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Electrochemical carboxylation of α-fluoroalkyl cyclopropane with CO_2 to mono- or difluoro pentenoic acid

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Supporting Information

1. General information

Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. Infrared (IR) spectra were obtained using a Bruker tensor 27 infrared spectrometer. High-resolution mass spectrometry was recorded with Waters Synapt (ESI) or GCT Premier (EI). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were obtained using a Bruker DPX 300 or 400 or 500 MHz Spectrometer. Chemical shifts were reported in ppm with TMS as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad.

Unless mentioned, all reactions were performed under an atmosphere of N_2 and carried out with dry solvents. $^{n}Bu_4NI$, $^{n}Bu_4NBr$, $^{n}Bu_4NCl$, $^{n}Bu_4NPF_6$, and $^{n}Bu_4NClO_4$ were purchased from Macklin and used as received. CO_2 (99.999%) was commercially available. As the eluent, the petroleum ether, EtOAc and CH_2Cl_2 were purchased from Shanghai Titan Scientific.

List of abbreviation:

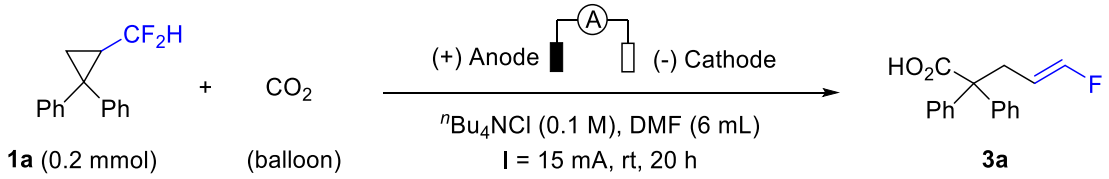
Entry	Chemical name	Abbreviation
1	Petroleum ether	PE
2	Ethyl acetate	EtOAc
3	Acetic acid	AcOH
4	Dimethyl sulfoxide	DMSO
5	*N,N*-Dimethylformamide	DMF
6	*N,N*-Dimethylaniline	DMA
7	*N*-Methyl-2-pyrrolidone	NMP
8	Graphite Felt	GF

2. Reaction condition optimization

2.1 Condition optimization for carboxylation with sacrificial anode

The defluorinative carboxylation of diphenyl substituted α-CF_2H cyclopropane **1a** with CO_2 was selected as the model reaction for condition optimization. Firstly, we examined the influence of electrode by conducting the reaction in DMF containing $^{n}Bu_4NCl$ at the constant current of 15 mA in an undivided cell under room temperature with CO_2 balloon (as shown in Table S1). By screening several typical anodes (entries 1-5), Mg-plate turned out to be the best and afford the desired carboxylic acid **3a** in 81% yield (entry 3). The performance of the typical cathode was also studied, and Ni-plate is still the best result (entries 6-9).

Table S1. Screening of anode and cathode



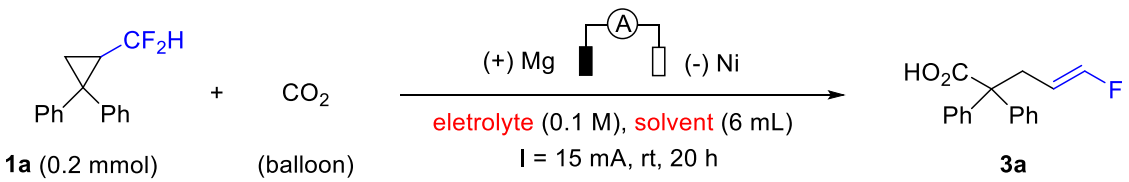
Entry	Anode	Cathode	Yield (%)[a]
1	Al	Ni	71
2	Zn	Ni	79
3	Mg	Ni	81[b]
4	Cu	Ni	NR
5	Fe	Ni	62
6	Mg	Pt	73
7	Mg	Graphite Felt (GF)	79
8	Mg	C rod	NR
9	Mg	Nb	42

[a] Trimethoxybenzene (3-5 mg) was used as the internal standard, and ^1H NMR was determined. [b] Isolated yield.

Then the solvent effects were examined using Ni-plate as cathode and Mg-plate as anode, $^{n}Bu_4NCl$ as the electrolyte, with typical results shown in Table S2. The reaction conducted in DMSO, CH_3CN and NMP gave lower yield than that in DMF (entries 1-4). The supporting electrolyte is

another important parameter in affecting the reaction outcome, and their influence was studied. By changing the electrolyte from $^{n}Bu_4NCl$ to $^{n}Bu_4NBr$, a similar 80% yield was obtained (entry 5). Further varying the counter anions in the tetrabutylammonium family had no positive impact on the reaction (entries 6-8). Another ammonium salt, such as Et_4NCl, was also tried, but no better result was obtained (entry 9).

Table S2. Screening of solvent and supporting electrolyte.



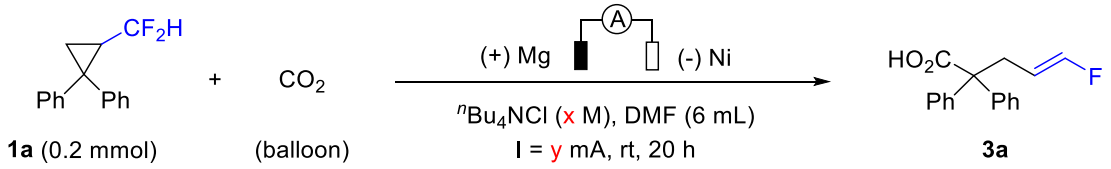
Entry	Solvent	Eletrolyte	Yield (%)[a]
1	DMF	$^{n}Bu_4NCl$	81[b]
2	DMSO	$^{n}Bu_4NCl$	75
3	CH_3CN	$^{n}Bu_4NCl$	53
4	NMP	$^{n}Bu_4NCl$	75
5	DMF	$^{n}Bu_4NBr$	80[b]
6	DMF	$^{n}Bu_4NBF_4$	25
7	DMF	$^{n}Bu_4NClO_4$	65
8	DMF	$^{n}Bu_4NI$	76
9	DMF	Et_4NCl	44

[a] Trimethoxybenzene (3-5 mg) was used as the internal standard, and ^1H NMR was determined. [b] Isolated yield.

Subsequently, the concentration of electrolyte was studied. As shown in Table S3, by decreasing the concentration of $^{n}Bu_4NCl$ to 0.05 M, the desired carboxylic acids **3a** was obtained in 65% yield, and further increasing the concentration to 0.15 M also gave no better results (entries 1 and 2). Since the intensity of the current may affect the reactions Then, the influence of current intensity was studied, and found that when the current intensity is increased to 15 mA or decreased to 20 mA, the yield of **3a** decreased to 54% and 74%, respectively (entry 4-5).

Finally, we determined to perform the defluorinative carboxylation of **1a** (0.2 mmol) under room temperature in DMF (6.0 mL) containing $^{n}Bu_4NCl$ (0.1 M) at constant current of 15 mA in an undivided cell with CO_2 balloon and Ni-plate as cathode and Mg-plate as anode.

Table S3. Screening of electrolyte concentration and current



Entry	Conc. of $^{n}Bu_4NCl$ (M)	I (mA)	Yield (%)[a]
1	0.10	15	81[b]
2	0.05	15	65
3	0.15	15	73
4	0.10	10	54
5	0.10	20	74

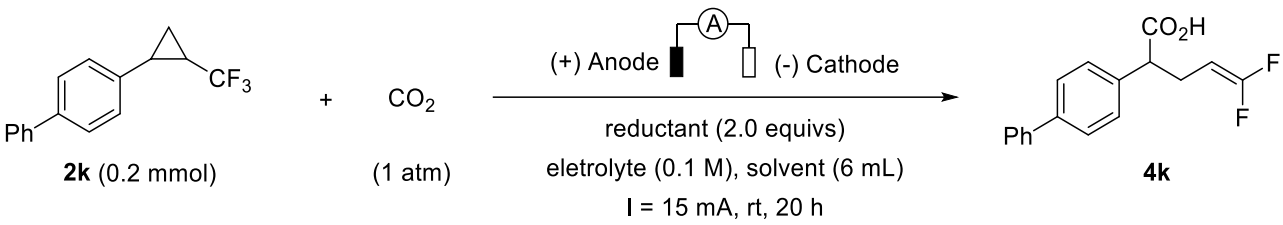
[a] Trimethoxybenzene (3-5 mg) was used as the internal standard, and ^1H NMR was determined. [b] Isolated yield.

2.2 Condition optimization for carboxylation with non-sacrificial anode

The defluorinative carboxylation of biphenyl substituted α-CF_3 cyclopropane **2k** with CO_2 was selected as the model reaction for condition optimization of non-sacrificial anode system. The influence of reductant was first studied by performing the reaction using Pt as anode and Graphite Felt (GF) cathode, in NMP with $^{n}Bu_4NI$ as the electrolyte at a constant current of 15 mA for 20 hours in an undivided cell at room temperature, with CO_2 bubbling. As detailed in Table S4, among the typical reductant tested, Na_2S was the best to give the desired carboxylic acid **4k** in 42% yield (entries 1-4). The study of solvent effect by conducting the reaction in DMSO or DMF gave no better result (entries 5-6). The performance of different electrode was then studied and found that the combination of C rod with GF cathode or Pt cathode could gave an improved 45% yield, and the cheaper GF cathode as selected for use (entries 7-11). The variation of electrolyte gave no better results (entries 12-14). Subsequent variations in the dosage of Na_2S did not yield improvements

(entries 17-18). Thus, the optimal reaction conditions for the defluorinative carboxylation under non-sacrificial anode system were established.

Table S4. Condition optimization of non-sacrificial anode



Entry	Anode	Cathode	Reductant	Eletrolyte	Solvent	Yield (%)[a]
1	Pt	GF	CH_3CO_2Na	$^nBu_4NI$	NMP	36
2	Pt	GF	Sodium ascorbate	$^nBu_4NI$	NMP	25
3	Pt	GF	Na_2SO_3	$^nBu_4NI$	NMP	33
4	Pt	GF	Na_2S	$^nBu_4NI$	NMP	42
5	Pt	GF	Na_2S	$^nBu_4NI$	DMSO	28
6	Pt	GF	Na_2S	$^nBu_4NI$	DMF	10
7	GF	GF	Na_2S	$^nBu_4NI$	NMP	41
8	Nb	GF	Na_2S	$^nBu_4NI$	NMP	45
9	C rod	GF	Na_2S	$^nBu_4NI$	NMP	45[b]
10	C rod	Ni	Na_2S	$^nBu_4NI$	NMP	29
11	C rod	Pt	Na_2S	$^nBu_4NI$	NMP	45
12	C rod	GF	Na_2S	$^nBu_4NBr$	NMP	18
13	C rod	GF	Na_2S	$^nBu_4NCl$	NMP	NR
14	C rod	GF	Na_2S	Et_4NI	NMP	44
17[c]	C rod	GF	Na_2S	$^nBu_4NI$	NMP	20
18[d]	C rod	GF	Na_2S	$^nBu_4NI$	NMP	36

[a] Determined by ^1H NMR with 4-(Trifluoromethoxy)anisole (3-5 mg) as internal standard. [b] Isolated yield. [c] With Na_2S (1.0 equiv). [d] With Na_2S (3.0 equivs).

3. Photographic guide for electrochemical reaction

Electrochemical reactions at the electrode were conducted in the following equipment: In a 10 mL three-necked flask using Ni-plate as cathode and Mg-plate as anode with the current supplied from a 36 V constant-current power supply purchased from Xiamen Bodong Biotechnology Ltd.

Photographic guide for the equipment (0.2 mmol)

Step 0. Overview of materials used.

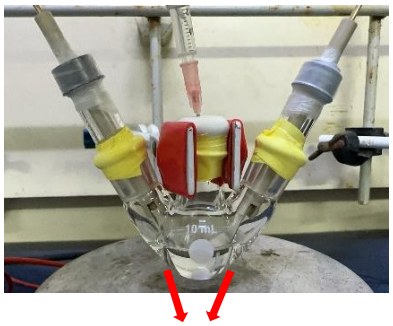
From left to right: (1) Ni-plate [cathode, 30 mm x 10 mm x 0.5 mm], Mg-plate [anode, 30 mm x 10 mm x 0.5 mm]; (2) 10 mL three-necked flask; (3) rubber stopper; (4) needle for CO_2 balloon.

Step 1. Assembling the cell

1) The electrodes are inserted into the two lateral openings of the three-neck flask; 2) The stopper is fitted into the central opening of the three-neck flask; 2) The rubber stopper is punctured to accommodate the needle.

Step 2. Electrolysis

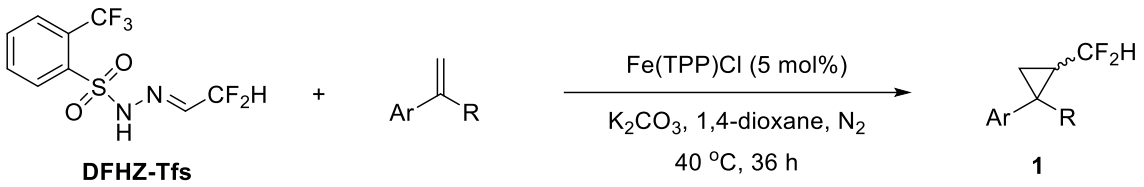
After the addition of all materials, the cell was evacuated and back-filled under CO_2 flow (this procedure was repeated three times) and then conducted constant current electrolysis (I = 15.0 mA) using a CO_2 balloon.



Effective area (Mg):
13 mm*10 mm*0.5 mm
Effective area (Ni):
13 mm*10 mm*0.1 mm

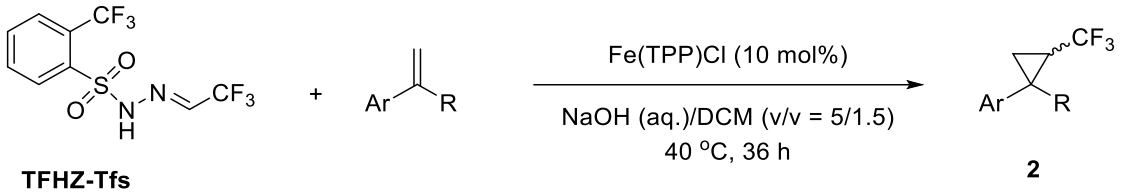
4. General procedure for the preparation of starting materials

4.1 General procedure A (for the synthesis of **1a-1o**)[1]



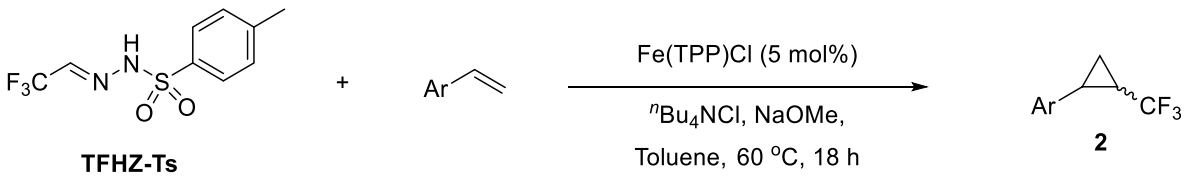
To a flame-dried screw-cap reaction tube equipped with a magnetic stir bar, DFHZ-Tfs (0.75 mmol, 253.5 mg), K_2CO_3 (0.9 mmol, 124.4 mg), and Fe(TPP)Cl (0.015 mmol, 10.6 mg) were added. A solution of styrene (0.3 mmol) in dry 1,4-dioxane (5.0 mL) was then added. The reaction mixture was degassed by freezing with liquid nitrogen to remove oxygen. The mixture was stirred at 40 °C for 36 hours. The crude reaction mixture was filtered through a short pad of celite and washed with EtOAc. The filtrate was evaporated under reduced pressure to obtain a crude mixture, which was purified by flash column chromatography using *n*-hexane as the eluent to yield the final product.

4.2 General procedure B (for the synthesis of **2a-2f**, **2j**)[2]

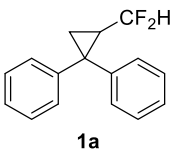


To a flame-dried screw-cap reaction tube equipped with a magnetic stir bar, TFHZ-Tfs (0.9 mmol, 207.0 mg) and Fe(TPP)Cl (0.03 mmol, 21.1 mg) were added. The tube was evacuated and back-filled with nitrogen three times. A solution of styrene (0.3 mmol) in CH_2Cl_2 (1.5 mL) and a 20 wt% aqueous NaOH solution (5 mL) were then successively added. The reaction mixture was stirred at 40 °C for 36 hours. Afterward, 10 mL of water was added to the mixture, and the layers were allowed to separate. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, then filtered through a short silica gel pad using CH_2Cl_2 as the eluent. The filtrate was evaporated under reduced pressure to obtain a crude mixture, which was purified by flash column chromatography using *n*-hexane as the eluent to yield the final product.

4.3 General procedure C (for the synthesis of **2g-2i, 2k**)[3]

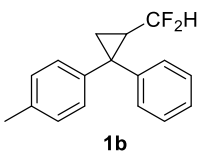


To a flame-dried screw-cap reaction tube equipped with a magnetic stir bar, TFHZ-Ts (2.2 mmol, 616.6 mg) and $^{n}Bu_4NCl$ (0.07 mmol, 19.5 mg) were added. The tube was evacuated and back-filled with nitrogen three times. A solution of styrene (0.3 mmol) in toluene (8 mL) was then added. The reaction mixture was stirred at 40 °C for 5 minutes, after which NaOMe (1.6 mmol, 86.4 mg) and Fe(TPP)Cl (0.05 mmol, 35.2 mg) were added. The mixture was stirred for an additional 18 hours at the same temperature. Subsequently, saturated aqueous NH_4Cl (10 mL) was added to quench the reaction. The aqueous layer was extracted with EtOAc (3 × 10 mL), and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography using *n*-hexane as the eluent to yield the desired product.



1a

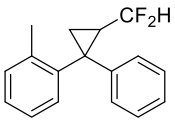
The reaction afforded **1a** in 81% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J = 7.2 Hz, 2H), 7.32-7.14 (m, 8H), 5.14-4.84 (m, 1H), 2.23-2.14 (m, 1H), 1.64 (td, J = 5.6 Hz, 2.4 Hz, 1H), 1.48-1.44 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.49, 139.65, 130.02, 128.75, 128.53, 127.78, 127.29, 126.63, 118.18 (t, $J_{C\text{-}F}$ = 234.6 Hz), 35.22 (d, $J_{C\text{-}F}$ = 9.3 Hz), 27.17 (dd, $J_{C\text{-}F}$ = 31.6 Hz, 28.1 Hz), 15.60 (d, $J_{C\text{-}F}$ = 7.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.98 (d, J = 283.5 Hz), -113.99 (d, J = 283.1 Hz); IR (neat): 3063, 3032, 2376, 1697, 1520, 1265, 1088, 1034, 756, 702 cm^{-1}; MS (EI): 244 (M^+, 100), 115 (96), 193 (88), 165 (71), 243 (53), 178 (48). HRMS (EI): Exact mass calcd for: $C_{16}H_{14}F_2$ $[M]^+$: 244.1064, Found: 244.1062.



1b

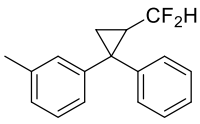
The reaction afforded **1b** in 70% yield as colorless oil. ^{1}H NMR analysis revealed that the dr vlues is 1:1; For the mixture: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.40 (m, 1H), 7.32-7.06 (m, 8H), 5.15-4.84 (m, 1H), 2.31 (s, 1.5H), 2.28 (s, 1.5H), 2.20-2.14 (m, 1H), 1.64-1.60 (m, 1H), 1.47-1.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.71, 141.63, 139.90, 136.94, 136.63, 136.29, 129.92, 129.87, 129.43, 129.20, 128.71, 128.49, 127.69, 127.19,

126.52, 118.30 (t, $J_{C\text{-}F}$ = 234.6 Hz), 118.25 (t, $J_{C\text{-}F}$ = 234.6 Hz), 34.82 (dd, $J_{C\text{-}F}$ = 10.8 Hz, 9.2 Hz), 27.27 (dd, $J_{C\text{-}F}$ = 28.0 Hz, 5.3 Hz), 26.95 (dd, $J_{C\text{-}F}$ = 28.0 Hz, 5.2 Hz), 21.00, 20.89, 15.57 (dd, $J_{C\text{-}F}$ = 14.4 Hz, 7.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.90 (d, J = 283.1 Hz), -107.91 (d, J = 283.1 Hz), -113.91 (d, J = 283.1 Hz), -114.07 (d, J = 283.1 Hz); IR (neat): 3024, 2924, 1651, 1512, 1427, 1088, 1034, 910, 741 cm^{-1}; MS (EI): 258 (M^+, 40), 243 (100), 165 (37), 115 (31), 192 (21), 178 (20). HRMS (EI): Exact mass calcd for: $C_{17}H_{16}F_2$ $[M]^+$: 258.1220, Found: 258.1217.



1c

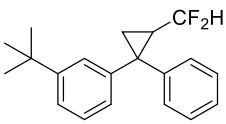
The reaction afforded **1c** in 72% yield as colorless oil. ^{13}C NMR analysis revealed that the dr vlues is 1.4:1; For the mixture: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 7.6 Hz, 1H), 7.44-7.35 (m, 2H), 7.28-7.14 (m, 4H), 7.08-7.03 (m, 2H), 4.93 (td, J = 55.2 Hz, 7.6 Hz, 2H), 2.28 (s, 3H), 2.23-2.15 (m, 1H), 1.90-1.87 (m, H), 1.37-1.26 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.99, 138.22, 137.77, 137.08, 131.18 (minor), 130.74, 129.96, 129.36, 128.40, 128.37, 127.79 (minor), 127.31, 126.85, 126.14, 126.13, 126.04, 126.01, 118.21 (t, $J_{C\text{-}F}$ = 234.0 Hz), 117.91 (t, $J_{C\text{-}F}$ = 235.3 Hz) (minor), 34.01 (d, $J_{C\text{-}F}$ = 9.0 Hz), 27.68 (dd, $J_{C\text{-}F}$ = 31.6 Hz, 28.0 Hz), 19.83 (minor), 19.50 (major), 13.85 (d, $J_{C\text{-}F}$ = 7.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -108.53 (d, J = 284.3 Hz), -114.25 (d, J = 284.3 Hz); IR (neat): 3024, 2978, 1690, 1427, 1180, 1088, 1034, 910, 756, 733 cm^{-1}; MS (EI): 258 (M^+, 38), 243 (100), 179 (63), 178 (51), 115 (36), 165 (32). HRMS (EI): Exact mass calcd for: $C_{17}H_{16}F_2$ $[M^+]$: 258.1220, Found: 258.1218.



1d

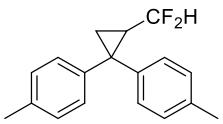
The reaction afforded **1d** in 75% yield as colorless oil. ^{1}H NMR analysis revealed that the dr vlues is 1:1; For the mixture: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 7.6 Hz, 1H), 7.33-7.13 (m, 6H), 7.09-6.98 (m, 2H), 5.15-4.84 (m, 1H), 2.32 (s, 1.5H), 2.30 (s, 1.5H), 2.22-2.14 (m, 1H), 1.64-1.61 (m, 1H), 1.48-1.43 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.62, 144.45, 139.82, 139.57, 138.34, 138.14, 130.69, 129.96, 128.69, 128.58, 128.54, 128.48, 128.41, 128.05, 127.77, 127.42, 127.20, 127.06, 126.55, 124.98, 118.24 (t, $J_{C\text{-}F}$ = 234.6 Hz), 35.19 (dd, $J_{C\text{-}F}$ = 9.4 Hz, 4.3 Hz), 27.21 (dd, $J_{C\text{-}F}$ = 31.6 Hz, 7.1 Hz), 26.93 (dd, $J_{C\text{-}F}$ = 31.7 Hz, 6.9 Hz), 21.35, 15.47 (dd, $J_{C\text{-}F}$ = 14.1 Hz, 7.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.92 (d, J = 283.1 Hz), -107.94 (d, J = 283.1 Hz), -113.95 (d, J = 283.1 Hz), -113.97 (d, J = 283.1 Hz); IR (neat): 3023, 2978, 1944, 1427, 1180, 1080, 1034, 910, 748, 702 cm^{-1}; MS (EI): 258 (M^+, 100), 243 (96), 207

(68), 115 (62), 165 (58), 129 (33). HRMS (EI): Exact mass calcd for: $C_{17}H_{16}F_2$ $[M]^+$: 258.1220, Found: 258.1223.



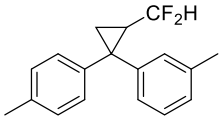
1e

The reaction afforded **1e** in 81% yield as colorless oil. ^{1}H NMR analysis revealed that the dr vlues is 2:1; For the mixture: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.42 (m, 1H), 7.33-7.08 (m, 8H), 5.15-4.84 (m, 1H), 2.22-2.13 (m, 1H), 1.65-1.59 (m, 1H), 1.51-1.47 (m, 1H) 1.30 (s, 6H), 1.28 (s, 3H) (minor); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.64, 151.42 (minor), 144.73, 144.12 (minor), 139.86 (minor), 139.17 (major), 130.00, 128.70, 128.49, 128.38, 128.16 (minor), 127.56, 127.29, 127.21, 127.18, 126.49, 125.06, 124.59, 124.19, 123.67 (minor), 118.36 (t, $J_{C\text{-}F}$ = 234.1 Hz), 118.27 (t, $J_{C\text{-}F}$ = 234.1 Hz) (minor), 35.47 (dd, $J_{C\text{-}F}$ = 9.6 Hz, 7.1 Hz), 34.68, 31.30 (s), 27.39 (dd, $J_{C\text{-}F}$ = 31.8 Hz, 28.1 Hz), 27.16 (dd, $J_{C\text{-}F}$ = 31.8 Hz, 28.0 Hz) (minor), 15.97 (d, $J_{C\text{-}F}$ = 7.8 Hz), 15.60 (d, $J_{C\text{-}F}$ = 7.8 Hz) (minor); ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.88 (d, J = 283.1 Hz) (minor), -107.94 (d, J = 283.1 Hz) (major), -113.91 (d, J = 283.1 Hz) (minor), -114.00 (d, J = 283.1 Hz) (major); IR (neat): 2963, 2315, 1427, 1258, 1088, 1034, 910, 741, 702 cm^{-1}; MS (EI): 300 (M^+, 12), 243 (100), 285 (36), 244 (18), 103 (13), 147 (13). HRMS (EI): Exact mass calcd for: $C_{20}H_{22}F_2$ $[M]^+$: 300.1690, Found: 300.1694.



1f

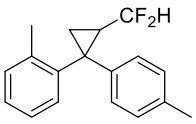
The reaction afforded **1f** in 83% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, J = 8.0 Hz, 2H), 7.15-7.04 (m, 6H), 5.12-4.83 (m, 1H), 2.29 (s, 3H), 2.16-2.10 (m, 1H), 2.27 (s, 3H), 1.60-1.56 (m, 1H), 1.42-1.38 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.84, 136.86, 136.85, 136.20, 129.77, 129.40, 129.17, 127.60, 118.37 (t, $J_{C\text{-}F}$ = 234.3 Hz), 34.49 (t, $J_{C\text{-}F}$ = 9.4 Hz), 27.04 (dd, $J_{C\text{-}F}$ = 31.6 Hz, 27.8 Hz), 21.01, 20.90, 15.56 (d, $J_{C\text{-}F}$ = 7.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.83 (d, J = 282.8 Hz), -114.00 (d, J = 282.8 Hz); IR (neat): 3024, 2376, 1651, 1512, 1180, 1080, 1034, 818, 756 cm^{-1}; MS (EI): 272 (M^+, 23), 257 (100), 129 (18), 178 (15), 165 (15), 206 (13). HRMS (EI): Exact mass calcd for: $C_{18}H_{18}F_2$ $[M]^+$: 272.1377, Found: 272.1380.



1g

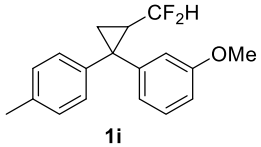
The reaction afforded **1g** in 80% yield as colorless oil. ^{1}H NMR analysis revealed that the dr vlues is 1:1; For the mixture: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.26 (m, 1H), 7.21-6.98 (m, 7H), 5.14-4.85 (m, 1H), 2.32 (s, 1.5H), 2.31 (s, 1.5H),

2.30 (s, 1.5H), 2.29 (s, 1.5H), 2.18-2.12 (m, 1H), 1.62-1.58 (m, 1H), 1.45-1.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.68, 141.76, 139.81, 138.30, 138.10, 136.84, 136.80, 136.20, 130.61, 129.80, 129.40, 129.17, 128.55, 128.47, 128.39, 127.96, 127.68, 127.34, 126.96, 124.91, 118.35 (t, $J_{C\text{-}F}$ = 234.3 Hz), 118.31 (t, $J_{C\text{-}F}$ = 234.4 Hz), 34.85 (dd, $J_{C\text{-}F}$ = 9.5 Hz, 6.5 Hz), 27.18 (dd, $J_{C\text{-}F}$ = 27.7 Hz, 1.9 Hz), 26.86 (dd, $J_{C\text{-}F}$ = 28.4 Hz, 1.8 Hz), 21.37, 20.98, 20.88, 15.47 (d, $J_{C\text{-}F}$ = 7.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.84 (d, J = 282.8 Hz), -107.86 (d, J = 282.8 Hz), -113.90 (d, J = 282.8 Hz), -114.03 (d, J = 282.8 Hz); IR (neat): 2924, 1991, 1512, 1180, 1088, 1034, 910, 733 cm^{-1}; MS (EI): 272 (M^+, 46), 257 (100), 129 (29), 178 (20), 165 (19), 258 (18). HRMS (EI): Exact mass calcd for: $C_{18}H_{18}F_2$ $[M]^+$: 272.1377, Found: 272.1375.



1h

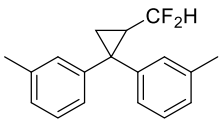
The reaction afforded **1h** in 72% yield as colorless oil. ^{13}C NMR analysis revealed that the dr vlues is 1.5:1; For the mixture: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.42 (m, 1H), 7.26-7.04 (m, 6H), 6.94-6.92 (m, 1H), 5.09-4.79 (m, 1H), 2.29 (s, 6H), 2.21-2.13 (m, 2H), 1.87-1.84 (m, 1H), 1.32-1.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.17, 140.13 (minor), 139.20 (minor), 137.65, 137.30, 136.43, 135.70, 135.20, 131.13 (minor), 130.71, 129.87, 129.19, 129.08, 129.04, 127.68 (minor), 127.19, 126.04, 126.00, 125.97, 118.33 (t, $J_{C\text{-}F}$ = 234.3 Hz), 117.98 (t, $J_{C\text{-}F}$ = 235.6 Hz) (minor), 33.65 (d, $J_{C\text{-}F}$ = 9.2 Hz), 27.55 (dd, $J_{C\text{-}F}$ = 31.6 Hz, 27.9 Hz), 20.83 (d, $J_{C\text{-}F}$ = 10.5 Hz), 19.82 (minor), 19.46 (major), 13.80 (d, $J_{C\text{-}F}$ = 7.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -108.44 (d, J = 283.9 Hz), -114.34 (d, J = 283.9 Hz); IR (neat): 3017, 2924, 2315, 1697, 1512, 1265, 1088, 1034, 756 cm^{-1}; MS (EI): 272 (M^+, 22), 257 (100), 178 (40), 272 (22), 258 (19), 165 (19). HRMS (EI): Exact mass calcd for: $C_{18}H_{18}F_2$ $[M]^+$: 272.1377, Found: 272.1375.



1i

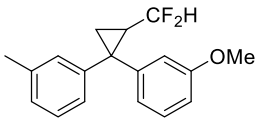
The reaction afforded **1i** in 70% yield as colorless oil. ^{1}H NMR analysis revealed that the dr vlues is 1.4:1; For the mixture: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.29 (m, 1H), 7.25-7.16 (m, 2H), 7.13-7.07 (m, 2H), 7.02-6.95 (m, 1H), 6.87-6.70 (m, 2H), 5.17-4.85 (m, 1H), 3.78 (s, 1.75H), 3.76 (s, 1.25H) (minor), 2.32 (s, 1.25H) (minor), 2.29 (s, 1.75H) (major), 2.20-2.13 (m, 1H), 1.61 (td, J = 5.6 Hz, 2.4 Hz, 1H), 1.47-1.40 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.69, 159.59 (minor), 146.32, 141.45, 141.42

(minor), 136.99, 136.49, 136.33, 129.84, 129.70, 129.49, 129.42, 129.19, 127.64, 122.19, 119.99 (minor), 118.25 (t, $J_{C\text{-}F}$ = 234.5 Hz), 118.23 (t, $J_{C\text{-}F}$ = 234.4 Hz) (minor), 115.75, 114.06 (minor), 112.51, 111.46 (minor), 55.12, 34.92 (d, $J_{C\text{-}F}$ = 9.5 Hz), 34.79 (d, $J_{C\text{-}F}$ = 9.6 Hz, 1C) (minor), 27.26 (dd, $J_{C\text{-}F}$ = 28.3 Hz, 5.9 Hz), 27.01 (dd, $J_{C\text{-}F}$ = 27.9 Hz, 5.8 Hz) (minor), 21.01 (minor), 20.90 (major), 15.65 (d, $J_{C\text{-}F}$ = 7.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.59 (d, J = 283.1 Hz), -107.86 (d, J = 283.1 Hz) (minor), -113.78 (d, J = 283.1 Hz), -114.02 (d, J = 283.5 Hz); IR (neat): 2932, 1991, 1713, 1520, 1273, 1034, 748, 702 cm^{-1}; MS (EI): 288 (M^+, 100), 273 (84), 237 (57), 165 (45), 129 (27), 178 (24). HRMS (EI): Exact mass calcd for: $C_{18}H_{18}F_2O$ $[M]^+$: 288.1326, Found: 288.1330.



1j

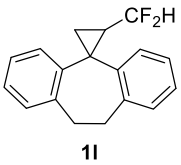
The reaction afforded **1j** in 39% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.13 (m, 4H), 7.11-6.97 (m, 4H), 5.19-4.79 (m, 1H), 2.32 (s, 3H), 2.31 (s, 3H), 2.22-2.10 (m, 1H), 1.60 (td, J = 7.6 Hz, 3.2 Hz, 1H), 1.46-1.40 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.57, 139.71, 138.32, 138.13, 130.62, 128.55, 128.39, 128.00, 127.39, 127.00, 125.02, 118.31 (t, $J_{C\text{-}F}$ = 234.1 Hz), 35.21 (d, $J_{C\text{-}F}$ = 9.4 Hz), 26.94 (dd, $J_{C\text{-}F}$ = 31.8 Hz, 28.0 Hz), 21.40, 15.40 (d, $J_{C\text{-}F}$ = 7.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -107.84 (d, J = 282.6 Hz), -113.94 (d, J = 282.6 Hz); IR (neat): 2978, 1991, 1605, 1427, 1265, 1080, 1034, 910, 748, 710 cm^{-1}; MS (EI): 272 (M^+, 81), 257 (100), 129 (53), 221 (41), 178 (27), 165 (25). HRMS (EI): Exact mass calcd for: $C_{18}H_{18}F_2$ $[M]^+$: 272.1377, Found: 272.1379.



1k

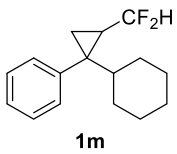
The reaction afforded **1k** in 75% yield as colorless oil. ^{1}H NMR analysis revealed that the dr vlues is 1.2:1; For the mixture: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.14 (m, 3H), 7.10-6.96 (m, 3H), 6.89-6.71 (m, 2H), 5.17-4.85 (m, 1H), 3.79 (s, 1.65H), 3.77 (s, 1.35H) (minor), 2.32 (s, 1.35H) (minor), 2.31 (s, 1.65H) (major), 2.22-2.12 (m, 1H), 1.61 (td, J = 5.6 Hz, 2.4 Hz, 1H), 1.47-1.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.67, 159.57 (minor), 146.19 (minor), 144.27 (major), 141.31, 139.41 (minor), 138.31 (minor), 138.12 (major), 130.64 (minor), 129.67, 129.46, 128.54, 128.47, 128.38, 128.06, 127.43, 127.00, 124.90, 122.19, 120.04, 118.24 (t, $J_{C\text{-}F}$ = 234.8 Hz), 118.17 (t, $J_{C\text{-}F}$ = 234.7 Hz) (minor), 115.82, 114.15, 112.43, 111.42, 55.03, 35.16 (dd, $J_{C\text{-}F}$ = 9.4 Hz, 5.4 Hz), 27.22 (dd, $J_{C\text{-}F}$ = 27.9 Hz, 6.3 Hz), 26.90 (dd, $J_{C\text{-}F}$ = 28.0 Hz, 6.2 Hz), 21.32, 15.53 (d, $J_{C\text{-}F}$ = 7.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ

-107.69 (d, J = 283.1 Hz), -107.94 (d, J = 283.1 Hz) (minor), -113.89 (d, J = 283.1 Hz), -114.00 (d, J = 283.1 Hz); IR (neat): 3750, 3009, 2376, 1520, 1273, 1088, 1034, 756 cm^{-1}; MS (EI): 288 (M^+, 100), 257 (77), 237 (67), 165 (43), 129 (39), 145 (26). HRMS (EI): Exact mass calcd for: $C_{18}H_{18}F_2O$ $[M]^+$: 288.1326, Found: 288.1322.



1l

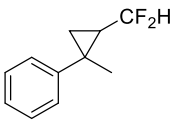
The reaction afforded **1l** in 54% yield as white solid, Mp 61.7-62.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.18 (m, 4H), 7.16-7.10 (m, 2H), 7.08-7.04 (m, 2H), 4.92 (td, J = 55.2 Hz, 7.6 Hz, 1H), 3.98 (td, J = 13.6 Hz, 5.6 Hz, 1H), 3.53 (dt, J = 17.6 Hz, 4.8 Hz, 1H), 3.07-2.98 (m, 1H), 2.85-2.79 (m, 1H), 1.84-1.70 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.71, 140.95, 139.81, 135.14, 131.39, 128.88, 127.58, 127.51, 127.26, 126.43, 126.29, 125.75, 118.34 (t, $J_{C\text{-}F}$ = 235.1 Hz), 32.94, 32.81 (t, $J_{C\text{-}F}$ = 9.0 Hz), 30.27 (t, $J_{C\text{-}F}$ = 28.7 Hz), 12.24, 12.17; ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.40 (d, J = 283.9 Hz), -113.19 (d, J = 284.3 Hz); IR (neat): 3017, 2940, 1697, 1427, 1273, 1088, 1034, 910, 748 cm^{-1}; MS (EI): 270 (M^+, 100), 269 (94), 255 (55), 203 (40), 204 (36), 189 (35). HRMS (EI): Exact mass calcd for: $C_{18}H_{16}F_2$ $[M]^+$: 270.1220, Found: 270.1224.



1m

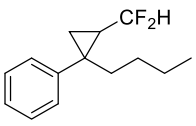
The reaction afforded **1m** in 69% yield as white solid, Mp 43.2-45.0 ºC. ^{1}H NMR analysis revealed that the dr vlues is 2.5:1; For the mixture: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.19 (m, 7H), 5.72 (td, J = 56.4 Hz, 7.6 Hz, 0.4H), 4.99-4.70 (m, 1H), 1.86-1.46 (m, 8.4H), 1.21-0.69 (m, 11.2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.58 (minor), 137.79 (major), 131.55, 131.53, 131.20, 127.85, 127.57 (minor), 127.02, 126.76 (minor), 118.52 (t, $J_{C\text{-}F}$ = 233.9 Hz), 117.89 (t, $J_{C\text{-}F}$ = 233.3 Hz) (minor), 48.26, 43.10 (minor), 36.27 (d, $J_{C\text{-}F}$ = 8.2 Hz, (minor), 36.06 (d, $J_{C\text{-}F}$ = 8.4 Hz) (major), 30.96 (minor), 30.53 (major), 30.42 (d, $J_{C\text{-}F}$ = 2.0 Hz, (minor), 29.82 (d, $J_{C\text{-}F}$ = 1.1 Hz) (major), 26.75 (minor), 26.57 (major), 26.47, 26.42 (minor), 26.10, 26.02 (minor), 26.58 (dd, $J_{C\text{-}F}$ = 31.8 Hz, 26.9 Hz), 15.21 (d, $J_{C\text{-}F}$ = 6.7 Hz) (minor), 14.16 (d, $J_{C\text{-}F}$ = 7.4 Hz) (major); ^{19}F NMR (376 MHz, $CDCl_3$): δ -102.10 (d, J = 284.6 Hz, (minor), -106.78 (d, J = 280.9 Hz) (major), -111.44 (d, J = 284.6 Hz) (minor), -113.01 (d, J = 280.9 Hz) (major); IR (neat): 2924, 2855, 2315, 1690, 1427, 1180, 1080, 1034, 764, 702 cm^{-1}; MS (EI): 250 (M^+, 78), 172 (100),

129 (75), 81 (69), 104 (65), 91 (63). HRMS (EI): Exact mass calcd for: $C_{16}H_{20}F_2$ $[M]^+$: 250.1533, Found: 250.1535.



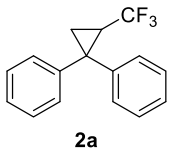
1n

The reaction afforded **1n** in 51% yield as colorless oil. ^{13}C NMR analysis revealed that the dr vlues is greater than 20:1; For the mixture: ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.28 (m, 4H), 7.24-7.20 (m, 1H), 5.69 (td, J = 56.0 Hz, 6.8 Hz, 1H), 1.66-1.56 (m, 1H), 1.48 (s, 3H), 1.32-1.28 (m, 1H), 0.97 (td, J = 5.6 Hz, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.71, 129.17 (minor), 128.61 (minor), 128.50, 127.54, 126.98 (minor), 126.51, 118.11 (t, $J_{C\text{-}F}$ = 235.1 Hz), 26.58 (dd, $J_{C\text{-}F}$ = 29.7 Hz, 27.5 Hz), 25.14 (d, $J_{C\text{-}F}$ = 7.6 Hz), 21.58 (s, 2C), 16.77 (dd, $J_{C\text{-}F}$ = 7.1 Hz, 1.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -106.21 (d, J = 285.0 Hz), -112.03 (d, J = 284.6 Hz); IR (neat): 3024, 2970, 2315, 1690, 1427, 1188, 1088, 1026, 764, 702 cm^{-1}; MS (EI): 182 (M^+, 34), 131 (100), 91 (41), 147 (37), 167 (37), 115 (25). HRMS (EI): Exact mass calcd for: $C_{11}H_{12}F_2$ $[M]^+$: 182.0907, Found: 182.0905.



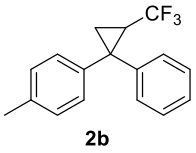
1o

The reaction afforded **1o** in 58% yield as colorless oil. ^1H NMR analysis revealed that the dr vlues is 4:1; For the mixture: ^1H NMR (400 MHz, $CDCl_3$): δ 7.29-7.18 (m, 6.25H), 5.68 (td, J = 56.0 Hz, 6.8 Hz, 1H), 4.91-4.61 (m, 0.25H) (minor), 1.88-1.82 (m, 0.25H) (minor), 1.74-1.69 (m, 1H) (major), 1.57-1.48 (m, 2.5H), 1.26-1.09 (m, 6H), 1.02-0.97 (m, 0.25H) (minor), 0.89 (td, J = 5.6 Hz, 2.4 Hz, 1H) (minor), 0.80-0.77 (m, 4H) (major); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.95, 139.70 (minor), 130.05 (minor), 129.14 (major), 128.40 (minor), 128.25 (major), 126.94 (minor), 126.61 (major), 118.53 (t, $J_{C\text{-}F}$ = 233.6 Hz) (minor), 118.01 (t, $J_{C\text{-}F}$ = 234.6 Hz) (major), 41.07 (minor), 35.21 (major), 30.99 (d, $J_{C\text{-}F}$ = 8.4 Hz) (minor), 30.78 (d, $J_{C\text{-}F}$ = 8.3 Hz) (major), 28.97, 28.68 (minor), 26.35 (dd, $J_{C\text{-}F}$ = 31.4 Hz, 26.8 Hz) (minor), 26.31 (dd, $J_{C\text{-}F}$ = 30.5 Hz, 27.3 Hz) (major), 22.74, 22.55 (minor), 15.26 (d, $J_{C\text{-}F}$ = 6.8 Hz), 13.53 (d, $J_{C\text{-}F}$ = 7.3 Hz) (minor), 13.95 (minor), 13.89 (major); ^{19}F NMR (376 MHz, $CDCl_3$): δ -104.67 (d, J = 284.6 Hz), -107.61 (d, J = 281.2 Hz) (minor), -111.79 (d, J = 284.3 Hz), -112.90 (d, J = 281.6 Hz) (minor); IR (neat): 3024, 2376, 1690, 1466, 1427, 1080, 1026, 910, 702 cm^{-1}; MS (EI): 224 (M^+, 40), 167 (100), 147 (63), 117 (37), 115 (31), 91 (27). HRMS (EI): Exact mass calcd for: $C_{14}H_{18}F_2$ $[M]^+$: 224.1377, Found: 224.1379.



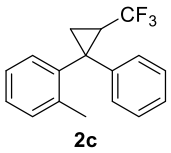
2a

The reaction afforded **2a** in 70% yield as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47-7.44 (m, 2H), 7.35-7.17 (m, 8H), 2.43-2.31 (m, 1H), 1.92 (t, J = 5.7 Hz, 1H), 1.56-1.52 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.48, 139.03, 129.63, 128.65, 128.36, 127.84, 127.13, 126.84, 125.91 (q, $J_{C\text{-}F}$ = 270.6 Hz), 35.91, 26.69 (q, J = 35.5 Hz), 15.48 (q, J = 0.6 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -61.45; IR (neat): 3063, 3032, 1412, 1273, 1126, 910, 748, 702 cm^{-1}; MS (EI): 262 (M^+, 100), 261 (91), 165 (63), 115 (49), 184 (39), 178 (32). HRMS (EI): Exact mass calcd for: $C_{16}H_{13}F_3$ $[M]^+$: 262.0969, Found: 262.0965.



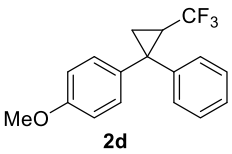
2b

The reaction afforded **2b** in 25% yield as colorless oil. ^{1}F NMR analysis revealed that the dr vlues is 1:1; For the mixture: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 7.6 Hz, 1H), 7.33-7.28 (m, 4H), 7.24-7.15 (m, 2H), 7.09 (t, J = 8.4 Hz, 2H), 2.36-2.30 (m, 1H), 2.30 (s, 1.5H), 2.29 (s, 1.5H), 1.88 (t, J = 5.6 Hz, 1H), 1.53-1.48 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.72, 141.64, 139.27, 136.75, 136.54, 136.03, 129.55, 129.46, 129.19, 129.08, 128.63, 128.33, 127.78, 127.71, 127.03, 126.74, 125.95 (q, $J_{C\text{-}F}$ = 270.4 Hz), 35.58 (d, $J_{C\text{-}F}$ = 1.4 Hz), 35.52 (d, $J_{C\text{-}F}$ = 1.4 Hz), 26.66 (q, $J_{C\text{-}F}$ = 35.4 Hz), 26.64 (q, $J_{C\text{-}F}$ = 35.3 Hz), 21.07, 20.92, 15.52 (q, $J_{C\text{-}F}$ = 2.4 Hz), 15.46 (q, $J_{C\text{-}F}$ = 2.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -61.37, -61.42; IR (neat): 3024, 2924, 2315, 1458, 1412, 1273, 1126, 910, 748, 702 cm^{-1}; MS (EI): 276 (M^+, 35), 261 (100), 165 (43), 165 (23), 183 (22), 178 (19). HRMS (EI): Exact mass calcd for: $C_{17}H_{15}F_3$ $[M]^+$: 276.1126, Found: 276.1122.



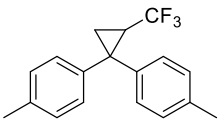
2c

The reaction afforded **2c** in 76% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.56 (m, 1H), 7.42-7.39 (m, 2H), 7.27-7.14 (m, 5H), 7.11-7.05 (m, 1H), 2.42-2.34 (m, 1H), 2.30 (s, 3H), 2.12 (t, J = 6.0 Hz, 1H), 1.41-1.37 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.13, 137.41, 137.10, 130.92, 129.63, 128.43, 127.93, 127.41, 126.77, 126.08, 126.02 (q, $J_{C\text{-}F}$ = 270.5 Hz), 34.66 (q, $J_{C\text{-}F}$ = 1.9 Hz), 27.53 (q, $J_{C\text{-}F}$ = 35.3 Hz), 19.41, 14.23 (q, $J_{C\text{-}F}$ = 2.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -61.33; IR (neat): 3063, 3024, 2932, 1404, 1273, 1126, 910, 748, 702 cm^{-1}; MS (EI): 276 (M^+, 31), 261 (100), 178 (46), 165 (19), 183 (18), 115 (18). HRMS (EI): Exact mass calcd for: $C_{17}H_{15}F_3$ $[M]^+$: 276.1126, Found: 276.1124.



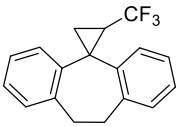
2d

The reaction afforded **2d** in 34% yield as colorless oil. ^{1}F NMR analysis revealed that the dr vlues is 1:1; For the mixture: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.40 (m, 1H), 7.36-7.32 (m, 1H), 7.30-7.16 (m, 5H), 6.84-6.78 (m, 2H), 3.77 (s, 1.5H), 3.75 (s, 1.5H), 2.36-2.25 (m, 1H), 1.86 (td, J = 1.4 Hz, 0.6 Hz, 1H), 1.53-1.47 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.58, 158.37, 144.82, 139.45, 136.80, 131.09, 130.67, 129.45, 128.94, 128.61, 128.32, 127.65, 126.99, 126.70, 122.95 (q, $J_{C\text{-}F}$ = 270.0 Hz), 113.97, 113.73, 55.24, 55.12, 35.18 (d, J = 27.4 Hz), 26.71 (q, J = 35.4 Hz), 15.76 (d, J = 2.4 Hz), 15.40 (d, J = 2.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -61.32, -61.42; IR (neat): 3032, 2839, 2060, 1512, 1458, 1412, 12773, 1250, 1126, 1042, 910, 748, 702 cm^{-1}; MS (EI): 292 (M^+, 100), 261 (69), 152 (37), 165 (25), 115 (22), 183 (22). HRMS (EI): Exact mass calcd for: $C_{17}H_{15}F_3O$ $[M]^+$: 292.1075, Found: 292.1070.



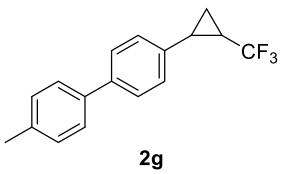
2e

The reaction afforded **2e** in 59% yield as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.29 (m, 2H), 7.20-7.18 (m, 2H), 7.10-7.05 (m, 4H), 2.36-2.24 (m, 1H), 2.30 (s, 3H), 2.80 (s, 3H), 1.85 (t, J = 5.7 Hz, 1H), 1.50-1.45 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.88, 136.63, 136.42, 136.27, 129.38, 129.28, 129.05, 127.63, 124.92 (q, $J_{C\text{-}F}$ = 270.4 Hz), 35.19, 26.61 (q, $J_{C\text{-}F}$ = 35.3 Hz), 21.06, 20.91, 15.49 (q, $J_{C\text{-}F}$ = 2.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -61.33; IR (neat): 3024, 2924, 1906, 1512, 1458, 1412, 1273, 1126, 1096, 910, 818, 748 cm^{-1}; MS (EI): 290 (M^+, 22), 275 (100), 152 (37), 178 (16), 183 (14), 129 (9). HRMS (EI): Exact mass calcd for: $C_{18}H_{17}F_3$ $[M]^+$: 290.1282, Found: 290.1283.



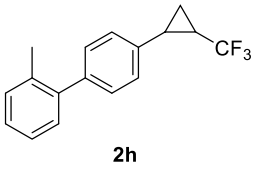
2f

The reaction afforded **2f** in 62% yield as white solid, Mp 42.8-43.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.16 (m, 4H), 7.14-7.10 (m, 2H), 7.07-7.02 (m, 2H), 3.96 (td, J = 13.6 Hz, 6.0 Hz, 1H), 3.58-3.52 (m, 1H), 3.10-3.01 (m, 1H), 2.88-2.82 (m, 1H), 2.09-2.02 (m, 1H), 1.93-1.84 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.90, 140.52, 139.25, 134.23, 131.11, 128.90, 127.75, 127.52, 127.41, 126.41, 125.97, 125.93 (q, $J_{C\text{-}F}$ = 271.1 Hz), 125.51, 33.34 (q, $J_{C\text{-}F}$ = 1.8 Hz), 32.89, 30.23, 29.84 (q, $J_{C\text{-}F}$ = 34.3 Hz), 12.61 (q, $J_{C\text{-}F}$ = 2.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -61.73; IR (neat): 3024, 2376, 2314, 1744, 1404, 1273, 1126, 1065, 910, 748 cm^{-1}; MS (EI): 288 (M^+, 100), 273 (72), 189 (35), 203 (34), 202 (29), 204 (24). HRMS (EI): Exact mass calcd for: $C_{18}H_{15}F_3$ $[M]^+$: 288.1126, Found: 288.1124.



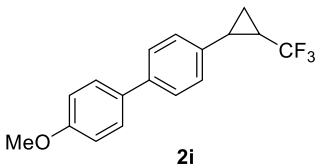
2g

The reaction afforded **2g** in 40% yield as white solid; Mp 98.1-98.4 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53-7.45 (m, 4H), 7.26-7.16 (m, 4H), 2.43-2.37 (m, 1H), 2.40 (s, 3H), 1.91-1.78 (m, 1H), 1.44-1.37 (m, 1H), 1.26-1.17 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.73, 137.78, 137.74, 137.10, 129.51, 127.10, 126.84, 126.81, 125.89 (q, $J_{C\text{-}F}$ = 269.1 Hz), 22.98 (q, $J_{C\text{-}F}$ = 36.5 Hz), 19.28 (q, $J_{C\text{-}F}$ = 2.8 Hz), 10.88 (q, $J_{C\text{-}F}$ = 2.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -66.73; IR (neat): 3024, 2924, 1420, 1342, 1273, 1150, 1126, 910, 810, 748 cm^{-1}; MS (EI): 276 (M^+, 100), 192 (41), 165 (26), 261 (22), 191 (20), 207 (17). HRMS (EI): Exact mass calcd for: $C_{17}H_{15}F_3$ $[M]^+$: 276.1126, Found: 276.1124.



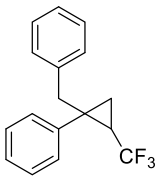
2h

The reaction afforded **2h** in 66% yield as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28-7.21 (m, 6H), 7.18-7.16 (m, 2H), 2.44-2.39 (m, 1H), 2.27 (s, 3H), 1.90-1.83 (m, 1H), 1.44-1.39 (m, 1H), 1.25-1.20 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.37, 140.51, 137.51, 135.31, 130.35, 129.73, 129.40, 127.31, 126.17, 125.92 (q, $J_{C\text{-}F}$ = 268.0 Hz), 125.81, 22.98 (q, $J_{C\text{-}F}$ = 36.5 Hz), 20.43, 19.33 (q, $J_{C\text{-}F}$ = 2.9 Hz), 10.90 (q, $J_{C\text{-}F}$ = 2.6 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -66.72; IR (neat): 3024, 2924, 2315, 1913, 1466, 1420, 1342, 1265, 1142, 833, 756 cm^{-1}; MS (EI): 276 (M^+, 100), 165 (51), 192 (29), 179 (28), 167 (26), 178 (23). HRMS (EI): Exact mass calcd for: $C_{17}H_{15}F_3$ $[M]^+$: 276.1126, Found: 276.1122.



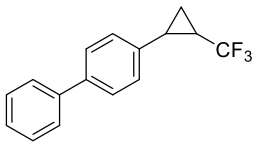
2i

The reaction afforded **2i** in 60% yield as white solid, Mp 116.1-117.9 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51-7.48 (m, 4H), 7.17 (d, J = 6.0 Hz, 2H), 6.97 (d, J = 6.3 Hz, 2H), 3.85 (s, 3H), 2.42-2.37 (m, 1H), 1.87-1.80 (m, 1H), 1.42-1.37 (m, 1H), 1.23-1.18 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.16, 139.40, 137.42, 133.16, 127.98, 126.85, 125.90 (q, $J_{C\text{-}F}$ = 269.1 Hz), 114.23, 55.32, 22.95 (q, $J_{C\text{-}F}$ = 36.6 Hz), 19.26 (q, $J_{C\text{-}F}$ = 2.9 Hz), 10.86 (q, $J_{C\text{-}F}$ = 2.6 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -66.72; IR (neat): 3032, 2955, 2839, 1906, 1605, 1504, 14420, 1273, 1250, 1134, 818 cm^{-1}; MS (EI): 292 (M^+, 100), 277 (24), 165 (16), 249 (13), 152 (12), 178 (11). HRMS (EI): Exact mass calcd for: $C_{17}H_{15}F_3O$ $[M]^+$: 292.1075, Found: 292.1079.



2j

The reaction afforded **2j** in 26% yield as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27-7.12 (m, 8H), 6.91-6.88 (m, 2H), 3.17 (d, J = 13.5 Hz, 1H), 2.70 (d, J = 13.5 Hz, 1H), 1.85-1.75 (m, 1H), 1.41 (t, J = 5.7 Hz, 1H), 1.26-1.21 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.68, 137.46, 129.91, 129.73, 129.71, 128.10, 128.00, 126.00 (q, $J_{C\text{-}F}$ = 270.0 Hz), 126.66, 46.94, 32.19, 25.26 (q, $J_{C\text{-}F}$ = 35.1 Hz), 12.69 (q, $J_{C\text{-}F}$ = 2.6 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -61.31; IR (neat): 3063, 3032, 1991, 1412, 1281, 1126, 1080, 764, 748, 702 cm^{-1}; MS (EI): 276 (M^+, 1), 292 (100), 261 (69), 152 (37), 165 (25), 115 (22). HRMS (EI): Exact mass calcd for: $C_{17}H_{15}F_3$ $[M]^+$: 276.1126, Found: 276.1123.

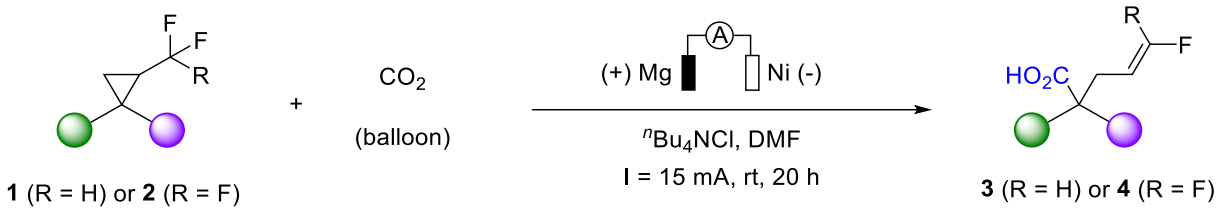


2k

The reaction afforded **2k** in 51% yield as white solid, Mp 75.9-77.8 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58-7.52 (m, 4H), 7.47-7.41 (m, 2H), 7.37-7.32 (m, 1H), 7.20 (d, J = 8.1 Hz, 2H), 2.44-2.37 (m, 1H), 1.90-1.79 (m, 1H), 1.44-1.38 (m, 1H), 1.25-1.18 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.64, 139.82, 138.11, 128.79, 127.32, 127.30, 126.99, 126.88, 125.88 (q, $J_{C\text{-}F}$ = 269.3 Hz), 23.02 (q, $J_{C\text{-}F}$ = 36.4 Hz), 19.29 (q, $J_{C\text{-}F}$ = 2.8 Hz), 10.93 (q, $J_{C\text{-}F}$ = 2.6 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -66.74; IR (neat): 2376, 2315, 1528, 1420, 1342, 1265, 1134, 910, 756 cm^{-1}; MS (EI): 262 (M^+, 100), 178 (66), 193 (43), 165 (42), 115 (18), 263 (18). HRMS (EI): Exact mass calcd for: $C_{16}H_{13}F_3$ $[M]^+$: 262.0969, Found: 262.0973.

5. General procedure for the defluorinative carboxylation reaction.

5.1 General procedure A. (carboxylation with sacrificial anode)

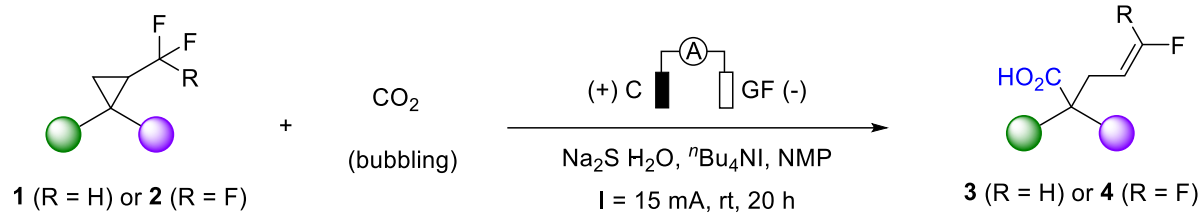


1 (R = H) or **2** (R = F) **3** (R = H) or **4** (R = F)

The electroreduction was carried out in an undivided cell equipped with a Mg plate anode (30 mm × 10 mm × 0.5 mm) and a Ni plate cathode (30 mm × 10 mm × 0.1 mm). To a 10 mL three-neck flask, $^{n}Bu_4NCl$ (166.8 mg, 0.6 mmol) and substrate **1** or **2** (0.2 mmol) were added. The cell was evacuated and back-filled under a CO_2 flow (this procedure was repeated three times), and anhydrous DMF (6 mL) was added via a syringe. The electroreduction was performed at a constant current of 15 mA for 15-20 hours with a CO_2 balloon at room temperature. After the reaction, the mixture was acidified with 2 N HCl (10 mL) at 0 °C. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were washed with saturated NaCl solution (2 × 20 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography using CH_2Cl_2 as the eluent to yield the desired product.

Note: For the synthesis of **3b**, **3d** and **3f**, $^{n}Bu_4NBr$ was used instead of $^{n}Bu_4NCl$. For the synthesis of **3m** and **3o**, an Nb plate was used as the cathode, and the reaction was carried out in NMP instead of DMF.

5.2 General procedure B. (carboxylation with non-sacrificial anode)

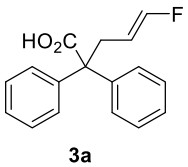


1 (R = H) or **2** (R = F) **3** (R = H) or **4** (R = F)

The electroreduction was carried out in an undivided cell using a carbon rod as the anode and GF[5] as the cathode. To a 10 mL three-neck flask, $^{n}Bu_4NI$ (221.0 mg, 0.6 mmol), $Na_2S{\cdot}H_2O$ (96.0 mg, 0.4 mmol), and NMP (6.0 mL) were added, followed by the addition of **1** or **2** (0.2 mmol). After bubbling CO_2 gas into the electrolyte for 10 minutes, the electroreduction was performed at a constant current of 15 mA for 12 hours at room temperature. The reaction mixture was acidified with

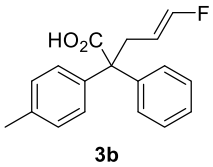
2 N HCl (10 mL). The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were washed with saturated NaCl solution (2 × 20 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography using dichloromethane as the eluent to yield the desired product.

5.3 Characterization data of products



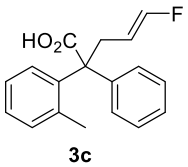
3a

The reaction afforded **3a** in 81% yield as white solid, Mp 113.4-114.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.26 (m, 10H), 6.24 (dd, J = 85.2 Hz, J = 11.2 Hz, 1H), 5.19-5.07 (m, 1H), 2.97 (dd, J = 8.0 Hz, J = 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.05, 150.68 (d, $J_{C\text{-}F}$ = 255.0 Hz), 141.47, 129.01, 128.03, 127.29, 107.01 (d, $J_{C\text{-}F}$ = 12.2 Hz), 60.33 (d, $J_{C\text{-}F}$ = 2.8 Hz), 34.07 (d, $J_{C\text{-}F}$ = 10.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.28; IR (neat): 3063, 3032, 1697, 1674, 1258, 1103, 910, 725, 694 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{17}H_{14}O_2F$ $[M\text{-}H]^-$: 269.0978, Found: 269.0992.



3b

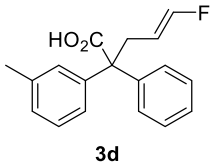
The reaction afforded **3b** in 80% yield as white solid, Mp 75.4-76.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.24 (m, 5H), 7.18-7.11 (m, 4H), 6.23 (dd, J = 85.2 Hz, J = 10.8 Hz, 1H), 5.17-5.06 (m, 1H), 2.99-2.87 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.79, 150.62 (d, $J_{C\text{-}F}$ = 254.7 Hz), 141.65, 138.45, 137.02, 128.99, 128.86, 128.75, 127.95, 127.16, 107.11 (d, $J_{C\text{-}F}$ = 12.1 Hz), 59.96 (d, $J_{C\text{-}F}$ = 3.1 Hz), 34.06 (d, $J_{C\text{-}F}$ = 10.0 Hz), 20.96; ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.46; IR (neat): 3055, 3032, 1697, 1512, 1265, 1103, 910, 741, 702 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{18}H_{16}O_2F$ $[M\text{-}H]^-$: 283.1134, Found: 283.1147.



3c

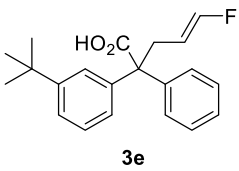
The reaction afforded **3c** in 48% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.39 (m, 2H), 7.33-7.22 (m, 6H), 7.15-7.13 (m, 1H), 6.33 (dd, J = 84.8 Hz, J = 11.2 Hz, 1H), 5.23-5.12 (m, 1H), 3.14-2.92 (m, 2H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.63, 150.32 (d, $J_{C\text{-}F}$ = 255.7 Hz), 141.06, 139.69, 137.38, 132.43, 128.63, 128.50, 127.99, 127.48, 127.05, 125.64, 107.13 (d, $J_{C\text{-}F}$ = 12.4 Hz), 59.40 (d, $J_{C\text{-}F}$ = 3.0 Hz), 34.33 (d, $J_{C\text{-}F}$ = 9.9 Hz), 21.28; ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.21; IR (neat): 3063, 3024, 1697, 1489,

1450, 1265, 1103, 910, 733 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{18}H_{16}O_2F$ $[M-H]^-$: 283.1134, Found: 283.1126.



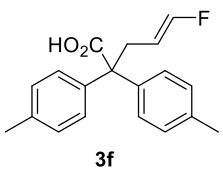
3d

The reaction afforded **3d** in 84% yield as white solid, Mp 52-54 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.32-7.19 (m, 6H), 7.11-7.08 (m, 3H), 6.25 (dd, J = 85.2 Hz, J = 11.2 Hz, 1H), 5.19-5.07 (m, 1H), 3.03-2.89 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.99, 150.62 (d, J_{C-F} = 254.9 Hz), 141.58, 141.35, 137.64, 129.54, 129.05, 128.09, 127.95, 127.91, 127.17, 126.07, 107.10 (d, J_{C-F} = 12.1 Hz), 60.23 (d, J_{C-F} = 3.0 Hz), 34.09 (d, J_{C-F} = 10.0 Hz), 21.58; ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.46; IR (neat): 3032, 2924, 1697, 1497, 1265, 1103, 910, 733, 702 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{18}H_{16}O_2F$ $[M-H]^-$: 283.1134, Found: 283.1126.



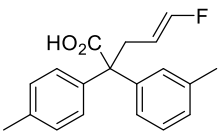
3e

The reaction afforded **3e** in 74% yield as white solid, Mp 96.4-97.8 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.32-7.25 (m, 8H), 7.10-7-07 (m, 1H), 6.22 (dd, J = 85.6 Hz, 11.2 Hz, 1H), 5.18-5.10 (m, 1H), 2.96 (dd, J = 8.4 Hz, 2.0 Hz, 2H), 1.27 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.45, 150.72, 150.61 (d, J_{C-F} = 254.8 Hz), 141.53, 140.77, 129.02, 127.94, 127.64, 127.21, 126.44, 126.02, 126.07, 107.14 (d, J_{C-F} = 12.3 Hz), 60.44 (d, J_{C-F} = 3.1 Hz), 34.74, 34.16 (d, J_{C-F} = 9.9 Hz), 31.26; ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.44; IR (neat): 3063, 2963, 2631, 1697, 1498, 1265, 1103, 910, 748, 702 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{21}H_{22}O_2F$ $[M-H]^-$: 325.1604, Found: 325.1607.



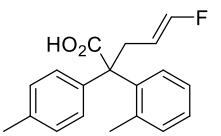
3f

The reaction afforded **3f** in 81% yield as white solid, Mp 159.4-161.8 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.17-7.11 (m, 8H), 6.25 (dd, J = 85.2 Hz, 11.2 Hz, 1H), 5.18-5.07 (m, 1H), 2.93 (dd, J = 8.0 Hz, 1.6 Hz, 2H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.78, 150.58 (d, J_{C-F} = 254.6 Hz), 138.61, 136.89, 128.85, 128.69, 107.20 (d, J_{C-F} = 12.1 Hz), 59.61 (d, J_{C-F} = 3.1 Hz), 34.06 (d, J_{C-F} = 10.1 Hz), 20.96; ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.65; IR (neat): 3024, 2924, 1991, 1697, 1512, 1265, 1103, 918, 810, 741 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{19}H_{18}O_2F$ $[M-H]^-$: 297.1291, Found: 297.1269.



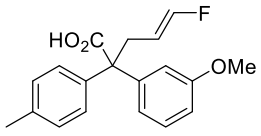
3g

The reaction afforded **3g** in 78% yield as white solid, Mp 147.5-149.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.15 (m, 3H), 7.13-7.05 (m, 5H), 6.26 (dd, J = 85.2 Hz, 10.8 Hz, 1H), 5.18-5.07 (m, 1H), 2.93 (dd, J = 8.0 Hz, 2.0 Hz, 2H), 2.35 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.02, 150.58 (d, $J_{C\text{-}F}$ = 254.7 Hz), 141.51, 138.53, 137.57, 136.89, 129.54, 128.91, 128.68, 127.98, 127.84, 126.06, 107.19 (d, $J_{C\text{-}F}$ = 12.0 Hz), 59.88 (d, $J_{C\text{-}F}$ = 2.9 Hz), 34.08 (d, $J_{C\text{-}F}$ = 10.1 Hz), 21.58, 20.96; ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.63; IR (neat): 3024, 2924, 1697, 1512, 1265, 1103, 910, 741 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{19}H_{18}O_2F$ [M-H]$^-$: 297.1291, Found: 297.1281.



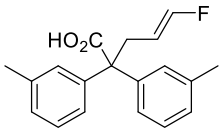
3h

The reaction afforded **3h** in 57% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.24 (m, 3H), 7.22-7.19 (m, 2H), 7.14-7.12 (m, 1H), 7.08 (d, J = 8.0 Hz, 2H), 6.31 (dd, J = 85.2 Hz, 11.2 Hz, 1H), 5.21-5.10 (m, 1H), 3.10-2.90 (m, 2H), 2.32 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 179.82, 150.24 (d, $J_{C\text{-}F}$ = 255.1 Hz), 139.85, 138.01, 137.31, 136.73, 132.35, 128.70, 128.63, 128.55, 127.36, 125.55, 107.27 (d, $J_{C\text{-}F}$ = 12.1 Hz), 59.12 (d, $J_{C\text{-}F}$ = 3.0 Hz), 34.04 (d, $J_{C\text{-}F}$ = 9.9 Hz), 21.30, 20.92; ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.43; IR (neat): 3017, 2924, 1697, 1512, 1265, 1103, 910, 741 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{19}H_{18}O_2F$ [M-H]$^-$: 297.1291, Found: 297.1286.



3i

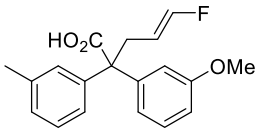
The reaction afforded **3i** in 72% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.10 (m, 1H), 7.17-7.10 (m, 4H), 6.87-6.79 (m, 3H), 6.26 (dd, J = 85.2 Hz, 11.2 Hz, 1H), 5.18-5.07 (m, 1H), 3.74 (s, 3H), 2.92 (dd, J = 8.0 Hz, 1.6 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.80, 159.13, 150.58 (d, $J_{C\text{-}F}$ = 254.9 Hz), 143.18, 138.28, 136.96, 128.86, 128.83, 128.70, 121.43, 115.55, 112.00, 107.14 (d, $J_{C\text{-}F}$ = 12.2 Hz), 59.93 (d, $J_{C\text{-}F}$ = 3.1 Hz), 55.20, 34.05 (d, $J_{C\text{-}F}$ = 10.0 Hz), 20.95; ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.52; IR (neat): 3001, 2940, 1697, 1674, 1489, 1250, 1103, 910, 733 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{19}H_{18}O_3F$ [M-H]$^-$: 313.1240, Found: 313.1229.



3j

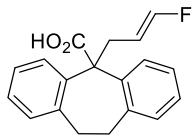
The reaction afforded **3j** in 78% yield as white solid, Mp 136.3-138.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.19 (m, 2H), 7.10-7.06 (m, 6H), 6.26 (dd, J = 85.2 Hz, 11.2 Hz, 1H), 5.18-5.07 (m, 1H), 2.95 (dd, J = 8.0 Hz, 1.6 Hz, 2H), 2.33 (s,

6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.94, 150.57 (d, $J_{C\text{-}F}$ = 254.7 Hz), 141.46, 137.55, 129.58, 127.99, 127.83, 126.14, 107.20 (d, $J_{C\text{-}F}$ = 12.0 Hz), 60.15 (d, $J_{C\text{-}F}$ = 2.9 Hz), 34.11 (d, $J_{C\text{-}F}$ = 10.0 Hz), 21.59; ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.62; IR (neat): 3009, 2376, 1744, 1697, 1651, 1528, 1497, 1396, 1265, 1103, 918, 748 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{19}H_{18}O_2F$ [M-H]$^-$: 297.1291, Found: 297.1308.



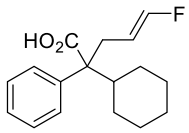
3k

The reaction afforded **3k** in 64% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.18 (m, 2H), 7.10-7.07 (m, 3H), 6.88-6.82 (m, 3H), 6.27 (dd, J = 85.6 Hz, 11.2 Hz, 1H), 5.20-5.08 (m, 1H), 3.76 (s, 3H), 2.97-2.93 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.59, 159.18, 150.64 (d, $J_{C\text{-}F}$ = 255.1 Hz), 143.17, 141.26, 137.64, 129.56, 128.90, 128.12, 127.92, 126.10, 121.55, 115.66, 112.08, 107.20 (d, $J_{C\text{-}F}$ = 12.0 Hz), 60.23 (d, $J_{C\text{-}F}$ = 3.1 Hz), 55.26, 34.16 (d, $J_{C\text{-}F}$ = 10.1 Hz), 21.63; ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.50; IR (neat): 3009, 2955, 1697, 1605, 1489, 1258, 1103, 910, 733, 702 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{19}H_{18}O_3F$ [M-H]$^-$: 313.1240, Found: 313.1260.



3l

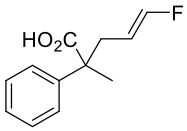
The reaction afforded **3l** in 89% yield as white solid, Mp 148.5-149.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.28 (m, 2H), 7.22-7.16 (m, 4H), 7.14-7.12 (m, 2H), 6.14 (dd, J = 84.8 Hz, 10.8 Hz, 1H), 5.21-5.12 (m, 1H), 3.22-3.14 (m, 2H), 3.10-3.04 (m, 2H), 3.03-2.99 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.05, 150.14 (d, $J_{C\text{-}F}$ = 255.8 Hz), 141.44, 138.56, 130.70, 127.81, 127.26, 126.37, 106.66 (d, $J_{C\text{-}F}$ = 11.9 Hz), 61.70, 38.09, 35.02; ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.09; IR (neat): 3063, 3017, 2623, 1697, 1497, 1258, 1103, 910, 733 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{19}H_{16}O_2F$ [M-H]$^-$: 295.1134, Found: 295.1113.



3m

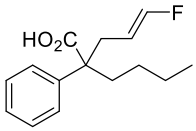
The reaction afforded **3m** in 45% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.30 (m, 2H), 7.26-7.20 (m, 3H), 6.38 (dd, J = 85.2 Hz, 11.2 Hz, 1H), 5.25-5.13 (m, 1H), 2.74-2.58 (m, 2H), 2.08-2.02 (m, 1H), 1.87-1.61 (m, 5H), 1.33-1.19 (m, 2H), 1.07-0.85 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 180.70, 150.16 (d, $J_{C\text{-}F}$ = 254.8 Hz), 138.73, 128.39, 127.78, 126.83, 107.24 (d, $J_{C\text{-}F}$ = 11.4 Hz), 59.39 (d, $J_{C\text{-}F}$ = 2.9 Hz, 1C), 43.63, 31.81 (d, $J_{C\text{-}F}$ = 9.6 Hz), 29.17, 28.13, 26.98, 26.96, 26.40; ^{19}F NMR (376 MHz, $CDCl_3$): δ -

124.94; IR (neat): 3063, 2932, 1697, 1450, 1265, 1103, 910, 748, 702 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{17}H_{20}O_2F$ $[M-H]^-$: 275.1447, Found: 275.1469.



3n

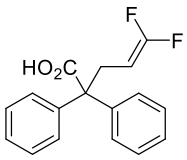
The reaction afforded **3n** in 39% yield as colorless oil, ^1H NMR analysis[6] revealed that the E/Z vlues is 6:1; For the mixture: ^1H NMR (400 MHz, $CDCl_3$): δ 7.38-7.34 (m, 4.64H), 7.30-7.26 (m, 1.16 H), 7.30-7.27 (m, 1.16H), 6.49 (dd, J = 85.2 Hz, 4.8 Hz, 0.16H) (minor), 6.47 (dd, J = 84.8 Hz, 11.2 Hz, 1.0H) (major), 5.25-5.13 (m, 1.0H), 4.69-4.54 (m, 0.16H) (minor), 2.89-2.75 (m, 0.32H) (minor), 2.67-2.47 (m, 2.0H) (major), 1.60 (s, 0.48H) (minor), 1.58 (s, 3.0H) (major); ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.74 (minor), 181.57 (major), 150.54 (d, J_{C-F} = 255.4 Hz), 149.52 (d, J_{C-F} = 258.0 Hz) (minor), 141.81 (minor), 141.72 (major), 128.58, 128.53 (minor), 127.29, 127.22 (minor), 126.12 (minor), 126.05 (major), 106.89 (d, J_{C-F} = 11.1 Hz), 106.27 (d, J_{C-F} = 4.1 Hz) (minor), 53.41, 49.73 (d, J_{C-F} = 3.1 Hz), 49.53 (d, J_{C-F} = 2.6 Hz) (minor), 34.94 (d, J_{C-F} = 9.6 Hz), 32.35 (d, J_{C-F} = 4.5 Hz) (minor), 22.00 (minor), 21.82 (major); ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.68, -127.67 (minor); IR (neat): 3063, 2986, 1697, 1528, 1497, 1273, 1103, 918, 748, 702 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{12}H_{12}O_2F$ $[M-H]^-$: 207.0821, Found: 207.0810.



3o

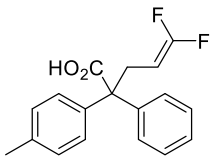
The reaction afforded **3o** in 68% yield as white solid, Mp 126.5-128.1 °C. ^1H NMR analysis[6] revealed that the E/Z vlues is 7:1; For the mixture: (500 MHz, $CDCl_3$): δ 7.37-7.27 (m, 5.7H), 6.46 (dd, J = 85.5 Hz, 5.0 Hz, 0.14H) (minor), 6.43 (dd, J = 85.0 Hz, 11.0 Hz, 1.0H) (major), 5.13-5.04 (m, 1.0H), 4.54-4.42 (m, 0.14H) (minor), 2.98-2.77 (m, 0.28H) (minor), 2.68-2.56 (m, 2.0H) (major), 2.08-1.95 (m, 2.28H), 1.38-1.29 (m, 2.28H), 1.18-1.10 (m, 2.28H), 0.91-0.88 (m, 3.42H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.79 (minor), 181.61 (major), 150.26 (d, J_{C-F} = 255.1 Hz), 149.37 (d, J_{C-F} = 256.8 Hz) (minor), 141.20 (minor), 141.03 (major), 128.49, 128.44 (minor), 127.17, 127.09 (minor), 126.52 (minor), 126.49 (major), 106.46 (d, J_{C-F} = 10.5 Hz), 105.92 (d, J_{C-F} = 4.4 Hz) (minor), 53.60 (d, J_{C-F} = 3.6 Hz), 53.28 (d, J_{C-F} = 2.3 Hz) (minor), 34.13 (minor), 33.50 (major), 30.56 (d, J_{C-F} = 9.8 Hz), 28.20 (d, J_{C-F} = 4.5 Hz) (minor), 26.15 (minor), 26.08 (major), 23.10 (minor), 23.06 (major), 13.91, 13.85 (minor); ^{19}F NMR (282 MHz, $CDCl_3$): δ

-124.71, -127.34 (minor); IR (neat): 2955, 2353, 1697, 1520, 1273, 11103, 918, 764, 748 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{15}H_{188}O_2F$ $[M-H]^-$: 249.1291, Found: 249.1310.



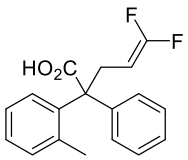
4a

The reaction afforded **4a** in 77% yield as white solid, Mp 85.3-86.5 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.36-7.26 (m, 10H), 4.09-3.98 (m, 1H), 3.06 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.08, 156.68 (dd, J_{C-F} = 287.3 Hz, 283.6 Hz, 1C), 141.24, 128.89, 128.09, 127.38, 74.37 (dd, J_{C-F} = 25.5 Hz, 18.5 Hz), 60.09 (t, J_{C-F} = 2.1 Hz), 31.65 (d, J_{C-F} = 5.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -86.43 (d, J = 41.4 Hz), -89.15 (d, J = 41.4 Hz); IR (neat): 3063, 2932, 2639, 1744, 1705, 1497, 1265, 1011, 756, 702 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{17}H_{13}O_2F_2$ $[M-H]^-$: 287.0884, Found: 287.0859.



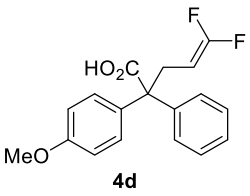
4b

The reaction afforded **4b** in 72% yield as colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.32-7.24 (m, 5H), 7.17-7.11 (m, 4H), 4.01 (dt, J = 25.6 Hz, 6.8 Hz, 1H), 3.03 (d, J = 6.0 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 180.07, 156.62 (dd, J_{C-F} = 287.1 Hz, 283.3 Hz), 141.53, 138.28, 137.09, 128.86, 128.80, 128.74, 128.00, 127.23, 74.50 (dd, J_{C-F} = 25.5 Hz, 18.4 Hz), 31.69, 20.96; ^{19}F NMR (376 MHz, $CDCl_3$): δ -86.79 (d, J = 41.4 Hz), -89.26 (d, J = 41.7 Hz); IR (neat): 3024, 2924, 2639, 1744, 1697, 1512, 1258, 910, 741 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{18}H_{15}O_2F_2$ $[M-H]^-$: 301.1040, Found: 301.1031.



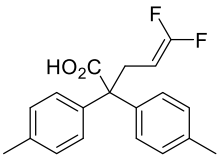
4c

The reaction afforded **4c** in 72% yield as colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40-7.37 (m, 2H), 7.30-7.12 (m, 7H), 4.06-3.95 (m, 1H), 3.19 (dd, J = 14.8 Hz, 8.0 Hz, 1H), 3.05 (dd, J = 14.4 Hz, 7.2 Hz, 1H), 1,95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 179.71, 156.61 (dd, J_{C-F} = 287.0 Hz, 283.8 Hz), 140.77, 139.44, 137.34, 132.48, 128.76, 128.60, 128.10, 127.51, 127.21, 125.54, 74.47 (dd, J_{C-F} = 25.4 Hz, 18.1 Hz), 59.23, 31.12 (d, J_{C-F} = 5.0 Hz), 21.23; ^{19}F NMR (376 MHz, $CDCl_3$): δ -86.43 (d, J = 41.4 Hz), -89.15 (d, J = 41.4 Hz); IR (neat): 3024, 2986, 2631, 1744, 1697, 1450, 1396, 1258, 910, 748 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{18}H_{15}O_2F_2$ $[M-H]^-$: 301.1040, Found: 301.1021.



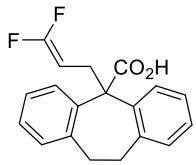
4d

The reaction afforded **4d** in 60% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.21 (m, 7H), 6.86 (d, J = 8.8 Hz, 2H), 4.08-3.97 (m, 1H), 3.81 (s, 3H), 3.03 (d, J = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 179.62, 158.67, 156.64 (dd, $J_{C\text{-}F}$ = 287.1 Hz, 283.3 Hz), 141.59. 133.15, 130.04, 128.79, 128.04, 127.26, 113.42, 74.44 (dd, $J_{C\text{-}F}$ = 25.4 Hz, 18.3 Hz), 59.37 (t, $J_{C\text{-}F}$ = 2.3 Hz), 55.23, 31.75 (d, $J_{C\text{-}F}$ = 4.9 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -86.69 (d, J = 41.5 Hz), -89.21 (d, J = 41.5 Hz); IR (neat): 3009, 2924, 2855, 1744, 1705, 1512, 1265, 1103, 910, 748 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{18}H_{15}O_3F_2$ $[M\text{-}H]^-$: 317.0989, Found: 317.0985.



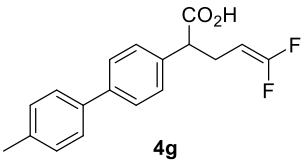
4e

The reaction afforded **4e** in 73% yield as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18-7.11 (m, 8H), 4.08-3.94 (m, 1H), 3.02 (dt, J = 7.8 Hz, 1.8 Hz, 2H), 2.34 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 179.94, 156.58 (dd, $J_{C\text{-}F}$ = 287.0 Hz, 283.0 Hz), 138.37, 137.00, 128.75, 128.72, 74.53 (dd, $J_{C\text{-}F}$ = 25.4 Hz, 18.3 Hz), 59.35 (t, $J_{C\text{-}F}$ = 2.1 Hz, 1C), 31.65 (d, $J_{C\text{-}F}$ = 5.0 Hz), 20.96; ^{19}F NMR (282 MHz, $CDCl_3$): δ -86.91 (d, J = 42.9 Hz), -89.32 (d, J = 42.6 Hz); IR (neat): 2978, 2924, 1744, 1697, 1512, 1265, 910, 741 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{19}H_{17}O_2F_2$ $[M\text{-}H]^-$: 315.1197, Found: 315.1172.



4f

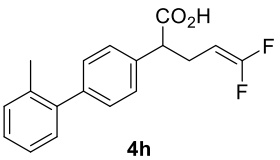
The reaction afforded **4f** in 77% yield as white solid, Mp 147.5-149.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.27 (m, 2H), 7.22-7.17 (m, 4H), 7.15-7.12 (m, 2H), 4.11-4.02 (m, 1H), 3.23-3.15 (m, 2H), 3.13-3.06 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 180.70, 156.77 (dd, $J_{C\text{-}F}$ = 287.5 Hz, 283.9 Hz), 141.37, 138.29, 130.75, 128.11, 127.38, 126.36, 74.10 (dd, $J_{C\text{-}F}$ = 25.4 Hz, 18.6 Hz), 61.48, 35.40, 35.10; ^{19}F NMR (376 MHz, $CDCl_3$): δ -86.44 (d, J = 42.9 Hz), -89.63 (d, J = 46.6 Hz); IR (neat): 3024, 2940, 2631, 1744, 1697, 1450, 1396, 1265, 1211, 910, 748 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{19}H_{15}O_2F_2$ $[M\text{-}H]^-$: 313.1040, Found: 313.1024.



4g

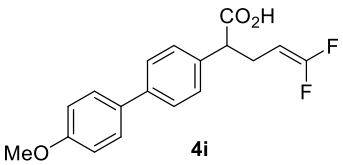
The reaction afforded **4g** in 45% yield as white solid, Mp 89.2-92.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 9.2 Hz, 2H), 4.20-4.09 (m, 1H), 3.64 (t, J = 8.0 Hz, 1H), 2.79-2.72 (m, 1H), 2.55-2.47 (m, 1H), 2.39 (s, 3H); ^{13}C NMR (125 MHz,

$CDCl_3$): δ 178.59, 156.77 (dd, $J_{C\text{-}F}$ = 287.1 Hz, 284.5 Hz), 140.83, 137.63, 137.27, 135.83, 129.54, 128.33, 127.41, 126.93, 75.31 (dd, $J_{C\text{-}F}$ = 24.3 Hz, 19.9 Hz), 50.91, 25.95 (d, $J_{C\text{-}F}$ = 4.9 Hz), 21.12; ^{19}F NMR (376 MHz, $CDCl_3$): δ -86.89 (d, J = 42.1 Hz), -88.93 (d, J = 42.1 Hz); IR (neat): 3024, 2924, 2376, 1744, 1697, 1497, 1412, 1265, 910, 748 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{18}H_{15}O_2F_2$ [M-H]$^-$: 301.1040, Found: 301.1071.



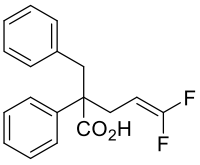
4h

The reaction afforded **4h** in 55% yield as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.29 (m, 4H), 7.27-7.20 (m, 5H), 4.25-4.11 (m, 1H), 3.67 (d, J = 7.8 Hz, 1H), 2.83-2.72 (m, 1H), 2.59-2.48 (m, 1H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 179.02, 156.77 (dd, $J_{C\text{-}F}$ = 287.3 Hz, 284.5 Hz), 141.58, 141.20, 135.57, 135.32, 130.35, 129.73, 129.66, 127.62, 127.37, 125.78, 75.29 (dd, $J_{C\text{-}F}$ = 24.1 Hz, 19.9 Hz), 51.03 (t, $J_{C\text{-}F}$ = 2.6 Hz), 26.05 (d, $J_{C\text{-}F}$ = 4.9 Hz), 20.45; ^{19}F NMR (282 MHz, $CDCl_3$): δ -86.95 (d, J = 42.3 Hz), -89.00 (d, J = 42.0 Hz); IR (neat): 3024, 2924, 2654, 1744, 1705, 1412, 1265, 910, 733 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{18}H_{15}O_2F_2$ [M-H]$^-$: 301.1040, Found: 301.1071.



4i

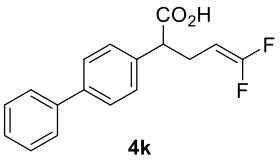
The reaction afforded **4i** in 39% yield as white solid, Mp 121.2-123.0 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53-7.50 (m, 4H), 7.35 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 9.0 Hz, 2H), 4.19-4.10 (m, 1H), 3.85 (s, 3H), 3.64 (t, J = 8.0 Hz, 1H), 2.79-2.72 (m, 1H), 2.54-2.48 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.12, 159.24, 156.72 (dd, $J_{C\text{-}F}$ = 286.8 Hz, 284.4 Hz), 140.44, 135.52, 133.01, 128.32, 128.29, 128.08, 127.11, 114.22, 75.30 (dd, $J_{C\text{-}F}$ = 24.0 Hz, 19.9 Hz), 55.33, 50.81, 25.93 (d, $J_{C\text{-}F}$ = 4.9 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -86.91 (d, J = 42.0 Hz), -88.96 (d, J = 42.3 Hz); IR (neat): 2924, 2855, 2315, 1744, 1713, 1273, 910, 748 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{18}H_{15}O_3F_2$ [M-H]$^-$: 317.0989, Found: 317.1006.



4j

The reaction afforded **4j** in 50% yield as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.28 (m, 3H), 7.26-7.14 (m, 5H), 6.92-6.89 (m, 2H), 4.16-4.02 (m, 1H), 3.35 (dd, J = 42.9 Hz, 13.5 Hz , 2H), 2.63 (dd, J = 7.5 Hz, 2.4 Hz , 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.91, 156.70 (dd, $J_{C\text{-}F}$ = 287.5 Hz, 284.5 Hz), 140.48, 136.02, 130.20, 128.55, 128.09, 127.49, 126.86, 126.70, 73.84 (dd, $J_{C\text{-}F}$ = 24.8 Hz, 19.0 Hz), 55.05,

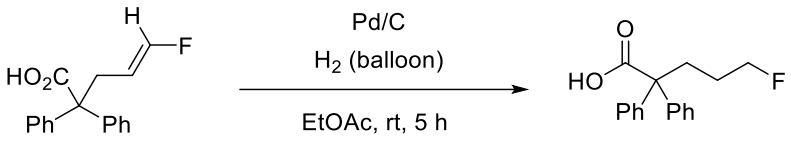
41.00, 27.39 (d, $J_{C\text{-}F}$ = 4.4 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -86.97 (d, J = 42.3 Hz), -89.02 (d, J = 42.3 Hz); IR (neat): 3348, 2924, 2855, 2315, 1667, 1396, 1273, 910, 748 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{18}H_{15}O_2F_2$ [M-H]$^-$: 301.1040, Found: 301.1071.



4k

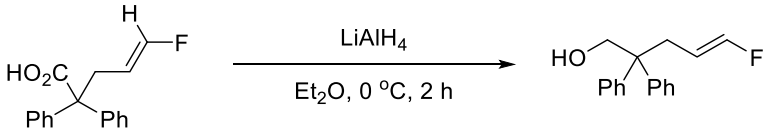
The reaction under condition B afforded **4k** in 45% yield as white solid, Mp 97.5-98.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 8.0 Hz, 4H), 7.46-7.35 (m, 5H), 4.21-4.10 (m, 1H), 3.66 (t, J = 8.0 Hz, 1H), 2.81-2.73 (m, 1H), 2.56-2.48 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.38, 156.74 (dd, $J_{C\text{-}F}$ = 286.9 Hz, 24.4 Hz), 140.86, 140.48, 136.15, 128.78, 128.34, 127.58, 127.43, 127.07, 75.26 (dd, $J_{C\text{-}F}$ = 24.1 Hz, 19.9 Hz), 50.88, 25.94 (d, $J_{C\text{-}F}$ = 4.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -86.89 (d, J = 42.1 Hz), -88.93 (d, J = 42.1 Hz); IR (neat): 3032, 2932, 1744, 1705, 1412, 1265, 910, 748 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{17}H_{13}O_2F_2$ [M-H]$^-$: 287.0884, Found: 287.0891.

6. Product elaboration



3a **5**

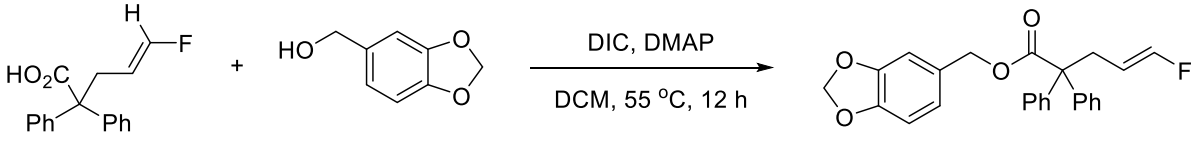
To a solution of **3a** (0.15 mmol, 40.5 mg) in EtOAc (3.0 mL), Pd/C (5.0 mg, 10 wt%) were added with H_2 balloon at room temperature. The reaction mixture was stirred for 5 h at room temperature and monitored by TLC until full conversion of **3a**. Then the reaction mixture was diluted with EtOAc, filtered, and dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography using CH_2Cl_2/MeOH (20:1, v/v) as the eluent to afford **5** in 39.5 mg with 97% yield as white solid. Mp 122.1-124.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.26 (m, 10H), 4.37 (dt, J = 47.5 Hz, 6.0 Hz, 2H), 2.51-2.48 (m, 2H), 1.53-1.45 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 179.83, 142.01, 128.95, 128.04, 127.12, 84.10 (d, $J_{C\text{-}F}$ = 164.3 Hz), 59.84, 33.74 (d, $J_{C\text{-}F}$ = 4.9 Hz), 26.55 (d, $J_{C\text{-}F}$ = 19.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -218.61; IR (neat): 3009, 2970, 2631, 1697, 1497, 1273, 764, 748 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{17}H_{16}O_2F$ $[M\text{-}H]^-$: 271.1134, Found: 271.1136.



3a **6**

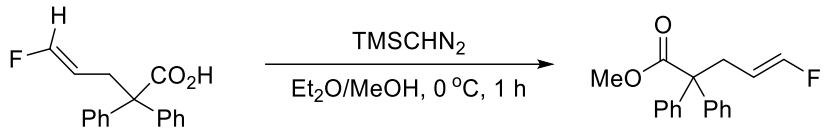
To a solution of **3a** (0.15 mmol, 40.5 mg) in Et_2O (2 mL), $LiAlH_4$ (6.8 mg, 0.18 mmol, 1.0 equiv) were added at 0 °C, then the resulting mixture was stirred for 0.5 h at 0 °C. After the full conversion of **3a** monitored by TLC analysis, the reaction was quenched with H_2O and extracted with Et_2O (10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography using PE/EtOAc (8:1, v/v) as eluent to afford **6** in 35.0 mg with 83% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.29 (m, 4H), 7.26-7.21 (m, 2H), 7.17-7.14 (m, 4H), 6.45 (dd, J = 85.6 Hz, 11.2 Hz, 1H), 5.01-4.90 (m, 1H), 4.14 (d, J = 6.8 Hz, 2H), 2.80 (dt, J = 8.0 Hz, 1.6 Hz, 2H), 1.05 (t, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 150.14 (d, $J_{C\text{-}F}$ = 254.7 Hz), 144.78, 128.33, 128.05, 126.58, 107.20 (d, $J_{C\text{-}F}$ = 10.9 Hz), 67.36, 51.46 (d, $J_{C\text{-}F}$ = 2.8 Hz), 31.78 (d, $J_{C\text{-}F}$ = 9.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -125.00; IR (neat): 3395, 3024, 2886, 1674, 1497, 1273, 1258, 1096, 748, 702 cm^{-1}; MS (EI): 256 (M^+, 0.1), 197 (100), 105 (68), 91 (47), 165 (20), 147 (20). HRMS (EI): Exact mass calcd for: $C_{17}H_{17}F_7O$ $[M]^+$:256.1263, Found: 256.1267.



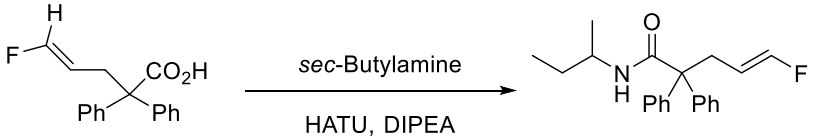
3a (1.2 equivs) **7**

To a solution of **3a** (0.15 mmol, 40.5 mg) in CH_2Cl_2 (2.0 mL), piperonyl alcohol (0.3 mmol, 27.0 mg), *N*,*N*'-diisopropylcarbodiimide (DIC, 0.20 mmol, 24.6 mg), and 4-dimethylaminopyridine (DMAP, 0.03 mmol, 6.6 mg) were added at room temperature. The resulting mixture was warmed to 55 °C and stirred until complete conversion of **3a** by TLC analysis. The solvent was then removed under reduced pressure, and the residue was purified by flash column chromatography using a elution (PE/EtOAc = 20/1 to 10/1, v/v). The desired product **7** was obtained as a colorless oil with a yield of 44% (26.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.19 (m, 10H), 6.69 (d, J = 8.0 Hz, 1H), 6.64-6.61 (m, 1H), 6.57 (d, J = 2.0 Hz, 1H), 6.16 (dd, J = 85.2 Hz, J = 11.2 Hz, 1H), 5.92 (s, 2H), 5.15-5.05 (m, 1H), 5.02 (s, 2H), 3.03-2.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.30, 150.51 (d, $J_{C\text{-}F}$ = 254.9 Hz), 147.61, 147.46, 141.83, 129.22, 128.96, 127.90, 127.01, 121.93, 108.71, 108.04, 107.18 (d, $J_{C\text{-}F}$ = 11.9 Hz), 101.05, 66.94, 60.43 (d, $J_{C\text{-}F}$ = 3.1 Hz), 34.22 (d, $J_{C\text{-}F}$ = 9.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.57; IR (neat): 3063, 2893, 2353, 1728, 1674, 1497, 1443, 1103, 1042, 918, 810, 764, 702 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{25}H_{21}O_4FNa$ $[M+Na]^+$: 427.1310, Found: 427.1316.



3a **8**

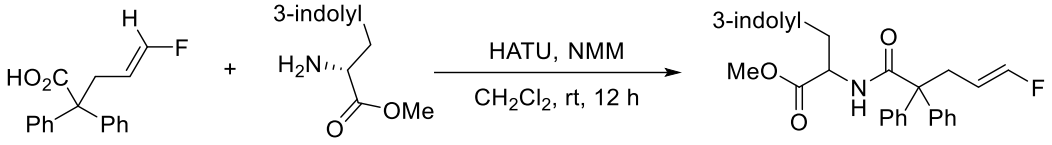
To a 10 mL flask were added **3a** (0.15 mmol, 40.5 mg), Et2O (2.0 mL) and MeOH (0.5 mL), and the hexane solution of TMSCHN2 (0.15 mL, 2 mol/L, 0.3 mmol) was added at 0 °C. The mixture was stirred at that temperature till full conversion of **3a**. Then the solvent was removed under reduced pressure, and the residue was purified by column chromatography using PE as eluent to afford **8** in 40.5 mg with 95% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.18 (m, 10H), 6.33-6.08 (m, 1H), 5.16-5.05 (m, 1H), 3.67 (s, 3H), 2.94 (dt, J = 8.0 Hz, 1.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.14, 150.50 (d, $J_{C\text{-}F}$ = 254.4 Hz), 142.01, 128.88, 127.95, 127.04, 107.30 (d, $J_{C\text{-}F}$ = 12.0 Hz), 60.43 (d, $J_{C\text{-}F}$ = 3.1 Hz), 52.44, 34.35 (d, $J_{C\text{-}F}$ = 10.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.66; IR (neat): 3063, 1728, 1674, 1497, 1258, 1227, 1103, 764, 748, 702 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{18}H_{17}O_2FNa$ $[M+Na]^+$: 307.1099, Found: 307.1105.



3a **9**

To a solution of **3a** (0.15 mmol, 40.5 mg) in DMF (2 mL), *sec*-butylamine (0.18 mmol, 13.2 mg, 1.2 equivs), *o*-(7-Azabenzotriazol-1-yl)-*N,N,N′,N′*-tramethyluronium hexafluorophosphate (HATU，0.3 mmol, 114.0 mg) and N,N-Diisopropylethylamine (DIPEA, 0.45 mmol, 58.0 mg) were added at room temperature. The resulting mixture was stirred for 12 h at room temperature till full conversion of **3a**. Then the reaction was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography using PE/EtOAc (10:1, v/v) as eluent to afford **9** in 44.5 mg with 91% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.24 (m, 10H), 6.23 (dd, J = 85.6 Hz, 11.2 Hz, 1H), 5.34-5.23 (m, 1H), 5.16 (d, J = 8.4 Hz, 1H), 3.93-3.83 (m, 1H), 2.99 (d, J = 8.0 Hz, 2H), 1.38-1.17 (m, 2H), 0.98 (d, J = 6.4 Hz, 3H), 0.67 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.92, 150.25 (d, $J_{C\text{-}F}$ = 254.0 Hz), 142.57, 142.31, 128.93, 128.87, 128.35,

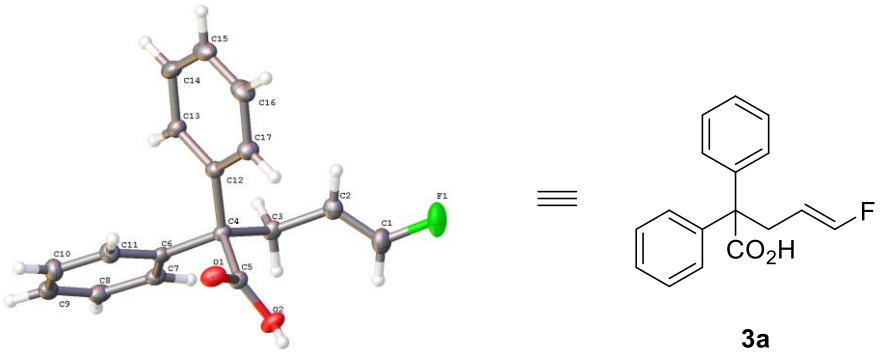
128.30, 127.10, 127.08, 108.19 (d, $J_{C\text{-}F}$ = 11.7 Hz), 60.79 (d, $J_{C\text{-}F}$ = 2.9 Hz), 47.00, 34.71 (d, $J_{C\text{-}F}$ = 9.9 Hz), 29.25, 20.08, 10.03; ^{19}F NMR (376 MHz, $CDCl_3$): δ -125.50; IR (neat): 3024, 2970, 1667, 1651, 1512, 1450, 1273, 1103, 918, 764, 748, 702 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{21}H_{24}ONFNa$ $[M+Na]^+$: 348.1739, Found: 348.1734.



To a solution of **3a** (0.15 mmol, 40.5 mg) in CH_2Cl_2 (2 mL), then *L*-Tryptophan ester (0.18 mmol, 39.2 mg, 1.2 equivs), HATU (0.3 mmol, 114.0 mg,) and 4-Methylmorpholine (NMM, 0.45 mmol, 45.5 mg) were added at room temperature. The resulting mixture was stirred for 12 h at room temperature till full conversion of **3a**. Then the reaction was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography using PE/EtOAc (10:1 to 2:1, v/v) as eluent to afford **10** in 60.5 mg with 86% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.26-7.23 (m, 3H), 7.21-7.15 (m, 6H), 7.08-7.02 (m, 3H), 6.46 (d, J = 2.4 Hz, 1H), 6.19 (dd, J = 85.6 Hz, 10.8 Hz, 1H), 5.98 (d, J = 7.6 Hz, 1H), 5.27-5.15 (m, 1H), 4.89 (dd, J = 12.8 Hz, 6.4 Hz, 1H), 3.65 (s, 3H), 3.19 (t, J = 4.8 Hz, 2H), 2.96-2.92 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.41, 172.16, 150.28 (d, $J_{C\text{-}F}$ = 253.9 Hz), 142.21, 141.84, 135.99, 129.00, 128.88, 128.25, 128.22, 127.21, 127.10, 126.95, 122.44, 122.28, 119.71, 118.47, 111.08, 109.70, 108.01 (d, $J_{C\text{-}F}$ = 12.0 Hz), 60.53 (d, $J_{C\text{-}F}$ = 2.8 Hz), 52.82, 52.29, 34.60 (d, $J_{C\text{-}F}$ = 10.0 Hz), 27.14; ^{19}F NMR (376 MHz, $CDCl_3$): δ -125.23; IR (neat): 3009, 1667, 1450, 1273, 1258, 1196, 1103, 764, 748 cm^{-1}; HRMS (ESI): Exact mass calcd for: $C_{29}H_{27}O_3N_2FNa$ $[M+Na]^+$: 493.1895, Found: 493.1898.

7. X-ray crystallographic data

Single crystals of **3a** were obtained by slow diffusion of the solution of **3a** in PE/EtOAc at room temperature. Data intensity of **3a** (CCDC 2337631) was collected using a 'Bruker APEX-II CCD' diffractometer at 150.00(10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically ideal positions and refined isotropically. Crystal data for $C_{17}H_{15}O_2F$ (M =270.29 g/mol): orthorhombic, space group Pccn (no. 33), a = 13.7828(3) Å, b = 27.4622(6) Å, c = 7.5425(2) Å, V = 2854.88(12) Å^3, Z = 8, T = 224.00 K, μ(Cu Kα) = 0.472 mm^{-1}, *Dcalc* = 1.258 g/cm^3, 24007 reflections measured (2.800° ≤ 2Θ ≤ 55.020°), 2715 unique (R_{int} = 0.0685) which were used in all calculations. The final R_1 was 0.0699 (I > 2σ(I)) and wR_2 was 0.1641 (all data).



X-ray of **3a**

Table S5 Crystal data and structure refinement for 3a.

Identification code	**3a**
Empirical formula	$C_{17}H_{15}FO_2$
Formula weight	270.29
Temperature/K	224.00
Wavelength	1.34139 Å
Crystal system	Orthorhombic
Space group	Pccn

a/ Å	a = 13.7828(3)
b/ Å	b = 27.4622(6)
b/ Å	c = 7.5425(2)
Volume/$Å^3$	2854.88(12)
Z	8
$\rho_{calc}g/cm^3$	1.258
μ/mm^{-1}	0.472
F(000)	1136
Crystal size/mm^3	0.17 × 0.17 × 0.05
2Θ range for data collection/°	2.800 to 55.020
Index ranges	-16≤h≤16, -33≤k≤29, -9≤l≤8
Reflections collected	26007
Independent reflections	2715 [R_{int} = 0.0685]
Completeness to theta = 53.594°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.6146
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2715/0/182
Goodness-of-fit on F^2	1.250
Final R indices [I>2sigma(I)]	R_1 = 0.0699, wR_2 = 0.1622
R indices (all data)	R_1 = 0.0748, wR_2 = 0.1641
Extinction coefficient	0.0034(3)

Table S6 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for 3a. Ueq is defined as 1/3 of the trace of the orthogonalised UIJ tensor.

Atom	X	y	z	U(eq)
F1	6441(2)	4774(1)	-1897(3)	74(1)

O1	4362(2)	4471(1)	4617(3)	40(1)
O2	5880(2)	4672(1)	3896(3)	41(1)
C1	6583(3)	4528(1)	-349(5)	50(1)
C2	6013(2)	4173(1)	122(5)	37(1)
C3	6188(2)	3883(1)	1772(4)	32(1)
C4	5344(2)	3870(1)	3130(4)	26(1)
C5	5180(2)	4378(1)	3898(4)	28(1)
C6	5607(2)	3555(1)	4760(4)	28(1)
C7	6530(2)	3363(1)	5025(4)	32(1)
C8	6713(2)	3064(1)	6474(5)	40(1)
C9	5999(3)	2955(1)	7683(5)	42(1)
C10	5083(3)	3156(1)	7459(5)	43(1)
C11	4894(2)	3451(1)	6011(4)	37(1)
C12	4439(2)	3666(1)	2210(4)	29(1)
C13	4308(2)	3164(1)	2116(4)	35(1)
C14	3527(3)	2964(1)	1205(5)	44(1)
C15	2878(3)	3263(2)	354(5)	48(1)
C16	2995(3)	3758(2)	412(5)	49(1)
C17	3779(2)	3962(1)	1337(5)	38(1)

Table S7 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
F1	98(2)	60(2)	64(2)	30(1)	17(2)	4(1)
O1	28(1)	36(1)	56(2)	-12(1)	3(1)	4(1)
O2	37(1)	29(1)	57(2)	-12(1)	10(1)	-7(1)
C1	63(2)	41(2)	47(2)	11(2)	4(2)	0(2)
C2	37(2)	37(2)	37(2)	-1(1)	6(2)	4(1)
C3	31(2)	26(1)	37(2)	-3(1)	6(1)	3(1)

C4	24(1)	24(1)	32(2)	-1(1)	0(1)	0(1)
C5	24(1)	26(1)	34(2)	1(1)	0(1)	2(1)
C6	31(2)	22(1)	31(2)	-4(1)	-3(1)	-1(1)
C7	30(2)	28(2)	39(2)	-4(1)	-4(1)	-1(1)
C8	40(2)	31(2)	48(2)	-2(2)	-15(2)	1(1)
C9	56(2)	32(2)	39(2)	5(2)	-12(2)	-5(2)
C10	49(2)	44(2)	36(2)	4(2)	5(2)	-4(2)
C11	35(2)	39(2)	37(2)	-1(1)	3(1)	2(1)
C12	26(1)	31(2)	31(2)	-3(1)	0(1)	-2(1)
C13	38(2)	32(2)	34(2)	-2(1)	3(1)	-6(1)
C14	47(2)	44(2)	39(2)	-6(2)	4(2)	-20(2)
C15	37(2)	68(2)	40(2)	-8(2)	1(2)	-18(2)
C16	36(2)	68(2)	43(2)	2(2)	-9(2)	2(2)
C17	35(2)	38(2)	42(2)	0(2)	-5(2)	0(1)

Table S8 Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C1	1.362(4)	C8	H8	0.9400
O1	C5	1.276(3)	C8	C9	1.375(5)
O2	H2	0.8300	C9	H9	0.9400
O2	C5	1.257(3)	C9	C10	1.388(5)
C1	H1	0.9400	C10	H10	0.9400
C1	C2	1.301(5)	C10	C11	1.386(5)
C2	H2A	0.9400	C11	H11	0.9400
C2	C3	1.497(4)	C12	C13	1.392(4)
C3	H3A	0.9800	C12	C17	1.387(4)
C3	H3B	0.9800	C13	H13	0.9400
C3	C4	1.551(4)	C13	C14	1.389(5)
C4	C5	1.527(4)	C14	H14	0.9400

C4	C6	1.547(4)	C14	C15	1.372(5)
C4	C12	1.534(4)	C15	H15	0.9400
C6	C7	1.391(4)	C15	C16	1.371(5)
C6	C11	1.393(4)	C16	H16	0.9400
C7	H7	0.9400	C16	C17	1.402(5)
C7	C8	1.389(4)	C17	H17	0.9400

Table S9 Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	O2	H2	109.5	C9	C8	C7	121.4(3)
F1	C1	H1	119.4	C9	C8	H8	119.3
C2	C1	F1	121.2(4)	C8	C9	H9	120.5
C2	C1	H1	119.4	C8	C9	C10	118.9(3)
C1	C2	H2A	119	C10	C9	H9	120.5
C1	C2	C3	121.9(3)	C9	C10	H10	120
C3	C2	H2A	119	C11	C10	C9	120.0(3)
C2	C3	H3A	108.3	C11	C10	H10	120
C2	C3	H3B	108.3	C6	C11	H11	119.3
C2	C3	C4	116.1(2)	C10	C11	C6	121.4(3)
H3A	C3	H3B	107.4	C10	C11	H11	119.3
C4	C3	H3A	108.3	C13	C12	C4	119.5(3)
C4	C3	H3B	108.3	C17	C12	C4	122.2(3)
C5	C4	C3	109.9(2)	C17	C12	C13	118.1(3)
C5	C4	C6	104.2(2)	C12	C13	H13	119.5
C5	C4	C12	112.7(2)	C14	C13	C12	121.1(3)
C6	C4	C3	111.2(2)	C14	C13	H13	119.5
C12	C4	C3	108.6(2)	C13	C14	H14	120
C12	C4	C6	110.2(2)	C15	C14	C13	120.1(3)
O1	C5	C4	118.3(2)	C15	C14	H14	120

O2	C5	O1	123.5(3)	C14	C15	H15	120
O2	C5	C4	118.1(2)	C16	C15	C14	120.0(3)
C7	C6	C4	122.8(3)	C16	C15	H15	120
C7	C6	C11	118.0(3)	C15	C16	H16	119.9
C11	C6	C4	119.2(3)	C15	C16	C17	120.2(3)
C6	C7	H7	119.9	C17	C16	H16	119.9
C8	C7	C6	120.2(3)	C12	C17	C16	120.5(3)
C8	C7	H7	119.9	C12	C17	H17	119.8
C7	C8	H8	119.3	C16	C17	H17	119.8

Table S10 Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F1	C1	C2	C3	176.9(3)	C6	C4	C5	O2	94.3(3)
C1	C2	C3	C4	123.2(4)	C6	C4	C12	C13	-36.9(4)
C2	C3	C4	C5	-65.9(3)	C6	C4	C12	C17	148.3(3)
C2	C3	C4	C6	179.3(2)	C6	C7	C8	C9	-0.6(5)
C2	C3	C4	C12	57.9(3)	C7	C6	C11	C10	-1.5(5)
C3	C4	C5	O1	159.9(3)	C7	C8	C9	C10	-1.1(5)
C3	C4	C5	O2	-24.9(4)	C8	C9	C10	C11	1.5(5)
C3	C4	C6	C7	7.1(4)	C9	C10	C11	C6	-0.2(5)
C3	C4	C6	C11	-171.9(3)	C11	C6	C7	C8	1.9(4)
C3	C4	C12	C13	85.1(3)	C12	C4	C5	O1	38.5(4)
C3	C4	C12	C17	-89.7(3)	C12	C4	C5	O2	-146.2(3)
C4	C6	C7	C8	-177.1(3)	C12	C4	C6	C7	127.6(3)
C4	C6	C11	C10	177.6(3)	C12	C4	C6	C11	-51.4(3)
C4	C12	C13	C14	-176.3(3)	C12	C13	C14	C15	1.0(5)
C4	C12	C17	C16	175.8(3)	C13	C12	C17	C16	0.9(5)
C5	C4	C6	C7	-111.3(3)	C13	C14	C15	C16	-0.5(5)
C5	C4	C6	C11	69.7(3)	C14	C15	C16	C17	0.1(6)

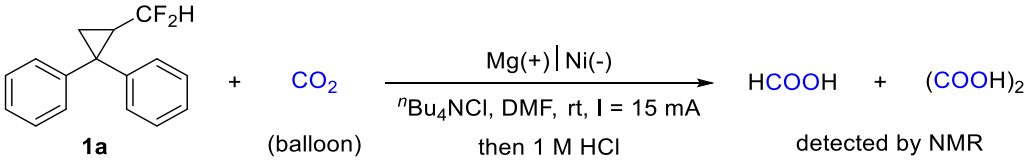
C5	C4	C12	C13	-152.8(3)	C15	C16	C17	C12	-0.4(5)
C5	C4	C12	C17	32.4(4)	C17	C12	C13	C14	-1.2(5)
C6	C4	C5	O1	-80.9(3)					

Table S11 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3a.

Atom	x	y	z	U(eq)
H2	5687	4946	4199	61
H1	7103	4617	391	60
H2A	5476	4097	-594	44
H3A	6763	4015	2366	38
H3B	6339	3548	1426	38
H7	7030	3435	4221	39
H8	7338	2934	6630	47
H9	6130	2748	8647	51
H10	4591	3091	8290	52
H11	4270	3584	5870	44
H13	4754	2956	2678	42
H14	3443	2625	1171	52
H15	2352	3127	-269	58
H16	2549	3962	-169	59
H17	3857	4302	1367	46

8. Mechanistic studies

8.1 Investigation of the formation of CO_2 radical anion



The electroreduction was carried out under the standard reaction conditions. After that, the reaction mixture was acidized with HCl aqueous (2 N). The aqueous layer was collected and concentrated in vacuo, and 2.0 mL D_2O was added. The aqueous phase was analyzed by crude ^1H NMR and ^{13}C NMR. The formic acid and oxalic acid were detected.[4] Therefore, the CO_2 radical anion might be generated through single electron transfer reduction at the cathode.

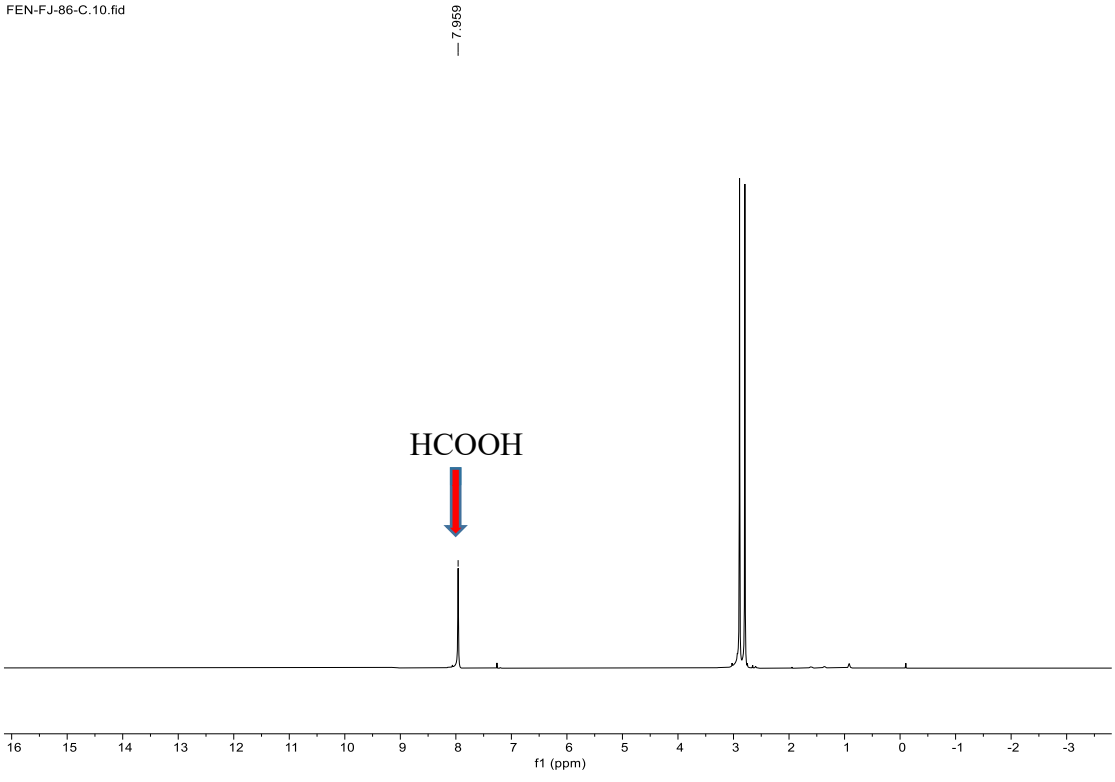


Figure S1. ^1H NMR spectrum of the aqueous

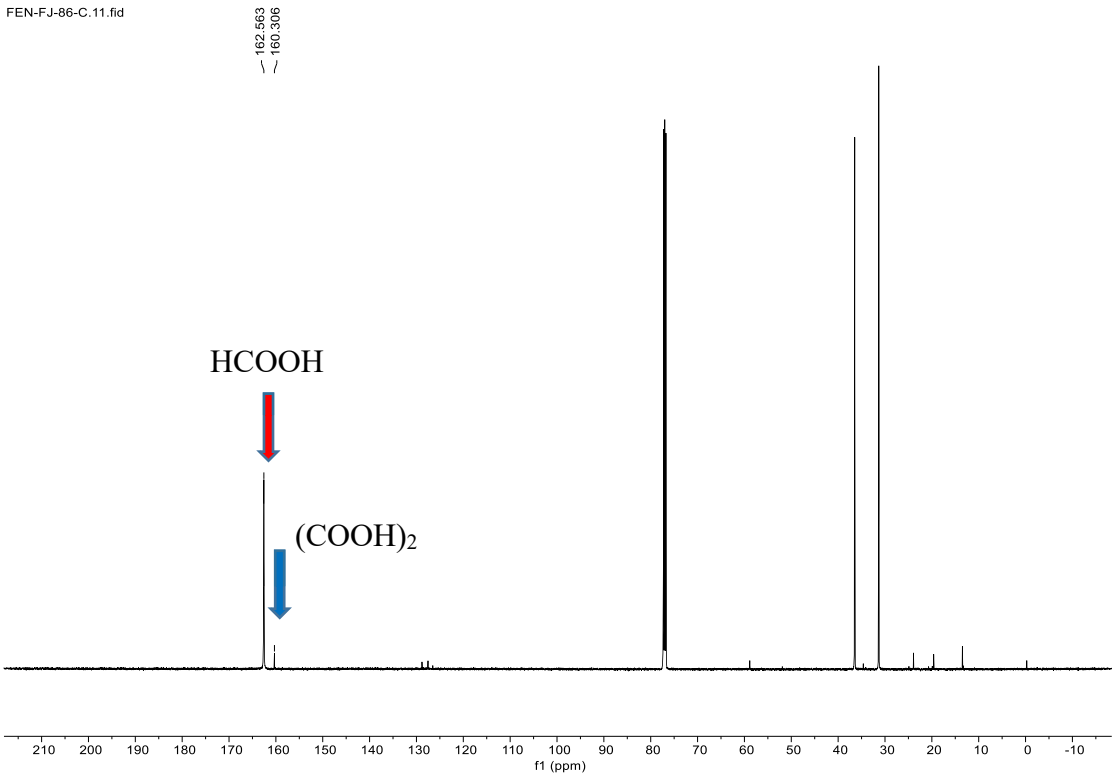
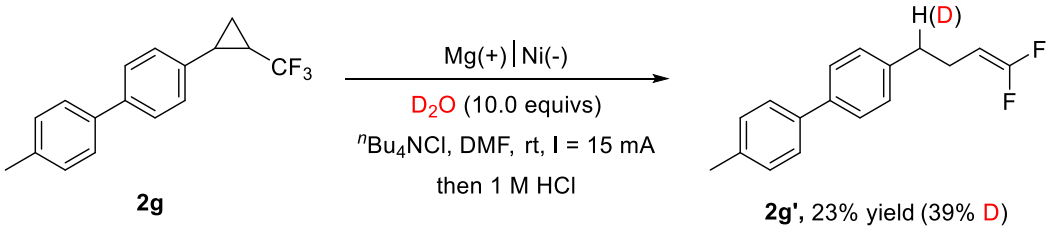


Figure S2. ^{13}C NMR spectrum of the aqueous

8.2 Trapping of carbanion intermediates with deuterium water



2g **2g'**, 23% yield (39% D)

To a 10 mL three-neck flask containing a stir bar was added $^{n}Bu_4NCl$ (166.8 mg, 0.6 mmol, 0.1 M), D_2O (10 equivs), followed by the addition of **2g** (0.2 mmol). Then the flask was installed with Mg-plate (30 mm x 10 mm x 0.5 mm) as anode and Ni-plate (30 mm x 10 mm x 0.5 mm) as cathode. Then the cell was evacuated and back-filled under N_2 flow (this procedure was repeated three times), and anhydrous DMF (6 mL) was added via a syringe. The electroreduction was performed at 15 mA of constant current for 12 h with N_2 balloon at room temperature. After that, the reaction mixture was transferred to a 50 mL Erlenmeyer flask and acidized with HCl (2 N, 10 mL) at 0 °C. The aqueous layer extracted with EtOAc (3 x 20 mL) and the combined organics were washed with saturated salt solution (2 x 20 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product

was purified by column chromatography using dichloromethane as the eluent to afford the desired product **2g'**. These results indicate that the carbanion intermediate could be formed in this electrochemical system. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53-7.48 (m, 4H), 7.25-7.23 (m, 4H), 4.27-4.21 (m, 1H), 2.72 (t, J = 9.0 Hz, 1.6H), 2.40 (s, 3H), 2.36-2.30 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.32 (dd, $J_{C\text{-}F}$ = 285.4 Hz, 283.3 Hz), 139.71, 139.02, 138.08, 136.84, 129.44, 128.76, 126.95, 126.82, 50.88, 35.28 (t, $J_{C\text{-}F}$ = 2.3 Hz), 23.96 (dd, $J_{C\text{-}F}$ = 9.4 Hz, 4.3 Hz), 21.07; ^{19}F NMR (282 MHz, $CDCl_3$): δ -88.89 (d, J = 47.1 Hz), -90.89 (dd, J = 47.1 Hz, 2.3 Hz); HRMS (EI): Exact mass calcd for: $C_{17}H_{15}DF_2$ $[M]^+$: 295.1283, Found: 295.1278.

8.3 Cyclic voltammetry studies

The cyclic voltammetry was carried out with a Shanghai Chenhua CHI760E workstation. A glassy-carbon electrode (3mm-diameter, disc-electrode) was used as the working electrode, a Pt plate was used as the auxiliary electrode and SCE (saturated calomel electrode) as the reference electrode. All of the samples should be bubbled with N_2 for 5 min before testing except the cases with CO_2. The measurements were carried out at a scan rate of 100 mV s^{-1} in DMF/$^{n}Bu_4NCl$ (0.1 M).

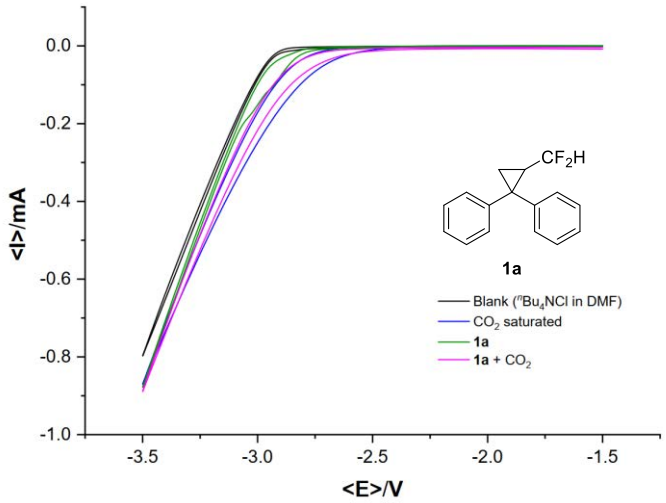


Figure S3. Cyclic voltammetry (DMF, 0.1M $^{n}Bu_4NCl$, 100 mVs^{-1}) using glassy carbon as the working electrode. Cyclic voltammograms of CO_2, **1a** (0.02 mmol), and their mixtures.

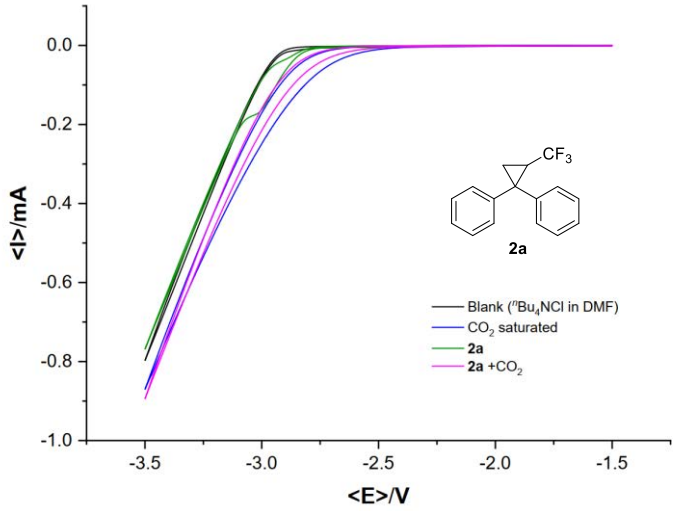


Figure S4. Cyclic voltammetry (DMF, 0.1M $^{n}Bu_4NCl$, 100 mVs^{-1}) using glassy carbon as the working electrode. Cyclic voltammograms of CO_2, **2a** (0.02 mmol), and their mixtures.

9. References

[1] Y.-Q. Ning, X.-Y. Zhang, Y. Gai, Y.-Q. Dong, P. Sivaguru, Y.-Y. Wang, B. R. P. Reddy, G. Zanoni and X.-H. Bi, *Angew. Chem. Int. Ed*. 2020, **59**, 6473-6481.

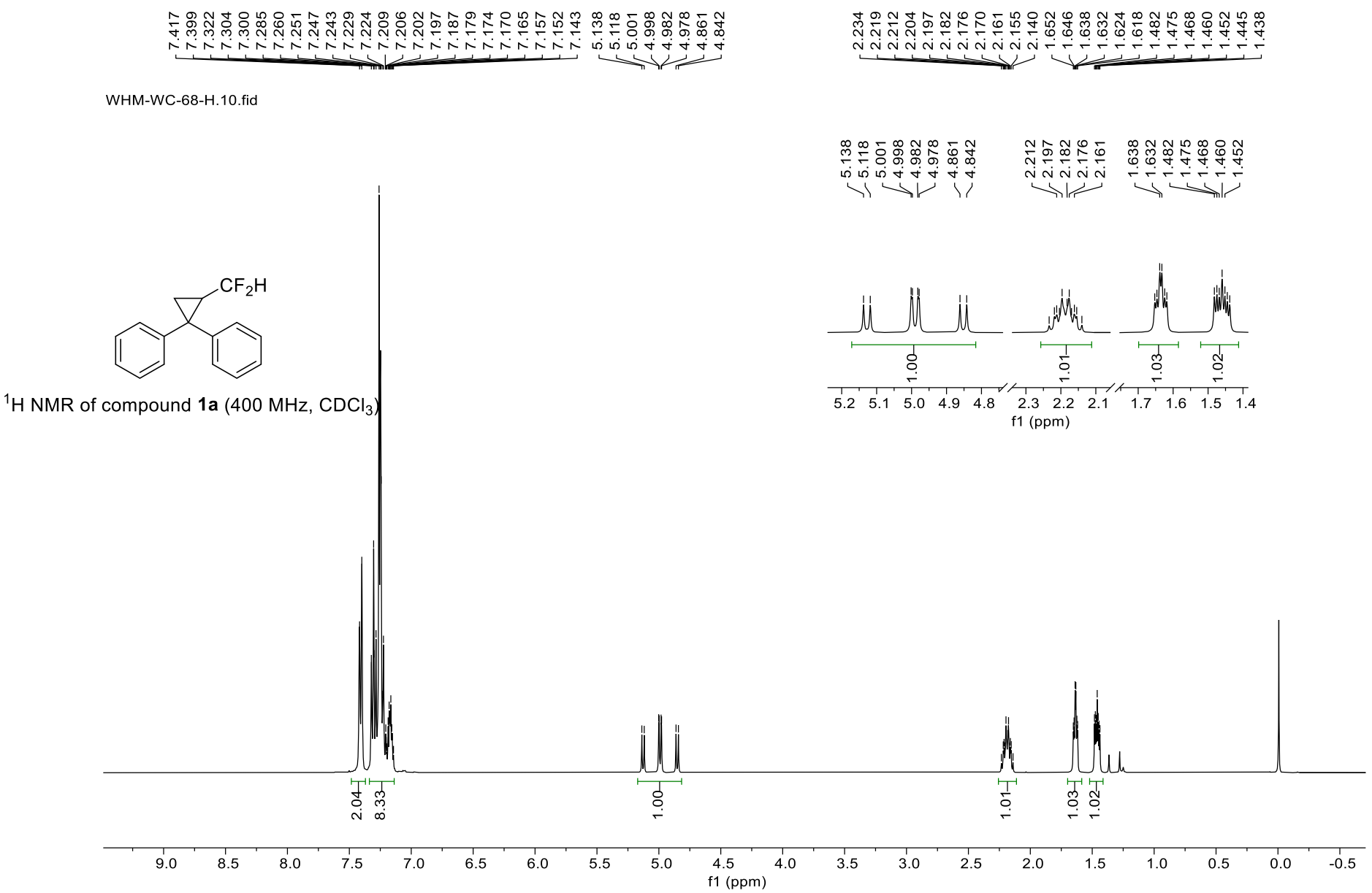
[2] X.-Y. Zhang, Z.-H. Liu, X.-Y. Yang, Y.-Q. Dong, E. Anderson, M. Virelli, G. Zanoni and X.-H. Bi, *Nat. Commun*. 2019, **10**, 284.

[3] K. Fuchibe, R. Oki, H. Hatta and J. Ichikawa, *Chem. Eur. J.* 2018, **24**, 17932-17935.

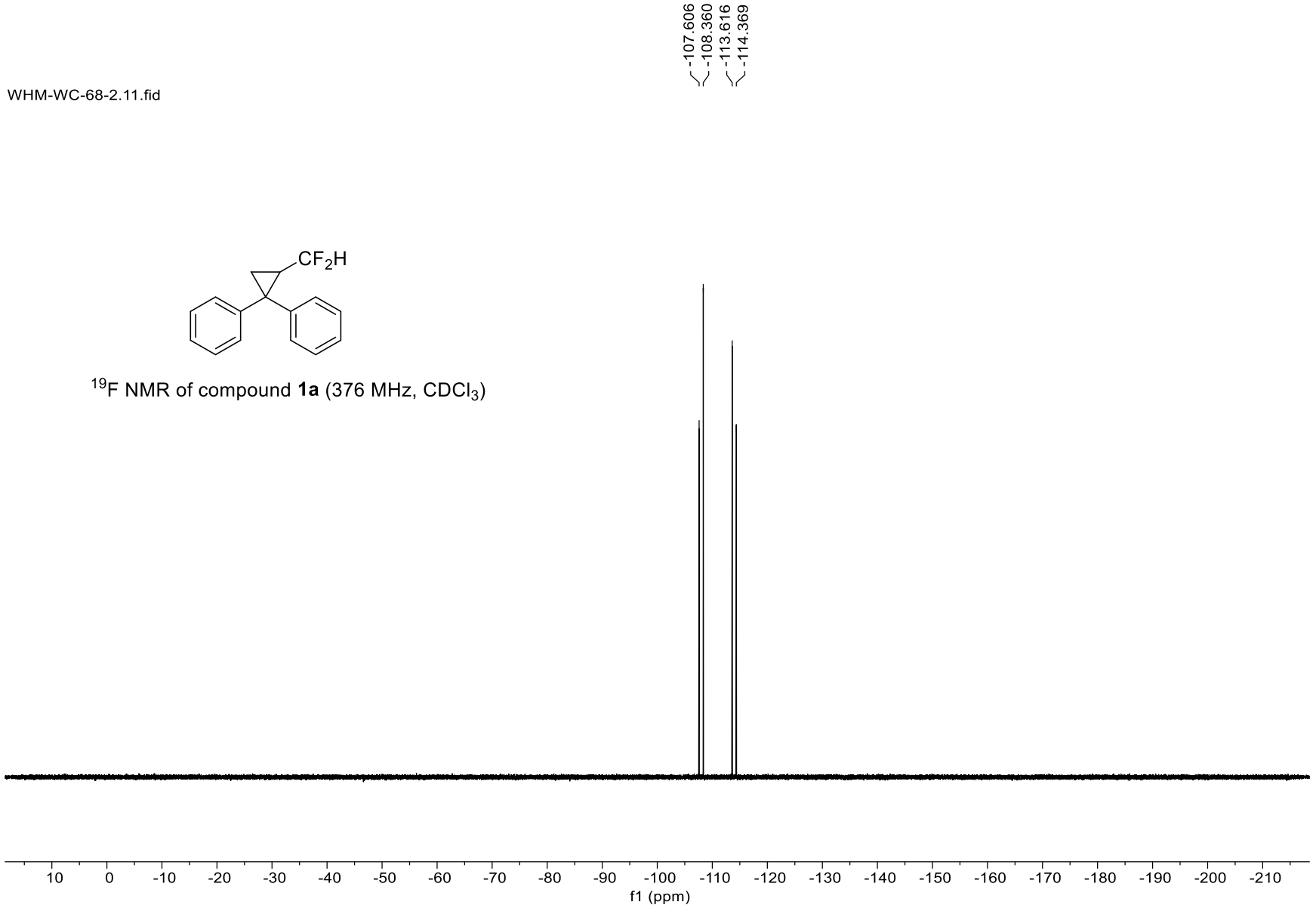
[4] Y. Wang, S. Tang, G. Yang, S. Wang, D. Ma and Y. Qiu, *Angew. Chem. Int. Ed.*, 2022, **61**, e202207746.

[5] a) X. Liu, R.-Y. Liu, J.-X. Qiu, X. Cheng, G.-G. Li, *Angew. Chem. Int. Ed*. **2020**, *59*, 13962-13967; b) J. Sheng, N. Wu, X. Liu, F. Liu, S. Liu, W.-J. Ding, C. Liu, X. Cheng, *Chin. J. Org. Chem.* **2020**, *40*, 3873-3880; c) L. F. Castanñeda, F. C. Walsh, J. L. Nava a, C. P. de León.

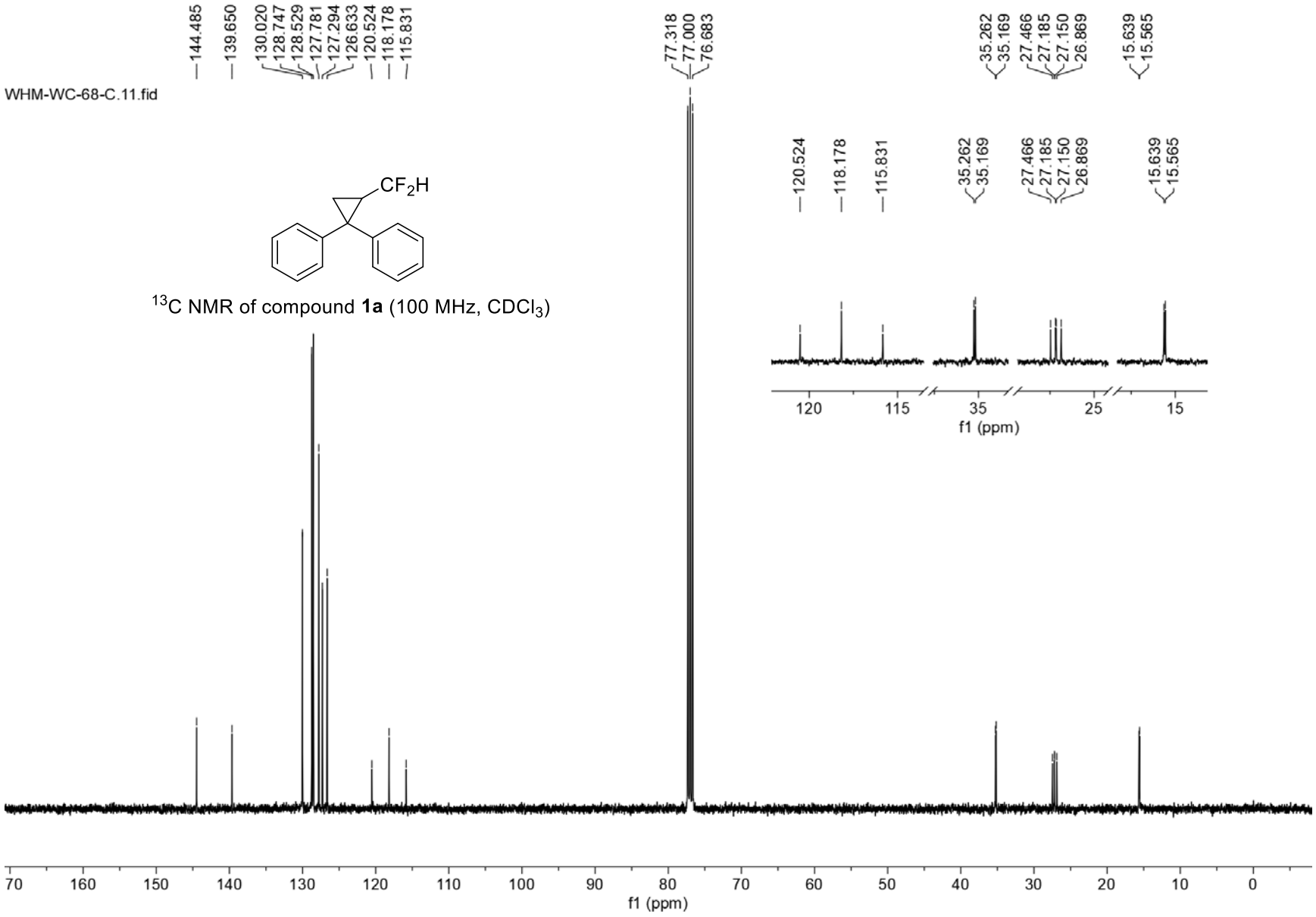
[6] a) I. Franzoni, L. Guénée, C. Mazet, *Chem. Sci*., **2013**, *4*, 2619-2624; b) F. Li, Y.-C. Luo, X.-J. Zhu, Y. Ye, Q.-J. Yuan, W.-B. Zhang, *Chem. Eur. J.* **2023**, *29*, e202300027.

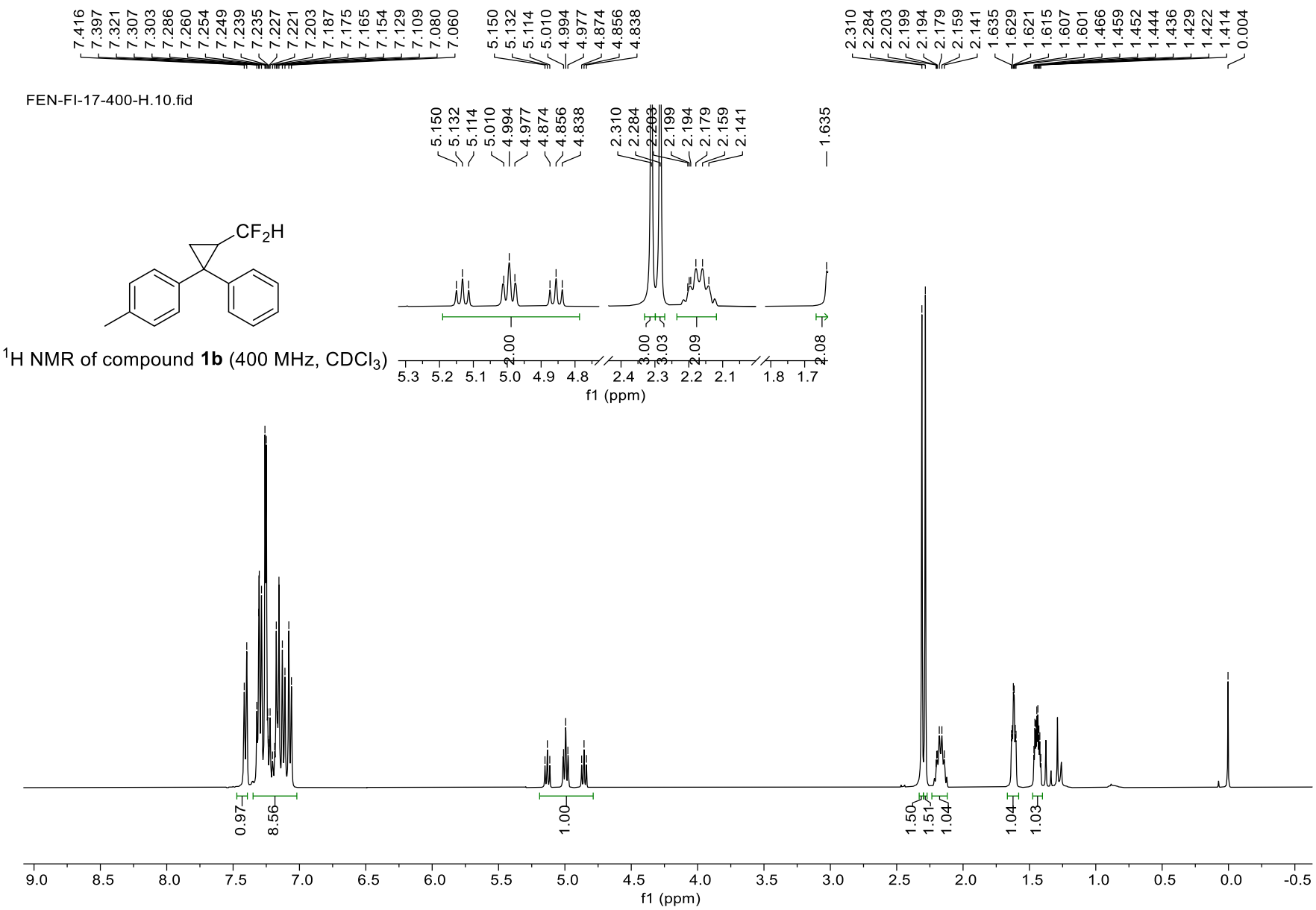

7.417
7.399
7.322
7.304
7.300
7.285
7.260
7.251
7.247
7.243
7.229
7.224
7.209
7.206
7.202
7.197
7.187
7.179
7.174
7.170
7.165
7.157
7.152
7.143
5.138
5.118
5.001
4.998
4.982
4.978
4.861
4.842
2.234
2.219
2.212
2.204
2.197
2.182
2.176
2.170
2.161
2.155
2.140
1.652
1.646
1.638
1.632
1.624
1.618
1.482
1.475
1.468
1.460
1.452
1.445
1.438
WHM-WC-68-H.10.fid
CF2H
1H NMR of compound 1a (400 MHz, CDCl3)
1.00
1.01
1.03
1.02
f1 (ppm)
2.04
8.33
1.00
1.01
1.03
1.02
f1 (ppm)

WHM-WC-68-2.11.fid



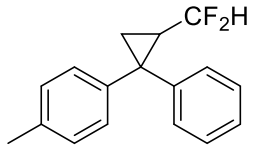
^{19}F NMR of compound **1a** (376 MHz, $CDCl_3$)


144.485
139.650
130.020
128.747
128.529
127.781
127.294
126.633
120.524
118.178
115.831
77.318
77.000
76.683
35.262
35.169
27.466
27.185
27.150
26.869
15.639
15.565
WHM-WC-68-C.11.fid
CF2H
13C NMR of compound 1a (100 MHz, CDCl3)
f1 (ppm)

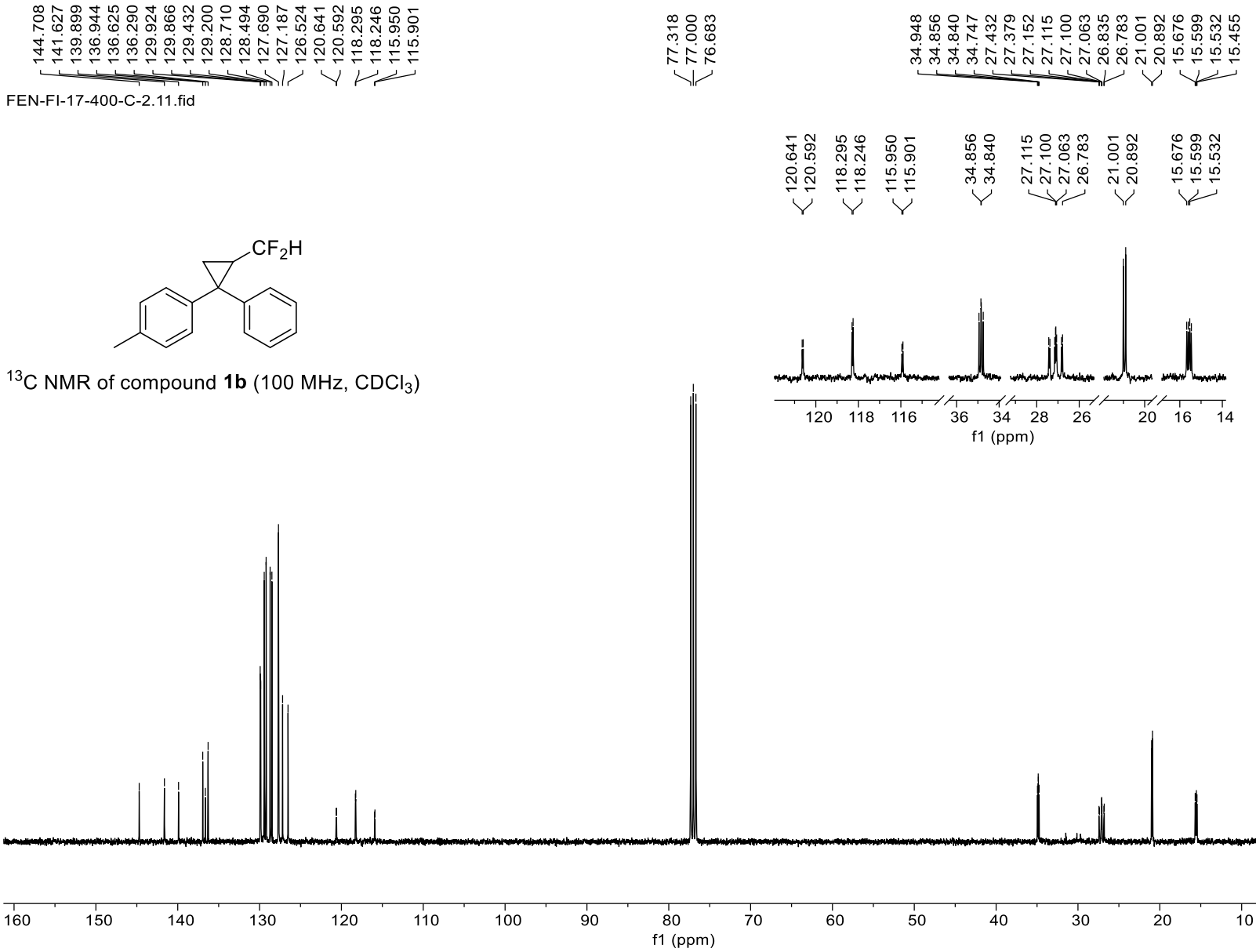

FEN-FI-17-400-H.10.fid
CF2H
1H NMR of compound 1b (400 MHz, CDCl3)
f1 (ppm)

FEN-FI-17-400-H.11.fid

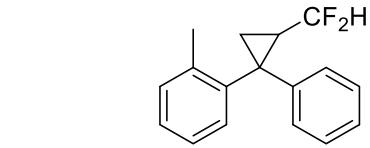
-107.522
-107.529
-108.275
-108.281
-113.538
-113.690
-114.291
-114.443



^{19}F NMR of compound **1b** (376 MHz, $CDCl_3$)


144.708
141.627
139.899
136.944
136.625
136.290
129.924
129.866
129.432
129.200
128.710
128.494
127.690
127.187
126.524
120.641
120.592
118.295
118.246
115.950
115.901
77.318
77.000
76.683
34.948
34.856
34.840
34.747
27.432
27.379
27.152
27.115
27.100
27.063
26.835
26.783
21.001
20.892
15.676
15.599
15.532
15.455
FEN-FI-17-400-C-2.11.fid
CF2H
13C NMR of compound 1b (100 MHz, CDCl3)
f1 (ppm)

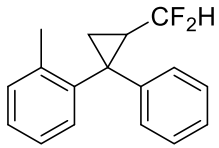
FEN-FI-42-400-H.10.fid



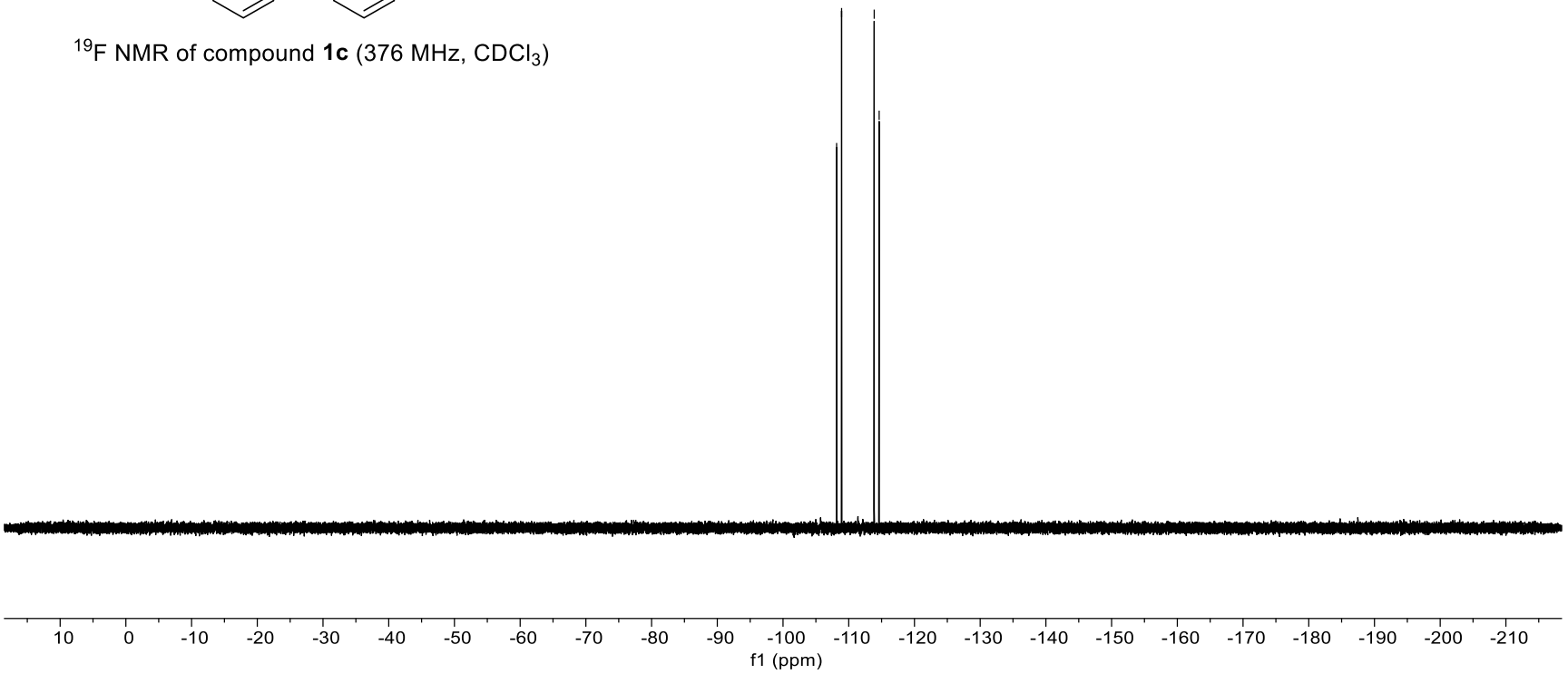
^{1}H NMR of compound **1c** (400 MHz, $CDCl_3$)

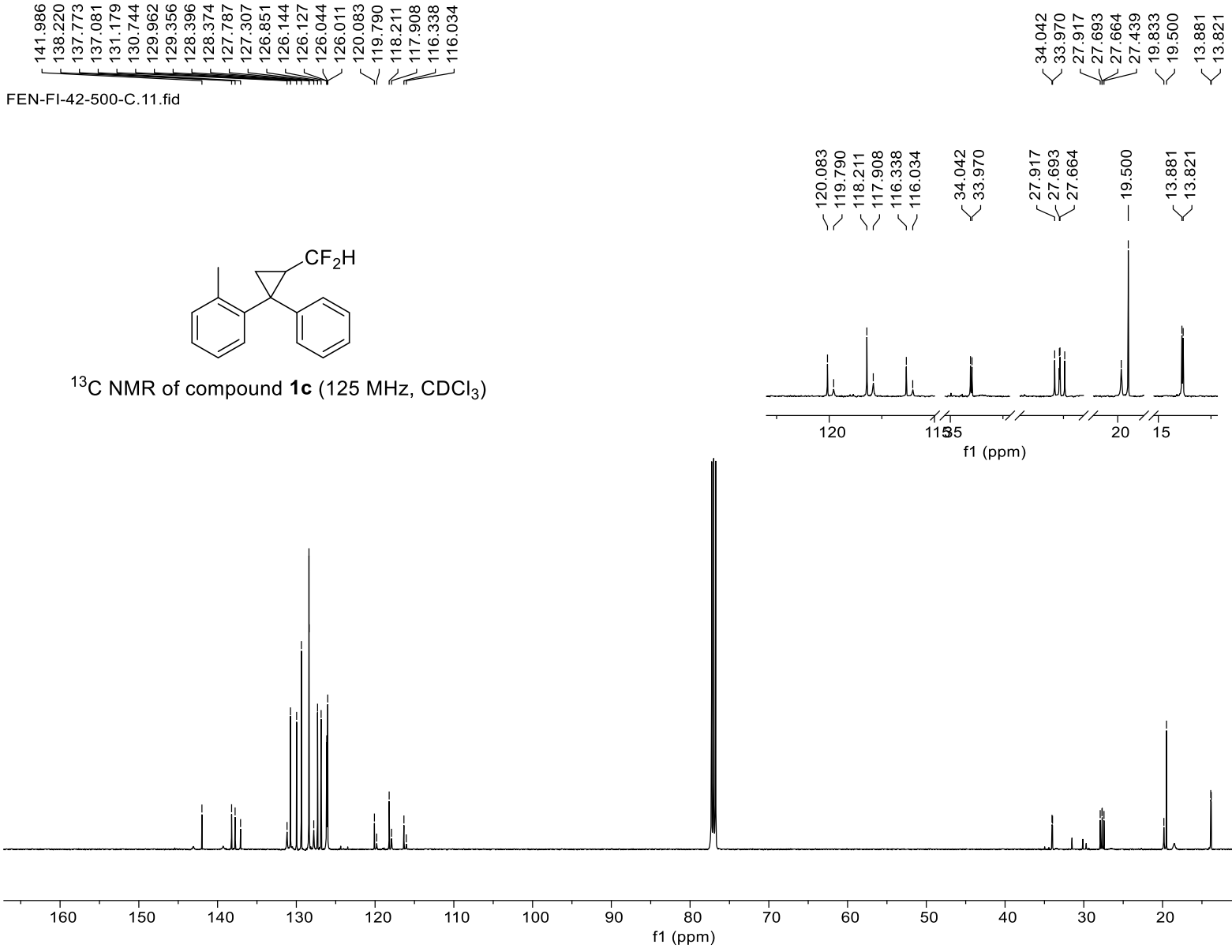
FEN-FI-42-400-H.11.fid

-108.156
-108.912
-113.875
-114.631

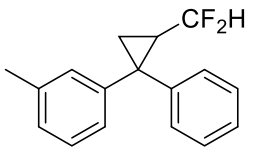


^{19}F NMR of compound **1c** (376 MHz, $CDCl_3$)



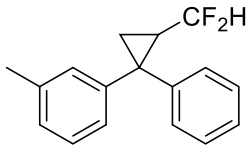

141.986
138.220
137.773
137.081
131.179
130.744
129.962
129.356
128.396
128.374
127.787
127.307
126.851
126.144
126.127
126.044
126.011
120.083
119.790
118.211
117.908
116.338
116.034
34.042
33.970
27.917
27.693
27.664
27.439
19.833
19.500
13.881
13.821
FEN-FI-42-500-C.11.fid
CF2H
13C NMR of compound 1c (125 MHz, CDCl3)
f1 (ppm)

FEN-FI-43.10.fid

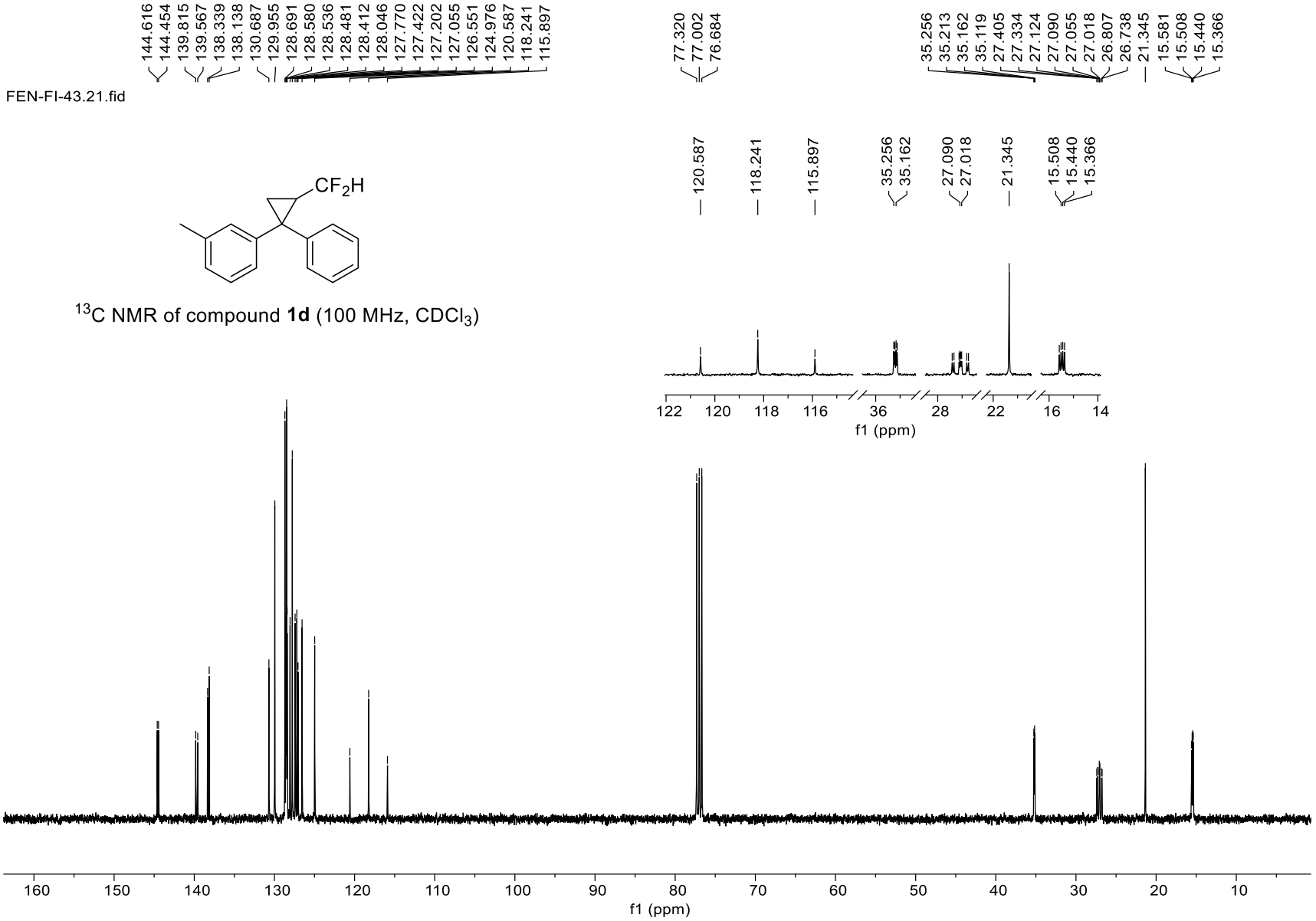


^{1}H NMR of compound **1d** (400 MHz, $CDCl_3$)

FEN-FI-43.11.fid



^{19}F NMR of compound **1d** (376 MHz, $CDCl_3$)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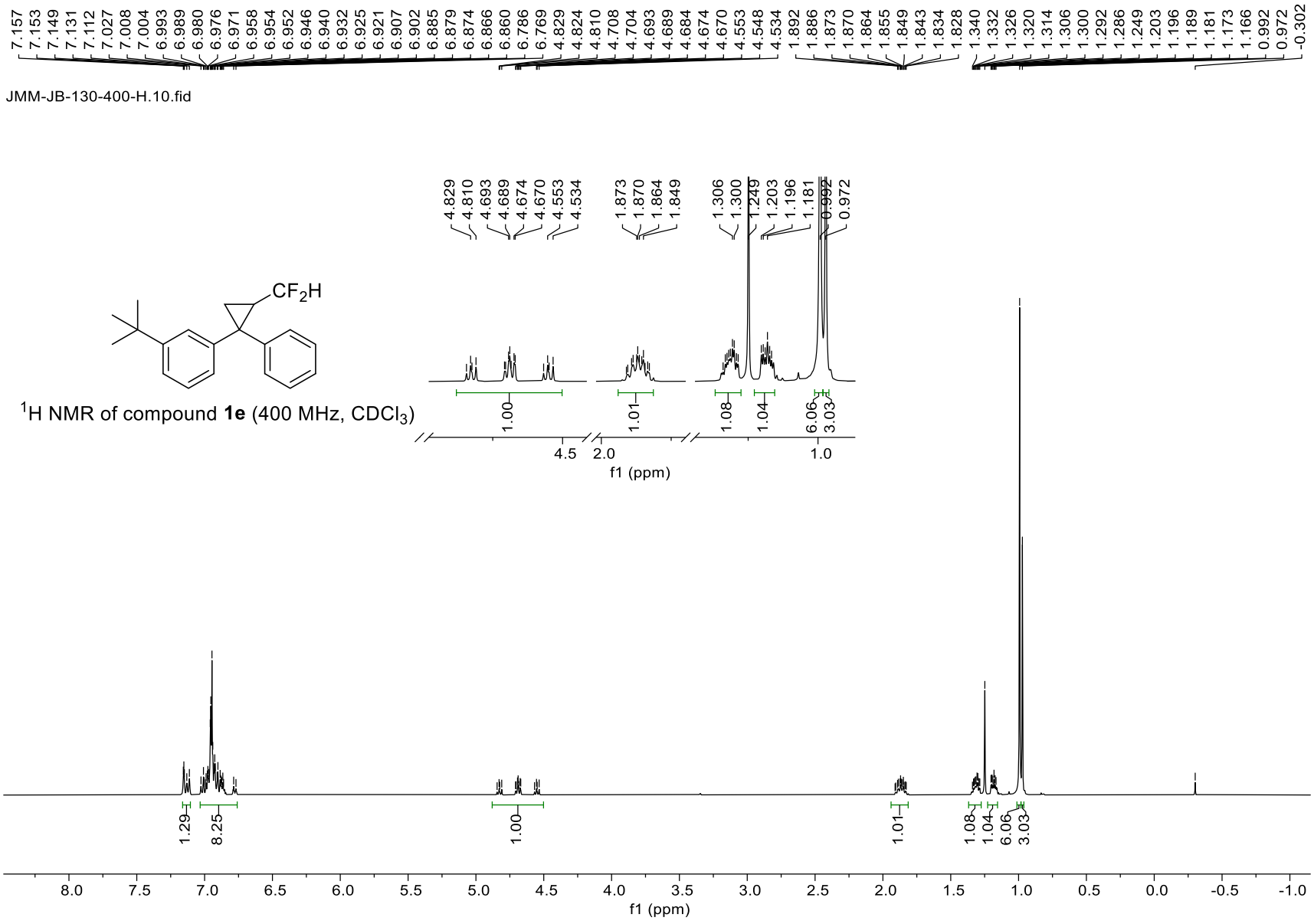
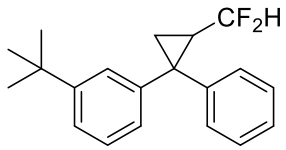
139.567
138.339
138.138
130.687
129.955
128.691
128.580
128.536
128.481
128.412
128.046
127.770
127.422
127.202
127.055
126.551
124.976
120.587
118.241
115.897
77.320
77.002
76.684
35.256
35.213
35.162
35.119
27.405
27.334
27.124
27.090
27.055
27.018
26.807
26.738
21.345
15.581
15.508
15.440
15.366
FEN-FI-43.21.fid
CF2H
13C NMR of compound 1d (100 MHz, CDCl3)
f1 (ppm)

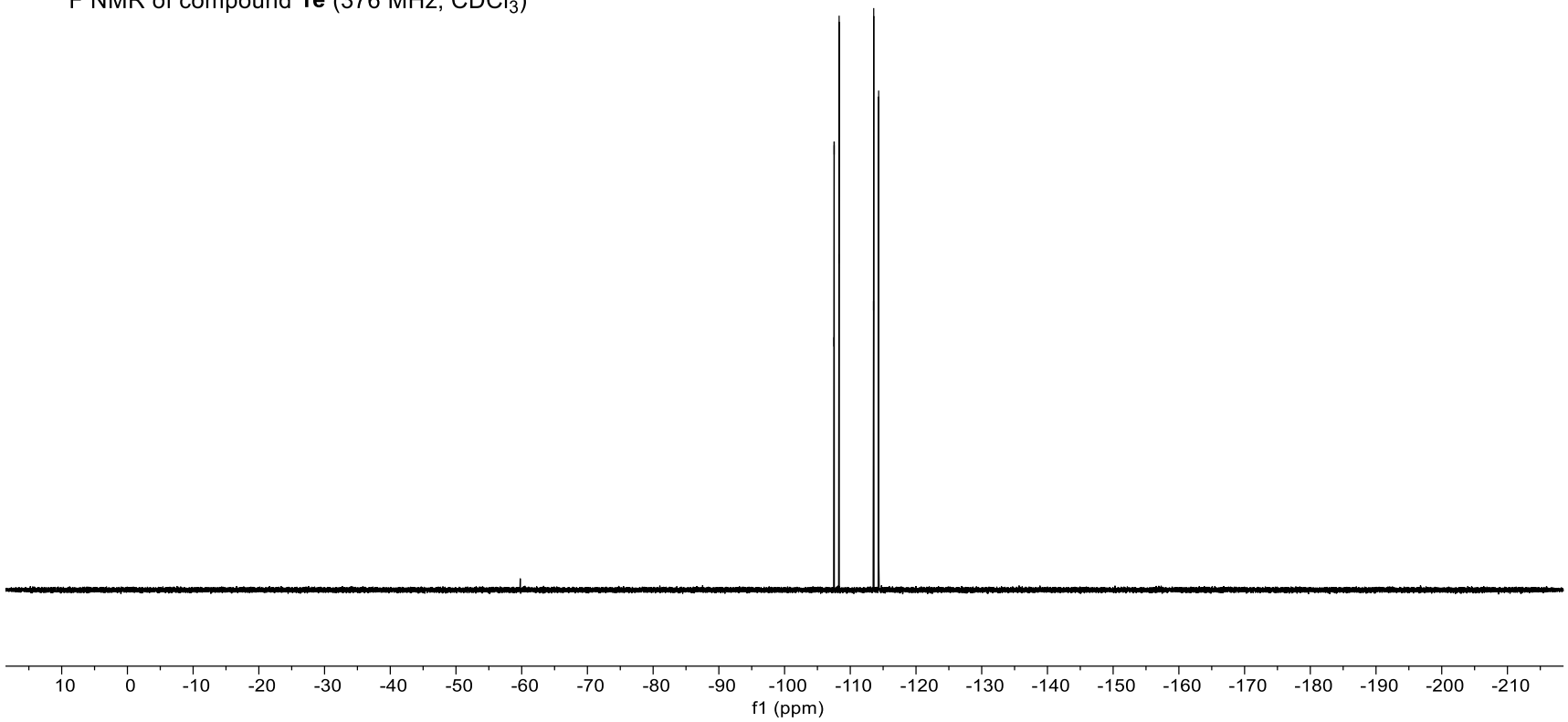

7.157 7.153 7.149 7.131 7.112 7.027 7.008 7.004 6.993 6.989 6.980 6.976 6.971 6.958 6.954 6.952 6.946 6.940 6.932 6.925 6.921 6.907 6.902 6.885 6.879 6.874 6.866 6.860 6.786 6.769 4.829 4.824 4.810 4.708 4.704 4.693 4.689 4.684 4.674 4.670 4.553 4.548 4.534 1.892 1.886 1.873 1.870 1.864 1.855 1.849 1.843 1.834 1.828 1.340 1.332 1.326 1.320 1.314 1.306 1.300 1.292 1.286 1.249 1.203 1.196 1.189 1.181 1.173 1.166 0.992 0.972 -0.302
JMM-JB-130-400-H.10.fid
CF2H
1H NMR of compound 1e (400 MHz, CDCl3)
4.829 4.810 4.693 4.689 4.674 4.670 4.553 4.534 1.873 1.870 1.864 1.849 1.306 1.300 1.249 1.203 1.196 1.181 0.992 0.972
1.00 1.01 1.08 1.04 6.06 3.03
4.5 2.0 1.0
f1 (ppm)
1.29 8.25 1.00 1.01 1.08 1.04 6.06 3.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

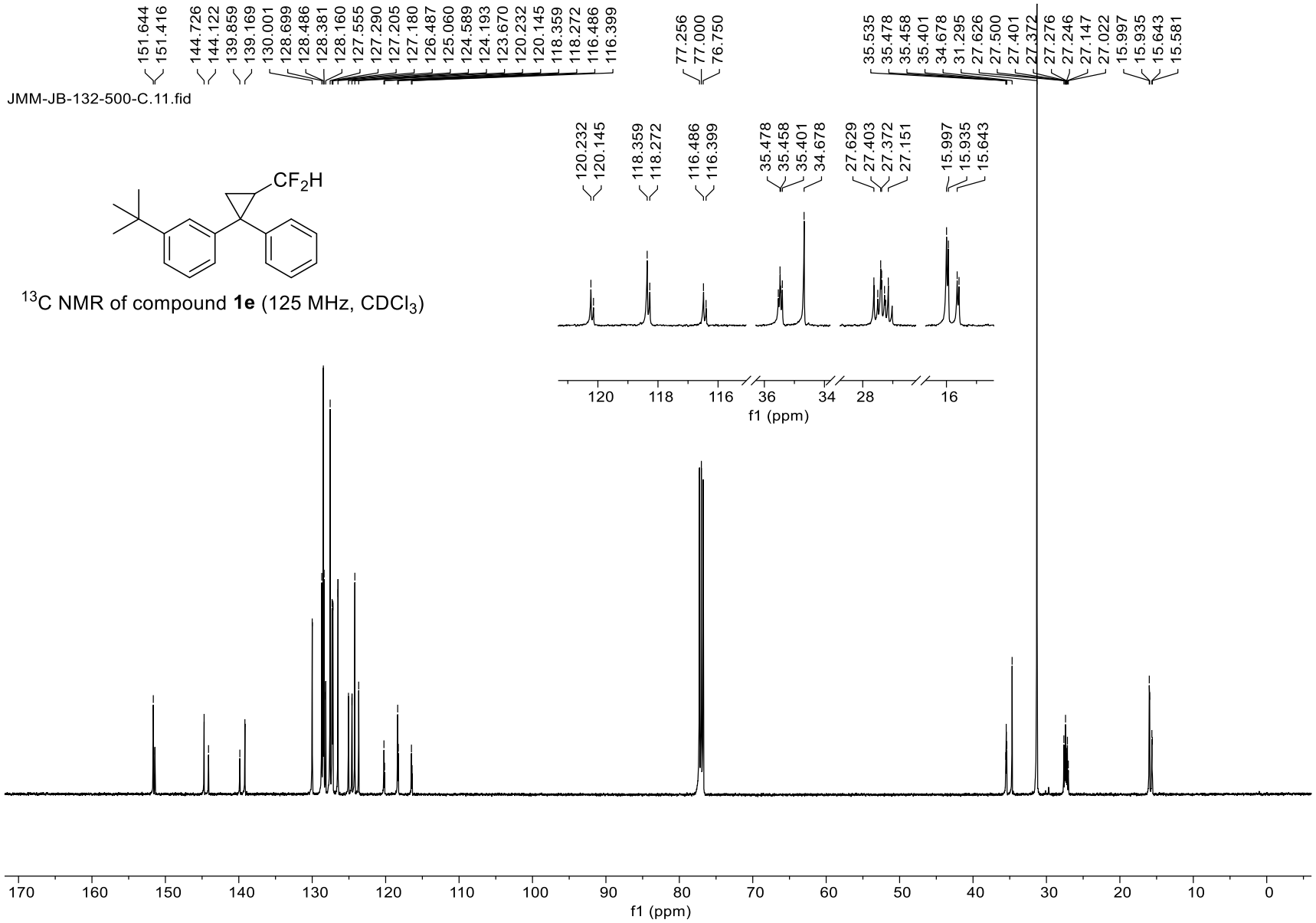
JMM-JB-130-400-H.11.fid

-107.504
-107.551
-108.257
-108.303
-113.536
-113.567
-114.289
-114.320



^{19}F NMR of compound **1e** (376 MHz, $CDCl_3$)




151.644
151.416
144.726
144.122
139.859
139.169
130.001
128.699
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128.381
128.160
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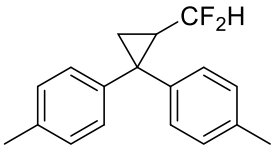
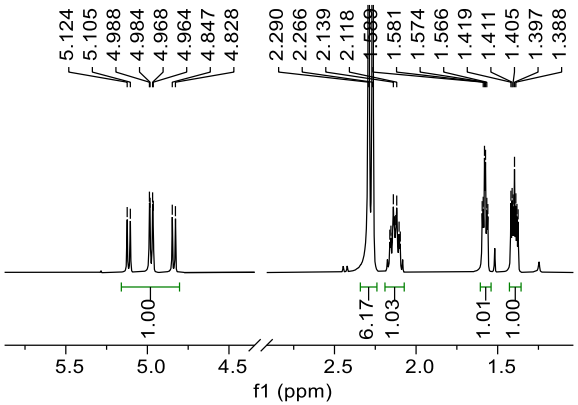
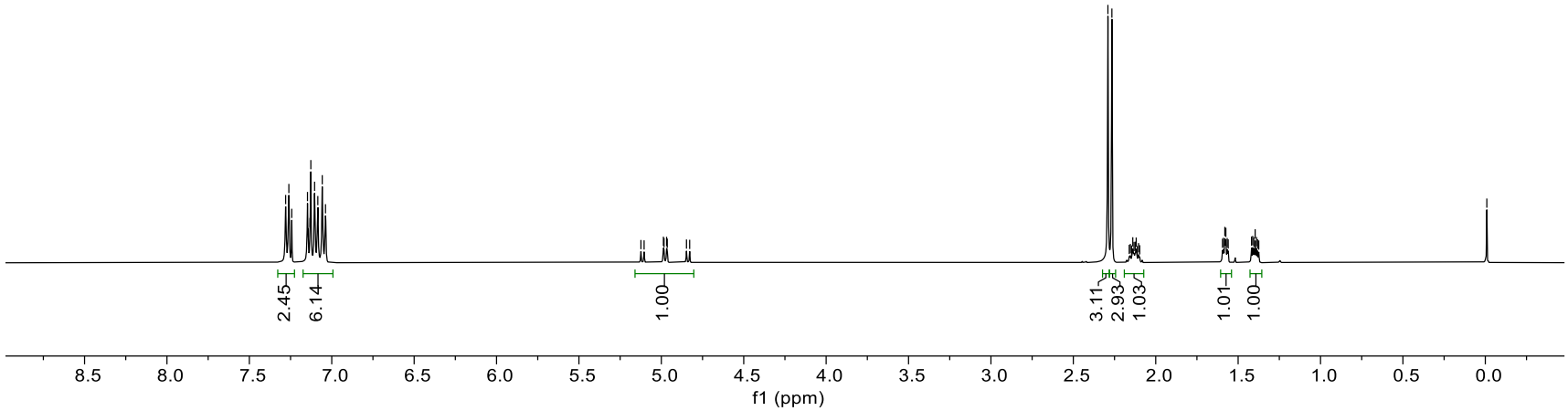
127.290
127.205
127.180
126.487
125.060
124.589
124.193
123.670
120.232
120.145
118.359
118.272
116.486
116.399
77.256
77.000
76.750
35.535
35.478
35.458
35.401
34.678
31.295
27.626
27.500
27.401
27.372
27.276
27.246
27.147
27.022
15.997
15.935
15.643
15.581
JMM-JB-132-500-C.11.fid
CF2H
13C NMR of compound 1e (125 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

FEN-FI-72-H-400.10.fid

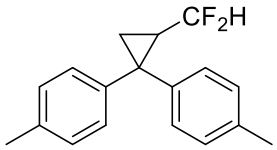


^{1}H NMR of compound **1f** (400 MHz, $CDCl_3$)

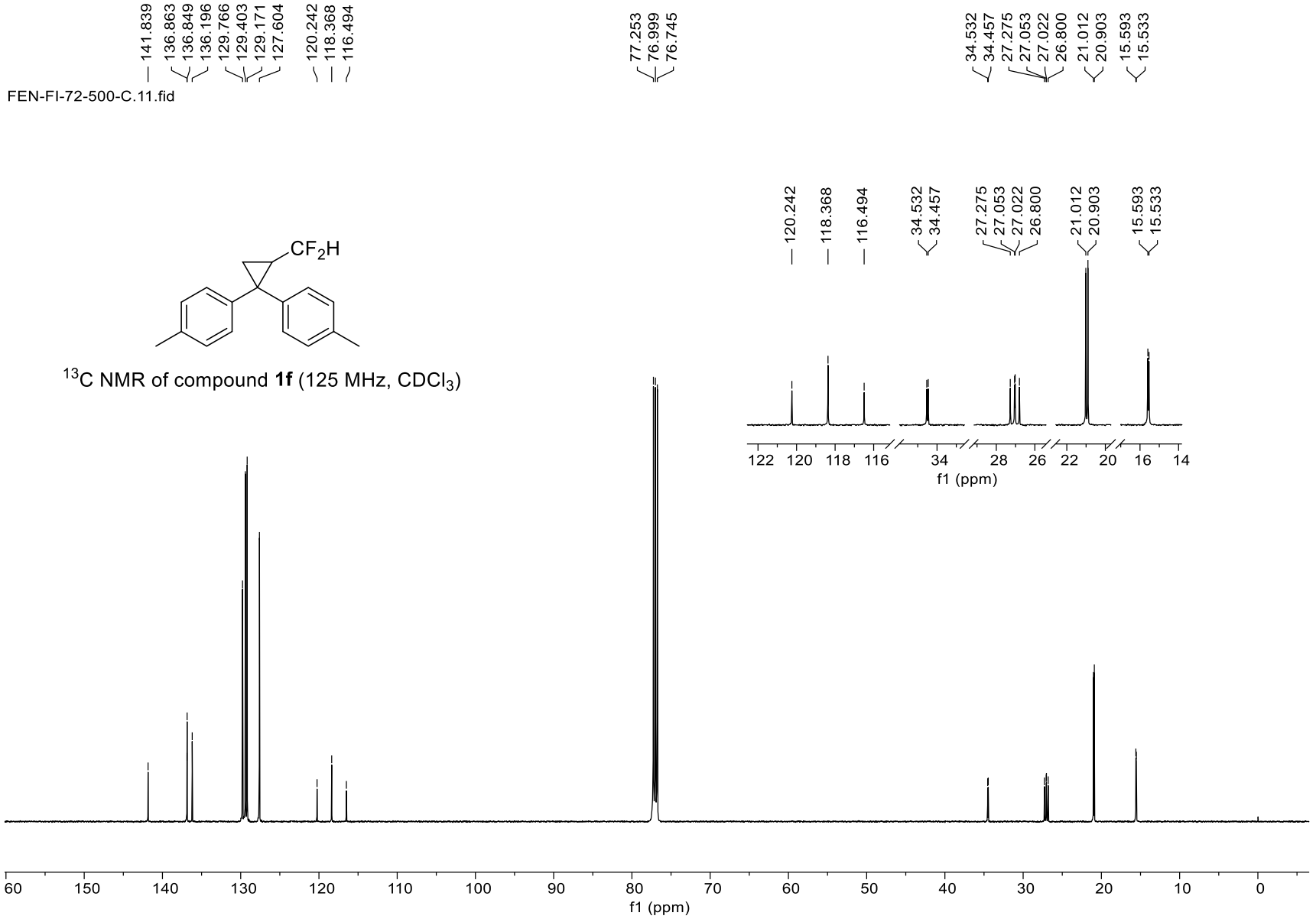




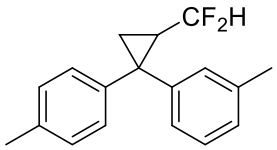
FEN-FI-72-H-400.11.fid



^{19}F NMR of compound **1f** (376 MHz, $CDCl_3$)


141.839
136.863
136.849
136.196
129.766
129.403
129.171
127.604
120.242
118.368
116.494
77.253
76.999
76.745
34.532
34.457
27.275
27.053
27.022
26.800
21.012
20.903
15.593
15.533
FEN-FI-72-500-C.11.fid
CF2H
13C NMR of compound 1f (125 MHz, CDCl3)
f1 (ppm)

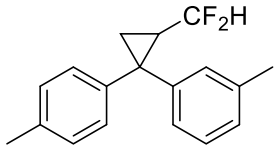
FEN-FI-87.10.fid



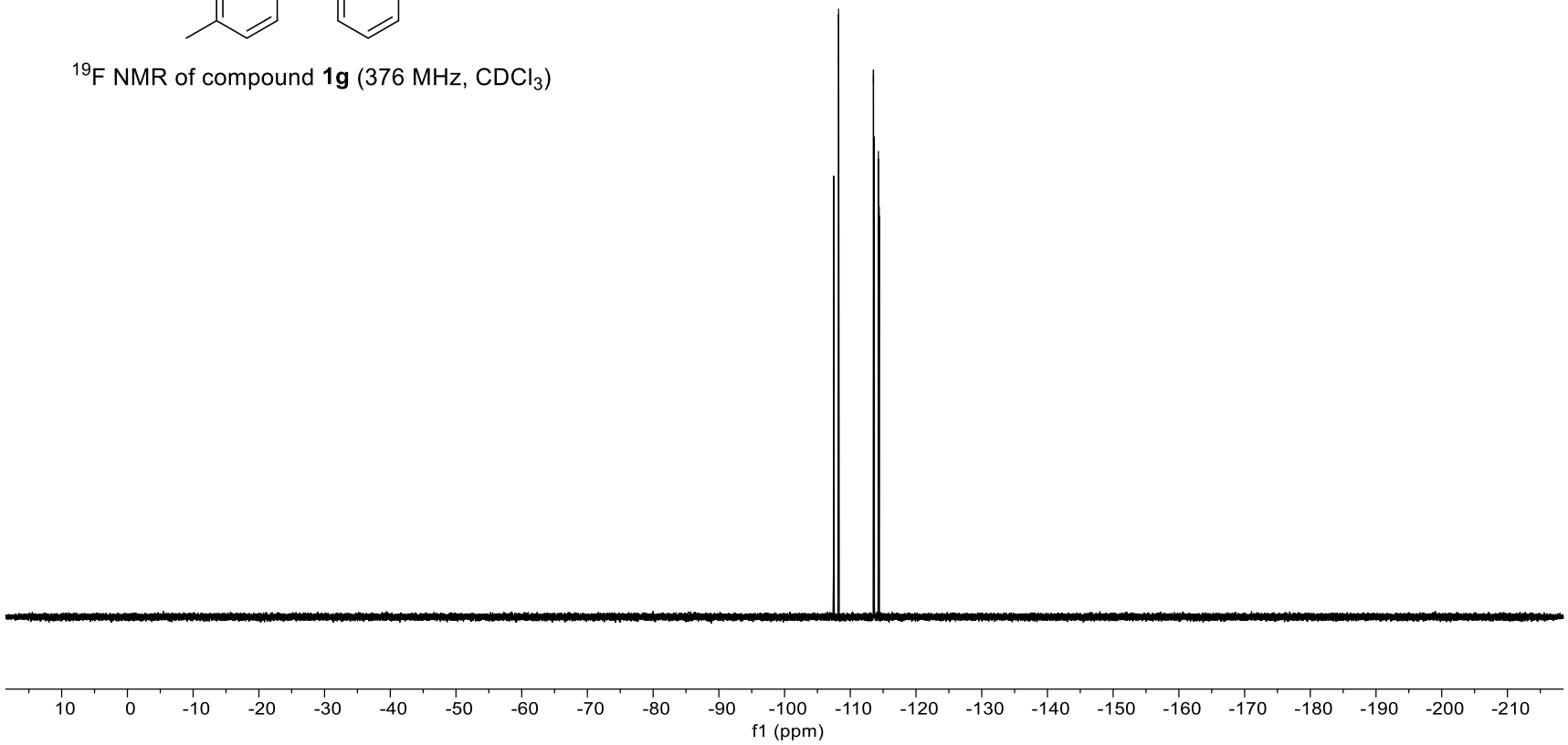
^{1}H NMR of compound **1g** (400 MHz, $CDCl_3$)

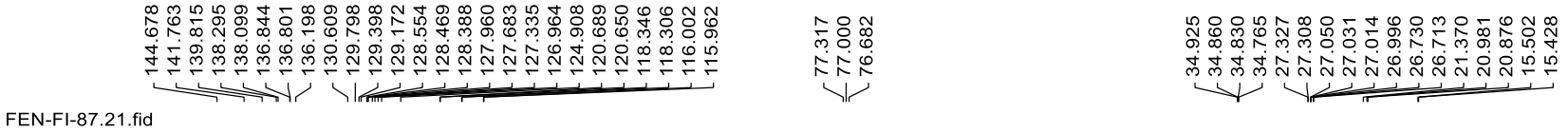
FEN-FI-87.11.fid

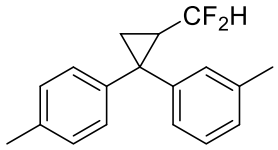
-107.467
-107.484
-108.219
-108.237
-113.521
-113.657
-114.273
-114.409



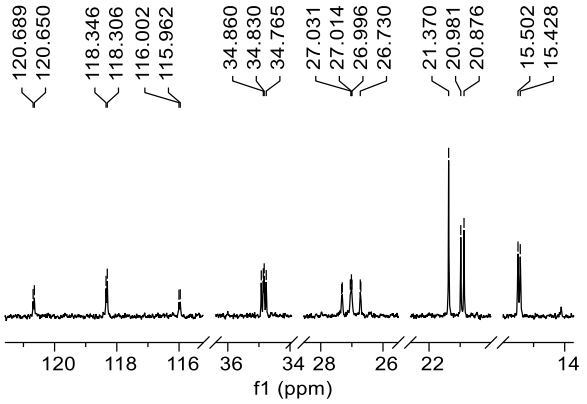
^{19}F NMR of compound **1g** (376 MHz, $CDCl_3$)

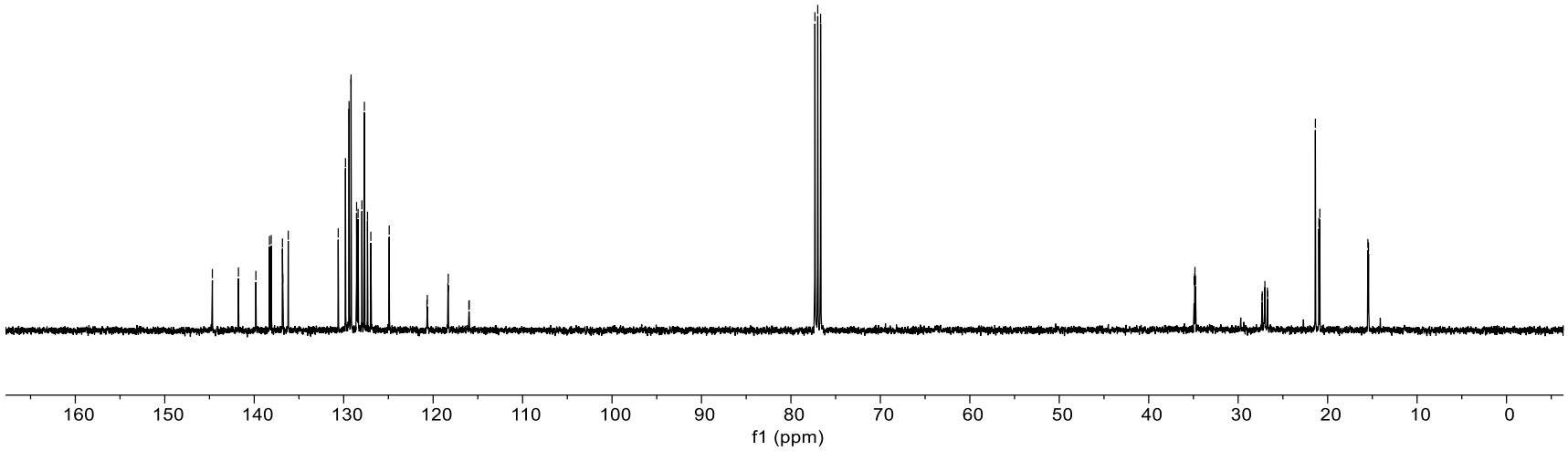


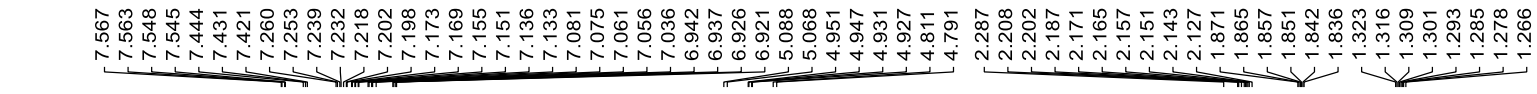




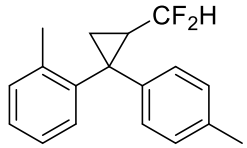
^{13}C NMR of compound **1g** (100 MHz, $CDCl_3$)







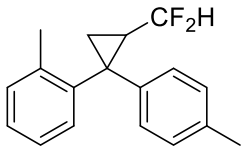
JMM-JB-112-400-H-2.10.fid



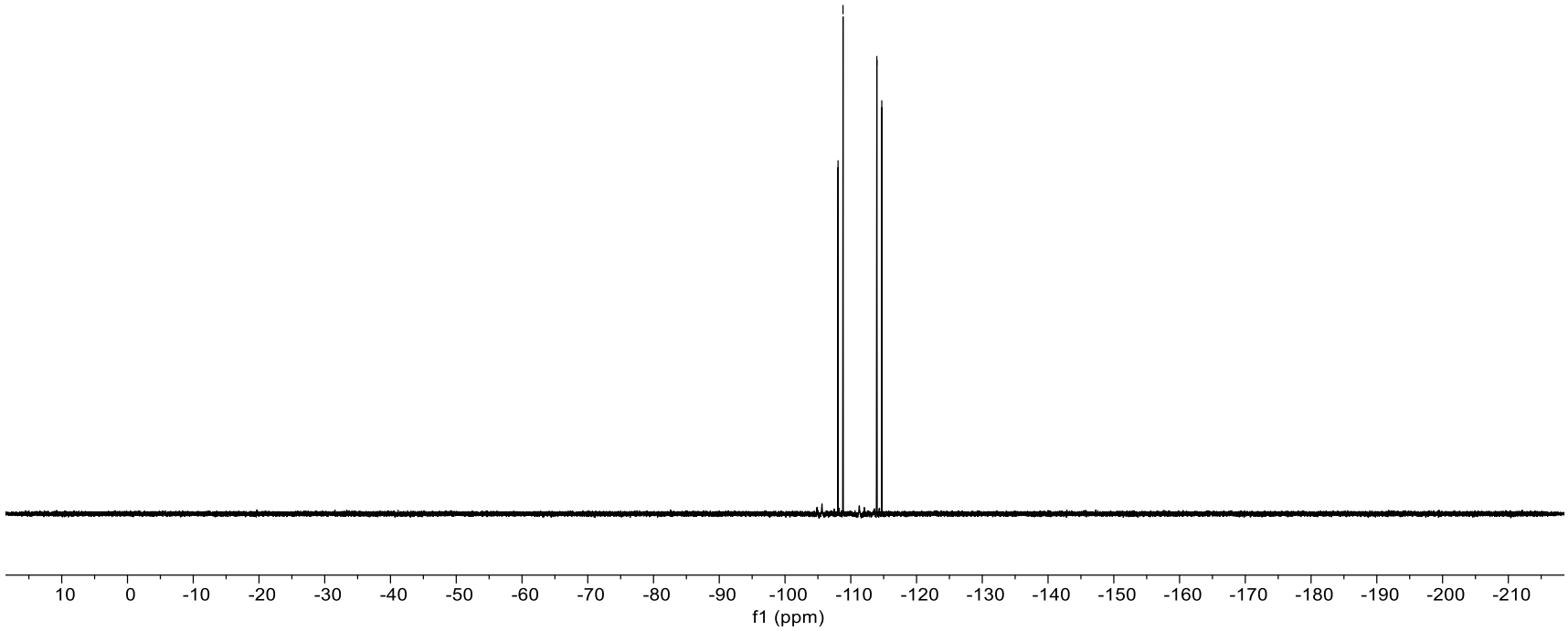
^{1}H NMR of compound **1h** (400 MHz, $CDCl_3$)

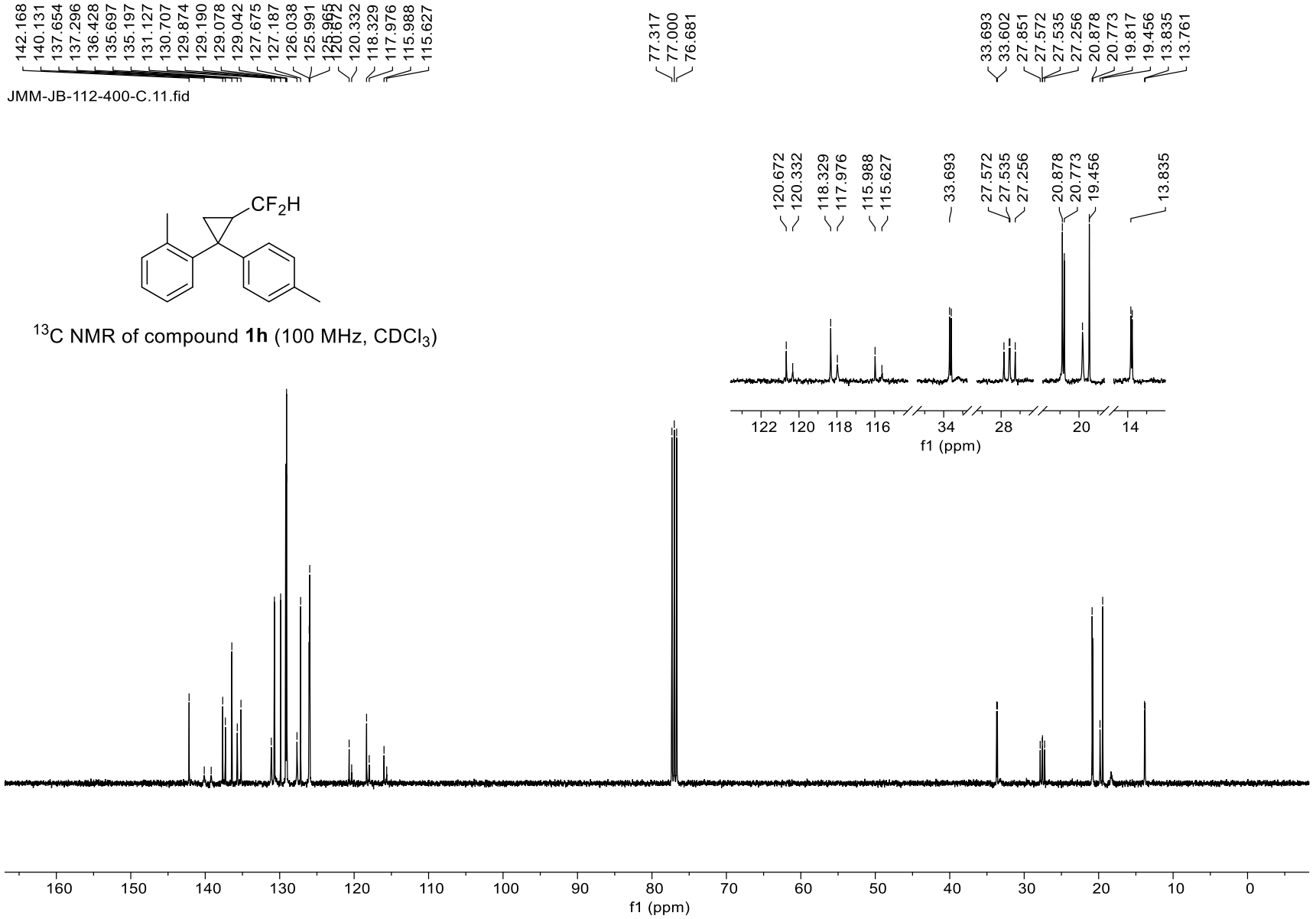
JMM-JB-112-400-H-2.11.fid

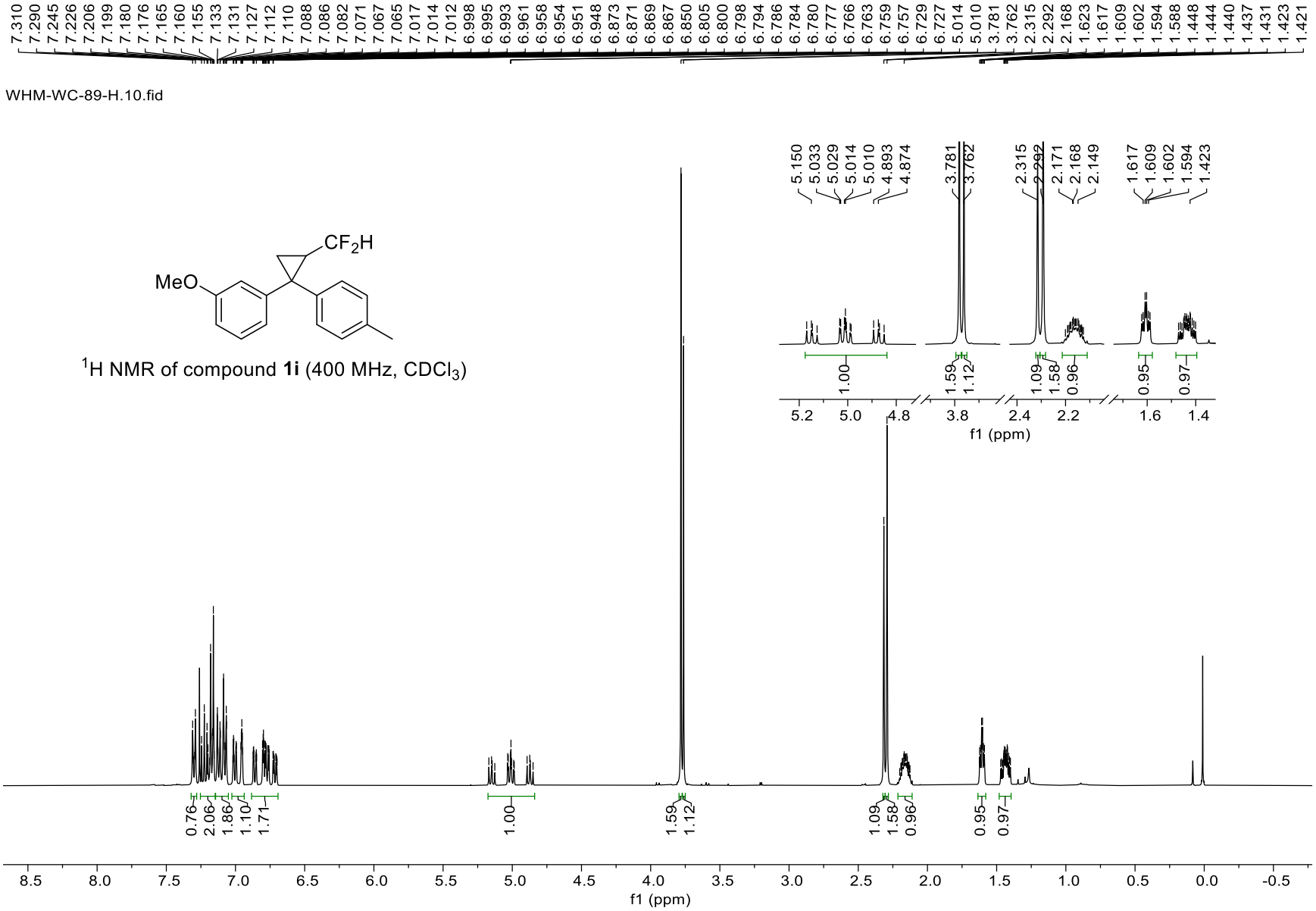
-108.064
-108.819
-113.961
-114.716



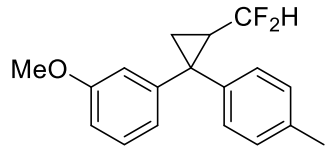
^{19}F NMR of compound **1h** (376 MHz, $CDCl_3$)



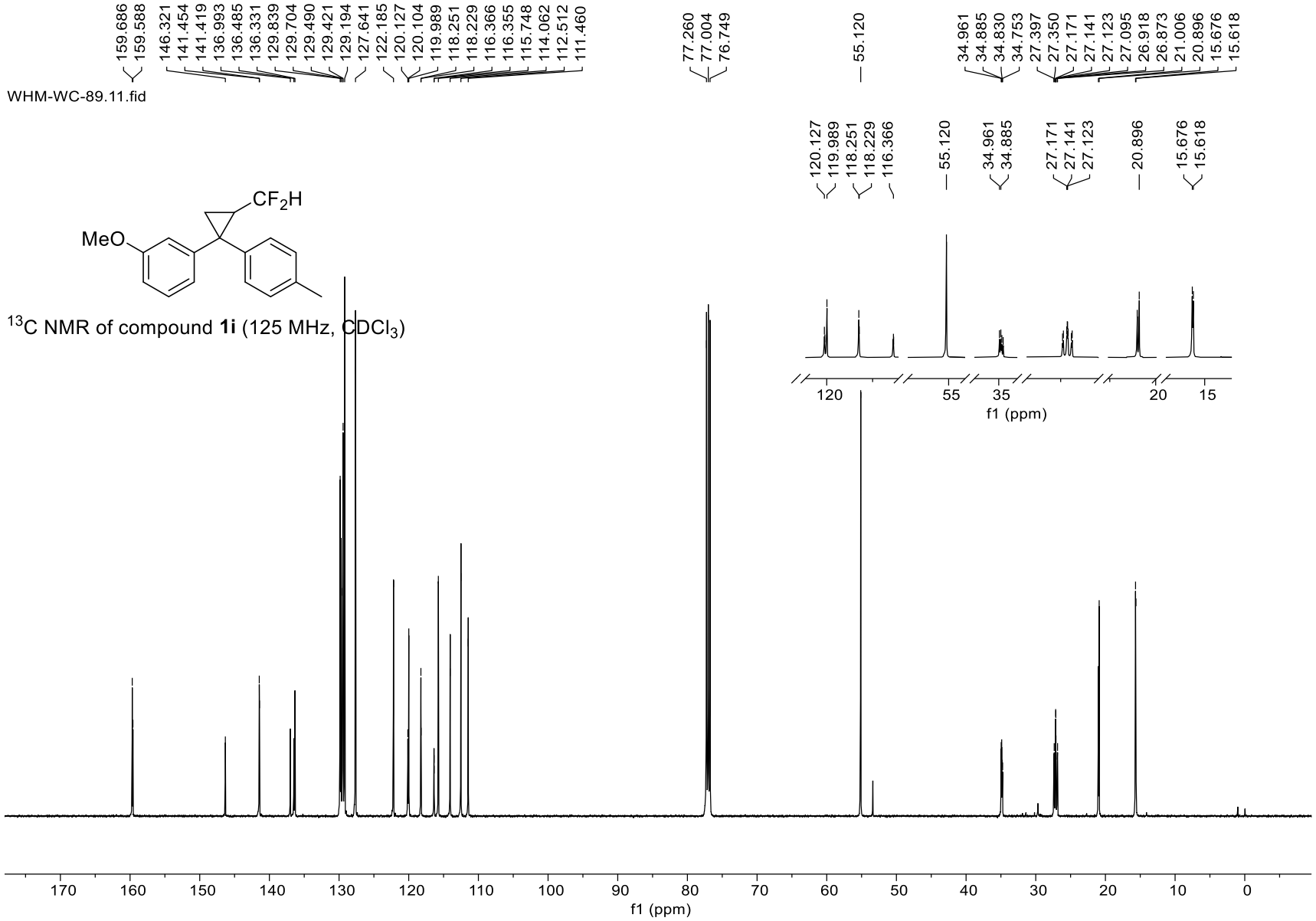

142.168
140.131
137.654
137.296
136.428
135.697
135.197
131.127
130.707
129.874
129.190
129.078
129.042
127.675
127.187
126.038
125.991
120.672
120.332
118.329
117.976
115.988
115.627
77.317
77.000
76.681
33.693
33.602
27.851
27.572
27.535
27.256
20.878
20.773
19.817
19.456
13.835
13.761
JMM-JB-112-400-C.11.fid
CF2H
13C NMR of compound 1h (100 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

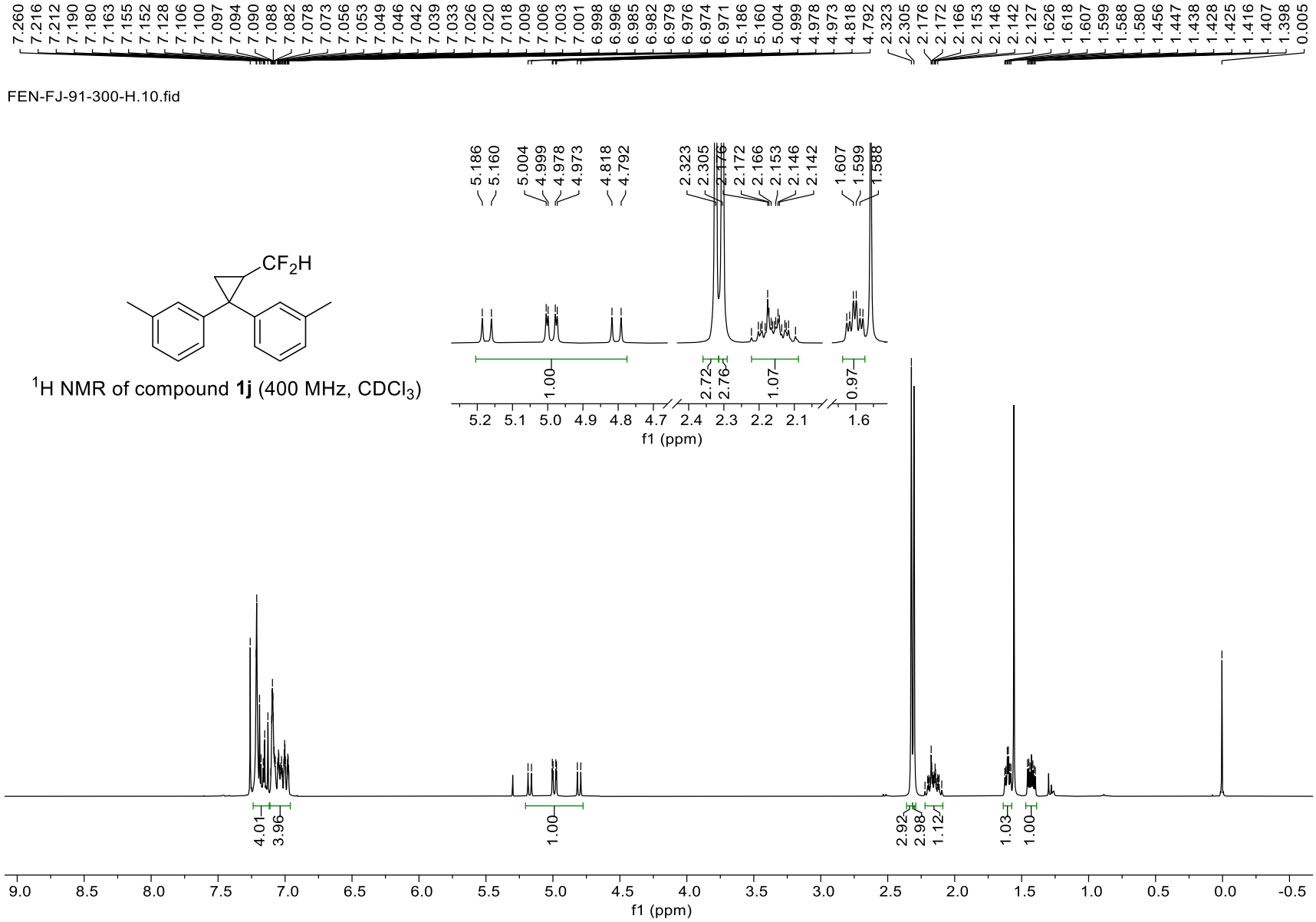

7.310 7.290 7.245 7.226 7.206 7.199 7.180 7.176 7.165 7.160 7.155 7.133 7.131 7.127 7.112 7.110 7.088 7.086 7.082 7.071 7.067 7.065 7.017 7.014 7.012 6.998 6.995 6.993 6.961 6.958 6.954 6.951 6.948 6.873 6.871 6.869 6.867 6.850 6.805 6.800 6.798 6.794 6.786 6.784 6.780 6.777 6.766 6.763 6.759 6.757 6.729 6.727 5.014 5.010 3.781 3.762 2.315 2.292 2.168 1.623 1.617 1.609 1.602 1.594 1.588 1.448 1.444 1.440 1.437 1.431 1.423 1.421
WHM-WC-89-H.10.fid
CF2H
MeO
1H NMR of compound 1i (400 MHz, CDCl3)
5.150 5.033 5.029 5.014 5.010 4.893 4.874 3.781 3.762 2.315 2.292 2.171 2.168 2.149 1.617 1.609 1.602 1.594 1.423
1.00 1.59 1.12 1.09 1.58 0.96 0.95 0.97
f1 (ppm)
0.76 2.06 1.86 1.10 1.71 1.00 1.59 1.12 1.09 1.58 0.96 0.95 0.97
f1 (ppm)

WHM-WC-89.11.fid



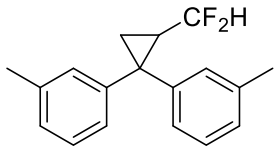
^{19}F NMR of compound **1i** (376 MHz, $CDCl_3$)


159.686
159.588
146.321
141.454
141.419
136.993
136.485
136.331
129.839
129.704
129.490
129.421
129.194
127.641
122.185
120.127
120.104
119.989
118.251
118.229
116.366
116.355
115.748
114.062
112.512
111.460
77.260
77.004
76.749
55.120
34.961
34.885
34.830
34.753
27.397
27.350
27.171
27.141
27.123
27.095
26.918
26.873
21.006
20.896
15.676
15.618
WHM-WC-89.11.fid
CF2H
MeO
13C NMR of compound 1i (125 MHz, CDCl3)
f1 (ppm)

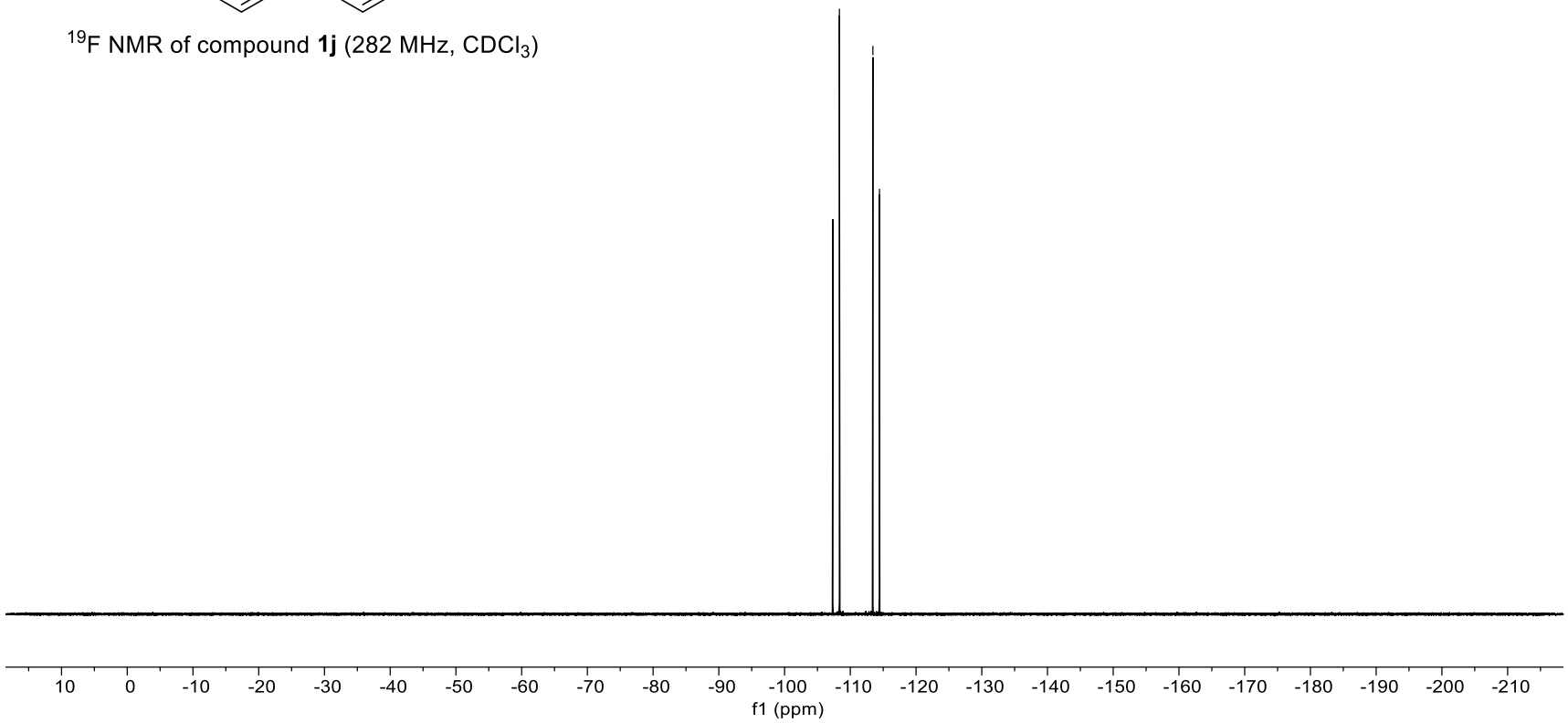

7.260 7.216 7.212 7.190 7.180 7.163 7.155 7.152 7.128 7.106 7.100 7.097 7.094 7.090 7.088 7.082 7.078 7.073 7.056 7.053 7.049 7.046 7.042 7.039 7.033 7.026 7.020 7.018 7.009 7.006 7.003 7.001 6.998 6.996 6.985 6.982 6.979 6.976 6.974 6.971 5.186 5.160 5.004 4.999 4.978 4.973 4.818 4.792 2.323 2.305 2.176 2.172 2.166 2.153 2.146 2.142 1.626 1.618 1.607 1.599 1.588 1.580 1.456 1.447 1.438 1.428 1.425 1.416 1.407 1.398 0.005
FEN-FJ-91-300-H.10.fid
CF2H
1H NMR of compound 1j (400 MHz, CDCl3)
5.186 5.160 5.004 4.999 4.978 4.973 4.818 4.792 2.323 2.305 2.176 2.172 2.166 2.153 2.146 2.142 1.607 1.599 1.588
1.00 2.72 2.76 1.07 0.97
5.2 5.1 5.0 4.9 4.8 4.7 2.4 2.3 2.2 2.1 1.6
f1 (ppm)
4.01 3.96 1.00 2.92 2.98 1.12 1.03 1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

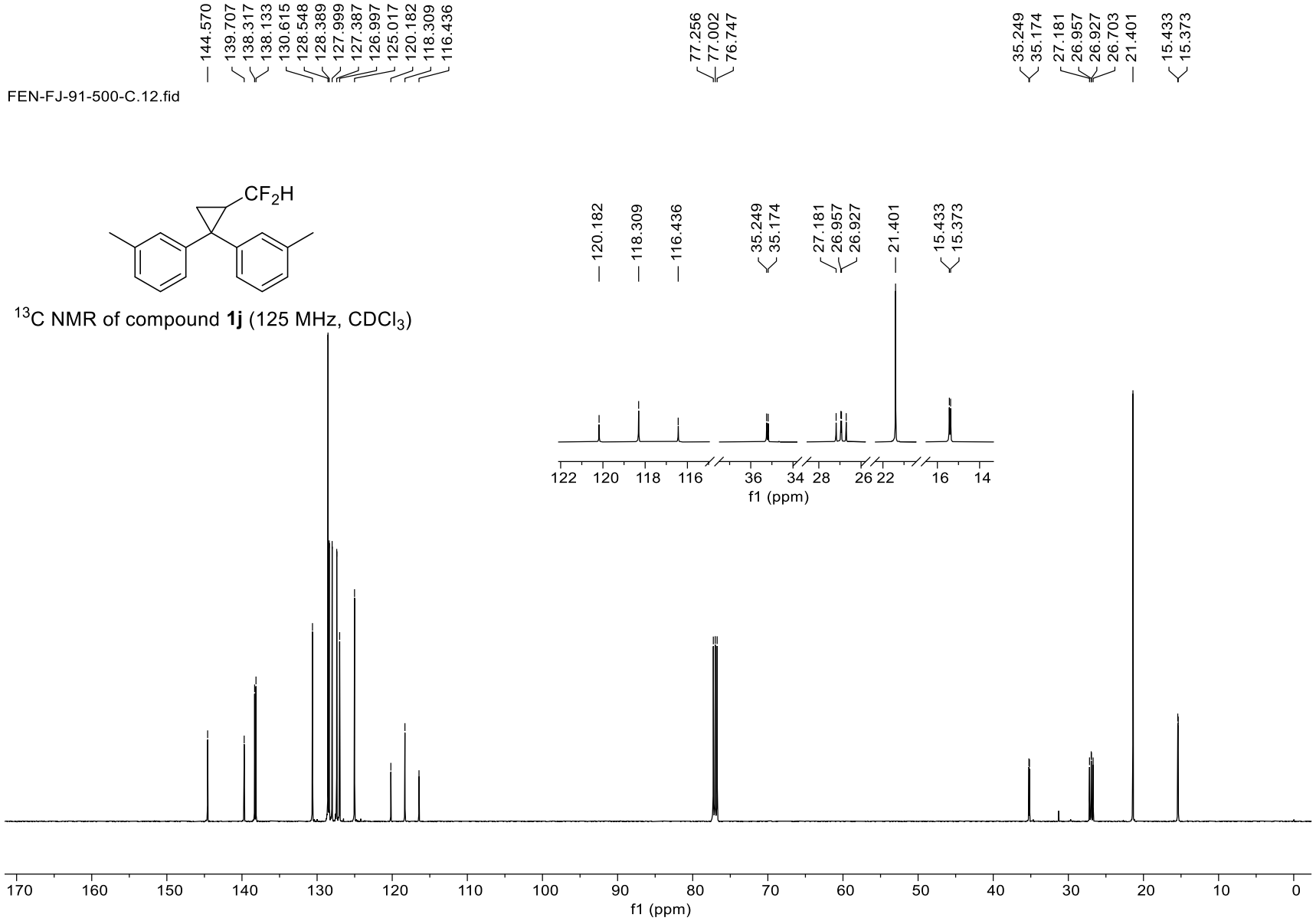
FEN-FJ-91-300-H.11.fid

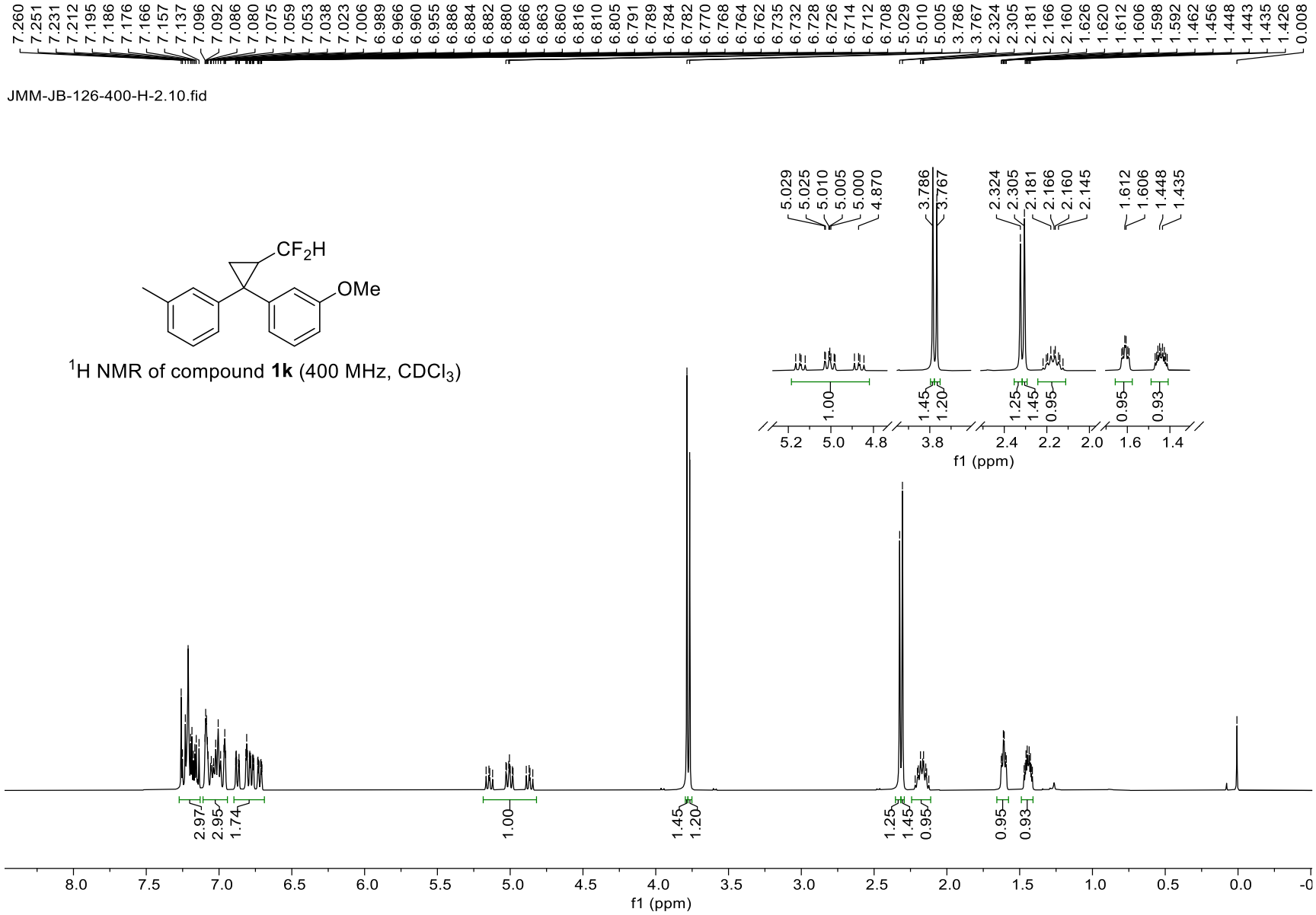
-107.343
-108.345
-113.437
-114.439



^{19}F NMR of compound **1j** (282 MHz, $CDCl_3$)

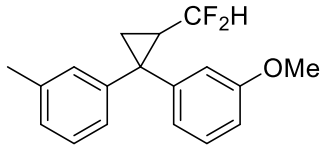



144.570
139.707
138.317
138.133
130.615
128.548
128.389
127.999
127.387
126.997
125.017
120.182
118.309
116.436
77.256
77.002
76.747
35.249
35.174
27.181
26.957
26.927
26.703
21.401
15.433
15.373
FEN-FJ-91-500-C.12.fid
CF2H
13C NMR of compound 1j (125 MHz, CDCl3)
f1 (ppm)

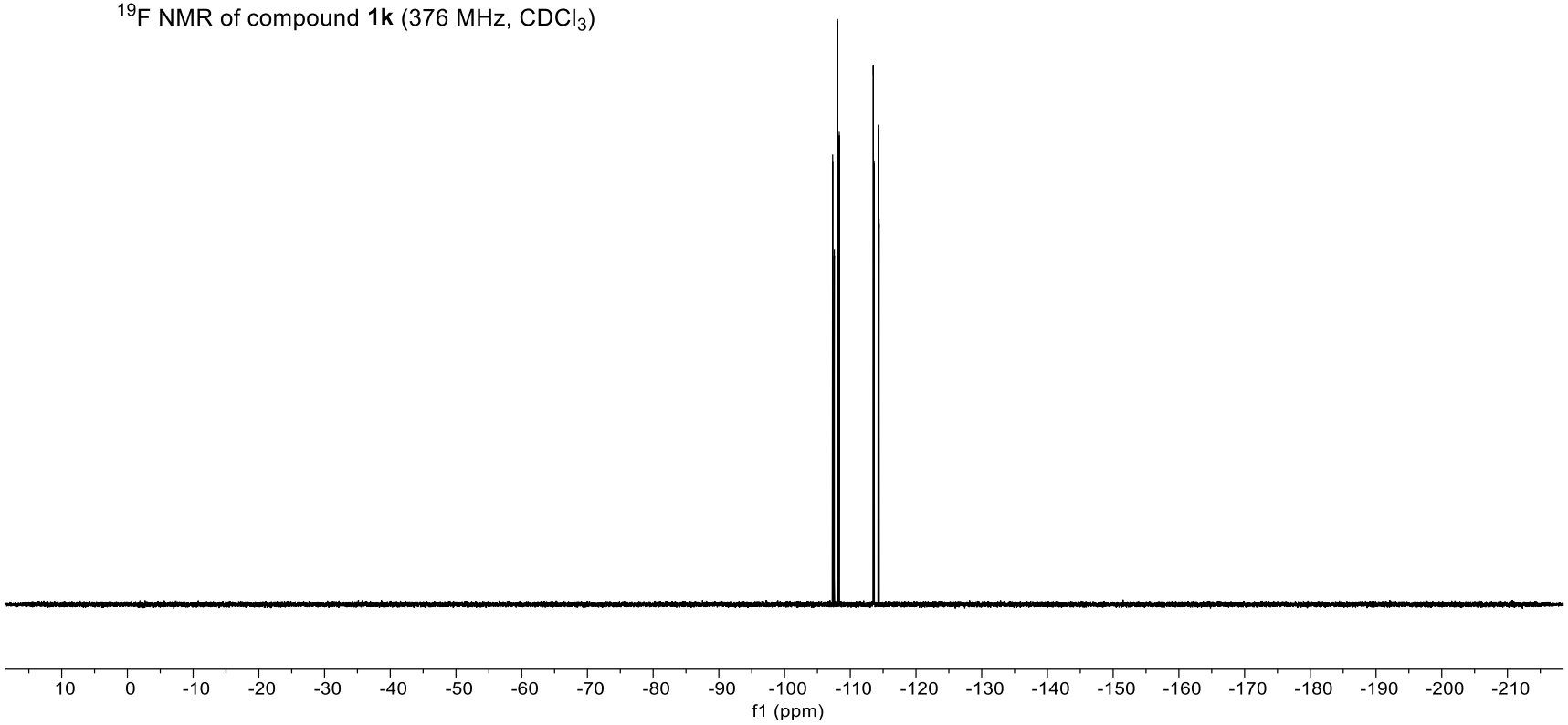

7.260 7.251 7.231 7.212 7.195 7.186 7.176 7.166 7.157 7.137 7.096 7.092 7.086 7.080 7.075 7.059 7.053 7.038 7.023 7.006 6.989 6.966 6.960 6.955 6.886 6.884 6.882 6.880 6.866 6.863 6.860 6.816 6.810 6.805 6.791 6.789 6.784 6.782 6.770 6.768 6.764 6.762 6.735 6.732 6.728 6.726 6.714 6.712 6.708 5.029 5.010 5.005 3.786 3.767 2.324 2.305 2.181 2.166 2.160 1.626 1.620 1.612 1.606 1.598 1.592 1.462 1.456 1.448 1.443 1.435 1.426 0.008
JMM-JB-126-400-H-2.10.fid
CF2H
OMe
1H NMR of compound 1k (400 MHz, CDCl3)
5.029 5.025 5.010 5.005 5.000 4.870 3.786 3.767 2.324 2.305 2.181 2.166 2.160 2.145 1.612 1.606 1.448 1.435
1.00 1.45 1.20 1.25 1.45 0.95 0.95 0.93
5.2 5.0 4.8 3.8 2.4 2.2 2.0 1.6 1.4
f1 (ppm)
2.97 2.95 1.74 1.00 1.45 1.20 1.25 1.45 0.95 0.95 0.93
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

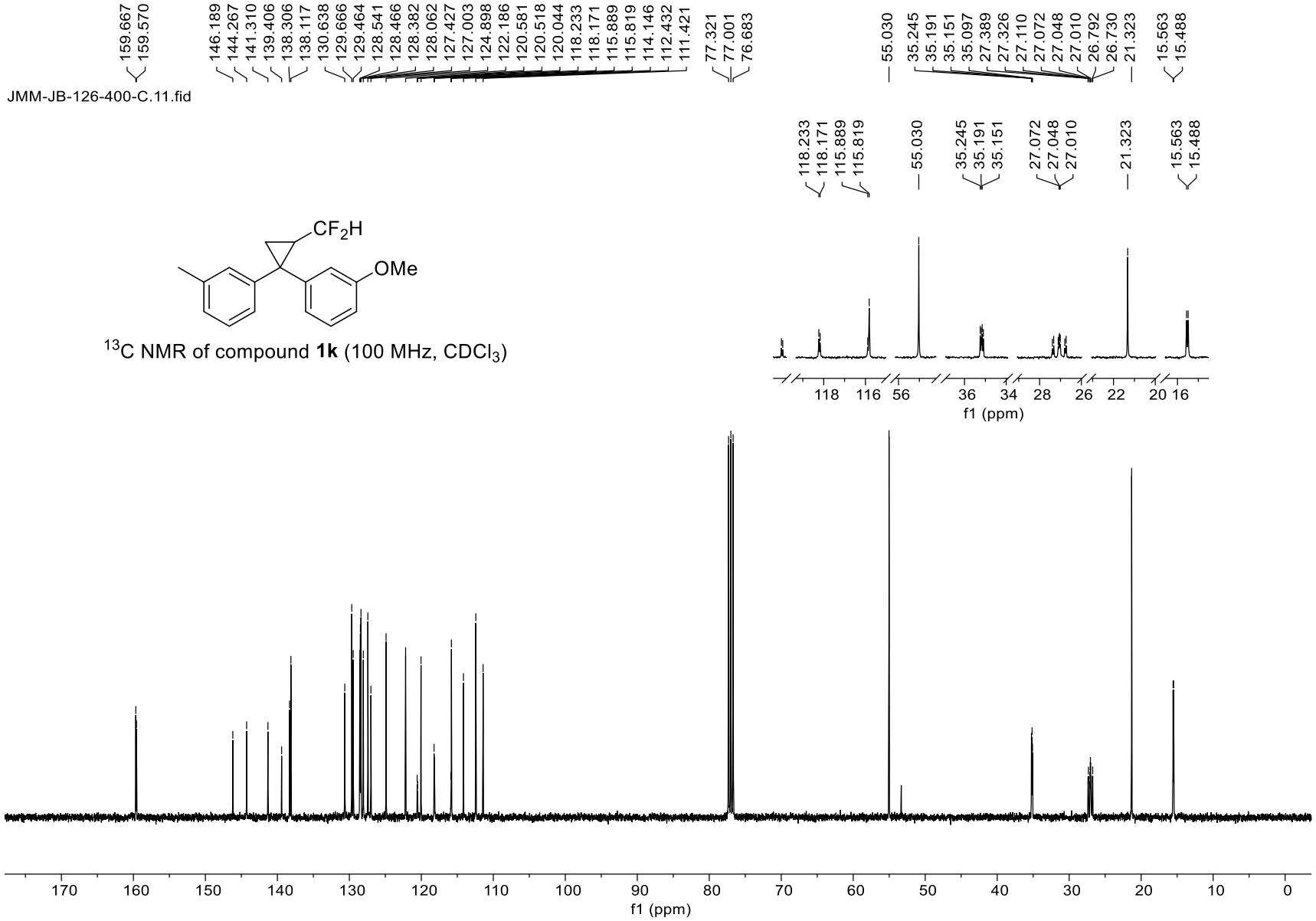
JMM-JB-126-400-H-2.11.fid

-107.316
-107.564
-108.069
-108.317
-113.509
-113.621
-114.262
-114.374

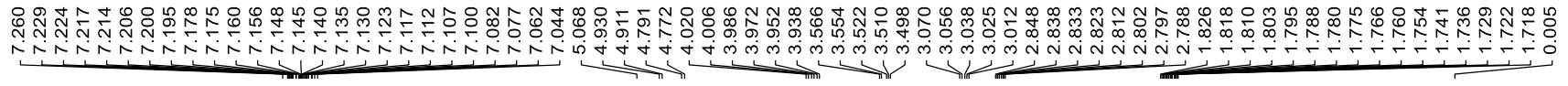


^{19}F NMR of compound **1k** (376 MHz, $CDCl_3$)

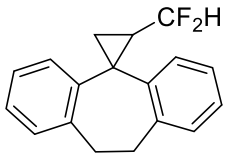




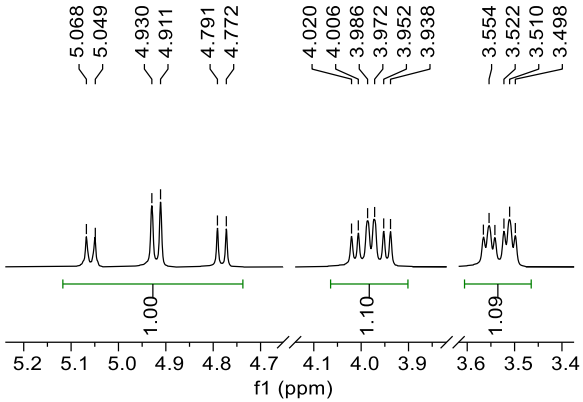
^{13}C NMR of compound **1k** (100 MHz, $CDCl_3$)

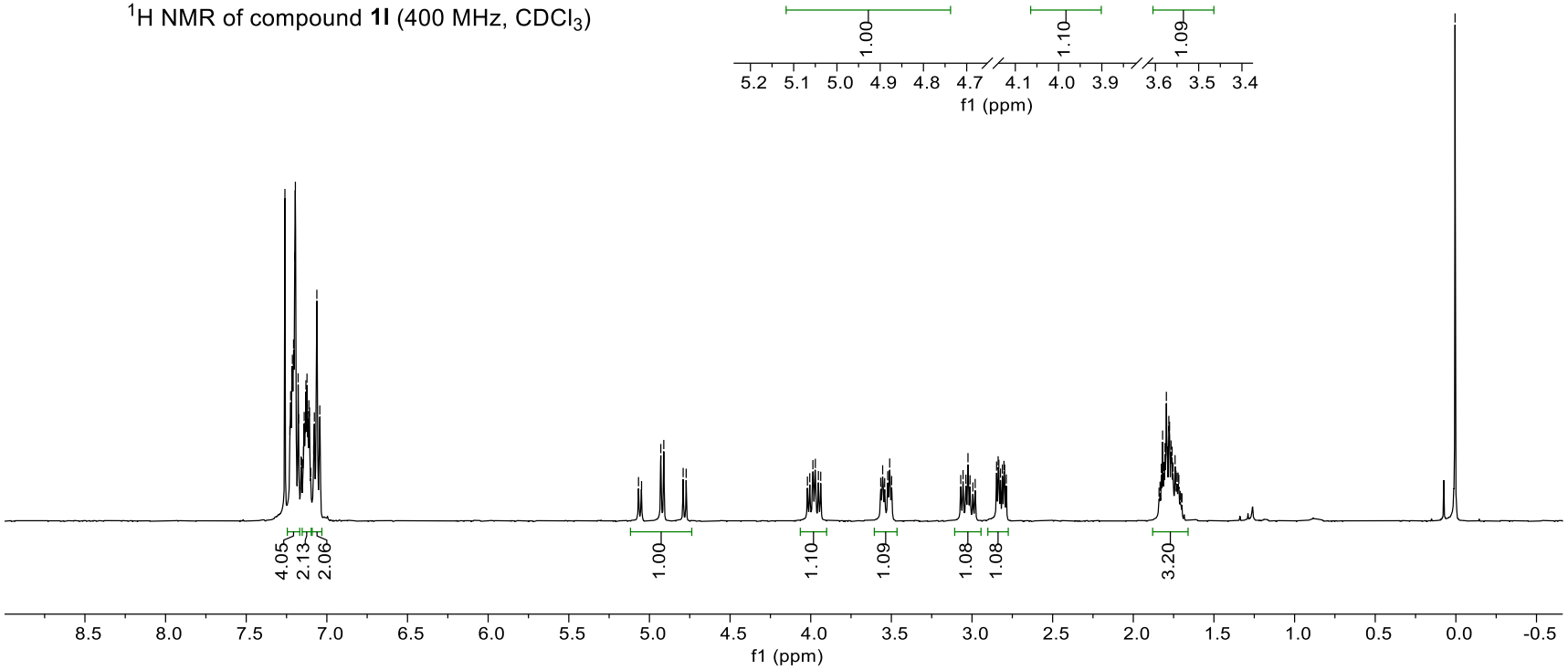


JMM-JB-110-400-H-re.10.fid



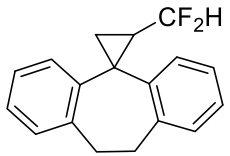
^{1}H NMR of compound **1l** (400 MHz, $CDCl_3$)



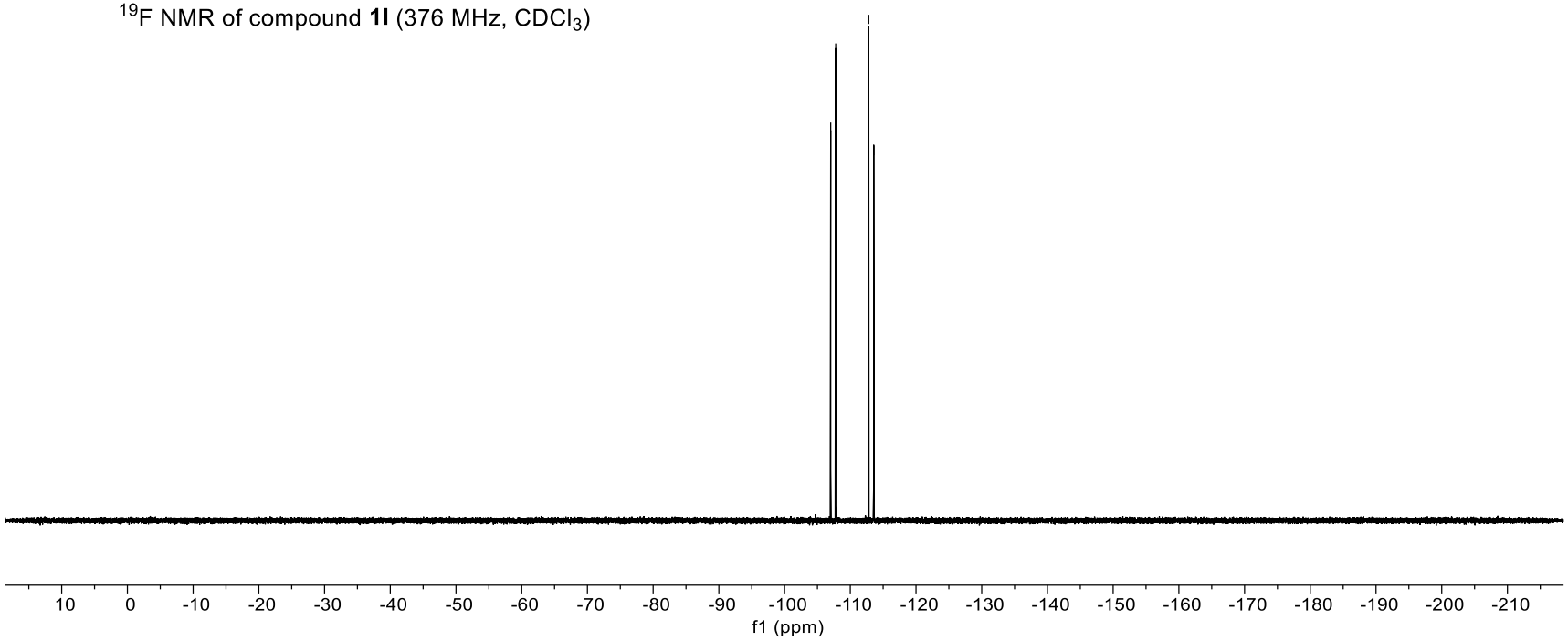


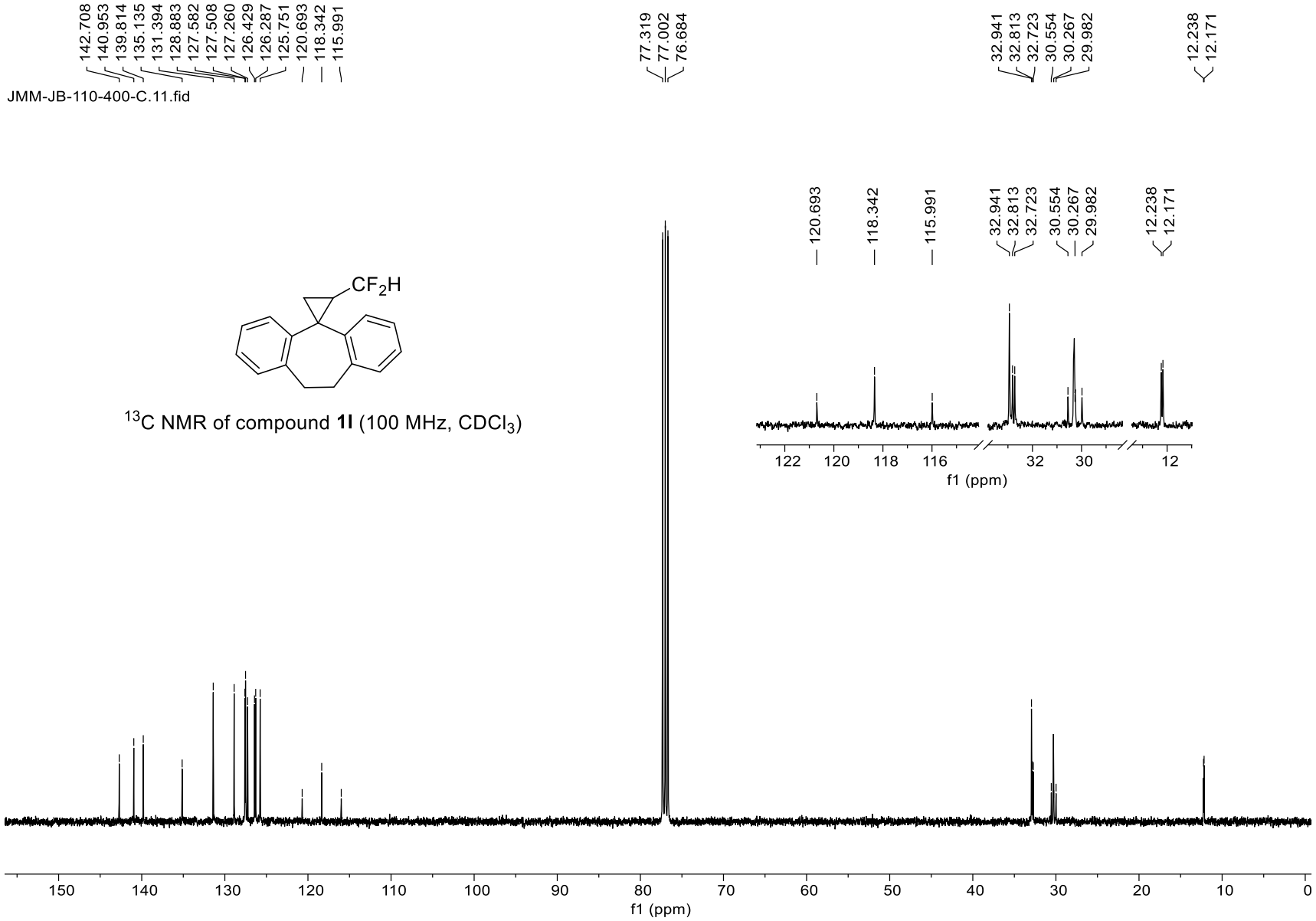
JMM-JB-110-400-H-re.12.fid

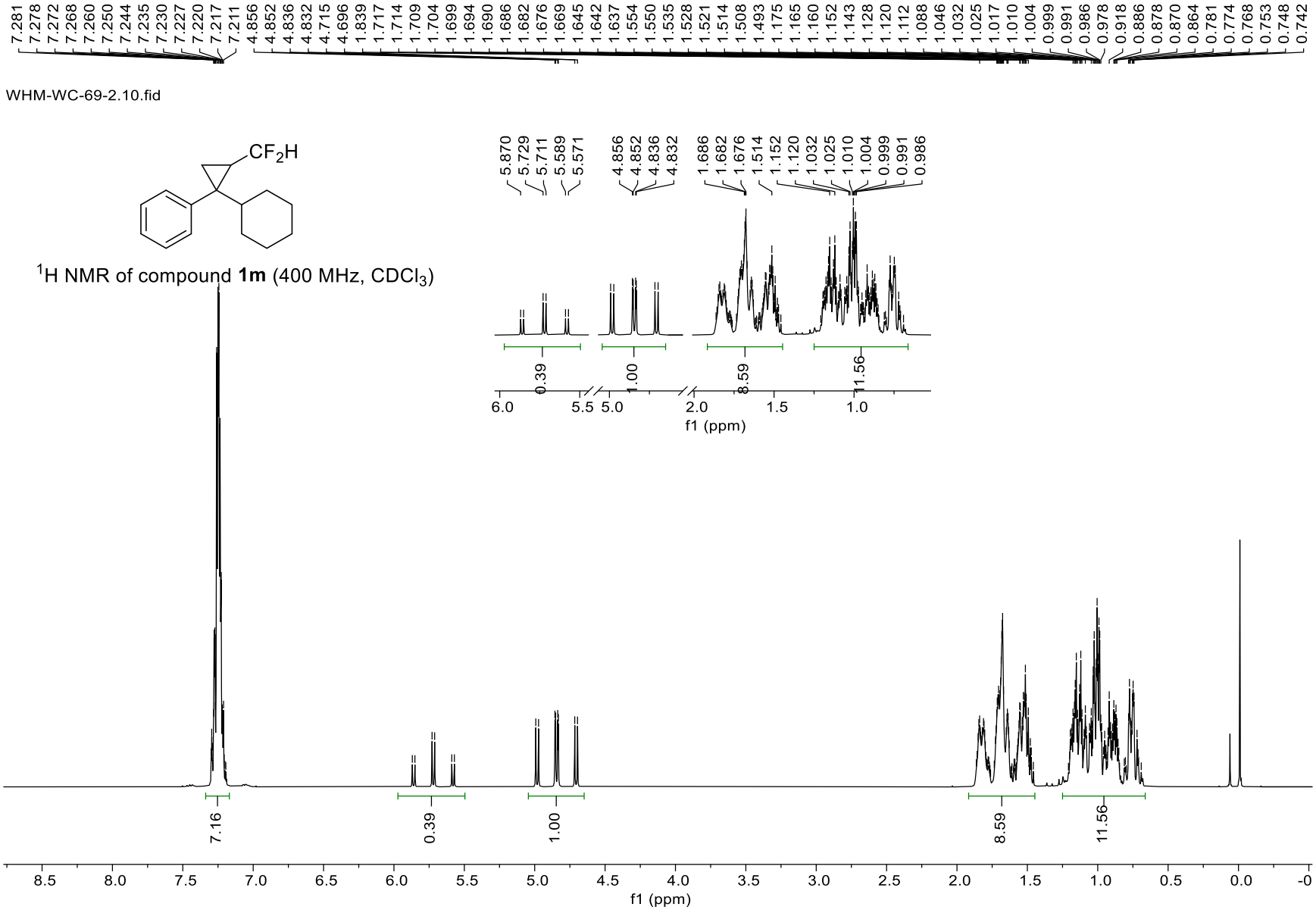
-107.021
-107.776
-112.814
-113.570



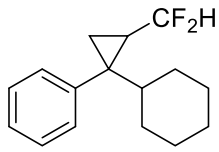
^{19}F NMR of compound **1l** (376 MHz, $CDCl_3$)



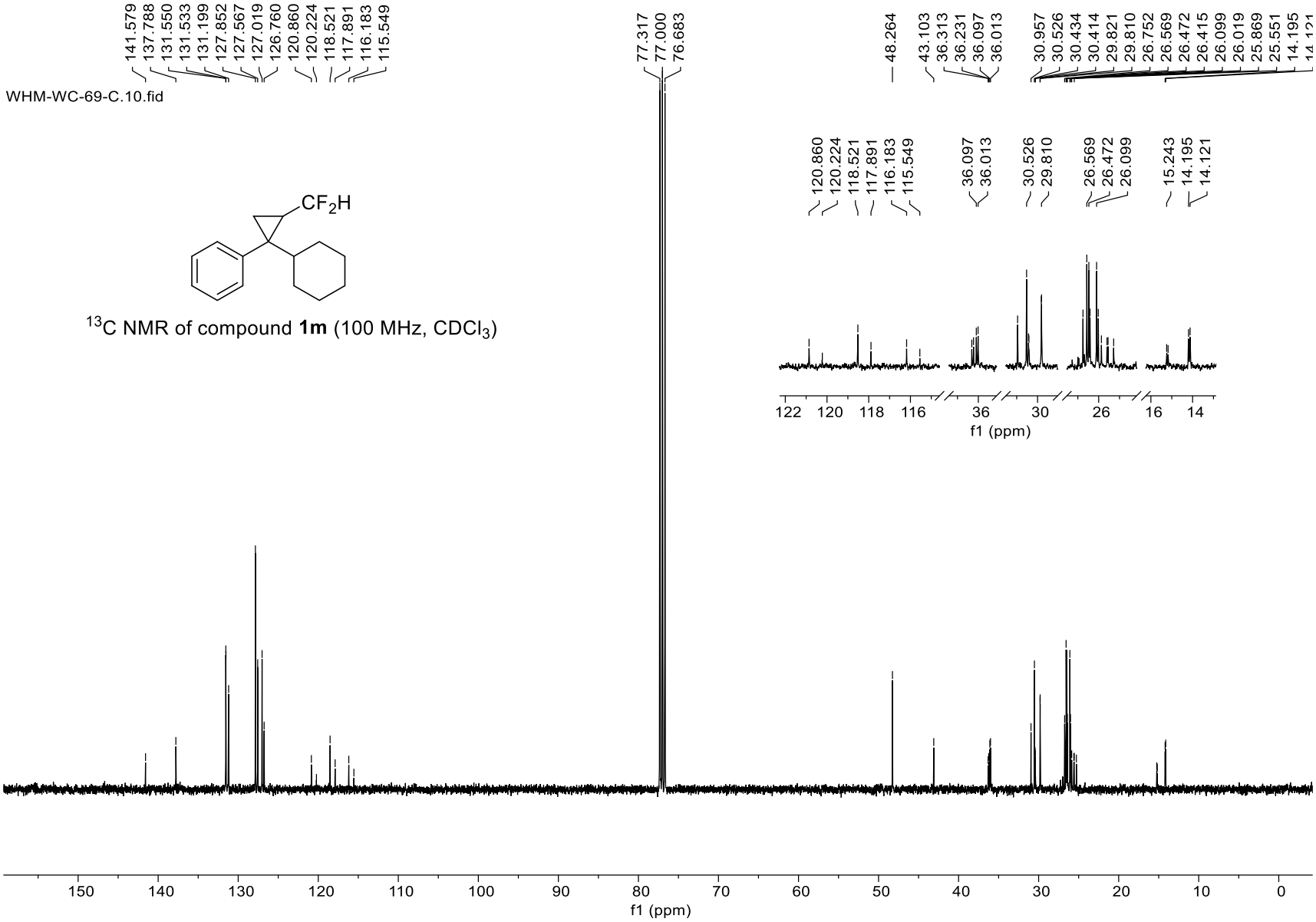

142.708
140.953
139.814
135.135
131.394
128.883
127.582
127.508
127.260
126.429
126.287
125.751
120.693
118.342
115.991
77.319
77.002
76.684
32.941
32.813
32.723
30.554
30.267
29.982
12.238
12.171
JMM-JB-110-400-C.11.fid
CF2H
13C NMR of compound 1l (100 MHz, CDCl3)
f1 (ppm)

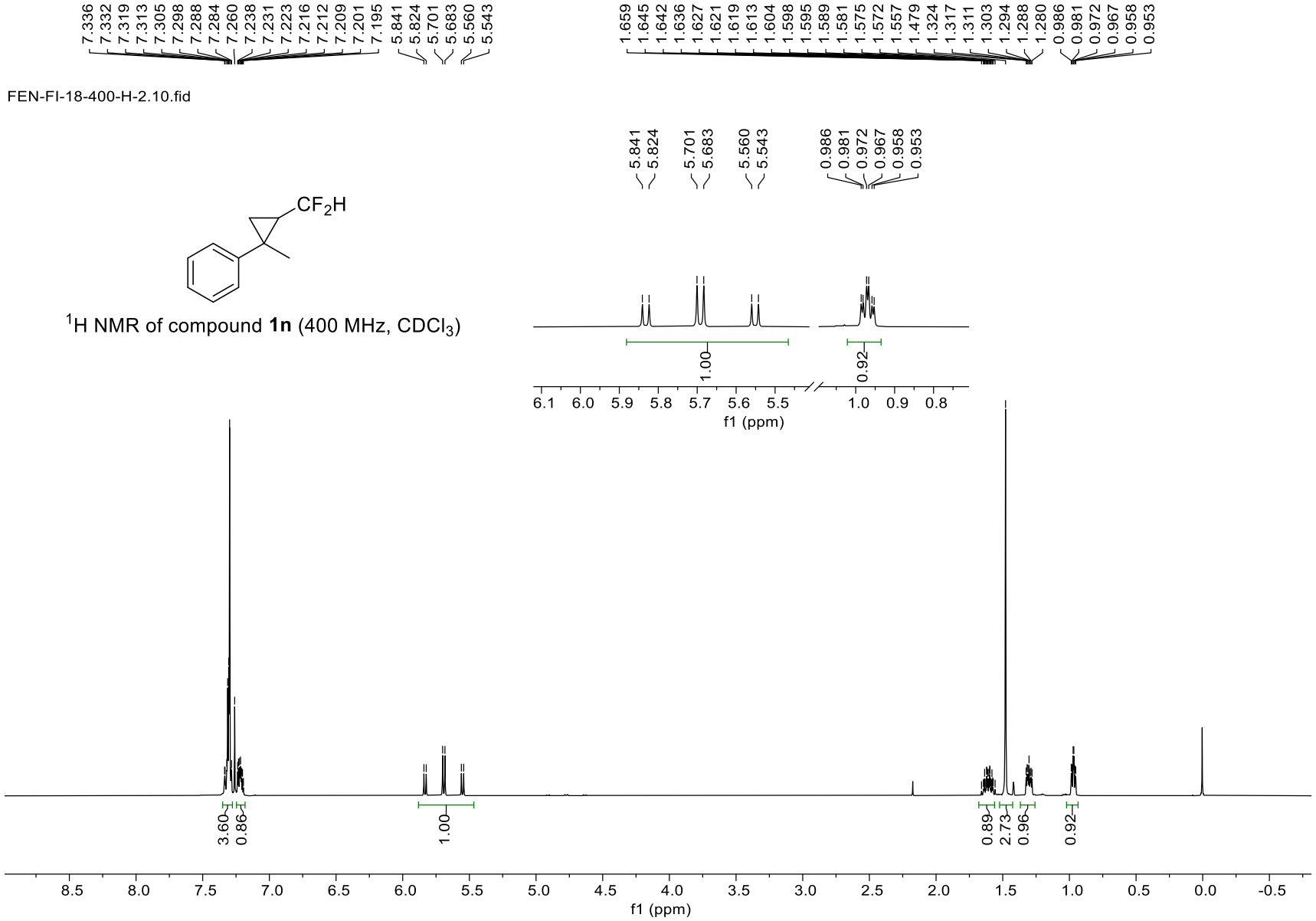

7.281 7.278 7.272 7.268 7.260 7.250 7.244 7.235 7.230 7.227 7.220 7.217 7.211 4.856 4.852 4.836 4.832 4.715 4.696 1.839 1.717 1.714 1.709 1.704 1.699 1.694 1.690 1.686 1.682 1.676 1.669 1.645 1.642 1.637 1.554 1.550 1.535 1.528 1.521 1.514 1.508 1.493 1.175 1.165 1.160 1.152 1.143 1.128 1.120 1.112 1.088 1.046 1.032 1.025 1.017 1.010 1.004 0.999 0.991 0.986 0.978 0.918 0.886 0.878 0.870 0.864 0.781 0.774 0.768 0.753 0.748 0.742
WHM-WC-69-2.10.fid
CF2H
1H NMR of compound 1m (400 MHz, CDCl3)
5.870 5.729 5.711 5.589 5.571 4.856 4.852 4.836 4.832 1.686 1.682 1.676 1.514 1.152 1.120 1.032 1.025 1.010 1.004 0.999 0.991 0.986
0.39 1.00 8.59 11.56
6.0 5.5 5.0 2.0 1.5 1.0
f1 (ppm)
7.16 0.39 1.00 8.59 11.56
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

WHM-WC-49.11.fid



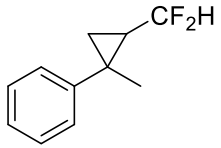
^{19}F NMR of compound **1m** (376 MHz, $CDCl_3$)


141.579
137.788
131.550
131.533
131.199
127.852
127.567
127.019
126.760
120.860
120.224
118.521
117.891
116.183
115.549
77.317
77.000
76.683
48.264
43.103
36.313
36.231
36.097
36.013
30.957
30.526
30.434
30.414
29.821
29.810
26.752
26.569
26.472
26.415
26.099
26.019
25.869
25.551
14.195
WHM-WC-69-C.10.fid
CF2H
13C NMR of compound 1m (100 MHz, CDCl3)
f1 (ppm)

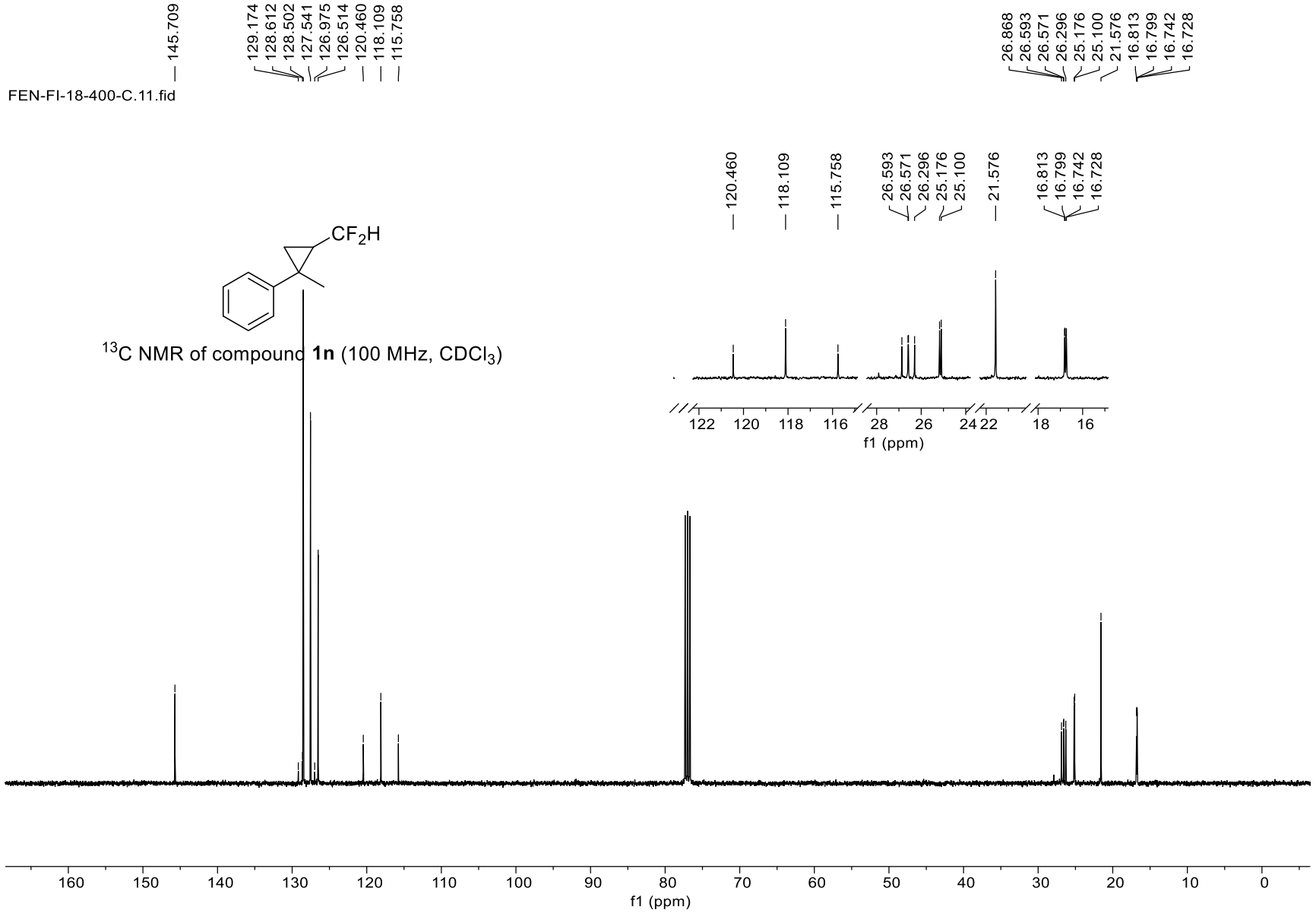

7.336
7.332
7.319
7.313
7.305
7.298
7.288
7.284
7.260
7.238
7.231
7.223
7.216
7.212
7.209
7.201
7.195
5.841
5.824
5.701
5.683
5.560
5.543
1.659
1.645
1.642
1.636
1.627
1.621
1.619
1.613
1.604
1.598
1.595
1.589
1.581
1.575
1.572
1.557
1.479
1.324
1.317
1.311
1.303
1.294
1.288
1.280
0.986
0.981
0.972
0.967
0.958
0.953
FEN-FI-18-400-H-2.10.fid
CF2H
1H NMR of compound 1n (400 MHz, CDCl3)
1.00
0.92
f1 (ppm)
3.60
0.86
1.00
0.89
2.73
0.96
0.92
f1 (ppm)

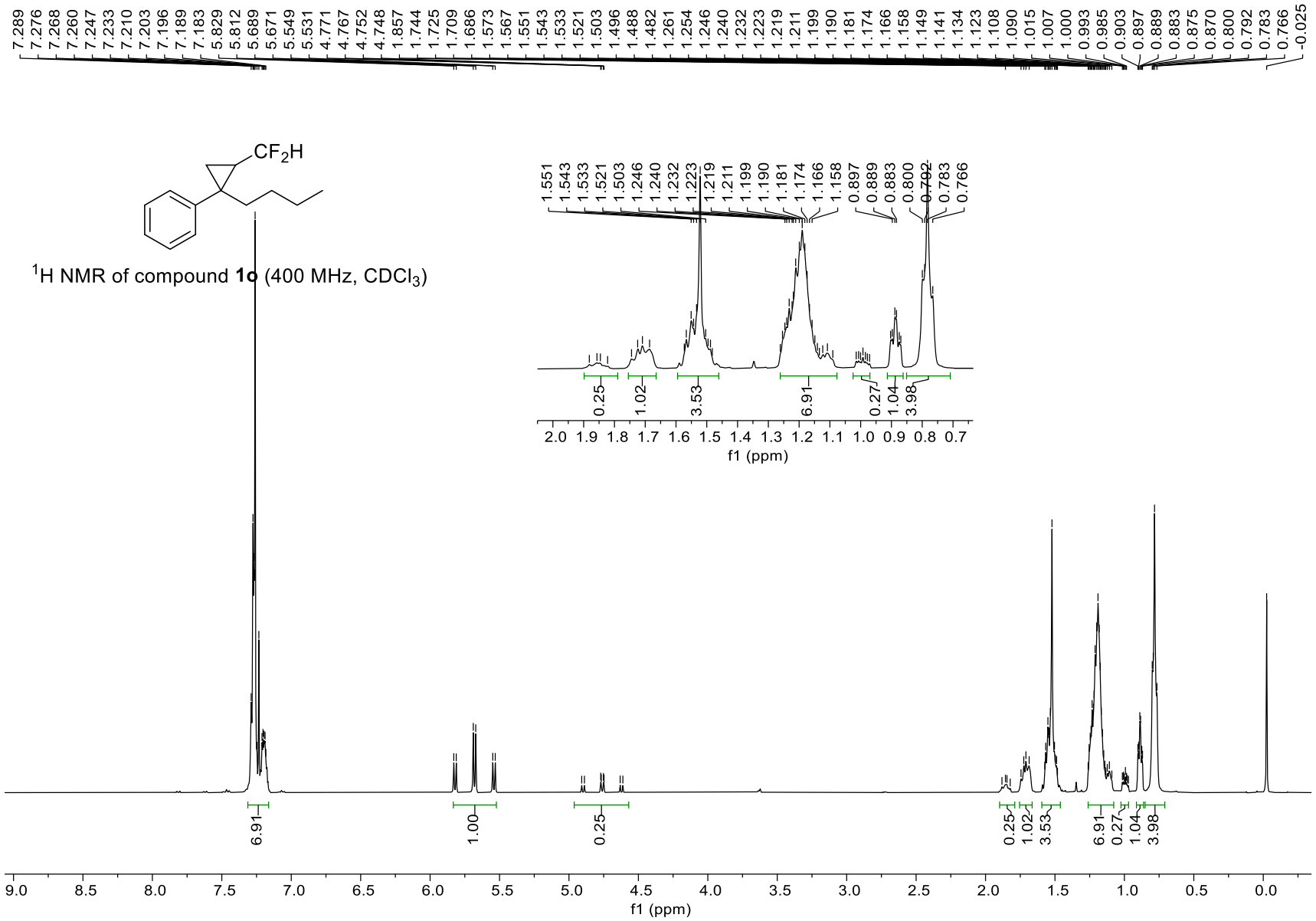
FEN-FI-18-400-H.11.fid

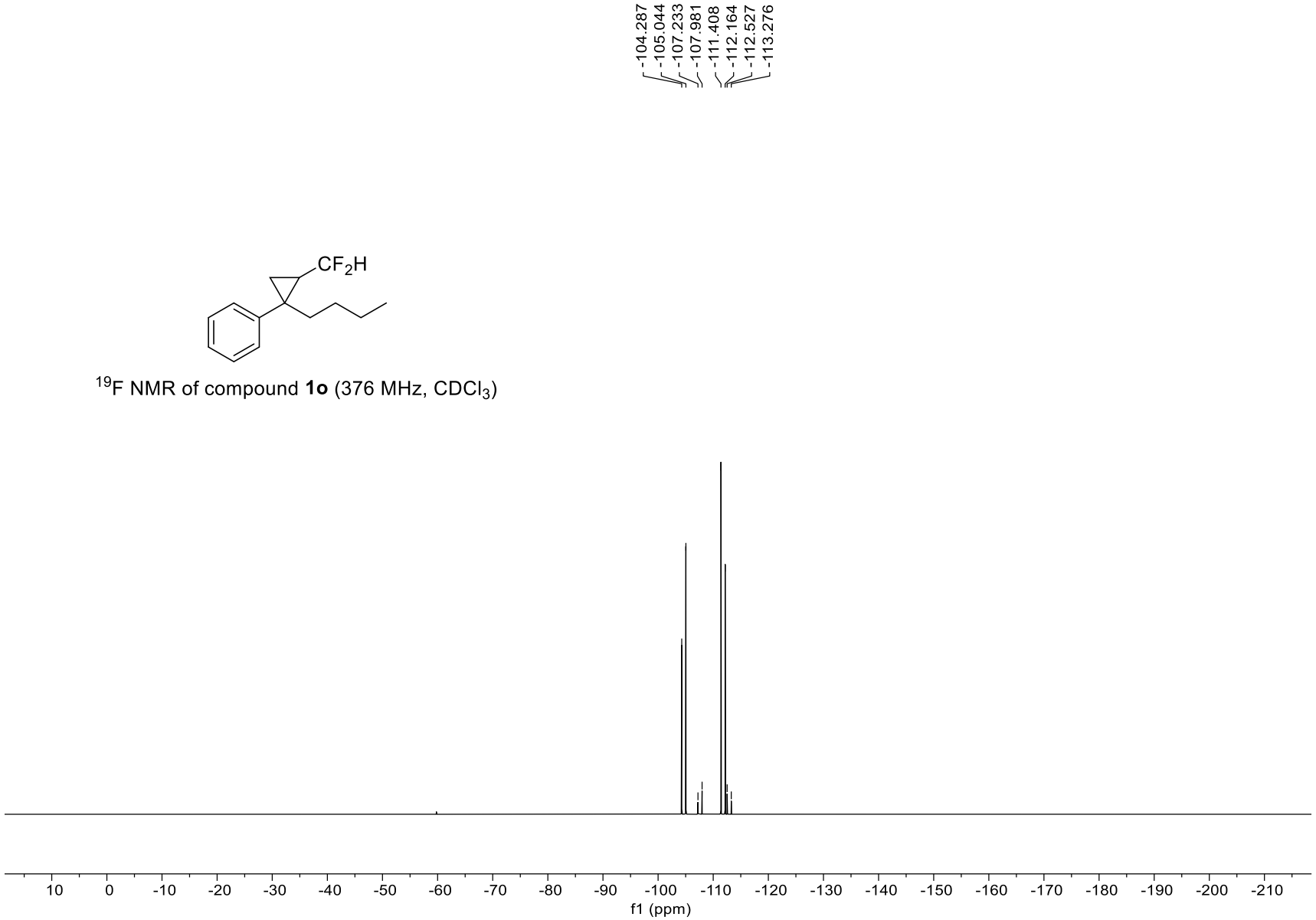
-105.826
-106.584
-111.650
-112.407



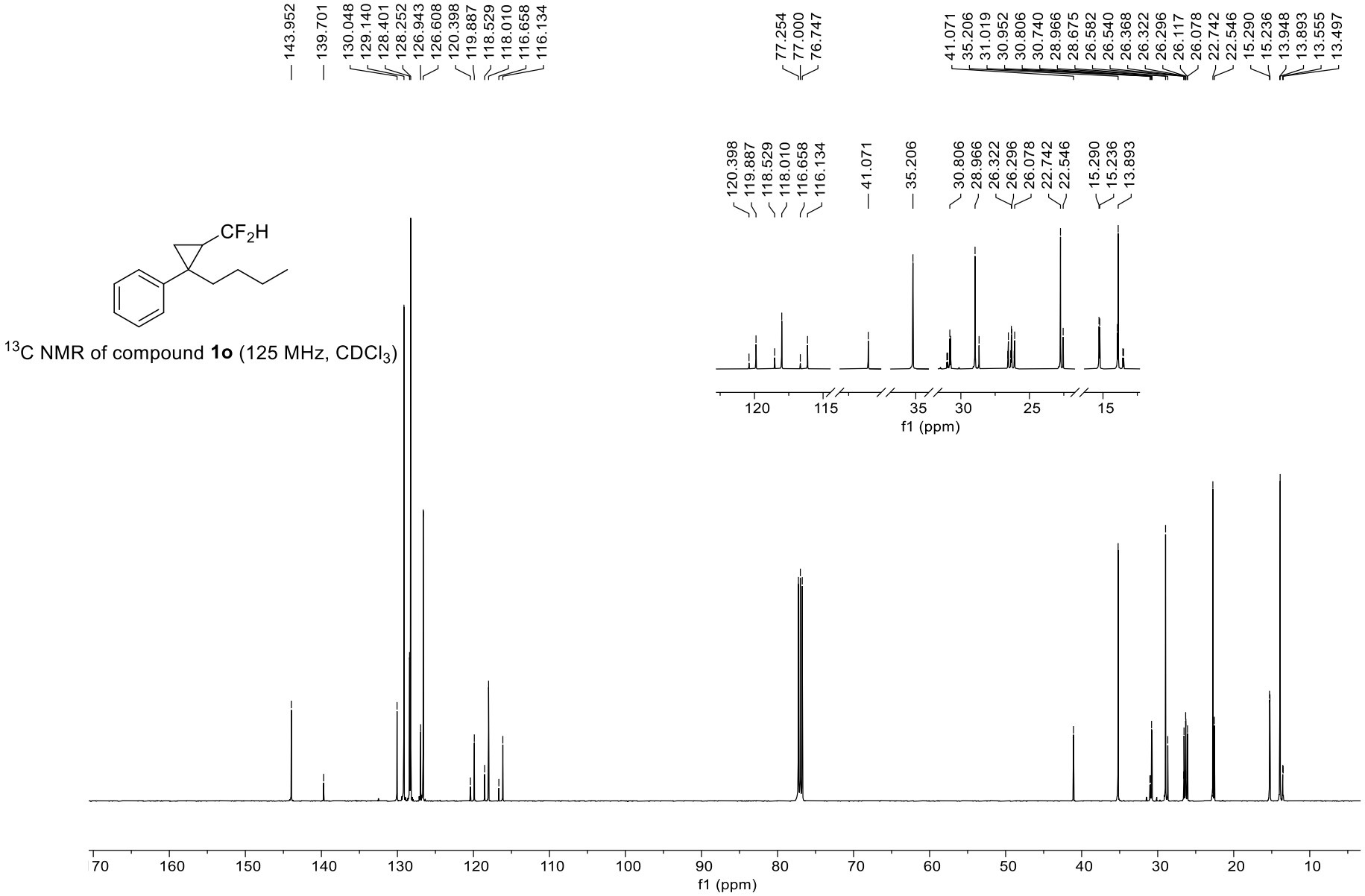
^{19}F NMR of compound **1n** (376 MHz, $CDCl_3$)

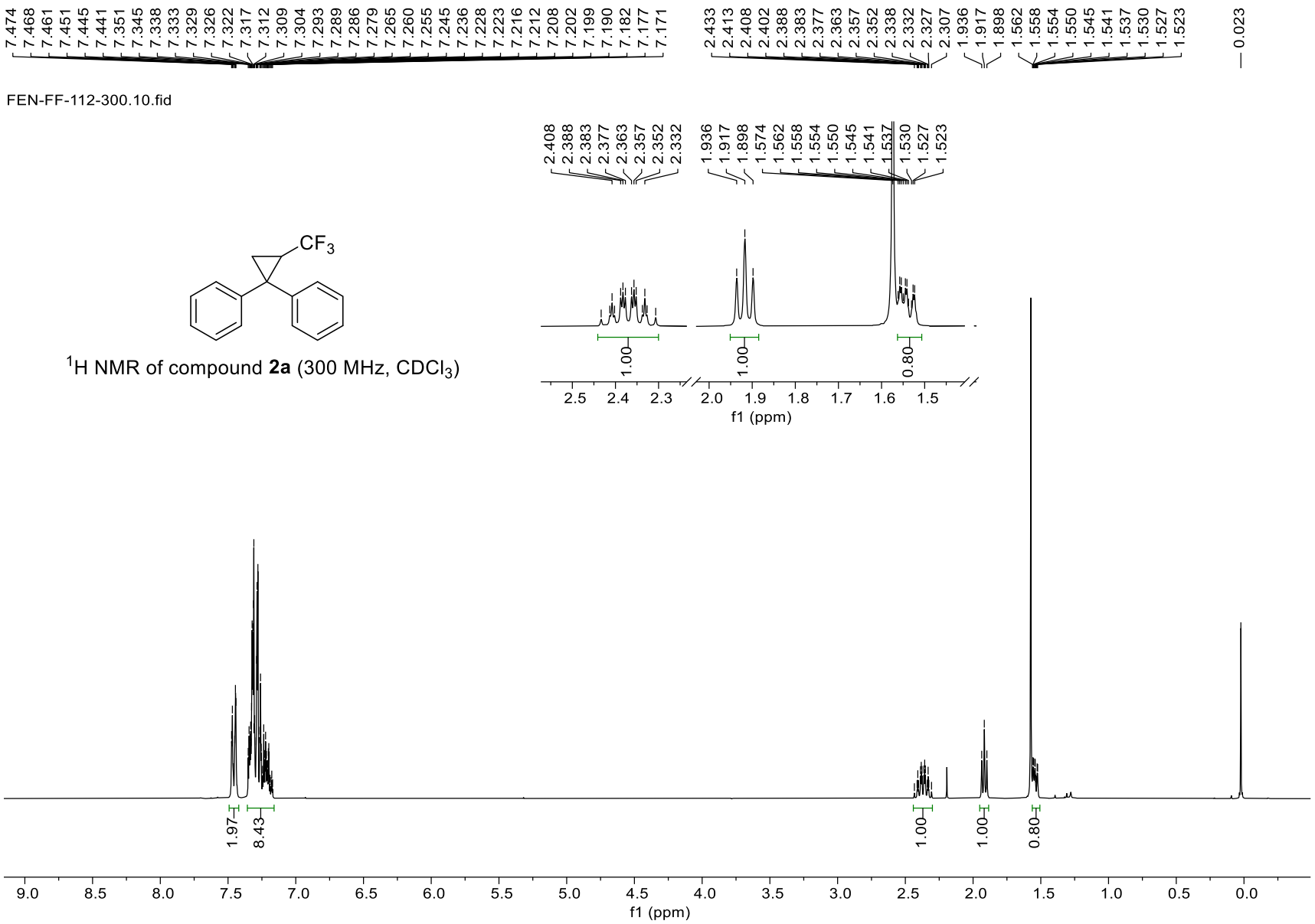

145.709
129.174
128.612
128.502
127.541
126.975
126.514
120.460
118.109
115.758
26.868
26.593
26.571
26.296
25.176
25.100
21.576
16.813
16.799
16.742
16.728
FEN-FI-18-400-C.11.fid
CF2H
13C NMR of compound 1n (100 MHz, CDCl3)
f1 (ppm)


CF2H
1H NMR of compound 1o (400 MHz, CDCl3)
f1 (ppm)



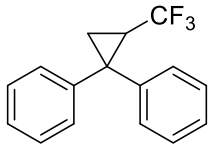
^{19}F NMR of compound **1o** (376 MHz, $CDCl_3$)


143.952
139.701
130.048
129.140
128.401
128.252
126.943
126.608
120.398
119.887
118.529
118.010
116.658
116.134
77.254
77.000
76.747
41.071
35.206
31.019
30.952
30.806
30.740
28.966
28.675
26.582
26.540
26.368
26.322
26.296
26.117
26.078
22.742
22.546
15.290
15.236
13.948
13.893
13.555
13.497
CF2H
13C NMR of compound 1o (125 MHz, CDCl3)
f1 (ppm)

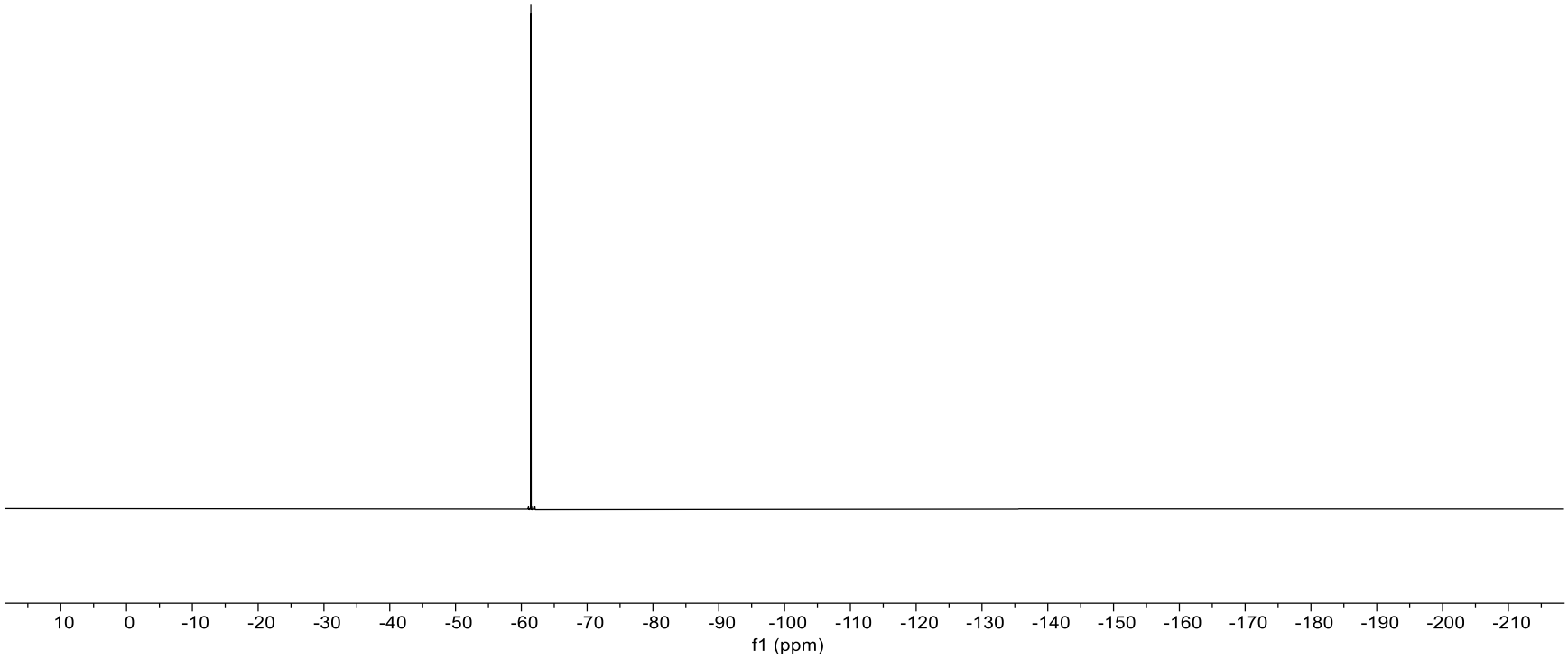

7.474 7.468 7.461 7.451 7.445 7.441 7.351 7.345 7.338 7.333 7.329 7.326 7.322 7.317 7.312 7.309 7.304 7.293 7.289 7.286 7.279 7.265 7.260 7.255 7.245 7.236 7.228 7.223 7.216 7.212 7.208 7.202 7.199 7.190 7.182 7.177 7.171
2.433 2.413 2.408 2.402 2.388 2.383 2.377 2.363 2.357 2.352 2.338 2.332 2.327 2.307 1.936 1.917 1.898 1.562 1.558 1.554 1.550 1.545 1.541 1.537 1.530 1.527 1.523
0.023
FEN-FF-112-300.10.fid
2.408 2.388 2.383 2.377 2.363 2.357 2.352 2.332
1.936 1.917 1.898 1.574 1.562 1.558 1.554 1.550 1.545 1.541 1.537 1.530 1.527 1.523
1.00 1.00 0.80
2.5 2.4 2.3 2.0 1.9 1.8 1.7 1.6 1.5
f1 (ppm)
CF3
1H NMR of compound 2a (300 MHz, CDCl3)
1.97 8.43 1.00 1.00 0.80
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

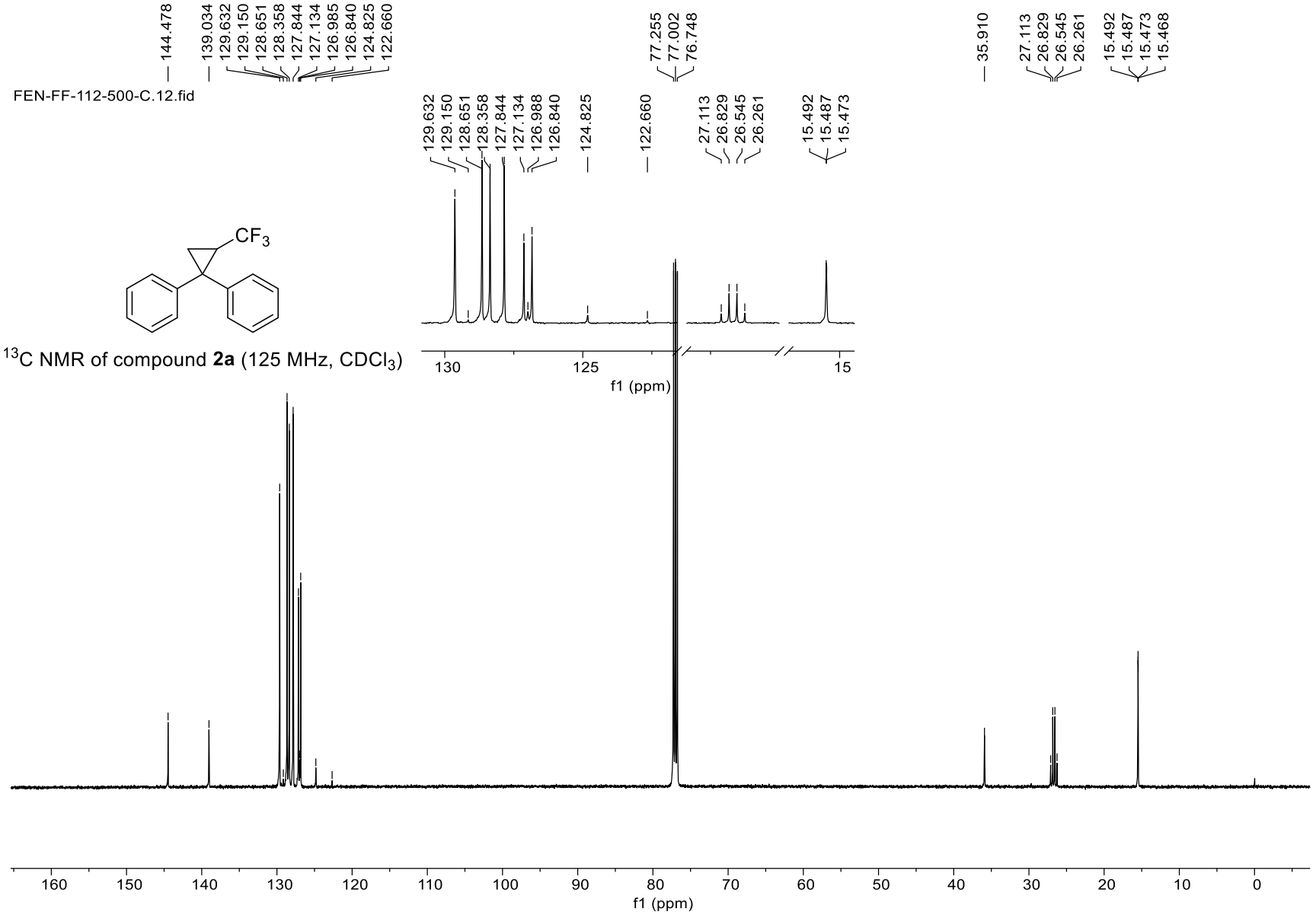
FEN-FF-112-300.11.fid

— -61.445

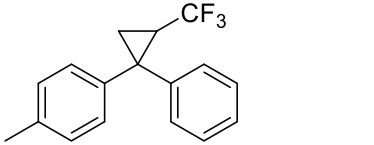


^{19}F NMR of compound **2a** (282 MHz, $CDCl_3$)




144.478
139.034
129.632
129.150
128.651
128.358
127.844
127.134
126.985
126.840
124.825
122.660
77.255
77.002
76.748
35.910
27.113
26.829
26.545
26.261
15.492
15.487
15.473
15.468
FEN-FF-112-500-C.12.fid
CF3
13C NMR of compound 2a (125 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

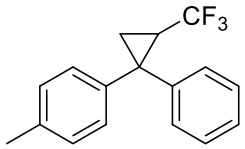
FEN-FJ-34-400-H.10.fid



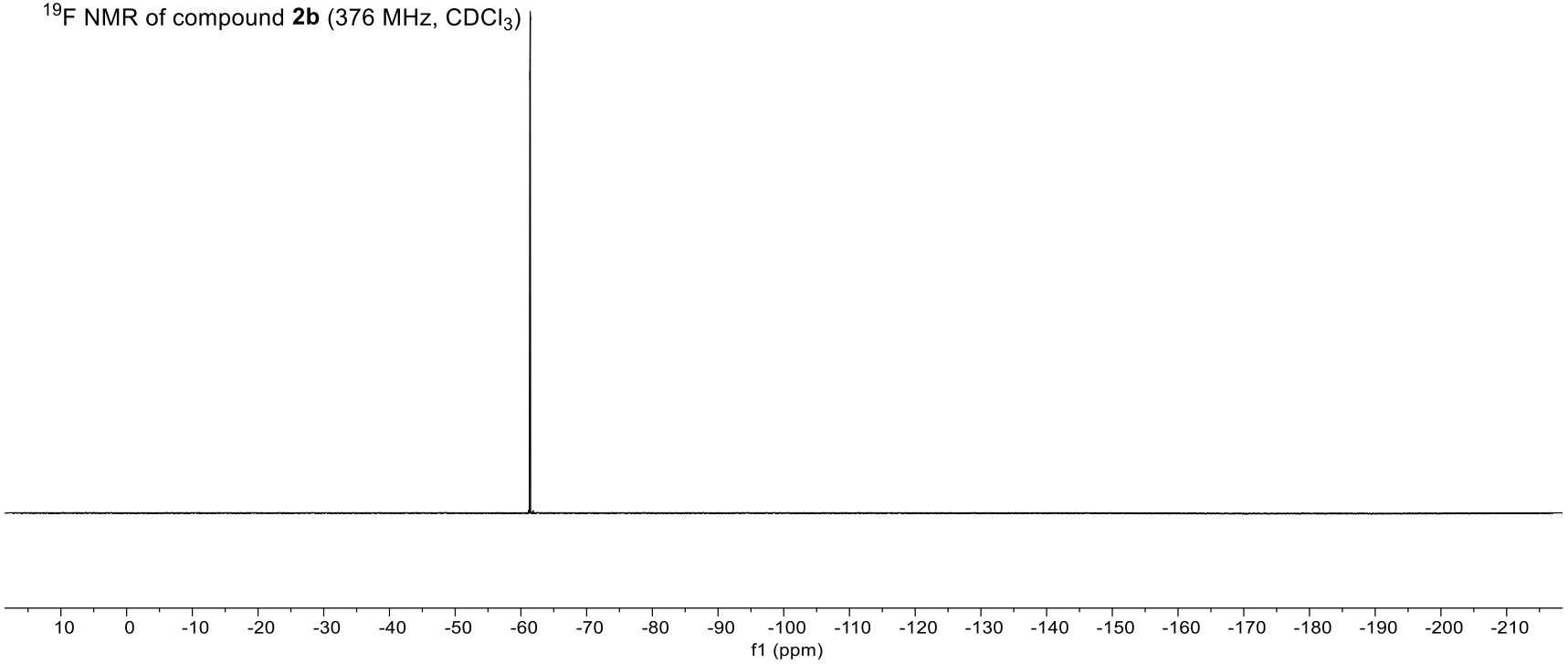
^{1}H NMR of compound **2b** (400 MHz, $CDCl_3$)

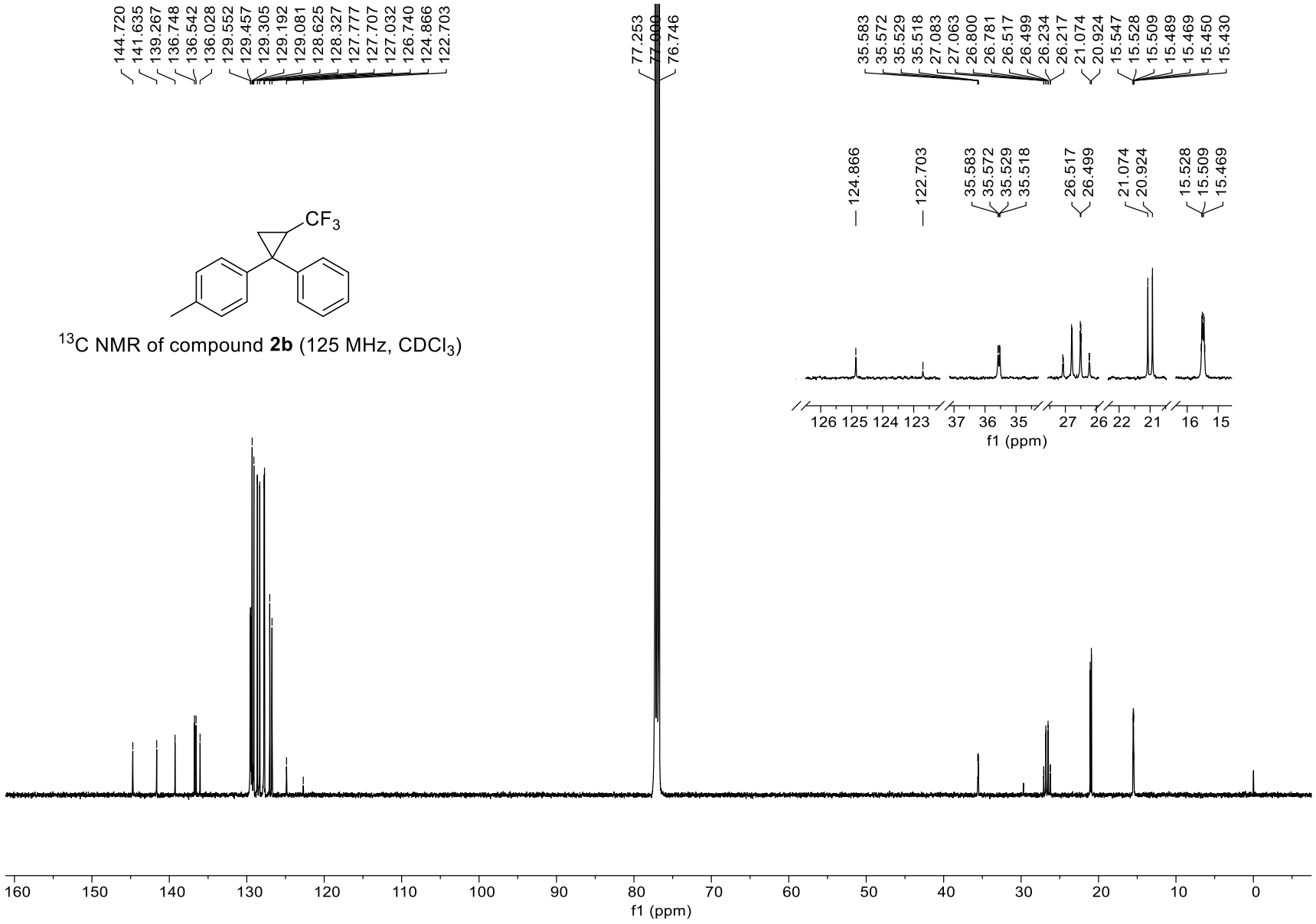
-61.368
-61.421

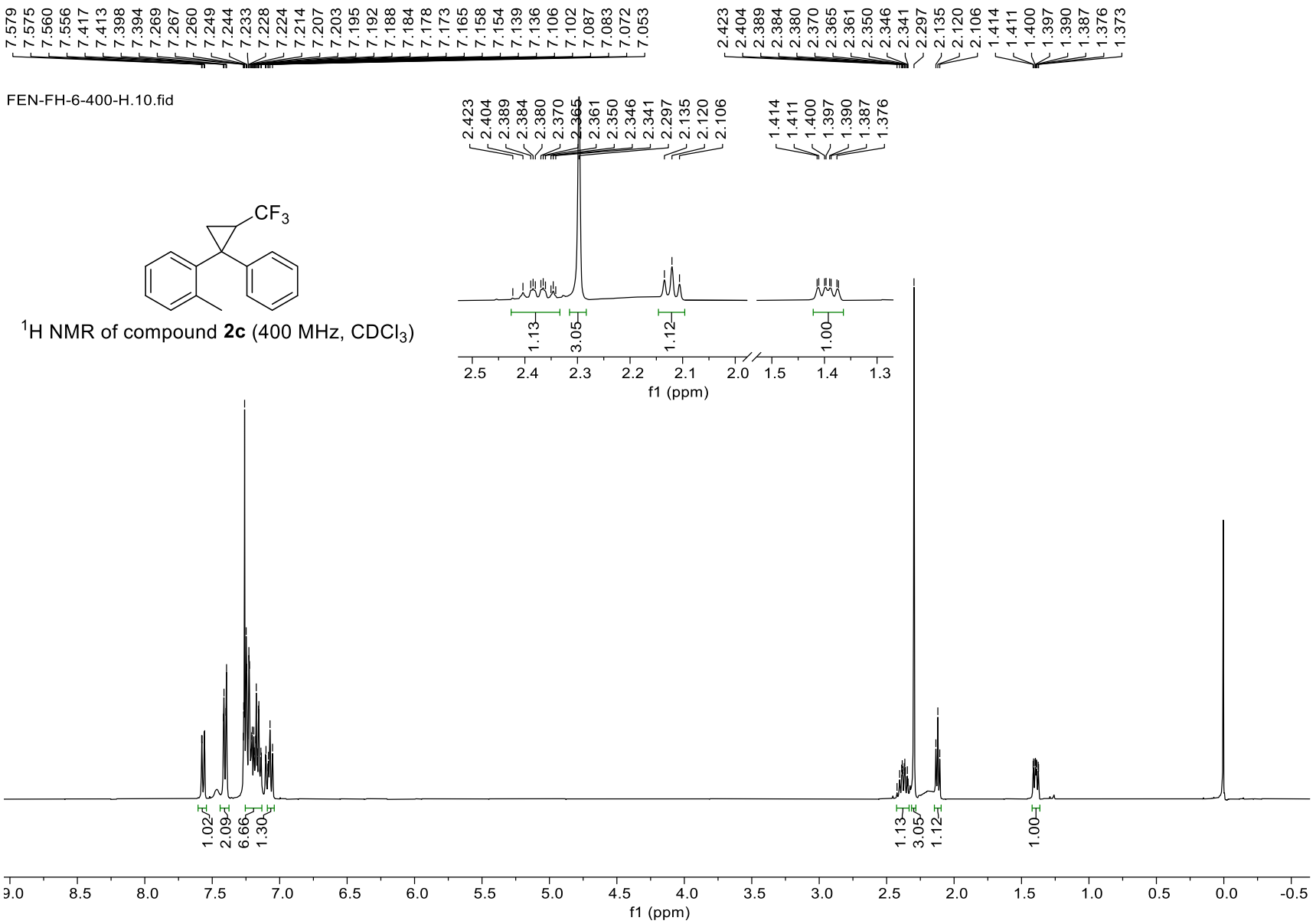
FEN-FJ-34-400-H.11.fid



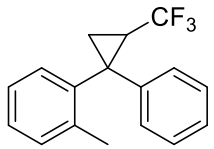
^{19}F NMR of compound **2b** (376 MHz, $CDCl_3$)



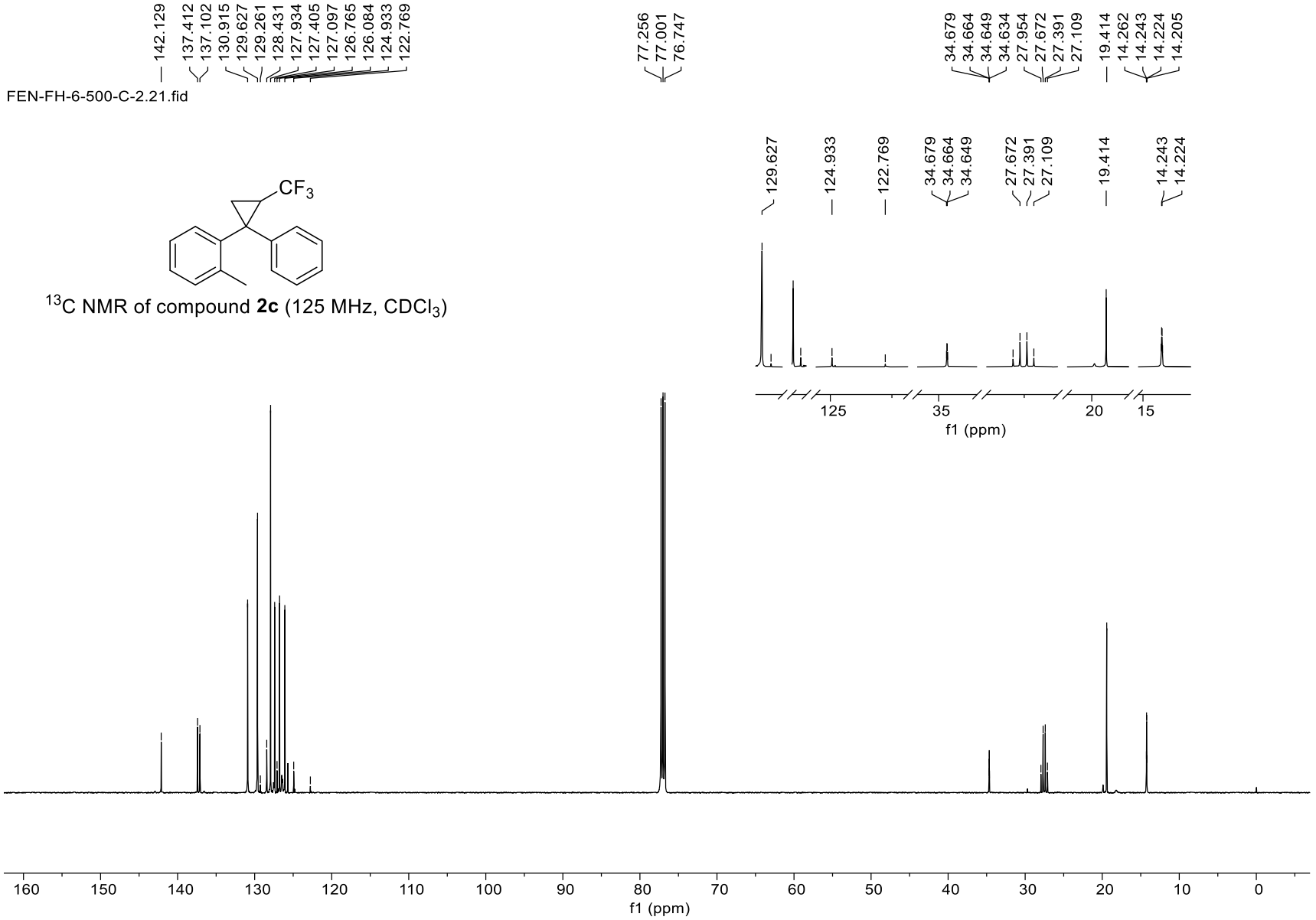

144.720
141.635
139.267
136.748
136.542
136.028
129.552
129.457
129.305
129.192
129.081
128.625
128.327
127.777
127.707
127.032
126.740
124.866
122.703
77.253
77.000
76.746
35.583
35.572
35.529
35.518
27.083
27.063
26.800
26.781
26.517
26.499
26.234
26.217
21.074
20.924
15.547
15.528
15.509
15.489
15.469
15.450
15.430
CF3
13C NMR of compound 2b (125 MHz, CDCl3)
f1 (ppm)


7.579 7.575 7.560 7.556 7.417 7.413 7.398 7.394 7.269 7.267 7.260 7.249 7.244 7.233 7.228 7.224 7.214 7.207 7.203 7.195 7.192 7.188 7.184 7.178 7.173 7.165 7.158 7.154 7.139 7.136 7.106 7.102 7.087 7.083 7.072 7.053
2.423 2.404 2.389 2.384 2.380 2.370 2.365 2.361 2.350 2.346 2.341 2.297 2.135 2.120 2.106 1.414 1.411 1.400 1.397 1.390 1.387 1.376 1.373
FEN-FH-6-400-H.10.fid
CF3
1H NMR of compound 2c (400 MHz, CDCl3)
1.13 3.05 1.12 1.00
f1 (ppm)
1.02 2.09 6.66 1.30 1.13 3.05 1.12 1.00
f1 (ppm)

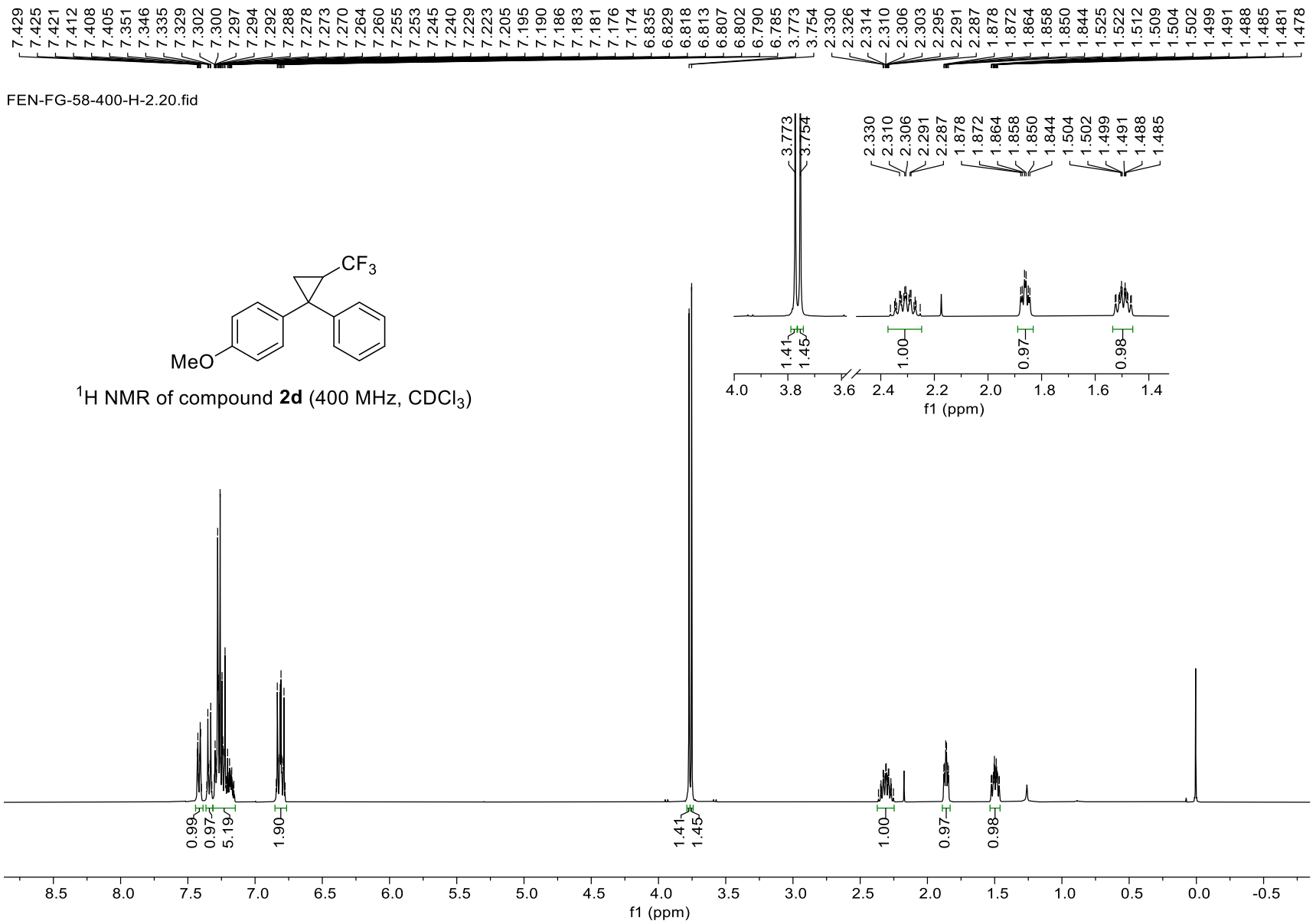
FEN-FH-6-400-H.11.fid



^{19}F NMR of compound **2c** (376 MHz, $CDCl_3$)

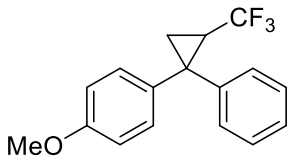


^{13}C NMR of compound **2c** (125 MHz, $CDCl_3$)

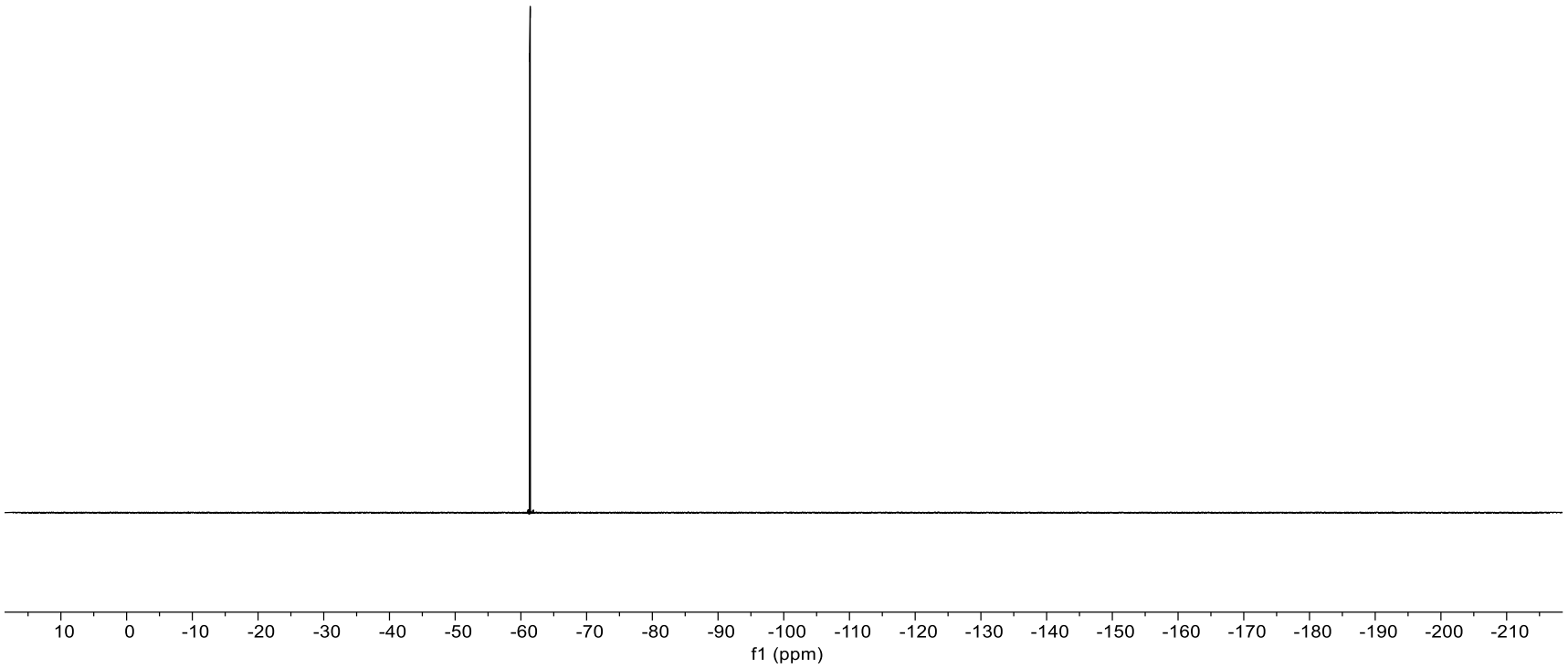

7.429 7.425 7.421 7.412 7.408 7.405 7.351 7.346 7.335 7.329 7.302 7.300 7.297 7.294 7.292 7.288 7.278 7.273 7.270 7.264 7.260 7.255 7.253 7.245 7.240 7.229 7.223 7.205 7.195 7.190 7.186 7.183 7.181 7.176 7.174 6.835 6.829 6.818 6.813 6.807 6.802 6.790 6.785 3.773 3.754 2.330 2.326 2.314 2.310 2.306 2.303 2.295 2.291 2.287 1.878 1.872 1.864 1.858 1.850 1.844 1.525 1.522 1.512 1.509 1.504 1.502 1.499 1.491 1.488 1.485 1.481 1.478
FEN-FG-58-400-H-2.20.fid
CF3
MeO
1H NMR of compound 2d (400 MHz, CDCl3)
3.773 3.754 2.330 2.310 2.306 2.291 2.287 1.878 1.872 1.864 1.858 1.850 1.844 1.504 1.502 1.499 1.491 1.488 1.485
1.41 1.45 1.00 0.97 0.98
4.0 3.8 3.6 2.4 2.2 2.0 1.8 1.6 1.4
f1 (ppm)
0.99 0.97 5.19 1.90 1.41 1.45 1.00 0.97 0.98
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

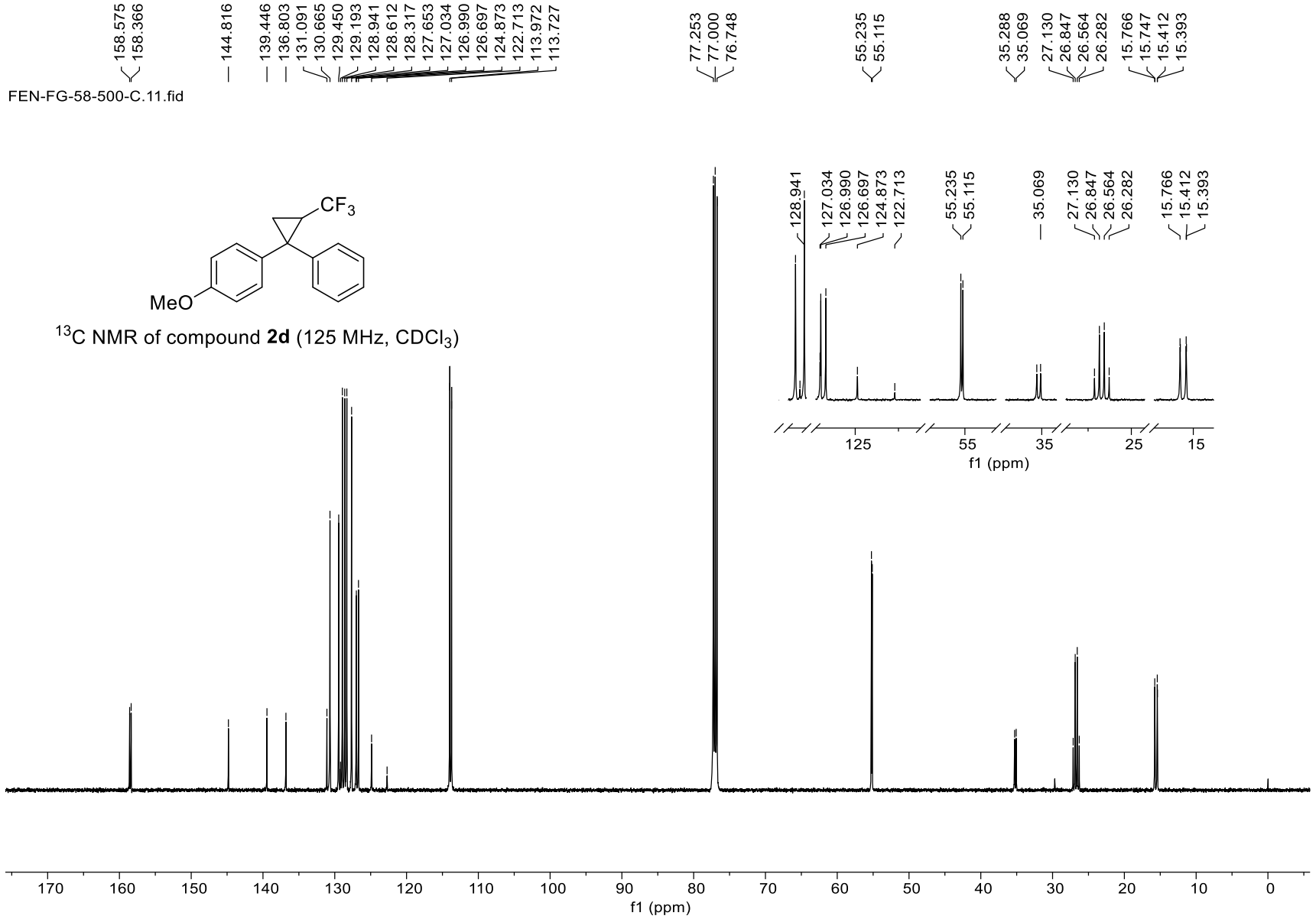
-61.321
-61.415

FEN-FG-58-400-H-2.21.fid

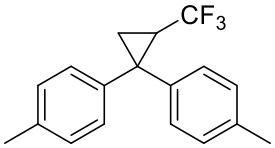


^{19}F NMR of compound **2d** (376 MHz, $CDCl_3$)



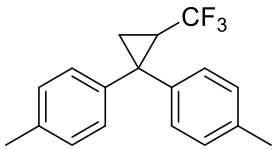

158.575
158.366
144.816
139.446
136.803
131.091
130.665
129.450
129.193
128.941
128.612
128.317
127.653
127.034
126.990
126.697
124.873
122.713
113.972
113.727
77.253
77.000
76.748
55.235
55.115
35.288
35.069
27.130
26.847
26.564
26.282
15.766
15.747
15.412
15.393
FEN-FG-58-500-C.11.fid
CF3
MeO
13C NMR of compound 2d (125 MHz, CDCl3)
f1 (ppm)

FEN-FG-64-1.10.fid
300M

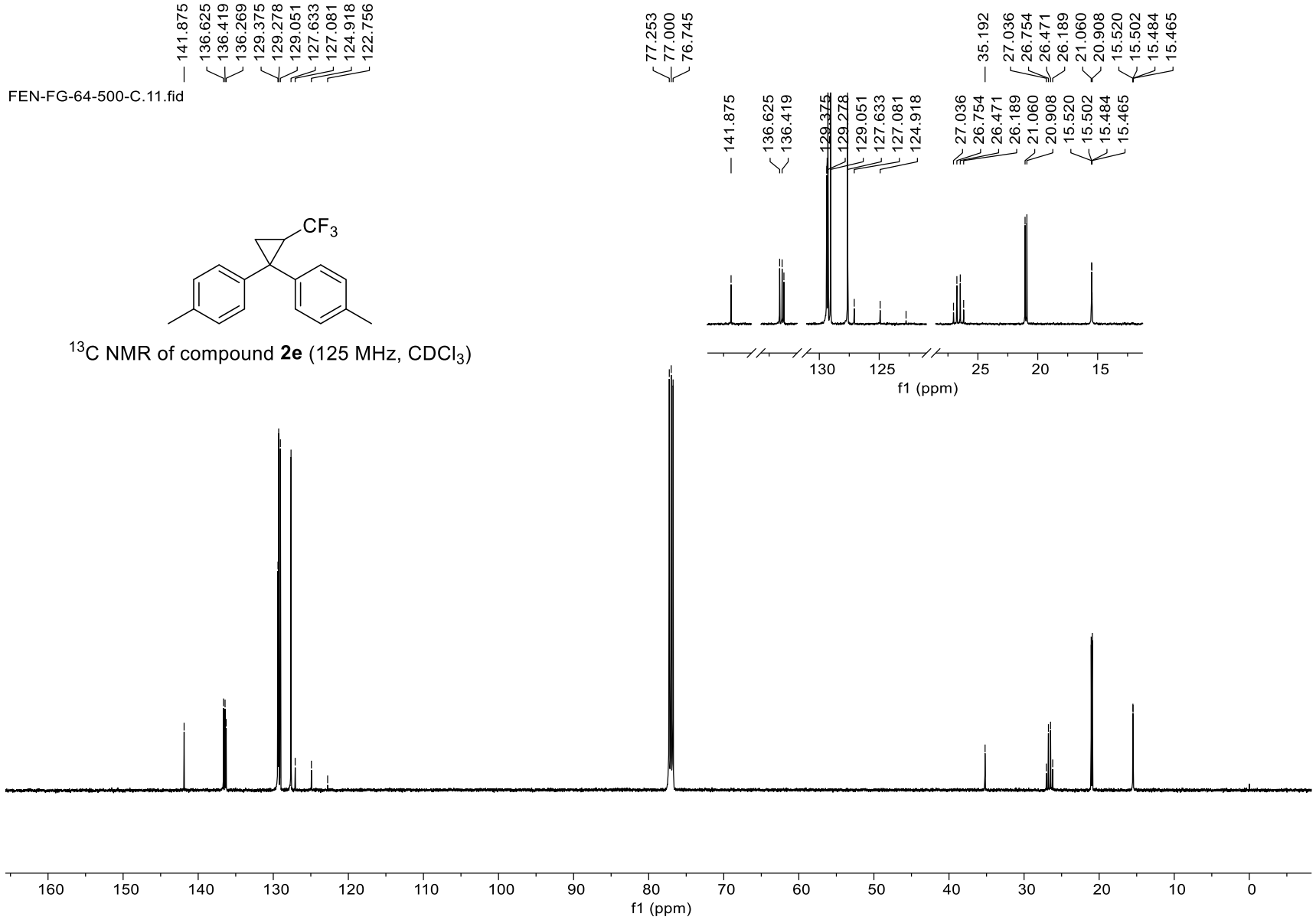


^{1}H NMR of compound **2e** (300 MHz, $CDCl_3$)

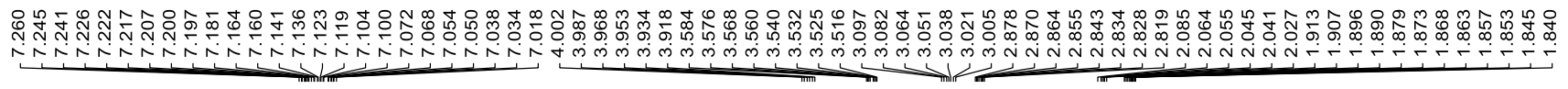
FEN-FG-64-1.11.fid
300M



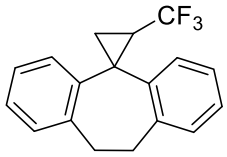
^{19}F NMR of compound **2e** (282 MHz, $CDCl_3$)



^{13}C NMR of compound **2e** (125 MHz, $CDCl_3$)

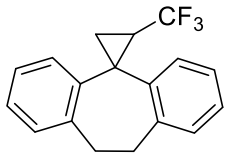


FEN-FG-90-400-H-2.20.fid

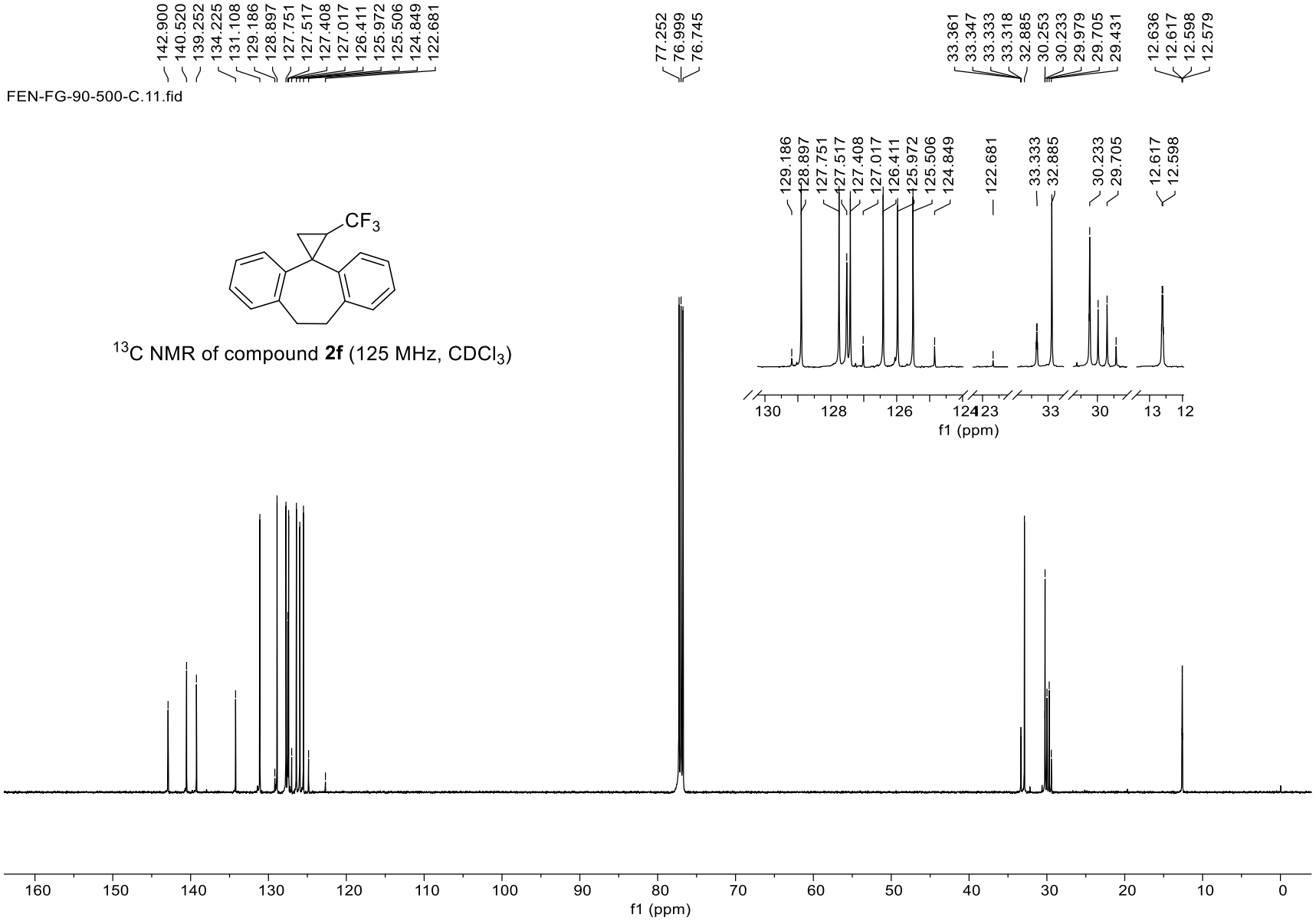


^{1}H NMR of compound **2f** (400 MHz, $CDCl_3$)

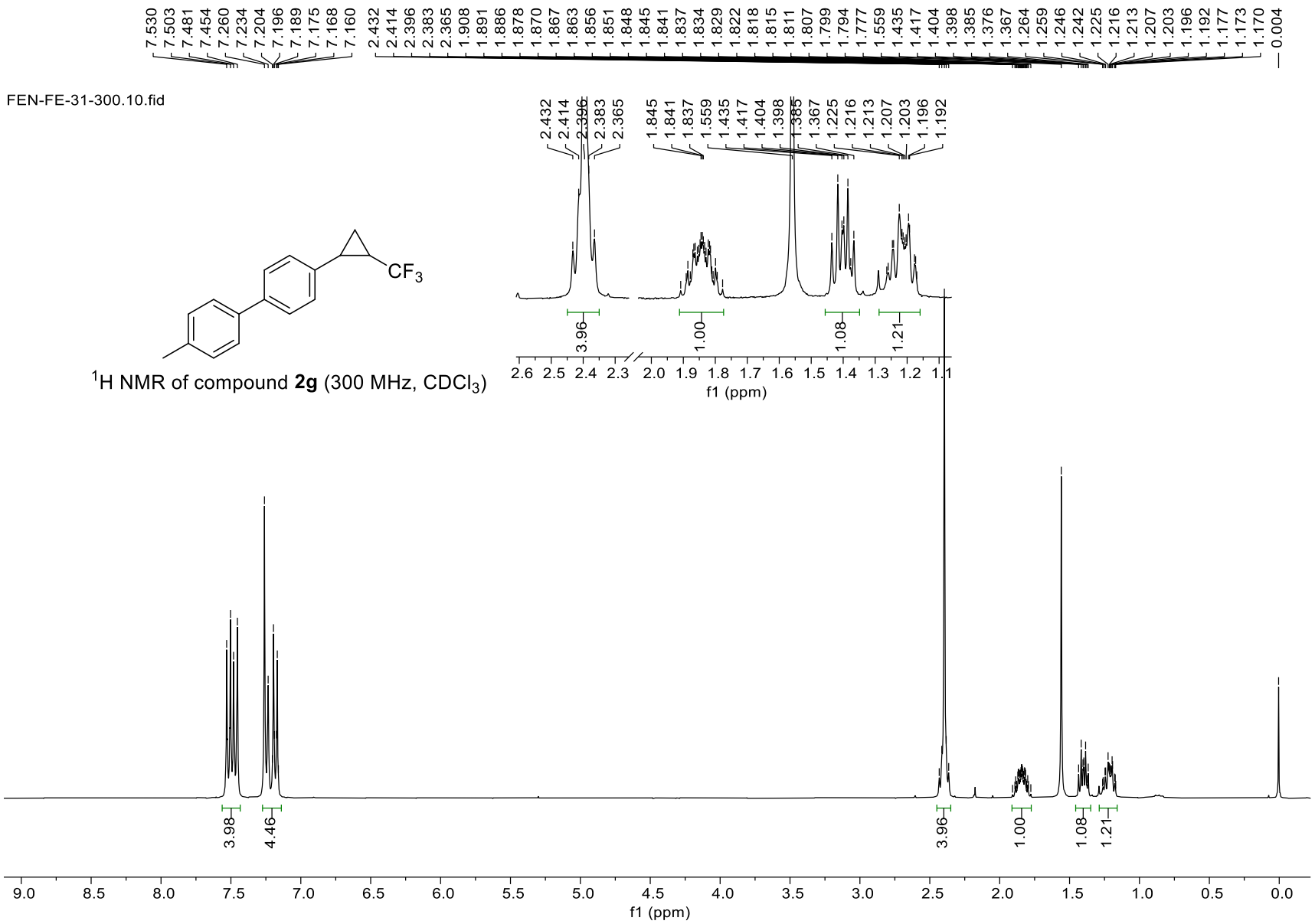
FEN-FG-90-400-H-2.21.fid



^{19}F NMR of compound **2f** (376 MHz, $CDCl_3$)



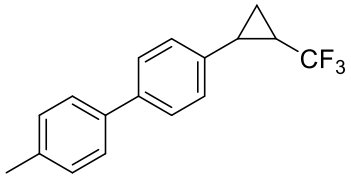
^{13}C NMR of compound **2f** (125 MHz, $CDCl_3$)



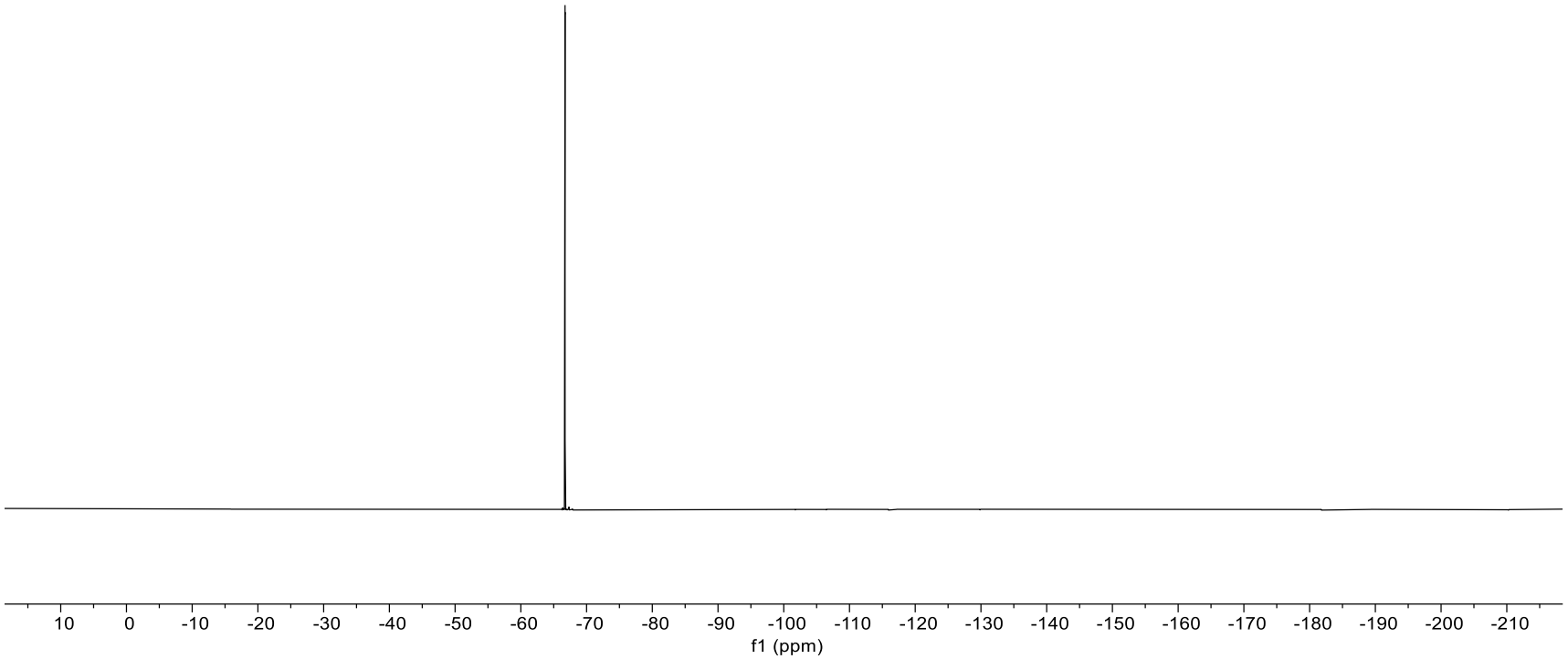
^{1}H NMR of compound **2g** (300 MHz, $CDCl_3$)

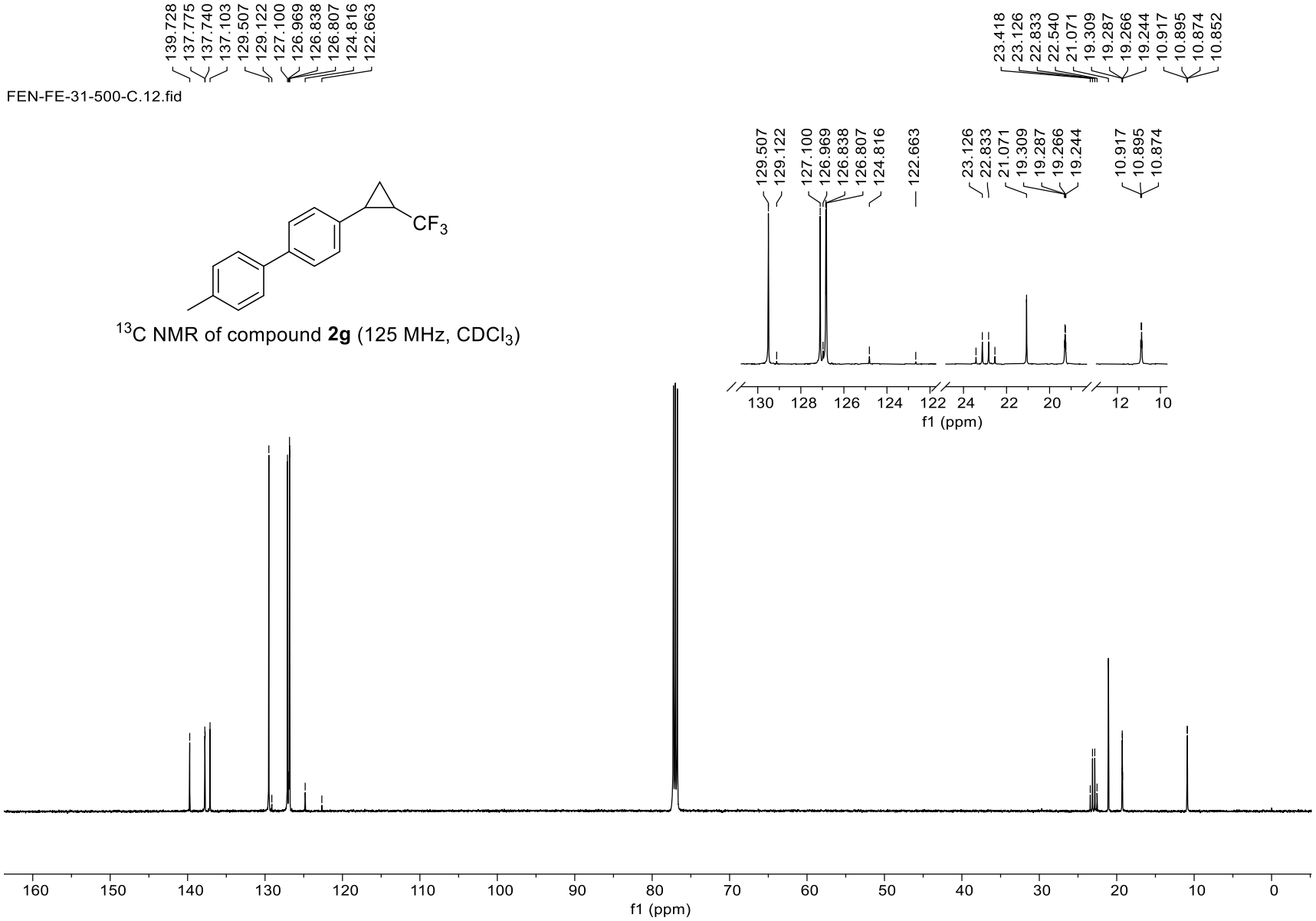
FEN-FE-31-300.11.fid

— -66.725



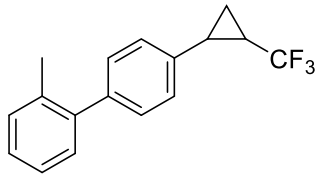
^{19}F NMR of compound **2g** (282 MHz, $CDCl_3$)





^{13}C NMR of compound **2g** (125 MHz, $CDCl_3$)

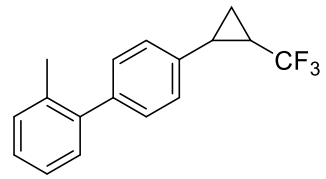
FEN-FG-100.10.fid



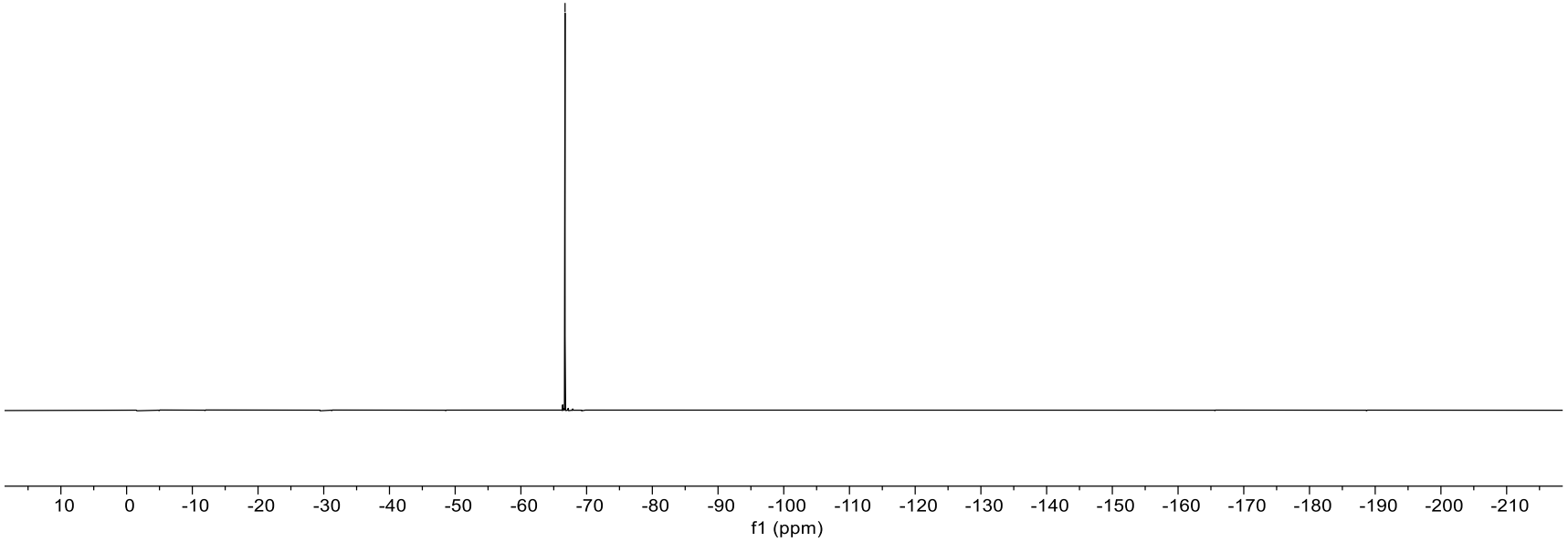
^{1}H NMR of compound **2h** (300 MHz, $CDCl_3$)

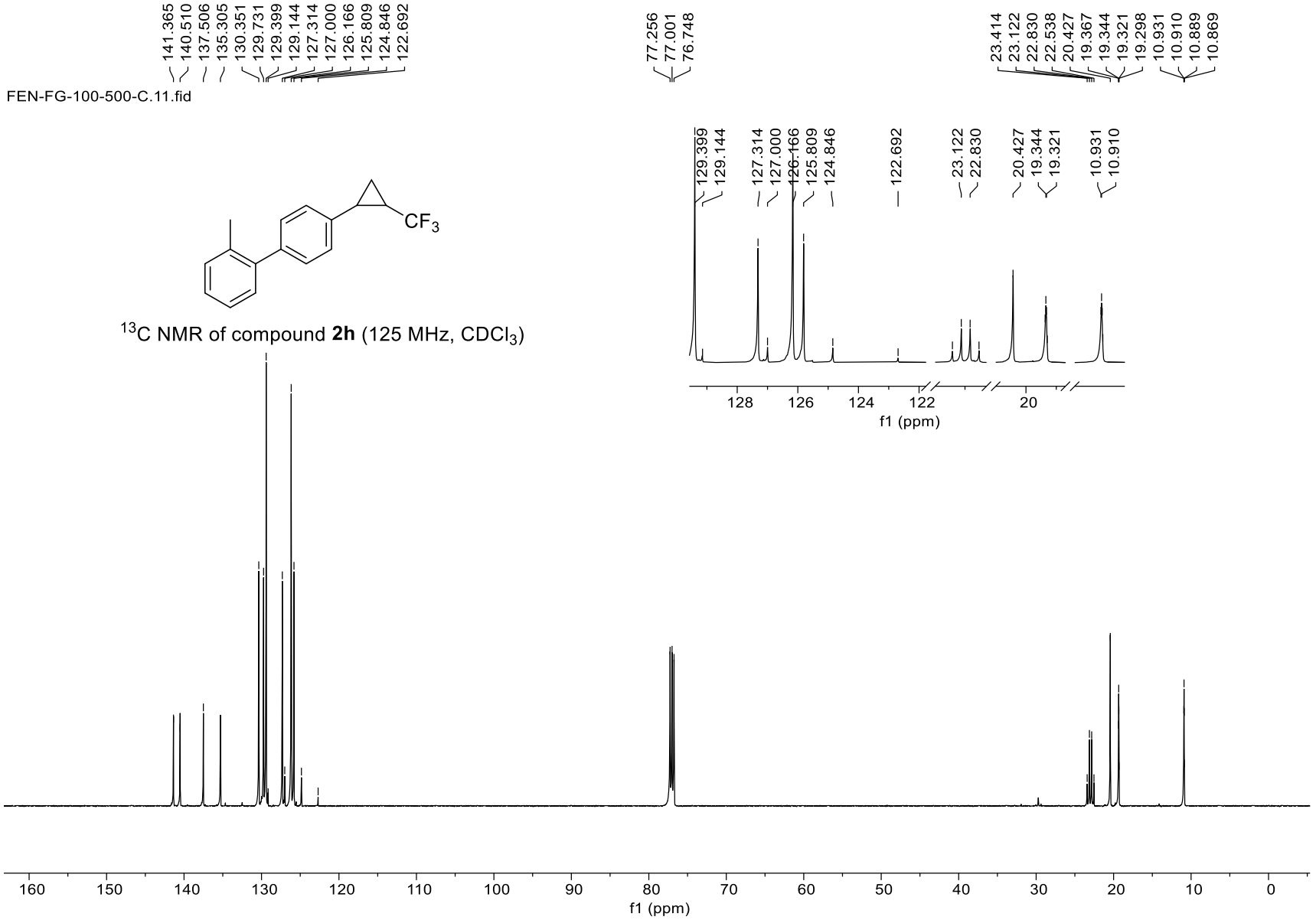
FEN-FG-100.11.fid

— -66.716

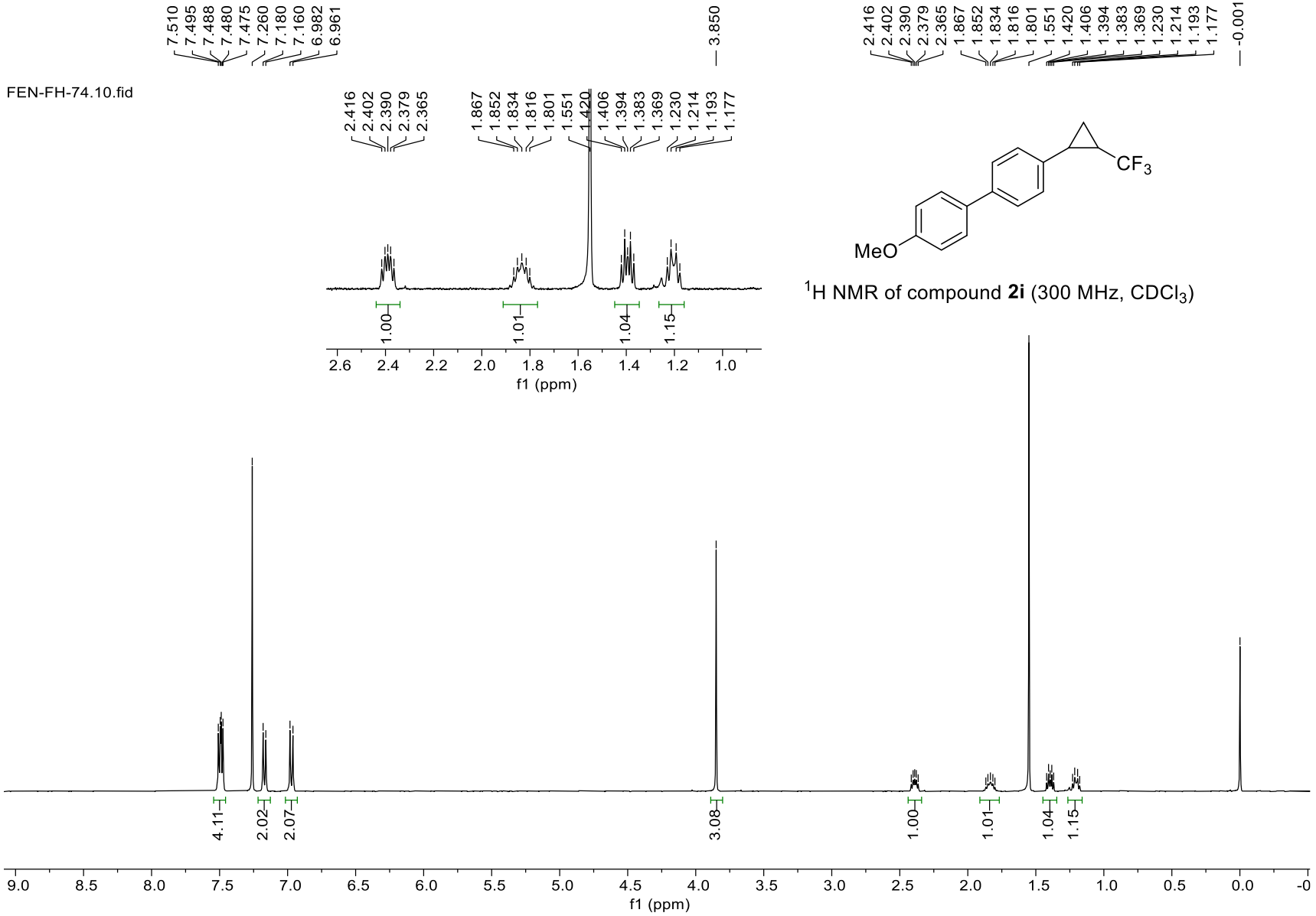


^{19}F NMR of compound **2h** (282 MHz, $CDCl_3$)




141.365
140.510
137.506
135.305
130.351
129.731
129.399
129.144
127.314
127.000
126.166
125.809
124.846
122.692
77.256
77.001
76.748
23.414
23.122
22.830
22.538
20.427
19.367
19.344
19.321
19.298
10.931
10.910
10.889
10.869
FEN-FG-100-500-C.11.fid
CF3
13C NMR of compound 2h (125 MHz, CDCl3)
f1 (ppm)

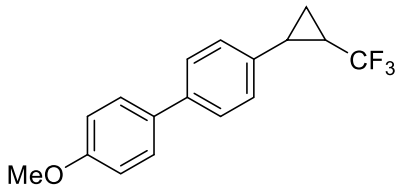
FEN-FH-74.10.fid



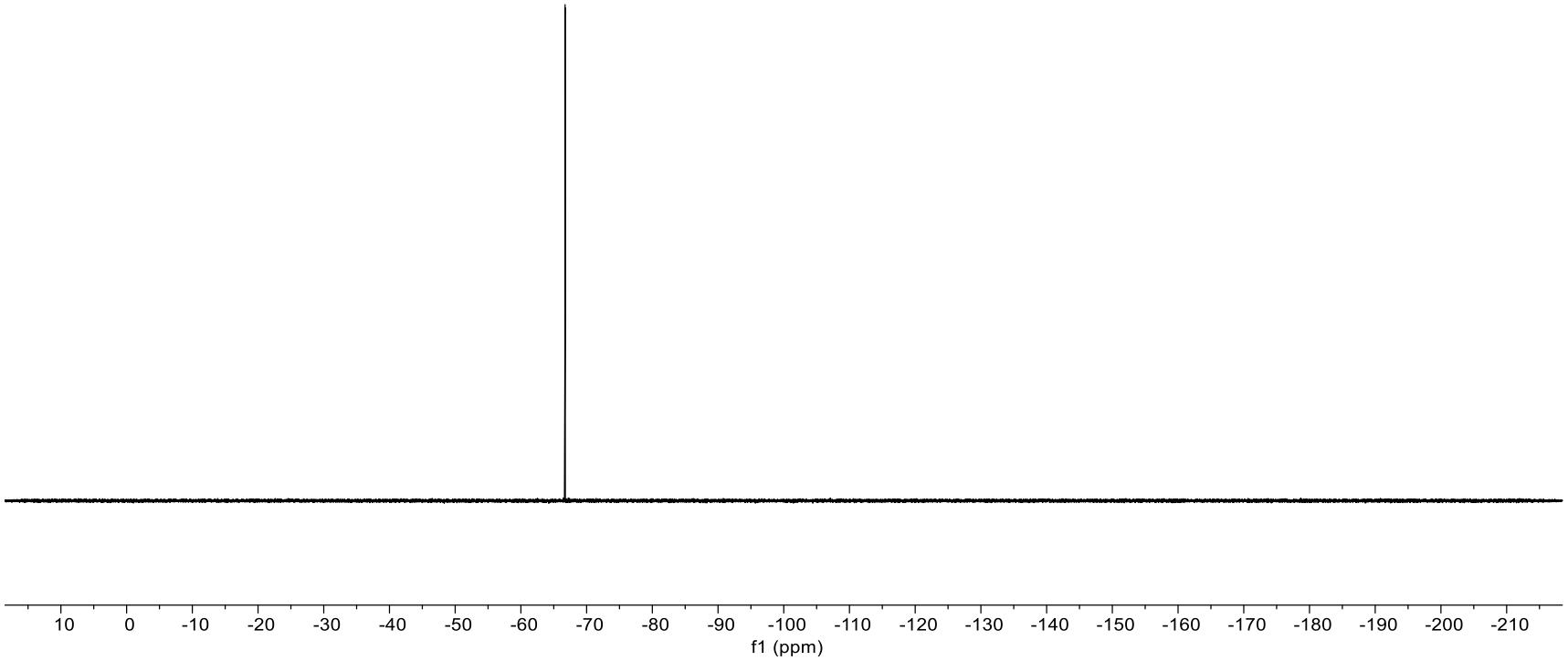
^{1}H NMR of compound **2i** (300 MHz, $CDCl_3$)

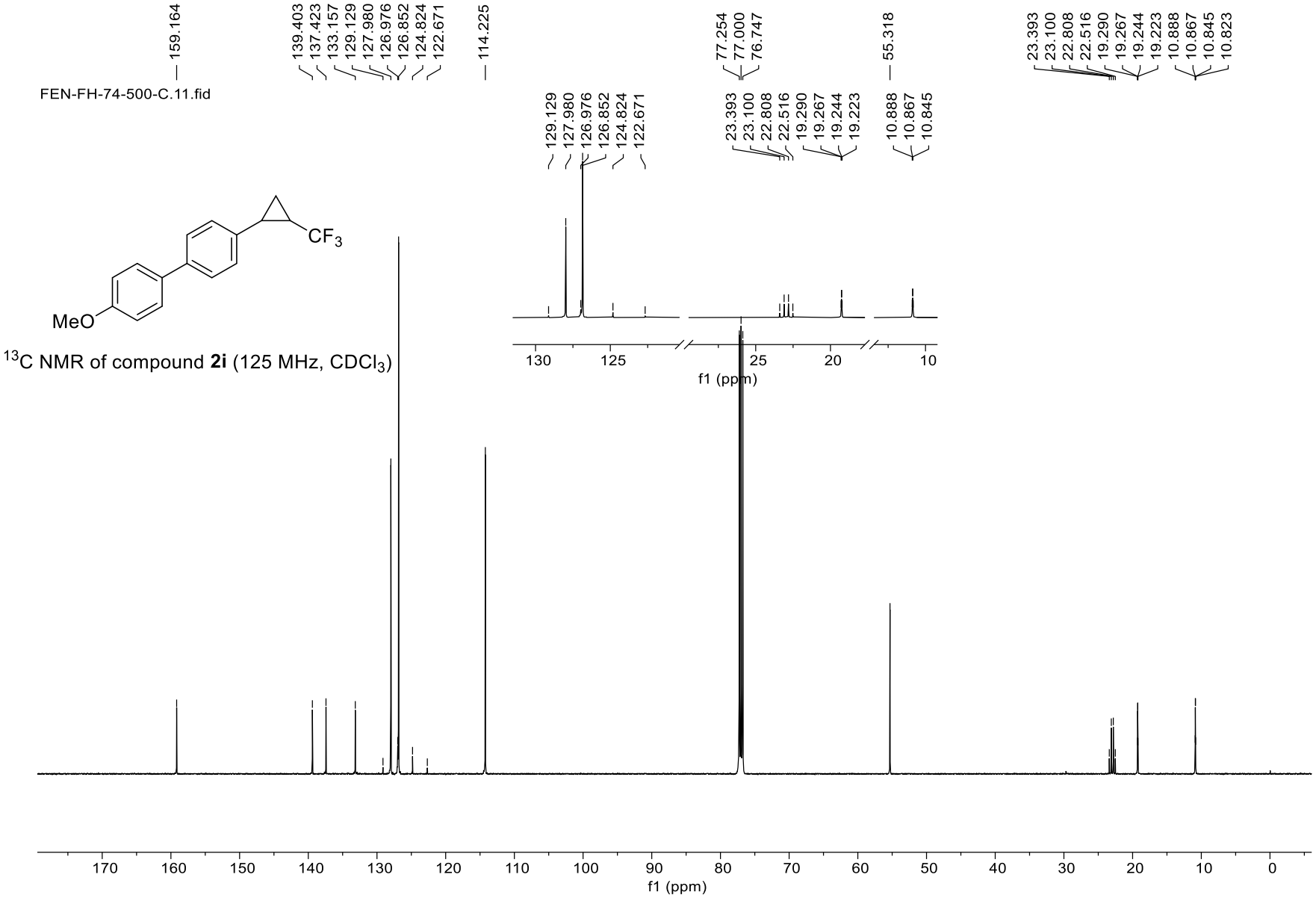
FEN-FH-74.11.fid

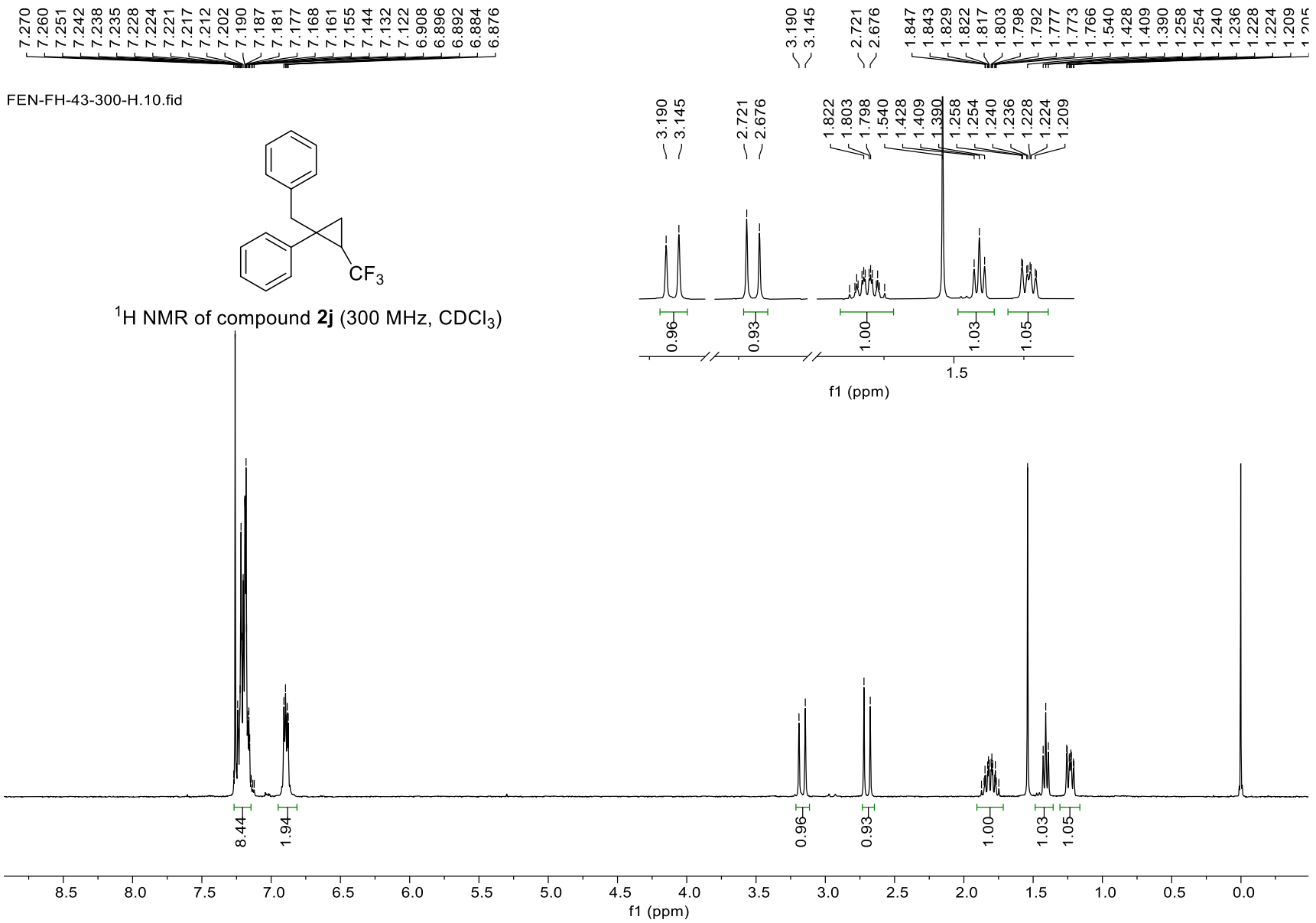
— -66.724



^{19}F NMR of compound **2i** (282 MHz, $CDCl_3$)

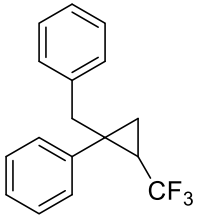



159.164
139.403
137.423
133.157
129.129
127.980
126.976
126.852
124.824
122.671
114.225
77.254
77.000
76.747
55.318
23.393
23.100
22.808
22.516
19.290
19.267
19.244
19.223
10.888
10.867
10.845
10.823
FEN-FH-74-500-C.11.fid
CF3
MeO
13C NMR of compound 2i (125 MHz, CDCl3)
f1 (ppm)

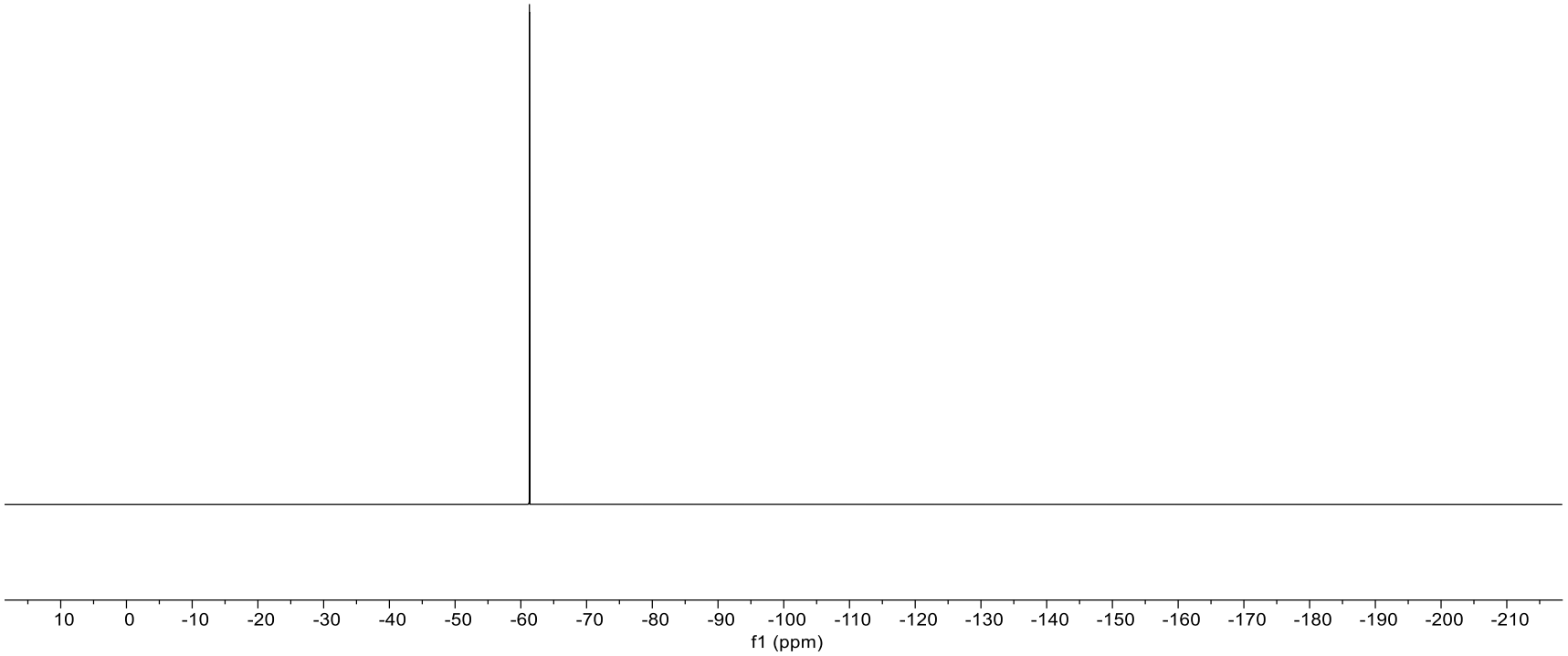

FEN-FH-43-300-H.10.fid
CF3
1H NMR of compound 2j (300 MHz, CDCl3)
f1 (ppm)

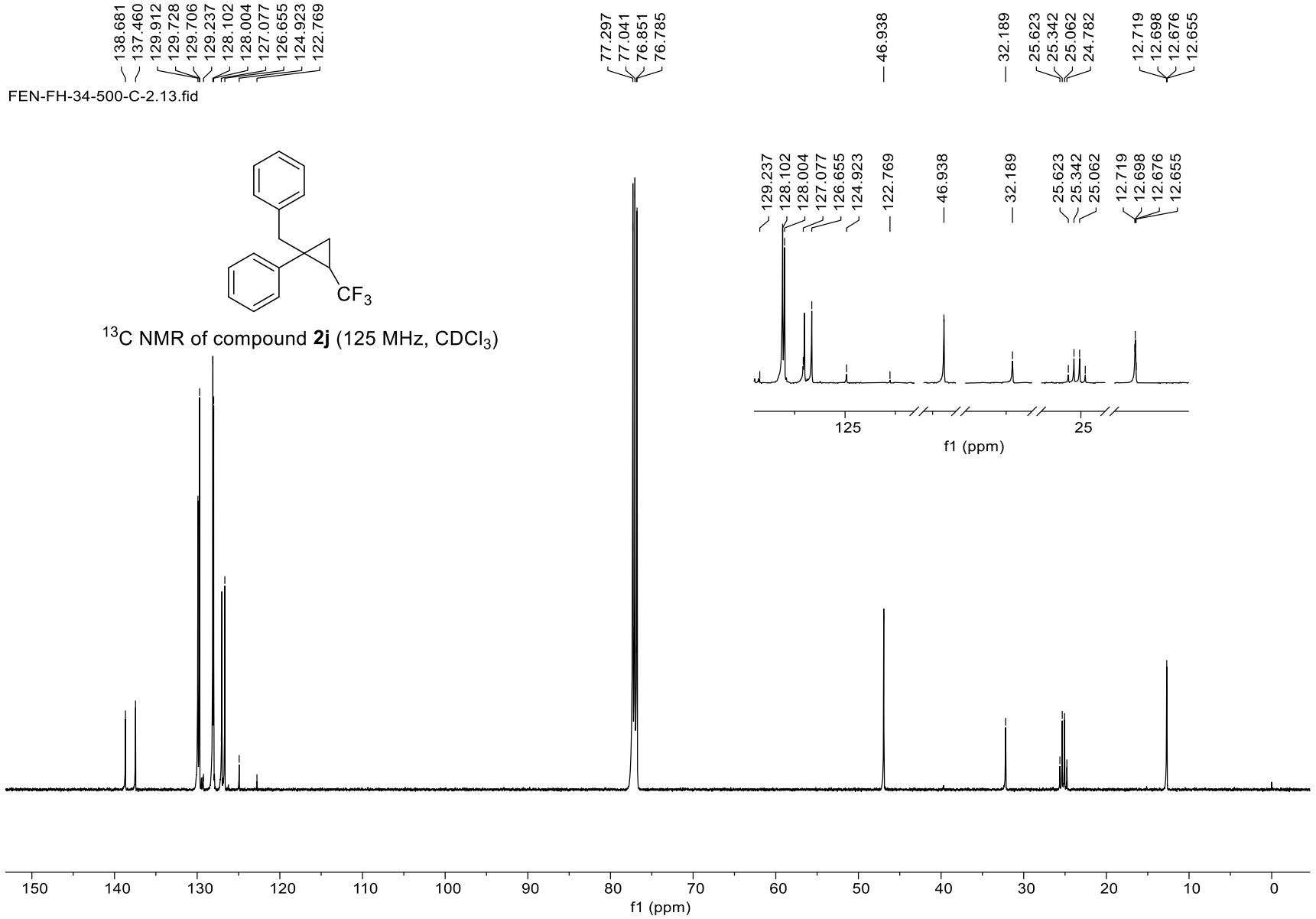
FEN-FH-43-300-H.11.fid

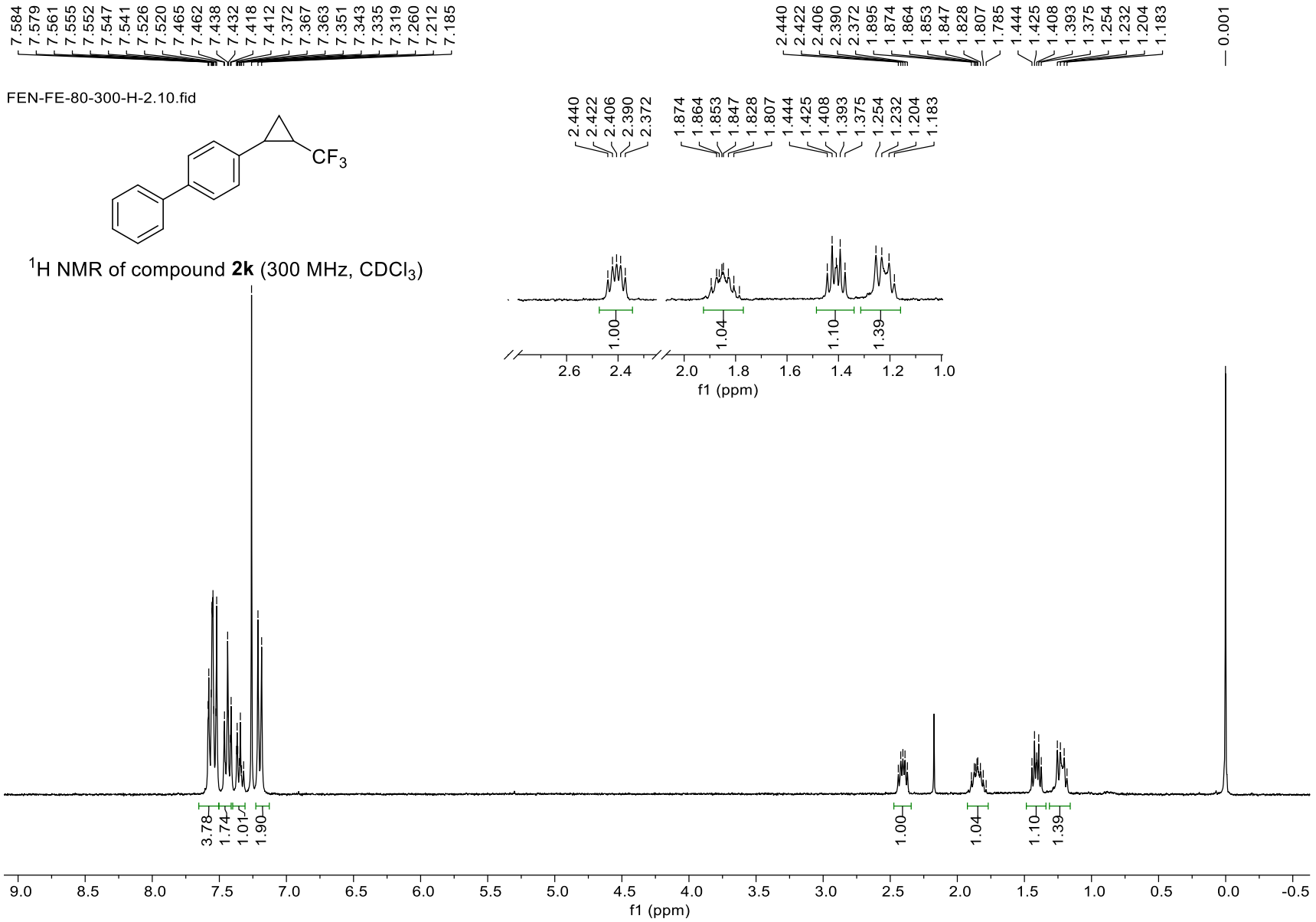
-61.306



^{19}F NMR of compound **2j** (282 MHz, $CDCl_3$)

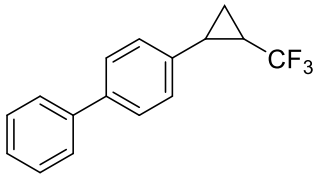



138.681
137.460
129.912
129.728
129.706
129.237
128.102
128.004
127.077
126.655
124.923
122.769
77.297
77.041
76.851
76.785
46.938
32.189
25.623
25.342
25.062
24.782
12.719
12.698
12.676
12.655
FEN-FH-34-500-C-2.13.fid
CF3
13C NMR of compound 2j (125 MHz, CDCl3)
f1 (ppm)

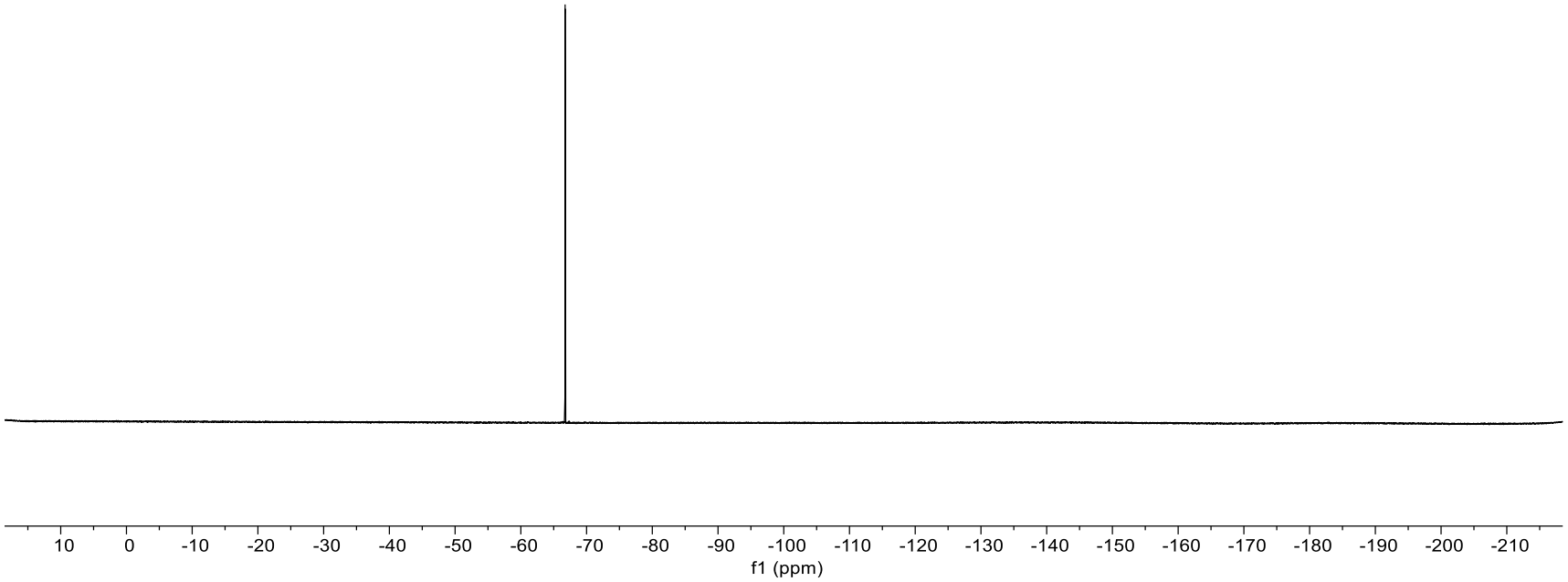

7.584
7.579
7.561
7.555
7.552
7.547
7.541
7.526
7.520
7.465
7.462
7.438
7.432
7.418
7.412
7.372
7.367
7.363
7.351
7.343
7.335
7.319
7.260
7.212
7.185
2.440
2.422
2.406
2.390
2.372
1.895
1.874
1.864
1.853
1.847
1.828
1.807
1.785
1.444
1.425
1.408
1.393
1.375
1.254
1.232
1.204
1.183
0.001
FEN-FE-80-300-H-2.10.fid
CF3
1H NMR of compound 2k (300 MHz, CDCl3)
1.00
1.04
1.10
1.39
f1 (ppm)
3.78
1.74
1.01
1.90
f1 (ppm)

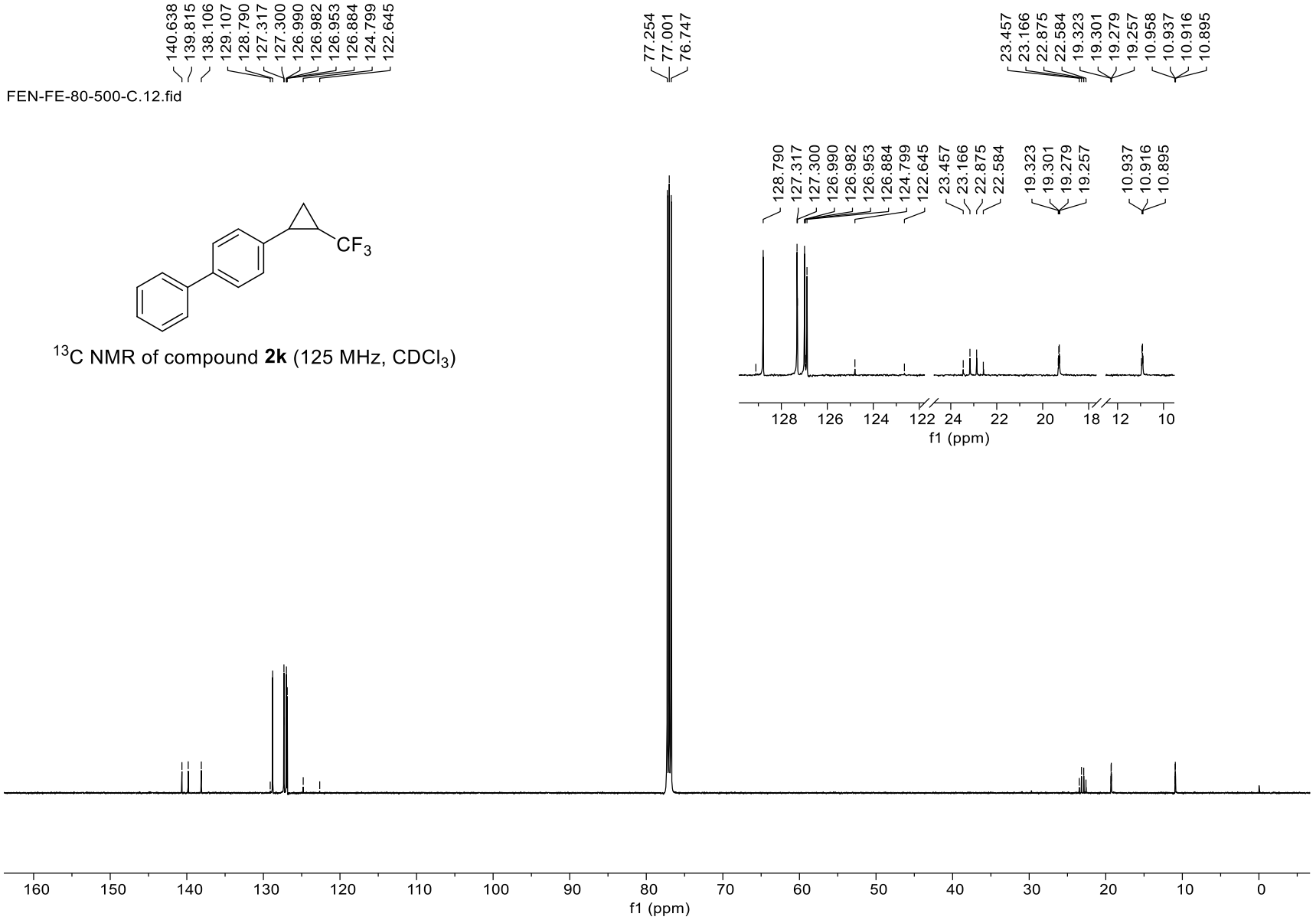
FEN-FE-80-300-H-2.12.fid

— -66.737

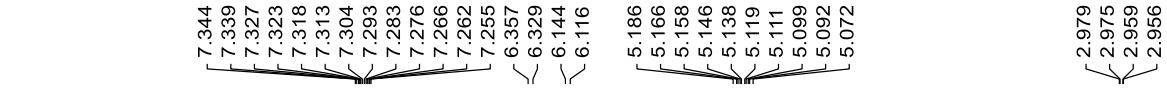


^{19}F NMR of compound **2k** (282 MHz, $CDCl_3$)

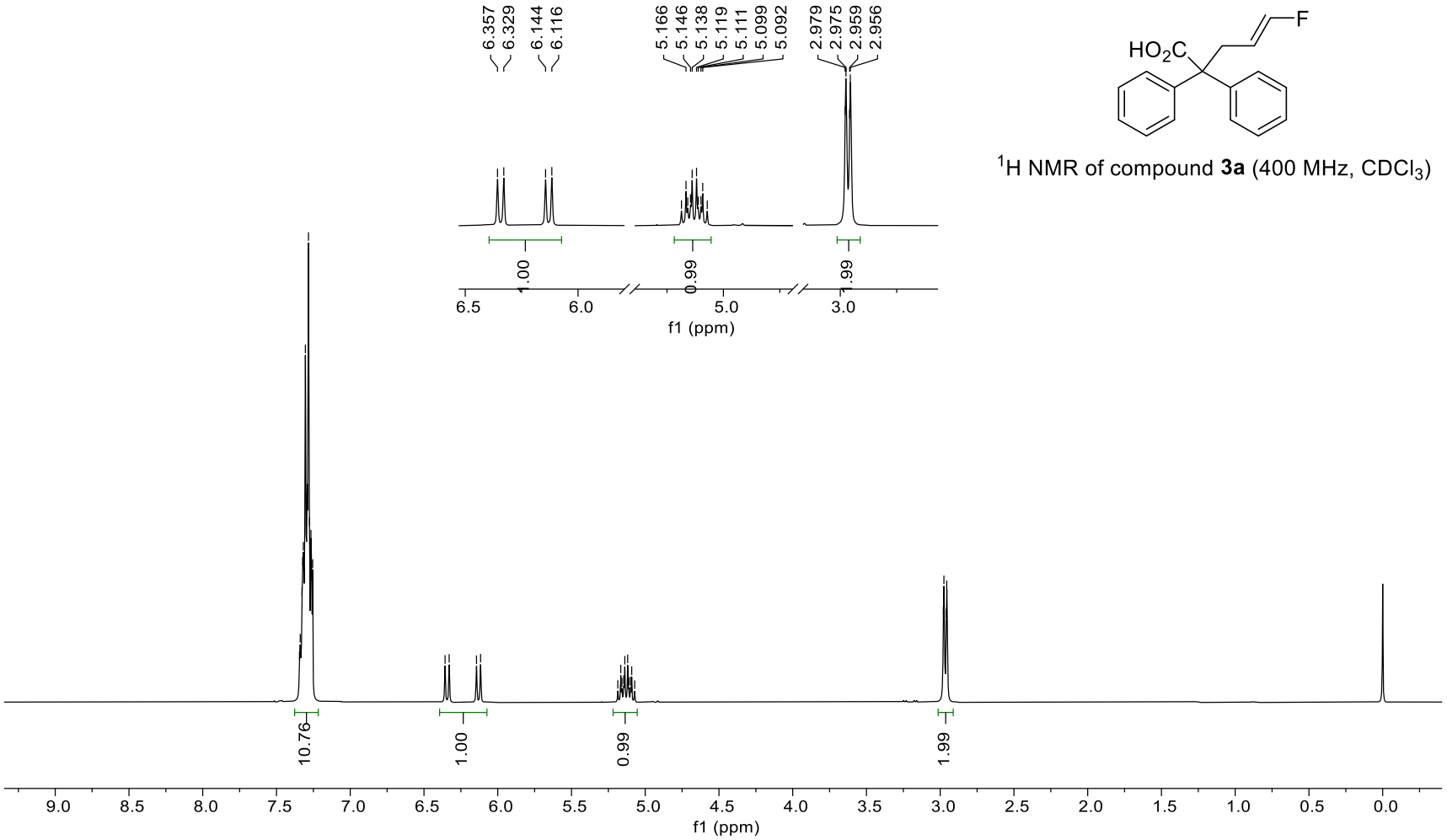




^{13}C NMR of compound **2k** (125 MHz, $CDCl_3$)

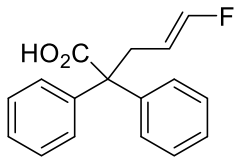


FEN-FI-98-400-H.10.fid

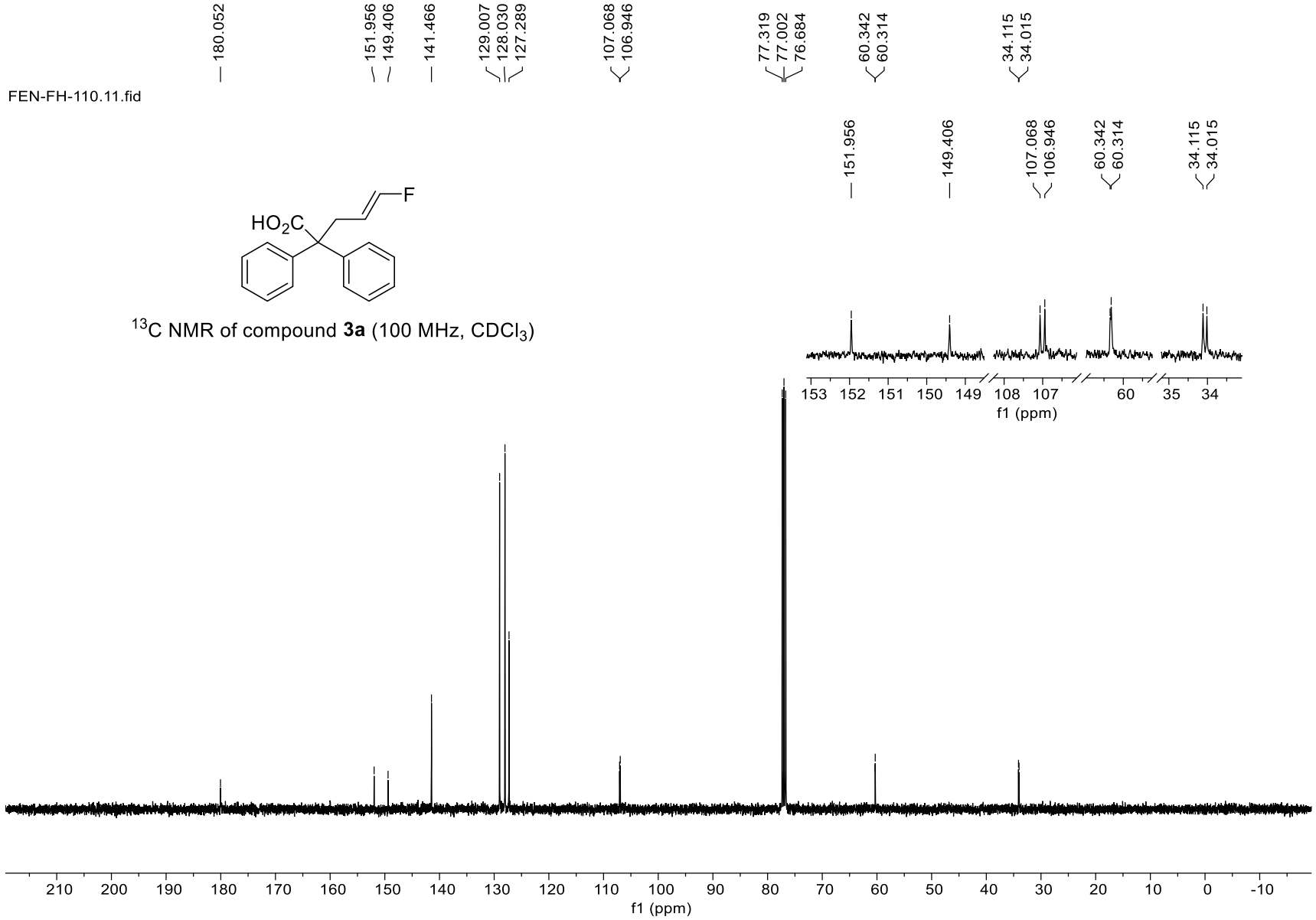


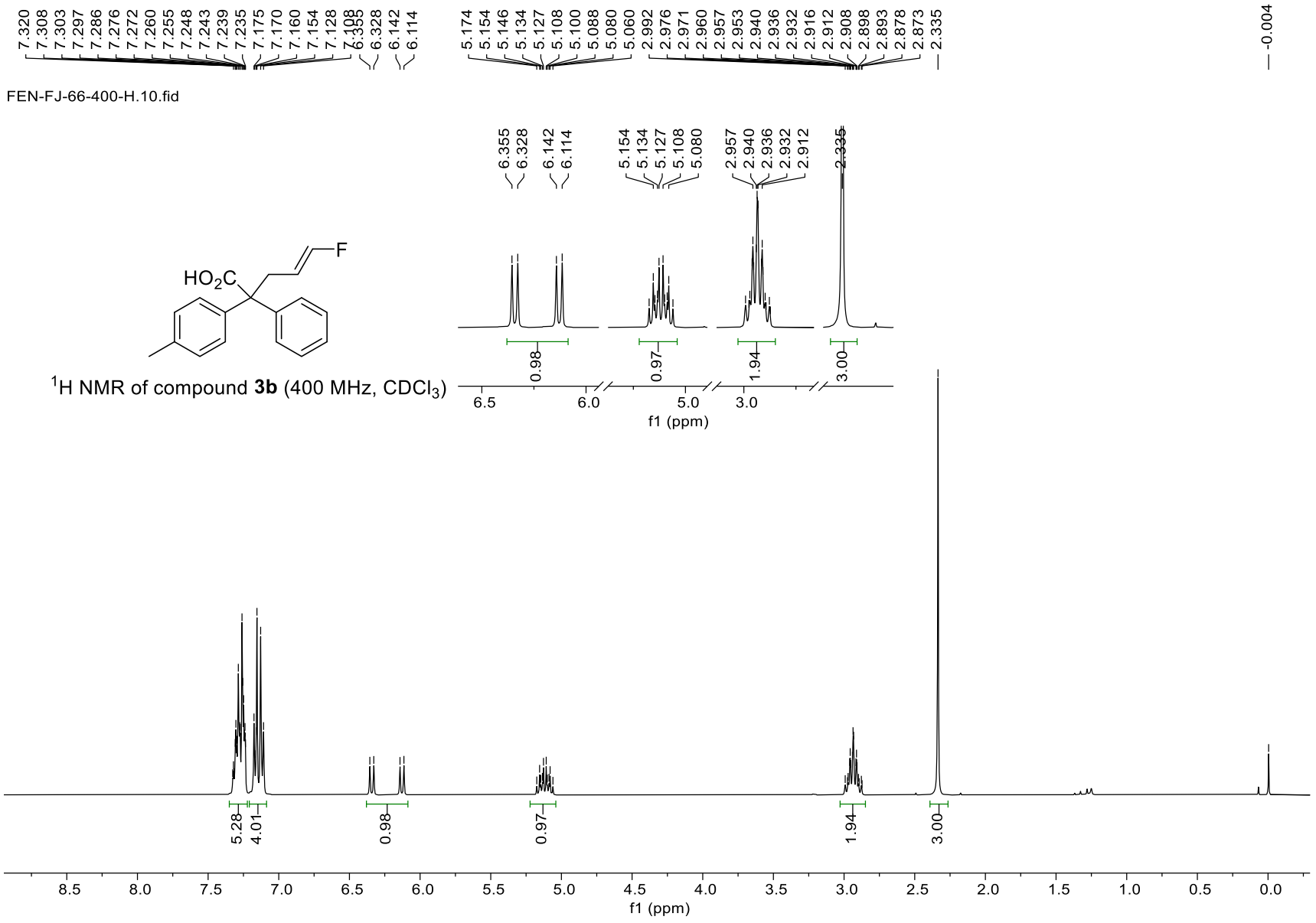
^{1}H NMR of compound **3a** (400 MHz, $CDCl_3$)

FEN-FI-98-400-H.11.fid

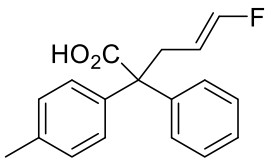


^{19}F NMR of compound **3a** (376 MHz, $CDCl_3$)

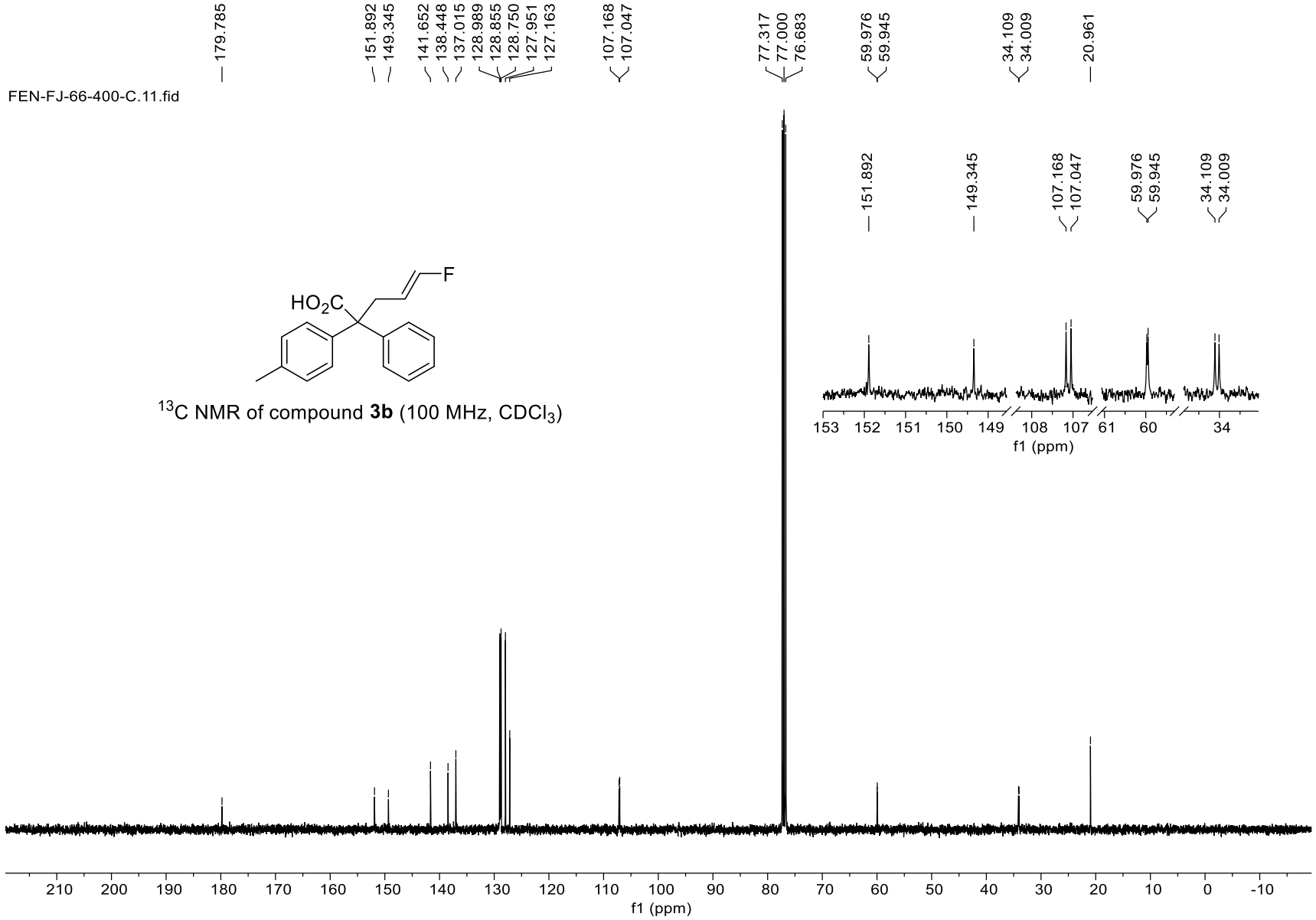

180.052
151.956
149.406
141.466
129.007
128.030
127.289
107.068
106.946
77.319
77.002
76.684
60.342
60.314
34.115
34.015
FEN-FH-110.11.fid
HO2C
F
13C NMR of compound 3a (100 MHz, CDCl3)
f1 (ppm)

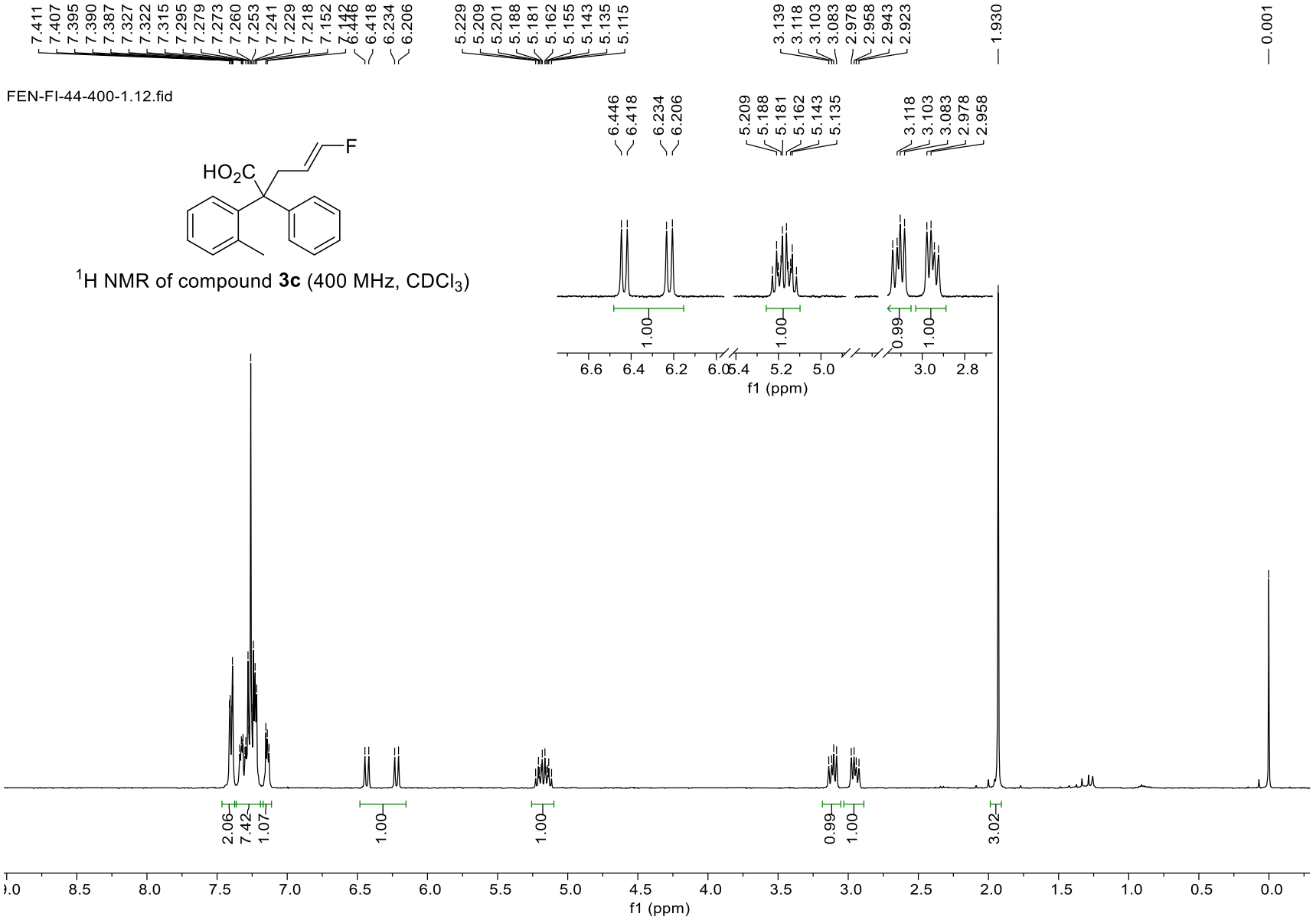

7.320
7.308
7.303
7.297
7.286
7.276
7.272
7.260
7.255
7.248
7.243
7.239
7.235
7.175
7.170
7.160
7.154
7.128
7.108
6.355
6.328
6.142
6.114
5.174
5.154
5.146
5.134
5.127
5.108
5.100
5.088
5.080
5.060
2.992
2.976
2.971
2.960
2.957
2.953
2.940
2.936
2.932
2.916
2.912
2.908
2.898
2.893
2.878
2.873
2.335
-0.004
FEN-FJ-66-400-H.10.fid
HO2C
F
1H NMR of compound 3b (400 MHz, CDCl3)
0.98
0.97
1.94
3.00
6.5
6.0
5.0
3.0
f1 (ppm)
5.28
4.01
0.98
0.97
1.94
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

FEN-FJ-66-400-H.11.fid

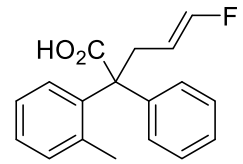


^{19}F NMR of compound **3b** (376 MHz, $CDCl_3$)

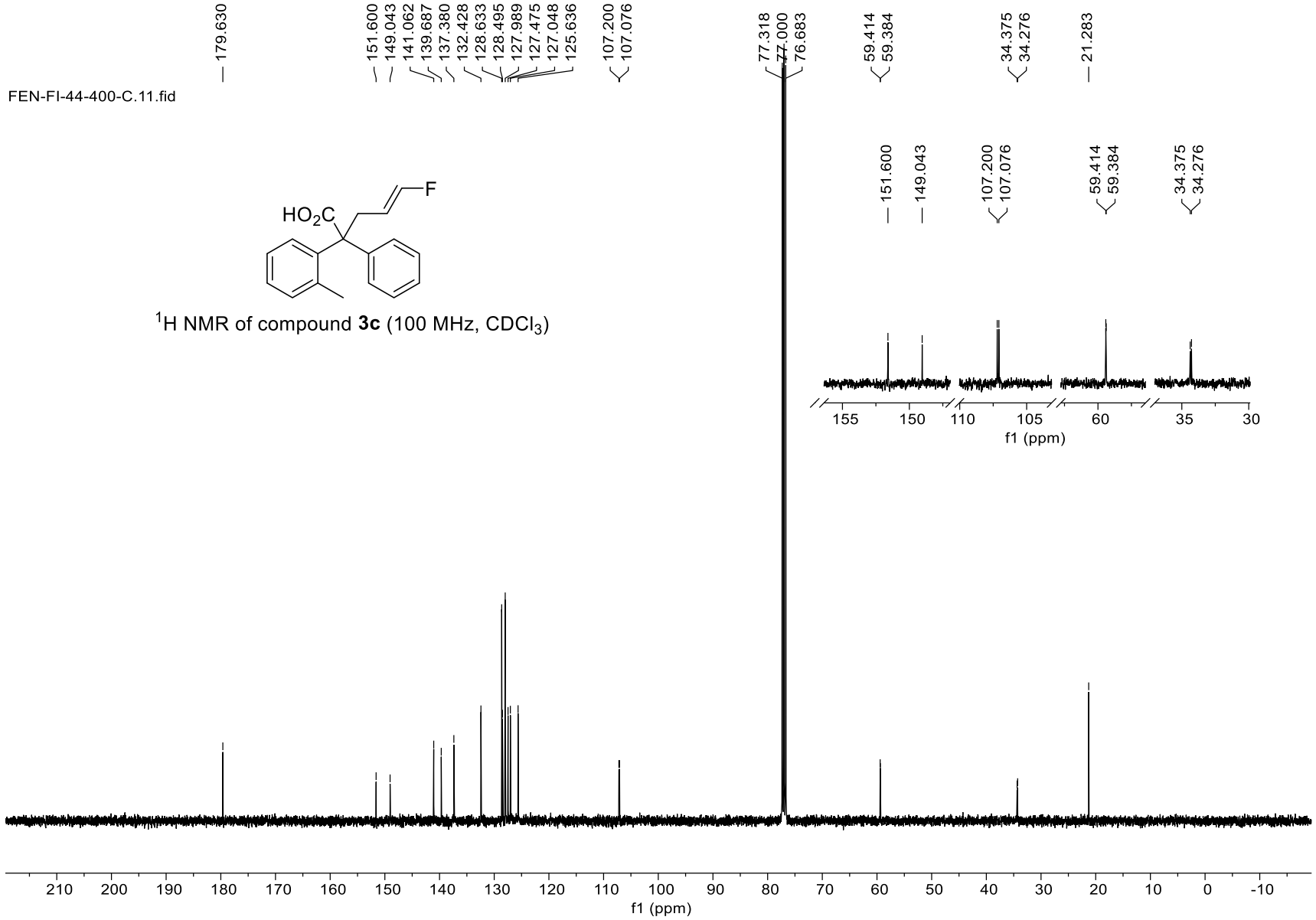

179.785
151.892
149.345
141.652
138.448
137.015
128.989
128.855
128.750
127.951
127.163
107.168
107.047
77.317
77.000
76.683
59.976
59.945
34.109
34.009
20.961
FEN-FJ-66-400-C.11.fid
HO2C
F
13C NMR of compound 3b (100 MHz, CDCl3)
f1 (ppm)

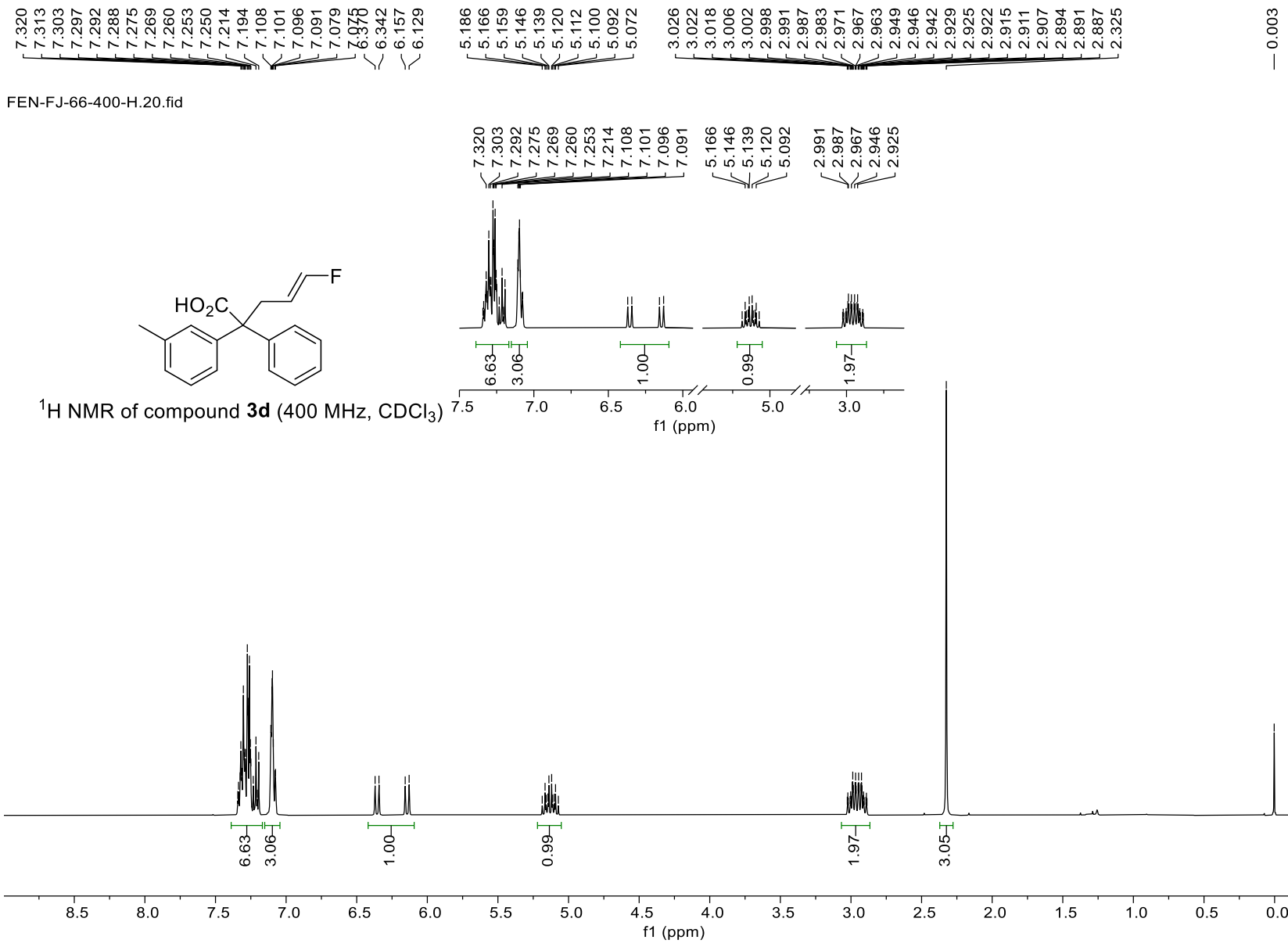

7.411
7.407
7.395
7.390
7.387
7.327
7.322
7.315
7.295
7.279
7.273
7.260
7.253
7.241
7.229
7.218
7.152
6.446
6.418
6.234
6.206
5.229
5.209
5.201
5.188
5.181
5.162
5.155
5.143
5.135
5.115
3.139
3.118
3.103
3.083
2.978
2.958
2.943
2.923
1.930
0.001
FEN-FI-44-400-1.12.fid
HO2C
F
1H NMR of compound 3c (400 MHz, CDCl3)
f1 (ppm)

FEN-FI-44-400-1.11.fid



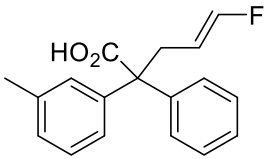
^{19}F NMR of compound **3c** (376 MHz, $CDCl_3$)


FEN-FI-44-400-C.11.fid
179.630
151.600
149.043
141.062
139.687
137.380
132.428
128.633
128.495
127.989
127.475
127.048
125.636
107.200
107.076
77.318
77.000
76.683
59.414
59.384
34.375
34.276
21.283
HO2C
F
1H NMR of compound 3c (100 MHz, CDCl3)
f1 (ppm)

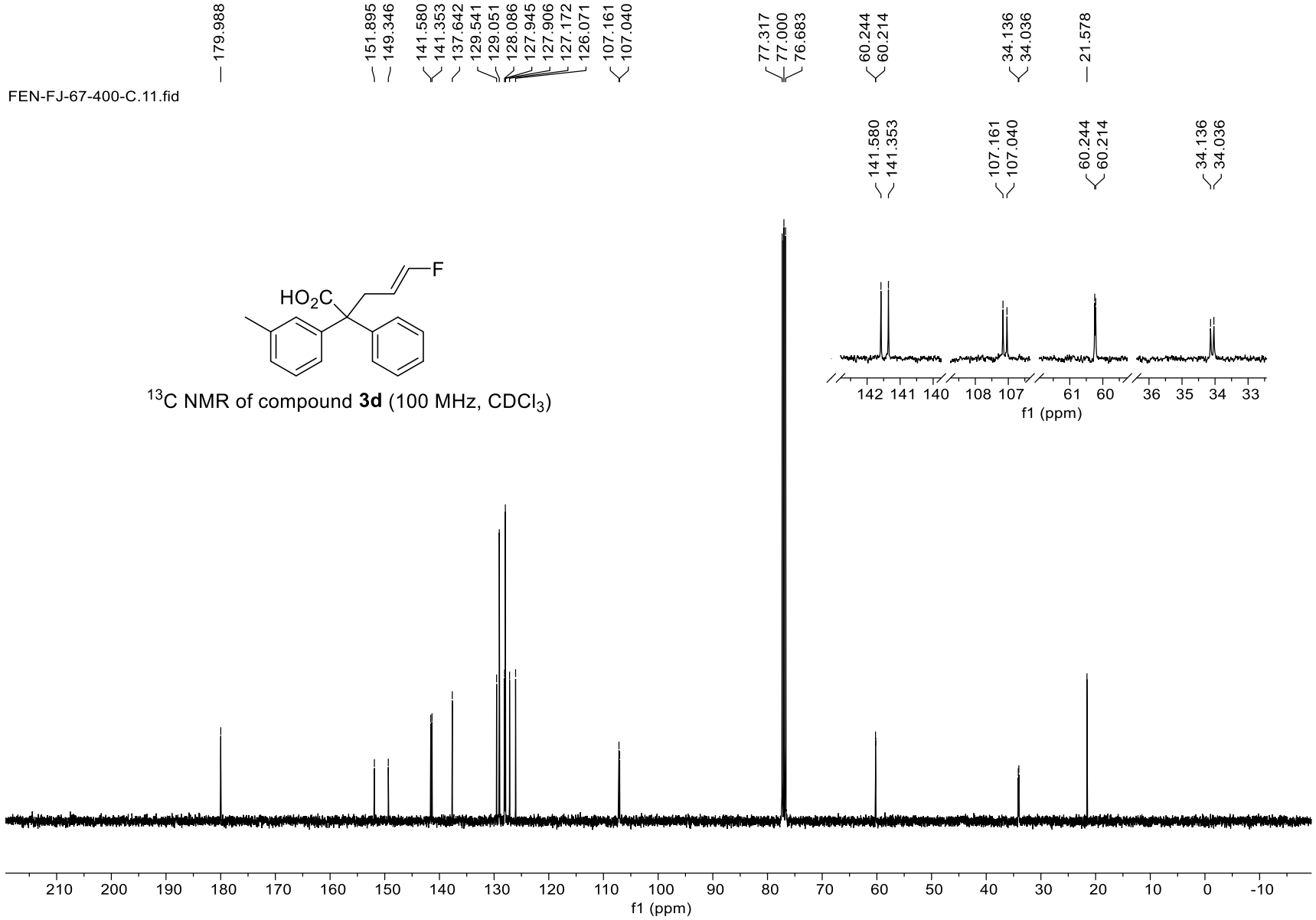


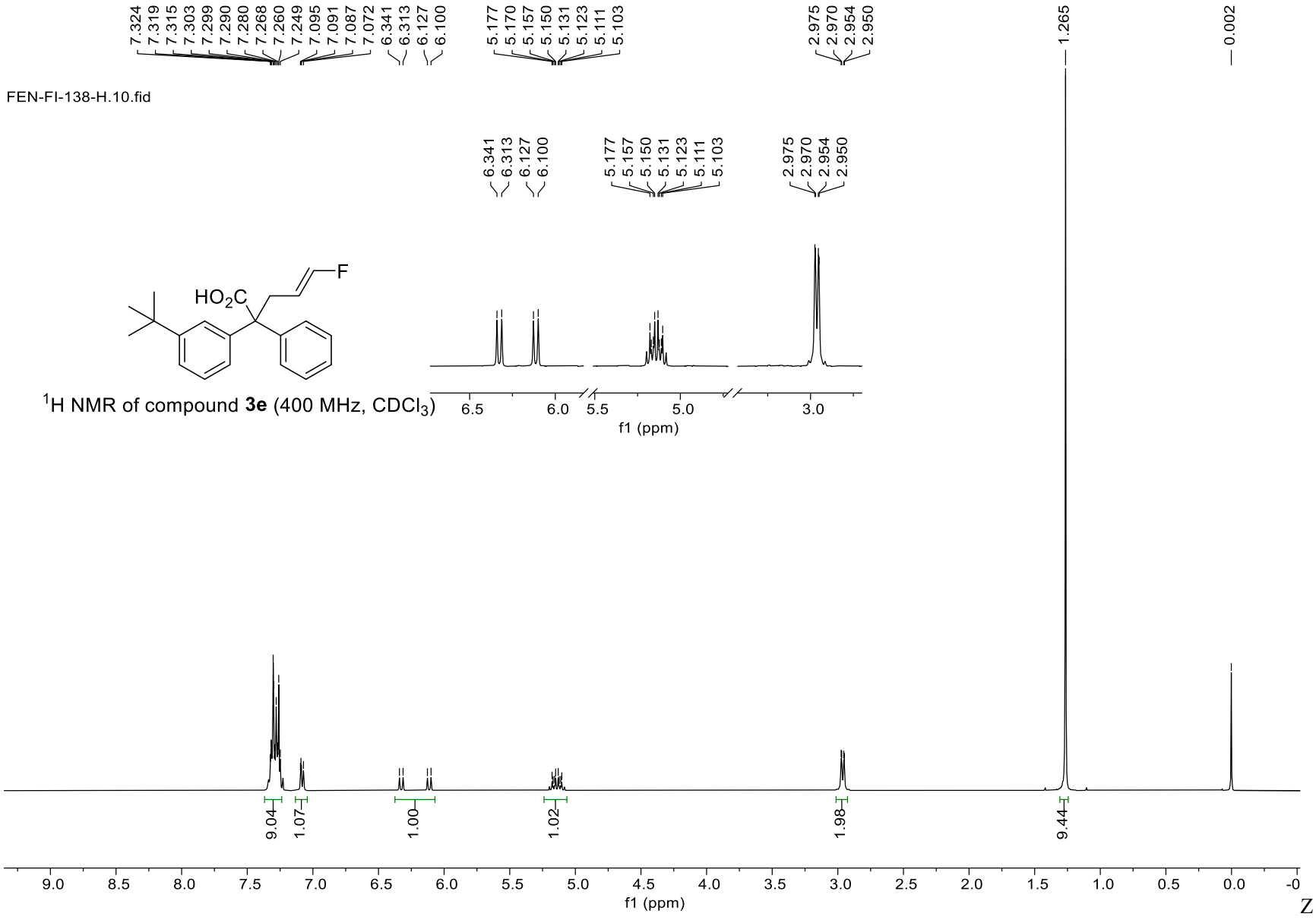
^{1}H NMR of compound **3d** (400 MHz, $CDCl_3$)

FEN-FJ-66-400-H.21.fid



^{19}F NMR of compound **3d** (376 MHz, $CDCl_3$)

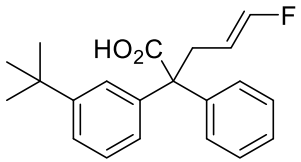

179.988
151.895
149.346
141.580
141.353
137.642
129.541
129.051
128.086
127.945
127.906
127.172
126.071
107.161
107.040
77.317
77.000
76.683
60.244
60.214
34.136
34.036
21.578
FEN-FJ-67-400-C.11.fid
HO2C
F
13C NMR of compound 3d (100 MHz, CDCl3)
f1 (ppm)



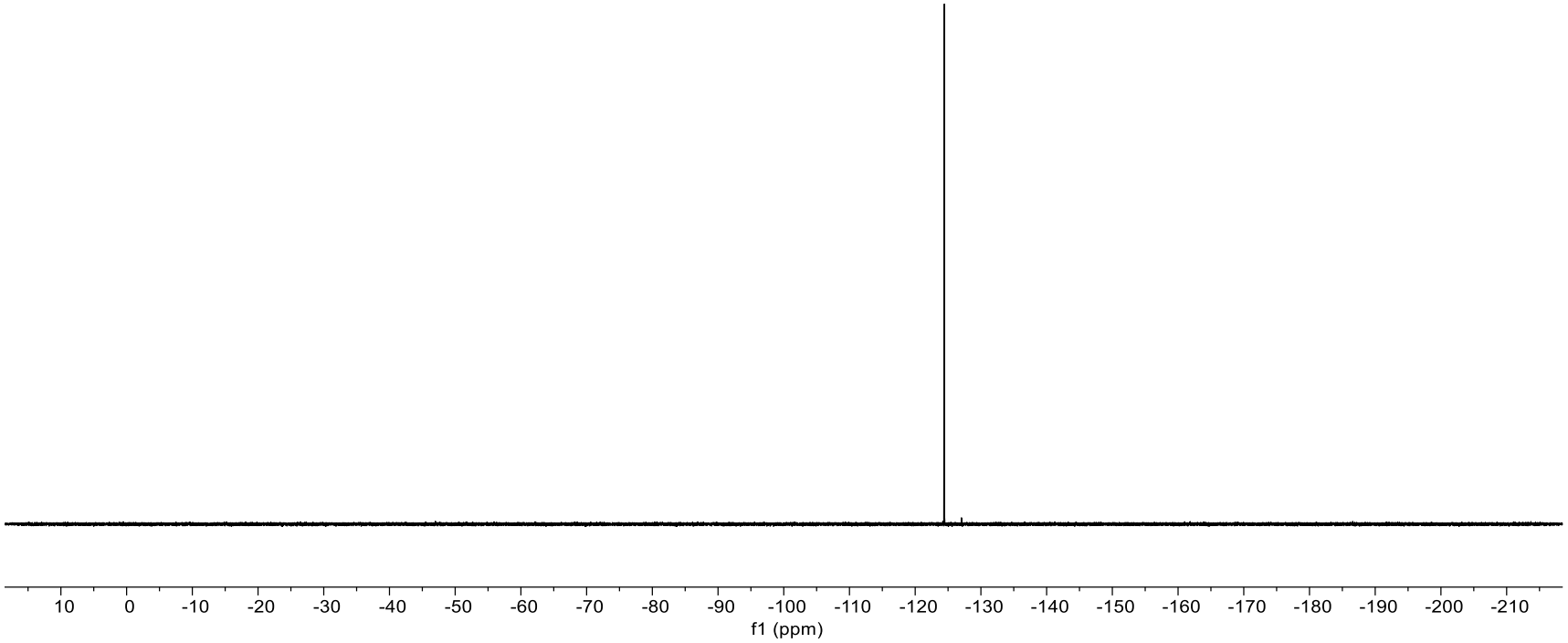
^{1}H NMR of compound **3e** (400 MHz, $CDCl_3$)

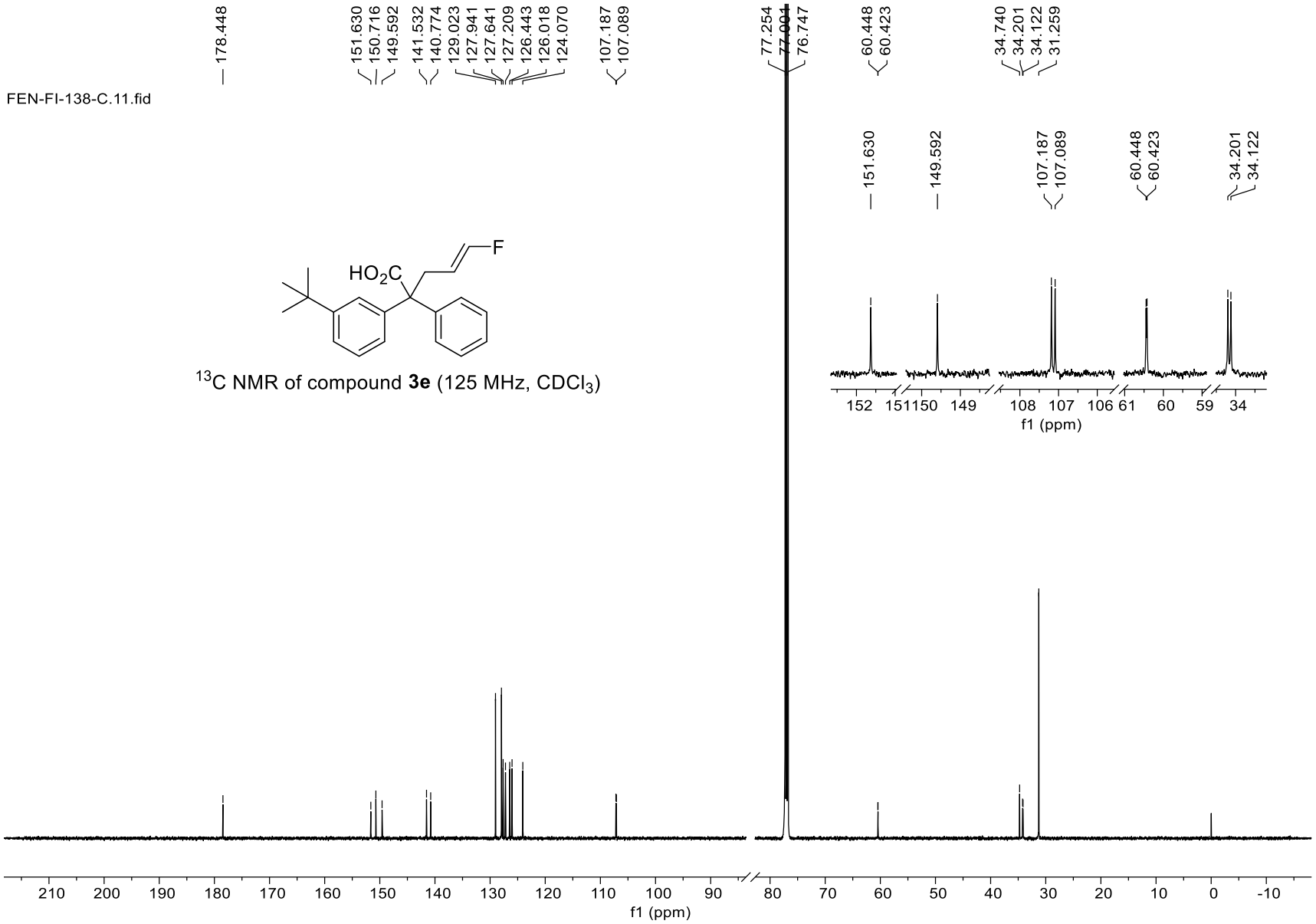
FEN-FI-138-F.11.fid

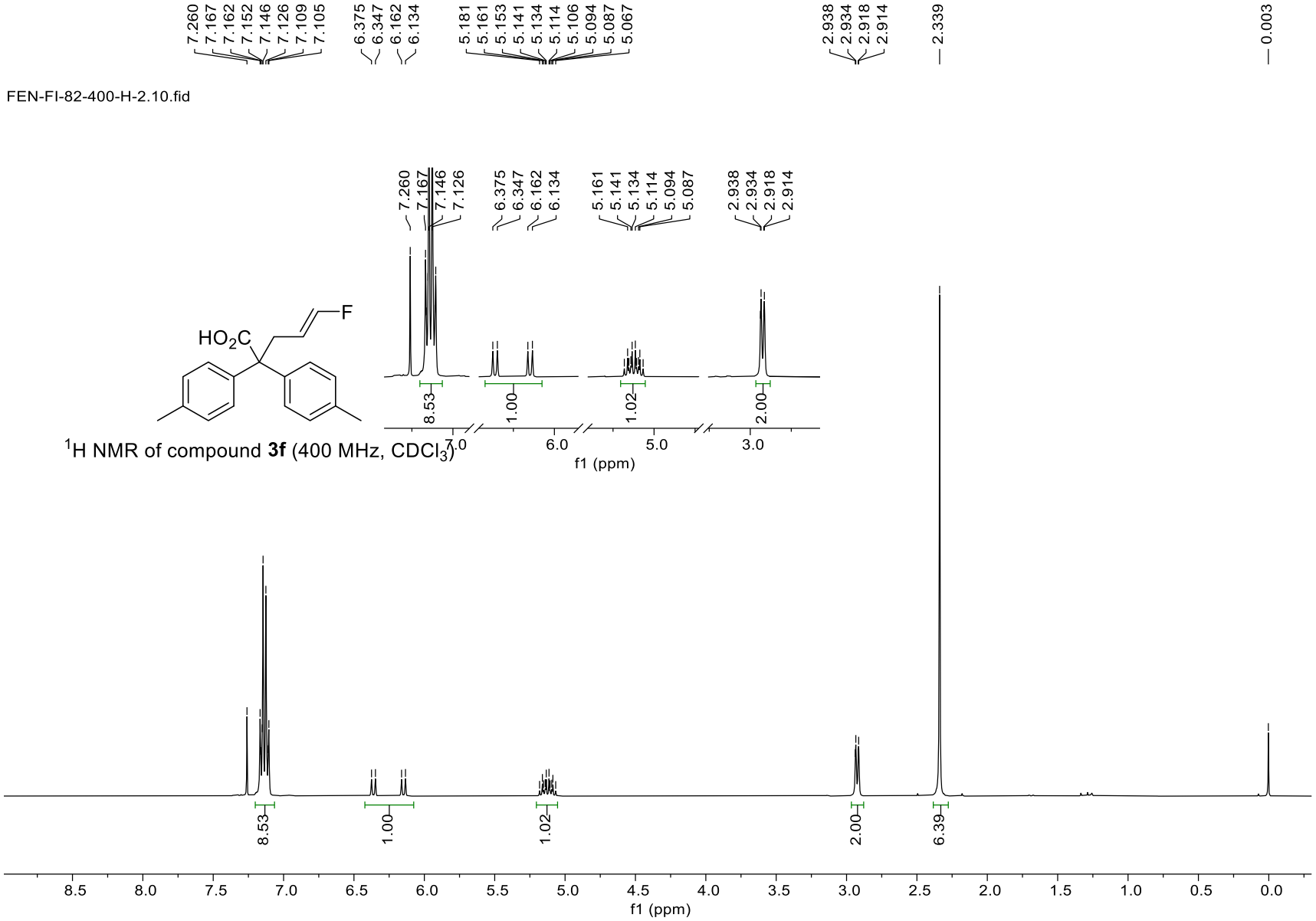
— -124.444



^{19}F NMR of compound **3e** (376 MHz, $CDCl_3$)



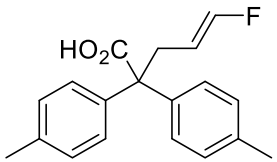

FEN-FI-138-C.11.fid
178.448
151.630
150.716
149.592
141.532
140.774
129.023
127.941
127.641
127.209
126.443
126.018
124.070
107.187
107.089
77.254
77.001
76.747
60.448
60.423
34.740
34.201
34.122
31.259
F
HO2C
13C NMR of compound 3e (125 MHz, CDCl3)
f1 (ppm)



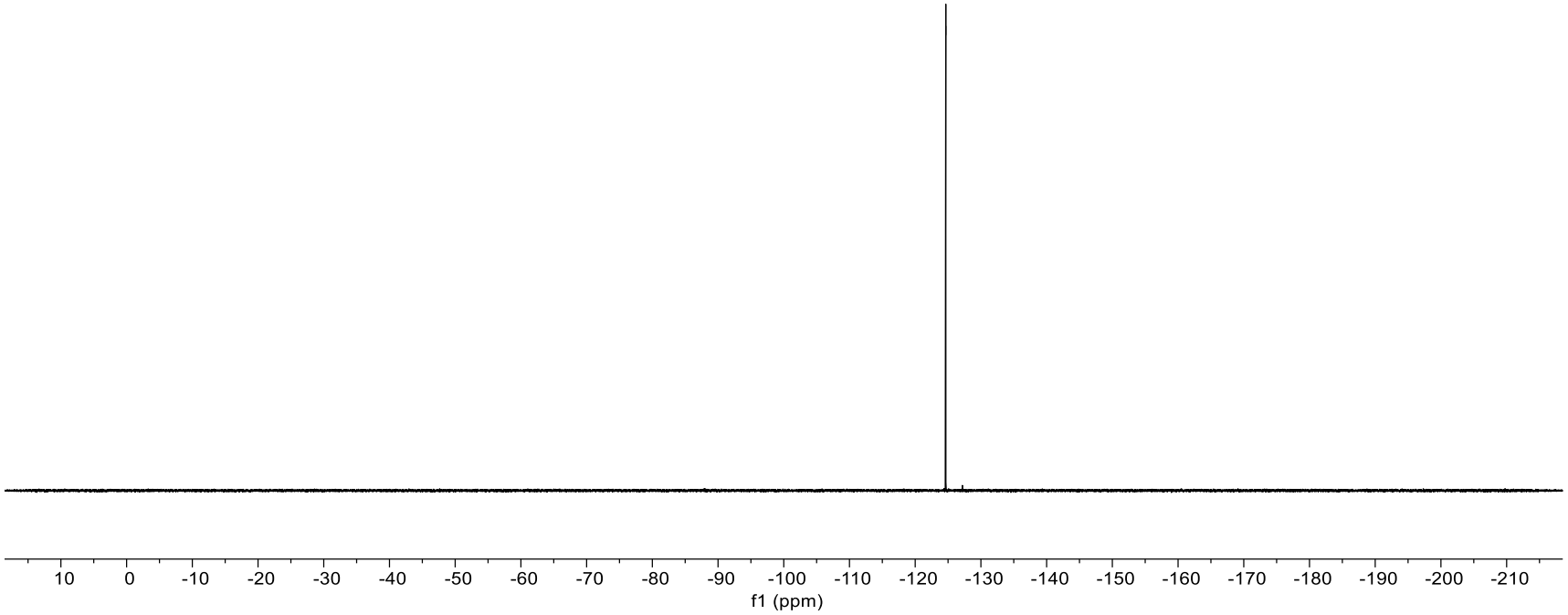
^{1}H NMR of compound **3f** (400 MHz, $CDCl_3$)

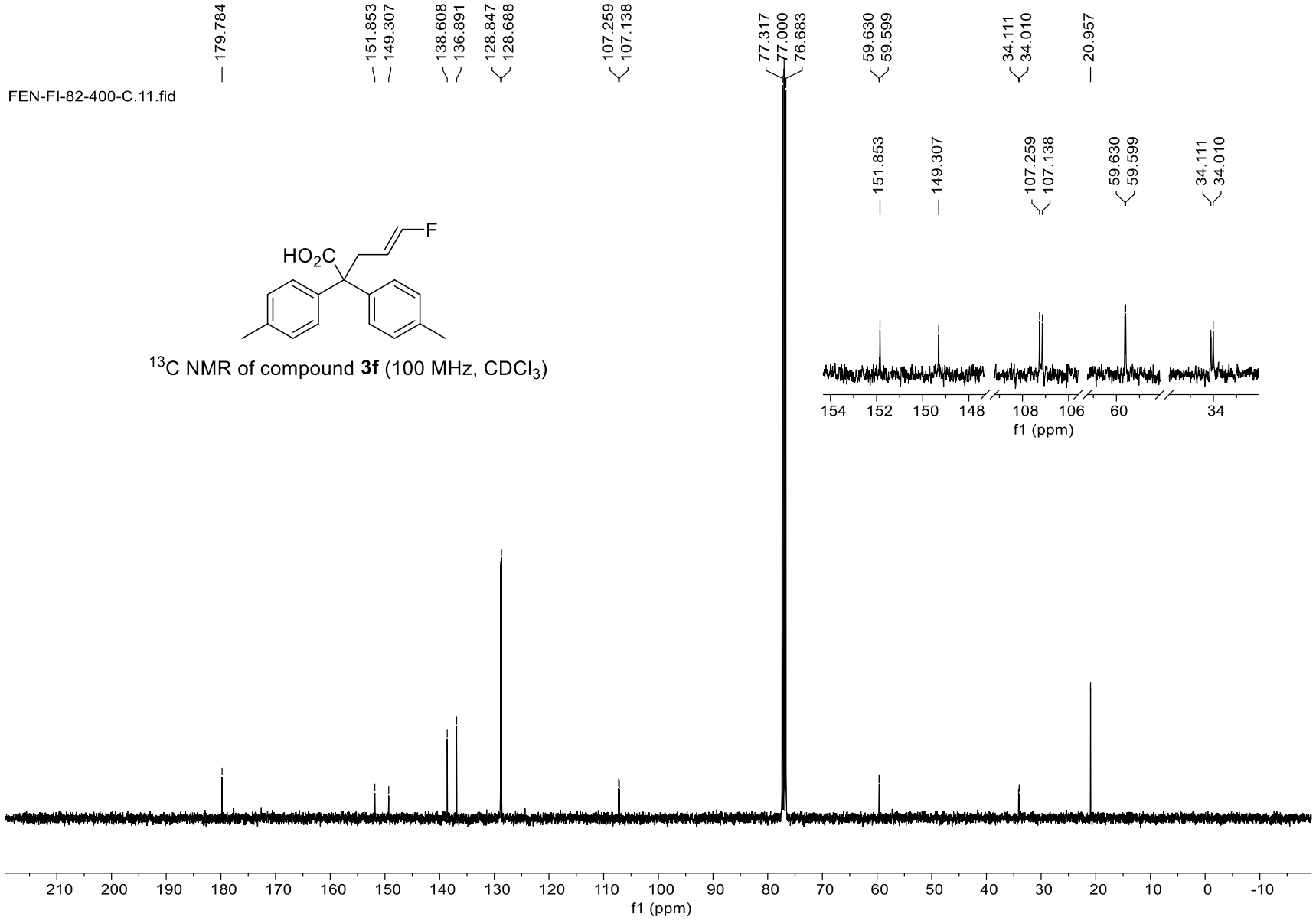
FEN-FI-82-400-H-2.11.fid

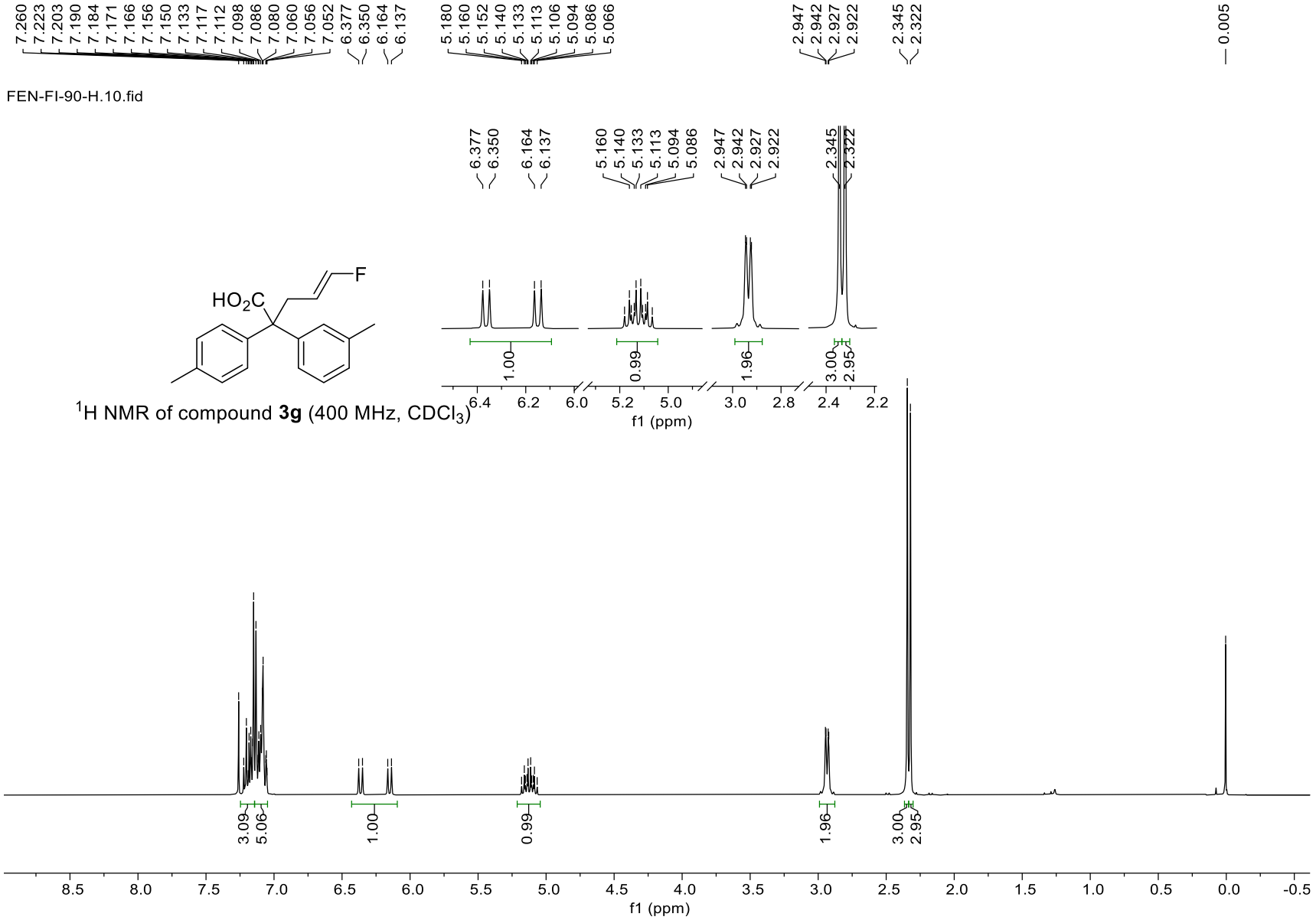
-124.654



^{19}F NMR of compound **3f** (376 MHz, $CDCl_3$)

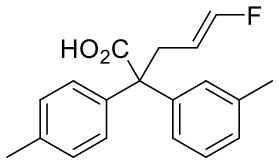



FEN-FI-82-400-C.11.fid
179.784
151.853
149.307
138.608
136.891
128.847
128.688
107.259
107.138
77.317
77.000
76.683
59.630
59.599
34.111
34.010
20.957
HO2C
F
13C NMR of compound 3f (100 MHz, CDCl3)
f1 (ppm)

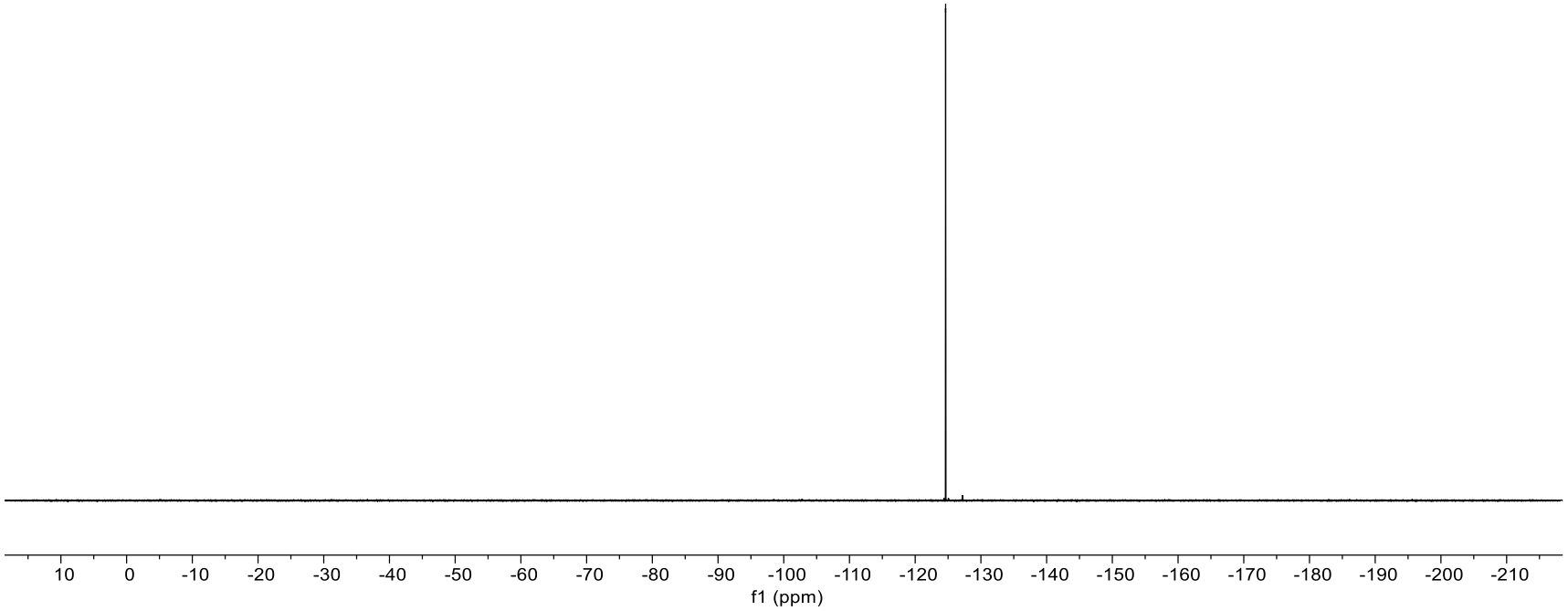


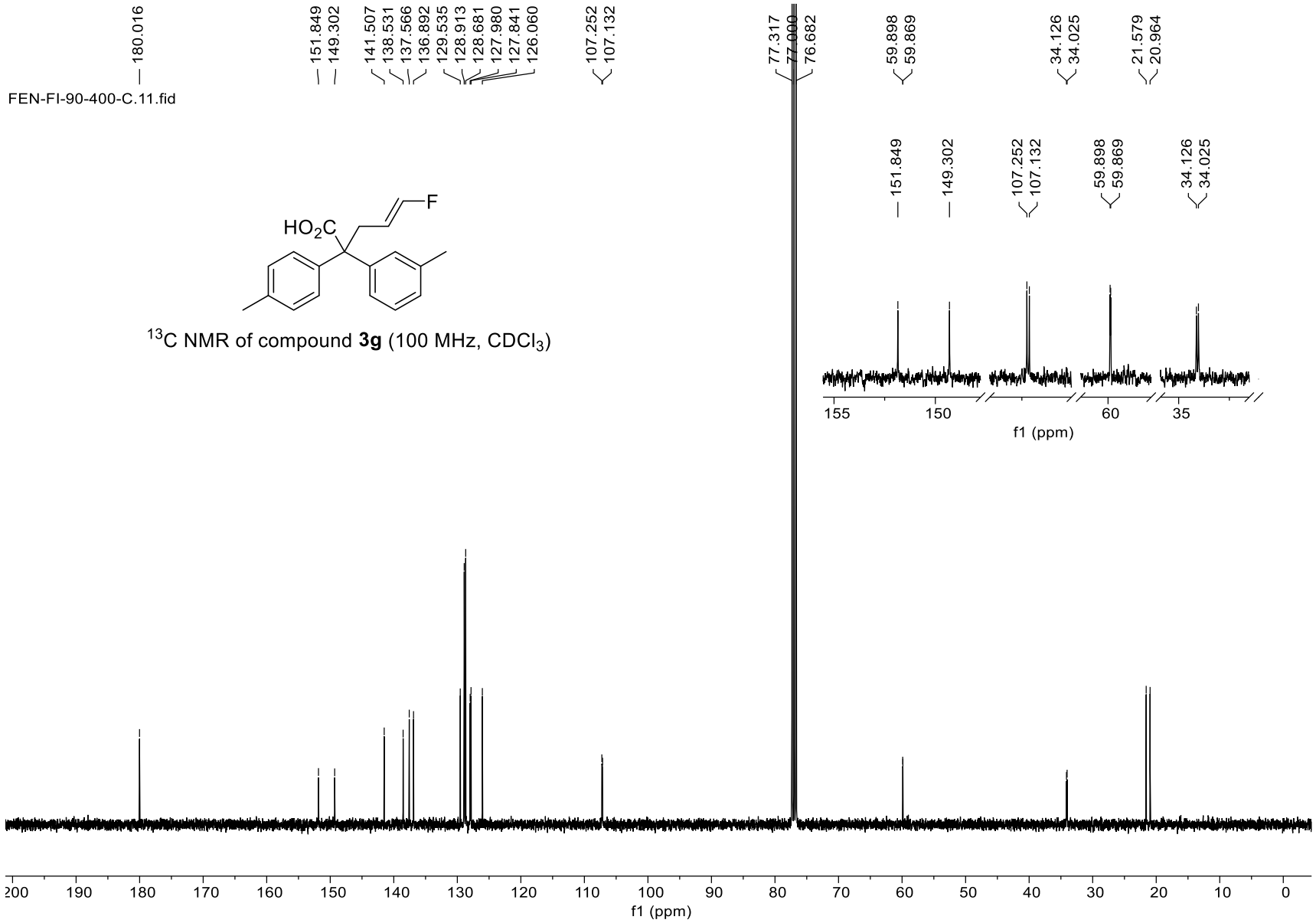
^{1}H NMR of compound **3g** (400 MHz, $CDCl_3$)

FEN-FI-90-F.11.fid

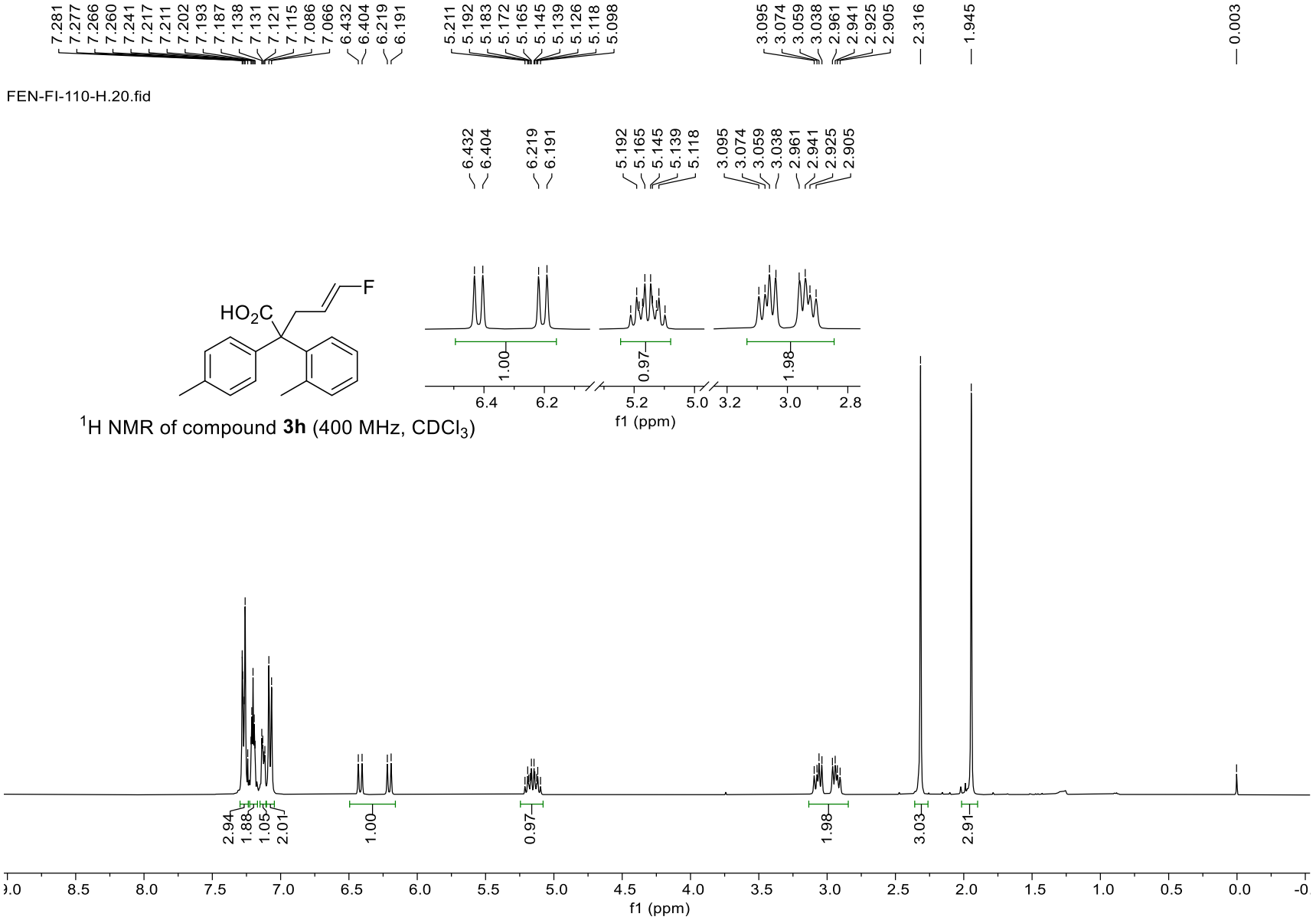


^{19}F NMR of compound **3g** (376 MHz, $CDCl_3$)



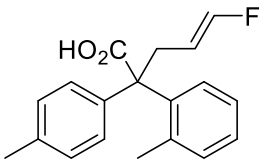


^{13}C NMR of compound **3g** (100 MHz, $CDCl_3$)

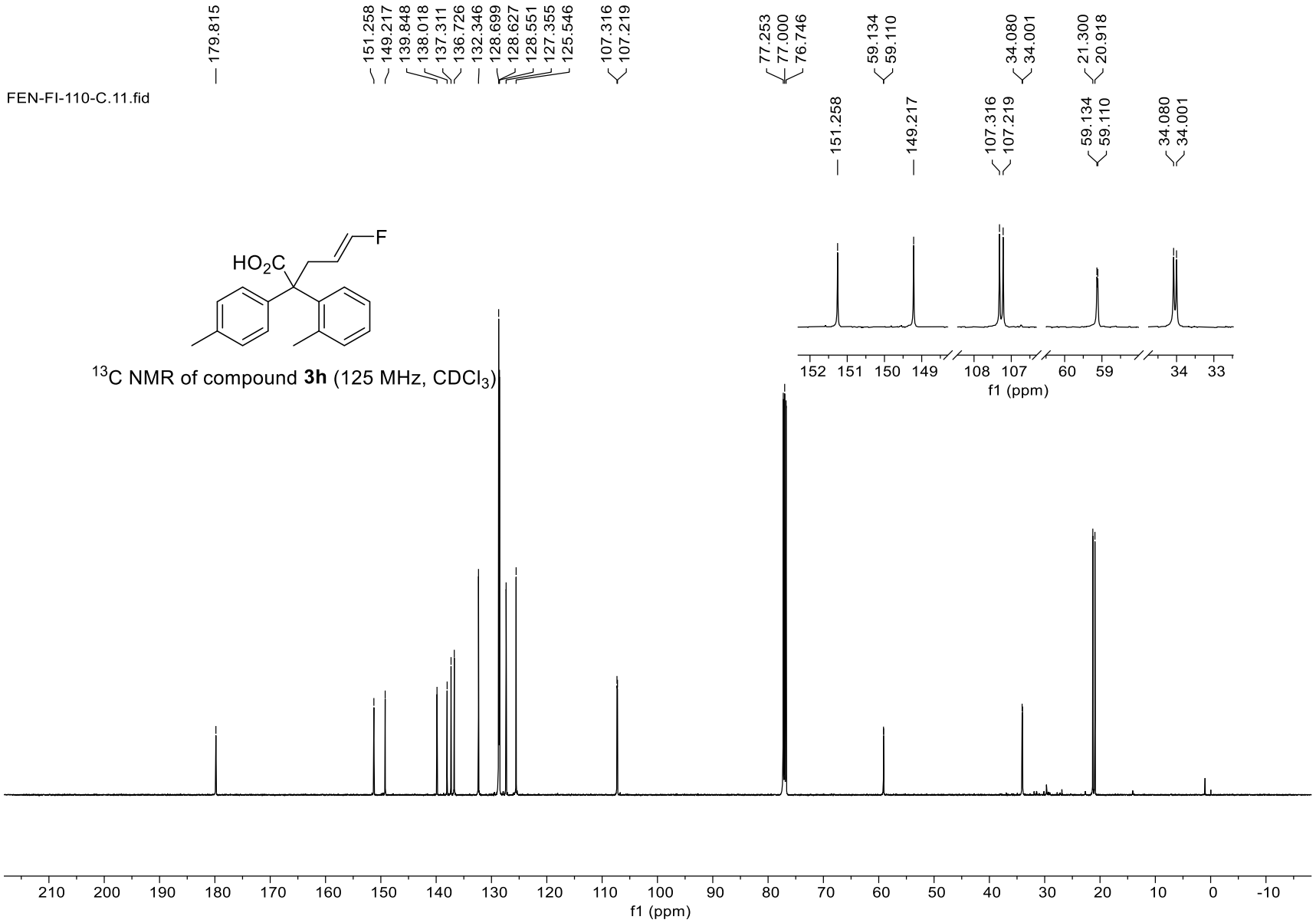


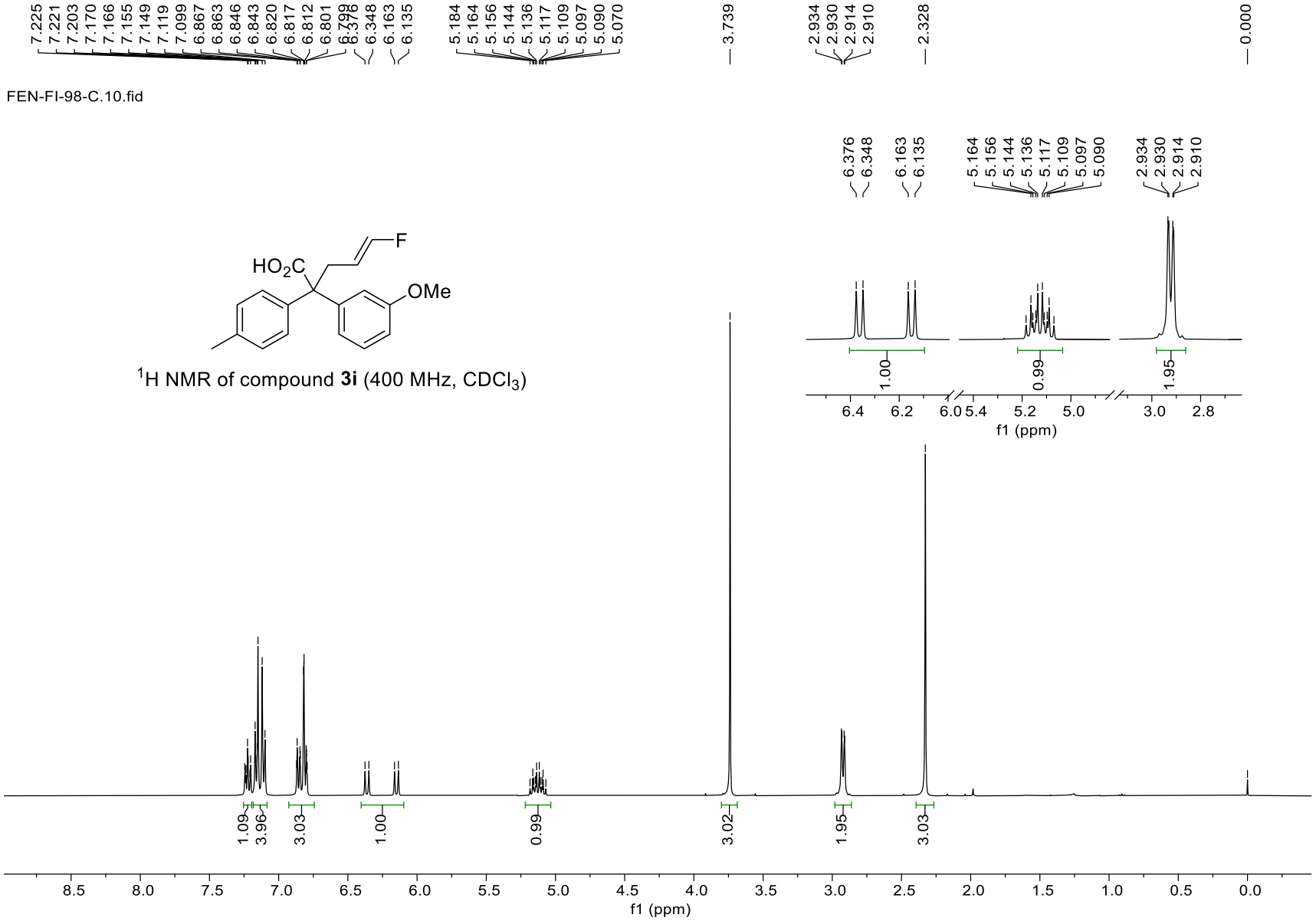
^{1}H NMR of compound **3h** (400 MHz, $CDCl_3$)

FEN-FI-110-H.21.fid

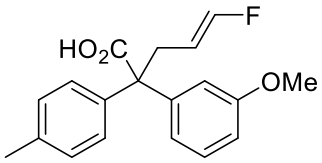


^{19}F NMR of compound **3h** (376 MHz, $CDCl_3$)

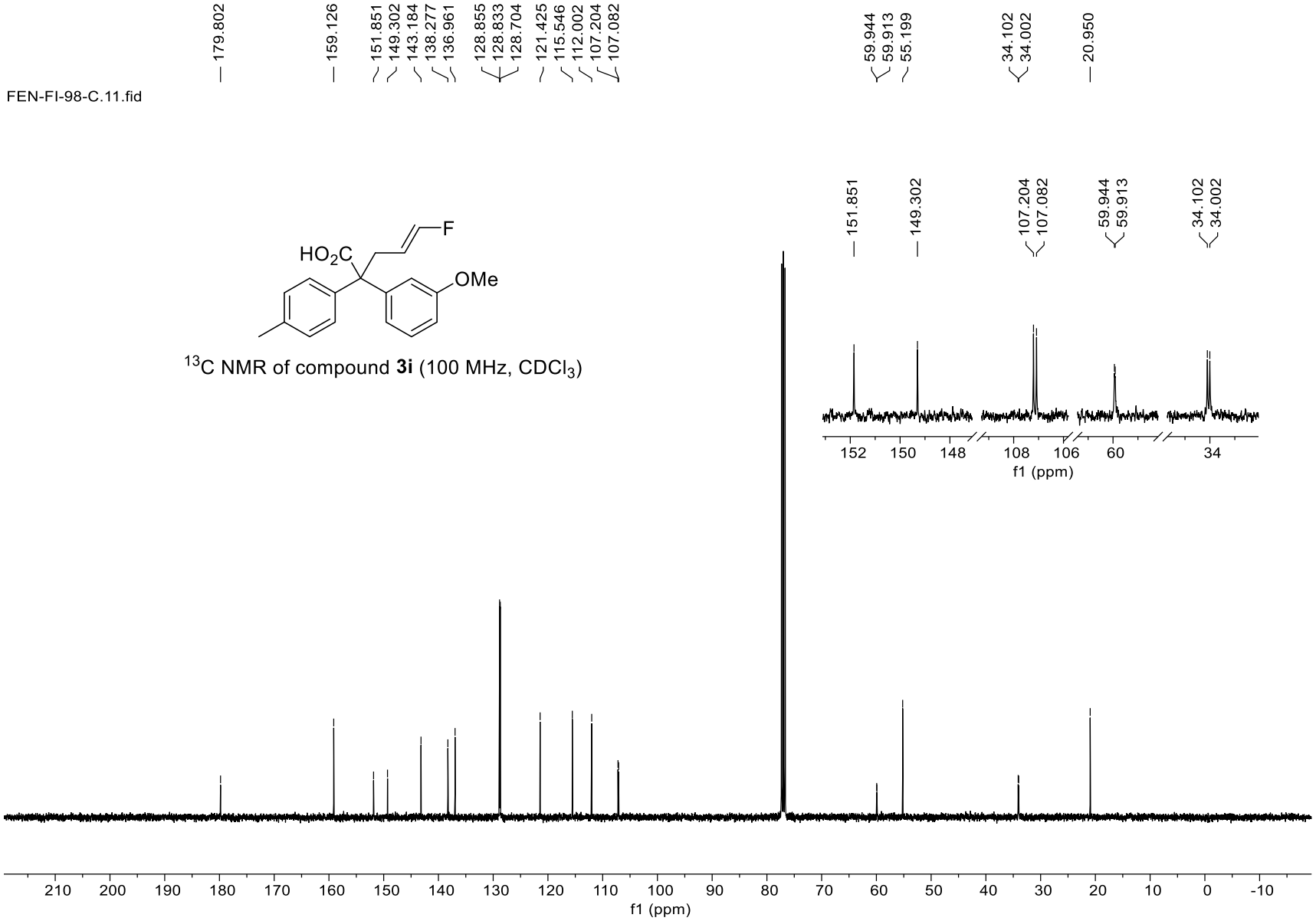

FEN-FI-110-C.11.fid
179.815
151.258
149.217
139.848
138.018
137.311
136.726
132.346
128.699
128.627
128.551
127.355
125.546
107.316
107.219
77.253
77.000
76.746
59.134
59.110
34.080
34.001
21.300
20.918
HO2C
F
13C NMR of compound 3h (125 MHz, CDCl3)
f1 (ppm)


7.225
7.221
7.203
7.170
7.166
7.155
7.149
7.119
7.099
6.867
6.863
6.846
6.843
6.820
6.817
6.812
6.801
6.799
6.348
6.163
6.135
5.184
5.164
5.156
5.144
5.136
5.117
5.109
5.097
5.090
5.070
3.739
2.934
2.930
2.914
2.910
2.328
0.000
FEN-FI-98-C.10.fid
F
HO2C
OMe
1H NMR of compound 3i (400 MHz, CDCl3)
6.376
6.348
6.163
6.135
5.164
5.156
5.144
5.136
5.117
5.109
5.097
5.090
2.934
2.930
2.914
2.910
1.00
0.99
1.95
6.4
6.2
6.0
5.4
5.2
5.0
3.0
2.8
f1 (ppm)
1.09
3.96
3.03
1.00
0.99
3.02
1.95
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

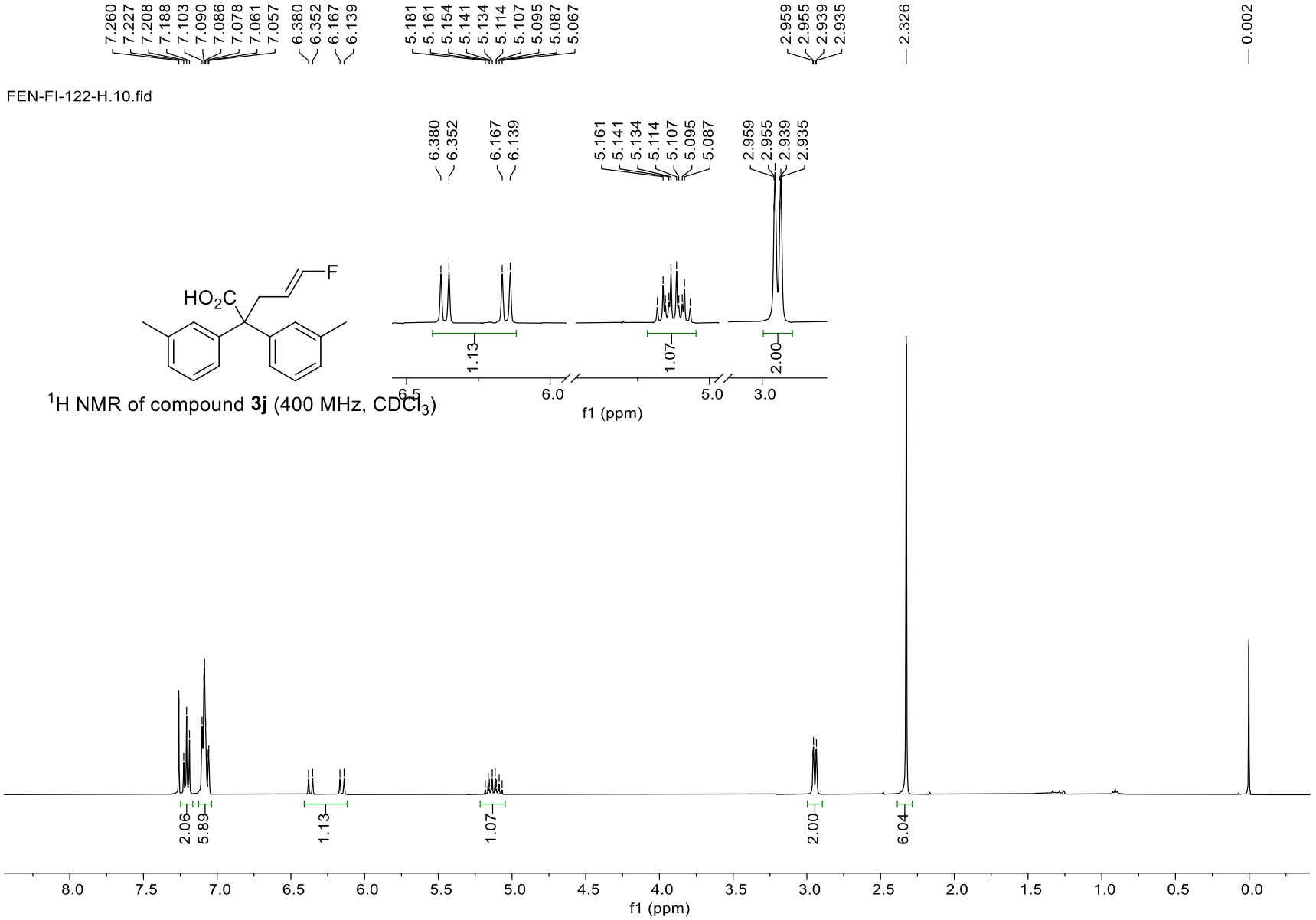
FEN-FI-98-H.11.fid



^{19}F NMR of compound **3i** (376 MHz, $CDCl_3$)

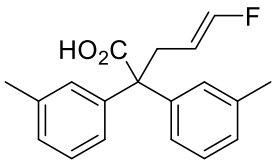


^{13}C NMR of compound **3i** (100 MHz, $CDCl_3$)

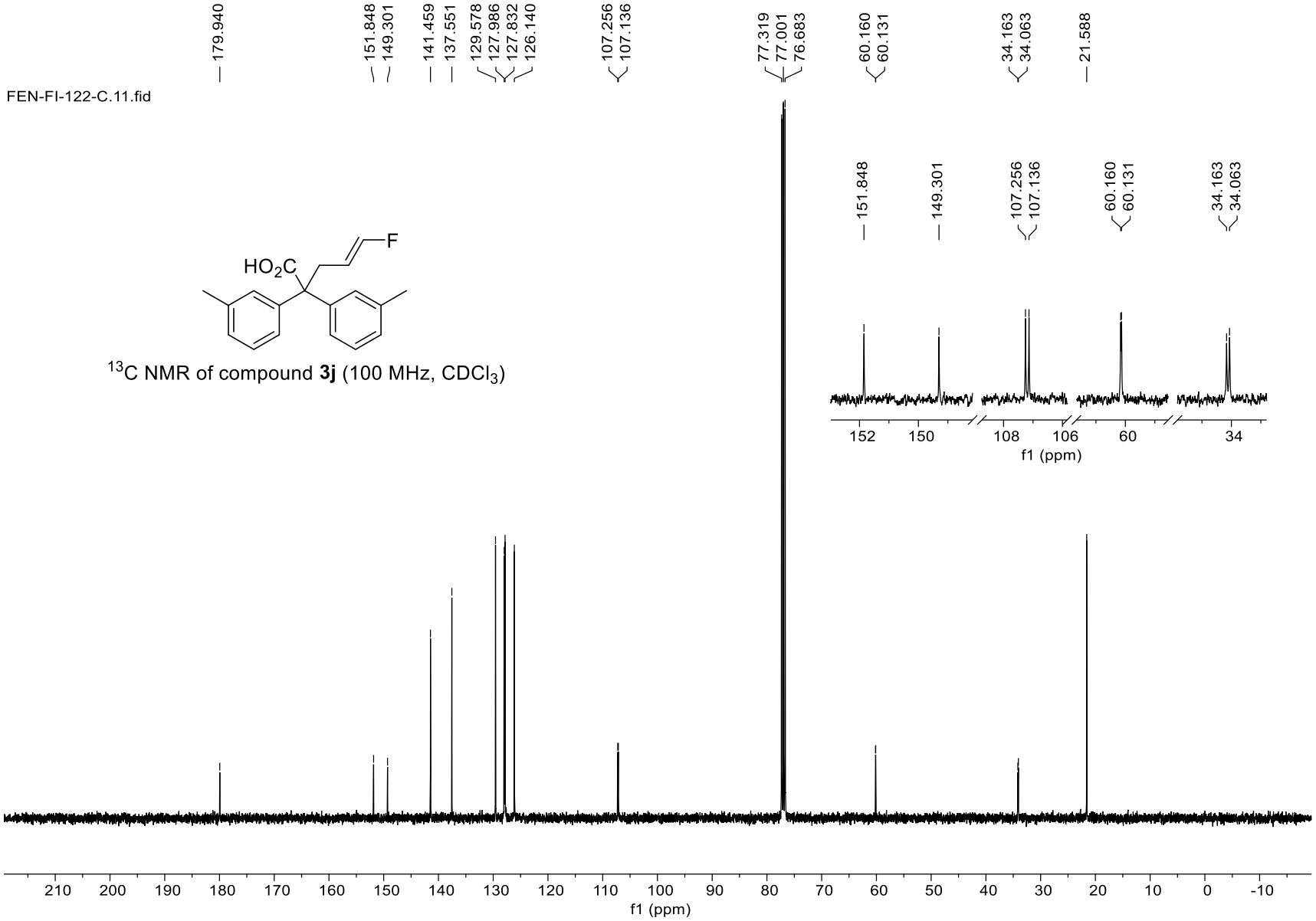


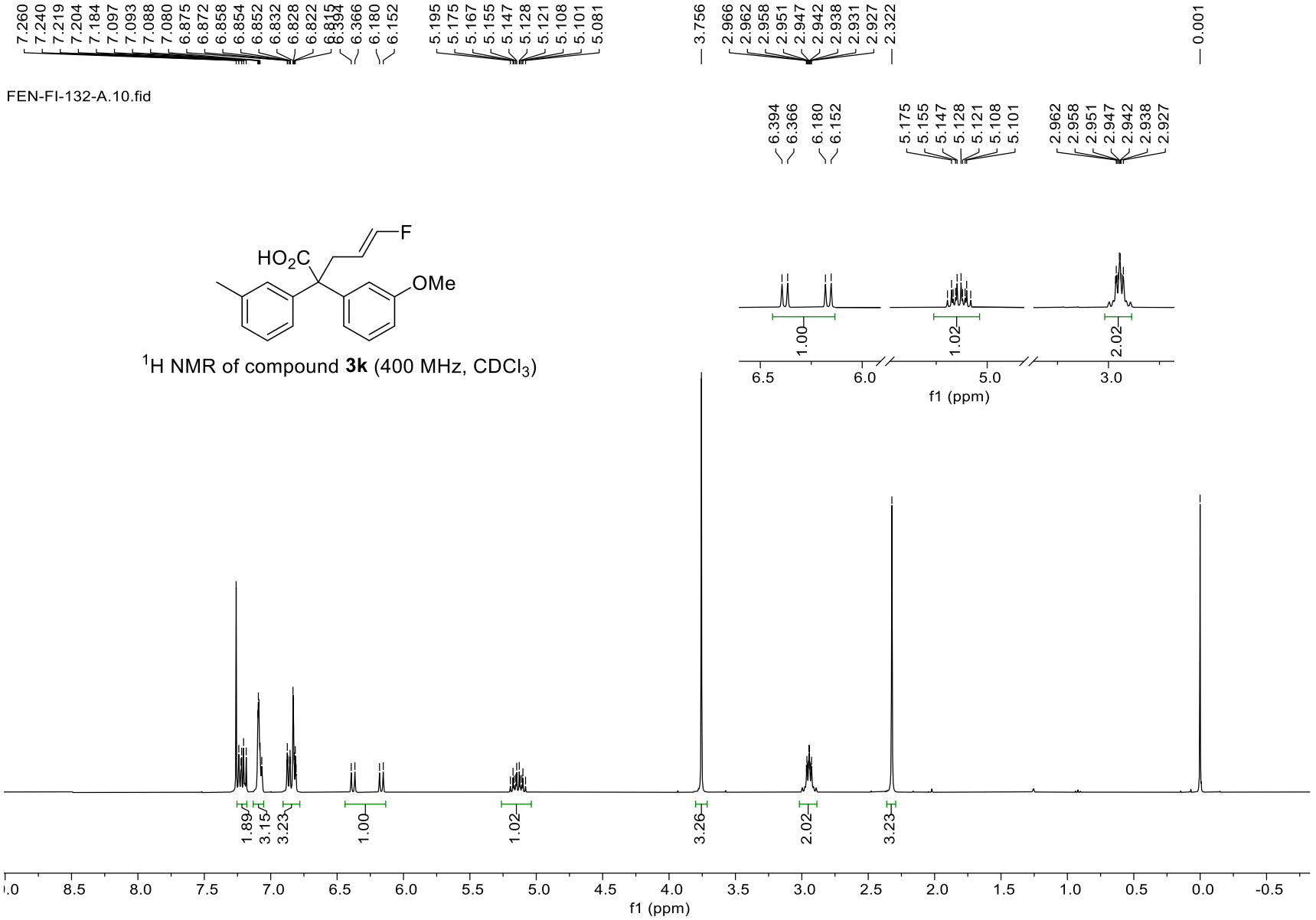
^{1}H NMR of compound **3j** (400 MHz, $CDCl_3$)

FEN-FI-122-H.11.fid

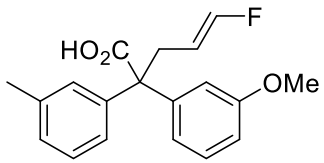


^{19}F NMR of compound **3j** (376 MHz, $CDCl_3$)

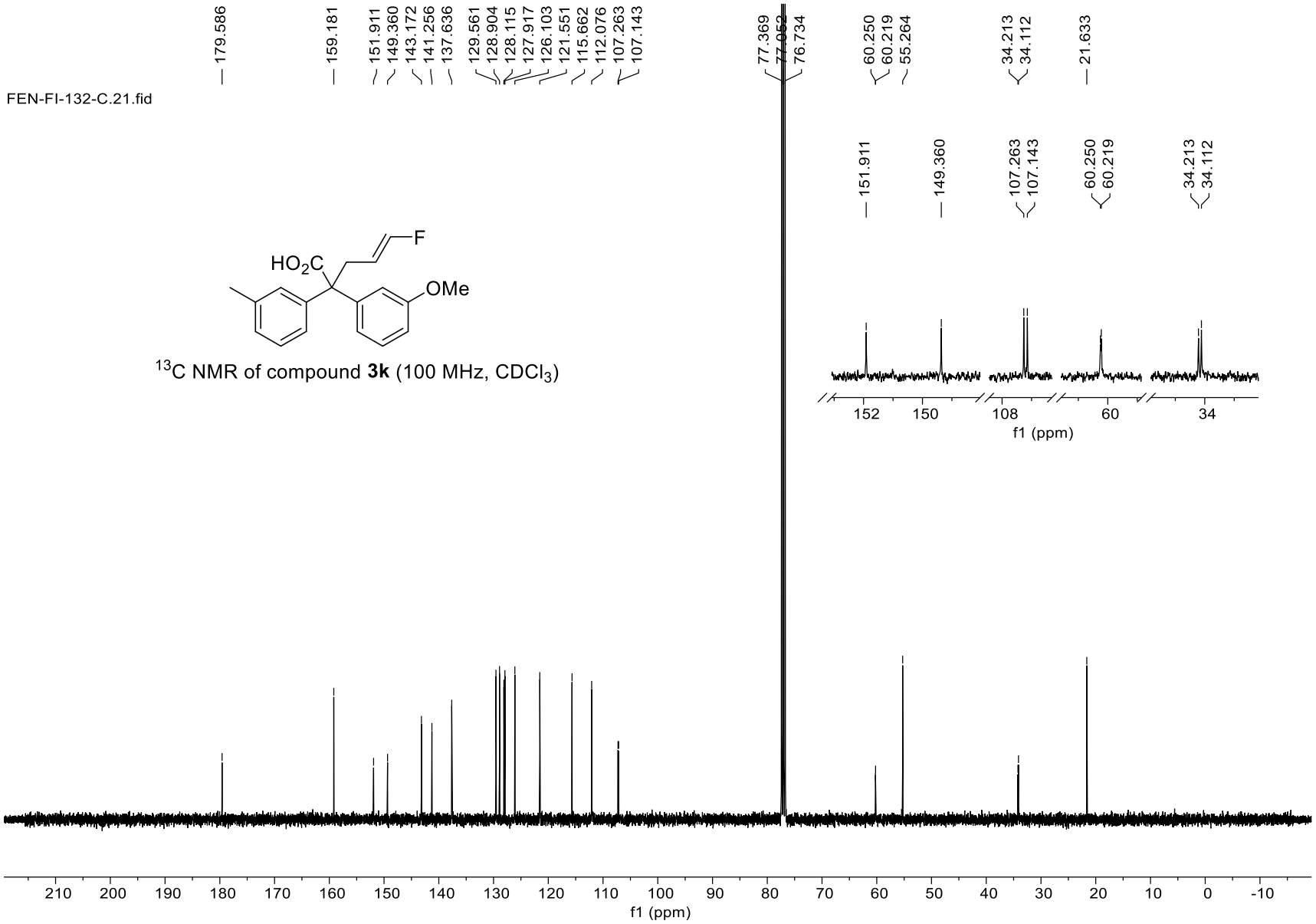

179.940
151.848
149.301
141.459
137.551
129.578
127.986
127.832
126.140
107.256
107.136
77.319
77.001
76.683
60.160
60.131
34.163
34.063
21.588
FEN-FI-122-C.11.fid
HO2C
F
13C NMR of compound 3j (100 MHz, CDCl3)
f1 (ppm)


7.260
7.240
7.219
7.204
7.184
7.097
7.093
7.088
7.080
6.875
6.872
6.858
6.854
6.852
6.832
6.828
6.822
6.815
6.394
6.366
6.180
6.152
5.195
5.175
5.167
5.155
5.147
5.128
5.121
5.108
5.101
5.081
3.756
2.966
2.962
2.958
2.951
2.947
2.942
2.938
2.931
2.927
2.322
0.001
FEN-FI-132-A.10.fid
F
HO2C
OMe
1H NMR of compound 3k (400 MHz, CDCl3)
1.00
1.02
2.02
6.5
6.0
5.0
3.0
f1 (ppm)
1.89
3.15
3.23
1.00
1.02
3.26
2.02
3.23
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

FEN-FI-132-A.11.fid

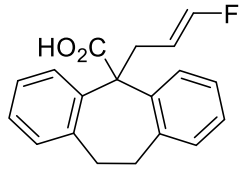


^{19}F NMR of compound **3k** (376 MHz, $CDCl_3$)



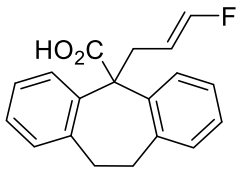
^{13}C NMR of compound **3k** (100 MHz, $CDCl_3$)

FEN-FI-104-H.10.fid

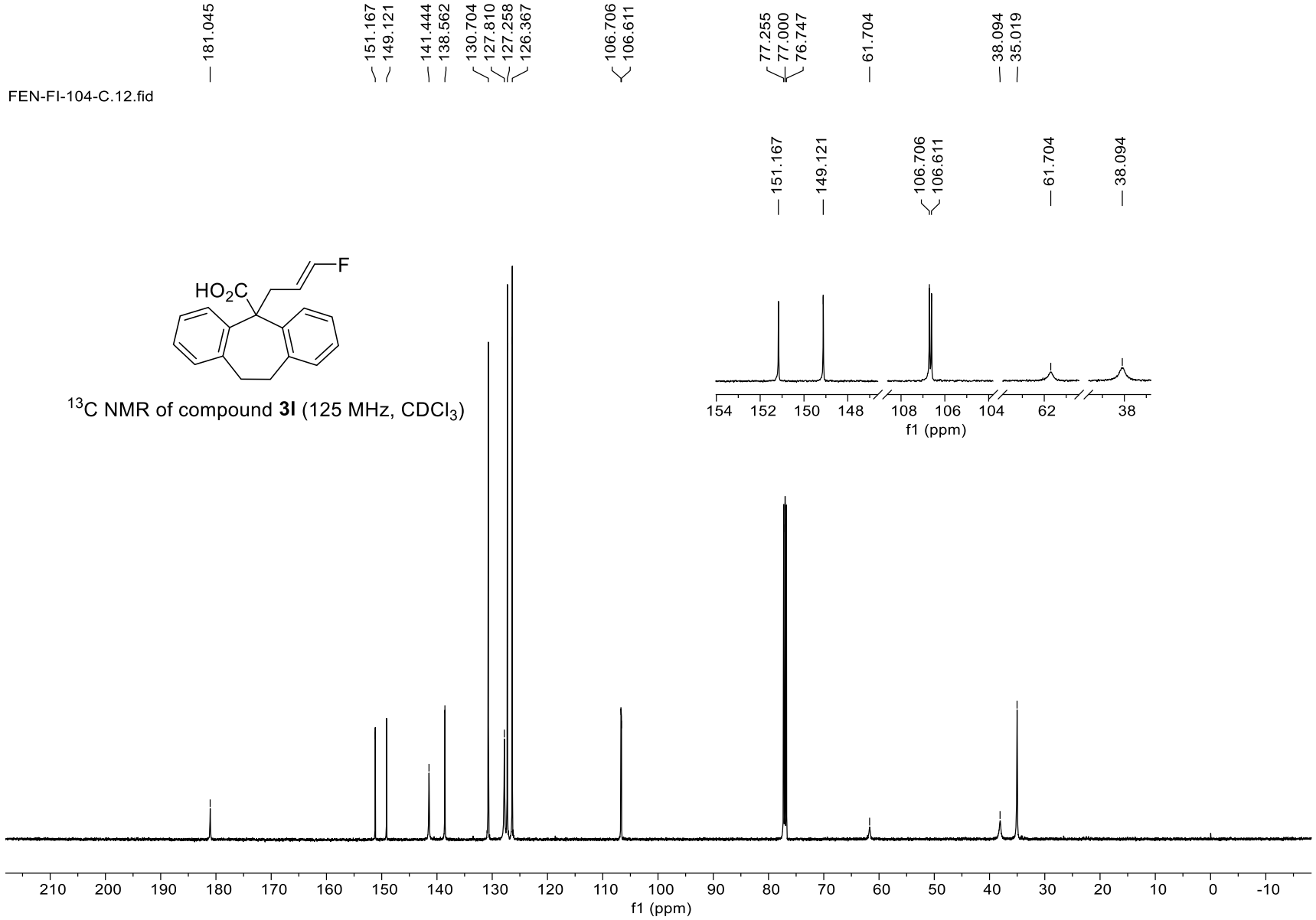


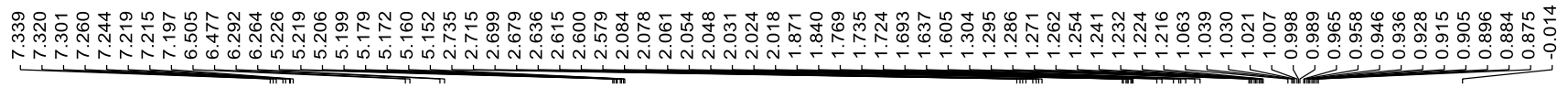
^{1}H NMR of compound **3l** (400 MHz, $CDCl_3$)

FEN-FI-104-H.11.fid

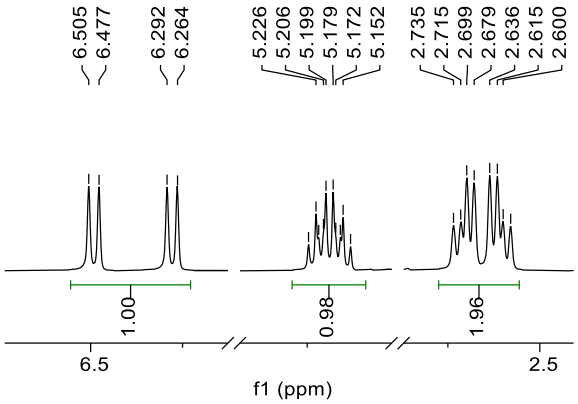


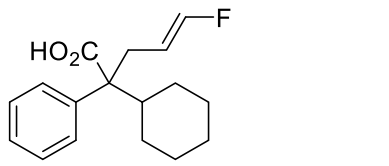
^{19}F NMR of compound **3l** (376 MHz, $CDCl_3$)


181.045
151.167
149.121
141.444
138.562
130.704
127.810
127.258
126.367
106.706
106.611
77.255
77.000
76.747
61.704
38.094
35.019
FEN-FI-104-C.12.fid
HO2C
F
13C NMR of compound 3l (125 MHz, CDCl3)
f1 (ppm)

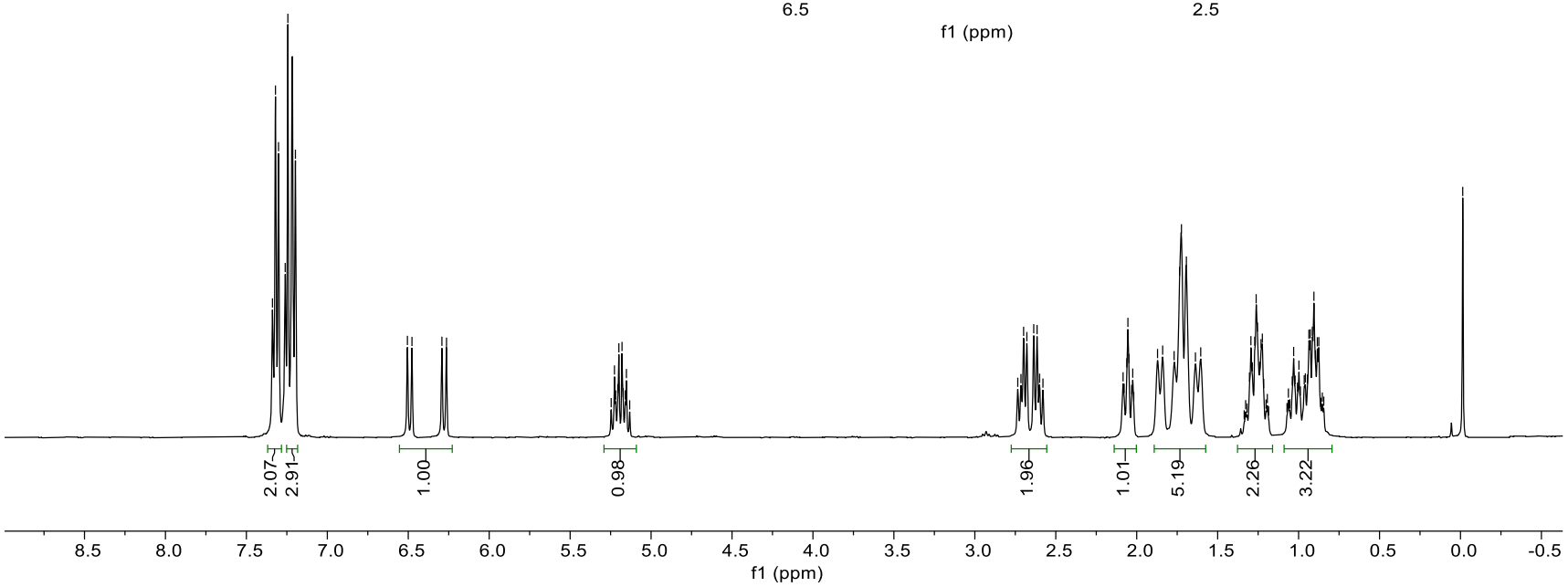


FEN-FJ-30-Nb-H-3.10.fid

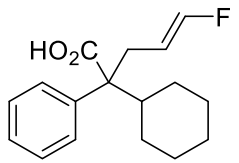




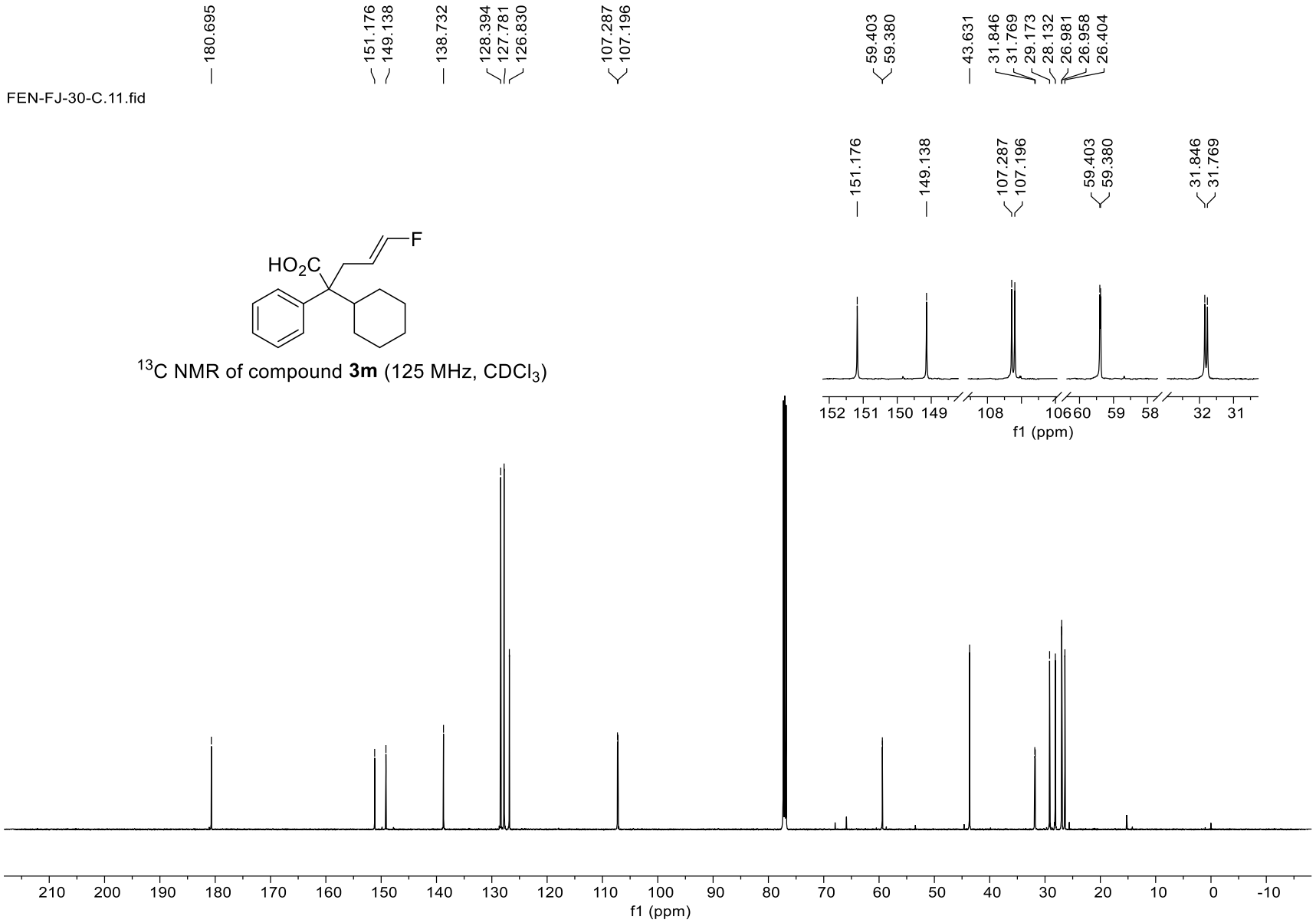
^{1}H NMR of compound **3m** (400 MHz, $CDCl_3$)

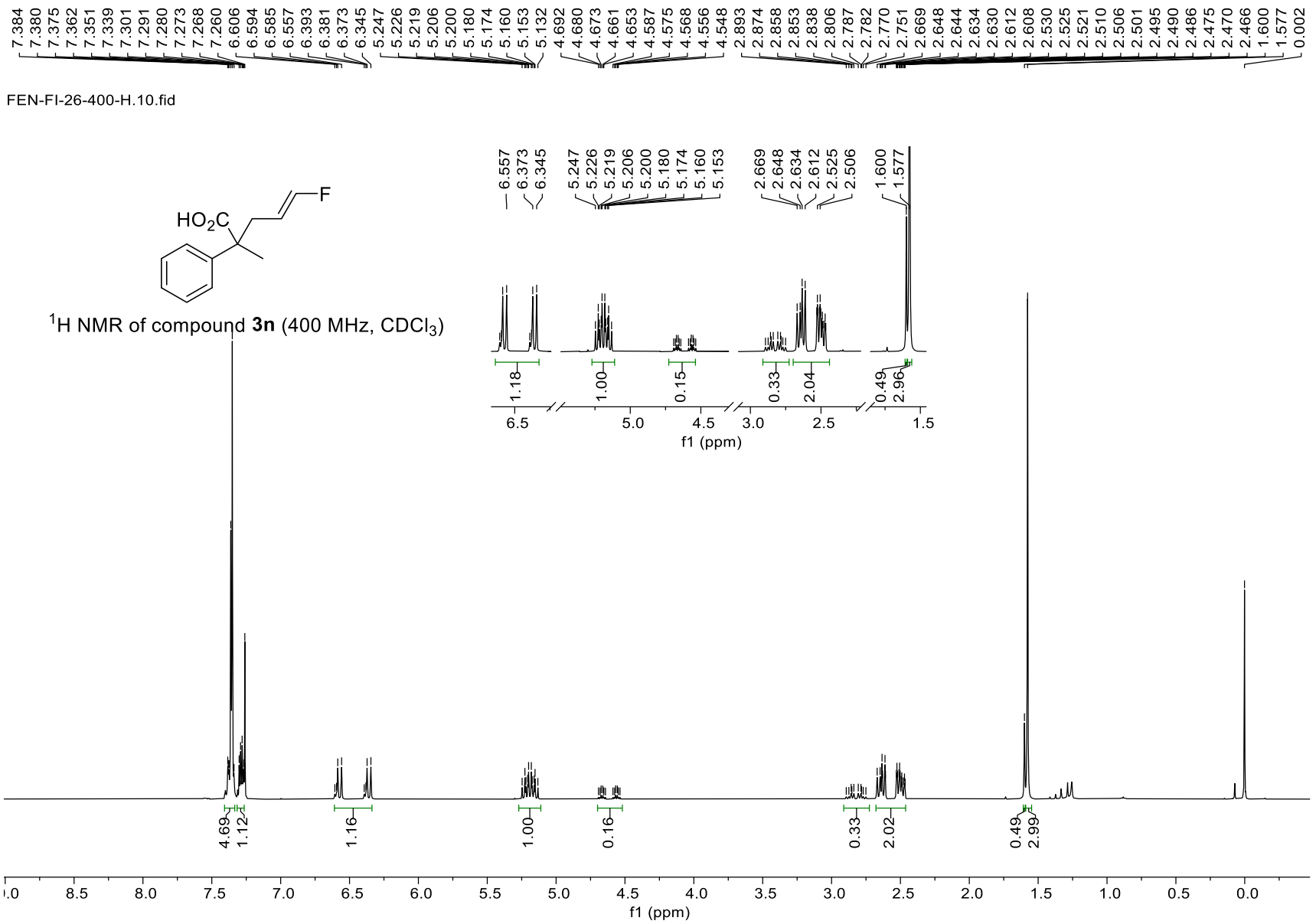


FEN-FJ-30-Nb-H-3.11.fid

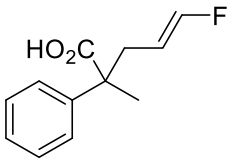


^{19}F NMR of compound **3m** (376 MHz, $CDCl_3$)

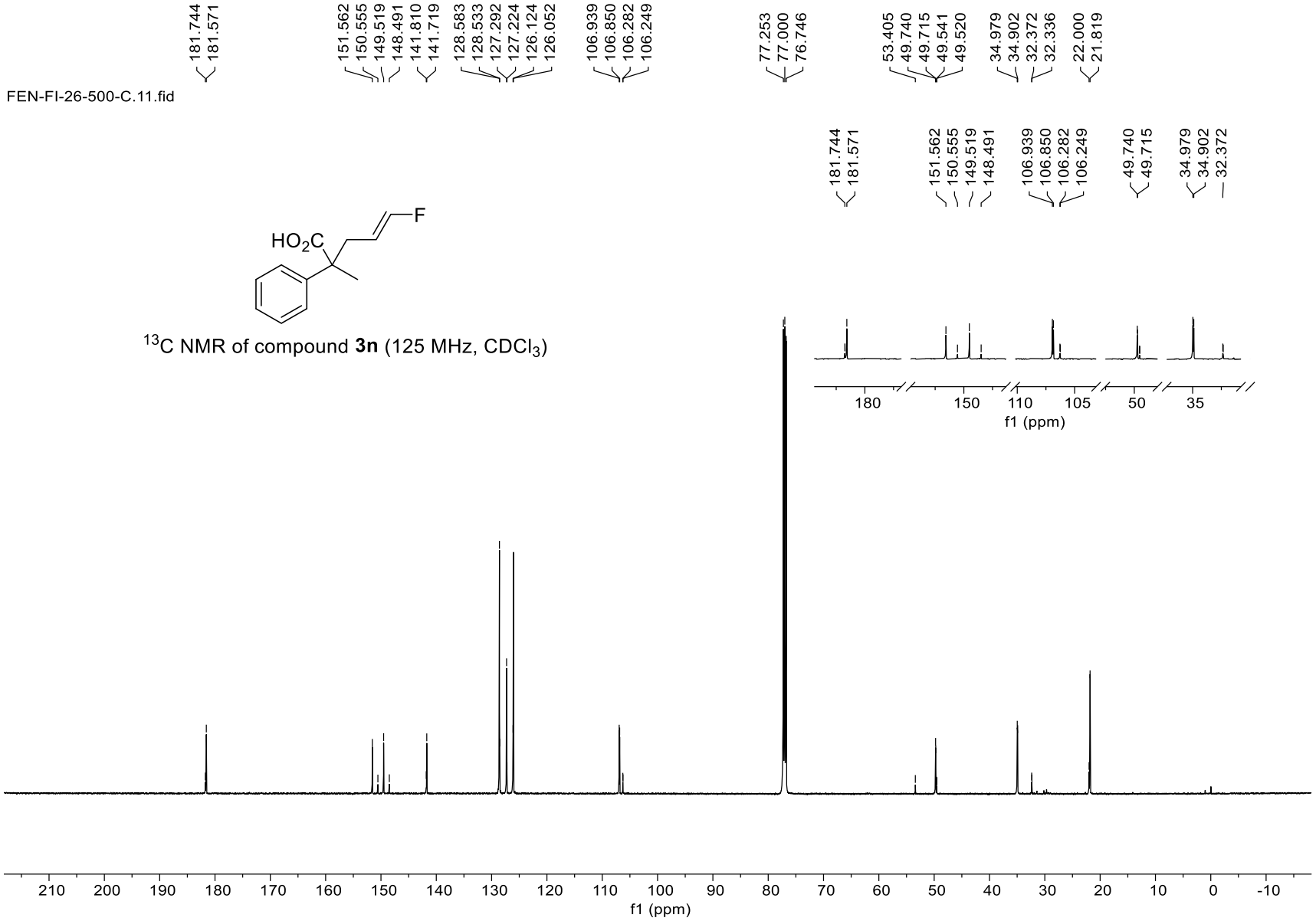

180.695
151.176
149.138
138.732
128.394
127.781
126.830
107.287
107.196
59.403
59.380
43.631
31.846
31.769
29.173
28.132
26.981
26.958
26.404
FEN-FJ-30-C.11.fid
HO2C
F
13C NMR of compound 3m (125 MHz, CDCl3)
f1 (ppm)


7.384 7.380 7.375 7.362 7.351 7.339 7.301 7.291 7.280 7.273 7.268 7.260 6.606 6.594 6.585 6.557 6.393 6.381 6.373 6.345 5.247 5.226 5.219 5.206 5.200 5.180 5.174 5.160 5.153 5.132 4.692 4.680 4.673 4.661 4.653 4.587 4.575 4.568 4.556 4.548 2.893 2.874 2.858 2.853 2.838 2.806 2.787 2.782 2.770 2.751 2.669 2.648 2.644 2.634 2.630 2.612 2.608 2.530 2.525 2.521 2.510 2.506 2.501 2.495 2.490 2.486 2.475 2.470 2.466 1.600 1.577 0.002
FEN-FI-26-400-H.10.fid
HO2C
F
1H NMR of compound 3n (400 MHz, CDCl3)
6.557 6.373 6.345 5.247 5.226 5.219 5.206 5.200 5.180 5.174 5.160 5.153 2.669 2.648 2.634 2.612 2.525 2.506 1.600 1.577
1.18 1.00 0.15 0.33 2.04 0.49 2.96
6.5 5.0 4.5 3.0 2.5 1.5
f1 (ppm)
4.69 1.12 1.16 1.00 0.16 0.33 2.02 0.49 2.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

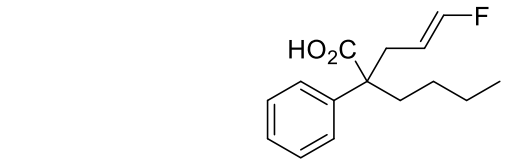
FEN-FI-26-400-H.11.fid



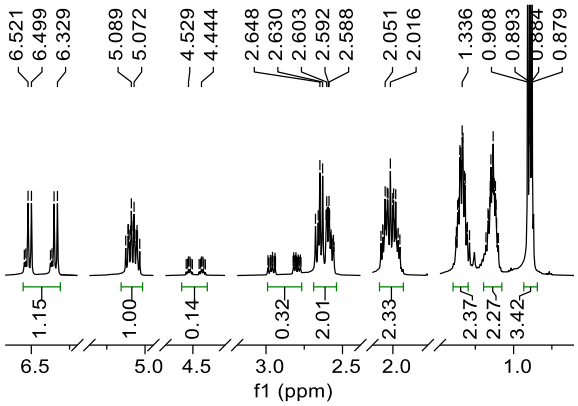
^{19}F NMR of compound **3n** (376 MHz, $CDCl_3$)

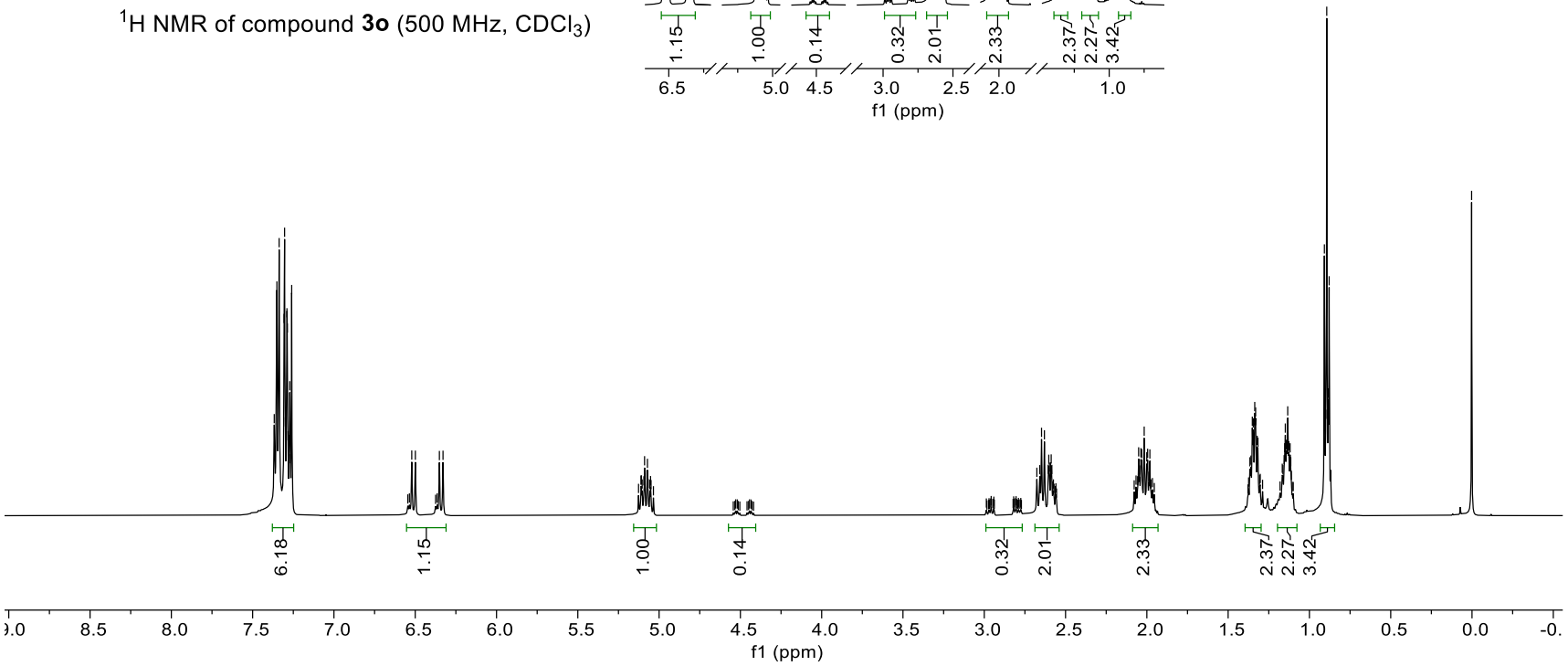

181.744
181.571
151.562
150.555
149.519
148.491
141.810
141.719
128.583
128.533
127.292
127.224
126.124
126.052
106.939
106.850
106.282
106.249
77.253
77.000
76.746
53.405
49.740
49.715
49.541
49.520
34.979
34.902
32.372
32.336
22.000
21.819
FEN-FI-26-500-C.11.fid
HO2C
F
13C NMR of compound 3n (125 MHz, CDCl3)
f1 (ppm)

FEN-FJ-71-500-H.10.fid

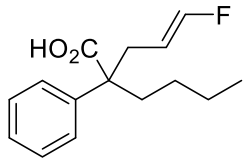


^{1}H NMR of compound **3o** (500 MHz, $CDCl_3$)

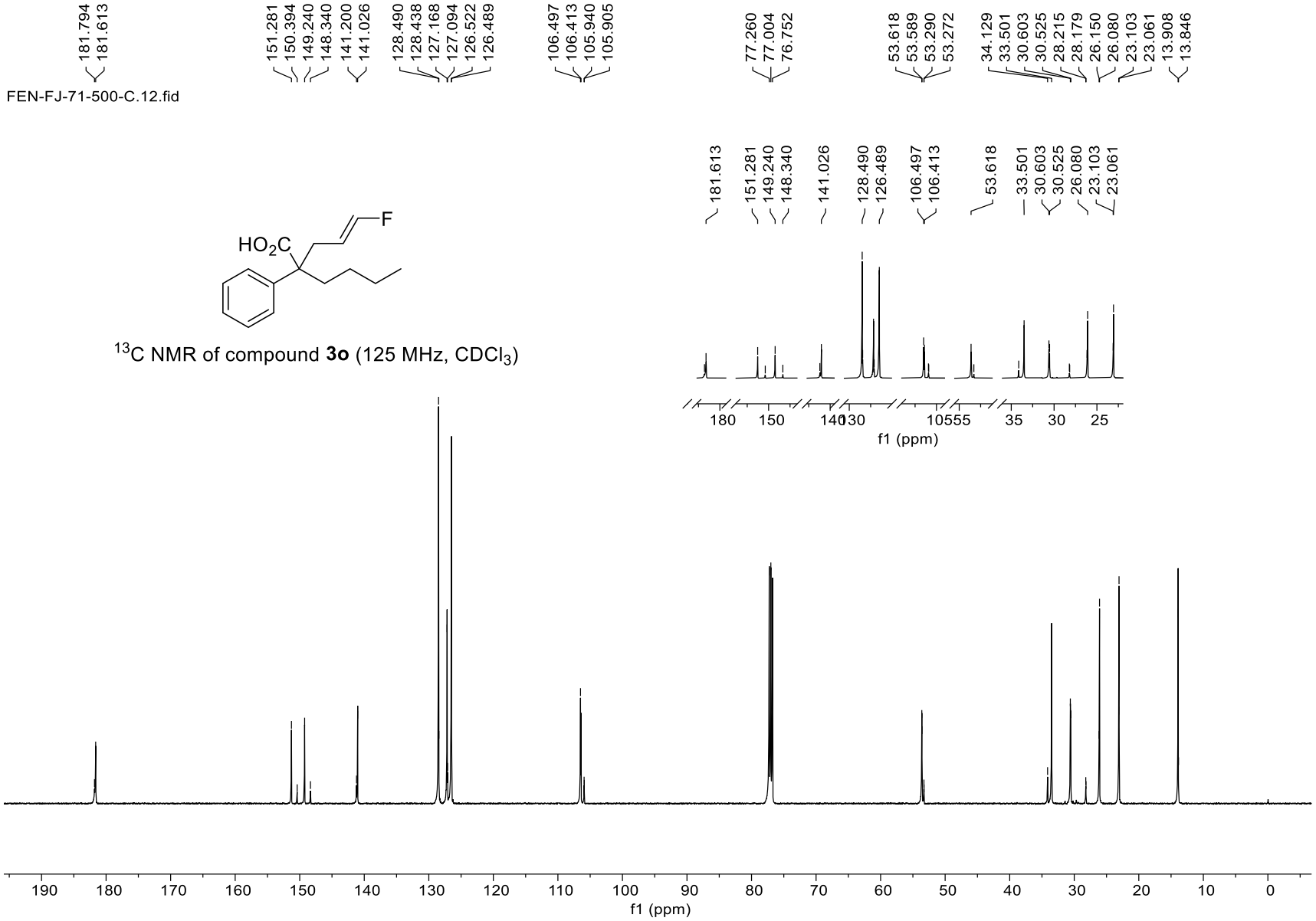




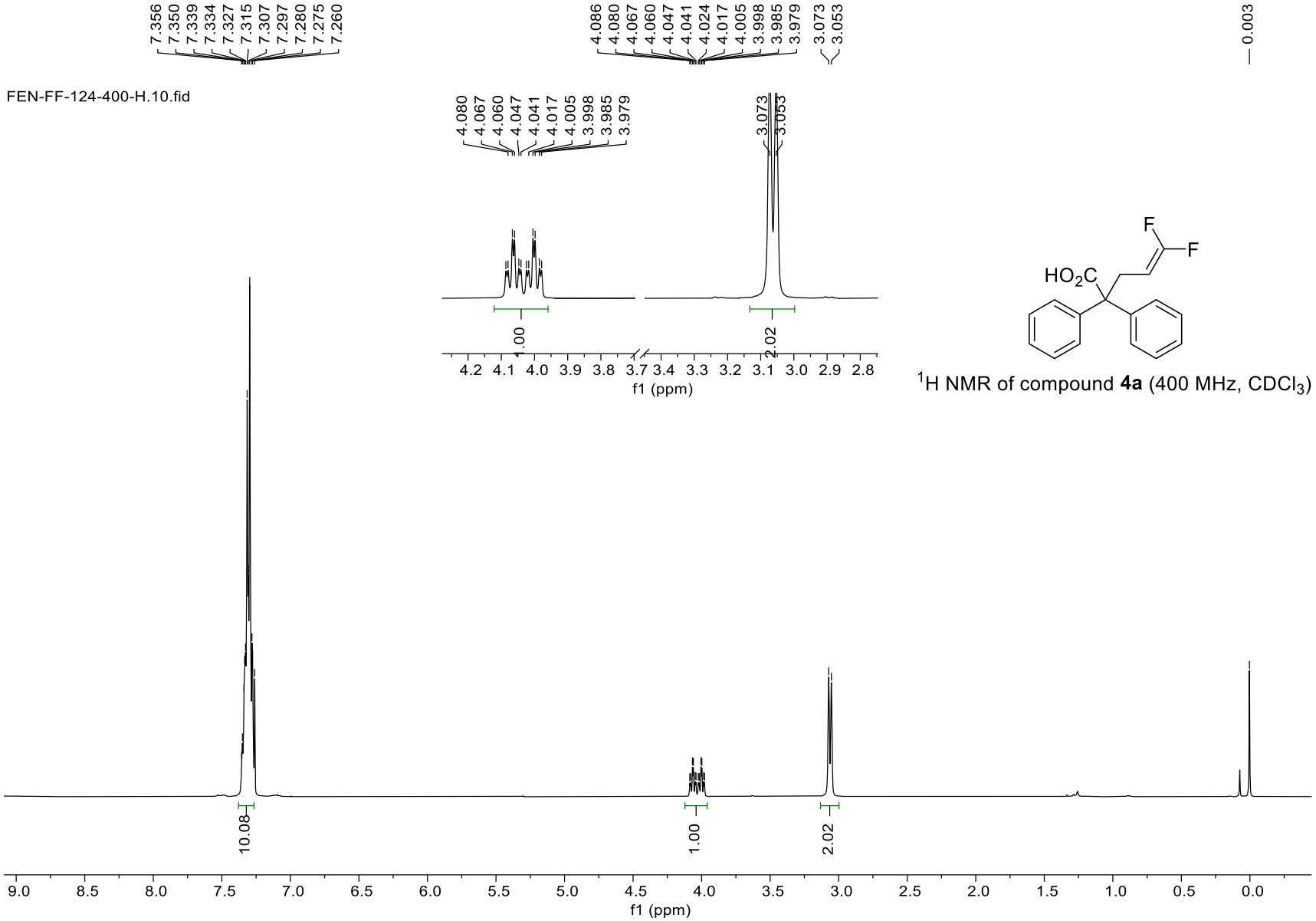
FEN-FJ-71-300.11.fid



^{19}F NMR of compound **3o** (282 MHz, $CDCl_3$)



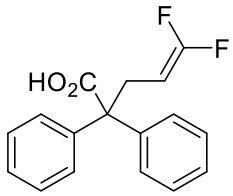
^{13}C NMR of compound **3o** (125 MHz, $CDCl_3$)



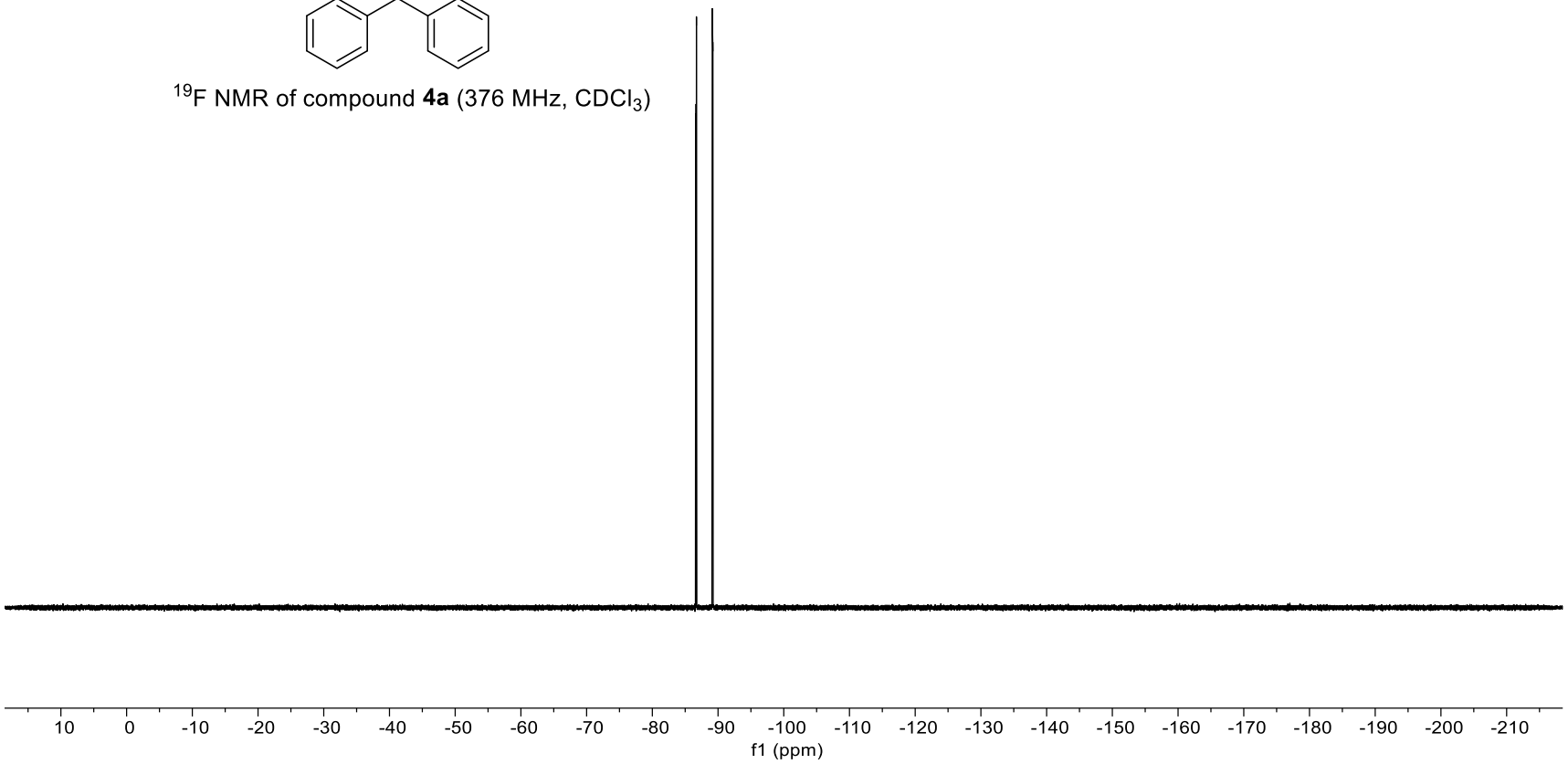
^{1}H NMR of compound **4a** (400 MHz, $CDCl_3$)

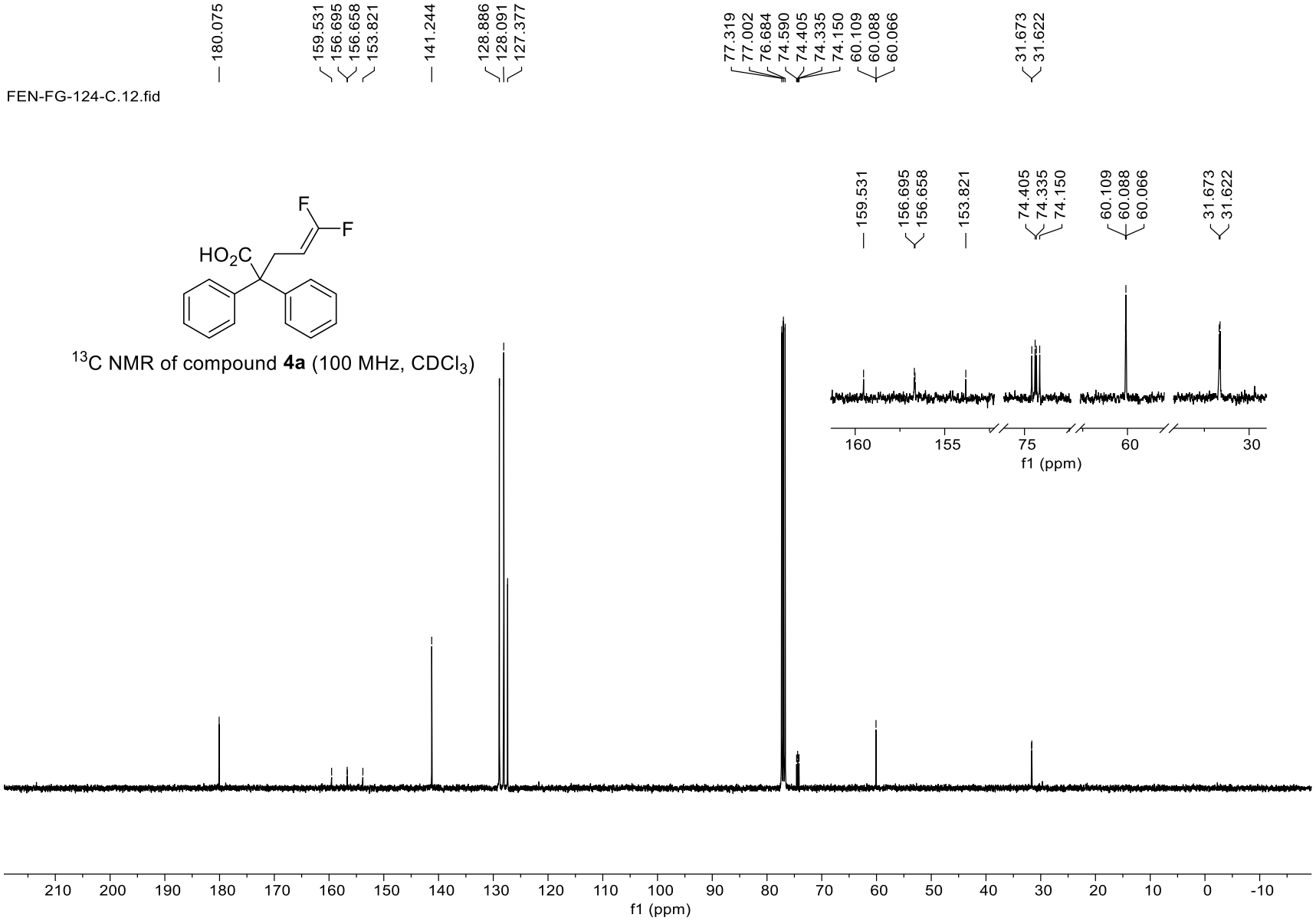
FEN-FF-124-400-H.11.fid

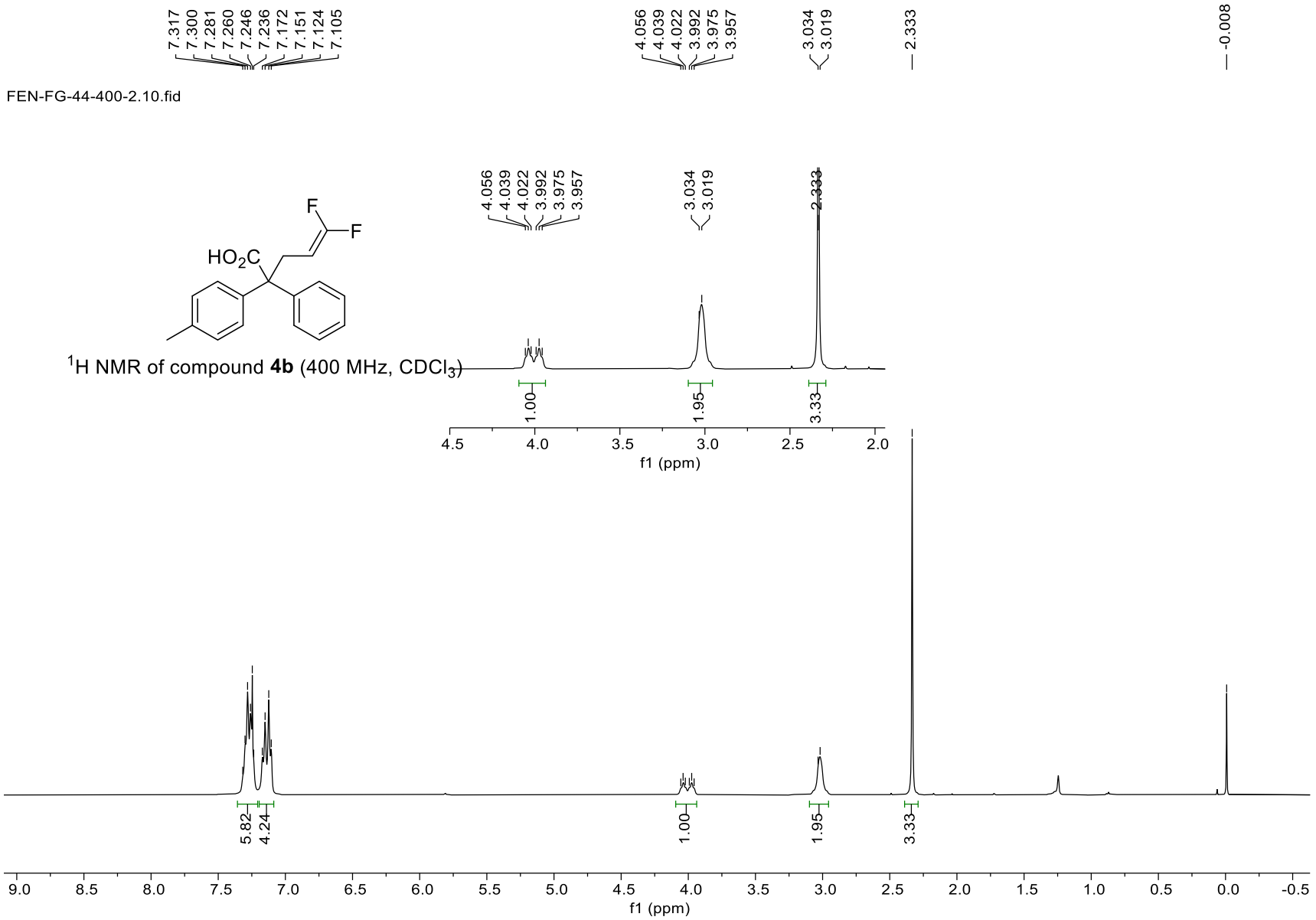
-86.598
-86.708
-89.115
-89.225



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

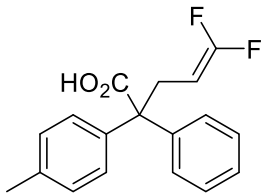



180.075
159.531
156.695
156.658
153.821
141.244
128.886
128.091
127.377
77.319
77.002
76.684
74.590
74.405
74.335
74.150
60.109
60.088
60.066
31.673
31.622
FEN-FG-124-C.12.fid
F
F
HO2C
13C NMR of compound 4a (100 MHz, CDCl3)
159.531
156.695
156.658
153.821
74.405
74.335
74.150
60.109
60.088
60.066
31.673
31.622
160
155
75
60
30
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

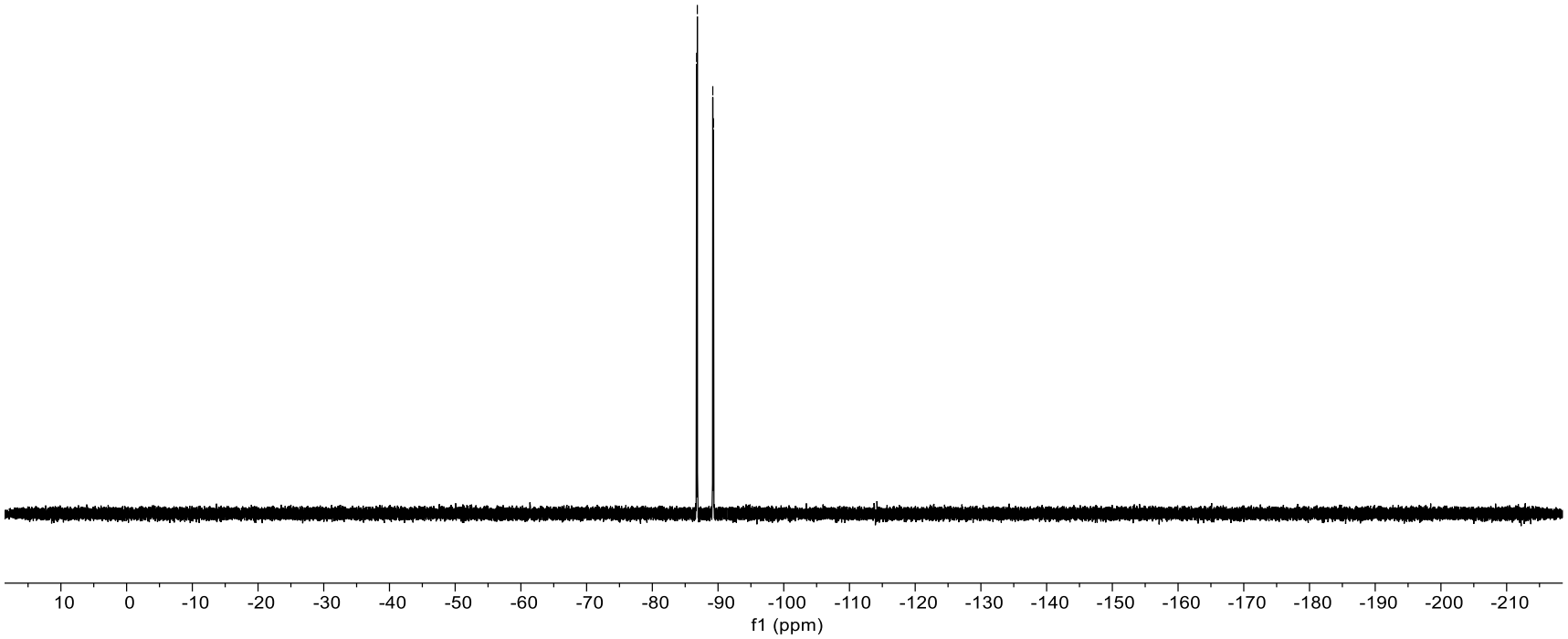

7.317
7.300
7.281
7.260
7.246
7.236
7.172
7.151
7.124
7.105
4.056
4.039
4.022
3.992
3.975
3.957
3.034
3.019
2.333
-0.008
FEN-FG-44-400-2.10.fid
F
F
HO2C
1H NMR of compound 4b (400 MHz, CDCl3)
1.00
1.95
3.33
f1 (ppm)
5.82
4.24
1.00
1.95
3.33
f1 (ppm)

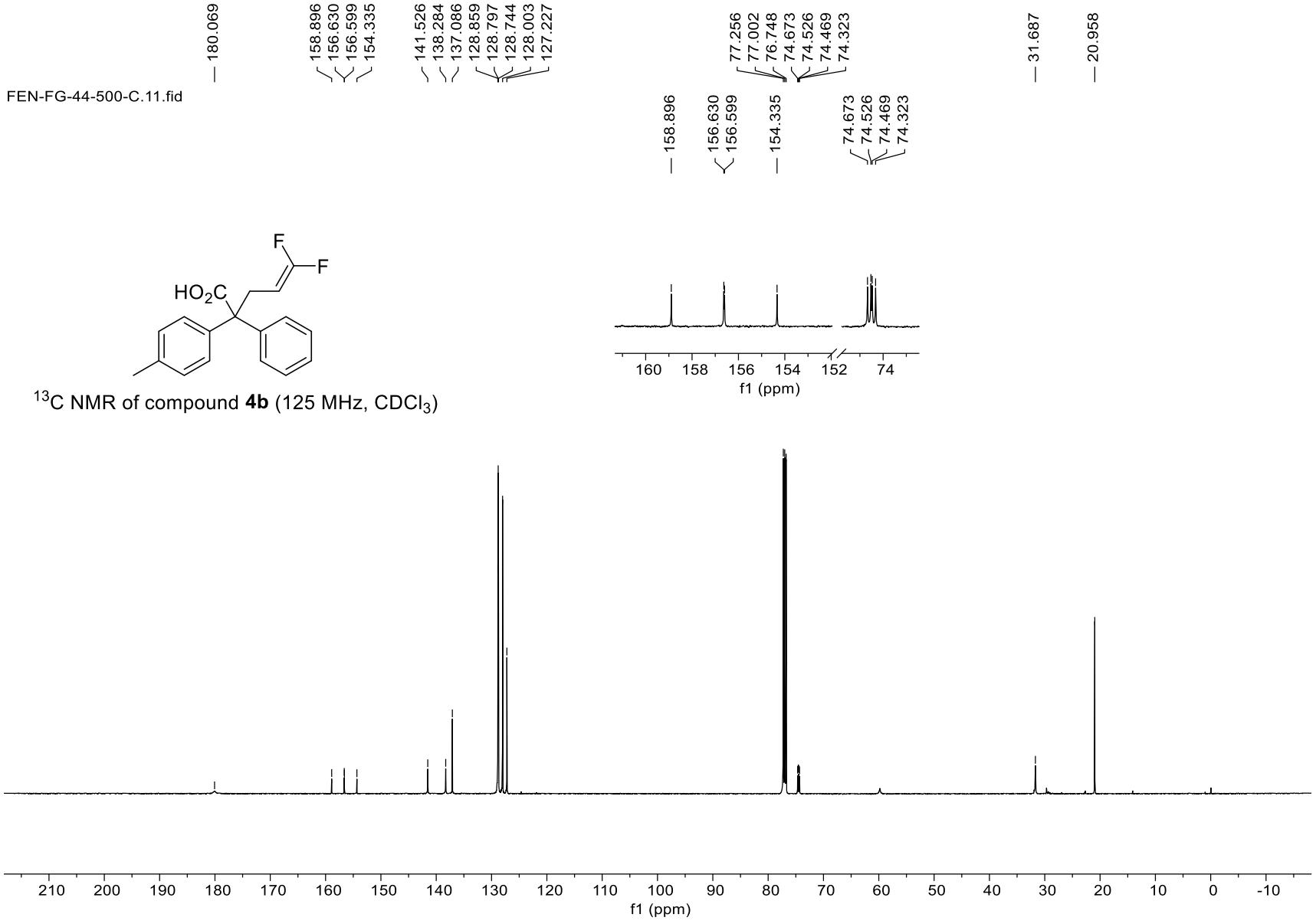
FEN-FG-44-400-2.11.fid

-86.737
-86.847
-89.201
-89.312

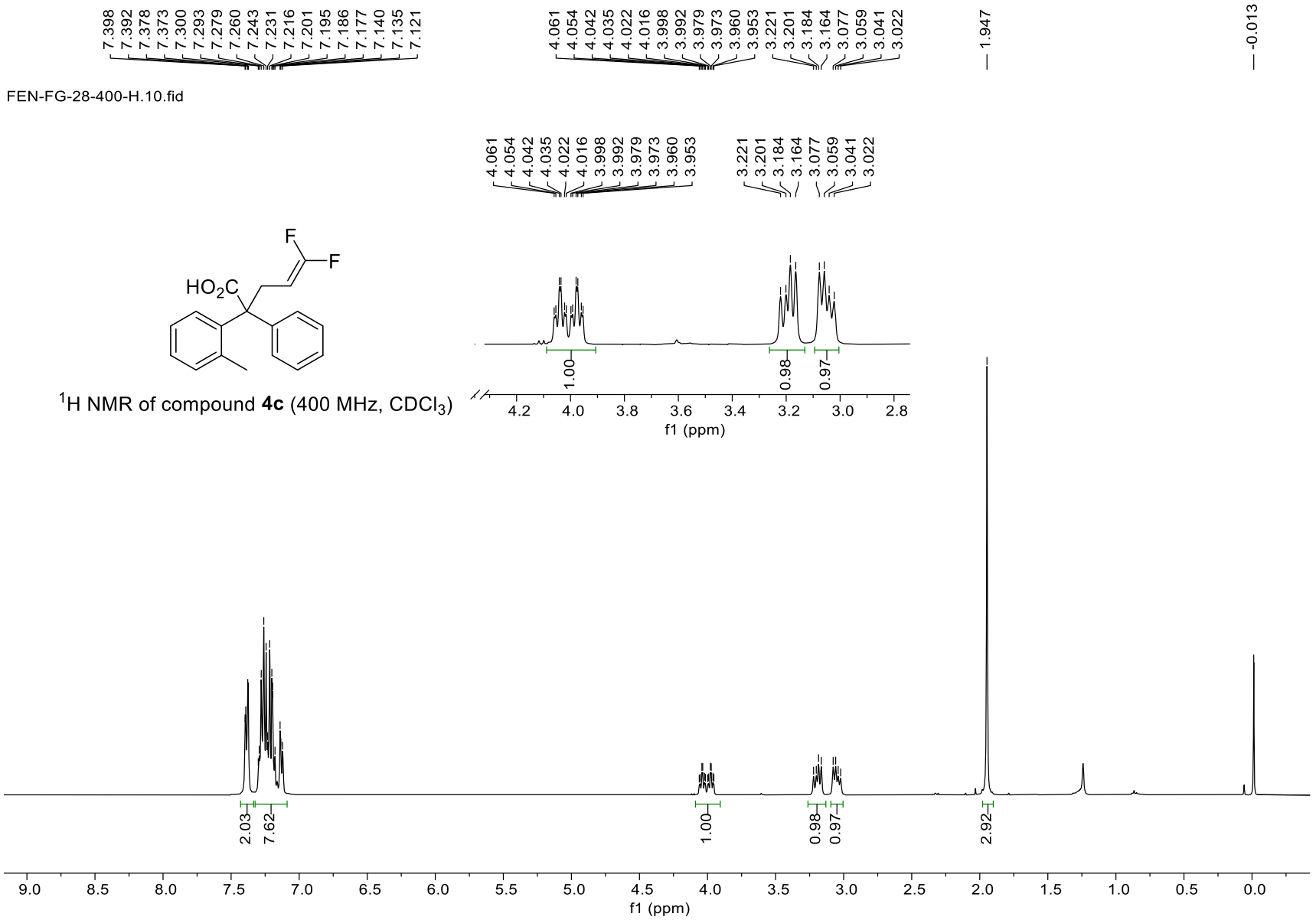


^{19}F NMR of compound **4b** (376 MHz, $CDCl_3$)



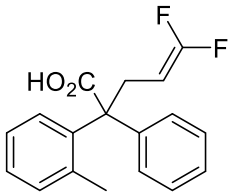


^{13}C NMR of compound **4b** (125 MHz, $CDCl_3$)

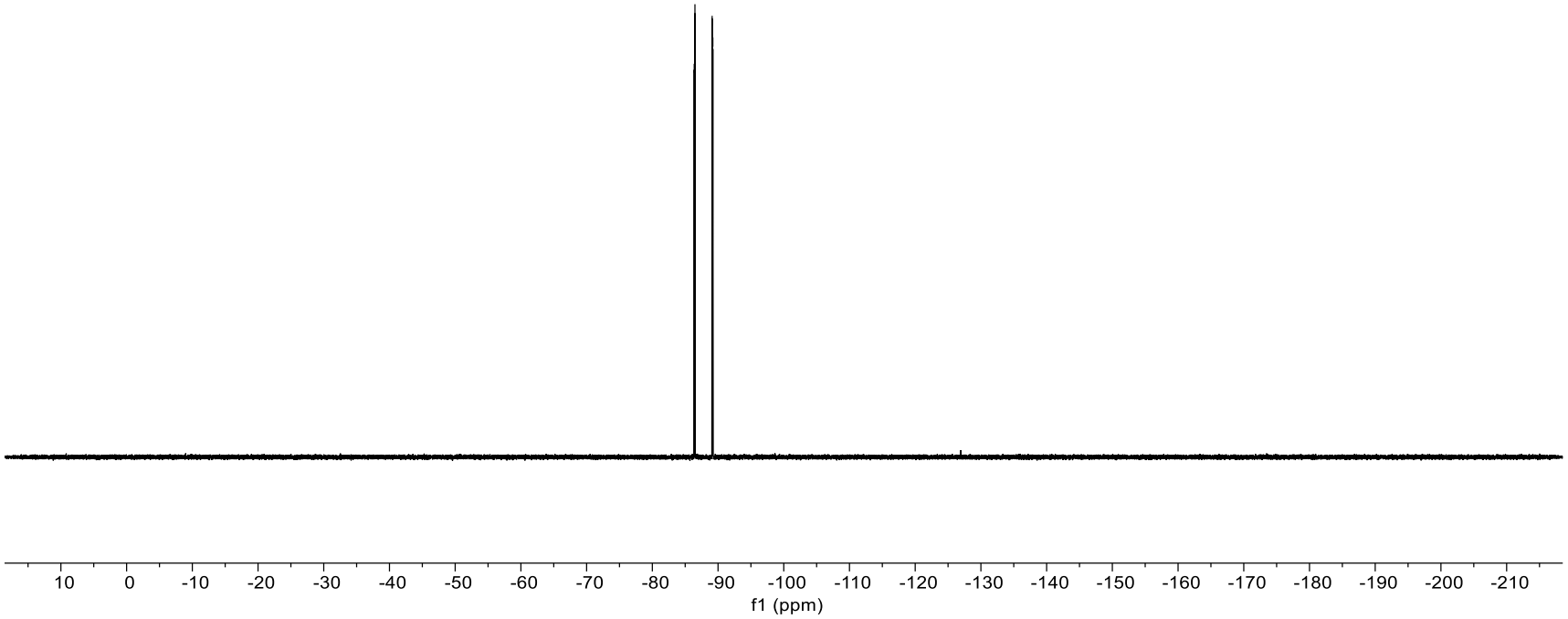


^{1}H NMR of compound **4c** (400 MHz, $CDCl_3$)

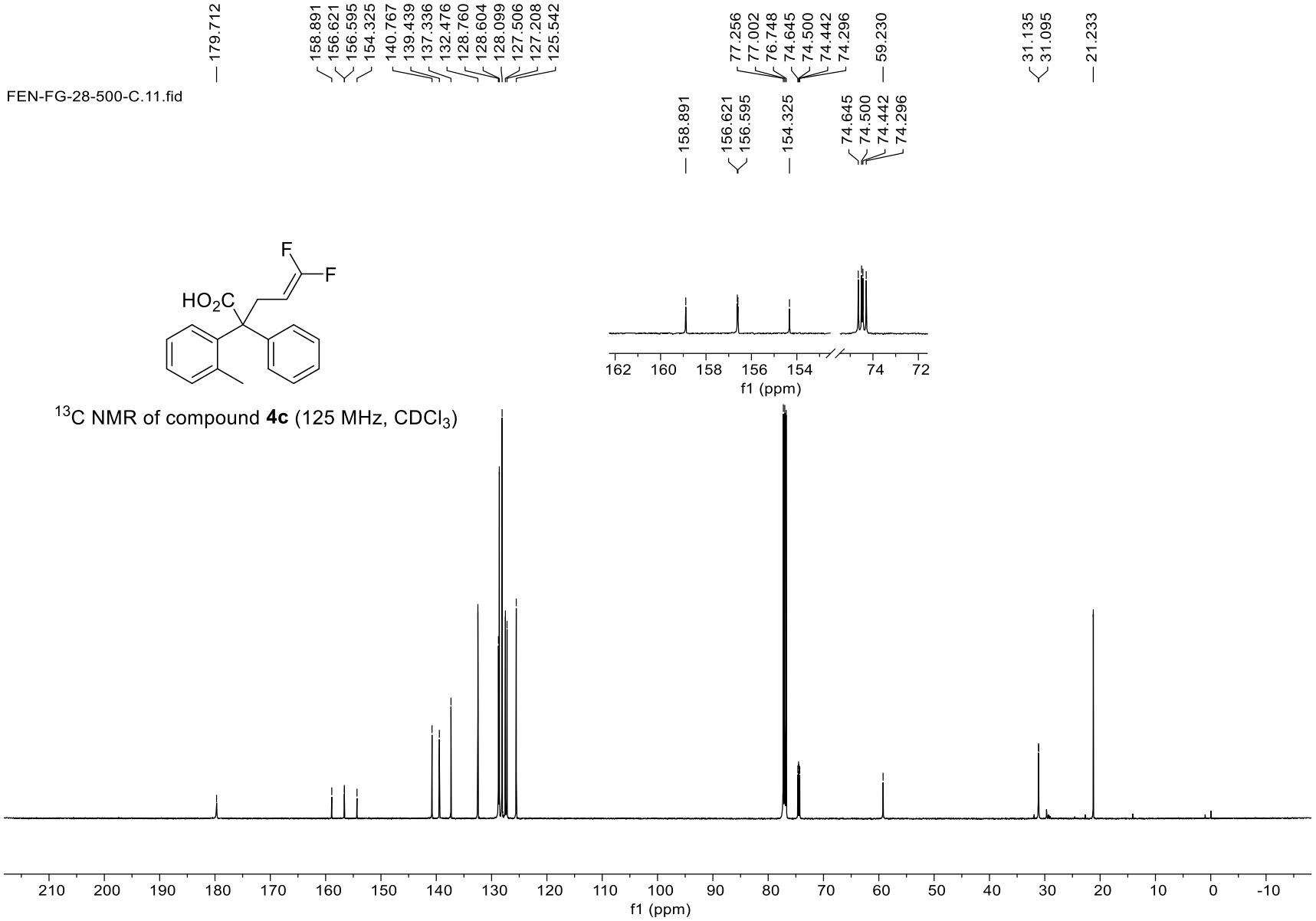
FEN-FG-28-400-H.11.fid



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

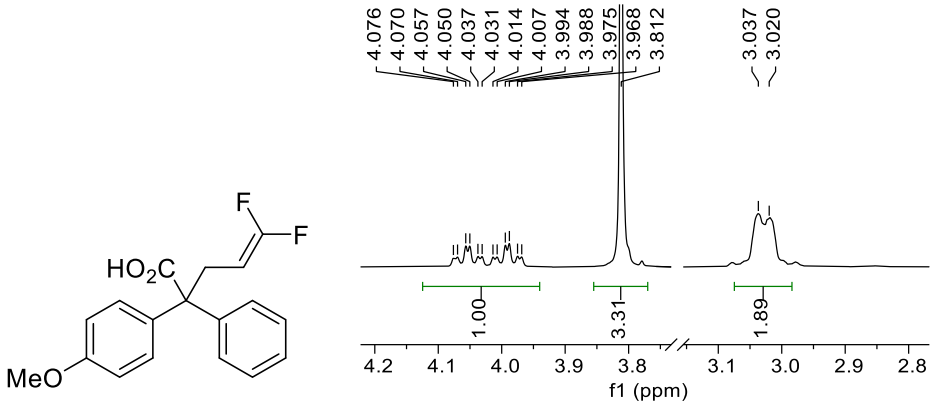


FEN-FG-28-500-C.11.fid

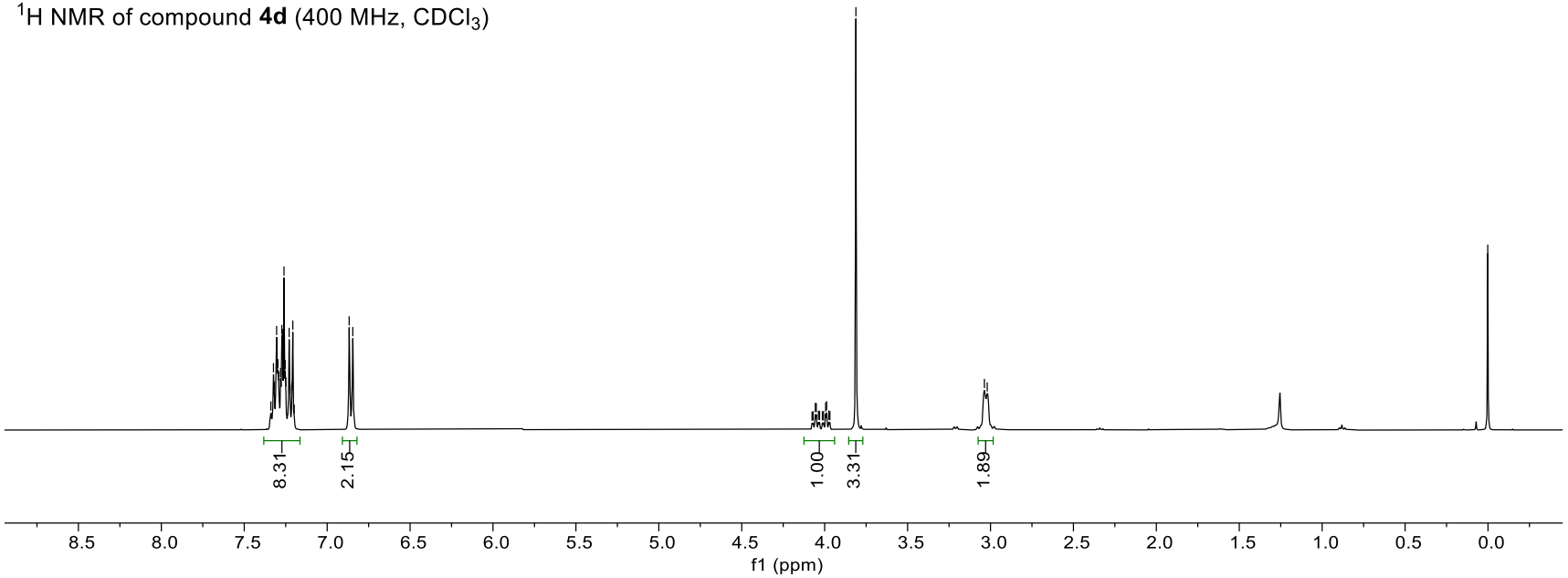


^{13}C NMR of compound **4c** (125 MHz, $CDCl_3$)

FEN-FG-62-400-2.10.fid

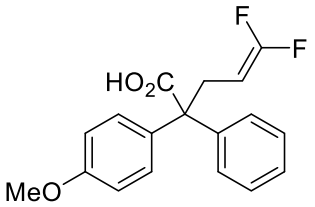


^{1}H NMR of compound **4d** (400 MHz, $CDCl_3$)

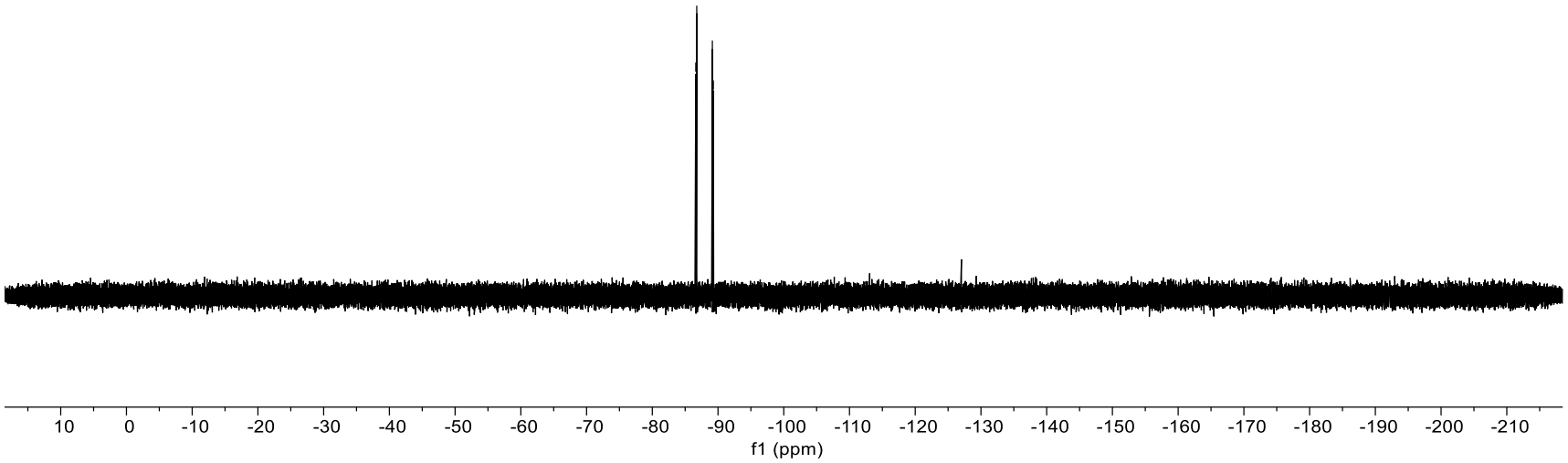


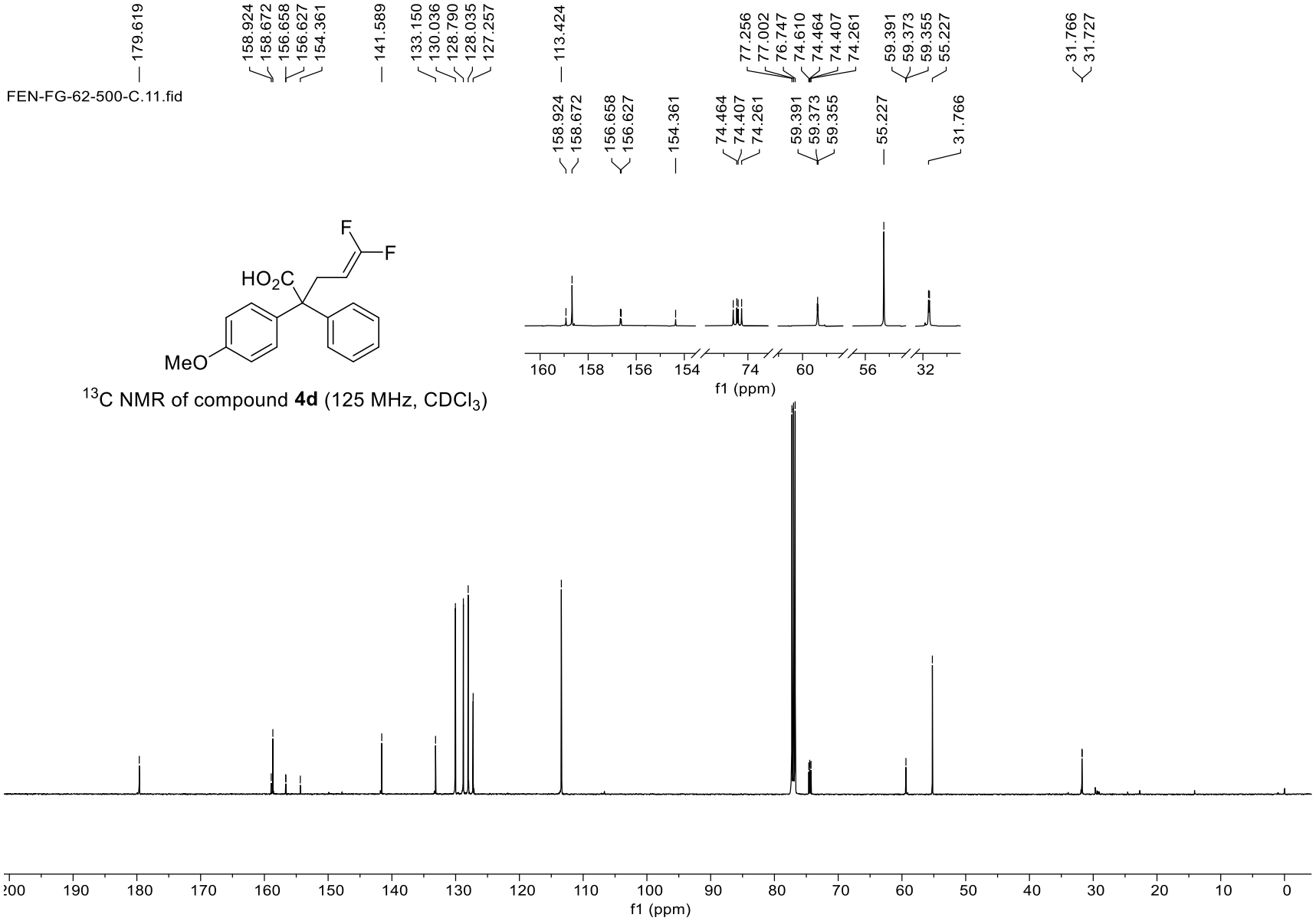
-86.613
-86.760
-89.139
-89.286

FEN-FG-62-300-F.11.fid

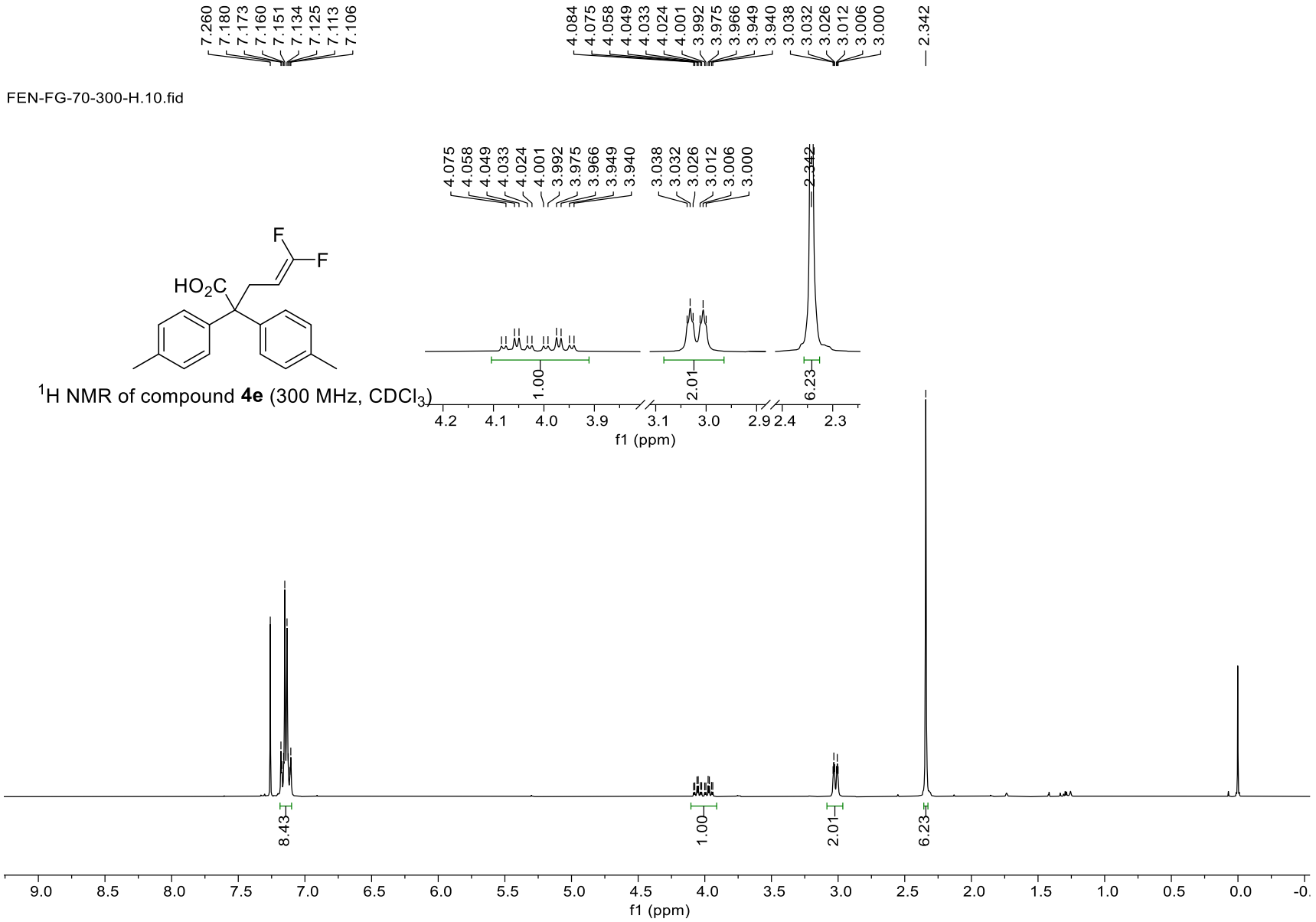


^{19}F NMR of compound **4d** (282 MHz, $CDCl_3$)





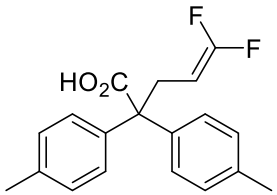
^{13}C NMR of compound **4d** (125 MHz, $CDCl_3$)



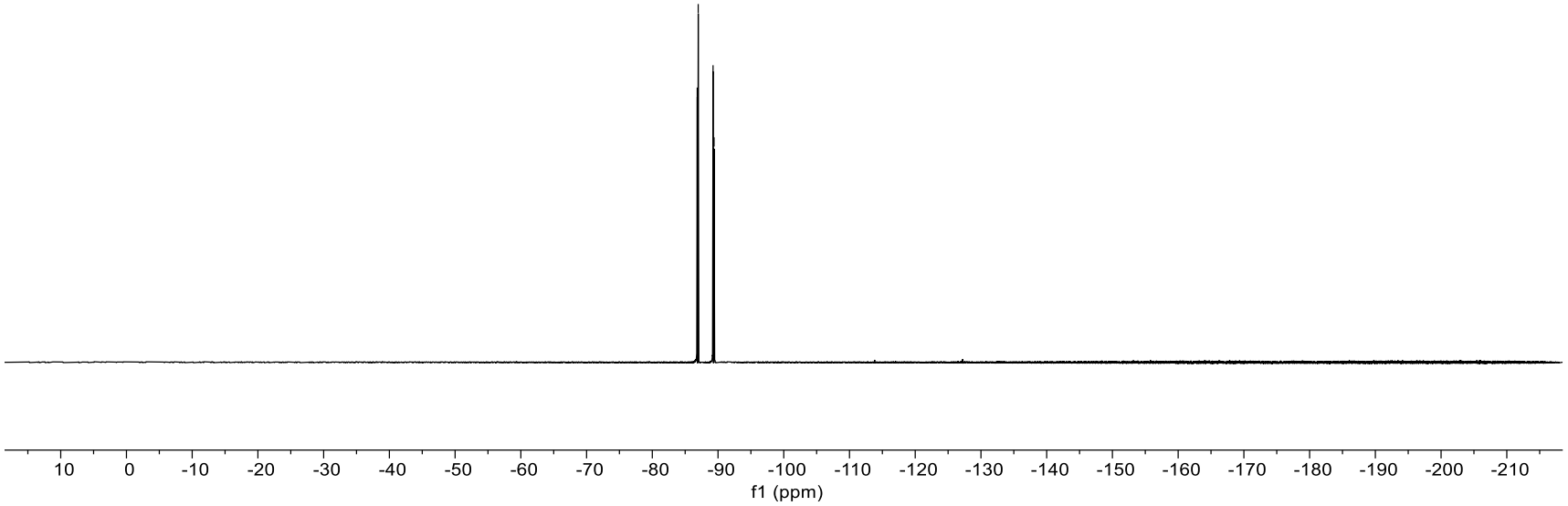
^{1}H NMR of compound **4e** (300 MHz, $CDCl_3$)

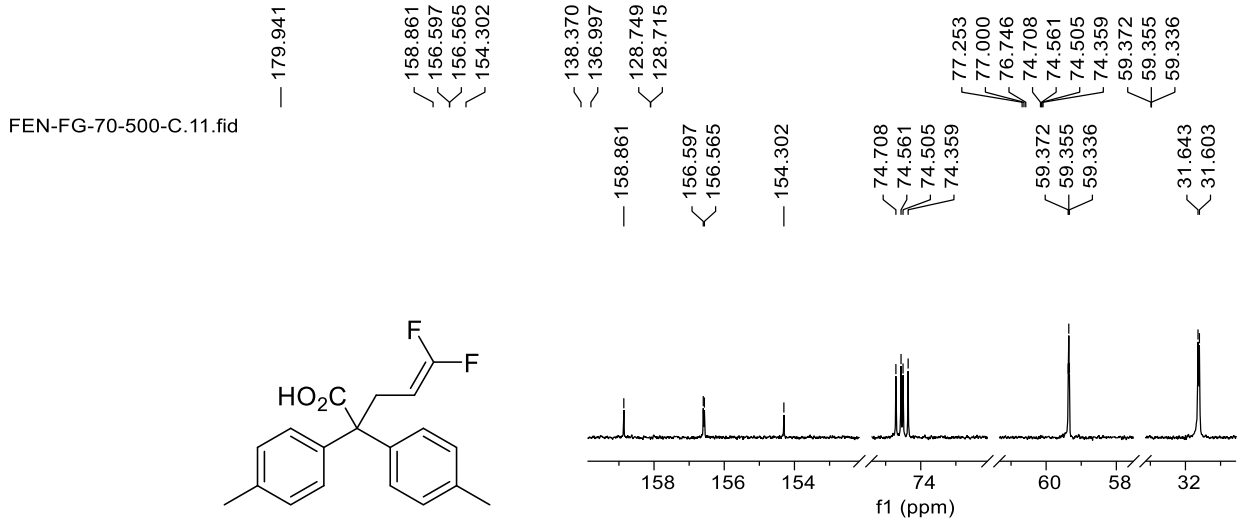
FEN-FG-70-300-F.11.fid

-86.834
-86.986
-89.243
-89.394

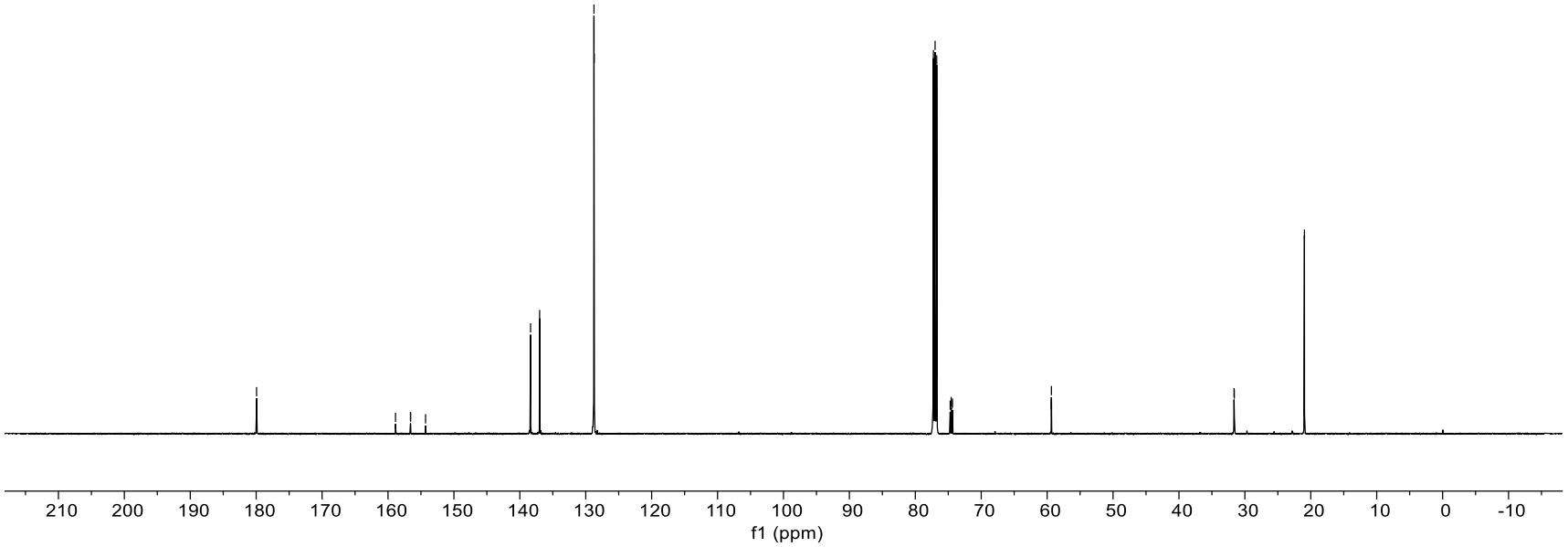


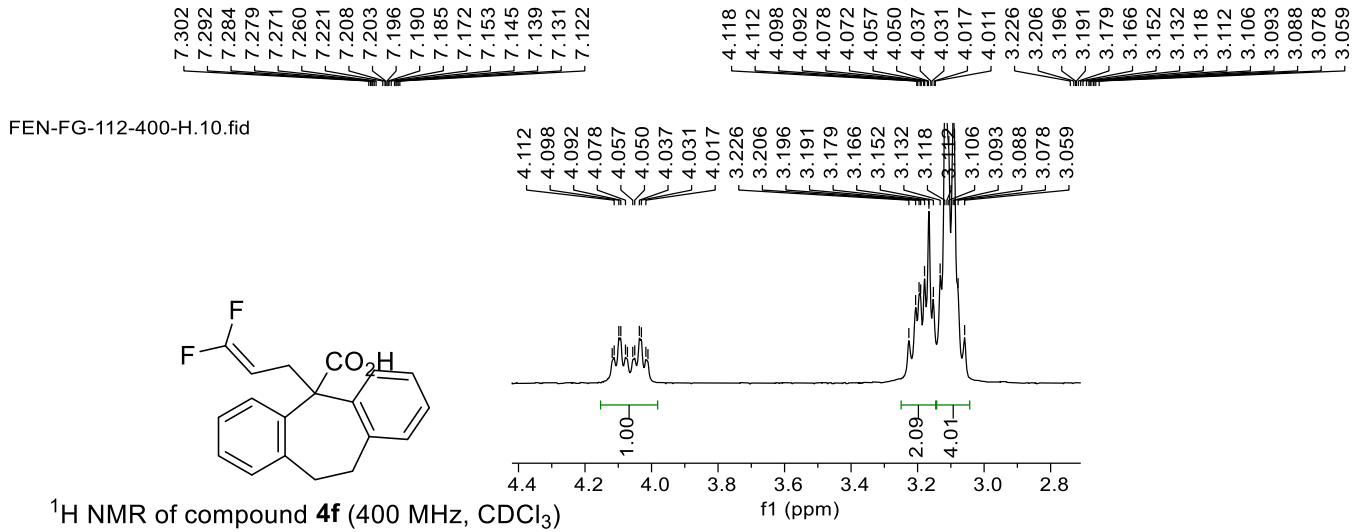
^{19}F NMR of compound **4e** (282 MHz, $CDCl_3$)



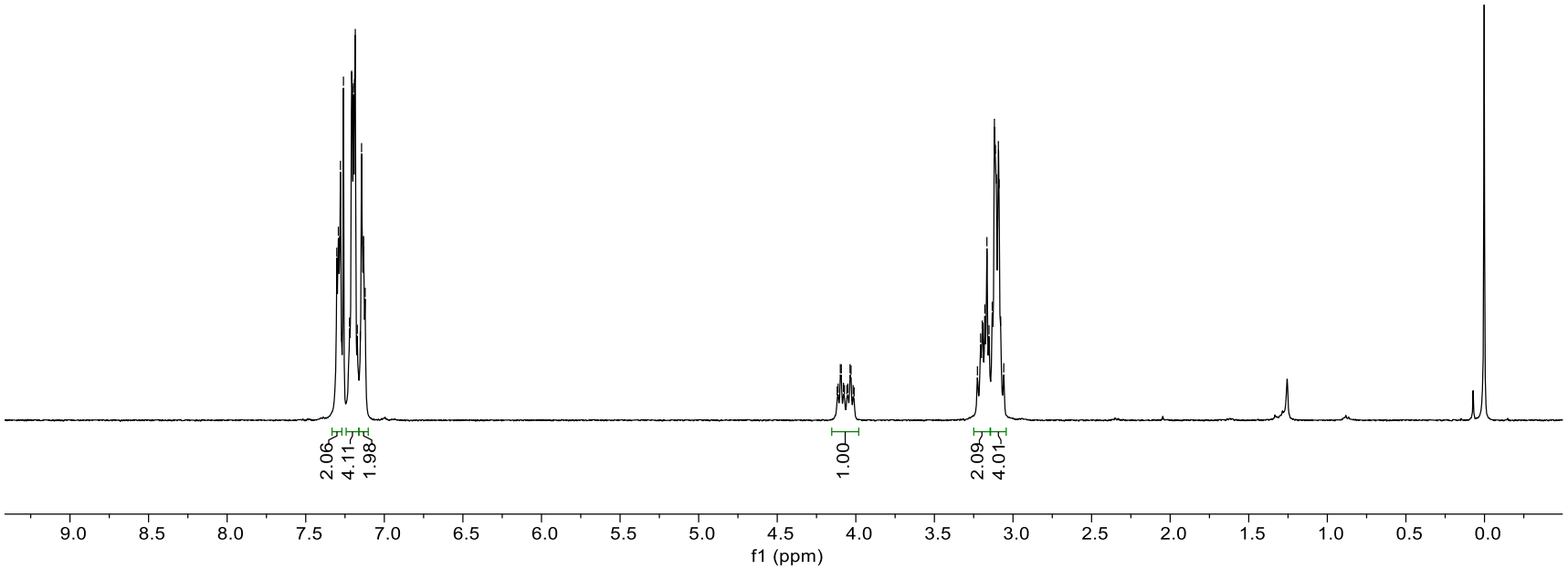


^{13}C NMR of compound **4e** (125 MHz, $CDCl_3$)



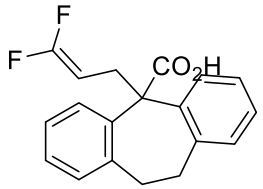


^{1}H NMR of compound **4f** (400 MHz, $CDCl_3$)

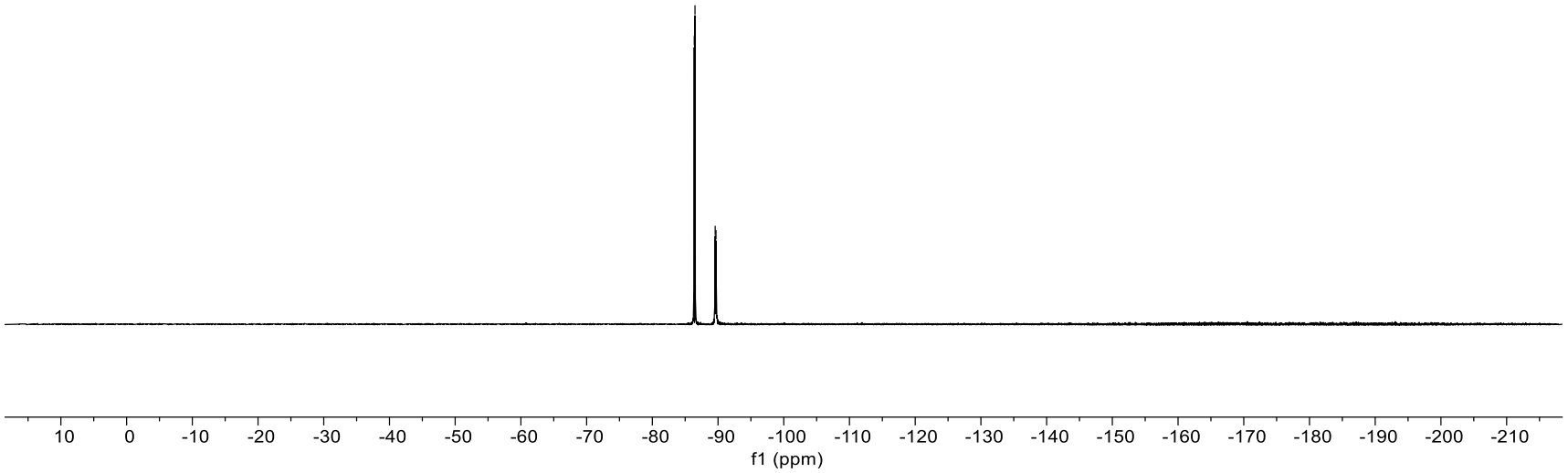


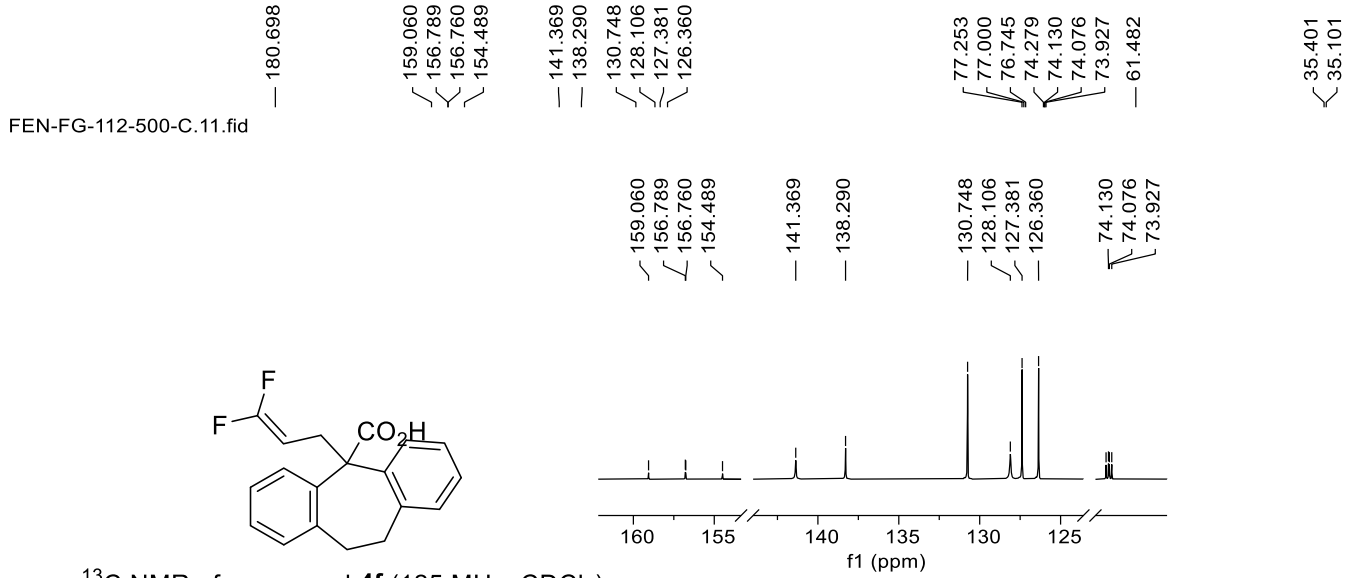
FEN-FG-112-400-H.11.fid

-86.379
-86.493
-89.564
-89.688

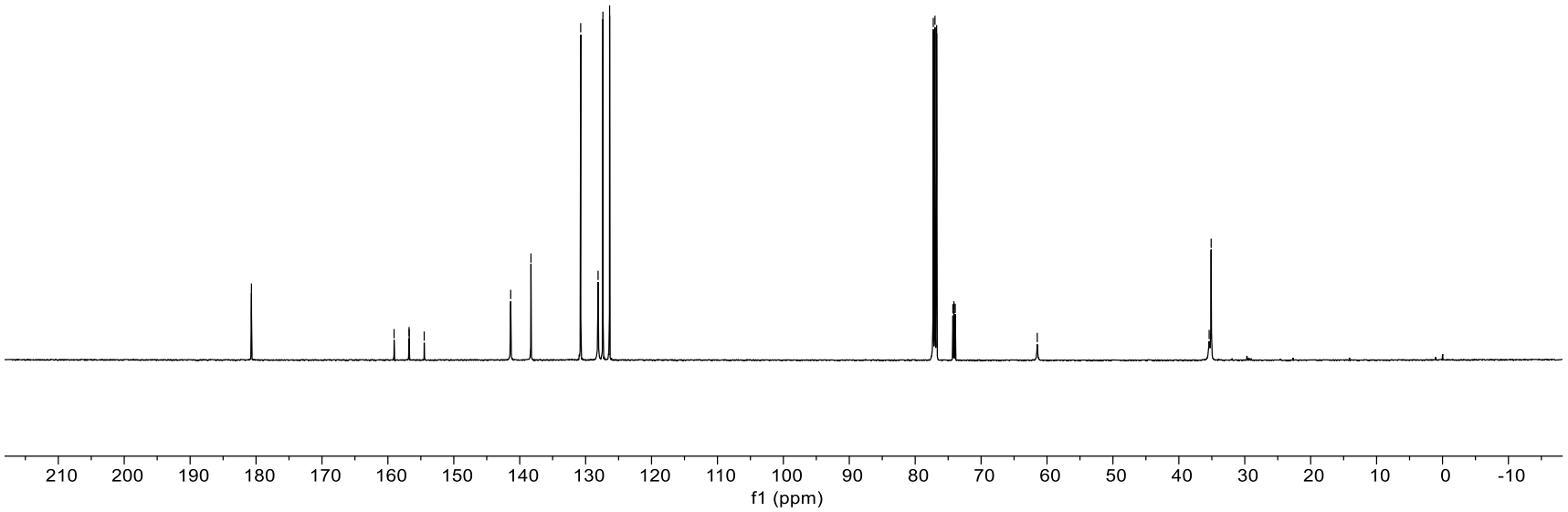


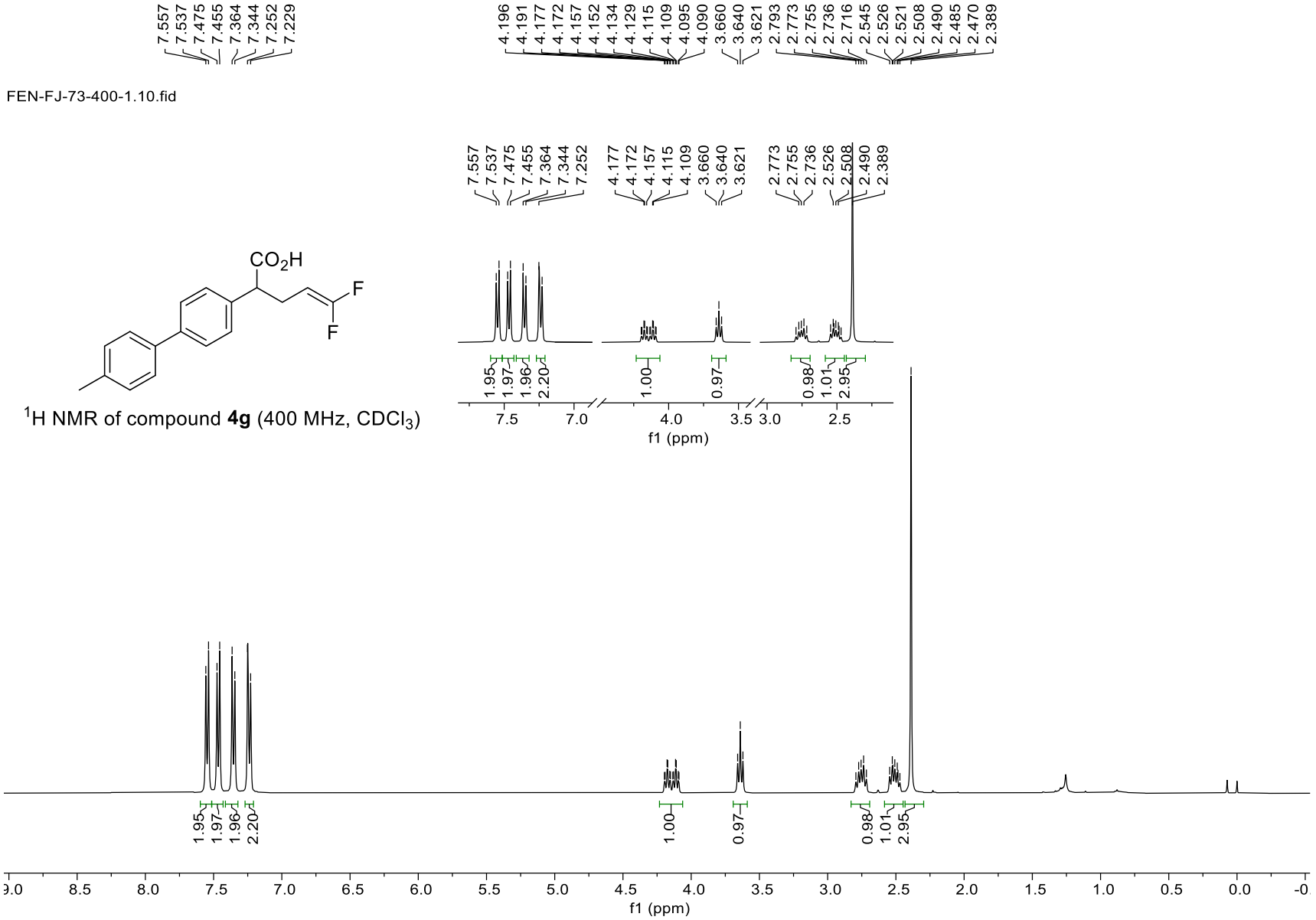
^{19}F NMR of compound **4f** (376 MHz, $CDCl_3$)





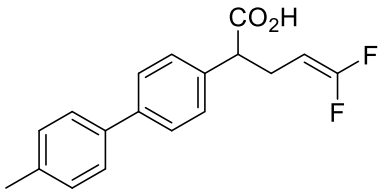
^{13}C NMR of compound **4f** (125 MHz, $CDCl_3$)



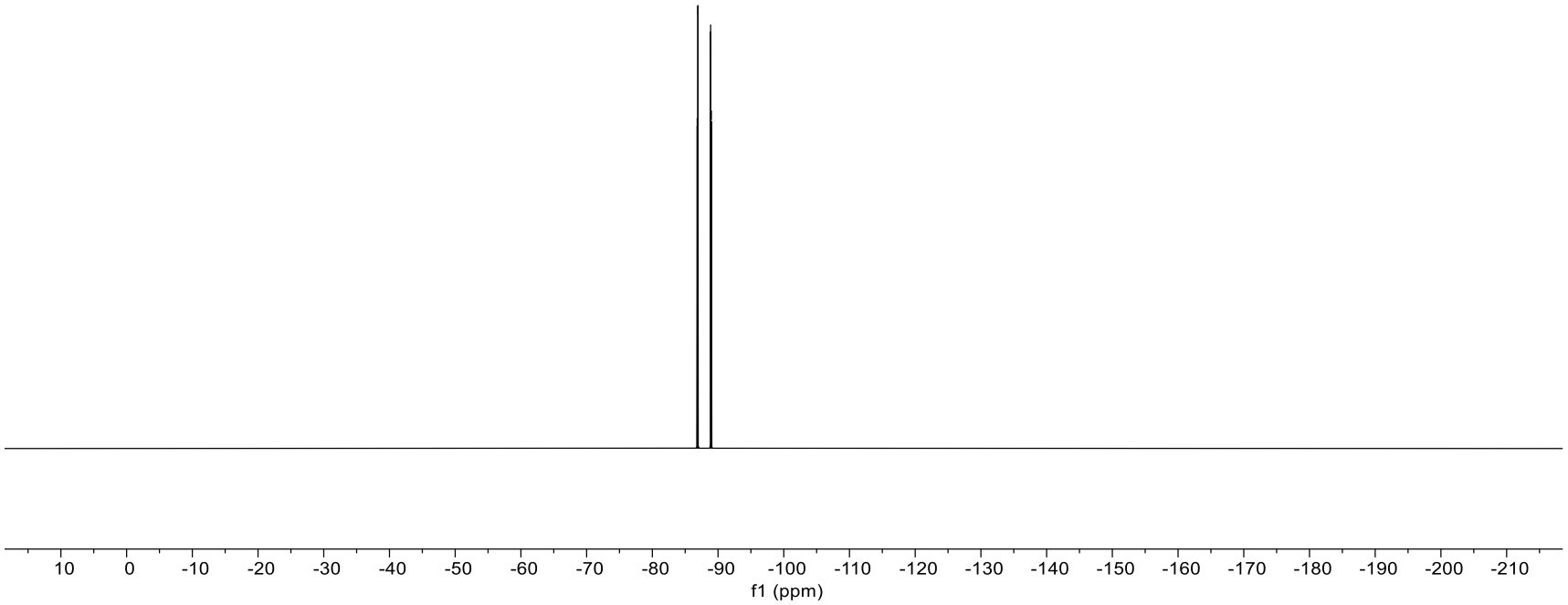

7.557
7.537
7.475
7.455
7.364
7.344
7.252
7.229
4.196
4.191
4.177
4.172
4.157
4.152
4.134
4.129
4.115
4.109
4.095
4.090
3.660
3.640
3.621
2.793
2.773
2.755
2.736
2.716
2.545
2.526
2.521
2.508
2.490
2.485
2.470
2.389
FEN-FJ-73-400-1.10.fid
CO2H
F
F
1H NMR of compound 4g (400 MHz, CDCl3)
1.95
1.97
1.96
2.20
1.00
0.97
0.98
1.01
2.95
f1 (ppm)

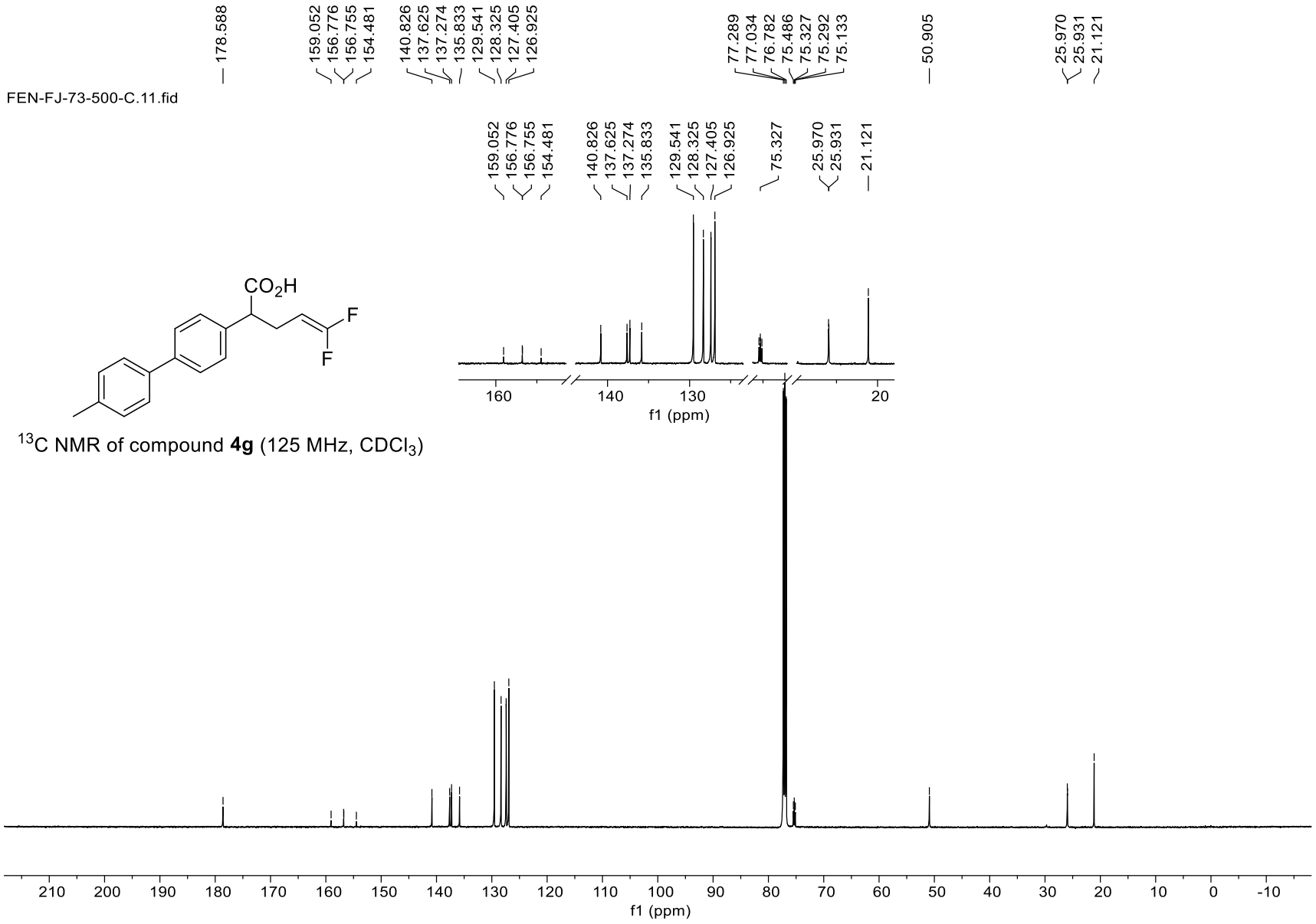
-86.830
-86.942
-88.872
-88.984

FEN-FJ-73-400-1.11.fid

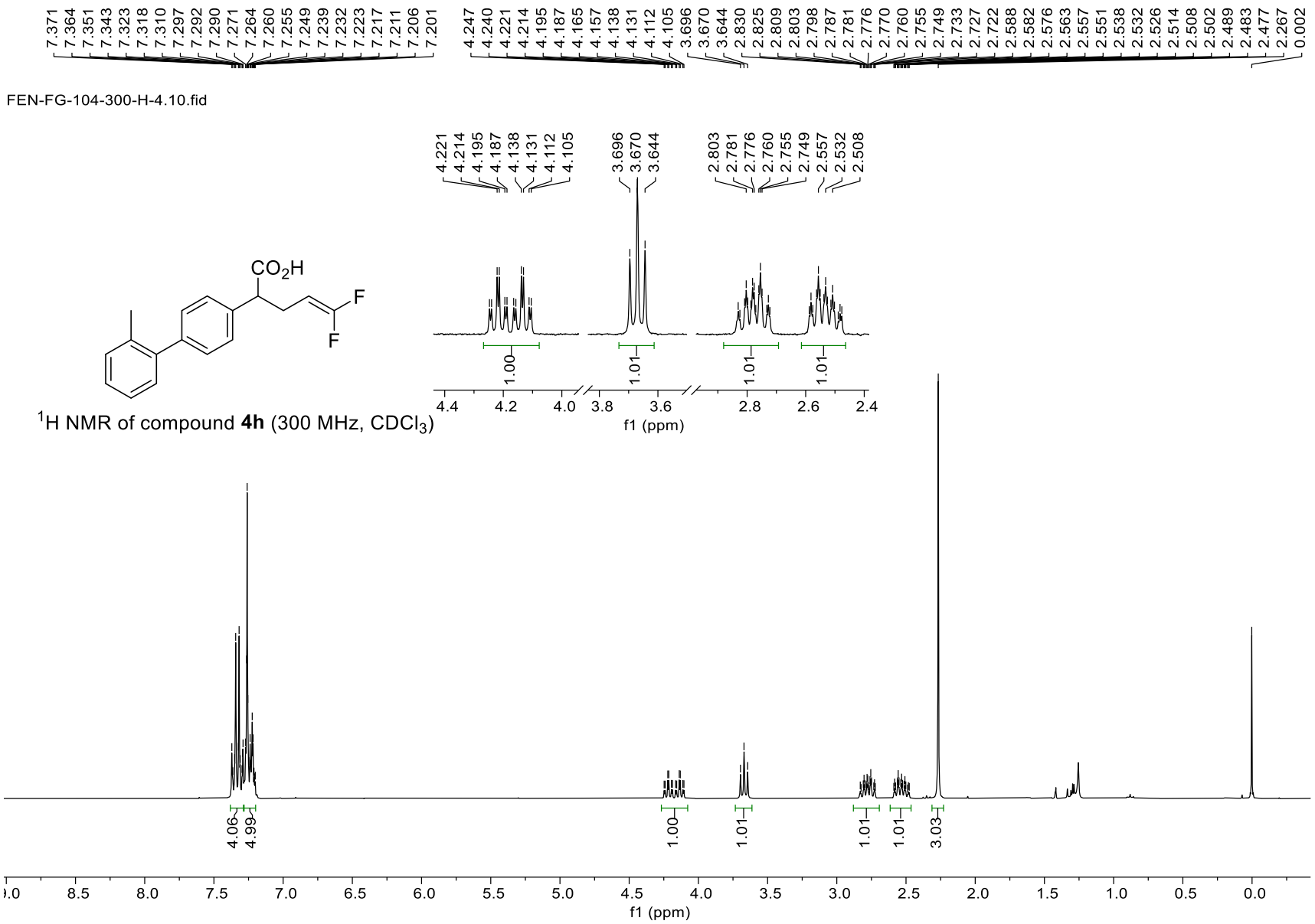


^{19}F NMR of compound **4g** (376 MHz, $CDCl_3$)





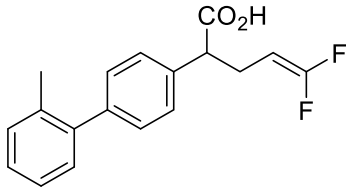
^{13}C NMR of compound **4g** (125 MHz, $CDCl_3$)



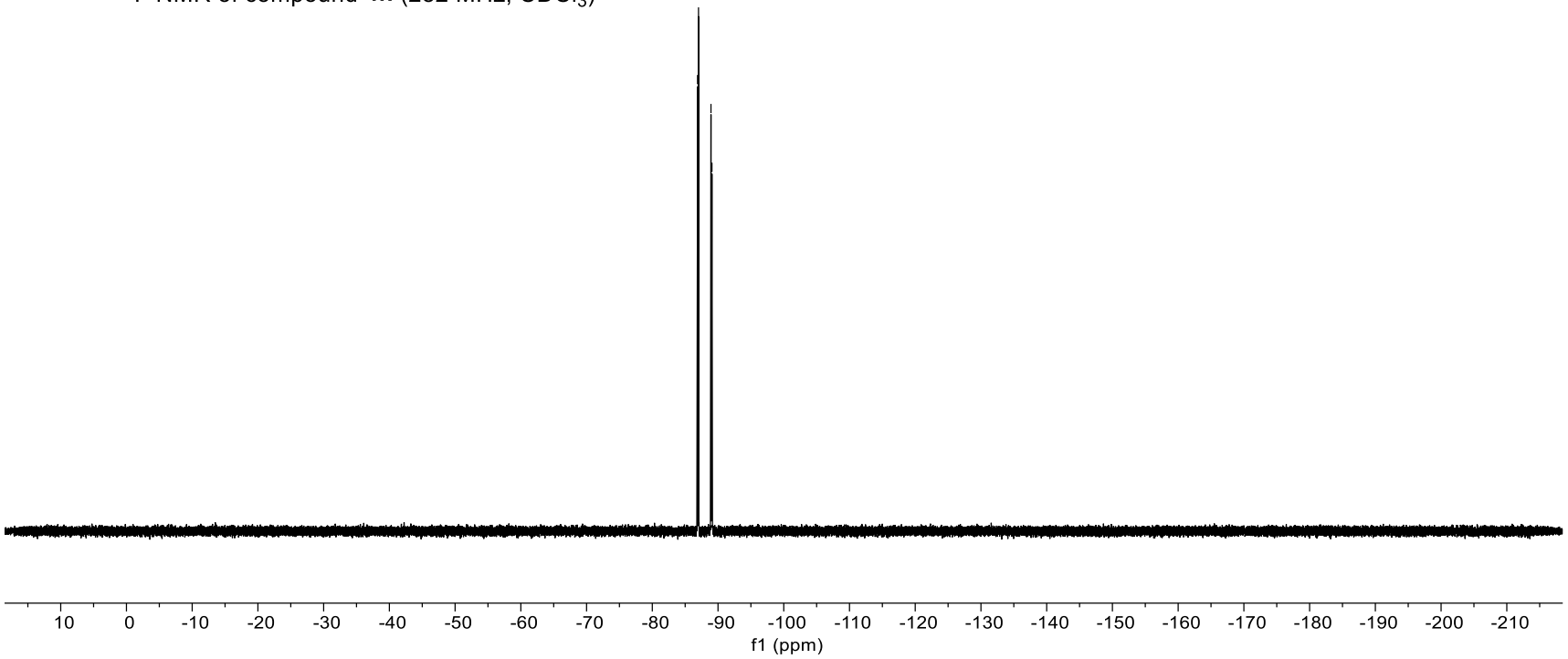
^{1}H NMR of compound **4h** (300 MHz, $CDCl_3$)

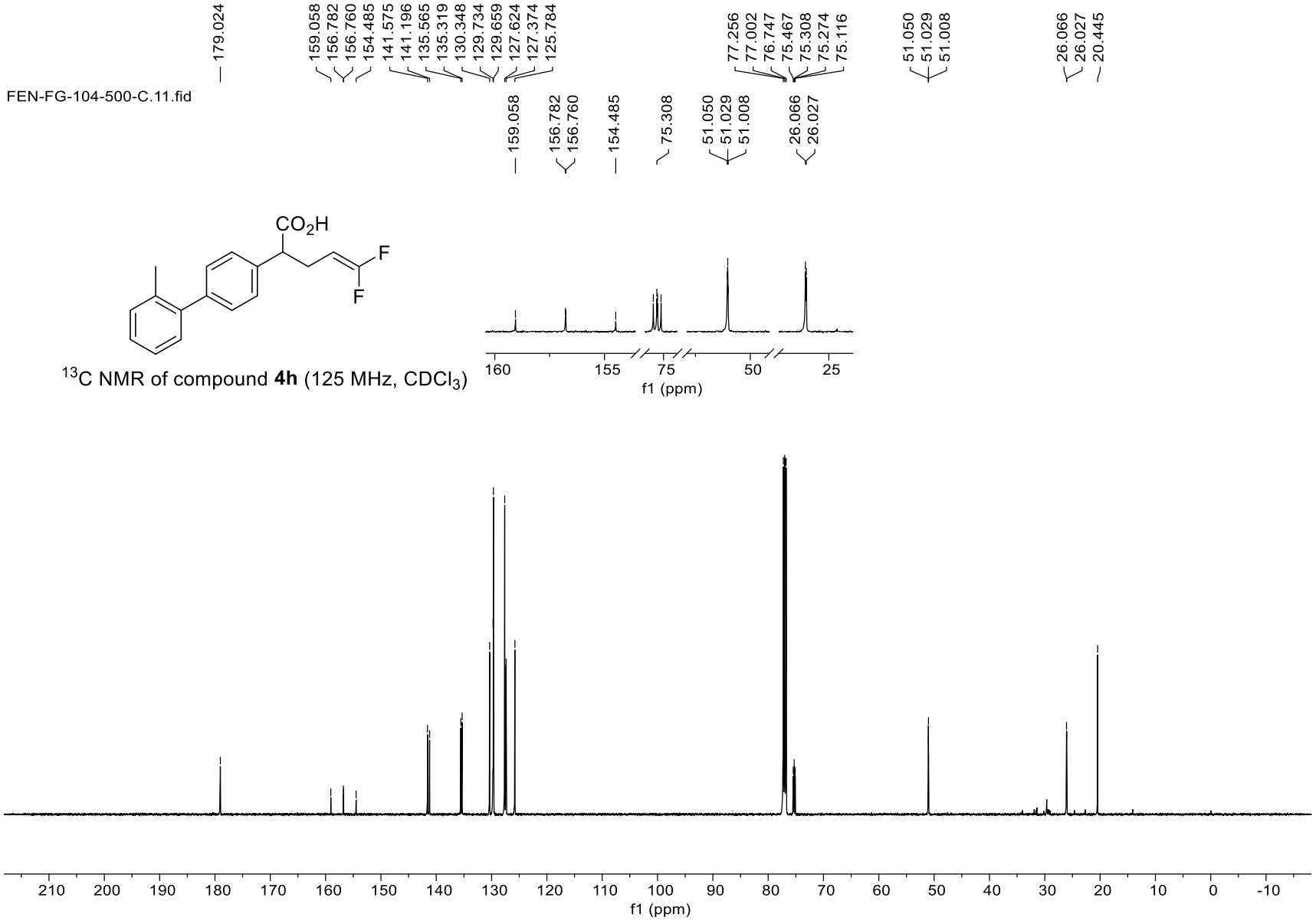
FEN-FG-104-300-F.11.fid

-86.879
-87.029
-88.927
-89.076

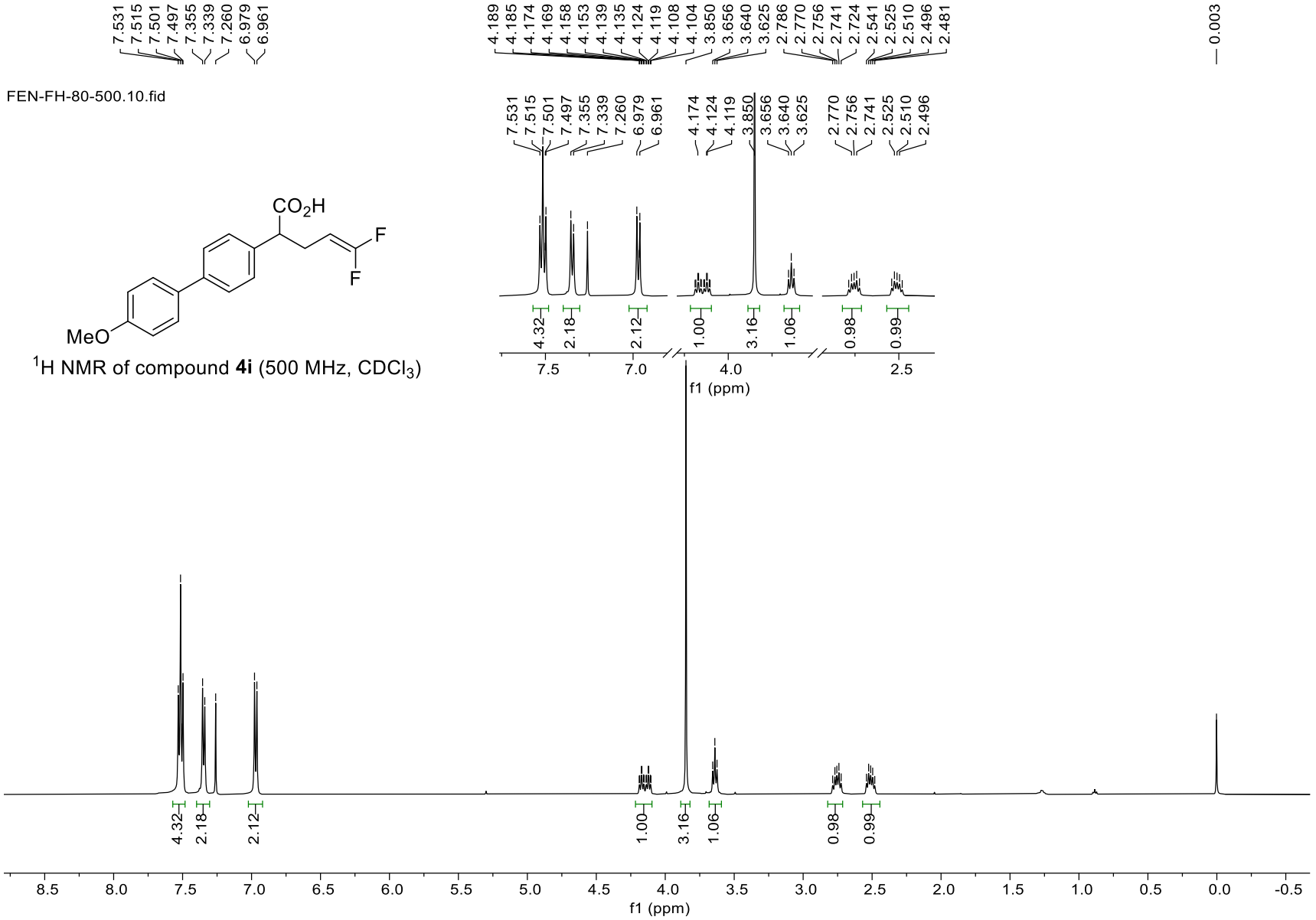


^{19}F NMR of compound **4h** (282 MHz, $CDCl_3$)





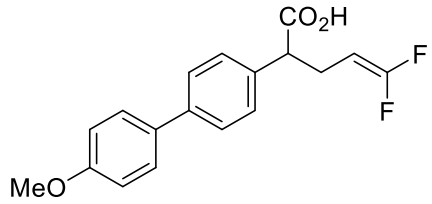
^{13}C NMR of compound **4h** (125 MHz, $CDCl_3$)



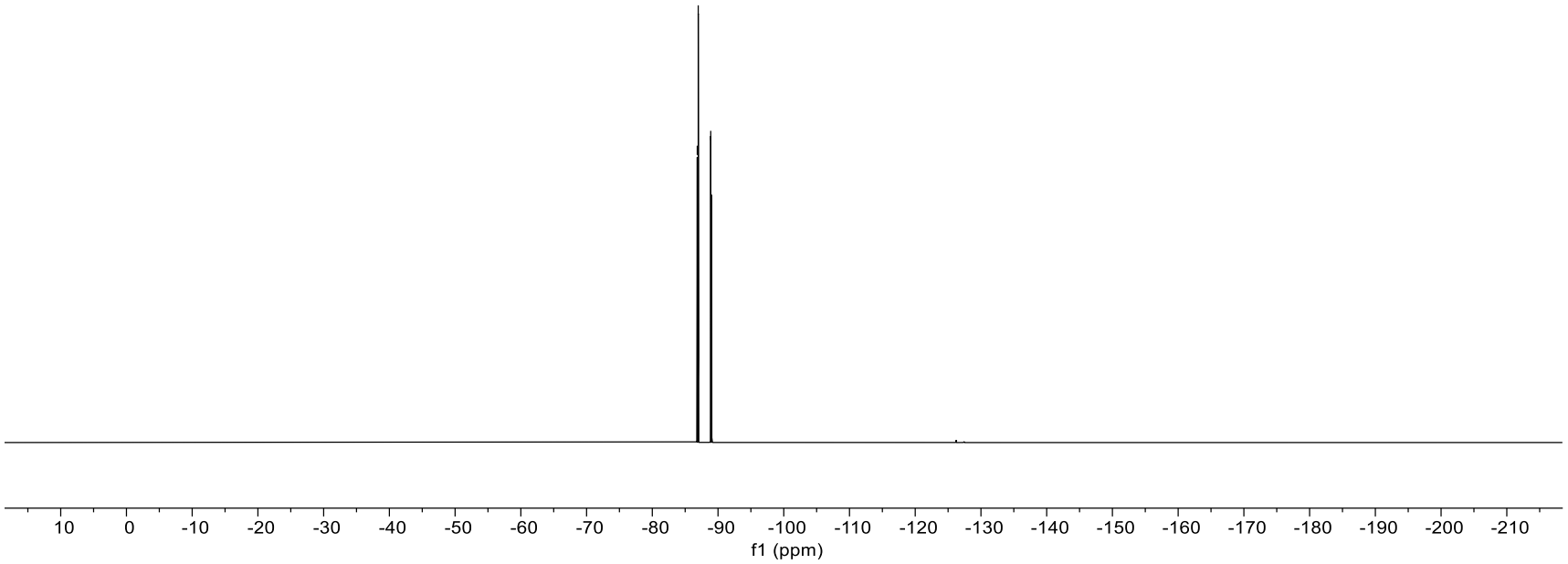
^{1}H NMR of compound **4i** (500 MHz, $CDCl_3$)

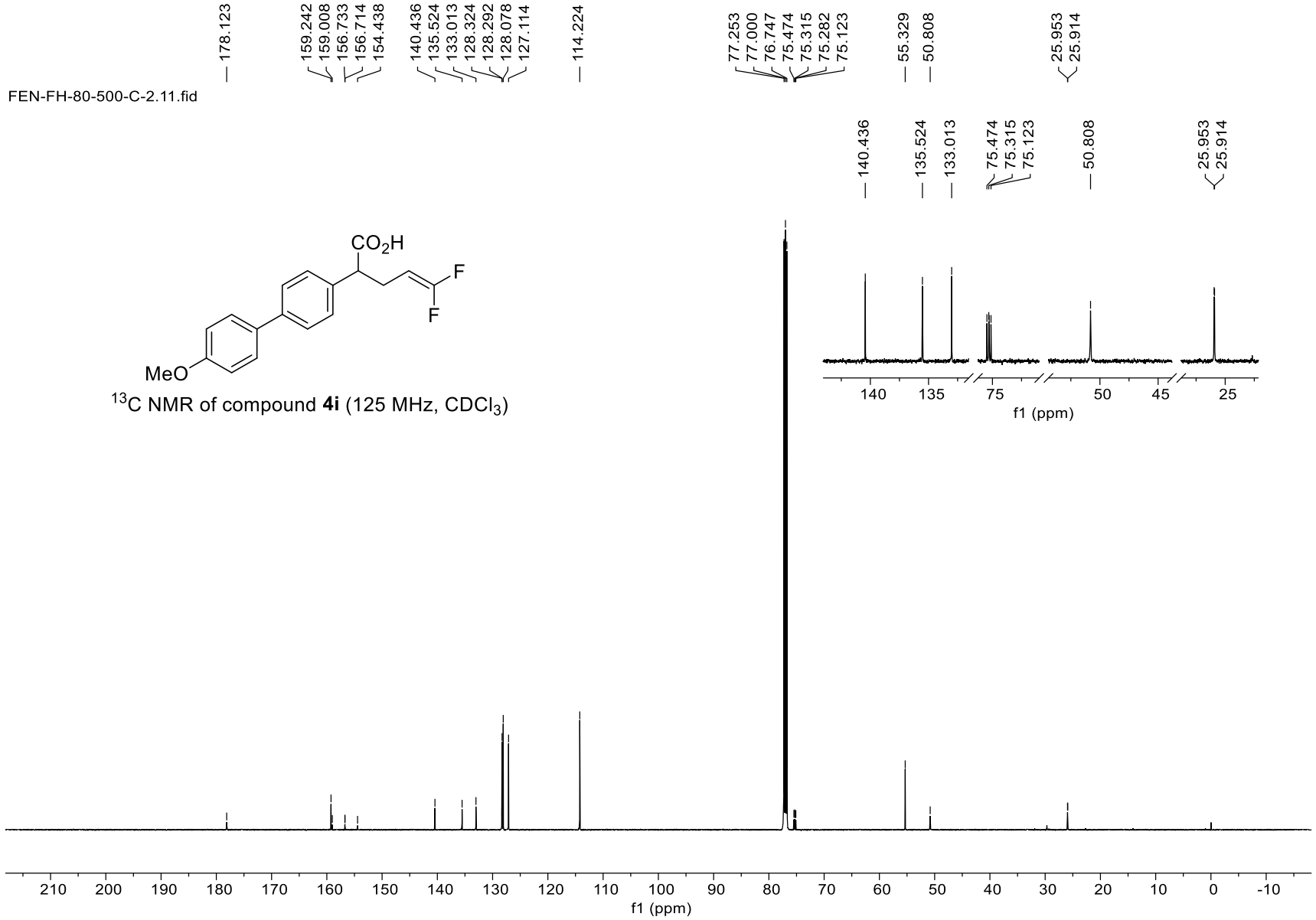
FEN-FH-80-300-F.11.fid

-86.840
-86.989
-88.888
-89.038

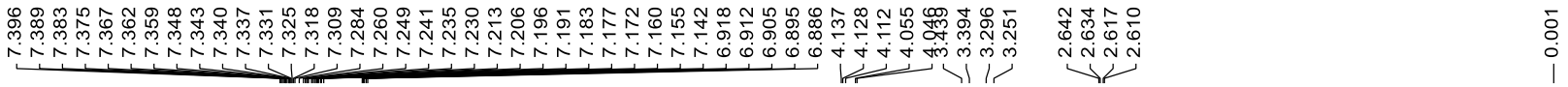


^{19}F NMR of compound **4i** (282 MHz, $CDCl_3$)

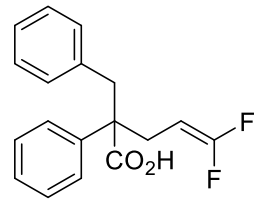




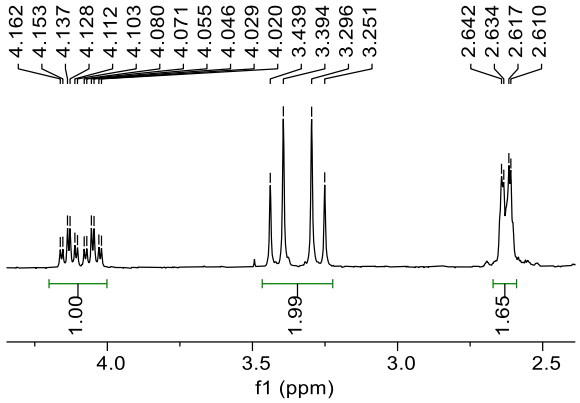
^{13}C NMR of compound **4i** (125 MHz, $CDCl_3$)

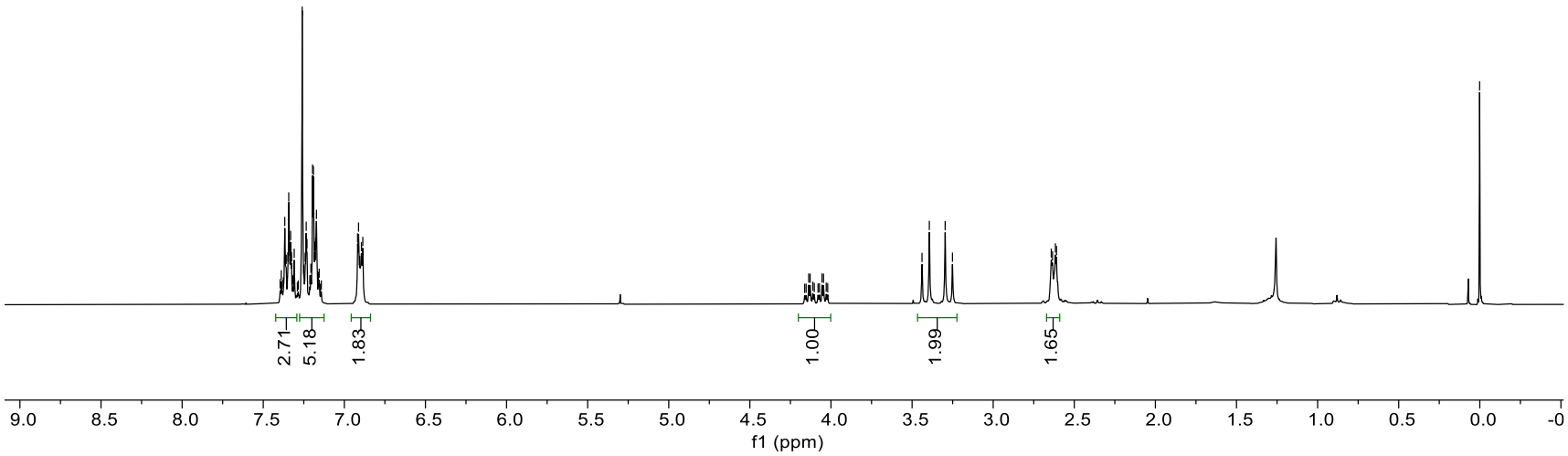


FEN-FH-48-300-H.11.fid



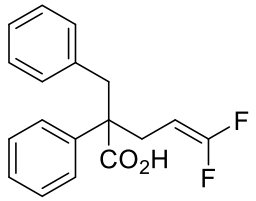
^{1}H NMR of compound **4j** (300 MHz, $CDCl_3$)



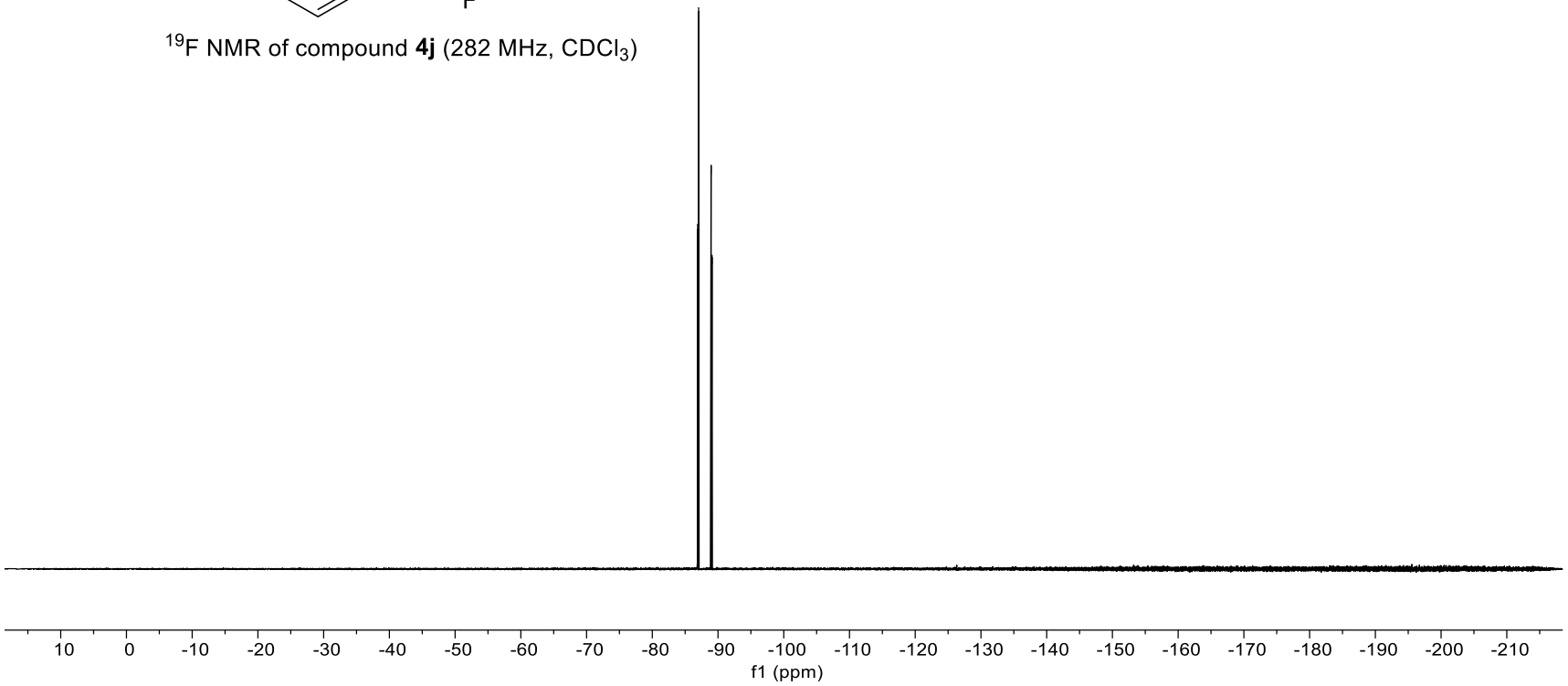


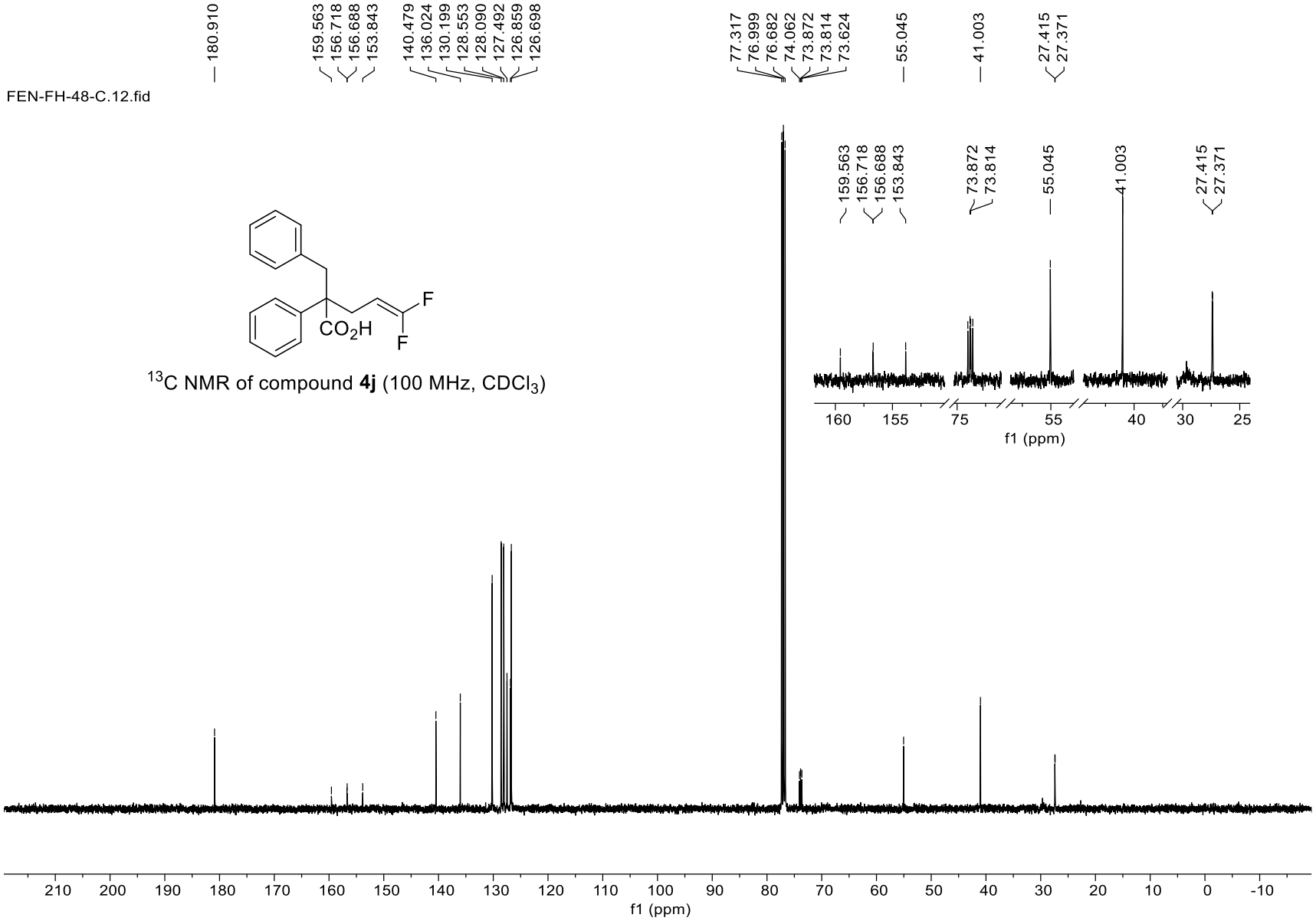
FEN-FH-48-F-300-2.11.fid

-86.898
-87.048
-88.940
-89.090

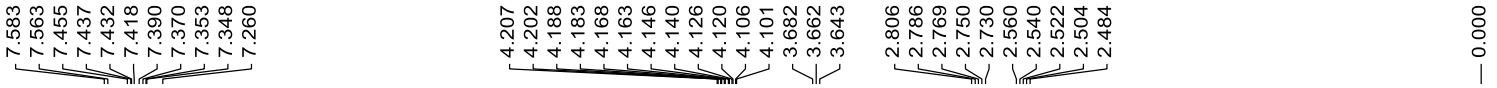


^{19}F NMR of compound **4j** (282 MHz, $CDCl_3$)

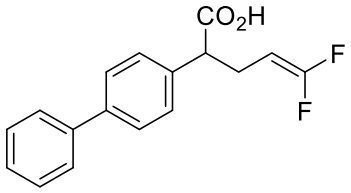




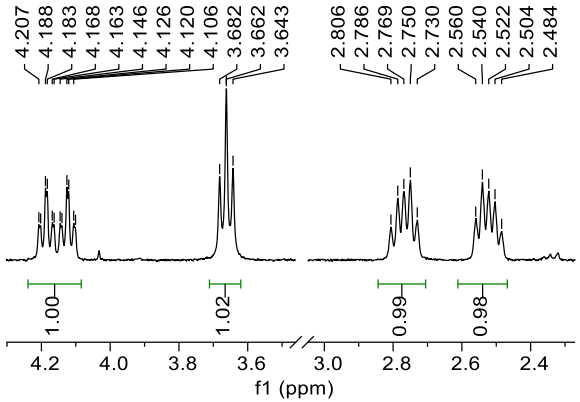
^{13}C NMR of compound **4j** (100 MHz, $CDCl_3$)

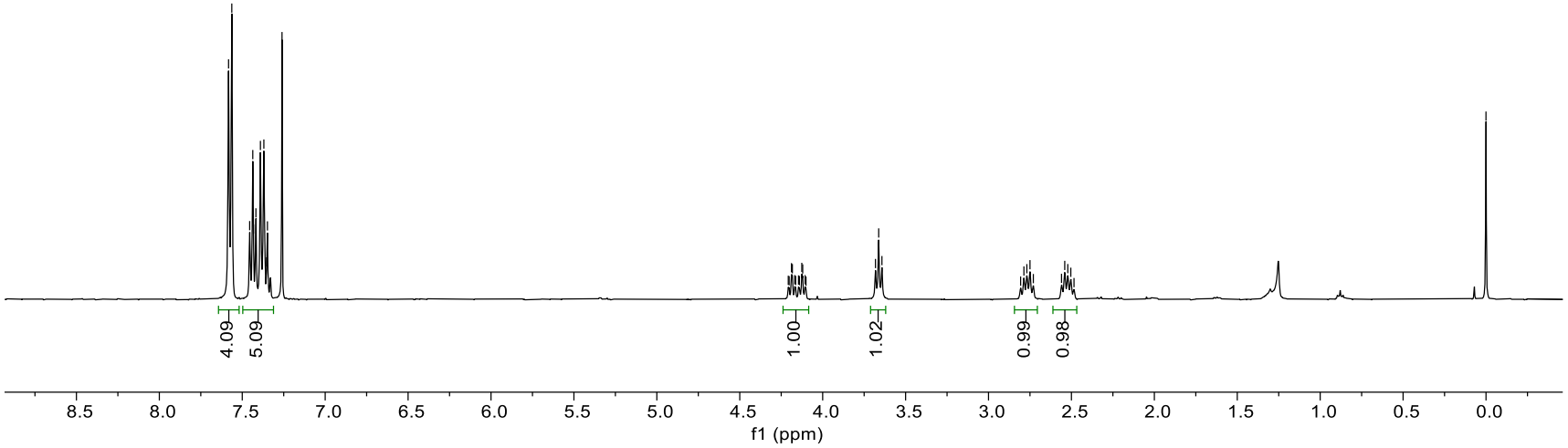


FEN-FJ-69-400-H.10.fid



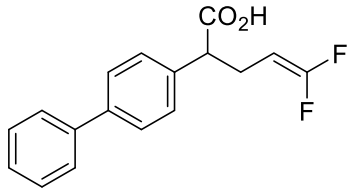
^{1}H NMR of compound **4k** (400 MHz, $CDCl_3$)



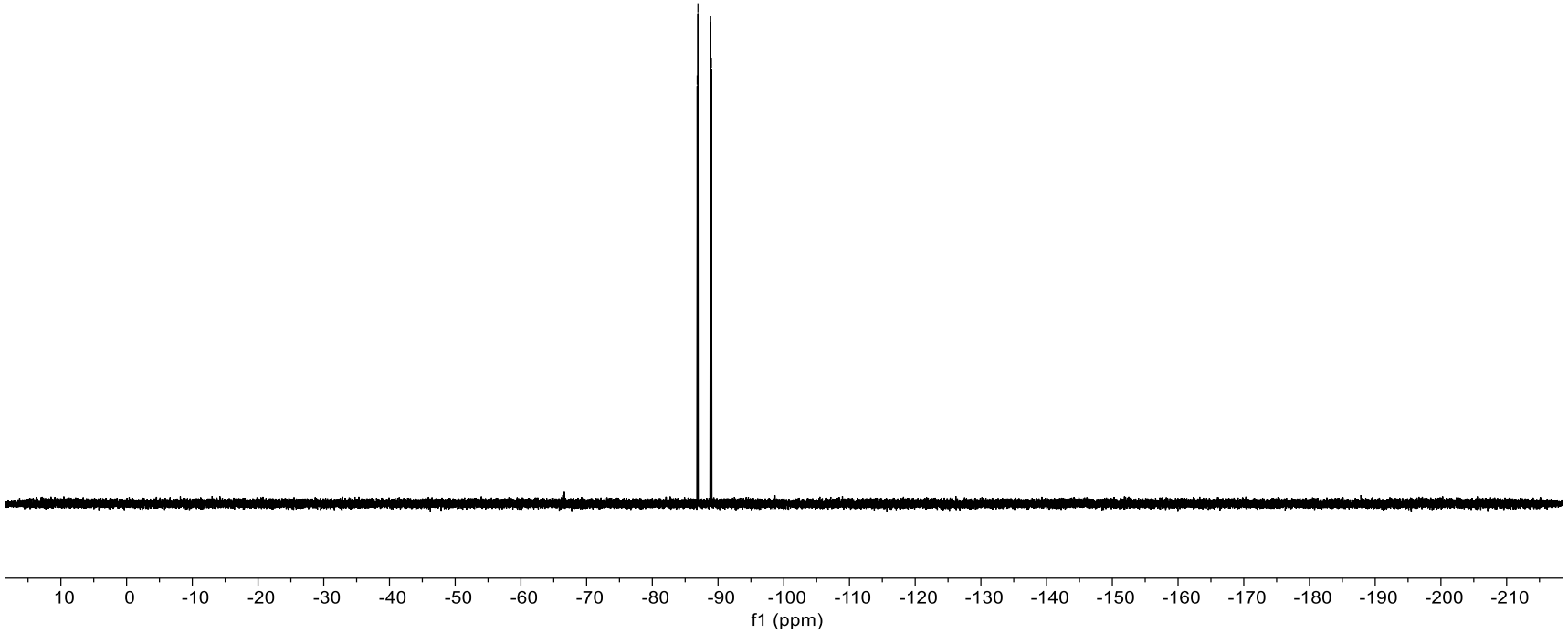


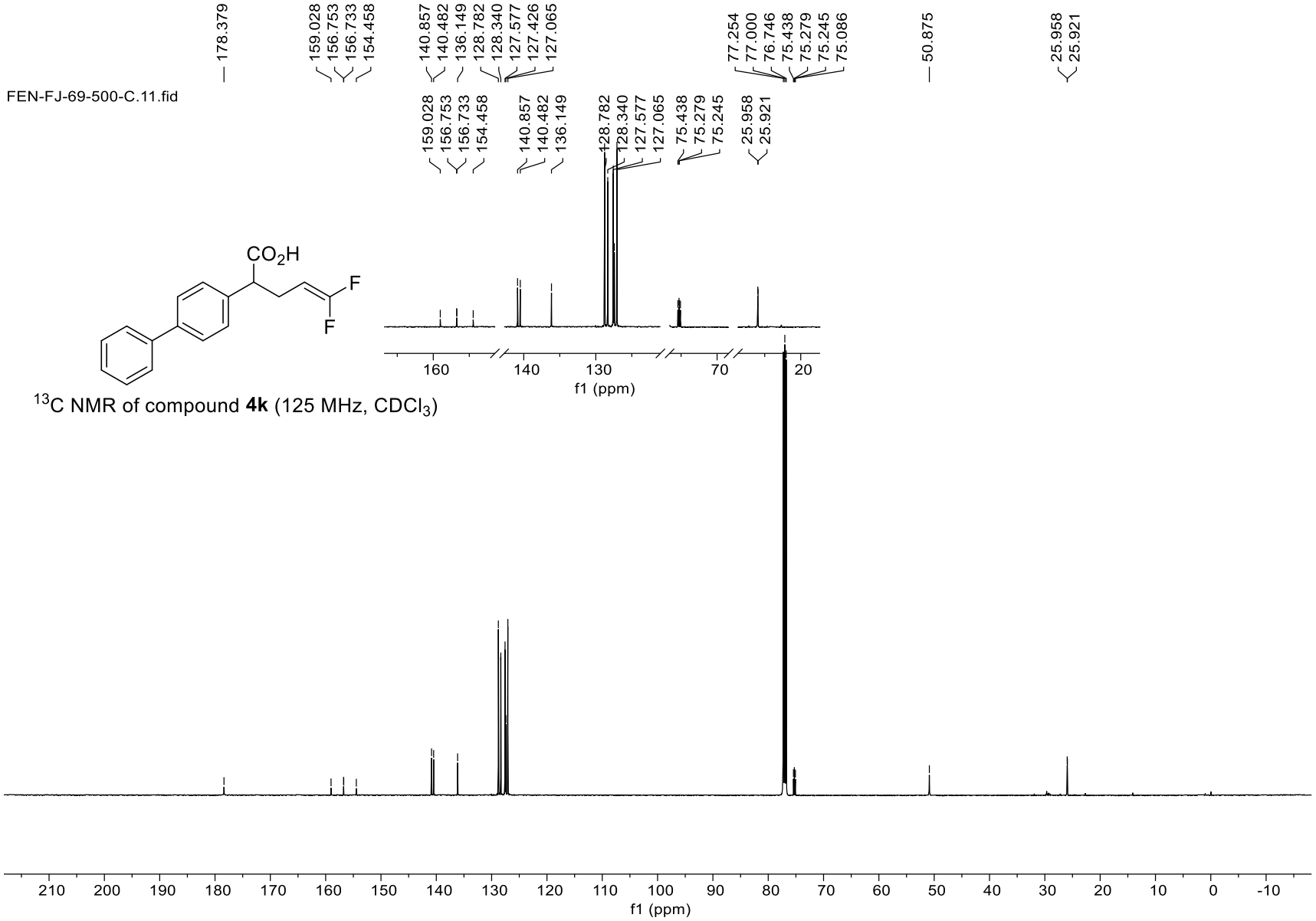
FEN-FJ-69-400-H.11.fid

-86.829
-86.941
-88.877
-88.989

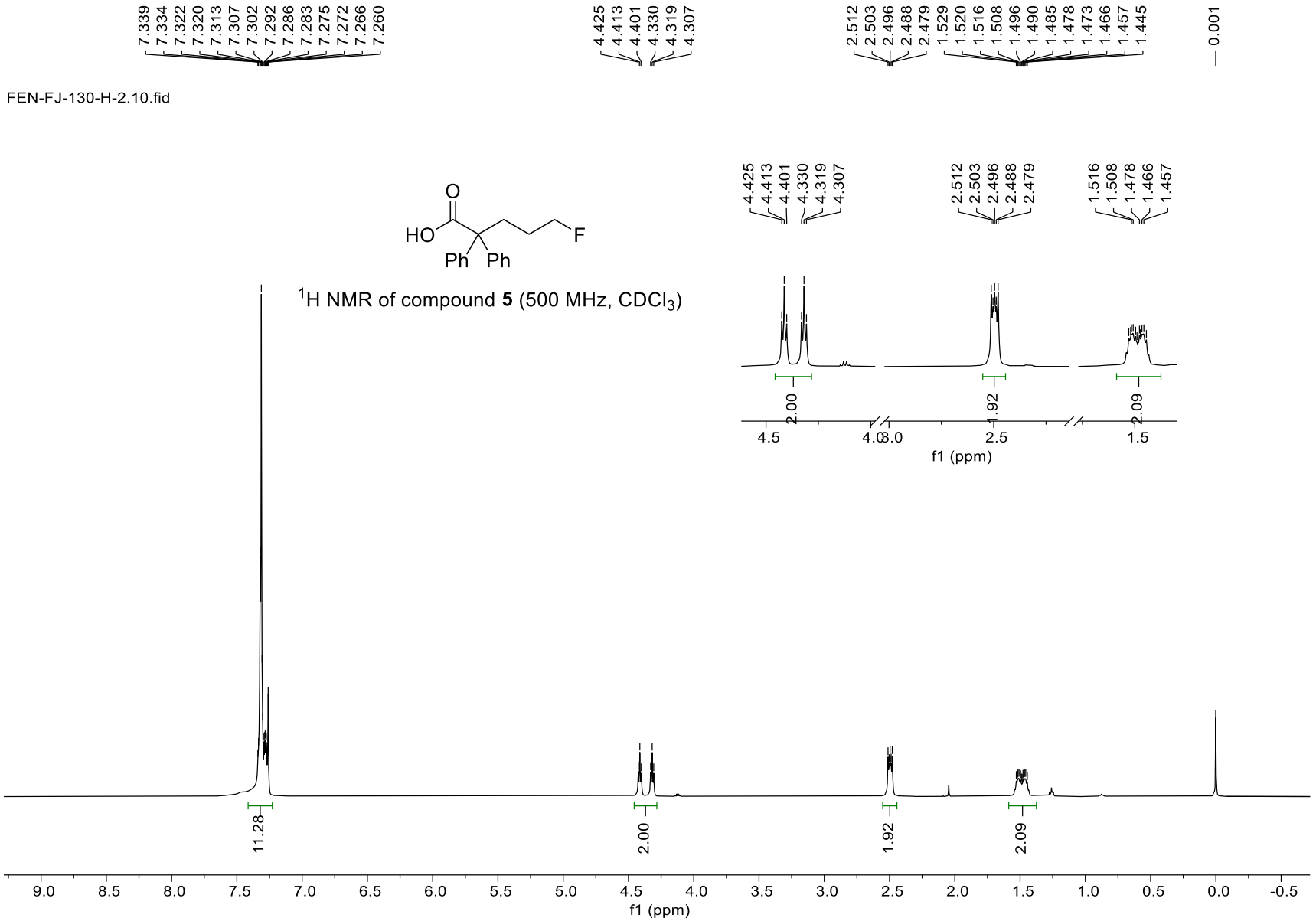


^{19}F NMR of compound **4k** (376 MHz, $CDCl_3$)

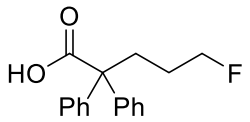




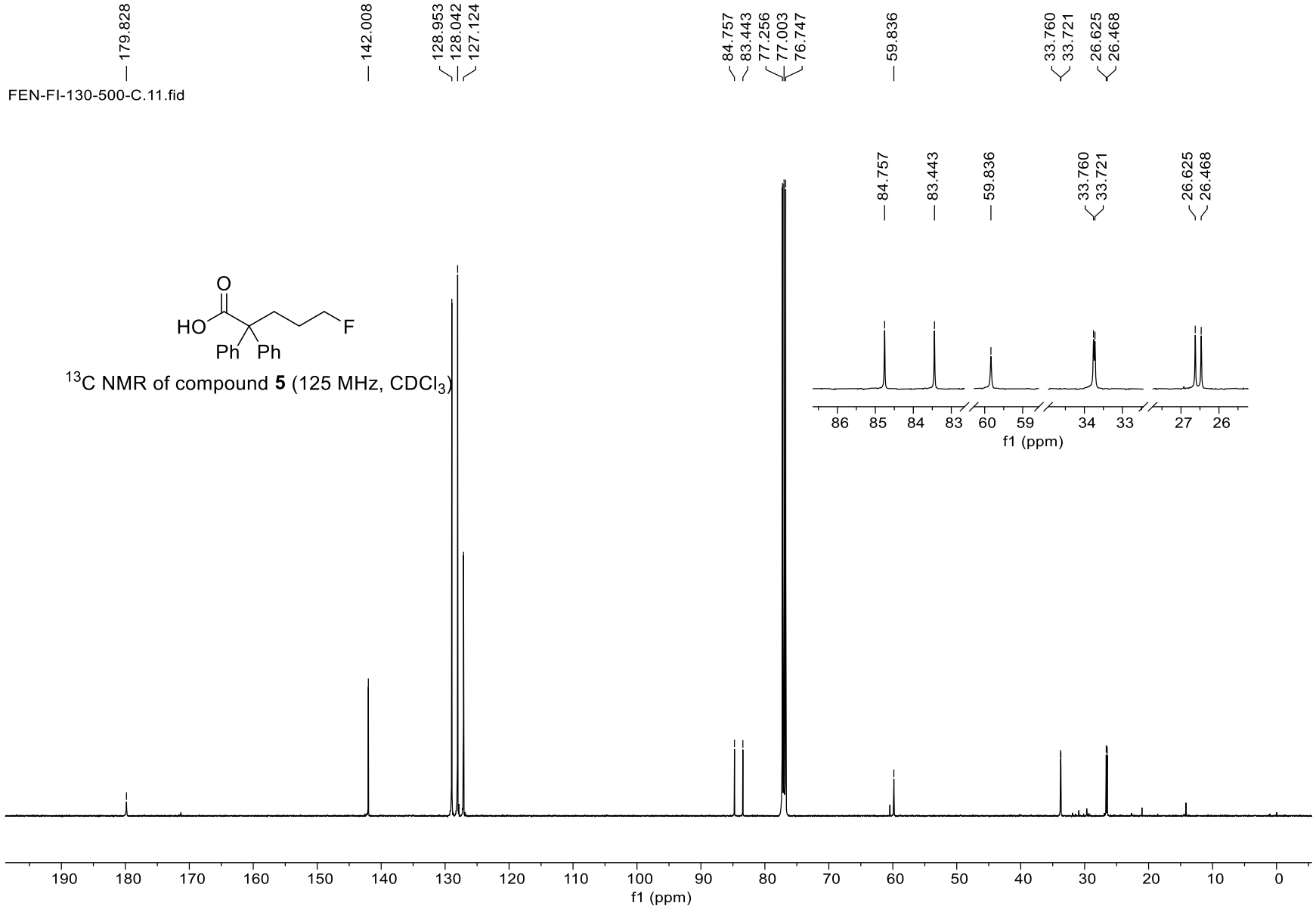
^{13}C NMR of compound **4k** (125 MHz, $CDCl_3$)

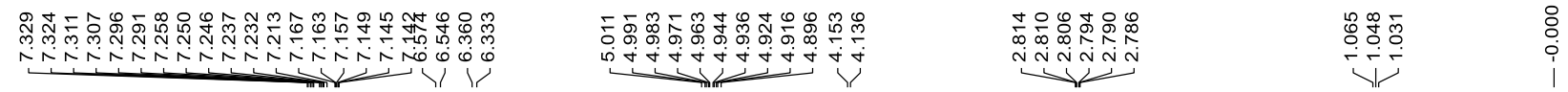

7.339
7.334
7.322
7.320
7.313
7.307
7.302
7.292
7.286
7.283
7.275
7.272
7.266
7.260
4.425
4.413
4.401
4.330
4.319
4.307
2.512
2.503
2.496
2.488
2.479
1.529
1.520
1.516
1.508
1.496
1.490
1.485
1.478
1.473
1.466
1.457
1.445
0.001
FEN-FJ-130-H-2.10.fid
HO
O
Ph
Ph
F
1H NMR of compound 5 (500 MHz, CDCl3)
11.28
2.00
1.92
2.09
f1 (ppm)

FEN-FI-130-F.11.fid

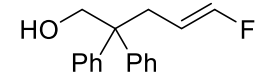


^{19}F NMR of compound **5** (376 MHz, $CDCl_3$)

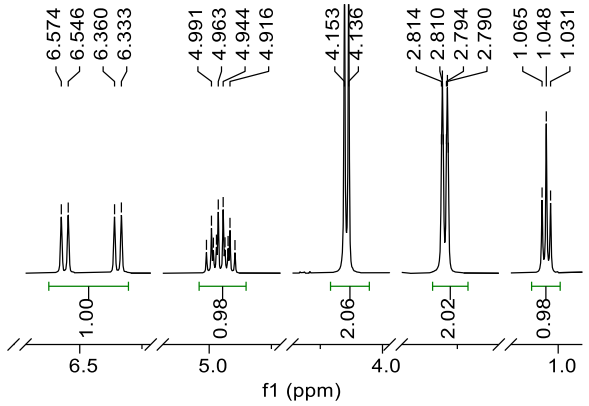

179.828
142.008
128.953
128.042
127.124
84.757
83.443
77.256
77.003
76.747
59.836
33.760
33.721
26.625
26.468
FEN-FI-130-500-C.11.fid
O
HO
F
Ph
Ph
13C NMR of compound 5 (125 MHz, CDCl3)
f1 (ppm)

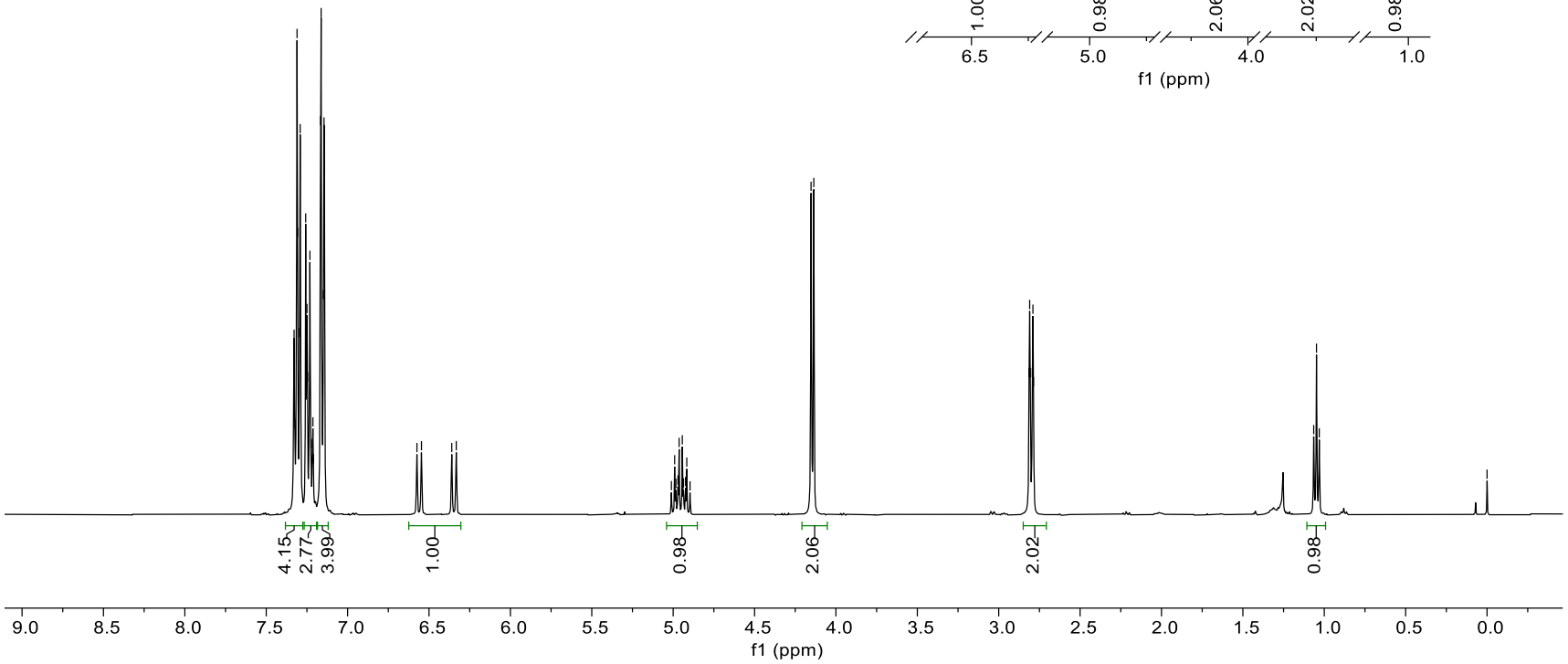


FEN-FI-118-H-400-2.10.fid



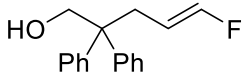
^{1}H NMR of compound **6** (400 MHz, $CDCl_3$)



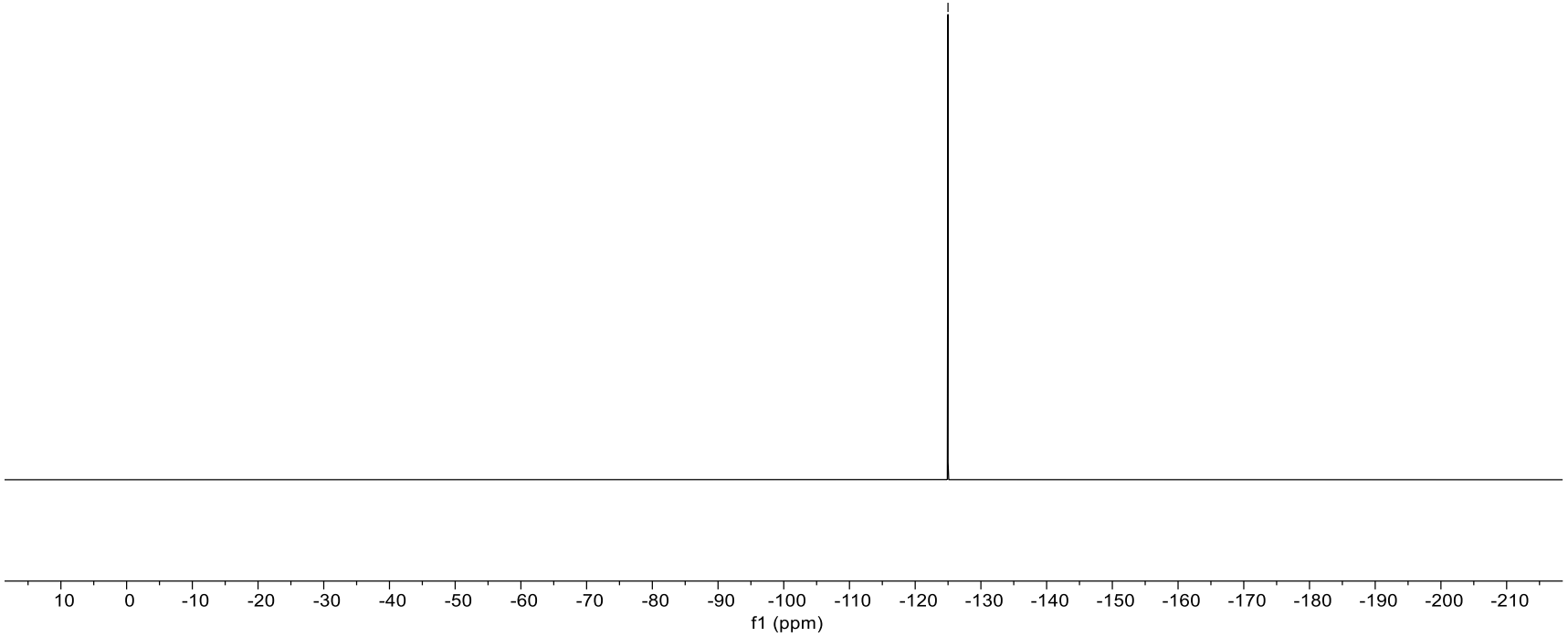


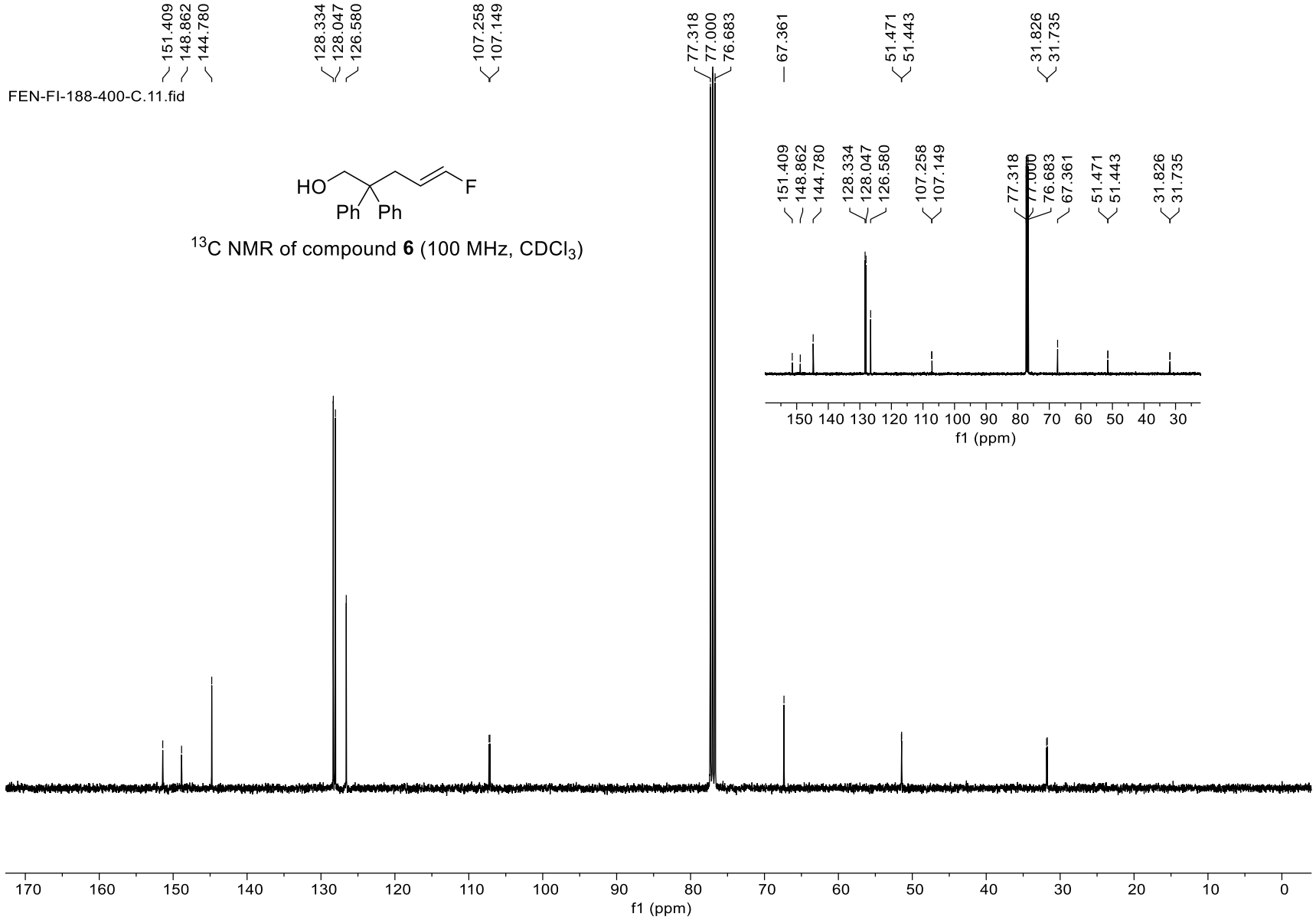
FEN-FI-118-H-400-2.11.fid

-124.993

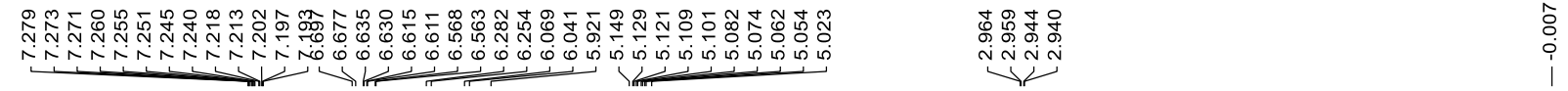


^{19}F NMR of compound **6** (376 MHz, $CDCl_3$)

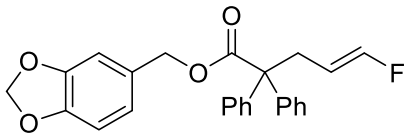




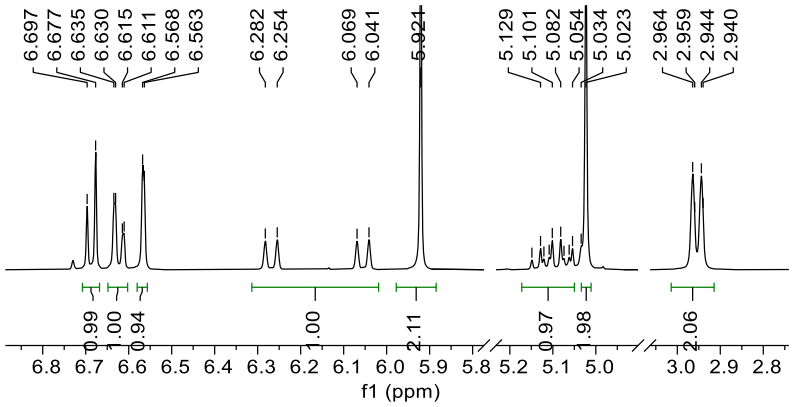
^{13}C NMR of compound **6** (100 MHz, $CDCl_3$)

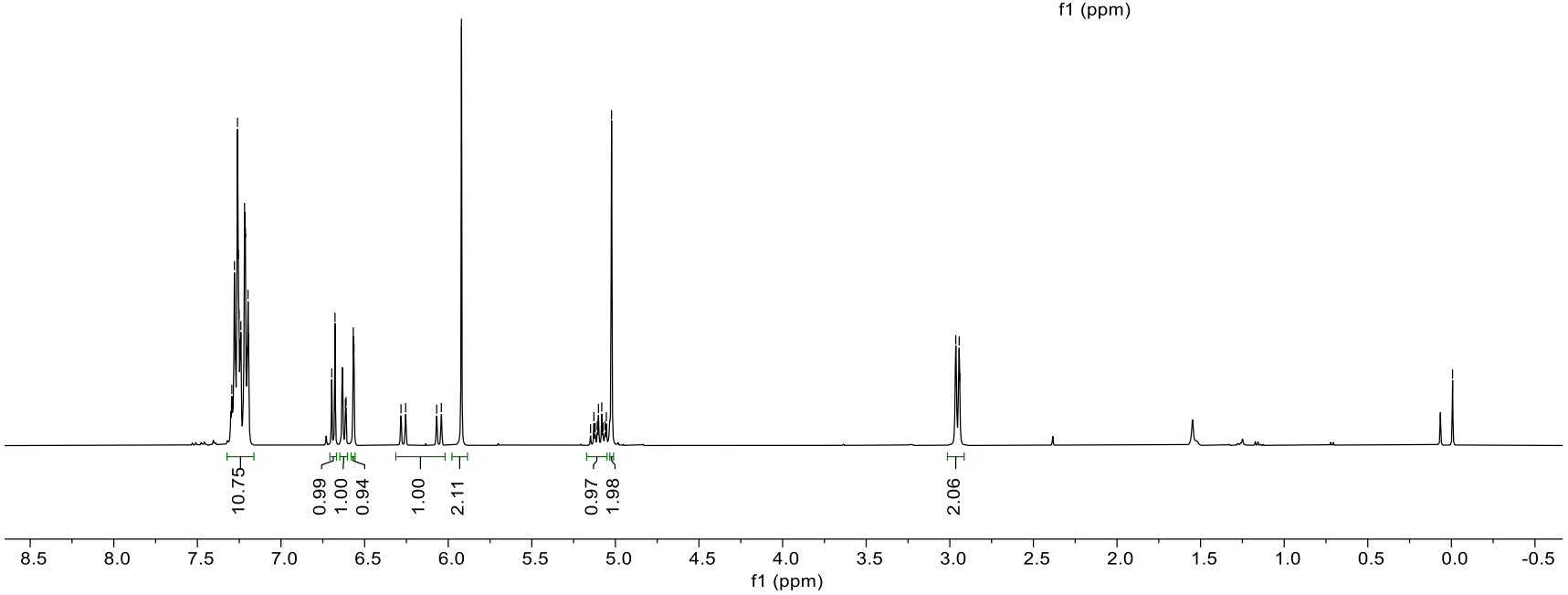


FEN-FJ-84-400-H.10.fid

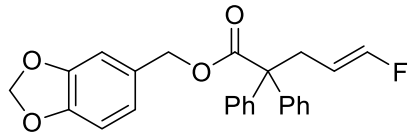


^{1}H NMR of compound **7** (400 MHz, $CDCl_3$)

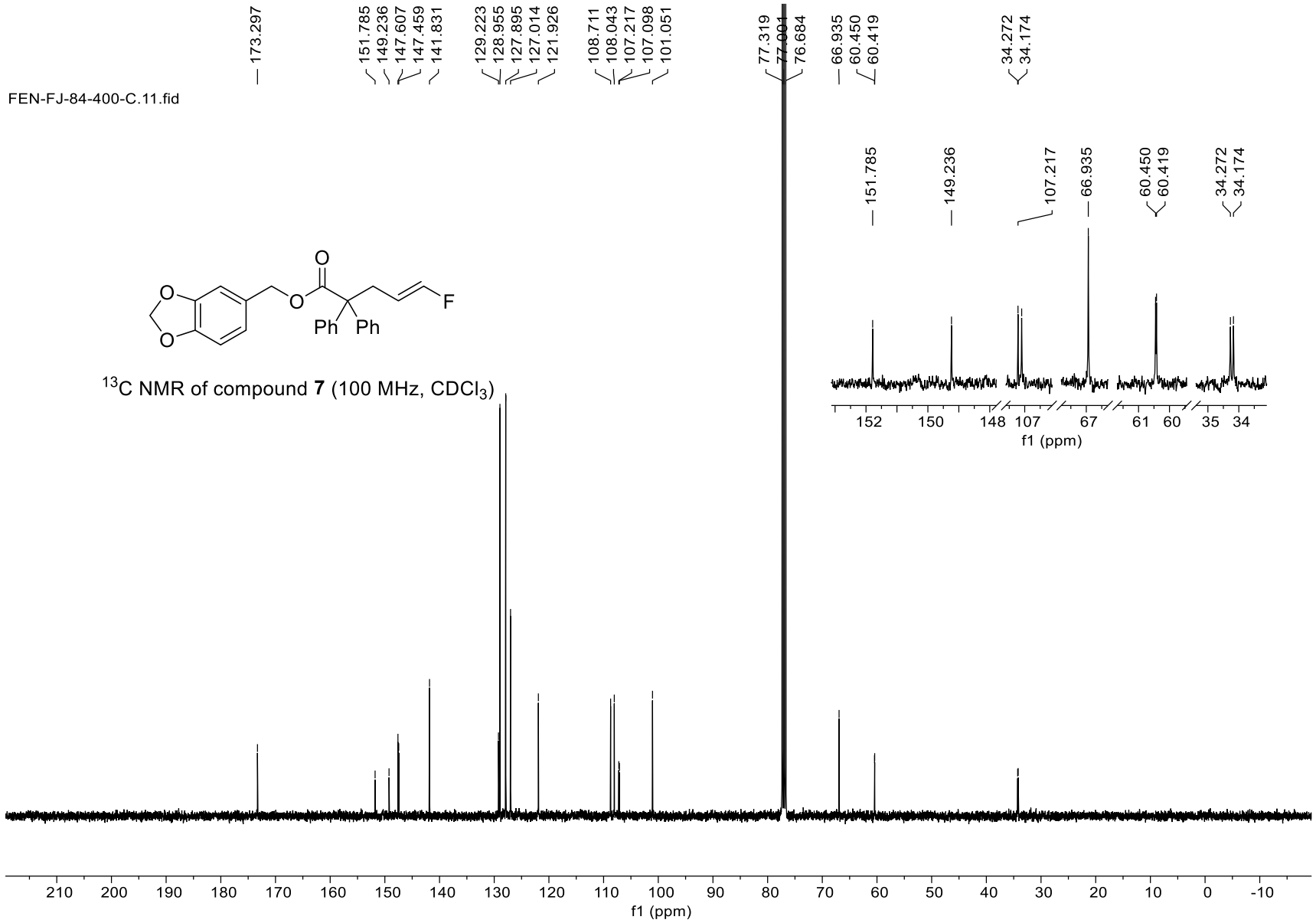


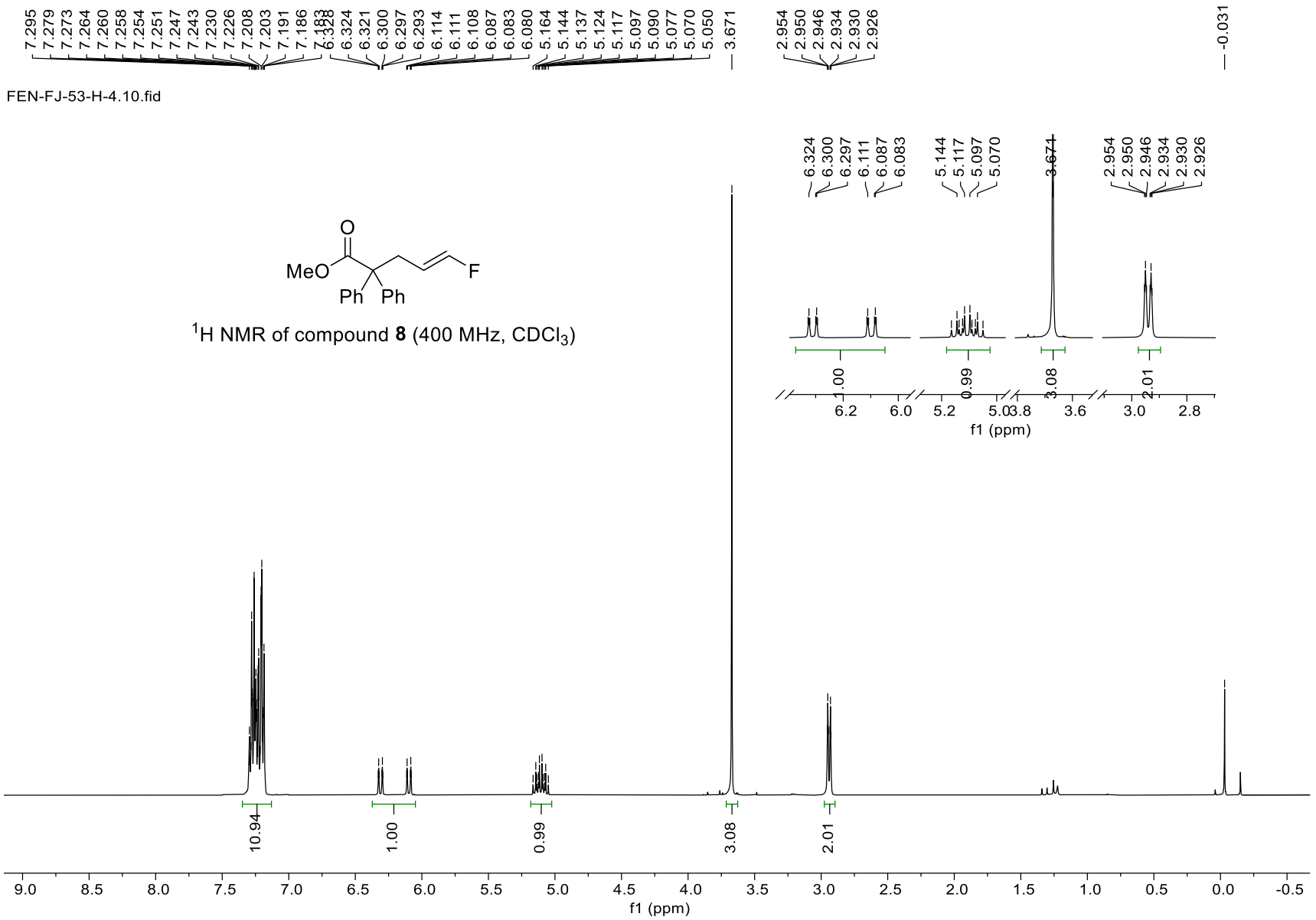


FEN-FJ-84-400-F.11.fid



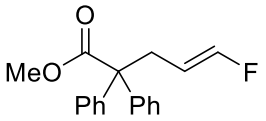
^{19}F NMR of compound **7** (376 MHz, $CDCl_3$)


FEN-FJ-84-400-C.11.fid
173.297
151.785
149.236
147.607
147.459
141.831
129.223
128.955
127.895
127.014
121.926
108.711
108.043
107.217
107.098
101.051
77.319
77.001
76.684
66.935
60.450
60.419
34.272
34.174
O
O
O
O
F
Ph
Ph
13C NMR of compound 7 (100 MHz, CDCl3)
f1 (ppm)

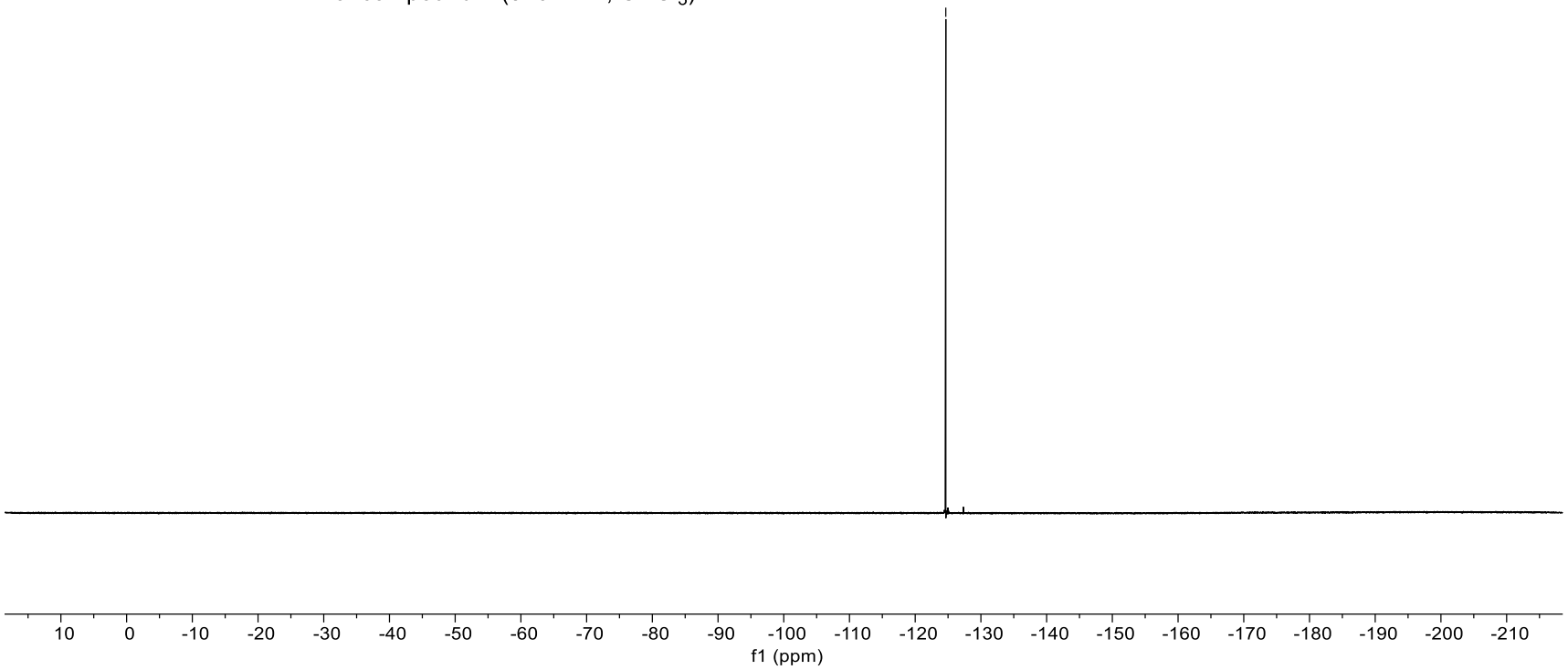

7.295 7.279 7.273 7.264 7.260 7.258 7.254 7.251 7.247 7.243 7.230 7.226 7.208 7.203 7.191 7.186 7.183 7.328 6.324 6.321 6.300 6.297 6.293 6.114 6.111 6.108 6.087 6.083 6.080 5.164 5.144 5.137 5.124 5.117 5.097 5.090 5.077 5.070 5.050 3.671 2.954 2.950 2.946 2.934 2.930 2.926 -0.031
FEN-FJ-53-H-4.10.fid
O
MeO
F
Ph Ph
1H NMR of compound 8 (400 MHz, CDCl3)
6.324 6.300 6.297 6.111 6.087 6.083 5.144 5.117 5.097 5.070 3.671 2.954 2.950 2.946 2.934 2.930 2.926
1.00 0.99 3.08 2.01
6.2 6.0 5.2 5.0 3.8 3.6 3.0 2.8
f1 (ppm)
10.94 1.00 0.99 3.08 2.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

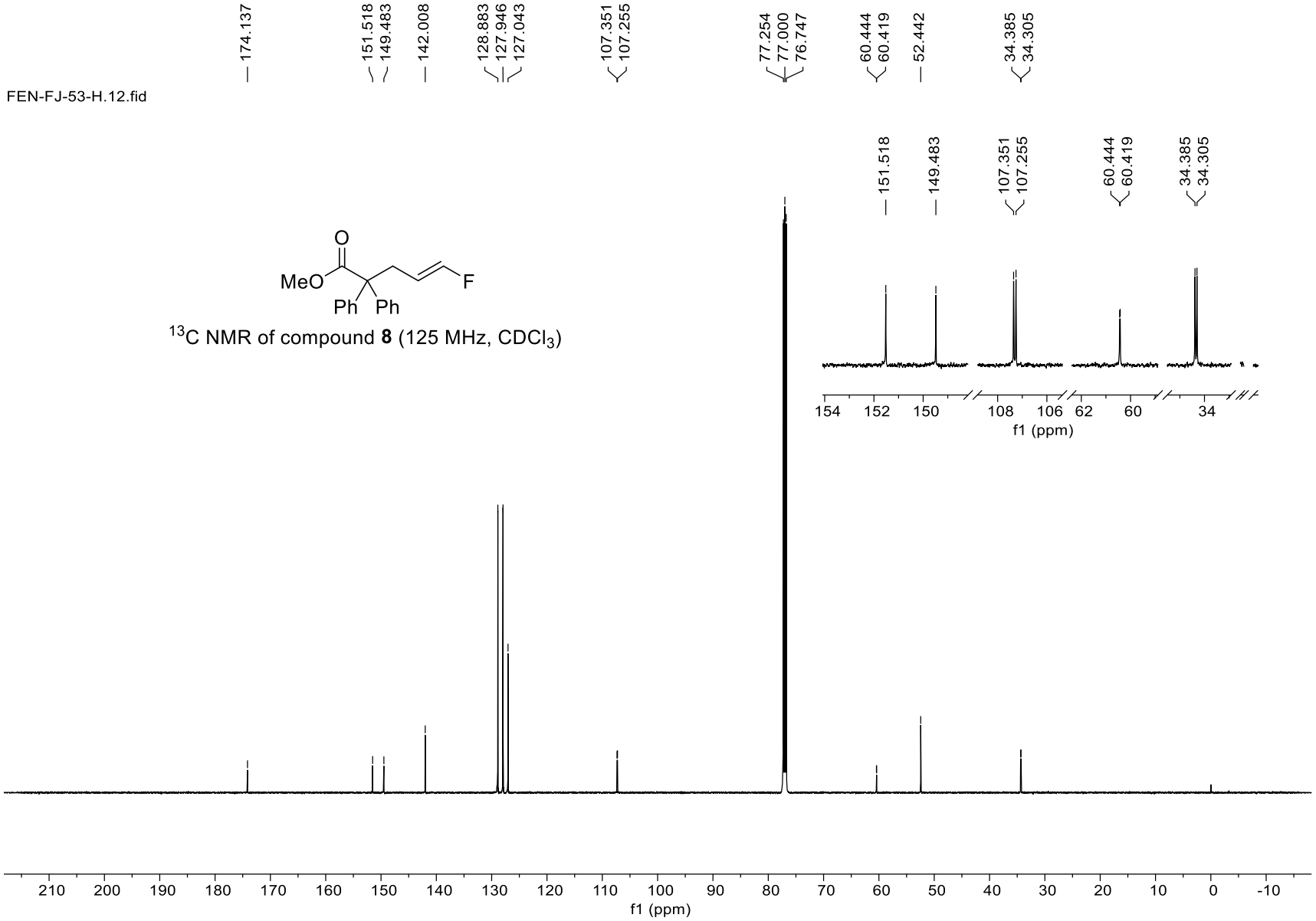
FEN-FJ-53-H-4.11.fid

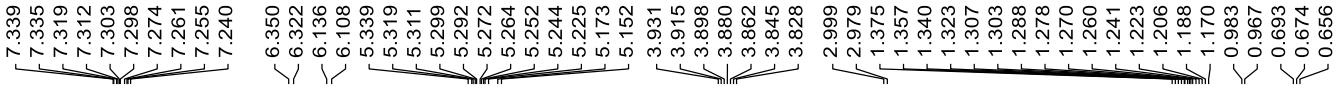
-124.656



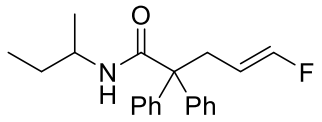
^{19}F NMR of compound **8** (376 MHz, $CDCl_3$)



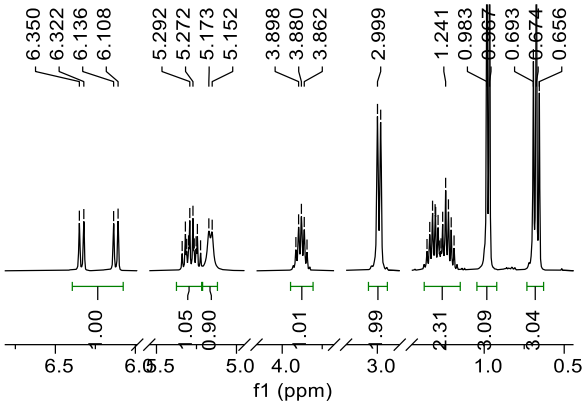

174.137
151.518
149.483
142.008
128.883
127.946
127.043
107.351
107.255
77.254
77.000
76.747
60.444
60.419
52.442
34.385
34.305
FEN-FJ-53-H.12.fid
O
MeO
F
Ph
Ph
13C NMR of compound 8 (125 MHz, CDCl3)
f1 (ppm)

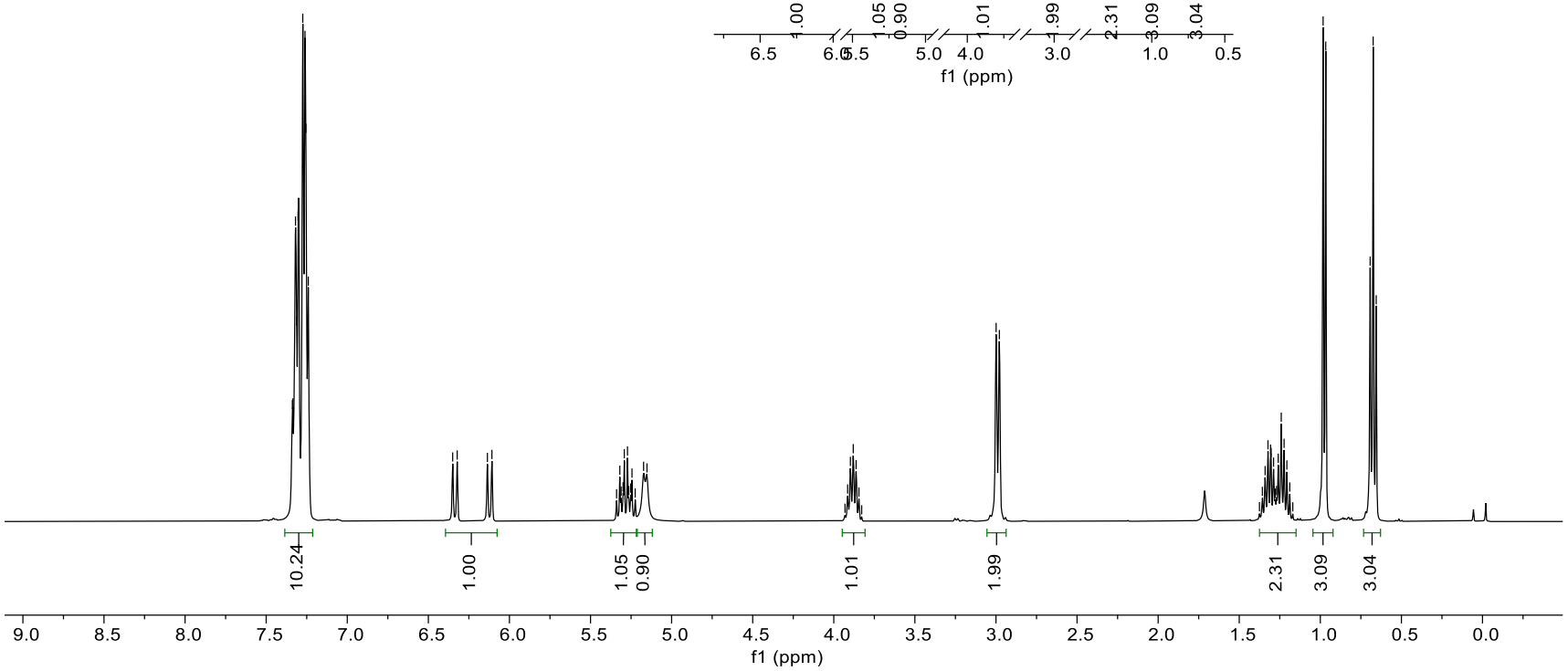


FEN-FJ-59-400-C.10.fid

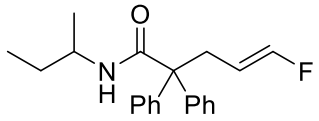


^{1}H NMR of compound **9** (400 MHz, $CDCl_3$)

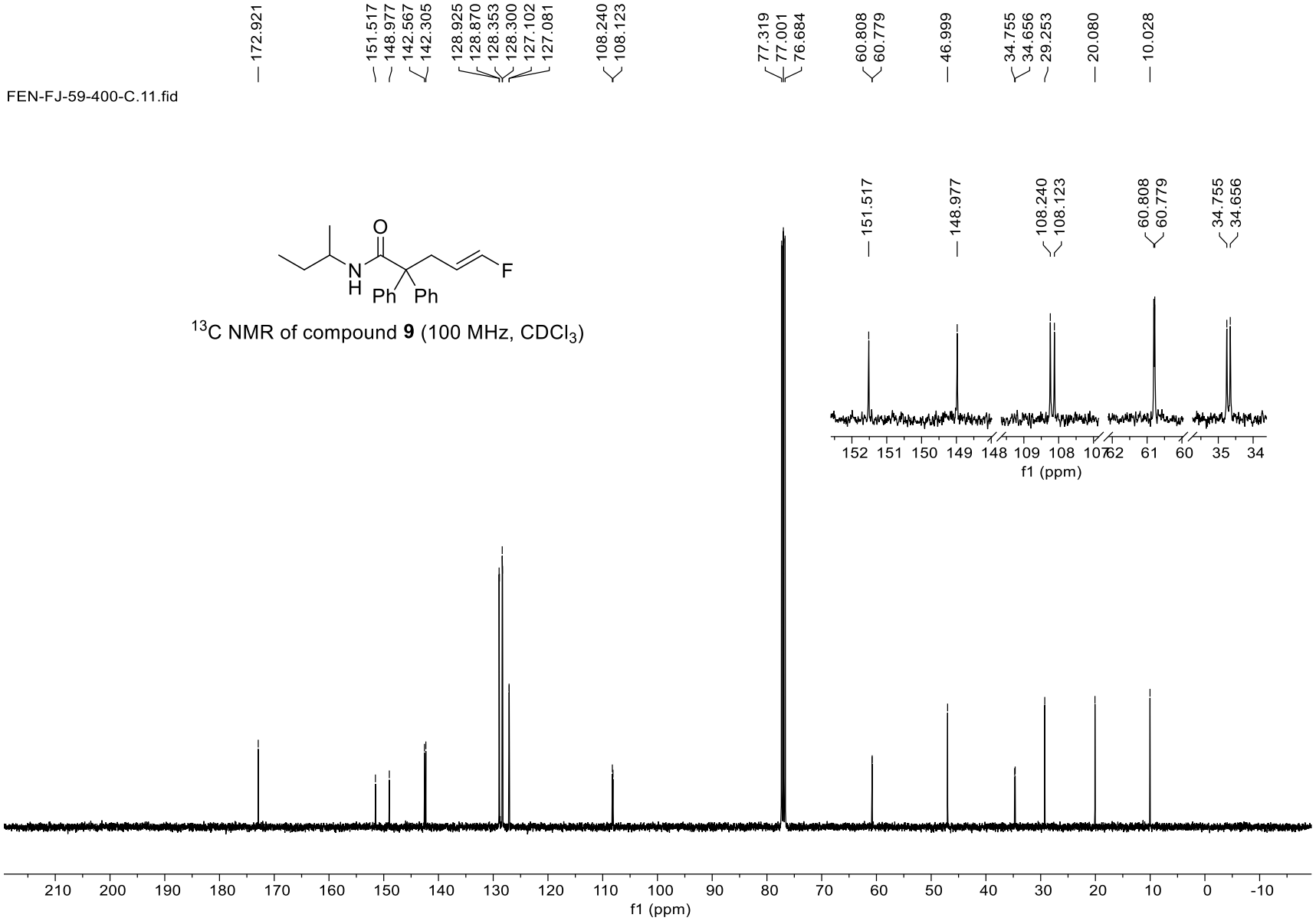


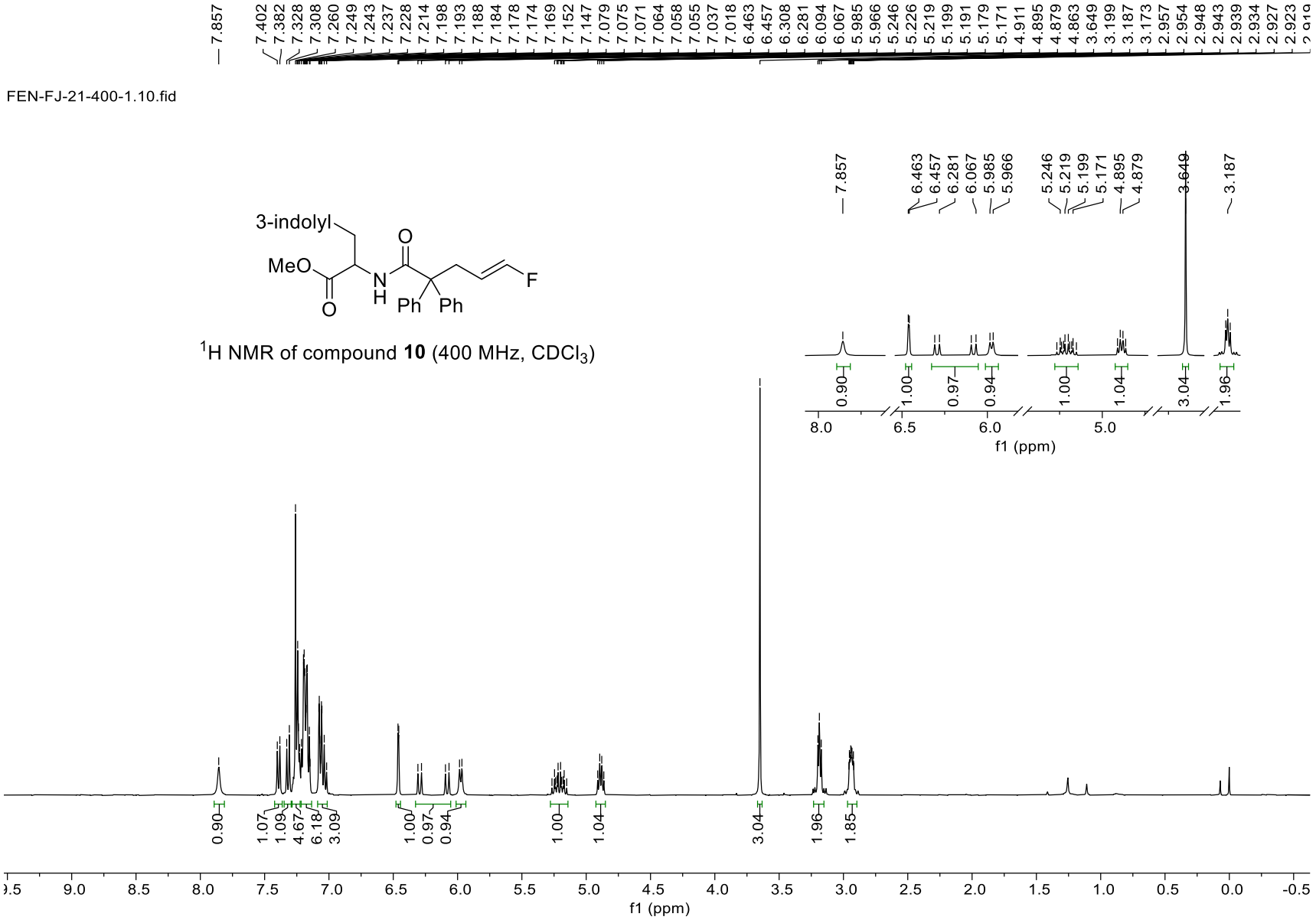


FEN-FJ-59-400-H-2.11.fid



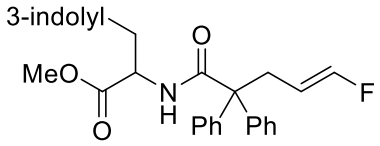
^{19}F NMR of compound **9** (376 MHz, $CDCl_3$)


172.921
151.517
148.977
142.567
142.305
128.925
128.870
128.353
128.300
127.102
127.081
108.240
108.123
77.319
77.001
76.684
60.808
60.779
46.999
34.755
34.656
29.253
20.080
10.028
FEN-FJ-59-400-C.11.fid
O
N
H
Ph
Ph
F
13C NMR of compound 9 (100 MHz, CDCl3)
f1 (ppm)

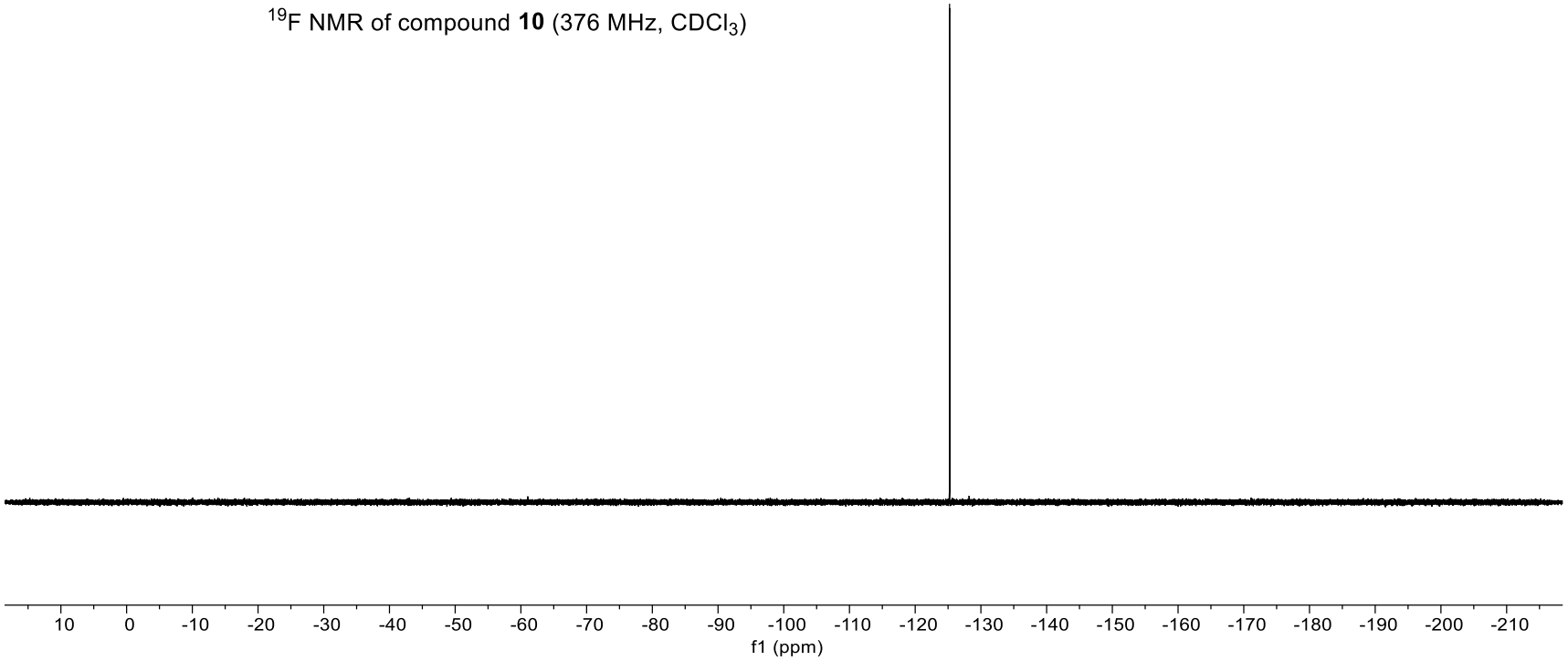

FEN-FJ-21-400-1.10.fid
3-indolyl
MeO
O
N
H
O
Ph
Ph
F
^{1}H NMR of compound **10** (400 MHz, $CDCl_3$)
f1 (ppm)

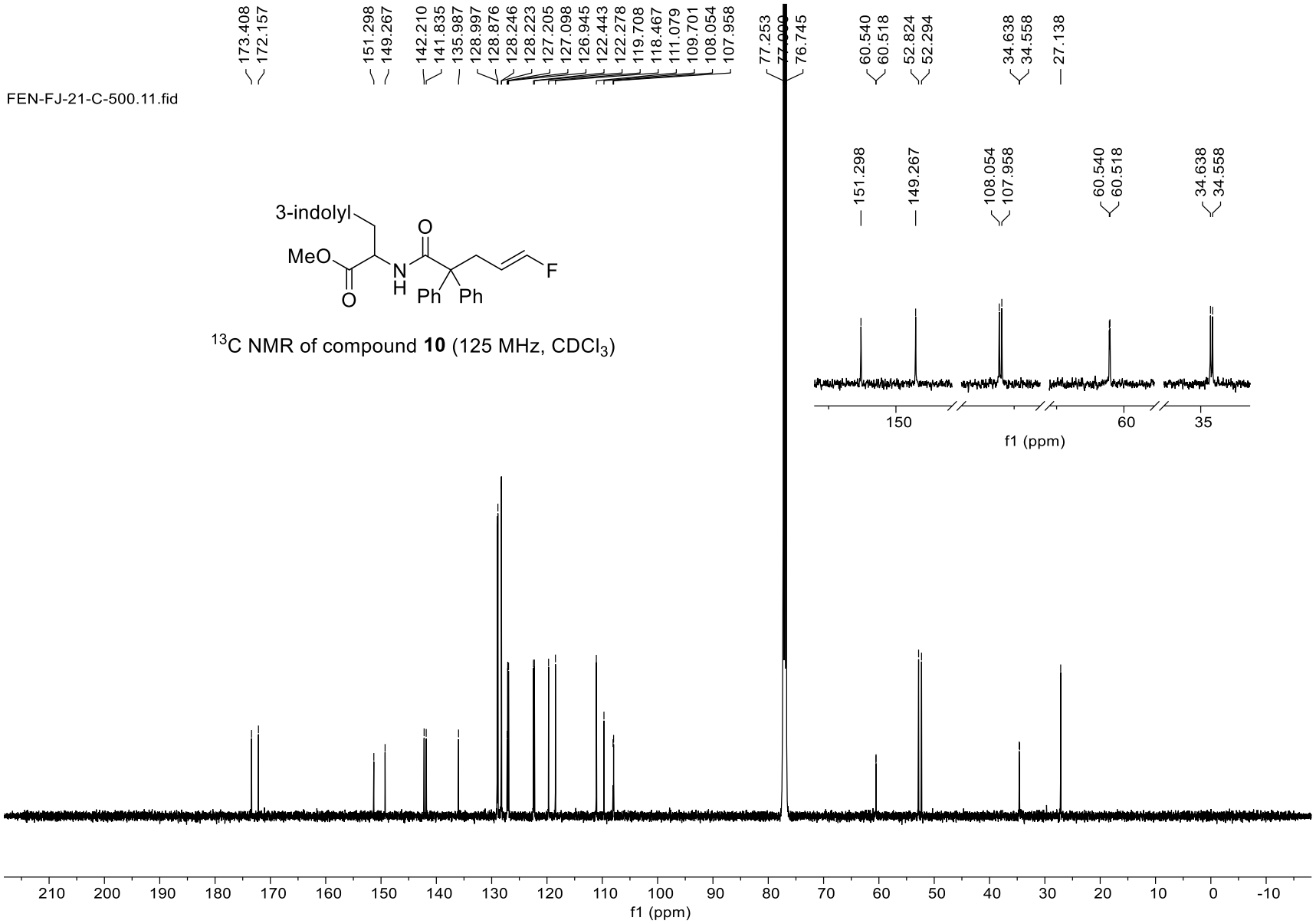
FEN-FJ-21-400-1.11.fid

— -125.230

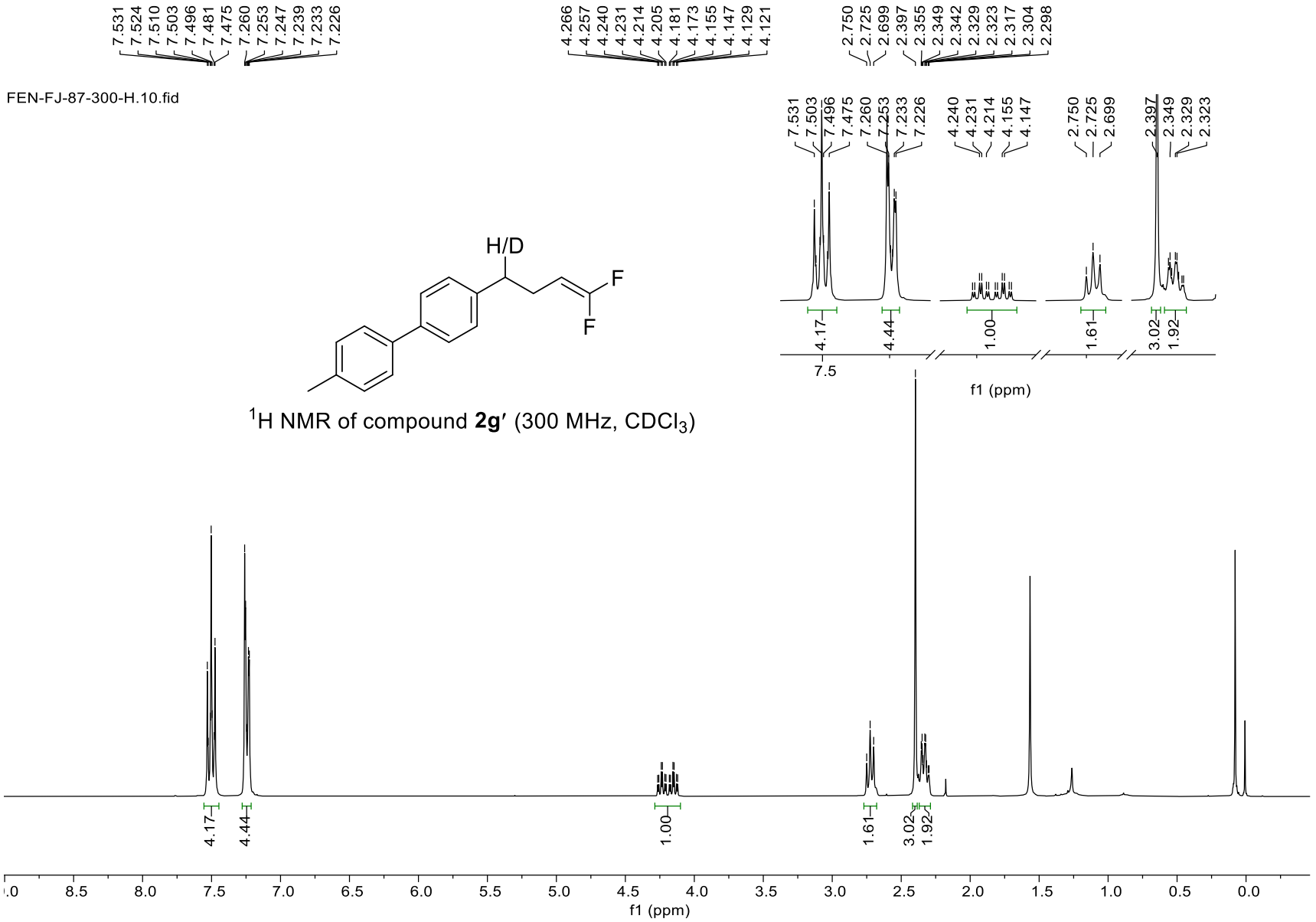


^{19}F NMR of compound **10** (376 MHz, $CDCl_3$)





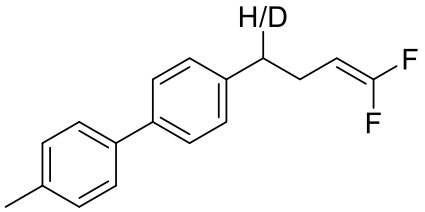
^{13}C NMR of compound **10** (125 MHz, $CDCl_3$)



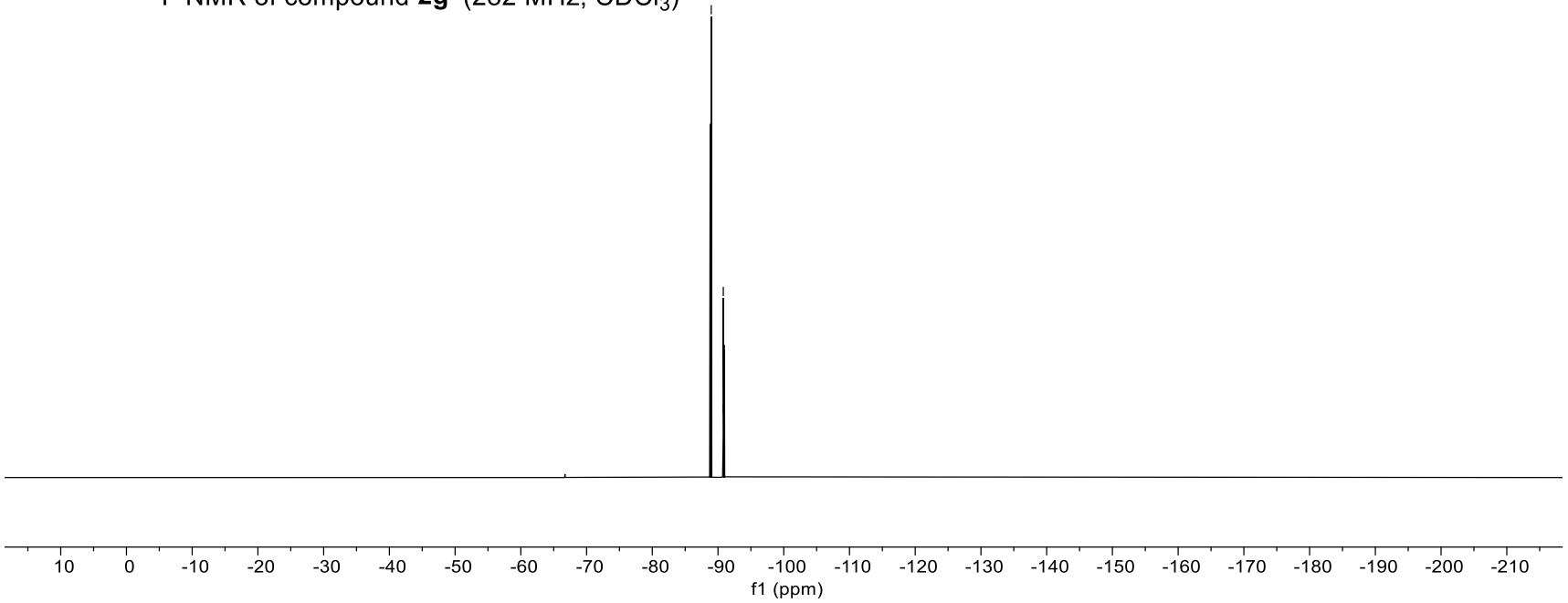
^{1}H NMR of compound **2g′** (300 MHz, $CDCl_3$)

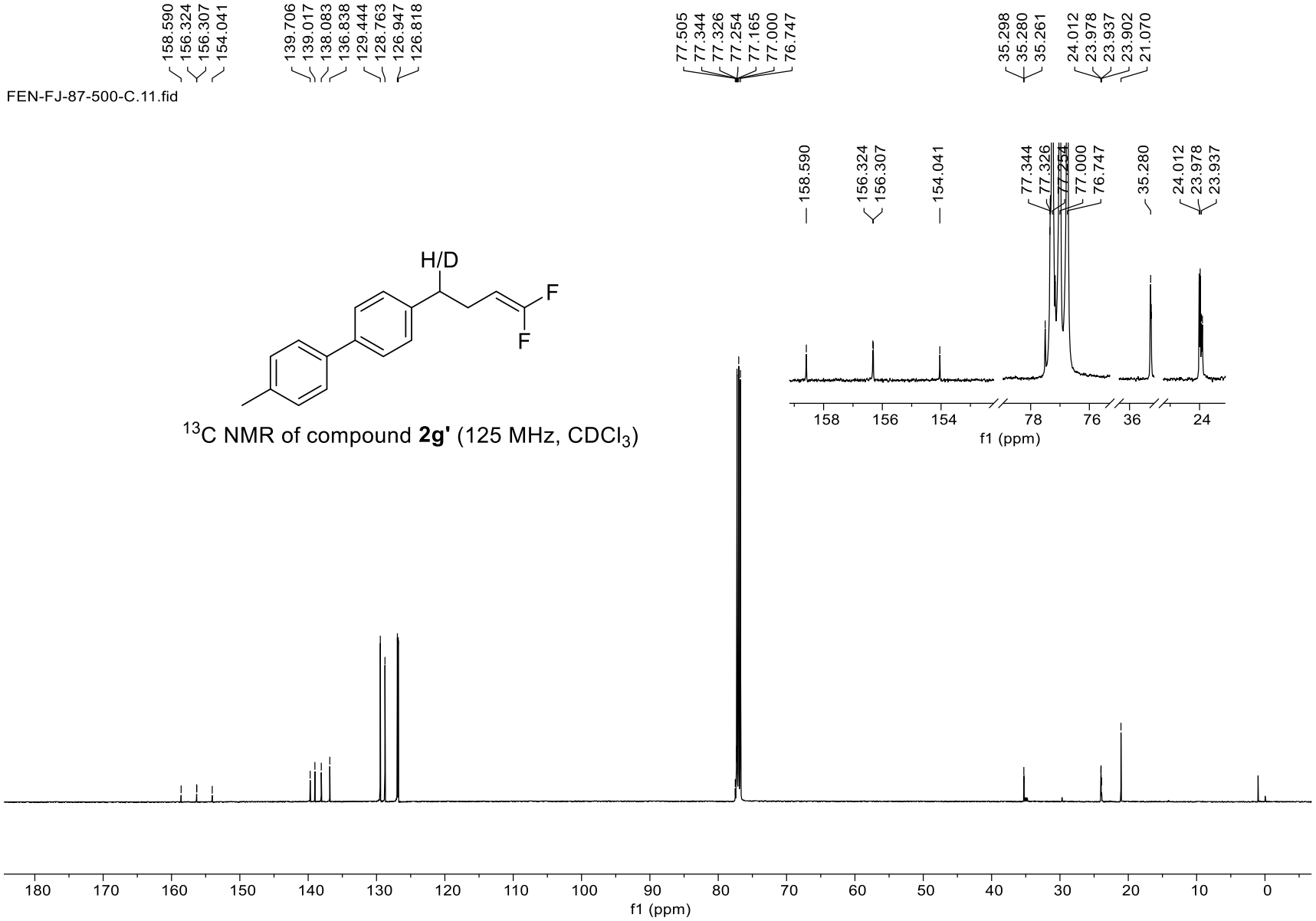
-88.804
-88.971
-90.799
-90.807
-90.966
-90.974

FEN-FJ-87-300-H.11.fid



^{19}F NMR of compound **2g'** (282 MHz, $CDCl_3$)




158.590
156.324
156.307
154.041
139.706
139.017
138.083
136.838
129.444
128.763
126.947
126.818
77.505
77.344
77.326
77.254
77.165
77.000
76.747
35.298
35.280
35.261
24.012
23.978
23.937
23.902
21.070
FEN-FJ-87-500-C.11.fid
H/D
F
F
13C NMR of compound 2g' (125 MHz, CDCl3)
f1 (ppm)