Supporting Information

Mechanochemical Fluorination of Unactivated Tertiary Alkyl Chlorides

Jiemin Wang[#], Xueyan Yang[#]*, Cheng Peng, Mengyao Pei and Xiaofeng Wei*

School of Pharmacy, Xi'an Jiaotong University, Xi'an, Shaanxi, 710061, P. R. China

E-mail: yangxueyan3553@126.com; xiaofeng.wei@xjtu.edu.cn

Table of contents

1. General Information

Unless otherwise stated, reactions were carried out using dry solvents under nitrogen or argon atmosphere. Commercial reagents were purchased from Adamas, Aladdin, Alfa Aesar, Bidepharm, Leyan and TCI, and used directly without further purification. Conversion was monitored by thin layer chromatography (TLC) using Silicycle 200 mm silica gel GF-254 plates and visualized by UV-light at 254 nm. Flash column chromatographic purification of products was performed over silica gel (200-300 mesh). All mechanochemical reactions were performed using grinding vessels in the Retsch MM 400. Both jars and balls were made of stainless steel (**Figure S1**). NMR spectra were recorded on JEOL 400MHz or Bruker 600MHz NMR spectrometers. Fluorobenzene was used as an internal standard to determine the NMR yields. Multiplicity was recorded as follows: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. High-resolution electrospray ionization and electronic impact mass spectrometry were performed on a WATERS I-Class VION IMS Qt of double focusing magnetic sector mass spectrometer. The above tests were conducted in the the Instrument Analysis Center of XJTU.

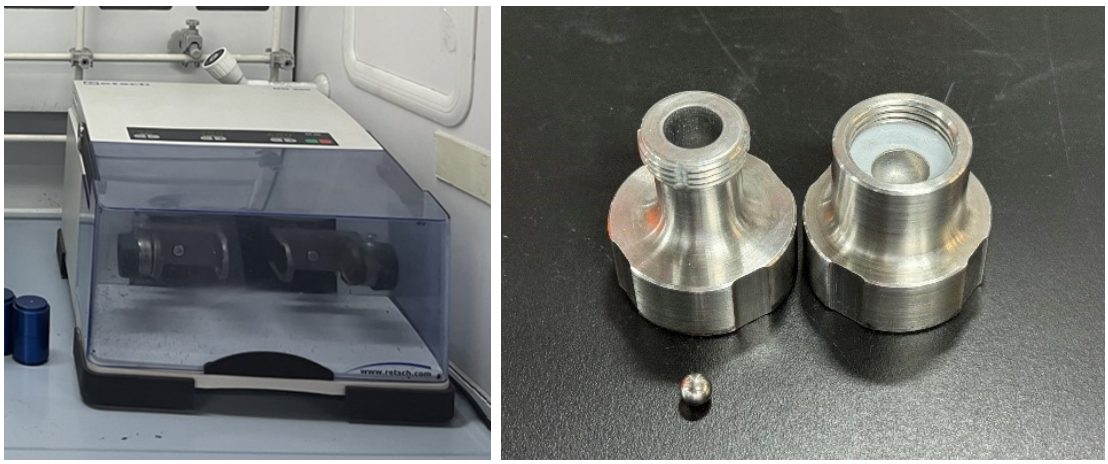


Fig.S1. Retsch MM400 (left), stainless jar (1.5 mL) and ball (6.0 mm diameter) (right) used in this study.

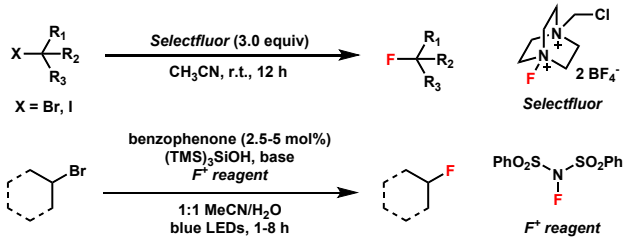
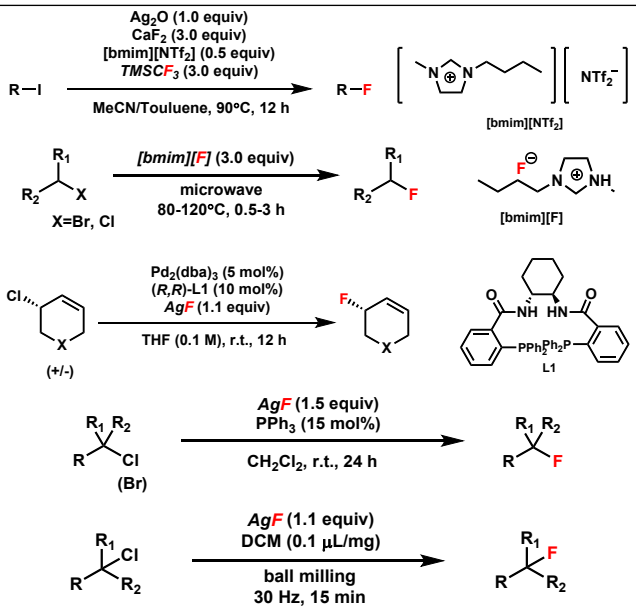
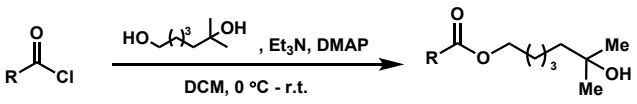
	Conditions	*Ref.*[a]
Radical pathway		15a 15b
Nucleophilic pathway		14a 14d 14g 18 this work

Table S1. Fluorination methods through halogen-exchange.

[a] References here refer to those in the manuscript.

2. Synthesis of Substrates

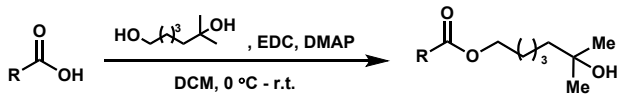
General procedure 1 (GP-1)



An oven-dried 50-mL round-bottom flask, equipped with a stir bar, was charged with 3-methyl-butane-1,3-diol[1] (878 mg, 6.0 mmol, 1.5 equiv.), DMAP (50 mg, 0.4 mmol, 0.1 equiv.), Et_3N (607 mg, 6.0 mmol, 1.5 equiv.) and DCM (20.0 mL). The mixture was cooled to 0°C and acyl chloride (4.0 mmol, 1.0 equiv.) was added dropwise. The reaction mixture was warmed to room temperature and stir for 4 h. After the completion of reaction, H_2O (25.0 mL) was added and the mixture was extracted with DCM (25.0

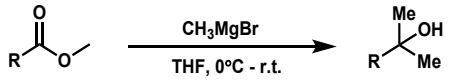
mL×3). The combined organic layers were washed with brine (10.0 mL), dried over Na_2SO_4 and filtrated. The solvent was removed by vacuum distillation and the residue was used for next step (GP-4) without further purification[2].

General procedure 2 (GP-2)



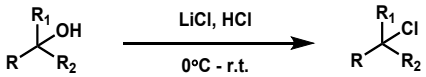
The carboxylic acid (4.0 mmol) was added to a solution of 1-(3-dimethylamino-propyl)-3-ethylcarbodiimide (EDC, 997 mg, 5.2 mmol, 1.2 equiv.) and DMAP (50 mg, 0.4 mmol, 0.1 equiv.) in CH_2Cl_2 (12.0 mL) at 0°C. The alcohol (702 mg, 4.8 mmol, 1.2 equiv.) was then added. The reaction mixture was warmed to room temperature and stirred overnight. After the completion of reaction, the solution was diluted with DCM (20.0 mL) and washed with 1N HCl (10.0 mL×2), sat. $NaHCO_3$ (20.0 mL), and brine (20.0 mL) sequentially. The organic layer was dried over Na_2SO_4 and filtrated. The solvent was removed by vacuum distillation and the residue was used for next step (GP-4) without further purification.[3]

General procedure 3 (GP-3)



A 50-mL round-bottom flask was charged with ester (4.0 mmol, 1.0 equiv.), followed by the addition of THF (8.0 mL). The resulting solution was cooled to 0°C and a 3 M solution of methyl magnesium bromide (4 mL, 12 mmol, 3.0 equiv.) in THF was added dropwise. The reaction was warmed to room temperature and stirred an additional 18 h. The reaction was quenched by slow addition of 5 mL of saturated NH_4Cl at 0°C and the resulting biphasic mixture was extracted with EtOAc (20.0 mL×3). The organic phase was dried over Na_2SO_4, filtered and concentrated. The crude product was used for next step (GP-4) without further purification[1].

General procedure 4 (GP-4)



A 50-mL round-bottom flask equipped with a stir bar was charged with LiCl (339 mg, 8.0 mmol, 2.0 equiv.) and concentrated hydrochloric acid (12 M, 8.0 mL). The solution was cooled to 0°C, and then the tertiary alcohol (4.0 mmol, 1.0 equiv.) was added dropwise, either neat or dissolved in a minimal amount of DCM, over 5 min. The reaction mixture was warmed to room temperature and stirred overnight. After the

completion of reaction, the mixture was then diluted with water (20.0 mL) and extracted with EtOAc (20.0 mL×3). The combined organic layers were washed with brine (10.0 mL), dried over Na_2SO_4 and filtrated. The residue was purified by flash silica gel chromatography to provide the substrates[4].

3. Comparative experiments and mechanistic experiments

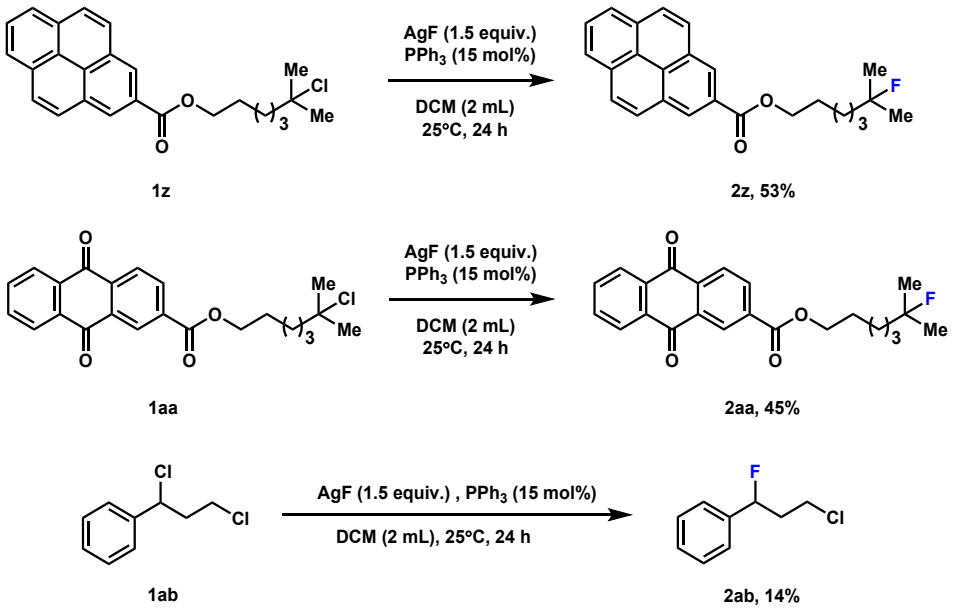
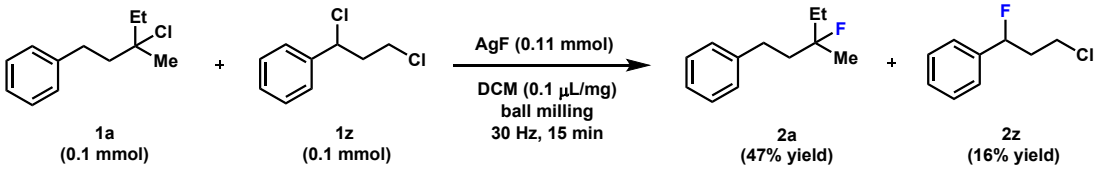


Fig. S2. Fluorination of **1z**, **1aa** and **1ab** utilizing Fu's method (*Ref.* 4).



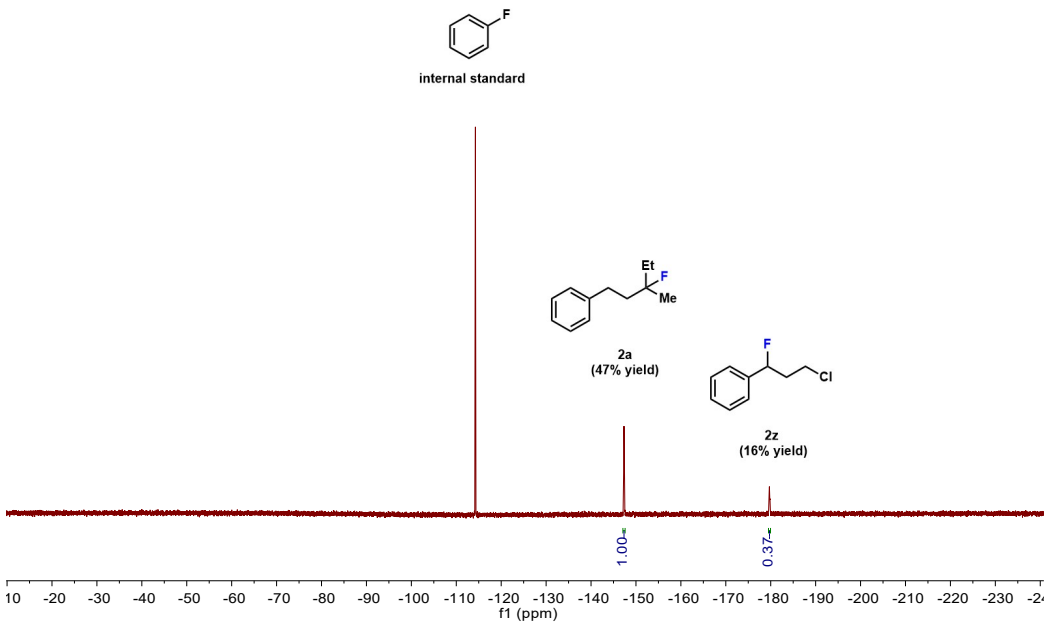
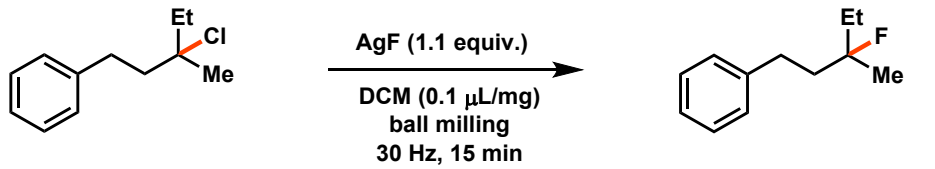


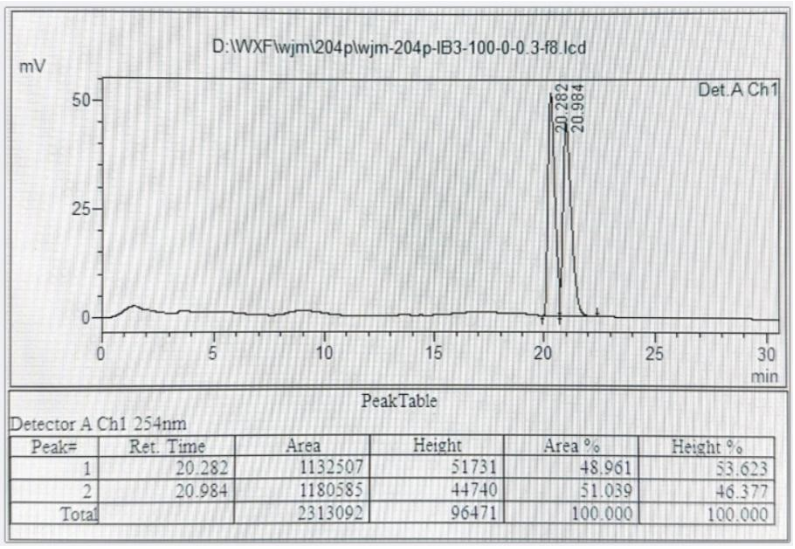
Fig. S3. Selectivity between activated benzylic chlorine and unactivated tertiary chlorine.



1a, >99% ee
enantioenriched (R or S)

2a (60% ee)
enantioenriched (S or R)

rac-**1a**, retention time: 20.3min, 21.0 min

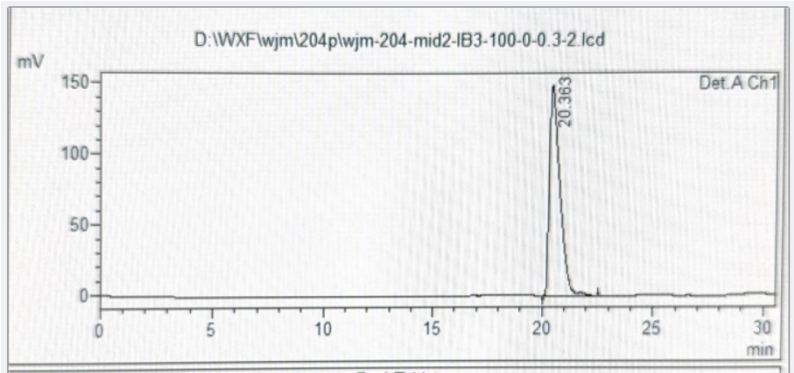


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.282	1132507	51731	48.961	53.623
2	20.984	1180585	44740	51.039	46.377
Total		2313092	96471	100.000	100.000

enantioenriched **1a** (> 99% ee), retention time: 20.3 min

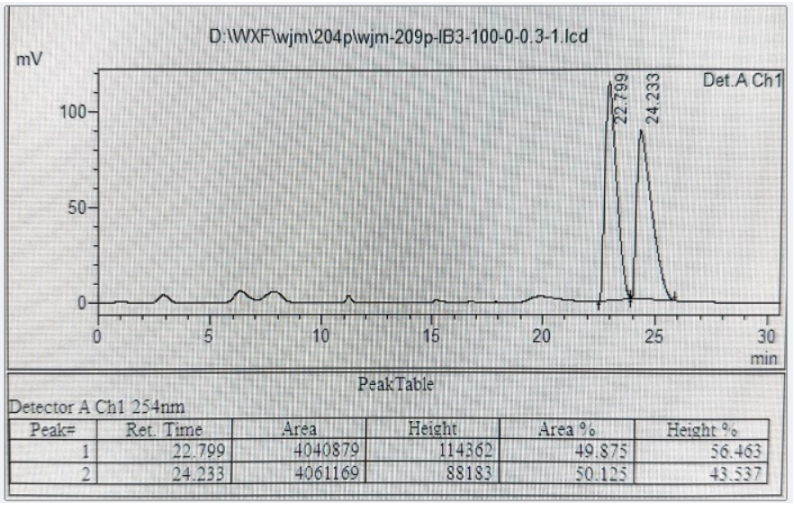


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.363	4938476	149791	100.000	100.000
Total		4938476	149791	100.000	100.000

rac-**2a** (from *rac*-**1a**), retention time: 22.8 min, 24.2 min

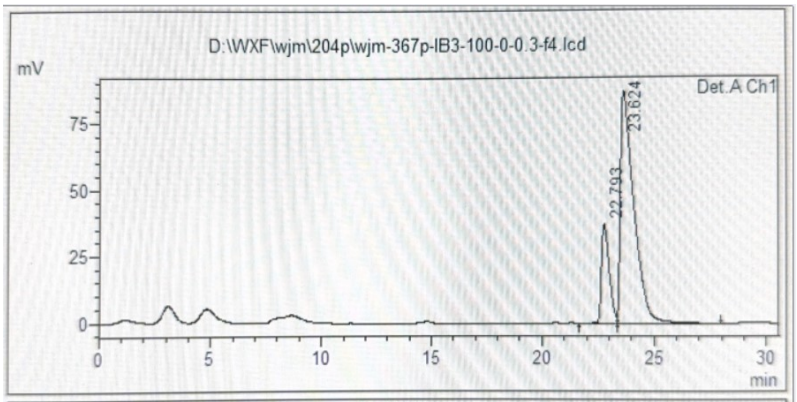


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.799	4040879	114362	49.875	56.463
2	24.233	4061169	88183	50.125	43.537

enantioenriched **2a** (61% ee, from enantioenriched **1a**), retention time: 22.8 min, 23.6 min



PeakTable

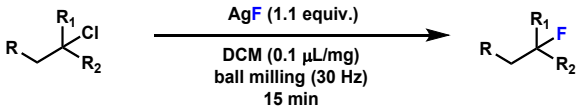
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.793	919631	37565	19.942	29.957
2	23.624	3691946	87833	80.058	70.043
Total		4611576	125399	100.000	100.000

Fig. S4. Fluorination of enantioenriched **1a**. (The ee was determined via HPLC analysis on a CHIRALPAK IB-3 column (100% hexanes, 0.3 mL/min).

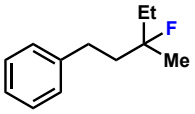
4. Fluorination of Chlorides/Bromides

General procedure 5 (GP-5)



Alkyl chlorides (0.2 mmol, 1.0 equiv.), AgF (28 mg, 0.22 mmol, 1.1 equiv.) and dry DCM (0.1 μL/mg) were added to a stainless-steel milling jar (1.5 mL) with a stainless-steel ball (6.0 mm diameter) in glove box and the reaction was carried out in a Retsch MM400 through 30 Hz ball milling. After grinding for 15 min, the mixture was eluted from silica gel with EtOAc, the solvent was removed by vacuum distillation, and the pure product was obtained by flash column chromatography.

(3-fluoro-3-methylpentyl)benzene (2a)



Compound **2a** was synthesized according to GP-5 and purified by flash column chromatography (100% hexanes). Colorless oil, 28.4 mg, 79% yield.

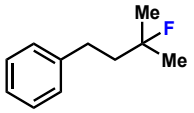
^{1}H NMR (400 MHz, CD_3CN) δ 7.29 – 7.23 (m, 2H), 7.22 – 7.13 (m, 3H), 2.68 – 2.61 (m, 2H), 1.90 – 1.79 (m, 2H), 1.73 – 1.60 (m, 2H), 1.31 (d, J = 21.9 Hz, 3H), 0.91 (t, J = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, CD_3CN) δ 143.39, 129.35, 129.23, 126.72, 98.27 (d, J = 166.9 Hz), 41.79 (d, J = 22.8 Hz), 32.80 (d, J = 23.6 Hz), 30.58 (d, J = 5.9 Hz), 23.93 (d, J = 24.8 Hz), 8.26 (d, J = 6.8 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -145.79.

Spectral data match those previously reported[4].

(3-fluoro-3-methylbutyl)benzene (2b)



Compound **2b** was synthesized according to GP-5 and purified by flash column chromatography (100% hexanes). Colorless oil, 23.6 mg, 71% yield.

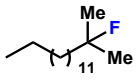
^{1}H NMR (400 MHz, CD_3CN) δ 7.29 – 7.24 (m, 2H), 7.22 – 7.13 (m, 3H), 2.71 – 2.63 (m, 2H), 1.90 – 1.82 (m, 2H), 1.36 (d, J = 21.5 Hz, 6H).

^{13}C NMR (151 MHz, CD_3CN) δ 143.32, 129.35, 129.21, 126.71, 96.23 (d, J = 164.6 Hz), 43.98 (d, J = 22.9 Hz), 30.88 (d, J = 5.7 Hz), 26.78 (d, J = 24.7 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -137.73.

Spectral data match those previously reported[3].

2-fluoro-2-methylpentadecane (2c)



Compound **2c** was synthesized according to GP-5 and purified by flash column chromatography (100% hexanes). Colorless oil, 41.1 mg, 84% yield.

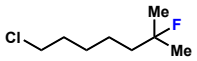
^{1}H NMR (400 MHz, CD_3CN) δ 1.62 – 1.50 (m, 2H), 1.37 – 1.21 (m, 28H), 0.89 – 0.82 (m, 3H).

^{13}C NMR (151 MHz, CD_3CN) δ 96.55 (d, J = 163.4 Hz), 42.01 (d, J = 22.6 Hz), 32.60, 30.66, 30.34, 30.31, 30.24, 30.21, 30.03, 26.78 (d, J = 24.8 Hz), 24.64 (d, J = 5.4 Hz), 23.35, 14.34.

^{19}F NMR (376 MHz, CD_3CN) δ -136.56.

Spectral data match those previously reported[1].

1-chloro-6-fluoro-6-methylheptane (2d)



Compound **2d** was synthesized according to GP-5 and purified by flash column chromatography (100% hexanes). Colorless oil, 20.3 mg, 61% yield.

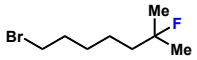
^{1}H NMR (400 MHz, CD_3CN) δ 3.57 (t, J = 6.7 Hz, 2H), 1.78 – 1.71 (m, 2H), 1.63 – 1.53 (m, 2H), 1.43 – 1.34 (m, 4H), 1.28 (d, J = 21.5 Hz, 6H).

^{13}C NMR (151 MHz, CD_3CN) δ 96.46 (d, J = 163.7 Hz), 46.11, 41.77 (d, J = 22.7 Hz), 33.22, 27.82, 26.76 (d, J = 24.8 Hz), 23.92 (d, J = 5.4 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -136.95.

Spectral data match those previously reported[3].

1-bromo-6-fluoro-6-methylheptane (2e)



Compound **2e** was synthesized according to GP-5 and purified by flash column chromatography (100% hexanes). Colorless oil, 35.1 mg, 83% yield.

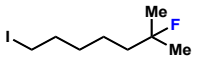
^{1}H NMR (400 MHz, CD_3CN) δ 3.47 (t, J = 6.8 Hz, 2H), 1.89 – 1.81 (m, 2H), 1.65 – 1.54 (m, 2H), 1.46 – 1.35 (m, 4H), 1.30 (d, J = 21.6 Hz, 6H).

^{13}C NMR (151 MHz, CD_3CN) δ 96.46 (d, J = 164.0 Hz), 41.75 (d, J = 22.7 Hz), 35.18, 33.44, 29.09, 26.76 (d, J = 24.8 Hz), 23.79 (d, J = 5.3 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -136.93.

Spectral data match those previously reported[3].

6-fluoro-1-iodo-6-methylheptane (2f)



Compound **2f** was synthesized according to GP-5 and purified by flash column chromatography (100% hexanes). Colorless oil, 42.7 mg, 83% yield.

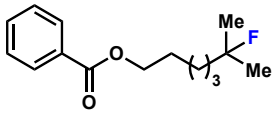
^{1}H NMR (400 MHz, CD_3CN) δ 3.23 (t, *J* = 6.9 Hz, 2H), 1.83 – 1.75 (m, 2H), 1.62 – 1.51 (m, 2H), 1.40 – 1.33 (m, 4H), 1.28 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (151 MHz, CD_3CN) δ 96.46 (d, *J* = 163.7 Hz), 41.72 (d, *J* = 22.9 Hz), 34.20, 31.39, 26.76 (d, *J* = 24.7 Hz), 23.56 (d, *J* = 5.1 Hz), 8.28.

^{19}F NMR (376 MHz, CD_3CN) δ -136.94.

Spectral data match those previously reported[3].

6-fluoro-6-methylheptyl benzoate (2g)



Compound **2g** was synthesized according to GP-5 and purified by flash column chromatography (5% EtOAc in hexanes). Colorless oil, 41.2 mg, 82% yield.

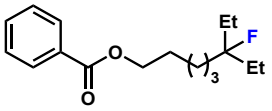
^{1}H NMR (400 MHz, CD_3CN) δ 8.02 – 7.95 (m, 2H), 7.64 – 7.55 (m, 1H), 7.50 – 7.42 (m, 2H), 4.26 (t, *J* = 6.6 Hz, 2H), 1.79 – 1.70 (m, 2H), 1.64 – 1.54 (m, 2H), 1.42 (m, 4H), 1.28 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (151 MHz, CD_3CN) δ 167.18, 133.90, 131.52, 130.14, 129.49, 96.48 (d, *J* = 163.6 Hz), 65.72, 41.86 (d, *J* = 22.7 Hz), 29.28, 26.97 (d, *J* = 34.2 Hz), 26.69, 24.34 (d, *J* = 5.3 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -138.35.

Spectral data match those previously reported[3].

6-ethyl-6-fluorooctyl benzoate (2h)



Compound **2h** was synthesized according to GP-5 and purified by flash column chromatography (5% EtOAc in hexanes). Colorless oil, 33.2 mg, 59% yield.

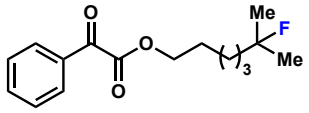
^{1}H NMR (400 MHz, CD_3CN) δ 8.01 – 7.95 (m, 2H), 7.62 – 7.55 (m, 1H), 7.50 – 7.42 (m, 2H), 4.26 (t, *J* = 6.6 Hz, 2H), 1.78 – 1.70 (m, 2H), 1.64 – 1.52 (m, 6H), 1.47 – 1.31 (m, 4H), 0.83 (t, *J* = 7.5 Hz, 6H).

^{13}C NMR (151 MHz, CD_3CN) δ 167.18, 133.90, 131.52, 130.14, 129.49, 100.37 (d, *J* = 168.2 Hz), 65.72, 36.52 (d, *J* = 23.1 Hz), 29.66 (d, *J* = 23.5 Hz), 29.28, 27.18, 23.66 (d, *J* = 5.7 Hz), 7.92 (d, *J* = 7.1 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -153.58.

Spectral data match those previously reported[3].

6-fluoro-6-methylheptyl 2-oxo-2-phenylacetate (2i)



Compound **2i** was synthesized according to GP-5 and purified by flash column chromatography (5% EtOAc in hexanes). Colorless oil, 48.4 mg, 86% yield.

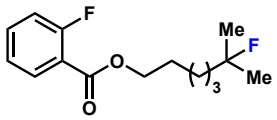
^{1}H NMR (400 MHz, CD_3CN) δ 7.97 – 7.93 (m, 2H), 7.75 – 7.69 (m, 1H), 7.59 – 7.53 (m, 2H), 4.36 (t, *J* = 6.6 Hz, 2H), 1.79 – 1.70 (m, 2H), 1.63 – 1.53 (m, 2H), 1.44 – 1.34 (m, 4H), 1.27 (d, *J* = 21.4 Hz, 6H).

^{13}C NMR (151 MHz, CD_3CN) δ 188.01, 165.05, 136.16, 133.28, 130.69, 130.07, 96.45 (d, *J* = 163.7 Hz), 67.19, 41.76 (d, *J* = 22.7 Hz), 28.96, 26.82 (d, *J* = 3.9 Hz), 26.67, 24.20 (d, *J* = 5.3 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -136.90.

Spectral data match those previously reported[1].

6-fluoro-6-methylheptyl 2-fluorobenzoate (2j)



Compound **2j** was synthesized according to GP-5 and purified by flash column chromatography (4% EtOAc in hexanes). Colorless oil, 43.4 mg, 80% yield.

^{1}H NMR (400 MHz, CD_3CN) δ 7.92 – 7.85 (m, 1H), 7.61 – 7.54 (m, 1H), 7.28 – 7.15 (m, 2H), 4.27 (t, *J* = 6.5 Hz, 2H), 1.77 – 1.69 (m, 2H), 1.65 – 1.52 (m, 2H), 1.46 – 1.34 (m, 4H), 1.28 (d, *J* = 21.5 Hz, 6H).

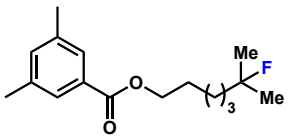
^{13}C NMR (151 MHz, CD_3CN) δ 164.94, 163.38, 161.67, 135.67, 132.77, 125.24, 117.81 (d, *J* = 22.4 Hz), 96.47 (d, *J* = 163.7 Hz), 66.01, 41.85 (d, *J* = 22.7 Hz), 29.19, 26.93 (d, *J* = 24.8 Hz), 26.68, 24.28 (d, *J* = 5.4 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -111.83, -136.81.

HRMS (ESI) m/z calcd for $C_{15}H_{20}F_2O_2$ $[M+Na]^+$: 293.13236, found 293.13226.

MIR (cm^{-1}): 2941, 1714, 1455, 1295, 1125, 1082, 866, 755.

6-fluoro-6-methylheptyl 3,5-dimethylbenzoate (2k)



Compound **2k** was synthesized according to GP-5 with 1.5 equiv. AgF added and

purified by flash column chromatography (4% EtOAc in hexanes). Colorless oil, 31.0 mg, 55% yield.

^{1}H NMR (400 MHz, CD_3CN) δ 7.58 (s, 2H), 7.22 (s, 1H), 4.22 (t, *J* = 6.6 Hz, 2H), 2.31 (s, 6H), 1.77 – 1.67 (m, 2H), 1.64 – 1.52 (m, 2H), 1.41 (m, 4H), 1.27 (d, *J* = 21.5 Hz, 6H).

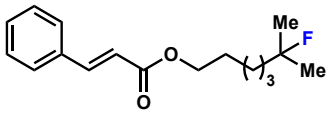
^{13}C NMR (151 MHz, CD_3CN) δ 167.18, 139.07, 135.10, 131.24, 127.56, 96.26 (d, *J* = 163.7 Hz), 65.38, 41.64 (d, *J* = 22.7 Hz), 29.06, 26.90, 26.55 (d, *J* = 24.4 Hz), 24.13 (d, *J* = 5.3 Hz), 20.91.

^{19}F NMR (376 MHz, CD_3CN) δ -136.76.

HRMS (ESI) m/z calcd for $C_{17}H_{25}FO_2$ $[M+Na]^+$: 303.17308, found 303.17306.

MIR (cm^{-1}): 2939, 1715, 1453, 1307, 1210, 767, 679.

6-fluoro-6-methylheptyl cinnamate (2l)



Compound **2l** was synthesized according to GP-5 and purified by flash column chromatography (5% EtOAc in hexanes). Colorless oil, 40.8 mg, 73% yield.

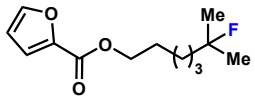
^{1}H NMR (400 MHz, CD_3CN) δ 7.68 – 7.57 (m, 3H), 7.42 – 7.36 (m, 3H), 6.48 (d, *J* = 16.1 Hz, 1H), 4.14 (t, *J* = 6.6 Hz, 2H), 1.71 – 1.52 (m, 4H), 1.44 – 1.32 (m, 4H), 1.28 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (151 MHz, CD_3CN) δ 167.51, 145.13, 135.40, 131.27, 129.87, 129.06, 119.27, 96.48 (d, *J* = 163.7 Hz), 65.18, 41.85 (d, *J* = 22.7 Hz), 29.32, 26.92 (d, *J* = 18.9 Hz), 26.70, 24.32 (d, *J* = 5.3 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -136.80.

Spectral data match those previously reported[4].

6-fluoro-6-methylheptyl furan-2-carboxylate (2m)



Compound **2m** was synthesized according to GP-5 and purified by flash column chromatography (5% EtOAc in hexanes). Colorless oil, 38.1 mg, 79% yield.

^{1}H NMR (400 MHz, CD_3CN) δ 7.66 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.15 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.54 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.21 (t, *J* = 6.6 Hz, 2H), 1.73 – 1.65 (m, 2H), 1.62 – 1.50 (m, 2H), 1.43 – 1.33 (m, 4H), 1.27 (d, *J* = 21.6 Hz, 6H).

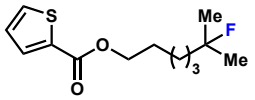
^{13}C NMR (151 MHz, CD_3CN) δ 159.37, 147.79, 145.78, 118.61, 112.86, 96.47 (d, *J* = 163.7 Hz), 65.54, 41.82 (d, *J* = 22.7 Hz), 29.24, 26.89 (d, *J* = 13.6 Hz), 26.68, 24.28 (d,

J = 5.3 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -136.83.

Spectral data match those previously reported[4].

6-fluoro-6-methylheptyl thiophene-2-carboxylate (2n)



Compound **2n** was synthesized according to GP-5 and purified by flash column chromatography (5% EtOAc in hexanes). Colorless oil, 40.7 mg, 79% yield.

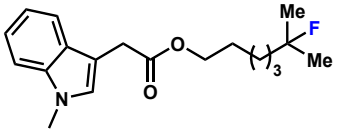
^{1}H NMR (400 MHz, CD_3CN) δ 7.75 (dd, J = 3.7, 1.3 Hz, 1H), 7.67 (dd, J = 5.0, 1.3 Hz, 1H), 7.13 (dd, J = 5.1, 3.8 Hz, 1H), 4.23 (t, J = 6.6 Hz, 2H), 1.77 – 1.66 (m, 2H), 1.63 – 1.52 (m, 2H), 1.44 – 1.36 (m, 4H), 1.28 (d, J = 21.5 Hz, 6H).

^{13}C NMR (151 MHz, CD_3CN) δ 162.88, 134.89, 134.17, 133.76, 129.02, 96.47 (d, J = 163.7 Hz), 65.89, 41.85 (d, J = 22.7 Hz), 29.25, 26.93 (d, J = 23.6 Hz), 26.68, 24.30 (d, J = 5.4 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -136.79.

Spectral data match those previously reported[4].

6-fluoro-6-methylheptyl 2-(1-methyl-1H-indol-3-yl)acetate (2o)



Compound **2o** was synthesized according to GP-5 and purified by flash column chromatography (10% EtOAc in hexanes). Colorless oil, 43.0 mg, 67% yield.

^{1}H NMR (400 MHz, CD_3CN) δ 7.50 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.3, 1H), 7.21 – 7.13 (m, 1H), 7.08 – 7.00 (m, 2H), 4.02 (t, J = 6.6 Hz, 2H), 3.72 (s, 3H), 3.69 (s, 2H), 1.61 – 1.45 (m, 4H), 1.32 – 1.23 (m, 10H).

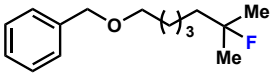
^{13}C NMR (151 MHz, CD_3CN) δ 172.87, 137.89, 129.01, 128.66, 122.39, 119.78, 119.72, 110.37, 107.99, 96.45 (d, J = 163.6 Hz), 65.20, 41.81 (d, J = 22.7 Hz), 32.98, 31.66, 29.27, 26.85 (d, J = 5.5 Hz), 26.67, 24.22 (d, J = 5.4 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -136.77.

HRMS (ESI) m/z calcd for $C_{19}H_{26}FNO_2$ $[M+K]^+$:358.15792, found 358.15850.

MIR (cm^{-1}): 2938, 1730, 1471, 1373, 1140, 868, 737.

(((6-fluoro-6-methylheptyl)oxy)methyl)benzene (2p)



Compound **2p** was synthesized according to GP-5 and purified by flash column chromatography (4% EtOAc in hexanes). Colorless oil, 34.0 mg, 71% yield.

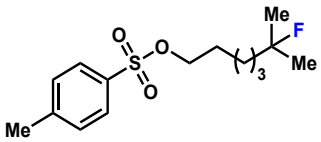
^{1}H NMR (400 MHz, CD_3CN) δ 7.35 – 7.22 (m, 5H), 4.43 (s, 2H), 3.43 (t, *J* = 6.5 Hz, 2H), 1.63 – 1.50 (m, 4H), 1.39 – 1.31 (m, 4H), 1.27 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (151 MHz, CD_3CN) δ 140.12, 129.20, 128.50, 128.28, 96.51 (d, *J* = 163.6 Hz), 73.19, 70.90, 41.95 (d, *J* = 22.7 Hz), 30.33, 27.07 (d, *J* = 65.0 Hz), 26.69, 24.46 (d, *J* = 5.4 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -136.64.

Spectral data match those previously reported[3].

6-fluoro-6-methylheptyl 4-methylbenzenesulfonate (2q)



Compound **2q** was synthesized according to GP-5 and purified by flash column chromatography (10% EtOAc in hexanes). Colorless oil, 53.9 mg, 89% yield.

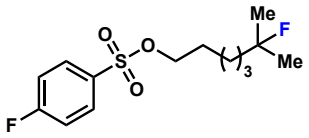
^{1}H NMR (400 MHz, CD_3CN) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 3.98 (t, *J* = 6.3 Hz, 2H), 2.41 (s, 3H), 1.64 – 1.54 (m, 2H), 1.54 – 1.41 (m, 2H), 1.31 – 1.16 (m, 10H).

^{13}C NMR (151 MHz, CD_3CN) δ 146.21, 133.97, 130.94, 128.66, 96.37 (d, *J* = 163.7 Hz), 71.90, 41.63 (d, *J* = 22.9 Hz), 29.21, 26.72 (d, *J* = 24.7 Hz), 26.24, 23.87 (d, *J* = 5.5 Hz), 21.57.

^{19}F NMR (376 MHz, CD_3CN) δ -136.94.

Spectral data match those previously reported[3].

6-fluoro-6-methylheptyl 4-fluorobenzenesulfonate (2r)



Compound **2r** was synthesized according to GP-5 and purified by flash column chromatography (10% EtOAc in hexanes). Colorless oil, 41.6 mg, 68% yield.

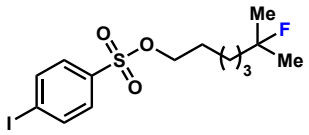
^{1}H NMR (400 MHz, CD_3CN) δ 7.95 – 7.91 (m, 2H), 7.37 – 7.30 (m, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 1.64 – 1.56 (m, 2H), 1.55 – 1.45 (m, 2H), 1.29 – 1.21 (m, 10H).

^{13}C NMR (151 MHz, CD_3CN) δ 166.69 (d, *J* = 253.7 Hz), 133.15 (d, *J* = 3.2 Hz), 131.79 (d, *J* = 9.9 Hz), 117.65 (d, *J* = 23.1 Hz), 96.37 (d, *J* = 163.7 Hz), 72.35, 41.63 (d, *J* = 22.7 Hz), 29.21, 26.72 (d, *J* = 24.8 Hz), 26.22, 23.87 (d, *J* = 5.2 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -105.59, -137.01.

Spectral data match those previously reported[3].

6-fluoro-6-methylheptyl 4-iodobenzenesulfonate (2s)



Compound **2s** was synthesized according to GP-5 with 1.5 equiv. AgF added and purified by flash column chromatography (5% EtOAc in hexanes). Colorless oil, 66.1 mg, 80% yield.

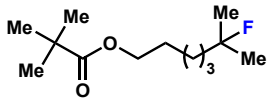
^{1}H NMR (400 MHz, CD_3CN) δ 8.01 – 7.96 (m, 2H), 7.62 – 7.57 (m, 2H), 4.02 (t, *J* = 6.3 Hz, 2H), δ 1.63 – 1.43 (m, 4H), 1.29 – 1.20 (m, 10H).

^{13}C NMR (151 MHz, CD_3CN) δ 139.72, 136.68, 130.10, 102.08, 96.37 (d, *J* = 163.8 Hz), 72.54, 41.62 (d, *J* = 22.8 Hz), 29.18, 26.74 (d, *J* = 24.7 Hz), 26.18, 23.84 (d, *J* = 5.4 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -136.98.

Spectral data match those previously reported[3].

6-fluoro-6-methylheptyl pivalate (2t)



Compound **2t** was synthesized according to GP-5 and purified by flash column chromatography (4% EtOAc in hexanes). Colorless oil, 38.0 mg, 82% yield.

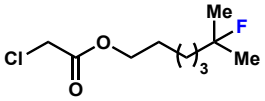
^{1}H NMR (400 MHz, CD_3CN) δ 3.99 (t, *J* = 6.5 Hz, 2H), 1.63 – 1.51 (m, 4H), 1.41 – 1.36 – 1.22 (m, 10H), 1.13 (s, 9H).

^{13}C NMR (151 MHz, CD_3CN) δ 178.96, 96.47 (d, *J* = 163.7 Hz), 64.90, 41.86 (d, *J* = 22.7 Hz), 39.28, 29.24, 27.37, 26.91 (d, *J* = 20.9 Hz), 26.68, 24.27 (d, *J* = 5.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -137.44.

Spectral data match those previously reported[1].

6-fluoro-6-methylheptyl 2-chloroacetate (2u)



Compound **2u** was synthesized according to GP-5 and purified by flash column chromatography (4% EtOAc in hexanes). Colorless oil, 31.1 mg, 69% yield.

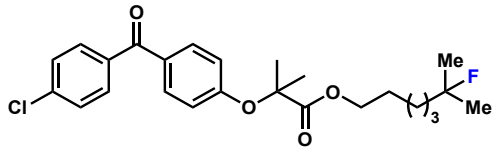
^{1}H NMR (400 MHz, CD_3CN) δ 4.15 – 4.09 (m, 4H), 1.67 – 1.51 (m, 4H), 1.42 – 1.32 (m, 4H), 1.28 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (151 MHz, CD_3CN) δ 168.35, 96.46 (d, *J* = 163.7 Hz), 66.73, 42.12, 41.80 (d, *J* = 22.8 Hz), 29.05, 26.80 (d, *J* = 13.7 Hz), 26.68, 24.22 (d, *J* = 5.4 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -136.89.

Spectral data match those previously reported[1].

6-fluoro-6-methylheptyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (2v)



Compound **2v** was synthesized according to GP-5 and purified by flash column chromatography (5% EtOAc in hexanes). Colorless oil, 69.2 mg, 77% yield.

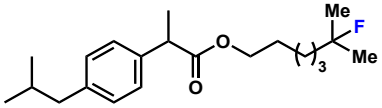
^{1}H NMR (400 MHz, CD_3CN) δ 7.70 – 7.63 (m, 4H), 7.50 – 7.46 (m, 2H), 6.86 – 6.81 (m, 2H), 4.10 (t, *J* = 6.3 Hz, 2H), 1.60 (s, 6H), 1.58 – 1.35 (m, 5H), 1.29 – 1.10 (m, 9H).

^{13}C NMR (151 MHz, CD_3CN) δ 194.63, 174.25, 160.64, 138.60, 137.60, 132.92, 132.12, 131.04, 129.40, 118.02, 96.37 (d, *J* = 163.7 Hz), 80.34, 66.36, 41.77 (d, *J* = 22.7 Hz), 28.99, 26.74 (d, *J* = 25.7 Hz), 26.57, 25.70, 24.15 (d, *J* = 5.3 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -136.95.

Spectral data match those previously reported[3].

6-fluoro-6-methylheptyl 2-(4-isobutylphenyl)propanoate (2w)



Compound **2w** was synthesized according to GP-5with 1.5 equiv. AgF added and purified by flash column chromatography (4% EtOAc in hexanes). Colorless oil, 38.4 mg, 57% yield.

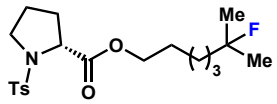
^{1}H NMR (400 MHz, CD_3CN) δ 7.19 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 4.09 – 3.96 (m, 2H), 3.70 (q, *J* = 7.2 Hz, 1H), 2.45 (d, *J* = 7.1 Hz, 2H), 1.83 (dp, *J* = 13.6, 6.8 Hz, 1H), 1.59 – 1.47 (m, 4H), 1.41 (d, *J* = 7.1 Hz, 3H), 1.36 – 1.19 (m, 4H), 1.28 (d, *J* = 21.5 Hz, 6H), 0.88 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, CD_3CN) δ 174.81, 140.92, 138.90, 129.67, 127.58, 95.90 (d, *J* = 163.7 Hz), 64.63, 45.26, 44.85, 41.31 (d, *J* = 22.7 Hz), 30.46, 28.66, 26.29 (d, *J* = 11.5 Hz), 26.17, 23.66 (d, *J* = 5.5 Hz), 22.01, 18.31.

^{19}F NMR (376 MHz, CD_3CN) δ -136.85.

Spectral data match those previously reported[4].

6-fluoro-6-methylheptyl tosyl-*L*-prolinate (2x)



Compound **2x** was synthesized according to GP-5 with 1.5 equiv. AgF added and purified by flash column chromatography (10% EtOAc in hexanes). Colorless oil, 40.0 mg, 50% yield.

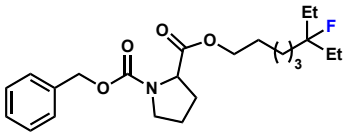
^{1}H NMR (400 MHz, CD_3CN) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 4.18 – 4.14 (m, 1H), 4.12 – 4.01 (m, 2H), 3.45 – 3.36 (m, 1H), 3.25 – 3.18 (m, 1H), 2.41 (s, 3H), 1.98 – 1.82 (m, 3H), 1.68 – 1.53 (m, 5H), 1.44 – 1.31 (m, 4H), 1.30 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (151 MHz, CD_3CN) δ 173.06, 144.96, 135.96, 130.72, 128.25, 96.48 (d, *J* = 163.7 Hz), 65.84, 61.66, 49.49, 41.83 (d, *J* = 22.7 Hz), 31.58, 29.12, 26.84 (d, *J* = 5.9 Hz), 26.70, 25.26, 24.24 (d, *J* = 5.4 Hz), 21.47.

^{19}F NMR (376 MHz, CD_3CN) δ -136.60 – -136.93 (m).

Spectral data match those previously reported[4].

1-benzyl 2-(6-ethyl-6-fluorooctyl) pyrrolidine-1,2-dicarboxylate (2y)



Compound **2y** was synthesized according to GP-5 with 1.5 equiv. AgF added and purified by flash column chromatography (16% EtOAc in hexanes). Colorless oil, 41.6 mg, 51% yield.

^{1}H NMR (400 MHz, CD_3OD) δ 7.38 – 7.28 (m, 5H), 5.19 – 4.99 (m, 2H), 4.38 – 4.30 (m, 1H), 4.16 – 3.93 (m, 2H), 3.61 – 3.42 (m, 2H), 2.36 – 2.21 (m, 1H), 2.02 – 1.89 (m, 3H), 1.81 – 1.70 (m, 2H), 1.68 – 1.47 (m, 6H), 1.41 – 1.22 (m, 4H), 0.97 – 0.84 (m, 6H).

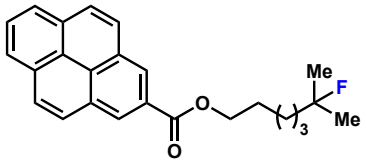
^{13}C NMR (151 MHz, CD_3CN) δ 173.72 (d, *J* = 42.8 Hz), 155.21 (d, *J* = 76.2 Hz), 138.14 (d, *J* = 29.4 Hz), 129.36 (d, *J* = 11.8 Hz), 128.80 (d, *J* = 8.7 Hz), 128.51 (d, *J* = 11.0 Hz), 100.33 (d, *J* = 168.5 Hz), 67.30, 65.60 (d, *J* = 20.3 Hz), 60.08 (d, *J* = 75.3 Hz), 47.50 (d, *J* = 71.2 Hz), 36.47 (d, *J* = 22.9 Hz), 31.54, 30.53, 29.64 (d, *J* = 23.8 Hz), 29.17 (d, *J* = 8.7 Hz), 26.90 (d, *J* = 2.0 Hz), 24.99, 24.12, 25.53 (d, *J* = 6.0 Hz), 7.92 (d, *J* = 7.0 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -153.64.

HRMS (ESI) m/z calcd for $C_{23}H_{34}FNO_4$ $[M+K]^+$: 446.21034, found 446.21120.

MIR (cm^{-1}): 2943, 1705, 1411, 1350, 1170, 735, 697.

6-fluoro-6-methylheptyl pyrene-2-carboxylate (2z)



Compound **2z** was synthesized according to GP-5 with 1.5 equiv. AgF and 0.4 μL/mg dry DCM added, 30 Hz ball milling for 1 h. White powder, 67.8 mg, 90% yield.

^{1}H NMR (400 MHz, CD_3CN) δ 9.10 (d, *J* = 9.4 Hz, 1H), 8.53 (d, *J* = 8.2 Hz, 1H), 8.28 (d, *J* = 7.7 Hz, 2H), 8.24 – 8.15 (m, 3H), 8.12 – 8.02 (m, 2H), 4.44 (t, *J* = 6.6 Hz, 2H), 1.85 (dq, *J* = 8.0, 6.5 Hz, 2H), 1.70 – 1.57 (m, 2H), 1.56 – 1.40 (m, 4H), 1.30 (d, *J* = 21.5 Hz, 6H).

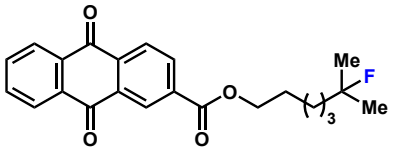
^{13}C NMR (151 MHz, Acetonitrile-d3) δ 168.70, 135.07, 131.98, 131.46, 131.26, 130.49, 130.20, 129.14, 128.13, 127.60, 127.40, 127.16, 125.58, 125.41, 125.29, 125.20, 124.80, 96.51 (d, J = 163.7 Hz), 66.11, 41.90 (d, J = 22.8 Hz), 29.39, 27.25, 26.80 (d, J = 24.8 Hz), 24.41 (d, J = 5.4 Hz).

^{19}F NMR NMR (376 MHz, CD_3CN) δ -136.54 – -136.99 (m).

HRMS (ESI) m/z calcd for $C_{25}H_{25}FO_2$ $[M+Na]^+$: 399.17308, found 399.17321.

MIR (cm^{-1}): 2939, 1706, 1372, 1145, 737.

6-fluoro-6-methylheptyl 9,10-dioxo-9,10-dihydroanthracene-2-carboxylate (2aa)



Compound **2aa** was synthesized according to GP-5 with 1.5 equiv. AgF and 0.4 μL/mg dry DCM added, 30 Hz ball milling for 1 h. White powder, 62.0 mg, 81% yield.

^{1}H NMR (400 MHz, CD_3CN) δ 8.66 (d, J = 1.7 Hz, 1H), 8.33 (dd, J = 8.1, 1.8 Hz, 1H), 8.26 (d, J = 8.1 Hz, 1H), 8.24 – 8.19 (m, 2H), 7.89 – 7.83 (m, 2H), 4.36 (t, J = 6.6 Hz, 2H), 1.82 (dq, J = 8.7, 6.7 Hz, 2H), 1.71 – 1.59 (m, 2H), 1.54 – 1.40 (m, 4H), 1.32 (d, J = 21.5 Hz, 6H).

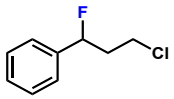
^{13}C NMR (151 MHz, CD_3CN) δ 183.33, 183.15, 165.73, 136.99, 136.38, 135.60, 135.57, 135.17, 134.51, 134.32, 128.46, 128.26, 127.90, 127.89, 96.50 (d, *J* = 163.7 Hz), 66.63, 41.87 (d, *J* = 22.7 Hz), 29.18, 27.05, 26.80 (d, *J* = 24.5 Hz), 24.34 (d, *J* = 5.4 Hz).

^{19}F NMR NMR (376 MHz, CD_3CN) δ -136.41 – -136.98 (m).

HRMS (ESI) m/z calcd for $C_{23}H_{23}FO_4$ $[M+Na]^+$: 405.14726, found 405.14925.

MIR (cm^{-1}): 2940, 1723, 1268, 1166, 705.

(3-chloro-1-fluoropropyl)benzene (2ab)



Compound **2ab** was synthesized according to GP-5 and purified by flash column chromatography (100% hexanes). Colorless oil, 20.3 mg, 59% yield.

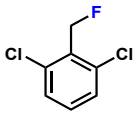
^{1}H NMR (400 MHz, CD_3CN) δ 7.47 – 7.32 (m, 5H), 5.68 (ddd, *J* = 48.1, 9.1, 3.9 Hz, 1H), 3.80 – 3.71 (m, 1H), 3.69 – 3.61 (m, 1H), 2.53 – 2.37 (m, 1H), 2.30 – 2.17 (m, 1H).

^{13}C NMR (151 MHz, CD_3CN) δ 140.24 (d, *J* = 19.3 Hz), 129.58, 126.71, 126.66, 92.56 (d, *J* = 168.8 Hz), 41.64 (d, *J* = 4.9 Hz), 40.39 (d, *J* = 24.3 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -177.90.

Spectral data match those previously reported[5].

1,3-dichloro-2-(fluoromethyl)benzene (2ac)



Compound **2ac** was synthesized according to GP-5 and purified by flash column chromatography (100% hexanes). Colorless oil, 20.5 mg, 57% yield.

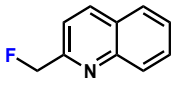
^{1}H NMR (400 MHz, CD_3CN) δ 7.50 – 7.44 (m, 2H), 7.42 – 7.34 (m, 1H), 5.68 (d, *J* = 47.5 Hz, 2H).

^{13}C NMR (151 MHz, CD_3CN) δ 137.69 (d, *J* = 3.9 Hz), 132.96 (d, *J* = 4.3 Hz), 132.02 (d, *J* = 14.7 Hz), 129.72 (d, *J* = 2.9 Hz), 79.89 (d, *J* = 163.2 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -211.56.

Spectral data match those previously reported[6].

2-(fluoromethyl)quinoline (2ad)



Compound **2ad** was synthesized according to GP-5 with 1.5 equiv. AgF added and purified by flash column chromatography (4% EtOAc in hexanes). Colorless oil, 25.3 mg, 78% yield.

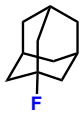
^{1}H NMR (400 MHz, CD_3CN) δ 8.35 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.63 – 7.55 (m, 2H), 5.62 (d, *J* = 47.0 Hz, 2H).

^{13}C NMR (151 MHz, CD_3CN) δ 157.65 (d, *J* = 20.4 Hz), 148.33, 138.09, 130.86, 129.82, 128.86, 128.61, 127.76, 119.66 (d, *J* = 4.4 Hz), 86.28 (d, *J* = 166.5 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -219.78.

Spectral data match those previously reported[7].

(3s,5s,7s)-1-fluoroadamantane (2ae)



Compound **2ae** was synthesized according to GP-5 and purified by thin layer chromatography (100% hexanes). White solid, 25.1 mg, 81% yield.

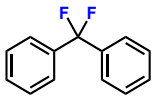
^{1}H NMR (400 MHz, CD_3CN) δ 2.20 (s, 3H), 1.89-1.83 (m, 6H), 1.71 – 1.55 (m, 6H).

^{13}C NMR (151 MHz, CD_3CN) δ 93.05 (d, J = 182.5 Hz), 43.33 (d, J = 17.2 Hz), 36.34 (d, J = 1.9 Hz), 32.40 (d, J = 9.6 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -127.68.

Spectral data match those previously reported[3].

Difluorodiphenylmethane (2af)



Compound **2af** was synthesized according to GP-5with AgF (56 mg, 0.44 mmol, 2.2 equiv.) and purified by flash column chromatography (5% EtOAc in hexanes). Colorless oil, 28.5 mg, 70% yield.

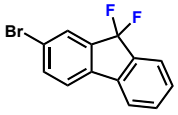
^{1}H NMR (400 MHz, CD_3CN) δ 7.56-7.50 (m, 4H), 7.50-7.44 (m, 6H).

^{13}C NMR (151 MHz, CD_3CN) δ 138.47 (t, J = 28.4 Hz), 131.09, 129.62, 126.36 (t, J = 5.8 Hz), 121.91 (t, J = 241.0 Hz).

^{19}F NMR (376 MHz, CD_3CN) δ -89.78.

Spectral data match those previously reported[8].

2-bromo-9,9-difluoro-9*H*-fluorene (2ag)



Compound **2ag** was synthesized according to GP-5with AgF (64 mg, 0.5 mmol, 2.5 equiv.) and purified by flash column chromatography (5% EtOAc in hexanes). Pale yellow solid, 40.1 mg, 71% yield.

^{1}H NMR (600 MHz, CD_3CN) δ 7.81 (t, J = 1.8 Hz, 1H), 7.70 – 7.66 (m, 2H), 7.63 (d, J = 7.6 Hz, 1H), 7.59 (d, J = 8.1 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H).

^{13}C NMR (151 MHz, CD_3CN) δ 140.31 (t, J = 25.4 Hz), 139.45 (t, J = 4.9 Hz), 139.23

(t, J = 5.1 Hz), 137.91 (t, J = 24.9 Hz), 136.43, 133.78, 130.48, 127.81, 124.61, 123.70, 123.64, 122.95, 122.12.

^{19}F NMR (376 MHz, CD_3CN) δ -111.63.

HRMS (ESI) m/z calcd for $C_{13}H_7BrF_2$ $[M+Li]^+$: 286.98537, found 286.98963.

MIR (cm^{-1}): 1450, 1416, 1354, 771, 758, 727, 665.

5. References

1 Bertrand, X., Pucheault, M., Chabaud, L. & Paquin, J.-F. Synthesis of Tertiary Fluorides through an Acid-Mediated Deoxyfluorination of Tertiary Alcohols. *J. Org. Chem.* **88**, 14527-14539 (2023).

2 Zhang, J. *et al.* Transition-metal free C–N bond formation from alkyl iodides and diazonium salts via halogen-atom transfer. *Nat. Commun.* **13**, 7961 (2022).

3 Zhang, W., Gu, Y.-C., Lin, J.-H. & Xiao, J.-C. Dehydroxylative Fluorination of Tertiary Alcohols. *Org. Lett.* **22**, 6642-6646 (2020).

4 Wang, Z.-Y., Freas, D. J. & Fu, G. C. Phosphine Catalysis of the Fluorination of Unactivated Tertiary Alkyl Chlorides under Mild and Convenient Conditions. *J. Am. Chem. Soc.* **145**, 25093-25097 (2023).

5 Cantillo, D., de Frutos, O., Rincón, J. A., Mateos, C. & Kappe, C. O. A Continuous-Flow Protocol for Light-Induced Benzylic Fluorinations. *J. Org. Chem.* **79**, 8486-8490 (2014).

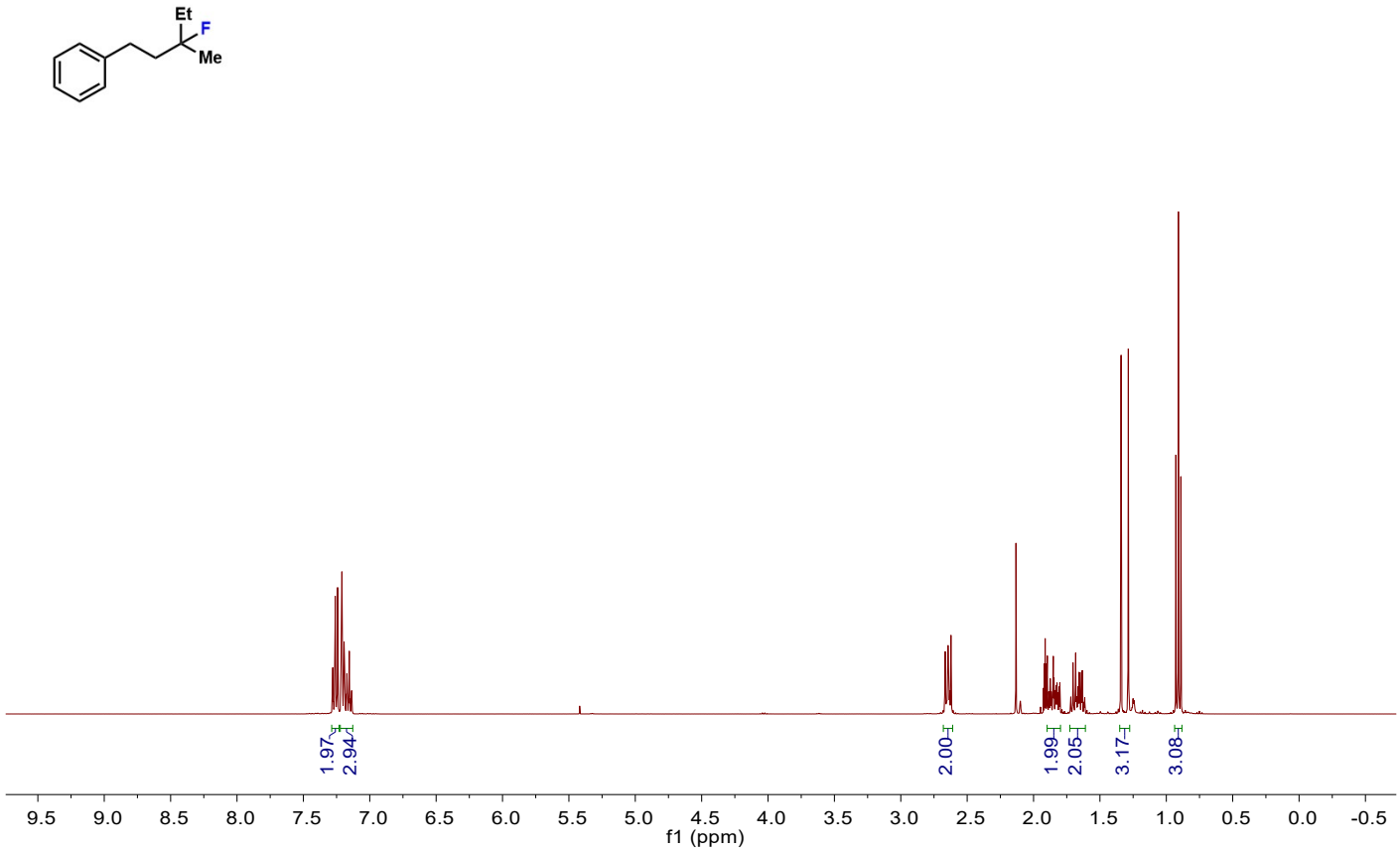
6 Alič, B., Petrovčič, J., Jelen, J., Tavčar, G. & Iskra, J. Renewable Reagent for Nucleophilic Fluorination. *J. Org. Chem.* **87**, 5987-5993 (2022).

7 Pang, X., Xiang, L., Ma, J., Yang, X. & Yan, R. Halogenations of substituted 2-alkylquinoline with iodine and halide exchange with AgF2. *RSC Adv.* **6**, 111713-111717 (2016).

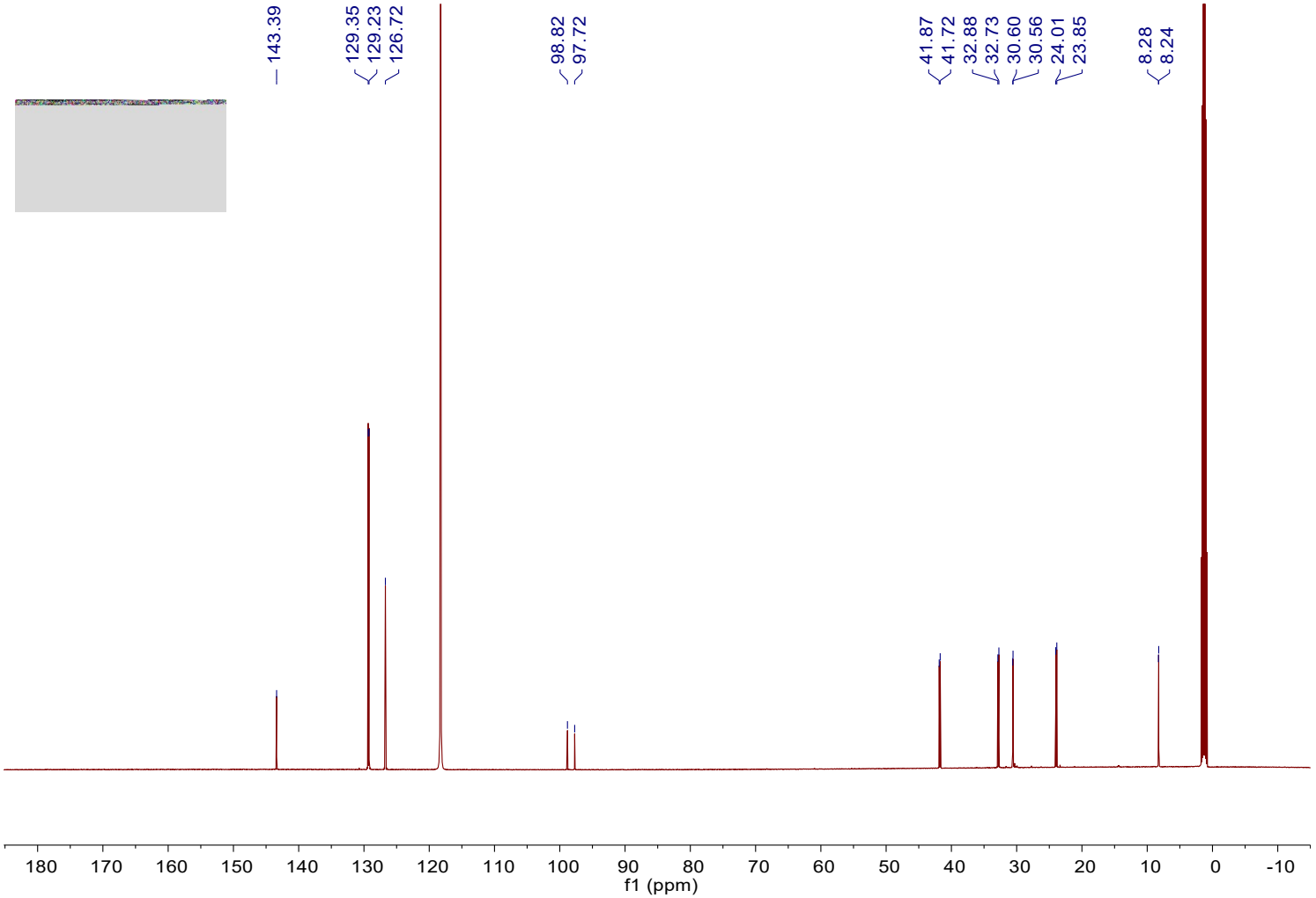
8 Geri, J. B., Wade Wolfe, M. M. & Szymczak, N. K. The Difluoromethyl Group as a Masked Nucleophile: A Lewis Acid/Base Approach. *J. Am. Chem. Soc.* **140**, 9404-9408 (2018).

6. NMR Spectra

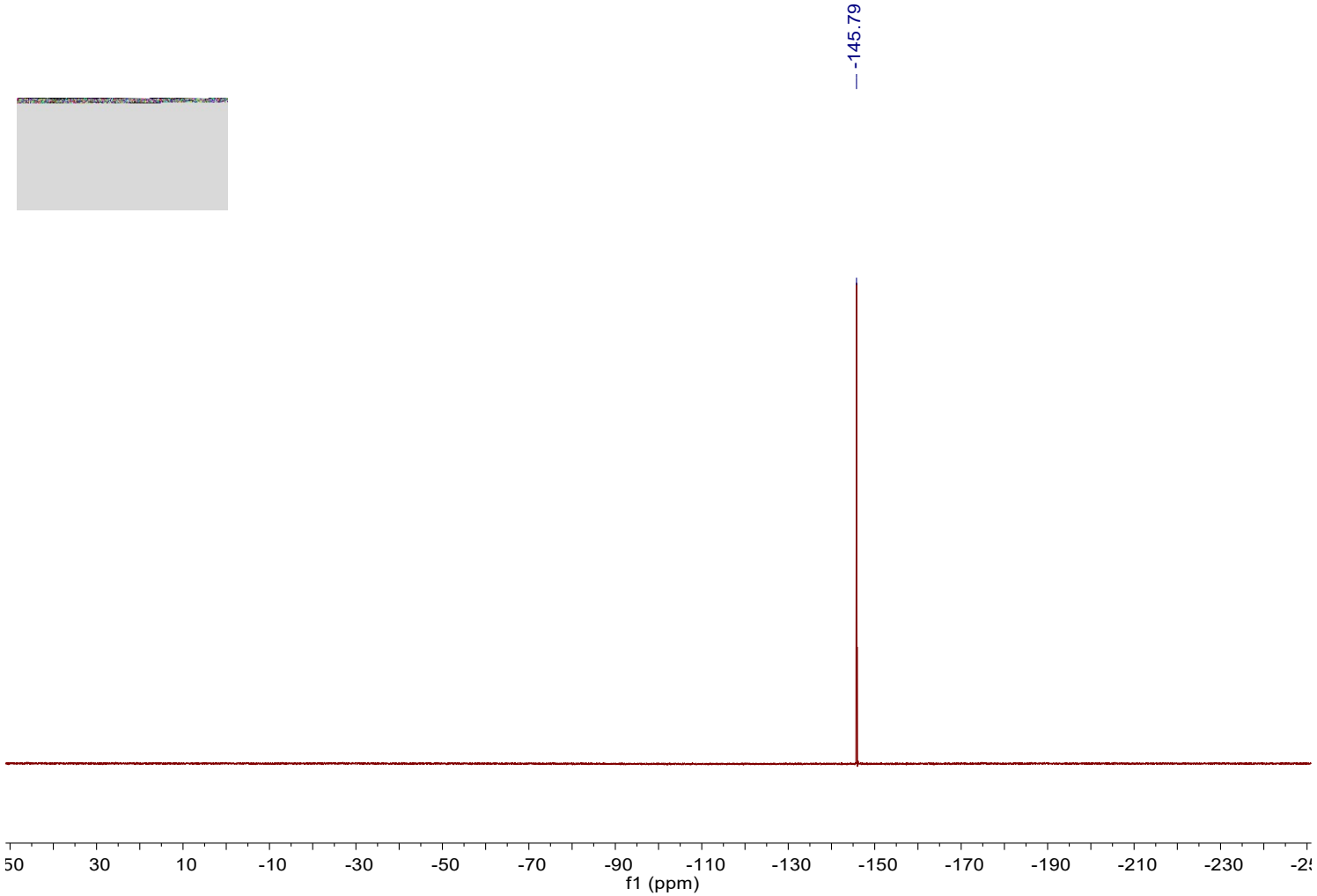
Compound **2a** ^{1}H NMR (400 MHz, CD_3CN)



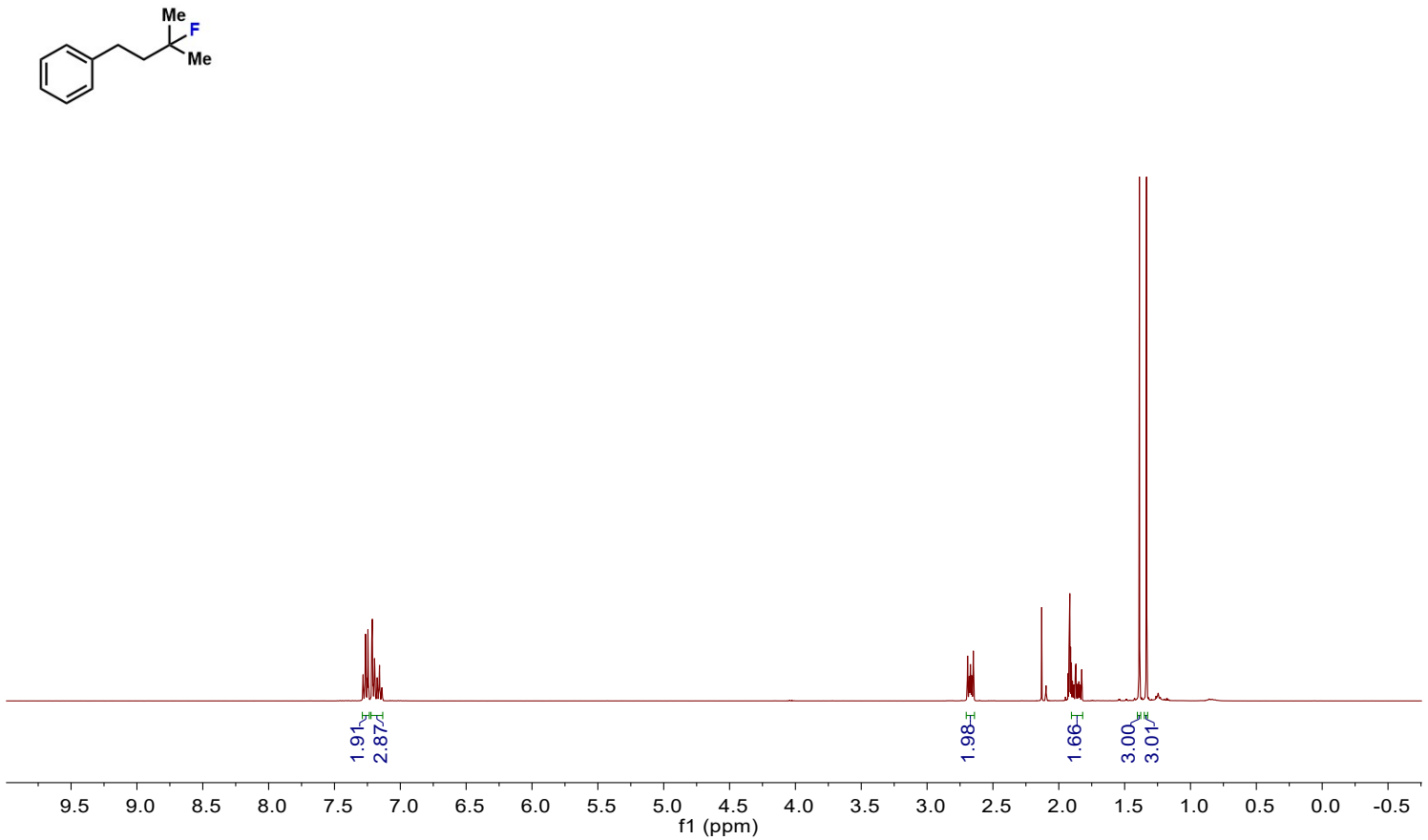
Compound **2a** ^{13}C NMR (151 MHz, CD_3CN)



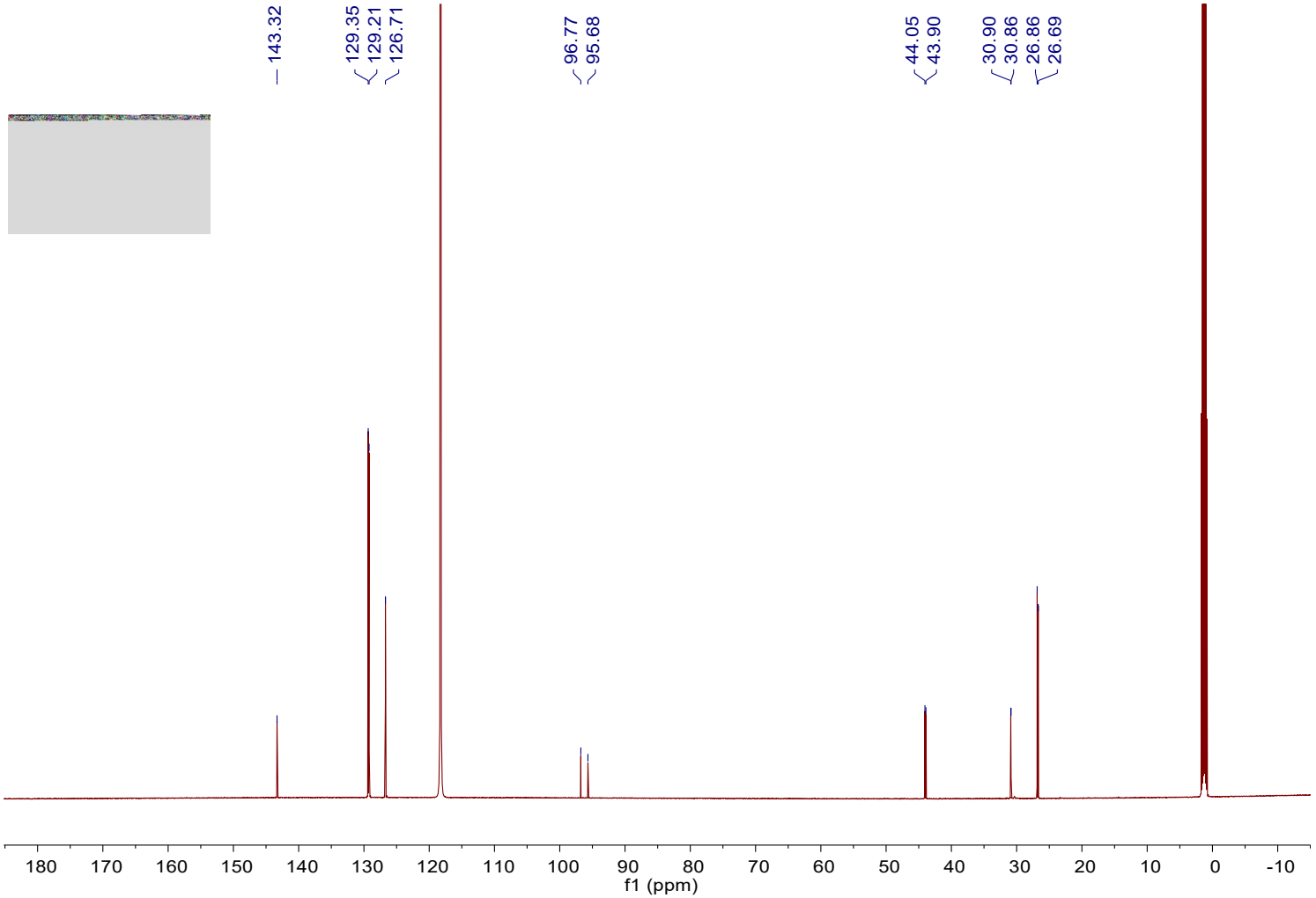
Compound **2a** ^{19}F NMR (376 MHz, CD_3CN)



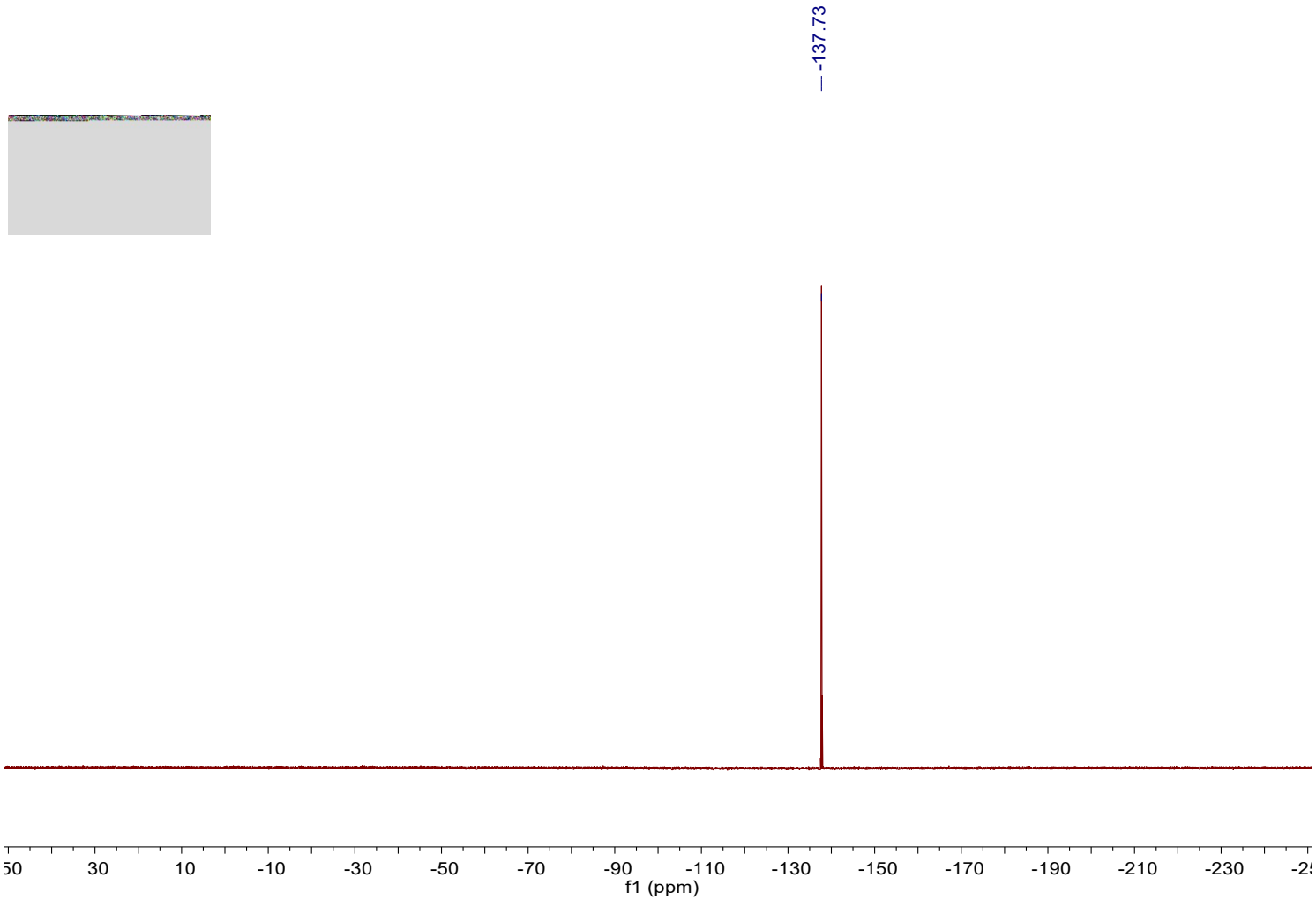
Compound **2b** ^{1}H NMR (400 MHz, CD_3CN)



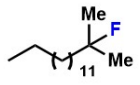
Compound **2b** ^{13}C NMR (151 MHz, CD_3CN)

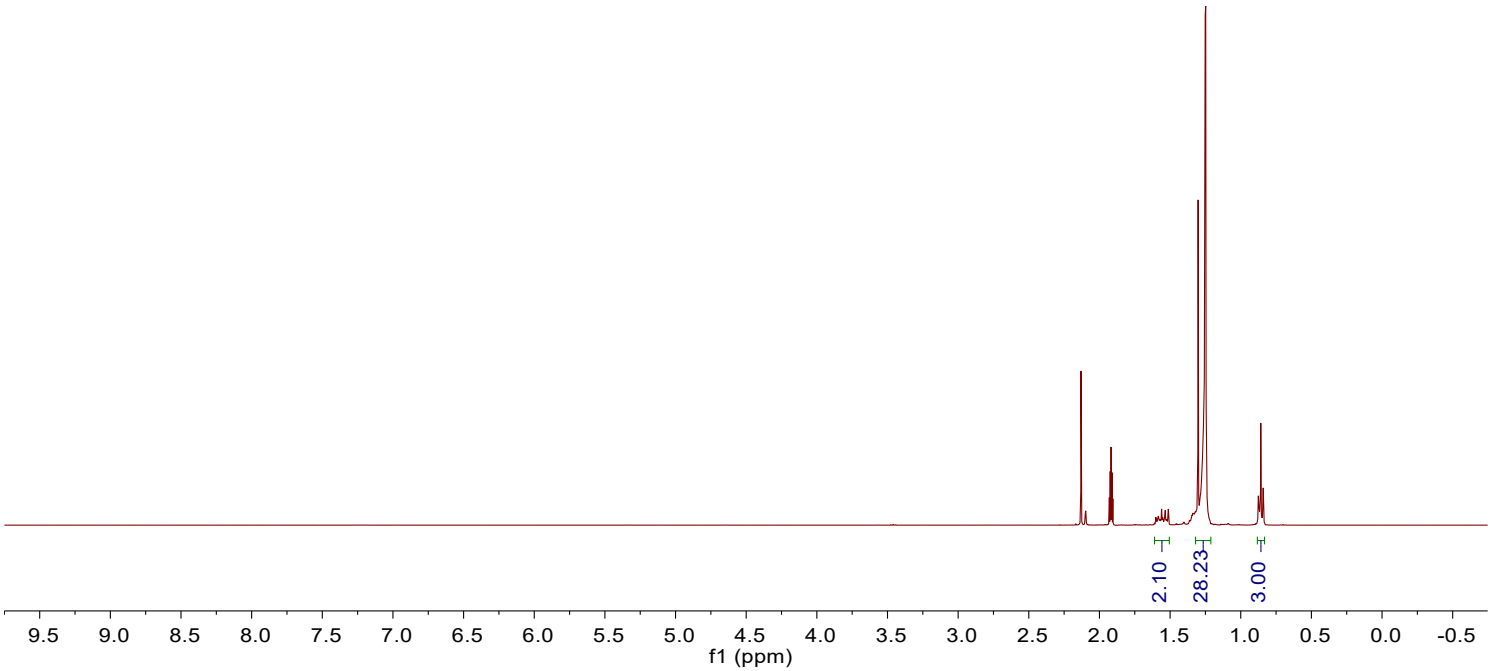


Compound **2b** ^{19}F NMR (376 MHz, CD_3CN)

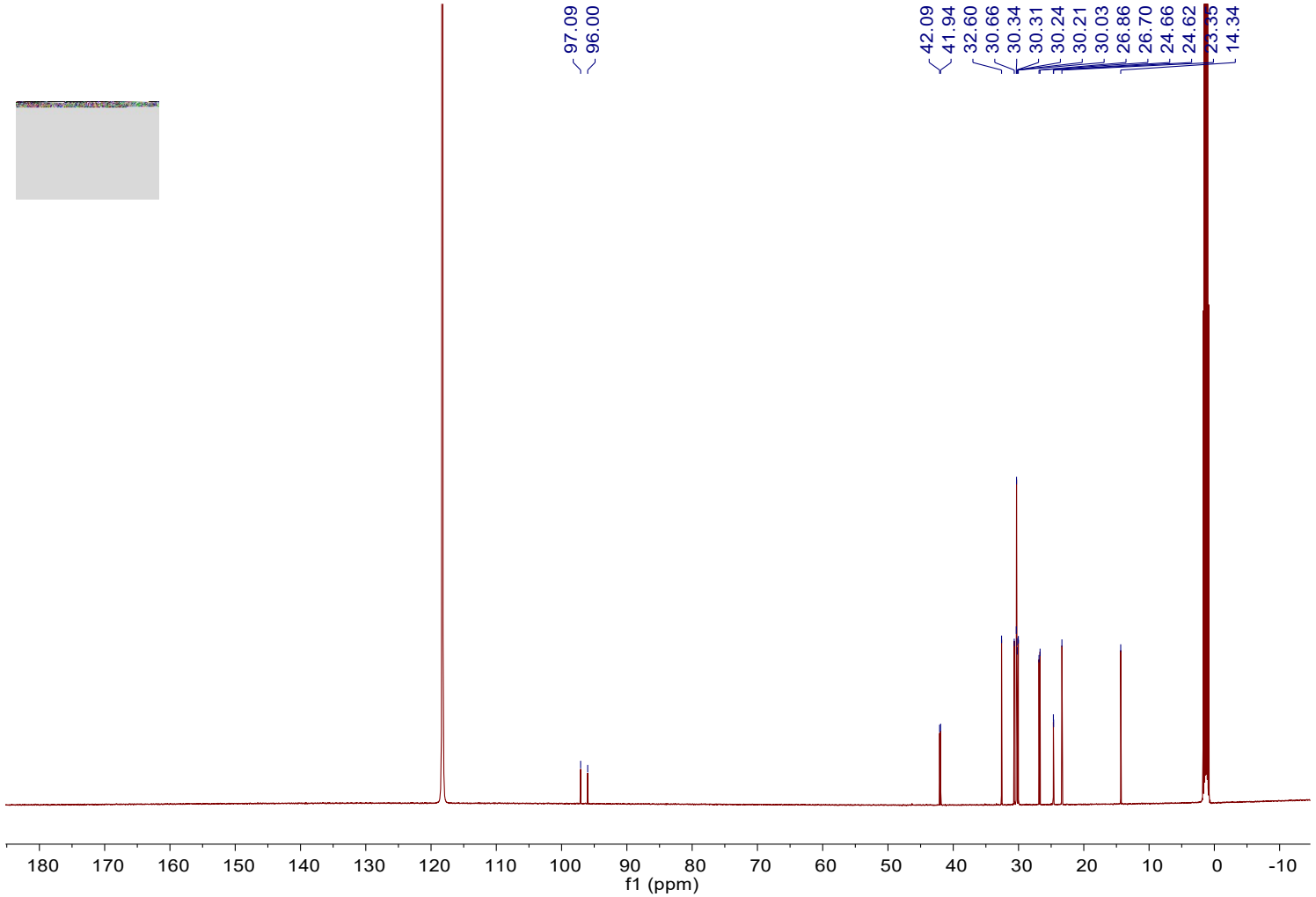


Compound **2c** ^{1}H NMR (400 MHz, CD_3CN)

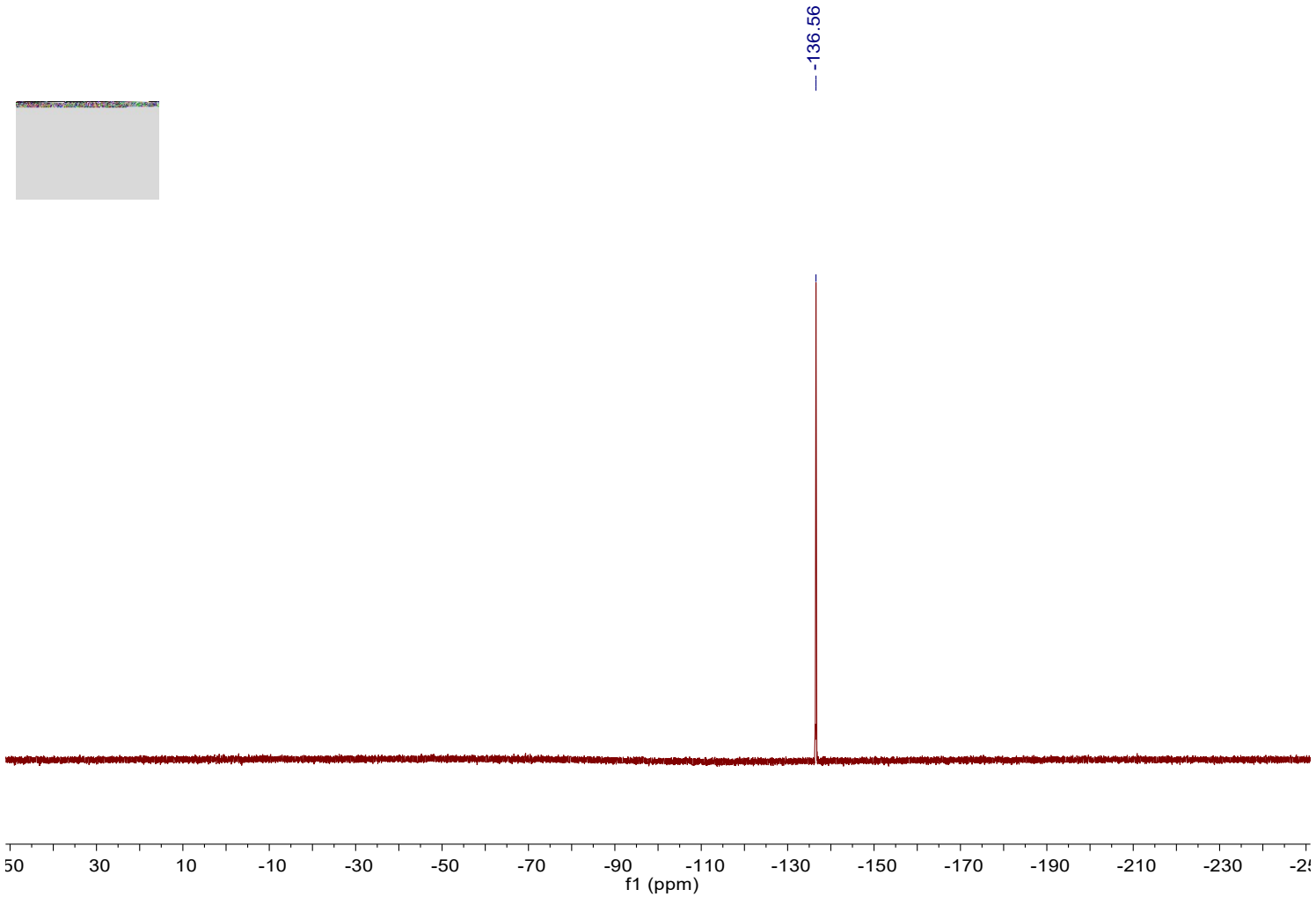




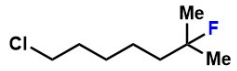
Compound **2c** ^{13}C NMR (151 MHz, CD_3CN)

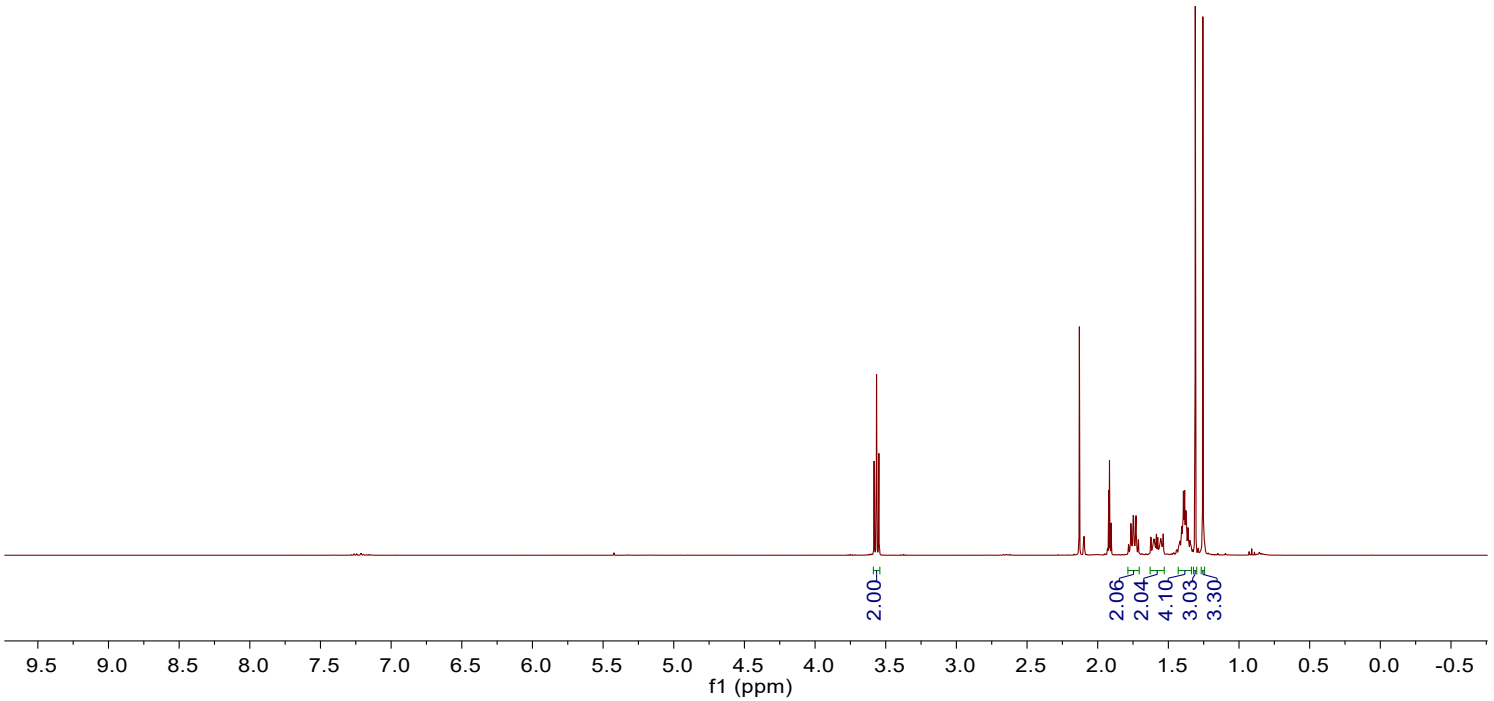


Compound **2c** ^{19}F NMR (376 MHz, CD_3CN)

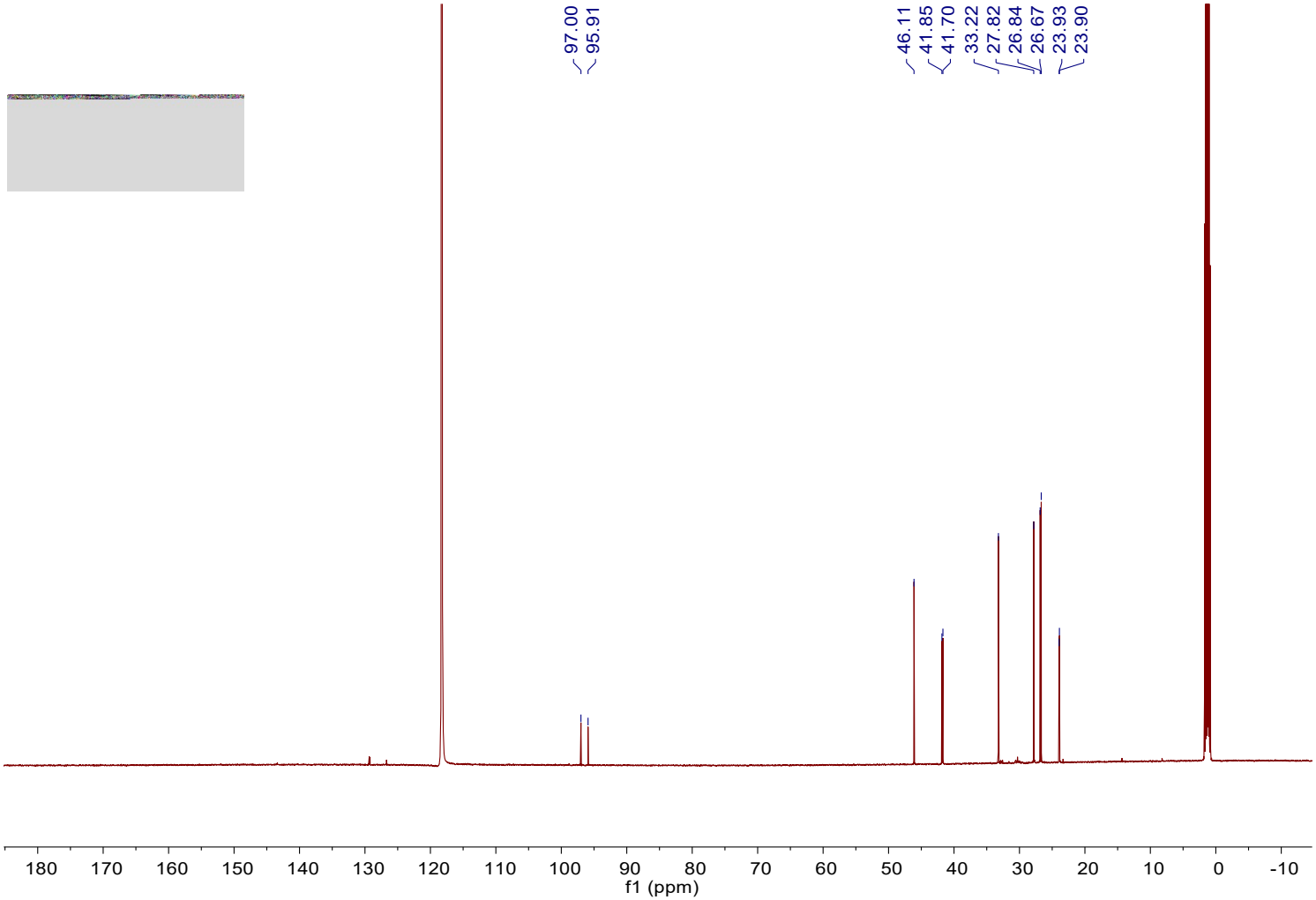


Compound **2d** ^{1}H NMR (400 MHz, CD_3CN)

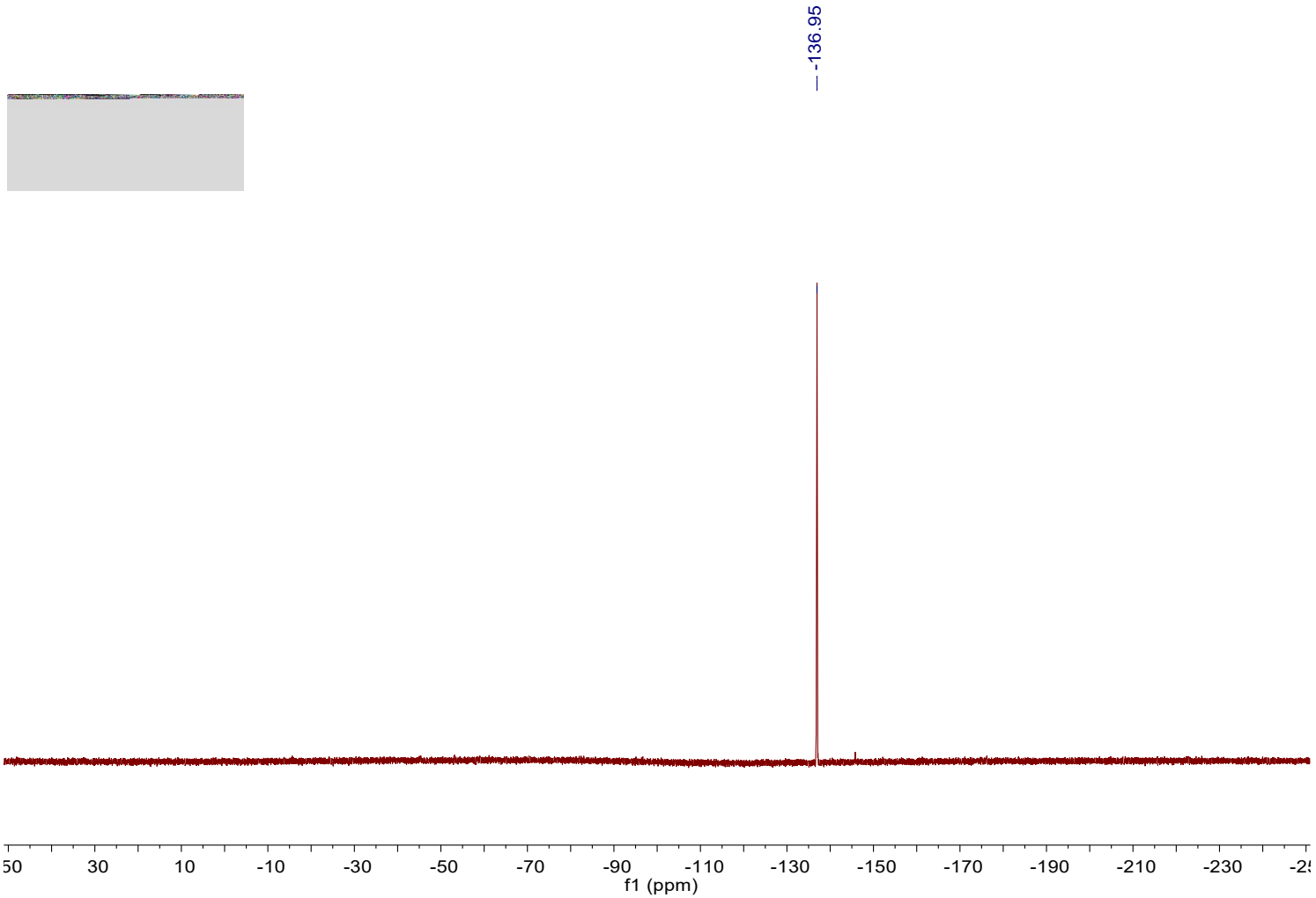




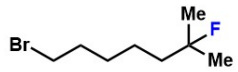
Compound **2d** ^{13}C NMR (151 MHz, CD_3CN)

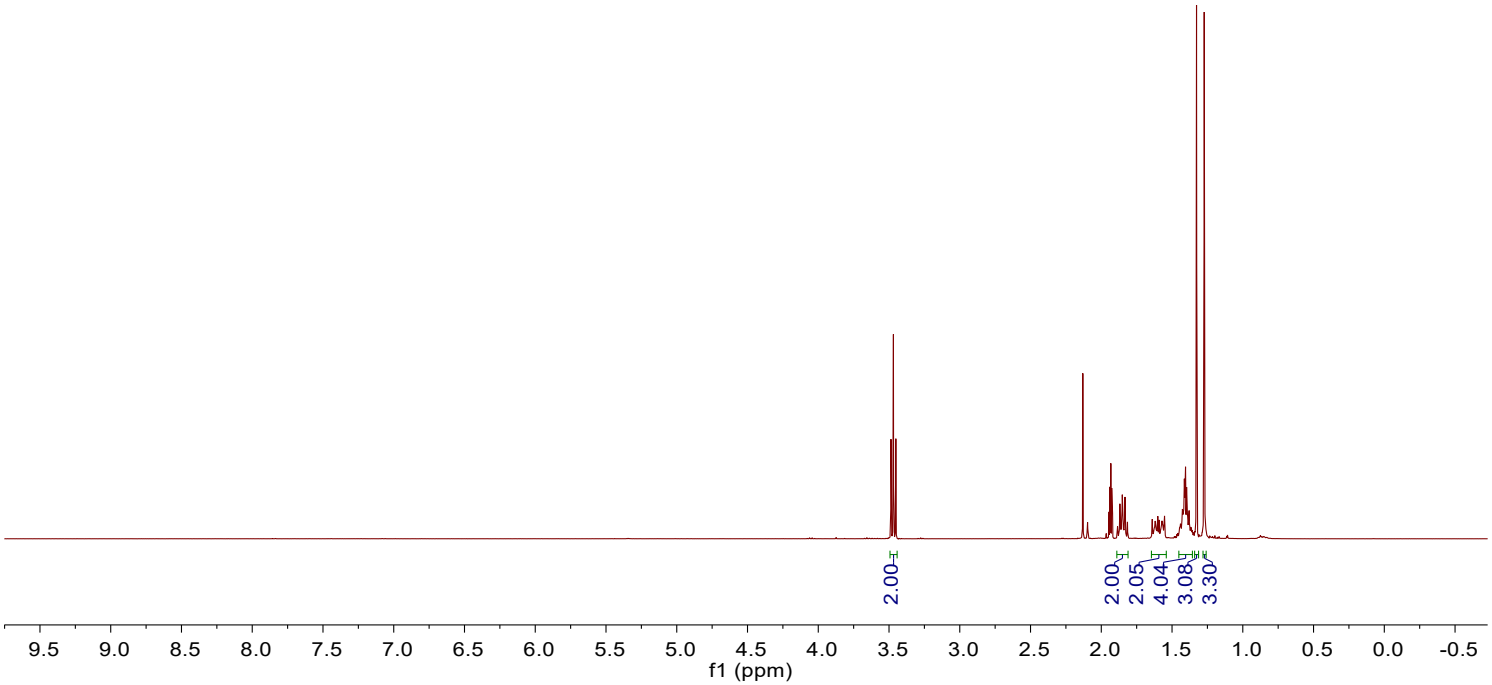


Compound **2d** ^{19}F NMR (376 MHz, CD_3CN)

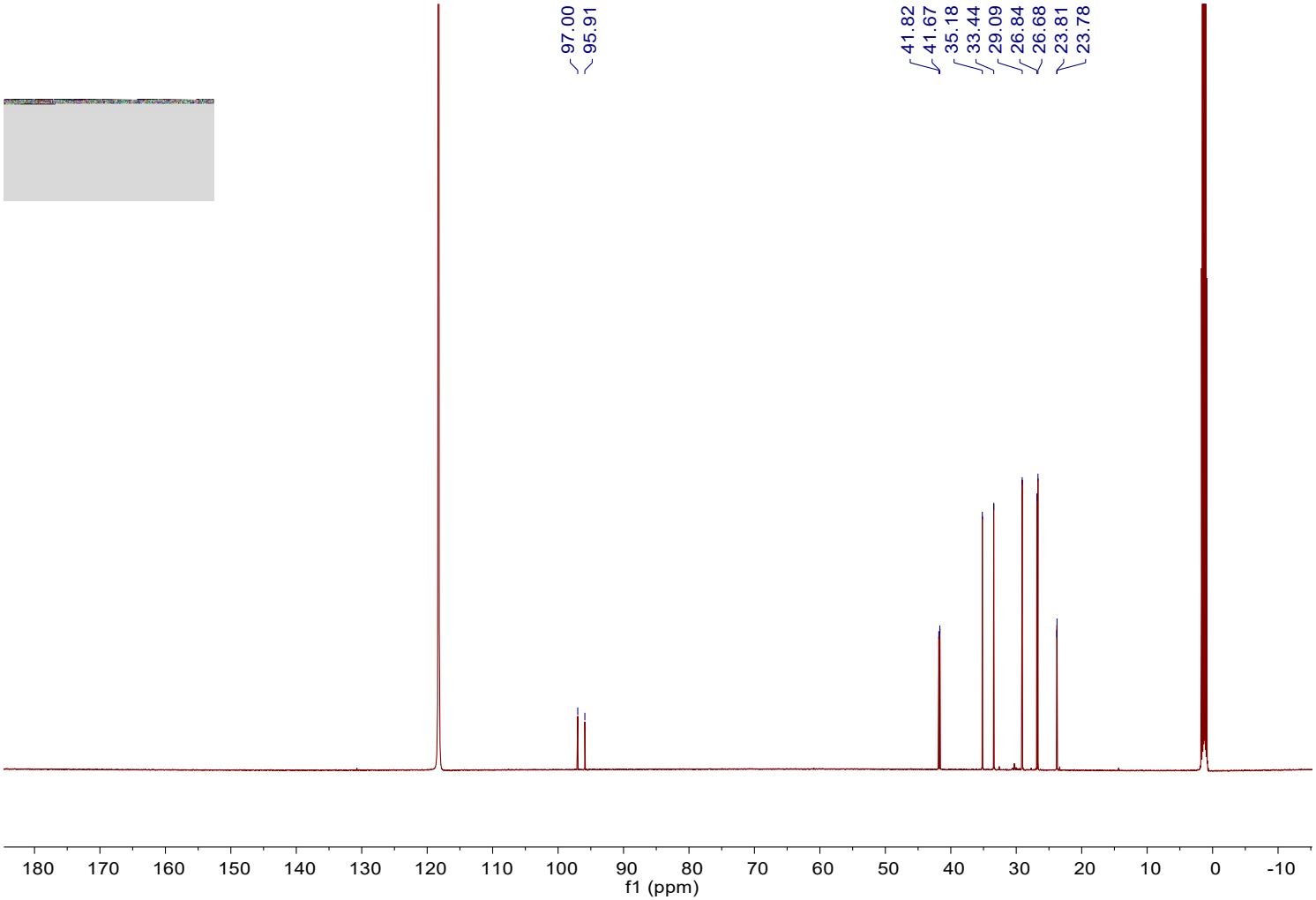


Compound **2e** ^{1}H NMR (400 MHz, CD_3CN)

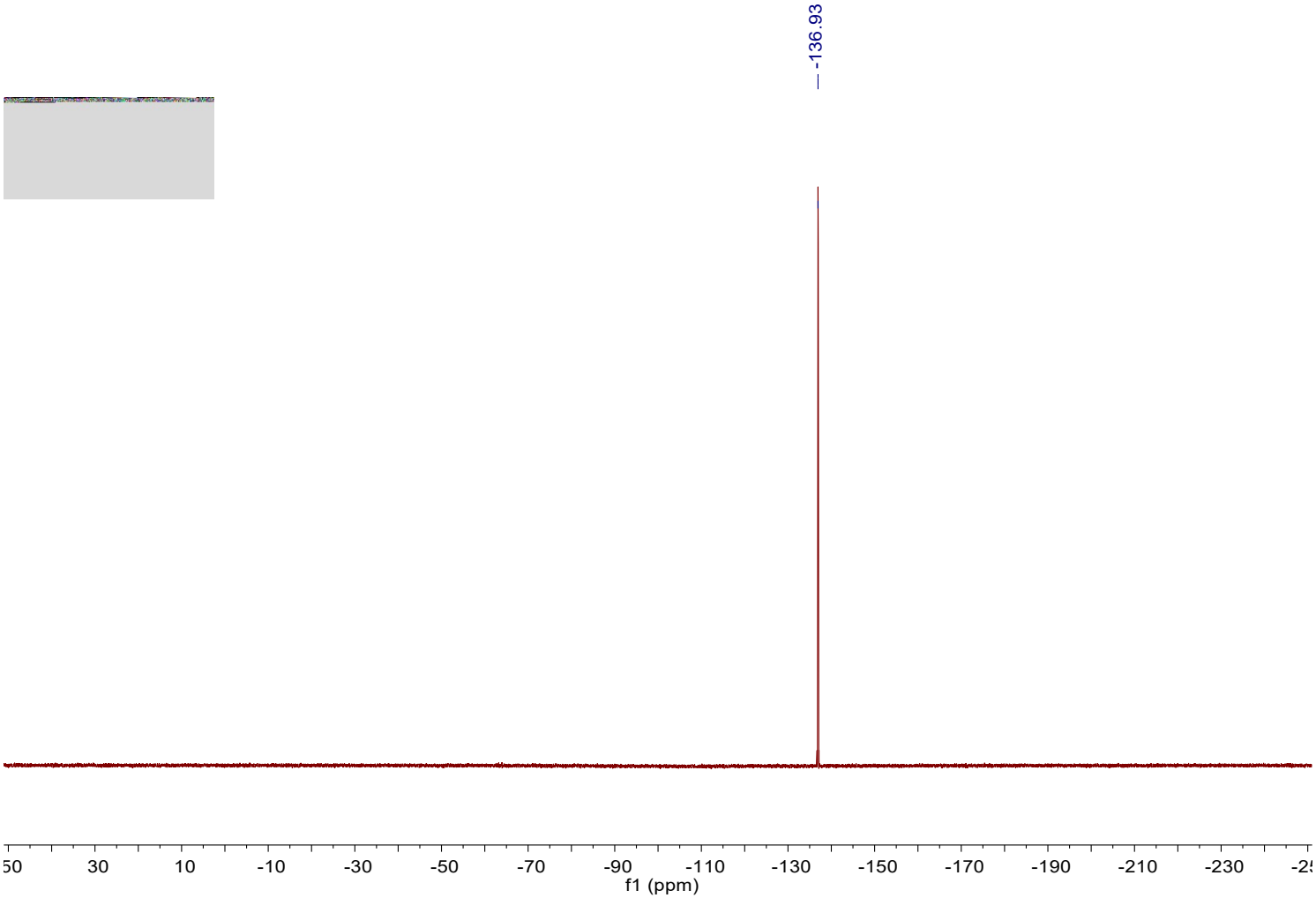




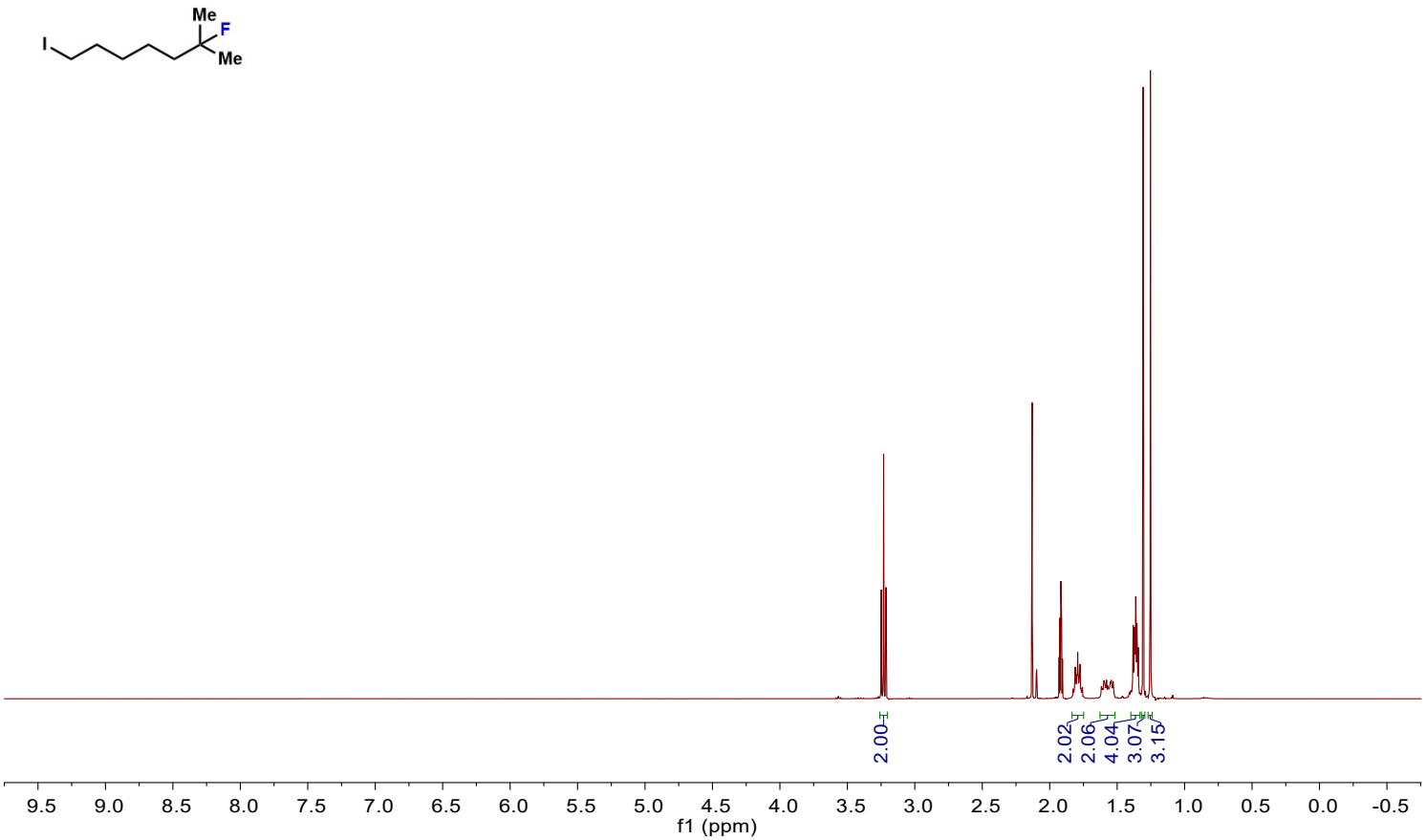
Compound **2e** ^{13}C NMR (151 MHz, CD_3CN)



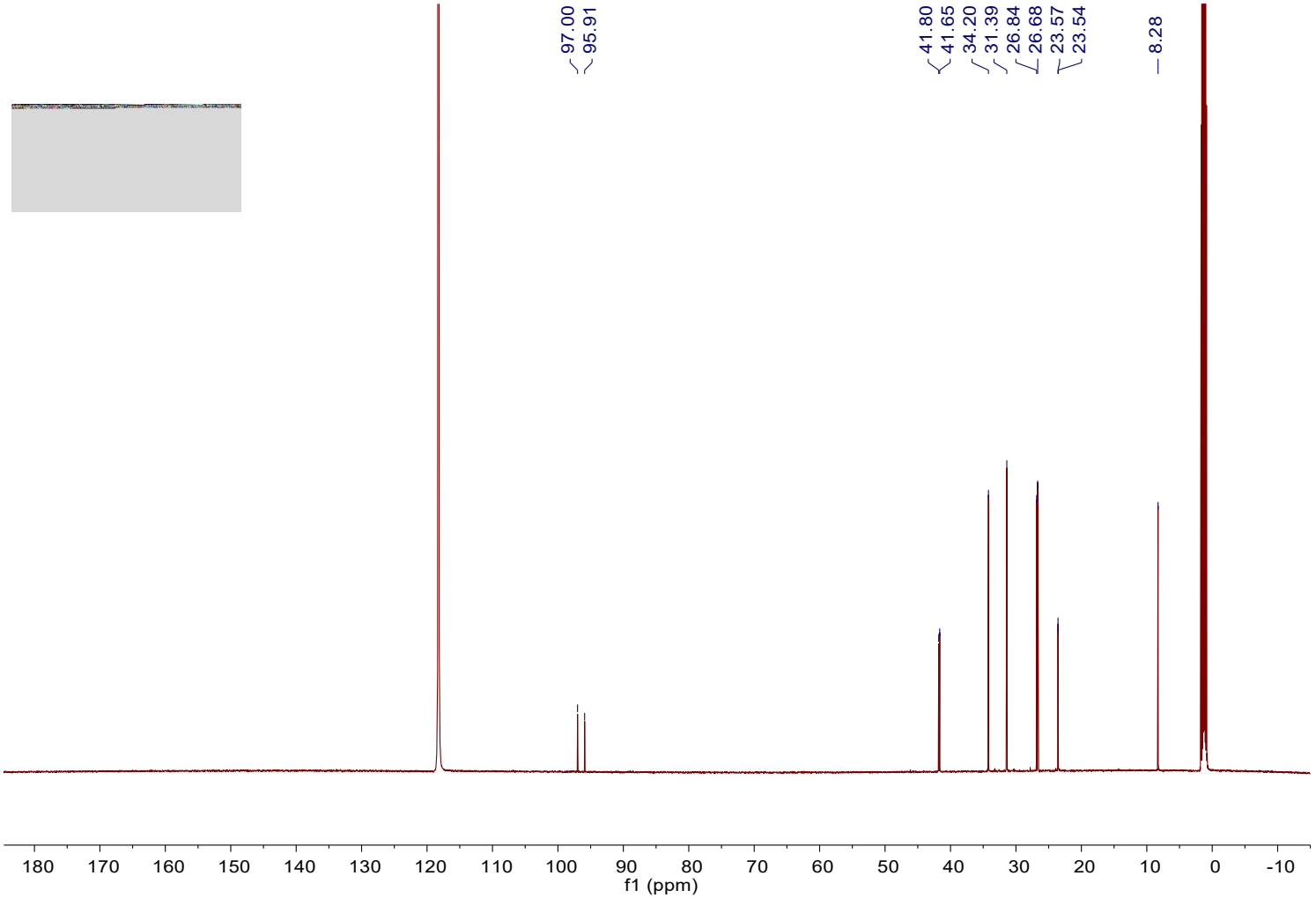
Compound **2e** ^{19}F NMR (376 MHz, CD_3CN)



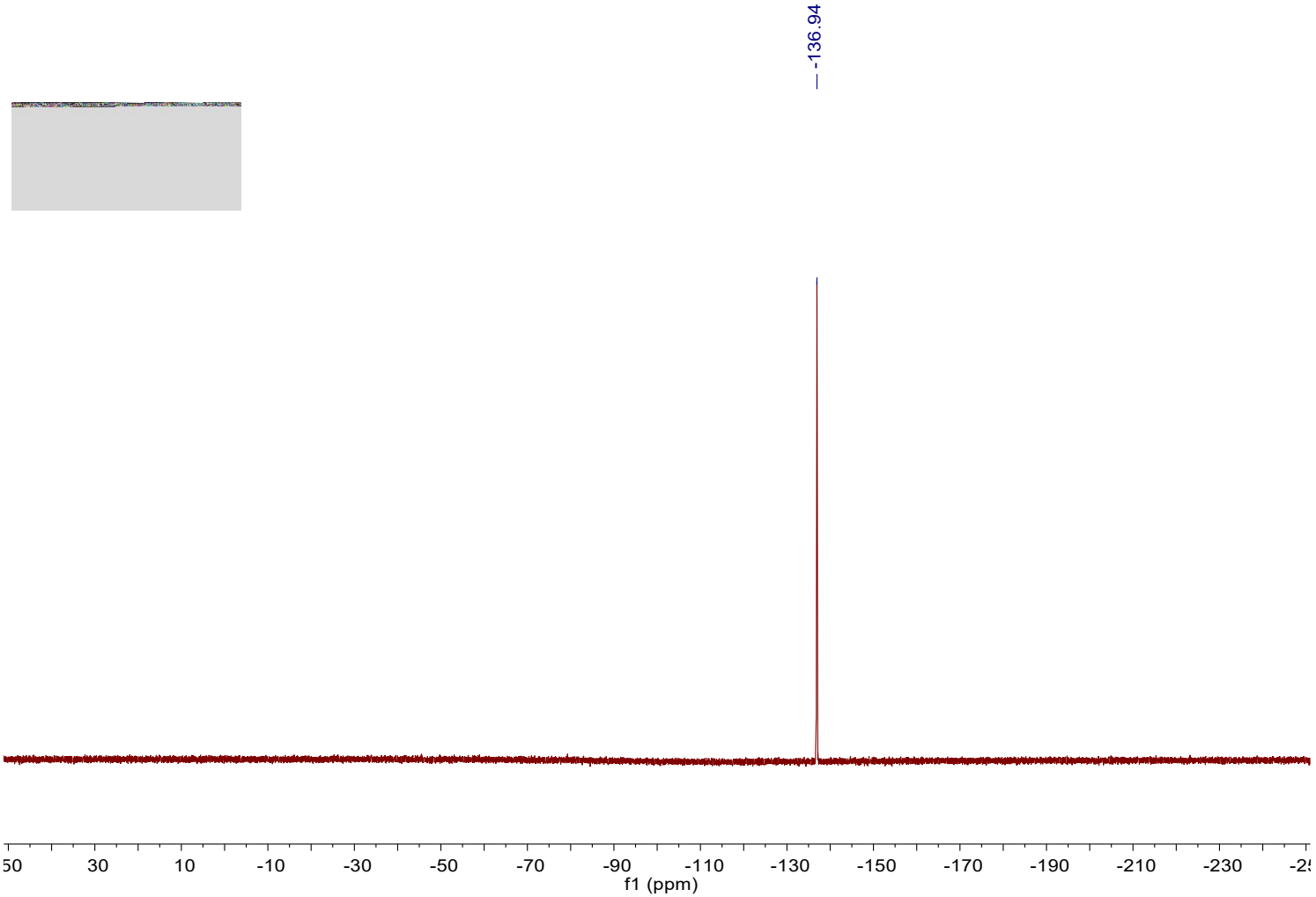
Compound **2f** ^{1}H NMR (400 MHz, CD_3CN)



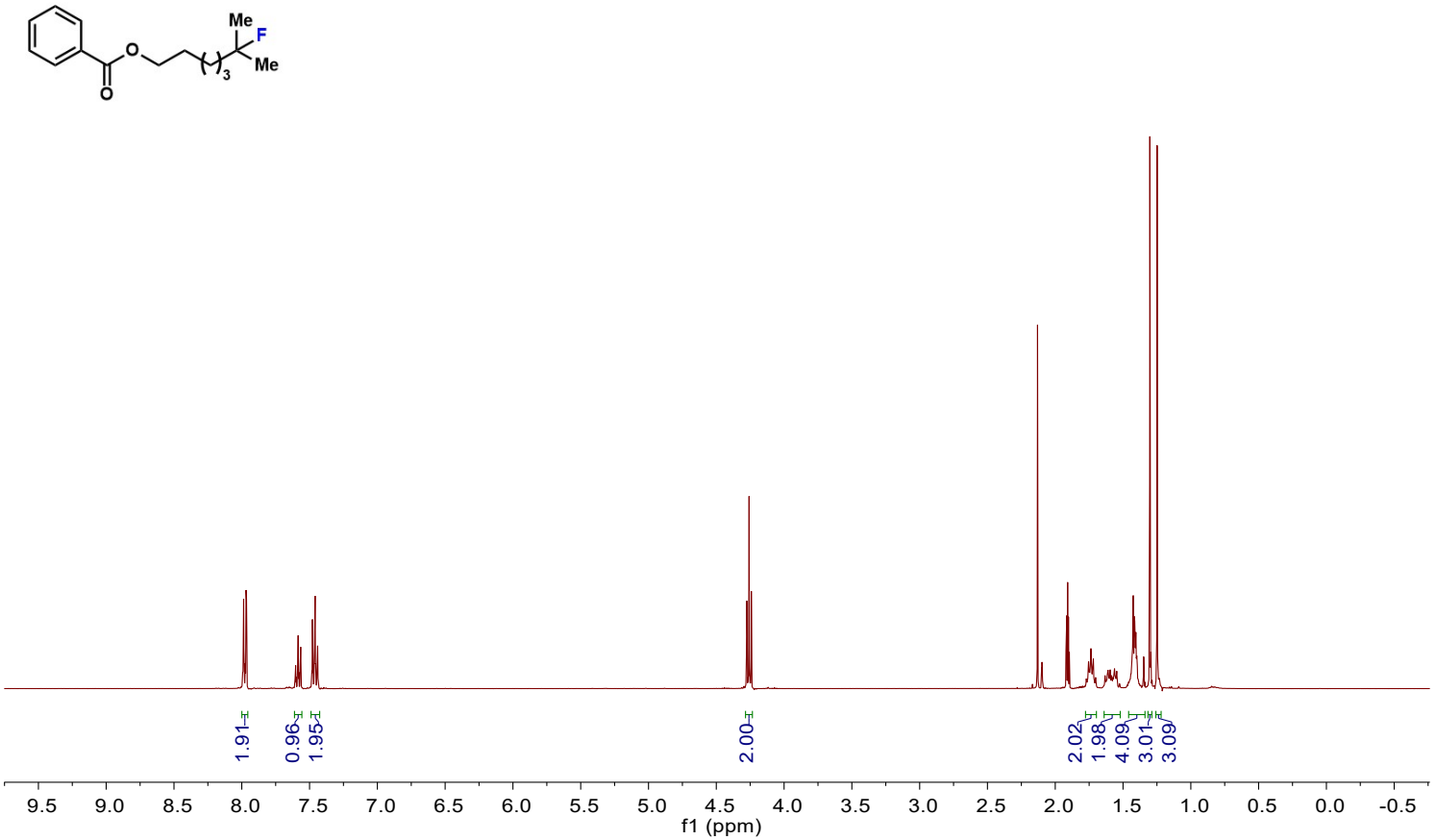
Compound **2f** ^{13}C NMR (151 MHz, CD_3CN)



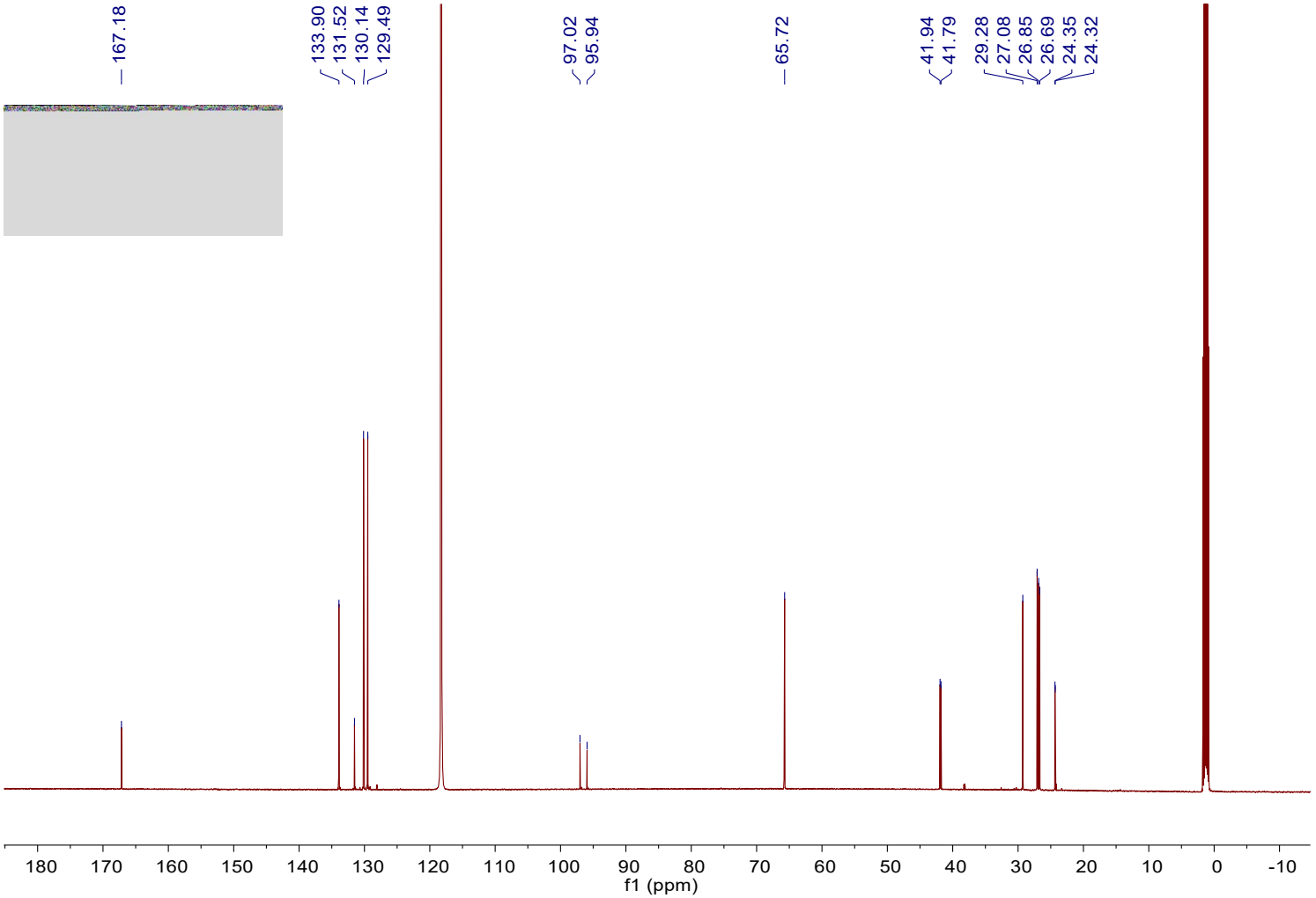
Compound **2f** ^{19}F NMR (376 MHz, CD_3CN)



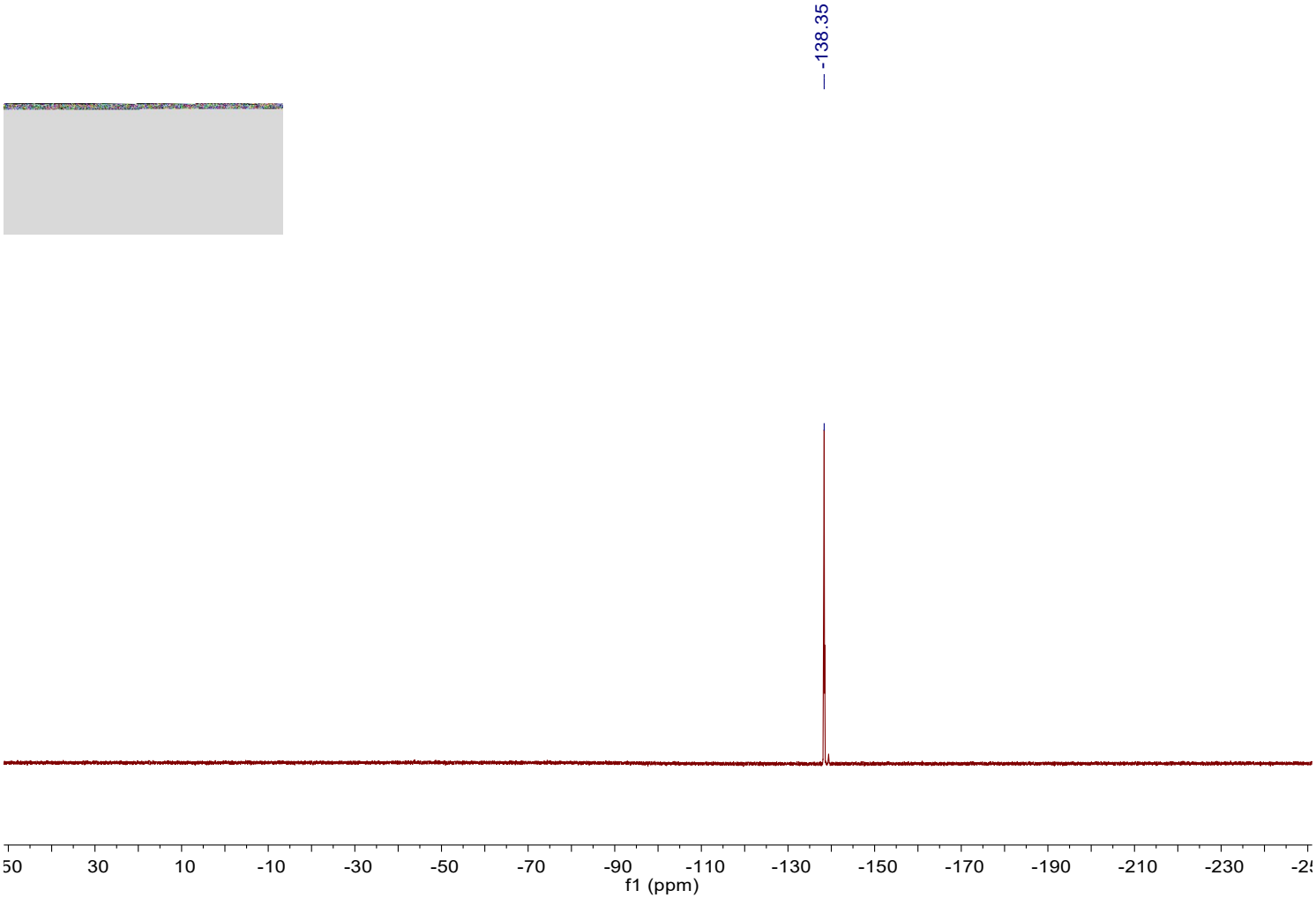
Compound **2g** ^{1}H NMR (400 MHz, CD_3CN)



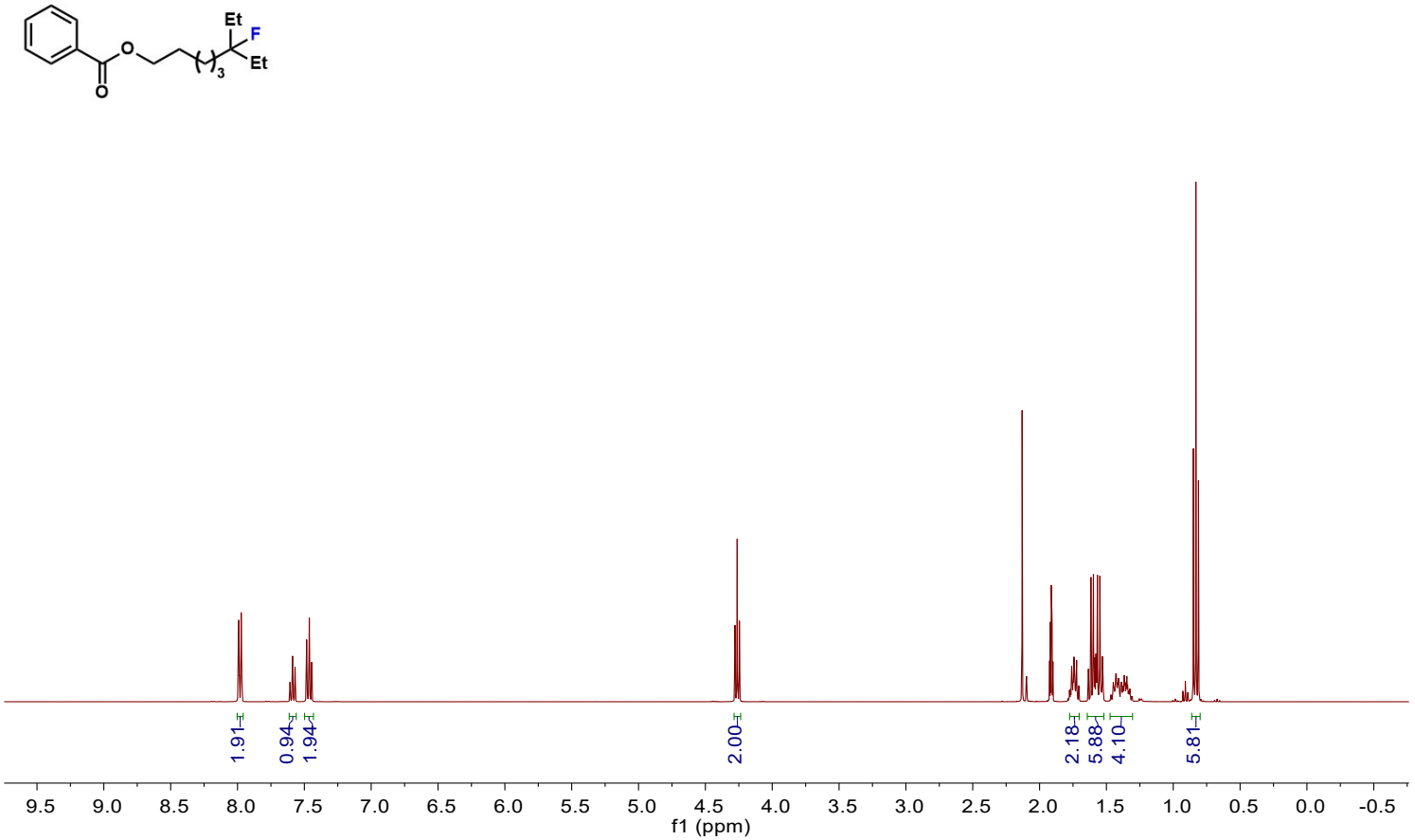
Compound **2g** ^{13}C NMR (151 MHz, CD_3CN)



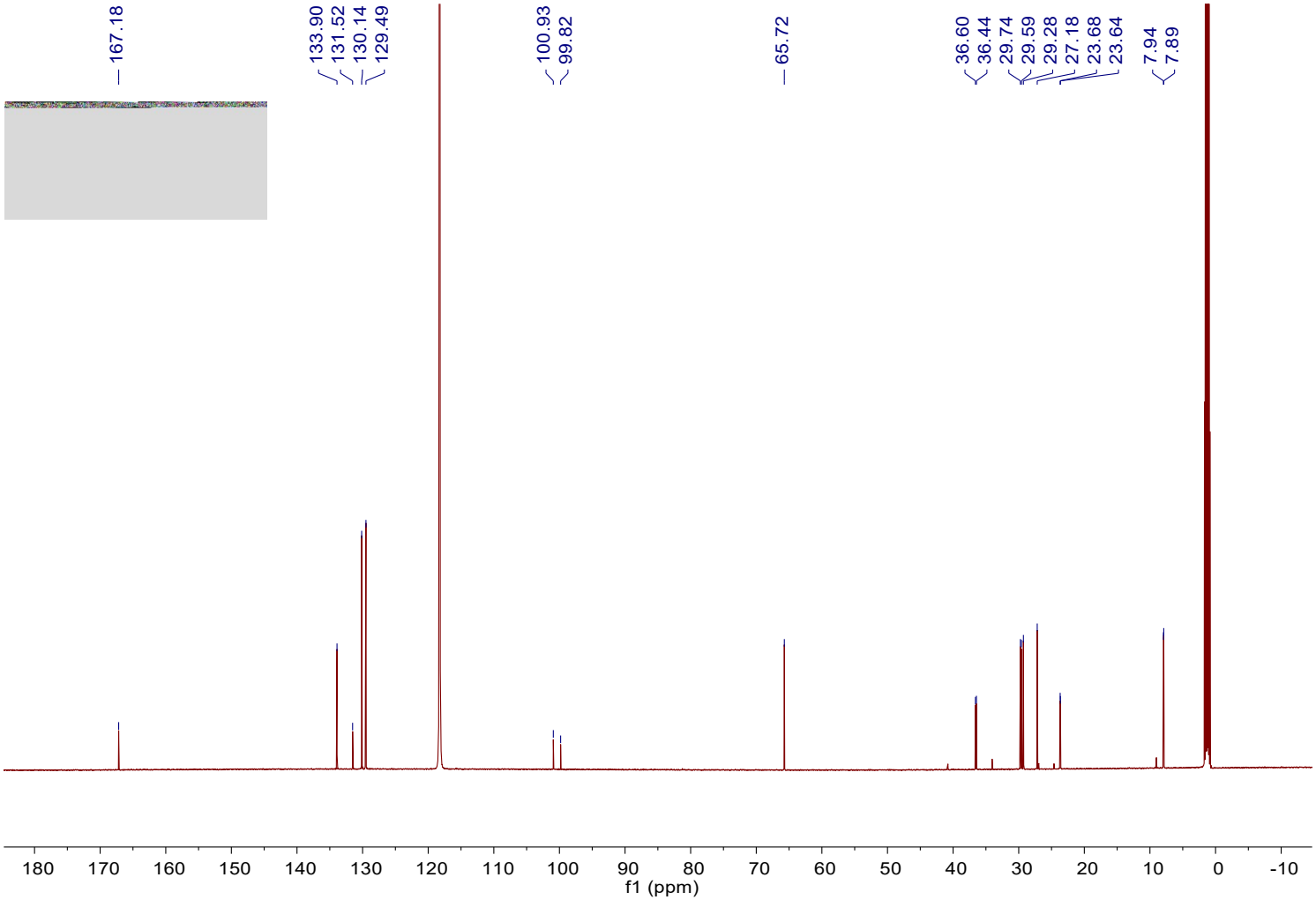
Compound **2g** ^{19}F NMR (376 MHz, CD_3CN)



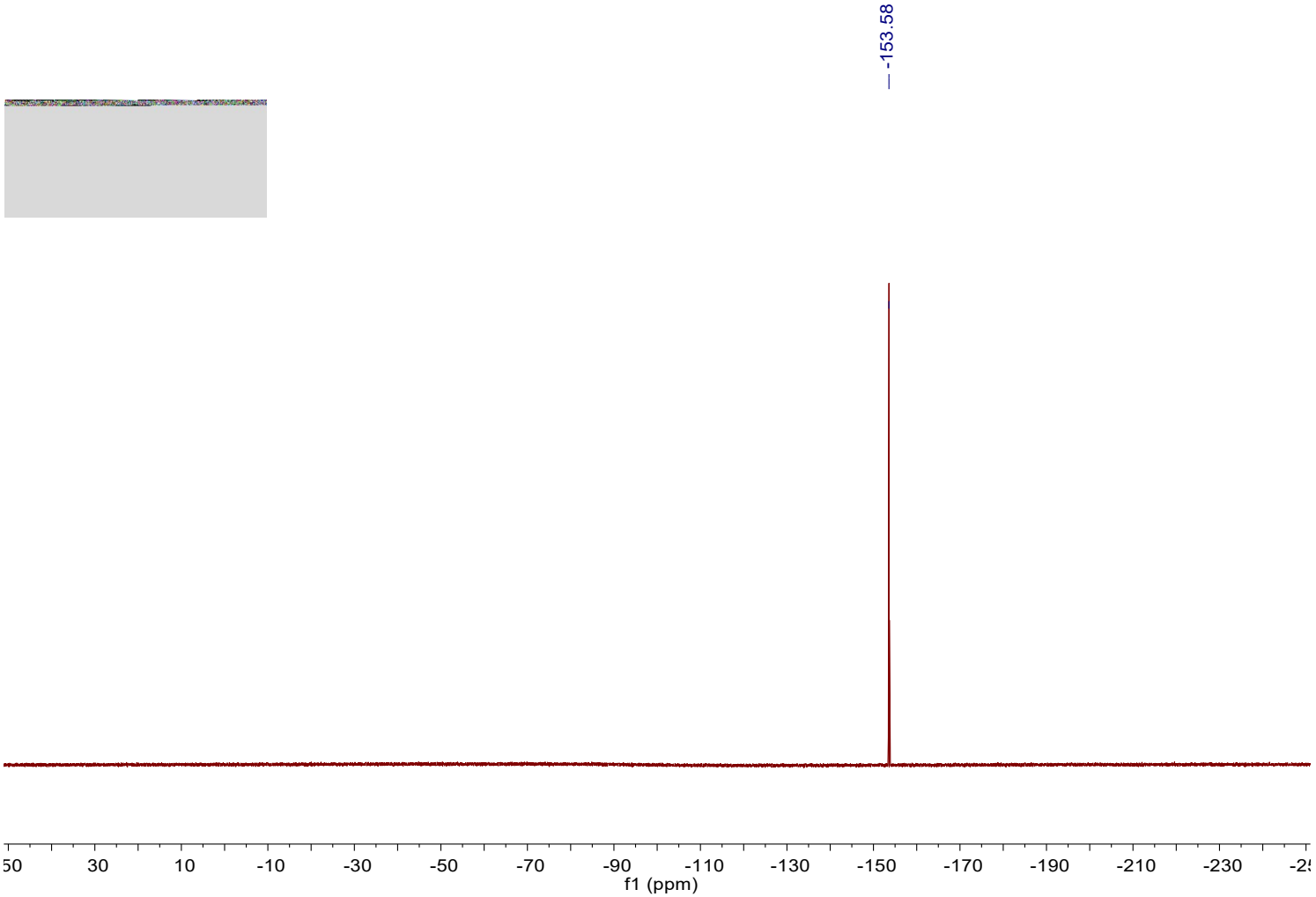
Compound **2h** ^{1}H NMR (400 MHz, CD_3CN)



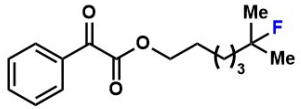
Compound **2h** ^{13}C NMR (151 MHz, CD_3CN)

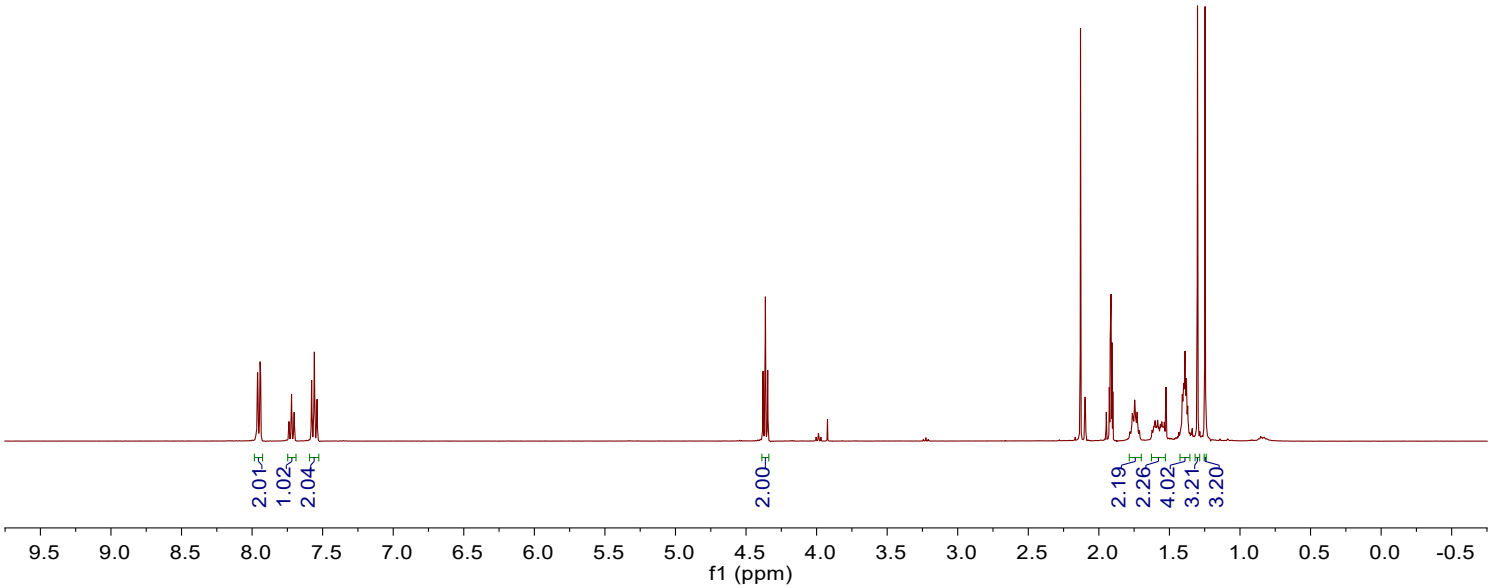


Compound **2h** ^{19}F NMR (376 MHz, CD_3CN)

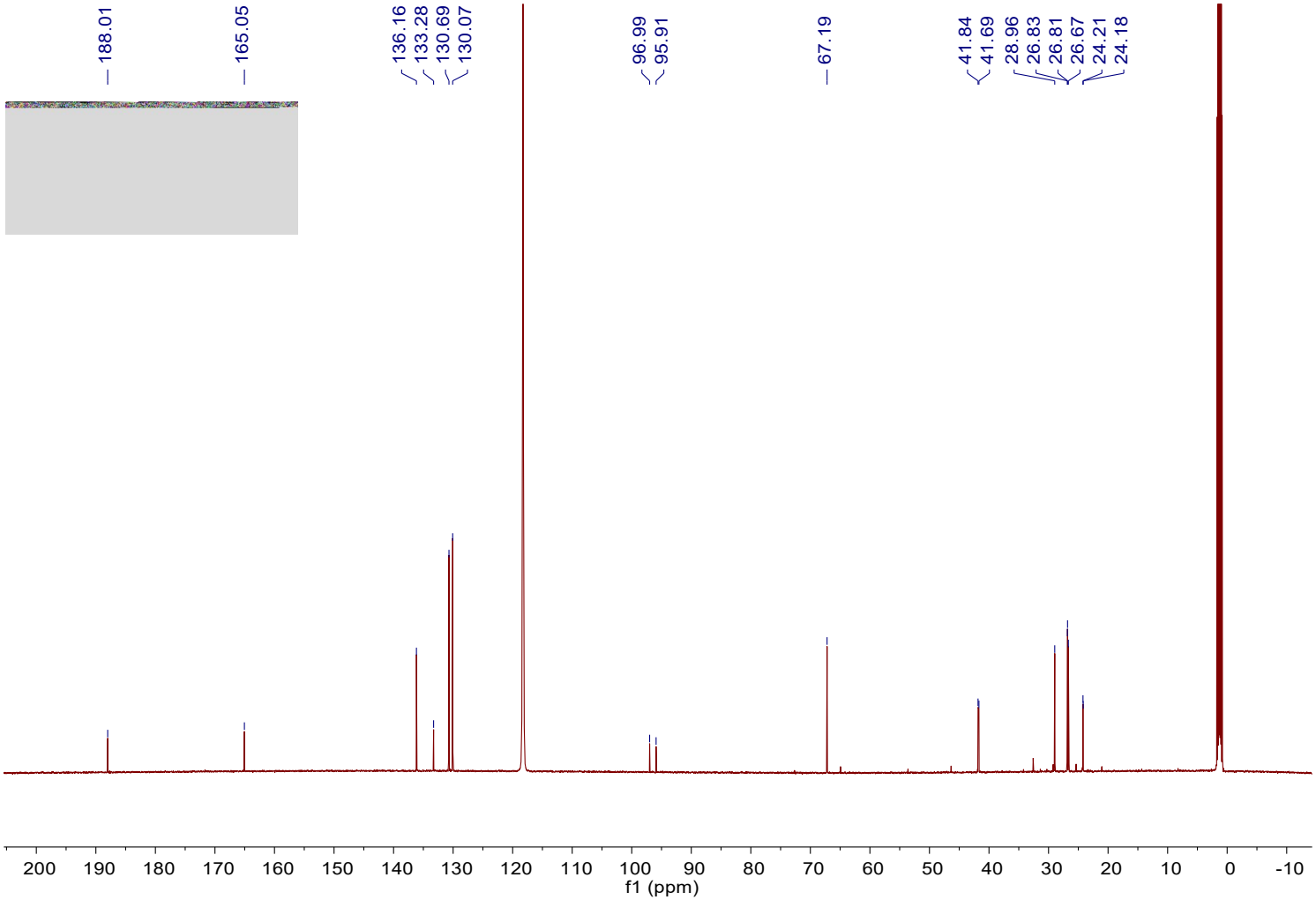


Compound **2i** ^{1}H NMR (400 MHz, CD_3CN)

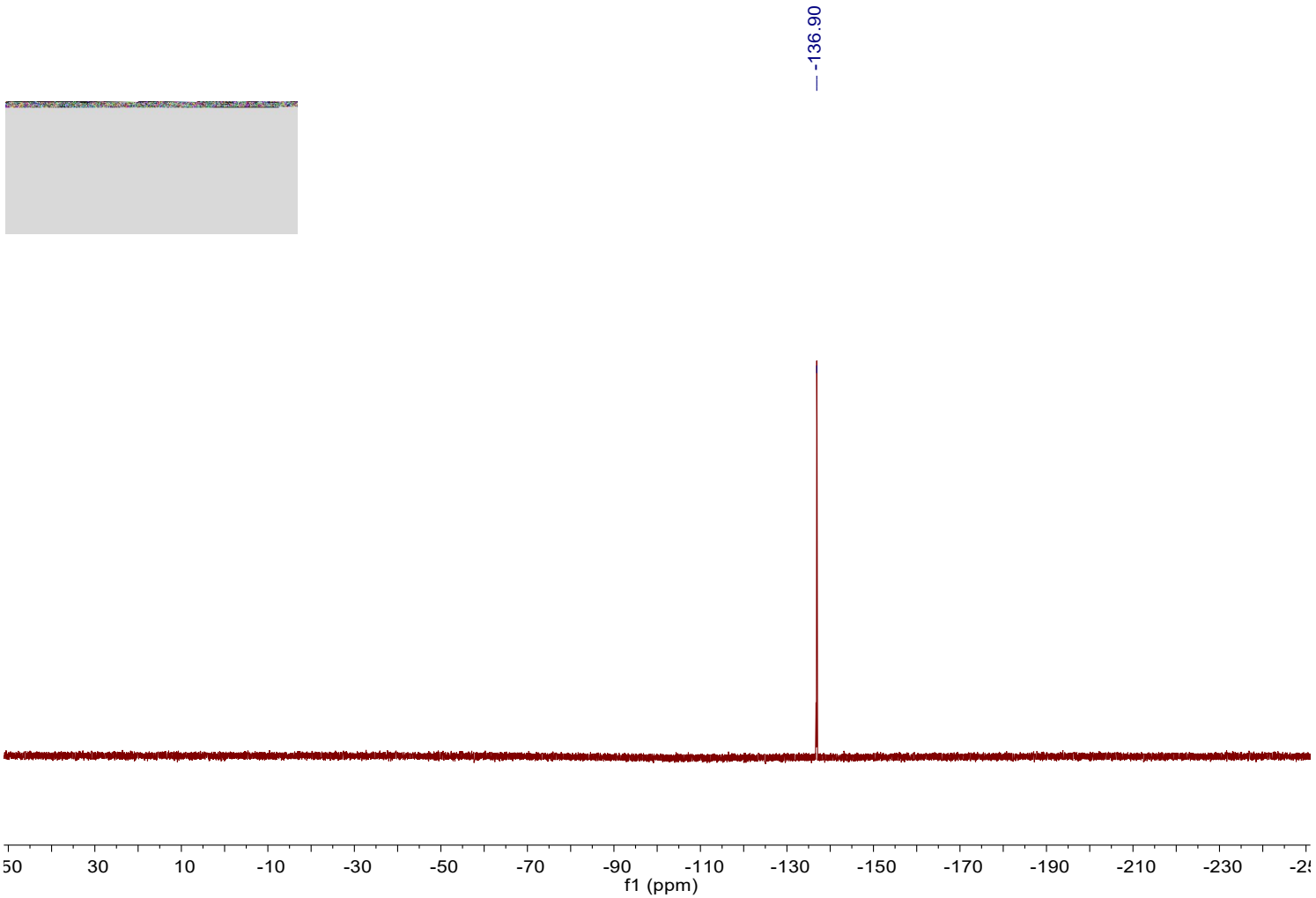




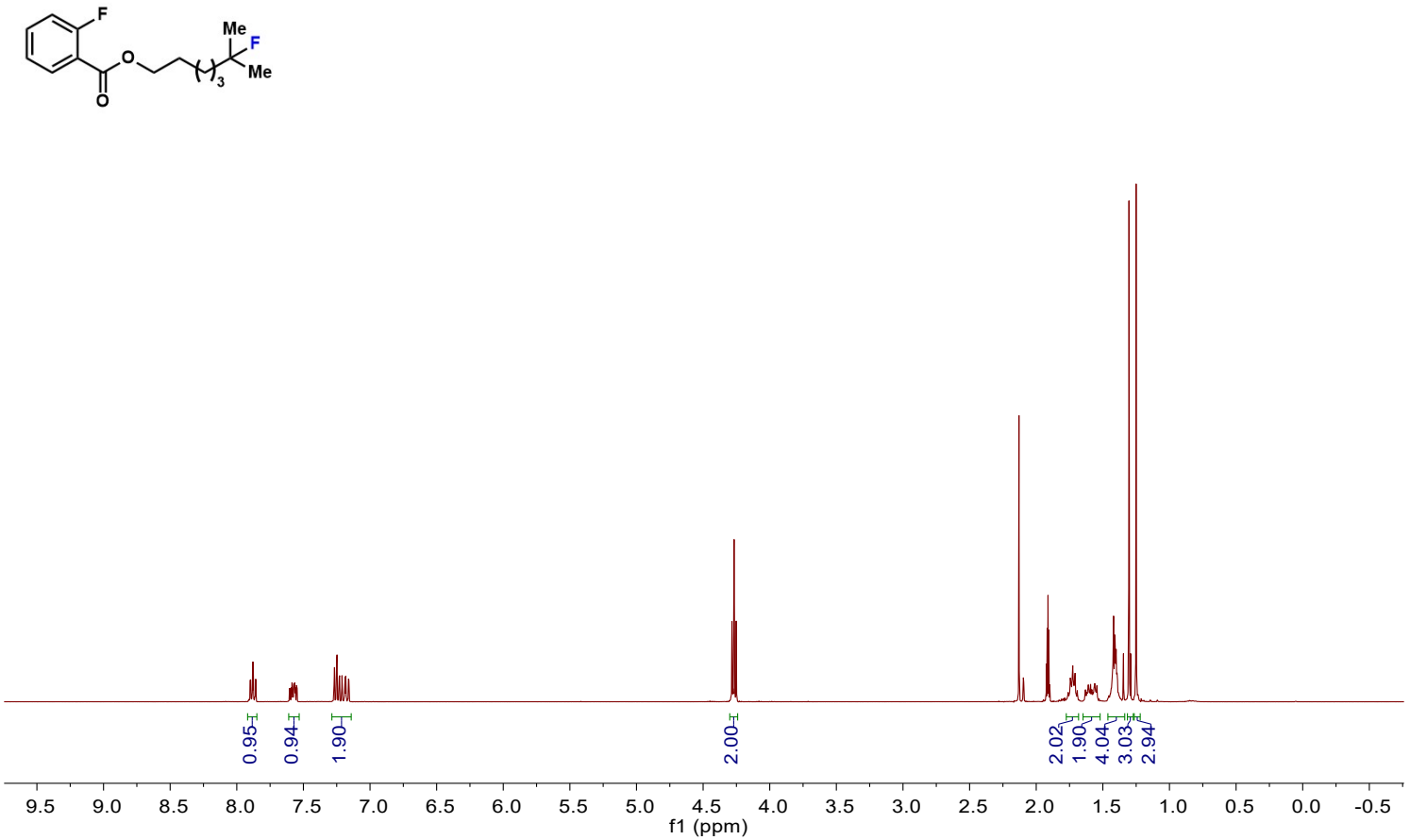
Compound **2i** ^{13}C NMR (151 MHz, CD_3CN)



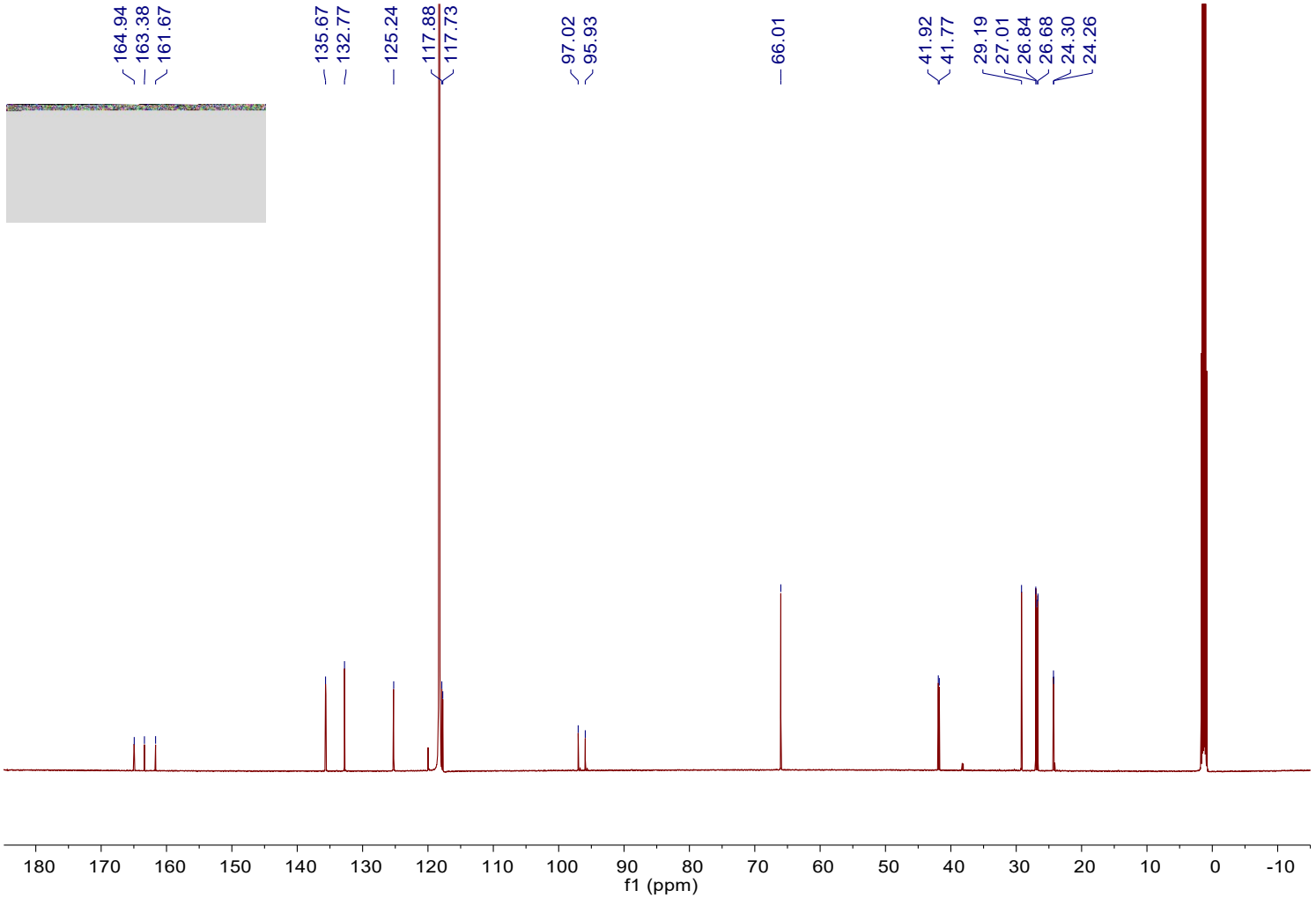
Compound **2i** ^{19}F NMR (376 MHz, CD_3CN)



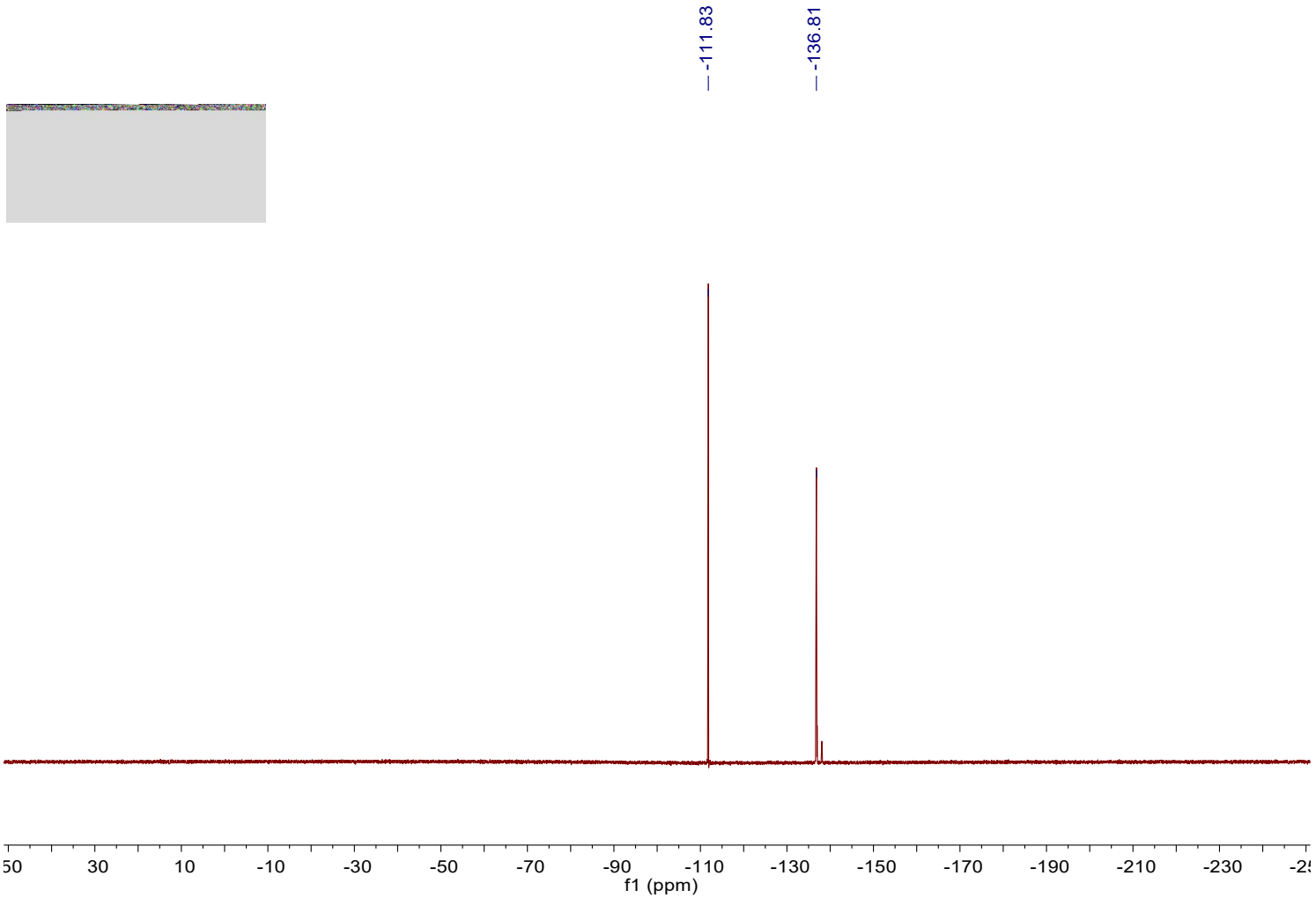
Compound **2j** ^{1}H NMR (400 MHz, CD_3CN)



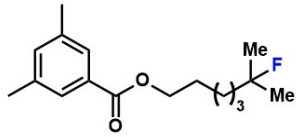
Compound **2j** ^{13}C NMR (151 MHz, CD_3CN)

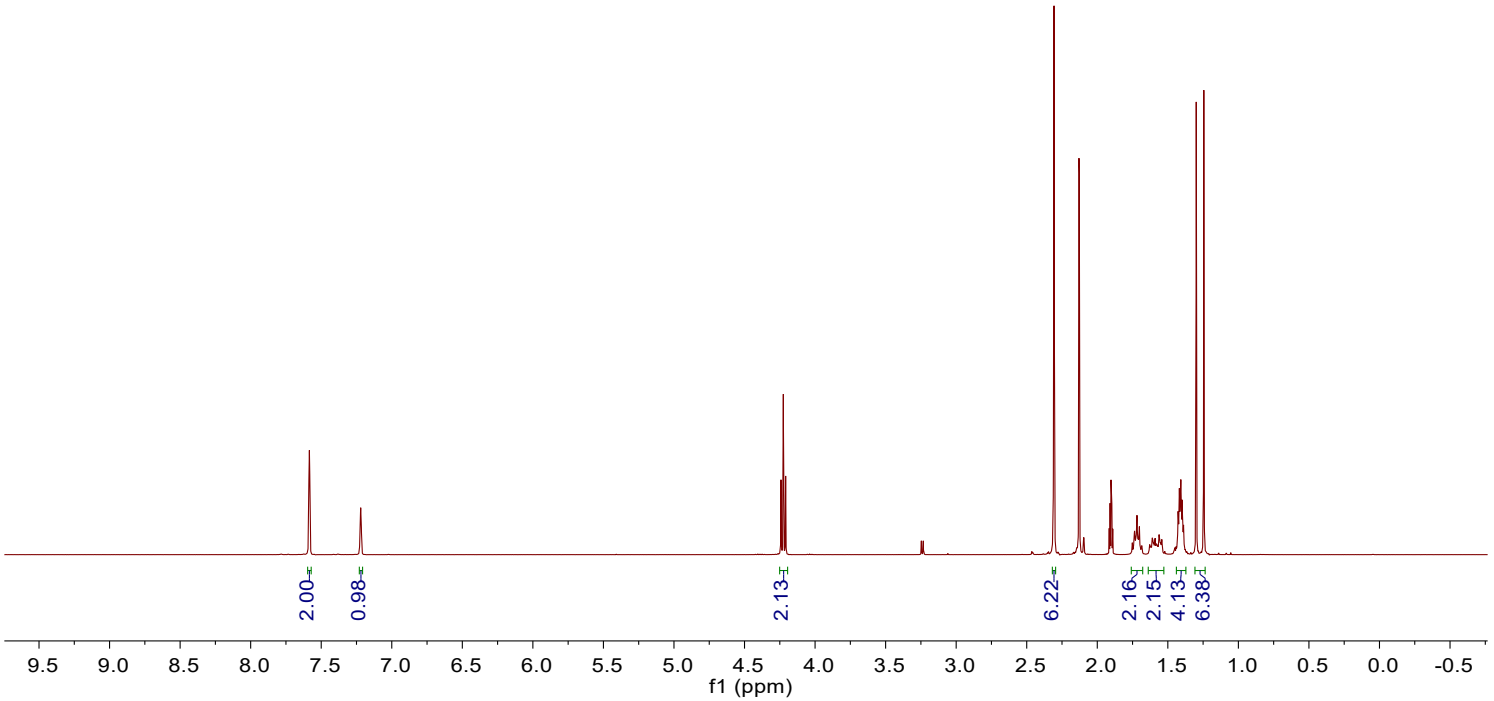


Compound **2j** ^{19}F NMR (376 MHz, CD_3CN)

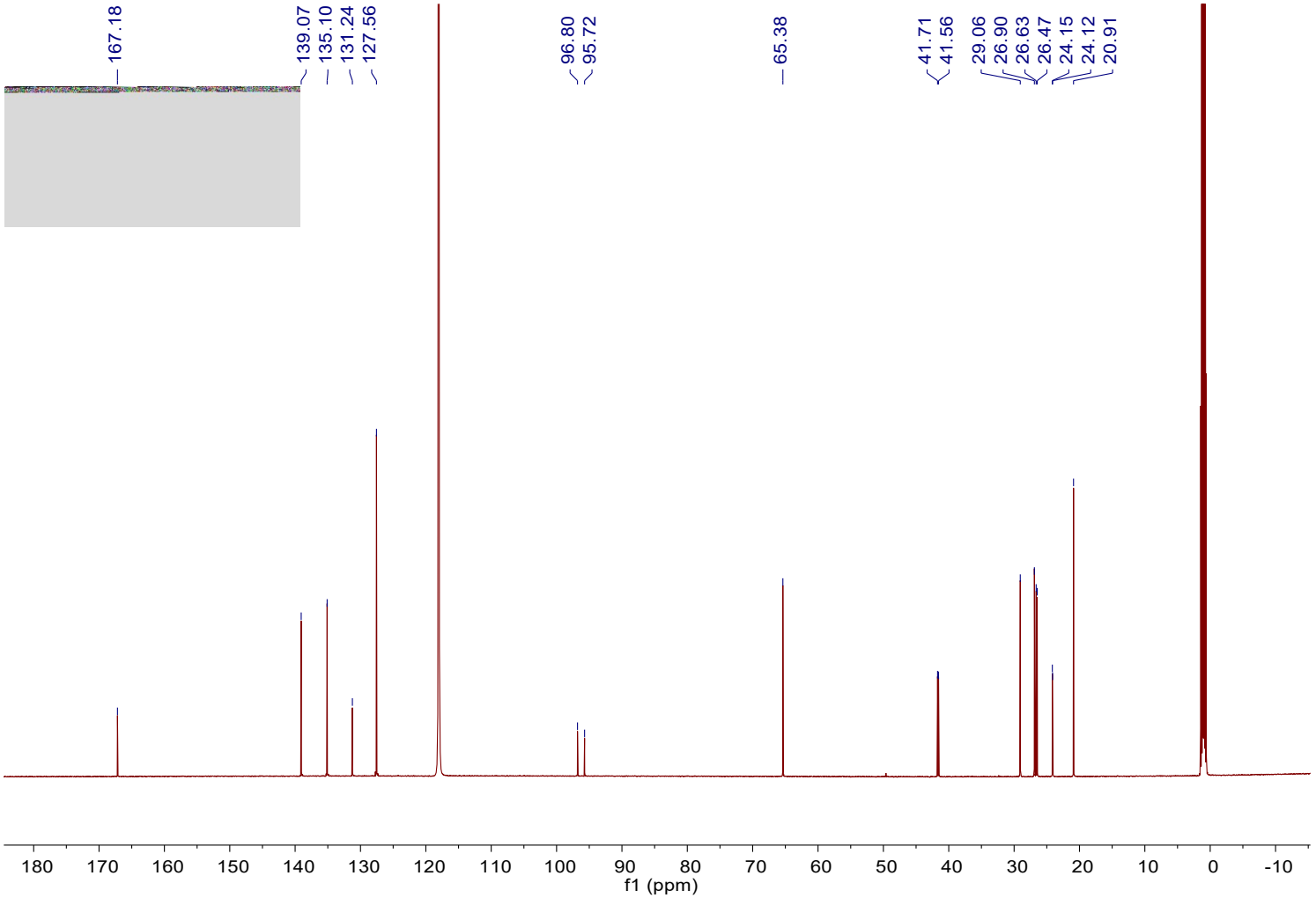


Compound **2k** ^{1}H NMR (400 MHz, CD_3CN)

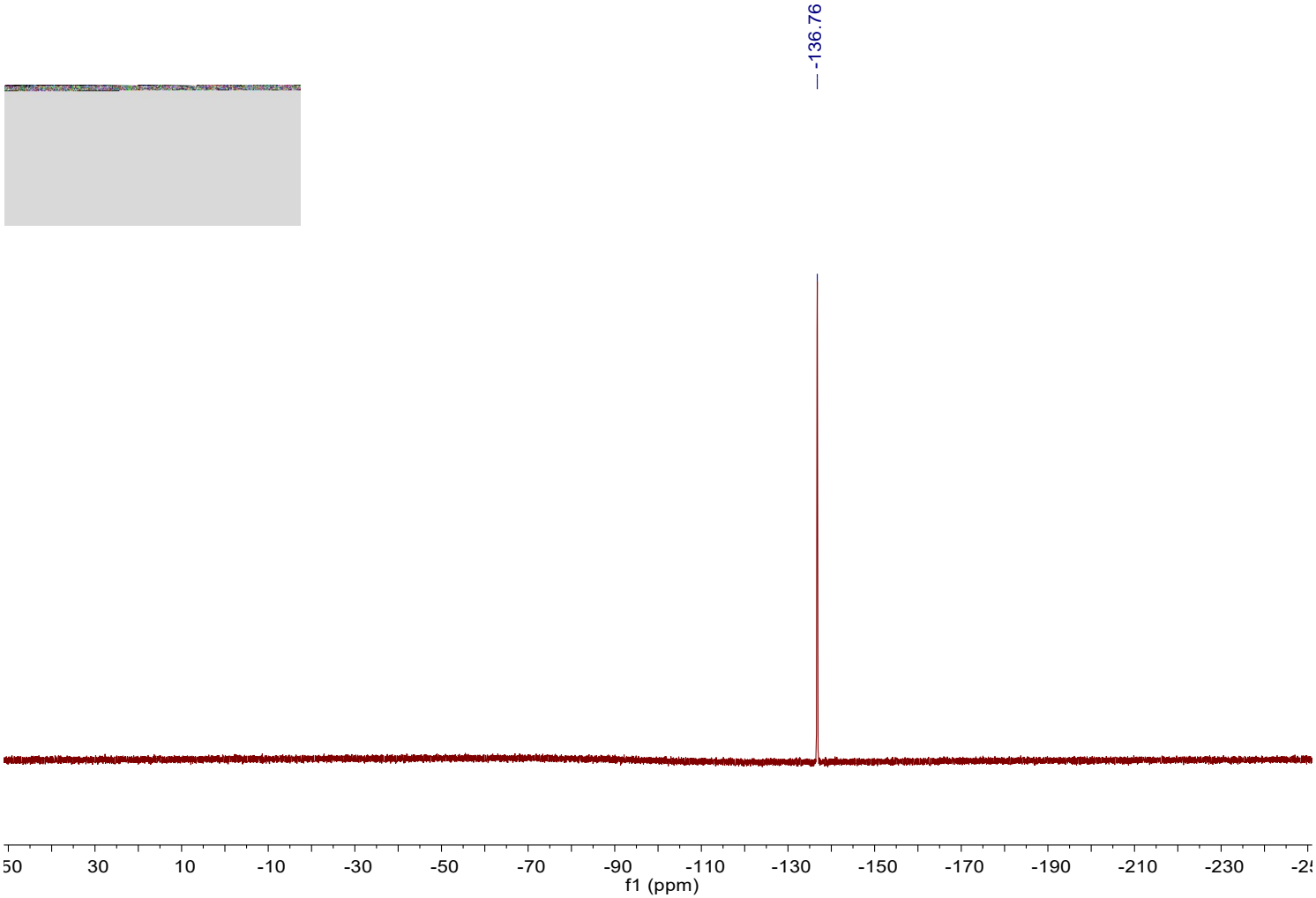




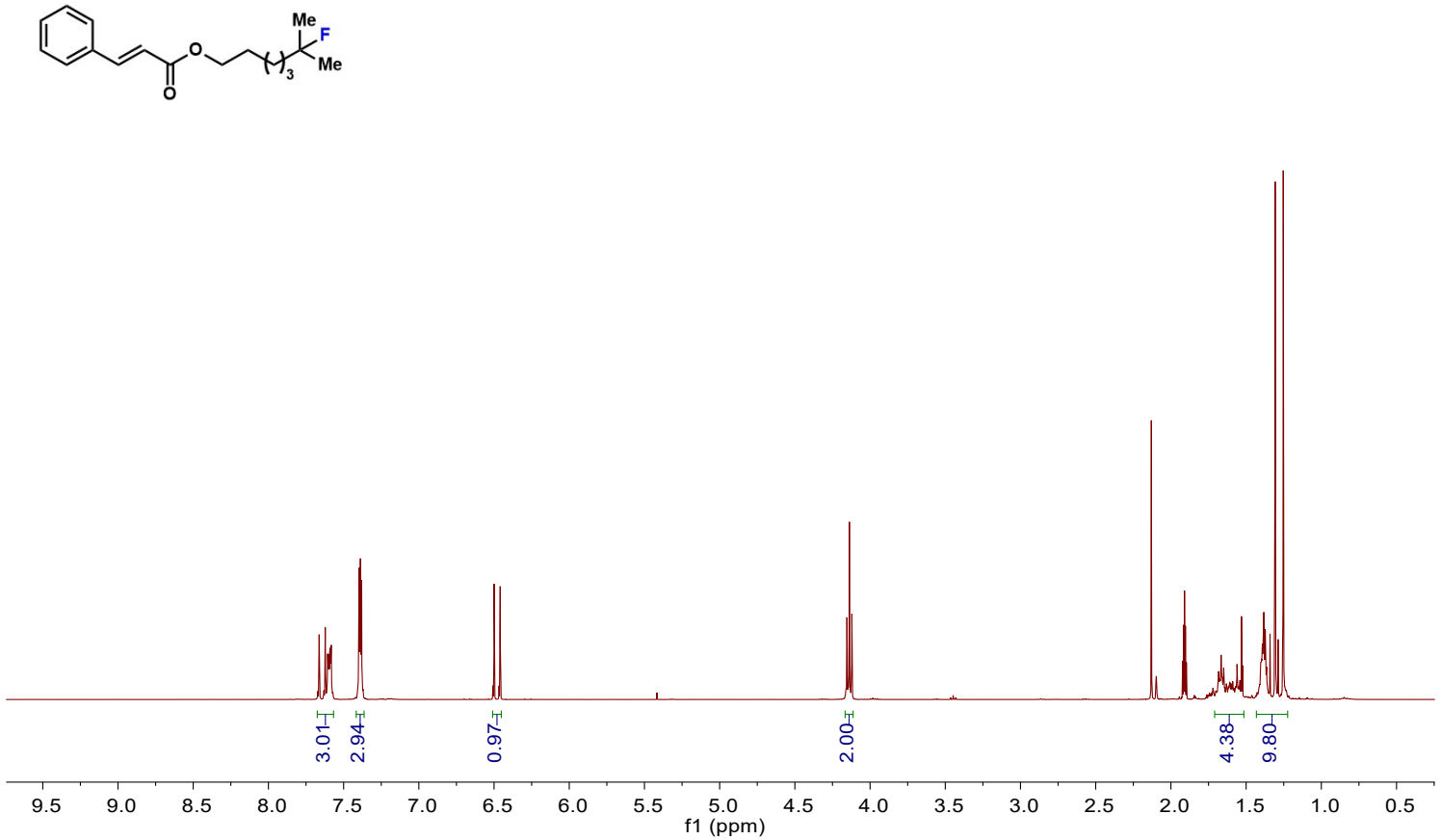
Compound **2k** ^{13}C NMR (151 MHz, CD_3CN)



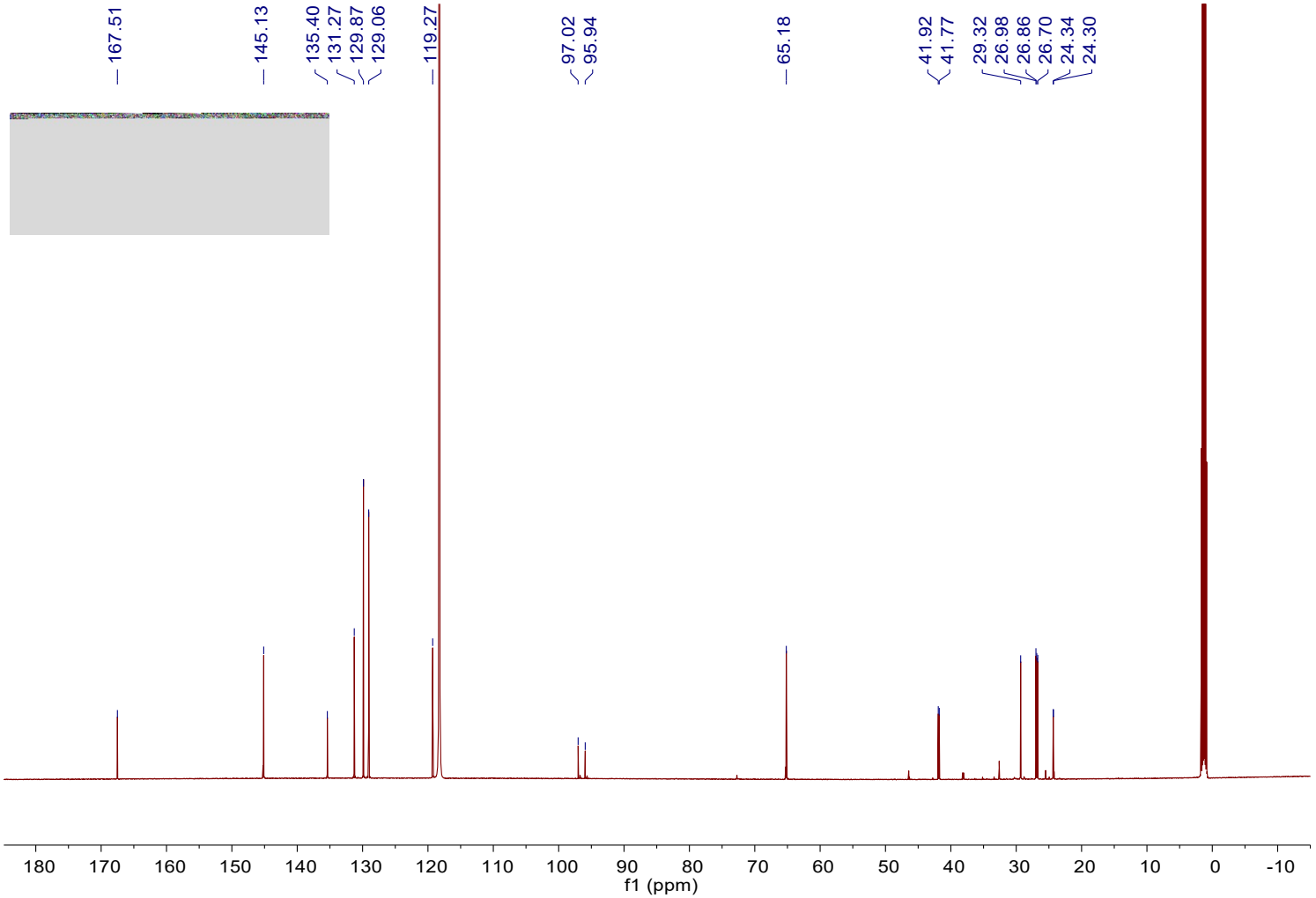
Compound **2k** ^{19}F NMR (376 MHz, CD_3CN)



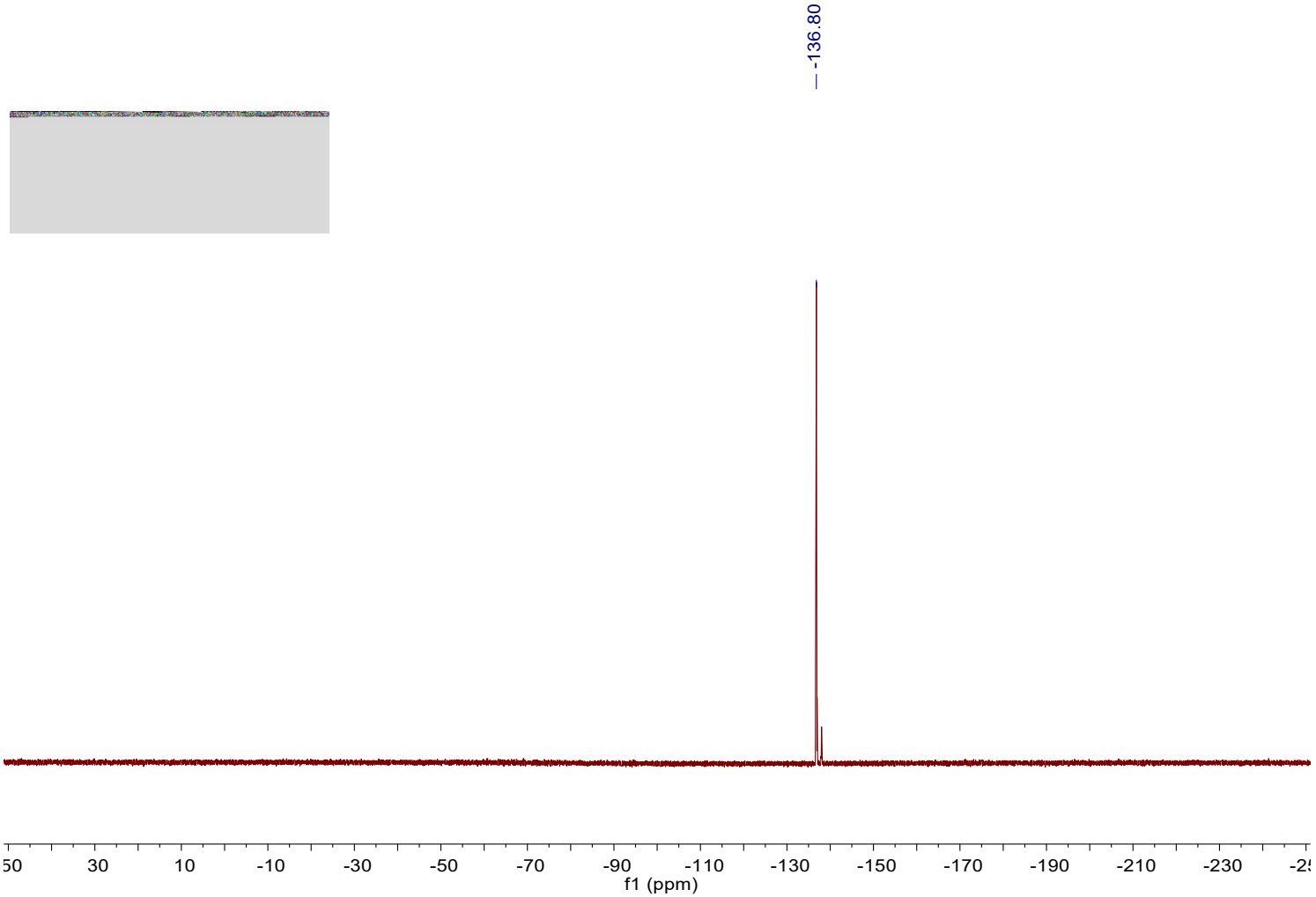
Compound **2l** ^{1}H NMR (400 MHz, CD_3CN)



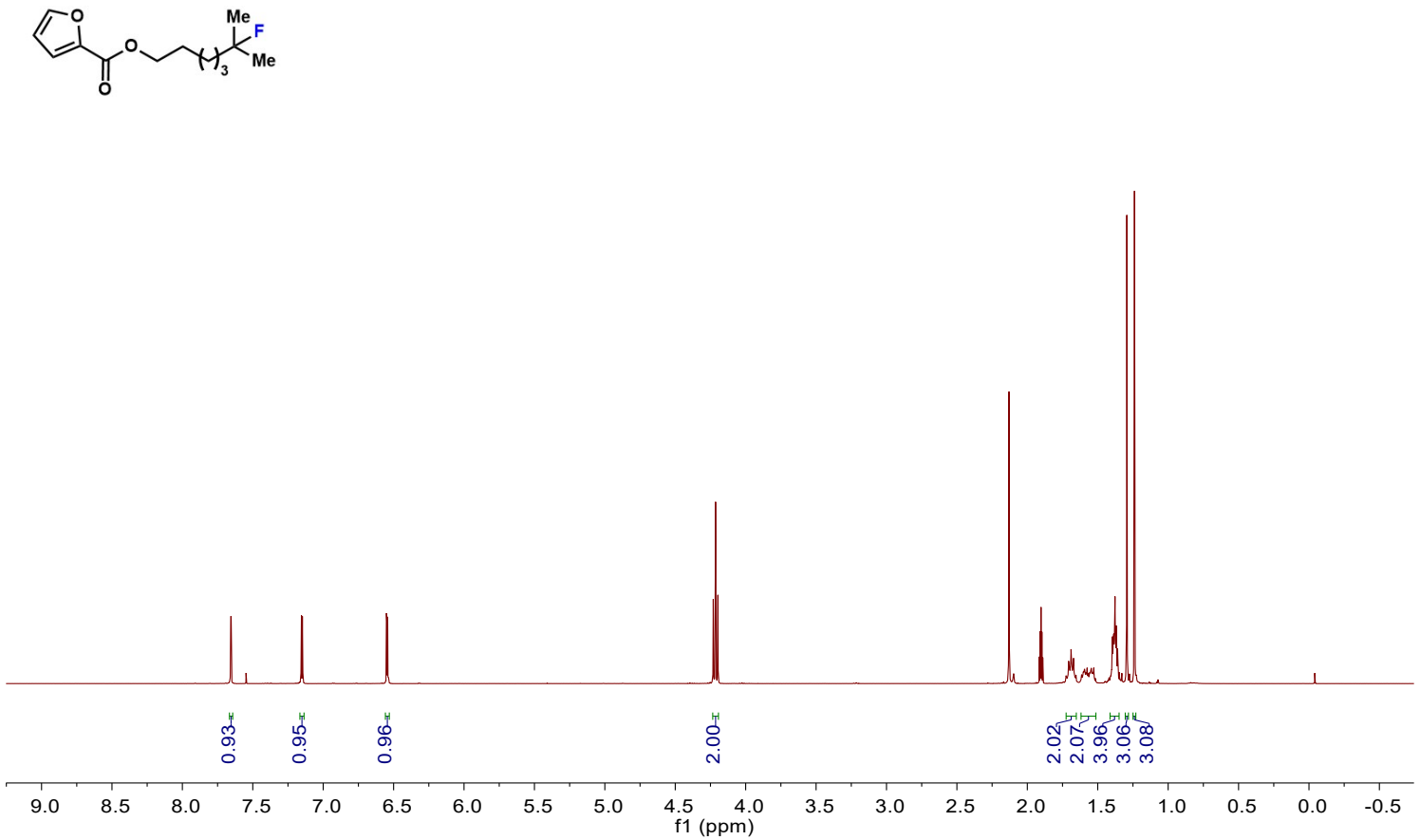
Compound **21** ^{13}C NMR (151 MHz, CD_3CN)



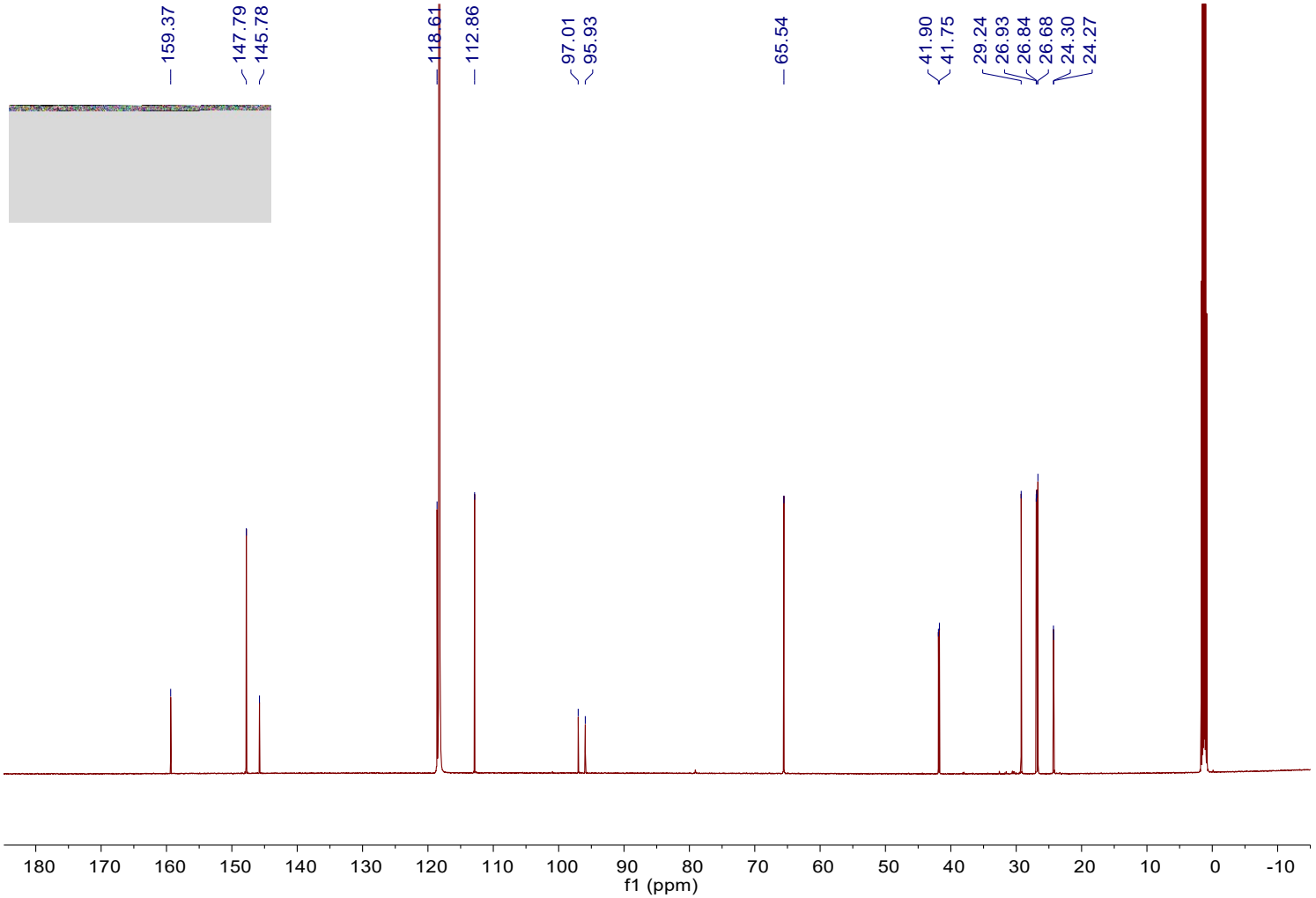
Compound **2l** ^{19}F NMR (376 MHz, CD_3CN)



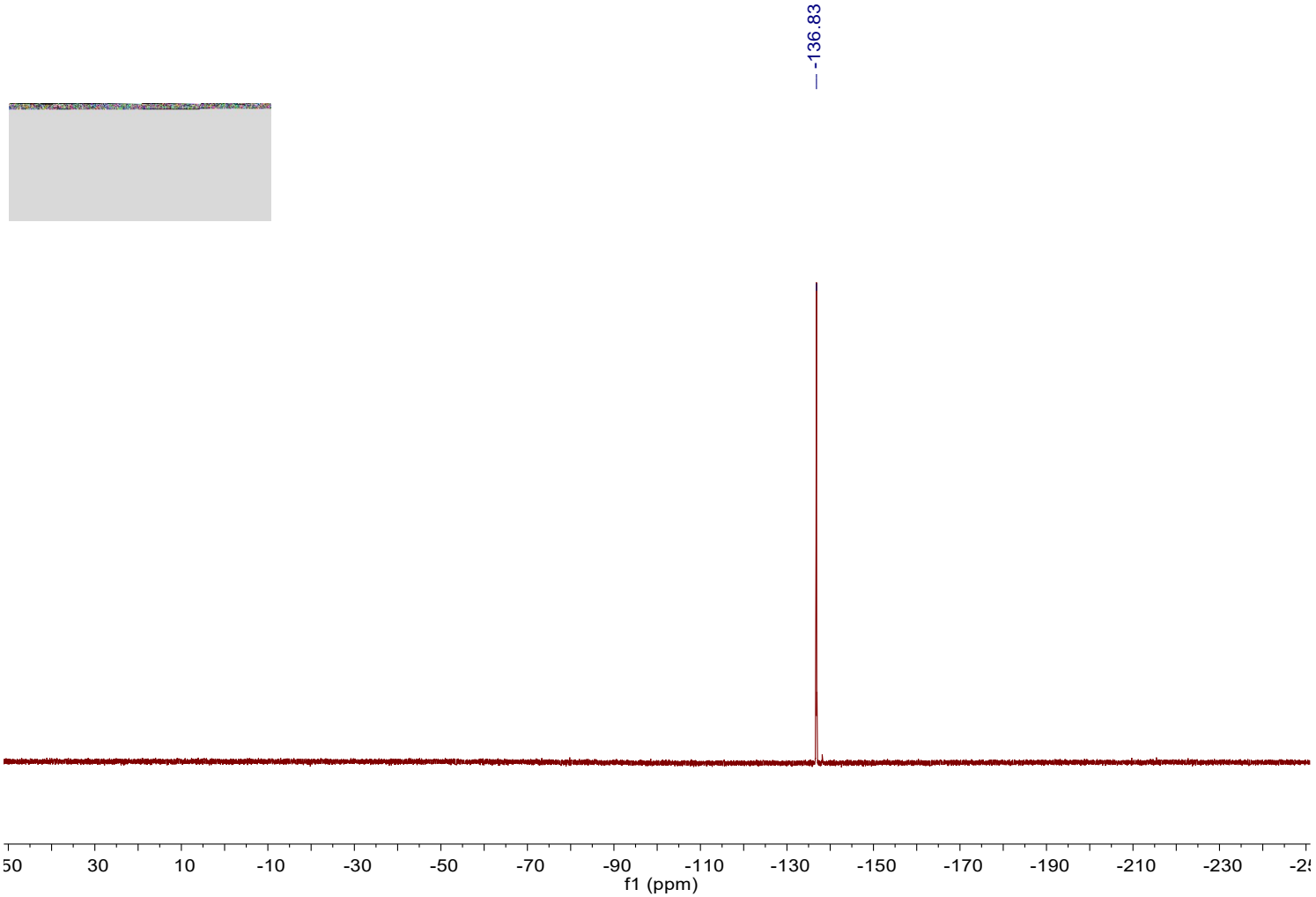
Compound **2m** ^{1}H NMR (400 MHz, CD_3CN)



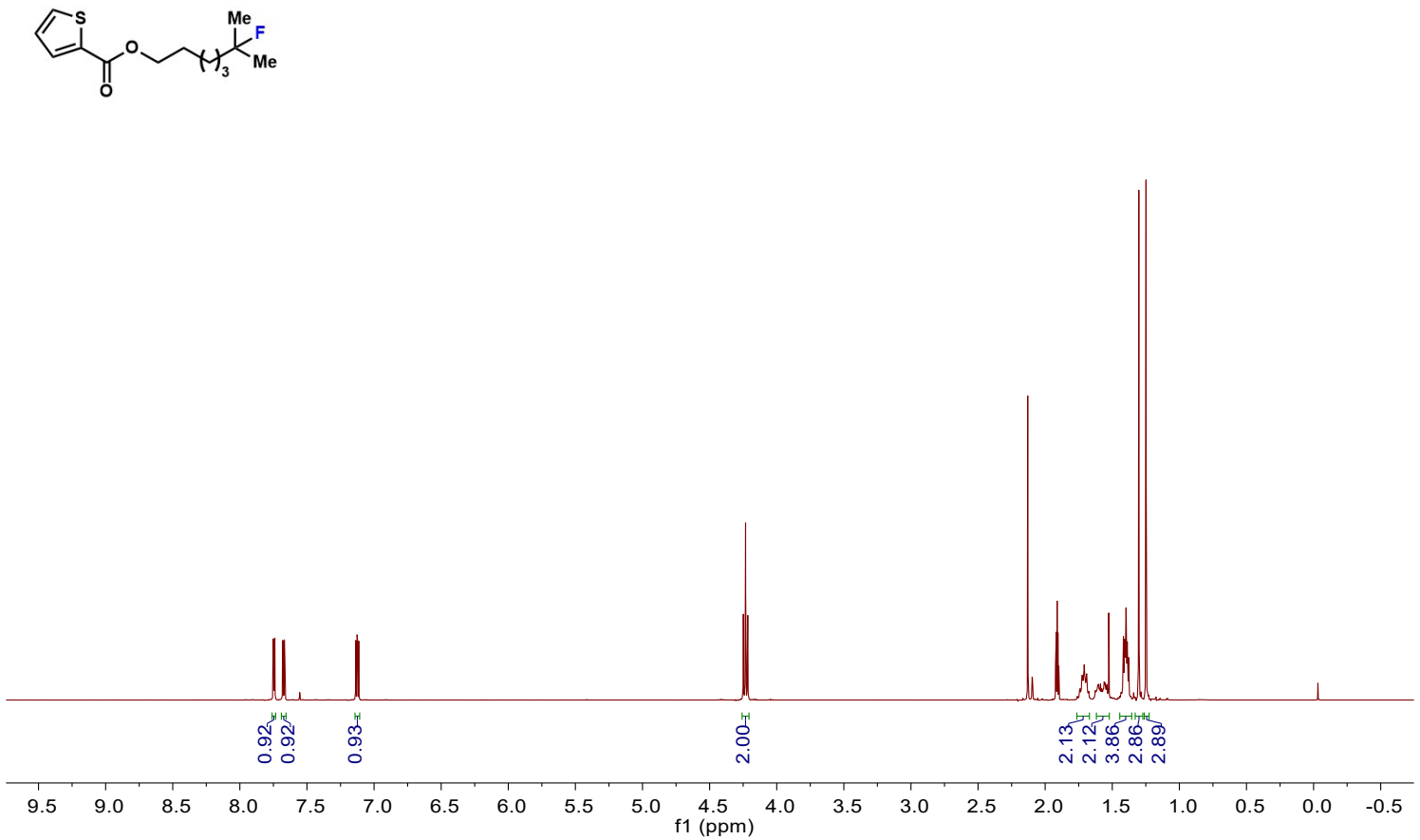
Compound **2m** ^{13}C NMR (151 MHz, CD_3CN)



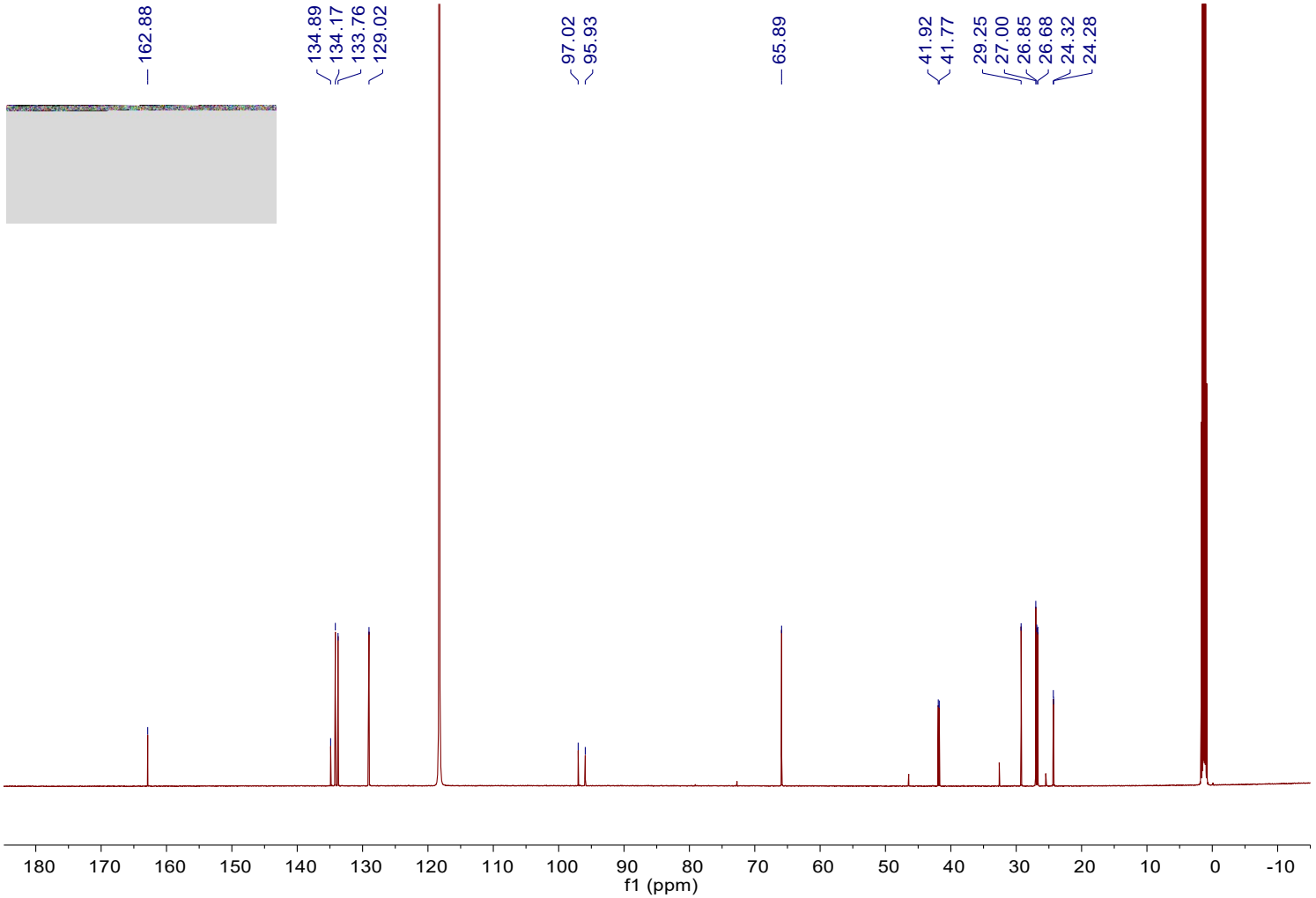
Compound **2m** ^{19}F NMR (376 MHz, CD_3CN)



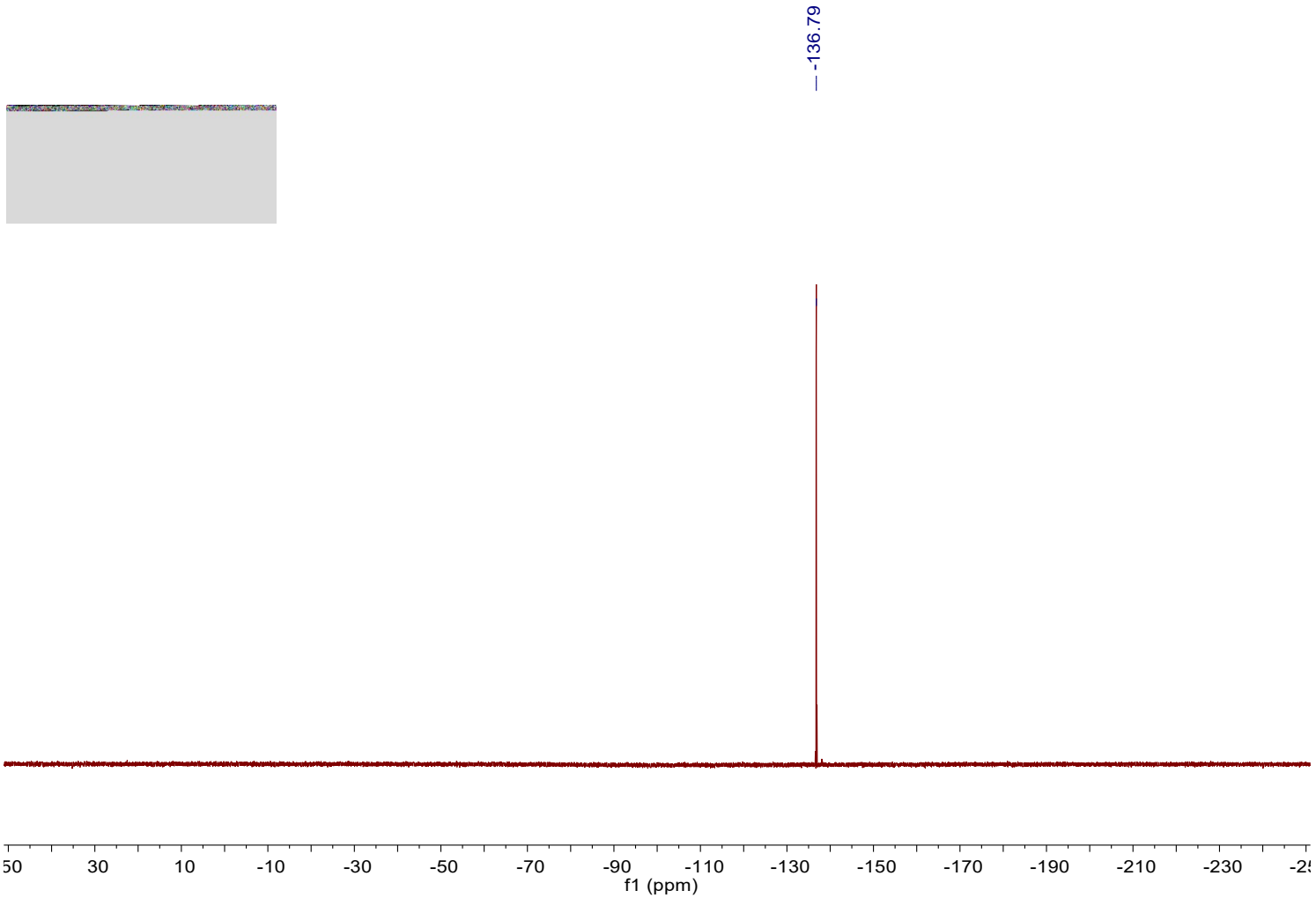
Compound **2n** ^{1}H NMR (400 MHz, CD_3CN)



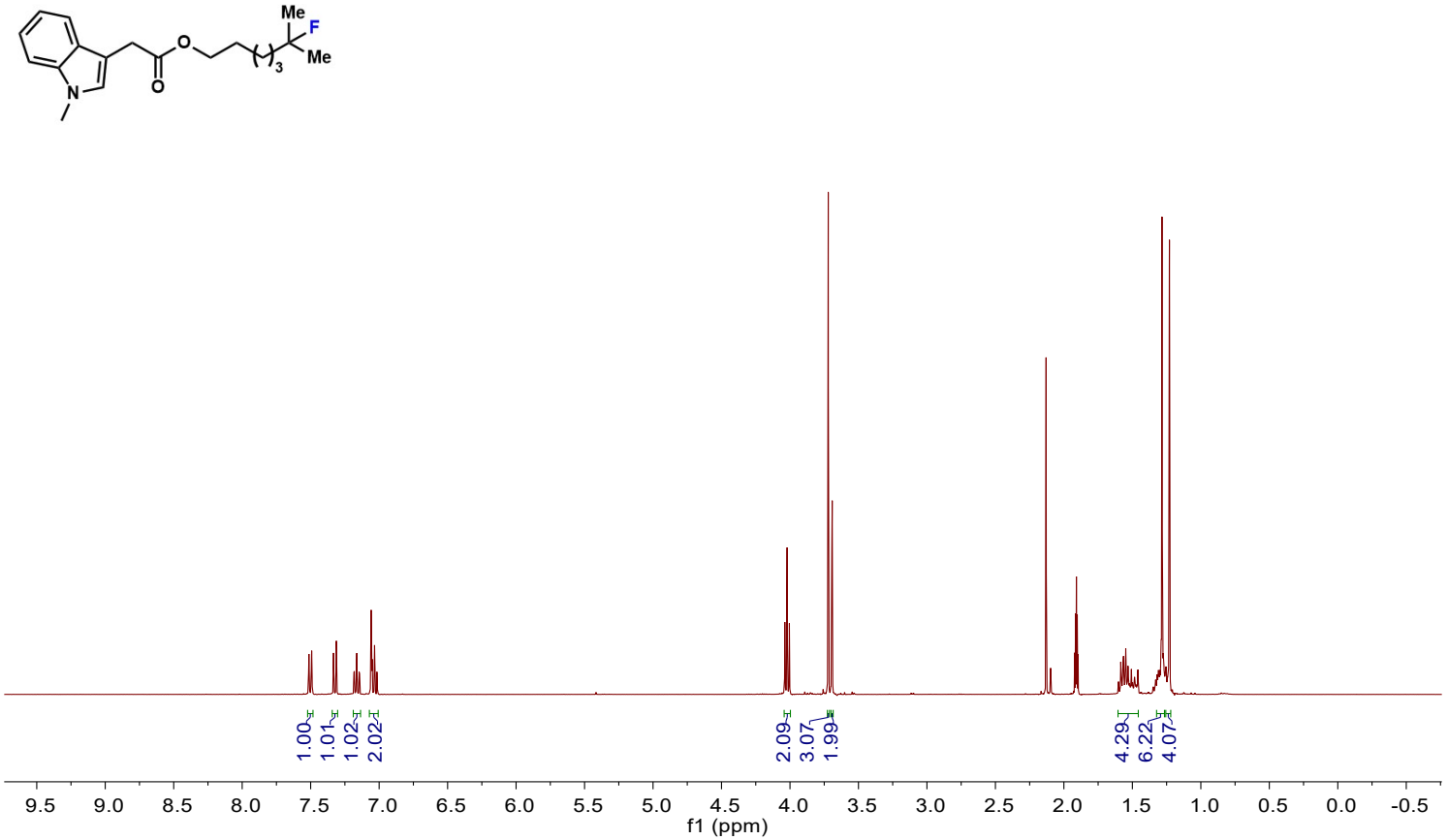
Compound **2n** ^{13}C NMR (151 MHz, CD_3CN)



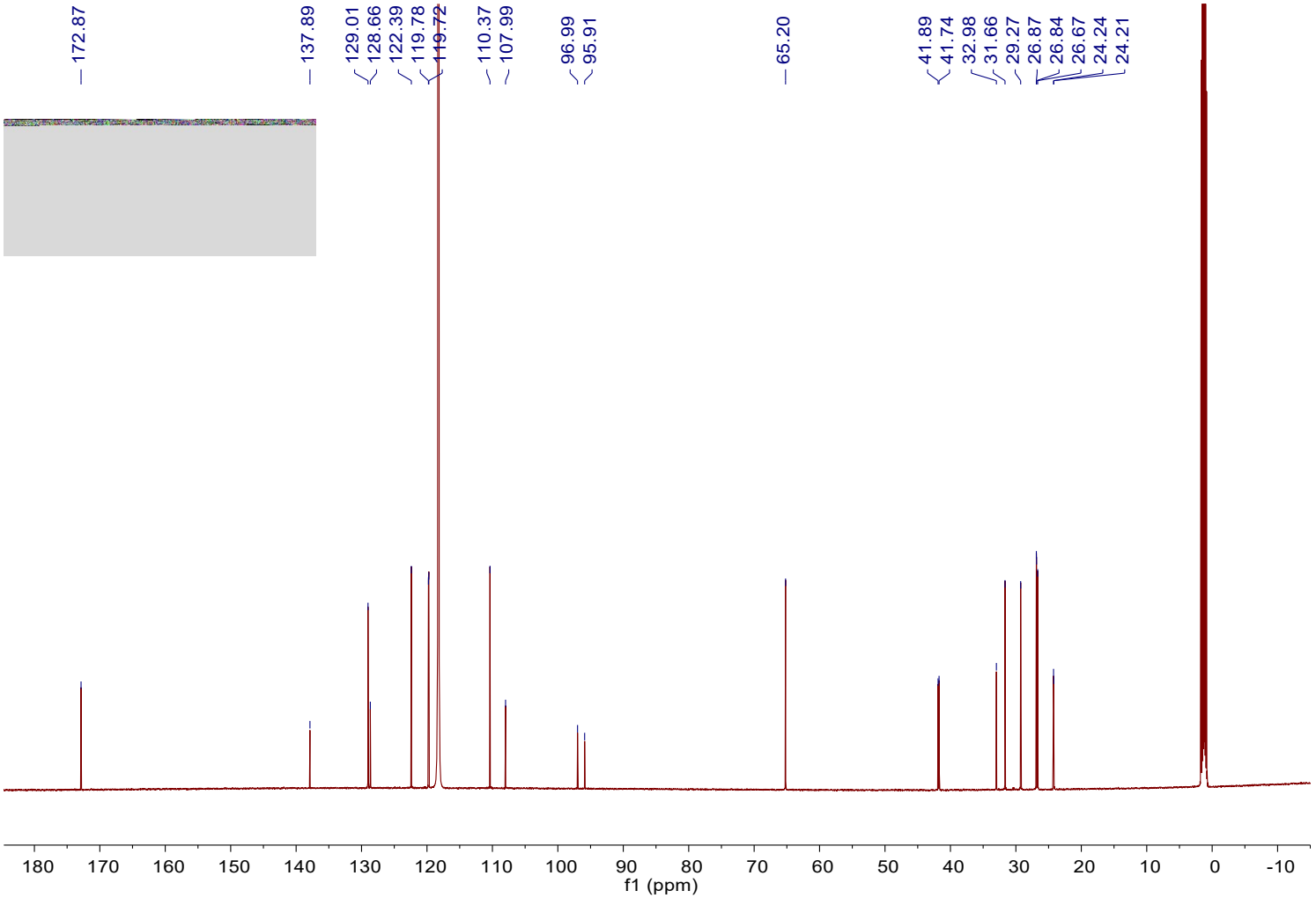
Compound **2n** ^{19}F NMR (376 MHz, CD_3CN)



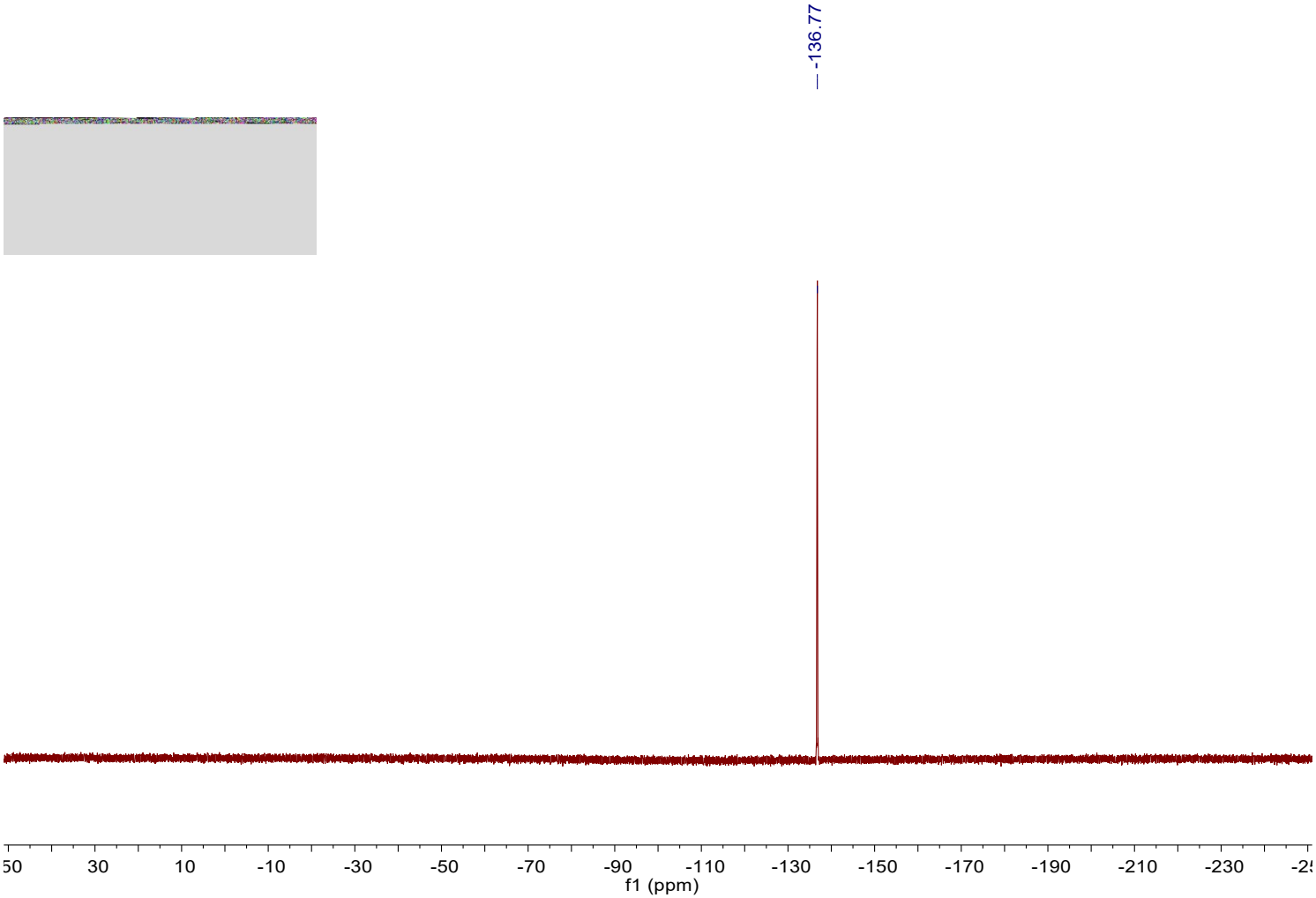
Compound **2o** ^{1}H NMR (400 MHz, CD_3CN)



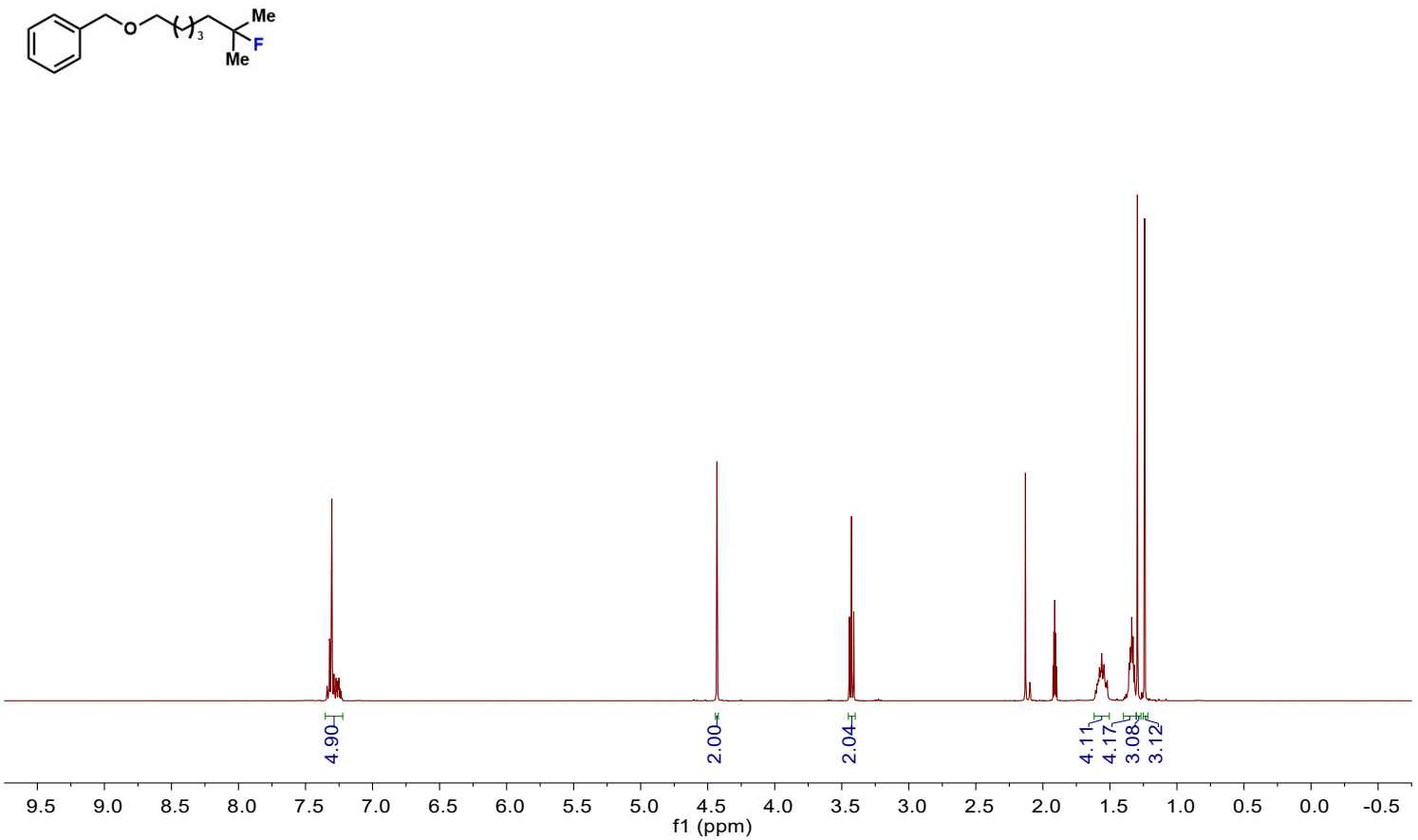
Compound **2o** ^{13}C NMR (151 MHz, CD_3CN)



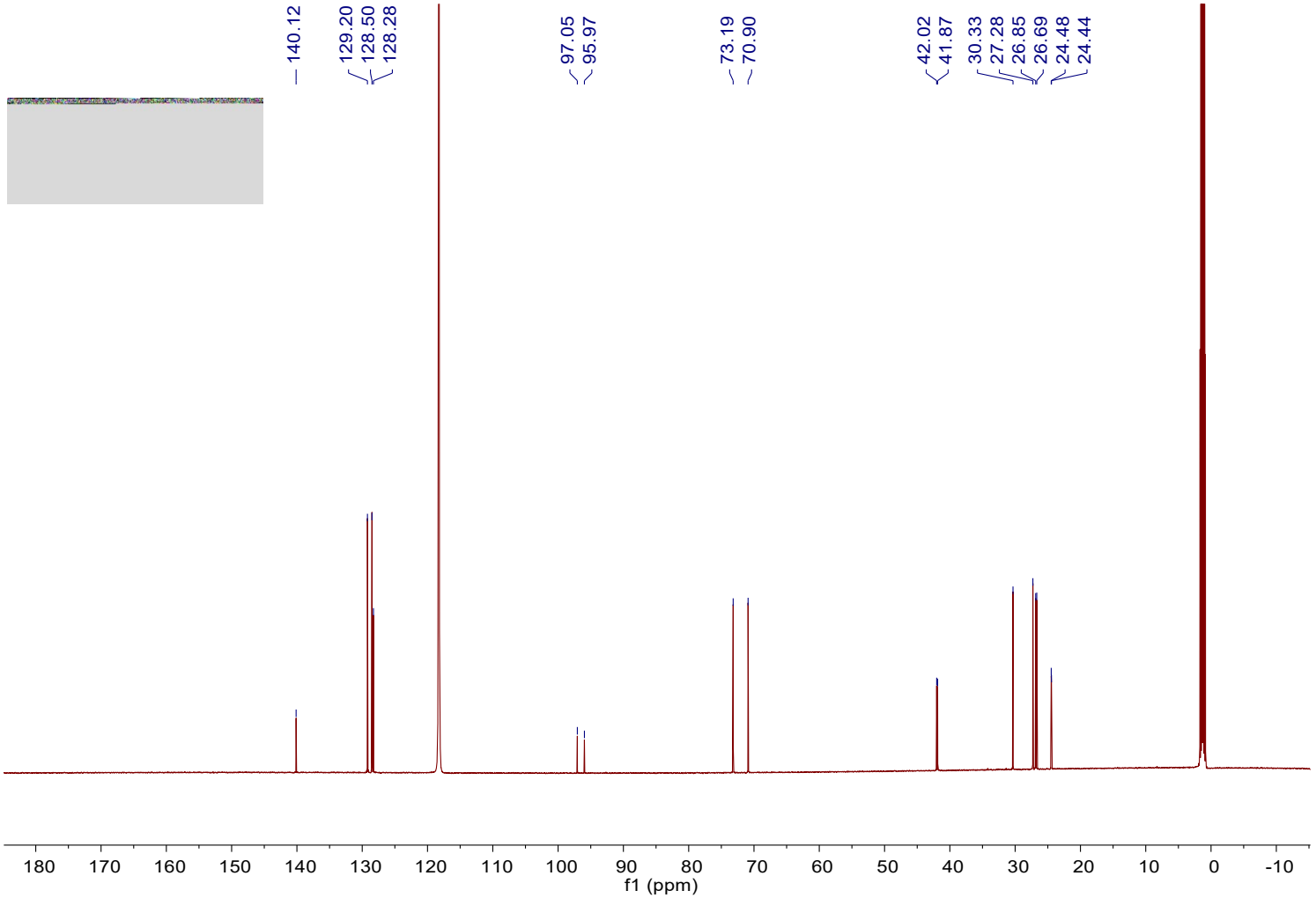
Compound **2o** ^{19}F NMR (376 MHz, CD_3CN)



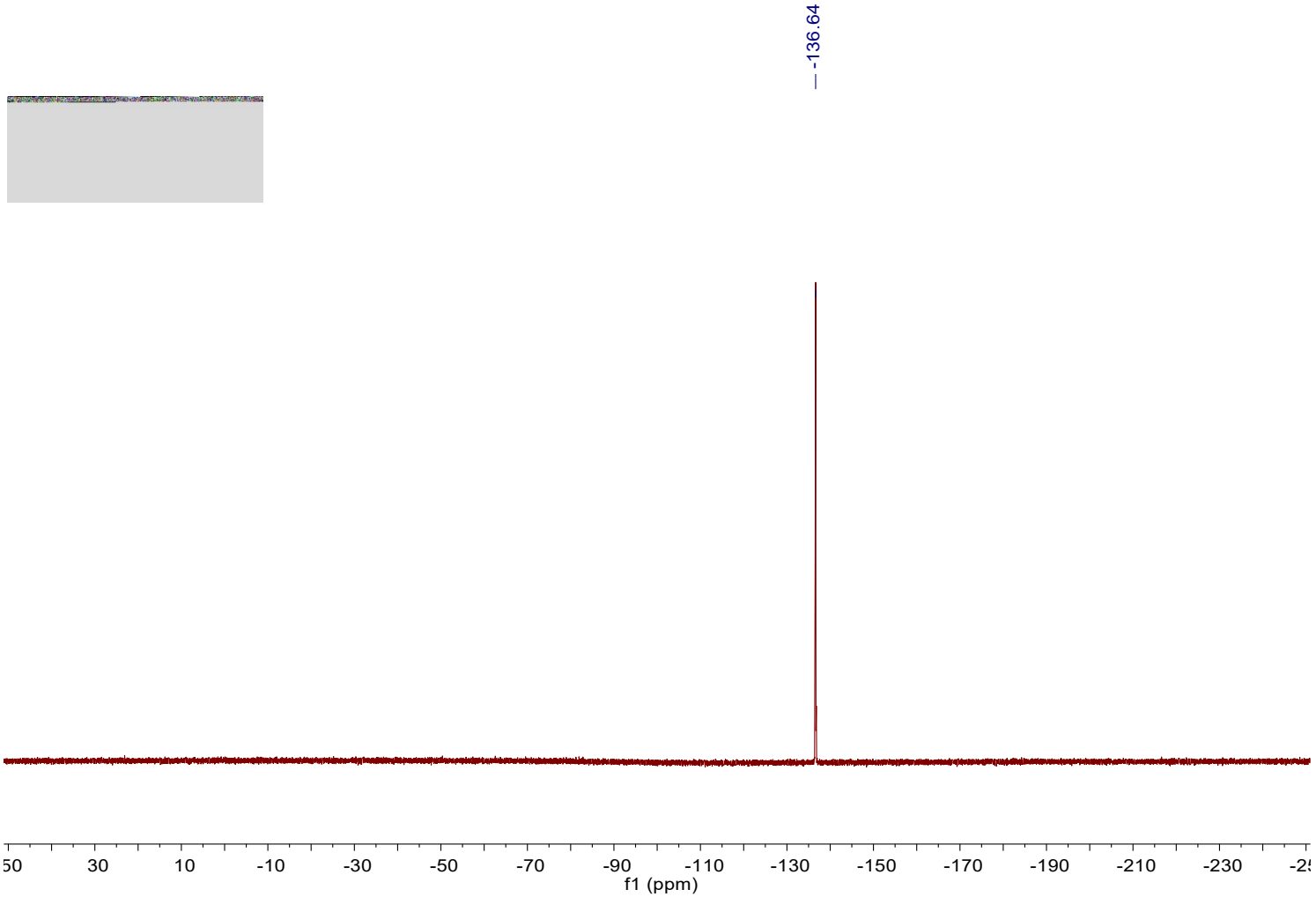
Compound **2p** ^{1}H NMR (400 MHz, CD_3CN)



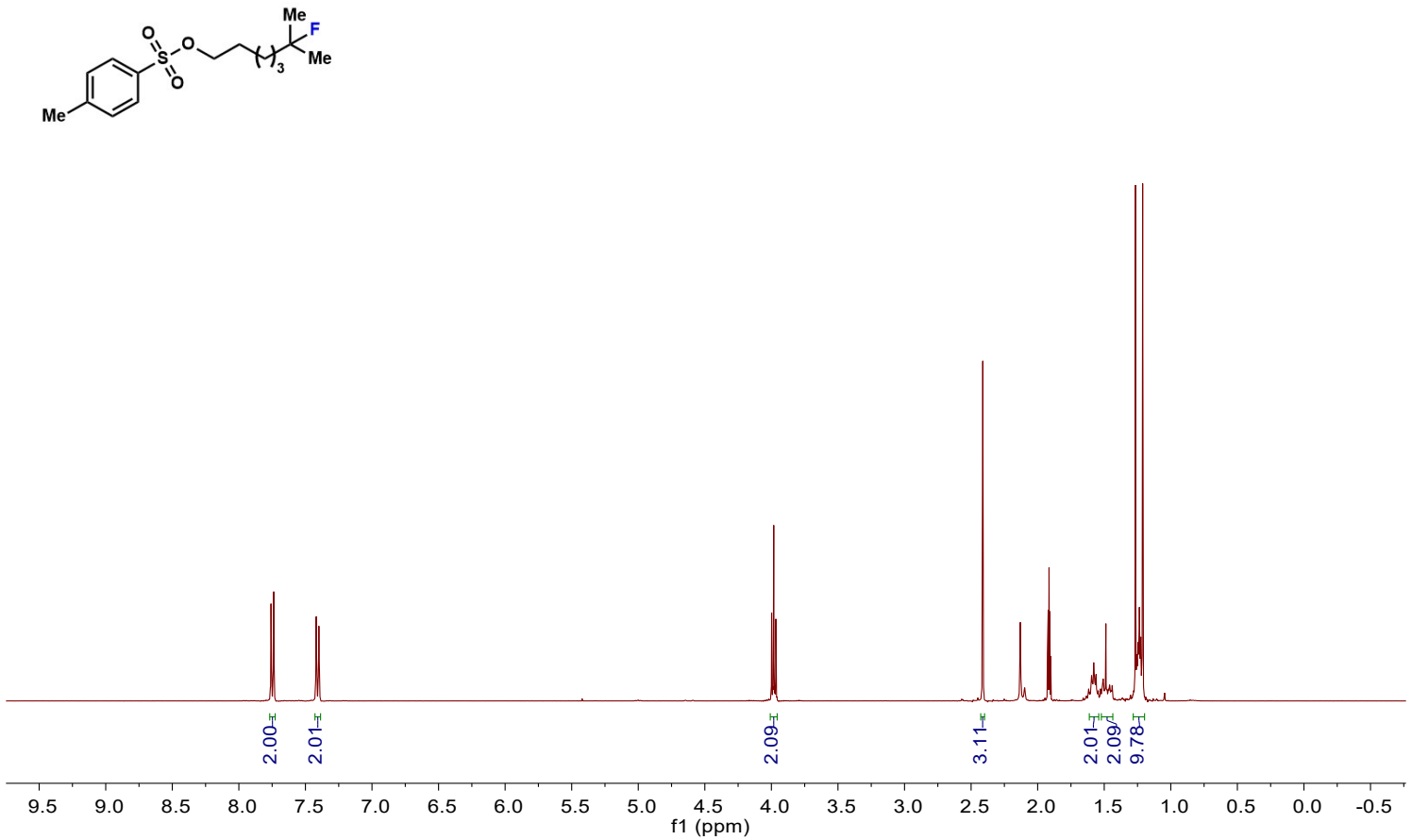
Compound **2p** ^{13}C NMR (151 MHz, CD_3CN)



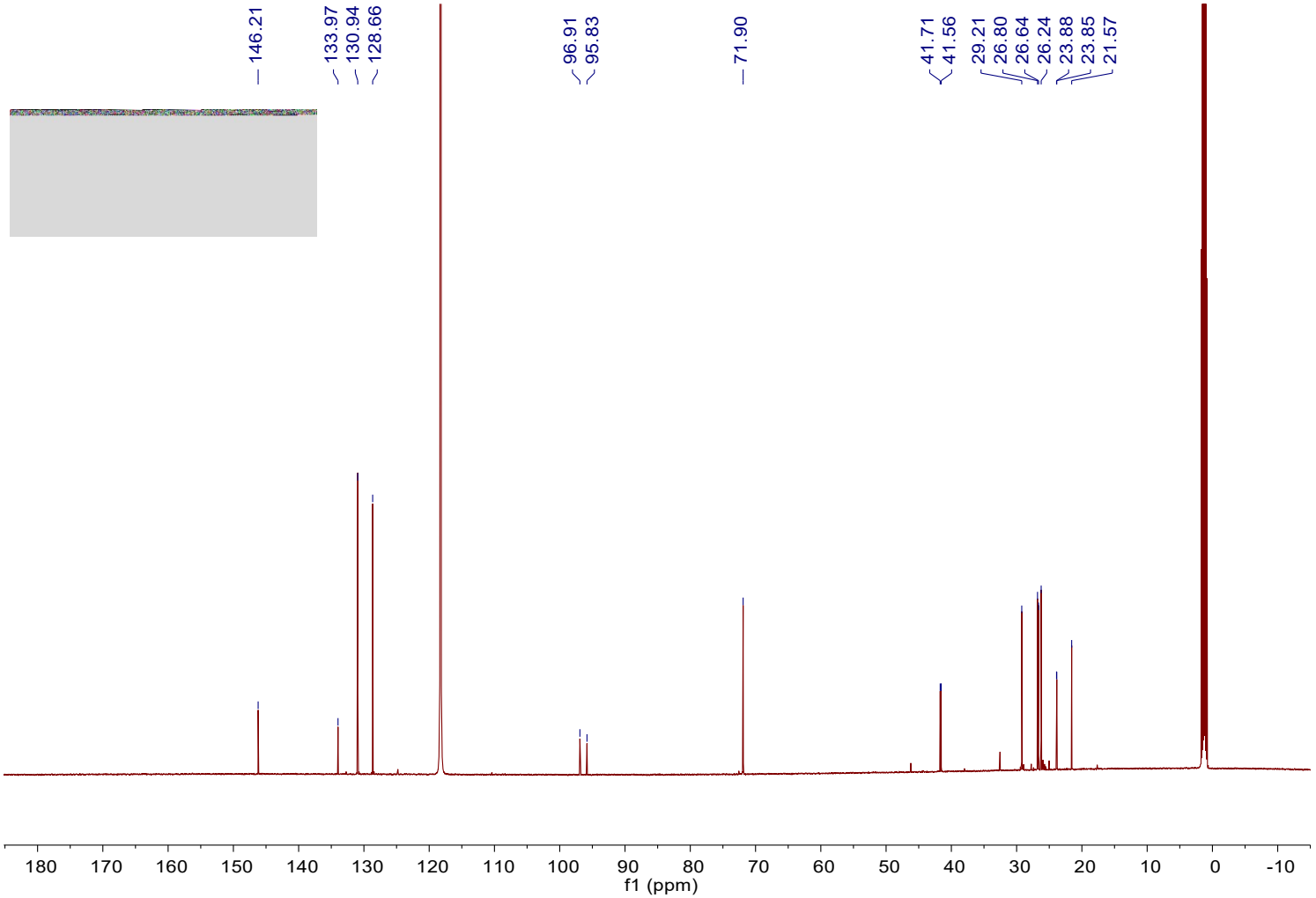
Compound **2p** ^{19}F NMR (376 MHz, CD_3CN)



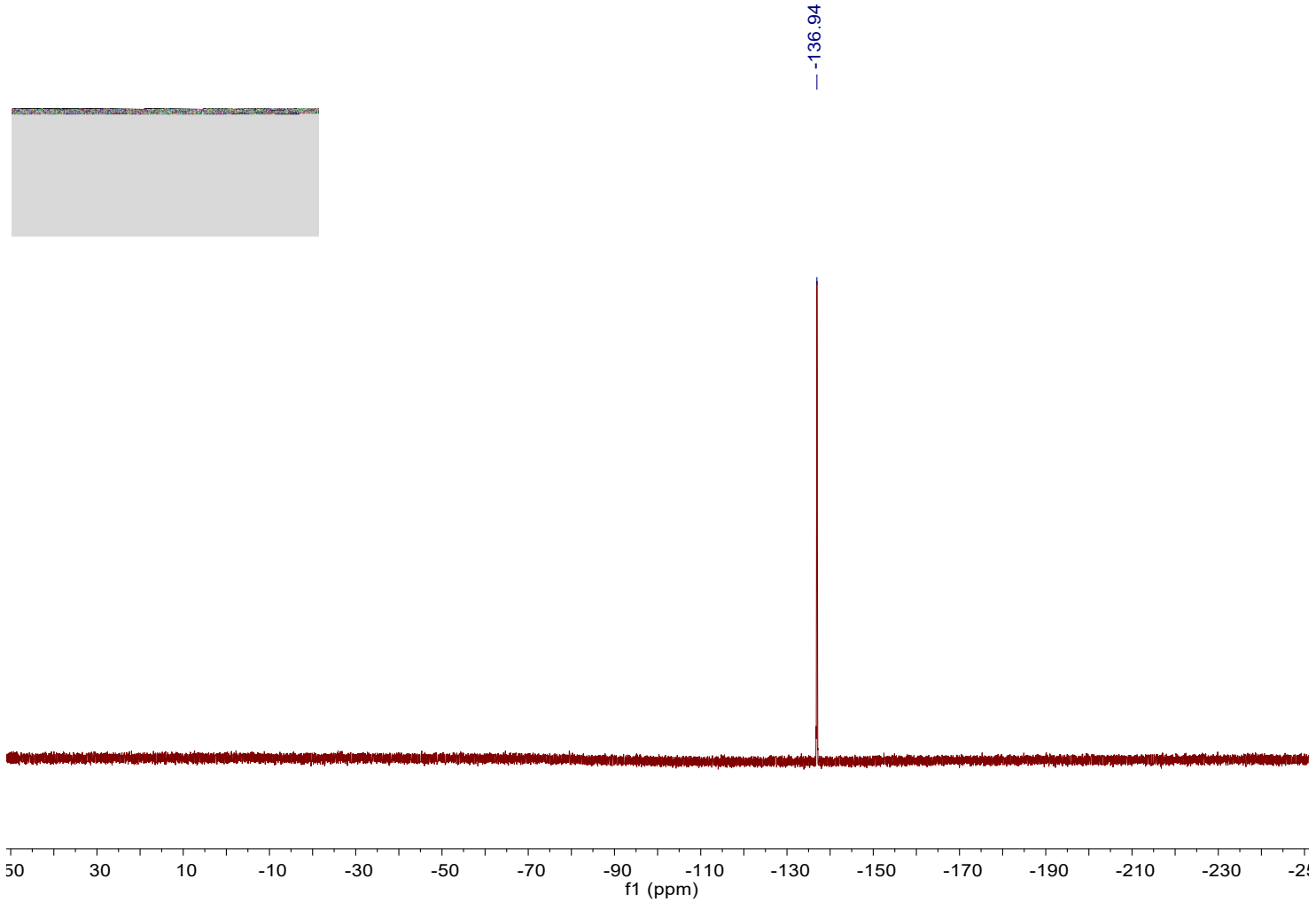
Compound **2q** ^{1}H NMR (400 MHz, CD_3CN)



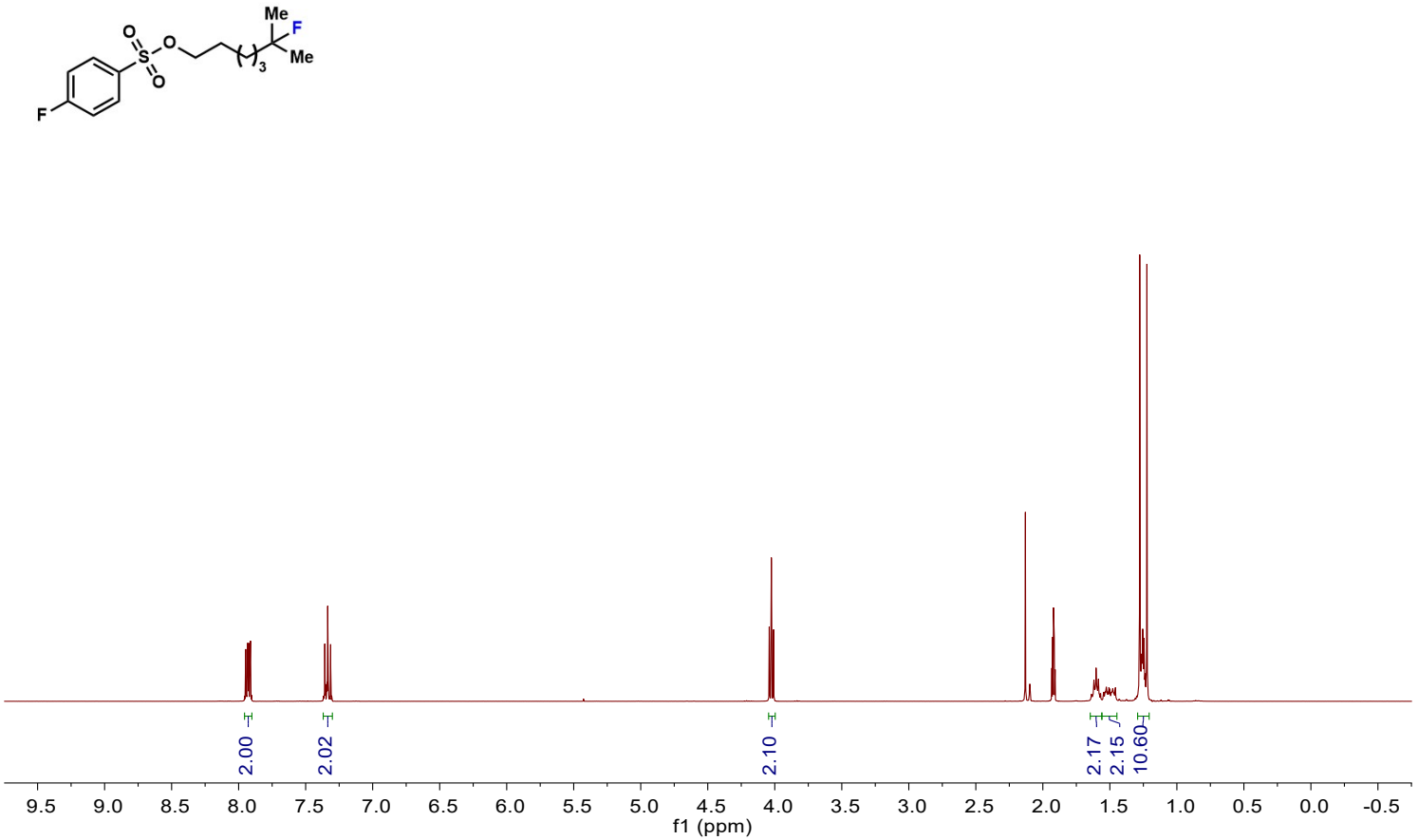
Compound **2q** ^{13}C NMR (151 MHz, CD_3CN)



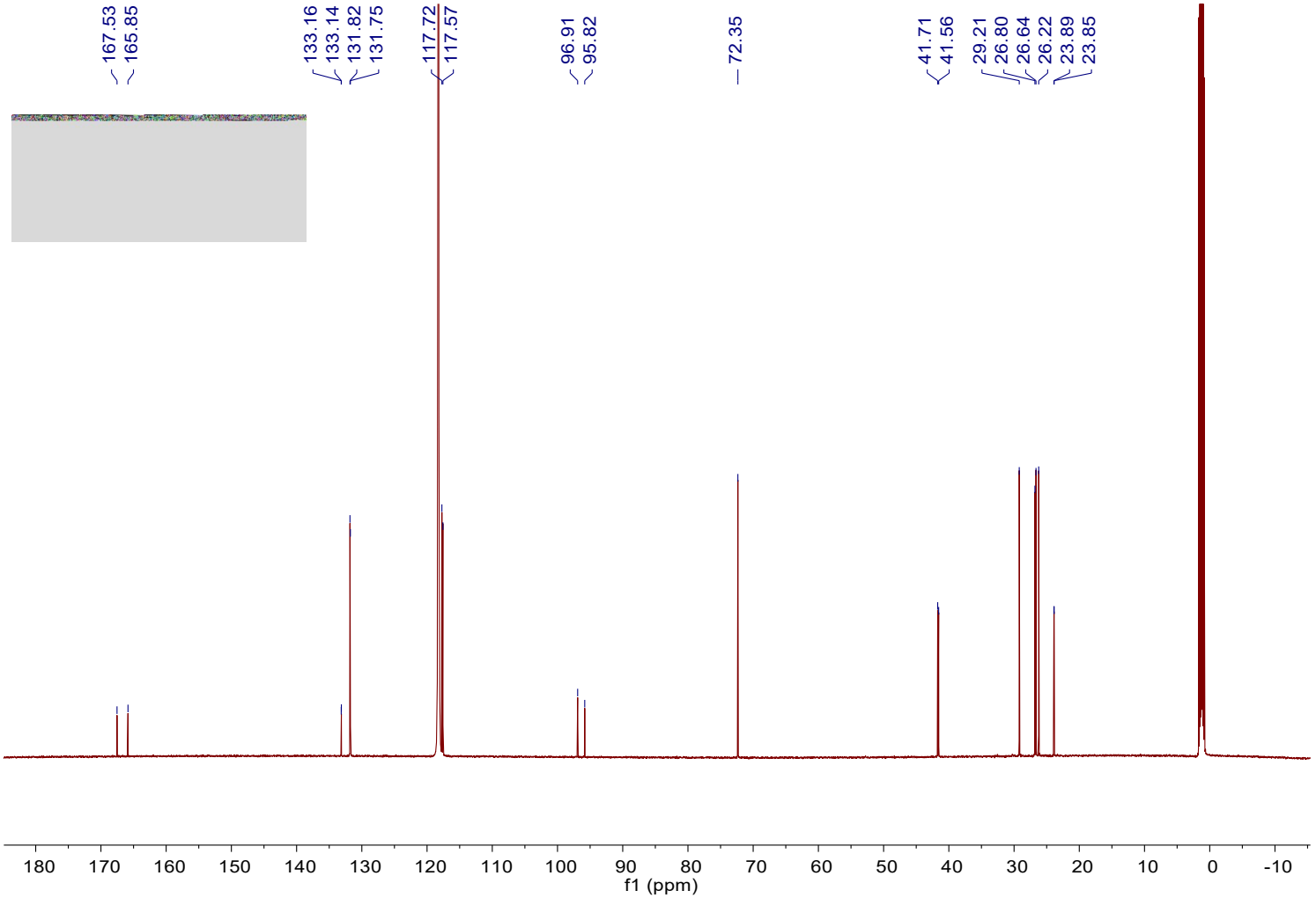
Compound **2q** ^{19}F NMR (376 MHz, CD_3CN)



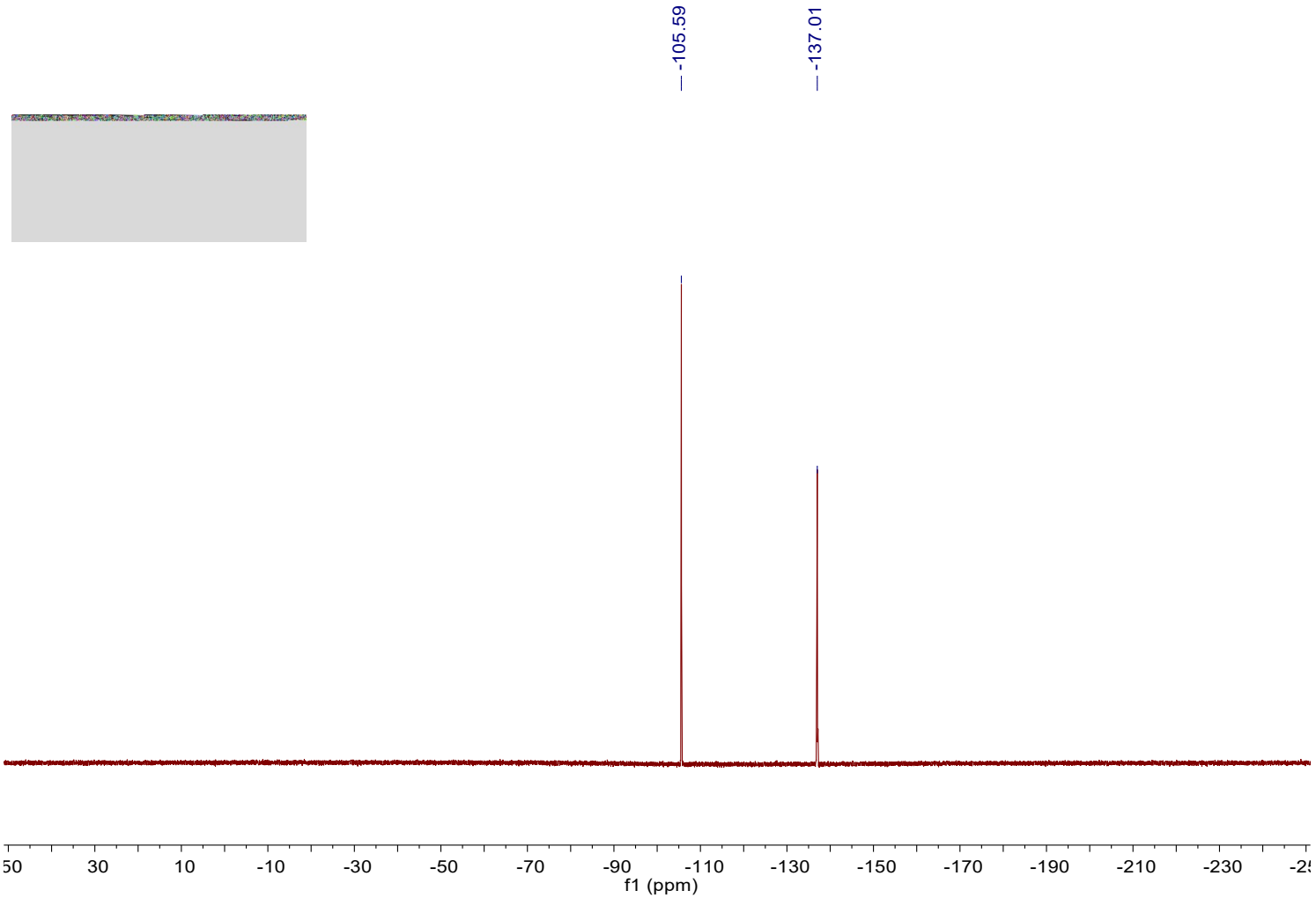
Compound **2r** ^{1}H NMR (400 MHz, CD_3CN)



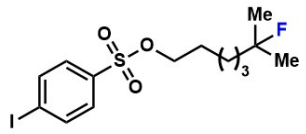
Compound **2r** ^{13}C NMR (151 MHz, CD_3CN)

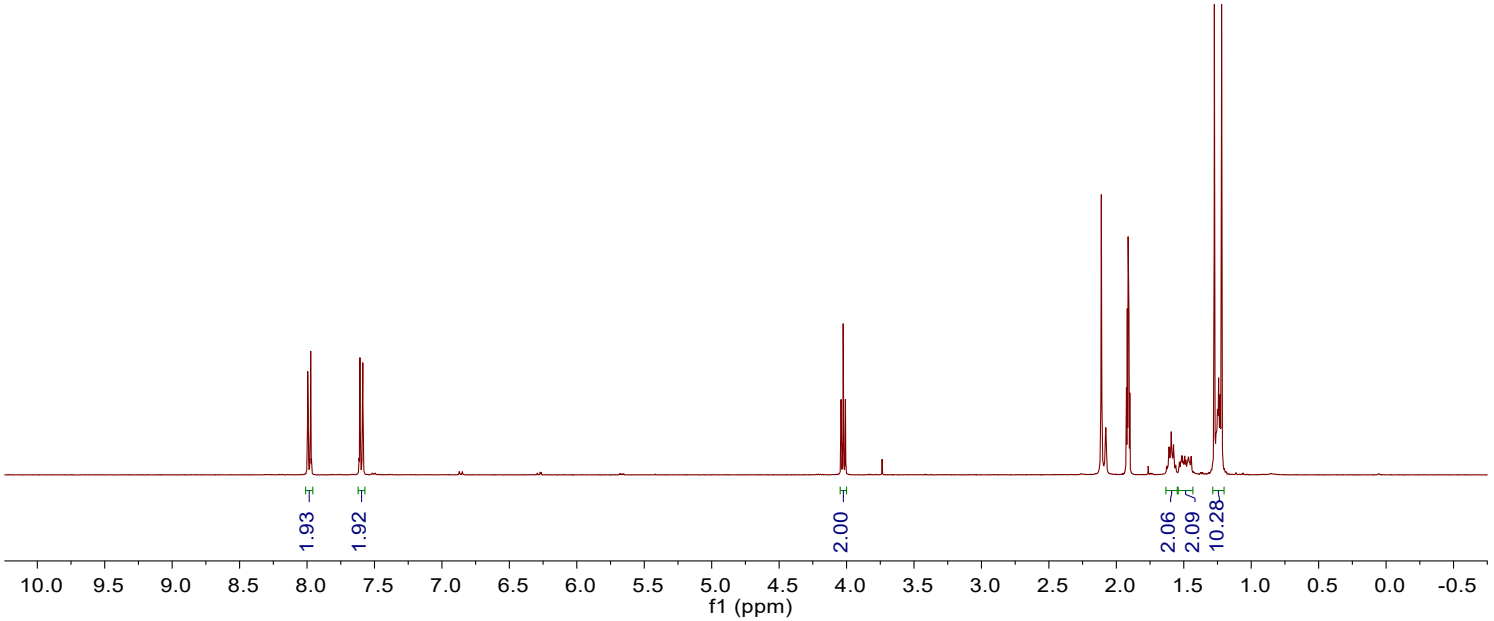


Compound **2r** ^{19}F NMR (376 MHz, CD_3CN)

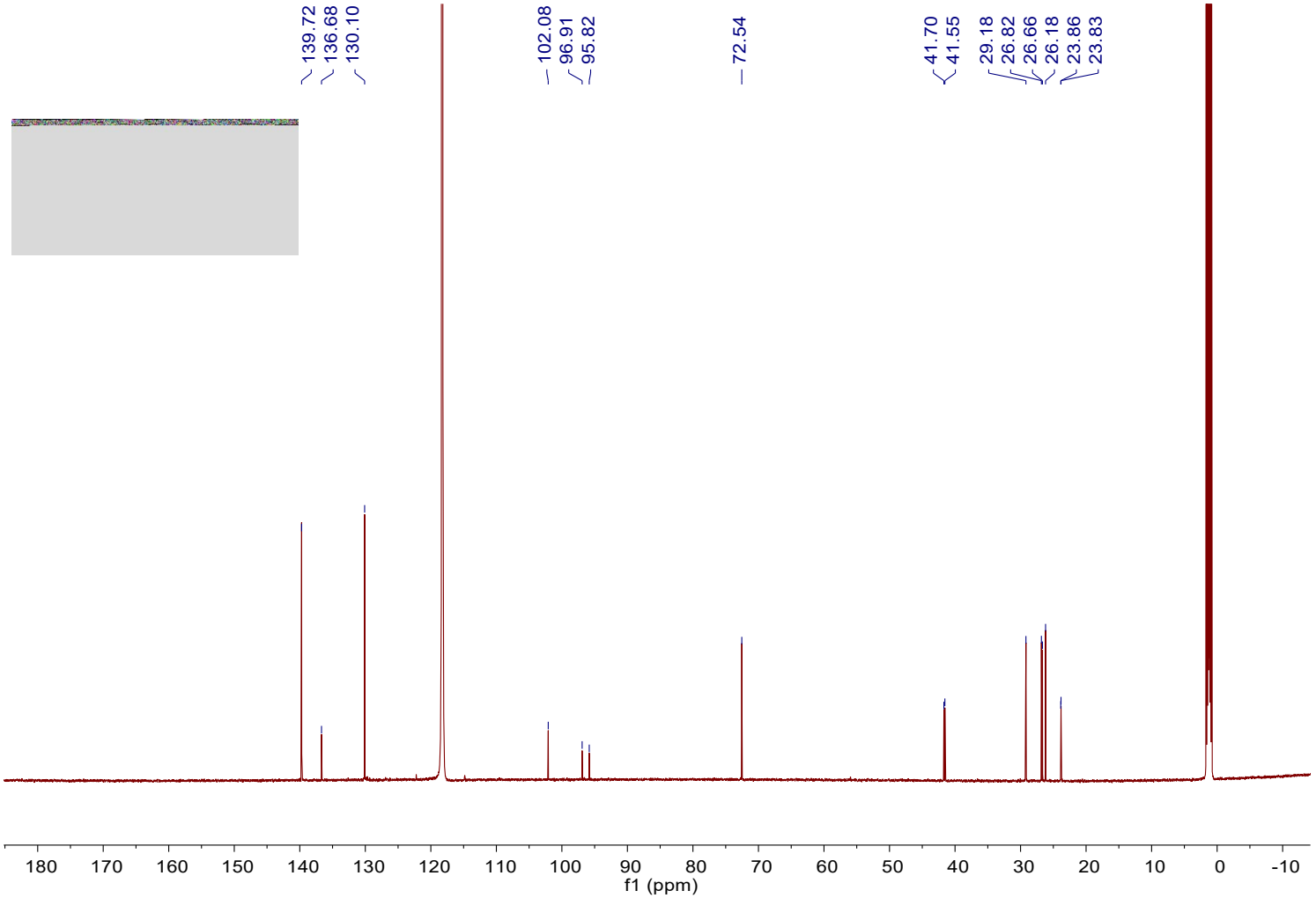


Compound **2s** ^{1}H NMR (400 MHz, CD_3CN)

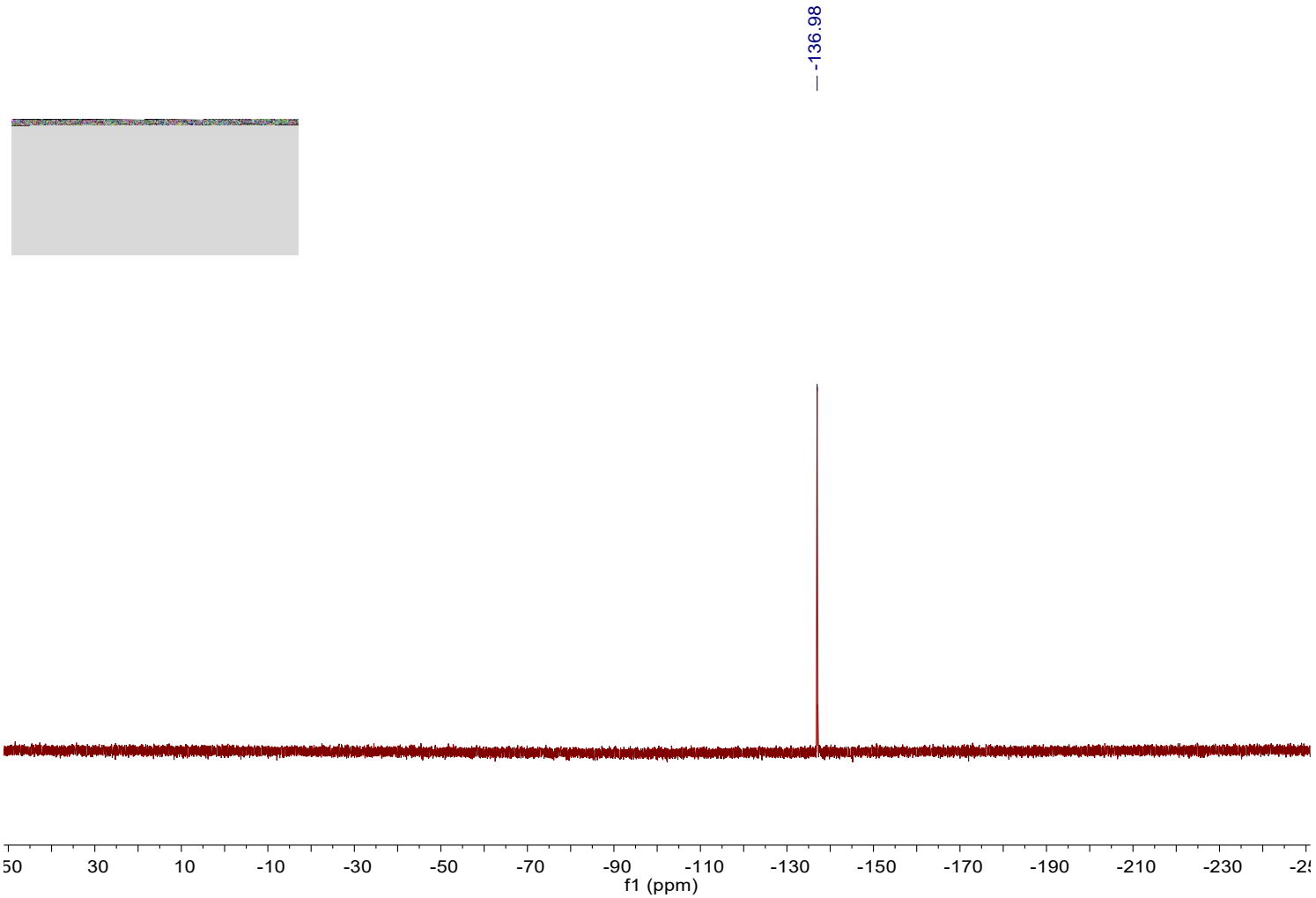




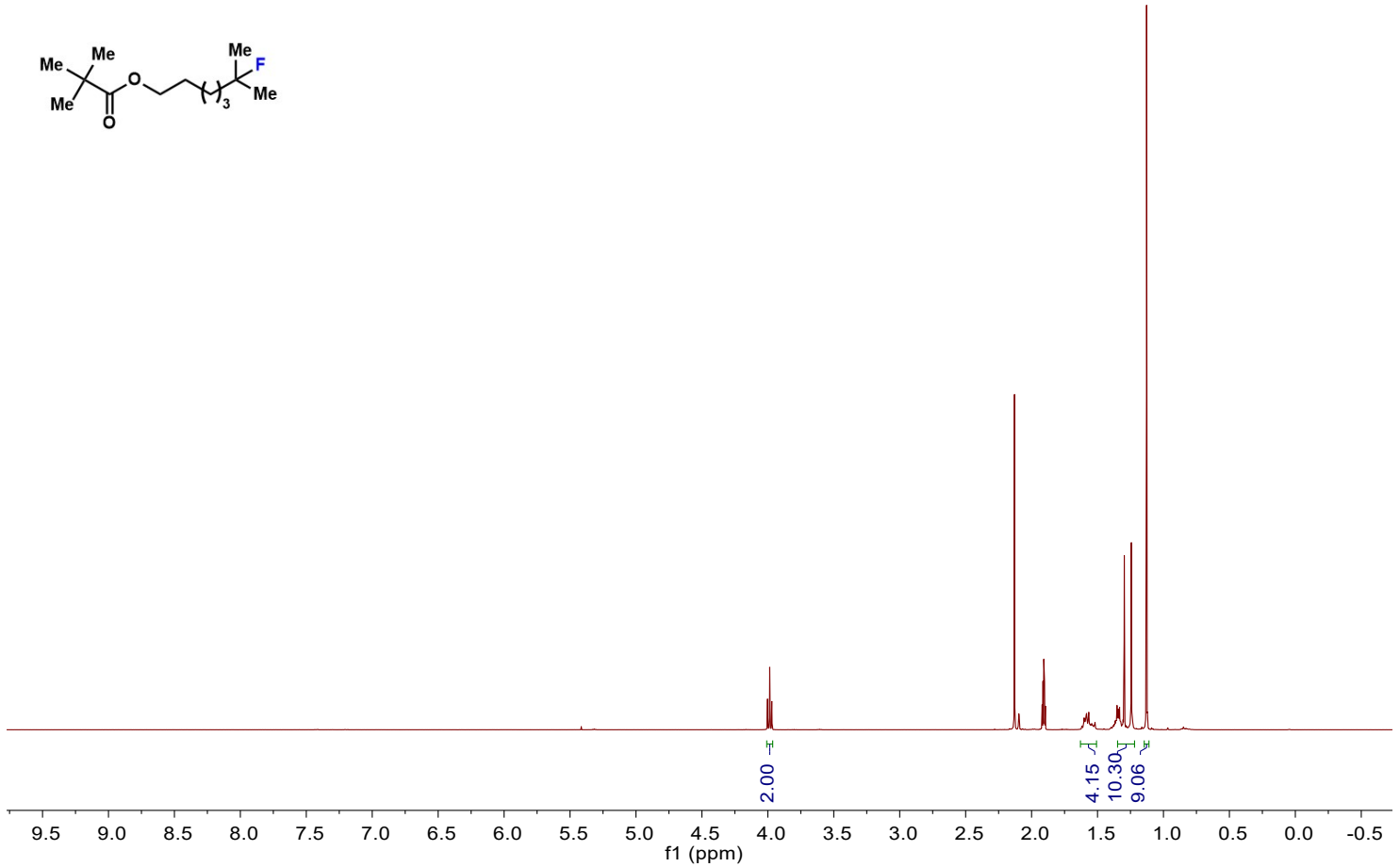
Compound **2s** ^{13}C NMR (151 MHz, CD_3CN)



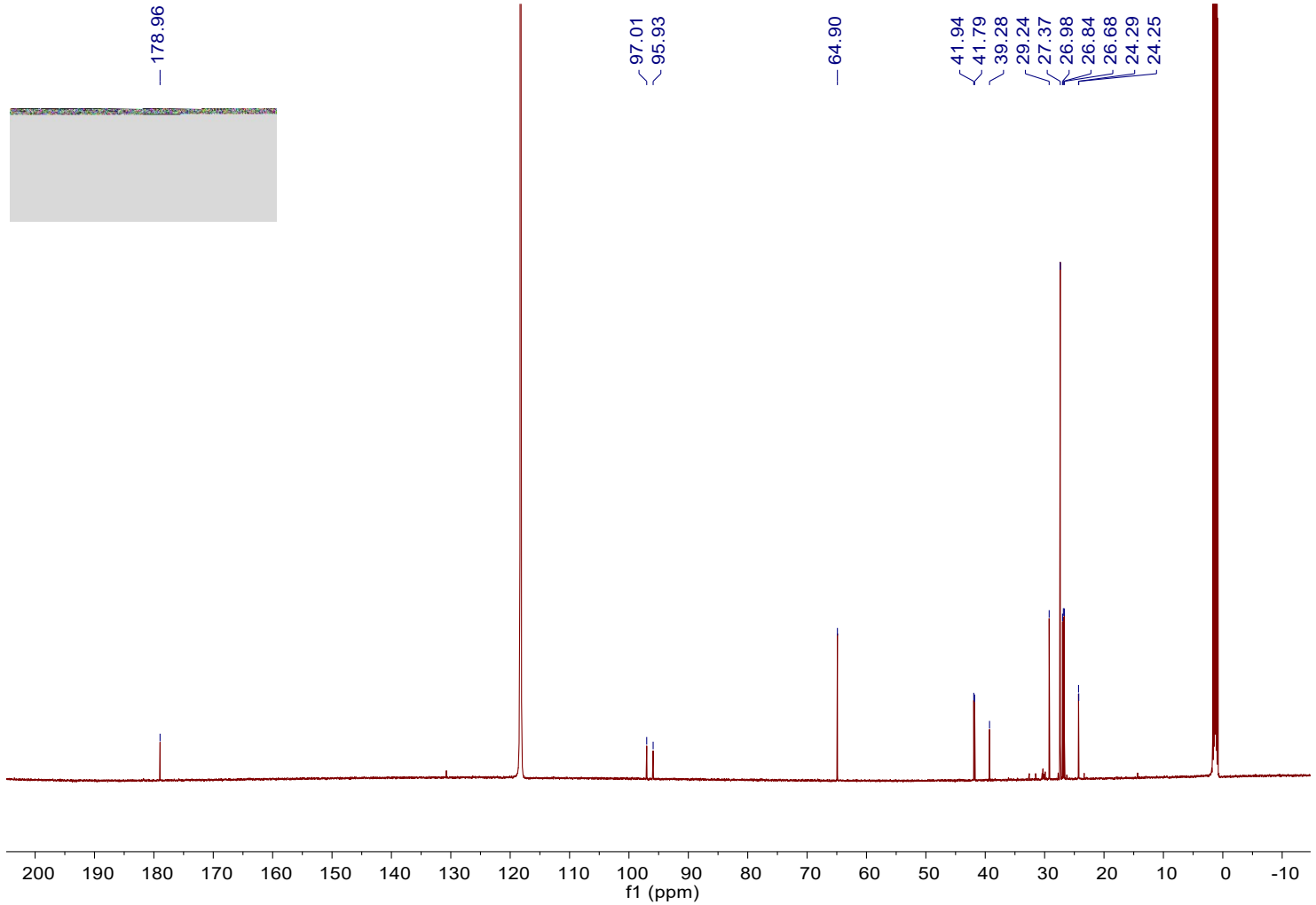
Compound **2s** ^{19}F NMR (376 MHz, CD_3CN)



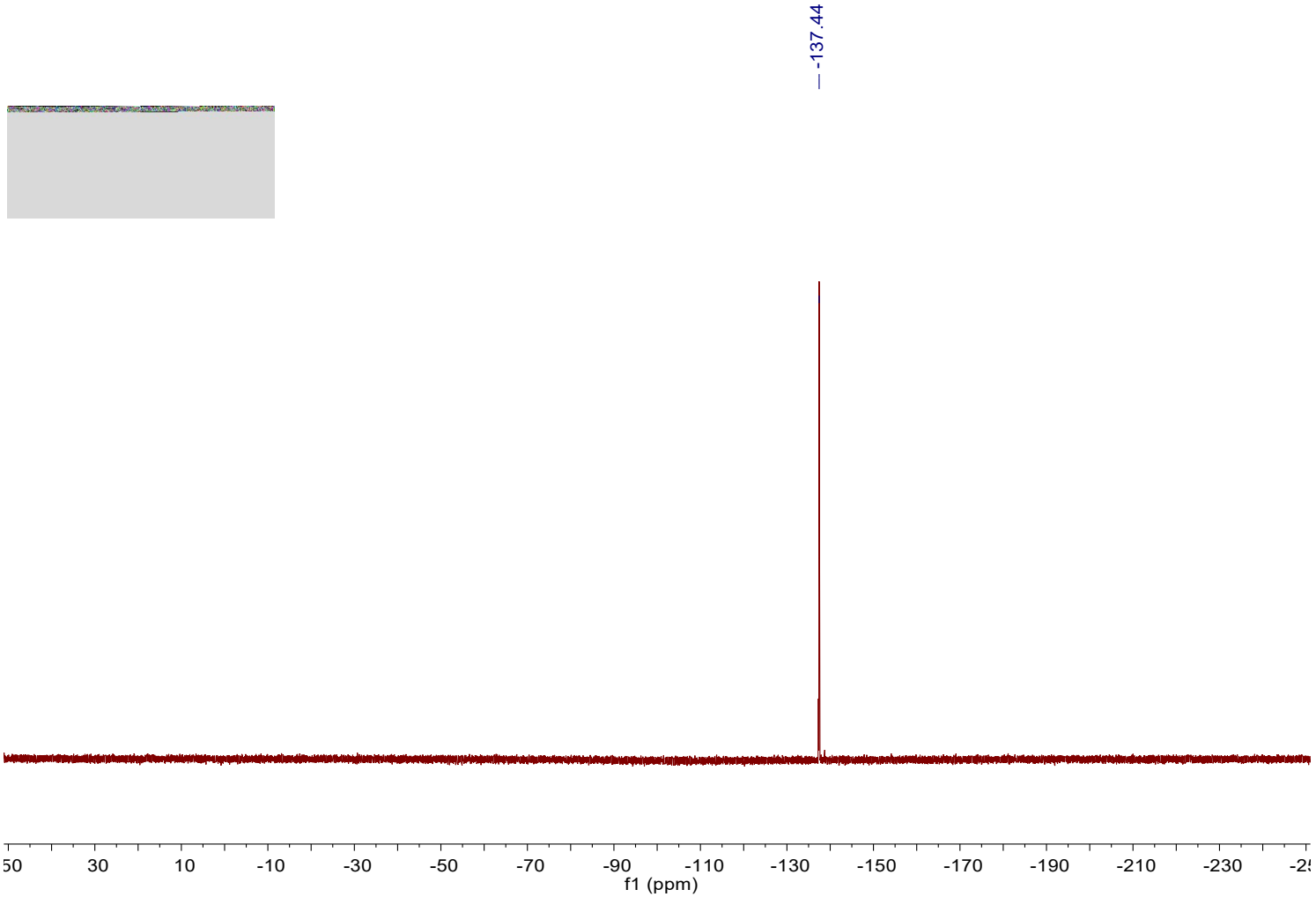
Compound **2t** ^{1}H NMR (400 MHz, CD_3CN)



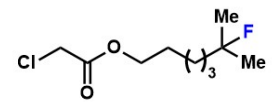
Compound **2t** ^{13}C NMR (151 MHz, CD_3CN)

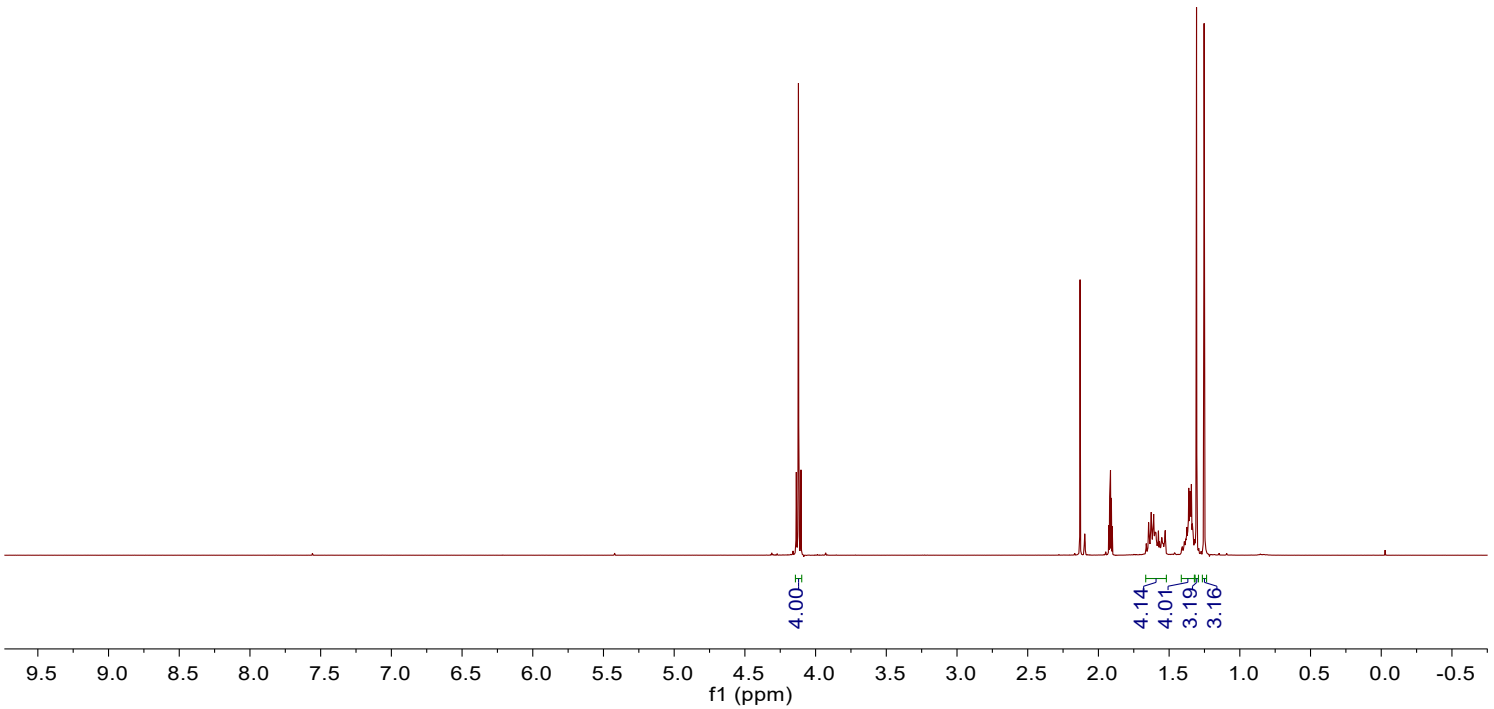


Compound **2t** ^{19}F NMR (376 MHz, $CDCl_3$)

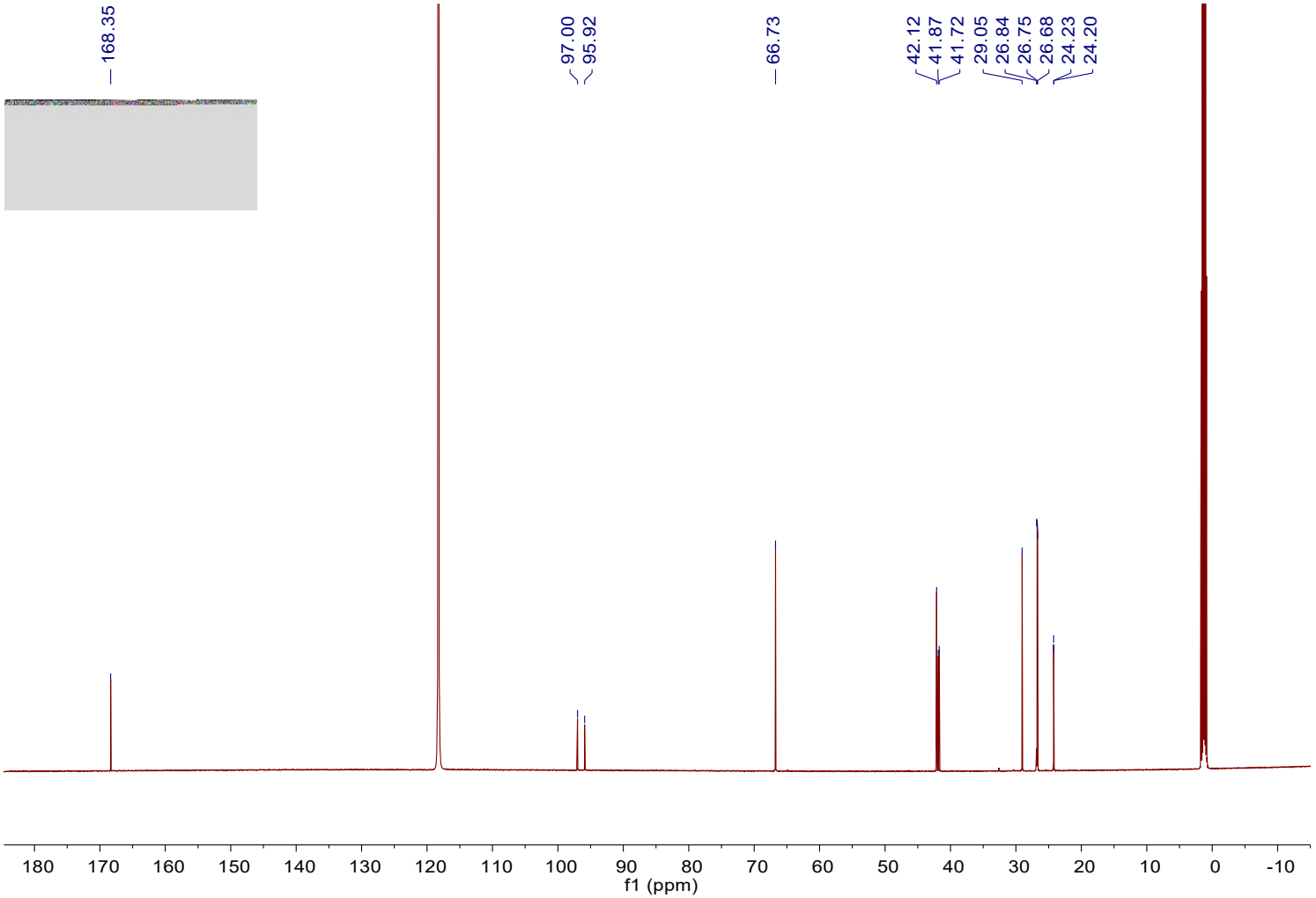


Compound **2u** ^{1}H NMR (400 MHz, CD_3CN)

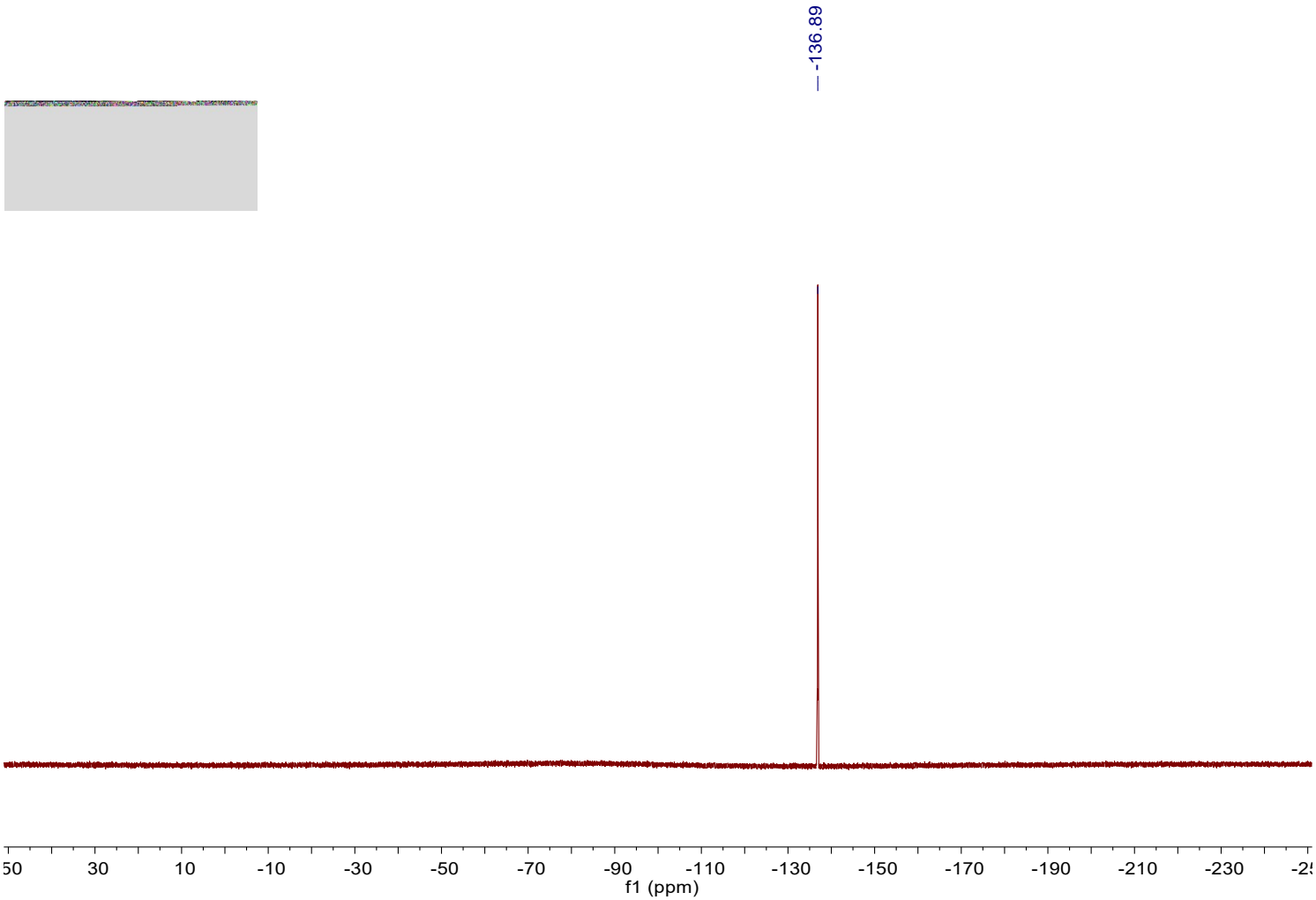




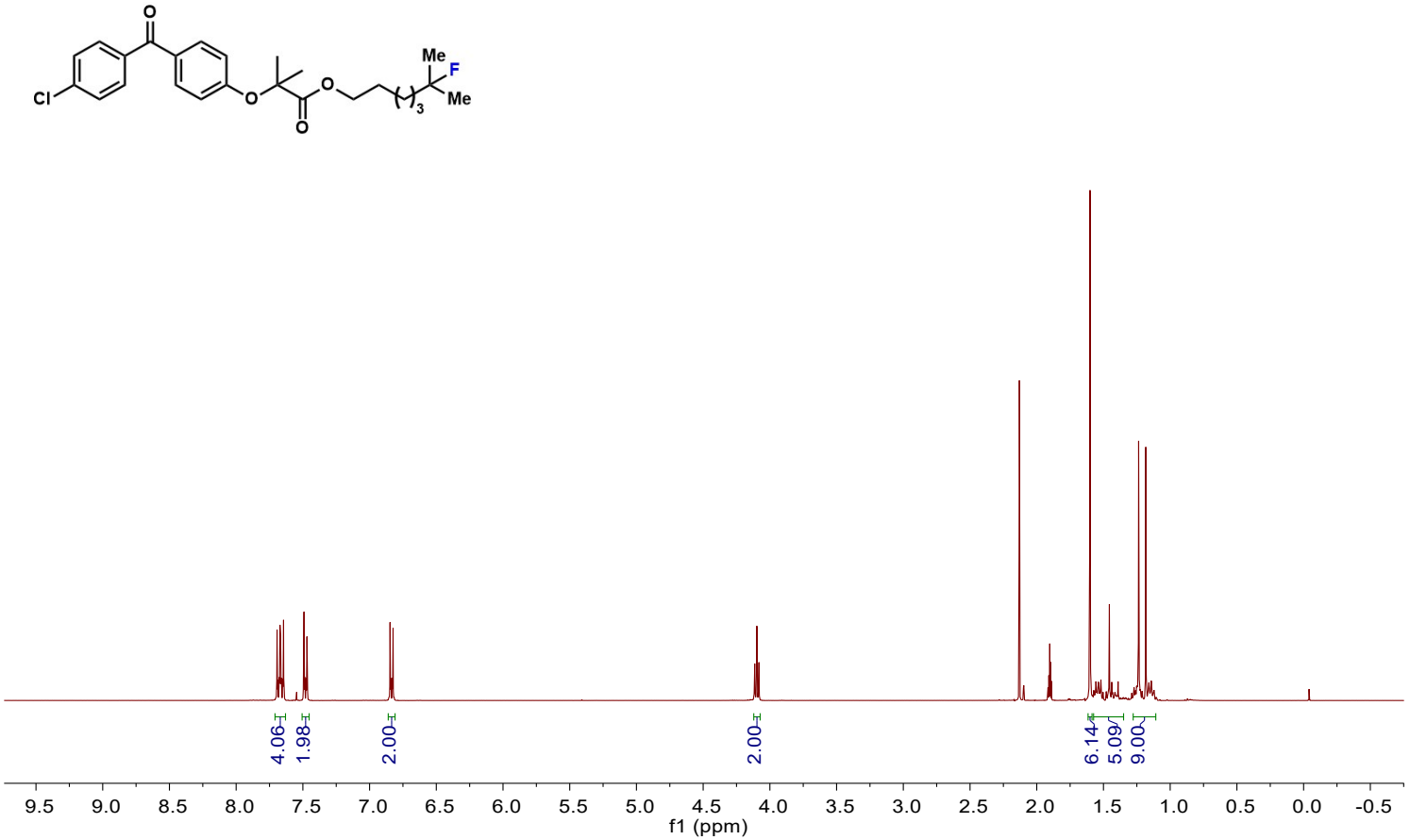
Compound **2u** ^{13}C NMR (151 MHz, CD_3CN)



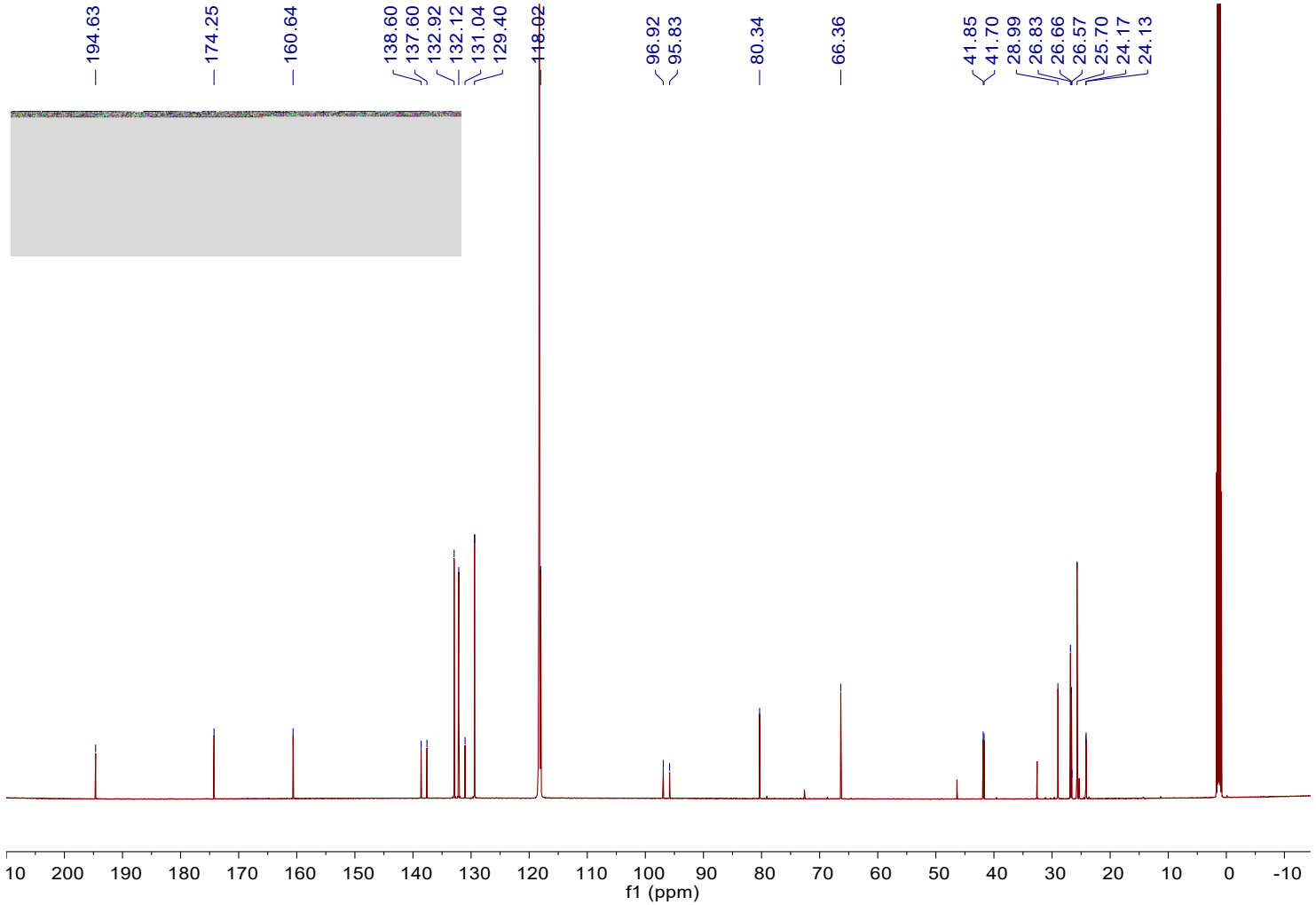
Compound **2u** ^{19}F NMR (376 MHz, CD_3CN)



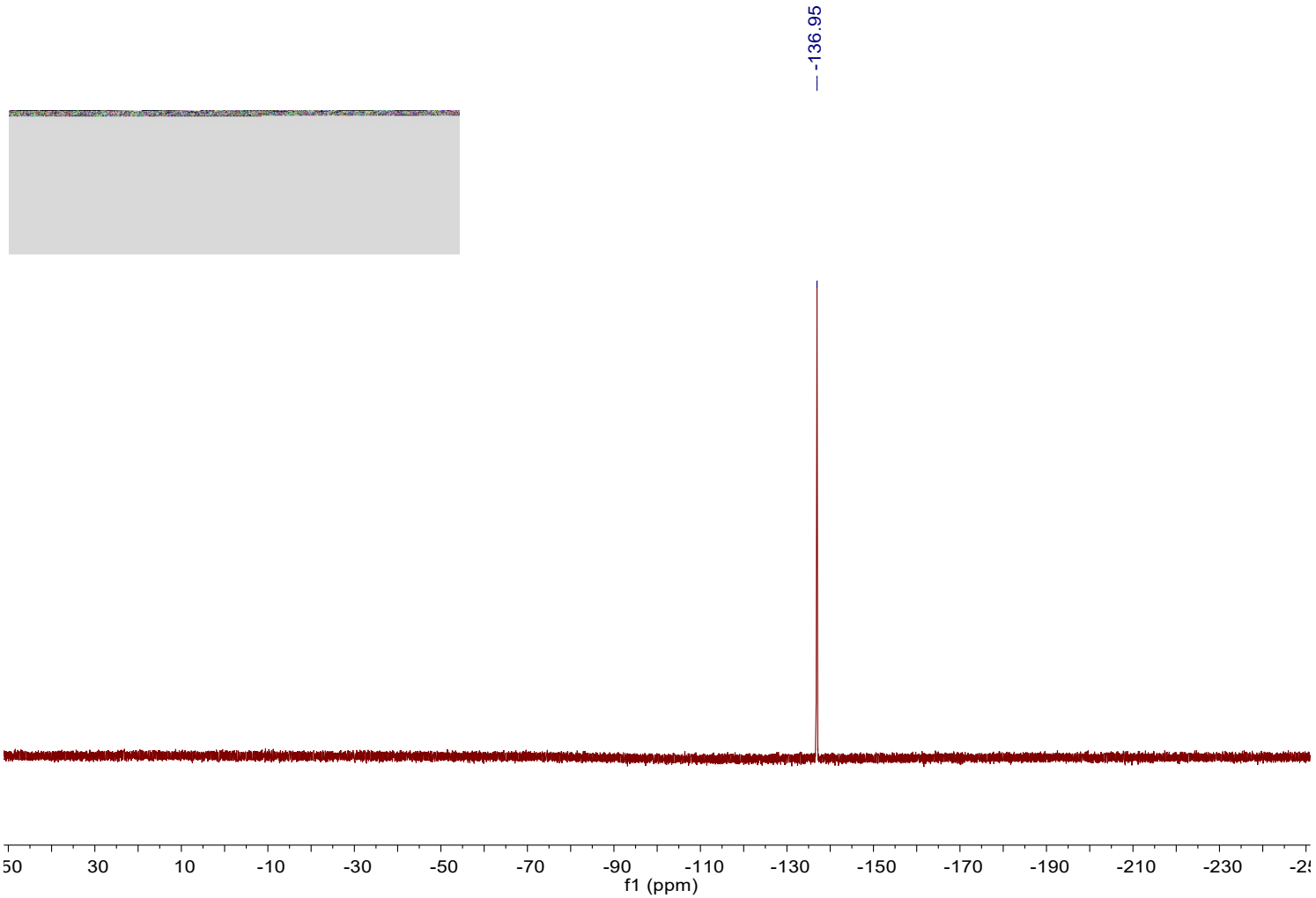
Compound **2v** ^{1}H NMR (400 MHz, CD_3CN)



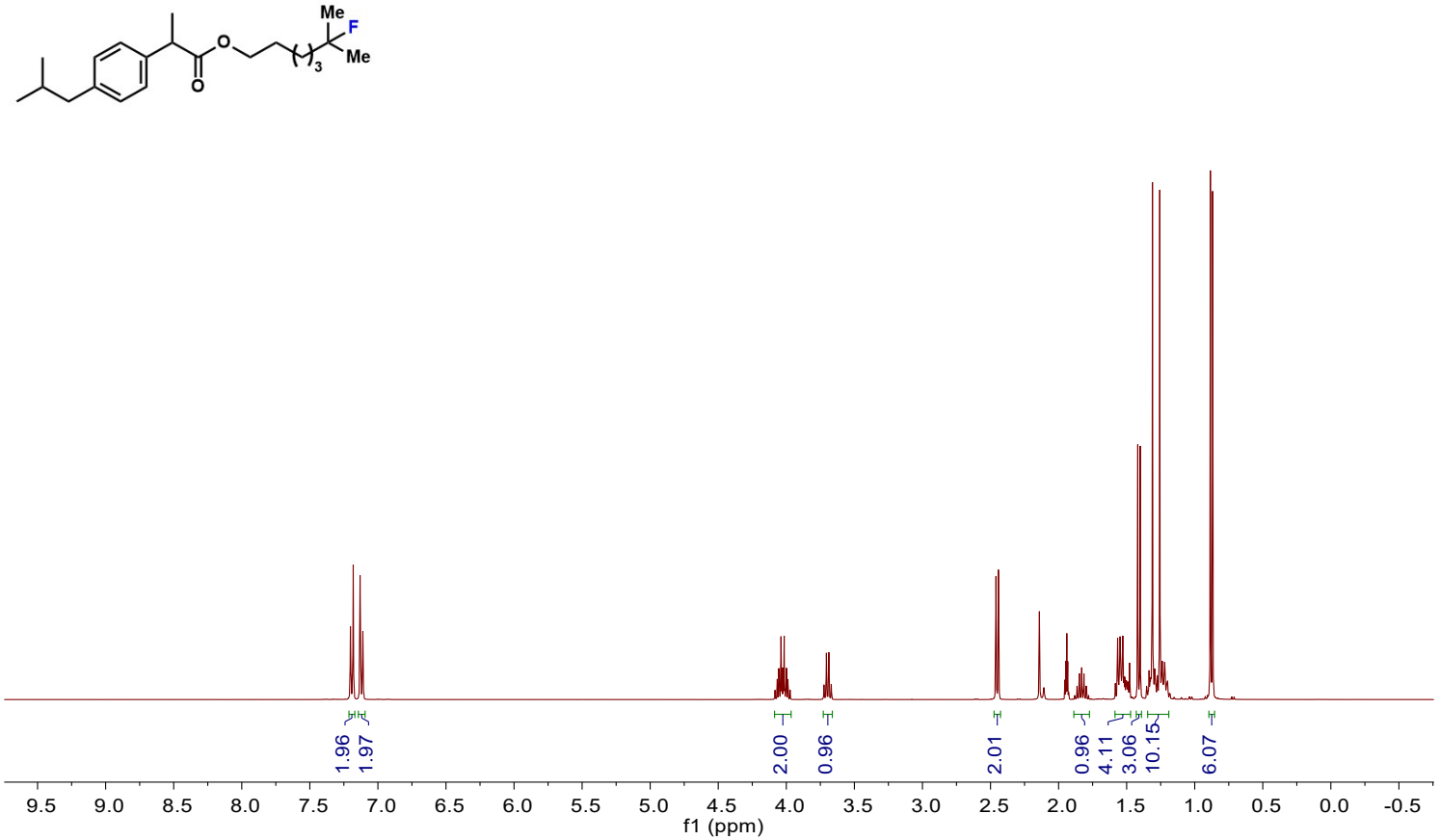
Compound **2v** ^{13}C NMR (151 MHz, CD_3CN)



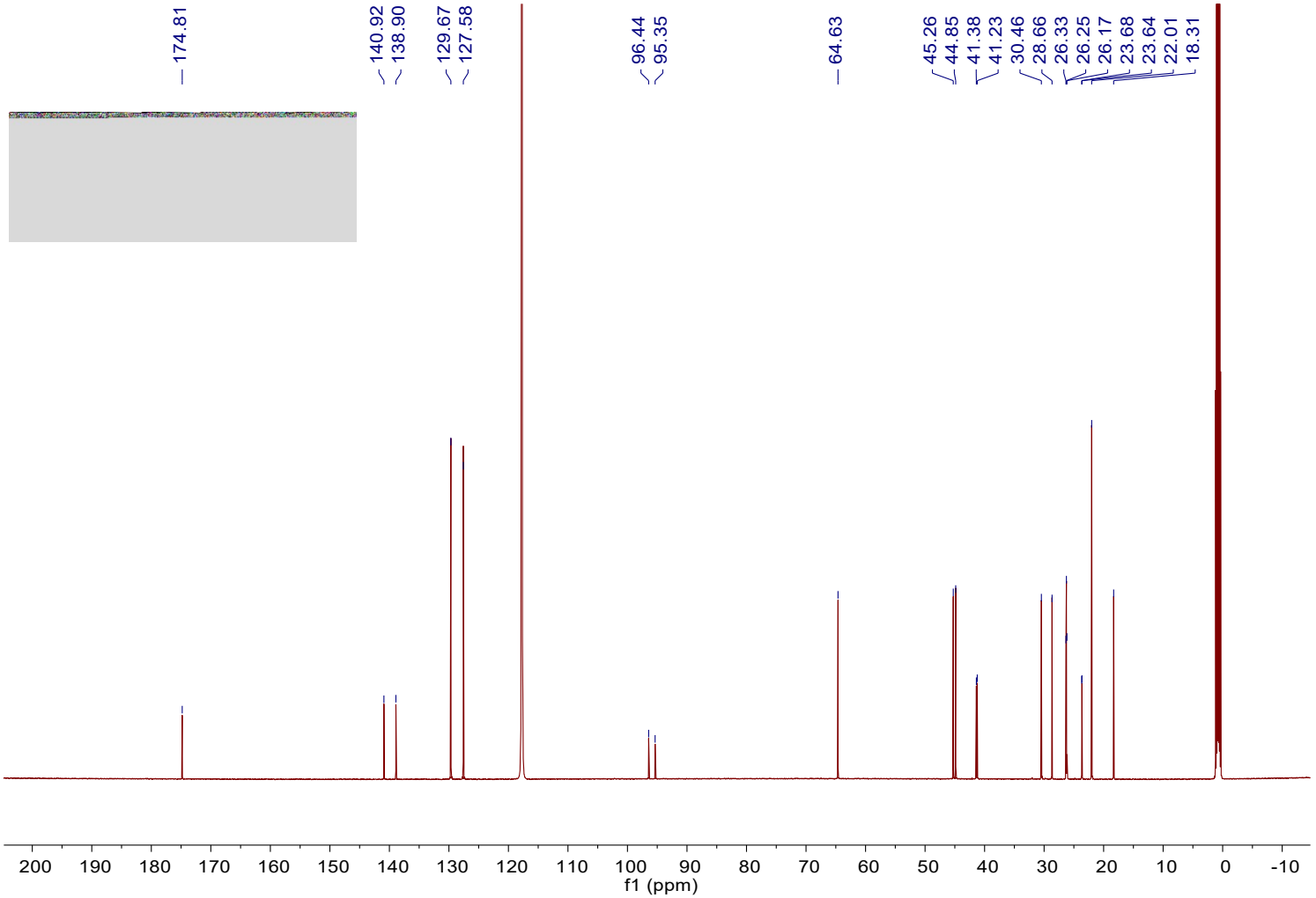
Compound **2v** ^{19}F NMR (376 MHz, CD_3CN)



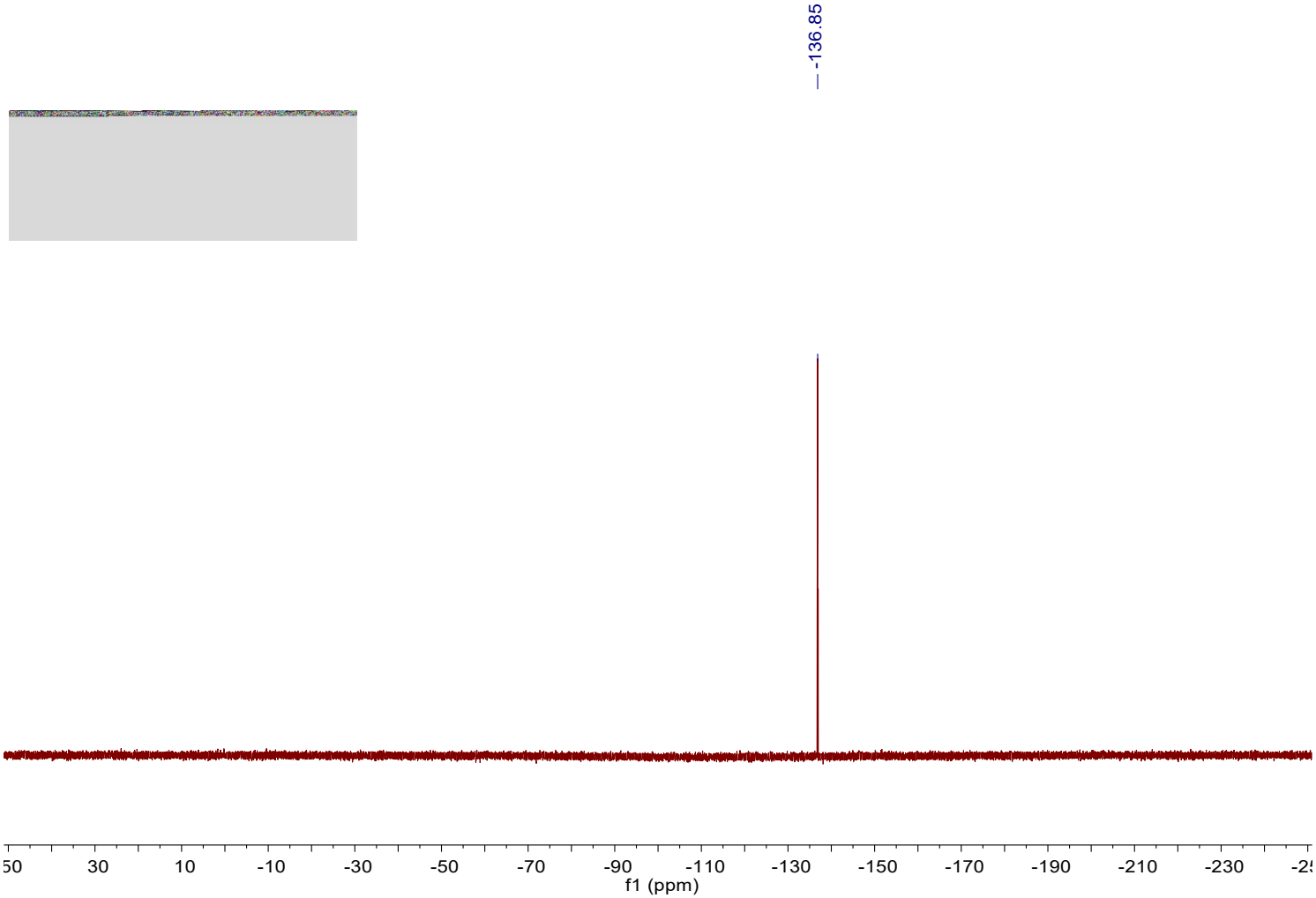
Compound **2w** ^{1}H NMR (400 MHz, CD_3CN)



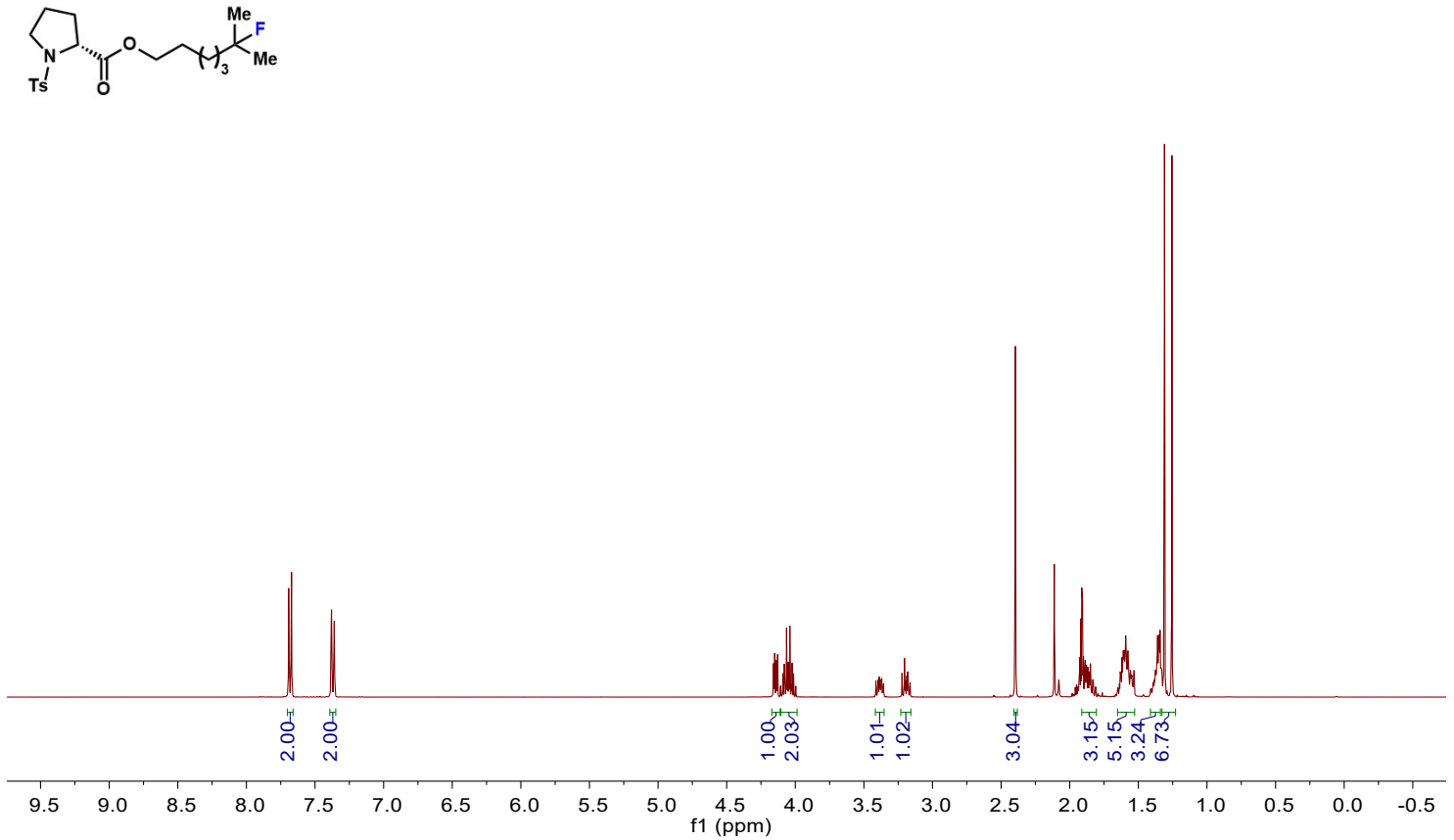
Compound **2w** ^{13}C NMR (151 MHz, CD_3CN)



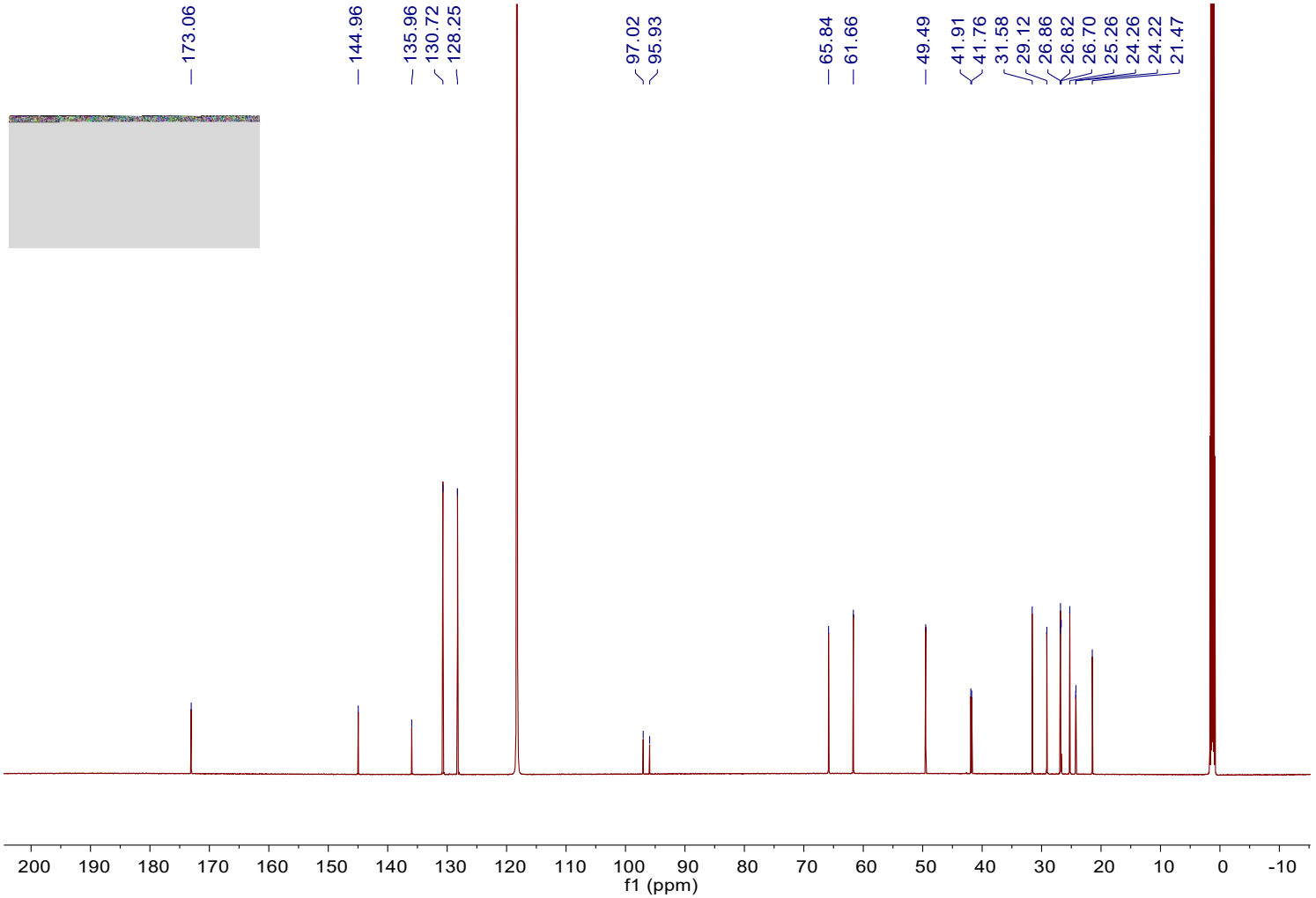
Compound **2w** ^{19}F NMR (376 MHz, CD_3CN)



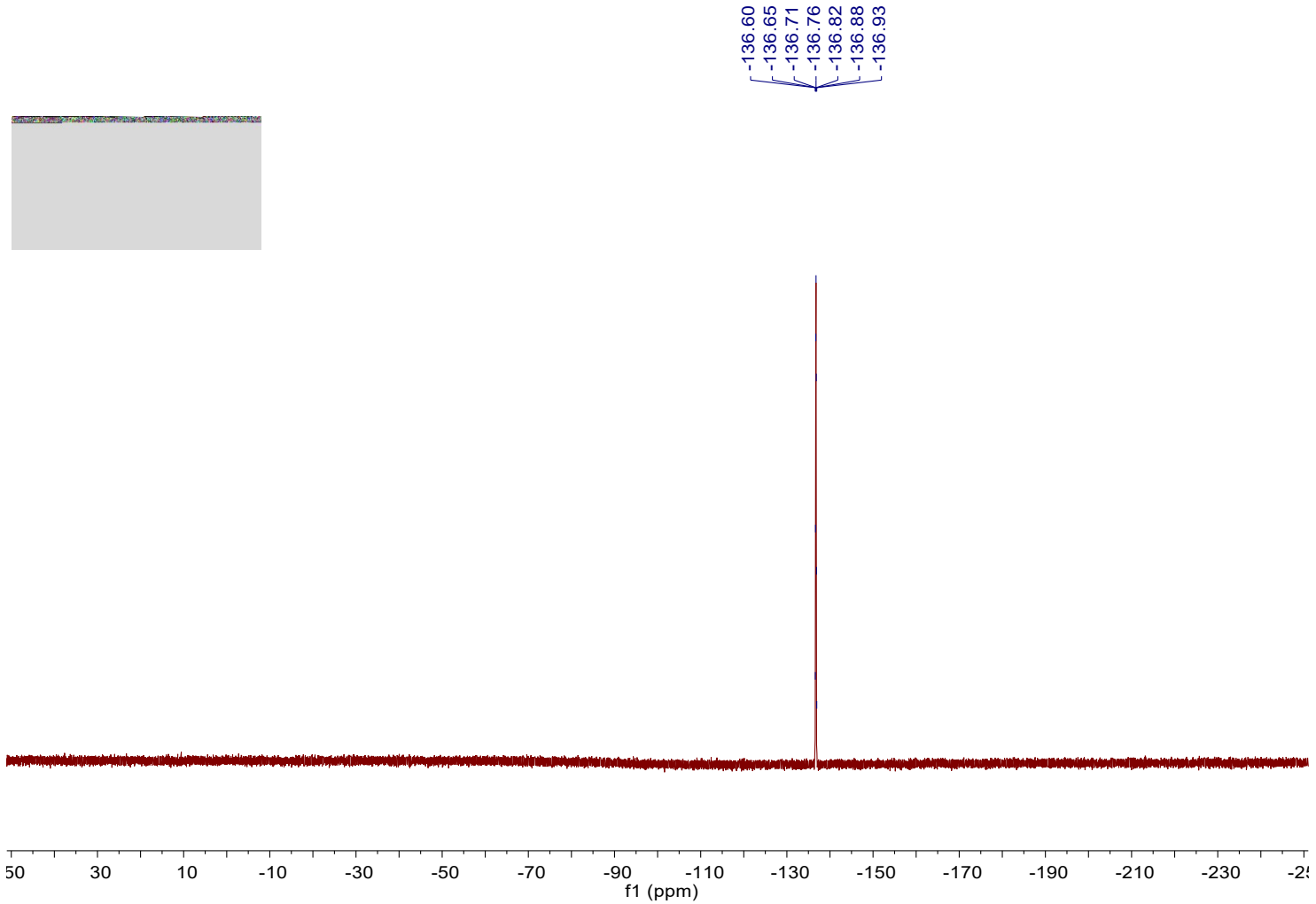
Compound **2x** ^{1}H NMR (400 MHz, CD_3CN)



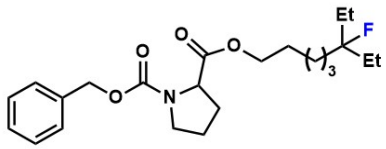
Compound **2x** ^{13}C NMR (151 MHz, CD_3CN)

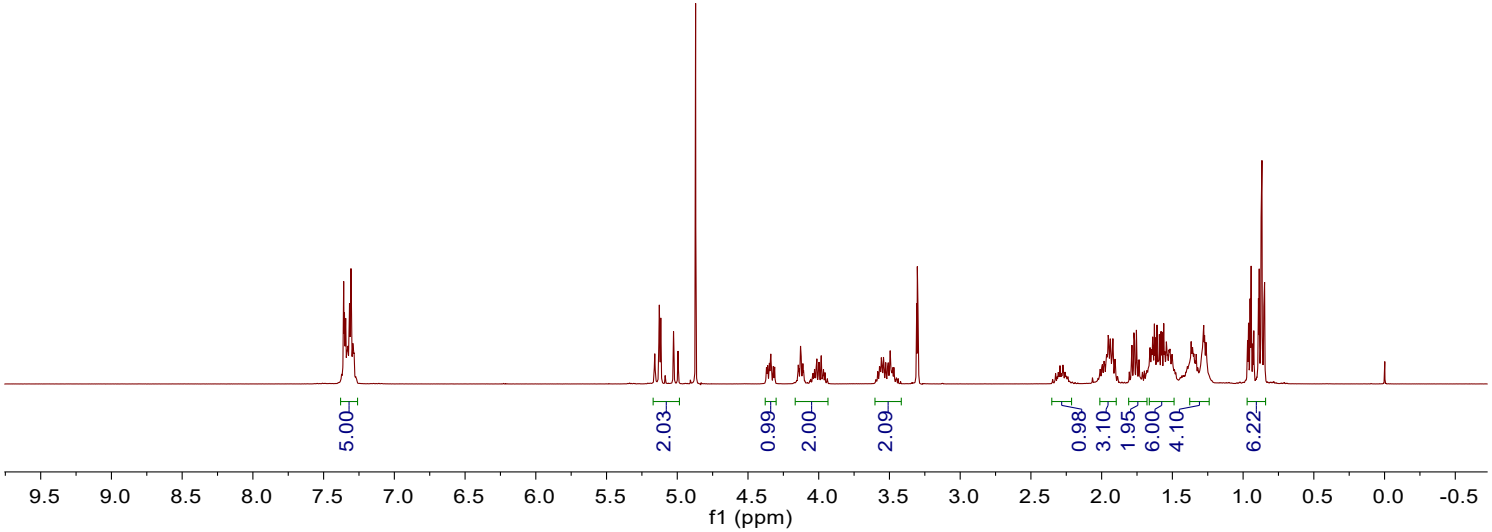


Compound **2x** ^{19}F NMR (376 MHz, CD_3CN)

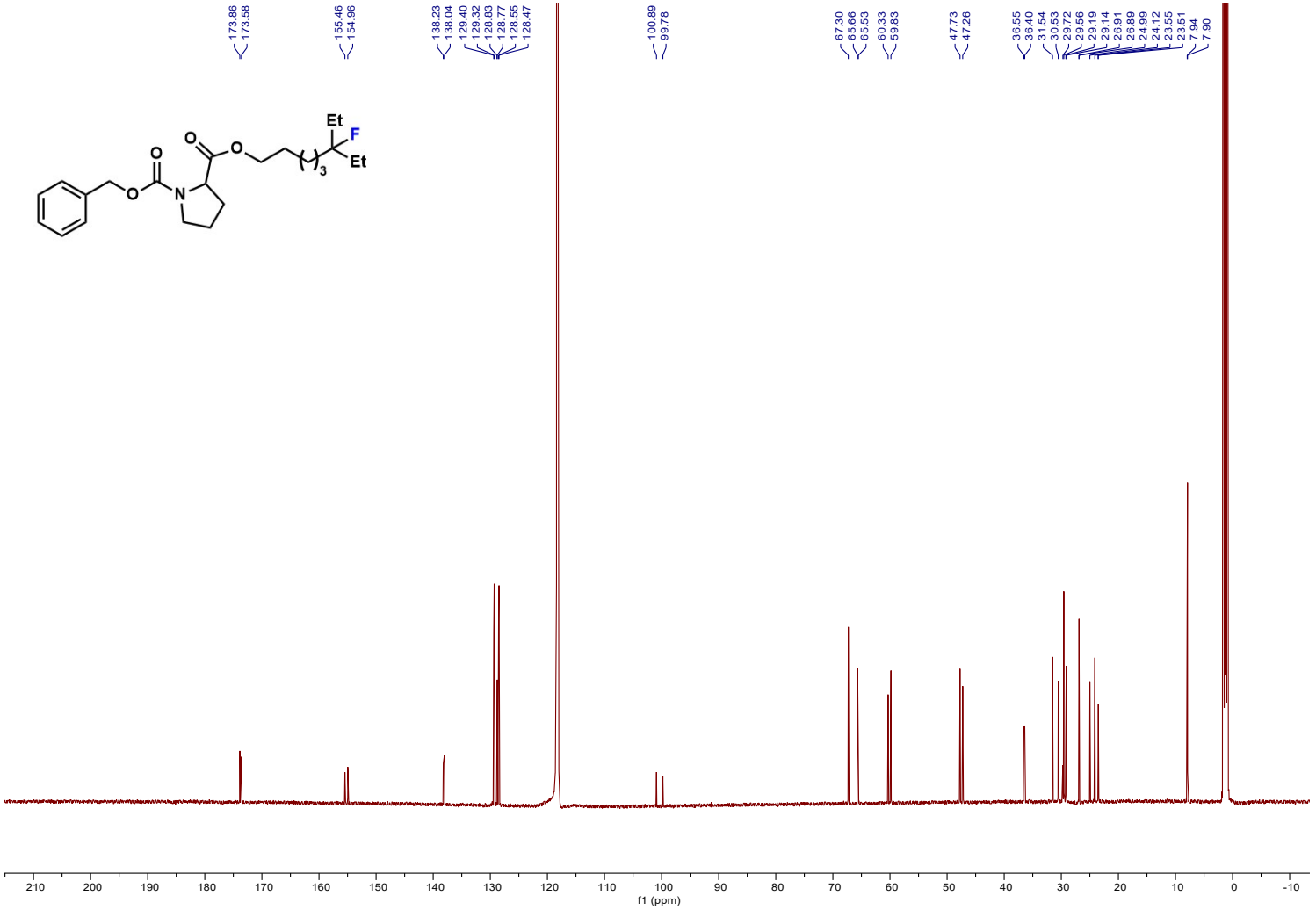


Compound **2y** ^{1}H NMR (400 MHz, CD_3OD)

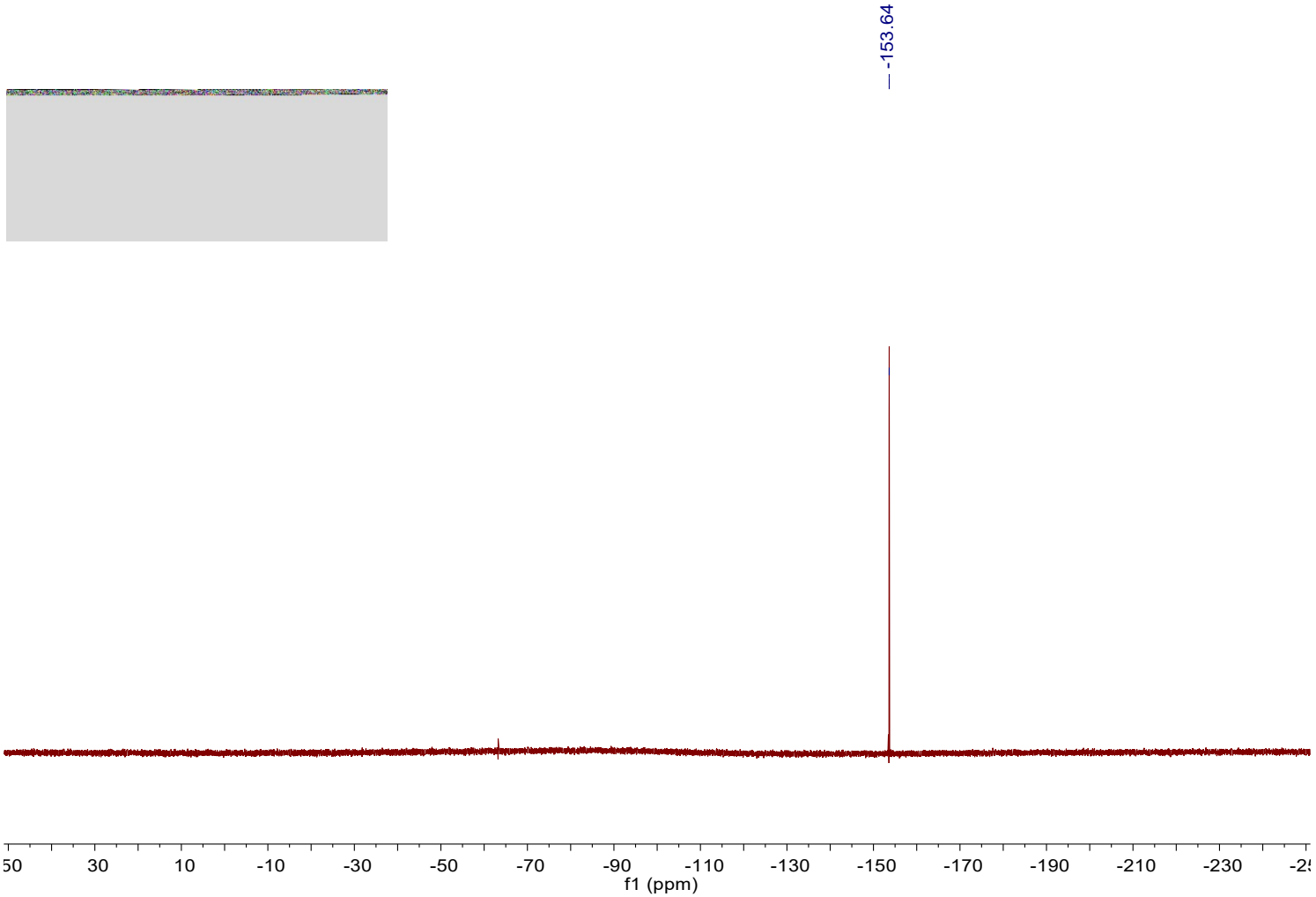




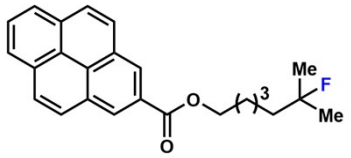
Compound **2y** ^{13}C NMR (151 MHz, CD_3CN)

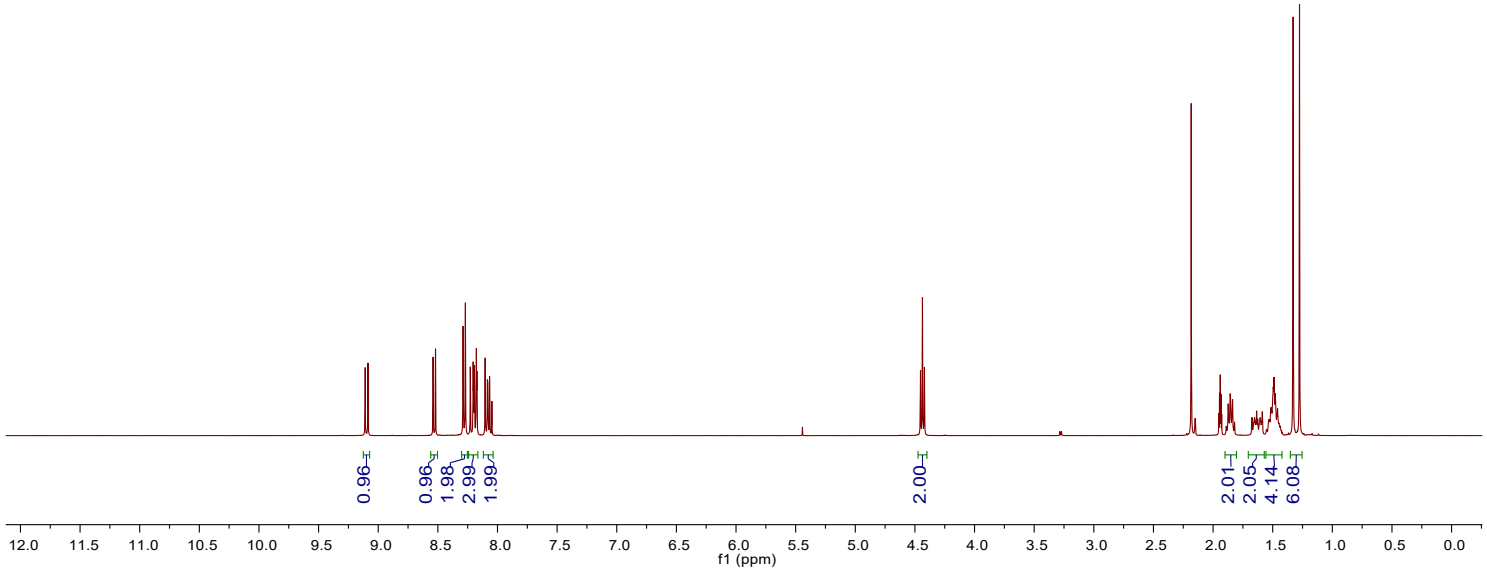


Compound **2y** ^{19}F NMR (376 MHz, CD_3CN)

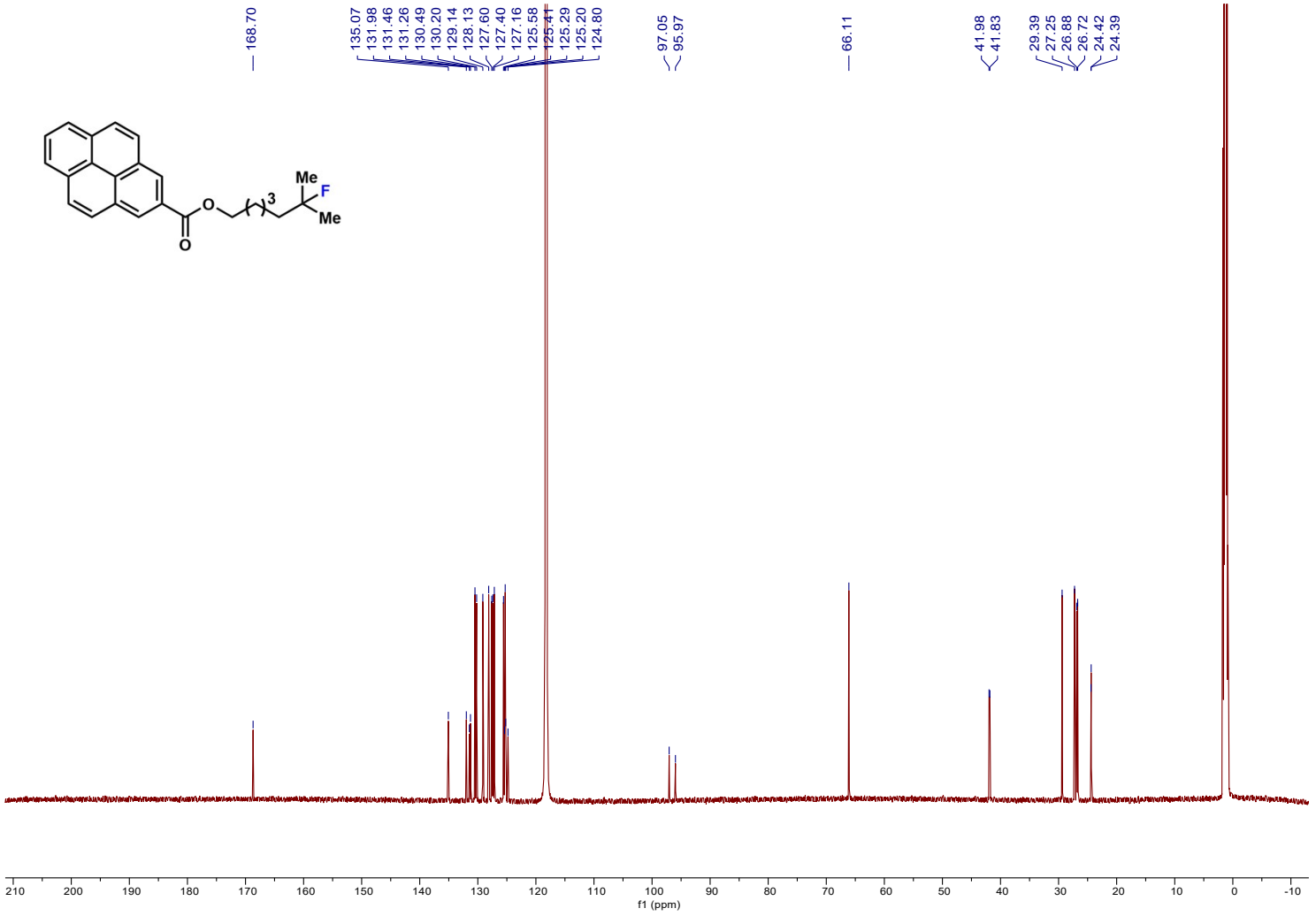


Compound **2z** ^{1}H NMR (400 MHz, CD_3CN)

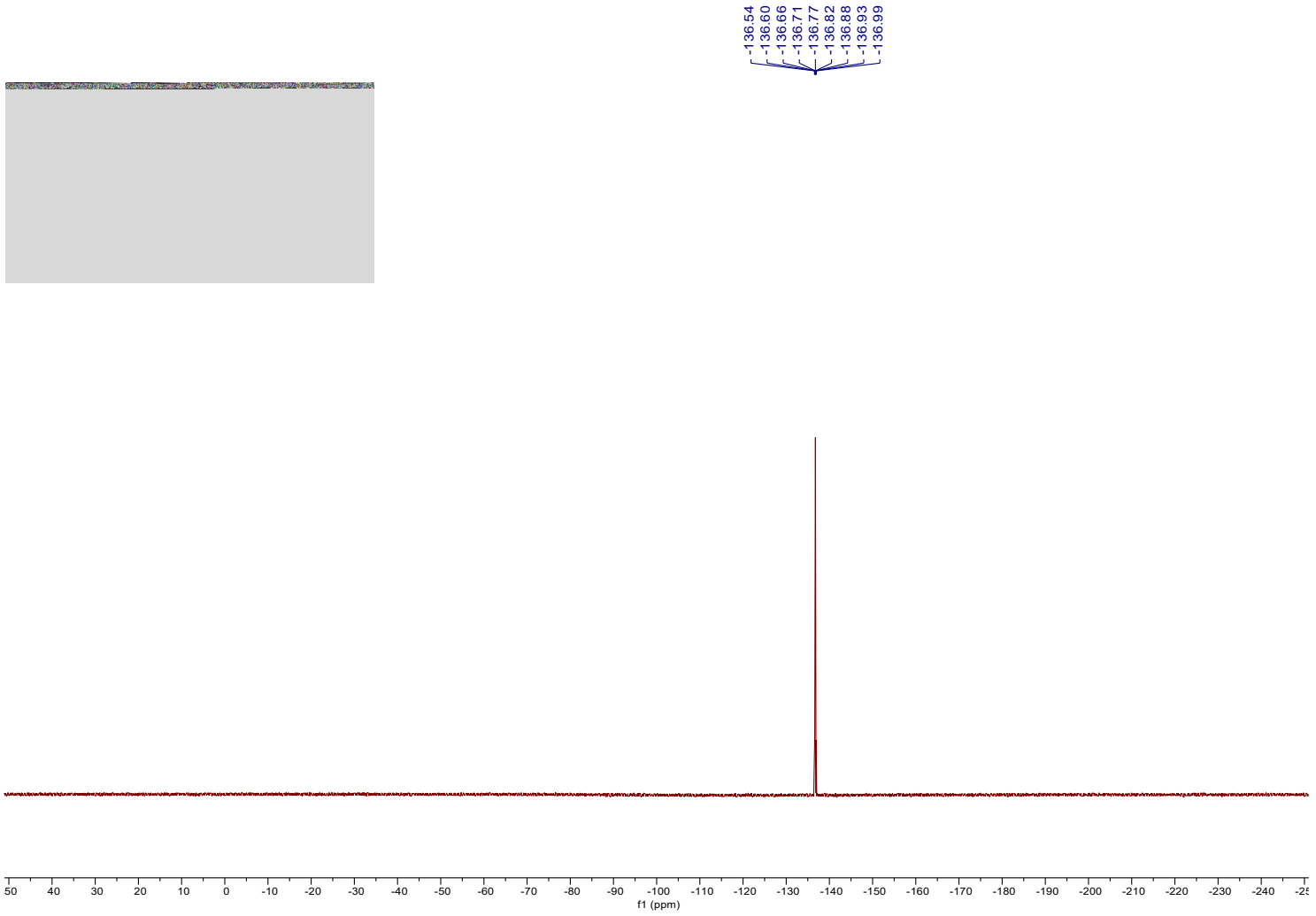




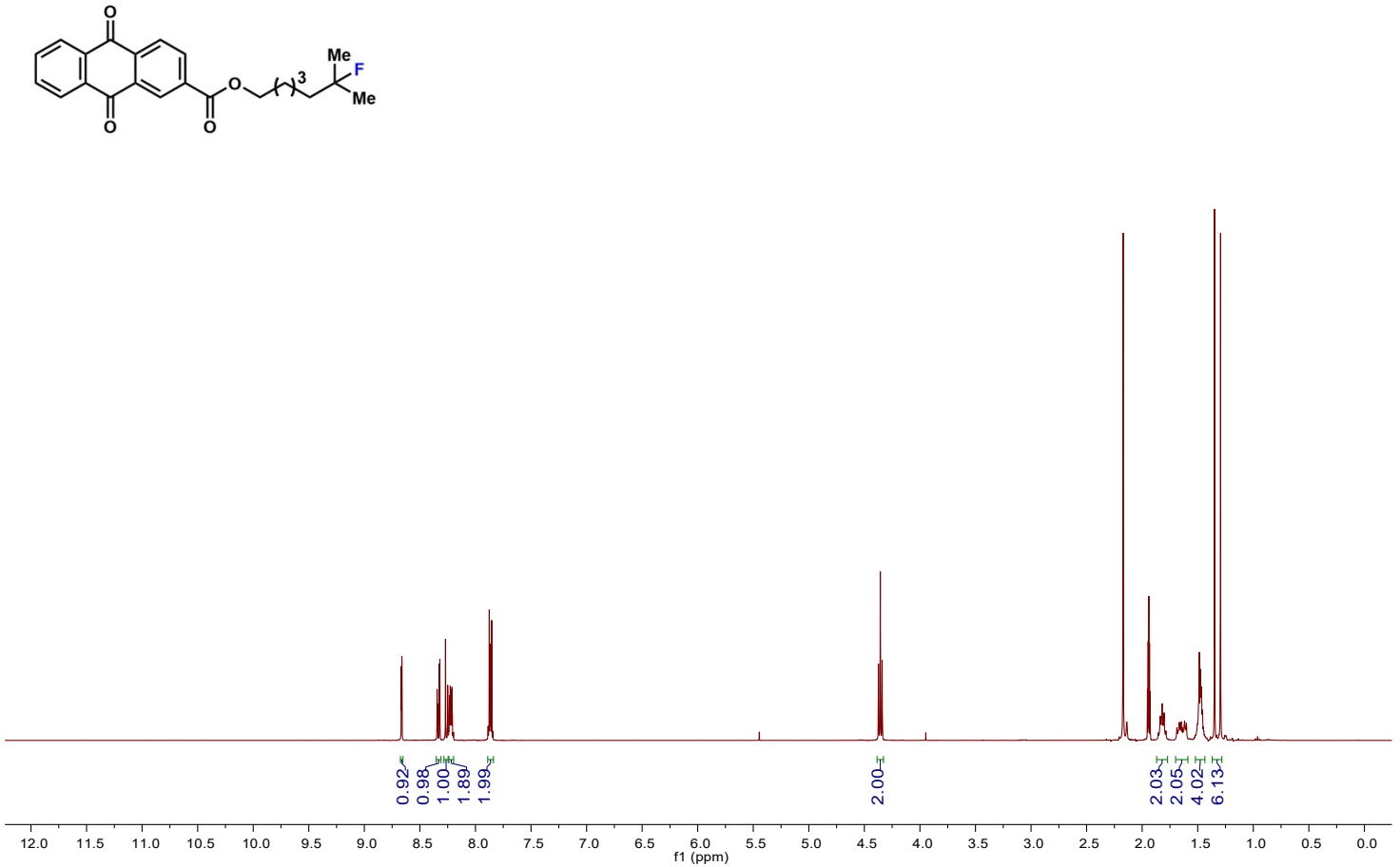
Compound **2z** ^{13}C NMR (151 MHz, CD_3CN)



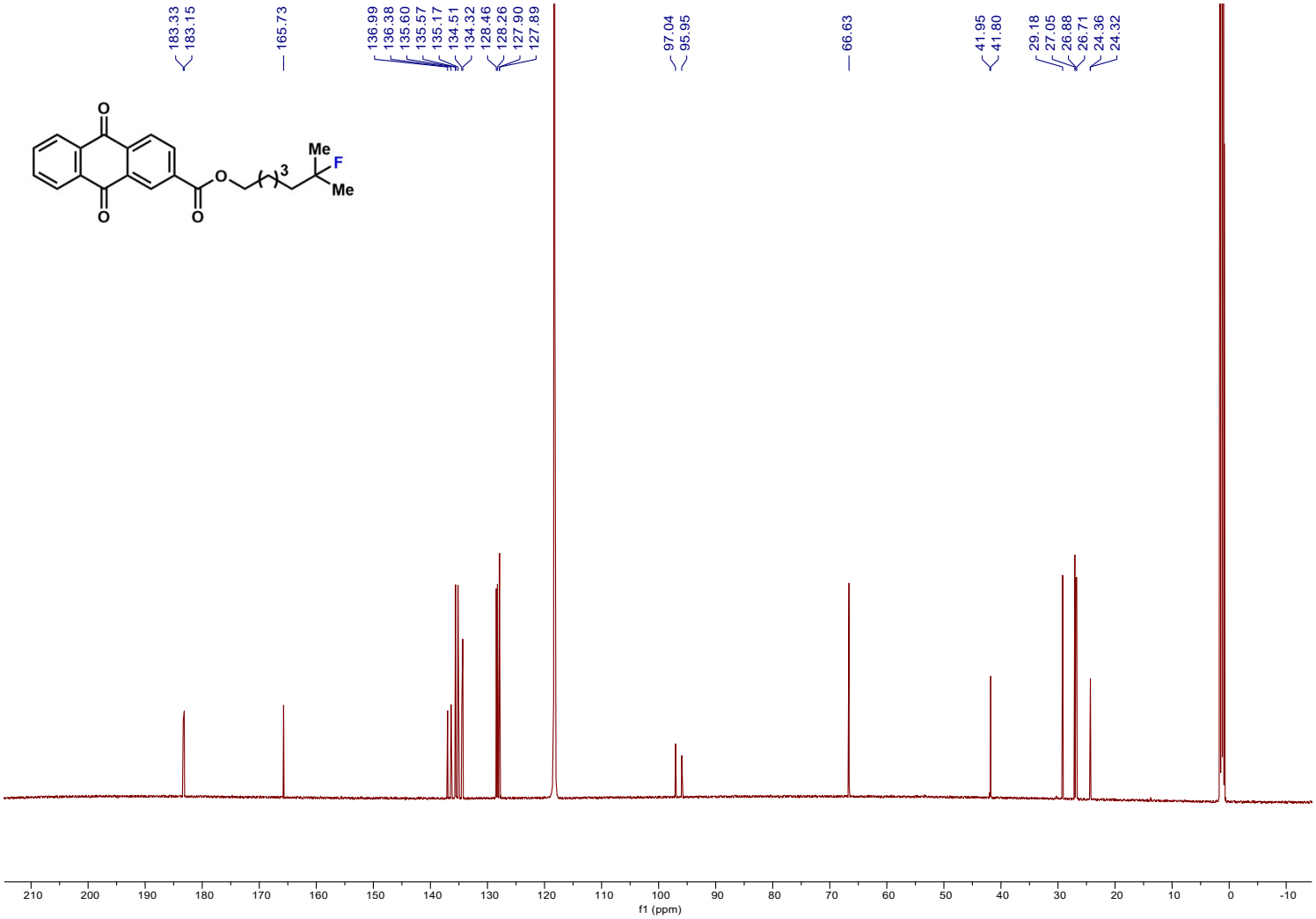
Compound **2z** ^{19}F NMR (376 MHz, CD_3CN)



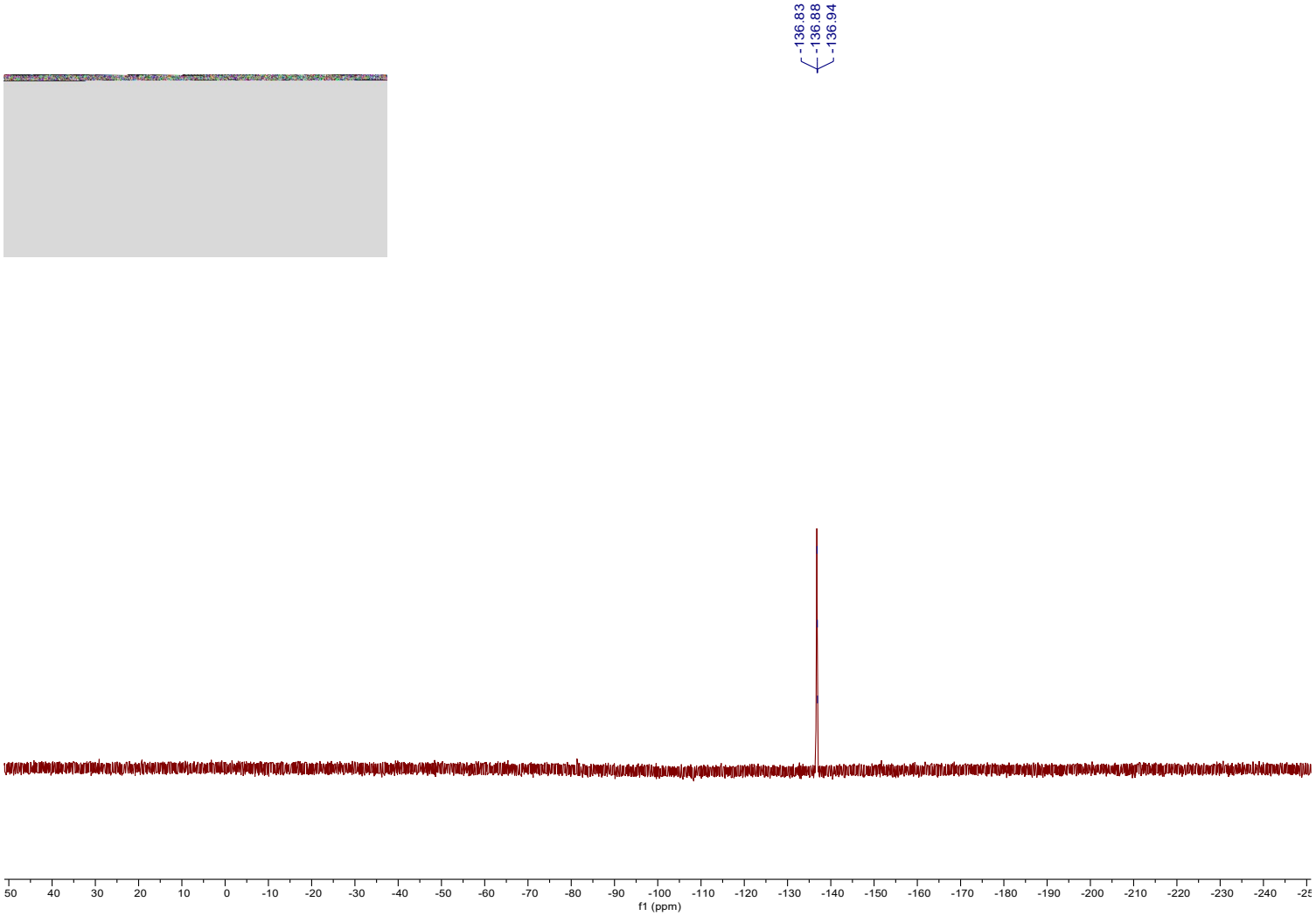
Compound **2aa** ^{1}H NMR (400 MHz, CD_3CN)



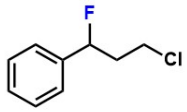
Compound **2aa** ^{13}C NMR (151 MHz, CD_3CN)

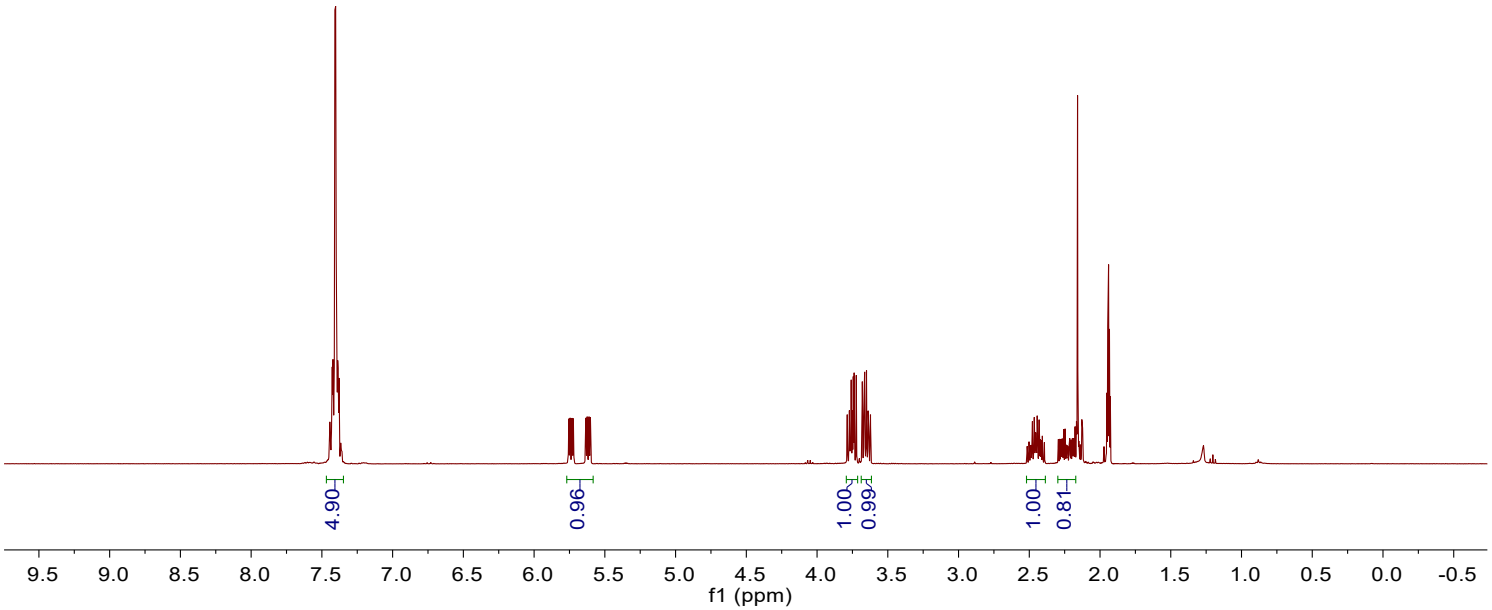


Compound **2aa** ^{19}F NMR (376 MHz, CD_3CN)

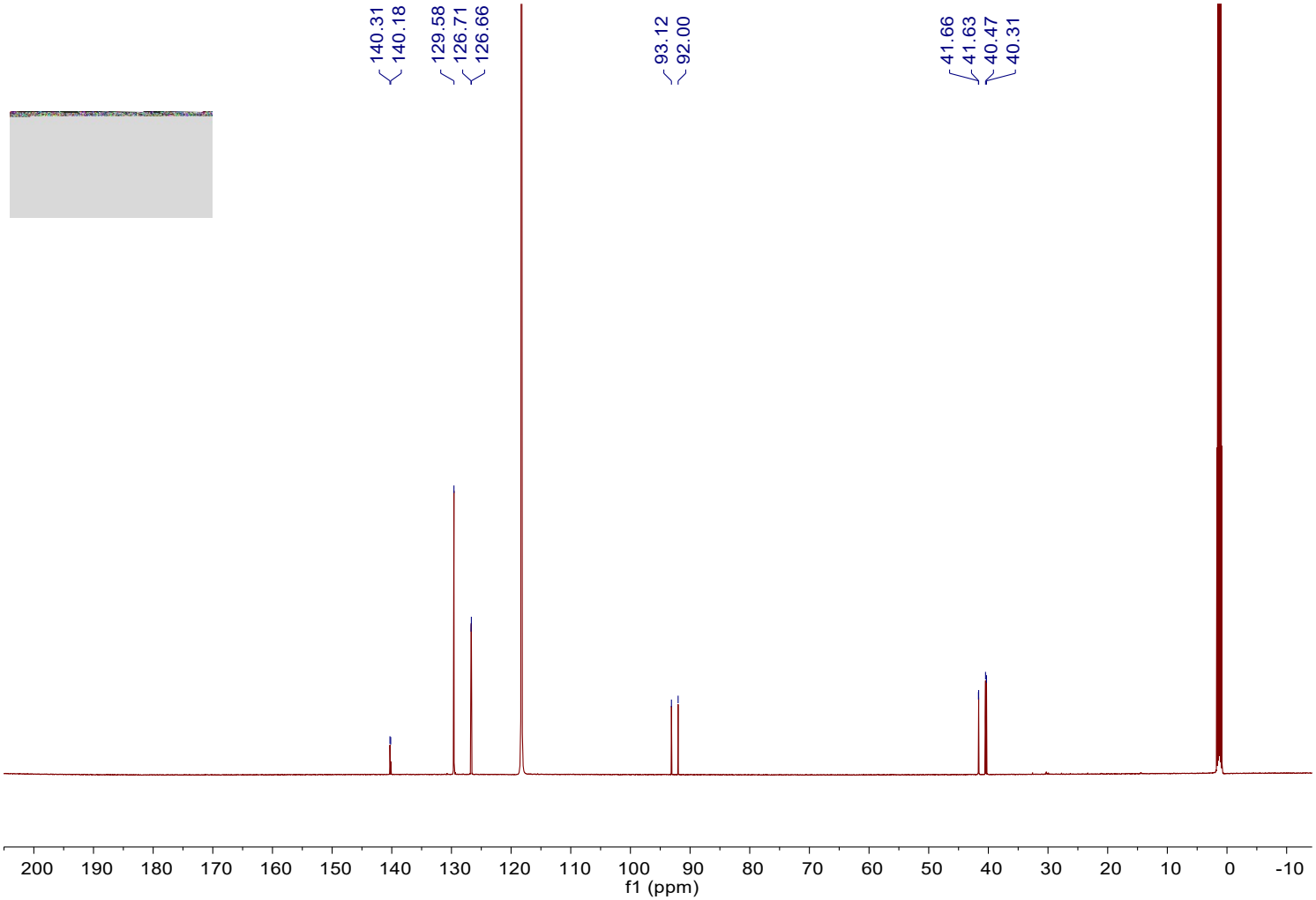


Compound **2ab** ^{1}H NMR (400 MHz, CD_3CN)

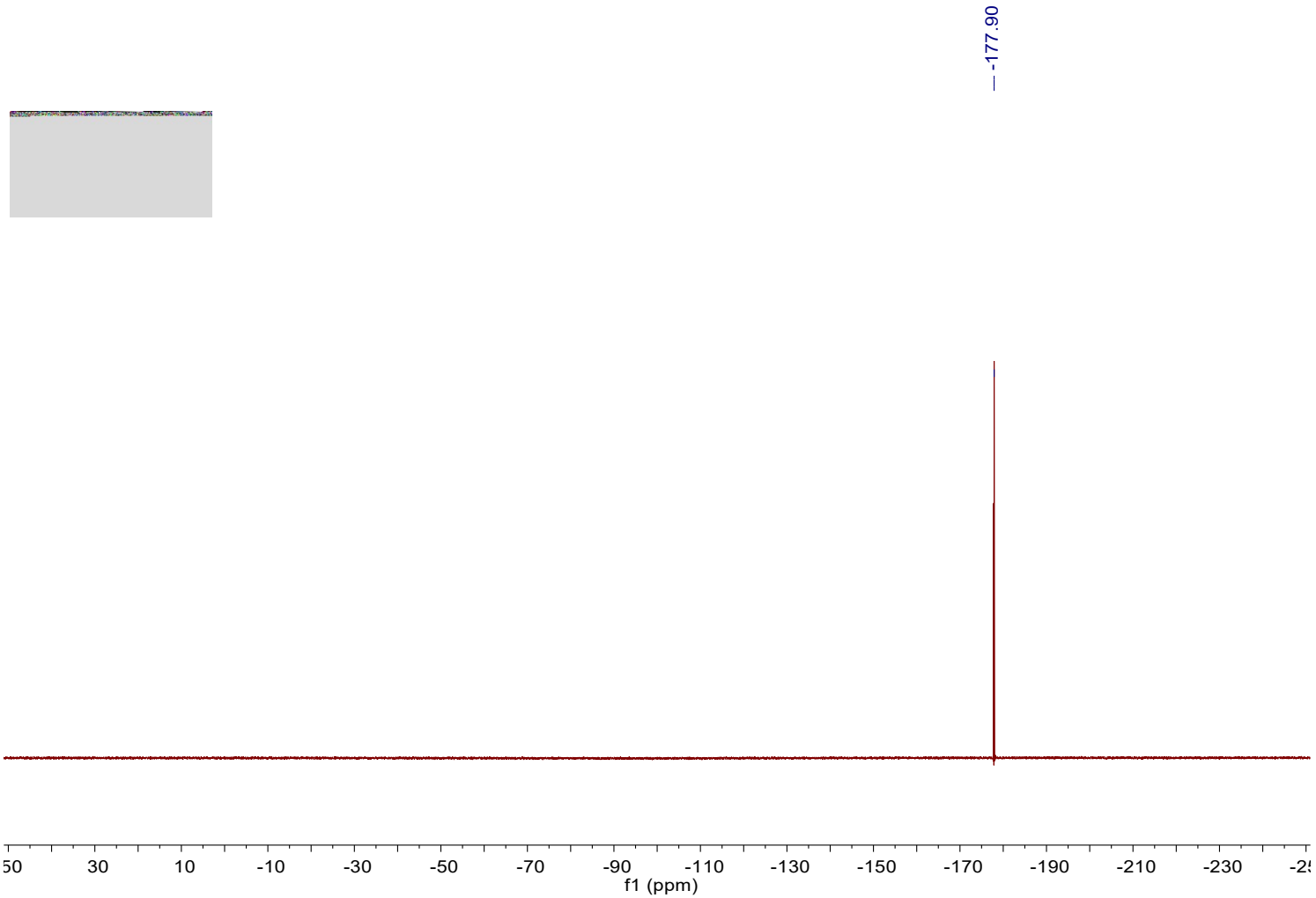




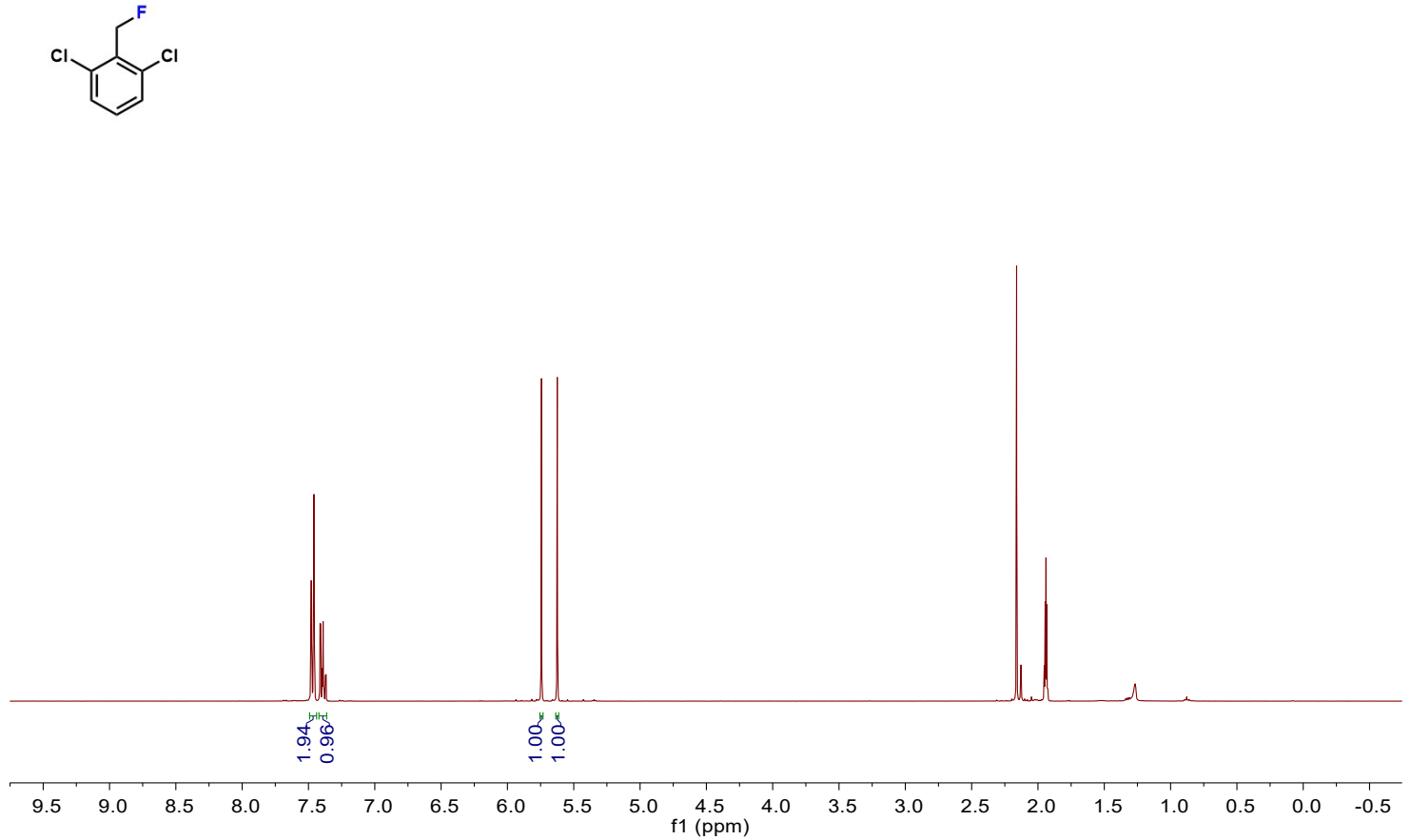
Compound **2ab** ^{13}C NMR (151 MHz, CD_3CN)



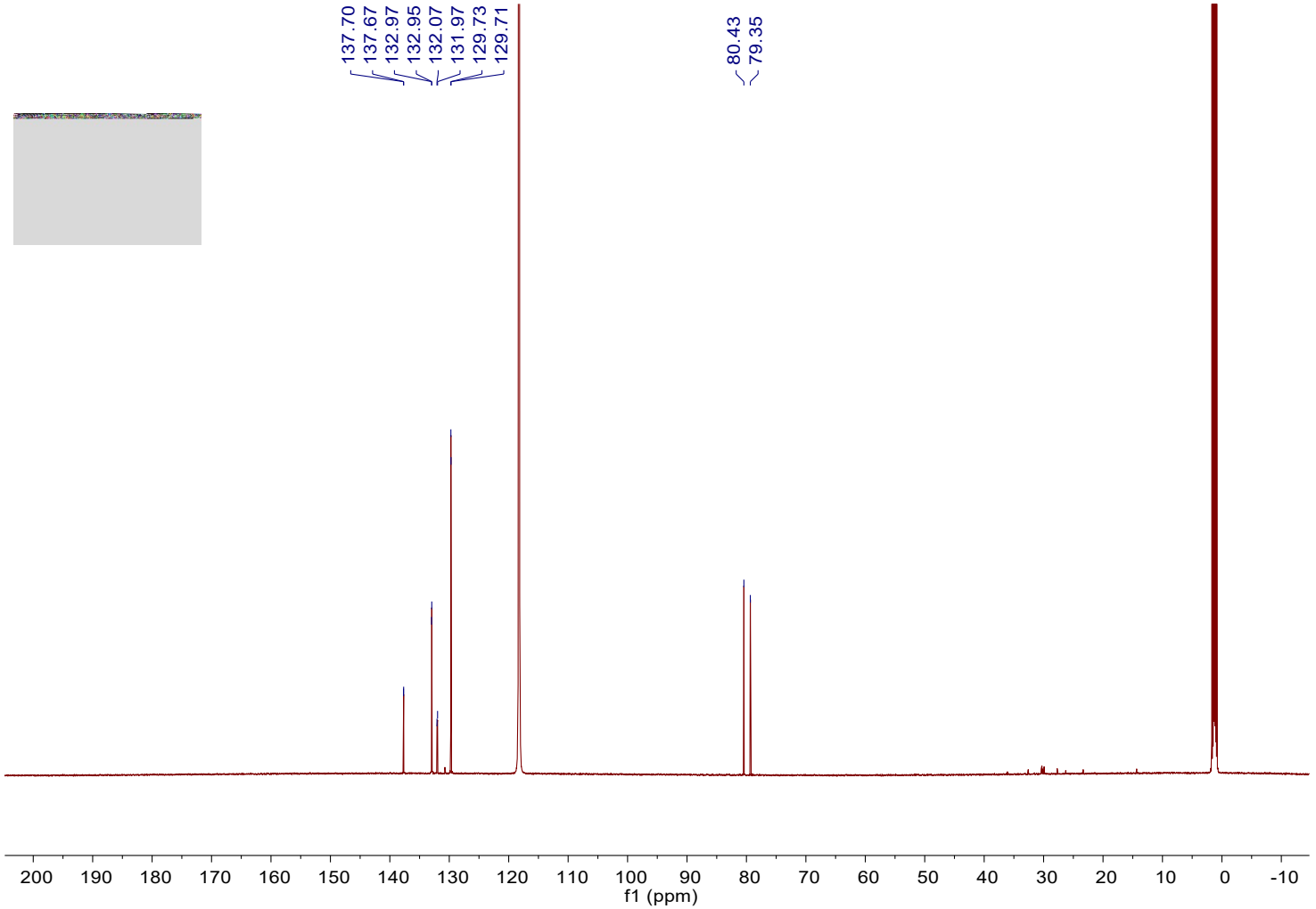
Compound **2ab** ^{19}F NMR (376 MHz, CD_3CN)



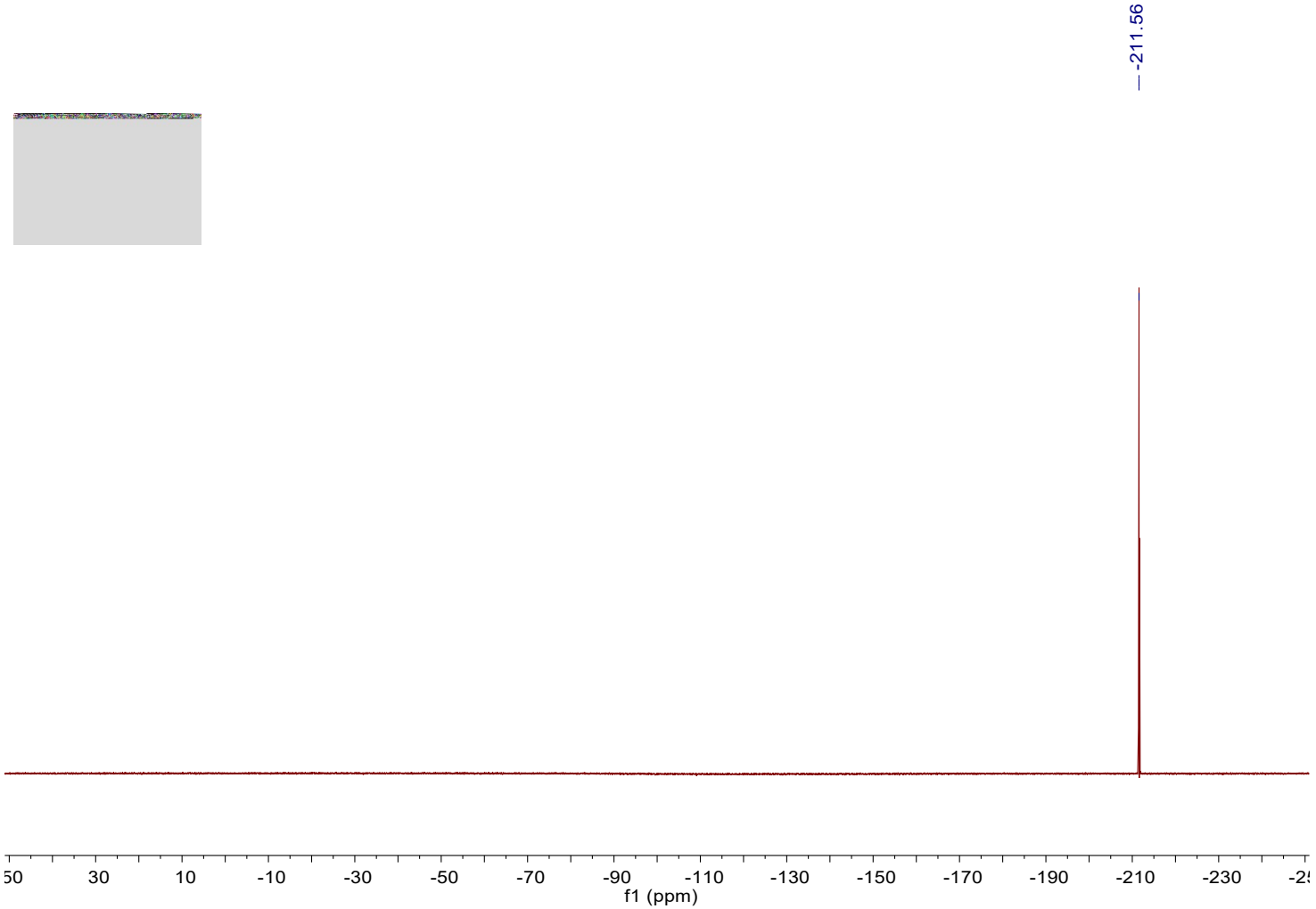
Compound **2ac** ^{1}H NMR (400 MHz, CD_3CN)



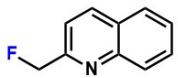
Compound **2ac** ^{13}C NMR (151 MHz, CD_3CN)

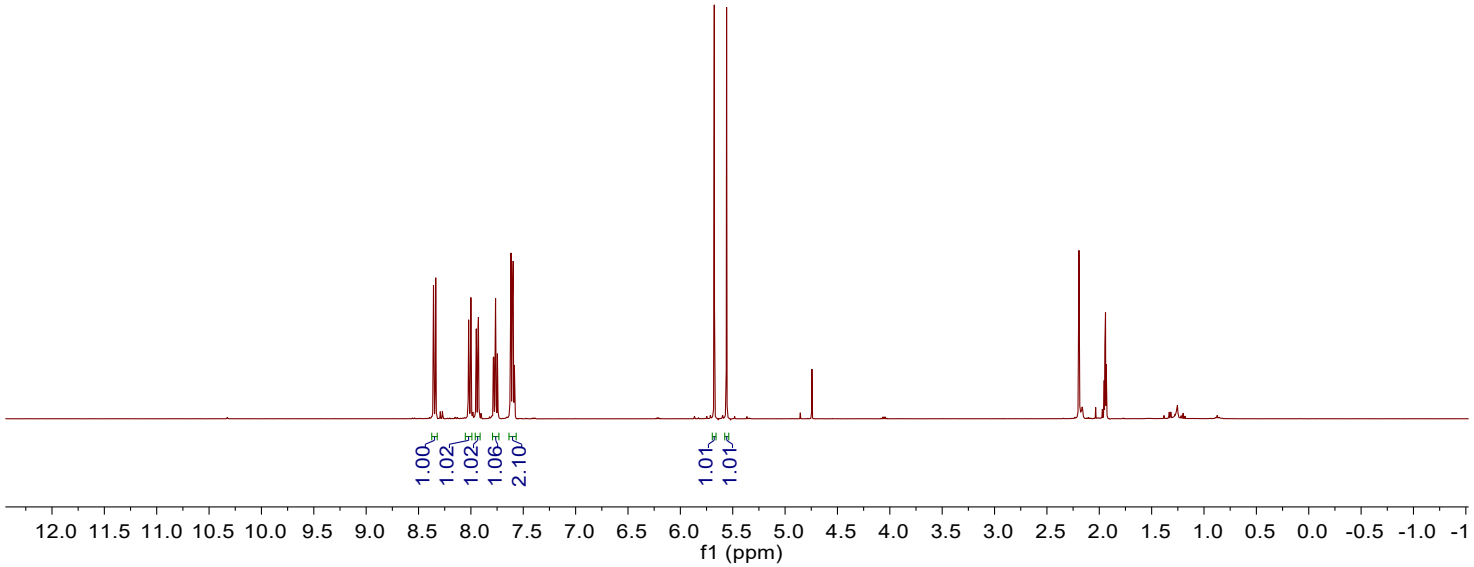


Compound **2ac** ^{19}F NMR (376 MHz, CD_3CN)

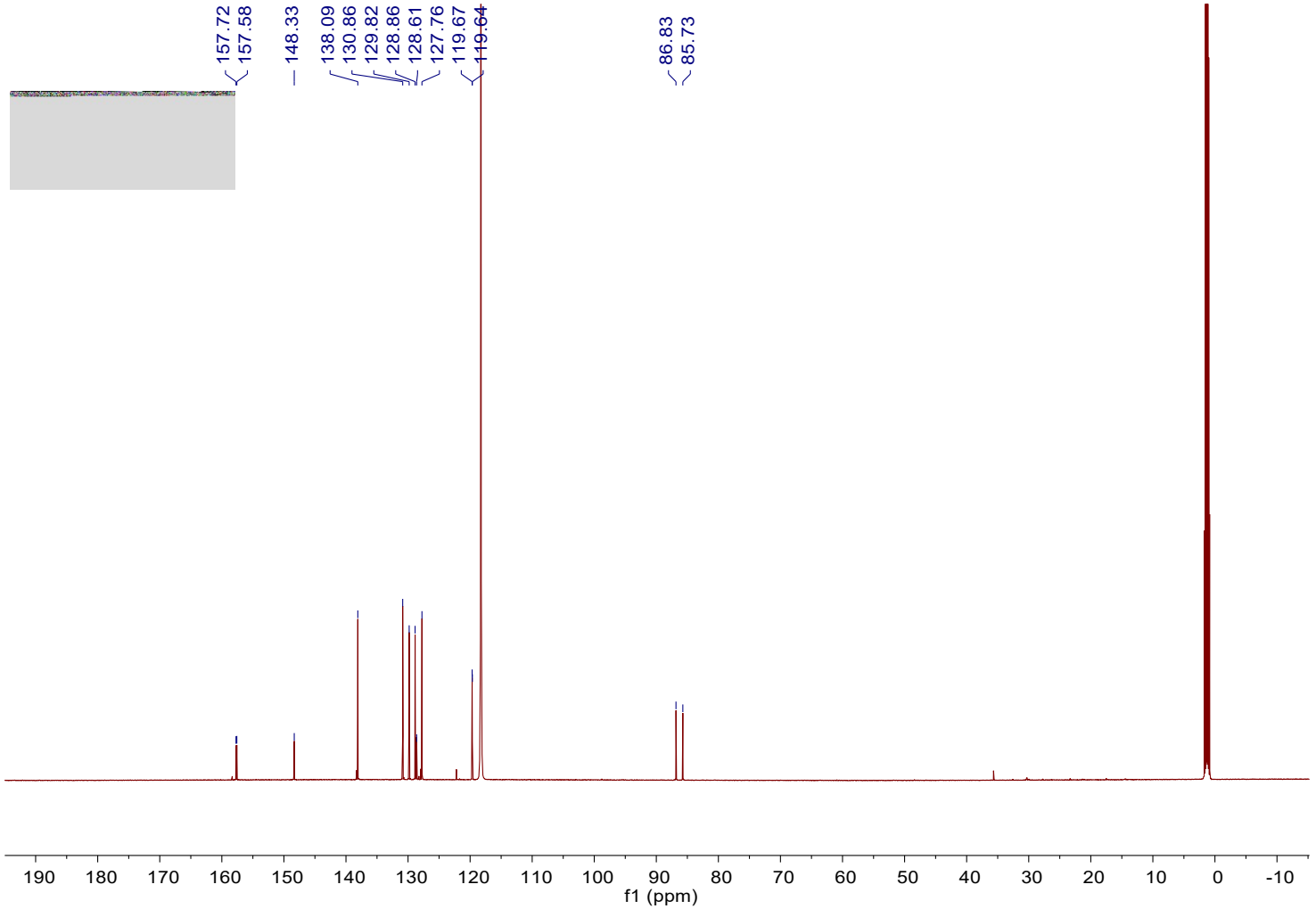


Compound **2ad** ^{1}H NMR (400 MHz, CD_3CN)

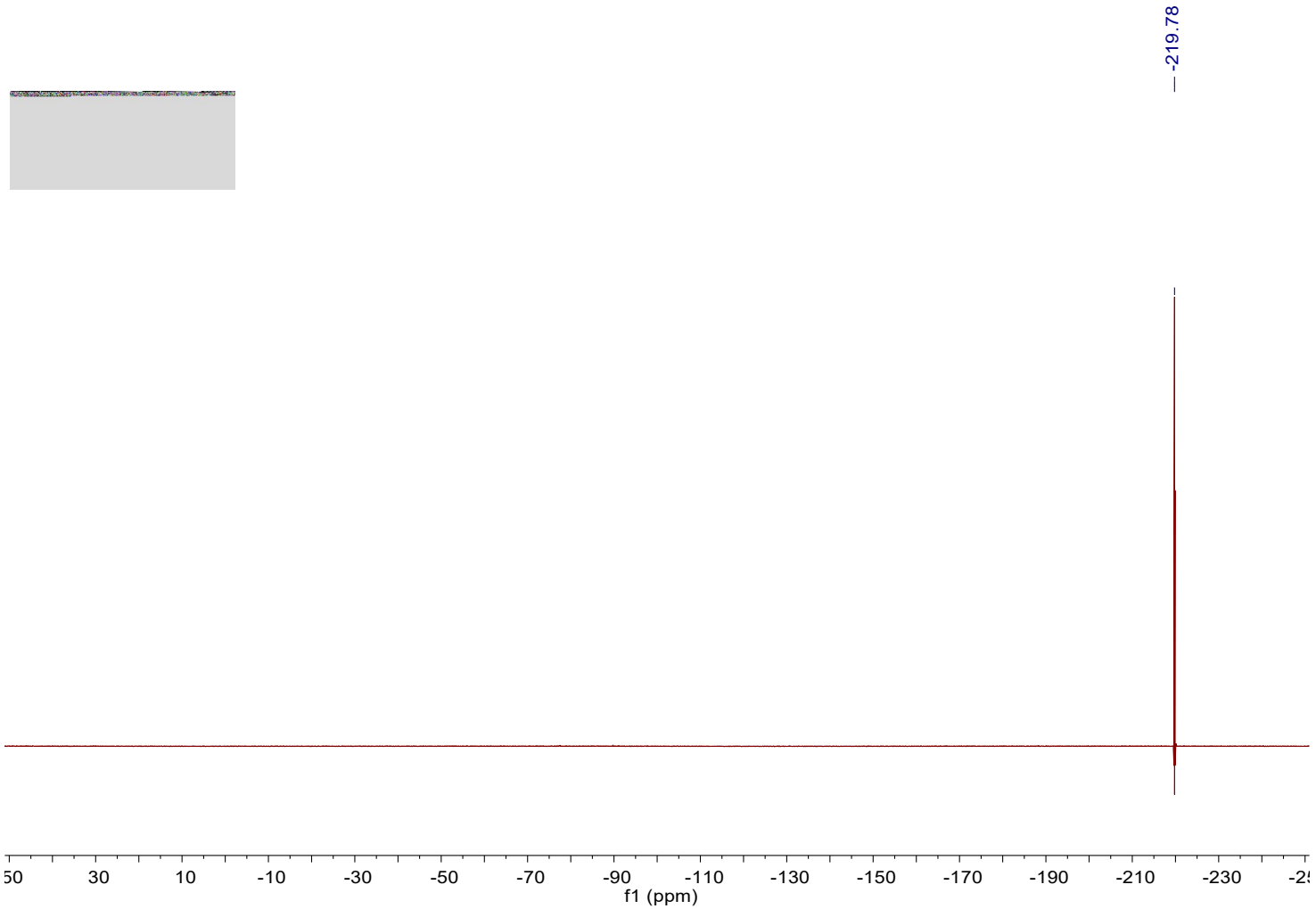




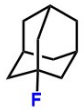
Compound **2ad** ^{13}C NMR (151 MHz, CD_3CN)

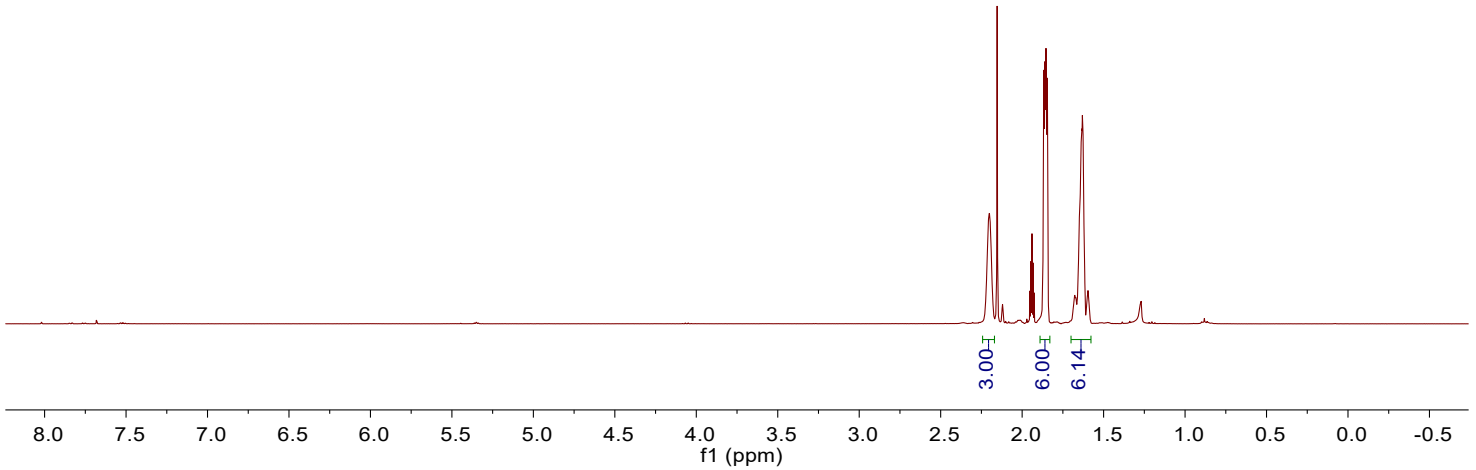


Compound **2ad** ^{19}F NMR (376 MHz, CD_3CN)

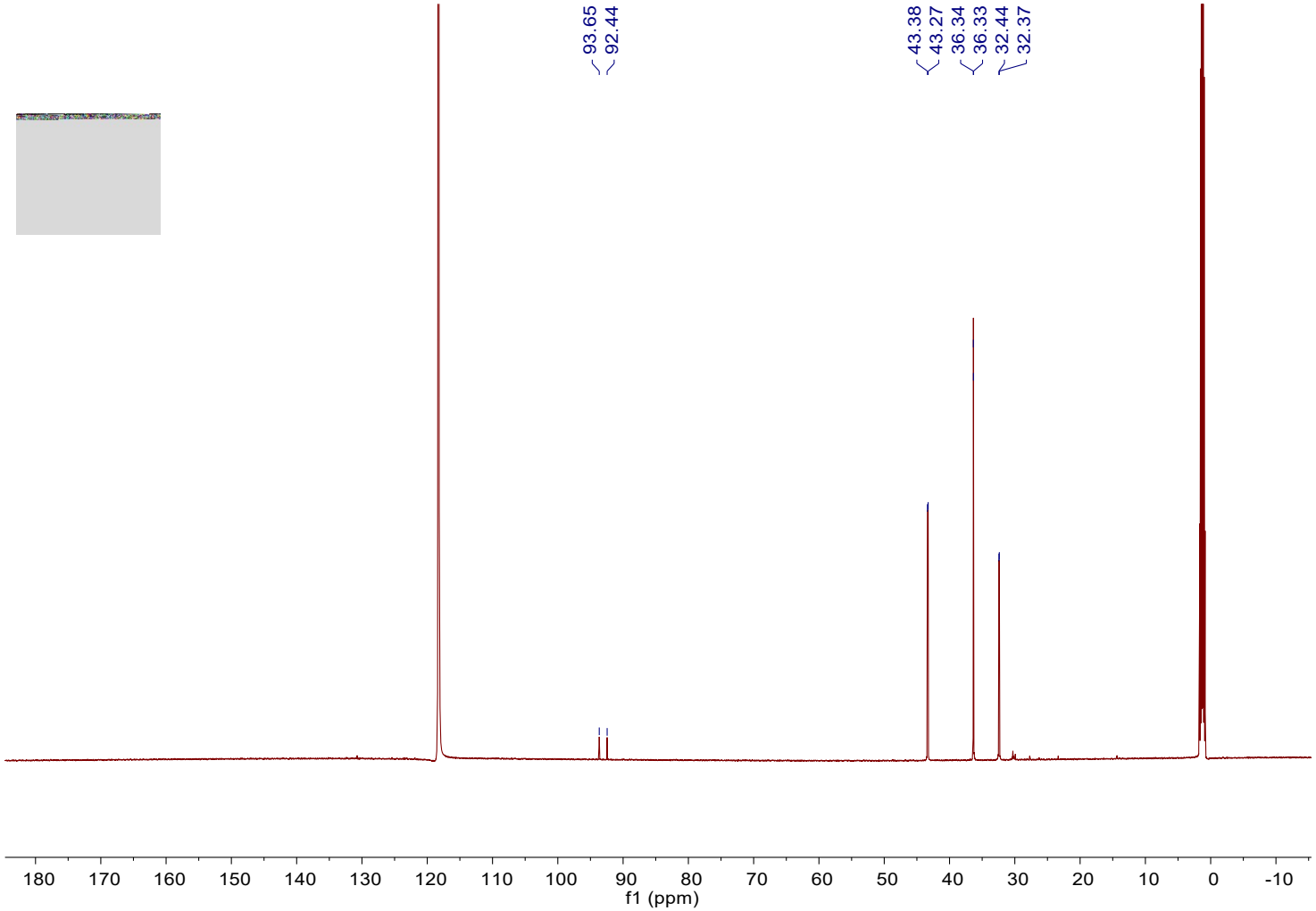


Compound **2ae** ^{1}H NMR (400 MHz, CD_3CN)

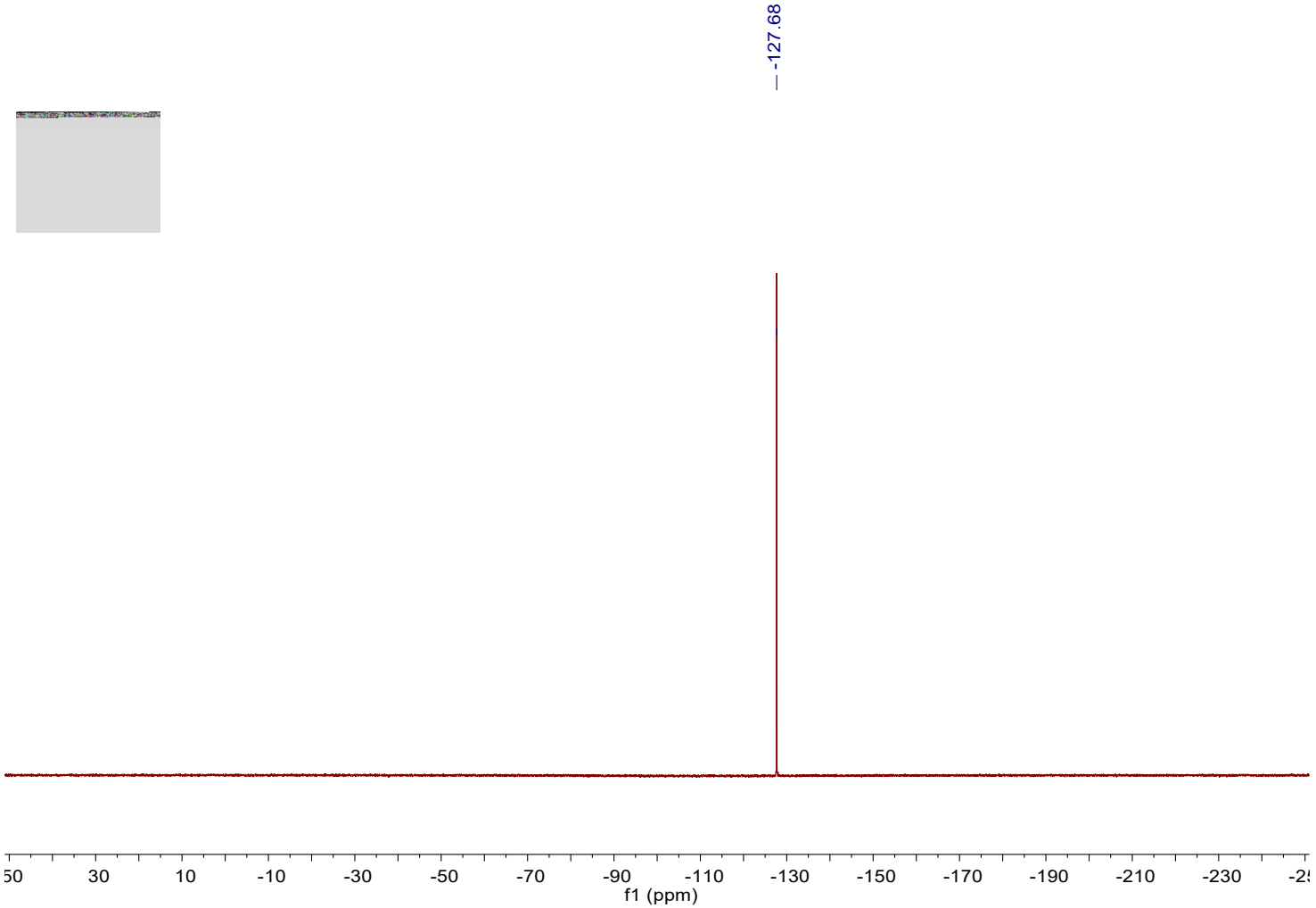




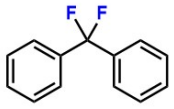
Compound **2ae** ^{13}C NMR (151 MHz, CD_3CN)

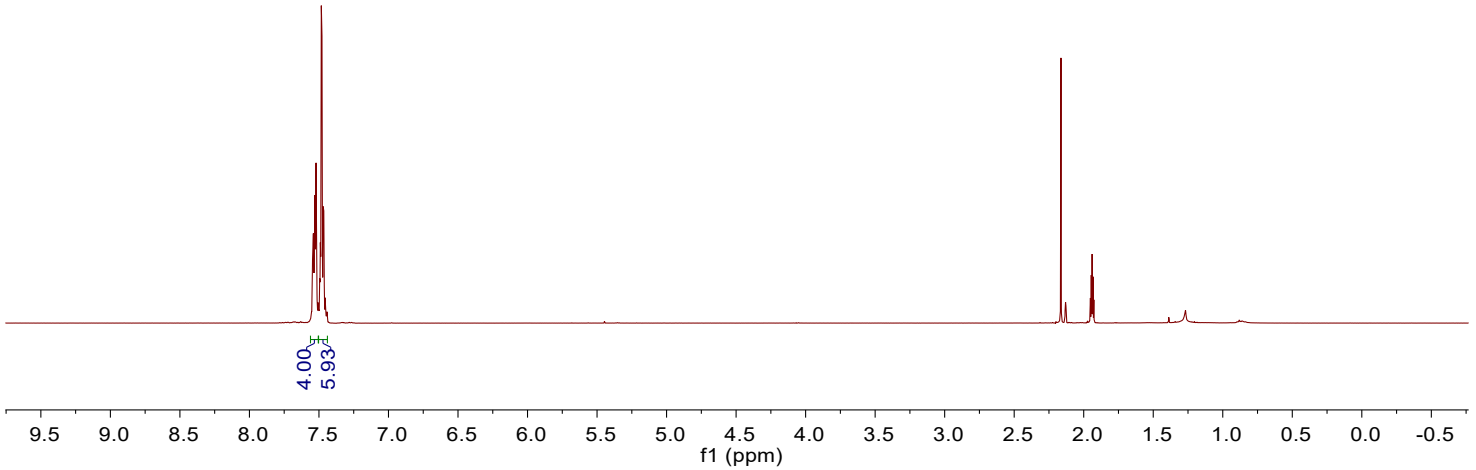


Compound **2ae** ^{19}F NMR (376 MHz, CD_3CN)

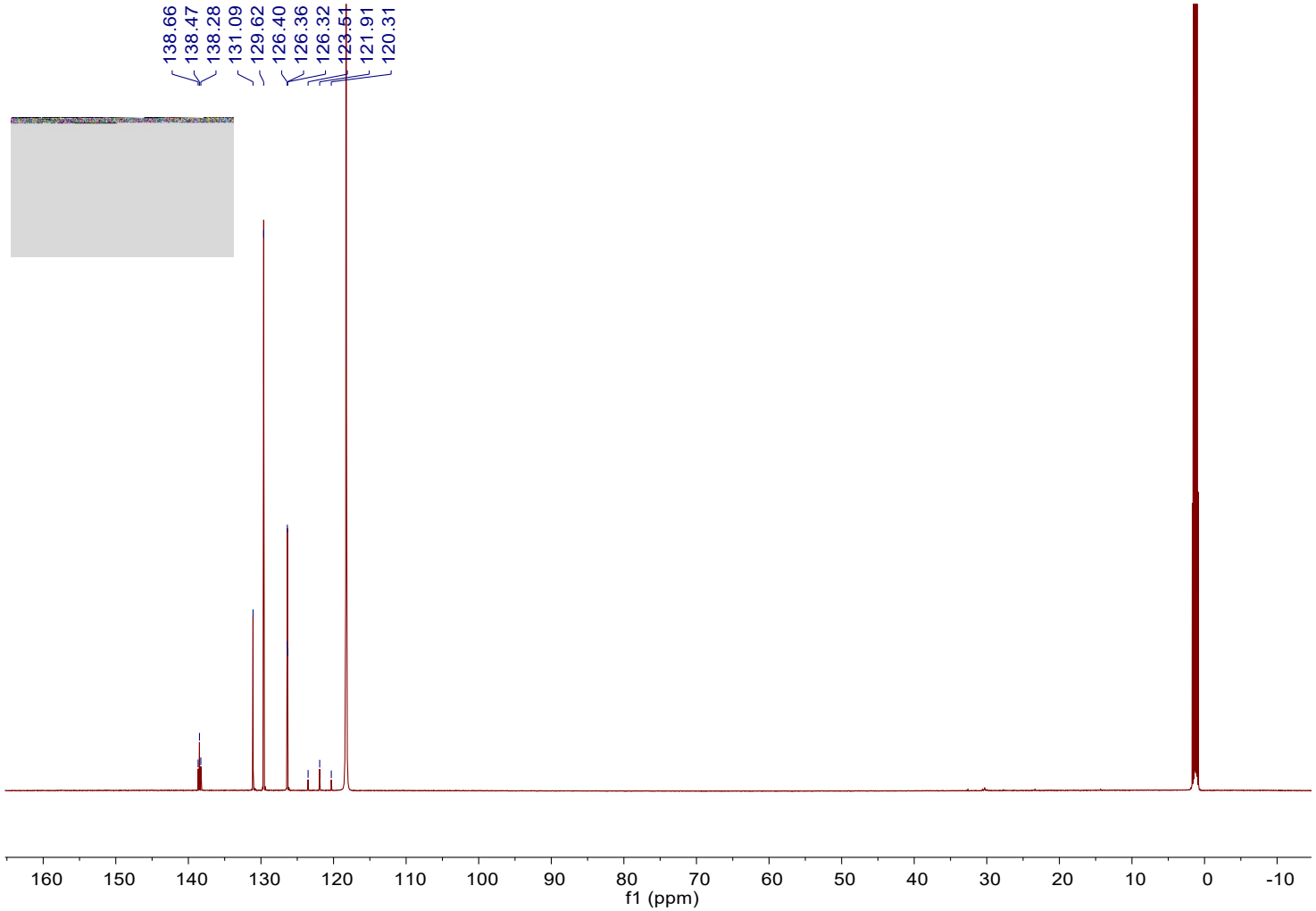


Compound **2af** ^{1}H NMR (400 MHz, CD_3CN)

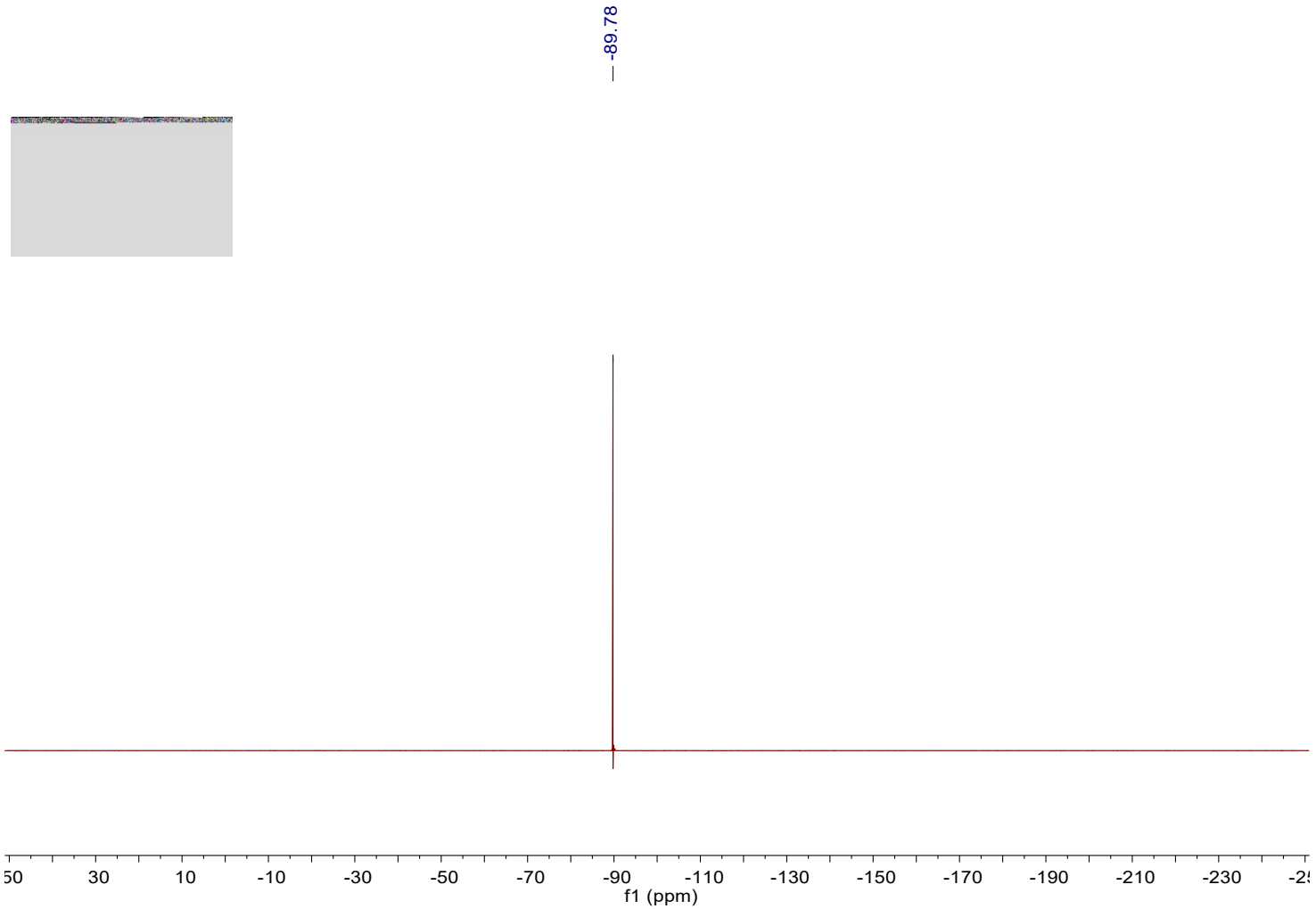




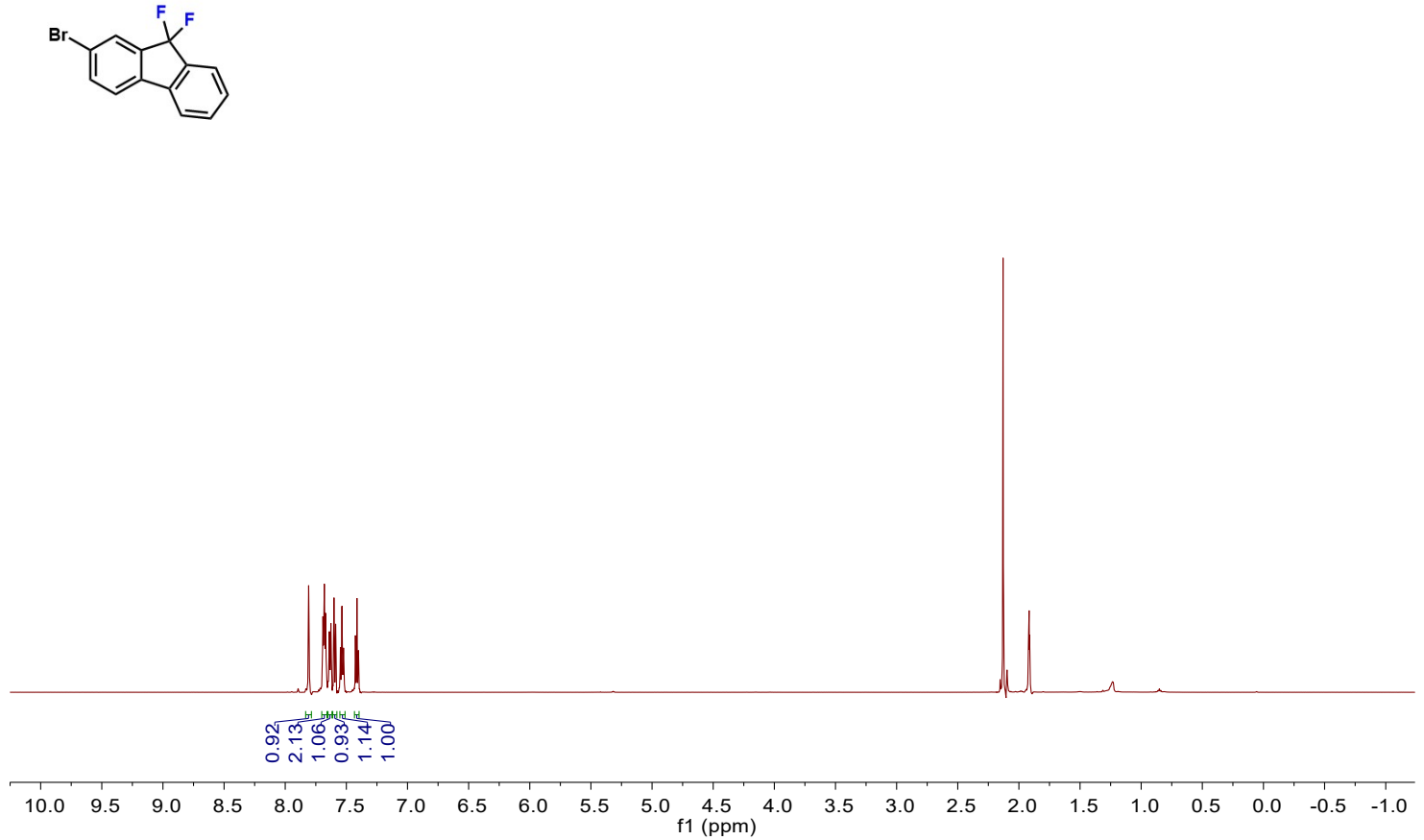
Compound **2af** ^{13}C NMR (151 MHz, CD_3CN)



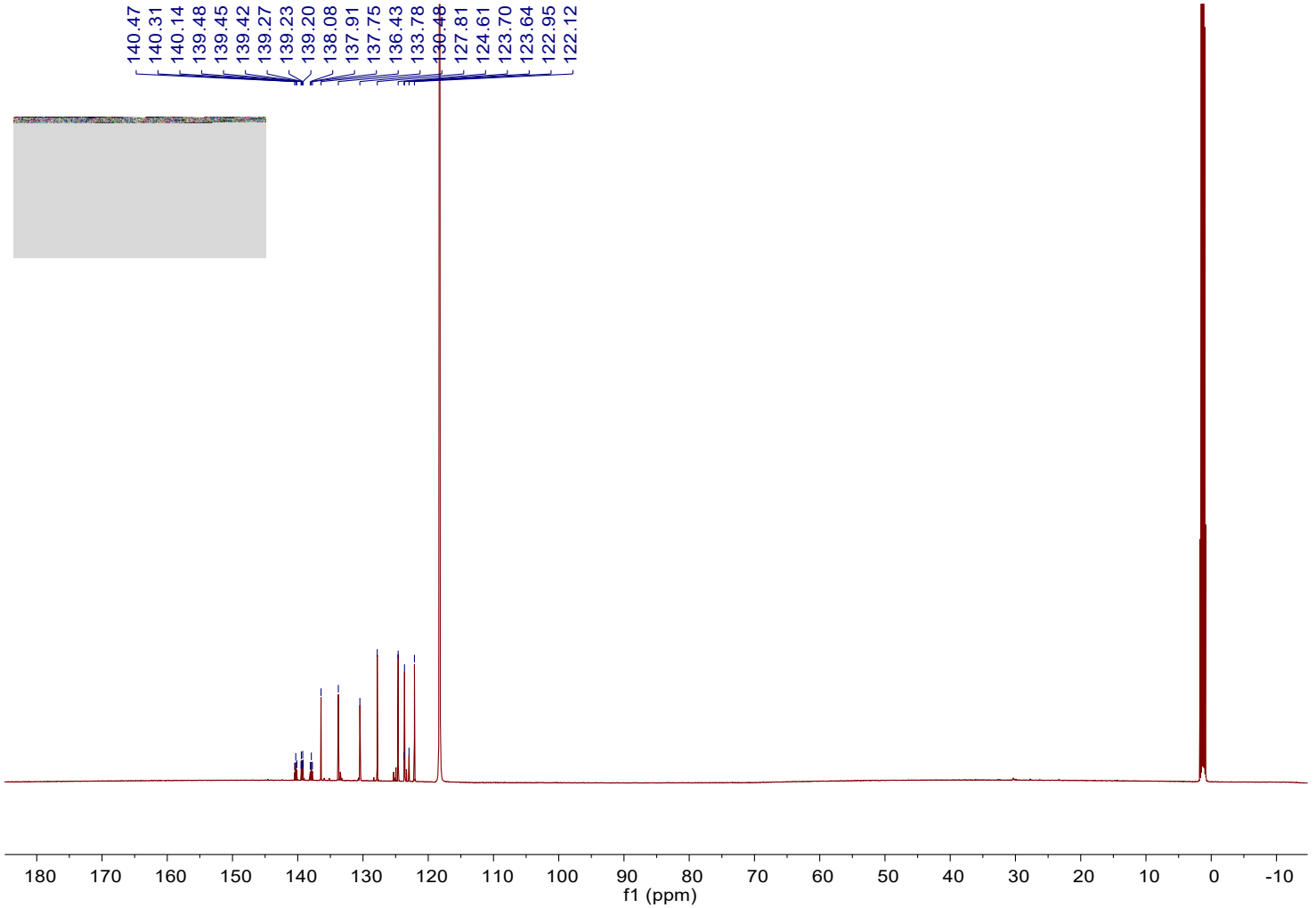
Compound **2af** ^{19}F NMR (376 MHz, CD_3CN)



Compound **2ag** ^{1}H NMR (600 MHz, CD_3CN)



Compound **2ag** ^{13}C NMR (151 MHz, CD_3CN)



Compound **2ag** ^{19}F NMR (376 MHz, CD_3CN)