Electronic Supplementary Material (ESI) for Green Chemistry.

C-H Fluorination Promoted by Pyridine *N*-Oxyl Radical

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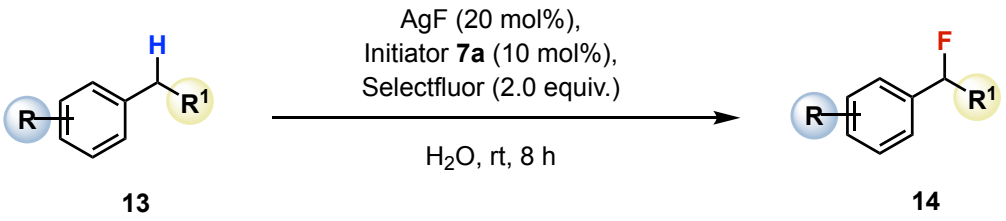
1. General Information

Flash chromatography was performed using silica gel purchased from Qingdao Haiyang. Mixtures of petroleum ether/ethyl acetate or dichloromethane/methanol were used as eluting solvents. AgF and Selectfluor were purchased from Energy Chemical and used as received. H_2O and *tert*-butanol served as reaction solvents, purchased from Adamas, and used as received.

All new compounds were characterized by NMR spectroscopy and high-resolution mass spectroscopy (HRMS). NMR spectra were recorded on a Bruker AMX 400 spectrometer and calibrated using TMS or residual deuterated solvent as an internal reference [$CDCl_3$: 7.26 ppm or 0.00 ppm (TMS) for ^1H NMR and 77.16 ppm for ^{13}C NMR]. The tabulated data were reported in ppm. HRMS spectra were recorded on a Waters Q-TOF Premier.

Figure S1. A Picture of Reaction Vials Used in this Study.

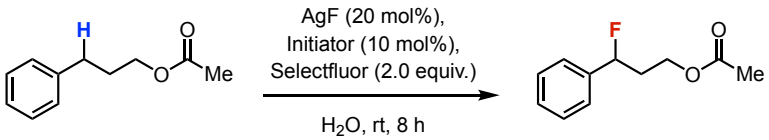
2. General Procedure for C-H Fluorination



General Procedure:

13 (1.0 equiv.), pyridine *N*-oxides **7** as initiator (10 mol%), Selectfluor (2.0 equiv.) and AgF (20 mol %.) were weighed into an 8 mL screw-capped vial equipped with a magnetic stir bar. The vial was loosely capped and transferred into a nitrogen-filled glovebox. The solvent was added to the vial. The vial was tightly sealed with a Teflon-lined cap and wrapped with black tape to stir for 8 hours. The reaction was extracted with ethyl acetate (2 mL x 3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subsequently subjected to silica gel chromatograph to give desired product **14.**

3. Condition Optimization

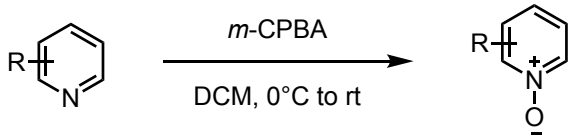


11 12

Entry	Deviation from standard situation	NMR Yield
1	none	85%
2	under air	n. d
3	with natural light	75%
4	2 h	34%
5	KF instead of Selectfluor	n. d
6	KF instead of AgF	n. d
7	add 2 equiv. KF	77%
8	*t*BuOH/H_2O = 1:4	84%
9	*t*BuOH/H_2O = 1:1	75%
10	MeCN	n. d
11	MeCN/H_2O = 1:1	22%
12	DCM	n. d

[a] Reactions were performed under N_2 atmosphere with 11 (0.1 mmol), Selectfluor (2.0 equiv.), AgF (20 mol%) and Initiator (10 mol%) in H_2O (1.0 mL) for 8 h. The reaction vial was encased with black tape to establish light-shielding conditions. NMR yields were determined by ^1H NMR spectroscopy with trimethyl benzene-1,3,5-tricarboxylate as an internal standard.

4. Procedure for the Preparation of Pyridine *N*-oxides



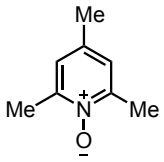
SI-1 **7**

The *N*-oxides used in this study were prepared following the reported procedures as shown below. All the *N*-oxides are known compounds, and the characterization data for these compounds were presented below. Data align consistently with previous reports. [1]

Procedure for the Preparation of Pyridine *N*-oxides:

m-CPBA (1.1 equiv.) was added slowly to a solution of pyridine (1.0 equiv.) in DCM at 0 °C, and the reaction mixture was stirred for 12 h at room temperature. The reaction mixture was concentrated, and the residue was subjected to flash-column chromatography (SiO_2, eluted with petroleum ether/ethyl acetate = 1:1 initially, then 5% MeOH in DCM, then 10% MeOH in DCM) to afford pyridine *N*-oxides.

5. Characterization Data for Pyridine *N*-oxides

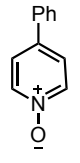


7a

2,4,6-trimethylpyridine 1-oxide (7a)

Following the **Procedure for the Preparation of Pyridine *N*-oxides**, **SI-1a** (1.2 g, 10 mmol), *m*-CPBA (2.4 g, 12 mmol), and DCM (30 mL) were used. The residue was purified by silica gel column chromatography (hexane: ethyl acetate = 1:1 initially, then 5% MeOH in DCM, then 10% MeOH in DCM) to afford the product as yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.96 (s, 2H), 2.51 (s, 6H), 2.28 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 148.32, 136.39, 132.15, 129.43, 127.90, 124.86, 20.28, 18.27.

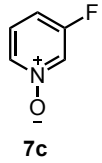


7b

4-phenylpyridine 1-oxide (7b)

Following the **Procedure for the Preparation of Pyridine *N*-oxides**, **SI-1b** (1.6 g, 10 mmol), *m*-CPBA (2.4 g, 12 mmol), and DCM (30 mL) were used. The residue was purified by silica gel column chromatography to afford the product as brown solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 7.1 Hz, 2H), 7.79–7.37 (m, 7H).

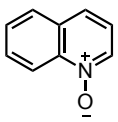


7c

3-fluoropyridine 1-oxide (7c)

Following the **Procedure for the Preparation of Pyridine *N*-oxides**, **SI-1c** (970 mg, 10 mmol), *m*-CPBA (2.4 g, 12 mmol), and DCM (30 mL) were used. The residue was purified by silica gel column chromatography to afford the product as white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (dt, *J* = 4.3, 2.0 Hz, 1H), 8.10 (d, *J* = 8.7 Hz, 1H), 7.33–7.25 (m, 1H), 7.15–7.07 (m, 1H).



7d

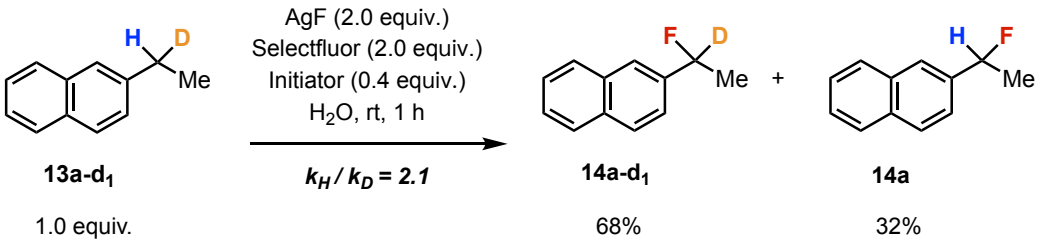
3-(trifluoromethyl)pyridine 1-oxide (7d)

Following the **Procedure for the Preparation of Pyridine *N*-oxides**, **SI-1d** (1.3 g, 10 mmol), *m*-CPBA (2.4 g, 12 mmol), and DCM (30 mL) were used. The residue was purified by silica gel column chromatography (hexane: ethyl acetate =1:1) to afford the product as brown solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 (d, *J* = 8.8 Hz, 1H), 8.54 (d, *J* = 6.0 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.82–7.70 (m, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.33–7.25 (m, 1H).

6. Mechanistic Studies

The Intramolecular Kinetic Isotope Effect Study



13a-d$_1$ 1.0 equiv.

k_H / k_D = 2.1

14a-d$_1$ 68%

14a 32%

13a-*d*$_1$ (1.0 equiv.), **7a** (0.4 equiv.), Selectfluor (2.0 equiv.) and AgF (2.0 equiv.) were weighed into an 8 mL screw-capped vial containing a magnetic stir bar. The vial was loosely capped and transferred into a nitrogen-filled glovebox. H_2O was added to the vial, and it was tightly sealed with a Teflon-lined cap. The entire setup was then wrapped with black tape and stirred for 1 hour. The ratio of **14a-*d*$_1$: 14a** was determined by ^{19}F NMR on a Bruker AMX 400 spectrometer instrument to be 68:32.

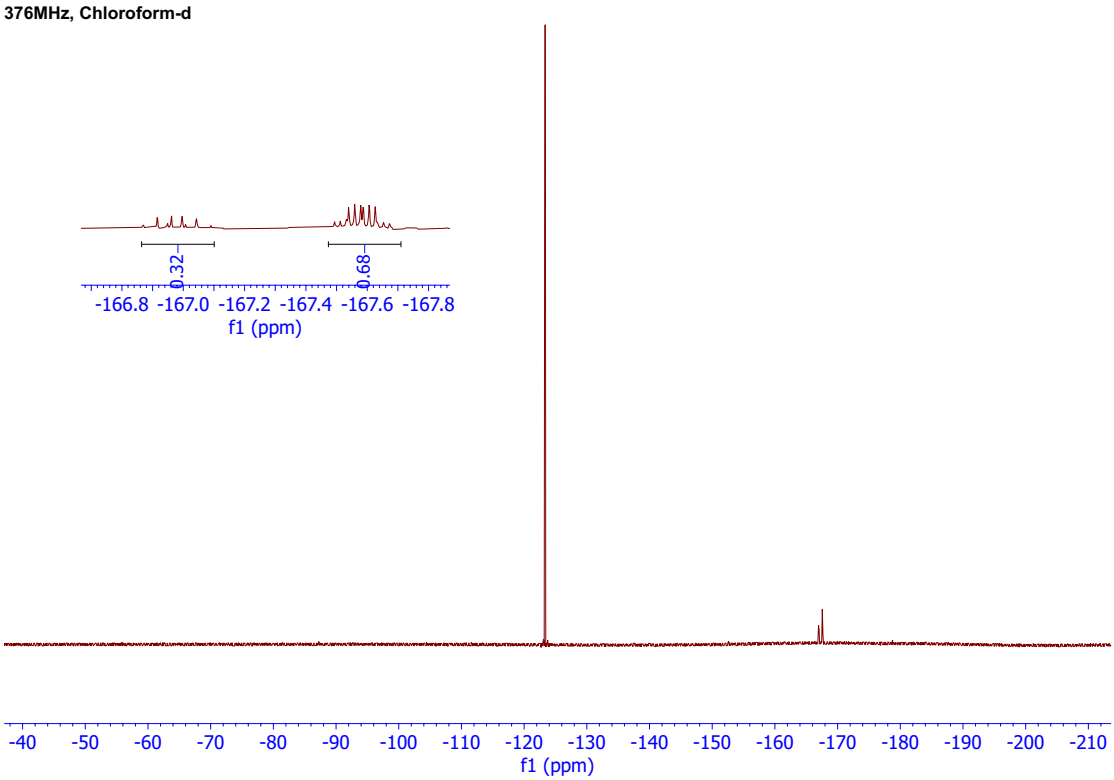
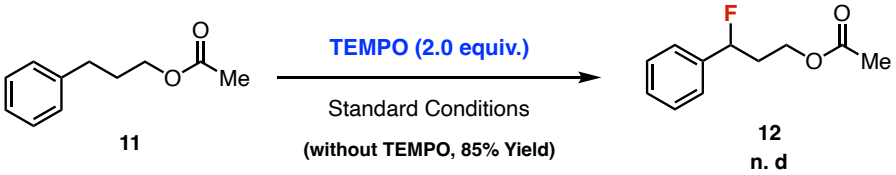


Figure S2. ^{19}F NMR of the Intramolecular Kinetic Isotope Effect Study.

Radical Trap Experiments

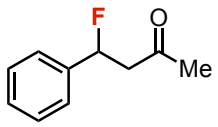


11

12
n. d

According to the **general procedure**，**11** (1.0 equiv.), pyridine *N*-oxides **7a** as initiator (10 mol%), Selectfluor (2.0 equiv.), AgF (20 mol %.) and TEMPO(2.0 equiv.) were weighed into an 8 mL screw-capped vial equipped with a magnetic stir bar. The vial was loosely capped and transferred into a nitrogen-filled glovebox. The solvent was added to the vial. The vial was tightly sealed with a Teflon-lined cap and wrapped with black tape to stir for 8 hours. The reaction was extracted with ethyl acetate (2 mL x 3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Fluorination product **12** was not detected.

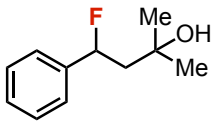
7. Characterization Data for C-H Fluorination Products



4-fluoro-4-phenylbutan-2-one (14a)

Following the **General Procedure, 13a** (14.8 mg, 0.1 mmol), AgF (2.5 mg, 20 mol%), **7a** (1.4 mg, 10 mol%), and H_2O (1 mL) were used. **14a** was obtained as yellow solid. (94% NMR yield). Once the residue was purified by silica gel column chromatography (hexane: EtOAc = 10:1), a 1:1 mixture of **14a** and trans-4-phenyl-3-buten-2-one (elimination product) was obtained when purified by silica gel chromatograph.[2]

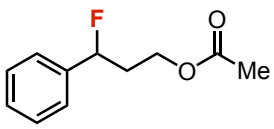
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41–7.33 (m, 5H), 5.95 (ddd, *J* = 46.9, 8.8, 4.0 Hz, 1H), 3.20 (ddd, *J* = 16.7, 14.7, 8.8 Hz, 1H), 2.82 (ddd, *J* = 32.1, 16.7, 4.0 Hz, 1H), 2.22 (s, 3H). **^{19}F NMR (376MHz, Chloroform-*d*)** δ -173.87 (d, *J* = 32.5 Hz), -173.96 – -174.46 (m). Characterization data are consistent with previous reports.[3]



4-fluoro-2-methyl-4-phenylbutan-2-ol (14b)

Following the **General Procedure, 13b** (16.4 mg, 0.1 mmol), AgF (2.5 mg, 20 mol%), **7a** (1.4 mg, 10 mol%), and H_2O (1 mL) were used. The residue was purified by silica gel column chromatography (hexane: EtOAc = 10:1) to afford the product as colorless oil (12.7 mg, 70% yield).

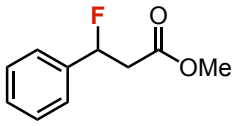
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45–7.24 (m, 5H), 5.79 (ddd, J = 49.1, 10.2, 2.4 Hz, 1H), 2.24 (td, J = 15.7, 10.2 Hz, 1H), 2.01–1.67 (m, 2H), 1.36 (d, J = 6.2 Hz, 6H).**^{13}C NMR (101 MHz, Chloroform-*d*)** δ 139.67, 139.47, 127.53, 127.49, 127.38, 127.34, 124.45, 124.39, 92.50, 92.48, 90.83, 90.81, 69.14, 49.30, 49.09, 29.73, 29.23. **^{19}F NMR (376MHz, Chloroform-*d*)** δ -173.31. Characterization data are consistent with previous reports. [4]



3-fluoro-3-phenylpropyl acetate (14c)

Following the **General Procedure, 13c** (17.8 mg, 0.1 mmol), AgF (2.5 mg, 20 mol%), **7a** (1.4 mg, 10 mol%), and H_2O (1 mL) were used. The residue was purified by silica gel column chromatography (hexane: EtOAc = 10:1) to afford the product as colorless oil (16.4mg, 84% yield).

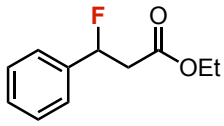
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (m, 5H), 5.57 (ddd, *J* = 47.8, 8.8, 4.3 Hz, 1H), 4.32–4.15 (m, 2H), 2.37–2.09 (m, 2H), 2.05 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.95, 139.58, 139.39, 128.61, 125.52, 125.45, 92.22, 90.59, 60.50, 60.45, 36.36, 36.12, 20.92. **^{19}F NMR (376MHz, Chloroform-*d*)** δ -177.39. Characterization data are consistent with previous reports. .[3]



Methyl-3-fluoro-3-phenylpropanoate (14d)

Following the **General Procedure, 13d** (16.4 mg, 0.1 mmol), AgF (2.5 mg, 20 mol%), **7a** (1.4 mg, 10 mol%), and H_2O (1 mL) were used. The residue was purified by silica gel column chromatography (hexane: EtOAc = 10:1) to afford the product as colorless oil. (14.6mg, 80% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47–7.31 (m, 5H), 5.93 (ddd, *J* = 46.9, 9.2, 4.1 Hz, 1H), 3.74 (s, 3H), 3.04 (ddd, *J* = 16.0, 13.5, 9.1 Hz, 1H), 2.80 (ddd, *J* = 32.6, 16.0, 4.1 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.26, 170.22, 138.80, 138.61, 128.98, 128.96, 128.79, 125.71, 125.65, 91.55, 89.84, 52.15, 42.50, 42.23. **^{19}F NMR (376MHz, Chloroform-*d*)** δ -173.18. Characterization data are consistent with previous reports. .[3]

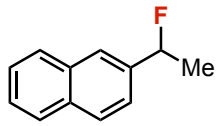


Ethyl-3-fluoro-3-phenylpropanoate (14e)

Following the **General Procedure, 13e** (17.8 mg, 0.1 mmol), AgF (2.5 mg, 20 mol%), **7a** (1.4 mg, 10 mol%), and H_2O (1 mL) were used. The residue was purified by silica gel column chromatography (hexane: EtOAc = 10:1) to afford the product as colorless oil (10.4mg, 53% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 6.0 Hz, 5H), 5.92 (ddd, *J* = 47.0, 9.1, 4.3 Hz, 1H), 4.19 (qd, *J* = 7.2, 1.8 Hz, 2H), 3.03 (ddd, *J* = 16.0, 13.6, 9.2 Hz, 1H), 2.79 (ddd, *J* = 32.3, 16.0, 4.2 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.74, 138.88, 138.69, 128.93, 128.75, 125.75, 125.68, 91.62, 89.90, 61.08, 42.74, 42.47, 14.22. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -173.02 (ddd, *J* = 46.4, 32.4, 13.2 Hz). Characterization data are consistent with previous reports. [5]

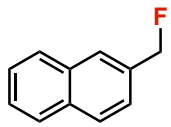
2-(1-fluoroethyl)naphthalene (14f)



Following the **General Procedure, 13f** (15.6 mg, 0.1 mmol), AgF (6.3 mg, 50 mol%), **7a** (1.4 mg, 10 mol%), and H_2O (1 mL) were used. The residue was purified by silica gel column chromatography (hexane) to afford the product as yellow oil (7.1mg, 41% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95–7.75 (m, 4H), 7.48 (ddd, J = 9.2, 5.8, 2.0 Hz, 3H), 5.79 (dq, J = 47.6, 6.4 Hz, 1H), 1.73 (dd, J = 23.8, 6.4 Hz, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)** δ 137.89, 137.70, 132.14, 132.06, 127.35, 127.06, 126.69, 125.29, 125.17, 123.19, 123.11, 122.12, 122.06, 90.95, 89.28, 22.07, 21.81. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -166.99 (d, *J* = 2.2 Hz). Characterization data are consistent with previous reports.[6]

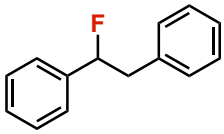
2-(fluoromethyl)naphthalene (14g)



Following the **General Procedures, 13g** (14.2 mg, 0.1 mmol), AgF (6.3 mg, 50 mol%), **7a** (1.4 mg, 10 mol%), and H_2O (1 mL) were used. The residue was purified by silica gel column chromatography (hexane) to afford the product as yellow oil (27% NMR yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92–7.81 (m, 4H), 7.56–7.44 (m, 3H), 5.54 (d, *J* = 47.8 Hz, 2H).**^{13}C NMR (101 MHz, Chloroform-*d*)** δ 133.80, 133.63, 133.47, 133.21, 128.60, 128.20, 127.87, 126.86, 126.79, 126.58, 126.50, 125.10, 85.71, 84.06. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -206.55, -206.62, -206.76, -206.82, -206.89, -207.03, -207.09. Characterization data are consistent with previous reports.[7]

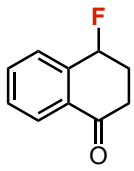
(1-fluoroethane-1,2-diyl)dibenzene (14h)



Following the **General Procedure, 13h** (18.2 mg, 0.1 mmol), AgF (12.1 mg, 1.0 equiv.), **7a** (1.4 mg, 10 mol%), and *t*BuOH/H_2O = 1:1 (1 mL) were used. The residue was purified by silica gel column chromatography (hexane: EtOAc = 49:1) to afford the product as colorless oil. (7.8mg, 39% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38–7.20 (m, 8H), 7.22–7.15 (m, 2H), 5.61 (ddd, *J* = 47.3, 8.1, 4.8 Hz, 1H), 3.27 (ddd, *J* = 17.5, 14.2, 8.1 Hz, 1H), 3.10 (ddd, *J* =

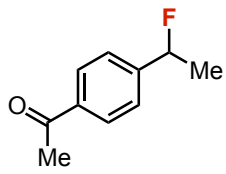
28.5, 14.2, 4.8 Hz, 1H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 138.86, 138.66, 135.68, 135.64, 128.49, 127.36, 127.35, 127.33, 125.67, 124.67, 124.60, 94.74, 94.71, 93.01, 92.98, 43.04, 42.80; **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -173.17. Characterization data are consistent with previous reports[8]



4-fluoro-3,4-dihydronaphthalen-1(2*H*)-one (14i)

Following the **General Procedure, 13i** (14.6 mg, 0.1 mmol), AgF (2.5 mg, 20 mol%), **7a** (1.4 mg, 10 mol%), and H_2O (1 mL) were used. The residue was purified by silica gel column chromatography (hexane: EtOAc = 8:1) to afford the product as yellow oil (5.9 mg, 36% yield).

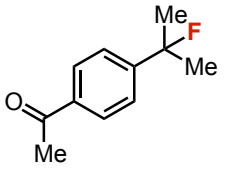
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.59–7.47 (m, 2H), 5.74 (dt, *J* = 50.4, 5.1 Hz, 1H), 3.03–2.92 (m, 1H), 2.65 (dt, *J* = 17.3, 6.4 Hz, 1H), 2.55–2.41 (m, 2H).**^{13}C NMR (101 MHz, Chloroform-*d*)** 196.68, 140.33, 140.15, 134.24, 131.48, 129.80, 129.77, 128.16, 128.10, 127.22, 88.65, 86.94, 34.03, 33.96, 29.80, 29.45, 29.23,. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -170.27 – -170.58 (m). Characterization data are consistent with previous reports.[9]



1-(4-(1-fluoroethyl)phenyl)ethan-1-one (14j)

Following the **General Procedure, 13j** (14.8 mg, 0.1 mmol), AgF (2.5 mg, 20 mol%), **7a** (1.4 mg, 10 mol%), and H_2O (1 mL) were used. The residue was purified by silica gel column chromatography (hexane: EtOAc = 97:3) to afford the product as yellow oil. (13.4 mg, 81% yield).

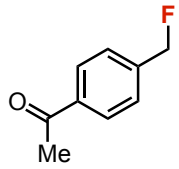
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 5.68 (dq, *J* = 47.6, 6.5 Hz, 1H), 2.61 (s, 3H), 1.65 (dd, *J* = 24.0, 6.5 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 197.84, 146.88, 146.68, 136.86, 128.71, 125.23, 125.15, 91.25, 89.56, 26.79, 23.23, 22.99. **^{19}F NMR (376 MHz, Chloroform-*d*)** -171.22, -170.88– -171.83 (m). Characterization data are consistent with previous reports. [2]



1-(4-(2-fluoropropan-2-yl)phenyl)ethan-1-one (14k)

Following the **General Procedure, 13k** (16.2mg, 0.1 mmol), AgF (2.5 mg, 20 mol%), **7a** (1.4 mg, 10 mol%), and H_2O (1 mL) were used. The residue was purified by silica gel column chromatography (hexane: EtOAc = 97:3) to afford the product as yellow oil. (7.4 mg, 41% yield).

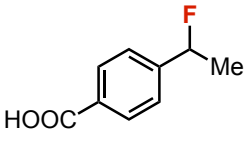
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.57–7.44 (m, 2H), 2.61 (s, 3H), 1.70 (d, *J* = 21.9 Hz, 6H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -138.79, -138.84, -138.89, -138.94, -138.99, -139.04, -139.09. Characterization data are consistent with previous reports. [2]



1-(4-(fluoromethyl)phenyl)ethan-1-one (14l)

Following the **General Procedure, 13l** (13.4 mg, 0.1 mmol), AgF (2.5 mg, 20 mol%), **7a** (1.4 mg, 10 mol%), and H_2O (1 mL) were used. The residue was purified by silica gel column chromatography (hexane: EtOAc = 97:3) to afford the product as yellow oil. (9.3mg, 61% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04–7.87 (m, 2H), 7.45 (dd, *J* = 8.3, 1.6 Hz, 2H), 5.44 (d, *J* = 47.2 Hz, 2H), 2.61 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 197.76, 141.53, 141.36, 137.21, 137.18, 128.70, 126.90, 126.84, 84.56, 82.88, 26.76. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -212.86 (d, *J* = 3.4 Hz), -213.02, -213.06 (t, *J* = 3.4 Hz), -213.25 (d, *J* = 3.4 Hz). Characterization data are consistent with previous reports. [10]

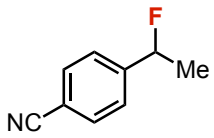


4-(1-fluoroethyl)benzoic acid (14m)

Following the **General Procedure, 13m** (15.0 mg, 0.1 mmol), AgF (2.5 mg, 20 mol%), **7a** (1.4 mg, 10 mol%), and H_2O (1 mL) were used. The residue was purified by preparative TLC (hexane: EtOAc = 7:3) to afford the product as white solid. (41% NMR yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 7.9 Hz, 2H), 7.44 (s, 2H), 5.70 (dq, *J* = 47.4, 6.3 Hz, 1H), 1.66 (dd, *J* = 24.1, 6.5 Hz, 3H). δ **^{19}F NMR (376 MHz,**

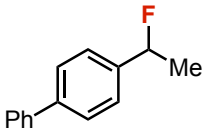
Chloroform-*d*) δ -171.66 (d, *J* = 4.2 Hz). Characterization data are consistent with previous reports.[4]



4-(1-fluoroethyl)benzonitrile (14n)

Following the **General Procedure, 13n** (13.1 mg, 0.1 mmol), AgF (2.5 mg, 20 mol%), **7b** (1.7 mg, 10 mol%), and H_2O (1 mL) were used. The residue was purified by silica gel column chromatography (hexane: EtOAc = 20:1) to afford the product as yellow oil. (9.4mg, 63% yield).

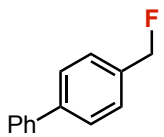
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 5.67 (dq, *J* = 47.4, 6.5 Hz, 1H), 1.64 (dd, *J* = 24.0, 6.4 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 146.91, 146.71, 132.50, 125.68 (d, *J* = 7.8 Hz), 118.69, 112.06, 90.82, 89.12, 23.18, 22.94. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -172.67 (d, *J* = 2.8 Hz). Characterization data are consistent with previous reports. [2]



4-(1-fluoroethyl)-1,1'-biphenyl (14o)

Following the **General Procedures, 13o** (18.2 mg, 0.1 mmol), AgF (2.5 mg, 20 mol%), **7a** (1.4 mg, 10 mol%), and *t*BuOH/H_2O = 1:1 (1 mL) were used. The residue was purified by silica gel column chromatography (hexane) to afford the product as white solid. (69% NMR yield).

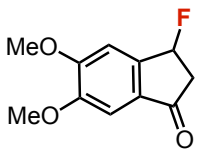
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 8.0, 5.8 Hz, 4H), 7.44 (t, *J* = 7.9 Hz, 4H), 7.41–7.30 (m, 1H), 5.68 (dq, *J* = 47.7, 6.4 Hz, 1H), 1.69 (dd, *J* = 23.8, 6.4 Hz, 3H). **^{19}F NMR (376 MHz, Chloroform-*d*)** -166.61 (dq, *J* = 15.2, 10.1 Hz). Characterization data are consistent with previous reports.[6]



4-(1-fluoroethyl)-1,1'-biphenyl (14p)

Following the **General Procedure, 13p** (16.8 mg, 0.1 mmol), AgF (6.3 mg, 50 mol%), **7a** (1.4 mg, 10 mol%), and *t*BuOH/H_2O=1:1 (1mL) were used. The residue was purified by silica gel column chromatography (hexane) to afford the product as white solid. (66% NMR yield).

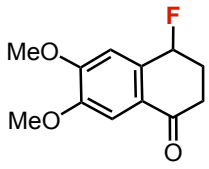
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66–7.55 (m, 4H), 7.50–7.42 (m, 4H), 7.40–7.34 (m, 1H), 5.42 (d, *J* = 47.9 Hz, 2H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -206.03 (d, *J* = 4.0 Hz), -206.23 (t, *J* = 3.8 Hz), -206.42 (d, *J* = 4.1 Hz). Characterization data are consistent with previous reports. [7]



3-fluoro-5,6-dimethoxy-2,3-dihydro-1*H*-inden-1-one (14q)

Following the **General Procedure, 13q** (19.2 mg, 0.1 mmol), AgF (6.3 mg, 50 mol%), **7a** (1.4 mg, 10 mol%), and H_2O (1 mL) were used. The residue was purified by silica gel column chromatography (hexane: EtOAc = 8:1) to afford the product as white solid. (9.2mg, 44% yield).

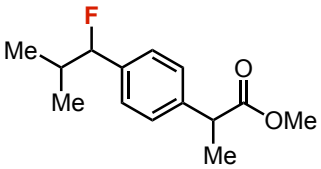
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24–7.10 (m, 2H), 6.10 (ddd, *J* = 56.4, 6.4, 1.9 Hz, 1H), 4.01 (s, 3H), 3.95 (s, 3H), 3.10 (ddd, *J* = 18.3, 11.5, 6.4 Hz, 1H), 2.85 (ddd, *J* = 23.2, 18.9, 2.0 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 198.78, 154.80, 154.77, 150.90, 144.32, 144.14, 129.39, 129.37, 106.12, 102.63, 87.90, 86.14, 55.44, 55.40, 55.27, 55.23, 43.23, 43.02. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -167.69. **HRMS (ESI)** calculated for $C_{11}H_{12}FO_3^+$ $[M+H]^+$ m/z 211.0765, found 211.0766.



4-fluoro-6,7-dimethoxy-3,4-dihydronaphthalen-1(2*H*)-one (14r)

Following the **General Procedure, 13r** (20.6 mg, 0.1 mmol), AgF (6.3 mg, 50 mol%), **7a** (1.4 mg, 10 mol%), and H_2O (1 mL) were used. The residue was purified by silica gel column chromatography (hexane: EtOAc = 8:1) to afford the product as yellow solid (8.9mg, 40% yield).

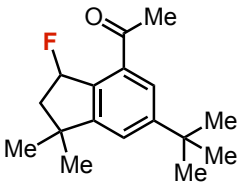
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (s, 1H), 6.98 (s, 1H), 5.84–5.57 (m, 1H), 3.97 (d, *J* = 16.6 Hz, 6H), 3.01–2.80 (m, 1H), 2.61 (dt, *J* = 10.3, 5.7 Hz, 1H), 2.52–2.33 (m, 2H).**^{13}C NMR (101 MHz, Chloroform-*d*)** δ 195.59, 154.01, 135.09, 134.92, 125.19, 109.53, 109.47, 108.44, 88.75, 87.04, 56.36, 56.24, 33.72, 33.65, 29.84, 29.62. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -169.30– -169.55 (m). Characterization data are consistent with previous reports.[11]



Methyl-2-(4-(1-fluoro-2-methylpropyl)-phenyl)propanoate (14s)

Following the **General Procedure, 13s** (22.0 mg, 0.1 mmol), AgF (6.3 mg, 50 mol %), **7a** (1.4 mg, 10 mol %), and *t*BuOH/H_2O = 1:1 (1 mL) were used. The residue was purified by silica gel column chromatography (hexane: EtOAc = 10:1) to afford the product as colorless oil (16.7mg, 70% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37–7.13 (m, 4H), 5.08 (dd, *J* = 47.0, 6.8 Hz, 1H), 3.73 (q, *J* = 7.2 Hz, 1H), 3.66 (s, 3H), 2.09 (ddt, *J* = 23.7, 13.6, 6.8 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 2H), 1.02 (d, *J* = 7.7 Hz, 2H), 0.85 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 173.88, 139.33, 139.31, 137.37, 137.16, 129.61, 126.30, 125.48, 125.41, 98.93, 98.91, 97.21, 97.18, 51.07, 51.04, 51.01, 50.98, 44.14, 44.11, 33.34, 33.12, 17.55, 17.35, 17.29, 16.54, 16.49. **^{19}F NMR (376 MHz, Chloroform-*d*)** -179.64 (d, *J* = 8.4 Hz). Characterization data are consistent with previous reports. [11]



1-(6-(tert-butyl)-3-fluoro-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)ethan-1-one (14t)

Following the **General Procedure, 13t** (24.4 mg, 0.1 mmol), AgF (6.3 mg, 50 mol%), **7a** (1.4 mg, 10 mol%), and *t*BuOH/H_2O = 1:1 (1 mL) were used. The residue was purified by silica gel column chromatography (hexane: EtOAc = 9:1) to afford the product as white solid. (11.0mg, 42% yield)[11]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, J = 1.8 Hz, 1H), 7.43 (t, J = 1.6 Hz, 1H), 6.44 (ddd, J = 54.0, 6.1, 1.5 Hz, 1H), 2.66 (s, 3H), 2.38–2.08 (m, 2H), 1.36 (d, J = 13.6 Hz, 15H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 198.64, 154.82, 154.77, 153.15, 153.11, 134.12, 133.96, 133.87, 124.56, 124.53, 122.55, 122.52, 93.56, 91.85, 47.46, 47.24, 41.70, 41.68, 34.07, 30.48, 30.34, 28.00, 27.95, 27.61, 27.57. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -158.61. Characterization data are consistent with previous reports. [11]

8. Reference

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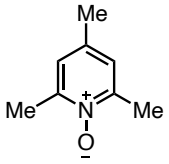
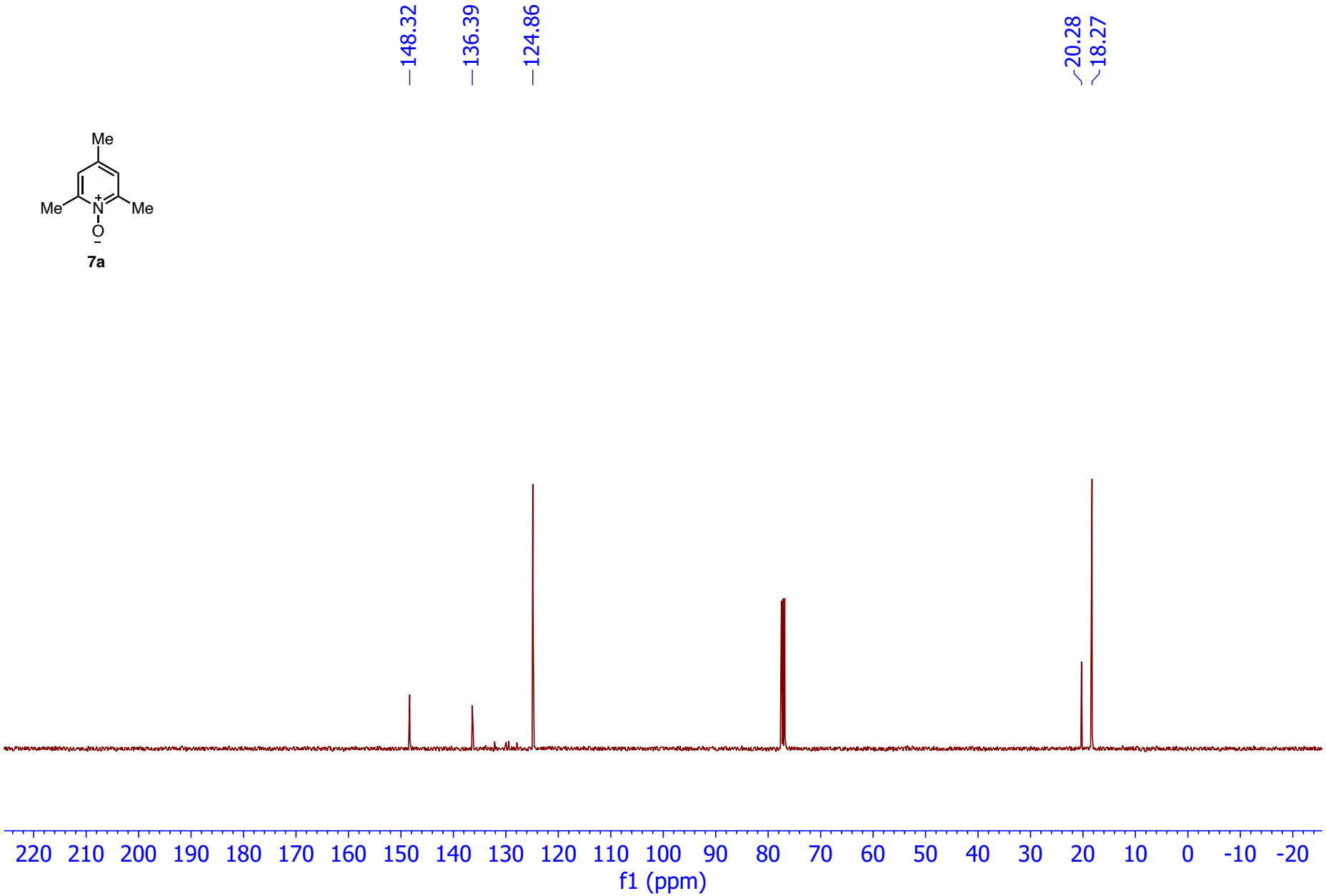
400 HMz, Chloroform-d



7a

^{1}H NMR of 7a

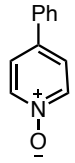
101 MHz, Chloroform-d



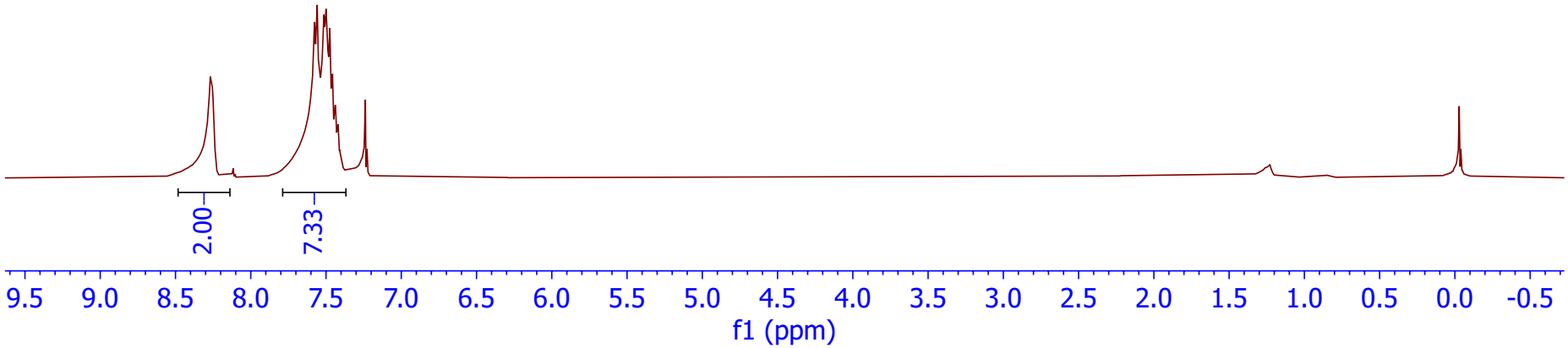
7a

^{13}C NMR of 7a

400 HMz, Chloroform-d

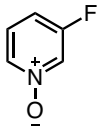


7b

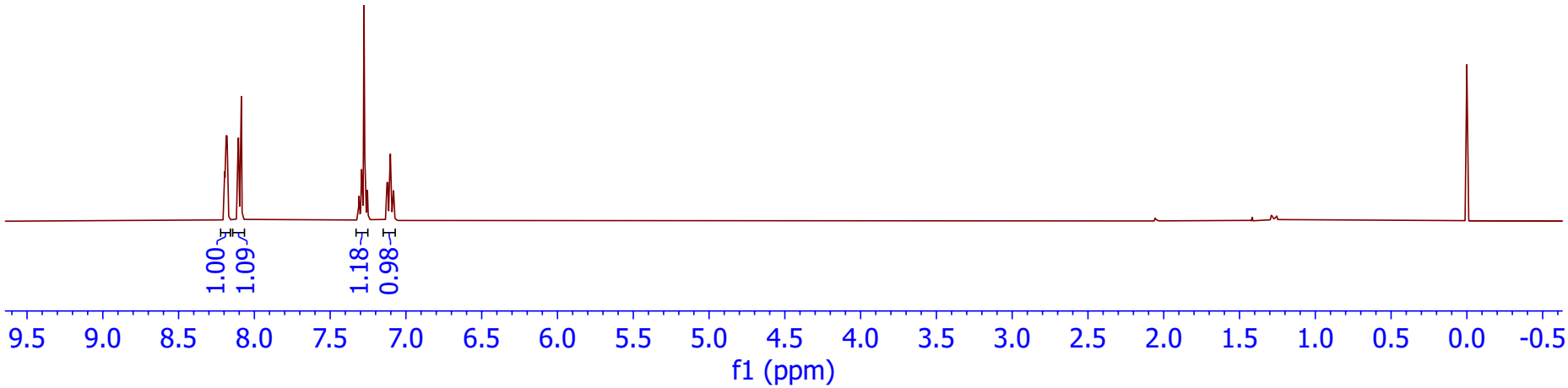


^{1}H NMR of 7b

400 HMz, Chloroform-d

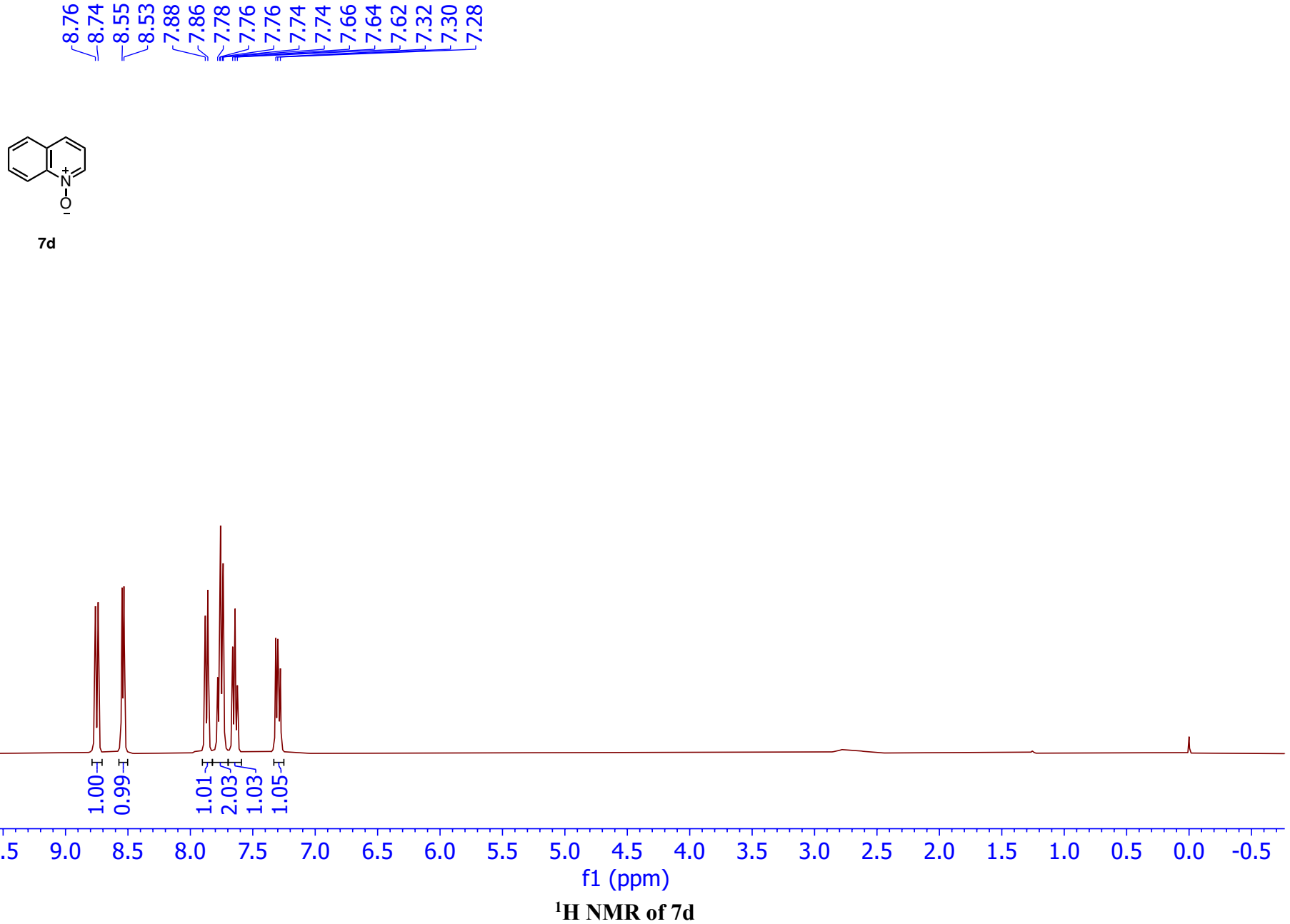


7c



^{1}H NMR of 7c

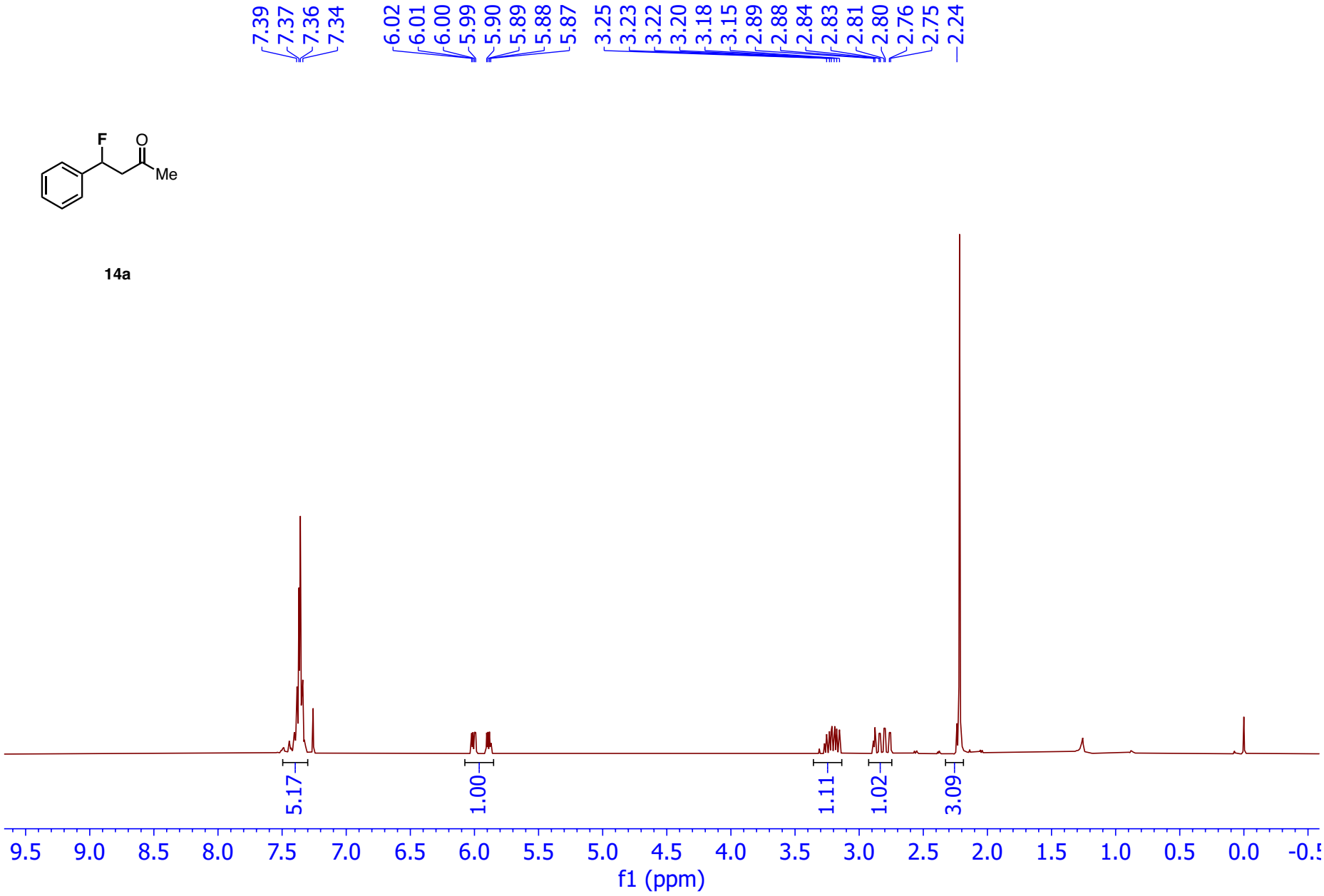
400 HMz, Chloroform-d



7d

^{1}H NMR of 7d

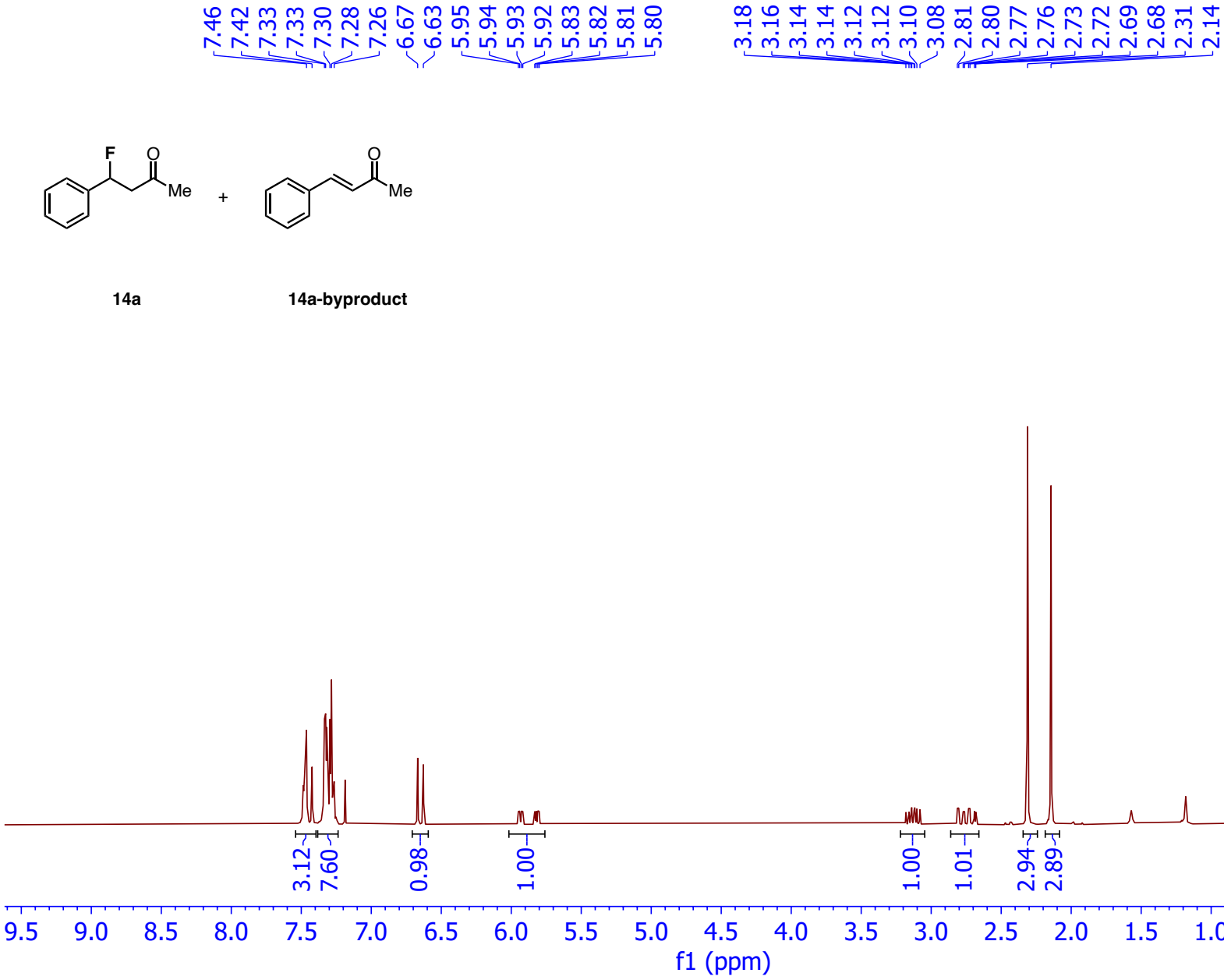
400 HMz, Chloroform-d



14a

^{1}H NMR of 14a

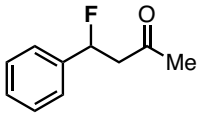
400 HMz, Chloroform-d



14a **14a-byproduct**

^{1}H NMR of 14a

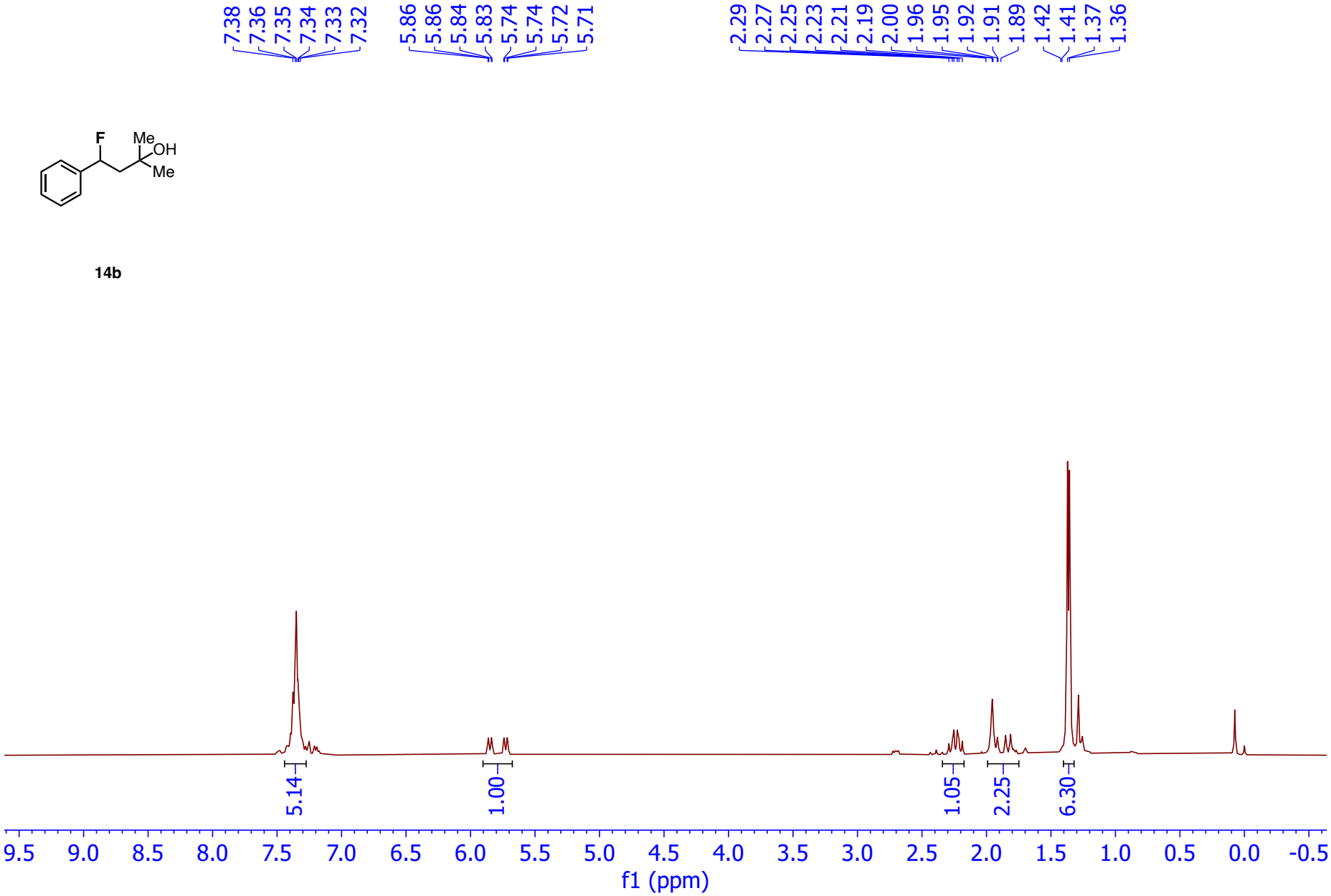
376MHz, Chloroform-d



14a

^{19}F NMR of 14a

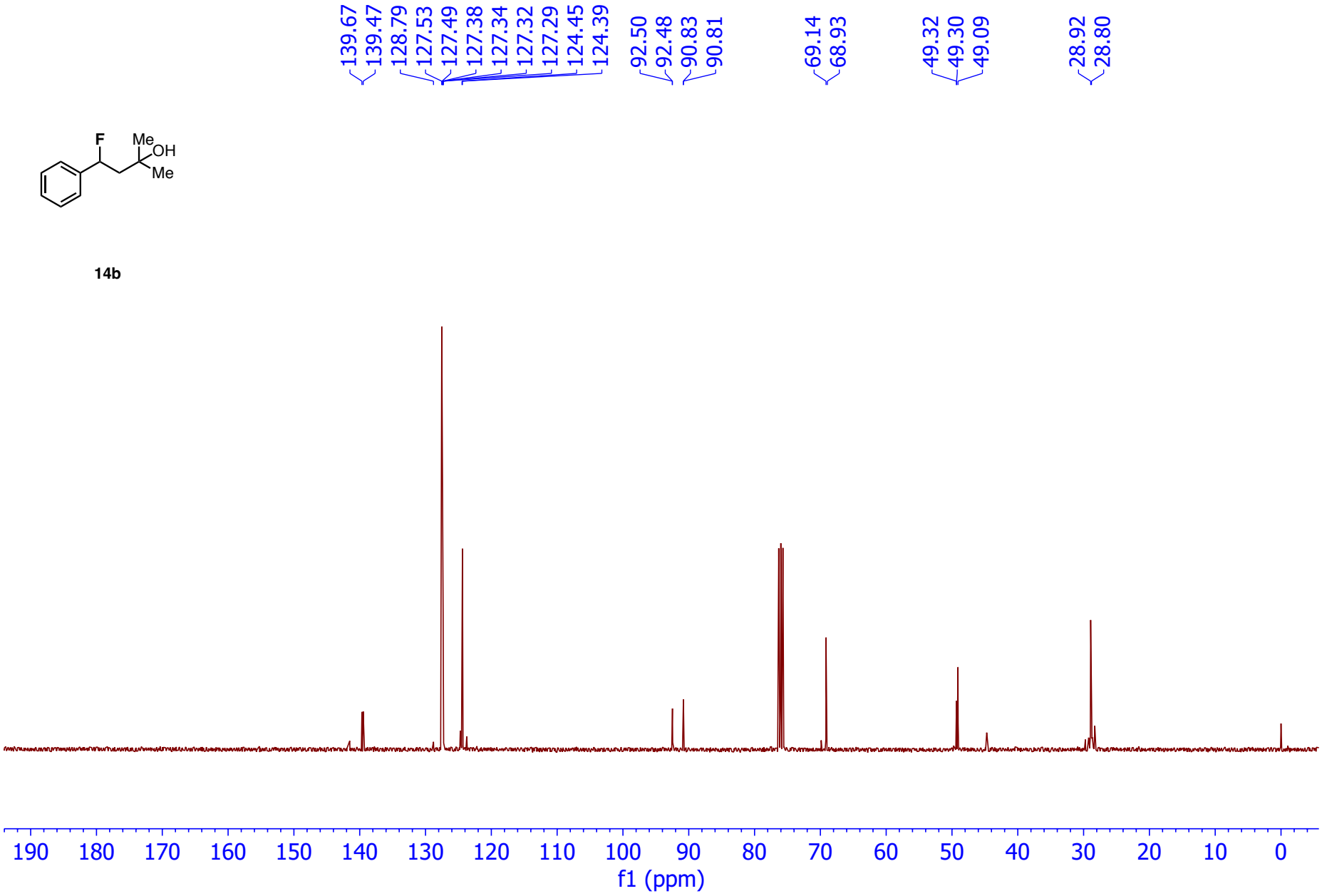
400 HMz, Chloroform-d



14b

^{1}H NMR of 14b

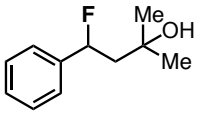
101 MHz, Chloroform-d



14b

^{13}C NMR of 14b

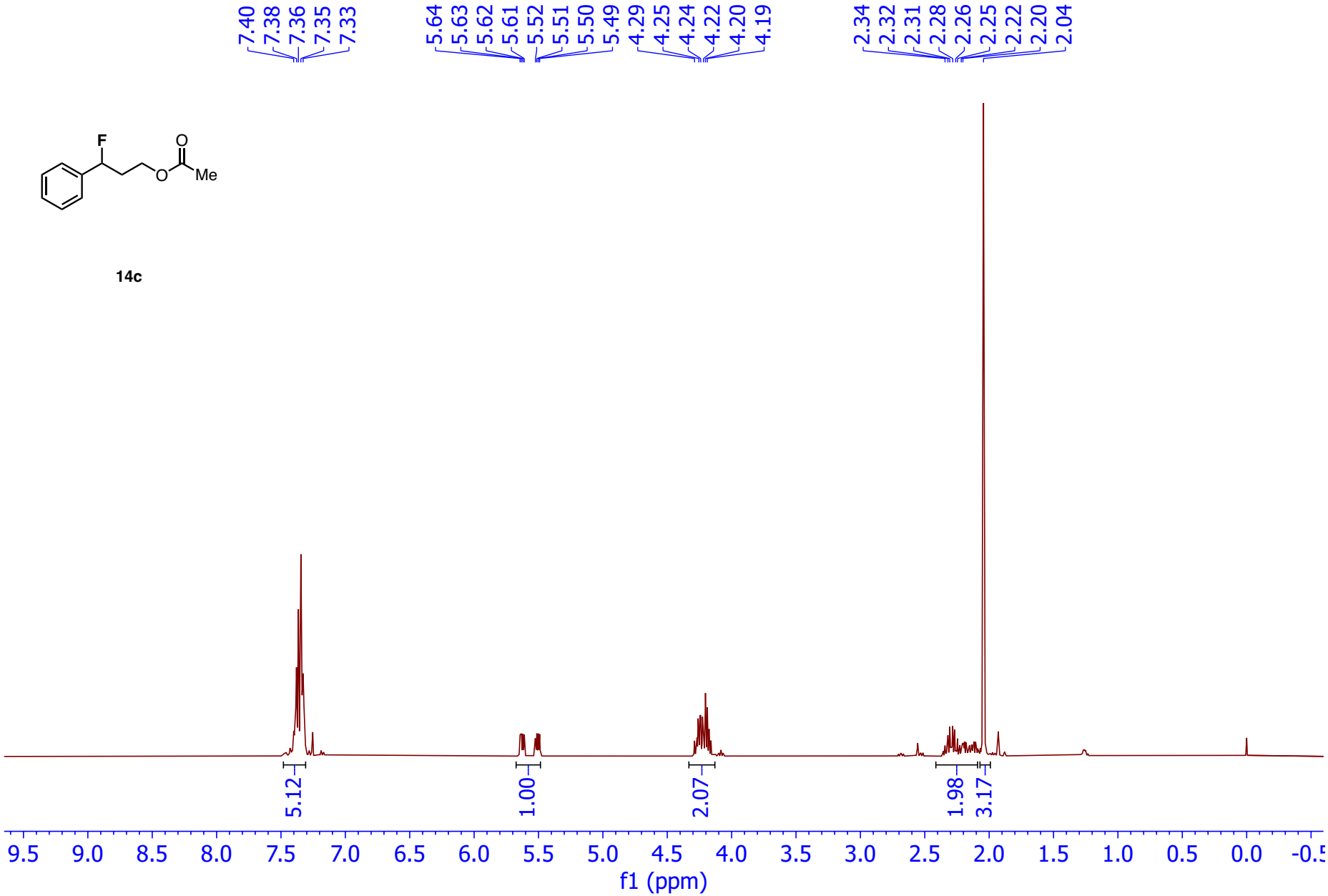
376MHz, Chloroform-d



14b

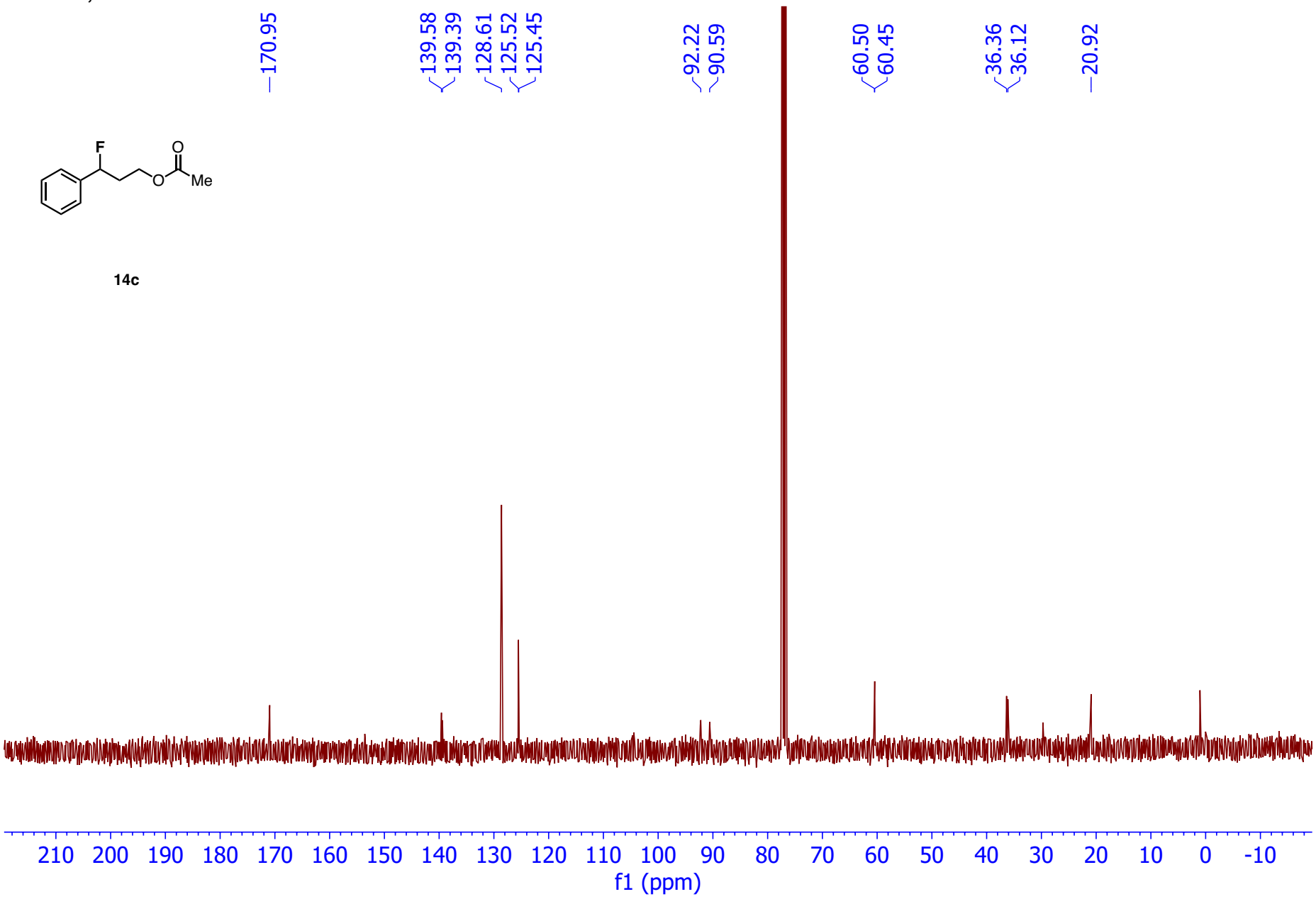
^{19}F NMR of 14b

400 HMz, Chloroform-d



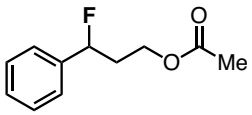
14c

^{1}H NMR of 14c



^{13}C NMR of 14c

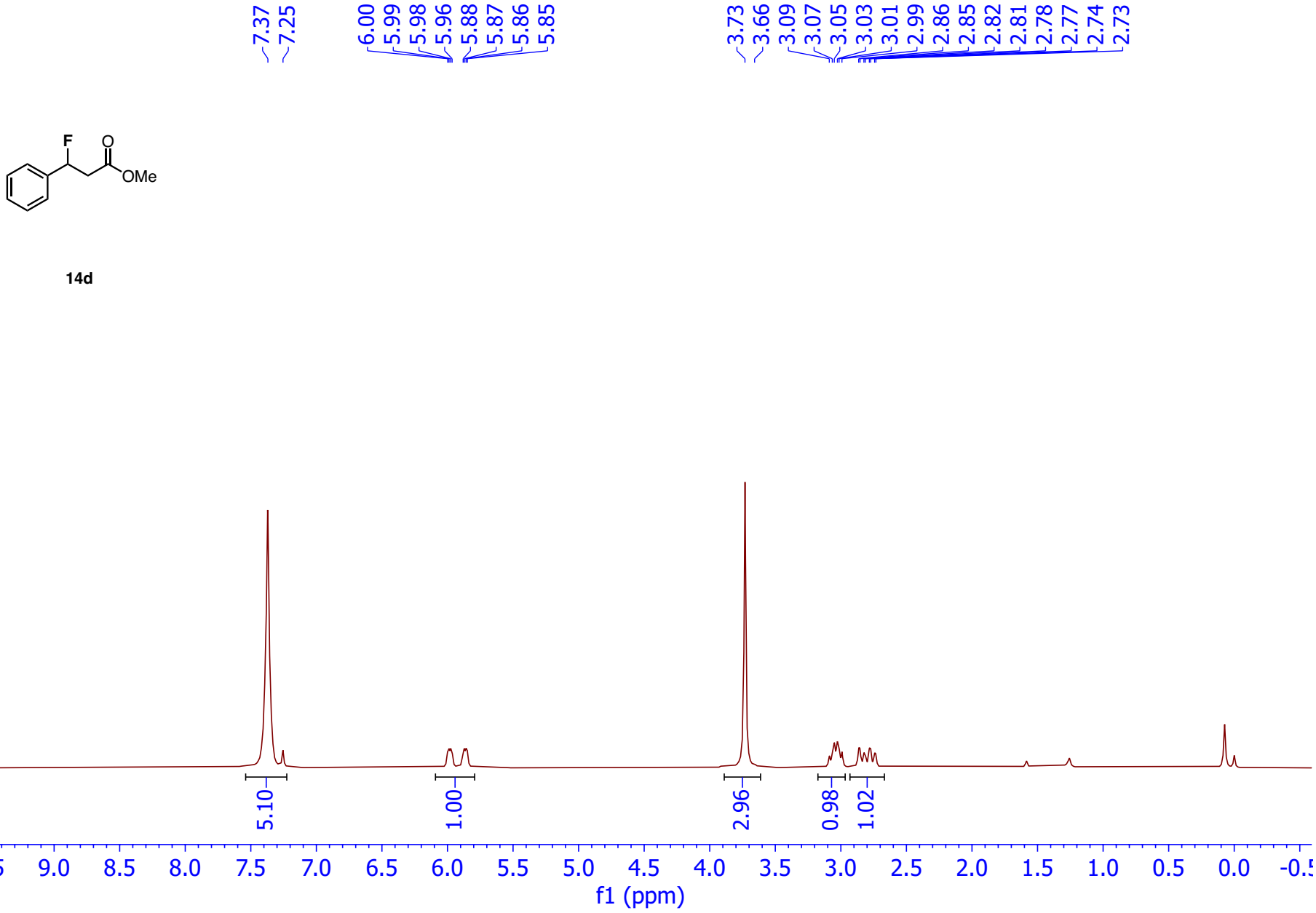
376MHz, Chloroform-d



14c

^{9}F NMR of 14c

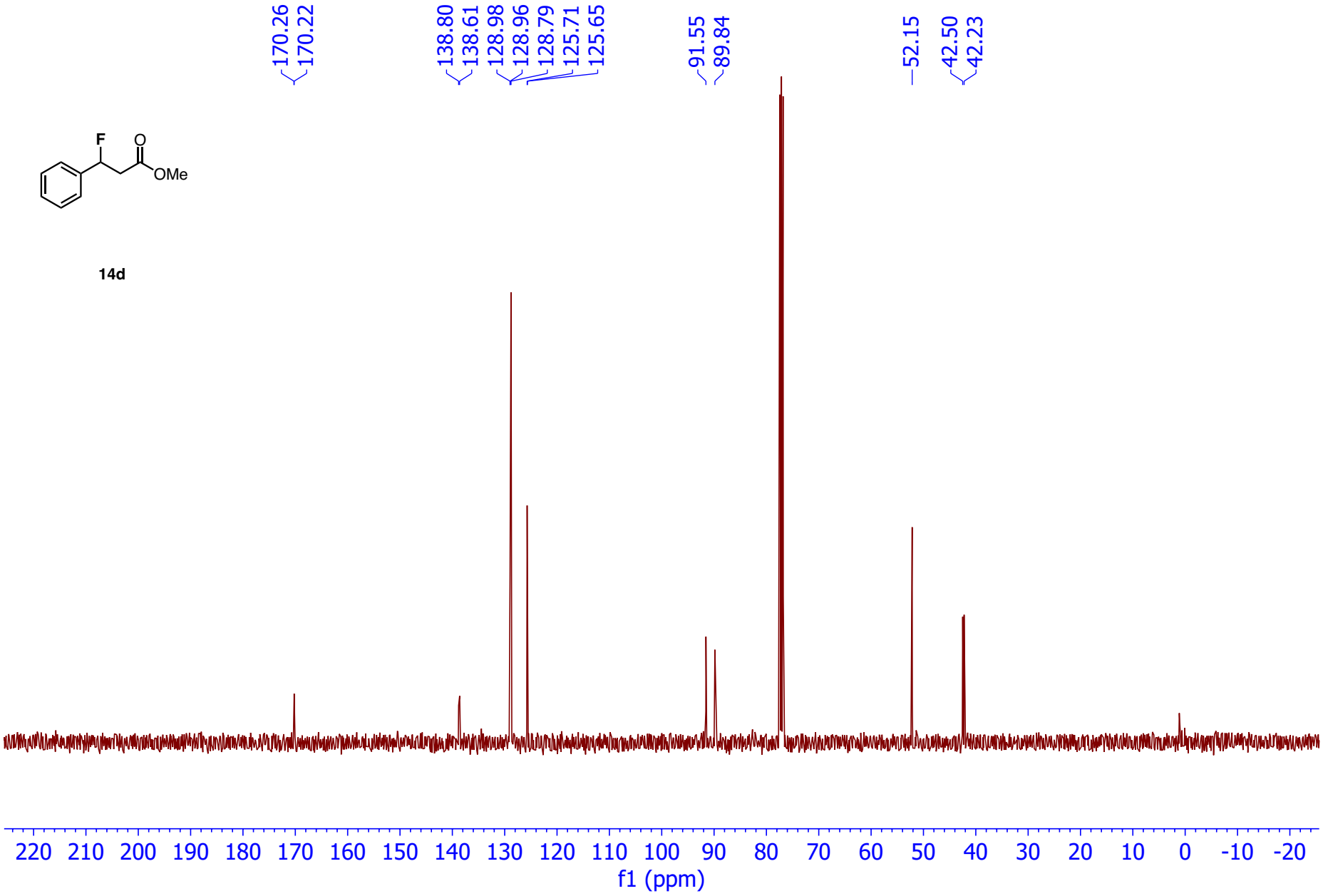
400 HMz, Chloroform-d



14d

^{1}H NMR of 14d

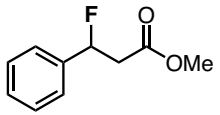
101 MHz, Chloroform-d



14d

^{13}C NMR of 14d

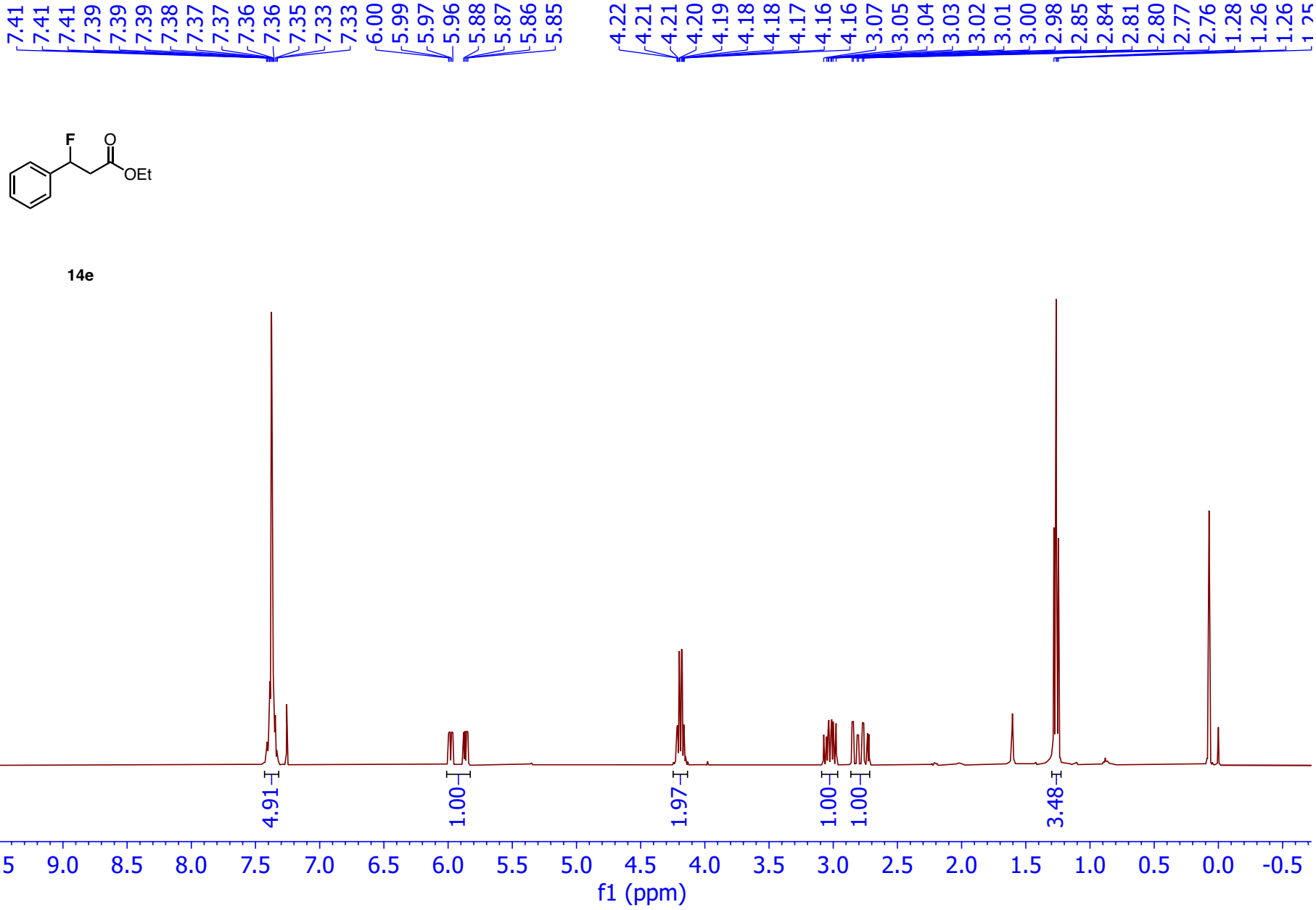
376MHz, Chloroform-d



14d

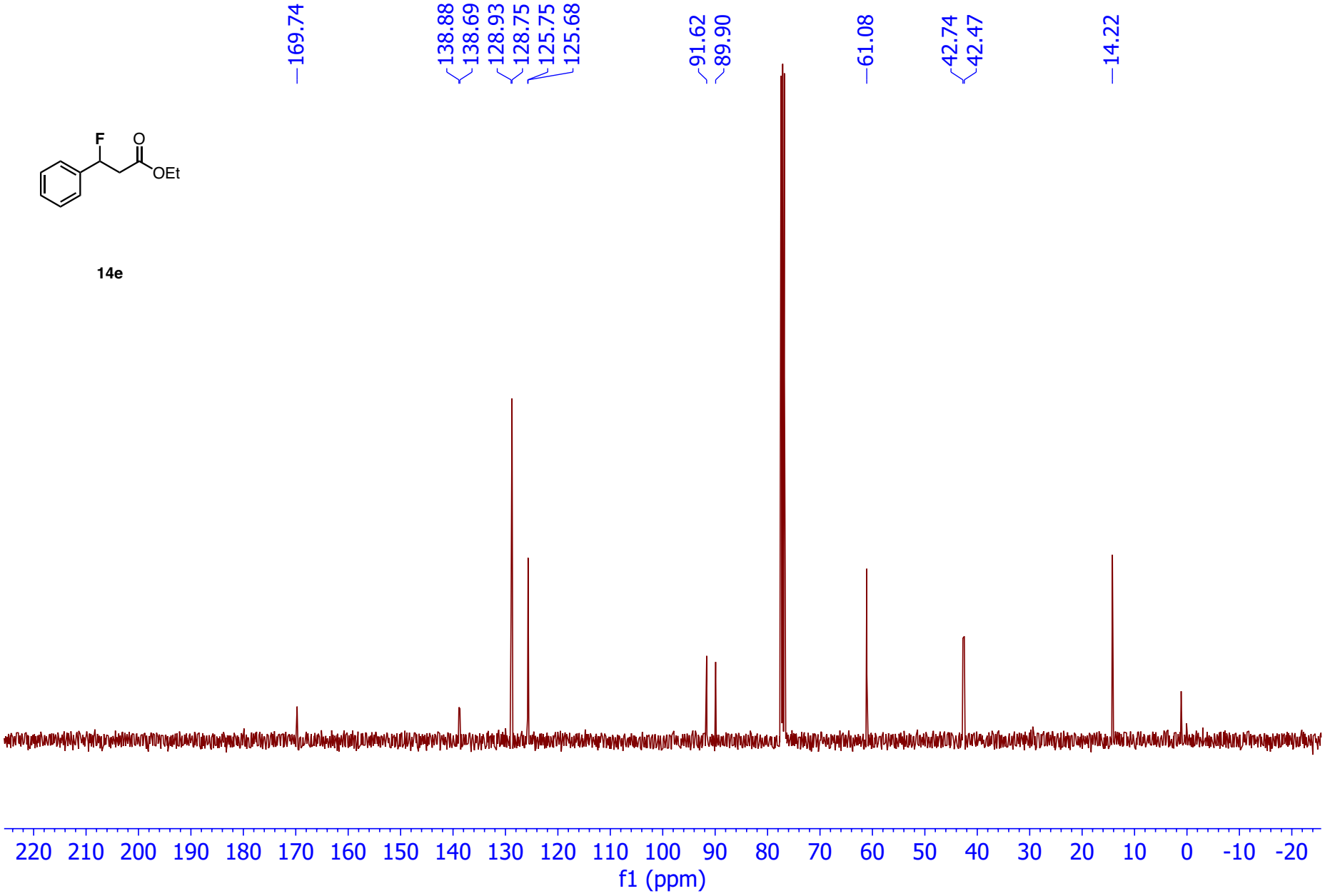
^{19}F NMR of 14d

400 HMz, Chloroform-d



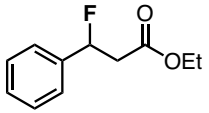
^{1}H NMR of 14e

101 MHz, Chloroform-d



^{13}C NMR of 14e

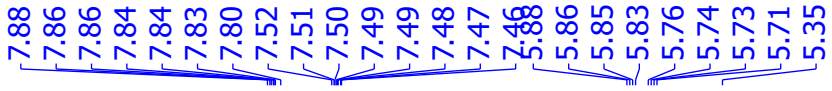
376MHz, Chloroform-d

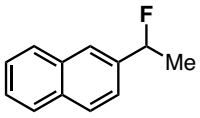


14e

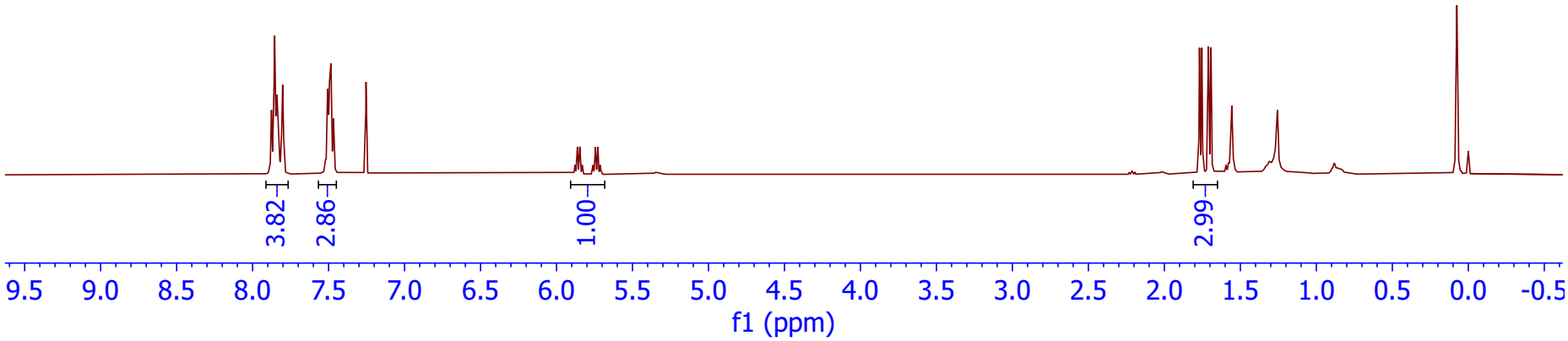
^{19}F NMR of 14e

400 HMz, Chloroform-d

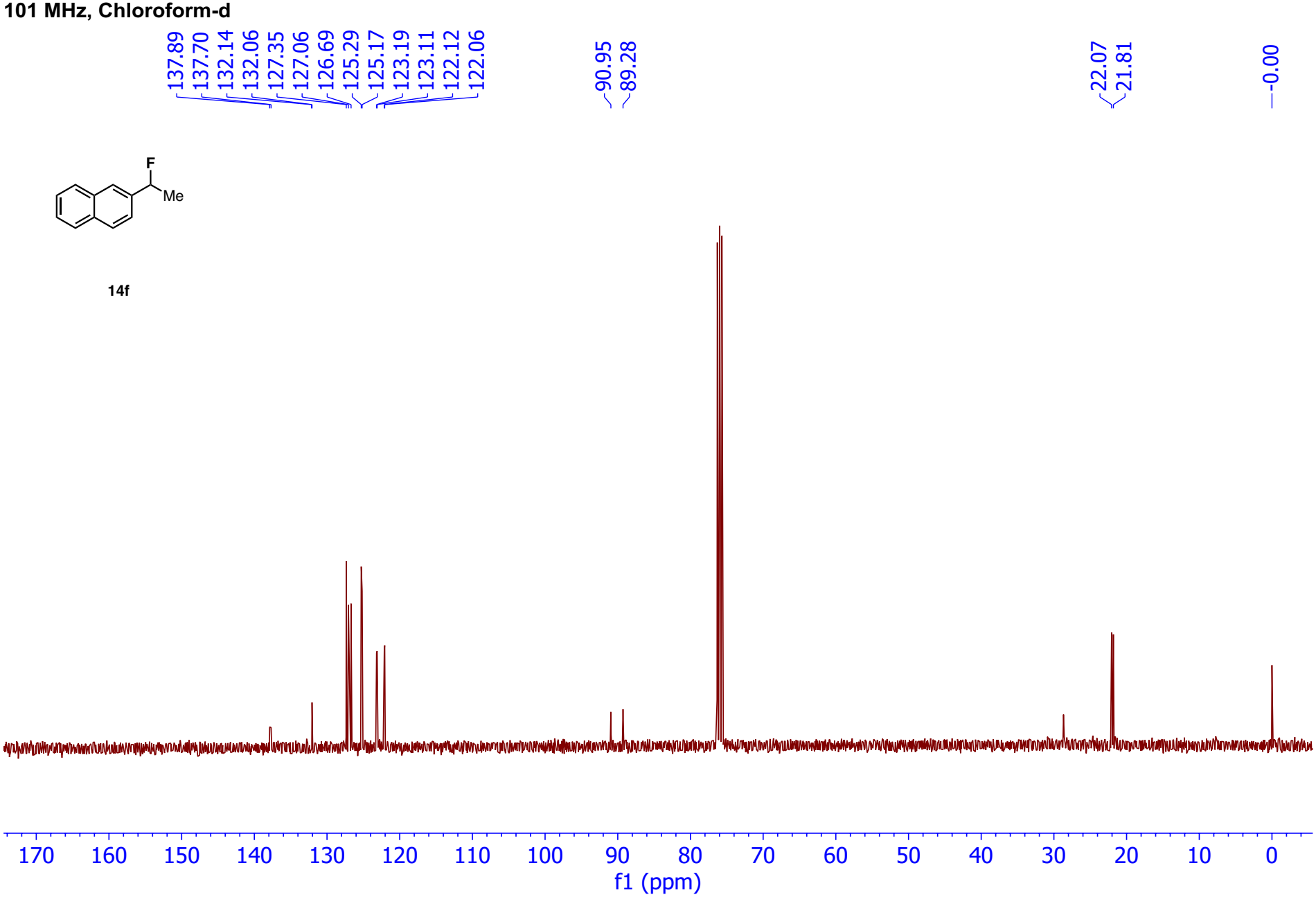




14f

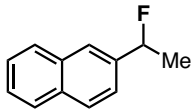


^{1}H NMR of 14f



^{13}C NMR of 14f

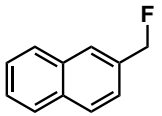
376MHz, Chloroform-d



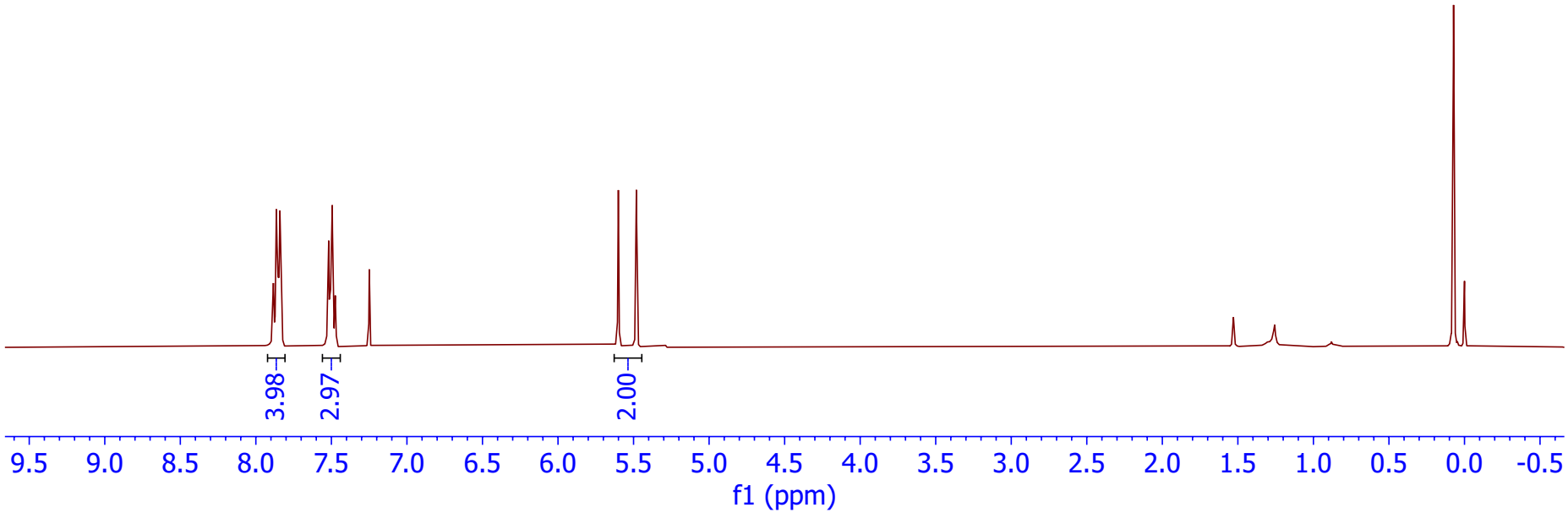
14f

^{19}F NMR of 14f

400 HMz, Chloroform-d

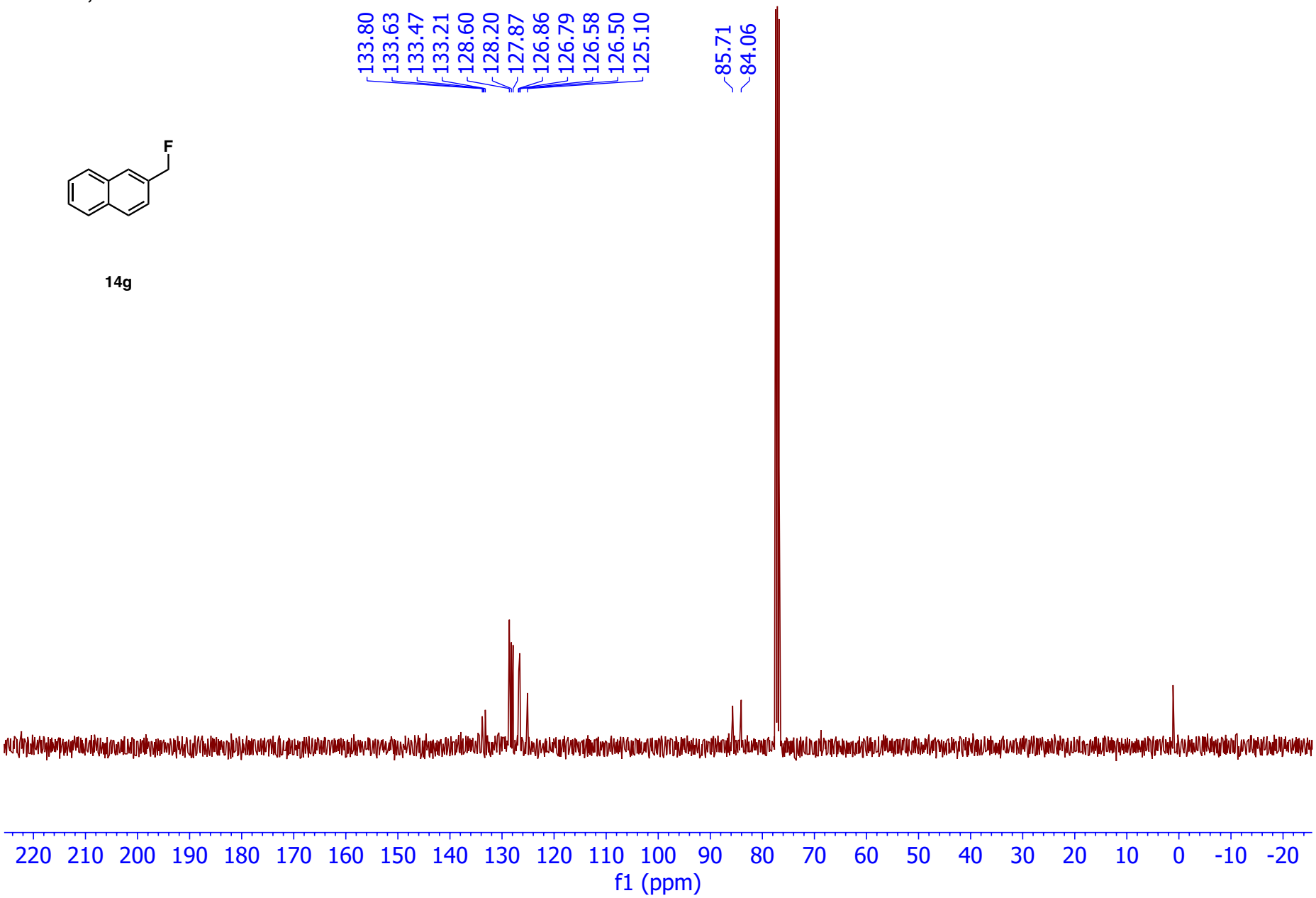


14g



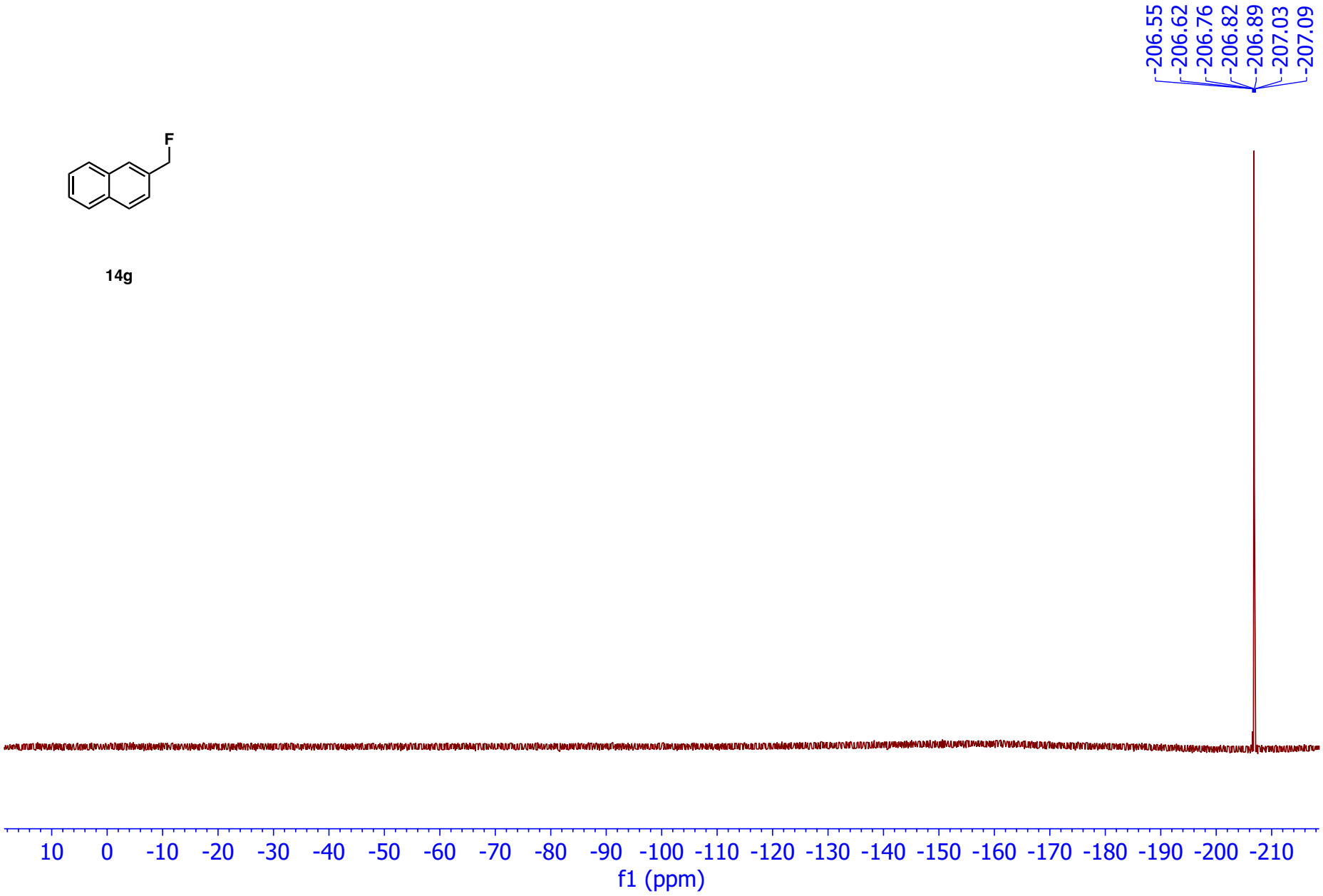
^{1}H NMR of 14g

101 MHz, Chloroform-d



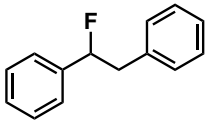
^{13}C NMR of 14g

376MHz, Chloroform-d

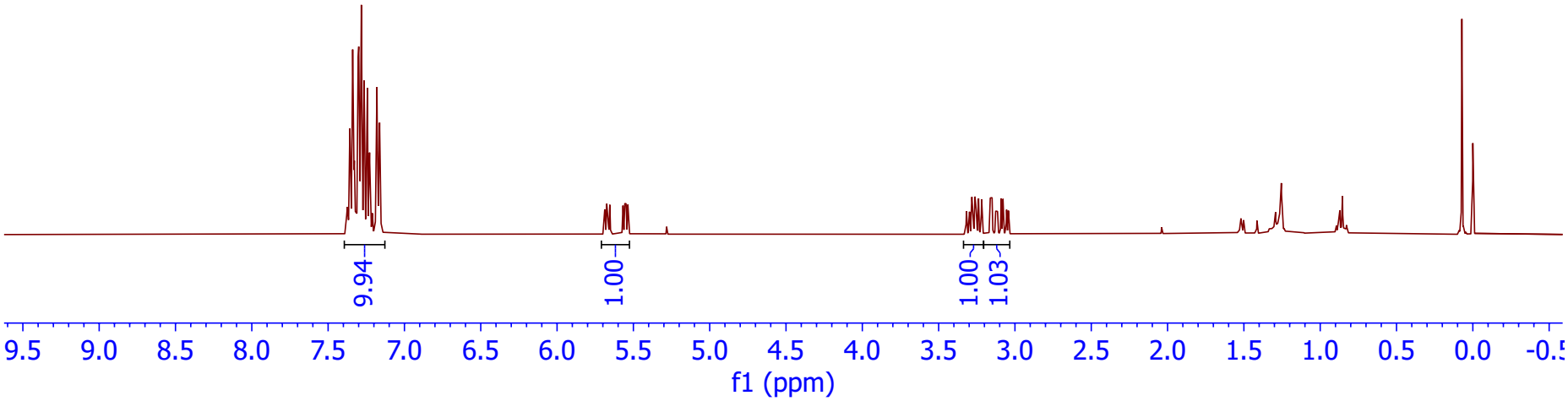


^{19}F NMR of 14g

400 HMz, Chloroform-d

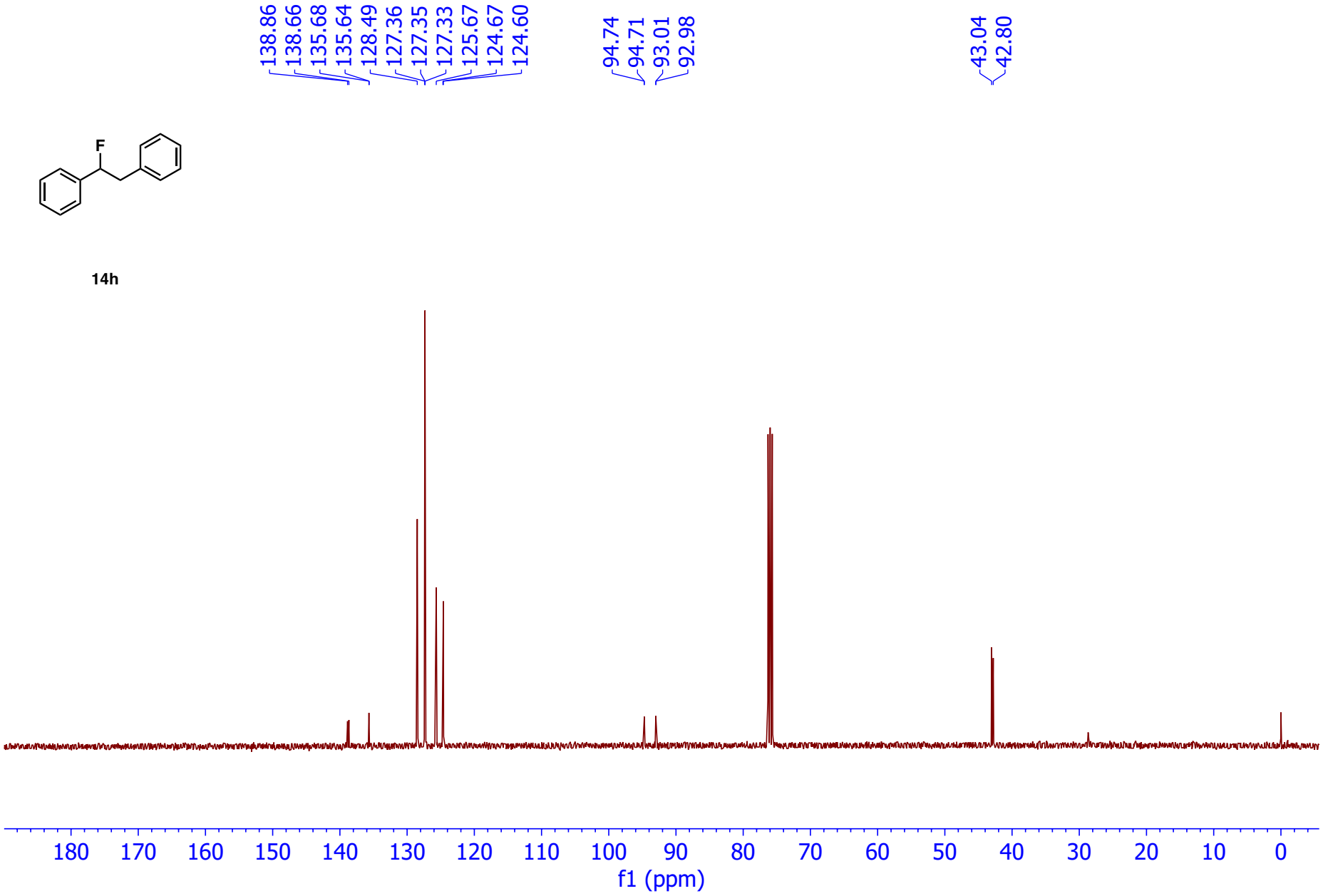


14h



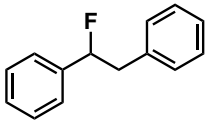
^{1}H NMR of 14h

101 MHz, Chloroform-d



^{13}C NMR of 14h

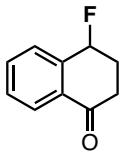
376MHz, Chloroform-d



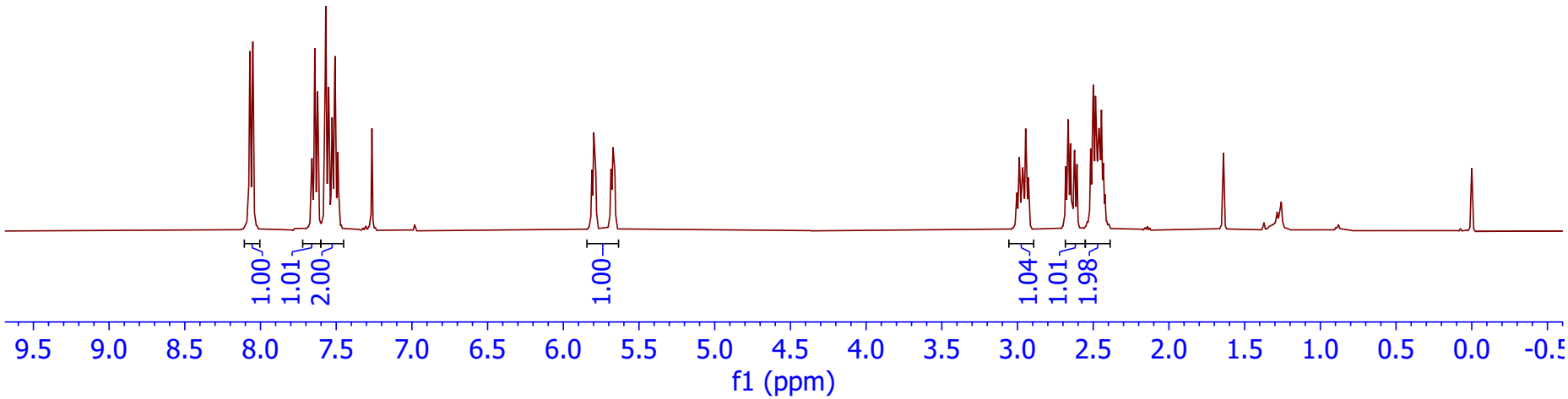
14h

^{19}F NMR of 14h

400 HMz, Chloroform-d

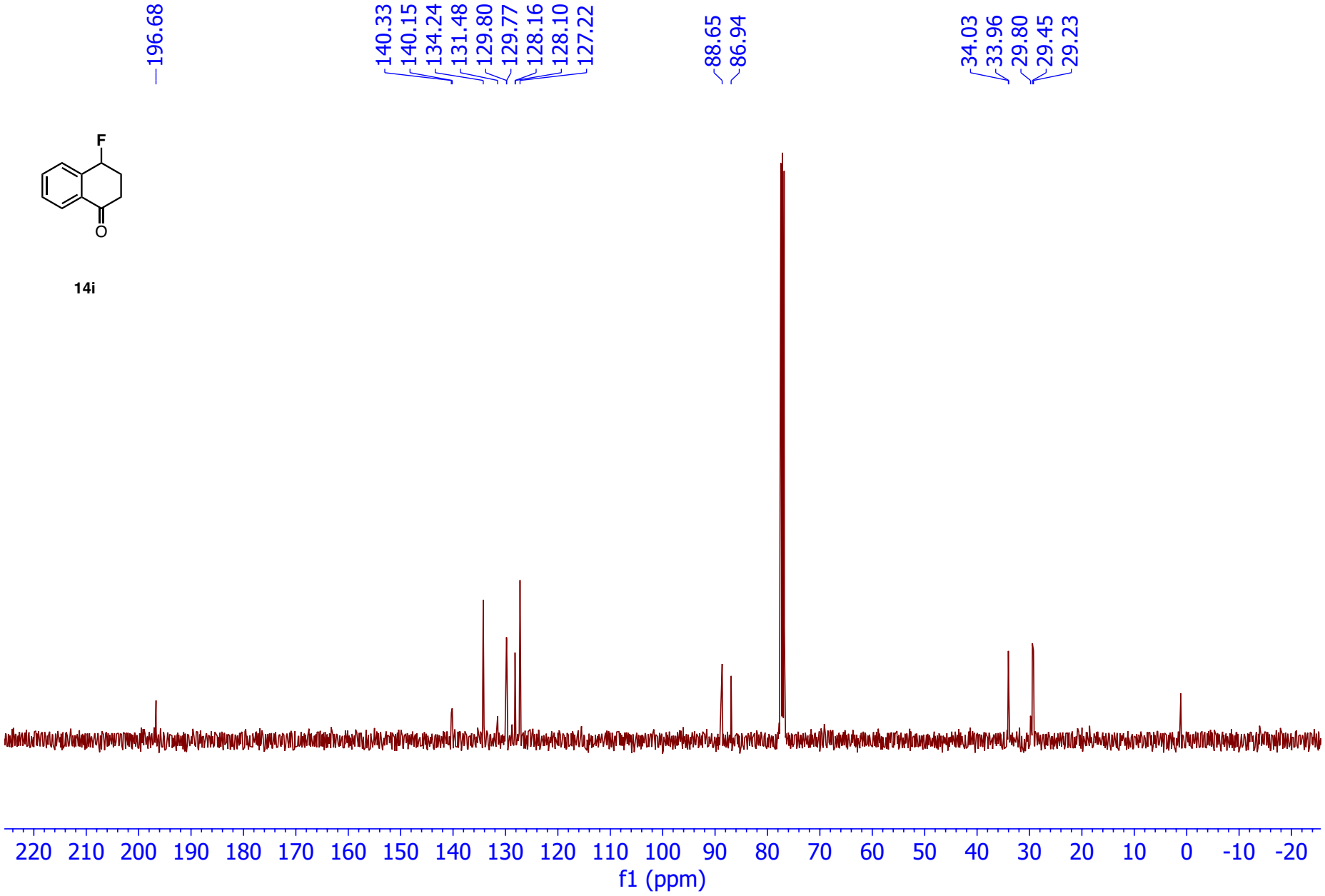


14i



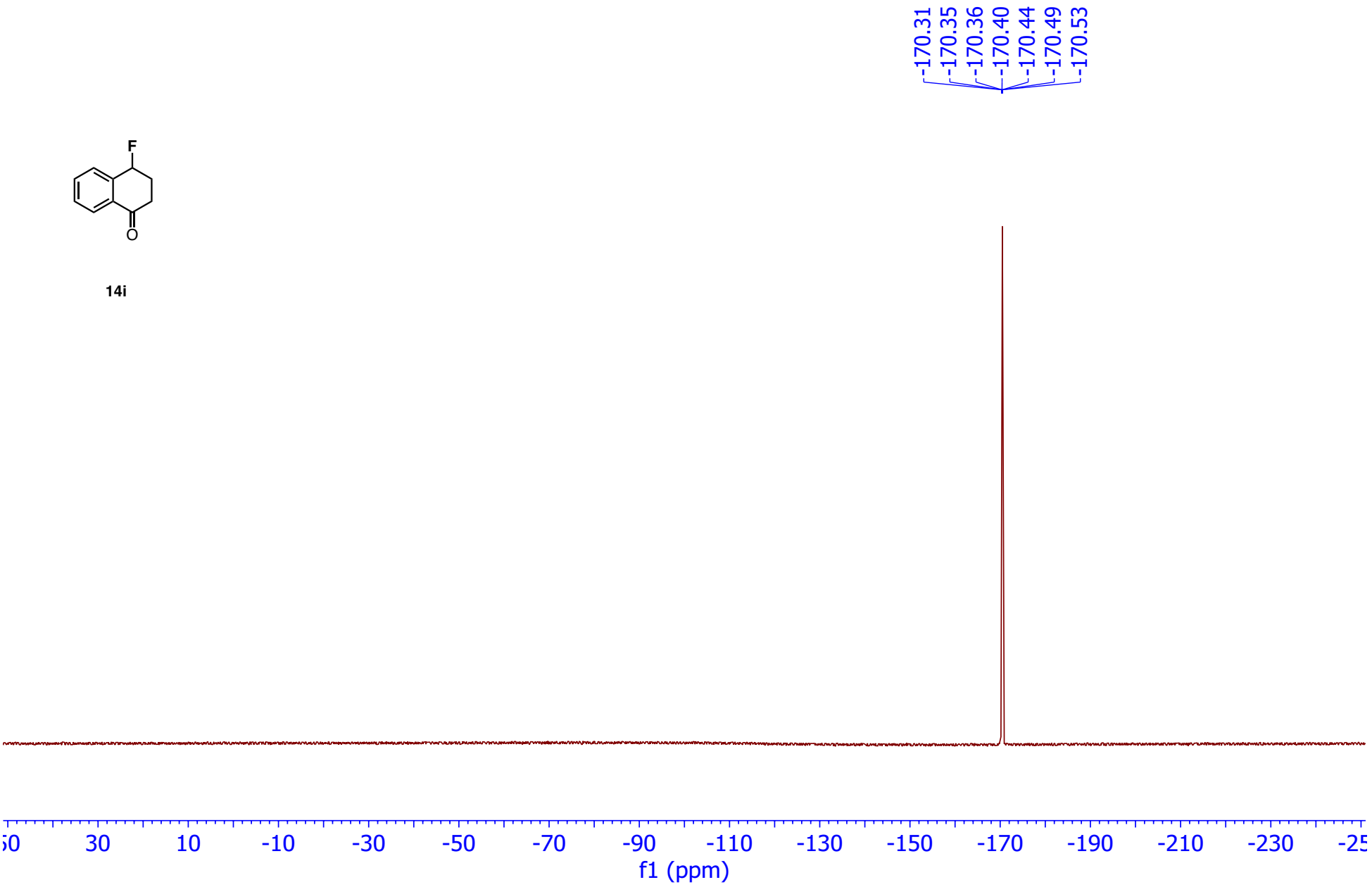
^{1}H NMR of 14i

101 MHz, Chloroform-d



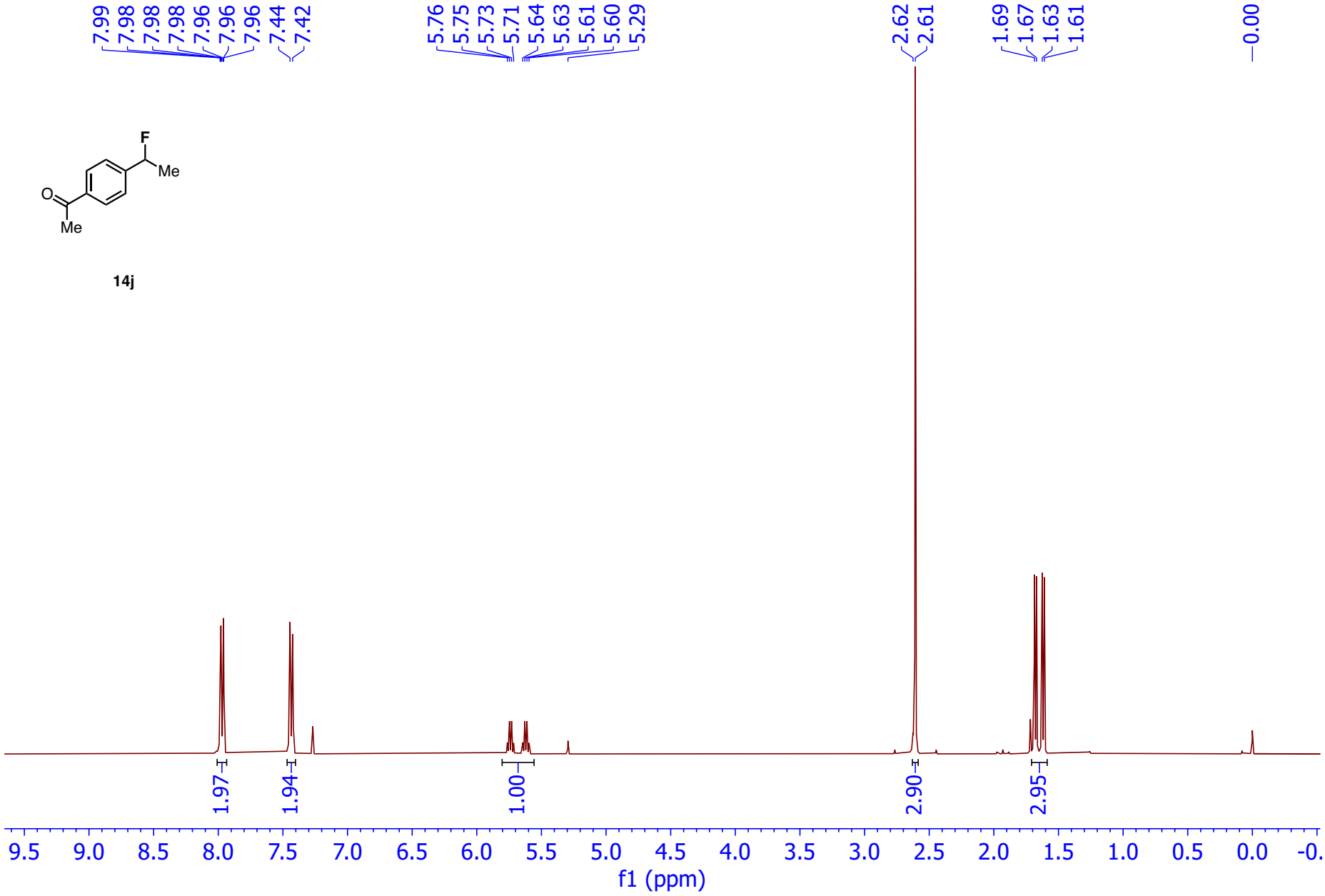
^{13}C NMR of 14i

376MHz, Chloroform-d



^{19}F NMR of 14i

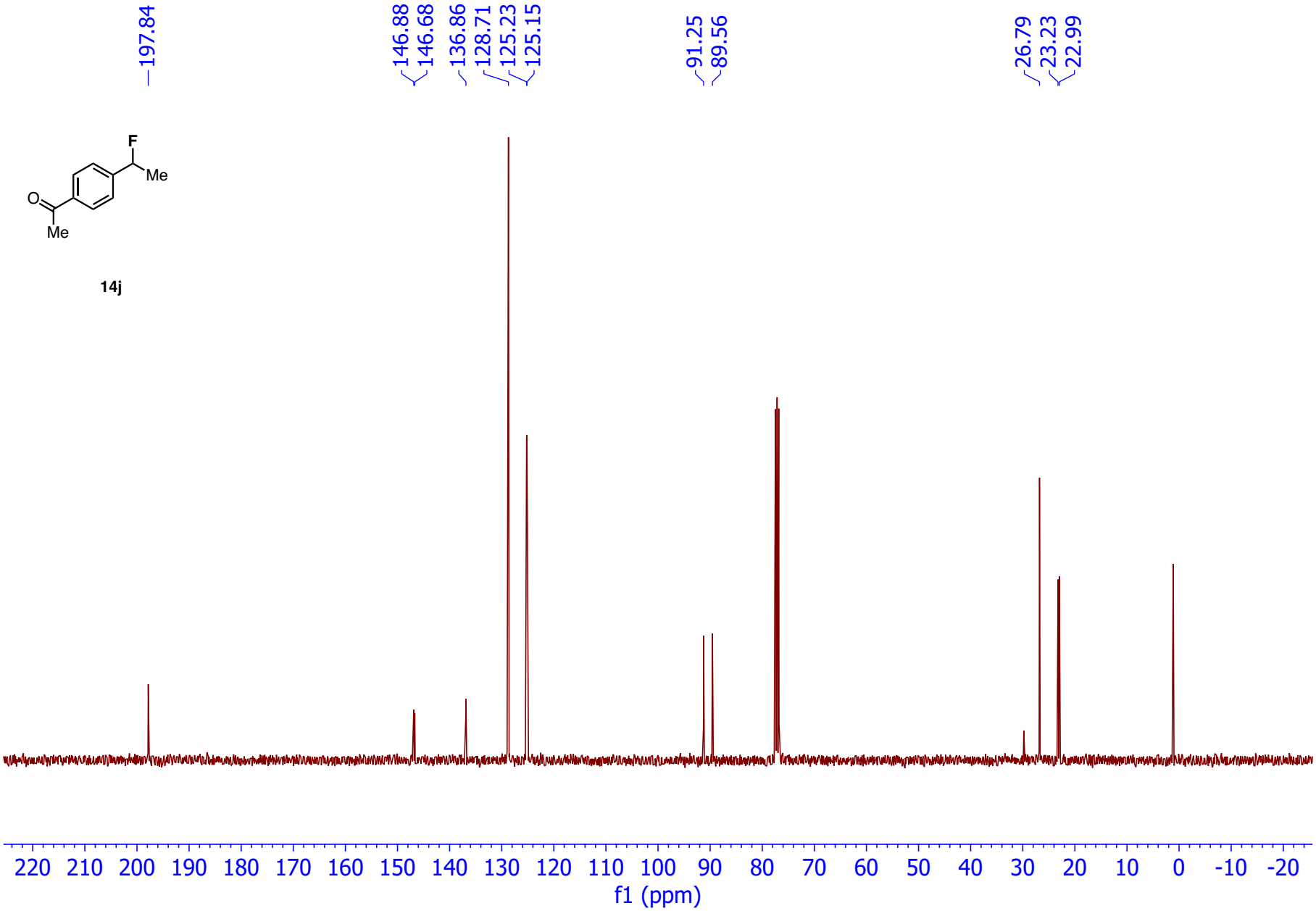
400 HMz, Chloroform-d



14j

^{1}H NMR of 14j

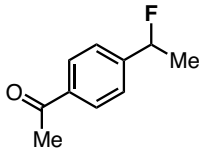
101 MHz, Chloroform-d



14j

^{13}C NMR of 14j

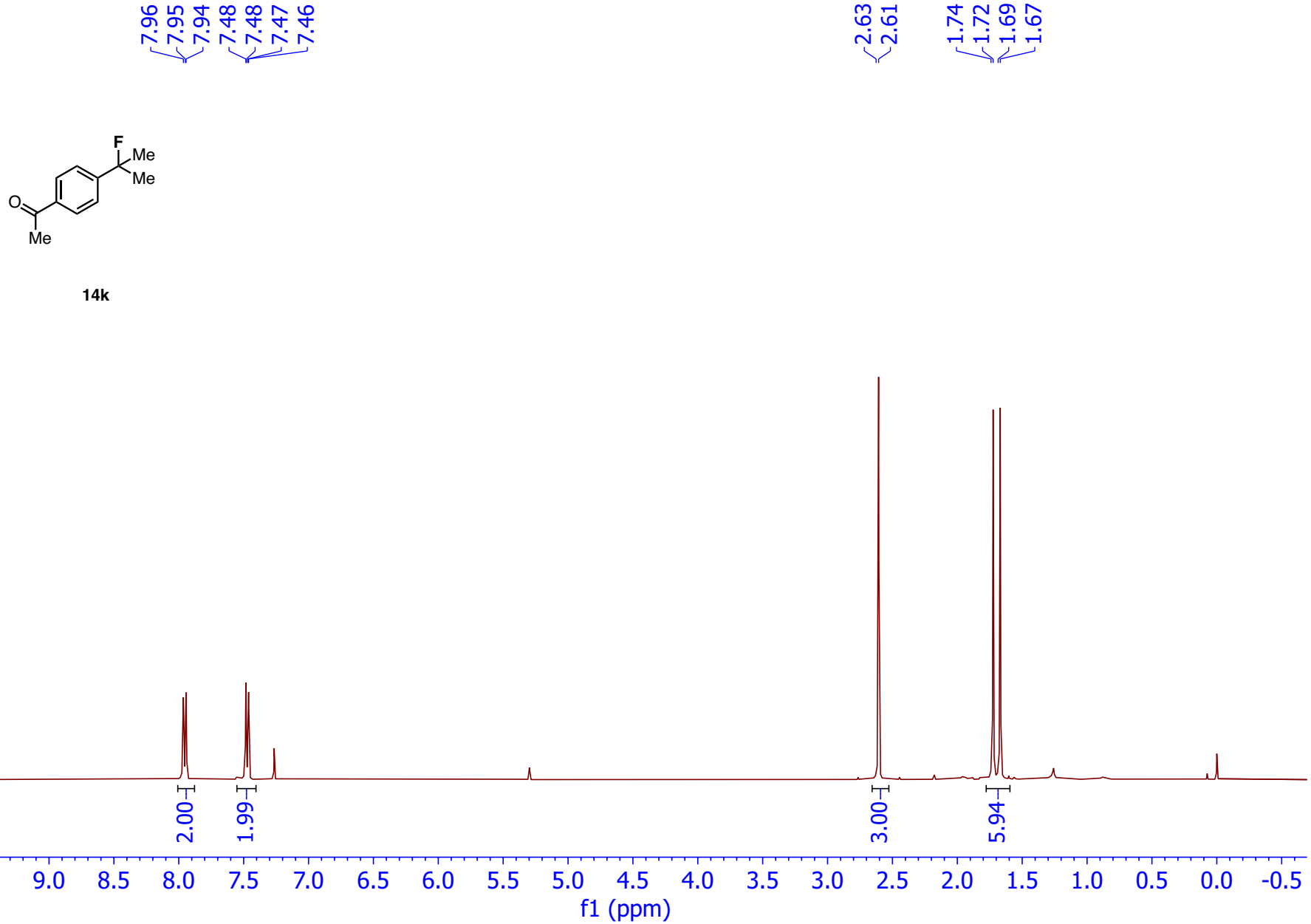
376MHz, Chloroform-d



14j

^{19}F NMR of 14j

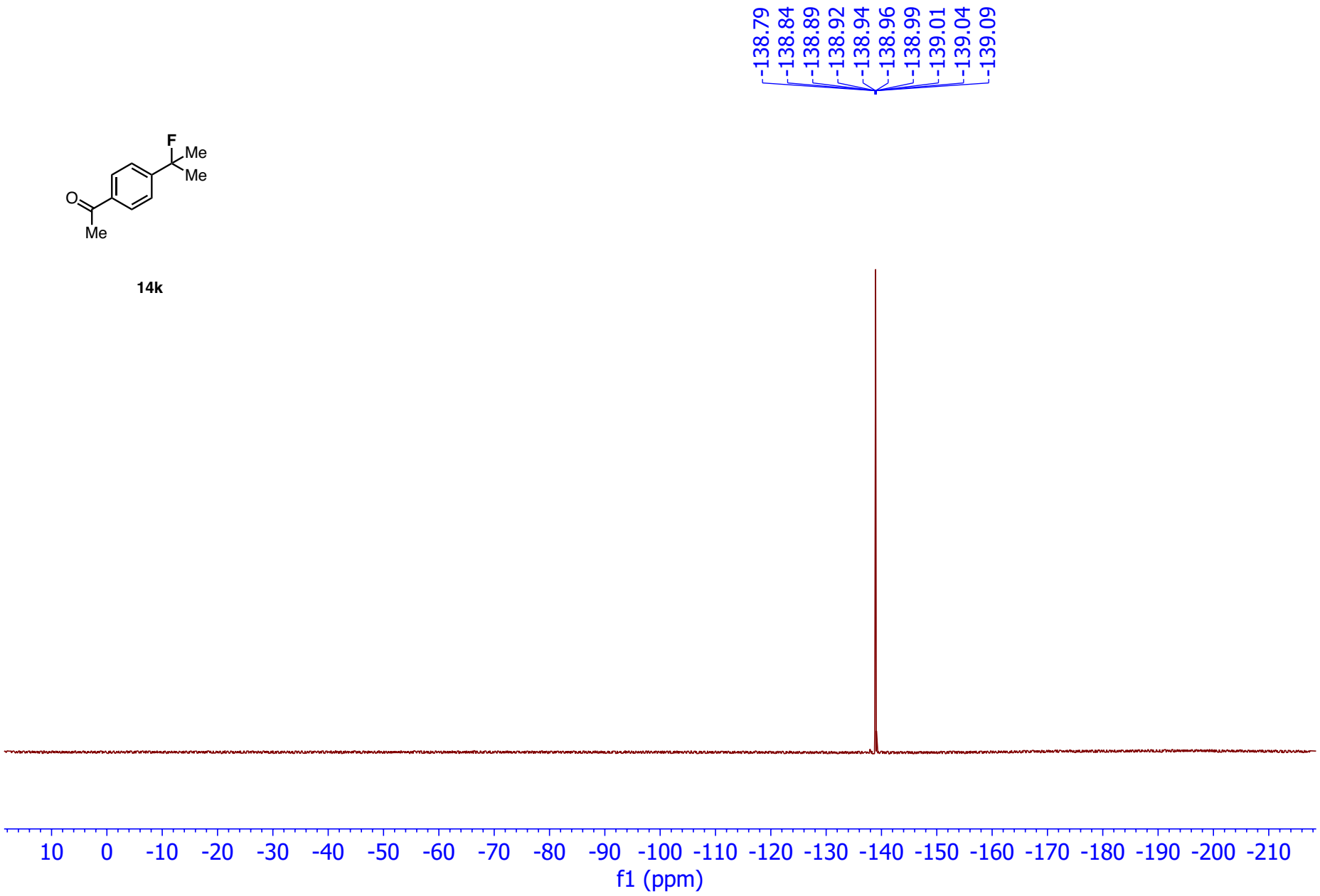
400 HMz, Chloroform-d



14k

^{1}H NMR of 14k

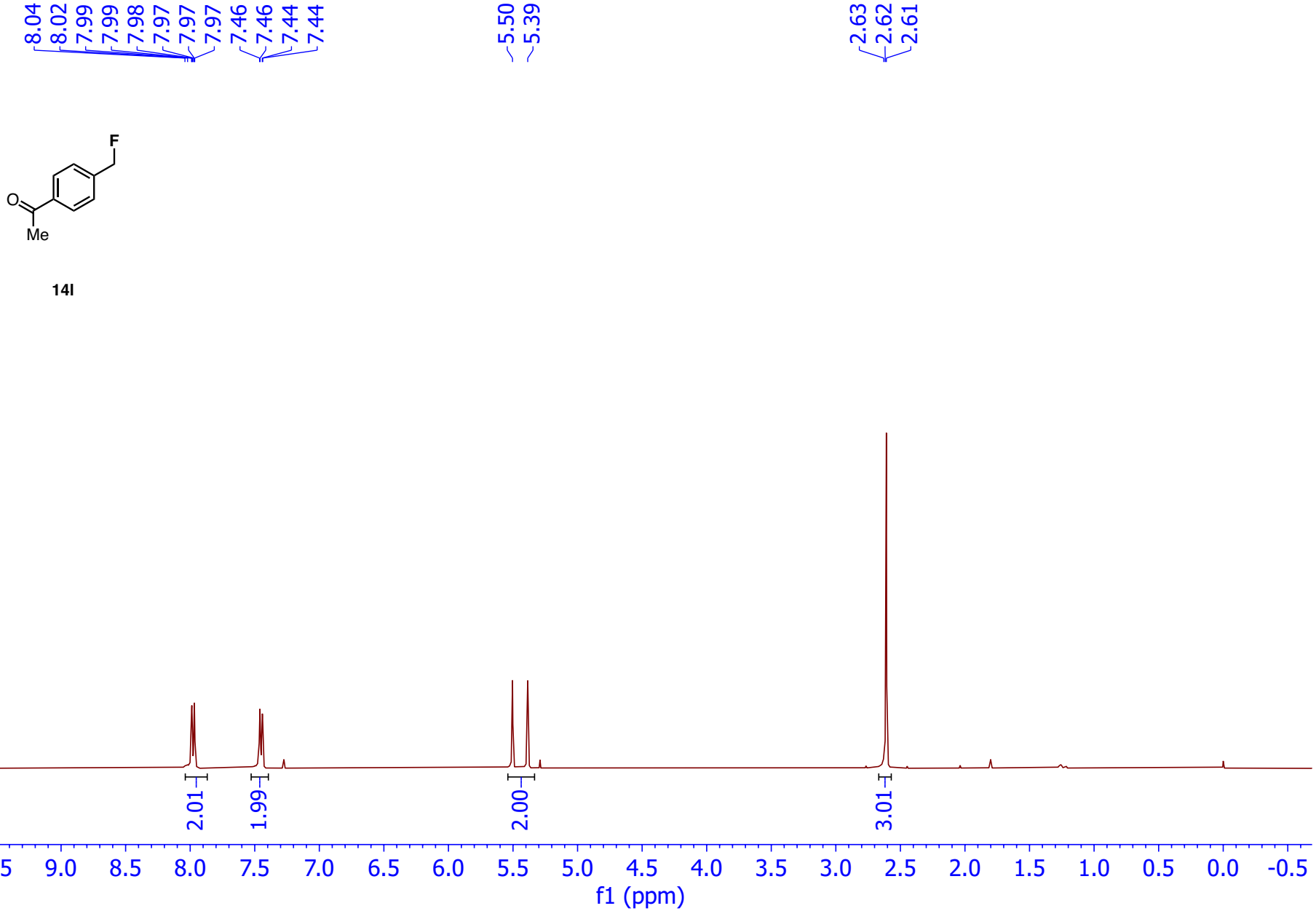
376MHz, Chloroform-d



14k

^{19}F NMR of 14k

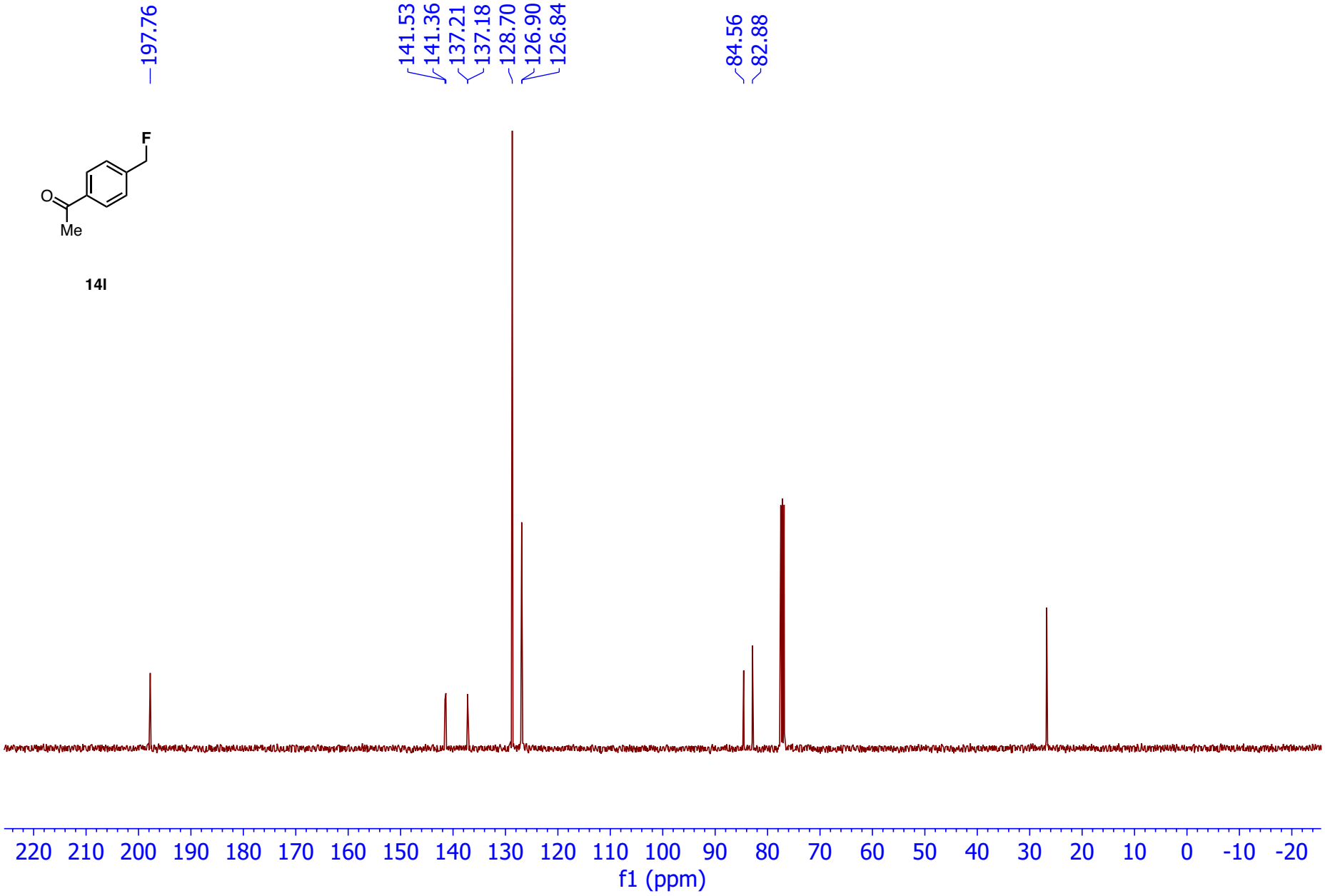
400 HMz, Chloroform-d



14l

^{1}H NMR of 14l

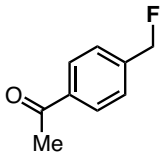
101 MHz, Chloroform-d



14l

^{13}C NMR of 14l

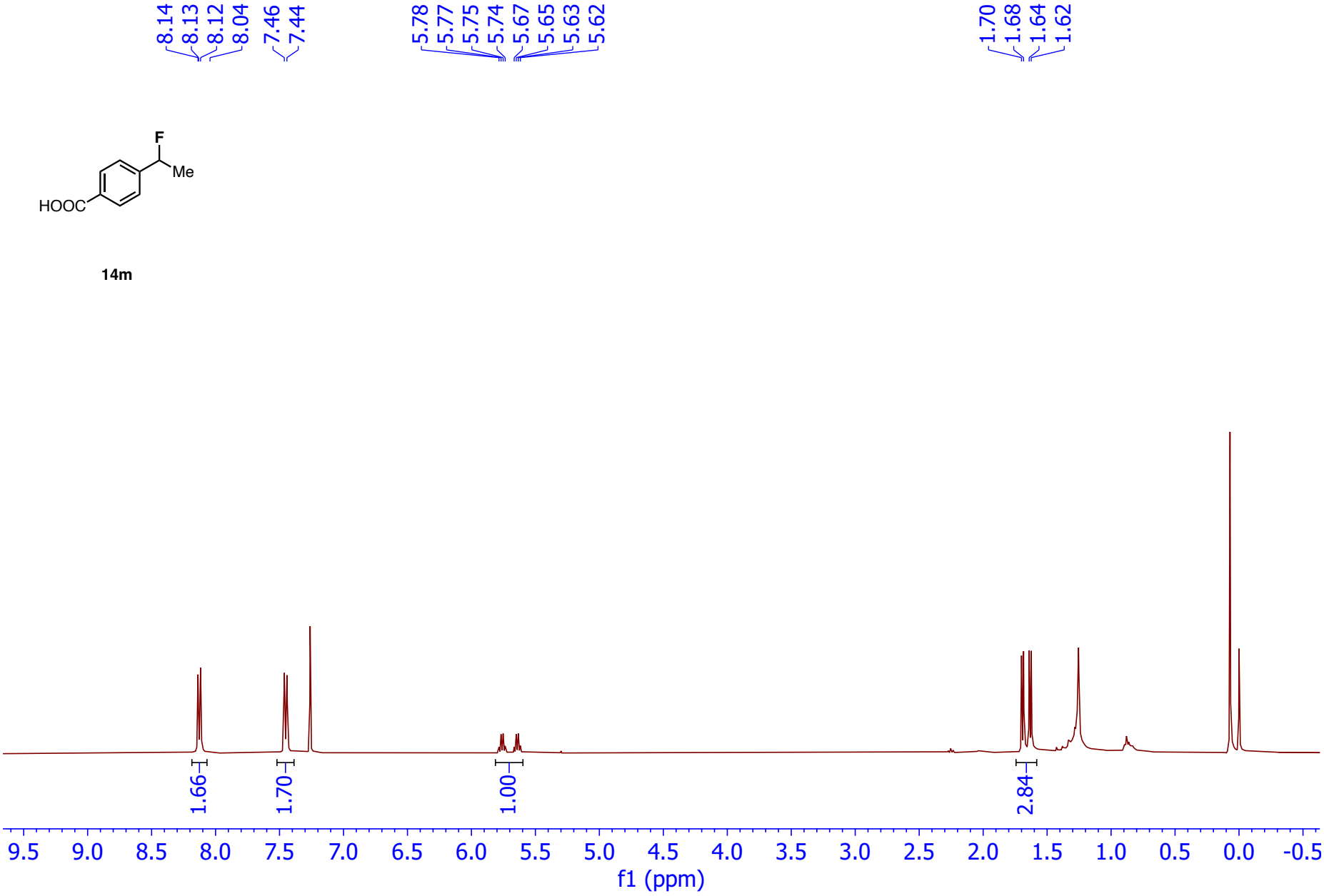
376MHz, Chloroform-d



14l

^{19}F NMR of 14l

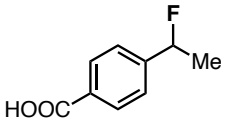
400 HMz, Chloroform-d



14m

^{1}H NMR of 14m

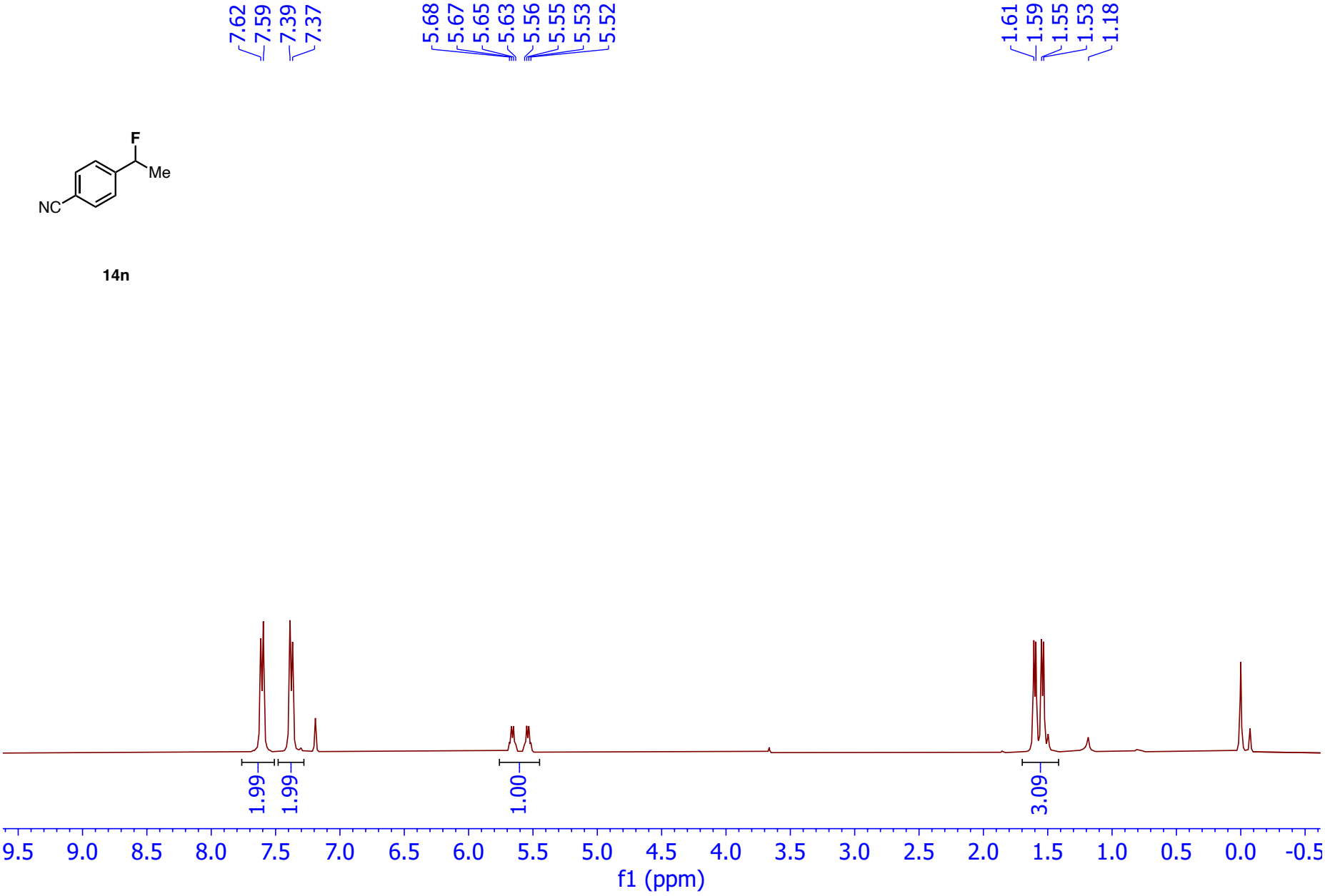
376MHz, Chloroform-d



14m

^{19}F NMR of 14m

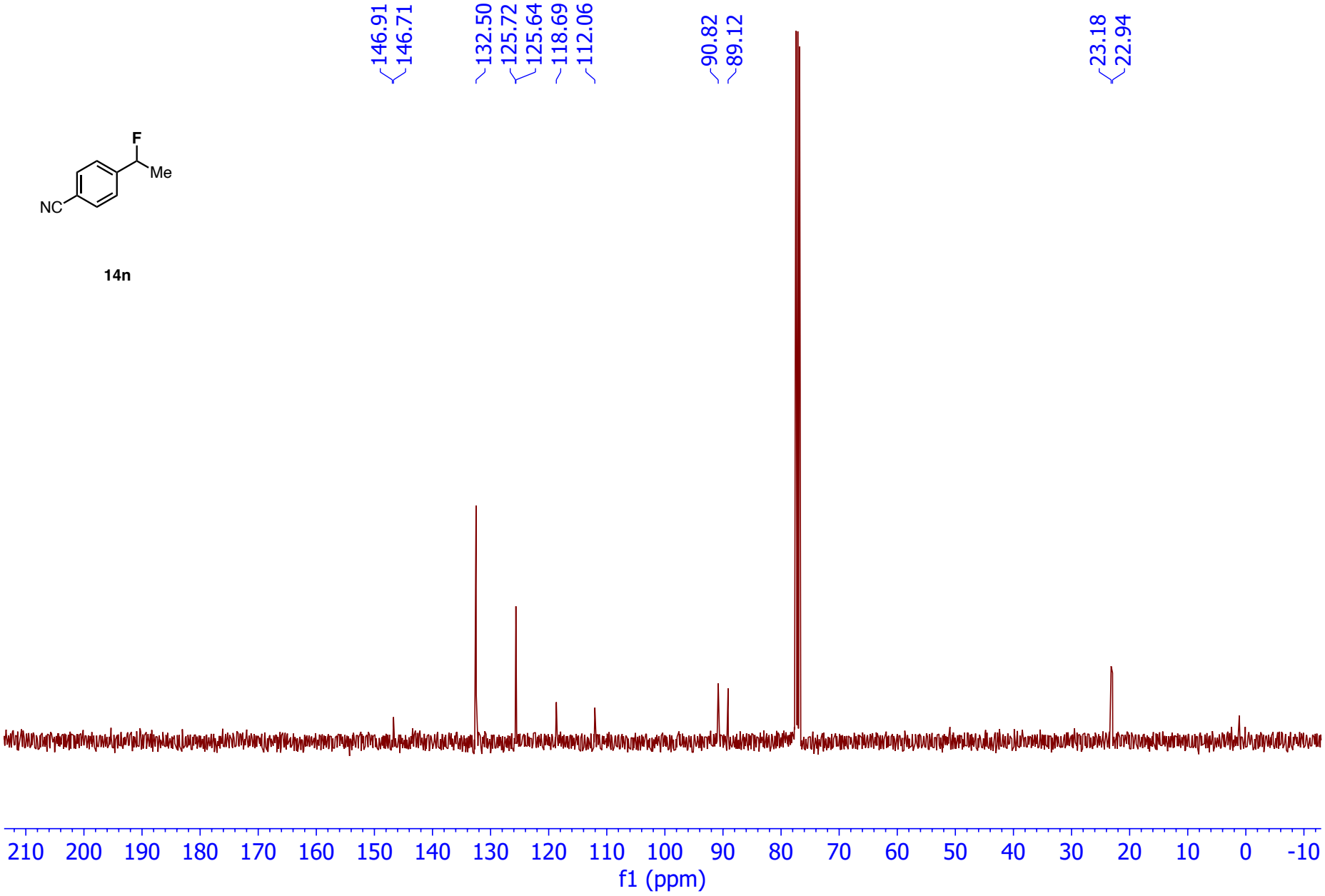
400 HMz, Chloroform-d



14n

^{1}H NMR of 14n

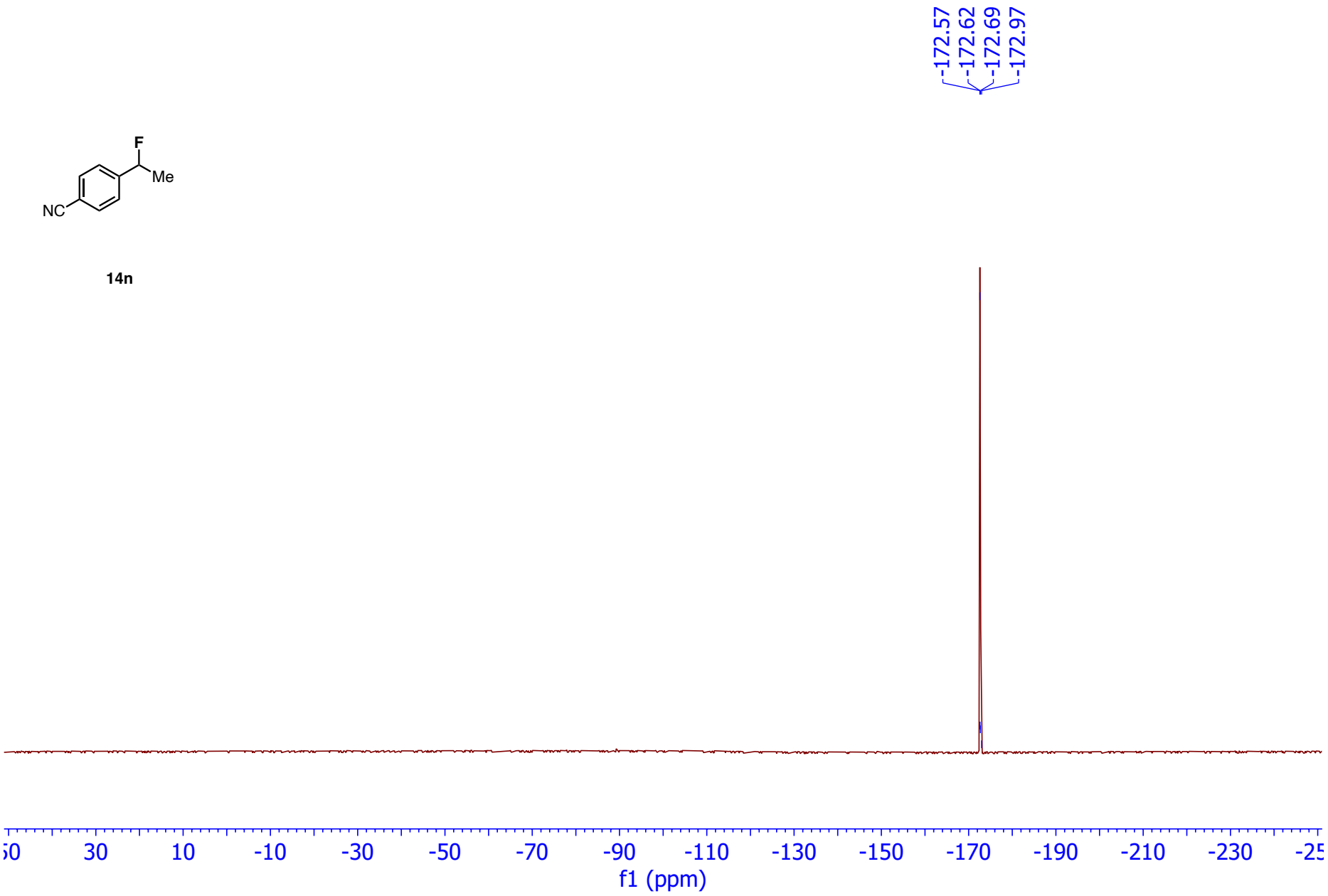
101 MHz, Chloroform-d



14n

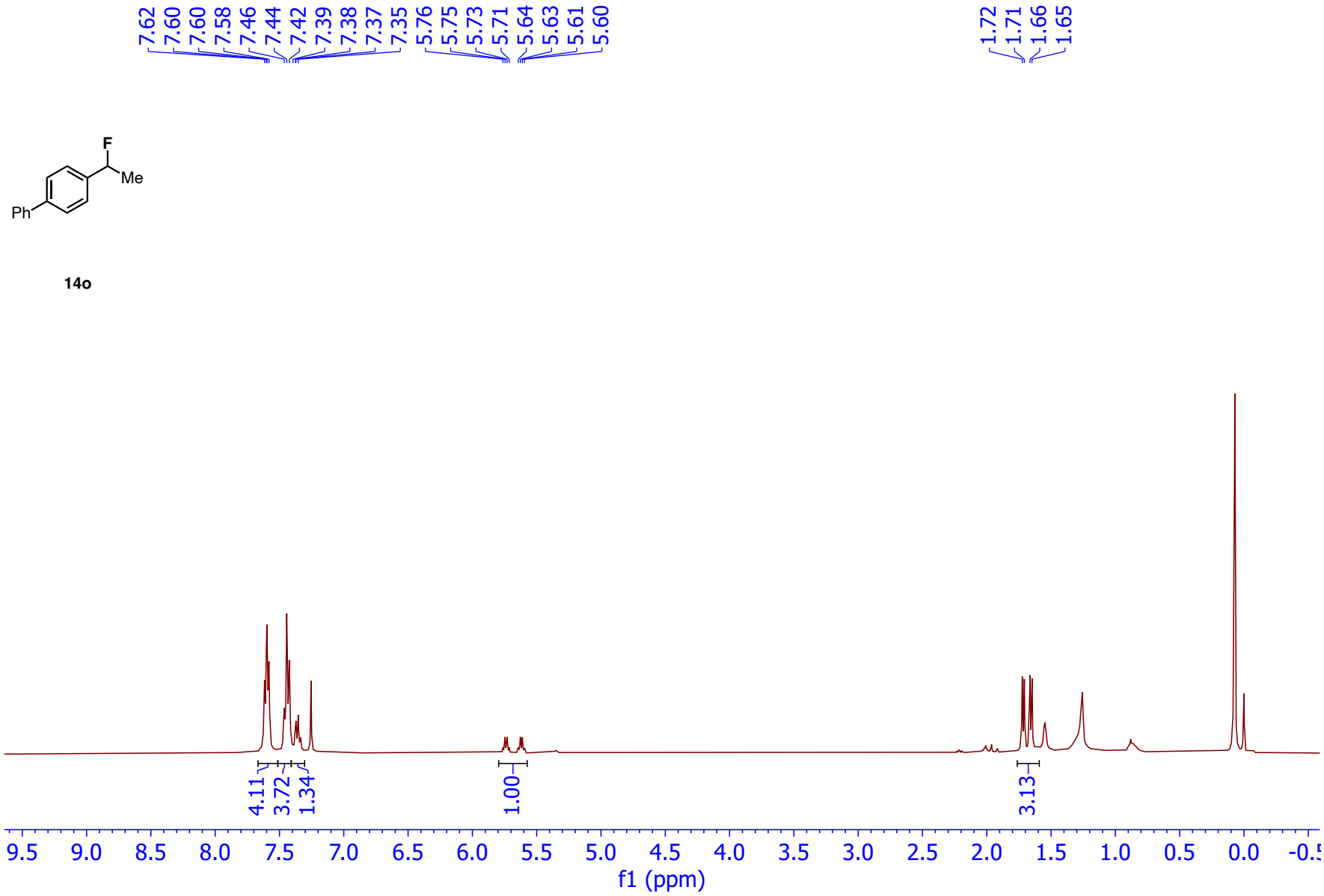
^{13}C NMR of 14n

376MHz, Chloroform-d



^{19}F NMR of 14n

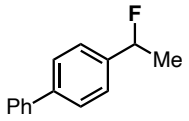
400 HMz, Chloroform-d



14o

^{1}H NMR of 14o

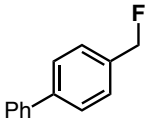
376MHz, Chloroform-d



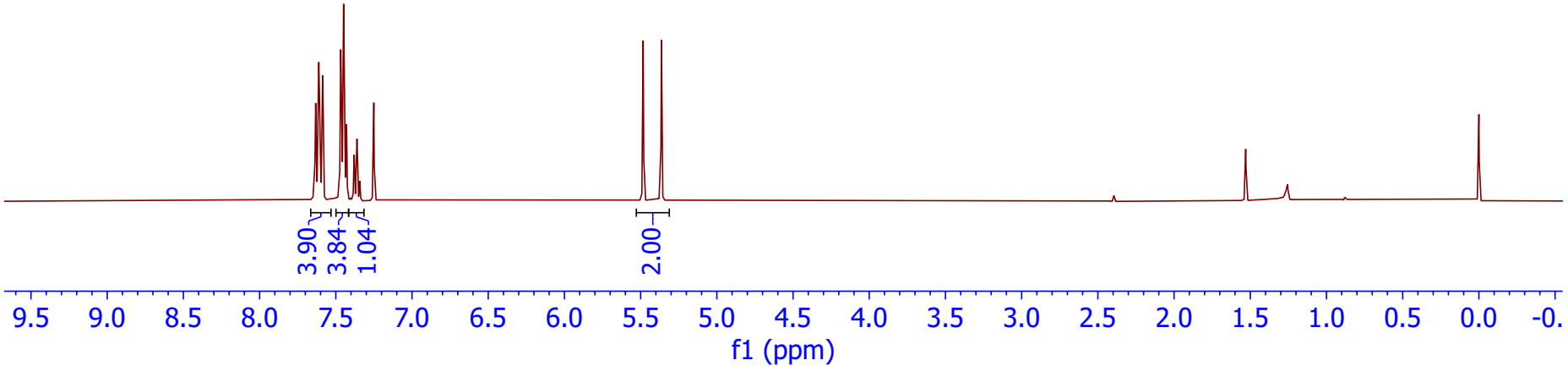
14o

^{19}F NMR of 14o

400 HMz, Chloroform-d

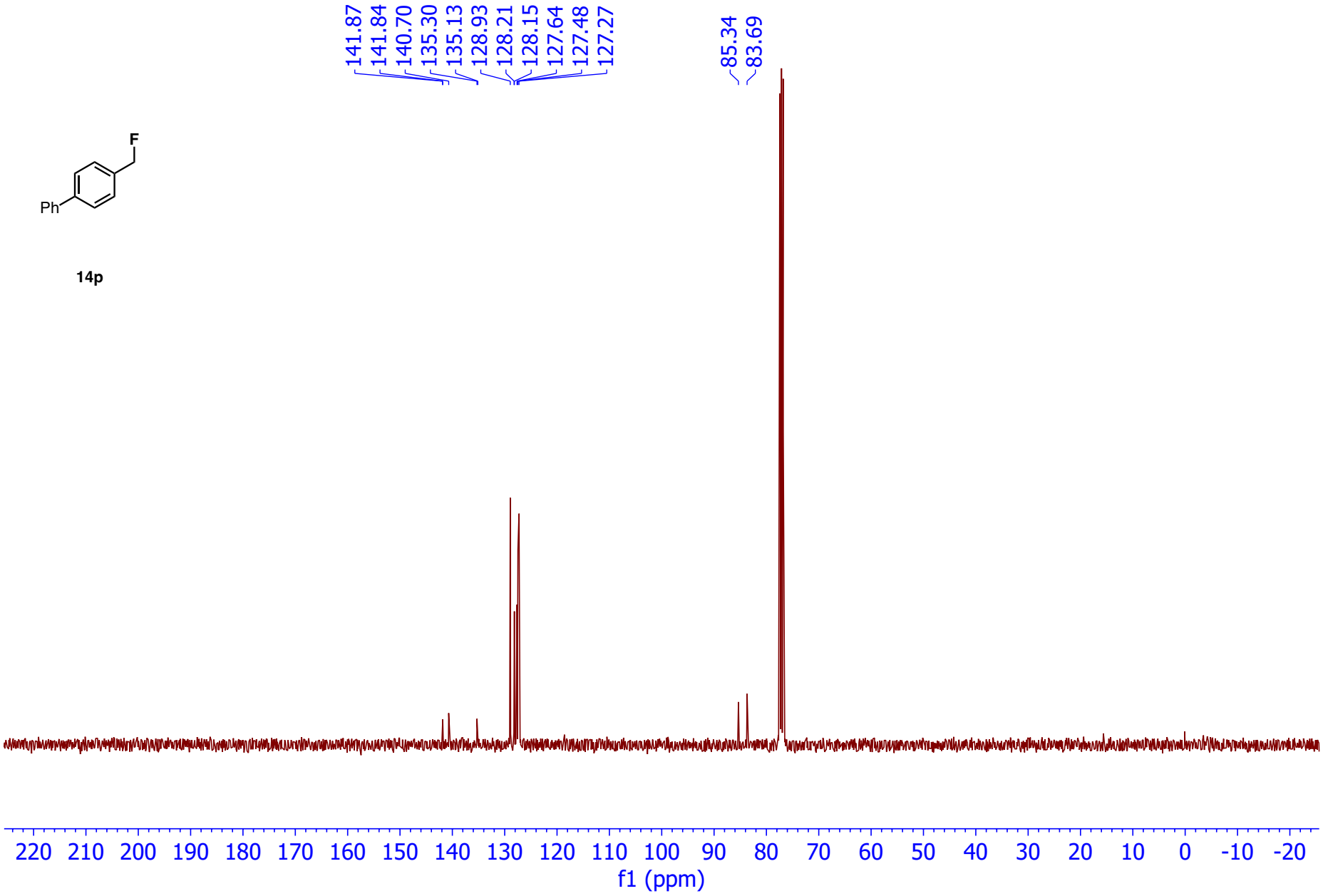


14p



^{1}H NMR of 14p

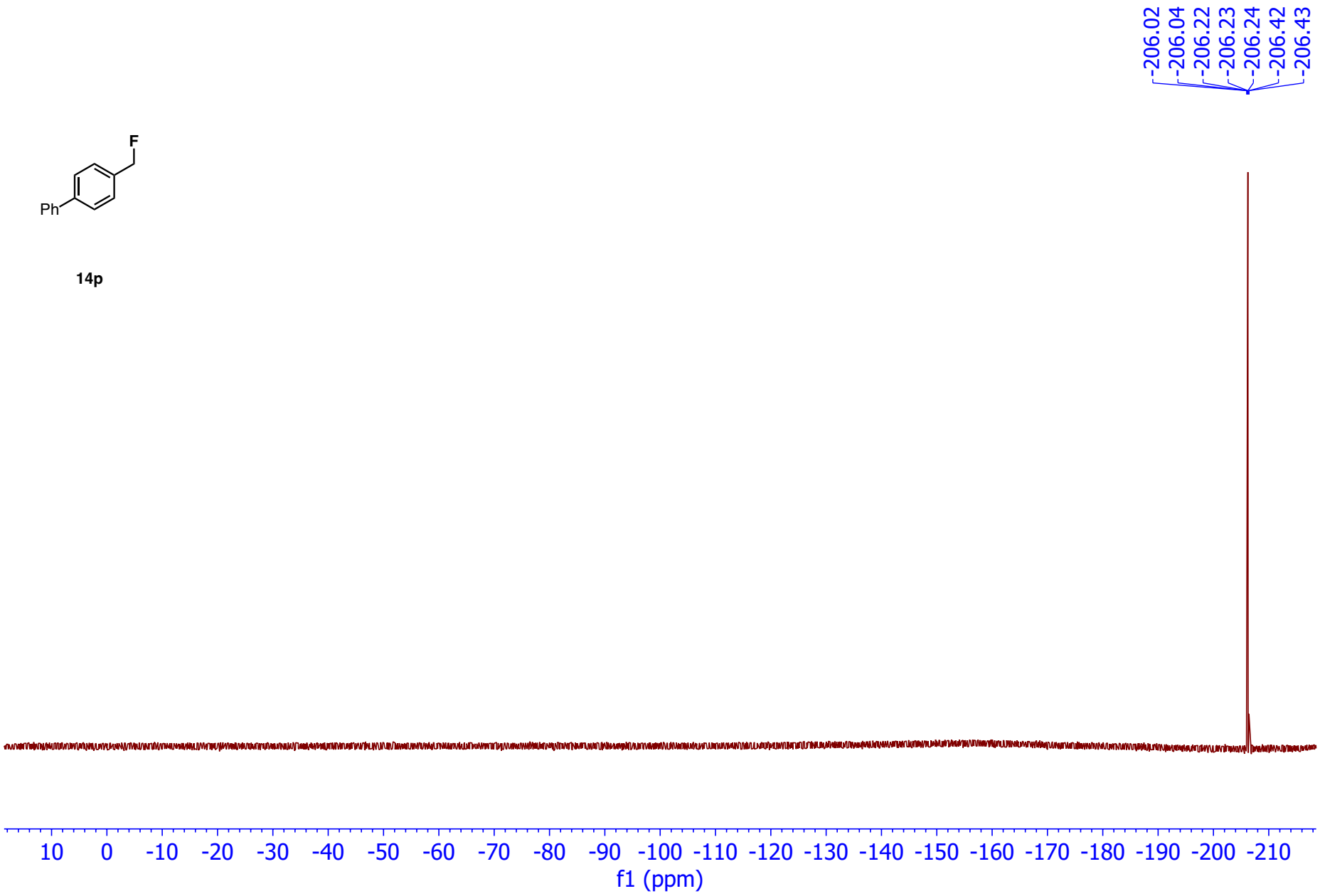
101 MHz, Chloroform-d



14p

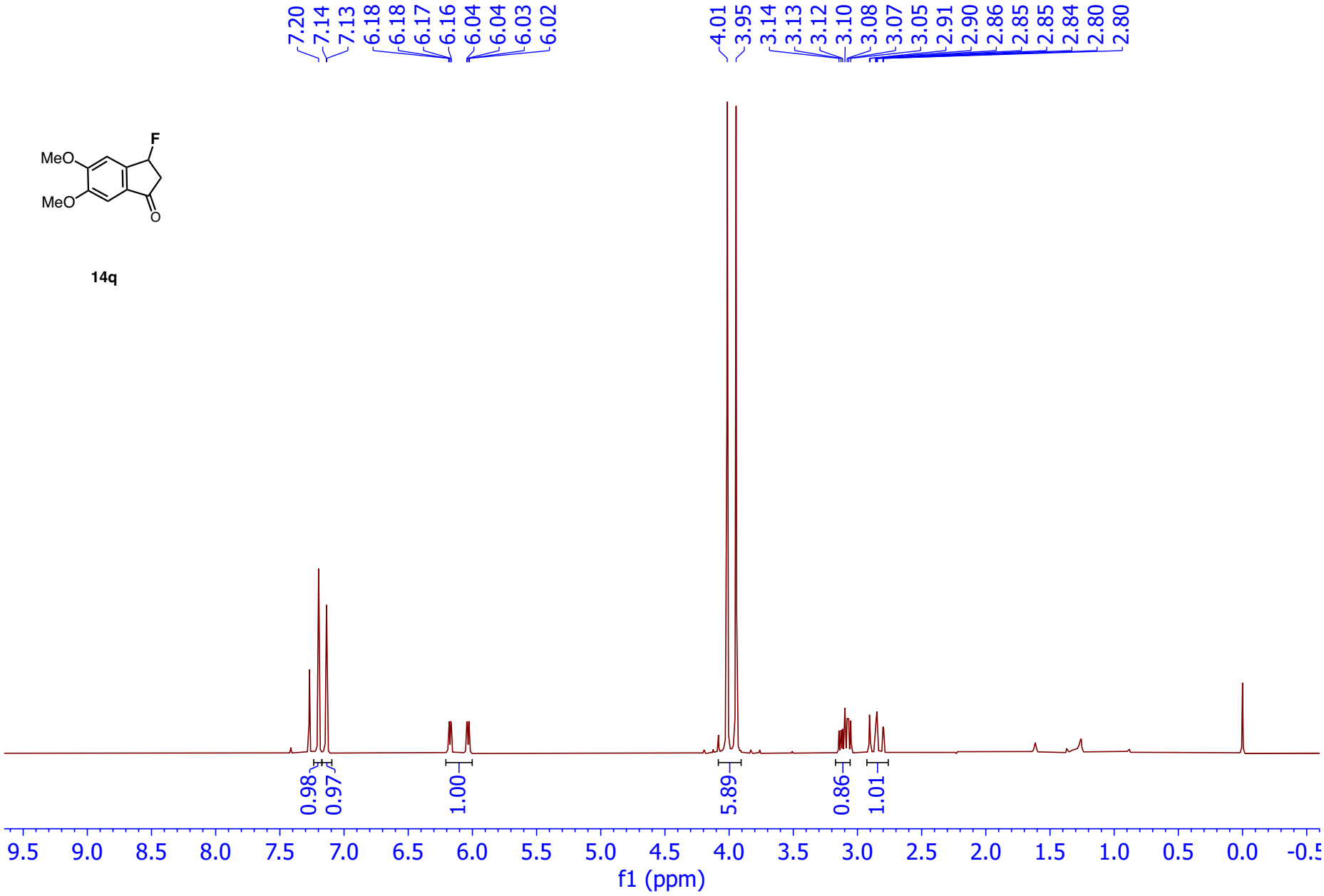
^{13}C NMR of 14p

376MHz, Chloroform-d



^{19}F NMR of 14p

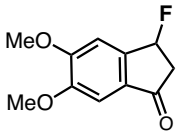
400 HMz, Chloroform-d



^{1}H NMR of 14q

101 MHz, Chloroform-d

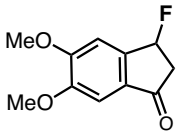
198.78
154.80
154.77
150.90
144.32
144.14
129.39
129.37
106.12
102.63
87.90
86.14
55.44
55.40
55.27
55.23
43.23
43.02



14q

^{13}C NMR of 14q

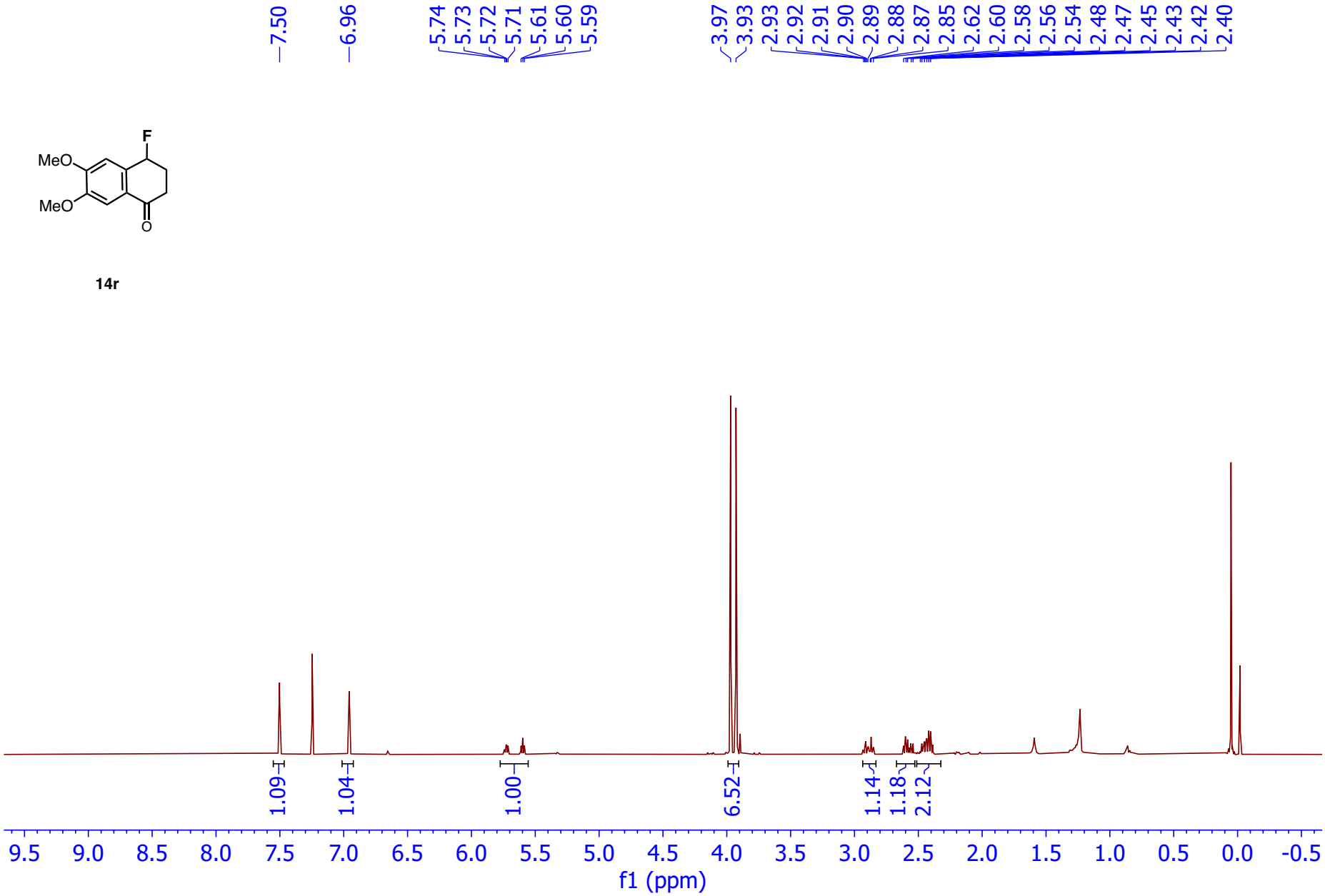
376MHz, Chloroform-d



14q

^{19}F NMR of 14q

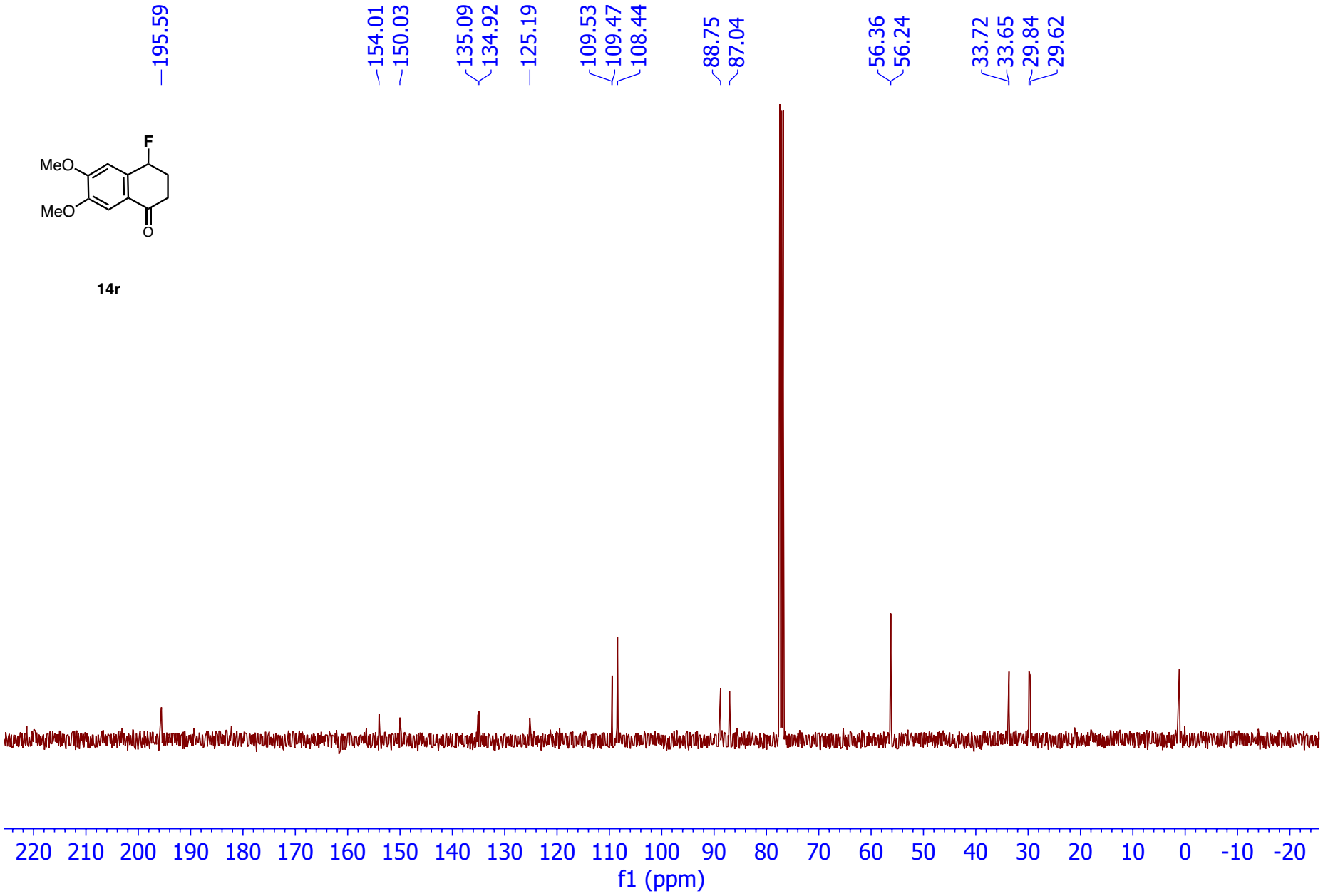
400 HMz, Chloroform-d



14r

^{1}H NMR of 14r

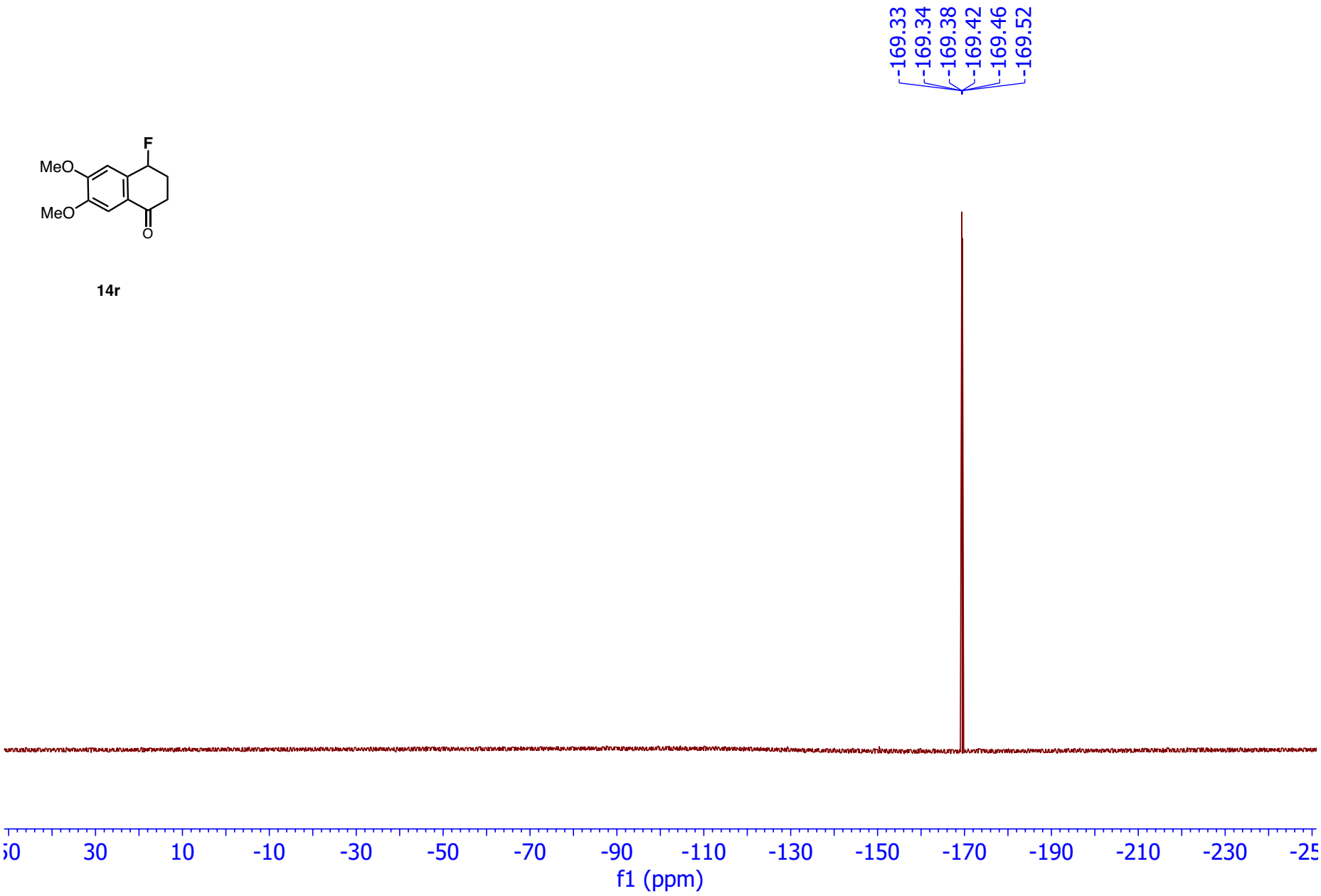
101 MHz, Chloroform-d



14r

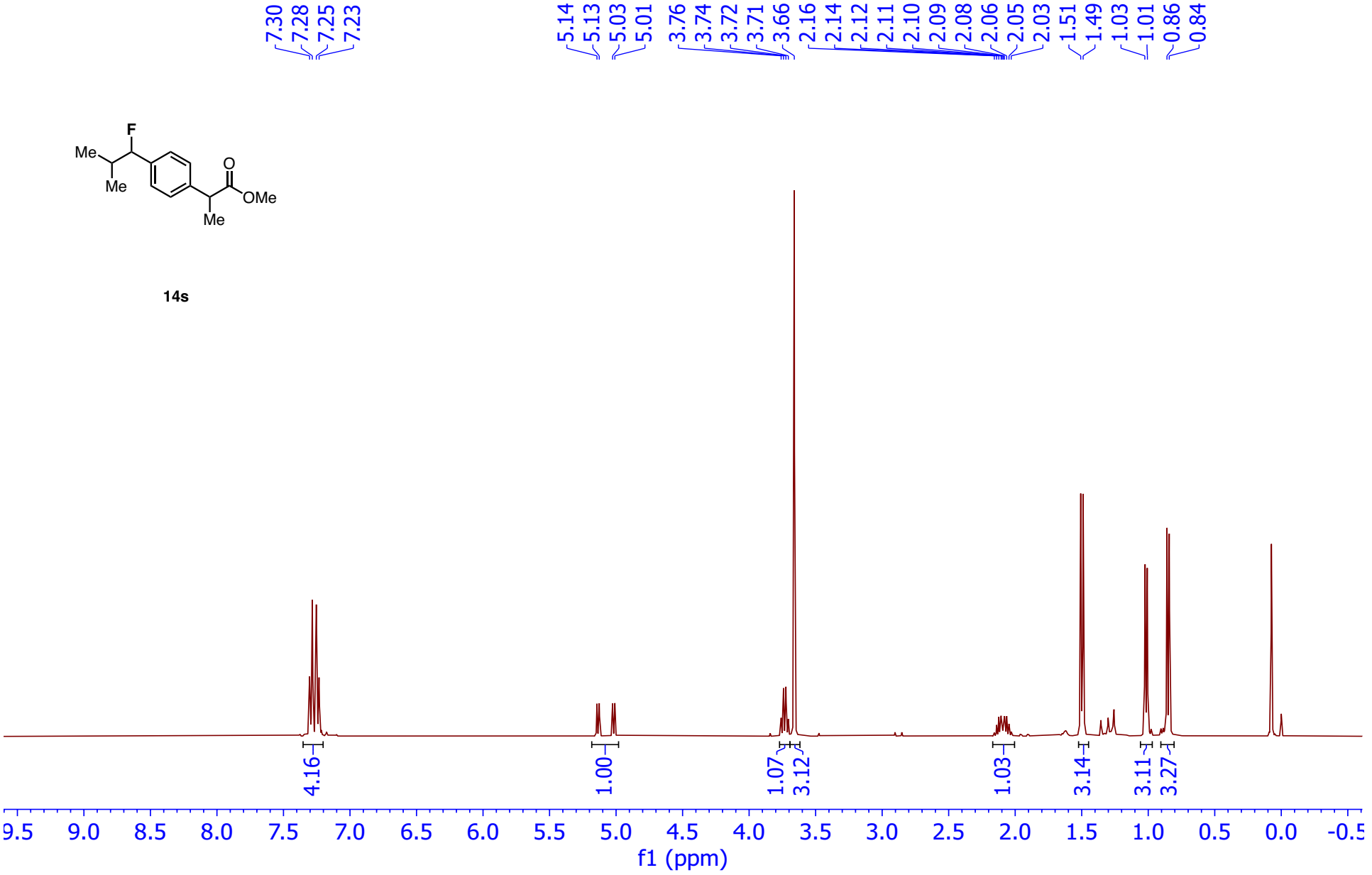
^{13}C NMR of 14r

376MHz, Chloroform-d



^{19}F NMR of 14r

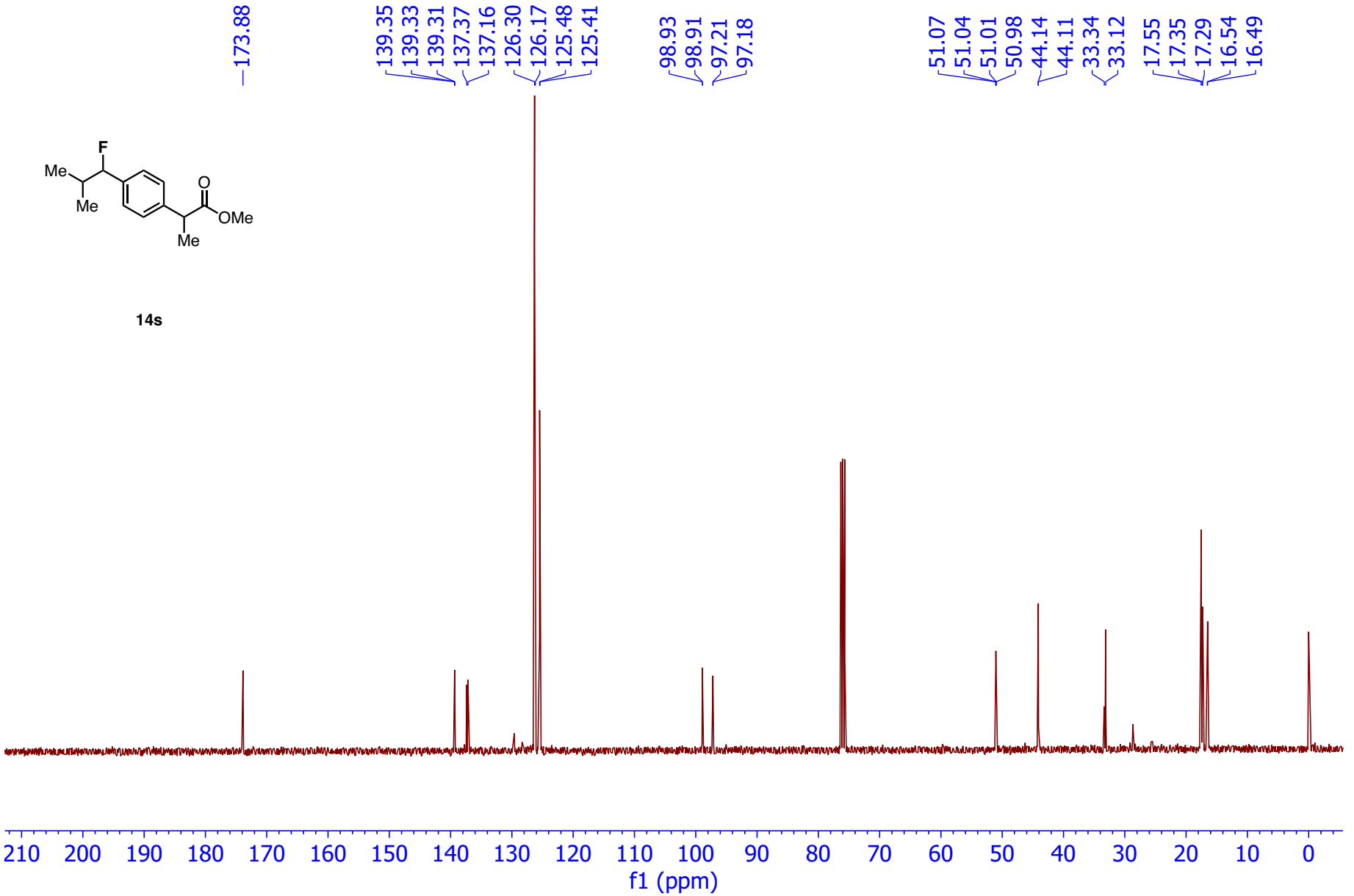
400 HMz, Chloroform-d



14s

^{1}H NMR of 14s

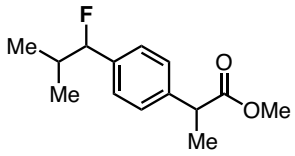
101 MHz, Chloroform-d



14s

^{13}C NMR of 14s

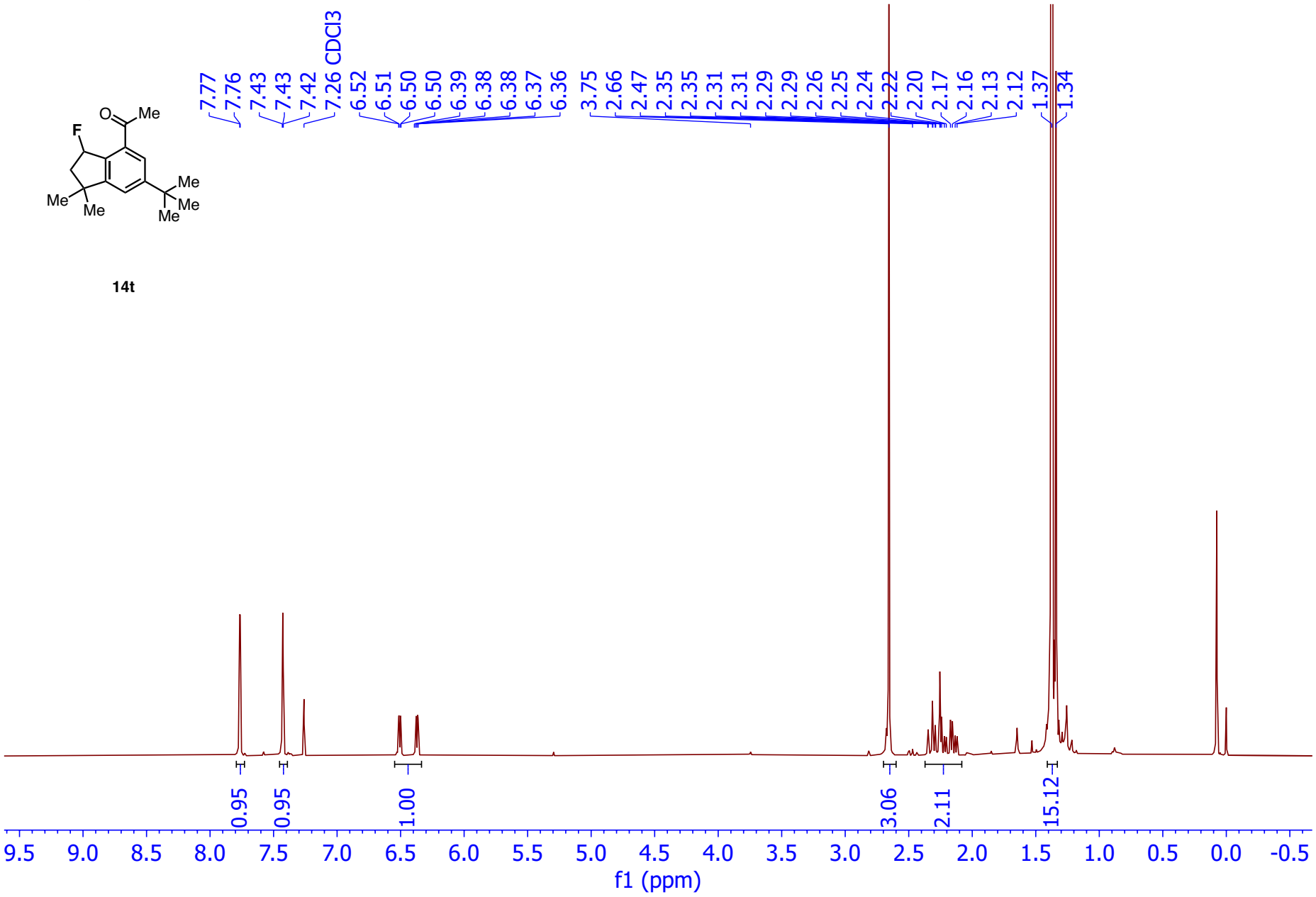
376MHz, Chloroform-d



14s

^{19}F NMR of 14s

400 HMz, Chloroform-d

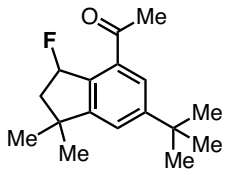


14t

^{1}H NMR of 14t

101 MHz, Chloroform-d

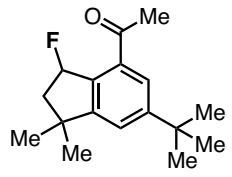
198.64
154.82
154.77
153.15
153.11
134.12
133.96
133.87
124.56
124.53
122.55
122.52
93.56
91.85
47.49
47.46
47.24
41.70
41.68
34.07
30.48
30.34
28.00
27.95
27.61
27.57
26.18



14t

^{13}C NMR of 14t

376MHz, Chloroform-d



14t

^{19}F NMR of 14t