SUPPORTING INFORMATION

Light Promoted Metal-free Regio- and Stereoselective Isoperfluoropropylation of Unactivated alkenes with *i*-C_3F_7-Iodine(III) Reagent

Yaxing Wu[a], Yunchen Jiang[a], Fei Wang[a], Bin Wang[a] and Chao Chen*[a]

a. Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, China.

* E-mail: chenchao01@mails.tsinghua.edu.cn. Tel: +86-10-62773684.

TABLE OF CONTENTS

MATERIALS AND METHODS

All reactions were carried out under ambient atmosphere unless otherwise stated. Concentration under reduced pressure was performed by rotary evaporation at 25-45 °C at an appropriate pressure. Purified compounds were further dried under vacuum (10^{-4}-10^{-1} KPa). Isolated yields refer to purified and spectroscopically pure compounds or mixtures of constitutional isomers. All air- and moisture-sensitive manipulations were performed using standard Schlenk- or glove-box techniques under an atmosphere of argon or dinitrogen.

Starting materials

All substrates and materials were used as received from commercial suppliers, or prepared according to published procedures, respectively, unless otherwise stated. AgF was purchased from Energy-Chemical, and stored in an anhydrous brown bottle. Various photocatalysts was purchased from Sigma-Aldrich, Bidepharm and Energy-Chemical.

Solvents

Dry THF, DCM and DME were purchased from Innochem (water content < 50 ppm). Dry MeCN and DMF were purchased from Energy-Chemical (water content < 30 ppm). Dry ether was obtained by post-treatment with 4 Å molecular sieve, which activated at 300 °C in muffle furnace. All deuterated solvents were purchased from Sigma-Aldrich. EtOAc and petroleum ether (boiling range 60-90 °C) was purchased from Tansoole.

Spectroscopy and instruments

NMR spectra were recorded on a JEOL AL-400MHz spectrometer operating at 400 MHz, 101 MHz, and 376 MHz, for 1H, 13C, and 19F acquisitions. Chemical shifts are reported in ppm with the solvent residual peak as the internal standard. For ^{1}H NMR: chloroform-*d*, δ 7.26; dimethyl sulfoxide-d_6, δ 2.50. For ^{13}C NMR: chloroform-*d*, δ 77.16; dimethyl sulfoxide-d_6, δ 39.52. ^{19}F NMR spectra were referenced using a unified chemical shift scale based on the ^{1}H NMR resonance of tetramethylsilane (1% (v/v) solution in the respective solvent). Data is reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; coupling constants in Hz; integration. HRMS spectra were obtained using Bruker Esquire ion trap mass spectrometer in positive mode. UV-vis absorption spectra were recorded on an UV 2700. Emission spectra were recorded on a Hitachi F-4600. EPR spectra were recorded on a JEOL JES FA-200 spectrometer (sensitivity, 7*109 spins; resolution, ≥ 2.35 μT).

Chromatography

Thin layer chromatography (TLC) was performed using TLC plates pre-coated with 200 μm thickness silica gel F254 plates and visualized by fluorescence quenching under 254 nm UV light, phosphomolybdic Acid, and $KMnO_4$ stain. Column chromatography was performed on silica gel (particle size 10-40 μm, Ocean Chemical Factory of Qingdao, China).

Photochemistry

All reactions with visible light were carried out using a photoreactor equipped with a LED module (25 W Power Green LED 525 nm, purchased from GreeThink), consisting out of 50 LED-chips. The power of the LED was adjusted using a linear regulator.

Cyclic voltammetry

Cyclic voltammetry experiments were conducted in a Schlenk tube that contained the substance dissolved in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in acetonitrile. A platinum wire working electrode and a platinum mesh counter electrode were used. The voltage was measured *via* a Luggin capillary against an Ag/Ag^+ reference and was referenced externally against the ferrocene/ferrocenium ion pair. The relevant parameters were controlled by a CHI660 electrochemical workstation.

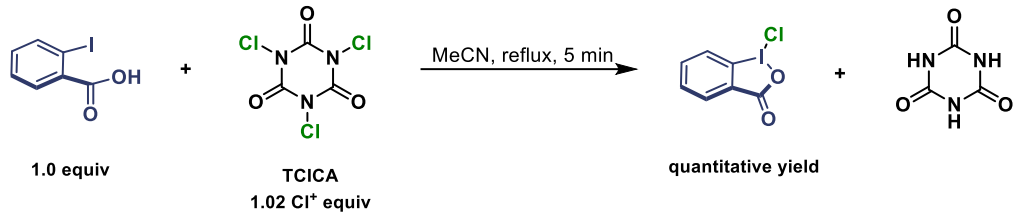
X-ray crystallographic Analysis

A crystal was mounted on a nylon loop using perfluoropolyether, and transferred to a XtaLAB FR-X diffractometer, Rigaku (Cu K_α radiation, λ=1.54178 Å) equipped with a nitrogen flow apparatus. The sample was held at 100(2) K or room temperature during the experiment.

EXPERIMENTAL DATA

The synthesis of *i*-C_3F_7-iodine(III) reagent (PFPI)

Chloroiodine(III) intermediate[1]



Scheme S1. Synthesis of chloroiodine(III) reagent.

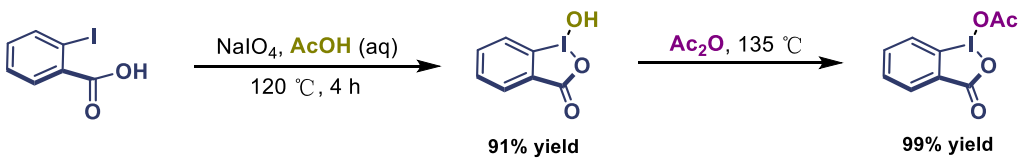
A 500 mL three-necked, round-bottom flask equipped with a teflon-coated magnetic stirring bar, nitrogen inlet and dropping funnel with pressure-equalizing side arm was charged under nitrogen with solid 2-iodobenzoic acid (20 g, 79.0 mmol, 1 equiv.), and anhydrous MeCN (150 mL) was added. The resulting stirred suspension was heated to 75 °C in an oil bath. The dropping funnel was charged with a solution of trichloroisocyanuric acid (6.37 g, 26.6 mol, 1.02 Cl^+ equiv.) in 30 mL of anhydrous MeCN. The solution of trichloroisocyanuric acid was dropped into the vigorously stirred reaction mixture within 5 min. The dropping funnel was rinsed with further anhydrous MeCN (10 mL). After addition was complete, the reaction mixture was refluxed for an additional 5 min. The reaction mixture was vacuum-filtered over an oven-preheated, sintered-glass funnel with a tightly packed pad of Celite (0.5 cm thick), and the filter cake was rinsed with additional hot MeCN (10-20 mL). The combined filtrates were evaporated to near-dryness, and the resulting yellow solid was filtered over a sintered-glass funnel and washed with a small amount of cold MeCN. The solid was dried for 1 h under high vacuum to give 1-chloro-1,2-benziodoxol-3-(1H)-one as free-flowing light yellow crystals in quantitative yield.

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.23 (ddd, *J* = 14.0, 8.0, 1.3 Hz, 2H), 7.98 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.82 - 7.76 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 117.1, 126.8, 128.9, 131.9, 133.4, 136.5, 167.3.

Acetoxyiodine(III) intermediate[2]



Scheme S2. Synthesis of acetoxyiodine(III) reagent.

To a suspension of 2-iodobenzoic acid (8.0 g, 32.2 mmol, 1.0 equiv.) in 30% v/v aq. AcOH (48 mL) was added $NaIO_4$ (7.24g, 33.8 mmol, 1.05 equiv.) at room temperature. The mixture was stirred at 120 °C for 4 h and then cooled down to room temperature followed by addition of water (50 mL). While avoiding exposure of ambient light, the precipitate was filtered, further washed with water (20 mL) and cold acetone (20 mL) and dried under vacuum to give 1-hydroxy-1,2-benziodoxol-3-(1*H*)-one as a white crystalline (7.78 g, 93% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Dimethyl sulfoxide-d_6, 298 K) δ 8.02 (dd, *J* = 7.7, 1.4 Hz, 1 H), 7.99 - 7.95 (m, 1 H), 7.85 (dd, *J* = 8.2, 0.7 Hz, 1 H), 7.71 (td, *J* = 7.6, 1.2 Hz, 1 H).

^{13}C NMR (101 MHz, Dimethyl sulfoxide-d_6, 298 K) δ 167.7, 134.5, 131.5, 131.1, 130.4, 126.3, 120.4.

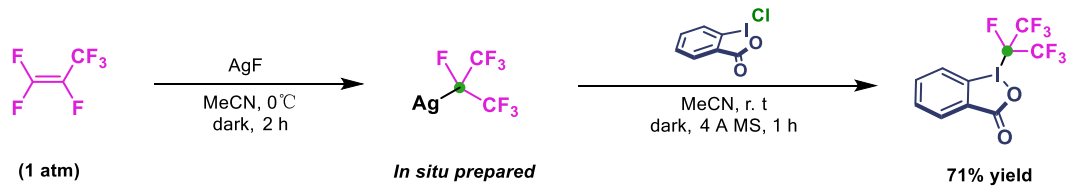
Acetic anhydride (25 mL) was added to 1-hydroxy-1,2-benziodoxol-3-(1*H*)-one (7.78 g, 29.5 mmol) at room temperature. The suspension was allowed to stir at 135 °C for 2 hours until fully dissolved. The resulting solution was slowly cooled down to -20 °C for crystallization. The white crystal was filtered and dried under vacuum to obtain 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (8.9 g, 99% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.23 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.00 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.92 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.71 (td, *J* = 7.3, 1.1 Hz, 1H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 176.4, 168.2, 136.2, 133.3, 131.5, 129.4, 129.1, 118.4, 20.3.

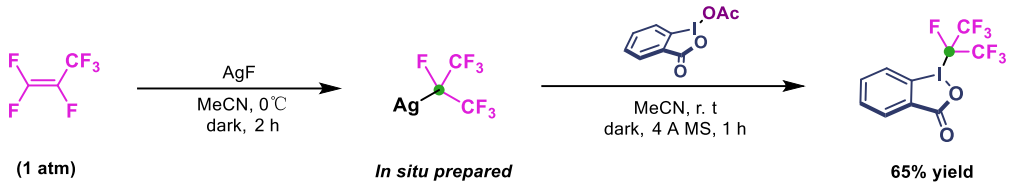
The *i*-C_3F_7-iodine(III)



Scheme S3. Synthesis of *i*-C_3F_7-iodine(III) (PFPI reagent) from chloroiodine(III) reagent.

In a nitrogen-filled glove box, an oven-dried crimp cap vessel with Teflon-coated stirrer bar was charged with silver fluoride (0.64 g, 5.0 mmol, 1.0 equiv.) and was brought under an atmosphere of dry nitrogen. To this vessel, anhydrous acetonitrile (20 mL) and hexafluoropropylene (1atm, balloon and adequate) were added, and the mixture was stirred at ice-water bath in the dark until silver fluoride precipitate dissolved completely. Then this solution was added to another oven-dried vessel, which filling with 1-chloro-1,2-benziodoxol-3-(1H)-one (1.44 g, 5.1 mmol, 1.02 equiv.) and 4 Å molecular sieves (100 mg). The reaction mixture was stirred at ambient temperature in the dark

for 1 hours. The reaction mixture was filtered over a sintered-glass funnel with a tightly packed pad of Celite (0.5 cm thick) under dry nitrogen atmosphere, and the filter cake was rinsed with additional anhydrous acetonitrile (5 - 10 mL). The solvent was evaporated under reduced pressure and crude solid product washed with anhydrous Et_2O (10 - 20 mL). Then, the product was obtained by anhydrous DCM leaching in ultrasonic generator under dry nitrogen atmosphere and vacuum evaporated of solvent. The solid was dried for 1 h under high vacuum to give 1-isoperfluoropropyl-1,2-benziodoxol-3-(1*H*)-one as off white solid (1.48 g, 71% yield).



Scheme S4. Synthesis of *i*-C_3F_7-iodine(III) (PFPI reagent) from acetoxyiodine(III) reagent.

In a nitrogen-filled glove box, an oven-dried crimp cap vessel with Teflon-coated stirrer bar was charged with silver fluoride (0.64 g, 5.0 mmol, 1.0 equiv.) and was brought under an atmosphere of dry nitrogen. To this vessel, anhydrous acetonitrile (20 mL) and hexafluoropropylene (1atm, balloon and adequate) were added, and the mixture was stirred at ice-water bath in the dark until silver fluoride precipitate dissolved completely. Then this solution was added to another oven-dried vessel, which filling with 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (1.56 g, 5.1 mmol, 1.02 equiv.) and 4 Å molecular sieves (100 mg). The reaction mixture was stirred at ambient temperature in the dark for 1 hours. The reaction mixture was filtered over a sintered-glass funnel with a tightly packed pad of Celite (0.5 cm thick) under dry nitrogen atmosphere, and the filter cake was rinsed with additional anhydrous acetonitrile (5 - 10 mL). The solvent was evaporated under reduced pressure and crude solid product washed with anhydrous Et_2O (10 - 20 mL). Then, the product was obtained by anhydrous DCM leaching in ultrasonic generator under dry nitrogen atmosphere and vacuum evaporated of solvent. The solid was dried for 1 h under high vacuum to give 1-isoperfluoropropyl-1,2-benziodoxol-3-(1*H*)-one as off white solid (1.35 g, 65% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.25 (dd, *J* = 7.6, 1.5 Hz, 1H), 8.01 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.78 - 7.70 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 167.9, 136.7, 133.1, 131.6, 127.99 (d, *J* = 6.7 Hz), 127.8, 120.5 (d, *J* = 10.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -71.21 (d, *J* = 11.8 Hz), -171.55 (p, *J* = 12.4 Hz).

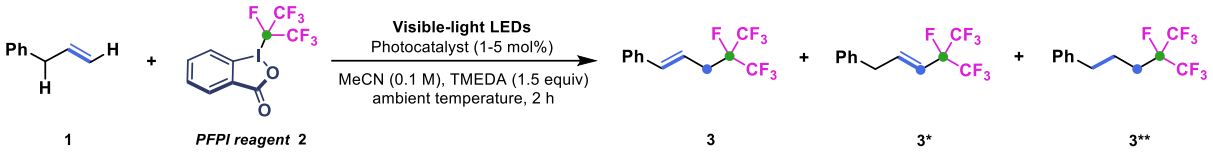
Elemental analysis: C%, theoretical value: 28.87%, measured value: 28.99%. H%, theoretical

value: 0.97%, measured value: 1.06%. O%, theoretical value: 7.69%, measured value: 7.54%.

Visible-light promoted isoperfluoropropylation of non-activated alkenes

Optimization of reaction conditions

Photocatalysts and photochemistry parameters screening



Scheme S5. Photocatalysts and photochemistry parameters screening.

Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, allylbenzene (**1**, 13.2 μL, 0.10 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (62.4 mg, 0.15 mmol, 1.5 equiv.), photocatalysts (PC, 1 - 5 mol%) were dissolved in dry MeCN (1 mL). Subsequently, TMEDA (22.4 μL, 0.15 mmol, 1.5 equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at visible light for 2 h, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, 10 μL of *n*-dodecane was added as an internal standard and the reaction mixture was diluted with EtOAc. The crude reaction mixture was filtered through a plug of silica then subjected to GC-MS analysis.

Entry	PC (1 - 5 mol%)	LEDs (Wavelength, Power)	Yield of **3** (%)	Yield ratio **3** : **3***	Yield of **3**** (%)
1	**Eosin Y (5 mol%)**	**Green LEDs (525 nm, 10 W)**	**80**	**> 99:1**	**< 5**
2	Eosin Y (5 mol%)	Green LEDs (525 nm, 25 W)	77	> 99:1	< 5
3	Eosin Y (5 mol%)	Blue LEDs (450 nm, 10 W)	69	> 99:1	< 5
4	Eosin Y (5 mol%)	White LEDs (100W)	47	> 99:1	< 5
5	Eosin Y (5 mol%)	UV (360-400nm)	42	96:4	< 5
6	*fac*-Ir(ppy)$_3$ (1 mol%)	Blue LEDs (450 nm, 10 W)	50	> 99:1	13
7	*fac*-Ir(ppy)$_3$ (1 mol%)	White LEDs (100W)	21	> 99:1	9
8	[Ir(dtbbpy)(ppy)$_2$]PF$_6$ (1 mol%)	Blue LEDs (450 nm, 10 W)	70	> 99:1	< 5
9	[Ru(bpy)$_3$](PF$_6$)$_2$ (1 mol%)	Blue LEDs (450 nm, 10 W)	65	> 99:1	< 5
10	[Ru(bpy)$_3$](PF$_6$)$_2$ (1 mol%)	UV (360-400nm)	30	92:8	< 5
11	PTH (5 mol%)	Blue LEDs (450 nm, 10 W)	trace	-	11
12	PTH (5 mol%)	UV (360-400nm)	trace	-	trace

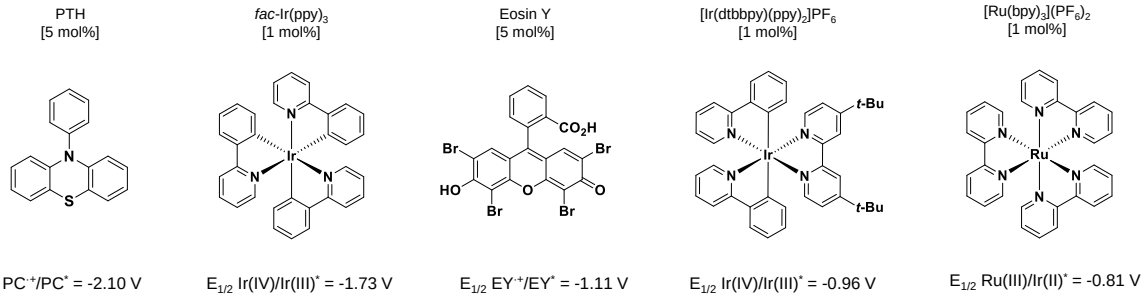
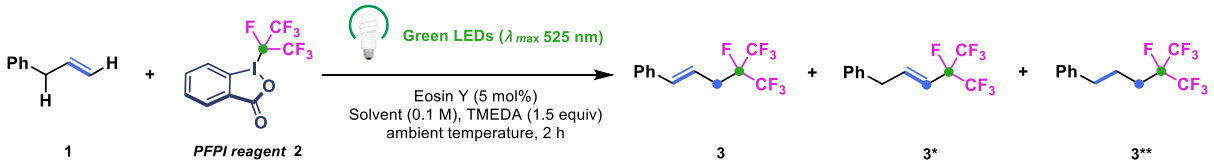


Table S1. Photocatalysts and photochemistry parameters screening

Solvent screening



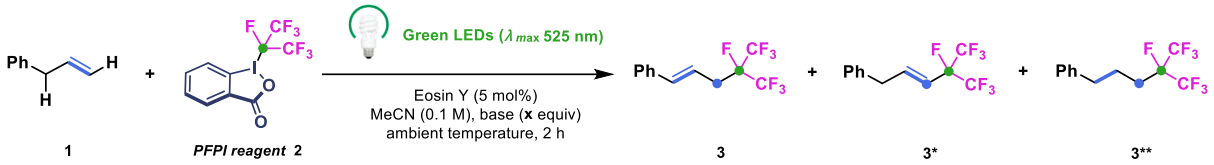
Scheme S6. Solvent screening.

Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, allylbenzene (**1**, 13.2 µL, 0.10 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (62.4 mg, 0.15 mmol, 1.5 equiv.), Eosin Y (5 mol%, 3.2 mg) were dissolved in dry solvent (1 mL). Subsequently, TMEDA (22.4 µL, 0.15 mmol, 1.5 equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at green light (525 nm) for 2 h, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, 10 µL of *n*-dodecane was added as an internal standard and the reaction mixture was diluted with EtOAc. The crude reaction mixture was filtered through a plug of silica then subjected to GC-MS analysis.

Entry	Solvent	Yield of **3** (%)	Yield ratio **3** : **3***	Yield of **3**** (%)
1	MeCN	**80**	**> 99:1**	**< 5**
2	DMF	44	> 99:1	< 5
3	DMA	55	> 99:1	< 5
4	THF	21	> 91:9	< 5
5	CH_2Cl_2	n. d	-	n. d

Table S2. Solvent screening.

Base screening



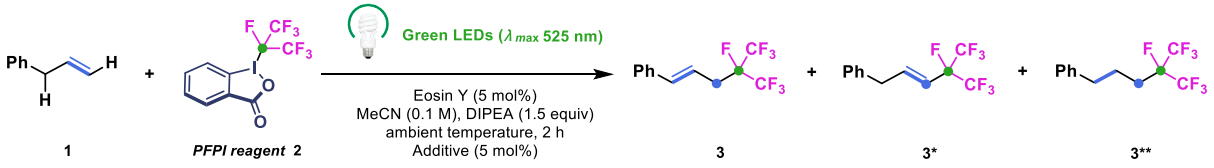
Scheme S7. Base screening.

Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, allylbenzene (**1**, 13.2 µL, 0.10 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (62.4 mg, 0.15 mmol, 1.5 equiv.), Eosin Y (5 mol%, 3.2 mg) were dissolved in dry MeCN (1 mL). Subsequently, base (x equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at green light (525 nm) for 2 h, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, 10 µL of *n*-dodecane was added as an internal standard and the reaction mixture was diluted with EtOAc. The crude reaction mixture was filtered through a plug of silica then subjected to GC-MS analysis.

Entry	Base (x equiv)	Yield of **3** (%)	Yield ratio **3** : **3***	Yield of **3**** (%)
1	**DIPEA (1.5 equiv)**	**87**	**> 99:1**	**< 5**
2	DIPEA (1.0 equiv)	74	> 99:1	< 5
3	TMEDA (1.5 equiv)	80	> 99:1	< 5
4	TMP (1.5 equiv)	37	96:4	10
5	TMG (1.5 equiv)	26	95:5	12
6	Cs_2CO_3 (1.0 equiv)	trace	-	n. d

Table S3. Base screening.

Additives screening



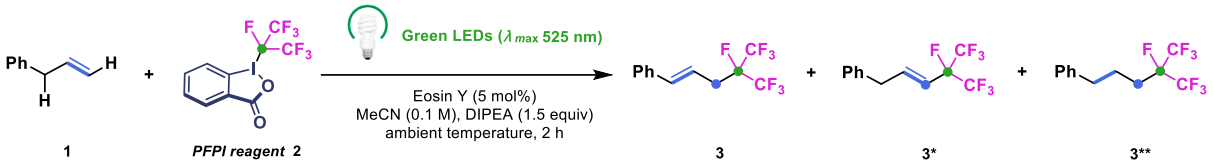
Scheme S8. Additives screening.

Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, allylbenzene (**1**, 13.2 μL, 0.10 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (62.4 mg, 0.15 mmol, 1.5 equiv.), Eosin Y (5 mol%, 3.2 mg), additive (5 mol%) were dissolved in dry MeCN (1 mL). Subsequently, DIPEA (26.1 μL, 0.15 mmol, 1.5 equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at green light (525 nm) for 2 h, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, 10 μL of *n*-dodecane was added as an internal standard and the reaction mixture was diluted with EtOAc. The crude reaction mixture was filtered through a plug of silica then subjected to GC-MS analysis.

Entry	Additive (5 mol%)	Yield of **3** (%)	Yield ratio **3** : **3***	Yield of **3****(%)
1	-	**87**	**> 99:1**	**< 5**
2	$Cu(CH_3CN)_4PF_6$	92[a]	89:11	n. d
3	$MeB(OH)_2$	68	> 99:1	< 5
4	$Zn(OTf)_2$	82	> 99:1	< 5

Table S4. Additives screening. [a] Total yield of **3** and **3***.

Control experiments under standard conditions



Scheme S9. Control experiments under standard conditions.

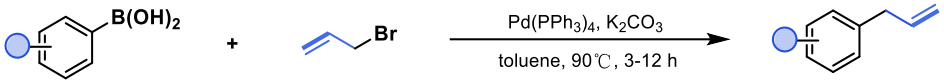
Entry[a]	Deviation from above	Yield of **3** (%)[a]	Yield ratio **3** : **3***[b]	Yield of **3****(%)[a]
1	**None (standard conditions)**	**87 (83[c])**	**> 99:1**	**< 5**
2	Reaction performed in CH_2Cl_2	n. d	-	n. d
3	Reaction performed in DMF	59	> 99:1	< 5
4	Reaction irradiated at 450 nm (blue light)	73	> 99:1	< 5
5	PTH instead of Eosin Y	trace	-	7
6	$[Ir(dtbbpy)(ppy)_2]PF_6$ instead of Eosin Y	82	> 99:1	< 5
7	*fac*-$Ir(ppy)_3$ instead of Eosin Y	58	> 99:1	14
8	$[Ru(bpy)_3](PF_6)_2$ instead of Eosin Y	71	> 99:1	< 5
9	TMEDA instead of DIPEA	80	> 99:1	< 5

10	TMP instead of DIPEA	37	96:4	10
11	TMG instead of DIPEA	26	95:5	12
12	Reaction performed in the dark	trace	-	n. d
13	5 mol% $Cu(CH_3CN)_4PF_6$ as additives	92[d]	89:11	n. d

Table S5. Control experiments under standard condition. [a]The yield was determined by GC-MS with *n*-dodecane as an internal standard. [b]The yield ritio was determined by GC-MS with *n*-dodecane as an internal standard or ^{19}F NMR analysis with $PhCF_3$ as an internal standard. [c]Yield of isolated product given. [d]Total yield of **3** and **3***.

Synthesis of the substrates

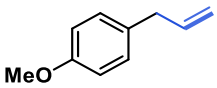
General procedure for preparation of allyl arenes



Scheme S10. Suzuki coupling for the synthesis of allyl arene.[3]

Under ambient atmosphere, a 50 mL borosilicate vial equipped with a magnetic stir bar was charged with arylboronic acid (5.0 mmol, 1.0 equiv.), allyl bromide (10.0 mmol, 2.0 equiv.), $Pd(PPh_3)_4$ (173.3 mg 0.15 mmol, 3.0 mol%), K_2CO_3 (1.38 g, 10.0 mmol, 2.0 equiv.) and toluene (20.0 mL, *c* = 0.25 M). The vial was sealed with a septum-cap and heated for 3 to 12 h at 90 °C. After cooling to room temperature, the reaction mixture was concentrated. The residue was dissolved in ethyl acetate (20 mL) and washed with brine (20 mL). The aqueous phase was extracted with ethyl acetate (2 × 20 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:30 to 1:100 (v:v)) to afford the title compound which was characterized by GC-MS analysis, ^1H NMR and ^{13}C NMR spectroscopy.

1-Allyl-4-methoxybenzene (**S1**)



S1

Known compound.

The title compound was prepared with 4-methoxyphenylboronic acid (759.8 mg, 5.0 mmol, 1.0 equiv.), allyl bromide (736.8 µL, 10.0 mmol, 2.0 equiv.), $Pd(PPh_3)_4$ (173.3 mg, 0.15 mmol, 3.0 mol%) and K_2CO_3 (1.38 g, 10.0 mmol, 2.0 equiv.) in toluene (20 mL, c = 0.25 M). The mixture was refluxed (90 °C) for 3 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:50 (v:v)) to afford the title compound as a colorless oil (606.8 mg, 82 %).

R_f = 0.45 (ethyl acetate: petroleum ether, 1:40 (v:v)).

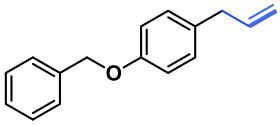
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.10 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.96 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.08 - 5.02 (m, 2H), 3.79 (s, 3H), 3.35 (d, *J* = 6.7 Hz, 2 H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 158.13, 138.06, 132.26, 129.68, 115.53, 114.01, 55.43, 39.50.

GC-MS: 148.

1-Allyl-4-(benzyloxy)benzene (**S2**)



S2

Known compound.

The title compound was prepared with 4-benzyloxyphenylboronic acid (1.14 g, 5.0 mmol, 1.0 equiv.), allyl bromide (736.8 µL, 10.0 mmol, 2.0 equiv.), $Pd(PPh_3)_4$ (173.3 mg, 0.15 mmol, 3.0 mol%) and K_2CO_3 (1.38 g, 10.0 mmol, 2.0 equiv) in toluene (20 mL, c = 0.25 M). The mixture was refluxed (90 °C) for 3 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:50 (v:v)) to afford the title compound as a colorless oil (795.2 mg, 71 %).

R_f = 0.58 (ethyl acetate: petroleum ether, 1:20 (v:v)).

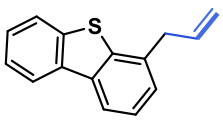
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.33 - 7.46 (m, 5H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 5.95 (ddt, *J* = 17.2 Hz, 10.1 Hz, 6.7 Hz, 1H), 5.07 - 5.11 (m, 4H), 3.36 (d, *J* = 6.8 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 157.3, 138.0, 137.3, 132.6, 129.6, 128.7, 128.0, 127.6, 115.6, 114.9, 70.2, 39.5.

GC-MS: 224.

4-Allyldibenzothiophene (**S3**)



S3

Known compound.

The title compound was prepared with dibenzothiophene-4-boronic acid (1.14 g, 5.0 mmol, 1.0 equiv.), allyl bromide (736.8 µL, 10.0 mmol, 2.0 equiv.), $Pd(PPh_3)_4$ (173.3 mg, 0.15 mmol, 3.0 mol%)

and K_2CO_3 (1.38 g, 10.0 mmol, 2.0 equiv) in toluene (20 mL, c = 0.25 M). The mixture was refluxed (90 °C) for 3 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:50 (v:v)) to afford the title compound as a colorless oil (0.896 g, 80 %).

R_f = 0.56 (ethyl acetate: petroleum ether, 1:100 (v:v)).

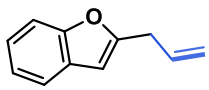
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.18 - 8.12 (m, 1H), 8.06 (d, 1H, *J* = 7.7 Hz), 7.90 - 7.86 (m, 1H), 7.50 - 7.45 (m, 2H), 7.45 (t, 1H, *J* = 7.2 Hz), 7.32 (d, 1H, *J* = 7.5 Hz), 6.25 - 6.02 (m, 1H), 5.23 (dq, 1H, *J* = 16.7 Hz, 1.5 Hz), 5.19 (dq, 1H, *J* = 9.9 Hz, 1.5 Hz), 3.67 (d, 2H, *J* = 6.3 Hz).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 146.1, 144.5, 143.5, 140.1, 135.1, 134.3, 126.8, 126.6, 125.1, 124.6, 123.0, 121.9, 119.8, 117.3, 39.6.

GC-MS: 224.

2-Allylbenzofuran (**S4**)



S4

Known compound.

The title compound was prepared with benzofuran-2-boronic acid (809.8 mg, 5.0 mmol, 1.0 equiv.), allyl bromide (736.8 µL, 10.0 mmol, 2.0 equiv.), $Pd(PPh_3)_4$ (173.3 mg, 0.15 mmol, 3.0 mol%) and K_2CO_3 (1.38 g, 10.0 mmol, 2.0 equiv.) in toluene (20 mL, c = 0.25 M). The mixture was refluxed (90 °C) for 3 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:50 (v:v)) to afford the title compound as a colorless oil (426.6 mg, 54 %).

R_f = 0.41 (ethyl acetate: petroleum ether, 1:50 (v:v)).

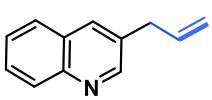
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.50 - 7.48 (m, 1H), 7.43 - 7.41 (m, 1H), 7.24 - 7.17 (m, 2H), 6.42 (d, *J* = 1.2 Hz, 1H), 6.06 - 5.99 (m, 1H), 5.24 (dq, *J* = 17.1 Hz, 1.8 Hz, 1H), 5.19 (dq, *J* = 9.9 Hz, 1.2 Hz, 1H), 3.55 (dd, *J* = 6.6 Hz, 1.2 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 157.0, 154.9, 133.1, 128.8, 123.3, 122.4, 120.3, 117.6, 110.7, 102.6, 33.0.

GC-MS: 158.

3-Allyl quinoline (**S5**)



S5

Known compound.

The title compound was prepared with quinoline-3-boronic acid (864.9 mg, 5.0 mmol, 1.0 equiv.), allyl bromide (736.8 µL, 10.0 mmol, 2.0 equiv.), $Pd(PPh_3)_4$ (173.3 mg, 0.15 mmol, 3.0 mol%) and K_2CO_3 (1.38 g, 10.0 mmol, 2.0 equiv.) in toluene (20 mL, c = 0.25 M). The mixture was refluxed (90 °C) for 3 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:40 (v:v)) to afford the title compound as a colorless oil (321.1 mg, 38 %).

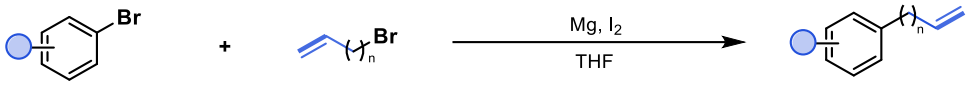
R_f = 0.28 (ethyl acetate: petroleum ether, 1:5 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.79 (s, 1 H), 8.10 (d, *J* = 8.5 Hz, 1 H), 7.95 (s, 1 H), 7.78 (d, *J* = 8.5 Hz, 1 H), 7.73 - 7.63 (m, 1 H), 7.57 - 7.50 (m, 1 H), 6.14 - 5.92 (m, 1 H), 5.25 - 4.97 (m, 2 H), 3.59 (d, *J* = 6.8 Hz, 2 H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 152.0, 146.9, 136.0, 134.6, 132.6, 129.2, 128.8, 128.1, 127.4, 126.6, 117.1, 37.3.

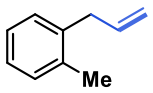
GC-MS: 169.



Scheme S11. Wurtz-Fittig coupling for the synthesis of allyl arene or 4-pentenyl-arene.[4]

Under ambient atmosphere, a flame-dried vial equipped with a magnetic stir bar was charged with Mg granules (115.2 mg, 4.8 mmol, 1.2 equiv.) and iodide grain and sealed with a septum. Part of a solution of bromoarene (4.0 mmol, 1.0 equiv.) in THF (5 mL) was added into the vial via a syringe. After the color suddenly faded, the rest of solution was added. The solution was stirred for 2 h under ambient atmosphere. The mixture was decanted into another dry flask. It was then cooled to 0 ℃ and alkyl bromide (6.0 mmol, 1.5 equiv.) was added carefully. The resulting solution was stirred for 45 min at 0 ℃ and quenched with saturated solution of NH_4Cl. The solution was then extracted with 3×10 mL diethyl ether and the combined organic layers were dried over Na_2SO_4. The solvent was then removed in vacuo and the residue was purified by flash column chromatography (silica gel, ethyl acetate: petroleum ether, 1:50 to 1:100 (v:v)) to afford the title compound which was characterized by GC-MS analysis, ^{1}H NMR and ^{13}C NMR spectroscopy.

1-Methyl-2-allylbenzene (**S6**)



S6

Known compound.

The title compound was prepared with 2-methyl bromobenzene (481.0 µL, 4.0 mmol, 1.0 equiv.), allyl bromide (442.1 µL, 6.0 mmol, 1.5 equiv.), Mg granules (115 mg, 4.8 mmol, 1.2 equiv.) and I_2 (20 mg) in THF (5 mL, *c* = 0.80 M). The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:100 (v:v)) to afford the title compound as a colorless oil (443.5 mg, 84 %).

R_f = 0.68 (ethyl acetate: petroleum ether, 1:100 (v:v)).

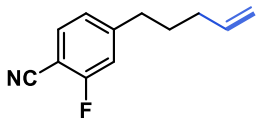
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.25 (m, 4H), 6.12 - 6.02 (m, 1H), 5.19 - 5.08 (m, 2H), 3.49 (d, *J* = 6.3 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 138.1, 136.7, 136.3, 130.1, 129.1, 126.3, 126.0, 115.6, 37.7, 19.3.

GC-MS: 132.

2-Fluro-4-pentenylbenzonitrile (**S7**)



S7

The title compound was prepared with 2-fluro-4-bromobenzonitrile (800.4 mg, 4.0 mmol, 1.0 equiv.), 5-bromopentene (710.7 µL, 6.0 mmol, 1.5 equiv.), Mg granules (115 mg, 4.8 mmol, 1.2 equiv.) and I_2 (20 mg) in THF (5 mL, c = 0.80 M). The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:50 - 1:100 (v:v)) to afford the title compound as a colorless oil (544.3 mg, 72 %).

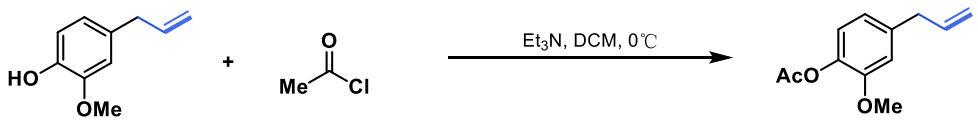
R_f = 0.64 (ethyl acetate: petroleum ether, 1:50 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.60 (dd, *J* = 8.0, 5.1 Hz, 1H), 7.11 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.02 (dd, *J* = 8.0, 2.1 Hz, 1H), 5.70 (tt, *J* = 17.0, 6.6 Hz, 1H), 5.20 - 4.89 (m, 2H), 2.62 (t, *J* = 8.7 Hz, 2H), 2.11 (td, *J* = 7.8, 6.7 Hz, 2H), 1.69 - 1.54 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 162.86 (d, *J* = 252.0 Hz), 145.44 (d, *J* = 8.2 Hz), 137.24, 133.29 (d, *J* = 8.1 Hz), 125.84 (d, *J* = 3.3 Hz), 116.21 (d, *J* = 20.0 Hz), 114.98, 114.74 (d, *J* = 4.1 Hz), 98.86 (d, *J* = 20.0 Hz), 35.35 (d, *J* = 4.2 Hz), 35.13, 29.63.

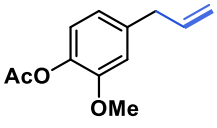
GC-MS: 189.



Scheme S12. Acetyloxylation of eugenol.

Acetyl chloride (298.6 µL, 4.2 mmol, 1.4 equiv.) was added to a solution of Et_3N (667.3 µL, 4.8 mmol, 1.6 equiv.) and eugenol (492.3 mg, 3 mmol, 1.0 equiv.) in CH_2Cl_2 (5 mL, 0.6 M) at 0 ºC. The mixture was stirred at this temperature until starting material is consumed. The reaction was poured into water (20 mL), and the mixture was stirred vigorously for 5 min. The aqueous phase was extracted with EtOAc (3×50 mL). The combined organic phases were washed with 1 M aq HCl (10 mL), saturated aq $NaHCO_3$ (15 mL), water (15 mL) and brine (15 mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure for giving the acetate ester which does not require purification (568.6 mg, 92 %).

Eugenyl acetate (**S8**)



S8

Known compound.

R_f = 0.43 (ethyl acetate: petroleum ether, 1:10 (v:v)).

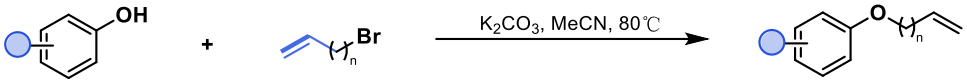
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ6.94 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 1.8 Hz, 1H), 6.77 (dd, *J* = 8.0, 1.9 Hz, 1H), 5.97 (ddt, *J* = 16.8, 10.1, 6.8 Hz, 1H), 5.12 (dq, *J* = 17.0, 1.7 Hz, 1H), 5.09 (dq, *J* = 10.1, 1.6 Hz, 1H), 3.82 (s, 3H), 3.38 (d, *J* = 6.7 Hz, 2H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 169.3, 150.8, 139.0, 137.9, 137.0, 122.4, 120.6, 116.1, 112.6, 55.8, 40.1, 20.6.

GC-MS: 206.

General procedure for preparation of allyl ethers and (pent-4-en-1-yloxy)benzene derivatives

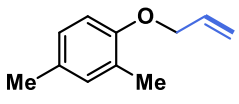


Scheme S13. Synthesis of allyl ethers and (pent-4-en-1-yloxy)benzene derivatives.[5]

To a solution of aromatic alcohol (5.0 mmol, 1.0 equiv.) and K_2CO_3 (2.07 g, 15.0 mmol, 3.0 equiv.) in CH_3CN (20.0 mL, 0.25 M) was added allyl bromide/5-bromopent-1-ene (10.0 mmol, 2.0 equiv.), and the mixture was refluxed for 12h. It was then cooled to 25°C and the solvent was removed in vacuo. The residue was partitioned between diethyl ether and water, and the aqueous layer was extracted with diethyl ether (3 x 20 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4. The solvent was then removed in vacuo and the residue was purified by flash column chromatography (silica gel, ethyl acetate: petroleum ether, 1:5 to 1:100 (v:v)) to

afford the corresponding alkenes which was characterized by GC-MS analysis, ^{1}H NMR and ^{13}C NMR spectroscopy.

2,4-Dimethyl(allyloxy)benzene (**S9**)



S9

Known compound.

The title compound was prepared with 2,4-dimethylphenol (610.1 mg, 5.0 mmol, 1.0 equiv.), K_2CO_3 (2.07 g, 15.0 mmol, 3.0 equiv.) and allyl bromide (736.8 µL, 10.0 mmol, 2.0 equiv.) in CH_3CN (20 mL, c = 0.25 M). The mixture was refluxed (80 °C) for 12 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:50 - 1:100 (v:v)) to afford the title compound as a colorless oil (761.4 mg, 94 %).

R_f = 0.65 (ethyl acetate: petroleum ether, 1:30 (v:v)).

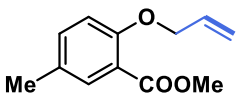
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.04 - 6.97 (m, 2H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.15 - 6.09 (m, 1H), 5.49 - 5.46 (m, 1H), 5.31 (dd, *J* = 10.9 Hz, 2.0 Hz, 1H), 4.57 - 4.55 (m, 2H), 2.31 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 154.8, 133.8, 131.4, 129.6, 126.6, 126.7, 116.7, 111.2, 68.9, 20.1, 16.2.

GC-MS: 162.

2-(Allyloxy)-5-methylbenzoate (**S10**)



S10

Known compound.

The title compound was prepared with 2-hydroxy-5-methylbenzoate (830.5 mg, 5.0 mmol, 1.0 equiv.), K_2CO_3 (2.07 g, 15.0 mmol, 3.0 equiv.) and allyl bromide (736.8 µL, 10.0 mmol, 2.0 equiv.) in CH_3CN (20 mL, c = 0.25 M). The mixture was refluxed (80 °C) for 12 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:30 - 1:80 (v:v)) to afford the title compound as a pale-yellow oil (927.2 mg, 90 %).

R_f = 0.55 (ethyl acetate: petroleum ether, 1:30 (v:v)).

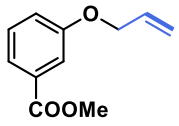
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.61 (s, 1H), 7.23 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.85 (d, 1H), 6.05 (ddt, *J* = 17.2, 10.5, 4.7 Hz, 1H), 5.50 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.29 (dd, *J* = 10.6, 1.2 Hz, 1H), 4.59 - 4.53 (m, 2H), 3.89 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 166.82, 157.78, 135.87, 132.91, 130.95, 127.32, 119.44, 116.37, 113.87, 70.98, 52.27, 22.11.

GC-MS: 206.

3-(Allyloxy)benzoate (**S11**)



S11

Known compound.

The title compound was prepared with 3-hydroxybenzoate (760.3 mg, 5.0 mmol, 1.0 equiv.), K_2CO_3 (2.07 g, 15.0 mmol, 3.0 equiv.) and allyl bromide (736.8 µL, 10.0 mmol, 2.0 equiv.) in CH_3CN (20 mL, c = 0.25 M). The mixture was refluxed (80 °C) for 12 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:30 - 1:80 (v:v)) to afford the title compound as a colorless oil (825.6 mg, 86 %).

R_f = 0.75 (ethyl acetate: petroleum ether, 1:10 (v:v)).

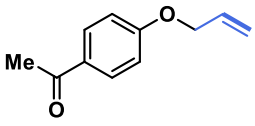
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.57 (s, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.11 (dd, *J* = 8.0, 2.7 Hz, 1H), 6.05 (ddt, *J* = 17.3, 10.5, 5.2 Hz, 1H), 5.42 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.29 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.57 (d, *J* = 5.2 Hz, 2H), 3.90 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 167.1, 158.6, 133.2, 131.5, 129.4, 122.3, 120.3, 118.0, 115.0, 69.1, 52.2.

GC-MS: 192.

1-(4-(Allyloxy)phenyl)ethanone (**S12**)



S12

Known compound.

The title compound was prepared with 4-hydroxyacetophenone (680.2 g, 5.0 mmol, 1.0 equiv.), K_2CO_3 (2.07 g, 15.0 mmol, 3.0 equiv.) and allyl bromide (736.8 µL, 10.0 mmol, 2.0 equiv.) in CH_3CN (20 mL, c = 0.25 M). The mixture was refluxed (80 °C) for 12 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:30 - 1:80 (v:v)) to afford the title compound as a pale-yellow oil (729.8 mg, 82 %).

R_f = 0.55 (ethyl acetate: petroleum ether, 1:30 (v:v)).

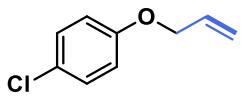
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.88 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 5.95 - 6.08 (m, 1H), 5.39 (dd, *J* = 16.4, 1.5 Hz, 1H), 5.29 (dd, *J* = 10.5 Hz, 1.3 Hz, 1H), 5.54 (td, *J* = 5.3 Hz, 1.5 Hz, 2H), 2.51 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 196.7, 162.3, 132.1, 130.4, 118.2, 114.2, 68.7, 26.1.

GC-MS: 176.

1-Chloro-4-(allyloxy)benzene (**S13**)



S13

Known compound.

The title compound was prepared with 4-chlorophenol (642.8 mg, 5.0 mmol, 1.0 equiv.), K_2CO_3 (2.07 g, 15.0 mmol, 3.0 equiv) and allyl bromide (736.8 µL, 10.0 mmol, 2.0 equiv.) in CH_3CN (20 mL, c = 0.25 M). The mixture was refluxed (80 °C) for 12 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:50 - 1:100 (v:v)) to afford the title compound as a colorless oil (812.0 mg, 97 %).

R_f = 0.60 (ethyl acetate: petroleum ether, 1:30 (v:v)).

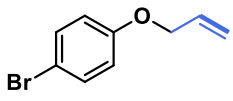
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.37 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 2H), 6.02 (ddt, *J* = 17.2, 10.1, 5.2 Hz, 1H), 5.42 (dd, *J* = 17.0, 1.4 Hz, 1H), 5.30 (dd, *J* = 10.2, 1.4 Hz, 1H), 4.50 (d, *J* = 5.2 Hz, 2 H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 157.3, 133.2, 132.7, 118.0, 116.8, 113.0, 68.8.

GC-MS: 168.

1-Bromo-4-(allyloxy)benzene (**S14**)



S14

Known compound.

The title compound was prepared with 4-bromophenol (859.8 mg, 5.0 mmol, 1.0 equiv.), K_2CO_3 (2.07 g, 15.0 mmol, 3.0 equiv) and allyl bromide (736.8 µL, 10.0 mmol, 2.0 equiv.) in CH_3CN (20 mL, c = 0.25 M). The mixture was refluxed (80 °C) for 12 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:50 - 1:100 (v:v)) to afford the title compound as a colorless oil (996.3 mg, 94 %).

R_f = 0.60 (ethyl acetate: petroleum ether, 1:30 (v:v)).

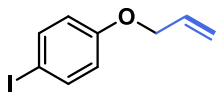
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.37 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 2H), 6.02 (ddt, *J* = 17.2, 10.1, 5.2 Hz, 1H), 5.42 (dd, *J* = 17.0, 1.4 Hz, 1H), 5.30 (dd, *J* = 10.2, 1.4 Hz, 1H), 4.50 (d, *J* = 5.2 Hz, 2 H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 157.3, 133.2, 132.7, 118.0, 116.8, 113.0, 68.8.

GC-MS: 212.

1-Iodo-4-(allyloxy)benzene (**S15**)



S15

Known compound.

The title compound was prepared with 4-iodophenol (1.10 g, 5.0 mmol, 1.0 equiv.), K_2CO_3 (2.07 g, 15.0 mmol, 3.0 equiv.) and allyl bromide (736.8 µL, 10.0 mmol, 2.0 equiv.) in CH_3CN (20 mL, c = 0.25 M). The mixture was refluxed (80 °C) for 12 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:50 - 1:100 (v:v)) to afford the title compound as a pale-yellow oil (1.196 g, 92 %).

R_f = 0.60 (ethyl acetate: petroleum ether, 1:30 (v:v)).

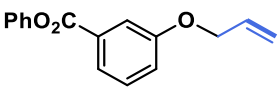
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.55 (d, *J* = 6.8 Hz, 2H), 6.69 (d, *J* = 6.8 Hz, 2H), 6.02 (ddt, *J* =17.8, 11.4, 5.8 Hz, 1H), 5.40 (dd, *J* = 17.3, 1.4 Hz, 1H), 5.28 (dd, *J* = 10.7, 1.4 Hz, 1H), 4.50 (d, *J* = 4.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 158.5, 138.2, 132.8, 118.0, 117.2, 82.9, 68.9.

GC-MS: 260.

3-(Allyloxy)phenyl benzoate (**S16**)



S16

The title compound was prepared with 3-(hydroxy)phenyl benzoate (1.07 g, 5.0 mmol, 1.0 equiv.), K_2CO_3 (2.07 g, 15.0 mmol, 3.0 equiv.) and allyl bromide (736.8 µL, 10.0 mmol, 2.0 equiv.) in CH_3CN (20 mL, c = 0.25 M). The mixture was refluxed (80 °C) for 12 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:30 - 1:80 (v:v)) to afford the title compound as a pale-yellow oil (1.03 g, 81 %).

R_f = 0.63 (ethyl acetate: petroleum ether, 1:10 (v:v)).

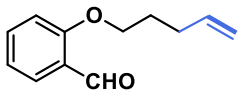
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.81 (ddd, *J* = 7.9, 2.5, 0.9 Hz, 1H), 7.54 (t, *J* = 2.2 Hz, 1H), 7.47 - 7.40 (m, 2H), 7.38 - 7.30 (m, 2H), 7.31 - 7.25 (m, 2H), 7.05 - 7.00 (m, 1H), 6.03 (dt, *J* = 11.4, 5.8 Hz, 1H), 5.39 - 5.31 (m, 2H), 4.51 (dt, *J* = 5.8, 1.0 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 164.25, 158.19, 148.72, 132.90, 130.75, 129.56, 127.52, 125.66, 124.44, 120.28, 119.72, 115.99, 114.61, 67.20.

GC-MS: 254.

2-(Pent-4-en-1-yloxy)benzaldehyde (**S17**)



S17

Known compound.

The title compound was prepared with 2-(hydroxy)benzaldehyde (610.2 mg, 5.0 mmol, 1.0 equiv.), K_2CO_3 (2.07 g, 15.0 mmol, 3.0 equiv.) and 5-bromopent-1-ene (1.18 mL, 10.0 mmol, 2.0 equiv.) in CH_3CN (20 mL, c = 0.25 M). The mixture was refluxed (80 °C) for 12 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:30 - 1:50 (v:v)) to afford the title compound as a pale-yellow oil (797.6 mg, 84 %).

R_f = 0.36 (ethyl acetate: petroleum ether, 1:10 (v:v)).

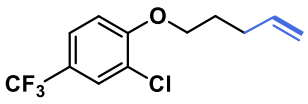
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 10.32 (s, 1H), 7.64 - 7.62 (m, 1H), 7.34 - 7.30 (t, *J* = 7.2 Hz, 1H), 6.81 - 6.76 (m, 2H), 5.70 - 5.60 (m, 1H), 4.89 - 4.81 (m, 2H), 3.85 - 3.82 (m, 2H), 2.08 (q, *J* = 6.8 Hz, 2H), 1.75 - 1.68 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 189.2, 161.2, 137.2, 135.7, 127.9, 124.7, 120.2, 115.2, 112.5, 67.5, 29.9, 28.0.

GC-MS: 190.

2-Chloro-4-trifluoromethyl-(allyloxy)benzene (**S18**)



S18

The title compound was prepared with 2-chloro-4-trifluoromethylphenol (980.3 mg, 5.0 mmol, 1.0 equiv), K_2CO_3 (2.07 g, 15.0 mmol, 3.0 equiv) and 5-bromopent-1-ene (1.18 mL, 10.0 mmol, 2.0 equiv.) in CH_3CN (20 mL, c = 0.25 M). The mixture was refluxed (80 °C) for 12 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:50 - 1:100 (v:v)) to afford the title compound as a colorless oil (1.02 g, 77 %).

R_f = 0.67 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

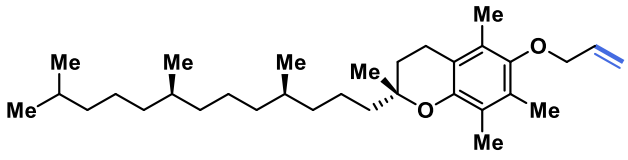
^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.62 (d, *J* = 2.3 Hz, 1H), 7.45 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.95 (d, *J* = 8.6 Hz, 1H), 5.85 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.12 - 4.97 (m, 2H), 4.07 (t, *J* = 6.4 Hz, 2H), 2.29 (q, *J* = 7.9, 7.5 Hz, 2H), 1.96 (dt, *J* = 13.3, 6.6 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 157.14, 137.45, 127.53, 125.10, 123.39, 115.67, 112.63, 68.48, 29.98, 28.11.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -61.61 (s, 3F).

GC-MS: 264.

D-α-tocopherol allyl ether (**S19**)



S19

Known compound.

The title compound was prepared with D-α-Tocopherol (2.15 g, 5.0 mmol, 1.0 equiv.), K_2CO_3 (2.07 g, 15.0 mmol, 3.0 equiv.) and allyl bromide (736.8 µL, 10.0 mmol, 2.0 equiv.) in CH_3CN (20 mL, c = 0.25 M). The mixture was refluxed (80 °C) for 12 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:20 - 1:50 (v:v)) to afford the title compound as a colorless oil (1.62 g, 69 %).

R_f = 0.34 (ethyl acetate: petroleum ether, 1:10 (v:v)).

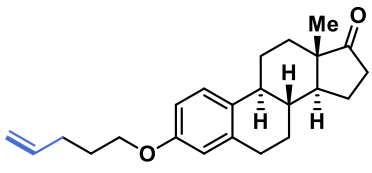
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 6.13 (ddt, *J* = 17.3, 10.8, 5.5 Hz, 1H), 5.45 (dd, *J* = 17.3, 1.6 Hz, 1H), 5.26 (dd, *J* = 10.7, 1.6 Hz, 1H), 4.20 (d, *J* = 5.5 Hz, 2H), 2.59 (t, *J* = 6.8 Hz, 2H), 2.19 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H), 1.88 - 1.72 (m, 2H), 1.61 - 1.50 (m, 3H), 1.48 - 1.36 (m, 4H), 1.32 - 1.22 (m, 10H), 1.18 - 1.04 (m, 6H), 0.91 - 0.83 (m, 13H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 148.4, 147.9, 134.6, 128.1, 126.0, 123.0, 117.6, 116.8, 74.9, 73.9, 40.2, 39.6, 37.7, 37.6, 37.4, 32.8, 32.8, 31.4, 28.1, 25.0, 24.7, 24.0, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 19.8, 13.0, 12.1, 12.0.

GC-MS: 470.

(*8R,9S,13S,14S*)-13-methyl-3-(allyloxy)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14*H*)-one (**S20**)



S20

Known compound.

The title compound was prepared with estrone (1.35 g, 5.0 mmol, 1.0 equiv.), K_2CO_3 (2.07 g, 15.0 mmol, 3.0 equiv.) and 5-bromopent-1-ene (1.18 mL, 10.0 mmol, 2.0 equiv.) in CH_3CN (20 mL, c = 0.25 M). The mixture was refluxed (80 °C) for 12 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:20 - 1:50 (v:v)) to afford the title compound as a white solid (1.22 g, 78 %).

R_f = 0.67 (ethyl acetate: petroleum ether, 1:5 (v:v)).

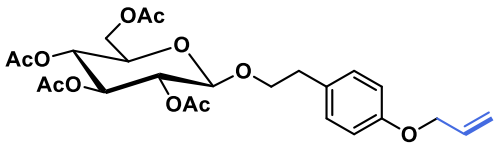
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.19 (d, *J* = 8.7 Hz, 1H), 6.71 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.64 (d, *J* = 2.5 Hz, 1H), 6.01 - 6.10 (m, 1H), 5.39 (d, *J* = 17.0 Hz, 1H), 5.26 (d, *J* = 10.3 Hz, 1H), 4.50 (d, *J* = 5.5 Hz, 2H), 3.72 (t, *J* = 8.3 Hz, 1H), 2.87 - 2.82 (m, 2H), 1.14-2.31 (m, 14H) 0.77 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 156.5, 137.9, 133.5, 132.8, 126.2, 117.4, 114.6, 112.0, 81.8, 68.7, 50.1, 43.9, 43.3, 38.8, 36.6, 30.5, 29.7, 27.0, 26.2, 23.1, 11.0.

GC-MS: 310.

2-(4-allyloxyphenyl)ethyl β-D-glucopyranoside tetraacetate (**S21**)



S21

The title compound was prepared with tetraacetyl salidroside (2.34 g, 5.0 mmol, 1.0 equiv.), K_2CO_3 (2.07 g, 15.0 mmol, 3.0 equiv.) and allyl bromide (736.8 µL, 10.0 mmol, 2.0 equiv.) in CH_3CN (20 mL, c = 0.25 M). The mixture was refluxed (80 °C) for 12 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:10 - 1:30 (v:v)) to afford the title compound as a colorless oil (1.07 g, 42 %).

R_f = 0.36 (ethyl acetate: petroleum ether, 1:2 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.10 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 2H), 6.07 - 6.01 (m, 1H), 5.40 (dt, *J* = 10.3, 8.2 Hz, 1H), 5.41 - 5.35 (m, 1H), 5.27 (dt, *J* = 10.3 Hz, 1.4 Hz, 1H), 5.21 (dd, *J* = 10.3 Hz, 8.2 Hz, 1H), 4.98 (dd, *J* = 9.6 Hz, 2.5 Hz, 1H), 4.50 (dd, *J* = 5.5 Hz, 1.4 Hz, 2H), 4.44 (d, *J* = 7.5 Hz, 1H), 4.18 (dd, *J* = 11.0 Hz, 6.2 Hz, 1H), 4.15 - 4.04

(m, 2H), 3.63 (dd, *J* = 15.8 Hz, 7.5 Hz, 1H), 3.39 (t, *J* = 6.9 Hz, 1H), 2.86 - 2.82 (m, 2H), 2.15 (s, 3H), 2.05 (s, 3H), 1.98 (s, 3H), 1.92 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 170.4 - 169.3, 157.2, 133.4, 130.7, 129.8, 117.6, 114.7, 101.3, 70.9, 70.7, 68.5, 68.7, 67.1, 61.3, 35.1, 20.8, 20.6.

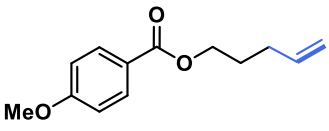
GC-MS: 508.

General procedure for preparation of other terminal alkenes

Scheme S14. Synthesis of pent-4-en-1-yl benzoates.[6]

Under ambient atmosphere, to a 0 °C solution of pent-en-1-ol (371.2 µL, 3.6 mmol, 1.2 equiv.), DMAP (5.00 mg, 0.0409 mmol), Et_3N (625.5 µL, 4.5 mmol, 1.5 equiv.) in 6.0 mL of CH_2Cl_2 was added acid chloride (3.0 mmol, 1.0 equiv.). The resulting mixture was warmed to room temperature and was stirred for 3 h. After this, the reaction mixture was diluted with saturated $NaHCO_3$ solution (5 mL) and stirred for an additional 10 min. The phases were separated and the organic layer was washed with saturated $NaHCO_3$ solution (3×10 mL) and brine solution (10 mL). The organic layer was dried (Na_2SO_4) and concentrated to give a crude residue that was purified by flash column chromatography (silica gel, ethyl acetate: petroleum ether, 1:50 to 1:100 (v:v)) to afford the title compound which was characterized by GC-MS analysis, ^{1}H NMR and ^{13}C NMR spectroscopy.

Pent-4-en-1-yl 4-methoxybenzoate (**S22**)



S22

Known compound.

The title compound was prepared with 4-methoxy-benzoylchlorid (406.2 µL, 3.0 mmol, 1.0 equiv.), Et_3N (625.5 µL, 4.5 mmol, 1.5 equiv.), DMAP (5.0 mg, 0.0409 mmol) and pent-en-1-ol (371.2 µL, 3.6 mmol, 1.2 equiv.), in DCM (6.0 mL, c = 0.50 M). The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:50 - 1:100 (v:v)) to afford the title compound as a colorless oil (600.6 mg, 91 %).

R_f = 0.41 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

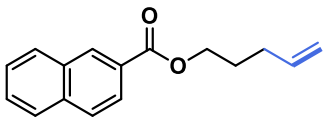
^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.05 (d, *J* = 9.7, 2H), 6.98 (d, *J* = 9.8, 2H), 5.89 (ddd, *J* = 18.1, 10.1, 8.3, 1H), 5.14 (d, *J* = 18.1, 1H), 5.05 (d, *J* = 10.0, 1H), 4.36 (t, *J* = 6.7,

2H), 3.91 (s, 3H), 2.27 (q, *J* = 7.1, 2H), 1.92 (q, *J* = 7.0, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 166.5, 163.3, 137.6, 131.5, 122.8, 115.4, 113.7, 64.1, 55.5, 30.3, 28.0.

GC-MS: 220.

Pent-4-en-1-yl 2-naphthoate (**S23**)



S23

Known compound.

The title compound was prepared with 2-naphthoic acid (571.8 mg, 3.0 mmol, 1.0 equiv.), Et_3N (625.5 µL, 4.5 mmol, 1.5 equiv.), DMAP (5.0 mg, 0.0409 mmol) and pent-en-1-ol (371.2 µL, 3.6 mmol, 1.2 equiv.) in DCM (6.0 mL, c = 0.50 M). The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:50 - 1:100 (v:v)) to afford the title compound as a colorless oil (626.4 mg, 87 %).

R_f = 0.54 (ethyl acetate: petroleum ether, 1:20 (v:v)).

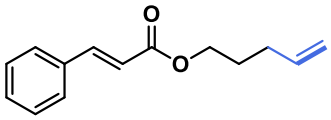
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.64 (s, 1H), 8.10 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.89 - 7.83 (m, 2H), 7.59 - 7.51 (m, 2H), 5.96 - 5.84 (m, 1H), 5.17 - 5.03 (m, 2H), 4.41 (t, *J* = 6.5 Hz, 2H), 2.27 (q, *J* = 7.6 Hz, 2H), 1.88 - 1.97 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 166.5, 137.4, 135.3, 132.3, 130.8, 129.2, 128.0, 127.9, 127.6, 127.5, 126.4, 125.0, 115.2, 64.3, 30.0, 27.8.

GC-MS: 240.

Pent-4-en-1-yl cinnamate (**S24**)



S24

The title compound was prepared with cinnamoyl chloride (499.8 mg, 3.0 mmol, 1.0 equiv.), Et_3N (625.5 µL, 4.5 mmol, 1.5 equiv.), DMAP (5.0 mg, 0.0409 mmol) and pent-en-1-ol (371.2 µL, 3.6 mmol, 1.2 equiv.) in DCM (6.0 mL, c = 0.50 M). The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:50 - 1:100 (v:v)) to afford the title compound as a colorless oil (570.2 mg, 88 %).

R_f = 0.58 (ethyl acetate: petroleum ether, 1:20 (v:v)).

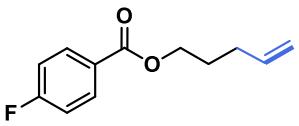
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.52 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.43 - 7.35 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 5.83 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.10 - 4.97 (m, 2H), 4.21 (t, *J* = 6.6 Hz, 2H), 2.18 (q, *J* = 7.2, 6.7 Hz, 2H), 1.81 (p, *J* = 6.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 167.13, 144.77, 137.61, 134.54, 130.35, 128.98, 128.16, 118.27, 115.42, 64.06, 30.19, 28.00.

GC-MS: 216.

Pent-4-en-1-yl 4-flurobenzoate (**S25**)



S25

Known compound.

The title compound was prepared with 4-fluro-benzoylchlorid (354.5 µL, 3.0 mmol, 1.0 equiv.), Et_3N (625.5 µL, 4.5 mmol, 1.5 equiv.), DMAP (5.0 mg, 0.0409 mmol) and pent-en-1-ol (371.2 µL, 3.6 mmol, 1.2 equiv.) in DCM (6.0 mL, c = 0.50 M). The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:50 - 1:100 (v:v)) to afford the title compound as a yellow oil (580.3 mg, 93 %).

R_f = 0.61 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

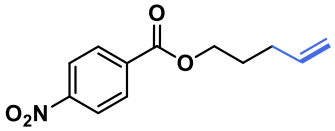
^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.10 - 7.99 (m, 2H), 7.15 - 7.04 (m, 2H), 5.84 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.05 (ddd, *J* = 17.1, 3.1, 1.6 Hz, 1H), 5.03 - 4.97 (m, 1H), 4.32 (t, *J* = 6.6 Hz, 2H), 2.25 - 2.16 (m, 2 H), 1.92 - 1.79 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 167.1, 165.1 (d, *J* = 117.2 Hz), 137.5, 132.1 (d, *J* = 9.3 Hz), 126.7 (d, *J* = 3.0 Hz), 115.7, 115.5 (d, *J* = 5.3 Hz), 64.6, 30.4, 28.0.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -106.01.

GC-MS: 208.

Pent-4-en-1-yl 4-nitrobenzoate (**S26**)



S26

Known compound.

The title compound was prepared with 4-nitro-benzoylchlorid (556.8 mg, 3.0 mmol, 1.0 equiv.), Et_3N (625.5 µL, 4.5 mmol, 1.5 equiv.), DMAP (5.0 mg, 0.0409 mmol) and pent-en-1-ol (371.2 µL, 3.6 mmol, 1.2 equiv.) in DCM (6.0 mL, c = 0.50 M). The crude product was purified by chromatography

(silica gel, ethyl acetate: petroleum ether, 1:50 - 1:80 (v:v)) to afford the title compound as a pale yellow solid (549.9 mg, 78 %).

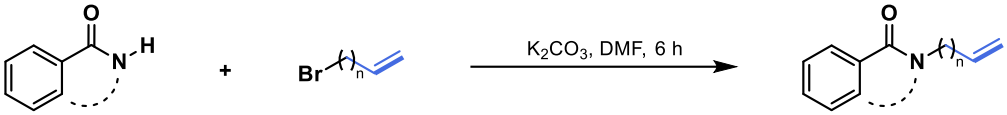
R_f = 0.38 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.30 (d, *J* = 9.2 Hz, 2H), 8.21 (d, *J* = 8.8 Hz, 2H), 5.91 - 5.81 (m, 1H), 5.12 - 5.03 (m, 2H), 4.41 (t, *J* = 6.7 Hz, 2H), 2.27 - 2.20 (m, 2H), 1.96 - 1.89 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 164.6, 150.4, 137.0, 135.7, 130.6, 123.5, 115.6, 65.3, 30.0, 27.8.

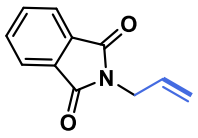
GC-MS: 235.



Scheme S15. Synthesis of benzamide.[7]

A reaction flask was charged with amide (5.0 mmol, 1.0 equiv.), 3-bromoprop-1-ene or 5-bromopent-1-ene (7.5 mmol, 1.5 equiv.), K_2CO_3 (1.04 g, 7.5 mmol, 1.5 equiv.), and DMF (20 mL, c = 0.25 M). The reaction mixture was allowed to stir at room temperature. After 6 h the reaction was completed, the reaction mixture was slowly poured into water (50 mL). The aqueous phase was extracted with CH_2Cl_2 (5 × 10 mL). The organic extracts were combined, washed with water (3 × 20 mL), and dried over Na_2SO_4. After filtration, the solution was evaporated under reduced pressure to give a crude residue that was purified by flash column chromatography (silica gel, ethyl acetate: petroleum ether, 1:10 to 1:50 (v:v)) to afford the title compound which was characterized by GC-MS analysis, ^{1}H NMR and ^{13}C NMR spectroscopy.

N-Allyl phthalimide (**S27**)



S27

Known compound.

The title compound was prepared with phthalimide (735.5 mg, 5.0 mmol, 1.0 equiv.), 3-bromoprop-1-ene (649.1 µL, 7.5 mmol, 1.5 equiv.) and K_2CO_3 (1.04 g, 7.5 mmol, 1.5 equiv.) in DMF (20 mL, c = 0.25 M). The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:10 - 1:30 (v:v)) to afford the title compound as a white solid (617.1 mg, 66 %).

R_f = 0.37 (ethyl acetate: petroleum ether, 1:2 (v:v)).

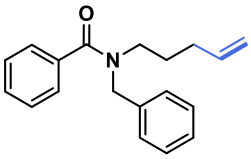
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.87-7.85 (m, 2H), 7.73 - 7.71 (m, 2H), 5.94 - 5.84 (m, 1H), 5.28 - 5.18 (m, 2H), 4.30 (dt, *J* = 6.0 Hz, 1.2 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 167.45, 134.43, 132.39, 131.54, 123.07, 116.31.

GC-MS: 187.

N-Pent-4-en-1-yl-*N*-benzylbenzamide (**S28**)



S28

The title compound was prepared with *N*-benzylbenzamide (1.06 g, 5.0 mmol, 1.0 equiv.), 5-bromopent-1-ene (888.3 μL, 7.5 mmol, 1.5 equiv.) and K_2CO_3 (1.04 g, 7.5 mmol, 1.5 equiv.) in DMF (20 mL, c = 0.25 M). The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:10 - 1:50 (v:v)) to afford the title compound as a colorless oil (753.3 mg, 54 %).

R_f = 0.46 (ethyl acetate: petroleum ether, 1:3 (v:v)).

NMR Spectroscopy:

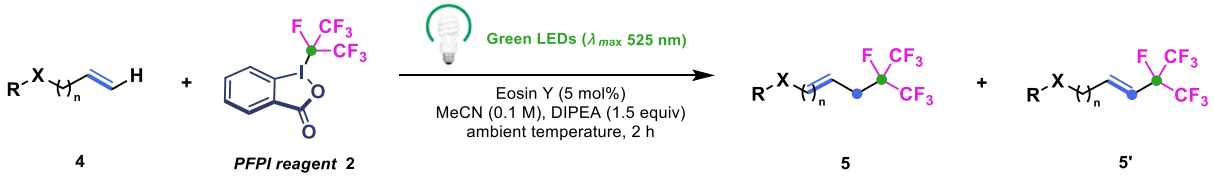
^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.44 - 7.12 (m, 10H), 5.91 - 5.40 (m, 1H), 5.07 - 4.81 (m, 2H), 4.82 - 4.44 (m, 2H), 3.56 - 3.05 (m, 2H), 2.20 - 1.43 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 172.15, 137.09, 136.78, 129.49, 128.83, 128.57, 128.17, 127.60, 126.93, 126.67, 115.19, 52.74, 44.46, 31.22, 27.43.

GC-MS: 279.

Substrate Scope

General procedure to access isoperfluoropropylated products.



Scheme S16. General procedure to access isoperfluoropropylated products.

Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, alkenes (**4**, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) were dissolved in dry MeCN (2.0 mL, 0.1 M). Subsequently, DIPEA (52.2 μL, 0.3 mmol, 1.5 equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at green light (525 nm) for 2 h, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, the reaction was quenched with 10 mL 5% $NaHCO_3$ aqueous

solution, then extracted with DCM (3 x 10 mL). The combined organic phase was dried with anhydrous Na_2SO_4 and concentrated under vacuum. The residue was further purified by column chromatography to afford corresponding isoperfluoropropylated products, which was characterized by GC-MS analysis, ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectroscopy. The 5/5' ratio and *Z/E* ratio was determined by ^{19}F NMR or GC-MS.

Figure S1-1. Fully assembled 525 nm photoreactor.

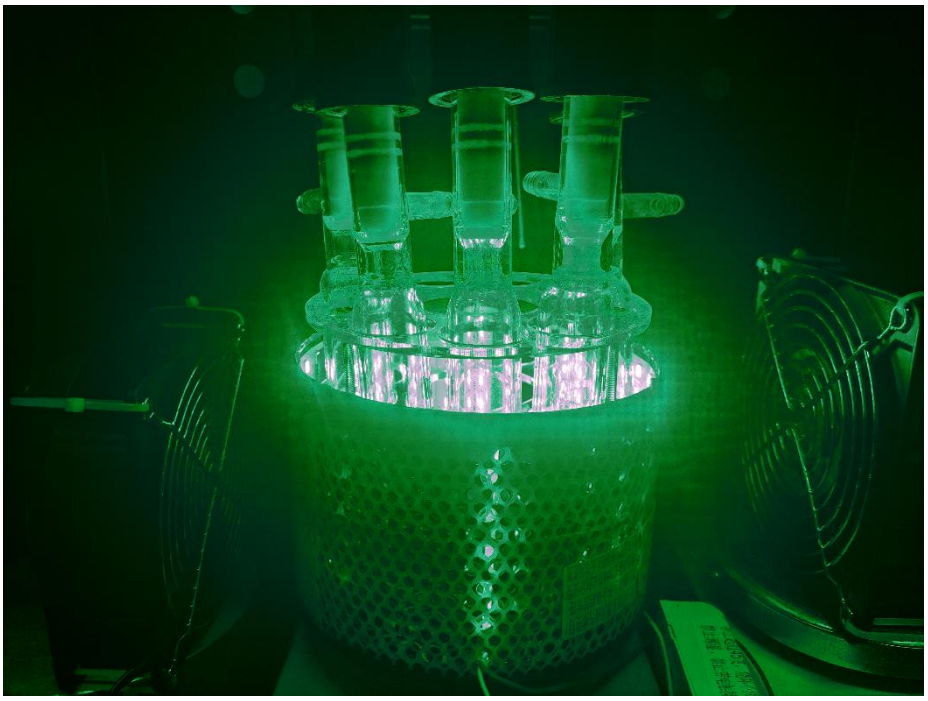
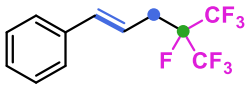


Figure S1-2. Fully assembled 525 nm photoreactor in operation.

Characterization of Products

(*E*)-(4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)benzene (**3**)



3

Known compound.

The title compound was prepared with allyl benzene (23.6 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (47.5 mg, 83 %, **3:3'** > 99:1, *E/Z* = 98:2).

R_f = 0.77 (ethyl acetate: petroleum ether, 1:50 (v:v)).

NMR Spectroscopy:

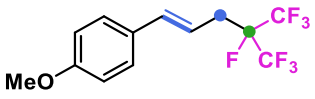
^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.42 - 7.27 (m, 5H), 6.62 (d, *J* = 15.7 Hz, 1H), 6.21 - 6.08 (m, 1 H), 3.04 (dd, *J* = 20.0, 7.5 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 136.70, 136.34, 128.75, 128.24, 126.56, 121.09 (qd, *J* = 285.9, 27.3 Hz, CF($\underline{C}F_3$)$_2$), 117.12 (d, *J* = 6.2 Hz), 93.15 - 89.94 (m, $\underline{C}F(CF_3)_2$), 32.90 (d, *J* = 21.1 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.95 (d, *J* = 7.1 Hz, CF($C\underline{F}_3$)$_2$, 6F), -181.74 – -182.23 (m, $C\underline{F}(CF_3)_2$, 1F).

GC-MS: 286

(*E*)-1-methoxy-4-(4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)benzene (**6**)



6

Known compound.

The title compound was prepared with 1-allyl-4-methoxybenzene (29.6 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (55.6 mg, 88 %, **6:6'** > 99:1, *E/Z* = 96:4).

R_f = 0.65 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

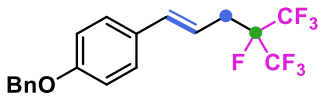
^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.32 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 5.7 Hz, 2H), 6.54 (d, *J* = 15.8 Hz, 1H), 5.97 (dt, *J* = 15.1, 7.0 Hz, 1H), 3.81 (s, 3H), 3.00 (dd, *J* = 20.0, 6.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 159.73, 136.08, 129.14, 127.77, 121.06 (qd, *J* = 285.2 Hz, 28.1 Hz, CF(*C*F_3)$_2$), 114.76 (d, *J* = 5.9 Hz), 114.14, 93.13 - 89.92 (m, *C*F(CF_3)$_2$), 55.33, 32.92 (d, *J* = 20.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.87 (d, *J* = 7.0 Hz, CF(C*F*$_3$)$_2$, 6F), -181.92 (th, *J* = 21.1, 7.1 Hz, C*F*(CF_3)$_2$, 1F).

GC-MS: 316

(*E*)-1-benzyloxy-4-(4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)benzene (**7**)



7

The title compound was prepared with 1-allyl-4-benzyloxy-benzene (44.8 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a yellow oil (65.9 mg, 84 %, **7:7'** > 99:1, *E/Z* = 96:4).

R_f = 0.59 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.44 - 7.35 (m, 4H), 7.35 - 7.26 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 15.7 Hz, 1H), 5.96 (dt, *J* = 14.6, 7.6 Hz, 1H), 5.06 (s, 2H), 2.98 (dd, *J* = 20.0, 7.5 Hz, 2H).

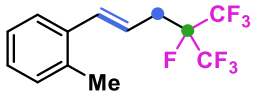
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 158.89, 136.91, 136.05, 129.36, 128.70, 128.11, 127.79, 127.53, 121.02 (qd, *J* = 286.5 Hz, 28.5 Hz, CF(*C*F_3)$_2$), 115.09, 114.88 (d, *J* = 5.1 Hz), 92.99 - 89.53 (m, *C*F(CF_3)$_2$), 70.11, 32.91 (d, *J* = 21.0 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.83 (d, *J* = 7.4 Hz, CF(C*F*$_3$)$_2$, 6F), -181.87 (th, *J* = 21.1, 7.0 Hz, C*F*(CF_3)$_2$, 1F).

GC-MS: 392

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{19}H_{16}F_7O^+$: 393.1084. Found: 393.1089.

(*E*)-2-methyl-(4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)benzene (**8**)



8

The title compound was prepared with 1-allyl-2-methylbenzene (26.4 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (46.2 mg, 77 %, **8:8'** = 97:3, *E/Z* > 99:1).

R_f = 0.57 (ethyl acetate: petroleum ether, 1:50 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.23 - 7.14 (m, 4H), 6.83 (d, *J* = 15.7 Hz, 1H), 5.99 (dt, *J* = 15.9, 7.5 Hz, 1H), 3.06 (dd, *J* = 19.9, 7.5 Hz, 2H), 2.35 (s, 3H).

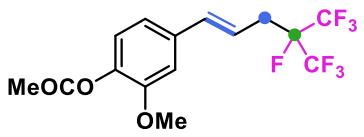
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 135.69, 135.56, 134.95, 130.38, 128.12, 126.30, 126.09, 121.05 (qd, *J* = 285.9 Hz, 27.3 Hz, CF($\underline{C}F_3$)$_2$), 118.64 (d, *J* = 5.9 Hz), 92.88 - 89.90 (m, $\underline{C}F(CF_3)_2$), 33.14 (d, *J* = 21.0 Hz), 19.70.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.79 (d, *J* = 7.1 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -181.74 (th, *J* = 21.1, 7.0 Hz, C$\underline{F}$(CF$_3$)$_2$, 1F).

GC-MS: 300

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{13}H_{12}F_7^+$: 301.0822. Found: 301.0814.

(*E*)-1-acetoxy-2-methoxy-4-(4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)benzene (**9**)



9

The title compound was prepared with eugenol acetate (41.2 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (54.6 mg, 73 %, **9:9'** > 99:1, *E/Z* = 97:3).

R_f = 0.41 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.04 - 6.92 (m, 3H), 6.55 (d, *J* = 15.7 Hz, 1H), 6.12 - 6.00 (m, 1H), 3.84 (s, 3H), 3.00 (dd, *J* = 20.0, 7.5 Hz, 2H), 2.31 (s, 3H).

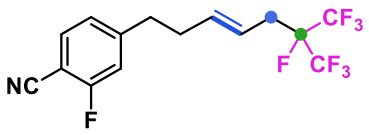
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 169.07, 151.32, 139.83, 136.10, 135.34, 123.03, 121.01 (qd, *J* = 287.4 Hz, 28.3 Hz, CF($\underline{C}F_3$)$_2$), 119.16, 117.40 (d, J = 6.0 Hz), 110.31, 93.43 - 89.48 (m, $\underline{C}F(CF_3)_2$), 55.83, 32.76 (d, J = 21.0 Hz), 20.59.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.94 (d, *J* = 7.1 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -181.92 – -182.08 (th, *J* = 21.0, 7.3 Hz, C$\underline{F}$(CF$_3$)$_2$, 1F).

GC-MS: 374

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{15}H_{14}F_7O_3^+$: 375.0826. Found: 375.0822.

(*E*)-2-fluro-4-(6,7,7,7-tetrafluoro-6-(trifluoromethyl)hept-3-en-1-yl)benzonitrile (**10**)



10

The title compound was prepared with 2-fluro-4-pentenylbenzonitrile (37.8 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (55.7 mg, 78 %, **10:10'** > 99:1, *E/Z* = 95:5).

R_f = 0.66 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.61 - 7.44 (m, 3H), 5.97 - 5.73 (m, 1H), 5.70 - 5.47 (m, 1H), 4.21 (td, *J* = 6.7, 1.9 Hz, 2H), 2.74 (dd, *J* = 19.7, 7.2 Hz, 2H), 2.48 (q, *J* = 6.8 Hz, 2H).

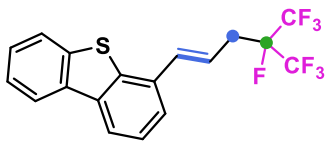
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 165.77 (d, *J* = 230.3 Hz), 145.15 (d, *J* = 6.1 Hz), 133.52, 130.32 (d, *J* = 9.2 Hz), 126.11 (d, *J* = 2.9 Hz), 120.94 (qd, *J* = 285.5 Hz, 27.3 Hz, CF(*C*F_3)$_2$), 120.62 (d, *J* = 6.0 Hz), 119.65, 115.53 (d, *J* = 21.9 Hz), 113.80, 92.66 – 89.61 (m, *C*F(CF_3)$_2$), 40.67, 33.69 (d, *J* = 22.9 Hz), 32.02.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.97 (d, *J* = 6.7 Hz, CF(C*F*$_3$)$_2$, 6F), -105.71 (tt, *J* = 9.4, 4.8 Hz), -182.21 (tp, *J* = 20.8, 7.0 Hz, C*F*(CF_3)$_2$, 1F).

GC-MS: 357

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{15}H_{12}F_8N^+$: 358.0837. Found: 358.0835.

(*E*)-4-(4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)dibenzothiophene (**11**)



11

The title compound was prepared with 4-allyldibenzothiophene (44.8 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (51.0 mg, 65 %, **11:11'** = 97:3, *E/Z* > 99:1).

R_f = 0.54 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.18 - 8.11 (m, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 7.92 - 7.84 (m, 1H), 7.53 - 7.39 (m, 4H), 6.87 (d, *J* = 15.7 Hz, 1H), 6.38 (dt, *J* = 15.3, 7.4 Hz, 1H), 3.14 (dd, *J* = 19.8, 7.4 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 139.08, 137.82, 136.43, 135.57, 134.64, 131.28,

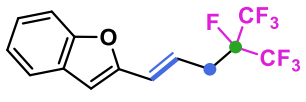
127.07, 125.01, 124.93, 124.70, 122.83, 121.81, 121.25, 121.05 (qd, *J* = 285.9 Hz, 28.3 Hz, CF(*C*F_3)$_2$), 120.13 (d, *J* = 5.9 Hz), 93.14 - 89.82 (m, *C*F(CF_3)$_2$), 33.22 (d, *J* = 20.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.69 (d, *J* = 7.1 Hz, CF(C*F*$_3$)$_2$, 6F), -181.78 (tp, *J* = 20.8, 7.1 Hz, C*F*(CF_3)$_2$, 1F).

GC-MS: 392

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{18}H_{12}F_7S^+$: 393.0542. Found: 393.0550.

(*E*)-2-(4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)benzofuran (**12**)



12

The title compound was prepared with 2-allylbenzofuran (31.6 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (36.5 mg, 56 %, **12:12'** = 97:3, *E*/*Z* > 99:1).

R_f = 0.38 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.65 (dd, *J* = 7.7, 5.9 Hz), 7.55 (d, *J* = 7.7 Hz), 7.48 (d, *J* = 8.3 Hz), 7.04, 6.50 (d, *J* = 15.7 Hz), 5.86 (dt, *J* = 15.7, 7.6 Hz), 2.98 (dd, *J* = 19.9, 7.5 Hz).

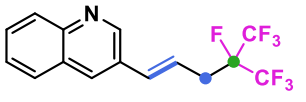
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 154.71, 152.78, 130.38, 129.58, 127.57, 127.28, 121.58 (d, *J* = 12.4 Hz), 121.05 (qd, *J* = 285.5 Hz, 27.3 Hz, CF(*C*F_3)$_2$), 118.64 (d, *J* = 5.9 Hz), 116.26, 108.41, 93.05 - 89.73 (m, *C*F(CF_3)$_2$), 34.52 (d, *J* = 20.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.85 (d, *J* = 6.7 Hz, CF(C*F*$_3$)$_2$, 6F), -181.86 (tp, *J* = 20.7, 6.9 Hz, C*F*(CF_3)$_2$, 1F).

GC-MS: 326

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{14}H_{10}F_7O^+$: 327.0614. Found: 327.0606.

(*E*)-3-(4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)quinoline (**13**)



13

The title compound was prepared with 3-allylquinoline (33.8 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (53.9 mg, 80 %, **13:13'** > 99:1, *E*/*Z* > 99:1).

R_f = 0.38 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.71 (s, 1H), 8.32 (s, 1H), 8.00 (d, *J* = 8.9 Hz, 2H), 7.67 - 7.49 (m, 2H), 6.60 (d, *J* = 15.7 Hz, 1H), 6.08 (dt, *J* = 15.7, 7.5 Hz, 1H), 3.02 (dd, *J* = 19.9, 7.3 Hz, 2H).

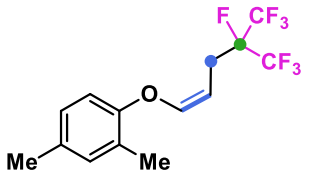
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 149.24, 146.05, 136.10, 135.34, 132.36, 131.17 (d, *J* = 5.9 Hz), 129.01, 127.16, 126.87, 123.03, 121.02 (qd, *J* = 286.4 Hz, 27.8 Hz, CF($\underline{C}F_3$)$_2$), 119.16, 93.12 - 89.63 (m, $\underline{C}F(CF_3)_2$), 34.89 (d, *J* = 20.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.90 (d, *J* = 7.6 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -184.04 (ddq, *J* = 24.5, 16.2, 7.9 Hz, C$\underline{F}(CF_3)_2$, 1F).

GC-MS: 337

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{15}H_{11}F_7N^+$: 338.0774. Found: 338.0773.

(*Z*)-2,4-dimethyl-((4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)oxy)benzene (**14**)



14

The title compound was prepared with 2,4-dimethyl(allyloxy)benzene (32.4 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (64.0 mg, 97 %, **14:14'** > 99:1, *Z/E* = 96:4).

R_f = 0.59 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.09 (d, *J* = 8.3 Hz, 1H), 6.82 (d, *J* = 2.9 Hz, 1H), 6.75 (dd, *J* = 8.2, 2.9 Hz, 1H), 6.58 (d, *J* = 6.2 Hz, 1H), 4.79 (q, *J* = 7.1, 6.6 Hz, 1H), 3.11 (dd, *J* = 19.8, 7.5 Hz, 2H), 2.27 (s, 3H), 2.24 (s, 3H).

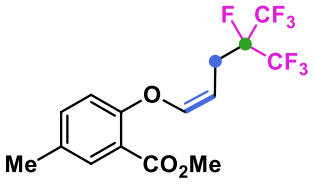
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 155.19, 145.52, 138.28, 131.69, 130.60, 121.12 (qd, *J* = 285.9 Hz, 27.3 Hz, CF($\underline{C}F_3$)$_2$), 118.13, 113.81, 98.30 (d, *J* = 6.7 Hz), 93.02 – 89.58 (m, $\underline{C}F(CF_3)_2$), 24.11 (d, *J* = 20.8 Hz), 19.94, 18.97.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.21 (d, *J* = 7.3 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -182.22 (th, *J* = 20.9, 7.3 Hz, C$\underline{F}(CF_3)_2$, 1F).

GC-MS: 330

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{14}H_{14}F_7O^+$: 331.0927. Found: 331.0924.

(*Z*)-2-((4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)oxy)-5-methylbenzoate (**15**)



15

The title compound was prepared with 2-(allyloxy)-5-methylbenzoate (41.2 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (65.8 mg, 88 %, **15:15'** > 99:1, *Z/E* > 99:1).

R_f = 0.44 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.77 (d, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.80, 6.56 (d, *J* = 6.0 Hz, 1H), 4.86 (q, *J* = 7.7 Hz, 1H), 3.86 (s, 3H), 3.13 (dd, *J* = 20.0, 8.0 Hz, 2H), 2.37 (s, 3H).

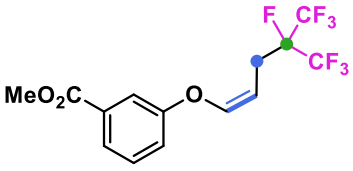
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 166.28, 156.15, 144.91, 132.13, 129.89, 124.19, 121.07 (qd, *J* = 284.0 Hz, 27.8 Hz, CF($\underline{C}F_3$)$_2$), 118.62, 117.81, 99.67 (d, *J* = 7.0 Hz), 93.11 – 89.60 (m, $\underline{C}F(CF_3)_2$), 52.04, 24.15 (d, *J* = 21.5 Hz), 21.66.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.18 (d, *J* = 6.8 Hz, CF($C\underline{F}_3$)$_2$, 6F), -182.40 (th, *J* = 21.4, 7.2 Hz, $C\underline{F}(CF_3)_2$, 1F).

GC-MS: 374

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{15}H_{14}F_7O_3^+$: 375.0826. Found: 375.0827.

(*Z*)-3-((4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)oxy)-benzoate (**16**)



16

The title compound was prepared with 3-(allyloxy)-benzoate (38.4 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (66.2 mg, 92 %, **16:16'** > 99:1, *Z/E* = 95:5).

R_f = 0.47 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.76 (d, *J* = 7.8 Hz, 1H), 7.64 (s, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 6.62 (d, *J* = 6.2 Hz, 1H), 4.89 (q, *J* = 7.2 Hz, 1H), 3.91 (s, 3H), 3.08 (dd, *J* = 19.6, 7.6 Hz, 2H).

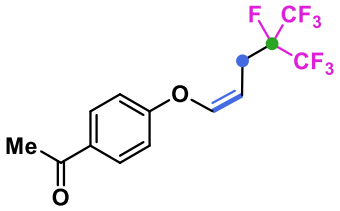
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 166.47, 156.83, 144.43, 131.95, 129.87, 124.63, 121.39, 121.02 (qd, *J* = 285.9 Hz, 27.3 Hz, CF(<u>*C*</u>F_3)$_2$), 117.26, 100.13 (d, *J* = 6.7 Hz), 92.97 – 89.60 (m), 52.39, 24.10 (d, *J* = 21.4 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.23 (d, *J* = 7.1 Hz, CF(C<u>*F*</u>$_3$)$_2$, 6F), -182.34 (th, *J* = 20.9, 7.0 Hz, C<u>*F*</u>(CF$_3$)$_2$, 1F).

GC-MS: 360

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{14}H_{12}F_7O_3^+$: 361.0669. Found: 361.0674.

(*Z*)-1-(4-((4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)oxy)phenyl)ethanone (**17**)



17

The title compound was prepared with 1-(4-(allyloxy)phenyl)ethanone (35.2 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a pale yellow oil (62.5 mg, 91 %, **17:17'** > 99:1, *Z/E* = 98:2).

R_f = 0.63 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.93 (d, *J* = 7.5 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 2H), 6.63 (d, *J* = 6.1 Hz, 1H), 4.94 (q, *J* = 7.4, 7.0 Hz, 1H), 3.06 (dd, *J* = 19.3, 7.3 Hz, 2H), 2.53 (s, 3H).

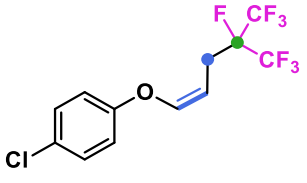
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 196.65, 160.27, 143.58, 130.69, 120.97 (qd, *J* = 285.1 Hz, 27.8 Hz, CF(<u>*C*</u>F_3)$_2$), 116.04, 114.43, 101.25 (d, J = 6.7 Hz), 92.79 – 89.62 (m, <u>*C*</u>F(CF$_3$)$_2$), 26.44, 24.08 (d, J = 21.4 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.30 (d, *J* = 7.3 Hz, CF(C<u>*F*</u>$_3$)$_2$, 6F), -182.36 (tp, *J* = 20.2, 6.8 Hz, C<u>*F*</u>(CF$_3$)$_2$, 1F).

GC-MS: 344

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{14}H_{12}F_7O_2^+$: 345.0720. Found: 345.0727.

(*Z*)-1-chloro-4-((4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)oxy)benzene (**18**)



18

The title compound was prepared with 1-chloro-4-(allyloxy)benzene (33.6 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (55.8 mg, 83 %, **18:18'** > 99:1, *Z/E* = 98:2).

R_f = 0.56 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.28 (dd, *J* = 8.8, 1.9 Hz, 1H), 6.92 (dd, *J* = 8.9, 1.8 Hz, 1H), 6.53 (d, *J* = 6.1 Hz, 1H), 4.87 (q, *J* = 7.1 Hz, 1H), 3.07 (dd, *J* = 19.6, 7.6 Hz, 2H).

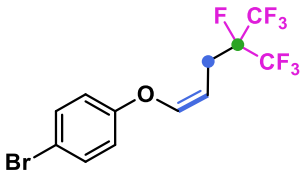
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 155.50, 144.63, 129.77, 128.63, 121.03 (qd, *J* = 285.5 Hz, 26.8 Hz, CF($\underline{C}F_3$)$_2$), 117.98, 116.02, 99.98 (d, *J* = 6.7 Hz), 93.01 – 89.49 (m, $\underline{C}F(CF_3)_2$), 24.07 (d, *J* = 21.1 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.25 (d, *J* = 7.2 Hz, CF($C\underline{F}_3$)$_2$, 6F), -182.31 (tp, *J* = 20.5, 6.9 Hz, $C\underline{F}(CF_3)_2$, 1F).

GC-MS: 336

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{12}H_9ClF_7O^+$: 337.0225. Found: 337.0219.

(*Z*)-1-bromo-4-((4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)oxy)benzene (**19**)



19

The title compound was prepared with 1-bromo-4-(allyloxy)benzene (42.4 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (63.8 mg, 84 %, **19:19'** > 99:1, *Z/E* = 98:2).

R_f = 0.59 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.43 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 7.9 Hz, 2H), 6.53 (d, *J* = 6.0 Hz, 1H), 4.87 (d, *J* = 7.4 Hz, 1H), 3.06 (dd, *J* = 20.2, 6.4 Hz, 2H).

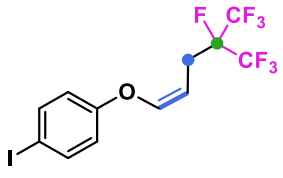
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 156.00, 144.49, 132.75, 121.01 (qd, *J* = 285.1 Hz, 27.0 Hz, CF($\underline{C}F_3$)$_2$), 118.43, 116.02, 100.13 (d, *J* = 6.9 Hz), 93.07 - 89.68 (m, $\underline{C}F(CF_3)_2$), 24.08 (d, *J* = 22.0 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.22 (d, *J* = 6.8 Hz, CF($C\underline{F}_3$)$_2$, 6F), -182.29 (tp, *J* = 21.4, 7.3 Hz, $C\underline{F}(CF_3)_2$, 1F).

GC-MS: 380

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{12}H_9BrF_7O^+$: 380.9720. Found: 380.9711.

(*Z*)-1-iodo-4-((4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)oxy)benzene (**20**)



20

The title compound was prepared with 1-iodo-4-(allyloxy)benzene (52.0 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a pale yellow oil (67.6 mg, 79 %, **20:20'** > 99:1, *Z/E* > 99:1).

R_f = 0.63 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.61 (d, *J* = 10.8 Hz, 2H), 6.76 (d, *J* = 9.0 Hz, 2H), 6.53 (d, *J* = 7.1 Hz, 1H), 4.88 (q, *J* = 7.2 Hz, 1H), 3.07 (dd, *J* = 19.6, 7.6 Hz, 2H).

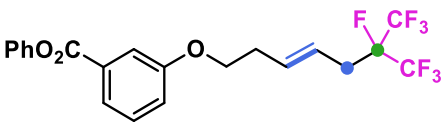
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 156.78, 144.34, 138.73, 121.01 (qd, *J* = 286.4 Hz, 26.9 Hz, $CF(\underline{C}F_3)_2$), 118.88, 100.24 (d, *J* = 7.2 Hz), 93.06 - 89.27 (m, $\underline{C}F(CF_3)_2$), 86.29, 24.09 (d, *J* = 21.1 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.25 (d, *J* = 7.2 Hz, $CF(C\underline{F}_3)_2$, 6F), -182.30 (th, *J* = 20.4, 7.2 Hz, $C\underline{F}(CF_3)_2$, 1F).

GC-MS: 428

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{12}H_9IF_7O^+$: 428.9581. Found: 428.9583.

(*E*)-3-((6,7,7,7-tetrafluoro-6-(trifluoromethyl)hept-3-en-1-yl)oxy)phenyl benzoate (**21**)



21

The title compound was prepared with 3-(pent-4-en-1-yloxy)phenyl benzoate (56.4 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a white solid (77.4 mg, 86 %, **21:21'** = 98:2, *E/Z* = 96:4).

R_f = 0.47 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.20 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 8.1 Hz, 1H), 6.85 - 6.74 (m, 3H), 5.87 - 5.73 (m, 1H), 5.55

(dt, *J* = 14.8, 7.3 Hz, 1H), 3.99 (t, *J* = 6.4 Hz, 2H), 2.83 (dd, *J* = 19.9, 7.3 Hz, 2H), 2.54 (q, *J* = 6.6 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 165.19, 159.84, 152.01, 133.84, 133.71, 130.26, 129.99, 129.63, 128.67, 120.99 (qd, *J* = 285.9 Hz, 26.8 Hz, CF($\underline{C}$F$_3$)$_2$), 120.33 (d, *J* = 5.9 Hz), 114.12, 112.44, 108.37, 92.93 - 89.78 (m, $\underline{C}$F(CF$_3$)$_2$), 67.16, 32.69, 32.44.

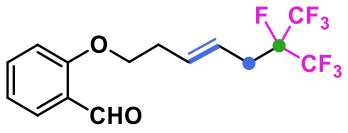
^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.83 (d, *J* = 7.2 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -182.06 (th, *J* = 21.0, 6.9 Hz, C$\underline{F}$(CF$_3$)$_2$, 1F).

GC-MS: 450

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{21}H_{18}F_7O_3^+$: 451.1139. Found: 451.1144.

Melt point: 55.2 - 55.8 ℃.

(*E*)-2-((6,7,7,7-tetrafluoro-6-(trifluoromethyl)hept-3-en-1-yl)oxy)phenyl aldehyde (**22**)



22

The title compound was prepared with 3-(pent-4-en-1-yloxy)phenyl aldehyde (38.0 mg, 0.20 mmol, 1.0 equiv.), *i*-C$_3$F$_7$-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 μL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (47.9 mg, 67 %, **22:22'** > 99:1, *E/Z* > 99:1).

R$_f$ = 0.32 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 10.47 (d, *J* = 0.8 Hz, 1H), 7.82 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.52 (ddd, *J* = 8.4, 7.3, 1.8 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 5.87 - 5.74 (m, 1H), 5.63 - 5.51 (m, 1H), 4.10 (t, *J* = 6.4 Hz, 2H), 2.83 (dd, *J* = 20.5, 7.8 Hz, 2H), 2.61 (q, *J* = 6.5 Hz, 2H).

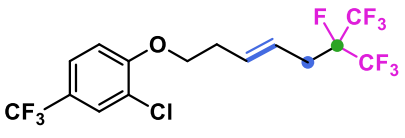
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 189.75, 161.20, 136.01, 133.47, 128.43, 125.02, 120.96 (qd, *J* = 284.5 Hz, 27.3 Hz, CF($\underline{C}$F$_3$)$_2$), 120.92, 120.80 (d, *J* = 6.1 Hz), 112.47, 92.97 - 89.83 (m, $\underline{C}$F(CF$_3$)$_2$), 67.47, 32.64, 32.37.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.87 (d, *J* = 6.7 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -182.16 (tp, *J* = 20.7, 6.9 Hz, C$\underline{F}$(CF$_3$)$_2$, 1F).

GC-MS: 358

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{15}H_{14}F_7O_2^+$: 359.0877. Found: 359.0885.

(*E*)-1-chloro-2-((6,7,7,7-tetrafluoro-6-(trifluoromethyl)hept-3-en-1-yl)oxy)-5-trifluromethylbenzene (**23**)



23

The title compound was prepared with 1-chloro-2-(pent-4-en-1-yloxy)-5-trifluromethylbenzene (52.8 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a pale-yellow oil (64.8 mg, 75 %, **23:23'** = 98:2, *E/Z* > 99:1).

R_f = 0.71 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.62 (d, *J* = 2.3 Hz, 1H), 7.46 (d, *J* = 8.6 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 1H), 5.83 (dt, *J* = 22.1, 7.4 Hz, 1H), 5.61 (dq, *J* = 14.9, 7.3, 6.8 Hz, 1H), 4.08 (t, *J* = 6.4 Hz, 2H), 2.84 (dd, *J* = 20.0, 7.2 Hz, 2H), 2.62 (q, *J* = 6.7 Hz, 2H).

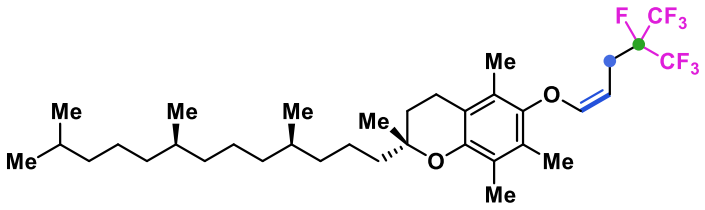
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 156.90, 133.09, 127.60 (d, *J* = 4.1 Hz), 125.10 (d, *J* = 3.9 Hz), 123.72 (q, *J* = 33.05 Hz), 123.51 (d, *J* = 7.5 Hz), 121.01 (q, *J* = 269.7 Hz), 120.97 (d, *J* = 5.9 Hz), 120.96 (qd, *J* = 286.4 Hz, 27.3 Hz, CF($\underline{C}F_3$)$_2$), 112.65, 92.64 - 89.61 (m, $\underline{C}F(CF_3)_2$), 68.34, 32.53 (d, *J* = 21.0 Hz), 32.17.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -61.80 (s, 3F), -75.98 (d, *J* = 6.8 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -182.23 (th, *J* = 20.3, 7.1, 6.5 Hz, C$\underline{F}(CF_3)_2$, 1F).

GC-MS: 432

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{15}H_{12}ClF_{10}O^+$: 433.0412. Found: 433.0421.

(*R*)-2,5,7,8-tetramethyl-6-(((*E*)-4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)oxy)-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chromane (**24**)



24

The title compound was prepared with D-α-tocopherol allyl ether (94.1 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a yellow oil (91.9 mg, 72 %, **24:24'** > 99:1, *Z/E* = 97:3).

R_f = 0.27 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 6.51 (d, *J* = 6.0 Hz, 1H), 5.12 (q, *J* = 7.2 Hz, 1H),

2.82 (dd, *J* = 19.6, 7.5 Hz, 2H), 2.61 (t, *J* = 7.1 Hz, 2H), 2.25 - 2.03 (m, 9H), 1.52 - 1.03 (m, 27H), 0.94 - 0.80 (m, 12H).

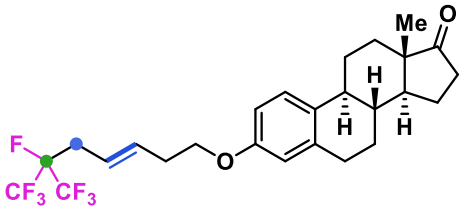
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 145.64, 144.69, 134.57, 122.69, 121.22, 117.42, 102.53 (d, *J* = 6.7 Hz), 74.59, 39.92, 39.49, 37.57, 37.40, 32.91, 32.81, 31.67, 28.09, 24.92, 24.56, 24.04 (d, *J* = 21.1 Hz), 23.90, 22.84, 22.75, 21.15, 20.88, 19.87, 19.77, 12.33, 11.88, 11.39.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.30 (d, *J* = 7.3 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -182.36 (tp, *J* = 20.2, 6.8 Hz, C$\underline{F}$(CF$_3$)$_2$, 1F).

GC-MS: 638

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{35}H_{54}F_7O_2^+$: 639.4007. Found: 639.4001.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(((*E*)-6,7,7,7-tetrafluoro-6-(trifluoromethyl)hept-3-en-1-yl)oxy)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (**25**)



25

The title compound was prepared with (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(allyloxy)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (67.7 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a white solid (67.8 mg, 67 %, **25:25'** = 96:4, *E/Z* > 99:1).

R_f = 0.24 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.20 (d, *J* = 8.5 Hz, 1H), 6.70 (d, *J* = 8.6 Hz, 1H), 6.64 (s, 1H), 5.80 (dt, *J* = 13.6, 6.7 Hz, 1H), 5.55 (dt, *J* = 15.0, 7.2 Hz, 1H), 3.97 (t, *J* = 5.6 Hz, 2H), 2.93 - 2.84 (m, 3H), 2.81 (d, *J* = 7.2 Hz, 1H), 2.57 - 2.44 (m, 3H), 2.39 (d, *J* = 8.9 Hz, 1H), 2.25 (d, *J* = 10.7 Hz, 1H), 2.19 - 2.10 (m, 1H), 2.10 - 1.89 (m, 3H), 1.64 - 1.41 (m, 6H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 220.95, 156.92, 137.87, 134.14, 132.29, 126.43, 121.01 (qd, *J* = 285.0 Hz, 27.3 Hz, CF(*C*F$_3$)$_2$), 120.05 (d, *J* = 6.1 Hz), 114.71, 112.24, 92.99 - 89.71 (m, *C*F(CF$_3$)$_2$), 66.93, 50.50, 48.09, 44.08, 38.47, 35.93, 32.61 (d, *J* = 21.1 Hz), 32.58, 31.69, 29.73, 26.63, 26.01, 21.66, 13.91.

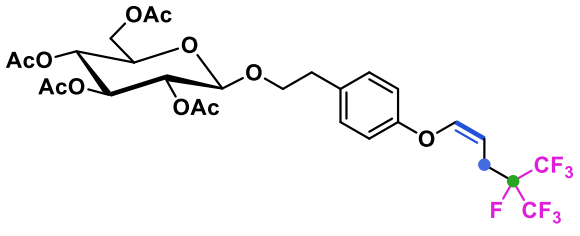
^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.84 (d, *J* = 7.3 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -182.04 (th,

J = 20.7, 6.8, 6.4 Hz, C*F*$(CF_3)_2$, 1F).

GC-MS: 506

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{26}H_{30}F_7O_2^+$: 507.2129. Found: 507.2134.

2-(4-(*Z*-(4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)oxy)phenyl)ethyl β-D-glucopyranoside tetraacetate (**26**)



26

The title compound was prepared with 2-(4-allyloxyphenyl)ethyl β-D-glucopyranoside tetraacetate (101.6 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (86.5 mg, 64 %, **26:26'** > 99:1, *Z/E* = 95:5).

R_f = 0.44 (MeOH: DCM, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.07 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 6.53 (d, *J* = 6.1 Hz, 1H), 5.38 (d, *J* = 12.9 Hz, 1H), 5.25 (d, *J* = 10.5 Hz, 1H), 5.15 (t, *J* = 9.5 Hz, 1H), 5.06 (t, *J* = 9.6 Hz, 1H), 5.00 - 4.94 (m, 1H), 4.87 (q, *J* = 7.2 Hz, 1H), 4.51 - 4.46 (m, 2H), 4.14 - 4.08 (m, 2H), 3.08 (dd, *J* = 19.6, 7.5 Hz, 2H), 2.84 - 2.75 (m, 2H), 2.06 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.90 (s, 3H).

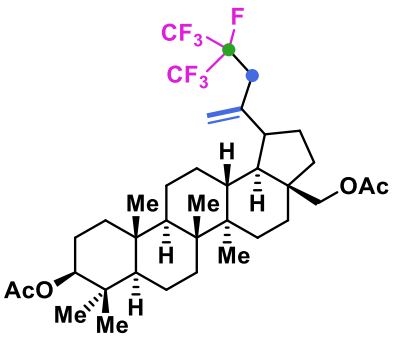
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 170.95, 170.40, 169.94, 169.65, 155.99, 142.01, 129.26, 128.01, 121.03 (qd, *J* = 285.5 Hz, 27.3 Hz, CF(*C*$F_3)_2$), 117.10, 99.47 (d, *J* = 20.3 Hz), 92.88 - 89.74 (m, *C*F$(CF_3)_2$), 73.96, 71.29, 70.57, 70.32, 70.02, 61.37, 37.75, 24.07 (d, *J* = 21.1 Hz), 21.18, 20.91, 20.60.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.70 (d, *J* = 7.7 Hz, CF(C*F*$_3)_2$, 6F), -184.14 (dh, *J* = 23.0, 7.9 Hz, C*F*$(CF_3)_2$, 1F).

GC-MS: 676

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{28}H_{32}F_{10}O_{11}^+$: 677.1827. Found: 677.1840.

((3a*S*,5a*R*,5b*R*,7a*R*,9*S*,11a*R*,11b*R*,13a*R*,13b*R*)-9-acetoxy-5a,5b,8,8,11a-pentamethyl-1-(4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-2-yl)icosahydro-3a*H*-cyclopenta[*a*]chrysen-3a-yl)methyl acetate (**29**)



29

The title compound was prepared with betulin acetate (105.2 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 μL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a white solid (56.9 mg, 41 %).

R_f = 0.22 (ethyl acetate: petroleum ether, 1:5 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 4.60 (d, J = 41.1 Hz, 2H), 4.44 (dt, J = 10.5, 5.1 Hz, 1H), 4.22 (d, J = 11.1 Hz, 1H), 3.81 (d, J = 11.1 Hz, 1H), 2.41 (tt, J = 10.9, 5.1 Hz, 1H), 2.07 - 1.97 (m, 6H), 1.83 - 1.09 (m, 23H), 1.10 - 0.69 (m, 19H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 171.63, 171.04, 150.18, 120.66 (qd, *J* = 286.3, 28.5 Hz, CF($\underline{C}F_3$)$_2$), 109.98, 93.24 (m, $\underline{C}F(CF_3)_2$), 80.95, 62.85, 55.44, 50.35, 48.83, 47.78, 46.37, 42.75, 38.45, 37.85, 37.62, 37.12, 34.61, 34.19, 29.72 (d, *J* = 17.0 Hz), 28.01, 27.12, 25.21, 23.76, 21.38, 21.11, 20.87, 19.18, 18.23, 16.56, 16.16 (d, *J* = 13.4 Hz), 14.79.

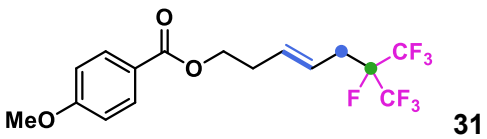
^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.65 (d, *J* = 7.0 Hz, CF($C\underline{F}_3$)$_2$, 6F), -182.09 (hept, *J* = 7.2 Hz, $C\underline{F}(CF_3)_2$, 1F).

GC-MS: 694

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{37}H_{54}F_7O_4^+$: 695.3905. Found: 695.3918.

Melt point: 99.2 - 100.7 ℃.

(*E*)-6,7,7,7-tetrafluoro-6-(trifluoromethyl)hept-3-en-1-yl 4-methoxybenzoate (**31**)



31

The title compound was prepared with pent-4-en-1-yl 4-methoxybenzoate (44.0 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 μL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (65.2 mg, 84 %, **31:31'** > 99:1, *E*/*Z* = 95:5).

R_f = 0.62 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.96 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 5.75 (dt, *J* = 14.2, 6.8 Hz, 1H), 5.54 (dt, *J* = 15.1, 7.2 Hz, 1H), 4.31 (t, *J* = 6.6 Hz, 2H), 3.84 (s, 3H), 2.81 (dd, *J* = 19.9, 7.3 Hz, 2H), 2.51 (q, *J* = 6.7 Hz, 2H).

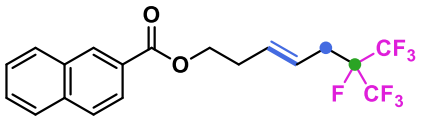
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 166.33, 163.49, 133.74, 131.65, 122.67, 120.96 (qd, *J* = 285.5 Hz, 26.3 Hz, CF($\underline{C}F_3$)$_2$), 120.42 (d, *J* = 6.0 Hz), 113.65, 92.81 - 89.76 (m, $\underline{C}F(CF_3)_2$), 63.45, 55.45, 32.55 (d, *J* = 20.8 Hz), 32.10.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.91 (d, *J* = 6.9 Hz, CF($C\underline{F}_3$)$_2$, 6F), -182.14 (th, *J* = 21.0, 6.9 Hz, $C\underline{F}(CF_3)_2$, 1F).

GC-MS: 388

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{16}H_{16}F_7O_3^+$: 389.0982. Found: 389.0977.

(*E*)-6,7,7,7-tetrafluoro-6-(trifluoromethyl)hept-3-en-1-yl 2-naphthoate (**32**)



32

The title compound was prepared with pent-4-en-1-yl 2-naphthoate (48.0 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (75.1 mg, 92 %, **32:32'** > 99:1, *E/Z* = 95:5).

R_f = 0.67 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.58 (s, 1H), 8.04 (d, *J* = 8.7 Hz, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.56 (dt, *J* = 19.4, 6.9 Hz, 2H), 5.80 (dt, *J* = 15.1, 7.4 Hz, 1H), 5.59 (dt, *J* = 14.9, 7.4 Hz, 1H), 4.46 - 4.36 (m, 2H), 2.84 (dd, *J* = 19.9, 7.3 Hz, 2H), 2.58 (q, *J* = 6.8 Hz, 2H).

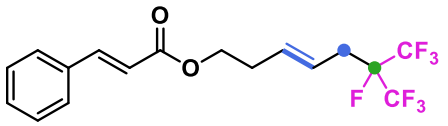
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 166.76, 135.65, 133.66, 132.58, 131.13, 129.42, 128.36, 128.23, 127.86, 127.48, 126.75, 125.27, 120.96 (qd, *J* = 286.8 Hz, 27.1 Hz, CF($\underline{C}F_3$)$_2$), 120.61 (d, *J* = 6.0 Hz), 92.92 - 89.76 (m, $\underline{C}F(CF_3)_2$), 63.89, 32.58 (d, *J* = 21.1 Hz), 32.12.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.82 (d, *J* = 7.3 Hz, CF($C\underline{F}_3$)$_2$, 6F), -182.08 (th, *J* = 21.1, 7.0 Hz, $C\underline{F}(CF_3)_2$, 1F).

GC-MS: 408

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{19}H_{16}F_7O_2^+$: 409.1033. Found: 409.1022.

(*E*)-6,7,7,7-tetrafluoro-6-(trifluoromethyl)hept-3-en-1-yl cinnamate (**33**)



33

The title compound was prepared with pent-4-en-1-yl cinnamate (43.2 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a pale-yellow oil (60.7 mg, 79 %, **33:33'** > 99:1, *E/Z* = 97:3).

R_f = 0.52 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.07 (d, *J* = 7.0 Hz, 1H), 7.68 (d, *J* = 16.0 Hz, 1H), 7.54 - 7.43 (m, 2H), 7.43 - 7.30 (m, 2H), 6.42 (d, *J* = 16.1 Hz, 1H), 5.78 - 5.66 (m, 1H), 5.66 - 5.47 (m, 1H), 4.24 (t, *J* = 6.6 Hz, 2H), 2.82 (dd, *J* = 19.9, 7.2 Hz, 2H), 2.46 (q, *J* = 6.8 Hz, 2H).

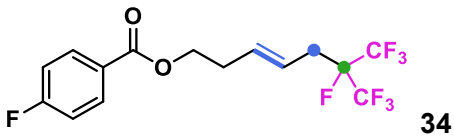
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 166.95, 145.01, 134.37, 130.40, 129.88, 128.98, 128.15, 120.99 (qd, *J* = 284.5 Hz, 26.8 Hz, CF($\underline{C}F_3$)$_2$), 120.48 (d, *J* = 6.1 Hz), 117.97, 92.83 - 89.79 (m, $\underline{C}F(CF_3)_2$), 63.31, 32.56 (d, *J* = 20.7 Hz), 32.03.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.87 (d, *J* = 6.8 Hz, CF($C\underline{F}_3$)$_2$, 6F), -182.05 (th, *J* = 21.0, 7.2 Hz, $C\underline{F}(CF_3)_2$, 1F).

GC-MS: 384

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{17}H_{16}F_7O_2^+$: 385.1033. Found: 385.1034.

(*E*)-6,7,7,7-tetrafluoro-6-(trifluoromethyl)hept-3-en-1-yl 4-flurobenzoate (**34**)



34

The title compound was prepared with pent-4-en-1-yl 4-flurobenzoate (41.6 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (67.7 mg, 90 %, **34:34'** = 98:2, *E/Z* = 97:3).

R_f = 0.69 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.08 - 7.98 (m, 2H), 7.14 - 7.04 (m, 2H), 5.83 - 5.68 (m, 1H), 5.62 - 5.47 (m, 1H), 4.33 (t, *J* = 6.5 Hz, 2H), 2.81 (dd, *J* = 20.0, 7.3 Hz, 2H), 2.52 (q, *J* = 6.7 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 165.88 (d, *J* = 253.8 Hz),165.59, 133.52, 132.15

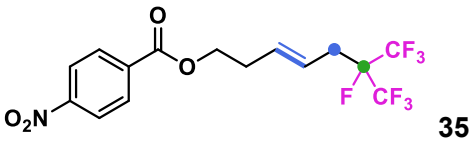
(d, *J* = 9.2 Hz), 126.47 (d, *J* = 2.9 Hz), 120.94 (qd, *J* = 285.5 Hz, 27.3 Hz, CF($\underline{C}F_3$)$_2$), 120.62 (d, *J* = 6.1 Hz), 115.53 (d, *J* = 22.1 Hz), 92.99 - 89.66 (m, $\underline{C}F(CF_3)_2$), 63.82, 32.51 (d, *J* = 21.1 Hz), 32.02.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.97 (d, *J* = 6.7 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -105.71, -182.22 (th, *J* = 21.2, 6.7 Hz, C$\underline{F}(CF_3)_2$, 1F).

GC-MS: 376

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{15}H_{13}F_8O_2^+$: 377.0782. Found: 377.0779.

(*E*)-6,7,7,7-tetrafluoro-6-(trifluoromethyl)hept-3-en-1-yl 4-nitrobenzoate (**35**)



35

The title compound was prepared with 4-pentenyl 4-nitrobenzoate (47.1 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 μL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a light-yellow oil (70.9 mg, 88 %, **35:35'** > 99:1, *E*/*Z* = 97:3).

R_f = 0.35 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.27 (d, *J* = 7.4 Hz, 2H), 8.17 (d, *J* = 8.9 Hz, 2H), 5.80 - 5.69 (m, 1H), 5.62 - 5.50 (m, 1H), 4.40 (t, *J* = 6.5 Hz, 2H), 2.82 (dd, *J* = 19.9, 7.2 Hz, 2H), 2.56 (d, *J* = 6.7 Hz, 2H).

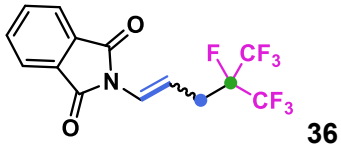
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 164.67, 150.66, 135.57, 133.21, 130.75, 123.61, 120.97 (d, *J* = 5.9 Hz), 120.92 (qd, *J* = 285.5 Hz, 27.8 Hz, CF($\underline{C}F_3$)$_2$), 92.86 - 89.60 (m, $\underline{C}F(CF_3)_2$), 64.58, 32.49 (d, *J* = 20.9 Hz), 31.94.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.89 (d, *J* = 7.0 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -182.07 - -182.39 (m, C$\underline{F}(CF_3)_2$, 1F).

GC-MS: 403

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{15}H_{13}F_7NO_4^+$: 404.0727. Found: 404.0720.

(*Z*)-2-(4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)isoindoline-1,3-dione (**36**)



36

The title compound was prepared with 2-allylisoindoline-1,3-dione (37.4 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 μL,

0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (51.1 mg, 72 %, **36:36'** = 96:4, *E/Z* = 54:46).

R_f = 0.22 (ethyl acetate: petroleum ether, 1:5 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.94 - 7.82 (m, 2H), 7.82 - 7.68 (m, 2H), 6.83 (dd, *J* = 14.6, 1.6 Hz, 0.54H), 6.63 (dt, *J* = 15.0, 7.7 Hz, 0.54H), 6.42 (dd, *J* = 8.9, 1.9 Hz, 0.46H), 5.74 (q, *J* = 7.6 Hz, 0.46H), 3.05 (dd, *J* = 19.7, 6.9 Hz, 0.92H), 2.95 (dd, *J* = 19.6, 7.7 Hz, 1.08H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 166.44, 166.23, 134.77, 131.89, 131.54, 124.03, 123.91, 123.03, 121.14, 117.33, 108.60, 31.41 (d, *J* = 21.2 Hz), 28.15 (d, *J* = 19.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.78 (d, *J* = 7.2 Hz, CF($C\underline{F}_3$)$_2$, 3.30F), -76.23 (d, *J* = 6.7 Hz, CF($C\underline{F}_3$)$_2$, 2.76F), -181.85 (tp, *J* = 20.6, 6.9 Hz, $C\underline{F}$(CF_3)$_2$, 0.54F), -183.49 (dtq, *J* = 20.4, 13.9, 6.9 Hz, $C\underline{F}$(CF_3)$_2$, 0.46F).

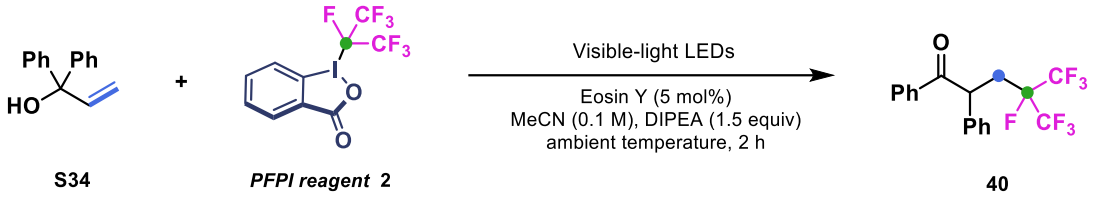
GC-MS: 355

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{14}H_9F_7NO_2^+$: 356.0516. Found: 356.0511.

Visible-light promoted neophyl rearrangement of allylic alcohols

Optimization of reaction conditions

Photochemistry parameters screening



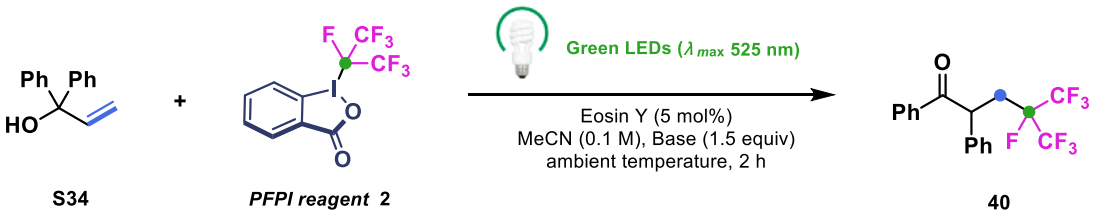
Scheme S17. Photochemistry parameters screening.

Under an ambient atmosphere, in a 10 mL screw-cap vial equipped with a magnetic stirring bar, 1,1-diphenylprop-2-en-1-ol (**S34**, 21.0 mg, 0.10 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (62.4 mg, 0.15 mmol, 1.5 equiv.), Eosin Y (3.2 mg, 5.0 mol%) were dissolved in dry MeCN (1 mL). Subsequently, DIPEA (26.1 μL, 0.15 mmol, 1.5 equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at visible light for 2 h, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, 10 μL of *n*-dodecane was added as an internal standard and the reaction mixture was diluted with EtOAc. The crude reaction mixture was filtered through a plug of silica then subjected to GC-MS analysis.

Entry	LEDs (Wavelength, Power)	Yield of **40** (%)[a]
1	**Green LEDs (525 nm, 10 W)**	**88**
2	Green LEDs (525 nm, 25 W)	83
3	Blue LEDs (450 nm, 10 W)	59
4	White LEDs (100W)	71
5	UV (360-400nm)	14

Table S6. Photochemistry parameters screening. [a]The yield was determined by GC-MS with *n*-dodecane as an internal standard.

Base screening



Scheme S18. Base screening.

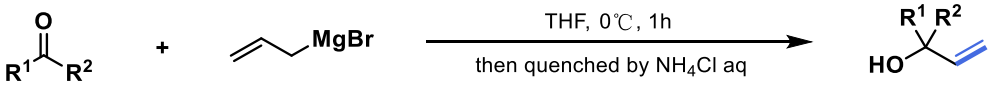
Under an ambient atmosphere, in a 10 mL screw-cap vial equipped with a magnetic stirring bar, 1,1-diphenylprop-2-en-1-ol (**S34**, 21.0 mg, 0.10 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (62.4 mg, 0.15 mmol, 1.5 equiv.), Eosin Y (3.2 mg, 5.0 mol%) were dissolved in dry MeCN (1 mL). Subsequently, base (0.15 mmol, 1.5 equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at green light (525 nm) for 2 h, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, 10 μL of *n*-dodecane was added as an internal standard and the reaction mixture was diluted with EtOAc. The crude reaction mixture was filtered through a plug of silica then subjected to GC-MS analysis.

Entry	Base	Yield of **40** (%)[a]
1	DIPEA	88
2	TEMDA	86
3	**TMP**	**93 (91[b])**
4	TMG	44
5	Et_3N	58

Table S7. Base screening. [a]The yield was determined by GC-MS with *n*-dodecane as an internal standard. [b]Yield of isolated product given.

Synthesis of the substrates

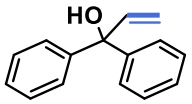
General procedure for preparation of allylic alcohols.



Scheme S19. Synthesis of allylic alcohols.[8]

To a solution of ketone (3.0 mmol, 1.0 equiv.) in THF (15 mL) at 0 °C was added vinylmagnesium bromide (4.5 mL, 1.0 M in THF, 1.5 equiv.) under an nitrogen atmosphere. After the reaction mixture was stirred at 0 °C for 1 h, the resulting solution was quenched by saturated aqueous NH_4Cl (5 mL) and H_2O (5 mL) and allowed to warm to room temperature. The resulting mixture was extracted with ethyl acetate (15 mL × 3), washed with brine (5 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:10 to 1:30 (v:v)) to afford the title compound which was characterized by GC-MS analysis, ^1H NMR and ^{13}C NMR spectroscopy.

1,1-Diphenylprop-2-en-1-ol (**S29**)



S29

Known compound.

The title compound was prepared with benzophenone (546.2 mg, 3.0 mmol, 1.0 equiv.), vinylmagnesium bromide (4.5 mL, 1.0 M in THF, 1.5 equiv.) in THF (15 mL). The mixture was stirred at 0 °C for 1 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:30 (v:v)) to afford the title compound as a colorless oil (573.3 mg, 91 %).

$\mathbf{R_f}$ = 0.21 (ethyl acetate: petroleum ether, 1:10 (v:v)).

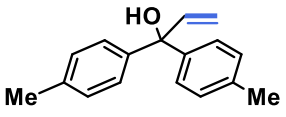
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.45 - 7.39 (m, 4H), 7.36 (m, 4H), 7.31 - 7.24 (m, 2H), 6.58 - 6.51 (m, 1H), 5.39 - 5.35 (m, 1H), 5.34 (m, 1H), 2.30 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 145.9, 143.5, 128.2, 127.3, 126.8, 114.0, 79.4.

GC-MS: 210.

1,1-Di-*p*-tolylprop-2-en-1-ol (**S30**)



S30

Known compound.

The title compound was prepared with 4,4'-dimethylbenzophenone (630.3 mg, 3.0 mmol, 1.0 equiv.), vinylmagnesium bromide (4.5 mL, 1.0 M in THF, 1.5 equiv.) in THF (15 mL). The mixture was stirred at 0 °C for 1 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:30 (v:v)) to afford the title compound as a colorless oil (642.6 mg, 90 %).

$\mathbf{R_f}$ = 0.23 (ethyl acetate: petroleum ether, 1:10 (v:v)).

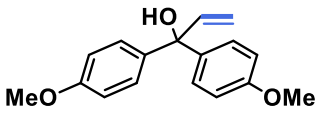
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.34 - 7.24 (m, 4H), 7.15 (m, 4H), 6.50 (dd, *J* = 17.1, 10.5 Hz, 1H), 5.34 (dd, *J* = 17.0, 1.2 Hz, 1H), 5.30 (dd, *J* = 10.6, 1.2 Hz, 1H), 2.36 (s, 6H), 2.24 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 143.8, 143.2, 136.9, 128.8, 126.9, 113.5, 79.2, 21.0.

GC-MS: 238.

1,1-Bis(4-methoxyphenyl)prop-2-en-1-ol (**S31**)



S31

Known compound.

The title compound was prepared with 4,4'-dimethyloxybenzophenone (726.3 mg, 3.0 mmol, 1.0 equiv.), vinylmagnesium bromide (4.5 mL, 1.0 M in THF, 1.5 equiv.) in THF (15 mL). The mixture was stirred at 0 °C for 1 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:30 (v:v)) to afford the title compound as a colorless oil (769.5 mg, 95 %).

R_f = 0.20 (ethyl acetate: petroleum ether, 1:10 (v:v)).

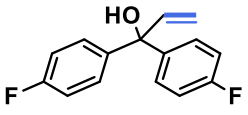
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.31 (d, *J* = 8.8 Hz, 4H), 6.85 (d, *J* = 8.8 Hz, 4H), 6.46 (dd, *J* = 17.2, 10.5 Hz, 1H), 5.30 (d, *J* = 17.3 Hz, 1H), 5.28 (d, *J* = 10.4 Hz, 1H), 3.81(s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 158.6, 143.9, 138.2, 128.1, 113.4, 78.8, 55.2.

GC-MS: 270.

1,1-Bis(4-fluorophenyl)prop-2-en-1-ol (**S32**)



S32

Known compound.

The title compound was prepared with 4,4'-difluorobenzophenone (654.2 mg, 3.0 mmol, 1.0 equiv.), vinylmagnesium bromide (4.5 mL, 1.0 M in THF, 1.5 equiv.) in THF (15 mL). The mixture was stirred at 0 °C for 1 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:30 (v:v)) to afford the title compound as a colorless oil (634.7 mg, 86 %).

R_f = 0.30 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

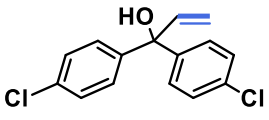
^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.39 - 7.29 (m, 4H), 7.05 - 6.94 (m, 4H), 6.45 (dd, *J* = 17.1, 10.5 Hz, 1H), 5.33 (dd, *J* = 10.6, 1.0 Hz, 1H), 5.27 (dd, *J* = 17.1, 1.0 Hz, 1H), 2.24 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 162.0 (d, *J* = 246.5 Hz), 143.2, 141.3 (d, *J* = 3.8 Hz), 128.7 (d, *J* = 8.0 Hz), 115.1 (d, *J* = 21.4 Hz), 114.5, 78.7.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -115.26 (tt, *J* = 8.6, 5.4 Hz, 2F).

GC-MS: 246.

1,1-Bis(4-chlorophenyl)prop-2-en-1-ol (**S33**)



S33

Known compound.

The title compound was prepared with 4,4'-dichlorobenzophenone (750.0 mg, 3.0 mmol, 1.0 equiv.), vinylmagnesium bromide (4.5 mL, 1.0 M in THF, 1.5 equiv.) in THF (15 mL). The mixture was stirred at 0 °C for 1 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:30 (v:v)) to afford the title compound as a pale-yellow oil (725.6 mg, 87 %).

R_f = 0.24 (ethyl acetate: petroleum ether, 1:10 (v:v)).

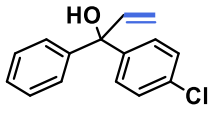
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.27 (s, 8H), 6.40 (dd, *J* = 17.2, 10.5 Hz, 1H), 5.33 (d, *J* = 10.4 Hz, 1H), 5.26 (d, *J* = 17.2 Hz, 1H), 2.35 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 143.7, 142.5, 133.3, 128.3, 128.4, 115.0, 78.7.

GC-MS: 278.

1-(4-Chlorophenyl)-1-phenyl-2-propenol (**S34**)



S34

Known compound.

The title compound was prepared with (4-chlorophenyl)(phenyl)methanone (648.1 mg, 3.0 mmol, 1.0 equiv.), vinylmagnesium bromide (4.5 mL, 1.0 M in THF, 1.5 equiv.) in THF (15 mL). The mixture was stirred at 0 °C for 1 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:30 (v:v)) to afford the title compound as a colorless oil (666.2 mg, 91 %).

R_f = 0.24 (ethyl acetate: petroleum ether, 1:10 (v:v)).

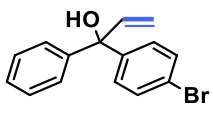
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.41 - 7.36 (m, 4H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.31 - 7.28 (m, 1H), 6.48 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.36 (dd, *J* = 10.4, 1.2 Hz, 1H), 5.33 (dd, *J* = 17.4, 1.2 Hz, 1H), 2.36 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 145.3, 144.0, 143.0, 133.1, 128.3, 128.3, 128.4, 127.5, 126.8, 114.5, 79.1.

GC-MS: 244.

1-(4-Bromophenyl)-1-phenyl-2-propenol (**S35**)



S35

The title compound was prepared with (4-bromophenyl)(phenyl)methanone (779.9 mg, 3.0 mmol, 1.0 equiv.), vinylmagnesium bromide (4.5 mL, 1.0 M in THF, 1.5 equiv.) in THF (15 mL). The mixture was stirred at 0 °C for 1 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:30 (v:v)) to afford the title compound as a colorless oil (820.8 mg, 95 %).

R_f = 0.27 (ethyl acetate: petroleum ether, 1:10 (v:v)).

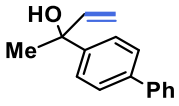
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.39 - 7.33 (m, 4H), 7.31 (d, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 2H), 7.26 - 7.23 (m, 1H), 6.44 (dd, *J* = 17.1, 10.6 Hz, 1H), 5.35 (dd, *J* = 10.1, 1.2 Hz, 1H), 5.28 (dd, *J* = 17.0, 1.2 Hz, 1H), 2.32 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 144.7, 143.1, 142.5, 133.2, 128.0, 127.7, 127.6, 127.0, 126.2, 113.5, 76.3.

GC-MS: 288.

1-Methyl-1-biphenyl-2-propenol (**S36**)



S36

The title compound was prepared with 4-acetylbiphenyl (588.3 mg, 3.0 mmol, 1.0 equiv.), vinylmagnesium bromide (4.5 mL, 1.0 M in THF, 1.5 equiv.) in THF (15 mL). The mixture was stirred at 0 °C for 1 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:30 (v:v)) to afford the title compound as a colorless oil (551.0 mg, 82 %).

R_f = 0.32 (ethyl acetate: petroleum ether, 1:10 (v:v)).

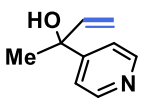
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.59 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.53 - 7.47 (m, 4H), 7.47 - 7.42 (m, 2H), 7.42 - 7.34 (m, 1H), 5.99 (tq, *J* = 11.7, 1.1 Hz, 1H), 5.21 (dd, *J* = 11.7, 2.4 Hz, 1H), 5.09 (d, *J* = 2.4 Hz, 1H), 4.39 (s, 1H), 1.67 (d, *J* = 1.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 145.71, 144.57, 140.84, 139.92, 129.09, 127.99, 127.26, 126.36, 111.95, 75.16, 28.51.

GC-MS: 224.

2-(Pyridin-4-yl)but-3-en-2-ol (**S37**)



S37

Known compound.

The title compound was prepared with methyl (4-pyridyl) ketone (363.2 mg, 3.0 mmol, 1.0 equiv.),

vinylmagnesium bromide (4.5 mL, 1.0 M in THF, 1.5 equiv.) in THF (15 mL). The mixture was stirred at 0 °C for 1 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:15 (v:v)) to afford the title compound as a light-yellow oil (339.7 mg, 76 %).

R_f = 0.40 (ethyl acetate: petroleum ether, 1:2 (v:v)).

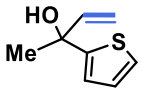
NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.58 (d, *J* = 4.0 Hz, 2H), 7.41 (d, *J* = 4.0 Hz, 2H), 6.18 - 6.10 (m, 1H), 5.32 (d, *J* = 16.1, 1H), 5.22 (d, *J* = 12.0, 1H), 2.36 (s, 1H), 1.64 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 155.5, 149.5,149.4, 143.4, 120.5, 113.6, 74.1, 29.2.

GC-MS: 149.

2-(Thiophen-2-yl)but-3-en-2-ol (**S38**)



S38

Known compound.

The title compound was prepared with 2-acetylthiophene (378.0 mg, 3.0 mmol, 1.0 equiv.), vinylmagnesium bromide (4.5 mL, 1.0 M in THF, 1.5 equiv.) in THF (15 mL). The mixture was stirred at 0 °C for 1 h. The crude product was purified by chromatography (silica gel, ethyl acetate: petroleum ether, 1:20 (v:v)) to afford the title compound as a pale-yellow oil (365.0 mg, 79 %).

R_f = 0.37 (ethyl acetate: petroleum ether, 1:5 (v:v)).

NMR Spectroscopy:

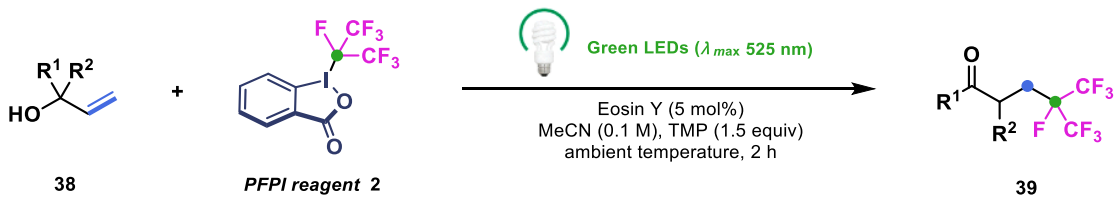
^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.24 (dd, *J* = 4.0, 2.4 Hz, 2H), 6.98 - 6.96 (m, 2H), 6.24 (d, *J* = 16.0, 8.0 Hz, 1H), 5.41 - 5.16 (m, 2H), 2.19 (s, 1H), 1.75 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 151.6, 144.2, 126.7, 124.6, 123.3, 112.5, 73.3, 30.1.

GC-MS: 154.

Substrate Scope

General procedure to access isoperfluoropropylated products.

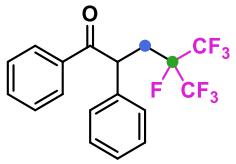


Scheme S20. General procedure to access isoperfluoropropylated products.

Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, allylic alcohols (**38**, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) were dissolved in dry MeCN (2.0 mL, 0.1 M). Subsequently, TMP (50.6 μL, 0.3 mmol, 1.5 equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at green light (525 nm) for 2 h, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, the reaction was quenched with 10 mL 5% $NaHCO_3$ aqueous solution, then extracted with DCM (3 x 10 mL). The combined organic phase was dried with anhydrous Na_2SO_4 and concentrated under vacuum. The residue was further purified by column chromatography to afford corresponding isoperfluoropropylated products **39**, which was characterized by GC-MS analysis, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectroscopy and HRMS.

Characterization of Products

4,5,5,5-Tetrafluoro-4-trifluoromethyl-1,2-diphenylbutan-1-one (**40**)



40

The title compound was prepared with 1,1-diphenylprop-2-en-1-ol (42.0 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and TMP (50.6 μL, 0.30 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (68.8 mg, 91 %).

R_f = 0.65 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.96 (dd, *J* = 7.1, 1.5 Hz, 2H), 7.55 - 7.45 (m, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.34 - 7.27 (m, 4H), 7.27 - 7.21 (m, 1H), 5.05 (d, *J* = 9.3 Hz, 1H), 3.65 (td, *J* = 15.4, 9.4 Hz, 1H), 2.36 (dd, *J* = 21.5, 15.7 Hz, 1H).

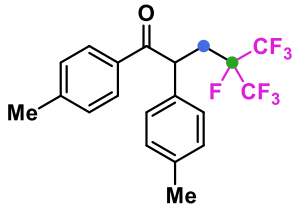
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 196.51, 138.13, 135.71, 133.41, 129.59, 128.79 (d, *J* = 6.6 Hz), 127.98 (d, *J* = 4.5 Hz), 121.12 (qt, *J* = 285.9, 29.2 Hz, CF($\underline{C}F_3$)$_2$), 92.89 - 89.20 (m, $\underline{C}F(CF_3)_2$), 46.63 (d, *J* = 5.5 Hz), 31.71 (d, *J* = 18.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.73 (qq, *J* = 29.2, 8.3 Hz, CF($C\underline{F}_3$)$_2$, 6F), -184.34 (dqt, *J* = 21.2, 14.3, 7.1 Hz, $C\underline{F}(CF_3)_2$, 1F).

GC-MS: 378

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{18}H_{14}F_7O^+$: 379.0927. Found: 379.0925.

4,5,5,5-Tetrafluoro-4-trifluoromethyl-1,2-di-*p*-tolylbutan-1-one (**41**)



41

The title compound was prepared with 1,1-di-*p*-tolylprop-2-en-1-ol (47.6 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and TMP (50.6 µL, 0.30 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (78.8 mg, 97 %).

R_f = 0.61 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.19 (dd, *J* = 8.2, 2.9 Hz, 4H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.00 (d, *J* = 9.3 Hz, 1H), 3.63 (td, *J* = 16.1, 15.6, 9.3 Hz, 1H), 2.34 (s, 3H), 2.28 (s, 3H).

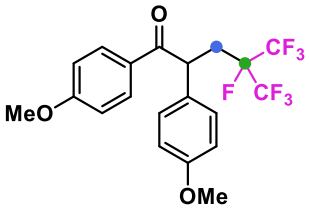
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 196.14, 144.27, 137.71, 135.42, 133.20, 130.21, 129.44, 128.97, 127.79, 121.16 (qt, *J* = 285.9, 27.3 Hz, CF($\underline{C}F_3$)$_2$), 92.90 - 89.41 (m, $\underline{C}$F(CF_3)$_2$), 46.06 (d, *J* = 5.1 Hz), 31.68 (d, *J* = 19.0 Hz), 21.61, 21.02.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.72 (dq, *J* = 29.4, 8.3 Hz, CF($C\underline{F}_3$)$_2$, 6F), -184.46 (dtp, *J* = 21.6, 14.2, 7.3 Hz, C$\underline{F}$(CF_3)$_2$, 1F).

GC-MS: 406

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{20}H_{18}F_7O^+$: 407.1240. Found: 407.1244.

4,5,5,5-Tetrafluoro-4-trifluoromethyl-1,2-bis(4-methoxyphenyl)butan-1-one (**42**)



42

The title compound was prepared with 1,1-bis(4-methoxyphenyl)prop-2-en-1-ol (54.0 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and TMP (50.6 µL, 0.30 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (84.9 mg, 97 %).

R_f = 0.56 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.94 (d, *J* = 8.9 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 4.94 (dd, *J* = 9.2, 2.9 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.59 (td, *J* = 15.5, 8.9 Hz, 1H), 2.31 (dd, *J* = 20.8, 16.3 Hz, 1H).

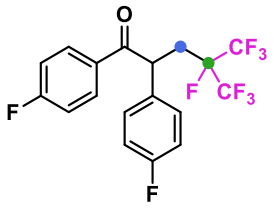
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 195.11, 163.71, 159.21, 131.14, 130.55, 128.97, 128.57, 121.15 (qt, *J* = 285.9, 27.8 Hz, CF($\underline{C}$F$_3$)$_2$), 114.88, 113.95, 92.90 - 89.47 (m, $\underline{C}$F(CF$_3$)$_2$), 55.45, 55.25, 45.36 (d, *J* = 5.0 Hz), 31.72 (d, *J* = 18.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.73 (dq, *J* = 25.3, 8.6 Hz, CF(C$\underline{F}$$_3$)$_2$, 6F), -184.59 (dtp, *J* = 21.3, 13.9, 7.1 Hz, C$\underline{F}$(CF$_3$)$_2$, 1F).

GC-MS: 438

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{20}H_{18}F_7O_3^+$: 439.1139. Found: 439.1139.

4,5,5,5-Tetrafluoro-4-trifluoromethyl-1,2-bis(4-fluorophenyl)butan-1-one (**43**)



43

The title compound was prepared with 1,1-bis(4-fluorophenyl)prop-2-en-1-ol (49.2 mg, 0.20 mmol, 1.0 equiv.), *i*-C$_3$F$_7$-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and TMP (50.6 µL, 0.30 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (73.7 mg, 89 %).

R$_f$ = 0.67 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.01 - 7.90 (m, 2H), 7.33 - 7.19 (m, 2H), 7.06 (t, *J* = 8.6 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 4.97 (dd, *J* = 9.2, 3.0 Hz, 1H), 3.58 (td, *J* = 15.6, 14.9, 9.1 Hz, 1H), 2.40 - 2.26 (m, 1H).

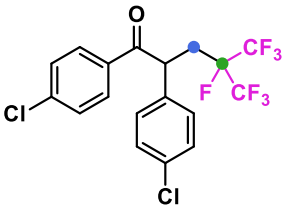
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 194.85, 165.97 (d, *J* = 255.9 Hz), 162.44 (d, *J* = 247.7 Hz), 133.66 (d, *J* = 3.4 Hz), 131.85 (d, *J* = 3.2 Hz), 131.45 (d, *J* = 9.5 Hz), 129.55 (d, *J* = 8.2 Hz), 121.05 (qt, *J* = 286.9, 29.2 Hz, CF($\underline{C}$F$_3$)$_2$), 116.62 (d, *J* = 21.7 Hz), 116.00 (d, *J* = 22.0 Hz), 92.73 - 89.42 (m, $\underline{C}$F(CF$_3$)$_2$), 45.76 (d, *J* = 5.4 Hz), 31.71 (d, *J* = 18.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.85 (dq, *J* = 41.5, 8.6 Hz, CF(C$\underline{F}$$_3$)$_2$, 6F), -104.12 (s, 1F), -113.60 (s, 1F), -184.45 (ddh, *J* = 21.3, 14.3, 7.1 Hz, C$\underline{F}$(CF$_3$)$_2$, 1F).

GC-MS: 414

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{18}H_{12}F_9O^+$: 415.0739. Found: 415.0730.

4,5,5,5-Tetrafluoro-4-trifluoromethyl-1,2-bis(4-chlorophenyl)butan-1-one (**44**)



44

The title compound was prepared with 1,1-bis(4-chlorophenyl)prop-2-en-1-ol (55.6 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and TMP (50.6 µL, 0.30 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (83.8 mg, 94 %).

R_f = 0.61 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.85 (d, *J* = 5.6 Hz, 2H), 7.37 (d, *J* = 5.6 Hz, 2H), 7.29 (d, *J* = 5.6 Hz, 2H), 7.19 (d, *J* = 5.6 Hz, 2H), 4.93 (d, *J* = 8.8 Hz, 1H), 3.56 (m, 1H), 2.41 - 2.22 (m, 1H).

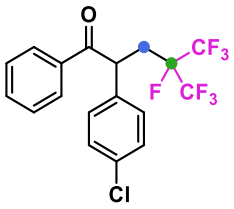
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 195.01, 140.25, 136.17, 134.32, 133.68, 130.15, 129.90, 129.23, 121.00 (qt, *J* = 285.9, 29.0 Hz, CF($\underline{C}F_3$)$_2$), 92.50 - 89.39 (m, $\underline{C}F(CF_3)_2$), 45.95 (d, *J* = 4.7 Hz), 31.52 (d, *J* = 18.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.74 (qq, *J* = 29.2, 8.2 Hz, CF($C\underline{F}_3$)$_2$, 6F), -184.34 (dqt, *J* = 21.2, 14.4, 7.1 Hz, $C\underline{F}(CF_3)_2$, 1F).

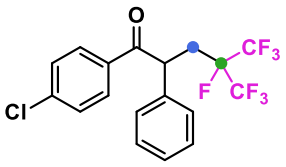
GC-MS: 446

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{18}H_{12}Cl_2F_7O^+$: 447.0148. Found: 447.0150.

4,5,5,5-Tetrafluoro-4-trifluoromethyl-1-phenyl-2-(4-chlorophenyl)-butan-1-one (**45**) and 4,5,5,5-tetra-fluoro-4-trifluoromethyl-2-phenyl-1-(4-chlorophenyl)-butan-1-one (**45***)



45



45*

The title compound was prepared with 1-(4-chlorophenyl)-1-phenyl-2-propenol (48.8 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and TMP (50.6 µL, 0.30 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (64.3 mg, 78 %). NMR yield ratio **45**/**45*** = 3.4/1.

R_f = 0.62 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.95 - 7.85 (m, 2H), 7.62 - 7.10 (m, 7H), 5.07 - 4.91 (m, 1H), 3.72 - 3.49 (m, 1H), 2.44 - 2.26 (m, 1H).

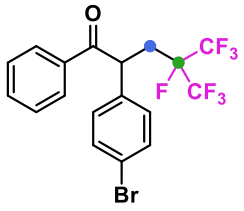
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 196.18, 195.26, 139.95, 137.79, 136.54, 135.42, 134.11, 133.97, 133.64, 130.20, 129.77, 129.70, 129.31, 129.11, 128.85, 128.78, 128.17, 127.87, 121.06 (qt, *J* = 286.4, 27.3 Hz, CF($\underline{C}F_3$)$_2$), 92.84 - 89.28 (m, $\underline{C}F(CF_3)_2$), 46.73, 31.68, 31.50.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.31 - -76.97 (m, CF($C\underline{F}_3$)$_2$, 6F), -184.05 - -184.60 (m, $C\underline{F}(CF_3)_2$, 1F).

GC-MS: 412

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{18}H_{13}ClF_7O^+$: 413.0538. Found: 413.0544.

4,5,5,5-Tetrafluoro-4-trifluoromethyl-1-phenyl-2-(4-bromophenyl)-butan-1-one (**46**)



46

The title compound was prepared with 1-(4-bromophenyl)-1-phenyl-2-propenol (57.6 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and TMP (50.6 μL, 0.30 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a white solid (64.7 mg, 71 %).

R_f = 0.64 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.92 (d, *J* = 7.1 Hz, 2H), 7.55 - 7.48 (m, 1H), 7.48 - 7.33 (m, 4H), 7.16 (d, *J* = 8.5 Hz, 2H), 4.99 (dd, *J* = 9.0, 3.1 Hz, 1H), 3.57 (td, *J* = 15.2, 14.4, 9.0 Hz, 1H), 2.40 - 2.26 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 196.12, 137.06, 135.39, 133.68, 132.75, 129.64, 128.88, 128.78, 122.20, 121.04 (qt, *J* = 286.4, 25.9 Hz, CF($\underline{C}F_3$)$_2$), 92.81 - 89.16 (m, $\underline{C}F(CF_3)_2$), 45.95, 31.51 (d, *J* = 18.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.72 (dq, *J* = 60.2, 8.6 Hz, CF($C\underline{F}_3$)$_2$, 6F), -184.30 (ddq, *J* = 29.2, 14.3, 7.1 Hz, $C\underline{F}(CF_3)_2$, 1F).

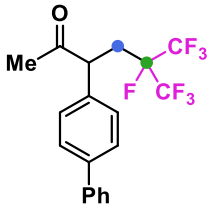
GC-MS: 456

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{18}H_{13}BrF_7O^+$: 457.0033. Found: 457.0039.

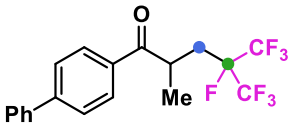
Melt point: 63.2 - 63.9 ℃.

5,6,6,6-Tetrafluoro-5-trifluoromethyl-2-(4-biphenyl)-penta-2-one (**47**) and 4,5,5,5-Tetrafluoro-4-

trifluoromethyl-1-(4-biphenyl)-2-methyl-butan-1-one (**47***)



47



47*

The title compound was prepared with 1-methyl-1-biphenyl-2-propenol (44.8 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and TMP (50.6 µL, 0.30 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (68.9 mg, 88 %). NMR yield ratio **47**/**47*** = 6.3/1.

R_f = 0.60 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.69 (s), 7.66 - 7.52 (m), 7.48 - 7.41 (m), 7.39 - 7.35 (m), 7.39 - 7.30 (m), 7.28 (d, *J* = 8.3 Hz), 4.15 (dd, *J* = 8.3, 3.6 Hz, 1H), 3.44 (td, *J* = 15.8, 7.7 Hz, 1H), 2.34 - 2.20 (m, 1H), 2.15 (s, 3H).

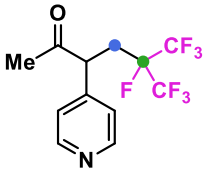
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 204.43, 204.25, 143.05, 141.26, 140.29, 139.62, 137.50, 136.49, 128.96, 128.68, 128.44, 128.32, 128.21, 127.73, 127.55, 127.14, 120.86 (q, *J* = 286.4, CF($\underline{C}F_3$)$_2$), 93.06 - 89.20 (m, $\underline{C}F(CF_3)_2$), 51.70 (d, *J* = 4.8 Hz), 30.23 (d, *J* = 19.1 Hz), 28.75.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.54 (d, *J* = 6.6 Hz, CF($C\underline{F}_3$)$_2$), -76.79 (dp, *J* = 103.7, 8.8 Hz, CF($C\underline{F}_3$)$_2$), -182.20 - -182.40 (m, $C\underline{F}(CF_3)_2$), -184.43 - -184.75 (m, $C\underline{F}(CF_3)_2$).

GC-MS: 392

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{19}H_{16}F_7O^+$: 393.1084. Found: 393.1084.

5,6,6,6-Tetrafluoro-5-trifluoromethyl-2-(pyridin-4-yl)-penta-2-one (**48**)



48

The title compound was prepared with 2-(pyridin-4-yl)but-3-en-2-ol (29.8 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and TMP (50.6 µL, 0.30 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a pale-yellow oil (34.9 mg, 55 %).

R_f = 0.42 (ethyl acetate: petroleum ether, 1:2 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.39 (d, *J* = 7.9 Hz, 2H), 7.84 (d, *J* = 7.9 Hz, 2H), 4.26 (dd, *J* = 8.4, 3.6 Hz, 1H), 3.54 (td, *J* = 17.3, 16.5, 9.1 Hz, 1H), 2.47 - 2.32 (m, 1H), 2.27 (s, 3H).

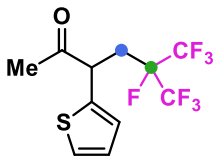
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 194.70, 136.54, 131.34, 131.09, 121.00 (qt, *J* = 285.9, 28.2 Hz, CF($\underline{C}$F$_3$)$_2$), 92.84 - 89.26 (m, $\underline{C}$F(CF$_3$)$_2$), 47.46, 33.40 (d, *J* = 18.8 Hz), 28.18.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -73.81 (d, *J* = 6.9 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -172.05 (m, C$\underline{F}$(CF$_3$)$_2$, 1F).

GC-MS: 317

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{12}H_{11}F_7NO^+$: 318.0723. Found: 318.0723.

5,6,6,6-Tetrafluoro-5-trifluoromethyl-2-(thiophen-2-yl)-penta-2-one (**49**)



49

The title compound was prepared with 2-(thiophen-2-yl)but-3-en-2-ol (30.8 mg, 0.20 mmol, 1.0 equiv.), *i*-C$_3$F$_7$-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and TMP (50.6 µL, 0.30 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (39.9 mg, 62 %).

R$_f$ = 0.57 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.39 - 7.26 (m, 1H), 7.03 - 6.85 (m, 2H), 4.86 (d, *J* = 11.5 Hz, 1H), 3.65 - 3.39 (m, 1H), 2.40 - 2.16 (m, 1H), 1.90 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 193.91, 131.14, 130.03, 127.88, 121.15 (qt, *J* = 285.5, 8.6 Hz, CF($\underline{C}$F$_3$)$_2$), 113.28, 92.81 -89.41 (m, $\underline{C}$F(CF$_3$)$_2$), 44.89 (d, *J* = 5.0 Hz), 31.20 (d, *J* = 18.8 Hz), 28.12.

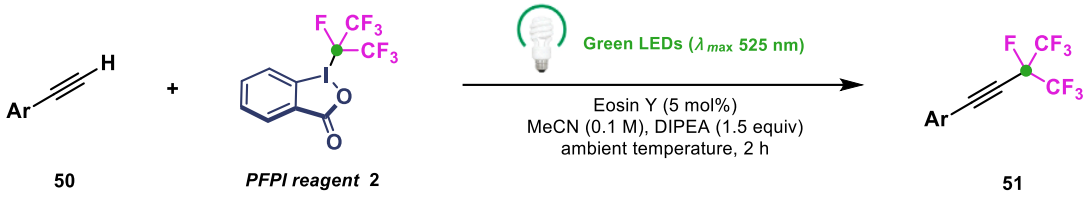
^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -77.04 (d, *J* = 7.8 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -184.73 (dp, *J* = 26.8, 7.7 Hz, C$\underline{F}$(CF$_3$)$_2$, 1F).

GC-MS: 322

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{11}H_{10}F_7OS^+$: 323.0335. Found: 323.0347.

Visible-light promoted isoperfluoropropylation of terminal alkynes

General procedure to access isoperfluoropropylated products.

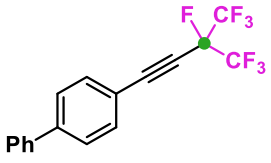


Scheme S21. General procedure to access isoperfluoropropylated products.

Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, terminal alkynes (**50**, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) were dissolved in dry MeCN (2.0 mL, 0.1 M). Subsequently, DIPEA (52.2 μL, 0.30 mmol, 1.5 equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at green light (525 nm) for 2 h, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, the reaction was quenched with 10 mL 5% $NaHCO_3$ aqueous solution, then extracted with DCM (3 x 10 mL). The combined organic phase was dried with anhydrous Na_2SO_4 and concentrated under vacuum. The residue was further purified by column chromatography to afford corresponding isoperfluoropropylated products **51**, which was characterized by GC-MS analysis, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectroscopy and HRMS.

Characterization of Products

4-(3,4,4,4-Tetrafluoro-3-(trifluoromethyl)but-1-yn-1-yl)-1,1'-biphenyl (**52**)



52

The title compound was prepared with 4-ethynyl-1,1'-biphenyl (35.5 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 μL, 0.3 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (33.2 mg, 48 %).

R_f = 0.69 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.67 - 7.56 (m), 7.47 (t, *J* = 7.5 Hz), 7.43 - 7.36 (m).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 143.92, 139.79, 133.13 (d, *J* = 2.9 Hz), 129.09,

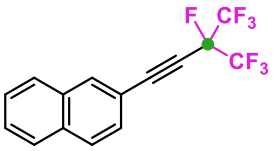
128.34, 127.37, 127.24, 119.48 (qd, *J* = 287.3, 29.4 Hz, CF(<u>*C*</u>F_3)$_2$), 117.60 (d, *J* = 4.0 Hz), 93.66 (d, *J* = 9.0 Hz), 73.62 (d, *J* = 26.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.77 (d, *J* = 11.6 Hz, CF(C<u>*F*</u>$_3$)$_2$, 6F), -165.19 (hept, *J* = 11.0 Hz, C<u>*F*</u>(CF$_3$)$_2$, 1F).

GC-MS: 346

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{17}H_{10}F_7^+$: 347.0665. Found: 347.0668.

2-(3,4,4,4-Tetrafluoro-3-(trifluoromethyl)but-1-yn-1-yl)naphthalene (**53**)



53

The title compound was prepared with 2-ethynylnaphthalene (30.4 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.30 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (39.0 mg, 61 %).

R_f = 0.72 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 8.13 (s, 1H), 7.84 (d, *J* = 9.0 Hz, 3H), 7.65 - 7.51 (m, 3H).

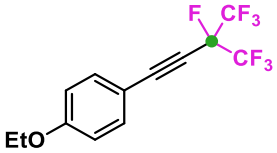
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 134.03, 133.94, 133.91, 132.60, 128.61, 128.22, 128.19, 128.01, 127.82, 127.25, 119.48 (dd, *J* = 289.6, 29.5 Hz, CF(<u>*C*</u>F_3)$_2$), 116.02 (d, *J* = 4.1 Hz), 94.08 (d, *J* = 8.3 Hz), 86.42 - 82.14 (m, <u>*C*</u>F(CF$_3$)$_2$).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.70 (d, *J* = 11.0 Hz, CF(C<u>*F*</u>$_3$)$_2$, 6F), -165.11 (hept, *J* = 10.9 Hz, C<u>*F*</u>(CF$_3$)$_2$, 1F).

GC-MS: 320

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{15}H_8F_7^+$: 321.0509. Found: 321.0501.

4-(3,4,4,4-Tetrafluoro-3-(trifluoromethyl)but-1-yn-1-yl)phenetole (**54**)



54

The title compound was prepared with 4-ethoxyphenylacetylene (29.2 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.30 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a pale-yellow oil (25.2 mg, 40 %).

R_f = 0.55 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.48 (d, *J* = 7.0 Hz, 2H), 6.87 (d, *J* = 6.9 Hz, 2H), 4.05 (q, *J* = 7.0 Hz, 2H), 1.42 (t, *J* = 6.9 Hz, 3H).

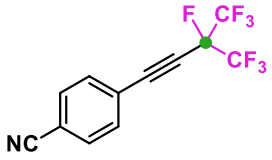
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 161.14, 134.41, 119.50 (qd, *J* = 287.5, 29.0 Hz, CF($\underline{C}F_3$)$_2$), 114.82, 110.53 (d, *J* = 3.8 Hz), 94.28 (d, *J* = 8.7 Hz), 86.91 - 83.96 (m, $\underline{C}$F(CF$_3$)$_2$), 72.08 (d, *J* = 26.8 Hz), 63.80, 14.65.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.89 (d, *J* = 11.6 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -164.22 (hept, *J* = 11.0 Hz, C$\underline{F}$(CF$_3$)$_2$, 1F).

GC-MS: 314

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{13}H_{10}F_7O^+$: 315.0614. Found: 315.0617.

4-(3,4,4,4-Tetrafluoro-3-(trifluoromethyl)but-1-yn-1-yl)benzonitrile (**55**)



55

The title compound was prepared with 4-cyanophenylacetylene (25.4 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.30 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (45.4 mg, 77 %).

R_f = 0.61 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.73 - 7.64 (m, 4H).

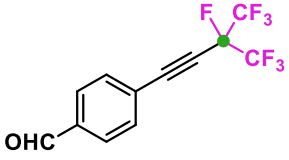
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 133.20 (d, *J* = 2.9 Hz), 132.40, 123.43 (d, *J* = 3.8 Hz), 119.24 (qd, *J* = 285.9, 29.2 Hz, CF($\underline{C}F_3$)$_2$), 117.71, 114.73, 91.08 (d, *J* = 8.3 Hz), 86.81 - 83.46 (m, $\underline{C}$F(CF$_3$)$_2$), 85.10.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.57 (d, *J* = 10.9 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -166.88 (hept, *J* = 10.7 Hz, C$\underline{F}$(CF$_3$)$_2$, 1F).

GC-MS: 295

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{12}H_5F_7N^+$: 296.0305. Found: 296.0300.

4-(3,4,4,4-Tetrafluoro-3-(trifluoromethyl)but-1-yn-1-yl)benzaldehyde (**56**)



56

The title compound was prepared with 4-ethynylbenzaldehyde (26.0 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and DIPEA (52.2 µL, 0.30 mmol, 1.5 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (37.0 mg, 62 %).

R_f = 0.34 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 10.02 (s, 1H), 8.22 (d, *J* = 6.7 Hz, 2H), 7.67 (d, *J* = 6.7 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 191.55, 137.12, 130.28, 129.19, 128.33, 120.24 (qd, *J* = 284.5, 27.5 Hz, CF($\underline{C}F_3$)$_2$), 117.15 (d, *J* = 29.1 Hz), 89.12 (d, *J* = 8.2 Hz).

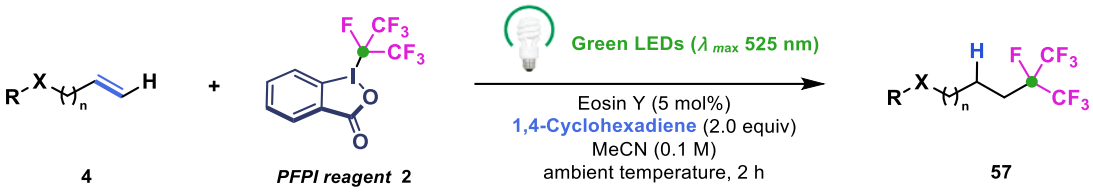
^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.91 (d, *J* = 6.8 Hz, CF($C\underline{F}_3$)$_2$, 6F), -182.14 (hept, *J* = 7.7, 7.1 Hz, $C\underline{F}(CF_3)_2$, 1F).

GC-MS: 298

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{12}H_6F_7O^+$: 299.0301. Found: 299.0300.

Visible-light promoted hydroisoperfluoropropylation of terminal alkenes

General procedure to access hydroisoperfluoropropylated products.

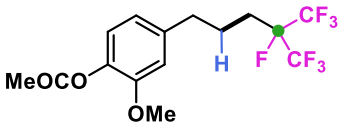


Scheme S22. General procedure to access hydroisoperfluoropropylated products.

Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, terminal alkenes (**4**, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) were dissolved in dry MeCN (2.0 mL, 0.1 M). Subsequently, 1,4-cyclohexadiene (37.8 μL, 0.40 mmol, 2.0 equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at green light (525 nm) for 2 h, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, the reaction was quenched with 10 mL 5% $NaHCO_3$ aqueous solution, then extracted with DCM (3 x 10 mL). The combined organic phase was dried with anhydrous Na_2SO_4 and concentrated under vacuum. The residue was further purified by column chromatography to afford corresponding isoperfluoropropylated products **57**, which was characterized by GC-MS analysis, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectroscopy and HRMS.

Characterization of Products

2-Methoxy-4-(4,5,5,5-tetrafluoro-4-(trifluoromethyl)pentyl)phenyl acetate (**58**)



58

The title compound was prepared with eugenol acetate (41.2 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and 1,4-cyclohexadiene (37.8 μL, 0.40 mmol, 2.0 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (69.9 mg, 93 %).

R_f = 0.44 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 6.96 (d, *J* = 7.9 Hz, 1H), 6.83 - 6.71 (m, 2H), 3.82 (s, 3H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.30 (s, 3H), 2.17 - 2.01 (m, 2H), 1.91 (p, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 169.26, 151.14, 139.47, 138.30, 122.83, 121.16

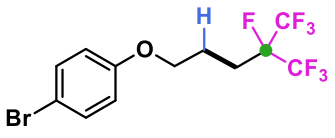
(qd, *J* = 284.5, 27.3 Hz, CF(*C*F_3)$_2$), 120.46, 112.46, 93.55 - 89.85 (m, *C*F(CF_3)$_2$), 55.86, 35.54, 28.52 (d, *J* = 20.6 Hz), 23.06, 20.67.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.29 (d, *J* = 6.8 Hz, CF(C*F*$_3$)$_2$, 6F), -183.61 (dtp, *J* = 20.4, 13.8, 7.0 Hz, C*F*(CF_3)$_2$, 1F).

GC-MS: 376

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{15}H_{16}F_7O_3^+$: 377.0982. Found: 377.0977.

1-Bromo-4-((4,5,5,5-tetrafluoro-4-(trifluoromethyl)pentyl)oxy)benzene (**59**)



59

The title compound was prepared with 1-bromo-4-(allyloxy)benzene (42.4 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and 1,4-cyclohexadiene (37.8 µL, 0.40 mmol, 2.0 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (61.3 mg, 80 %).

R_f = 0.61 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.37 (d, *J* = 8.9 Hz, 2H), 6.76 (d, *J* = 9.0 Hz, 2H), 3.96 (t, *J* = 5.8 Hz, 2H), 2.37 - 2.23 (m, 2H), 2.06 (dt, *J* = 16.9, 6.0 Hz, 2H).

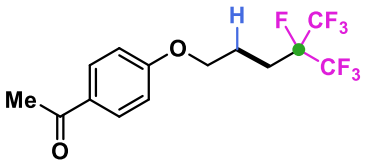
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 157.75, 132.43, 121.16 (qd, *J* = 287.2, 27.5 Hz, CF(*C*F_3)$_2$), 116.31, 113.37, 93.56 - 89.94 (m, *C*F(CF_3)$_2$), 66.95, 26.00 (d, *J* = 20.7 Hz), 21.81.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.33 (d, *J* = 6.9 Hz, CF(C*F*$_3$)$_2$, 6F), -184.22 (ddh, *J* = 26.9, 13.2, 6.6 Hz, C*F*(CF_3)$_2$, 1F).

GC-MS: 382

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{12}H_{11}BrF_7O^+$: 382.9876. Found: 382.9879.

1-(4-((4,5,5,5-Tetrafluoro-4-(trifluoromethyl)pentyl)oxy)phenyl)ethan-1-one (**60**)



60

The title compound was prepared with 1-(4-(allyloxy)phenyl)ethanone (35.2 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and 1,4-cyclohexadiene (37.8 µL, 0.40 mmol, 2.0 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (59.5 mg, 86 %).

R_f = 0.57 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.93 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 7.0 Hz, 2H), 4.07 (t, *J* = 5.8 Hz, 2H), 2.57 (s, 3H), 2.38 - 2.24 (m, 2H), 2.09 (dq, *J* = 11.9, 5.8 Hz, 2H).

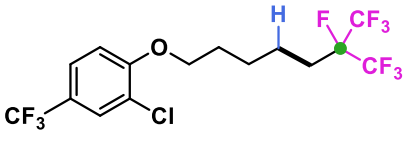
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 197.95, 162.75, 130.94, 121.13 (qd, *J* = 286.9, 27.6 Hz, CF($\underline{C}F_3$)$_2$), 114.25, 93.51 - 89.84 (m, $\underline{C}F(CF_3)_2$), 66.95, 26.29, 25.95 (d, *J* = 20.6 Hz), 21.73.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.32 (d, *J* = 6.6 Hz, CF($C\underline{F}_3$)$_2$, 6F), -184.24 (dtq, *J* = 20.1, 13.5, 6.8 Hz, $C\underline{F}(CF_3)_2$, 1F).

GC-MS: 346

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{14}H_{14}F_7O_2^+$: 347.0877. Found: 347.0865.

2-Chloro-1-((6,7,7,7-tetrafluoro-6-(trifluoromethyl)heptyl)oxy)-4-(trifluoromethyl)benzene (**61**)



61

The title compound was prepared with 1-chloro-2-(pent-4-en-1-yloxy)-5-trifluromethylbenzene (52.8 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and 1,4-cyclohexadiene (37.8 µL, 0.40 mmol, 2.0 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (82.4 mg, 95 %).

R_f = 0.65 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.62 (d, *J* = 2.4 Hz, 1H), 7.46 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.94 (d, *J* = 8.6 Hz, 1H), 4.07 (t, *J* = 6.2 Hz, 2H), 2.19 - 2.04 (m, 1H), 1.95 - 1.85 (m, 1H), 1.75 - 1.52 (m, 2H).

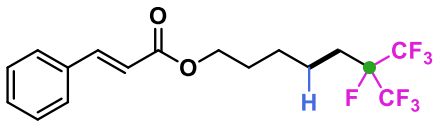
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 157.05, 137.42, 127.54 (d, *J* = 3.8 Hz), 125.11 (d, *J* = 3.8 Hz), 123.40, 123.07 (q, *J* = 135.6 Hz), 121.20 (qd, *J* = 285.5, 27.8 Hz, CF($\underline{C}F_3$)$_2$), 112.55, 92.56 - 89.11 (m, $\underline{C}F(CF_3)_2$), 68.86, 28.99 (d, *J* = 20.7 Hz), 28.59, 26.25, 21.29 (d, *J* = 5.1 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -61.81 (s, 3F), -76.42 (d, *J* = 6.7 Hz, CF($C\underline{F}_3$)$_2$, 6F), -183.82 (tdp, *J* = 20.3, 13.8, 7.1, 6.7 Hz, $C\underline{F}(CF_3)_2$, 1F).

GC-MS: 434

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{15}H_{14}ClF_{10}O^+$: 435.0568. Found: 435.0565.

6,7,7,7-Tetrafluoro-6-(trifluoromethyl)heptyl cinnamate (**62**)



62

The title compound was prepared with pent-4-en-1-yl cinnamate (43.2 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and 1,4-cyclohexadiene (37.8 µL, 0.40 mmol, 2.0 equiv.) in MeCN (2.0 mL, 0.1 M). The product was obtained as a colorless oil (67.2 mg, 87 %).

R_f = 0.48 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.69 (d, *J* = 16.1 Hz, 1H), 7.54 - 7.49 (m, 2H), 7.38 (t, *J* = 3.4 Hz, 3H), 6.43 (d, *J* = 16.3 Hz, 1H), 4.22 (d, *J* = 2.8 Hz, 2H), 2.08 (dt, *J* = 17.5, 7.0 Hz, 2H), 1.77 - 1.72 (m, 2H), 1.68 - 1.58 (m, 2H), 1.53 - 1.42 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 167.09, 144.94, 134.47, 130.40, 128.98, 128.16, 121.19 (qd, *J* = 286.8, 27.4 Hz, CF($\underline{C}F_3$)$_2$), 118.08, 93.42 - 90.01 (m, $\underline{C}F(CF_3)_2$), 64.21, 29.00 (d, *J* = 20.6 Hz), 28.40, 26.30, 21.26.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.28 (d, *J* = 6.1 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -183.68 (dq, *J* = 21.2, 13.7 Hz, C$\underline{F}(CF_3)_2$, 1F).

GC-MS: 386

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{17}H_{18}F_7O_2^+$: 387.1190. Found: 387.1181.

Mechanistic investigations

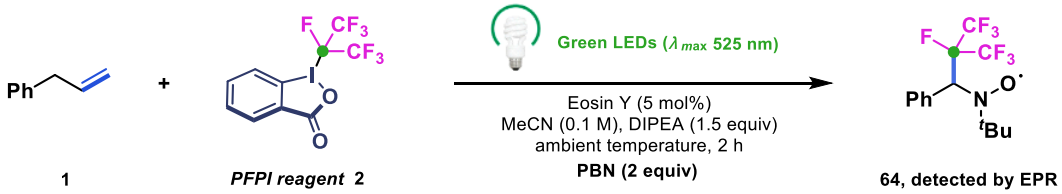
Radical trap experiment

Scheme S23. Radical trap reaction of TEMPO.

Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, allyl benzene (**1**, 26.5 μL, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (6.4 mg, 5 mol%) and 2, 2, 6, 6-tetramethylpiperidinyl-1-oxide (TEMPO, 62.4 mg, 0.40 mmol, 2.0 equiv.) were dissolved in dry MeCN (2 mL). Subsequently, DIPEA (52.2 μL, 0.30 mmol, 1.5 equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at green LEDs (525 nm) for 2 h, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, the crude reaction mixture was diluted with EtOAc and filtered through a plug of silica then subjected to LC-HRMS analysis.

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{12}H_{19}F_7NO^+$: 326.1349. Found: 326.1357.

Electron paramagnetic resonance (EPR) experiment



Scheme S24. Radical trap reaction of PBN.

Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, allyl benzene (**1**, 26.5 μL, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.40 mmol, 1.5 equiv.), Eosin Y (6.4 mg, 5.0 mol%) and phenyl *tert*-butyl nitrone (PBN, 70.8 mg, 0.40 mmol, 2.0 equiv.) were dissolved in dry MeCN (2 mL). Subsequently, DIPEA (52.2 μL, 0.40 mmol, 2.0 equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at green LEDs (525 nm) for 2 h, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, the crude reaction mixture was filtered through a plug of silica then analyzed by EPR. The EPR showed a EPR signal of nitroxide (g = 2.0063, a^N= 14.76, a^H= 2.08) which indicated that the isoperfluoropropyl group must be substituted at the β-carbon atom of nitroxide. The hyperfine coupling constants could not be calculated due to the poor resolution of the spectrum.

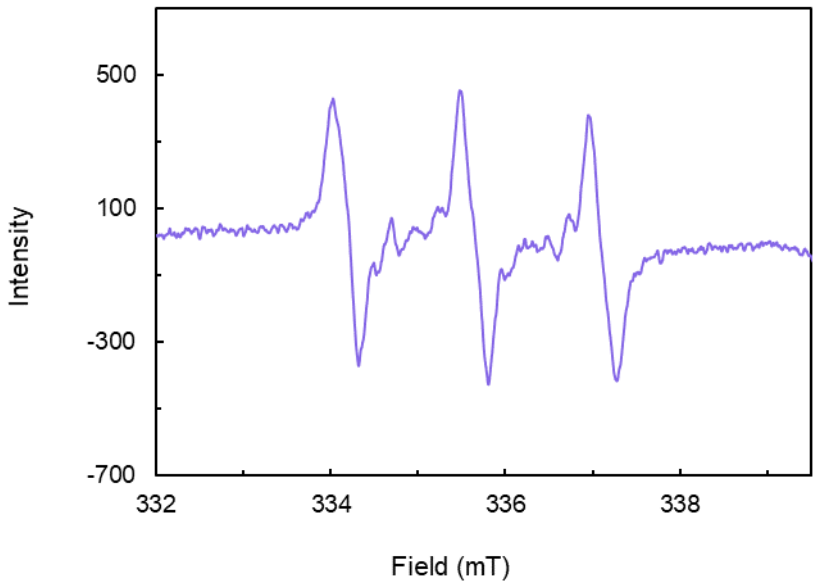
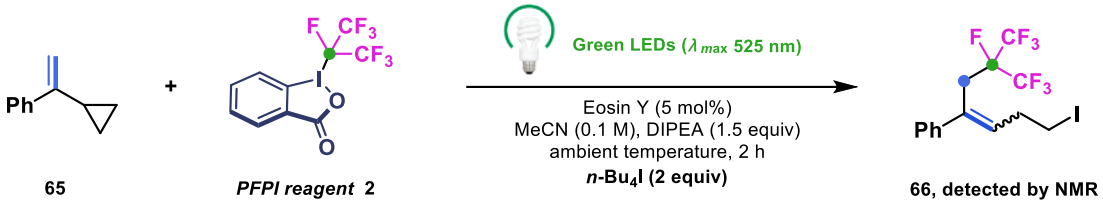


Figure S2. The EPR spectrum of *N-O* radical **64**.

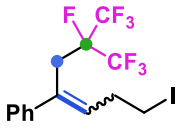
Radical clock experiment



Scheme S25. Radical clock reaction of cyclopropyl styrene derivatives.

Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, cyclopropyl styrene (**65**, 28.8 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (5 mol%, 6.4 mg) and *n*-Bu_4NI (147.8 mg, 0.40 mmol, 2.0 equiv.) were dissolved in dry MeCN (2.0 mL, 0.1 M). Subsequently, DIPEA (52.2 μL, 0.3 mmol, 1.5 equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at green light (525 nm) for 2 h, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, the reaction was quenched with 10 mL 5% $NaHCO_3$ aqueous solution, then extracted with DCM (3 x 10 mL). The combined organic phase was dried with anhydrous Na_2SO_4 and concentrated under vacuum. The residue was further purified by column chromatography to afford corresponding isoperfluoropropylated product **66**, which was characterized by GC-MS analysis, ^1H NMR, ^{13}C NMR, ^{19}F NMR spectroscopy and HRMS.

6-iodide-1,1,1,2-Tetrafluoro-2-(trifluoromethyl)-2-phenylhept-2-ene (**66**)



66

The product was obtained as a colorless oil (67.8 mg, 77 %).

R_f = 0.78 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.40 - 7.26 (m, 5H), 5.83 (t, *J* = 7.3 Hz, 1H), 3.37 (d, *J* = 22.0 Hz, 2H), 3.24 (t, *J* = 6.9 Hz, 2H), 2.83 (q, *J* = 7.0 Hz, 2H).

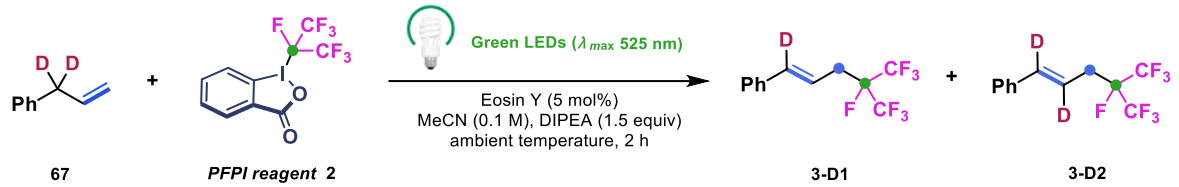
^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 142.10, 135.04, 132.24, 128.43, 127.65, 126.55, 120.87 (qd, *J* = 287.4, 286.6, 27.9 Hz, CF($\underline{C}F_3$)$_2$), 93.71 - 89.86 (m, $\underline{C}F(CF_3)_2$), 33.06, 28.72 (d, *J* = 19.4 Hz), 4.01.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.07 (d, *J* = 6.7 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -182.22 (tdp, *J* = 21.7, 14.1, 7.2 Hz, C$\underline{F}$(CF$_3$)$_2$, 1F).

GC-MS: 440

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{14}H_{13}F_7I^+$: 440.9945. Found: 440.9939.

Deuterium-labeling experiment



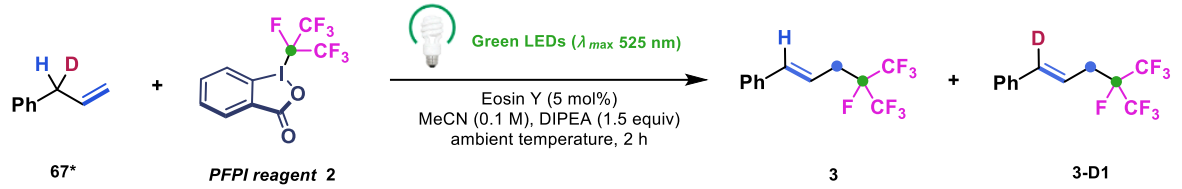
Scheme S26. Deuterium-labeling experiment of α-deuterated allyl benzene.

Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, α-deuterated allyl benzene (**67**, 24.0 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.) and Eosin Y (6.4 mg, 5 mol%) were dissolved in dry MeCN (2 mL). Subsequently, DIPEA (52.2 μL, 0.30 mmol, 1.5 equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at green LEDs (525 nm) for 2 h, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, 10 μL of *n*-dodecane was added as an internal standard. The crude reaction mixture was diluted with EtOAc and filtered through a plug of silica then subjected to GC-MS analysis.

GC-MS: 287; GC yield 74%, *n*-dodecane as internal standard.

GC-MS: 288; GC yield <1%, *n*-dodecane as internal standard.

Isotopic (H/D) kinetic experiment

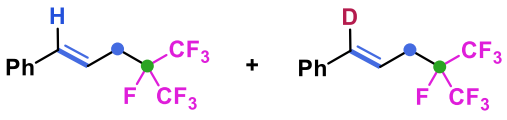


Scheme S27. Isotopic H/D kinetic experiment

Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, α-deuterated allyl benzene (**67***, 23.8 mg, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.) and Eosin Y (6.4 mg, 5 mol%) were dissolved in dry MeCN (2 mL). Subsequently, DIPEA (52.2 μL, 0.30 mmol, 1.5 equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at green LEDs (525 nm) for 20 min - 2 h, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, 10 μL of 1,2-dibromoethane was added as an internal standard. The reaction was quenched with 10 mL 5% $NaHCO_3$ aqueous solution, then extracted with DCM (3 x 10 mL). The combined organic phase was dried with anhydrous Na_2SO_4 and concentrated under vacuum. The crude products subjected to NMR analysis. The yield was determined by ^{1}H NMR and average yields was obtained by measuring three times.

Entry	Time (min)	NMR yield of **3** (%)	NMR yield of **3D-1** (%)
1	20	17	13
2	40	29	20
3	60	36	27
4	80	41	31
5	100	45	33
6	120	47	36

Table S8. Photochemistry parameters screening



3 **3-D1** (Yield ratio, 47:36)

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.46 - 7.26 (m, 5H), 6.62 (d, *J* = 15.7 Hz, **0.57 H**), 6.15 (dt, *J* = 15.9, 7.5 Hz, 1H), 3.04 (dd, *J* = 20.0, 7.5 Hz, 2H).

GC-MS: 286 and 287.

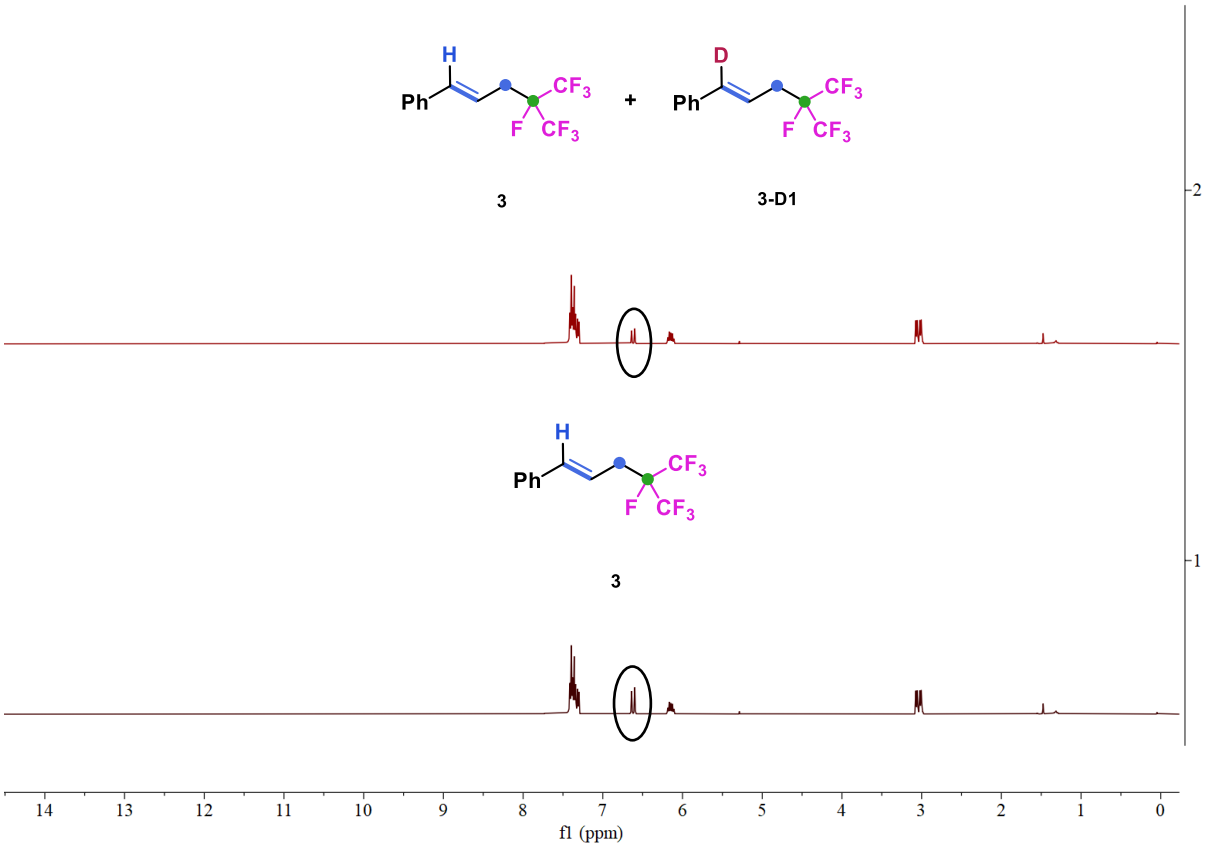


Figure S3. The ^{1}H NMR spectrum of **3** and **3-D1**.

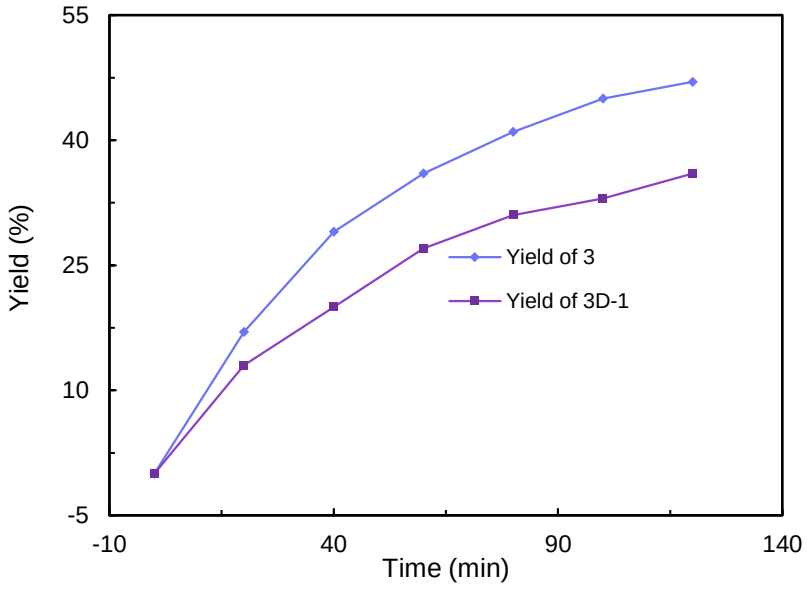
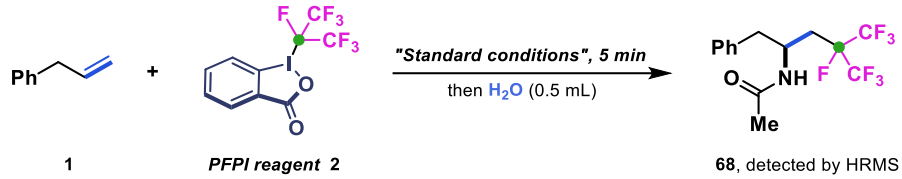


Figure S4. The reaction time-course curve.

Intermediate **D** trap experiment

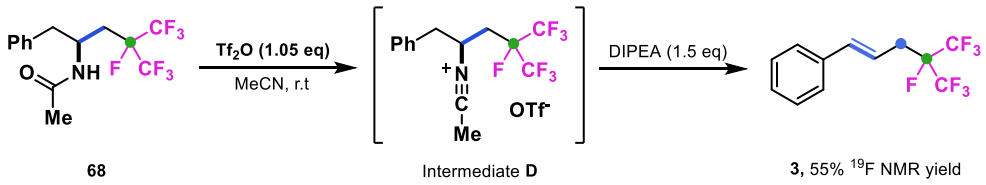


Scheme S28. Intermediate **D** trap experiment

Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, allyl benzene (**1**, 26.5 μL, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (6.4 mg, 5 mol%) were dissolved in dry MeCN (2 mL). Subsequently, DIPEA (52.2 μL, 0.30 mmol, 1.5 equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at green LEDs (525 nm) for 5 min, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, the crude reaction mixture was quenched by H_2O (0.5 mL) and stirred for another 1 h. Finally, the mixture was diluted with EtOAc and filtered through a plug of silica then subjected to LC-HRMS analysis.

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{14}H_{15}F_7NO^+$: 346.1036. Found: 346.1022.

Stoichiometric reactivity of Intermediate **D**



Scheme S29. Stoichiometric reactivity of Intermediate **D**

Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, amide (**68**, 34.5 mg, 0.10 mmol, 1.0 equiv.) were dissolved in dry MeCN (1 mL). Next, a solution of the triflic anhydride (0.105 mmol, 17.7μL, 1.05 equiv) in MeCN (1 mL) was added to the mixture at -40℃ and stirred for 10 min. Next, DIPEA (26.1 μL, 0.15 mmol, 1.5 equiv.) was added into the vial and stirred for another 1 h. Finally, 10 μL of benzotrifluoride was added as an internal standard and the reaction mixture was diluted with EtOAc. The crude reaction mixture was filtered through a plug of silica then subjected to ^{19}F NMR analysis.

Electrochemical studies[9]

Cyclic voltammetry (CV) experiments were conducted in a Schlenk tube that contained the substance dissolved in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in dry acetonitrile. A platinum wire working electrode and a platinum mesh counter electrode were used.

The voltage was measured via a Luggin capillary against an Ag/Ag^+ reference and was referenced externally against the ferrocene/ferrocenium ion pair. The scan rate used in each CV experiment is indicated case by case. The relevant parameters were controlled by a CHI660E electrochemical workstation.

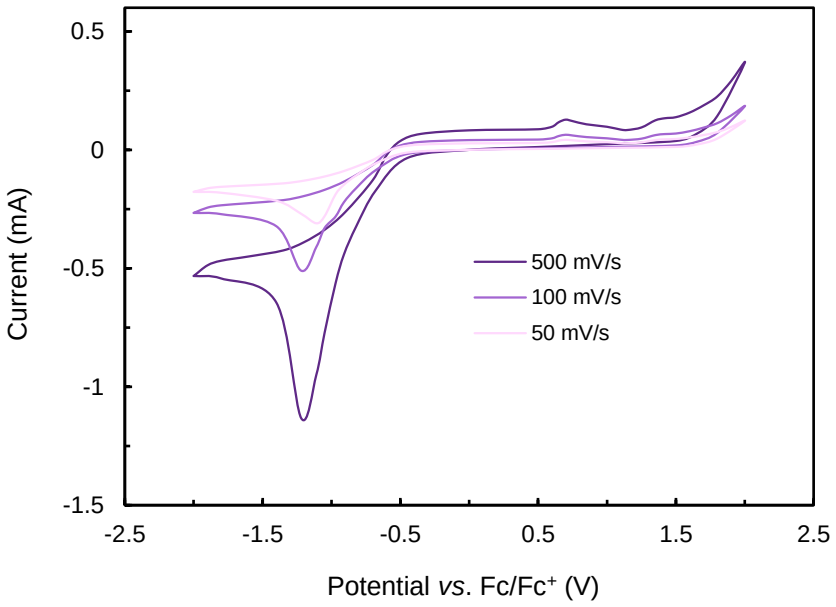


Figure S5. Cyclic voltammogram for PFPI reagent **2** [0.1M] in [0.1 M] $TBAPF_6$ in dry CH_3CN. Measurement started by oxidation from 0 to -2.0 V and finishing at 0 V. Platinum wire working electrode, Ag/Ag^+ reference electrode, platinum mesh counter electrode. One irreversible reduction observed at -1.22 V.

Absorption spectroscopy analysis.

The absorption profiles of the different reaction component were recorded in order to identify the photoactive species (Figure S6).

UV-visible absorption spectra were recorded on an UV-2700 spectrophotometer, equipped with a temperature control unit at 25 °C. The samples were measured in Starna Fluorometer Microquartz cuvettes (volume: 1.8 ml, path length: 10 mm) equipped with a PTFE-stopper. The spectra were aquired from 250 to 700 nm using 1.0 nm steps. All measurements were performed in MeCN at the following concentrations: allylbenzene, DIPEA and *i*-C_3F_7-iodine(III) reagent (1/100 of the reaction concentration); Eosin Y (0.1 mM, 1/10 of the reaction concentration).

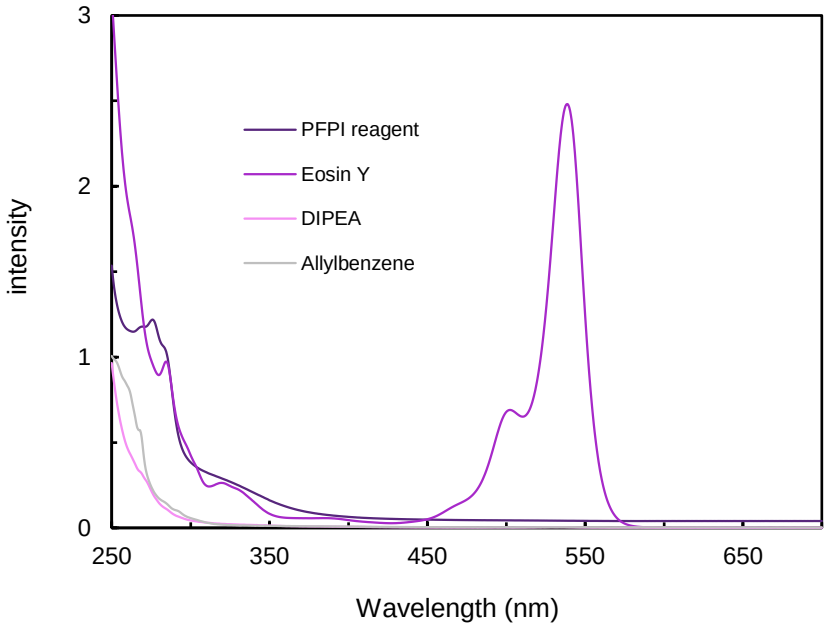
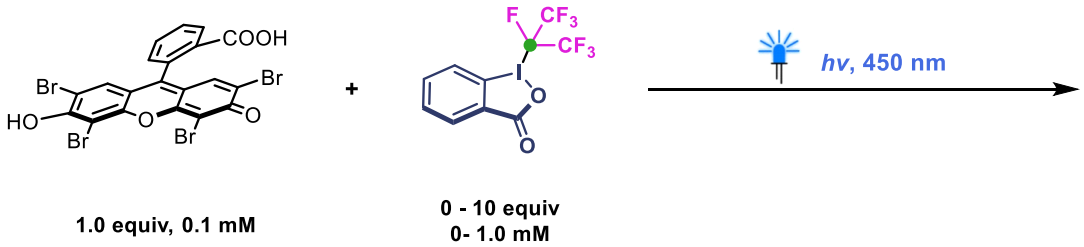


Figure S6. Optical absorption spectra of the reaction components, recorded in acetonitrile in 10 mm path quartz cuvettes using a Shimadzu UV-2700 spectrophotometer.

Stern-Volmer luminescence quenching experiments[10]

Fluorescence quenching studies were performed using a Hitachi F-4600 spectrofluorometer. In each experiment, Eosin Y and various concentrations of *i*-C_3F_7-iodine(III) reagent or DIPEA were combined in MeCN in Starna Fluorometer Microquartz cuvettes (volume: 1.8 ml, path length: 10 mm) equipped with a PTFE-stopper. The excitation wavelength was fixed at 450 nm (incident light slit regulated to 5 mm); the emission light was acquired from 500 nm to 800 nm (emission light slit regulated to 5 mm). A solvent blank was subtracted from all the measurements. The excitation wavelength was chosen in order to avoid saturation of the emission detector. The results shown in Figure S8-S11 indicate that *i*-C_3F_7-iodine(III) reagent quenches the excited state of Eosin Y and its emission. No change in the absorption spectra of the solution was observed during the addition of *i*-C_3F_7-iodine(III) reagent.



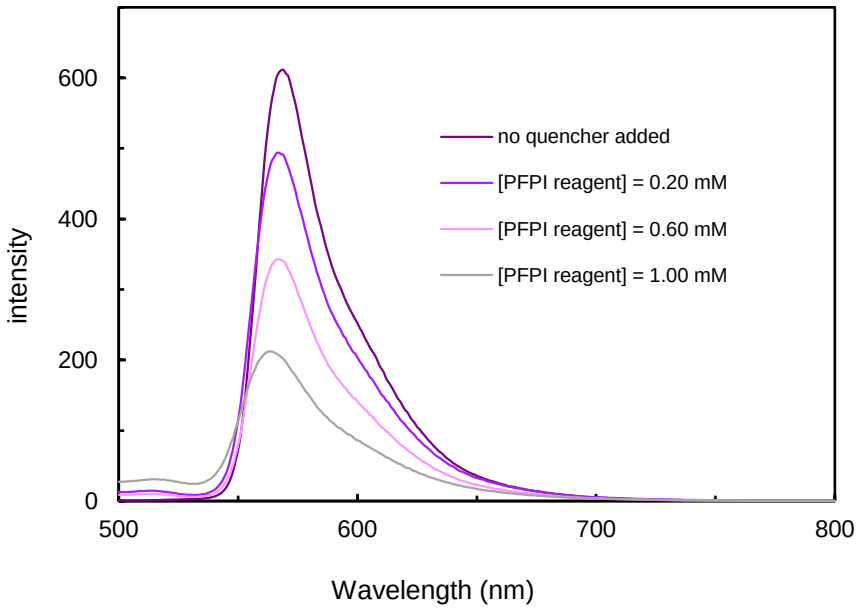


Figure S7. Quenching of the emission of Eosin Y*(0.10 mM in acetonitrile) in the presence of increasing amounts of *i*-C_3F_7-iodine(III) reagent.

The Stern-Volmer plot, reported in Figure S8, shows a linear correlation between the amounts of *i*-C_3F_7-iodine(III) reagent and the ratio I^0/I. On the basis of the following Equation 1, it is possible to calculate the Stern-Volmer constant K_{SV}.

$$I^0/I = 1 + K_{SV}[Q] \text{ [Eq. 1]}$$

We calculated a Stern-Volmer quenching constant of 1860.2 M^{-1}

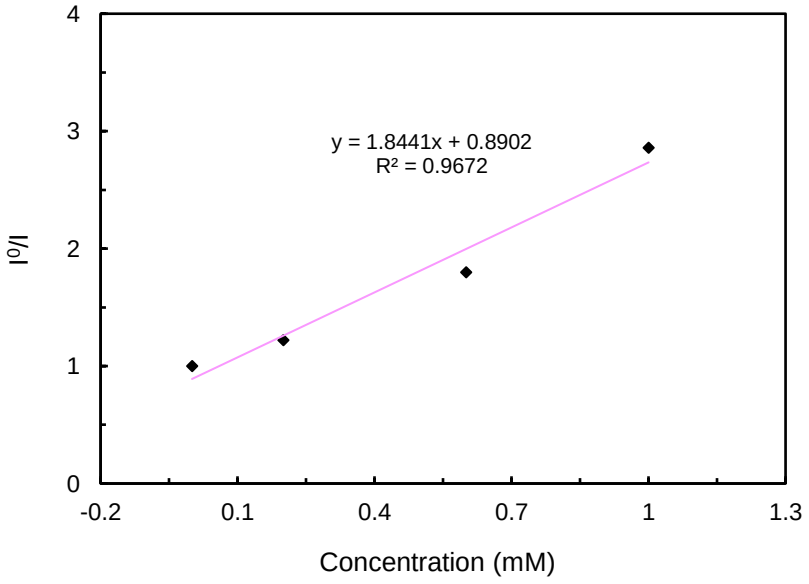
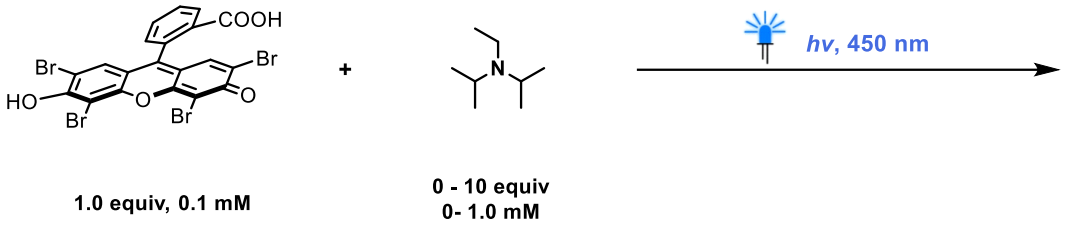


Figure S8. Stern-Volmer quenching plot using *i*-C_3F_7-iodine(III) reagent as a quencher.



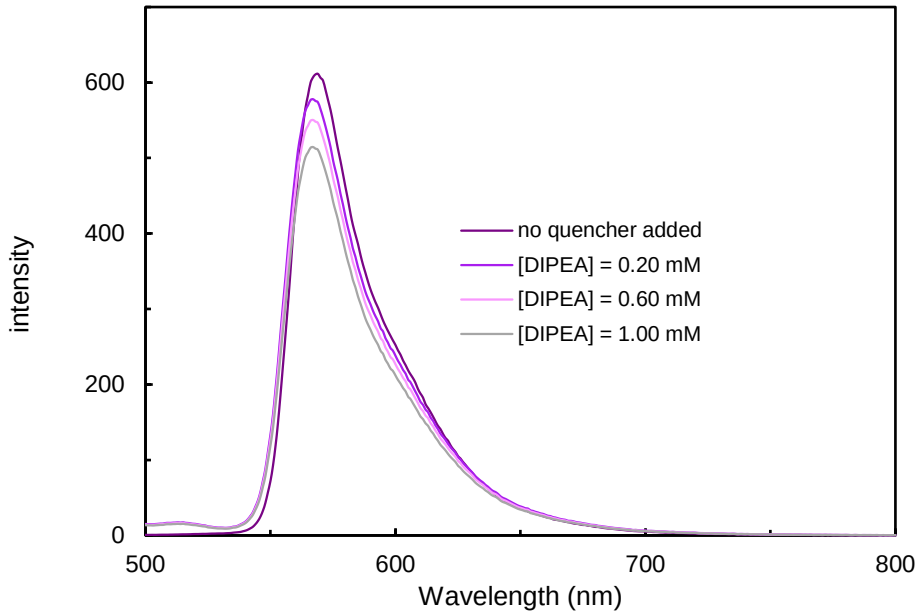


Figure S9. Quenching of the emission of Eosin Y*(0.10 mM in acetonitrile) in the presence of increasing amounts of DIPEA.

The Stern-Volmer plot, reported in Figure S9, shows a linear correlation between the amounts of DIPEA and the ratio I^0/I. On the basis of the following Equation 1, it is possible to calculate the Stern-Volmer constant K_{SV}.

$$I^0/I = 1 + K_{SV}[Q] \text{ [Eq. 1]}$$

We calculated a Stern-Volmer quenching constant of 180 M^{-1}

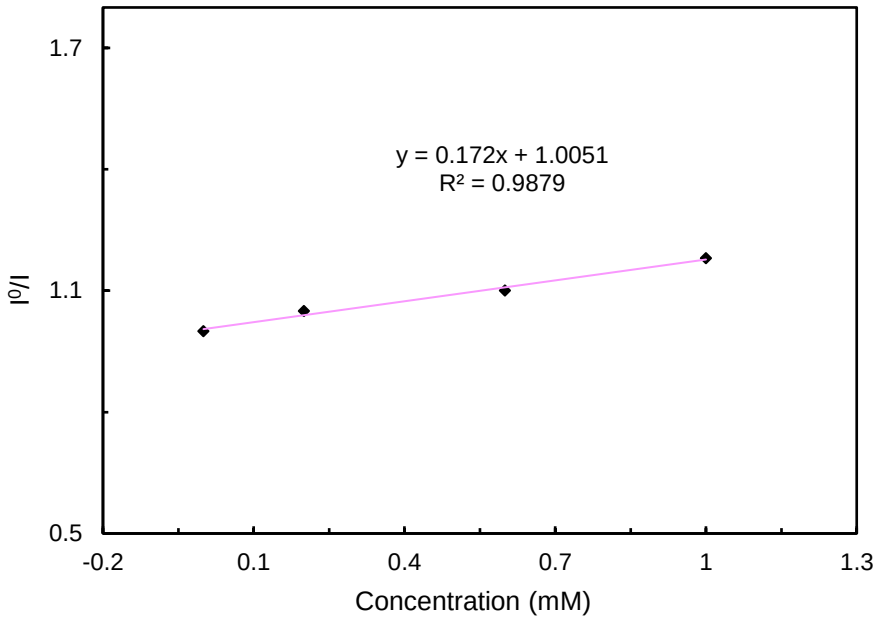


Figure S10. Stern-Volmer quenching plot using DIPEA as a quencher.

Quantum yield measurement [11]

The quantum yield Φ of the visible light-mediated isoperfluoropropylation of allyl benzene (**1**) with *i*-C_3F_7-Iodine(III) reagent (**2**) was determined using a method developed by Riedle and co-workers. For irradiation, a green LED (λ_{max} = 525 nm) was used. The radiant power was detected with a commercial optical power meter (PowerMax USB - PS19Q Power Sensor from Coherent) using computer-aided read out with PowerMax software.

Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, allyl benzene (**1**, 26.5 µL, 0.20 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (124.8 mg, 0.30 mmol, 1.5 equiv.), Eosin Y (6.4 mg, 5 mol%) and 2, 2, 6, 6-tetramethylpiperidinyl-1-oxide (TEMPO, 62.4 mg, 0.40 mmol, 2.0 equiv.) were dissolved in dry MeCN (2.0 mL). Subsequently, DIPEA (52.2 µL, 0.30 mmol, 1.5 equiv.) was added into the vial. An oven-dried fluorescence cuvette equipped with a magnetic stirring bar and a septum was flushed with nitrogen. Immediately prior to the quantum yield measurement, 2.0 mL of the reaction solution was transferred to the fluorescence cuvette under nitrogen atmosphere. The whole measurement was carried out in a dark room to minimize ambient light. First of all, the radiant power of light transmitted by a fluorescence cuvette with blank solution P_{ref} was measured. Following the fluorescence cuvette with the blank solution was exchanged by the fluorescence cuvette containing the prepared reaction mixture and the transmitted radiant power P_{sample} was determined for an irradiation time of Δt = 30 min. Afterwards the reaction yield or rather the molar amount of product molecules generated $n_{product}$ was determined by ^{19}F-NMR analysis using trifluoromethylbenzene as internal standard.

The quantum yield Φ was calculated as the following:

$$\Phi = \frac{N_{product}}{N_{ph,abs}} = \frac{n_{product} \cdot N_A \cdot h \cdot c}{P_{abs} \cdot \Delta t \cdot \lambda} = \frac{n_{product} \cdot N_A \cdot h \cdot c}{(P_{ref} - P_{sample}) \cdot \Delta t \cdot \lambda \cdot f} \quad \text{[Eq. 2]}$$

Here, Φ is the quantum yield, $N_{product}$ is the number of created molecules, $N_{ph,abs}$ is the number of absorbed photons, $n_{product}$ is the molar amount of product molecules generated in [mol], N_A is Avogadro's constant in [mol^{-1}], *h* is Planck's constant in [Js], *c* is the speed of light in [m/s], P_{abs} is the radiant power absorbed in [W], Δt is the irradiation time in [s], λ is the wavelength of the irradiation source in [m], P_{ref} is the radiant power transmitted by a fluorescence cuvette with blank solution in [W], P_{sample} is the radiant power transmitted by the fluorescence cuvette containing the reaction sample in [W] and f is a correction factor depending on the reflection coefficient R of the air-glass-interface.

Neglecting second order effects, the correction factor f can be calculated from:

$$f = \frac{1 + R \cdot \frac{P_{sample}}{P_{ref}}}{1-R} \quad \text{[Eq. 3]}$$

The reflection coefficient R for a fused silica cuvette and an irradiation wavelength of λ = 525 nm is equal to R = 0.0354.

Having this formula in hands, the preceding data obtained from the measurement could be used to calculate the final value for the quantum yield Φ as the following:

$n_{product}$	$0.068 \cdot 10^{-3}$ mol	N_A	$6.022 \cdot 10^{23}$ mol^{-1}
P_{sample}	$1.17 \cdot 10^{-3}$ W	h	$6.626 \cdot 10^{-34}$ Js
P_{ref}	$37.4 \cdot 10^{-3}$ W	c	$2.998 \cdot 10^{8}$ m/s
Δt	1800 s	R	0.0354
λ	$525 \cdot 10^{-9}$ m		

$$f = \frac{1 + R \cdot \frac{P_{sample}}{P_{ref}}}{1-R} = \frac{1 + 0.0354 \cdot \frac{1.17 \cdot 10^{-3}\ W}{37.4 \cdot 10^{-3}\ W}}{1-0.0354} = 1.038 \quad \text{[Eq. 4]}$$

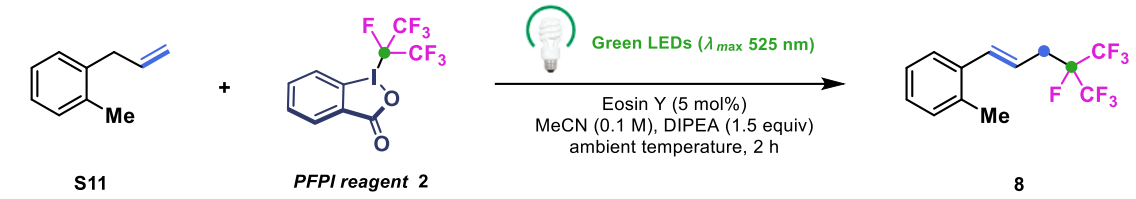
$$\Phi = \frac{n_{product} \cdot N_A \cdot h \cdot c}{(P_{ref} - P_{sample} \cdot \Delta t \cdot \lambda \cdot f} =$$

$$= \frac{0.068 \cdot 10^{-3}\ \text{mol} \cdot 6.022 \cdot 10^{23}\ \text{mol}^{-1} \cdot 6.626 \cdot 10^{-34}\ \text{Js} \cdot 2.998 \cdot 10^{8}\ \text{m/s}}{(37.4 \cdot 10^{-3}\ \text{W} - 1.3 \cdot 10^{-3}\ \text{W} \cdot 1800\ \text{s} \cdot 525 \cdot 10^{-9}\ \text{m} \cdot 1.038}$$

$$= \mathbf{0.2297} \cong \mathbf{23.0}\% \quad \text{[Eq. 5]}$$

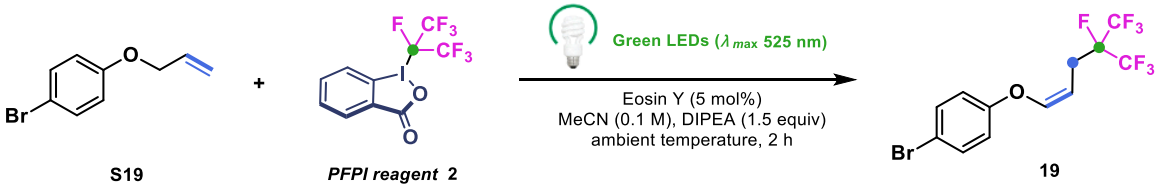
Gram-scale reactions and further transformations

Gram-scale reactions



Scheme S30. Gram-scale synthesis of **8**.

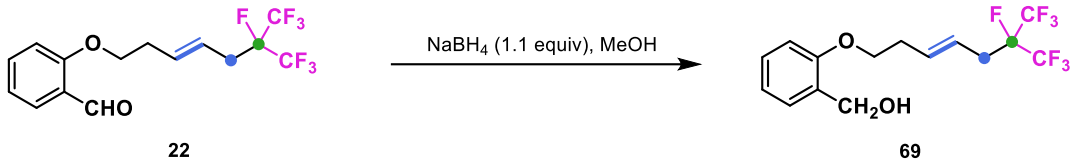
Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, 1-1-methyl-2-allylbenzene (**S11**, 396.3 mg, 3.0 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (1.87 g, 4.5 mmol, 1.5 equiv.), Eosin Y (5 mol%, 96.2 mg) were dissolved in dry MeCN (15 mL, c = 0.2 M). Subsequently, DIPEA (783.6 μL, 4.5 mmol, 1.5 equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at green light (525 nm) for 2 h, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, the reaction was quenched with 50 mL 5% $NaHCO_3$ aqueous solution, then extracted with DCM (3 x 30 mL). The combined organic phase was dried with anhydrous Na_2SO_4 and concentrated under vacuum. The obtained residue was purified by chromatography on silica gel eluting with EtOAc: petroleum ether (1: 100 - 1: 50 (v/v)) to afford 657.2 mg of **8** as a colorless oil (73% yield).



Scheme S31. Gram-scale synthesis of **19**.

Under an ambient atmosphere, in a 25 mL screw-cap vial equipped with a magnetic stirring bar, 1-1-bromo-4-(allyloxy)benzene (**S19**, 635.9 mg, 3.0 mmol, 1.0 equiv.), *i*-C_3F_7-iodine(III) (1.87 g, 4.5 mmol, 1.5 equiv.), Eosin Y (5 mol%, 96.2 mg) were dissolved in dry MeCN (15 mL, 0.2 M). Subsequently, DIPEA (783.6 μL, 4.5 mmol, 1.5 equiv.) was added into the vial. The vial was sealed and the reaction was irradiated at green light (525 nm) for 2 h, the temperature of the reaction systems was controlled within 25 - 35 °C by using the drum fan. After this, the reaction was quenched with 50 mL 5% $NaHCO_3$ aqueous solution, then extracted with DCM (3 x 30 mL). The combined organic phase was dried with anhydrous Na_2SO_4 and concentrated under vacuum. The obtained residue was purified by chromatography on silica gel eluting with EtOAc: petroleum ether (1: 50 - 1: 30 (v/v)) to afford 1.01 g of **19** as a colorless oil (89% yield).

Further transformations



22 69

Scheme S32. Reduction of aldehyde **22**.

In a 25 mL screw-cap vial equipped with a magnetic stirring bar, (*E*)-2-((6,7,7,7-tetrafluoro-6-(trifluoromethyl)hept-3-en-1-yl)oxy)phenyl aldehyde (**22**, 35.8 mg, 0.1 mmol, 1.0 equiv.) and $NaBH_4$ (4.2 mg, 0.11 mmol, 1.1 equiv.) were dissolved in dry MeOH (1 mL, 0.1 M) at 0 ℃. The mixture was stirred for 0.5 hours and then quenched with 5 mL water. After this, the reaction mixture was extracted with DCM (3 x 5 mL). The combined organic phase was dried with anhydrous Na_2SO_4 and concentrated under vacuum. The obtained residue was purified by chromatography on silica gel eluting with EtOAc: petroleum ether (1: 30 - 1: 10 (v/v)) to afford 33.8 mg of **69** as a pale-yellow oil (94% yield).

R_f = 0.30 (ethyl acetate: petroleum ether, 1:10 (v:v)).

NMR Spectroscopy:

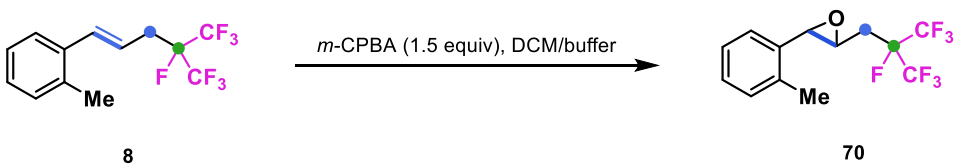
^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.30 - 7.21 (m, 2H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 5.84 - 5.73 (m, 1H), 5.62 - 5.54 (m, 1H), 4.66 (s, 1H), 4.11 - 3.94 (m, 2H), 2.83 (dd, *J* = 19.9, 6.8 Hz, 2H), 2.59 (t, *J* = 6.1 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 156.70, 133.94, 129.30, 129.02, 128.87, 120.96, 120.71, 120.95 (qd, *J* = 284.5, 27.4 Hz, CF($\underline{C}F_3$)$_2$), 111.10, 92.95 - 89.81 (m, $\underline{C}F(CF_3)_2$), 66.83, 62.31, 32.62, 32.36 (d, *J* = 8.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -75.85 (d, *J* = 6.7 Hz, CF($C\underline{F}_3$)$_2$, 6F), -182.25 (ddh, *J* = 27.4, 20.9, 6.9 Hz, $C\underline{F}(CF_3)_2$, 1F).

GC-MS: 360

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{15}H_{16}F_7O_2^+$: 361.1033. Found: 361.1027.



8 70

Scheme S33. Epoxidation of alkene **8**.

In a 25 mL screw-cap vial equipped with a magnetic stirring bar, (*E*)-2-methyl-(4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)benzene (**8**, 30.0 mg, 0.1 mmol, 1.0 equiv.) and 3-

chloroperbenzoic acid (*m*-CPBA, 25.9 mg, 0.15 mmol, 1.5 equiv.) were dissolved in CH_2Cl_2 (2 mL) and phosphate buffer (2 mL, pH= 7.0) at room temperature. The mixture was stirred for 12 hours and then quenched with 5 mL water. After this, the reaction mixture was extracted with DCM (3 x 5 mL). The combined organic phase was dried with anhydrous Na_2SO_4 and concentrated under vacuum. The obtained residue was purified by chromatography on silica gel eluting with EtOAc: petroleum ether (1: 50 - 1: 30 (v/v)) to afford 24.3 mg of **70** as a colorless oil (77% yield).

R_f = 0.48 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

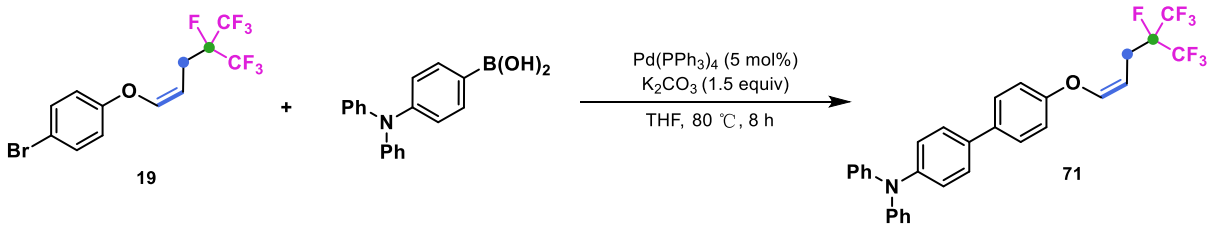
^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.39 - 7.11 (m, 4H), 4.38 (d, *J* = 11.7 Hz, 1H), 3.55 (dt, *J* = 11.5, 5.5 Hz, 1H), 3.23 (d, *J* = 13.4 Hz, 1H), 3.05 (d, *J* = 13.4 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 135.19, 135.07, 130.17, 127.78, 125.42, 125.21, 120.76 (qd, *J* = 285.5, 27.7 Hz, CF($\underline{C}F_3$)$_2$), 93.03 - 89.41 (m, $\underline{C}F(CF_3)_2$), 60.85, 55.90 (d, *J* = 6.0 Hz), 32.44 (d, *J* = 20.9 Hz), 19.25.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.90 (d, *J* = 7.6 Hz, CF(C$\underline{F}_3$)$_2$, 6F), -184.05 (dhept, *J* = 23.3, 7.5 Hz, C$\underline{F}$(CF$_3$)$_2$, 1F).

GC-MS: 316

HRMS (ESI) m/z $[M+H]^+$: Calculated for $C_{13}H_{12}F_7O^+$: 317.0771. Found: 317.0766.



Scheme S34. Suzuki coupling of **19**.

Under an ambient atmosphere, in a 10 mL screw-cap vial equipped with a magnetic stirring bar, (*Z*)-1-bromo-4-((4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)oxy)benzene (**19**, 38.0 mg, 0.1 mmol, 1.0 equiv.), [4-(diphenylamino)phenyl]boronic acid (34.7 mg, 0.12 mmol, 1.2 equiv.), K_2CO_3 (20.7 mg, 0.15 mmol, 1.5 equiv.) and $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol, 5.0 mol%) were dissolved in dry THF (2 mL, 0.05 M). The mixture was stirred at 80℃ for 8 hours and then quenched with 5 mL water. After this, the reaction mixture was extracted with DCM (3 x 10 mL). The combined organic phase was dried with anhydrous Na_2SO_4 and concentrated under vacuum. The obtained residue was purified by chromatography on silica gel eluting with EtOAc: petroleum ether (1: 30 - 1: 10 (v/v)) to afford 43.5 mg of **71** as an off-white solid (80% yield).

R_f = 0.37 (ethyl acetate: petroleum ether, 1:5 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.47 - 7.38 (m, 4H), 7.31

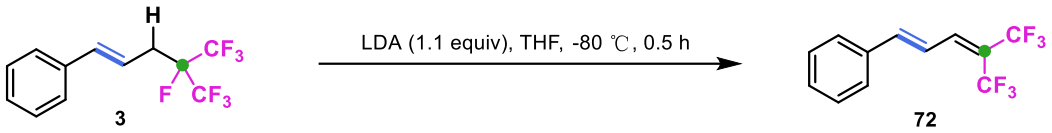
- 7.20 (m, 4H), 7.17 - 7.08 (m, 5H), 7.07 - 6.99 (m, 3H), 6.63 (d, *J* = 5.7 Hz, 1H), 4.85 (d, *J* = 6.4 Hz, 1H), 3.10 (dd, *J* = 19.7, 7.1 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 147.79 (d, *J* = 6.1 Hz), 129.37 (d, *J* = 3.7 Hz), 128.00, 127.61, 127.39, 124.49, 124.40, 124.17, 124.06, 123.04, 122.91, 116.99, 24.15 (d, *J* = 22.5 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -76.11 (d, *J* = 6.8 Hz, CF(C<u>*F*</u>$_3$)$_2$, 6F), -182.20 (ddp, *J* = 20.8, 14.3, 7.3 Hz, C<u>*F*</u>(CF$_3$)$_2$, 1F).

GC-MS: 545

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{30}H_{23}F_7NO^+$: 546.1662. Found: 546.1669.



Scheme S35. β-fluorine elimination of **3**.

Under an ambient atmosphere, in a 10 mL screw-cap vial equipped with a magnetic stirring bar, a solution of (*E*)-(4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-en-1-yl)benzene (**3**, 28.6 mg, 0.1 mmol, 1.0 equiv.) in anhydrous THF (1 mL) was cooled to - 80 °C. LDA (0.11 mmol, 1.1 equiv. 0.5 M in THF) was added at -80 °C slowly under stirring. Then, the mixture was stirred at - 80℃ for 0.5 hours and then quenched with 5 mL saturated ammonium chloride solution. After this, the reaction mixture was extracted with DCM (3 x 10 mL). The combined organic phase was dried with anhydrous Na_2SO_4 and concentrated under vacuum. The obtained residue was purified by chromatography on silica gel eluting with EtOAc: petroleum ether (1: 100 - 1: 50 (v/v)) to afford 10.9 mg of **72** as a colorless oil (41% yield).

R_f = 0.79 (ethyl acetate: petroleum ether, 1:20 (v:v)).

NMR Spectroscopy:

^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ 7.55 - 7.49 (m, 2H), 7.44 - 7.37 (m, 3H), 7.17 (d, *J* = 10.1 Hz, 2H), 7.09 - 6.99 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ 146.91, 141.63, 134.95, 130.53, 129.13, 128.54 (d, *J* = 29.0 Hz, <u>*C*</u>(CF$_3$)$_2$), 128.07, 121.74 (qd, *J* = 273.0, 11.7 Hz, C(<u>*C*</u>F$_3$)$_2$), 120.03.

^{19}F NMR (376 MHz, Chloroform-*d*, 298 K) δ -57.45 (d, *J* = 6.9 Hz, 3F), -63.17 (d, *J* = 6.8 Hz, 3F).

GC-MS: 266

HRMS (ESI) m/z [M+H]$^+$: Calculated for $C_{12}H_9F_6^+$: 267.0603. Found: 267.0601.

X-Ray crystal structures

Crystal Structure of $C_{18}H_{12}BrF_7O$

The low temperature (109±2°K) single-crystal X-ray experiments were performed on a Rigaku diffractometer with Cu K_α radiation. Unit cell was obtained and refined by 7515 reflections with 4.1° < θ < 66.7°. No decay was observed in data collection. Raw intensities were corrected for Lorentz and polarization effects, and for absorption by empirical method. Direct phase determination yielded the positions of all non-hydrogen atoms. All non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms of carbons were generated geometrically with C-H bonds of 0.95-1.00 Å according to criteria described in the SHELXTL manual (Bruker, 1997). They were included in the refinement with $U_{iso}(H) = 1.2U_{eq}$ of their parent atoms. The final full-matric least-square refinement on F^2 converged with $R1 = 0.0674$ and $wR2 = 0.1726$ for 2715 observed reflections [$I \geq 2\sigma(I)$]. The final difference electron density map shows no features. Details of crystal parameters, data collection and structure refinement are given in Table 1.

Data collection was controlled by CrysAlisPro, Agilent Technologies, Version 1.171.36.32 (Oxford, 2013). Computations were performed using the SHELXTL NT ver. 5.10 program package (Bruker, 1997) on an IBM PC 586 computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated (*International Tables for X-ray Crystallography*, 1989). Crystal drawings were produced with XP (Bruker, 1997).

References

Bruker. (1997) SHELXTL. Structure Determination Programs, Version 5.10, Bruker AXS Inc.,6300 Enterprise Lane, Madison, WI 53719-1173, USA.

International Tables for X-ray Crystallography: (1989) Vol. C (Kluwer Academic Publishers, Dordrecht) Tables 4.2.6.8 and 6.1.1.4.

Oxford. (2013) CrysAlisPro, Agilent Technologies, Version 1.171.36.32, Oxford Diffraction Ltd., 68 Milton Park, Abingdon, Oxfordshire, OX14 4RX, UK.

Table 1. Details of Data Collection, Processing and Structure Refinement

Sample code	**46**
CCDC No	2262771
Molecular formula	$C_{18}H_{12}BrF_7O$
Molecular weight	457.19
Color and habit	colorless prism
Crystal size	0.01 × 0.02 × 0.05 mm
Crystal system	monoclinic
Space group	*C*2/*c* (No. 15)
Unit cell parameters	*a* = 28.7901(4) Å α = 90.00° *b* = 11.39160(10) Å β = 107.1140(10)° *c* = 11.1231(2) Å γ = 90.00° *V* = 3486.46(9) Å^3 *Z* = 8 *F*(000) = 1808
Density (calcd)	1.742 g/cm^3
Diffractometer	XtaLAB AFC11 (RINC): quarter-chi single
Radiation	Cu K$_\alpha$, λ = 1.54178 Å
Temperature	109±2K
Scan type	ω-scan
Data collection range	-34 < *h* < 28, -13 < *k* < 13, -8 < *l* < 12; θ_{max} = 66.6°
Reflections measured	Total: 12043 Unique (*n*): 2981 Observed [I ≥ 2σ(I)]: 2715
Absorption coefficient	3.950 mm^{-1}
Minimum and maximum transmission	0.643, 1.000
No. of variables, *p*	244
Weighting scheme	$w = \frac{1}{\sigma^2(F_o^2) + (0.0784P)^2 + 28.3095P}$ $P = (F_o^2 + 2F_c^2)/3$
$R1 = \frac{\Sigma\|\|F_o\|-\|F_c\|\|}{\Sigma\|F_o\|}$ (for all reflections)	0.0713 0.0674 (for observed data)
$wR2 = \sqrt{\frac{\Sigma[w(F_o^2 - F_c^2)^2]}{\Sigma w(F_o^2)^2}}$ (for all reflections)	0.1757 0.1726 (for observed data)
Goof = S = $\sqrt{\frac{\Sigma[w(F_o^2 - F_c^2)^2]}{n - p}}$	1.085
Largest and mean Δ/σ	0.000, 0.000
Residual extrema in final difference map	-0.953 to 1.207 *e* Å^{-3}

Table 2. Atomic coordinates and equivalent isotropic temperature factors* (Å^2)

Atoms	*x*	*y*	*z*	$U_{eq.}$
Br(1)	0.05964(2)	0.54794(5)	0.63703(7)	0.0541(3)
F(1)	0.24003(11)	0.2560(3)	0.7063(5)	0.0764(14)
F(2)	0.28410(16)	0.2199(7)	0.9539(6)	0.141(3)
F(3)	0.33392(12)	0.2334(3)	0.8461(4)	0.0637(10)
F(4)	0.31854(14)	0.0719(5)	0.9182(4)	0.0931(17)
F(5)	0.30965(13)	0.1453(5)	0.6219(4)	0.0789(13)
F(6)	0.23907(16)	0.0871(9)	0.5432(4)	0.155(3)
F(7)	0.2895(3)	-0.0163(5)	0.6797(8)	0.147(3)
O(1)	0.14749(11)	-0.0524(3)	0.8378(3)	0.0251(7)
C(1)	0.13609(14)	-0.0214(4)	0.7284(4)	0.0188(8)
C(2)	0.16678(14)	0.0712(4)	0.6858(4)	0.0200(8)
C(3)	0.21707(14)	0.0763(4)	0.7841(4)	0.0225(9)
C(4)	0.25631(15)	0.1462(4)	0.7488(4)	0.0274(9)
C(5)	0.29926(18)	0.1685(6)	0.8672(6)	0.0478(15)
C(6)	0.2741(2)	0.0881(7)	0.6480(5)	0.0566(18)
C(7)	0.09127(14)	-0.0674(3)	0.6362(4)	0.0195(8)
C(8)	0.08121(15)	-0.0501(4)	0.5067(4)	0.0240(9)
C(9)	0.04015(15)	-0.0987(4)	0.4240(4)	0.0283(10)
C(10)	0.00825(15)	-0.1637(4)	0.4691(4)	0.0285(10)
C(11)	0.01748(15)	-0.1803(4)	0.5969(4)	0.0272(9)
C(12)	0.05872(15)	-0.1332(4)	0.6801(4)	0.0234(9)
C(13)	0.13899(14)	0.1870(4)	0.6717(4)	0.0215(8)
C(14)	0.12559(15)	0.2324(4)	0.7722(4)	0.0268(9)
C(15)	0.10113(17)	0.3388(4)	0.7625(5)	0.0344(11)
C(16)	0.09039(17)	0.3984(4)	0.6500(5)	0.0361(11)
C(17)	0.10231(17)	0.3549(4)	0.5475(5)	0.0340(11)
C(18)	0.12657(15)	0.2484(4)	0.5584(4)	0.0267(9)

*$U_{eq.}$ defined as one third of the trace of the orthogonalized **U** tensor.

Table 3. Bond lengths (Å) and bond angles (°)

Br(1)-C(16)	1.906(5)	C(4)-C(6)	1.516(8)
F(1)-C(4)	1.370(6)	C(4)-C(5)	1.539(7)
F(2)-C(5)	1.308(7)	C(7)-C(8)	1.397(6)
F(3)-C(5)	1.317(6)	C(7)-C(12)	1.396(6)
F(4)-C(5)	1.287(8)	C(8)-C(9)	1.381(6)
F(5)-C(6)	1.315(7)	C(9)-C(10)	1.384(7)
F(6)-C(6)	1.297(7)	C(10)-C(11)	1.380(7)
F(7)-C(6)	1.282(10)	C(11)-C(12)	1.381(6)
O(1)-C(1)	1.216(5)	C(13)-C(14)	1.386(6)
C(1)-C(7)	1.488(5)	C(13)-C(18)	1.392(6)
C(1)-C(2)	1.538(5)	C(14)-C(15)	1.390(7)
C(2)-C(13)	1.527(6)	C(15)-C(16)	1.376(7)
C(2)-C(3)	1.537(5)	C(16)-C(17)	1.375(7)
C(3)-C(4)	1.524(6)	C(17)-C(18)	1.387(7)
O(1)-C(1)-C(7)	120.8(4)	F(7)-C(6)-C(4)	111.5(5)
O(1)-C(1)-C(2)	119.8(4)	F(6)-C(6)-C(4)	109.0(5)
C(7)-C(1)-C(2)	119.3(3)	F(5)-C(6)-C(4)	113.7(6)
C(13)-C(2)-C(3)	113.3(3)	C(8)-C(7)-C(12)	118.7(4)
C(13)-C(2)-C(1)	107.1(3)	C(8)-C(7)-C(1)	122.4(4)
C(3)-C(2)-C(1)	108.3(3)	C(12)-C(7)-C(1)	118.9(4)
C(4)-C(3)-C(2)	116.8(3)	C(9)-C(8)-C(7)	120.4(4)
F(1)-C(4)-C(6)	107.3(5)	C(8)-C(9)-C(10)	120.2(4)
F(1)-C(4)-C(3)	111.2(4)	C(11)-C(10)-C(9)	120.0(4)
C(6)-C(4)-C(3)	113.6(4)	C(12)-C(11)-C(10)	120.2(4)
F(1)-C(4)-C(5)	104.6(4)	C(11)-C(12)-C(7)	120.5(4)
C(6)-C(4)-C(5)	110.1(4)	C(14)-C(13)-C(18)	119.0(4)
C(3)-C(4)-C(5)	109.6(4)	C(14)-C(13)-C(2)	120.0(4)
F(4)-C(5)-F(2)	104.6(7)	C(18)-C(13)-C(2)	121.0(4)
F(4)-C(5)-F(3)	107.9(5)	C(13)-C(14)-C(15)	121.2(4)
F(2)-C(5)-F(3)	108.3(5)	C(16)-C(15)-C(14)	118.3(4)
F(4)-C(5)-C(4)	111.7(5)	C(17)-C(16)-C(15)	122.1(4)
F(2)-C(5)-C(4)	110.3(5)	C(17)-C(16)-Br(1)	118.9(4)
F(3)-C(5)-C(4)	113.6(5)	C(15)-C(16)-Br(1)	119.0(4)
F(7)-C(6)-F(6)	110.7(8)	C(16)-C(17)-C(18)	119.0(4)
F(7)-C(6)-F(5)	106.9(6)	C(17)-C(18)-C(13)	120.4(4)
F(6)-C(6)-F(5)	104.9(5)		

Table 4. Anisotropic thermal parameters* (Å^2)

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br(1)	0.0426(4)	0.0311(4)	0.0764(5)	-0.0036(3)	-0.0013(3)	0.0124(2)
F(1)	0.0276(16)	0.046(2)	0.149(4)	0.052(2)	0.015(2)	0.0028(14)
F(2)	0.054(3)	0.243(7)	0.128(4)	-0.145(5)	0.031(3)	-0.054(3)
F(3)	0.0313(16)	0.060(2)	0.088(3)	0.0080(19)	-0.0002(16)	-0.0239(15)
F(4)	0.042(2)	0.128(4)	0.080(3)	0.060(3)	-0.0275(19)	-0.029(2)
F(5)	0.044(2)	0.139(4)	0.064(2)	0.016(2)	0.0321(18)	-0.015(2)
F(6)	0.051(3)	0.378(10)	0.041(2)	-0.067(4)	0.019(2)	-0.062(4)
F(7)	0.249(8)	0.055(3)	0.226(7)	-0.034(4)	0.206(7)	-0.010(4)
O(1)	0.0233(15)	0.0327(17)	0.0172(16)	0.0026(11)	0.0025(12)	-0.0020(12)
C(1)	0.0161(18)	0.0231(19)	0.017(2)	-0.0003(15)	0.0038(15)	0.0033(15)
C(2)	0.0169(19)	0.025(2)	0.017(2)	-0.0012(15)	0.0029(15)	-0.0015(16)
C(3)	0.021(2)	0.028(2)	0.016(2)	0.0007(16)	0.0013(16)	-0.0006(16)
C(4)	0.020(2)	0.028(2)	0.031(2)	0.0061(18)	0.0011(17)	-0.0009(17)
C(5)	0.024(2)	0.066(4)	0.053(4)	-0.029(3)	0.012(2)	-0.019(3)
C(6)	0.035(3)	0.109(6)	0.028(3)	-0.012(3)	0.012(2)	-0.025(3)
C(7)	0.0174(18)	0.0184(18)	0.020(2)	-0.0018(15)	0.0017(16)	0.0041(15)
C(8)	0.020(2)	0.030(2)	0.021(2)	0.0010(16)	0.0030(16)	0.0000(16)
C(9)	0.022(2)	0.040(3)	0.016(2)	-0.0036(17)	-0.0042(16)	-0.0015(19)
C(10)	0.019(2)	0.030(2)	0.031(3)	-0.0073(18)	-0.0010(17)	-0.0006(17)
C(11)	0.019(2)	0.029(2)	0.034(3)	-0.0035(18)	0.0068(18)	-0.0021(17)
C(12)	0.023(2)	0.025(2)	0.020(2)	-0.0001(16)	0.0039(16)	0.0008(16)
C(13)	0.0171(19)	0.024(2)	0.020(2)	-0.0010(16)	-0.0003(15)	-0.0027(16)
C(14)	0.024(2)	0.029(2)	0.025(2)	-0.0029(17)	0.0023(17)	-0.0022(17)
C(15)	0.029(2)	0.031(2)	0.041(3)	-0.010(2)	0.007(2)	-0.0017(19)
C(16)	0.027(2)	0.021(2)	0.051(3)	-0.002(2)	-0.002(2)	0.0015(18)
C(17)	0.029(2)	0.029(2)	0.036(3)	0.0062(19)	-0.003(2)	-0.0041(19)
C(18)	0.023(2)	0.029(2)	0.023(2)	0.0003(17)	-0.0004(17)	-0.0046(17)

*The exponent takes the form: $-2\pi^2\Sigma\Sigma U_{ij}h_ih_j\mathbf{a}_i^*\mathbf{a}_j^*$

Table 5. Coordinates and isotropic temperature factors* (Å^2) for H atoms

Atoms	*x*	*y*	*z*	$U_{eq.}$
H(2)	0.1706	0.0479	0.6026	0.024
H(3A)	0.2131	0.1101	0.8624	0.027
H(3B)	0.2289	-0.0051	0.8032	0.027
H(8)	0.1028	-0.0047	0.4752	0.029
H(9)	0.0338	-0.0874	0.3361	0.034
H(10)	-0.0200	-0.1969	0.4122	0.034
H(11)	-0.0046	-0.2244	0.6278	0.033
H(12)	0.0650	-0.1456	0.7679	0.028
H(14)	0.1333	0.1900	0.8491	0.032
H(15)	0.0921	0.3697	0.8317	0.041
H(17)	0.0941	0.3972	0.4705	0.041
H(18)	0.1348	0.2171	0.4881	0.032

*The exponent takes the form: $-8\pi^2 U \sin^2\theta/\lambda^2$

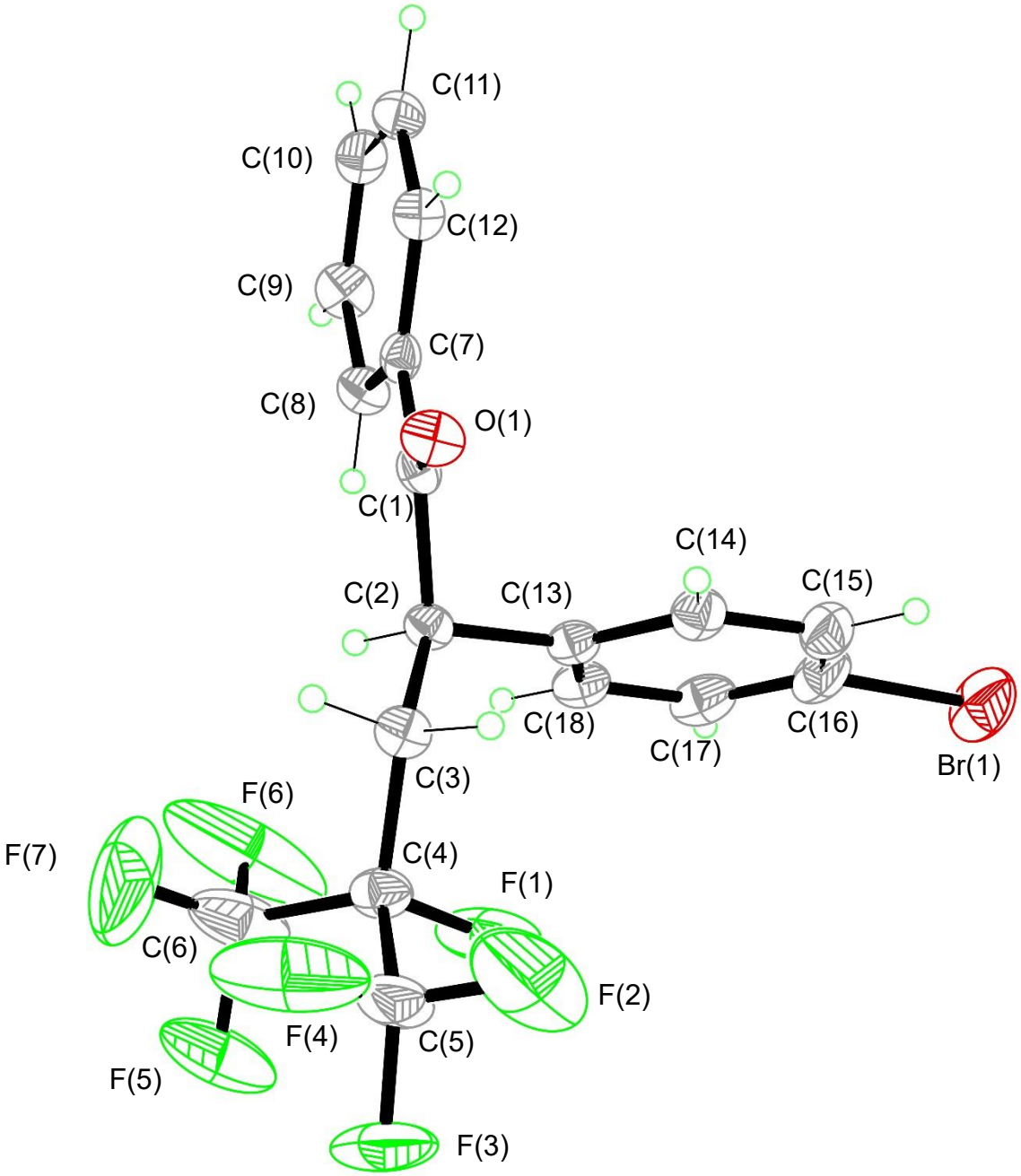


Figure S11. ORTEP drawing of $C_{18}H_{12}BrF_7O$ with 50% probability ellipsoids, showing the atomic numbering scheme.

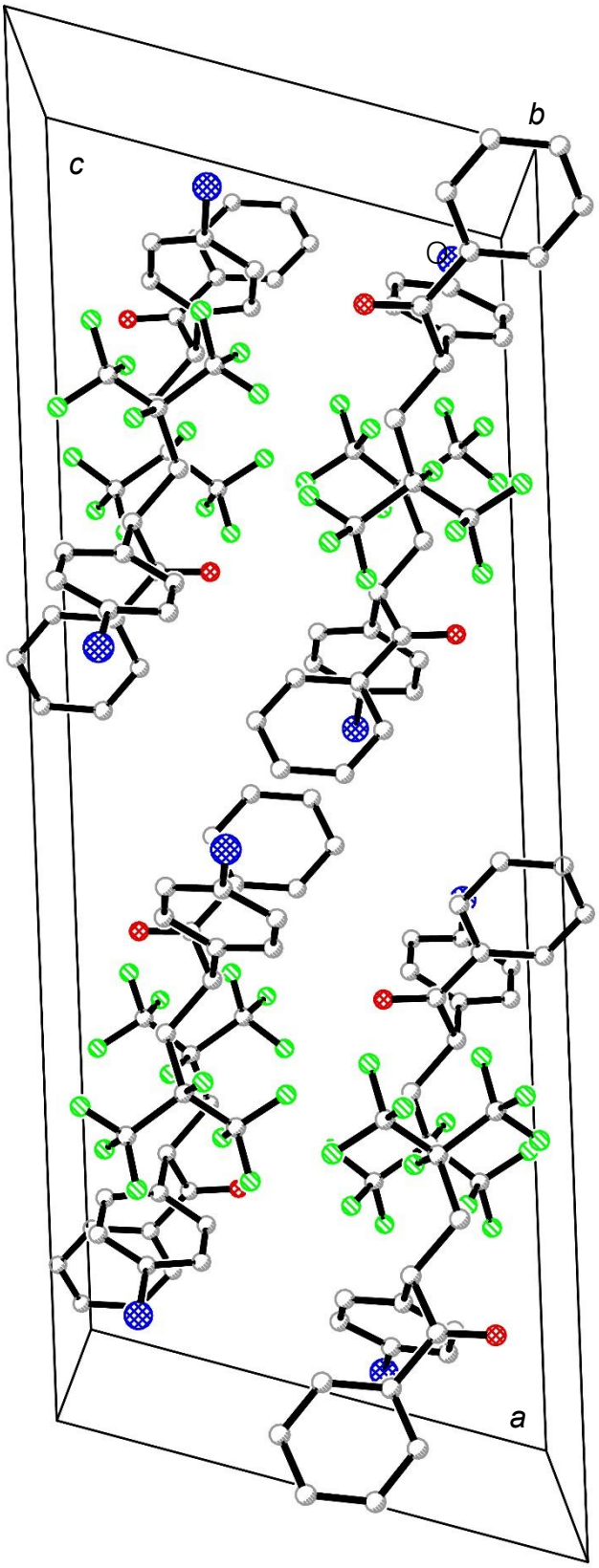
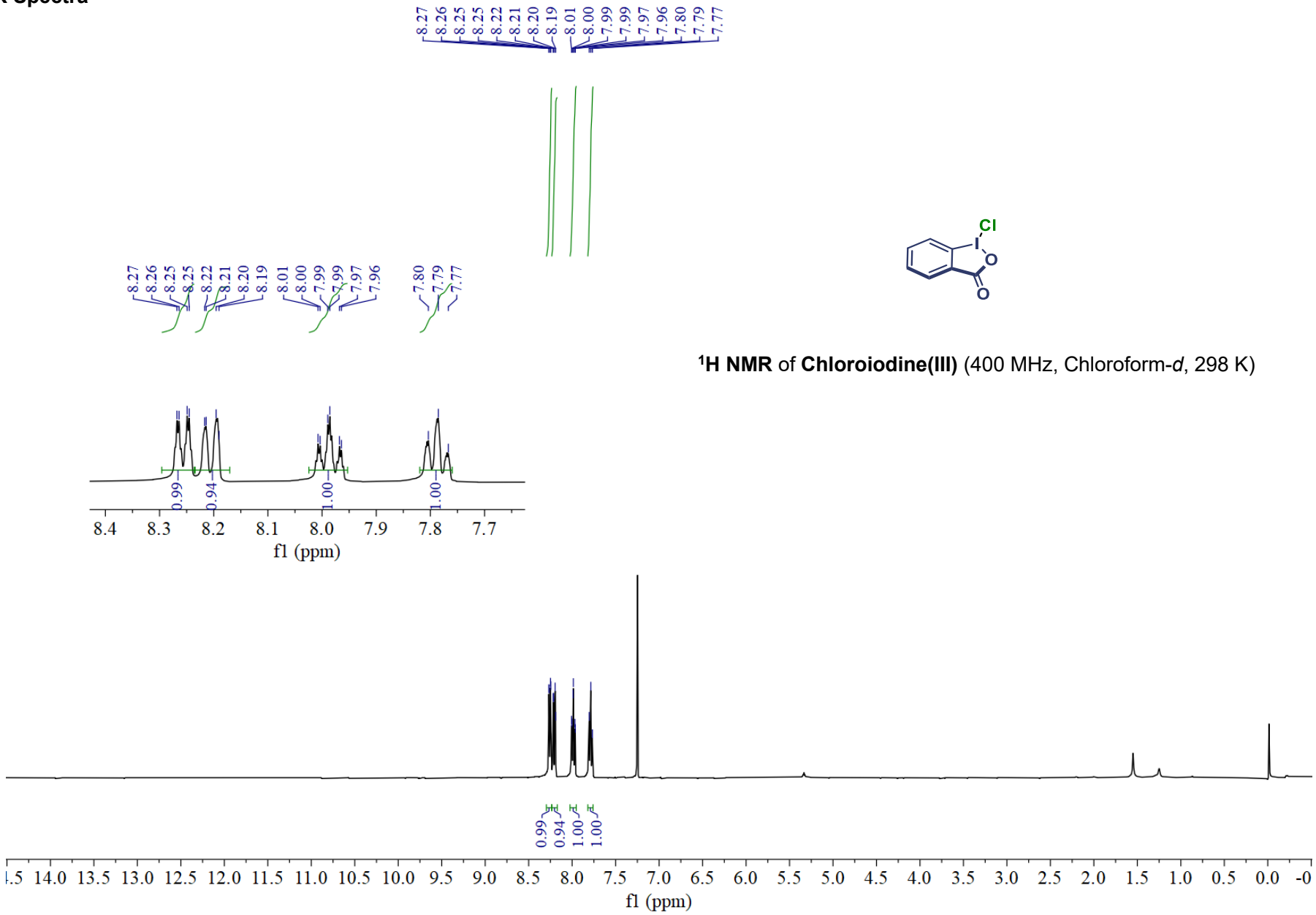
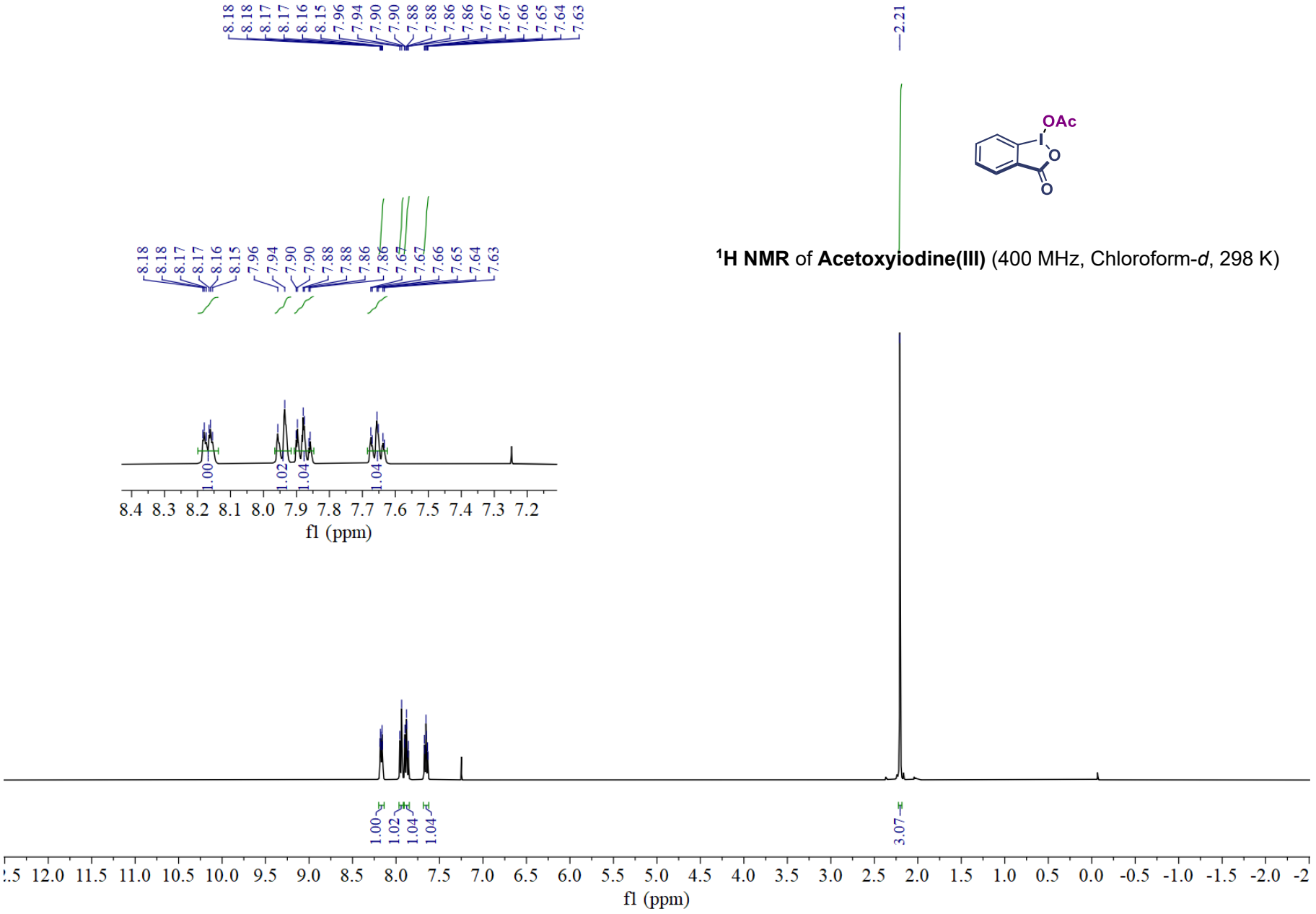


Figure S12. A packing view along the *b* direction

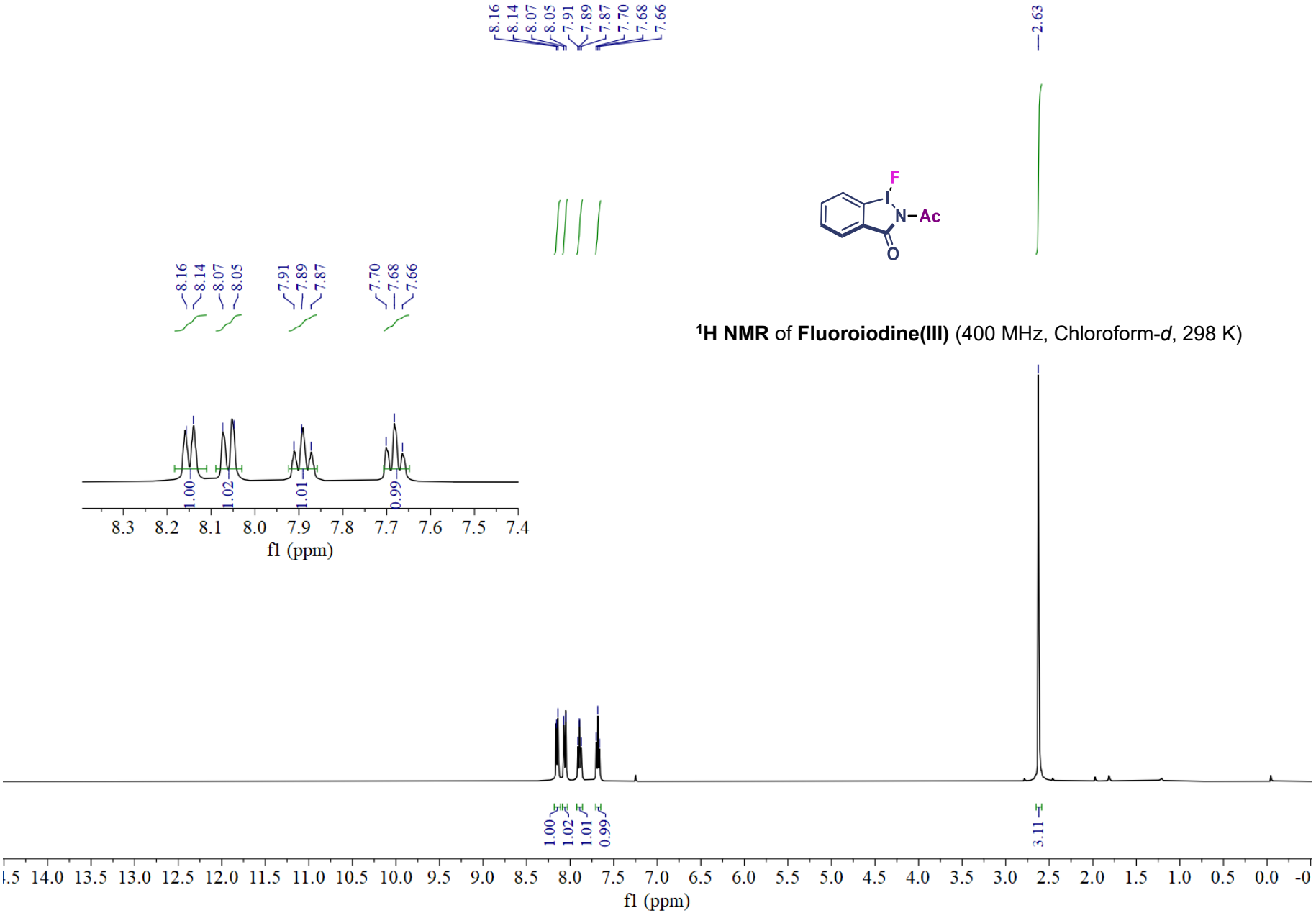
NMR Spectra



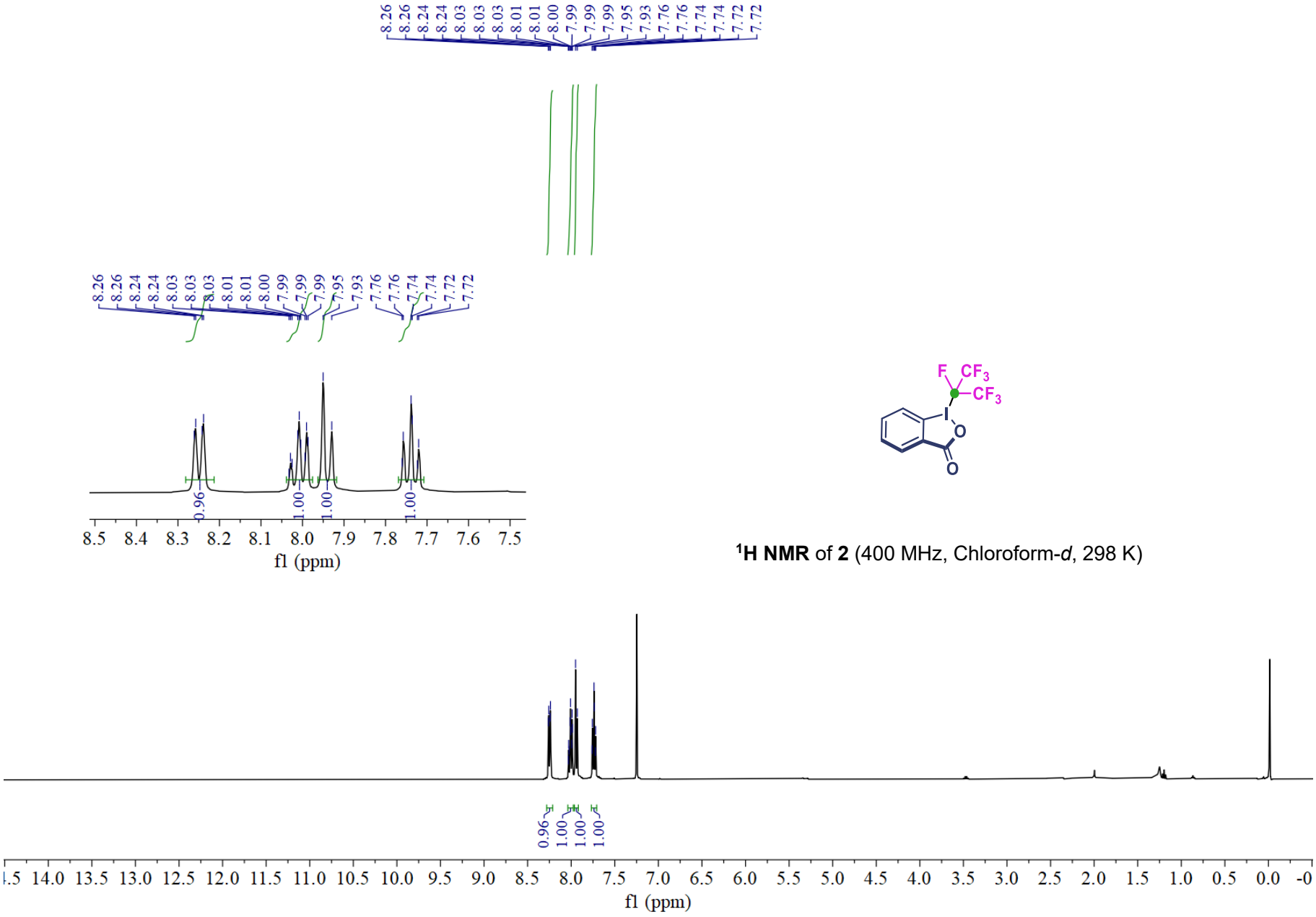
^{1}H NMR of **Chloroiodine(III)** (400 MHz, Chloroform-*d*, 298 K)



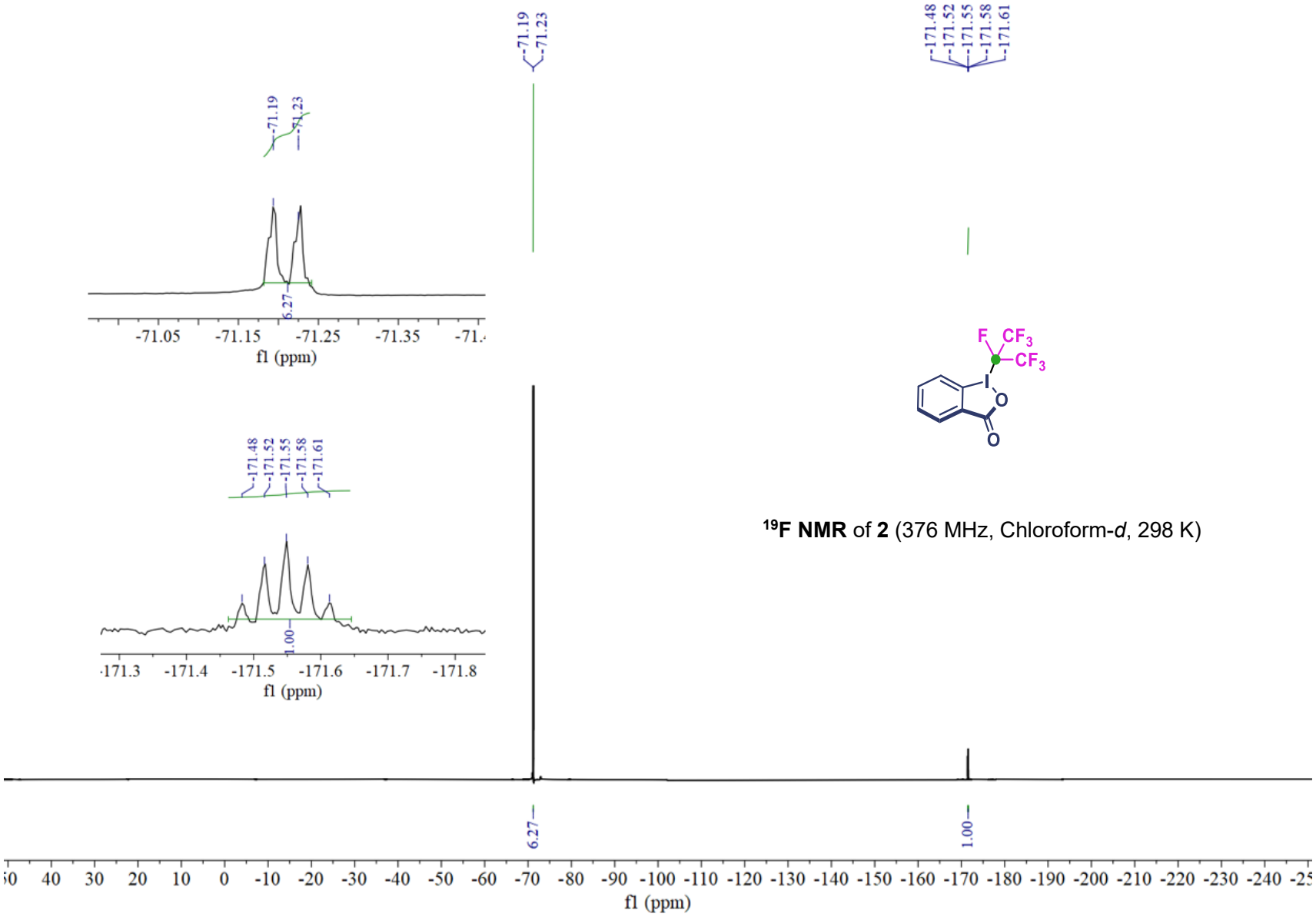
^{1}H NMR of **Acetoxyiodine(III)** (400 MHz, Chloroform-*d*, 298 K)



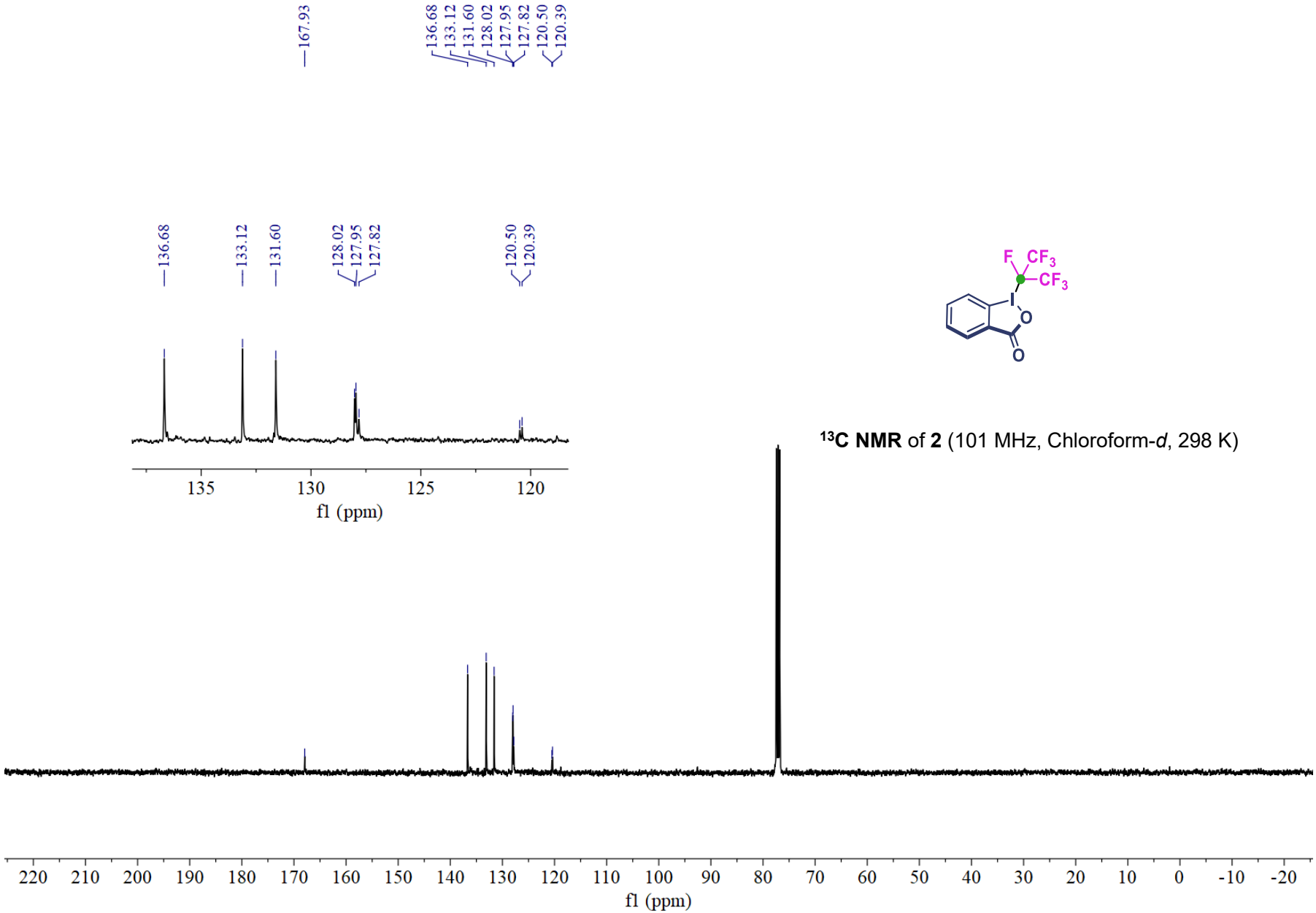
^{1}H NMR of **Fluoroiodine(III)** (400 MHz, Chloroform-*d*, 298 K)



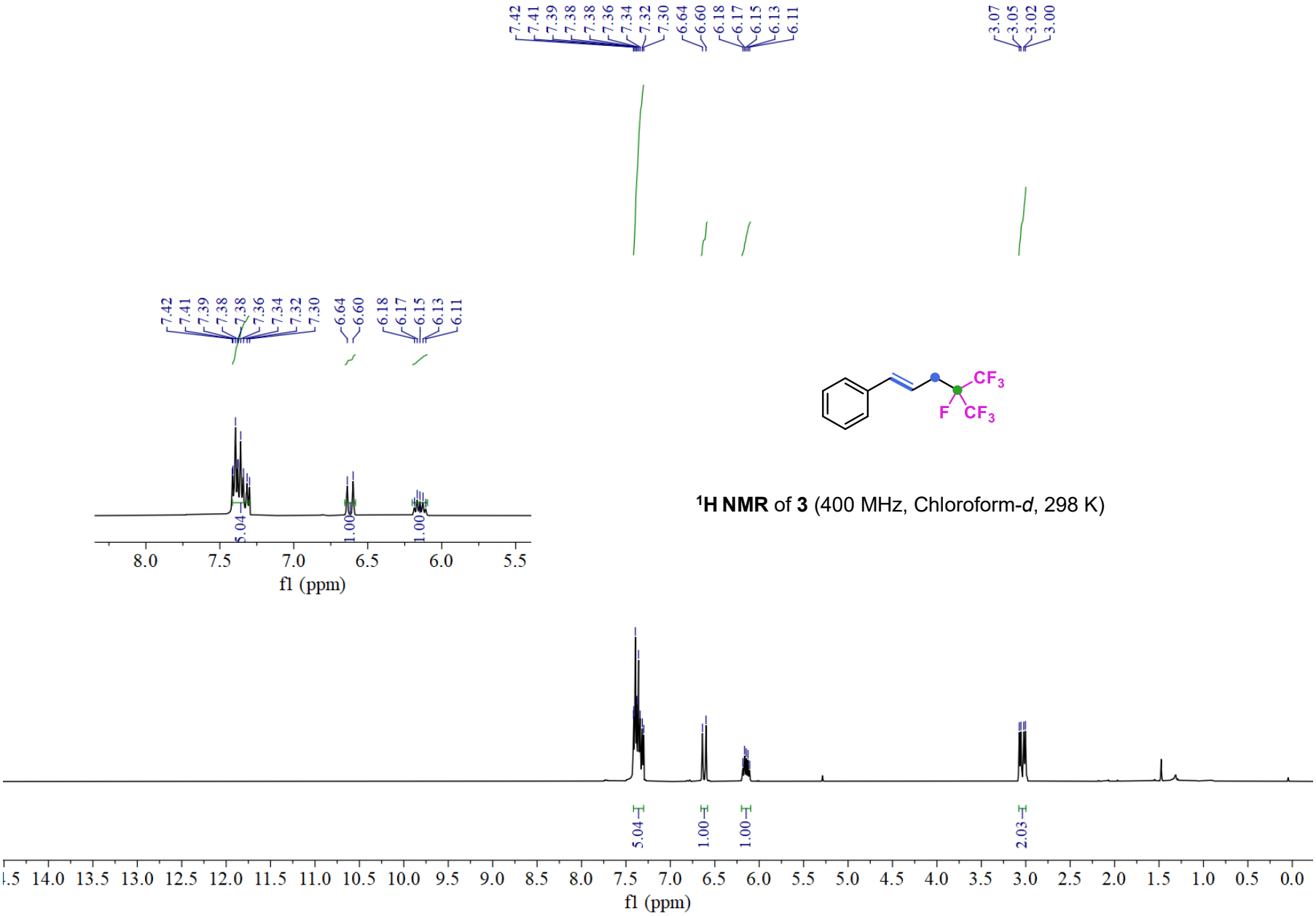
^{1}H NMR of **2** (400 MHz, Chloroform-*d*, 298 K)



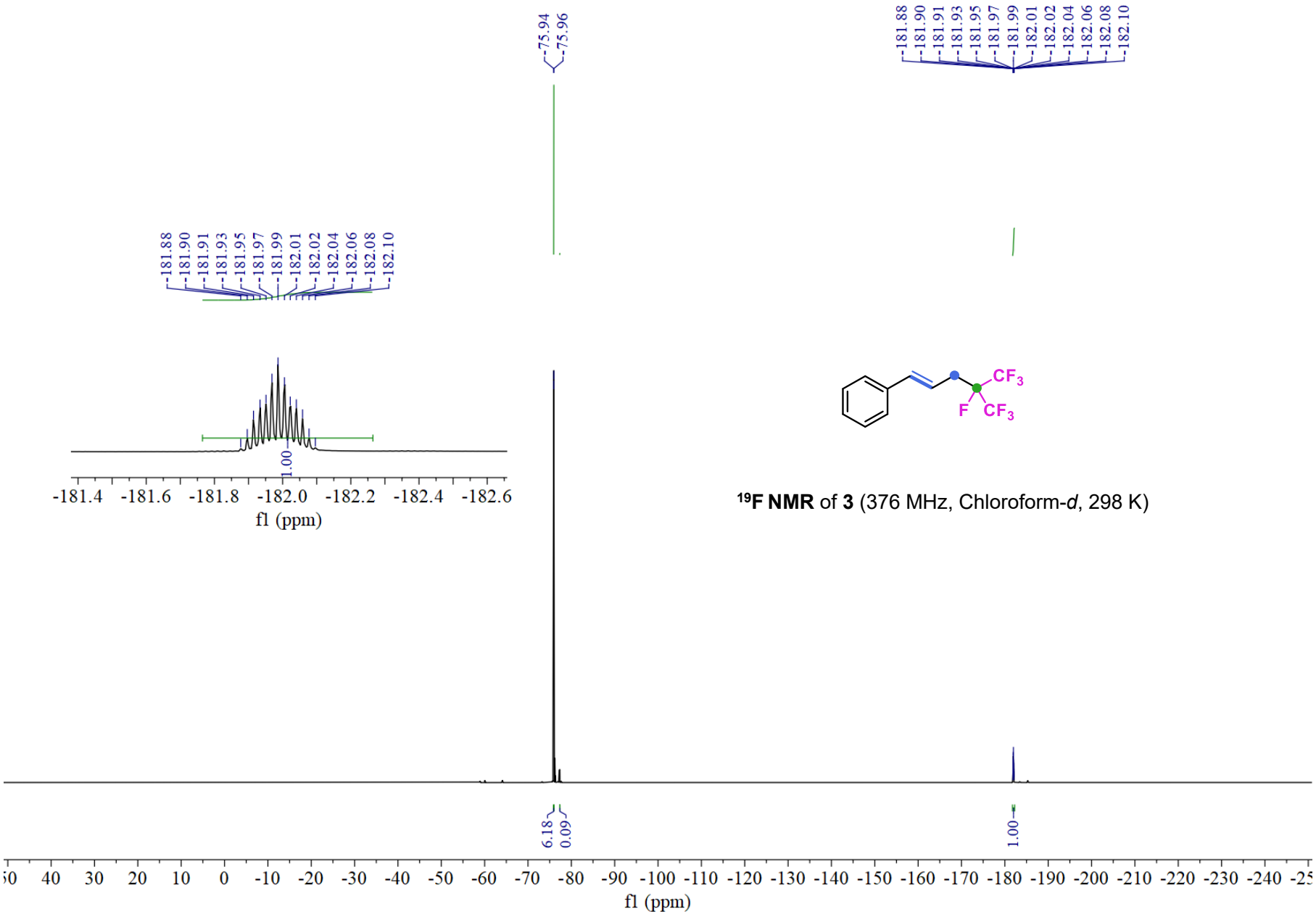
^{19}F NMR of **2** (376 MHz, Chloroform-*d*, 298 K)



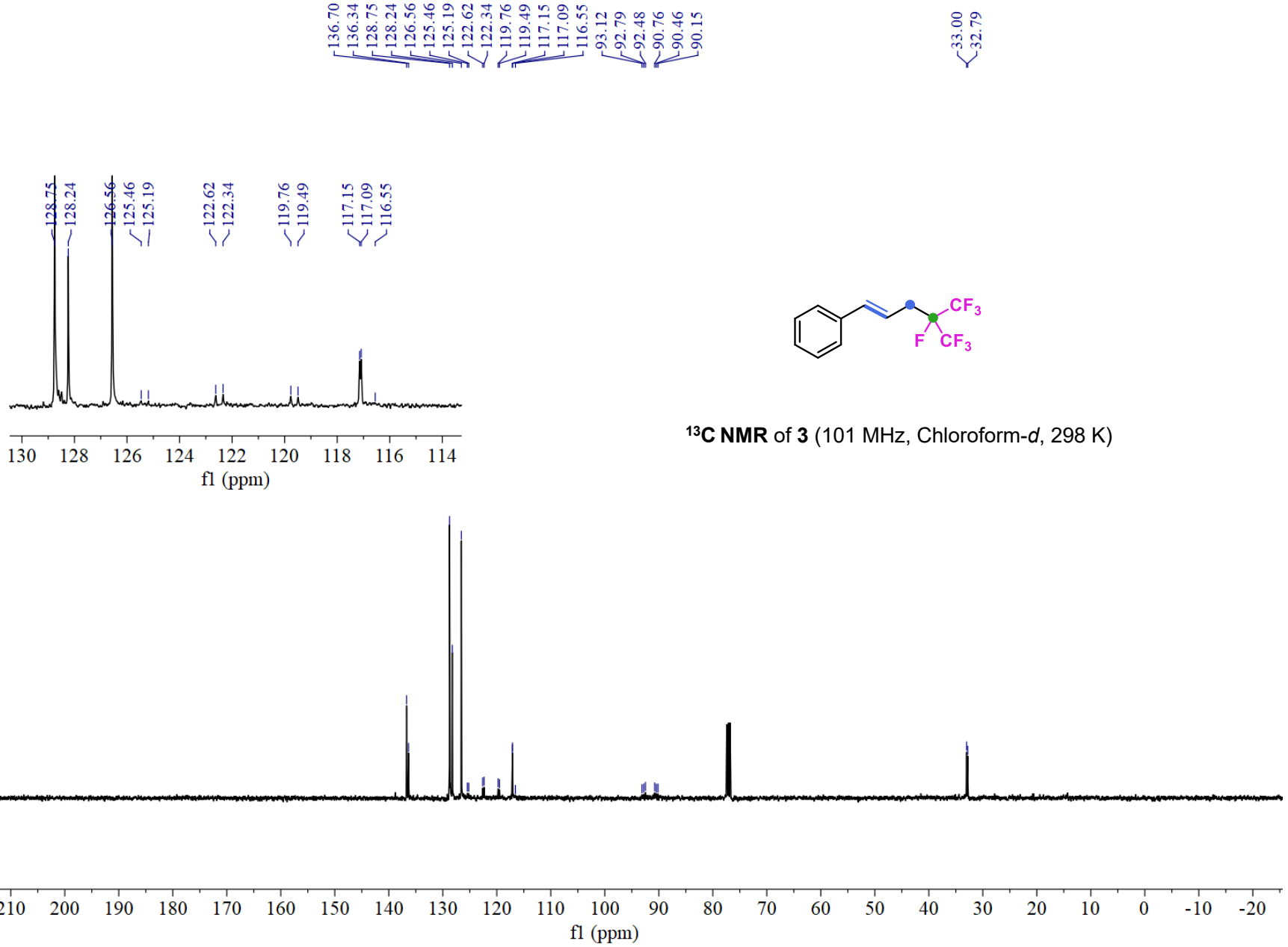
^{13}C NMR of **2** (101 MHz, Chloroform-*d*, 298 K)



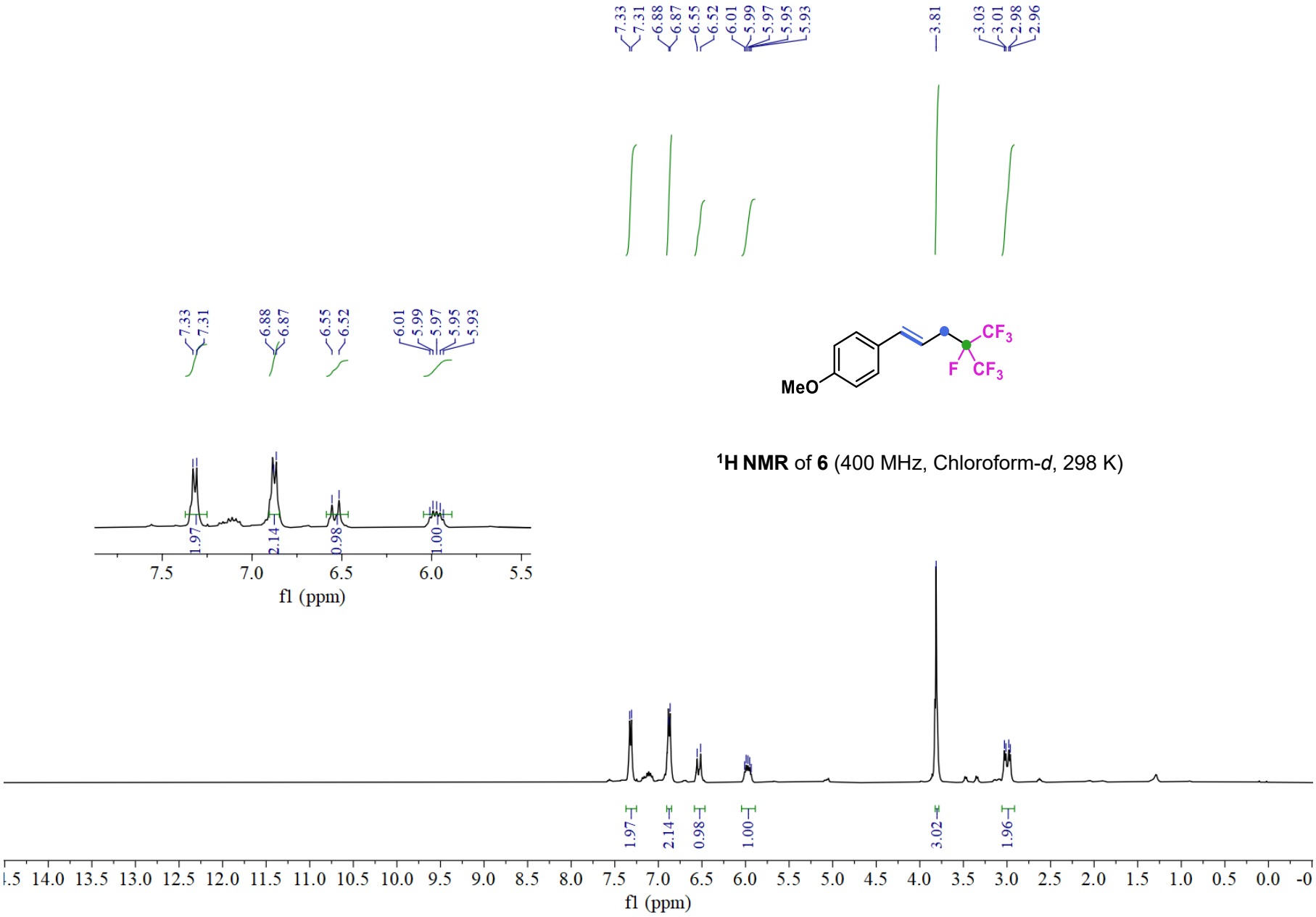
^{1}H NMR of **3** (400 MHz, Chloroform-*d*, 298 K)



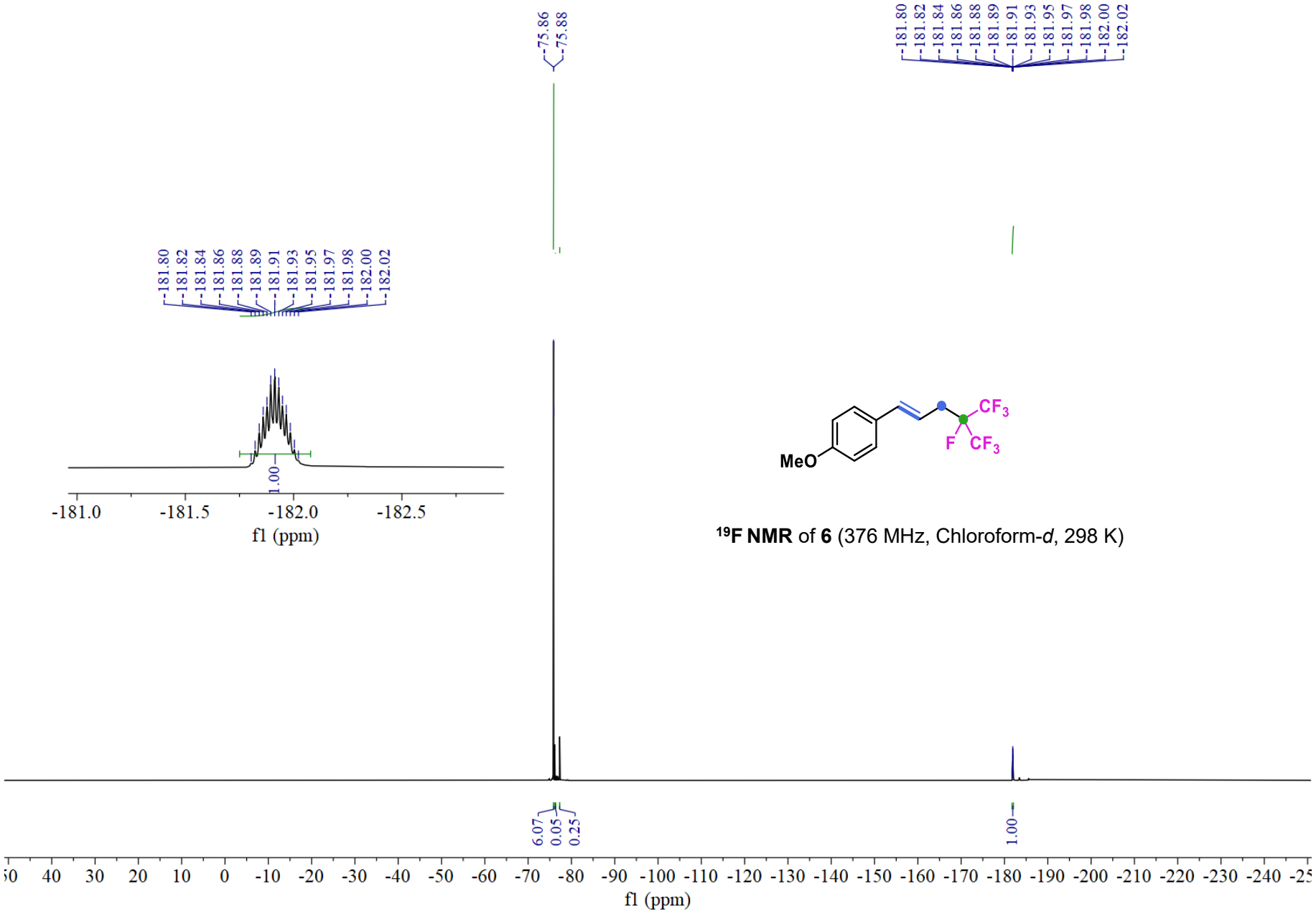
^{19}F NMR of **3** (376 MHz, Chloroform-*d*, 298 K)



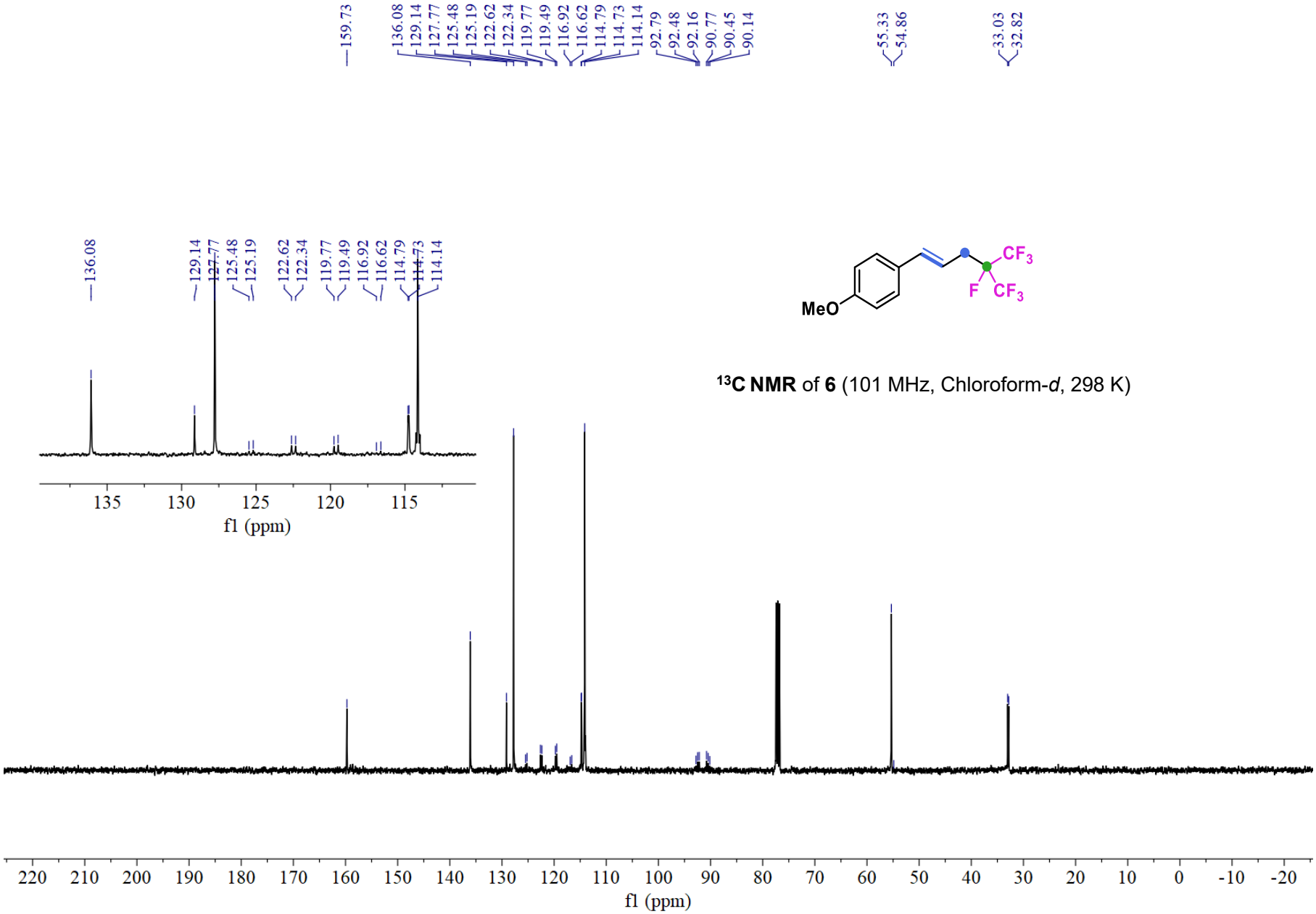
^{13}C NMR of **3** (101 MHz, Chloroform-*d*, 298 K)



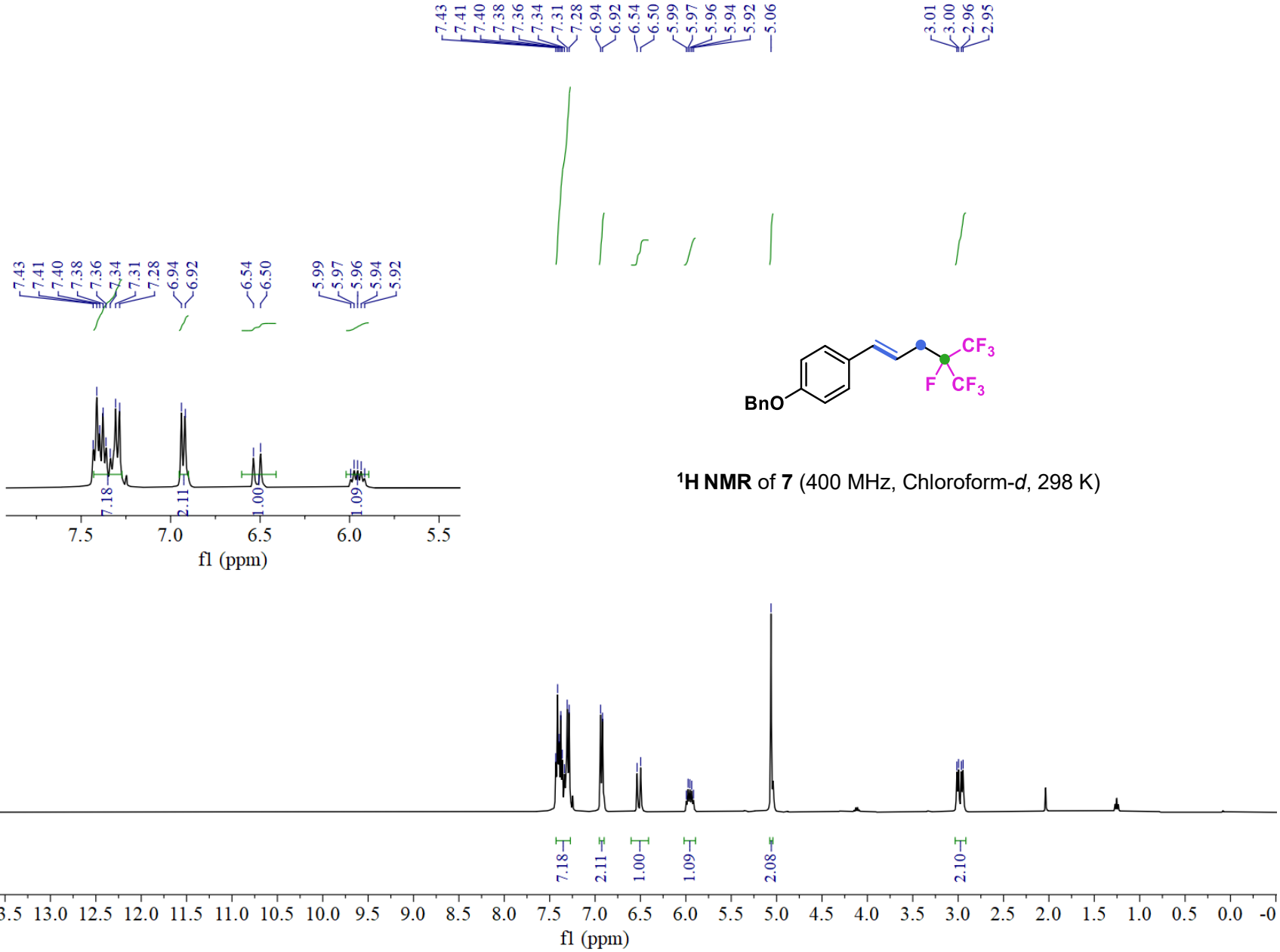
^{1}H NMR of **6** (400 MHz, Chloroform-*d*, 298 K)



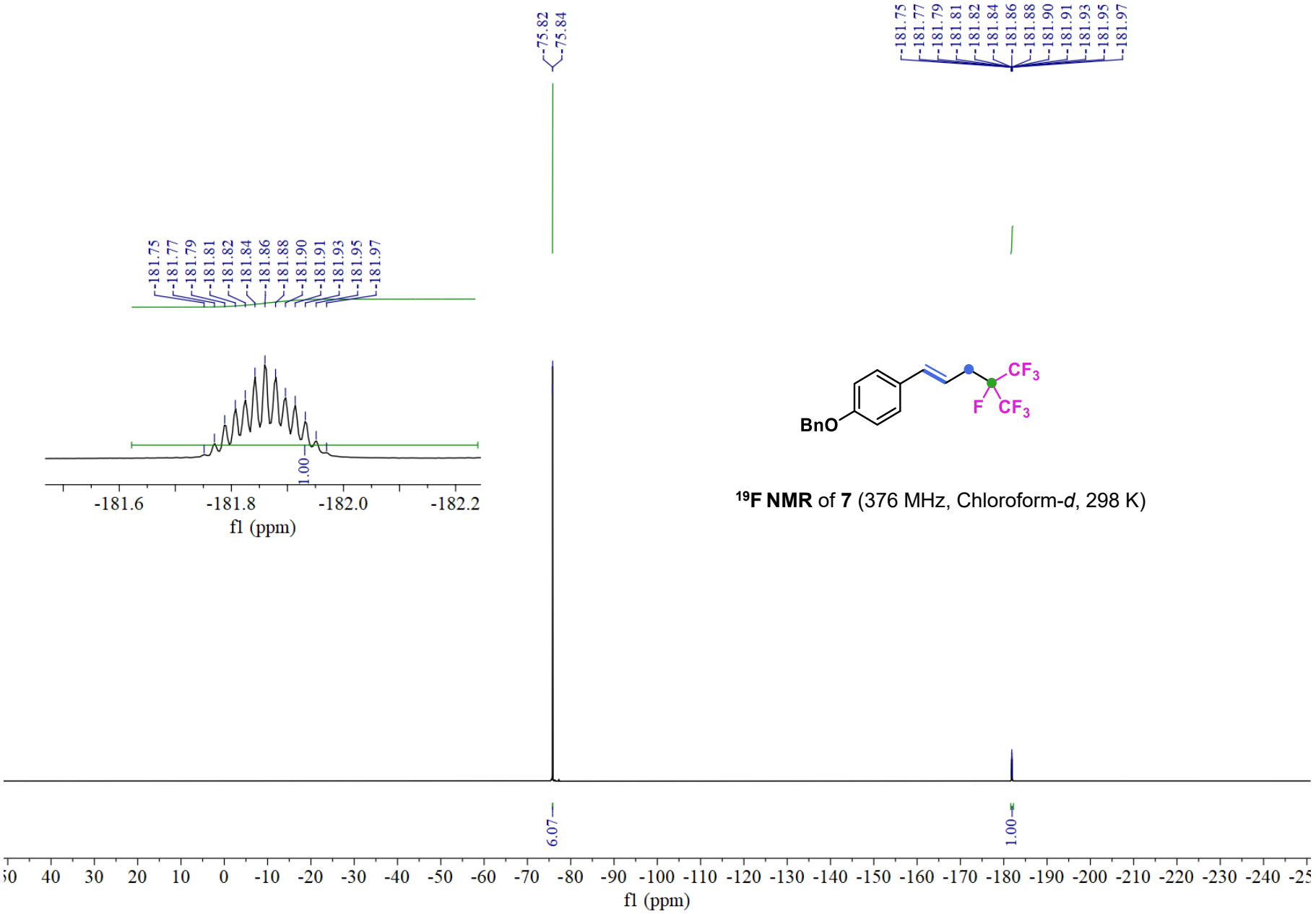
^{19}F NMR of **6** (376 MHz, Chloroform-*d*, 298 K)



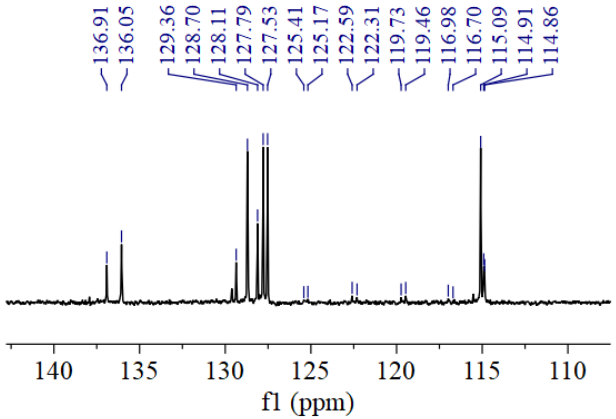
^{13}C NMR of **6** (101 MHz, Chloroform-*d*, 298 K)

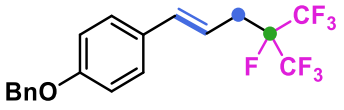


^{1}H NMR of **7** (400 MHz, Chloroform-*d*, 298 K)

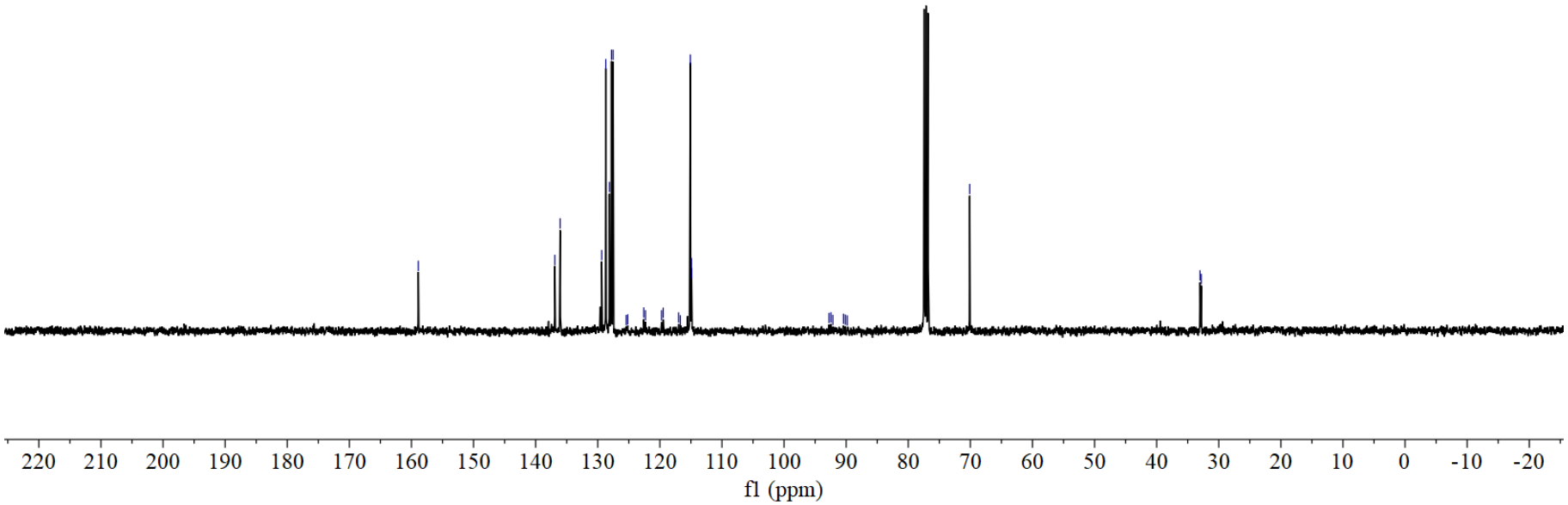


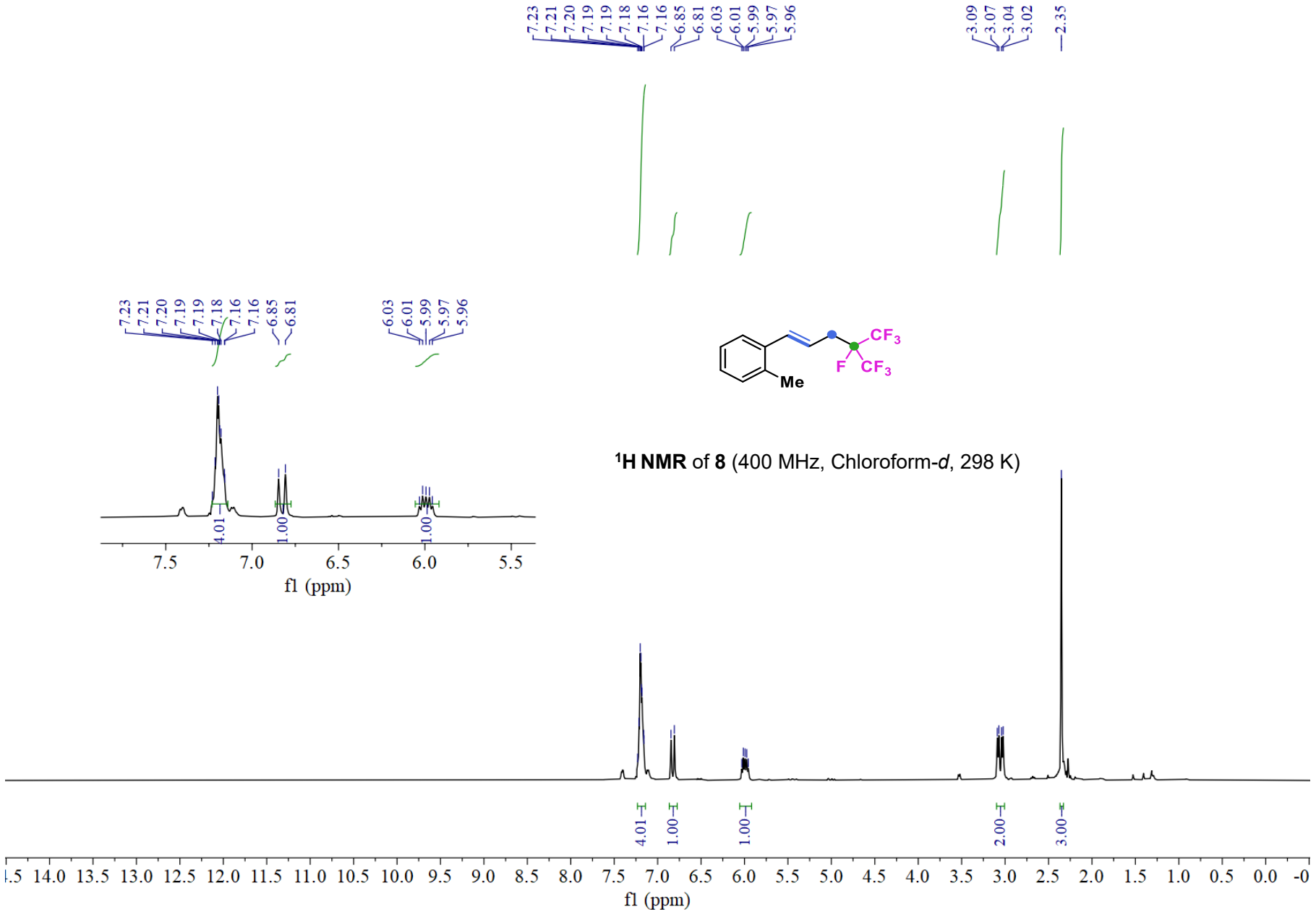
^{19}F NMR of **7** (376 MHz, Chloroform-*d*, 298 K)



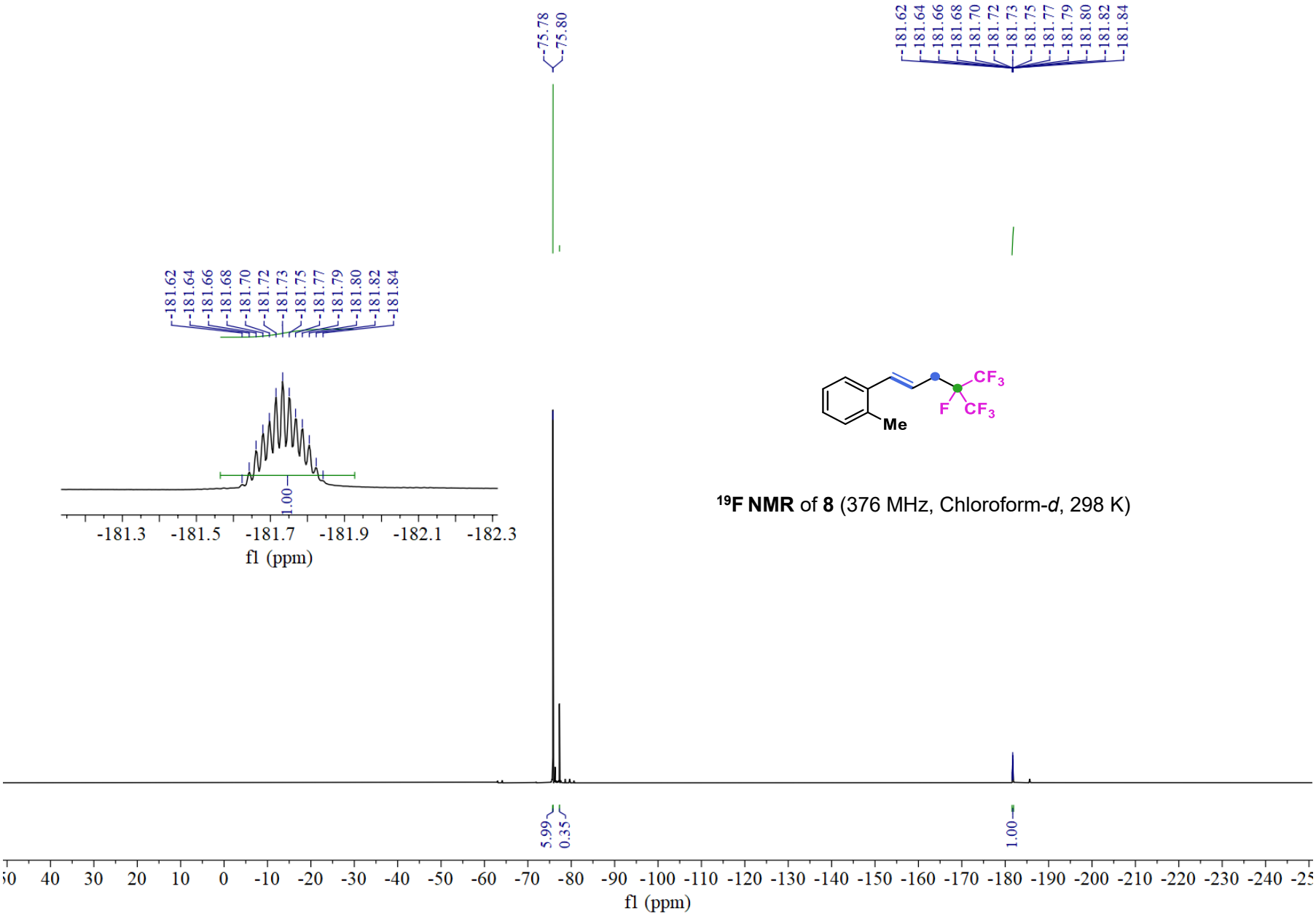


^{13}C NMR of **7** (101 MHz, Chloroform-*d*, 298 K)

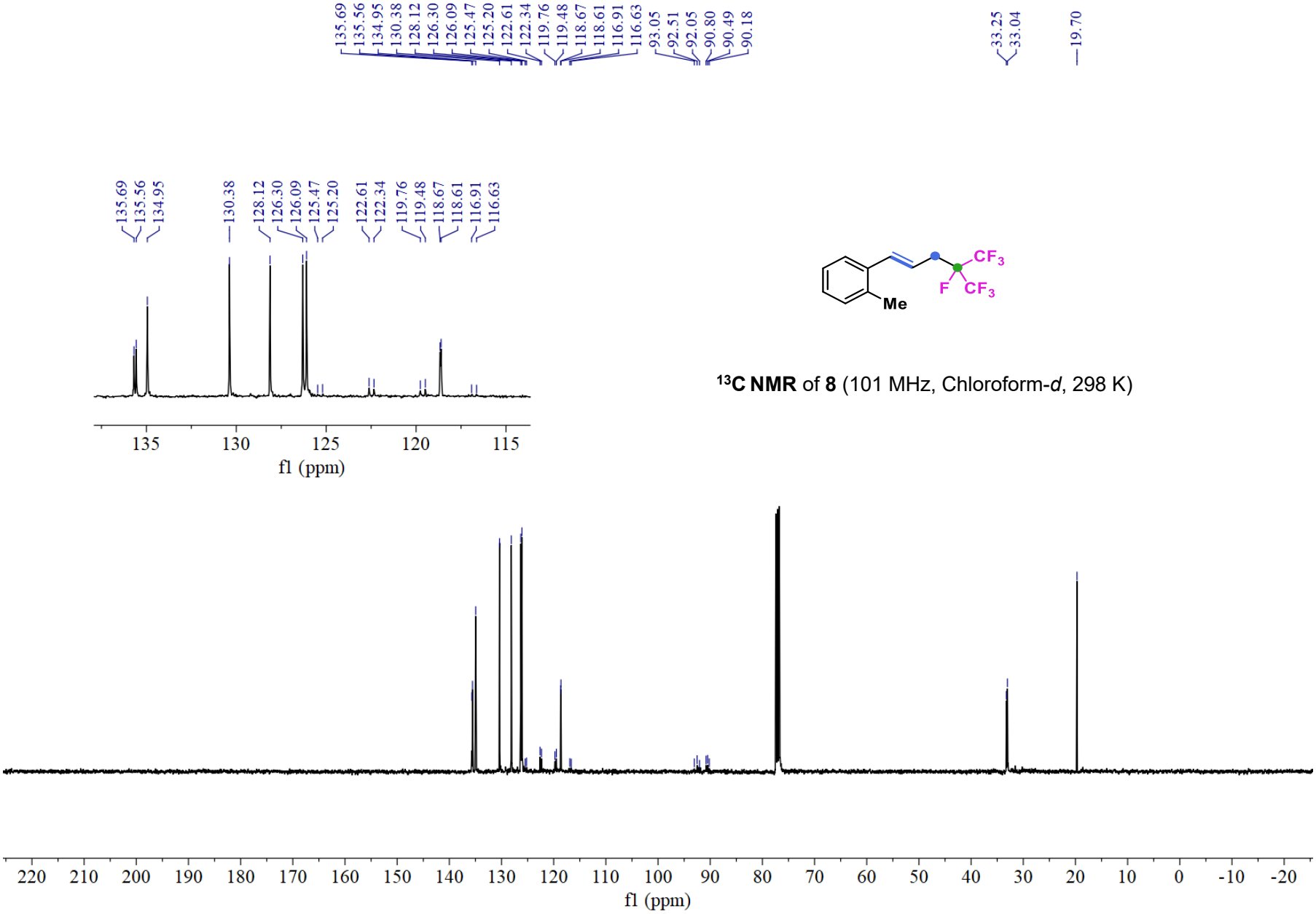




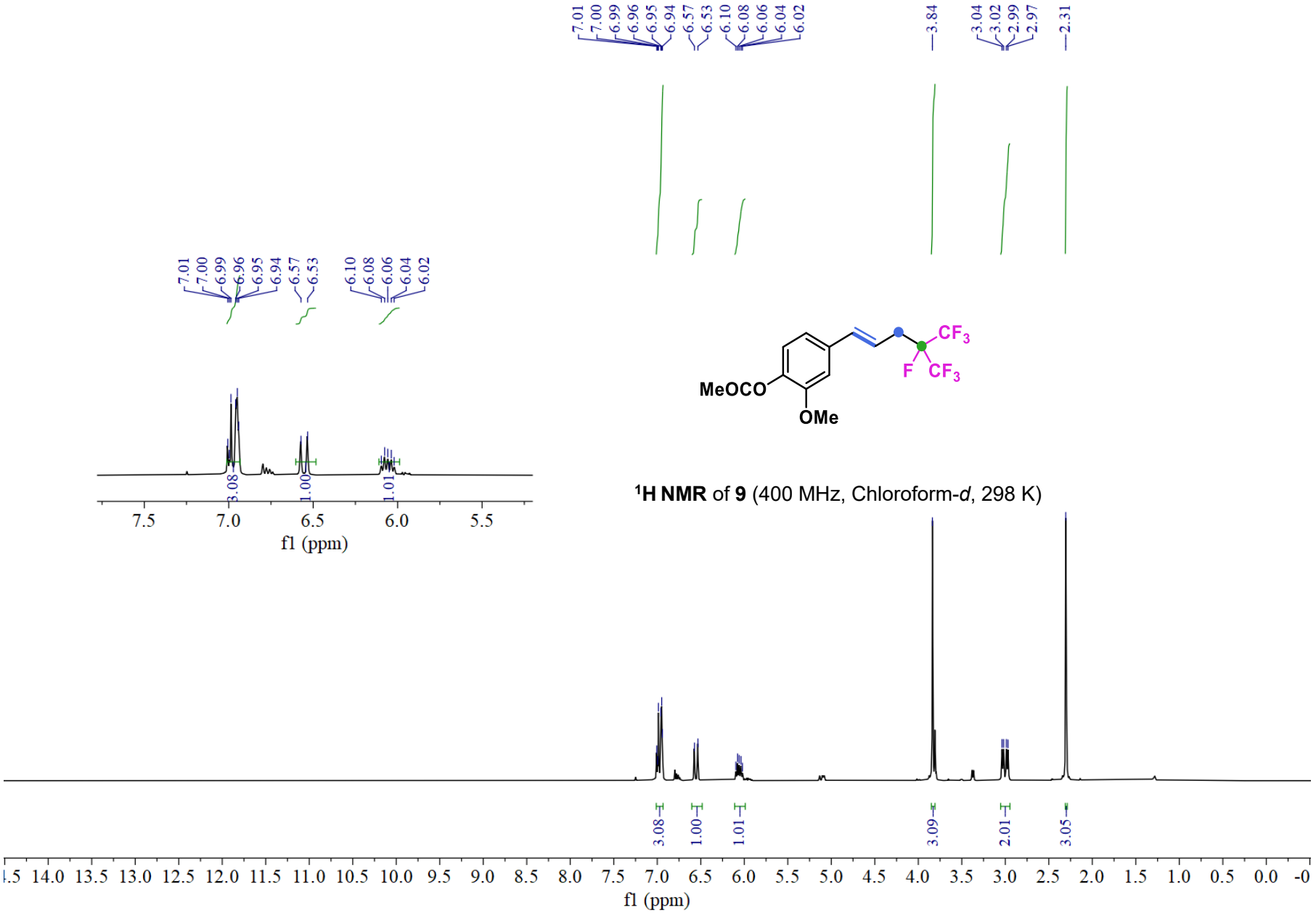
^{1}H NMR of **8** (400 MHz, Chloroform-*d*, 298 K)



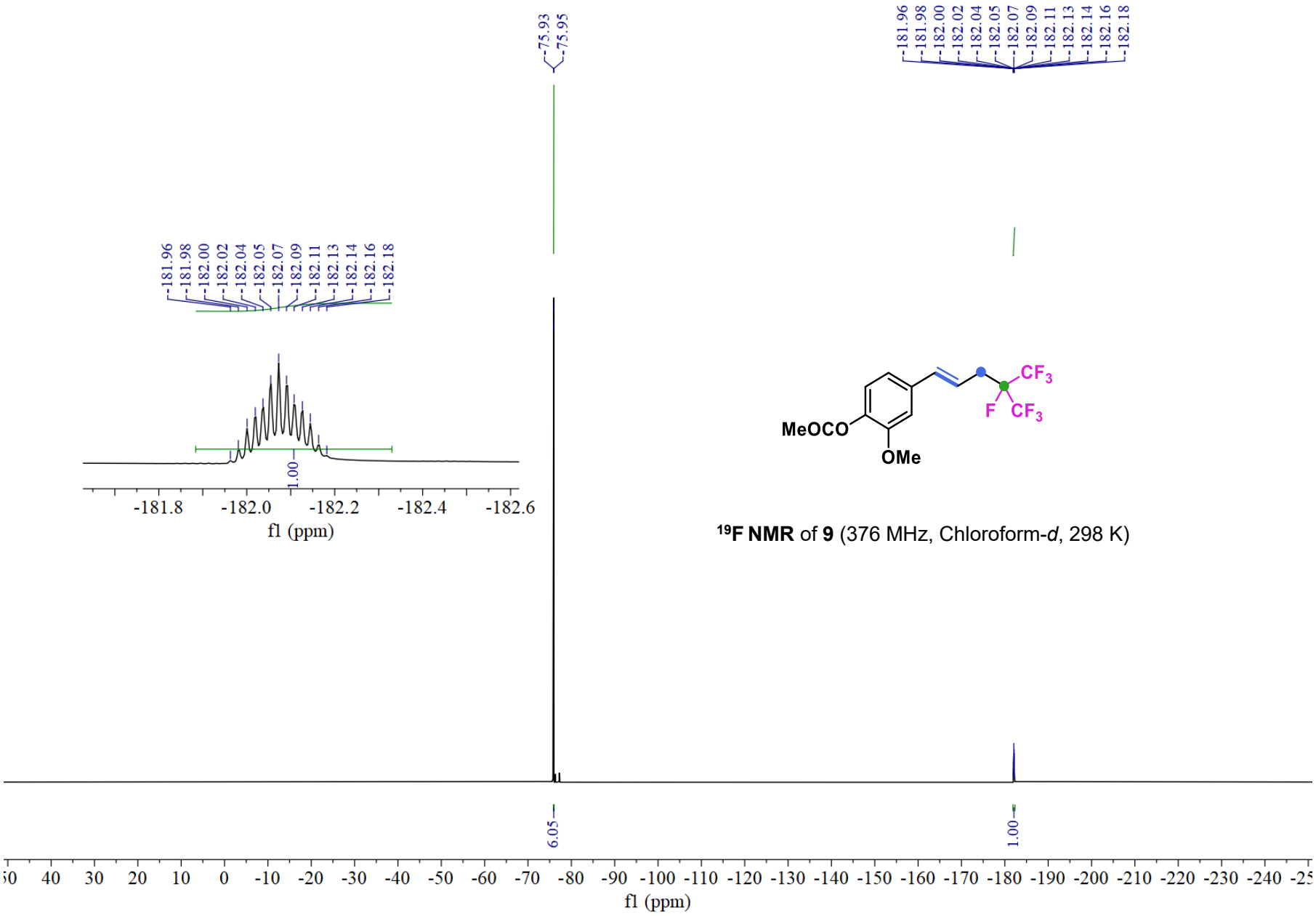
^{19}F NMR of **8** (376 MHz, Chloroform-*d*, 298 K)



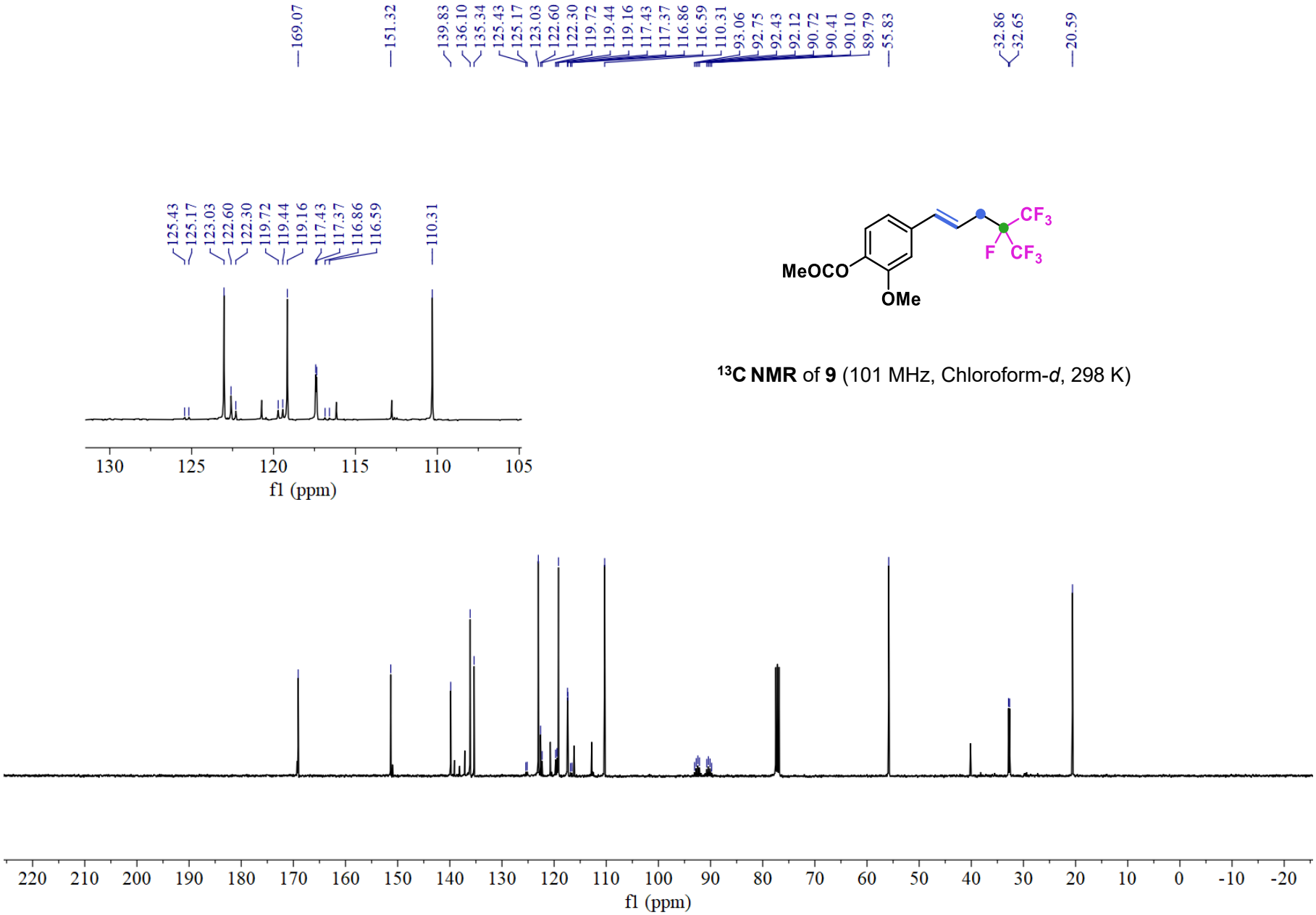
^{13}C NMR of **8** (101 MHz, Chloroform-*d*, 298 K)



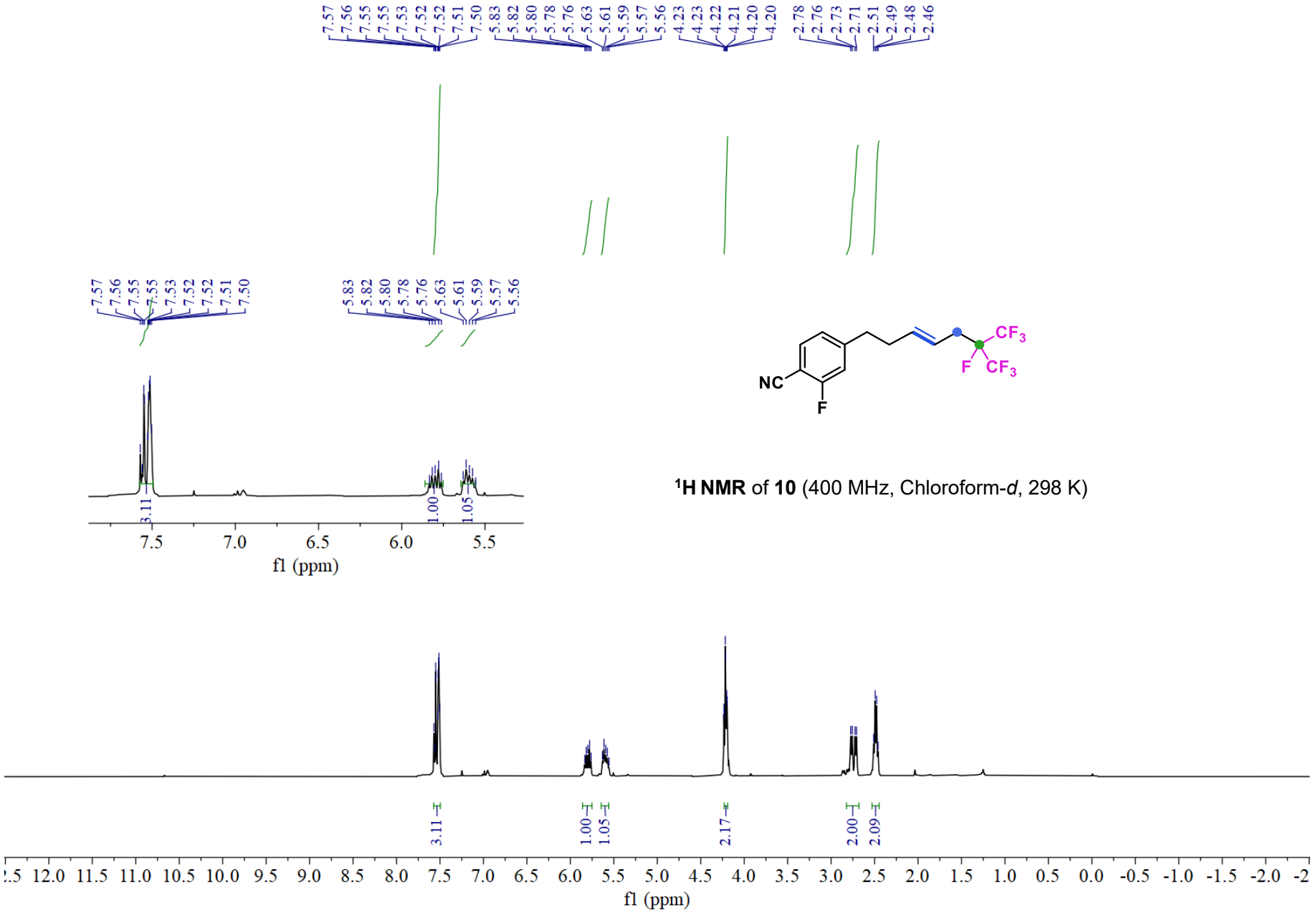
^{1}H NMR of **9** (400 MHz, Chloroform-*d*, 298 K)



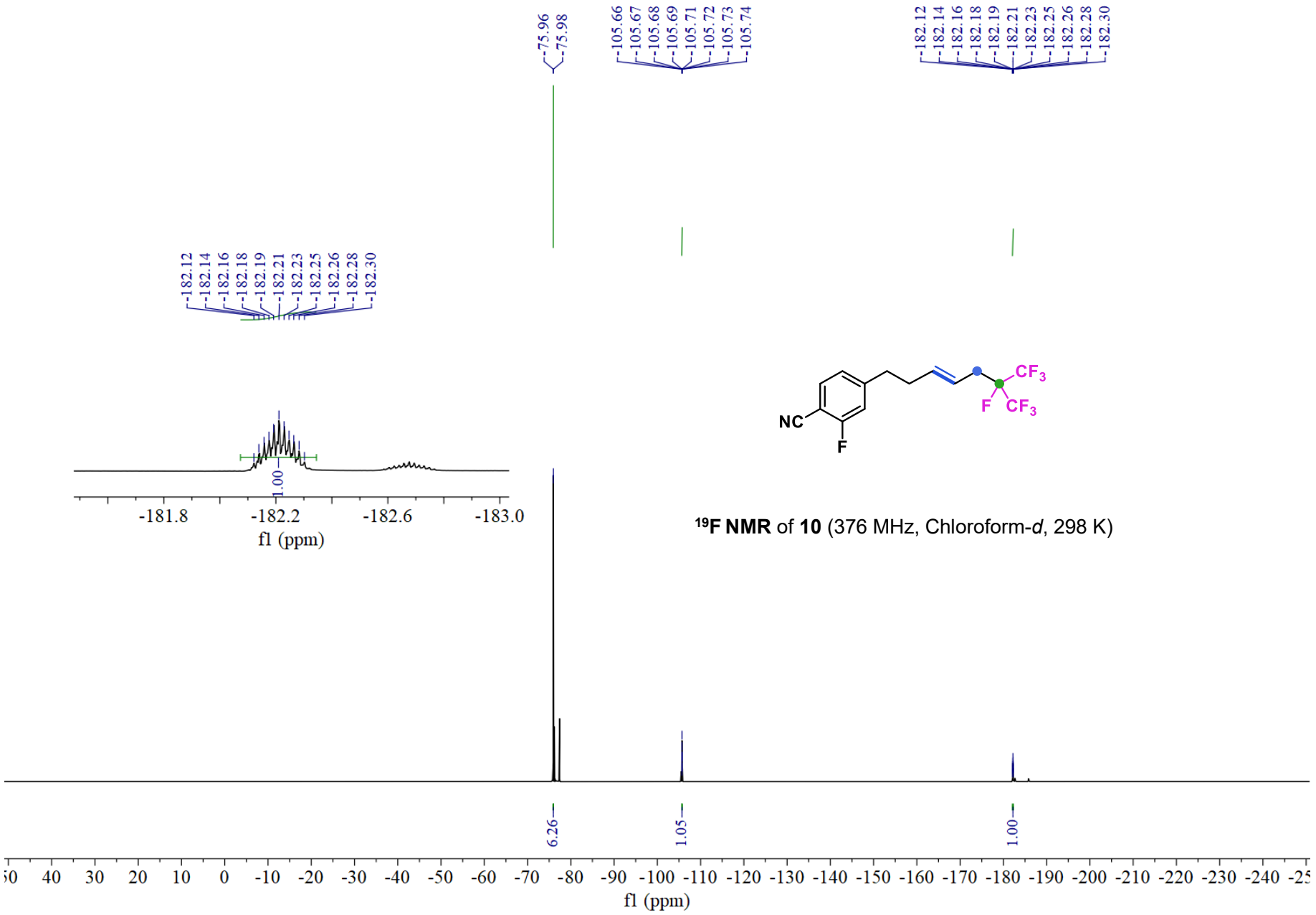
^{19}F NMR of **9** (376 MHz, Chloroform-*d*, 298 K)



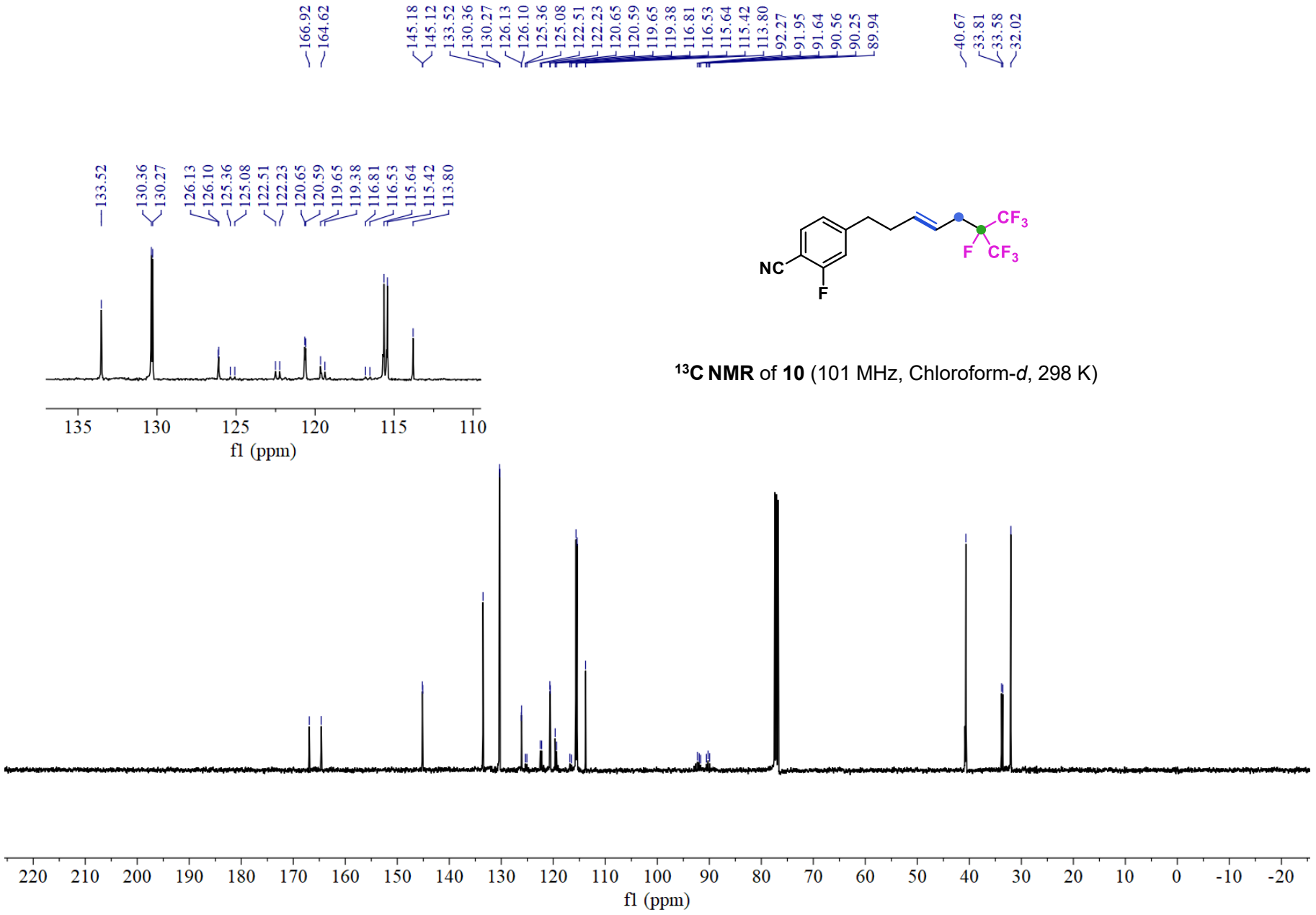
^{13}C NMR of **9** (101 MHz, Chloroform-*d*, 298 K)



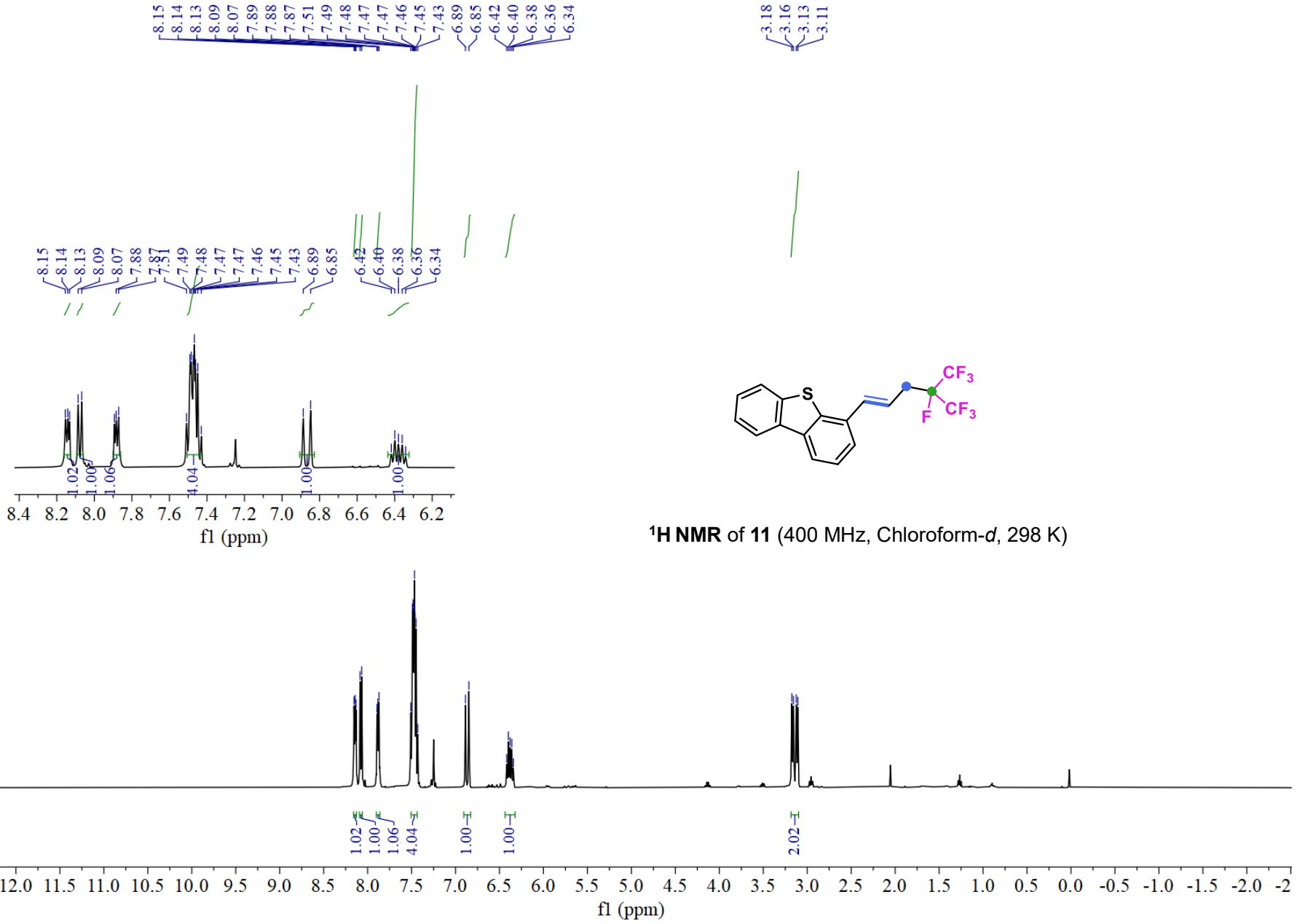
^{1}H NMR of **10** (400 MHz, Chloroform-*d*, 298 K)



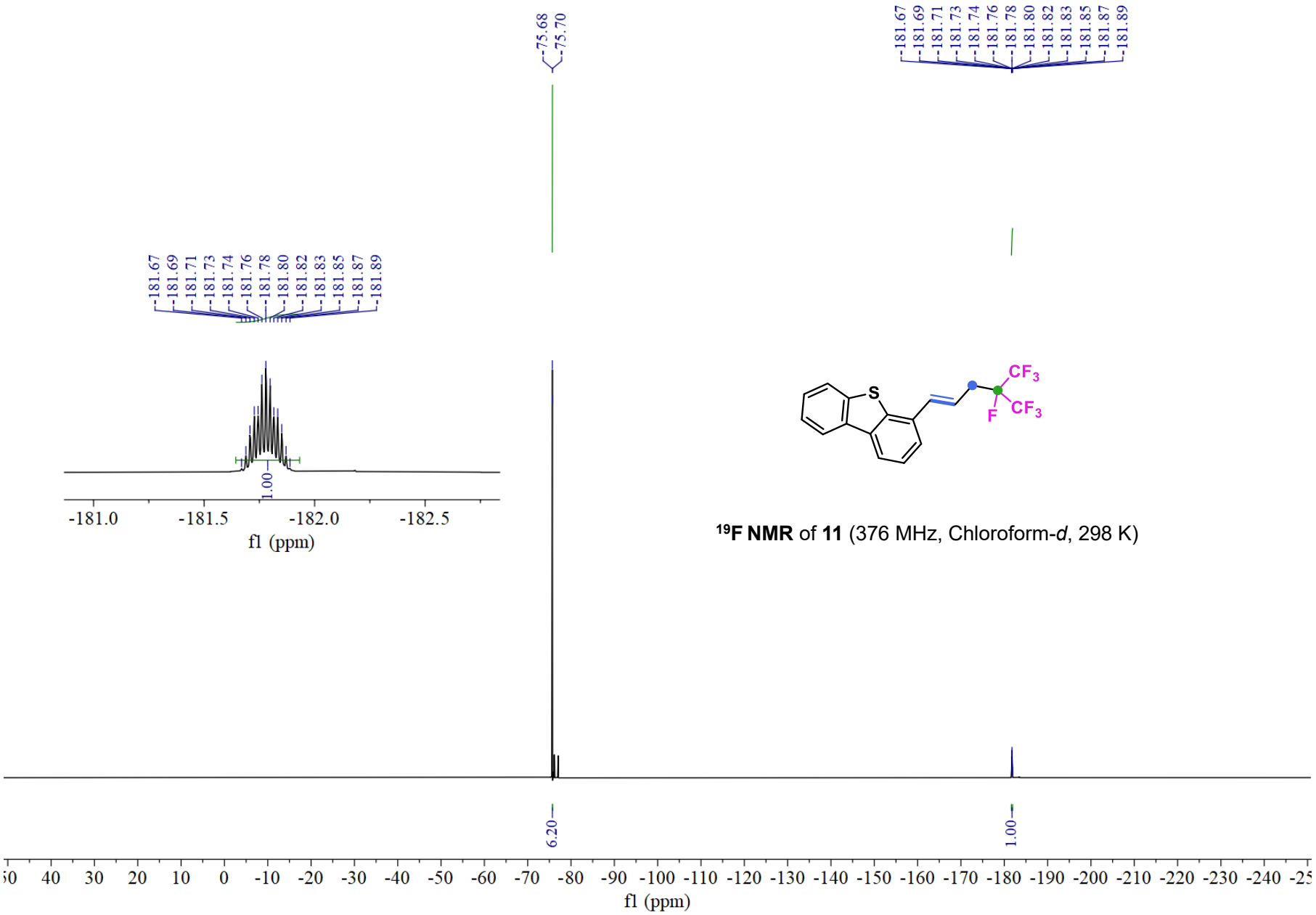
^{19}F NMR of **10** (376 MHz, Chloroform-*d*, 298 K)



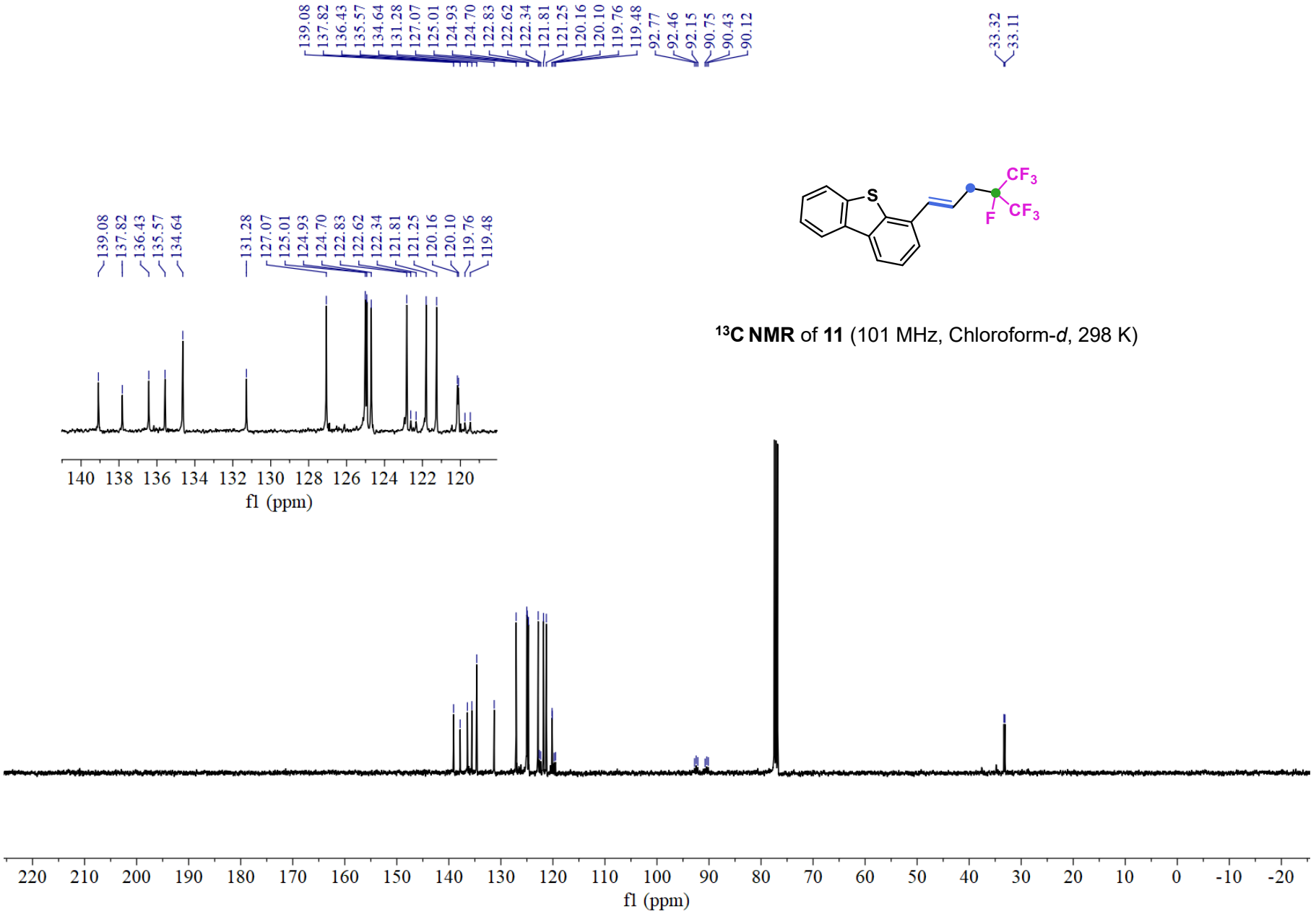
^{13}C NMR of **10** (101 MHz, Chloroform-*d*, 298 K)



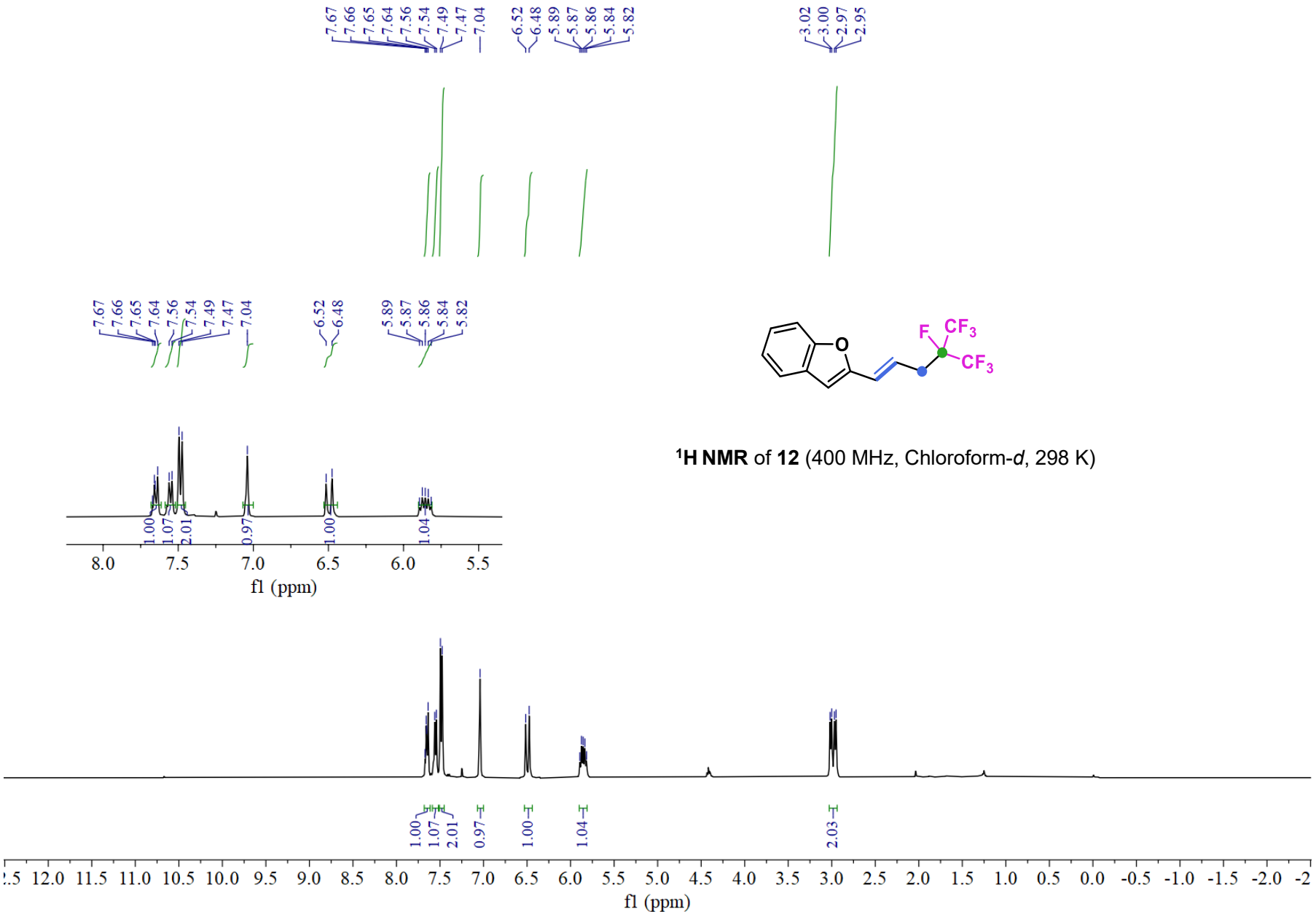
^{1}H NMR of **11** (400 MHz, Chloroform-*d*, 298 K)



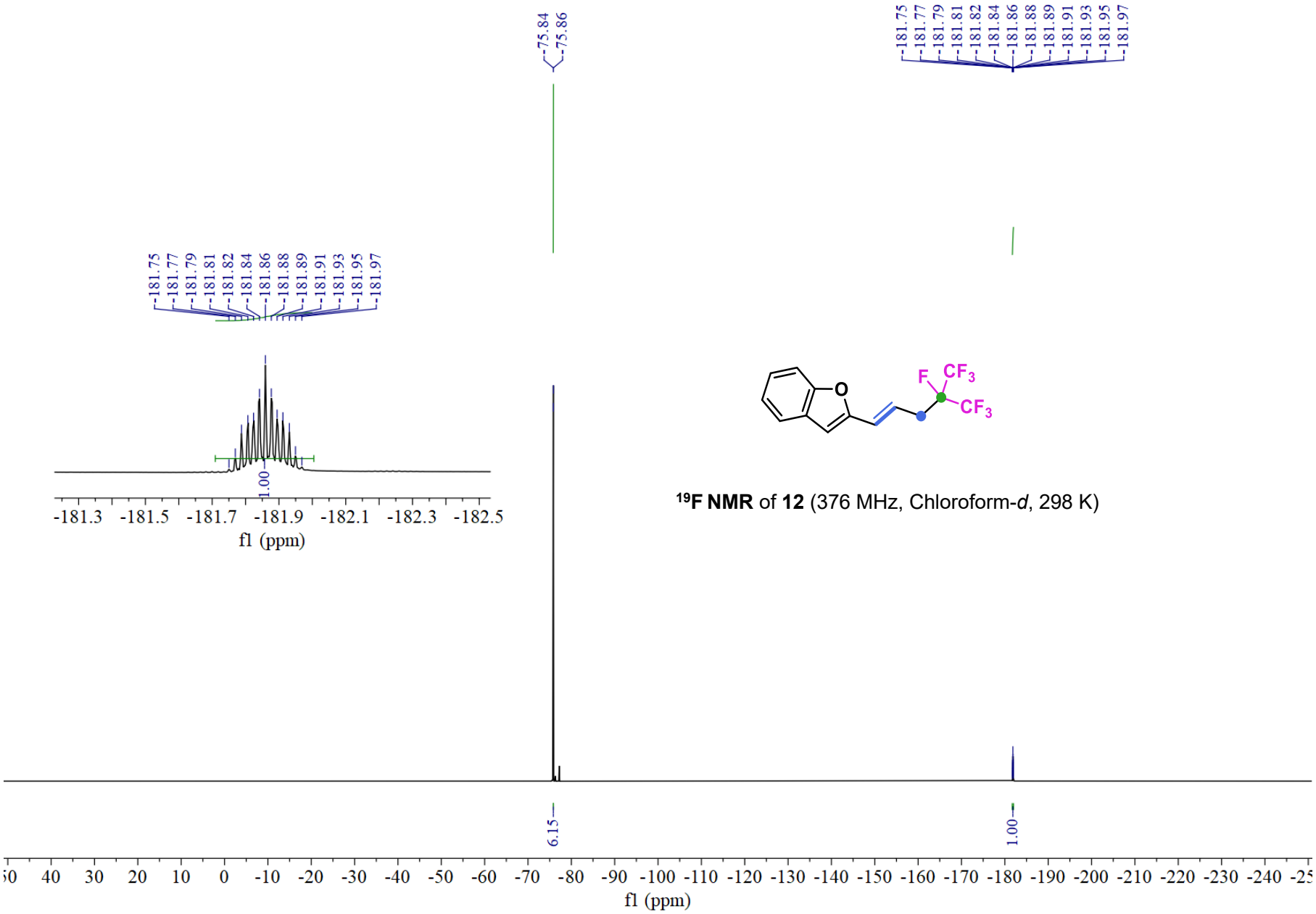
^{19}F NMR of **11** (376 MHz, Chloroform-*d*, 298 K)



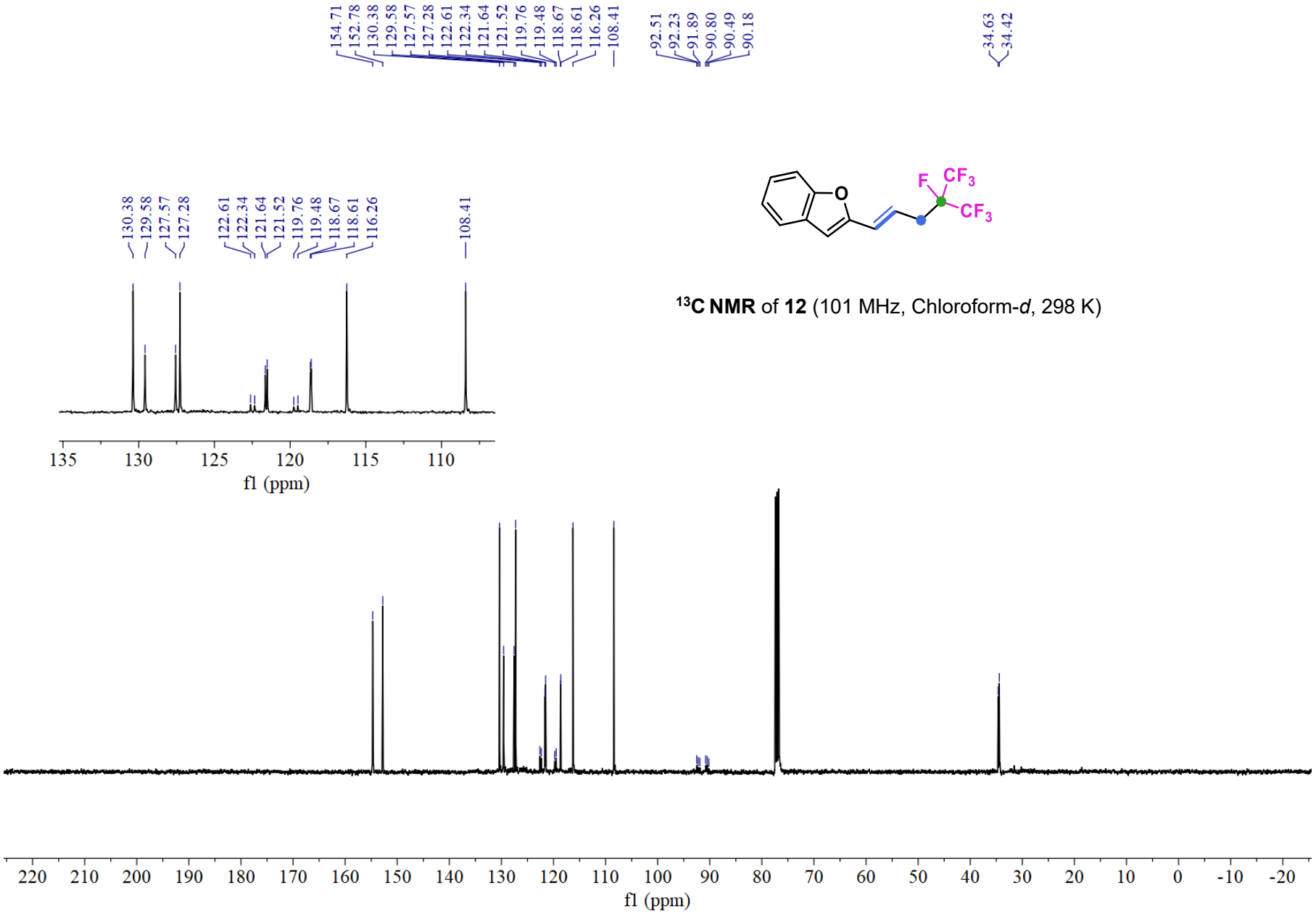
^{13}C NMR of **11** (101 MHz, Chloroform-*d*, 298 K)



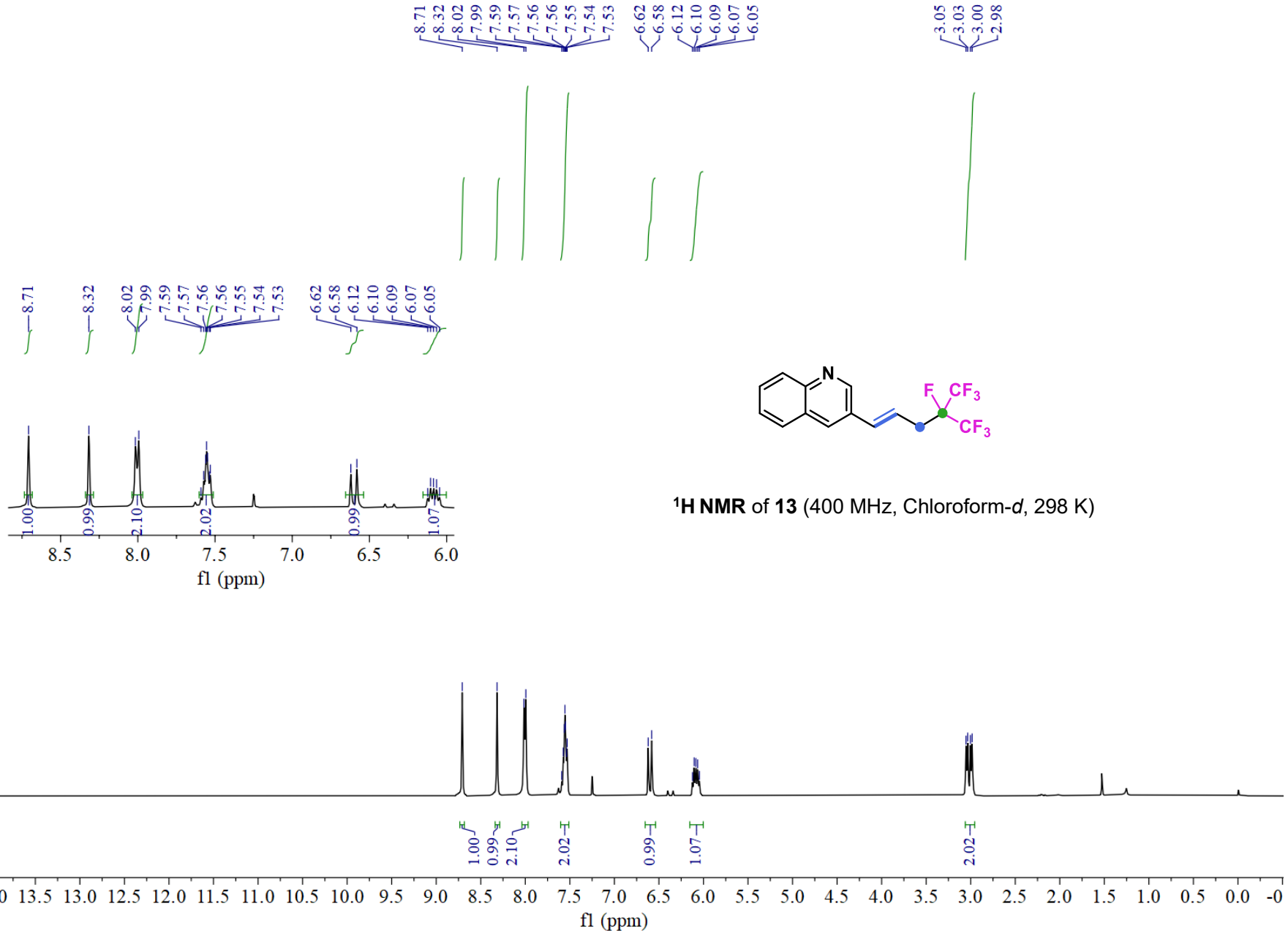
^{1}H NMR of **12** (400 MHz, Chloroform-*d*, 298 K)



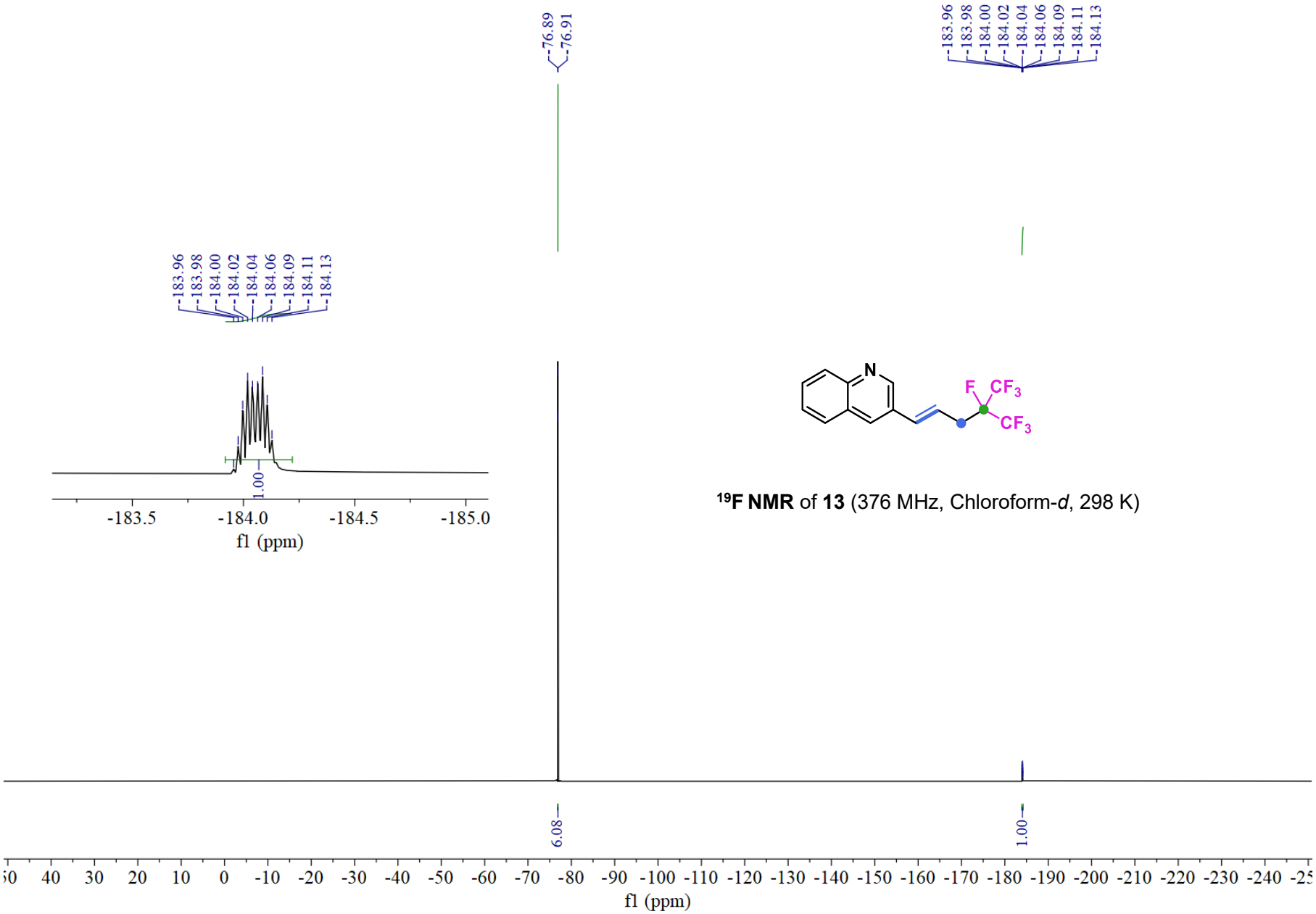
^{19}F NMR of **12** (376 MHz, Chloroform-*d*, 298 K)



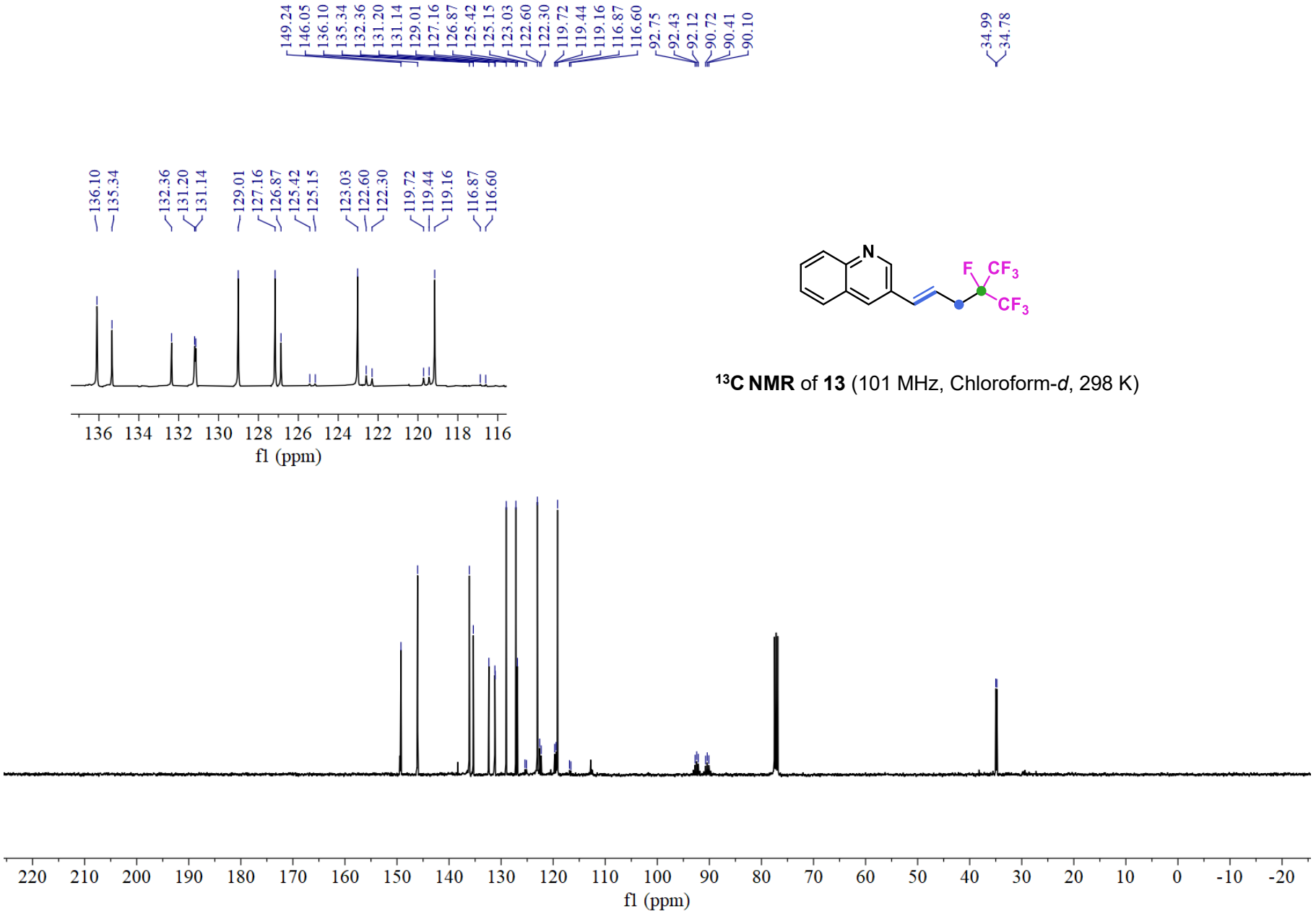
^{13}C NMR of **12** (101 MHz, Chloroform-*d*, 298 K)



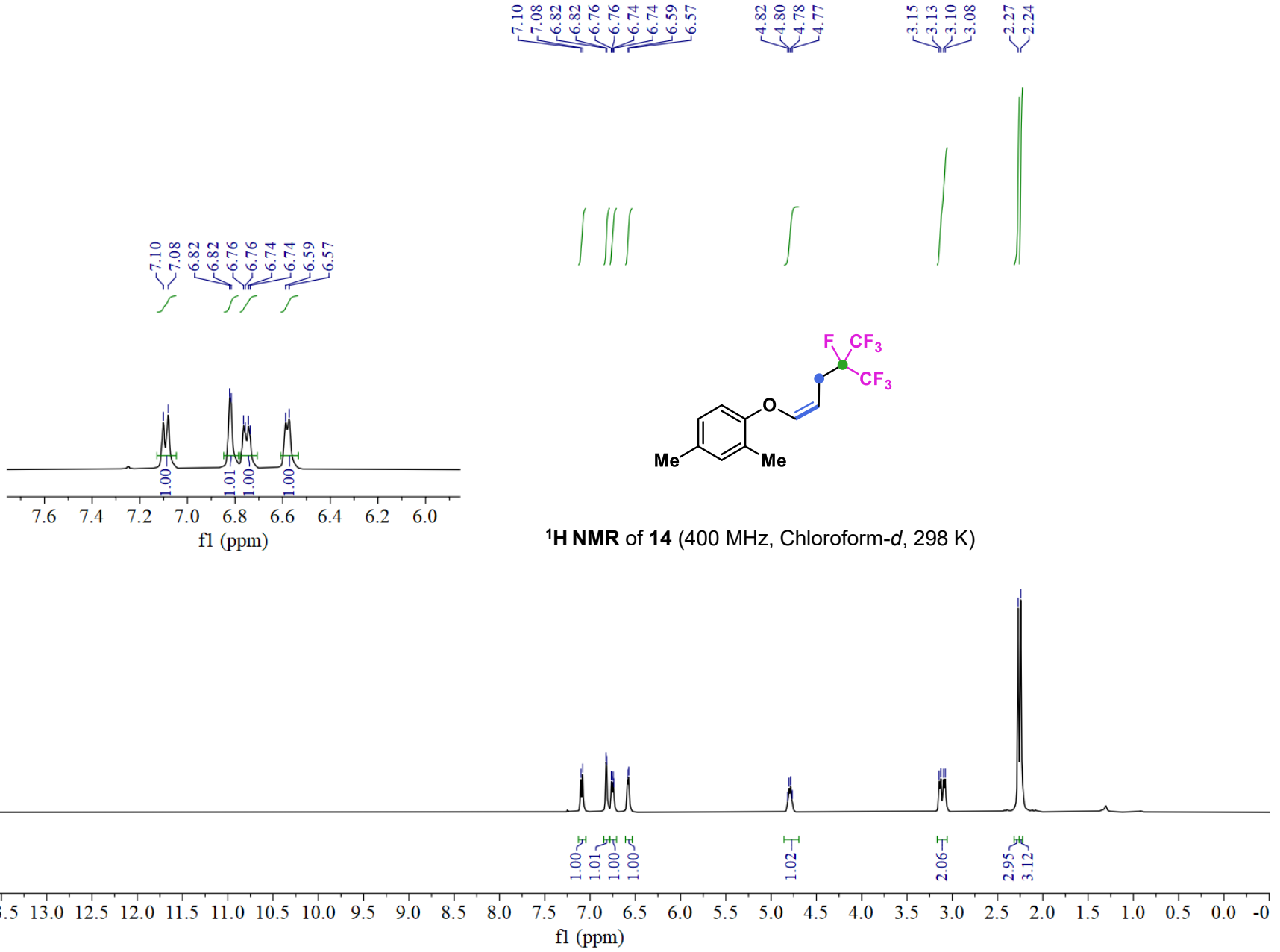
^{1}H NMR of **13** (400 MHz, Chloroform-*d*, 298 K)



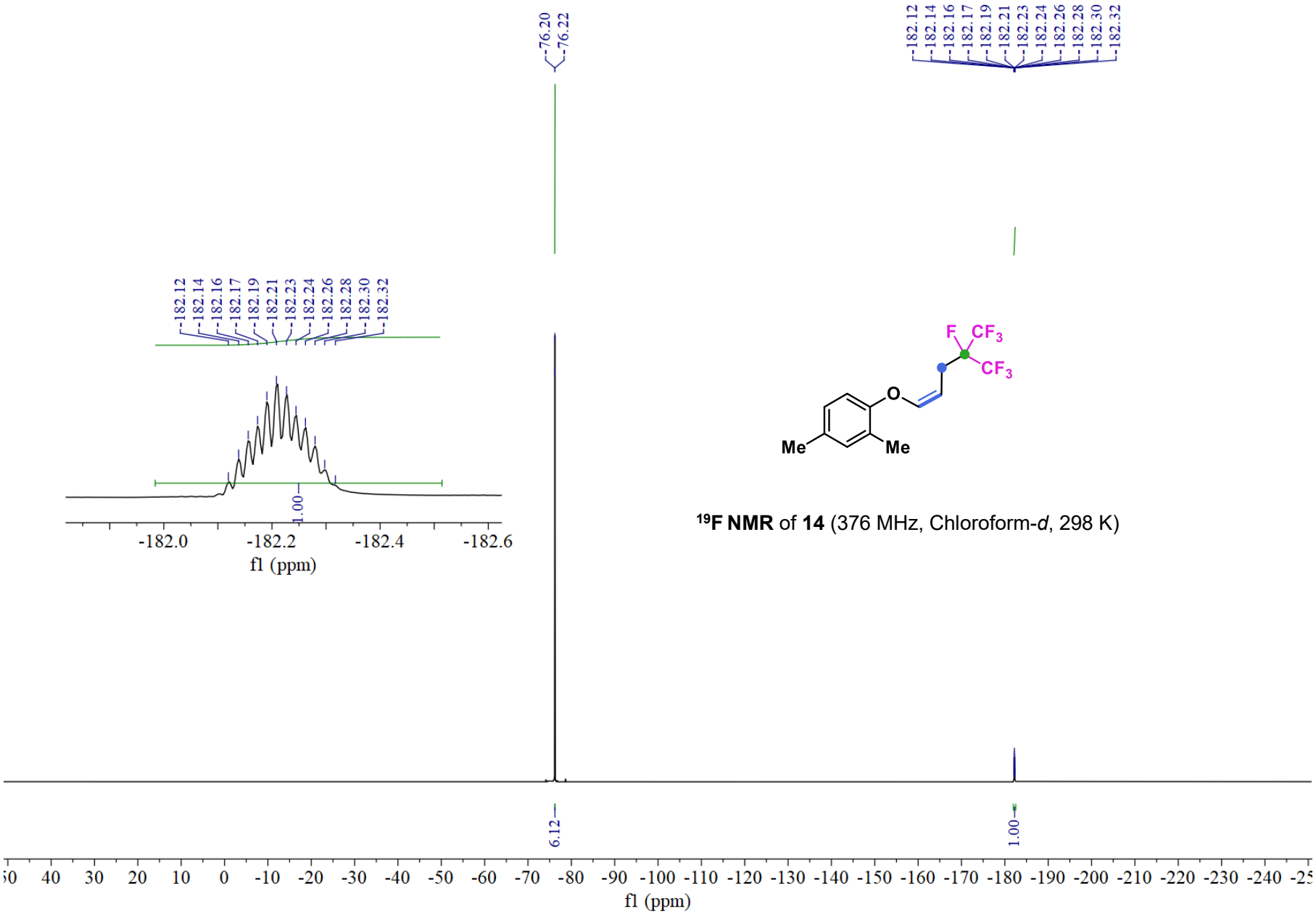
^{19}F NMR of **13** (376 MHz, Chloroform-*d*, 298 K)



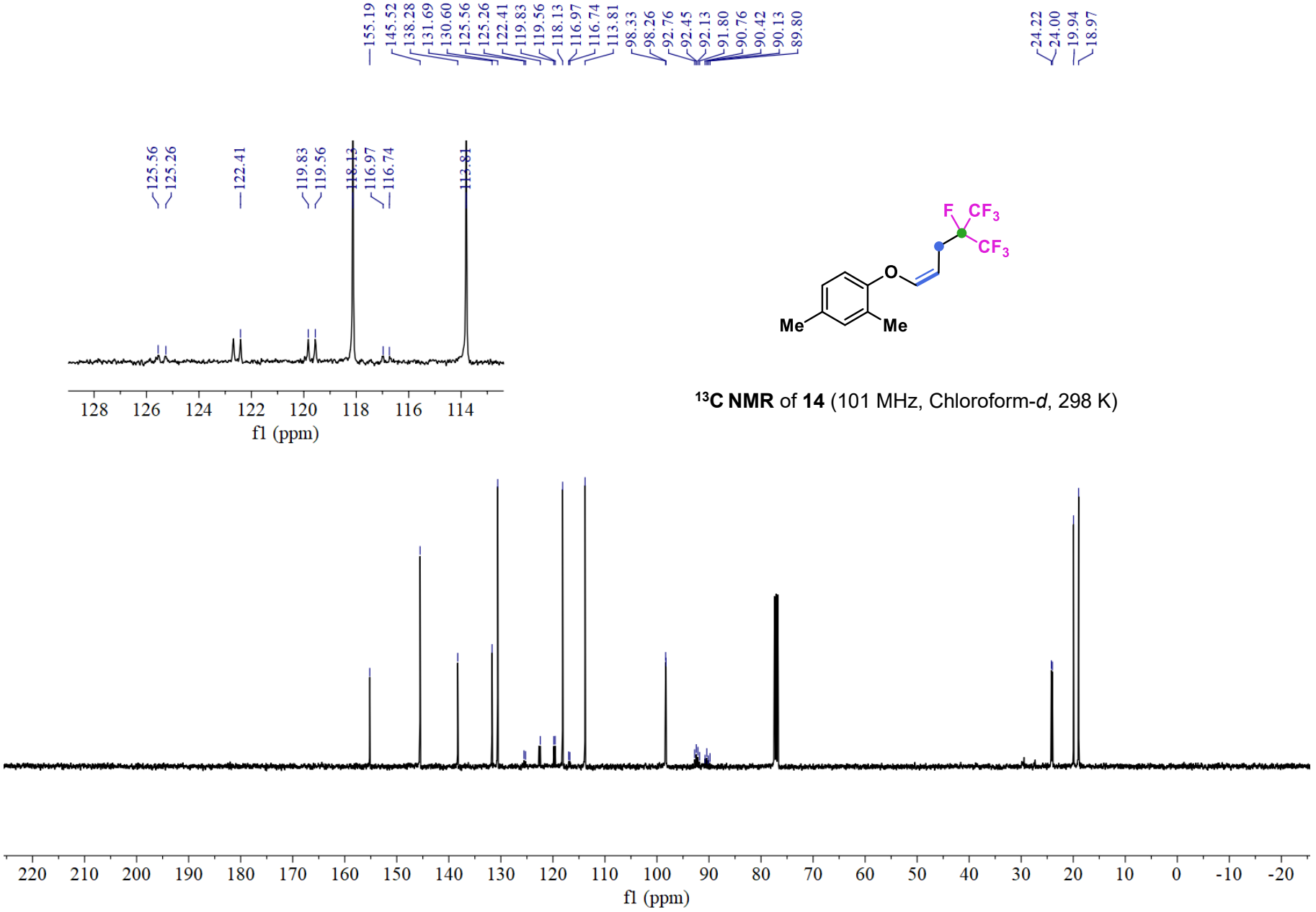
^{13}C NMR of **13** (101 MHz, Chloroform-*d*, 298 K)



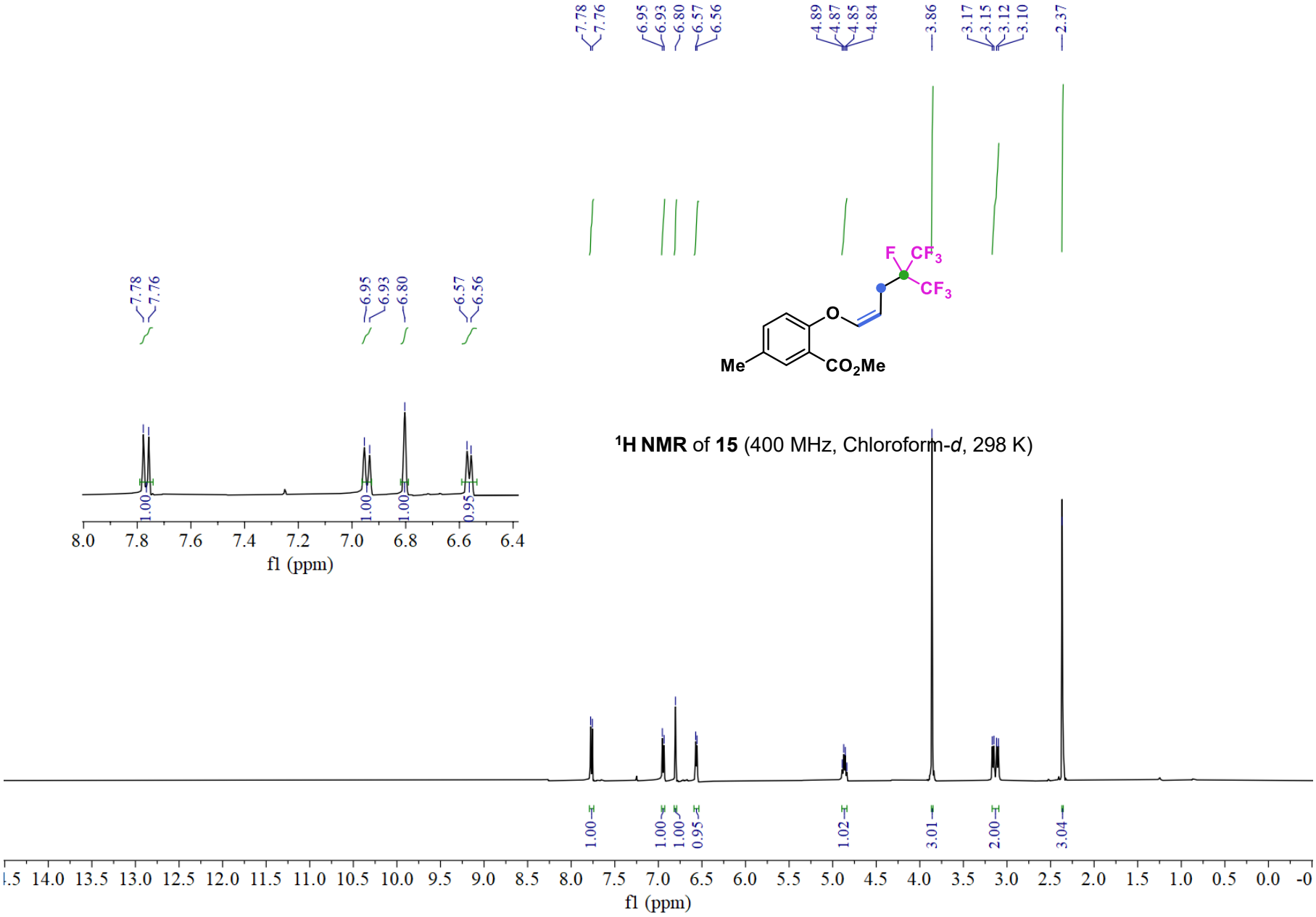
^{1}H NMR of **14** (400 MHz, Chloroform-*d*, 298 K)



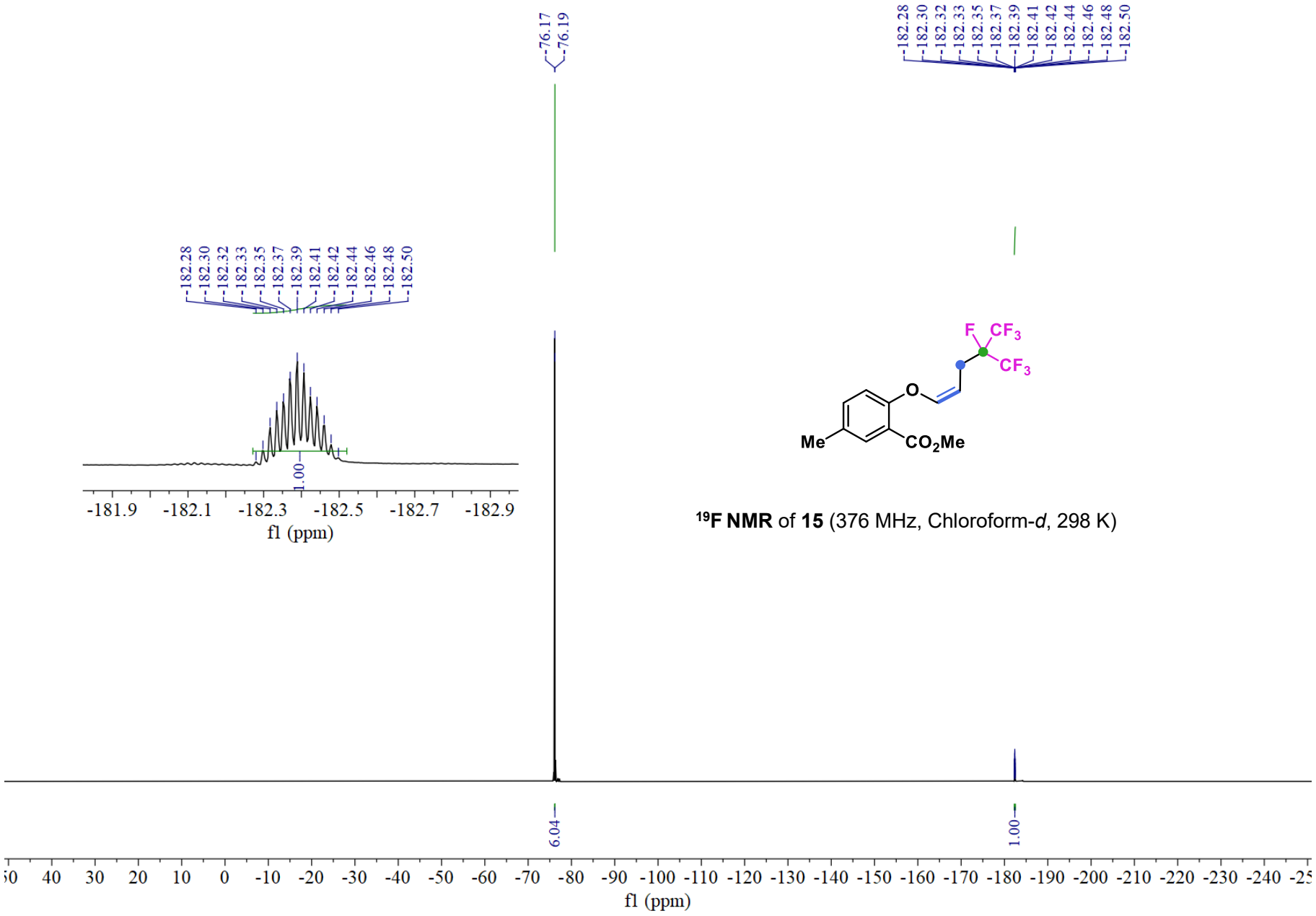
^{19}F NMR of **14** (376 MHz, Chloroform-*d*, 298 K)



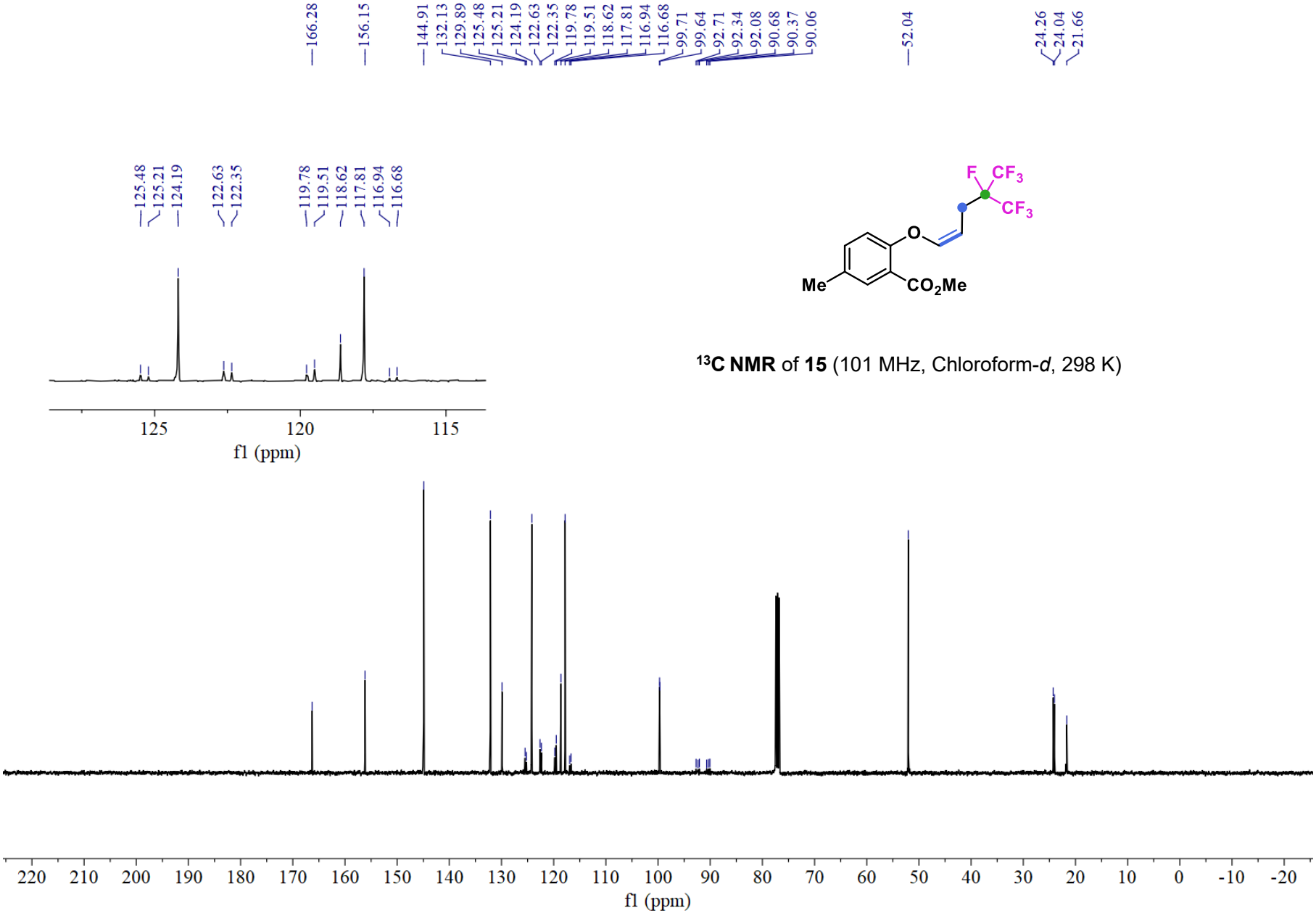
^{13}C NMR of **14** (101 MHz, Chloroform-*d*, 298 K)



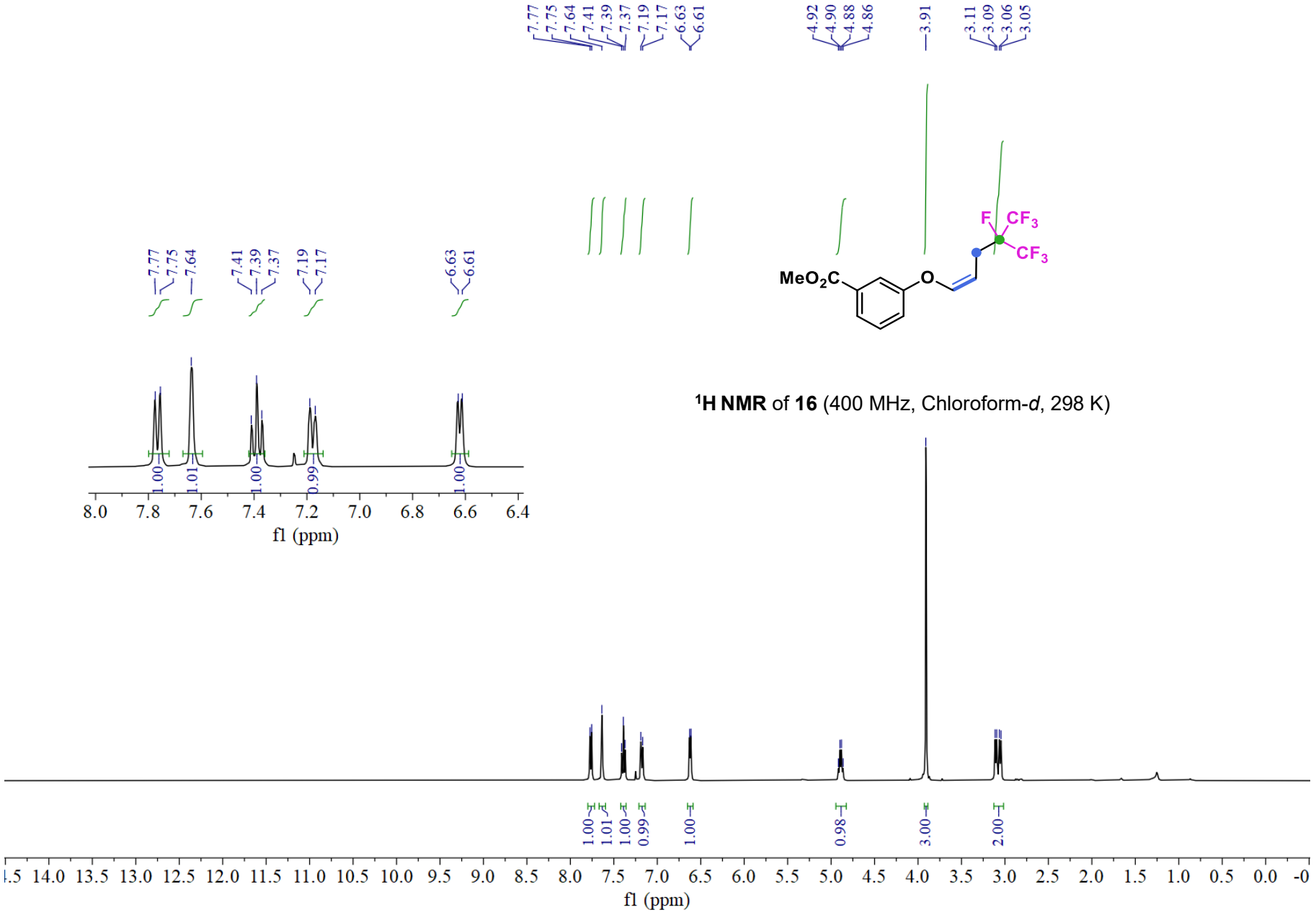
^{1}H NMR of **15** (400 MHz, Chloroform-*d*, 298 K)



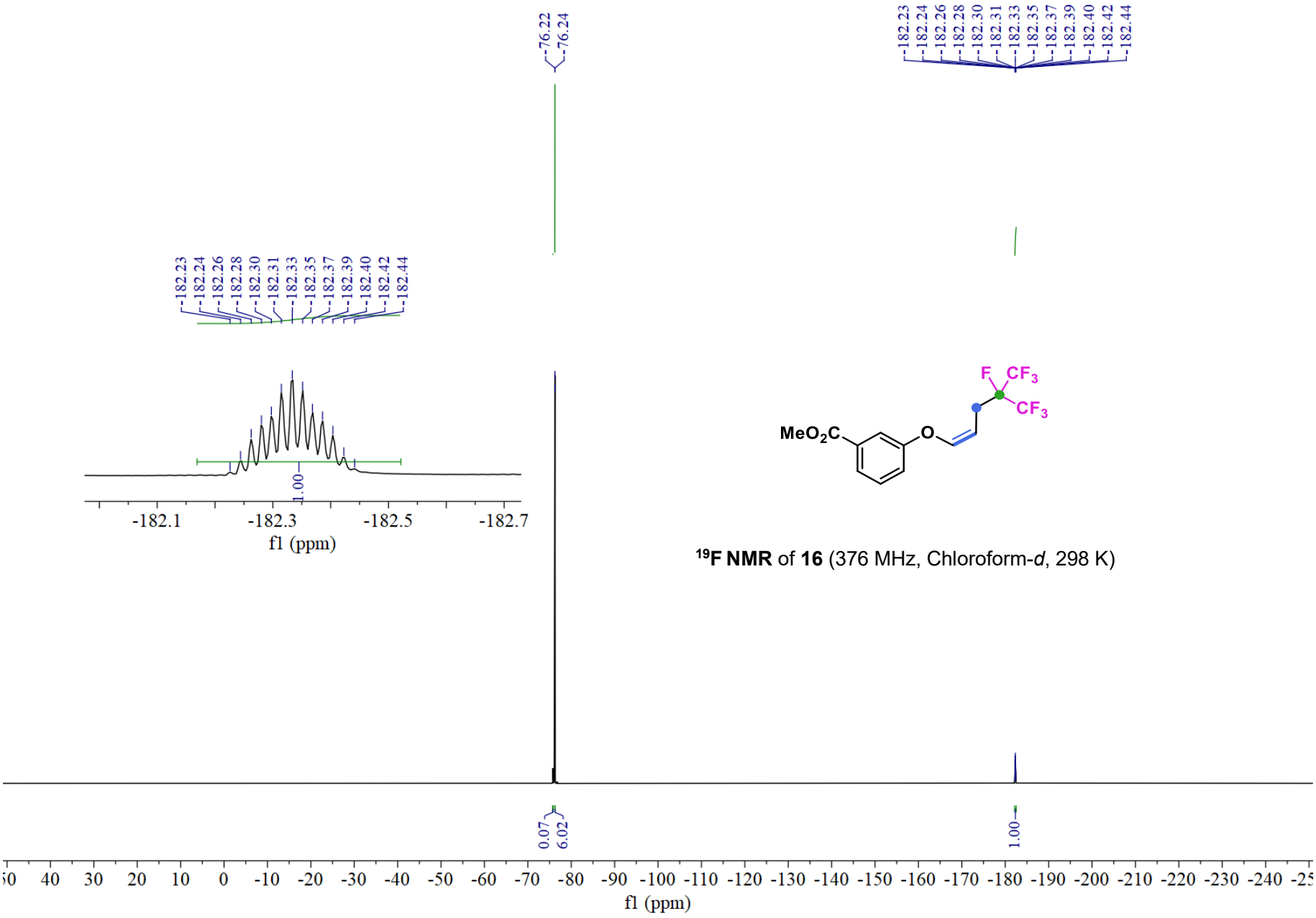
^{19}F NMR of **15** (376 MHz, Chloroform-*d*, 298 K)



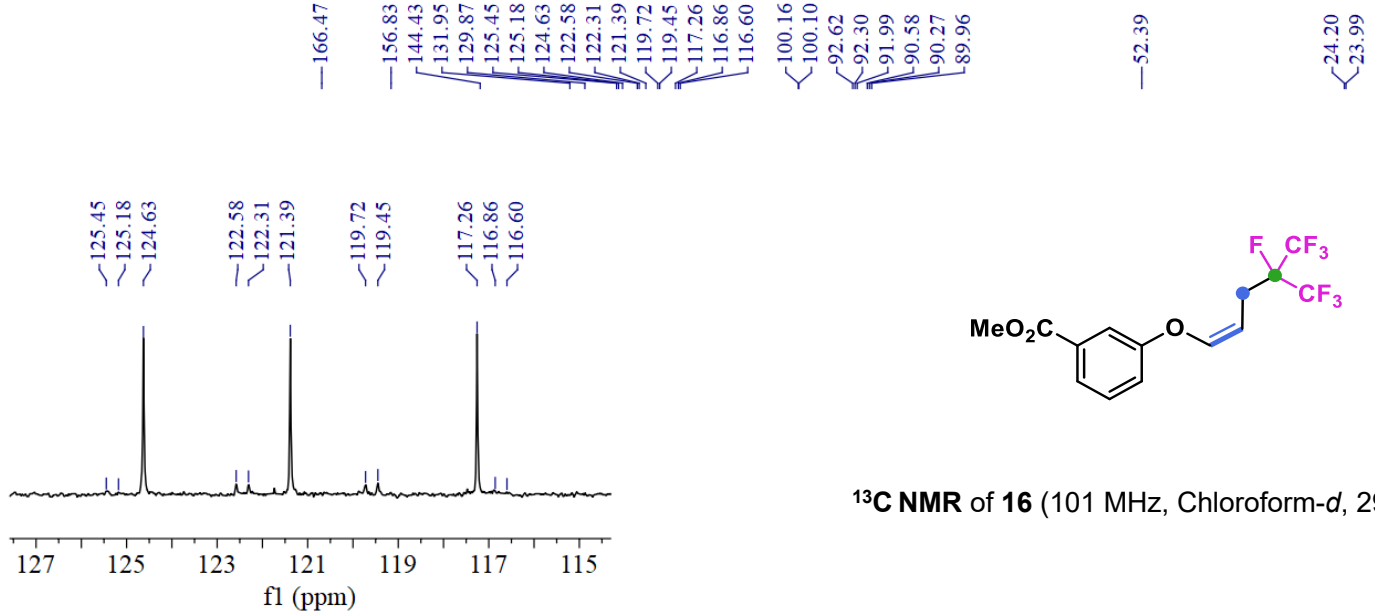
^{13}C NMR of **15** (101 MHz, Chloroform-*d*, 298 K)



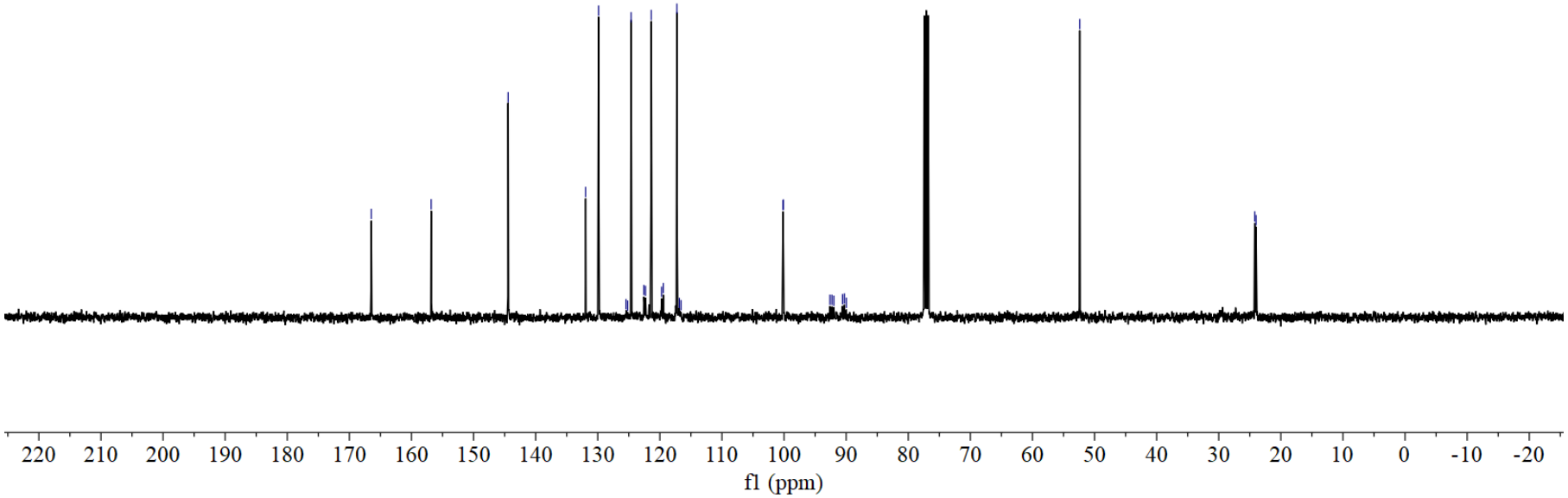
^{1}H NMR of **16** (400 MHz, Chloroform-*d*, 298 K)

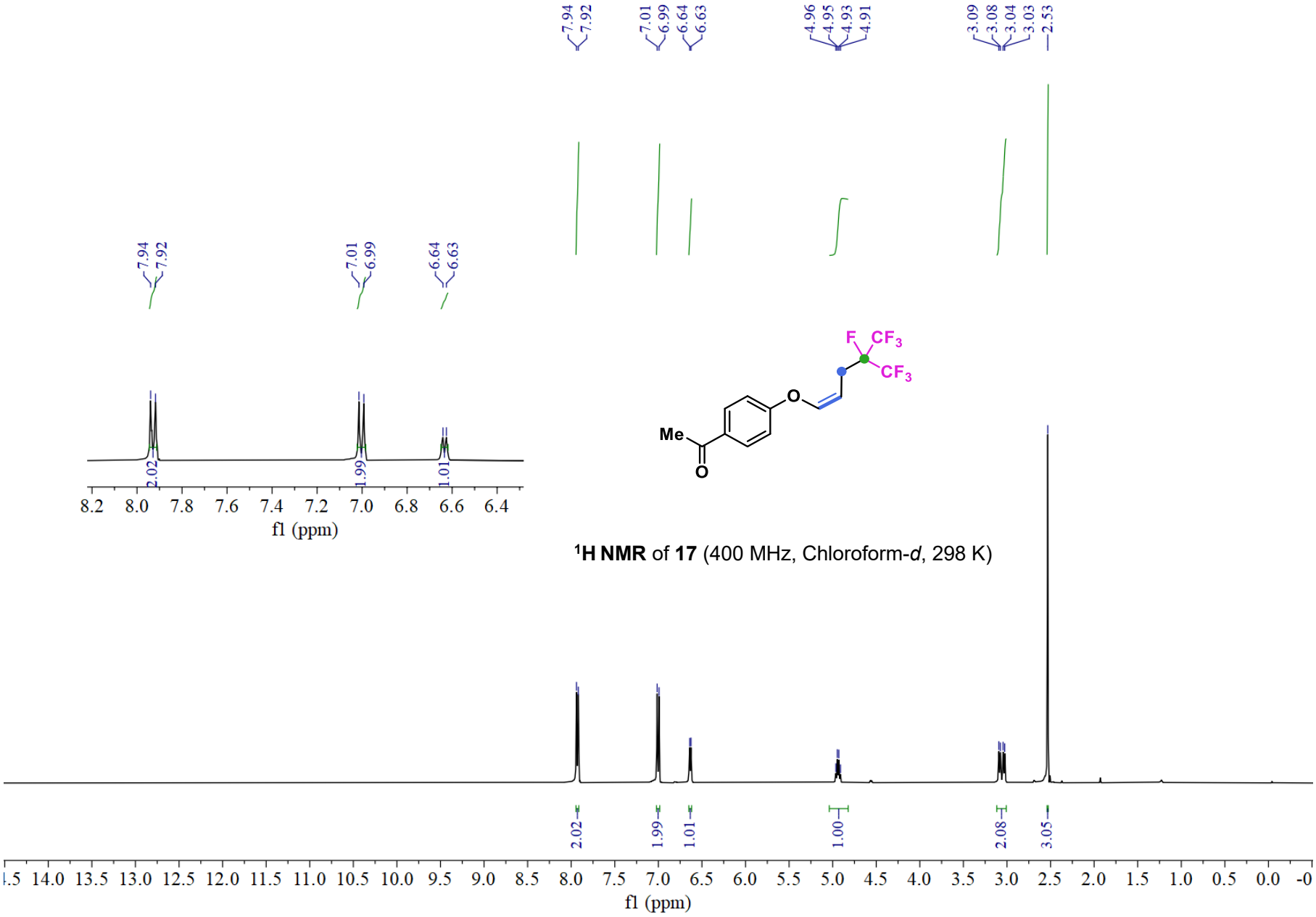


^{19}F NMR of **16** (376 MHz, Chloroform-*d*, 298 K)

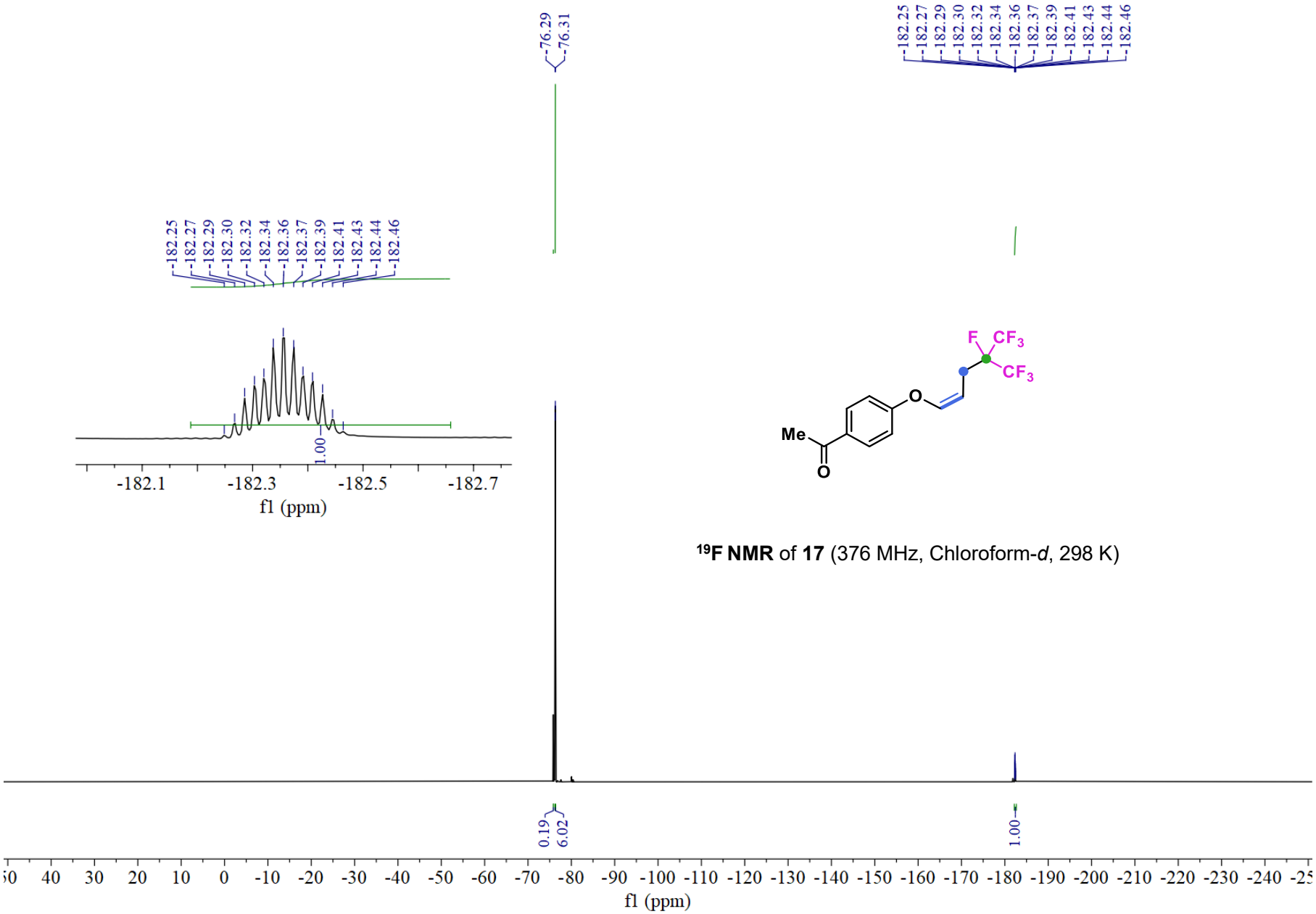


^{13}C NMR of **16** (101 MHz, Chloroform-*d*, 298 K)

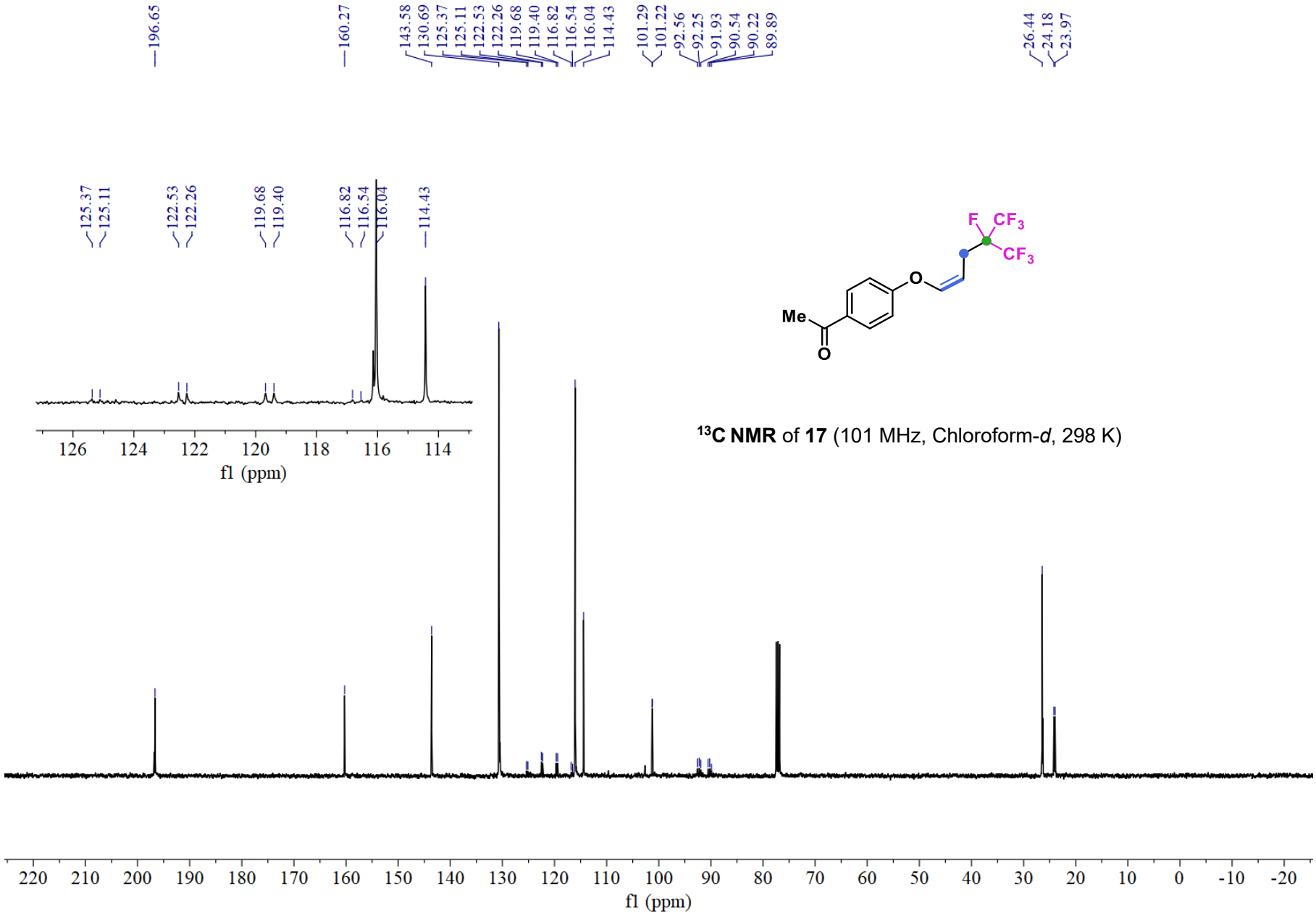




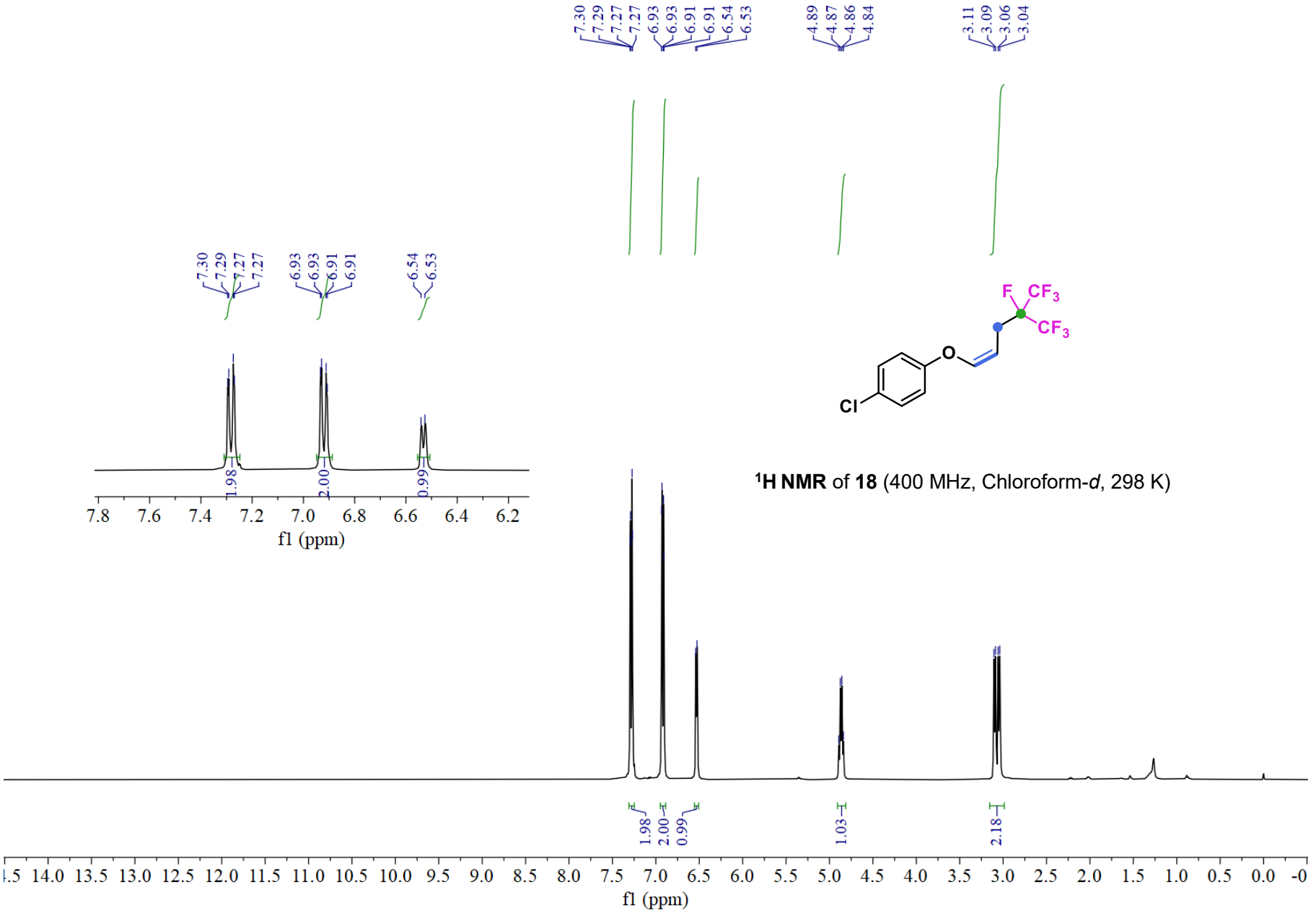
^{1}H NMR of **17** (400 MHz, Chloroform-*d*, 298 K)



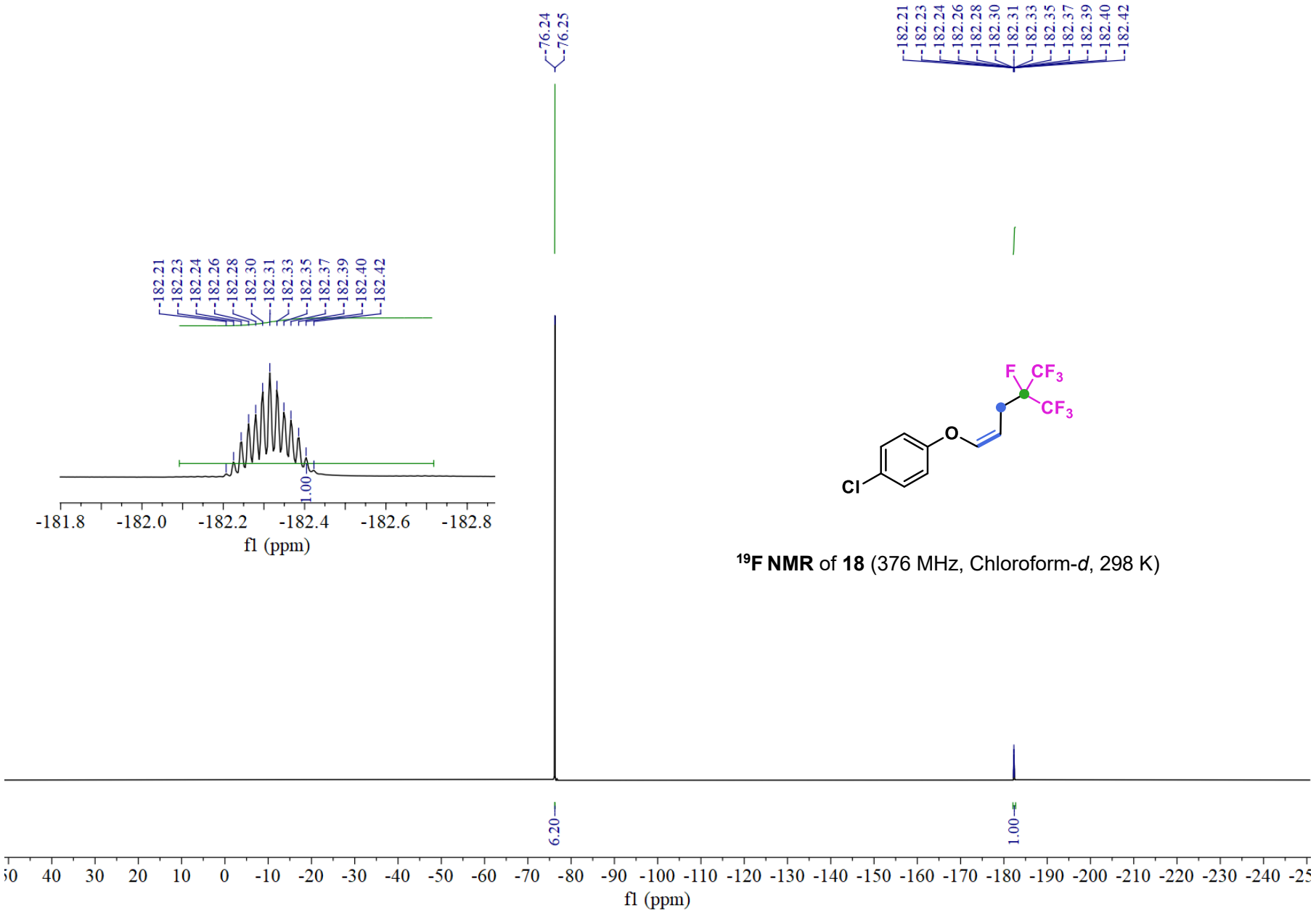
^{19}F NMR of **17** (376 MHz, Chloroform-*d*, 298 K)



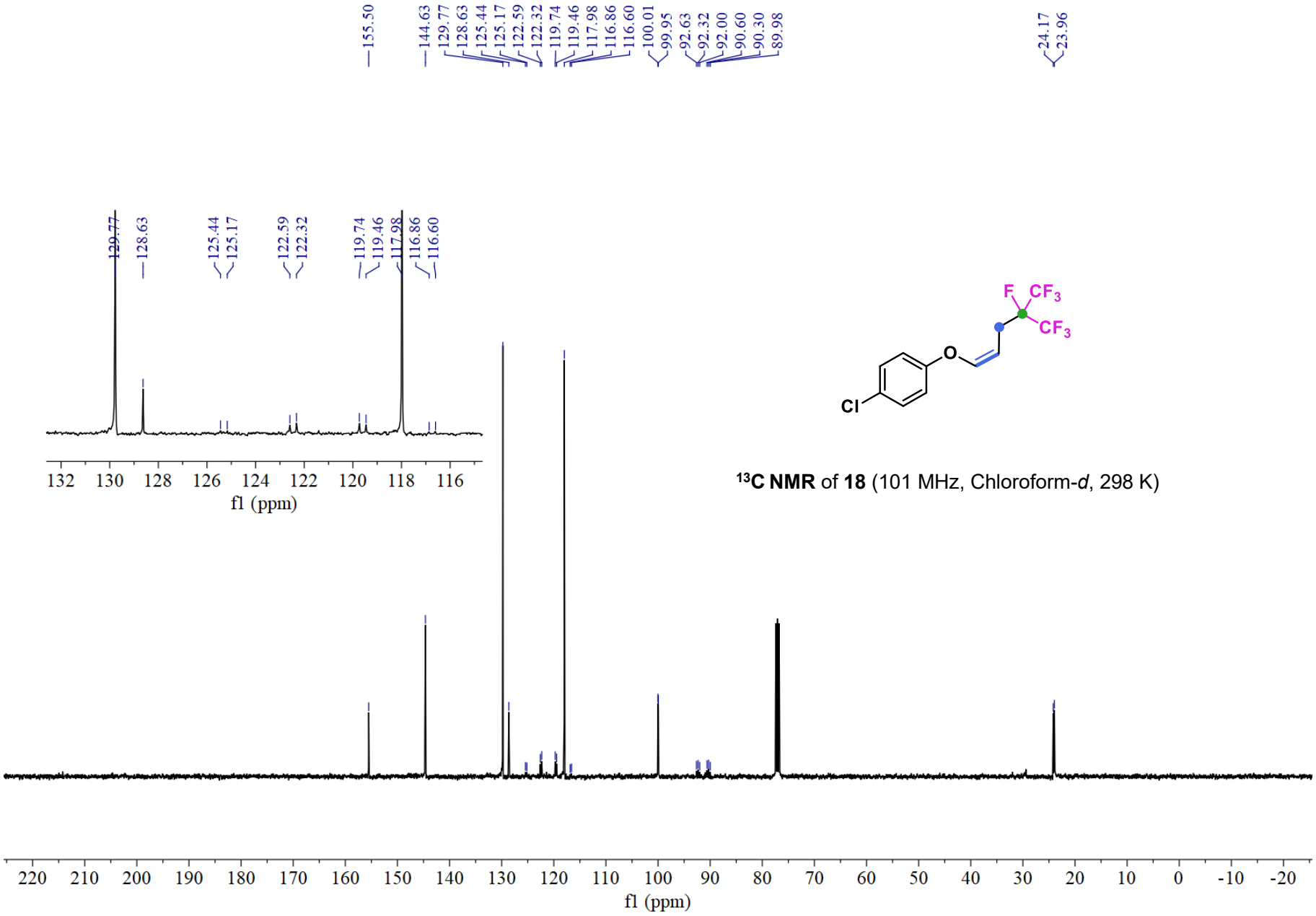
^{13}C NMR of **17** (101 MHz, Chloroform-*d*, 298 K)



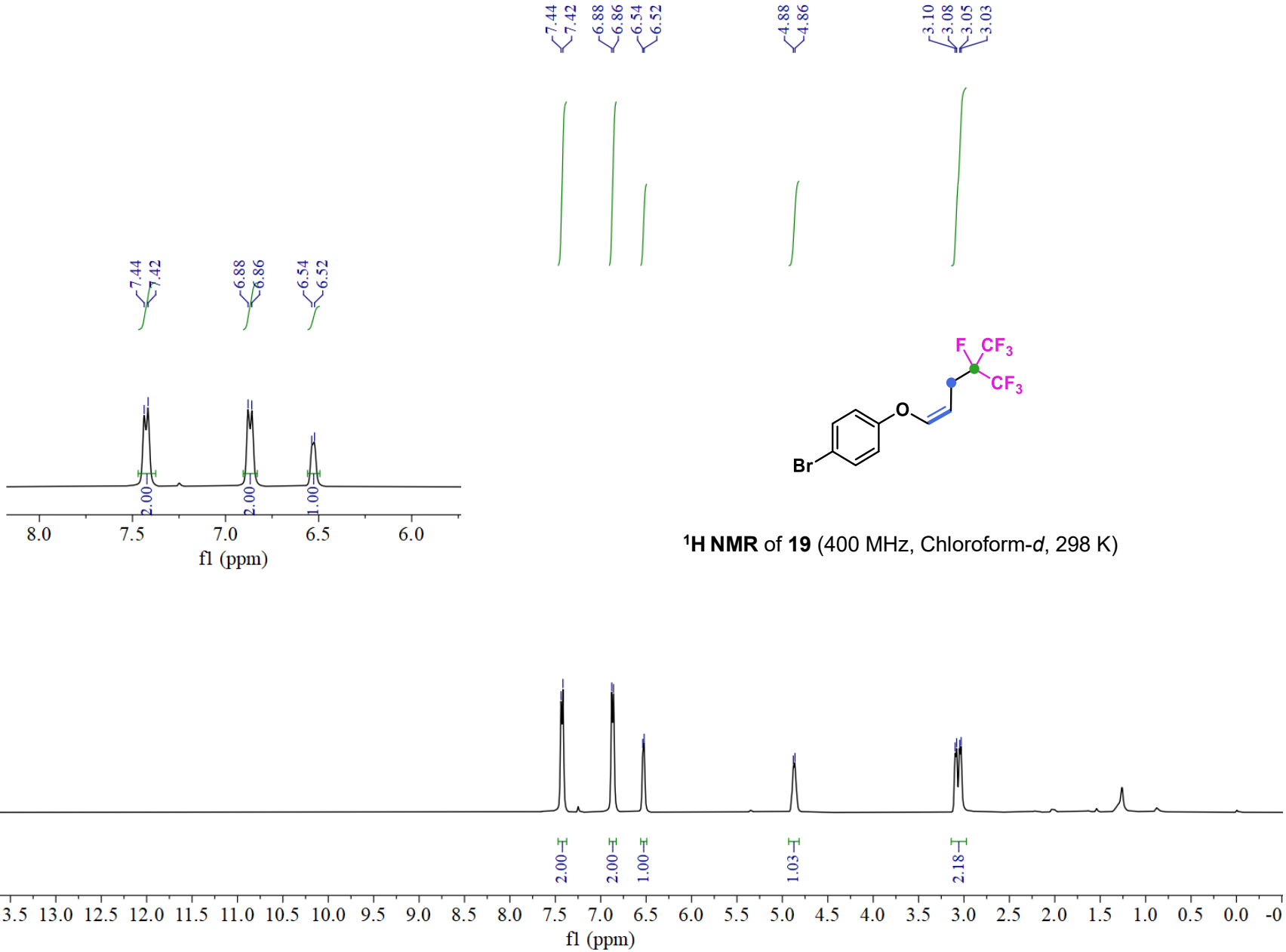
^{1}H NMR of **18** (400 MHz, Chloroform-*d*, 298 K)



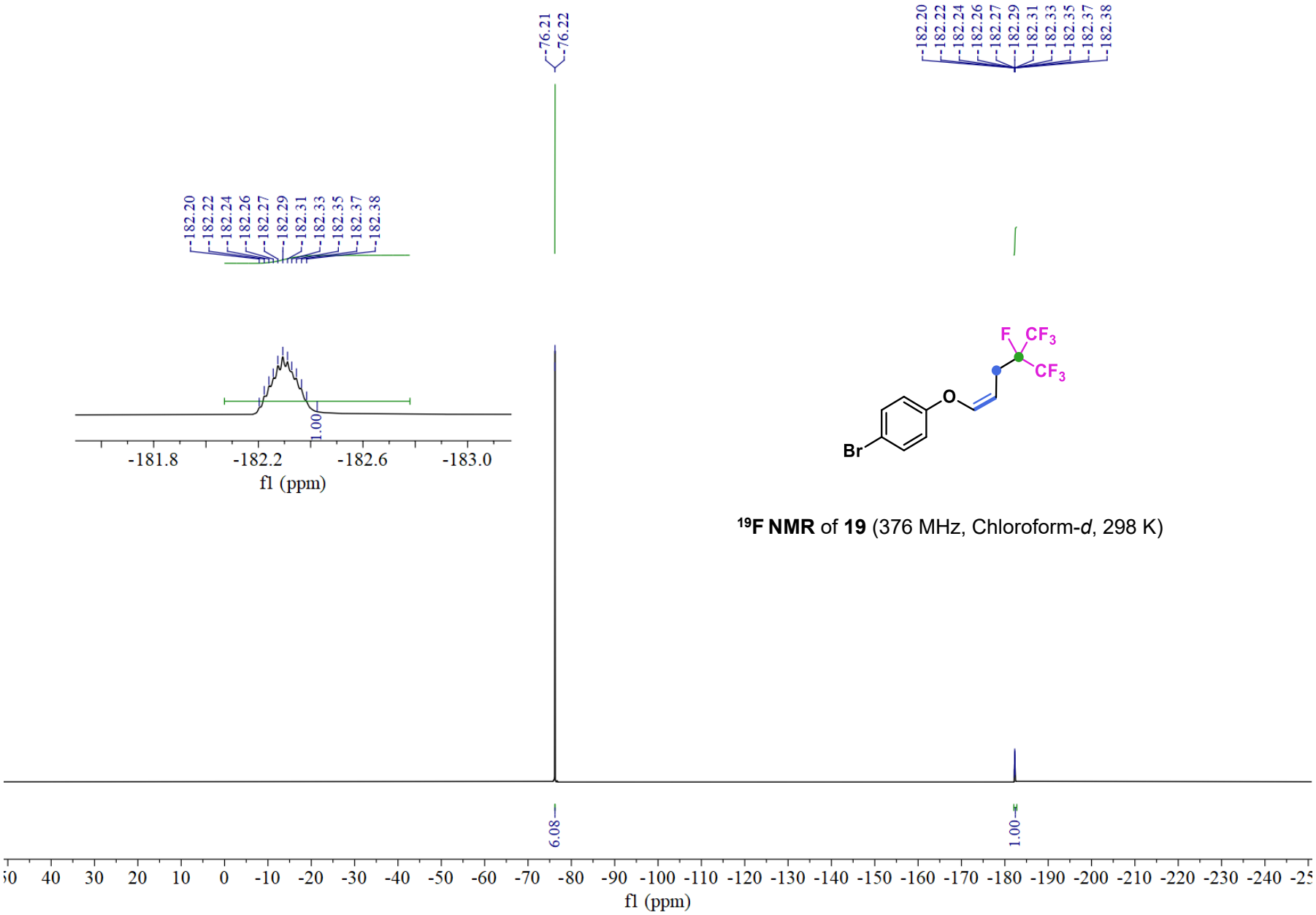
^{19}F NMR of **18** (376 MHz, Chloroform-*d*, 298 K)



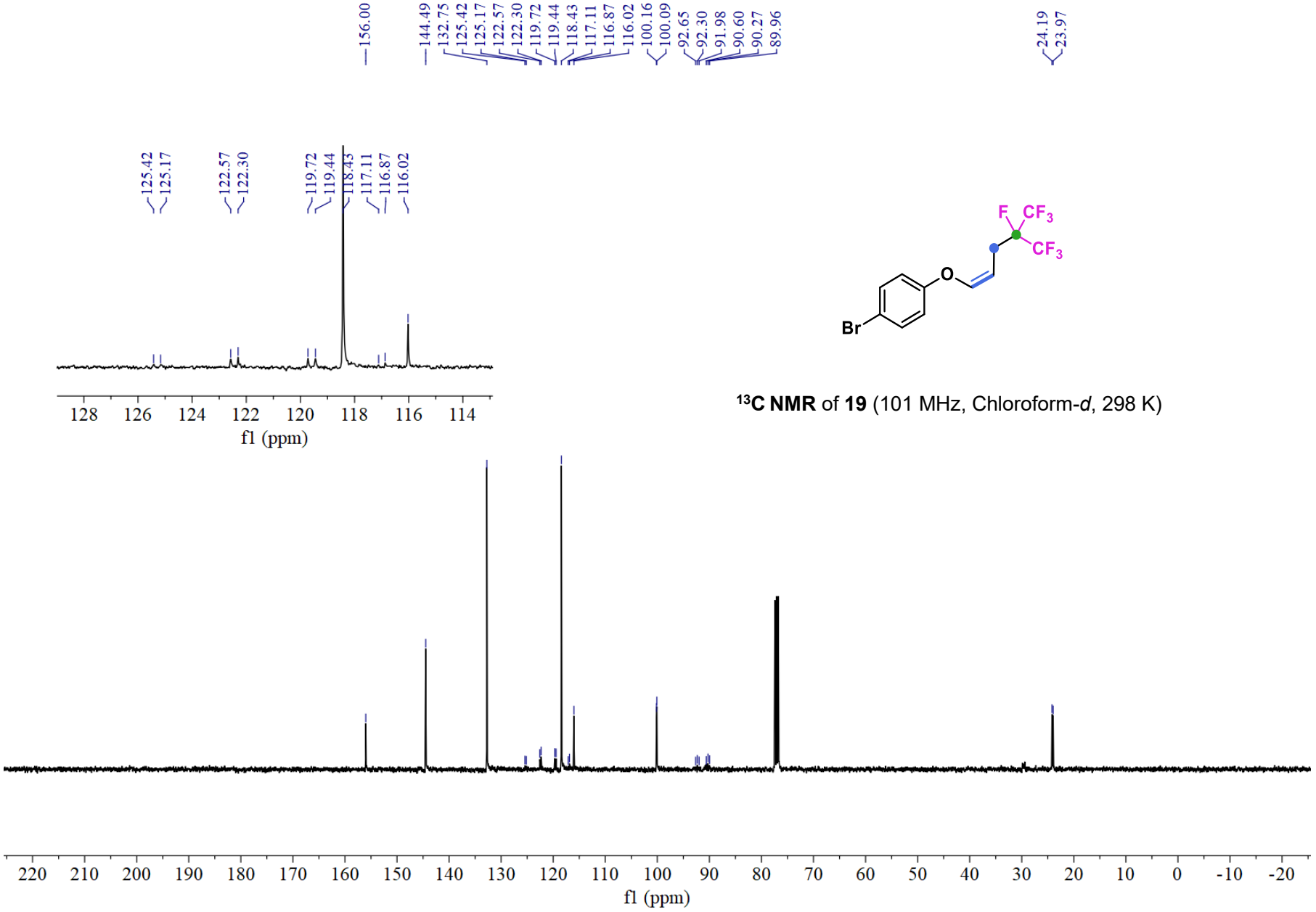
^{13}C NMR of **18** (101 MHz, Chloroform-*d*, 298 K)



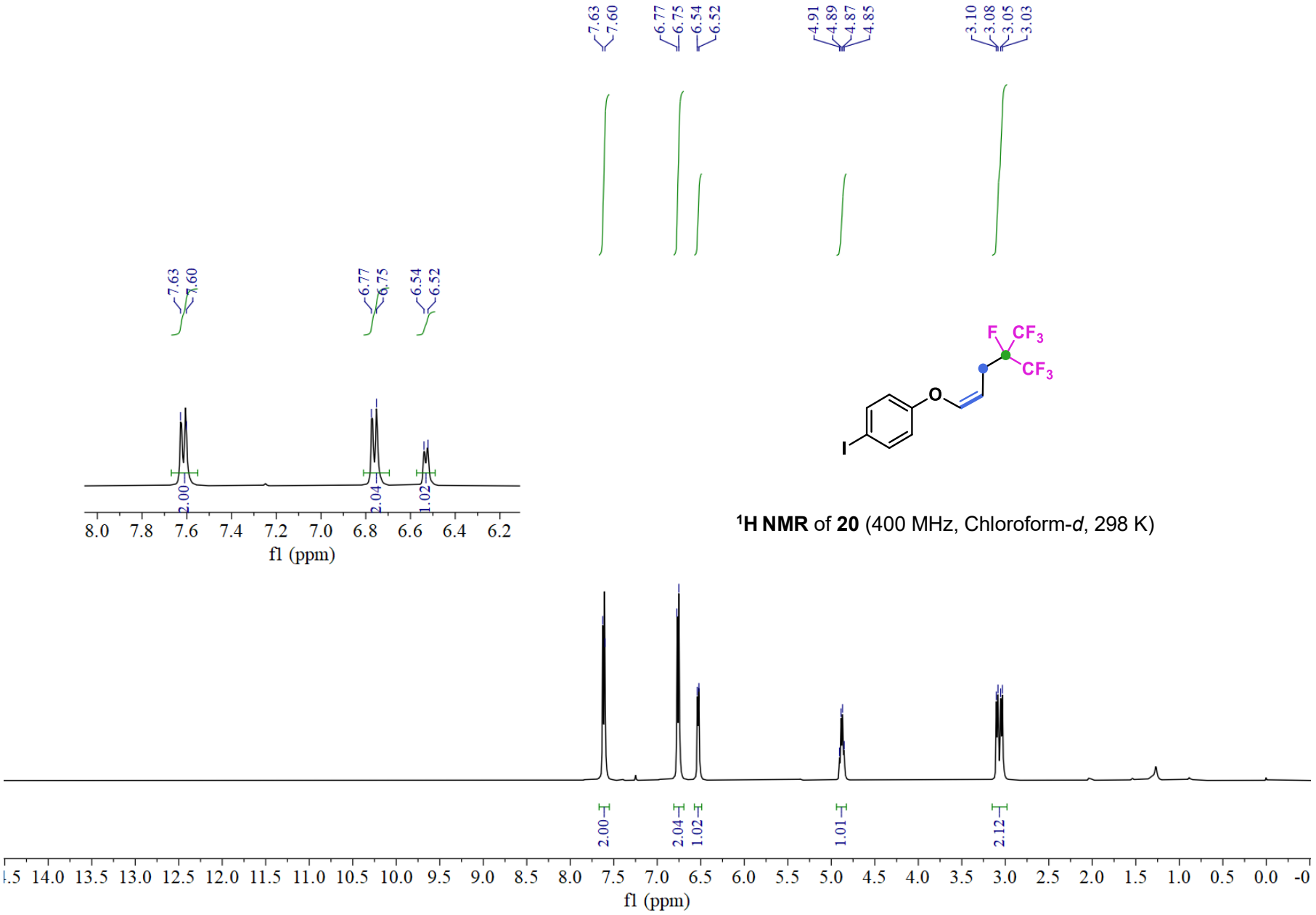
^{1}H NMR of **19** (400 MHz, Chloroform-*d*, 298 K)



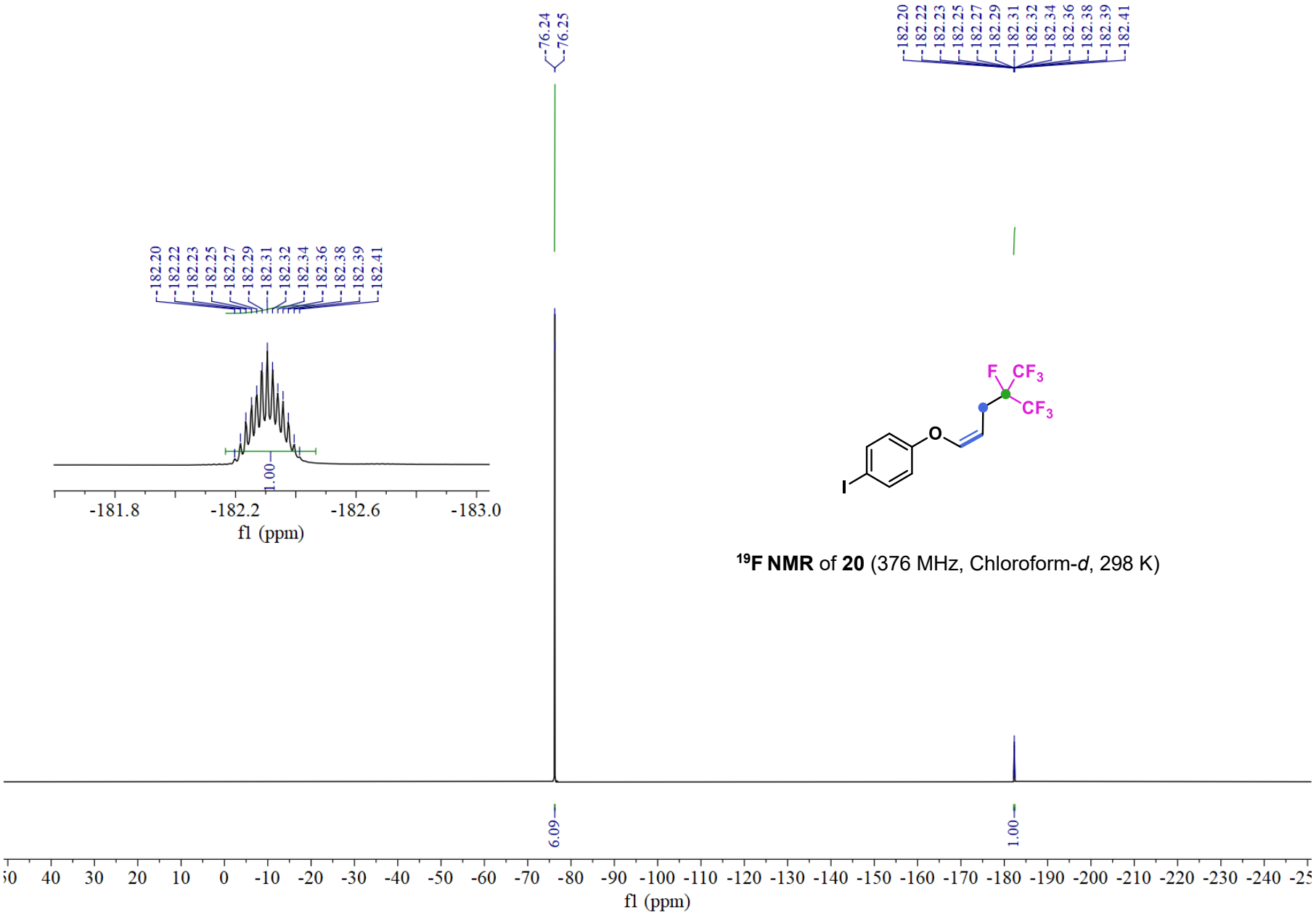
^{19}F NMR of **19** (376 MHz, Chloroform-*d*, 298 K)



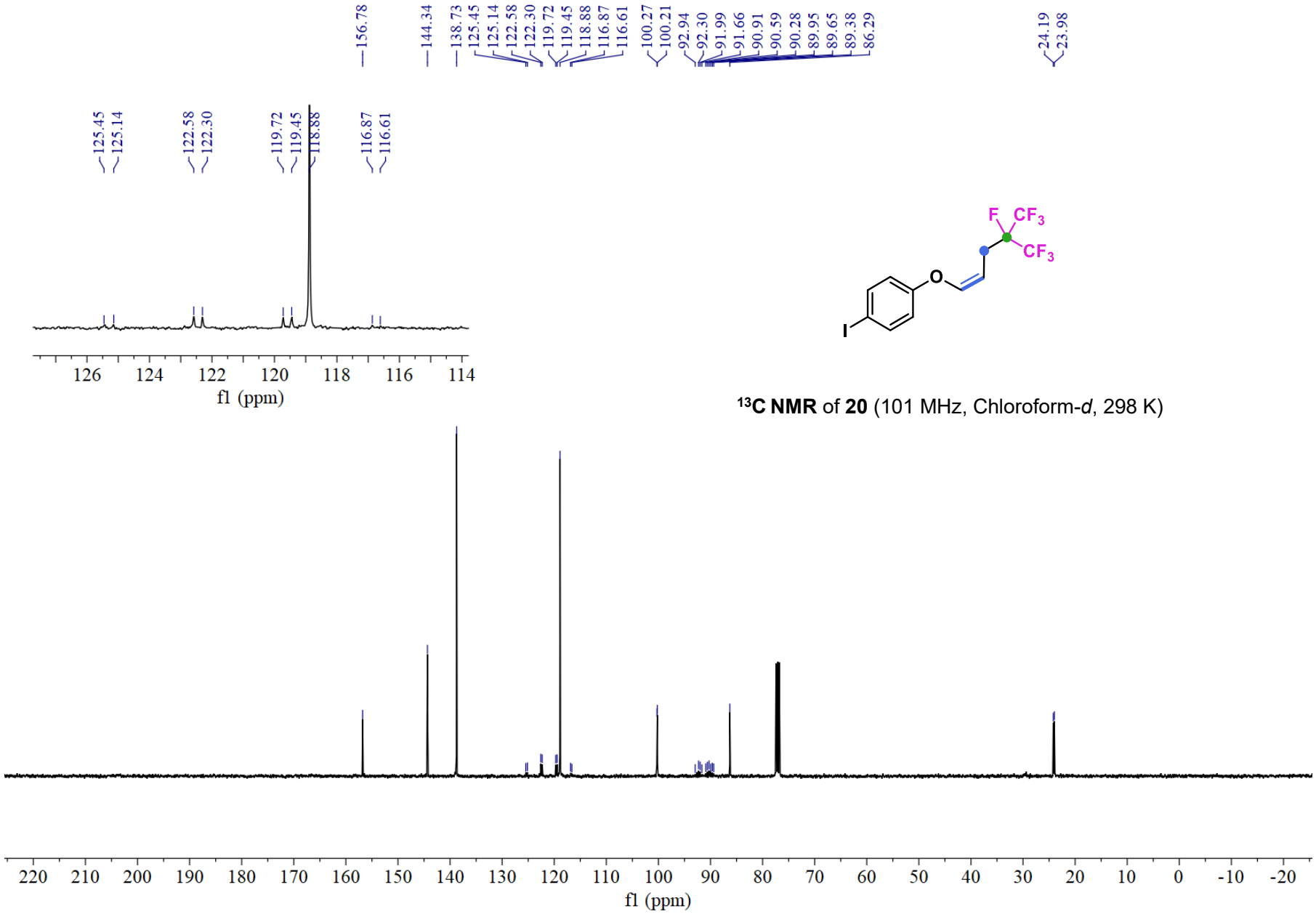
^{13}C NMR of **19** (101 MHz, Chloroform-*d*, 298 K)



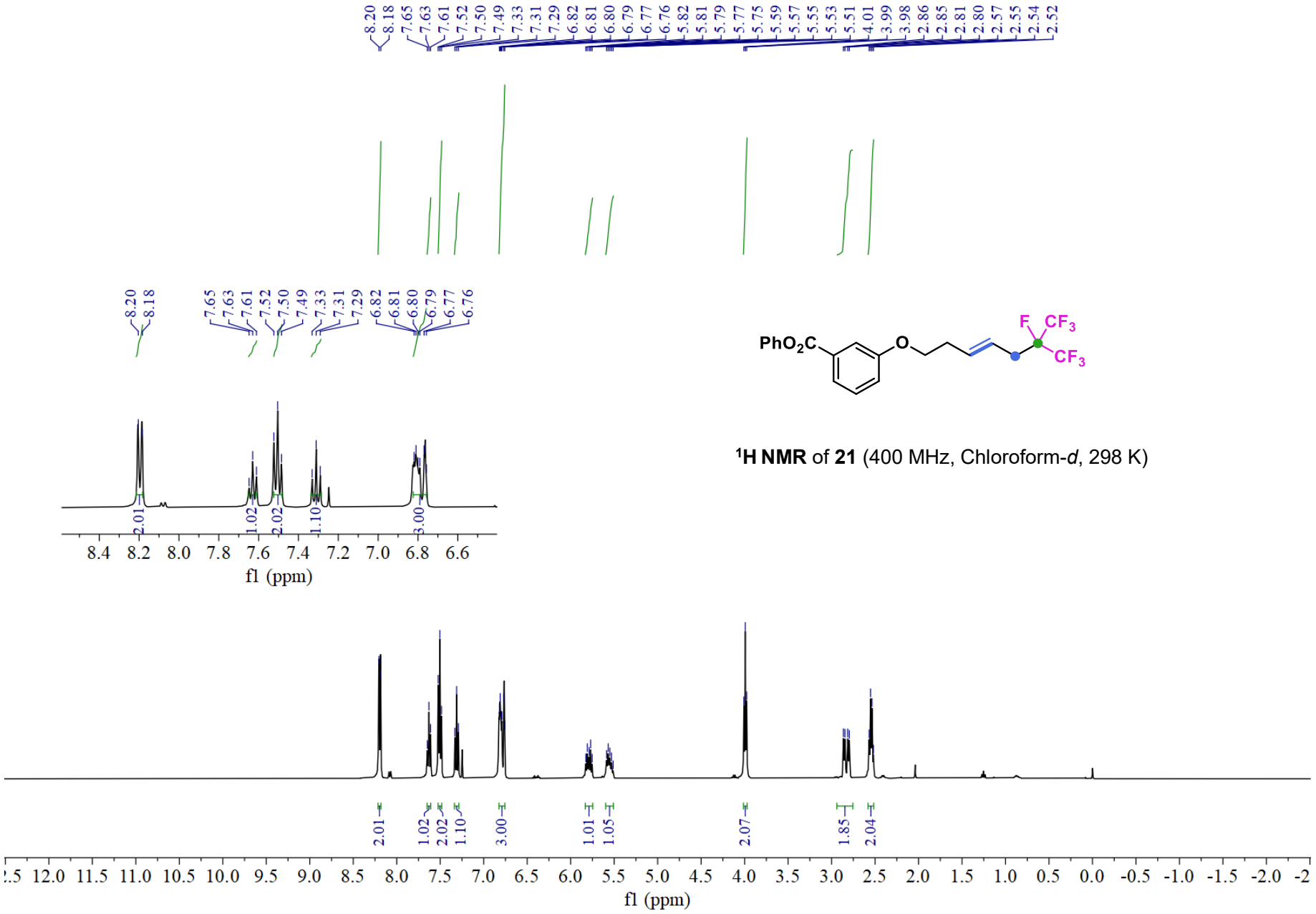
^{1}H NMR of **20** (400 MHz, Chloroform-*d*, 298 K)



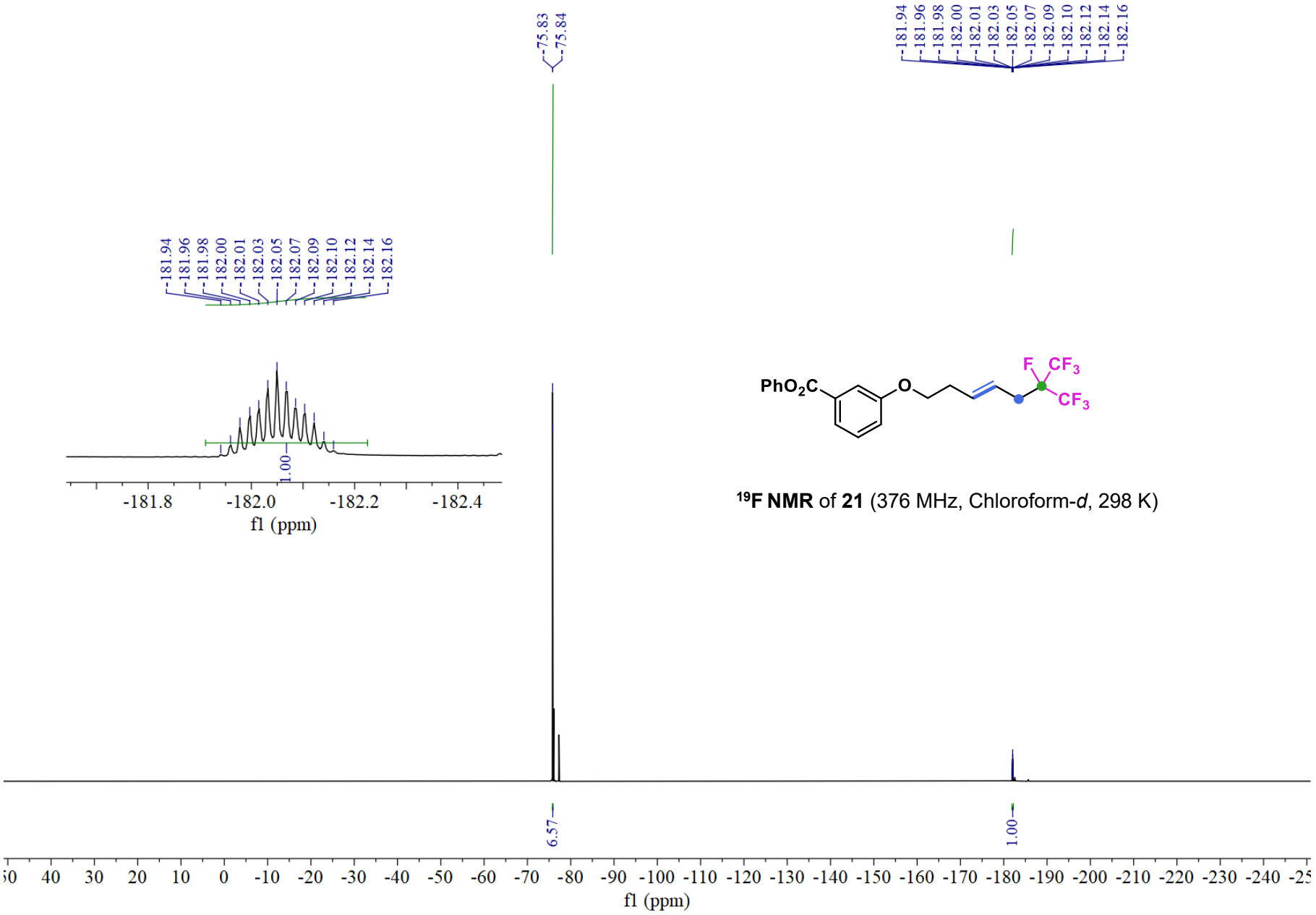
^{19}F NMR of **20** (376 MHz, Chloroform-*d*, 298 K)



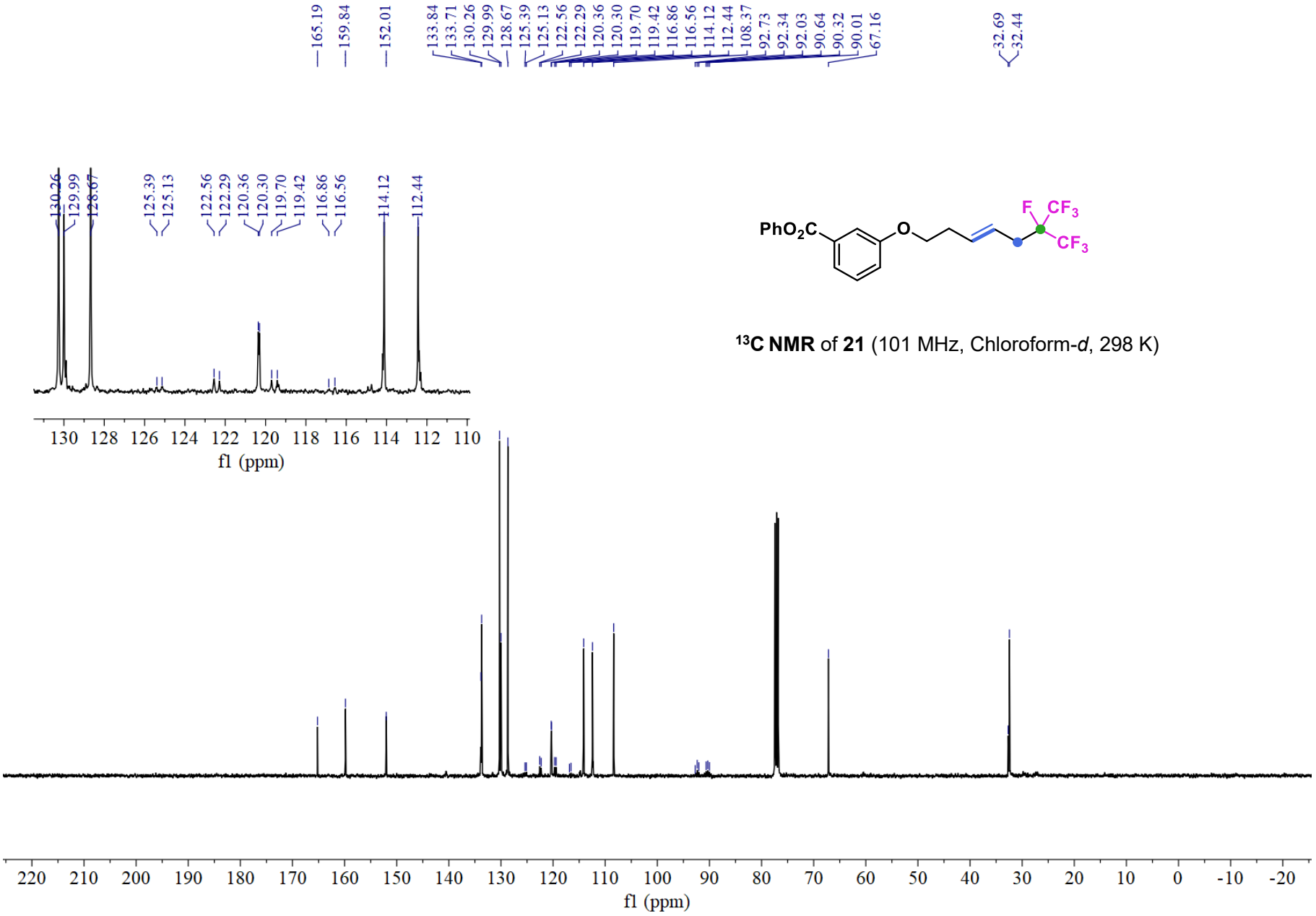
^{13}C NMR of **20** (101 MHz, Chloroform-*d*, 298 K)



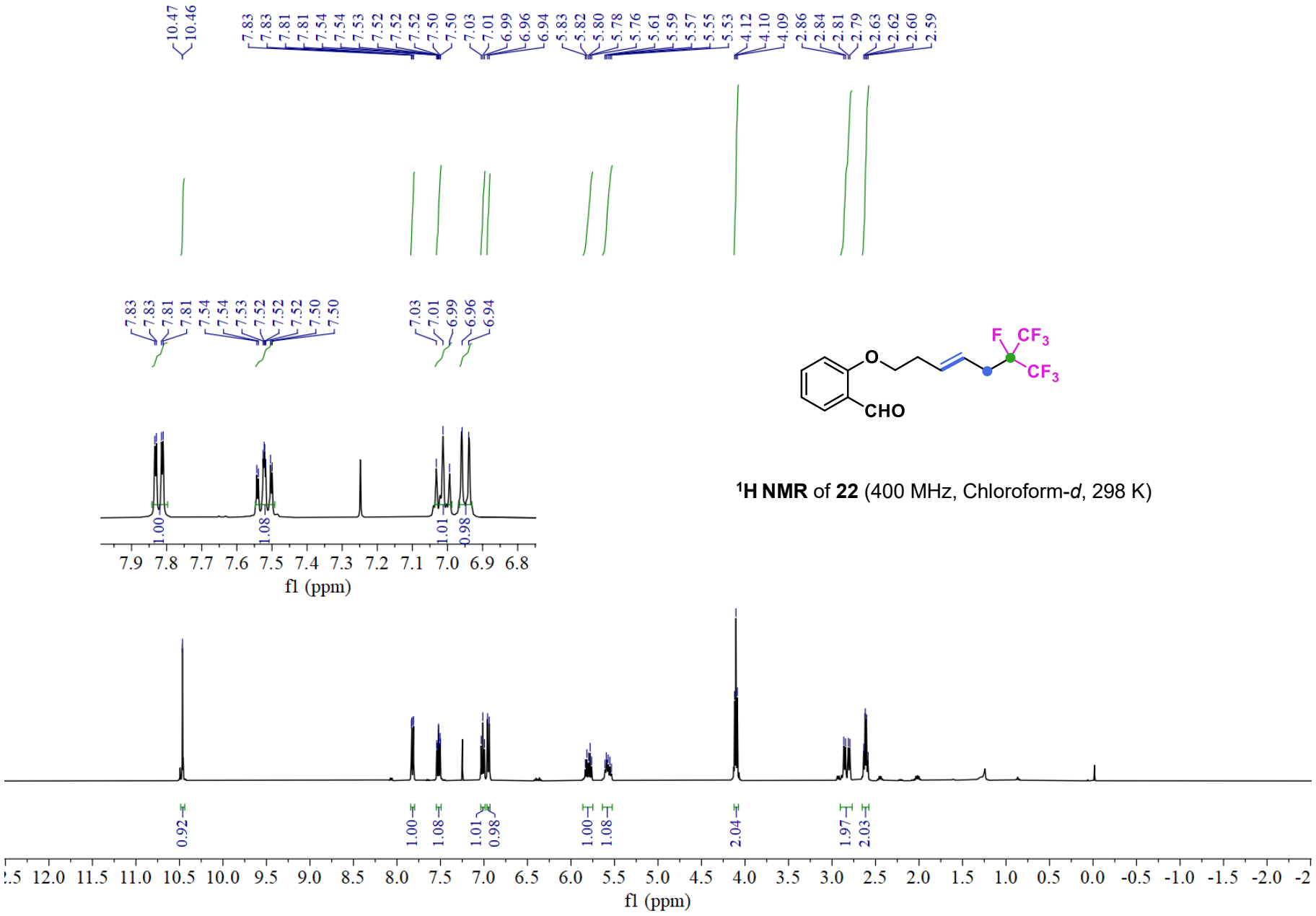
^{1}H NMR of **21** (400 MHz, Chloroform-*d*, 298 K)



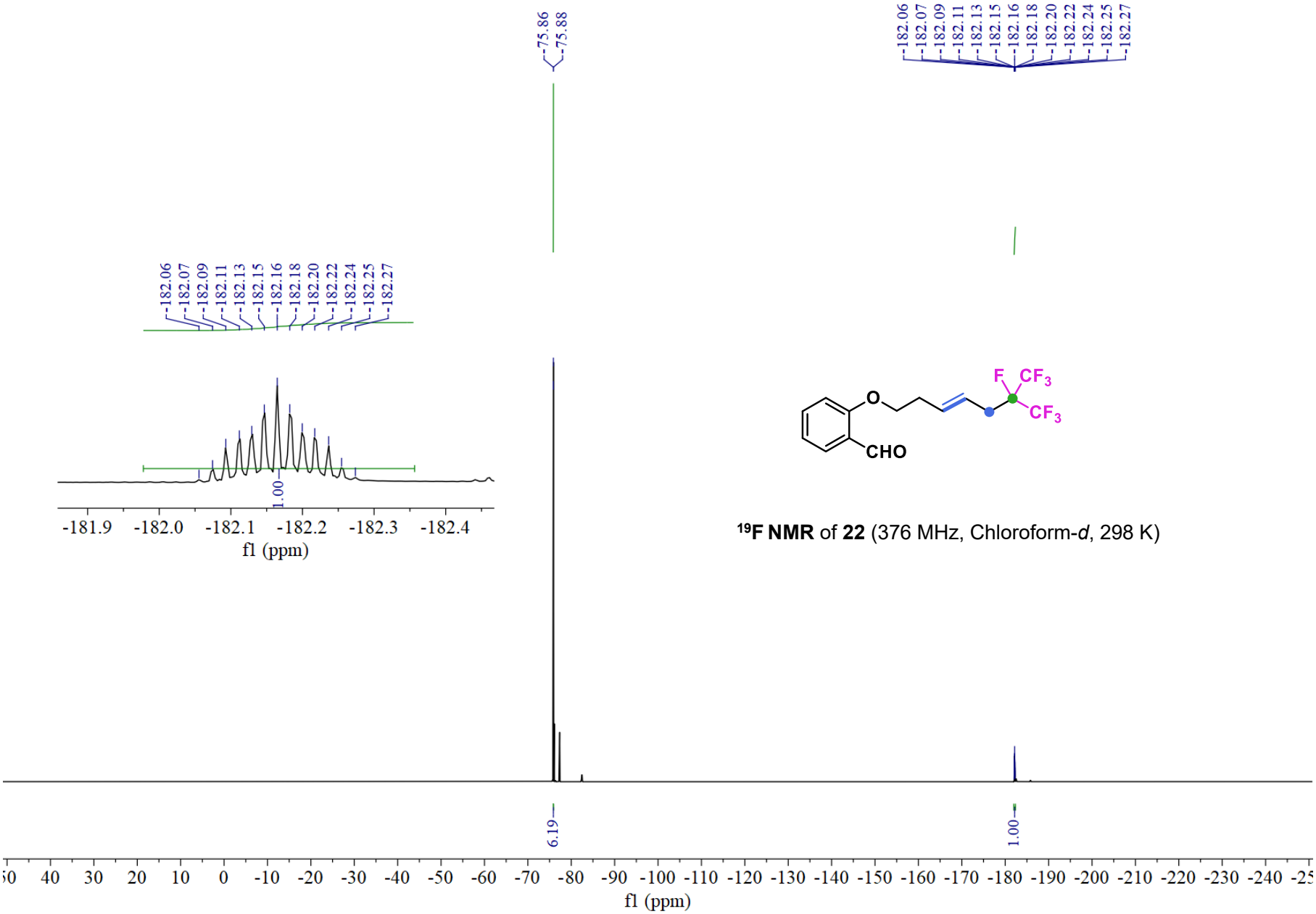
^{19}F NMR of **21** (376 MHz, Chloroform-*d*, 298 K)



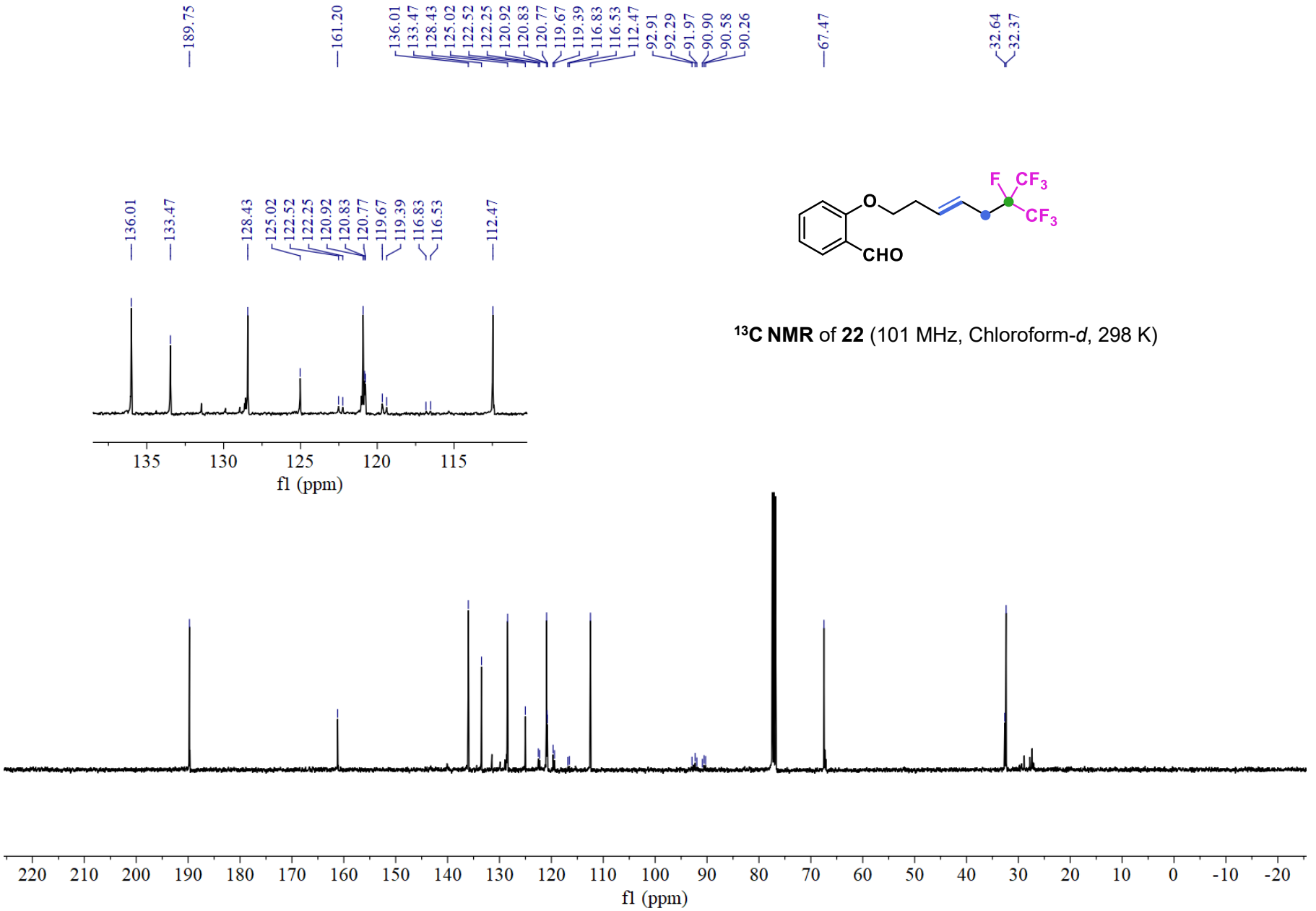
^{13}C NMR of **21** (101 MHz, Chloroform-*d*, 298 K)



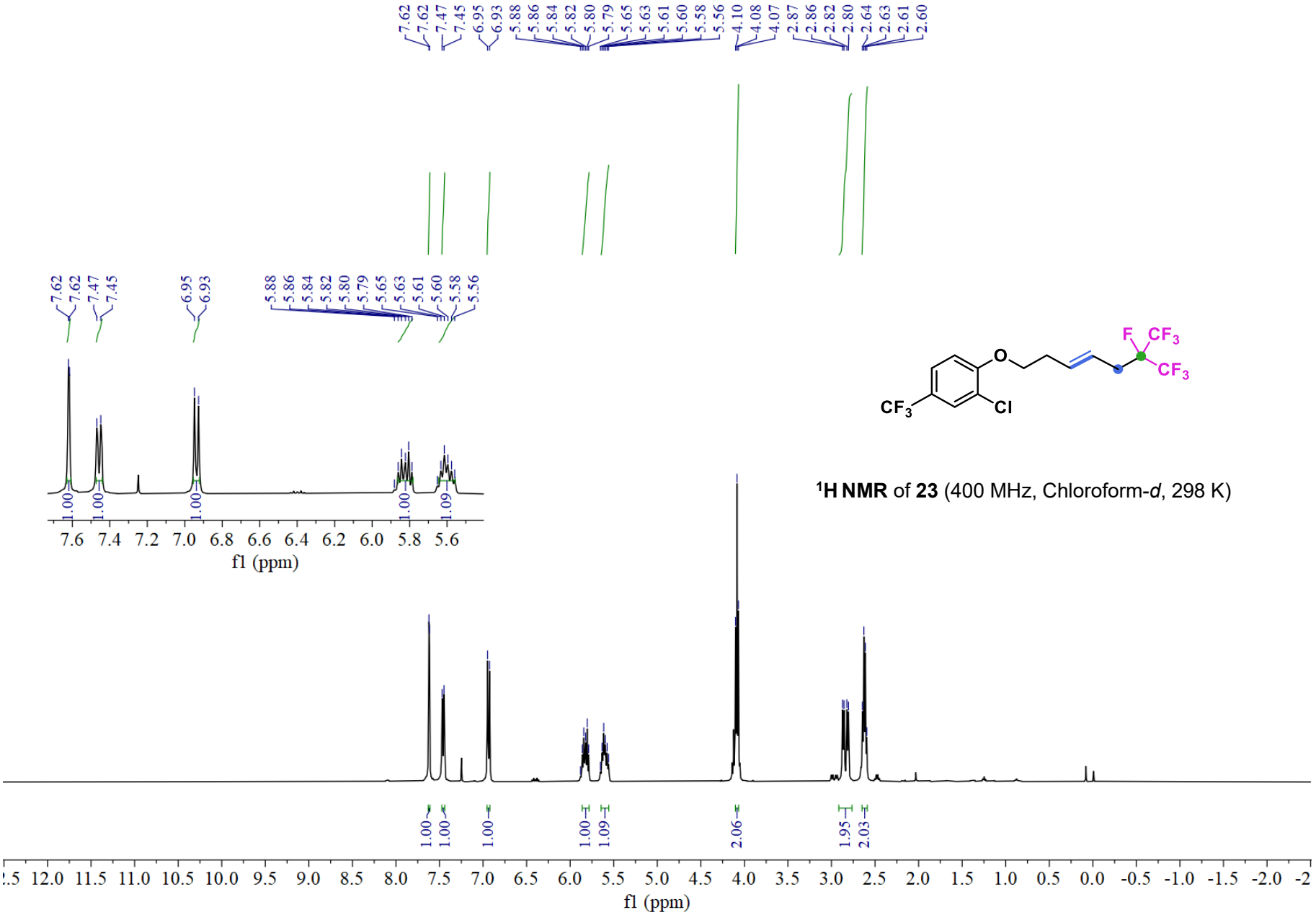
^{1}H NMR of **22** (400 MHz, Chloroform-*d*, 298 K)



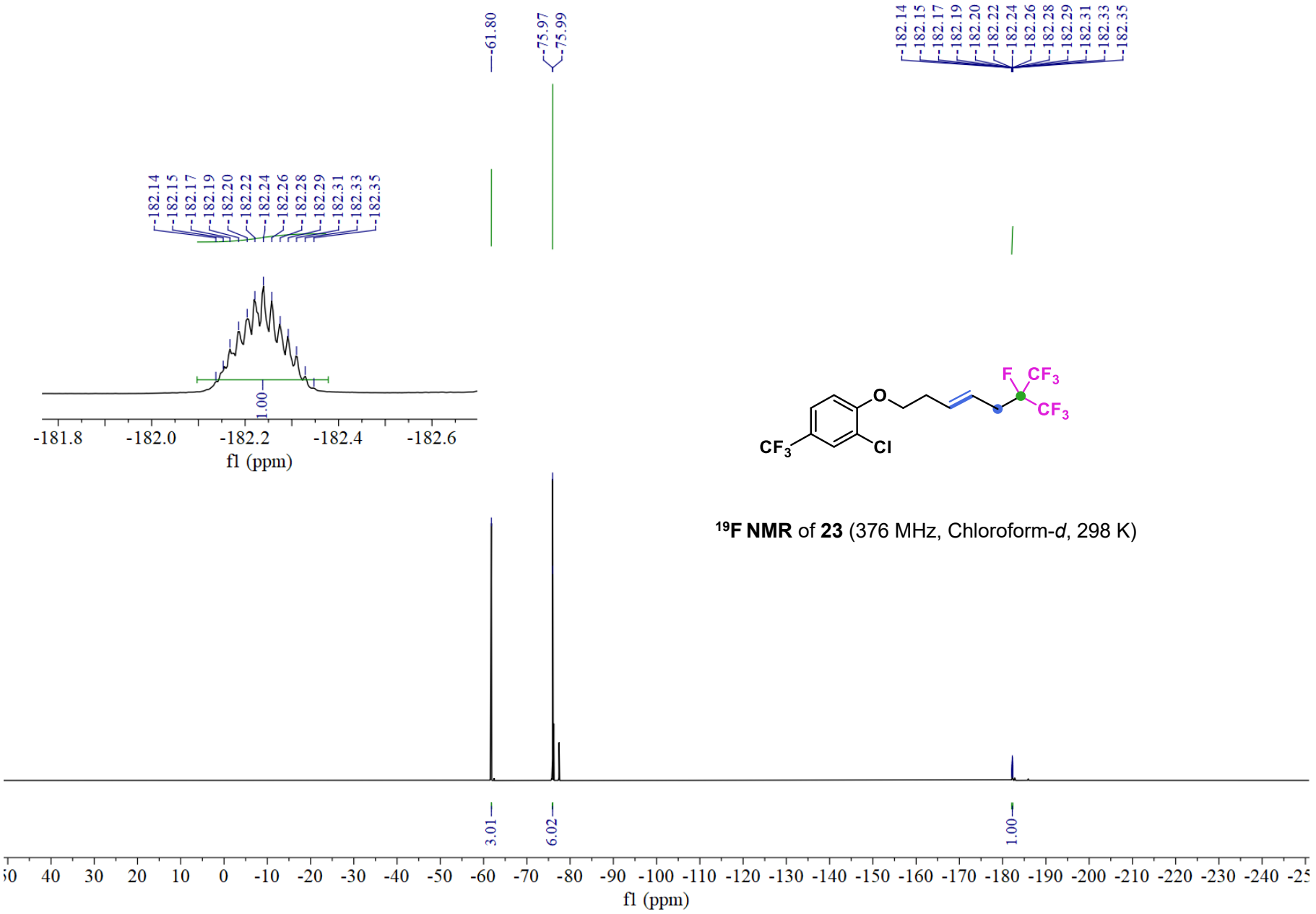
^{19}F NMR of **22** (376 MHz, Chloroform-*d*, 298 K)



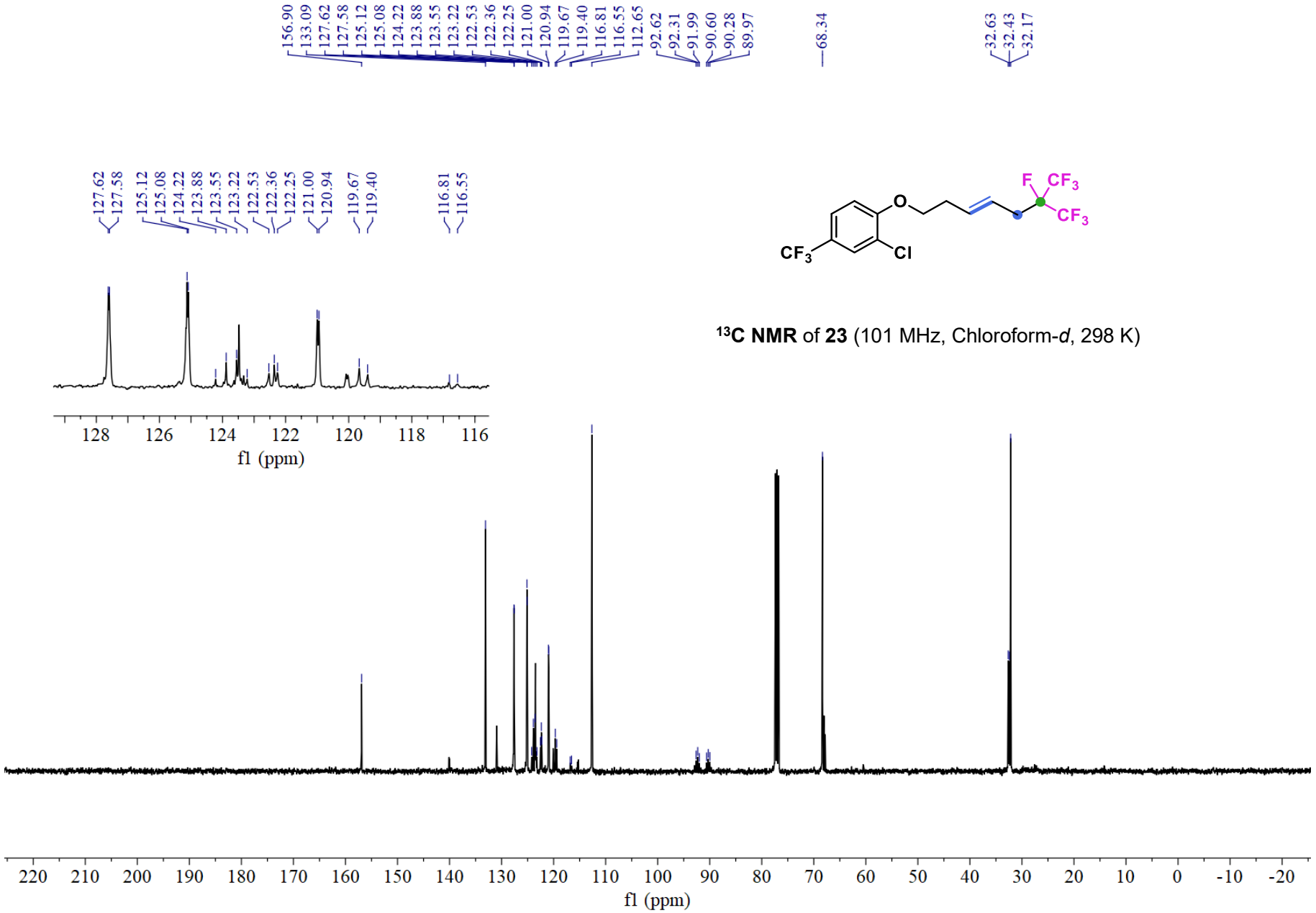
^{13}C NMR of **22** (101 MHz, Chloroform-*d*, 298 K)



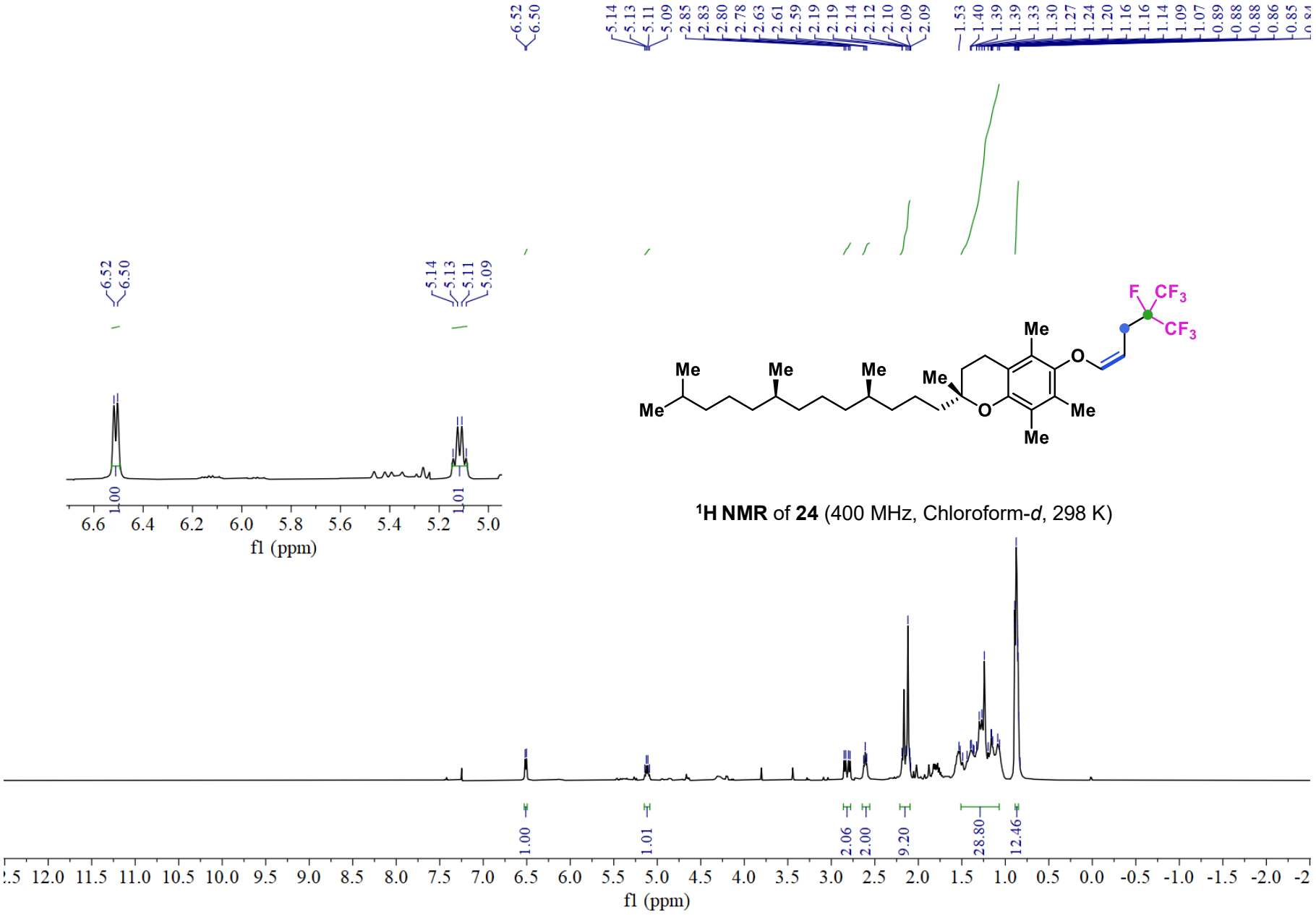
^{1}H NMR of **23** (400 MHz, Chloroform-*d*, 298 K)



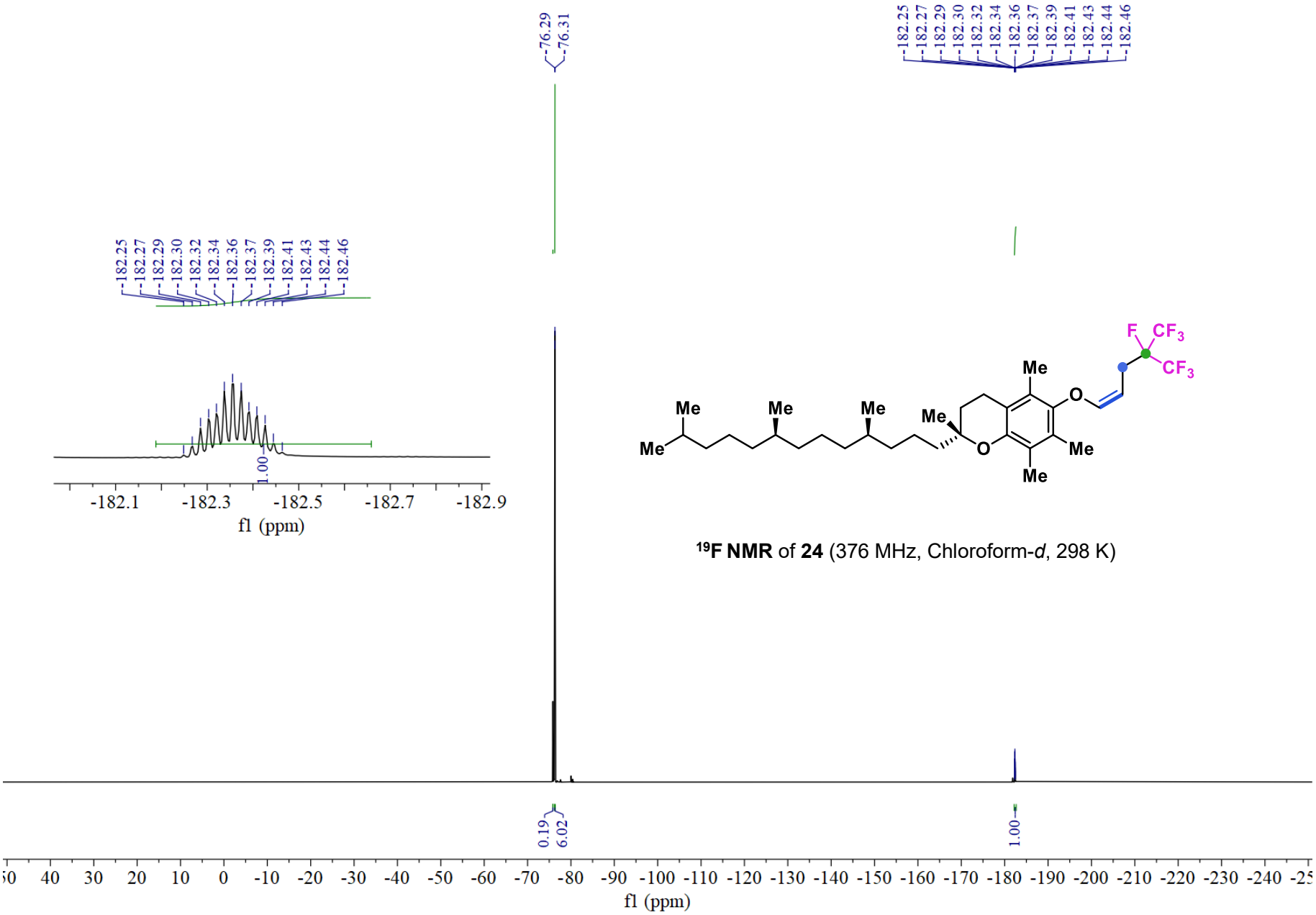
^{19}F NMR of **23** (376 MHz, Chloroform-*d*, 298 K)



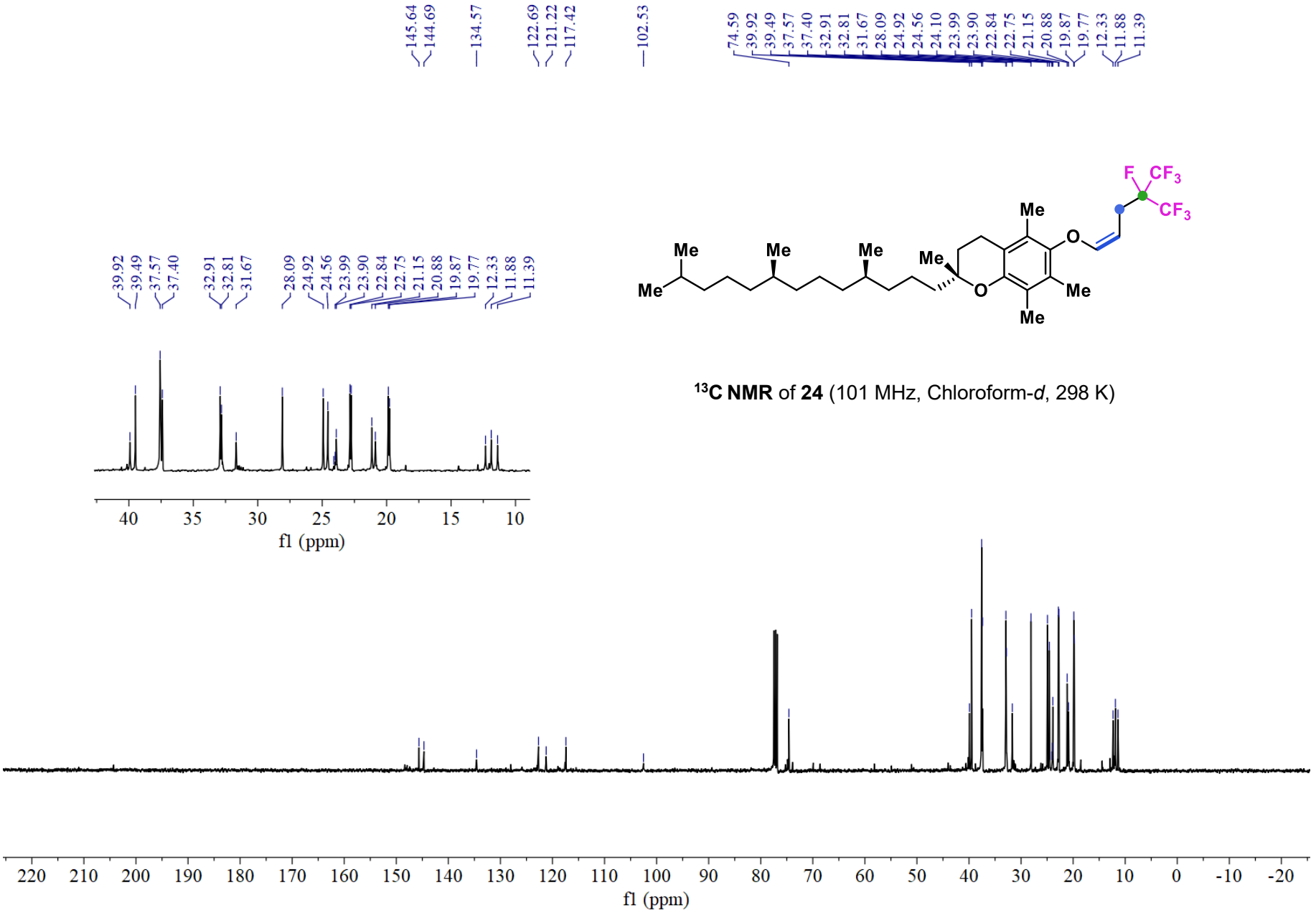
^{13}C NMR of **23** (101 MHz, Chloroform-*d*, 298 K)



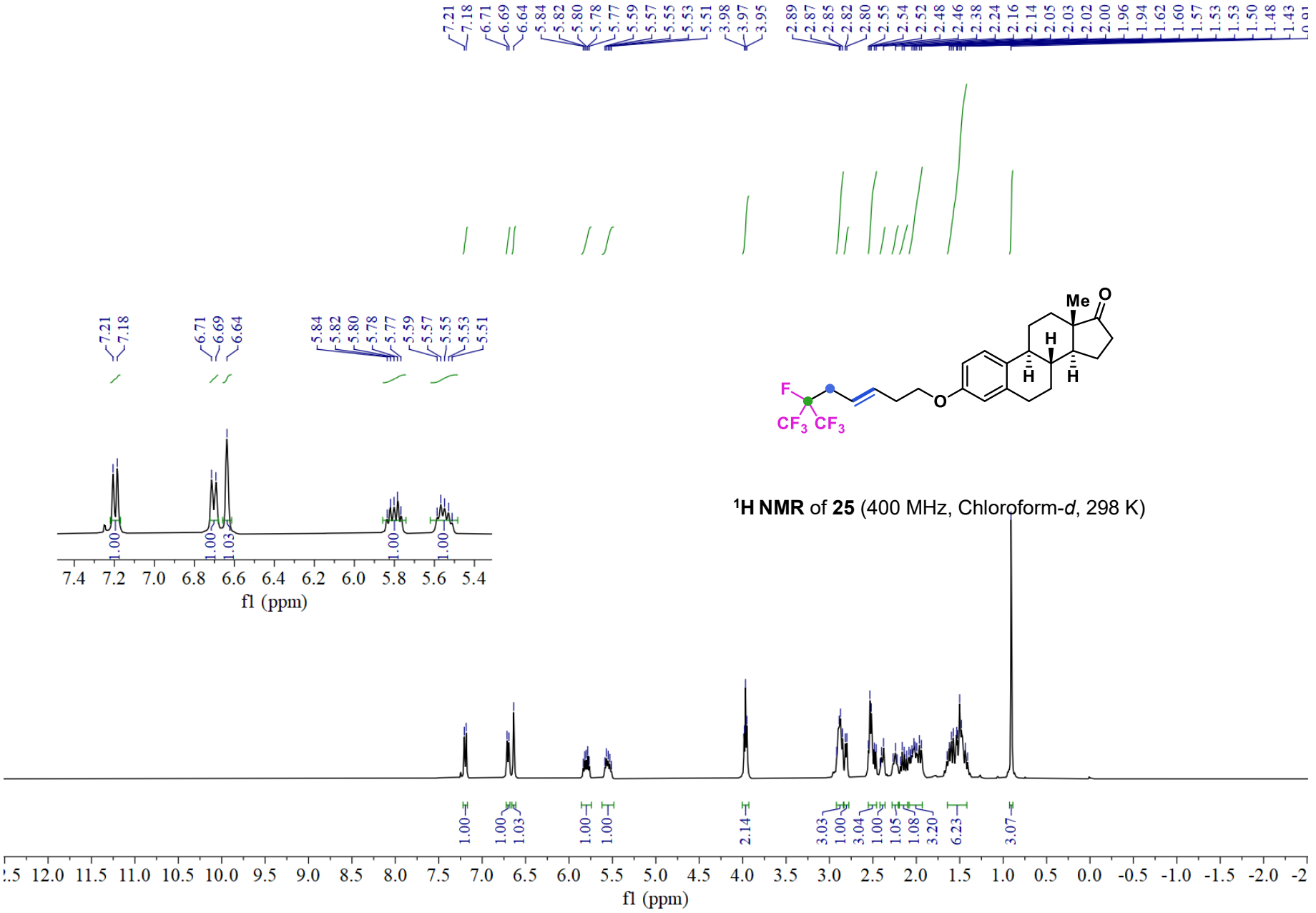
^{1}H NMR of **24** (400 MHz, Chloroform-*d*, 298 K)



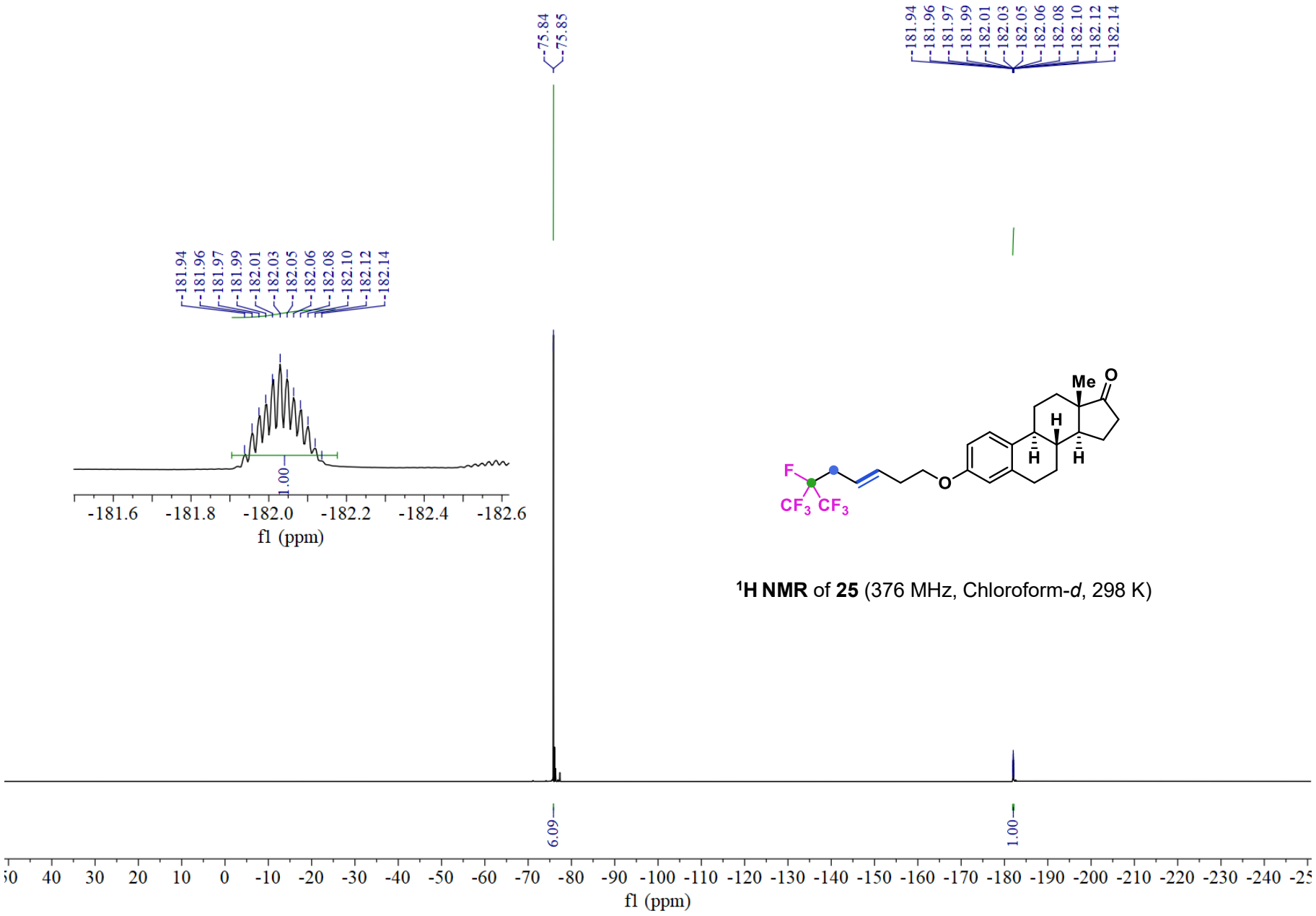
^{19}F NMR of **24** (376 MHz, Chloroform-*d*, 298 K)



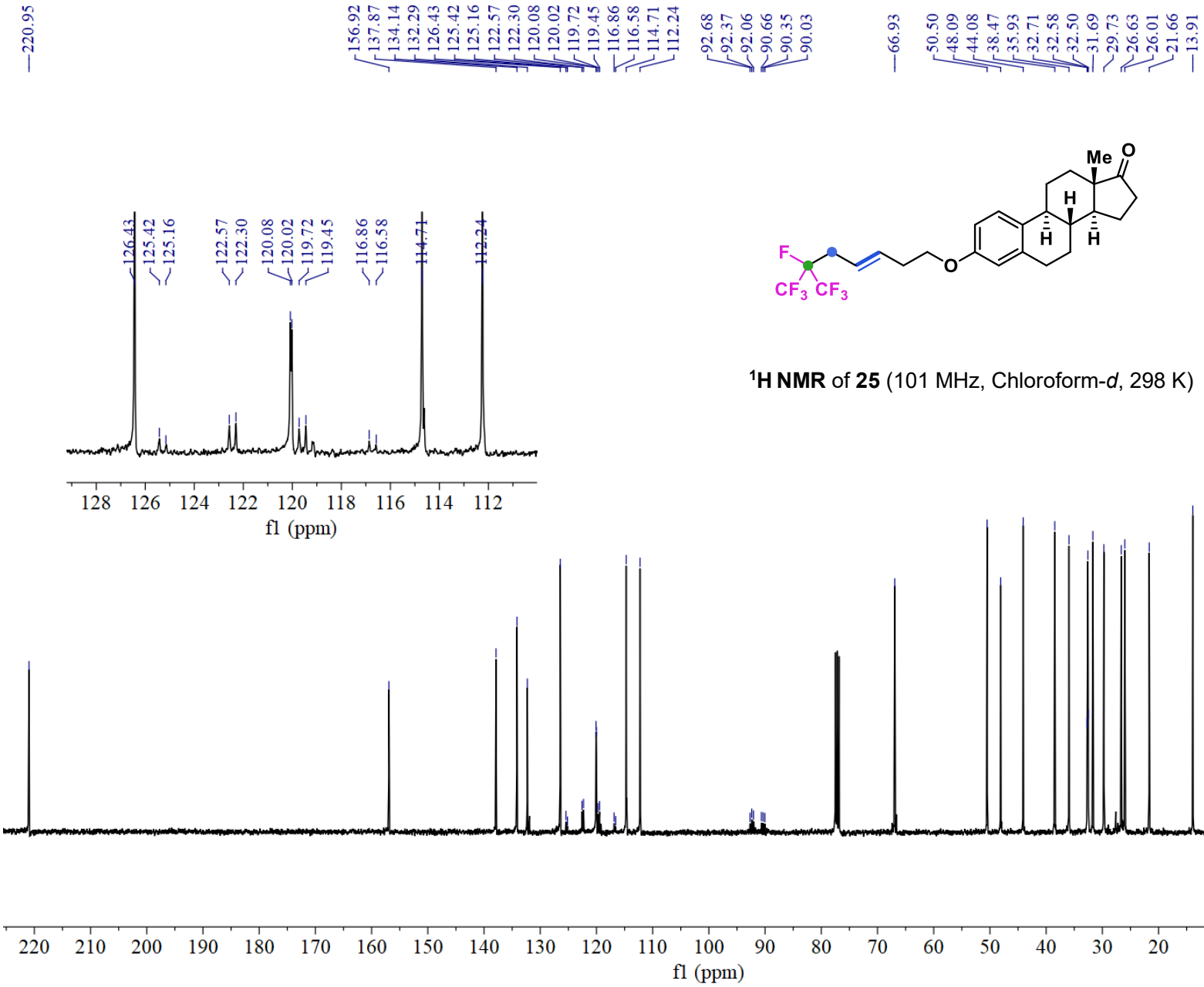
^{13}C NMR of **24** (101 MHz, Chloroform-*d*, 298 K)



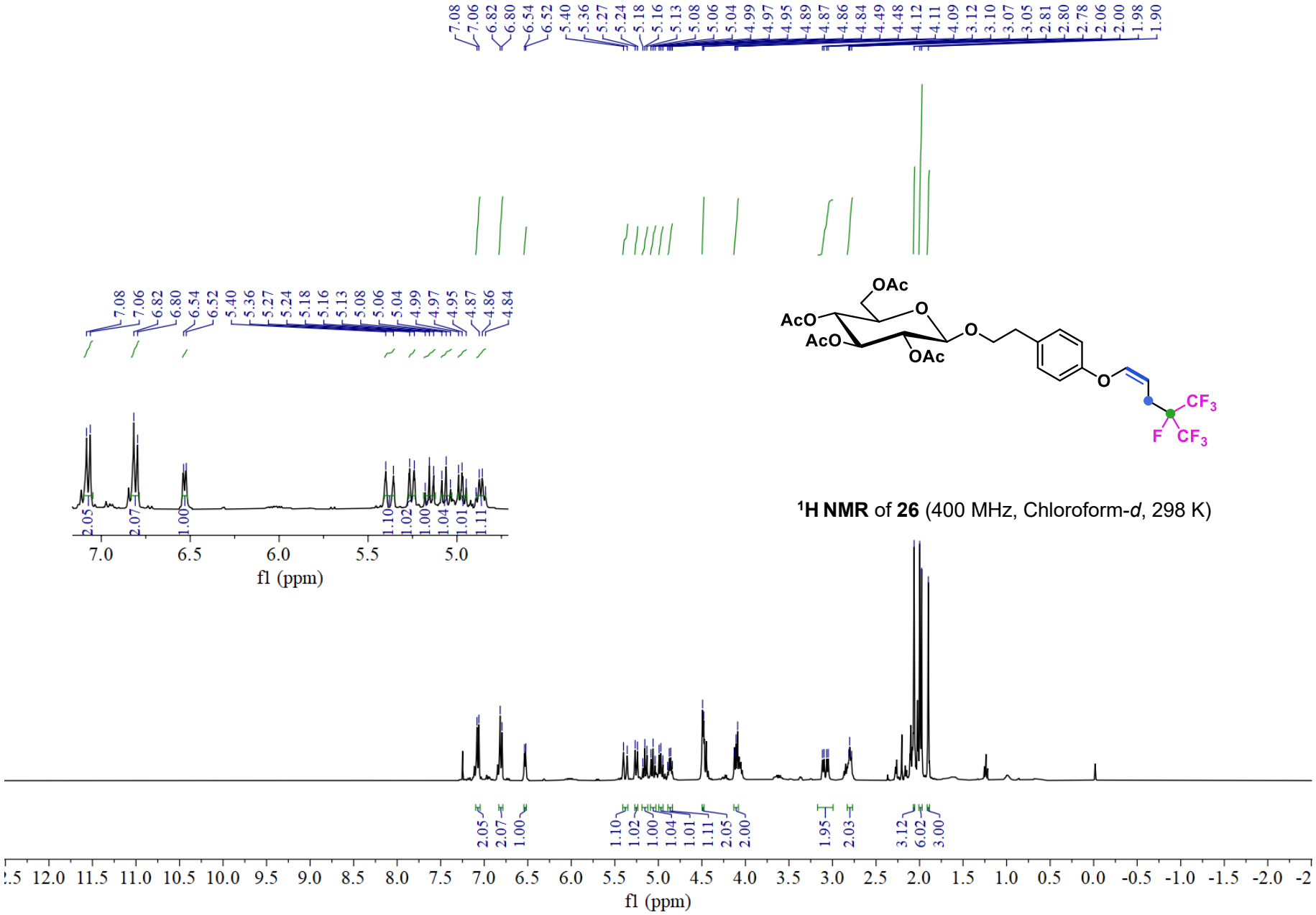
^{1}H NMR of **25** (400 MHz, Chloroform-*d*, 298 K)



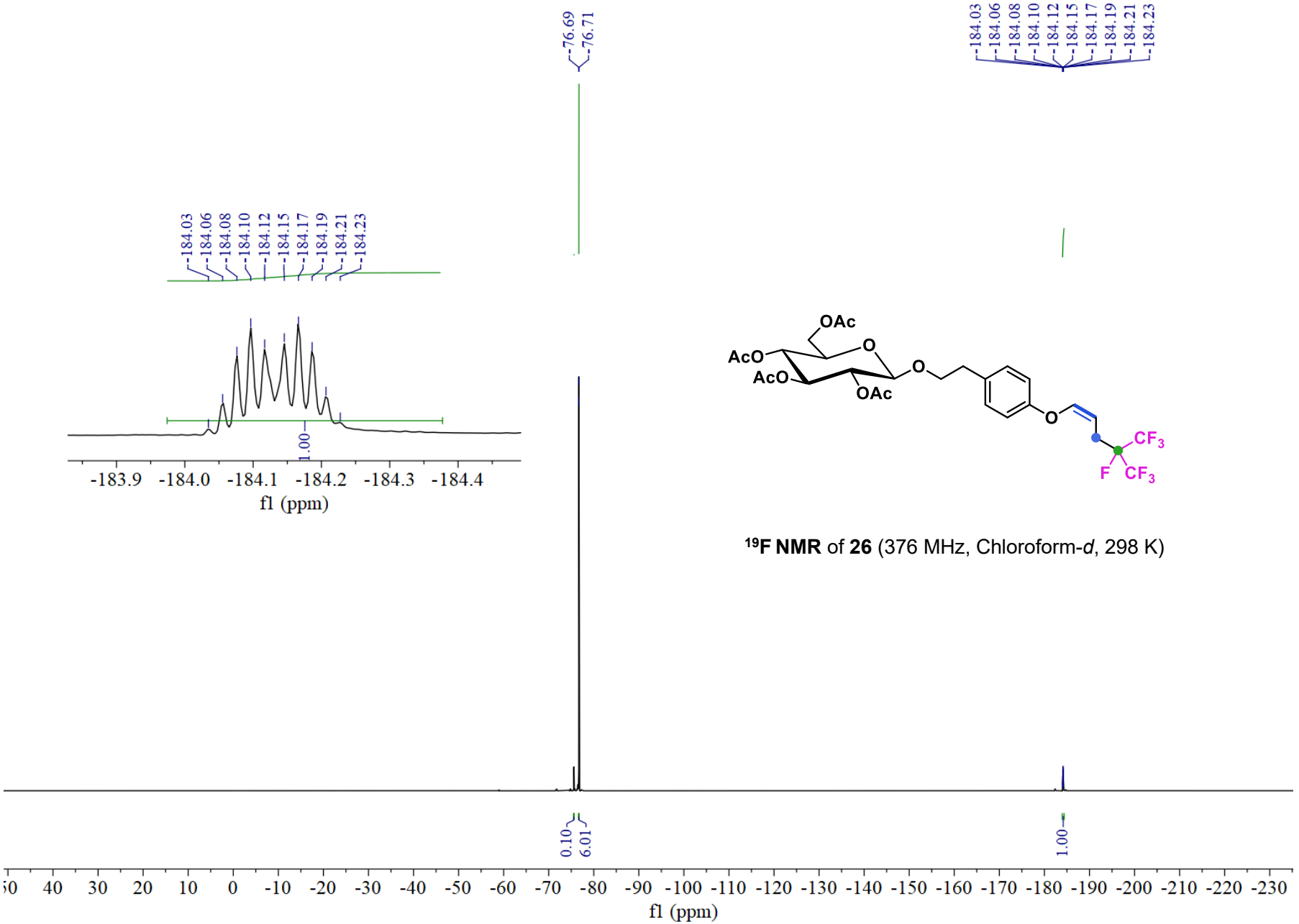
^{1}H NMR of **25** (376 MHz, Chloroform-*d*, 298 K)



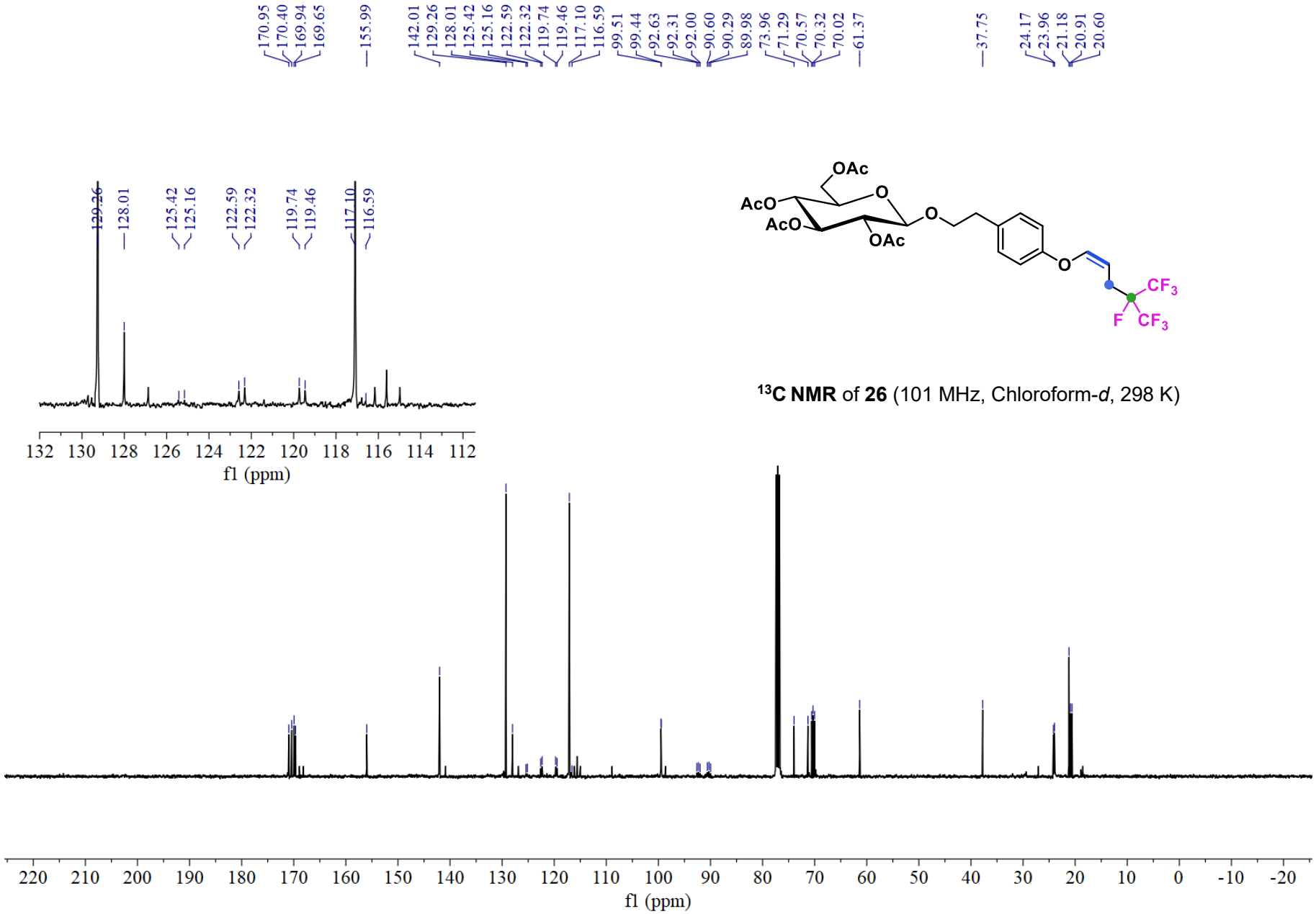
^{1}H NMR of **25** (101 MHz, Chloroform-*d*, 298 K)



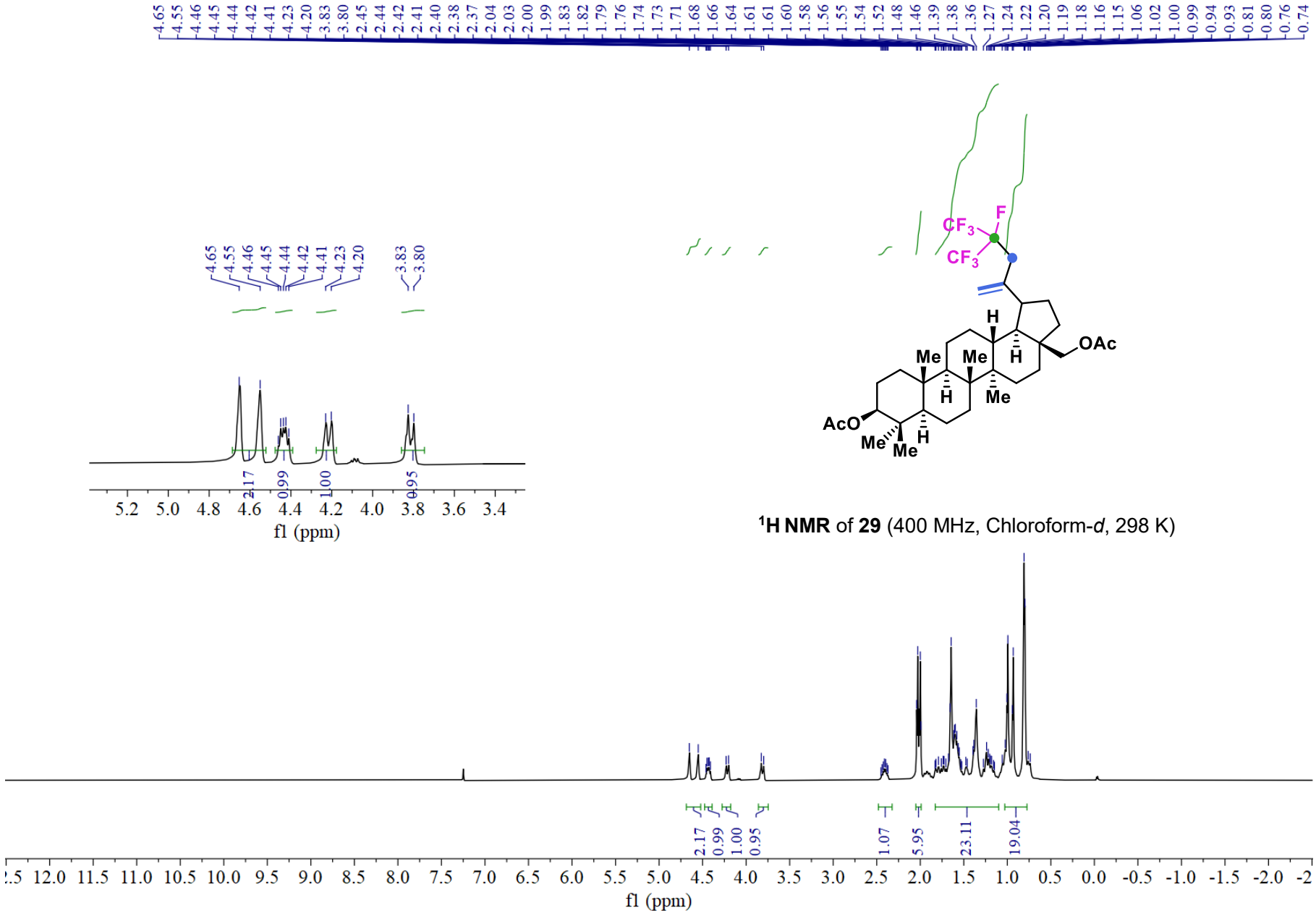
^{1}H NMR of **26** (400 MHz, Chloroform-*d*, 298 K)



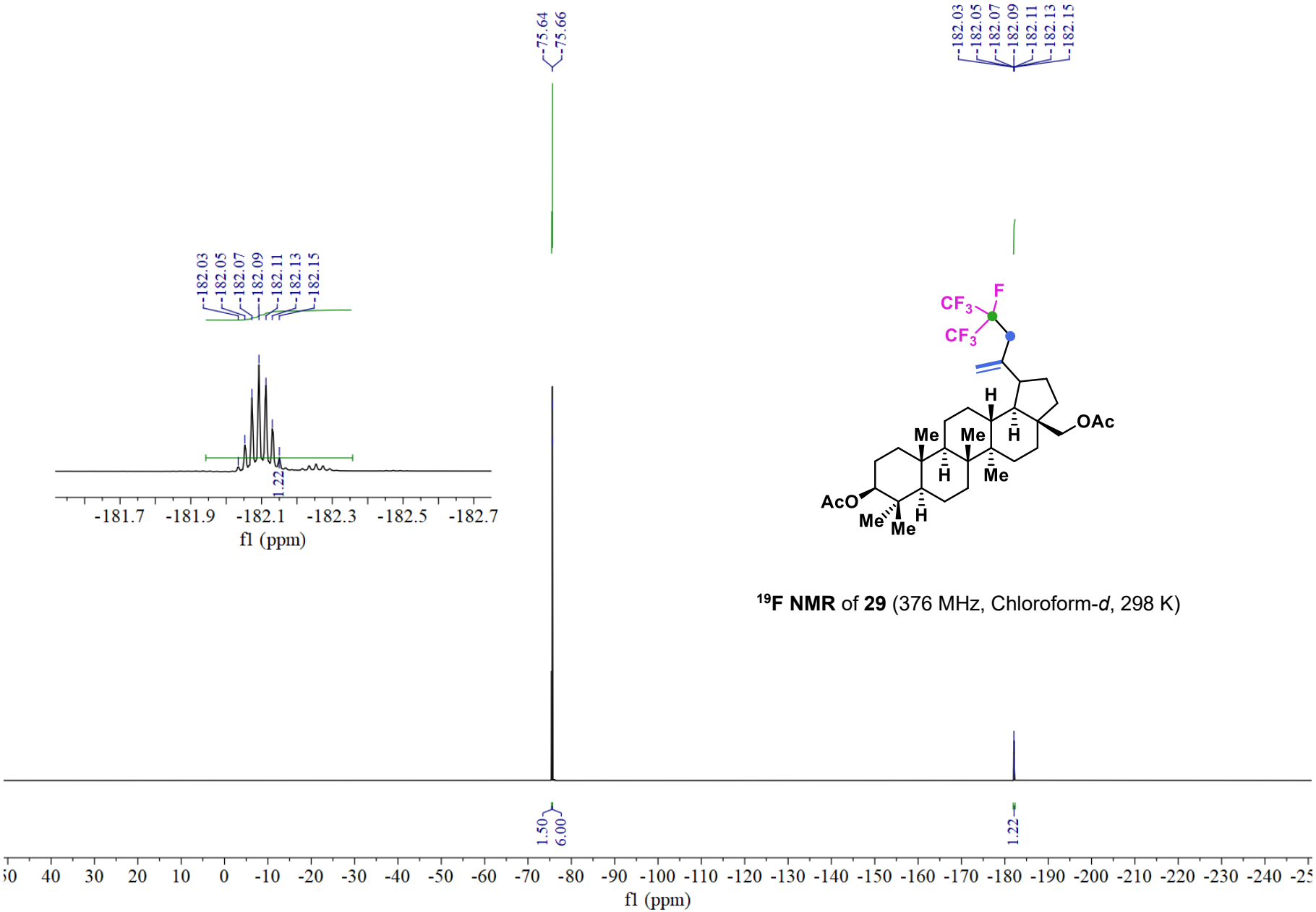
^{19}F NMR of **26** (376 MHz, Chloroform-*d*, 298 K)



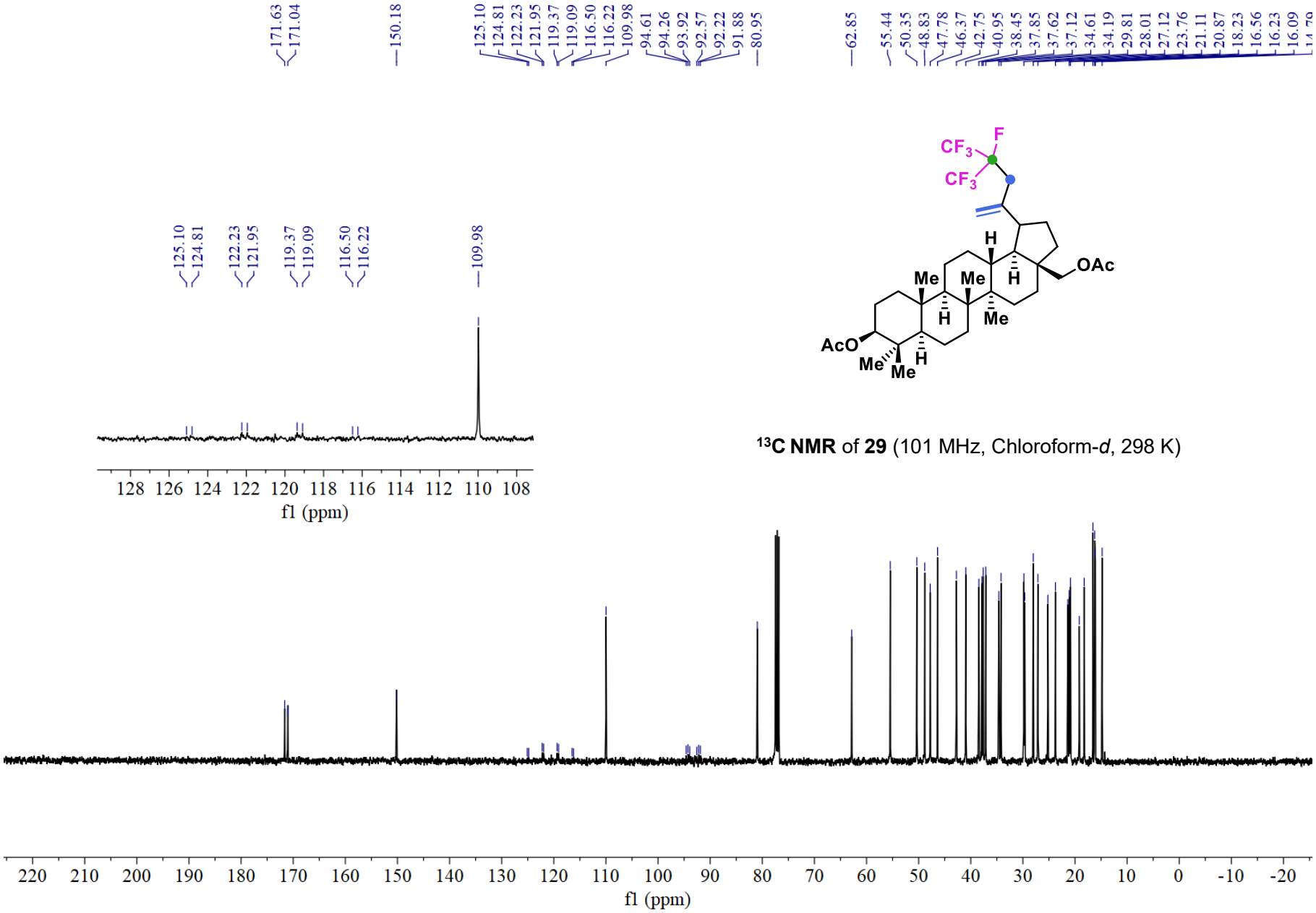
^{13}C NMR of **26** (101 MHz, Chloroform-*d*, 298 K)



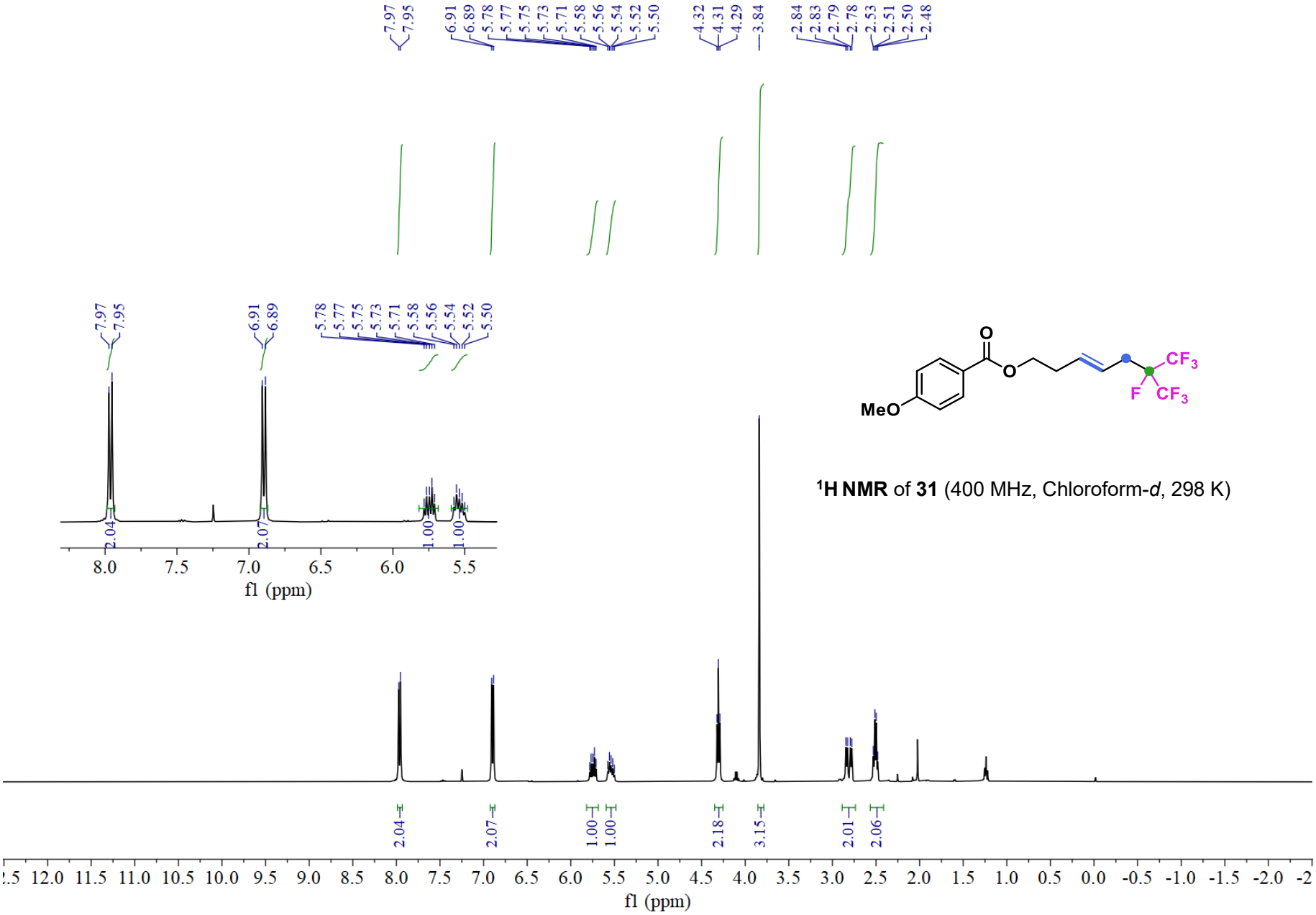
^{1}H NMR of **29** (400 MHz, Chloroform-*d*, 298 K)



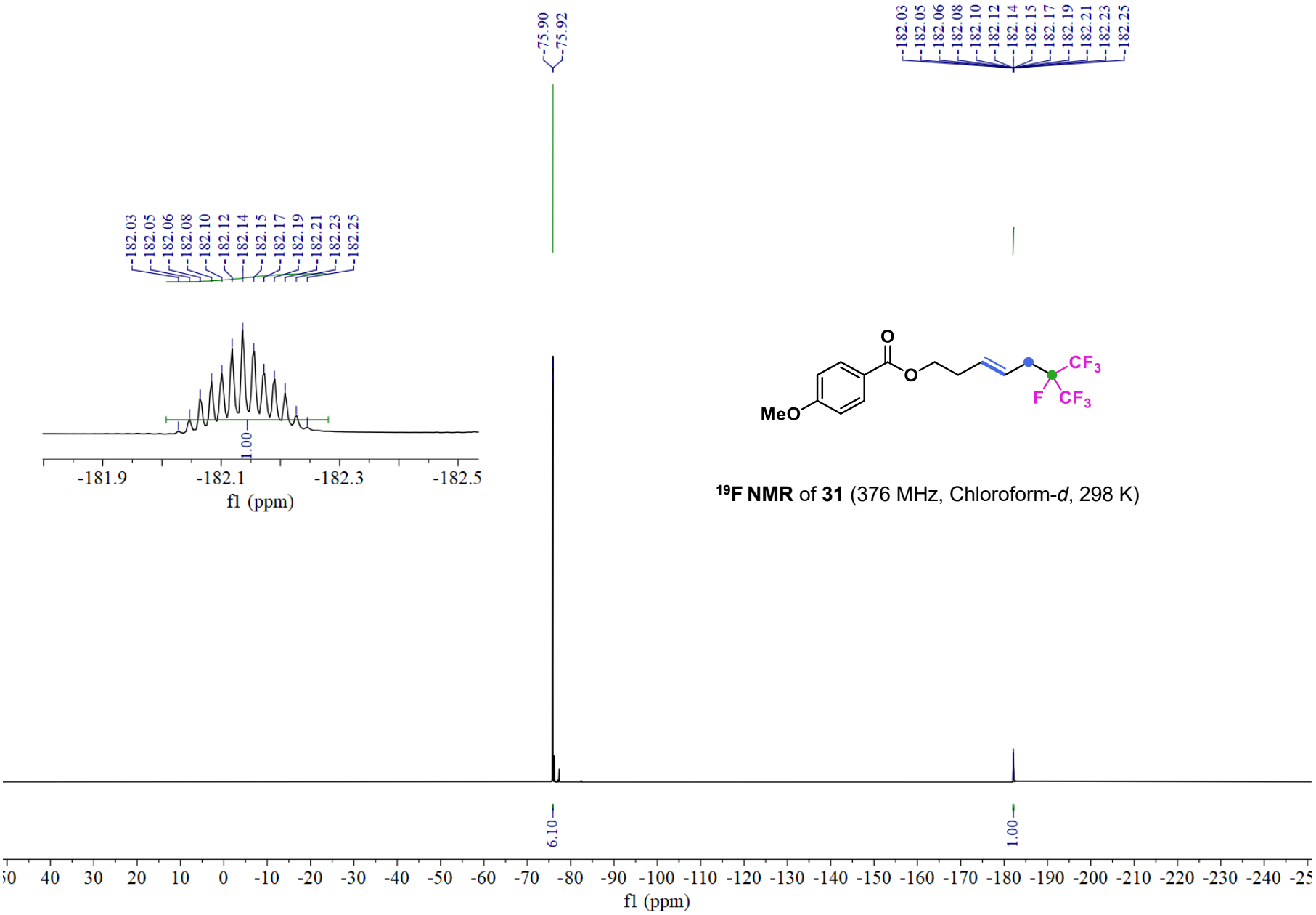
^{19}F NMR of **29** (376 MHz, Chloroform-*d*, 298 K)



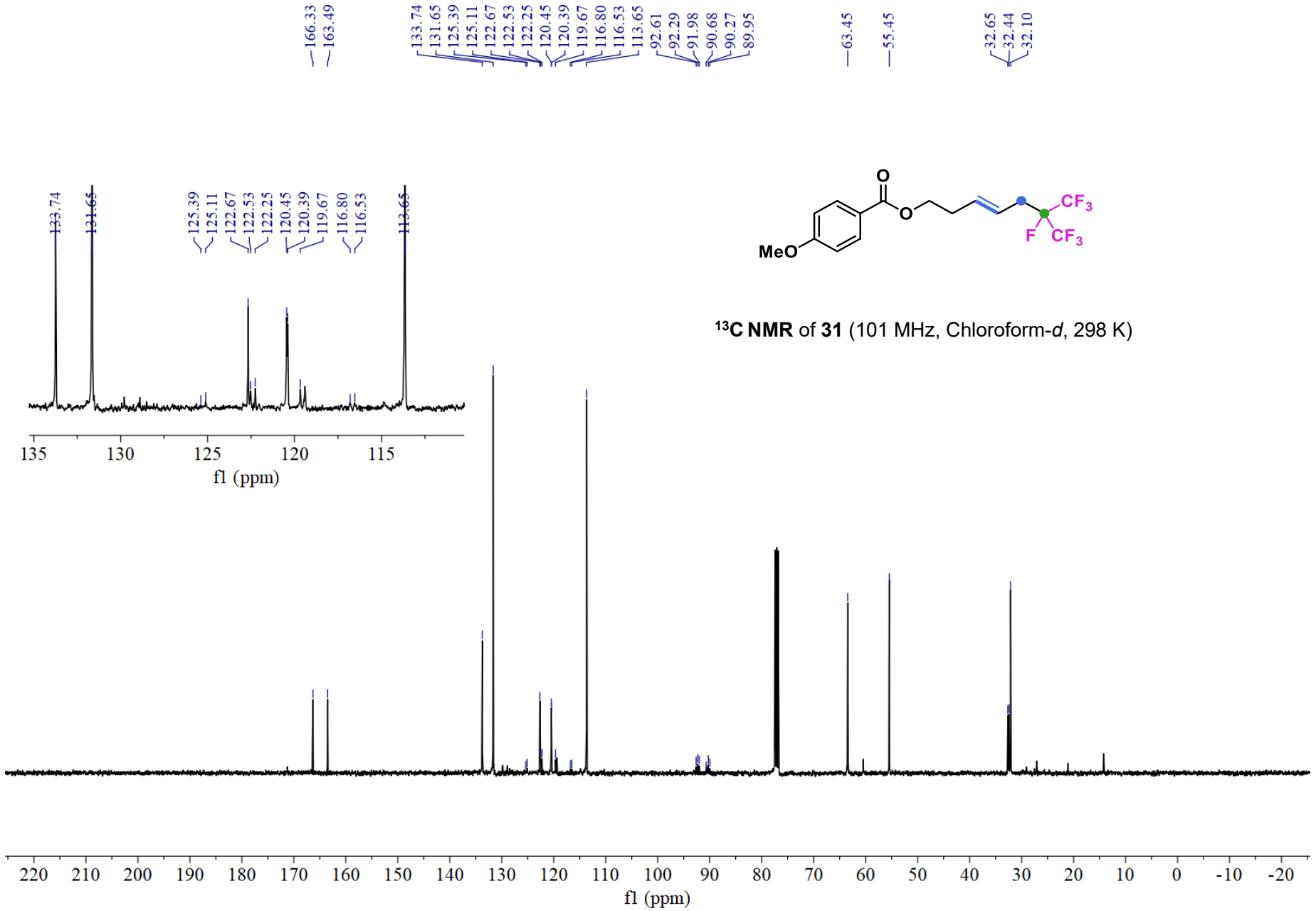
^{13}C NMR of **29** (101 MHz, Chloroform-*d*, 298 K)



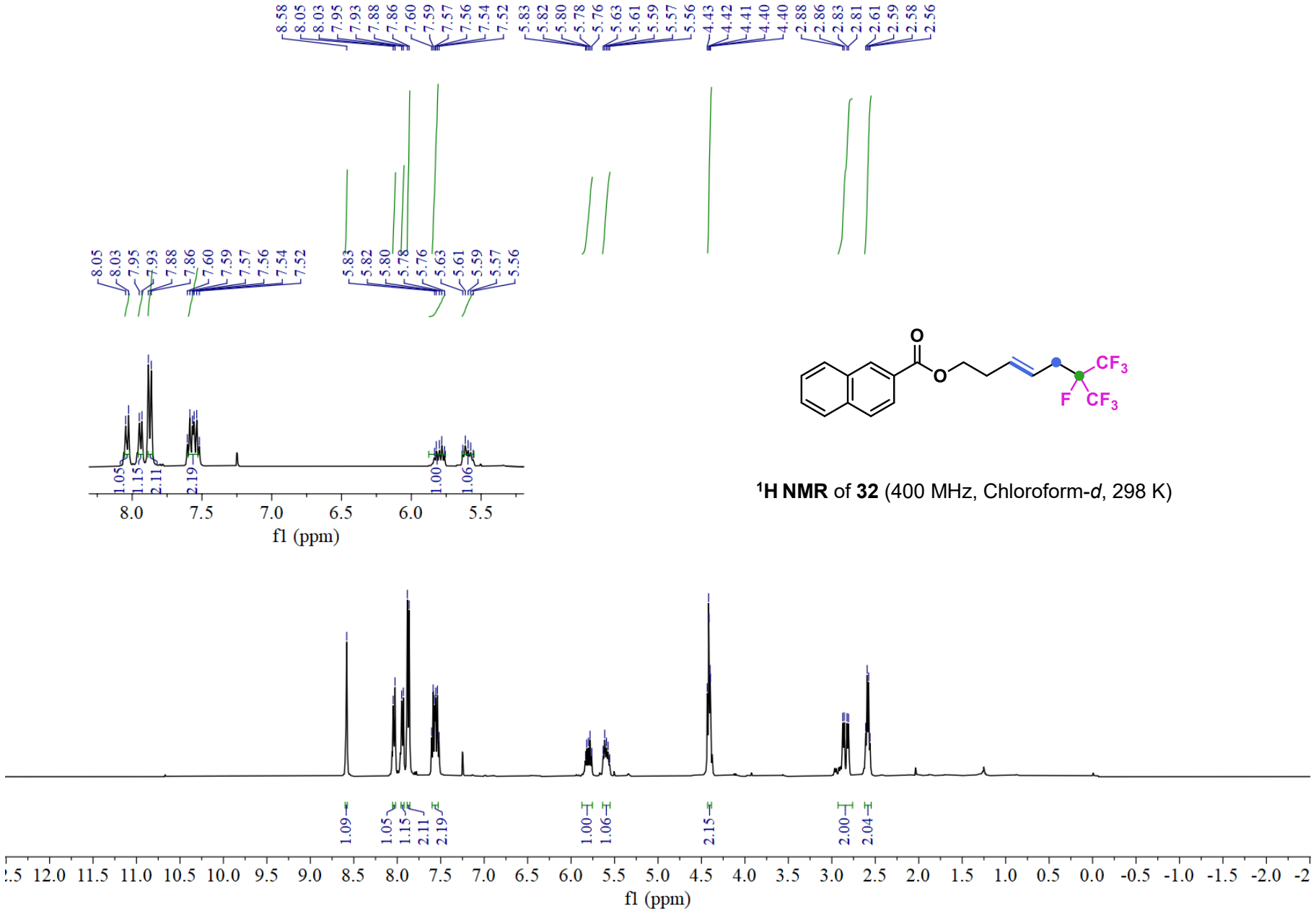
^{1}H NMR of **31** (400 MHz, Chloroform-*d*, 298 K)



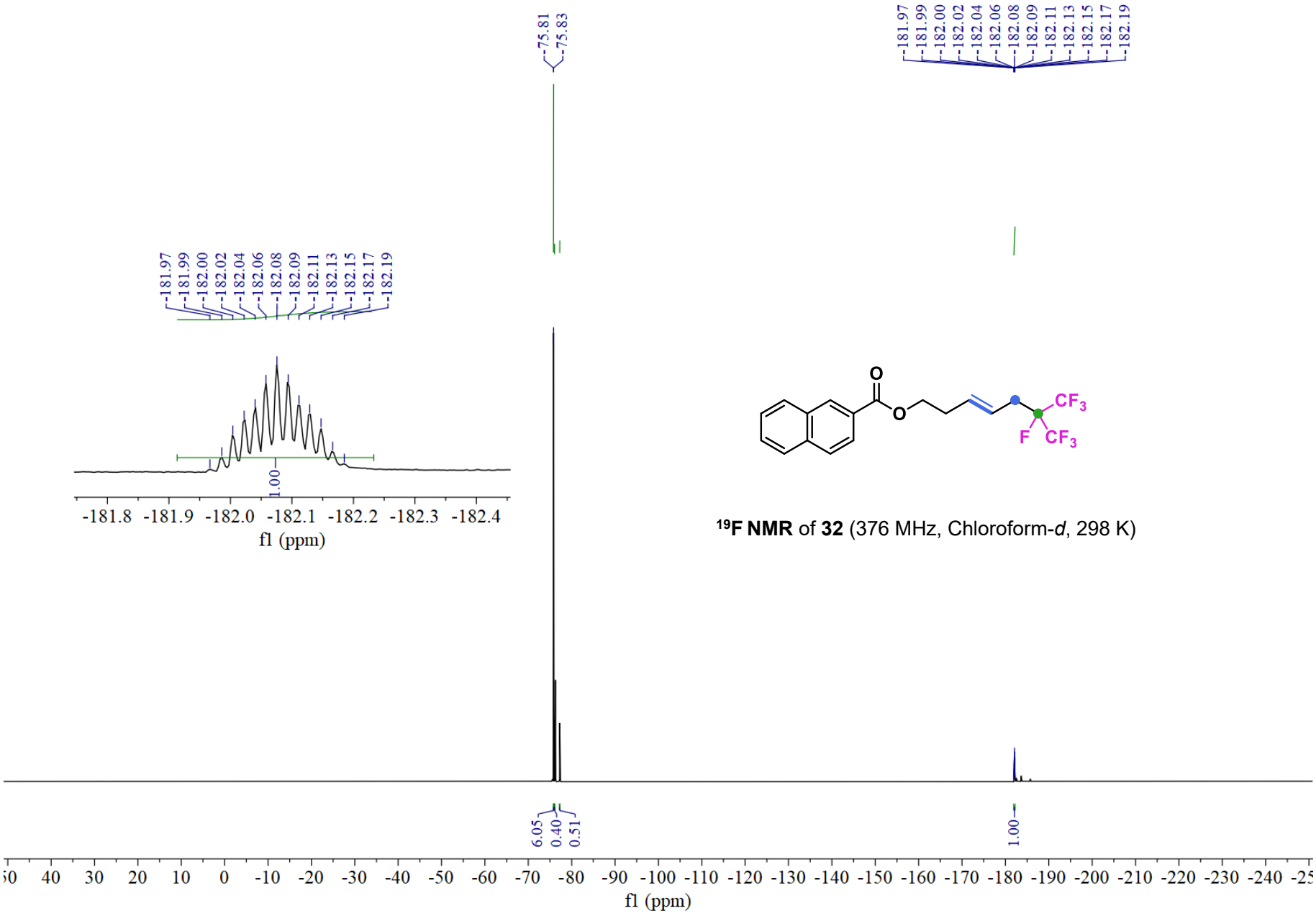
^{19}F NMR of **31** (376 MHz, Chloroform-*d*, 298 K)



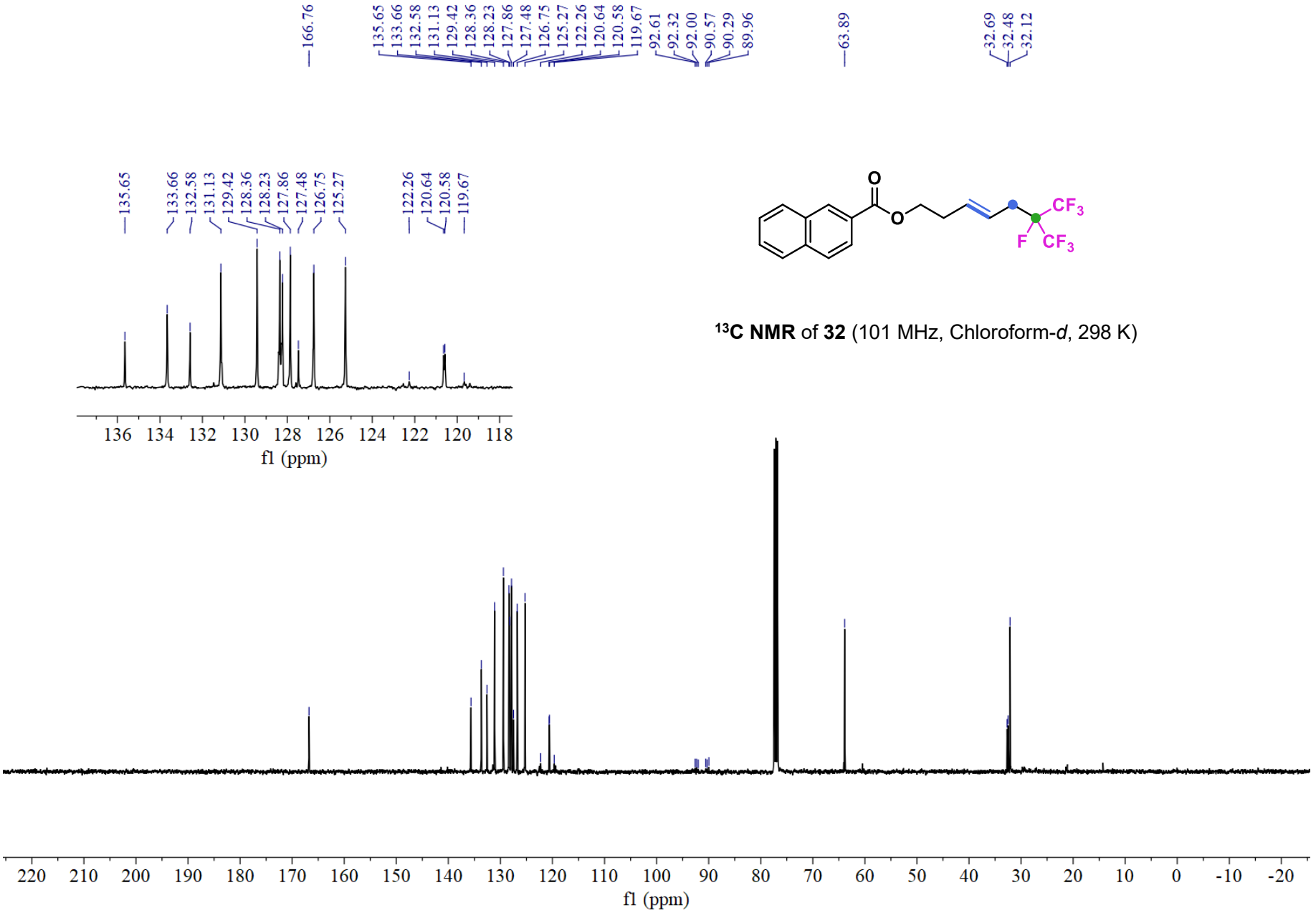
^{13}C NMR of **31** (101 MHz, Chloroform-*d*, 298 K)



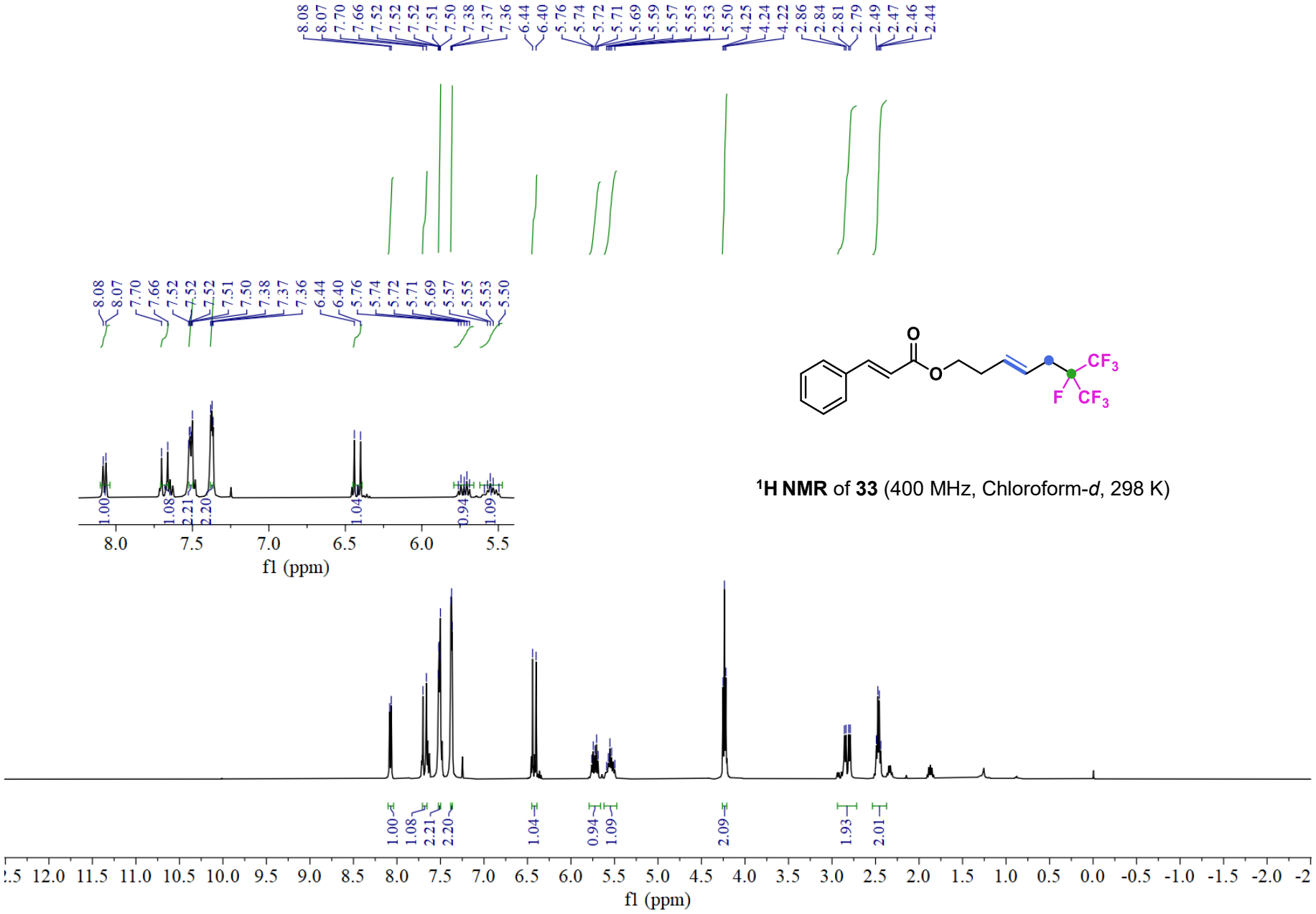
^{1}H NMR of **32** (400 MHz, Chloroform-*d*, 298 K)



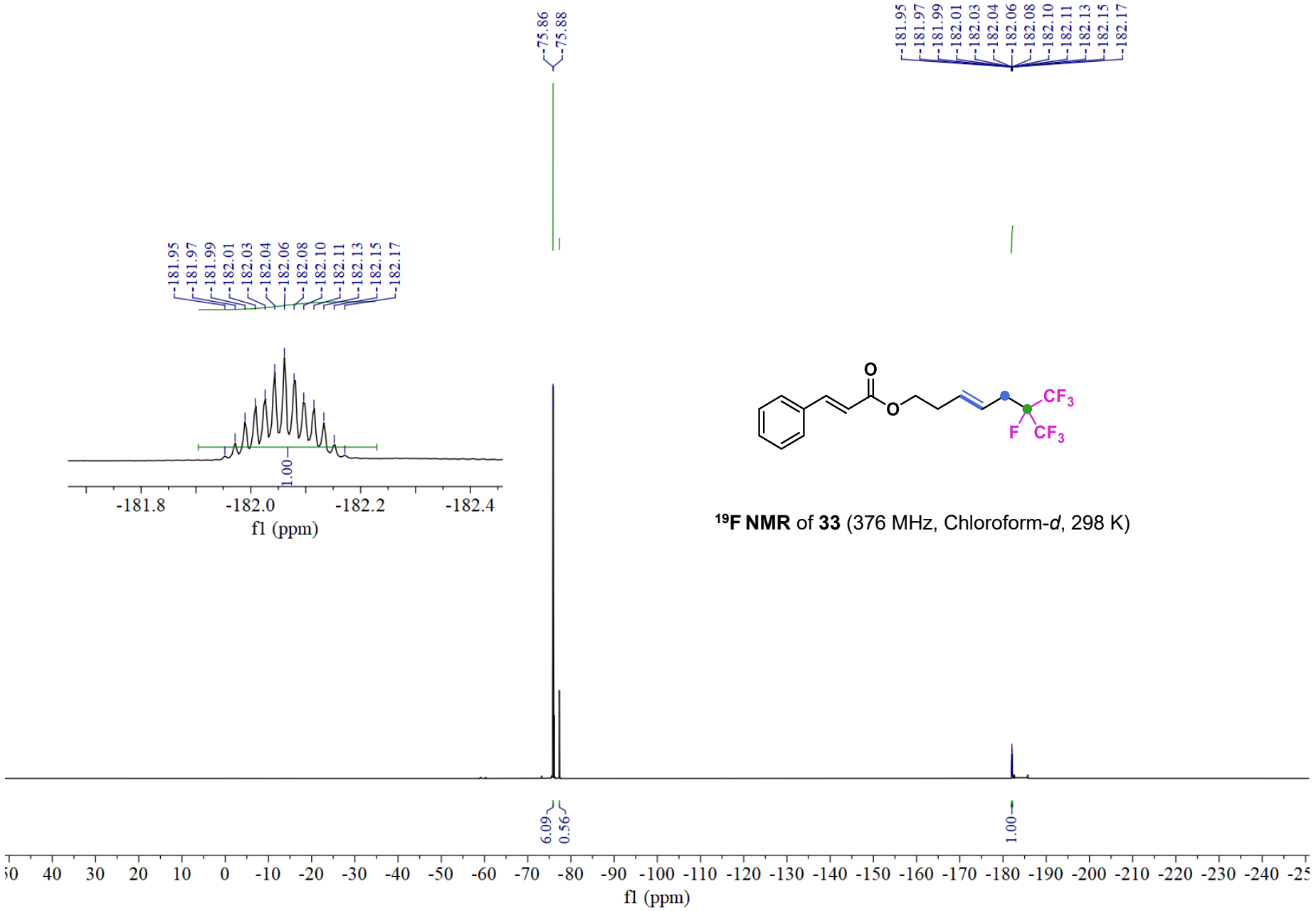
^{19}F NMR of **32** (376 MHz, Chloroform-*d*, 298 K)



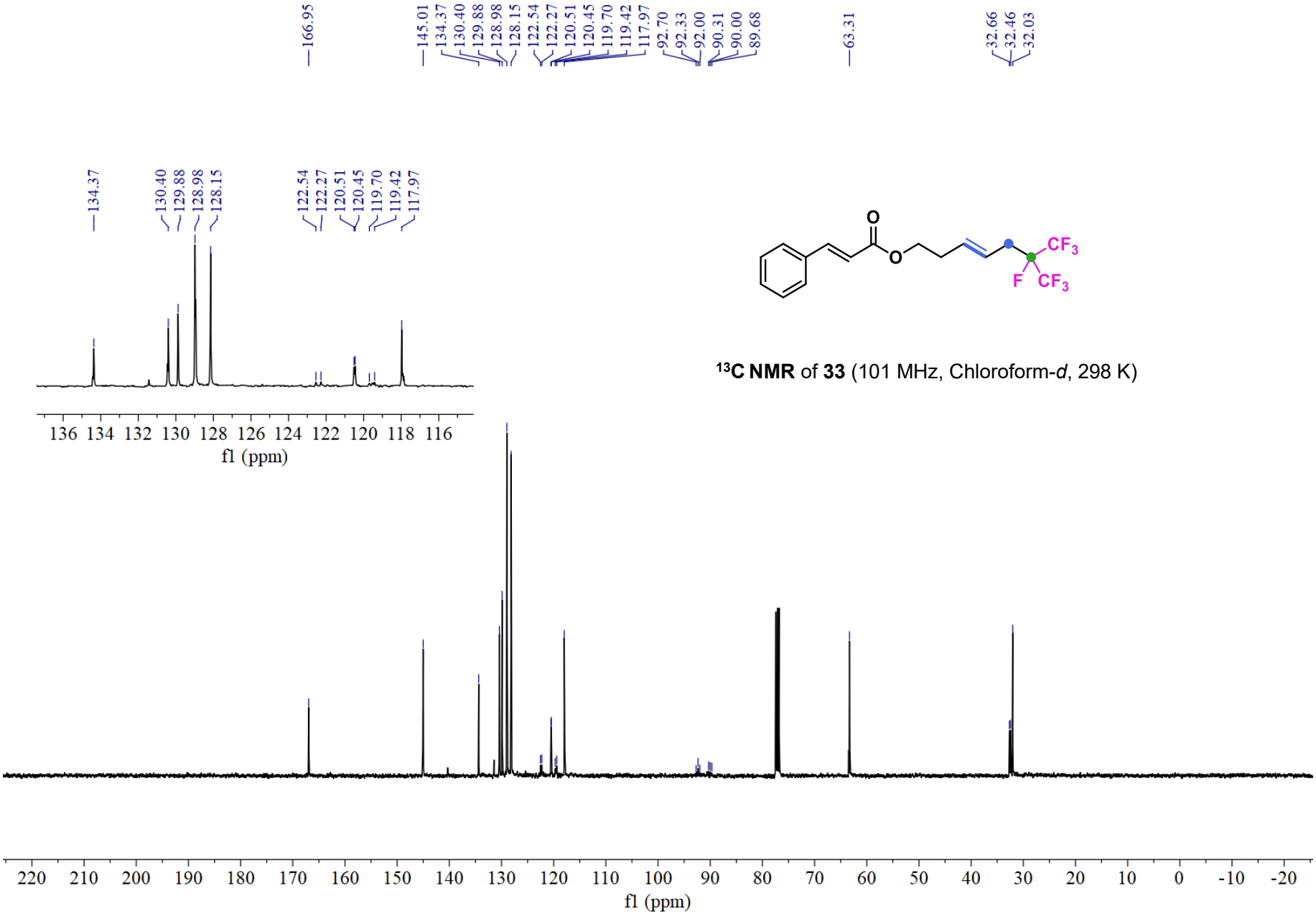
^{13}C NMR of **32** (101 MHz, Chloroform-*d*, 298 K)



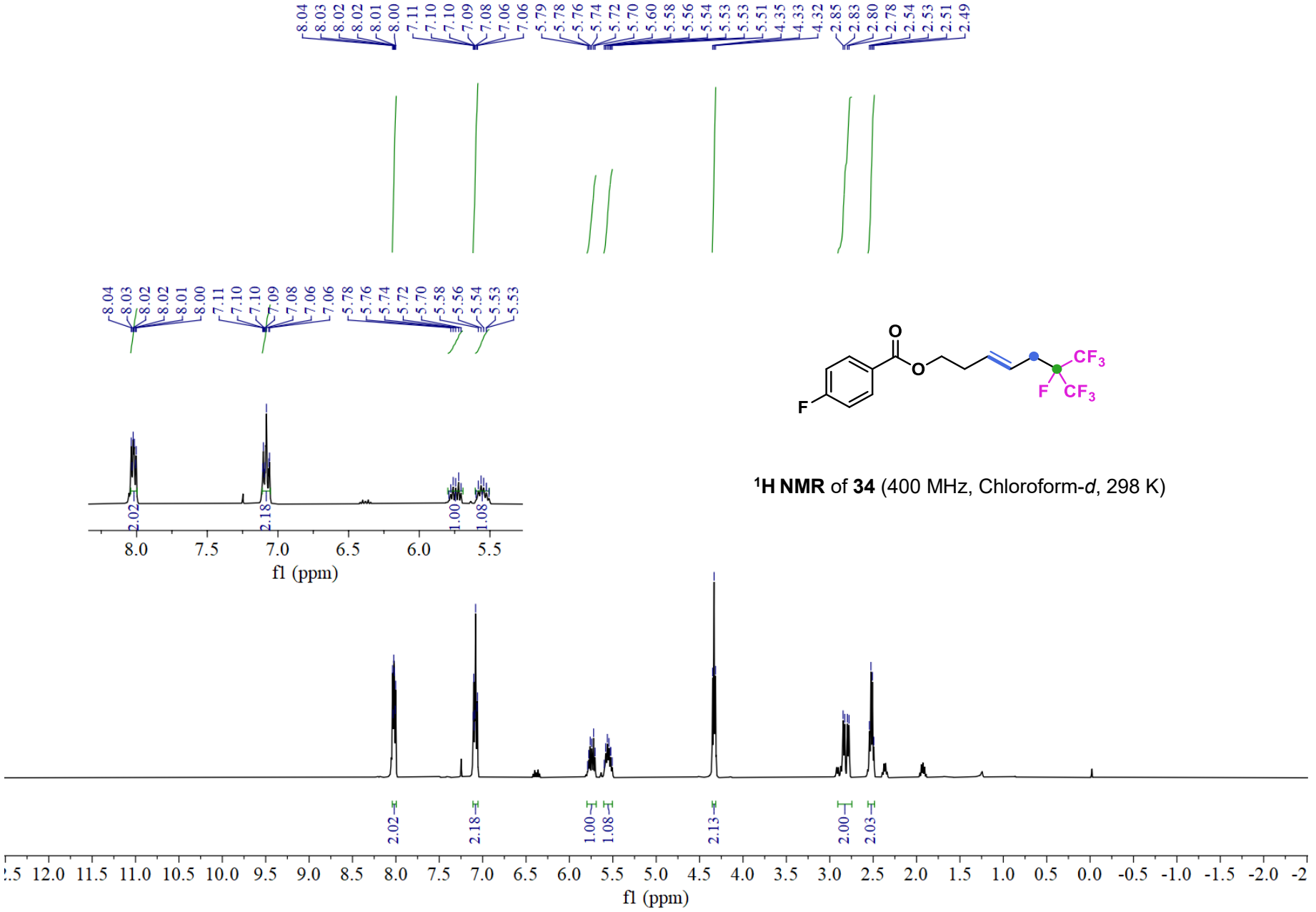
^{1}H NMR of **33** (400 MHz, Chloroform-*d*, 298 K)



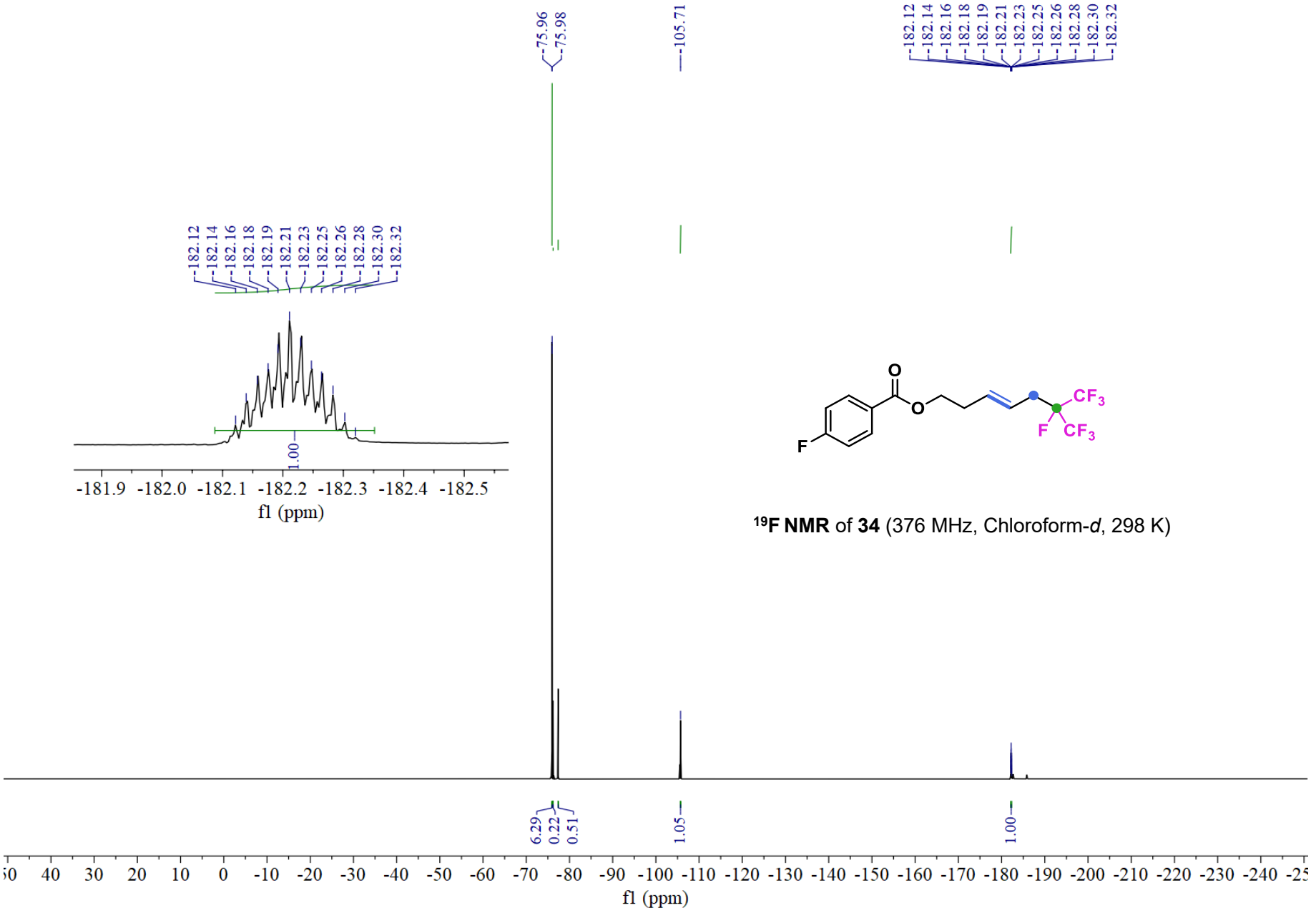
^{19}F NMR of **33** (376 MHz, Chloroform-*d*, 298 K)



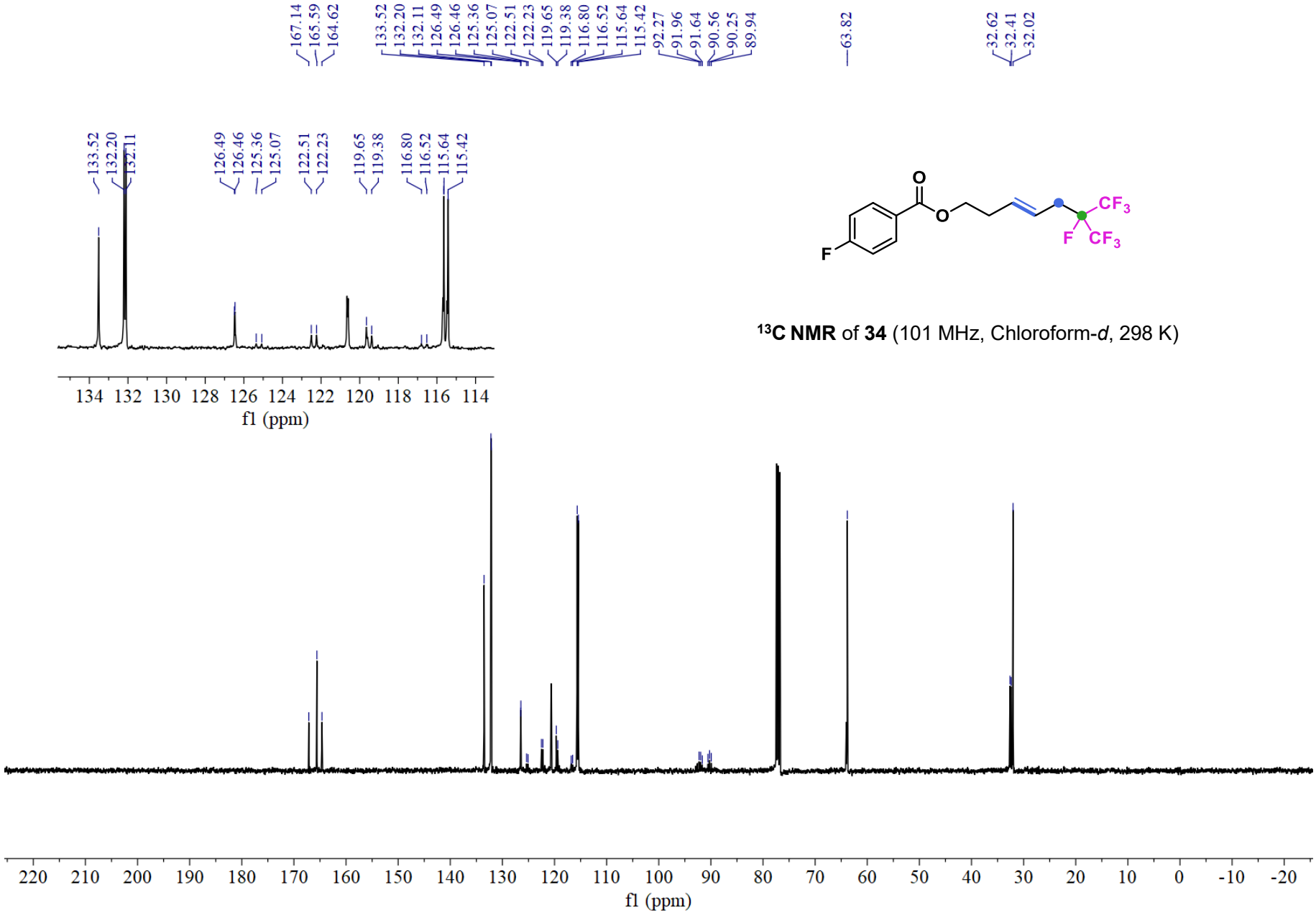
^{13}C NMR of **33** (101 MHz, Chloroform-*d*, 298 K)



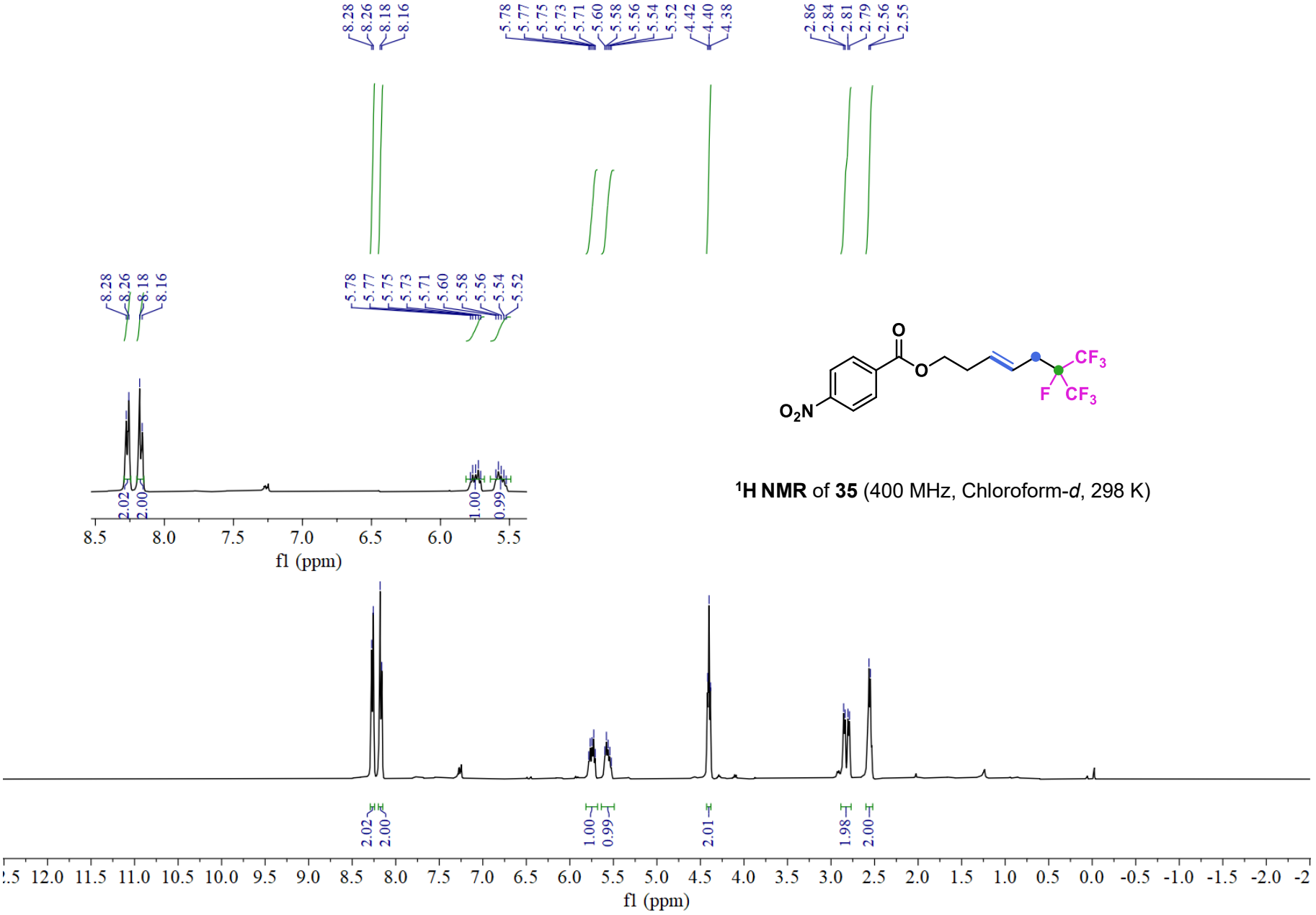
^{1}H NMR of **34** (400 MHz, Chloroform-*d*, 298 K)



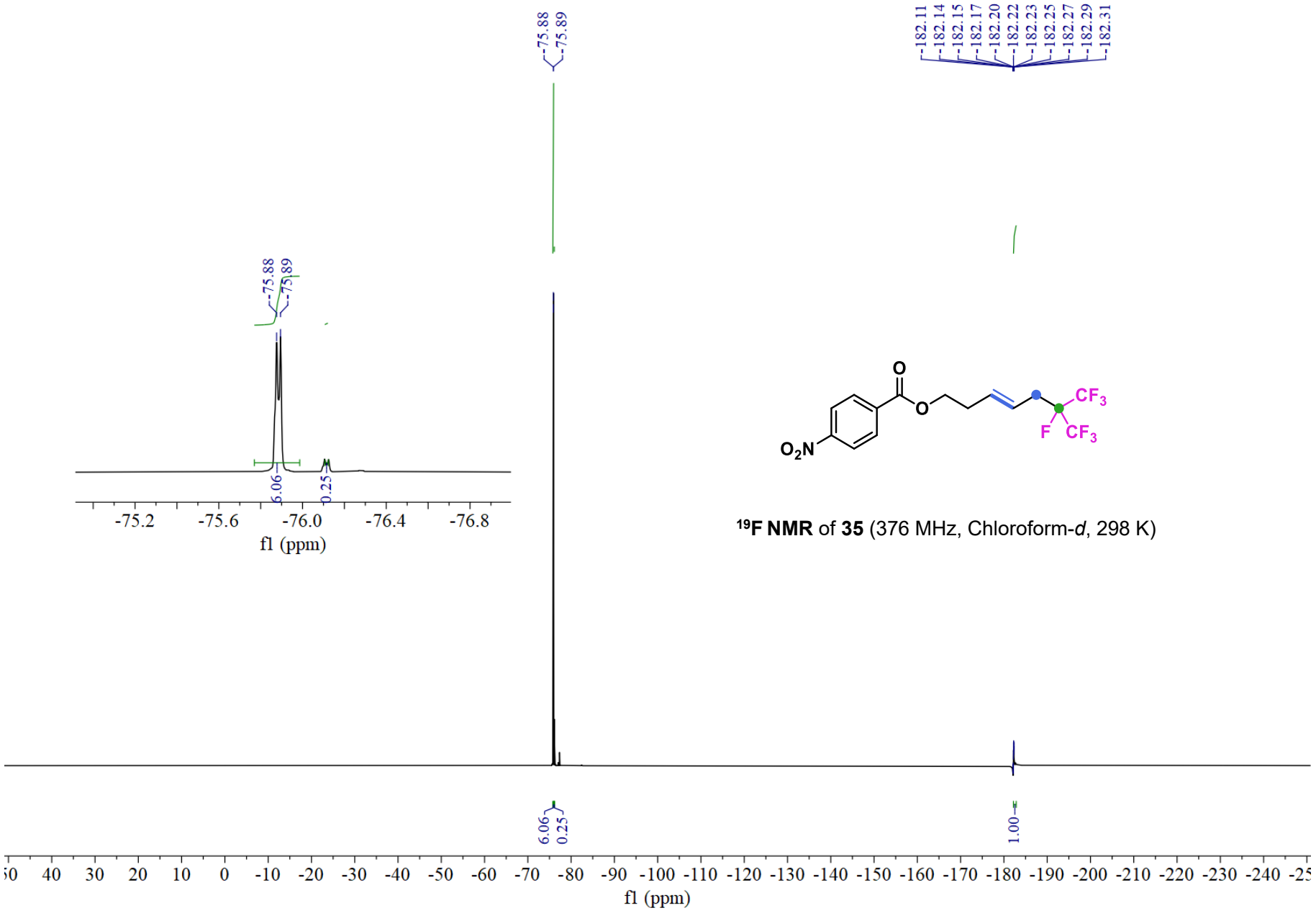
^{19}F NMR of **34** (376 MHz, Chloroform-*d*, 298 K)



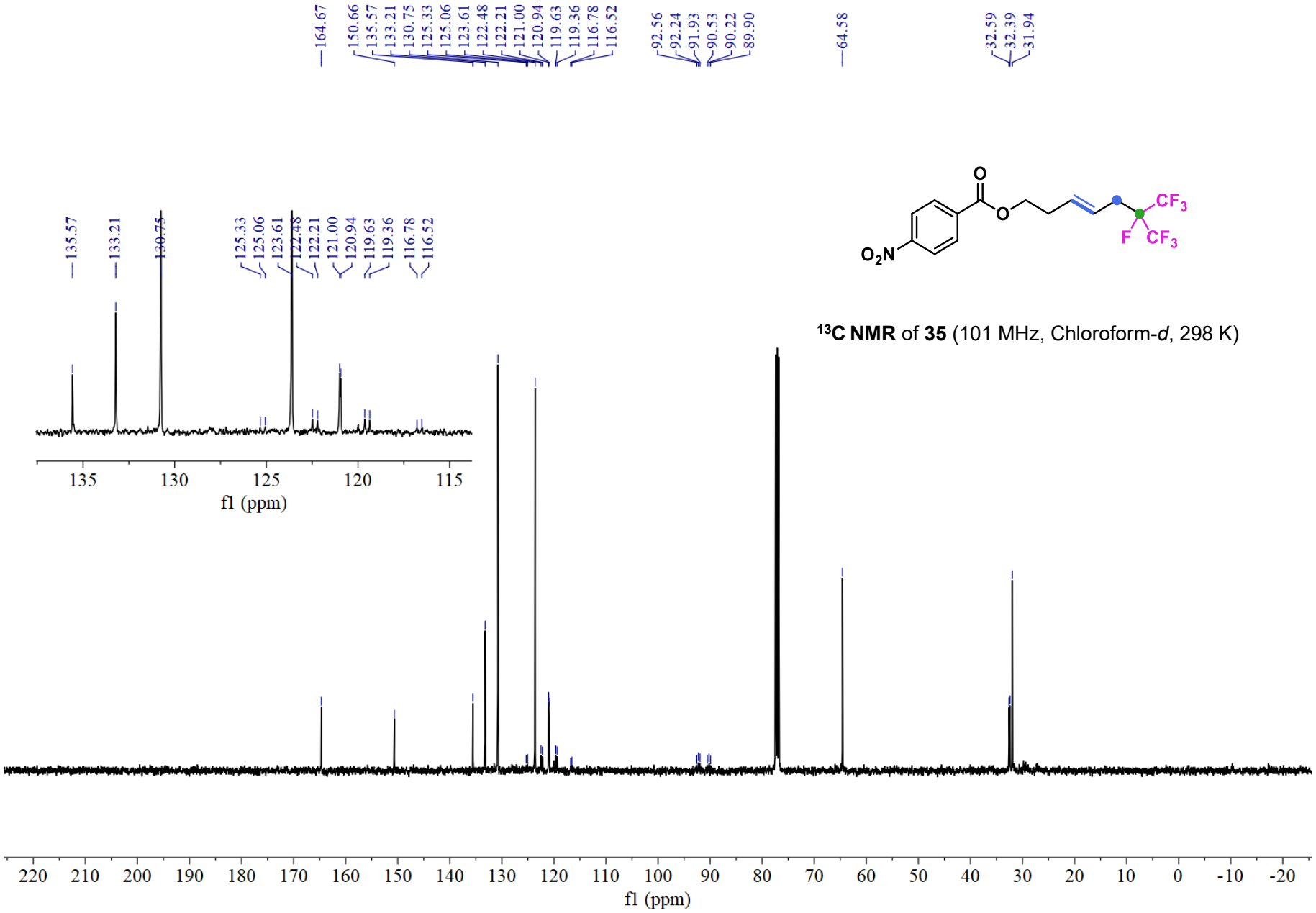
^{13}C NMR of **34** (101 MHz, Chloroform-*d*, 298 K)



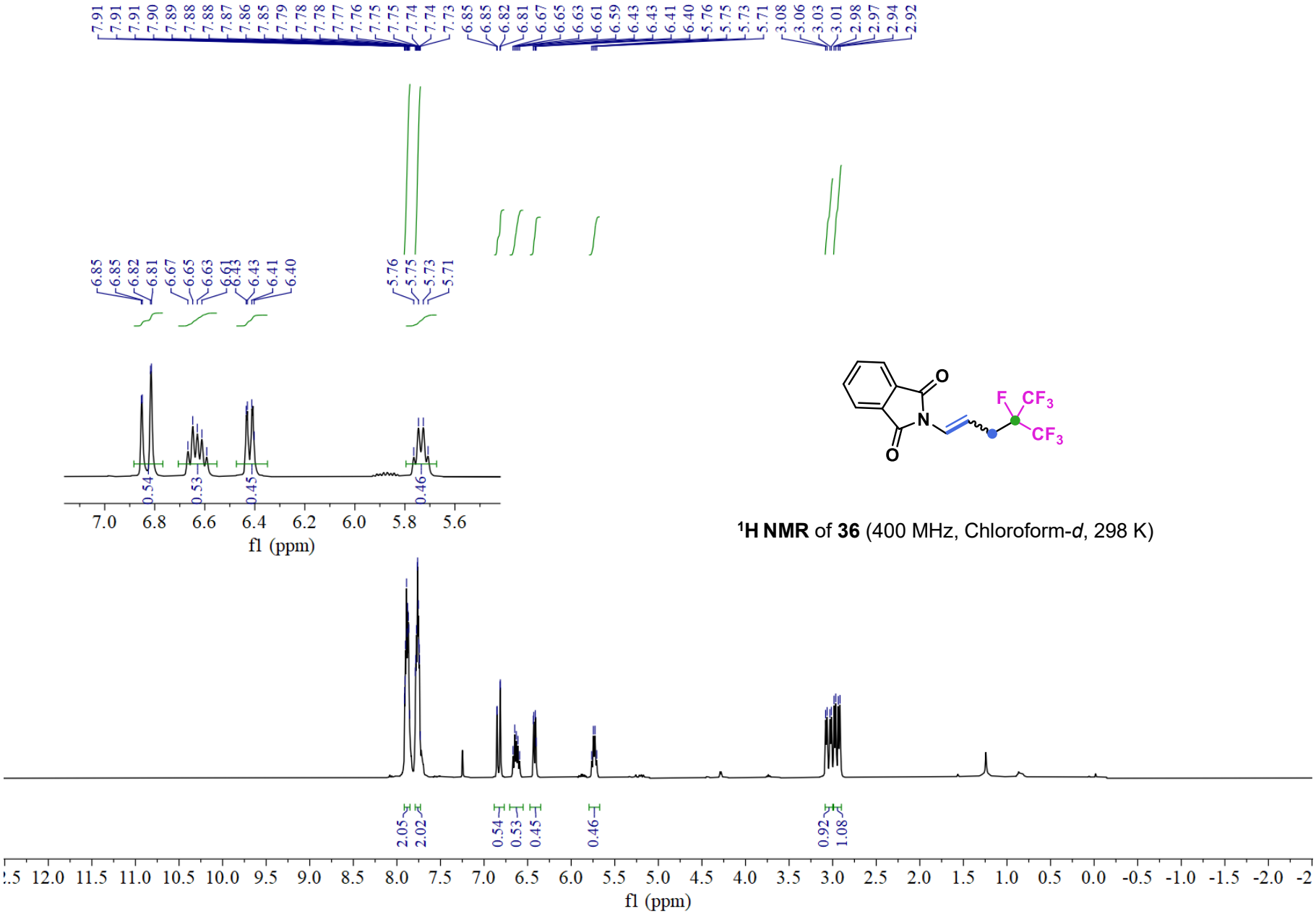
^{1}H NMR of **35** (400 MHz, Chloroform-*d*, 298 K)



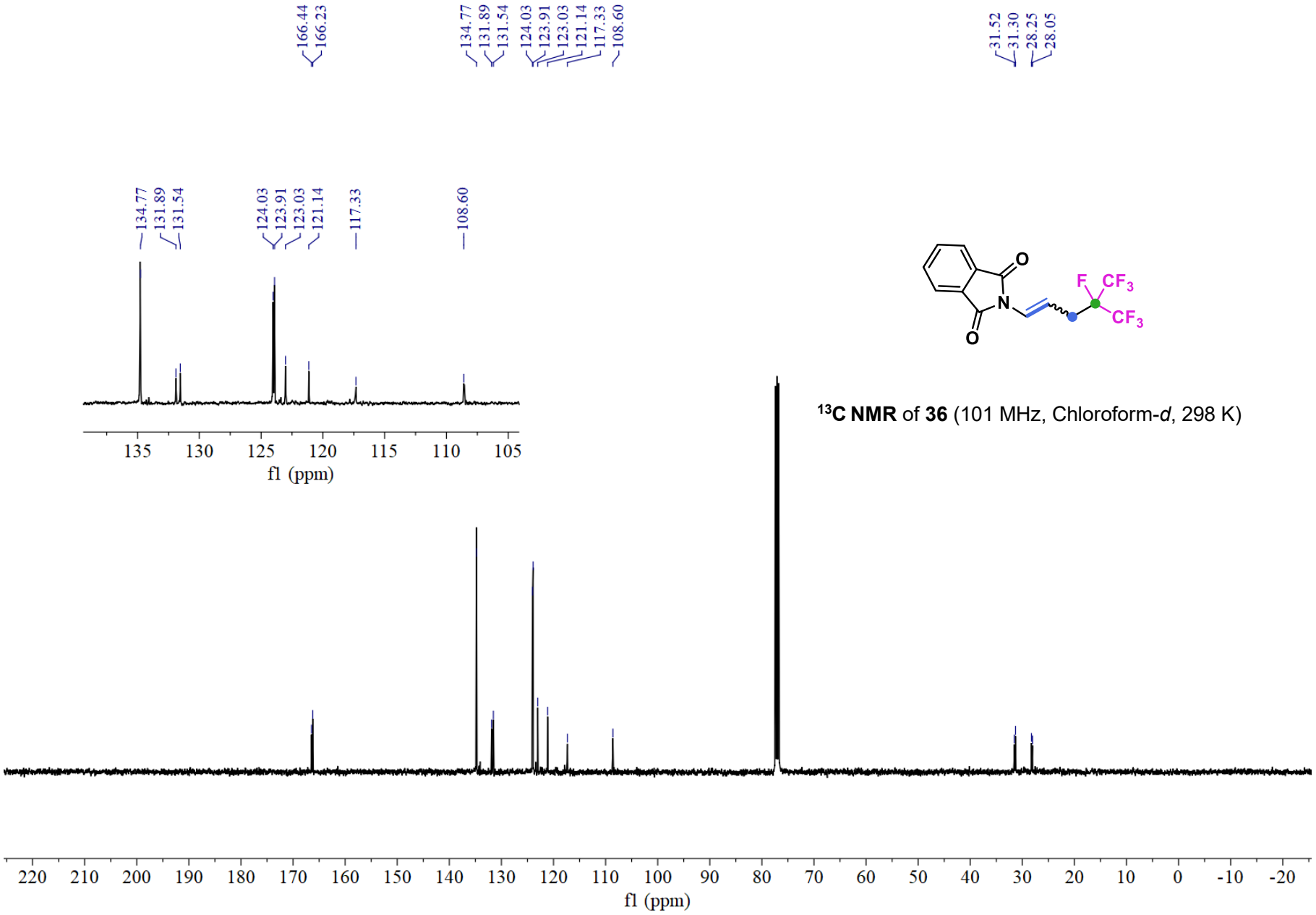
^{19}F NMR of **35** (376 MHz, Chloroform-*d*, 298 K)



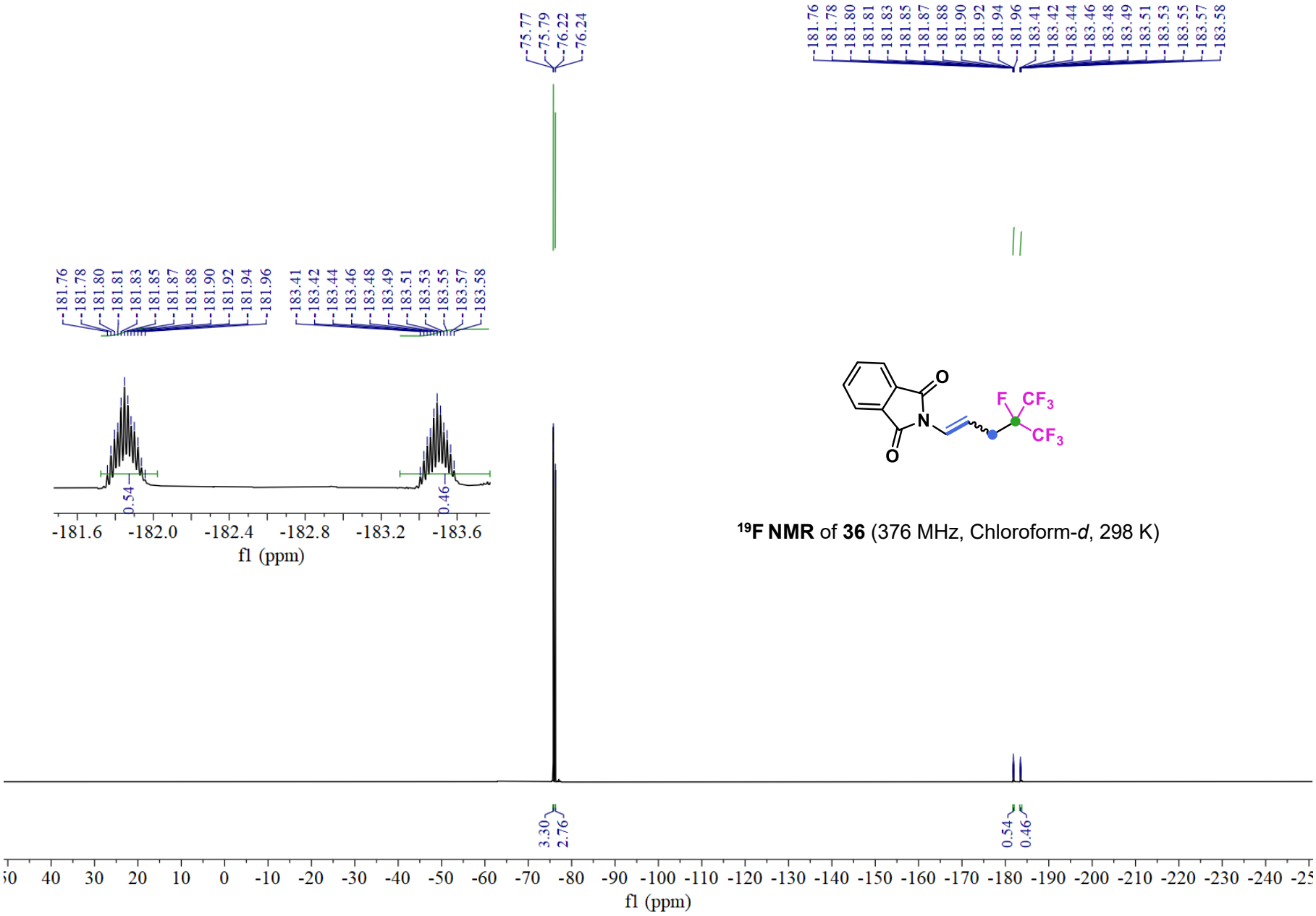
^{13}C NMR of **35** (101 MHz, Chloroform-*d*, 298 K)



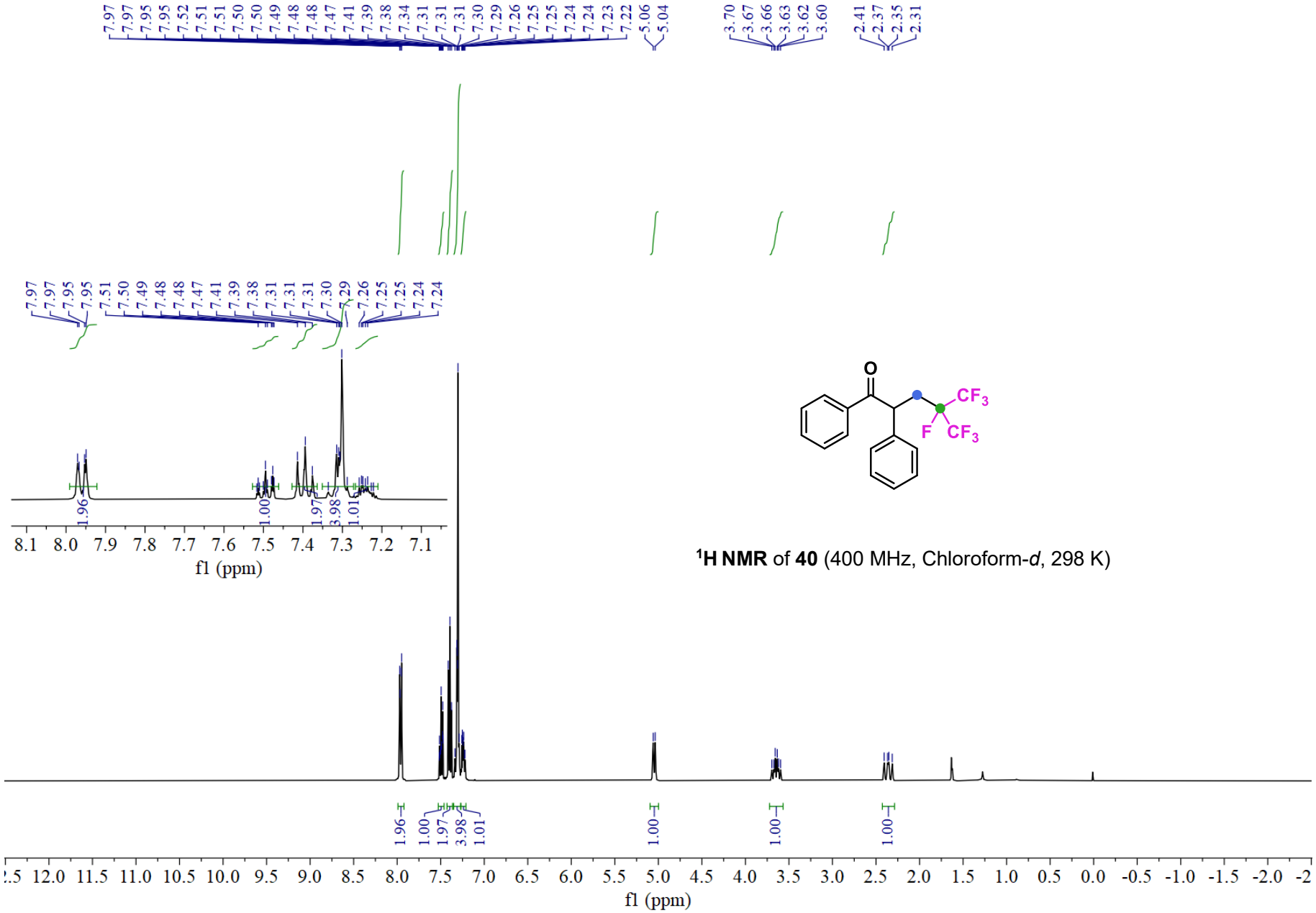
^{1}H NMR of **36** (400 MHz, Chloroform-*d*, 298 K)



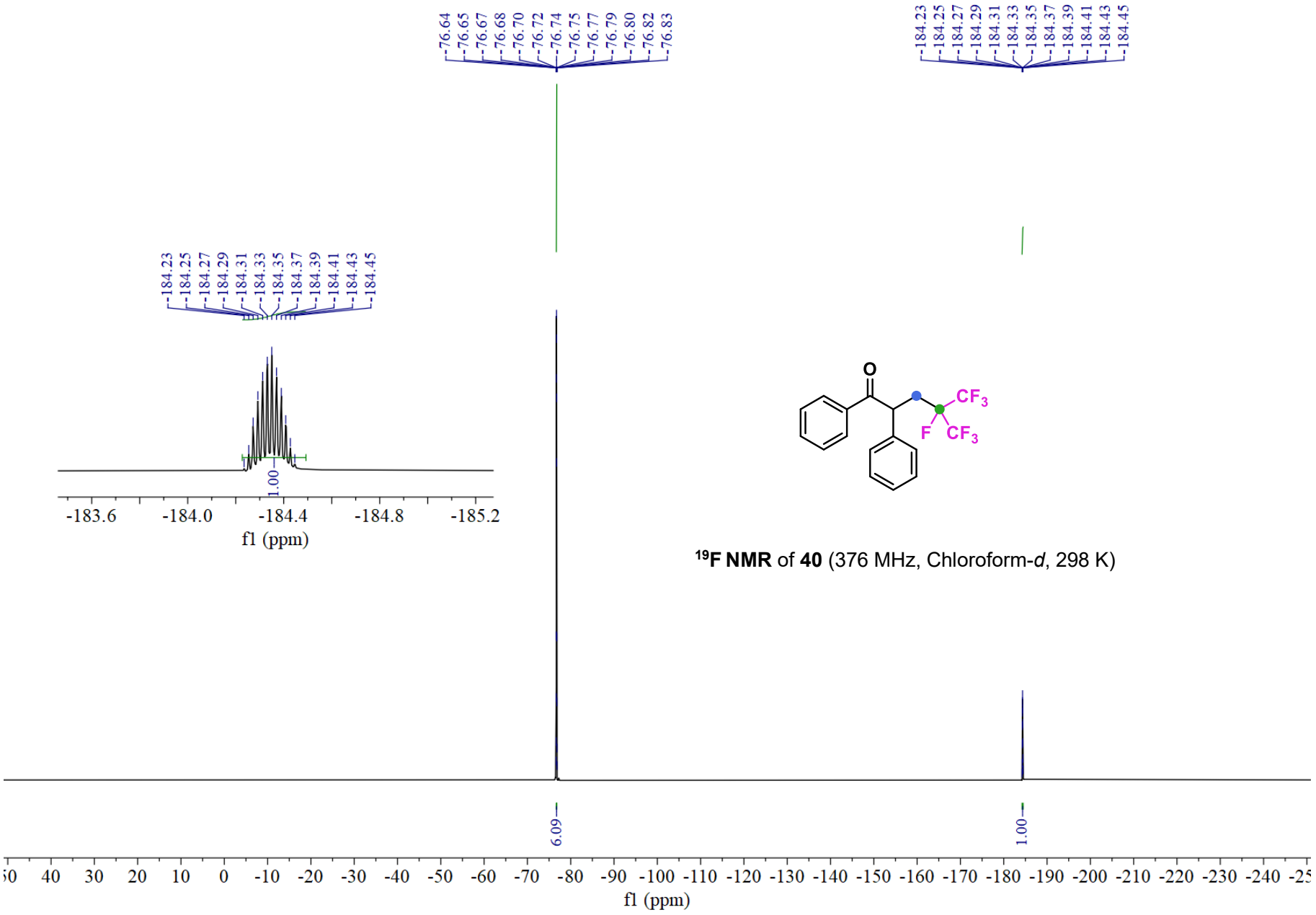
^{13}C NMR of **36** (101 MHz, Chloroform-*d*, 298 K)



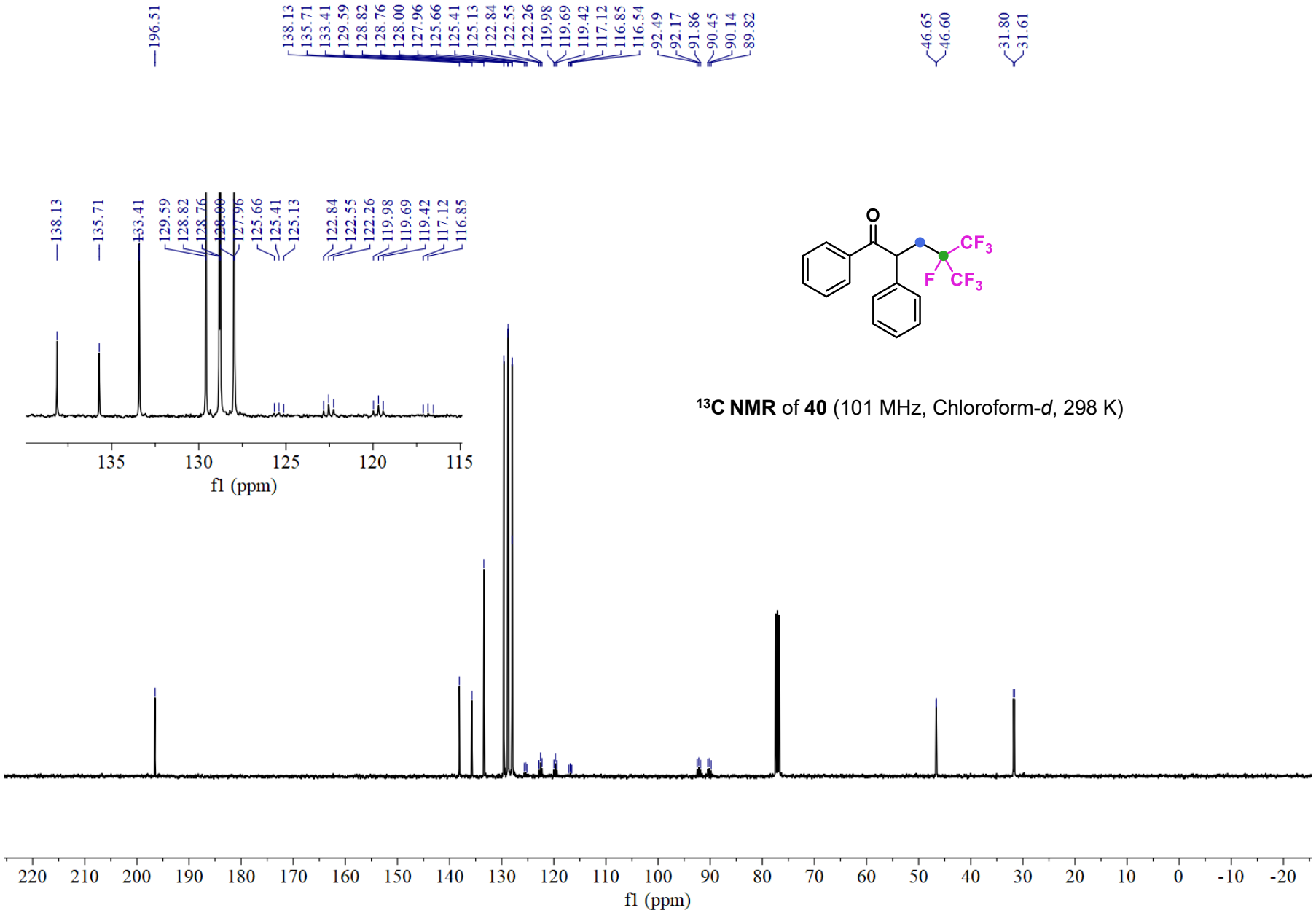
^{19}F NMR of **36** (376 MHz, Chloroform-*d*, 298 K)



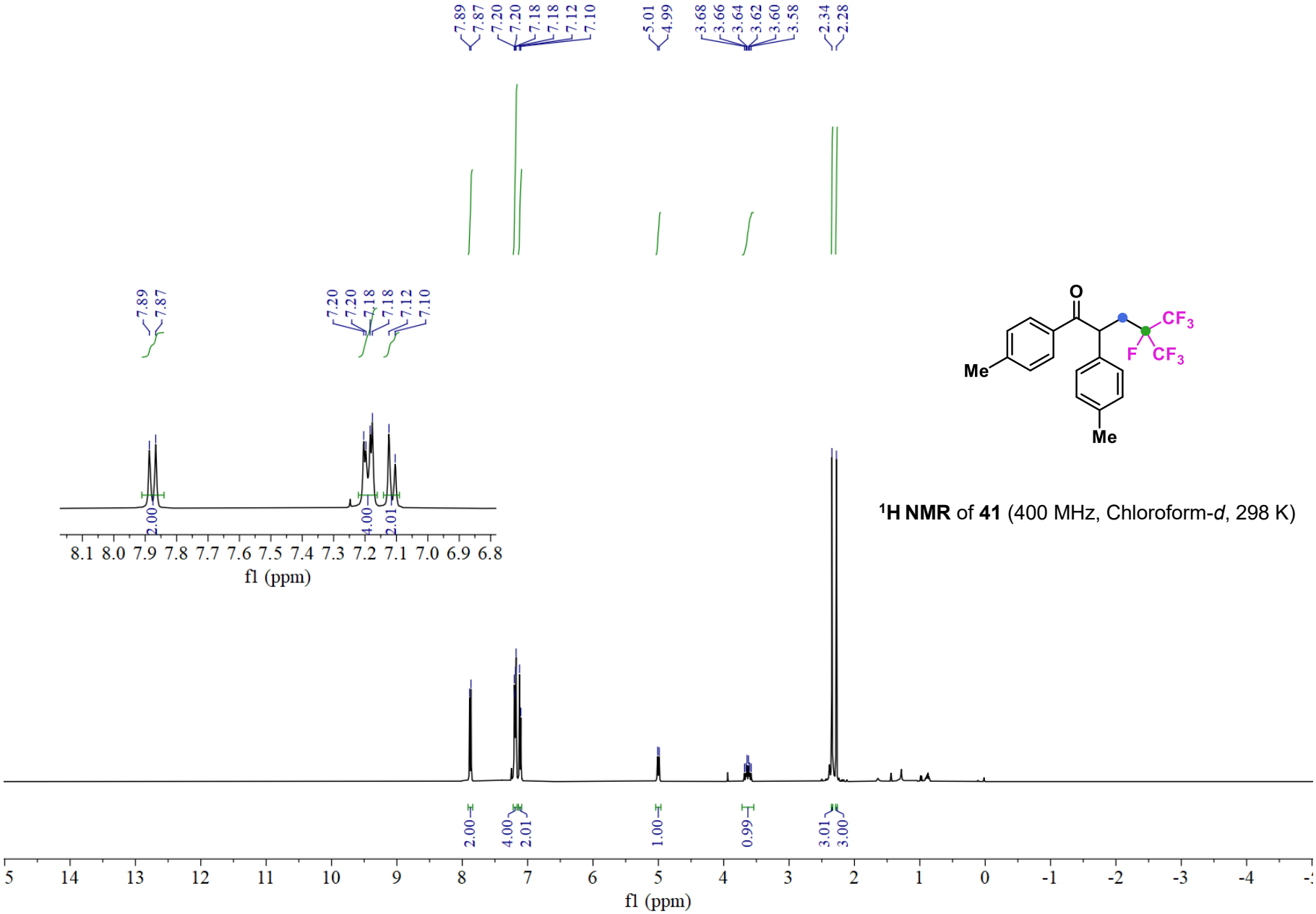
^{1}H NMR of **40** (400 MHz, Chloroform-*d*, 298 K)



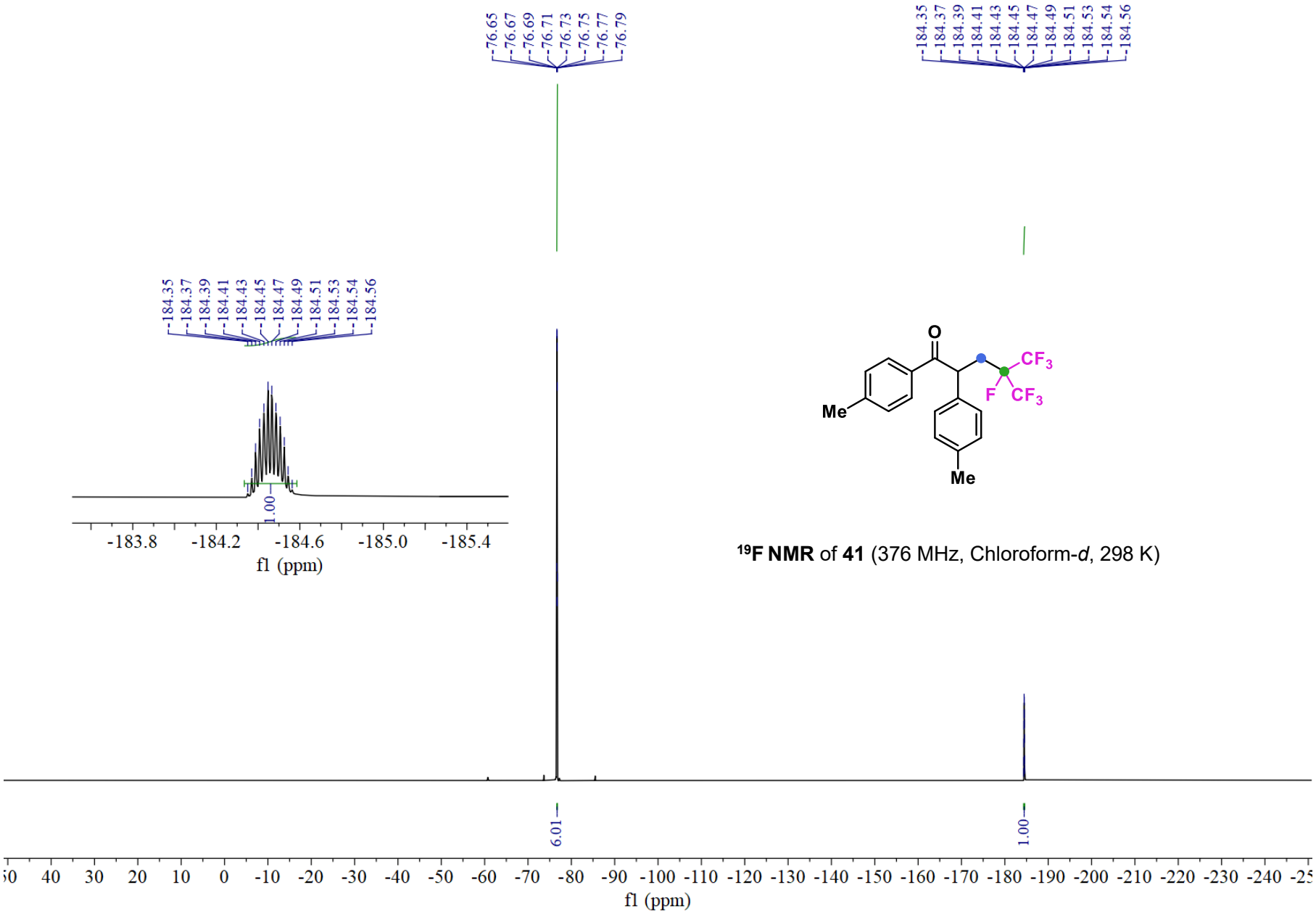
^{19}F NMR of **40** (376 MHz, Chloroform-*d*, 298 K)



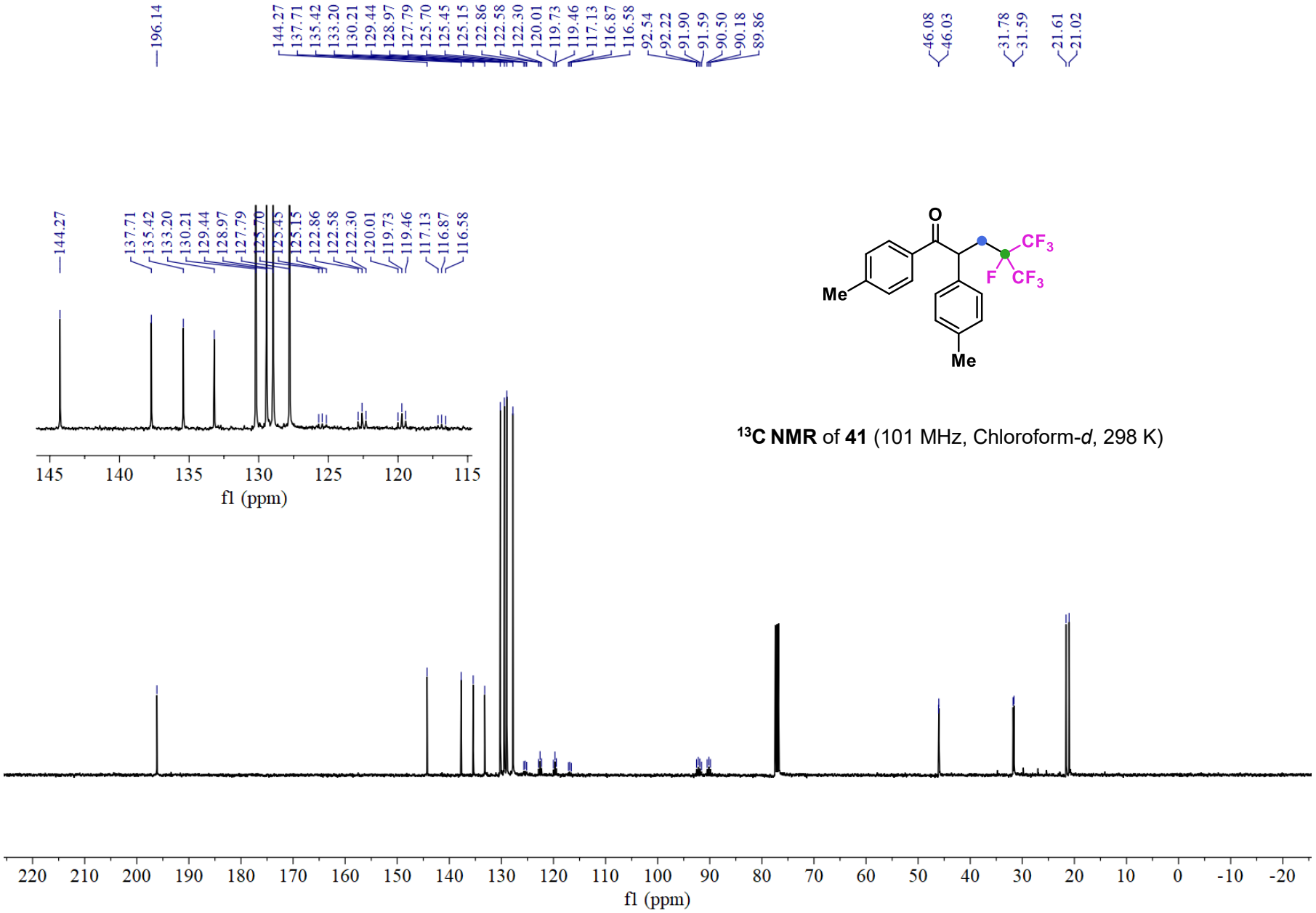
^{13}C NMR of **40** (101 MHz, Chloroform-*d*, 298 K)



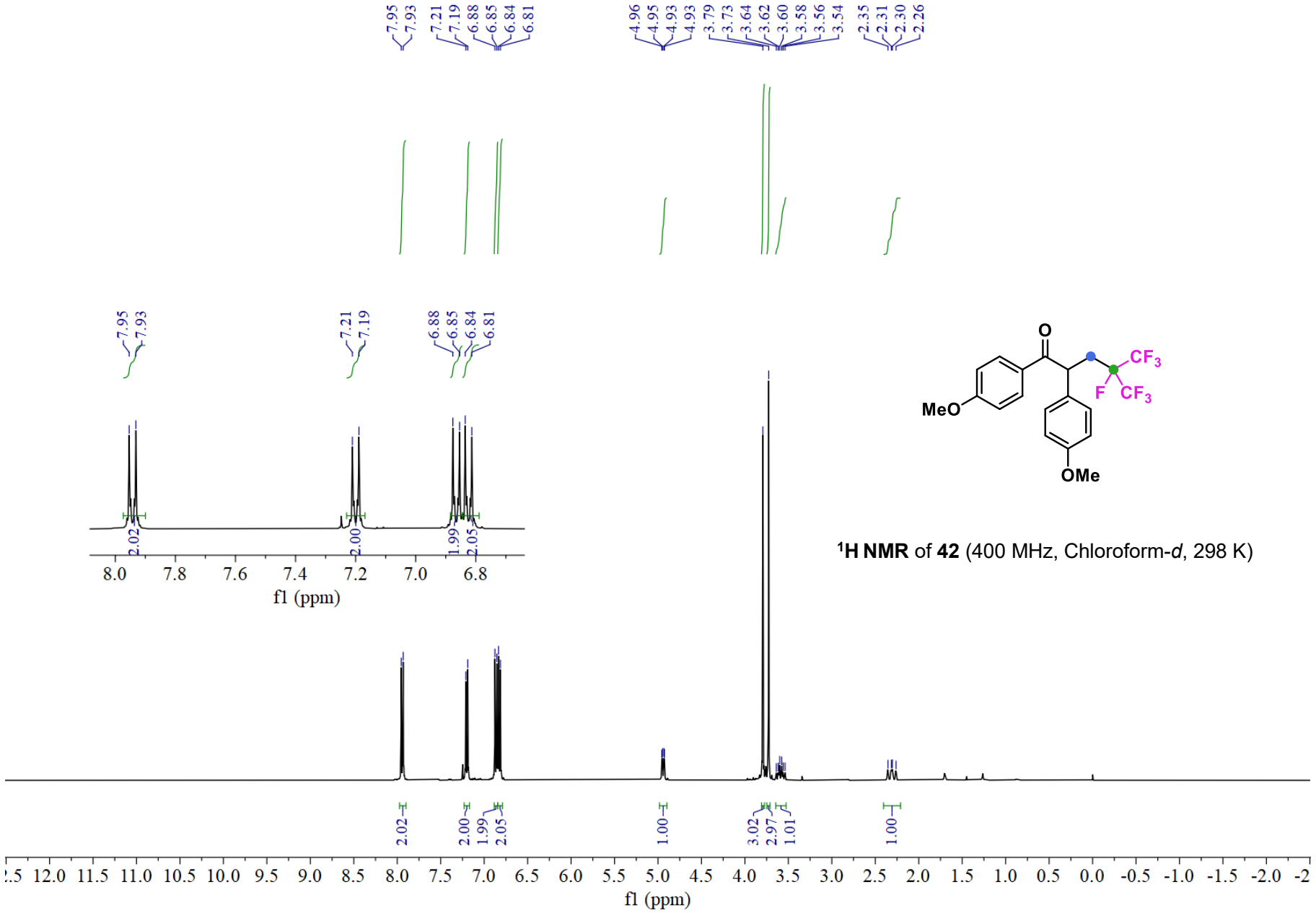
^{1}H NMR of **41** (400 MHz, Chloroform-*d*, 298 K)



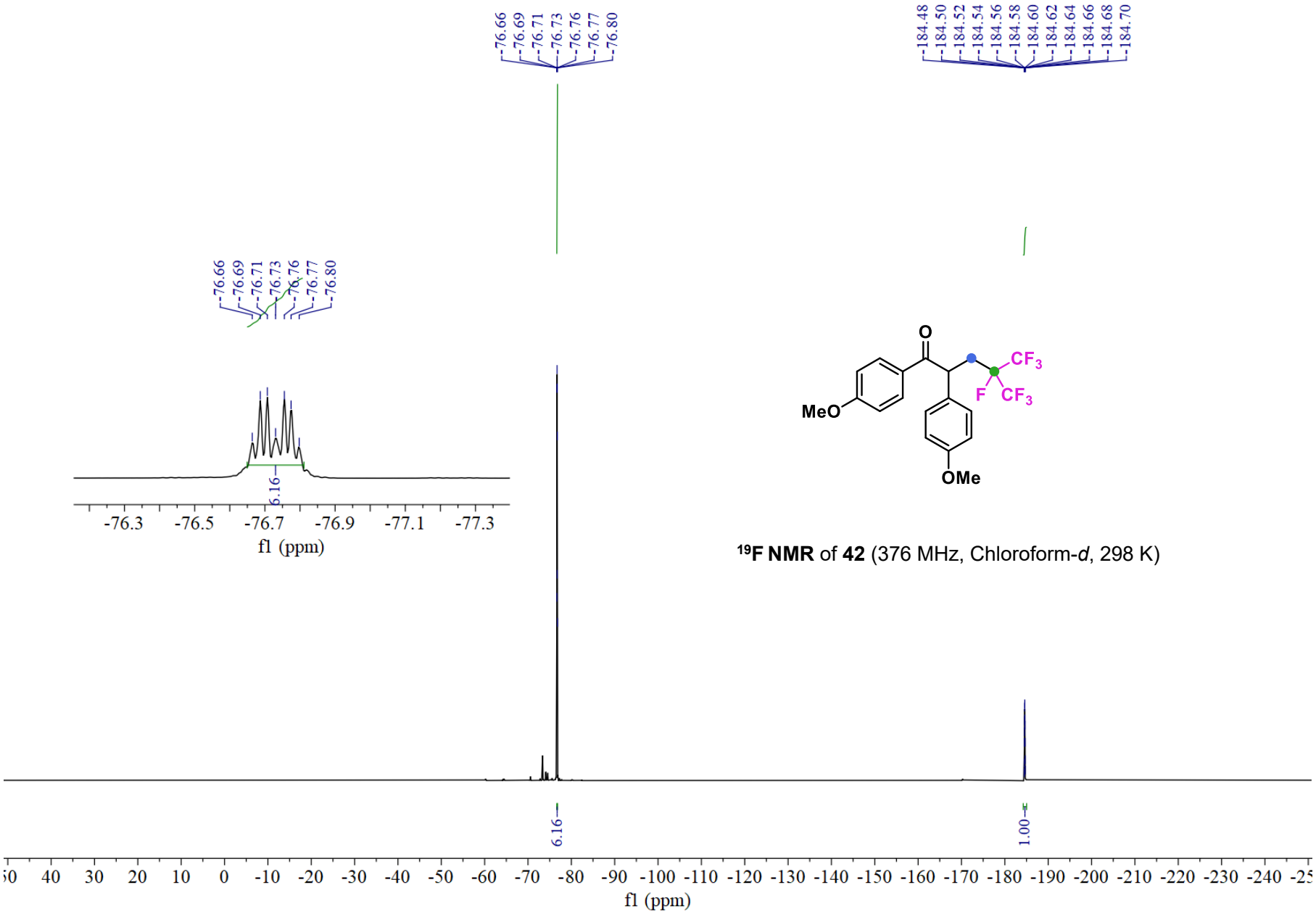
^{19}F NMR of **41** (376 MHz, Chloroform-*d*, 298 K)



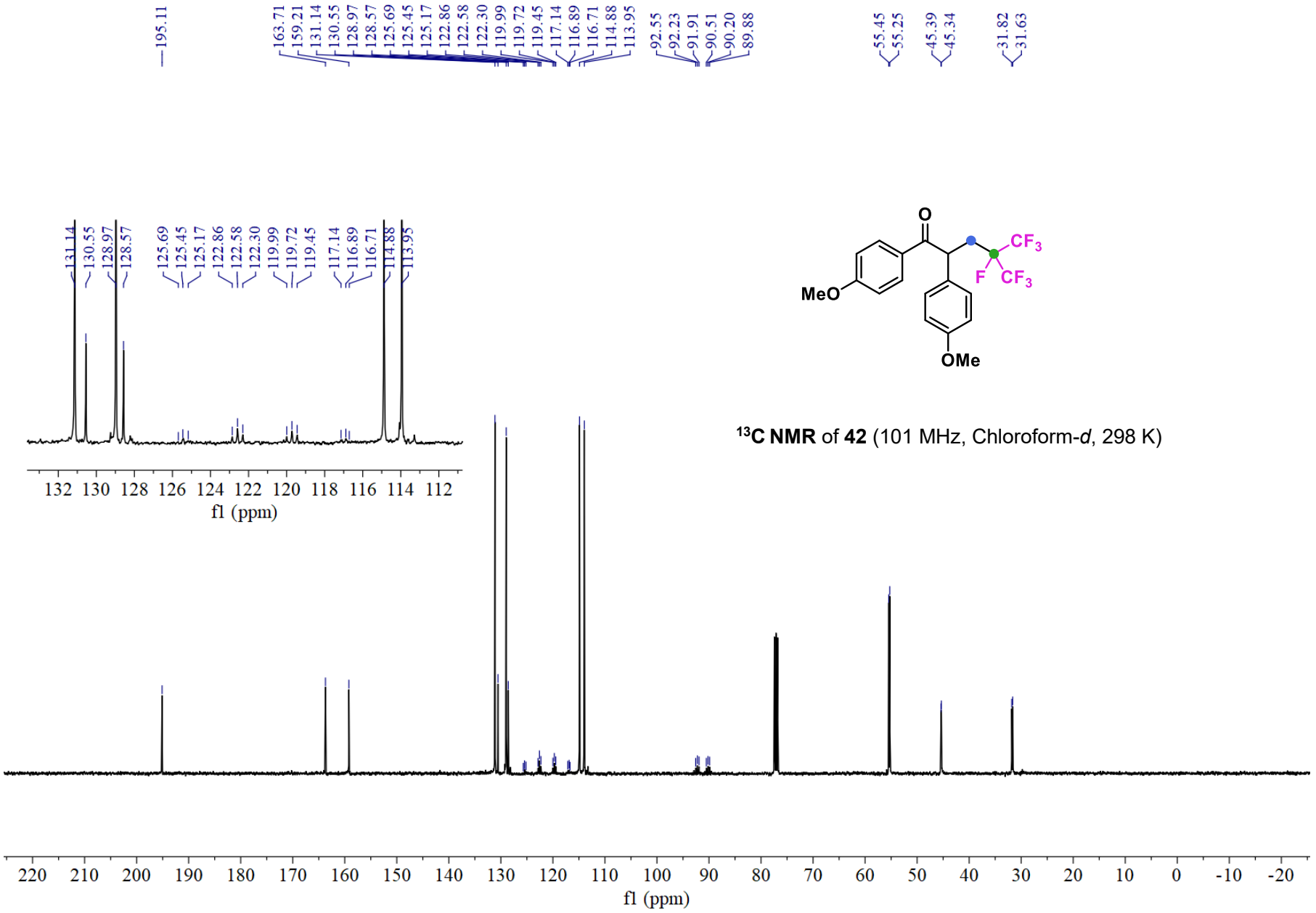
^{13}C NMR of **41** (101 MHz, Chloroform-*d*, 298 K)



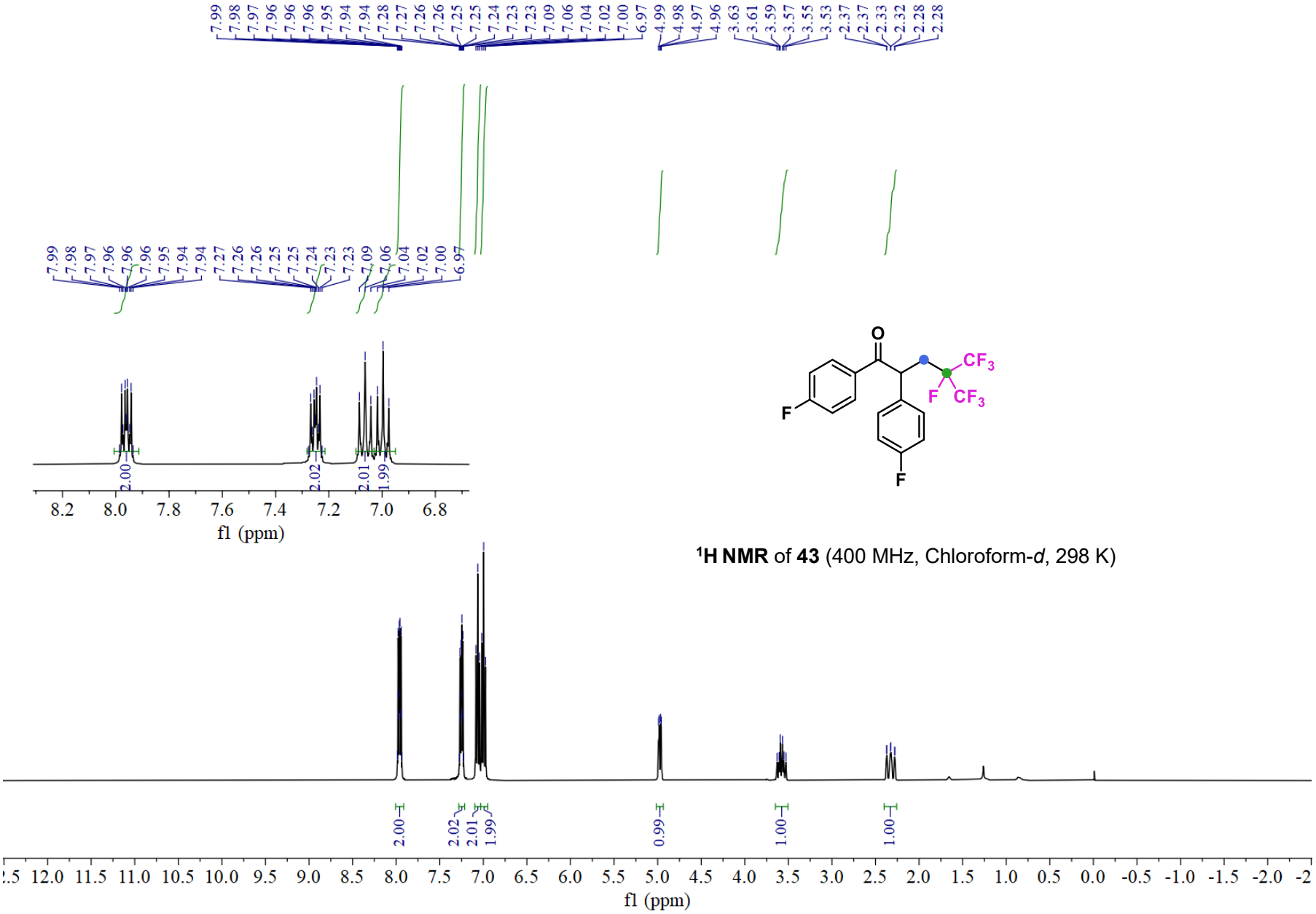
^{1}H NMR of **42** (400 MHz, Chloroform-*d*, 298 K)



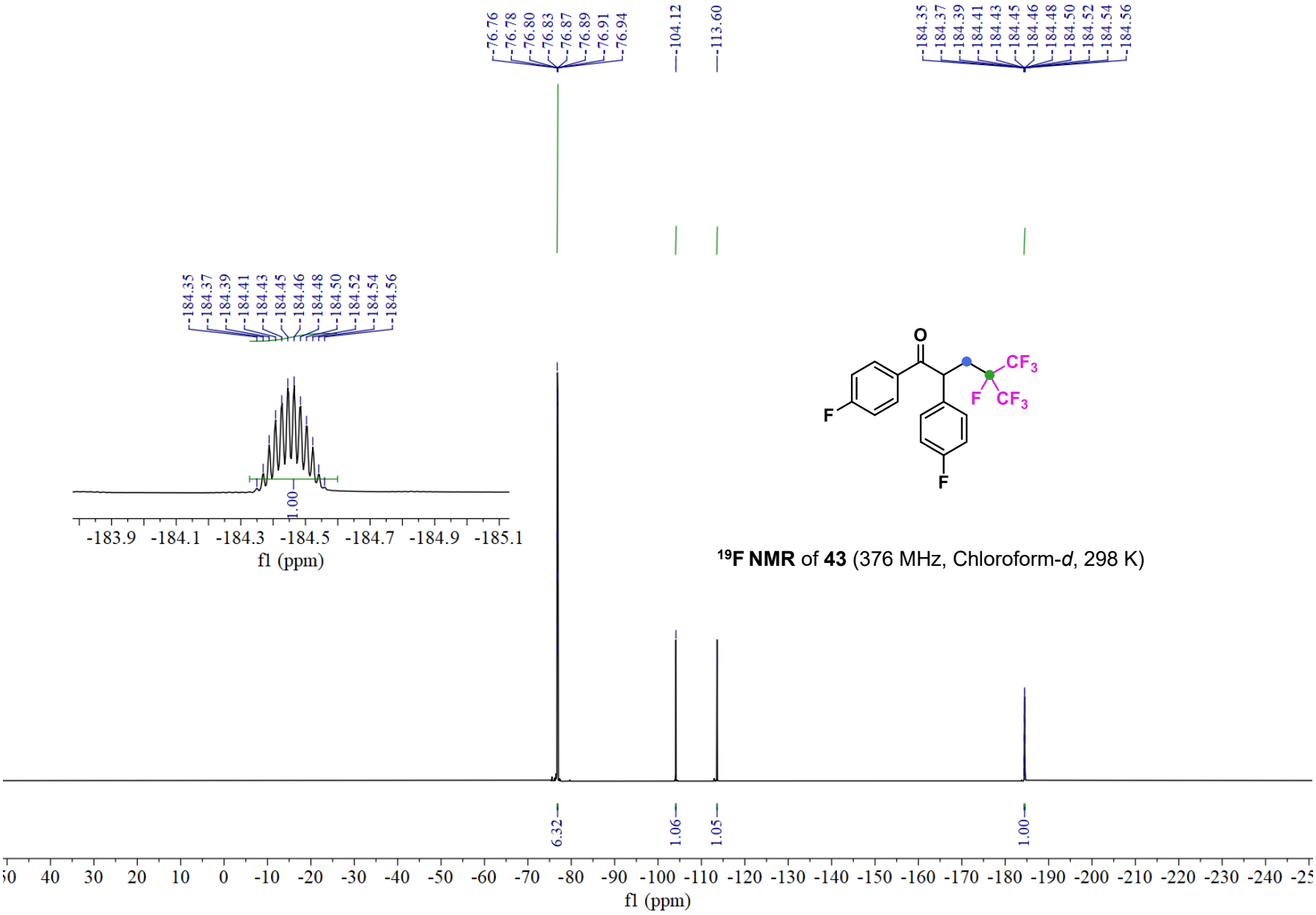
^{19}F NMR of **42** (376 MHz, Chloroform-*d*, 298 K)



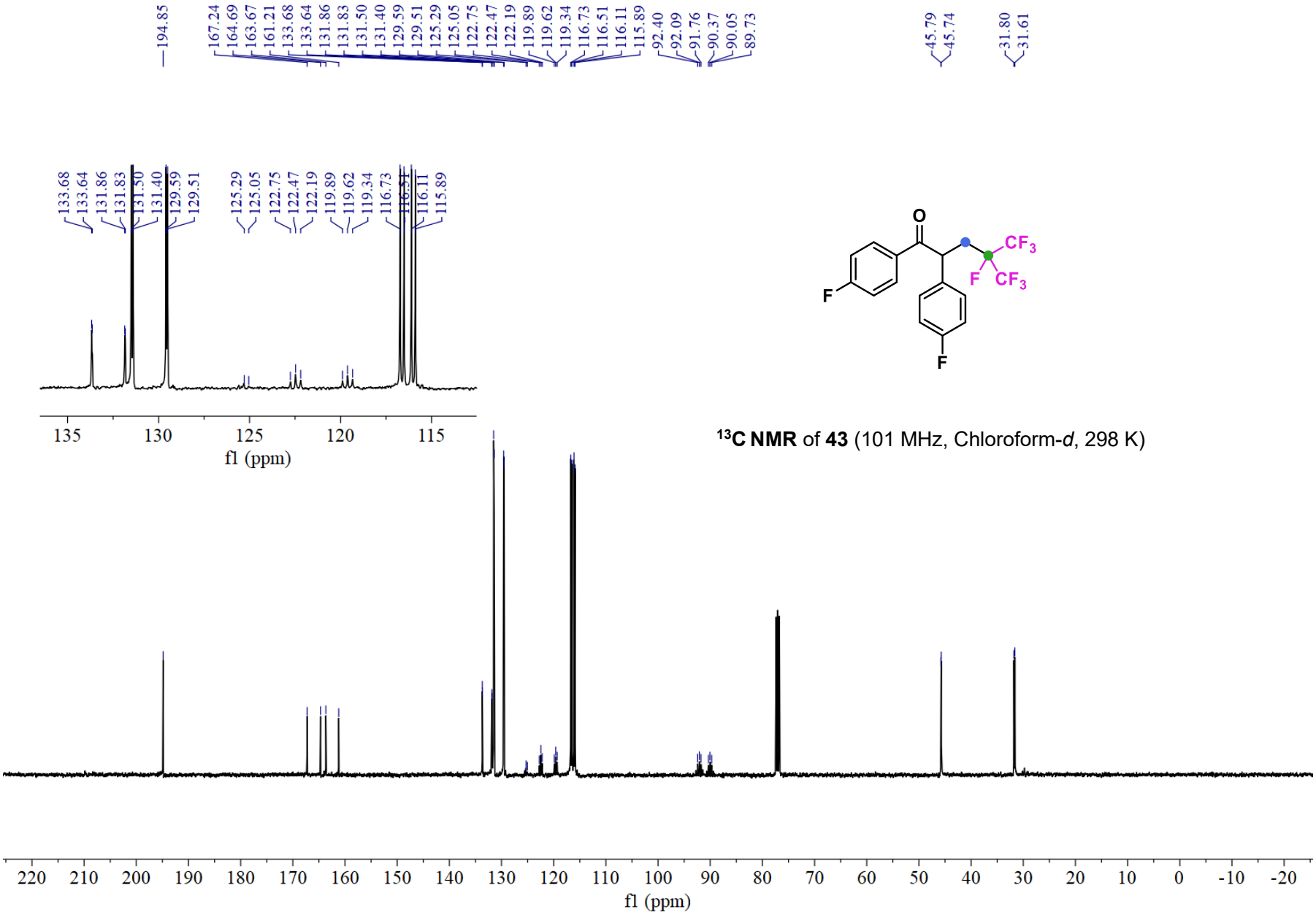
^{13}C NMR of **42** (101 MHz, Chloroform-*d*, 298 K)



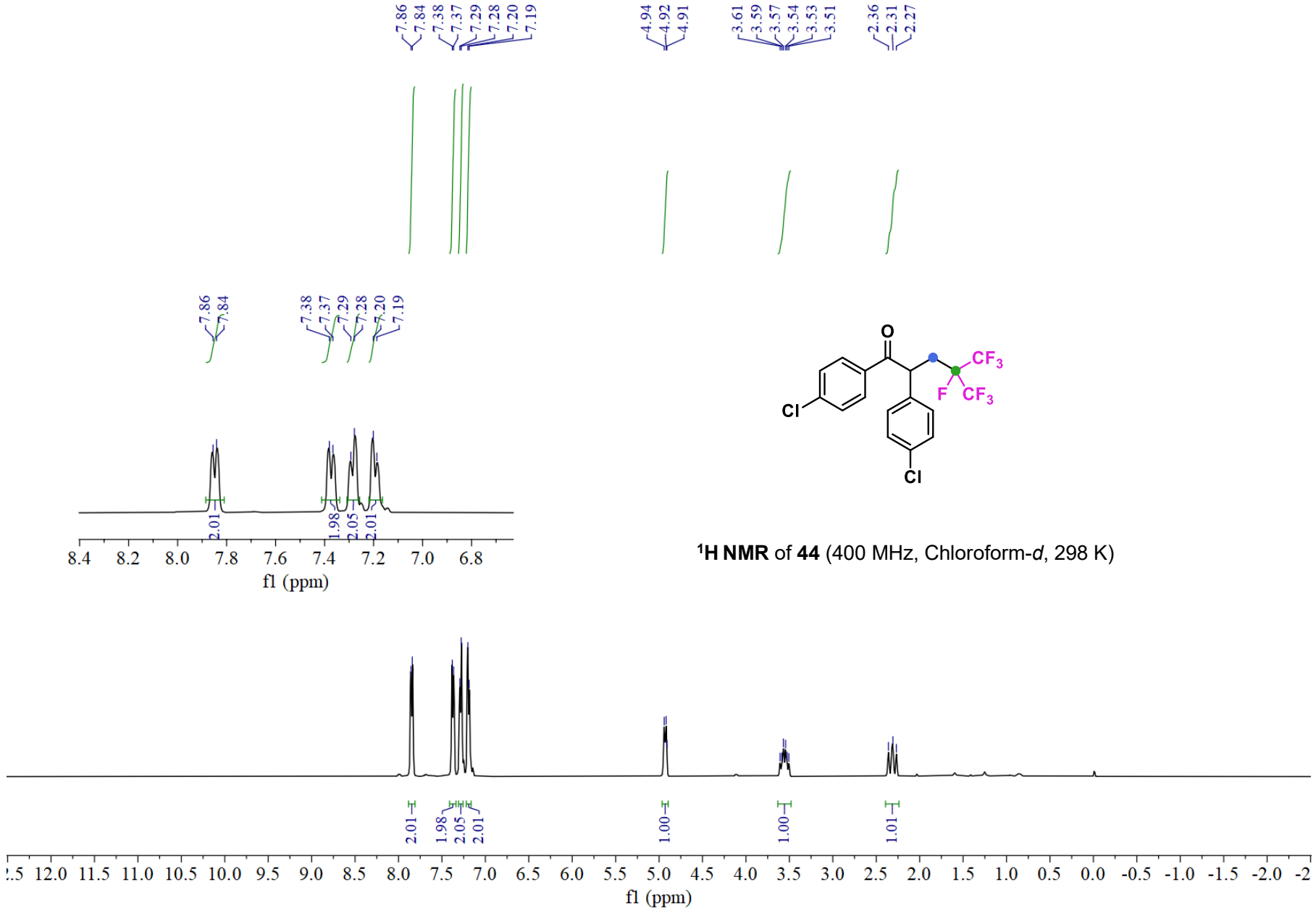
^{1}H NMR of **43** (400 MHz, Chloroform-*d*, 298 K)



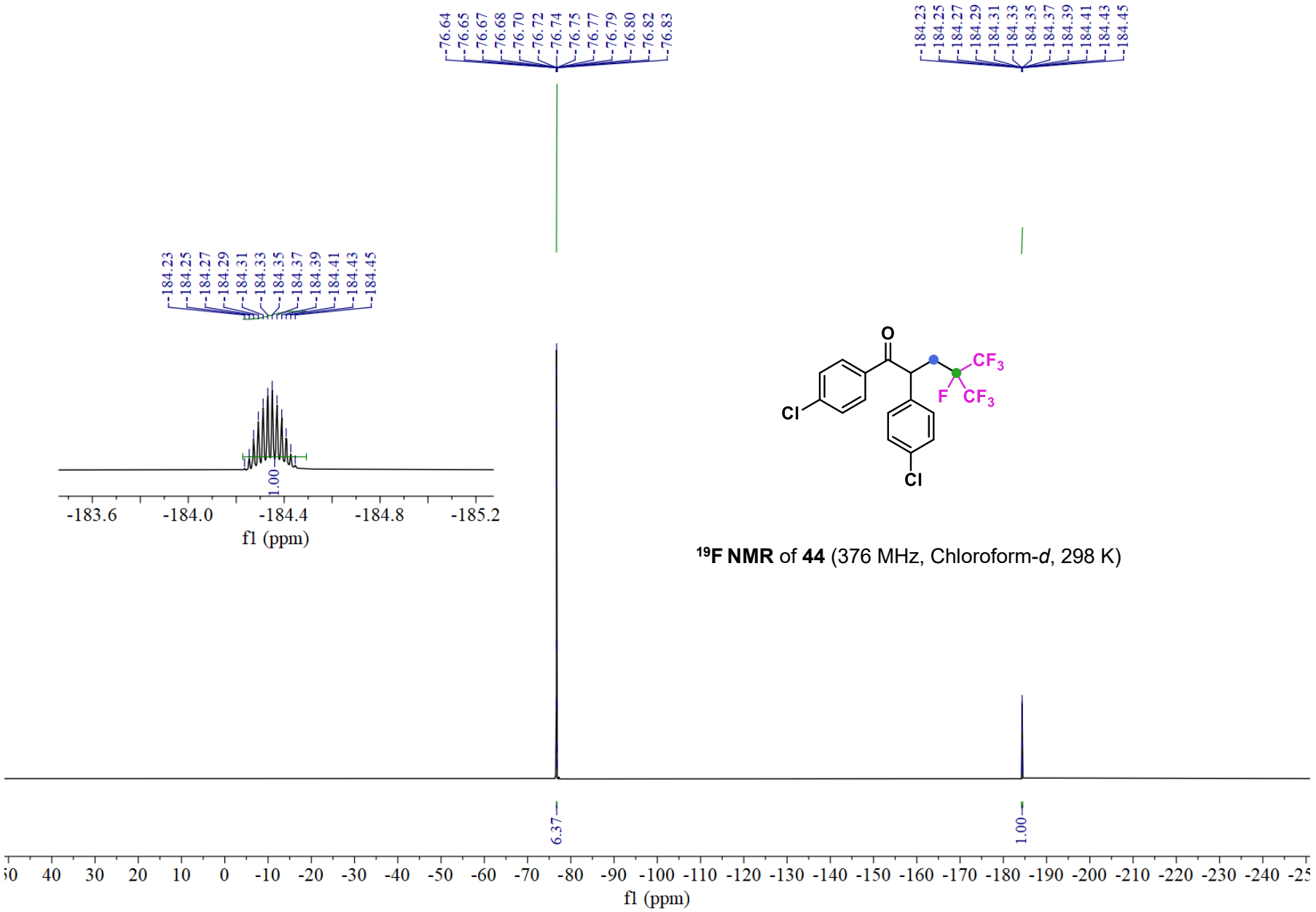
^{19}F NMR of **43** (376 MHz, Chloroform-*d*, 298 K)



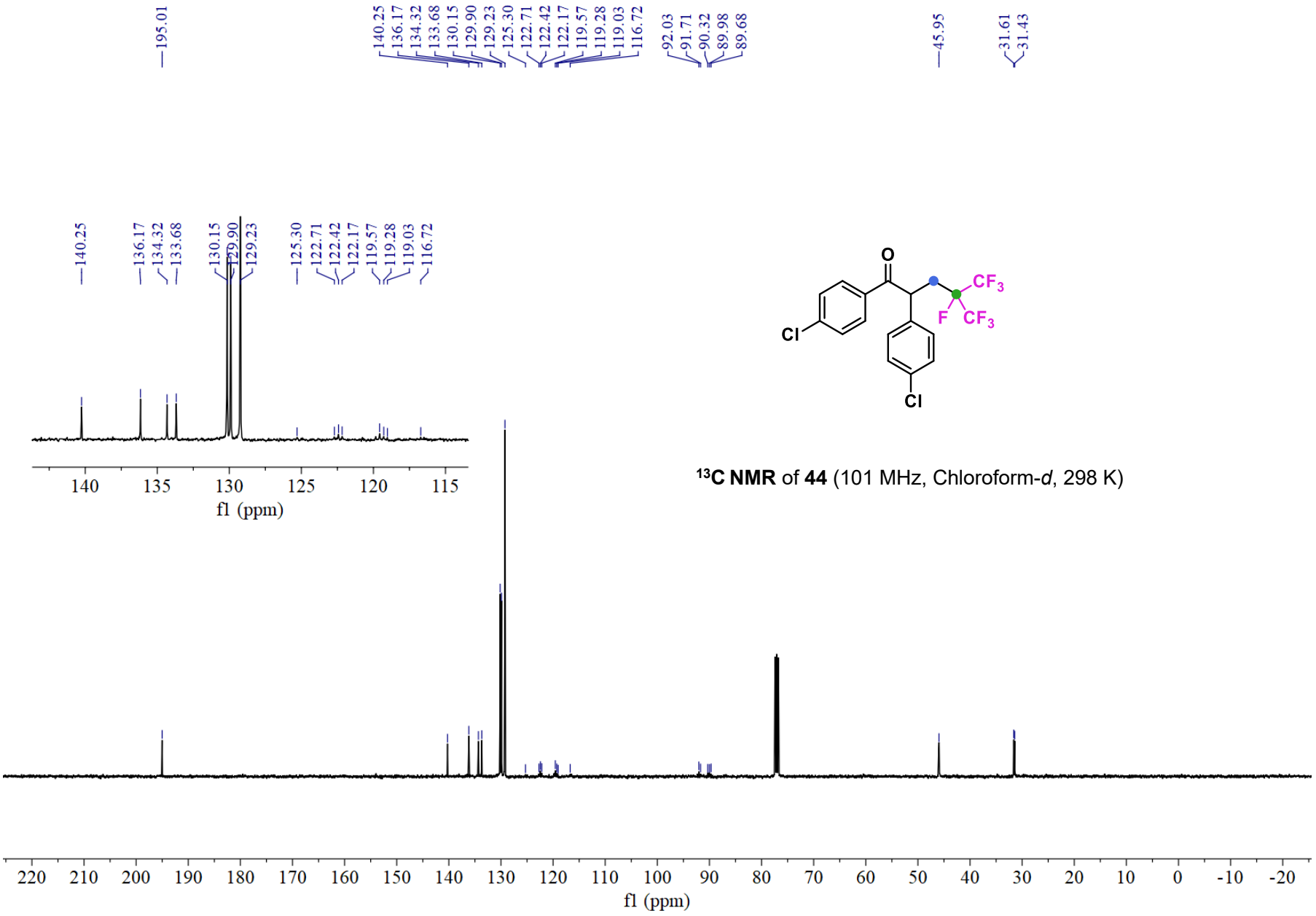
^{13}C NMR of **43** (101 MHz, Chloroform-*d*, 298 K)



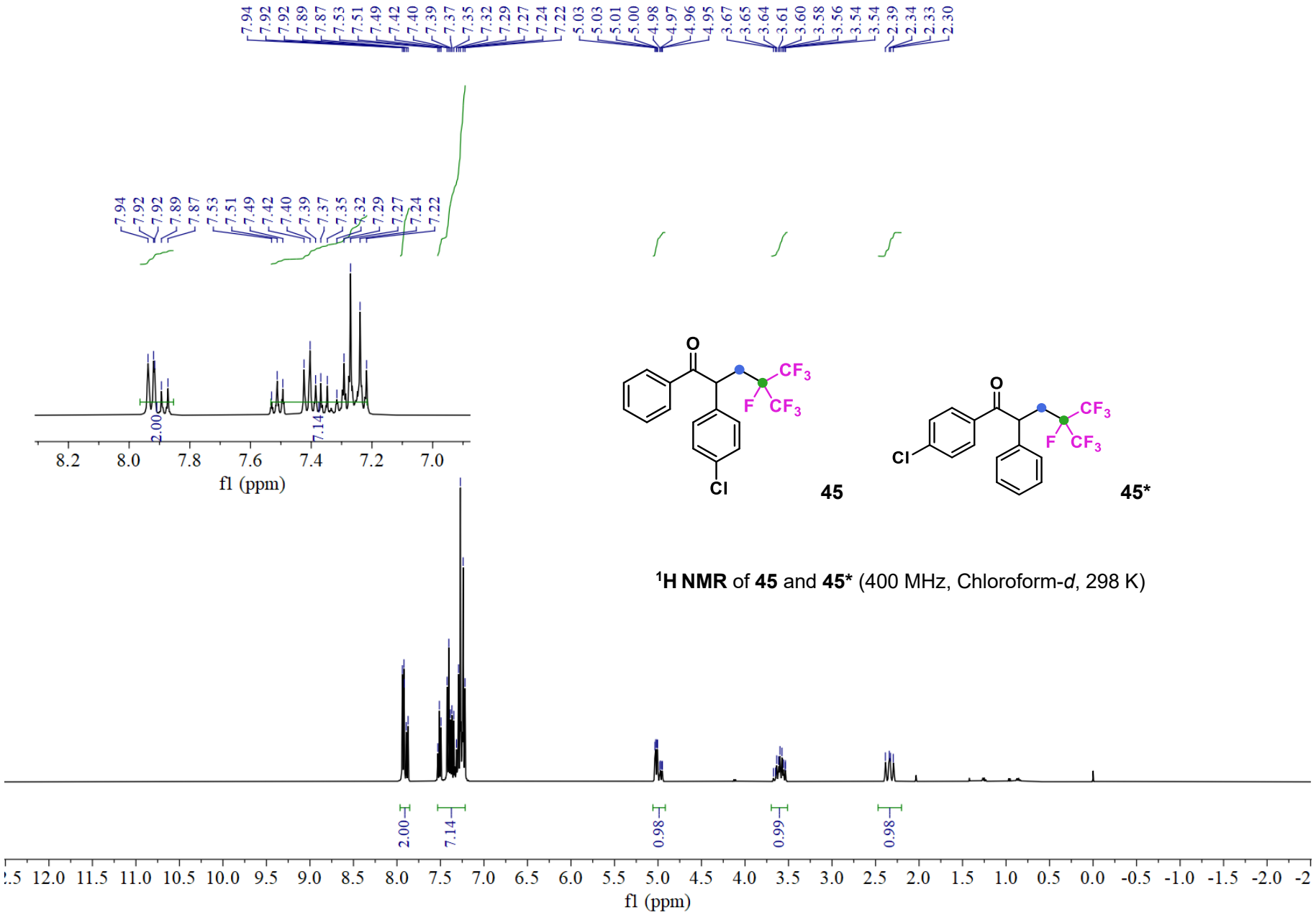
^{1}H NMR of **44** (400 MHz, Chloroform-*d*, 298 K)



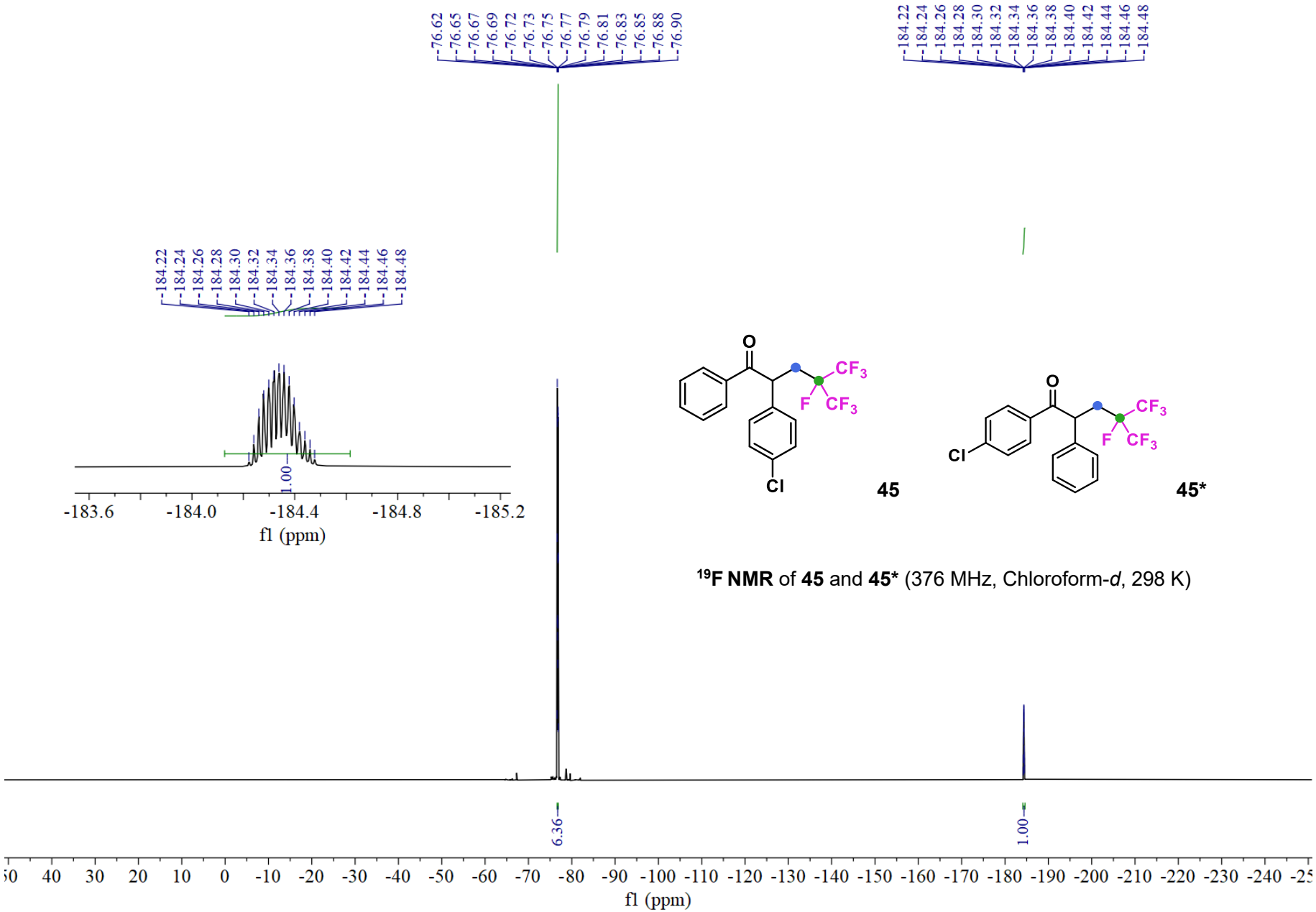
^{19}F NMR of **44** (376 MHz, Chloroform-*d*, 298 K)



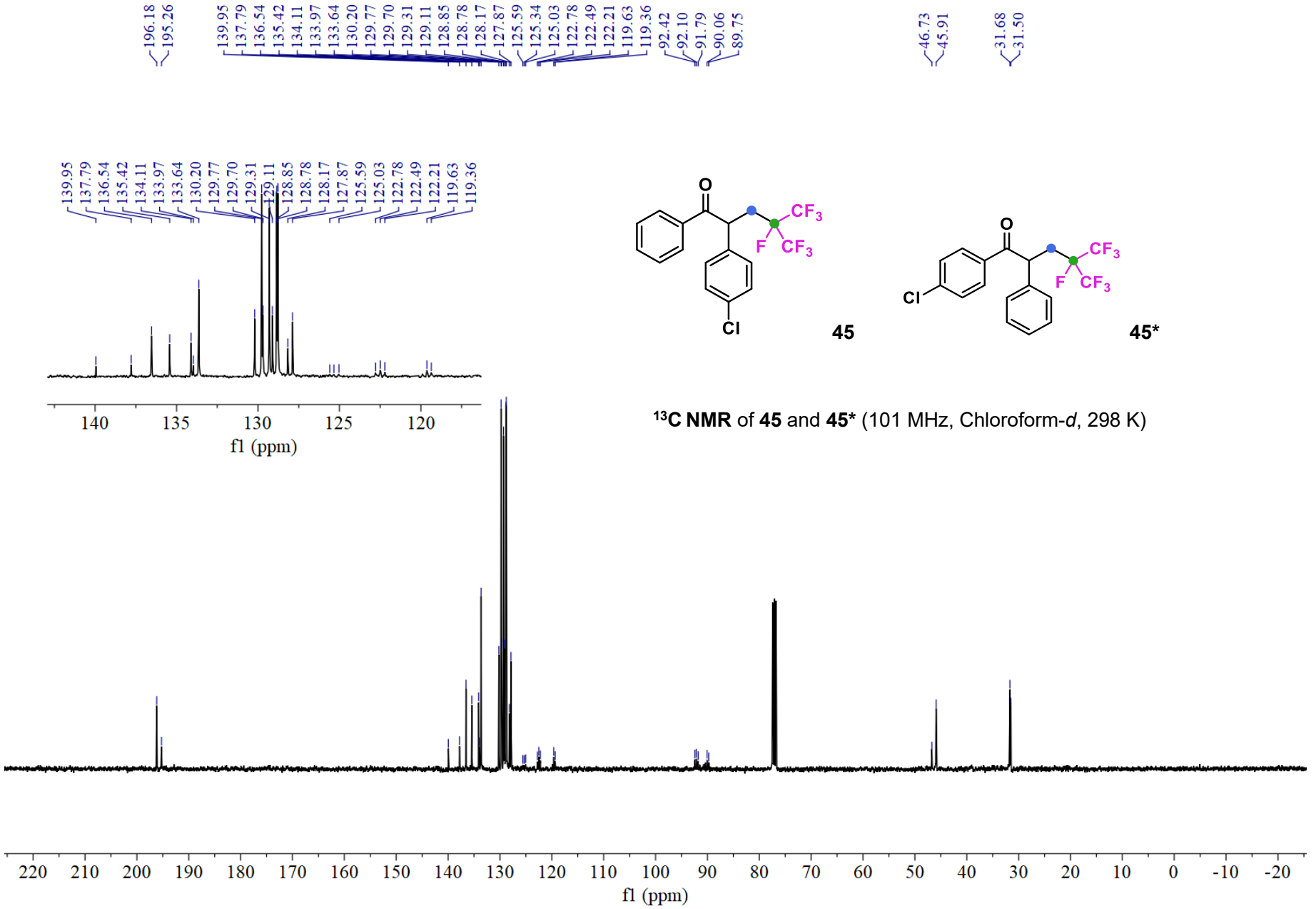
^{13}C NMR of **44** (101 MHz, Chloroform-*d*, 298 K)



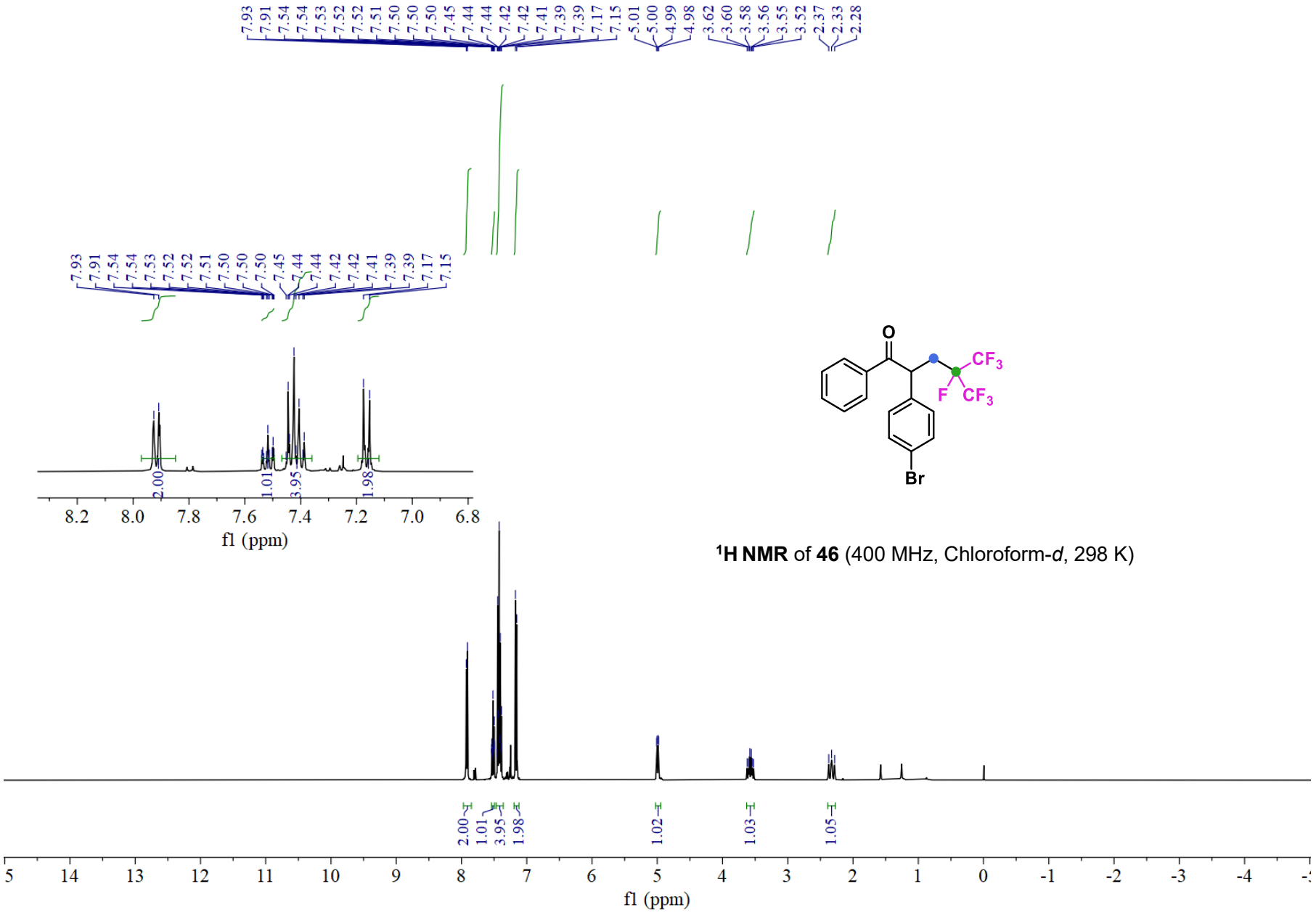
^{1}H NMR of **45** and **45*** (400 MHz, Chloroform-*d*, 298 K)



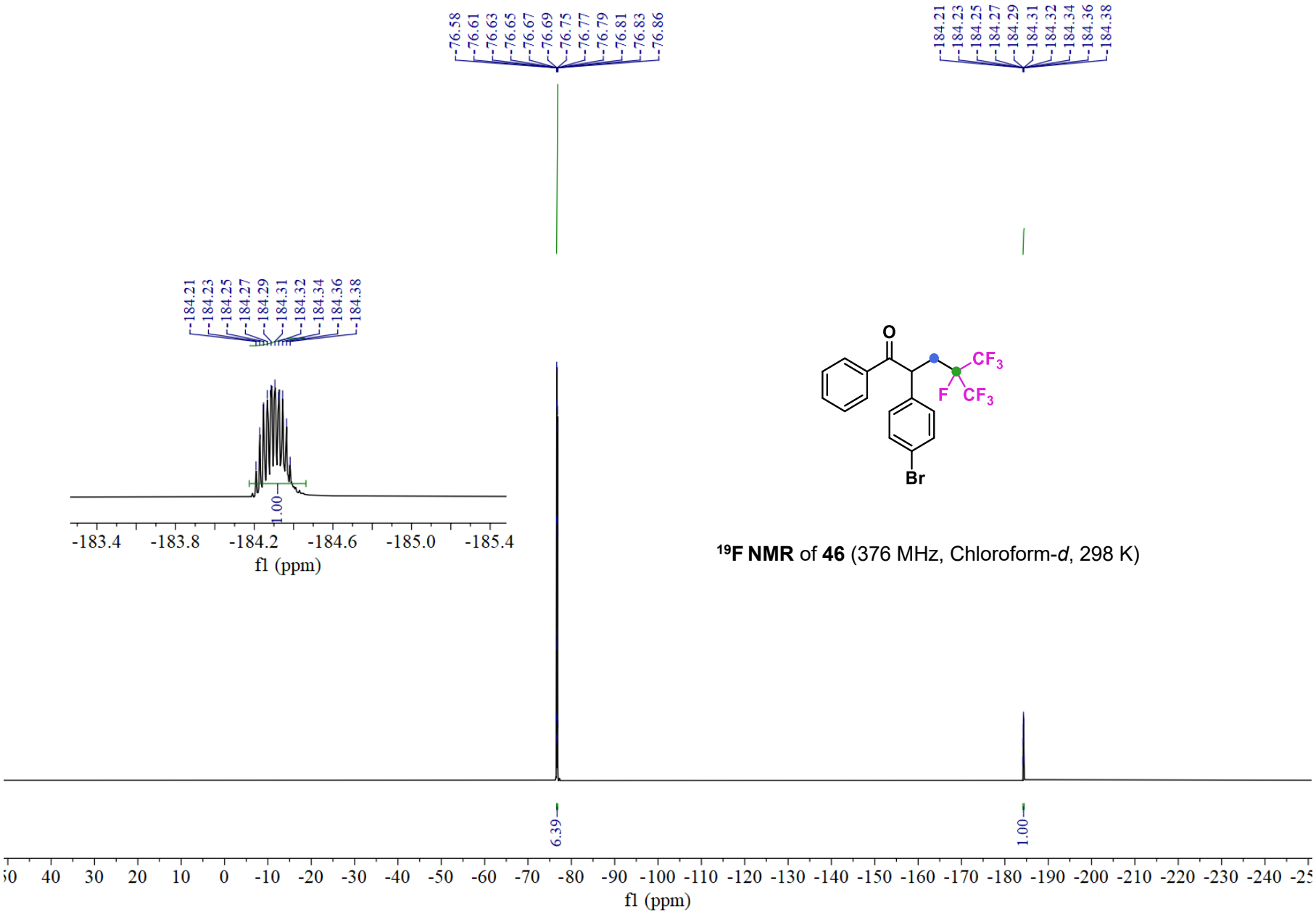
^{19}F NMR of **45** and **45*** (376 MHz, Chloroform-*d*, 298 K)



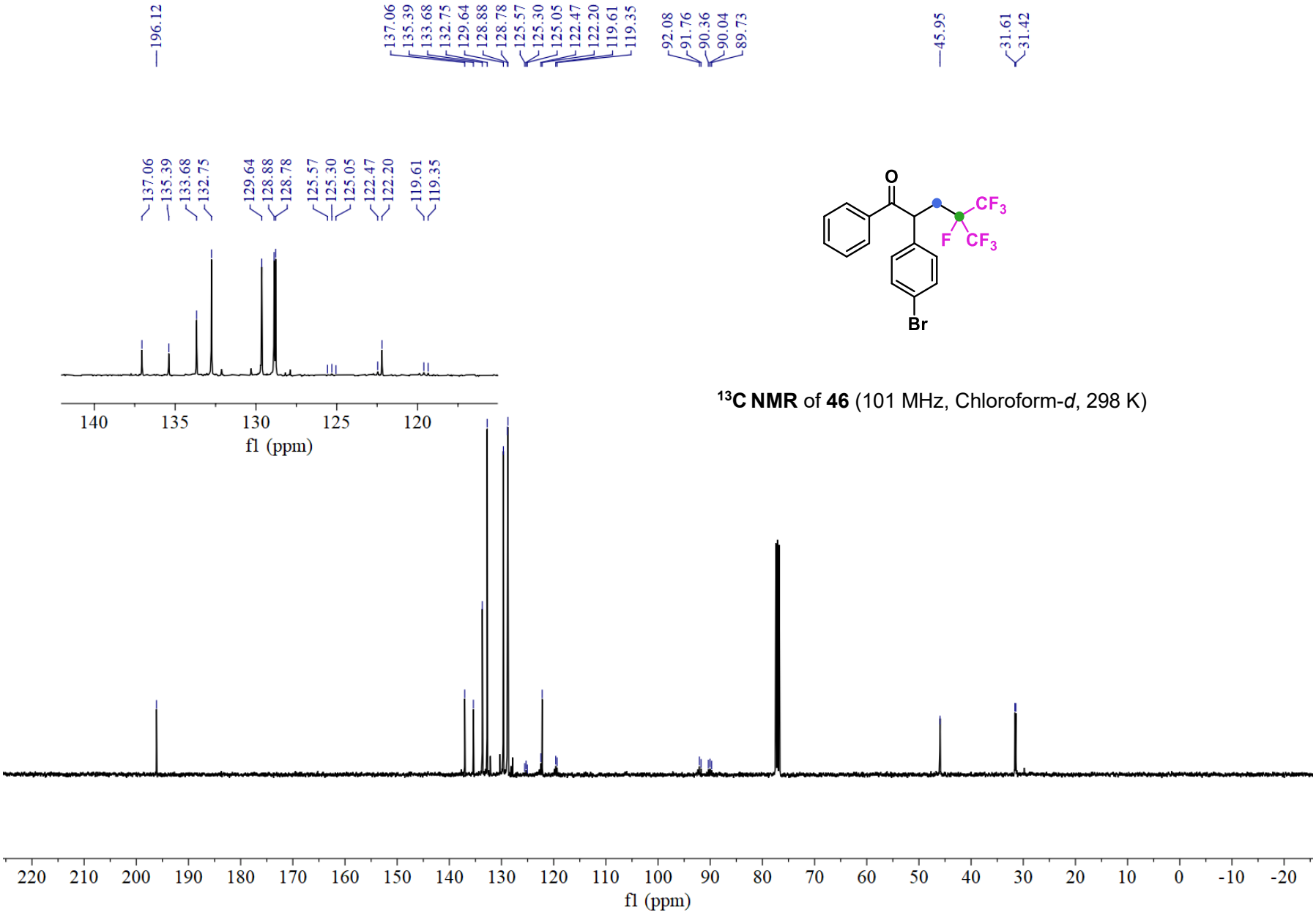
^{13}C NMR of **45** and **45*** (101 MHz, Chloroform-*d*, 298 K)



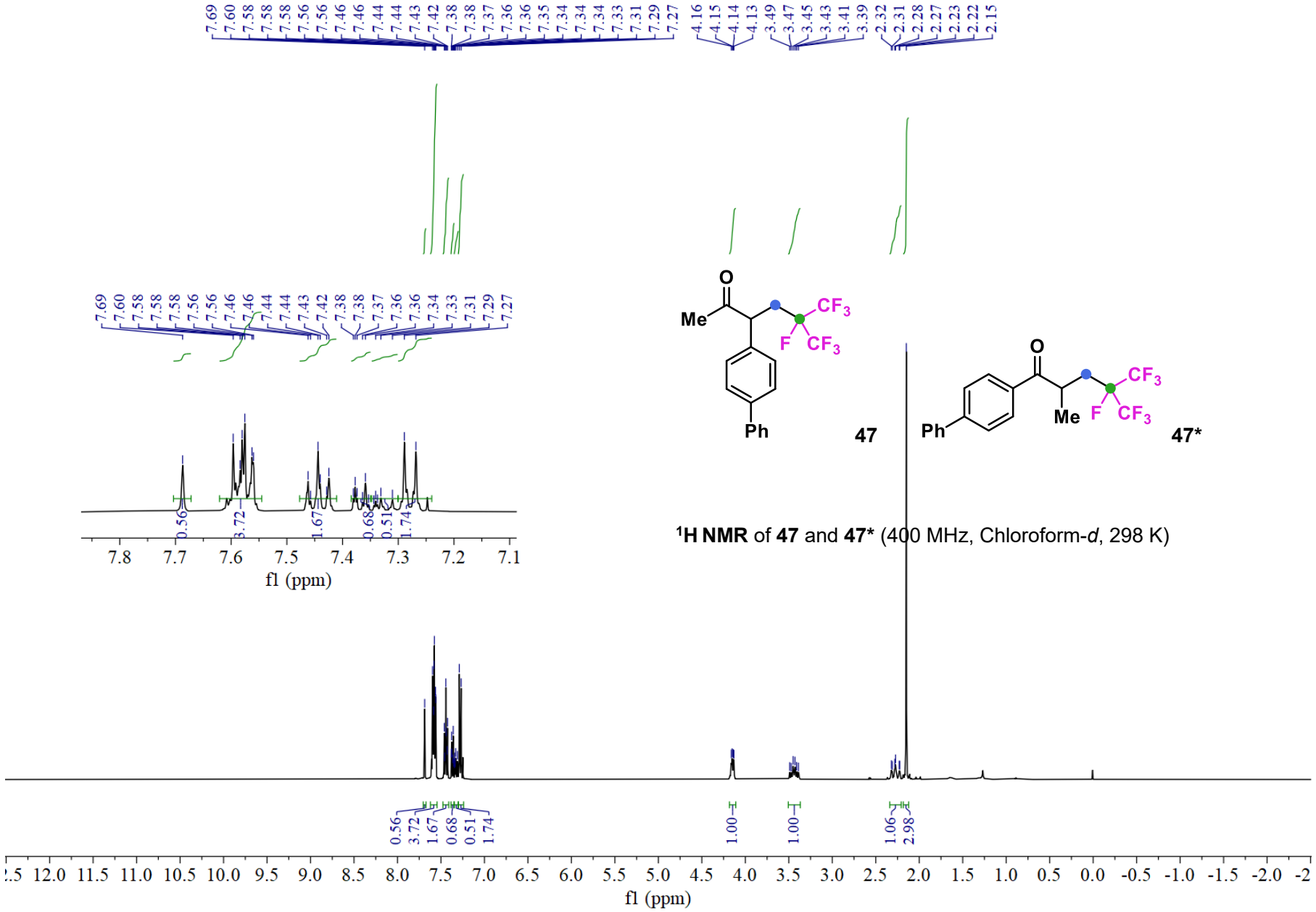
^{1}H NMR of **46** (400 MHz, Chloroform-*d*, 298 K)



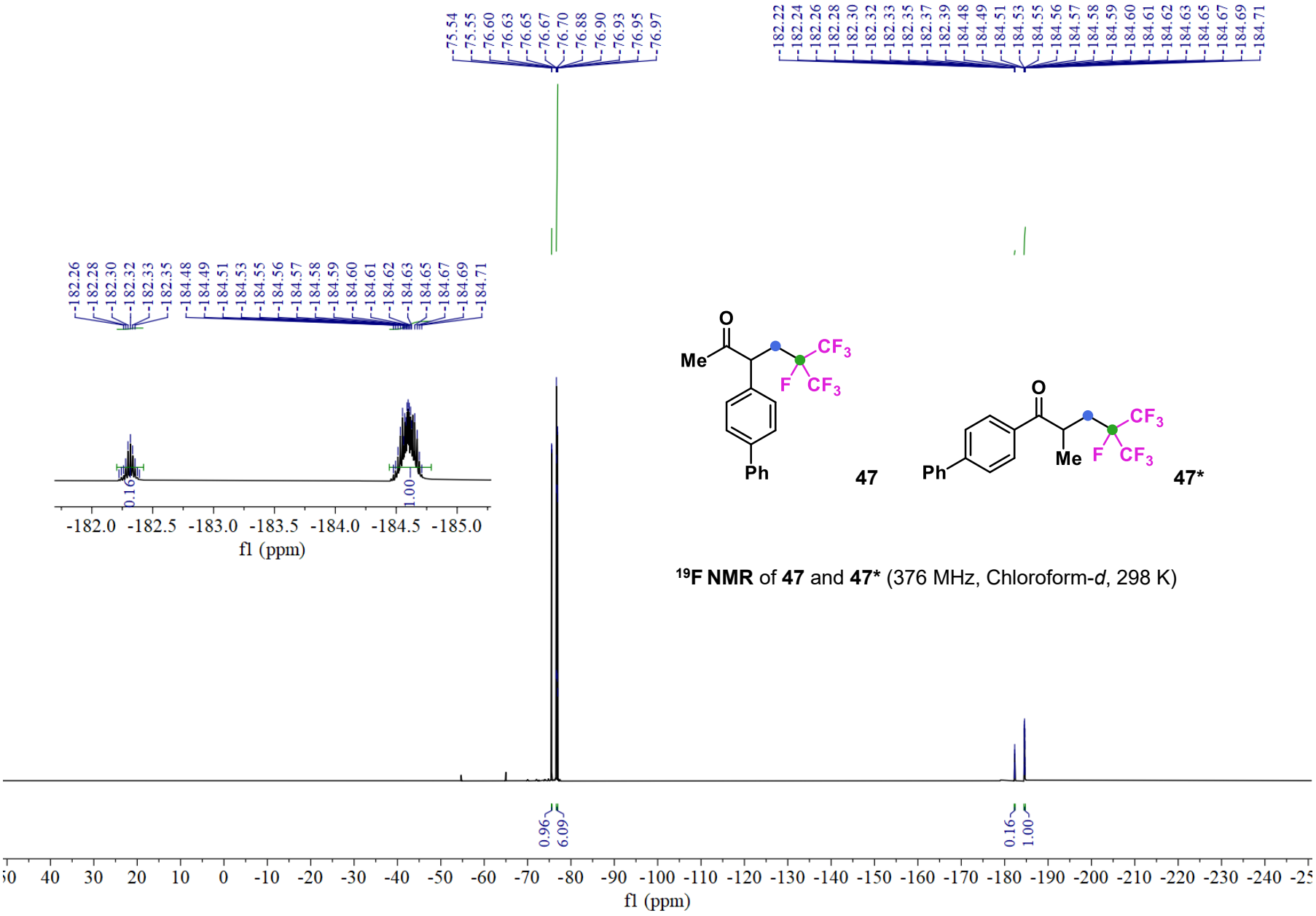
^{19}F NMR of **46** (376 MHz, Chloroform-*d*, 298 K)



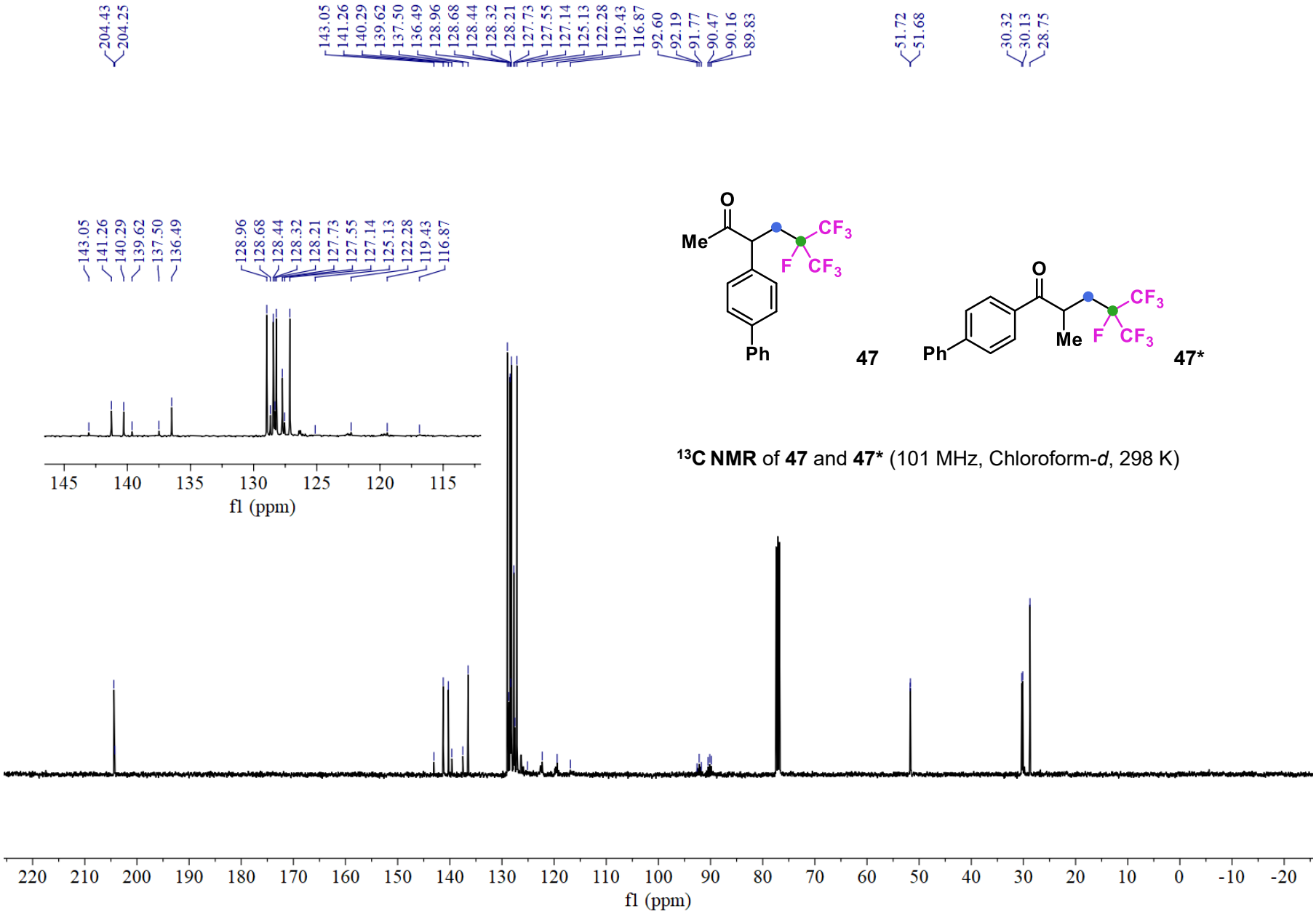
^{13}C NMR of **46** (101 MHz, Chloroform-*d*, 298 K)



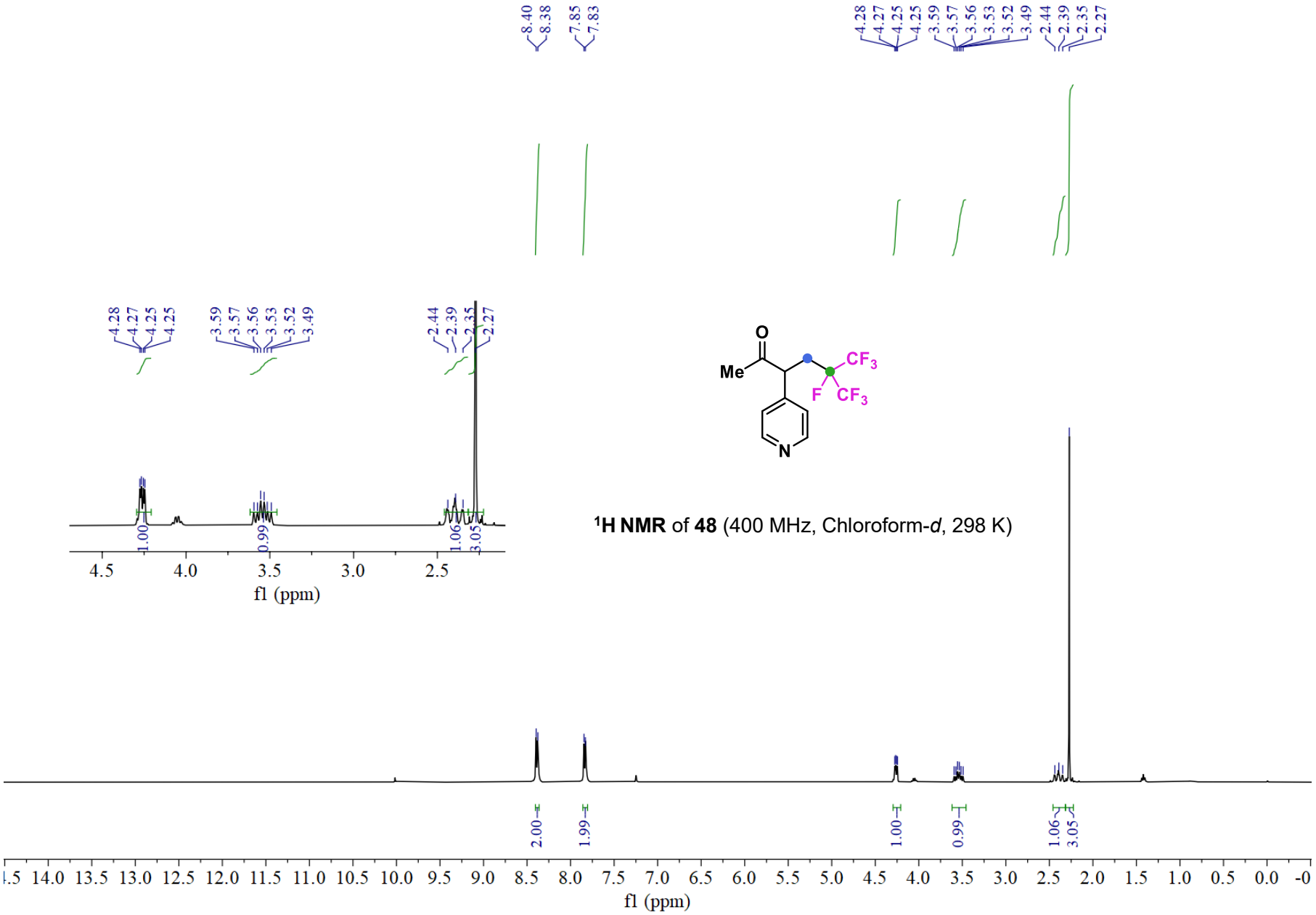
^{1}H NMR of **47** and **47*** (400 MHz, Chloroform-*d*, 298 K)



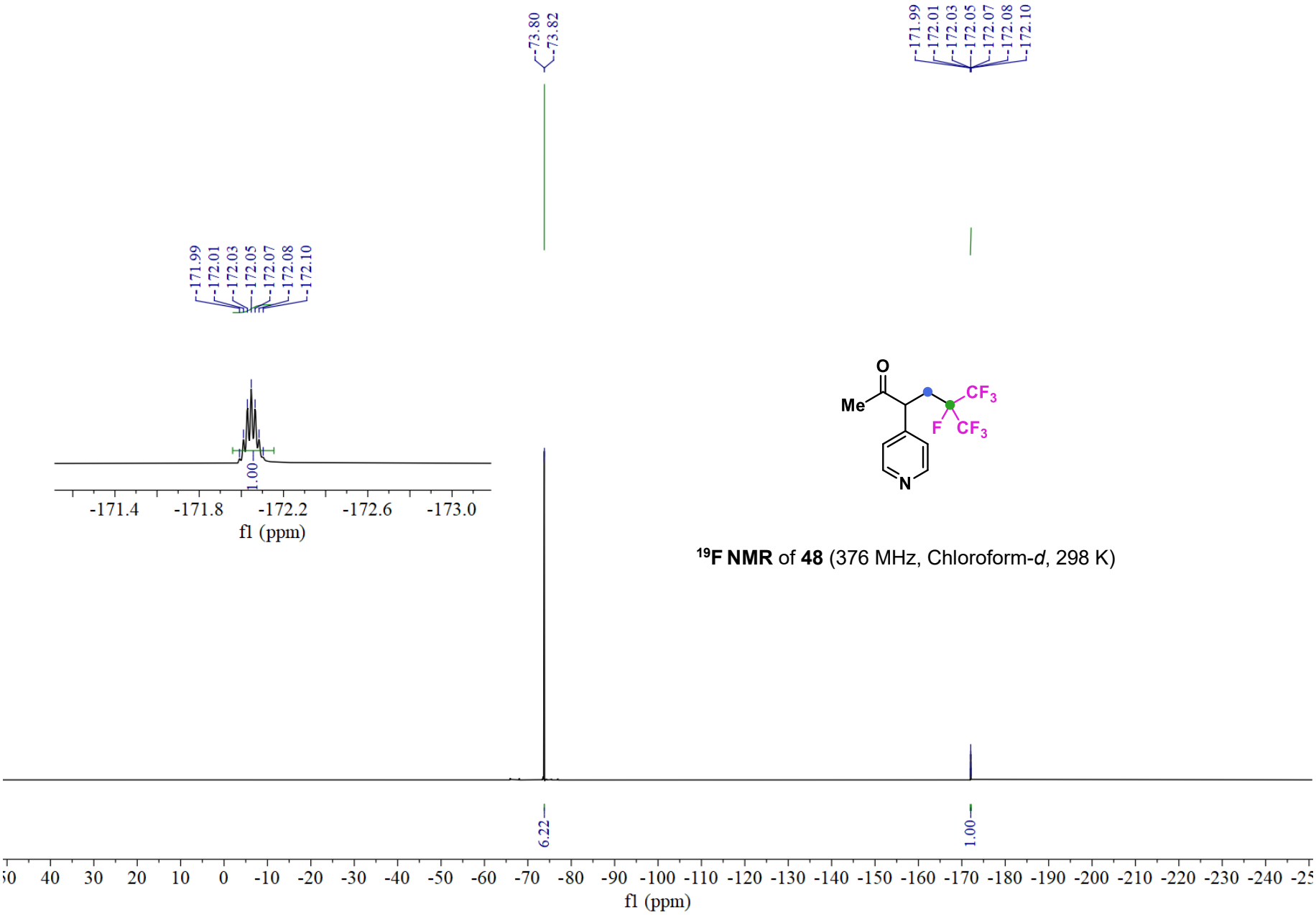
^{19}F NMR of **47** and **47*** (376 MHz, Chloroform-*d*, 298 K)



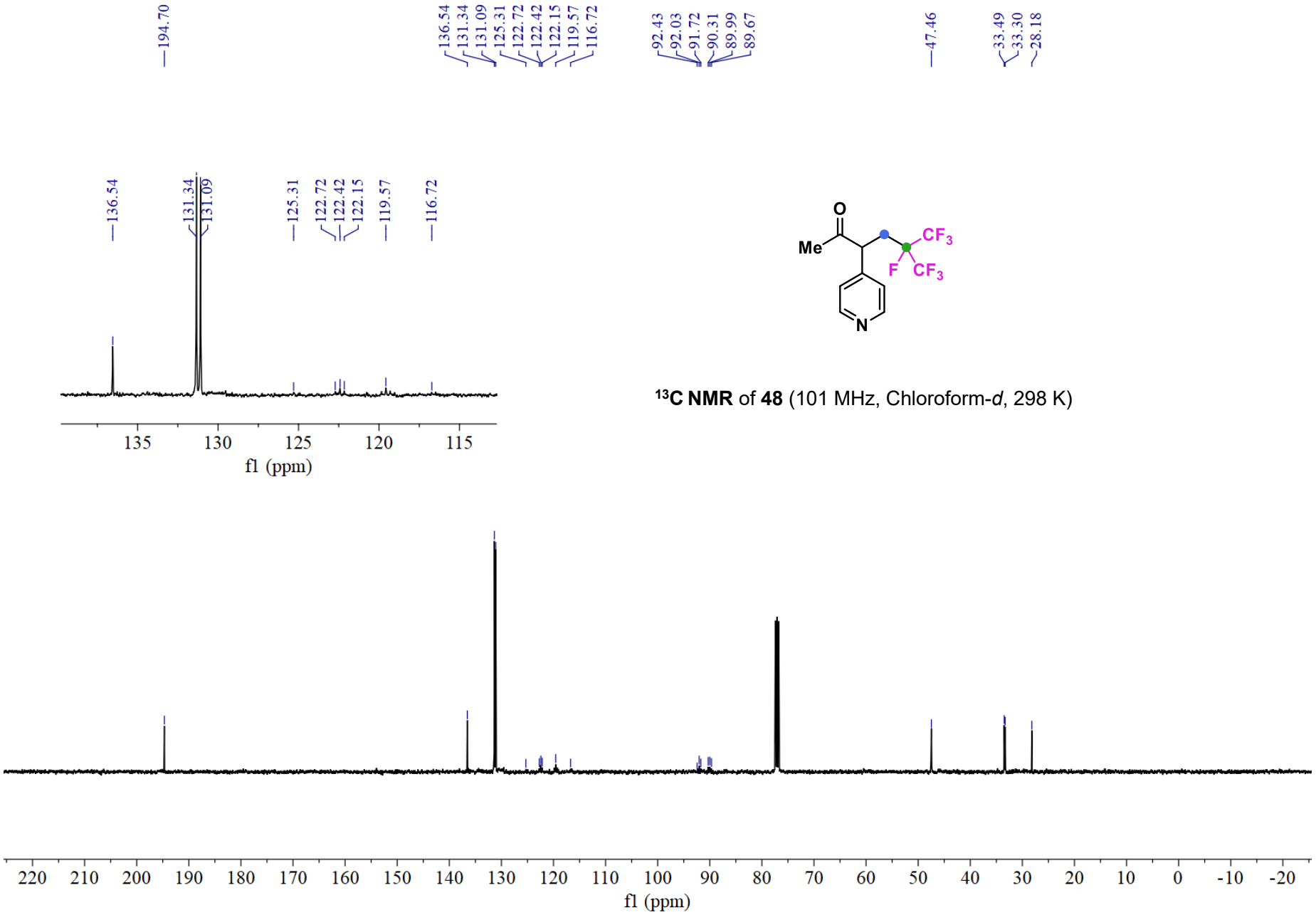
^{13}C NMR of **47** and **47*** (101 MHz, Chloroform-*d*, 298 K)



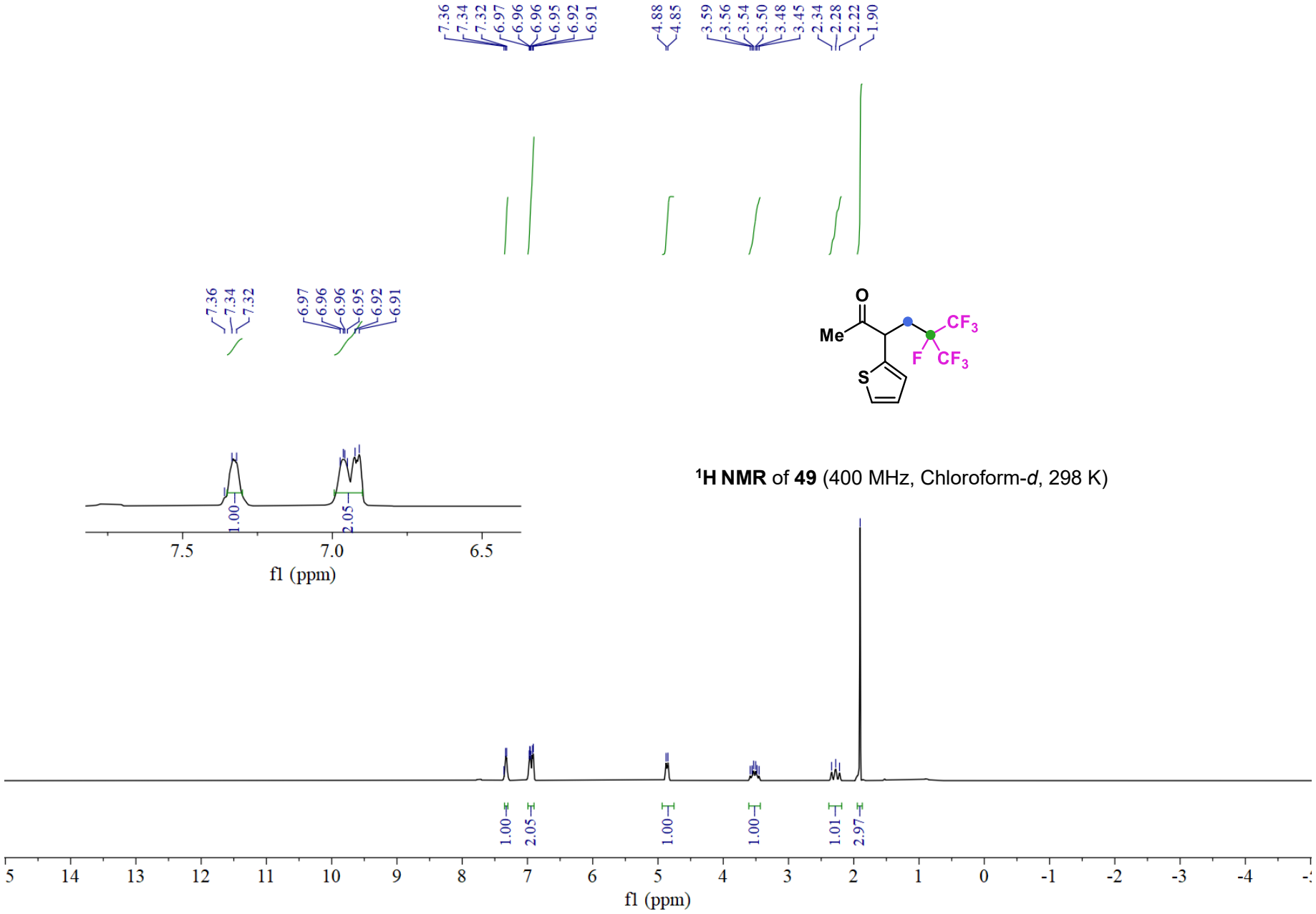
^{1}H NMR of **48** (400 MHz, Chloroform-*d*, 298 K)



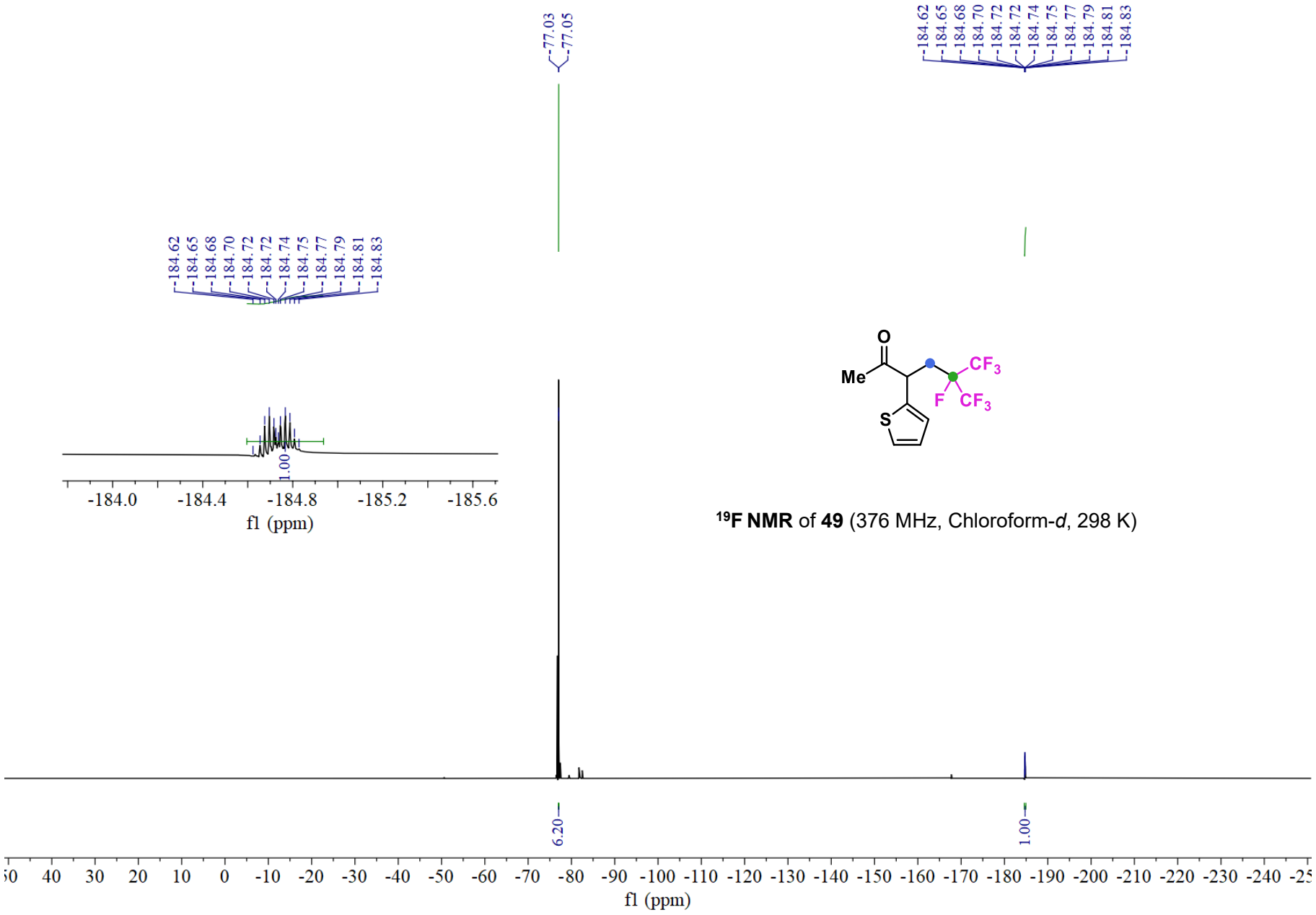
^{19}F NMR of **48** (376 MHz, Chloroform-*d*, 298 K)



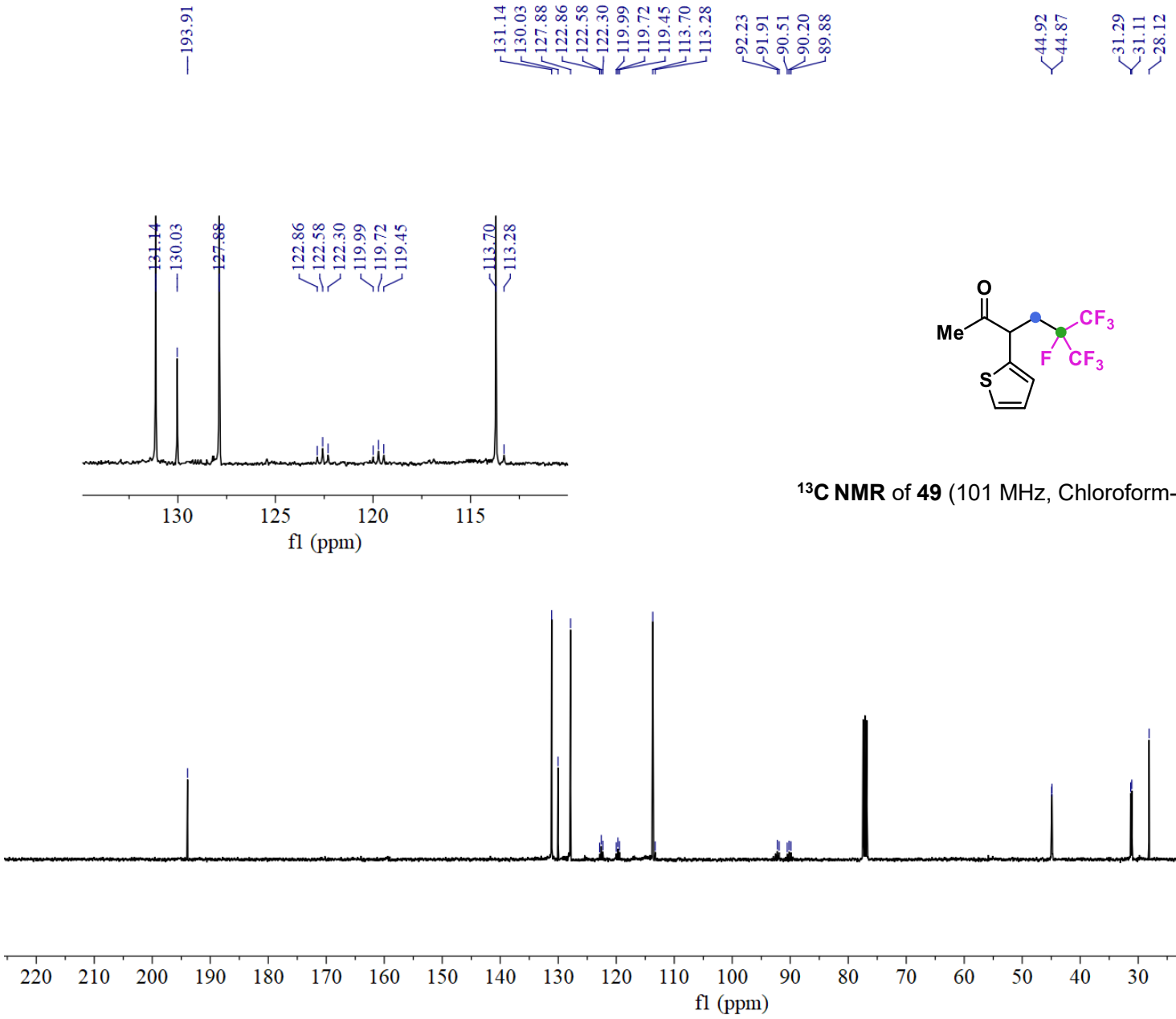
^{13}C NMR of **48** (101 MHz, Chloroform-*d*, 298 K)



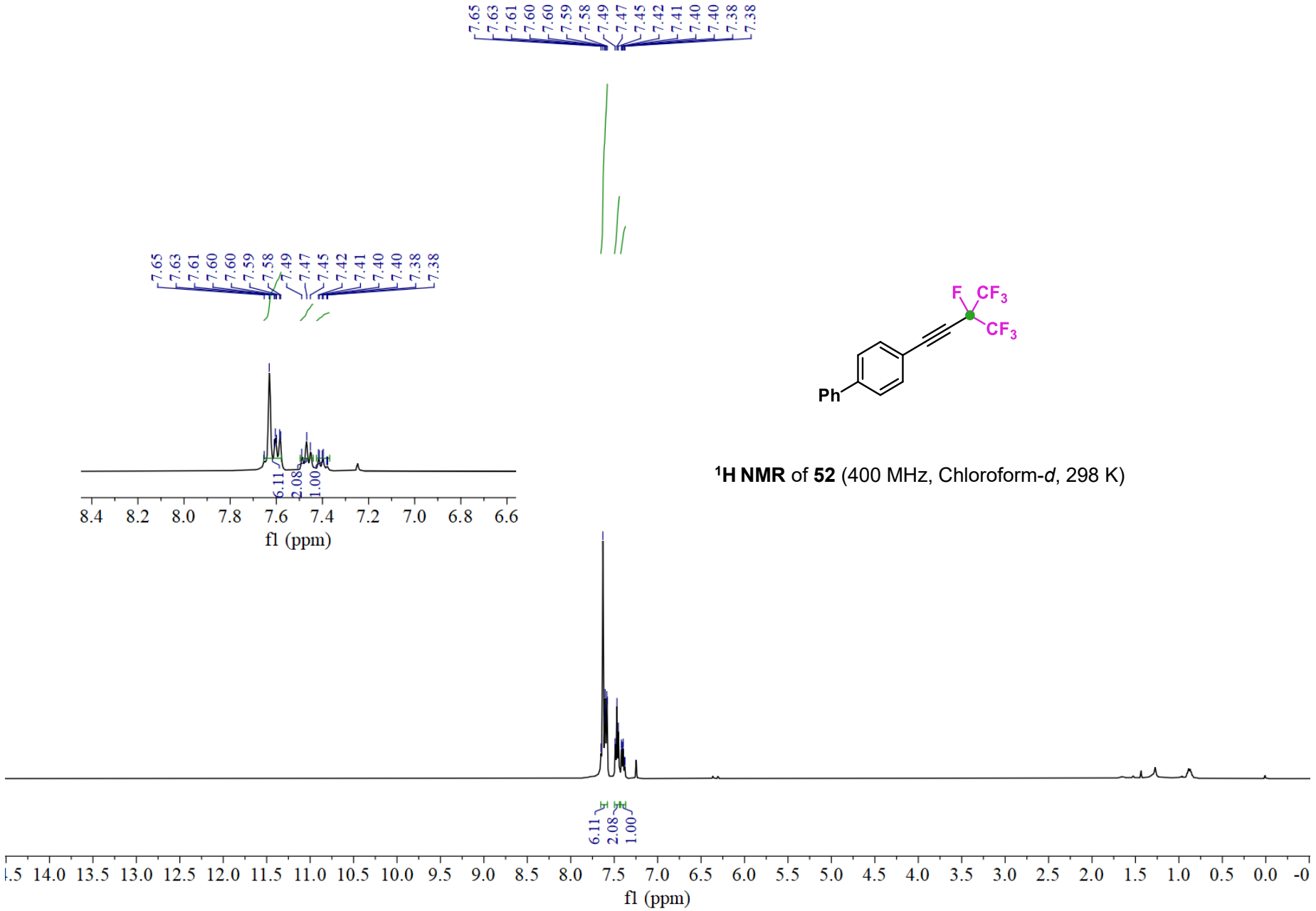
^{1}H NMR of **49** (400 MHz, Chloroform-*d*, 298 K)



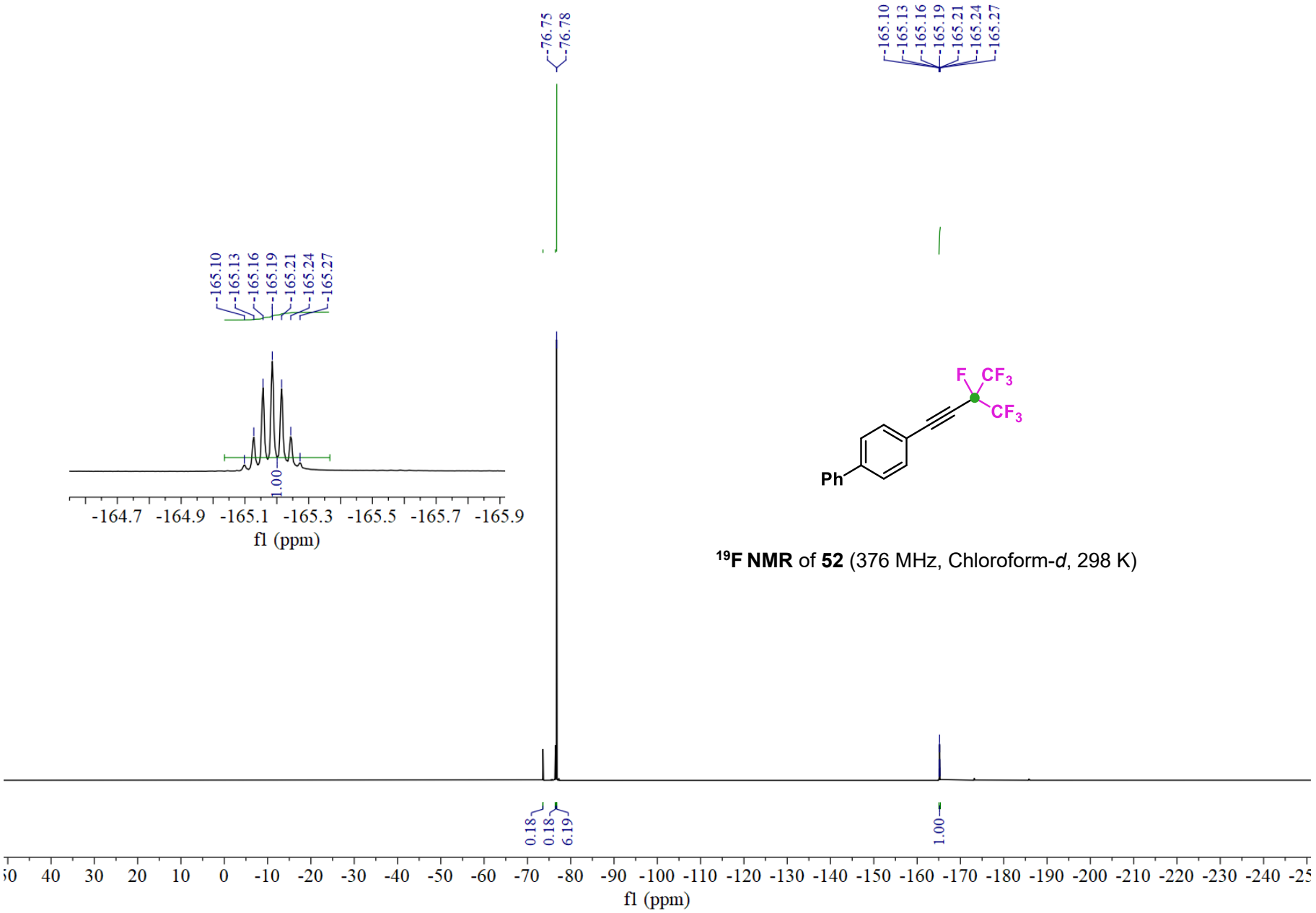
^{19}F NMR of **49** (376 MHz, Chloroform-*d*, 298 K)



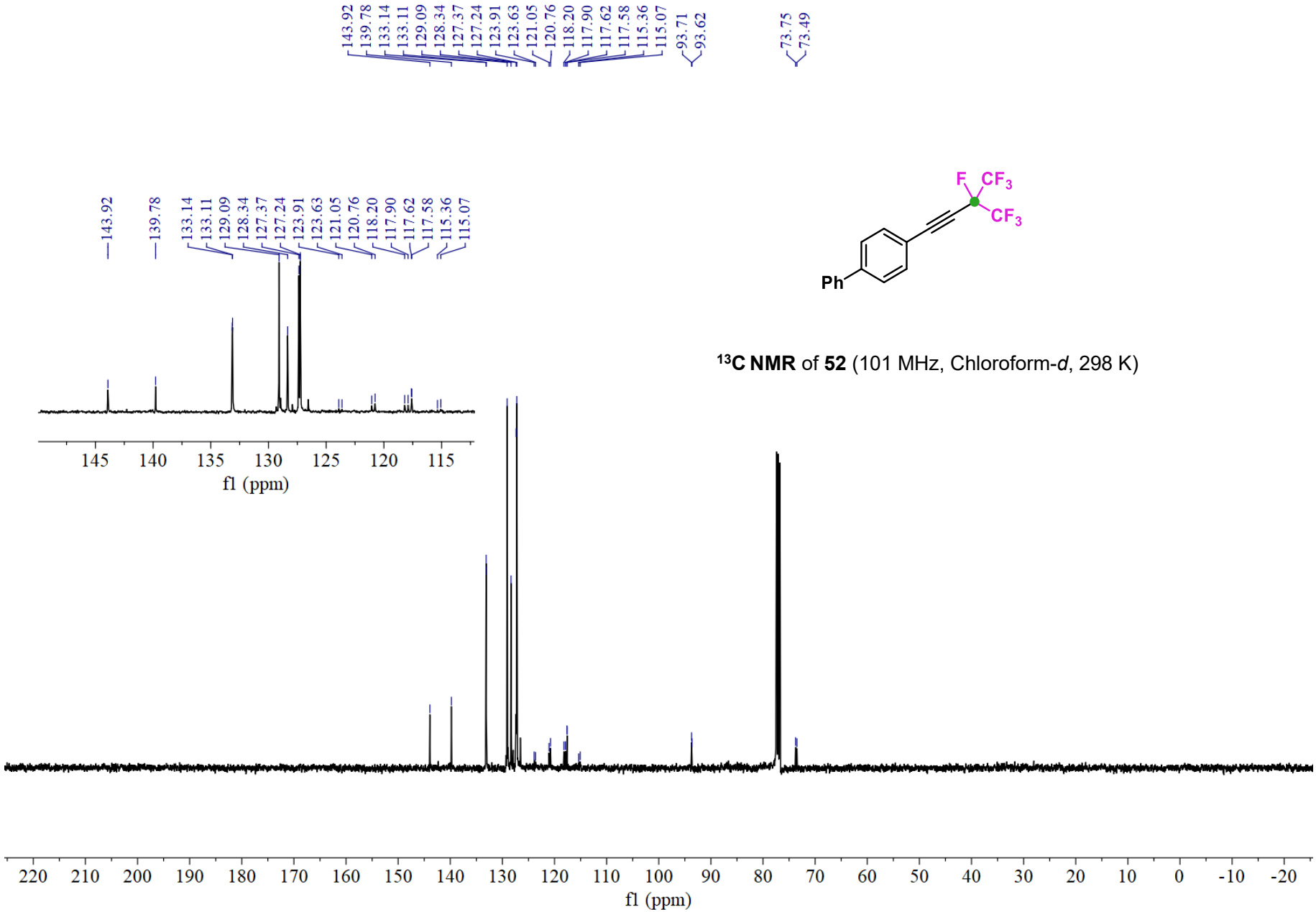
^{13}C NMR of **49** (101 MHz, Chloroform-*d*, 298 K)



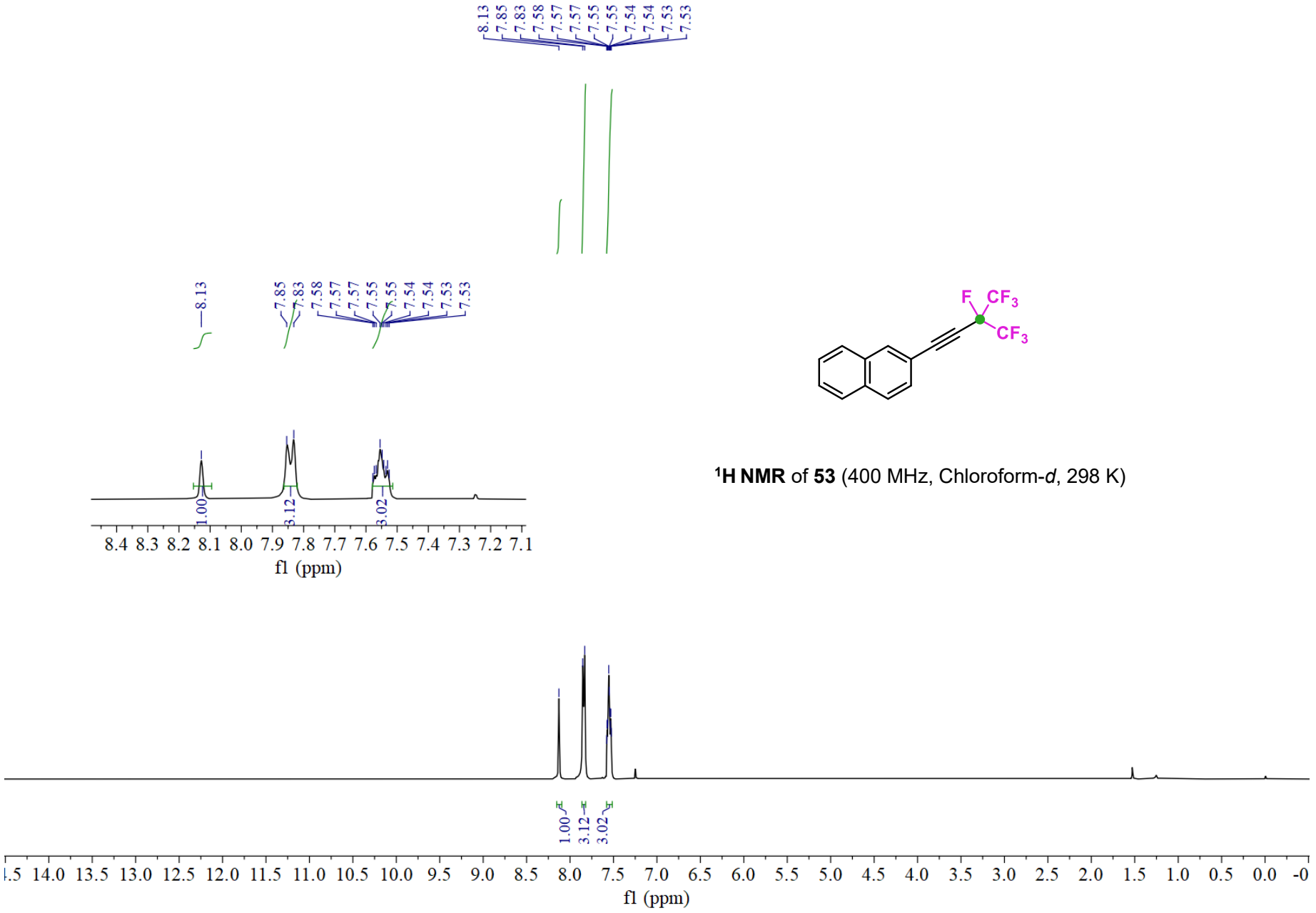
^{1}H NMR of **52** (400 MHz, Chloroform-*d*, 298 K)



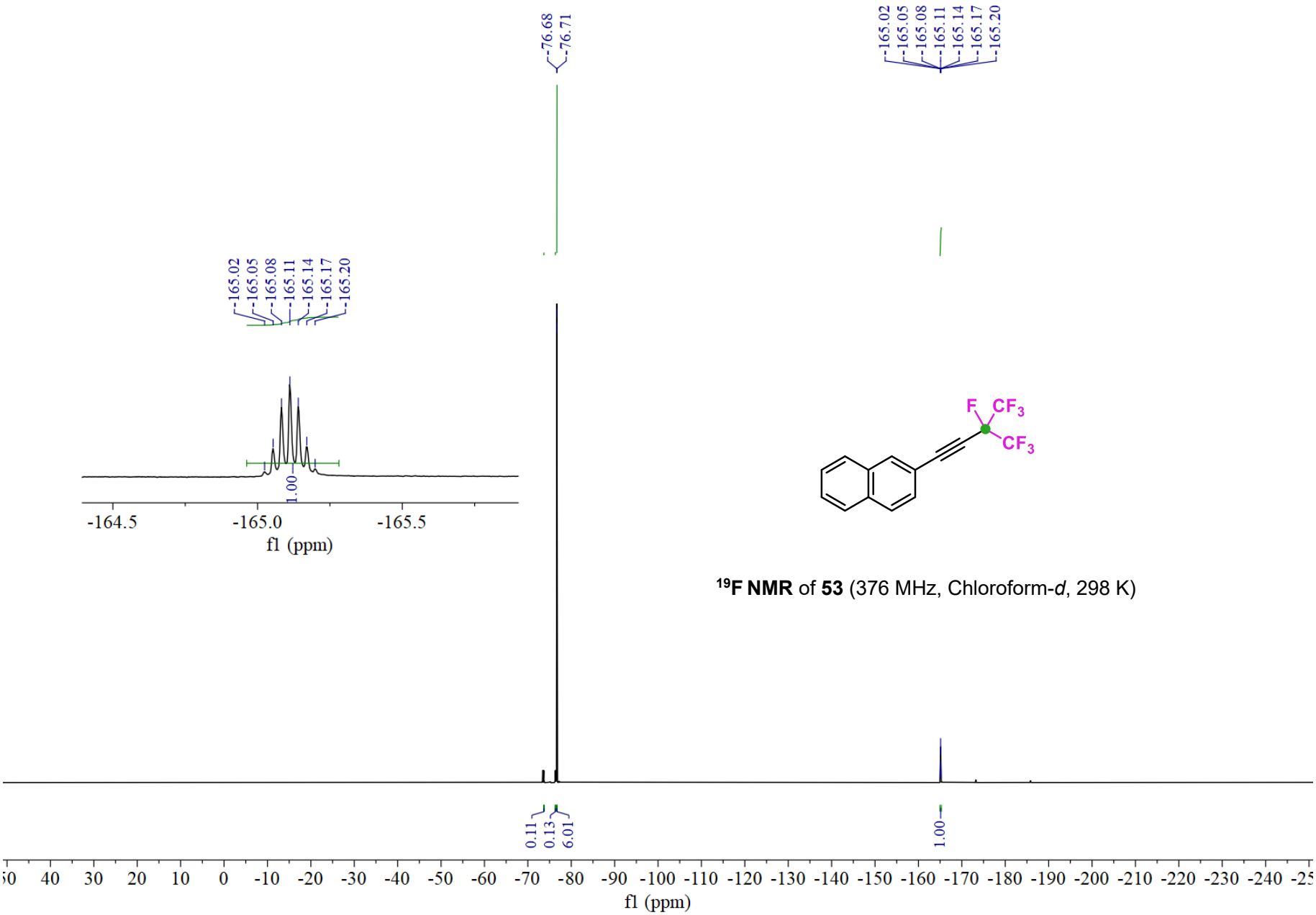
^{19}F NMR of **52** (376 MHz, Chloroform-*d*, 298 K)



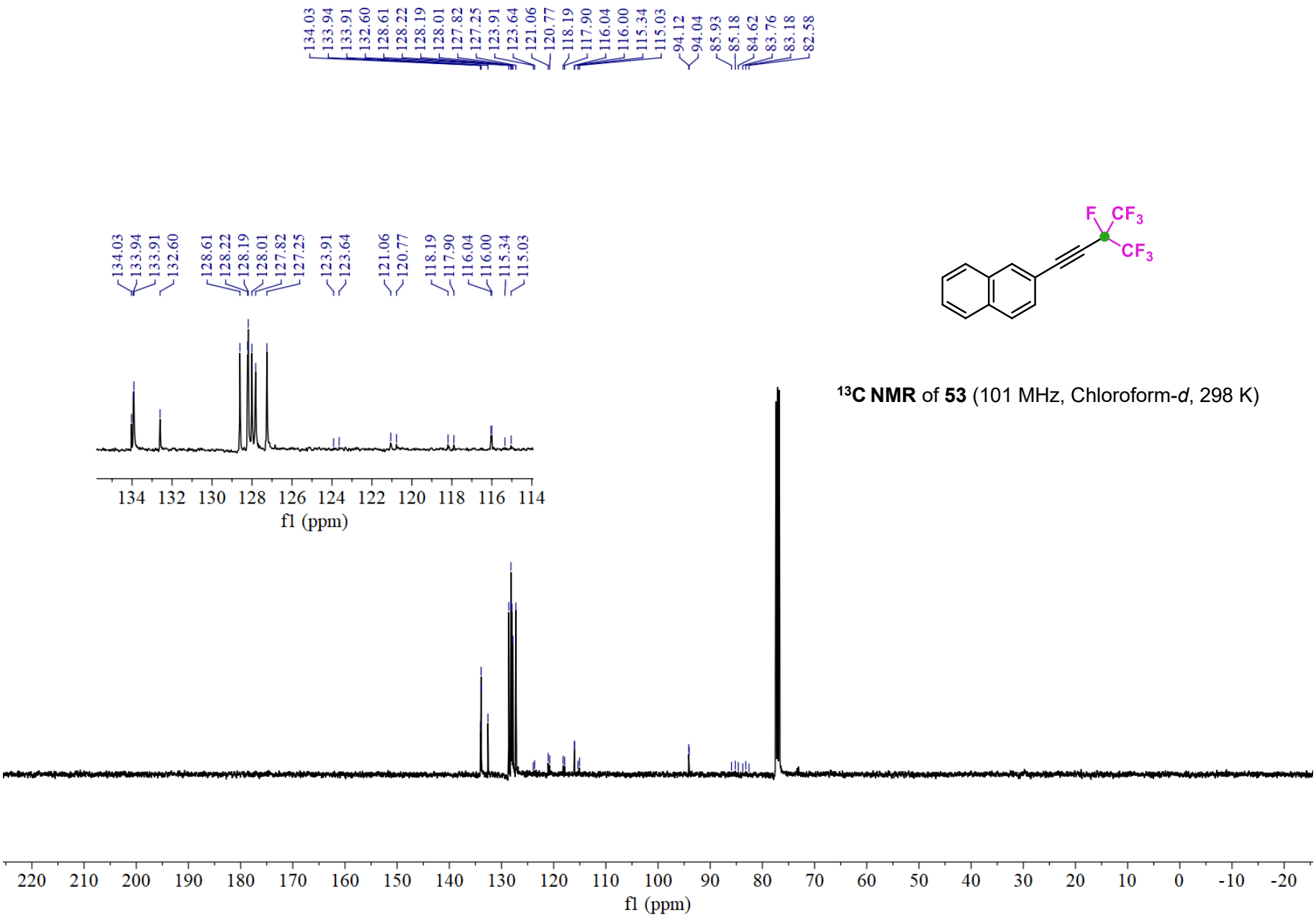
^{13}C NMR of **52** (101 MHz, Chloroform-*d*, 298 K)



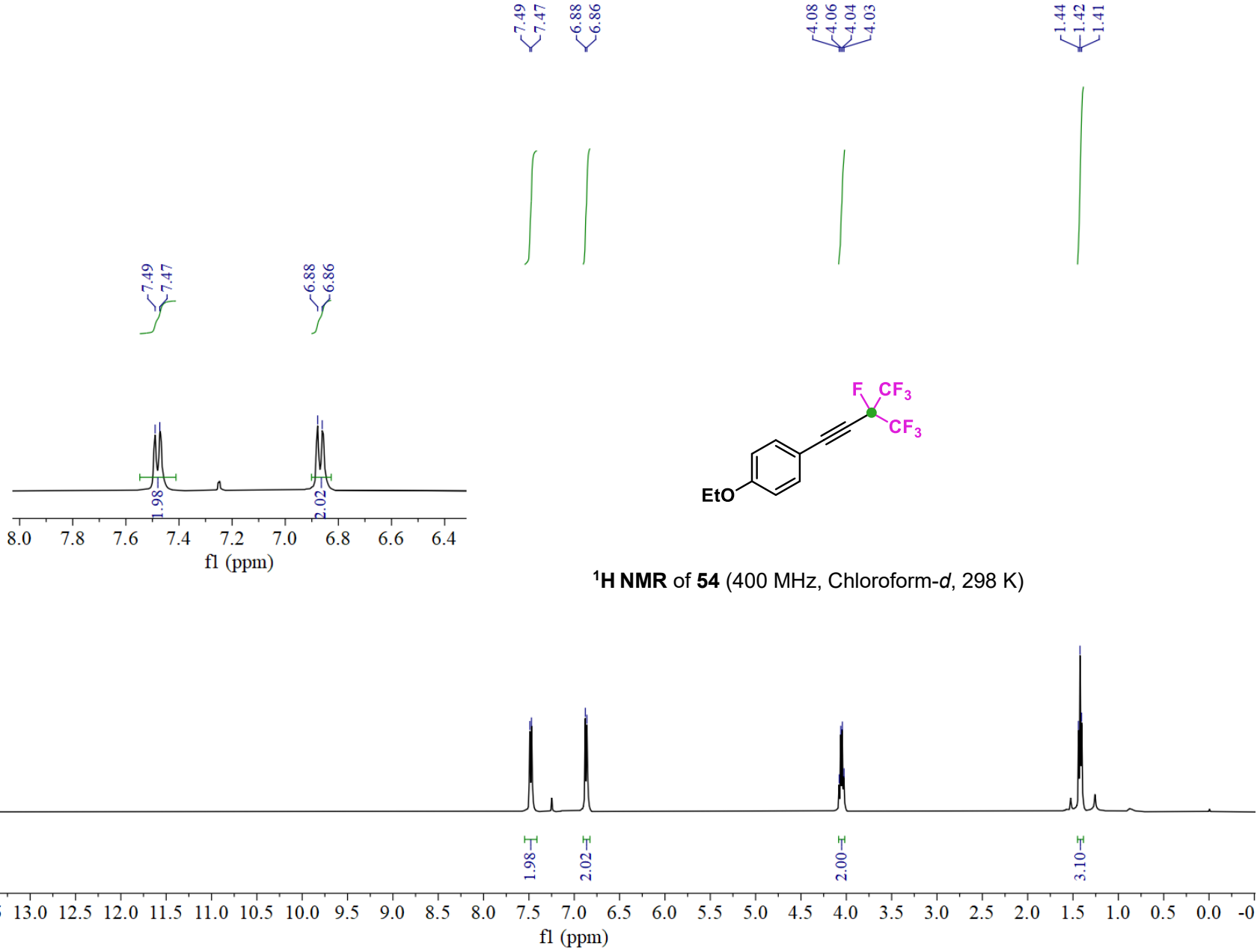
^{1}H NMR of **53** (400 MHz, Chloroform-*d*, 298 K)



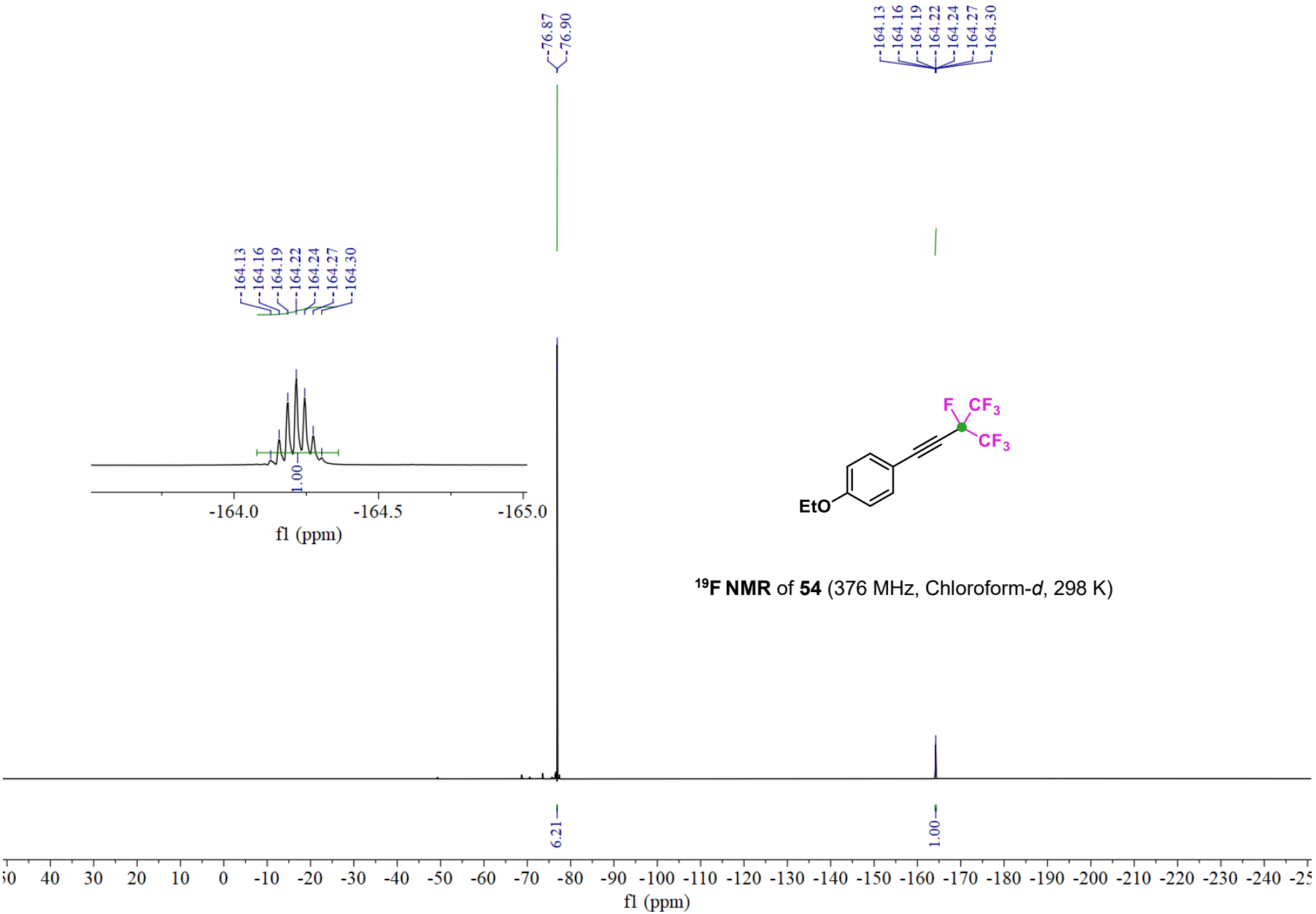
^{19}F NMR of **53** (376 MHz, Chloroform-*d*, 298 K)



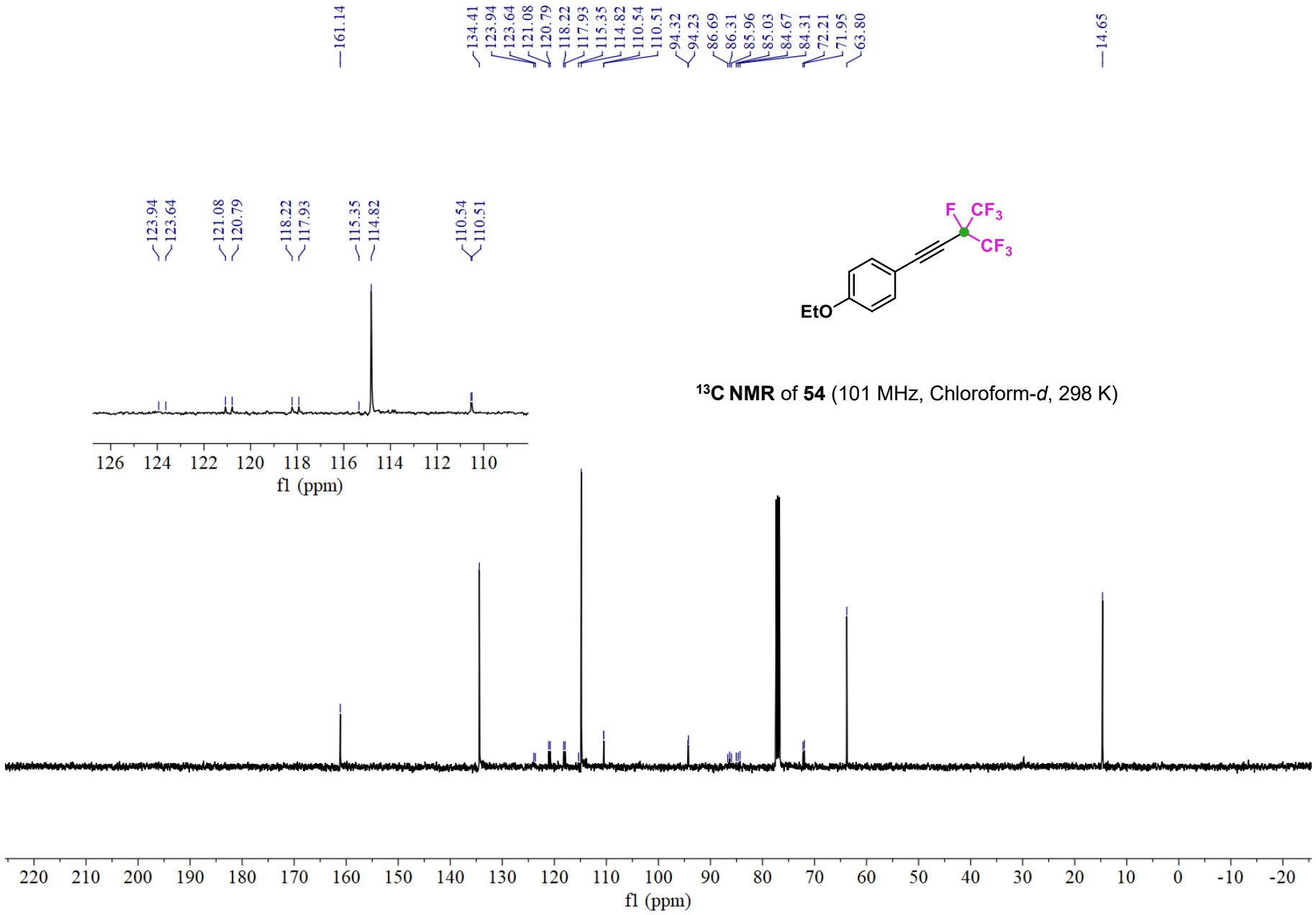
^{13}C NMR of **53** (101 MHz, Chloroform-*d*, 298 K)



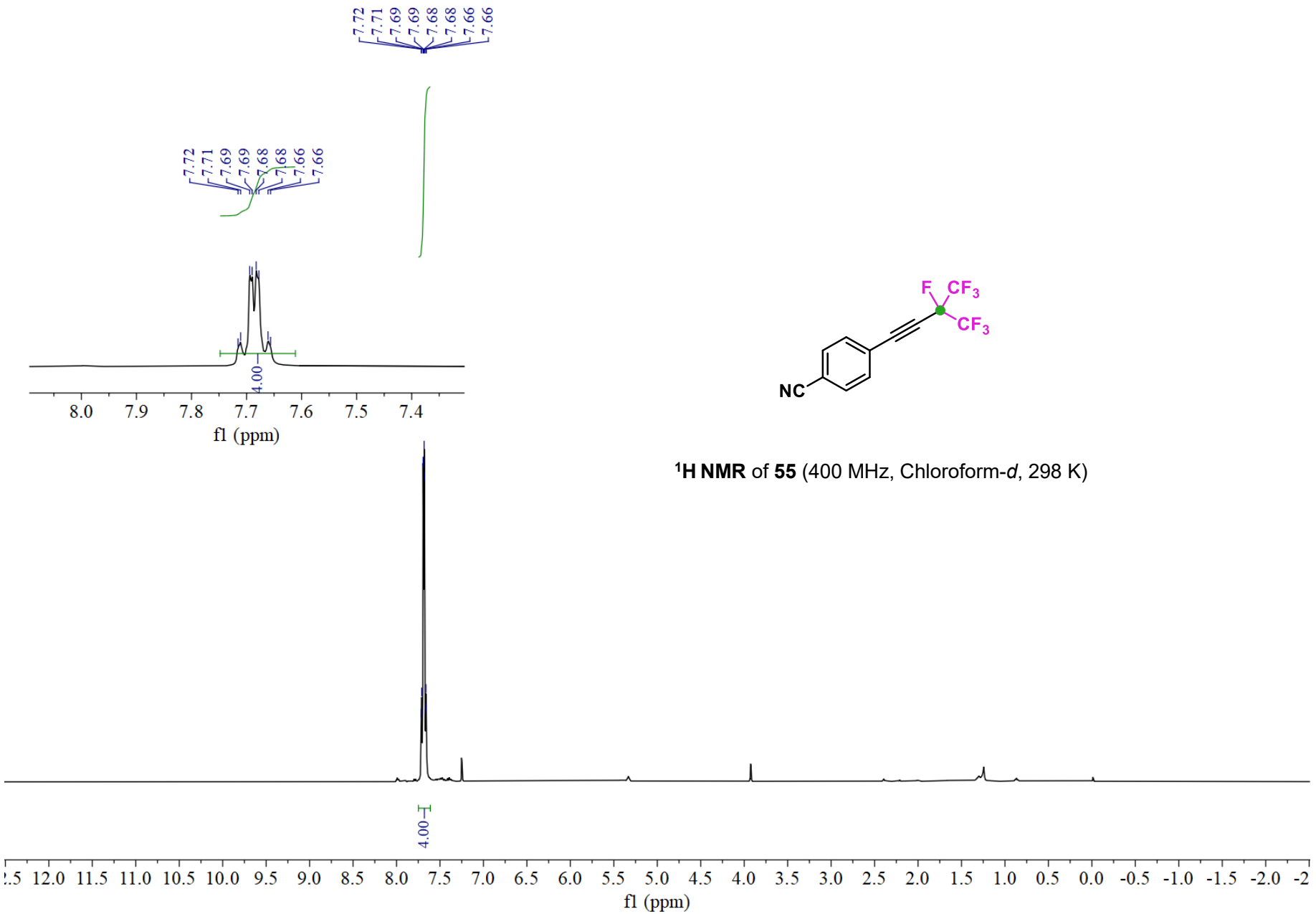
^{1}H NMR of **54** (400 MHz, Chloroform-*d*, 298 K)



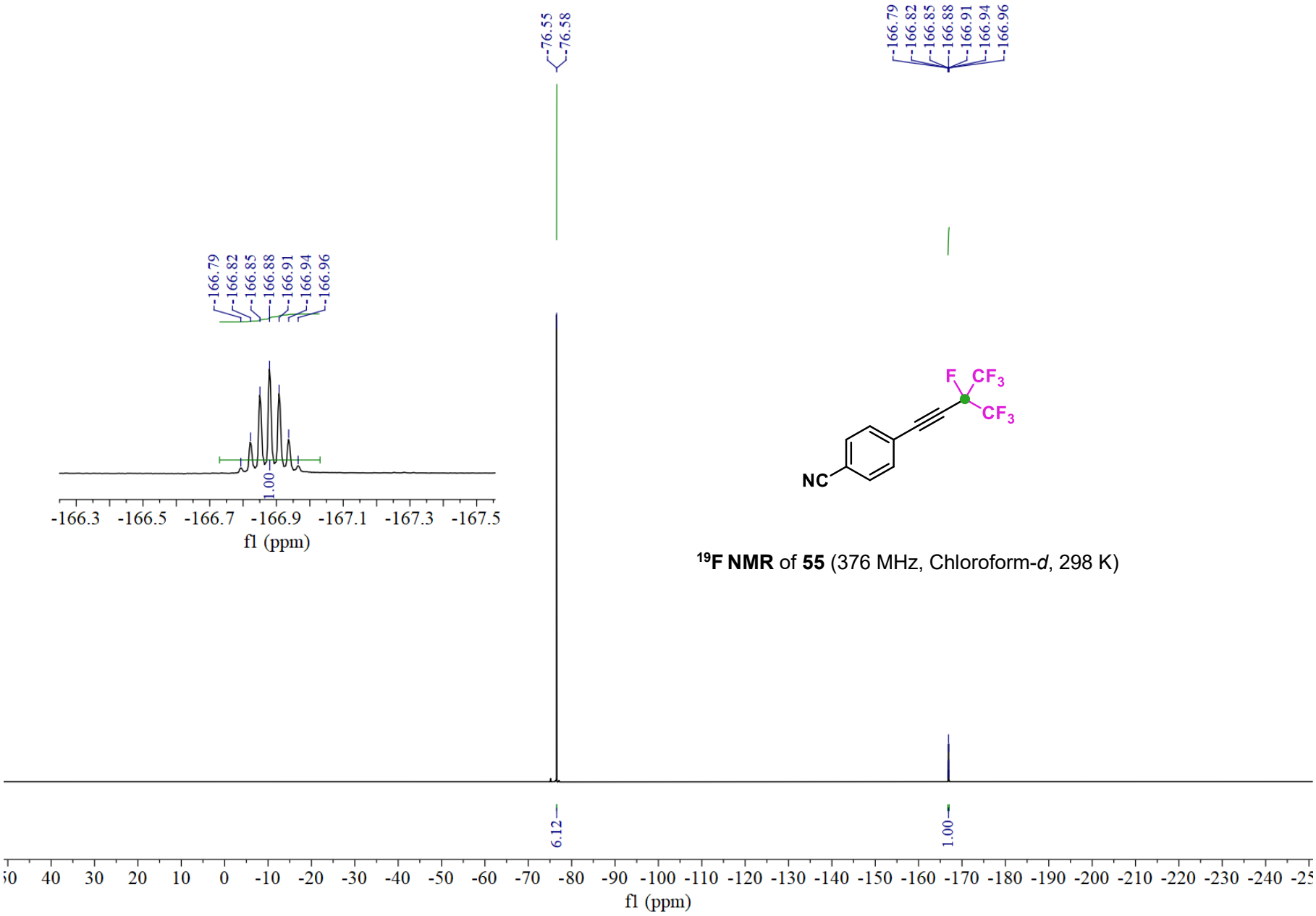
^{19}F NMR of **54** (376 MHz, Chloroform-*d*, 298 K)



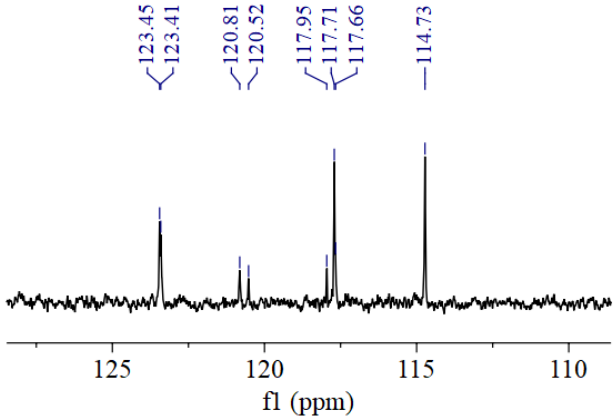
^{13}C NMR of **54** (101 MHz, Chloroform-*d*, 298 K)

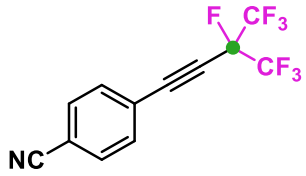


^{1}H NMR of **55** (400 MHz, Chloroform-*d*, 298 K)

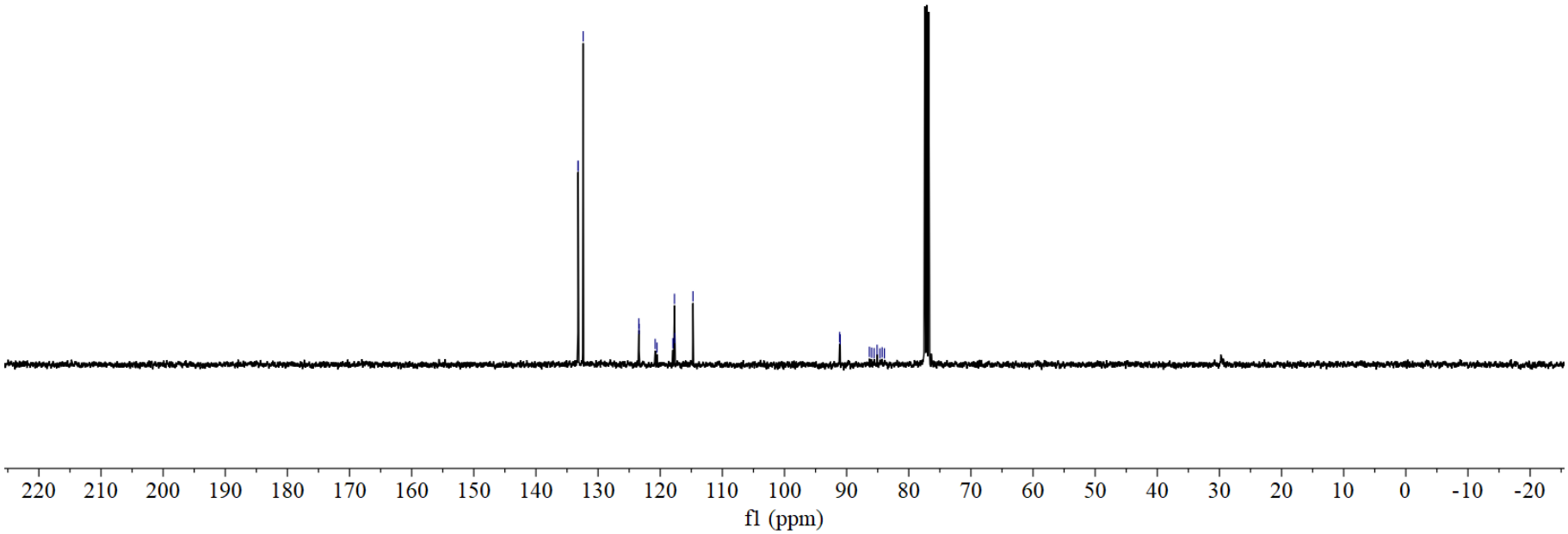


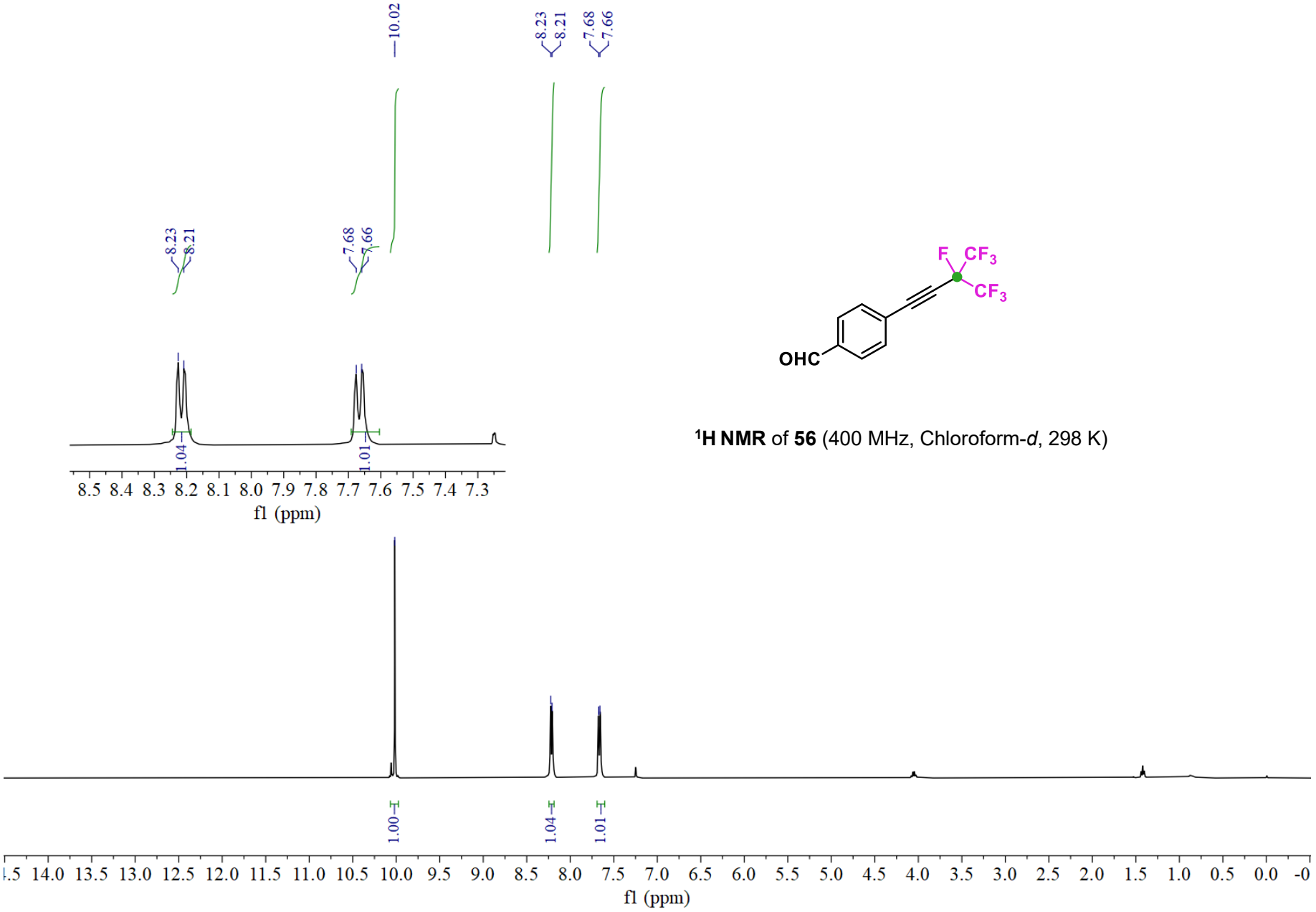
^{19}F NMR of **55** (376 MHz, Chloroform-*d*, 298 K)



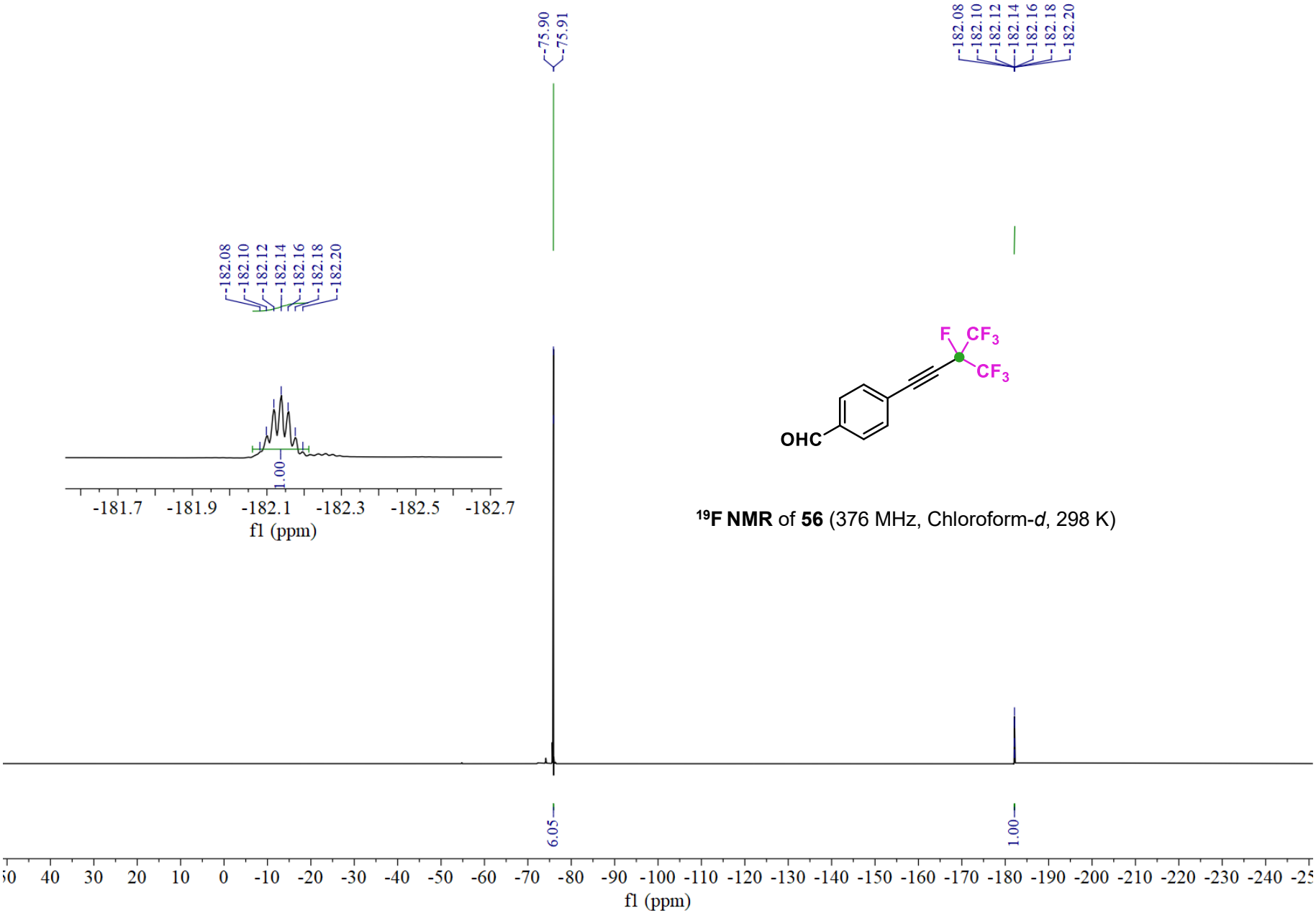


^{13}C NMR of **55** (101 MHz, Chloroform-*d*, 298 K)

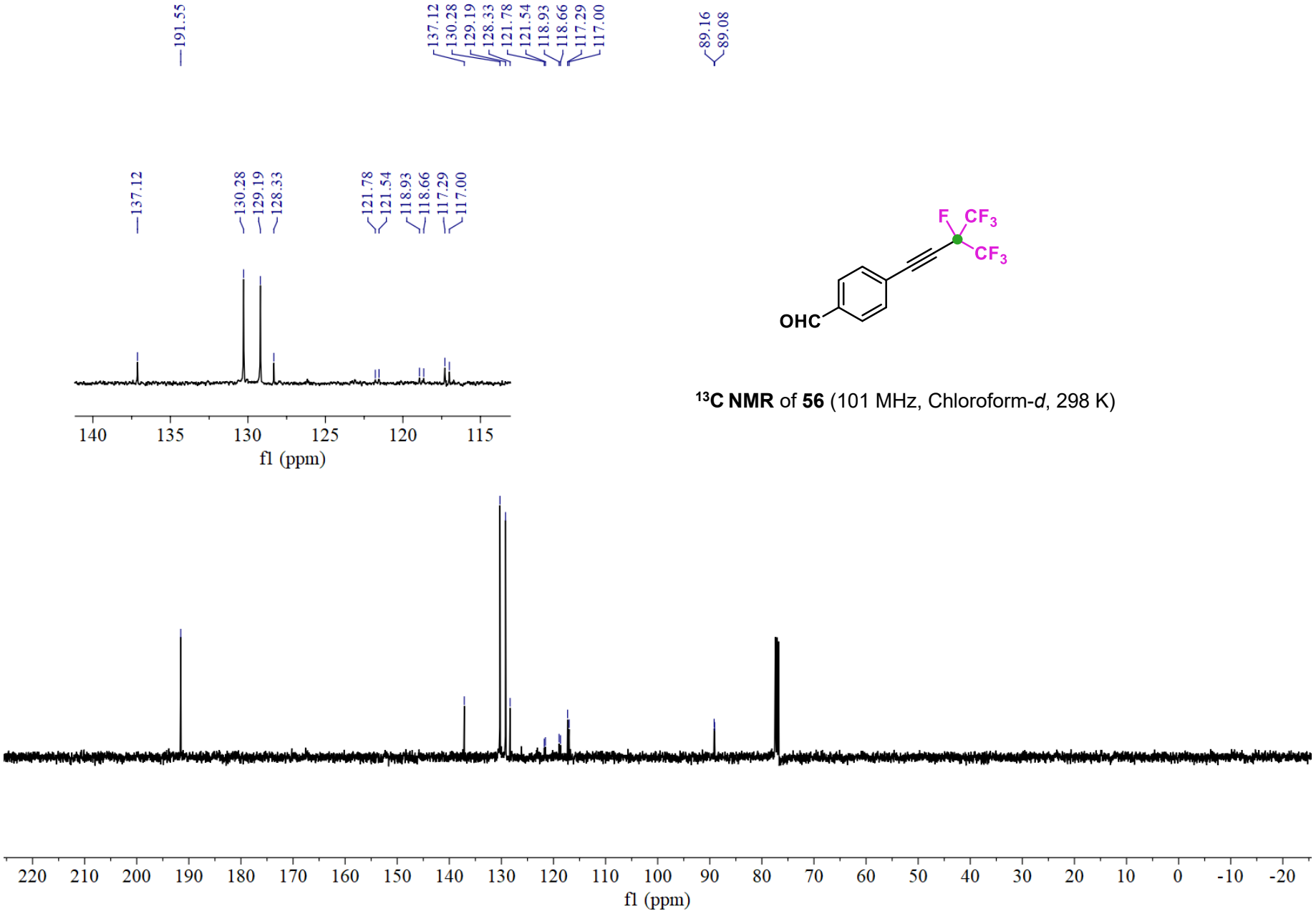




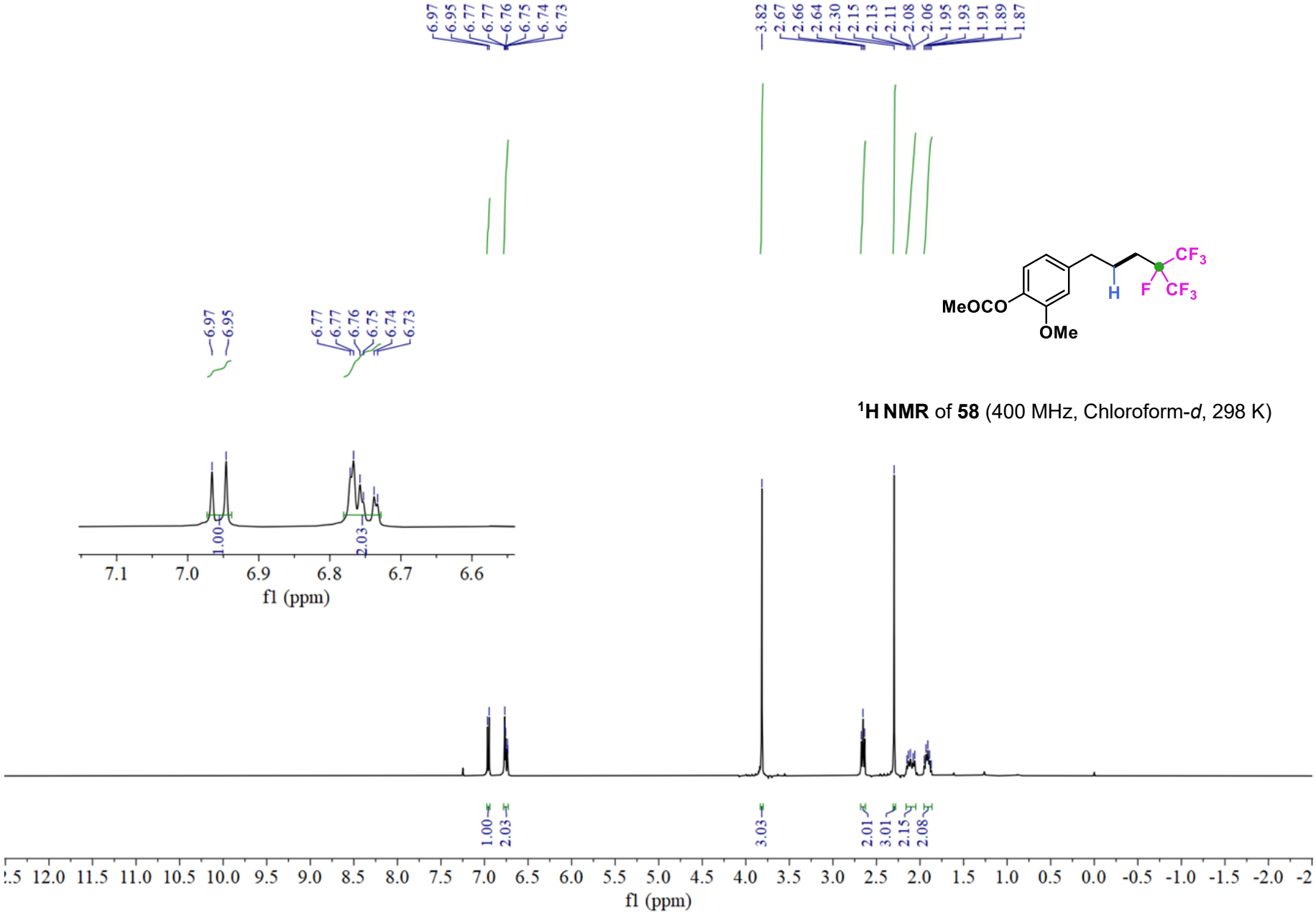
^{1}H NMR of **56** (400 MHz, Chloroform-*d*, 298 K)



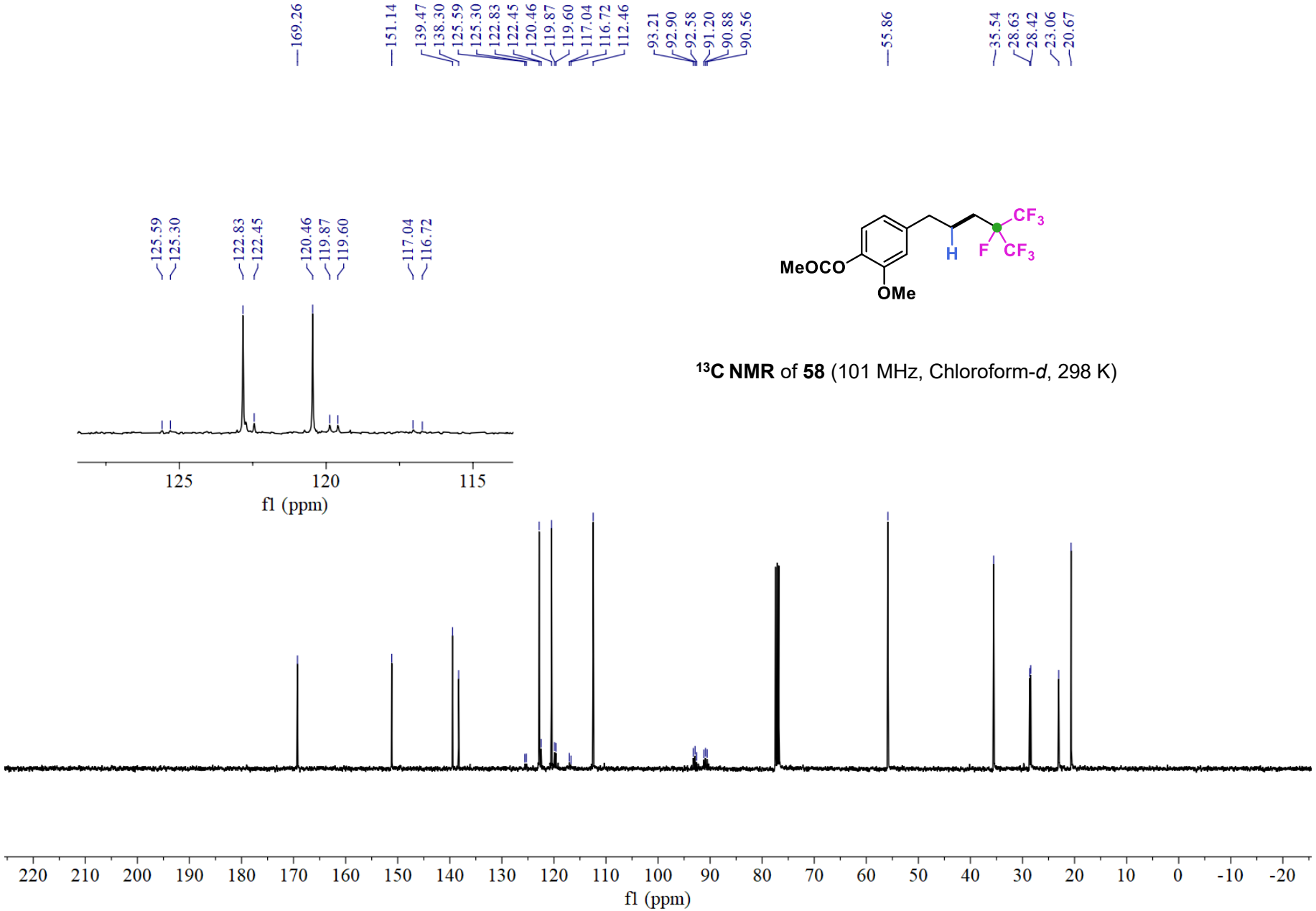
^{19}F NMR of **56** (376 MHz, Chloroform-*d*, 298 K)



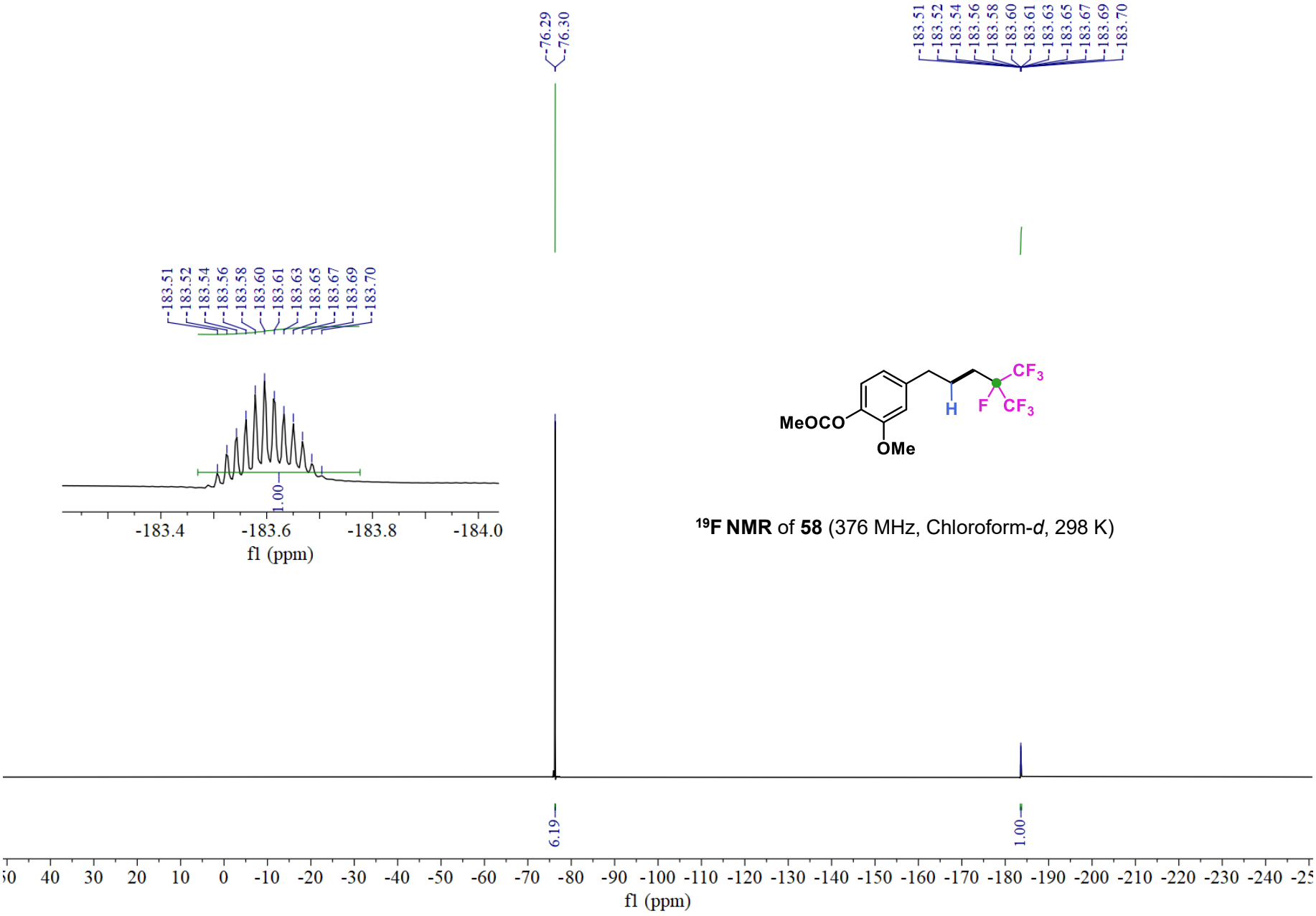
^{13}C NMR of **56** (101 MHz, Chloroform-*d*, 298 K)



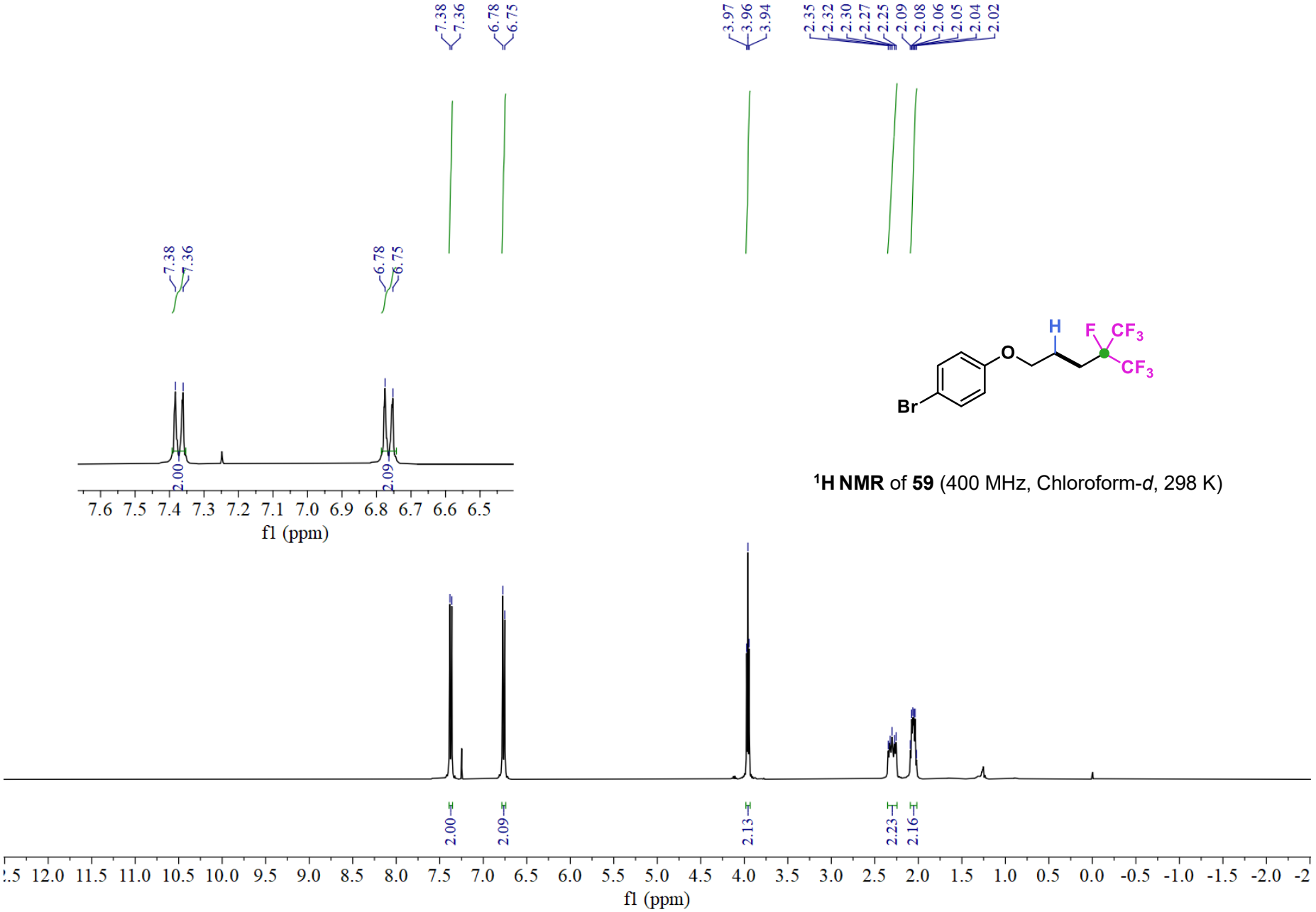
^{1}H NMR of **58** (400 MHz, Chloroform-*d*, 298 K)



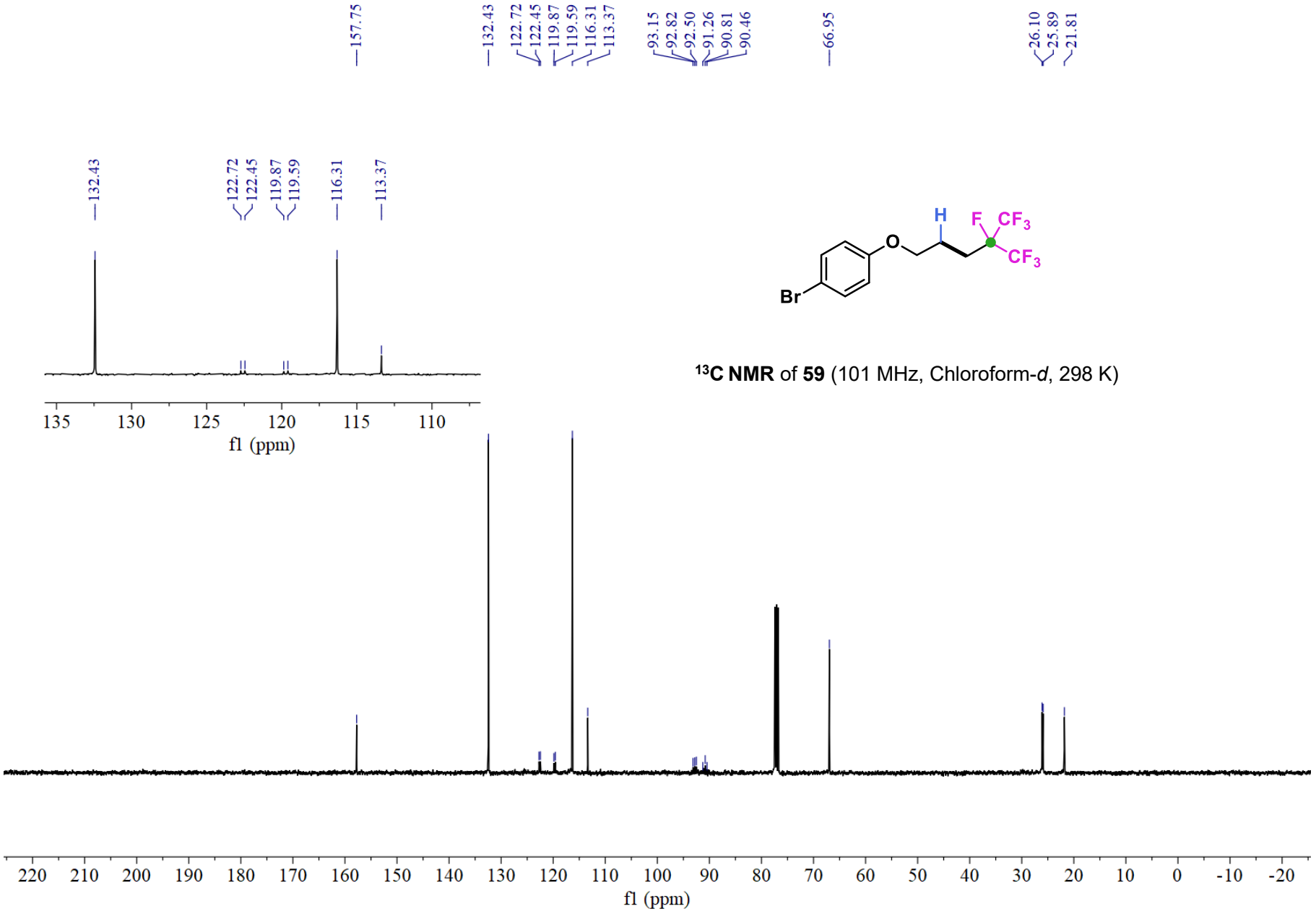
^{13}C NMR of **58** (101 MHz, Chloroform-*d*, 298 K)



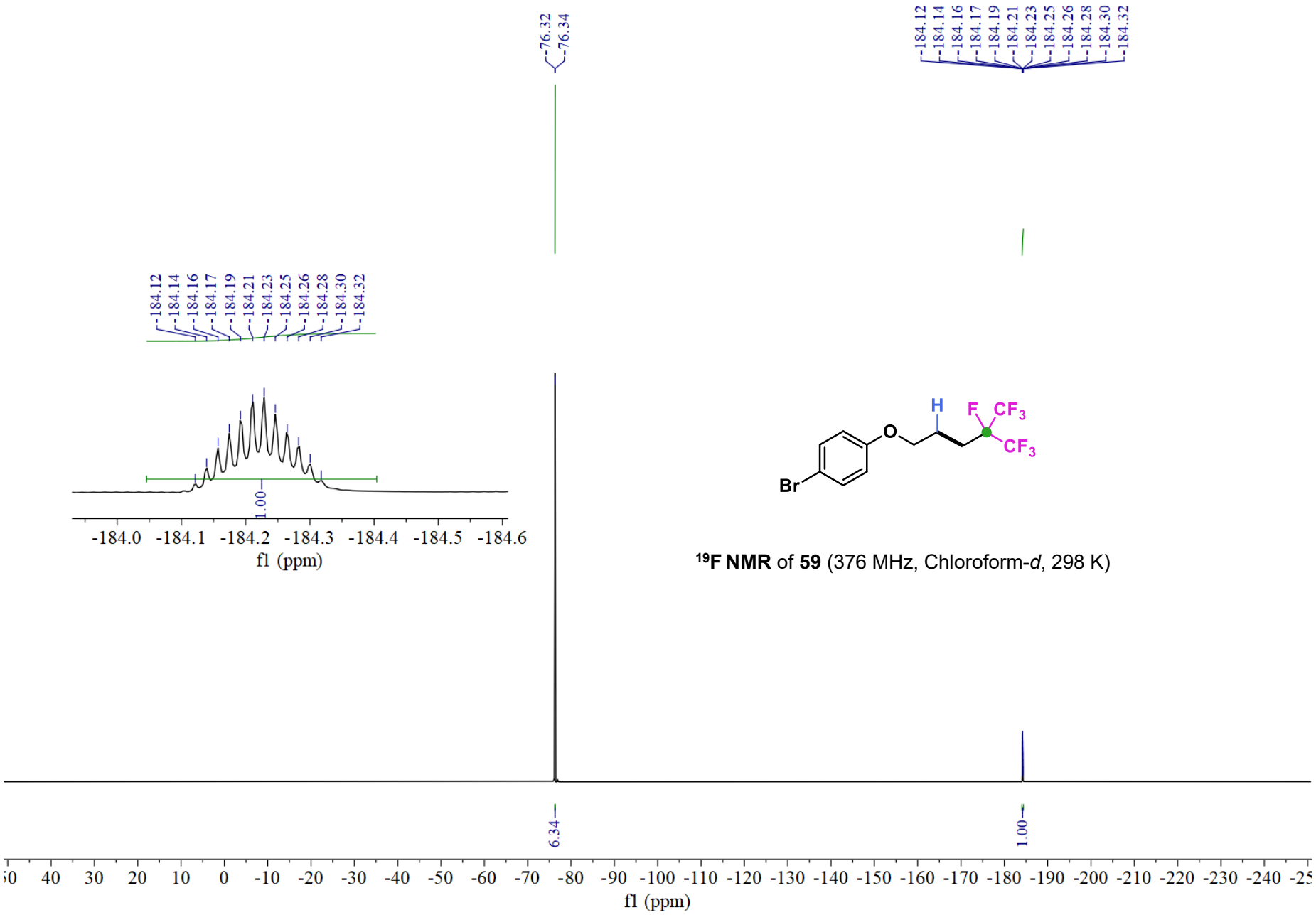
^{19}F NMR of **58** (376 MHz, Chloroform-*d*, 298 K)



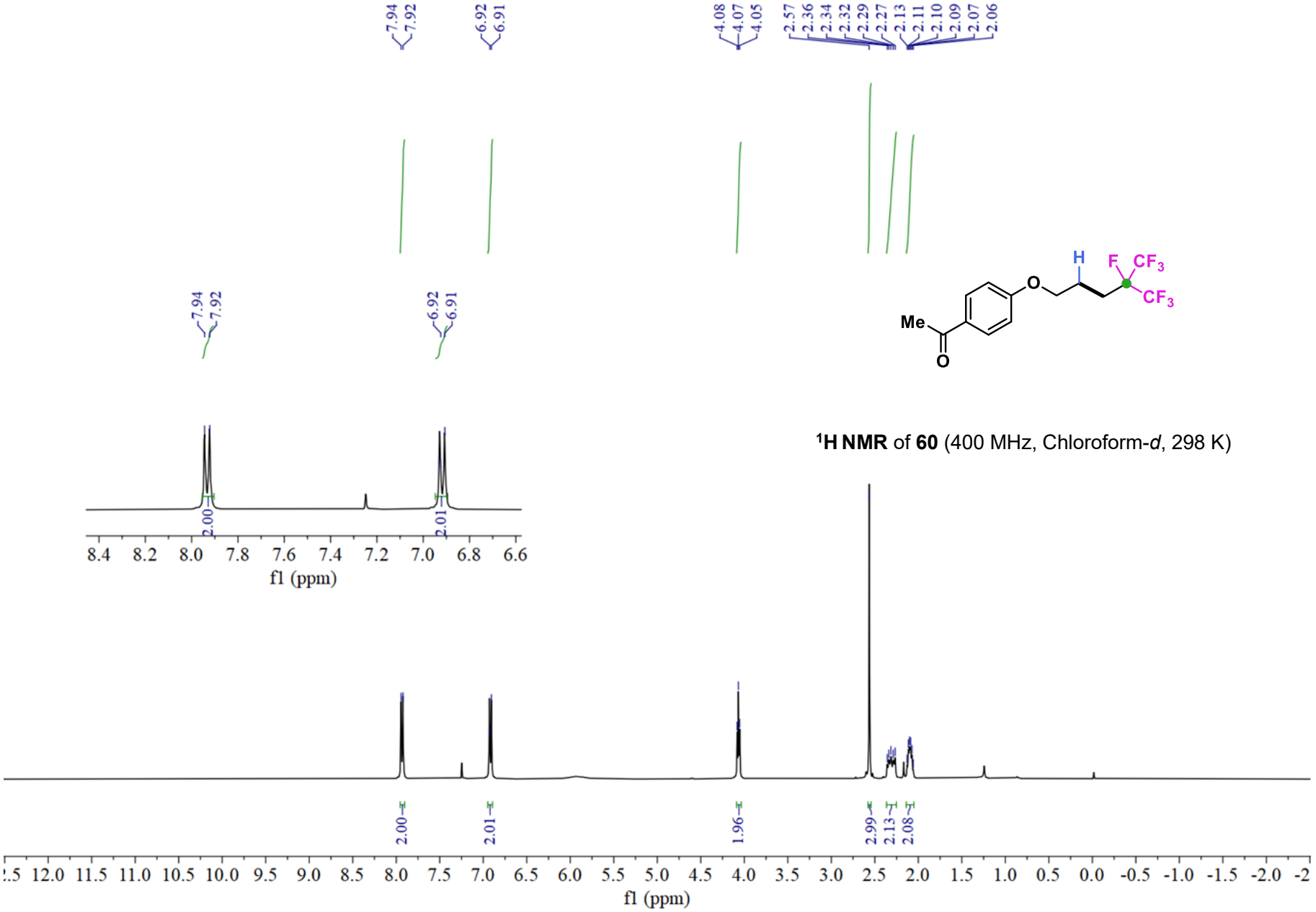
^{1}H NMR of **59** (400 MHz, Chloroform-*d*, 298 K)



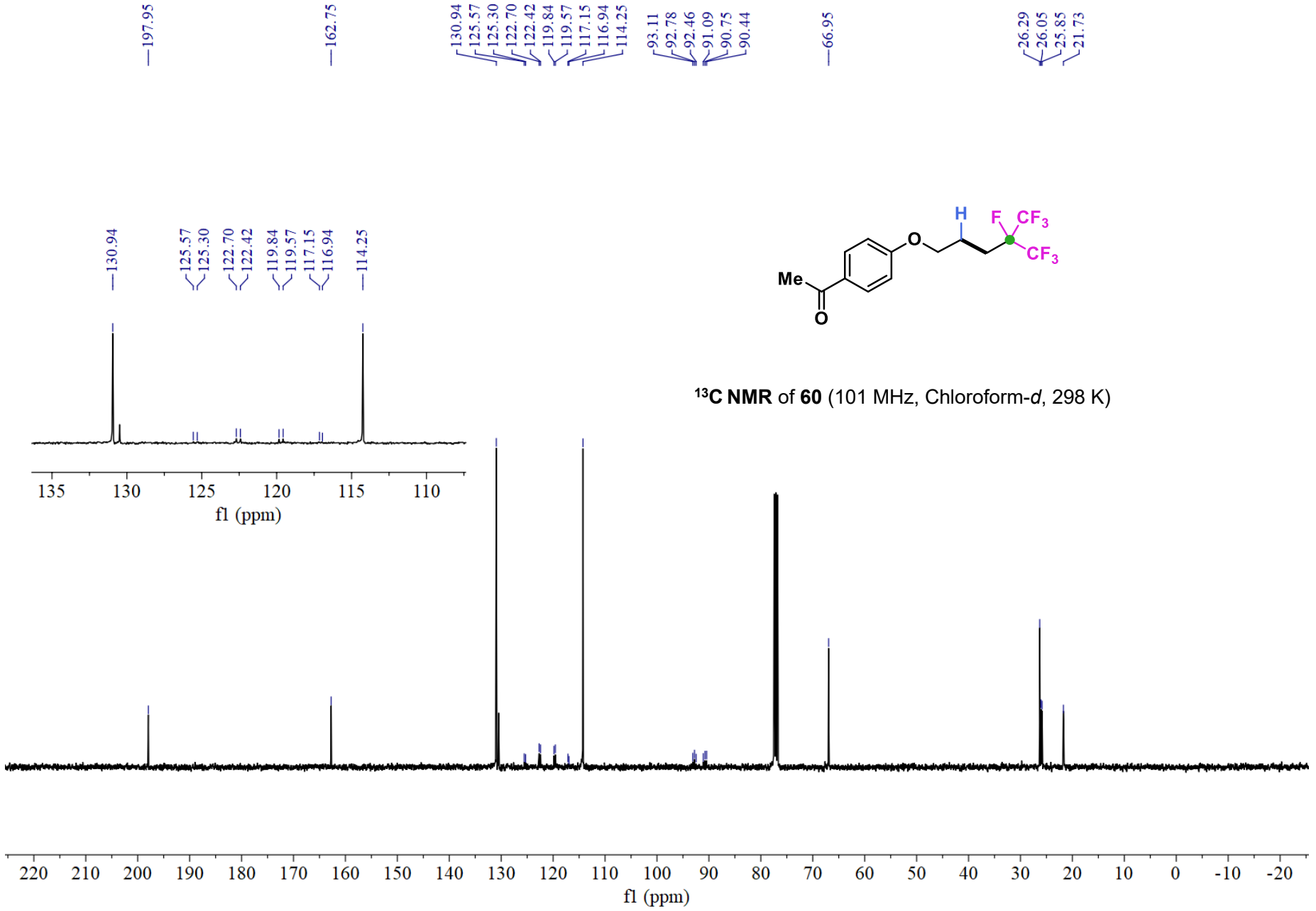
^{13}C NMR of **59** (101 MHz, Chloroform-*d*, 298 K)



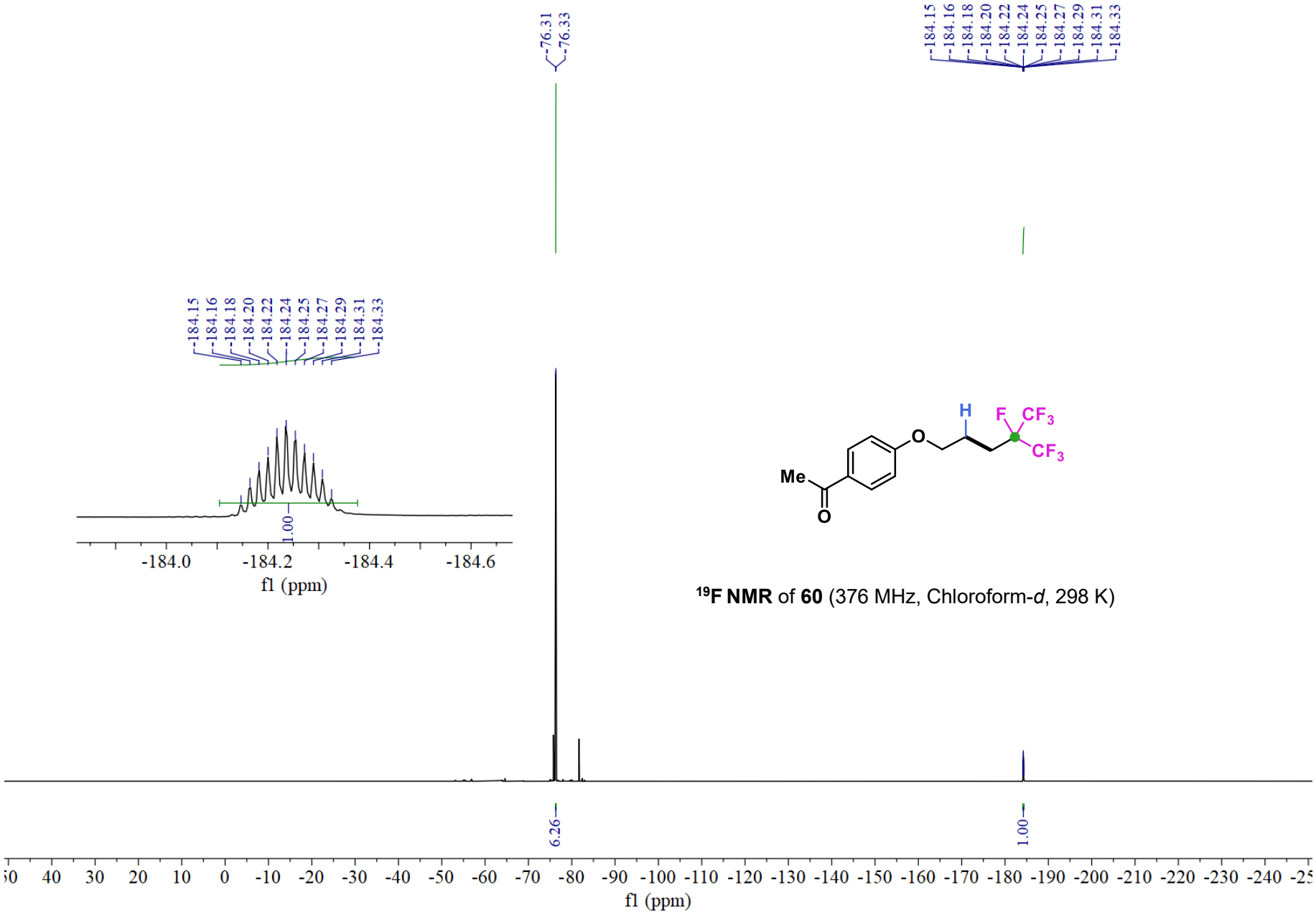
^{19}F NMR of **59** (376 MHz, Chloroform-*d*, 298 K)



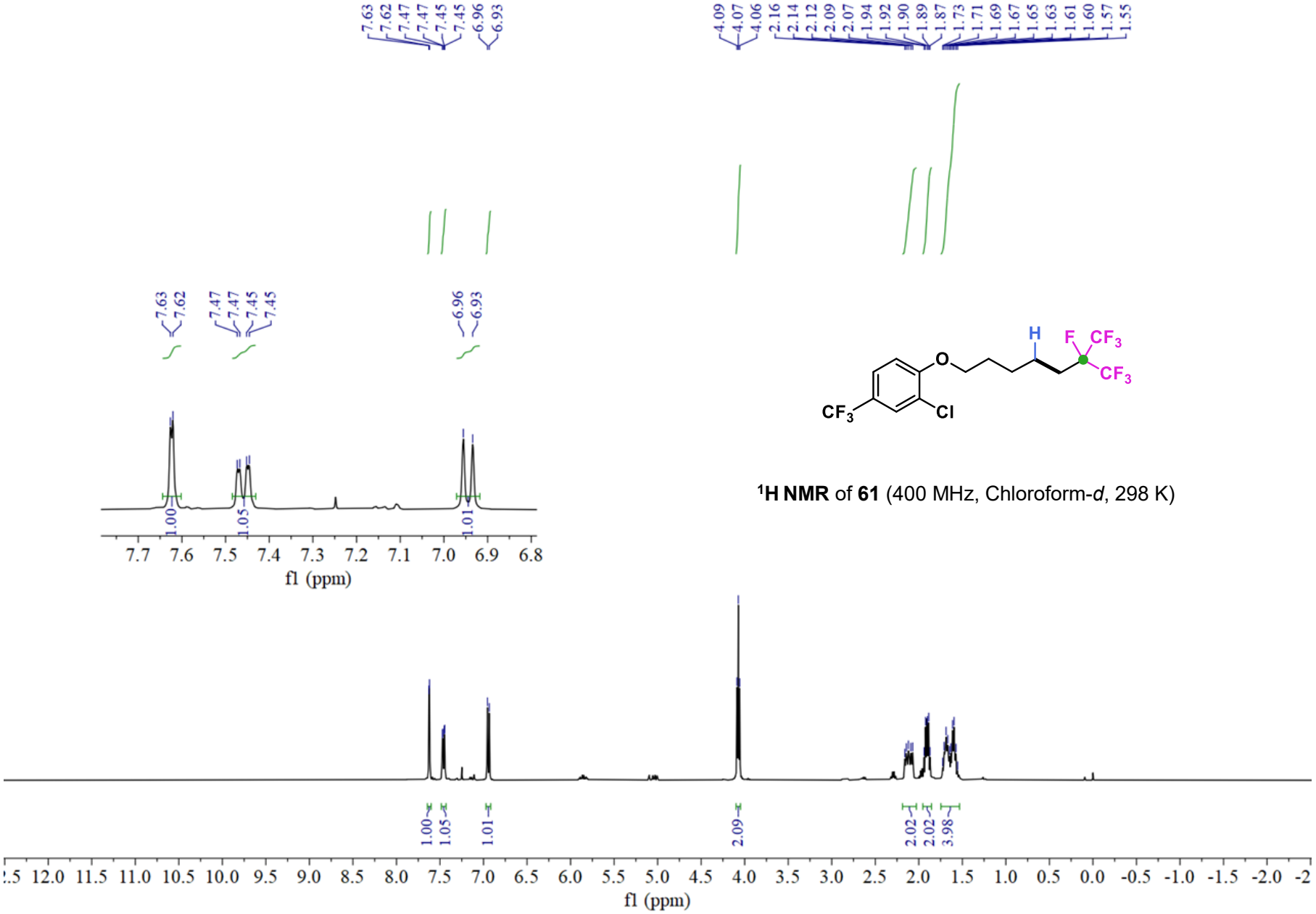
^{1}H NMR of **60** (400 MHz, Chloroform-*d*, 298 K)



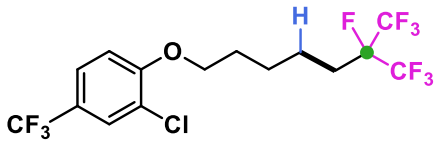
^{13}C NMR of **60** (101 MHz, Chloroform-*d*, 298 K)



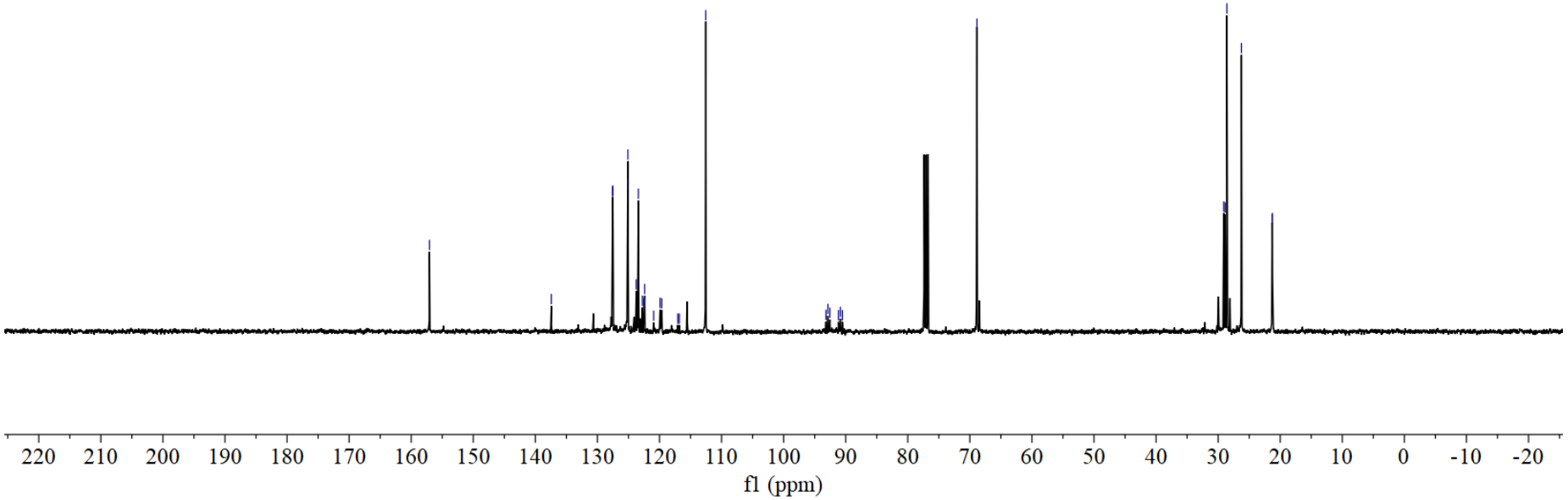
^{19}F NMR of **60** (376 MHz, Chloroform-*d*, 298 K)

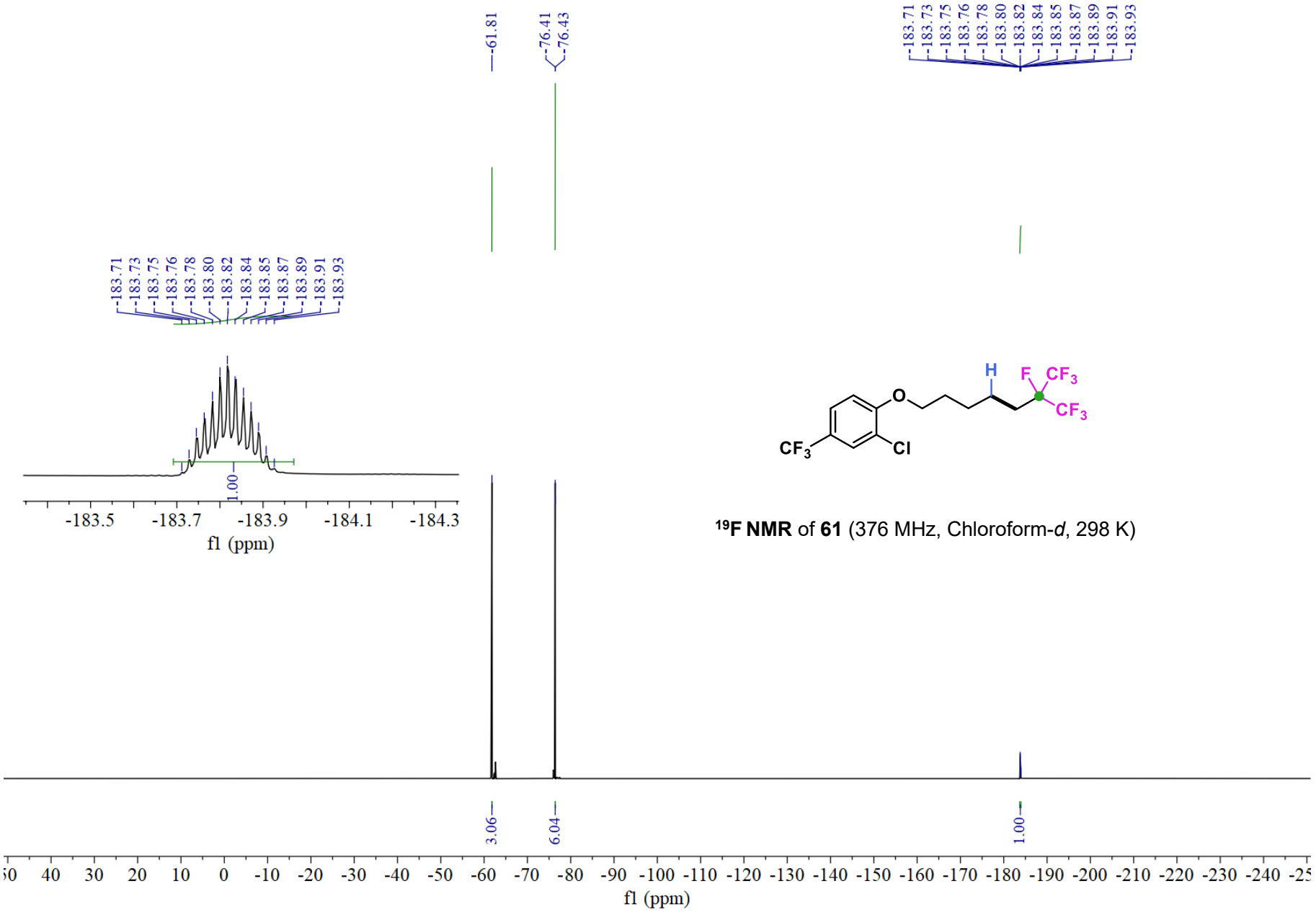


^{1}H NMR of **61** (400 MHz, Chloroform-*d*, 298 K)

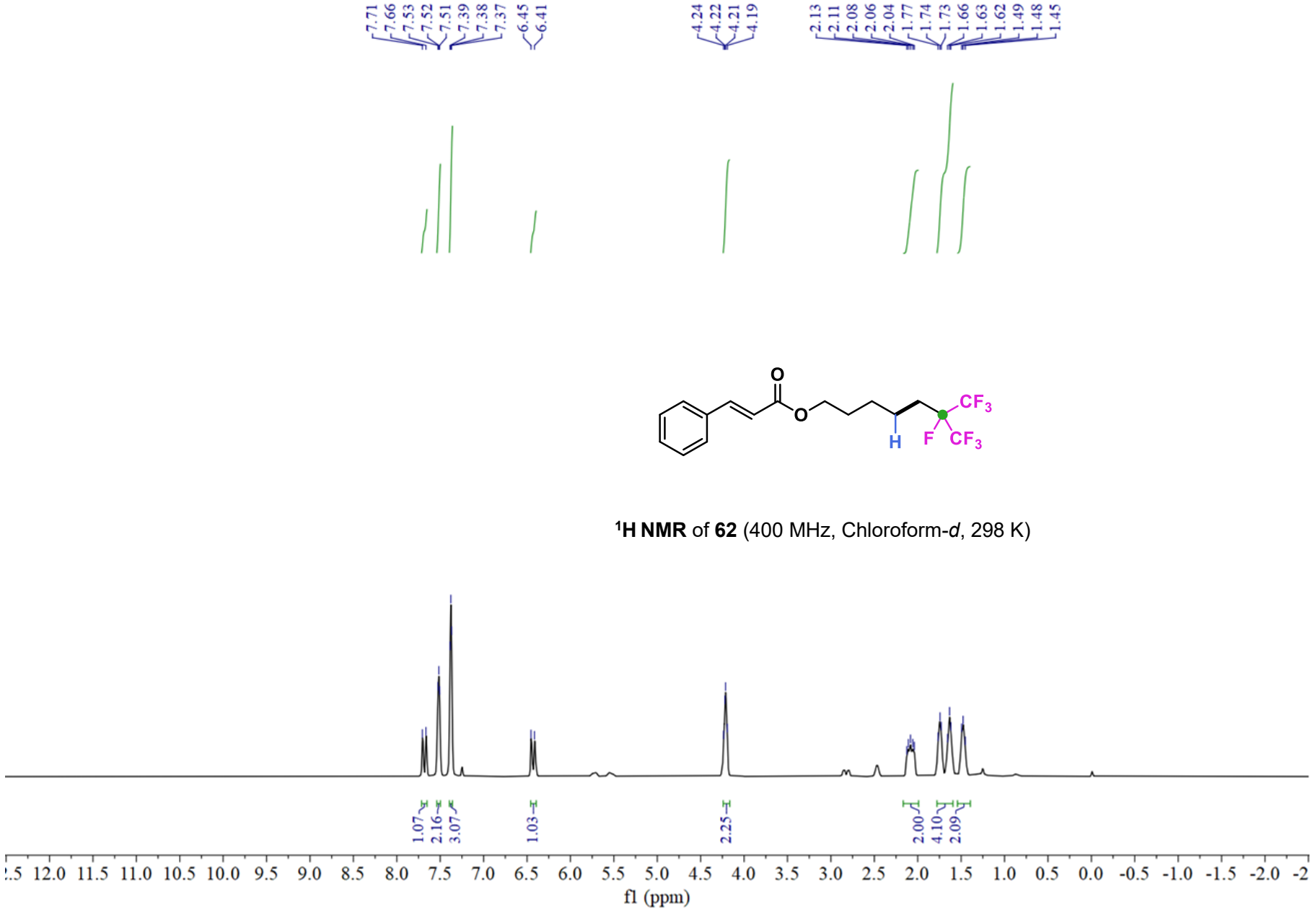


^{13}C NMR of **61** (101 MHz, Chloroform-*d*, 298 K)

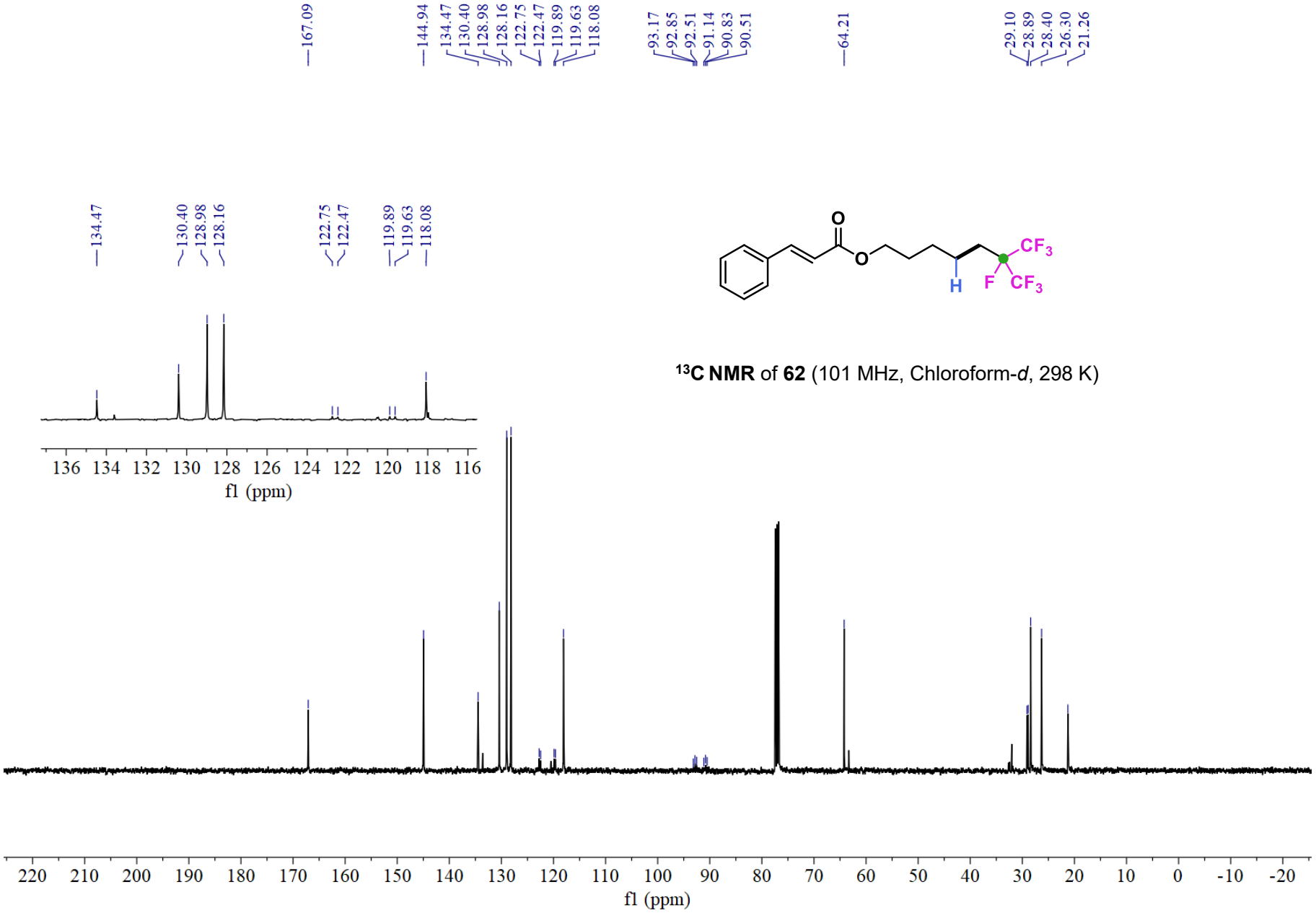




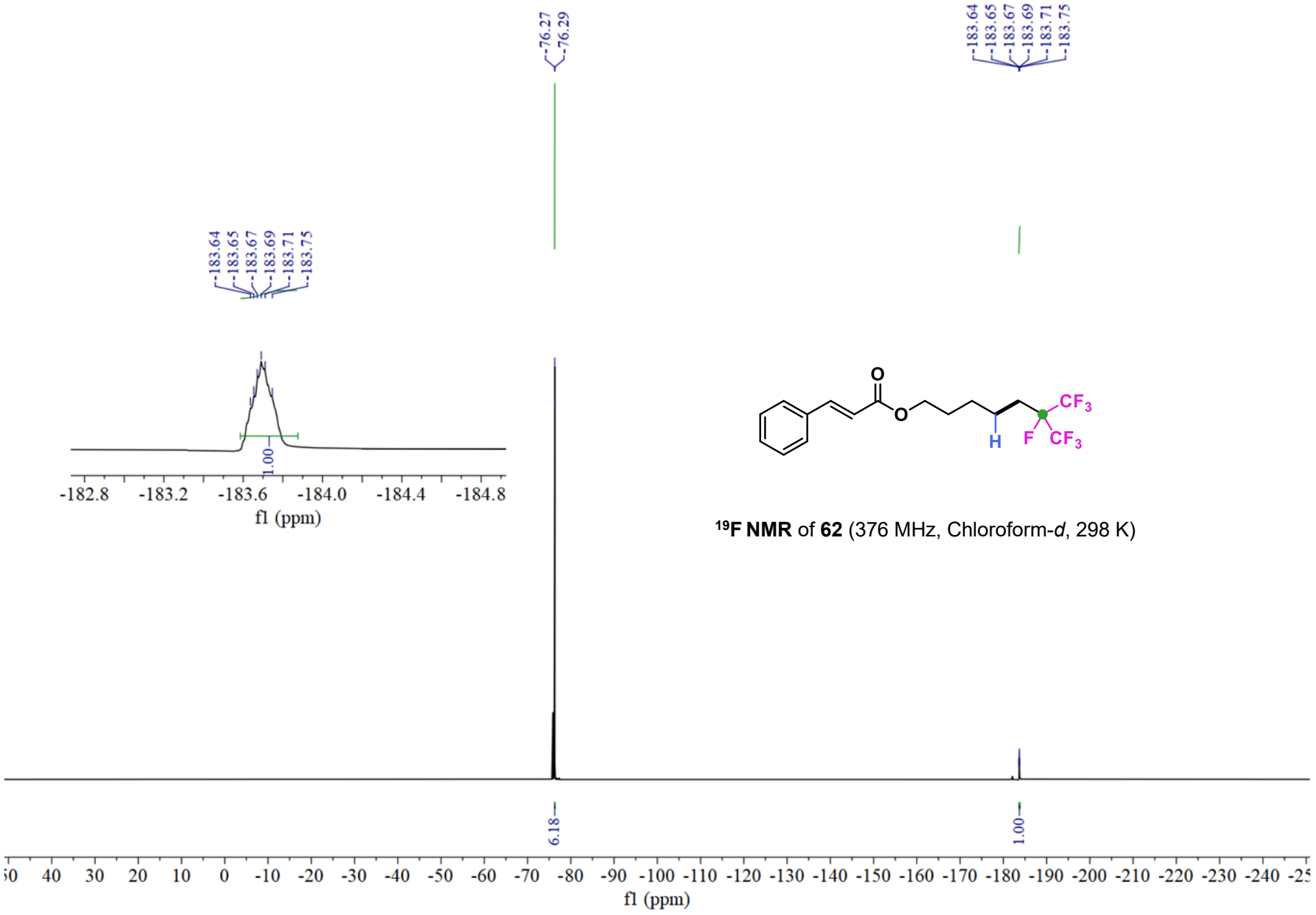
^{19}F NMR of **61** (376 MHz, Chloroform-*d*, 298 K)



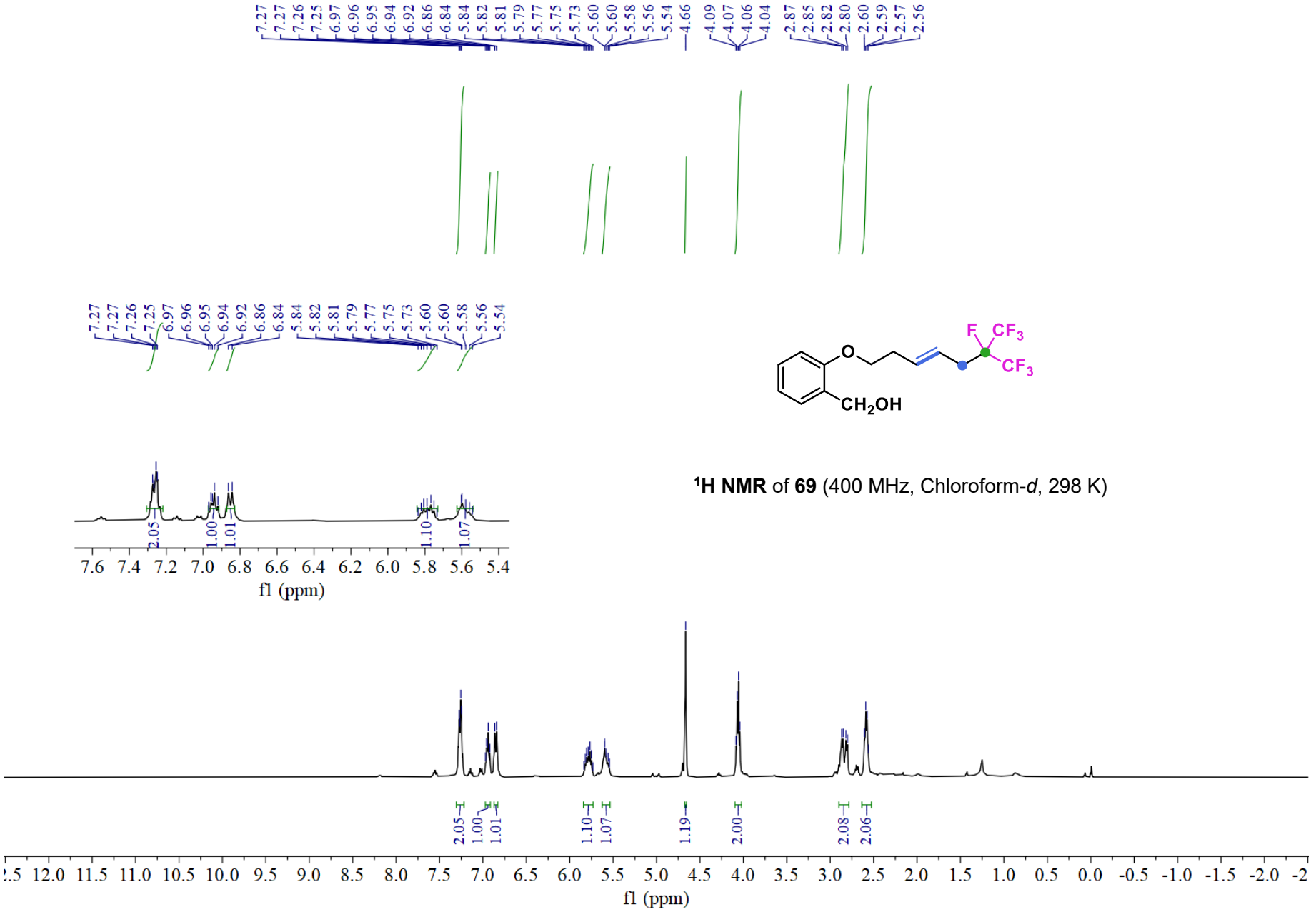
^{1}H NMR of **62** (400 MHz, Chloroform-*d*, 298 K)



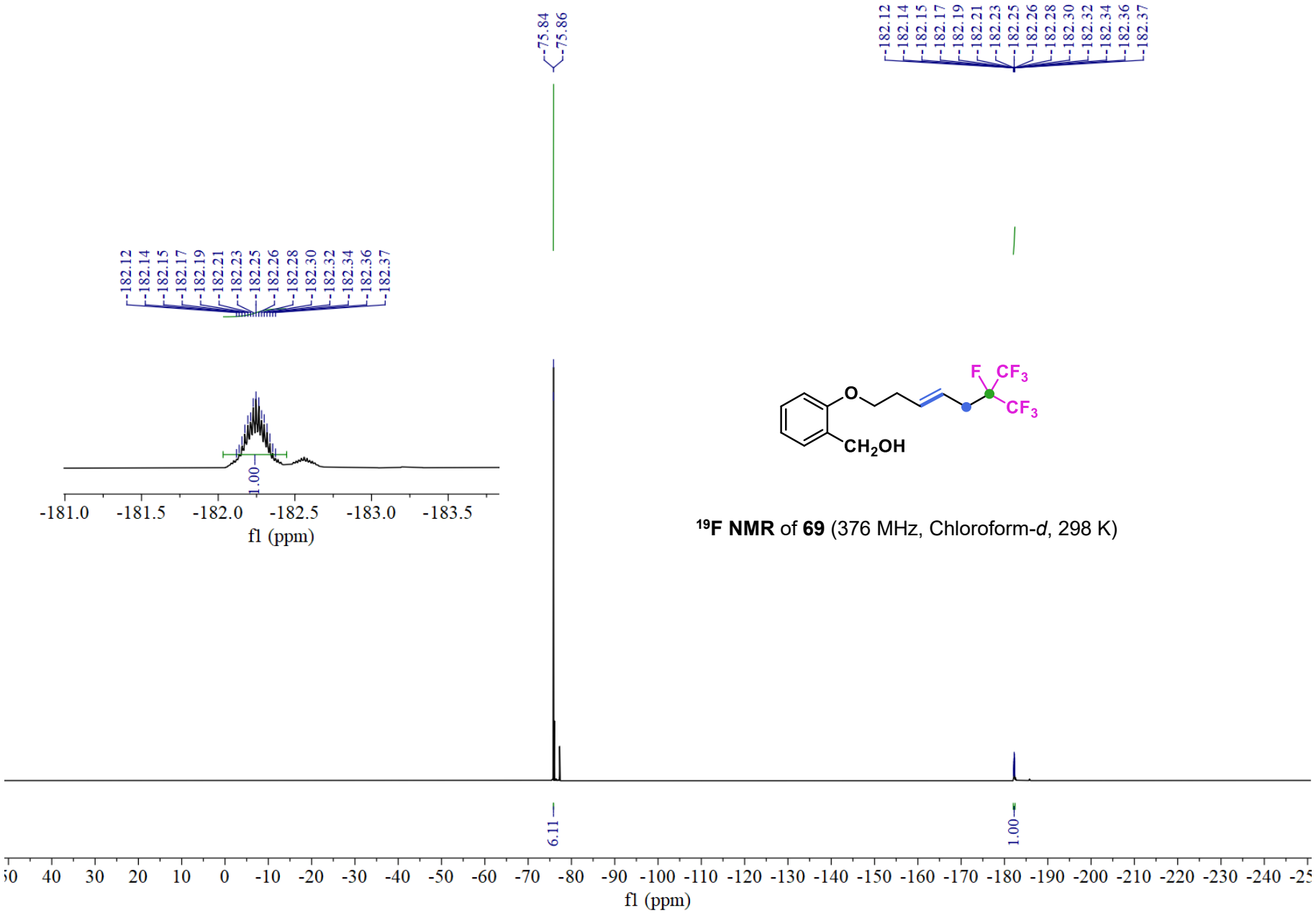
^{13}C NMR of **62** (101 MHz, Chloroform-*d*, 298 K)



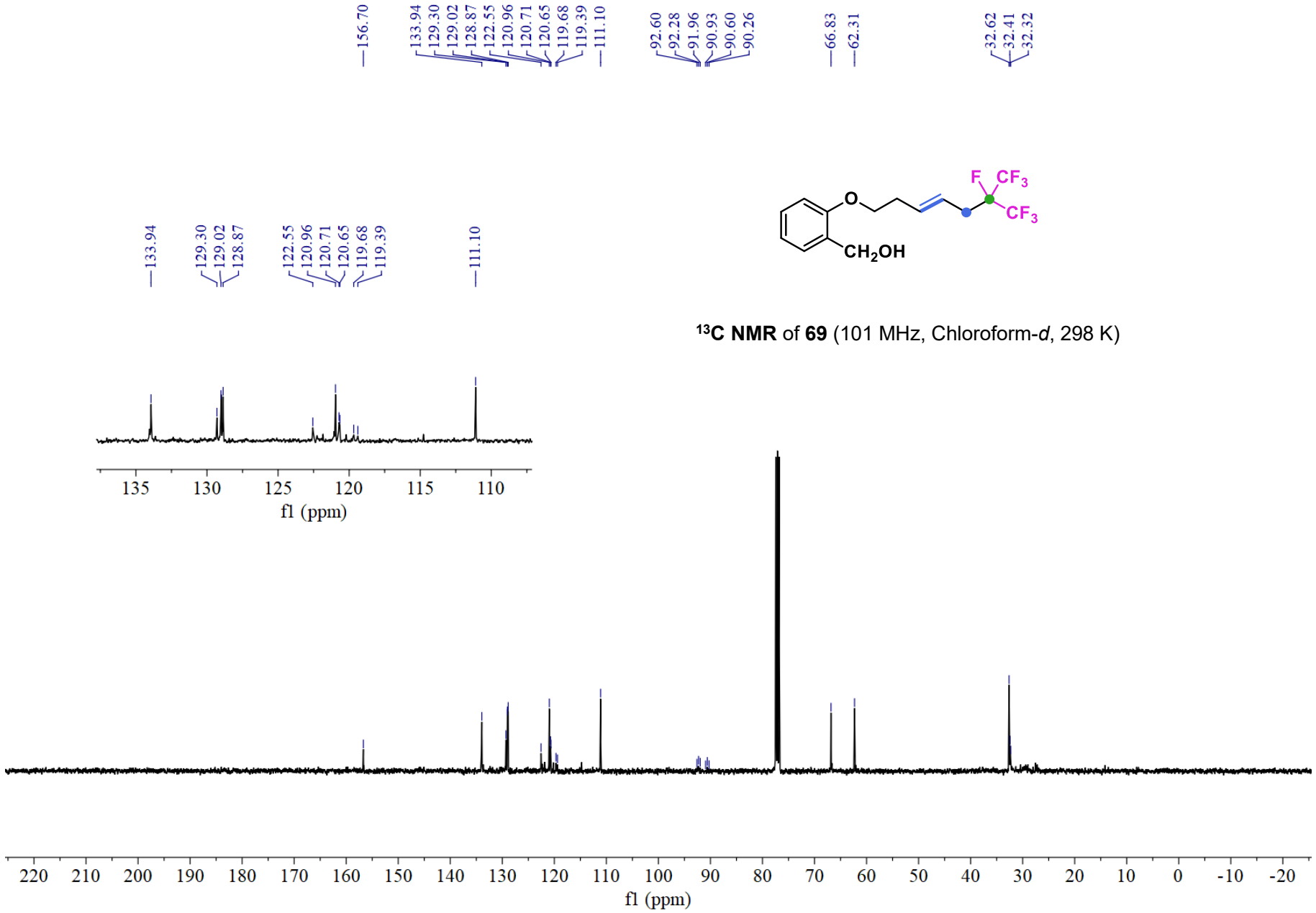
^{19}F NMR of **62** (376 MHz, Chloroform-*d*, 298 K)



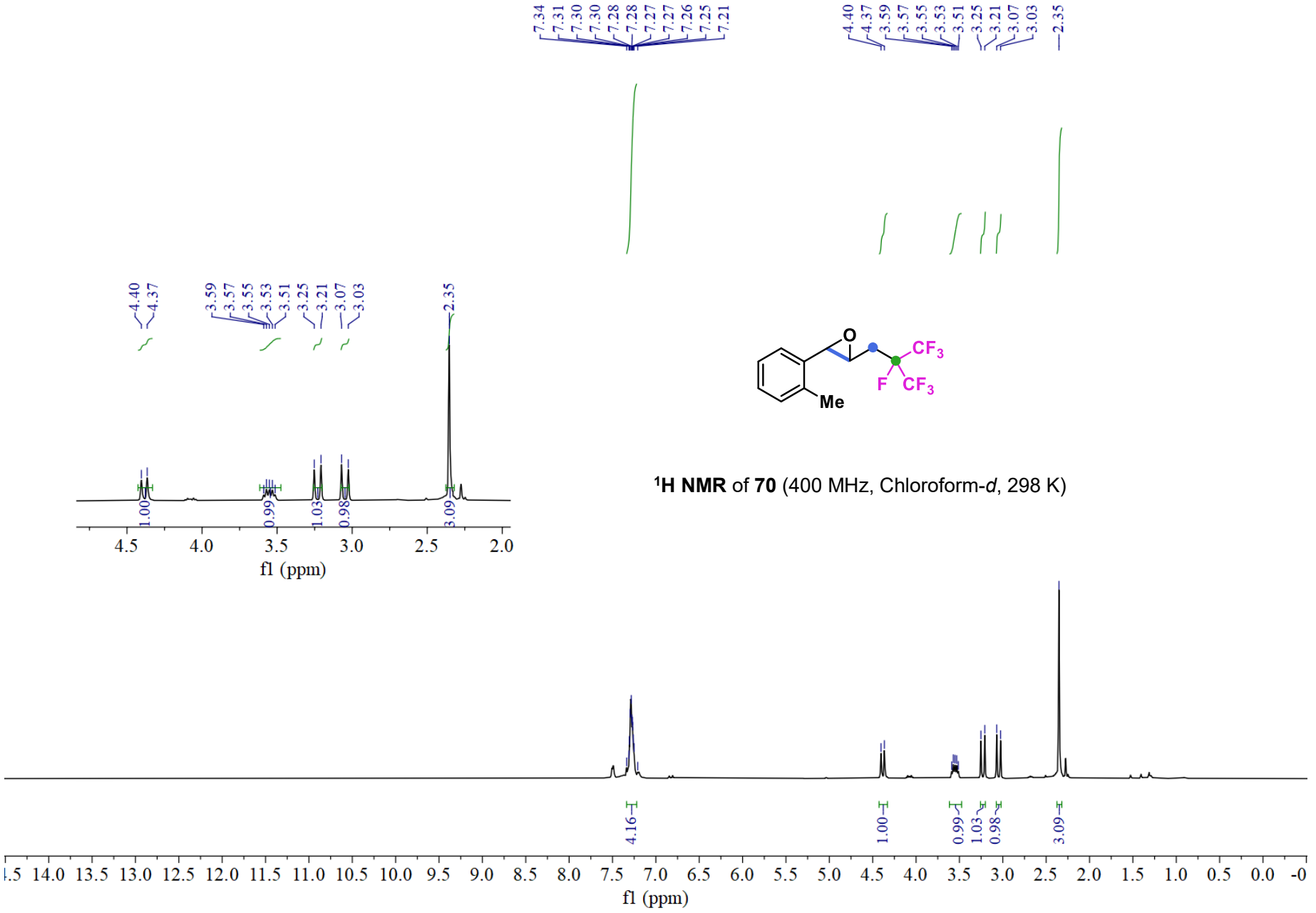
^{1}H NMR of **69** (400 MHz, Chloroform-*d*, 298 K)



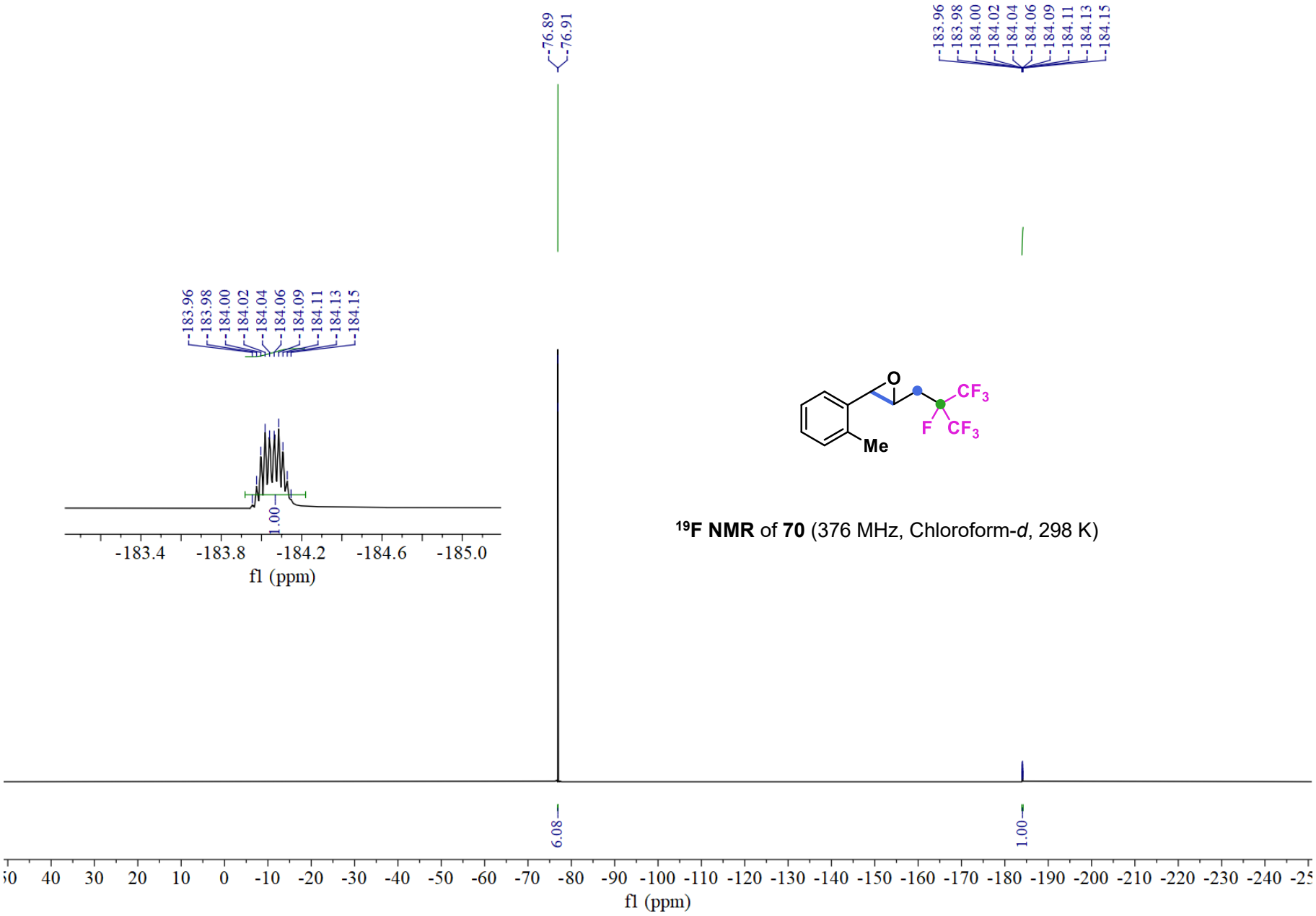
^{19}F NMR of **69** (376 MHz, Chloroform-*d*, 298 K)



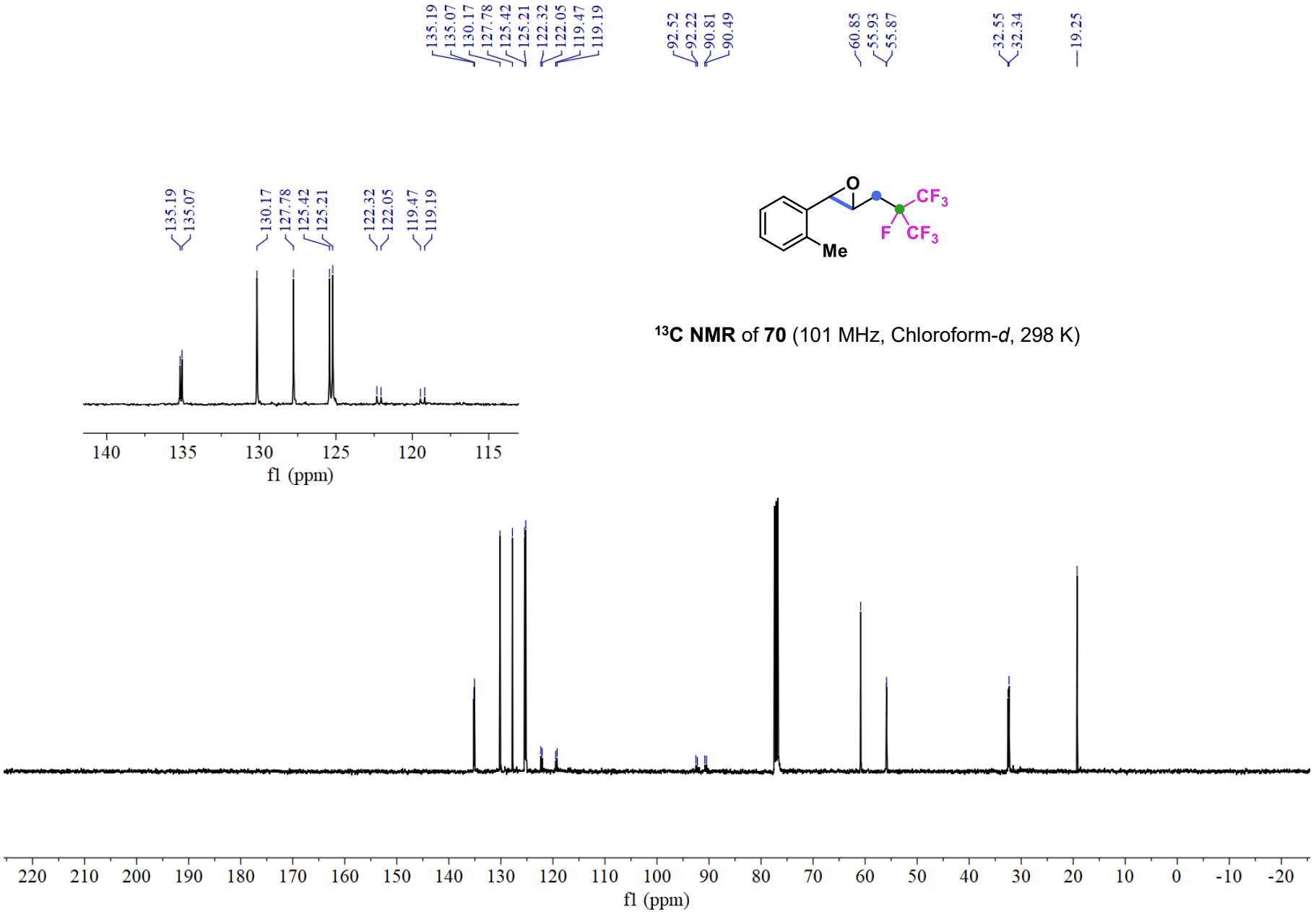
^{13}C NMR of **69** (101 MHz, Chloroform-*d*, 298 K)



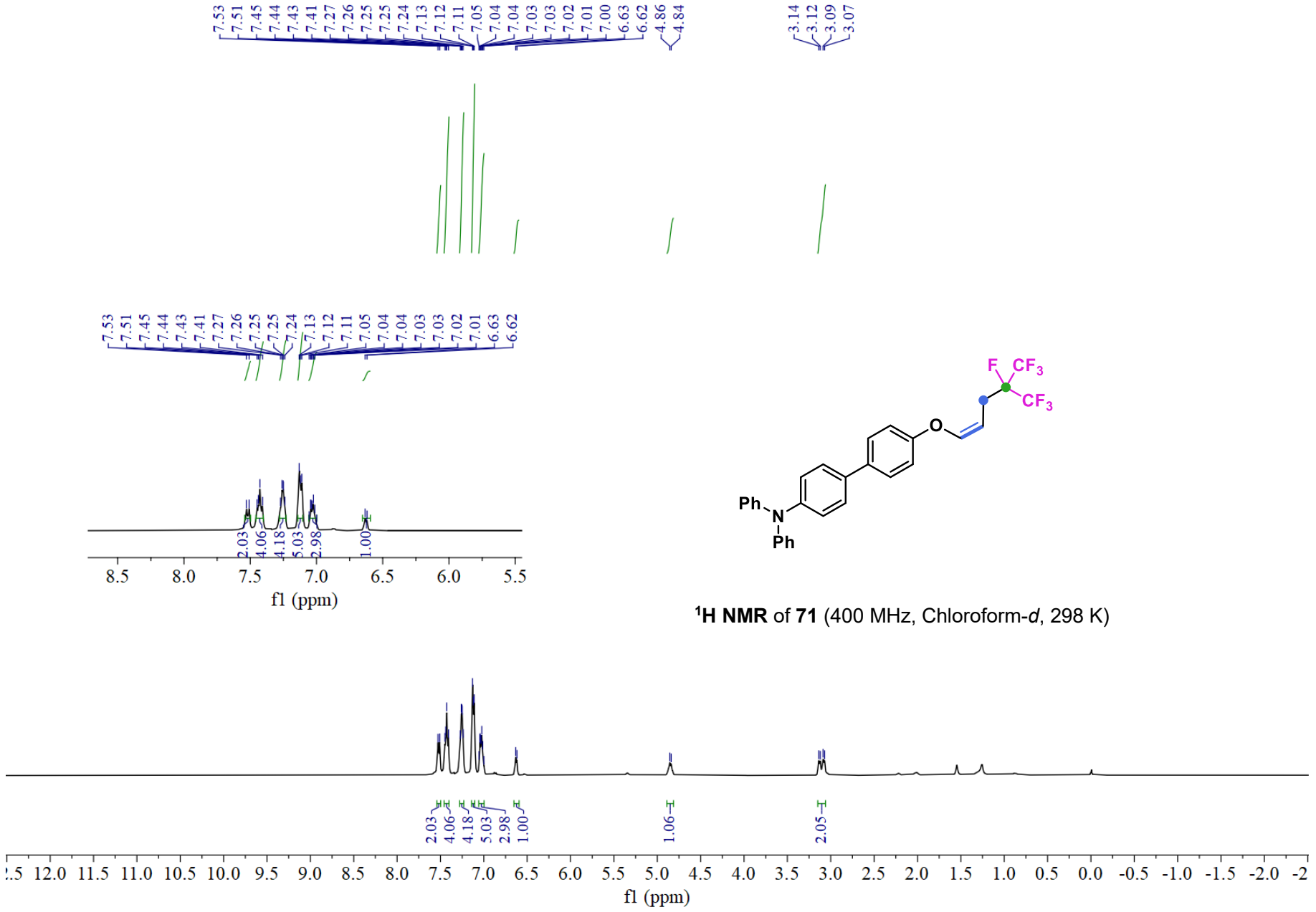
^{1}H NMR of **70** (400 MHz, Chloroform-*d*, 298 K)



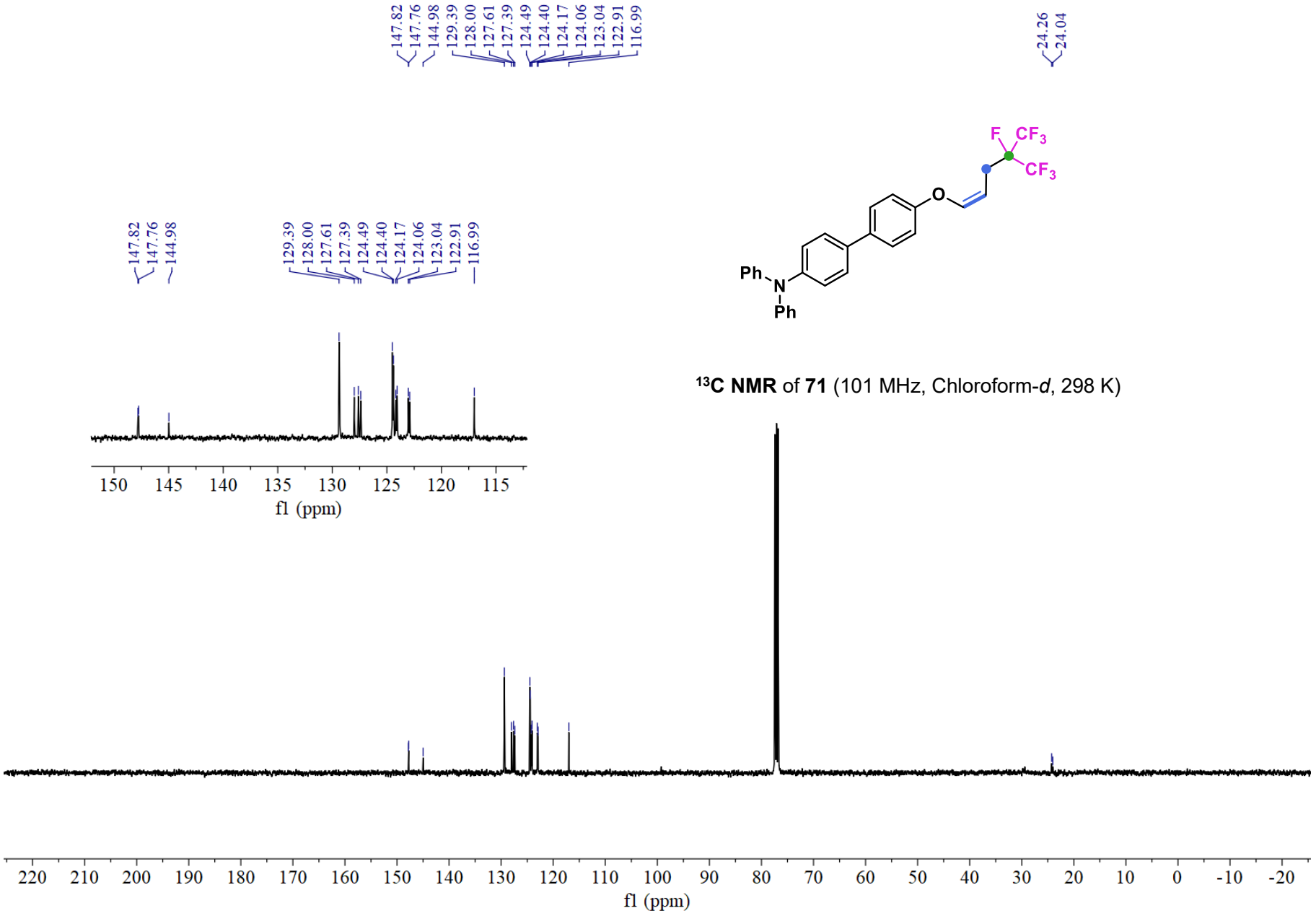
^{19}F NMR of **70** (376 MHz, Chloroform-*d*, 298 K)



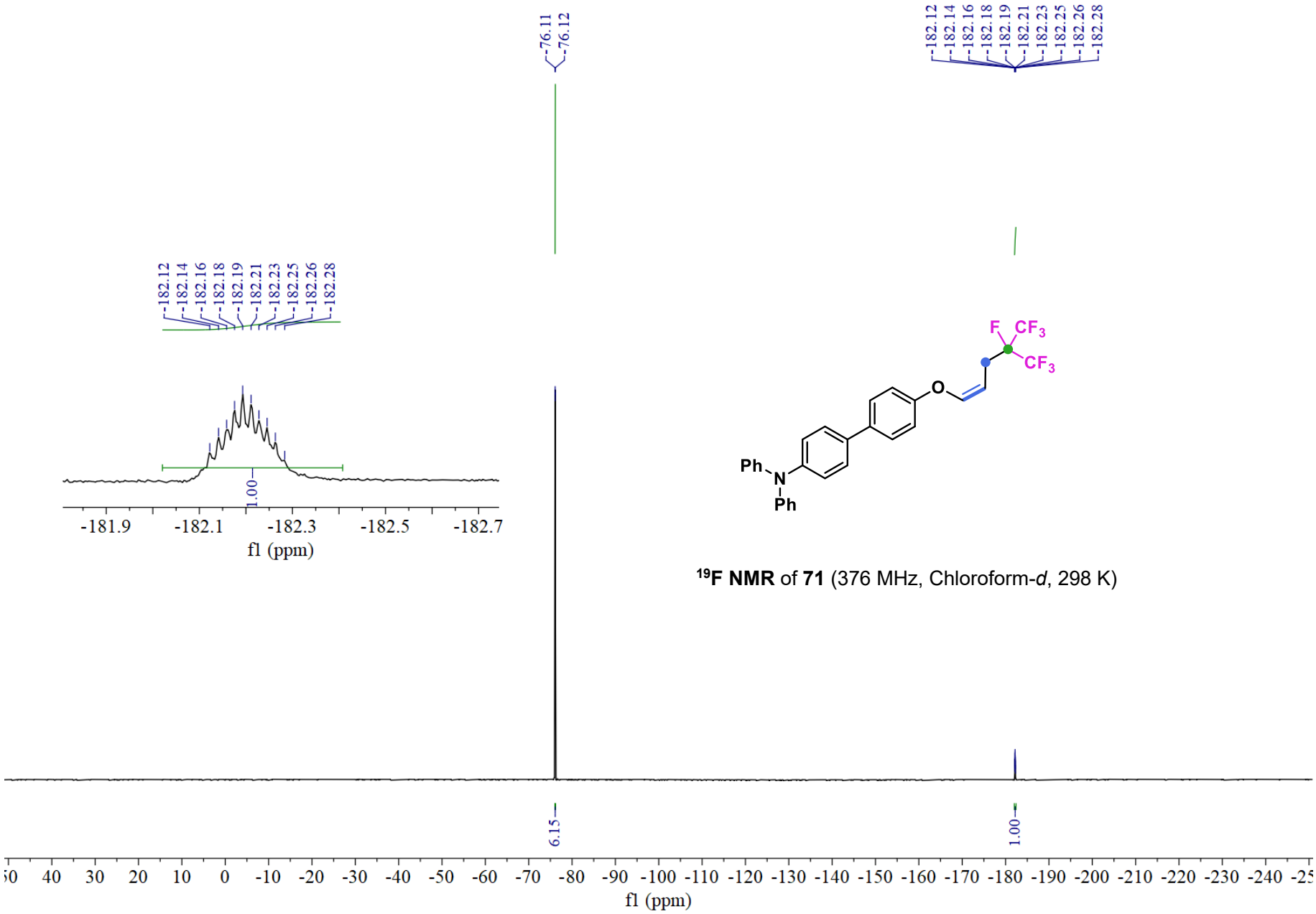
^{13}C NMR of **70** (101 MHz, Chloroform-*d*, 298 K)



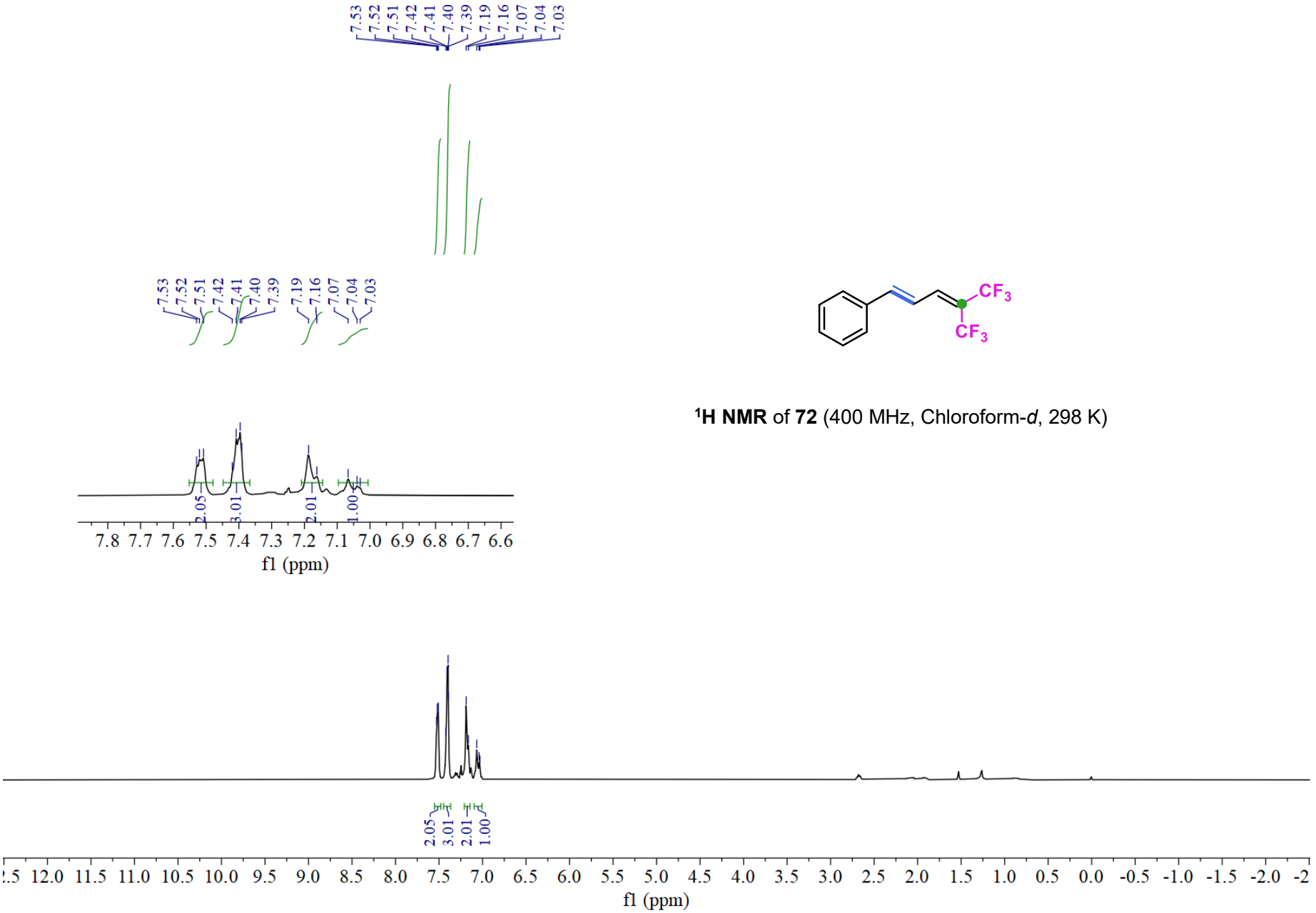
^{1}H NMR of **71** (400 MHz, Chloroform-*d*, 298 K)



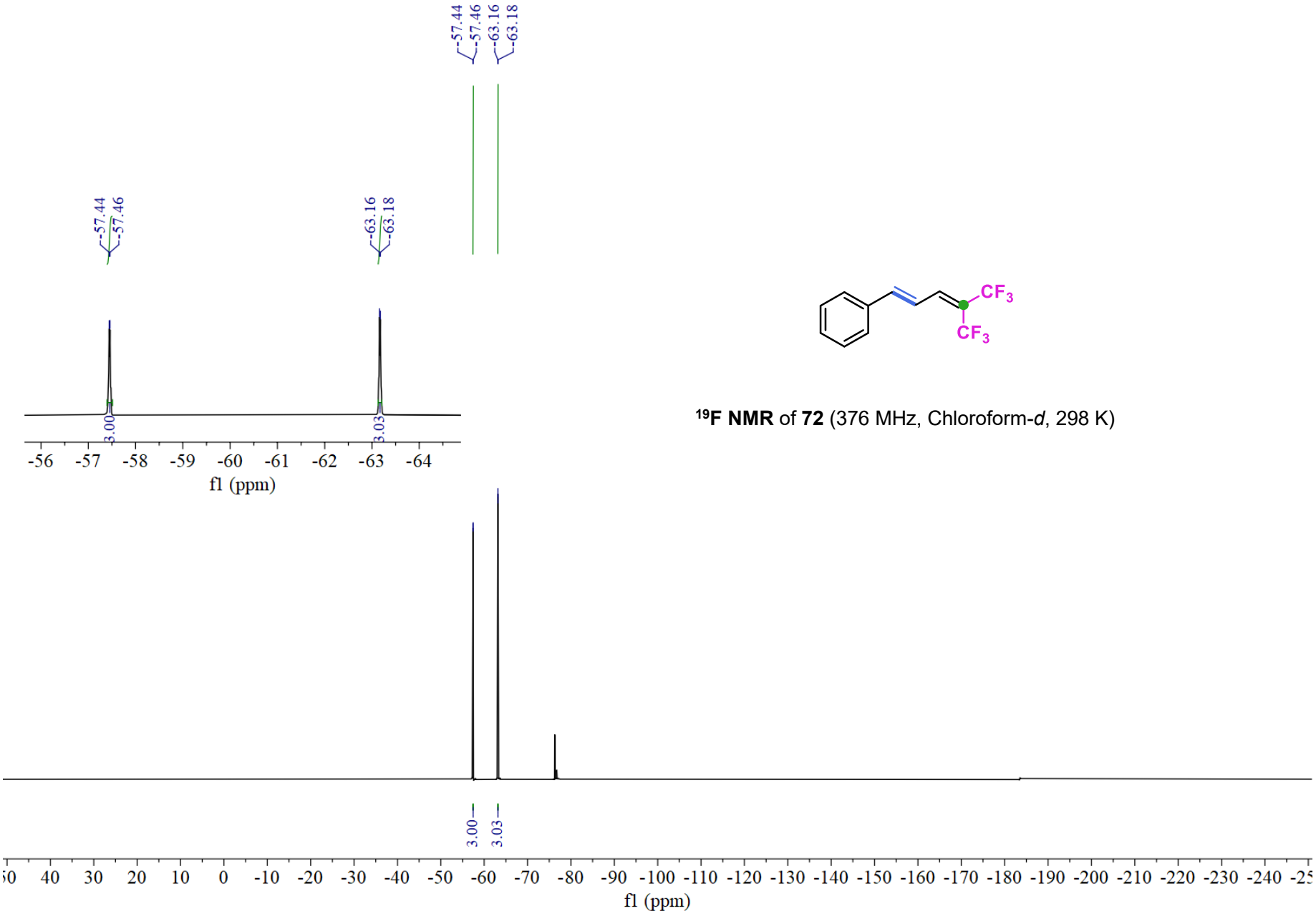
^{13}C NMR of **71** (101 MHz, Chloroform-*d*, 298 K)



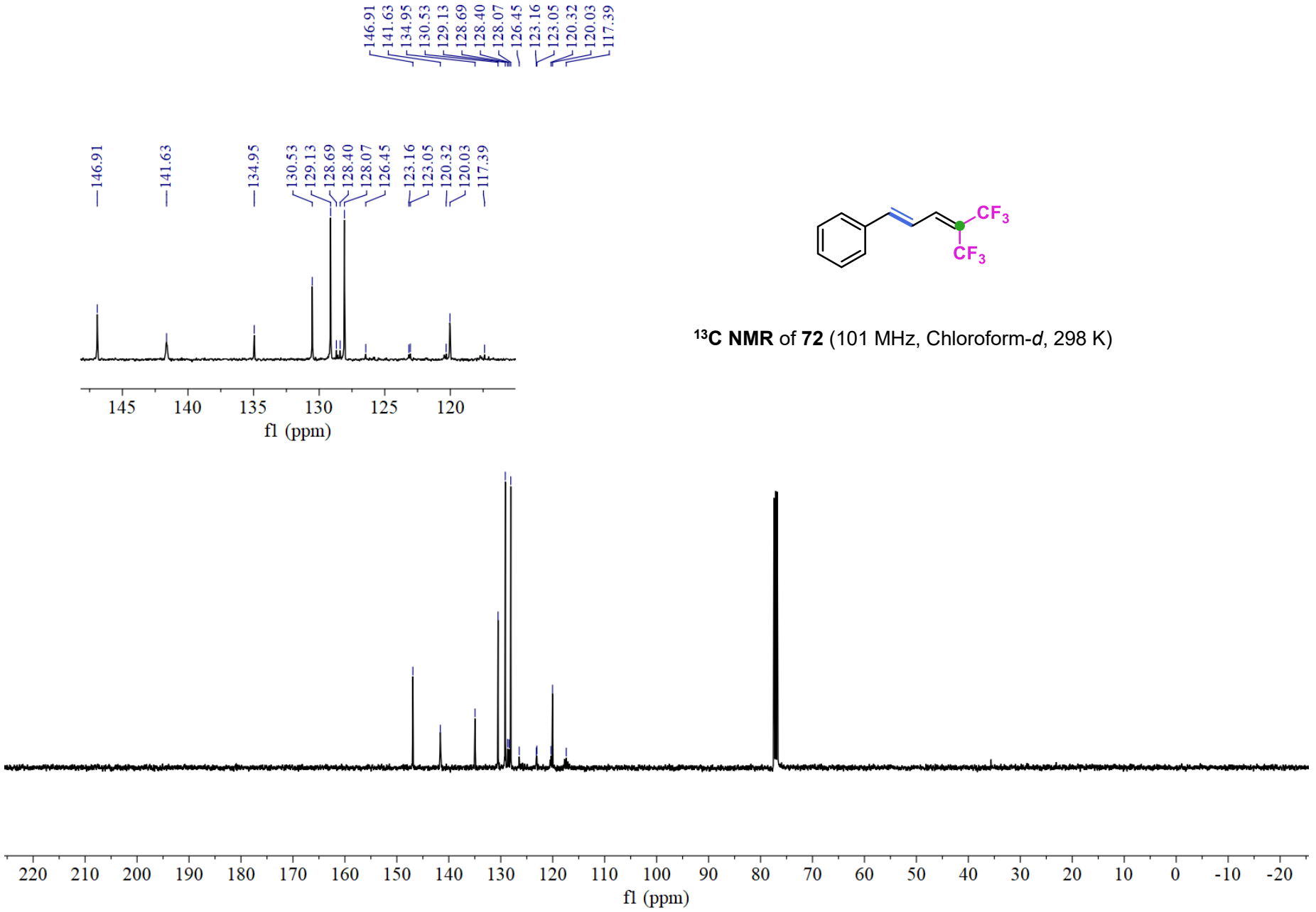
^{19}F NMR of **71** (376 MHz, Chloroform-*d*, 298 K)



^{1}H NMR of **72** (400 MHz, Chloroform-*d*, 298 K)



^{19}F NMR of **72** (376 MHz, Chloroform-*d*, 298 K)



^{13}C NMR of **72** (101 MHz, Chloroform-*d*, 298 K)

REFERENCRS

1. Matoušek, V.; Pietrasiak, E.; Schwenk, R.; Togni, A. *J. Org. Chem.* 2013, **78**, 6763.
2. Borrel, J.; Waser. J. *Org. Lett.* 2022, **24**, 142.
3. Li, Y.; Wang, X.; Guo, Y.; Zhu, Z.; Wu, Y.; Gong, Y. *Chem. Commun.* 2016, **52**, 796.
4. Wang, X.; Ye, Y.; Zhang, S.; Feng, J.; Xu, Y.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* 2011, **133**, 16410.
5. Zhang, K.; Liu, J. B.; Qing, F. L. *Chem. Commun*. 2014, **50**, 14157.
6. Wu, X.; Chu, L.; Qing, F. L. *Angew. Chem. Int. Ed.* 2013, **52**, 2198.
7. Gourab, K.; Theresa, S.; Kari, R.; Franziska, S. *Angew. Chem. Int. Ed.* 2020, **59**, 21930.
8. Wu, Z.; Wang, D.; Liu, Y.; Huan, L.; Zhu, C. *J. Am. Chem. Soc.* 2017, **139**, 1388.
9. Emilien, L. S.; Eleni, G.; Igor, A. D.; Will, C. H.; Paolo, M. *J. Am. Chem. Soc.* 2023, **145**, 47.
10. Peter, B.; Huang, H. M.; Teresa, F.; Laskar, R.; Glorius F. *Chem. Sci.* 2022, **13**, 7855.
11. Megerle, U.; Lechner, R.; König, B.; Riedle, E. *Photochem. Photobiol. Sci.* 2010, **9**, 1400.