Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Photoredox Activation of Anhydrides for the Solvent-Controlled Switchable Synthesis of *gem*-Difluoro Compounds

*R. Giri, I. Mosiagin, I. Franzoni, N. Y. Nötel, S. Patra, D. Katayev**

Table of Contents

1. General Information

1.1. Material and methods

All reactions were performed in flame-dried glassware under inert (Ar or N_2) atmosphere containing a Teflon-coated stirring bar and dry septum. In addition, glassware was dried overnight at 150 °C before use. Commercially available starting materials were purchased from Thermoscientific – Acros, Sigma Aldrich, Apollo Scientific, Fluorochem, and TCI unless otherwise noted. All commercially available olefins were analyzed by ^{1}H NMR spectroscopy before use. Anhydrous acetonitrile was distilled over CaH_2 and stored over pre-conditioned 3 Å mol sieves for at least 12 h before use. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 F254 TLC glass plates and visualized with 254 nm light and potassium permanganate staining solutions followed by heating. Purification of reaction products was carried out by flash chromatography using Brunschwig silica 32-63, 60Å under 0.3-0.5 bar overpressure. Medium pressure liquid chromatography (MPLC) was performed on a CombiFlash Rf200 System from Teledyne ISCO with a built-in UV-detector and fraction collector or manually using silica gel SilicaFlash P60, 40-63 µm. Teledyne ISCO RediSep Rf flash columns used having 0.035–0.070 mm particle size and 230–400 mesh. Normal phase preparatory HPLC purification was conducted on a Teledyne Isco CombiFlash EZ Prep system using a Macherey-Nagel VP 250/21 Nucleosil 50-5 columns. ^{1}H- and ^{13}C-NMR spectra were recorded on Bruker Ultrashield 300 (operating at 300.1 MHz and 75.5 MHz, respectively), Bruker Ascend 400 (operating at 400.1 MHz and 100.6 MHz, respectively), Bruker AVANCE III 500 (operating at 500.1 MHz and 125.6 MHz, respectively), and Bruker Ascend LH 600 (operating at 600.1 MHz and 151.6 MHz, respectively), ^{19}F-NMR spectra on Bruker DPX-300 and Bruker Ultrashield 300 (at 282 MHz) and Bruker DPX-400 and Bruker Ascend 400 (at 376 MHz) Bruker DPX-500 and Bruker AVANCE III 500 (at 477 MHz). The chemical shifts are reported in parts per million (ppm) and coupling constants (*J*) are given in Hertz (Hz). ^{1}H-NMR spectra are reported with the solvent resonance as the reference unless noted otherwise ($CDCl_3$ at 7.26 ppm). Peaks are reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). ^{13}C-NMR spectra were recorded with ^{1}H-decoupling and are reported with the solvent resonance as the reference unless noted otherwise ($CDCl_3$ at 77.16 ppm). ^{19}F-NMR spectra were recorded with ^{1}H-decoupling unless noted otherwise. A Bruker Tensor III spectrometer equipped with a golden gate was used to record infrared spectra. Melting points were measured by using OptiMelt Automated Melting Point System Type K/°C. HR-MS (ESI+) mass spectra were measured on a Bruker FTMS 4.7T BioAPEX II and Thermo Scientific LTQ Orbitrap XL equipped with a static nanospray ion source and mass spectrometry service operated on VG-TRIBRID for electron impact ionization (EI), or Varian IonSpec Spectrometer for electrospray ionization (ESI) and are reported as (*m/z*,). Electron impact ionization mass spectra (EI-MS) were run on a gas chromatography – mass spectrometry (GC-MS) instrument of Agilent 8890 series GC system and Agilent 5977B GC/MSD. Single crystals for X-ray diffraction were measured on XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer with CuKα radiation (λ = 1.54184Å). All measurements were carried out at 100 K. The structures were solved using SHELXS.1, SHELXT51 or Superflip1 and refined by full-matrix leastsquares analysis (SHELXL) using the program package OLEX2.2 Unless otherwise indicated below, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters (in terms of a riding model). Solid-state structures were visualized using the ORTEP3 program. All SC-XRD specific details and deposited CCDC numbers can be located in Section 14 (X-Ray Diffraction Data) of this Supporting Information. UV-VIS absorption spectra were recorded on Perkin Elmer Lambda 35 UV/VIS spectrometer. Fluorescence spectroscopy was measured on JASCO FP-6200 spectrofluorometer. Cyclic voltammetry was measured using the Osilla potentiostat, an Ag^+ (0.01M $AgNO_3$)/Ag reference electrode, a platinum disc working electrode, and a platinum counter electrode. All measurements were carried out in MeCN (0.1 M NBu_4PF_6) unless stated otherwise.

1.2. High intensity blue LEDs photoreactors

The photoreactor was custom designed and built by Katayev and co-workers in coordination with the mechanical workshop in the Department of Chemistry and Applied Biosciences at ETH Zürich having blue LEDs, equally spaced in a circular design, powered by a 10.3 A power supply, emitting 350 W of light with the measured UV-Vis spectrum (Figure 1). The LEDs were water-cooled and further cooled by built-in fans to maintain an ambient temperature.

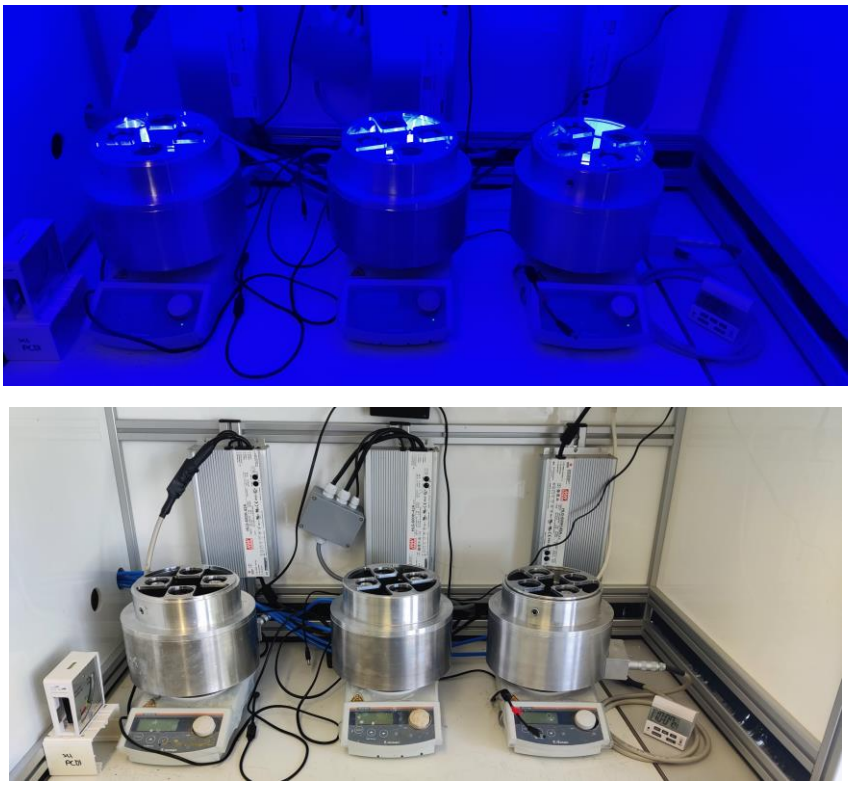


Figure 1.1. Custom-made high-intensity, blue LEDs photoreactors.

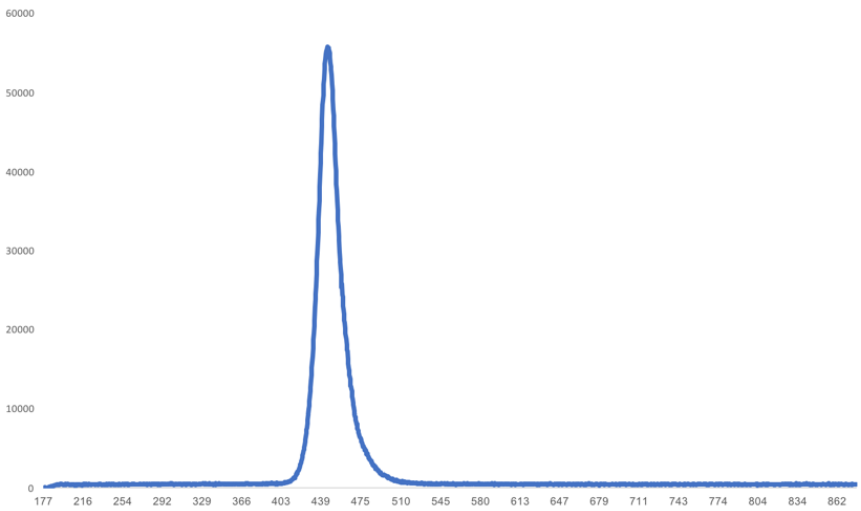


Figure 1.2. UV-Vis emission spectrum of high-intensity, blue LED photoreactor (λ_{max} = 440 nm, FWHM = 20 nm). The figure is taken from.[4]

1.3. Graphical representation of the reaction setup

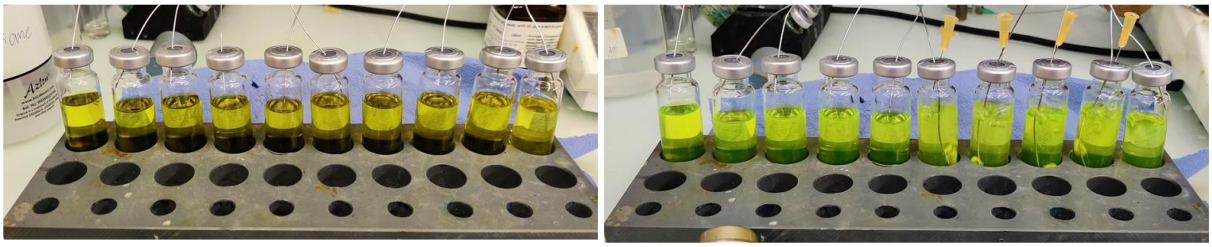
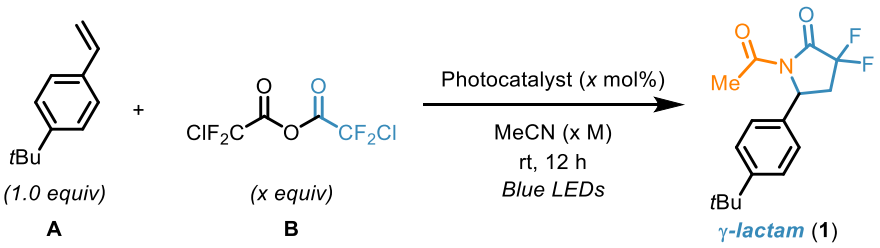


Figure 1.3. Colour of the reaction mixture before degassing **(left),** colour of the reaction mixture after degassing (**right**).

Figure 1.4. Before irradiation **(left),** after irradiation (**right**).

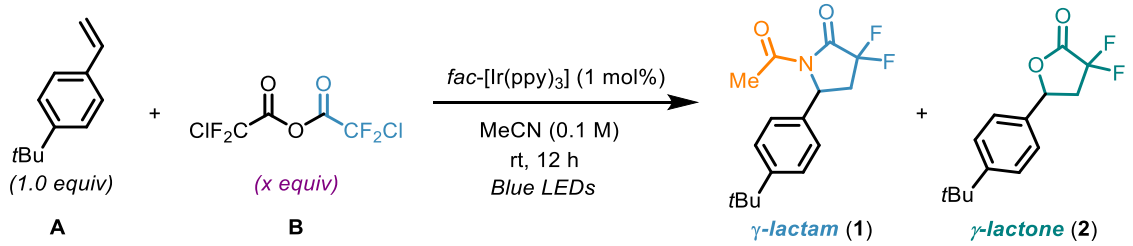
2. Development of the Reaction Conditions



A flame-dried 20 mL crimp cap vial was charged with photocatalyst (*x* mol%) and equipped with a magnetic stirring bar. The content of the vial was then subjected to three vacuum/argon cycles. Anhydrous MeCN (*x* mL) was added under an argon atmosphere, and the yellow solution was degassed for 6 min. 4-*tert*-Butylstyrene, (94%, stab. with 50 ppm *4-tert*-butylcatechol, commercially available at Thermoscientific - Alfa Aesar, 95 µL, 0.5 mmol, 1.0 equiv) and chlorodifluoroacetic anhydride (*CDFAA*, *x* equiv.) were introduced to the solution *via* microsyringes. The reaction mixture was irradiated at ambient conditions under blue LEDs for 12 h. An internal standard of *n*-decane (96 µL, 0.5 mmol, 1.0 equiv) was added with a microsyringe once the reaction is completed. An aliquot was taken and analysed by GC to obtain the calibrated yields and characterization for the desired product.

Note: Optimization of reaction conditions was done at 0.5 mmol of styrene (**A**).

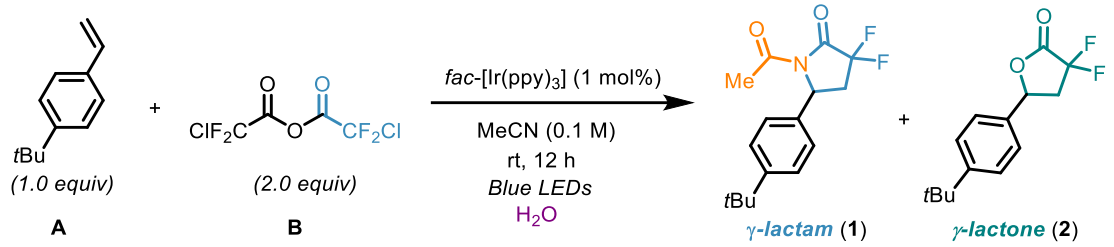
2.1. *CDFAA* loading



Entry[a]	*CDFAA* (equiv)	Yield of 1 [%][b]	Yield of 2 [%][b]
1	1.0	39	9
2	1.5	40	10
3	2.0	56	5
4	3.0	54	6
5	4.0	55	6

Table 2.1. a. Reaction conditions: 4-*tert*-butylstyrene (1.0 equiv), *fac*-[Ir(ppy)$_3$] (1.0 mol%), *CDFAA* (x equiv), MeCN (0.1 M), rt, blue LEDs (350 W), 12 h. **b.** Yields of **1** and **2** are determined by GC against an internal standard of *n*-decane.

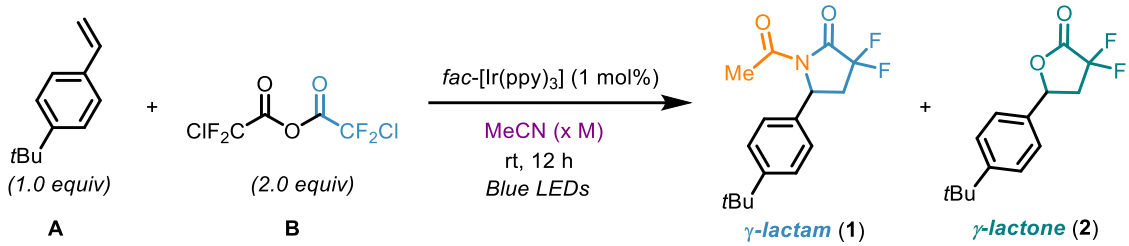
2.2. Effect of H_2O



Entry[a]	H_2O	Yield of 1 [%][b]	Yield of 2 [%][b]
1	Yes[c]	32	13
2	No	56	5

Table 2.2. a. Reaction conditions: 4-*tert*-butylstyrene (1.0 equiv), *fac*-[Ir(ppy)$_3$] (1.0 mol%), CDFAA (2.0 equiv), MeCN (0.1 M), rt, blue LEDs (350 W), 12 h. b. Yields of **1** and **2** are determined by GC against an internal standard of *n*-decane. **c.** Addition of 1.0 equiv of H_2O prior to LEDs irradiation.

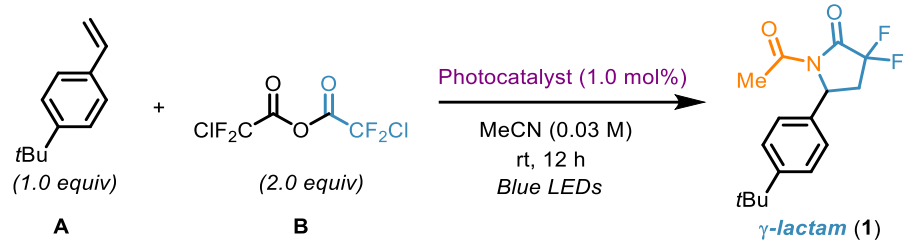
2.3. Concentration effect on 1

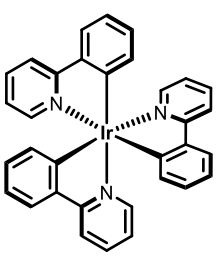


Entry[a]	Concentration [M]	Yield of 1 [%][b]	Yield of 2 [%][b]
1	0.100	56	5
2	0.070	79	8
3	0.050	87	7
4	0.045	86	5
5	0.040	90	4
6	0.030	92	2

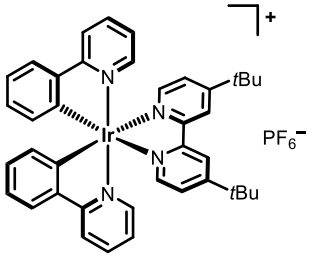
Table 2.3. a. Reaction conditions: 4-*tert*-butylstyrene (1.0 equiv), *fac*-[Ir(ppy)$_3$] (1.0 mol%), *CDFAA* (2.0 equiv), MeCN (x M), rt, blue LEDs (350 W), 12 h. **b.** Yields of **1** and **2** are determined by GC against an internal standard of *n*-decane.

2.4. Photocatalyst effect

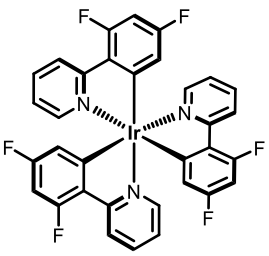




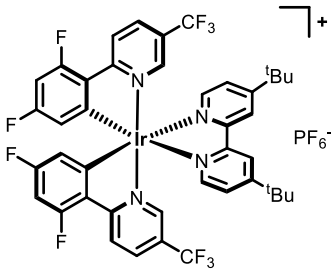
92%
fac-[Ir(ppy)$_3$]



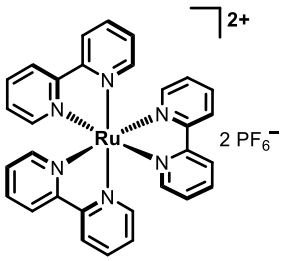
30%
[Ir(dtbbpy)(ppy)$_2$]PF$_6$



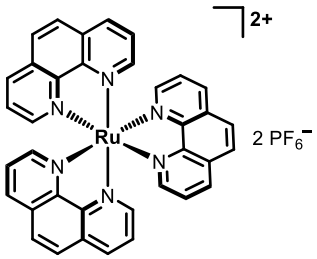
88%
Ir(dFppy)$_3$



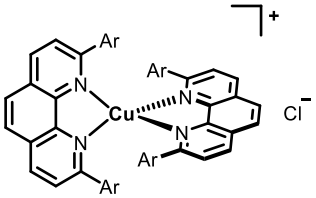
18%
(Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$



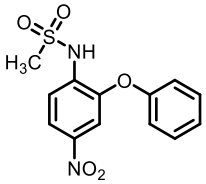
4%
Ru(bpy)$_3$(PF$_6$)$_2$



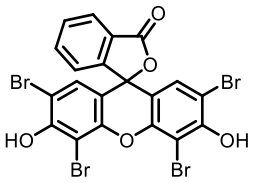
11%
Ru(phen)$_3$(PF$_6$)$_2$



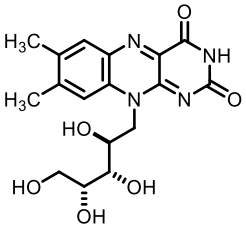
Ar= *p*-OMe-C$_6$H$_4$
80%
[Cu(dap)$_2$Cl]



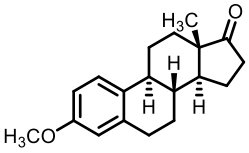
7%
Nimesulide



0%
Eosin Y



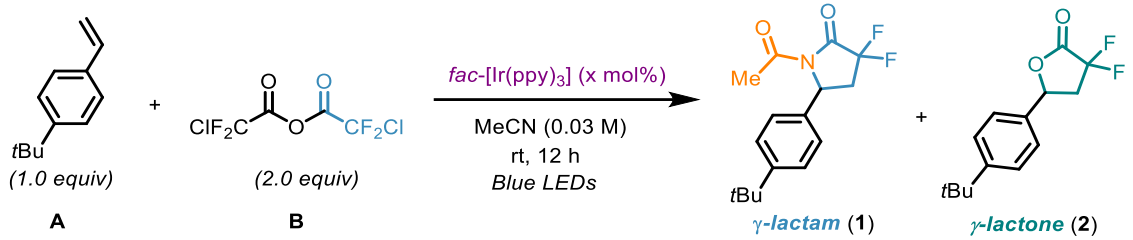
7%
Riboflavin



0%
Estrone 3-methyl ether

Table 2.4. Reaction conditions: 4-*tert*-butylstyrene (1.0 equiv), *CDFAA* (2.0 equiv), photocatalyst (1.0 mol%), MeCN (0.03 M), blue LEDs (350 W), 12 h, rt. Yield of **1** is determined by GC against an internal standard of *n*-decane.

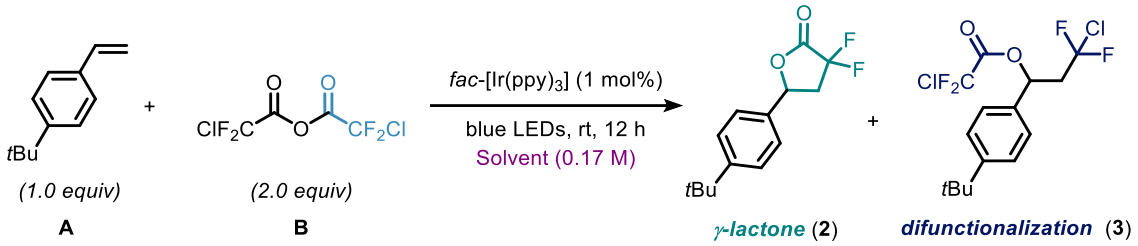
2.5. *fac*-[Ir(ppy)$_3$] loading



Entry[a]	*fac*-[Ir(ppy)$_3$] [mol %]	Yield of 1 [%][b]	Yield of 2 [%][b]
1	5.0	80	5
2	3.0	85	4
3	2.5	83	6
4	2.0	84	4
5	1.0	92 (90)[c]	2

Table 2.5. a. Reaction conditions: 4-*tert*-butylstyrene (1.0 equiv), *fac*-[Ir(ppy)$_3$] (x mol%), *CDFAA* (2.0 equiv), MeCN (0.03 M), blue LEDs (350 W), 12 h, rt. **b.** Yield of **1** and **2** is determined by GC against an internal standard of *n*-decane. **c.** Isolated yield is reported in parentheses.

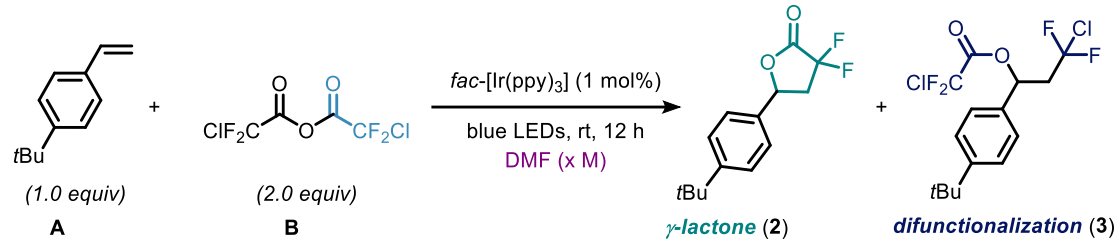
2.6. Solvent optimization



Entry[a]	Solvent	Yield of 2 [%][b]	Yield of 3 [%][b]
1	EtOAc	15	62
2	DMF	80	3
3	THF	17	15
4	$CHCl_3$	56	28
5	1,4-Dioxane	17	42
6	Et_2O	9	75
7	DMSO	5	-
8	DCM	30	53
9	HFIP	5	-
10	1,2 DCE	9	46
11	DMA	6	-
12	Acetone	8	-
13	THF: $CHCl_3$ (1:1)	44	14
14	Toluene	16	76
15	Ethylbenzene	10	70
16	Benzene	12	68
17	Hexafluorobenzene	-	-
18	Pentafluorobenzene	-	traces
19	Trifluorotoluene	-	-

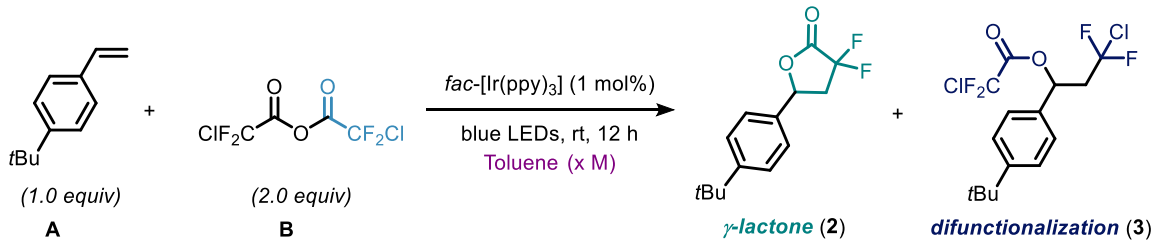
Table 2.6. a. Reaction conditions: 4-*tert*-butylstyrene (1.0 equiv), *CDFAA* (2.0 equiv), *fac*-[Ir(ppy)$_3$] (1.0 mol%), solvent (0.03 M), rt, blue LEDs (350 W), 12 h. **b.** Yields of **2** and **3** are determined by GC against an internal standard of *n*-decane.

2.7. Concentration effect on 2 and 3



Entry[a]	Concentration [M]	Yield of 2 [%][b]	Yield of 3 [%][b]
1	0.500	79	2
2	0.250	84	2
3	0.170	86 (81)[c]	3
4	0.100	81	-
5	0.050	83	2
6	0.033	80	3

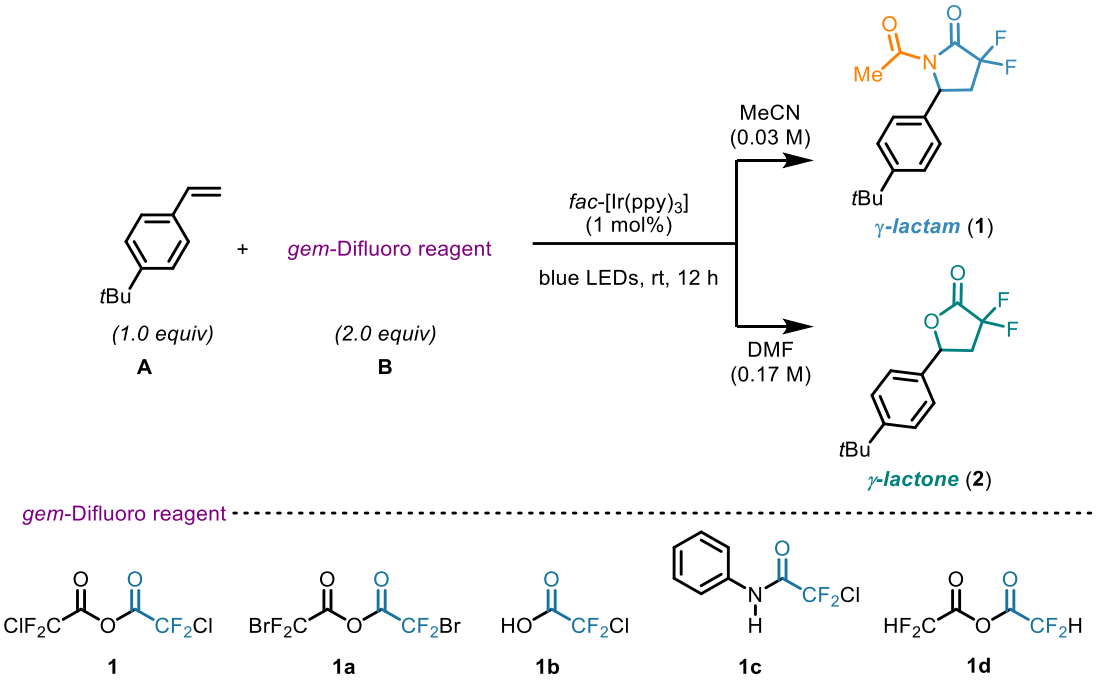
Table 2.7. a. Reaction conditions: 4-*tert*-butylstyrene (1.0 equiv), *CDFAA* (2.0 equiv), *fac*-[Ir(ppy)$_3$] (1.0 mol%), (1.0 mol%), DMF (x M), blue LEDs (350 W), 12 h, rt. **b.** Yield of **2** is determined by GC against an internal standard of *n*-decane. **c.** Isolated yield is reported in parentheses.



Entry[a]	Concentration [M]	Yield of 2 [%][b]	Yield of 3 [%][b]
1	0.500	18	70
2	0.250	16	72
3	0.170	14	81 (75) [c]
4	0.100	19	74
5	0.050	10	69
6	0.033	16	70

Table 2.8. a. Reaction conditions: 4-*tert*-butylstyrene (1.0 equiv), *CDFAA* (2.0 equiv), *fac*-[Ir(ppy)$_3$] (1.0 mol%), Toluene (x M), blue LEDs (350 W), 12 h, rt. **b.** Yield of **3** is determined by GC against an internal standard of *n*-decane. **c.** Isolated yield is reported in parentheses.

2.8. Screening of reagents

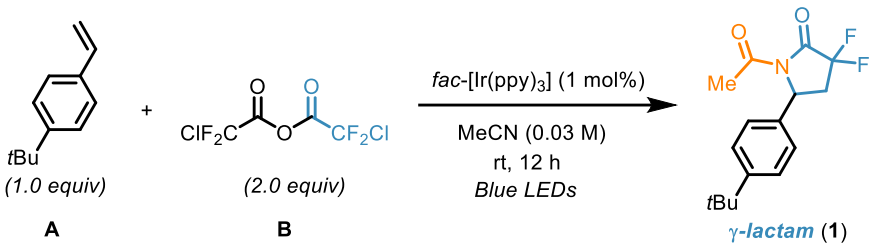


Entry[a]	Solvent	*Reagent*	γ-lactam (1) [%][b]	γ -lactone (2) [%][b]
1	MeCN	1	92 (90)[c]	2
2	MeCN	1a	64	10
3	MeCN	1b	43	10
4	MeCN	1c	-	-
5	MeCN	1d	-	-
6	DMF	1	-	86 (81)[c]
7	DMF	1a	-	60 (54)[c]
8	DMF	1b	-	58
9	DMF	1c	-	-
10	DMF	1d	-	traces

Table 2.9. a. Reaction conditions: 4-*tert*-butylstyrene (1.0 equiv), *gem*-difluoro reagent (2.0 equiv), *fac*-[Ir(ppy)$_3$] (1.0 mol%), solvent (x M), blue LEDs (350 W), 12 h, rt. **b.** Yield of **1** and **2** are determined by GC against an internal standard of *n*-decane. **c.** Isolated yields are reported in parentheses.

2.9. Control experiments

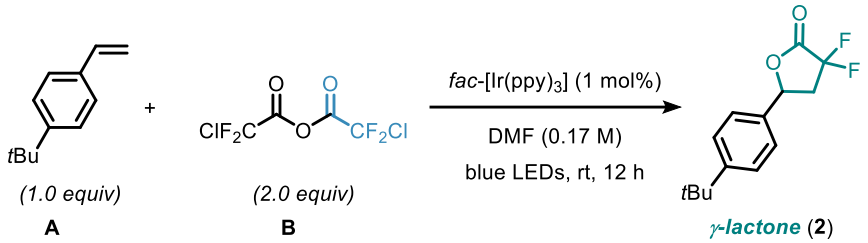
2.9.1. For γ-lactam **1**



Entry[a]	Variables	Yield of 1 [%][b]	Side products
1	Standard conditions	92	2% of (**2**)
2	Under air	81	5% of (**2**)
3	Without LEDs	-	unreacted SM[c]
4	Without catalyst	-	unreacted SM[c]
5	Heating at 90 ˚C without light	-	unreacted SM[c]

Table 2.10. a. Standard reaction condition: 4-*tert*-butylstyrene (1.0 equiv), *CDFAA* (2.0 equiv), *fac*-[Ir(ppy)$_3$] (1.0 mol%), MeCN (0.03 M), rt, blue LEDs (350 W), 12 h. **b.** Yields are determined by GC against an internal standard of *n*-decane. SM-**c.** starting material **A**.

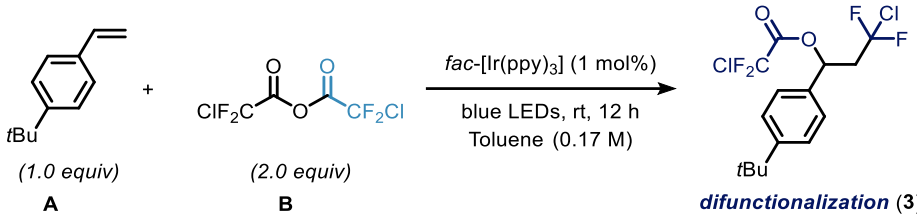
2.9.2. For γ-lactone **2**



Entry[a]	Variables	Yield of 2 [%][b]]	Side products
1	Standard conditions	86	3% of (**3**)
2	Under air	80	5% of (**3**)
3	Without LEDs	-	unreacted SM[c]
4	Without catalyst	-	unreacted SM[c]
5	Heating at 90 ˚C without light	-	unreacted SM[c]

Table 2.11. a. Standard reaction condition: 4-*tert*-butylstyrene (1.0 equiv), *CDFAA* (2.0 equiv), *fac*-[Ir(ppy)$_3$] (1.0 mol%), DMF (0.17 M), rt, blue LEDs(350 W), 12 h. **b.** Yield of **2** is determined by GC against an internal standard of *n*-decane. SM-**c.** starting material **A**.

2.9.3. For oxy-fluoroalkylation reaction to form product **3**



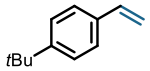
Entry[a]	Variables	Yield of 3 [%][b]	Side products
1	Standard conditions	81	14% of (**2**)
2	Under air	52	19% of (**2**)
3	Without LEDs	-	unreacted SM[c]
4	Without catalyst	-	unreacted SM[c]
5	Heating at 90 ˚C without light	-	unreacted SM[c]

Table 2.12. a. Standard reaction condition: 4-*tert*-butylstyrene (1.0 equiv), *CDFAA* (2.0 equiv), *fac*-[Ir(ppy)$_3$] (1.0 mol%), Toluene (0.17 M), rt, blue LEDs (350 W), 12 h. **b.** Yield of **3** is determined by GC against an internal standard of *n*-decane. **c.** SM-starting material **A**.

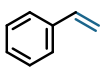
3. Synthesis of Starting Materials

3.1. Commercially available starting materials

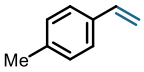
Commercially available starting materials are mostly purchased from Thermoscientific – Acros, Sigma Aldrich, Apollo Scintific, Fluorochem and TCI.



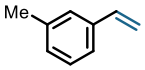
CAS 1746-23-2



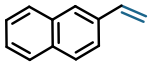
CAS 100-42-5



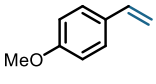
CAS 622-97-9



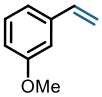
CAS 100-80-1



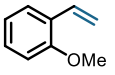
CAS 827-54-3



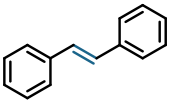
CAS 637-69-4



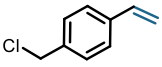
CAS 626-20-0



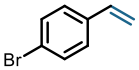
CAS 612-15-7



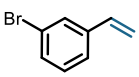
CAS 103-30-0



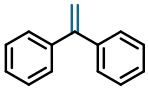
CAS 1592-20-7



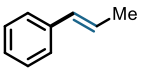
CAS 2039-82-9



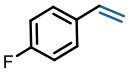
CAS 2039-86-3



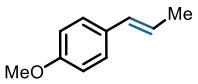
CAS 530-48-3



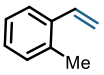
CAS 873-66-5



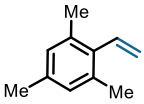
CAS 405-99-2



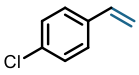
CAS 4180-23-8



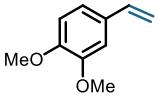
CAS 611-15-4



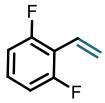
CAS 769-25-5



CAS 1073-67-2



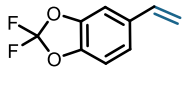
CAS 6380-23-0



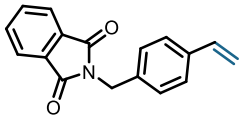
CAS 207226-37-7

3.2. Prepared starting materials

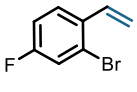
Starting materials from S_1-S_{23} were synthesized according to published procedures. According to the following references.[1-17]



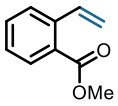
ref 1, S-1



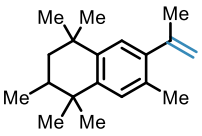
ref 1, S-2



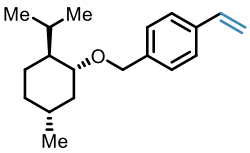
ref 2, S-3



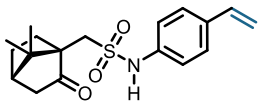
ref 3, S-4



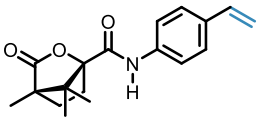
ref 4, S-5
From AHTN



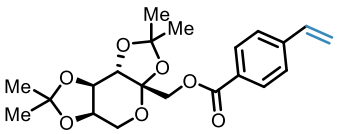
ref 4, S-6
From L-Menthol



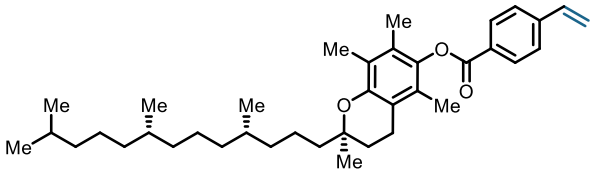
ref 4, S-7
From (–)-10-Camphorsulfonyl



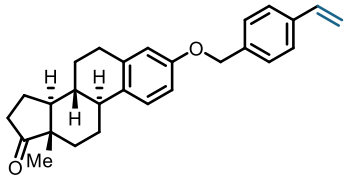
ref 4, S-8
From L-Camphanic



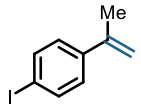
ref 5, S-9
From D-Fructopyranose diacetonide



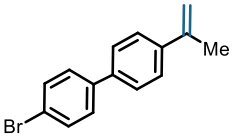
ref 6, S-10
From α-Tocopherol



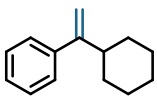
ref 7, S-11
From Estrone



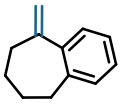
ref 8, S-12



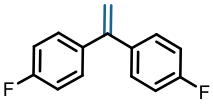
ref 9, S-13



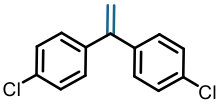
ref 10, S-14



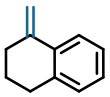
ref 10, S-15



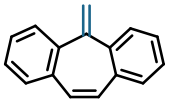
ref 10, S-16



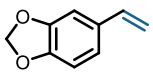
ref 10, S-17



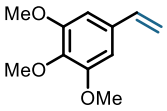
ref 11, S-18



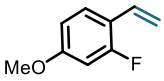
ref 12, S-19



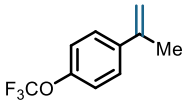
ref 13, S-20



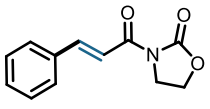
ref 14, S-21



ref 15, S-22



ref 17, S-23



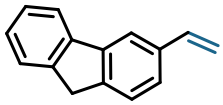
ref 17, S-24

3.3. Synthesis of starting materials

General procedure

Methyltriphenylphosphonium bromide (3.0 equiv) was suspended in dry THF (0.2 M) and the solution was cooled to 0 °C. *tert*-BuOK (3.0 equiv) was added in one portion and the reaction was stirred at 0 °C for 30 min. Subsequently the corresponding ketone or aldehyde (1.0 equiv) was introduced, and the final mixture was naturally warmed to RT and stirred until consumption of starting material (controlled by TLC (2 to 16 h). The reaction was quenched with H_2O and extracted with EtOAc (3x50 mL). The combined organic layers were washed with water and dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to give the pure alkene **S-25** to **S-29.**

3-Vinyl-9*H*-fluorene (S-25)

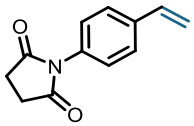


Synthesized using 9H-fluorene-3-carbaldehyde. Isolated as a white solid with 76% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.71 (m, 2H), 7.63 – 7.60 (m, 1H), 7.58 – 7.52 (m, 1H), 7.47 – 7.40 (m, 1H), 7.40 – 7.33 (m, 1H), 7.32 – 7.27 (m, 1H), 6.80 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.80 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.25 (dd, *J* = 10.9, 0.9 Hz, 1H), 3.91 (s, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 176.2, 138.2, 136.0, 131.3, 127.1, 126.6, 115.4, 28.6.

1-(4-Vinylphenyl)pyrrolidine-2,5-dione (S-26)

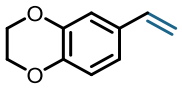


Synthesized using 4-pyrrolylbenzaldehyde. Isolated as a white solid with 70% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.45 (m, 2H), 7.31 – 7.21 (m, 2H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.77 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.31 (dd, *J* = 10.9, 0.8 Hz, 1H), 2.90 (s, 4H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 143.6, 136.3, 131.6, 119.8, 117.4, 114.9, 112.3, 64.5.

6-Vinyl-2,3-dihydrobenzo[*b*][1,4]dioxine (S-27)

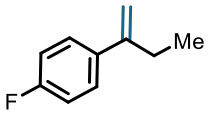


Synthesized using 2,3-dihydrobenzo[*b*][1,4]dioxine-6-carbaldehyde. Isolated as a colorless oil with 82% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.96 – 6.93 (m, 1H), 6.92 – 6.88 (m, 1H), 6.86 – 6.76 (m, 1H), 6.60 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.59 (dd, *J* = 17.5, 0.9 Hz, 1H), 5.13 (dd, *J* = 10.9, 0.9 Hz, 1H), 4.26 (s, 4H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 163.5, 161.0, 149.1, 137.6, 127.6 , 115.0, 110.9, 28.2, 12.9.

1-(But-1-en-2-yl)-4-fluorobenzene (S-28)

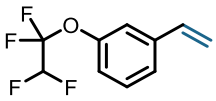


Synthesized using 1-(4-fluorophenyl)propan-1-one. Isolated as a colorless oil with 76% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.30 (m, 1H), 7.11 – 6.91 (m, 1H), 5.23 (d, *J* = 1.2 Hz, 1H), 5.06 (d, *J* = 1.5 Hz, 1H), 2.68 – 2.28 (m, 1H), 1.37 – 0.95 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.5, 153.7, 146.5, 134.7, 130.8, 128.9 (d, *J* = 24.6 Hz), 116.7, 62.2, 43.0.

1-(1,1,2,2-Tetrafluoroethoxy)-3-vinylbenzene (S-29)

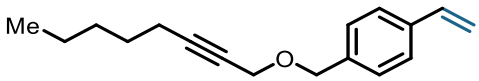


Synthesized using 3-(1,1,2,2-tetrafluoroethoxy)benzaldehyde. Isolated as a colorless oil with (80%, 1.4 g).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.32 (m, 2H), 7.29 (s, 1H), 7.18 – 7.11 (m, 1H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.11 – 5.74 (m, 2H), 5.36 (dd, *J* = 10.9, 0.7 Hz, 1H).

^{19}F-NMR (377 MHz, $CDCl_3$): δ -88.1 (d, *J* = 5.5 Hz), -136.8 (t, *J* = 5.5 Hz).

1-(1,1,2,2-Tetrafluoroethoxy)-2-vinylbenzene (S-30)

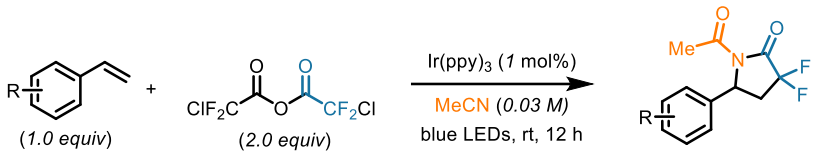


To a solution of 2-octyn-1-ol (2.08 g, 6.9 mmol) in THF (10 mL) was added sodium hydride (1.5 equiv, 60% dispersion) and Bu_4NI (0.5 equiv) stirred for 10 min at 0 ˚C. Later, 4-vinylbenzyl chloride (1.0 g, 6.6 mmol) was dissolved in 10 mL THF and slowly introduced to the reaction mixture via syringe. The resulting mixture was stirred at 50 ˚C for 16 h. The mixture was carefully added to 50 mL of cold water and extracted three times with 40 mL portions of ether. The Et_2O layer was washed with H_2O and brine, and further dried over Na_2SO_4. The crude product was purified by flash column chromatography on silica gel (hexane/EA = 5:1) to afford the corresponding **S-30** as a yellow gel (70%, 1.1 g).

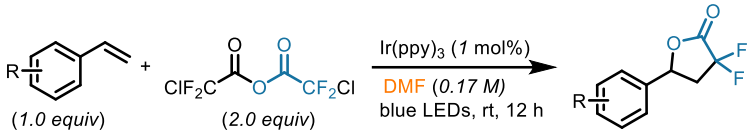
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.37 (m, 2H), 7.35 – 7.30 (m, 2H), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.75 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.24 (dd, *J* = 10.9, 1.0 Hz, 1H), 4.58 (s, 2H), 4.16 (t, *J* = 2.2 Hz, 2H), 2.24 (tt, *J* = 7.1, 2.2 Hz, 2H), 1.66 – 1.46 (m, 2H), 1.48 – 1.22 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 137.4, 137.3, 136.7, 128.4, 126.4, 114.0, 87.5, 75.9, 71.2, 57.8, 31.2, 28.5, 22.3, 18.9, 14.1.

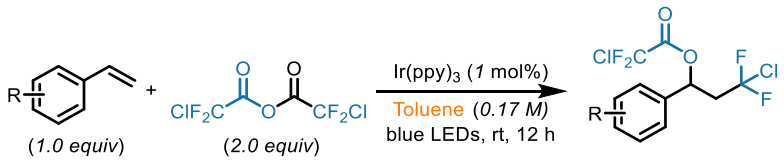
4. General Procedures for the Synthesis of γ-Lactams, γ-Lactones and Chlorodifluoro-alkanes



General Procedure 1: A flame dried 20 mL crimp cap vial was charged with *fac*-[Ir(ppy)$_3$] (3.3 mg, 5 µmol, 1.0 mol%) and equipped with a magnetic bar. The contents of the vial were then subjected to three vacuum/argon cycles. Anhydrous MeCN (15 mL) was added under an argon atmosphere, and the solution was sparged for 5 min. The substrate[a] (0.5 mmol, 1.0 equiv) and *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv) were introduced to the solution *via* microsyringes. The reaction mixture was stirred at room temperature under blue LEDs irradiation for 12 h. The solvent was evaporated under reduced pressure, and the crude product was purified by flash column chromatography or manually over silica gel as indicated to get γ-lactams.



General Procedure 2: A flame dried 5 mL crimp cap vial was charged with *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%) and equipped with a magnetic bar. The contents of the vial were then subjected to three vacuum/argon cycles. Anhydrous DMF (3 mL) was added under an argon atmosphere, and the solution was sparged for 6 min. The substrate[a] (0.5 mmol, 1.0 equiv) and *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv) were introduced to the solution *via* microsyringes. The reaction mixture was irradiated at room temperature under blue LEDs for 12 h. Reaction contents were added to an appropriately sized separatory funnel and 10 mL EtOAc was added and washed with water (3×5) mL; further organic layer was washed with 3 mL brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography or manually over silica gel as indicated to afford γ-lactone derivatives.



General Procedure 3: A flame dried 5 mL crimp cap vial was charged with *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%) and equipped with a magnetic bar. The contents of the vial were then subjected to three vacuum/argon cycles. Anhydrous Toluene (3 mL) was added, and the yellow solution was sparged for 5 min. Substrate[a] (0.5 mmol, 1.0 equiv) and *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv) were introduced to the solution *via* microsyringes. The reaction mixture was irradiated at room temperature under blue LEDs irradiation for 12 h and then solvent was evaporated under reduced pressure. Crude product was purified by flash column chromatography or manually over silica gel as indicated to afford difunctionalized derivatives.

[a] The solid substrates were added to the vial prior to vacuum/argon cycling.

5. Calibration Data for Yield Determination of Compound 1

The yield of **1** for the optimization reactions reported in Section 2 was determined by GC against an internal standard of *n*-decane. The response factor of **1** (0.4281) with respect to the internal standard was computed by plotting the area ratios of eight samples against the respective molar ratios.

Sample	Compound 1			Standard		
	[mL]	[mmol]	Area	[mL]	[mmol]	Area
A	1	0.03664	3.3734	1	0.05130	2.0727
B	0.9	0.03297	2.4935	1	0.05130	1.9474
C	0.8	0.02931	3.3159	1	0.05130	2.1733
D	0.7	0.02565	2.3088	1	0.05130	2.0296
E	0.6	0.02198	1.6951	1	0.05130	1.8543
F	0.5	0.01832	2.2264	1	0.05130	2.4588
G	0.4	0.01466	1.4900	1	0.05130	2.0263
H	0.3	0.01100	0.9224	1	0.05130	1.5479

Table 5.1. Calibration data.

Sample	Molar Ratio [Compound/Standard]	Area Ratio [Compound/Standard]
A	0.714	1.62753896
B	0.643	1.28042518
C	0.571	1.52574426
D	0.500	1.13756405
E	0.428	0.91414550
F	0.357	0.90548235
G	0.286	0.73533041
H	0.214	0.59590413

Table 5.2. Molar and area ratios.

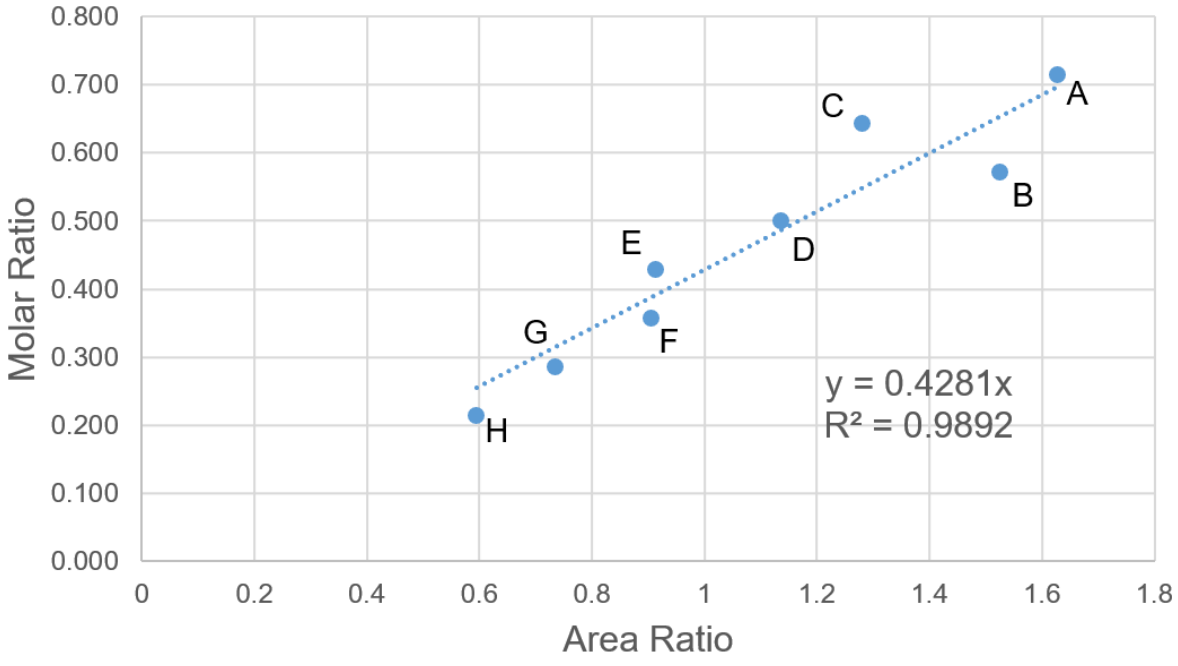


Figure 5.1. The response factor was determined by plotting the area ratios against the molar ratios.

6. Mechanistic Investigations

6.1 Stern-Volmer quenching studies

To investigate the dynamics of the excited state in more detail, Stern-Volmer quenching studies were carried out. The quenching efficiency can be defined as the following which has been deduced by Stern and Volmer.

$$(I_0 \div I) - 1 = k_q \tau_0 \,[\text{quencher}]$$

Where I_0 is the luminescence intensity in the absence of any quencher, I is the luminescence intensity in the presence of a predefined quencher concentration while τ_0 is the excited state lifetime of photocatalyst which has been previously reported as 1.90 x 10^{-6} s for *fac*-[Ir(ppy)$_3$] in acetonitrile at 25 °C.[18-20]

Preparation of stock solutions for Stern-Volmer measurements

A stock solution of the photocatalyst was prepared by dissolving *fac*-[Ir(ppy)$_3$] (0.3 mg, 0.5 µmol, 50.0 µM) in oxygen- and water-free acetonitrile (10 mL) under argon. A stock solution of *CDFAA* was prepared by dissolving 44.2 µL (62.2 mg, 25.4 µmol, 25.0 mM) in acetonitrile to give a total volume of 10 mL. A stock solution of 4-*tert*-butylstyrene was prepared by dissolving 34 µL (38.5 mg, 24.0 µmol, 24.0 mM) in 10 mL acetonitrile.

For evaluation of the quenching ability of TFAA and 4-*tert*-butylstyrenerene, samples of *fac*-[Ir(ppy)$_3$] and the reagent were prepared under argon in dark. Quartz cuvettes (1.5 mL, 10 mm x 4 mm, PTFE cap) were filled with photocatalyst stock solution (0.5 mL), the relevant amount of the reagent stock solution (or pure reagent), and acetonitrile to obtain a total volume of 1.5 mL. The samples were further put into a secondary container (Schott wide screw cap bottle or a screwcap Falcon). All samples have been kept in the dark and were only taken out of the secondary container directly before mounting the samples on the spectrometer under the exclusion of light. Fluorescence Emission spectra were acquired as fast as possible after sample preparation (excitation at 430 ± 2 nm, 1 nm steps, excitation slit, and emission slit: 2 nm).

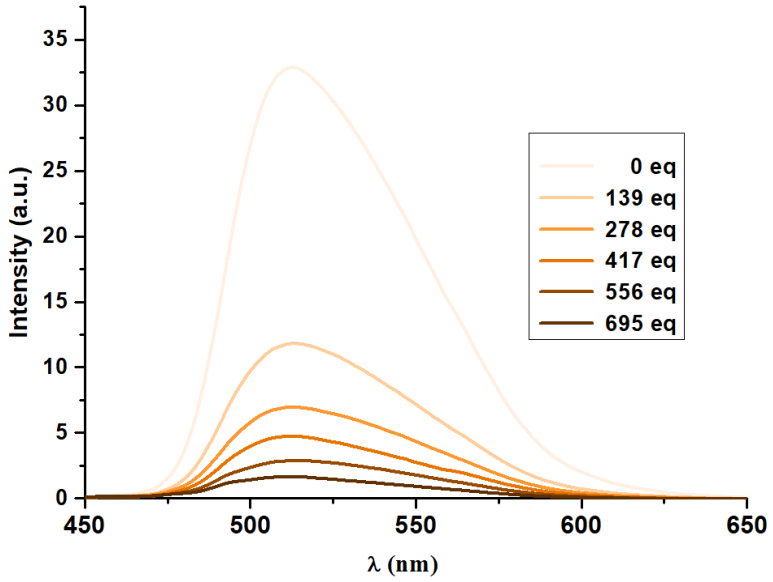


Figure 6.1. Emission quenching of *fac*-[Ir(ppy)$_3$]. with *CDFAA* in acetonitrile (acetonitrile, 47 µM *fac*-[Ir(ppy)$_3$]. 20°C, d_{em} = 2 nm, d_{ex} = 2 nm, λ_{ex} = 430 nm).

First, the influence on the emission of the catalyst by *CDFAA* was investigated. The emission quenching data clearly show that quenching of the excited state of the catalyst by *CDFAA* is highly efficient and happening with a calculated quenching constant of $k_q = 2.0 \times 10^9\ M^{-1}s^{-1}$ (Figures 6.1 and 6.2). Calculation of the quenching constants was performed for *CDFAA* according to the following equation:

$(I_0 \div I) - 1 = k_q \tau_0\,[\text{quencher}]$

Where $\tau_0 = 1.90 \times 10^{-6}$ s

Thus $k_q \tau_0 = 336$

$k_q = 2.0 \times 10^9\ M^{-1}\ s^{-1}$

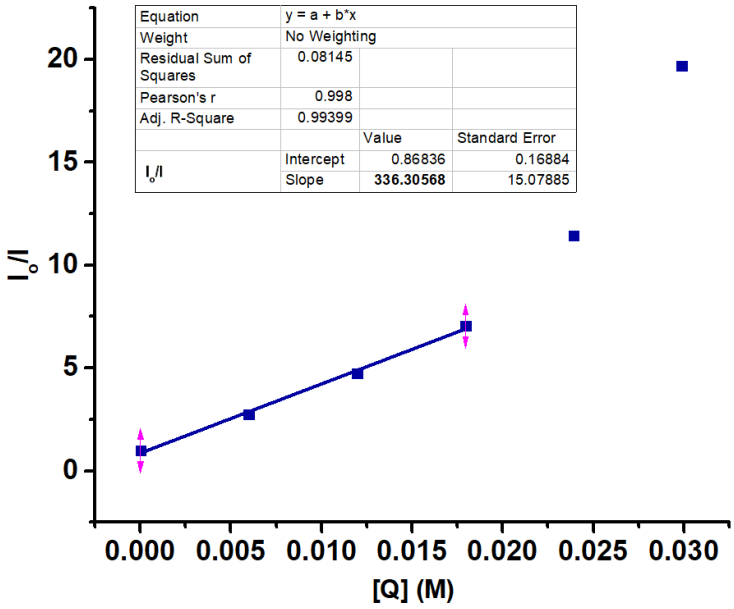


Figure 6.2. Correlation between emission intensity and concentration of *CDFAA*.

Next, the same quenching experiment was carried out in the presence of *t*Bu-styrene as a quencher. In presence of the substrate small quenching of the excited state of the catalyst was observed, only on a weak level not able to compete with the efficient quenching of *CDFAA* (Figure 6.3).

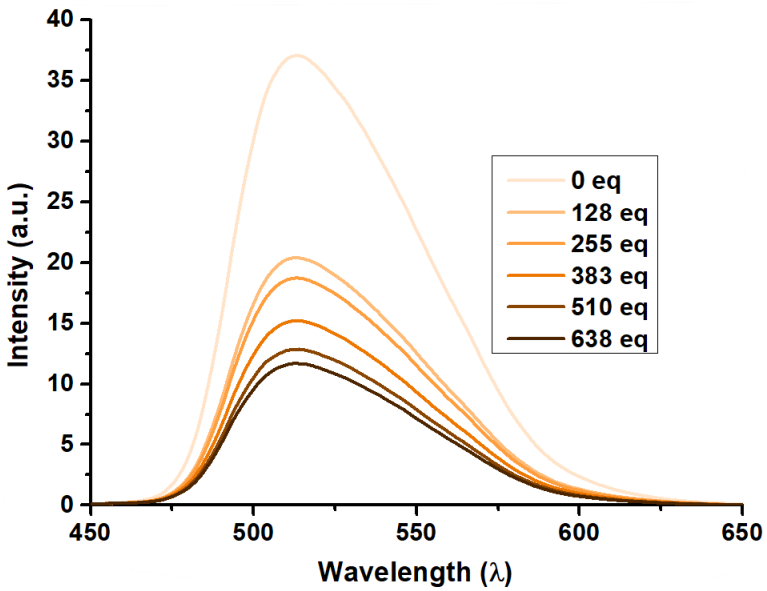


Figure 6.3. Emission quenching of *fac*-[Ir(ppy)$_3$] with 4-*tert*-butylstyrene in acetonitrile (acetonitrile, 50 µM *fac*-[Ir(ppy)$_3$]. 20°C, d_{em} = 2 nm, d_{ex} = 2 nm, λ_{ex} = 430 nm).

6.2 Cyclic voltammetry

Cyclic voltammetry data for halogenated anhydrides

1.94 g (5.0 mmol, 0.1 M) NBu_4PF_6 was dissolved in 50 mL anhydrous acetonitrile in a volumetric flask and the solution was degassed for 20 min by bubbling Ar. For each measurement, 10 mL of the solution was taken to the cyclovoltammetric cell and 0.1 mmol of analyte was added. The resulting solution was stirred for 1 min to ensure homogeneity. Before each measurement, the solution was purged with Ar and the glassy carbon electrode was rotated to homogenize the probe solution. During the measurement, the solution was protected by a positive Ar stream.

The cyclovoltammetry setup was built from a Pt-counter electrode and Ag^+ (0.01 M $AgNO_3$ in 0.1 M NBu_4PF_6)/Ag reference electrode. The working electrode was chosen as Pt disc electrode (2 mm diameter). A short introduction to cyclic voltammetry was taken from the following references.[4,21] Generally, a scan rate of 100 mV/s was applied to measure the reaction components. However, more detailed measurements using scan rates, ranging from 400mV/s to 50 mV/s were also carried out.

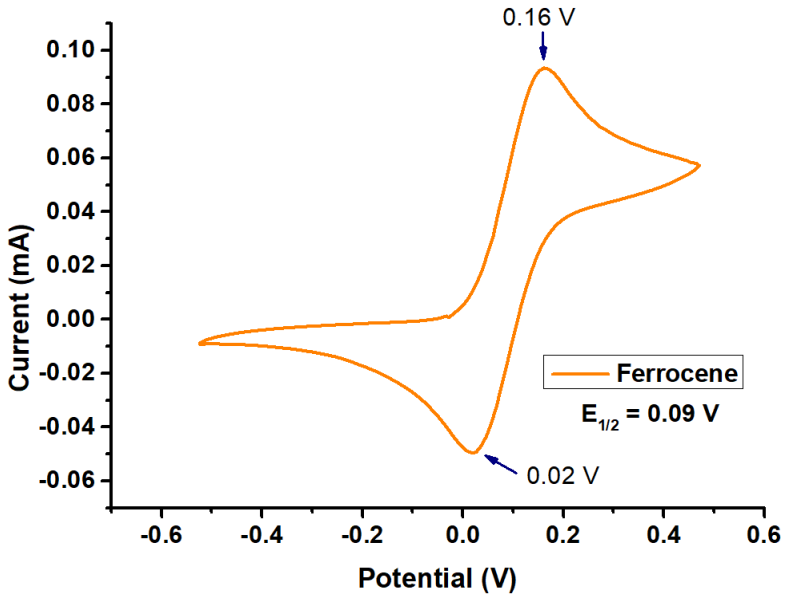


Figure 6.4. Cyclic voltammogram of ferrocene (0.1 mmol) was recorded in 10 mL, 0.1M $(NBu_4)PF_6$ MeCN solution. The cyclovoltammetry setup was built from a Pt-counter electrode and an Ag^+/Ag (0.01 M) reference electrode. The working electrode was chosen as Pt electrode (2 mm diameter).

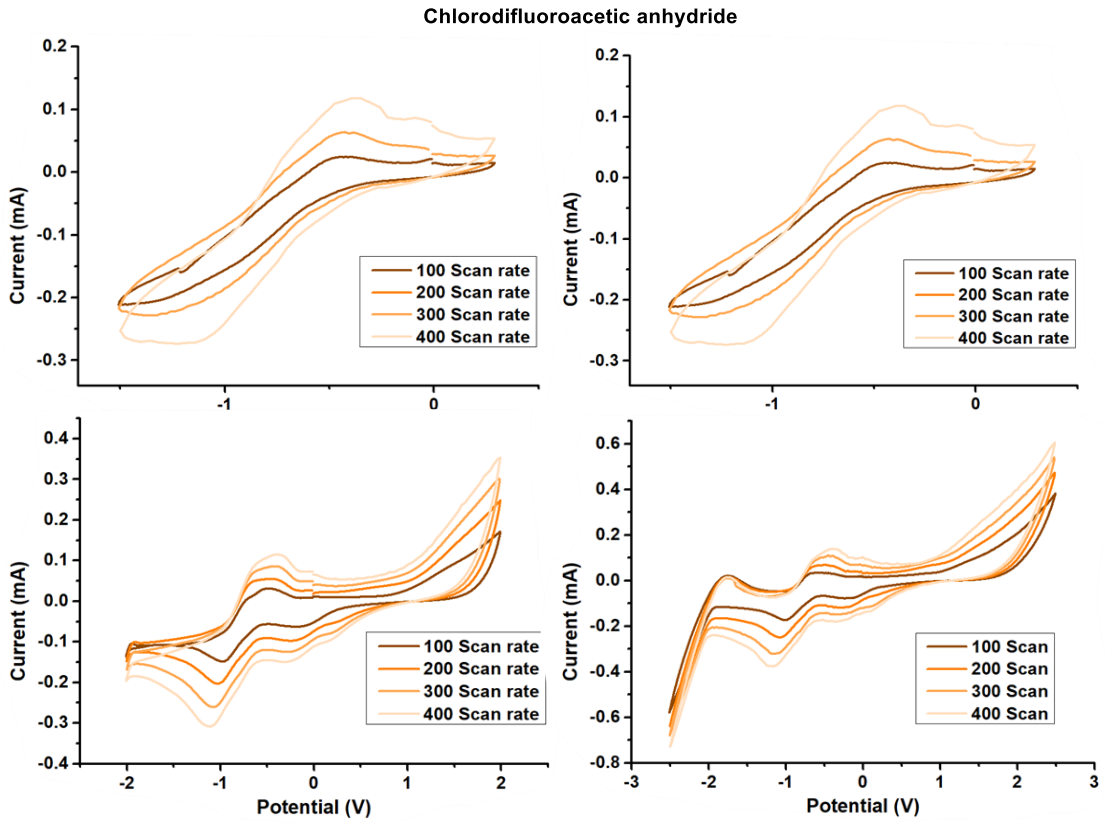


Figure 6.5. Cyclic voltammogram of *CDFAA* (0.1 mmol) recorded in 10 mL 0.1M $(NBu_4)PF_6$ MeCN solution at different scan rates. The cyclovoltammetry setup was built from a Pt-counter electrode and an Ag^+/Ag (0.01 M) reference electrode. The working electrode was chosen as Pt electrode (2 mm diameter).

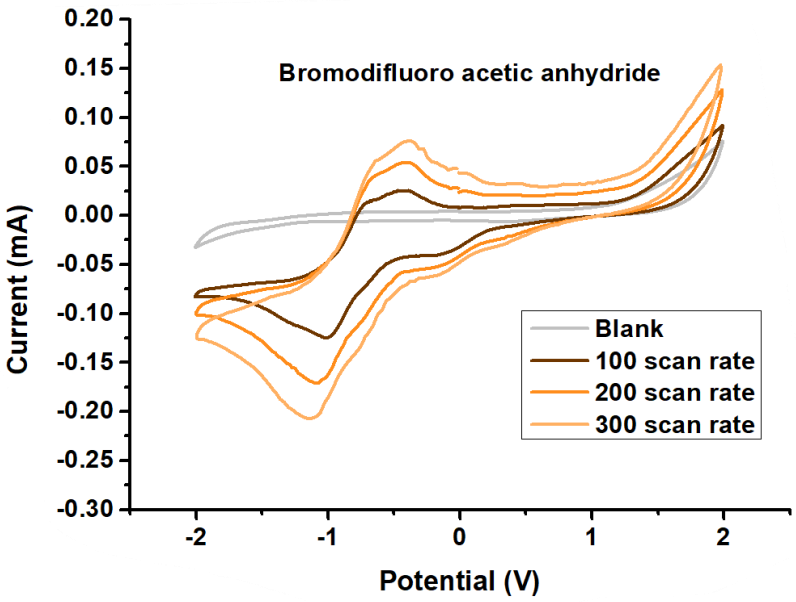


Figure 6.6. Cyclic voltammogram of bromodifluoro acetic anhydride (0.1 mmol) recorded in 10 mL, 0.1M $(NBu_4)PF_6$ MeCN solution at different sweep rates. The cyclovoltammetry setup was built from a Pt-counter electrode and an Ag^+/Ag (0.01 M) reference electrode. The working electrode was chosen as Pt electrode (2 mm diameter).

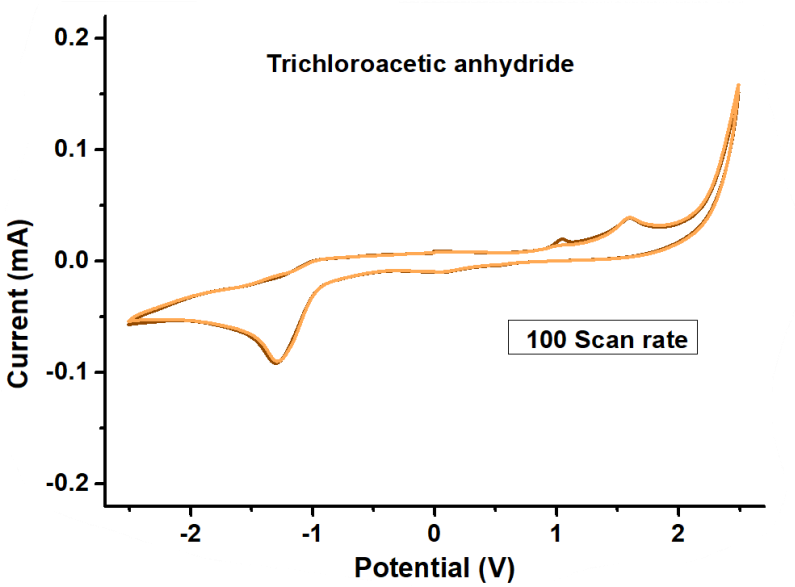


Figure 6.7. Cyclic voltammogram of trichloroacetic anhydride (0.1 mmol) recorded in 10 mL, 0.1M $(NBu_4)PF_6$ MeCN solution. The cyclovoltammetry setup was built from a Pt-counter electrode and an Ag^+/Ag (0.01 M) reference electrode. The working electrode was chosen as Pt electrode (2 mm diameter).

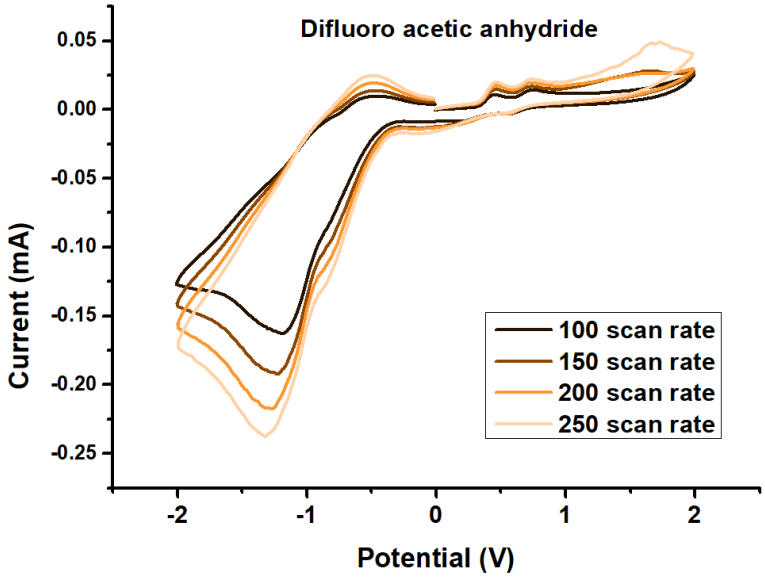


Figure 6.8. Cyclic voltammogram of difluoro acetic anhydride (0.1 mmol) recorded in 10 mL, 0.1M $(NBu_4)PF_6$ MeCN solution at different sweep rates. The cyclovoltammetry setup was built from a Pt-counter electrode and an Ag^+/Ag (0.01 M) reference electrode. The working electrode was chosen as Pt electrode (2 mm diameter).

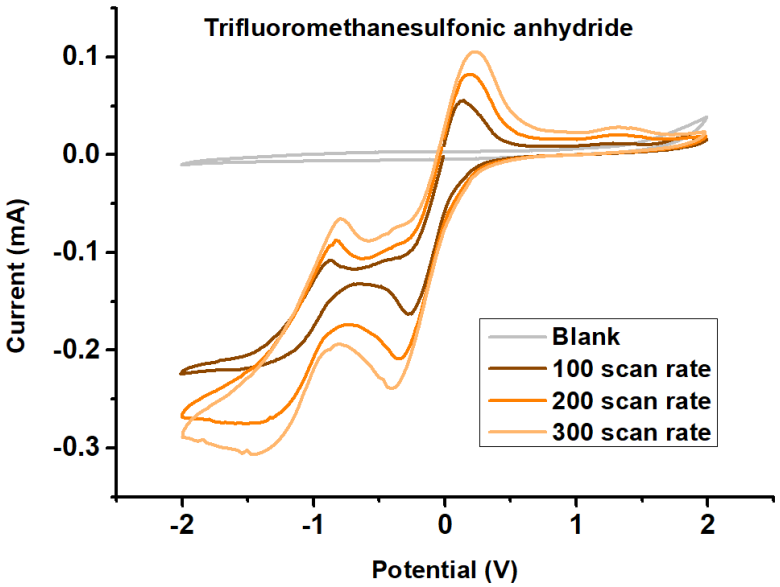


Figure 6.9. Cyclic voltammogram of trifluoromethanesulfonic anhydride (0.1 mmol) recorded in 10 mL, 0.1M $(NBu_4)PF_6$ MeCN solution at different sweep rates. The cyclovoltammetry setup was built from a Pt-counter electrode and an Ag^+/Ag (0.01 M) reference electrode. The working electrode was chosen as Pt electrode (2 mm diameter).

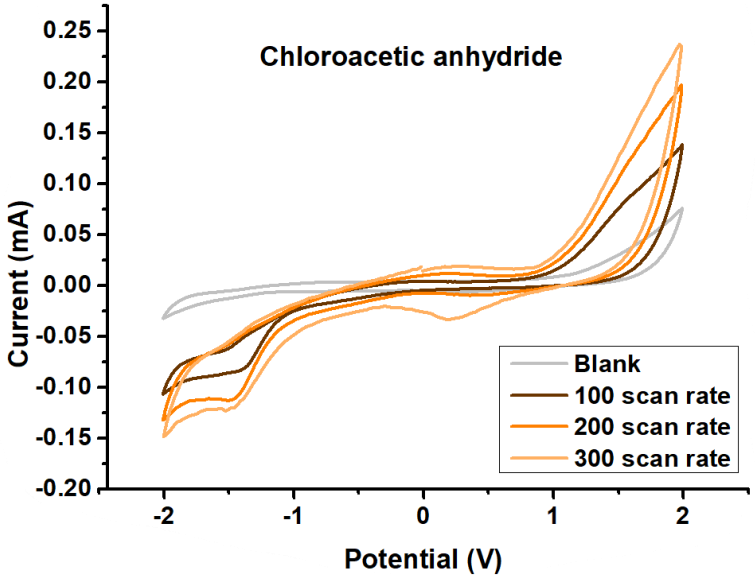


Figure 6.10. Cyclic voltammogram of chloroacetic anhydride (0.1 mmol) recorded in 10 mL, 0.1M $(NBu_4)PF_6$ MeCN solution at different sweep rates. The cyclovoltammetry setup was built from a Pt-counter electrode and an Ag^+/Ag (0.01 M) reference electrode. The working electrode was chosen as Pt electrode (2 mm diameter).

List for the conversion of reduction potential vs SCE.

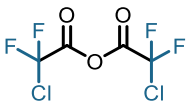
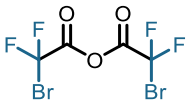
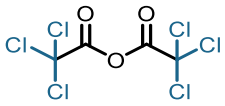
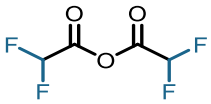
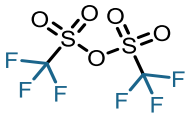
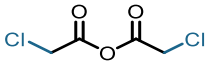
Numbers	Anhydride	E_{pc} vs $AgNO_3/Ag$	E_{pc} vs Ferrocene (Fc^+/Fc)[a]	E_{pc} vs SCE[b]
B		-1.12 V	-1.21 V	-0.83 V
C		-1.14 V	-1.23 V	-0.85 V
D		-1.30 V	-1.39 V	-1.01 V
E		-1.32 V	-1.41 V	-1.03 V
F		-1.41 V	-1.50 V	-1.12 V
G		-1.43 V	-1.52 V	-1.14 V

Table 6.1. a. Cyclovoltammtery was measured against Ag^+/Ag as a reference; cathodic peak potential, (E_{pc} vs $AgNO_3$ (0.01M) /Ag). **b.** E_{pc} values converted to SCE by adding 0.38 in E_{pc} vs Fc^+/Fc or 0.29 is added to E_{pc} (V vs $AgNO_3/Ag$).[22]

Photo cyclovoltammetry studies of reaction mixtures

A series of cyclovoltammetry measurements were carried out using a ossila cyclic voltammetry setup. Therefore 774.0 mg tetrabutyl ammonium hexafluorophophate (purchased from Sigma Aldrich, for electrochemical analysis, ≥ 99.0%) was dissolved in 40 mL of anhydrous acetonitrile. The solution was degassed by sparging with Ar for 20 min. Then the analyte was added and cyclic voltammetric measurements were carried out. The electrodes have been picked like described below. A platinium disc working electrode, a Pt-counter electrode as well as Ag^+ (0.01 M $AgNO_3$ in 0.05 M NBu_4PF_6)/Ag was used as reference electrode. Scan rate of 100 mV/s was applied to measure the reaction components (Figure 6.12).

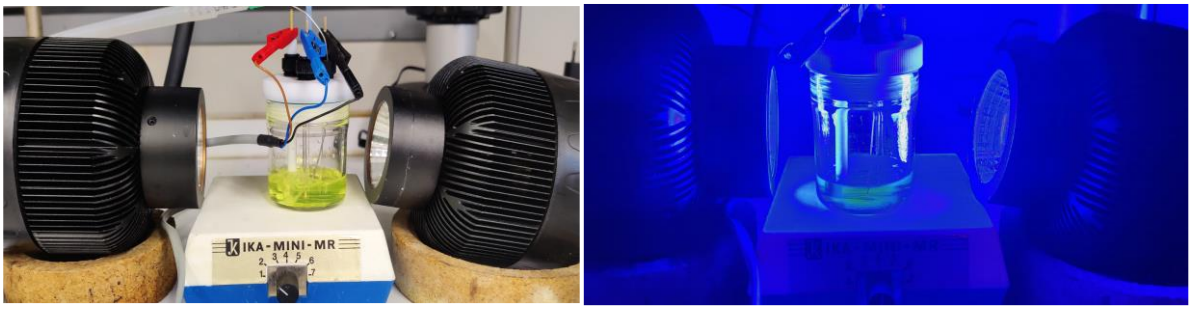


Figure 6.11. Cyclic voltammetry measurements under irradiation at 440 nm.

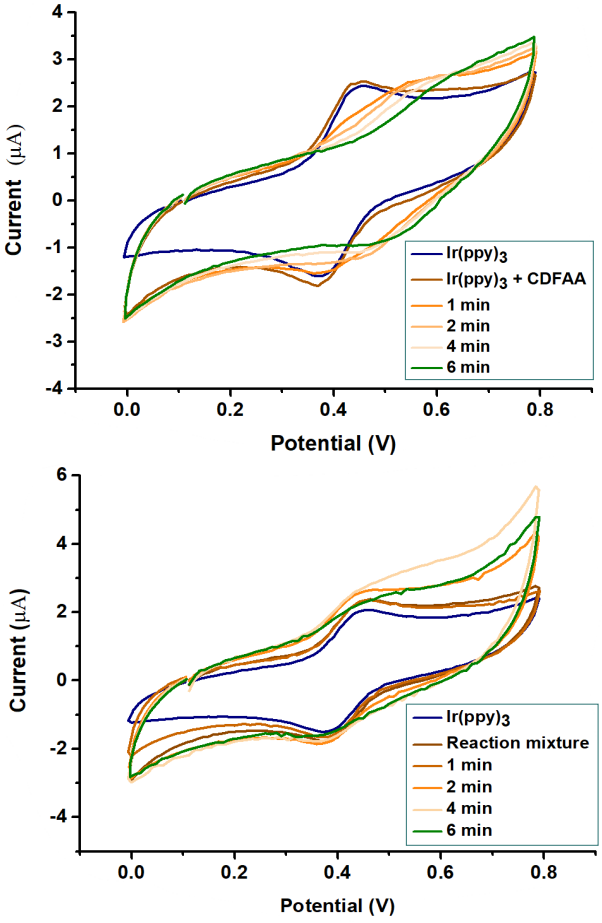


Figure 6.12. **a. Top**: *fac*-[Ir(ppy)$_3$] (5.4 mg), *CDFAA* (12 mM) in MeCN (0.05 M NBu_4PF_6). 100 mV/s. **b. Bottom**: *fac*-[Ir(ppy)$_3$] (5.4 mg), *CDFAA* (12 mM), 4-*tert*-butylstyrene (24 mM) in MeCN (0.05 M NBu_4PF_6). Scan rate: 100 mV/s.

6.3. UV-Vis studies

To investigate the mechanism of the reaction in more detail, the reaction was investigated by means of absorption spectroscopy in the UV-Vis region. Therefore, absorption spectra of starting materials in acetonitrile were measured first (Figure 6.13).

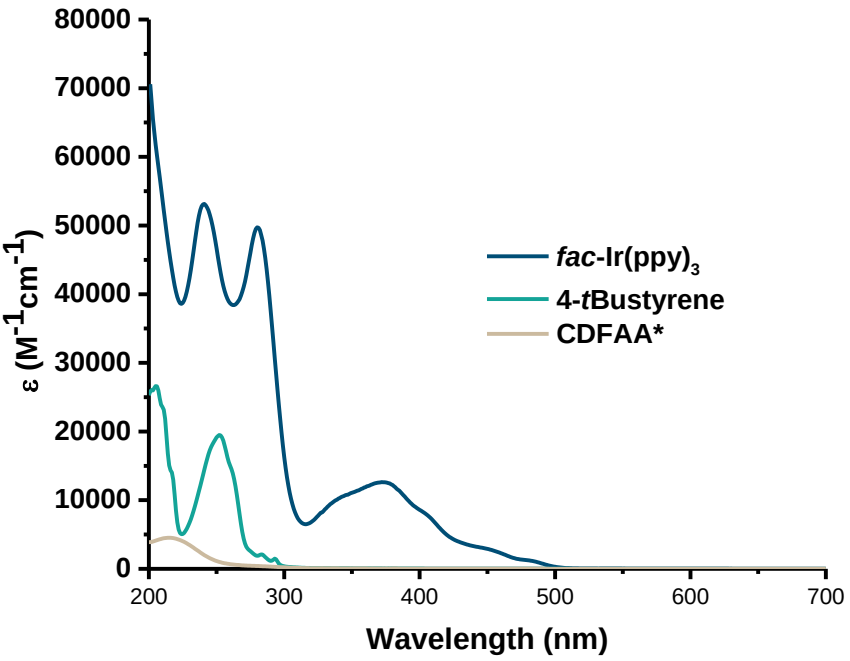


Figure 6.13. UV-Vis spectra of starting materials in MeCN. *Note: extinction coefficients for *CDFAA* are multiplied by 10 times for representation reasons.

Compound	C (mM)	Absorption maximum, nm (ε, $M^{-1}cm^{-1}$)
fac-[Ir(ppy)$_3$]	0.032	240 (53000), 280 (50000), 372 (13000), 440 (sh, 3000)
4-*tert*-Bustyrene	0.1	207 (27000), 252 (19000)
CDFAA	1.3	217 (470)

Table 6.2. Properties of starting materials

To further monitor reaction progress and to analyse reactivity of the starting materials with reaction components, several solutions with pure and mixed starting materials were prepared in screw-cap UV-Vis cuvettes under argon. Those solutions were irradiated in the photoreactor, and absorption spectra was collected over the course of reaction. Unfortunately, quantification of the data was found to be complicated due to the bleaching of the photocatalyst (Figure 6.14) under irradiation with blue LEDs. For a reaction mixture consisting of *CDFAA* and styrene, it can be clearly stated that there is no absorption change over time (Figure 6.15), thus no reaction takes place between styrene and *CDFAA*. It can also be observed that there is a reaction between Ir(ppy)$_3$ and *CDFAA* under light irradiation (Figure 6.16). However, no reaction is seen between styrene and Ir(ppy)$_3$ (Figure 6.17), which was also confirmed by control experiments in absence of CDFAA – no conversion of styrene was detected.

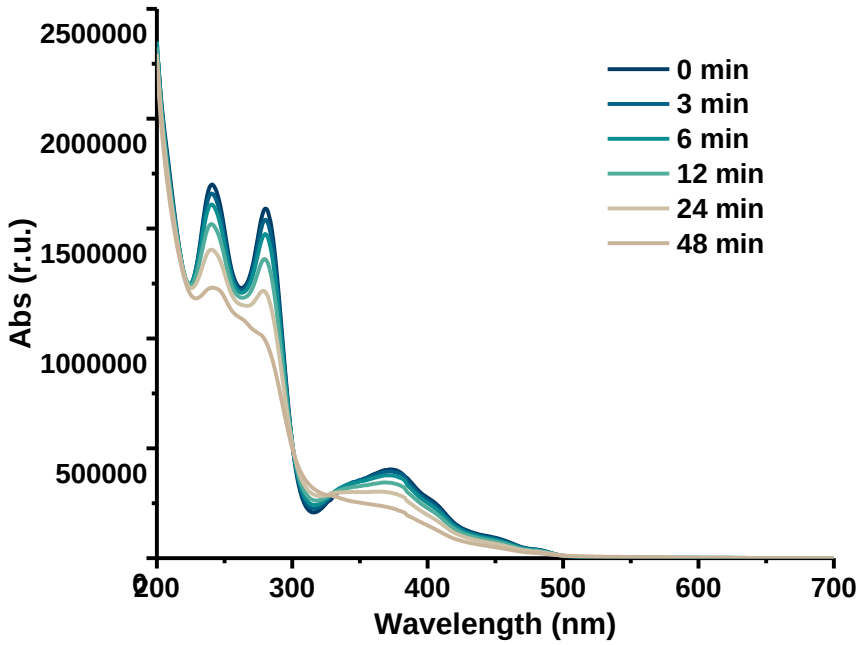


Figure 6.14. UV-Vis spectra for the solution of fac-[Ir(ppy)$_3$] in MeCN (0.032 mM) upon irradiation in the photoreactor.

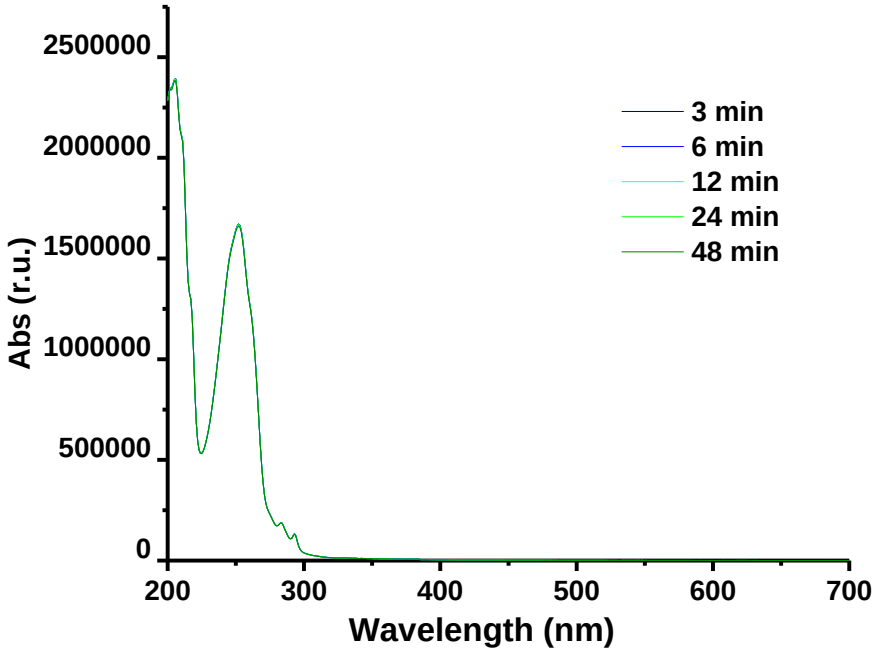


Figure 6.15. UV-Vis spectra for solution of *CDFAA* and 4-*tert*-bustylstyrene in MeCN (1.3 and 1.3 mM respectively) in MeCN upon irradiation in the photoreactor.

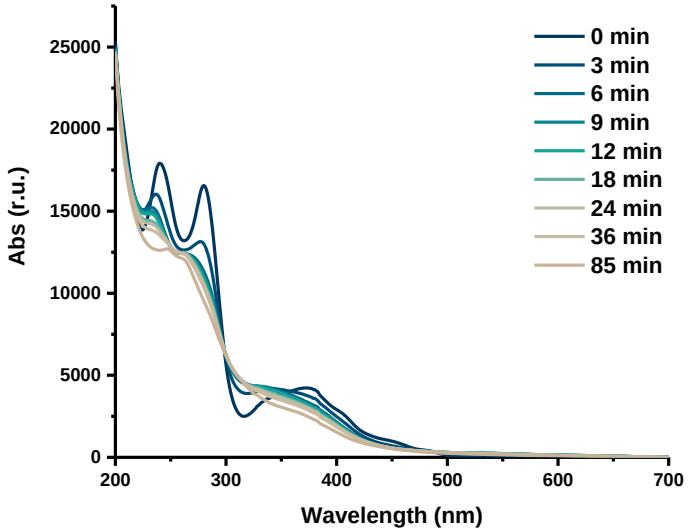


Figure 6.16. UV-Vis spectra of solution of *CDFAA* and *fac*-[Ir(ppy)$_3$] in MeCN (0.064 and 0.032 mM respectively) in MeCN upon irradiation in the photoreactor.

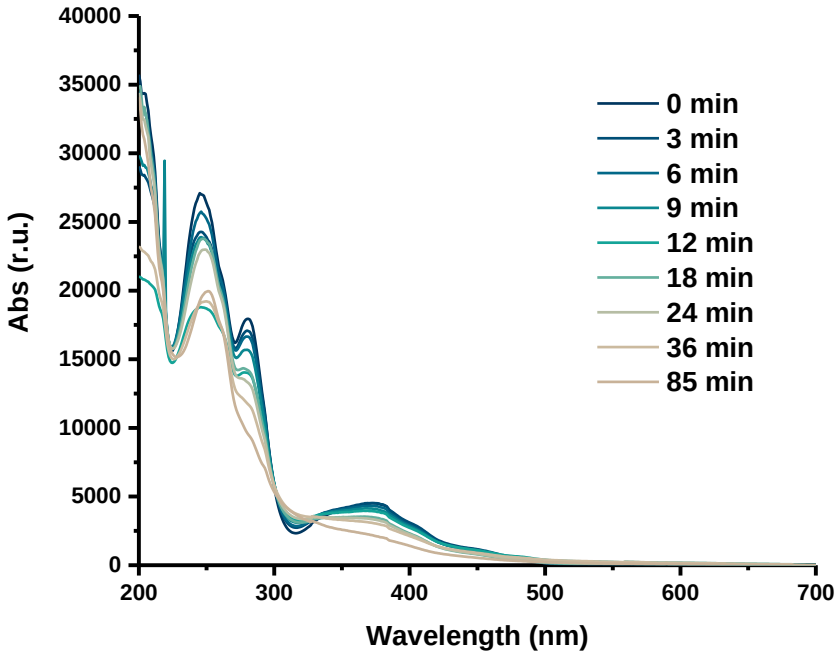


Figure 6.17. UV-Vis spectra of solution of *fac*-[Ir(ppy)$_3$] and 4-*tert*-bustylstyrene in MeCN (0.032 and 0.064 mM respectively) in MeCN upon irradiation in the photoreactor.

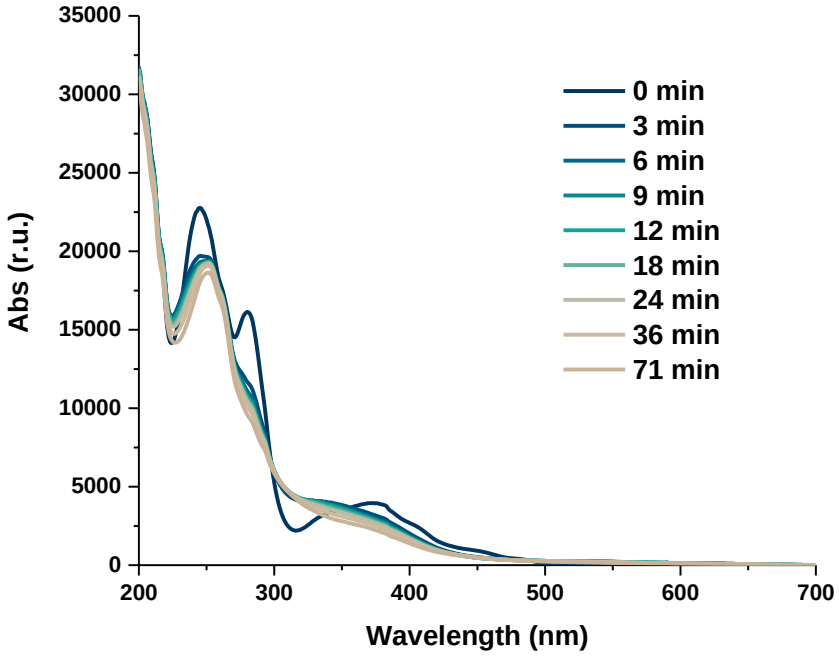


Figure 6.18. UV-Vis spectra of solution of *fac*-[Ir(ppy)$_3$], *CDFAA* and 4-*tert*-bustylstyrene in MeCN (0.032, 0.064 and 0.064 mM respectively) in MeCN upon irradiation in the photoreactor.

6.4. Hammett studies

The radical nature of initial addition of reactive species to the olefin was also indicated by Hammett studies The experiments were performed in accordance with the method described by Harper and co-workers.[23] Signal resolution on GC-MS of the signals of styrene derivatives and n-decane was initially evaluated by stepwise addition of each styrene derivatives in MeCN with n-decane to determine the feasibility of using GC-MS techniques in these experiments. Similarly, signal resolution was determined for the corresponding products in the presence of n-decane. No substantial signal overlap was observed between all components of the reaction mixture. A 25 mL round flame-dried vial was charged with *fac*-[Ir(ppy)$_3$] (1.0 mol%, 9.9 mg, 0.015 mmol) and the vial was sealed under argon atmosphere. It was further subjected to 3 argon/vacuum cycles. Anhydrous MeCN (15 mL) for lactam or anhydrous DMF for lactone (3 mL) was added, and the reaction mixture was sparged with Ar for 3 min. Finally, six styrene derivatives (0.25 mmol p-*t*Bu, 0.25 mmol *p*-Me, 0.25 mmol *p*-H, 0.25 mmol *p*-F, 0.25 mmol *p*-Cl, 0.25 mmol *p*-Br) (total amount of styrene derivatives = 1.50 mmol), *CDFAA* (2.0 equiv, 3.00 mmol, 0.52 mL) and *n*-decane (0.25 mmol, 49 μL) were subsequently introduced to the reaction mixture *via* microsyringe. The obtained yellow solution was irradiated at room temperature under blue LEDs irradiation (440 nm), 30 min for lactones (Table 6.3) and 120 min (Table 6.4) for lactams. The amount of the corresponding styrenes were determined by GC-MS analysis with respect to *n*-decane.

Data analysis for *para*-substituted styrene derivatives (DMF as solvent)

Name	T_{peak} (GC-MS)	Initial area (S_o)	Final area (S)	S/S_o	$\ln_{(S/S0)}$	$\ln(S/S0)/\ln(S_H/S_{H0})$ = K_{rel}	log10 (K_{rel})	σ_{para}
*t*Bu	7.24	16511884	9310245	0.563851163	-0.572965	1.178008	0.071148	-0.20
Me	5.33	13044801	7458943	0.571794311	-0.558976	1.149247	0.060413	-0.17
H	4.22	7017253	4314525	0.614845296	-0.486385	1	0	0
F	4.28	9794061	6273929	0.640585044	-0.445373	0.915682	-0.03826	0.06
Cl	6.03	8649761	5955668	0.688535556	-0.373188	0.76727	-0.11505	0.24
Br	6.79	11668561	8370282	0.717336268	-0.332211	0.68302	-0.16557	0.36

Table 6.3. a. Relative rate constants determined from the relative integrations of GC-MS diagrams for the competitive *gem*-difluoro-γ-lactone formation between various *para*-substituted styrene and *CDFAA* under general photoredox reaction condition 1.

Data analysis for *para*-substituted styrene derivatives (MeCN as solvent)

Name	T_{peak} (GC-MS)	Initial area (S_o)	Final area (S)	S/S_o	$\ln_{(S/S0)}$	$\ln(S/S0)/\ln(S_H/S_{H0})$ = K_{rel}	log10 (K_{rel})	σ_{para}
*t*Bu	7.24	20886781	2947671	0.141126151	-1.958101	1.407771	0.148532	-0.20
Me	5.33	15375506	2421549	0.157493939	-1.848368	1.328879	0.123485	-0.17
H	4.22	10432859	2596169	0.248845403	-1.390923	1	0	0
F	4.28	14392507	4320317	0.300178211	-1.203379	0.865165	-0.0629	0.06
Cl	6.03	15872771	5435583	0.342447012	-1.071638	0.770451	-0.11325	0.24
Br	6.79	16983048	6150263	0.362141295	-1.015721	0.730249	-0.13652	0.36

Table 6.4. a. Relative rate constants determined from the relative integrations of GC-MS diagrams for the competitive reactions for the formation of *gem*-difluoro-γ-lactam between various *para*-substituted styrene and *CDFAA* under general photoredox reaction condition 2.

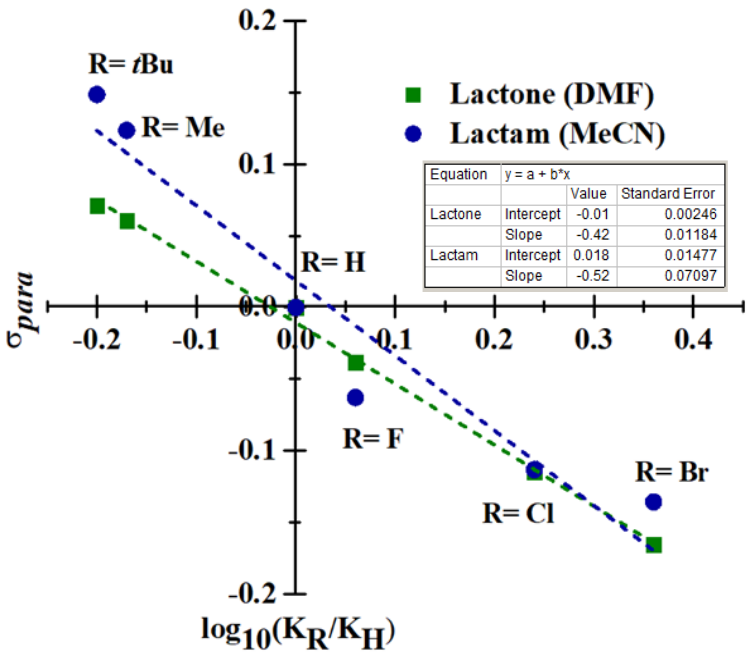


Figure 6.19. Values of $\log_{10}(K_R/K_H)$ vs σ_x for the *gem*-difluoro reaction of styrenes using *CDFAA*.

7. Competition Experiments

7.1. Solvent competition experiment

Effect of MeCN and DMF on the formation of products 1 and 2.

A set of 14 flame dried 20 mL crimp cap vial was taken and each of them are charged with *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 μmol, 1.0 mol%) and equipped with a magnetic stirring bar. The content of the vial was then subjected to three vacuum/argon cycles. Different compositions of solvents mixture ranging from 0% DMF to 100% DMF in anhydrous MeCN making a total volume of (15 mL) were prepared under an argon atmosphere, and the solution was sparged for 5 min. The substrate (0.5 mmol, 1.0 equiv) and *CDFAA* (170 μL, 1.0 mmol, 2.0 equiv) were introduced subsequently to each solution *via* microsyringes. The reaction mixture was stirred at room temperature under blue LEDs irradiation for 12 h. Further GC-MS analysis was performed, and ratio of product yields of γ-lactam and lactone was plotted against the composition of solvent (Figure 7.1).

Entry	% of DMF added	Relative yield of γ-lactam (1)	Relative yield of γ-lactone (2)
1	0	98	2
2	2.5	76	24
3	5	51	49
4	7.5	26	74
5	10	18	82
6	20	11	89
7	30	5	95
8	40	4	95
9	50	3	97
10	60	2	98
11	70	1	99
12	80	0.5	99.5
13	90	0	100
14	100	0	100

Table 7.1. Relative yields of lactam and lactone formation with solvent mixture experiments.

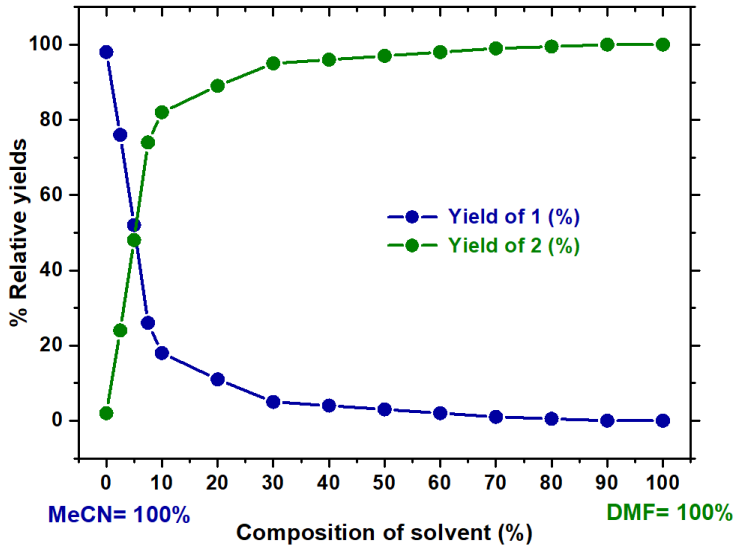


Figure 7.1. Graphical representation of the competition b/w γ–lactam and lactone formation.

Effect of Toluene and DMF on the formation of products 2 and 3.

A set of 11 flame dried 20 mL crimp cap vial was taken and each of them are charged with *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 μmol, 1.0 mol%) and equipped with a magnetic bar. The content of the vial was then subjected to three vacuum/argon cycles. Different compositions of solvents mixture ranging from 0% toluene to 100% toluene in anhydrous DMF making a total volume of (15 mL) were prepared under an argon atmosphere, and the solution was sparged for 5 min. The substrate (0.5 mmol, 1.0 equiv) and *CDFAA* (170 μL, 1.0 mmol, 2.0 equiv) were introduced to each solution *via* microsyringes. The reaction mixture was stirred at room temperature under blue LEDs irradiation for 12 h. Further GC-MS analysis was performed, and ratio of product yields of γ- lactone and difunctionalization was plotted against the composition of solvent (Figure 7.2).

Entry	% of toluene added	Relative yield of γ- lactone (2)	Relative yield of difunctionalization (3)
1	0	84	16
2	10	60	40
3	20	49	51
4	30	39	61
5	40	29	71
6	50	17	83
7	60	14	86
8	70	11	88
9	80	7	93
10	90	5	95
11	100	3	97

Table 7.2. Relative yields of lactone and difunctionalization with solvent mixture experiments.

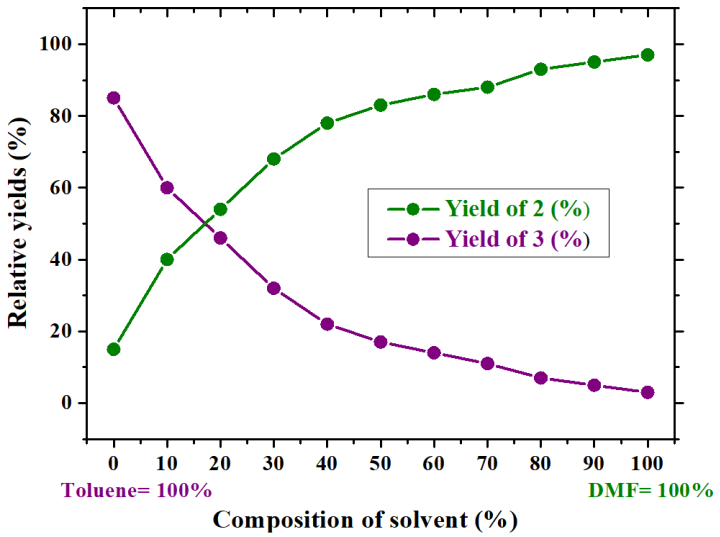


Figure 7.2. Graphical representation of the competition b/w difunctionalization and γ–lactone formation.

Effect of MeCN and Toluene on the formation of products 1, 2, and 3.

A set of 11 flame dried 20 mL crimp cap vial was taken and each of them are charged with *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 μmol, 1.0 mol%) and equipped with a magnetic bar. The content of the vial was then subjected to three vacuum/argon cycles. Different compositions of solvent mixture ranging from 0% MeCN to 100% MeCN in anhydrous Toluene making a total volume of (15 mL) were prepared under an argon atmosphere, and the solution was sparged for 5 min. The substrate (0.5 mmol, 1.0 equiv) and *CDFAA* (170 μL, 1.0 mmol, 2.0 equiv) were introduced to each solution *via* microsyringes. The reaction mixture was stirred at room temperature under blue LEDs irradiation for 12 h. Further GC-MS analysis was performed, and ratio of product yields of γ- lactam, γ- lactone and difunctionalization was plotted against the composition of solvent (Figure 7.3).

Entry	% of MeCN added	Relative yield of γ-lactam (1)	Relative yield of γ-lactone (2)	Relative yield of difunctionalization (3)
1	0	100	0	0
2	10	93	6	1
3	20	91	7	2
4	30	90	7	3
5	40	88	8	4
6	50	86	10	4
7	60	84	12	4
8	70	79	15	6
9	80	49	29	21
10	90	12	39	48
11	100	0	16	84

Table 7.3. Relative yields of lactam, lactone and difunctionalization with solvent mixture experiments.

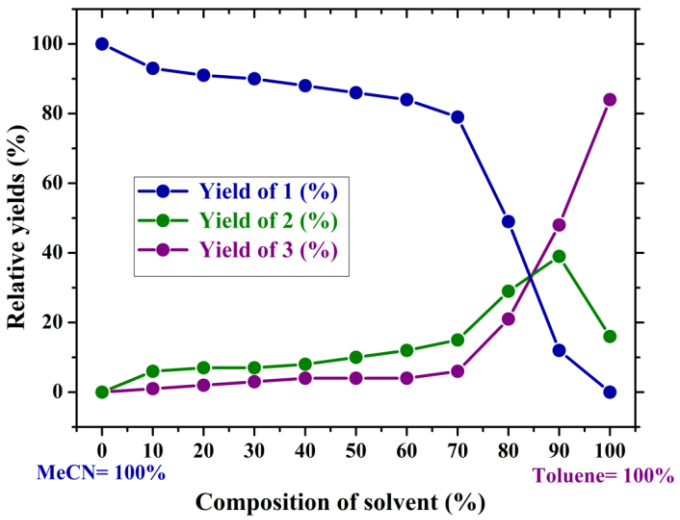


Figure 7.3. Graphical representation of the competition between difunctionalization, γ–lactone and γ–lactam formation.

7.2. Equilibrium constants ratio for 1 vs 2

This switchability of the divergent protocol can be explained by solvent stabilization of carbocation **III**, which has been further confirmed with theoretical studies. Theoretically computed Gibbs free energies revealed that coordination of DMF is energetically more favourable than coordination of MeCN to species **III**. To further justify these calculated ΔG values, additional experiments were performed in solvent mixtures, which suggested that even small amounts of DMF in MeCN shifte the reaction equlibrium towards the formation of **2** as major product (Figure 7.4).

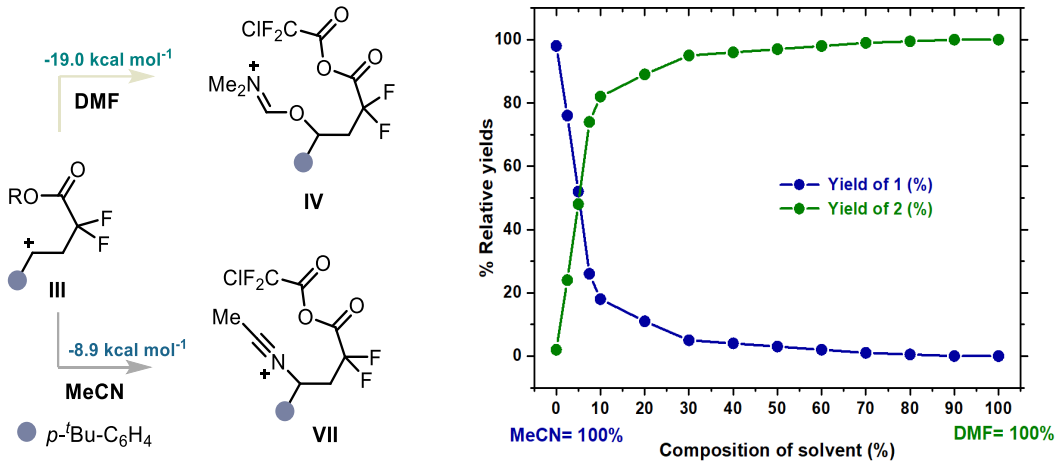


Figure 7.4. Calculated ΔG_{DMF} and ΔG_{MeCN} values and experimental data for lactam-lactone competition experiment.

Even though qualitative agreement of experiment and calculations were excellent , we decided to further quantify it by calculating equilibrium constants. Since coordination of solvents is an equilibrium process, the only irreversible step is the formation of final products, as a result, the ratio of products is determined by the original reaction equilibrium ratios. Utilizing this assumption, we calculated equilibrium constants ratio for reaction of DMF and MeCN as presented below:

$$\Delta G = -RTlnk$$

$$k = \exp(-\frac{\Delta G}{RT})$$

$$\frac{k_{DMF}}{k_{MeCN}} = \frac{\exp(-\frac{\Delta G_{DMF}}{RT})}{\exp(-\frac{\Delta G_{MeCN}}{RT})} = \exp\left(-\frac{\Delta G_{DMF}}{RT} + \frac{\Delta G_{MeCN}}{RT}\right) = \exp\left(\frac{\Delta G_{MeCN} - \Delta G_{DMF}}{RT}\right)$$

$$\frac{k_{DMF}}{k_{MeCN}} = \exp\left(\frac{-8900 + 19000}{8.31 * 298}\right) = \exp(4.08) = \mathbf{59}$$

Thus, calculated ratio based on computated Gibbs free energies of equilibrium constants is **59**.

For the experimental equilibrium constants ratio of final products can be calculated.

$$\frac{C_{lactone}(\mathbf{2})}{C_{lactam}(\mathbf{1})} = \frac{k_{DMF}}{k_{MeCN}}\frac{C_{DMF}}{C_{MeCN}}$$

$$\frac{k_{DMF}}{k_{MeCN}} = \frac{C_{lactone}(\mathbf{2})}{C_{lactam}(\mathbf{1})}\frac{C_{MeCN}}{C_{DMF}}$$

Neglecting changes in volume after mixing, the concentration of solvents can be easily determined as follows:

$$C_{solv} = \frac{V_{solv}}{V_{system}} \frac{p_{solvent}}{M_{solvent}}$$

Concentration of solvents can be considered constant during the reaction process since they are in big excess to reagents. Thus, the concentration ratio can be calculated as follows:

$$\frac{\mathrm{C}_{MeCN}}{\mathrm{C}_{DMF}} = \frac{V_{MeCN}}{V_{system}} \frac{p_{MeCN}}{M_{MeCN}} \frac{V_{system}}{V_{DMF}} \frac{M_{DMF}}{p_{DMF}} = \frac{V_{MeCN}}{V_{DMF}} \frac{p_{MeCN}}{M_{MeCN}} \frac{M_{DMF}}{p_{DMF}}$$

$$\frac{\mathrm{C}_{MeCN}}{\mathrm{C}_{DMF}} == \frac{V_{MeCN}}{V_{DMF}} \frac{0.786}{41.0} \frac{73.1}{0.944} = 1.48 \frac{V_{MeCN}}{V_{DMF}}$$

Experimental ratio between equilibrium constants can be found as follows:

$$\frac{\mathrm{k}_{DMF}}{\mathrm{k}_{MeCN}} = 1.48 \frac{V_{MeCN}}{V_{DMF}} \frac{\mathrm{C}_{lactone}(\mathbf{2})}{\mathrm{C}_{lactam}(\mathbf{1})} = 1.48 \frac{V_{MeCN}}{V_{DMF}} \frac{\mathrm{Yield}_{lactone(\mathbf{2})}}{\mathrm{Yield}_{lactam(\mathbf{1})}}$$

Solvent volumes are specified during set up of the experiment and the yields which are analysed by GC-MS correspond to concentration of lactone **1** and lactam **2**. Thus, ratios of equilibrium constants can be calculated for each experimental point, as it is presented in table 7.4. The distribution of calculated rate constant ratios can be graphically represented (Figure 7.5).

DMF volume fraction (%)	$\boldsymbol{\frac{V_{MeCN}}{V_{DMF}}}$	**Lactam yield (1) (%)**	**Lactone yield (2) (%)**	$\boldsymbol{\frac{\mathrm{Yield}_{lactone(2)}}{\mathrm{Yield}_{lactam(1)}}}$	$\boldsymbol{\frac{\mathrm{k}_{DMF}}{\mathrm{k}_{MeCN}}}$
0	–	98	2	0.0204	–
2.5	39	76	24	0.316	18.2
5	19	51	49	0.961	27.0
7.5	12.3	26	74	2.85	52.0
10	9	18	82	4.56	60.7
20	4	11	89	8.09	47.9
30	2.3	5	95	19	65.6
40	1.5	4	95	23.8	52.7
50	1	3	97	32.3	47.8
60	0.667	2	98	49	48.3
70	0.429	1	99	99	62.8
80	0.25	0.5	99.5	199	73.6
90	0.111	0	100	–	–
100	0	0	100	–	–

Table 7.4. Experimentally found ratio between equilibrium constants.

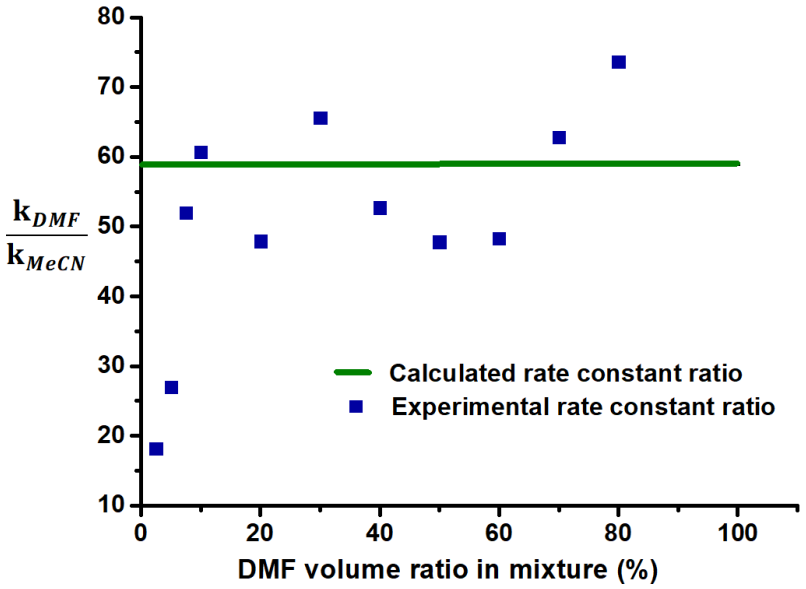


Figure 7.5. Comparison of experimental and calculated equilibrium constant ratio.

The average experimental ratio of rate constants was calculated and found to be **51** (Table 7.5). Nonetheless, two points appear out of the trend line due to the low concentration of DMF. This can be attributed to the solvation of DMF by MeCN, resulting in a slower reaction with the carbocation at lower DMF concentrations. We propose that deviation seen at low DMF concentrations is attributed to many solvation processes in which it can participate (e.g., chloride anion and anhydride). This reduces the concentration of DMF that is available for coordination to the carbocation. Therefore, product lactam is dominated, and two points are out of the trend. For this reason, the first two measures were excluded, and the experimentally found ratio of equilibrium constants is **57** (experimental), which is in excellent agreement with the computational value of **59** (calculated) (Figure 7.5).

Entry	Full range	Without first two values	Computated ratio
Sum of values	556	511	–
Number of dots	11	9	–
Average ratio	**51**	**57**	**59**

Table 7.5. Calculated ratio between equilibrium constants.

8. Scale-Up Synthesis

8.1. Gram-scale synthesis in flow

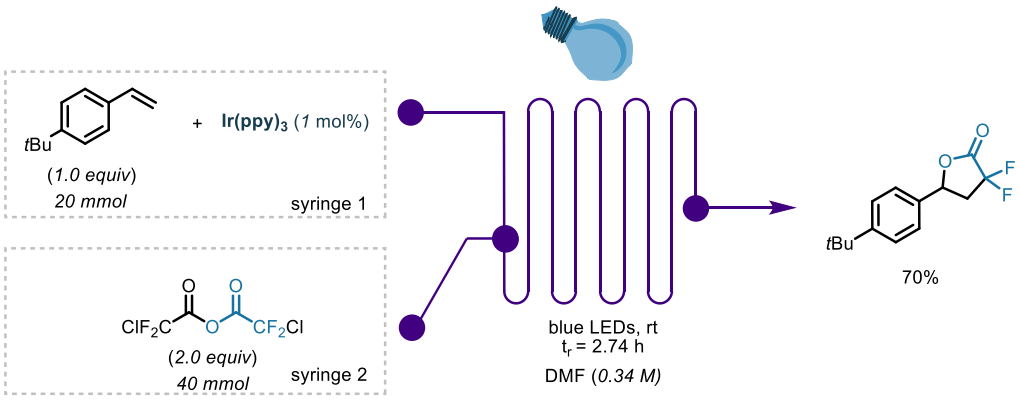


Figure 8.1. Pictorial representation of flow setup.

Components of flow reactor.

Syringe pump: Fusion 4000 syringe pump

Tubing components:

1. Tubing PFA 1/16″ OD (0.04″ ID) [Item #: 1507L], length =100ft

2. Nut PEEK 1/16″ [LT-115X]

3. Ferrule SF [P-250X]

4. SS Ring 1/16″ [included with P-250X]

5. Y Assembly PEEK ¼-28 0.20” [P-512]

Components of tubing were taken from this tutorial (https://chem.uncg.edu/croatt/flow-chemistry/designing-and-connecting-the-tubing/) (accessed on 01.04.2022).

Tube volume

$V = \pi r^2 h$

$V = 3.14(0.04)^2 (1200)\ in^3$

$V = 6.0288\ in^3$ or $98.79\ cm^3$

$V = 6.0288\ (16.387)\ mL$

$V = 98.78\ mL$

Retention time = Tube volume / Flow rate

$\tau_R = 98.78 / 0.6$

$\tau_R = 164.63\ min$

$\tau_R = 2.74\ h$

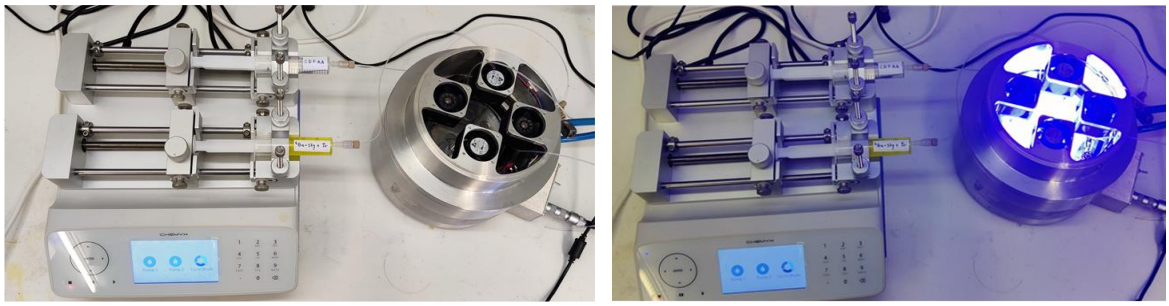


Figure 8.2. Flow setup for scale-up lactone in DMF.

Procedure for reaction in flow: In an oven dried flask, 4-*tert*-butylstyrene, (94%, stab. with 50 ppm 4-*tert*-butylcatechol commercially available at Thermoscientific - Alfa Aesar, 3.9 gram, 20.0 mmol, 1.0 equiv) and *fac*-[Ir(ppy)$_3$] (131.0 mg, 0.2 mmol, 1.0 mol%) were dissolved in 30 mL DMF while in another flask *CDFAA* (40.0 mmol, 6.9 mL) was dissolved in 30 mL DMF. Both liquids were taken up with a syringe and mounted on a syringe pump. The syringes were connected to a 98.8 mL flow coil tubing (PFA tubing, 1/16" outer diameter and 0.04" inner diameter, [1507L]) *via* a PEEK Y-mixer (Y Assembly PEEK [P-512]). Stock solutions were pumped into the flow reactor with a flow rate of 0.3 mL/min through each syringe (corresponding to 2.74 hour residence time). When the syringe was fully empty, again stock solution was loaded into a syringe and injected to collect all product at the end of the reactor in a flask. The reaction mixture was added to an appropriately sized separatory funnel and 130 mL EtOAc was added and washed with water (4×60) mL; further organic layer was washed with 60 mL brine. The combined organic layers were then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel as indicated to afford γ–lactone as a pale-yellow solid (4.97 g, 14.0 mmol, 70% yield).

8.2. Gram-scale synthesis in batch

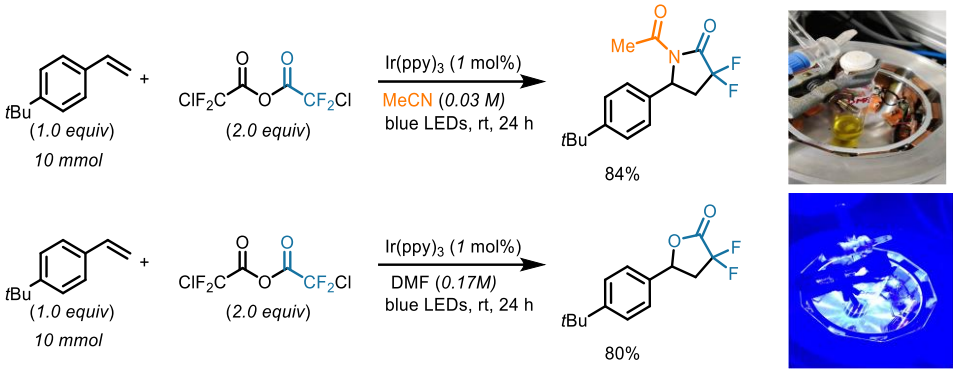


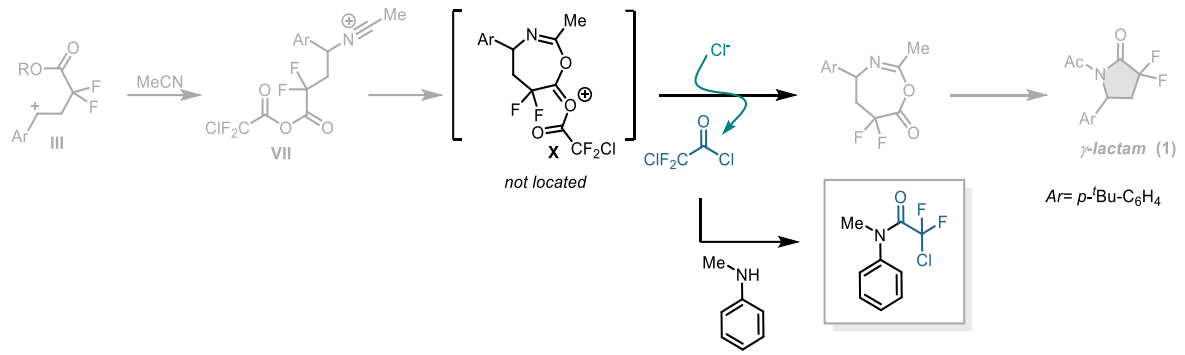
Figure 8.3. Batch setup for scale-up lactam in MeCN and lactone in DMF.

Procedure 1: A flame dried 250 mL slank tube was charged with *fac*-[Ir(ppy)$_3$] (65.0 mg, 0.1 mmol, 1.0 mol%) and equipped with a magnetic stirring bar. The content of the tube was then subjected to three vacuum/argon cycles. Anhydrous MeCN (150 mL) was added under an argon atmosphere, and the solution was sparged for 5 min. 4-*tert*-butylstyrene, (94%, stab. with 50 ppm 4-*tert*-butylcatechol commercially available at Thermoscientific - Alfa Aesar, 1.95 gram, 10.0 mmol, 1.0 equiv) and *CDFAA* (4.9 mL, 20.0 mmol, 2.0 equiv) were introduced to the solution. The reaction mixture was stirred at room temperature under blue LEDs irradiation for 24 h. The solvent was evaporated under reduced pressure, and the crude product was purified by flash column chromatography over silica gel as indicated to get γ-lactams as a white solid (2.47 g, 8.4 mmol, 84% yield).

Procedure 2: A flame dried 150 mL slank tube was charged with *fac*-[Ir(ppy)$_3$] (65.0 mg, 0.1 mmol, 1.0 mol%) and equipped with a magnetic bar. The content of the tube was then subjected to three vacuum/argon cycles. Anhydrous DMF (30 mL) was added under an argon atmosphere, and the solution was sparged for 5 min. 4-*tert*-butylstyrene, (94%, stab. with 50 ppm 4-*tert*-butylcatechol commercially available at Thermoscientific - Alfa Aesar, 1.95 gram, 10.0 mmol, 1.0 equiv) and *CDFAA* (4.84 mL, 20.0 mmol, 2.0 equiv) were introduced to the solution. The reaction mixture was stirred at room temperature under blue LEDs irradiation for 24 h. The reaction contents were added to an appropriately sized separatory funnel and 100 mL EtOAc was added and washed with water (3×50) mL; further organic layer was washed with 30 mL brine. The combined organic layers were then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel as indicated to afford γ–lactone as a yellow solid (2.03 g, 8.0 mmol, 80% yield).

9. Trapping Experiments

9.1. Side product trapping



In the reaction sequence we observed by-product formation - 2-chloro-2,2-difluoroacetyl chloride. In order to confirm it, a trapping experiment using N-Benzylmethylamine was performed. The formed product, 2-chloro-2,2-difluoro-*N*-methyl-*N*-phenylacetamide was observed in GC-MS. The following procedure was used: 4-*tert*-Butylstyrene (94%, 95 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (85 µL, 0.5 mmol, 1.0 equiv), and anhydrous MeCN (15 mL). After 12 h, 1.0 equivalent of PhNHMe (64 µL, 0.5 mmol, 1.0 equiv) was added under argon. The final reaction mixture was stirred for 1 h and analyzed with GC-MS (Figure 9.1).

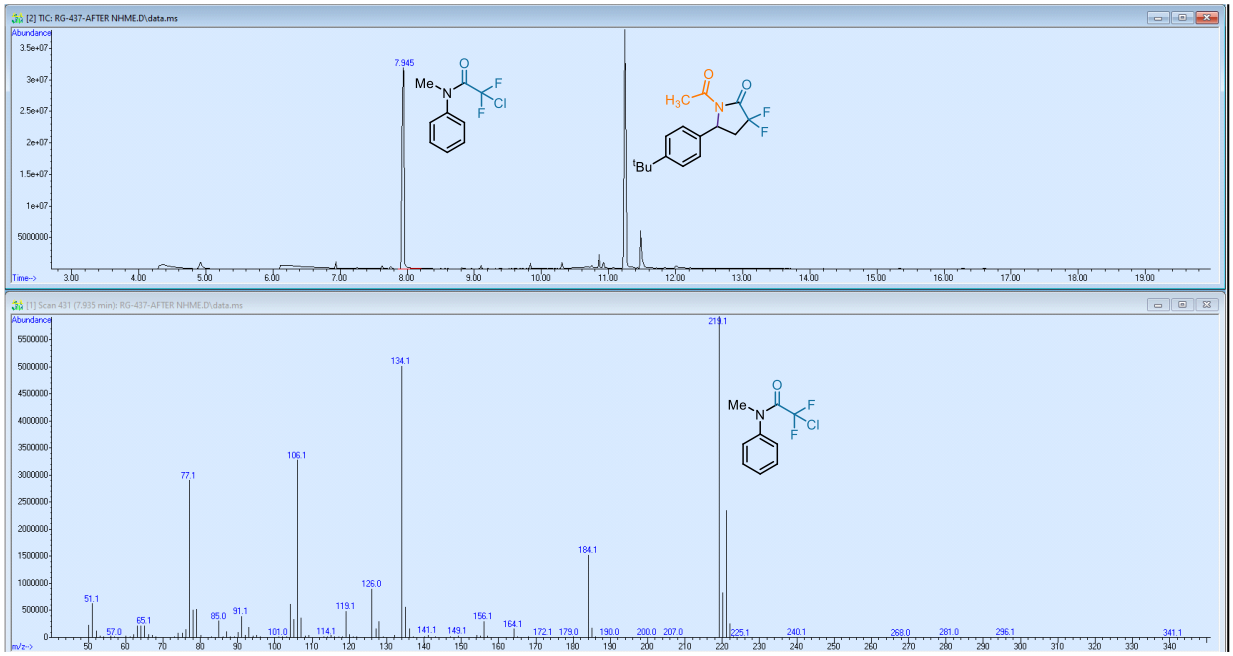
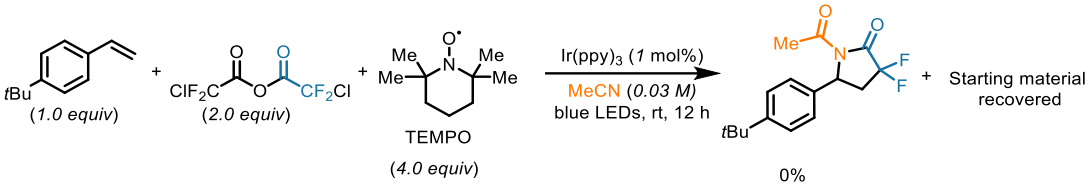


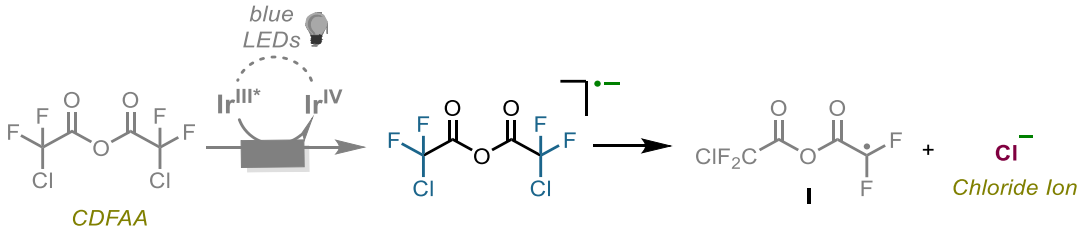
Figure 9.1. GC-MS spectrum for side product trapping experiment.

9.2. Procedure of the radical trapping experiment with TEMPO



A flame dried 20 mL crimp cap vial was charged with *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%) and equipped with a magnetic bar. The content of the vial was then subjected to three vacuum/argon cycles. Anhydrous MeCN (15 mL) was added under an argon atmosphere, and the solution was sparged for 5 min. 4-*tert*-butylstyrene (95 µL, 0.5 mmol, 1.0 equiv), 2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) (312.5 mg, 2.0 mmol, 4.0 equiv) and *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv) were introduced to the solution *via* microsyringes. The reaction mixture was stirred at room temperature under blue LEDs irradiation for 12 h. When reaction mixture was analyzed with GC-MS and ^{1}H-NMR only starting material was detected.

10. Determination of Chloride Ion Concentration (Mohr's Method)



The presence of chloride ions in solution before and after reaction was determined by titration with silver nitrate. Potassium chromate was utilized as indicator. Silver nitrate solution was prepared by mixing 1.35 g of silver nitrate and 100 mL distilled H_2O (C = 0.079 M) in a volumetric flask, while indicator solution was prepared from 0.50 g of K_2CrO_4 and 10 mL of water.

Samples were prepared according to the following method:

A blank sample (Entry 1) was prepared from *fac*-[Ir(ppy)$_3$], 4-*tert*-butylstyrene and *CDFAA* (amounts according to general procedure 1) and 5 mL of water and was kept in dark for 24 h.

Difunctionalization reaction with styrene and *CDFAA* in toluene was analysed for the presence of chloride ions by preparing two different samples of the reaction mixture containing *fac*-[Ir(ppy)$_3$], 4-*tert*-butylstyrene, *CDFAA* and toluene (amounts according to general procedure 3). The first sample was placed in dark for 24 h (Entry 2), and the second was irradiated with blue LEDs for 24 h (Entry 4).

γ-Lactone formation with styrene and *CDFAA* in DMF was analysed for the presence of chloride ions by preparing two different samples consisting of *fac*-[Ir(ppy)$_3$], 4-*tert*-butylstyrene, *CDFAA* and DMF (amounts according to general procedure 2). The first sample was kept in the dark for 24 h (Entry 3), and the second sample was irradiated with blue LEDs for 24 h (Entry 5).

Titration was performed according to the following procedure:

Sample (Entry 1-5) was diluted with 50 mL of water. Sodium hydrogen carbonate was then added in small portions until pH become neutral. Next, 0.5 mL of indicator solution was introduced dropwise. Solution of silver nitrate was added *via* burette until brown-red precipitate formation was detected (equivalence point). This method was adapted from Kahler's work[24]. Additional information on the use

of this method to determine chloride ion can be find using the following link: https://www.canterbury.ac.nz/media/documents/science-outreach/chloride_mohr.pdf. (acsessed on 20.03.2022). The results of our experiments are summarized in table 10.1.

Entry	Sample	$AgNO_3$ solution used V (mL)	No. of moles of Cl^- (mmol)	Ratio of Cl^- to substrate (%)
1	Dark, water	0.05 (1 drop)	≤0.004	≤0.8%
2	Dark, PhMe	0.05 (1 drop)	≤0.004	≤0.8%
3	Dark, DMF	0.05 (1 drop)	≤0.004	≤0.8%
4	Irradiated in PhMe	1.5	0.12	24%
5	Irradiated in DMF	6.1	0.53	106%

Table 10.1. Determination of chloride ion concentration by titration (Mohr's method).

Due to the complexity of the system and the presence of an organic solvent, the quantitative analysis of the samples (entry 4-5) is not accurate. However, from a qualitative point of view, it can be clearly stated that in the case of reaction in toluene (entry 4), chloride ions are generated similarly to the reaction in DMF (entry 5), only after the application of light irradiation. This supports our proposed mechanism and the fact that dissociation of *CDFAA* occurs *via* homolytic cleavage of the Cl–CF_2R bond in all solvent systems.

11.Formation of XVII

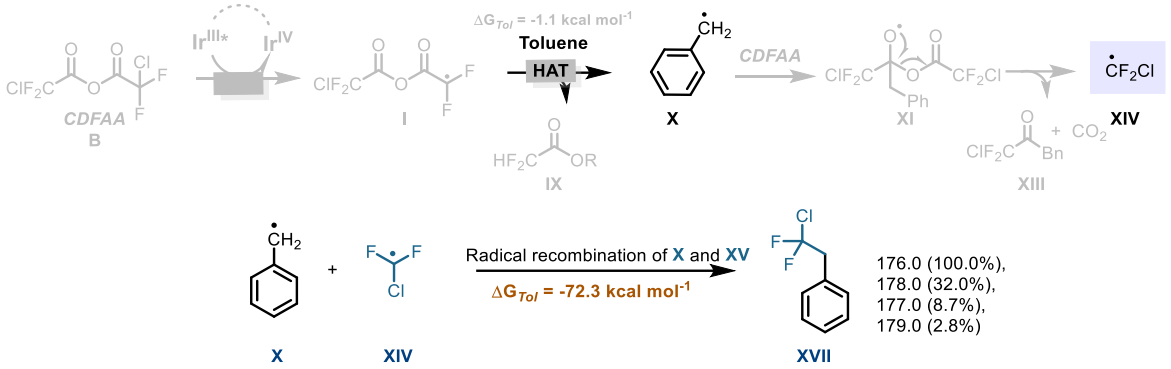


Figure 11.1. Radical recommendation and calculated ΔG value.

Careful analysis of the photocatalytic reaction in toluene revealed the formation of species **XVII**, presumably due to radical recombination of **X** and **XIV** (Figure 11.2). This observation further supports our hypothesis on hydrogen atom abstraction (HAT) process by the *gem*-difluoroalkyl radical **I** from toluene. This HAT process is also validated by theoretical calculations with estimated Gibbs free energy of -72.3 kcal mol^{-1} (Figure 11.1).

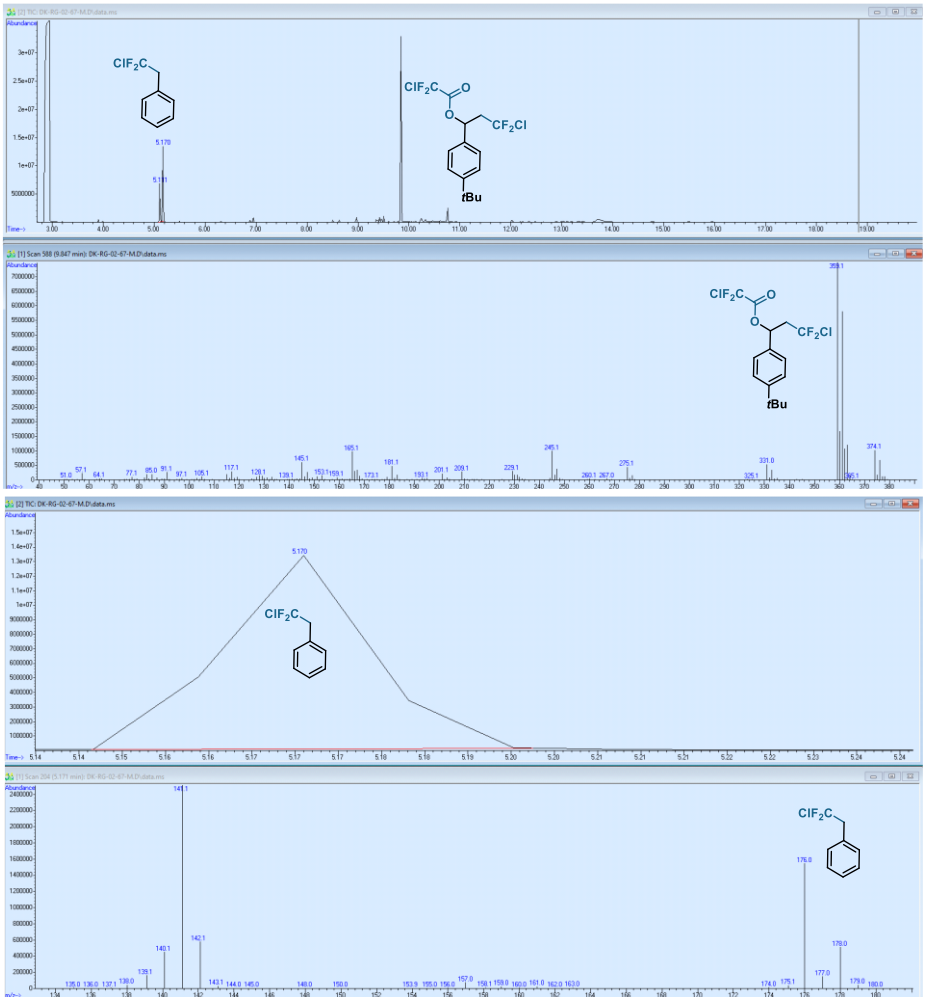
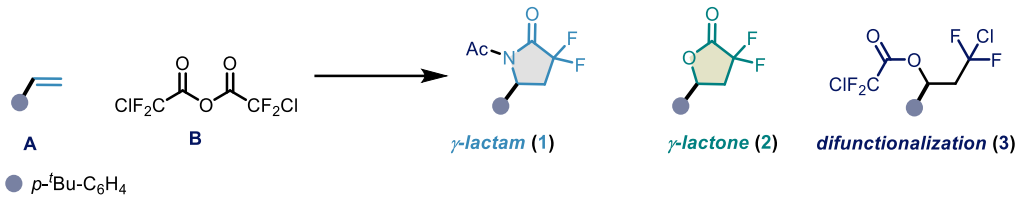


Figure 11.2. GC-MS spectrum for **XVII** formation.

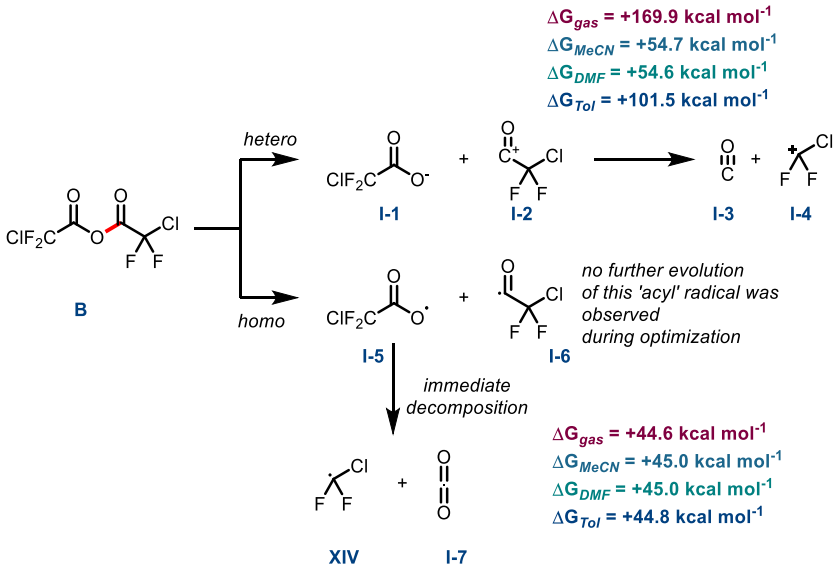
12. Detailed Mechanistic Proposals

General reaction scheme

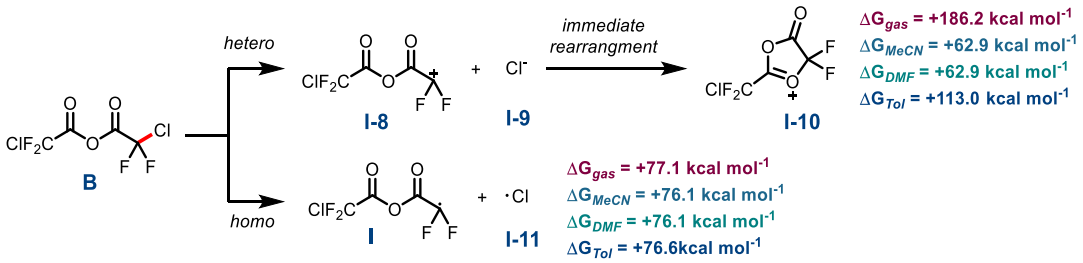


12.1. *CDFAA*: Direct heterolytic and homolytic bond cleavage

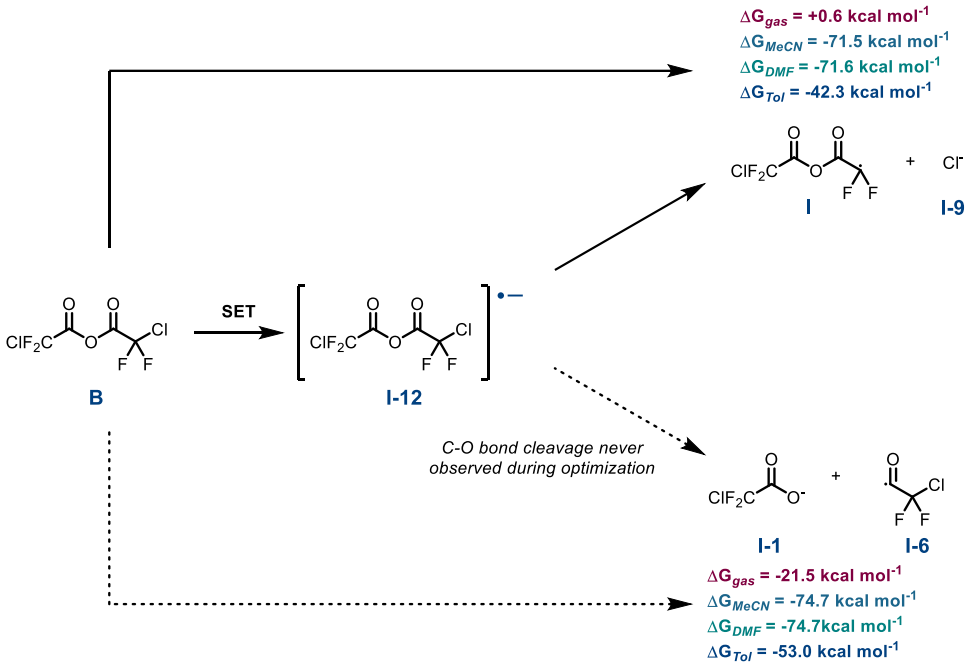
C-O Bond cleavage



C-Cl Bond cleavage



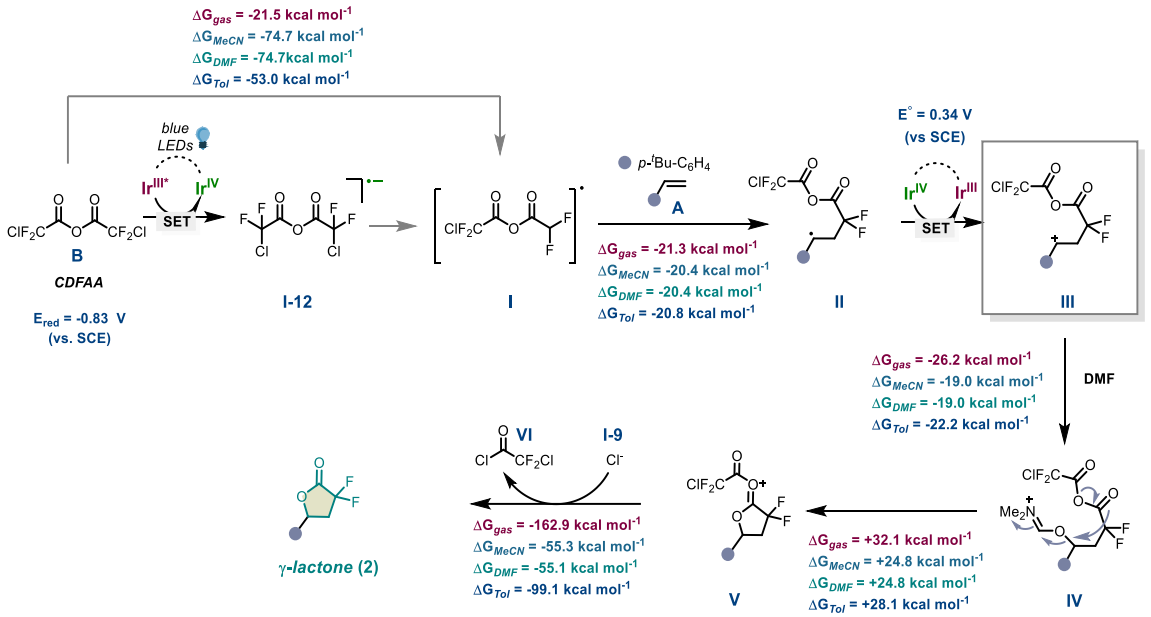
Anhydride SET evolution



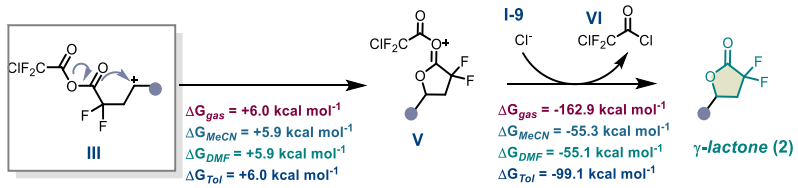
Note: a, Computational optimization of the radical anion **I-12** was unsuccessful and in any scenario C-Cl bond cleavage was observed. **b**, ΔG values are calculated by inclusion of the G for the free electron (-0.867 kcal mol^{-1})[25-26] **c**, In no case C-O bond cleavage was observed during the optimization of intermediate **I-12**, even when optimizations were attempted including implicit solvent model for either DMF, acetonitrile, or toluene.

12.2. Detailed mechanistic proposals for the formation of *gem*-difluoro-γ-lactone

Mechanistic scenario 1 (DMF coordination)

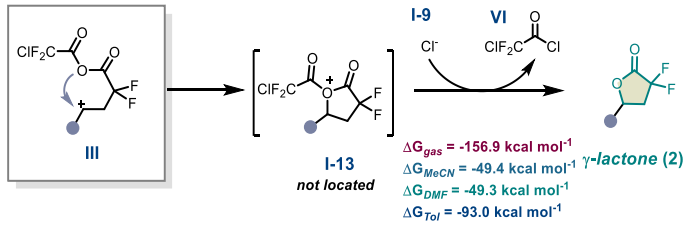


Mechanistic scenario 2 (without DMF coordination)



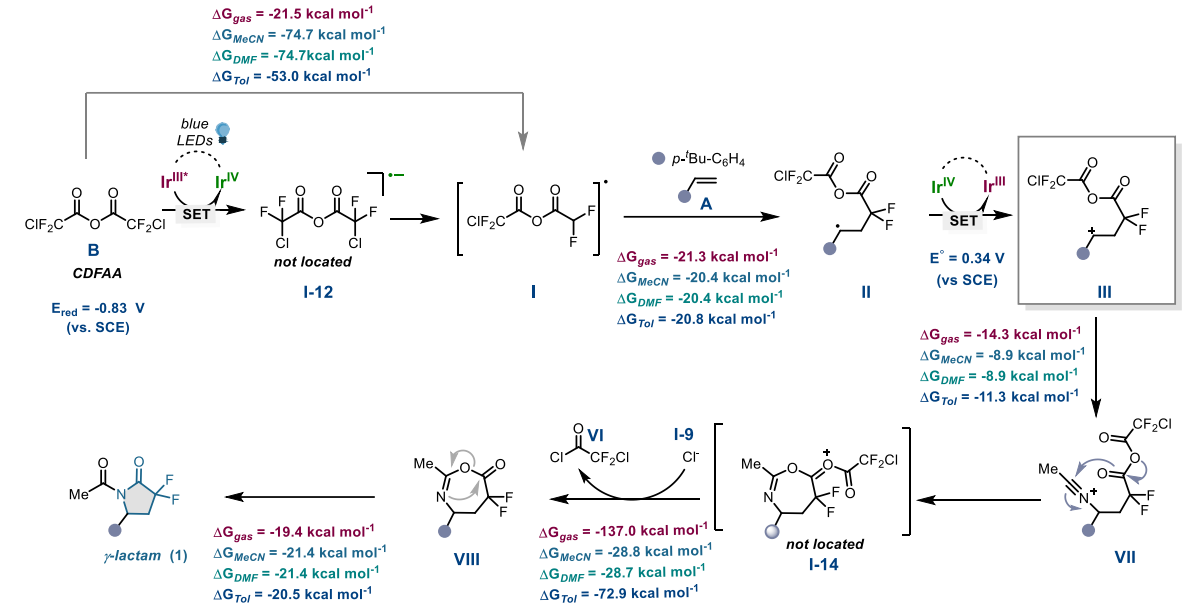
Note: (III to **V)** and (**III** to **IV** to **V)** are energetically equivalent: given that direct coordination of DMF to intermediate **III** is exergonic, it is presumably that the corresponding intermediate **IV** is generated in the presence of DMF as solvent.

Mechanistic proposal 3 (without DMF coordination)

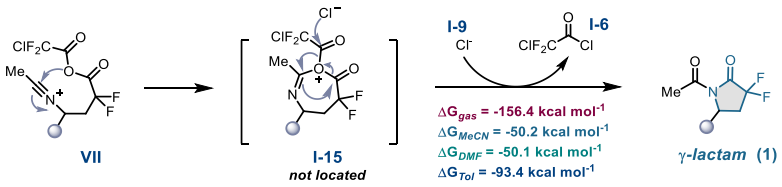


12.3. Detailed mechanistic proposals for formation of γ-lactam

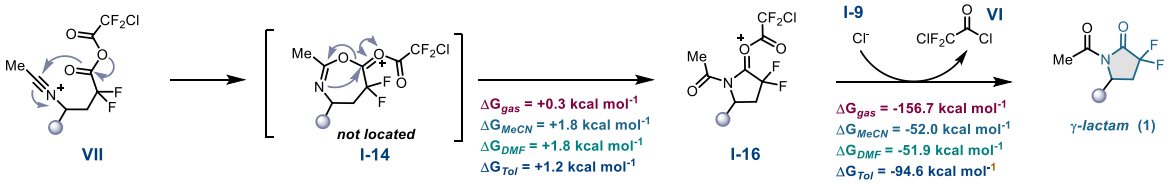
Mechanistic proposal 1



Mechanistic proposal 2

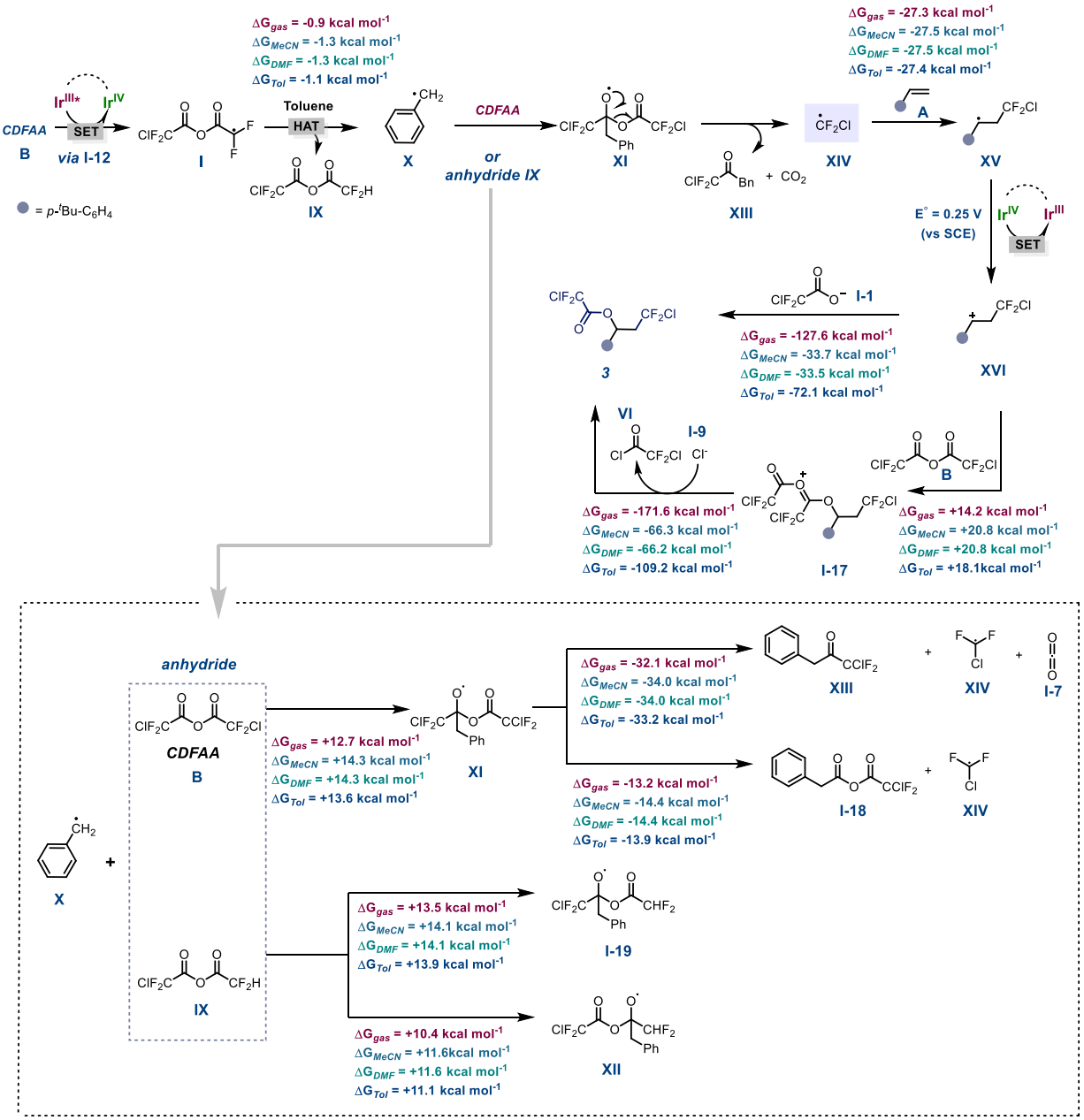


Mechanistic proposal 3

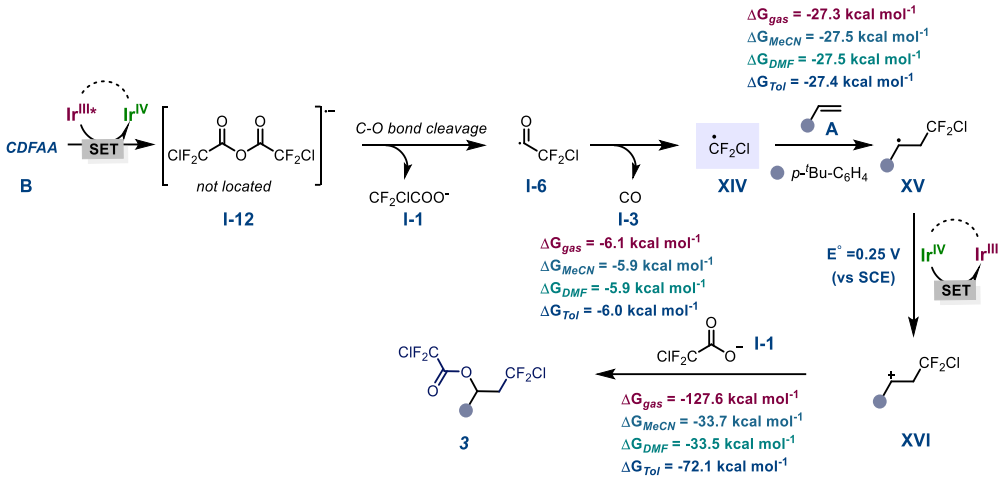


12.4. Detailed mechanistic proposals for oxy-fluoroalkylation of alkenes

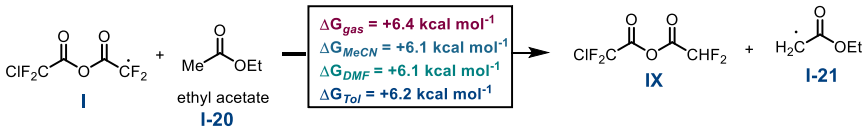
Mechanistic proposal 1

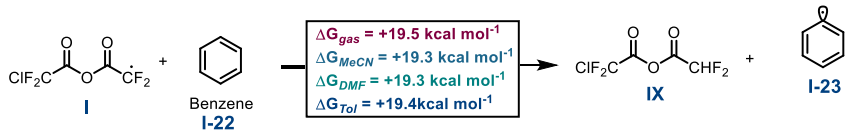


Mechanistic proposal 2: Direct C-O Bond cleavage

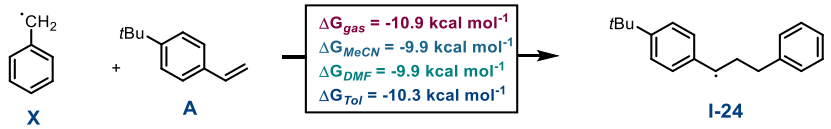


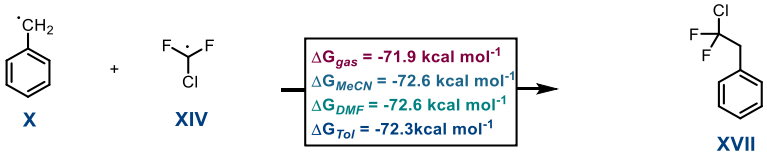
12.5. HAT step for other solvents:





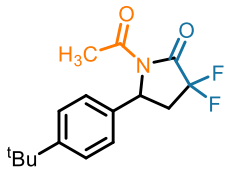
12.6. Radical recombination possibilities:





13. NMR Data

1-Acetyl-5-(4-(*tert*-butyl)phenyl)-3,3-difluoropyrrolidin-2-one (1)



Compound **1** was obtained according to general procedure **1** from 4-*tert*-butylstyrene (94%, 95.0 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white crystalline solid (133.0 mg, 0.45 mmol, 90% yield) after purification by flash column chromatography (24 g SiO_2, hexane/EA = 20:1).

R_f Value: 0.5 in 10% in EtOAc: Hexane.

Melting point: 102–104 °C

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.42 – 7.32 (m, 2H), 7.17 – 7.08 (m, 2H), 5.42 – 5.23 (m, 1H), 3.01 – 2.80 (m, 1H), 2.61 – 2.47 (m, 1H), 2.59 (s, 3H), 1.30 (s, 9H).

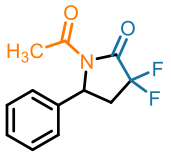
^{13}C-NMR (101 MHz, $CDCl_3$): δ 170.1, 164.3 (t, *J* = 33.3 Hz), 151.4, 136.4, 126.1, 125.3 (d, *J* = 1.9 Hz), 117.4 (dd, *J* = 253.2, 251.7 Hz), 54.5 (dd, *J* = 5.0, 1.8 Hz), 37.5 (t, *J* = 21.2 Hz), 34.7, 31.4, 25.7.

^{19}F-NMR (282 MHz, $CDCl_3$): δ -99.60 (d, *J* = 275.7 Hz), -103.52 (d, *J* = 275.7 Hz)

FT-IR (ATR, neat; cm^{-1}): 2965, 2900, 2866, 1755, 1723, 1380, 1316, 1306, 1242, 1070.

HRMS (ESI) *m/z*, $[M+Na]^+$ calcd for $C_{16}H_{19}F_2NO_2+Na^+$: 318.1276; found: 318.1277.

1-Acetyl-3,3-difluoro-5-phenylpyrrolidin-2-one (4)



Compound **4** was obtained according to general procedure **1** from styrene (57.0 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL) . Compound **4** was isolated as a white solid (90.8 mg, 0.38 mmol, 76% yield) after purification by column chromatography (40 g SiO_2, hexane/EA = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.32 – 7.11 (m, 5H), 5.38 – 5.25 (m, 1H), 2.96 – 2.74 (m, 1H), 2.52 (s, 3H), 2.50 – 2.40 (m, 1H)

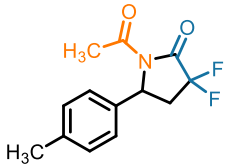
^{13}C-NMR (75 MHz, $CDCl_3$): δ 170.1, 164.3 (t, *J* = 31.8 Hz), 139.5, 129.2, 128.5, 125.6 (d, *J* = 1.6 Hz), 117.3 (t, *J* = 252.5 Hz), 54.8 (dd, *J* = 5.0, 1.9 Hz), 37.5 (t, *J* = 21.3 Hz), 25.7

^{19}F-NMR (282 MHz, $CDCl_3$): δ -99.7 (d, *J* = 275.8 Hz), -103.7 (d, *J* = 275.8 Hz)

FT-IR (ATR, neat; cm^{-1}): 3034, 1754, 1716, 1316, 1205, 1057.

HRMS (ESI) *m/z*, $[M+NH_4]^+$ calcd for $C_{12}H_{11}F_2NO_2+NH_4^+$: 257.1096; found 257.1096.

1-Acetyl-3,3-difluoro-5-(*p*-tolyl)pyrrolidin-2-one (5)



Compound **5** was obtained according to general procedure **1** from 1-methyl-4-vinylbenzene (66.0 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (97.7 mg, 0.39 mmol, 77% yield) after purification by flash column chromatography (24 g SiO_2, hexane/EA = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.21 – 7.13 (m, 2H), 7.12 – 7.06 (m, 2H), 5.40 – 5.30 (m, 1H), 3.01 – 2.80 (m, 1H), 2.58 (s, 3H), 2.56 – 2.45 (m, 1H), 2.33 (s, 3H).

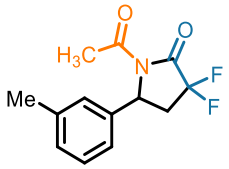
^{13}C-NMR (75 MHz, $CDCl_3$): δ 170.1, 164.3 (t, *J* = 24.8 Hz), 138.4, 136.6, 129.9, 125.6 (d, *J* = 1.6 Hz), 117.4 (t, *J* = 252.8 Hz), 54.6 (dd, *J* = 5.0, 1.9 Hz), 37.6 (t, *J* = 21.2 Hz), 25.7, 21.2.

^{19}F-NMR (282 MHz, $CDCl_3$): δ -99.7 (d, *J* = 275.7 Hz), -103.6 (d, *J* = 275.7 Hz).

FT-IR (ATR, neat; cm^{-1}): 3037, 1754, 1716, 1317, 1206, 1066, 754.

HRMS (ESI) *m/z*, $[M+H]^+$ calcd for $C_{13}H_{13}F_2NO_2+H^+$: 254.0987; found 254.0985.

1-Acetyl-3,3-difluoro-5-(*m*-tolyl)pyrrolidin-2-one (6)



Compound **6** was obtained according to general procedure **1** from 1-methyl-3-vinylbenzene (66.0 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170.0 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (78.4 mg, 0.31 mmol, 62% yield) after purification by column chromatography (40 g SiO_2, hexane/EA = 5:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.35 – 7.27 (m, 1H), 7.22 – 7.15 (m, 1H), 7.09 – 7.02 (m, 2H), 5.49 – 5.33 (m, 1H), 3.08 – 2.88 (m, 1H), 2.67 (s, 3H), 2.65 – 2.52 (m, 1H), 2.42 (s, 3H).

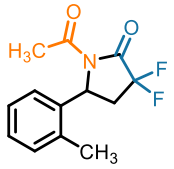
^{13}C-NMR (75 MHz, $CDCl_3$): δ 170.1, 164.3 (t, *J* = 32.1 Hz), 139.5, 139.0, 129.3, 129.1, 126.3 (d, *J* = 1.6 Hz), 122.5 (d, *J* = 1.6 Hz), 117.3 (t, *J* = 252.7 Hz), 54.8 (dd, *J* = 5.0, 1.9 Hz), 37.6 (t, *J* = 21.2 Hz), 25.7, 21.6.

^{19}F-NMR [^{1}H Coupled] (282 MHz, $CDCl_3$): δ -99.7 (ddd, *J* = 275.5, 16.7, 7.5 Hz), -103.5 (ddd, *J* = 275.5, 16.7, 7.5 Hz).

FT-IR (ATR, neat; cm^{-1}): 2965, 2927, 1761, 1712, 1303, 1252, 1202, 1068.

HRMS (ESI) *m/z*, $[M+NH_4]^+$ calcd for $C_{13}H_{13}F_2NO_2+NH_4^+$: 271.1253; found 271.1252.

1-Acetyl-3,3-difluoro-5-(*o*-tolyl)pyrrolidin-2-one (7)



Compound **7** was obtained according to general procedure **1** from 1-methyl-2-vinylbenzene (59.1 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 μmol, 1.0 mol%), *CDFAA* (170 μL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL) . Isolated as a white solid (93.6 mg, 0.37 mmol, 74% yield) after purification by column chromatography (24 g SiO_2, hexane to hexane/EA = 5:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.22 – 7.15 (m, 3H), 6.95 – 6.90 (m, 1H), 5.49 – 5.33 (m, 1H), 2.91 (m, 1H), 2.62 (s, 3H), 2.48 – 2.35 (m, 4H).

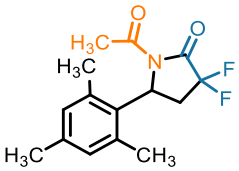
^{13}C-NMR (100 MHz, $CDCl_3$): δ 170, 164.5 (t, *J* = 32.2 Hz), 137.7, 134.6, 131.2, 128.2, 126.9, 122.8 (d, *J* = 2.2 Hz), 117.4 (d, *J* = 253.6 Hz), 51.4 (dd, *J* = 4.9, 1.7 Hz), 36.5 (t, *J* = 21.1 Hz), 25.6, 19.3.

^{19}F-NMR (375 MHz, $CDCl_3$): δ -99.5 (d, *J* = 275.3 Hz), -103.5 (d, *J* = 275.3 Hz).

FT-IR (ATR, neat; cm^{-1}): 2965, 1756, 1718, 1374, 1310, 1246, 758.

HRMS (ESI) *m/z*, $[M+H]^+$ calcd for $C_{13}H_{13}F_2NO_2+H^+$: 254.0986; found 254.0987.

1-Acetyl-3,3-difluoro-5-mesitylpyrrolidin-2-one (8)



Compound **8** was obtained according to general procedure **1** from 1, 1,3,5-trimethyl-2-vinylbenzene (73.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5M.0 μmol, 1.0 mol%), *CDFAA* (170 μL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL) . Isolated as an off-white solid (102.6 mg, 0.365 mmol, 73% yield) after purification by column chromatography (24 g SiO_2, hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.88 (s, 1H), 6.79 (s, 1H), 5.69 – 5.50 (m, 1H), 2.97 (m, 1H), 2.59 – 2.39 (m, 7H), 2.24 (d, *J* = 2.1 Hz, 3H), 2.13 (d, *J* = 2.0, 3H).

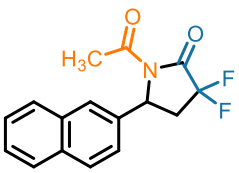
^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.0, 164.4 (dd, *J* = 33.4, 31.1 Hz), 137.8, 136.5, 133.5, 132.1, 131.4, 130.1, 116.9 (dd, *J* = 256.4, 248.1 Hz), 51.5 (d, *J* = 4.8 Hz), 34.3 (dd, *J* = 22.5, 20.5 Hz), 25.3, 20.9, 20.8, 20.7.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -99.7 (d, *J* = 275.6 Hz), -106.1 (d, *J* = 275.6 Hz).

FT-IR (ATR, neat; cm^{-1}): 2973, 2951,2925,1748, 1722, 1611, 1357,1324, 1229.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{15}H_{17}O_2NF_2+H^+$: 282.1295; found 282.1300.

1-Acetyl-3,3-difluoro-5-(naphthalen-2-yl)pyrrolidin-2-one (9)



Compound **9** was obtained according to general procedure **1** from 2-vinylnaphthalene (77.1 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL) . Isolated as a beige solid (81.0 mg, 0.28 mmol, 56% yield) after purification by column chromatography (40 g SiO_2, hexane/EA = 5:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.88 – 7.80 (m, 3H), 7.66 (s, 1H), 7.54 – 7.46 (m, 2H), 7.33 – 7.28 (m, 1H), 5.61 – 5.47 (m, 1H), 3.10 – 2.90 (m, 1H), 2.69 – 2.55 (m, 1H), 2.63 (s, 3H).

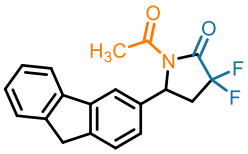
^{13}C-NMR (75 MHz, $CDCl_3$): δ 170.2, 164.3 (t, *J* = 27.8 Hz), 136.8, 133.3, 133.2, 129.5, 128.1, 127.9, 126.9, 126.7, 124.9 (d, *J* = 1.4 Hz), 123.0 (d, *J* = 1.7 Hz), 117.3 (t, *J* = 251.9 Hz), 55.0 (dd, *J* = 4.9, 1.9 Hz), 37.5 (t, *J* = 21.3 Hz), 25.7.

^{19}F-NMR (282 MHz, $CDCl_3$): δ -99.5 (d, *J* = 275.7 Hz), -103.5 (d, *J* = 275.7 Hz).

FT-IR (ATR, neat; cm^{-1}): 2969, 1751, 1716, 1320, 1250, 1064, 745.

HRMS (ESI) *m/z*, $[M+NH_4]^+$ calcd for $C_{16}H_{13}F_2NO_2+NH_4^+$: 307.1253; found 307.1252.

1-Acetyl-5-(*9H*-fluoren-3-yl)-3,3-difluoropyrrolidin-2-one (10)



Compound **10** was obtained according to general procedure **1** from 3-vinyl-*9H*-fluorene (96.0 mg, 0.5 mmol, 1.0 equiv.), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv.), and anhydrous MeCN (15 mL). Isolated as a white solid (75.3 mg, 0.23 mmol, 46% yield) after purification by column chromatography (24 g SiO_2, hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.79 – 7.73 (m, 2H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.40 – 7.34 (m, 2H) 7.34 – 7.28 (m, 1H), 7.25 – 7.19 (m, 1H), 5.50 – 5.42 (m, 1H), 4.04 – 3.75 (m, 2H), 3.07 – 2.83 (m, 1H), 2.68 – 2.50 (m, 4H).

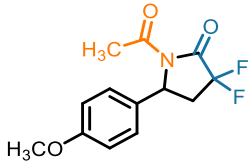
^{13}C-NMR (126 MHz, $CDCl_3$): δ 170.2, 164.3 (t, *J* = 32.3 Hz), 144.3, 143.5, 142.3, 141.0, 138.0, 127.2, 127.0, 125.2, 124.4, 122.3, 120.5, 120.2, 117.4 (t, *J* = 253.0 Hz), 55.1 (d, *J* = 4.4 Hz), 37.7 (t, *J* = 21.2 Hz), 37.0, 25.8.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -99.6 (d, *J* = 275.9 Hz), -103.5 (d, *J* = 275.9 Hz).

FT-IR (ATR, neat; cm^{-1}): 2925, 2853, 1762, 1716, 1421, 1299, 1250, 1094, 767, 739.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{19}H_{15}O_2NF_2+H^+$: 328.1135; found 328.1144.

1-Acetyl-3,3-difluoro-5-(4-methoxyphenyl)pyrrolidin-2-one (11)



Compound **11** was obtained according to general procedure **1** from 1-methoxy-4-vinylbenzene (67.0 mg, 0.5 mmol, 1.0 equiv.), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv.), and anhydrous MeCN (15 mL). Isolated as a white solid (53.3 mg, 0.2 mmol, 40% yield) after purification by column chromatography (24 g SiO_2, hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.20 – 7.09 (m, 2H), 6.93 – 6.83 (m, 2H), 5.41 – 5.27 (m, 1H), 3.79 (s, 3H), 2.98 – 2.82 (m, 1H), 2.60 – 2.48 (m, 4H).

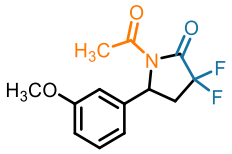
^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.2, 164.2 (m), 159.7, 131.5, 127.1 (d, *J* = 1.8 Hz), 117.4 (dd, *J* = 251.8, 3.6 Hz),114.6, 55.5, 54.4 (dd, *J* = 5.1, 1.8 Hz), 37.5 (t, *J* = 21.1 Hz), 25.7.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -99.6 (d, *J* = 275.7 Hz), -103.7 (d, *J* = 275.7 Hz).

FT-IR (ATR, neat; cm^{-1}): 3026, 2967, 2936, 2841, 2365, 2337, 1759, 1720, 1616, 1548, 1515, 1244.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{13}H_{13}O_3N+H^+$: 270.0938; found 270.0936.

1-Acetyl-3,3-difluoro-5-(3-methoxyphenyl)pyrrolidin-2-one (12)



Compound **12** was obtained according to general procedure **1** from 1-methoxy-3-vinylbenzene (67.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as an off-white solid (91.5 mg, 0.34 mmol, 68% yield) after purification by column chromatography (24 g SiO_2, hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.20 – 7.09 (m, 2H), 6.93 – 6.82 (m, 2H), 5.38 – 5.31 (m, 1H), 3.79 (s, 3H), 3.00 – 2.83 (m, 1H), 2.60 – 2.47 (m, 4H).

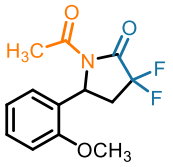
^{13}C-NMR (126 MHz, $CDCl_3$): δ 170.2, 164.2 (d, *J* = 32.5 Hz), 159.7, 131.5, 127.1 (d, *J* = 1.8 Hz), 117.4 (dd, *J* = 252.2, 2.7 Hz), 114.6, 55.5, 54.4 (dd, *J* = 5.1, 1.8 Hz), 37.5 (t, *J* = 21.1 Hz), 25.7.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -99.6 (d, *J* = 275.8 Hz), -103.7 (d, *J* = 275.8 Hz).

FT-IR (ATR, neat; cm^{-1}): 3357, 2956, 2843, 1759, 1718, 1603, 1496, 1373, 1313, 1243.

HRMS (ESI) *m/z*, $[M+H]^+$ calcd for $C_{13}H_{13}O_3NF_2+H^+$: 270.0934; found 270.0936.

1-Acetyl-3,3-difluoro-5-(2-methoxyphenyl)pyrrolidin-2-one (13)



Compound **13** was obtained according to general procedure **1** from 1-methoxy-2-vinylbenzene (67.1 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (96.8 mg, 0.36 mmol, 72% yield) after purification by column chromatography (24 g SiO_2, hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.26 (m, 1H), 7.04 – 7.01 (m, 1H), 6.94 – 6.91 (m, 2H), 5.62 – 5.45 (m, 1H), 3.85 (s, 3H), 2.94 – 2.86 (m, 1H), 2.59 (s, 3H), 2.58 – 2.51 (m, 1H).

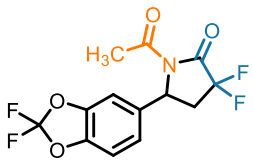
^{13}C-NMR (126 MHz, $CDCl_3$) = 170.1, 164.9 (t, *J* = 32.3 Hz), 156.2, 129.6, 127.6, 126.9, 120.8, 117.6 (t, *J* = 253.2 Hz), 111.1, 55.4, 51.6 (t, *J* = 3.6 Hz), 35.9 (t, *J* = 21.4 Hz), 25.5.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -100.7 (d, *J* = 274.3 Hz), -102.4 (d, *J* = 274.3 Hz).

FT-IR (ATR, neat; cm^{-1}): 2847, 1756, 1718, 1494, 1243, 761.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{13}H_{13}O_3NF_2+H^+$: 270.0935; found 270.0936.

1-Acetyl-5-(2,2-difluorobenzo[*d*][1,3]dioxol-5-yl)-3,3-difluoropyrrolidin-2-one (14)



Compound **14** was obtained according to general procedure **1** from 1, 2,2-difluoro-5-vinylbenzo[*d*][1,3]dioxole (92.0 mg, 0.5 mmol, 1.0 equiv.), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (166.4 mg, 0.365 mmol, 73% yield) after purification by column chromatography (24 g SiO_2, hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.06 – 7.01 (m, 1H), 6.93 – 6.98 (m, 2H), 5.41 – 5.32 (m, 1H), 3.00 – 2.78 (m, 1H), 2.60 (s, 3H), 2.56 – 2.46 (m, 1H).

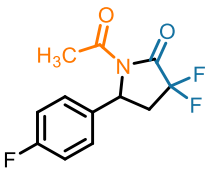
^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.1, 163.9 (t, *J* = 32.5 Hz), 144.4, 143.7, 135.7, 131.8 (t, *J* = 256.4 Hz), 121.3 (d, *J* =1.8 Hz), 117.0 (dd, *J* = 254.4, 3.7 Hz), 110.1, 107.3 (d, *J* = 1.8 Hz), 54.4 (dd, *J* = 5.5, 1.8 Hz), 37.4 (t, *J* = 21.4 Hz), 25.7.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -49.7 (d, *J* = 3.7 Hz), -99.0 (d, *J* = 277.3 Hz), -104.2 (d, *J* = 277.3 Hz).

FT-IR (ATR, neat; cm^{-1}): 3347, 2362, 2333, 1760, 1722, 1502, 1451, 1310, 1229, 1203, 1138 1101.

HRMS (EI) m/z, $[M]^+$ calcd for $C_{13}H_9O_4NF_4$: 319.0461; found 319.0462.

1-Acetyl-3,3-difluoro-5-(4-fluorophenyl)pyrrolidin-2-one (15)



Compound **15** was obtained according to general procedure **1** from 4-fluorostyrene (97%, 62.0 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a beige solid (70.3 mg, 0.27 mmol, 55% yield) after purification by column chromatography (40 g SiO_2, hexane/EA = 5:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.24 – 7.14 (m, 2H), 7.12 – 6.99 (m, 2H), 5.45 – 5.28 (m, 1H), 3.09 – 2.76 (m, 1H), 2.64 – 2.40 (m, 4H).

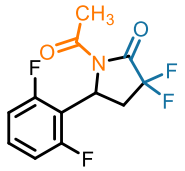
^{13}C-NMR (75 MHz, $CDCl_3$): δ 170.2, 164.3 (t, *J* = 22.5 Hz), 161.0, 135.3 (d, *J* = 3.2 Hz), 127.6 (dd, *J* = 8.3, 1.9 Hz), 117.2 (dd, *J* = 253.9, 251.2 Hz), 116.4, 116.1, 54.9 – 53.6 (m), 37.3 (d, *J* = 21.4 Hz), 25.7.

^{19}F-NMR (282 MHz, $CDCl_3$): δ -99.4 (d, *J* = 276.3 Hz), -103.9 (d, *J* = 276.3 Hz), -113.3 (s).

FT-IR (ATR, neat; cm^{-1}): 3072, 1776, 1759, 1752, 1715, 1512, 1309, 1067, 836.

HRMS (ESI) *m/z*, $[M+NH_4]^+$ calcd for $C_{12}H_{10}F_3NO_2+NH_4^+$: 275.1002; found 275.1002.

1-Acetyl-5-(2,6-difluorophenyl)-3,3-difluoropyrrolidin-2-one (16)



Compound **16** was obtained according to general procedure **1** from 1,3-difluoro-2-vinylbenzene (70.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (100.0 mg, 0.365 mmol, 73% yield) after purification by column chromatography (24 g SiO_2, hexane to hexane/EA=10:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.26 (m, 1H), 6.92 (t, *J* = 9.2 Hz, 2H), 5.71 – 5.56 (m, 1H), 3.13 – 2.92 (m, 1H), 2.72 – 2.50 (m, 4H).

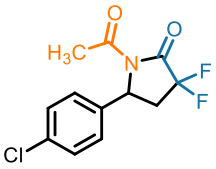
^{13}C-NMR (126 MHz, $CDCl_3$): δ 170.1, 163.6 (t, *J* = 32.2 Hz), 161.4 (d, *J* = 7.0 Hz), 159.4 (d, *J* = 7.0 Hz), 130.2 (t, *J* = 10.9 Hz), 117.3 (dd, *J* = 255.7, 5.8 Hz), 115.1 (t, *J* = 14.1 Hz), 112.1 (dd, *J* = 22.1, 3.5 Hz), 46.0 (t, *J* = 3.5 Hz), 35.2 (t, *J* = 22.1 Hz), 25.2.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -115.7 (m), -100.6 (d, *J* = 275.5 Hz), -104.6 (dt, *J* = 275.5, 6.9 Hz).

FT-IR (ATR, neat; cm^{-1}): 3100, 1766, 1714, 1626, 1576, 1463, 1390, 1311, 1263.

HRMS (ESI) m/z, $[M+Na]^+$ calcd for $C_{12}H_9O_2NF_4+Na^+$: 298.0464; found 298.0462.

1-Acetyl-5-(4-chlorophenyl)-3,3-difluoropyrrolidin-2-one (17)



Compound **17** was obtained according to general procedure **1** from 1-chloro-4-vinylbenzene (60.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (116.0 mg, 0.425 mmol, 85% yield) after purification by column chromatography (24 g SiO_2, hexane to hexane/EA=10:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.31 (m, 2H), 7.18 – 7.12 (m, 2H), 5.41 – 5.30 (m, 1H), 3.01 – 2.84 (m, 1H), 2.59 (s, 3H), 2.56 – 2.45 (m, 1H).

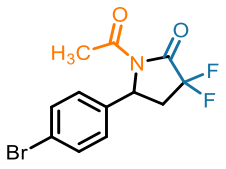
^{13}C-NMR (126 MHz, $CDCl_3$): δ 170.1, 164.0 (t, *J* = 32.8 Hz), 138.0, 134.5, 129.5, 127.1 (d, *J* = 2.3 Hz), 117.1 (dd, *J* = 254.1, 251.3 Hz), 54.2 (dd, *J* = 4.9, 1.7 Hz), 37.3 (t, *J* = 21.4 Hz), 25.6.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -99.5 (d, *J* = 276.5 Hz), -103.9 (d, *J* = 276.5 Hz).

FT-IR (ATR, neat; cm^{-1}): 3328, 1768, 1716, 1480, 1370, 1254, 1068.

HRMS (ESI) *m/z*, $[M+Na]^+$ calcd for $C_{12}H_{10}O_2NClF_2+Na^+$: 296.0256; found 296.0260.

1-Acetyl-5-(4-bromophenyl)-3,3-difluoropyrrolidin-2-one (18)



Compound **18** was obtained according to general procedure **1** from 4-bromostyrene (97%, 67.0 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (124.0 mg, 0.39 mmol, 78% yield) after purification by flash column chromatography (24 g SiO_2, hexane/EA=10:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.59 – 7.41 (m, 2H), 7.18 – 6.97 (m, 2H), 5.43 – 5.21 (m, 1H), 3.09 – 2.76 (m, 1H), 2.63 – 2.41 (m, 4H).

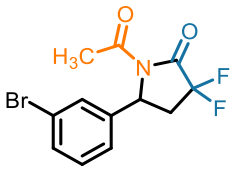
^{13}C-NMR (75 MHz, $CDCl_3$): δ 170.0, 164.0 (t, *J* = 31.9 Hz), 138.5, 132.4, 127.4 (d, *J* = 1.8 Hz), 122.4, 117.1 (dd, *J* = 254.1, 251.2 Hz), 54.2 (dd, *J* = 5.2, 1.8 Hz), 37.2 (t, *J* = 21.5 Hz), 25.6.

^{19}F-NMR (282 MHz, $CDCl_3$): δ -99.4 (d, *J* = 275.9 Hz), -104.0 (d, *J* = 275.9 Hz).

FT-IR (ATR, neat; cm^{-1}): 2972, 1757, 1714, 1295, 1250, 1205, 1066.

Elemental analysis calcd (%) for $C_{12}H_{10}BrF_2NO_2$: [C] 45.31, [H] 3.17, [Br] 25.12, [F] 11.94, [N] 4.40, [O] 10.06; found: [C] 45.29, [H] 3.15, [Br] 23.56, [F] 11.60, [N] 4.48.

1-Acetyl-5-(3-bromophenyl)-3,3-difluoropyrrolidin-2-one (19)



Compound **19** was obtained according to general procedure **1** from 1-bromo-3-vinylbenzene (91.5 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (112.9 mg, 0.35 mmol, 71% yield) after purification by column chromatography (24 g SiO_2, hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.45 (ddd, *J* = 8.0, 1.9, 1.0, 1H), 7.35 (t, *J* = 1.9 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.13 (dt, *J* = 8.0, 1.0 Hz, 1H), 5.43 – 5.21 (m, 1H), 2.99 – 2.85 (m, 1H), 2.61 (s, 3H), 2.54 – 2.39 (m, 1H).

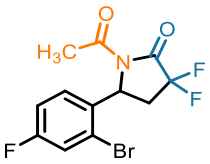
^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.0, 164.0 (t, *J* = 32.4 Hz), 141.8, 131.8, 130.8, 128.9 (d, *J* = 1.8 Hz), 124.1 (d, *J* = 1.8 Hz), 123.53, 117.0 (dd, *J* = 254.0, 251.5 Hz), 54.2 (dd, *J* = 5.2, 1.8 Hz), 37.3 (t, *J* = 21.6 Hz), 25.6.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -99.6 (d, *J* = 276.5 Hz), -104.0 (d, *J* = 276.5 Hz).

FT-IR (ATR, neat; cm^{-1}): 3331, 1763, 1715, 1572, 1237, 895.

HRMS (ESI) m/z, $[M+Na]^+$ calcd for $C_{12}H_{10}BrF_2NO_2+Na^+$: 339.9753; found 339.9755.

1-Acetyl-5-(2-bromo-4-fluorophenyl)-3,3-difluoropyrrolidin-2-one (20)



Compound **20** was obtained according to general procedure **1** from 2-bromo-4-fluoro-1-vinylbenzene (100.5 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as an off-white solid (116.9 mg, 0.35 mmol, 70% yield) after purification by column chromatography (24 g SiO_2, hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.37 (dd, *J* = 8.2, 2.6, 1H), 7.01 (td, *J* = 8.2, 2.6 Hz, 1H), 6.97– 6.91 (m, 1H), 5.73 – 5.63 (m, 1H), δ 3.10 – 2.82 (m, 1H), 2.64 (s, 2H), 2.59 – 2.44 (m, 1H).

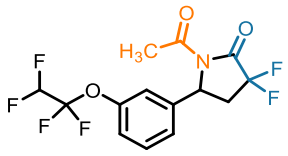
^{13}C-NMR (126 MHz, $CDCl_3$): δ 169.8, 164.3 (t, *J* = 32.2 Hz), 163.0, 161, 134.0 (d, *J* = 3.8 Hz), 126.3, 122.2 (d, *J* = 9.5 Hz), 121.1 (d, *J* = 21. Hz), 116.9 (t, *J* = 253.6 Hz), 115.3 (d, *J* = 21.3 Hz) δ 53.8 (d, *J* = 5.4 Hz), 36.2 (t, *J* = 21.3 Hz), 25.4.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -99.6 (d, *J* = 277.8 Hz), -105.1 (d, *J* = 276.0 Hz), -111.5.

FT-IR (ATR, neat; cm^{-1}): 3093, 3017, 2362, 1769, 1718, 1598, 1482, 1373.

HRMS (ESI) m/z, $[M+Na]^+$ calcd for $C_{12}H_9O_2NBrF_3+Na^+$: 357.9654; found 357.9661.

1-Acetyl-3,3-difluoro-5-(3-(1,1,2,2-tetrafluoroethoxy)phenyl)pyrrolidin-2-one (21)



Compound **21** was obtained according to general procedure **1** from 1-(1,1,2,2-tetrafluoroethoxy)-3-vinylbenzene (110 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 μmol, 1.0 mol%), *CDFAA* (170 μL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a yellow oil (141.0 mg, 0.4 mmol, 79% yield) after purification by column chromatography (40 g SiO_2, hexane/EA = 5:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.39 (t, *J* = 8.0 Hz, 1H), 7.22 – 7.09 (m, 2H), 7.05 (s, 1H), 5.90 (tt, *J* = 53.0, 2.8 Hz, 1H), 5.46 – 5.32 (m, 1H), 3.12 – 2.78 (m, 1H), 2.67 – 2.43 (m, 4H).

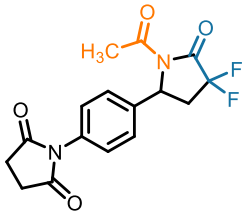
^{13}C-NMR (75 MHz, $CDCl_3$): δ 170.2, 164.1 (t, *J* = 32.1 Hz), 149.5, 141.7, 130.7, 123.5, 121.5, 119.1, 117.1 (t, *J* = 252.0 Hz), 116.6 (t, *J* = 271.5 Hz), 107.8 (tt, *J* = 251.7, 41.3 Hz), 54.3 (d, *J* = 5.2 Hz), 37.3 (t, *J* = 21.6 Hz), 25.5.

^{19}F-NMR (282 MHz, $CDCl_3$): δ -88.2 (t, *J* = 5.6 Hz), -99.5 (d, *J* = 276.4 Hz), -104.2 (d, *J* = 276.4 Hz), -136.8 (t, *J* = 5.6 Hz).

FT-IR (ATR, neat; cm^{-1}): 1767, 1723, 1317, 1191,1118, 1074, 759.

HRMS (ESI) *m/z*, $[M+NH_4]^+$ calcd for $C_{14}H_{11}F_6NO_3+NH_4^+$: 373.0981; found 373.0983.

3-(4,4-Difluoro-5-oxo-2-phenyltetrahydrofuran-3-carbonyl)oxazolidin-2-one (22)



Compound **22** was obtained according to general procedure **1** from 1-(4-vinylphenyl)pyrrolidine-2,5-dione (100.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 μmol, 1.0 mol%), *CDFAA* (170 μL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (114.2 mg, 0.34 mmol, 68% yield) after purification by column chromatography (24 g SiO_2, hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.33 (s, 4H), 5.45 – 5.38 (m, 1H), 3.02 – 2.84 (m, 5H), 2.63 – 2.50 (m, 4H).

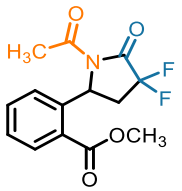
^{13}C-NMR (151 MHz, $CDCl_3$): δ 176.1, 169.9, 164.05 (t, *J* = 31.2 Hz), 139.8, 132.0, 127.1, 126.6 (d, *J* = 1.7), 117.2 (dd, *J* = 253.9, 251.5 Hz), 54.3 (d, *J* = 5.1 Hz), 37.1 (t, *J* = 21.5 Hz), 28.5, 25.6.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -99.2 (d, *J* = 276.5 Hz), -103.7 (d, *J* = 276.5 Hz).

FT-IR (ATR, neat; cm^{-1}): 3550, 2944, 1768, 1697, 1656, 1612, 1518, 1425, 1389, 1370, 1232.

HRMS (ESI) m/z, $[M+Na]^+$ calcd for $C_{17}H_{14}ON_3F_2+Na^+$: 337.0999; found 337.0994.

Methyl 2-(1-acetyl-4,4-difluoro-5-oxopyrrolidin-2-yl)benzoate (23)



Compound **23** was obtained according to general procedure **1** from methyl 2-vinylbenzoate (81.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 μmol, 1.0 mol%), *CDFAA* (170 μL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (87.8 mg, 0.295 mmol, 59% yield) after purification by column chromatography (24 g SiO_2,hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.07 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.51 (td, *J* = 7.7, 1.5 Hz, 1H), 7.38 (td, *J* = 7.7, 1.5 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 6.27 – 6.16 (m, 1H), 3.92 (s, 3H), 3.18 – 3.00 (m, 1H), 2.63 (s, 3H), 2.56 – 2.45 (m, 1H).

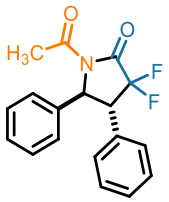
^{13}C-NMR (126 MHz, $CDCl_3$): δ 170.0, 167.0, 164.9 (t, *J* = 38.5 Hz), 141.8, 133.2, 131.8, 128.1, 127.5, 124.0, 117.3 (dd, *J* = 253.9, 249.8 Hz), 52.7 (d, *J* = 19.0), 37.7 (t, *J* = 19.0 Hz), 25.6.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -99.1 (d, *J* = 277.8 Hz), -105.1 (d, *J* = 277.8 Hz).

FT-IR (ATR, neat; cm^{-1}): 3041, 2958, 1765, 1718, 1706, 1602, 1579, 1437,1242, 1072.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{14}H_{13}O_4NF_2+H^+$: 298.0884; found 298.0885.

1-Acetyl-3,3-difluoro-4,5-diphenylpyrrolidin-2-one (24)



Compound **24** was obtained according to general procedure **1** from *trans*-stilbene (90.1 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 μmol, 1.0 mol%), *CDFAA* (170 μL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (86.6 mg, 0.275 mmol, 55% yield) after purification by column chromatography (40 g SiO_2, hexane/EA = 5:1). Crude d.r. = 10:1, isolated d.r. > 20:1.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.32 – 7.03 (m, 10H,), 5.37 – 5.26 (m, 1H), 3.49 (ddd, *J* = 17.1, 15.0, 6.8 Hz, 1H) 2.58 (s, 3H).

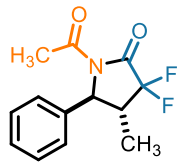
^{13}C-NMR (75 MHz, $CDCl_3$): δ 170.1, 164.2 (t, *J* = 31.9 Hz), 138.5, 130.6, 129.2, 129.2, 129.1, 128.5, 125.4, 115.8 (t, *J* = 257.5 Hz), 62.3, 62.3, 54.8 (t, *J* = 19.8 Hz), 26.0.

^{19}F-NMR (282 MHz, $CDCl_3$): δ -106.7 (d, *J* = 270.0 Hz), -111.7 (d, *J* = 270.0 Hz).

FT-IR (ATR, neat; cm^{-1}): 3041, 2969, 1774, 1709, 1246, 1065, 745.

HRMS (ESI) *m/z*,$[M+NH_4]^+$ calcd for $C_{18}H_{15}F_2NO_2+NH_4^+$: 333.1409; found 333.1409.

1-Acetyl-3,3-difluoro-4-methyl-5-phenylpyrrolidin-2-one (25)



Compound **25** was obtained according to general procedure **1** from (*E*)-prop-1-en-1-ylbenzene (59.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 μmol, 1.0 mol%), *CDFAA* (170 μL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (126.6 mg, 0.34 mmol, 68% yield) after purification by column chromatography (24 g SiO_2, 100% of hexane to hexane/EA = 5:1). Crude d.r. = 9:1, isolated d.r. > 20:1.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.29 (m, 2H), 7.33 – 7.29 (m, 1H), 7.21 – 7.18 (m, 2H), 4.72 – 4.67 (m, 1H), 2.57 (s, 3H), 2.48 – 2.41 (m, 1H), 1.25 (dd, *J* = 7.1, 1.6 Hz, 3H).

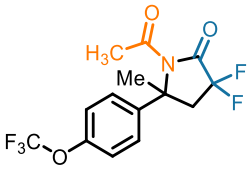
^{13}C-NMR (126 MHz, $CDCl_3$): δ 170.2, 164.5 (t, *J* = 32.1 Hz), 138.7, 129.2, 128.5, 125.6, 117.1 (dd, *J* = 255.8, 252.8 Hz), 63.3 (d, *J* = 5.2 Hz), 43.5 (t, *J* = 20.2 Hz), 25.9, 9.7 (d, *J* = 8.1 Hz).

^{19}F-NMR (471 MHz, $CDCl_3$): δ -108.9 (d, *J* = 271.1 Hz), -118.2 (d, *J* = 271.1 Hz).

FT-IR (ATR, neat; cm^{-1}): 3065, 2980, 2937, 1766, 1715, 1346, 1259, 1233.

HRMS (ESI) m/z, $[M+Na]^+$ calcd for $C_{13}H_{13}O_2NF_2+Na^+$: 276.0804; found 276.0807.

1-Acetyl-3,3-difluoro-5-methyl-5-(4-(trifluoromethoxy)phenyl)pyrrolidin-2-one (26)



Compound **26** was obtained according to general procedure **1** from 1-(prop-1-en-2-yl)-4-(trifluoromethoxy)benzene (101.1 mg, 0.5 mmol, 1.0 equiv.), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 μmol, 1.0 mol%), *CDFAA* (170 μL, 1.0 mmol, 2.0 equiv.), and anhydrous MeCN (15 mL). Isolated as a white solid (102.8 mg, 0.305 mmol, 61% yield) after purification by column chromatography (24 g SiO_2, hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.29 – 7.26 (m, 2H), 7.23 – 7.19 (m, 2H), 2.73 – 2.60 (m, 2H), 2.57 (s, 3H), 2.03 (s, 3H).

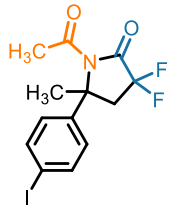
^{13}C-NMR (126 MHz, $CDCl_3$): δ 170.3, 164.7 (t, *J* = 32.0 Hz), 148.6 (d, *J* = 1.8 Hz), 142.0 (d, *J* = 1.8 Hz), 126.0, 121.3, 116.9 (m), 62.1 (dd, *J* = 4.4, 2.3 Hz), 47.1 (t, *J* = 20.2 Hz), 26.7, 25.4.

^{19}F-NMR (471 MHz, $CDCl_3$): -57.9, -101.6 (d, *J* = 276.6 Hz), -103.8 (d, *J* = 276.5 Hz).

FT-IR (ATR, neat; cm^{-1}): 3086, 2359, 2333, 1763, 1710, 1510, 1326, 1204, 1033.

HRMS (EI) m/z, $[M]^+$ calcd for $C_{14}H_{12}O_3NF_5$: 337.0732; found 337.0731.

1-Acetyl-3,3-difluoro-5-(4-iodophenyl)-5-methylpyrrolidin-2-one (27)



Compound **27** was obtained according to general procedure **1** from 1-iodo-4-(prop-1-en-2-yl)benzene (122.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 μmol, 1.0 mol%), *CDFAA* (170 μL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (128.9 mg, 0.34 mmol, 68% yield) after purification by column chromatography (24 g SiO_2, 100% of hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.70 – 7.65 (m, 2H), 7.01 – 6.96 (m, 2H), 2.71 – 2.58 (m, 2H), 2.55 (s, 3H), 1.98 (s, 3H).

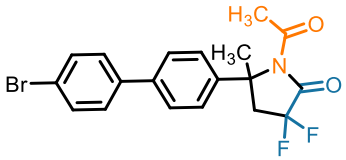
^{13}C-NMR (126 MHz, $CDCl_3$): δ 170.3, 164.7 (t, *J* = 32.0 Hz), 143.2 (d, *J* = 1.9 Hz), 138.1, 126.3, 116.2 (dd, *J* = 253.1, 250.1 Hz), 93.4, 62.2 (dd, *J* = 4.4, 2.2 Hz), 46.9 (t, *J* = 20.1 Hz), 26.9, 25.1.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -101.5 (d, *J* = 276.5 Hz), -103.8 (d, *J* = 276.5 Hz).

FT-IR (ATR, neat; cm^{-1}): 2940, 1752, 1710, 1323, 1209, 811.

HRMS (EI) m/z, $[M]^+$ calcd for $C_{13}H_{12}F_2INO_2$: 378.9873; found 378.9875.

1-Acetyl-5-(4'-bromo-[1,1'-biphenyl]-4-yl)-3,3-difluoro-5-methylpyrrolidin-2-one (28)



Compound **28** was obtained according to general procedure 1 from 4-bromo-4'-(prop-1-en-2-yl)-1,1'-biphenyl (136.5 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 μmol, 1.0 mol%), *CDFAA* (170 μL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (146.9 mg, 0.36 mmol, 72% yield) after purification by column chromatography (24 g SiO_2, 100% of hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): 7.70 – 7.66 (m, 4H), 7.01 – 6.96 (m, 4H), 2.71 – 2.58 (m, 2H), 2.55 (s, 3H), 1.98 (s, 3H).

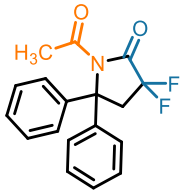
^{13}C-NMR (101 MHz, $CDCl_3$): δ 170.4, 164.9 (t, *J* = 32.0 Hz), 142.8 (d, *J* = 1.8 Hz), 139.4 (d, *J* = 1.8 Hz), 139.2, 132.1, 129.1, 128.8, 128.4, 127.6, 127.5, 124.9, 122.0, 116.4 (dd, *J* = 253.1, 249.9 Hz), 62.4 (dd, *J* = 4.3, 2.2 Hz), 47.2 (t, *J* = 20.0 Hz), 27.0, 25.3.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -101.3 (d, *J* = 276.3), -103.8 (d, *J* = 276.3).

FT-IR (ATR, neat; cm^{-1}): 3031, 1749, 1729, 1587, 1458, 1366, 1358, 1329, 1275.

HRMS (EI) m/z, $[M]^+$ calcd for $C_{19}H_{16}O_2NBrF_2$: 407.0327; found 407.0327.

1-Acetyl-3,3-difluoro-5,5-diphenylpyrrolidin-2-one (29)



Compound **29** was obtained according to general procedure **1** from ethene-1,1-diyldibenzene (90.1 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 μmol, 1.0 mol%), *CDFAA* (170 μL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL) . Isolated as a white solid (118.2 mg, 0.375 mmol, 75% yield) after purification by column chromatography (24 g SiO_2, 100% of hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.37 (m, 4H), 7.34 (m, 2H), 7.26 (m, 4H), 3.26 (t, *J*=14.4, 2H), 2.59 (s, 3H).

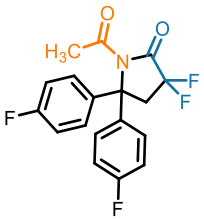
^{13}C-NMR (126 MHz, $CDCl_3$): δ 170.3, 165.2 (t, *J* = 31.7 Hz), 140.5, 128.5, 128.2, 127.9, 116.2 (t, *J* = 251.6 Hz), 69.6, 49.8 (t, *J* = 20.0 Hz), 27.0.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -103.7.

FT-IR (ATR, neat; cm^{-1}): 3037, 3024, 1751, 1725, 1446, 1318, 1206, 1076, 698.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{18}H_{15}O_2NF_2+H^+$: 316.1142; found 316.1144.

1-Acetyl-3,3-difluoro-5,5-bis(4-fluorophenyl)pyrrolidin-2-one (30)



Compound **30** was obtained according to general procedure **1** from 4,4'-(ethene-1,1-diyl)bis(fluorobenzene) (108.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 μmol, 1.0 mol%), *CDFAA* (170 μL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (126.0 mg, 0.36 mmol, 72% yield) after purification by column chromatography (24 g SiO_2, 100% of hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.21 (m, 4H), 7.07 (m, 4H), 3.21 (t, *J* = 14.4 Hz, 2H), 2.58 (s, 3H).

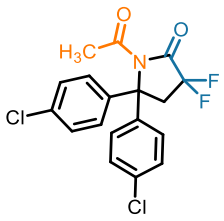
^{13}C-NMR (126 MHz, $CDCl_3$): δ 170.4, 164.8 (t, *J* = 31.8 Hz), 163.3, 161.3, 136.0 (d, *J* = 3.5 Hz), 129.7, 129.6, 115.6 (dd, *J* = 251.9, 129.4 Hz), 115.5 (d, *J* = 21.8 Hz), 68.7 (d, *J* = 3.5 Hz), 49.6 (t, *J* = 20.0 Hz), 27.1.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -103.8, -113.5.

FT-IR (ATR, neat; cm^{-1}): 3084, 2903, 1766, 1716, 1604, 1510, 1372, 1315, 1202.

HRMS (ESI) m/z, $[M+Na]^+$ calcd for $C_{18}H_{13}O_2NF_4+Na^+$: 374.0775; found 374.0775.

1-Acetyl-5,5-bis(4-chlorophenyl)-3,3-difluoropyrrolidin-2-one (31)



Compound **31** was obtained according to general procedure **1** from 4,4'-(ethene-1,1-diyl)bis(chlorobenzene) (124.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (128.7 mg, 0.25 mmol, 67% yield) after purification by column chromatography (24 g SiO_2, hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.35 (m, 4H), 7.16 (m, 4H), 3.19 (t, *J* = 14.2 Hz, 2H), 2.58 (s, 3H).

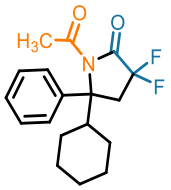
^{13}C-NMR (126 MHz, $CDCl_3$): δ 170.3, 164.7 (t, *J* = 31.8 Hz), 138.6, 134.5, 129.2, 128.8, 115.8 (d, *J* = 251.9 Hz), 68.6, 49.3 (t, *J* = 20.2 Hz), 27.0.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -103.62.

FT-IR (ATR, neat; cm^{-1}): 2959, 2925, 1811, 1722, 1597, 1493, 1434, 1404, 1343.

HRMS (ESI) m/z, $[M+Na]^+$ calcd for $C_{18}H_{13}O_2NCl_2F_2+Na^+$: 406.0182; found 406.0184.

1-Acetyl-5-cyclohexyl-3,3-difluoro-5-phenylpyrrolidin-2-one (32)



Compound **32** was obtained according to general procedure **1** from (1-cyclohexylvinyl)benzene (93.1 mg, 0.5 mmol, 1.0 equiv.), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv.), and anhydrous MeCN (15 mL). Isolated as a white solid (104.4 mg, 0.325 mmol, 65% yield) after purification by column chromatography (24 g SiO_2, hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.50 – 7.44 (m, 2H), 7.39 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 3.30 – 3.20 (m, 1H), 2.97 – 2.76 (m, 2H), 2.45 (s, 3H), 1.91 – 1.74 (m, 4H), 1.47 – 1.33 (m, 3H), 1.24 – 1.13 (m, 1H), 1.12 – 0.93 (m, 2H).

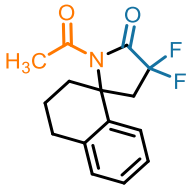
^{13}C-NMR (126 MHz, $CDCl_3$): δ 171.1, 165.2 (t, *J* = 31.9 Hz), 141.3, 128.5, 127.6 (d, *J* = 2.3 Hz), 125.7, 117.0 (t, *J* = 248.6 Hz), 68.7 (d, *J* = 5.1 Hz), 40.3, 39.0 (t, *J* = 21.5 Hz), 29.0, 27.1, 26.5 (d, *J* = 1.6 Hz), 26.2, 26.1.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -98.1 (d, *J* = 278.2 Hz), -99.7 (d, *J* = 278.2 Hz).

FT-IR (ATR, neat; cm^{-1}): 3086, 1776, 1712, 1590, 1565, 1490,1325, 1093.

HRMS (ESI) m/z, $[M+Na]^+$ calcd for $C_{18}H_{21}O_2NF_2+Na^+$: 344.1425; found 344.1433.

1'-Acetyl-4',4'-difluoro-3,4-dihydro-*2H*-spiro[naphthalene-1,2'-pyrrolidin]-5'-one (33)



Compound **33** was obtained according to general procedure **1** from 1-methylene-1,2,3,4-tetrahydronaphthalene (72.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (90.6 mg, 0.33 mmol, 66% yield) after purification by column chromatography (24 g SiO_2, hexane to hexane/EA = 5:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.19 – 7.13 (m, 2H), 7.13 – 7.08 (m, 1H), 7.03 – 6.97 (m, 1H), 2.96 – 2.84 (m, 2H), 2.84 – 2.75 (m, 1H), 2.69 – 2.56 (m, 1H), 2.54 (s, 3H), 2.52 – 2.42 (m, 1H), 2.11 – 2.02 (m, 1H), 2.01 – 1.91 (m, 1H), 1.86 – 1.72 (m, 1H).

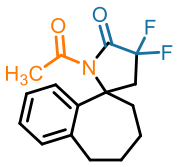
^{13}C-NMR (101 MHz, $CDCl_3$): δ 170.1, 165.1 (m), 138.6 (d, *J* = 2.1 Hz), 137.5, 129.5, 127.5, 127.3, 123.7, 116.8 (dd, *J* = 254.1, 248.9 Hz), 62.7 (d, *J* = 5.6 Hz), 46.0 (t, *J* = 19.6 Hz), 33.0, 29.2, 27.1, 20.9.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -99.1 (d, *J* = 276.5 Hz), -104.2 (d, *J* = 276.5 Hz).

FT-IR (ATR, neat; cm^{-1}): 2954, 2931, 2872, 1759, 1722, 1490, 1453, 1368.

HRMS (EI) m/z, [M]+ calcd for $C_{15}H_{15}O_2NF_2^+$: 279.1068; found 279.1065.

1'-Acetyl-4',4'-difluoro-6,7,8,9-tetrahydrospo[benzo[7]annulene-5,2'-pyrrolidin]-5'-one (34)



Compound **34** was obtained according to general procedure **1** from 5-methylene-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene (79.1 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (101.0 mg, 0.345 mmol, 69% yield) after purification by column chromatography (24 g SiO_2, hexane to hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.22 – 7.08 (m, 3H), 6.90 – 6.79 (m, 1H), 3.07 – 2.97 (m, 2H), 2.87 – 2.77 (m, 3H), 2.65 (s, 3H), 2.02 – 1.94 (m, 1H), 1.92 – 1.76 (m, 3H), 1.75 – 1.64 (m, 1H).

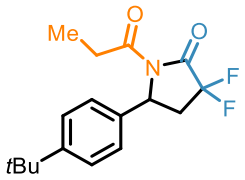
^{13}C-NMR (126 MHz, $CDCl_3$): δ 171.2, 165.2 (t, *J* = 31.8 Hz), 140.3, 139.3, 132.1, 127.9, 126.6, 125.7, 116.2 (t, *J* = 251.0 Hz), 68.8 – 68.6 (m), 42.5 (t, *J* = 19.9 Hz), 37.9, 36.1, 27.5, 26.8, 24.9.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -102.4 (d, *J* = 274.9 Hz), -104.4 (d, *J* = 275.0 Hz).

FT-IR (ATR, neat; cm^{-1}): 2925, 2910, 2852, 1765, 1704, 1374, 1320.

HRMS (ESI) m/z, $[M+Na]^+$ calcd for $C_{16}H_{17}NO_2F_2$+Na^+: 316.1117; found 316.1120.

5-(4-(*tert*-Butyl)phenyl)-3,3-difluoro-1-propionylpyrrolidin-2-one (35)



Compound **35** was obtained according to general procedure **1** from 4-*tert*-butylstyrene (94%) , (96 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and PrCN (15 mL). isolated as a white solid (114.0 mg, 0.38 mmol, 74% yield) after purification by column chromatography (12 g SiO_2, hexane to hexane/EA = 5:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36 (m, 2H), 7.13 (m, 2H), 5.44 – 5.31 (m, 1H), 3.11 – 3.01 (m, 1H), 2.91 (m, 2H), 2.53 (m, 1H), 1.30 (s, 9H), 1.13 (t, *J* = 7.3 Hz, 3H).

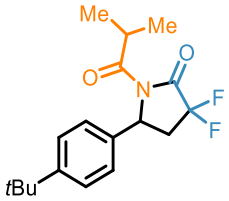
^{13}C-NMR (101 MHz, $CDCl_3$): δ 174.1, 164.2 (t, *J* = 32.1 Hz), 151.4, 136.6, 126.1, 125.3 (d, *J* =1.5), 117.4 (t, *J* = 252.4 Hz), 54.6 (dd, *J* = 5.1, 1.8 Hz), 37.5 (t, *J* = 21.2 Hz), 34.7, 31.5, 31.4, 8.0.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -99.6 (d, *J* = 275.1 Hz), -103.4 (d, *J* = 275.1 Hz).

FT-IR (ATR, neat; cm^{-1}): 2967, 1750, 1721, 1510, 1459, 1384, 1314, 1304, 1221.

HRMS (ESI) m/z, $[M+Na]^+$ calcd for $C_{17}H_{21}O_2NF_2+Na^+$: 332.1433; found 332.1431.

5-(4-(*tert*-Butyl)phenyl)-3,3-difluoro-1-isobutyrylpyrrolidin-2-one (36)



Compound **36** was obtained according to general procedure **1** from 4-*tert*-butylstyrene (94%) , (96 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and *i*PrCN (15 mL). Isolated as a white solid (122.8 mg, 0.38 mmol, 76% yield) after purification by column chromatography (12 g SiO_2, hexane to hexane/EA = 5:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.38 – 7.33 (m, 2H), 7.14 – 7.08 (m, 2H), 5.40 – 5.33 (m, 1H), 3.72 (hept, *J* = 6.6 Hz, 1H), 3.02 – 2.78 (m, 1H), 2.60 – 2.39 (m, 1H), 1.30 (s, 9H), 1.16 (dd, *J* = 6.6, 5.8 Hz, 6H).

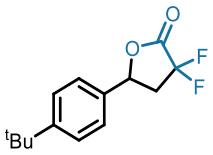
^{13}C-NMR (75 MHz, $CDCl_3$): δ 177.4, 163.7 (t, *J* = 32.0 Hz), 151.4, 136.7, 126.1, 125.1 (d, *J* = 1.4 Hz), 117.4 (d, *J* = 251.4 Hz), 54.7 (dd, *J* = 4.8, 2.2 Hz), 37.5 (t, *J* = 21.1 Hz), 35.0, 34.7, 31.4, 19.0, 17.9.

^{19}F-NMR (282 MHz, $CDCl_3$): δ -100.0 (d, *J* = 274.3 Hz), -103.4 (d, *J* = 274.3 Hz).

FT-IR (ATR, neat; cm^{-1}): 2962, 1752, 1726, 1516, 1463, 1390, 1314, 1224.

HRMS (ESI) m/z, $[M+Na]^+$ calcd for $C_{18}H_{23}F_2NO_2+Na^+$: 346.1588; found 346.1589.

5-(4-(*tert*-Butyl)phenyl)-3,3-difluorodihydrofuran-2(3*H*)-one (2)



Compound **2** was obtained according to general procedure **2** from 4-*tert*-butylstyrene (94%, 95 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a white solid (102.9 mg, 0.405 mmol, 81% yield) after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 10:1).

R_f Value: 0.4 in 10% EtOAc: Hexane.

Melting point: 64-66 °C

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.52 – 7.42 (m, 2H), 7.31 – 7.26 (m, 2H), 5.59 (dd, *J* = 9.0, 6.2 Hz, 1H), 3.17 – 3.03 (m, 1H), 2.75 – 2.58 (m, 1H), 1.33 (s, 9H).

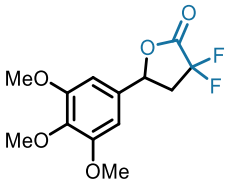
^{13}C-NMR (126 MHz, $CDCl_3$): δ 165.0 (dd, *J* = 33.9, 31.8 Hz), 153.0, 133.1, 126.1, 125.7, 115.7 (dd, *J* = 259.0, 249.8 Hz), 39.8 (dd, *J* = 22.2, 20.5 Hz), 34.8, 31.2.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -106.5 (d, *J* = 279.1 Hz), -109.2 (d, *J* = 279.1 Hz).

FT-IR (ATR, neat; cm^{-1}): 2962, 1805, 1509, 1463, 1418, 1361, 1319, 1251, 1211.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{14}H_{16}F_2O_2+H^+$: 255.1197; found: 255.1194.

3,3-Difluoro-5-(3,4,5-trimethoxyphenyl)dihydrofuran-2(*3H*)-one (37)



Compound **37** was obtained according to general procedure **2** from 1,2,3-trimethoxy-5-vinylbenzene (97.0 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a colourless oil (93.6 mg, 0.325 mmol, 65% yield), after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 10:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.19 (s, 1H), 6.93 (s, 1H), 5.29 (dd, *J* = 8.5, 5.2 Hz, 1H), 3.92 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H), 3.10 – 2.98 (m, 1H), 2.86 – 2.68 (m, 1H).

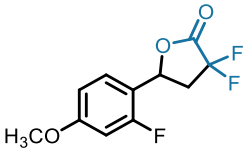
^{13}C-NMR (126 MHz, $CDCl_3$): δ 181.3 (t, *J* = 25.9 Hz), 159.1, 156.0, 143.7, 139.2, 117.2 (d, *J* = 2.5 Hz), 111.7 (dd, *J* = 253.3, 245.6 Hz), 107.9, 62.0, 61.4, 56.5, 52.2 (dd, *J* = 7.7, 5.4 Hz), 41.7 (t, *J* = 23.7 Hz).

^{19}F-NMR (471 MHz, $CDCl_3$): δ -105.9 (d, *J* = 274.0 Hz), -107.1 (d, *J* = 274.0 Hz).

FT-IR (ATR, neat; cm^{-1}): 2942, 1692, 1585, 1490, 1457, 1457, 1332, 1225, 1124, 1056, 967.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{13}H_{14}F_2O_5+H^+$:289.0917; found: 289.0918.

3,3-Difluoro-5-(2-fluoro-4-methoxyphenyl)dihydrofuran-2(*3H*)-one (38)



Compound **38** was obtained according to general procedure **2** from 2-fluoro-4-methoxy-1-vinylbenzene (76 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a colourless oil (70.1 mg, 0.285 mmol, 57% yield), after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 10:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.33 – 7.19 (m, 1H), 6.77 – 6.65 (m, 2H), 5.76 (dd, *J* = 8.6, 6.5 Hz, 1H), 3.82 (s, 3H), 3.19 – 3.05 (m, 1H), 2.82 – 2.62 (m, 1H).

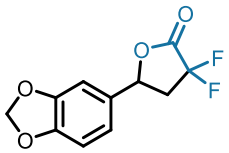
^{13}C-NMR (75 MHz, $CDCl_3$): δ 164.9 (dd, *J* = 34.0, 32.1 Hz), 162.2 (d, *J* = 11.4 Hz), 161.1 (d, *J* = 248.3 Hz), 128.1 (d, *J* = 5.1 Hz), 115.7 (dd, *J* = 258.1, 249.6 Hz), 115.4 (d, *J* = 12.6 Hz), 110.6 (d, *J* = 2.9 Hz), 102.4 (d, *J* = 24.5 Hz), 72.6 (dt, *J* = 7.3, 2.6 Hz), 55.9, 39.3 – 38.4 (m).

^{19}F-NMR (282 MHz, $CDCl_3$): δ -106.0 (d, *J* = 279.4 Hz), -108.9 (d, *J* = 279.4 Hz), -115.6 (s).

FT-IR (ATR, neat; cm^{-1}): 2901, 1744, 1322, 1314, 1314, 1231, 1055.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{11}H_9F_3O_3+H^+$: 247.0577; found 247.0577.

5-(Benzo[*d*][1,3]dioxol-5-yl)-3,3-difluorodihydrofuran-2(*3H*)-one (39)



Compound **39** was obtained according to general procedure **2** from 5-vinylbenzo[*d*][1,3]dioxole (74.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a colourless oil (99.3 mg, 0.41 mmol, 82% yield) after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 10:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.91 – 6.73 (m, 3H), 6.01 (s, 2H), 5.51 (dd, *J* = 8.9, 6.2 Hz, 1H), 3.15 – 3.01 (m, 1H), 2.72 – 2.52 (m, 1H).

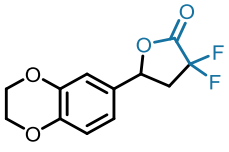
^{13}C-NMR (126 MHz, $CDCl_3$): δ 165.0 (t, *J* = 33.0, 31.5 Hz), 148.8 (d, *J* = 34.1 Hz), 129.8, 120.3, 115.8 (dd, *J* = 259.1, 250.0 Hz), 108.8, 106.3, 101.8, 77.3 – 77.2 (m), 40.1 (dd, *J* = 22.6, 20.4 Hz).

^{19}F-NMR (471 MHz, $CDCl_3$): δ -106.6 (d, *J* = 278.9 Hz), -109.1 (d, *J* = 278.9 Hz).

FT-IR (ATR, neat; cm^{-1}): 2918, 2848, 1806, 1609, 2586, 1511, 1462, 1441, 1304.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{11}H_8O_4F_2+H^+$: 242.0391; found 242.0387.

5-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-3,3-difluorodihydrofuran-2(*3H*)-one (40)



Compound **40** was obtained according to general procedure **2** from 6-vinyl-2,3-dihydrobenzo[*b*][1,4]dioxine (81 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a (79.4 mg, 0.31 mmol, 62% yield), after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 10:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.91 (d, *J* = 8.4, 1H), 6.86 (d, *J* = 2.2 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.2 Hz, 1H), 5.49 (dd, *J* = 8.9, 6.2, 1H), 4.27 (s, 4H), 3.13 – 3.00 (m, 1H), 2.71 – 2.56 (m, 1H).

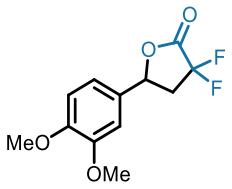
^{13}C-NMR (126 MHz, $CDCl_3$): δ 165.0 (t, *J* = 34.1, 32.4 Hz), 144.9, 144.2, 129.3, 119.2, 118.1, 115.9 (dd, *J* = 258.9, 250.0 Hz), 115.3, 77.1 – 77.0 (m), 64.5 (d, *J* = 8.0 Hz), 39.9 (dd, *J* = 22.2, 20.6 Hz).

^{19}F-NMR (471 MHz, $CDCl_3$): δ -106.6 (d, *J* = 279.2 Hz), -109.1 (d, *J* = 279.2 Hz).

FT-IR (ATR, neat; cm^{-1}): 2926, 2886, 2852, 1806, 1733, 1591, 1572, 1507, 1436, 1285.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{12}H_{10}F_2O_4+H^+$: 257.0623; found 257.0622.

5-(3,4-Dimethoxyphenyl)-3,3-difluorodihydrofuran-2(3*H*)-one (41)



Compound **41** was obtained according to general procedure **2** from 1,2-dimethoxy-4-vinylbenzene (82.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a colourless oil (81.3 mg, 0.315 mmol, 63% yield) after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 10:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.94 – 6.86 (m, 2H), 6.85 – 6.82 (m, 1H), 5.56 (dd, *J* = 9.0, 6.1 Hz, 1H), δ 3.90 (s, 3H), 3.90 (s, 3H), 3.16 – 3.04 (m, 1H), 2.75 – 2.59 (m, 1H).

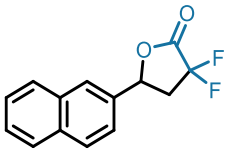
^{13}C-NMR (126 MHz, $CDCl_3$): δ 165.1 (t, *J* = 33.2, 32.2 Hz), 150.3, 149.7, 128.3, 118.9, 115.9 (dd, *J* = 259.1, 250.0 Hz), 111.3, 108.8, 77.5 – 77.5 (m), 56.2 (d, *J* = 4.6 Hz), 40.0 (dd, *J* = 22.2, 20.5 Hz).

^{19}F-NMR (471 MHz, $CDCl_3$): δ -106.60 (d, *J* = 279.2 Hz), -109.08 (d, *J* = 279.2 Hz).

FT-IR (ATR, neat; cm^{-1}): 2927, 2849, 1733, 1592, 1512, 1455, 1259.

HRMS (EI) m/z, $[M]^+$ calcd for $C_{12}H_{12}O_4F_2^+$: 258.0700; found 258.0698.

3,3-Difluoro-5-(naphthalen-2-yl)dihydrofuran-2(3*H*)-one (42)



Compound **42** was obtained according to general procedure **2** from 2-vinylnaphthalene (77.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a white solid (74.4 mg, 0.30 mmol, 60% yield) after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 10:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.5 Hz, 1H), 7. 85 – 7.90 (m, 2H), 7. 84 (m, 1H), 7.59 – 7.53 (m, 2H), 7. 41 (dd, *J* = 8.5, 1.9 Hz, 1H), 5. 79 (dd, *J* = 8.9, 6.3 Hz, 1H), 3.35 – 3.09 (m, 1H), 2.87 – 2.53 (m, 1H).

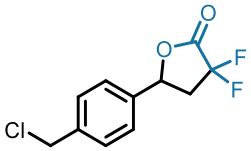
^{13}C-NMR (151 MHz, $CDCl_3$): δ 165.1 (dd, *J* = 34.0, 31.9 Hz), 133.8, 133.5, 133.1, 129.6, 128.3, 128.0, 127.2 (d, *J* = 18.7 Hz), 125.6, 122.5, 115.8 (dd, *J* = 259.2, 250.0 Hz), 77.3 – 77.3 (m), 40.5 – 39.9 (m).

^{19}F-NMR (471 MHz, $CDCl_3$): δ -106.3 (d, *J* = 279.2 Hz), -109.0 (d, *J* = 279.2 Hz).

FT-IR (ATR, neat; cm^{-1}): 2959, 1812, 1603, 1508, 1490, 1474, 1434, 1335.

HRMS (EI) m/z, $[M]^+$ calcd for $C_{14}H_{10}O_2F_2^+$: 248.0644; found 248.0643.

5-(4-(chloromethyl)phenyl)-3,3-difluorodihydrofuran-2(*3H*)-one (43)



Compound **43** was obtained according to general procedure **2** from 1-(chloromethyl)-4-vinylbenzene (76.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a colourless oil (72.6 mg, 0.295 mmol, 59% yield) after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 10:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.52 – 7.43 (m, 2H), 7.38 – 7.32 (m, 2H), 5.62 (dd, *J* = 8.8, 6.3 Hz, 1H), 4.60 (s, 2H), 3.21 – 3.09 (m, 1H), 2.72 – 2.55 (m, 1H).

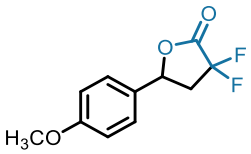
^{13}C-NMR (126 MHz, $CDCl_3$): δ 164.88 (dd, *J* = 33.8, 32.0 Hz), 139.19, 136.56, 129.49, 126.19, 115.63 (dd, *J* = 258.9, 250.2 Hz), 76.69 (dd, *J* = 7.1, 1.9 Hz), 45.50, 41.02 – 38.42 (m).

^{19}F-NMR (471 MHz, $CDCl_3$): δ -106.6 (d, *J* = 279.2 Hz), -109.1 (d, *J* = 279.2 Hz).

FT-IR (ATR, neat; cm^{-1}): 2961, 1794, 1431, 1423, 1321, 1315.

HRMS (EI) m/z, $[M]^+$ calcd for $C_{11}H_9O_2ClF_2$: 246.0255; found 246.0254.

3,3-Difluoro-5-(4-methoxyphenyl)dihydrofuran-2(*3H*)-one (44)



Compound **44** was obtained according to general procedure **2** from 1-methoxy-4-vinylbenzene (67 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a brown solid (59.3 mg, 0.26 mmol, 52% yield) after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 10:1).

^{1}H-NMR (400 MHz, $CDCl_3$): 7.30 – 7.25 (m, 2H), 6.99 – 6.91 (m, 2H), 5.56 (dd, *J* = 9.0, 6.1 Hz, 1H), 3.83 (s, 3H), 3.15 – 3.02 (m, 1H), 2.76 – 2.58 (m, 1H).

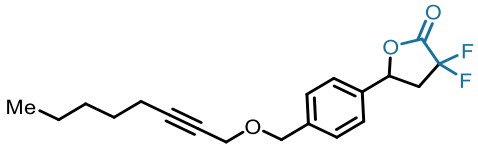
^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.2 – 164.7 (m), 160.7, 127.8, 127.6, 115.8 (dd, *J* = 258.9, 250.0 Hz), 77.22 – 77.15 (m), 55.4, 39.8 (dd, *J* = 18.2, 17.2 Hz).

^{19}F-NMR (377 MHz, $CDCl_3$): δ -106.6 (d, *J* = 279.1 Hz), -109.2 (d, *J* = 279.1 Hz).

FT-IR (ATR, neat; cm^{-1}): 2919, 2848, 1807, 1610, 1586, 1511, 1462, 1442.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{11}H_{10}O_3F_2+H^+$: 229.0669; found 229.0669.

3,3-Difluoro-5-(4-((oct-2-yn-1-yloxy)methyl)phenyl)dihydrofuran-2(*3H*)-one (45)



Compound **45** was obtained according to general procedure **2** from 1-((oct-2-yn-1-yloxy)methyl)-4-vinylbenzene (121 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a colourless oil (114.0 mg, 0.34 mmol, 68% yield) after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 10:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.47 –7.41 (m, 2H), 7.36 –7.30 (m, 2H), 5.61 (dd, *J* = 8.8, 6.2 Hz, 1H), 4.61 (s, 2H), 4.18 (t, *J* = 2.2 Hz, 2H), 3.19 – 3.06 (m, 1H), 1.71 – 2.56 (m, 1H), 2.29 – 2.18 (m, 2H), 1.54 (s, 2H), 1.43 – 1.30 (m, 4H), 0.90 (s, 3H).

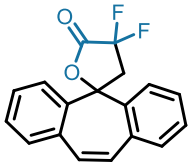
^{13}C-NMR (151 MHz, $CDCl_3$): δ 165.0 (dd, *J* = 33.9, 31.9 Hz), 139.8, 135.7, 128.8, 125.9, 115.7 (dd, *J* = 259.3, 250.1 Hz), 87.9, 75.6, 70.8, 58.2, 40.3 – 40.0 (m), 31.2, 28.5, 22.3, 18.9, 14.1.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -106.5 (d, *J* = 279.3 Hz), -109.1 (d, *J* = 279.3 Hz).

FT-IR (ATR, neat; cm^{-1}): 2931, 2658, 1730, 1630, 1512, 1465, 1406, 1354.

HRMS (ESI) m/z, $[M+OH]^-$ calcd for $[C_{19}H_{22}F_2O_3+OH]$: 353.1570; found 353.1570.

4',4'-Difluoro-3',4'-dihydro-5'*H*-spiro[dibenzo[*a,d*][7]annulene-5,2'-furan]-5'-one (46)



Compound **46** was obtained according to general procedure **2** from 5-methylene-*5H*-dibenzo[*a,d*][7]annulene (102.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a white solid (126.7 mg, 0.425 mmol, 85% yield) after purification by column chromatography (12 g SiO_2, pure hexane to hexane/EA= 10:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.74 – 7.70 (m, 2H), 7.48 – 7.40 (m, 4H), 7.38 – 7.33 (m, 2H), 7.12 (s, 2H), 2.97 (t, *J* = 14.8 Hz, 2H).

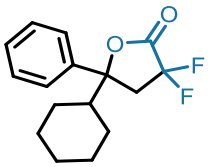
^{13}C-NMR (126 MHz, $CDCl_3$): δ 164.6 (t, *J* = 33.8 Hz), 138.6, 131.8, 131.4, 129.7, 129.4, 128.0, 122.3, 115.3 (t, *J* = 253.6 Hz), 84.2, 42.6 (t, *J* = 20.7 Hz).

^{19}F-NMR (471 MHz, $CDCl_3$): δ -104.3.

FT-IR (ATR, neat; cm^{-1}): 3032, 1808, 1487, 1459, 1432, 1240, 1105.

HRMS (ESI) *m/z*, , $[M+H]^+$ calcd for $C_{18}H_{12}O_2F_2+H^+$: 299.0878; found 299.0878.

5-Cyclohexyl-3,3-difluoro-5-phenyldihydrofuran-2(3*H*)-one (47)



Compound **47** was obtained according to general procedure **2** from (1-cyclohexylvinyl)benzene (93.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a white solid (60.0 mg, 0.215 mmol, 43% yield) after purification by column chromatography (12 g SiO_2, pure hexane to hexane/EA= 10:1).

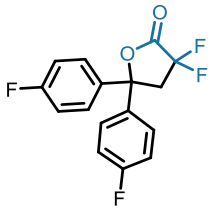
^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.43 – 7.31 (m, 3H), 7.29 – 7.24 (m, 2H), 3.17 – 2.89 (m, 2H), 1.98 – 1.67 (m, 4H), 1.66 – 1.58 (m, 2H), 1.24 – 1.14 (m, 2H), 1.07 – 0.90 (m, 2H), 0.86 – 0.77 (m, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ 164.9 (t, *J* = 33.1 Hz), 139.8, 128.4, 128.3, 125.7, 115.8 (dd, *J* = 254.4, 1.3 Hz), 88.9 – 88.8 (m), 48.7, 41.6 (t, *J* = 20.8 Hz), 27.3, 26.6, 26.2, 26.0, 25.9.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -101.9 (d, *J* = 280.9 Hz), -103.8 (d, *J* = 280.9 Hz).

HRMS (ESI) *m/z*, $[M+Na]^+$ calcd for $C_{16}H_{18}O_2F_2+Na^+$: 303.1169; found 303.1167.

3,3-Difluoro-5,5-bis(4-fluorophenyl)dihydrofuran-2(*3H*)-one (48)



Compound **48** was obtained according to general procedure **2** from 4,4'-(ethene-1,1-diyl)bis(fluorobenzene) (108.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a white solid (88.4 mg, 0.285 mmol, 57% yield) after purification by column chromatography (12 g SiO_2, pure hexane to hexane/EA= 10:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.35 – 7.29 (m, 4H), 7.11 – 7.04 (m, 4H), 3.39 (t, *J* = 13.7 Hz, 2H).

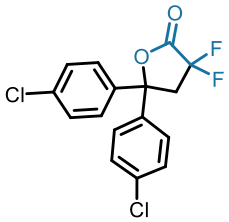
^{13}C-NMR (126 MHz, $CDCl_3$): δ 164.2 (t, *J* = 33.0 Hz), 163.8, 161.8, 137.4 (d, *J* = 3.5 Hz), 127.4 (d, *J* = 8.5 Hz), 116.1 (d, *J* = 21.9 Hz), 115.5 (t, *J* = 254.7 Hz), 85.9 (t, *J* = 4.5 Hz), 44.8 (t, *J* = 20.8 Hz).

^{19}F-NMR (471 MHz, $CDCl_3$): δ -104.6, -112.4.

FT-IR (ATR, neat; cm^{-1}): 3079, 1802, 1602, 1506, 1417, 1345.

HRMS (EI) *m/z*, $[M]^+$ calcd $C_{16}H_{10}O_2F_4$: 310.0609; found 310.0610.

5,5-Bis(4-chlorophenyl)-3,3-difluorodihydrofuran-2(*3H*)-one (49)



Compound **49** was obtained according to general procedure **2** from 4,4'-(ethene-1,1-diyl)bis(chlorobenzene) (124.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a white solid (106.3 mg, 0.31 mmol, 62% yield) after purification by column chromatography (12 g SiO_2, pure hexane to hexane/EA= 10:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.46 – 7.36 (m, 4H), 7.28 – 7.18 (m, 4H), 3.41 (t, *J* = 13.6, 2H).

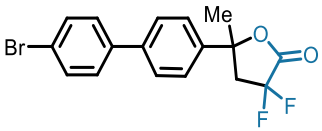
^{13}C-NMR (126 MHz, $CDCl_3$): δ 164.0 (t, *J* = 33.1 Hz), 139.8, 135.2, 129.4, 126.8, 115.3 (t, *J* = 254.8 Hz), 85.6 (t, *J* = 4.5 Hz), 44.5 (t, *J* = 21.0 Hz).

^{19}F-NMR (471 MHz, $CDCl_3$): δ -104.7.

FT-IR (ATR, neat; cm^{-1}): 2959, 2925, 1810, 1721, 1596, 1492, 1433, 1404, 1342, 1296.

HRMS (EI) *m/z*, $[M]^+$ calcd $C_{16}H_{10}O_2Cl_2F_2$: 342.0018; found 342.0020.

5-(4'-Bromo-[1,1'-biphenyl]-4-yl)-3,3-difluoro-5-methyldihydrofuran-2(*3H*)-one (50)



Compound **50** was obtained according to general procedure **2** from 4-bromo-4'-(prop-1-en-2-yl)-1,1'-biphenyl (136.5, 0.5 mmol, 1.0 equiv), *fac*-$[Ir(ppy)_3]$ (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as white solid (131.7 mg, 0.36 mmol, 72% yield), after purification by column chromatography (12 g SiO_2, pure hexane to hexane/EA= 10:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.62 – 7.54 (m, 4H), 7.47 – 7.38 (m, 4H), 3.07 – 2.90 (m, 1H), 1.86 (s, 1H).

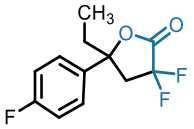
^{13}C-NMR (126 MHz, $CDCl_3$): δ 164.7 (t, *J* = 33.0 Hz), 142.0, 140.3, 139.1, 132.2, 128.8, 127.6, 125.4, 124.6, 122.2, 116.0 (dd, *J* = 255.7, 252.9 Hz), 83.9 (dd, *J* = 5.2, 3.5 Hz), 45.1 (t, *J* = 20.6 Hz), 30.3.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -101.9 (d, *J* = 282.0 Hz), -104.8 (d, *J* = 282.0 Hz).

FT-IR (ATR, neat; cm^{-1}): 1802, 1586, 1482, 1433, 1388, 1344, 1307, 1281.

HRMS (EI) *m/z*, $[M]^+$ calcd $C_{17}H_{13}O_2BrF_2$: 366.0059; found 366.0060.

5-Ethyl-3,3-difluoro-5-(4-fluorophenyl)dihydrofuran-2(*3H*)-one (51)



Compound **51** was obtained according to general procedure **2** from 1-(but-1-en-2-yl)-4-fluorobenzene (75.0 mg, 0.5 mmol, 1.0 equiv), *fac*-$[Ir(ppy)_3]$ (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as pale-yellow gel (74.4 mg, 0.305 mmol, 61% yield), after purification by column chromatography (12 g SiO_2, pure hexane to hexane/EA= 10:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.26 (m, 2H), 7.14 – 7.06 (m, 2H), 3.01 – 2.87 (m, 2H), 2.13 – 1.99 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H).

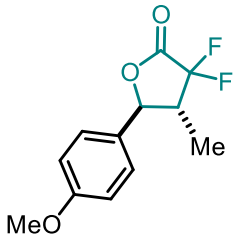
^{13}C-NMR (126 MHz, $CDCl_3$): δ 164.4 (t, *J* = 33.4 Hz), 163.4, 161.4, 136.6, 126.4 (d, *J* = 8.2 Hz), 115.9, 115.7, 115.7 (t, *J* = 254.1 Hz), 86.3 (t, *J* = 4.4 Hz), 43.7 (t, *J* = 20.7 Hz), 36.0, 7.8.

^{19}F-NMR [^{1}H Coupled] (471 MHz, $CDCl_3$): δ -103.0 – 102.0 (m), -104.1 – 102.9 (m), -113.5 – 112.4 (m).

FT-IR (ATR, neat; cm^{-1}): 2966, 2949, 1797, 1752, 1605, 1512, 1465, 1349.

HRMS (EI) *m/z*, $[M]^+$ calcd $C_{12}H_{11}F_3O_2$: 244.0710; found 244.0710.

3,3-Difluoro-5-(4-methoxyphenyl)-4-methyldihydrofuran-2(*3H*)-one (52)



Compound **52** was obtained according to general procedure **2** from anethole (74.0 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as colourless oil (81.1 mg, 0.34 mmol, 67% yield), after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 10:1). Crude d.r. = 9:1, isolated d.r. > 20:1.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.47 – 7.25 (m, 2H), 7.12 – 6.90 (m, 2H), 5.08 (d, *J* = 9.7 Hz, 1H), 3.90 (s, 3H), 2.88 – 2.50 (m, 1H), 1.31 – 1.22 (m, 3H).

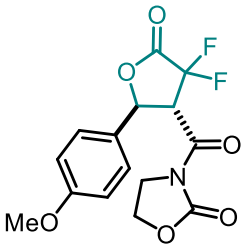
^{13}C-NMR (75 MHz, $CDCl_3$): δ 165.3 (t, *J* = 31.3 Hz), 161.0, 128.3, 126.5, 115.9 (dd, *J* = 260.3, 250.7 Hz), 114.6, 83.7 (d, *J* = 9.5 Hz), 55.5, 45.8 (t, *J* = 20.3 Hz), 6.8 (d, *J* = 6.9 Hz).

^{19}F-NMR (282 MHz, $CDCl_3$): δ -116.32 (d, *J* = 274.0, 11.2 Hz), -121.39 (d, *J* = 274.0, 22.7 Hz).

FT-IR (ATR, neat; cm^{-1}): 2941, 2842, 1805, 1517, 1252, 1205, 1132.

HRMS (ESI) *m/z*, $[M+H]^+$ calcd for $C_{12}H_{12}F_2O_3+H^+$: 243.0827; found 243.0825.

3-(4,4-Difluoro-5-oxo-2-phenyltetrahydrofuran-3-carbonyl)oxazolidin-2-one (53)



Compound **53** was obtained according to general procedure **2** reaction time was 24 h, from 3-cinnamoyloxazolidin-2-one (108.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as white solid (91.7 mg, 0.295 mmol, 59% yield), after purification by column chromatography (12 g SiO_2, hexane/EA= 10:1). Crude d.r. = 8:1, isolated d.r. > 20:1.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.40 (m, 3H), 7.40 – 7.35 (m, 2H), 6.07 (d, *J* = 7.7 Hz, 1H), 5.44 – 5.32 (m, 1H), 4.55 – 4.40 (m, 2H), 4.17 – 4.02 (m, 2H).

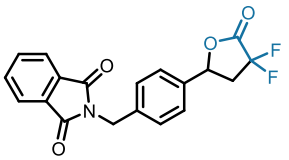
^{13}C-NMR (75 MHz, $CDCl_3$): δ 163.1 – 163.0 (m), 162.9 (dd, *J* = 32.6, 31.3 Hz), 152.9, 134.8, 130.1, 129.4, 126.5, 114.2 (dd, *J* = 266.7, 257.3 Hz), 78.8 (dd, *J* = 5.5, 1.3 Hz), 62.5, 52.9 (dd, *J* = 20.3, 18.4 Hz), 42.9.

^{19}F-NMR (377 MHz, $CDCl_3$) δ -107.4 (d, *J* = 274.9 Hz), -111.5 (d, *J* = 274.9 Hz).

FT-IR (ATR, neat; cm^{-1}): 2995, 2930, 1815, 1775, 1693, 1476, 1390, 1365, 1293.

HRMS (ESI) *m/z*, $[M+H]^+$ calcd $C_{11}H_9F_3O_3+H^+$: 247.0577; found 247.0577.

5-(3,4-Dimethoxyphenyl)-3,3-difluorodihydrofuran-2(*3H*)-one (54)



Compound **54** was obtained according to general procedure **2** reaction time was 24 h, from 2-(4-vinylbenzyl)isoindoline-1,3-dione (131.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a colourless oil (114.2 mg, 0.32 mmol, 64% yield) after purification by column chromatography (12 g SiO_2, hexane/EA= 10:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.86 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.52 – 7.49 (m, 2H), 7.31 – 7.28 (m, 2H), 5.58 (dd, *J* = 8.9, 6.2 Hz, 1H), 4.86 (s, 2H), 3.15 – 3.04 (m, 1H), 2.66 – 2.52 (m, 1H).

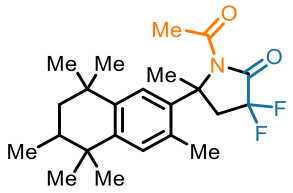
^{13}C-NMR (126 MHz, $CDCl_3$): δ 168.0, 164.8 (dd, *J* = 33.6, 32.2 Hz), 138.0, 135.8, 134.2, 132.0, 129.4, 126.0, 123.5, 115.5 (dd, *J* = 259.3, 246.3 Hz), 76.7 – 76.6 (m), 41.1, 40.4 – 39.4 (m).

^{19}F-NMR (471 MHz, $CDCl_3$): δ -106.6 (d, *J* = 279.9 Hz), -109.1 (d, *J* = 279.2 Hz).

FT-IR (ATR, neat; cm^{-1}): 2943, 1816, 1760, 1709, 1610, 1466, 1432, 1334.

HRMS (EI) *m/z*, $[M]^+$ calcd for $C_{12}H_{12}O_4F_2$: 258.0700; found 258.0698.

1-Acetyl-3,3-difluoro-5-methyl-5-(5,5,6,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)pyrrolidin-2-one (55)



Compound **55** was obtained according to general procedure **1** from 1,1,2,4,4-pentamethyl-6-(prop-1-en-2-yl)-1,2,3,4-tetrahydronaphthalene (121.1 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (96.1 mg, 0.25 mmol, 51% yield) after purification by column chromatography (40 g SiO_2, hexane/EA = 5:1)

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.22 (d, *J* = 6.4 Hz, 1H), 7.05 (s, 1H), 2.89 – 2.74 (m, 1H), 2.67 – 2.56 (m, 1H), 2.55 (d, *J* = 1.2 Hz, 3H), 2.16 (s, 3H), 2.04 (s, 3H), 1.91 – 1.78 (m, 1H), 1.67 – 1.55 (m, 1H), 1.42 – 1.33 (m, 1H), 1.32 – 1.22 (m, 9H), 1.03 (d, *J* = 8.9 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H).

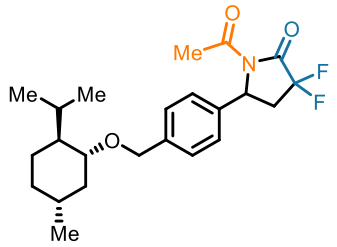
^{13}C-NMR (126 MHz, $CDCl_3$): δ 169.8 (d, *J* = 3.1 Hz), 165.0 (t, *J* = 32.3 Hz), 145.5 (d, *J* = 2.3 Hz), 142.6 (d, *J* = 9.2 Hz), 136.7 (dd, *J* = 9.2, 2.0 Hz), 131.9 (d, *J* = 15.5 Hz), 129.9 (d, *J* = 3.1 Hz), 124.5 (d, *J* = 16.5 Hz), 116.6 (dd, *J* = 253.7, 248.5 Hz), 62.9 (d, *J* = 5.0 Hz), 44.6 (t, *J* = 19.8 Hz), 43.7 (d, *J* = 9.7 Hz), 37.4 (d, *J* = 3.2 Hz), 34.6 (d, *J* = 24.4 Hz), 34.3 (d, *J* = 3.1 Hz), 32.5, 32.1 (d, *J* = 6.4 Hz), 28.5 (d, *J* = 39.6 Hz), 27.1 (d, *J* = 7.3 Hz), 26.4 (d, *J* = 2.5 Hz), 25.0 (d, *J* = 24.6 Hz), 21.8, 16.9 (d, *J* = 4.4 Hz).

^{19}F-NMR (471 MHz, $CDCl_3$): δ -99.1 (d, *J* = 277.8 Hz), -105.1 (d, *J* = 276.5 Hz).

FT-IR (ATR, neat; cm^{-1}): 2964, 2904, 1754, 1720, 1455, 1371, 1317, 1299.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{23}H_{31}O_2NF_2+H^+$: 392.2390; found 392.2396.

1-Acetyl-3,3-difluoro-5-(4-((((*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)phenyl)-pyrrolidine-2-one (56)



Compound **56** was obtained according to general procedure **1** from 1-((((*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)-4-vinylbenzene (123.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (130.0 mg, 0.32 mmol, 64% yield) after purification by column chromatography (40 g SiO_2, hexane/EA = 5:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.31 (m, 2H), 7.21 – 7.13 (m, 2H), 5.42 – 5.32 (m, 1H), 4.64 (dd, *J* = 11.5, 1.9 Hz, 1H), 4.36 (dd, *J* = 11.5, 2.8 Hz, 1H), 3.24 – 3.11 (m, 1H), 3.01 – 2.82 (m, 1H), 2.58 (d, *J* = 0.8 Hz, 3H), 2.55 – 2.43 (m, 1H), 2.34 – 2.22 (m, 1H), 2.22 – 2.13 (m, 1H), 1.71 – 1.58 (m, 2H), 1.44 – 1.24 (m, 2H), 1.01 – 0.83 (m, 9H), 0.71 (t, *J* = 6.6 Hz, 3H).

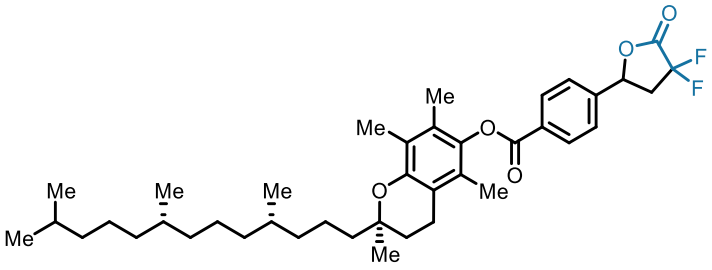
^{13}C-NMR (101 MHz, $CDCl_3$): δ 170.0, 164.2 (t, *J* = 32.6, 31.6 Hz), 139.6, 138.6, 128.6 (d, *J* = 4.7 Hz), 125.6 (d, *J* = 1.7 Hz), 117.3 (dd, *J* = 253.5, 251.7 Hz), 79.2 (d, *J* = 5.0 Hz), 70.0, 54.6 (d, *J* = 5.1 Hz), 48.4, 40.4, 37.5 (t, *J* = 21.2 Hz), 34.7, 31.7, 26.4 – 24.5 (m), 23.4, 22.5, 21.1.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -99.6 (dd, *J* = 275.6, 5.5 Hz), -103.7 (dd, *J* = 275.6, 11.9 Hz).

FT-IR (ATR, neat; cm^{-1}): 2953, 2929, 2866, 1804, 1726, 1567, 1455, 1422, 1385.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{23}H_{31}F_2NO_3+H^+$: 408.2345; found 408.3002.

(*S*)-2,5,7,8-Tetramethyl-2-((*4S,8S*)-4,8,12-trimethyltridecyl)chroman-6-yl-4-(4,4-difluoro-5-oxotetrahydrofuran-2-yl)benzoate (57)



Compound **57** was obtained according to general procedure **2** from (*S*)-2,5,7,8-tetramethyl-2-((*4S,8S*)-4,8,12-trimethyltridecyl)chroman-6-yl-4-vinylbenzoate (280.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a colourless oil (186.4 mg, 0.285 mmol, 57% yield) after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 10:1).

^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.36 – 8.28 (m, 2H), 7.54 – 7.46 (m, 2H), 5.72 (dd, *J* = 8.7, 6.5 Hz, 1H), 3.27 – 3.17 (m, 1H), 2.72 – 2.59 (m, 3H), 2.12 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.88 – 1.74 (m, 2H), 1.65 – 1.01 (m, 24H), 0.90 – 0.83 (m, 12H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ 164.6 (d, *J* = 33.1 Hz), 164.3, 149.6, 141.6, 140.5, 131.0, 130.8, 126.8, 125.6, 125.0, 123.3, 117.6, 115.3 (dd, *J* = 258.6, 251.0 Hz), 76.1 (d, *J* = 6.3 Hz), 75.2, 40.5, 40.0 (t, *J* =

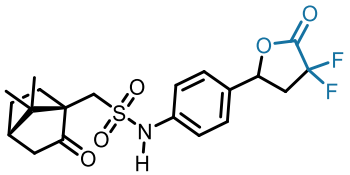
21.6 Hz), 39.7 (d, *J* = 13.9 Hz), 39.4 (d, *J* = 4.3 Hz), 37.4 (t, *J* = 12.3 Hz), 32.8, 31.1 (d, *J* = 30.1 Hz), 28.0, 24.8, 24.5, 24.2, 23.7, 22.7 (d, *J* = 13.9 Hz), 21.1, 20.7, 19.7 (t, *J* = 8.0 Hz), 13.1, 12.2, 11.9.

^{19}F-NMR [^{1}H Coupled] (565 MHz, $CDCl_3$): δ -105.8 – -107.2 (m), -108.4 – -109.4 (m).

FT-IR (ATR, neat; cm^{-1}): 2949, 2926, 2667, 2367, 2343, 1817, 1713, 1615, 1579, 1460, 1414, 1378.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{40}H_{56}F_2O_5+H^+$: 655.4169; found 655.4182.

N-(4-(4,4-Difluoro-5-oxotetrahydrofuran-2-yl)phenyl)-1-((*1S*,*4S*)-7,7-dimethyl-2-oxobicyclo-[2.2.1]heptan-1-yl)methanesulfonamide (58)



Compound **58** was obtained according to general procedure **2** from 1-((*1S*,*4S*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-(4-vinylphenyl)methanesulfonamide (166.5 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a white solid (162.3 mg, 0.38 mmol, 76% yield), after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 3:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.41 – 7.35 (m, 2H), 7.35 – 7.30 (m, 2H), 5.59 (dd, *J* = 8.9, 6.2 Hz, 1H), 3.33 (d, *J* = 15.3 Hz, 1H), 3.18 – 3.07 (m, 1H), 2.91 (d, *J* = 15.4 Hz, 1H), 2.72 – 2.58 (m, 1H), 2.49 – 2.42 (m, 1H), 2.21 – 2.05 (m, 4H), 1.99 (d, *J* = 15.3 Hz, 1H), 1.54 – 1.44 (m, 1H), 0.97 (s, 3H), 0.86 (s, 3H).

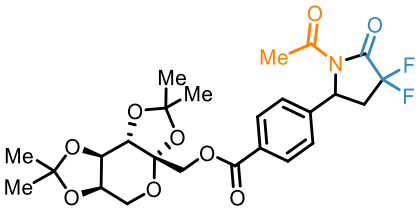
^{13}C-NMR (126 MHz, $CDCl_3$): δ 218.0, 164.9 (t, *J* = 32.8 Hz), 139.1 (d, *J* = 3.2 Hz), 133.1, 127.2 (d, *J* = 5.6 Hz), 122.4 (d, *J* = 1.8 Hz), 115.7 (dd, *J* = 259.2, 250.2 Hz), 76.8 (dd, *J* = 7.1, 1.7 Hz), 60.0, 49.9, 49.4, 43.3, 43.0, 40.1 – 39.7 (m), 27.8, 27.2, 20.1, 19.4.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -106.5 (d, *J* = 279.3 Hz), -109.0 (m).

FT-IR (ATR, neat; cm^{-1}): 3324, 3304, 2968, 2942, 2880, 1808, 1785, 1682, 1600, 1532, 1421, 3121.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{23}F_2NO_5S+H^+$: 428.1338; found 428.1339.

((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-Tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 4-(1-acetyl-4,4-difluoro-5-oxopyrrolidin-2-yl)benzoate (59)



Compound **59** was obtained according to general procedure **1** from (((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl-4-vinylbenzoate (195.0 mg, 0.5 mmol), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (189.0 mg, 0.36 mmol, 72% yield) after purification by column chromatography (40 g SiO_2, hexane/EA = 5:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.11 – 8.03 (m, 2H), 7.30 – 7.24 (m, 3H), 5.47 – 5.37 (m, 1H), 4.70 – 4.59 (m, 2H), 4.47 – 4.39 (m, 1H), 4.38 – 4.31 (m, 1H), 4.28 – 4.21 (m, 1H), 4.02 – 3.90 (m, 1H), 3.84

– 3.77 (m, 1H), 3.08 – 2.85 (m, 1H), 2.61 (s, 3H), 2.51 (m, 1H), 1.55 (s, 3H), 1.45 (d, *J* = 2.9 Hz, 3H), 1.38 (s, 3H), 1.34 (s, 3H).

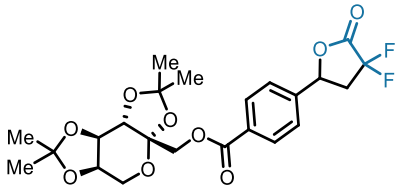
^{13}C-NMR (101 MHz, $CDCl_3$): δ 169.9, 165.3, 163.9 (dd, *J* = 31.5, 1.7 Hz), 144.4, 130.6, 130.1 (d, *J* = 2.0 Hz), 125.5, 116.9 (dd, *J* = 251.3 Hz), 109.2, 108.9, 101.6, 70.8, 70.6, 70.1, 65.7 (d, *J* = 2.2 Hz), 61.4, 54.3 (d, *J* = 5.2 Hz), 37.1 (t, *J* = 21.5 Hz), 26.5, 25.9 (d, *J* = 1.6 Hz), 25.6, 25.4, 24.0.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -99.8 (dd, *J* = 276.2, 25.5 Hz), -104.0 (dd, *J* = 276.2, 4.2 Hz).

FT-IR (ATR, neat; cm^{-1}): 2991, 2942, 1765, 1722, 1662, 1614, 1537, 1375.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{25}H_{29}F_2NO_9+H^+$: 526.1883; found 526.1881.

((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-Tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3*a*-yl)methyl 4-(4,4-difluoro-5-oxotetrahydrofuran-2-yl)benzoate (60)



Compound **60** was obtained according to general procedure **2** from ((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3*a*-yl)methyl 4-vinylbenzoate (195.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a white solid (179.8 mg, 0.37 mmol, 74% yield) after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 5:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.18 – 8.11 (m, 1H), 7.47 – 7.38 (m, 2H), 5.67 (dd, *J* = 8.7, 6.4 Hz, 1H), 4.72 – 4.67 (m, 1H), 4.64 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.44 (d, *J* = 2.6 Hz, 1H), 4.39 – 4.32 (m, 1H), 4.30 – 4.22 (m, 1H), 4.00 – 3.91 (m, 1H), 3.87 – 3.75 (m, 1H), 3.25 – 3.12 (m, 1H), 2.73 – 2.53 (m, 1H), 1.55 (s, 3H), 1.46 (s, 3H), 1.36 (d, *J* = 4.2 Hz, 6H).

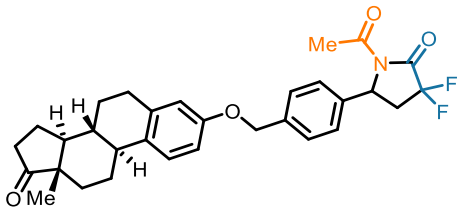
^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.3, 164.5 (m), 141.4, 131.2 (m), 130.8, 127.7 (m), 125.6, 109.4, 109.0, 101.7, 76.2 (m), 70.8 (d, *J* = 13.0 Hz), 70.2, 65.9, 61.5, 40.0 (t, *J* = 21.8 Hz), 26.7, 26.0, 25.6, 24.2.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -106.5 (dd, *J* = 280.1, 3.1 Hz), -109.1 (dd, *J* = 280.1, 10.3 Hz).

FT-IR (ATR, neat; cm^{-1}): 2942, 2936, 1722, 1664, 1613, 1531, 1423, 1317.

HRMS (ESI) m/z, $[M]^-$ calcd for $C_{23}H_{26}F_2O_9$+OH:501.1578; found 501.1580.

1-Acetyl-3,3-difluoro-5-(4-((((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)methyl)phenyl)pyrrolidin-2-one (61)



Compound **61** was obtained according to general procedure **1** from 1(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-((4-vinylbenzyl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (193.3 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0

equiv), and anhydrous MeCN (15 mL). Isolated as white solid (104.3 mg, 0.205 mmol, 41% yield)after purification by column chromatography (40 g SiO_2, hexane/EA = 5:1)

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.43 (m, 2H), 7.23 (s, 1H), 7.21 (m, 2H), 6.77 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.71 (m, 1H), 5.45 – 5.35 (m, 1H), 5.01 (s, 2H), 3.03 – 2.83 (m, 3H), 2.60 (s, 3H), 2.56 – 2.46 (m, 2H), 2.43 – 2.37 (m, 1H), 2.33 – 2.20 (m, 1H), 2.20 – 2.08 (m, 1H), 2.08 – 1.92 (m, 3H), 1.68 – 1.52 (m, 4H), 1.50 – 1.37 (m, 2H), 0.91 (s, 3H).

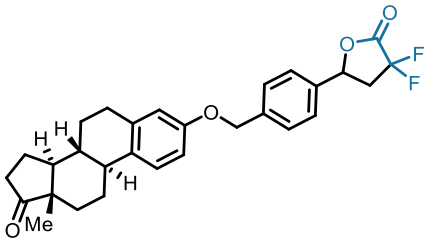
^{13}C-NMR (101 MHz, $CDCl_3$): δ 221.0, 170.0, 164.2 (dd, *J* = 33.0, 32.1 Hz), 139.6, 138.6, 128.6 (d, *J* = 4.7 Hz,), 125.6 (d, *J* = 1.7 Hz), 117.3 (dd, *J* = 253.5, 251.7 Hz), 79.2 (d, *J* = 5.0 Hz), 70.0, 54.6 (d, *J* = 5.1 Hz), 48.4, 40.4, 37.5 (t, *J* = 21.2 Hz), 34.7, 31.7, 25.6, 23.4, 22.5, 21.1, 16.2.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -99.6 (d, *J* = 276.1 Hz), -103.7 (d, *J* = 276.1 Hz).

FT-IR (ATR, neat; cm^{-1}): 2925, 2891, 2857, 1757, 1721, 1610, 1577, 1498, 1460, 1429, 1373.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{31}H_{33}O_4NF_2+H^+$: 522.2449; found 522.2450.

3,3-Difluoro-5-(4-((((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)methyl)phenyl)dihydrofuran-2(3*H*)-one (62)



Compound **62** was obtained according to general procedure **2** from (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-((4-vinylbenzyl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (193.3 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a white solid (117.6 mg, 0.245 mmol, 49% yield), after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 10:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.47 (m, 2H), 7.40 – 7.33 (m, 2H), 7.21 (dd, *J* = 8.6, 1.0 Hz, 1H), 6.78 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.74 – 6.69 (m, 1H), 5.62 (dd, *J* = 8.8, 6.2 Hz, 1H), 5.06 (s, 2H), 3.22 – 3.06 (m, 1H), 2.93 – 2.85 (m, 2H), 2.65 (m, 1H), 2.56 – 2.46 (m, 1H), 2.44 – 2.35 (m, 1H), 2.31 – 2.21 (m, 1H), 2.20 – 2.11 (m, 1H), 2.11 – 1.98 (m, 2H), 1.98 – 1.92 (m, 1H), 1.70 – 1.51 (m, 4H), 1.50 – 1.37 (m, 2H), 0.91 (s, 3H).

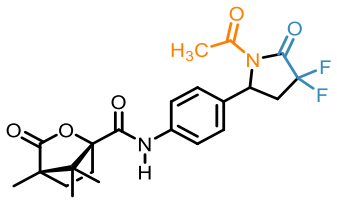
^{13}C-NMR (101 MHz, $CDCl_3$): δ 221.0, 165.0 (dd, *J* = 34.1, 2.0 Hz), 156.7, 139.2, 138.1, 135.9, 132.8, 128.2, 126.6, 126.1, 115.7 (dd, *J* = 258.9, 250.2 Hz), 115.0, 112.5, 69.4, 50.6, 48.1, 44.1, 40.1 (dd, *J* = 22.2, 20.8 Hz), 38.5, 36.0, 31.7, 29.8, 26.7, 26.0, 21.7, 14.0.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -106.5 (d, *J* = 279.4), -109.0 (d, *J* = 279.4).

FT-IR (ATR, neat; cm^{-1}): 2928, 2857, 1810, 1732, 1607, 1574, 1498, 1449.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{29}H_{30}F_2O_4+H^+$: 481.2185; found 481.2175.

(1*R*)-*N*-(4-(1-Acetyl-4,4-difluoro-5-oxopyrrolidin-2-yl)phenyl)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxamide (63)



Compound **63** was obtained according to general procedure **1** from (1*R*)-4,7,7-trimethyl-3-oxo-*N*-(4-vinylphenyl)-2-oxabicyclo[2.2.1]heptane-1-carboxamide (148.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (132.0 mg, 0. 305 mmol, 61% yield) after purification by column chromatography (40 g SiO_2, hexane/EA = 5:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.62 – 7.55 (m, 2H), 7.22 – 7.16 (m, 2H), 5.40 – 5.30 (m, 1H), 3.00 – 2.83 (m, 1H), 2.58 (s, 3H), 2.56 – 2.45 (m, 1H), 2.03 – 1.94 (m, 2H), 1.85 – 1.64 (m, 2H), 1.17 – 1.12 (m, 6H), 0.96 (s, 3H).

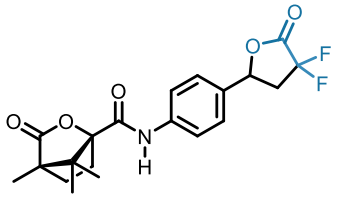
^{13}C-NMR (126 MHz, $CDCl_3$): δ 178.0, 170.1, 165.5, 164.1 (t, *J* = 32.1 Hz), 137.0, 136.0, 126.6, 120.6, 117.2 (dd, *J* = 253.8, 251.5 Hz), 92.5, 55.6, 54.6, 54.4 (d, *J* = 4.9 Hz), 37.4 (t, *J* = 21.3 Hz), 30.6 (d, *J* = 3.1 Hz), 29.2, 25.7, 16.9, 16.7, 9.8.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -99.6 (dd, *J* = 275.8, 22.5), -103.9 (dd, *J* = 275.8, 6.0).

FT-IR (ATR, neat; cm^{-1}): 3341, 2967, 1785, 1759, 1719, 1678, 1601, 1536, 1421.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{22}H_{24}F_2N_2O_5+H^+$: 435.1726; found 435.1722.

(1*R*)-*N*-(4-(4,4-Difluoro-5-oxotetrahydrofuran-2-yl)phenyl)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxamide (64)



Compound **64** was obtained according to general procedure **2** from ((1*R*)-4,7,7-trimethyl-3-oxo-*N*-(4-vinylphenyl)-2-oxabicyclo[2.2.1]heptane-1-carboxamide (150.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a white solid (143.0 mg, 0.365 mmol, 73% yield) after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 10:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.71 – 7.65 (m, 2H), 7.40 – 7.30 (m, 2H), 5.59 (dd, *J* = 8.9, 6.3 Hz, 1H), 3.19 – 3.04 (m, 1H), 2.73 – 2.55 (m, 2H), 2.08 – 1.96 (m, 2H), 1.86 – 1.71 (m, 1H), 1.16 (d, *J* = 8.7 Hz, 6H), 0.98 (s, 3H).

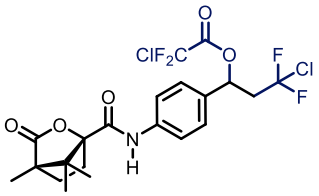
^{13}C-NMR (126 MHz, $CDCl_3$): δ 177.9, 165.7, 164.9 (dd, *J* = 31.6, 2.4 Hz), 138.1, 132.6, 126.9, 120.6, 115.7 (dd, *J* = 259.0, 250.1 Hz), 92.5, 55.7, 54.6, 40.0 (dd, *J* = 22.3, 20.7 Hz), 30.7, 29.2, 16.9, 16.7, 9.9.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -106.6 (d, *J* = 279.5 Hz), -109.1 (dd, *J* = 279.5, 3.5 Hz).

FT-IR (ATR, neat; cm^{-1}): 3304, 2971, 2938, 2878, 1809, 1785, 1681, 1600, 1535, 1422, 1321.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{20}H_{21}O_5NF_2+H^+$: 394.1460; found 394.1461.

3-Chloro-3,3-difluoro-1-(4-((1*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxamido)phenyl)propyl 2-chloro-2,2-difluoroacetate (65)



Compound **65** was obtained according to general procedure **3** from 1-((1*S*,4*S*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-(4-vinylphenyl)methanesulfonamide (166.5 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and toluene (3 mL). Isolated as a yellow oil (194.0 mg, 0.38 mmol, 76% yield) after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 5:1).

^{1}H-NMR (400 MHz, $CDCl_3$): 8.21 (s, 1H), 7.69 – 7.63 (m, 2H), 7.43 – 7.35 (m, 2H), 6.22 (dd, *J* = 9.2, 3.3 Hz, 1H), 3.26 – 3.10 (m, 1H), 2.89 – 2.73 (m, 1H), 2.65 – 2.54 (m, 1H), 2.07 – 1.95 (m, 2H), 1.81 – 1.69 (m, 1H), 1.16 (d, *J* = 6.6 Hz, 6H), 0.98 (s, 3H).

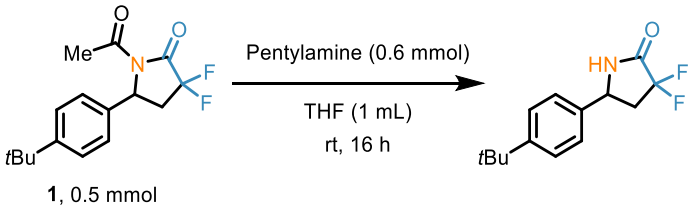
^{13}C-NMR (101 MHz, $CDCl_3$): δ 177.9, 165.7, 157.9 (t, *J* = 35.1 Hz), 138.2, 132.7, 127.6, 127.0 (t, *J* = 292.9 Hz), 120.6 (d, *J* = 1.4 Hz), 116.7 (t, *J* = 300.6 Hz), 92.5, 74.4 (t, *J* = 3.1 Hz), 55.7, 54.6, 47.7 – 47.2 (m), 30.7, 29.2, 16.9, 16.7, 9.8.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -49.8 (m), -50.4 (m), -64.3 (m).

FT-IR (ATR, neat; cm^{-1}): 3322, 2974, 2937, 1778, 1675, 1599, 1529, 1425, 1323.

HRMS (ESI) m/z, $[M+Na]^+$ calcd for $C_{21}H_{21}Cl_2F_4NO_5+Na^+$:536.0623; found 536.0625.

5-(4-(*tert*-Butyl)phenyl)-3,3-difluoropyrrolidin-2-one (66)



Compound **1** (0.5 mmol, 147.0 mg, 1.0 equiv) was dissolved in 1 mL of pentylamine and stirred at rt for 16 h. After completion of the reaction, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography (12 g SiO_2, hexane to hexane/EA=1:1) to afford **66** as a white solid (134.0 mg, 0.46 mmol, 92% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.40 (m, 2H), 7.28 – 7.20 (m, 2H), 6.52 (s, 1H), 4.84 – 4.73 (m, 1H), 3.08 – 2.91 (m, 1H), 2.52 – 2.30 (m, 1H), 1.32 (s, 9H).

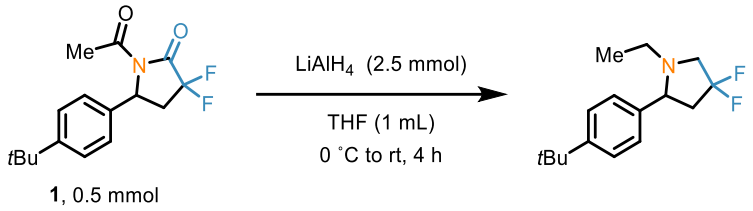
^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.7 (t, *J* = 30.6 Hz), 152.30 (m), 136.1, 126.3 (m), 125.7, 118.7 (m), 52.3, 40.6 (m), 34.7, 31.3.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -106.4, -106.5.

FT-IR (ATR, neat; cm^{-1}): 3220, 3209, 3129, 2963, 1736, 1510, 1424, 1414.

HRMS (EI) m/z, $[M]^+$ calcd for $C_{14}H_{17}F_2NO^+$: 253.1274; found 253.1273.

2-(4-(*tert*-Butyl)phenyl)-1-ethyl-4,4-difluoropyrrolidine (67)



1, 0.5 mmol

Compound **1** (0.5 mmol, 147.0 mg, 1.0 equiv) was dissolved in 1 mL of THF and solution was cooled to 0 ˚C. Then, solid $LiAlH_4$ (2.5 mmol, 5.0 equiv, 98.0 mg) was added in portions and the reaction was stirred for 4 h at rt. After the reaction was complete, excess of $LiAlH_4$ was quenched with ice at 0 ˚C. The formed precipitate was filtered, and washed with additional 10 mL of EtOAc. The organic phase was dried over anhydrious Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (12 g SiO_2, hexane to hexane/EA=1:1) to afford **67** as a white solid (91.0 mg, 0.34 mmol, 68% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): 7.44 – 7.37 (m, 2H), 7.33 – 7.27 (m, 2H), 4.99 (dd, *J* = 10.4, 1.9 Hz, 2H), 4.00 – 3.73 (m, 3H), 3.22 (t, *J* = 7.3 Hz, 1H), 2.60 – 2.56 (m, 2H), 2.56 – 2.43 (m, 1H), 2.32 – 2.18 (m, 1H), 1.32 (s, 9H).

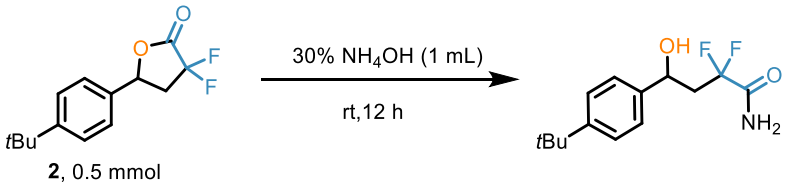
^{13}C-NMR (101 MHz, $CDCl_3$): δ 150.9, 137.7, 128.5 (dd, *J* = 250.8, 6.3 Hz), 127.3, 67.7 (m), 61.3 (t, *J* = 28.4 Hz), 47.3, 45.9 (t, *J* = 23.1 Hz), 34.7, 31.5, 13.2.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -91.2 (d, *J* = 227.9), -93.5 (d, *J* = 227.9).

FT-IR (ATR, neat; cm^{-1}): 2964, 2905, 2871, 2808, 2357, 1706, 1367, 1268.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{16}H_{23}F_2N+H^+$: 268.1869; found 268.1871.

4-(4-(*tert*-Butyl)phenyl)-2,2-difluoro-4-hydroxybutanamide (68)



2, 0.5 mmol

Compound **2** (0.5 mmol, 133.0 mg, 1.0 equiv) was suspended in 1 mL of aq. NH_4OH (30%) and stirred at 50 °C overnight (14 h). After the reaction was completed, the solution was quenched with 0.1 M HCl, and 10 mL of EtOAc was added. The organic phase was separated and the solvent was removed under reduced pressure. The white solid product **68** (127.0 mg, 0.47 mmol, 94% yield) was dried and characterized without further purification.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.36 (m, 2H), 7.34 – 7.28 (m, 2H), 6.43 (s, 1H), 5.94 (s, 1H), 5.04 (dd, *J* = 10.5, 2.6 Hz, 1H), 2.77 (s, 1H), 2.74 – 2.59 (m, 1H), 2.53 – 2.35 (m, 1H), 1.31 (s, 9H).

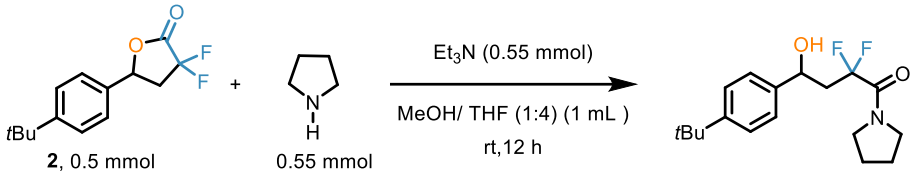
^{13}C-NMR (101 MHz, $CDCl_3$): δ 167.0 (t, *J* = 30.1 Hz), 151.2, 139.9, 125.5 (d, *J* = 23.8 Hz), 116.8 (t, *J* = 268.6 Hz), 68.6 (dd, *J* = 7.1, 4.5 Hz), 43.2 (t, *J* = 22.3 Hz), 34.6, 31.3.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -99.8 (d, *J* = 262.8 Hz), -105.6 (d, *J* = 262.8 Hz).

FT-IR (ATR, neat; cm^{-1}): 3642, 3394, 3227, 2959, 2902, 2868, 1810, 1690, 1618, 1512, 1447.

HRMS (ESI) m/z, $[M-H]^-$ calcd for $C_{14}H_{19}F_2NO_2-H^-$: 270.1311; found 270.1313.

2-(4-(*tert*-Butyl)phenyl)-1-ethyl-4,4-difluoropyrrolidine (69)



Compound **2** (0.5 mmol, 133.0 mg, 1.0 equiv), pyrrolidine (1.0 mmol, 71.1 mg, 2.0 equiv) and Et_3N (1.5 mmol, 101.0 mg, 3.0 equiv) were dissolved in a mixture of MeOH/THF (1:4) 1 mL and heated overnight at 80 °C. After completion of the reaction, the solution was cooled to rt, diluted with an additional 10 mL of EtOAc, and dried over anhydrous Na_2SO_4. The crude obtained after evapotaration of the organic solvent was purified by column chromatography (12 g SiO_2, hexane to hexane/EA=1:1) to afford **69** as a white solid (99.0 mg, 0.305 mmol, 61 % yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.32 (m, 4H), 5.00 (dt, *J* = 9.4, 1.7 Hz, 1H), 4.19 (s, 1H), 3.81 – 3.68 (m, 2H), 3.63 – 3.50 (m, 2H), 2.87 – 2.65 (m, 1H), 2.53 – 2.36 (m, 1H), 2.04 – 1.93 (m, 2H), 1.93 – 1.83 (m, 2H), 1.32 (s, 9H).

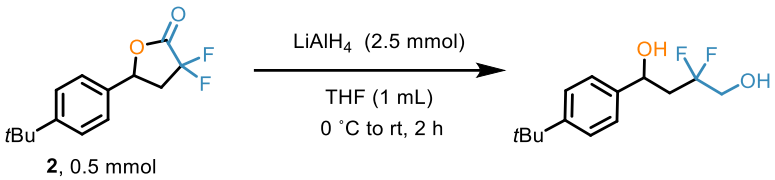
^{13}C-NMR (101 MHz, $CDCl_3$): δ 163.1 (t, *J* = 30.2 Hz), 150.7, 141.0, 125.5 (d, *J* = 3.4 Hz), 118.6 (m), 68.1 (dd, *J* = 8.5, 3.4 Hz), 47.8, 46.8 (t, *J* = 6.2 Hz), 45.0 (t, *J* = 22.1 Hz), 34.7, 31.5, 26.6 (d, *J* = 1.9 Hz), 23.4.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -94.8 (d, *J* = 286.9), -102.8 (d, *J* = 286.9).

FT-IR (ATR, neat; cm^{-1}): 3448, 3340, 2950, 2950, 2905, 2883, 2956, 1636, 1476, 1467, 1454.

HRMS (ESI) m/z, $[M+Na]^+$ calcd for $C_{18}H_{25}F_2NO_2+Na^+$: 348.1746; found 348.1744.

1-(4-(*tert*-Butyl)phenyl)-3,3-difluorobutane-1,4-diol (70)



Compound **2** (0.5 mmol, 133.0 mg, 1.0 equiv) was dissolved in 1 mL of dry THF and the solution was cooled to 0 ˚C with ice-bath. Then solid $LiAlH_4$ (2.5 mmol, 98.0 mg, 5.0 equiv) was introduced in small portions and the final solution was stirred for 2 h at room temperature. After the reaction was completed (checked by TLC), $LiAlH_4$ was quenched with ice at 0 ˚C. The reaction solution was extracted with 10 mL of EtOAc and the organic phase was further dried over Na_2SO_4. Under reduced pressure, the organic layer was concentrated and the residue was purified by column chromatography (12 g SiO_2, hexane to hexane/EA=1:1) to afford **70** as a white solid (118.0 mg, 0.46 mmol, 92% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.37 (m, 2H), 7.33 – 7.27 (m, 2H), 4.99 (dd, *J* = 10.4, 1.9 Hz, 1H), 4.00 – 3.74 (m, 2H), 3.22 (t, *J* = 7.3 Hz, 1H), 2.57 (s, 1H), 2.58 – 2.42 (m, 1H), 2.33 – 2.18 (m, 1H), 1.32 (s, 9H).

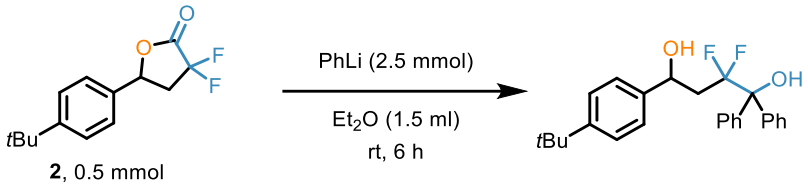
^{13}C-NMR (101 MHz, $CDCl_3$): δ 151.6, 140.2, 125.9, 125.5, 122.7 (t, *J* = 243.5 Hz), 69.5 (dd, *J* = 10.6, 2.3 Hz), 64.5 (dd, *J* = 34.4, 32.1 Hz), 43.4 (dd, *J* = 25.2, 23.8 Hz), 34.7, 31.4.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -98.8. -107.3 (m).

FT-IR (ATR, neat; cm^{-1}): 3357, 3272, 2961, 2902, 2867, 1509, 1455.

HRMS (EI) m/z, $[M]^+$ calcd for $C_{14}H_{20}F_2O_2^+$: 258.1428; found 258.1426.

4-(4-(*tert*-Butyl)phenyl)-2,2-difluoro-1,1-diphenylbutane-1,4-diol (71)



Compound **2** (0.5 mmol, 127.0 mg, 1.0 equiv) was dissolved in 2 mL of dry Et_2O. The a solution of PhLi in ether (1.9 M, 2.5 mmol, 5 equiv, 1.3 mL) was added dropwise at 0 ˚C, and the reaction was stirred for 6 h, warming naturally to rt. After the reaction was completed (checked by TLC), excess of PhLi was quenched with H_2O at 0 ˚C. The solution was extracted with 10 mL of EtOAc and the organic phase was dried over Na_2SO_4. Under reduced pressure, the resulting organic layer was concentrated, and the residue was purified by column chromatography (12 g SiO_2, hexane to hexane/EA = 5:1) to afford **71** as a white solid (174.0 mg, 0.425 mmol, 85 % yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.67 – 7.52 (m, 4H), 7.40 – 7.27 (m, 8H), 7.21 (d, *J* = 8.4 Hz, 2H), 5.23 – 5.08 (m, 1H), 4.10 (s, 1H), 2.59 (d, *J* = 2.4 Hz, 1H), 2.57 – 2.41 (m, 1H), 2.41 – 2.21 (m, 1H), 1.31 (s, 9H).

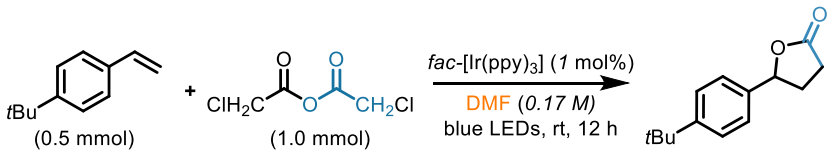
^{13}C-NMR (101 MHz, $CDCl_3$): δ 151.0, 141.9, 141.3, 140.3, 128.3, 128.1, 128.3 – 125.6 (m), 127.5 (t, *J* = 2.7 Hz), 125.6 (d, *J* = 4.7 Hz), 124.8 (t, *J* = 254.4 Hz), 80.2 (t, *J* = 25.7 Hz), 69.2 (dd, *J* = 6.9, 4.7 Hz), 43.0 (t, *J* = 23.4 Hz), 34.7, 31.4.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -98.5 (d, *J* = 255.4), -104.8 (d, *J* = 255.4).

FT-IR (ATR, neat; cm^{-1}): 2964, 2905, 2871, 2808, 2357, 1706, 1367, 1268.

HRMS (ESI) m/z, $[M-H]^-$ calcd for $C_{26}H_{28}F_2O_2$-H^-: 409.1985 found 409.1986.

5-(4-(*tert*-Butyl)phenyl)dihydrofuran-2(3*H*)-one (72)



Compound **72** was obtained according to general procedure **2** from 4-*tert*-butylstyrene (95.0 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *2-chloroacetic anhydride* (108.2 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a white solid (89.4 mg, 0.41 mmol, 82%) after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 10:1).

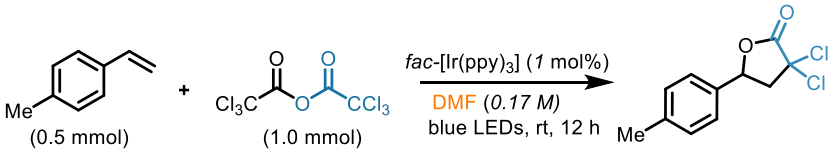
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.29 (m, 2H), 7.28 – 7.07 (m, 2H), 5.42 (dd, *J* = 8.0, 5.9 Hz, 1H), 2.67 – 2.45 (m, 3H), 2.31 – 2.04 (m, 1H), 1.25 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 177.1, 151.7, 136.4, 125.8, 125.3, 81.4, 34.8, 31.4, 30.9, 29.2.

FT-IR (ATR, neat; cm^{-1}): 2957, 2903, 2870, 1760, 1616, 1510, 1459, 1412, 1359.

HRMS (ESI) m/z, $[M+H]^+$ calcd for $C_{14}H_{18}O_2$+H^+: 219.1380; found 219.1380.

3,3-Dichloro-5-(*p*-tolyl)dihydrofuran-2(3*H*)-one (73)



Compound **73** was obtained according to general procedure **2** from 1-methyl-4-vinylbenzene, (65.6 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5 µmol, 1.0 mol%), *2,2,2-trichloroacetic anhydride* (180.9 µL, 1.0 mmol, 2.0 equiv), and DMF (3 mL). Isolated as a yellow oil (102.0 mg, 0.42 mmol, 84%) after purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 10:1).

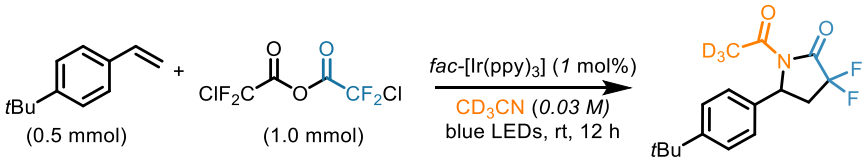
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.22 – 7.03 (m, 4H), 5.46 (dd, *J* = 10.0, 5.0 Hz, 1H), 3.29 (dd, *J* = 14.3, 5.0 Hz, 1H), 2.81 (dd, *J* = 14.3, 10.0 Hz, 1H), 2.26 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 167.7, 139.8, 132.5, 129.8, 126.1, 78.9, 77.8, 52.3, 21.3.

FT-IR (ATR, neat; cm-1): 3032, 2926, 1801, 1616, 1518, 1435.

HRMS (ESI) m/z, $[M+Na]^+$ calcd for $C_{11}H_{10}Cl_2O_2$+Na^+: 266.9950; found 266.9950.

1-(Acetyl-d$_3$)-5-(4-(*tert*-butyl)phenyl)-3,3-difluoropyrrolidin-2-one (74)



Compound **74** was obtained according to general procedure **1** from4-*tert*-butylstyrene (95.0 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and CD_3CN (15 mL). Isolated as a white solid (132.6 mg, 0.445 mmol, 89% yield) after purification by column chromatography (40 g SiO_2, hexane/EA = 5:1)

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.33 (m, 2H), 7.18 – 7.06 (m, 2H), 5.42– 5.32 (m, 1H), 2.99 – 2.83 (m, 1H), 2.65 – 2.47 (m, 1H), 1.30 (s, 9H).

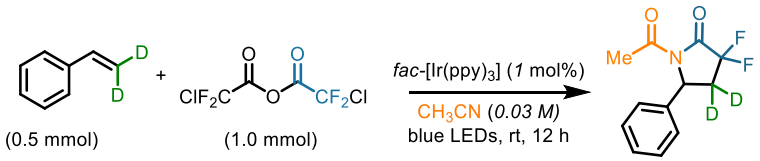
^{13}C-NMR (126 MHz, $CDCl_3$): δ 170.2, 164.3 (t, *J* = 32.1 Hz), 151.4, 136.4, 126.1, 125.3 (d, *J* = 1.6 Hz), 117.4 (t, *J* = 252.4 Hz), 54.5 (m), 37.5 (t, *J* = 21.1 Hz), 34.7, 31.4.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -99.6 (d, *J* = 275.4 Hz), -103.6 (d, *J* = 275.4 Hz).

FT-IR (ATR, neat; cm^{-1}): 2963, 1754, 1720, 1515, 1382, 1317.

HRMS (ESI) m/z, $[M+Na]^+$ calcd for $C_{16}H_{16}D_3F_2NO_2$+Na^+: 321.1457; found 321.1464.

1-Acetyl-3,3-difluoro-5-phenylpyrrolidin-2-one-4,4-*d*$_2$ (75)



Compound **75** was obtained according to general procedure **1** from Ethenyl-*2,2-d*$_2$benzene (95% D isotope), (53.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5.0 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and anhydrous MeCN (15 mL). Isolated as a white solid (84.3 mg, 0.35 mmol, 70% yield) after purification by column chromatography (40 g SiO_2, hexane/EA = 5:1)

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.37 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 6.9 Hz, 2H), 5.38 (s, 1H), 2.60 (s, 3H).

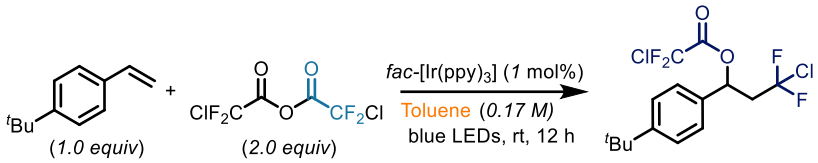
^{13}C-NMR (126 MHz, $CDCl_3$): δ 170.1, 164.3 (t, *J* = 32.0), 139.5, 129.2, 128.5, 125.6 (d, *J* = 1.6), 117.3 (t, *J* = 249.7), 54.6 (dd, *J* = 5.0, 1.8), 25.7.

^{19}F-NMR (471 MHz, $CDCl_3$): δ -100.0 (d, *J* = 275.9 Hz), -104.0 (dd, *J* = 275.9, 2.5 Hz).

FT-IR (ATR, neat; cm^{-1}): 1752, 1714, 1494, 1451, 1426, 1382.

HRMS (ESI) m/z, $[M+Na]^+$ calcd for $C_{12}H_9D_2O_2NF_2+Na^+$: 264.0777; found 264.0776.

1-(4-(*tert*-Butyl)phenyl)-3-chloro-3,3-difluoropropyl 2-chloro-2,2-difluoroacetate (3)



Compound **3** was obtained according to general procedure **3** from 4-*tert*-butylstyrene (94%, 95.0 µL, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and toluene (3 mL). After purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 5:1), compound **3** was isolated as colourless oil (140.0 mg, 0.642 mmol, 75% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.44**–** 7.09 (m, 2H), 7.15 – 7.08 (m, 2H), 6.26 (dd, *J* = 9.6, 2.8 Hz, 1H), 3.25 – 3.13 (m, 1H), 2.86 – 2.75 (m, 1H), 1.33 (s, 9H).

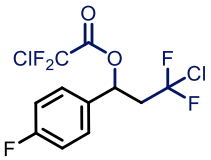
^{13}C-NMR (101 MHz, $CDCl_3$): δ 158.0 (t, *J* = 35.0 Hz), 153.0, 133.4, 127.2 (t, *J* = 293.1 Hz), 126.3, 126.1, 116.9 (t, *J* = 300.6 Hz), 74.7, 47.8 (t, *J* = 24.5 Hz), 34.9, 31.4.

^{19}F-NMR (377 MHz, $CDCl_3$): δ -49.8 (d, *J* = 164.8 Hz), -50.8 (d, *J* = 164.8 Hz), -64.2 (d, *J* = 10.3 Hz).

FT-IR (ATR, neat; cm^{-1}): 2965, 1783, 1758, 1724, 1381, 1302, 1097, 972.

HRMS (ESI) *m/z*, $[M]^+$ calcd for $C_{15}H_{16}Cl_2F_4O_2^+$: 374.0458; found: 374.0447.

3-Chloro-3,3-difluoro-1-(4-fluorophenyl)propyl 2-chloro-2,2-difluoroacetate (76)



Compound **76** was obtained according to general procedure **3** from 1-fluoro-4-vinylbenzene (61.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and toluene (3 mL). After purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 5:1) compound **76** was isolated as a yellow oil (131.4 mg, 0.39 mmol, 78% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.34 (m, 2H), 7.15 – 7.06 (m, 2H), 6.24 (dd, *J* = 9.2, 3.4 Hz, 1H), 3.28 – 3.09 (m, 1H), 2.91 – 2.73 (m, 1H).

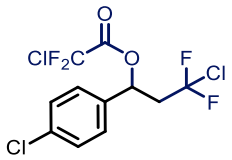
^{13}C-NMR (101 MHz, $CDCl_3$): δ 164.7, 162.2, 157.9 (t, *J* = 35.3 Hz), 132.3 (d, *J* = 3.3 Hz), 128.6 (d, *J* = 8.6 Hz), 127.0 (t, *J* = 292.9 Hz), 116.8 (t, *J* = 300.6 Hz), 116.6, 116.4, 74.2 (t, *J* = 3.1 Hz), 47.6 (t, *J* = 24.6 Hz).

^{19}F-NMR (377 MHz, $CDCl_3$): δ -49.3 – -50.1 (m), -50.3 – -51.0 (m), -64.4 (d, *J* = 4.0 Hz), -110.9.

FT-IR (ATR, neat; cm^{-1}): 1783, 1608, 1513, 1421, 1379, 1298, 1232.

HRMS (EI) *m/z*, $[M\text{-}OC(O)CF_2Cl]^+$ calcd for $[C_9H_7ClF_3\text{-}OC(O)CF_2Cl]^+$: 207.0188; found: 207.0183.

3-Chloro-1-(4-chlorophenyl)-3,3-difluoropropyl 2-chloro-2,2-difluoroacetate (77)



Compound **77** was obtained according to general procedure **3** from 1-chloro-4-vinylbenzene (69.0 mg, 0.5 mmol, 1.0 equiv) (61.0 mg, 0.5 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (3.3 mg, 5 µmol, 1.0 mol%), *CDFAA* (170 µL, 1.0 mmol, 2.0 equiv), and toluene (3 mL). After purification by column chromatography (12 g SiO_2, hexane to hexane/EA= 5:1), compound **77** was isolated as a yellow oil (105.0 mg, 0.30 mmol, 60% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.38 (m, 2H), 7.36 – 7.30 (m, 2H), 6.22 (dd, *J* = 9.2, 3.4 Hz, 1H), 3.25 – 3.05 (m, 1H), 2.88 – 2.71 (m, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 157.8 (t, *J* = 35.3 Hz), 135.9, 134.8, 129.6, 127.9, 128.3 – 126.8 (m), 124.0, 116.7 (t, *J* = 300.6 Hz), 74.1 (t, *J* = 3.1 Hz), 47.5 (t, *J* = 24.7 Hz).

^{19}F-NMR [^{1}H Coupled] (377 MHz, $CDCl_3$): δ -49.3 – -50.1 (m), -50.2 – -51.1 (m), -64.3 – -64.6 (m).

FT-IR (ATR, neat; cm^{-1}): 1783, 1608, 1513, 1421, 1379, 1298, 1232.

HRMS (EI) *m/z*, $[M\text{-}OC(O)CF_2Cl]^+$ calcd for $[C_9H_7Cl_2F_2\text{-}OC(O)CF_2Cl]^+$: 222.9893; found: 222.9886.

14. X-Ray Diffraction Data

Crystal data for CCDC 2048568 1-acetyl-5-(4-(*tert*-butyl)phenyl)-3,3-difluoropyrrolidin-2-one (1)

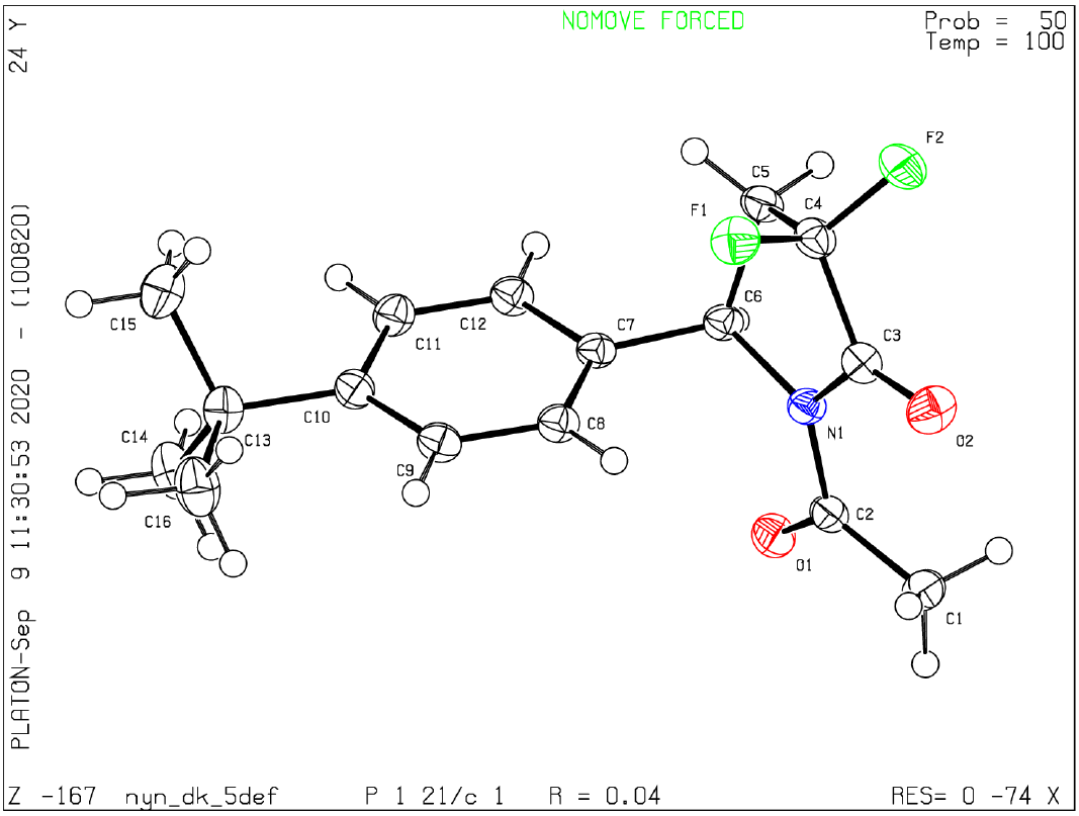


Figure 14.1. Crystal data and structure refinement for **1**.

CCDC	2048568
Empirical formula	$C_{16}H_{19}F_2NO_2$
Formula weight	295.32
Temperature/K	99.95
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	20.880(4)
b/Å	6.3145(11)
c/Å	11.6089(19)
α/°	90
β/°	98.261(2)
γ/°	90
Volume/Å^3	1514.8(4)
Z	4
ρcalc g/.cm^3	1.295
μ/mm^{-1}	0.101
F(000)	624.0
Crystal size/mm^3	0.712 × 0.602 × 0.07
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.942 to 57.068
Index ranges	-28 ≤ h ≤ 27, -8 ≤ k ≤ 8, -15 ≤ l ≤ 15

Reflections collected	39408
Independent reflections	3833 [R_{int} = 0.0395, R_{sigma} = 0.0201]
Data/restraints/parameters	3833/0/194
Goodness-of-fit on F^2	1.091
Final R indexes [I>=2σ (I)]	R_1 = 0.0437, wR_2 = 0.1118
Final R indexes [all data]	R_1 = 0.0508, wR_2 = 0.1162
Largest diff. peak/hole/e Å^{-3}	0.36/-0.20

Crystal data for CCDC-2050590 1-Acetyl-3,3-difluoro-4,5-diphenylpyrrolidin-2-one (24)

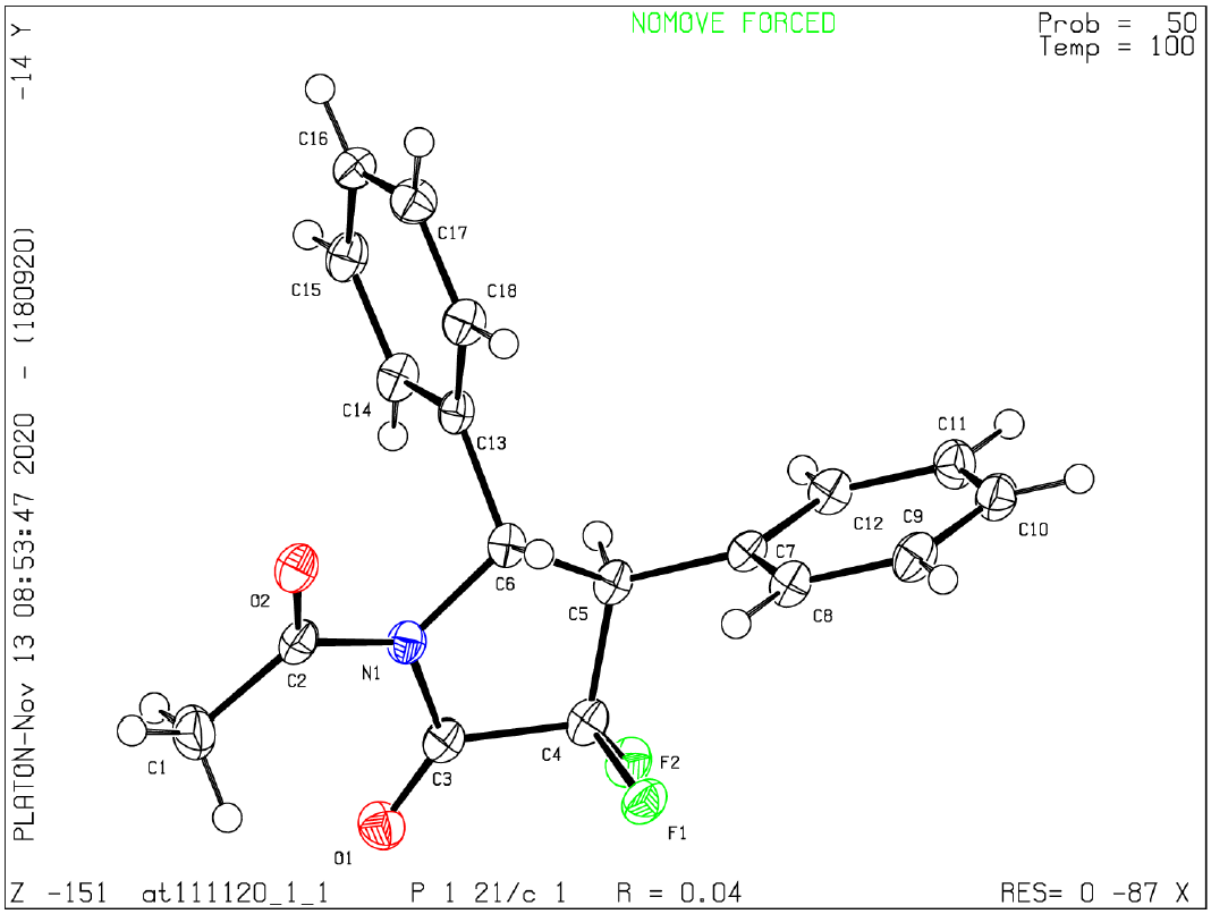


Figure 14.2. Crystal data and structure refinement for **24**.

CCDC	2050590
Empirical formula	$C_{18}H_{15}F_2NO_2$
Formula weight	315.31
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.0365(3)
b/Å	5.5281(1)
c/Å	15.6934(3)
α/°	90
β/°	101.292(2)
γ/°	90
Volume/Å^3	1449.39(5)

Z	4
ρ_{calc} g/.cm^3	1.445
μ/mm^{-1}	0.940
F(000)	656.0
Crystal size/mm^3	0.15 × 0.052 × 0.026
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.29 to 159.9
Index ranges	$-18 \leq h \leq 21$, $-6 \leq k \leq 6$, $-20 \leq l \leq 19$
Reflections collected	16452
Independent reflections	3091 [R_{int} = 0.0346, R_{sigma} = 0.0265]
Data/restraints/parameters	3091/0/209
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0365, wR_2 = 0.0948
Final R indexes [all data]	R_1 = 0.0403, wR_2 = 0.0980
Largest diff. peak/hole/e Å^{-3}	0.25/-0.23

15. Computational Studies

15.1. Computational Details

All geometries were fully optimized in gas-phase at the M06-2X[27] level of theory without any constraints, at 298K and 1 atm using an ultra-fine integration grid. The Berny algorithm was used for geometry optimizations.[28,29] The Karlsruhe def2-TZVP basis set[30-32] was used on all atoms and dispersion effects were accounted for by the inclusion of the D3 version of Grimme's dispersion with the original D3 damping function (GD3).[33] Frequency calculations were performed at the same level of theory for all intermediates to confirm minima (no imaginary frequencies). Single-point energies were calculated on the gas-phase optimized geometries at 298 K and 1 atm at the same level of theory while solvent effects were taken into account through the CPCM[34,35] solvation model of the integral equation formalism variant of the polarizable continuum model (IEFPCM)[36] with default parameters for Acetonitrile, DMF, or Toluene (**SP-1**). Zero-point corrected energies, enthalpies, and Gibbs free energies were obtained by adding the respective gas-phase thermal corrections to the single-point energies. All Gibbs free energies were subjected to state correction from gas-phase to solution at room temperature by addition of 1.89 kcal mol^{-1} to all species according to ΔG_{atm} to mol L^{-1} = RT*ln*(24.5).[37] Gibbs free energy corrections were adjusted to account for the reaction temperature at 298 K and Grimme's quasi-harmonic approximations were applied with the frequency cut-off value of 100 cm^{-1} to correct the effect of small frequency vibrational modes.[38] All calculations have been checked for occupation and negative energies of SOMO and HOMO orbitals and expectation values of $<S^2>$ as close as possible to 0.75 or at least <0.81. All relative energies are reported in kcal mol^{-1}. All calculations were carried out using the Gaussian16, revision C.01 software.[39]

In order to evaluate the impact of other combinations of DFT methods and basis sets, additional single-point calculations were carried out on the gas-phase optimized geometries at different levels of theory as follow:

SP-2 [CPCM(MeCN)/M06L/GD3/def2-TZVP]

SP-3 [CPCM(MeCN)/B3LYP/GD3/def2-TZVP]

SP-4 [CPCM(MeCN)/BP86/GD3/def2-TZVP]

SP-5 [CPCM(MeCN)/M06-2X/GD3/6-311++G(d,p)]

SP-6 [CPCM(MeCN)/M06-2X/GD3/aug-cc-pVTZ]

Computational Prediction of Reduction Potentials

Reduction potentials for selected species have been calculated against two independent redox reference couples in acetonitrile: NO^+/NO and TCNE/$TCNE^{\cdot-}$. The energies of all the selected species and redox reference couples were obtained as described before with the difference that, in order to account for

geometry relaxations and solvent stabilization effects, the CPCM solvation model with default parameters for acetonitrile was included during the optimization stage.

The corresponding Gibbs free energies differences were then converted to potentials E^{cell} against the redox reference by application of the Nerst equation:

$$\Delta G = -nFE^{cell}$$

that is

$$E^{cell} = - \Delta G / nF$$

where n is the number of electrons involved in the process (n=1 in all the cases presented in this study), and F is the Faraday constant of 23.061 kcal per volt-gram-equivalent.

The resulting calculated potentials were corrected against the ferrocene **Fc^+/Fc** reference by the known experimental values reported in the literature:[40]

Fc^+/Fc = 0.00V NO^+/NO = +0.87V TCNE/$TCNE^{\cdot -}$ = -0.27V

and finally corrected against **SCE** by the known correspondence:

Fc^+/Fc = 0.00V SCE = +0.40V

15.2. Computed Energies and Thermal Correction for all the Species Considered

	Gas-phase optimization and frequency analysis						
Species	**Total energy**	**ZPE corr.**	**H corr.**	**G corr.**	**SP-1 (MeCN) Total energy**	**SP-1 (DMF) Total energy**	**SP-1 (Toluene) Total energy**
1	-1,026.058545	0.328344	0.349300	0.282442	-1,026.071618	-1,026.071635	-1,026.065878
2	-893.268290	0.277916	0.295401	0.235427	-893.279482	-893.279497	-893.274533
3	-2,051.492896	0.293094	0.317111	0.241912	-2,051.501552	-2,051.501564	-2,051.497804
A	-466.851403	0.247390	0.260478	0.210509	-466.855637	-466.855643	-466.853800
B	-1,697.918345	0.050380	0.063753	0.010694	-1,697.923749	-1,697.923756	-1,697.921427
DMF	-248.496390	0.103270	0.110283	0.074247	-248.505442	-248.505455	-248.501328
I	-1,237.664260	0.047519	0.059758	0.009098	-1,237.670283	-1,237.670291	-1,237.667680
I-1	-886.659305	0.024669	0.032036	-0.006729	-886.747809	-886.747916	-886.711616
I-10	-1,237.371811	0.050302	0.061405	0.013875	-1,237.459413	-1,237.459519	-1,237.423518
I-9	-460.255959	-	-	-	-460.370291	-460.370426	-460.324034
VI	-1,271.536641	0.023354	0.030965	-0.008592	-1,271.539136	-1,271.539139	-1,271.538076
I-16	-1,837.113875	0.352117	0.379623	0.298285	-1,837.181996	-1,837.182081	-1,837.153562
I-17	-2,862.526371	0.316650	0.346956	0.259657	-2,862.591092	-2,862.591173	-2,862.564161
I-18	-1,270.865781	0.157805	0.172797	0.117338	-1,270.873330	-1,270.873340	-1,270.870111
I-19	-1,509.204654	0.180882	0.198995	0.136162	-1,509.213537	-1,509.213549	-1,509.209706
XII	-1,509.208784	0.180556	0.198839	0.135211	-1,509.216552	-1,509.216562	-1,509.213234
I-20	-307.693980	0.119123	0.127410	0.088044	-307.700033	-307.700041	-307.697402
I-21	-307.029285	0.105693	0.113568	0.074666	-307.035575	-307.035583	-307.032821
I-22	-232.224751	0.101202	0.106519	0.073755	-232.227815	-232.227819	-232.226497
I-23	-231.538983	0.088115	0.093399	0.060095	-231.541988	-231.541992	-231.540683
I-24	-737.776237	0.368238	0.387158	0.324240	-737.782360	-737.782368	-737.779660
I-3	-113.322295	0.005196	0.008500	-0.013913	-113.322899	-113.322899	-113.322648
I-4	-697.626496	0.012680	0.017129	-0.014198	-697.726329	-697.726448	-697.685880
I-6	-811.268872	0.019495	0.026237	-0.011378	-811.270506	-811.270508	-811.269821
I-7	-188.596936	0.011971	0.015511	-0.008703	-188.599389	-188.599392	-188.598360
I-11	-460.132584	-	-	-	-460.133557	-460.133558	-460.133159
II	-1,704.575524	0.298550	0.322948	0.248511	-1,704.584346	-1,704.584358	-1,704.580480
III	-1,704.320779	0.300145	0.324967	0.248625	-1,704.391410	-1,704.391497	-1,704.362129
IV	-1,952.885019	0.409091	0.440056	0.351967	-1,952.953237	-1,952.953322	-1,952.924881
IX	-1,238.319538	0.060882	0.072976	0.023277	-1,238.325846	-1,238.325854	-1,238.323163
MeCN	-132.746905	0.045743	0.050284	0.022780	-132.755395	-132.755408	-132.751556
Toluene	-271.535298	0.128669	0.135801	0.098773	-271.538385	-271.538389	-271.537051
V	-1,704.313415	0.301632	0.325727	0.250845	-1,704.384245	-1,704.384333	-1,704.354711
VII	-1,837.111557	0.350219	0.378667	0.295442	-1,837.182000	-1,837.182088	-1,837.152660
VIII	-1,026.027580	0.327996	0.348728	0.282392	-1,026.037483	-1,026.037496	-1,026.033202
X	-270.882471	0.115295	0.121891	0.085644	-270.885885	-270.885890	-270.884411
XI	-1,968.805808	0.170615	0.189745	0.124655	-1,968.812208	-1,968.812216	-1,968.809467
XIII	-1,082.281059	0.142859	0.155290	0.105051	-1,082.287264	-1,082.287272	-1,082.284558
XIV	-697.939660	0.010650	0.015318	-0.017094	-697.940372	-697.940373	-697.940076
XV	-1,164.856059	0.260914	0.278096	0.217901	-1,164.861375	-1,164.861382	-1,164.859082
XVI	-1,164.605612	0.263258	0.280402	0.220953	-1,164.675447	-1,164.675533	-1,164.646614
XVII	-968.963483	0.133361	0.143766	0.098275	-968.968594	-968.968601	-968.966373

Table 15.1. Energies (gas-phase and solvated single-point) and thermal corrections (gas-phase, 298K) expressed in Hartree.

Species	SP-2 (MeCN) Total energy	SP-3 (MeCN) Total energy	SP-4 (MeCN) Total energy	SP-5 (MeCN) Total energy	SP-6 (MeCN) Total energy
1	-1,026.333305	-1,026.524491	-1,026.509576	-1,025.964609	-1,026.069387
2	-893.502144	-893.669779	-893.654727	-893.183753	-893.277101
3	-2,051.778001	-2,052.027564	-2,052.075953	-2,051.374885	-2,051.511801
A	-467.002054	-467.104061	-467.078413	-466.807476	-466.857450
B	-1,698.090144	-1,698.249318	-1,698.324497	-1,697.827684	-1,697.930216
DMF	-248.580830	-248.631174	-248.626580	-248.480427	-248.506475
I	-1,237.836877	-1,237.972572	-1,238.017654	-1,237.574901	-1,237.669100
I-1	-886.833944	-886.927401	-886.966658	-886.700946	-886.754486
I-10	-1,237.631724	-1,237.755870	-1,237.805809	-1,237.355472	-1,237.455962
I-9	-460.378046	-460.403176	-460.431174	-460.378369	-460.384710
VI	-1,271.625989	-1,271.720634	-1,271.789599	-1,271.492289	-1,271.550215
I-16	-1,837.524324	-1,837.782914	-1,837.807439	-1,837.027716	-1,837.182150
I-17	-2,862.953955	-2,863.269241	-2,863.358094	-2,862.417268	-2,862.604124
I-18	-1,271.067665	-1,271.223202	-1,271.255121	-1,270.780074	-1,270.875128
I-19	-1,509.452062	-1,509.650749	-1,509.683873	-1,509.095731	-1,509.214129
XII	-1,509.455528	-1,509.654920	-1,509.687616	-1,509.098260	-1,509.216898
I-20	-307.791398	-307.851147	-307.843465	-307.668098	-307.700842
I-21	-307.126167	-307.185172	-307.178112	-307.003626	-307.036219
I-22	-232.296547	-232.345000	-232.332280	-232.201842	-232.227512
I-23	-231.612458	-231.655475	-231.644860	-231.516032	-231.541625
I-24	-738.010654	-738.164847	-738.131429	-737.707135	-737.784331
I-3	-113.344471	-113.363163	-113.359236	-113.310621	-113.320868
I-4	-697.794235	-697.840044	-697.876159	-697.686738	-697.728002
I-6	-811.348904	-811.426650	-811.461244	-811.226872	-811.273877
I-7	-188.655723	-188.672475	-188.677905	-188.577826	-188.596761
I-11	-460.139211	-460.167954	-460.192300	-460.133796	-460.142134
II	-1,704.890414	-1,705.127672	-1,705.149039	-1,704.447756	-1,704.586365
III	-1,704.707597	-1,704.942342	-1,704.962348	-1,704.250101	-1,704.391860
IV	-1,953.322507	-1,953.613418	-1,953.628452	-1,952.788455	-1,952.954368
IX	-1,238.485477	-1,238.627190	-1,238.666896	-1,238.232788	-1,238.325622
MeCN	-132.796565	-132.819691	-132.812960	-132.741414	-132.755785
Toluene	-271.622194	-271.679165	-271.664199	-271.508837	-271.538584
V	-1,704.693113	-1,704.926759	-1,704.950682	-1,704.240669	-1,704.384032
VII	-1,837.525059	-1,837.782959	-1,837.799201	-1,837.027735	-1,837.182455
VIII	-1,026.296006	-1,026.485829	-1,026.470814	-1,025.928388	-1,026.035275
X	-270.970637	-271.027520	-271.013183	-270.856230	-270.886120
XI	-1,969.057648	-1,969.272564	-1,969.341875	-1,968.691342	-1,968.819682
XIII	-1,082.439245	-1,082.572151	-1,082.595188	-1,082.215908	-1,082.291074
XIV	-697.992839	-698.054963	-698.086532	-697.907441	-697.945043
XV	-1,165.057310	-1,165.219380	-1,165.227820	-1,164.784952	-1,164.868930
XVI	-1,164.879855	-1,165.039180	-1,165.047053	-1,164.596645	-1,164.681917
XVII	-969.092407	-969.210702	-969.229552	-968.909826	-968.973652

Table 15.2. Single-point total energies calculated at different levels of theory expressed in Hartree.

Step	Gas-phase	SP-1 (MeCN)	SP-1 (DMF)	SP-1 (Toluene)	SP-2	SP-3	SP-4	SP-5	SP-6
B to I and I-9	0.6	-71.5	-71.6	-42.3	-76.5	-77.6	-76.3	-77.0	-75.8
B to I and I-11	77.1	76.1	76.1	76.6	72.5	69.2	72.8	75.6	75.6
B to I-1 and I-6	-21.5	-74.7	-74.7	-53.0	-73.5	-81.0	-80.2	-78.1	-76.9
B to I-1, I-3, and I-4	169.9	54.7	54.6	101.5	48.9	49.7	52.0	56.4	54.8
B to I-9 and I-10	186.2	62.9	62.8	113.0	54.3	60.5	58.8	62.8	60.1
B to I-6, XIV, and I-7	44.6	45.0	45.0	44.8	31.9	33.5	35.8	46.3	45.6
I and A to II	-21.3	-20.4	-20.4	-20.8	-16.1	-15.8	-17.0	-24.8	-21.3
I and A to II	-21.3	-20.4	-20.4	-20.8	-16.1	-15.8	-17.0	-24.8	-21.3
I and I-20 to IX and I-21	6.4	6.1	6.1	6.2	10.9	7.6	10.6	4.6	5.6
I and I-22 to IX to I-23	19.5	19.3	19.3	19.4	22.6	22.2	24.3	17.8	18.8
I and Toluene to IX and X	-0.9	-1.3	-1.3	-1.1	2.5	-1.2	1.8	-2.7	-1.9
I-16 and I-9 to 1 and VI	-156.7	-52.0	-51.9	-94.6	-51.1	-52.4	-53.3	-47.2	-48.4
I-17 and I-9 to VI and 3	-171.6	-66.3	-66.2	-109.2	-61.7	-64.1	-64.4	-61.4	-62.4
I-6 to I-3 and XIV	-6.1	-5.9	-5.9	-6.0	-3.1	-5.1	-0.7	-4.9	-5.4
III and DMF to IV	-26.2	-19.0	-19.0	-22.2	-5.0	-8.7	-8.4	-20.0	-18.8
III and MeCN to VII	-14.3	-8.9	-8.9	-11.3	0.1	0.1	-1.8	-9.5	-8.7
III to 2	-156.9	-49.4	-49.3	-93.0	-40.3	-41.8	-45.6	-43.5	-45.5
III to V	6.0	5.9	5.9	6.0	10.5	11.2	8.7	7.3	6.3
IV to V	32.1	24.8	24.8	28.1	15.5	19.8	17.2	27.3	25.1
V to 2	-162.9	-55.3	-55.1	-99.1	-50.8	-53.0	-54.3	-50.8	-51.8
VII and I-9 to 1 and I-11	-156.4	-50.2	-50.1	-93.4	-48.8	-50.6	-56.7	-45.4	-46.5
VII and I-9 to VIII and VI	-137.0	-28.8	-28.7	-72.9	-25.4	-26.3	-32.4	-22.7	-25.1
VII to I-16	0.3	1.8	1.8	1.2	2.2	1.8	-3.4	1.8	2.0
VIII to 1	-19.4	-21.4	-21.4	-20.5	-23.4	-24.2	-24.3	-22.7	-21.4
X and A to I-24	-10.9	-9.9	-9.9	-10.3	-8.1	-5.1	-9.3	-11.5	-9.8
X and B to XI	12.7	14.3	14.3	13.6	17.8	18.6	13.2	11.2	13.8
X and IX to I-19	13.5	14.1	14.1	13.9	17.7	17.7	12.8	11.0	13.7
X and IX to XII	10.4	11.6	11.6	11.1	15.0	14.5	9.9	8.8	11.4
X and XIV to XVII	-71.9	-72.6	-72.6	-72.3	-64.1	-63.7	-64.7	-75.0	-72.7
XI to I-18 and XIV	-13.2	-14.4	-14.4	-13.9	-15.2	-16.9	-13.3	-11.0	-13.7
XI to XIII, XIV, and I-7	-32.1	-34.0	-34.0	-33.2	-43.6	-41.7	-35.8	-30.9	-33.0
XIV and A to XV	-27.3	-27.5	-27.5	-27.4	-25.7	-24.4	-26.0	-30.5	-28.2
XVI and B to I-17	14.2	20.8	20.8	18.1	25.7	27.8	24.1	20.1	20.7
XVI and I-1 to 3	-127.6	-33.7	-33.5	-72.1	-24.8	-22.8	-23.6	-33.0	-31.8

Table 15.3. Computed ΔG for each step at all the levels of theory considered expressed in kcal mol^{-1}.

CPCM (MeCN)/M06-2X/GD3/def2-TZVP optimization and frequency analysis				
Species	**Total energy**	**ZPE corr.**	**H corr.**	**G corr.**
II	-1704.584528	0.298019	0.322410	0.248022
III	-1704.392762	0.299754	0.324593	0.248470
XV	-1164.861442	0.260592	0.277766	0.217477
XVI	-1164.675821	0.263095	0.280227	0.220779
X	-270.885896	0.115289	0.121874	0.085641
IX	-1238.325992	0.060425	0.072567	0.022731
A	-466.855657	0.247188	0.260235	0.210491
NO^+	-129.669325	0.005940	0.009245	-0.013220
NO	-129.895848	0.004722	0.008027	-0.015246
TCNE	-447.538405	0.047667	0.057767	0.013895
$TCNE^{\cdot-}$	-447.718870	0.046484	0.056518	0.012093

Table 15.4. Solvated energies and thermal corrections (298K) for the species re-optimized in acetonitrile (CPCM).

Redox pair	Reference System	ΔG *vs* ref. (kcal mol^{-1})	E^0 *vs* ref.	E^0 *vs* Fc^+/Fc	E^0 *vs* SCE	Average E^0 *vs* SCE
II/III	$TCNE/TCNE^{\cdot-}$	-6.24	0.27	0.00	0.40	**0.34**
	NO^+/NO	22.80	-0.99	-0.12	0.28	
XV/XVI	$TCNE/TCNE^{\cdot-}$	-4.18	0.18	-0.09	0.31	**0.25**
	NO^+/NO	24.87	-1.08	-0.21	0.19	

Table 15.5. Calculation of the reduction potential for the **II**/**III** and **XV**/**XVI** couples.

15.3. Cartesian Coordinates – Gas-Phase Optimizations

	1		
N	2.27793	0.69980	0.22556
C	1.39743	0.04443	1.20363
H	1.48268	0.58080	2.14692
C	2.00127	-1.37154	1.32220
H	1.25200	-2.13298	1.52250
H	2.76479	-1.39117	2.09959
C	2.68678	-1.59072	-0.00326
C	3.04434	-0.17755	-0.51330
C	2.23866	2.10537	0.11415
C	3.08768	2.74108	-0.94457
H	2.92125	3.81294	-0.89829
H	2.82796	2.34909	-1.92727
H	4.13872	2.50371	-0.78636
O	1.53302	2.71920	0.86957
O	3.83069	0.05910	-1.38464
F	1.86060	-2.16713	-0.91328
F	3.78661	-2.35819	0.07543
C	-0.05486	0.05137	0.77986
C	-1.04159	0.07094	1.75276
H	-0.76202	0.13552	2.79853
C	-2.38624	0.02548	1.40784
H	-3.12145	0.04875	2.19976
C	-2.78734	-0.03386	0.07637
C	-1.78310	-0.04575	-0.89382
H	-2.04935	-0.08699	-1.94276
C	-0.44183	-0.00525	-0.55424
H	0.30253	-0.01786	-1.34138
C	-4.25313	-0.07885	-0.34996
C	-5.20261	-0.05453	0.84765
H	-5.04415	-0.91266	1.50345
H	-6.23378	-0.09183	0.49319
H	-5.08472	0.85765	1.43539
C	-4.51008	-1.36694	-1.14464
H	-5.55574	-1.41200	-1.45620
H	-4.29436	-2.24618	-0.53512
H	-3.88986	-1.41661	-2.04004
C	-4.56199	1.13589	-1.23630
H	-4.38021	2.06547	-0.69428
H	-5.60903	1.11617	-1.54586
H	-3.94568	1.14351	-2.13571
	2		
C	-3.43175	0.86854	-0.48716
O	-2.21889	0.67247	-1.03014
C	-1.60167	-0.54104	-0.54310
H	-1.81321	-1.32834	-1.26972
C	-2.32492	-0.83295	0.77970
H	-1.87779	-0.24516	1.58250
H	-2.32974	-1.88671	1.04697
C	-3.69996	-0.29538	0.49125
O	-4.14651	1.78142	-0.72999
F	-4.38499	0.11243	1.56729
F	-4.45973	-1.21838	-0.15575
C	-0.12066	-0.35261	-0.40728
C	0.40923	0.84346	0.06824
H	-0.24952	1.67591	0.28392
C	1.77385	0.97915	0.24095
H	2.15917	1.92428	0.60282
C	2.65829	-0.06660	-0.04343
C	2.11319	-1.25451	-0.51864
H	2.75301	-2.09089	-0.76177
C	0.74199	-1.39404	-0.70410
H	0.34745	-2.32749	-1.08970
C	4.15755	0.13478	0.16556
C	4.64147	1.29211	-0.71954
H	5.71377	1.44484	-0.58102
H	4.13458	2.22558	-0.47345
H	4.45796	1.07544	-1.77327
C	4.96257	-1.11441	-0.19169
H	4.83788	-1.38666	-1.24134
H	4.67484	-1.96795	0.42495
H	6.02295	-0.92269	-0.02144
C	4.42242	0.47565	1.63887
H	5.49215	0.62229	1.80150
H	4.08341	-0.33247	2.28941
H	3.90906	1.38962	1.93903
	3		
C	0.56419	-0.78005	0.31864
O	1.31639	0.32689	-0.21918
H	0.83634	-0.89313	1.36791
C	0.98078	-2.00997	-0.46926
H	0.69235	-1.90578	-1.51779
H	0.45853	-2.87355	-0.05742
C	2.46264	-2.32778	-0.46362
Cl	3.17670	-2.29755	1.16561
F	2.65109	-3.55702	-0.97253
F	3.15622	-1.48312	-1.23440
C	-0.91540	-0.52030	0.20311
C	-1.46196	-0.05644	-0.98456
H	-0.81551	0.15829	-1.82807
C	-2.82965	0.15549	-1.09550
H	-3.21841	0.52350	-2.03433
C	-3.68953	-0.09591	-0.02852

C	-3.12224	-0.55974	1.16029	H	3.76934	-0.95417	1.26380
H	-3.75404	-0.75469	2.01781	H	2.24405	-1.84282	1.28178
C	-1.75843	-0.76393	1.27990	H	2.37989	-0.31587	2.15744
H	-1.34287	-1.10188	2.22211				
C	-5.19864	0.12450	-0.11025			**B**	
C	-5.92057	-1.20043	0.17283	C	1.08823	-0.46460	0.65775
H	-7.00137	-1.05579	0.11651	O	-0.00000	-0.00002	-0.02882
H	-5.68456	-1.58285	1.16629	O	1.09278	-0.89489	1.75211
H	-5.63678	-1.95931	-0.55845	C	-1.08822	0.46458	0.65775
C	-5.61537	1.16564	0.93824	O	-1.09276	0.89488	1.75211
H	-6.69305	1.33429	0.88863	C	2.33359	-0.36363	-0.24254
H	-5.10964	2.11628	0.76109	F	3.30768	-1.09130	0.27909
H	-5.37263	0.83748	1.94931	F	2.06560	-0.82356	-1.46373
C	-5.63498	0.62560	-1.48683	Cl	2.82733	1.32625	-0.33713
H	-5.17617	1.58573	-1.72966	C	-2.33359	0.36364	-0.24254
H	-6.71727	0.76241	-1.49556	F	-3.30767	1.09131	0.27910
H	-5.38275	-0.08843	-2.27304	F	-2.06559	0.82357	-1.46372
C	1.47185	1.36749	0.58550	Cl	-2.82735	-1.32624	-0.33713
C	2.31079	2.45333	-0.11740				
F	1.86892	2.65555	-1.36123			**DMF**	
Cl	4.00117	1.94666	-0.16951	C	0.86249	-0.64323	-0.00000
F	2.20909	3.59498	0.54903	H	0.76307	-1.74200	0.00010
O	1.06677	1.48611	1.69763	O	1.93881	-0.09230	0.00000
				N	-0.34108	-0.02188	-0.00002
		A		C	-0.42151	1.42149	0.00001
C	-1.31104	1.38148	0.00001	H	-0.95450	1.77269	-0.88693
H	-1.78583	2.35598	0.00001	H	-0.95389	1.77317	0.88718
C	0.07659	1.29990	-0.00001	H	0.58852	1.82191	-0.00040
H	0.64642	2.21856	-0.00002	C	-1.58131	-0.75721	0.00001
C	0.72458	0.07039	-0.00001	H	-1.37440	-1.82631	0.00033
C	-0.08016	-1.07546	0.00003	H	-2.17498	-0.51687	0.88587
H	0.38314	-2.05472	0.00005	H	-2.17477	-0.51735	-0.88611
C	-1.45784	-0.99717	0.00004				
H	-2.03691	-1.91166	0.00007			**I**	
C	-2.10642	0.24128	0.00002	C	-1.24880	-0.20657	-0.00328
C	-3.56974	0.38294	0.00002	O	-1.69030	-0.41750	1.12715
H	-3.92591	1.40904	0.00008	O	-1.69211	-0.37603	-1.13996
C	-4.46650	-0.59711	-0.00006	C	0.21827	0.40021	0.00674
H	-5.52545	-0.37831	-0.00005	F	0.47934	1.14679	1.09196
H	-4.18623	-1.64278	-0.00014	F	0.47906	1.18332	-1.05249
C	2.24454	-0.07222	-0.00001	Cl	1.44806	-0.92850	-0.01609
C	2.68268	-0.84508	-1.25216				
H	2.24403	-1.84292	-1.28167			**I-10**	
H	3.76933	-0.95428	-1.26375	C	-0.25934	0.11052	-0.24843
H	2.37989	-0.31603	-2.15744	C	-1.78570	-0.01065	-0.39132
C	2.95074	1.28331	-0.00006	Cl	-2.36691	-0.09108	1.25016
H	4.03105	1.12994	-0.00002	F	-2.05551	-1.10509	-1.06893
H	2.69624	1.86816	0.88571	F	-2.22992	1.05149	-1.02633
H	2.69630	1.86806	-0.88592	O	0.30611	1.24091	-0.12823
C	2.68268	-0.84498	1.25220	O	0.46584	-0.93950	-0.19831

C	1.75426	0.99491	0.07215
C	1.85168	-0.55346	0.02947
F	2.23231	-1.05905	1.16195
F	2.56028	-0.98184	-0.96781
O	2.51650	1.84246	0.21231

VI

C	0.75501	0.57716	-0.25571
Cl	1.93236	-0.64924	0.13150
O	0.98645	1.54328	-0.88129
C	-0.65456	0.25453	0.29716
F	-1.39564	1.35160	0.24733
F	-0.58164	-0.14729	1.56364
Cl	-1.38522	-1.00812	-0.69016

I-16

C	-1.10802	2.28702	-0.24218
F	-0.73547	2.25165	-1.53302
F	-2.16930	3.08903	-0.13406
C	0.02646	2.62157	0.70606
H	-0.36459	3.26811	1.49004
H	0.82874	3.13212	0.18011
C	0.49676	1.26895	1.28818
H	0.54036	1.31591	2.37594
N	-0.62934	0.33491	0.94397
C	-1.49478	0.85968	0.15412
C	4.25679	-0.19927	-0.24987
C	3.10643	-0.21737	-1.03682
H	3.14574	-0.59283	-2.04899
C	1.88941	0.24021	-0.54979
H	1.02172	0.20929	-1.20094
C	1.79332	0.72733	0.74698
C	2.93014	0.74751	1.54985
H	2.87322	1.12468	2.56535
C	4.13893	0.29481	1.05325
H	5.00840	0.32443	1.69695
O	-2.57094	0.33245	-0.35372
C	-3.38426	-0.55958	0.37520
C	-4.39964	-1.20119	-0.58542
Cl	-5.60923	-0.00588	-1.00147
F	-4.94642	-2.23156	0.03088
F	-3.76118	-1.62291	-1.67076
O	-3.29479	-0.70571	1.53329
C	-0.55363	-1.13804	1.27995
C	0.00385	-1.41841	2.62545
H	-0.57192	-0.87414	3.37707
H	1.04461	-1.09120	2.67238
H	-0.05515	-2.48772	2.80485
O	-0.94031	-1.88412	0.45232
C	5.60988	-0.69300	-0.75124
C	6.08517	-1.84628	0.14486
H	7.05235	-2.20906	-0.20582
H	6.20442	-1.53214	1.18229
H	5.37901	-2.67795	0.11746
C	6.62026	0.46175	-0.68053
H	7.59228	0.12096	-1.03981
H	6.30041	1.29855	-1.30359
H	6.75150	0.82540	0.33905
C	5.54144	-1.19299	-2.19375
H	4.85662	-2.03668	-2.29814
H	5.23300	-0.40357	-2.88168
H	6.53013	-1.53157	-2.50355

I-17

C	-0.57204	0.84527	-0.43316
H	-0.04627	0.25983	-1.18418
O	0.08408	0.45204	0.91985
C	-0.31702	2.32823	-0.59265
H	-0.65107	2.88143	0.28713
H	-0.90839	2.66481	-1.44539
C	1.12647	2.71887	-0.84776
F	1.90365	2.36701	0.20559
F	1.21775	4.03632	-0.97584
Cl	1.80734	1.95223	-2.29352
C	-1.99462	0.43693	-0.32132
C	-2.45495	-0.62348	-1.08953
H	-1.77811	-1.14535	-1.75681
C	-3.78587	-1.01271	-1.02327
H	-4.11477	-1.83457	-1.64224
C	-4.68459	-0.36485	-0.17994
C	-4.19811	0.69515	0.59822
H	-4.86750	1.21772	1.26869
C	-2.88088	1.09749	0.53103
H	-2.54356	1.91733	1.15407
C	-6.15302	-0.76070	-0.07557
C	-6.50056	-1.93230	-0.99311
H	-7.55742	-2.17451	-0.88116
H	-5.92869	-2.82737	-0.74124
H	-6.32762	-1.68927	-2.04313
C	-7.02296	0.44334	-0.46740
H	-8.07707	0.17073	-0.39976
H	-6.81654	0.75675	-1.49204
H	-6.85711	1.29652	0.19101
C	-6.45987	-1.16578	1.37409
H	-5.84685	-2.01518	1.67997
H	-7.50859	-1.45380	1.45929
H	-6.28238	-0.34689	2.07180
C	1.17677	-0.12368	1.00369
O	1.82065	-0.49452	-0.04200

C	1.67730	-0.44643	2.43345
Cl	2.53597	0.92699	3.06010
F	2.45992	-1.52231	2.35616
F	0.62451	-0.73552	3.17544
C	3.24236	-0.80809	-0.08689
C	3.41644	-2.07522	-0.94023
O	4.03616	-0.11992	0.40263
Cl	3.06560	-1.68531	-2.61033
F	4.65536	-2.49431	-0.79997
F	2.57707	-3.00540	-0.49073

I-18

C	-1.35921	0.47075	0.53326
O	-1.00826	1.29370	-0.45752
C	-2.02412	-0.79351	-0.04670
Cl	-0.77318	-1.82323	-0.74422
F	-2.91560	-0.47138	-0.98322
F	-2.65197	-1.44493	0.92239
O	-1.21435	0.64302	1.69913
C	-0.10356	2.35762	-0.24901
C	1.08499	2.05739	0.63037
H	0.75569	2.11514	1.66783
H	1.78683	2.87132	0.45066
O	-0.30782	3.35950	-0.83859
C	2.77575	-0.80263	-1.19770
H	3.14392	-1.01581	-2.19271
C	2.88801	-1.75578	-0.19274
H	3.34455	-2.71414	-0.40298
C	2.41318	-1.47534	1.07961
H	2.49466	-2.21458	1.86563
C	1.82354	-0.24702	1.34790
H	1.43752	-0.03445	2.33749
C	1.71227	0.71286	0.34863
C	2.19312	0.42504	-0.92668
H	2.10853	1.16813	-1.71250

I-19

C	1.72269	-1.20309	-0.28701
C	1.10611	-0.18548	0.71990
O	0.65602	0.87535	-0.12965
O	2.04661	0.18220	1.58339
Cl	3.21849	-0.56653	-0.97837
F	1.99262	-2.34248	0.35334
F	0.87353	-1.47553	-1.27086
C	-0.04977	-0.82753	1.56757
H	0.37448	-1.72368	2.01481
H	-0.25844	-0.11196	2.35965
C	-1.29263	-1.13676	0.77998
C	-2.28596	-0.17452	0.62155
H	-2.16872	0.80064	1.07915
C	-3.43649	-0.46308	-0.09755
H	-4.19931	0.29510	-0.21557
C	-3.60946	-1.72104	-0.65627
H	-4.50772	-1.94772	-1.21546
C	-2.63074	-2.69187	-0.48877
H	-2.76508	-3.67805	-0.91332
C	-1.47892	-2.39983	0.22399
H	-0.71412	-3.15749	0.34938
C	0.15426	1.98727	0.42014
C	-0.20298	2.96820	-0.70507
H	0.62774	3.11913	-1.39684
O	-0.01142	2.20255	1.57751
F	-0.56815	4.13842	-0.17001
F	-1.25463	2.46189	-1.38695

XII

C	-1.96523	-1.72447	0.13895
C	-1.74022	-0.28647	-0.36993
O	-0.71827	0.26301	0.27414
O	-2.39894	0.20436	-1.23026
F	-1.91276	-1.76655	1.47172
Cl	-0.71060	-2.76693	-0.53347
F	-3.15936	-2.15188	-0.24484
C	-0.18815	1.50023	-0.25552
C	-1.19126	2.64296	0.05774
O	0.07005	1.44908	-1.54886
C	1.14528	1.73172	0.52087
H	1.55517	2.67442	0.16528
H	0.85191	1.83968	1.56550
C	2.10843	0.59408	0.33581
C	2.16197	-0.44114	1.26239
H	1.50528	-0.42076	2.12408
C	3.04080	-1.50031	1.08321
H	3.07400	-2.30039	1.81105
C	3.87087	-1.53324	-0.02767
H	4.55633	-2.35862	-0.16881
C	3.82009	-0.50395	-0.95915
H	4.46488	-0.52535	-1.82789
C	2.94298	0.55372	-0.77726
H	2.89910	1.35406	-1.50717
F	-0.60058	3.81813	-0.22257
F	-1.47983	2.62241	1.37444
H	-2.10986	2.54528	-0.51878

I-20

C	2.13092	-0.87777	0.00001
H	3.09179	-0.37339	-0.00029
H	2.03743	-1.51462	-0.87905
H	2.03777	-1.51414	0.87947

C	1.03019	0.14427	-0.00002
O	1.18440	1.33405	0.00001
O	-0.17711	-0.44112	-0.00005
C	-1.30107	0.44839	-0.00001
H	-1.24036	1.09001	-0.88017
H	-1.24031	1.09000	0.88016
C	-2.55058	-0.39787	0.00002
H	-3.43174	0.24362	0.00011
H	-2.58481	-1.03353	0.88435
H	-2.58493	-1.03344	-0.88436

I-21

C	-2.12960	-0.92006	0.00005
H	-1.88967	-1.97107	-0.00003
H	-3.15250	-0.58121	0.00025
C	-1.08207	0.07842	-0.00009
O	-1.27502	1.27232	0.00007
O	0.14649	-0.47264	-0.00012
C	1.23692	0.45484	-0.00007
H	1.15377	1.09495	0.87982
H	1.15394	1.09482	-0.88008
C	2.51554	-0.34657	0.00010
H	2.57223	-0.98019	0.88470
H	3.37329	0.32589	0.00013
H	2.57239	-0.98033	-0.88439

I-22

C	1.20243	-0.69423	-0.00000
H	2.13977	-1.23554	-0.00000
C	-0.00006	-1.38844	-0.00000
H	-0.00003	-2.47088	-0.00000
C	-1.20242	-0.69426	0.00000
H	-2.13991	-1.23533	0.00000
C	-1.20239	0.69430	0.00000
H	-2.13984	1.23542	0.00000
C	-0.00000	1.38843	0.00000
H	0.00004	2.47088	0.00000
C	1.20246	0.69421	-0.00000

I-23

C	-1.21843	0.76627	0.00006
H	-2.14989	1.31767	0.00011
C	0.00000	1.39328	-0.00008
C	1.21843	0.76627	-0.00015
H	2.14989	1.31767	-0.00027
C	1.20690	-0.62861	-0.00007
H	2.14299	-1.17315	-0.00013
C	-0.00000	-1.31695	0.00008
H	-0.00000	-2.39898	0.00013
C	-1.20690	-0.62861	0.00015
H	-2.14299	-1.17315	0.00026

I-24

C	1.89365	-1.52158	-0.73204
H	2.67007	-1.89339	-1.38645
C	2.13579	-0.41710	0.08841
C	1.08546	0.00364	0.91674
H	1.22755	0.85808	1.56769
C	-0.13911	-0.62262	0.92242
H	-0.92163	-0.23648	1.56166
C	-0.39850	-1.72937	0.07894
C	0.66936	-2.16061	-0.73792
H	0.51263	-3.00980	-1.39312
C	3.45983	0.33934	0.10353
C	4.48335	-0.26829	-0.85537
H	4.12867	-0.24521	-1.88741
H	4.71432	-1.30221	-0.59225
H	5.41111	0.30432	-0.80802
C	4.05107	0.31309	1.52035
H	4.99804	0.85712	1.54227
H	4.23580	-0.71352	1.84136
H	3.37965	0.77694	2.24344
C	3.21179	1.79651	-0.31456
H	2.79162	1.84059	-1.32109
H	2.51587	2.29340	0.36231
H	4.15025	2.35557	-0.30680
C	-1.65453	-2.37150	0.00292
H	-1.74701	-3.18708	-0.70604
C	-2.88372	-1.98077	0.74845
H	-2.63292	-1.53696	1.71475
H	-3.47994	-2.87297	0.95360
C	-3.77538	-0.98013	-0.03278
H	-4.71149	-0.84961	0.51454
H	-4.02037	-1.41089	-1.00582
C	-3.09542	0.34880	-0.21056
C	-2.30459	0.60668	-1.32647
H	-2.23477	-0.13908	-2.11010
C	-1.58290	1.78718	-1.42947
H	-0.96145	1.96396	-2.29801
C	-1.64797	2.73382	-0.41658
H	-1.08204	3.65317	-0.49358
C	-2.44890	2.49730	0.69300
H	-2.51478	3.23553	1.48216
C	-3.16672	1.31392	0.79121
H	-3.78459	1.12863	1.66354

I-3

C	0.00000	0.00000	-0.64009
O	0.00000	0.00000	0.48007

		I-4	
C	0.00051	-0.37795	-0.00000
F	-0.00009	-1.03926	1.05375
F	-0.00009	-1.03926	-1.05375
Cl	-0.00009	1.23379	-0.00000
		I-6	
C	0.12860	-0.42508	-0.00007
F	0.48292	-1.11581	-1.07949
F	0.48108	-1.11523	1.08033
Cl	0.92850	1.13968	0.00007
C	-1.43777	-0.32032	-0.00115
O	-2.07570	0.64715	-0.00019
		I-7	
C	0.00000	0.00000	0.00000
O	0.00000	0.00000	1.15457
O	0.00000	0.00000	-1.15457
		I	
C	-0.39792	-0.41452	0.50612
O	0.35978	-0.68050	-0.57061
O	-0.01282	-0.27021	1.61729
C	1.74816	-0.74885	-0.37481
O	2.35738	-1.76269	-0.55069
C	-1.87528	-0.28489	0.09209
F	-2.21572	-1.24908	-0.75910
F	-2.64173	-0.37927	1.16739
Cl	-2.10748	1.29117	-0.67055
C	2.32483	0.50295	-0.03207
F	1.64431	1.59633	0.11162
F	3.59021	0.63527	0.17824
		II	
C	-0.67324	1.07704	0.60040
O	-0.16311	0.67465	1.58290
O	-1.83211	0.64636	0.03162
C	-2.69269	-0.16583	0.74987
C	-3.45656	-1.07574	-0.23204
O	-2.83420	-0.13003	1.91691
C	-2.53565	-1.87167	-1.14372
H	-3.16657	-2.62345	-1.62484
H	-2.17250	-1.19046	-1.90982
F	-4.29326	-0.29425	-0.96046
F	-4.21952	-1.90009	0.50688
C	-1.42889	-2.48318	-0.35148
H	-1.70483	-3.24981	0.36252
C	-0.09084	-2.03356	-0.35557
C	0.41578	-1.08148	-1.26727
H	-0.20889	-0.70378	-2.06565
C	1.70671	-0.59904	-1.15850
H	2.03661	0.14066	-1.87509
C	2.56991	-1.03024	-0.14945
C	2.08499	-2.00954	0.73133
H	2.72335	-2.37728	1.52493
C	0.80774	-2.50409	0.63279
H	0.45755	-3.24136	1.34510
C	3.97375	-0.46977	0.03973
C	4.32845	0.56811	-1.02484
H	3.65142	1.42351	-0.99221
H	4.30032	0.13983	-2.02870
H	5.33982	0.93674	-0.84768
C	4.99896	-1.61011	-0.03353
H	4.82193	-2.36220	0.73570
H	6.00618	-1.21392	0.11082
H	4.95987	-2.10396	-1.00606
C	4.05294	0.20246	1.41910
H	3.31571	1.00306	1.49982
H	5.04744	0.62755	1.57036
H	3.86398	-0.50982	2.22283
C	-0.10059	2.23513	-0.24079
F	1.19101	2.37825	0.02543
F	-0.23770	2.00979	-1.54804
Cl	-0.96267	3.71428	0.18918
		III	
C	-3.50526	-0.98399	-0.66675
O	-2.83862	-1.81393	-1.15682
O	-3.08698	0.31798	-0.40279
C	-1.80492	0.55722	-0.10364
C	-1.47434	2.06295	-0.14370
O	-0.98175	-0.23440	0.23017
C	0.01183	2.28184	-0.39848
H	0.24411	2.01563	-1.42737
H	0.17488	3.36145	-0.27668
F	-1.80537	2.56507	1.06754
F	-2.19401	2.69418	-1.07276
C	0.85179	1.58312	0.59669
H	0.47875	1.60104	1.61780
C	2.07158	0.98711	0.38638
C	2.74008	0.41279	1.50678
H	2.26741	0.46866	2.48017
C	3.95228	-0.20430	1.36152
H	4.43516	-0.63450	2.22565
C	4.56820	-0.28453	0.09845
C	3.90906	0.28884	-1.01936
H	4.37475	0.23136	-1.99296
C	2.70061	0.90189	-0.89270
H	2.22066	1.32383	-1.76518
C	5.90193	-0.96326	-0.10563

C	6.48111	-1.53028	1.18957
H	6.66222	-0.74975	1.93049
H	7.43820	-2.00283	0.97184
H	5.83220	-2.29094	1.62682
C	6.88936	0.06941	-0.68488
H	6.56304	0.45865	-1.64878
H	7.85450	-0.41625	-0.83091
H	7.02943	0.90699	-0.00035
C	5.71049	-2.11443	-1.11345
H	6.66951	-2.61227	-1.25884
H	5.36768	-1.76077	-2.08528
H	4.99741	-2.85021	-0.73958
C	-4.97247	-1.14019	-0.23285
F	-5.68766	-0.10052	-0.65121
F	-5.46100	-2.24453	-0.76454
Cl	-5.01215	-1.23413	1.52528
H	5.36768	-1.76077	-2.08528
H	4.99741	-2.85021	-0.73958
C	-4.97247	-1.14019	-0.23285
F	-5.68766	-0.10052	-0.65121
F	-5.46100	-2.24453	-0.76454
Cl	-5.01215	-1.23413	1.52528

IV

C	-4.93753	0.12770	1.15711
F	-4.83627	-0.78565	2.11707
Cl	-6.11795	-0.37035	-0.04283
F	-5.28448	1.28431	1.69870
C	-3.58369	0.30149	0.44723
O	-3.00872	-0.91458	0.21533
O	-3.10377	1.34489	0.16699
C	-2.16401	-1.06136	-0.84654
C	-1.16286	-2.20208	-0.60477
F	-0.83900	-2.69584	-1.81494
F	-1.74132	-3.17714	0.11153
C	0.09842	-1.72281	0.09699
H	0.76925	-2.58295	0.12088
H	-0.13681	-1.44713	1.12590
C	0.78284	-0.57240	-0.62684
O	0.07360	0.65966	-0.19750
C	-0.24182	1.53206	-1.09400
H	-0.18092	1.26400	-2.14527
N	-0.64658	2.70996	-0.77624
C	-1.14011	3.63084	-1.79975
H	-2.20160	3.80253	-1.62527
H	-0.99752	3.20061	-2.78728
H	-0.59714	4.57083	-1.72153
C	-0.74019	3.17170	0.60853
H	-0.19279	4.10941	0.69001
H	-0.31363	2.43047	1.27479
H	-1.78938	3.33220	0.84945
H	0.63664	-0.66810	-1.70579
O	-2.15865	-0.37300	-1.81012
C	4.97896	-0.10891	0.24165
C	4.02759	-0.16378	1.26926
H	4.34916	-0.09241	2.30024
C	2.68195	-0.31570	1.00260
H	1.97576	-0.35768	1.82429
C	2.23726	-0.41090	-0.31590
C	3.16318	-0.35208	-1.34491
H	2.83656	-0.43668	-2.37564
C	4.51798	-0.20659	-1.06716
H	5.21292	-0.17457	-1.89376
C	6.45573	0.04696	0.59092
C	6.89139	-1.13852	1.46491
H	6.75344	-2.08311	0.93633
H	7.94799	-1.04018	1.71842
H	6.32810	-1.18423	2.39748
C	7.34109	0.08370	-0.65419
H	8.38253	0.19535	-0.35185
H	7.26250	-0.83824	-1.23318
H	7.09308	0.92630	-1.30244
C	6.65226	1.35633	1.36900
H	6.08173	1.36567	2.29825
H	7.70599	1.47841	1.62412
H	6.34462	2.21511	0.76979

IX

C	1.72825	-0.79547	-0.29245
C	2.28689	0.46411	0.39560
H	2.32463	0.35019	1.47880
F	1.50838	1.52113	0.08288
F	3.51695	0.67977	-0.08354
O	0.34588	-0.83146	-0.44055
O	2.39432	-1.65710	-0.73349
C	-0.44393	-0.42822	0.57072
C	-1.89310	-0.26038	0.07863
Cl	-2.01051	1.25230	-0.81612
F	-2.70556	-0.23187	1.12412
F	-2.24394	-1.27811	-0.70452
O	-0.10234	-0.22867	1.68775

MeCN

C	0.00000	-0.00000	0.28215
N	0.00000	-0.00000	1.42744
C	0.00000	-0.00000	-1.17536
H	-1.02402	0.00000	-1.54425
H	0.51201	0.88683	-1.54425
H	0.51201	-0.88683	-1.54425

Toluene

C	-1.19604	1.19728	0.00188
C	0.19217	1.19659	-0.00826
C	0.90764	0.00284	-0.01098
C	0.19559	-1.19438	-0.00834
C	-1.19136	-1.19993	0.00192
C	-1.89322	-0.00203	0.00793
H	-1.73330	2.13713	0.00161
H	0.73001	2.13760	-0.01672
H	0.73718	-2.13346	-0.01689
H	-1.72570	-2.14145	0.00174
H	-2.97536	-0.00407	0.01312
C	2.41161	0.00101	0.00872
H	2.78422	-0.12304	1.02794
H	2.81218	-0.81786	-0.58898
H	2.81239	0.93695	-0.37902

V

C	-1.60105	2.37940	-0.28652
F	-2.16632	2.77152	-1.42048
F	-2.25631	2.93488	0.74840
C	-0.10507	2.58258	-0.20328
H	0.13179	3.56053	0.21221
H	0.31767	2.50264	-1.20372
C	0.39170	1.46338	0.69863
H	0.20747	1.65988	1.75275
O	-0.72617	0.33815	0.42455
C	-1.72508	0.85530	-0.09459
C	4.24998	-0.29135	0.10158
C	3.44012	0.04581	-0.99287
H	3.79438	-0.14124	-1.99780
C	2.19873	0.61898	-0.82313
H	1.60781	0.85729	-1.69979
C	1.71263	0.86517	0.46417
C	2.49734	0.52172	1.55982
H	2.13235	0.70242	2.56431
C	3.75142	-0.04005	1.37832
H	4.33990	-0.28335	2.25066
O	-2.80931	0.25390	-0.41945
C	-2.94164	-1.18919	-0.35300
C	-4.44340	-1.51416	-0.26987
Cl	-4.98972	-1.10133	1.34452
F	-4.59512	-2.80029	-0.50724
F	-5.10086	-0.81106	-1.18239
O	-2.03054	-1.90987	-0.36921
C	5.62124	-0.90895	-0.14226
C	6.46718	0.06894	-0.97230
H	6.59776	1.01605	-0.44635
H	7.45366	-0.36168	-1.14915
H	6.01580	0.27575	-1.94305
C	6.35935	-1.20751	1.16213
H	6.53601	-0.30116	1.74414
H	5.81426	-1.92212	1.78153
H	7.33067	-1.64525	0.93208
C	5.44489	-2.22315	-0.91846
H	6.42146	-2.67604	-1.09474
H	4.83714	-2.93183	-0.35358
H	4.97263	-2.06360	-1.88820

VII

C	-0.44520	-1.80927	-0.09378
H	-0.58829	-2.88293	-0.21968
C	0.46918	-1.27496	-1.20081
H	0.59084	-0.19361	-1.11856
H	-0.03982	-1.47339	-2.14586
C	1.83709	-1.94288	-1.29791
C	2.82445	-1.42335	-0.23904
O	3.18055	-0.11934	-0.51942
C	0.76204	-1.55151	2.18903
N	0.21725	-1.67612	1.19832
C	1.47904	-1.41291	3.43250
H	1.07275	-2.11426	4.16107
H	1.37664	-0.38547	3.78128
H	2.52906	-1.63034	3.22756
C	3.05963	0.79831	0.46950
O	2.47996	0.63090	1.49093
O	3.19428	-2.01647	0.71005
F	1.72098	-3.27072	-1.13532
F	2.35805	-1.69990	-2.51173
C	-1.77567	-1.09868	-0.05008
C	-1.84476	0.25954	0.25124
H	-0.94603	0.81970	0.49177
C	-3.06619	0.90297	0.25272
H	-3.09896	1.95754	0.49337
C	-4.25277	0.22400	-0.05376
C	-4.15964	-1.13177	-0.35309
H	-5.04721	-1.69861	-0.59383
C	-2.93612	-1.79192	-0.34687
H	-2.89709	-2.84983	-0.57948
C	-5.57638	0.98214	-0.04717
C	-5.81253	1.56588	1.35365
H	-5.85984	0.77391	2.10297
H	-6.75890	2.10828	1.37079
H	-5.02487	2.26302	1.64156
C	-5.50384	2.12324	-1.07277
H	-6.44703	2.67136	-1.07961
H	-5.32805	1.73408	-2.07698
H	-4.70918	2.83183	-0.83690
C	-6.75742	0.08057	-0.40447
H	-6.65544	-0.34187	-1.40576

	VIII		
C	-2.80703	1.59407	0.33334
C	-3.50467	2.88614	0.09892
H	-2.80845	3.60413	-0.32216
H	-3.91283	3.25984	1.03821
H	-4.33868	2.72536	-0.58581
N	-1.61870	1.35774	0.02336
C	-1.04236	0.05584	0.32276
H	-1.32146	-0.24596	1.34149
C	-1.59591	-0.99573	-0.64921
H	-1.25057	-1.98612	-0.35206
H	-1.25112	-0.79439	-1.66526
C	-3.11406	-1.00858	-0.67053
F	-3.57391	-2.22326	-1.01112
F	-3.59057	-0.13338	-1.60158
C	-3.73293	-0.61797	0.68764
O	-3.64824	0.69643	1.00315
O	-4.26243	-1.39306	1.40924
C	3.28011	0.01584	0.03906
C	2.58914	-0.87716	0.86235
H	3.13678	-1.61057	1.44140
C	1.21006	-0.84401	0.96468
H	0.70490	-1.54615	1.61996
C	0.46621	0.08565	0.24407
C	1.13733	0.97930	-0.57411
H	0.57162	1.71795	-1.12640
C	2.52415	0.94230	-0.67260
H	3.01030	1.65944	-1.31915
C	4.80387	-0.05395	-0.04126
C	5.22217	-1.44162	-0.54745
H	4.80981	-1.63063	-1.54014
H	6.31063	-1.50558	-0.60896
H	4.87608	-2.23289	0.11828
C	5.38031	0.99731	-0.98939
H	6.46724	0.90551	-1.01466
H	5.01029	0.86546	-2.00779
H	5.13832	2.00983	-0.66136
C	5.39807	0.17761	1.35515
H	5.10999	1.15775	1.73908
H	5.05884	-0.57649	2.06597
H	6.48828	0.13184	1.31056
	X		
C	-1.12767	-1.20454	0.00001
C	0.25116	-1.20992	0.00003
C	0.98501	-0.00003	-0.00004
C	0.25117	1.20994	0.00004
C	-1.12759	1.20457	-0.00000
C	-1.82845	-0.00000	-0.00003
H	-1.66843	-2.14232	0.00003
H	0.79243	-2.14836	0.00011
H	0.79255	2.14832	0.00009
H	-1.66840	2.14233	0.00000
H	-2.91024	0.00007	-0.00006
C	2.39130	-0.00003	-0.00007
H	2.94624	0.92672	0.00017
H	2.94623	-0.92676	0.00002
	XI		
C	-1.49635	-0.58907	0.77651
C	-2.70765	-0.57052	-0.18090
Cl	-2.71021	0.94429	-1.08921
F	-3.82541	-0.66583	0.52514
F	-2.65582	-1.59746	-1.02793
O	-0.38609	-0.81578	0.08329
O	-1.60310	-0.39818	1.94450
C	0.85596	-0.98391	0.78413
C	1.31759	0.30832	1.54766
H	2.35196	0.12695	1.83126
H	0.71369	0.34169	2.45175
C	1.84264	-1.37781	-0.35687
Cl	1.48229	-2.99400	-0.96234
F	3.08903	-1.35907	0.12127
F	1.77571	-0.51069	-1.36130
O	0.82878	-1.95714	1.68563
C	0.92012	3.97280	-0.64990
H	0.82271	4.90062	-1.19822
C	2.09754	3.23975	-0.72649
H	2.92084	3.59563	-1.33173
C	2.22197	2.05167	-0.02484
H	3.14192	1.48218	-0.08578
C	1.17260	1.58193	0.76177
C	0.00188	2.32974	0.84501
H	-0.80843	1.98987	1.47928
C	-0.12548	3.51788	0.13961
H	-1.04134	4.08969	0.21353
	XIII		
C	-0.93944	0.89344	-0.28687
C	0.01318	0.31631	-1.30653
H	0.09851	1.04896	-2.10906
H	-0.38242	-0.61468	-1.71132
C	-1.80333	-0.12723	0.48995
Cl	-3.16552	-0.60043	-0.54694
F	-2.26525	0.38696	1.61802
F	-1.09094	-1.22173	0.78713
O	-1.05679	2.05507	-0.04071
C	3.85037	-0.33574	0.52646
H	4.81664	-0.49621	0.98633
C	3.35432	0.95305	0.37917

H	3.93240	1.80014	0.72459
C	2.11697	1.15910	-0.21101
H	1.72499	2.16348	-0.32135
C	1.36464	0.07767	-0.66125
C	1.86231	-1.21035	-0.50502
H	1.27527	-2.05585	-0.84287
C	3.10215	-1.41665	0.08388
H	3.48136	-2.42371	0.19836

XIV

C	0.42101	-0.00000	0.32644
F	1.05215	-1.07900	-0.07914
F	1.05215	1.07901	-0.07914
Cl	-1.26264	-0.00000	-0.03141

XV

C	2.46654	0.75174	-0.18507
H	2.28988	1.26677	0.76294
H	2.38345	1.50511	-0.97950
C	1.51243	-0.37244	-0.39274
H	1.91139	-1.33365	-0.68903
C	0.11586	-0.22749	-0.26271
C	-0.49824	0.99469	0.07788
H	0.10993	1.87449	0.24737
C	-1.87273	1.09892	0.19575
H	-2.29175	2.06034	0.45830
C	-2.71234	0.00501	-0.01525
C	-2.10346	-1.21355	-0.35680
H	-2.71868	-2.08800	-0.53041
C	-0.74064	-1.33307	-0.47891
H	-0.30245	-2.28807	-0.74345
C	-4.23041	0.08250	0.10791
C	-4.70868	1.48446	0.48484
H	-4.42431	2.22175	-0.26817
H	-4.30577	1.80035	1.44887
H	-5.79709	1.48809	0.56081
C	-4.86972	-0.30156	-1.23463
H	-5.95807	-0.25350	-1.15795
H	-4.59825	-1.31441	-1.53361
H	-4.54952	0.38114	-2.02358
C	-4.70262	-0.89694	1.19252
H	-5.78948	-0.85200	1.28950
H	-4.25993	-0.64602	2.15796
H	-4.42890	-1.92471	0.95227
C	3.90969	0.31175	-0.19142
F	4.72087	1.37307	-0.06540
F	4.22714	-0.28526	-1.35164
Cl	4.28255	-0.82307	1.12664

XVI

C	1.52590	0.57352	-0.63159
H	1.88179	1.60050	-0.57480
C	2.56404	-0.43499	-0.92961
H	2.80557	-0.36330	-1.99982
H	2.26748	-1.45691	-0.70923
C	3.85726	-0.12243	-0.18449
Cl	3.59729	-0.12174	1.56498
F	4.78171	-1.02377	-0.49609
F	4.31096	1.08262	-0.55190
C	0.18623	0.36354	-0.44735
C	-0.42667	-0.93029	-0.48919
H	0.17611	-1.81026	-0.66753
C	-1.76718	-1.05592	-0.30390
H	-2.21819	-2.03743	-0.33739
C	-2.59042	0.07630	-0.06063
C	-1.99404	1.35325	-0.01449
H	-2.60260	2.22525	0.17060
C	-0.64904	1.49846	-0.20109
H	-0.19293	2.48079	-0.16474
C	-4.07077	-0.12578	0.14268
C	-4.82003	1.18219	0.39218
H	-5.87817	0.96237	0.52849
H	-4.73454	1.86816	-0.45224
H	-4.47154	1.68543	1.29561
C	-4.64497	-0.79928	-1.12118
H	-5.71638	-0.94249	-0.97914
H	-4.20024	-1.77580	-1.30959
H	-4.49876	-0.17300	-2.00206
C	-4.26948	-1.05677	1.35700
H	-3.81830	-2.03690	1.20656
H	-5.33931	-1.20153	1.50900
H	-3.85290	-0.61593	2.26344

XVII

C	0.86892	-0.00006	-0.54827
C	-0.57488	-0.00011	-0.97767
C	-1.51545	-0.00000	0.21150
Cl	-3.21886	0.00000	-0.30887
F	-1.32142	1.07772	0.98525
F	-1.32146	-1.07762	0.98540
C	1.54166	1.19935	-0.33820
C	2.86649	1.20081	0.07237
C	3.53145	0.00005	0.27813
C	2.86658	-1.20075	0.07242
C	1.54174	-1.19940	-0.33817
H	-0.81145	0.88228	-1.57175
H	-0.81144	-0.88261	-1.57158
H	1.02226	2.13716	-0.49580
H	3.37987	2.14022	0.23042
H	4.56575	0.00011	0.59633

H	3.38000	-2.14013	0.23049	
H	1.02242	-2.13726	-0.49571	

15.4. Cartesian coordinates – solvent re-optimized structures for the calculation of reduction potentials

II - reoptimized in solvent			
C	-0.71435	1.09533	0.61008
O	-0.21382	0.71885	1.61053
O	-1.85318	0.63076	0.03451
C	-2.69701	-0.20182	0.73912
C	-3.44333	-1.11899	-0.24968
O	-2.83759	-0.18538	1.90964
C	-2.50408	-1.90953	-1.14376
H	-3.11474	-2.68013	-1.62021
H	-2.14766	-1.23293	-1.91705
F	-4.28302	-0.34637	-0.98468
F	-4.21093	-1.94240	0.49128
C	-1.39339	-2.49211	-0.33355
H	-1.65543	-3.27352	0.36944
C	-0.06163	-2.02250	-0.33515
C	0.42998	-1.05392	-1.23892
H	-0.20177	-0.67469	-2.03104
C	1.71992	-0.56504	-1.13578
H	2.03898	0.18294	-1.84880
C	2.59708	-1.00623	-0.14220
C	2.12574	-1.99901	0.73293
H	2.77572	-2.37886	1.51159
C	0.84866	-2.49896	0.64139
H	0.51233	-3.25279	1.34327
C	4.00576	-0.45125	0.02902
C	4.34145	0.60486	-1.02372
H	3.66336	1.45836	-0.96583
H	4.29563	0.19359	-2.03387
H	5.35553	0.97046	-0.85608
C	5.02562	-1.59359	-0.08484
H	4.86241	-2.35694	0.67653
H	6.03625	-1.20075	0.04352
H	4.96395	-2.06936	-1.06540
C	4.11889	0.19492	1.41846
H	3.39856	1.00887	1.52316
H	5.12235	0.60225	1.55791
H	3.93402	-0.52881	2.21309
C	-0.14876	2.25311	-0.23633
F	1.14081	2.40507	0.03871
F	-0.27798	2.01692	-1.54054
Cl	-1.02506	3.72399	0.18452
III - reoptimized in solvent			
C	-3.73023	-0.99855	-0.54462
O	-3.19492	-1.98077	-0.91164
O	-3.14960	0.21500	-0.30809
C	-1.80883	0.33284	-0.12878
C	-1.39519	1.81768	-0.12864
O	-1.04050	-0.54531	0.07175
C	0.08592	1.99165	-0.39591
H	0.30223	1.70541	-1.42317
H	0.28687	3.06721	-0.29693
F	-1.71849	2.30464	1.09346
F	-2.11057	2.49606	-1.03791
C	0.93085	1.29578	0.59623
H	0.53477	1.23103	1.60610
C	2.18811	0.78985	0.38527
C	2.86950	0.20583	1.49303
H	2.37191	0.17454	2.45418
C	4.12930	-0.30724	1.34627
H	4.62238	-0.74721	2.19901
C	4.77637	-0.26203	0.09902
C	4.10602	0.32194	-1.00446
H	4.59755	0.36260	-1.96586
C	2.84947	0.82963	-0.87965
H	2.35832	1.26569	-1.73808
C	6.16950	-0.81515	-0.10379
C	6.75229	-1.43083	1.16725
H	6.84424	-0.69479	1.96734
H	7.75002	-1.81061	0.94789
H	6.14810	-2.26615	1.52462
C	7.08384	0.33620	-0.56383
H	6.74992	0.77245	-1.50456
H	8.09097	-0.05587	-0.71069
H	7.12645	1.12347	0.18991
C	6.11366	-1.89651	-1.19902
H	7.11670	-2.30056	-1.34086
H	5.77283	-1.49702	-2.15339
H	5.45143	-2.71220	-0.90610
C	-5.24201	-0.89063	-0.26467
F	-5.74101	0.21767	-0.80926
F	-5.85299	-1.93720	-0.80174
Cl	-5.50049	-0.86957	1.47596
NO_cation - optimized in solvent			
N	0.00000	0.00000	-0.55862

O	0.00000	0.00000	0.48879

NO_radical_neutral - optimized in solvent

N	0.00000	0.00000	-0.60563
O	0.00000	0.00000	0.52993

TCNE_neutral - optimized in solvent

C	0.00001	0.67412	0.00000
C	-0.00001	-0.67412	0.00000
C	-1.22401	-1.41731	0.00000
N	-2.20343	-2.01093	0.00000
C	-1.22401	1.41731	0.00000
N	-2.20343	2.01093	0.00000
C	1.22401	1.41731	0.00000
N	2.20343	2.01093	0.00000
C	1.22401	-1.41731	0.00000
N	2.20343	-2.01093	0.00000

TCNE_radical_anion - optimized in solvent

C	-0.00000	0.71171	0.00000
C	-0.00000	-0.71171	0.00000
C	-1.20586	-1.44003	0.00000
N	-2.20150	-2.02414	0.00000
C	-1.20586	1.44003	0.00000
N	-2.20151	2.02413	0.00000
C	1.20586	1.44003	0.00000
N	2.20150	2.02414	0.00000
C	1.20586	-1.44003	0.00000
N	2.20151	-2.02413	0.00000

XV - reoptimized in solvent

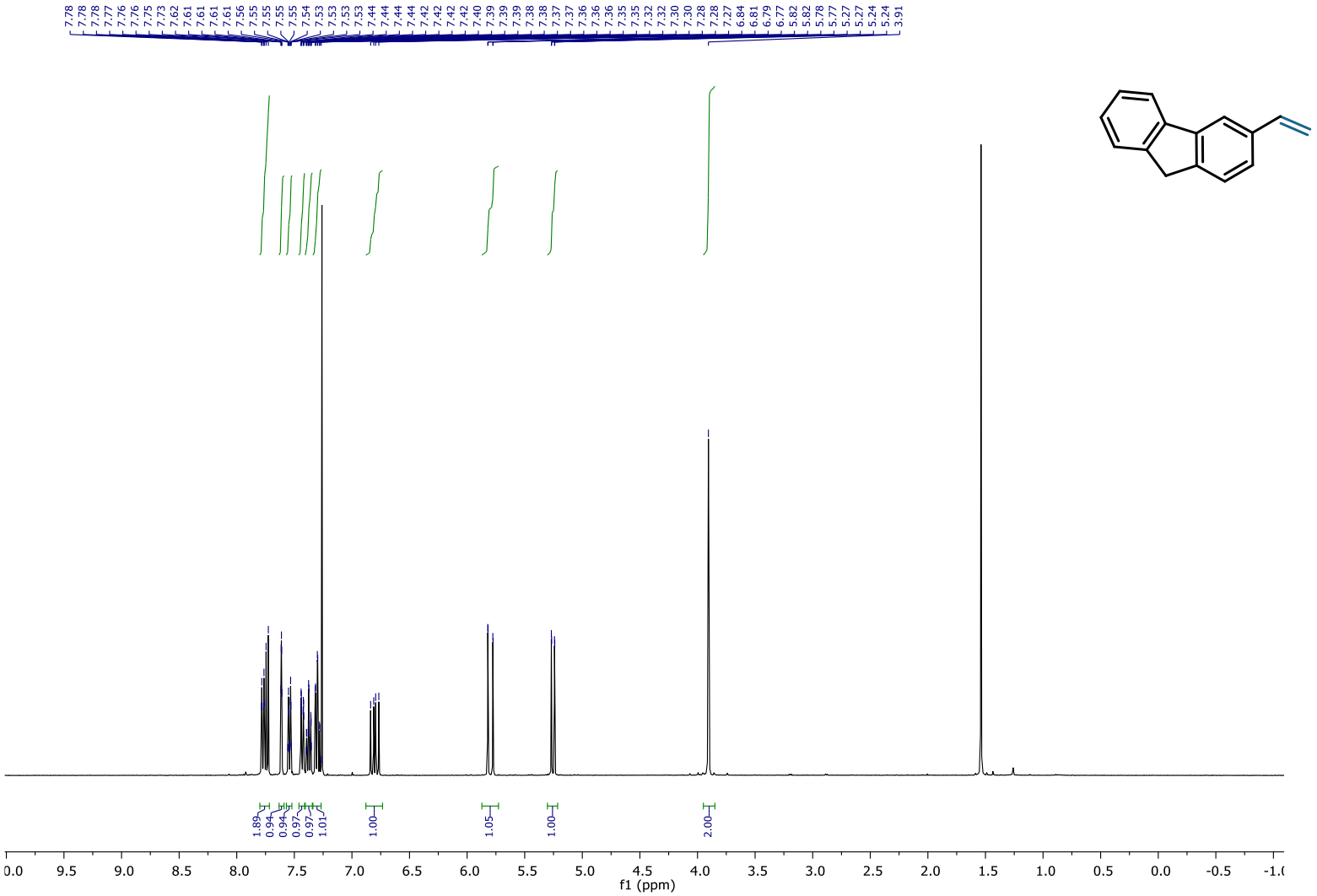
C	2.48029	0.75700	-0.28999
H	2.26862	1.34336	0.60670
H	2.45410	1.45149	-1.13993
C	1.51728	-0.36570	-0.46526
H	1.90398	-1.32872	-0.77354
C	0.12217	-0.21879	-0.31250
C	-0.48980	1.00610	0.02673
H	0.11664	1.89048	0.17655
C	-1.86364	1.10669	0.16553
H	-2.28044	2.06992	0.42544
C	-2.70431	0.00792	-0.02234
C	-2.09741	-1.21292	-0.36352
H	-2.71198	-2.09108	-0.52067
C	-0.73514	-1.32955	-0.50657
H	-0.29928	-2.28589	-0.77088
C	-4.22052	0.08348	0.12372
C	-4.69584	1.48683	0.49942
H	-4.42453	2.22011	-0.26234
H	-4.27801	1.80974	1.45480
H	-5.78296	1.48608	0.59190
C	-4.87927	-0.31132	-1.20657
H	-5.96612	-0.26560	-1.11069
H	-4.60922	-1.32560	-1.50253
H	-4.57555	0.36977	-2.00385
C	-4.67436	-0.89145	1.22056
H	-5.75977	-0.84625	1.33147
H	-4.21982	-0.63215	2.17865
H	-4.40266	-1.92005	0.98086
C	3.90992	0.29076	-0.19118
F	4.74498	1.33860	-0.09775
F	4.27795	-0.39576	-1.28791
Cl	4.19673	-0.75797	1.22004

XVI - reoptimized in solvent

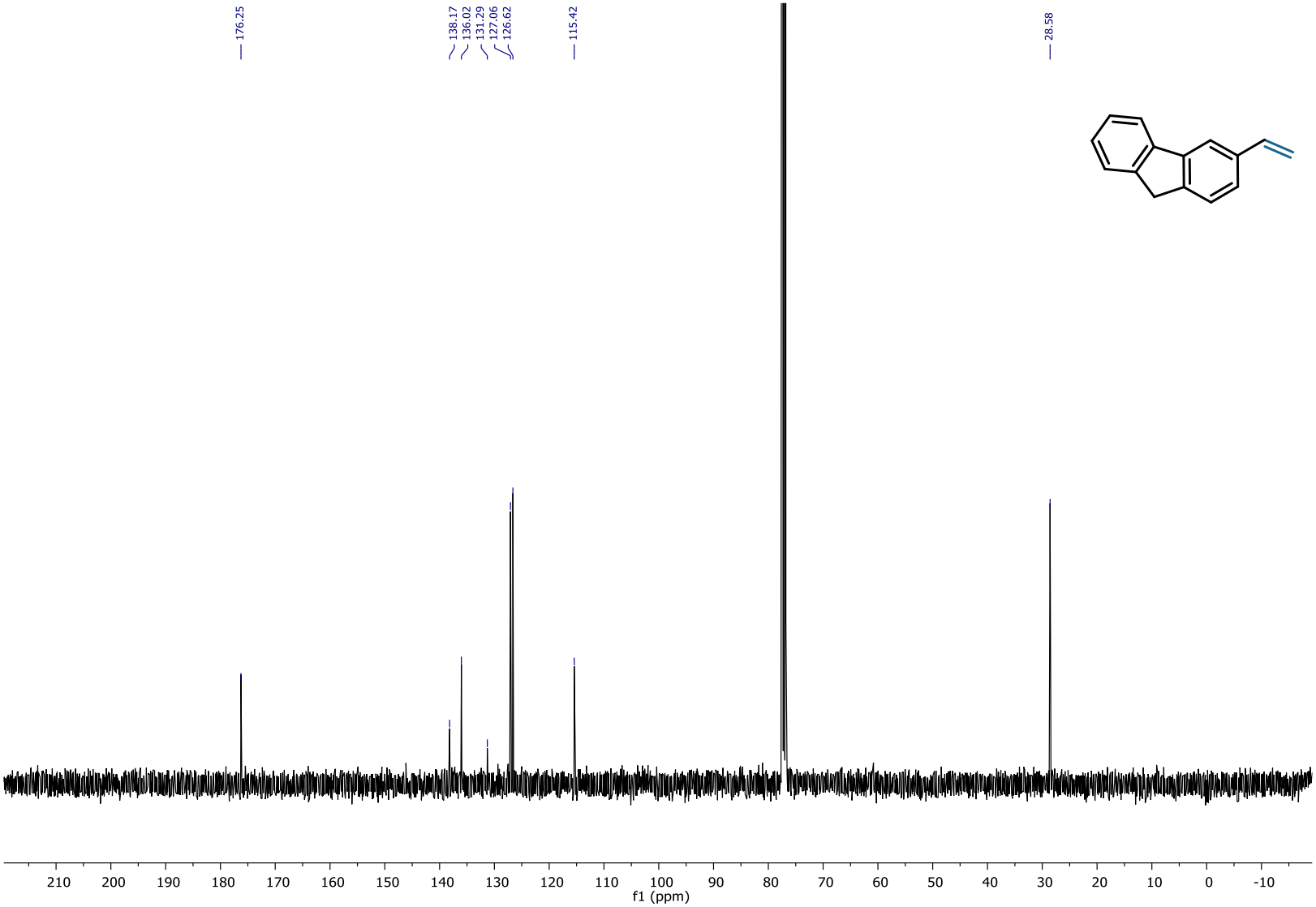
C	1.50326	0.54394	-0.58988
H	1.85549	1.57259	-0.58437
C	2.52860	-0.48898	-0.84700
H	2.70044	-0.51108	-1.93251
H	2.23906	-1.48698	-0.52986
C	3.86045	-0.13628	-0.21216
Cl	3.73631	-0.01711	1.55283
F	4.77106	-1.06527	-0.51585
F	4.31439	1.03588	-0.67975
C	0.16325	0.34081	-0.40538
C	-0.44438	-0.95435	-0.38450
H	0.16064	-1.84194	-0.50236
C	-1.78840	-1.07031	-0.21485
H	-2.23552	-2.05381	-0.20085
C	-2.61122	0.07321	-0.05200
C	-2.02098	1.35068	-0.06630
H	-2.63052	2.23212	0.05735
C	-0.67209	1.48787	-0.23657
H	-0.21546	2.46947	-0.24932
C	-4.09796	-0.12067	0.13578
C	-4.85201	1.19853	0.29358
H	-5.91278	0.98329	0.42072
H	-4.74337	1.83302	-0.58730
H	-4.51644	1.75297	1.17125
C	-4.65053	-0.86609	-1.09427
H	-5.72391	-1.00618	-0.96136
H	-4.19451	-1.84741	-1.21877
H	-4.48798	-0.28767	-2.00455
C	-4.31991	-0.97555	1.39851
H	-3.86192	-1.96026	1.31336
H	-5.39262	-1.11192	1.54051
H	-3.91547	-0.47753	2.28058

16. NMR Spectra of Isolated Compounds

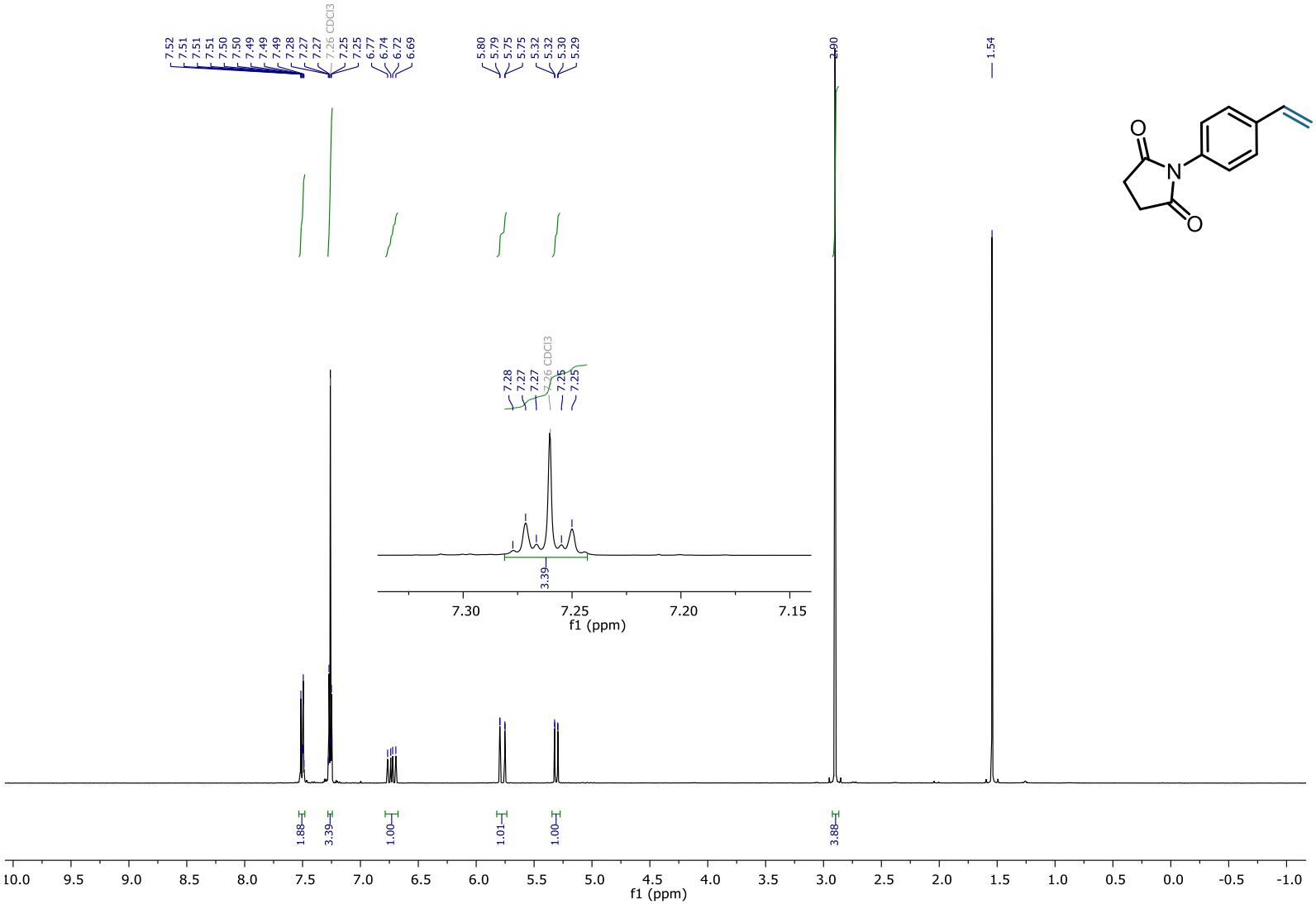
^{1}H-NMR (400 MHz, $CDCl_3$) of **S-25**



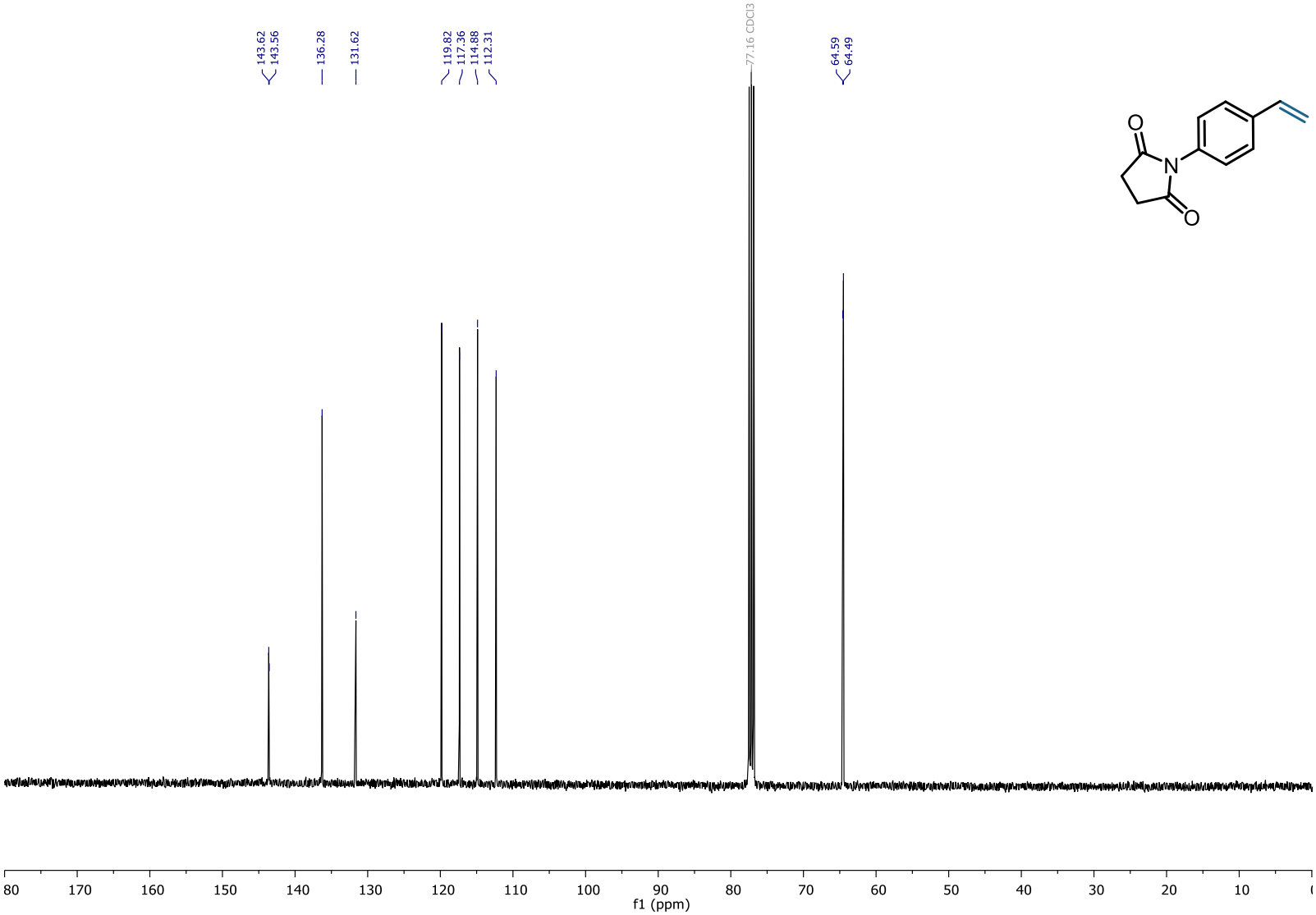
^{1}H-NMR (100 MHz, $CDCl_3$) of **S-25**



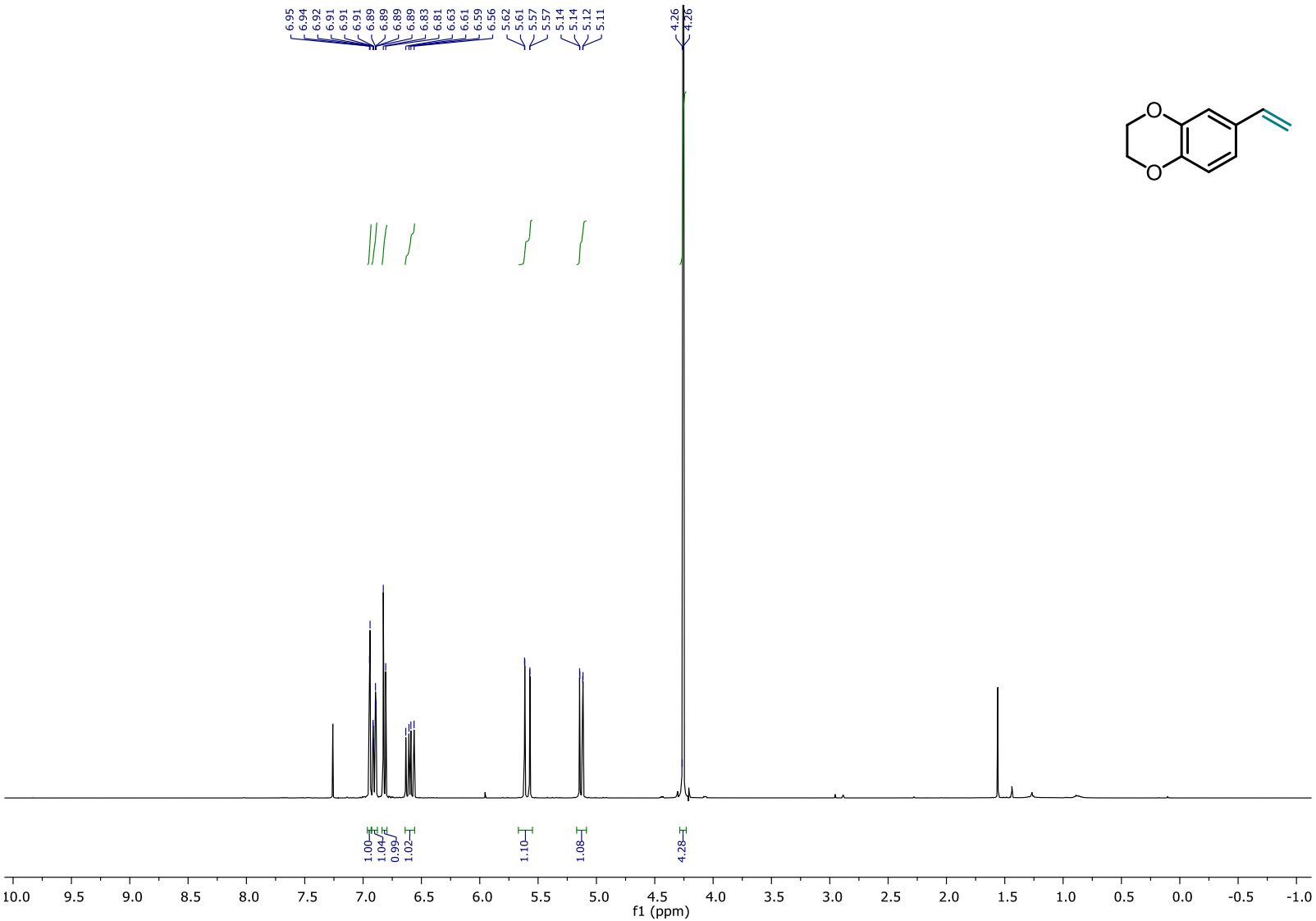
^{1}H-NMR (400 MHz, $CDCl_3$) of **S-26**



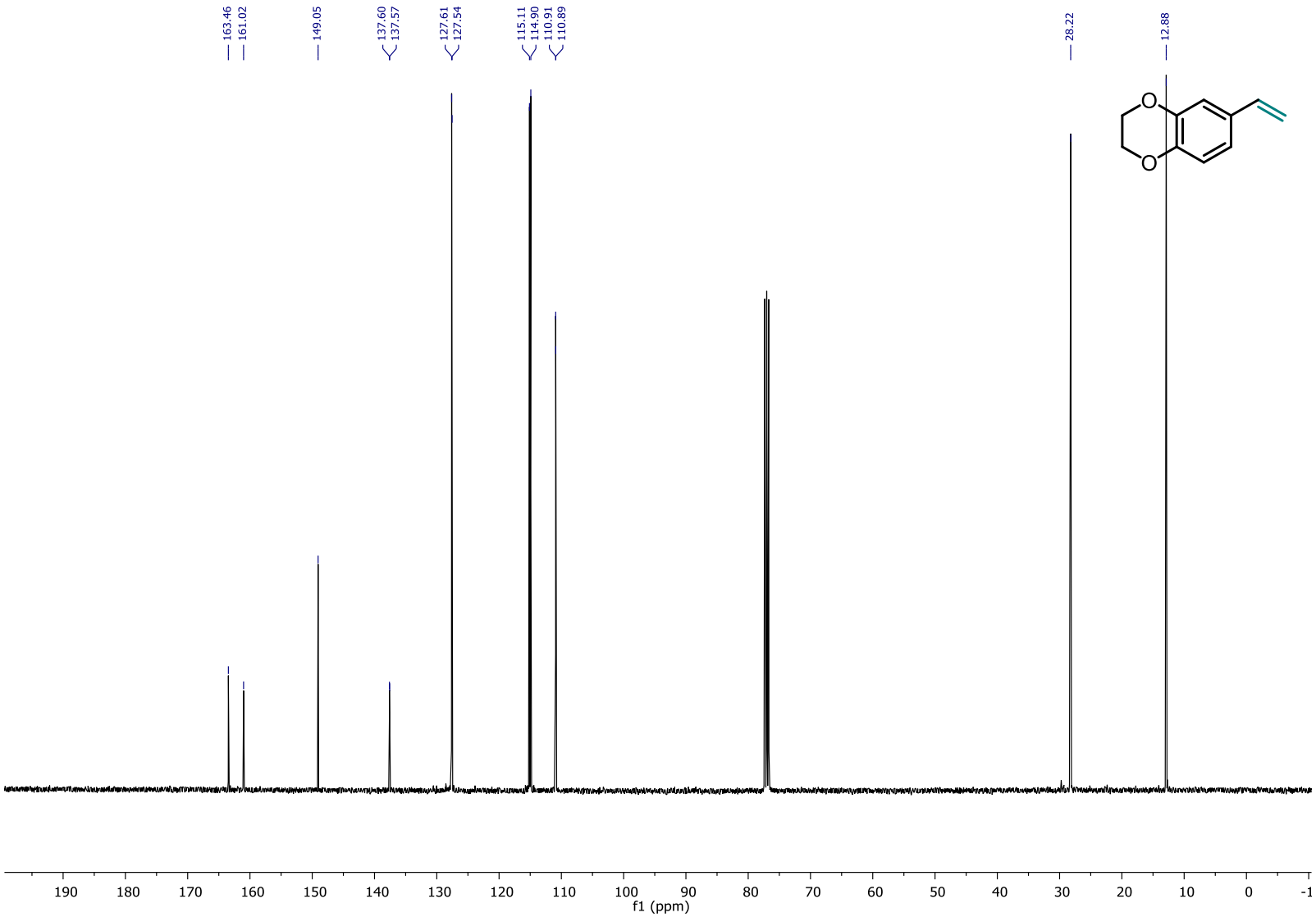
^{13}C-NMR (100 MHz, $CDCl_3$) of **S-26**



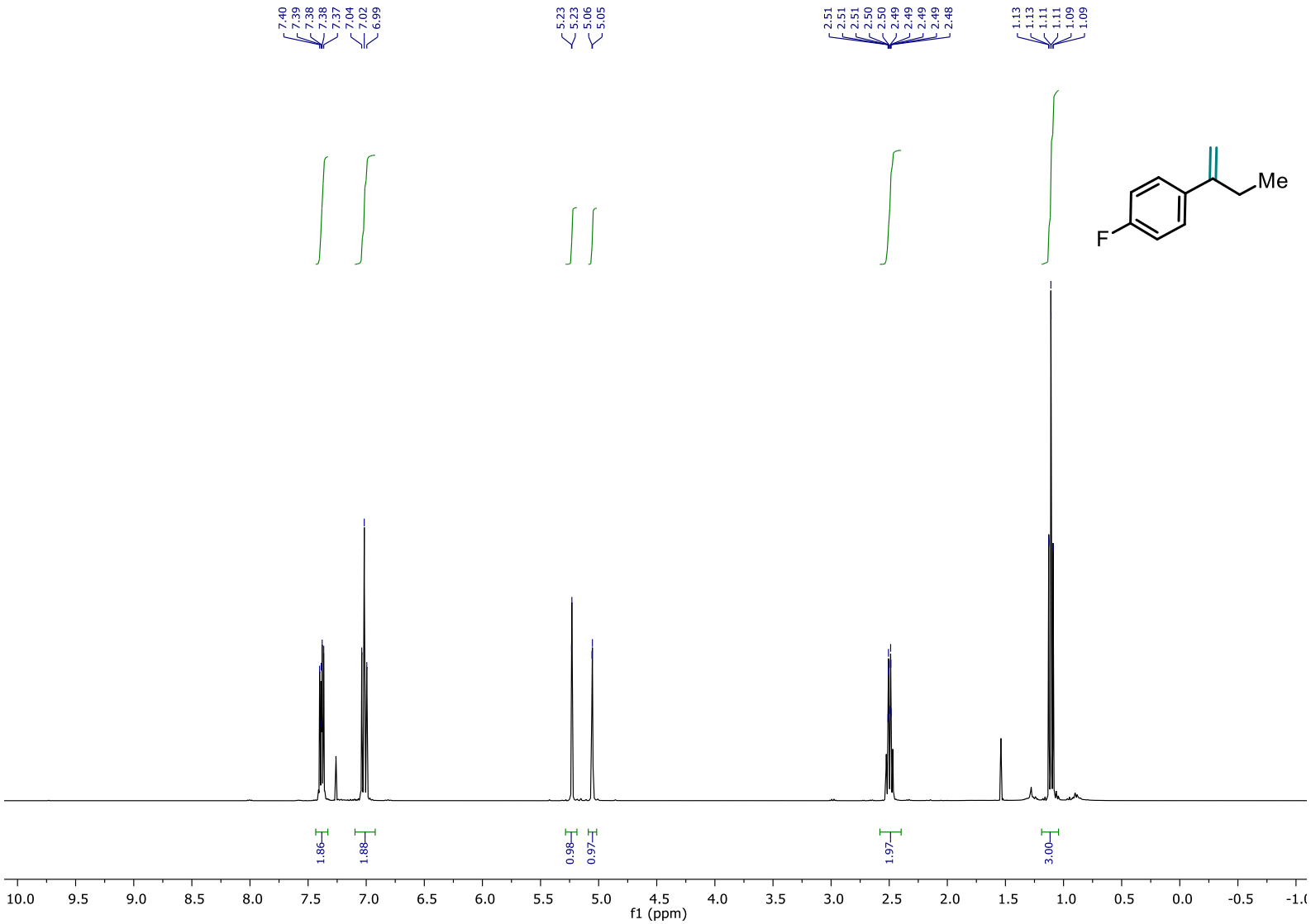
^{1}H-NMR (400 MHz, $CDCl_3$) of **S-27**



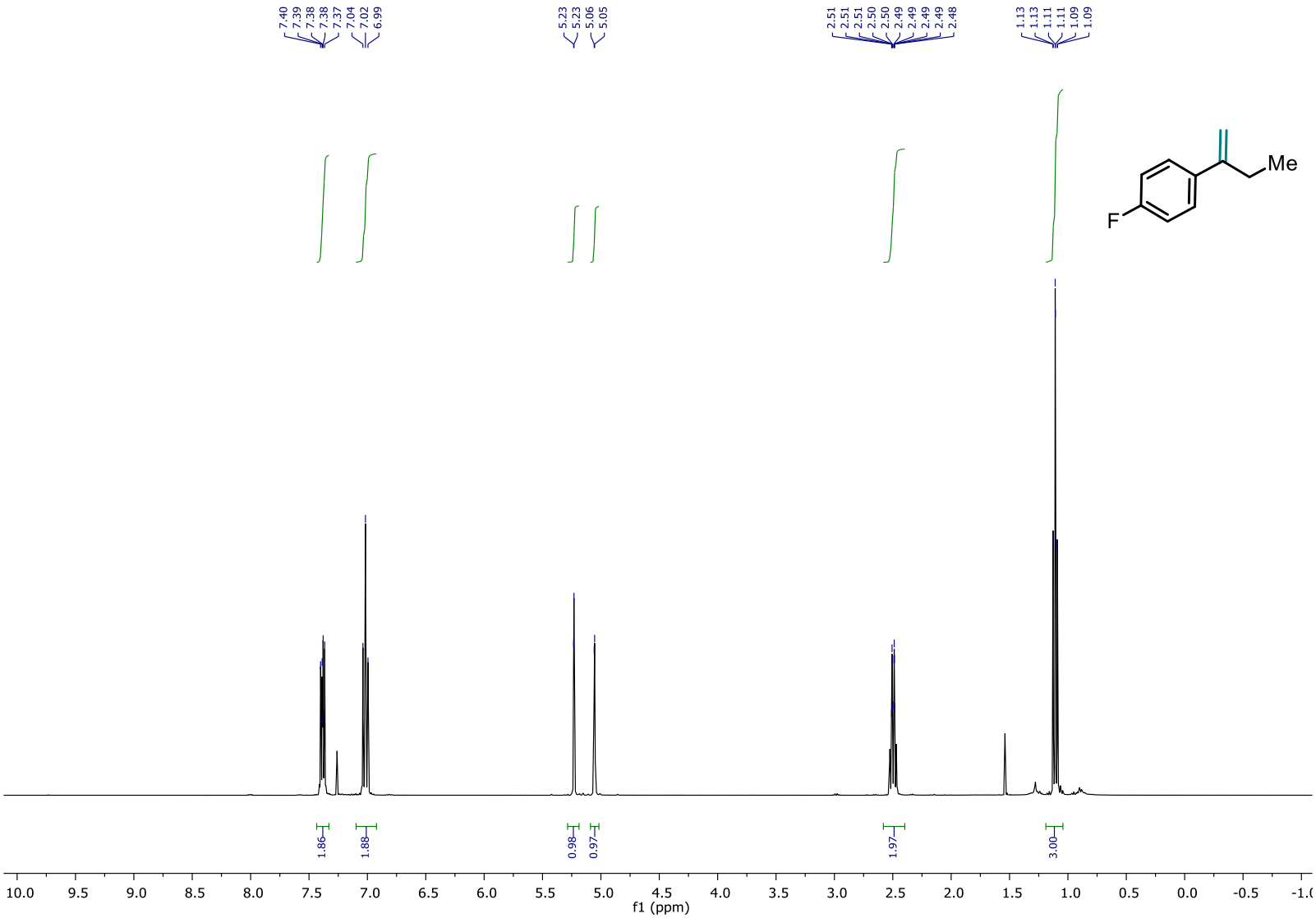
^{13}C-NMR (100 MHz, $CDCl_3$) of **S-27**



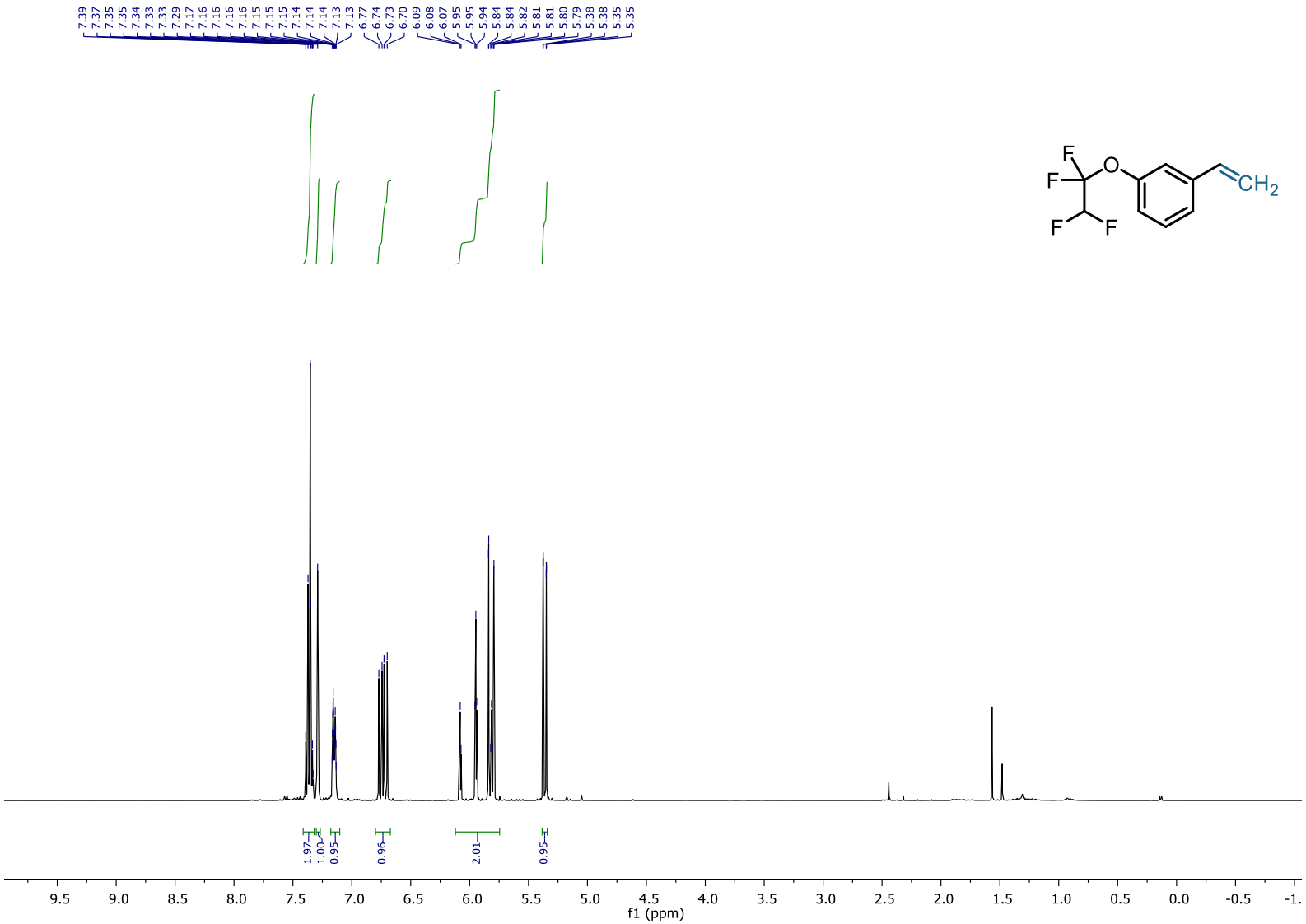
^{1}H-NMR (400 MHz, $CDCl_3$) of **S-28**



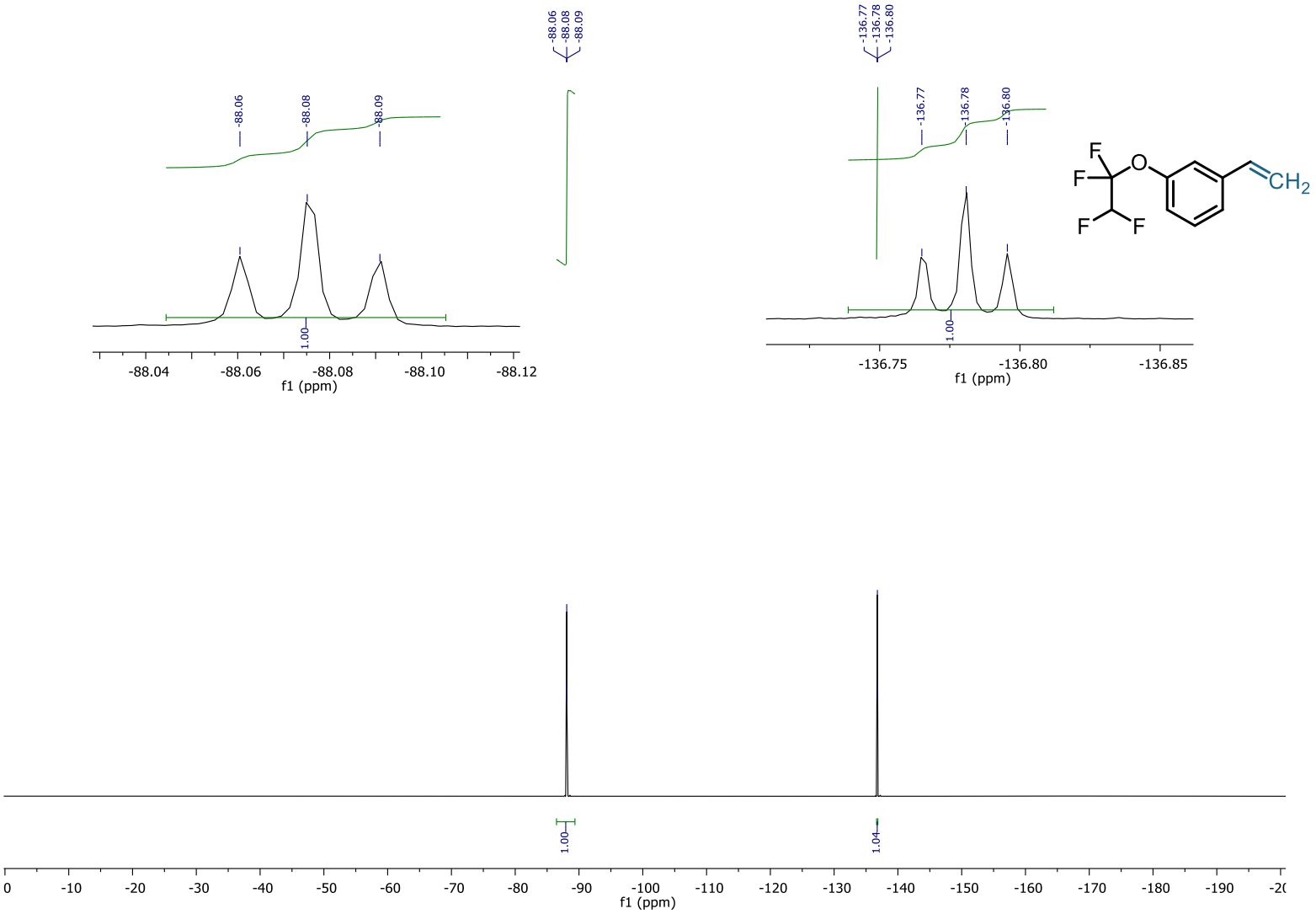
^{13}C-NMR (101 MHz, $CDCl_3$) of **S-28**



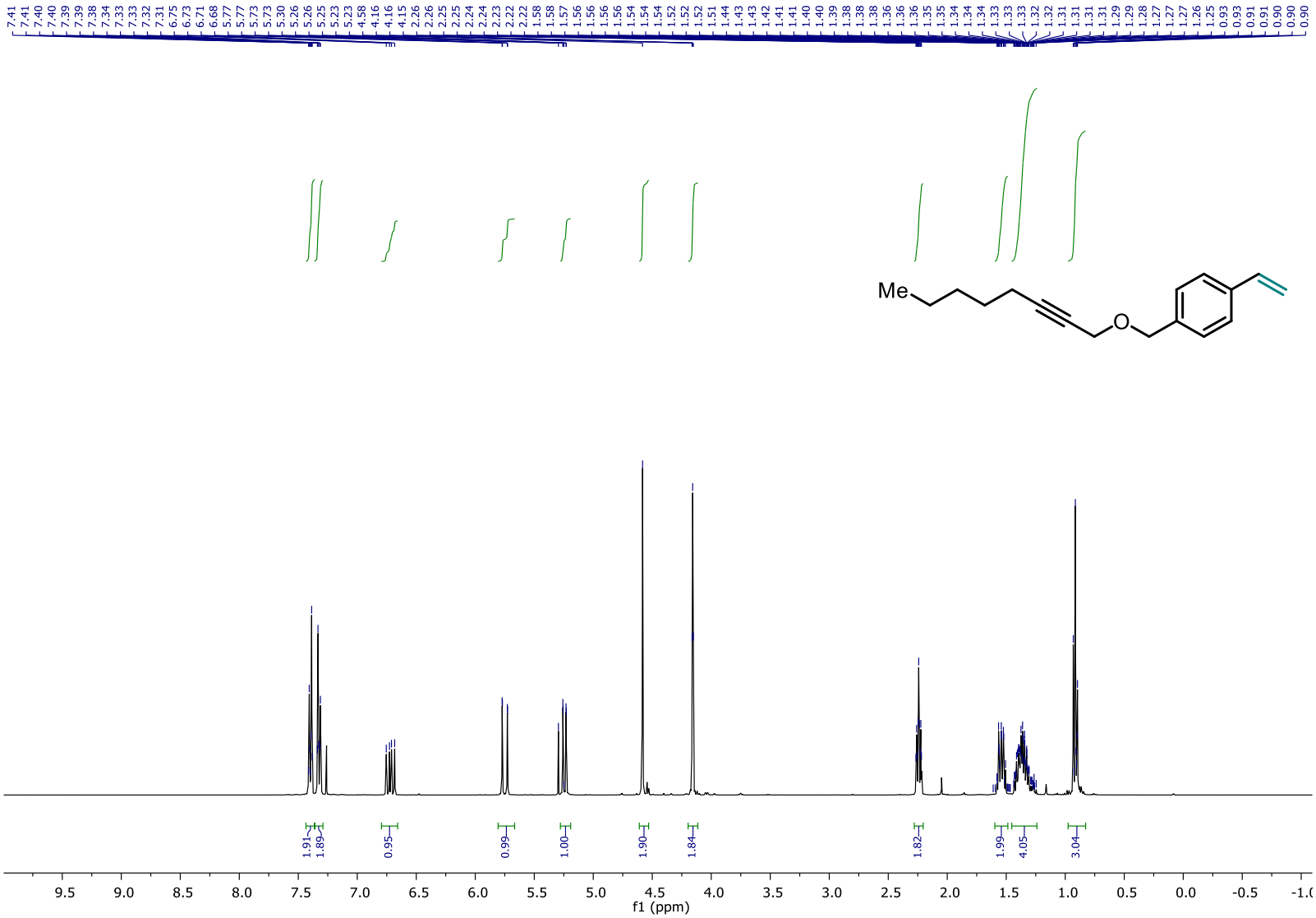
^{1}H-NMR (400 MHz, $CDCl_3$) of **S-29**



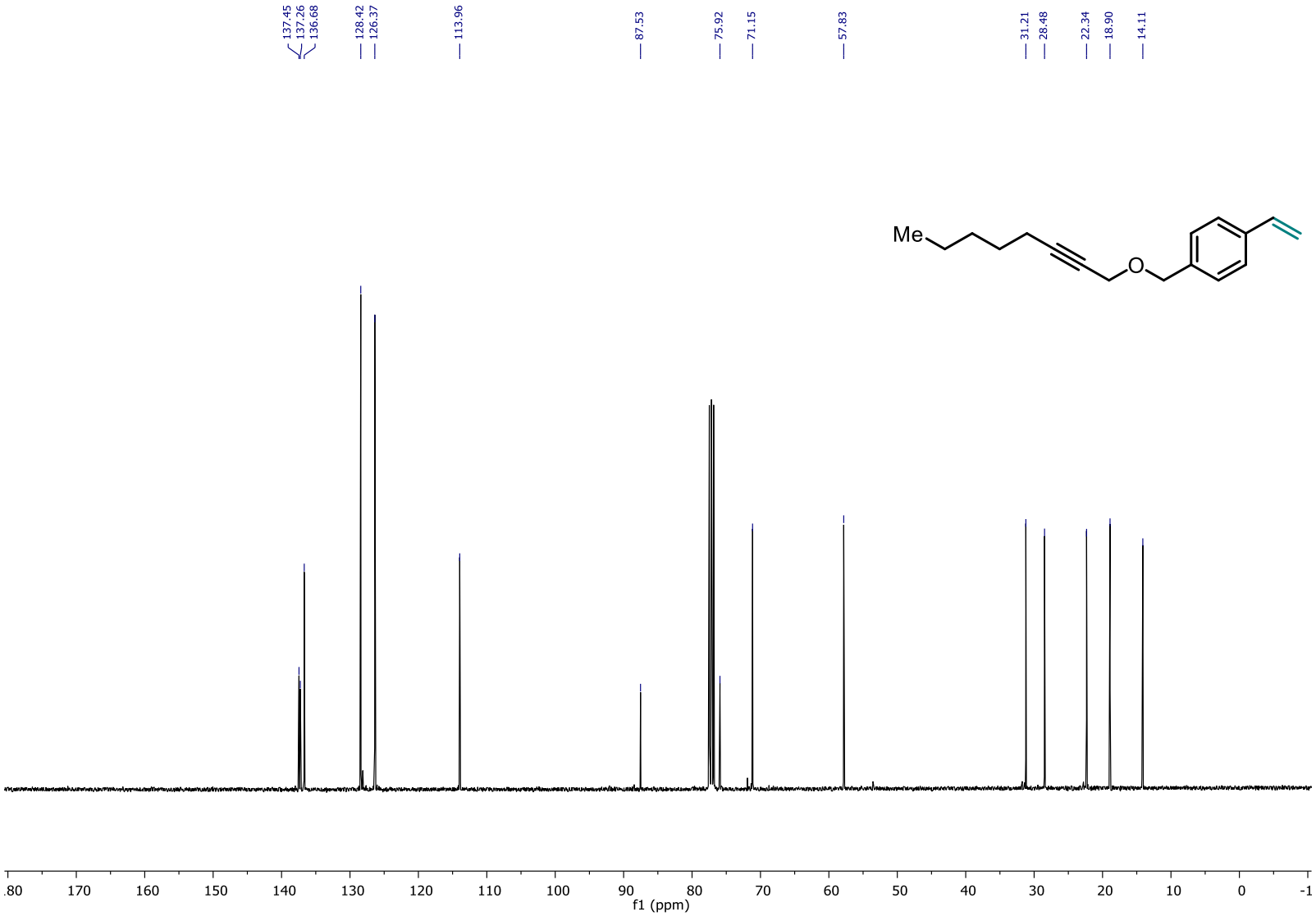
^{19}F-NMR (377 MHz, $CDCl_3$) of **S-29**



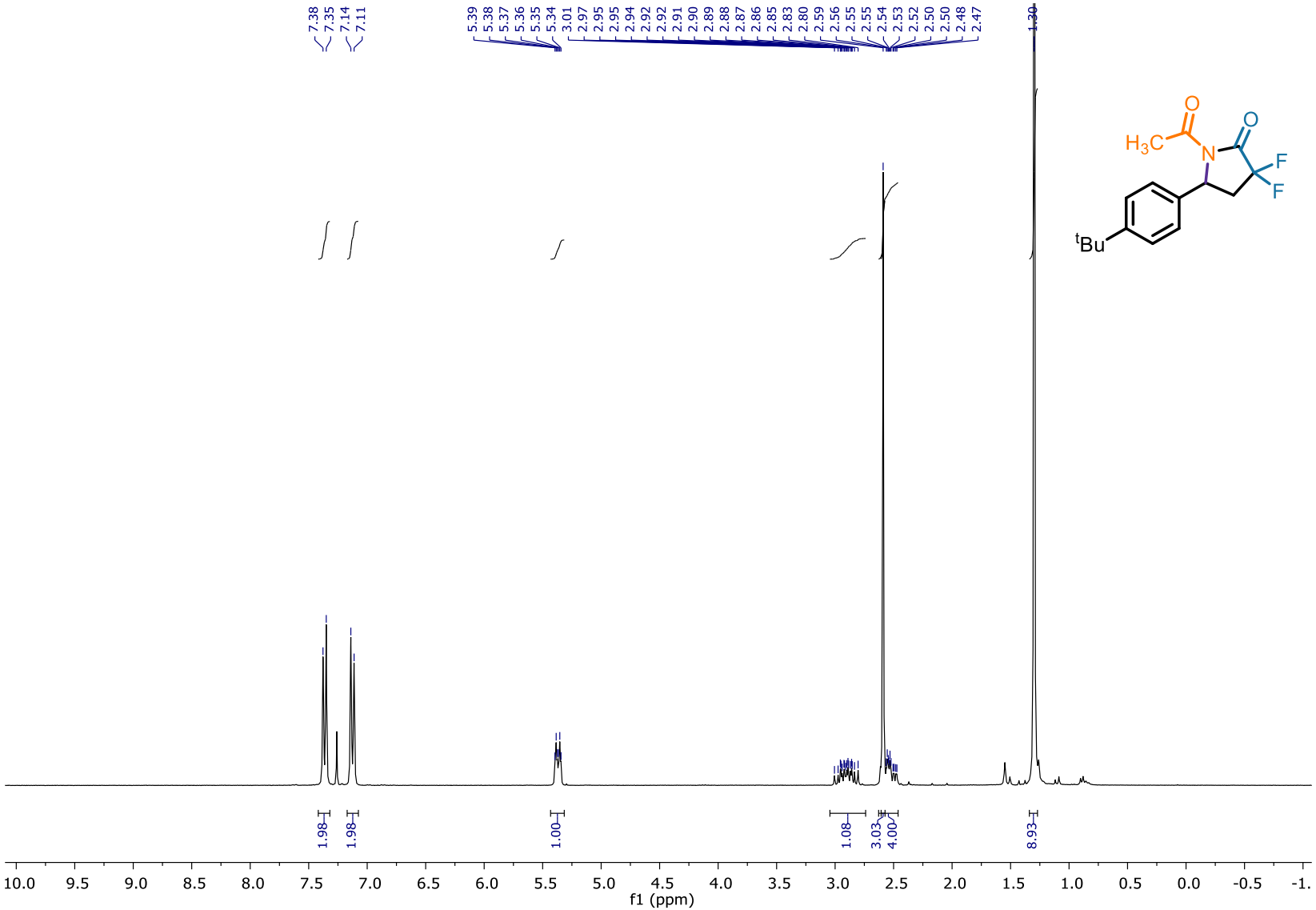
^{1}H-NMR (300 MHz, $CDCl_3$) of **S-30**



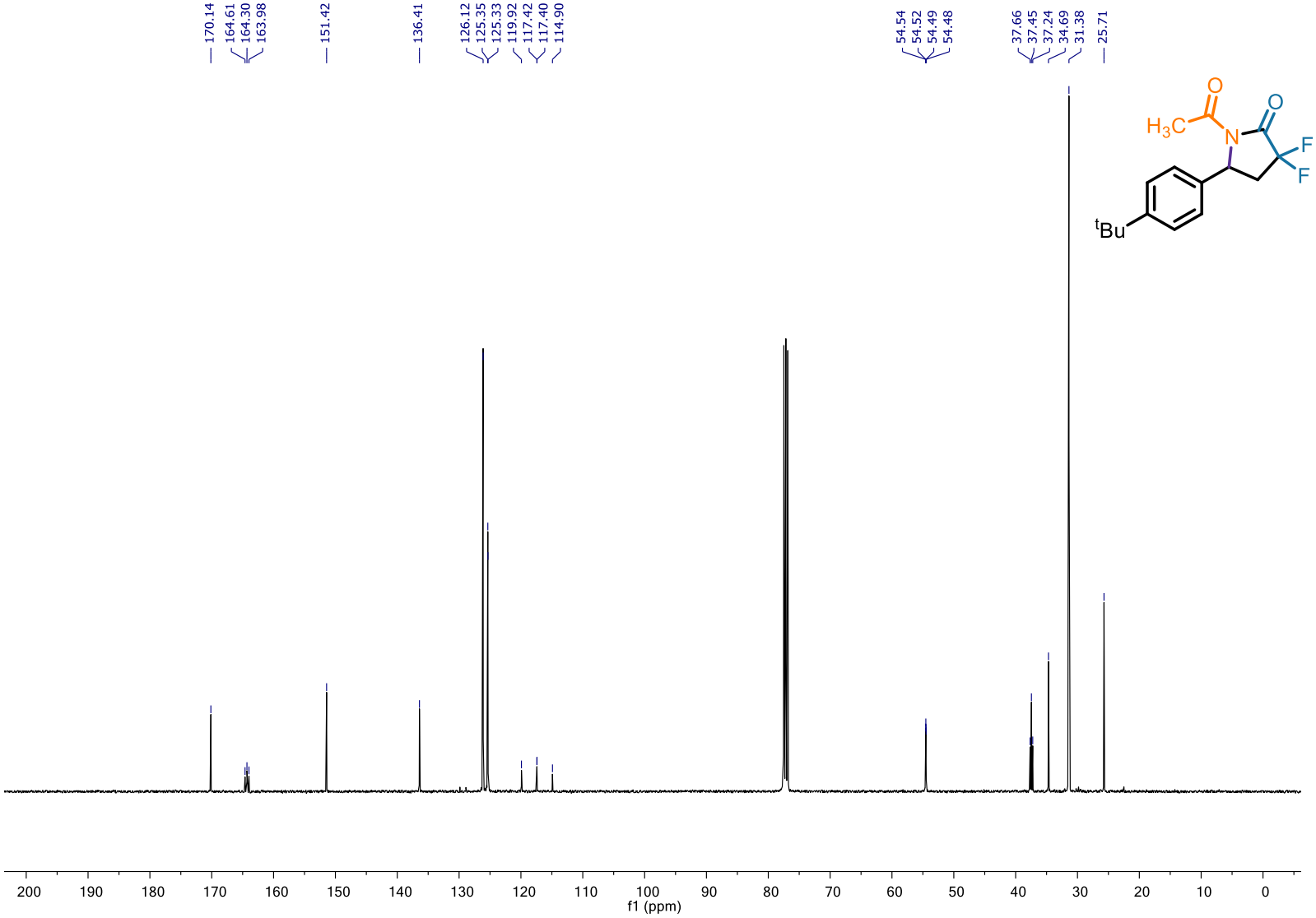
^{13}C-NMR (101 MHz, $CDCl_3$) of **S-30**



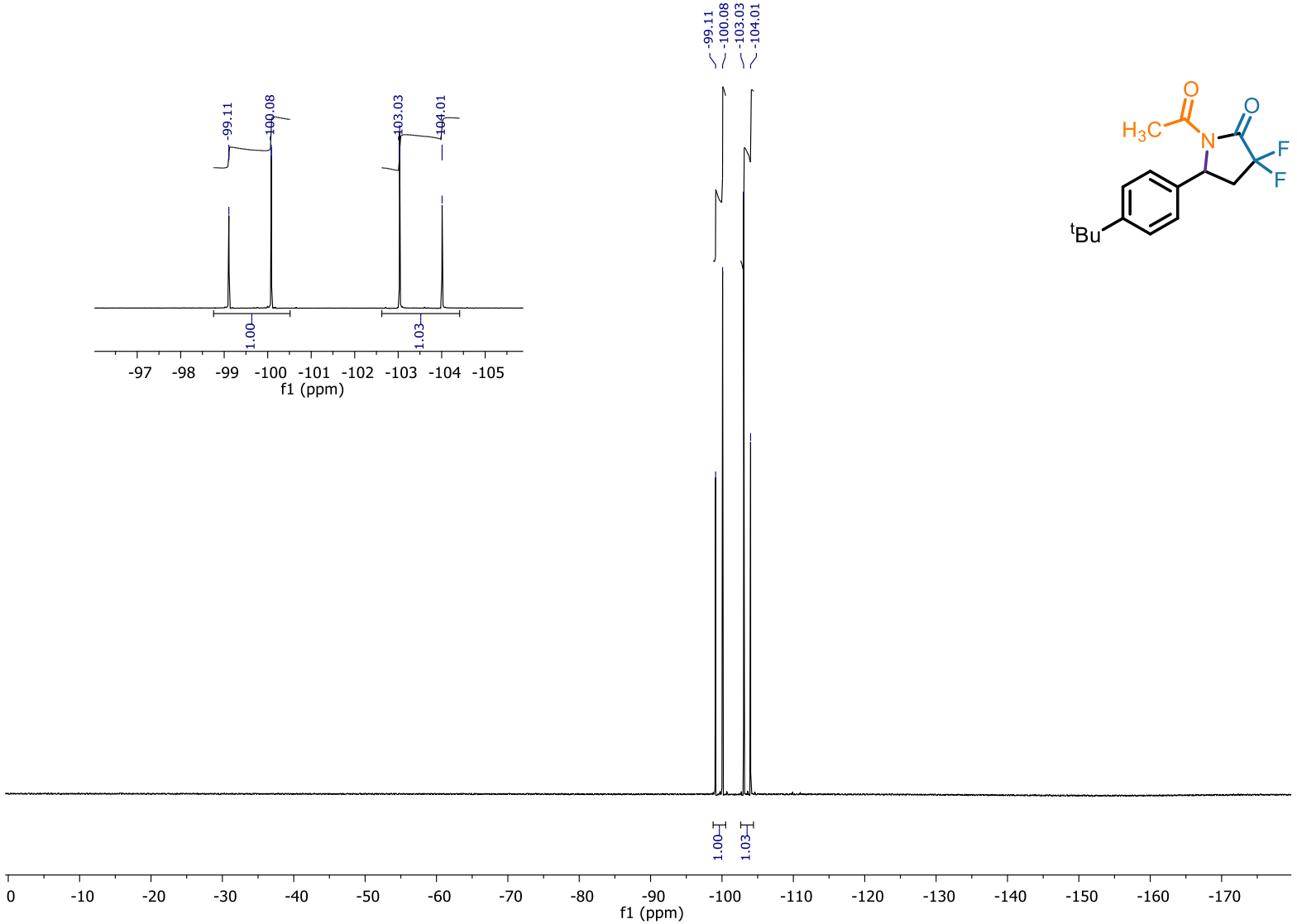
^{1}H-NMR (300 MHz, $CDCl_3$) of **1**



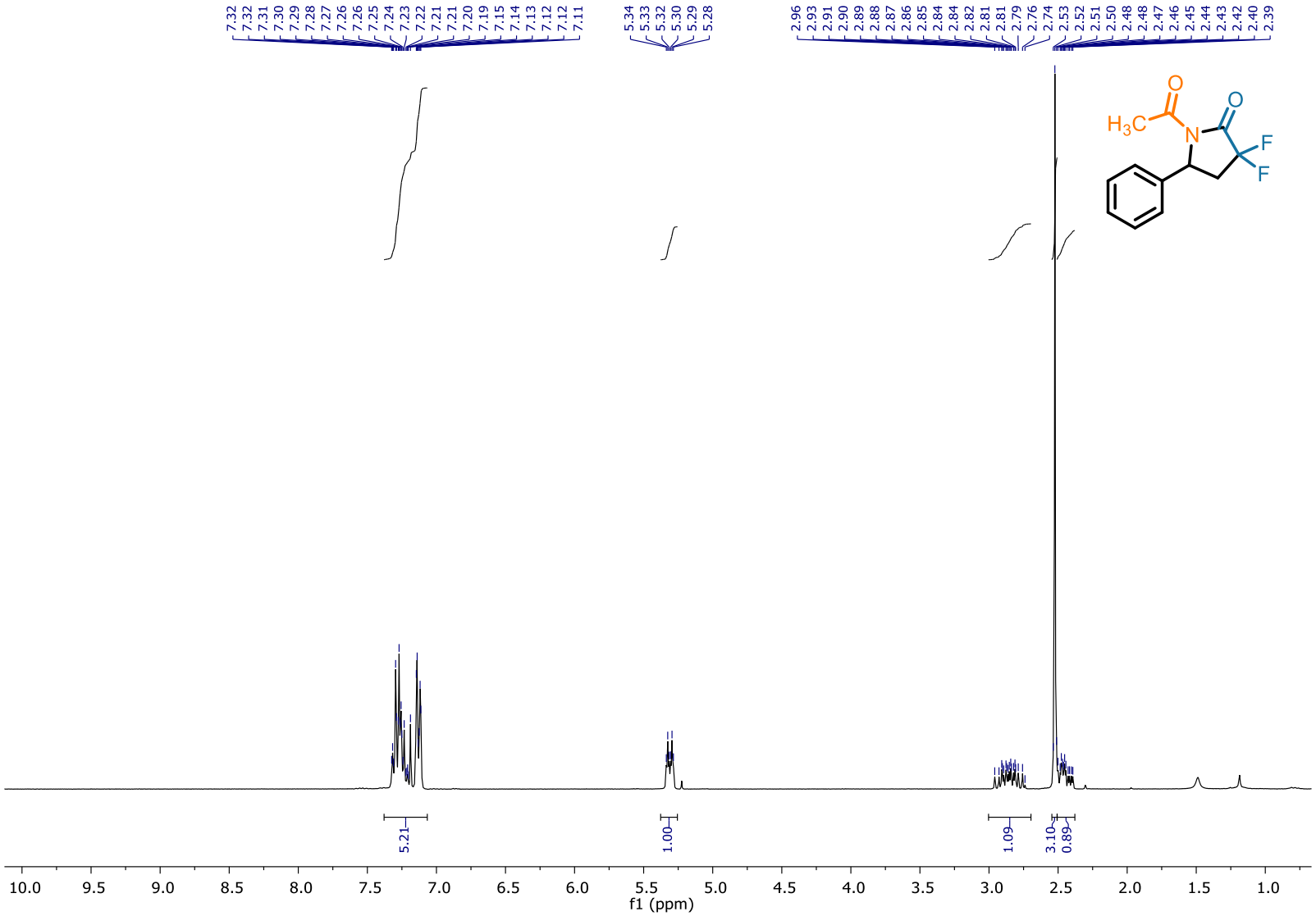
^{13}C-NMR (101 MHz, $CDCl_3$) of **1**



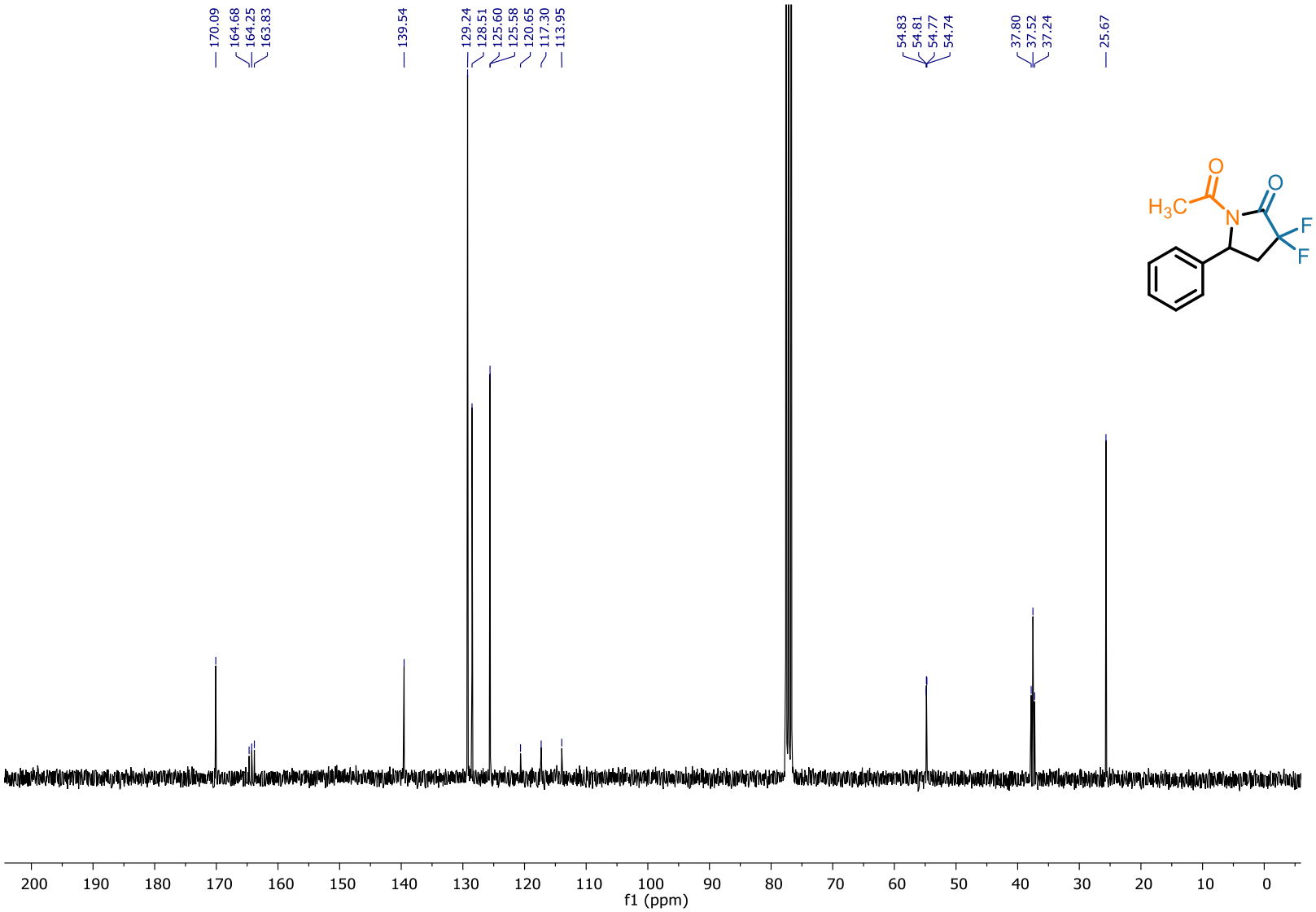
^{19}F-NMR (282 MHz, $CDCl_3$) of **1**



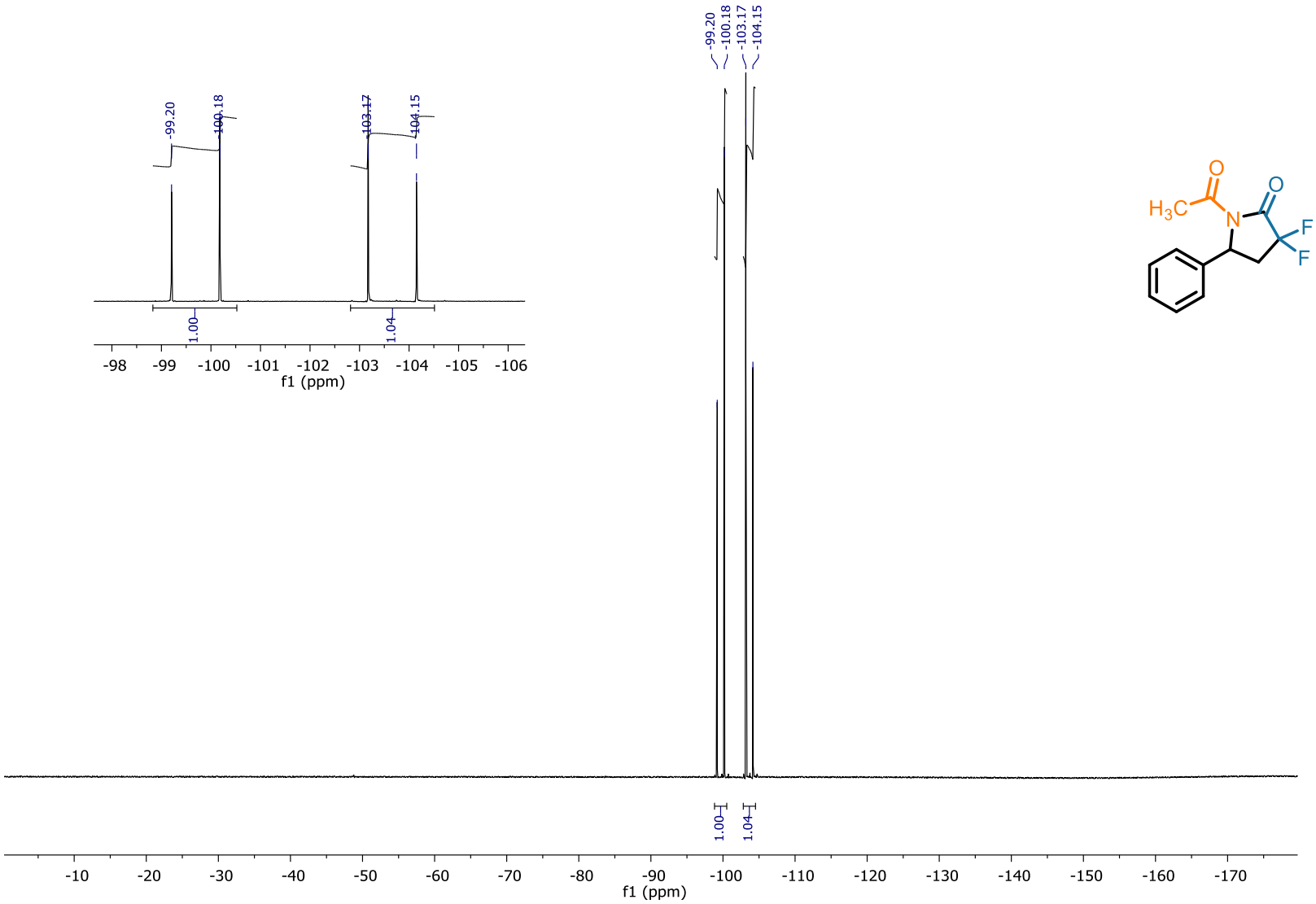
^{1}H-NMR (300 MHz, $CDCl_3$) of **4**



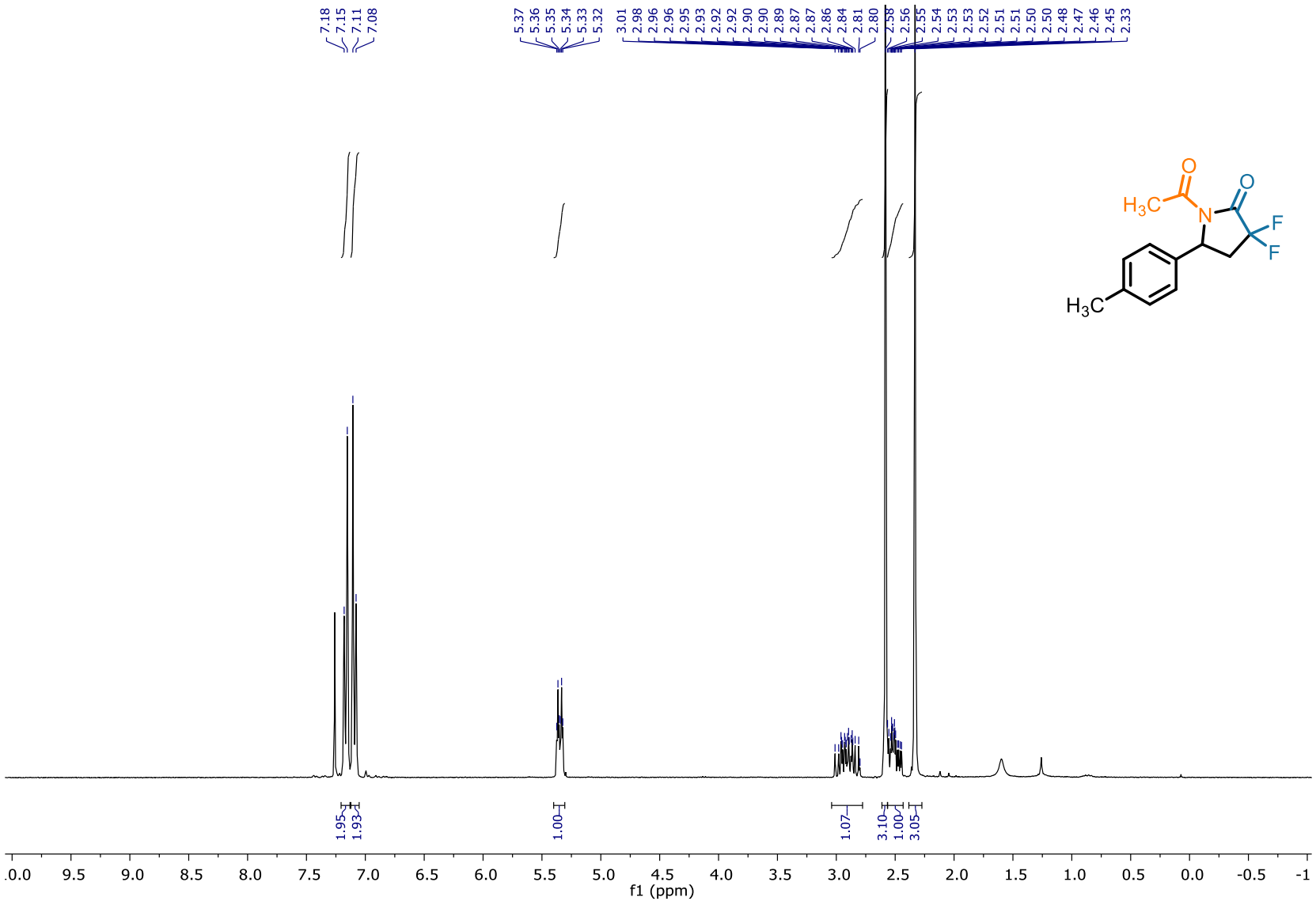
^{13}C-NMR (75 MHz, $CDCl_3$) of **4**



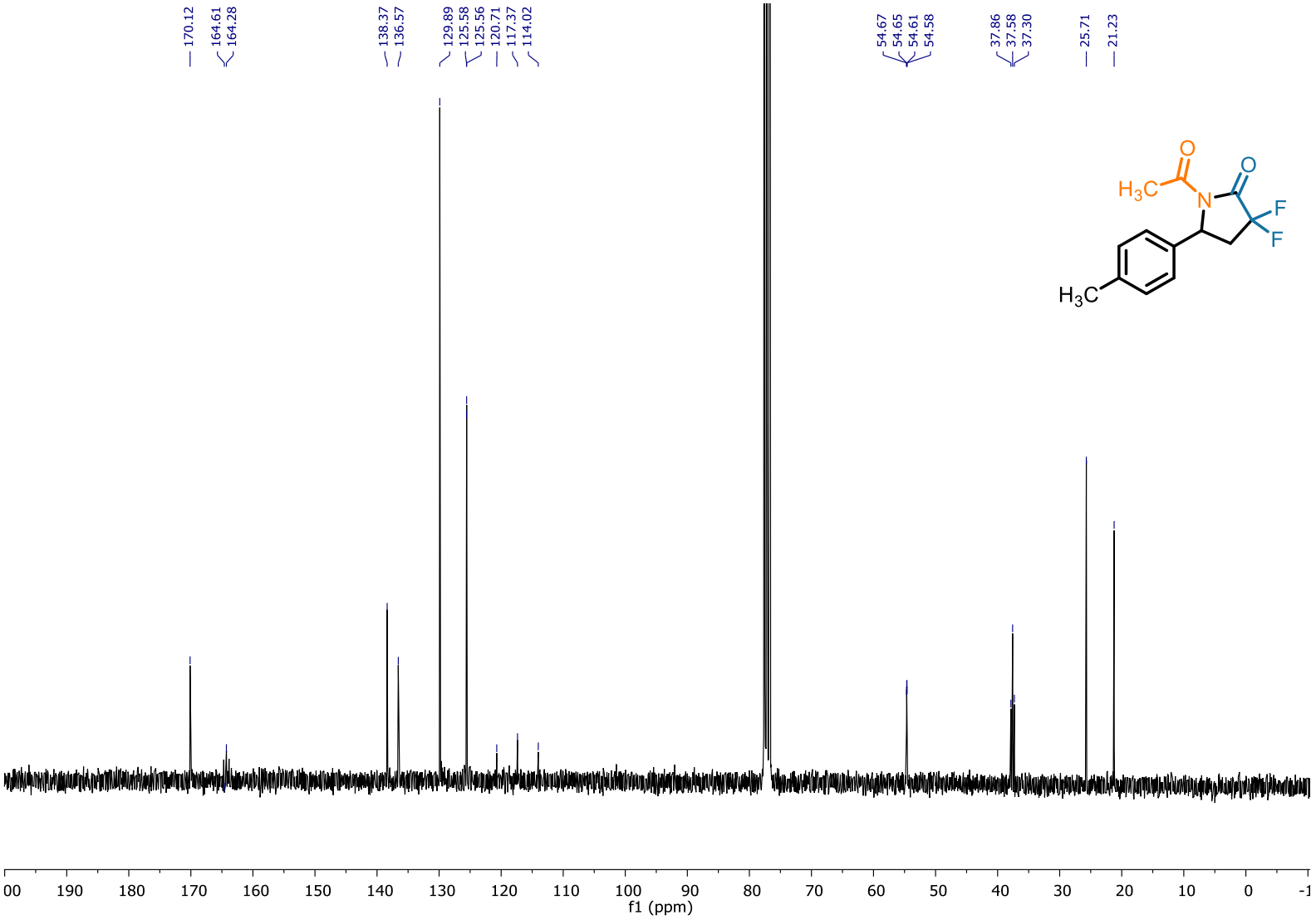
^{19}F-NMR (282 MHz, $CDCl_3$) of **4**



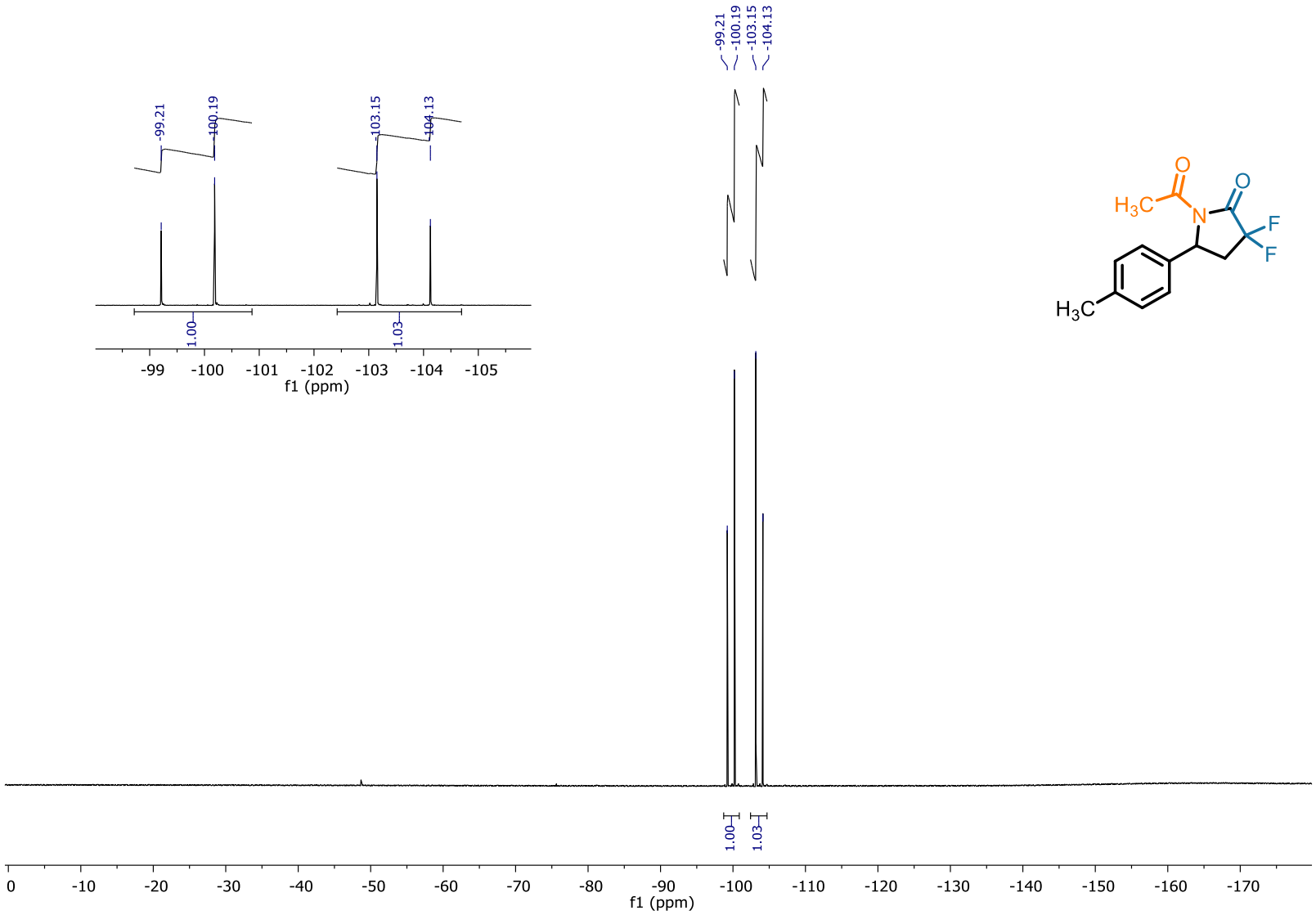
^{1}H-NMR (300 MHz, $CDCl_3$) of **5**



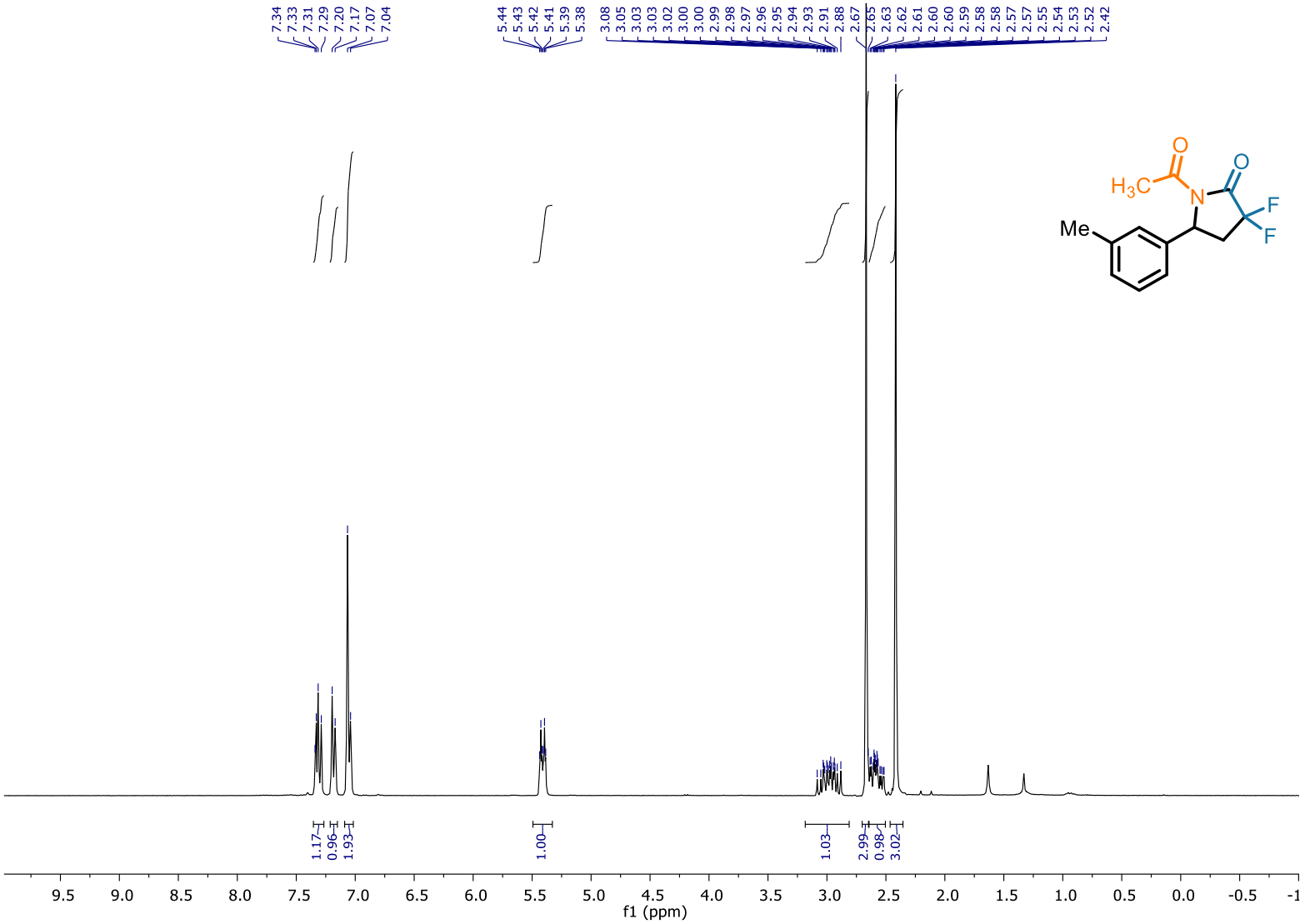
^{13}C-NMR (75 MHz, $CDCl_3$) of **5**



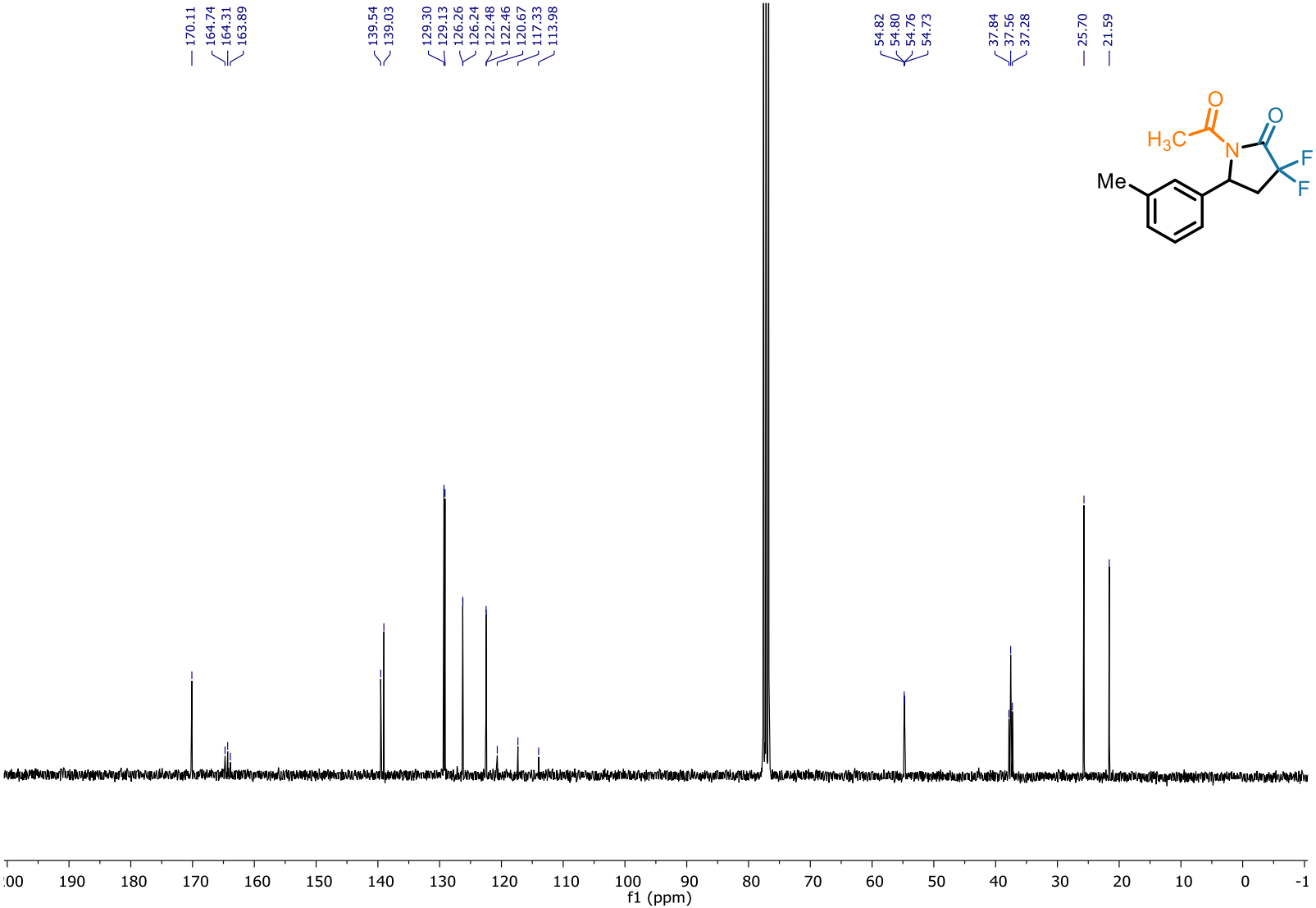
^{19}F-NMR (282 MHz, $CDCl_3$) of **5**



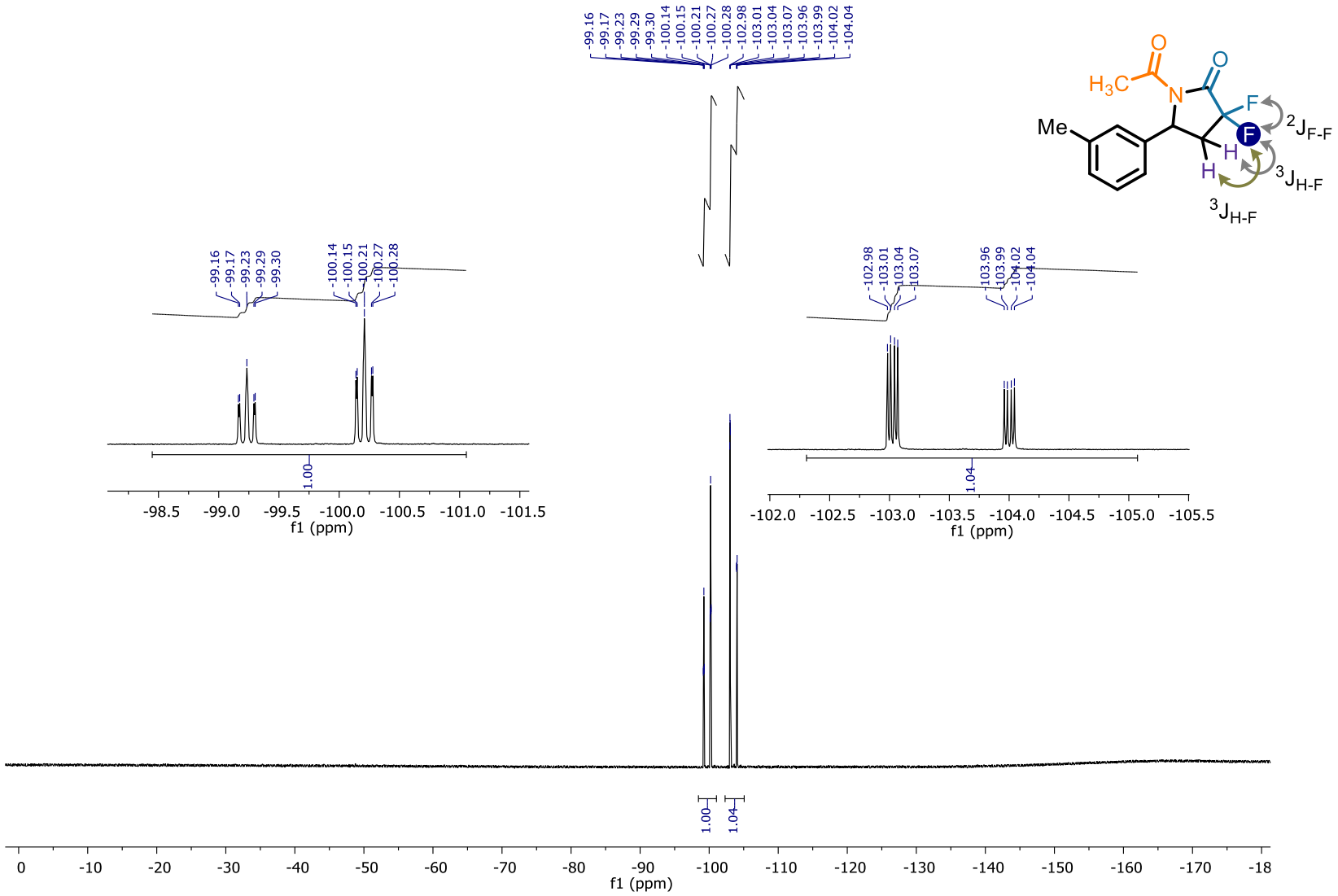
^{1}H-NMR (300 MHz, $CDCl_3$) of **6**



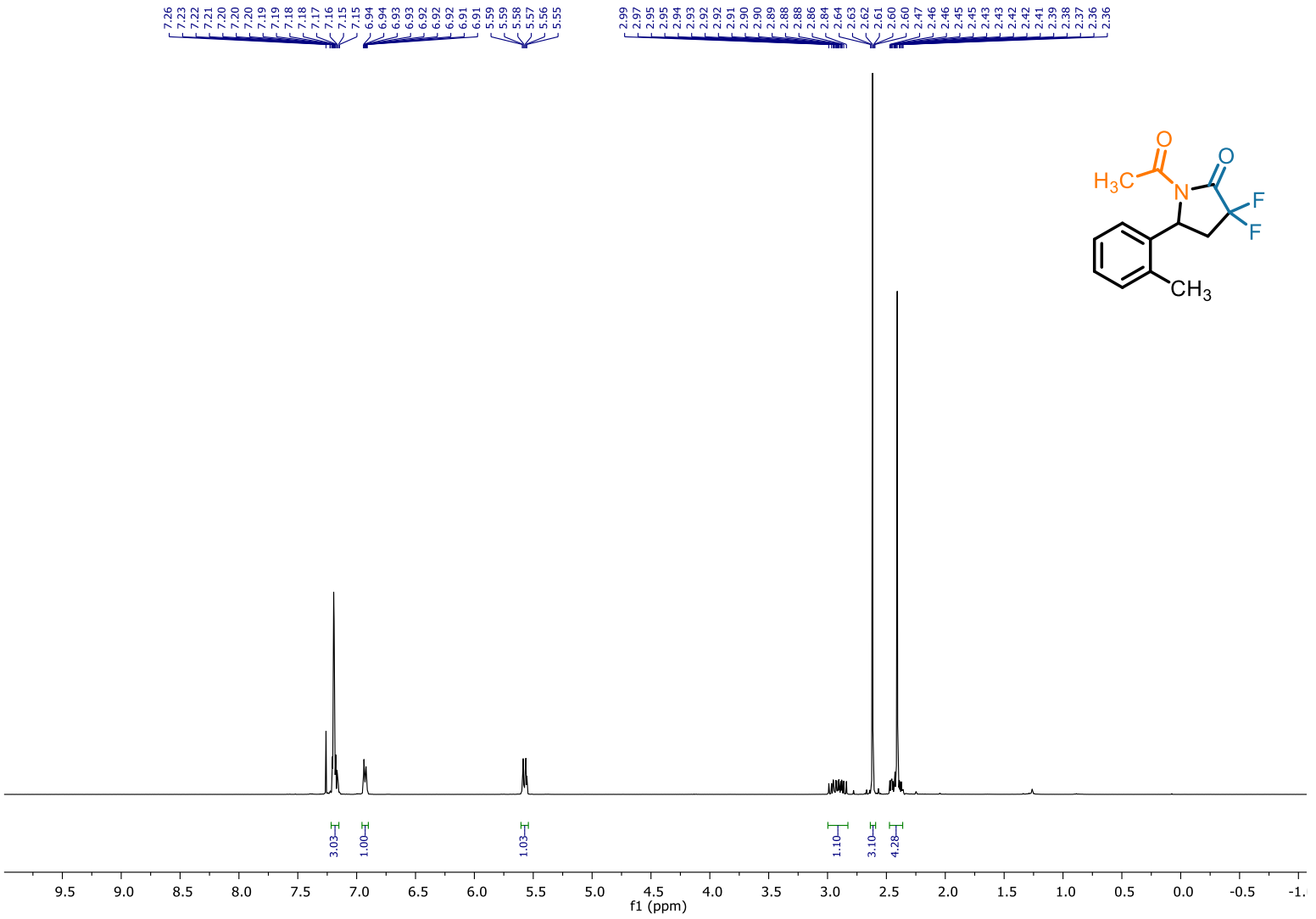
^{13}C-NMR (75 MHz, $CDCl_3$) of **6**



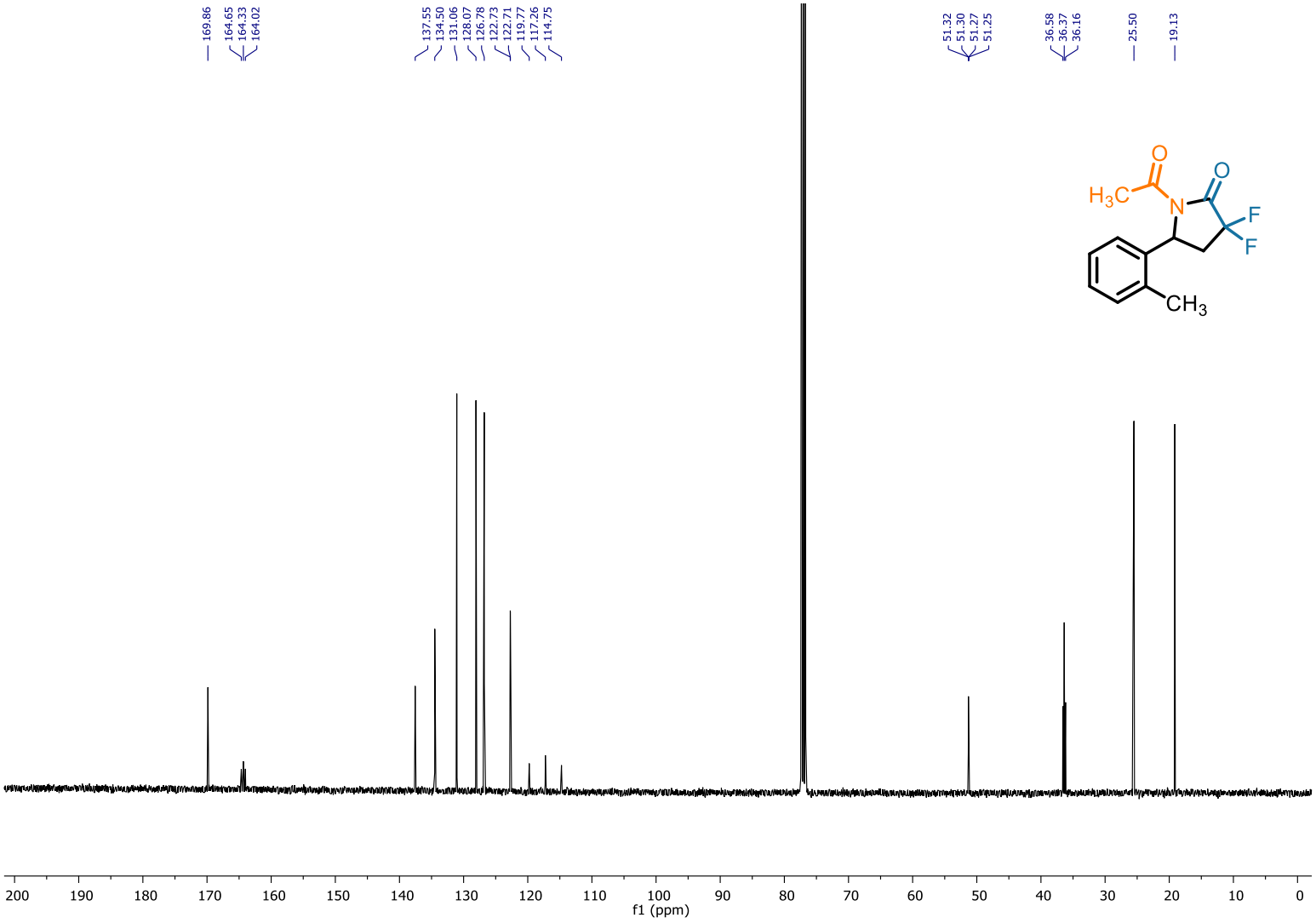
[^{1}H Coupled] ^{19}F-NMR (282 MHz, $CDCl_3$) of **6**



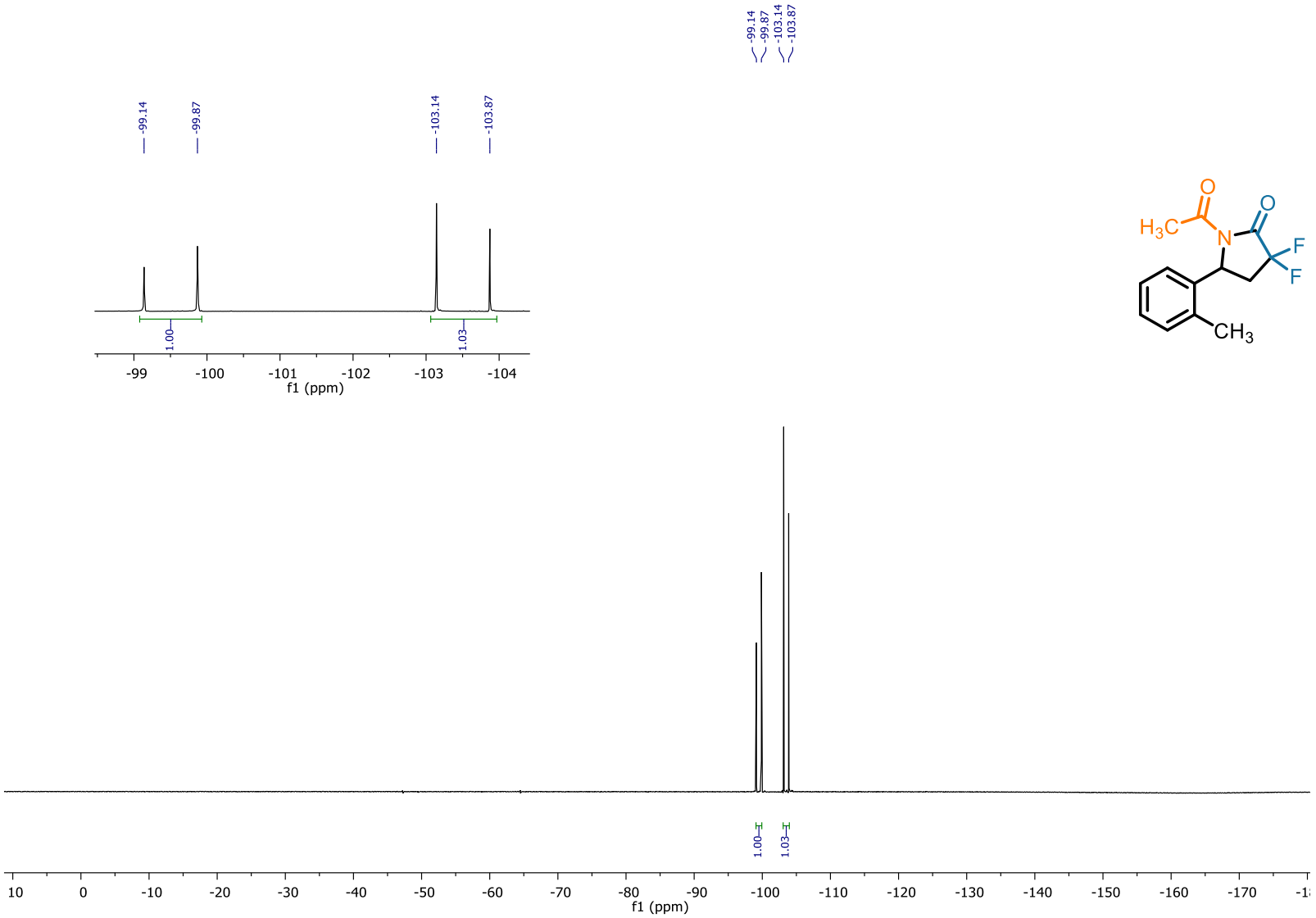
^{1}H-NMR (400 MHz, $CDCl_3$) of **7**



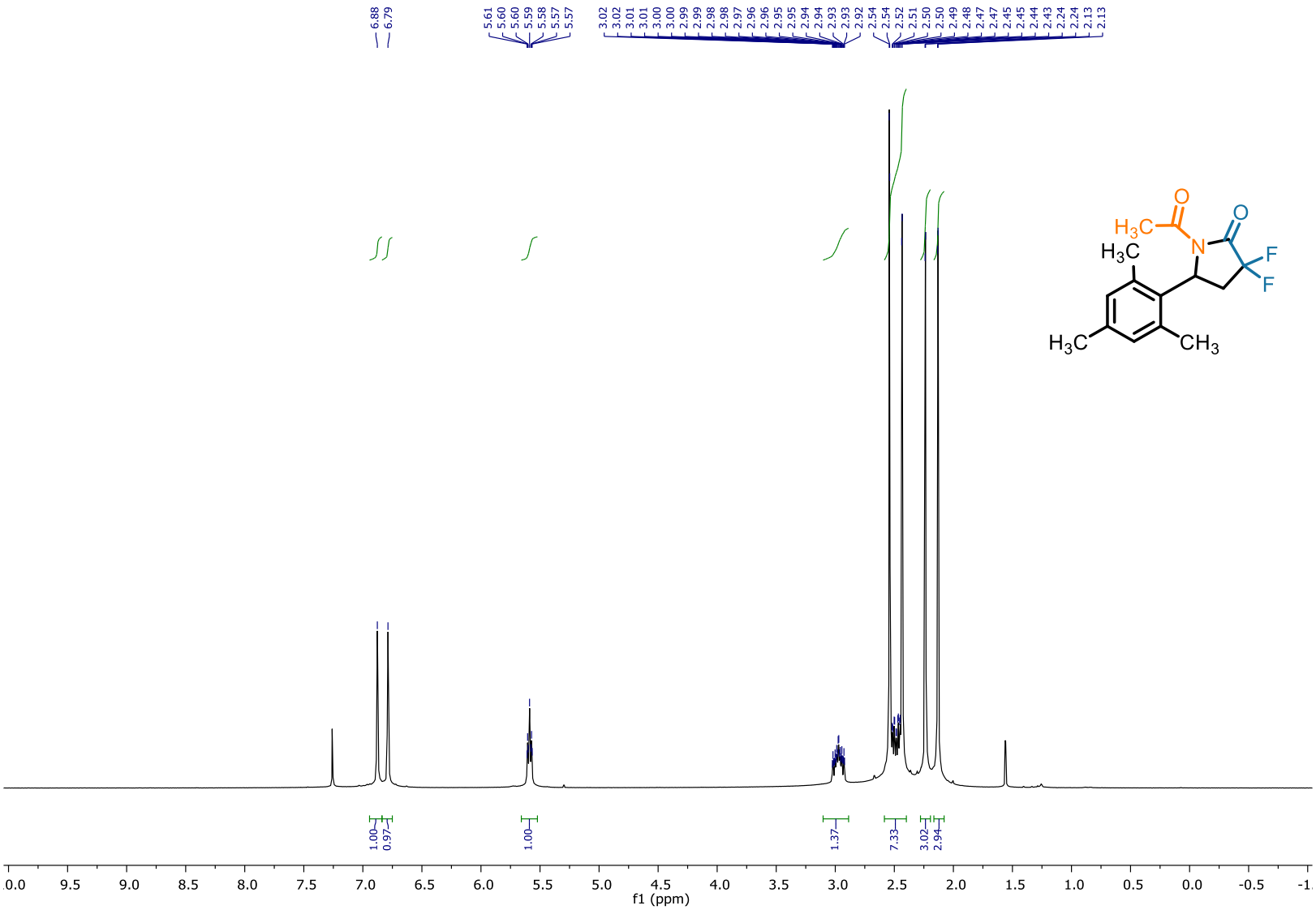
^{13}C-NMR (100 MHz, $CDCl_3$) of **7**



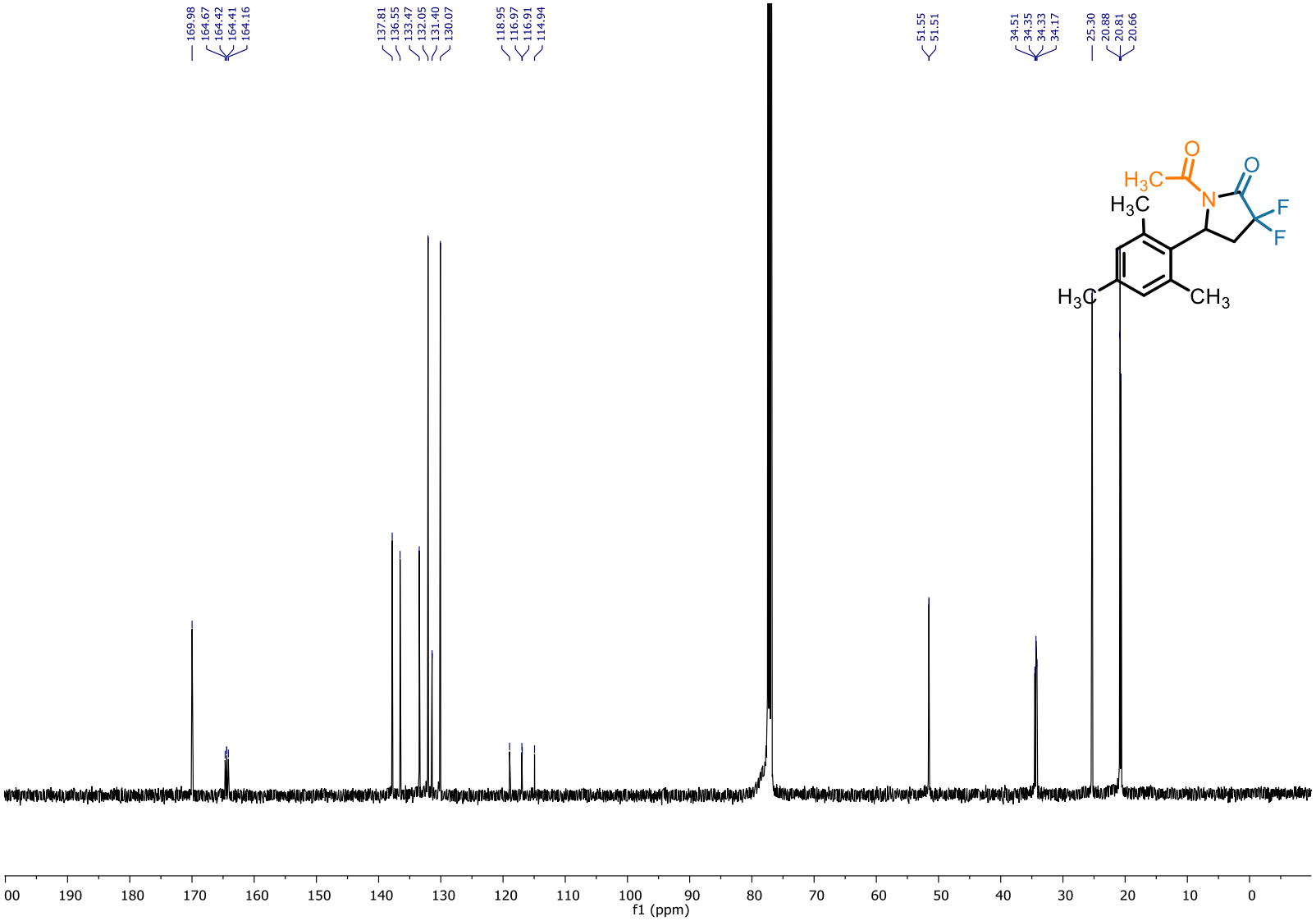
^{19}F-NMR (375 MHz, $CDCl_3$) of **7**



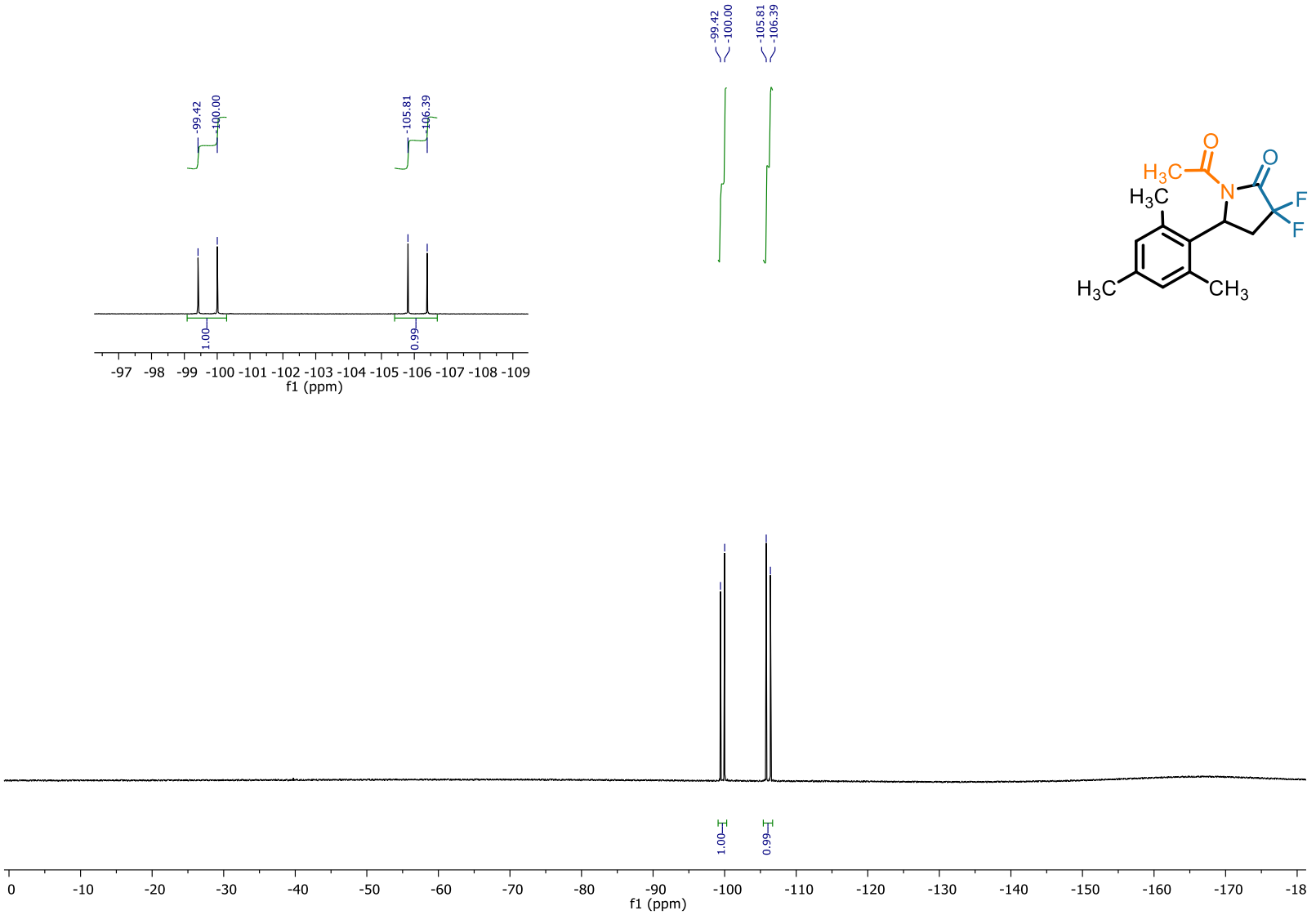
^{1}H-NMR (500 MHz, $CDCl_3$) of **8**



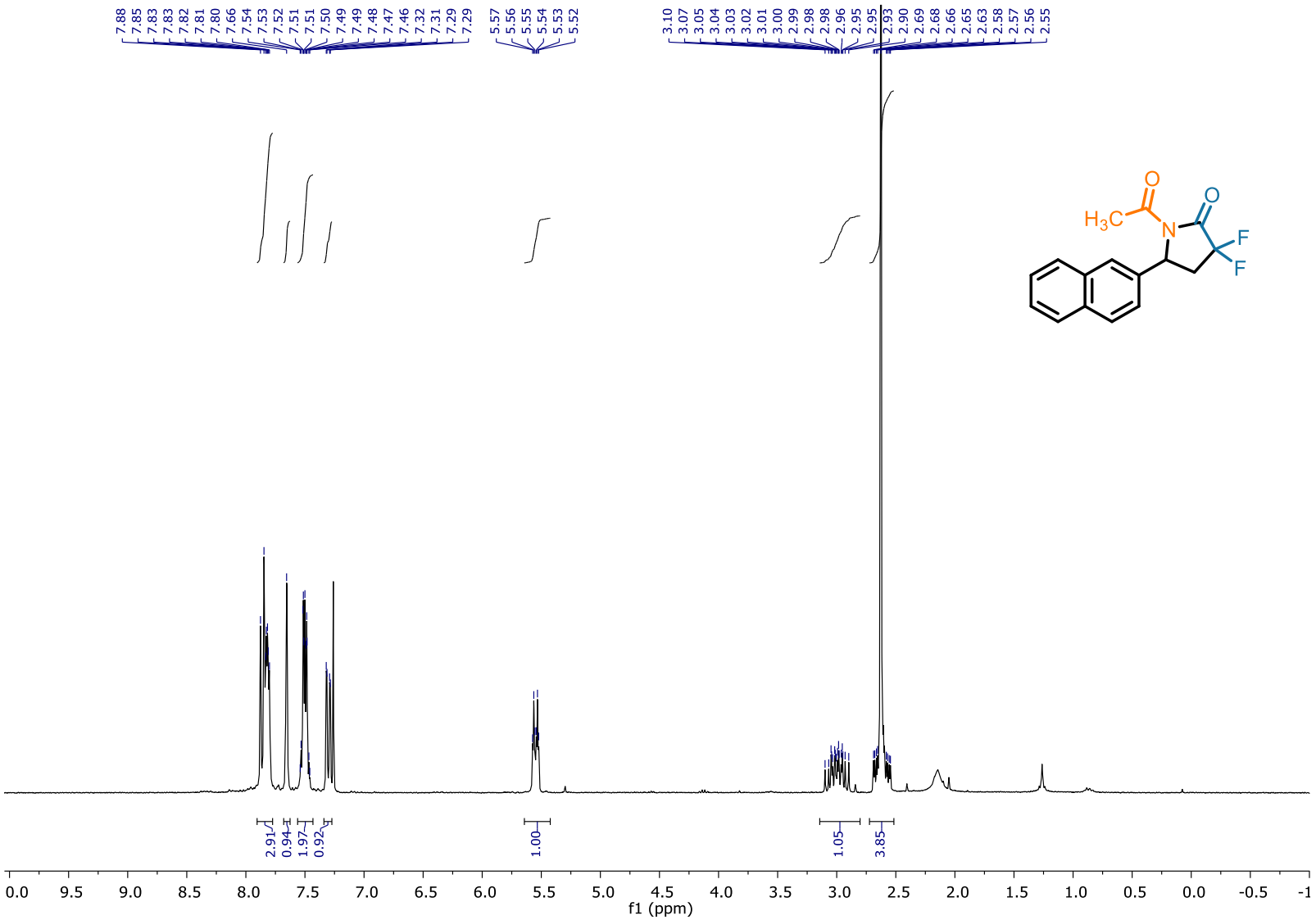
^{13}C-NMR (126 MHz, $CDCl_3$) of **8**



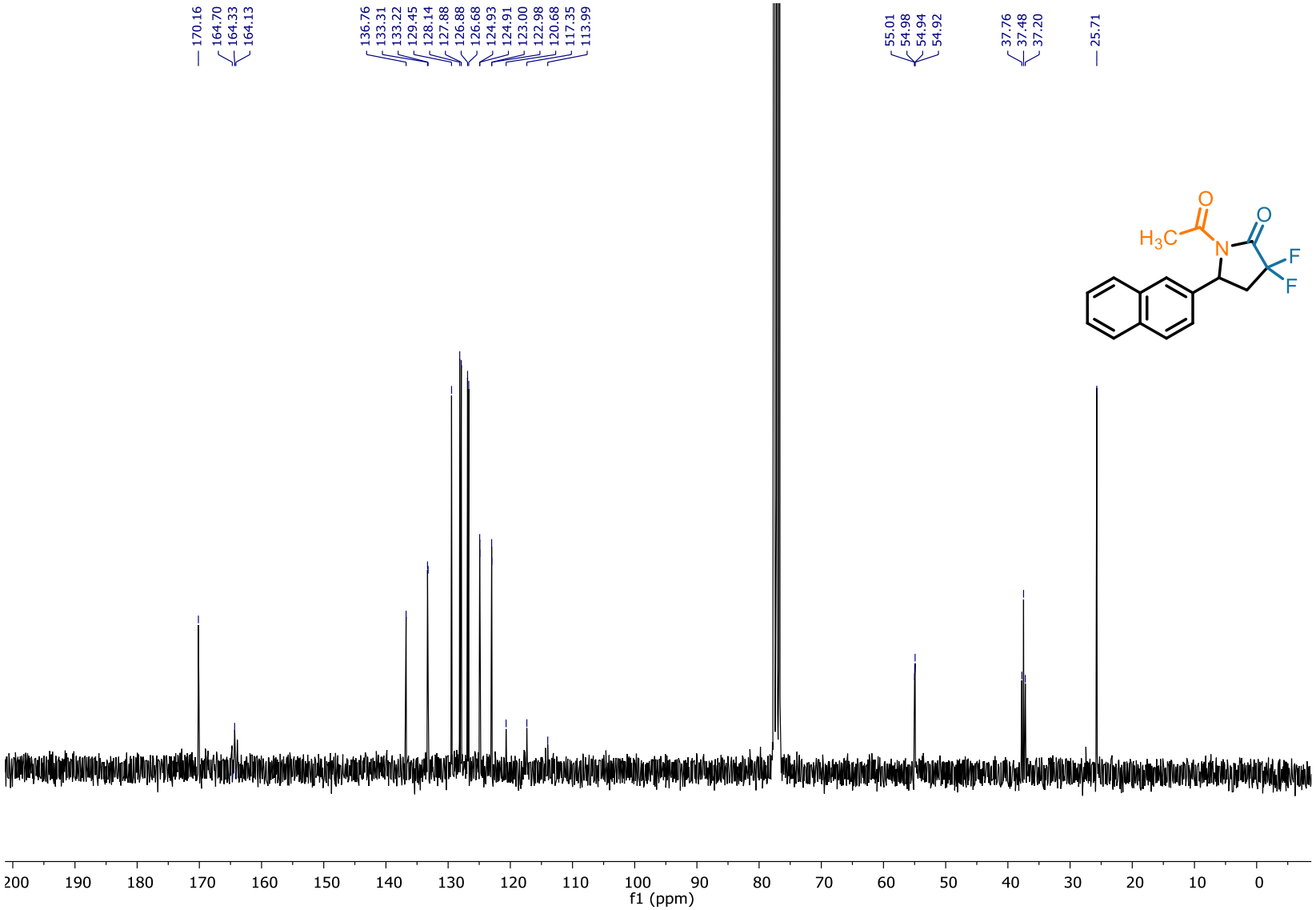
^{19}F-NMR (471 MHz, $CDCl_3$) of **8**



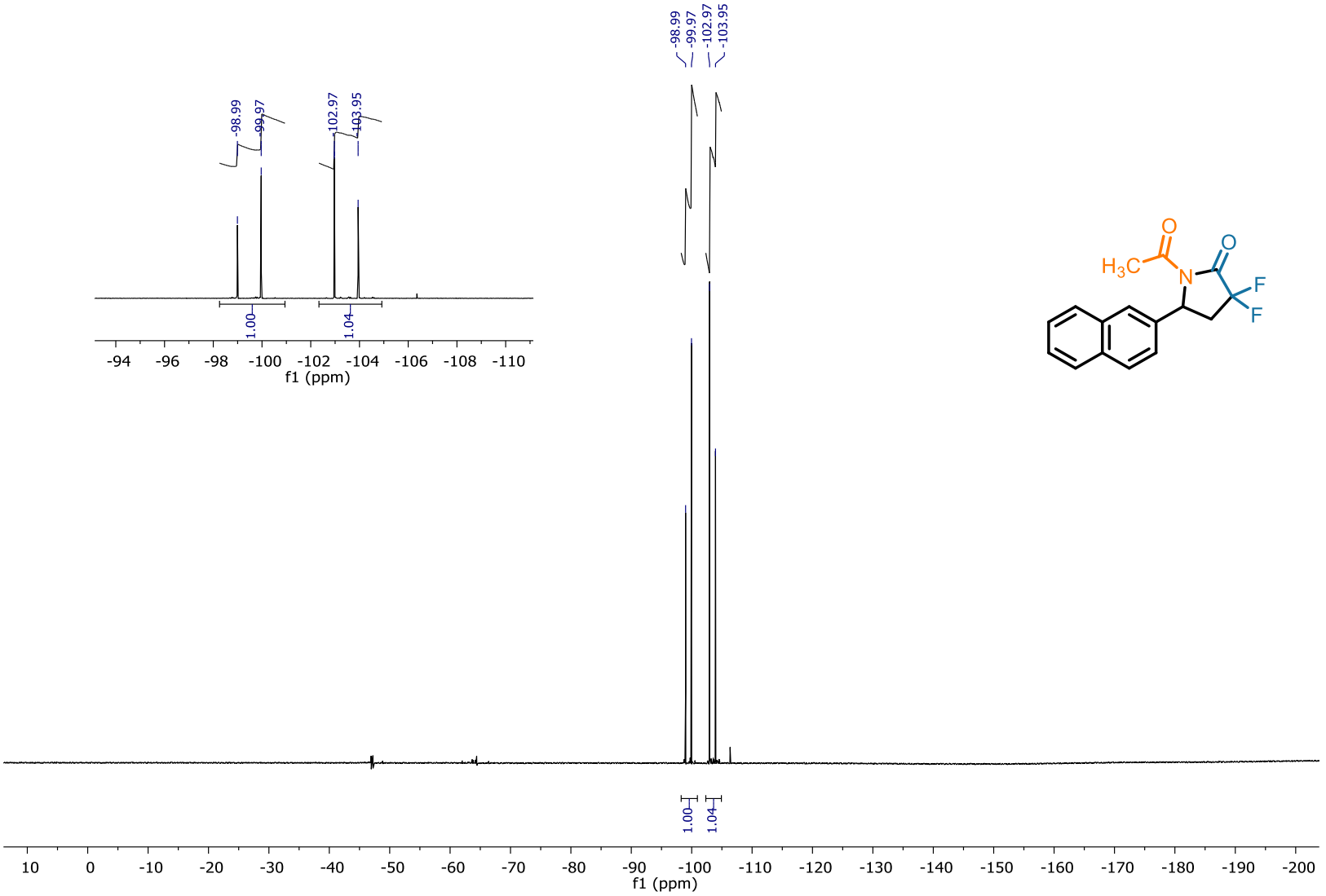
^{1}H-NMR (300 MHz, $CDCl_3$) of **9**



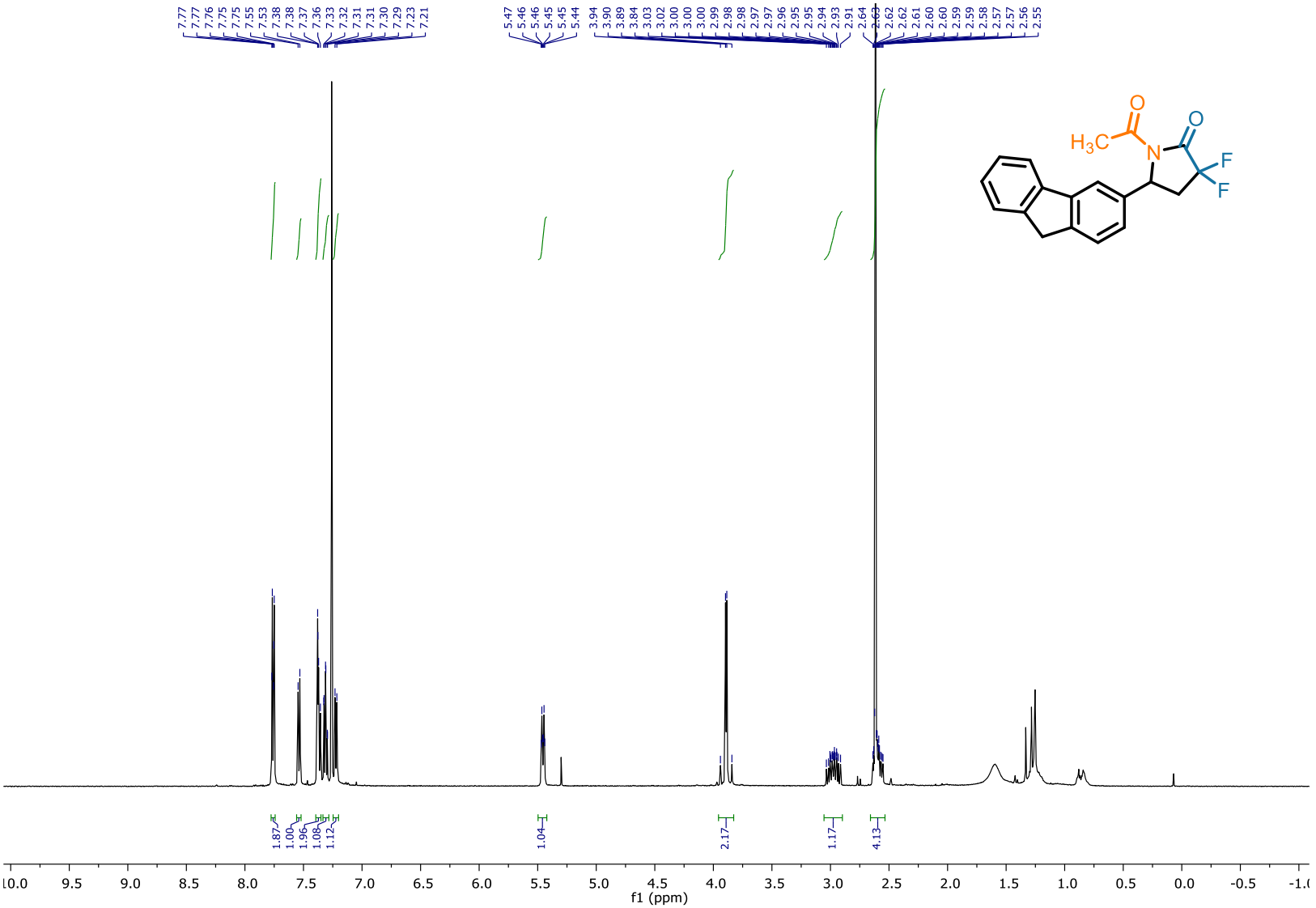
^{13}C-NMR (75 MHz, $CDCl_3$) of **9**



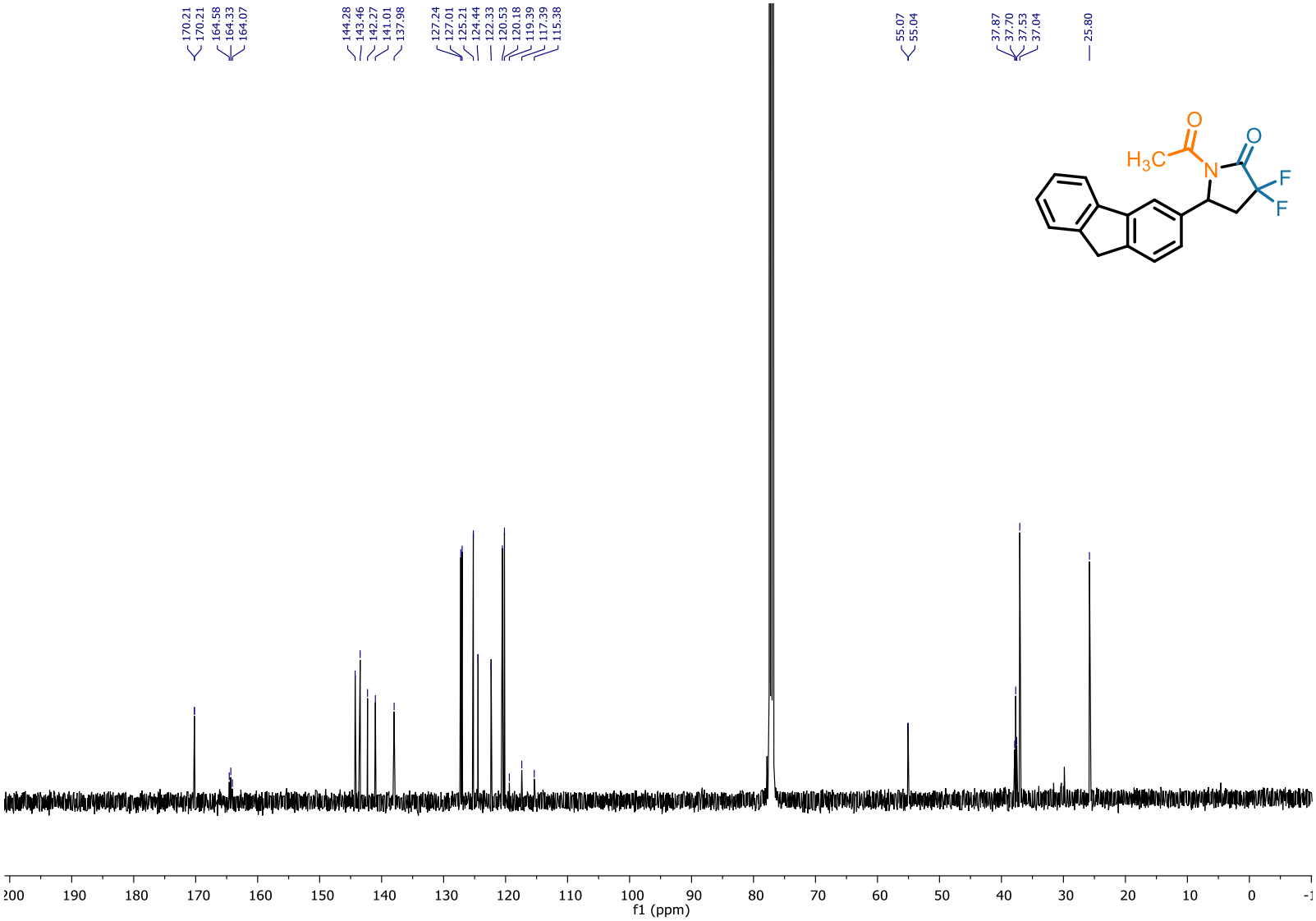
^{19}F-NMR (282 MHz, $CDCl_3$) of **9**



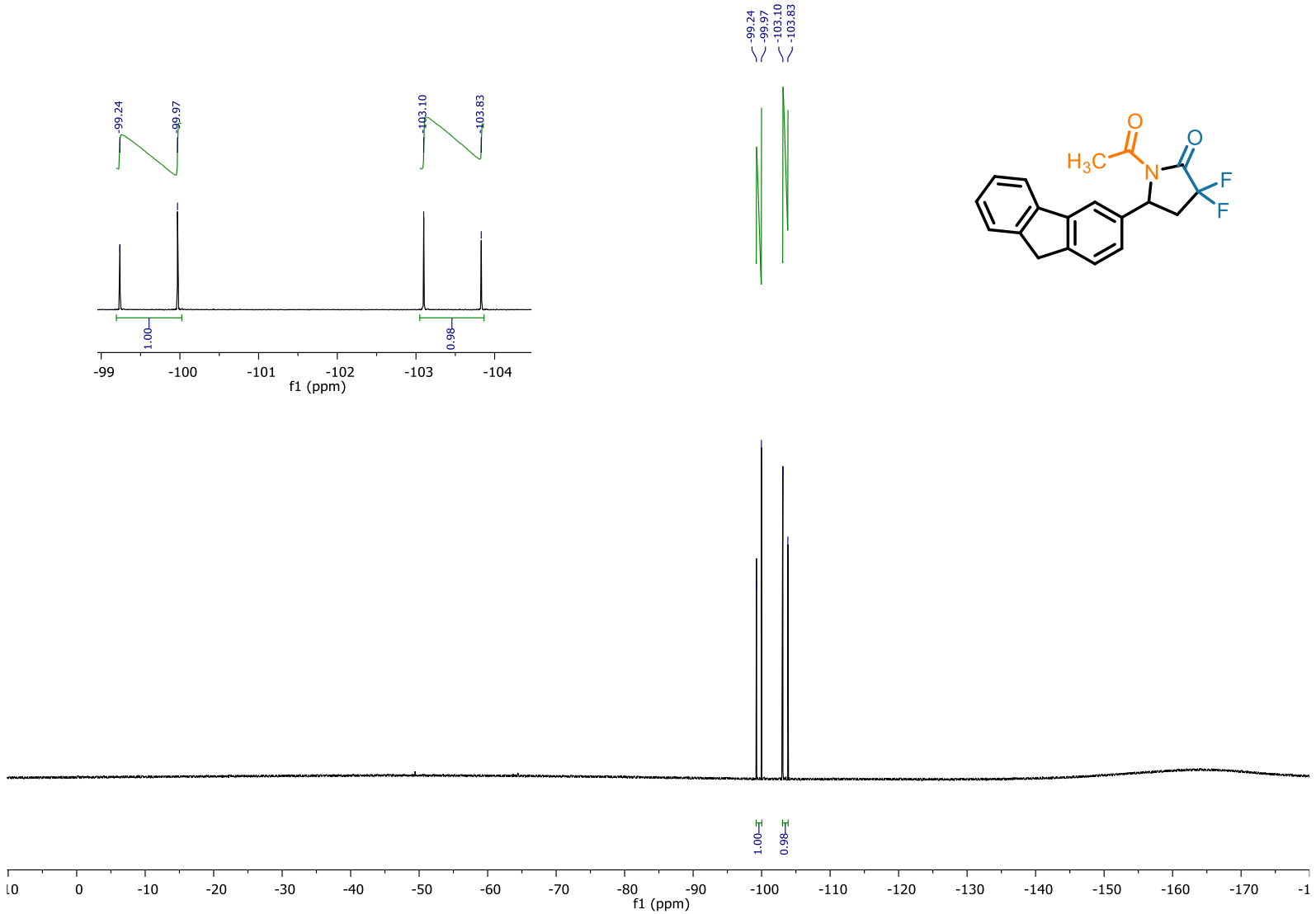
^{1}H-NMR (500 MHz, $CDCl_3$) of **10**



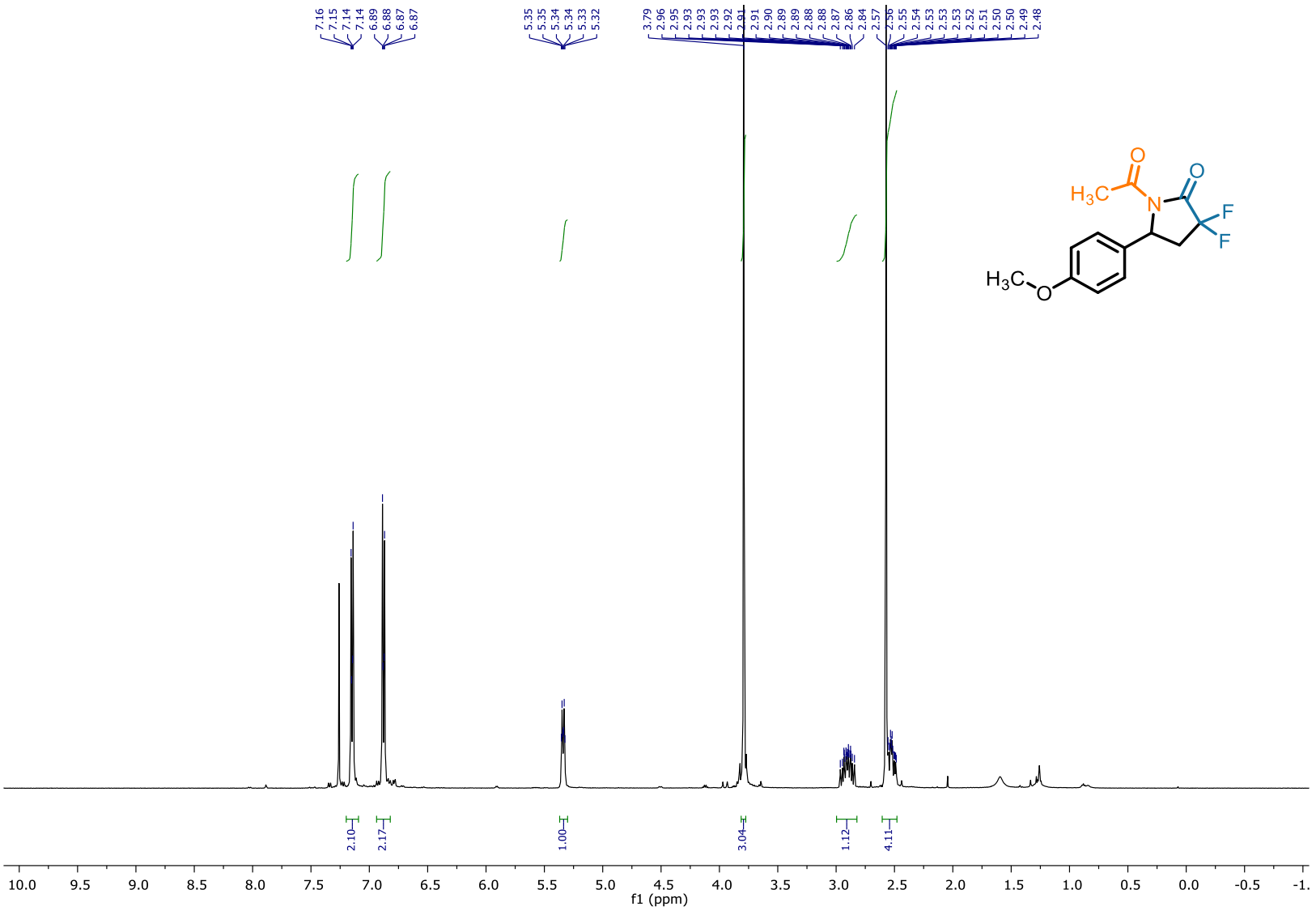
^{13}C-NMR (126 MHz, $CDCl_3$) of **10**



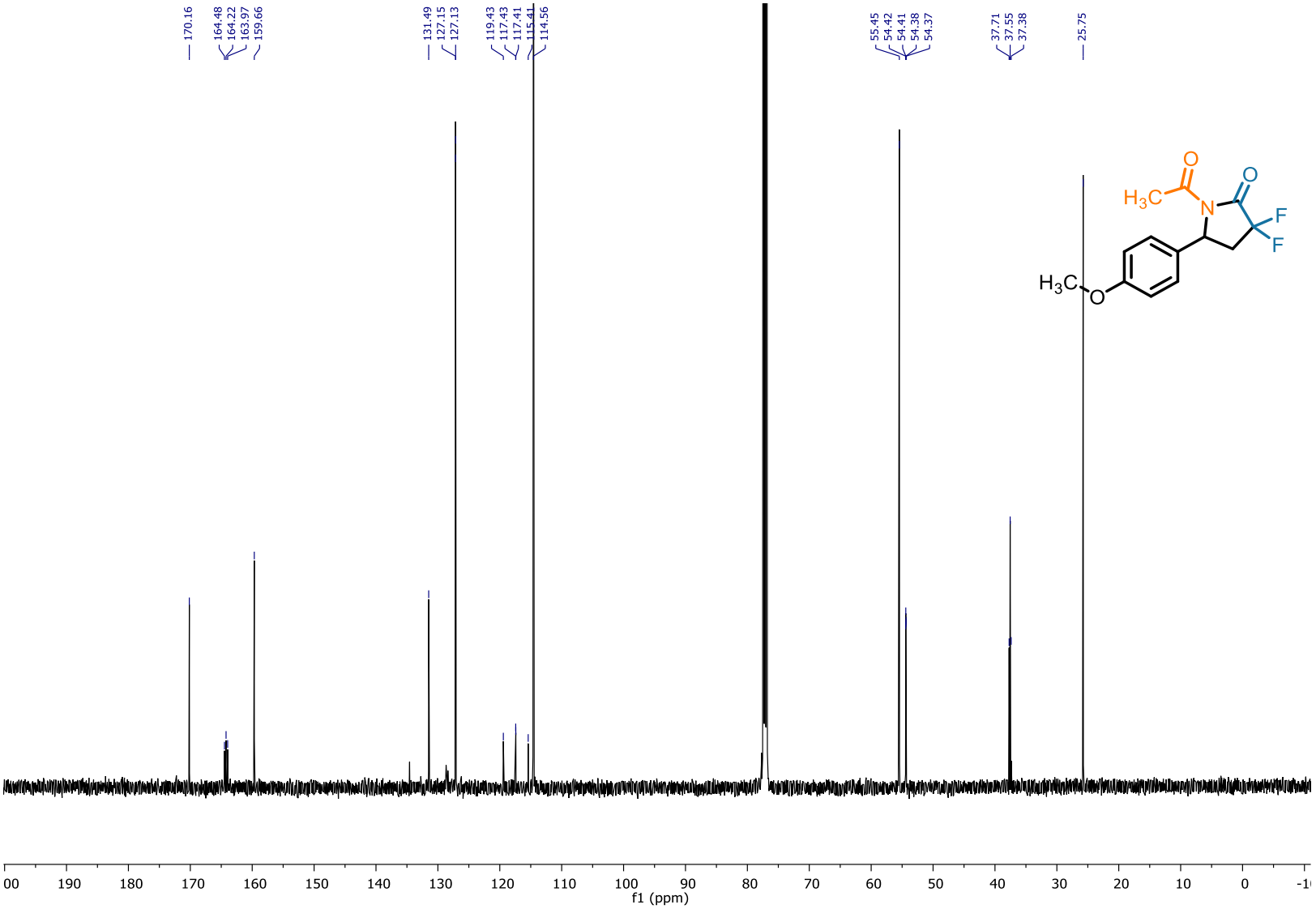
^{19}F-NMR (471 MHz, $CDCl_3$) of **10**



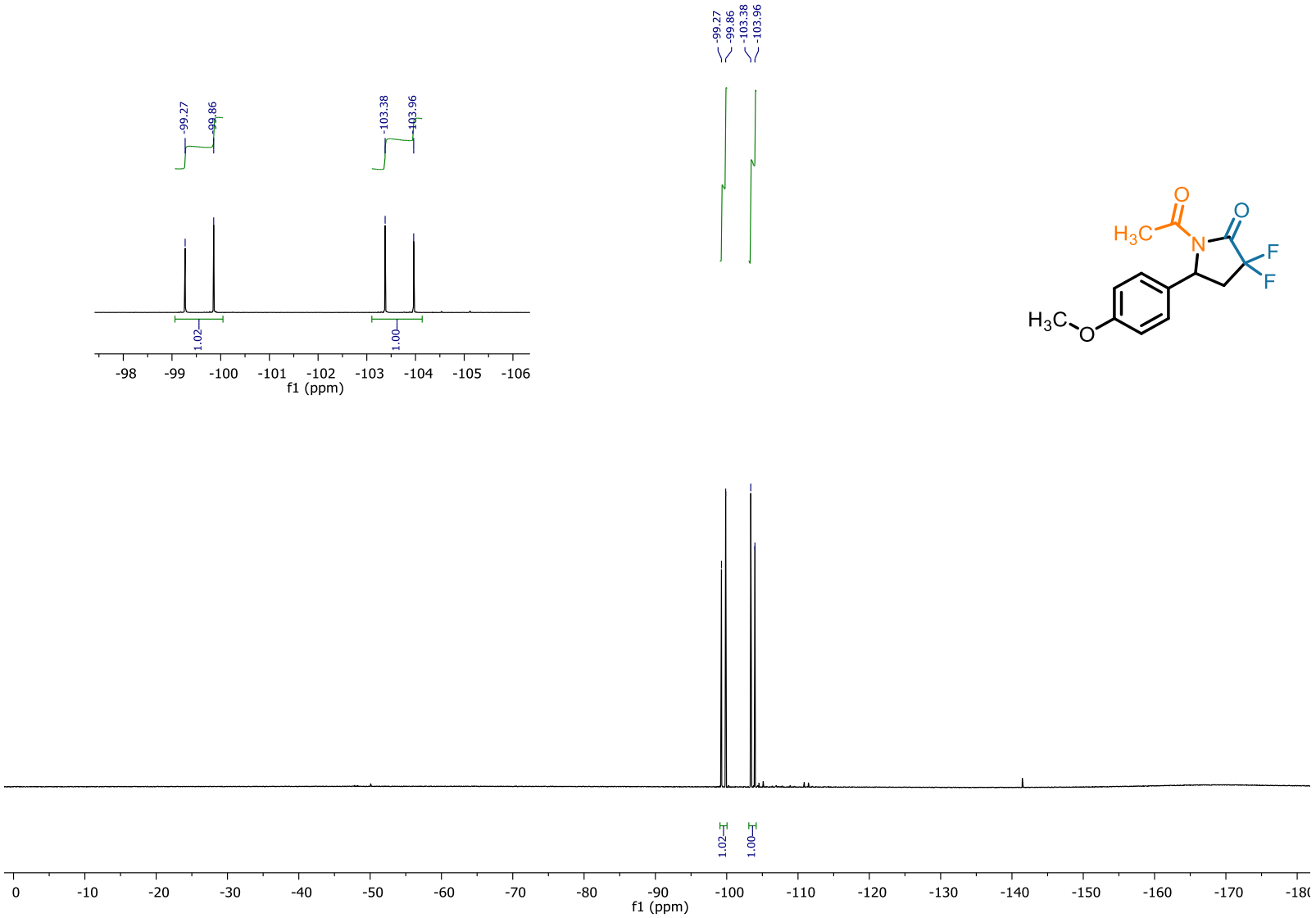
^{1}H-NMR (500 MHz, $CDCl_3$) of **11**



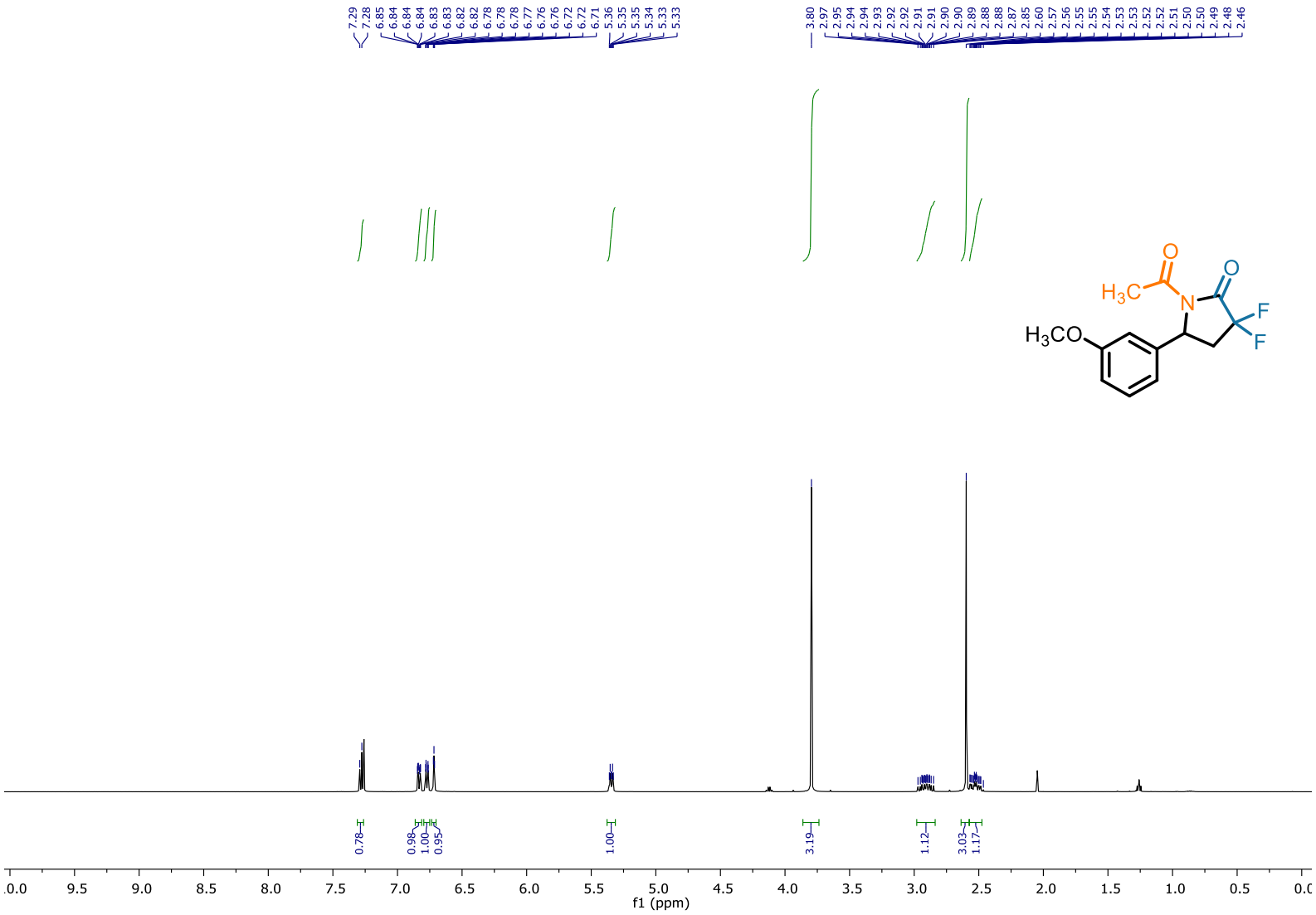
^{13}C-NMR (126 MHz, $CDCl_3$) of **11**



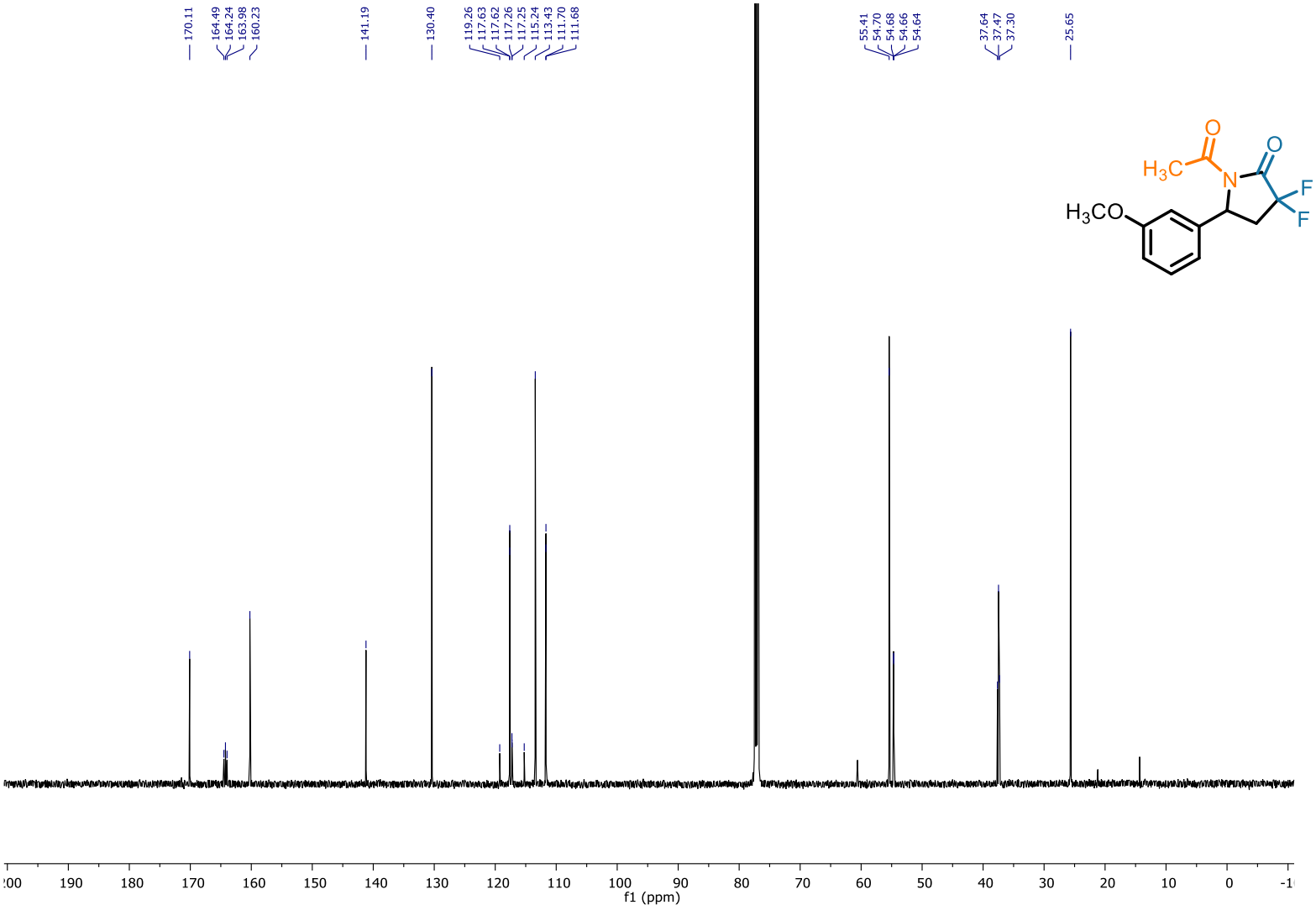
^{19}F-NMR (471 MHz, $CDCl_3$) of **11**



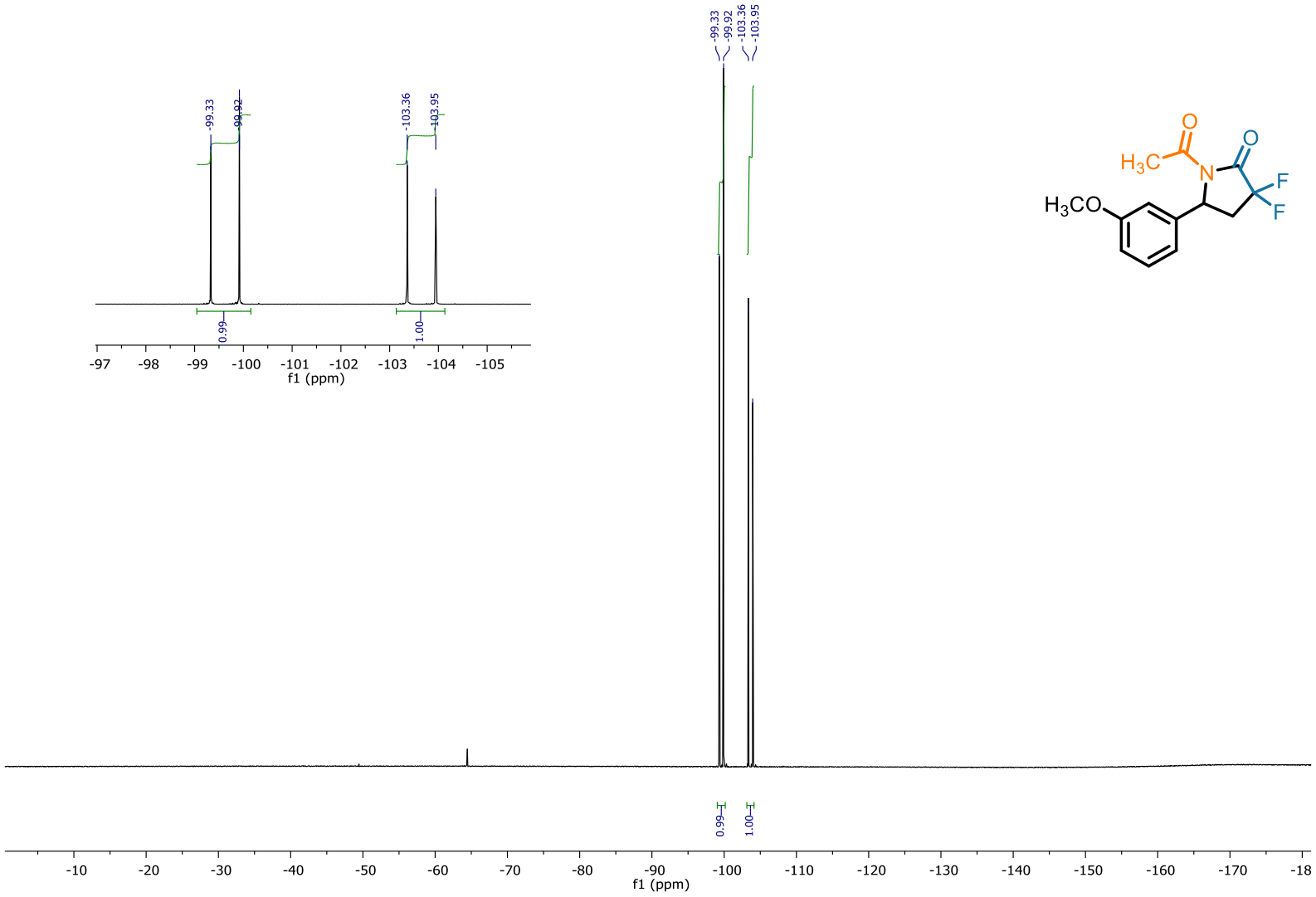
^{1}H-NMR (500 MHz, $CDCl_3$) of **12**



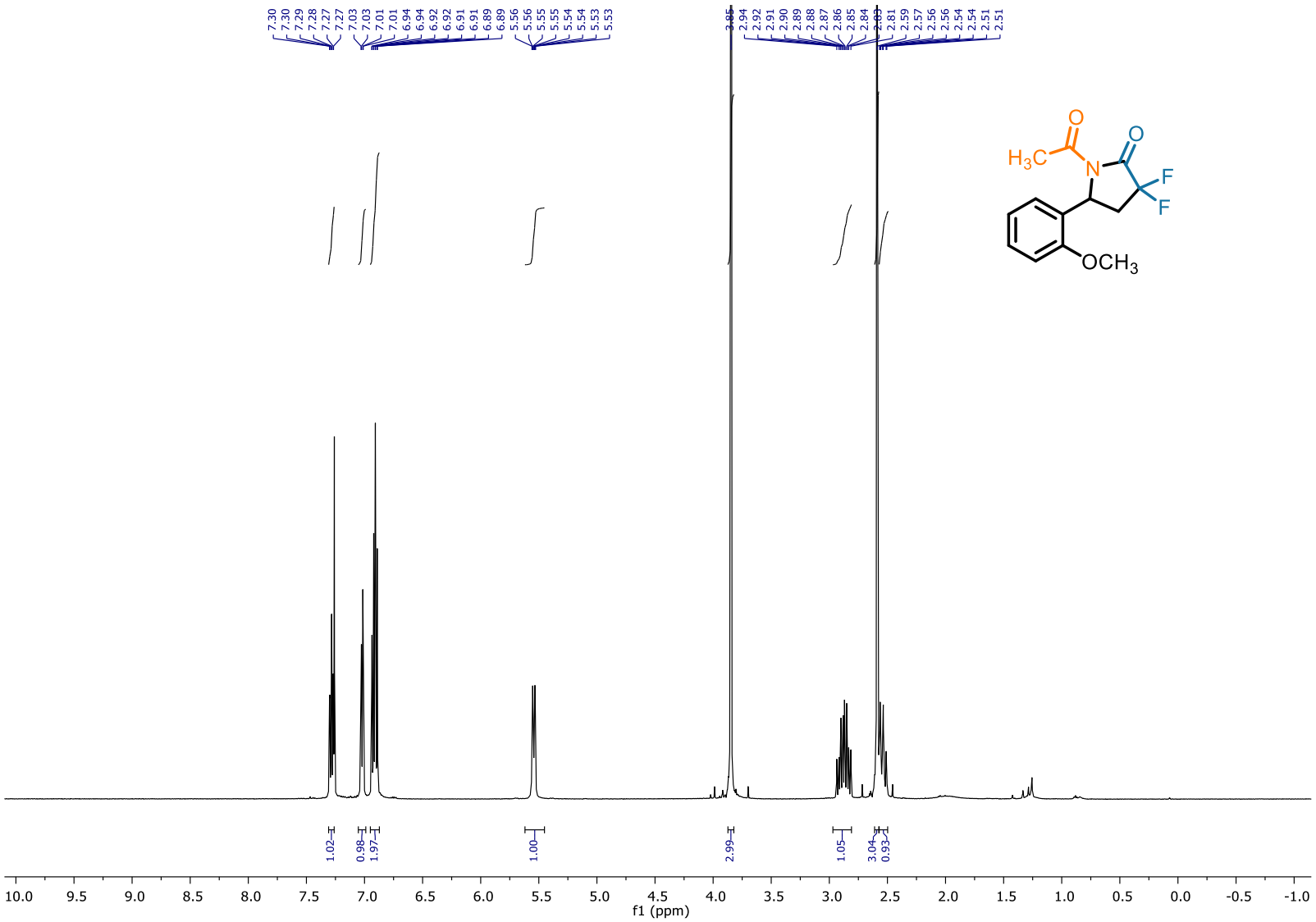
^{13}C-NMR (126 MHz, $CDCl_3$) of **12**



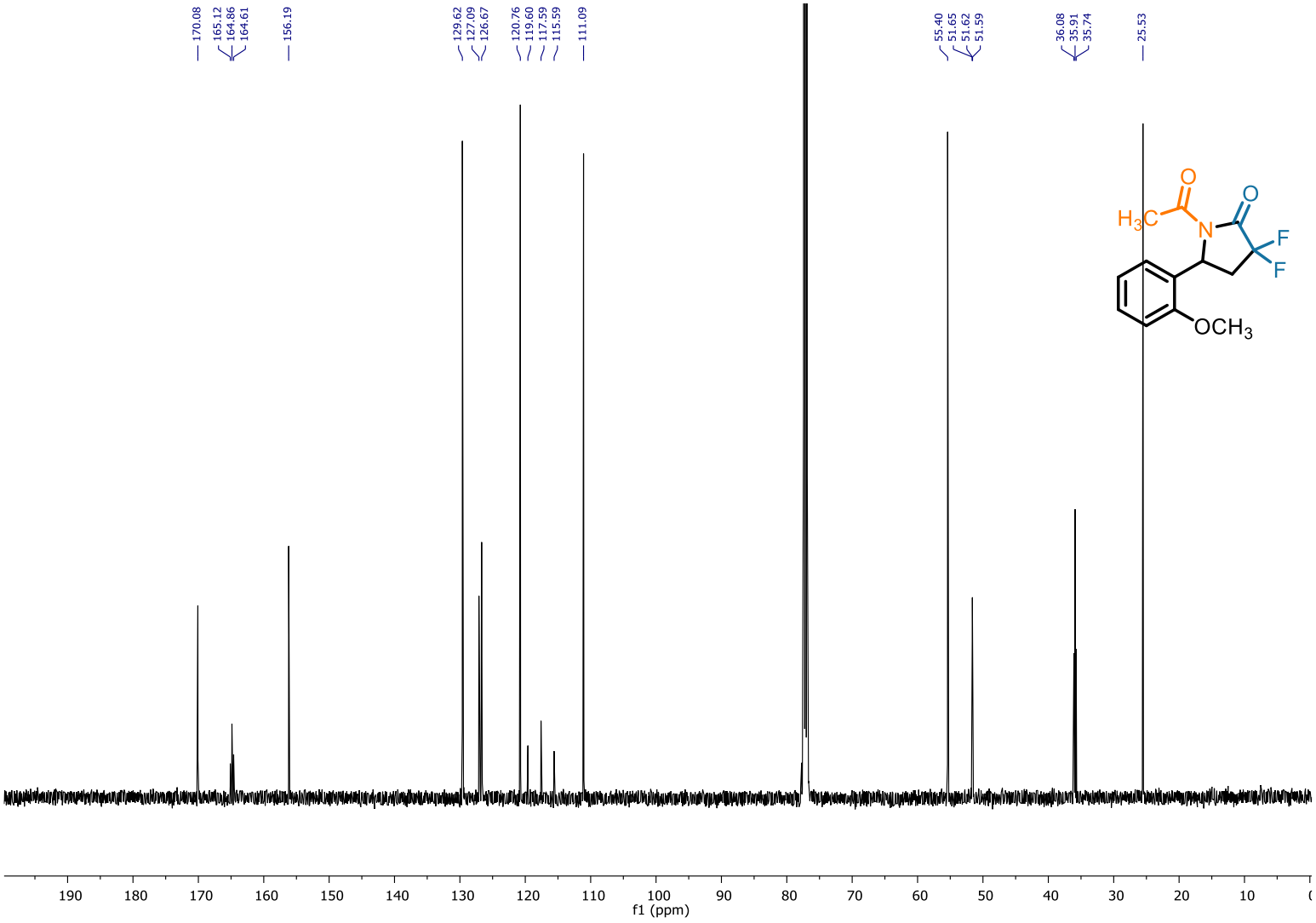
^{19}F-NMR (471 MHz, $CDCl_3$) of **12**



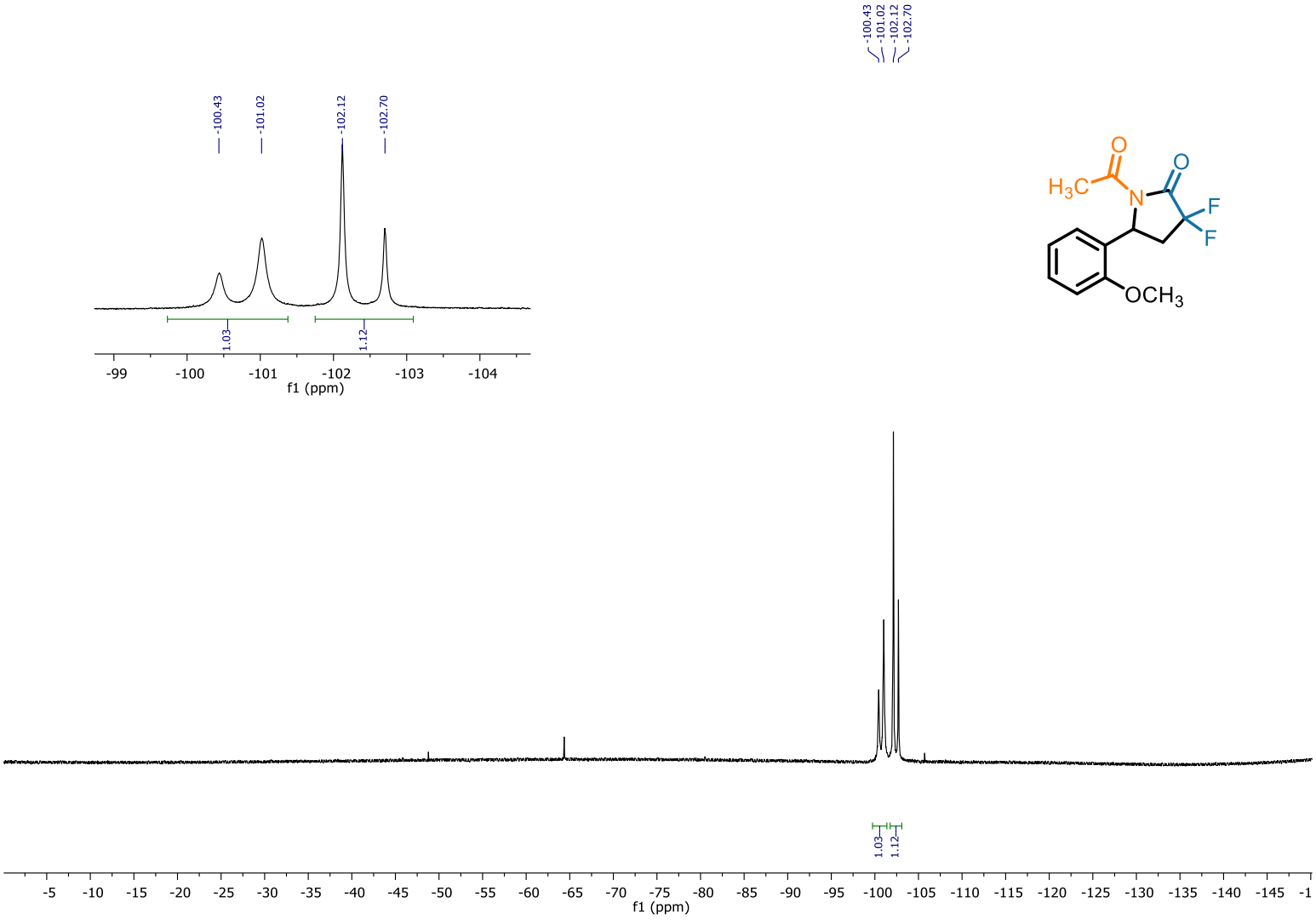
^{1}H-NMR (500 MHz, $CDCl_3$) of **13**



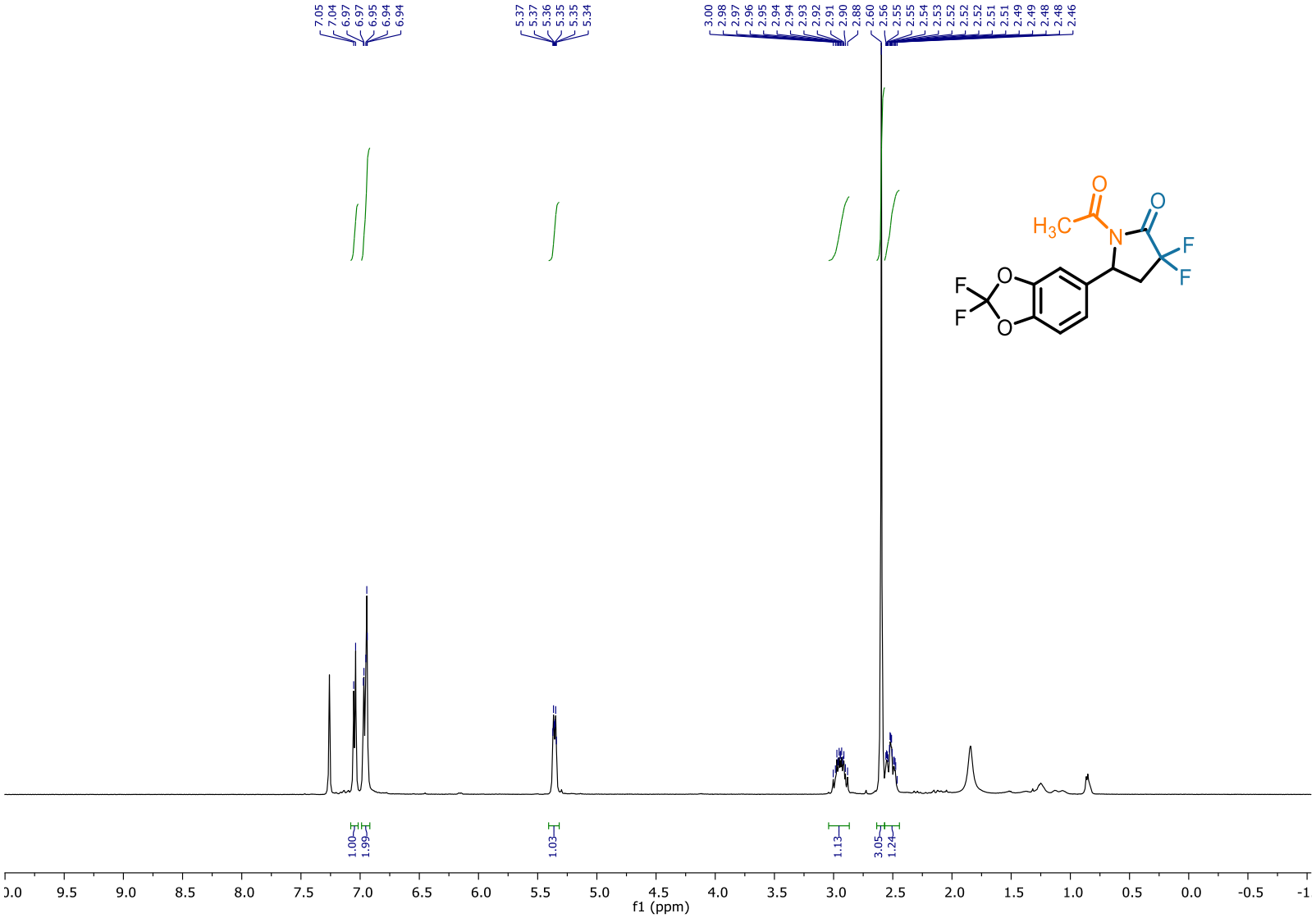
^{13}C-NMR (126 MHz, $CDCl_3$) of **13**



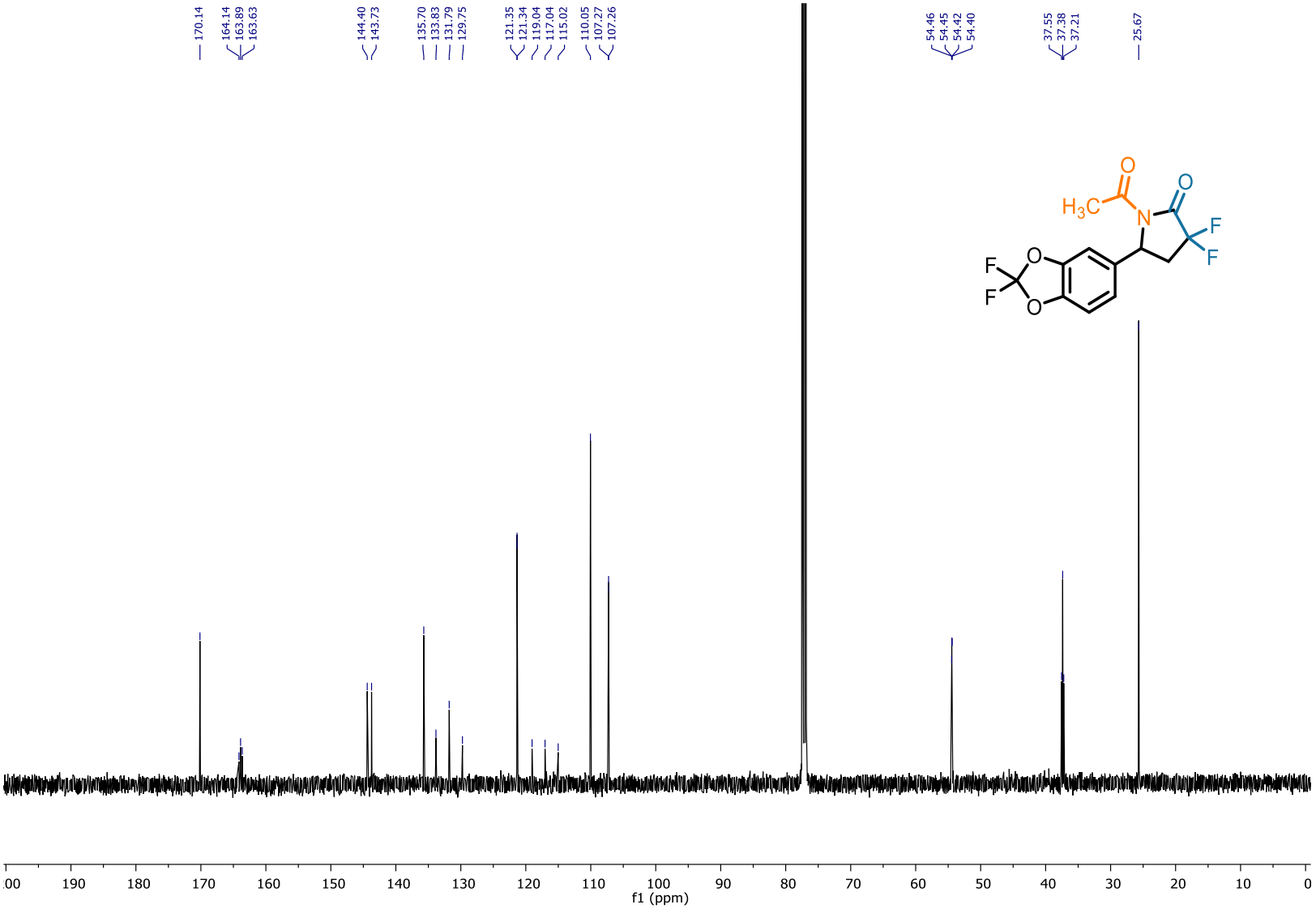
^{19}F-NMR (471 MHz, $CDCl_3$) of **13**



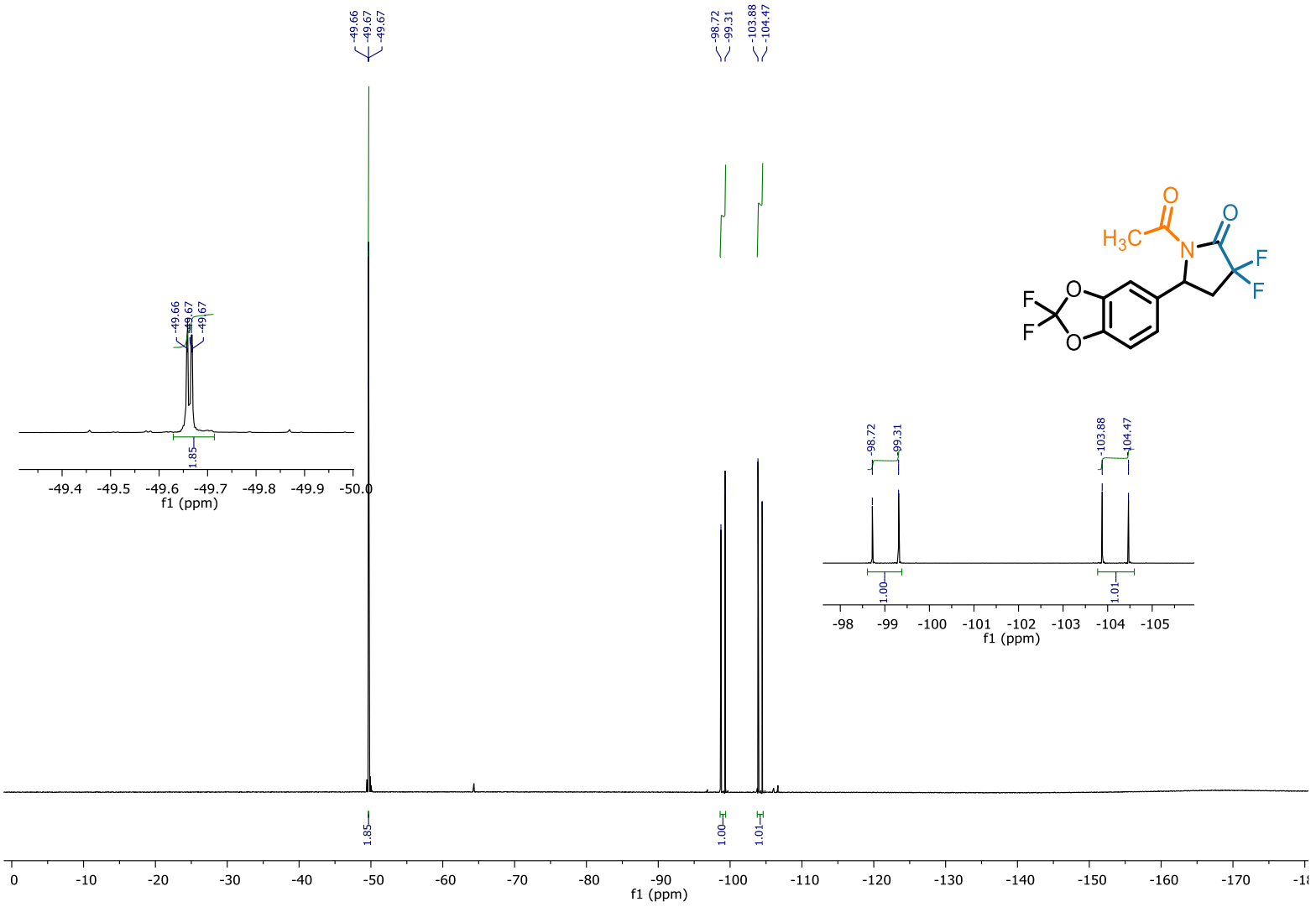
^{1}H-NMR (500 MHz, $CDCl_3$) of **14**



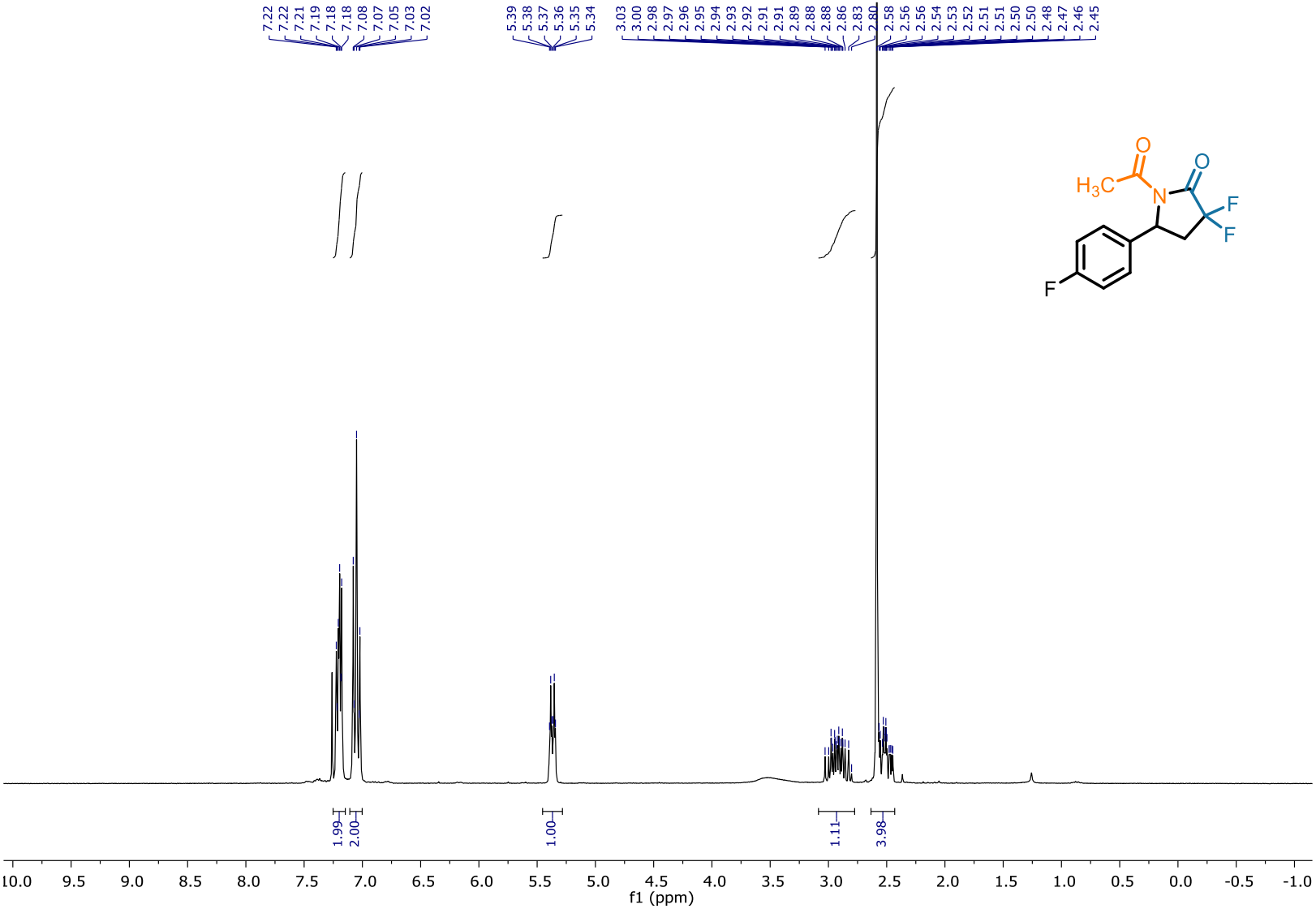
^{13}C-NMR (126 MHz, $CDCl_3$) of **14**



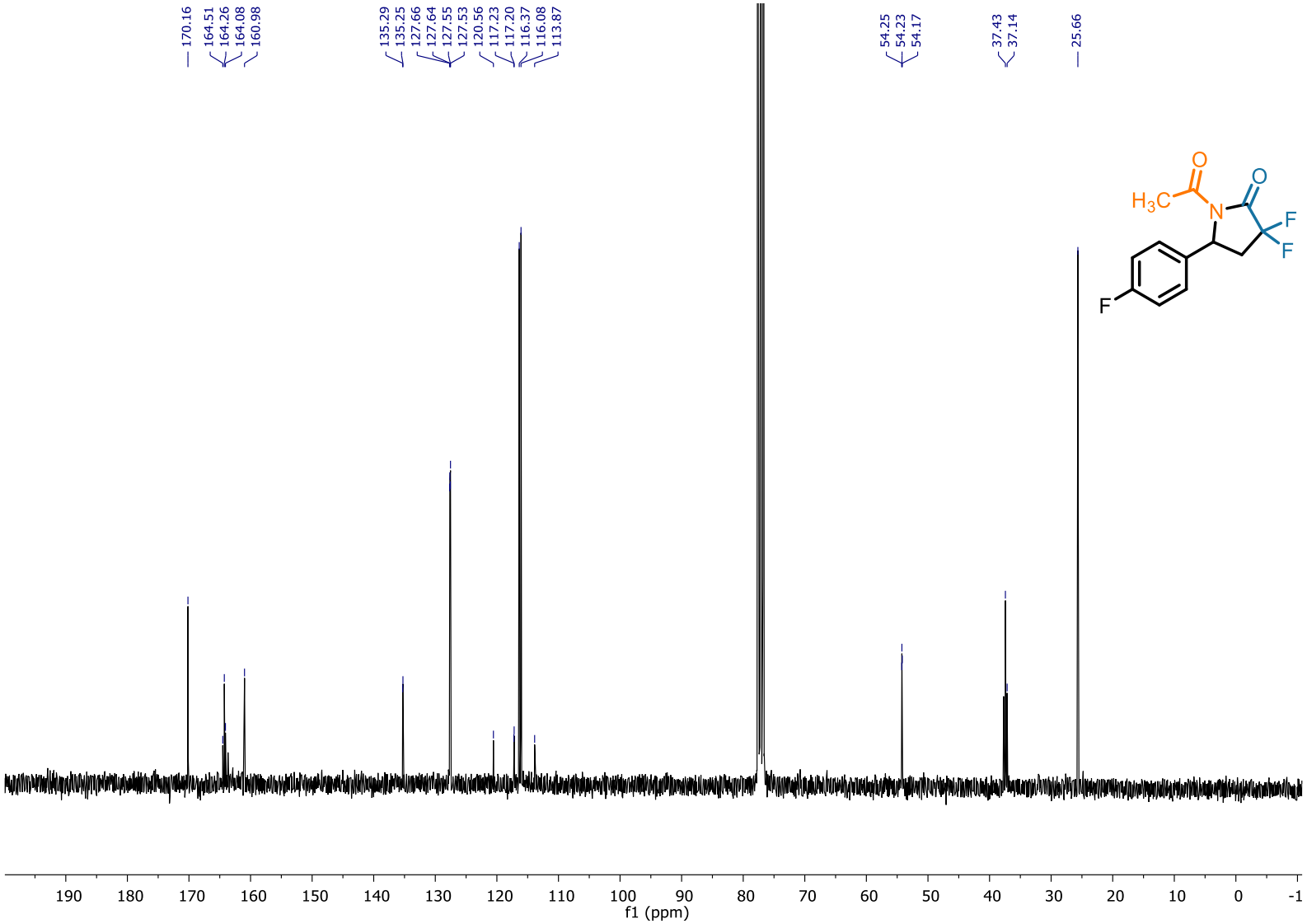
^{19}F-NMR (471 MHz, $CDCl_3$) of **14**



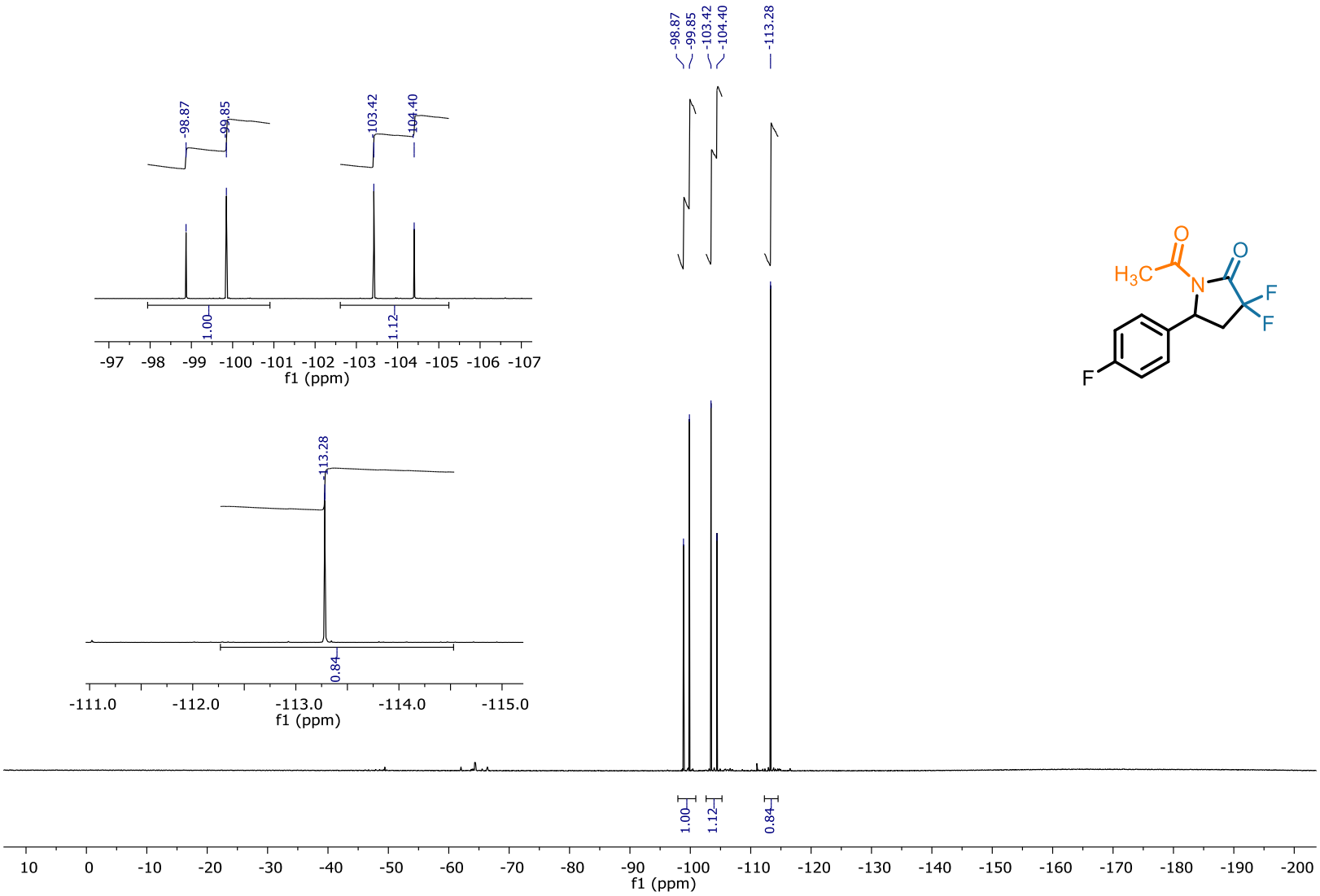
^{1}H-NMR (300 MHz, $CDCl_3$) of **15**



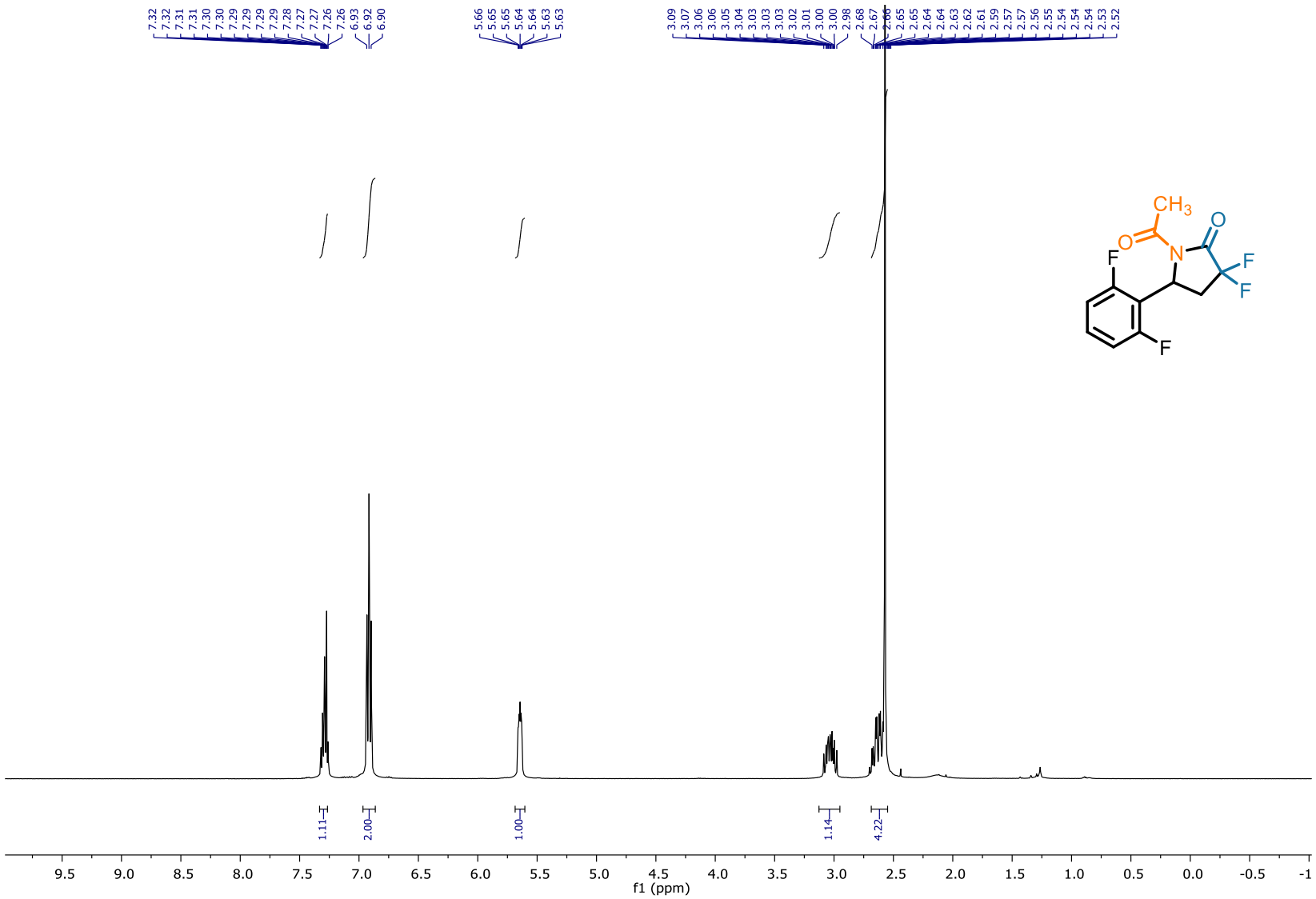
^{13}C-NMR (75 MHz, $CDCl_3$) of **15**



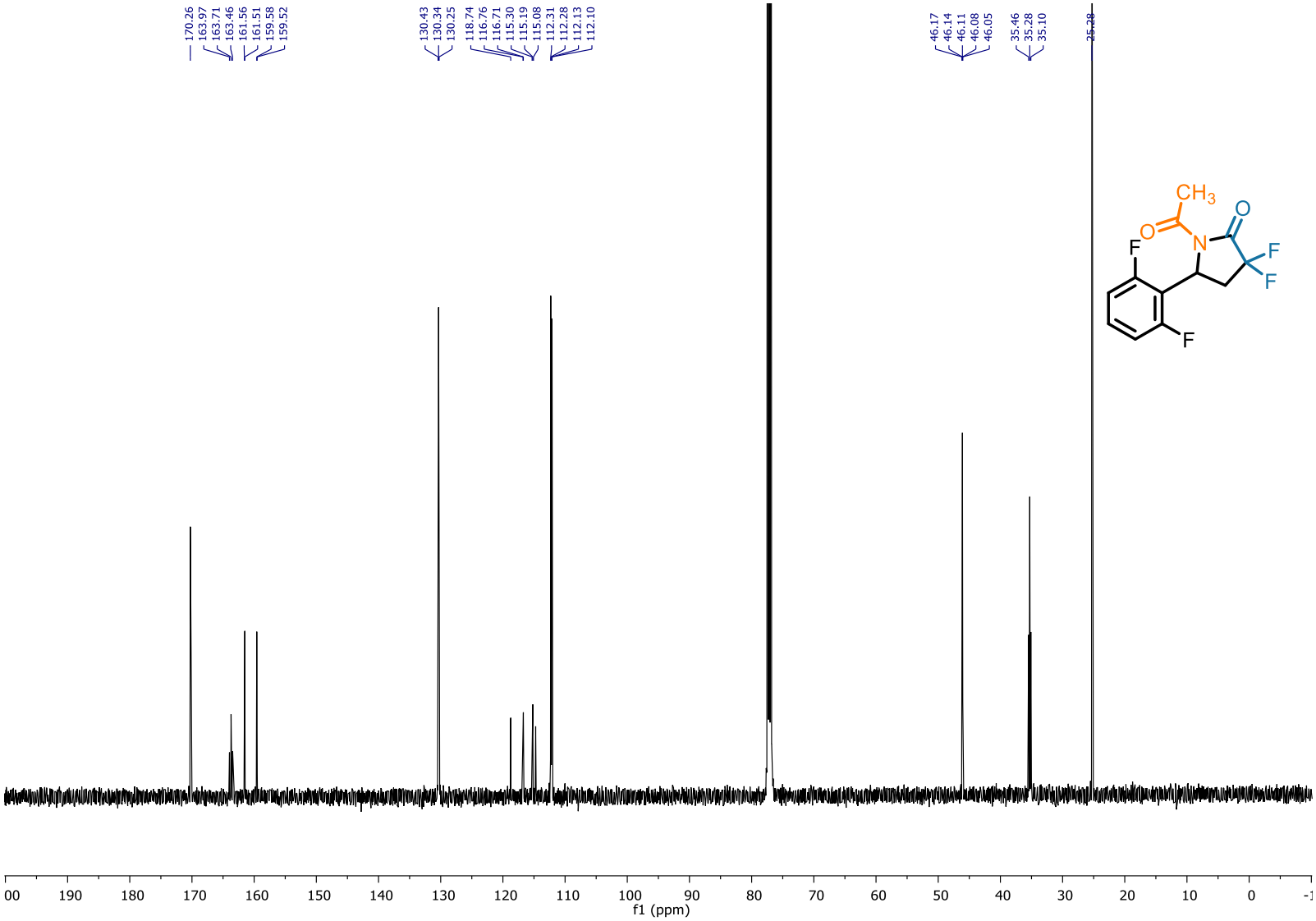
^{19}F-NMR (282 MHz, $CDCl_3$) of **15**



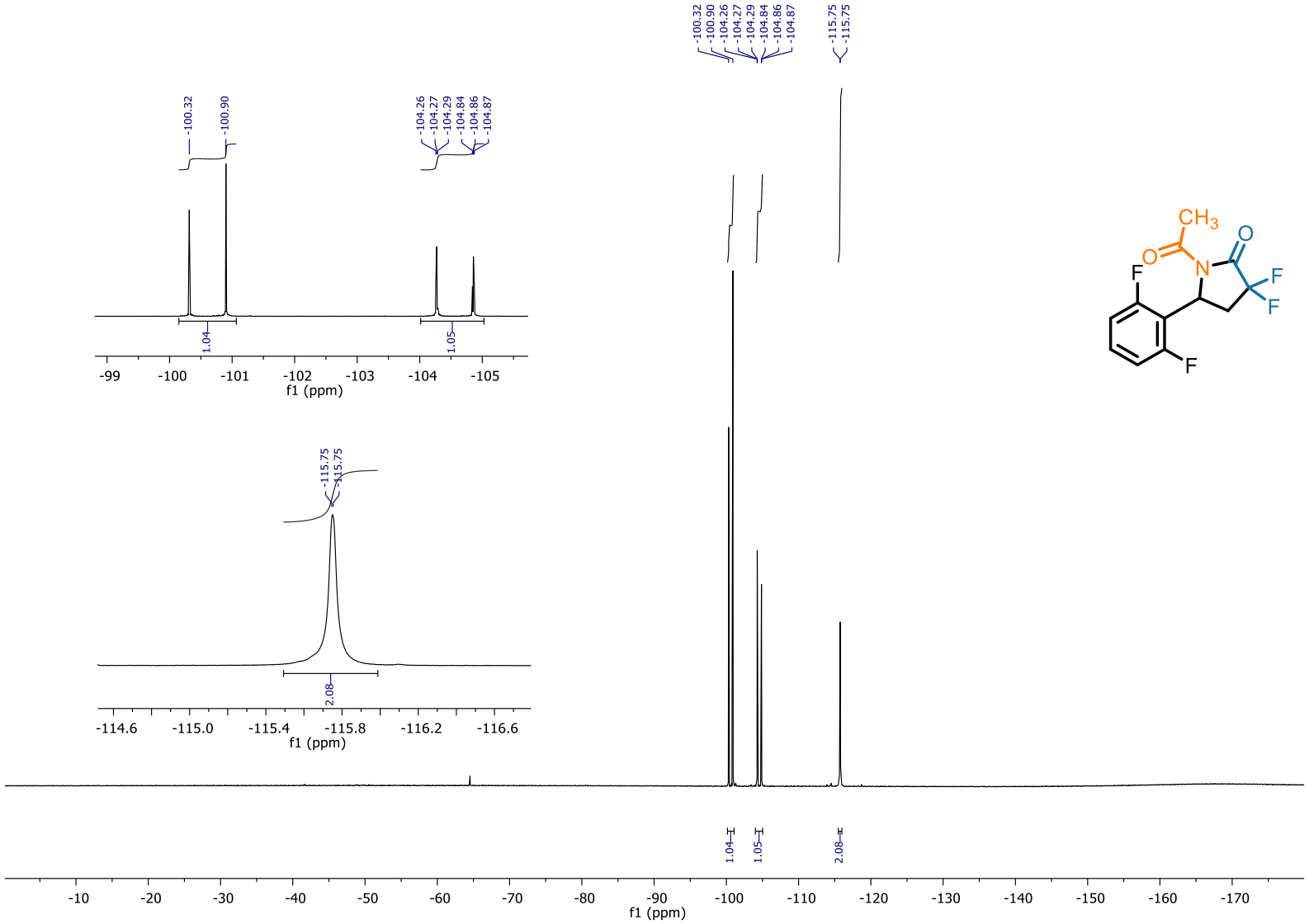
^{1}H-NMR (500 MHz, $CDCl_3$) of **16**



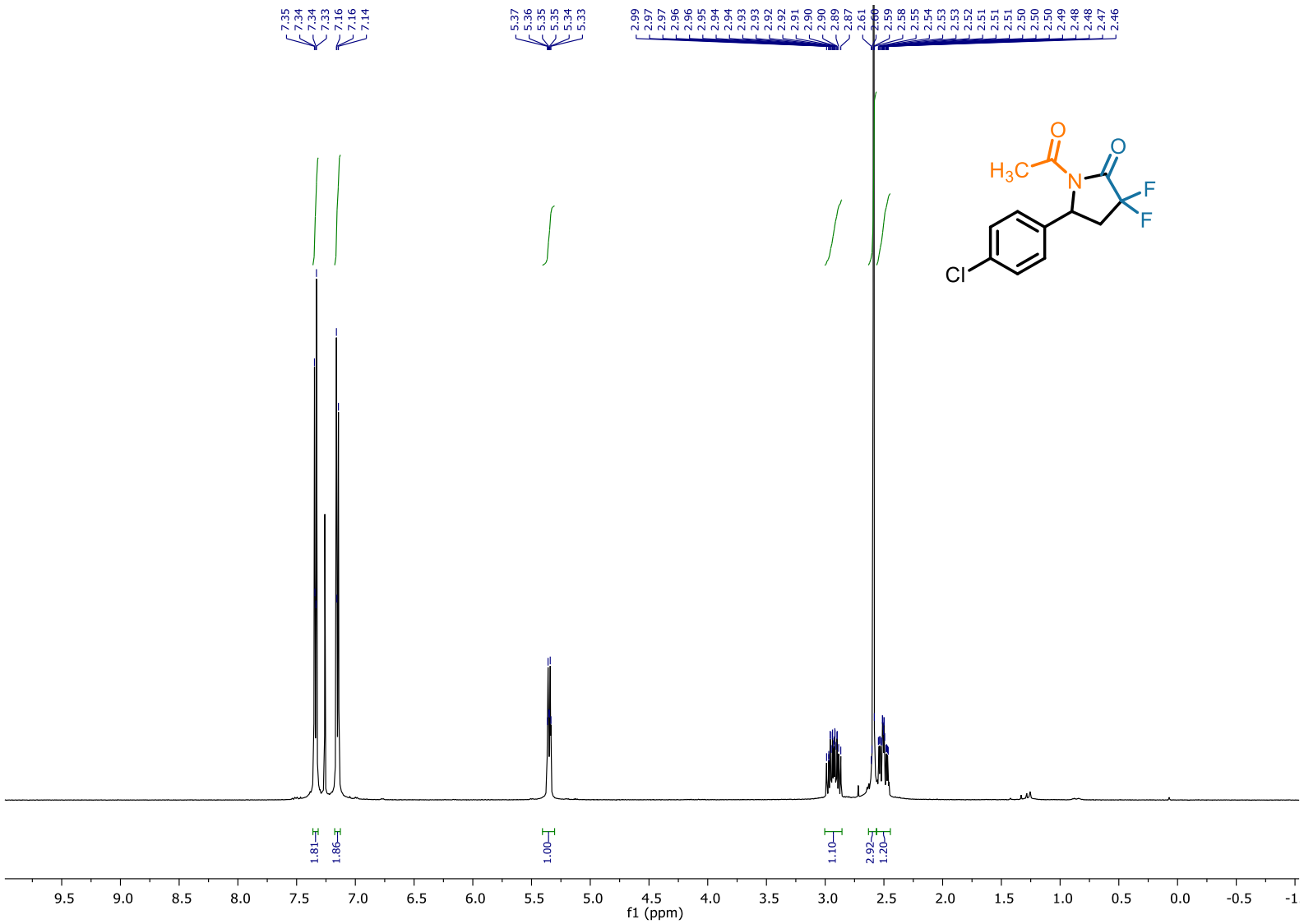
^{13}C-NMR (126 MHz, $CDCl_3$) of **16**



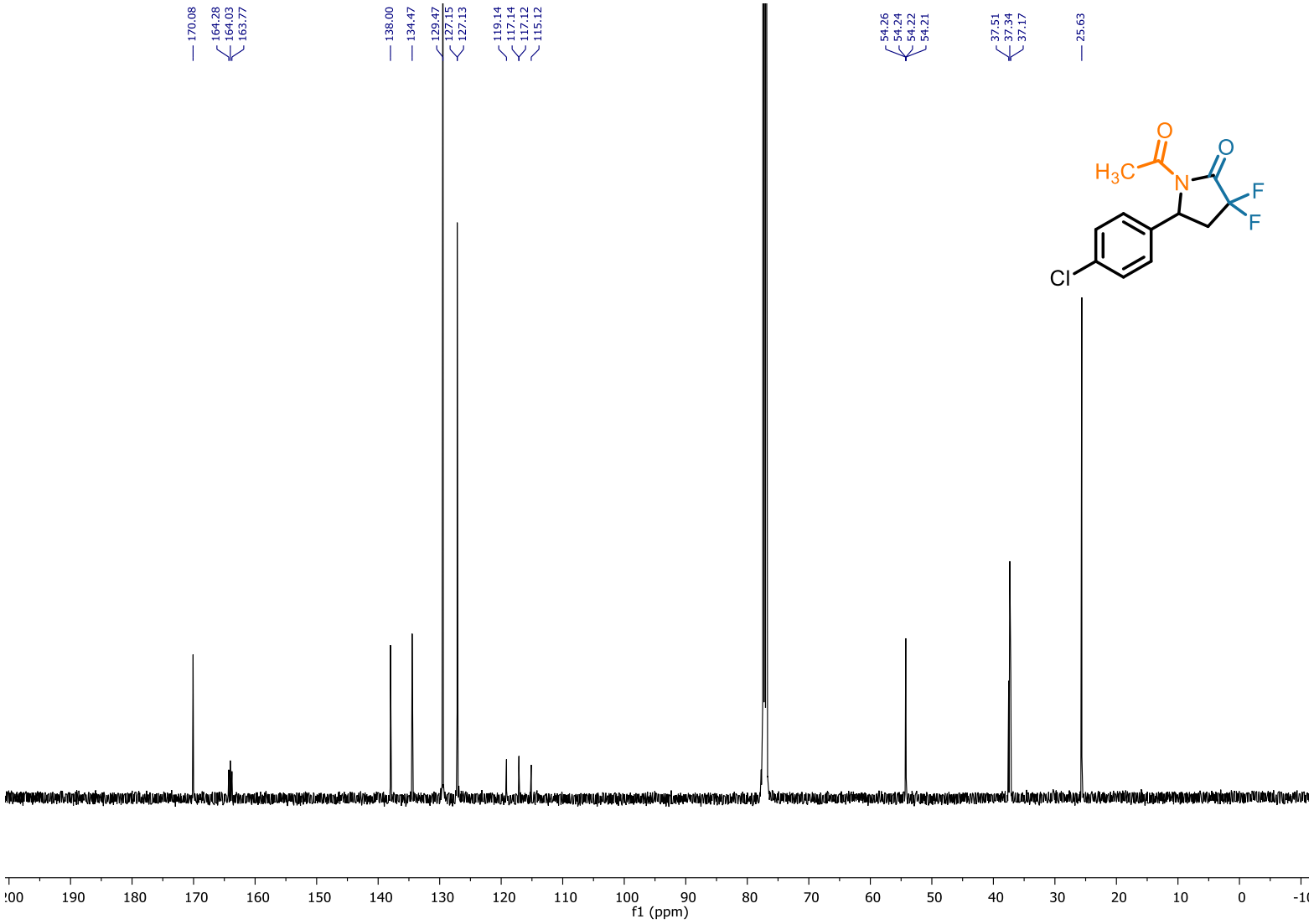
^{19}F-NMR (471 MHz, $CDCl_3$) of **16**



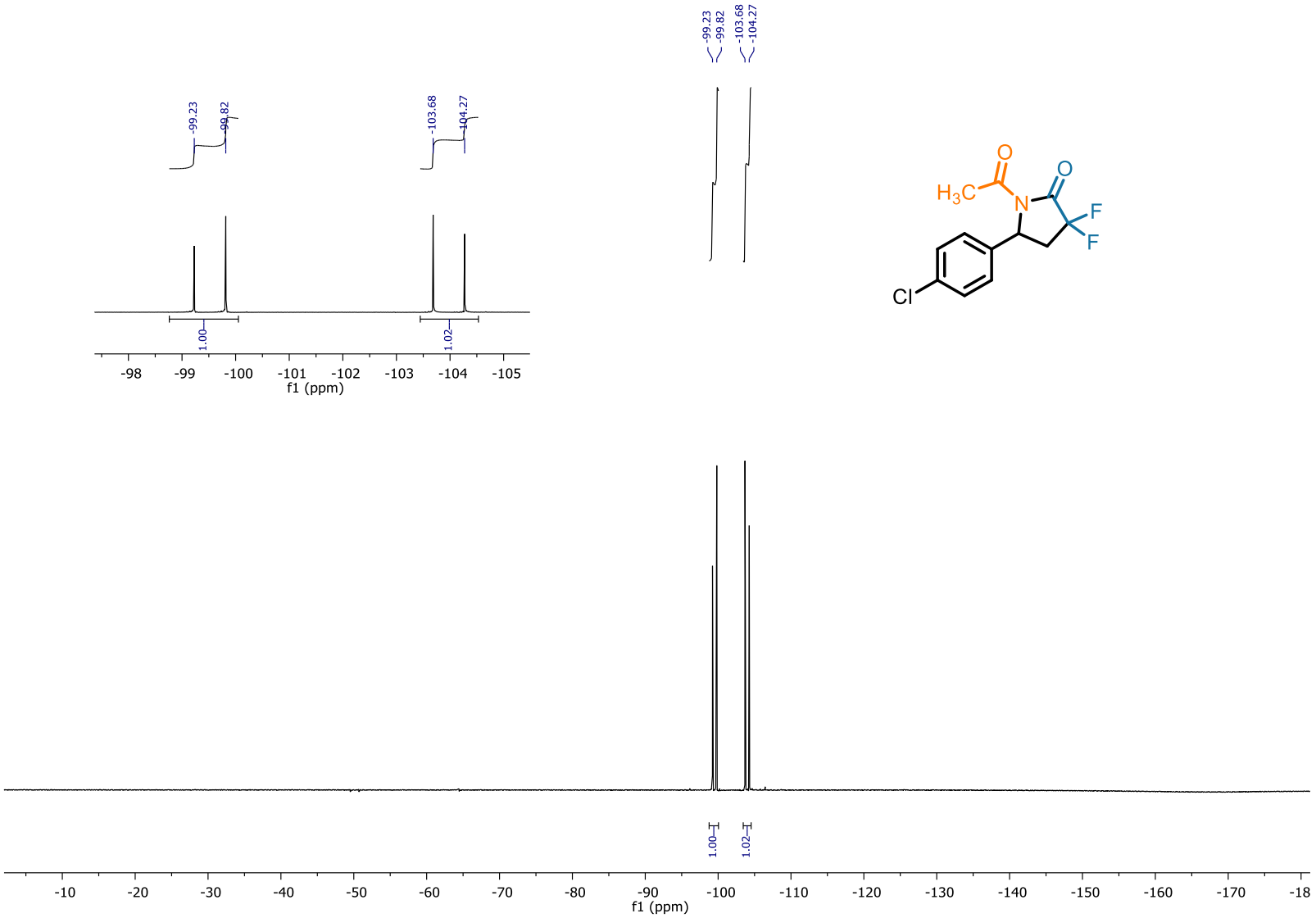
^{1}H-NMR (500 MHz, $CDCl_3$) of **17**



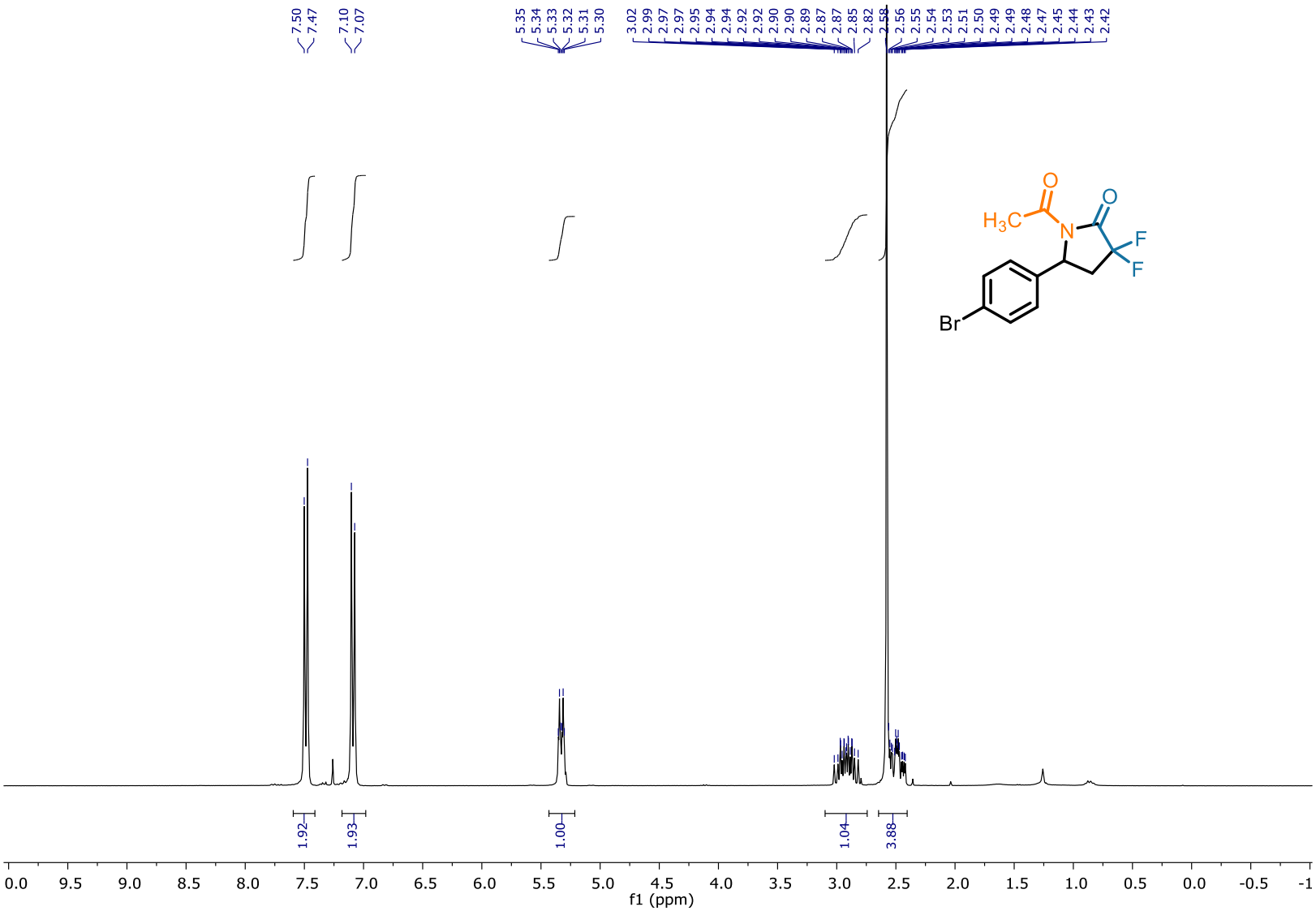
^{13}C-NMR (126 MHz, $CDCl_3$) of **17**



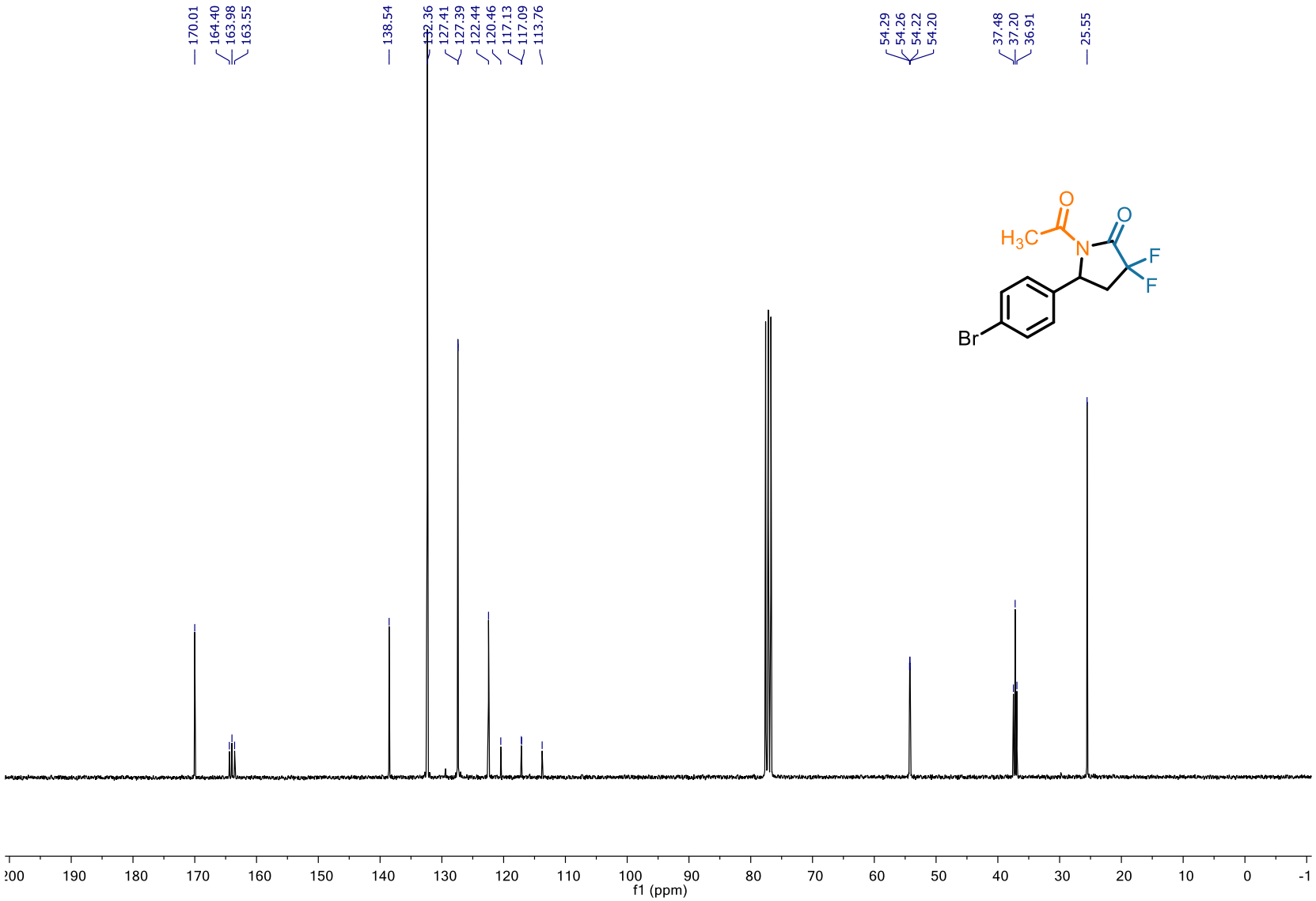
^{19}F-NMR (471 MHz, $CDCl_3$) of **17**



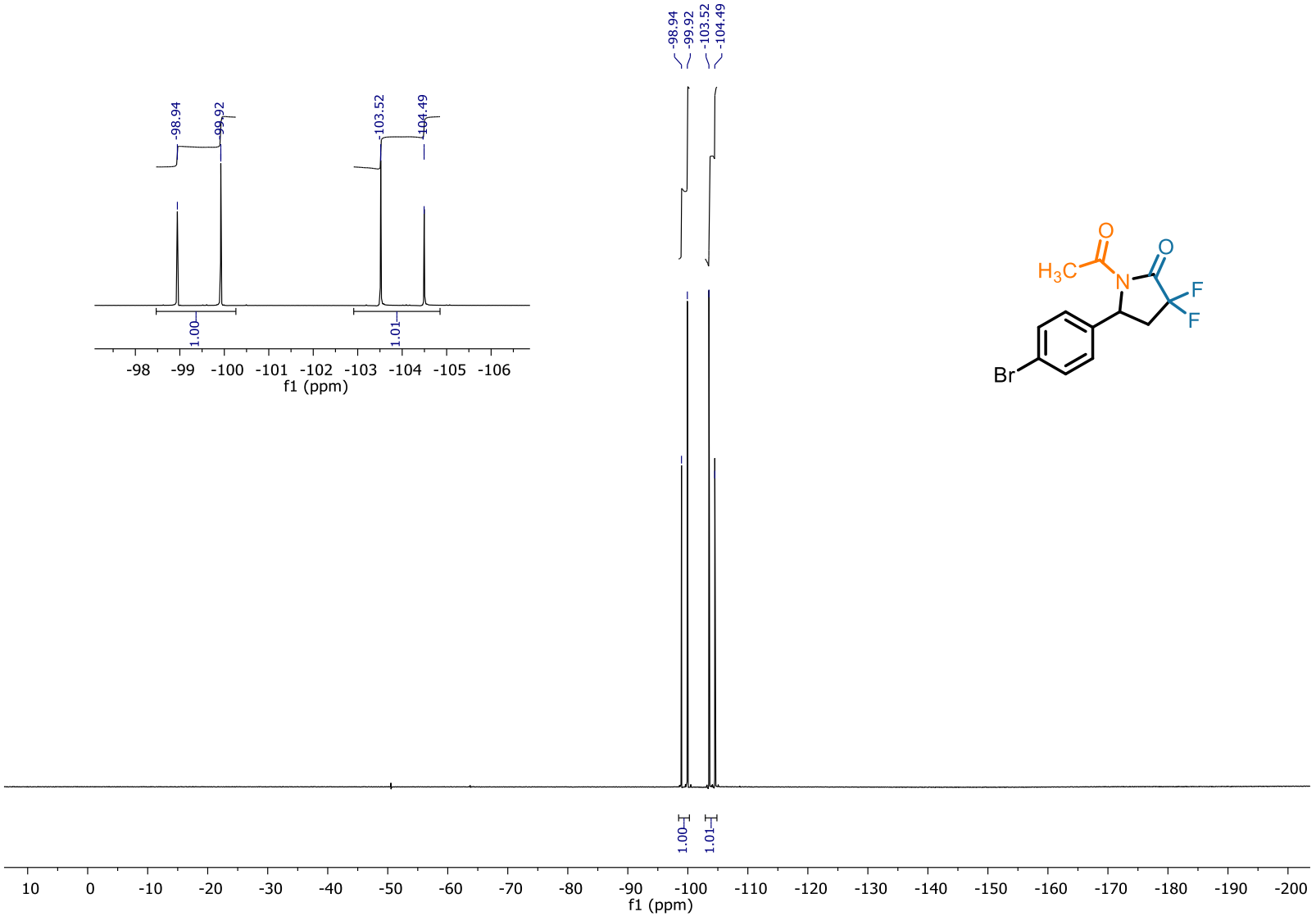
^{1}H-NMR (300 MHz, $CDCl_3$) of **18**



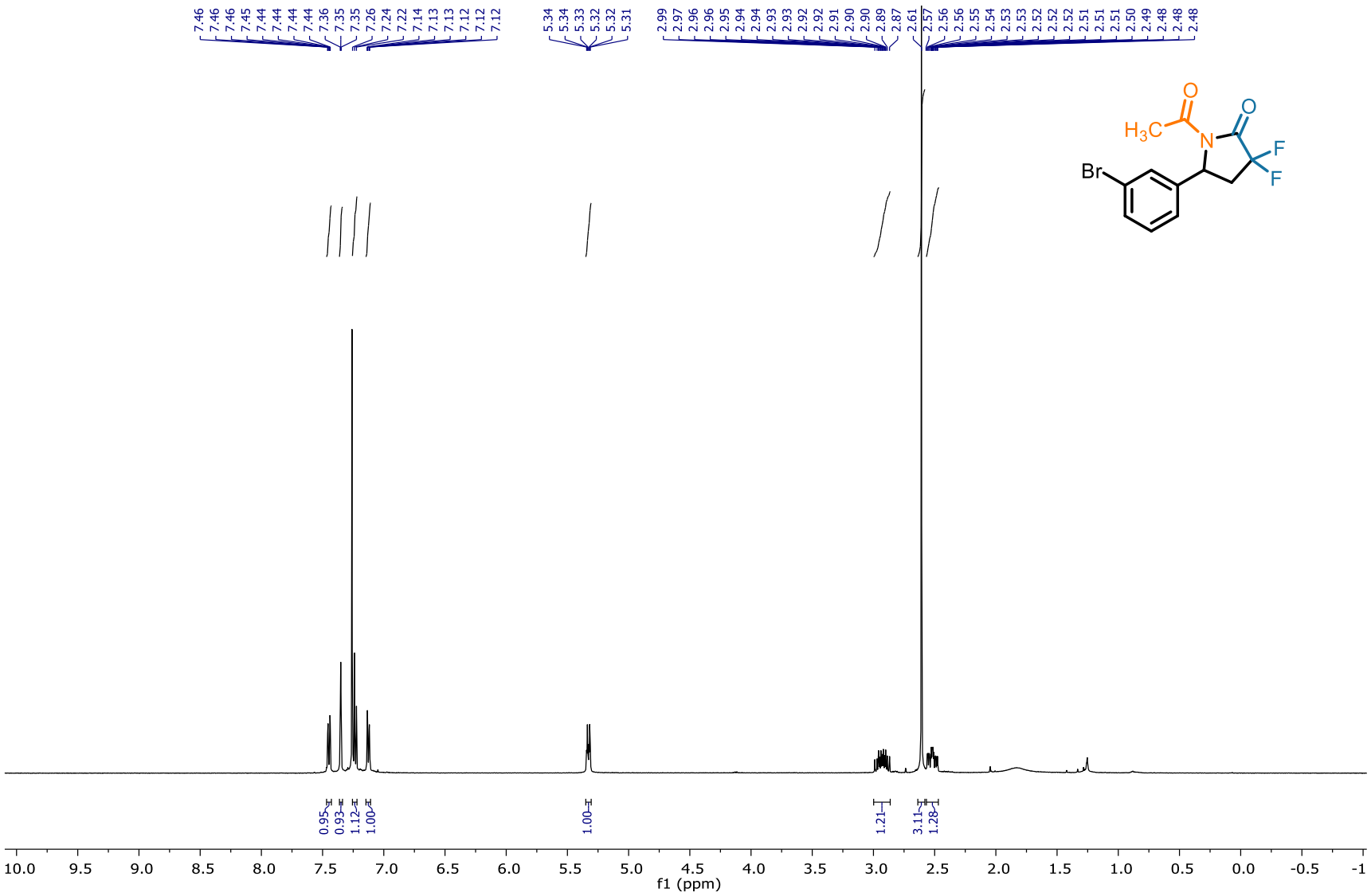
^{13}C-NMR (75 MHz, $CDCl_3$) of **18**



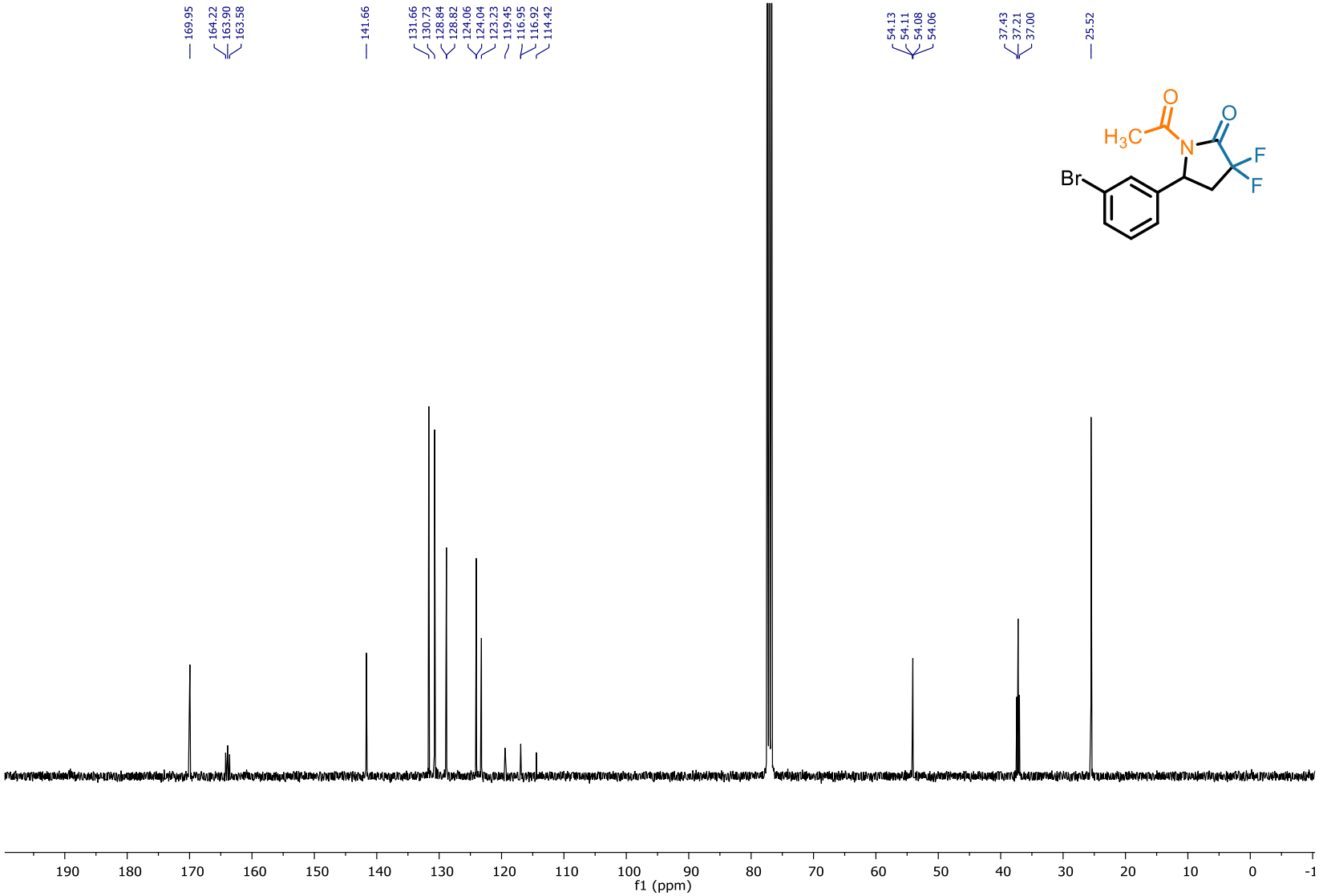
^{19}F-NMR (282 MHz, $CDCl_3$) of **18**



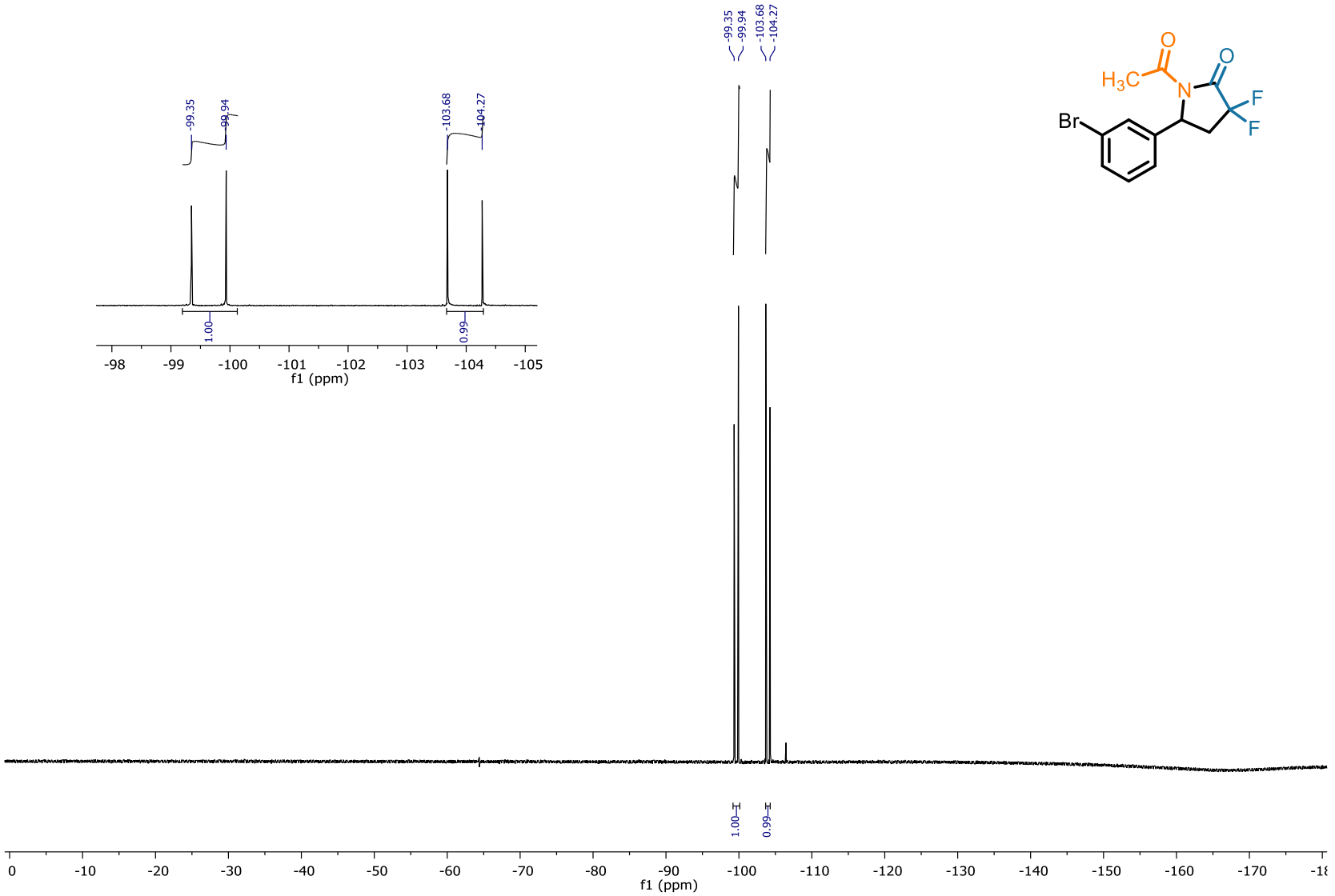
^{1}H-NMR (500 MHz, $CDCl_3$) of **19**



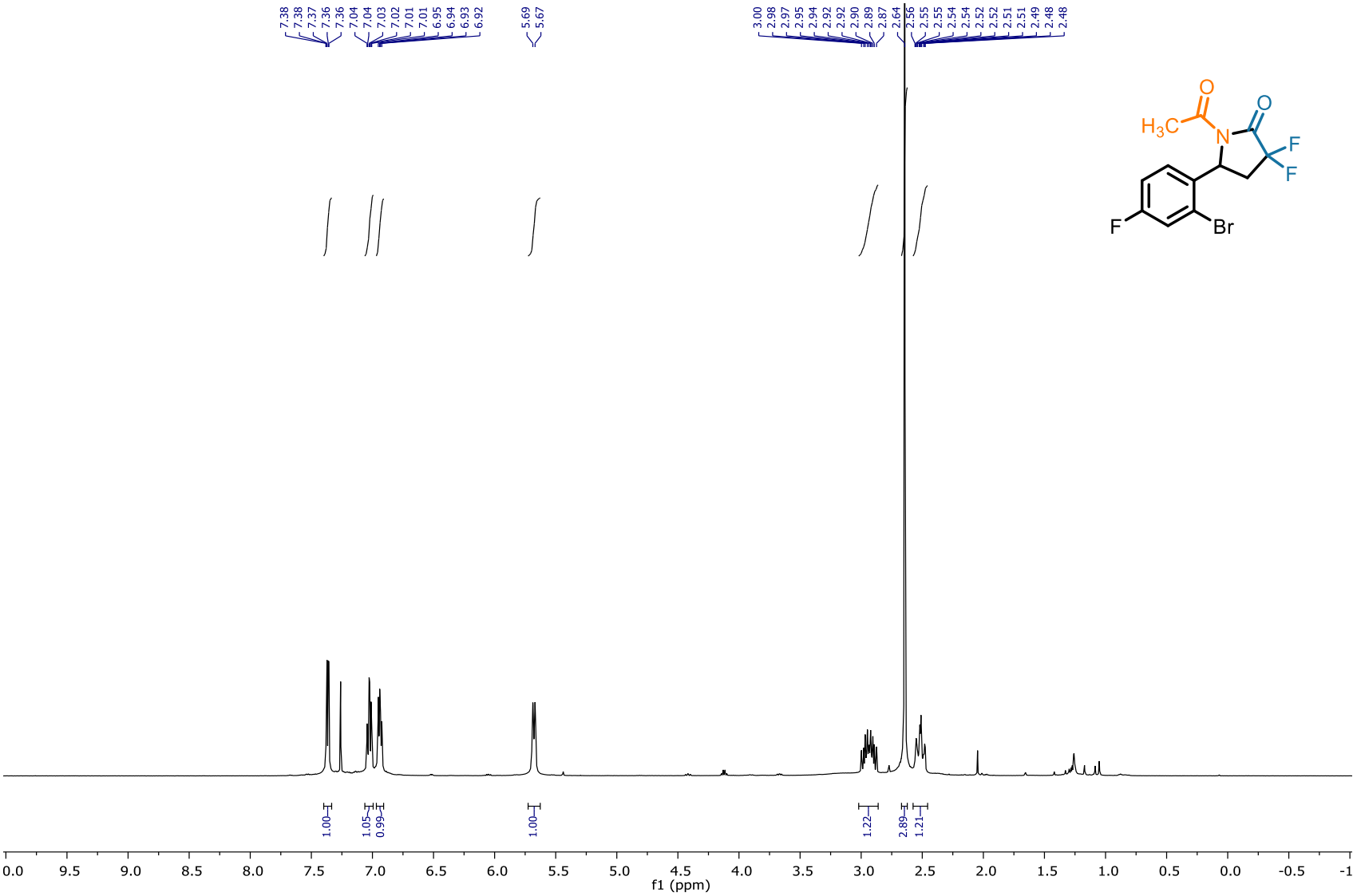
^{13}C-NMR (126 MHz, $CDCl_3$) of **19**



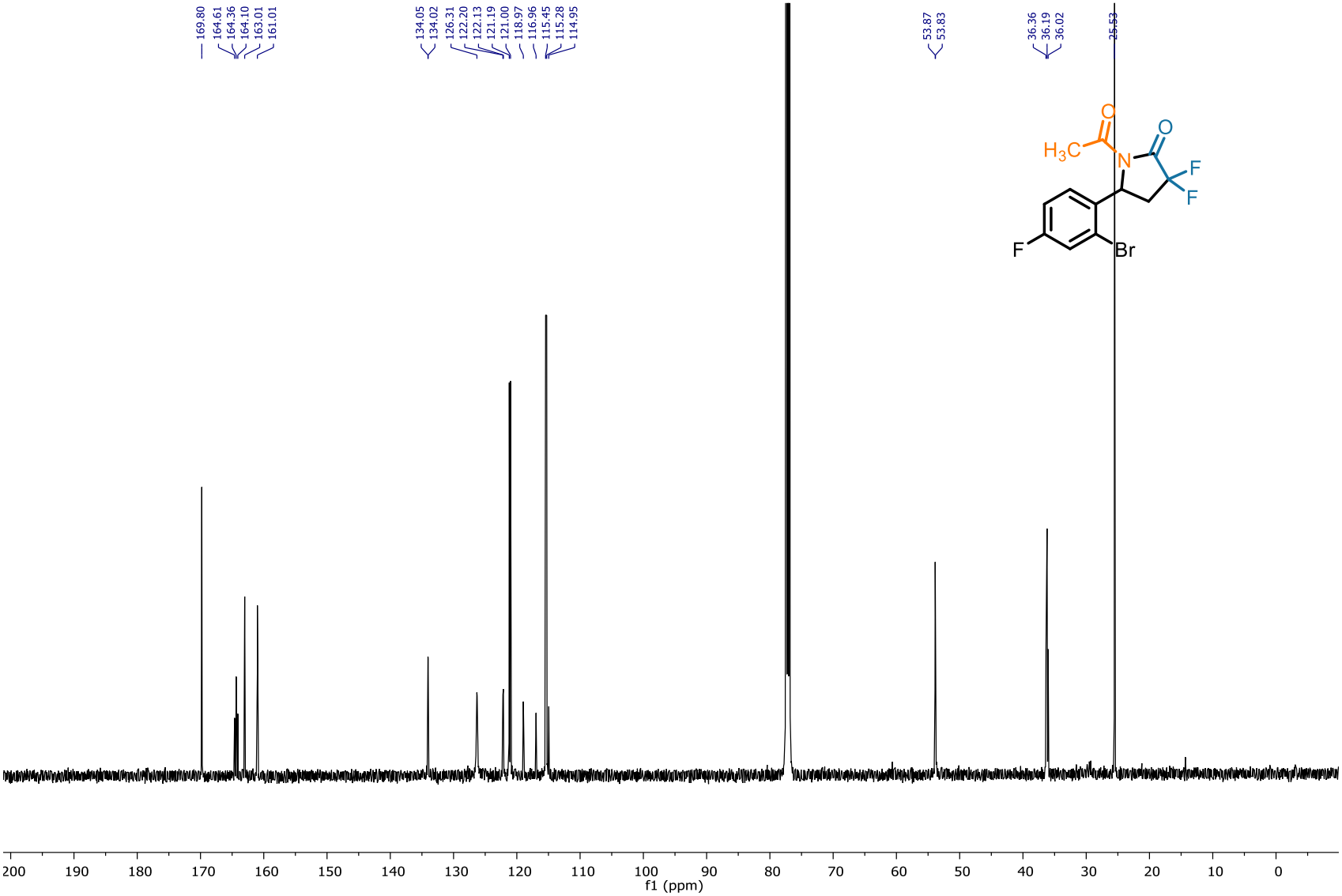
^{19}F-NMR (471 MHz, $CDCl_3$) of **19**



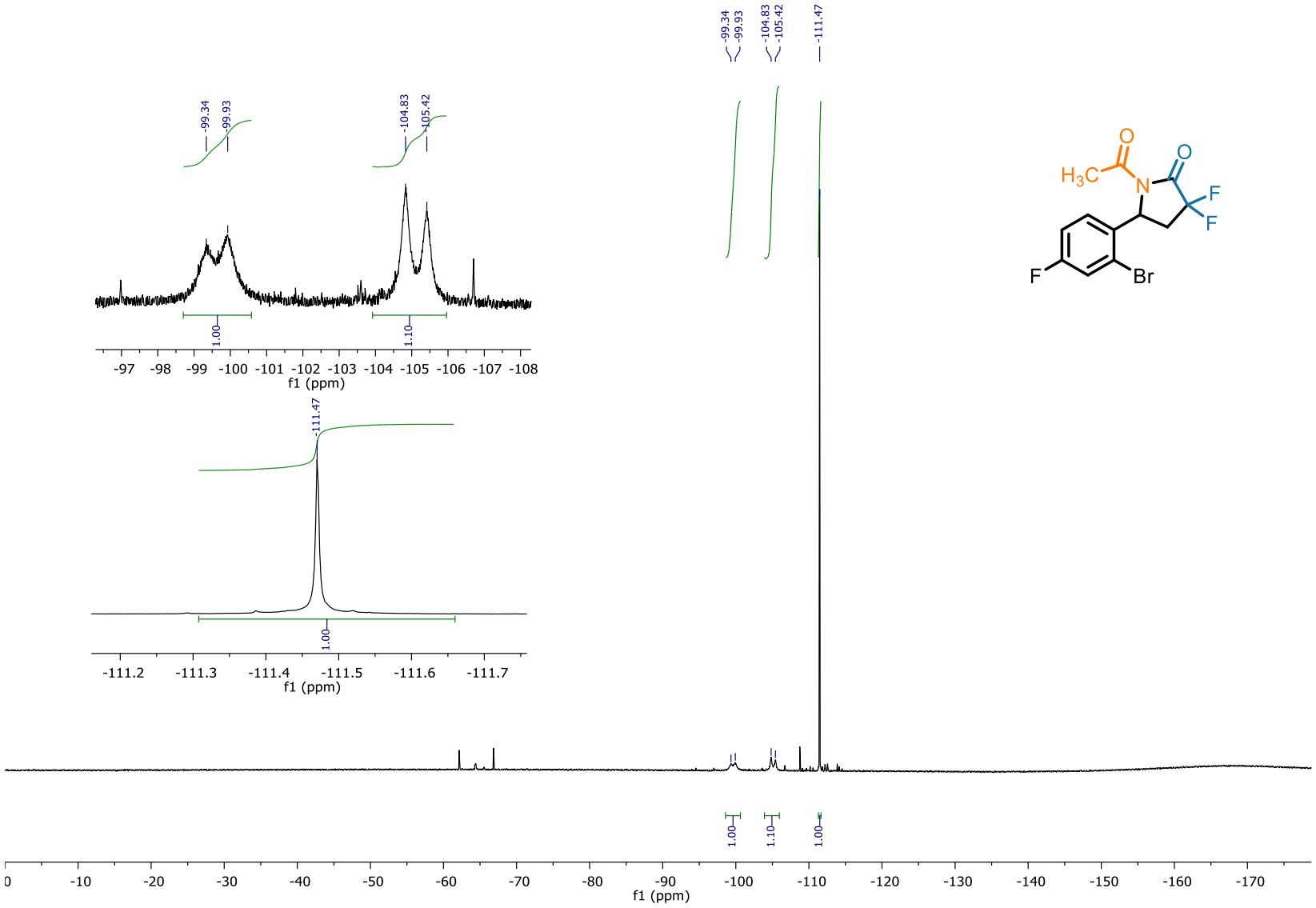
^{1}H-NMR (500 MHz, $CDCl_3$) of **20**



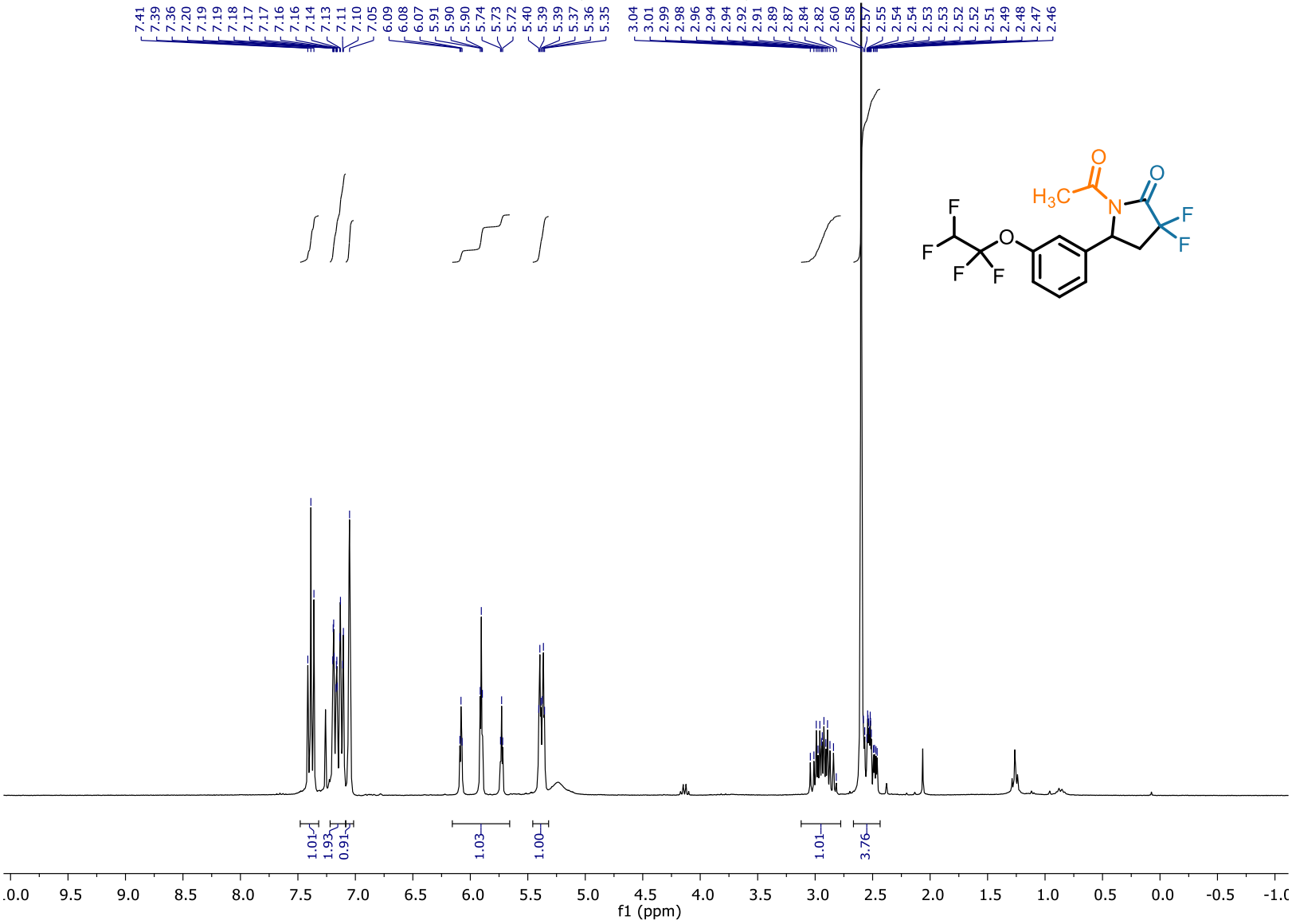
^{13}C NMR (126 MHz, $CDCl_3$) of **20**



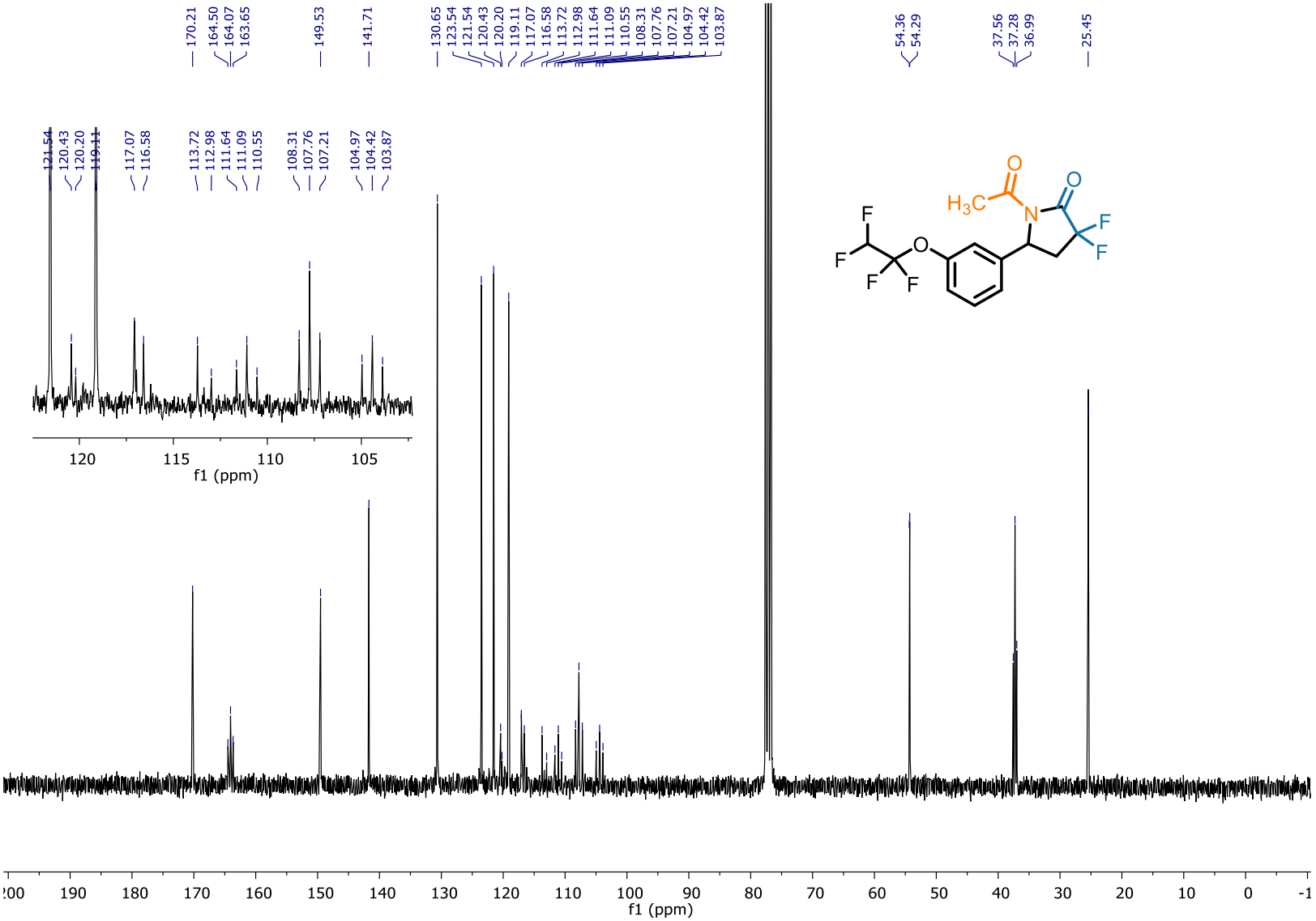
^{19}F-NMR (471 MHz, $CDCl_3$) of **20**



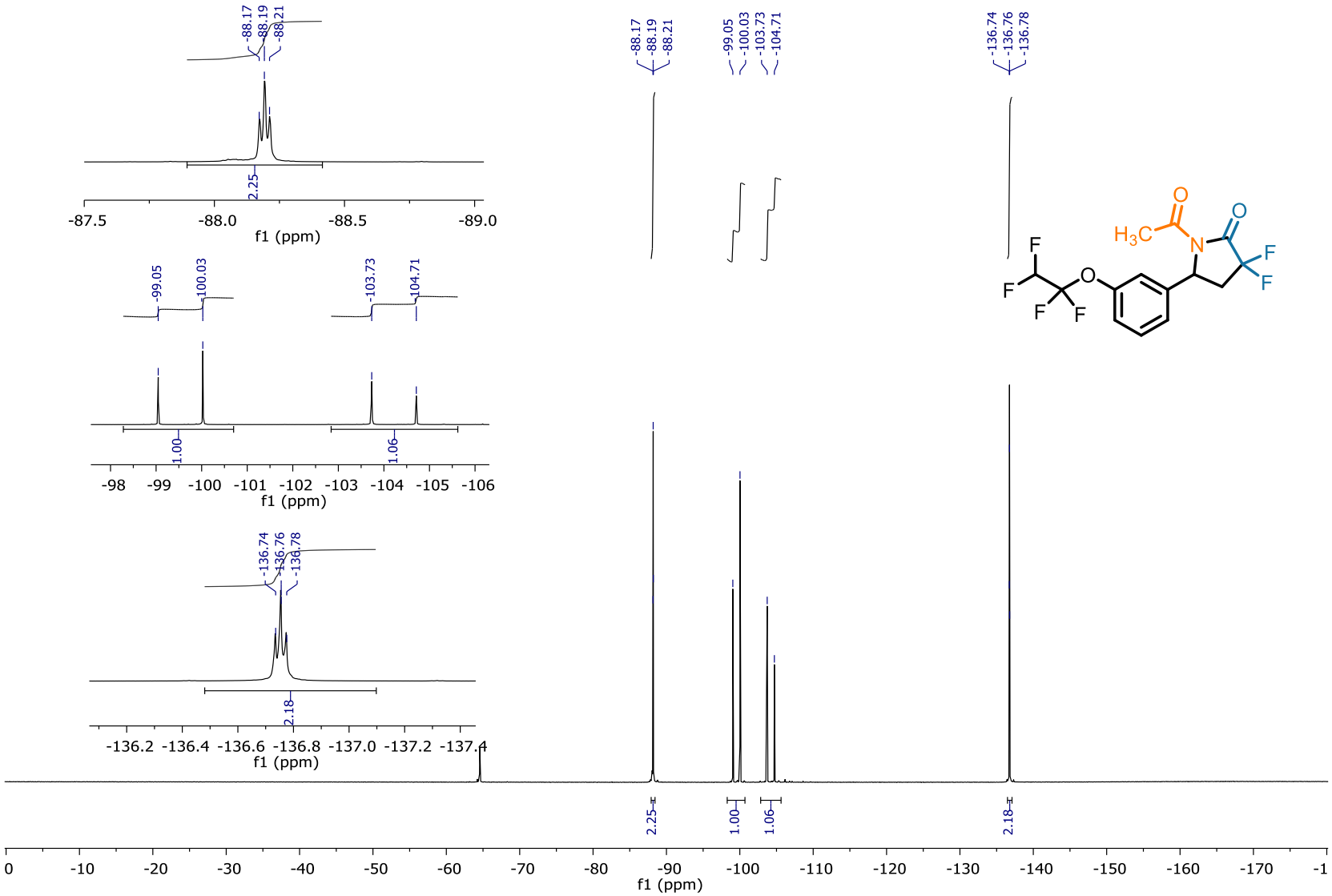
^{1}H-NMR (300 MHz, $CDCl_3$) of **21**



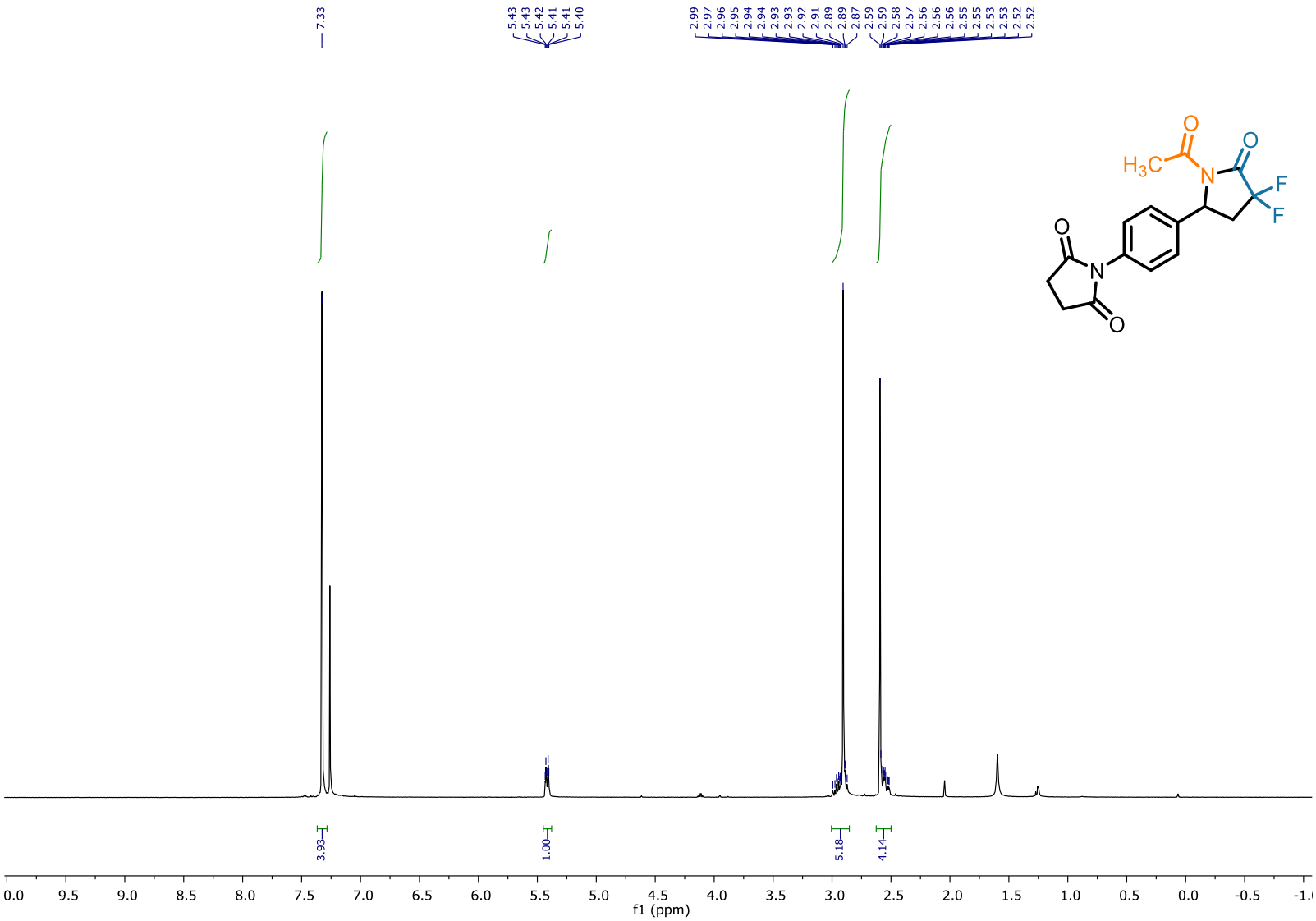
^{13}C-NMR (75 MHz, $CDCl_3$) of **21**



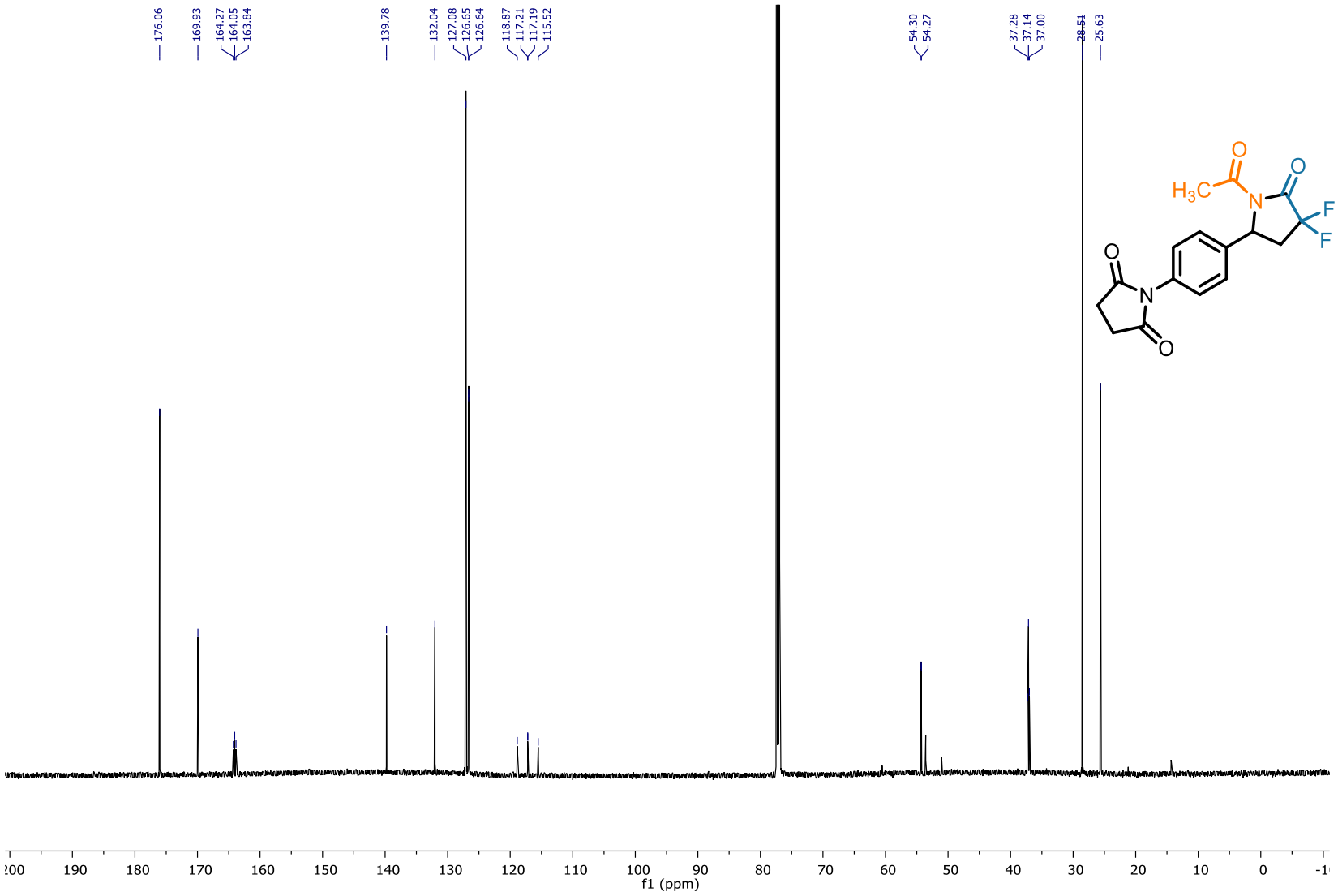
^{19}F-NMR (282 MHz, $CDCl_3$) of **21**



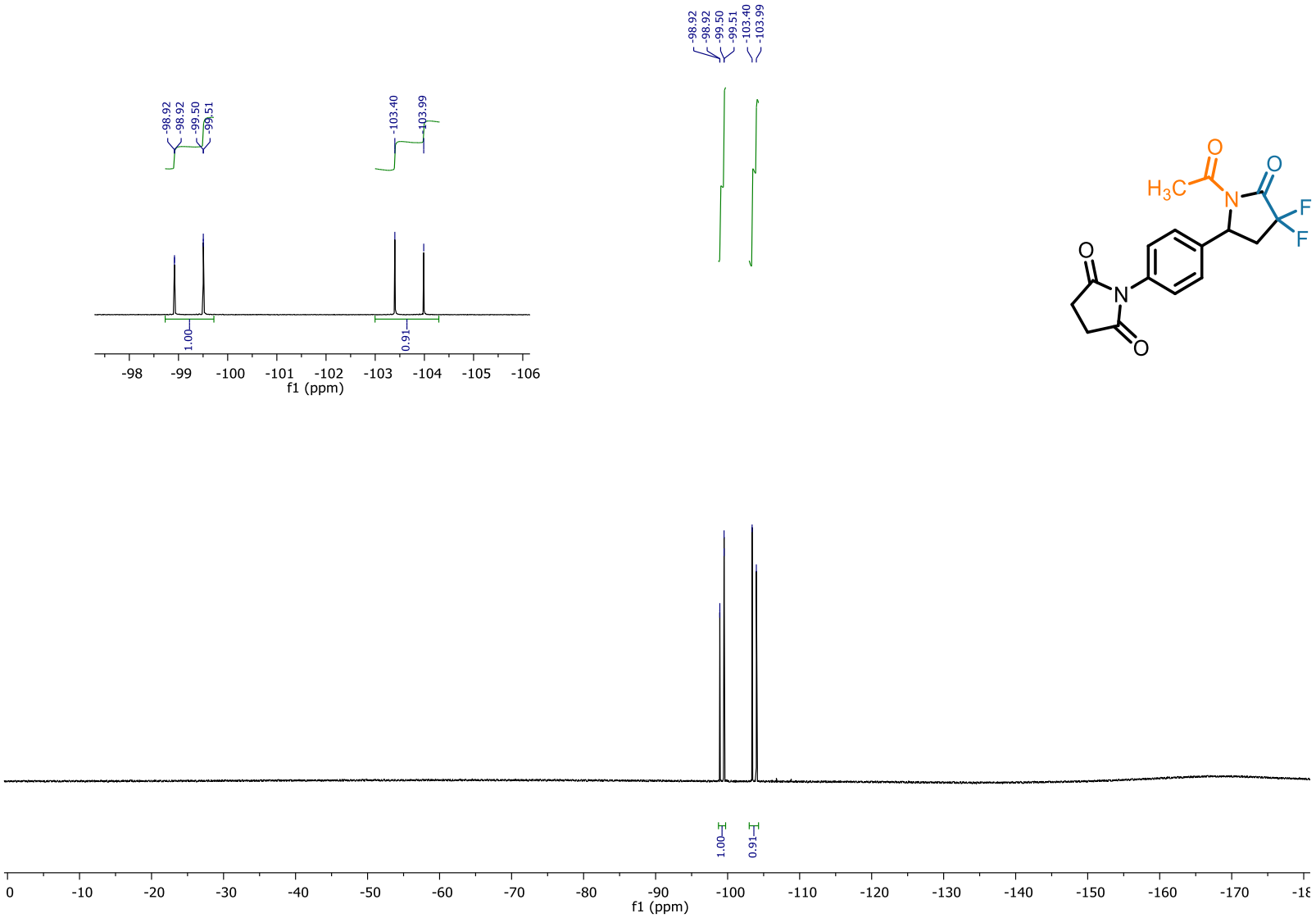
^{1}H-NMR (500 MHz, $CDCl_3$) of **22**



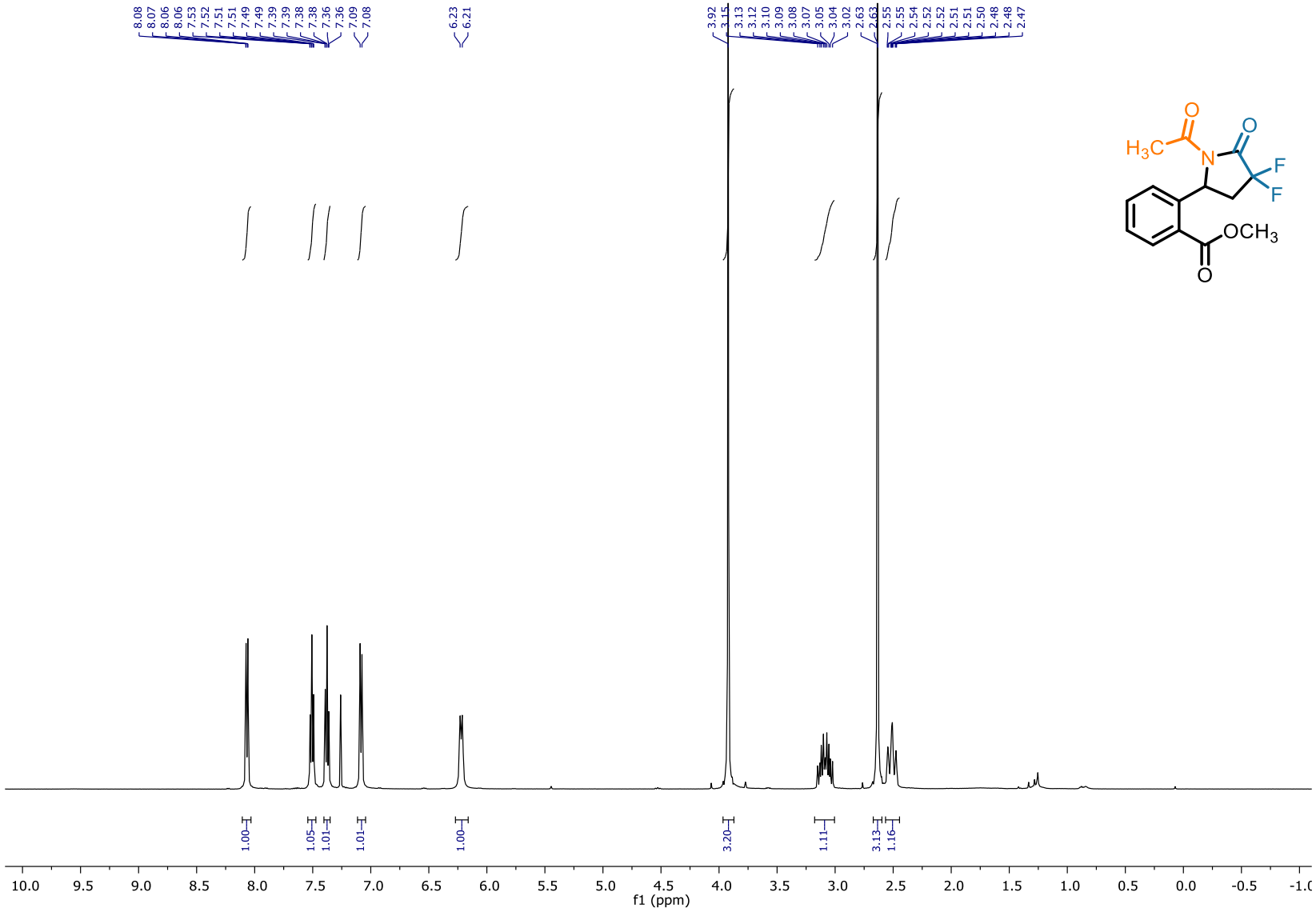
^{13}C-NMR (151 MHz, $CDCl_3$) of **22**



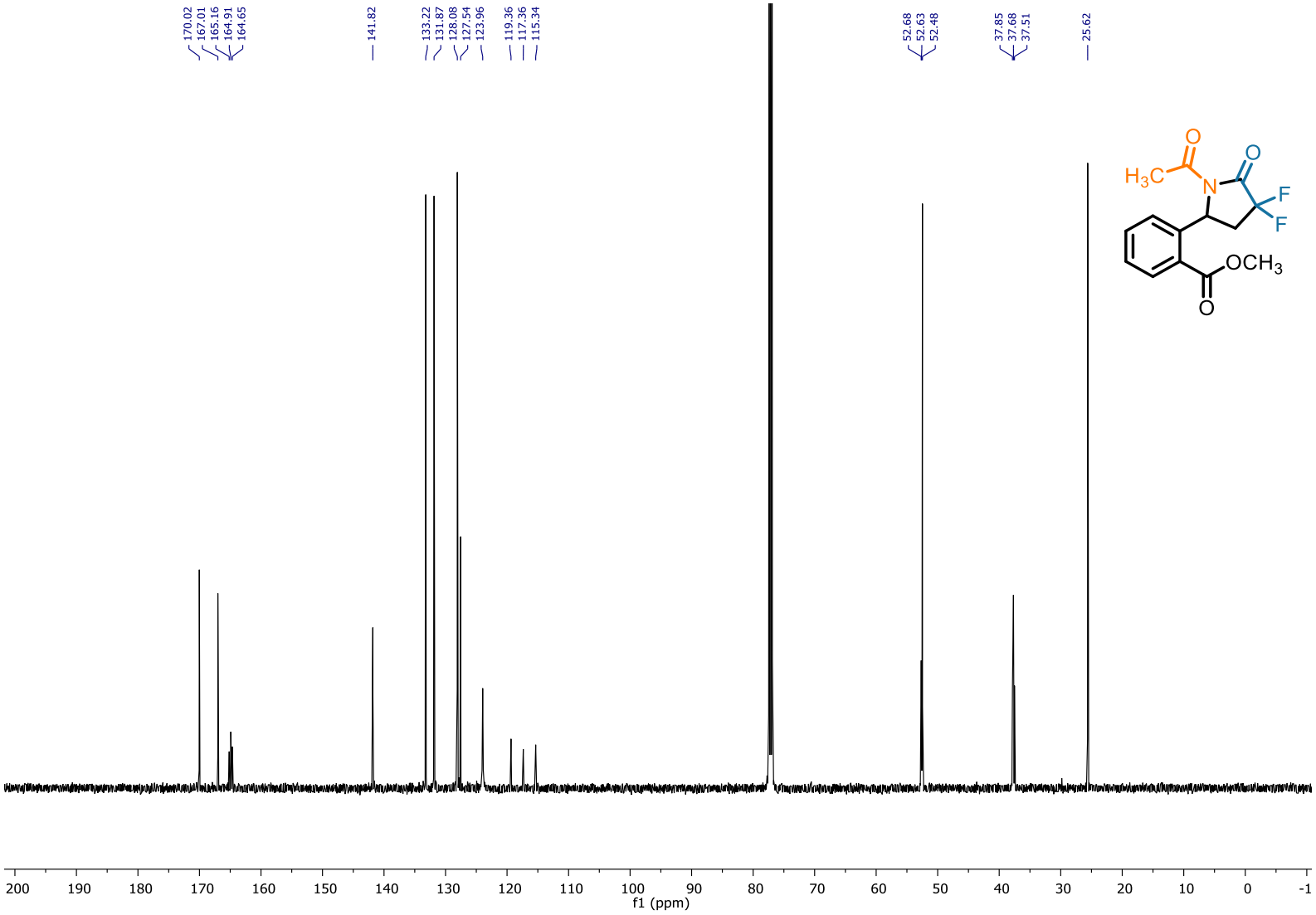
^{19}F-NMR (471 MHz, $CDCl_3$) of **22**



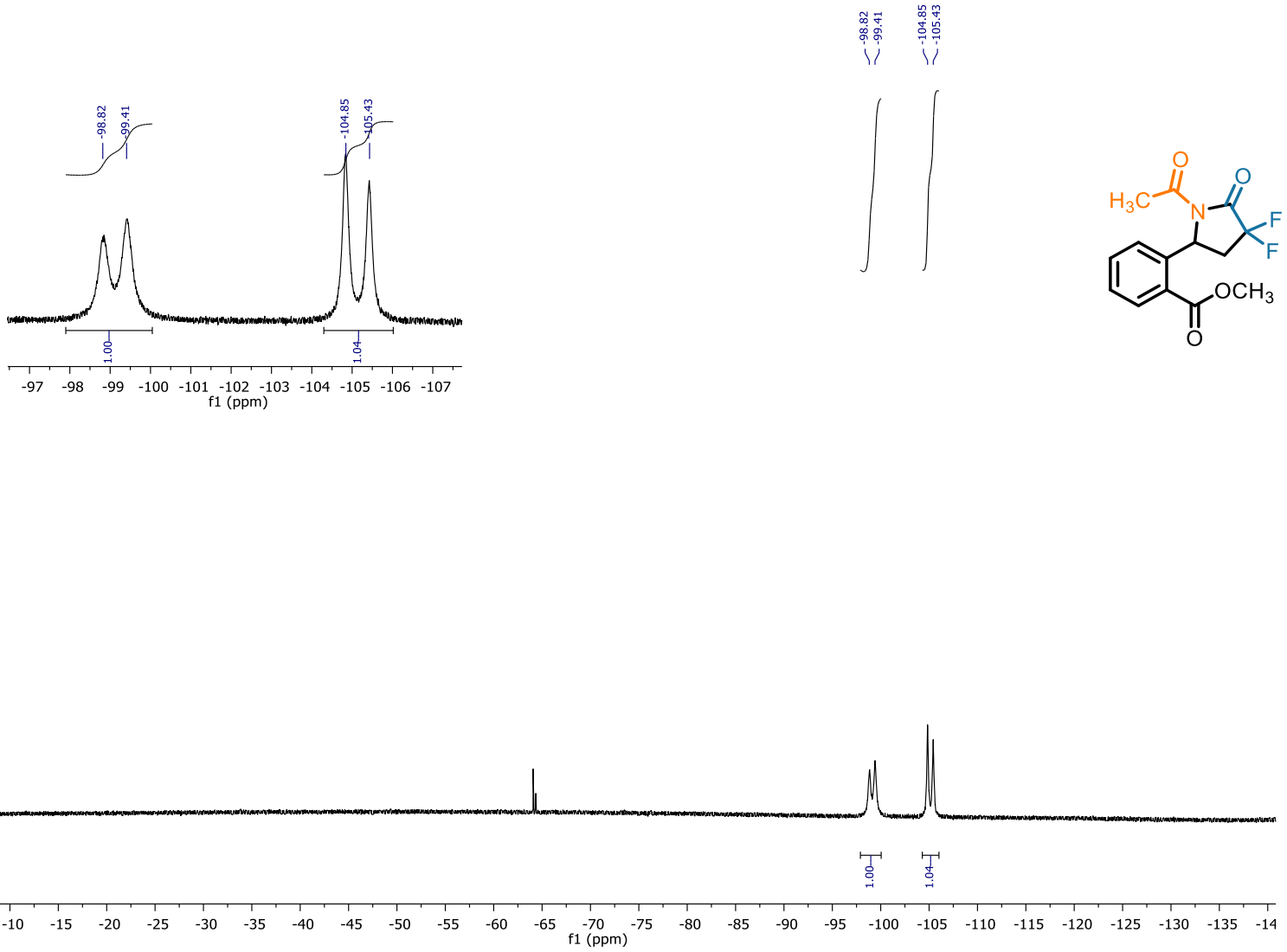
^{1}H-NMR (500 MHz, $CDCl_3$) of **23**



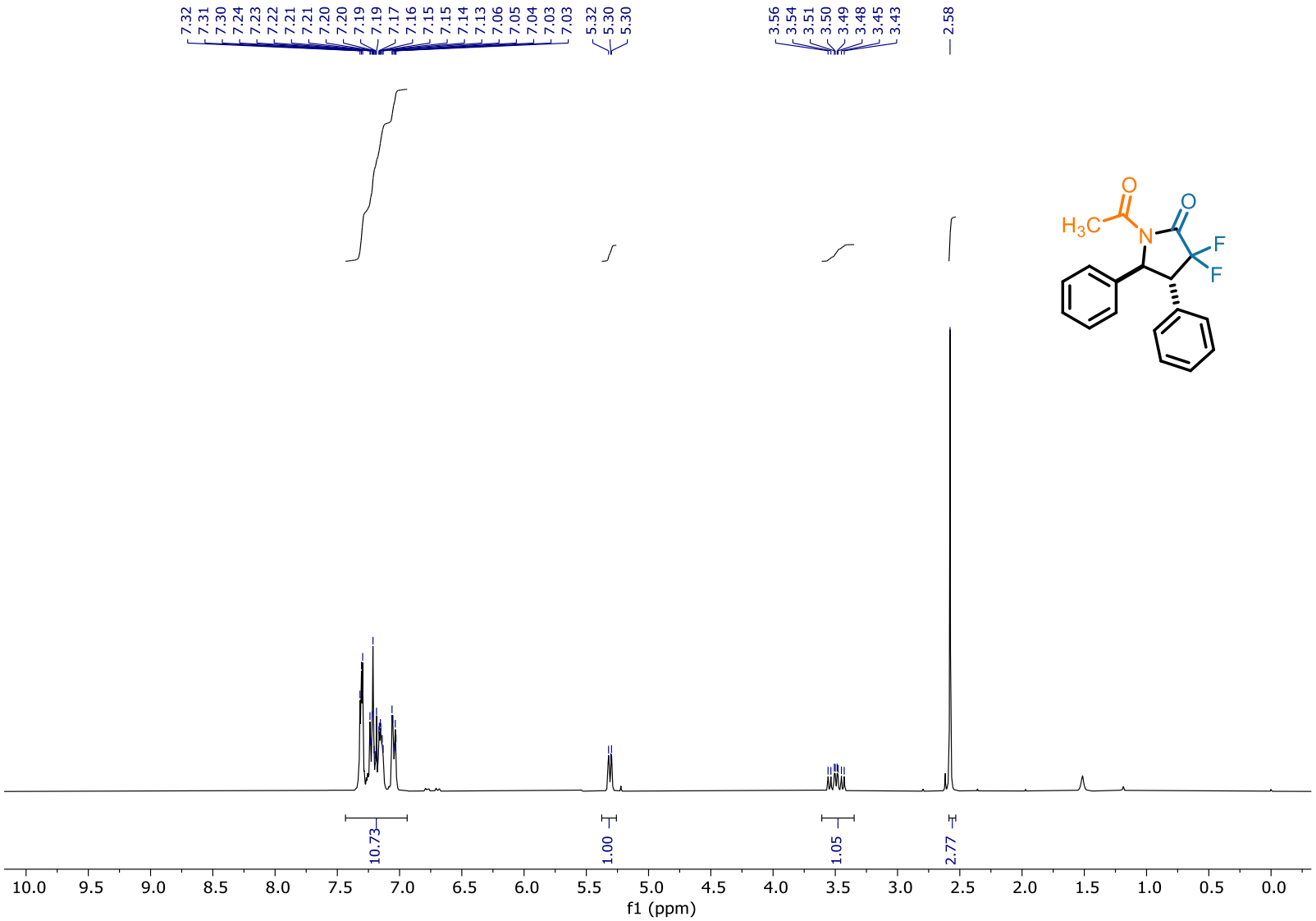
^{13}C-NMR (126 MHz, $CDCl_3$) of **23**



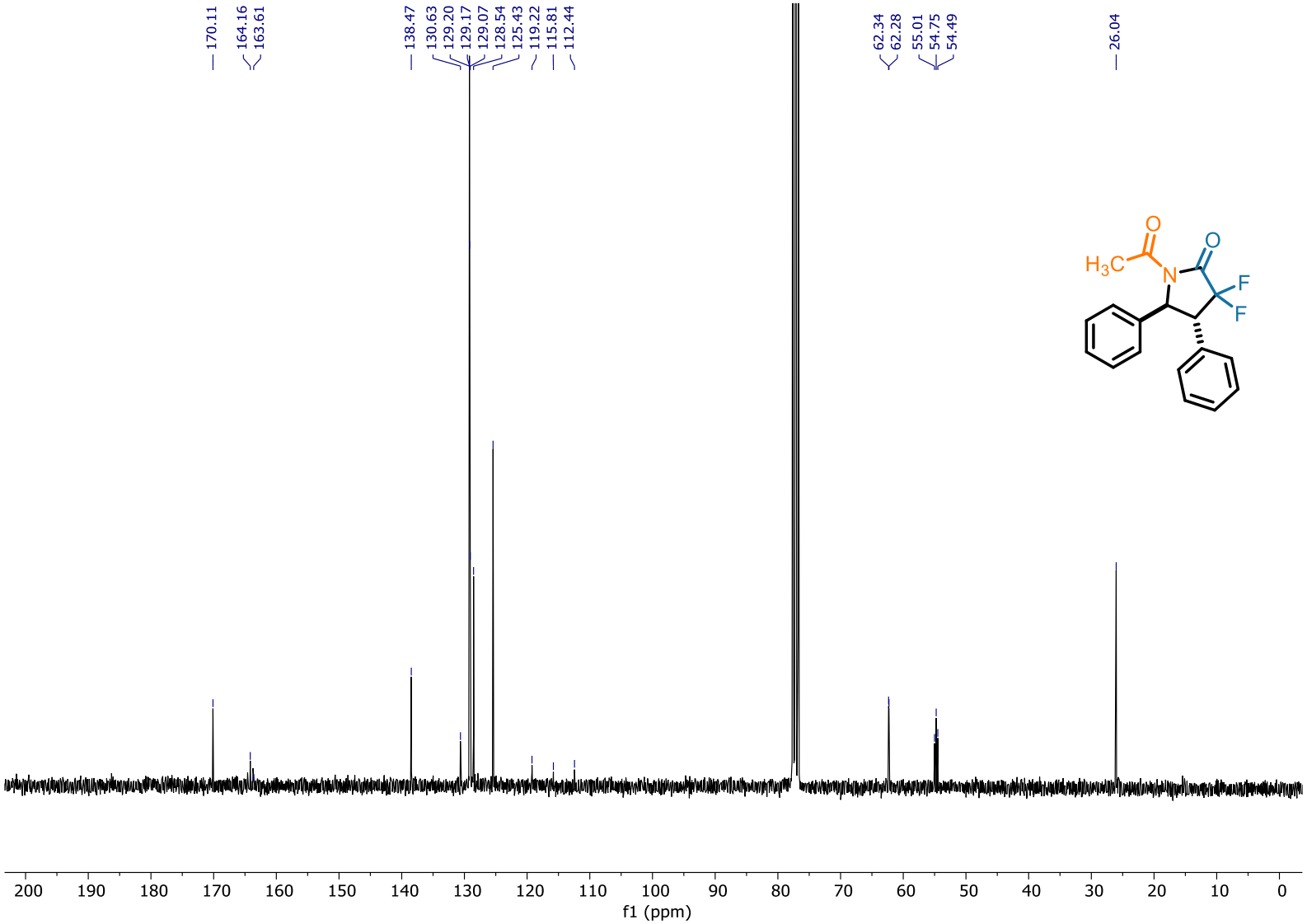
^{19}F-NMR (471 MHz, $CDCl_3$) of **23**



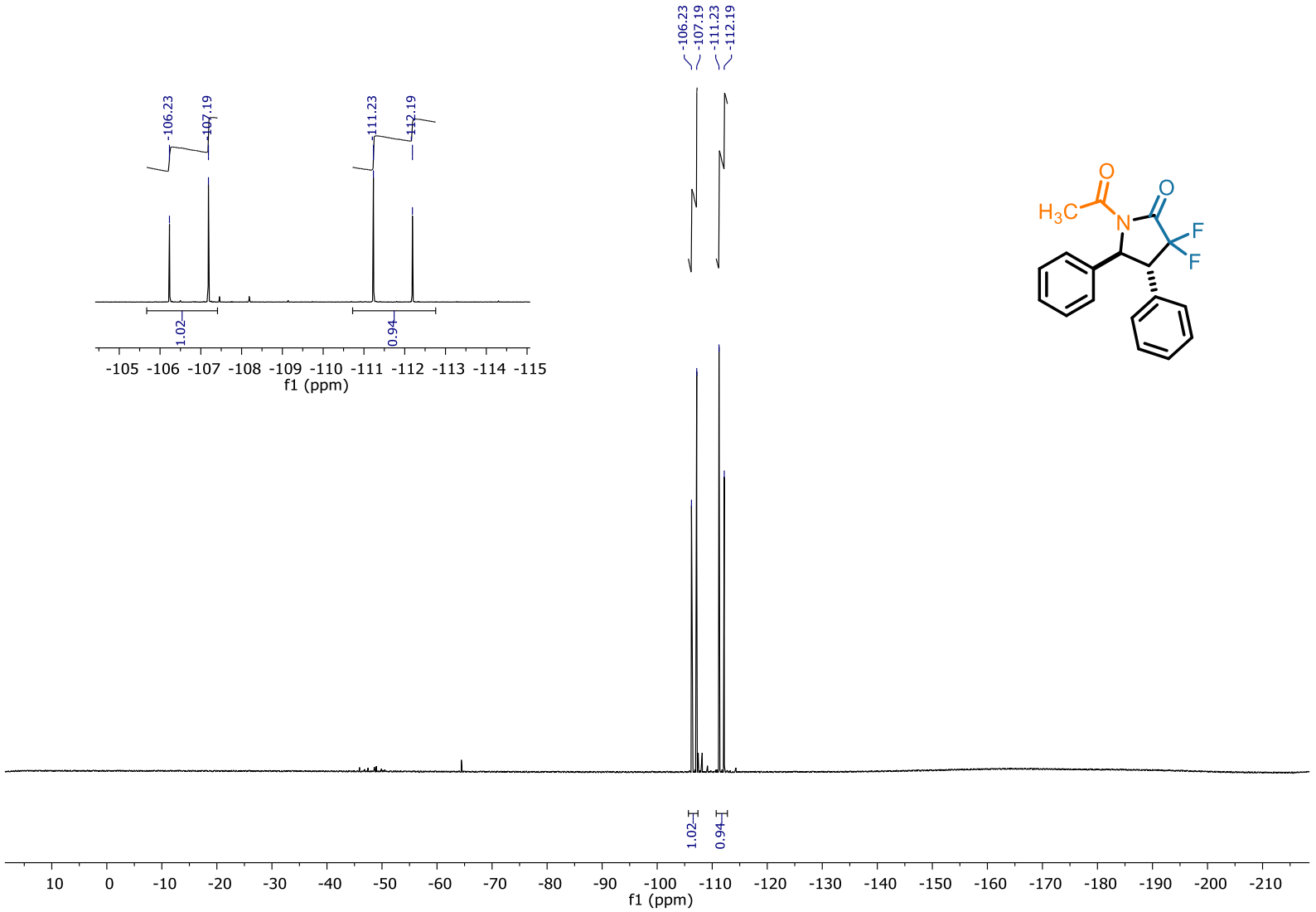
^{1}H-NMR (300 MHz, $CDCl_3$) of **24**



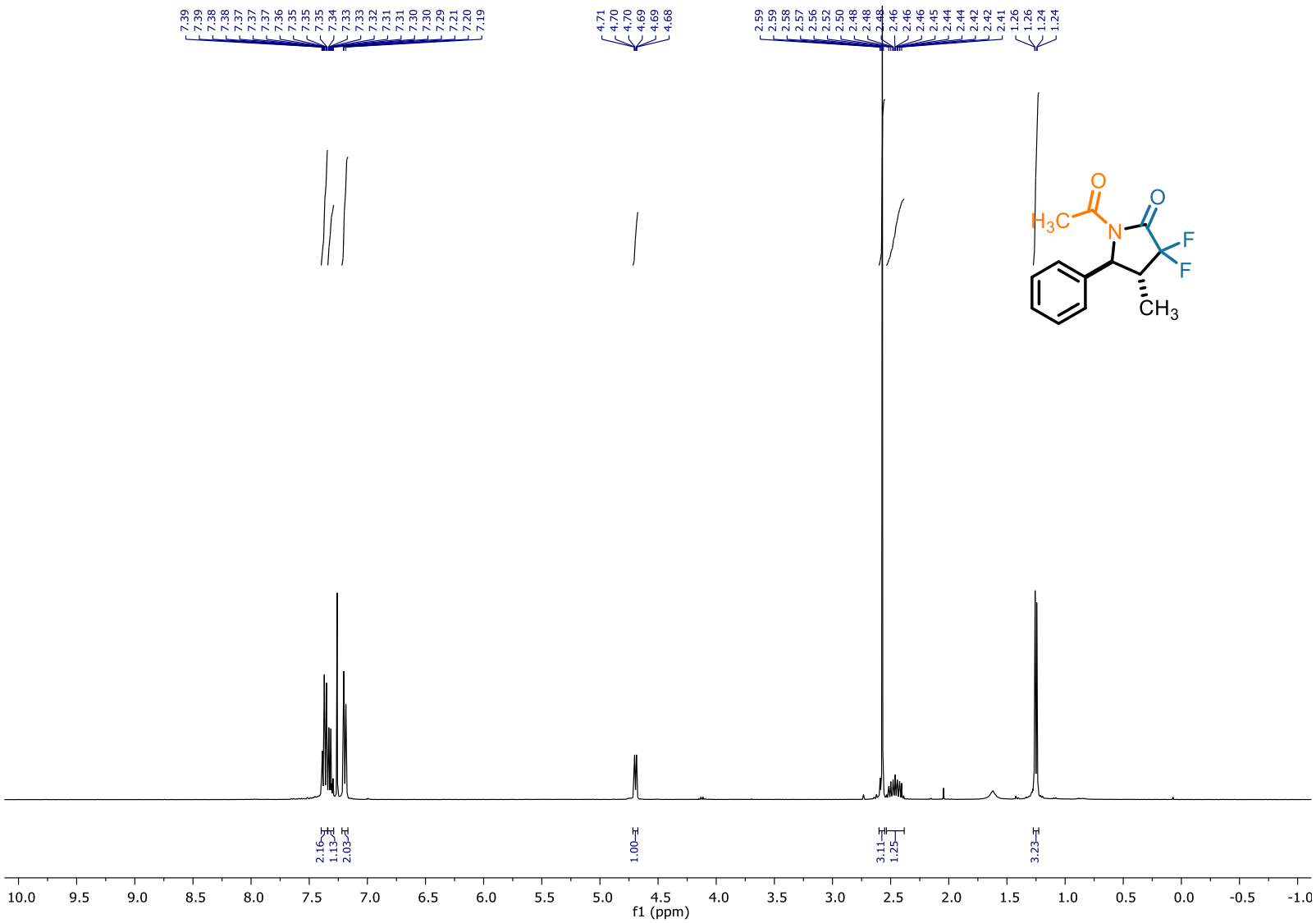
^{13}C-NMR (75 MHz, $CDCl_3$) of **24**



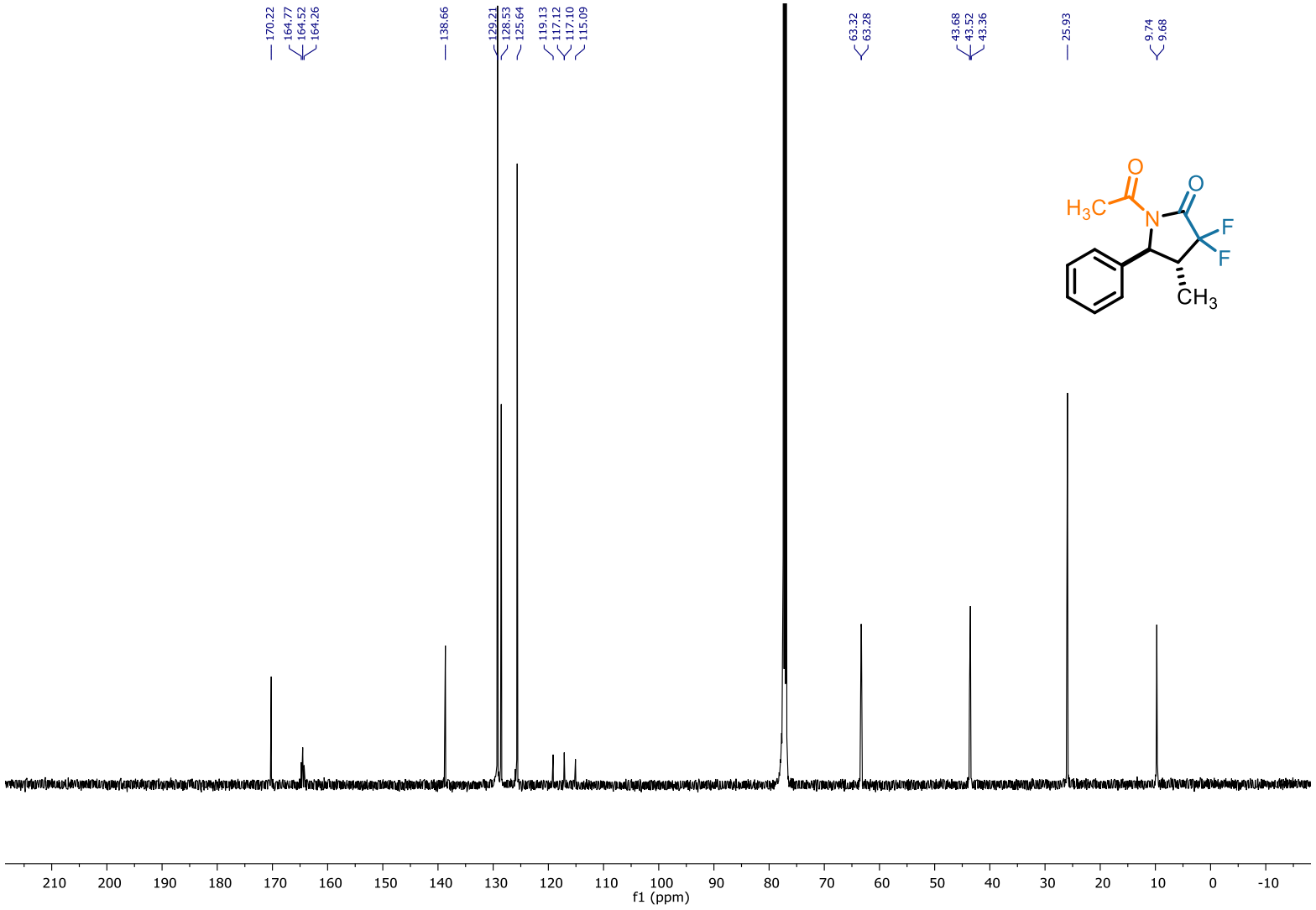
^{19}F-NMR (282 MHz, $CDCl_3$) of **24**



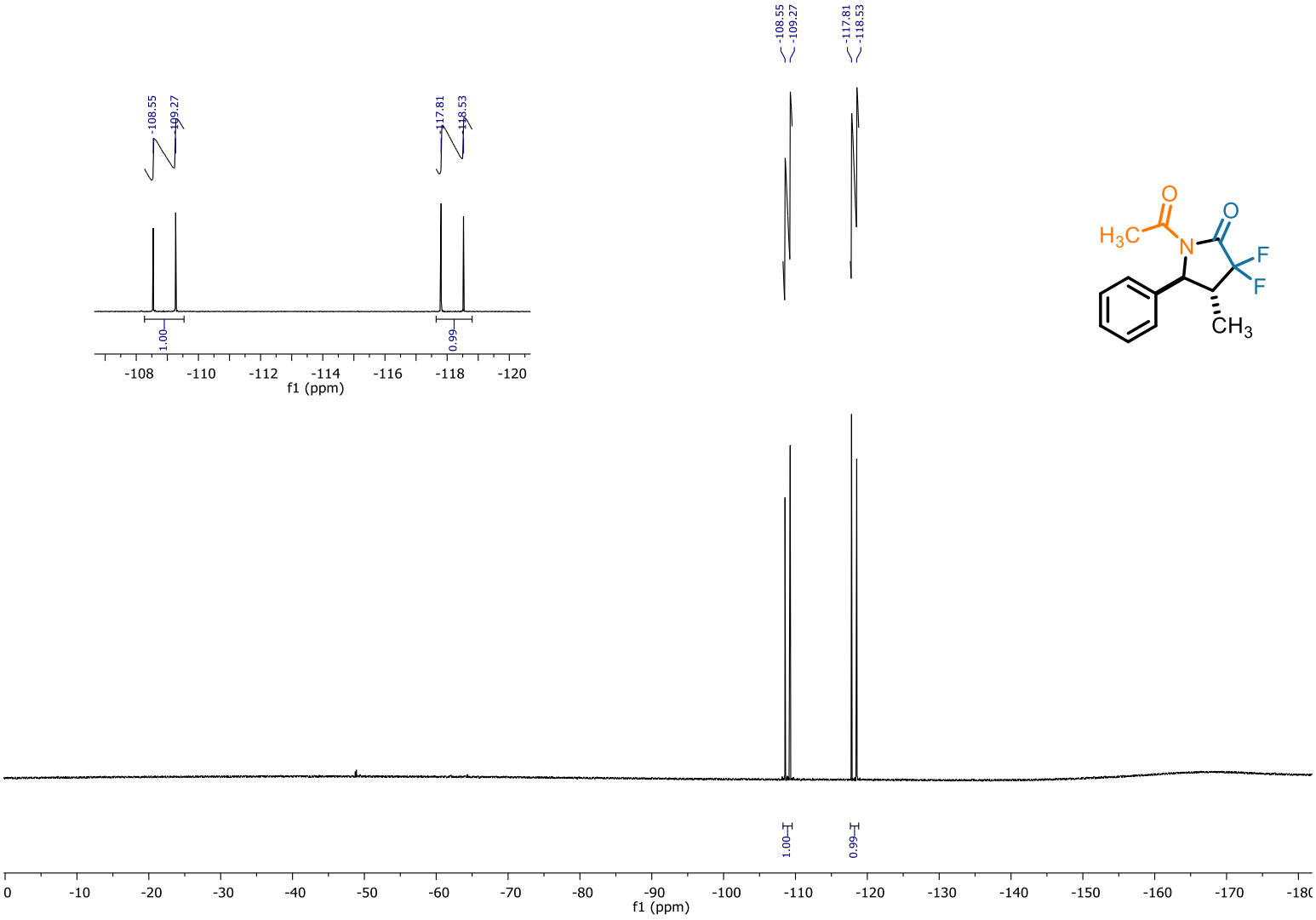
^{1}H-NMR (500 MHz, $CDCl_3$) of **25**



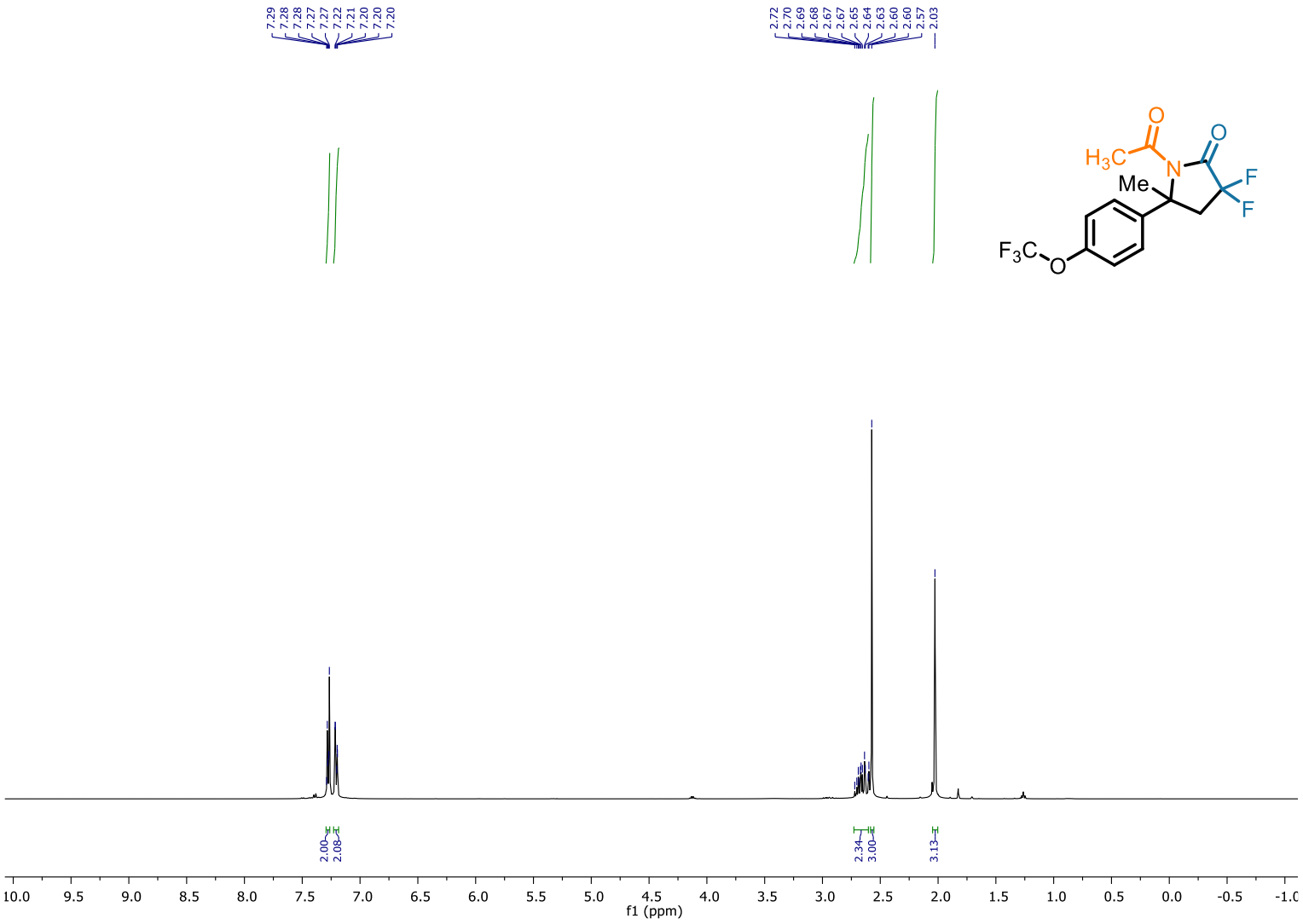
^{13}C-NMR (126 MHz, $CDCl_3$) of **25**



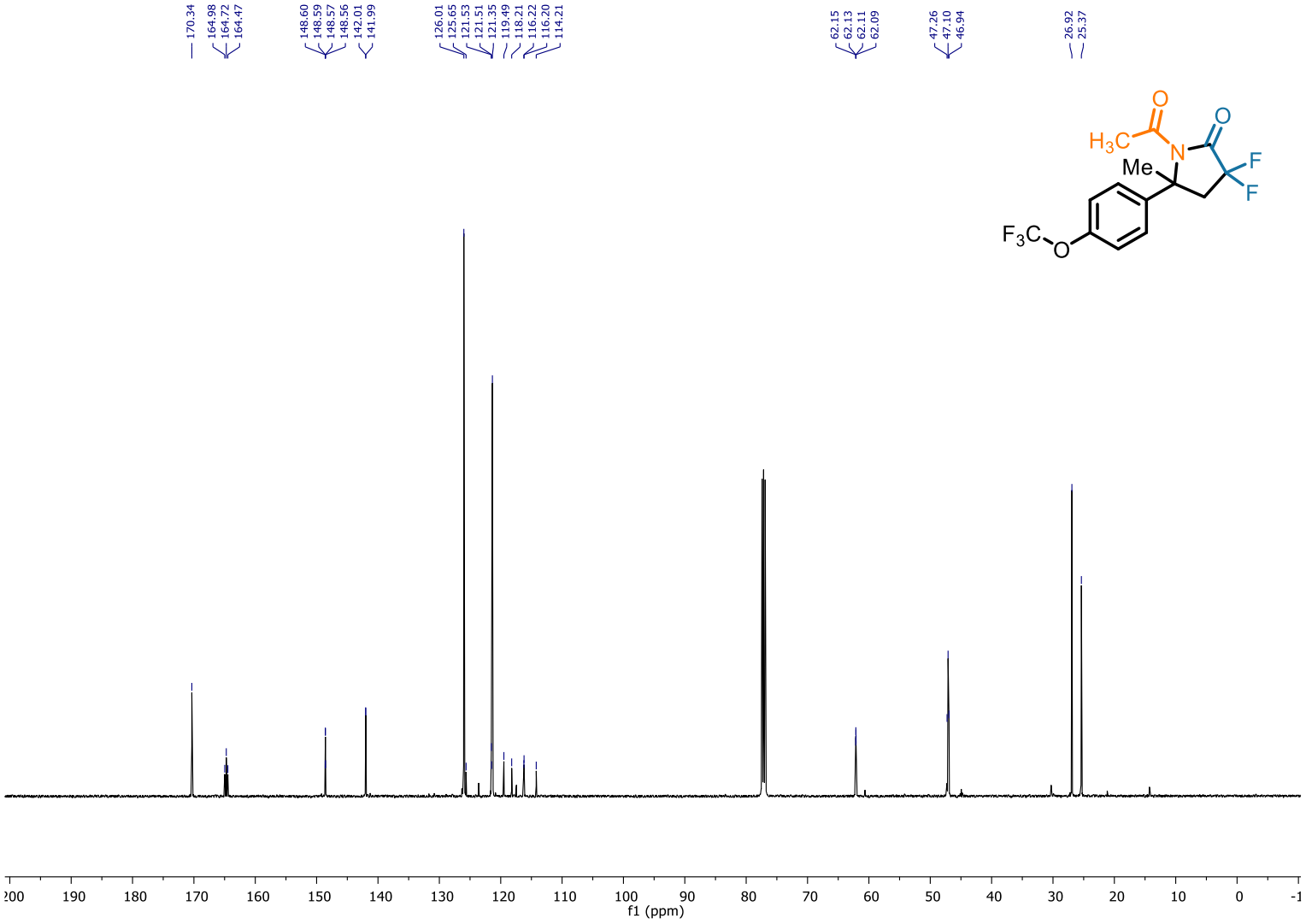
^{19}F-NMR (471 MHz, $CDCl_3$) of **25**



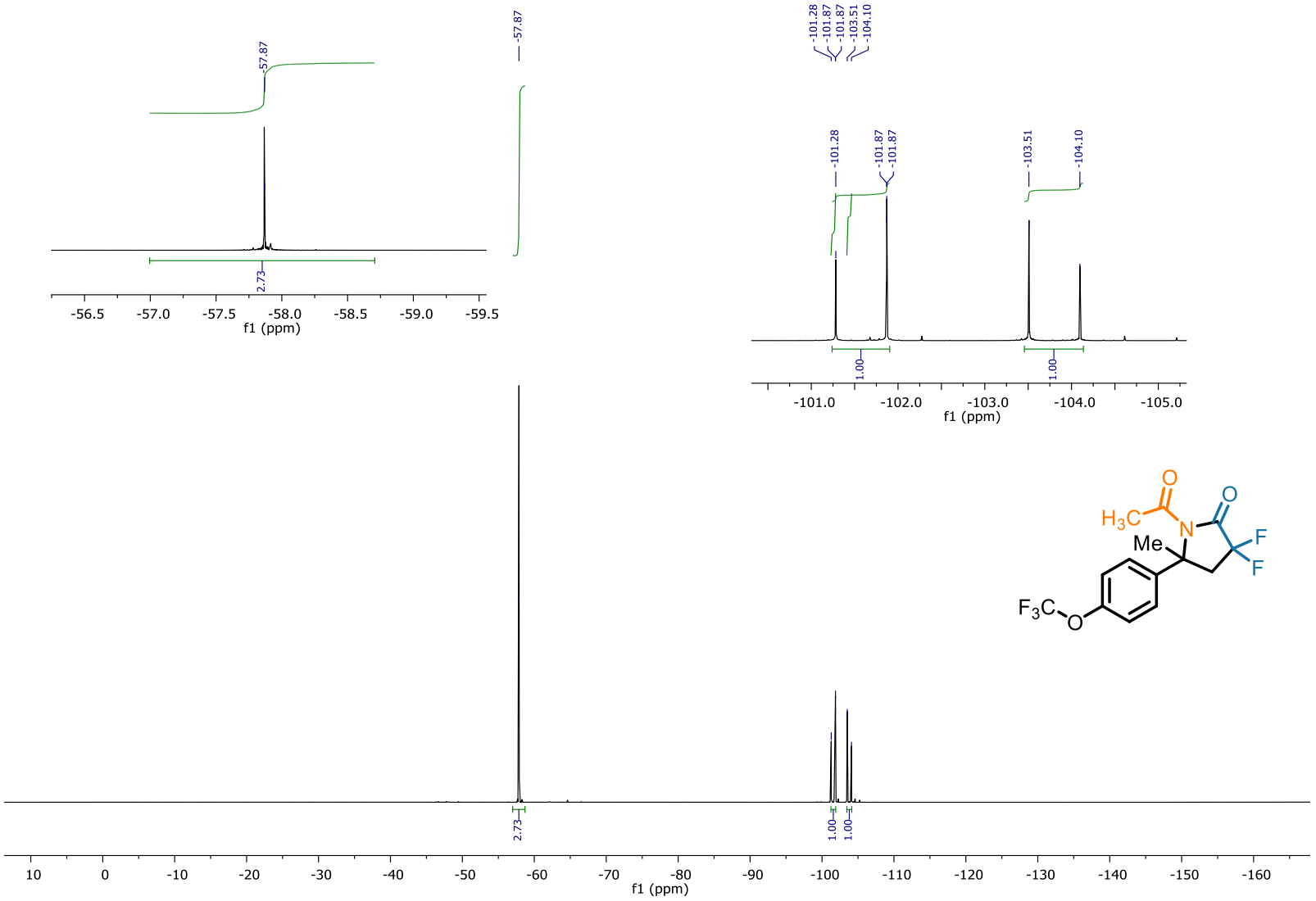
^{1}H-NMR (500 MHz, $CDCl_3$) of **26**



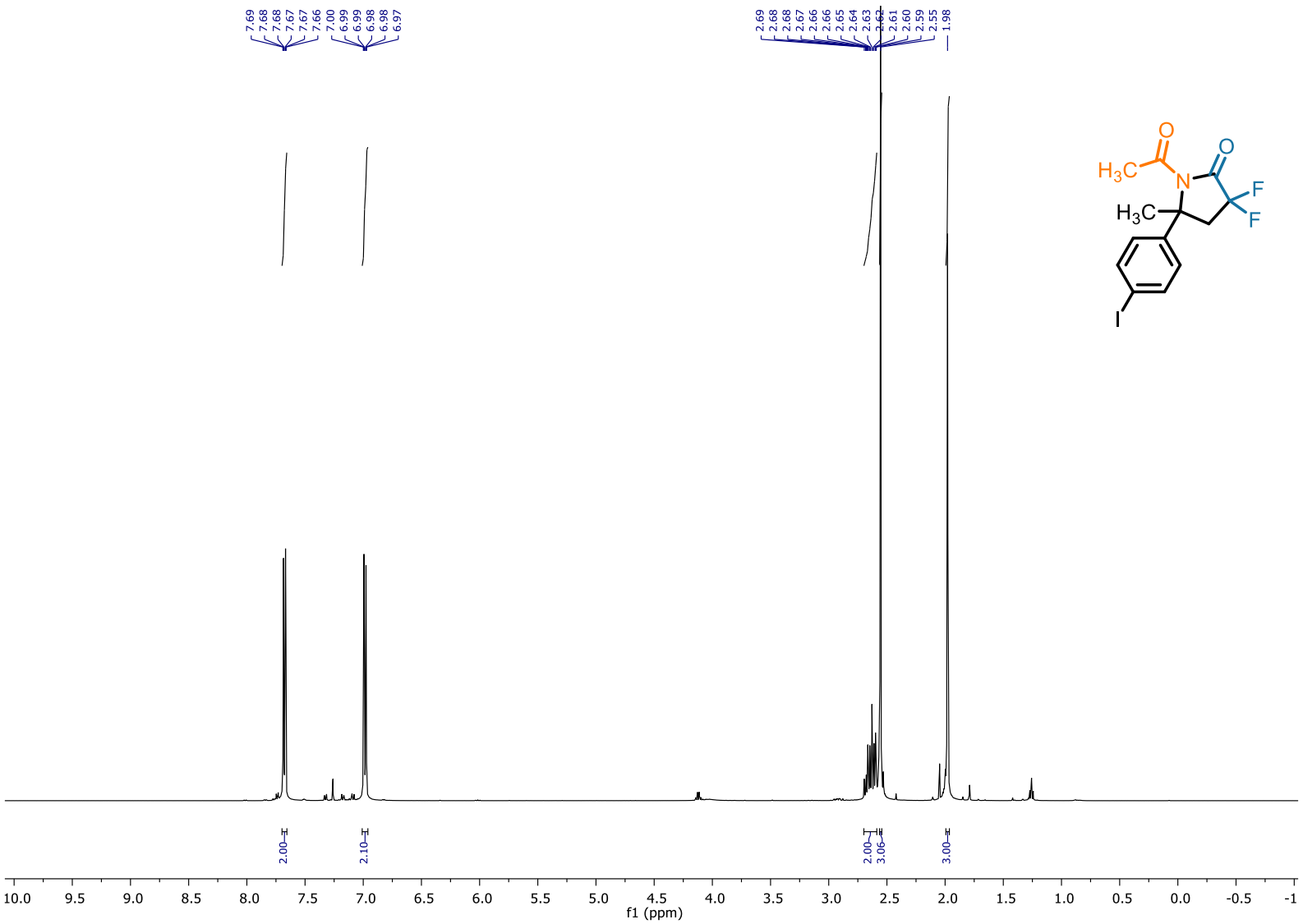
^{13}C-NMR (126 MHz, $CDCl_3$) of **26**



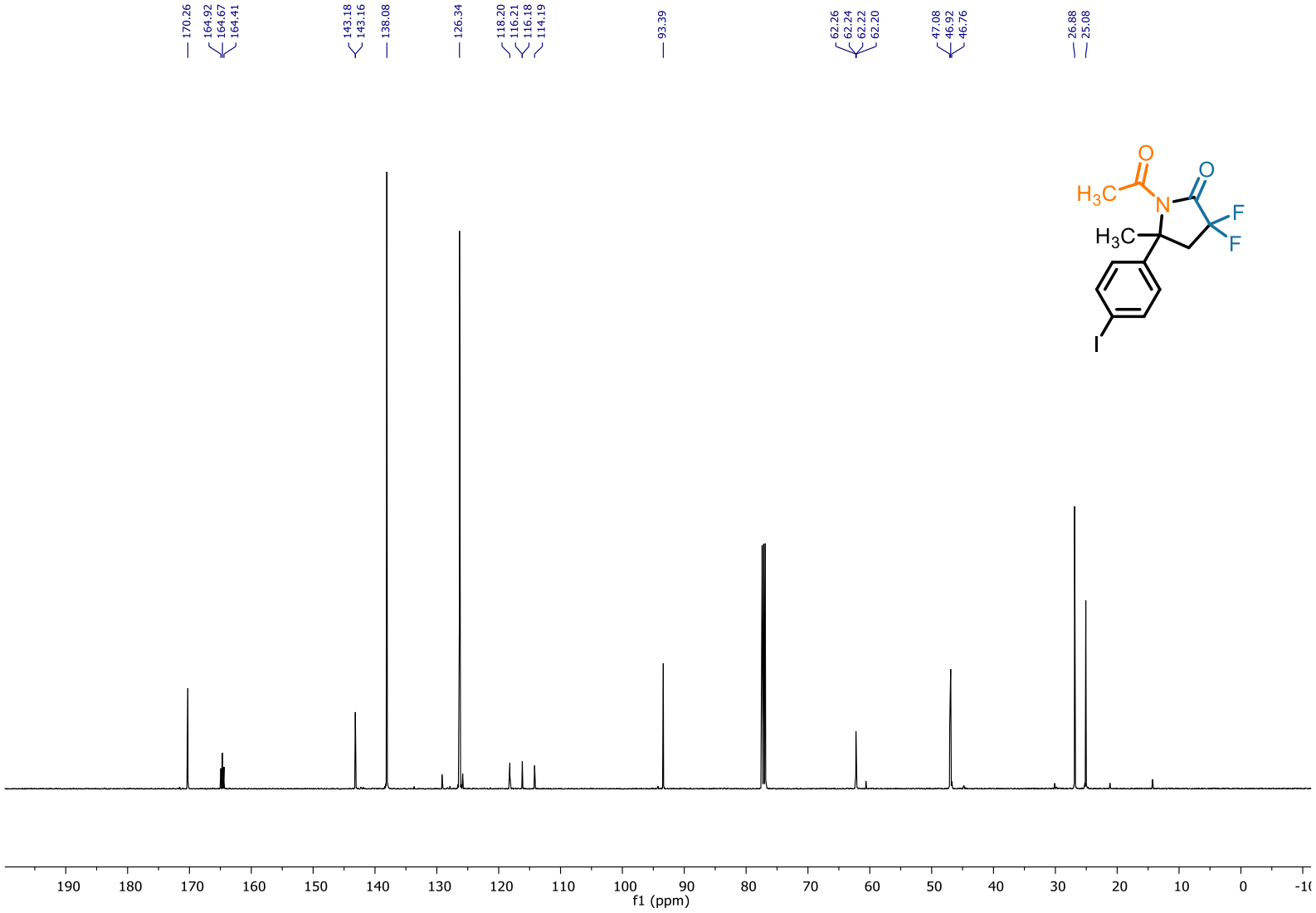
^{19}F-NMR (471 MHz, $CDCl_3$) of **26**



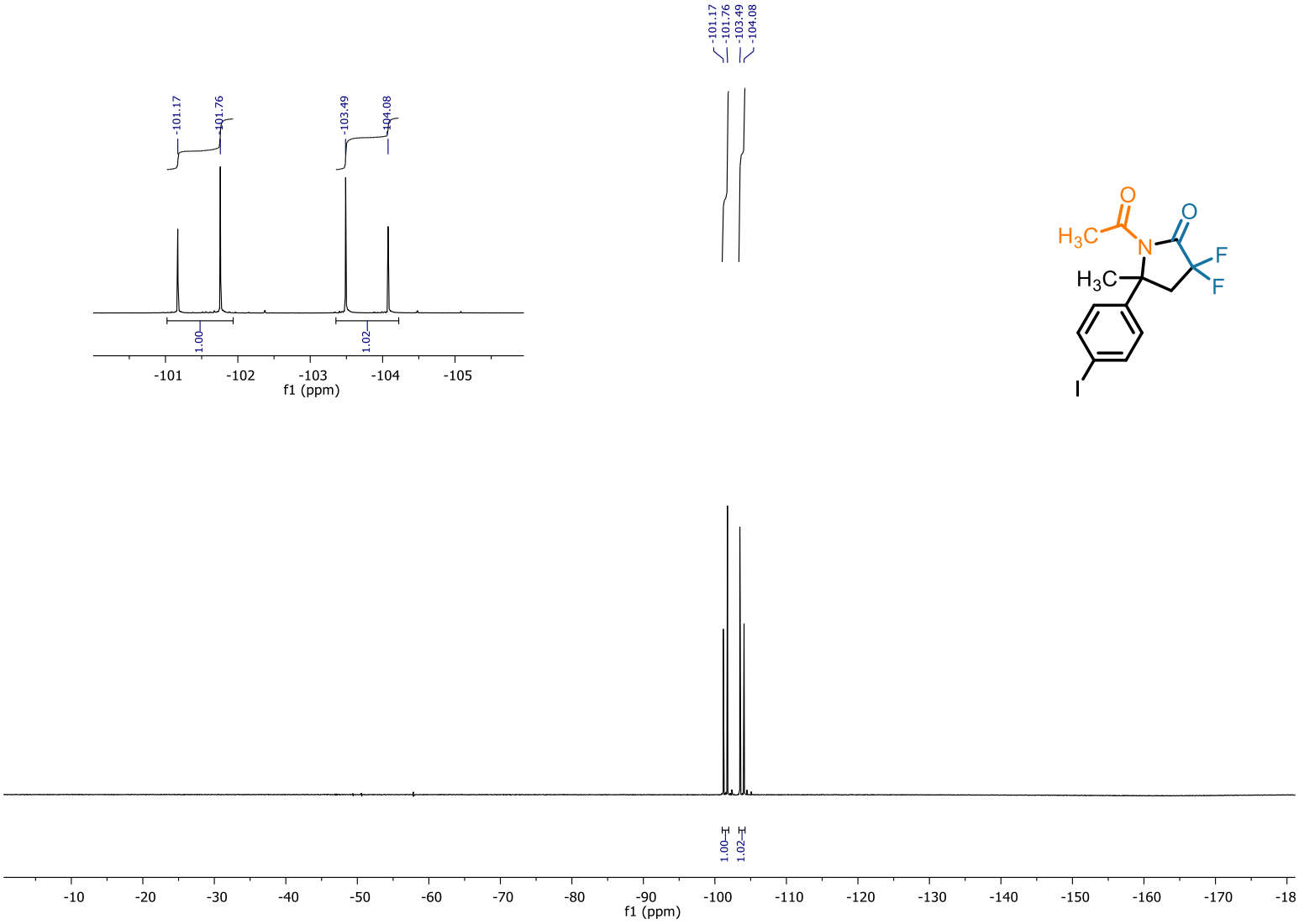
^{1}H-NMR (500 MHz, $CDCl_3$) of **27**



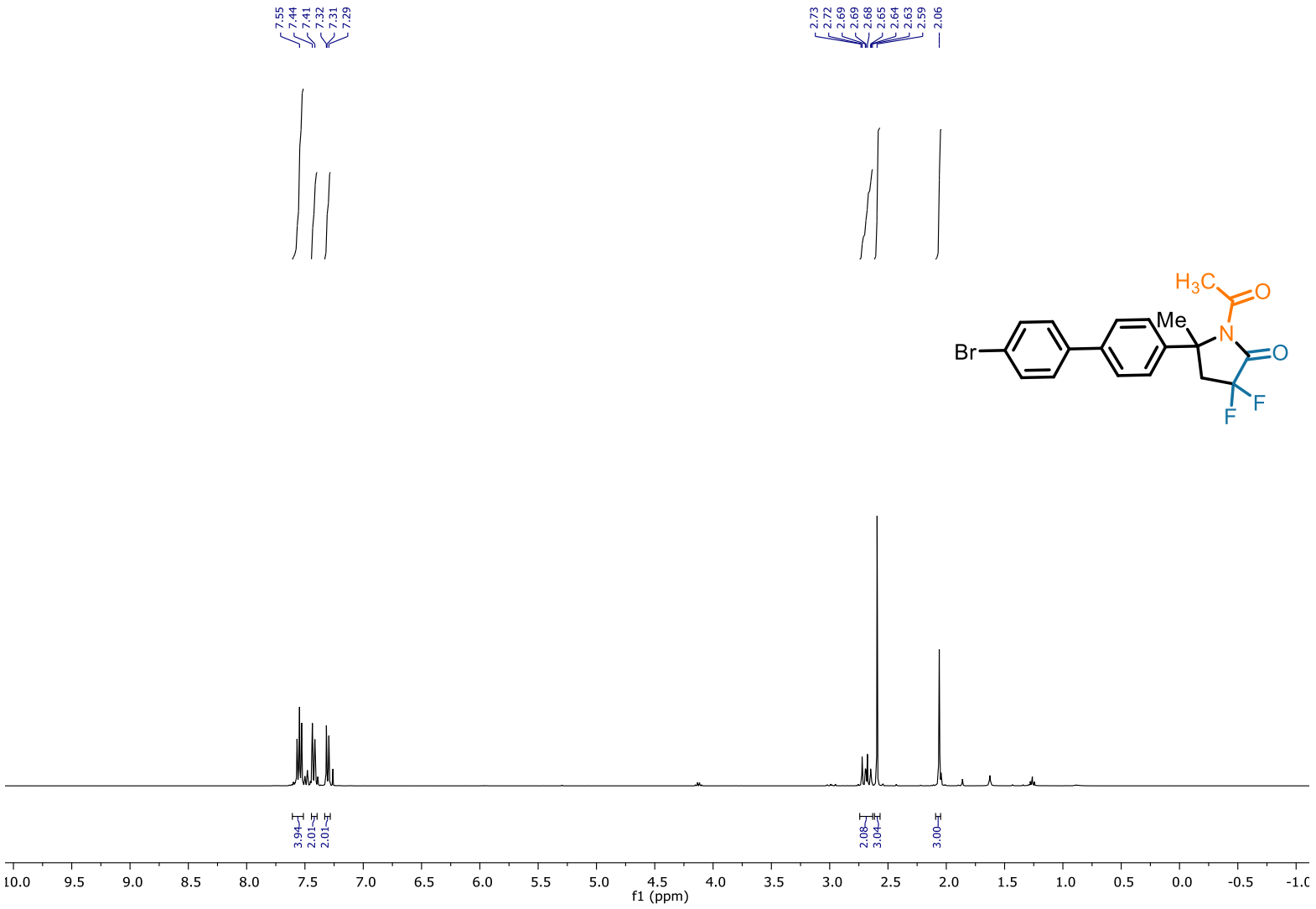
^{13}C-NMR (126 MHz, $CDCl_3$) of **27**



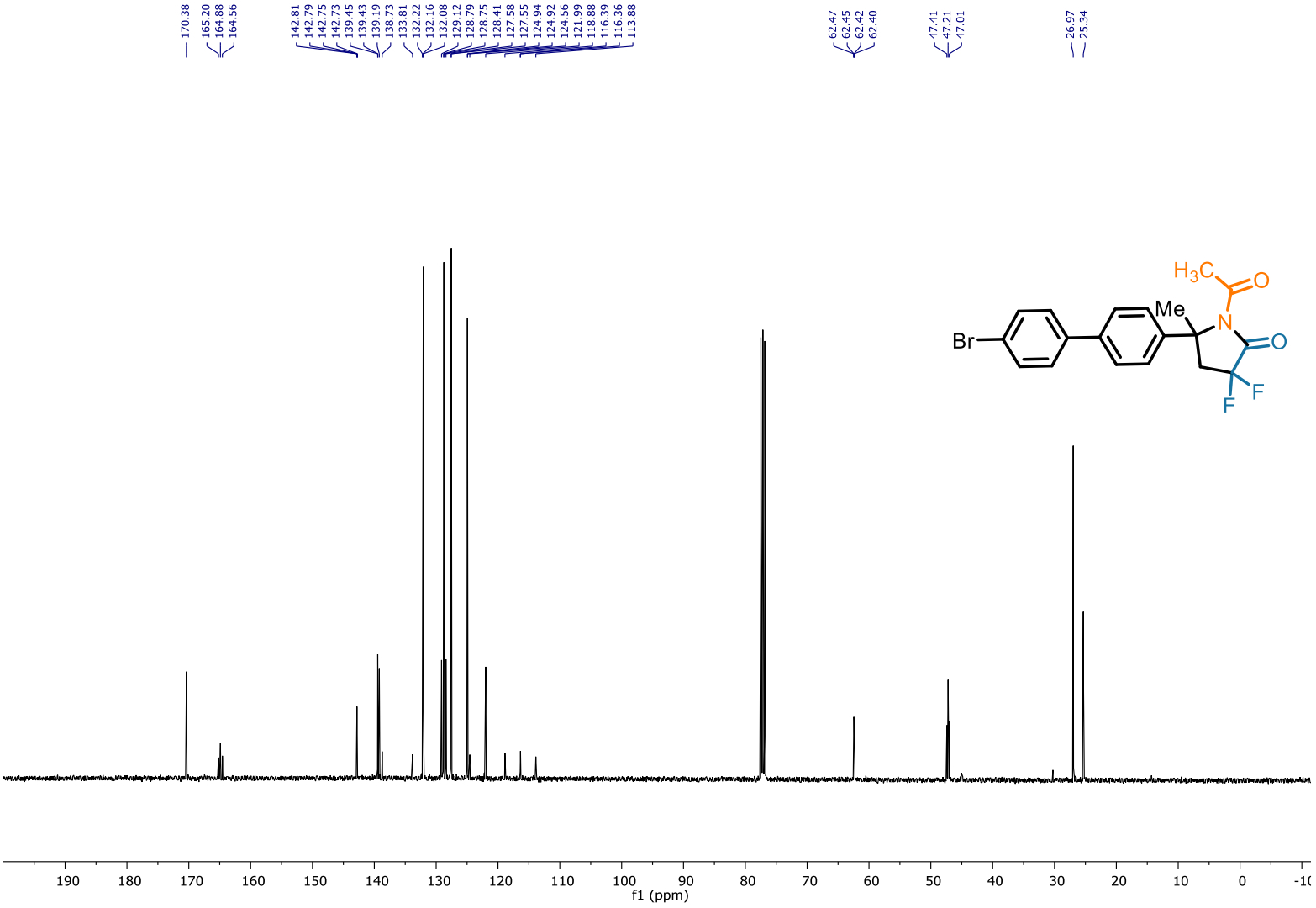
^{19}F-NMR (471 MHz, $CDCl_3$) of **27**



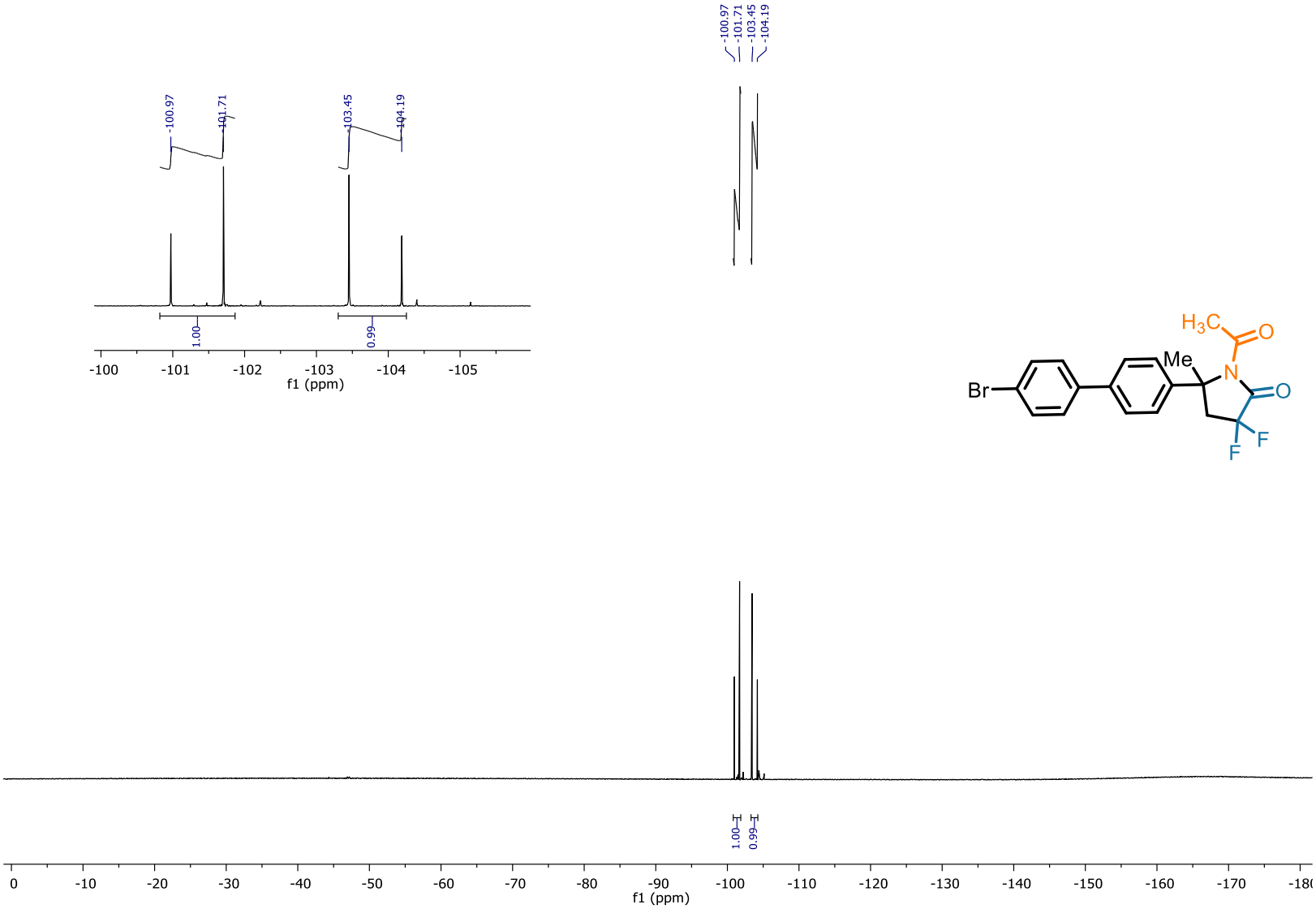
^{1}H-NMR (500 MHz, $CDCl_3$) of **28**



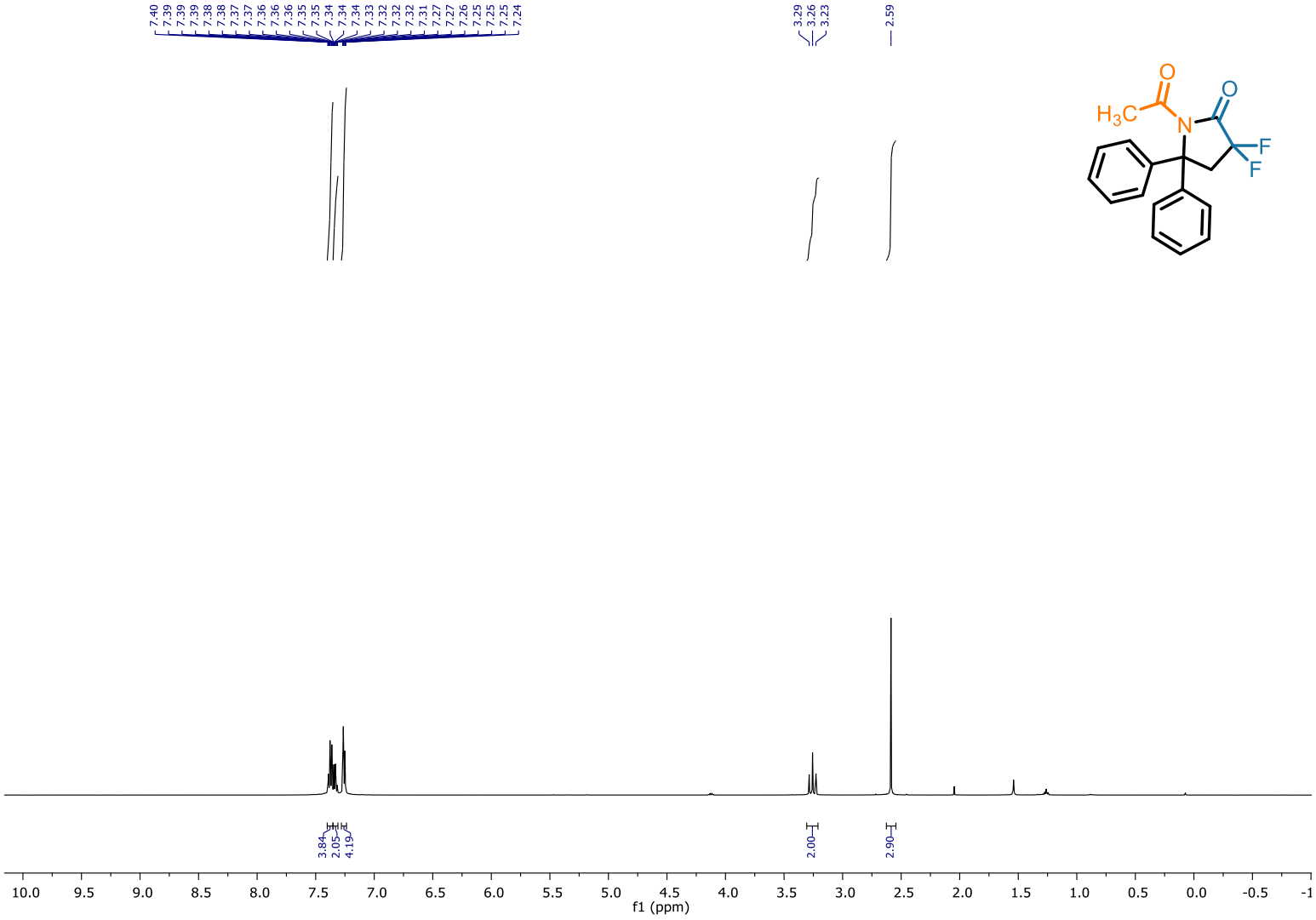
^{13}C-NMR (101 MHz, $CDCl_3$) of **28**



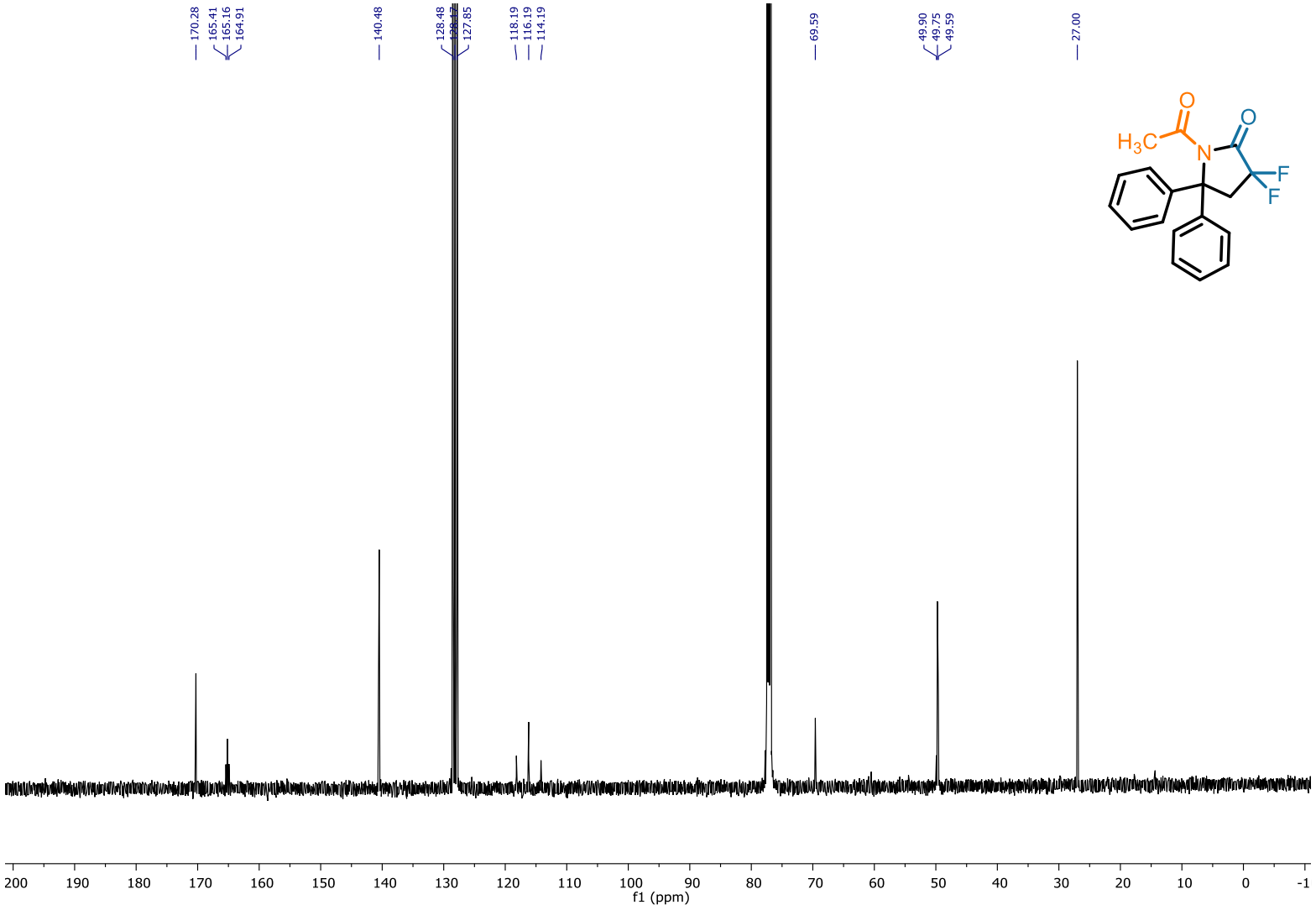
^{19}F-NMR (377 MHz, $CDCl_3$) of **28**



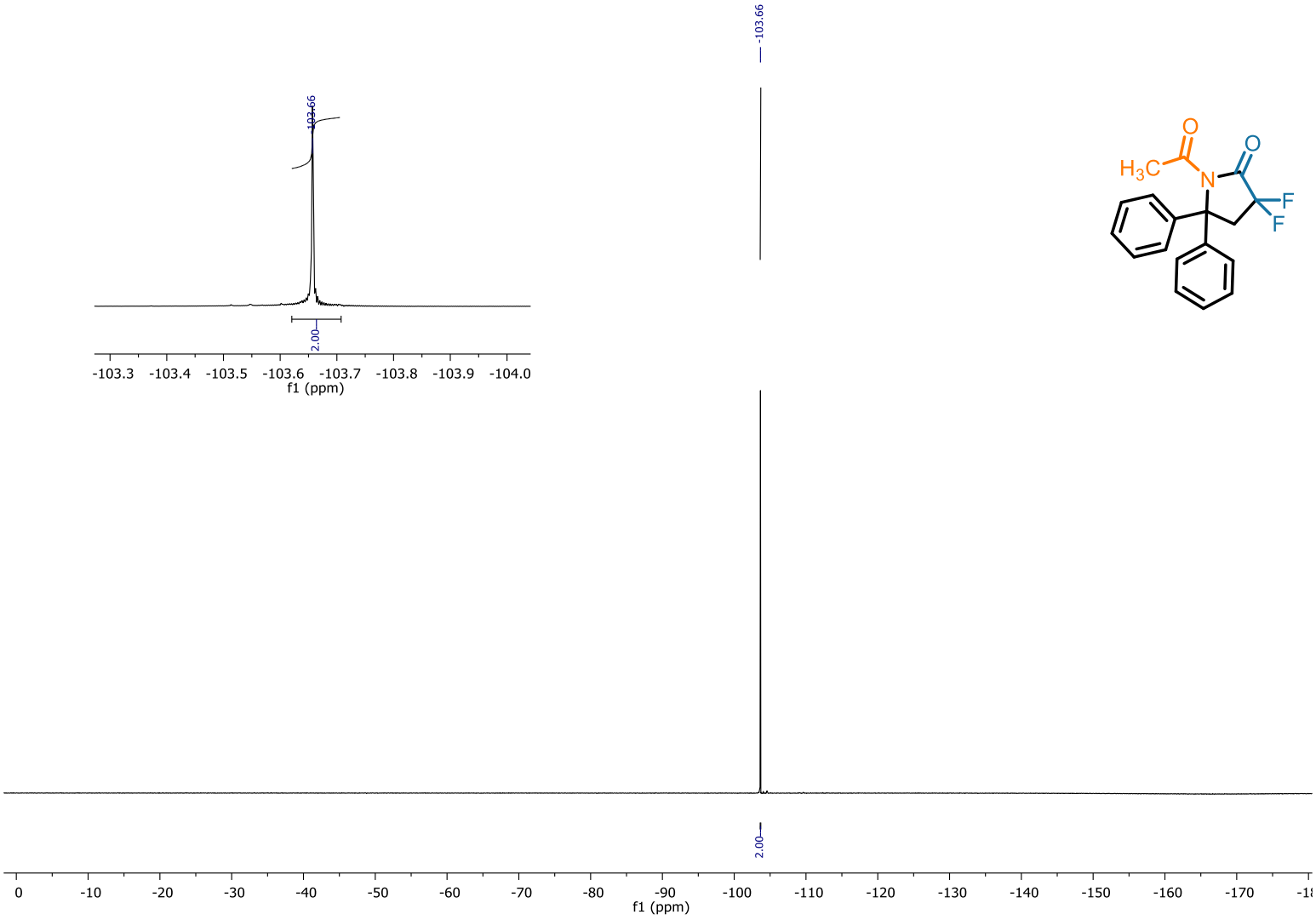
^{1}H-NMR (500 MHz, $CDCl_3$) of **29**



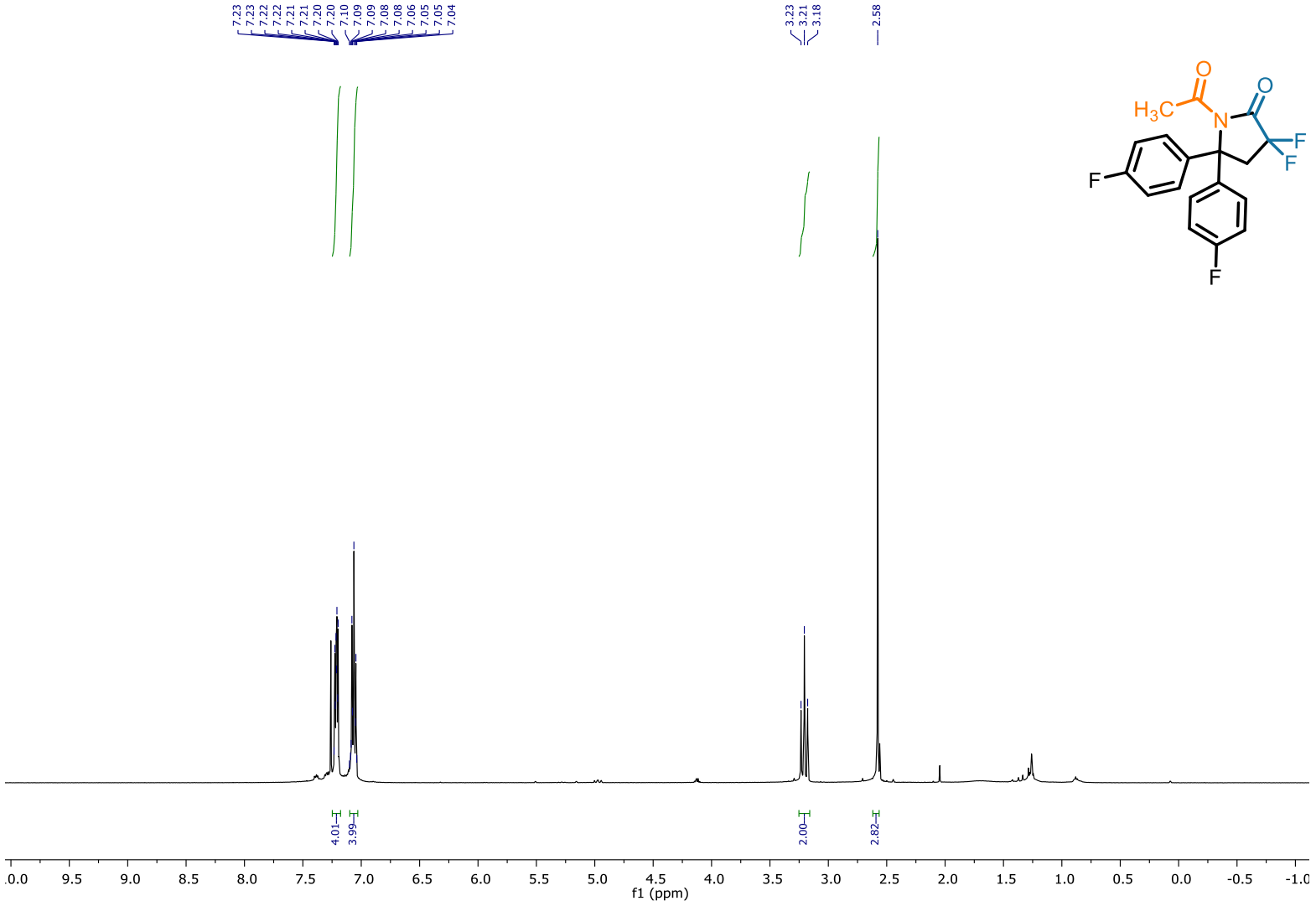
^{13}C-NMR (125 MHz, $CDCl_3$) of **29**



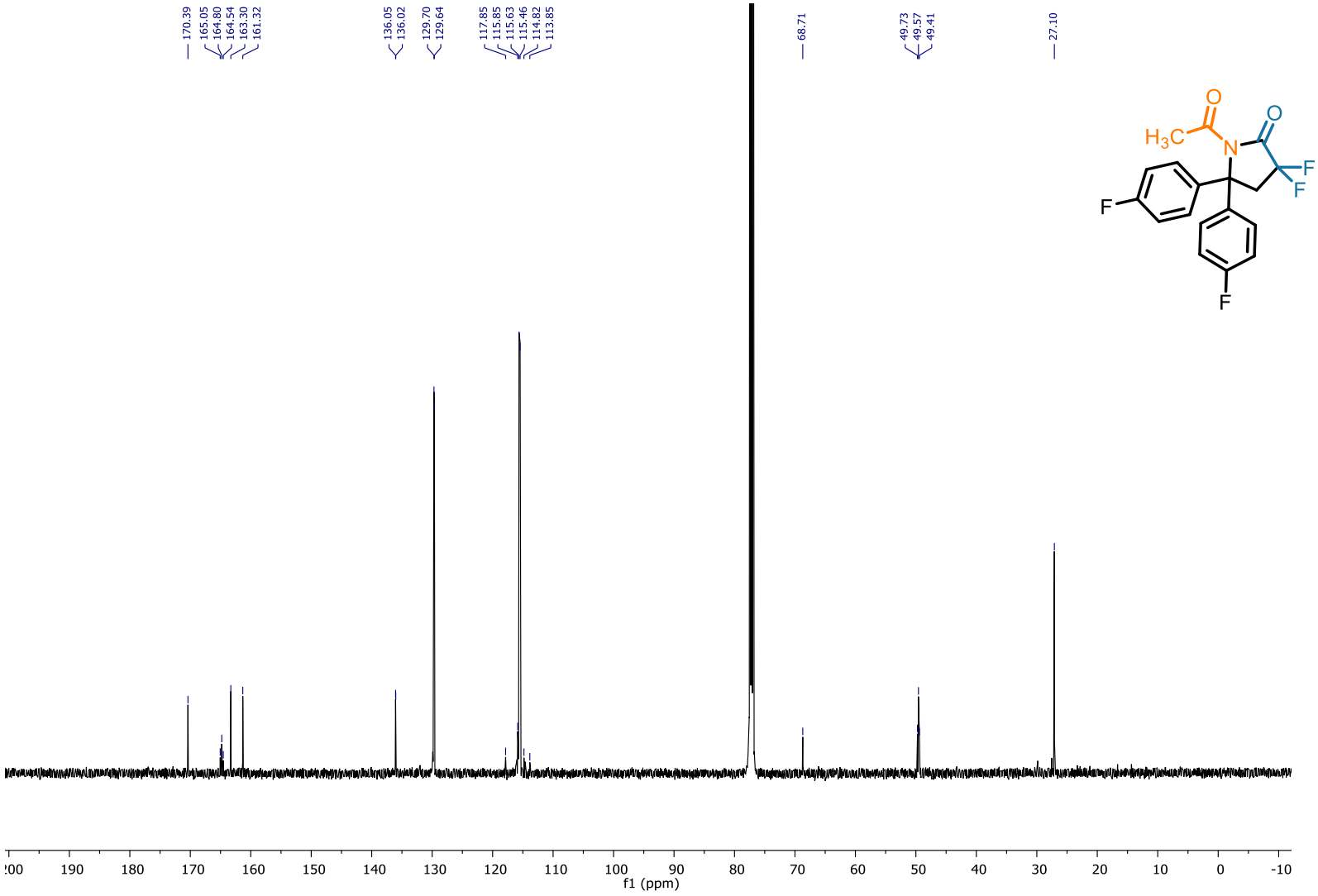
^{19}F-NMR (471 MHz, $CDCl_3$) of **29**



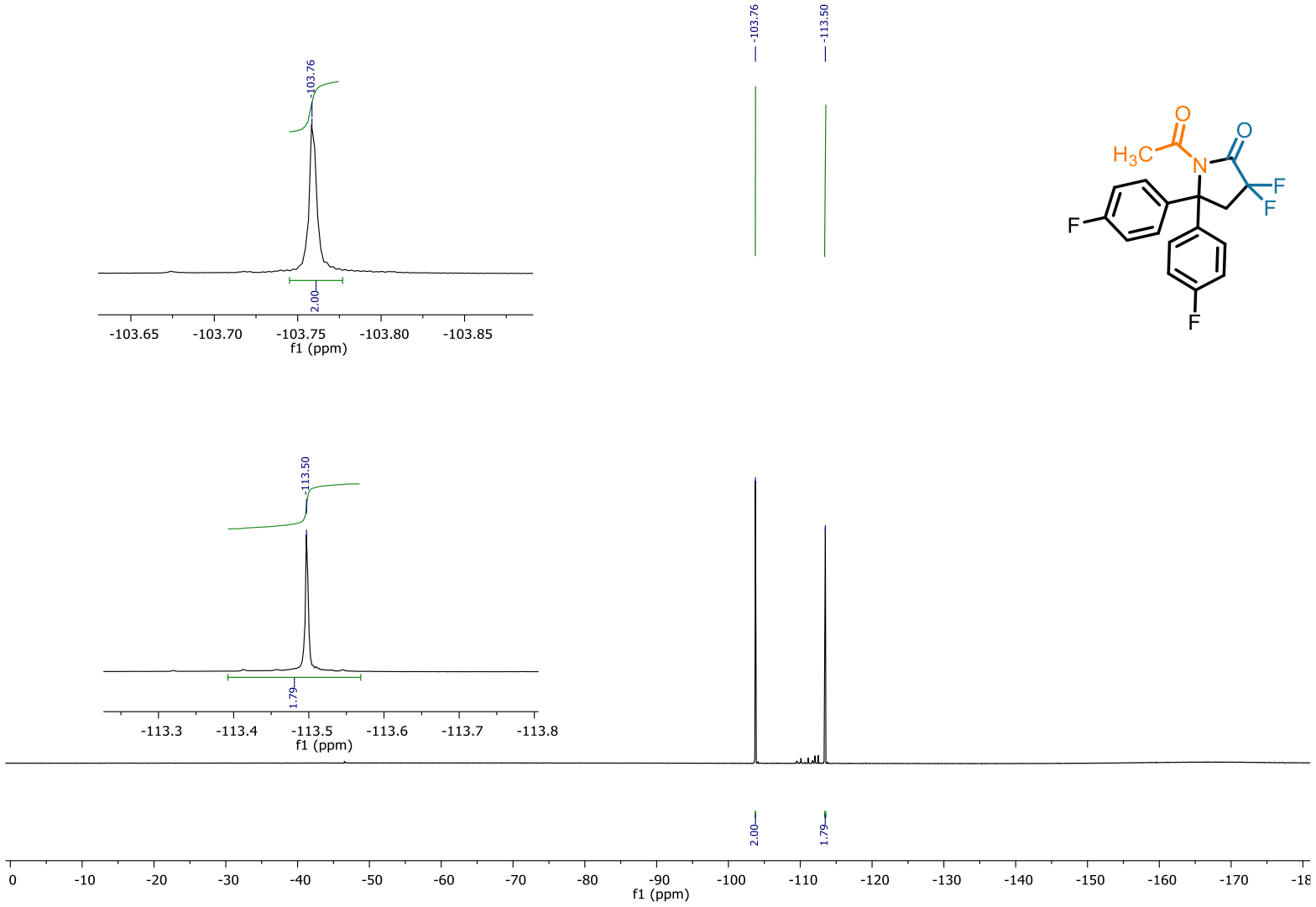
^{1}H-NMR (500 MHz, $CDCl_3$) of **30**



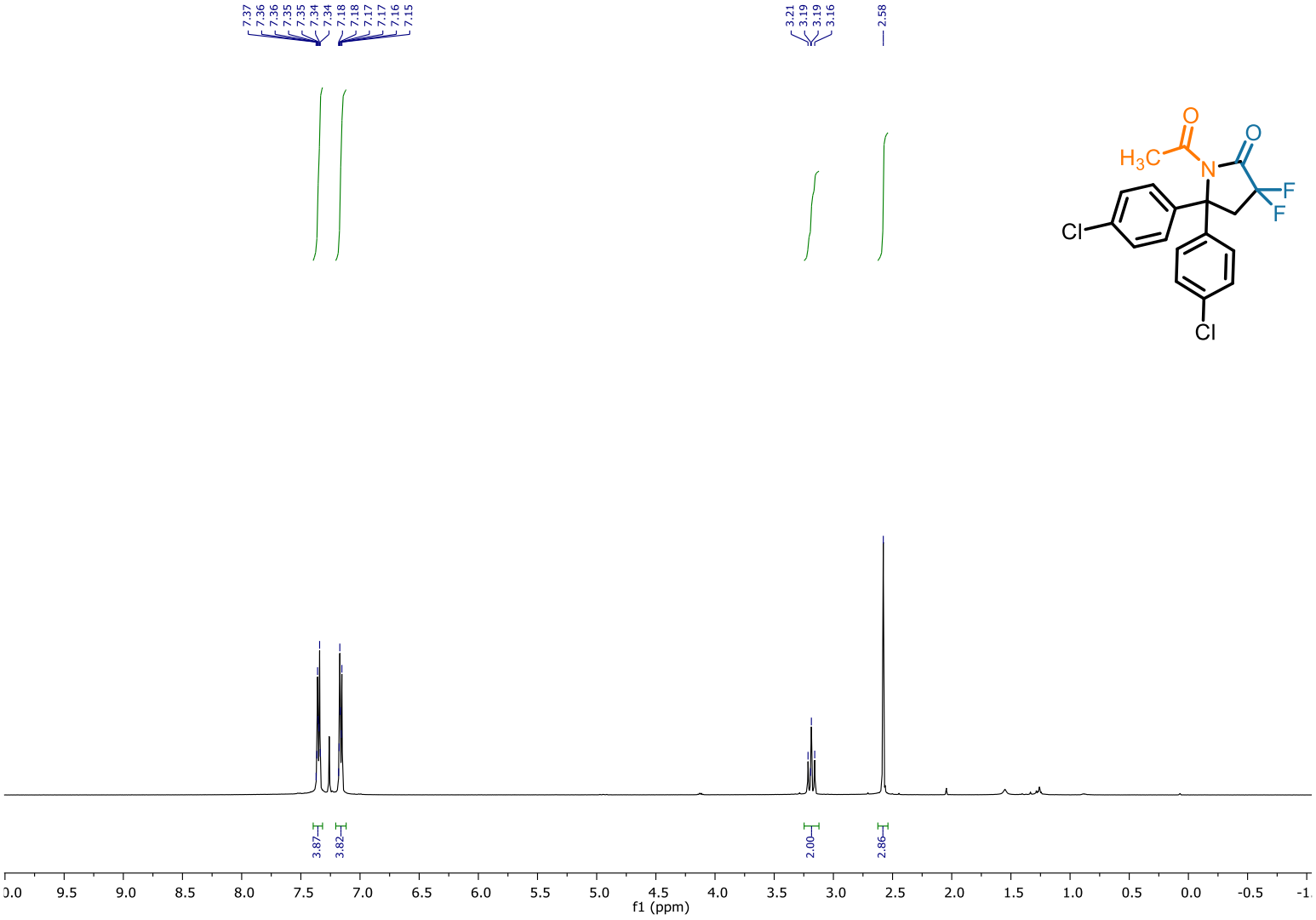
^{13}C-NMR (126 MHz, $CDCl_3$) of **30**



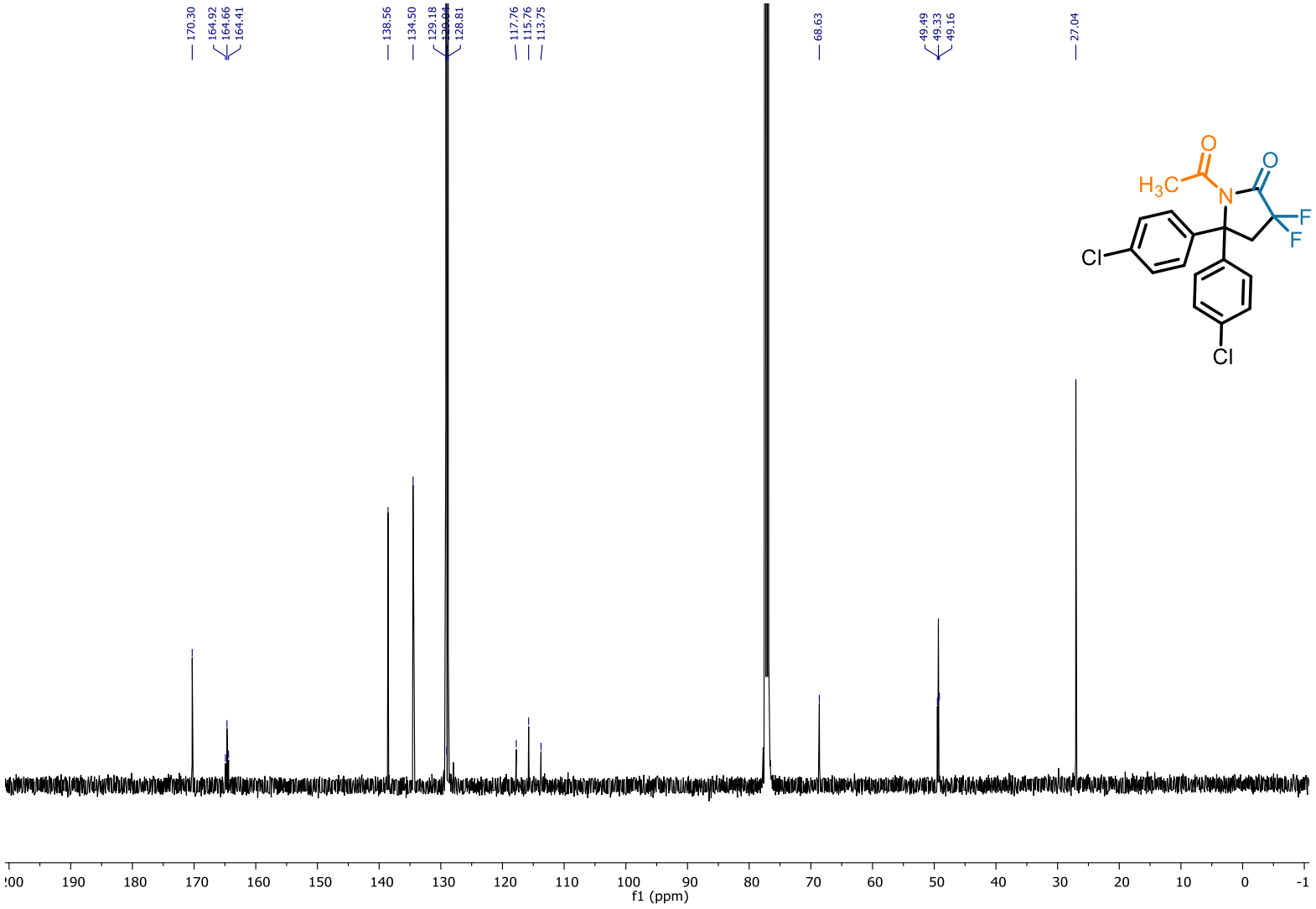
^{19}F-NMR (471 MHz, $CDCl_3$) of **30**



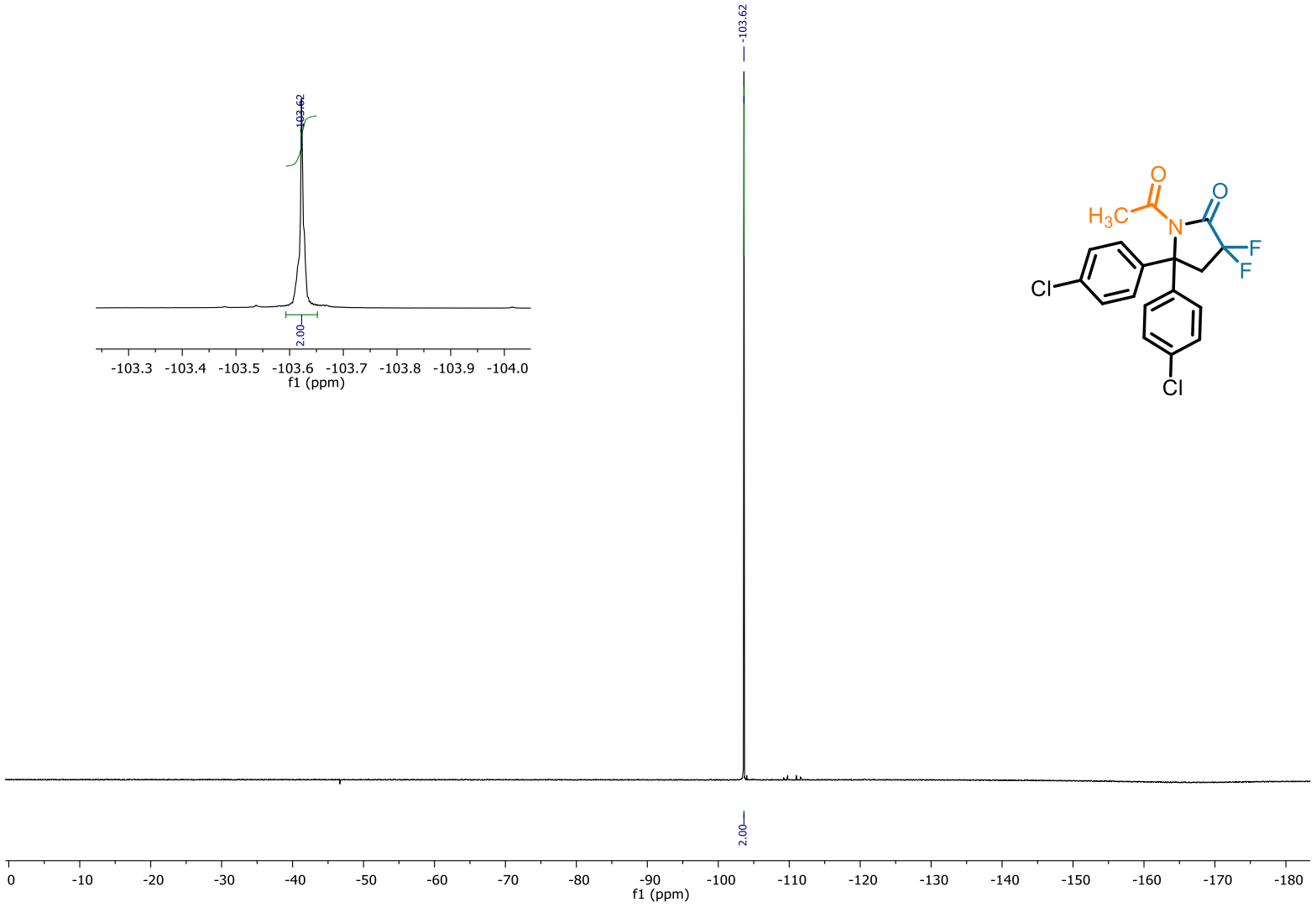
^{1}H-NMR (500 MHz, $CDCl_3$) of **31**



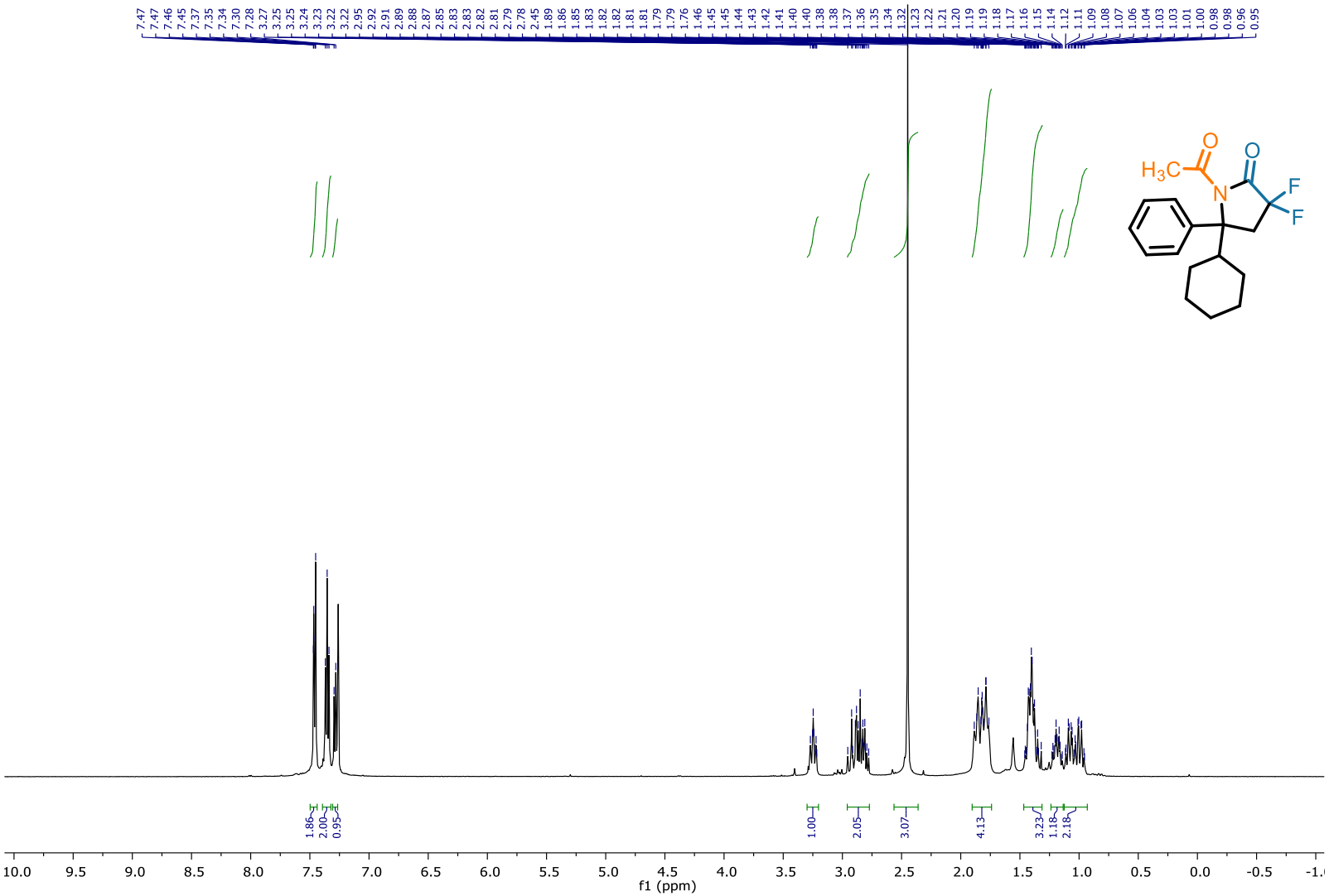
^{13}C-NMR (126 MHz, $CDCl_3$) of **31**



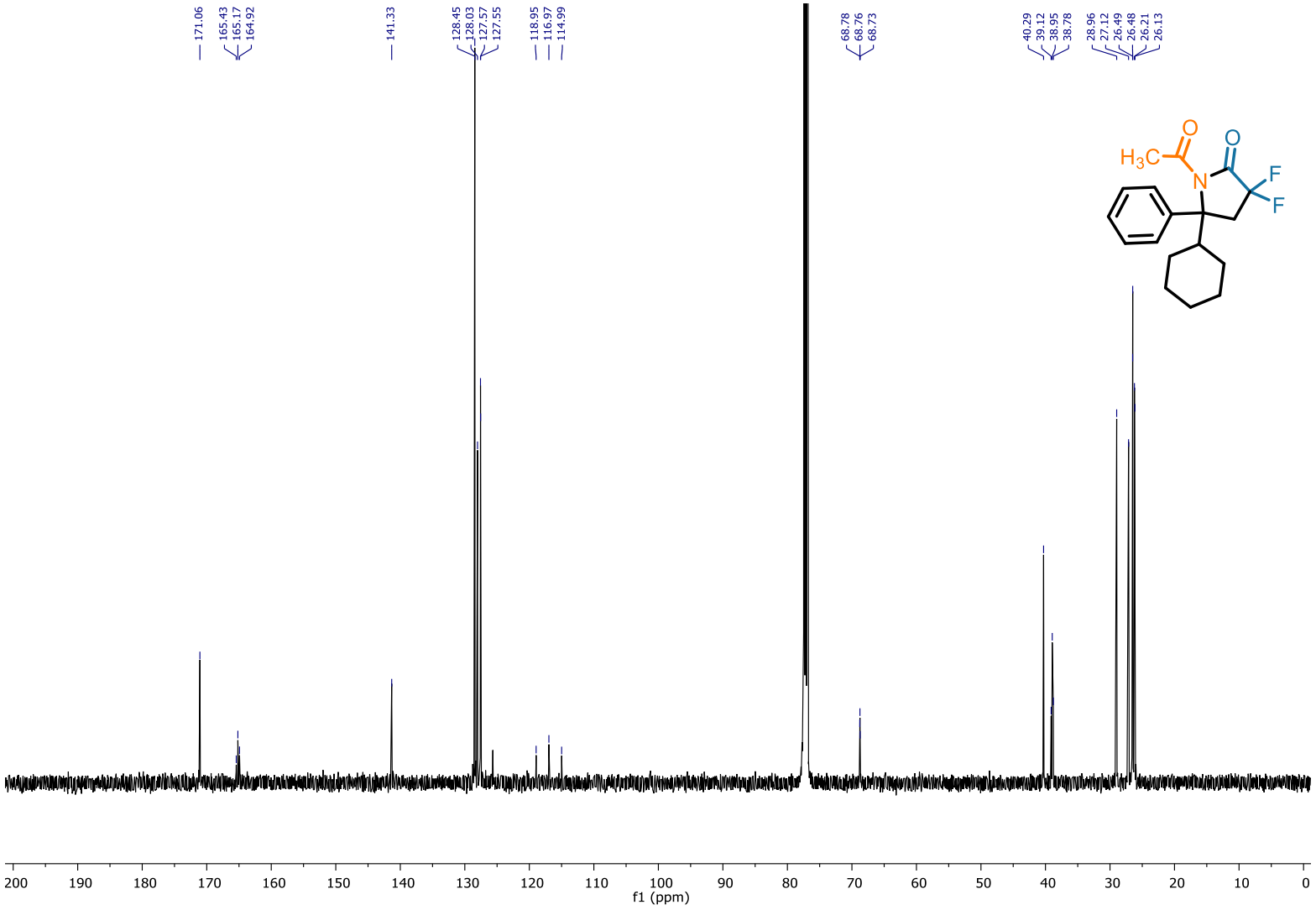
^{19}F-NMR (471 MHz, $CDCl_3$) of **31**



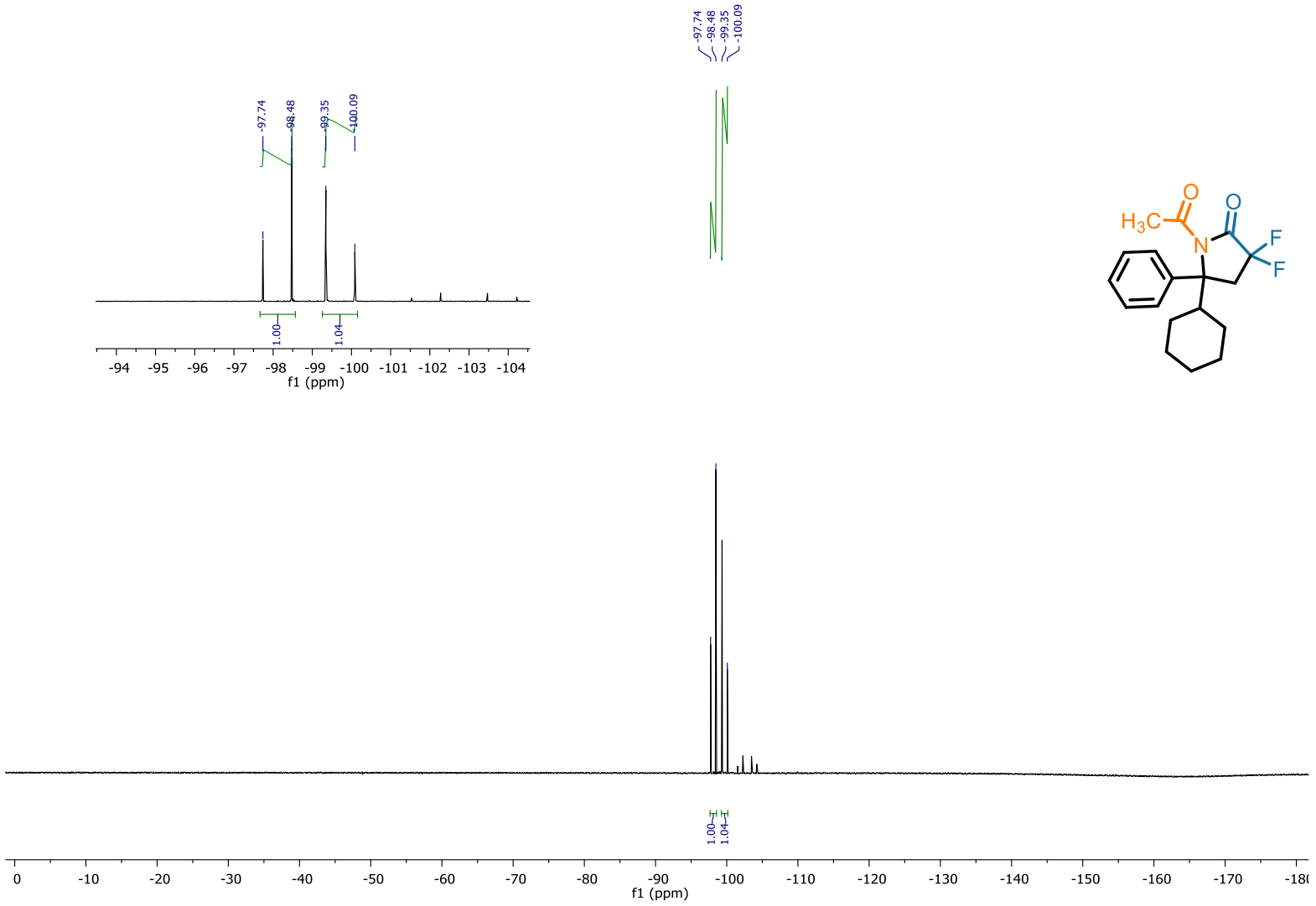
^{1}H-NMR (500 MHz, $CDCl_3$) of **32**



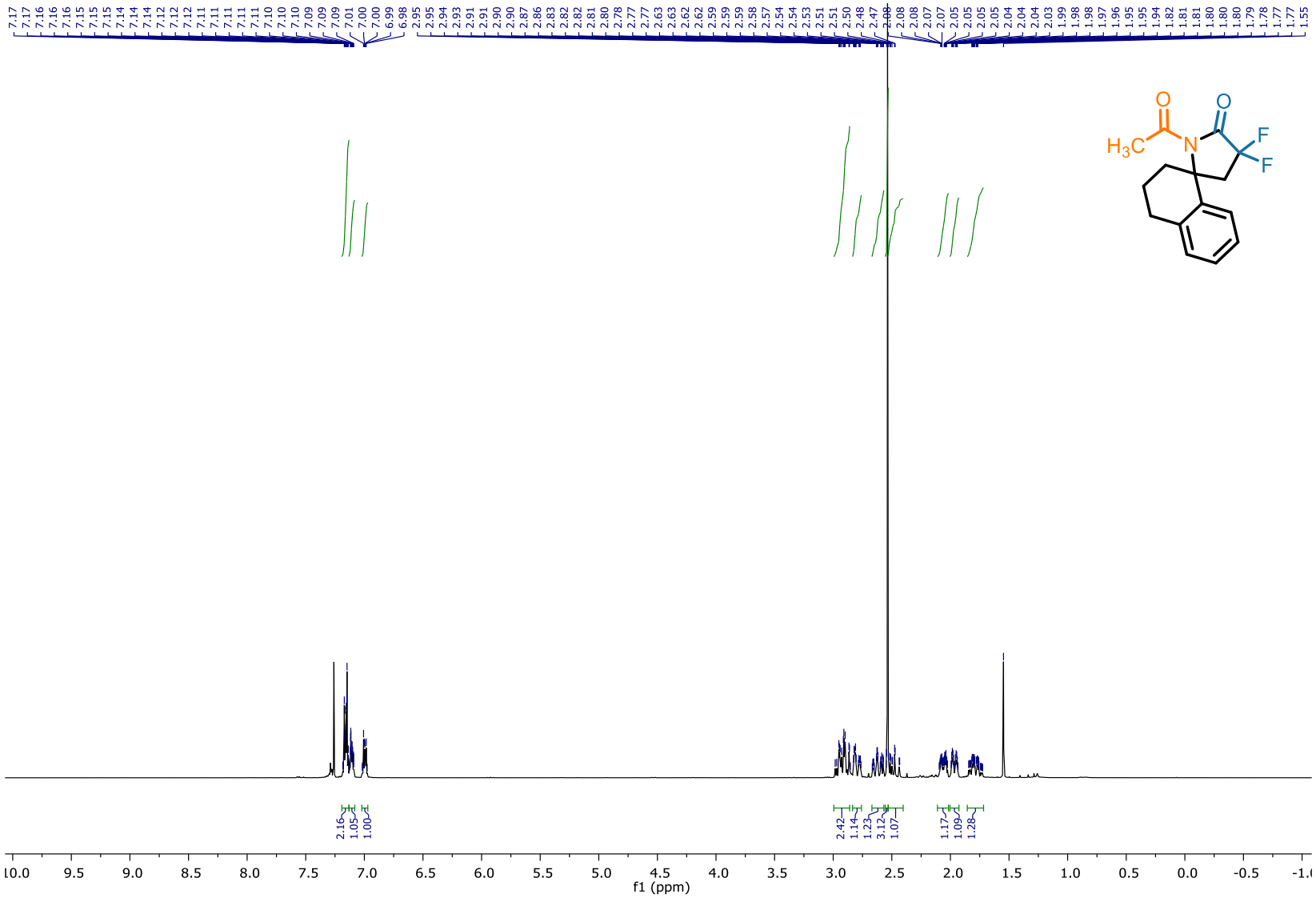
^{13}C-NMR (126 MHz, $CDCl_3$) of **32**



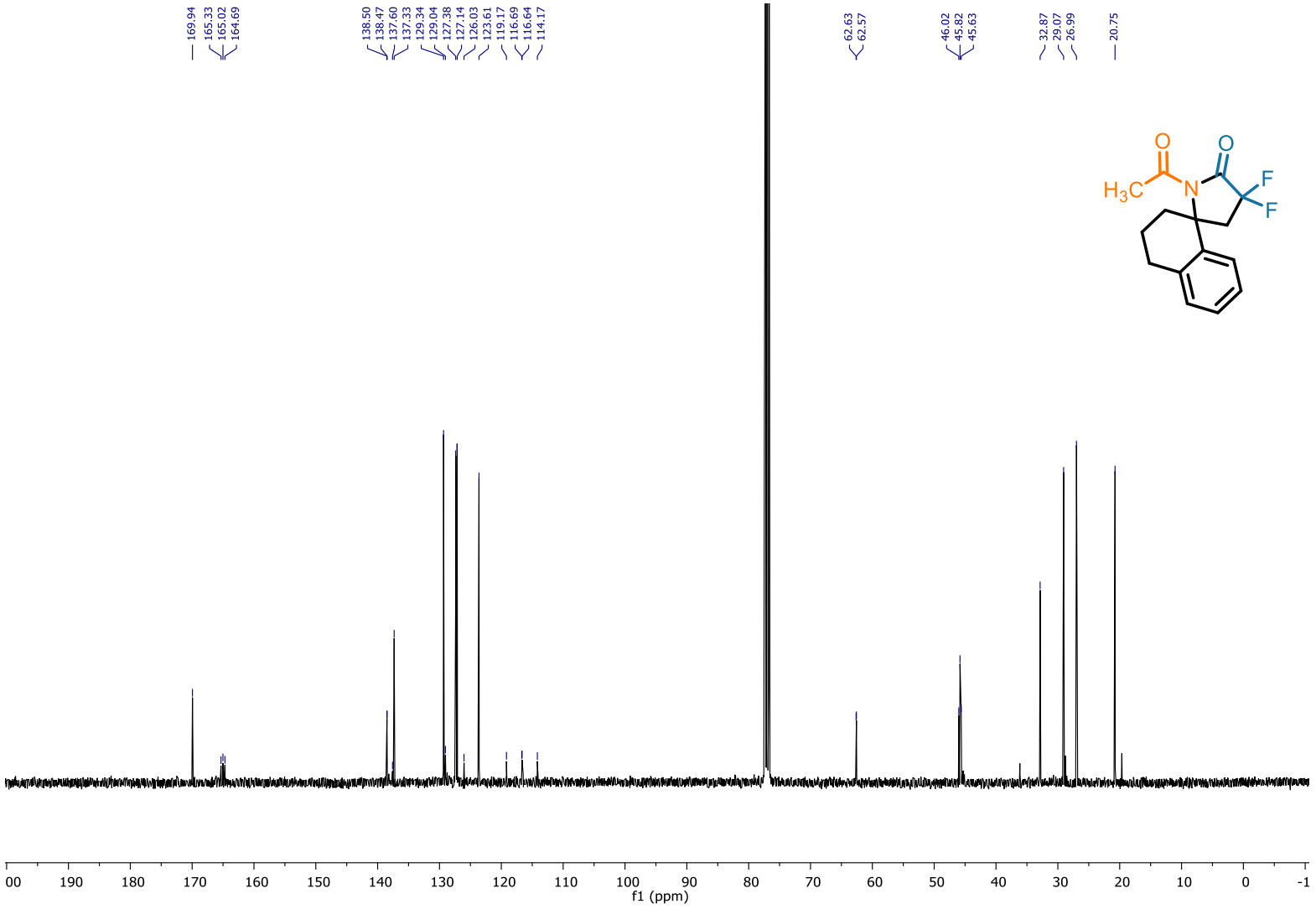
^{19}F-NMR (471 MHz, $CDCl_3$) of **32**



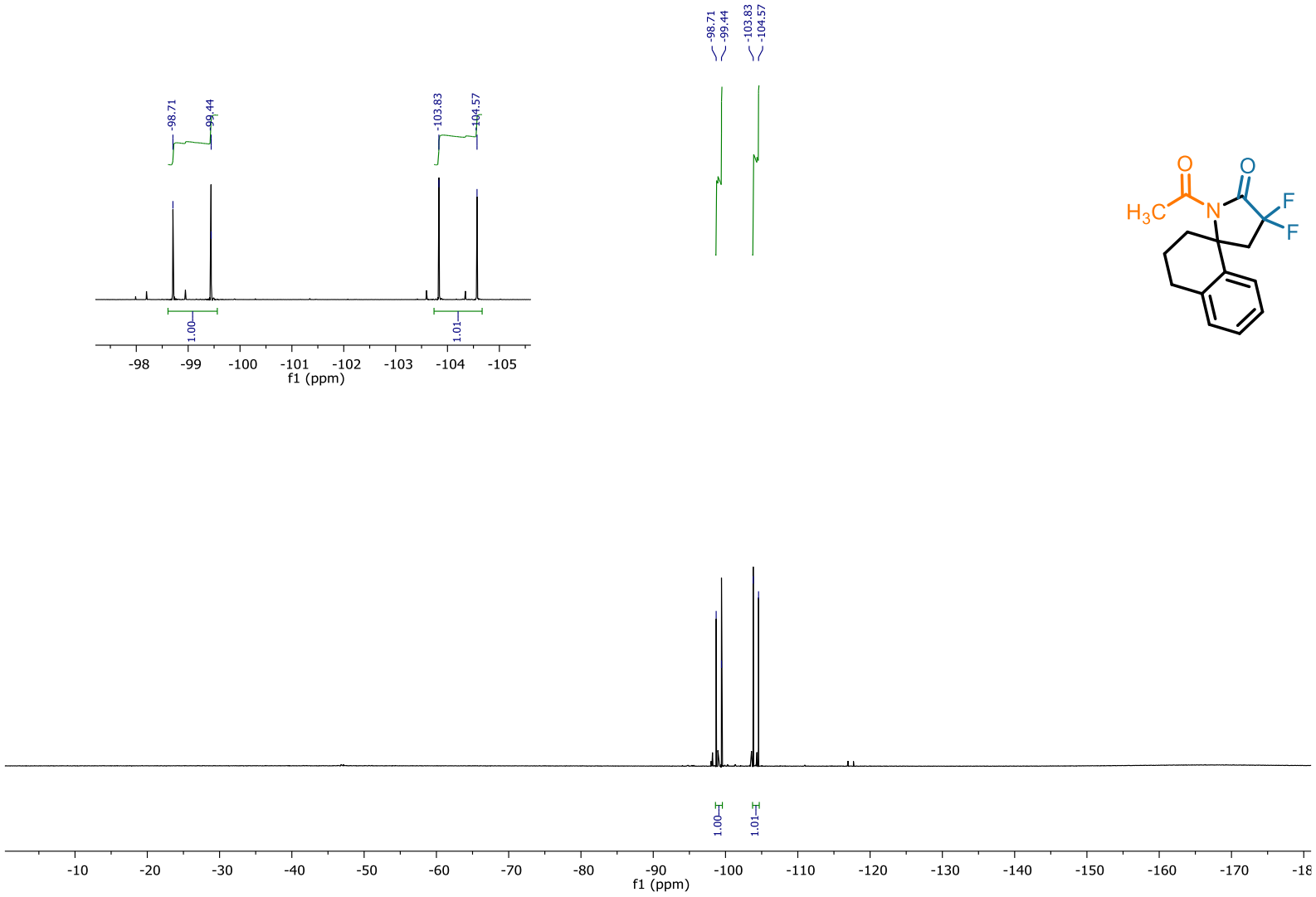
^{1}H-NMR (400 MHz, $CDCl_3$) of **33**



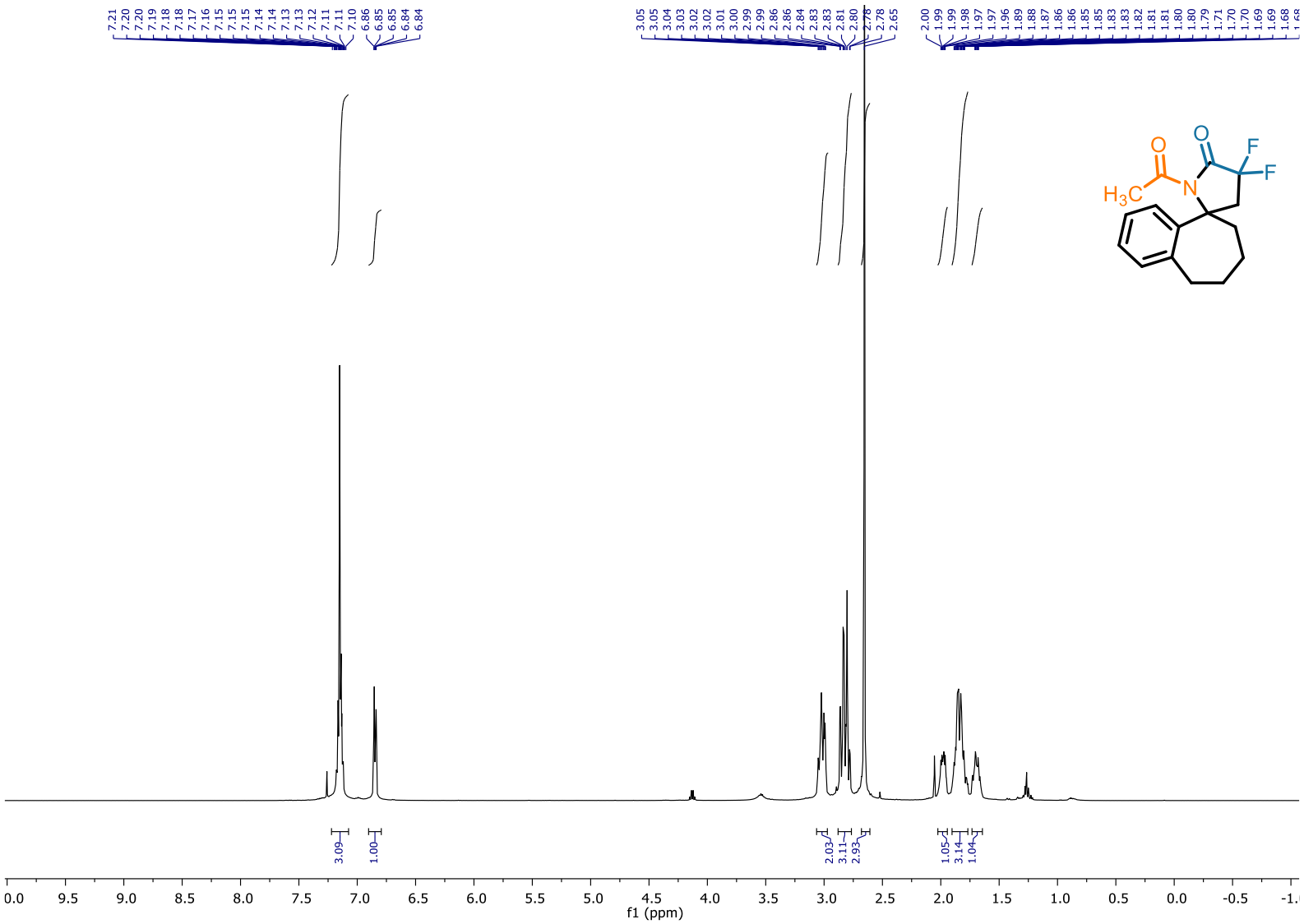
^{13}C-NMR (101 MHz, $CDCl_3$) of **33**



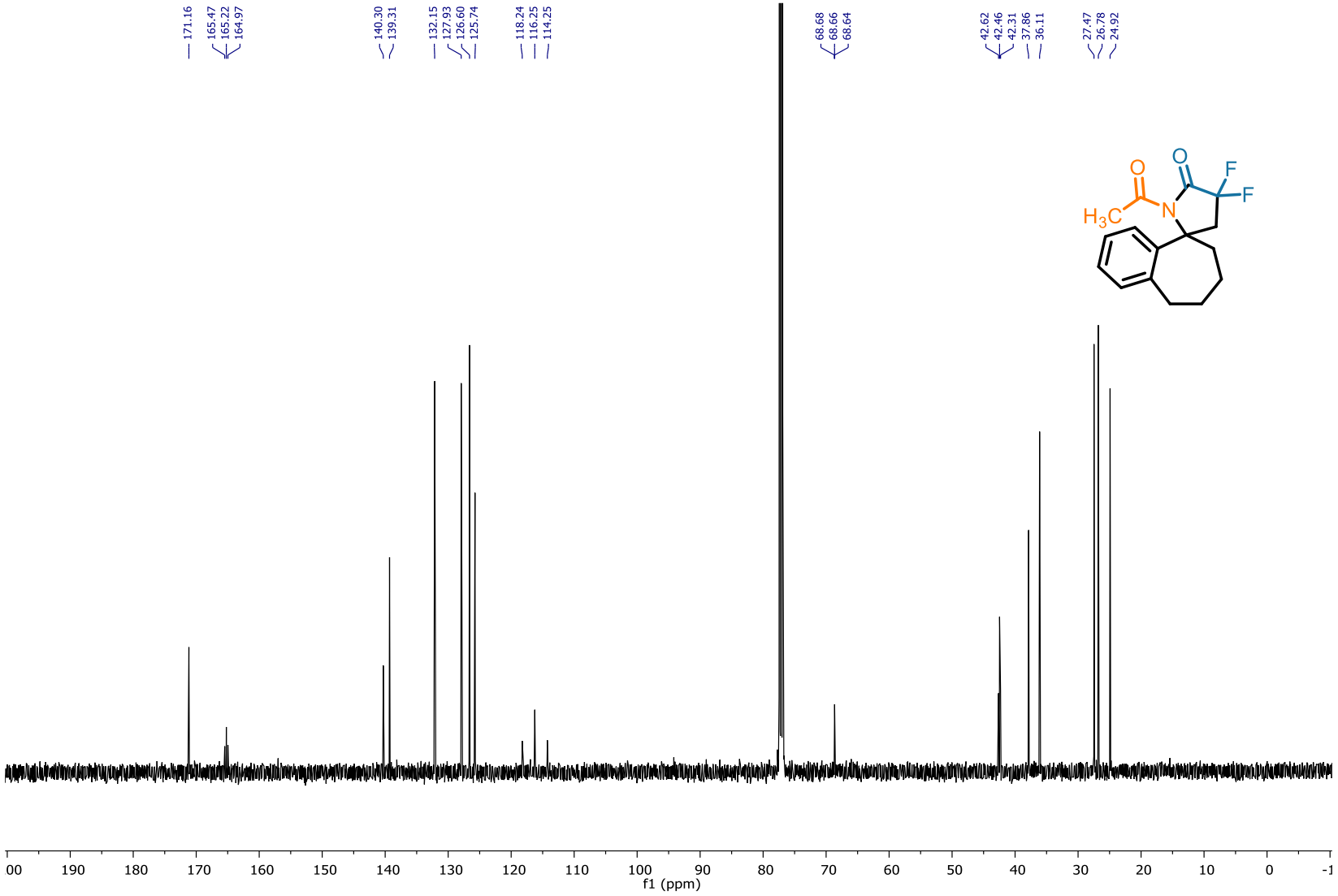
^{19}F-NMR (377 MHz, $CDCl_3$) of **33**



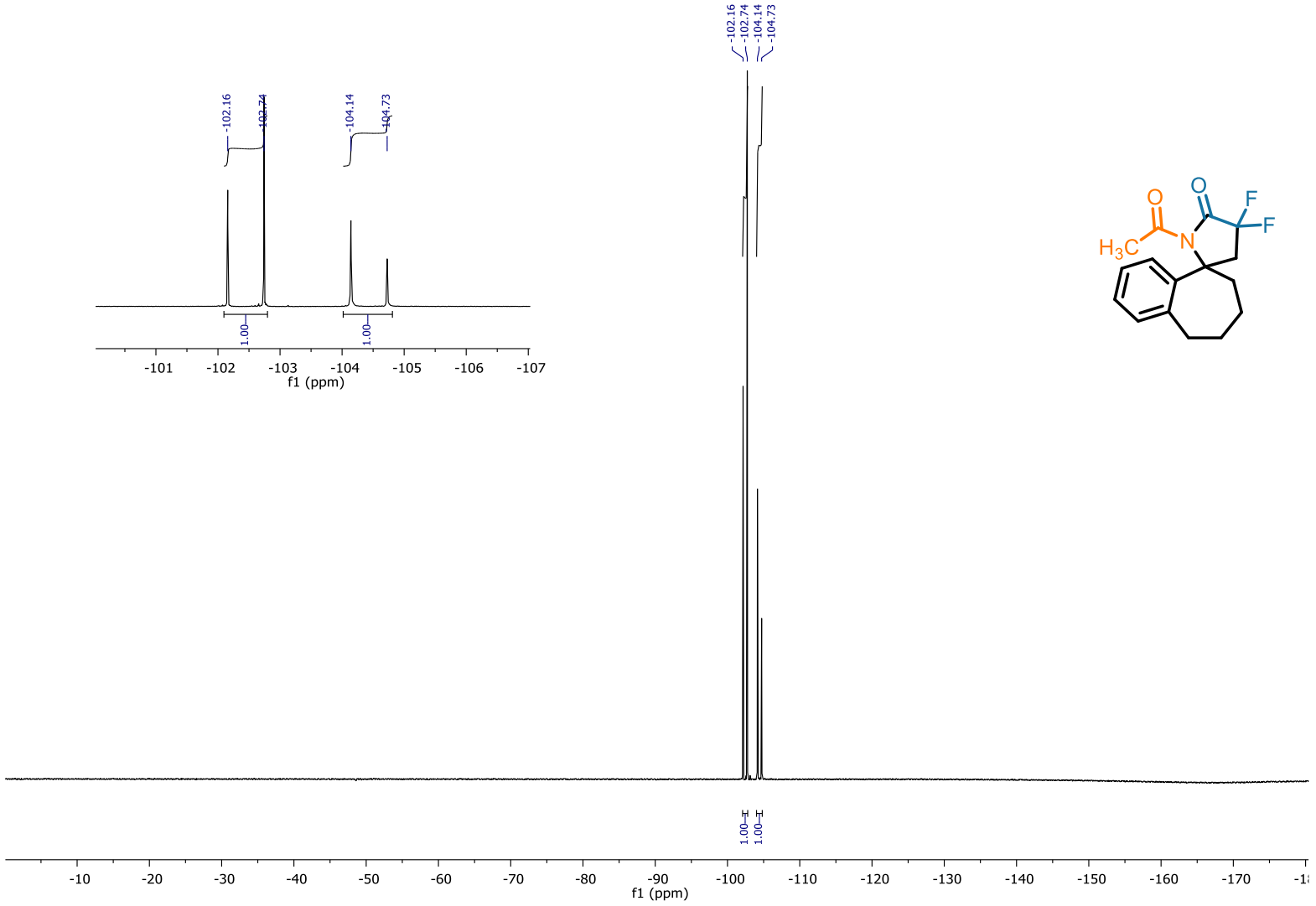
^{1}H-NMR (500 MHz, $CDCl_3$) of **34**



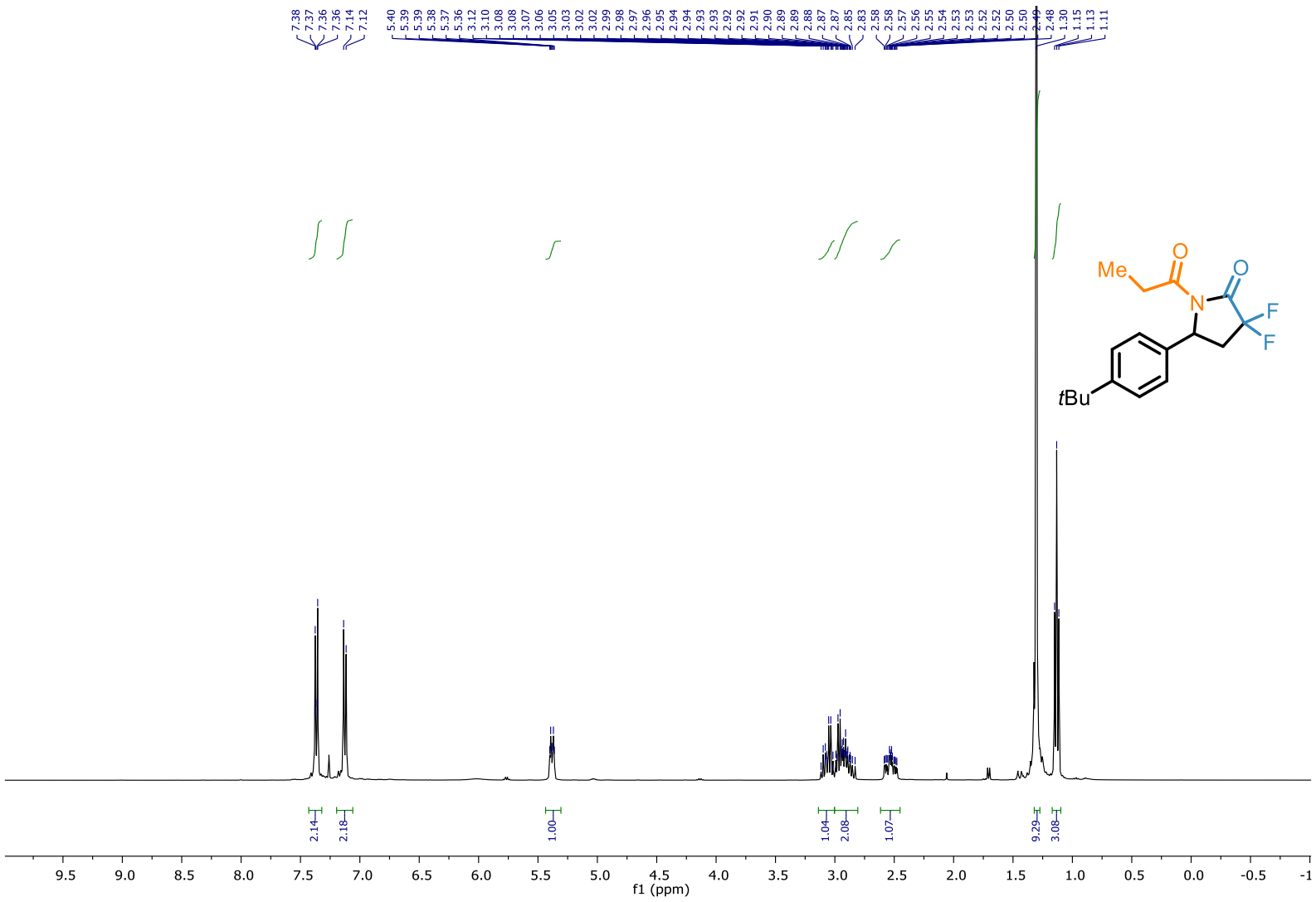
^{13}C-NMR (126 MHz, $CDCl_3$) of **34**



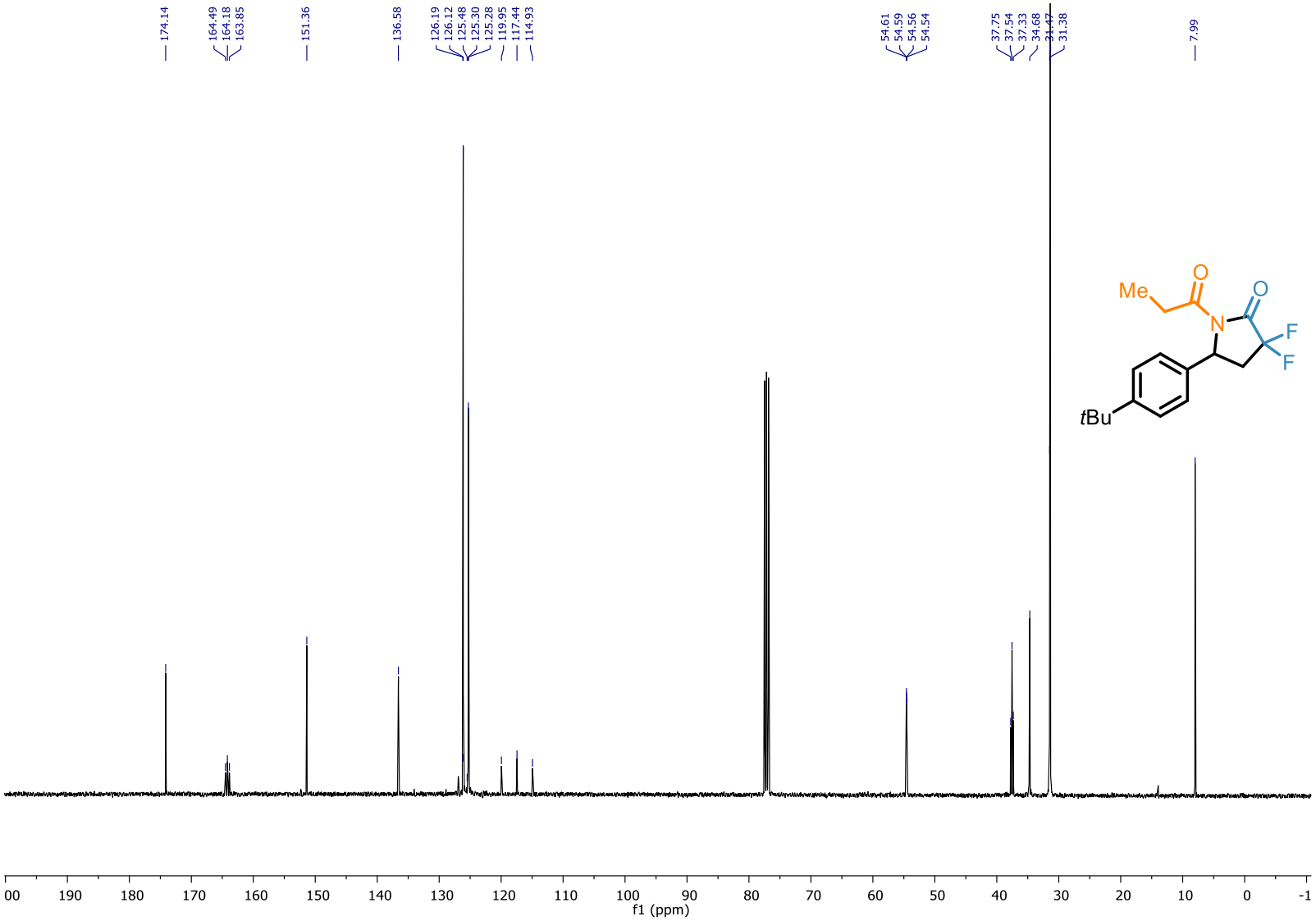
^{19}F-NMR (471 MHz, $CDCl_3$) of **34**



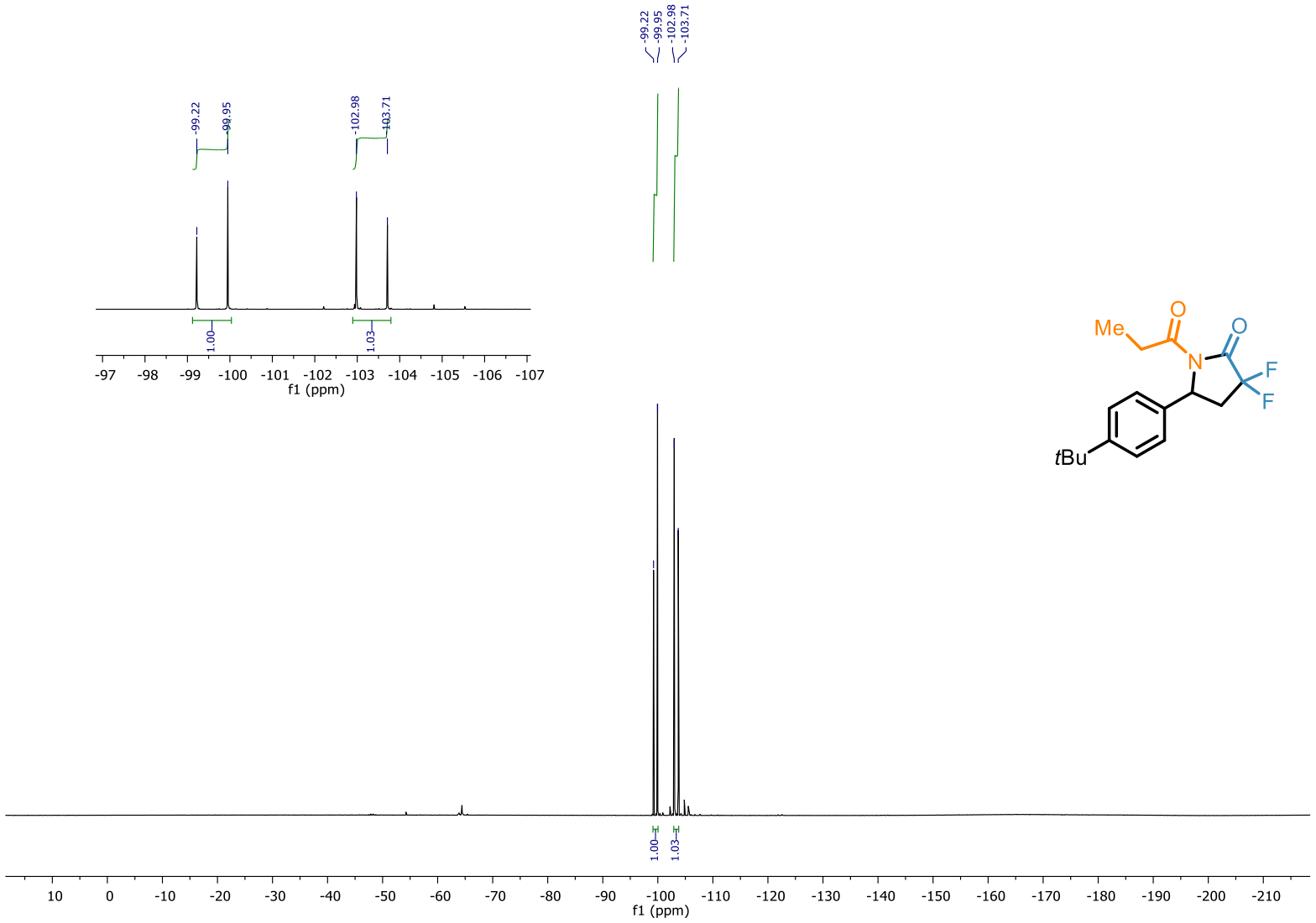
^{1}H-NMR (400 MHz, $CDCl_3$) of **35**



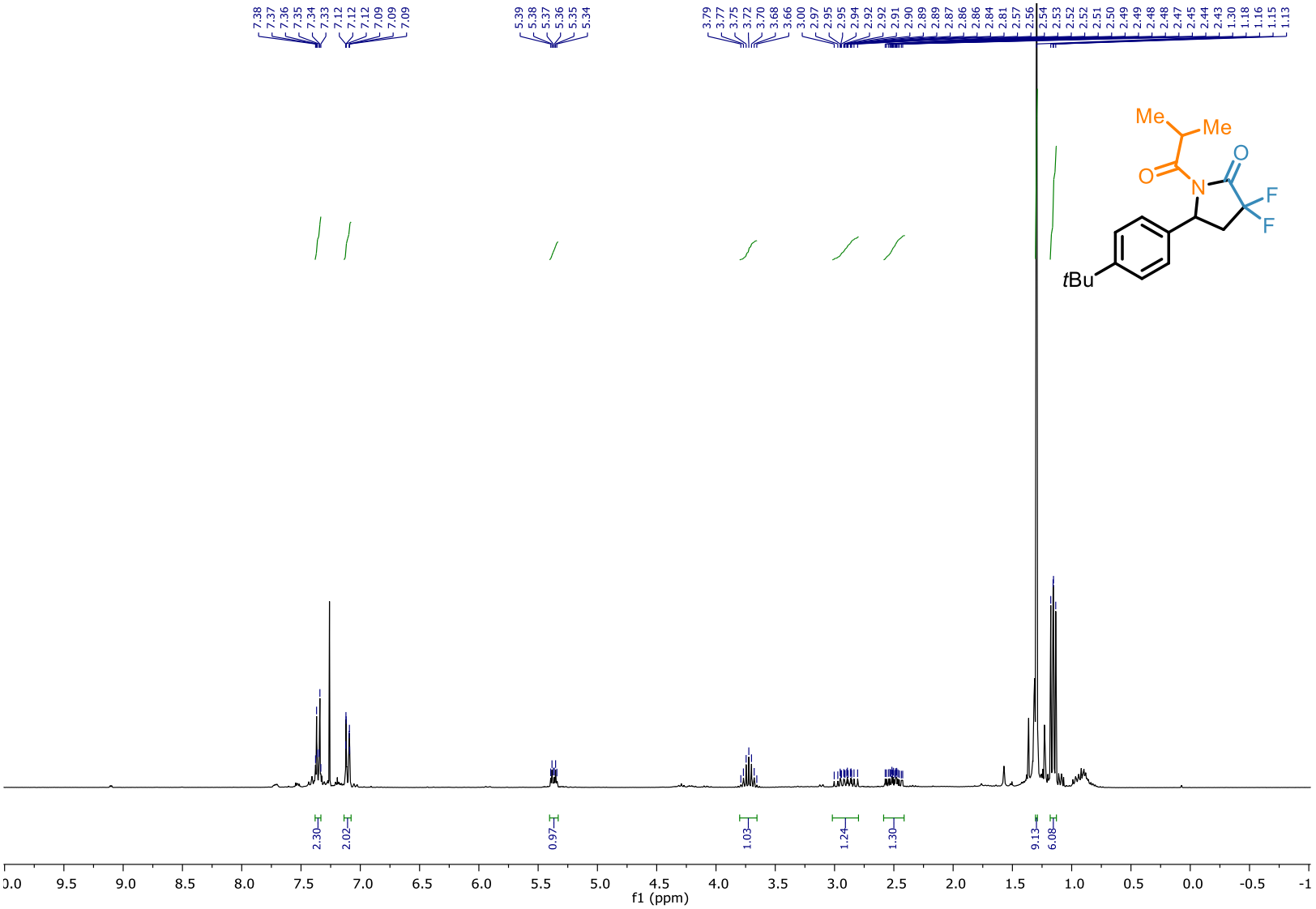
^{13}C-NMR (101 MHz, $CDCl_3$) of **35**



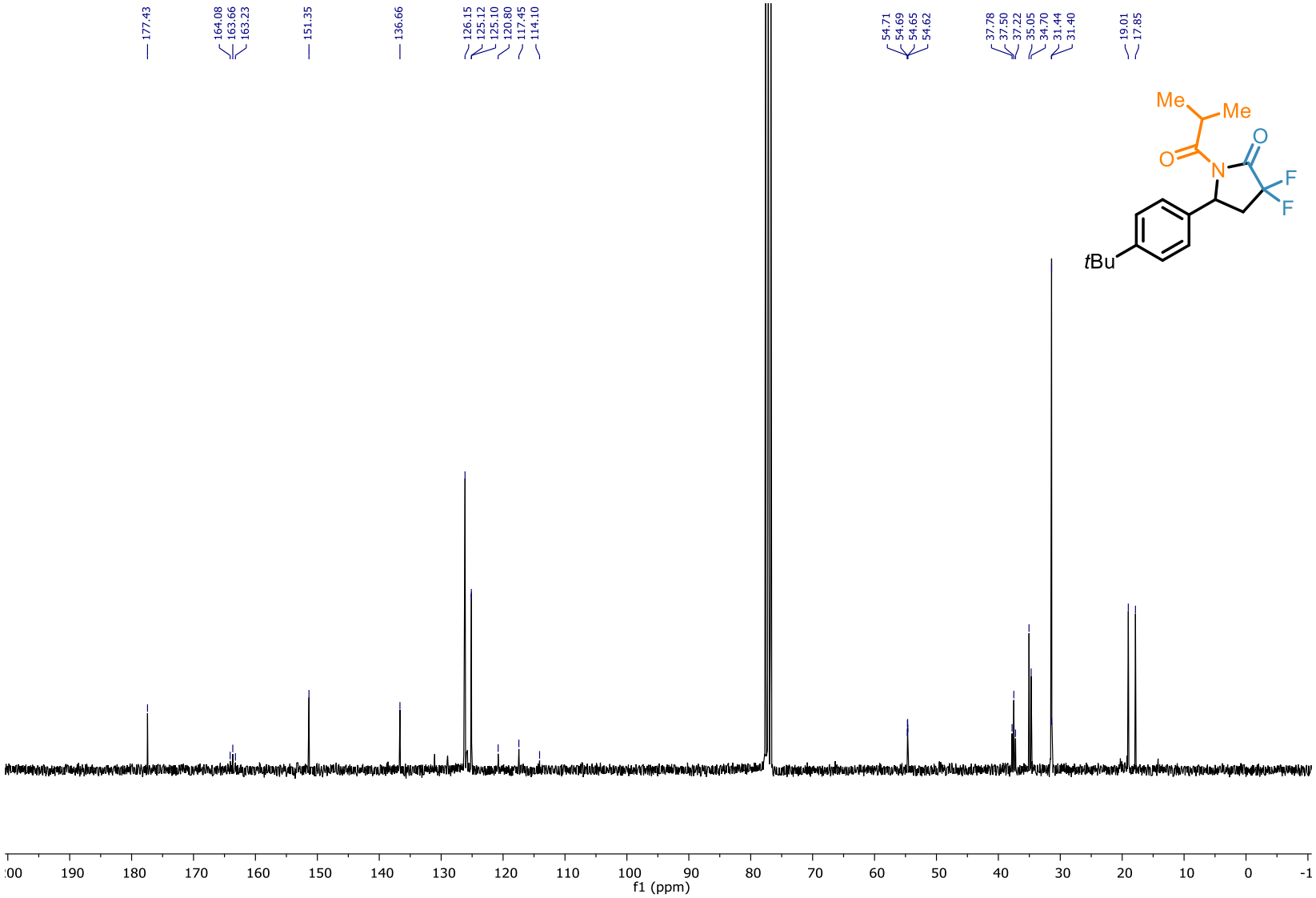
^{19}F-NMR (377 MHz, $CDCl_3$) of **35**



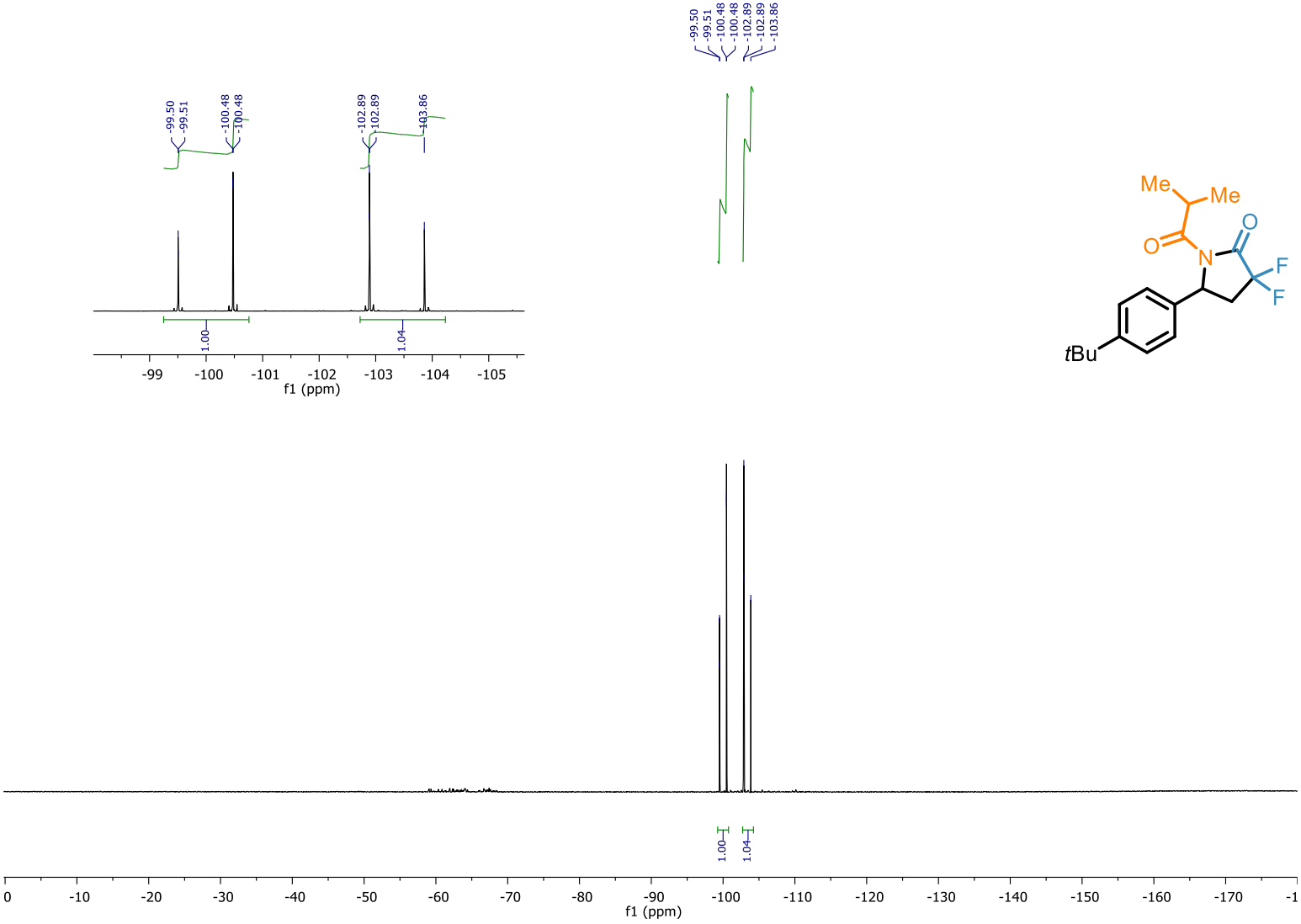
^{1}H-NMR (300 MHz, $CDCl_3$) of **36**



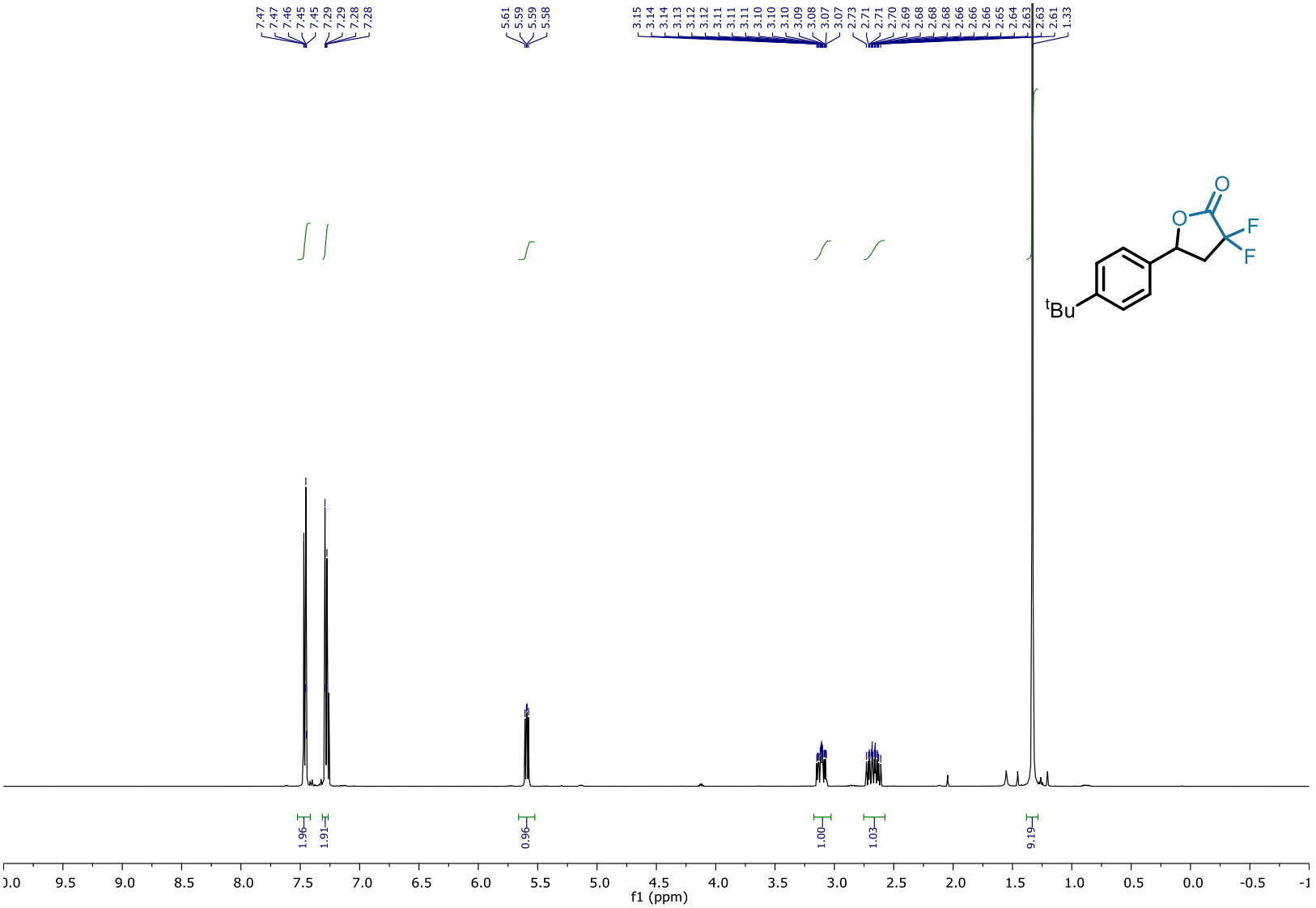
^{13}C-NMR (75 MHz, $CDCl_3$) of **36**



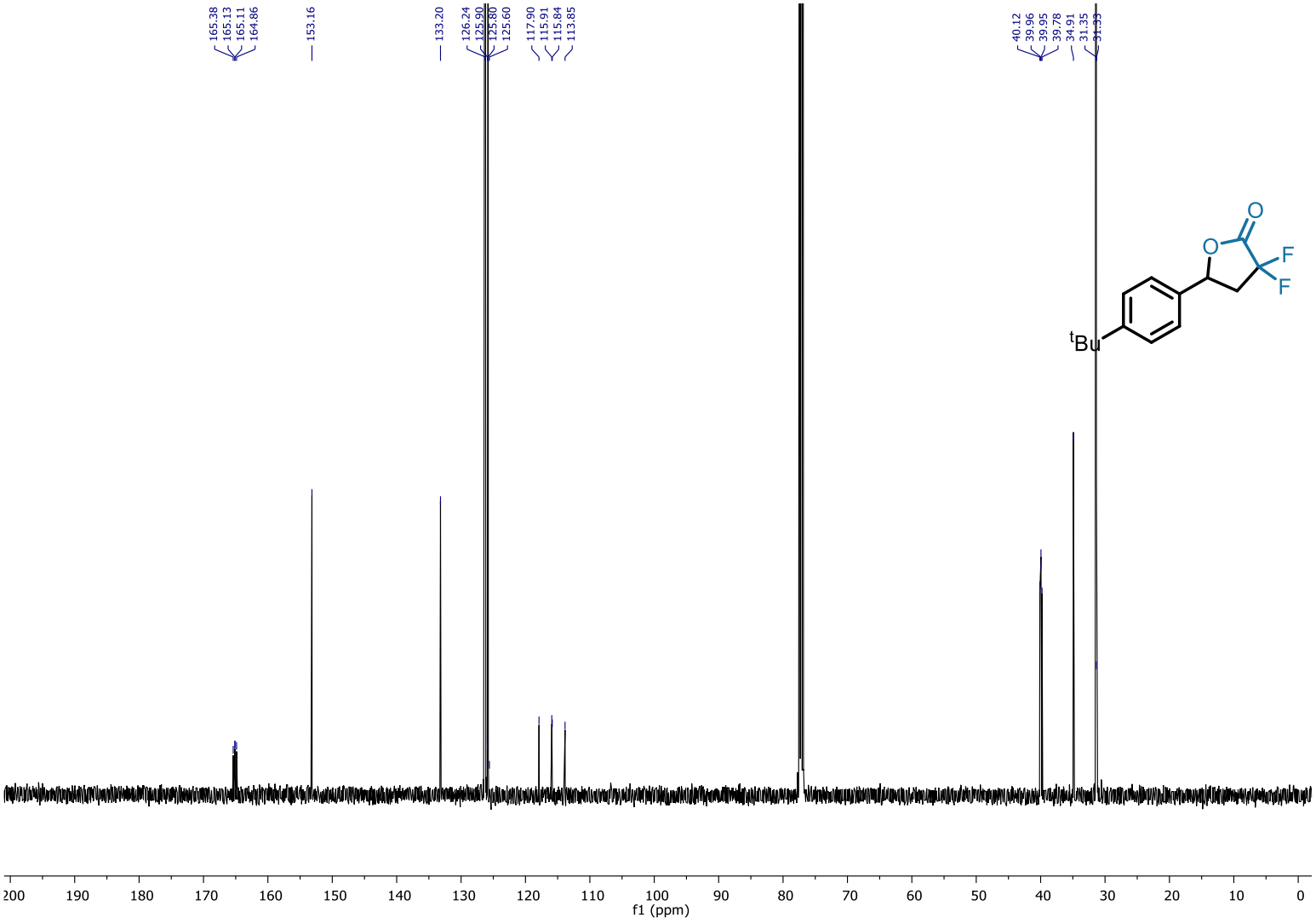
^{19}F-NMR (282 MHz, $CDCl_3$) of **36**



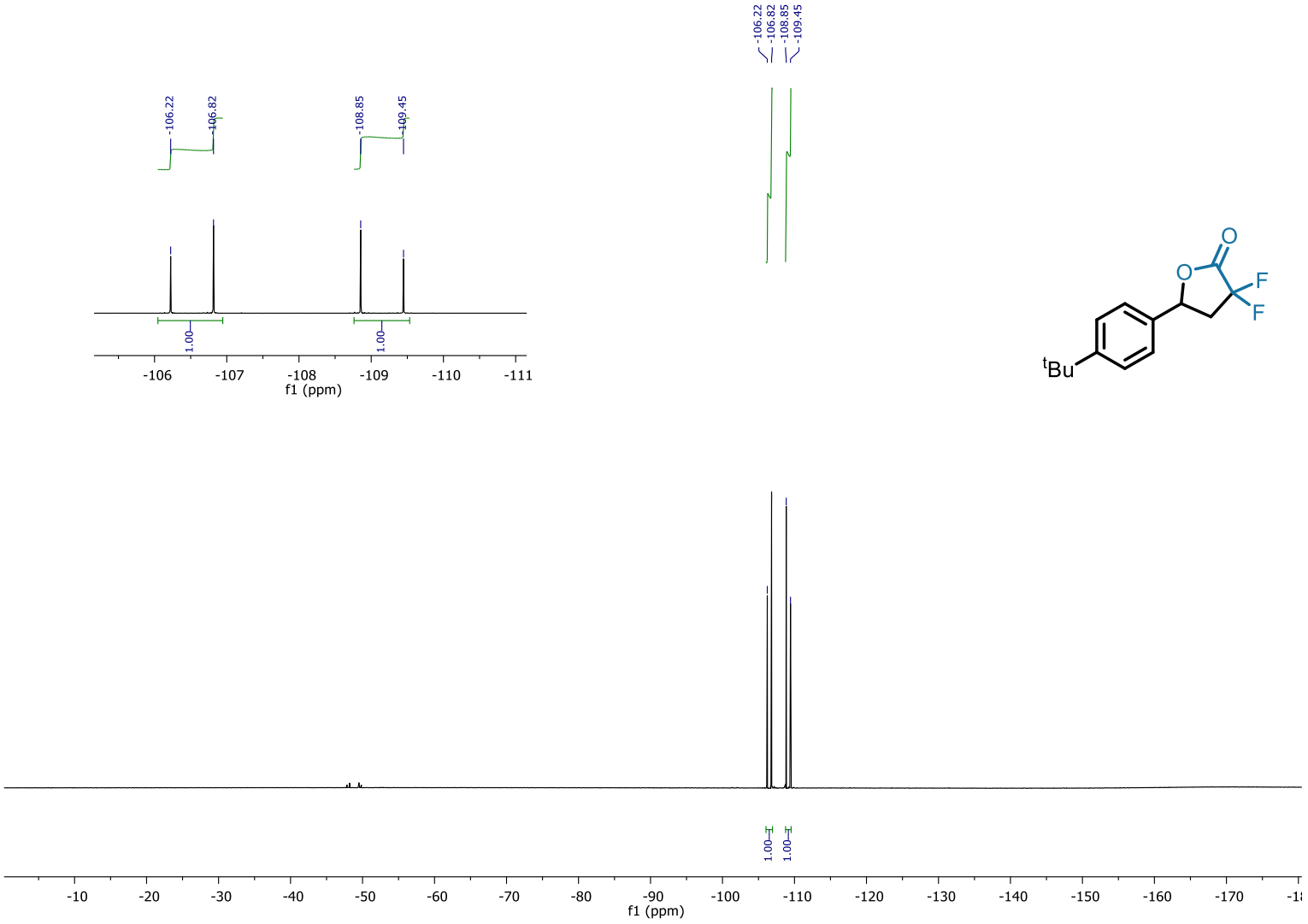
^{1}H-NMR (500 MHz, $CDCl_3$) of **2**



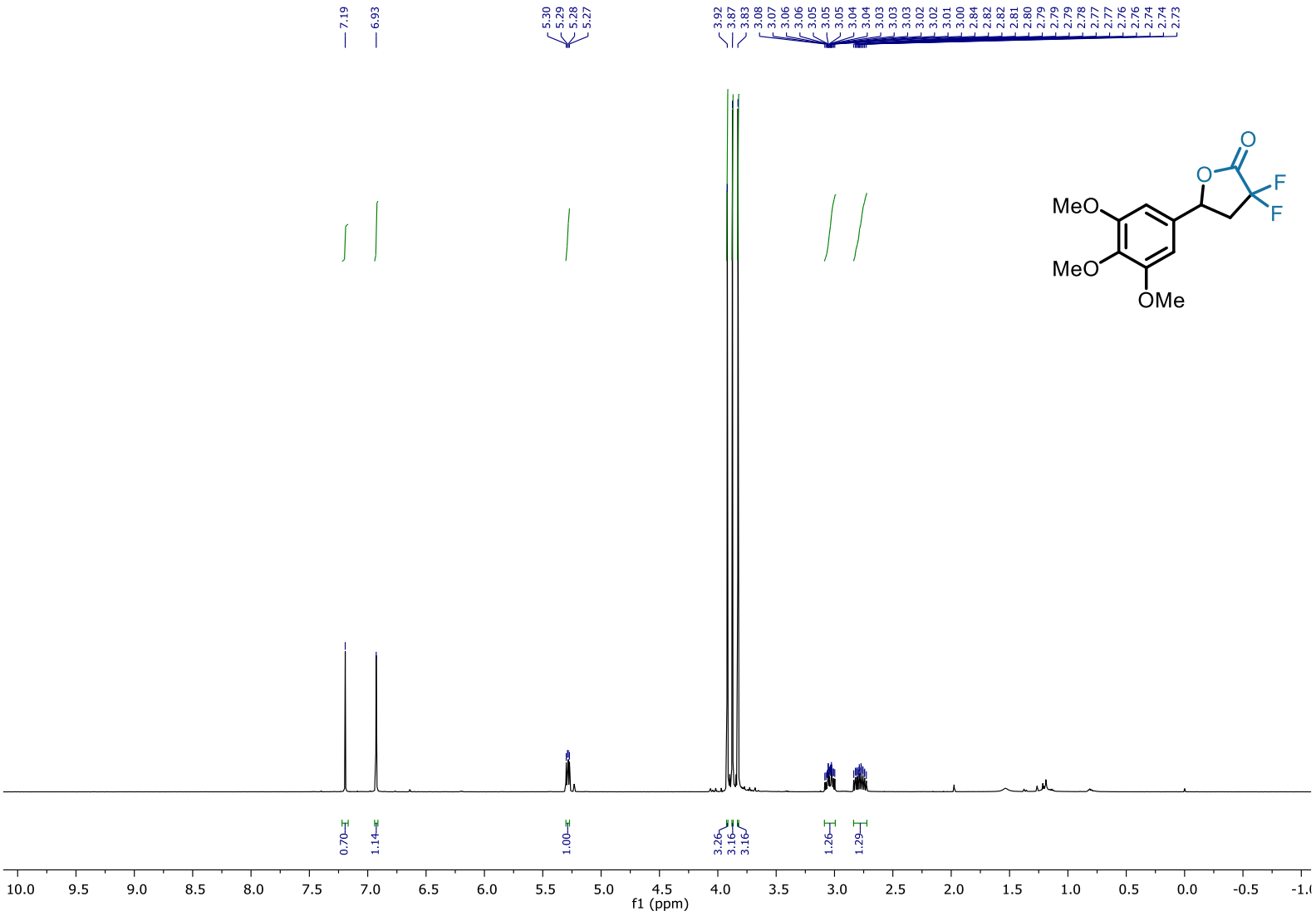
^{13}C-NMR (126 MHz, $CDCl_3$) of **2**



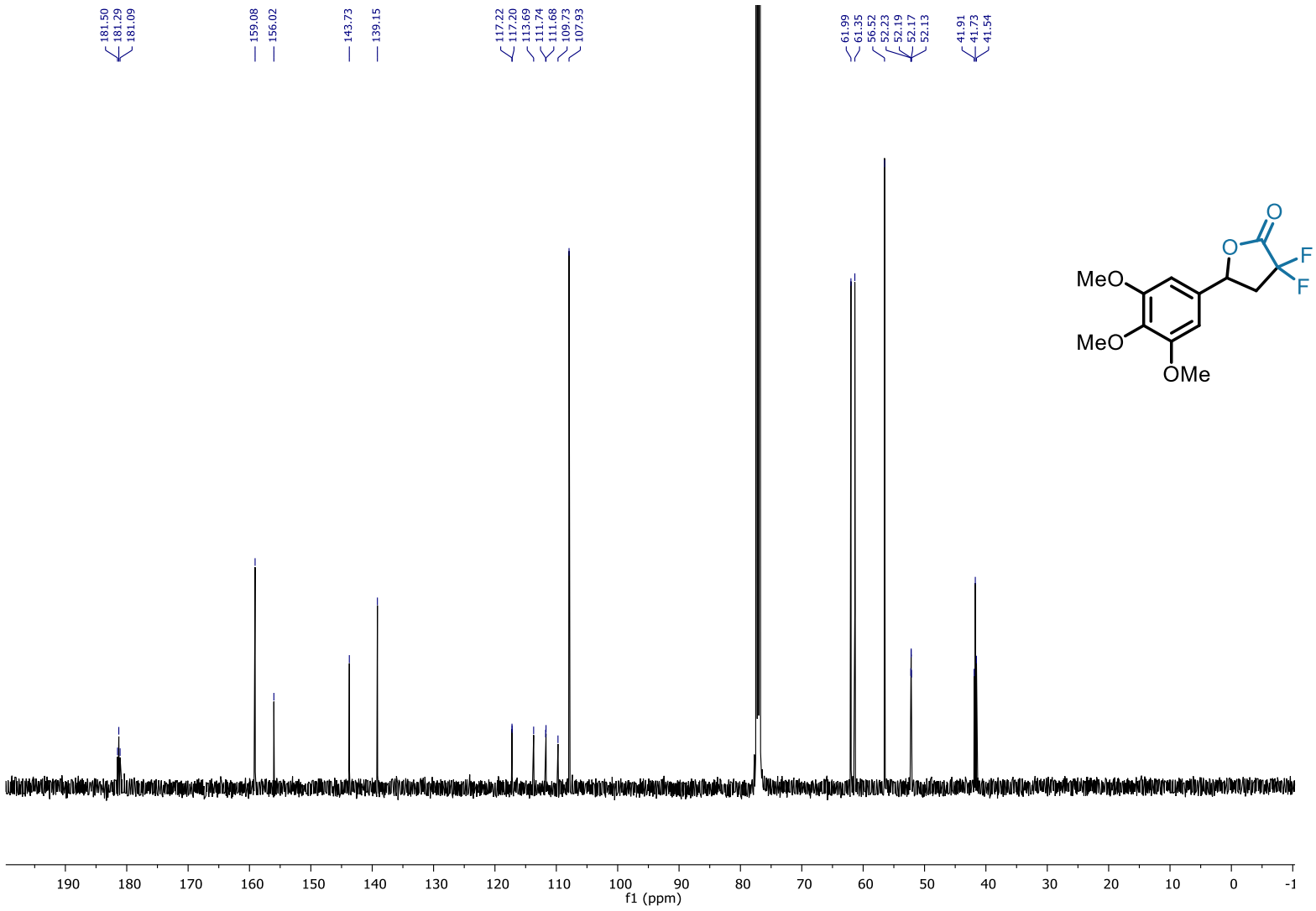
^{19}F-NMR (471 MHz, $CDCl_3$) of **2**



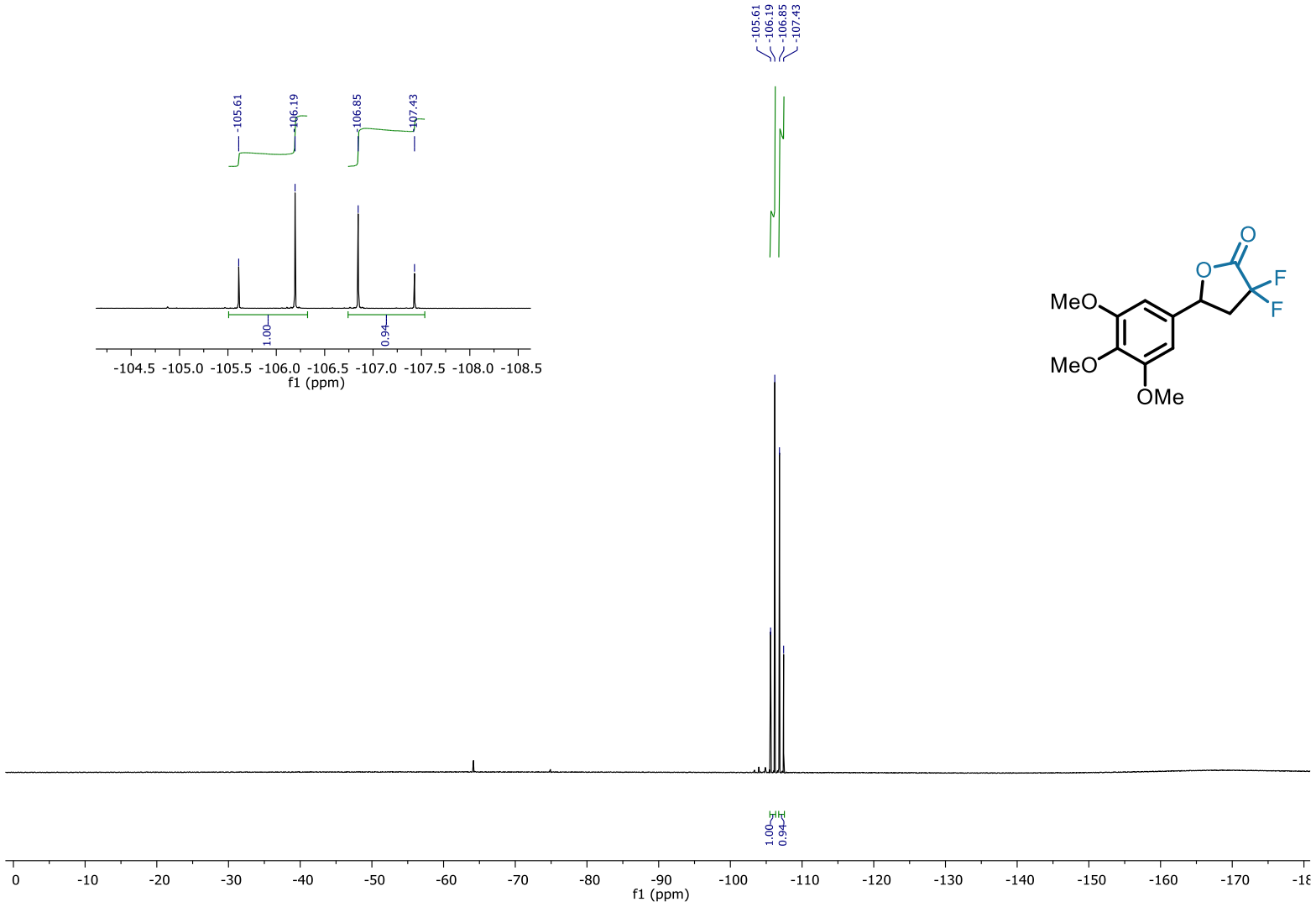
^{1}H-NMR (500 MHz, $CDCl_3$) of **37**



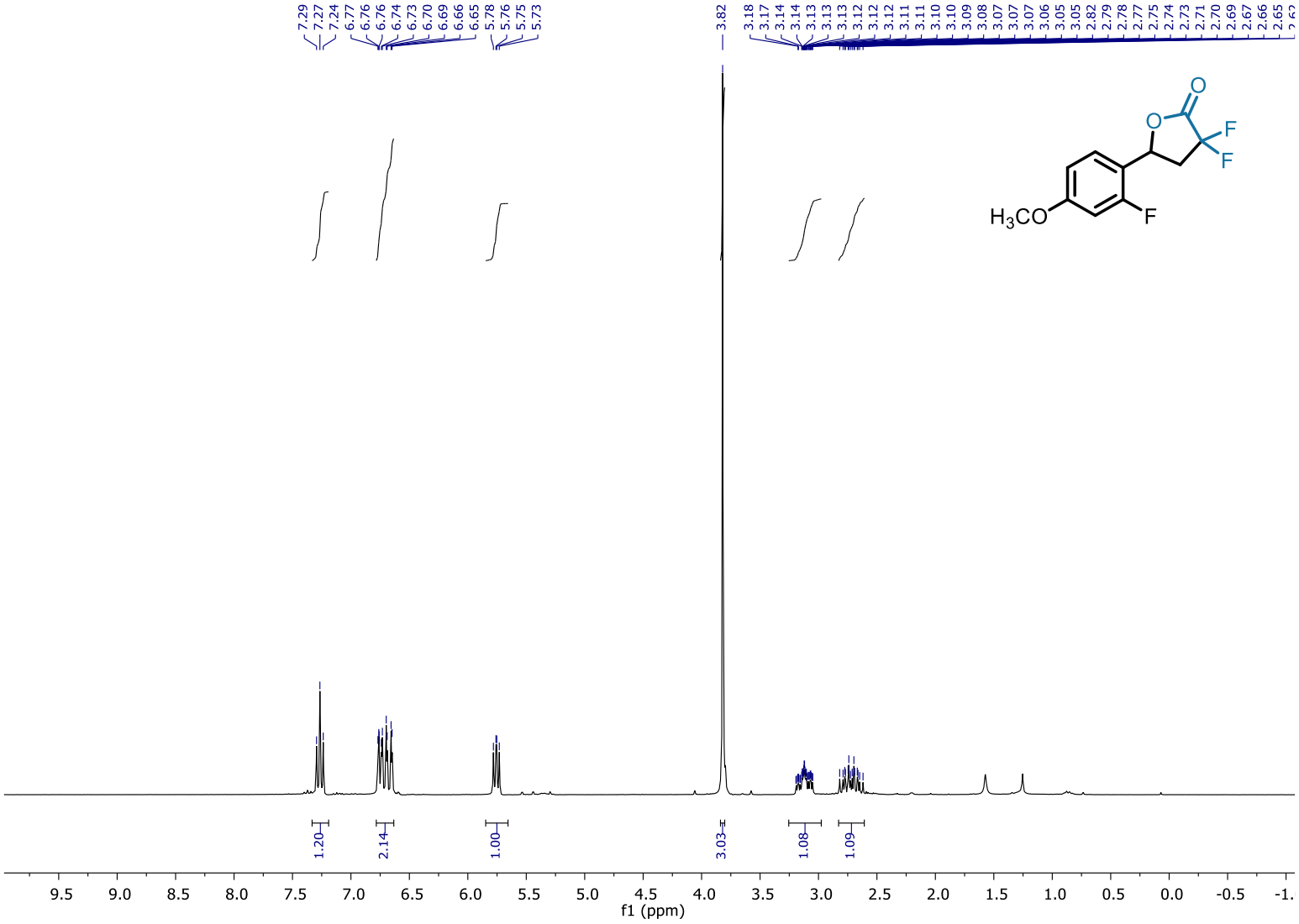
^{13}C-NMR (126 MHz, $CDCl_3$) of **37**



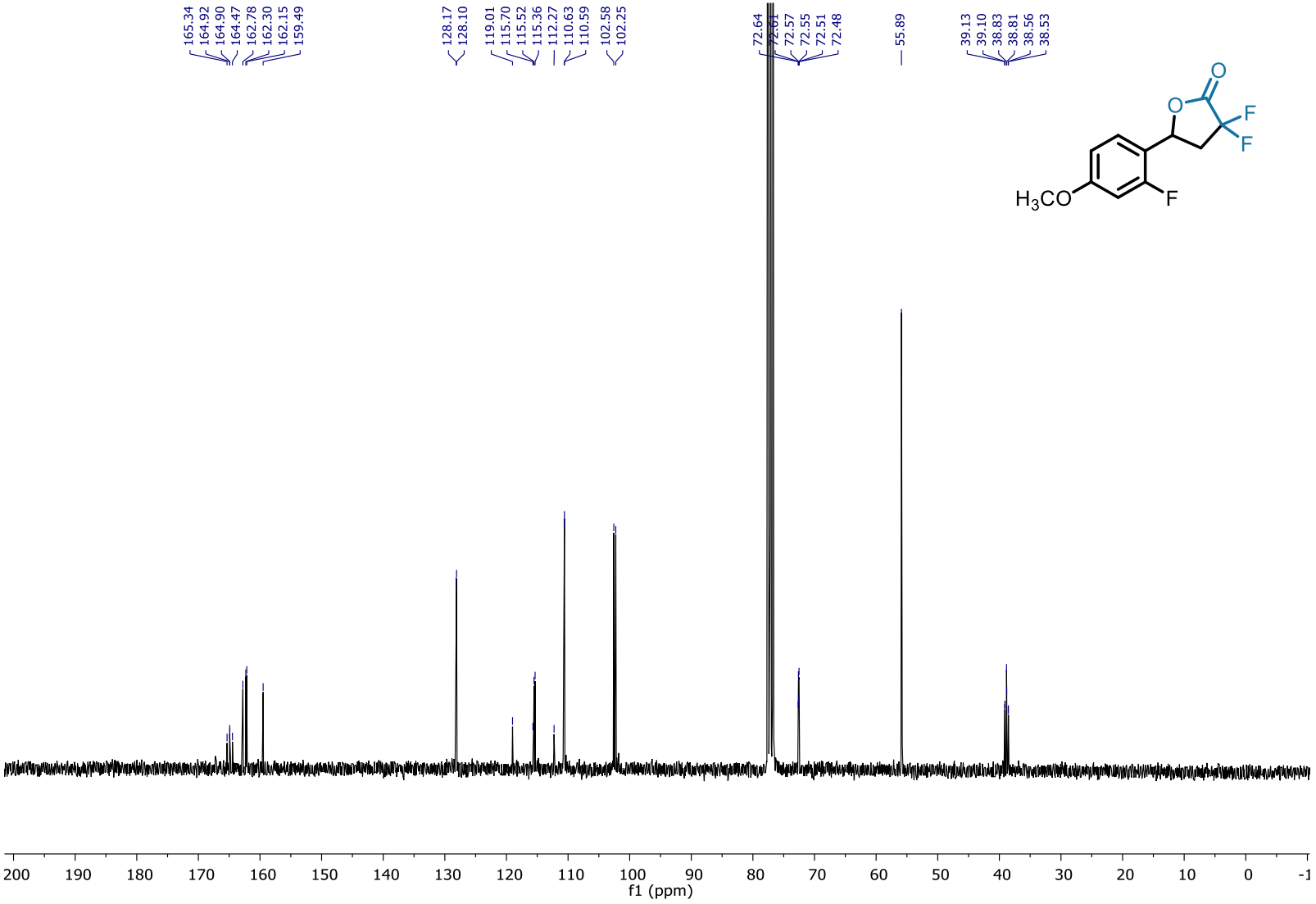
^{19}F-NMR (471 MHz, $CDCl_3$) of **37**



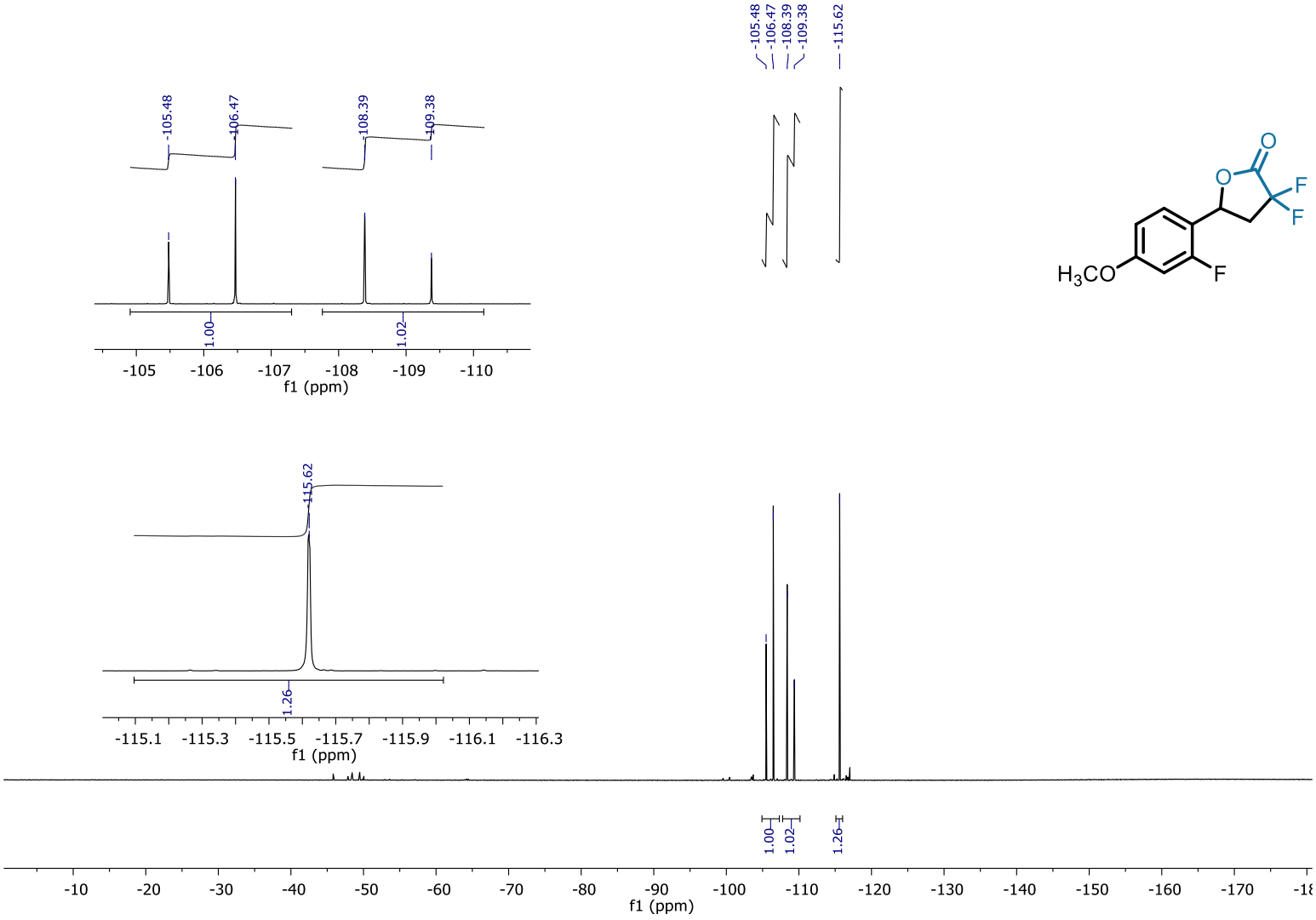
^{1}H-NMR (300 MHz, $CDCl_3$) of **38**



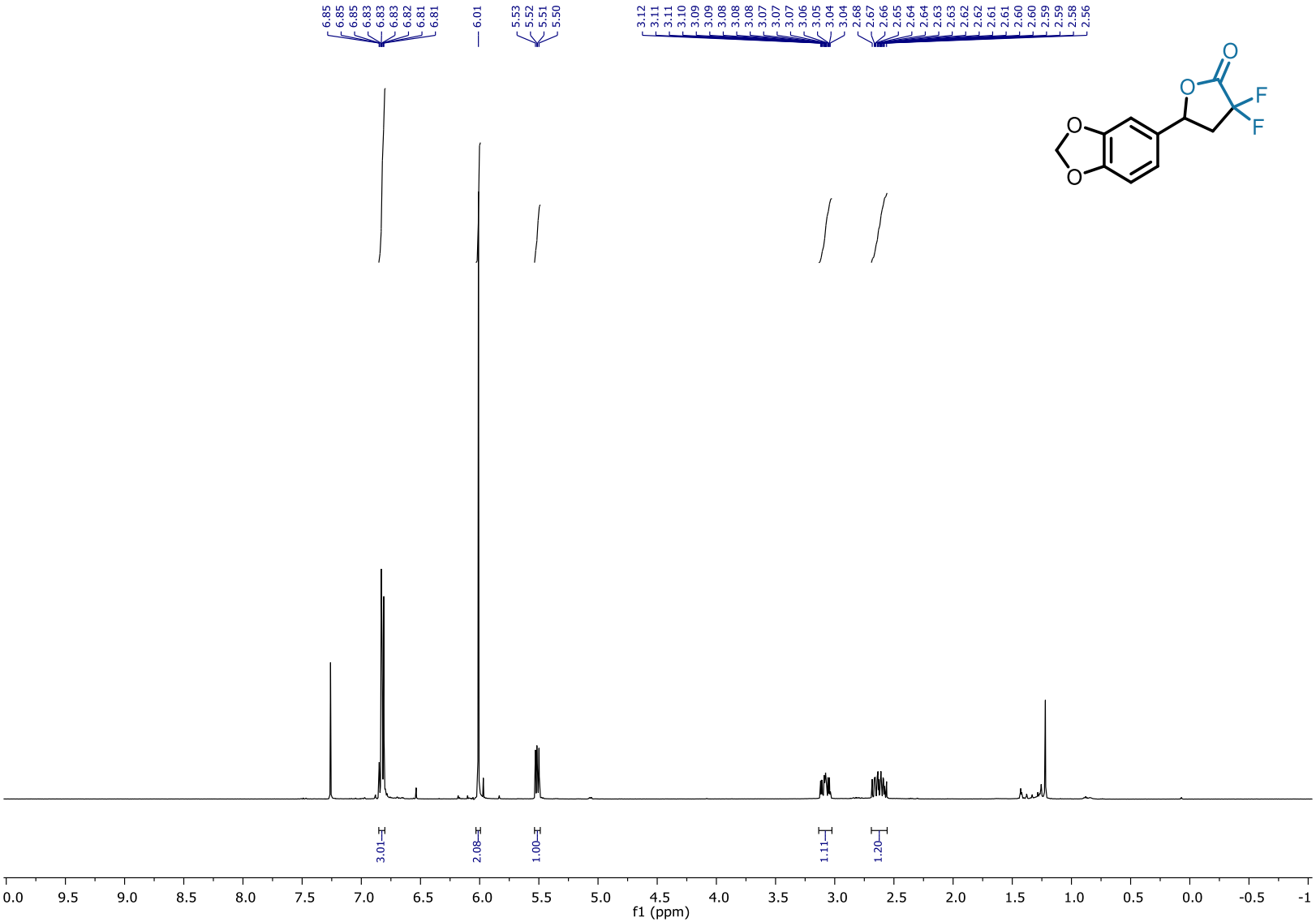
^{13}C-NMR (75 MHz, $CDCl_3$) of **38**



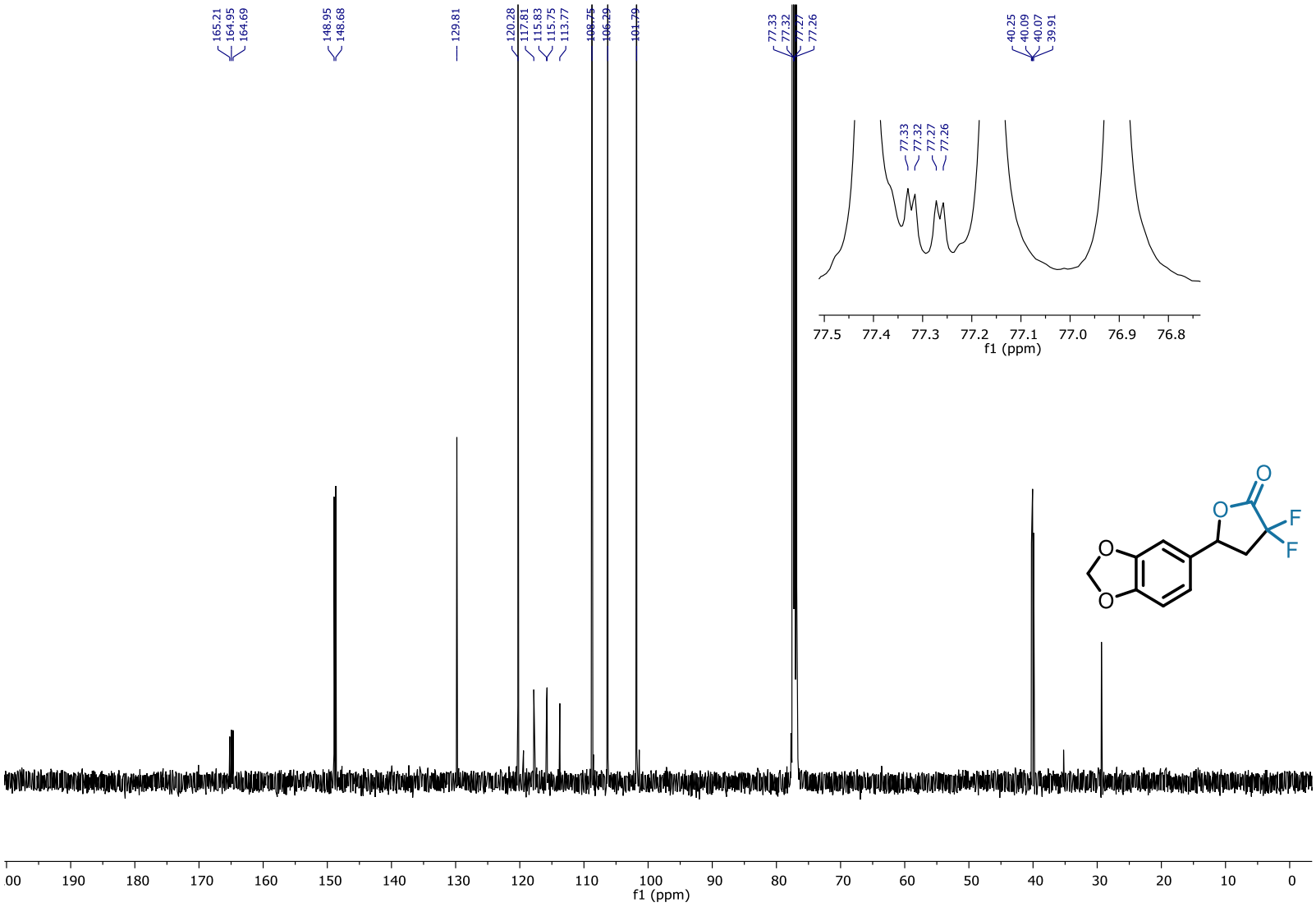
^{19}F-NMR (282 MHz, $CDCl_3$) of **38**



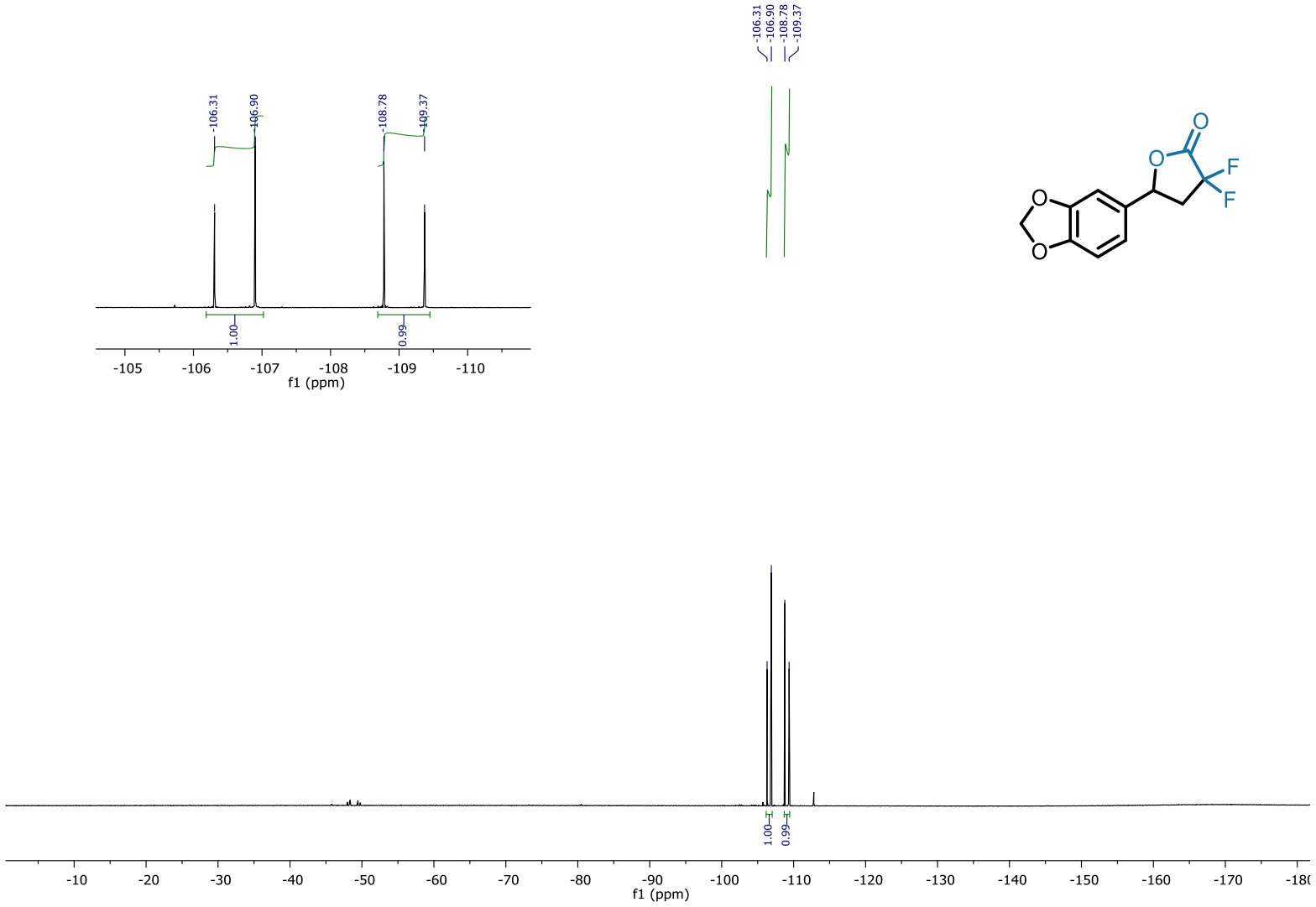
^{1}H-NMR (500 MHz, $CDCl_3$) of **39**



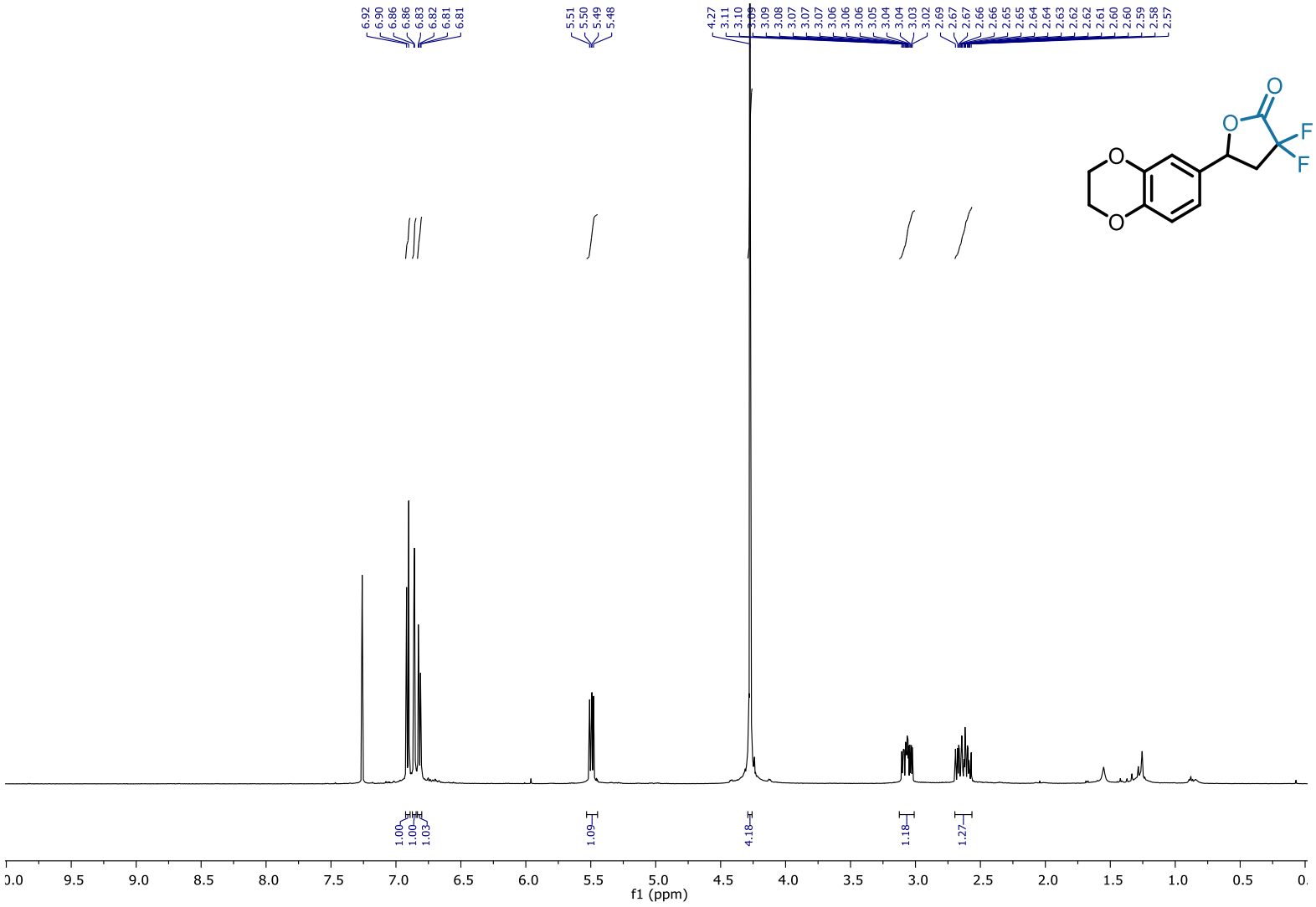
^{13}C-NMR (126 MHz, $CDCl_3$) of **39**



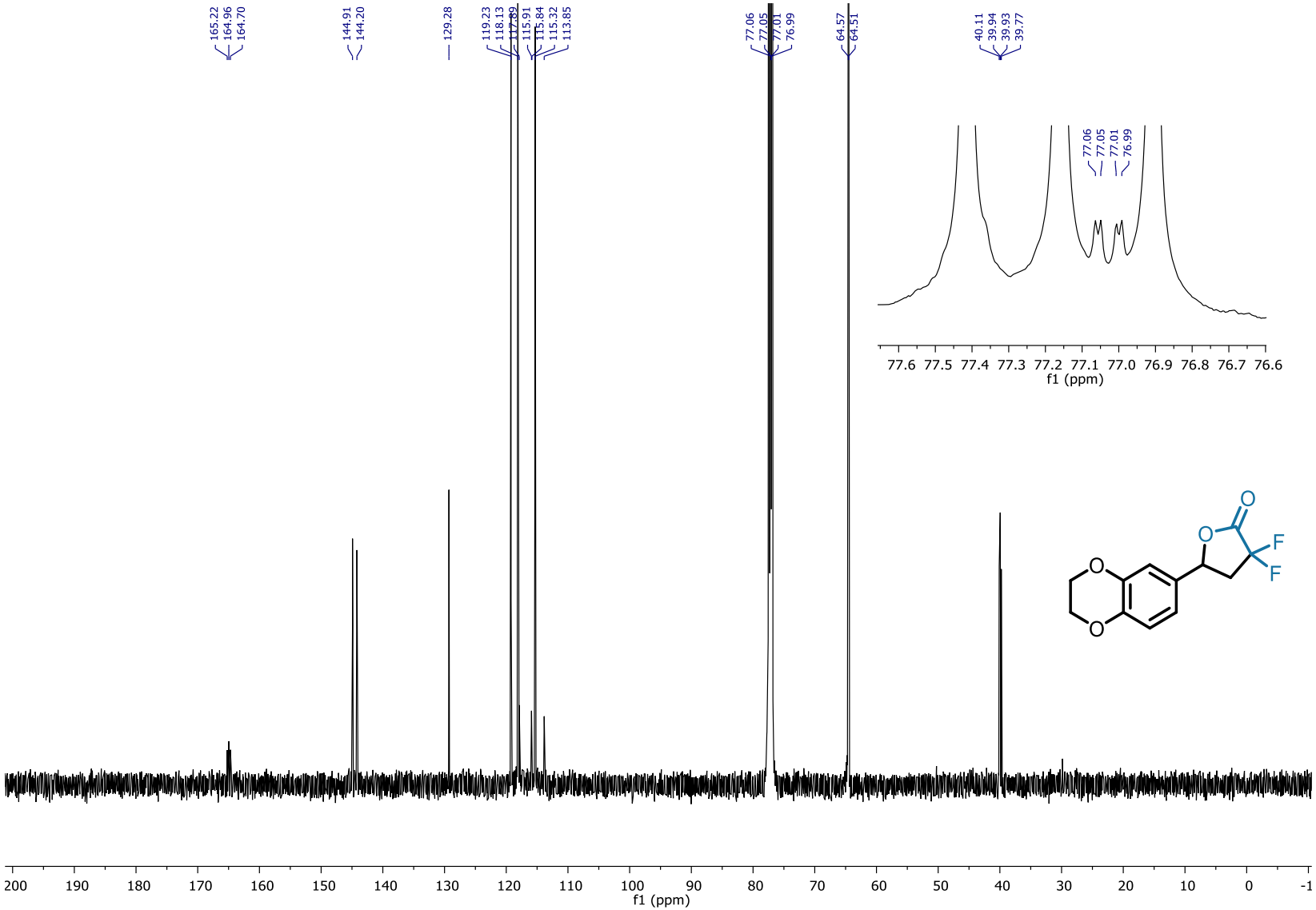
^{19}F-NMR (471 MHz, $CDCl_3$) of **39**



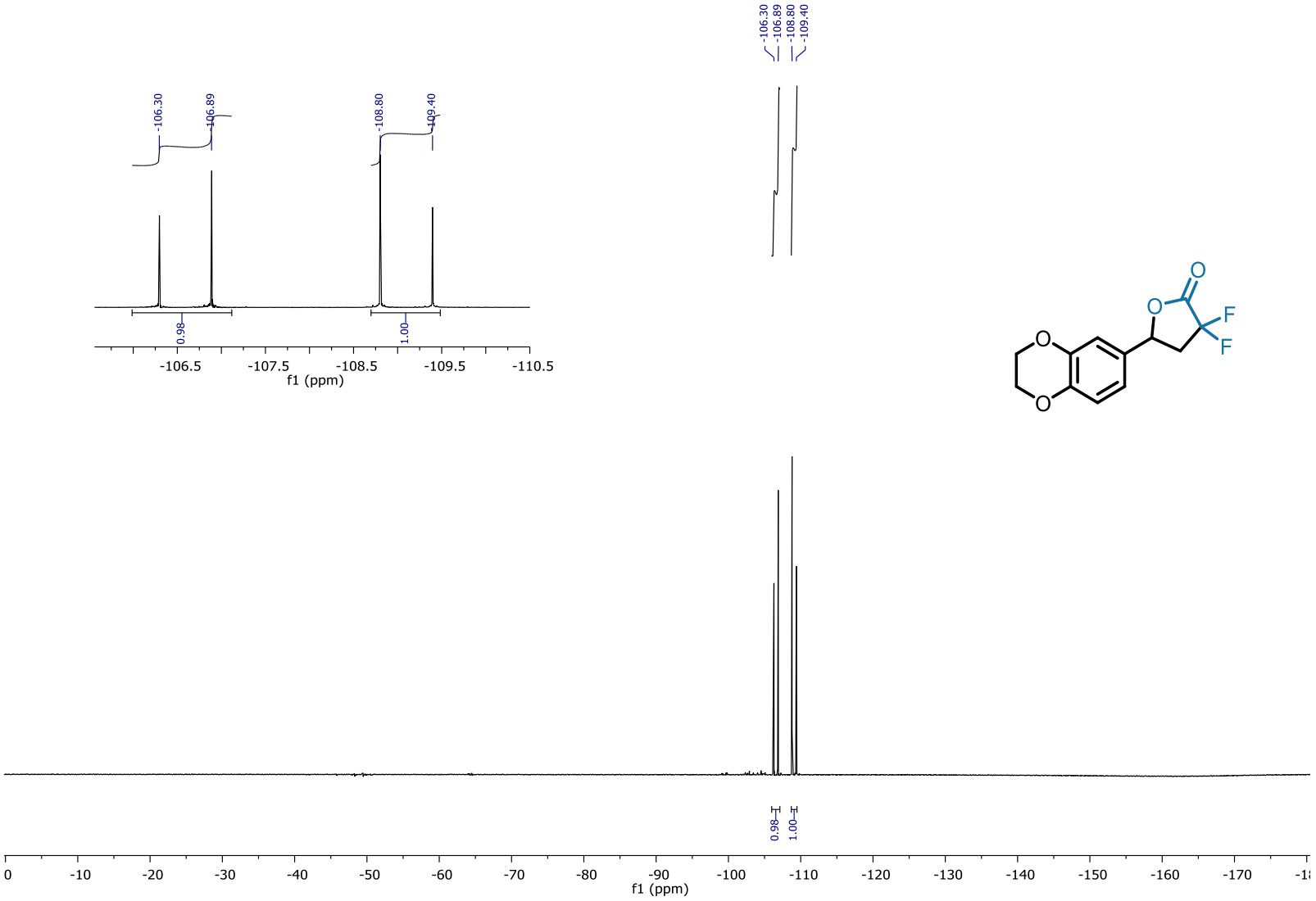
^{1}H-NMR (500 MHz, $CDCl_3$) of **40**



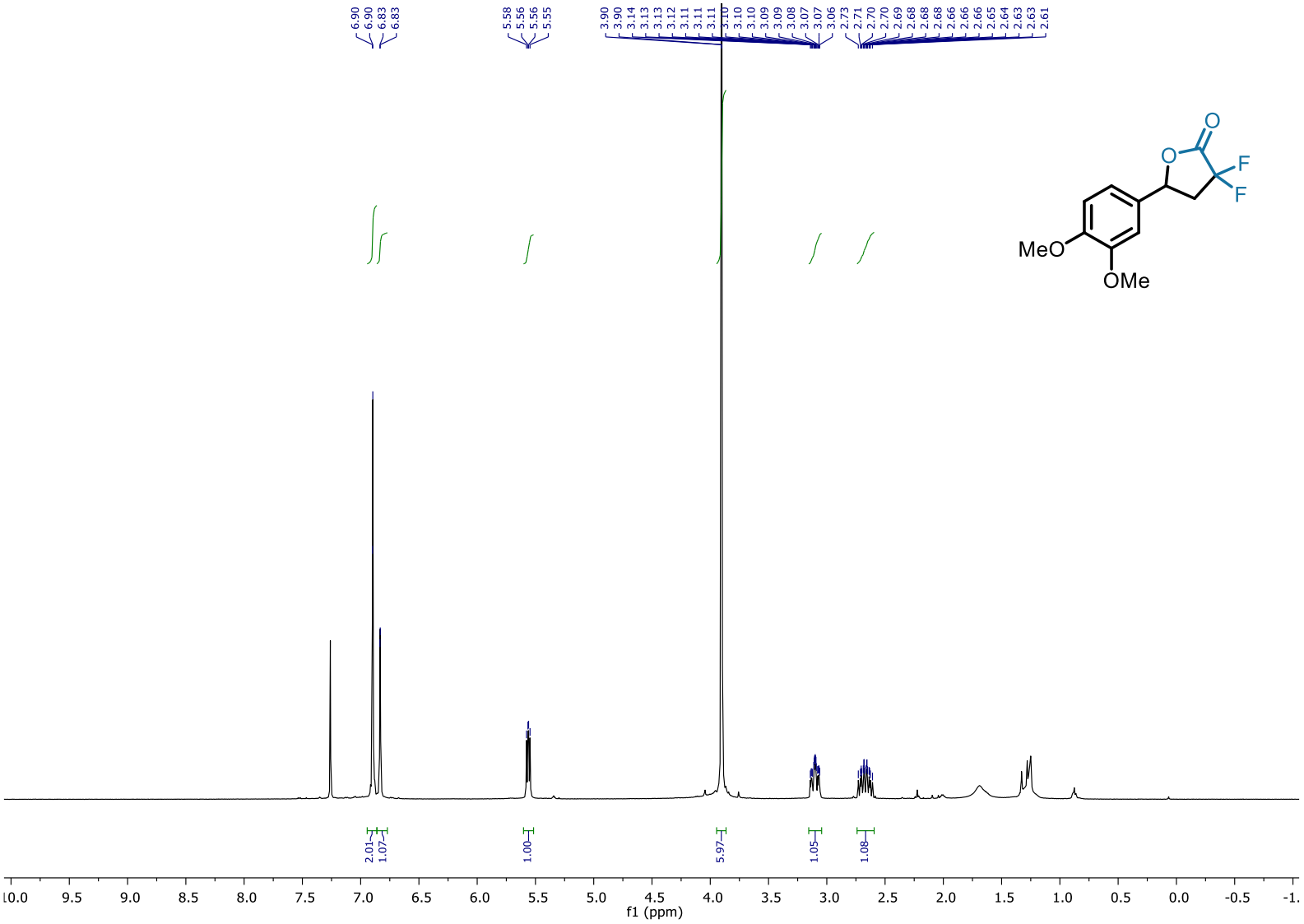
^{13}C-NMR (126 MHz, $CDCl_3$) of **40**



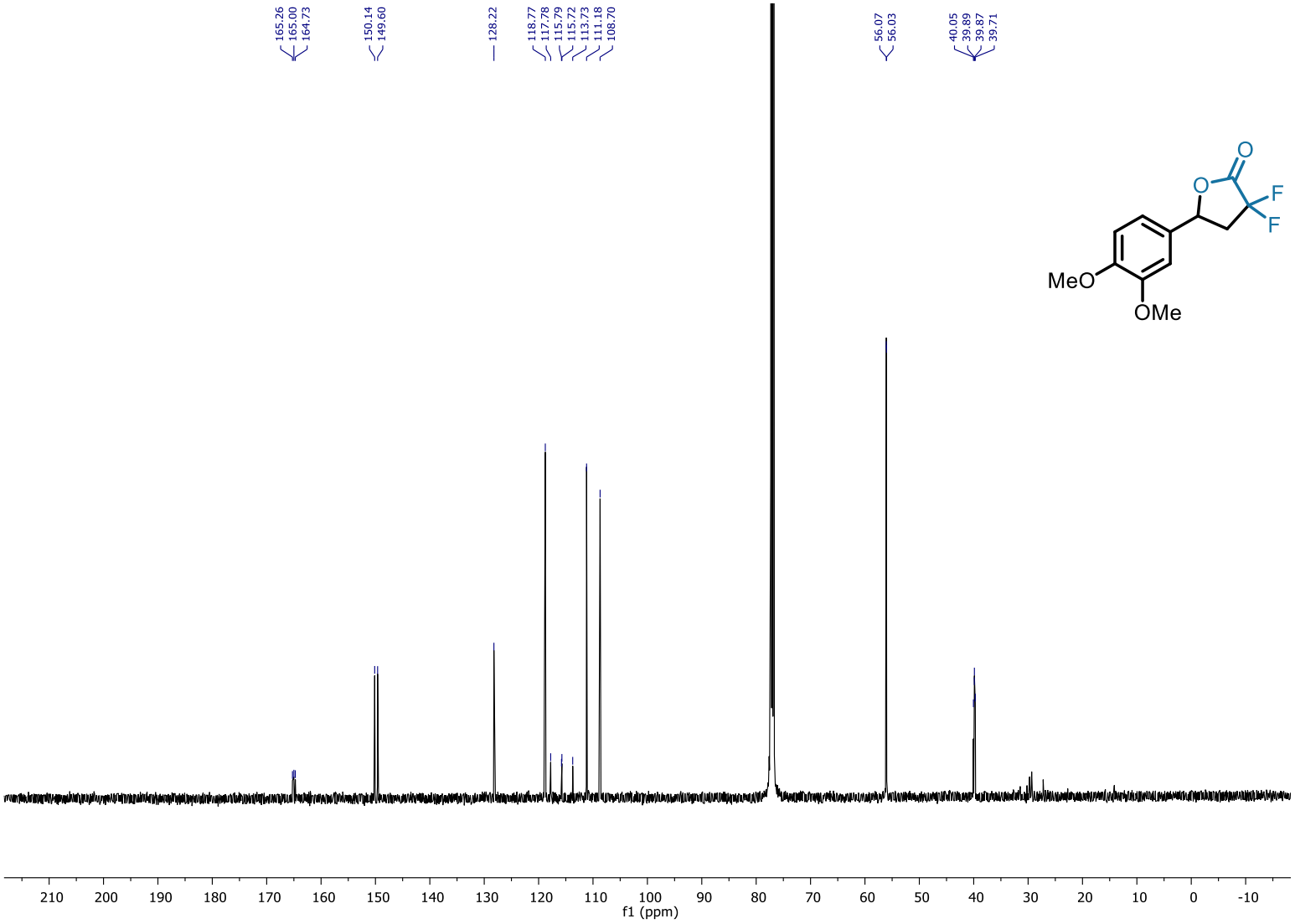
^{19}F-NMR (471 MHz, $CDCl_3$) of **40**



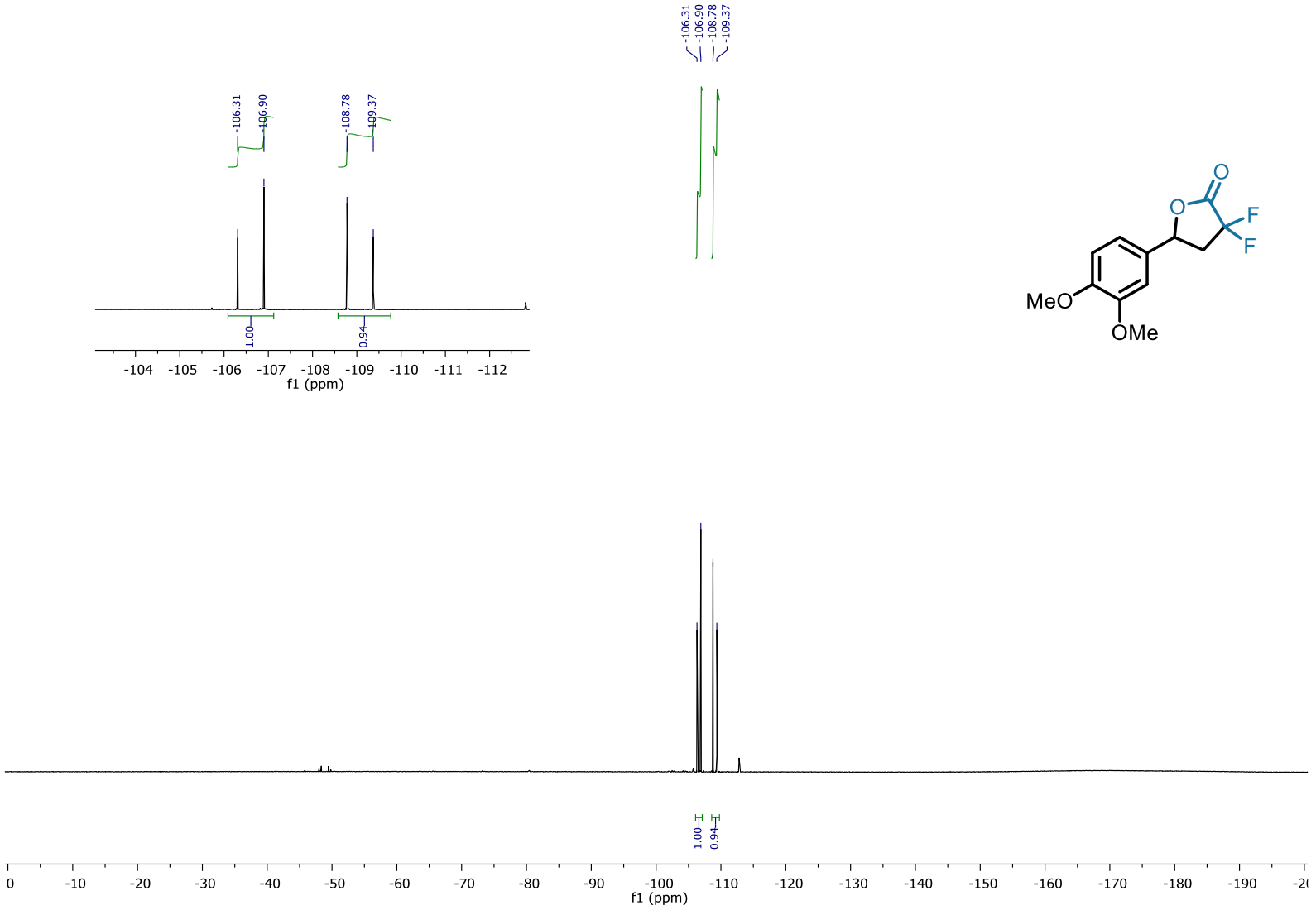
^{1}H-NMR (500 MHz, $CDCl_3$) of **41**



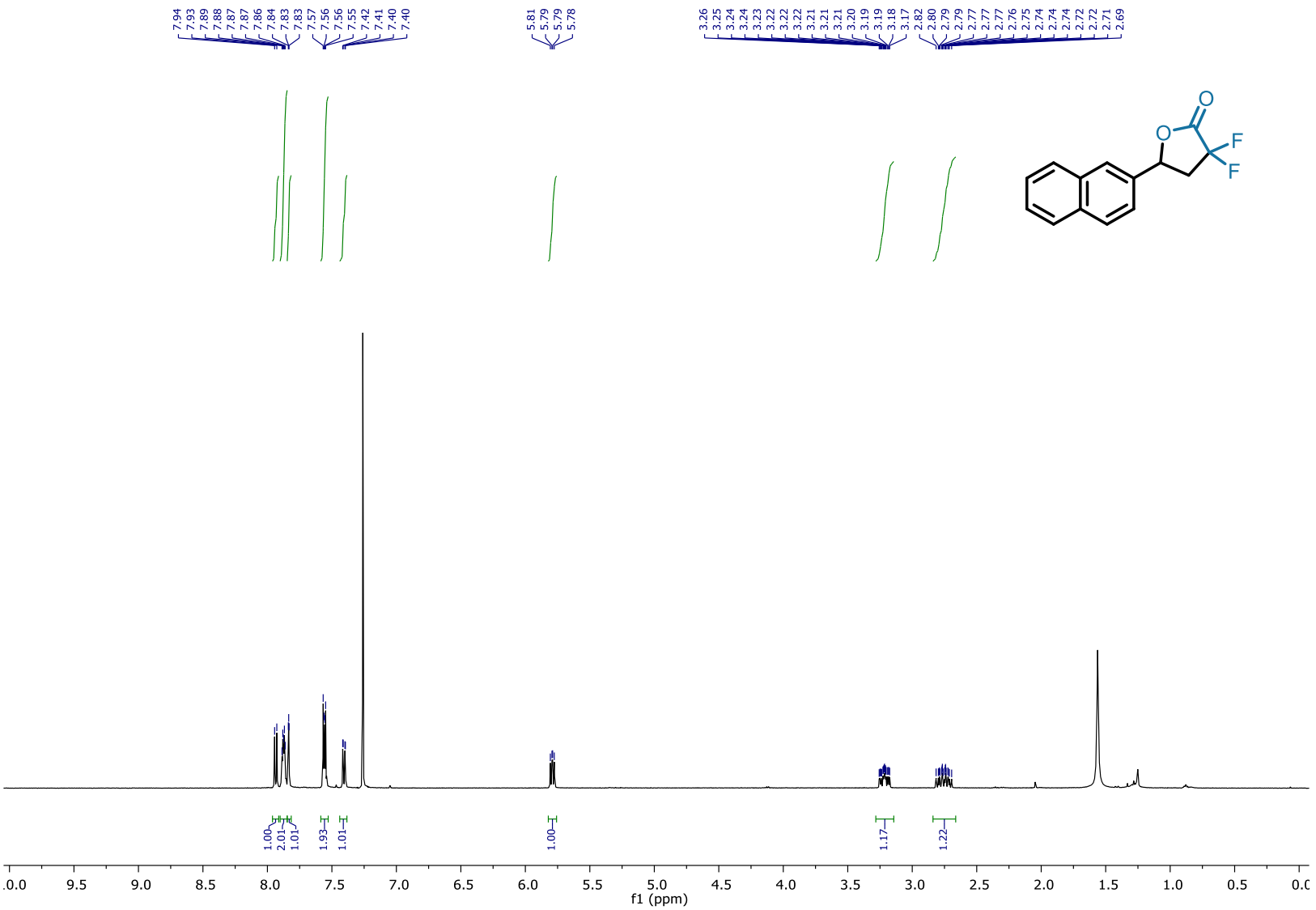
^{13}C-NMR (126 MHz, $CDCl_3$) of **41**



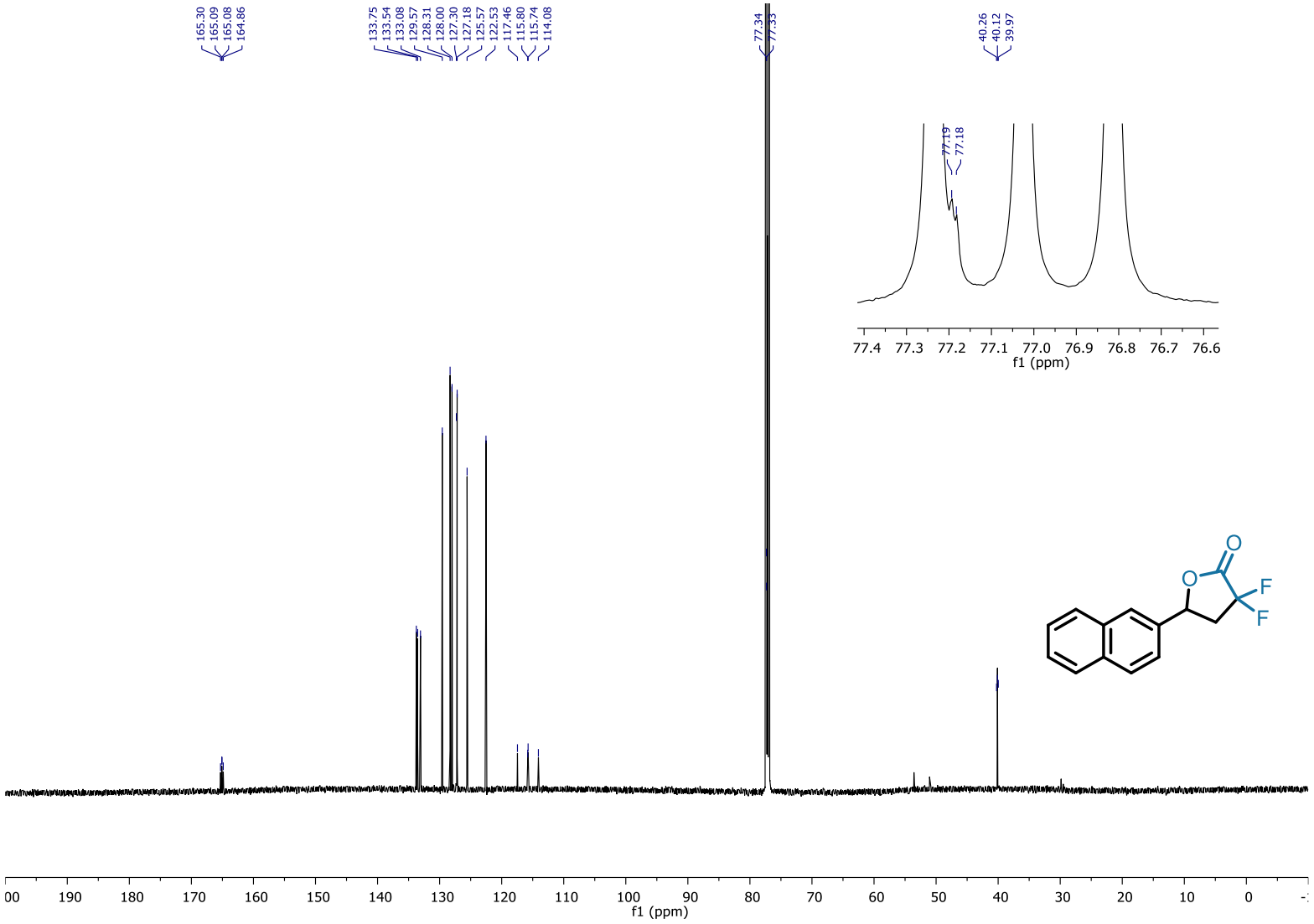
^{19}F-NMR (471 MHz, $CDCl_3$) of **41**



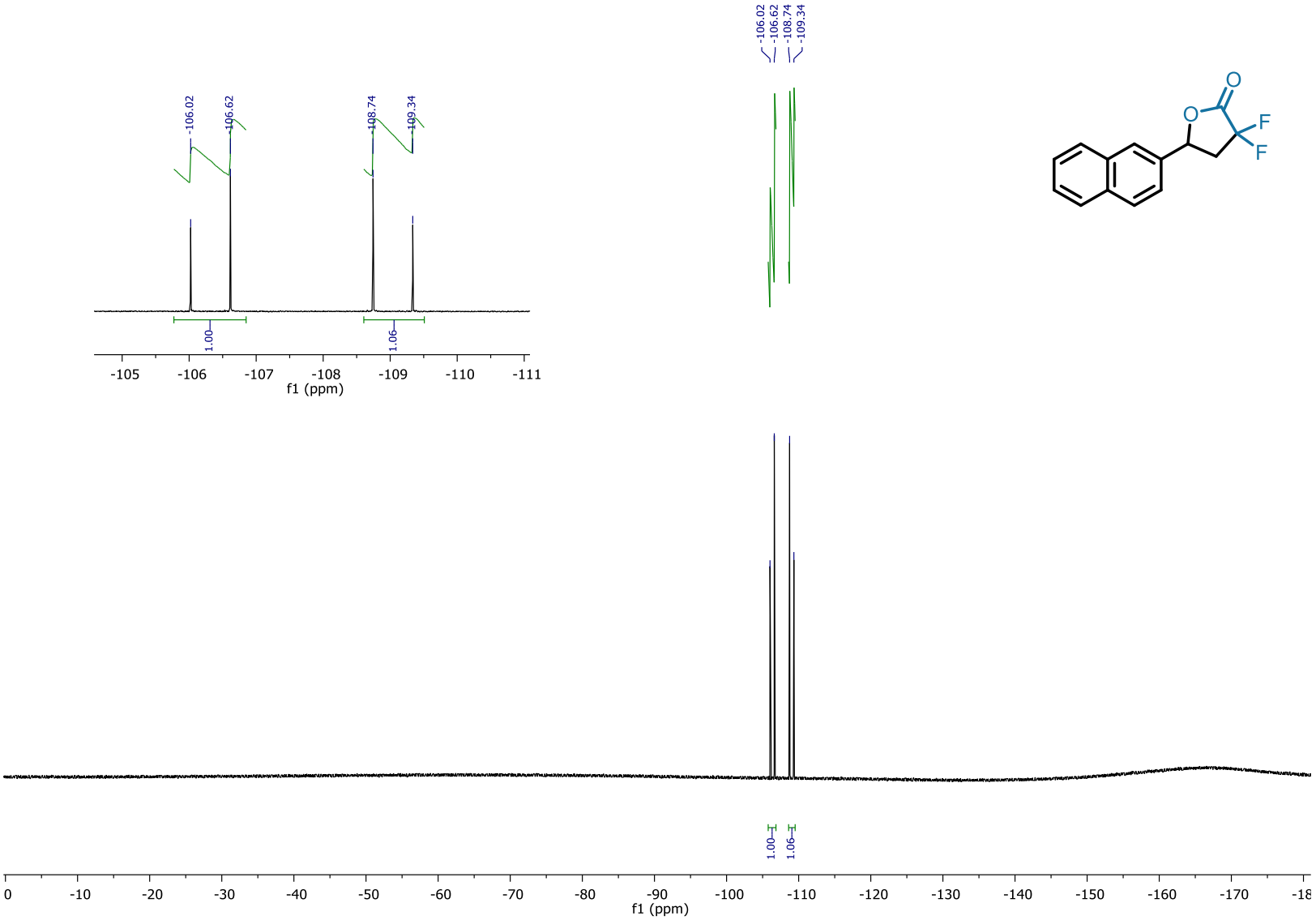
^{1}H-NMR (500 MHz, $CDCl_3$) of **42**



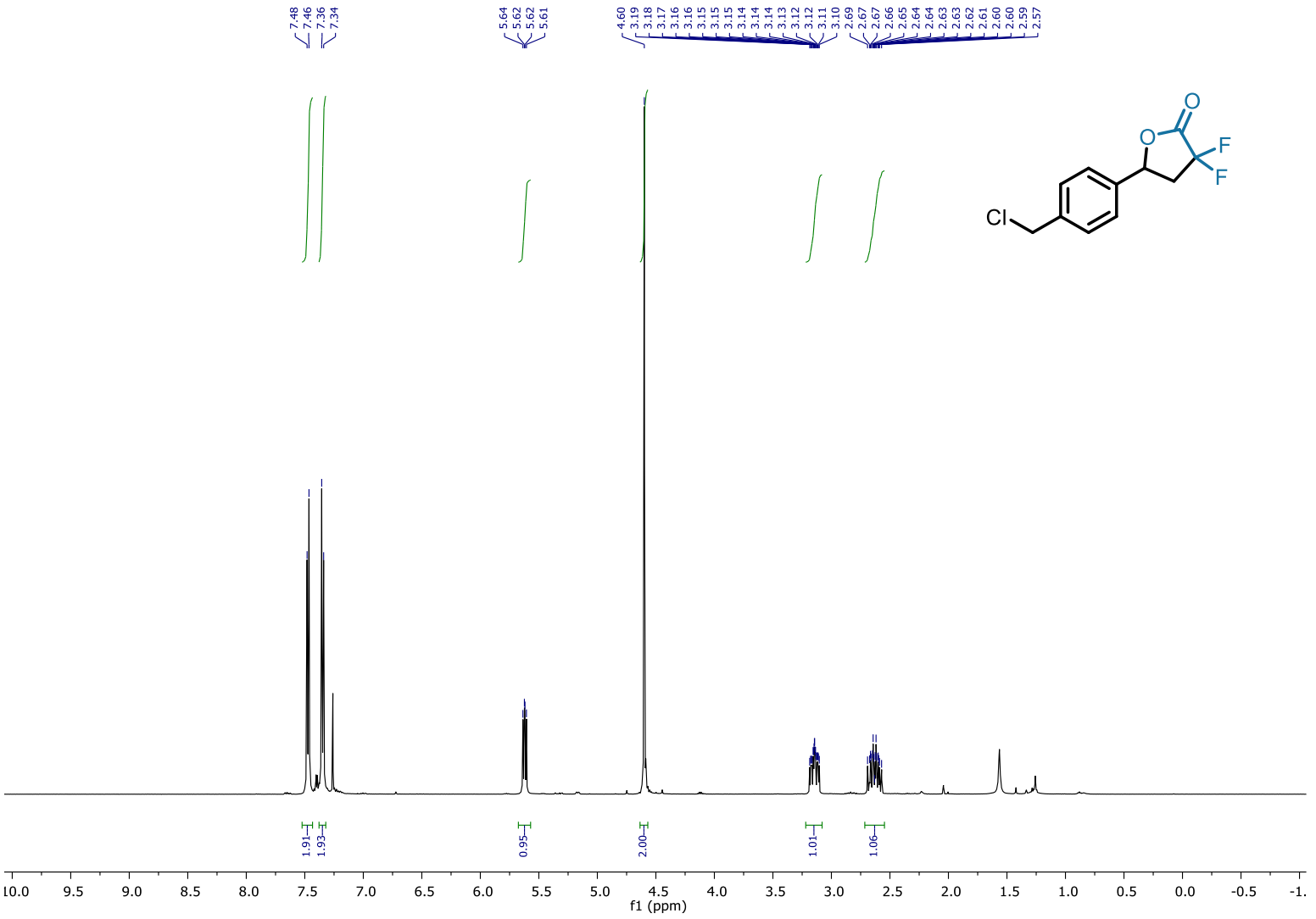
^{13}C-NMR (151 MHz, $CDCl_3$) of **42**



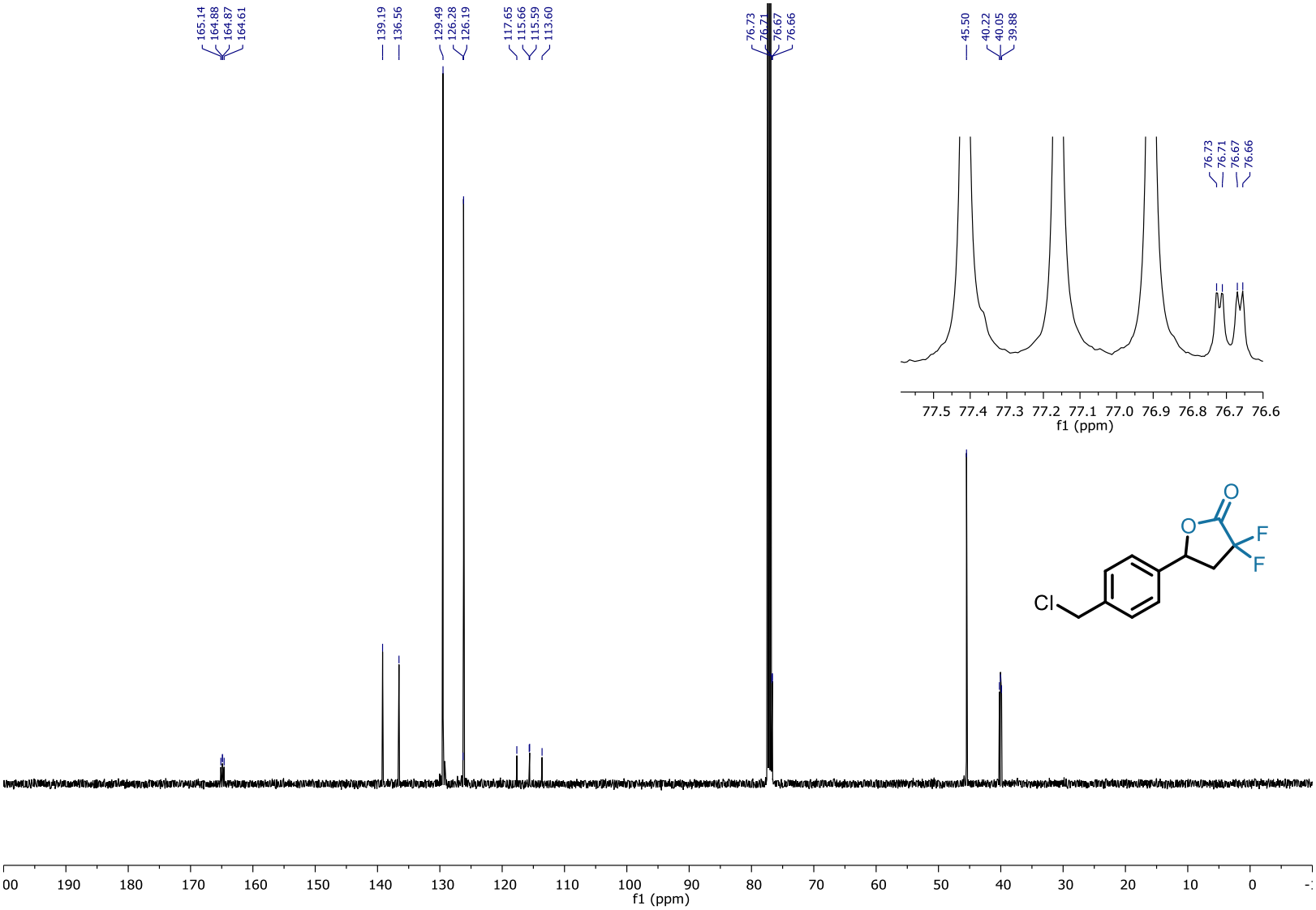
^{19}F-NMR (471 MHz, $CDCl_3$) of **42**



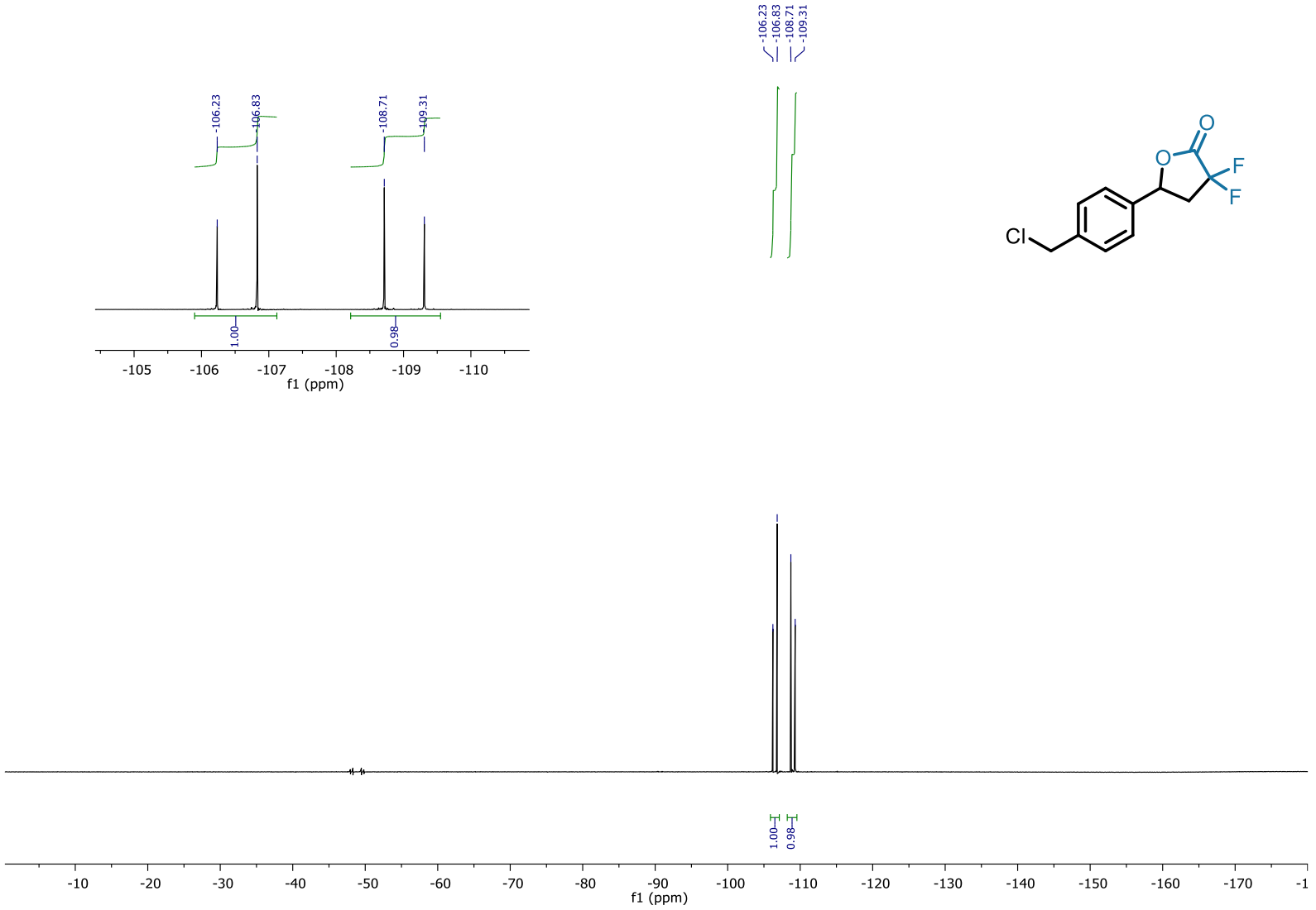
^{1}H-NMR (500 MHz, $CDCl_3$) of **43**



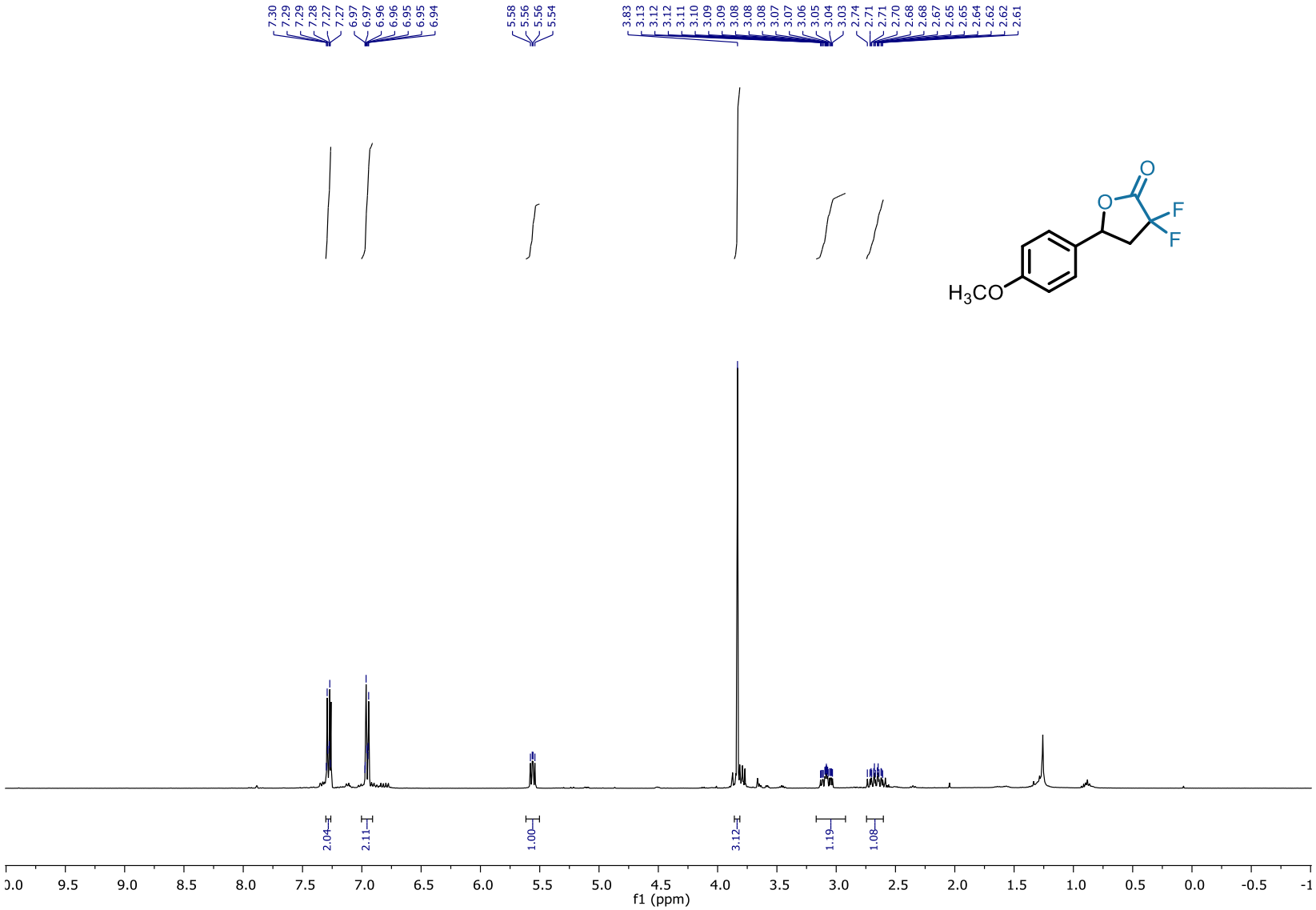
^{13}C-NMR (126 MHz, $CDCl_3$) of **43**



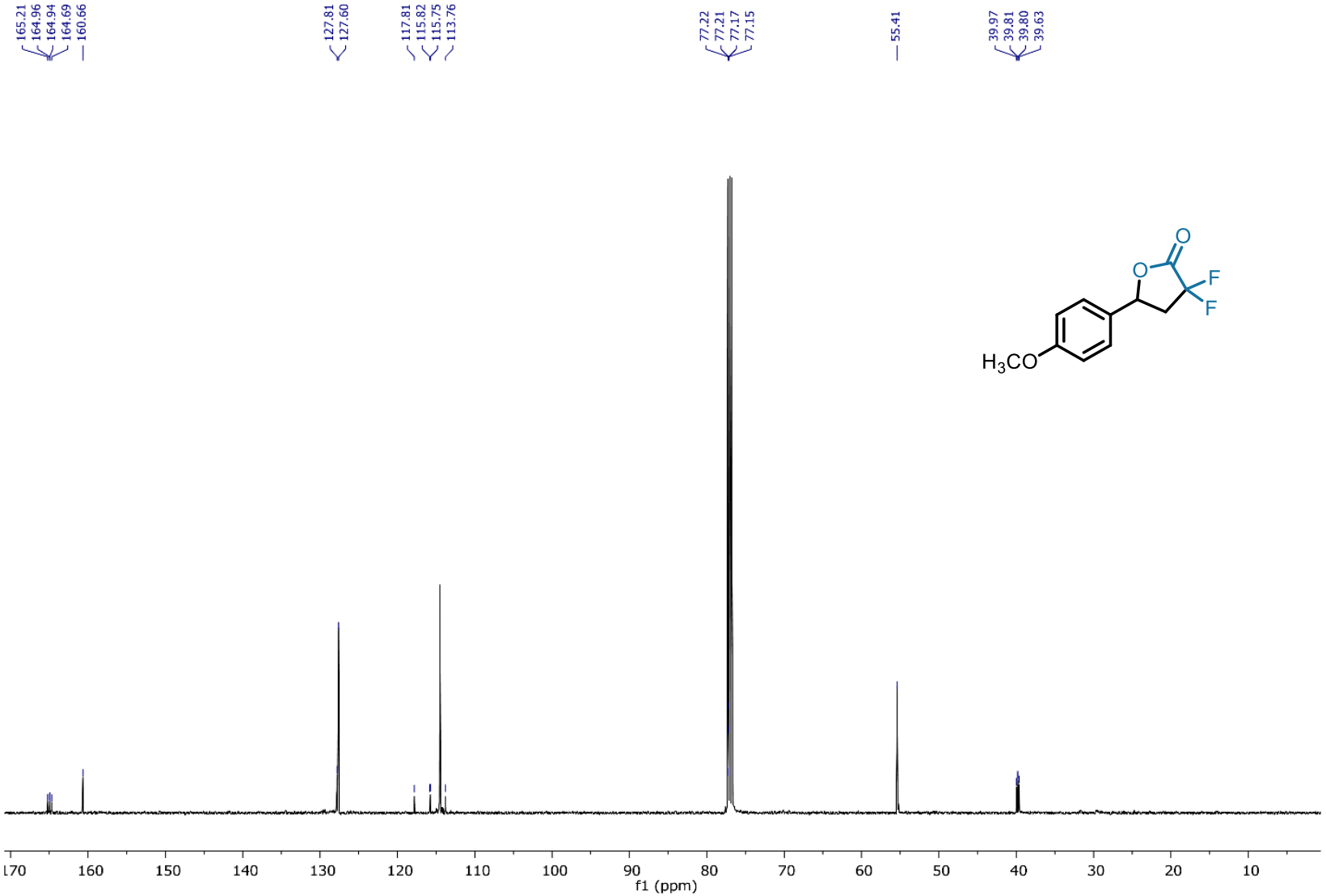
^{19}F-NMR (471 MHz, $CDCl_3$) of **43**



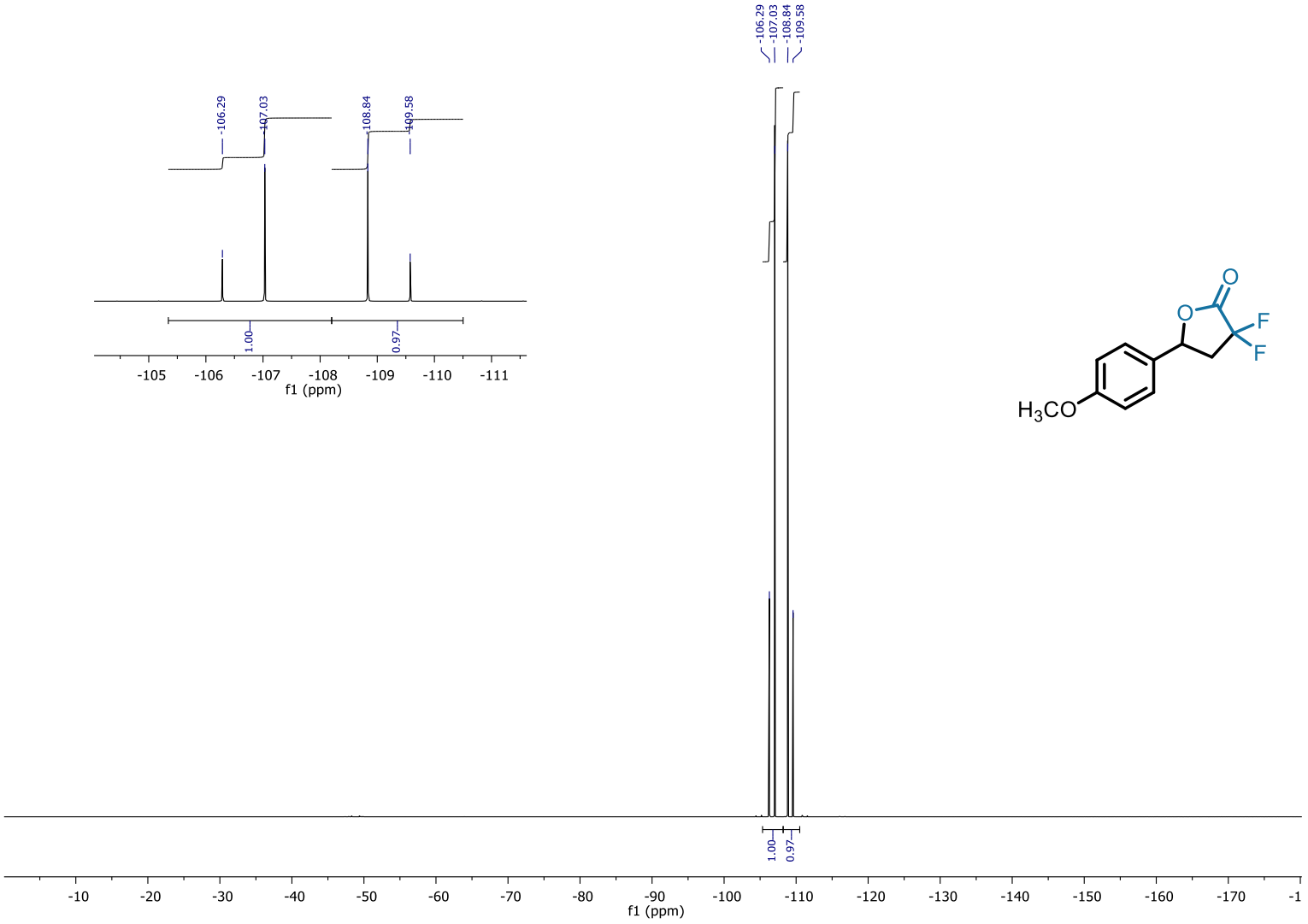
^{1}H-NMR (300 MHz, $CDCl_3$) of **44**



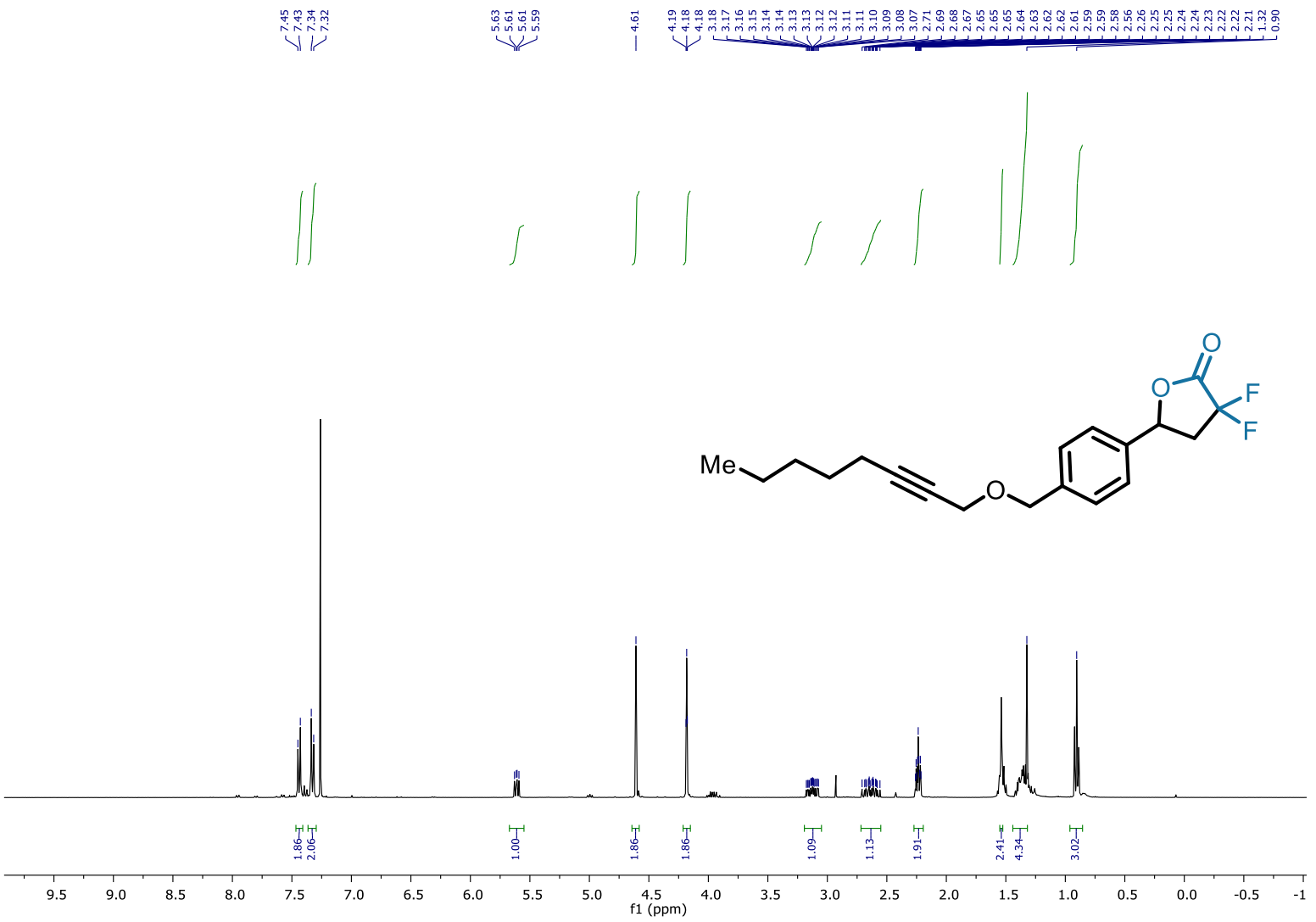
^{13}C-NMR (101 MHz, $CDCl_3$) of **44**



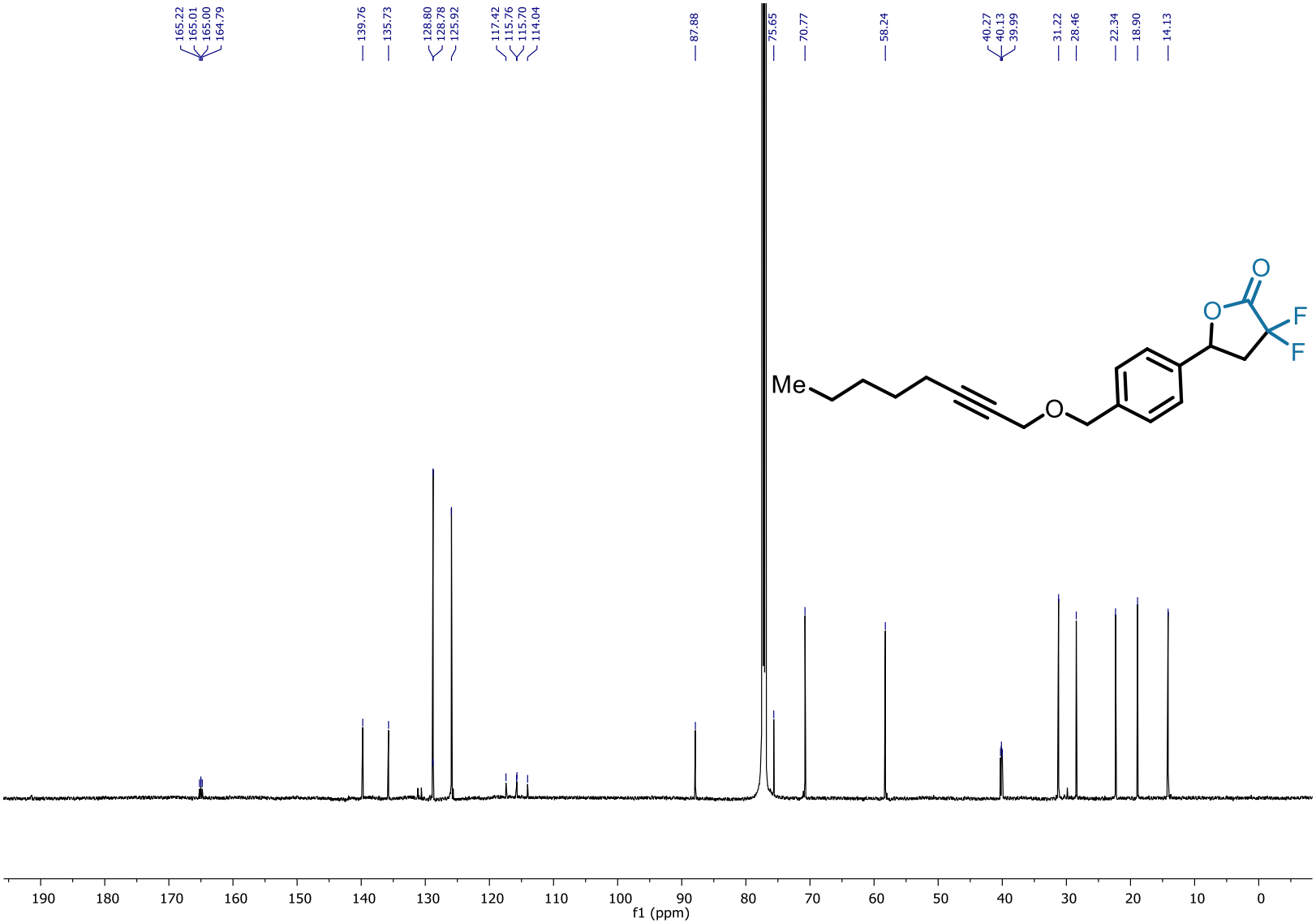
^{19}F-NMR (377 MHz, $CDCl_3$) of **44**



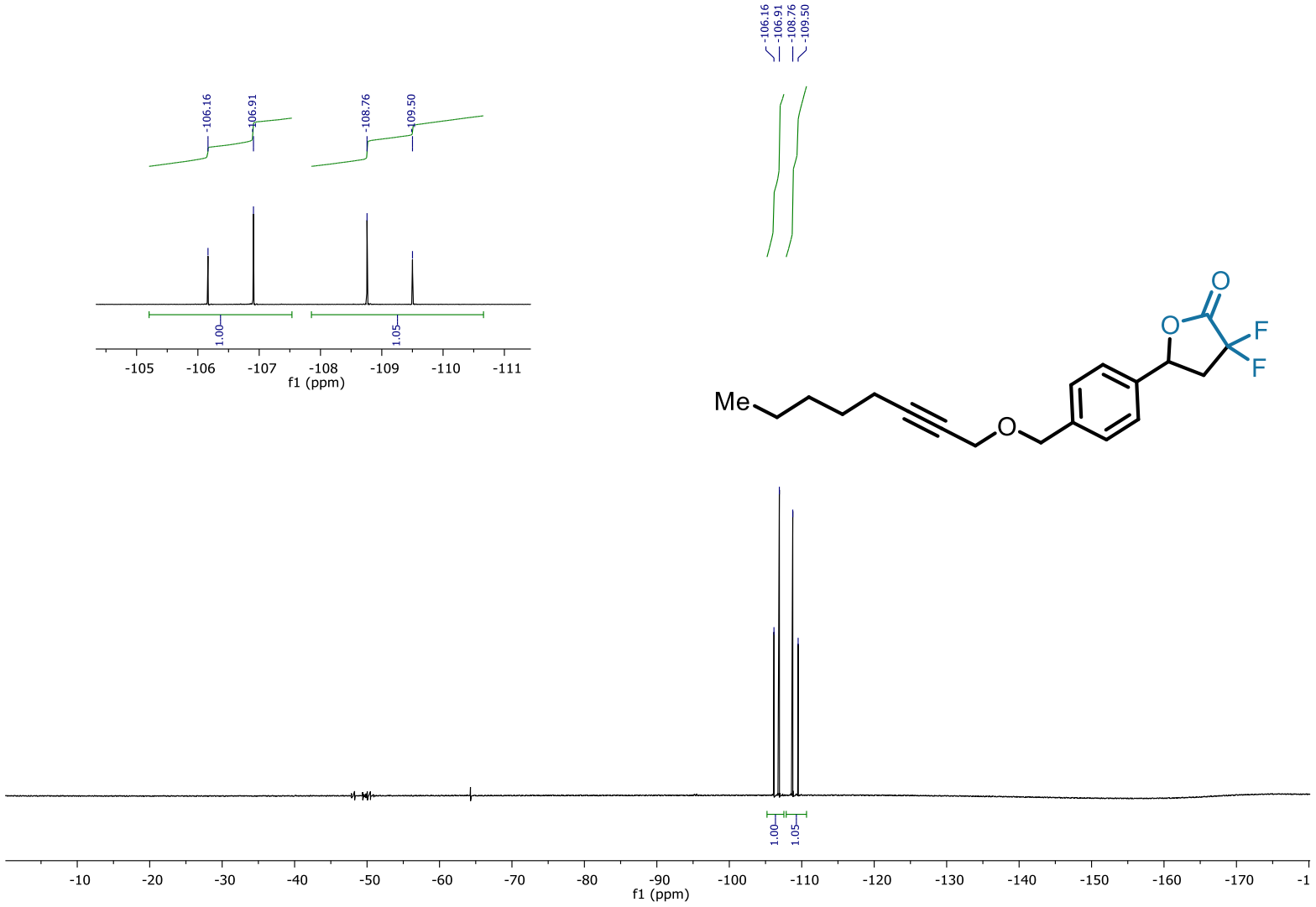
^{1}H-NMR (400 MHz, $CDCl_3$) of **45**



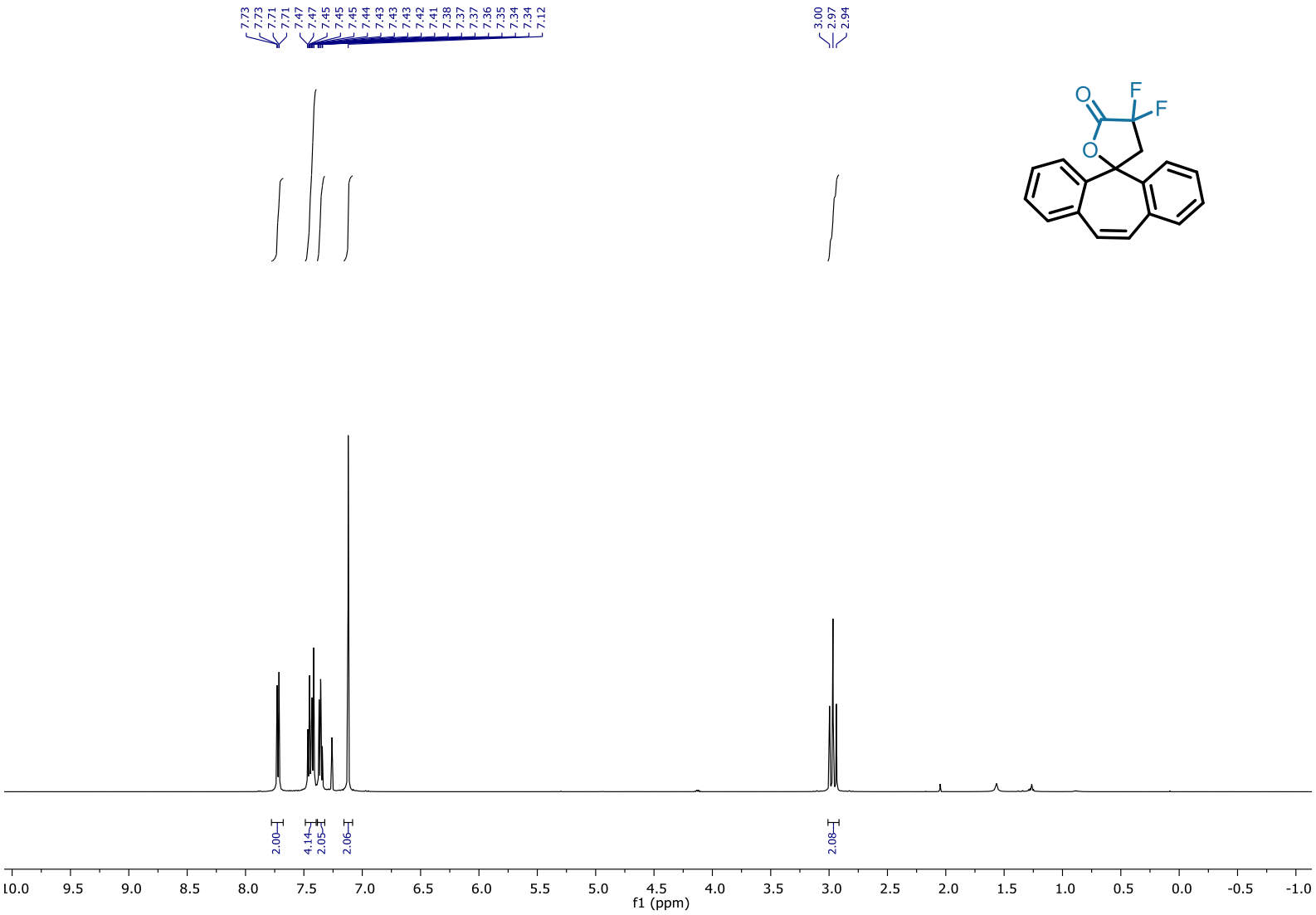
^{13}C-NMR (151 MHz, $CDCl_3$) of **45**



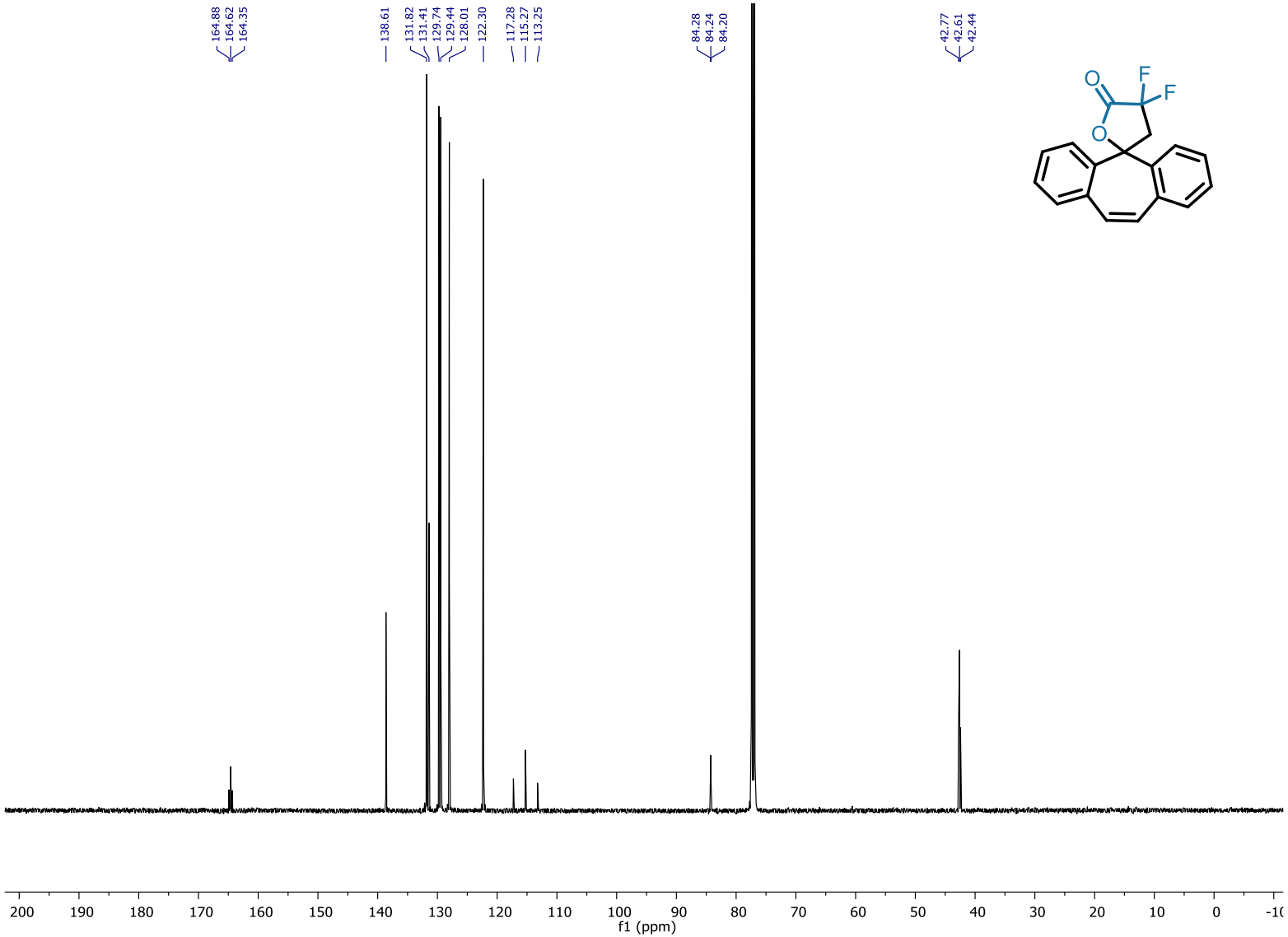
^{19}F-NMR (377 MHz, $CDCl_3$) of **45**



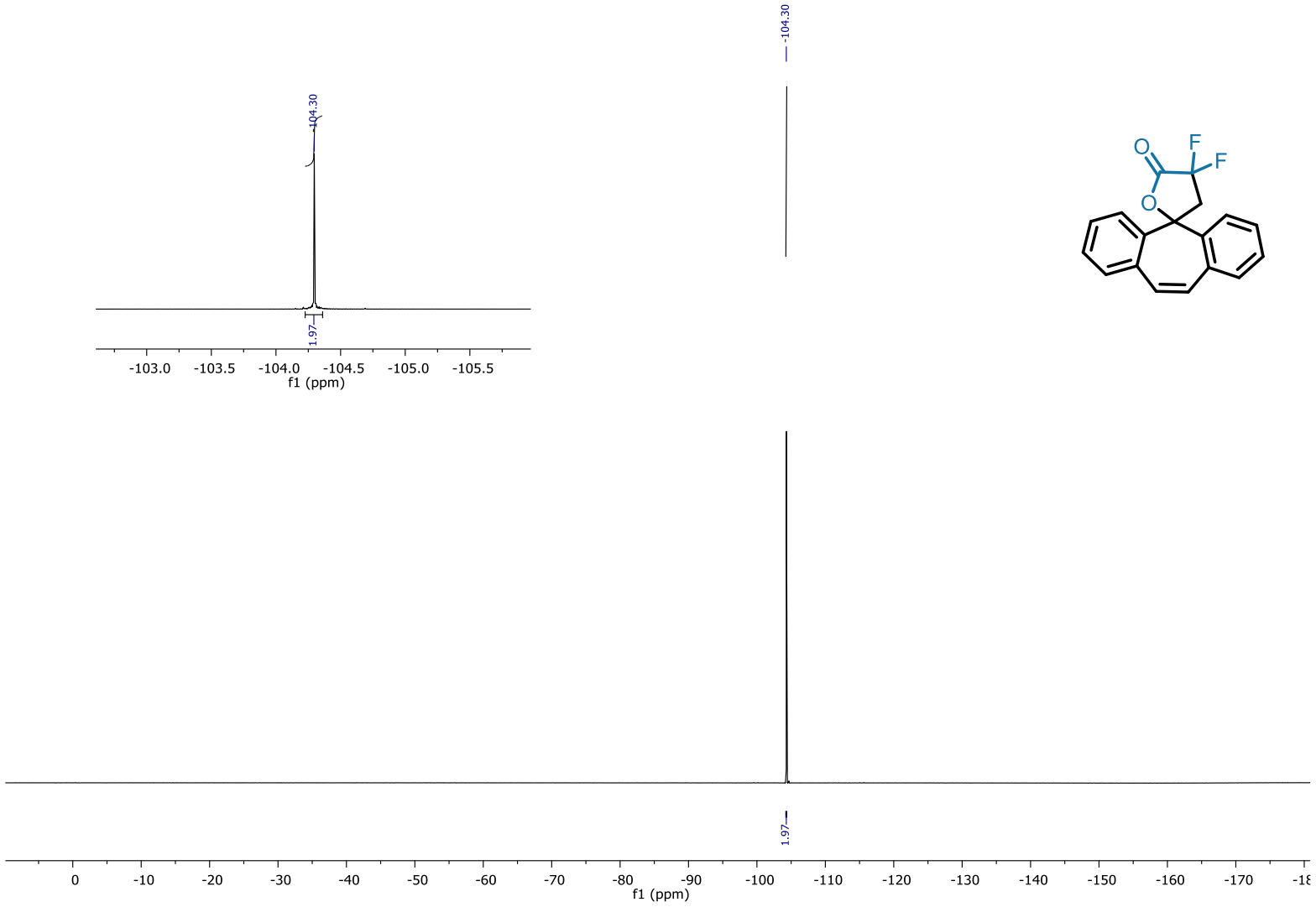
^{1}H-NMR (500 MHz, $CDCl_3$) of **46**



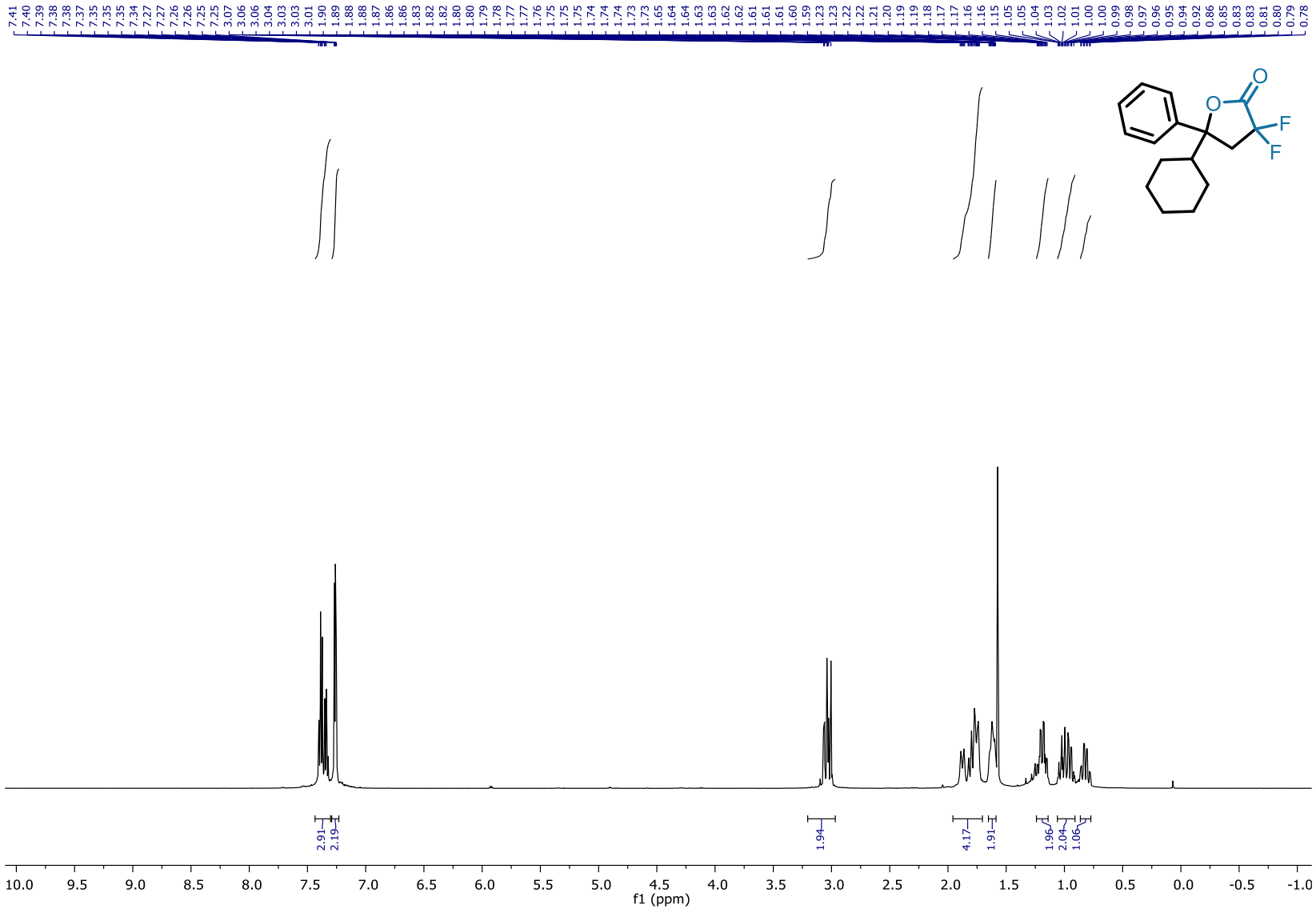
^{13}C-NMR (126 MHz, $CDCl_3$) of **46**



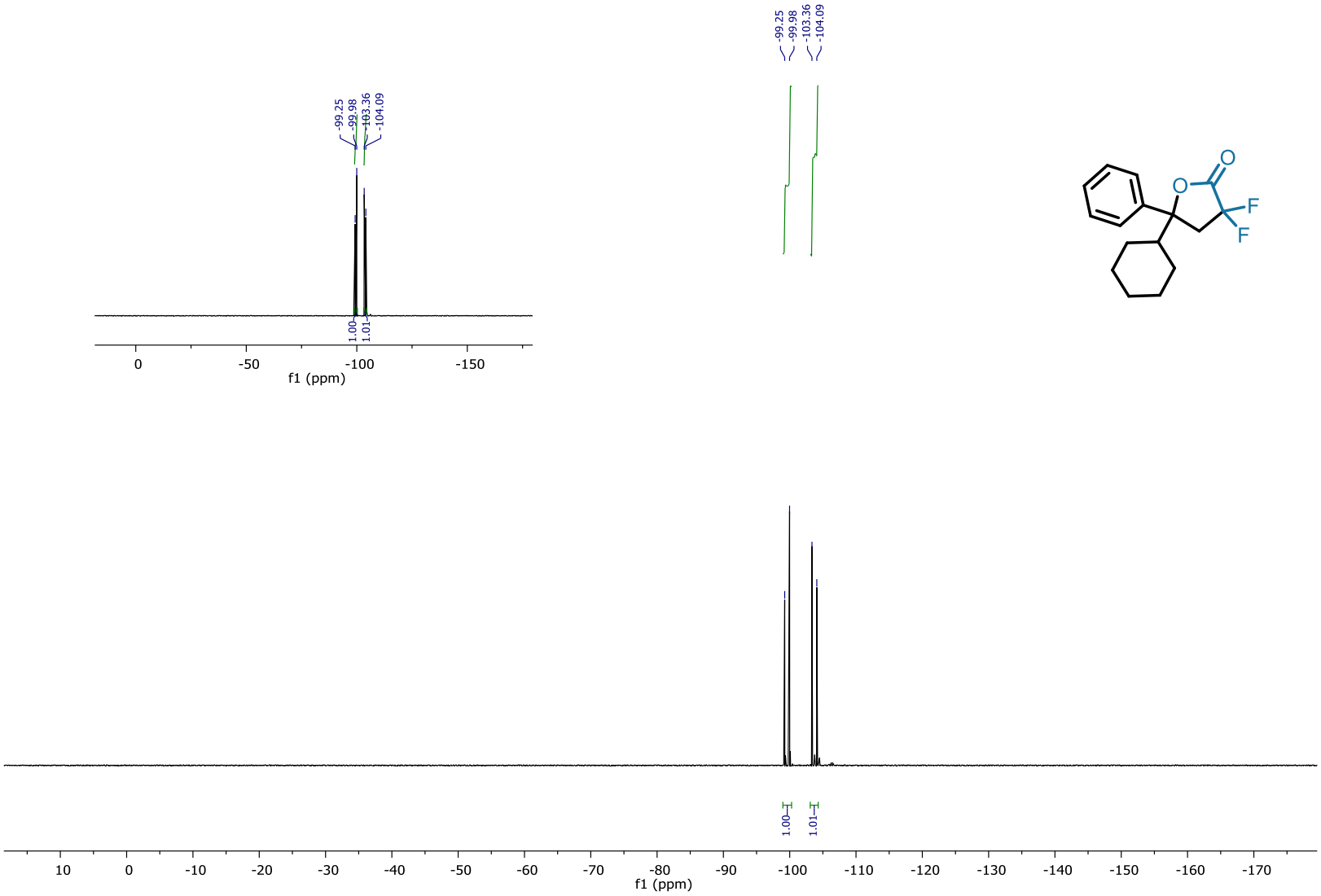
^{19}F-NMR (471 MHz, $CDCl_3$) of **46**



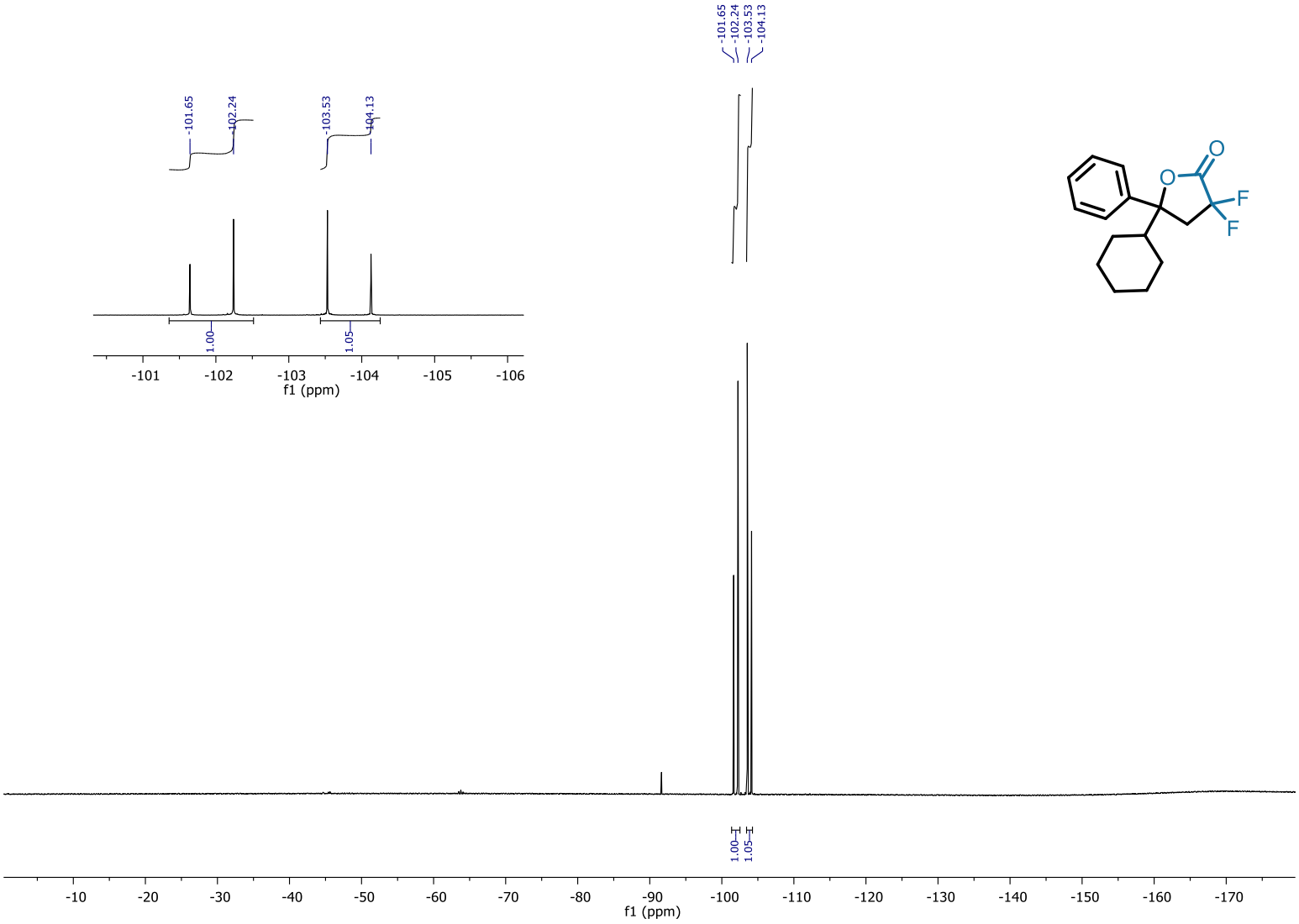
^{1}H-NMR (500 MHz, $CDCl_3$) of **47**



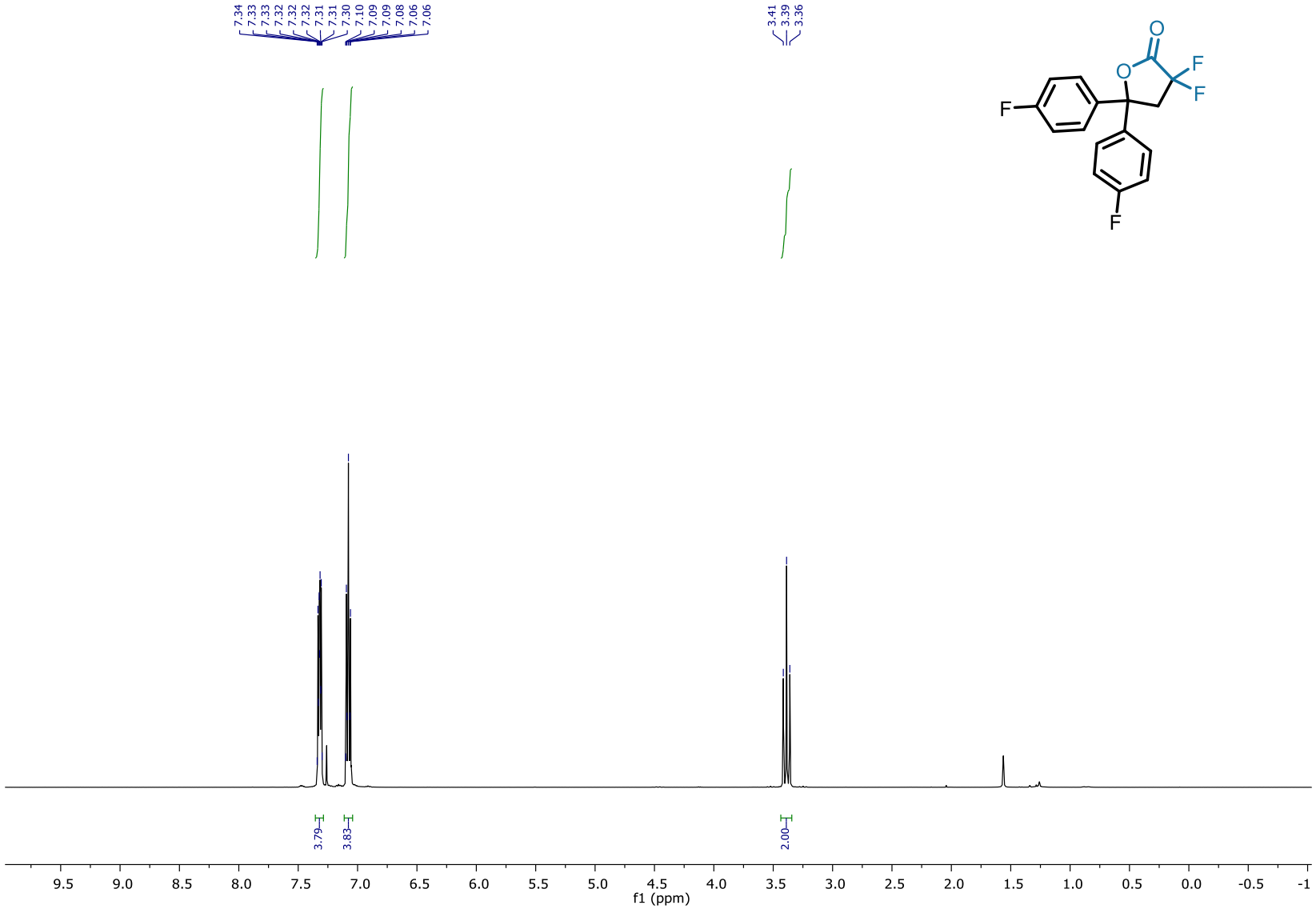
^{13}C-NMR (126 MHz, $CDCl_3$) of **47**



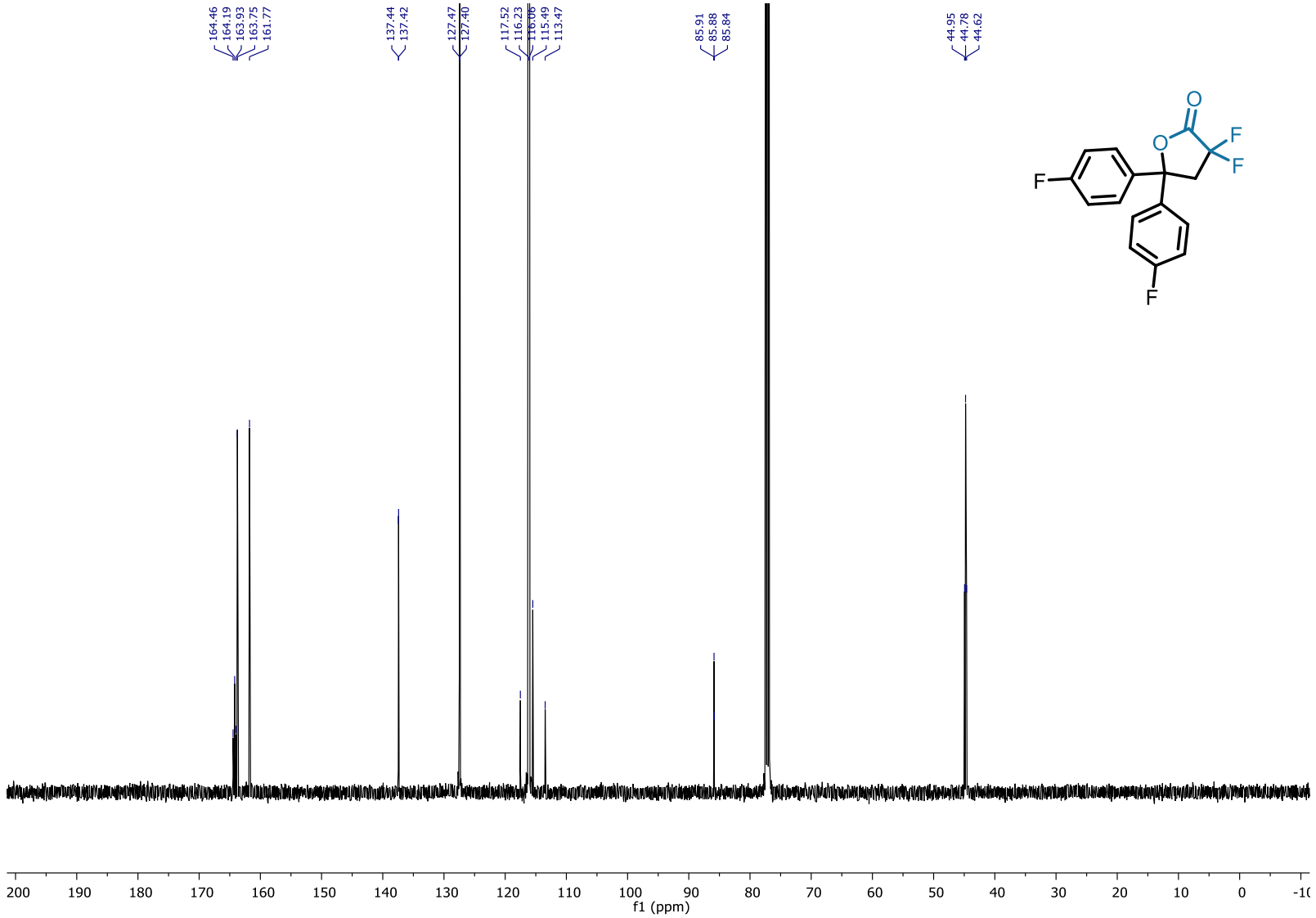
^{19}F-NMR (471 MHz, $CDCl_3$) of **47**



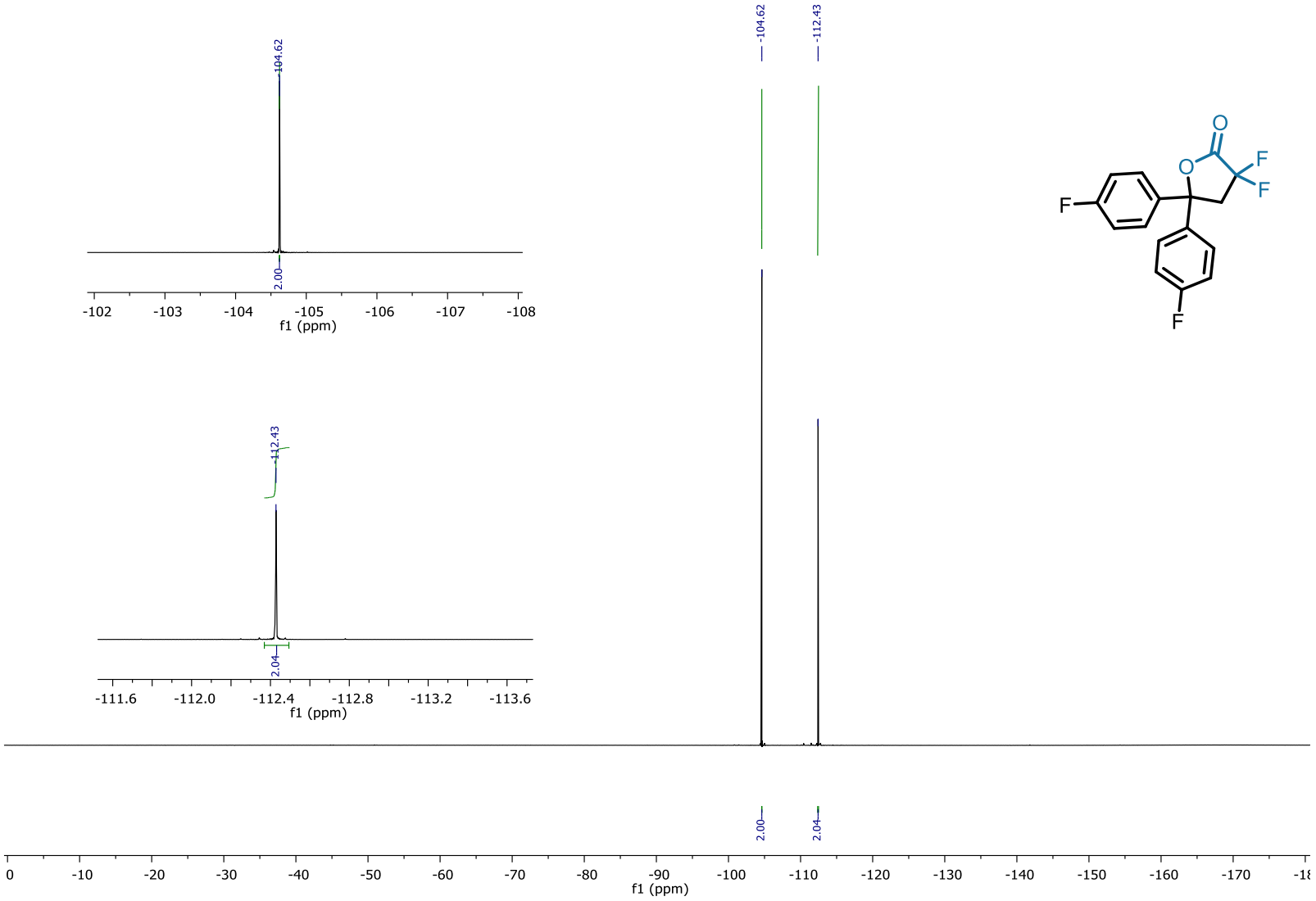
^{1}H-NMR (500 MHz, $CDCl_3$) of **48**



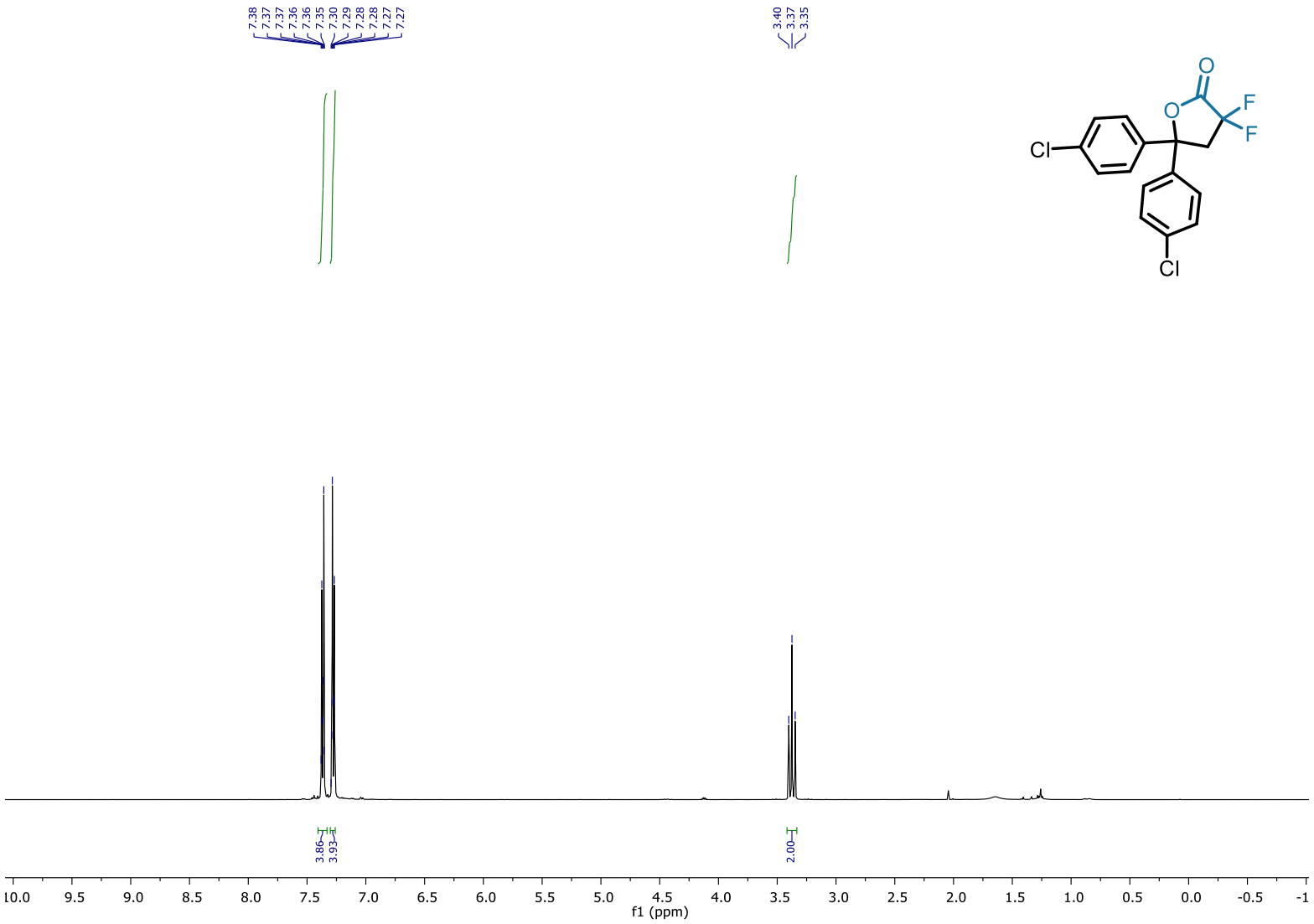
^{13}C-NMR (126 MHz, $CDCl_3$) of **48**



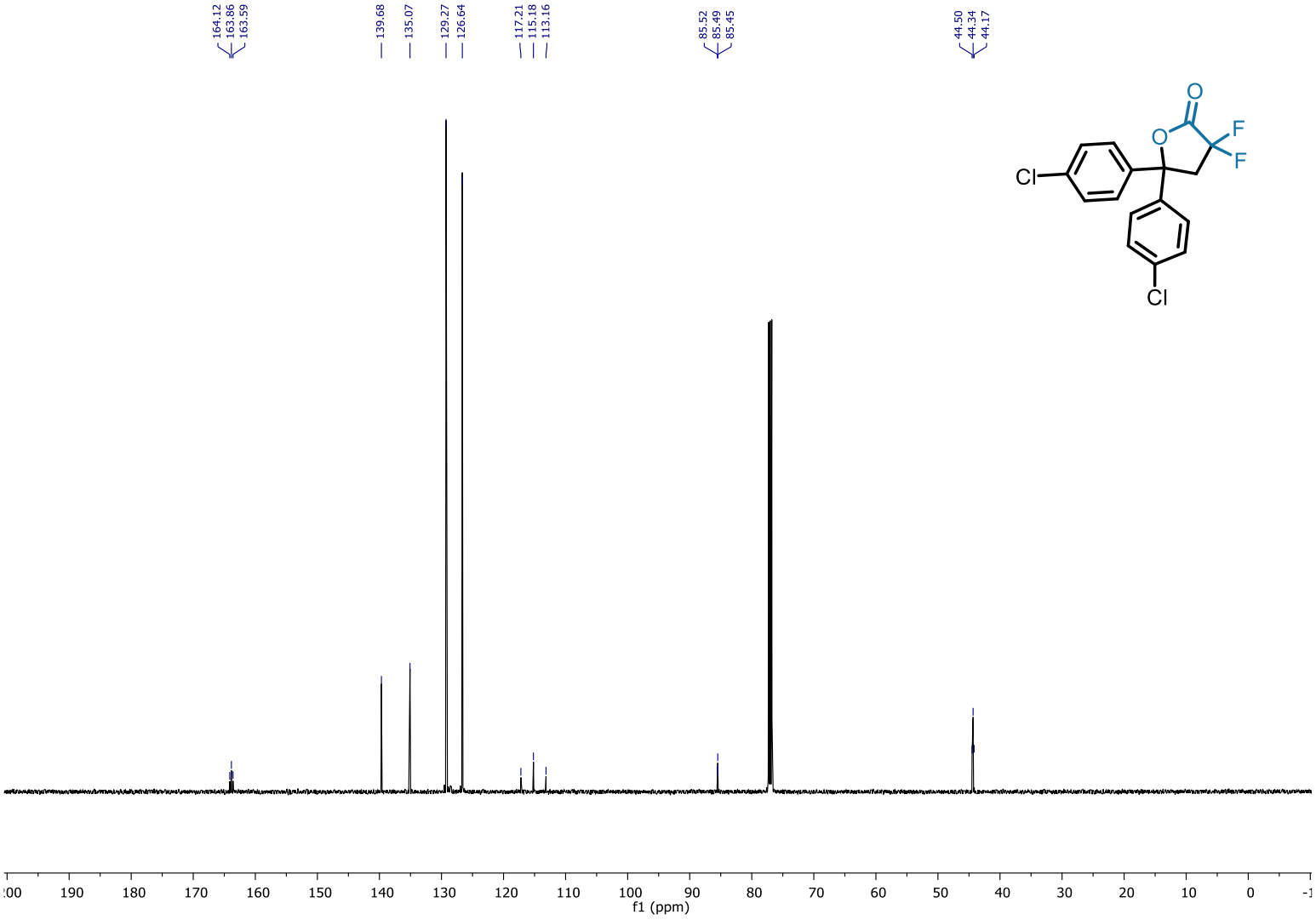
^{19}F-NMR (471 MHz, $CDCl_3$) of **48**



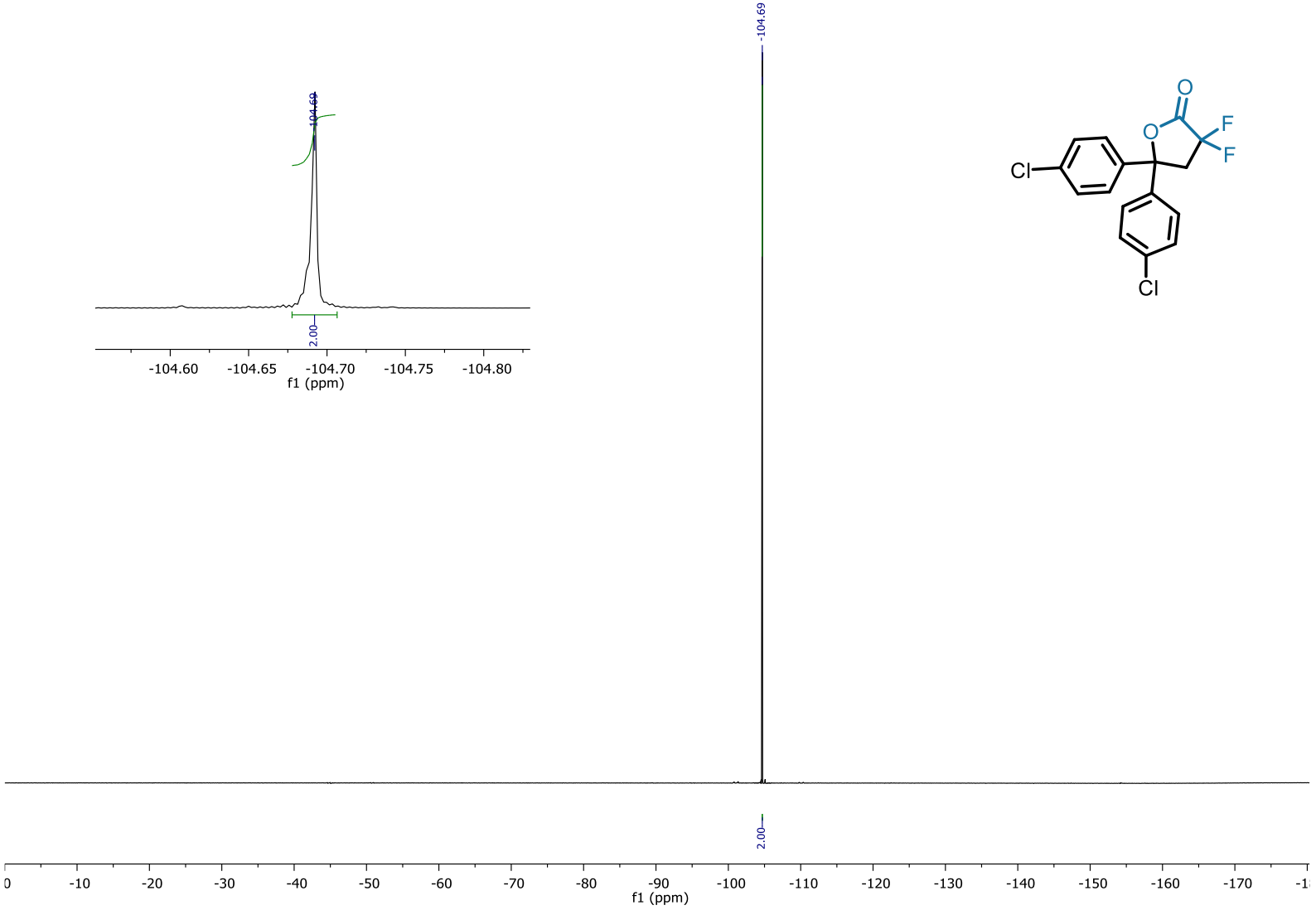
^{1}H-NMR (500 MHz, $CDCl_3$) of **49**



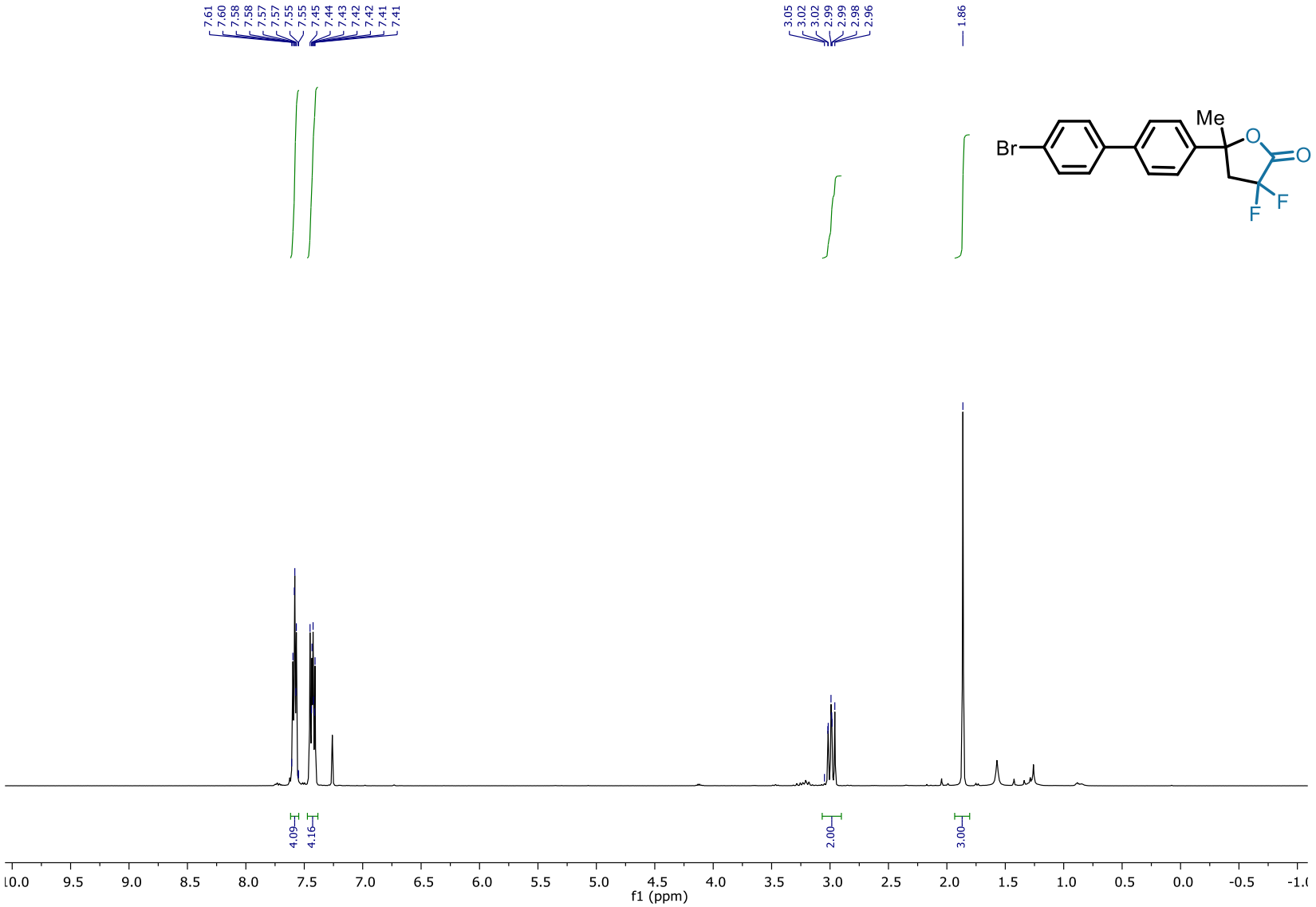
^{13}C-NMR (126 MHz, $CDCl_3$) of **49**



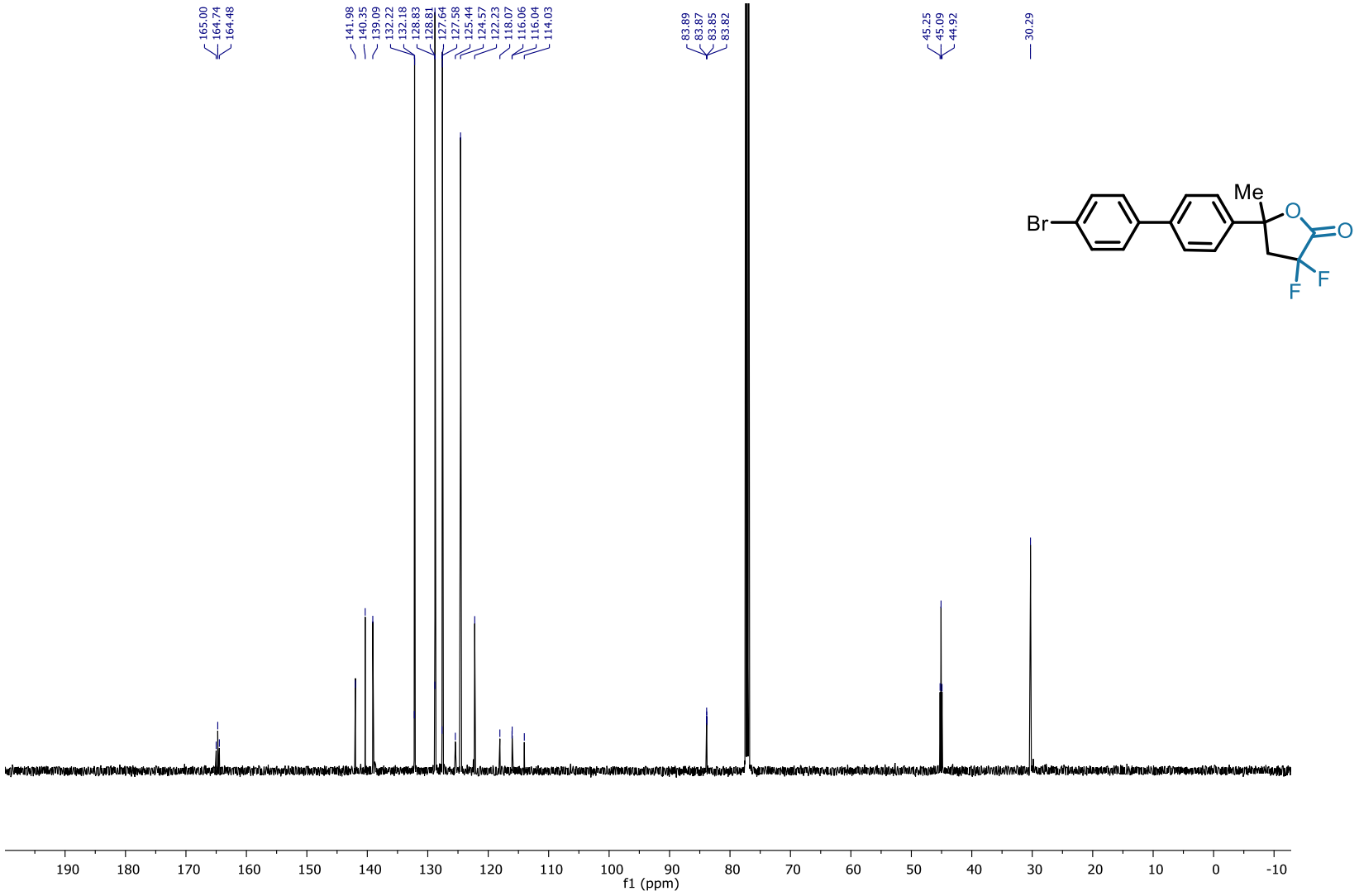
^{19}F-NMR (471 MHz, $CDCl_3$) of **49**



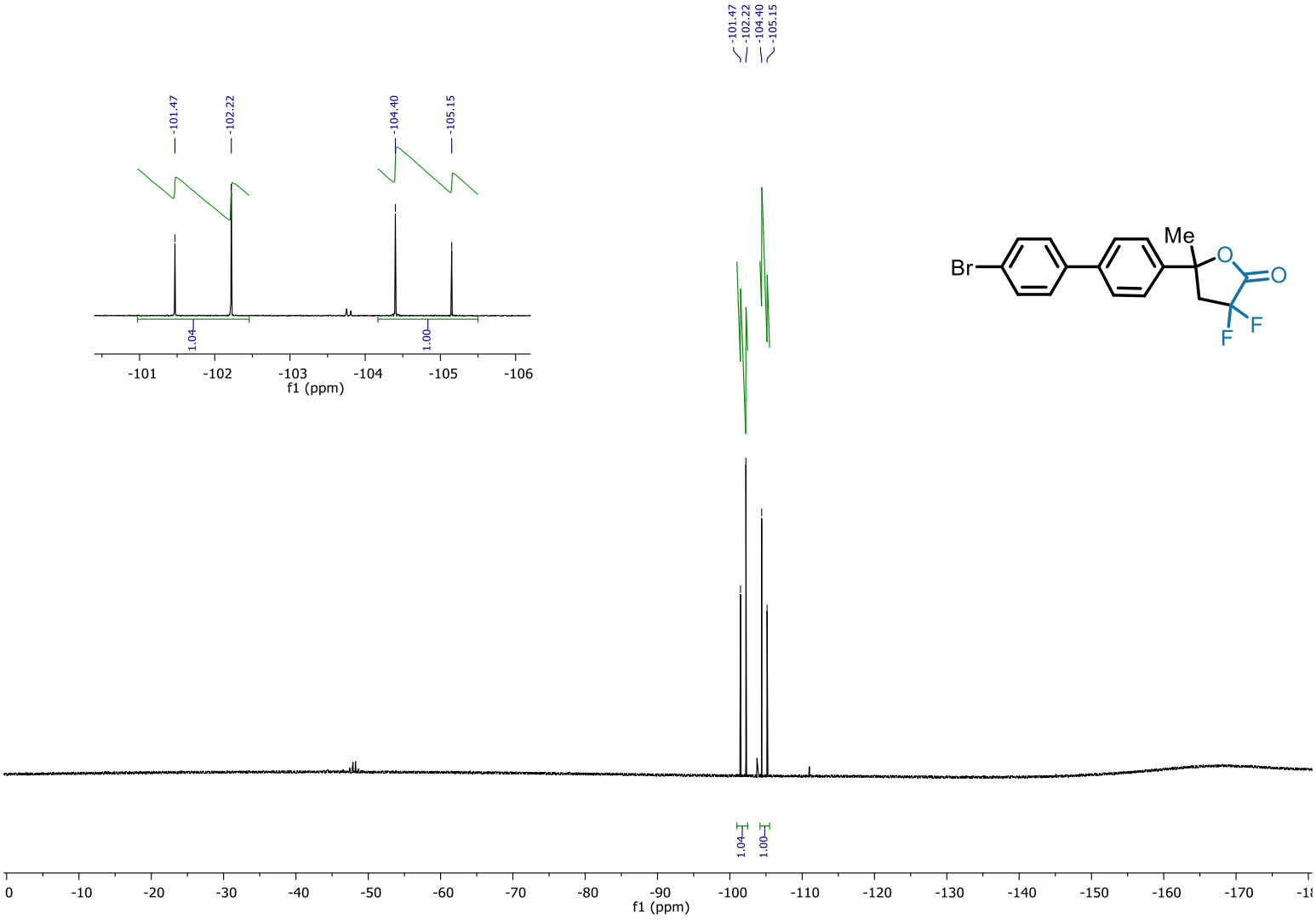
^{1}H-NMR (500 MHz, $CDCl_3$) of **50**



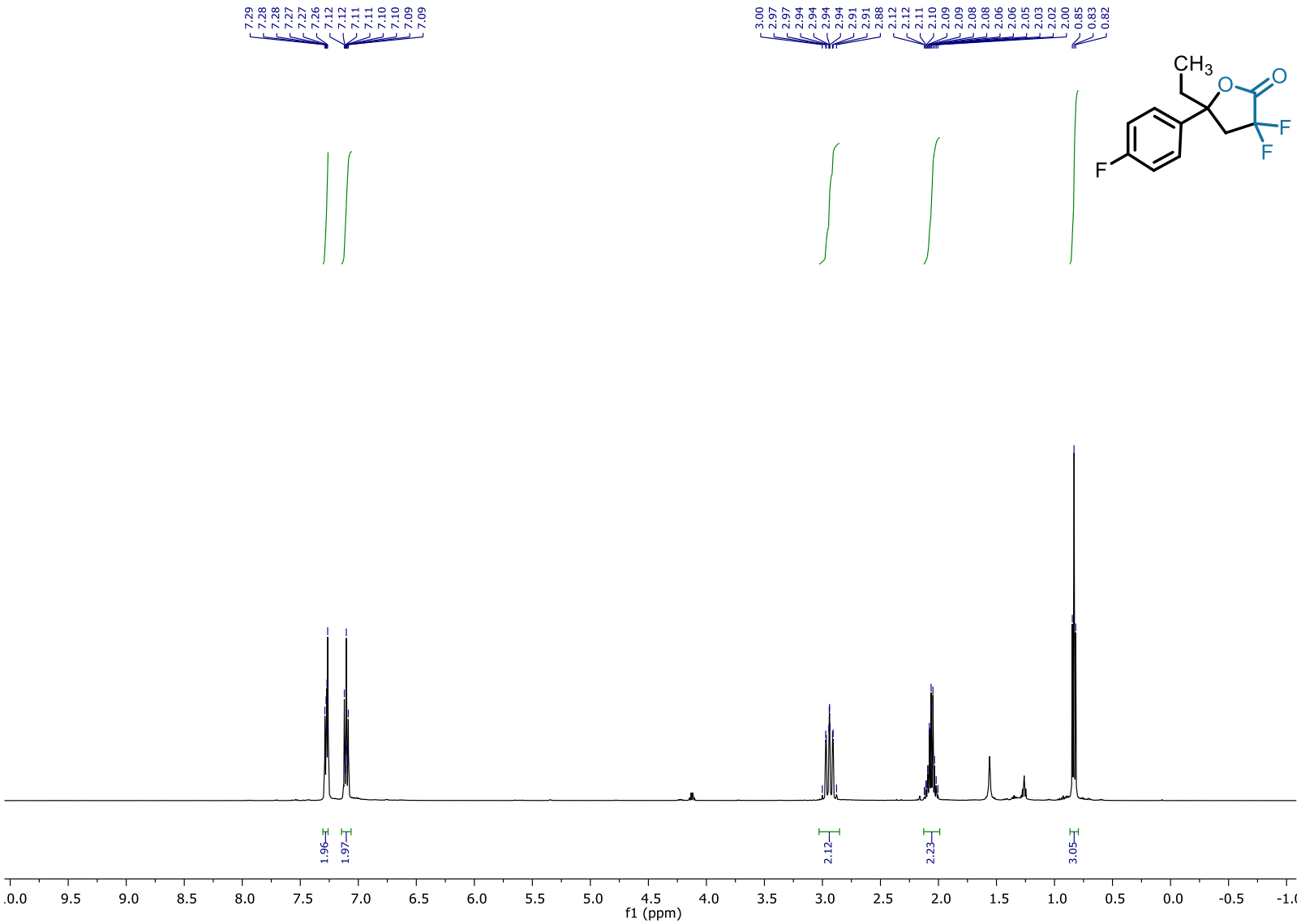
^{13}C-NMR (126 MHz, $CDCl_3$) of **50**



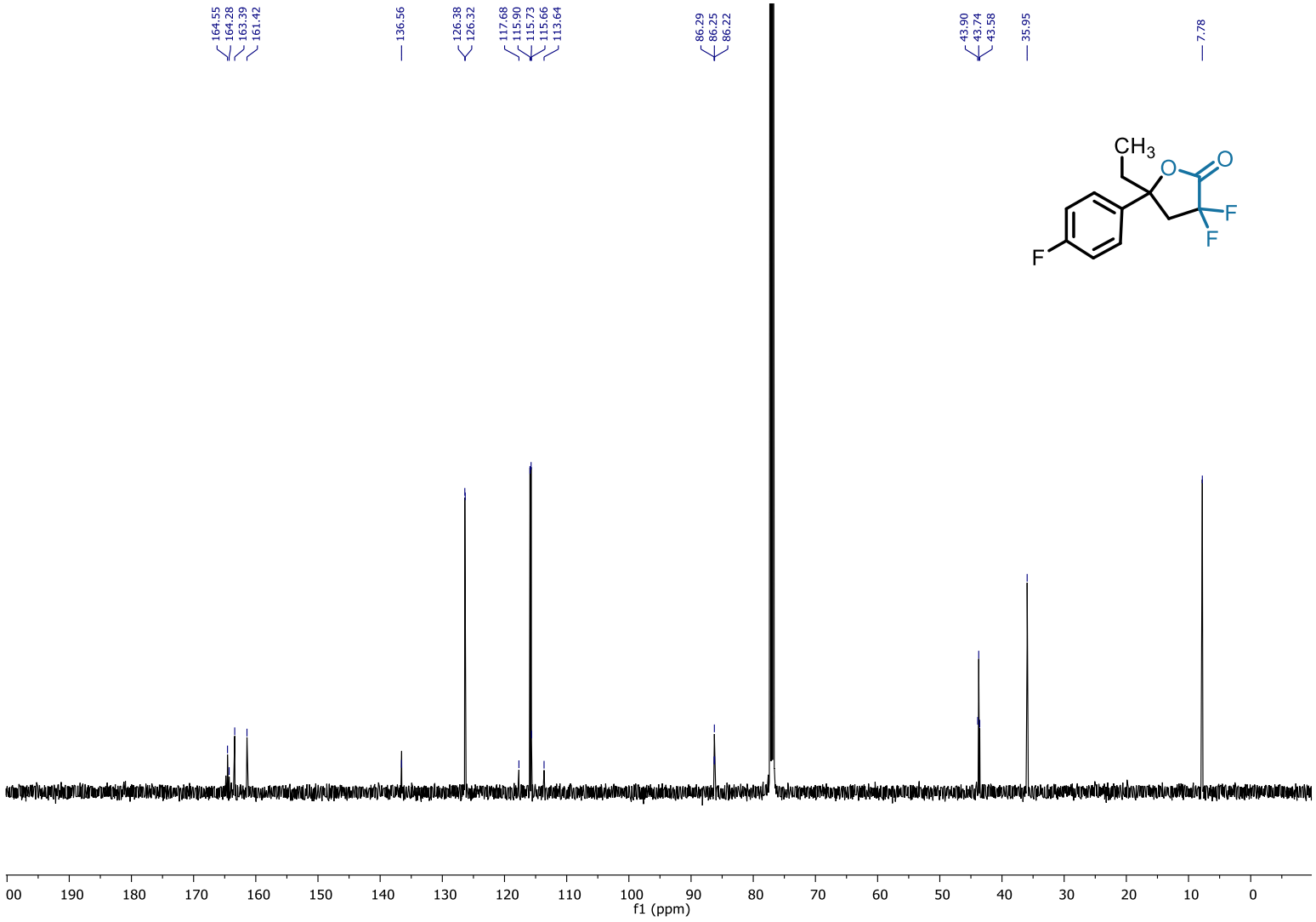
^{19}F-NMR (377 MHz, $CDCl_3$) of **50**



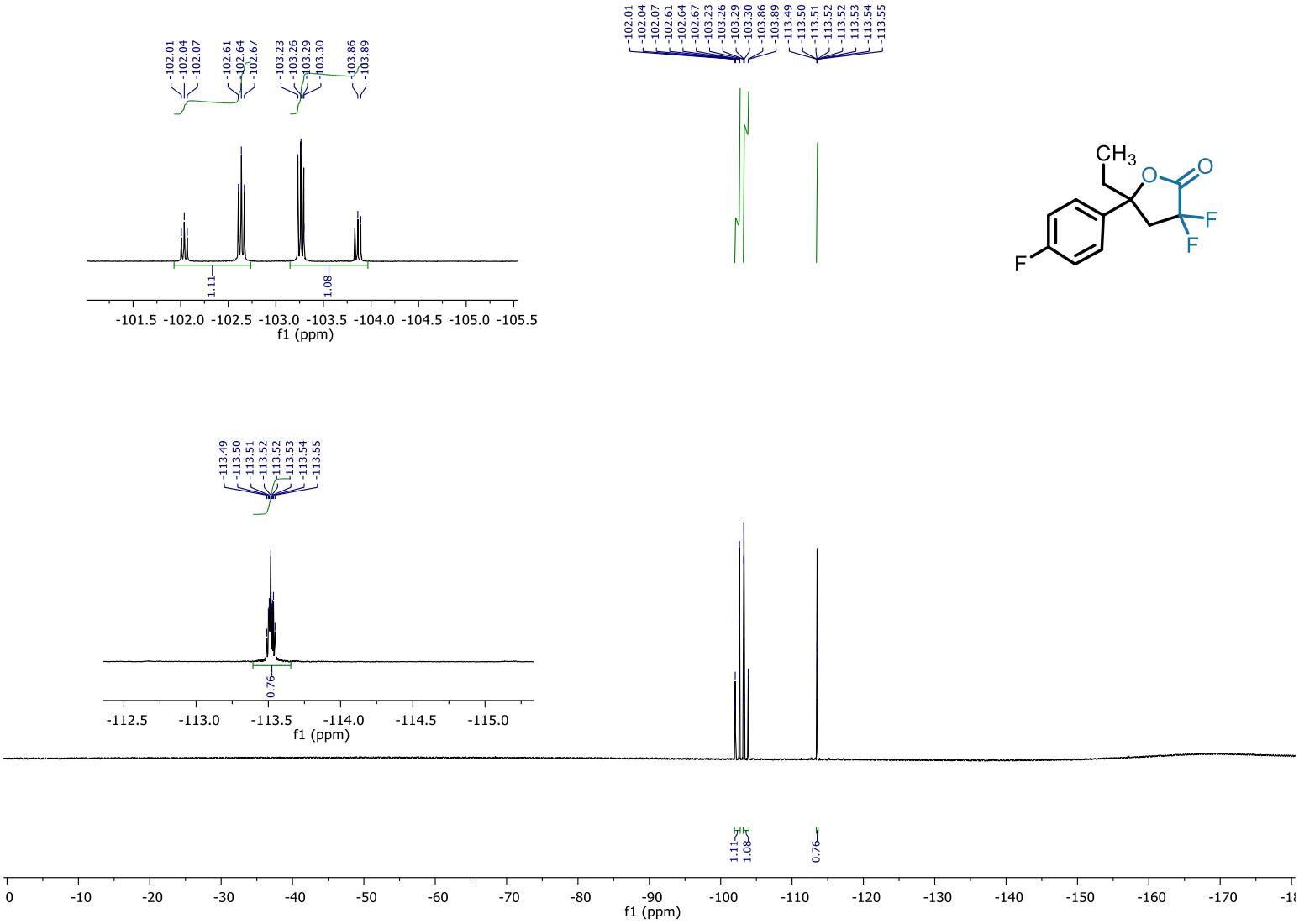
^{1}H-NMR (500 MHz MHz, $CDCl_3$) of **51**



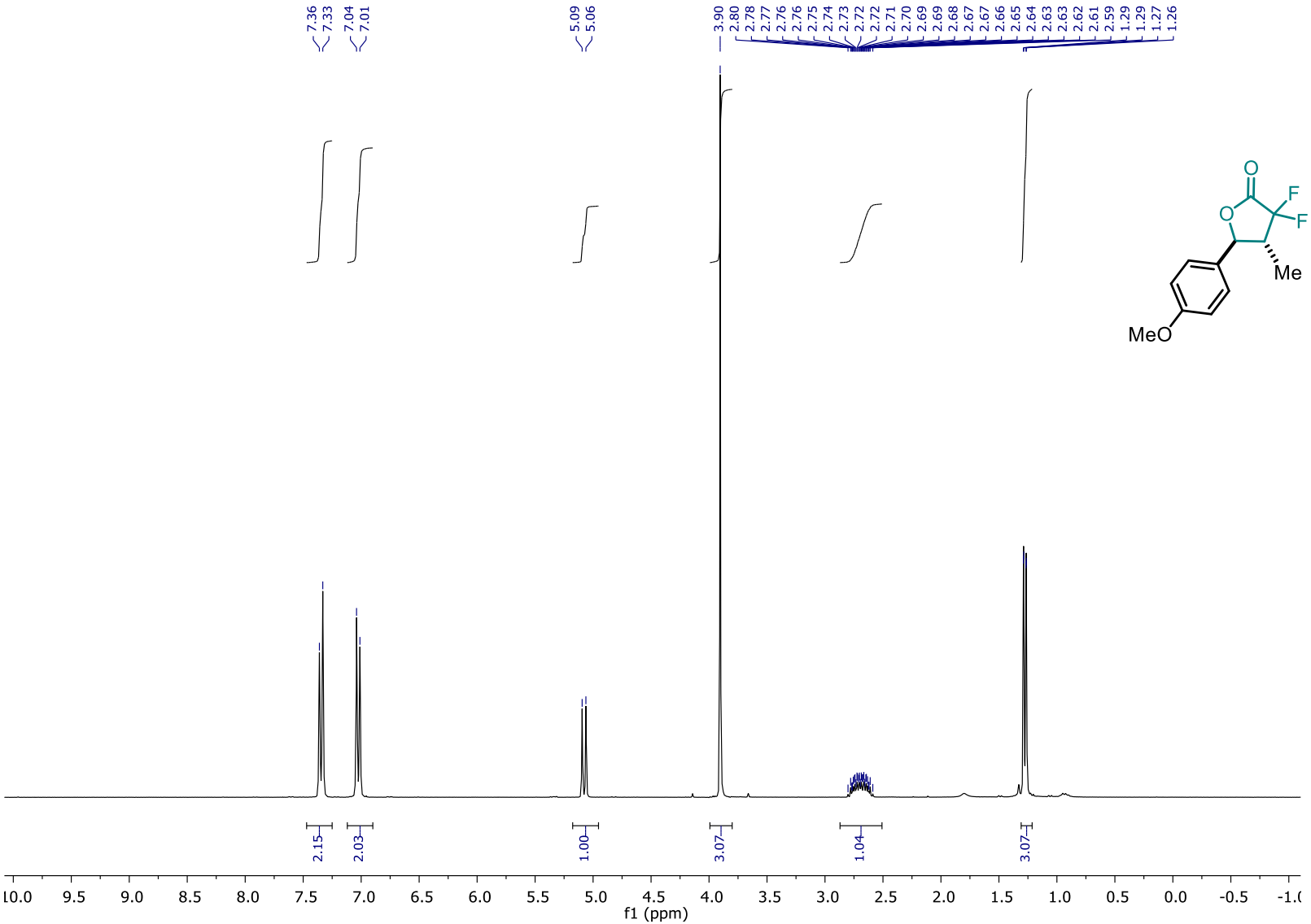
^{13}C-NMR (126 MHz, $CDCl_3$) of **51**



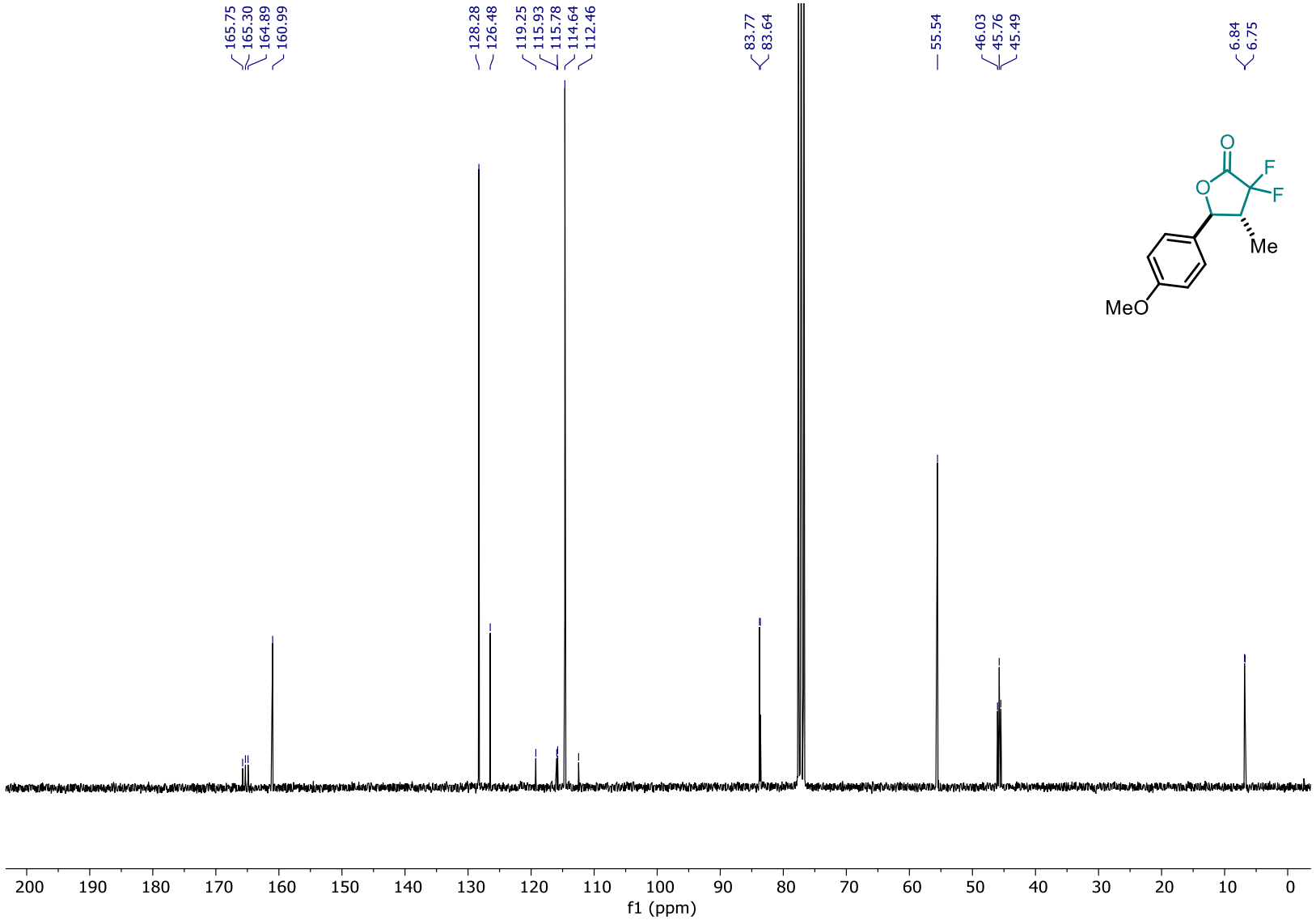
[1H Coupled] ^{19}F-NMR (471 MHz, $CDCl_3$) of **51**



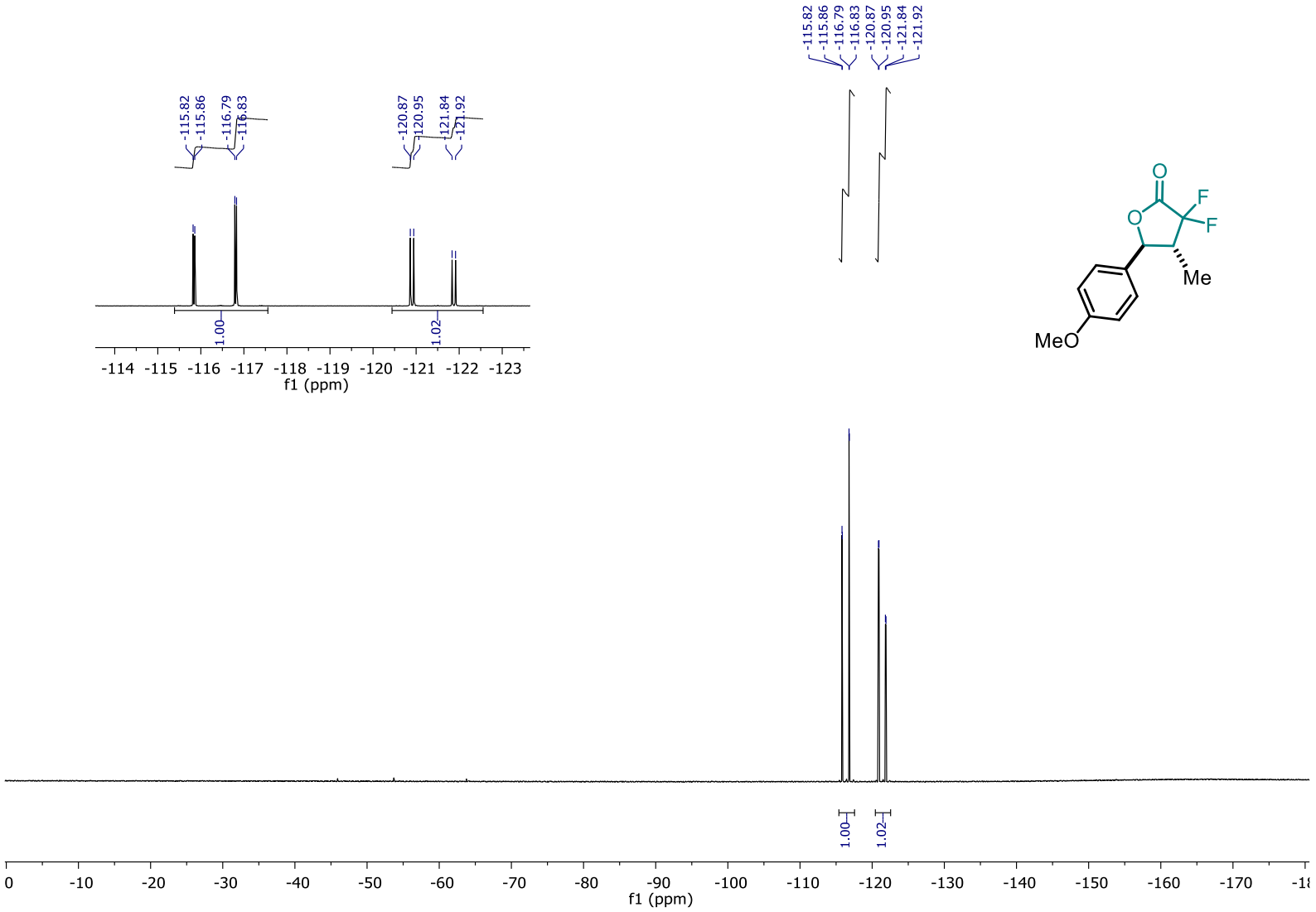
^{1}H-NMR (300 MHz, $CDCl_3$) of **52**



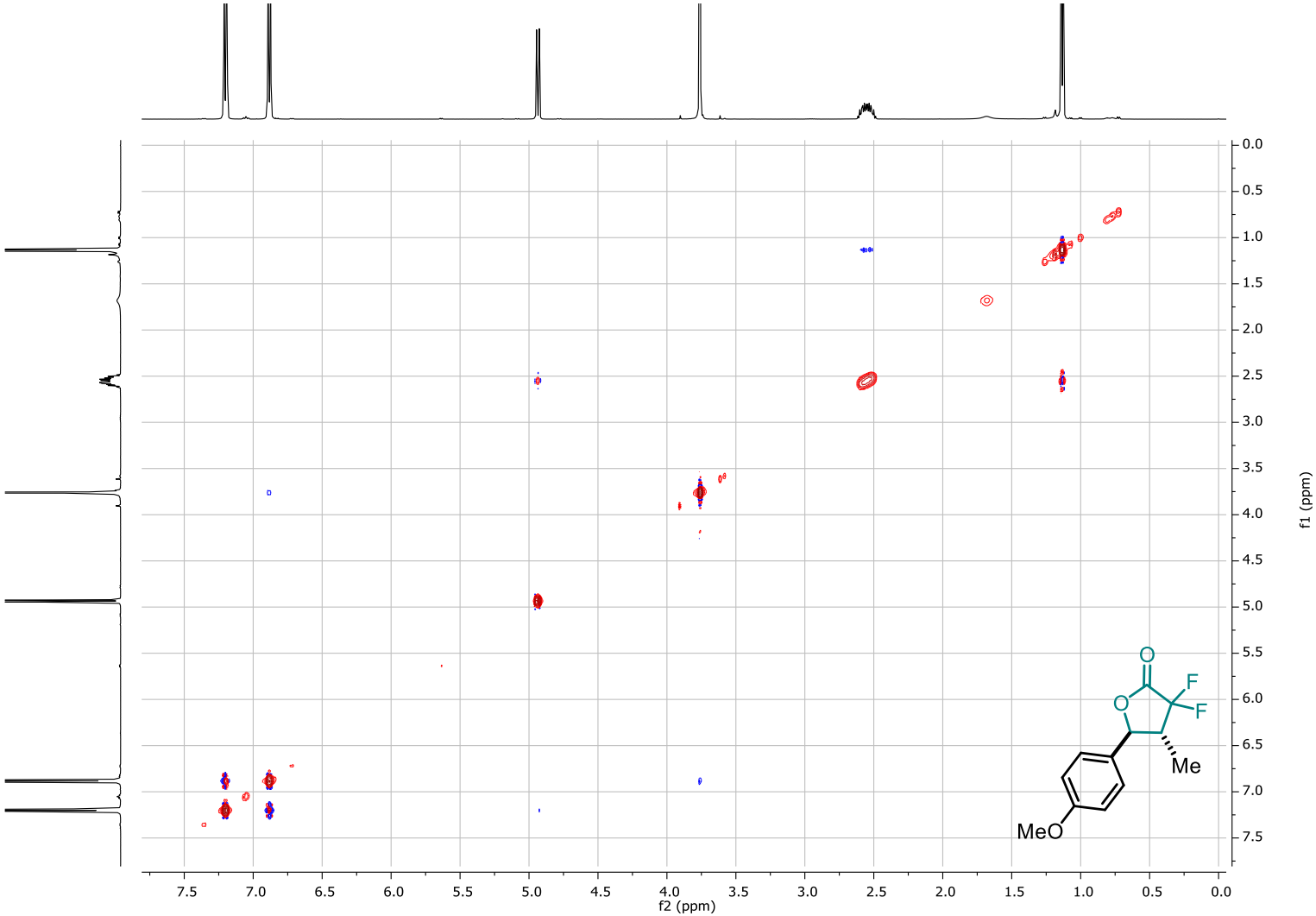
^{13}C-NMR (75 MHz, $CDCl_3$) of **52**



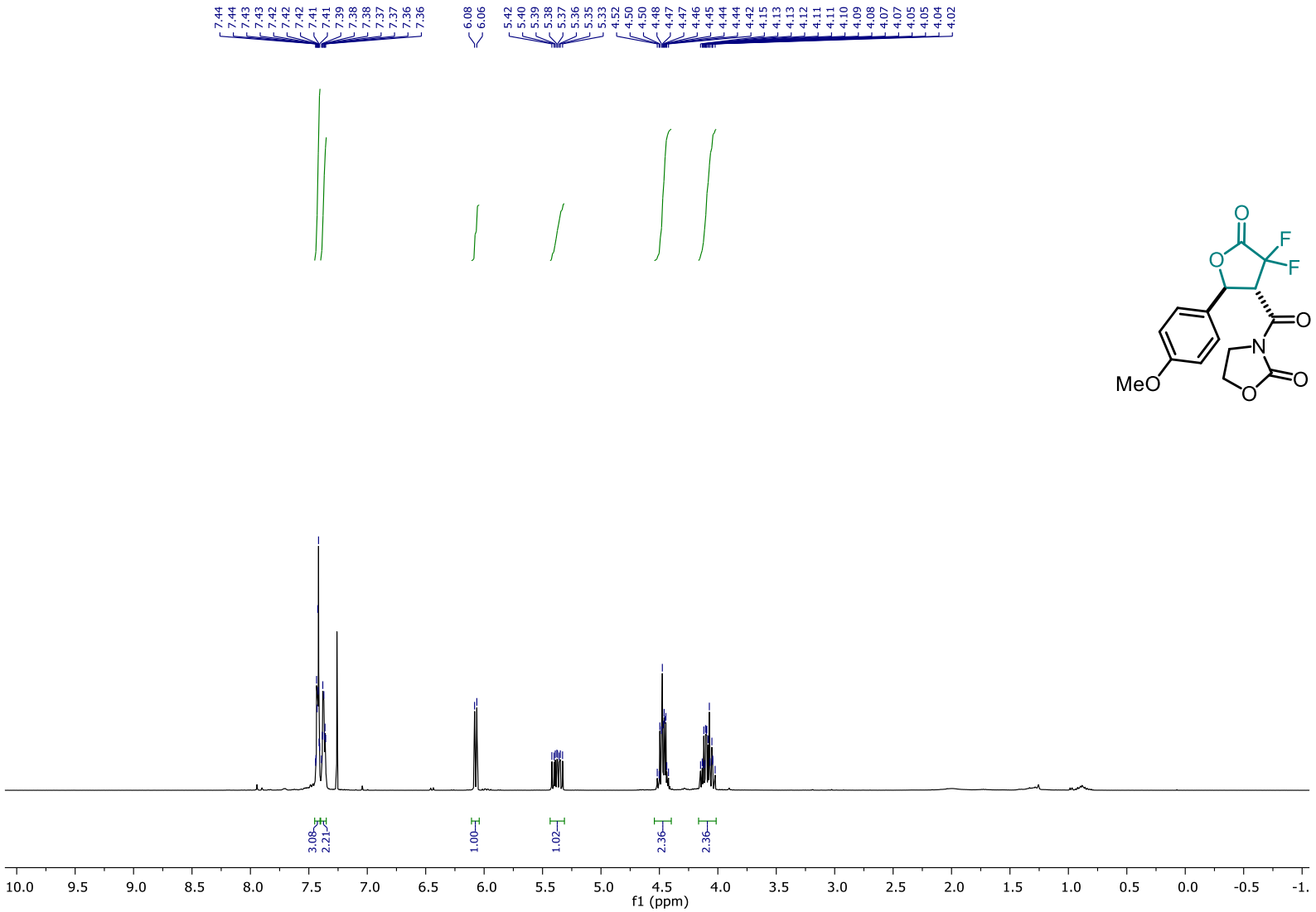
^{19}F-NMR (282 MHz, $CDCl_3$) of **52**



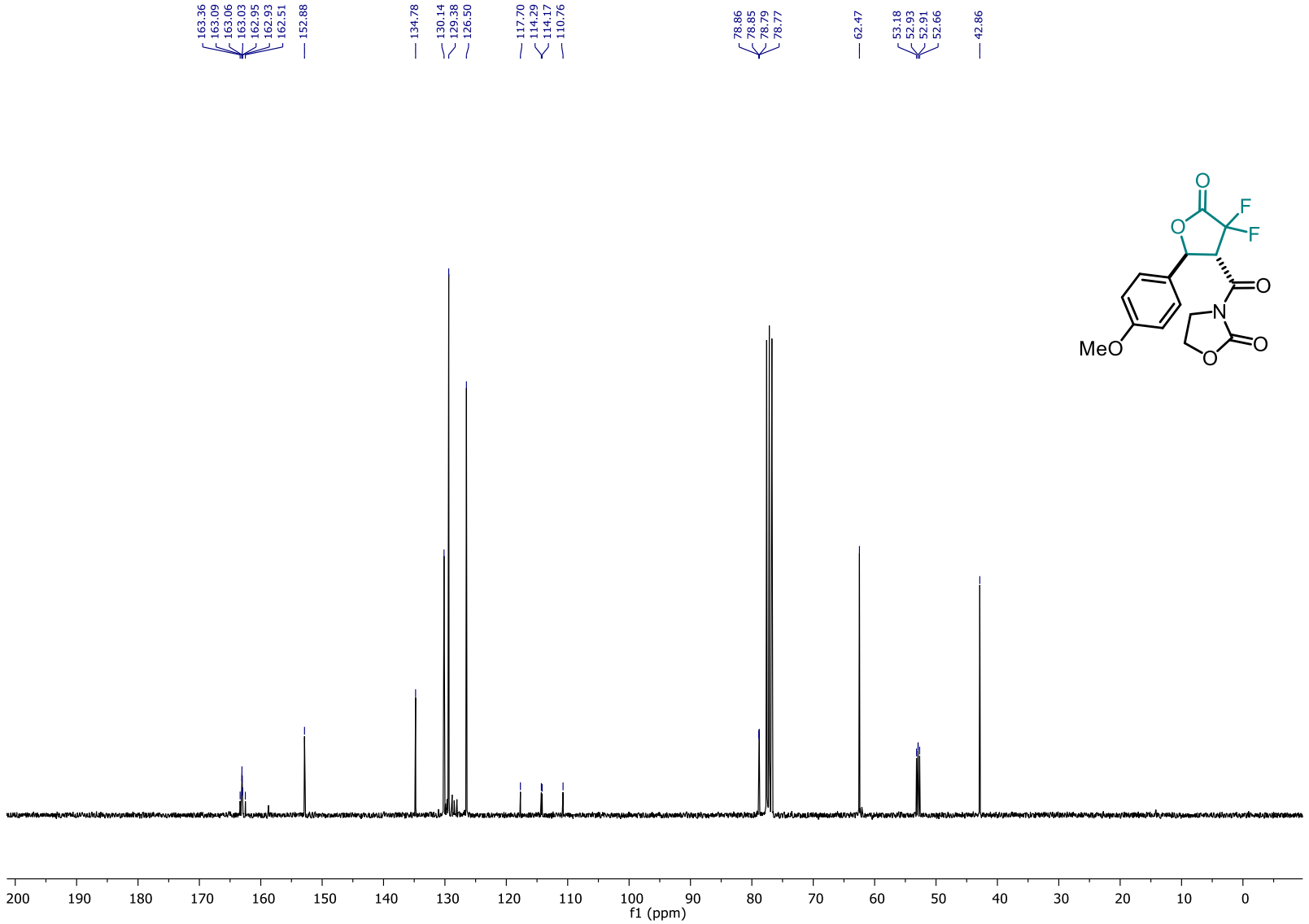
^{1}H-NOESY NMR (500 MHz, $CDCl_3$) of **52**



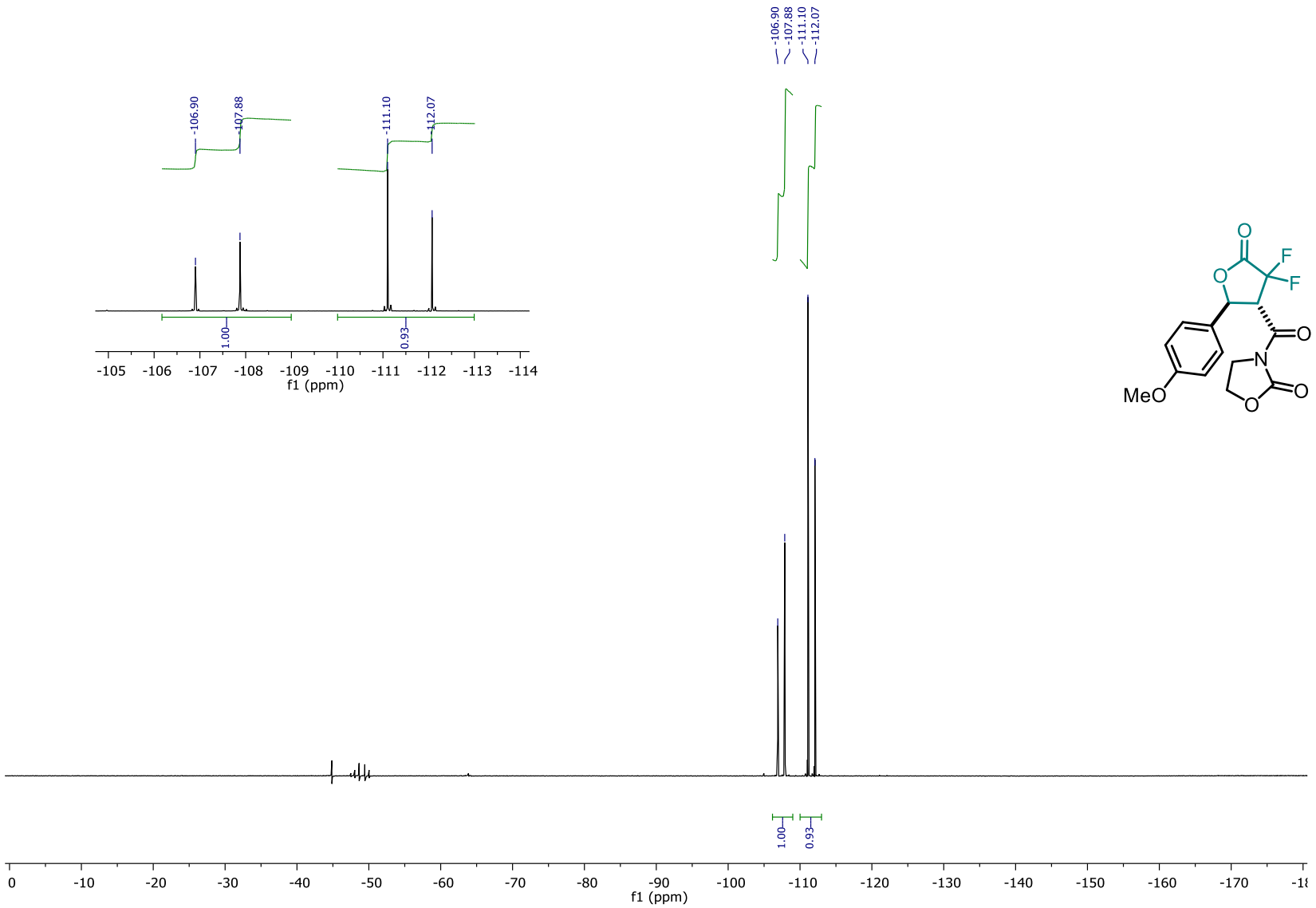
^{1}H-NMR (400 MHz, $CDCl_3$) of **53**



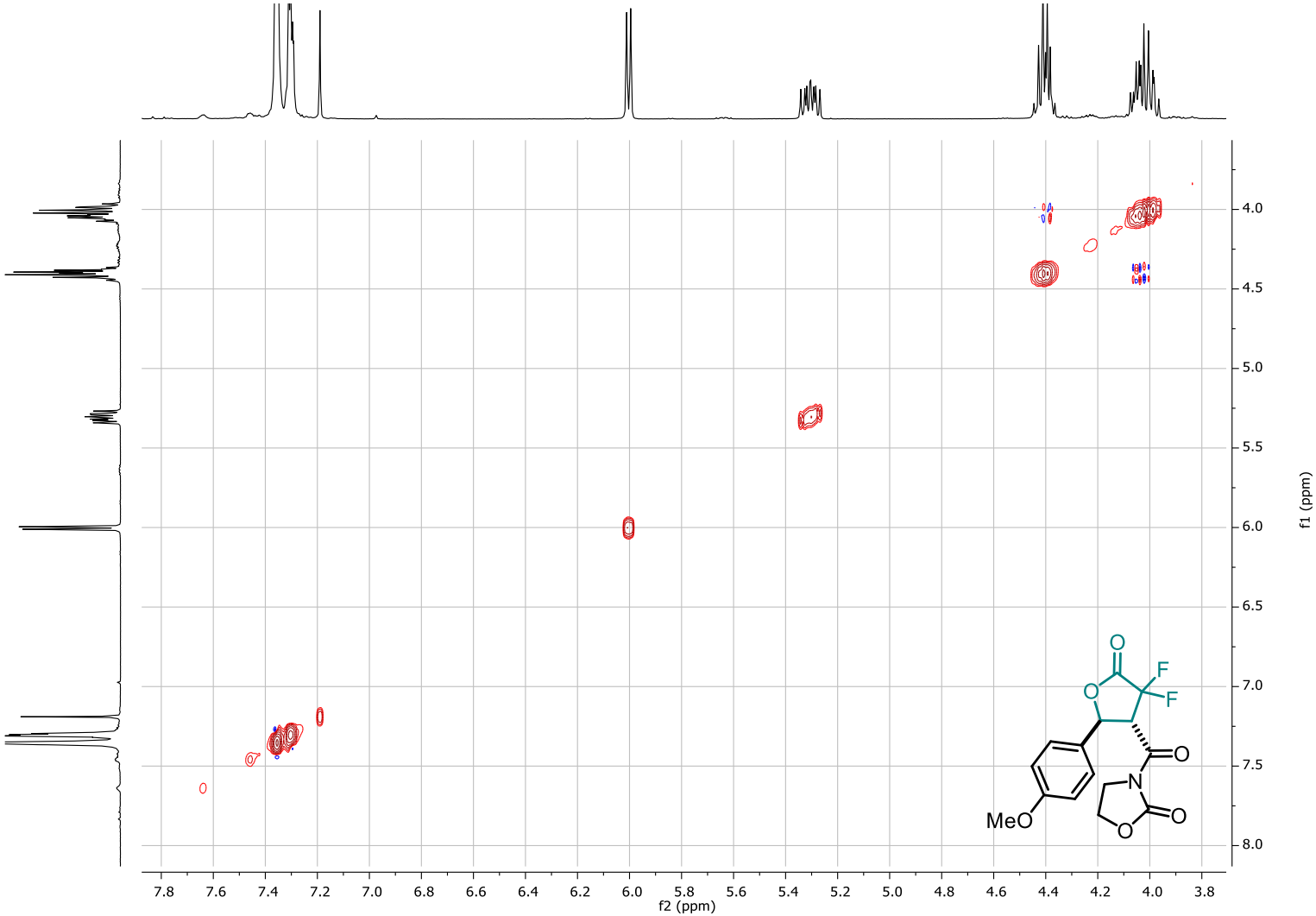
^{13}C-NMR (75 MHz, $CDCl_3$) of **53**



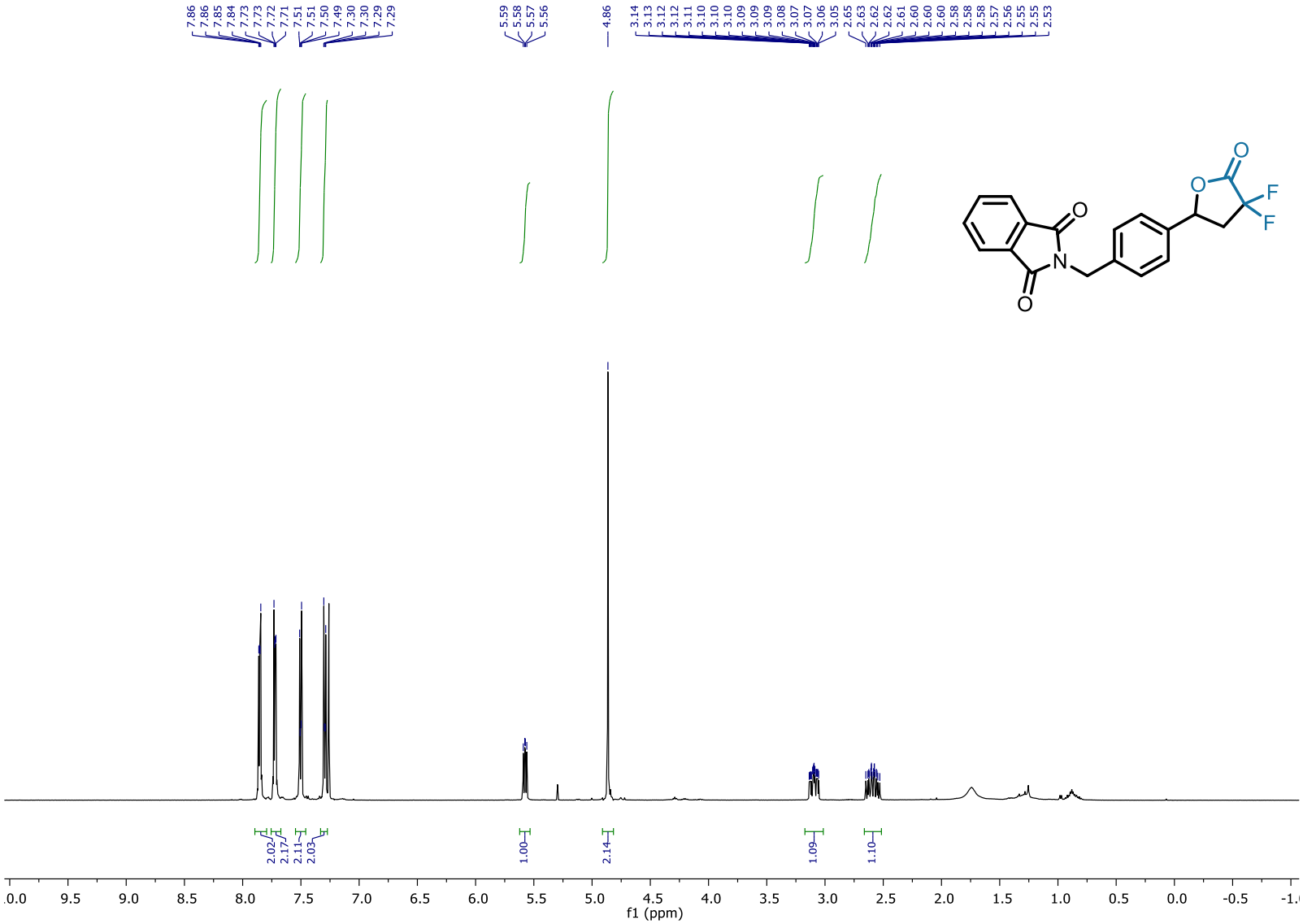
^{19}F-NMR (377 MHz, $CDCl_3$) of **53**



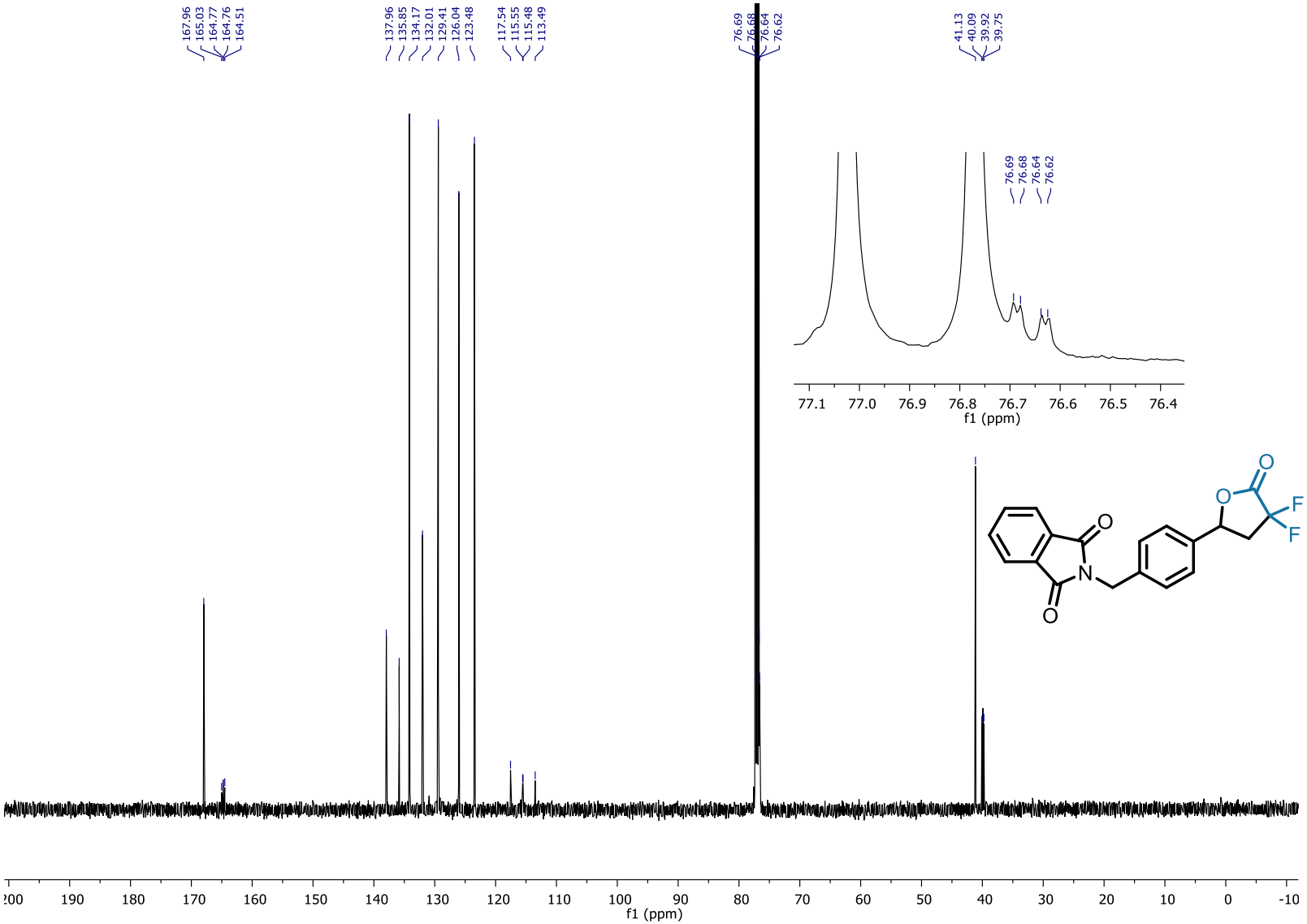
^{1}H-NOESY NMR (500 MHz, $CDCl_3$) of **53**



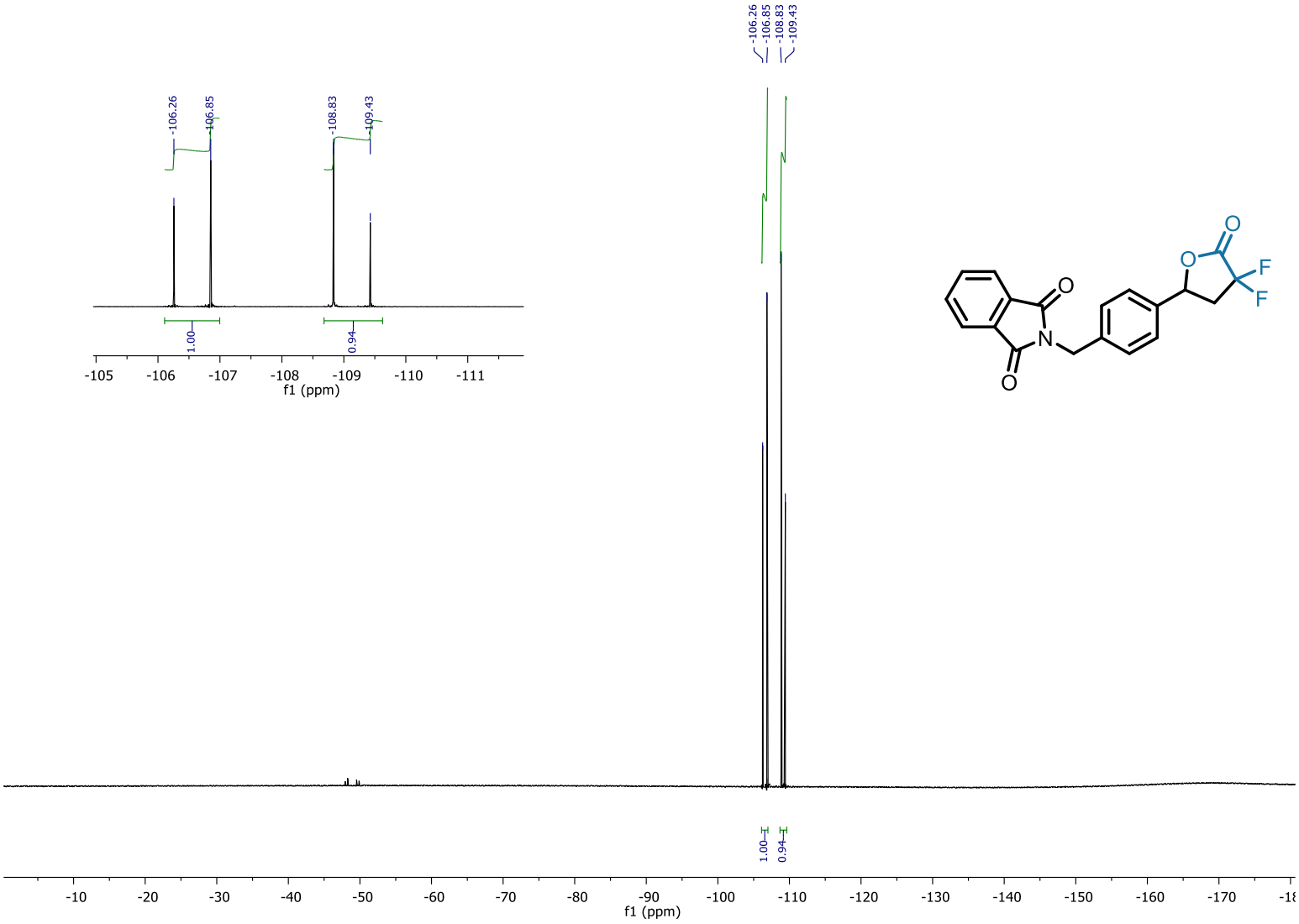
^{1}H-NMR (500 MHz, $CDCl_3$) of **54**



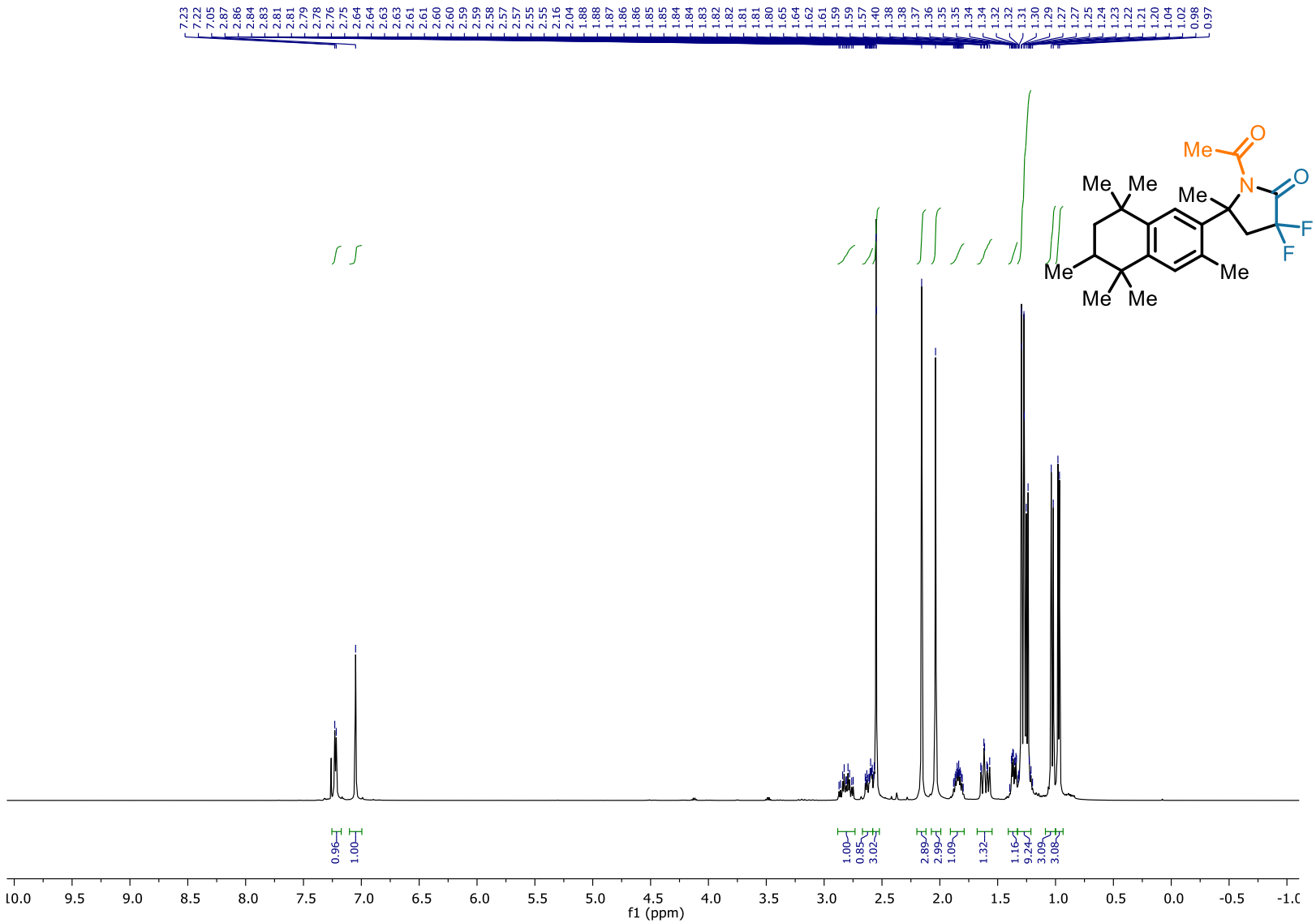
^{13}C-NMR (126 MHz, $CDCl_3$) of **54**



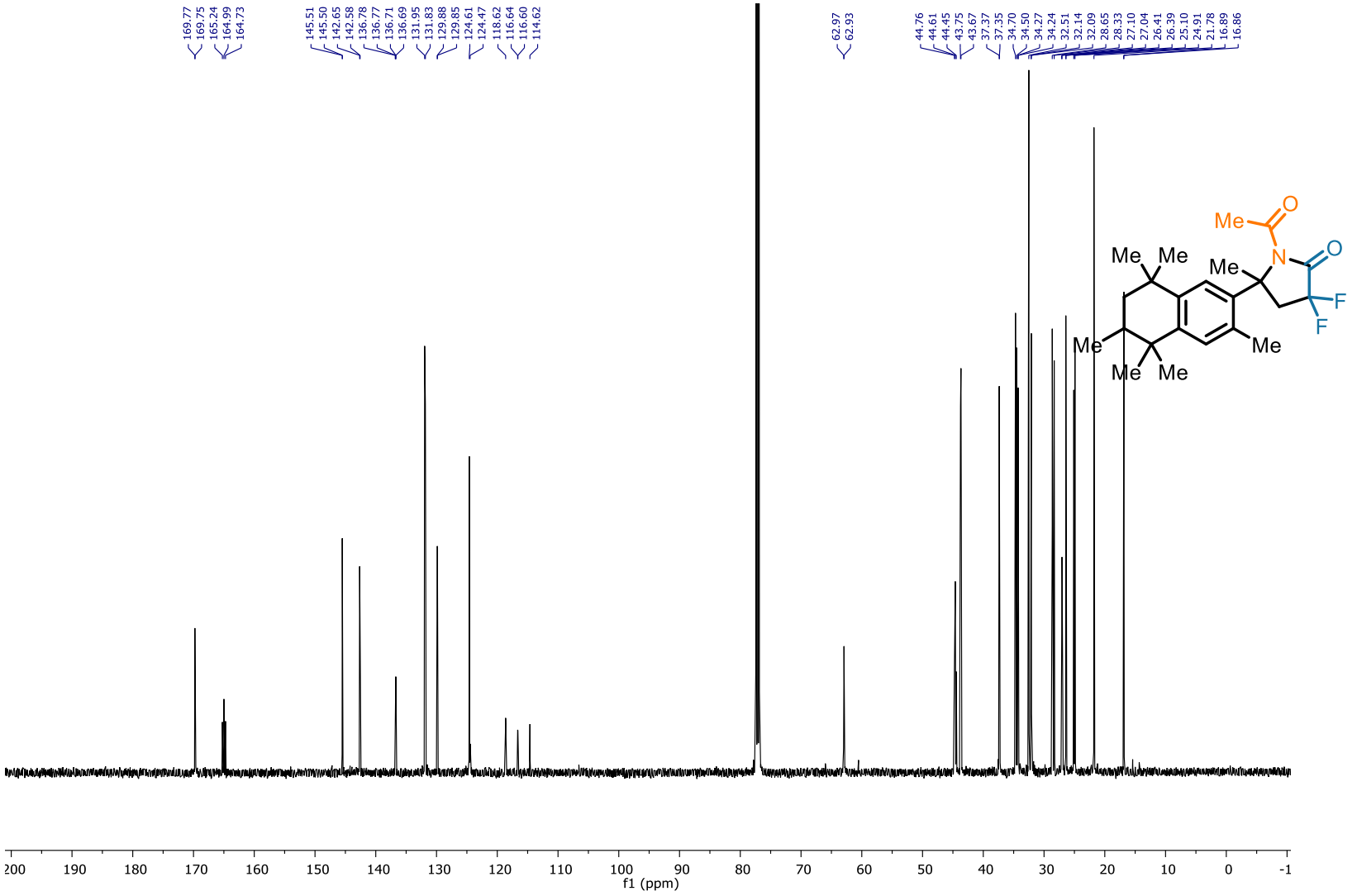
^{19}F-NMR (471 MHz, $CDCl_3$) of **54**



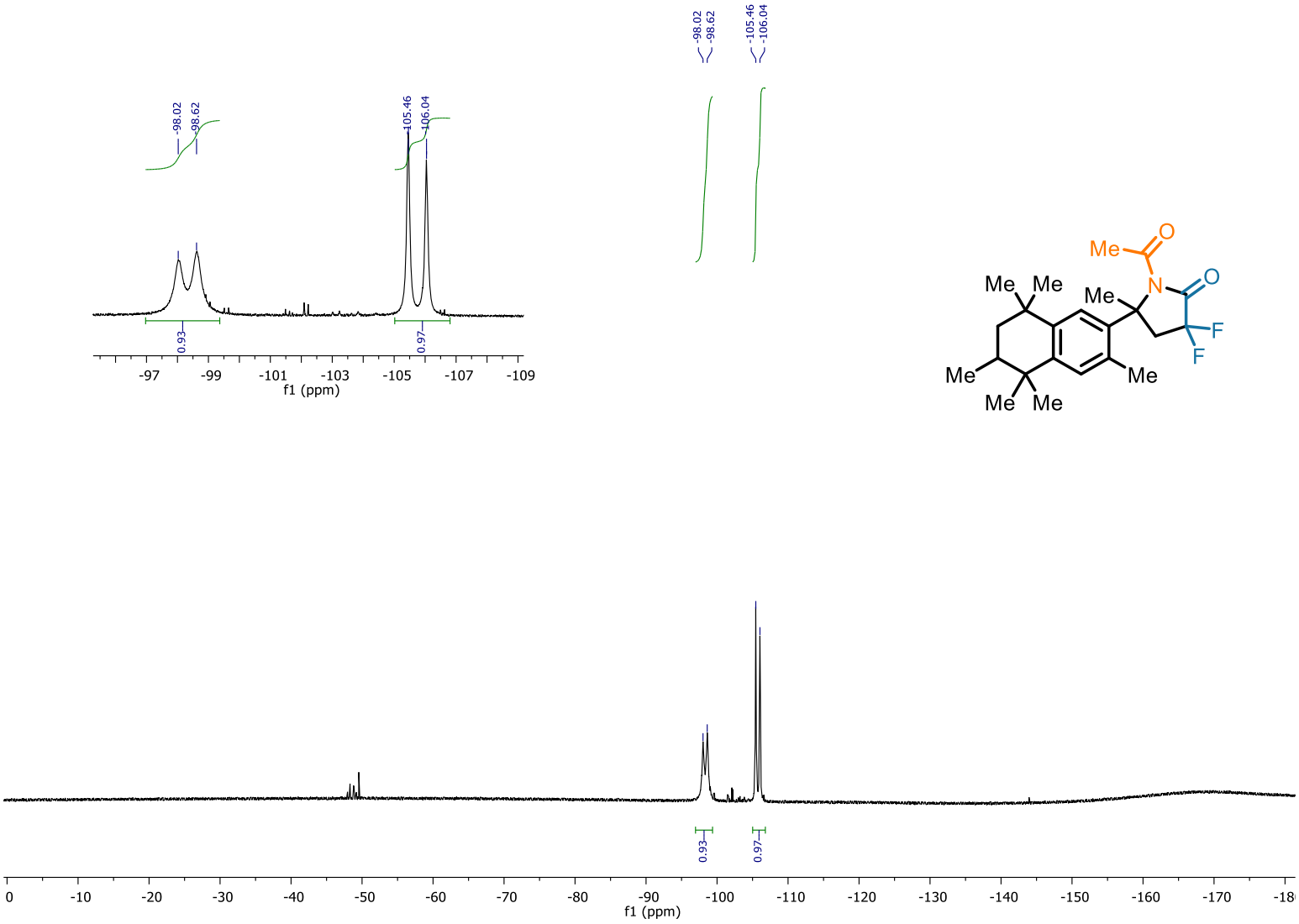
^{1}H-NMR (500 MHz, $CDCl_3$) of **55**



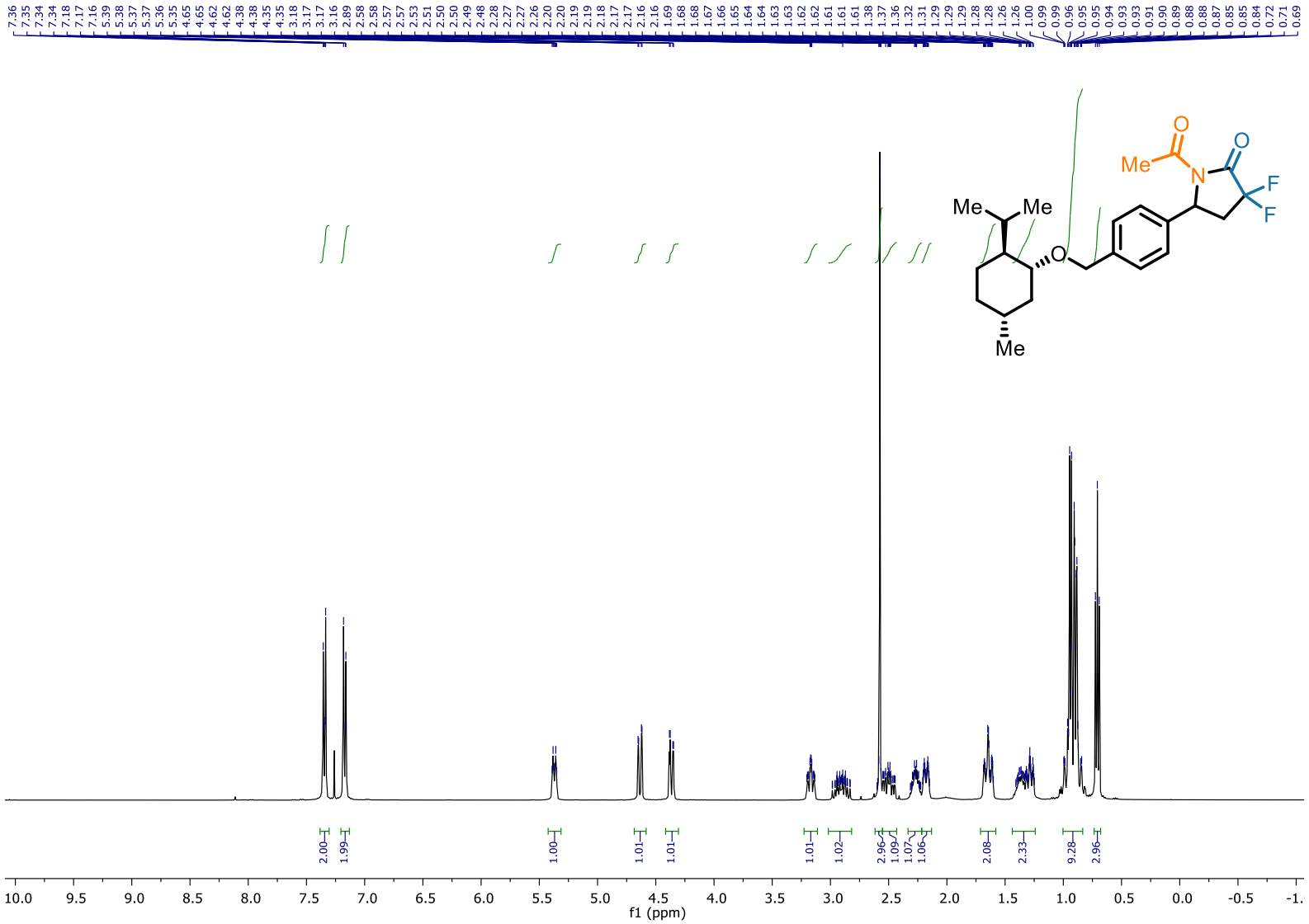
^{13}C-NMR (126 MHz, $CDCl_3$) of **55**



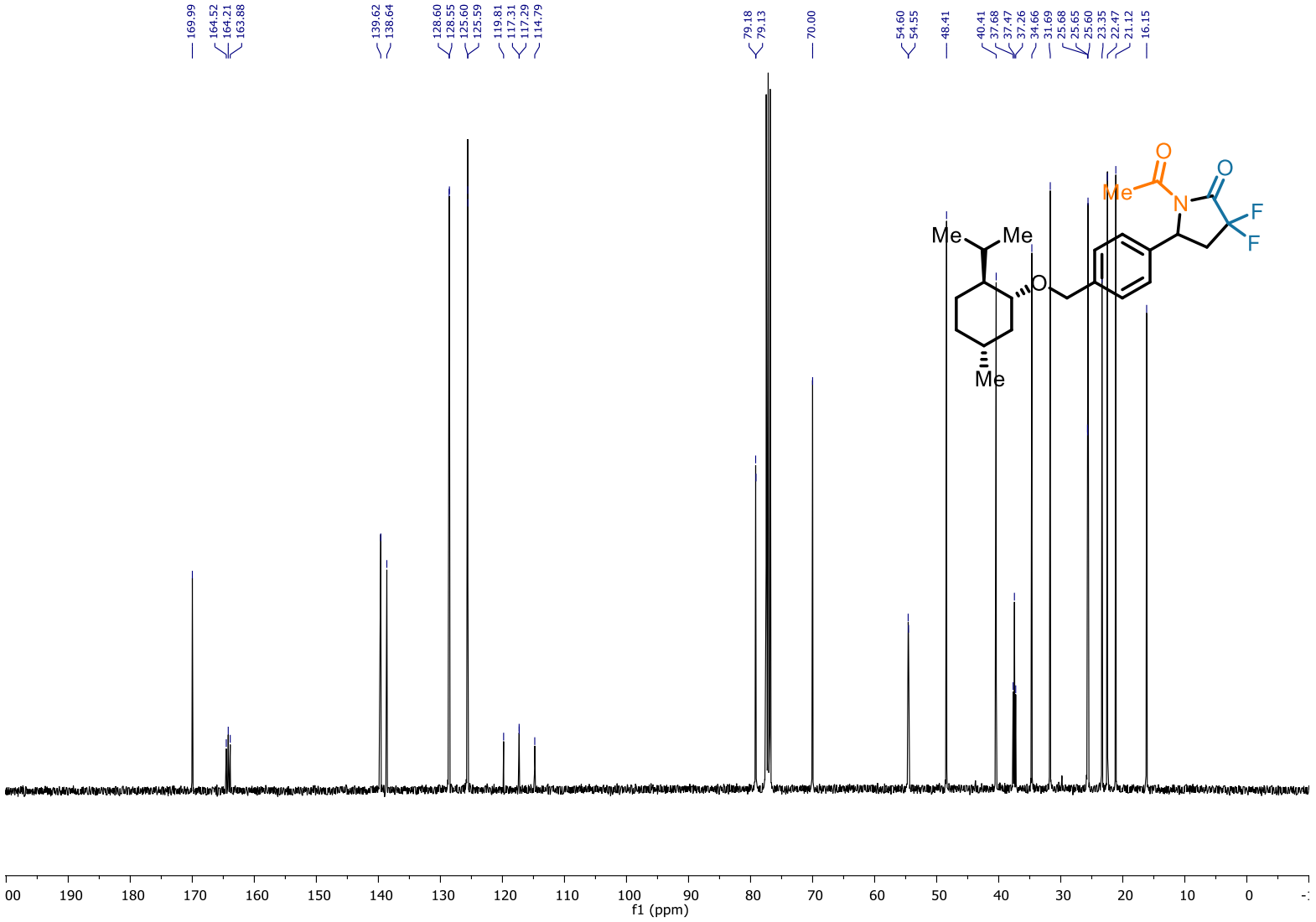
^{19}F-NMR (471 MHz, $CDCl_3$) of **55**



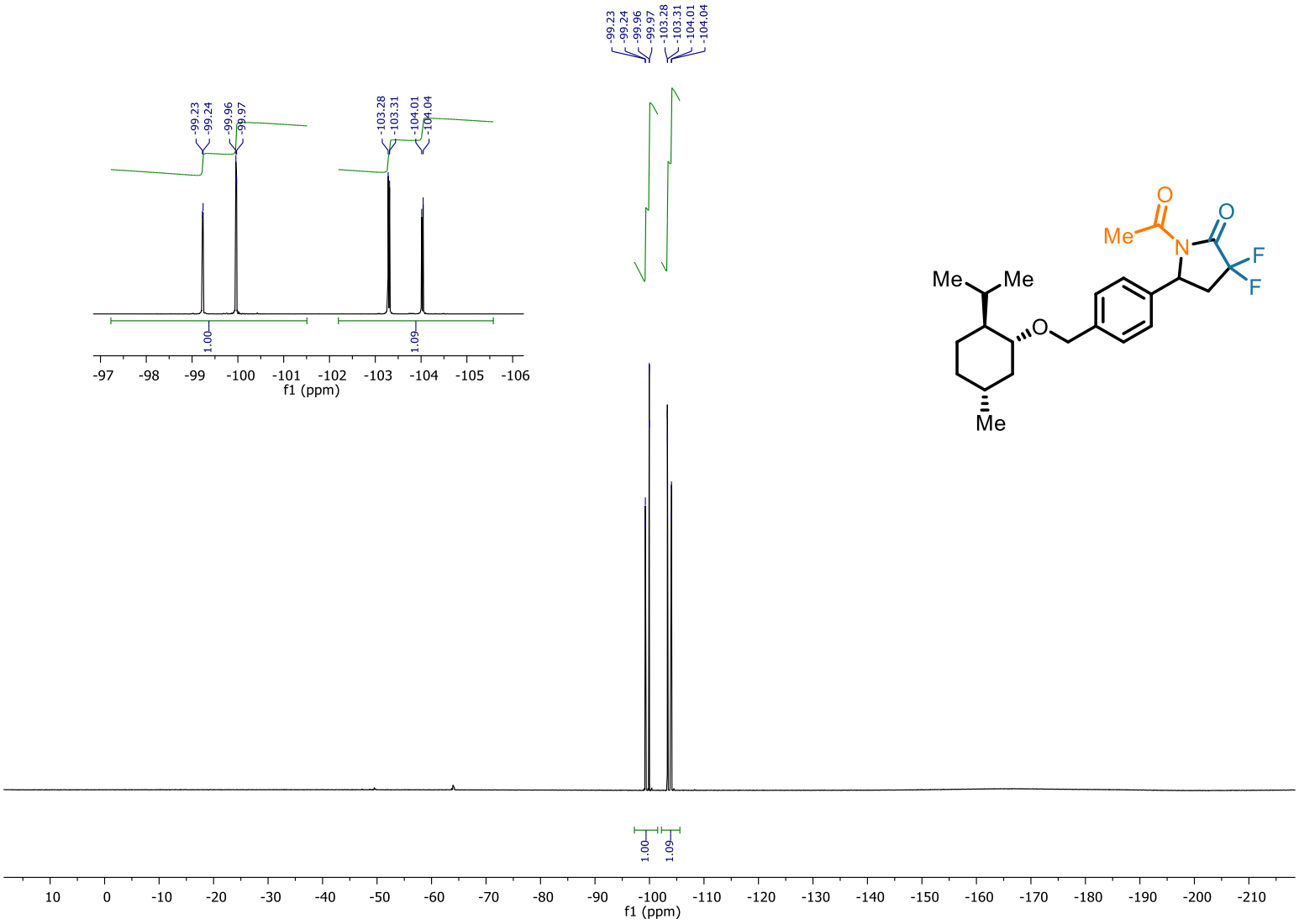
^{1}H-NMR (400 MHz, $CDCl_3$) of **56**



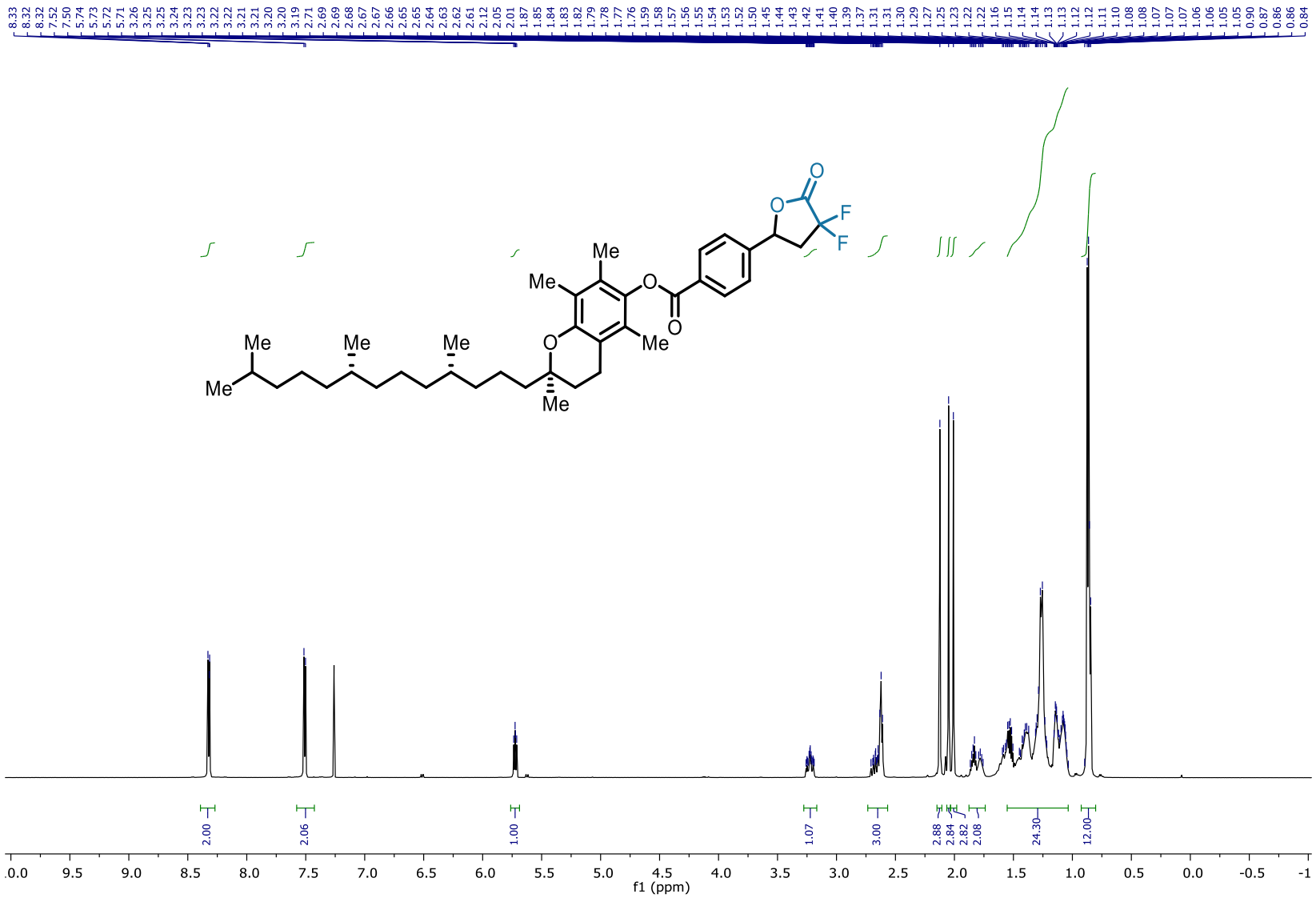
^{13}C-NMR (101 MHz, $CDCl_3$) of **56**



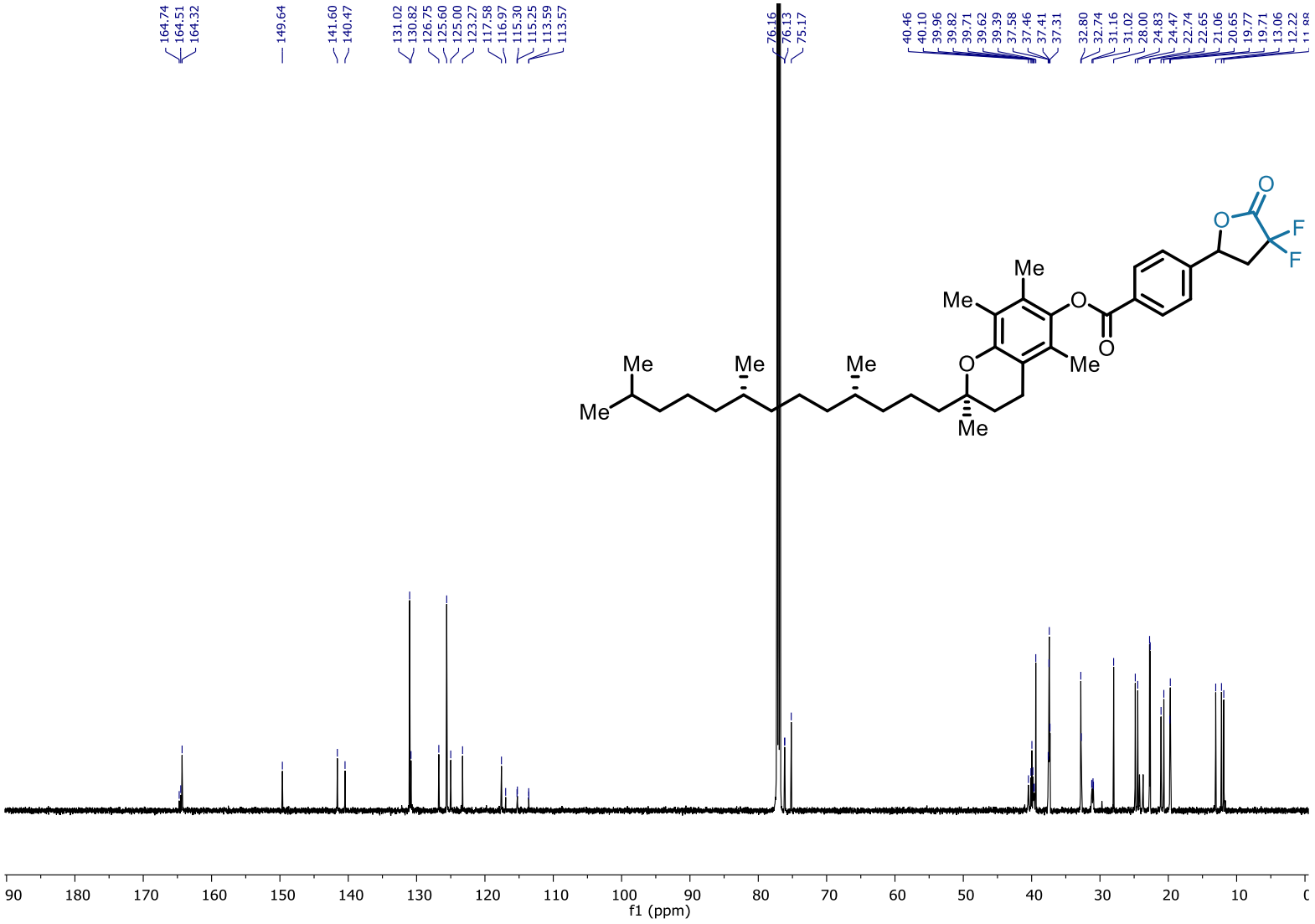
^{19}F-NMR (377 MHz, $CDCl_3$) of **56**



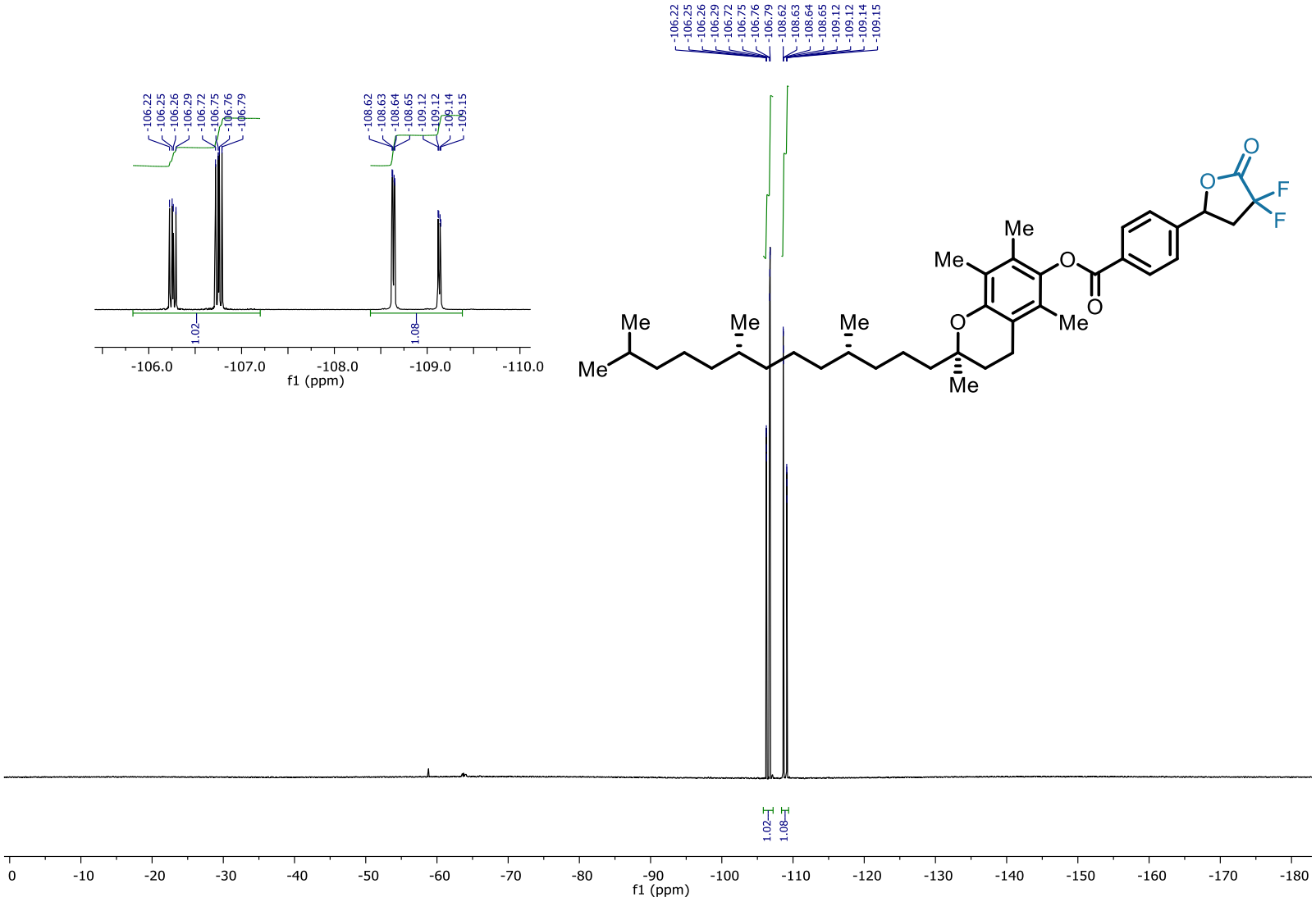
^{1}H-NMR (600 MHz, $CDCl_3$) of **57**



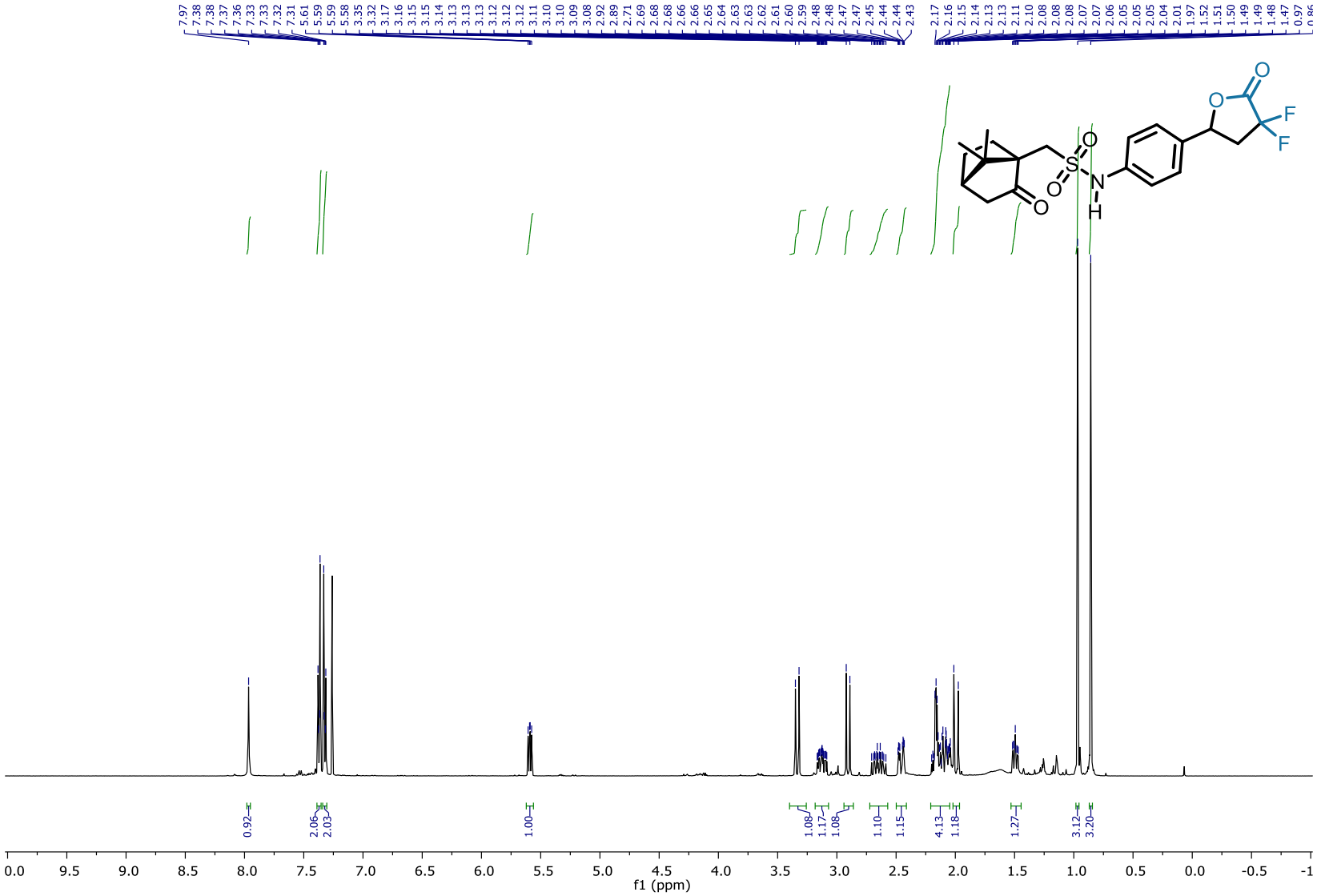
^{13}C-NMR (151 MHz, $CDCl_3$) of **57**



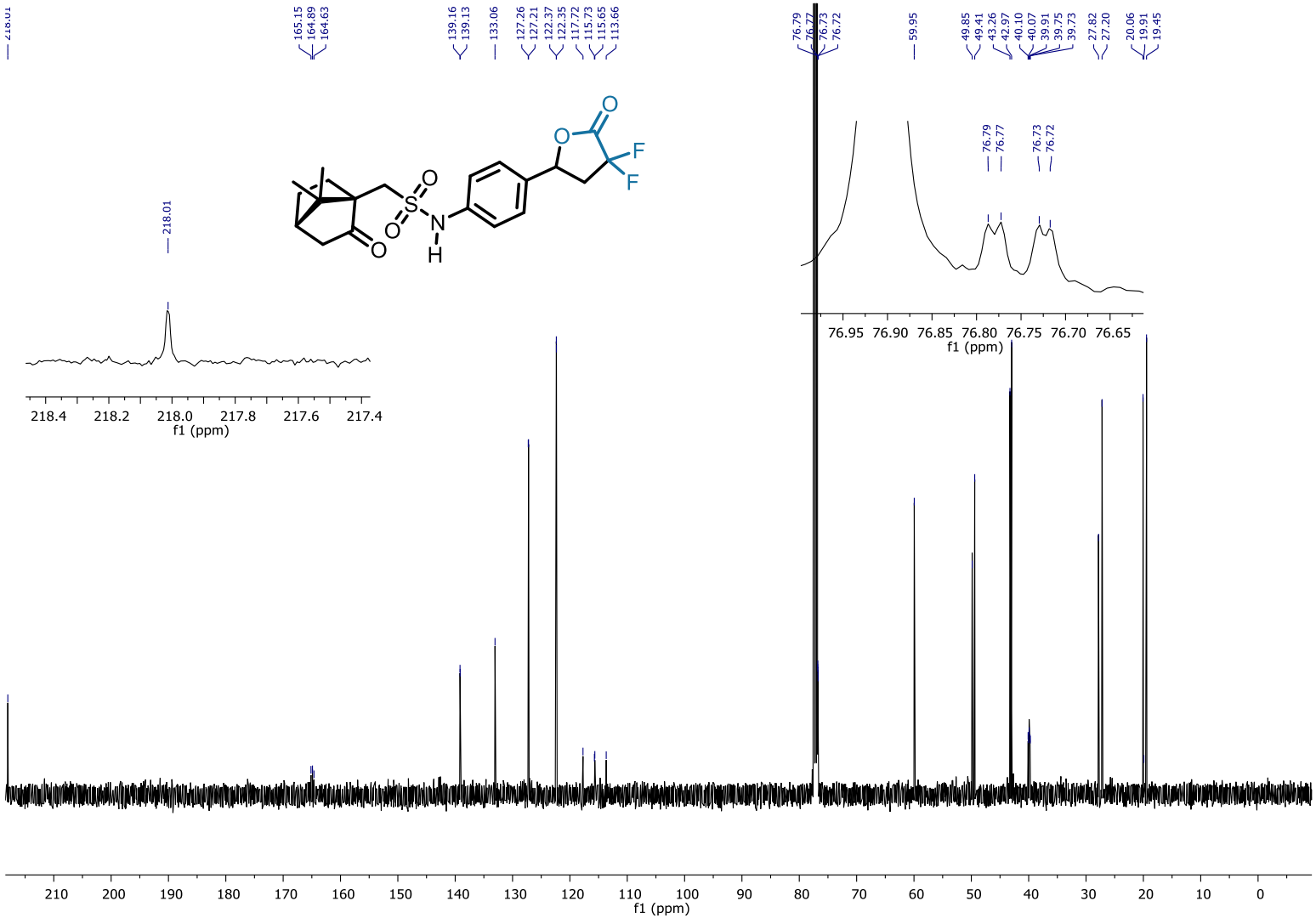
[^{1}H Coupled] ^{19}F-NMR (565 MHz, $CDCl_3$) of **57**



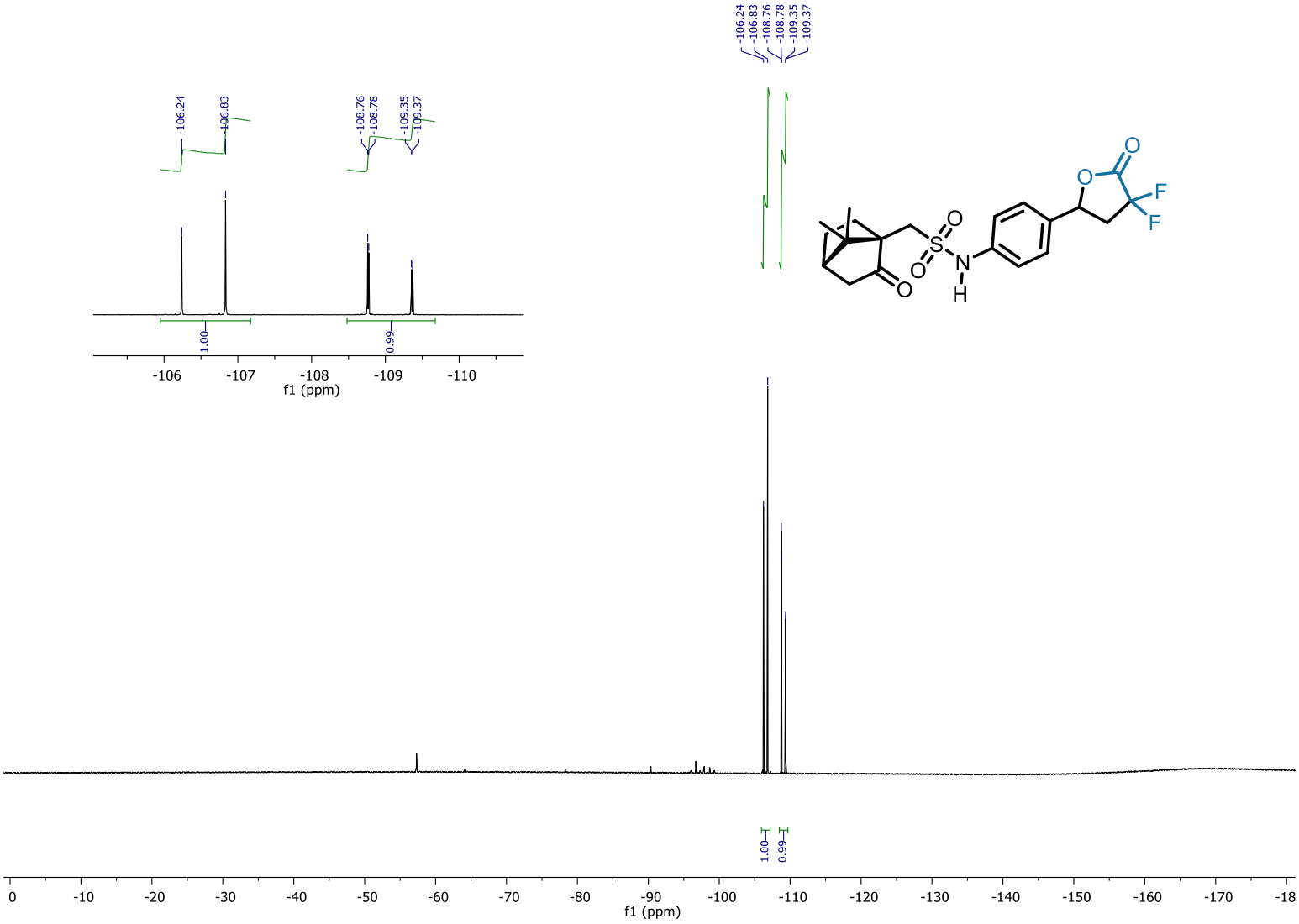
^{1}H-NMR (500 MHz, $CDCl_3$) of **58**



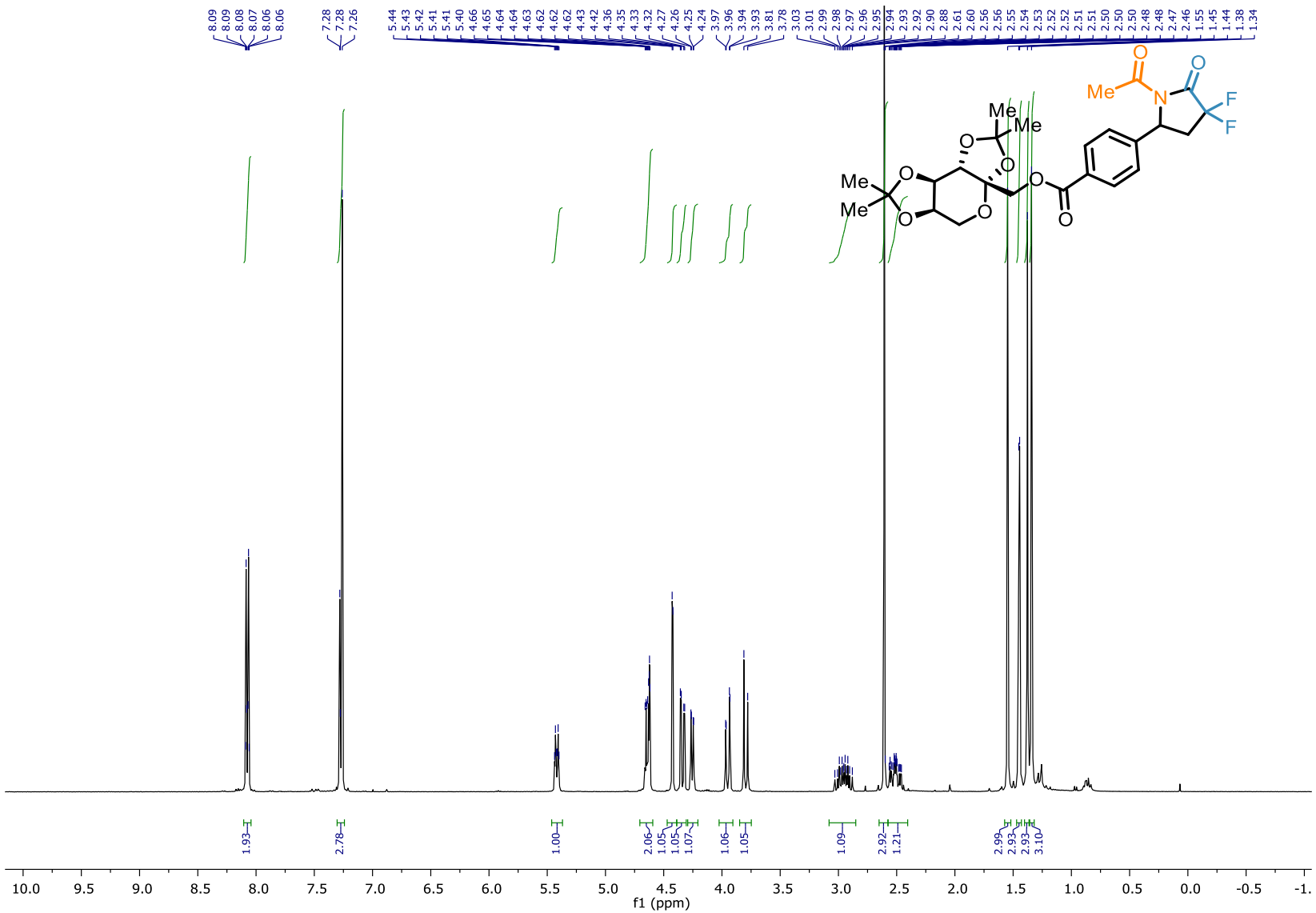
^{13}C-NMR (126 MHz, $CDCl_3$) of **58**



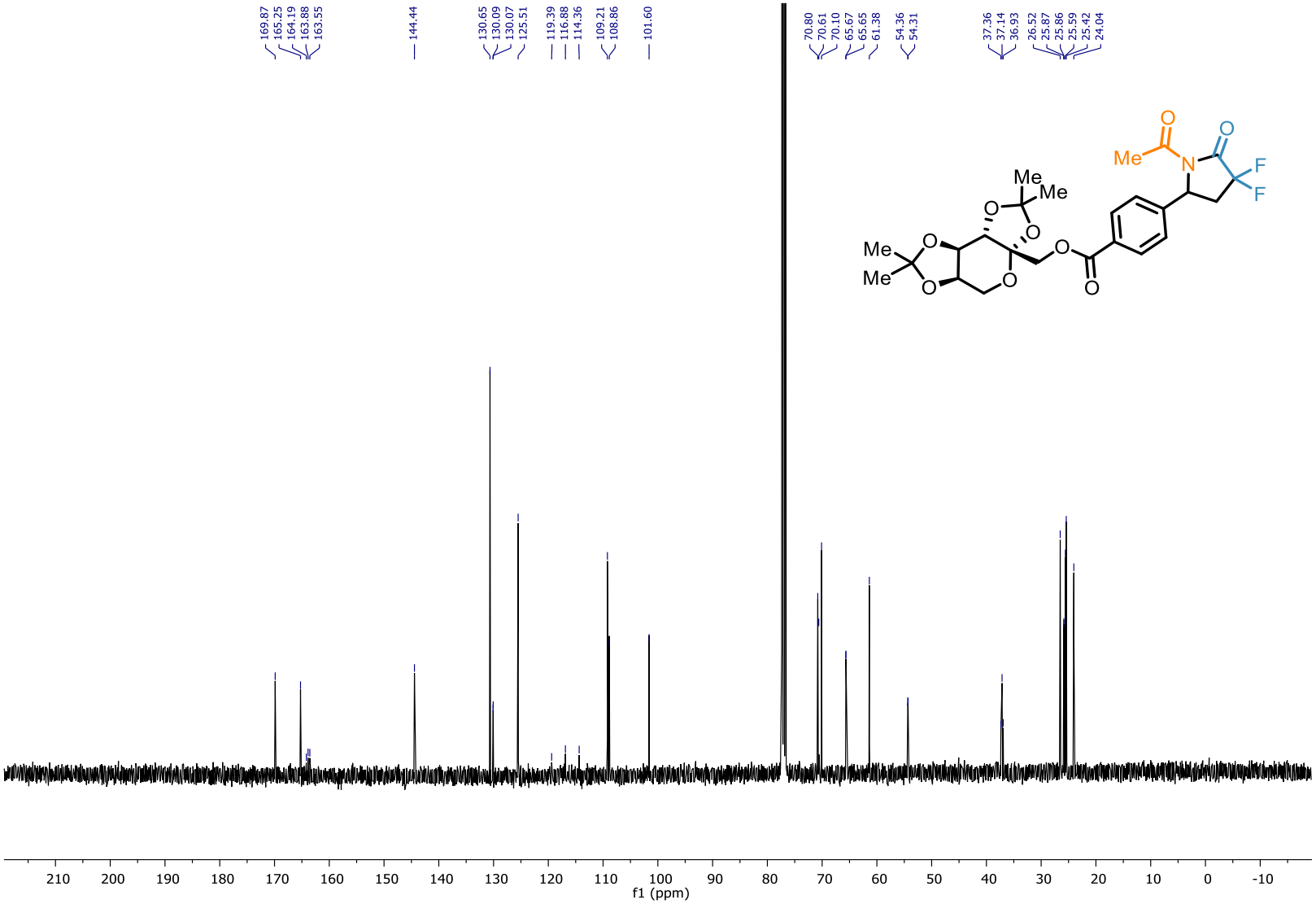
^{19}F-NMR (471 MHz, $CDCl_3$) of **58**



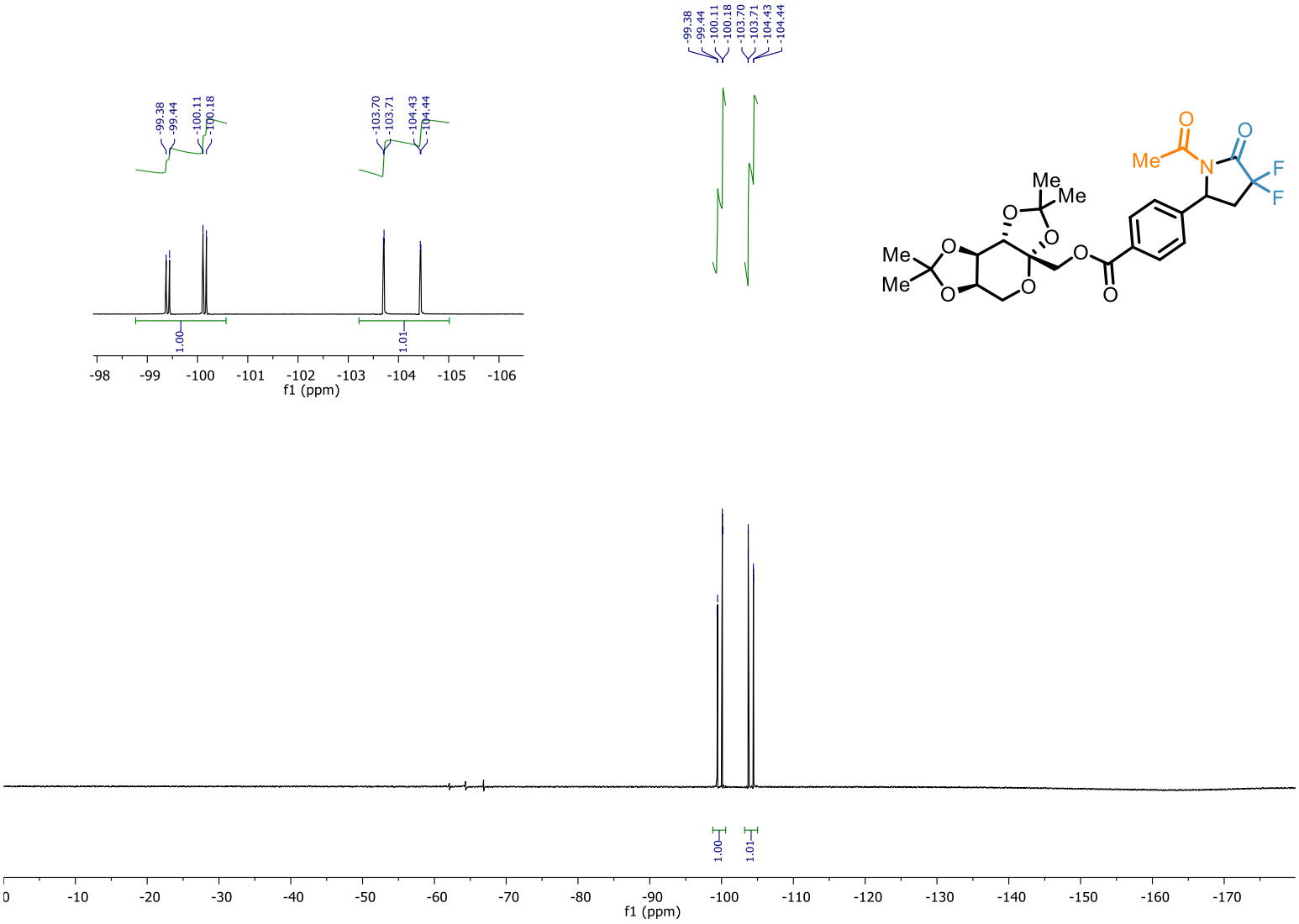
^{1}H-NMR (400 MHz, $CDCl_3$) of **59**



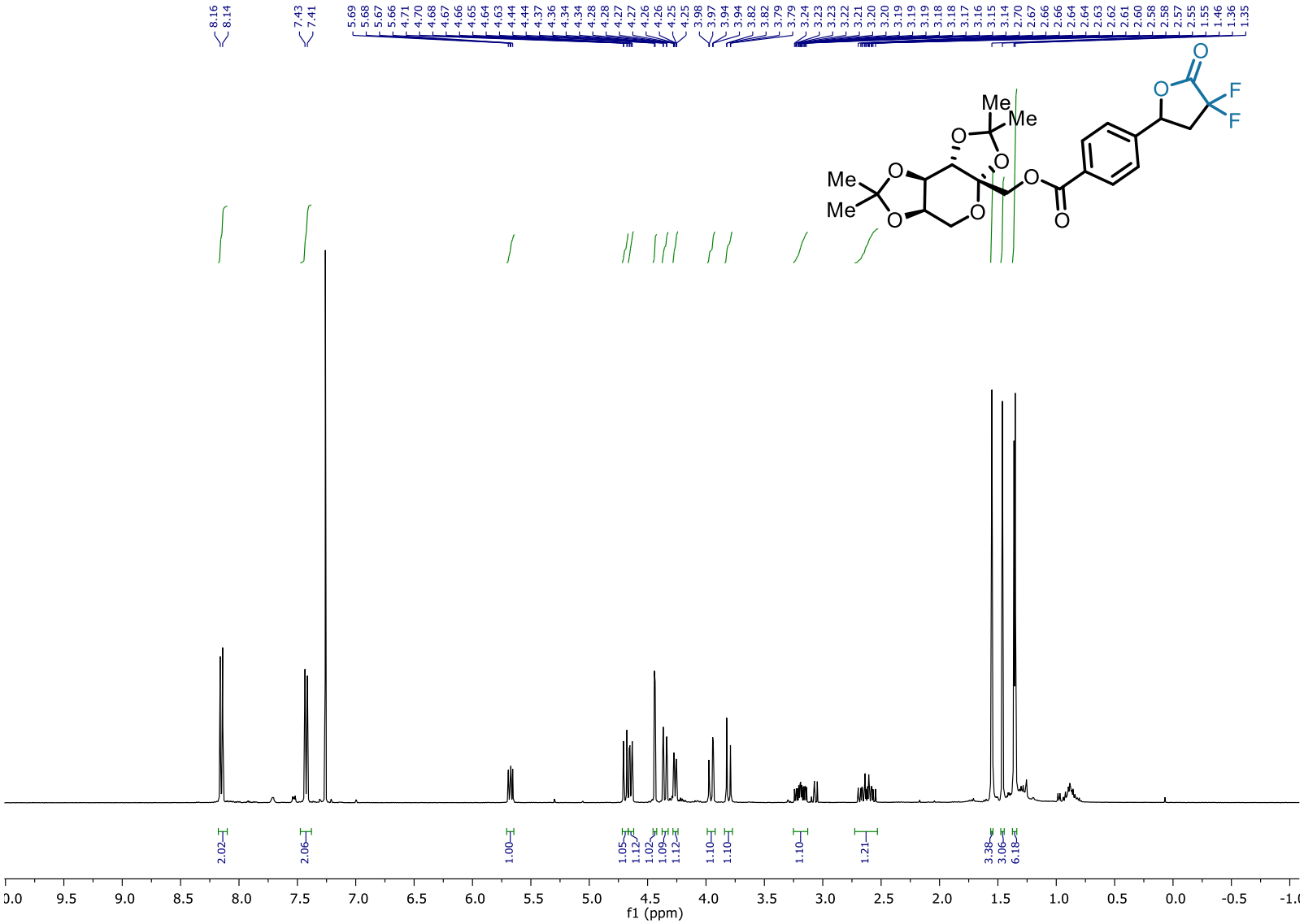
^{13}C-NMR (101 MHz, $CDCl_3$) of **59**



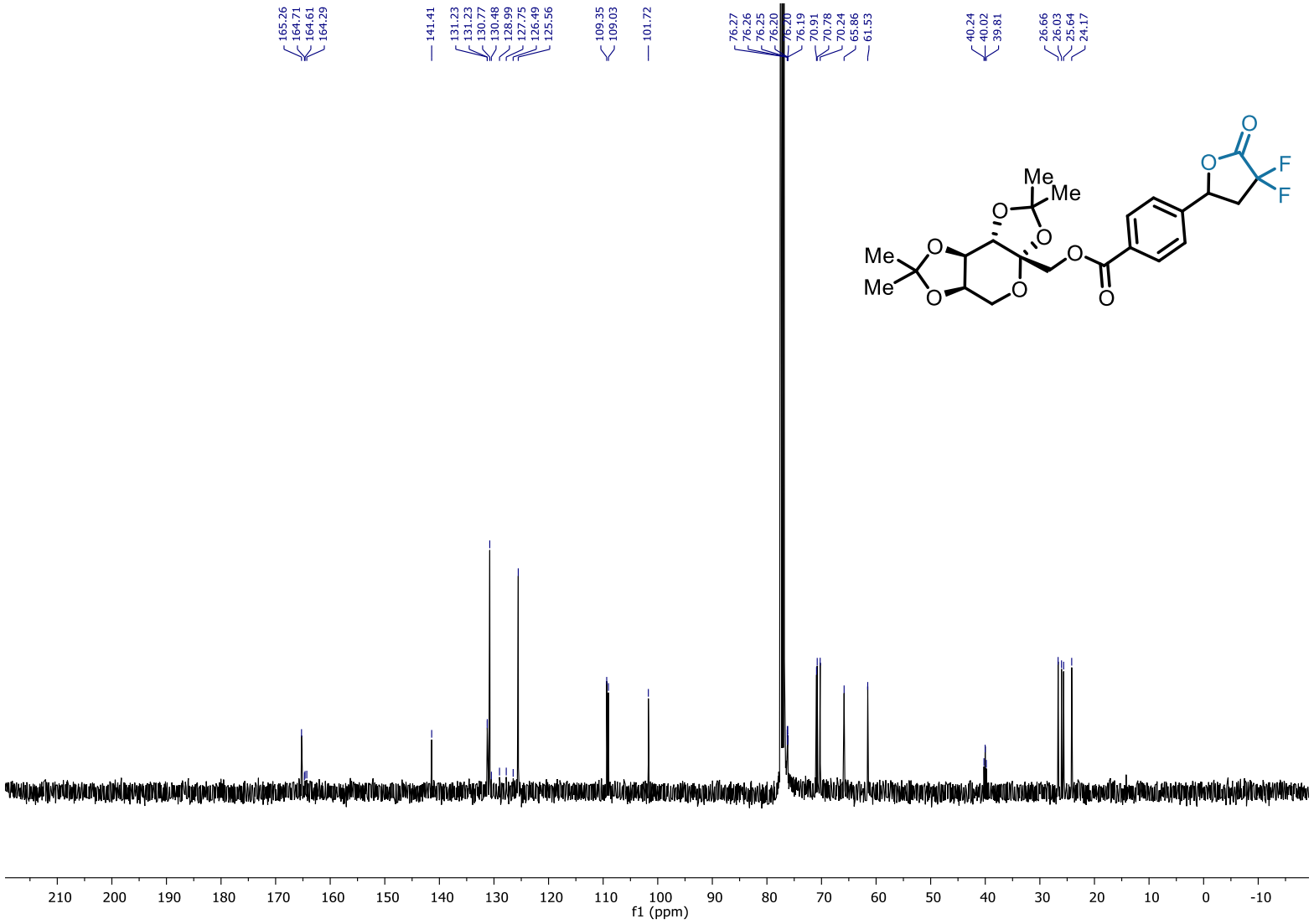
^{19}F-NMR (377 MHz, $CDCl_3$) of **59**



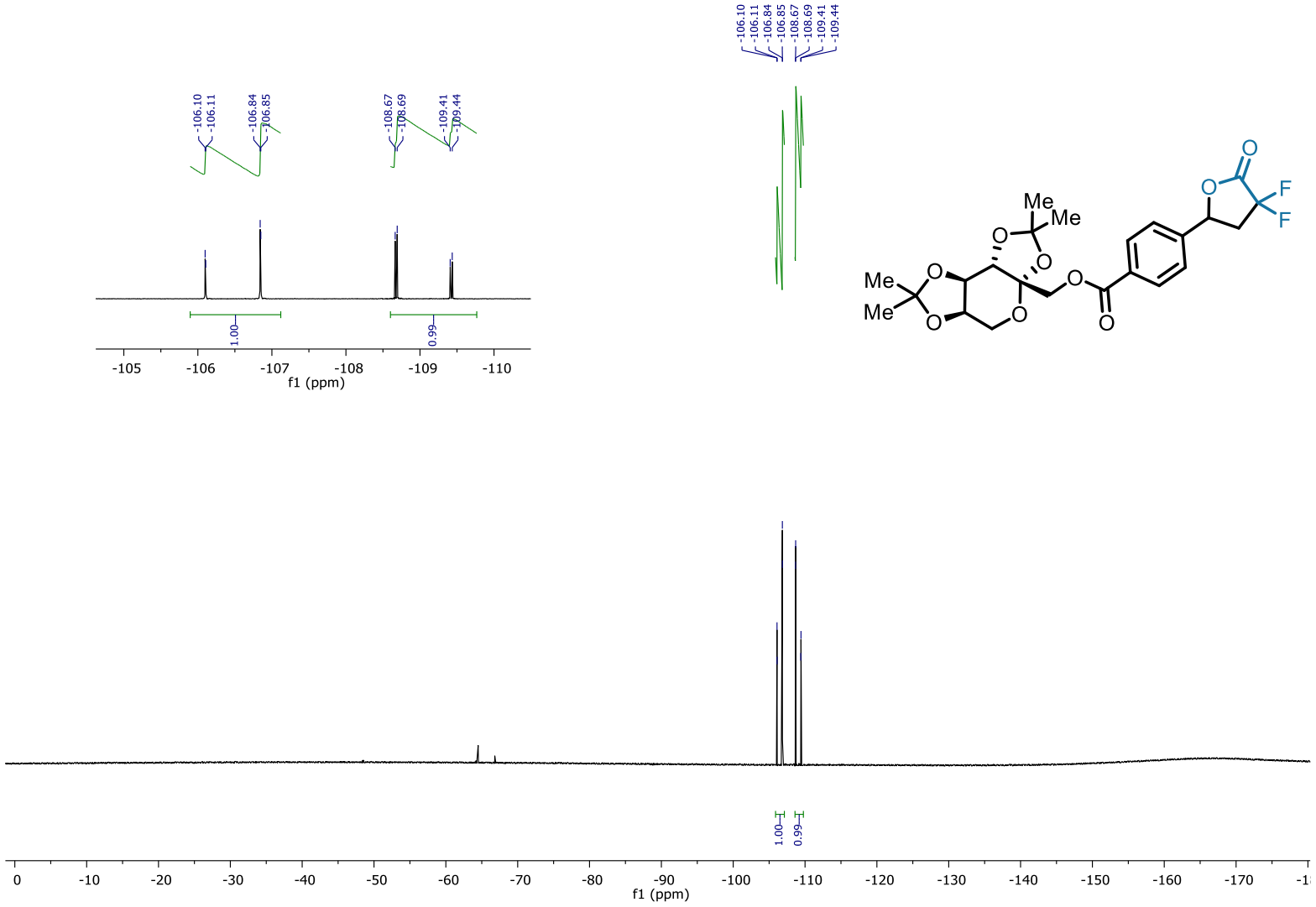
^{1}H-NMR (400 MHz, $CDCl_3$) of **60**



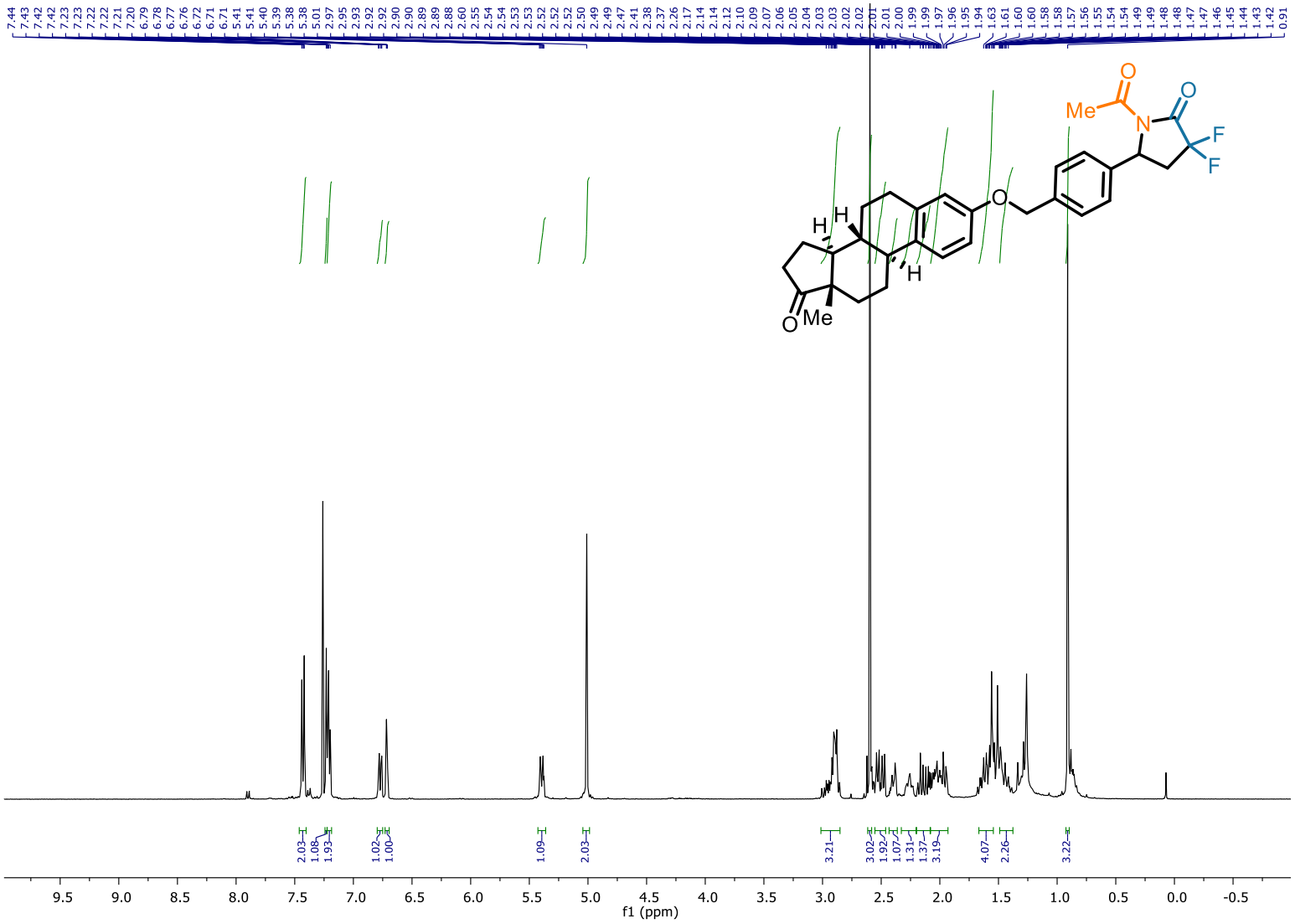
^{13}C-NMR (101 MHz, $CDCl_3$) of **60**



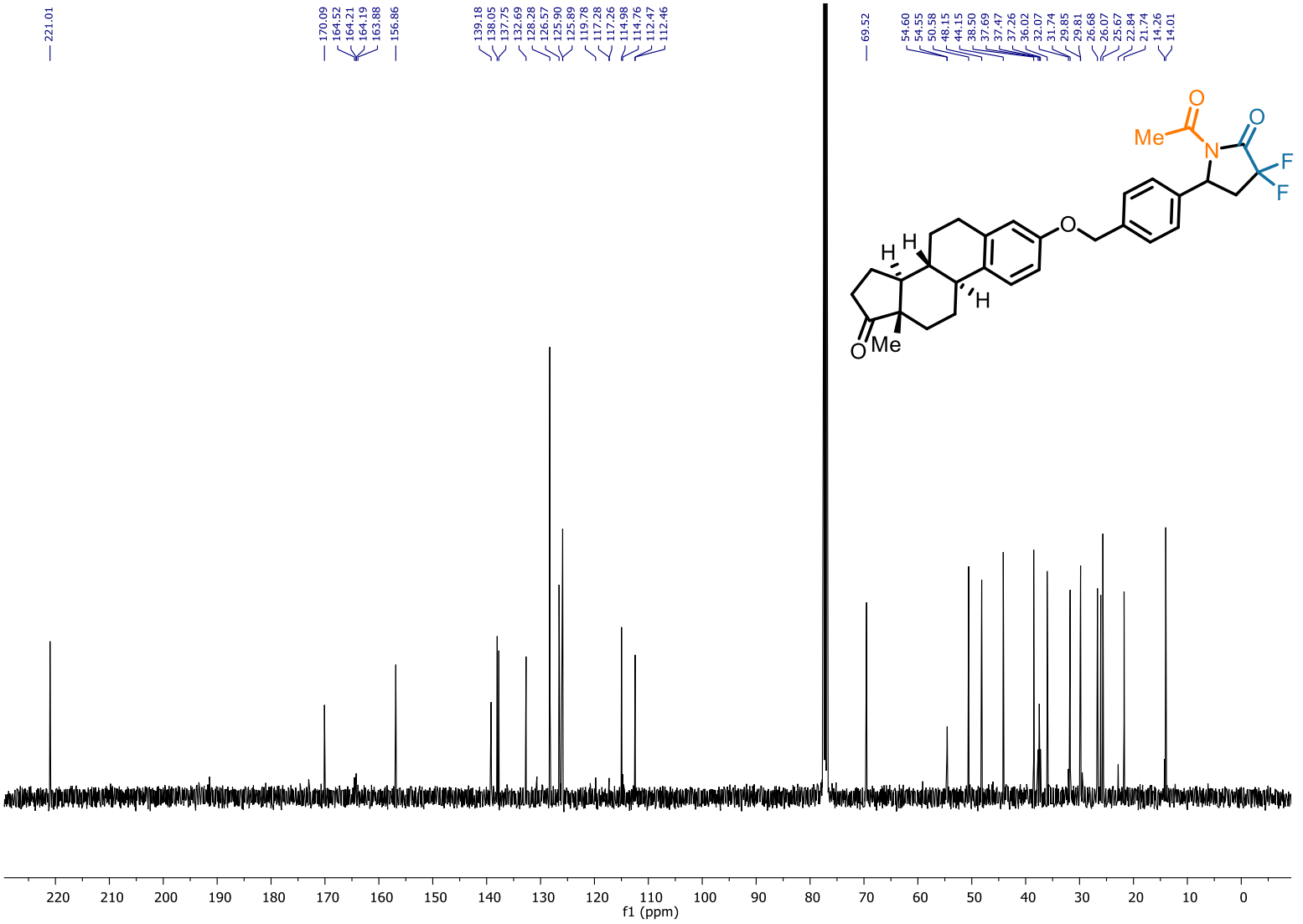
^{19}F-NMR (377 MHz, $CDCl_3$) of **60**



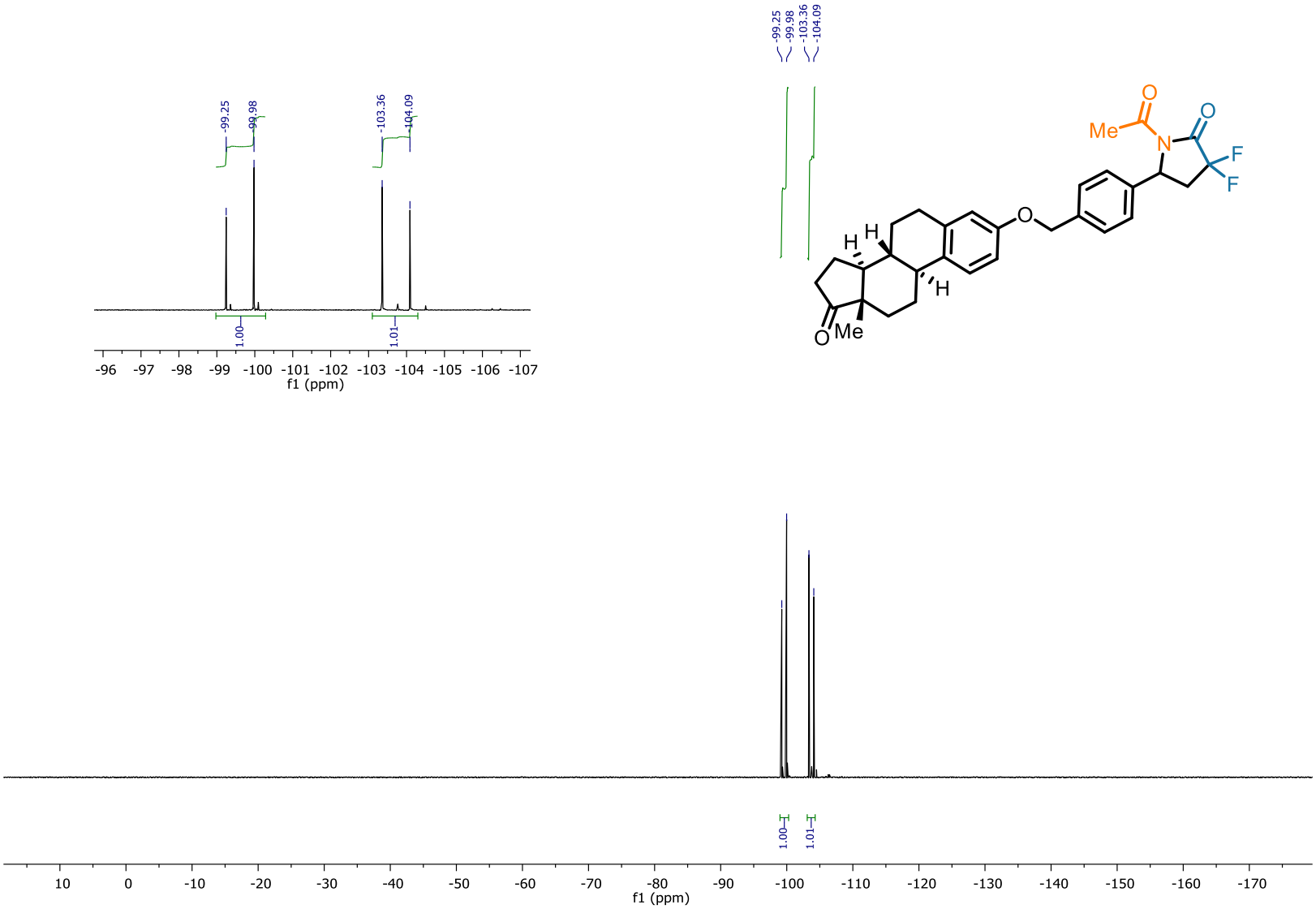
^{1}H-NMR (400 MHz, $CDCl_3$) of **61**



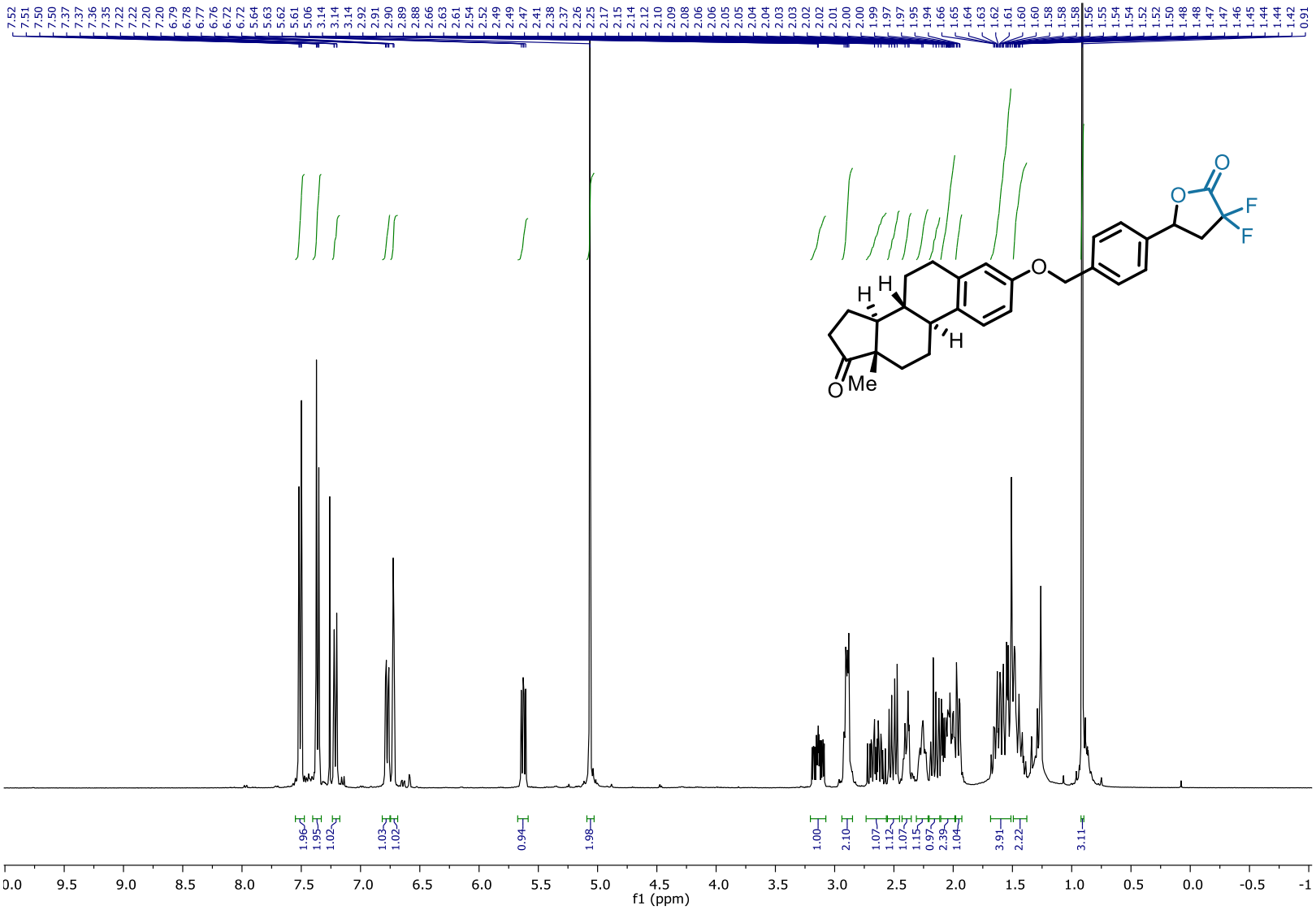
^{13}C-NMR (101 MHz, $CDCl_3$) of **61**



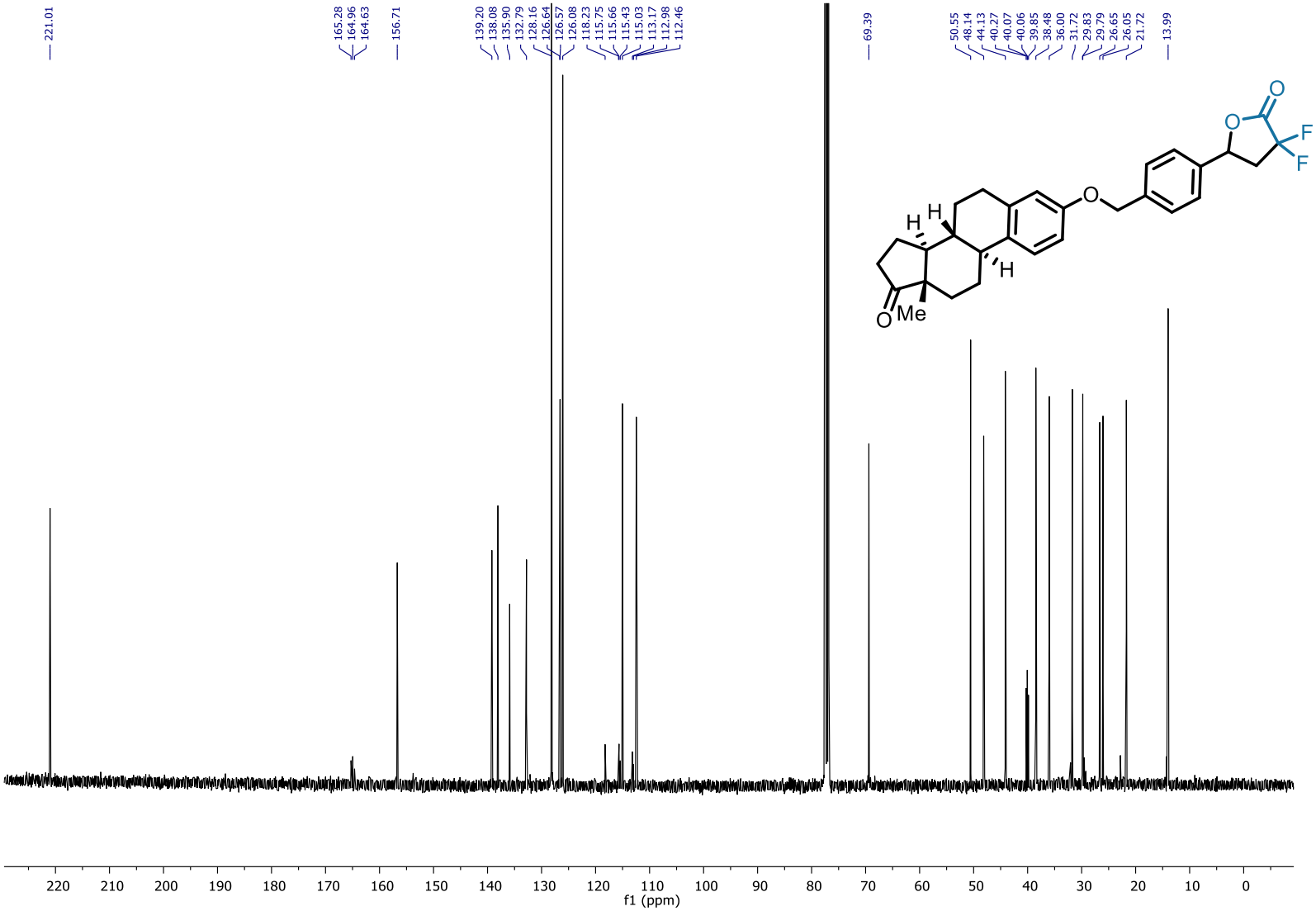
^{19}F-NMR (377 MHz, $CDCl_3$) of **61**



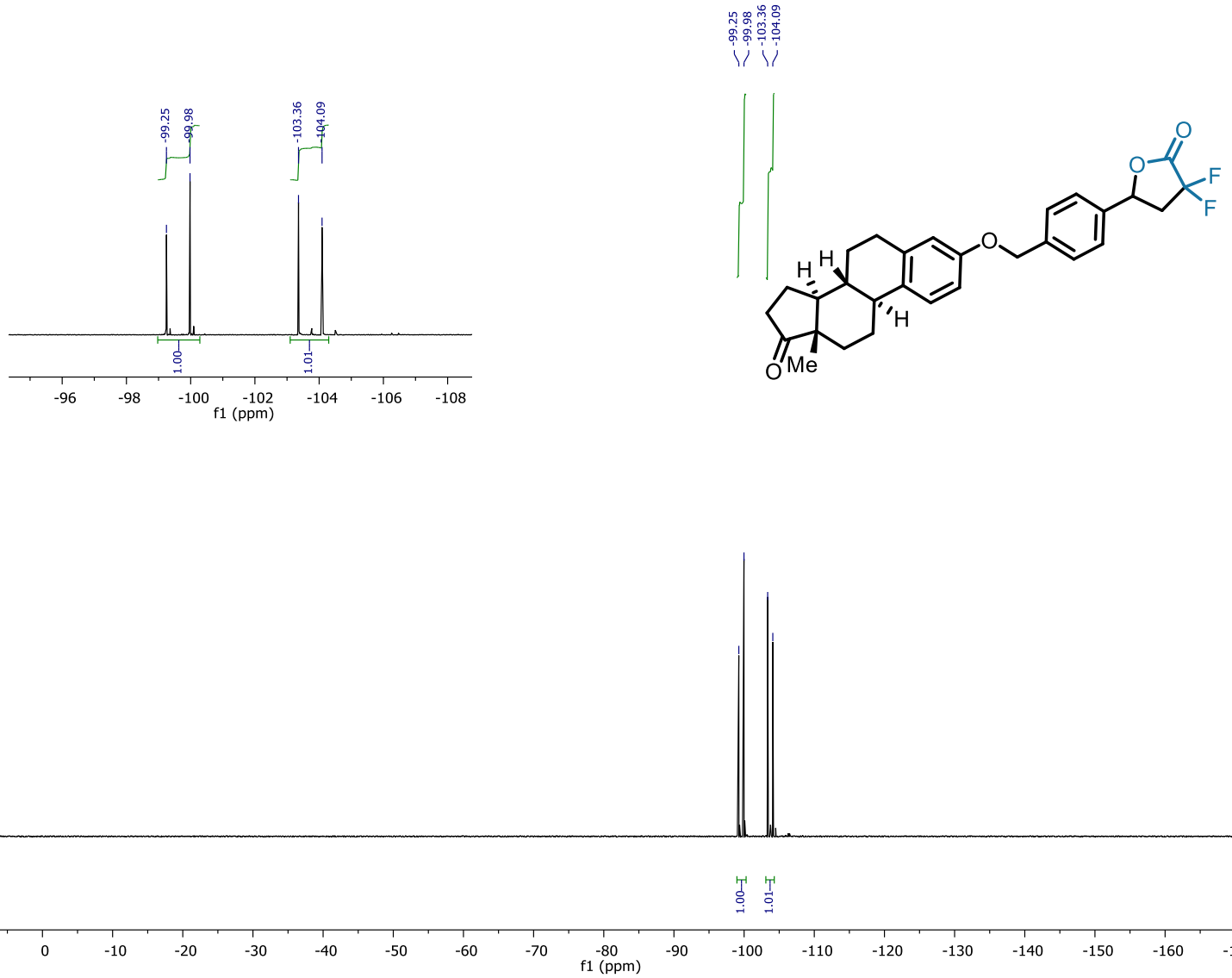
^{1}H-NMR (400 MHz, $CDCl_3$) of **62**



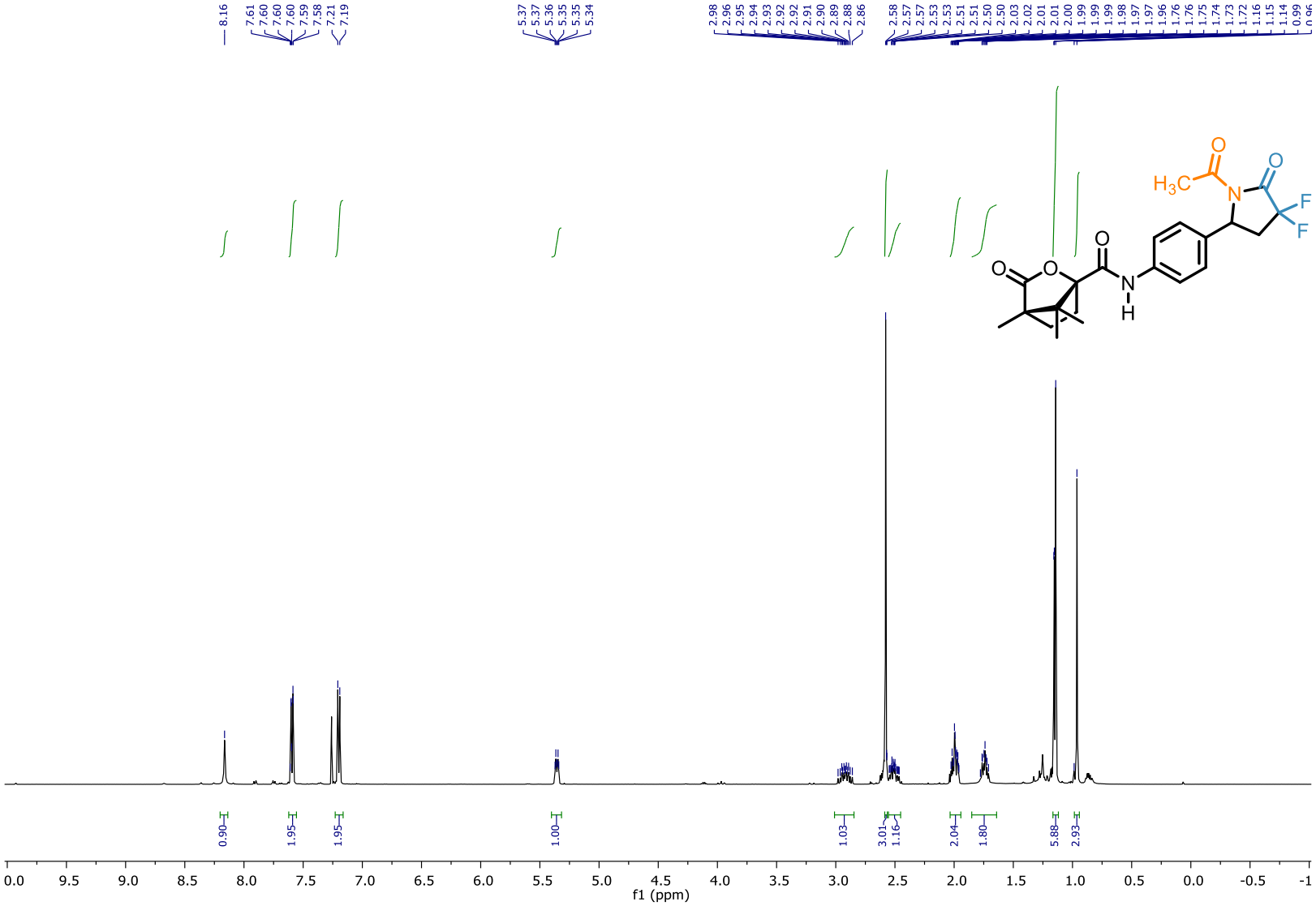
^{13}C-NMR (101 MHz, $CDCl_3$) of **62**



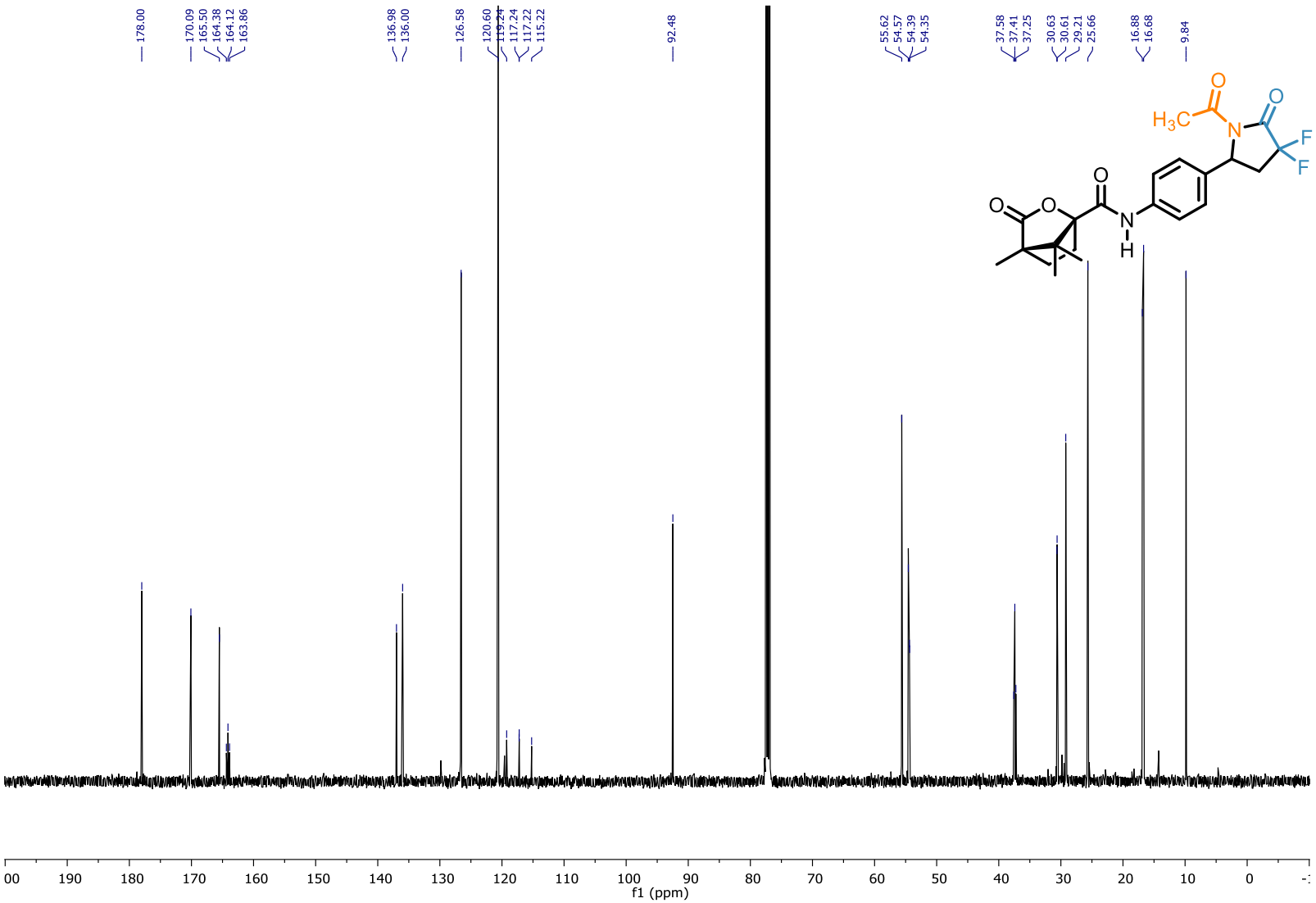
^{19}F-NMR (377 MHz, $CDCl_3$) of **62**



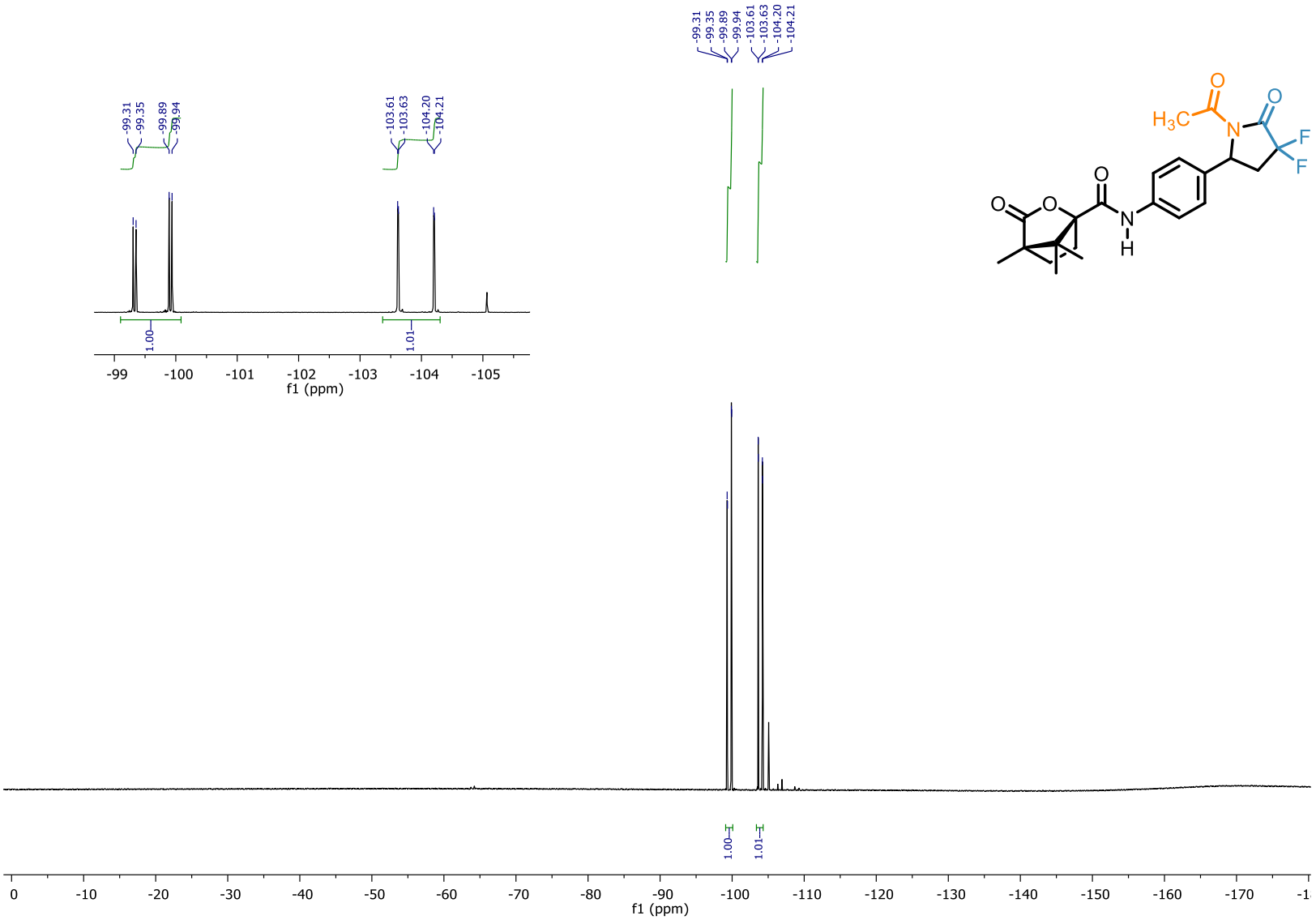
^{1}H-NMR (500 MHz, $CDCl_3$) of **63**



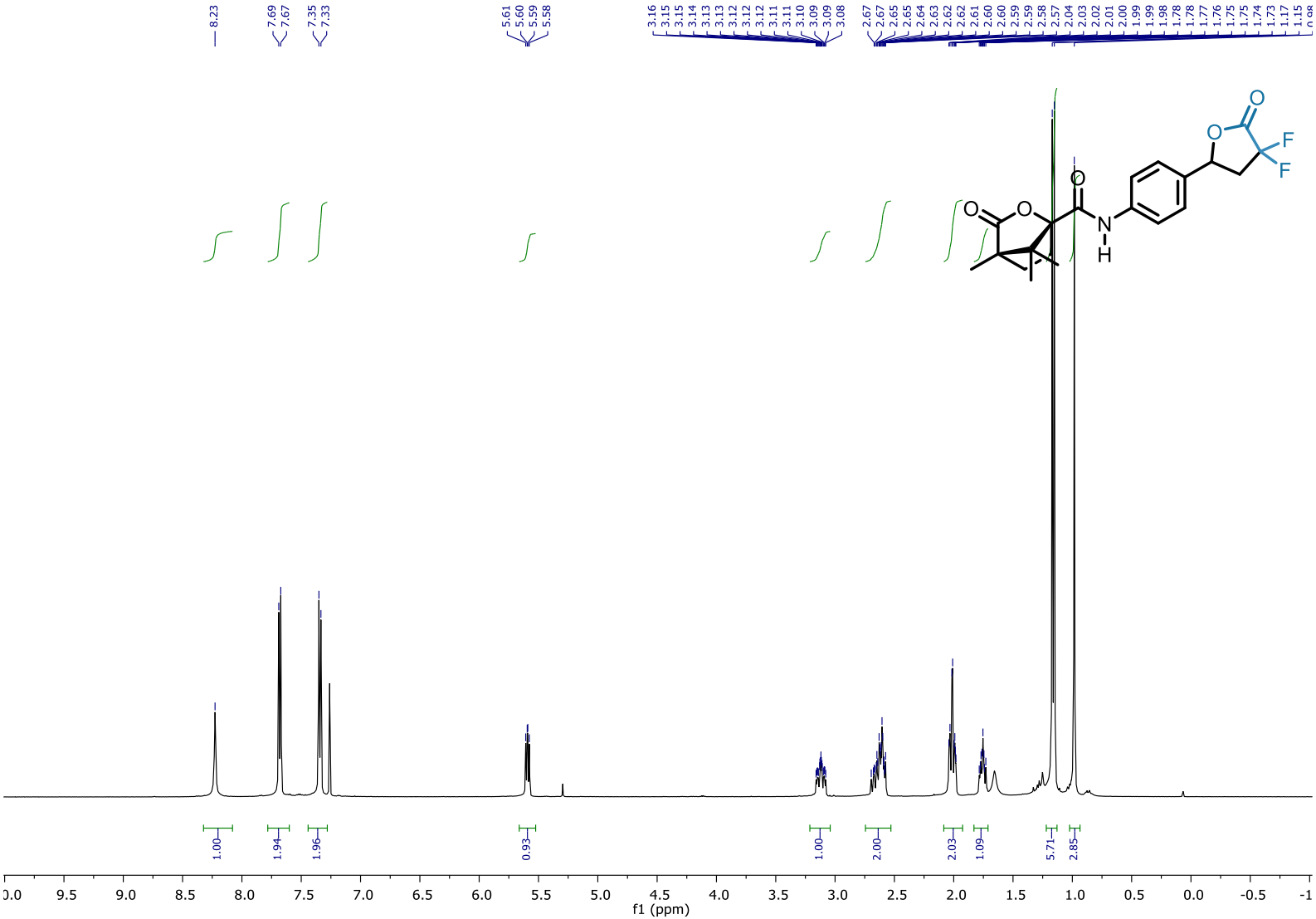
^{13}C-NMR (126 MHz, $CDCl_3$) of **63**



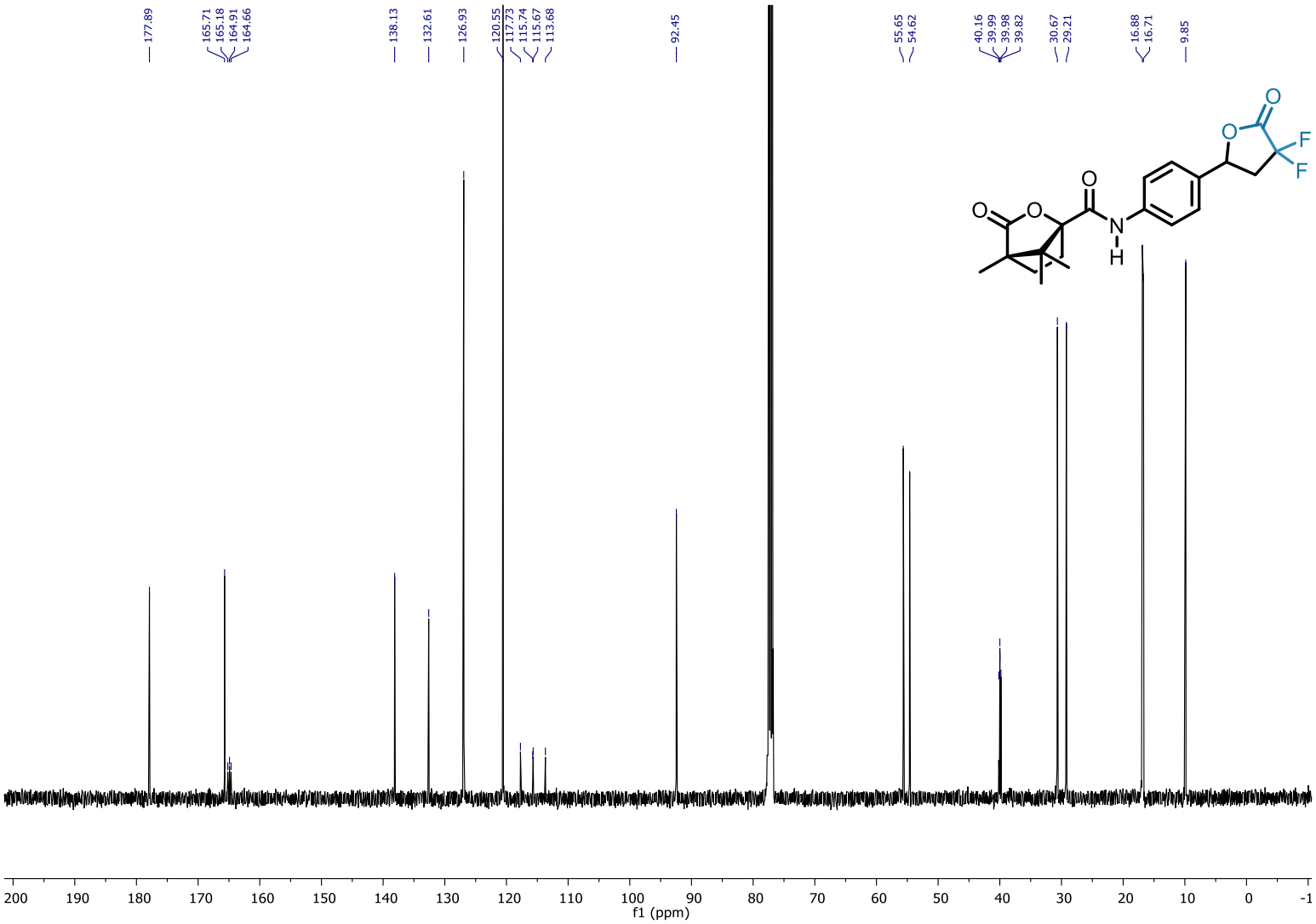
^{19}F-NMR (377 MHz, $CDCl_3$) of **63**



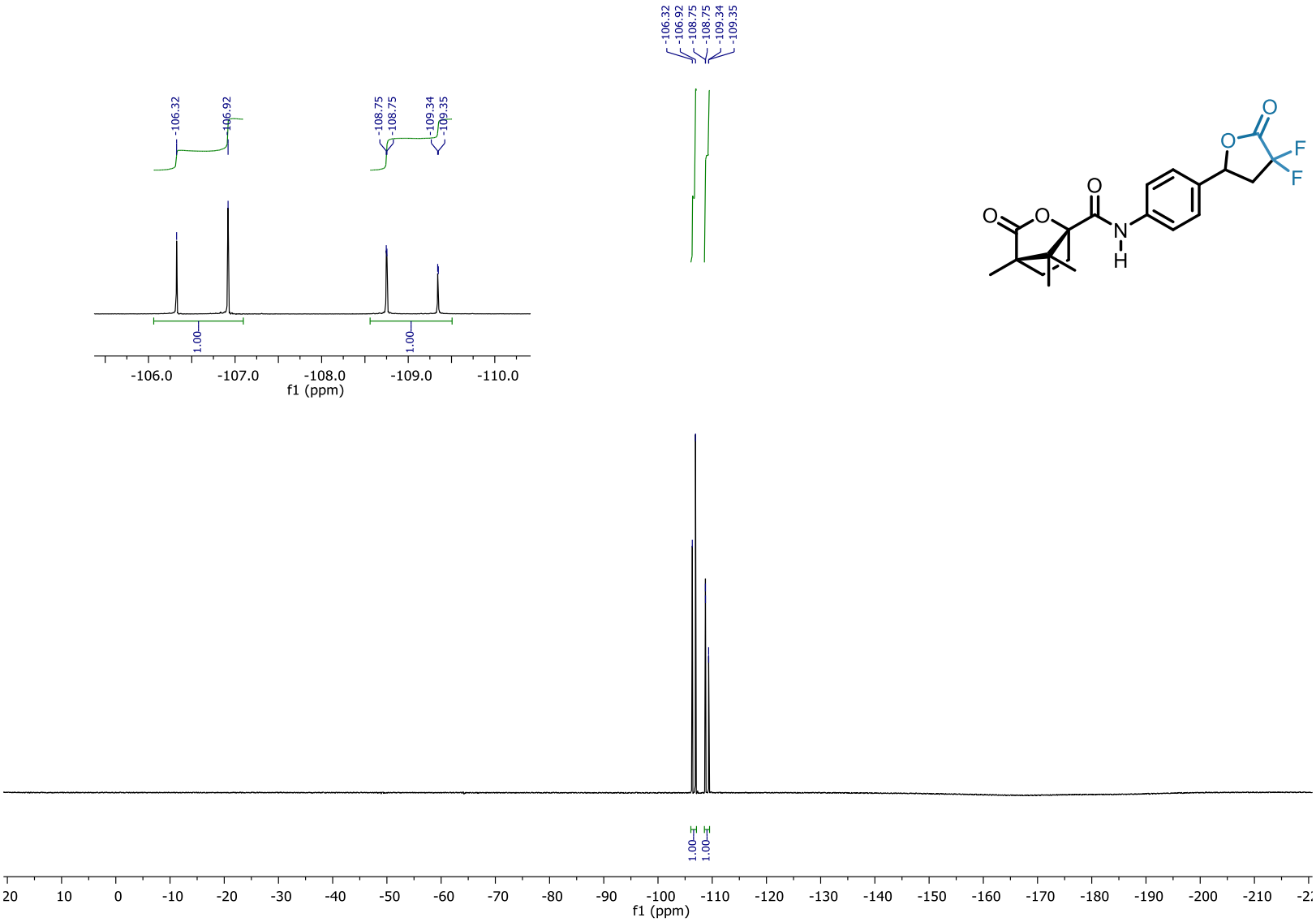
^{1}H-NMR (500 MHz, $CDCl_3$) of **64**



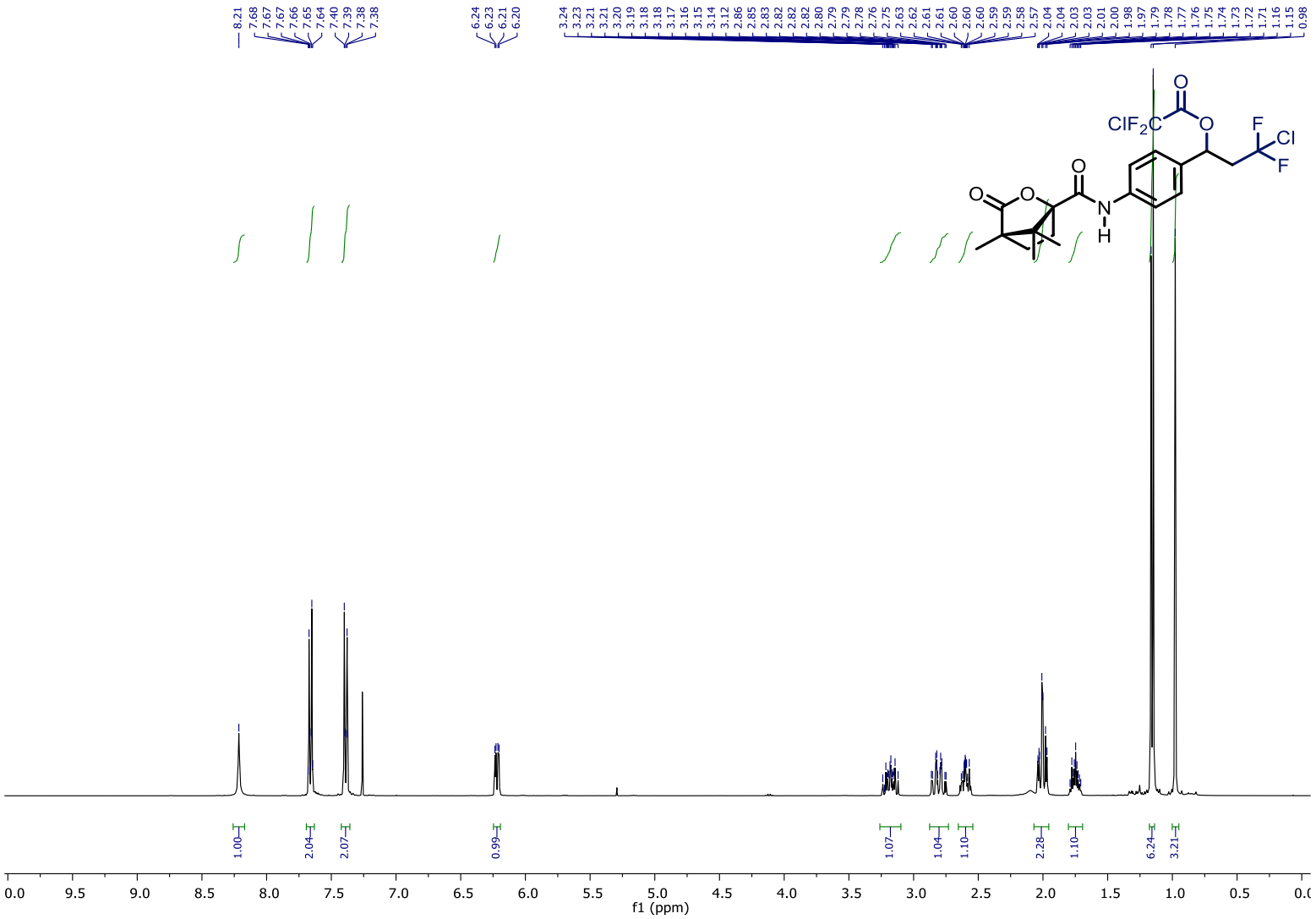
^{13}C-NMR (126 MHz, $CDCl_3$) of **64**



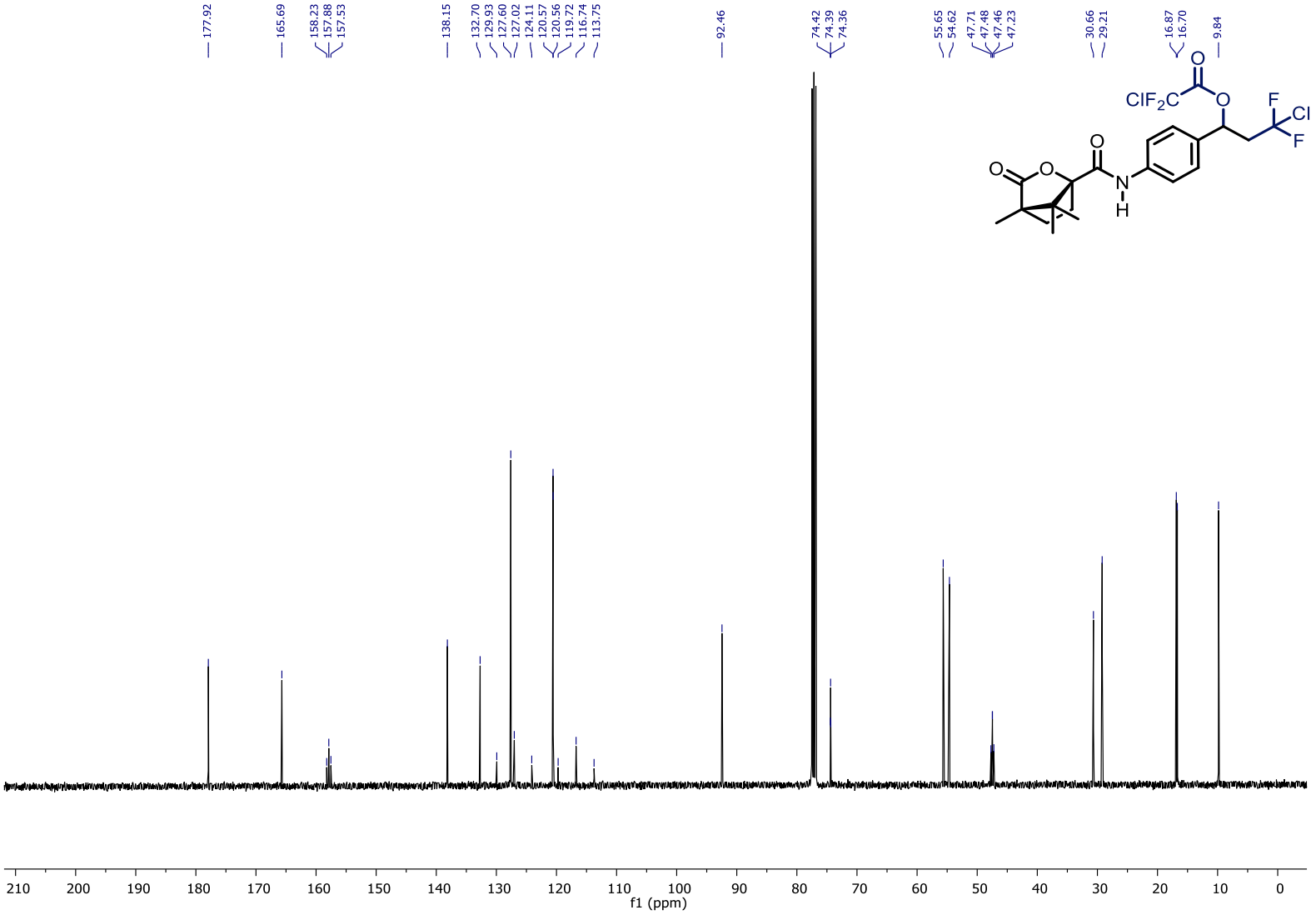
^{19}F-NMR (377 MHz, $CDCl_3$) of **64**



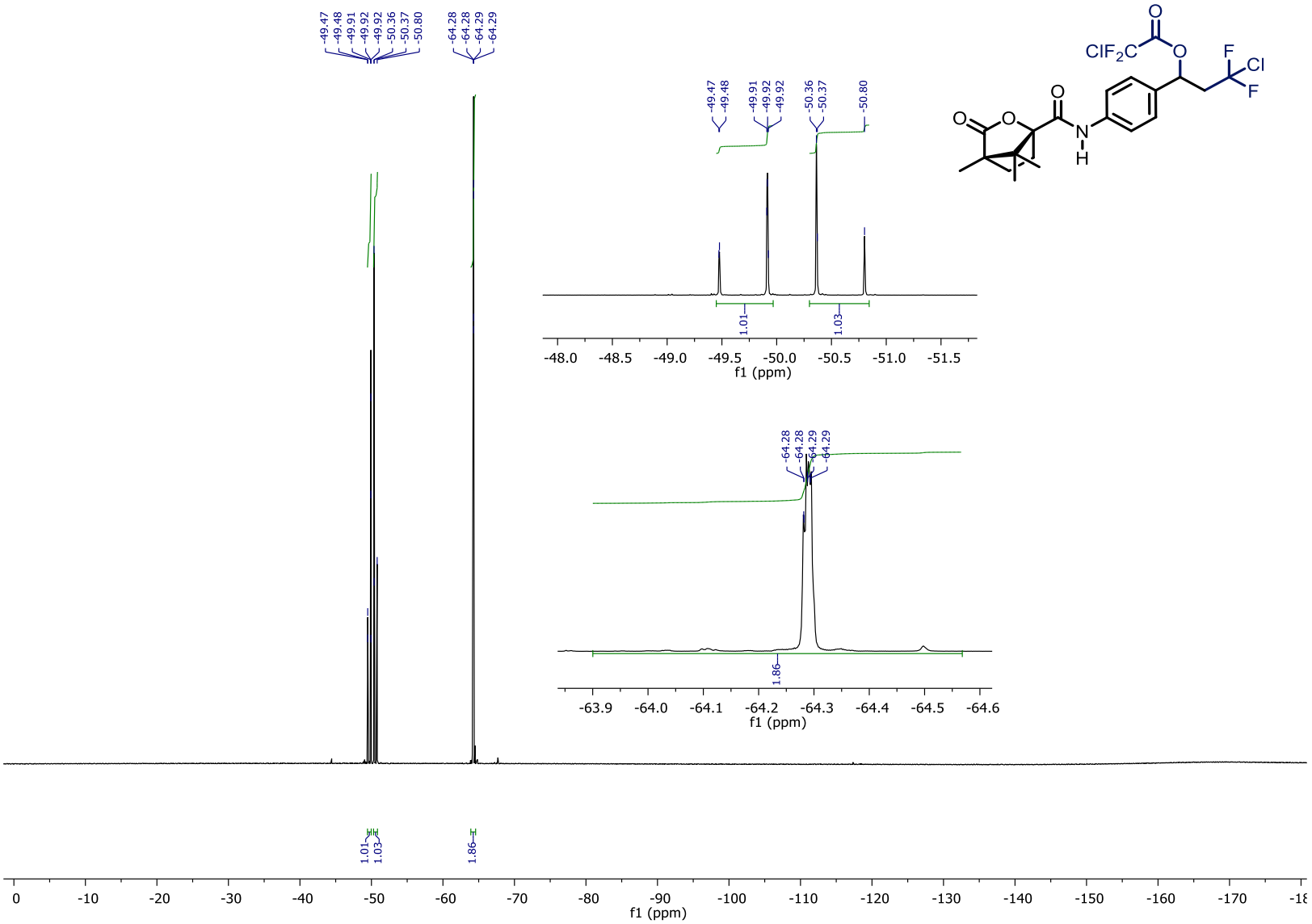
^{1}H-NMR (400 MHz, $CDCl_3$) of **65**



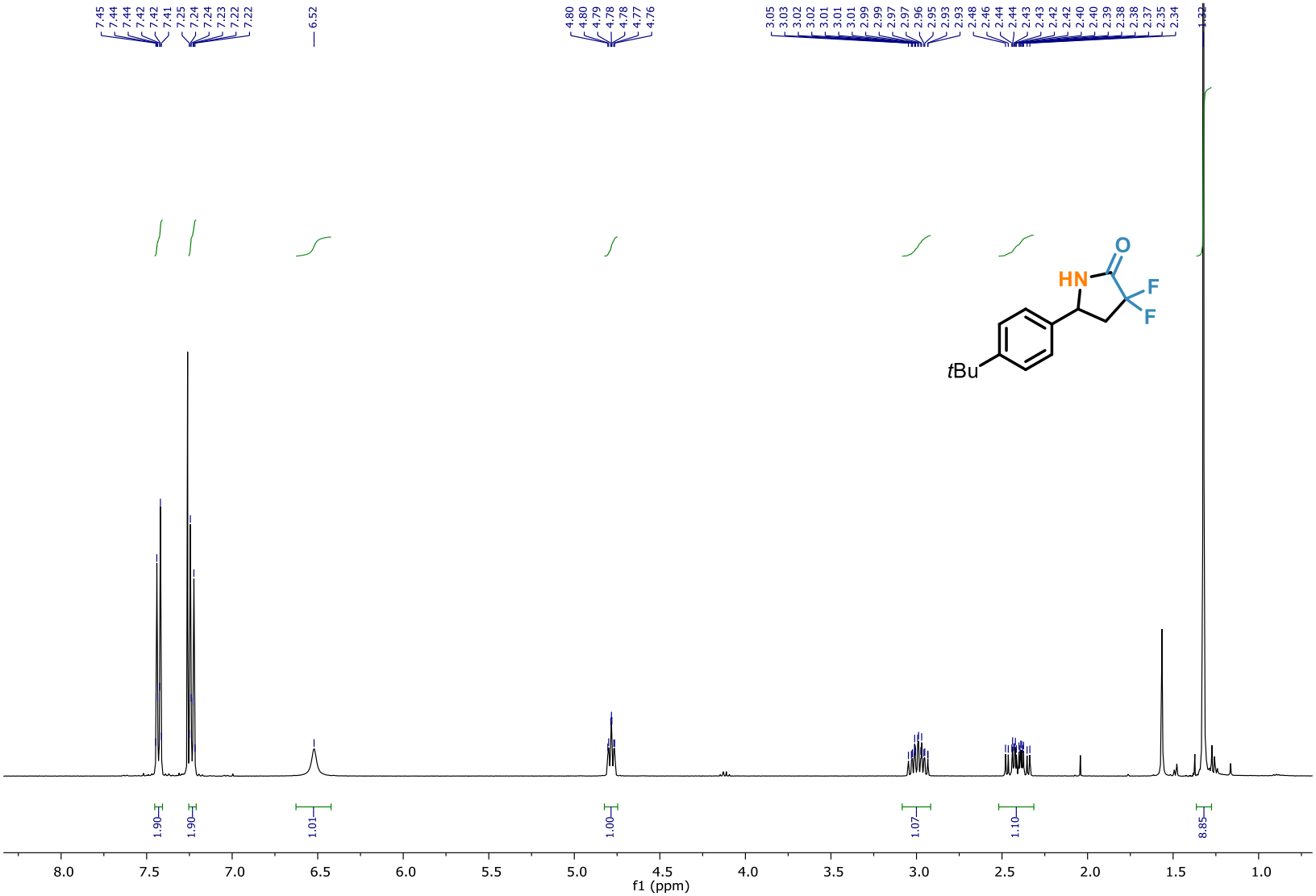
^{13}C-NMR (101 MHz, $CDCl_3$) of **65**



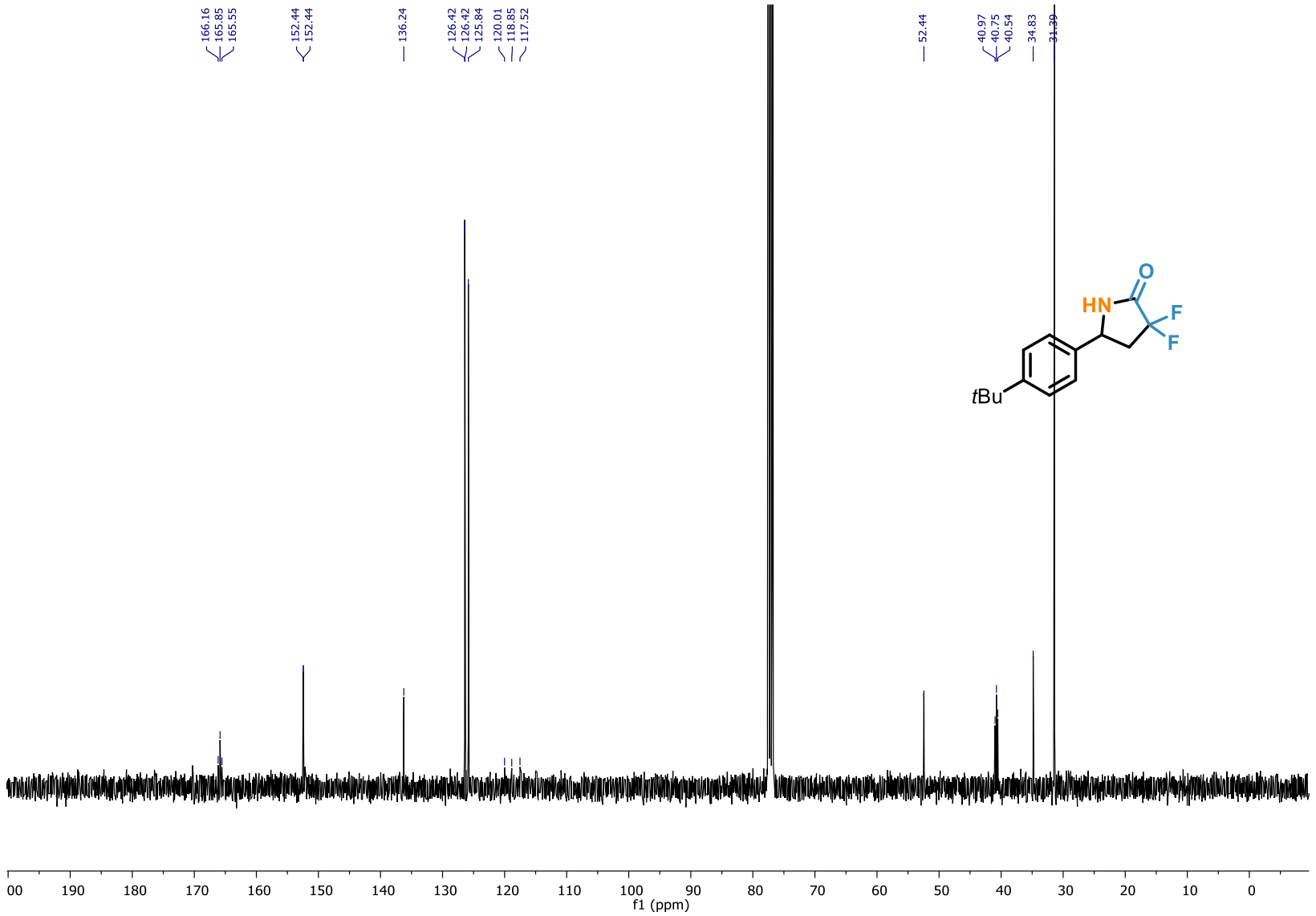
^{19}F-NMR (377 MHz, $CDCl_3$) of **65**



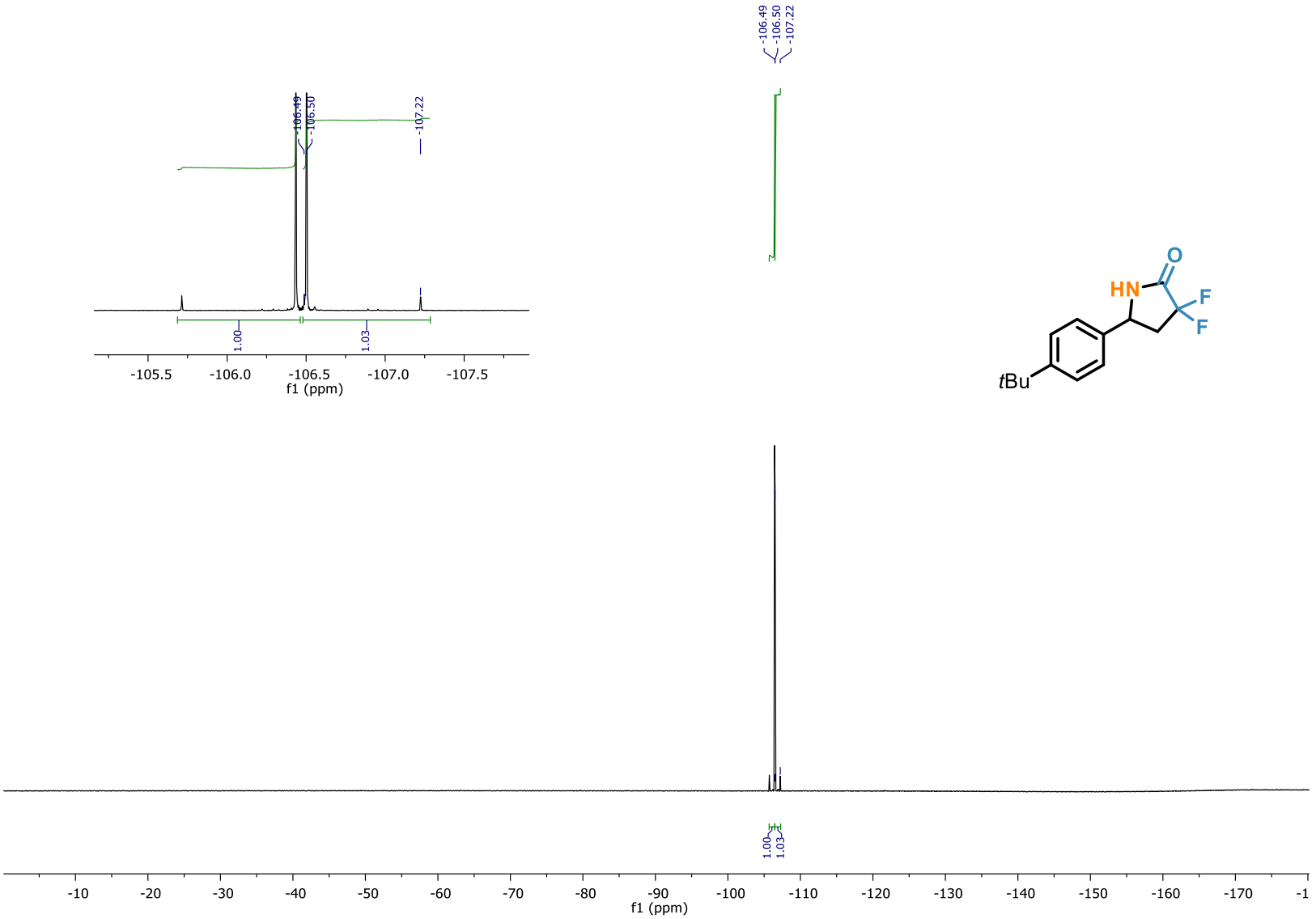
^{1}H-NMR (400 MHz, $CDCl_3$) of **66**



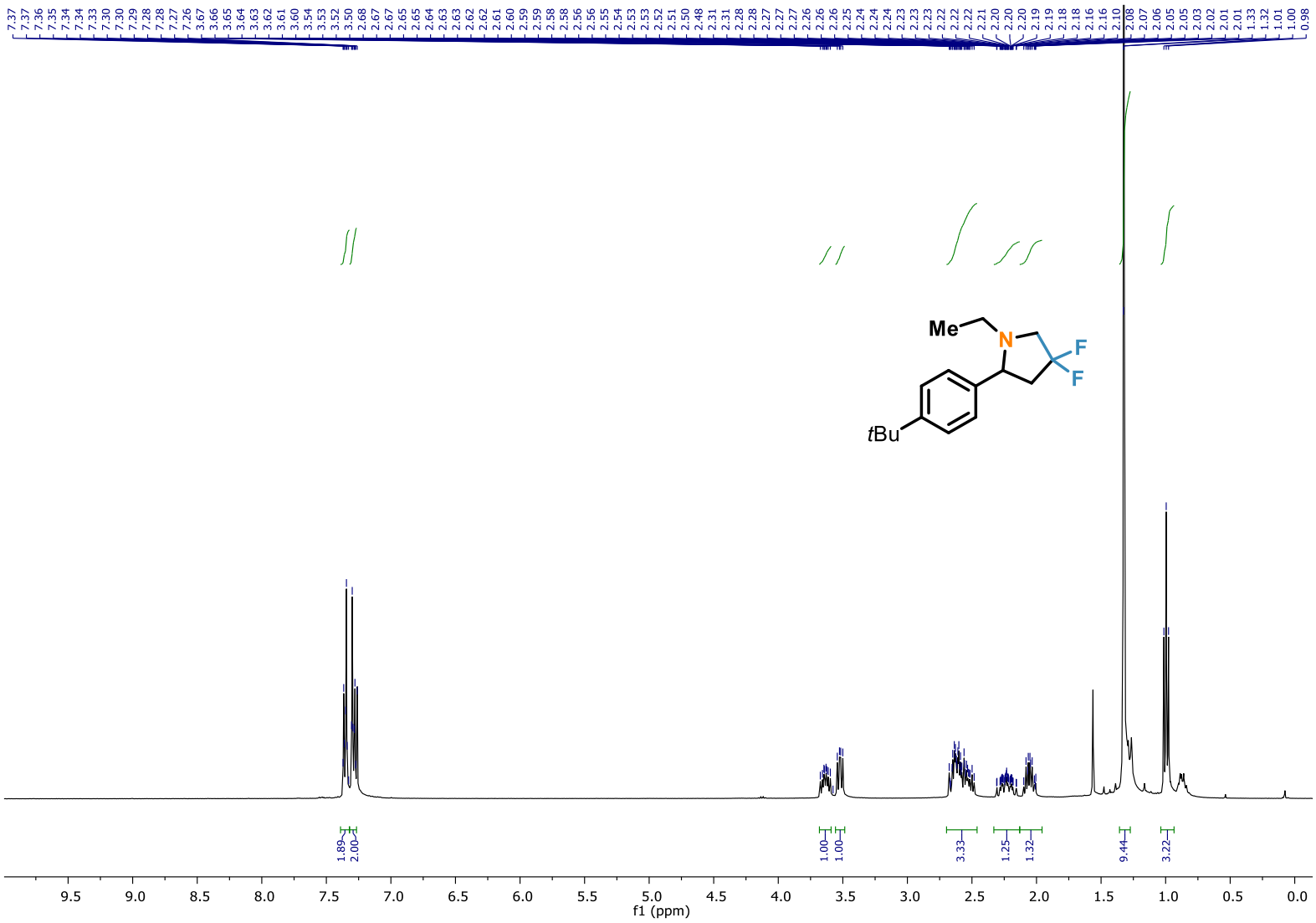
^{13}C-NMR (101 MHz, $CDCl_3$) of **66**



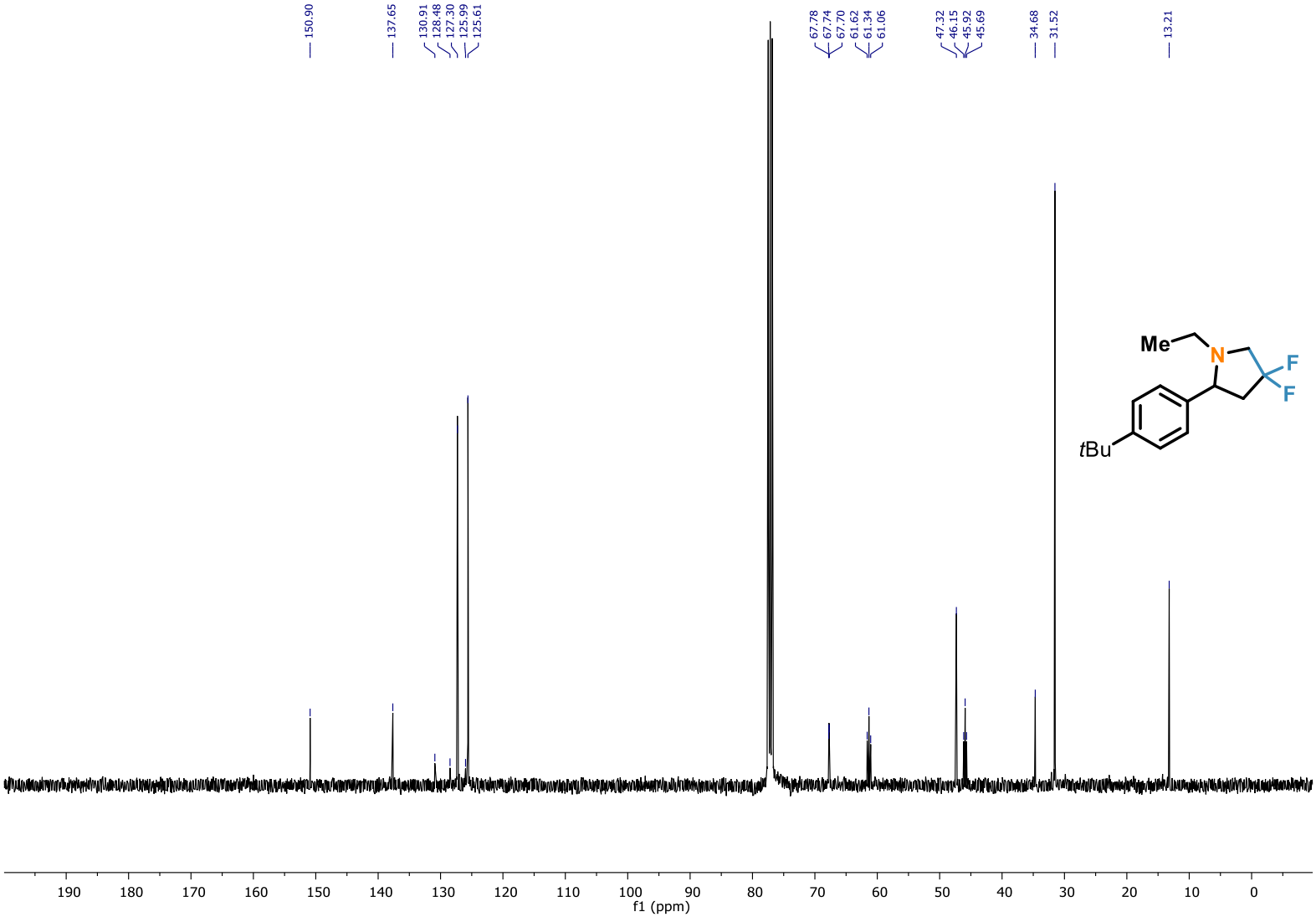
^{19}F-NMR (377 MHz, $CDCl_3$) of **66**



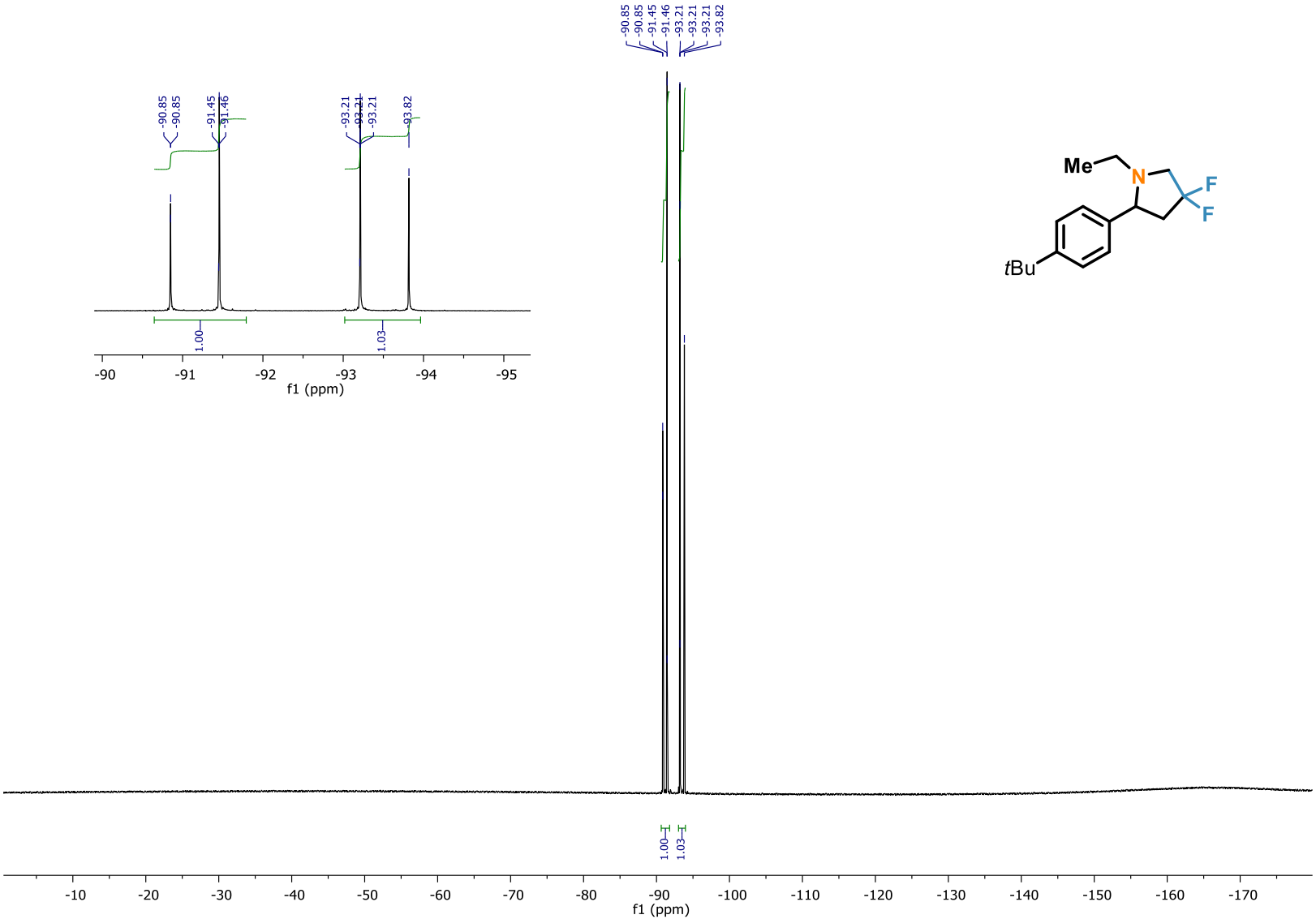
^{1}H-NMR (400 MHz, $CDCl_3$) of **67**



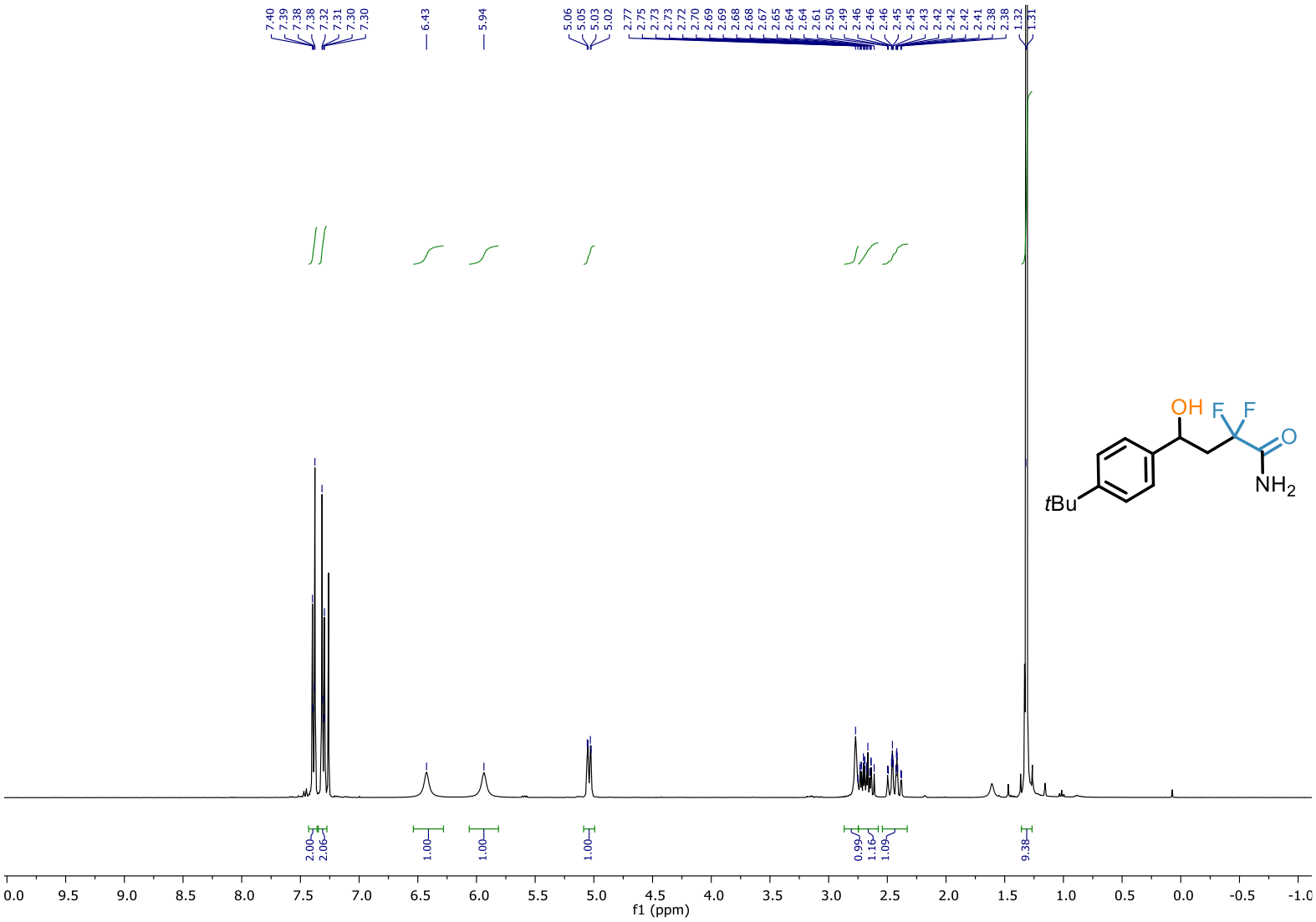
^{13}C-NMR (101 MHz, $CDCl_3$) of **67**



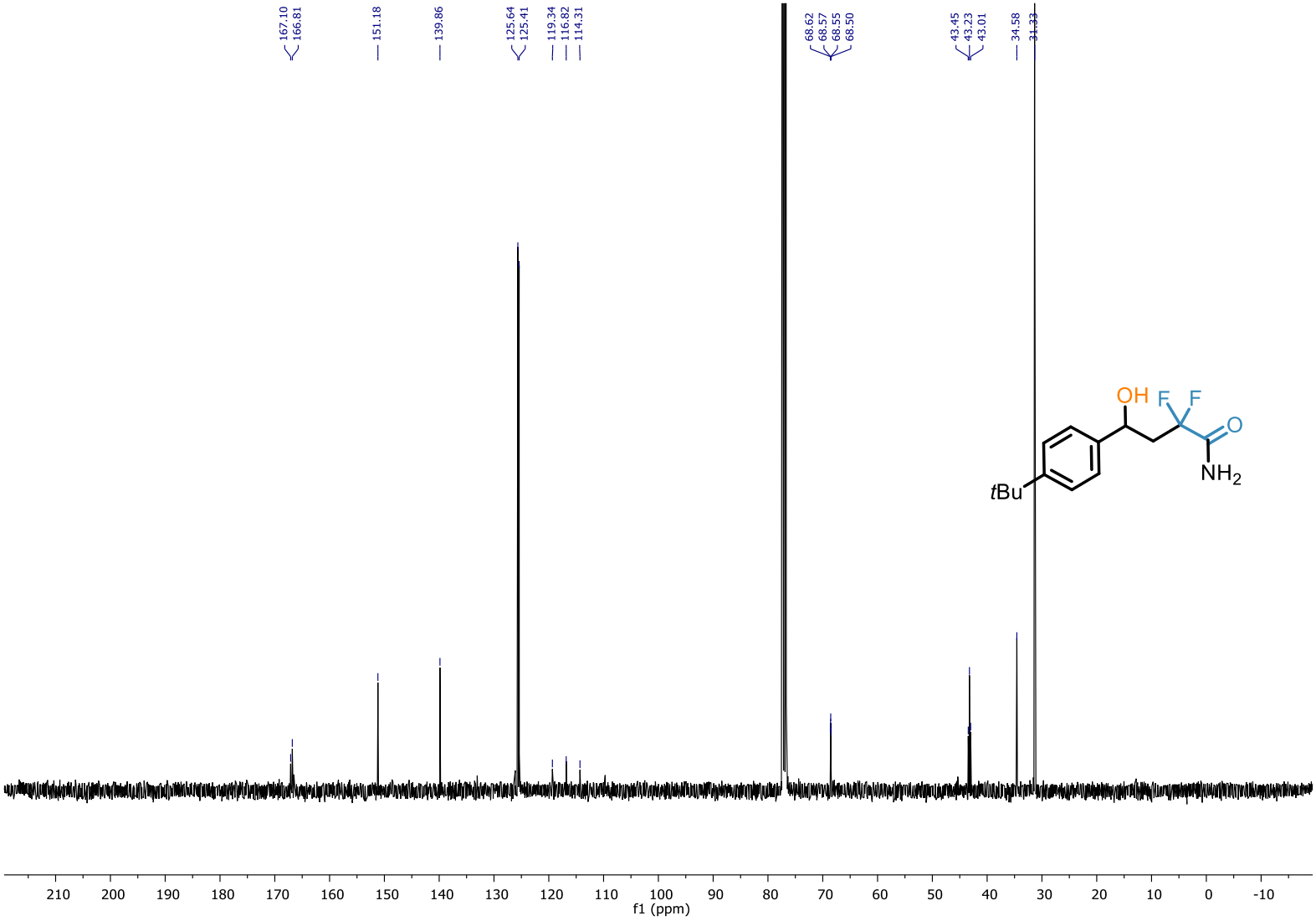
^{19}F-NMR (377 MHz, $CDCl_3$) of **67**



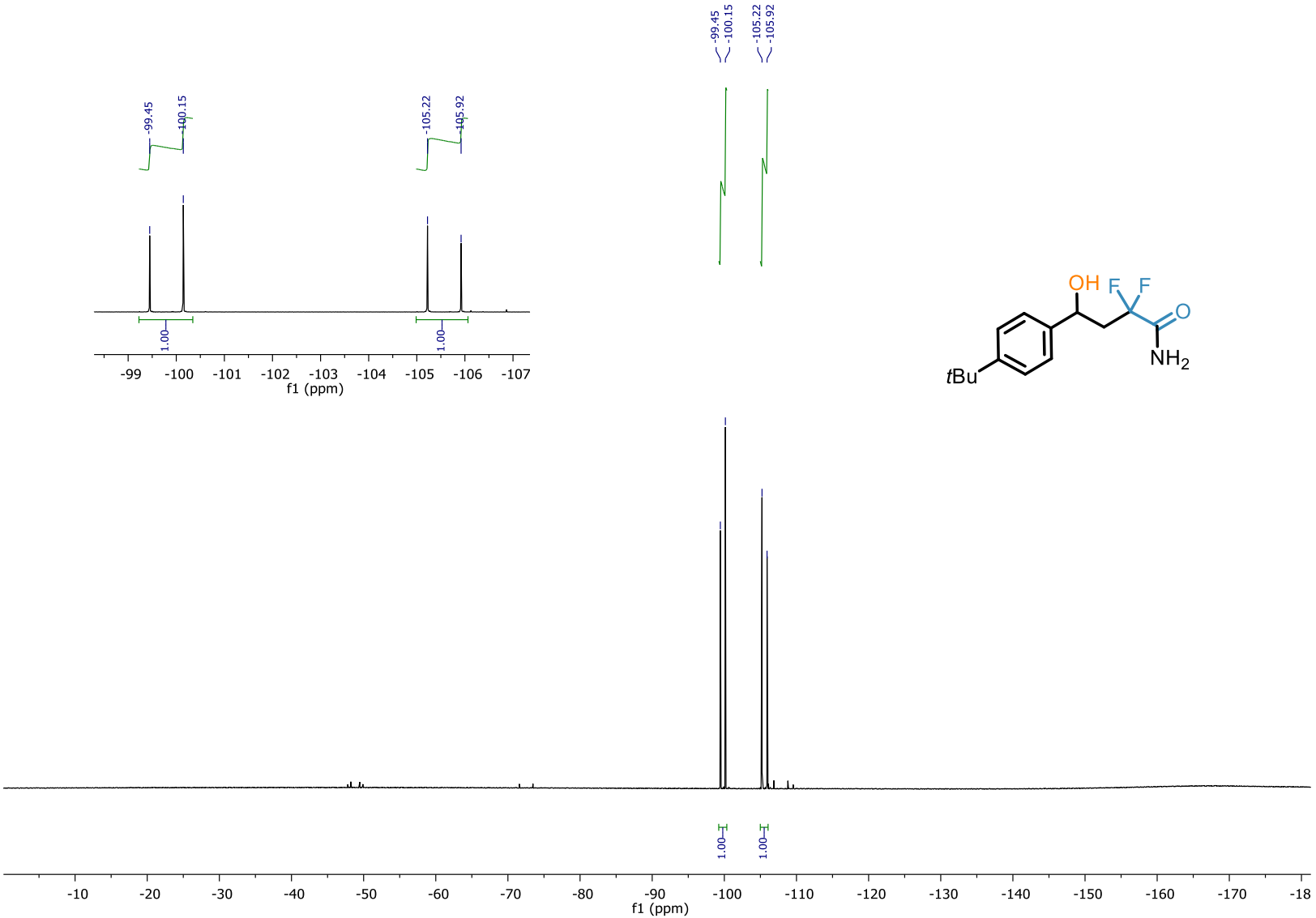
^{1}H-NMR (400 MHz, $CDCl_3$) of **68**



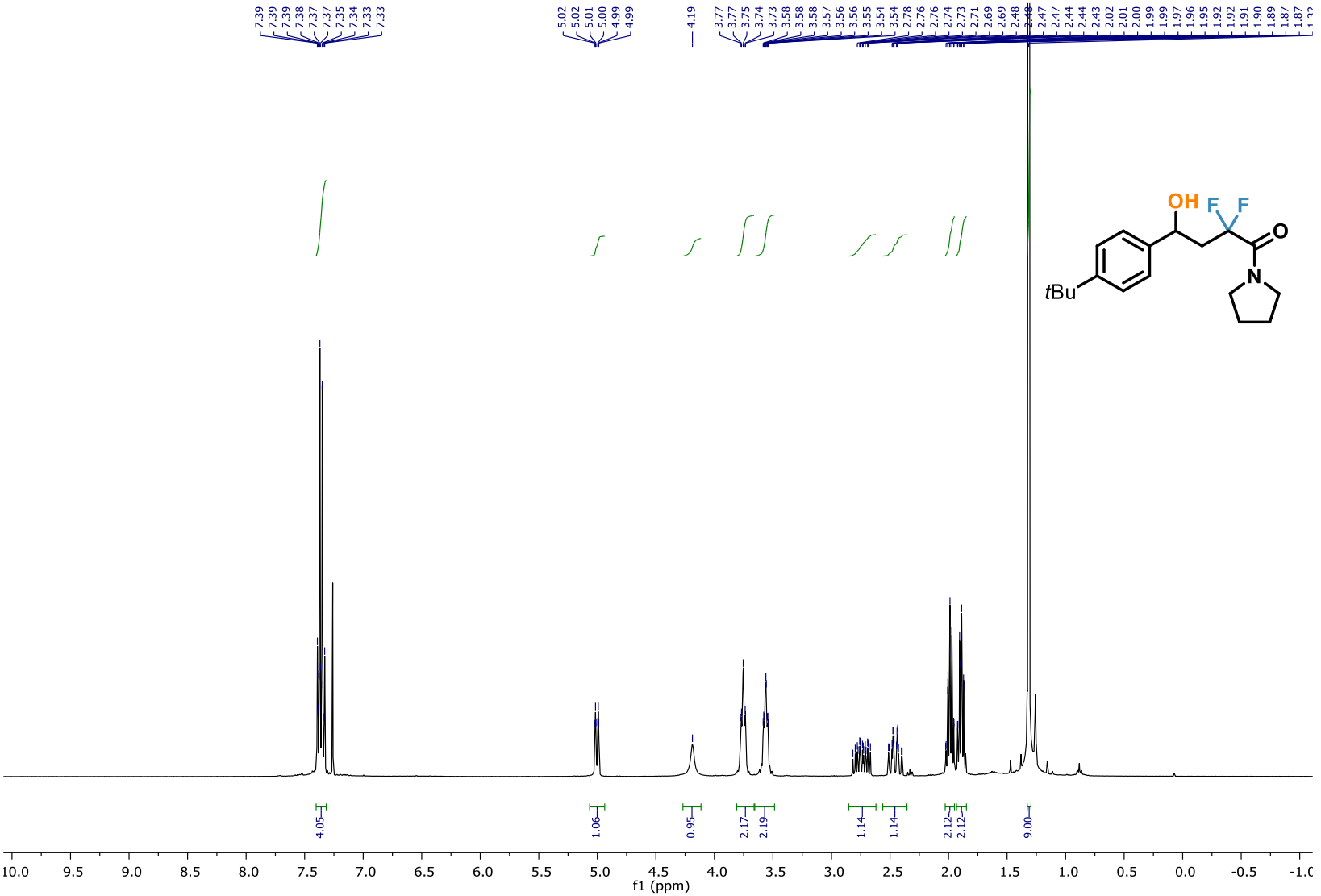
^{13}C-NMR (101 MHz, $CDCl_3$) of **68**



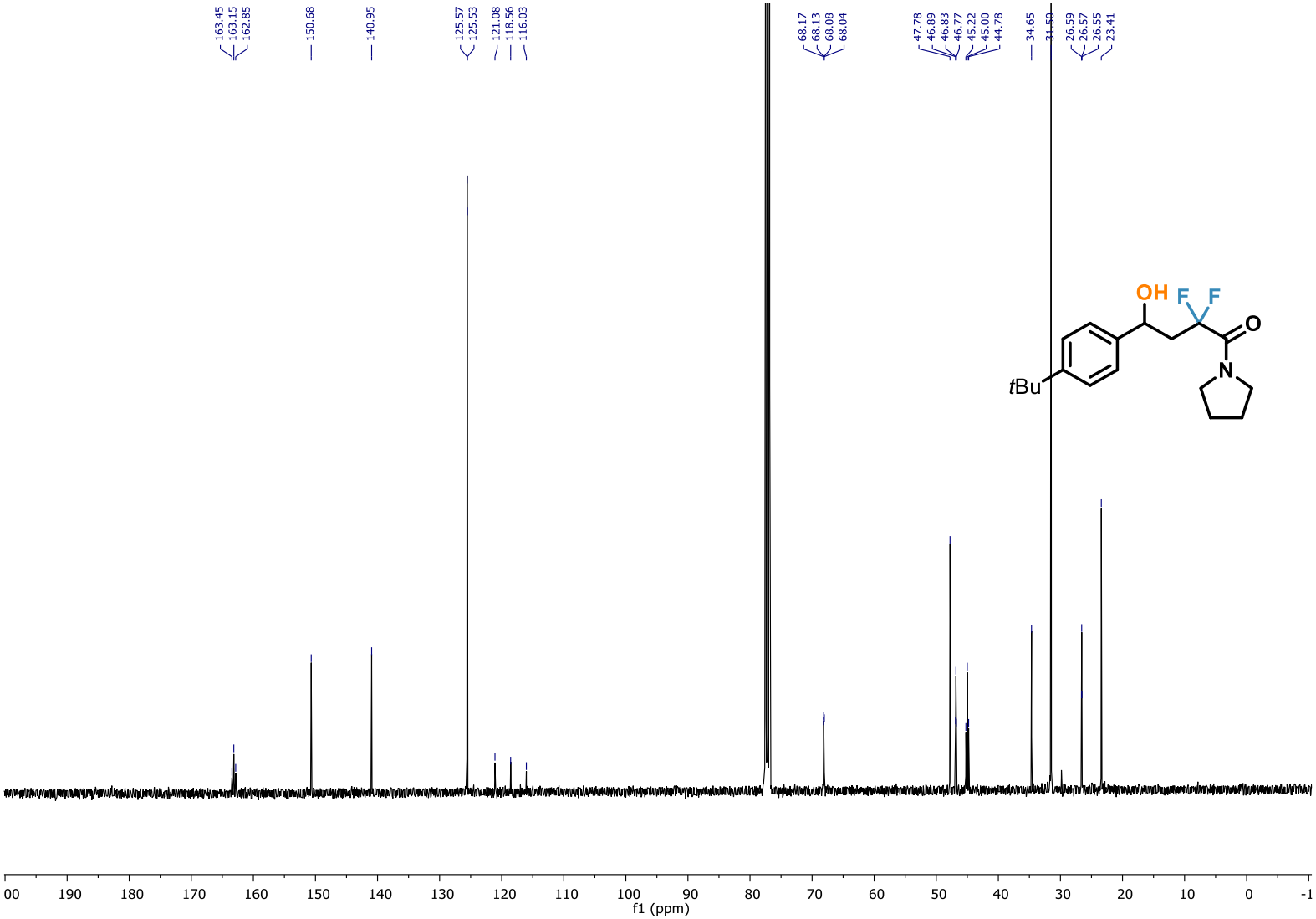
^{19}F-NMR (377 MHz, $CDCl_3$) of **68**



^{1}H-NMR (400 MHz, $CDCl_3$) of **69**

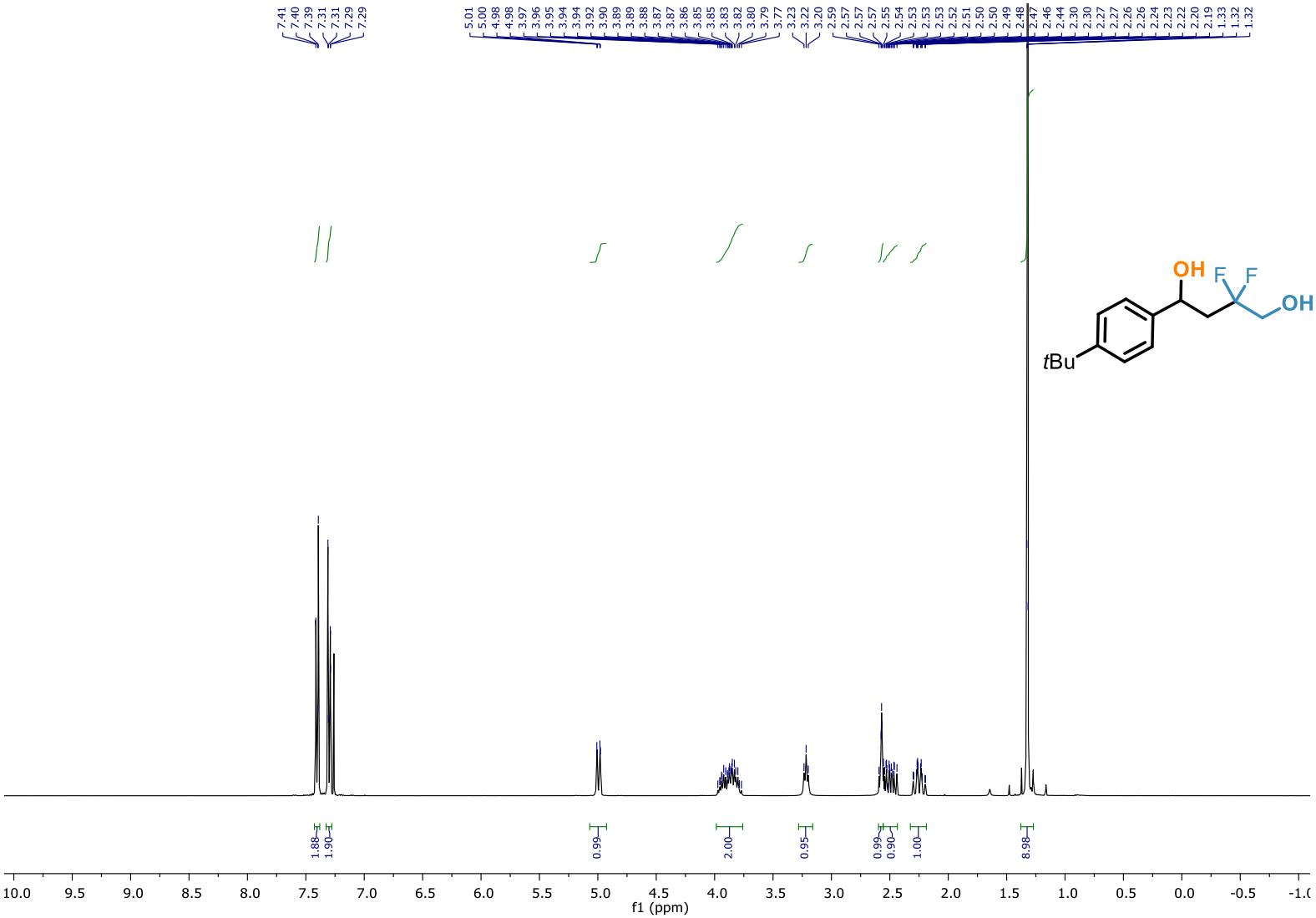


^{13}C-NMR (101 MHz, $CDCl_3$) of **69**

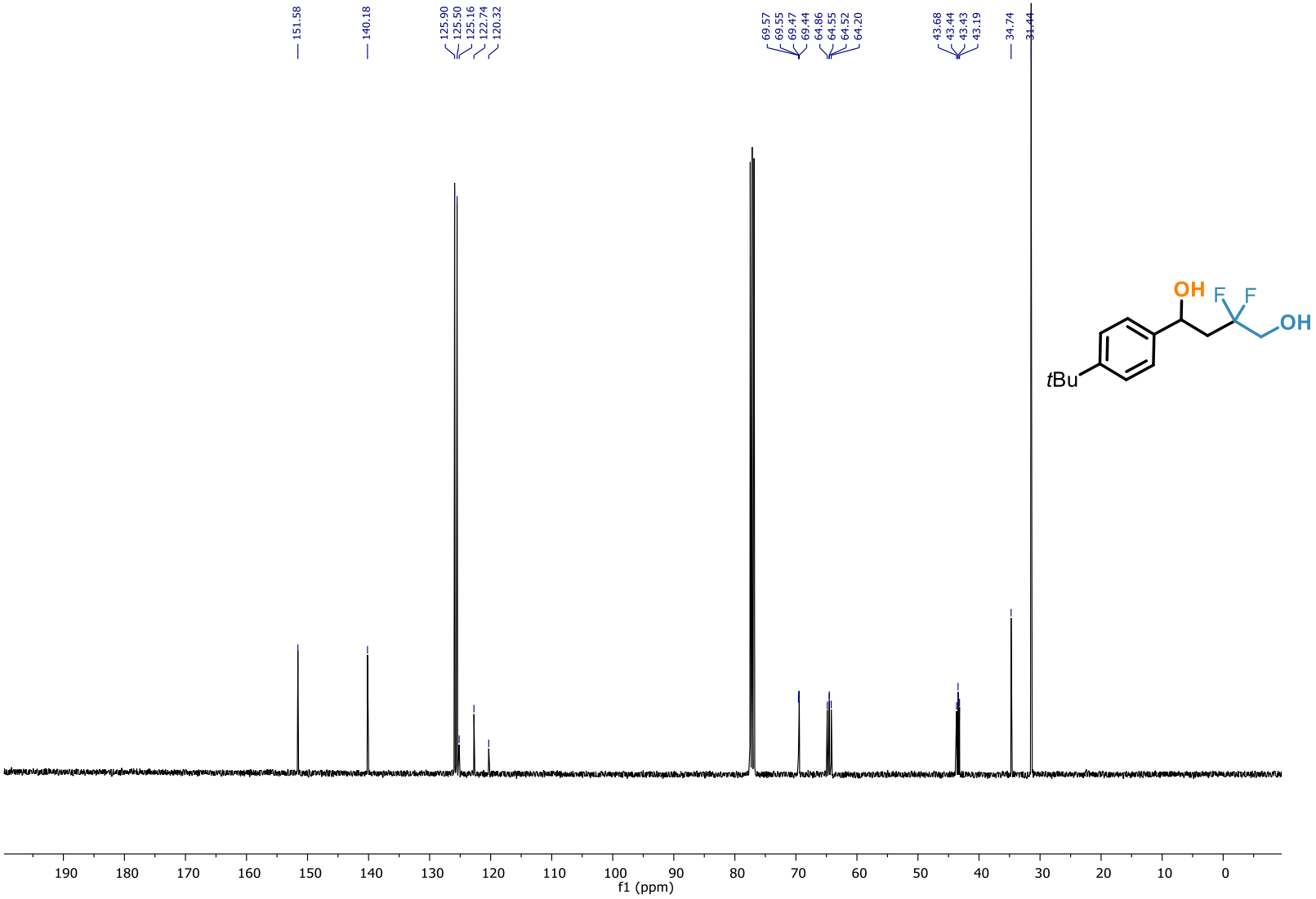


^{19}F-NMR (377 MHz, $CDCl_3$) of **69**

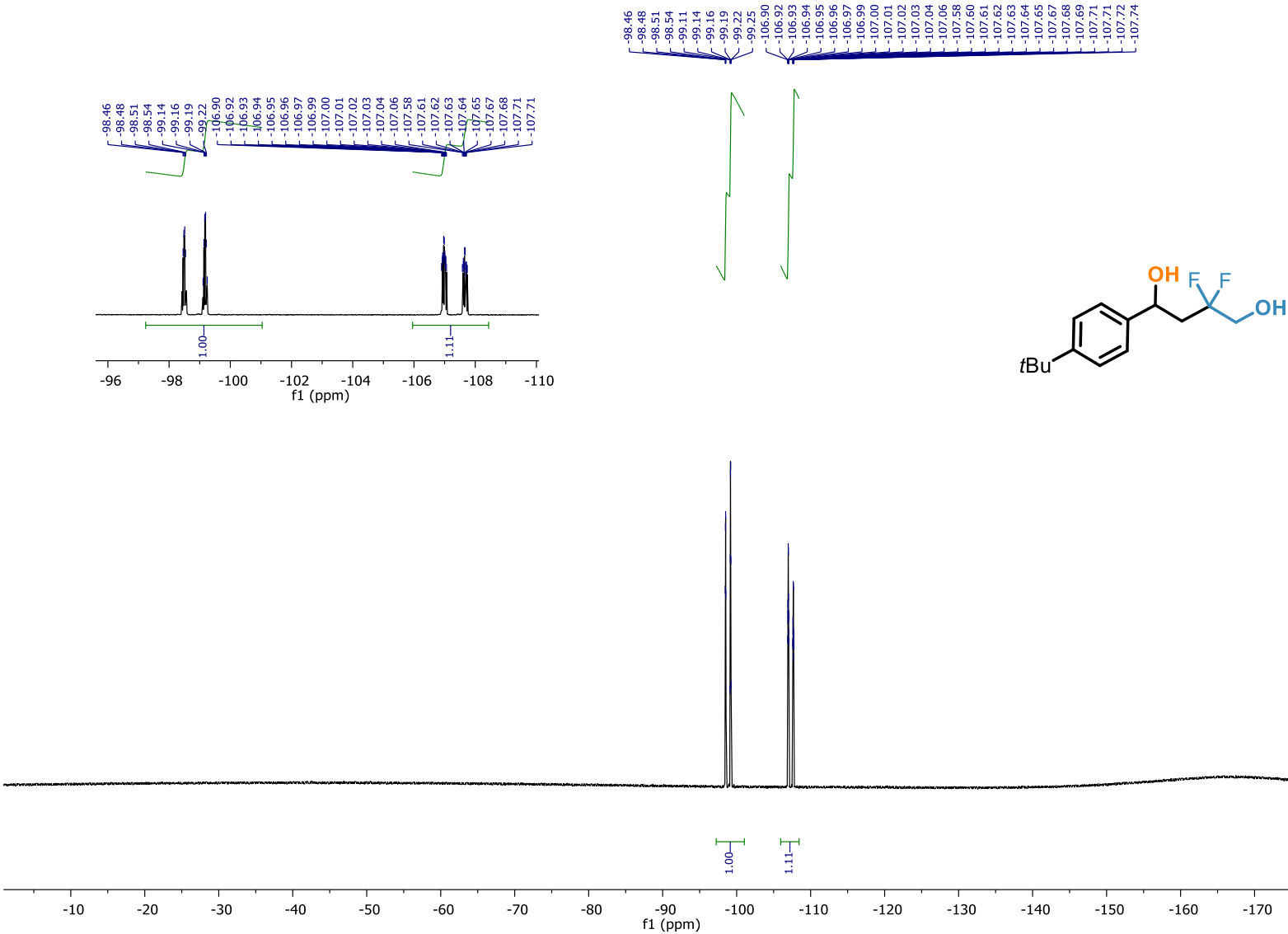
^{1}H-NMR (400 MHz, $CDCl_3$) of **70**



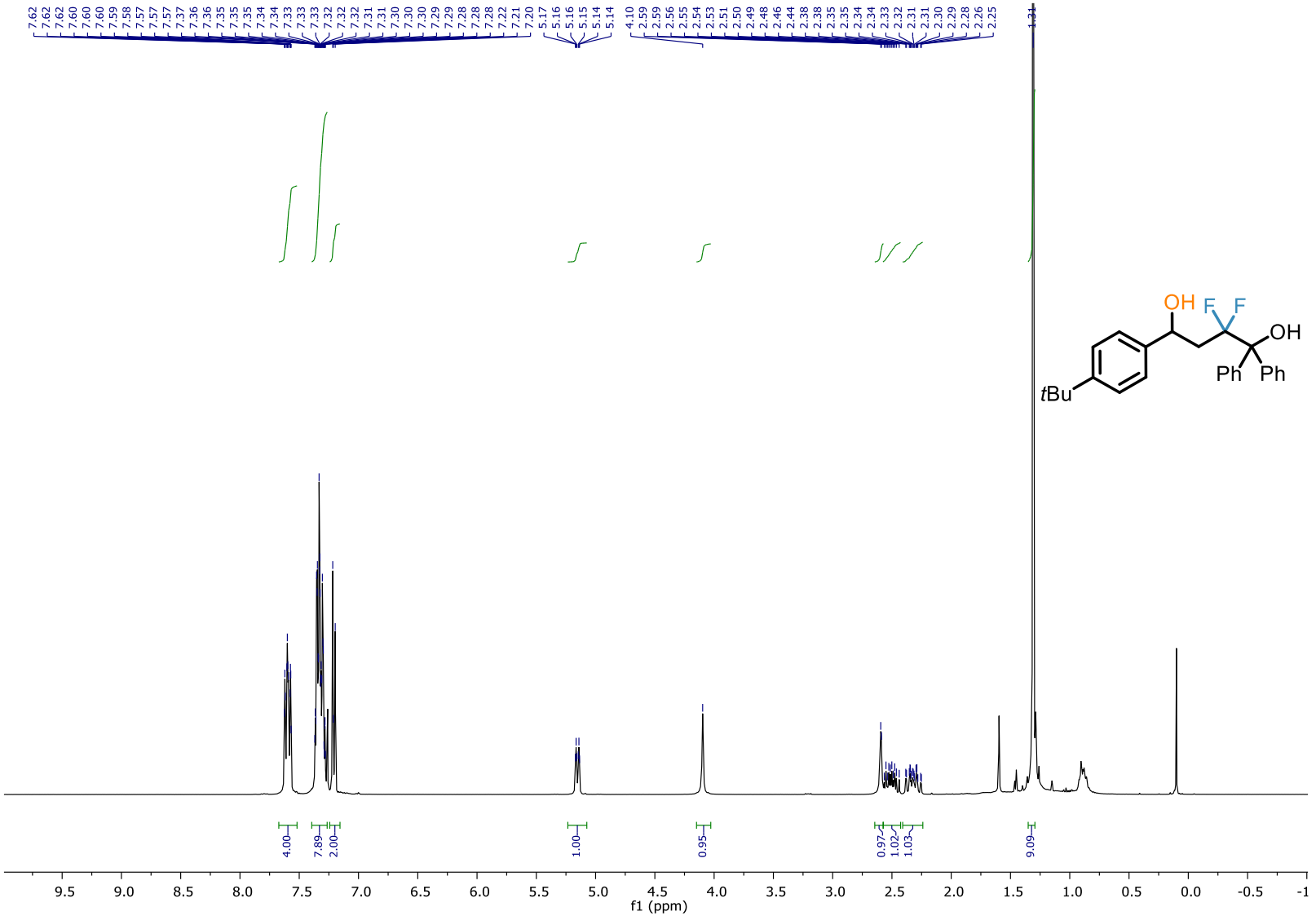
^{13}C-NMR (101 MHz, $CDCl_3$) of **70**



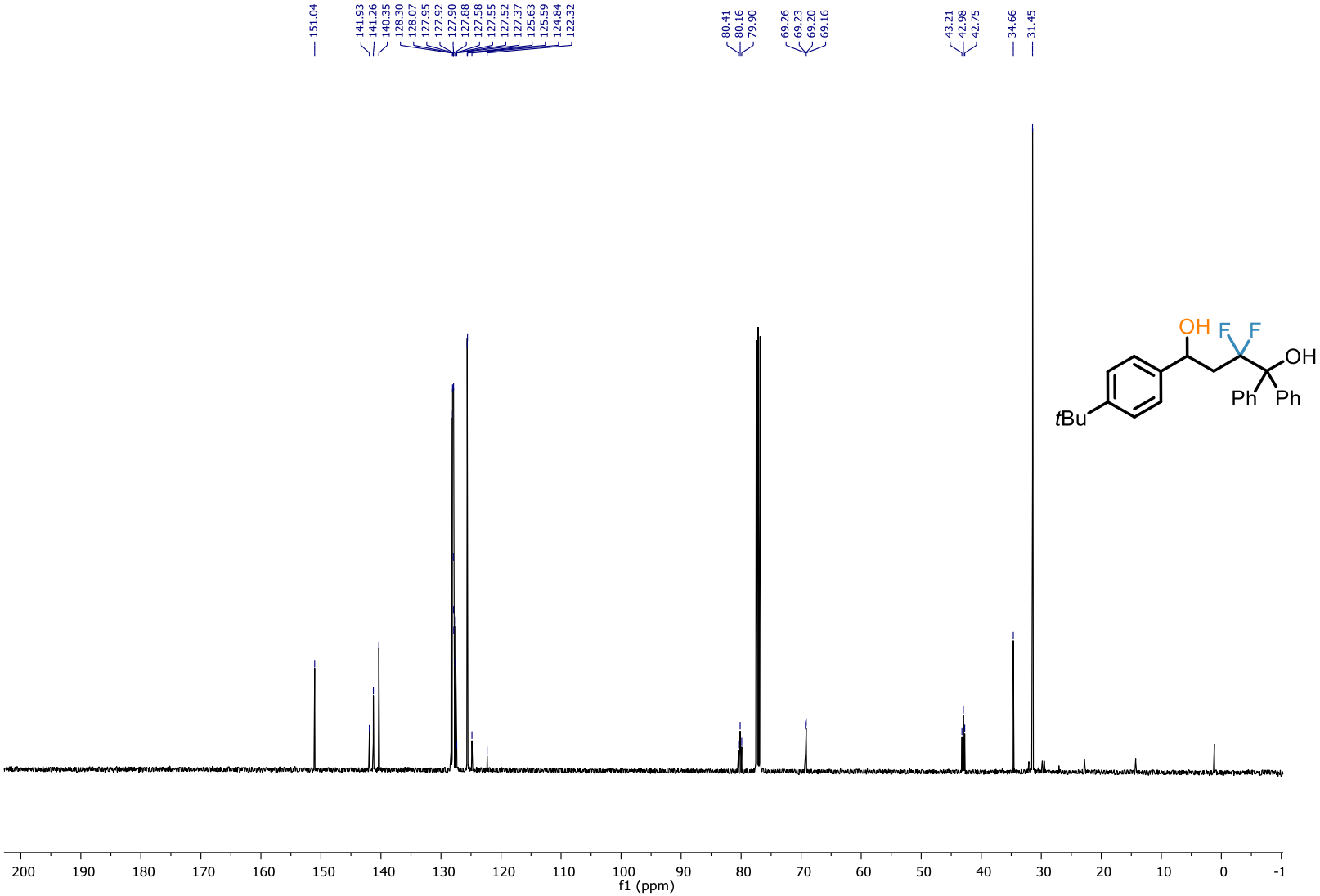
^{19}F-NMR (377 MHz, $CDCl_3$) of **70**



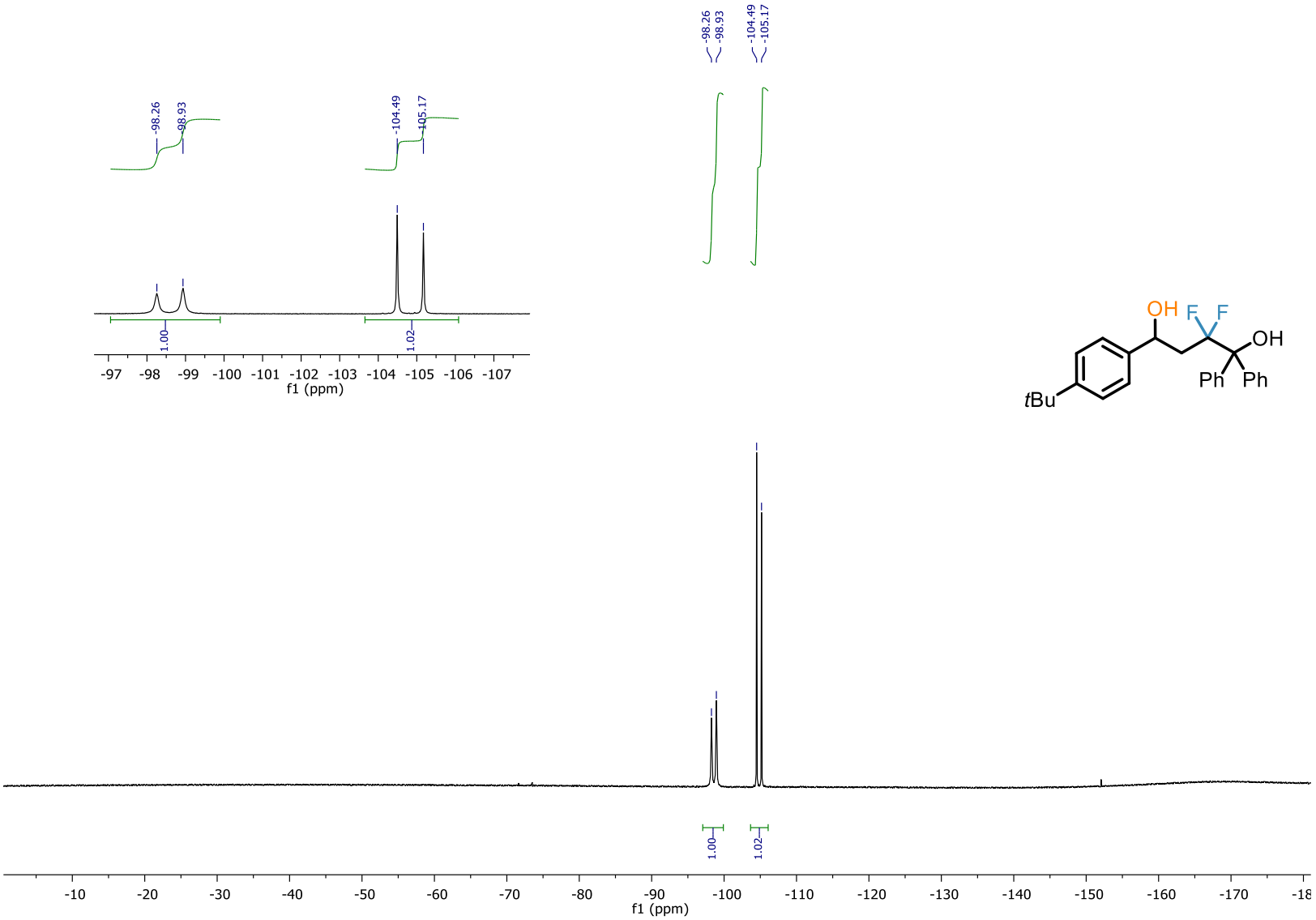
^{1}H-NMR (400 MHz, $CDCl_3$) of **71**



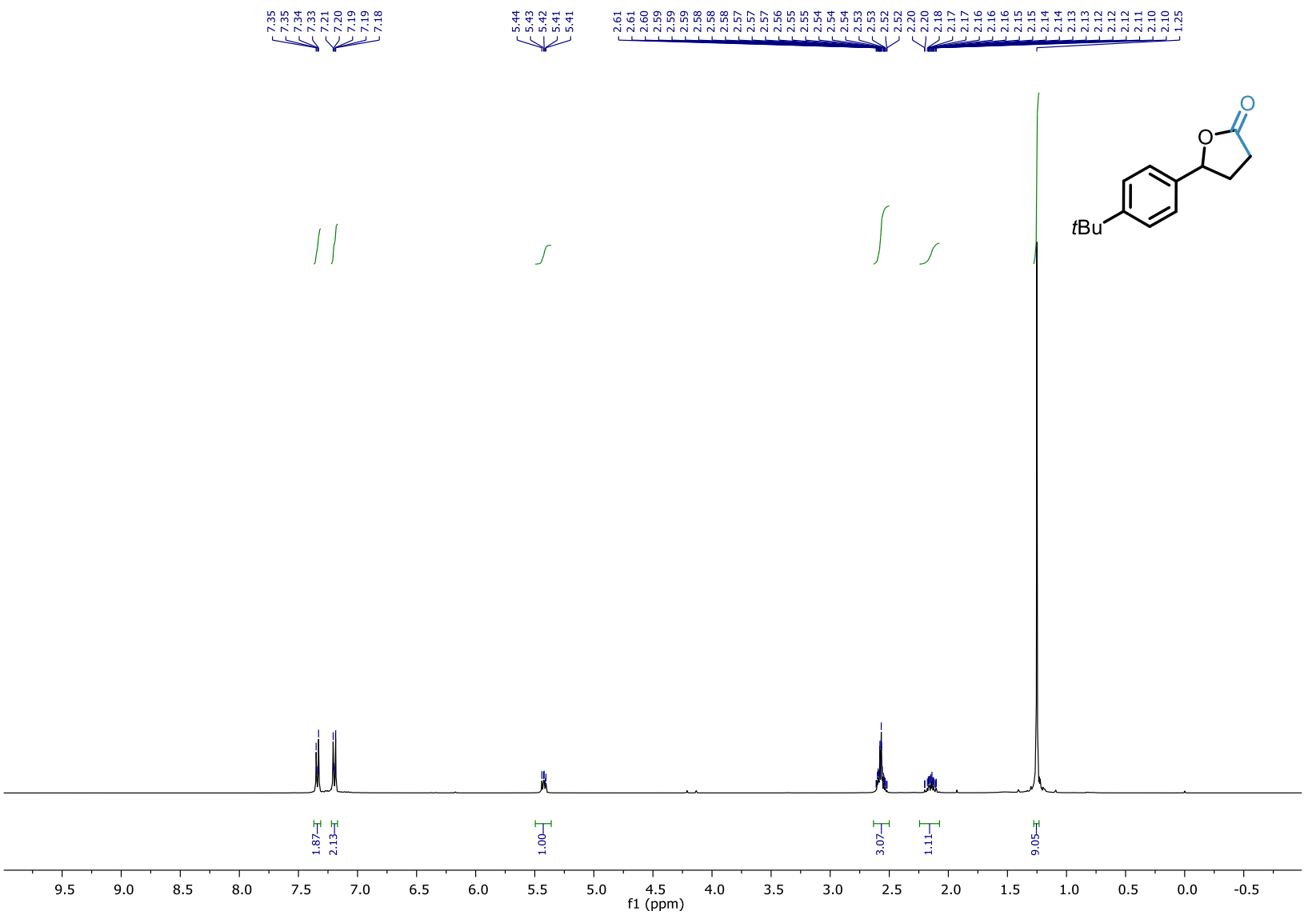
^{13}C-NMR (101 MHz, $CDCl_3$) of **71**



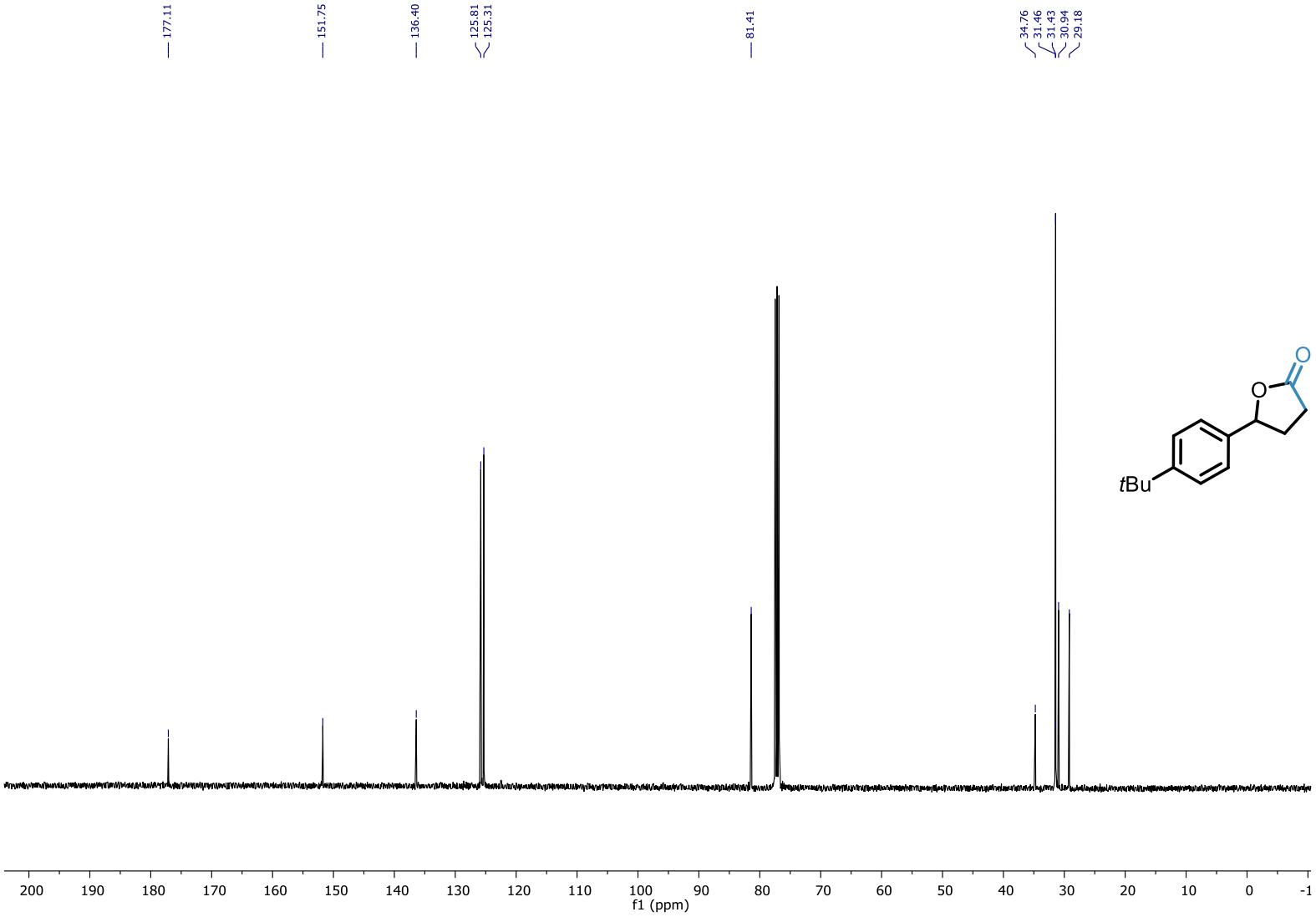
^{19}F-NMR (377 MHz, $CDCl_3$) of **71**



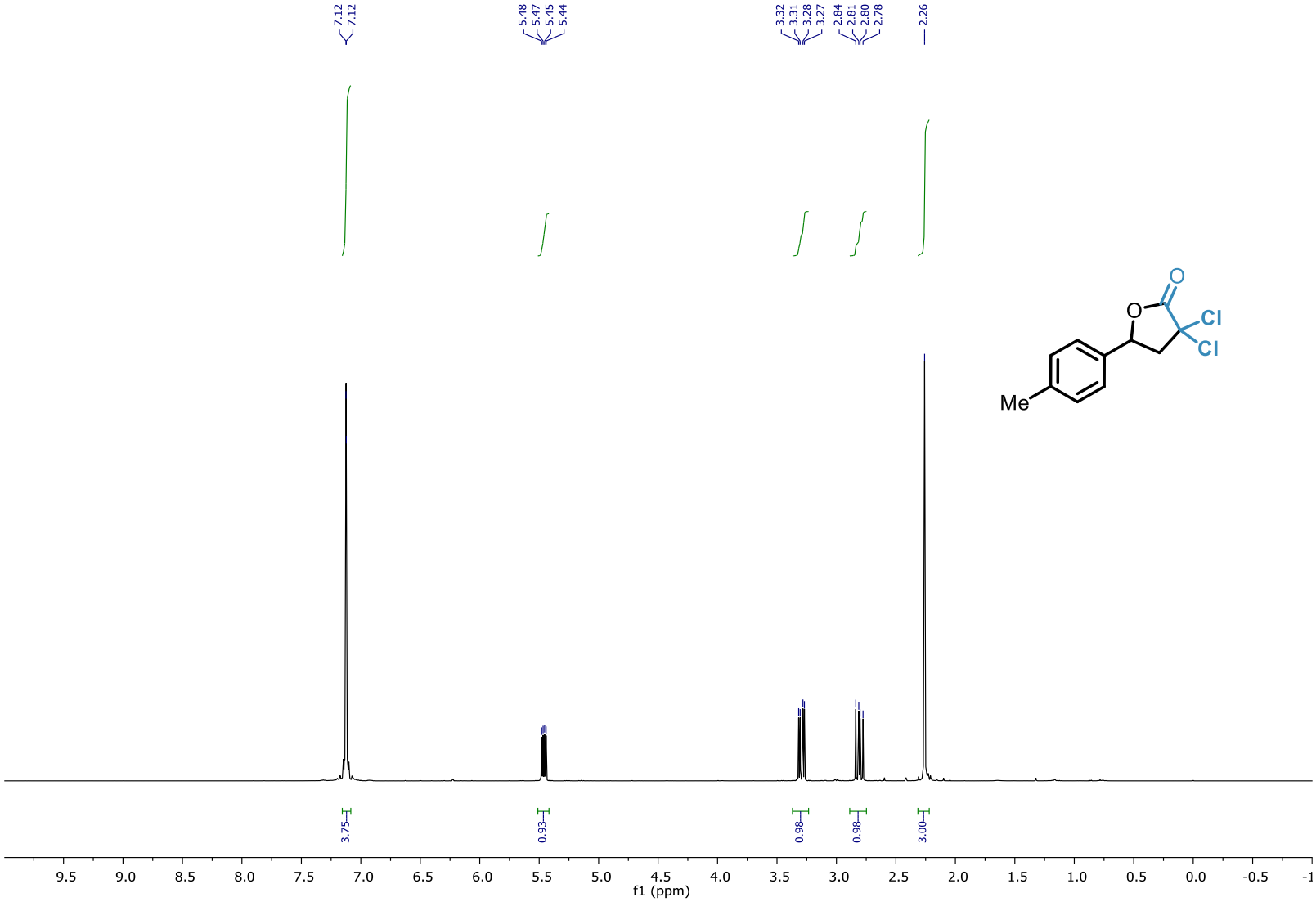
^{1}H-NMR (400 MHz, $CDCl_3$) of **72**



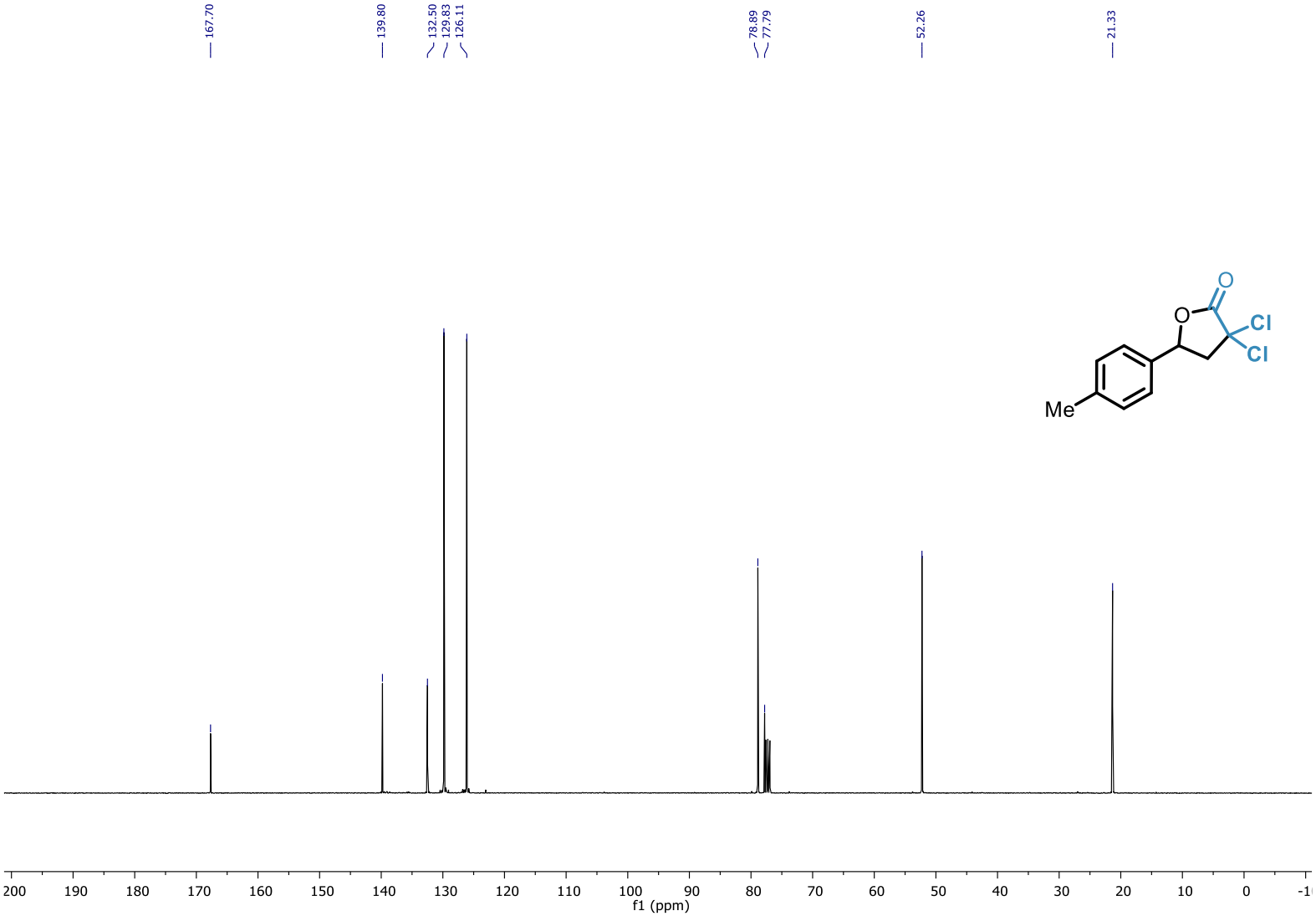
^{13}C-NMR (101 MHz, $CDCl_3$) of **72**



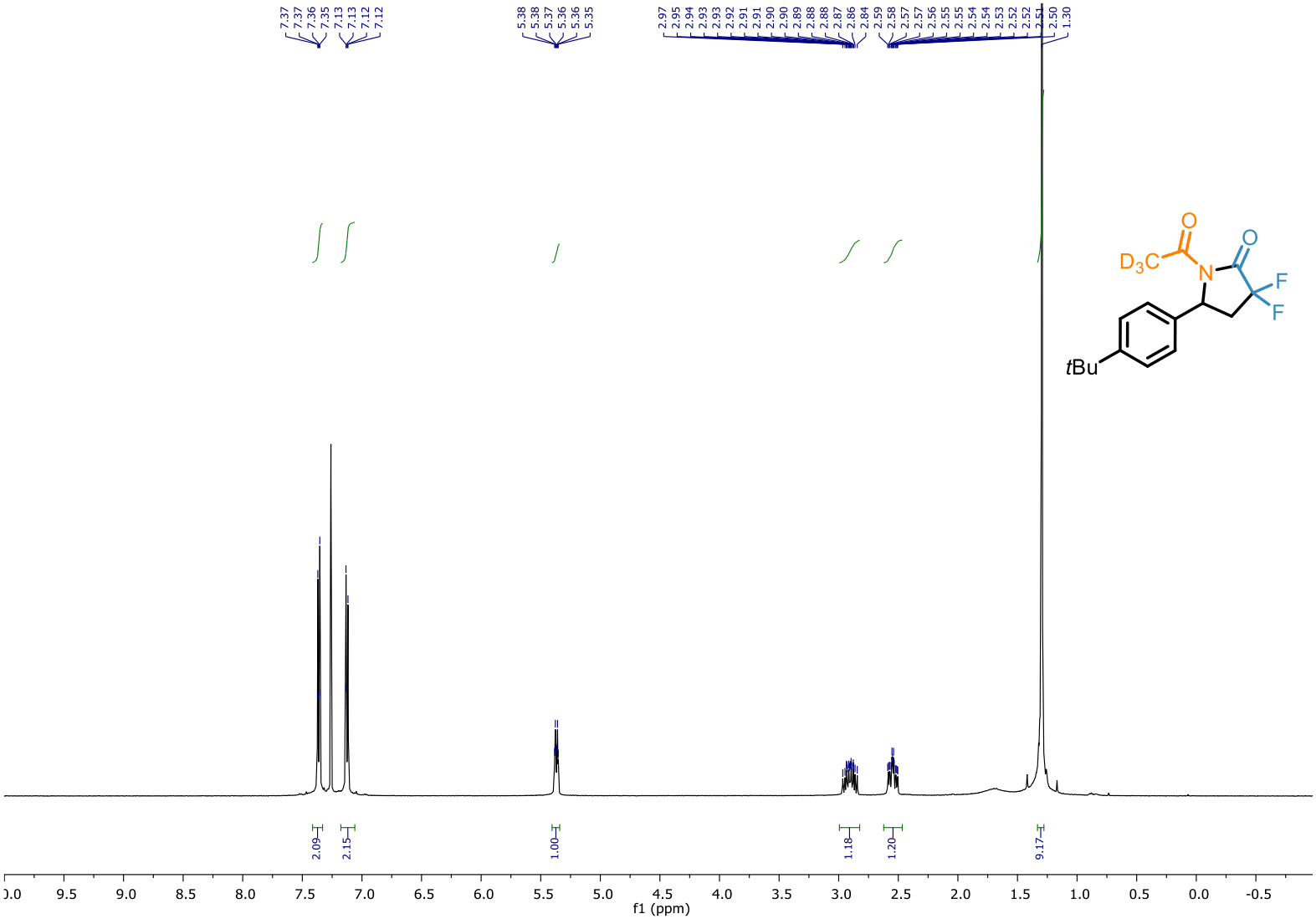
^{1}H-NMR (400 MHz, $CDCl_3$) of **73**



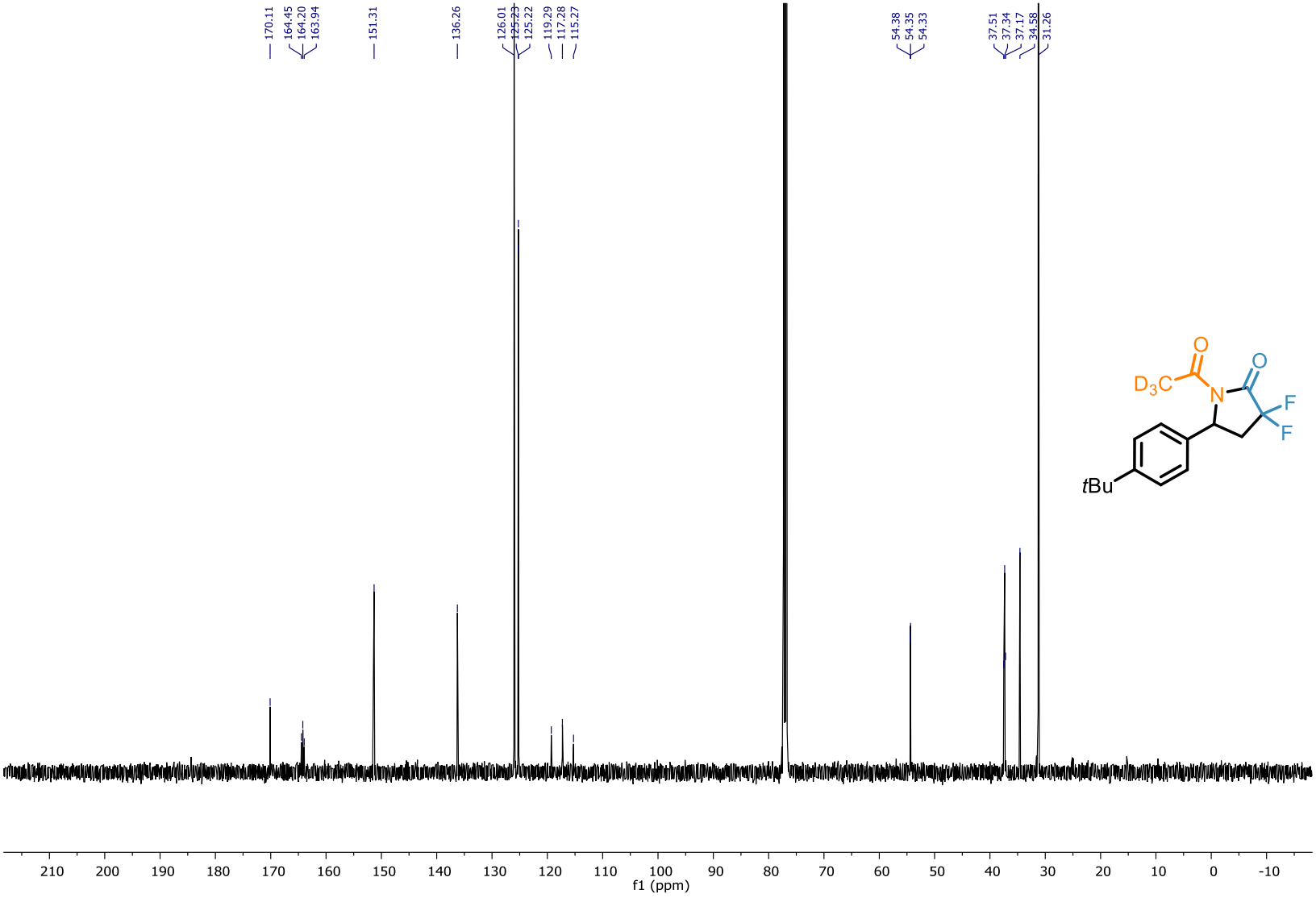
^{13}C-NMR (101 MHz, $CDCl_3$) of **73**



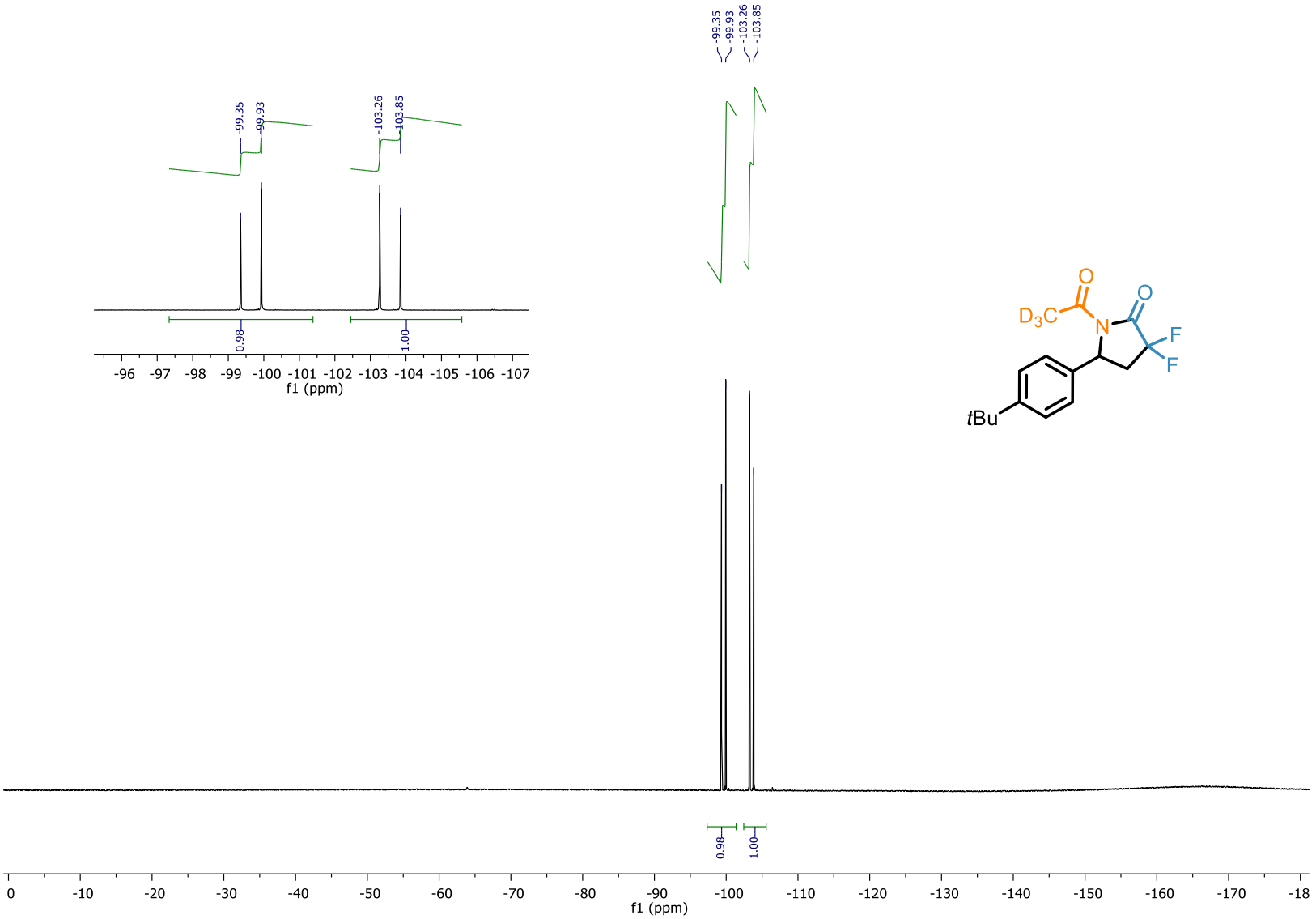
^{1}H-NMR (500 MHz, $CDCl_3$) of **74**



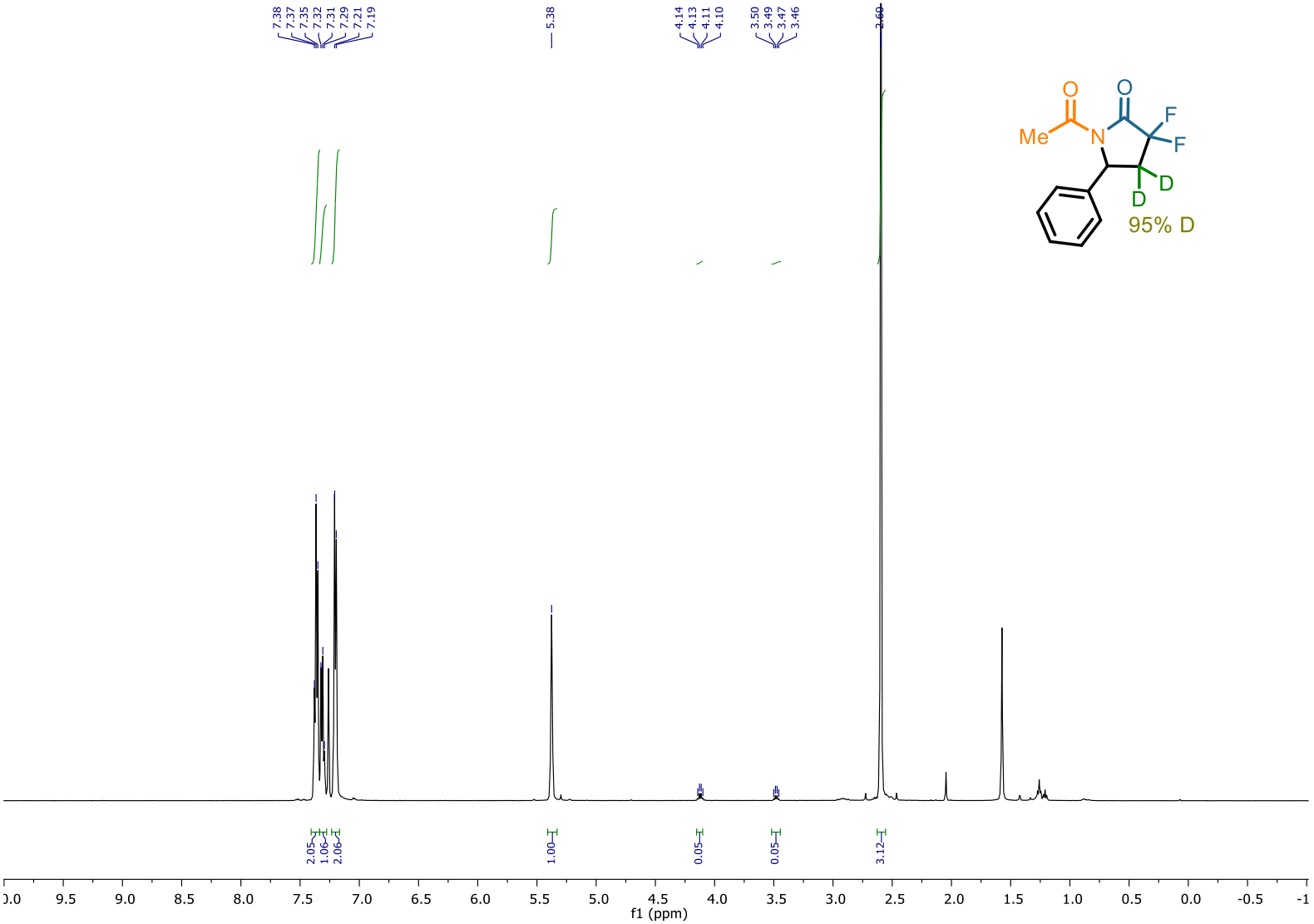
^{13}C-NMR (126 MHz, $CDCl_3$) of **74**



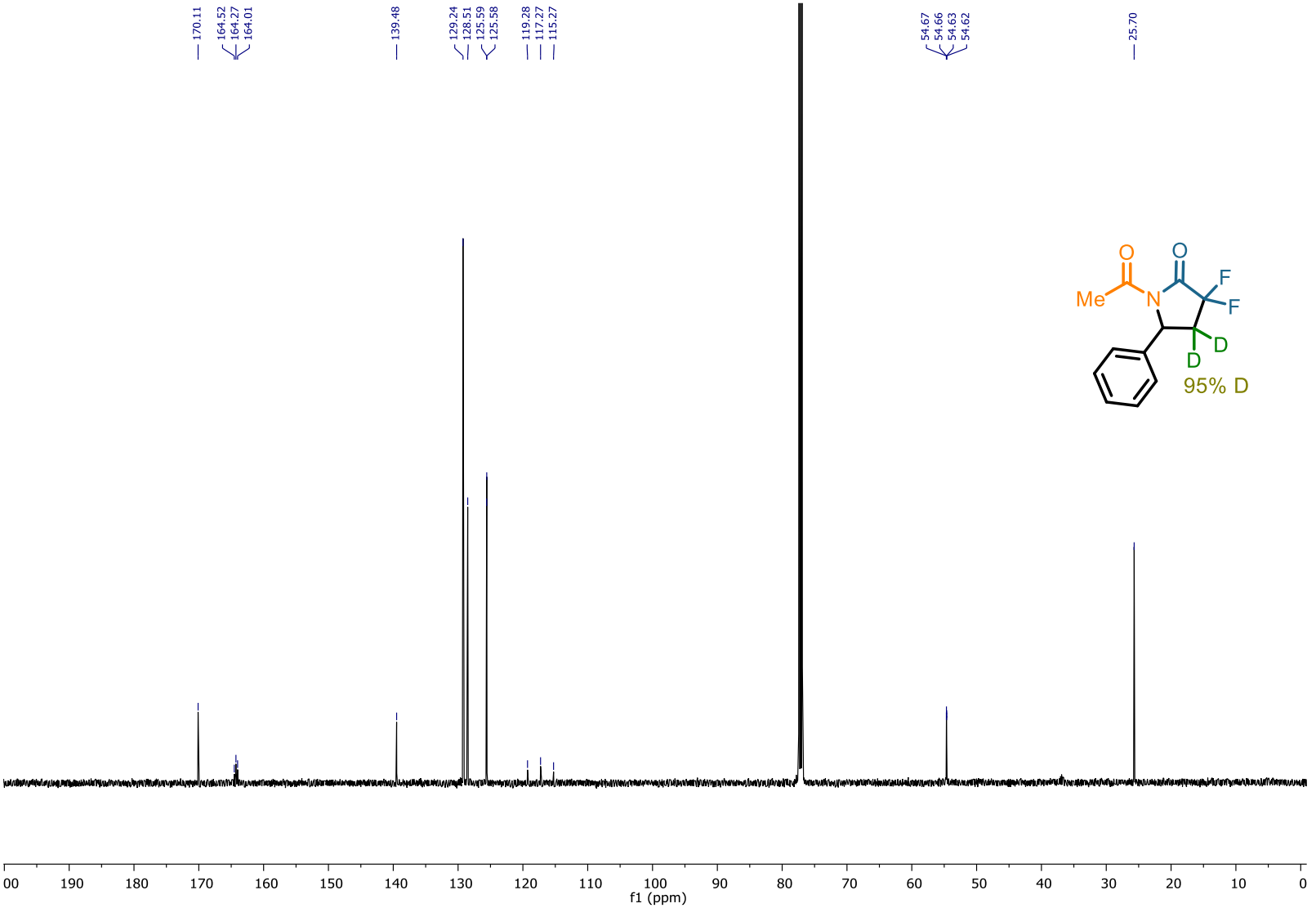
^{19}F-NMR (471 MHz, $CDCl_3$) of **74**



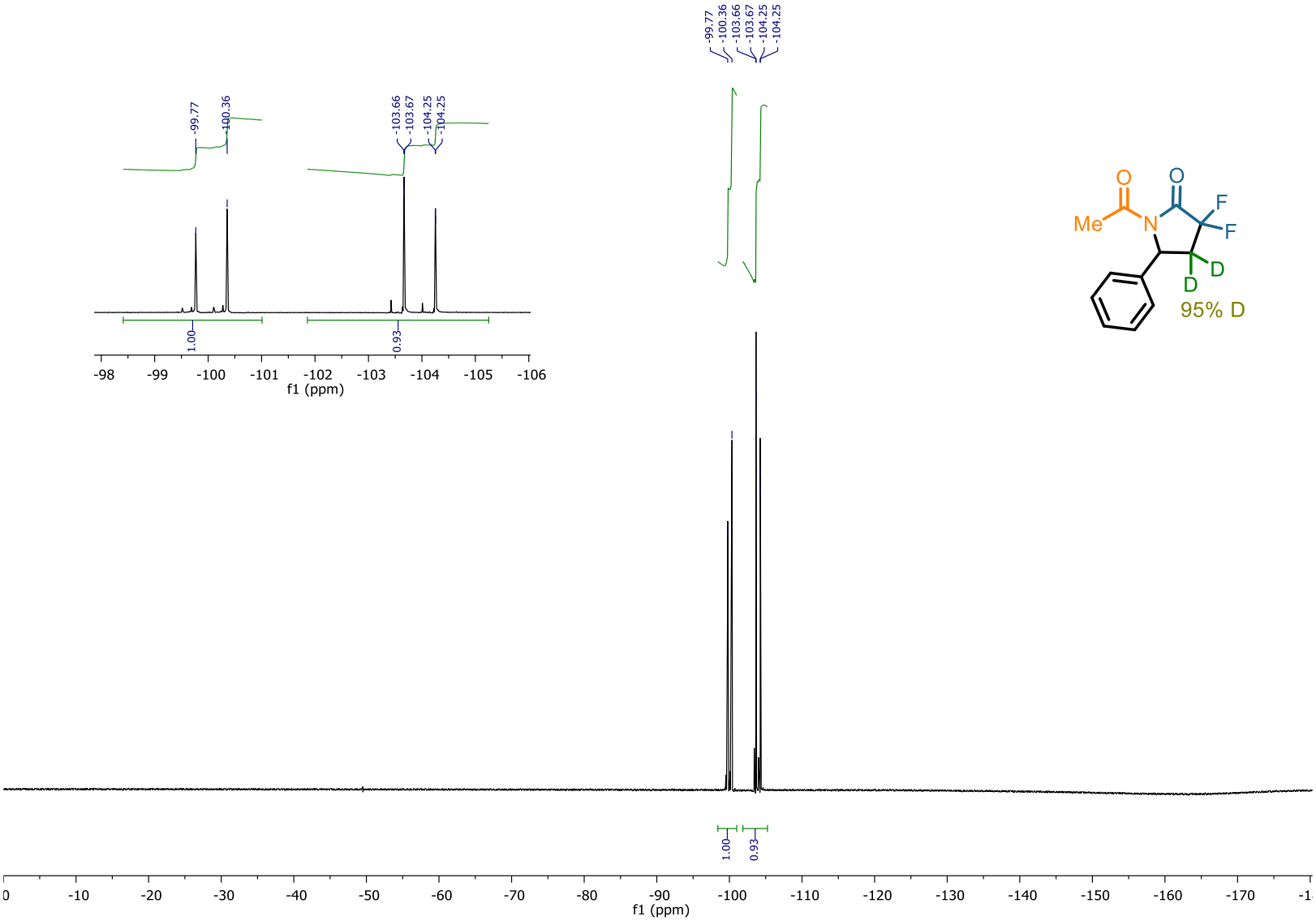
^{1}H-NMR (500 MHz, $CDCl_3$) of **75**



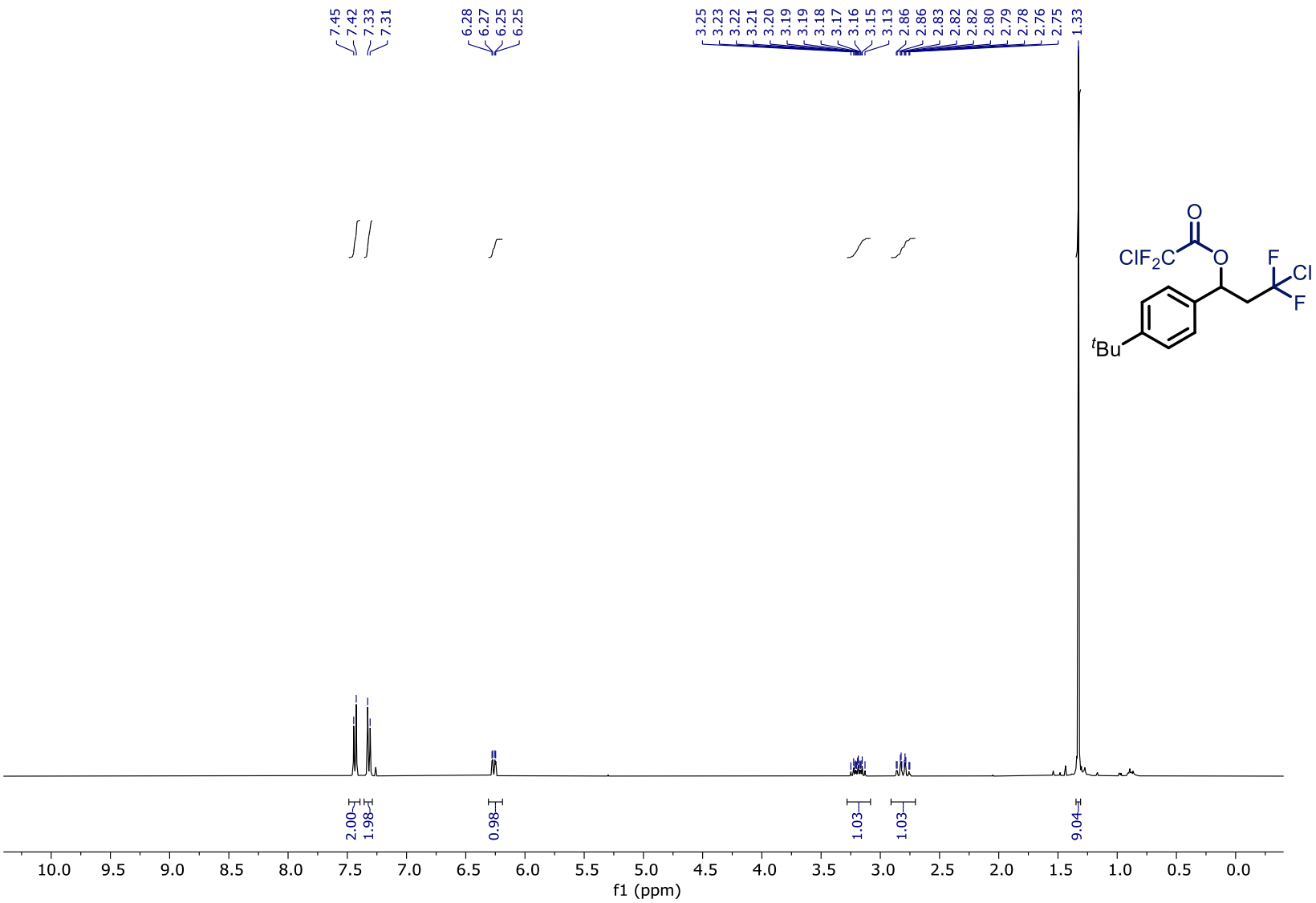
^{13}C-NMR (126 MHz, $CDCl_3$) of **75**



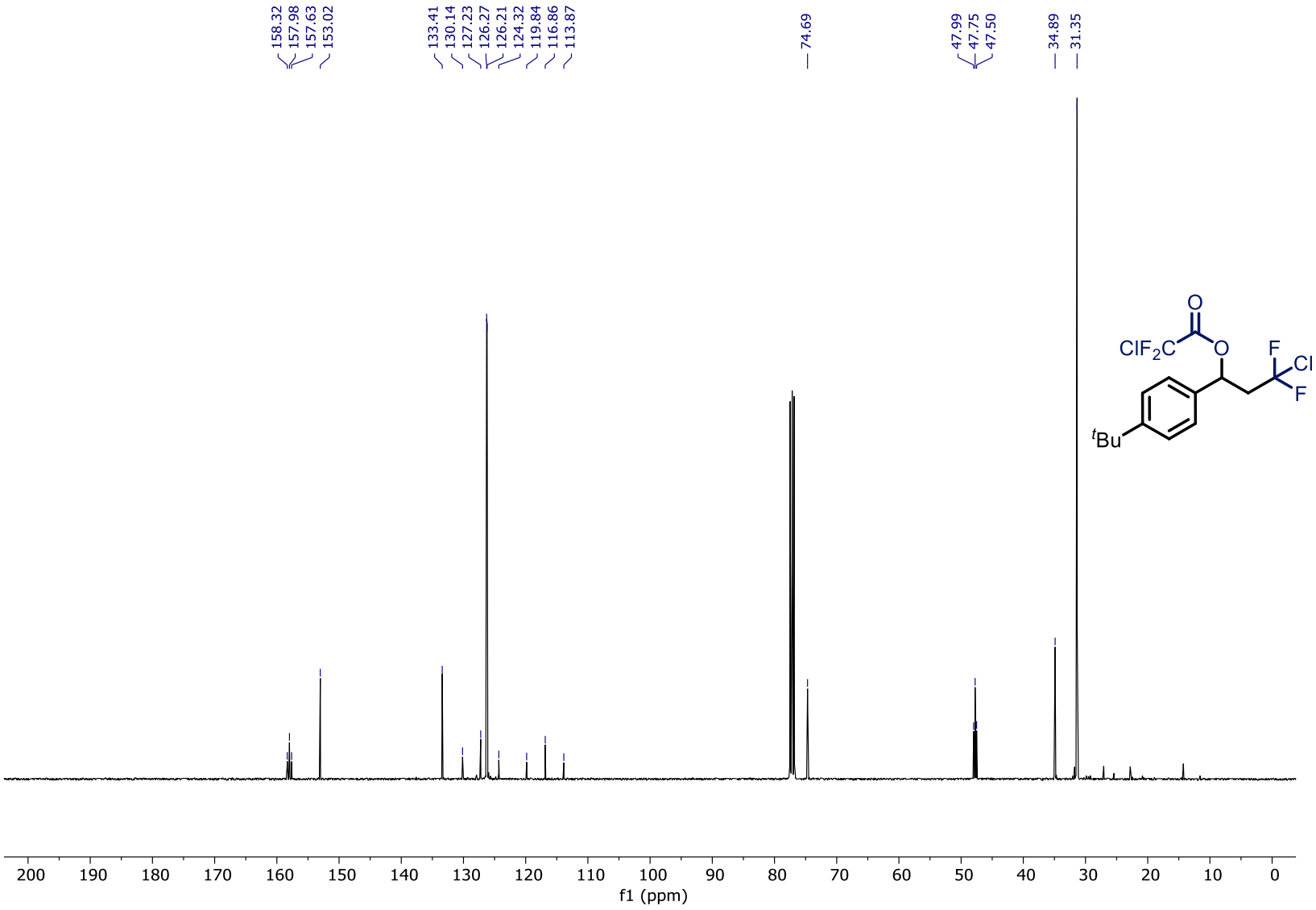
^{19}F-NMR (471 MHz, $CDCl_3$) of **75**



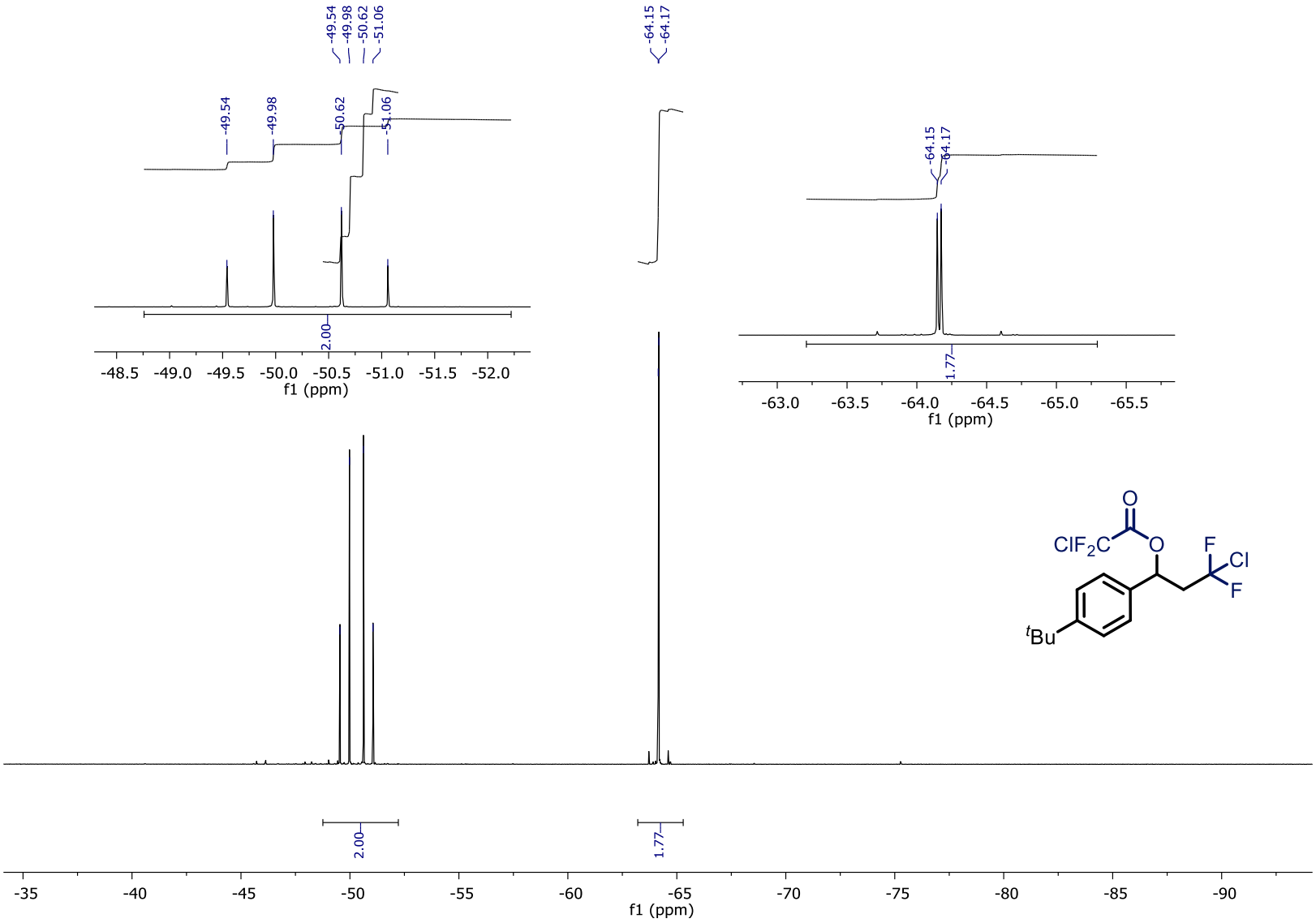
^{1}H-NMR (400 MHz, $CDCl_3$) of **3**



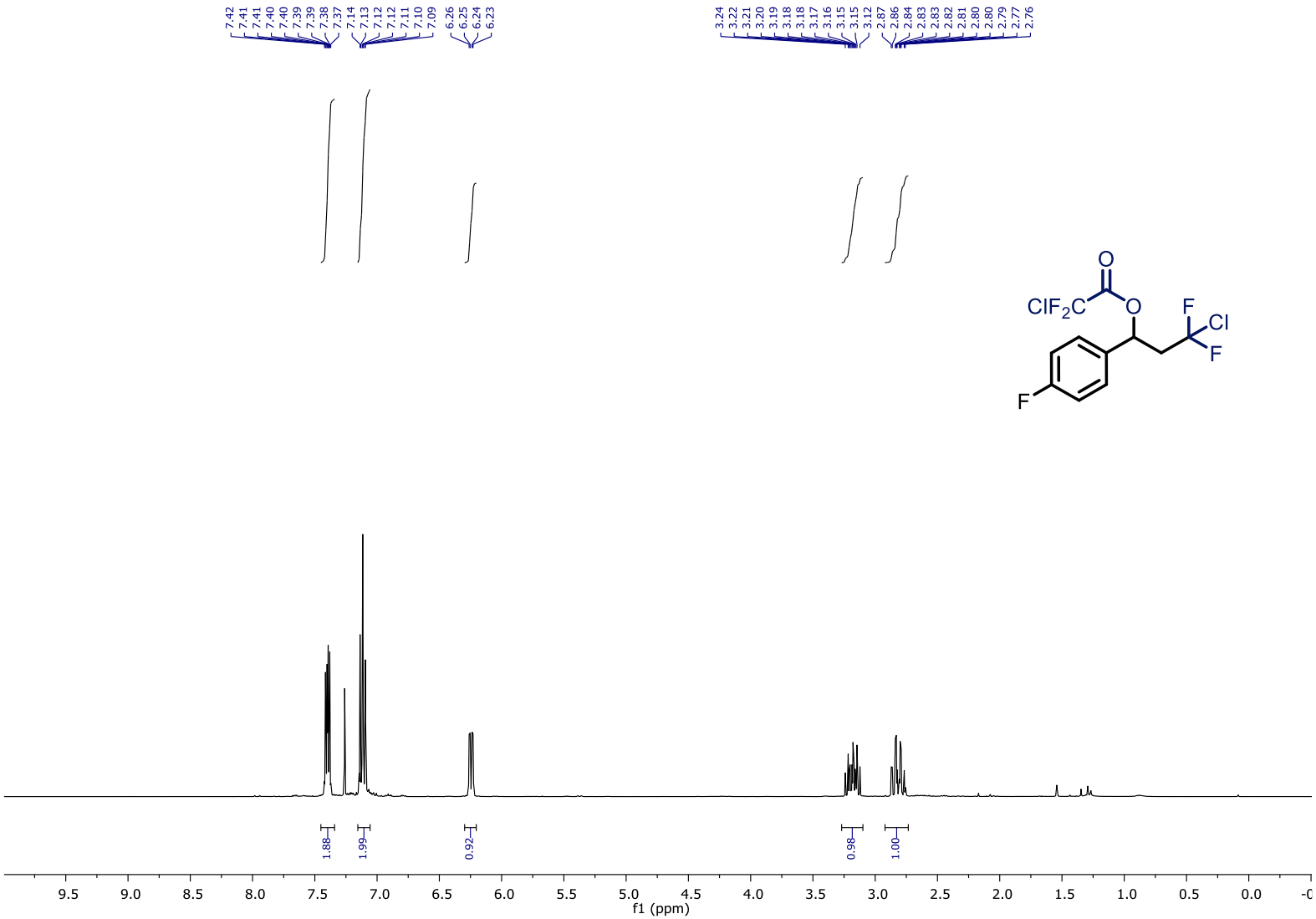
^{13}C-NMR (101 MHz, $CDCl_3$) of **3**



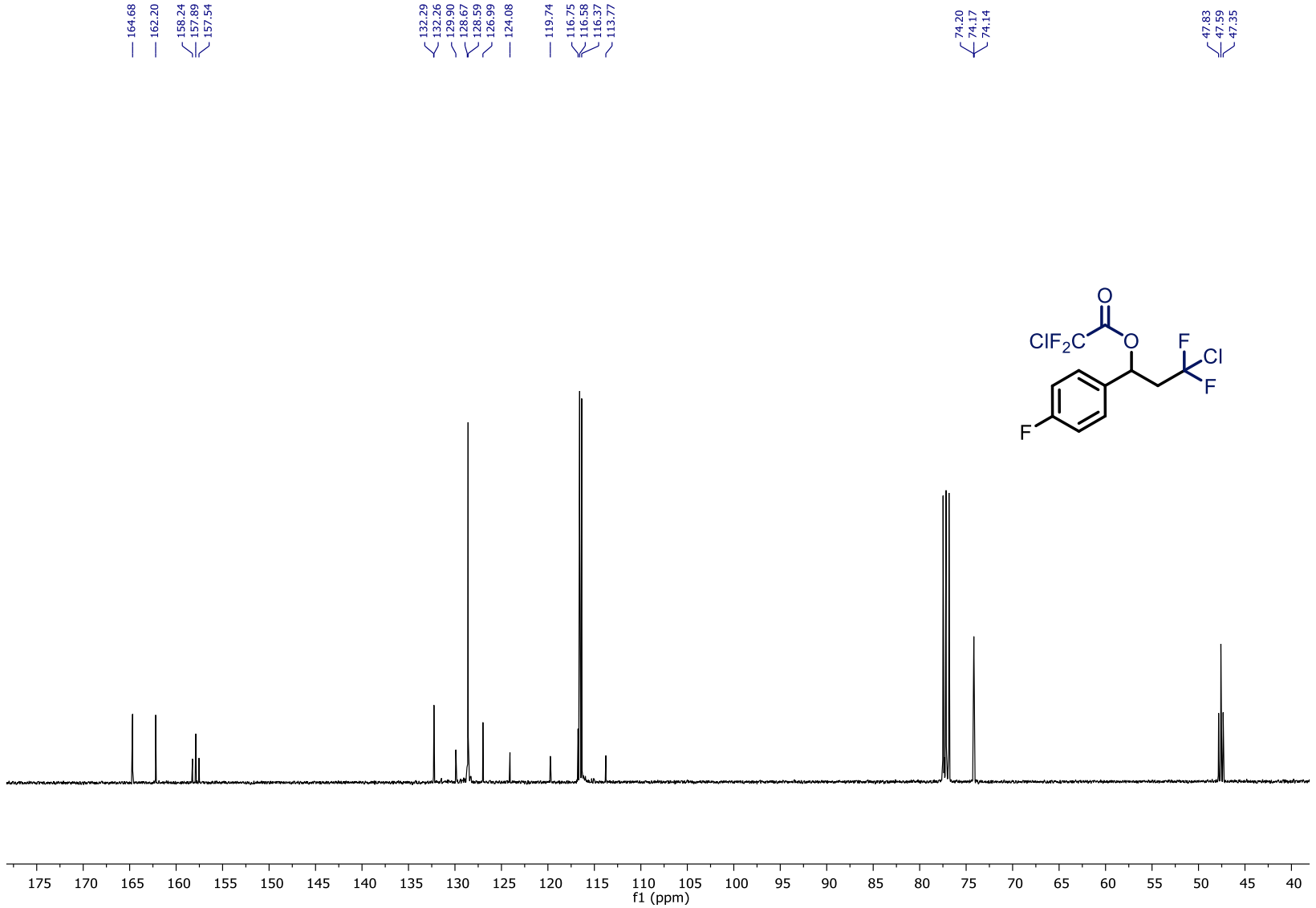
^{19}F-NMR (377 MHz, $CDCl_3$) of **3**



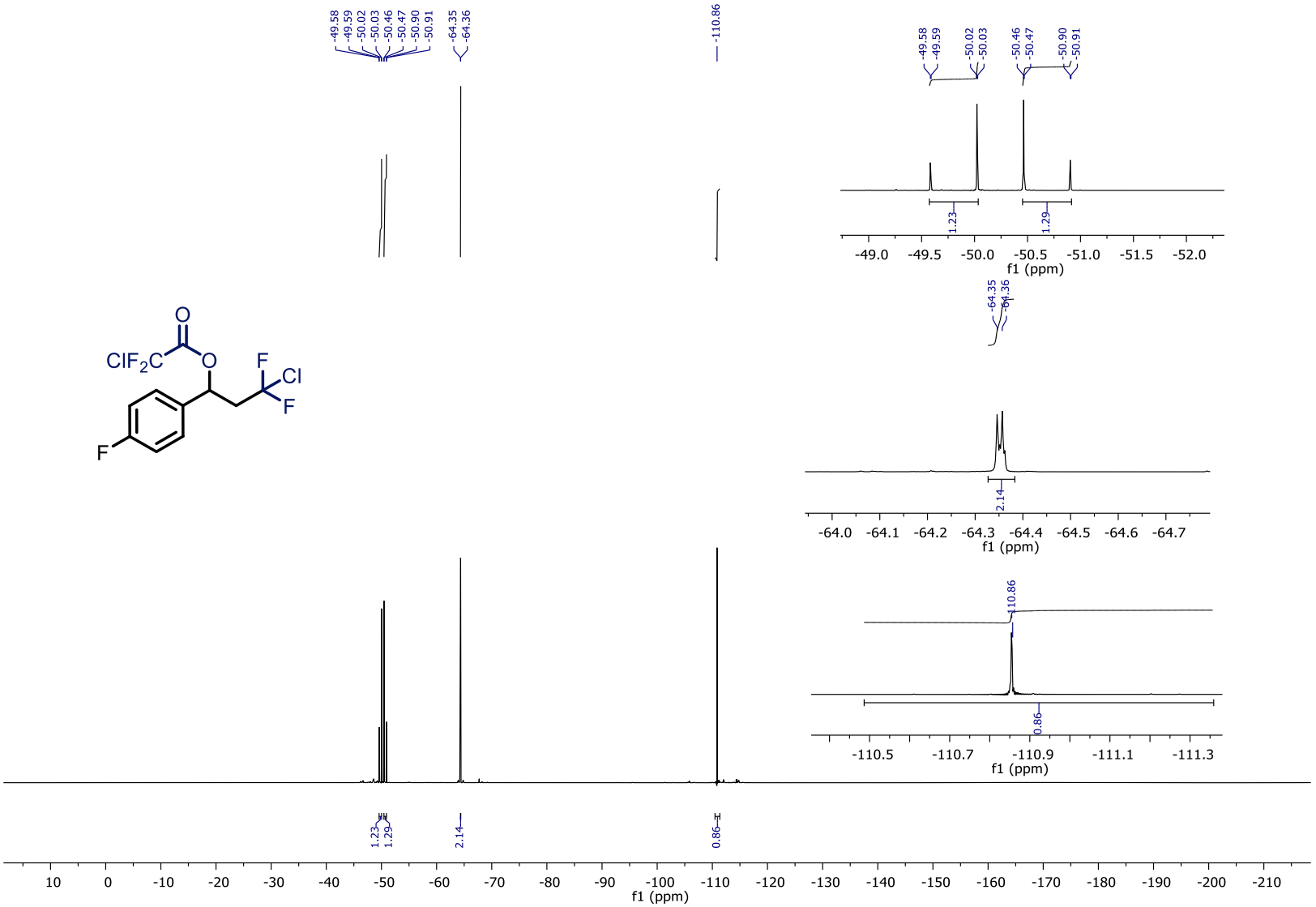
^{1}H-NMR (400 MHz, $CDCl_3$) of **76**



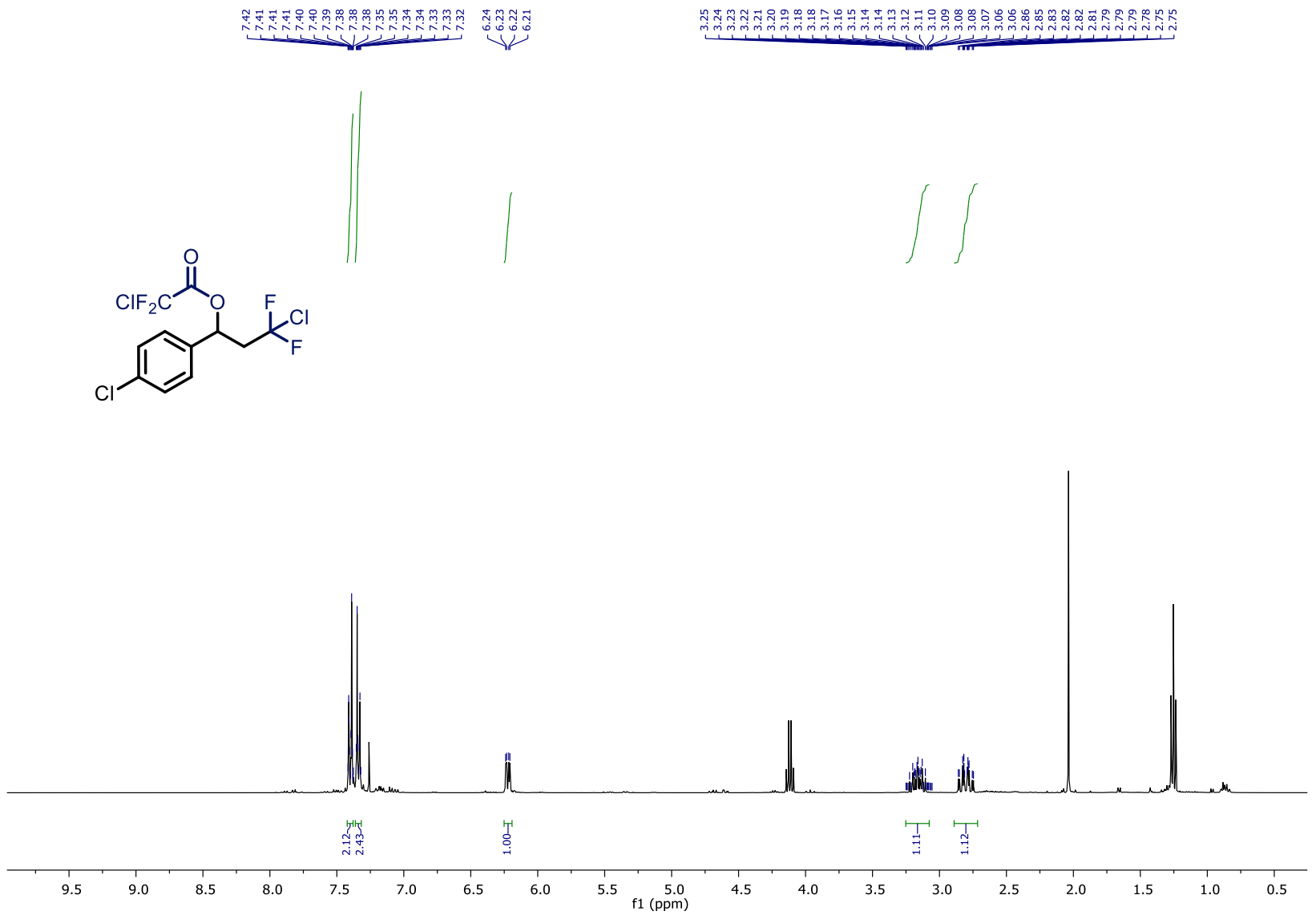
^{13}C-NMR (101 MHz, $CDCl_3$) of **76**



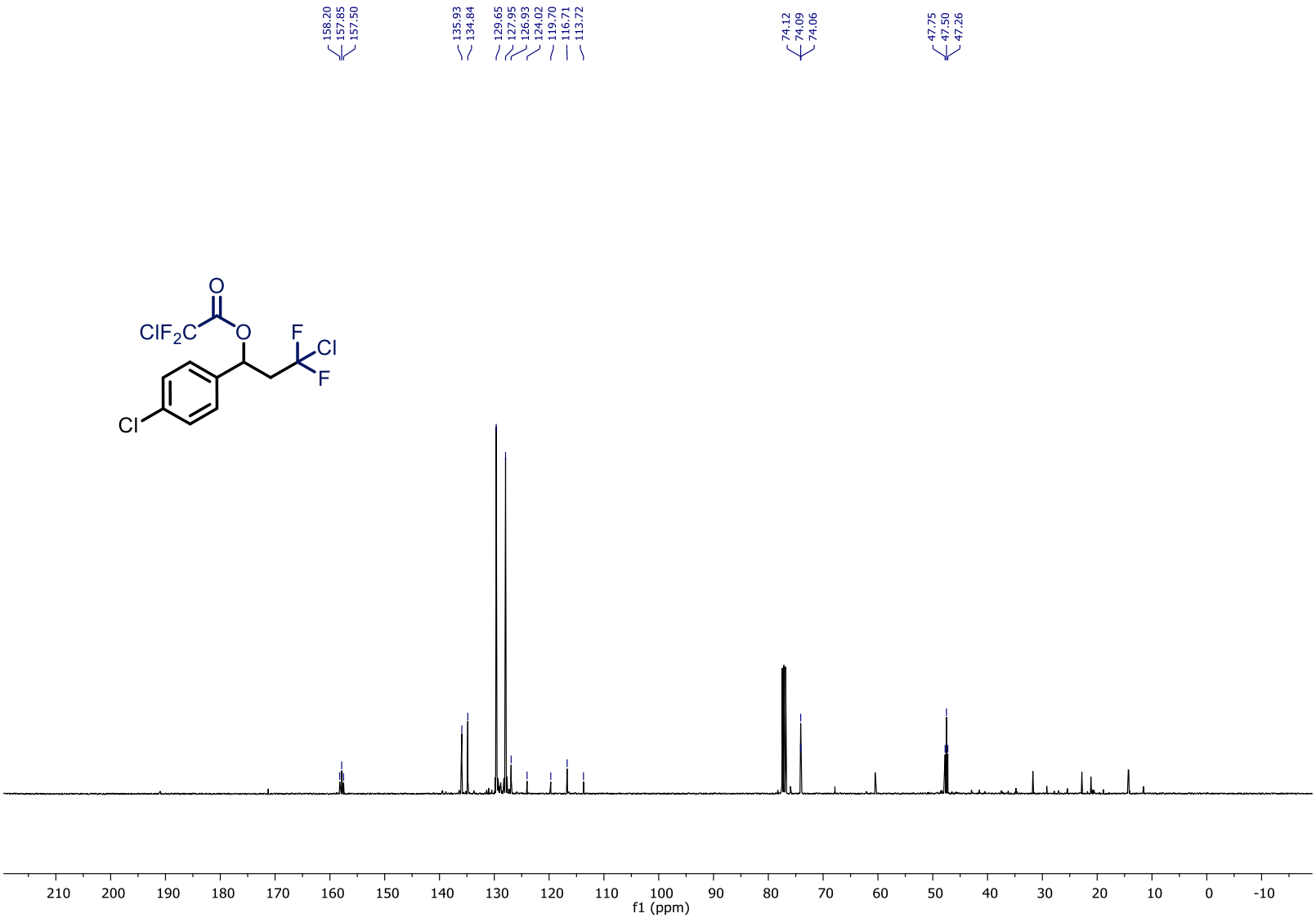
^{19}F-NMR (377 MHz, $CDCl_3$) of **76**



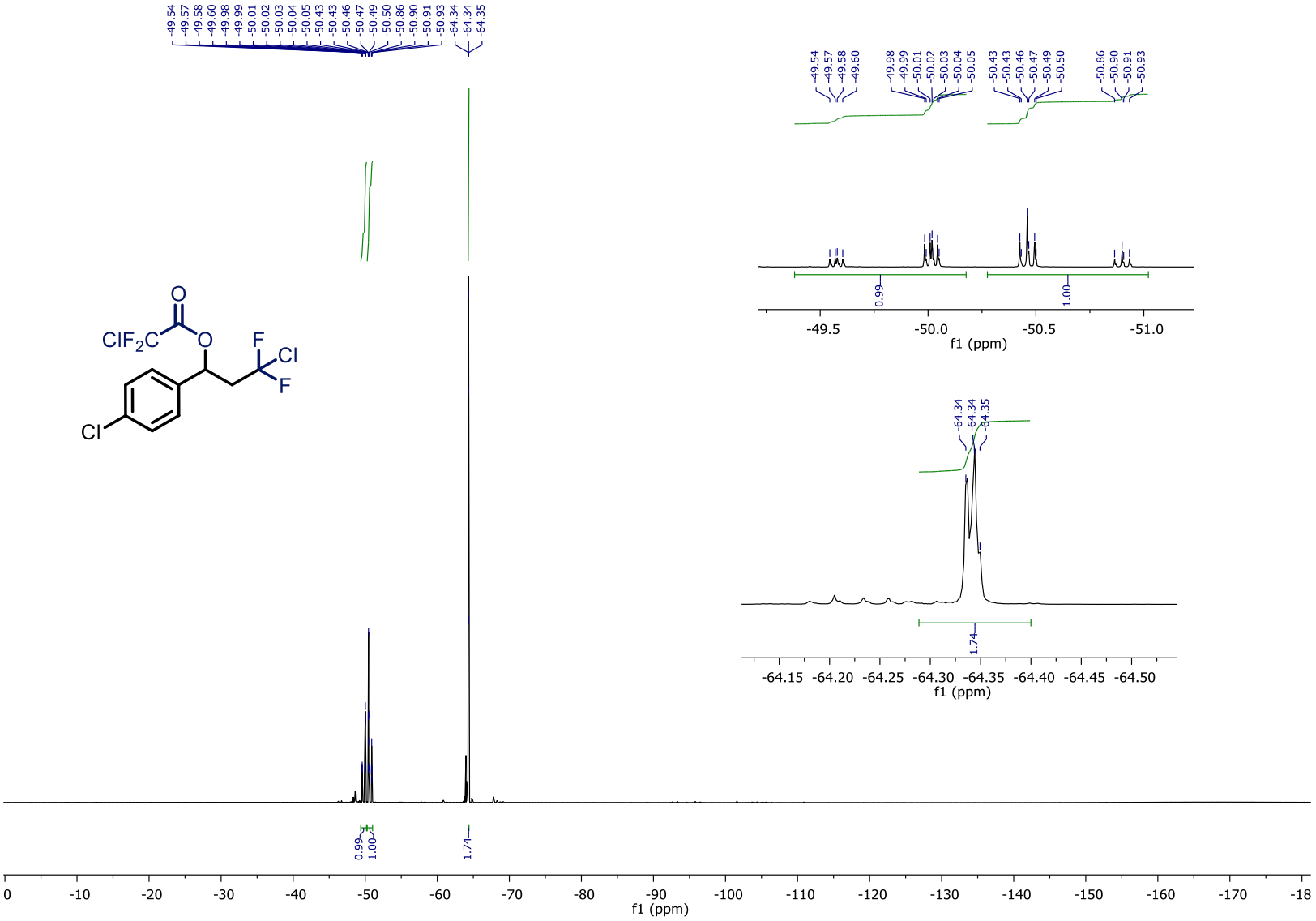
^{1}H-NMR (400 MHz, $CDCl_3$) of **77**



^{13}C-NMR (101 MHz, $CDCl_3$) of **77**



[^{1}H Coupled] ^{19}F-NMR (377 MHz, $CDCl_3$) of **77**



17. References

1. G. Z. Wang, R. Shang, Y. Fu, *Org. Lett.* **2018**, *20*, 888–891.
2. Z. Wu, S. N. Gockel, K. L. Hull, *Nat. Commun.* **2021**, *12*, 5956–5965.
3. R. O. McCourt, E. M. Scanlan, *Org. Lett.* **2019**, *21*, 3460–3464.
4. K. Zhang, D. Rombach, N. Y. Nötel, G. Jeschke, D. Katayev, *Angew. Chem. Int. Ed.* **2021**, *60*, 22487–22495. *Angew. Chem.* **2021**, *133*, 22661–22669.
5. J. L. Tu, W. Tang, W. Xu, F. Liu, *J. Org. Chem.* **2021**, *86*, 2929–2940.
6. S. Chen, J. Wang, L. G. Xie, *Org. Biomol. Chem.* **2021**, *19*, 4037–4042.
7. Y. Chen, Y. Ma, L. Li, H. Jiang, Z. Li, *Org. Lett.* **2019**, *21*, 1480–1483.
8. N. A. Magnus, J. A. Ailins, J. S. Cronin, W. D. Diseroad, A. D. Hargis, M. E. LeTourneau, B. E. Parker, S. M. Reurzel-Edens, J. P. Schafer, M. A. Staszak, G. A. Stephenson, S. L. Tameze, L. M. H. Zollars, *Org. Process Res. Dev.* **2005**, *9*, 621–628.
9. M. M. Amer, O. Olaizola, J. Carter, H. Abas, J. Clayden, *Org. Lett.* **2020**, *22*, 253–256.
10. C. Chatalova-Sazepin, Q. Wang, G. M. Sammis, J. Zhu, *Angew. Chem. Int. Ed.* **2015**, *54*, 5443–5446; *Angew. Chem.* **2015**, *127*, 5533–5536.
11. R. Iwai, S. Suzuki, S. Sasaki, A. S. Sairi, K. Igawa, T. Suenobu, K. Morokuma, G.-I. Konishi, *Angew. Chem. Int. Ed.* **2020**, *59*, 10566–10573; *Angew. Chem.* **2020**, *132*, 10653–10660.
12. H. J. Tang, B. Zhang, F. Xue, C. Feng, *Org. Lett.* **2021**, *23*, 4040–4044.
13. A. Hryniewicka, J. W. Morzycki, S. Witkowski, *J. Organomet. Chem.* **2010**, *695*, 1265–1270.
14. S. J. Plamondon, J. M. Warnica, D. Kaldre, J. L. Gleason, *Angew. Chem. Int. Ed.* **2020**, *132*, 253–258; *Angew. Chem.* **2020**, *132*, 259–564.
15. S. Chen, L. Yang, Y. Shang, J. Mao, P. J. Walsh, *Org. Lett.* **2021**, *23*, 1594–1599.
16. Y. Lou, J. Qiu, K. Yang, F. Zhang, C. Wang, Q. Song, *Org. Lett.* **2021**, *23*, 4564–4569.
17. S. Lauzon, H. Keipour, V. Gandon, T. Ollevier, *Org. Lett.* **2017**, *19*, 6324–6327.
18. G. J. Hedley, A. Ruseckas, I. D. W. Samuel, *Chem. Phys. Lett.* **2008**, *450*, 292–296.
19. K. C. Tang, K. L. Liu, I. C. Chen, *Chem. Phys. Lett.* **2004**, *386*, 437–441.
20. M. Kleinschmidt, C. van Wüllen, C. M. Marian, *J. Chem. Phys.* **2015**, *142*, 094301.
21. N. Elgrishi, N. et al, *J. Chem. Educ.* **2018**, *95*, 197–206.
22. V. V: Pavlishchuk, A. W. Addison, *Inorg. Chim. Acta* **2000**, *298*, 97–102.
23. H. M. Yau, R. S. Haines, J. B. Harper, *J. Chem. Educ.* **2015**, *92*, 538–542.
24. R. T: Sheen, H. L. Kahler, *Ind. Eng. Chem. Anal. Ed.* **1938**, *10*, 628–629.
25. S. L. Clegg, K. S. Pitzer, P. Brimblecombe, *J. Phys. Chem.* **1995**, *99*, 6755.
26. J. E. Bartmess, *J. Phys. Chem.* **1994**, *98*, 6420–6424.
27. Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157–167.
28. H. B. Schlegel, *J. Comput. Chem.* **1982**, *3*, 214–218.
29. X. Li, M. J. Frisch, *J. Chem. Theory Comput.* **2006**, *2*, 835–839.
30. A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.***1992**, *97*, 2571–2577.
31. A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829–5835.
32. F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
33. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
34. V. Barone, M. Cossi, *J. Phys. Chem. A.* **1998**, *102*, 1995–2001.
35. M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669–681.
36. G. Scalmani, M. J. Frisch, *J. Chem. Phys.* **2010**, *132*, 114110.
37. R. E. Skyner, J. L. McDonagh, C. R. Groom, T. van Mourik, J. B. O. Mitchell, *Phys. Chem. Chem. Phys.* **2015**, *17*, 6174–6191.
38. These calculations were carried out with the Python script *GoodVibes*. I. Funes-Ardoiz and R. S. Paton GoodVibes.py, DOI: 10.5281/zeonodo.1247565.
39. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov,

J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

40. N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877–910.