SUPPORTING INFORMATION

AlkylFluor: Deoxyfluorination of Alcohols

Nathaniel W. Goldberg, Xiao Shen, Jiakun Li, Tobias Ritter*

Department of Chemistry and Chemical Biology, Harvard University
Cambridge, Massachusetts 02138

Max-Planck-Institut für Kohlenforschung
Mülheim an der Ruhr, Germany

*E-mail: ritter@mpi-muelheim.mpg.de

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MATERIALS AND METHODS

All manipulations were performed using oven-dried glassware (130 °C for a minimum of 12 hours) and standard Schlenk techniques under an atmosphere of nitrogen, unless otherwise stated.

Solvents

Dioxane was distilled from deep purple sodium benzophenone ketyl. Acetonitrile, dichloromethane, and toluene were dried by filtration through a drying column on an mBraun solvent system. Dimethylsulfoxide and *N*,*N*-dimethylformamide were dried by distillation from calcium hydride. Deuterated solvents were purchased from Cambridge Isotope Laboratories.

Chromatography

Thin layer chromatography (TLC) was performed using EMD TLC plates pre-coated with 250 μm thickness silica gel 60 F_{254} plates and visualized by fluorescence quenching under UV light and staining with potassium permanganate, cerium ammonium molybdate, or 2,4-dinitrophenylhydrazine. Flash chromatography was performed using silica gel (230-400 mesh) purchased from Silicycle Inc.

Spectroscopy and Instruments

NMR spectra were recorded on a Varian Unity/Inova 500 spectrometer operating at 500 MHz, 125 MHz, and 470 MHz for ^{1}H, ^{13}C, and ^{19}F acquisitions, respectively. Chemical shifts are reported in ppm with the solvent resonance as the internal standard. For ^{1}H NMR: $CDCl_3$, δ 7.26; C_6D_6, δ 7.16, CD_2Cl_2 δ 5.32. For ^{13}C NMR: $CDCl_3$, δ 77.16; C_6D_6, δ 128.06, CD_2Cl_2, δ 53.8. Data is reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, spt = septet, m = multiplet, br = broad; coupling constants in Hz; integration.

Starting materials

All compounds were used as received from commercial suppliers, unless otherwise stated. 1,3-Bis(2,6-diisopropylphenyl)-2-chloroimidazolium chloride was prepared according to the literature method[1]. DAST was purchased from Acros Organics. XtalFluor-M, 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose, *N*-boc-*trans*-4-hydroxyproline methyl ester, benzyl (*S*)-mandelate, epiandrosterone, and Disperse Red 1 were purchased from Aldrich. Metronidazole was purchased from Santa Cruz Biotechnology. Lumefantrine was purchased from TCI. 4-Nitrobenzyl alcohol was purchased from Eastman Organic Chemicals. Testosterone was purchased from CalBioChem. 2,3,4,6-Tetra-*O*-benzylglucopyranose was obtained from the laboratory of Professor Daniel Kahne. Tolvaptan was purchased from Oakwood Chemicals.

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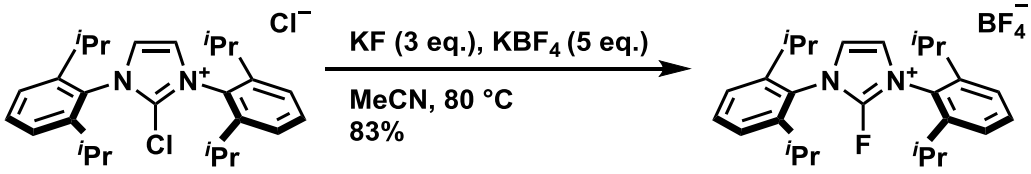
[1] Fujimoto, T.; Becker, F.; Ritter, T. *Org. Proc. Res. Develop.* **2014**, *18*, 1041.

EXPERIMENTAL DATA

Preparation of reagent

1,3-Bis(2,6-diisopropylphenyl)-2-fluoroimidazolium tetrafluoroborate (AlkylFluor)



1 **AlkylFluor**

All reagents were thoroughly dried before use. Under nitrogen atmosphere, 1,3-bis(2,6-diisopropylphenyl)-2-chloroimidazolium chloride (**1**) (21.0 g, 45.7 mmol, 1.00 equiv.), potassium fluoride (7.97 g, 137 mmol, 3.00 equiv.), and potassium tetrafluoroborate (28.8 g, 229 mmol, 5.00 equiv.) were suspended in dry acetonitrile (300 mL) in a 350 mL pressure flask. The mixture was heated at 80 °C for 16 hours with vigorous stirring. The reaction mixture was cooled to room temperature, then filtered through a pad of Celite, eluting with dichloromethane (3 × 25 mL). The filtrate was concentrated *in vacuo*, and the residue was dissolved in dichloromethane (200 mL) and filtered again through Celite, eluting with dichloromethane (3 × 25 mL). The filtrate was concentrated *in vacuo* and the residual solid was washed with diethyl ether (3 × 15 mL) to afford the title compound as a colorless solid (18.8 g, 83%).

NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.88 (d, *J* = 2.4 Hz, 2 H), 7.65 (t, *J* = 7.8 Hz, 2 H), 7.41 (d, *J* = 7.8 Hz, 4 H), 2.50 (spt, *J* = 6.8 Hz, 4 H), 1.35 (d, *J* = 6.7 Hz, 12 H), 1.19 (d, *J* = 6.8 Hz, 12 H)

^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 145.5, 143.1 (d, J_{CF} = 278.8 Hz), 133.3, 125.7, 125.5, 122.2 (d, J_{CF} = 5.7 Hz), 29.6, 24.2, 23.7

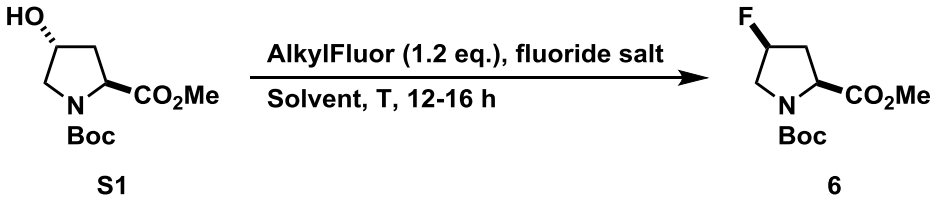
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC, δ): –108.0 (1 F), –152.9, –153.0 (4 F)

HRMS-FIA (m/z) calc'd for $C_{27}H_{36}FN_2$ $[M–BF_4]^+$, 407.2857; found, 407.2778

Optimization of deoxyfluorination reaction

In a nitrogen-filled glovebox, a 4 mL vial was charged with *N*-boc-*trans*-4-hydroxyproline methyl ester (12.3 mg, 50.0 µmol, 1.00 equiv.), fluoride salt, and AlkylFluor (29.7 mg, 60.0 µmol, 1.20 equiv.). Solvent (1.5 mL) was added, then the vial was sealed and removed from the glovebox. The mixture was heated to the appropriate temperature overnight with vigorous stirring, then cooled to room temperature. Benzotrifluoride (5.0 µL, 41 µmol, 0.81 equiv.) was added as a standard. The yield was determined by comparing the integration of the ^{19}F NMR resonance of the fluorinated product (δ –173 ppm) with that of benzotrifluoride (δ − 62.6 ppm).

Table S1: Optimization of deoxyfluorination reaction



S1 **6**

Entry	Solvent	Fluoride salt	T (° C)	Yield of 6 (%)
1	DMSO	KF (3 eq.)	80	23
2	DMSO	CsF (3 eq.)	80	32
3	DMF	KF (3 eq.)	80	25
4	DMF	CsF (3 eq.)	80	57
5	Acetonitrile	KF (3 eq.)	80	58
6	Acetonitrile	CsF (3 eq.)	80	78
7	Toluene	KF (3 eq.)	80	62
8	Toluene	CsF (3 eq.)	80	80
9	Dioxane	KF (3 eq.)	80	79
10	Dioxane	CsF (3 eq.)	80	83
11	Dioxane	None	80	<1
12	Dioxane	KF (3 eq.)	23	35
13	Dioxane	CsF (3 eq.)	23	54
14	Dioxane	KF (3 eq.)	40	79
15	Dioxane	KF (5 eq.)	40	89
16	Dioxane	KF (10 eq.)	40	95

Evaluation of commercial deoxyfluorination reagents

DAST[2]: Alcohol (50. µmol, 1.0 equiv.) was dissolved in dry dichloromethane under nitrogen. The solution was cooled to 0 °C. DAST (9.9 µL, 75 µmol, 1.5 equiv.) was added. The reaction mixture was then warmed to 23 °C and stirred for 18 hours. Benzotrifluoride (5.0 µL, 41 µmol, 0.81 equiv.) was added as a standard, and the yield was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of benzotrifluoride (δ –62.6 ppm). In all cases, TLC analysis of the reaction mixture showed complete consumption of the alcohol starting material. For 4-hydroxyproline, elimination was the major side reaction. For testosterone, a complex mixture of unidentified products was observed.

[2] Singh, R. P.; Shreeve, J. M. *Synthesis*. **2002**, *17*, 2561-2578.

XtalFluor-M procedure A[3]: Alcohol (50. μmol, 1.0 equiv.) was dissolved in dry dichloromethane under nitrogen. The solution was cooled to 0 °C. XtalFluor-M (18.2 mg, 75 μmol, 1.5 equiv.) was added, then DBU (11.2 μL, 75 μmol, 1.5 equiv.). The reaction mixture was warmed to 23 °C and stirred for 18 hours. Benzotrifluoride (5.0 μL, 41 μmol, 0.81 equiv.) was added as a standard, and the yield was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of benzotrifluoride (δ –62.6 ppm). In all cases, TLC analysis of the reaction mixture showed complete consumption of the alcohol starting material, with elimination as the major side reaction.

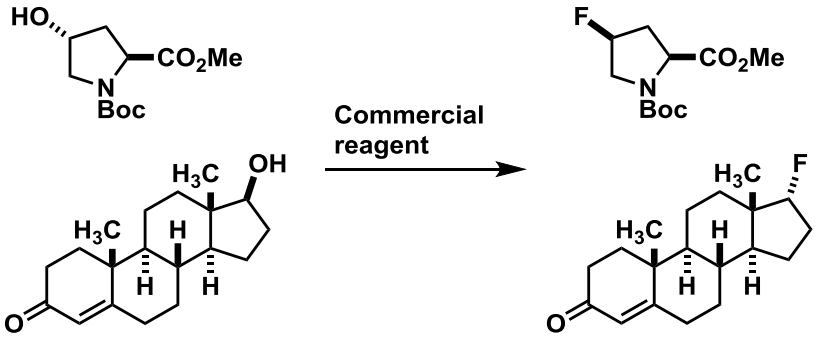
XtalFluor-M procedure B[3]: Alcohol (50. μmol, 1.0 equiv.) was dissolved in dry dichloromethane under nitrogen. The solution was cooled to 0 °C. XtalFluor-M (18.2 mg, 75 μmol, 1.5 equiv.) was added, then triethylamine trihydrofluoride (16.3 μL, 100 μmol, 2.0 equiv.). The reaction mixture was warmed to 23 °C and stirred for 18 hours. Benzotrifluoride (5.0 μL, 41 μmol, 0.81 equiv.) was added as a standard, and the yield was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of benzotrifluoride (δ –62.6 ppm). In all cases, TLC analysis of the reaction mixture showed complete consumption of the alcohol starting material, with elimination as the major side reaction.

PyFluor[4]: Alcohol (0.200 mmol, 1.00 equiv.) was dissolved in dry toluene (1.0 mL). PyFluor (25.3 μL, 0.220 mmol, 1.10 equiv.) was added, followed by base (0.400 mmol, 2.00 equiv.). The reaction was heated with vigorous stirring for 48 hours under ambient atmosphere. The reaction was cooled to room temperature and, benzotrifluoride (10.0 μL, 81.4 μmol, 0.407 equiv.) was added as a standard. The yield was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of benzotrifluoride (δ − 62.6 ppm). In all cases, ^{19}F NMR showed complete consumption of PyFluor.

[3] L'Heureux, A.; Beaulieu, F., Bennett, C.; Bill, D. R.; Clayton, S.; LaFlamme, F.; Mirmehrabi, M.; Tayadon, S.; Tovell, D.; Couturier, M. *J. Org. Chem*. **2010**, *75*(10), 3401-3411.

[4] Nielsen, M. K.; Ugaz, C. R.; Li, W.; Doyle, A. G. *J. Am. Chem. Soc.* **2015**, *137*, 9571-9574.

Table S2: Evaluation of commercial deoxyfluorination reagents

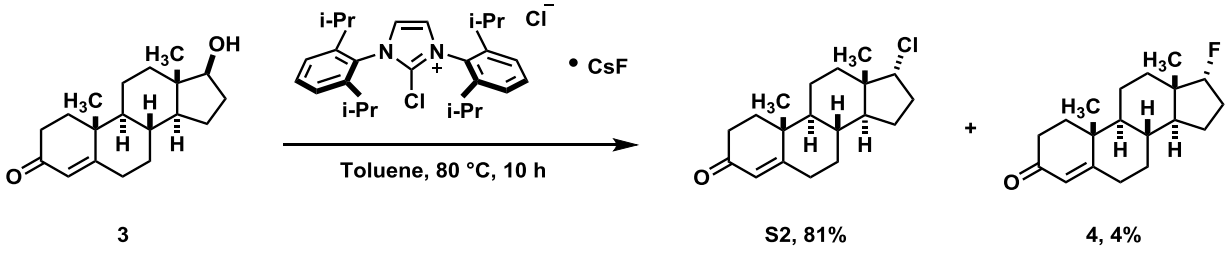


Reagent	Additive	T (°C)	Yield (%)	
			4-Fluoroproline (δ –173)	Fluorodeoxytestosterone (δ –178)
DAST	—	0 → 23	73	17
XtalFluor-M	DBU	0 → 23	40	7
XtalFluor-M	NEt_3·3HF	0 → 23	53	10
PyFluor	DBU	50	73[a]	<1
PyFluor	MTBD	50		<1
PyFluor	DBU	80		7
PyFluor	MTBD	80		<1

[a] Reported isolated yield[4]

Evaluation of PhenoFluorMix[5]

17-*epi*-17-Chloro-17-deoxytestosterone (S2)



3 **S2, 81%** **4, 4%**

In an argon-filled glovebox, an oven-dried vial was charged with 1,3-bis(2,6-diisopropylphenyl)-2-chloroimidazolium chloride (138 mg, 0.30 mmol, 1.5 equiv.), previously dried (200 °C, 24 hours) cesium fluoride (303 mg, 2.00 mmol,10.0 equiv.) and testosterone (58 mg, 0.20 mmol, 1.0 equiv.). Toluene (4.0 mL) was added, then the vial was sealed and removed from the glovebox. The mixture was stirred at 80 °C for

[5] Fujimoto, T.; Ritter. T. *Org. Lett.* **2015**, *17*, 544-547.

10 hours. Purification by flash column chromatography on silica (ethyl acetate in hexanes = 11%) afforded the inseparable mixture of compound **S2**[6] and **4** (53 mg, the ratio of **S2**/**4** = 20:1) as a white solid.

NMR Spectroscopy:

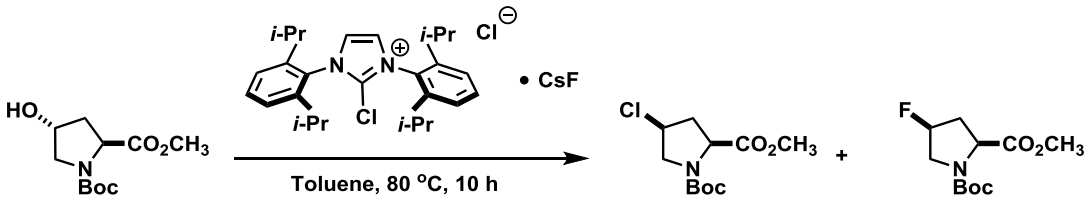
^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 5.71 (s, 1 H), 4.10–4.03 (d, *J* = 6.3 Hz, 1 H), 2.47–2.24 (m, 5 H), 2.05–0.96 (m, 14 H), 1.17 (s, 3H), 0.82 (s, 3 H)

^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ: 199.5, 171.0, 124.0, 70.9, 53.3, 47.9, 46.1, 38.7, 36.1, 35.8, 34.3, 34.0, 33.6, 32.9, 32.2, 24.6, 20.9, 18.0, 17.6

^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC, δ): –177.6

HRMS-FIA (m/z) calc'd for $C_{19}H_{27}ClNaO$ $[M+Na]^+$, 329.1643; found, 329.1641

N-Boc-*cis*-4-chloro-L-proline methyl ester (S3)



S1 **S3**, 95% **6**, trace

In an argon-filled glovebox, an oven-dried vial was charged with 1,3-bis(2,6-diisopropylphenyl)-2-chloroimidazolium chloride (35 mg, 0.075 mmol, 1.5 equiv.), previously dried (200 °C, 24 hours) cesium fluoride (76 mg, 0.50 mmol,10.0 equiv.) and *N*-boc-*trans*-4-hydroxyproline methyl ester **S1** (12.3 mg, 0.05 mmol, 1.0 equiv.). Toluene (1.0 mL) was added, then the vial was sealed and removed from the glovebox. The mixture was stirred at 80 °C for 10 hours. Purification by flash column chromatography on silica (ethyl acetate in hexanes = 17%) afforded 20 mg of the title compound **S3**[7] as a colorless oil, along with trace **6**.

NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 4.46–4.32 (m, 2 H), 4.00–3.90 (m, 1 H), 3.76 (s, 3 H), 3.67–3.60 (m, 1 H), 2.76–2.67 (m, 1 H), 2.38–2.34 (m, 1 H), 1.42 (s, 9 H)

[6] Cahiez, J.; Lefèvre, N.; Poizat, M.; Moyeux, A. *Synthesis* **2013**, *45*(2), 231–236.

[7] Chiba, J.; Takayama, G.; Takashi, T.; Yokoyama, M.; Nakayama, A.; Baldwin, J. J.; McDonald, E.; Moriarty, K. J.; Sarko. C. S.; Saionz, K. W.; Swanson, R.; Wong, A.; Machinaga, N. *Bioorg. Med. Chem.* **2006**, *14*(8), 2725–2746.

General procedures for the deoxyfluorination of alcohols

General Procedure A

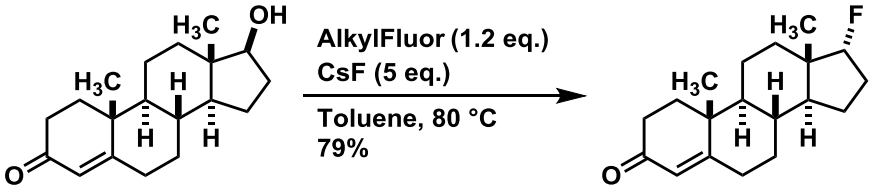
Potassium fluoride was pre-dried at 200 °C under high vacuum for 24 hours and stored in a desiccator. An oven-dried 4 mL vial was charged with a magnetic stir bar, potassium fluoride (58.1 mg, 1.00 mmol, 5.00 equiv.) and AlkylFluor (118.7 mg, 0.240 mmol, 1.20 equiv.), and heated at 100 °C for 1 hour under vacuum (~0.1 mbar). The mixture was cooled to room temperature, then alcohol (0.200 mmol, 1.00 equiv.) was added quickly. The vial was sealed, then evacuated and backfilled three times with nitrogen. Dioxane (3.0 mL) was added by syringe. The reaction mixture was heated at the appropriate temperature with vigorous stirring. Upon completion, the reaction mixture was cooled to room temperature and filtered through a pad of Celite, eluting with dichloromethane (3 × 1 mL). The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography to afford the desired alkyl fluoride.

General Procedure B

Anhydrous cesium fluoride was stored in a desiccator. An oven-dried 4 mL vial was charged with cesium fluoride (152 mg, 1.00 mmol, 5.00 equiv.) and AlkylFluor (118.7 mg, 0.240 mmol, 1.20 equiv.) and heated at 120 °C for 1 hour under vacuum (~0.1 mbar). The vial was backfilled with nitrogen, and toluene (1.5 mL) was added by syringe. The mixture was heated to 100 °C with vigorous stirring until the suspension became visibly less cloudy (1-2 hours), indicating conversion of insoluble AlkylFluor to soluble PhenoFluor[1]. In a separate 4 mL vial, under nitrogen, a solution of alcohol (0.200 mmol, 1.00 equiv.) in toluene (1.0 mL) was prepared, and transferred to the reaction vial by syringe, rinsing with toluene (2 × 0.25 mL). The reaction was heated at the appropriate temperature with vigorous stirring. Upon completion, the reaction mixture was cooled to room temperature and filtered through a pad of Celite, eluting with dichloromethane (3 × 1 mL). The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography to afford the desired alkyl fluoride.

Deoxyfluorination of alcohols

17-*epi*-17-Fluoro-17-deoxytestosterone (4)



According to general procedure B, testosterone (57.7 mg, 0.200 mmol, 1.00 equiv.), cesium fluoride (152 mg, 1.00 mmol, 5.00 equiv.), and AlkylFluor (118.7 mg, 0.240 mmol, 1.20 equiv.) were stirred in toluene (3.0 mL) at 80 °C for 16 hours. The reaction was cooled to room temperature and concentrated *in vacuo*, and the residue was purified by flash column chromatography on silica eluting with hexanes/ethyl acetate (10:1 to 6:1 v/v), to afford the title compound as a colorless crystalline solid (45.7 mg, 79%).

R_f = 0.13 (hexanes/ethyl acetate 8:1 v/v, UV quenching)

NMR Spectroscopy:

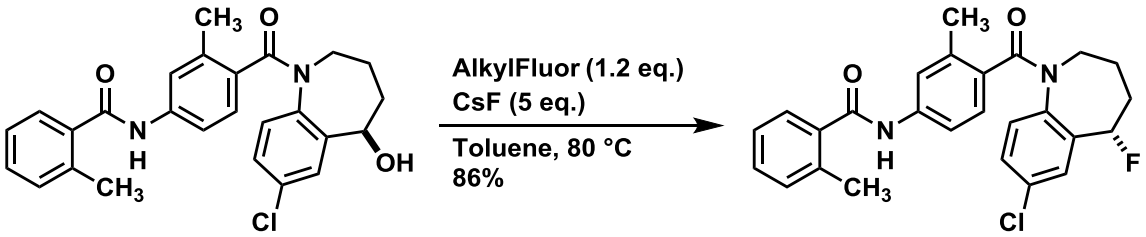
^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 5.74 (s, 1 H), 4.52 (dd, *J* = 55.3, 5.4 Hz, 1 H), 2.48–2.00 (m, 6 H), 1.92–1.41 (m, 10 H), 1.29–1.07 (m, 2 H), 1.19 (s, 3 H), 1.03–0.95 (m, 1 H), 0.71 (d, *J* = 2.4 Hz, 3 H)

^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ: 199.6, 171.1, 124.0, 201.8 (d, J_{CF} = 179.8 Hz), 53.6, 48.6, 45.2, (d, J_{CF} = 17.7 Hz), 38.8, 35.8 (d, J_{CF} = 9.1 Hz), 34.1, 33.0, 30.8 (d, J_{CF} = 5.8 Hz), 30.4, 30.2, 24.4, 20.5, 17.6, 15.5 (d, J_{CF} = 7.7 Hz)

^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC, δ): –177.7 (dt, *J* = 55.3, 34.3 Hz)

HRMS-FIA (m/z) calc'd for $C_{19}H_{28}FO$ $[M+H]^+$, 291.2119; found, 291.2146

Fluorodeoxytolvaptan (5)



According to general procedure B, tolvaptan (44.9 mg, 0.100 mmol, 1.00 equiv.), cesium fluoride (76.0 mg, 0.500 mmol, 5.00 equiv.), and AlkylFluor (59.4 mg, 0.120 mmol, 1.20 equiv.) were stirred in toluene (3.0 mL) at 80 °C for 17 hours. The reaction was cooled to room temperature and concentrated *in vacuo*, and the residue was purified by flash column chromatography on silica eluting with hexanes/ethyl acetate (5:1 to 3:2 v/v), to afford the title compound as a colorless solid (38.8 mg, 86%).

R_f = 0.17 (hexanes/ethyl acetate 2:1 v/v, UV quenching)

NMR Spectroscopy:

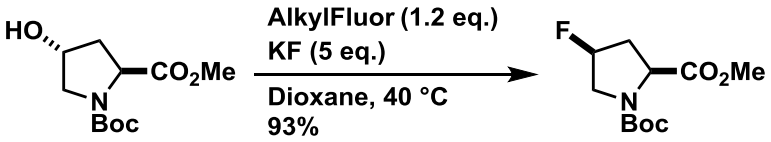
^{1}H NMR (500 MHz, CD_2Cl_2, –20 ºC, δ): [mixture of rotamers] 8.51–8.11 (m, 1 H), 7.59–7.41 (m, 1 H), 7.38–7.29 (m, 2 H), 7.27–7.11 (m, 3 H), 7.04–6.96 (m, 1 H), 6.89–6.81 (m, 0.3 H), 6.62–6.53 (m, 1 H), 6.42–6.36 (m, 0.2 H), 6.19–6.12 (m, 0.2 H), 5.79–5.47 (m, 1 H), 4.91–4.74 (m, 1 H), 2.92–2.74 (m, 1 H), 2.68–2.17 (m, 8 H), 2.09–1.87 (m, 1 H), 1.86–1.63 (m, 1 H), 1.32–1.17 (m, 1 H), 0.96–0.79 (m, 1 H)

^{13}C NMR (125 MHz, CD_2Cl_2, –20 ºC, δ: [mixture of rotamers] 169.1, 169.0, 168.3, 168.1, 139.9, 139.8, 139.1, 139.0, 138.6, 137.9 (d, J_{CF} = 5.7 Hz), 137.1, 137.0, 136.6, 136.5, 136.3, 136.2, 136.2, 134.6, 133.0 (d, J_{CF} = 2.9 Hz), 132.0, 131.7, 131.3, 131.2, 131.2, 130.3, 130.1, 129.6, 129.3, 128.0, 126.9, 125.8, 125.8, 124.4 (d, J_{CF} = 16.2 Hz), 121.1, 120.9, 116.0, 115.9, 94.6 (d, J_{CF} = 171.7 Hz), 92.0 (d, J_{CF} = 177.4 Hz), 47.3, 46.1, 45.0, 33.1 (d, J_{CF} = 21.9 Hz), 31.5, 31.2, 31.0, 25.4 (d, J_{CF} = 11.4 Hz), 22.8, 19.9, 19.8

^{19}F NMR (470 MHz, CD_2Cl_2, –20 ºC, δ): [mixture of rotamers] –176.9 (br s), –178.7 (br s), –179.8 (br m)

HRMS-FIA (m/z) calc'd for $C_{26}H_{25}ClFN_2O_2$ $[M+H]^+$, 451.1583; found, 451.1578

N-Boc-*cis*-4-fluoro-L-proline methyl ester (6)



According to general procedure A, *N*-boc-*trans*-4-hydroxyproline methyl ester (49.1 mg, 0.200 mmol, 1.00 equiv.), potassium fluoride (58.1 mg, 1.00 mmol, 5.00 equiv.), and AlkylFluor (118.7 mg, 0.240 mmol, 1.20 equiv.) were heated in dioxane (3.0 mL) at 40 °C for 17 hours. The reaction was cooled to room temperature and concentrated *in vacuo*, and the residue was purified by flash column chromatography on silica eluting with hexanes/ethyl acetate (8:1 to 4:1 v/v), to afford the title compound as a colorless oil (45.7 mg, 93%).

R_f = 0.17 (hexanes/ethyl acetate 4:1 v/v, $KMnO_4$ stain)

NMR Spectroscopy:

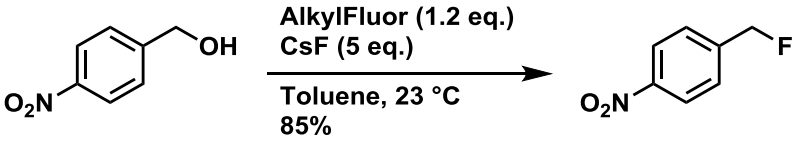
^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): [mixture of 2 rotamers] 5.20 (d, *J* = 52.7 Hz, 1 H, major + minor), 4.54 (d, *J* = 9.3 Hz, 1 H, minor), 4.42 (d, *J* = 9.8 Hz, 1 H major), 3.90–3.57 (m, 2 H, major + minor), 3.74 (s, 3 H, major + minor), 2.53-2.22 (m, 2 H, major + minor), 1.48 (s, 9 H, minor), 1.43 (s, 9 H, major)

^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 172.4, 172.0, 154.1, 153.7, 92.3 (d, J_{CF} = 177.4), 91.2 (d, J_{CF} = 177.4 Hz), 80.5, 57.8, 57.3, 53.3 (d, J_{CF} = 24.0 Hz), 53.0 (d, J_{CF} = 24.0 Hz), 52.5, 52.3, 37.6 (d, J_{CF} = 22.1 Hz), 36.7 (d, J_{CF} = 22.1 Hz), 28.5, 28.4

^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC, δ): –172.9 (m, minor), –173.2 (m, major)

HRMS-FIA (m/z) calc'd for $C_{11}H_{18}FNaO_4$ $[M+Na]^+$, 270.1112; found, 270.1149

4-Nitrobenzyl fluoride (7)



According to general procedure B, 4-nitrobenzyl alcohol (30.6 mg, 0.200 mmol, 1.00 equiv.), cesium fluoride (152 mg, 1.00 mmol, 5.00 equiv.), and AlkylFluor (118.7 mg, 0.240 mmol, 1.20 equiv.) were stirred in toluene (3.0 mL) at 23 °C for 16 hours. The reaction was cooled to room temperature and concentrated *in vacuo*, and the residue was purified by flash column chromatography on silica eluting with hexanes/ethyl acetate (15:1 to 12:1 v/v), to afford the title compound as a colorless oil (26.3 mg, 85%).

R_f = 0.33 (hexanes/ethyl acetate 10:1 v/v, UV quenching)

NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.26 (d, *J* = 8.3 Hz, 2 H) 7.53 (d, *J* = 8.3 Hz, 2 H) 5.51 (d, *J* =

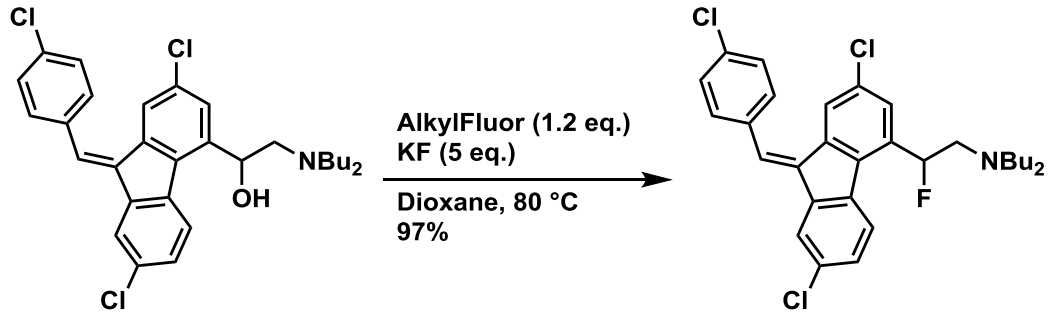
47.0 Hz, 2 H)

^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ: 148.1, 143.5 (d, J_{CF} = 17.7 Hz), 127.2 (d, J_{CF} = 6.7 Hz), 124.0, 83.0 (d, J_{CF} = 171.2 Hz)

^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC, δ): –215.7 (t, J = 46.7 Hz)

The compound does not form detectable ions under ESI conditions, so HRMS analysis was unsuccessful. NMR data match those reported[4].

Fluorodeoxylumefantrine (8)



According to general procedure A, lumefantrine (52.9 mg, 0.100 mmol, 1.00 equiv.), potassium fluoride (29.1 mg, 0.50 mmol, 5.00 equiv.), and AlkylFluor (59.3 mg, 0.120 mmol, 1.20 equiv.) were heated in dioxane (3.0 mL) at 80 °C for 17 hours. The reaction was cooled to room temperature and concentrated *in vacuo*, and the residue was purified by flash column chromatography on silica eluting with hexanes/ethyl acetate (20:1 v/v), to afford the title compound as a crystalline yellow solid (51.6 mg, 97%).

R_f = 0.62 (hexanes/ethyl acetate 9:1 v/v, UV quenching)

NMR Spectroscopy:

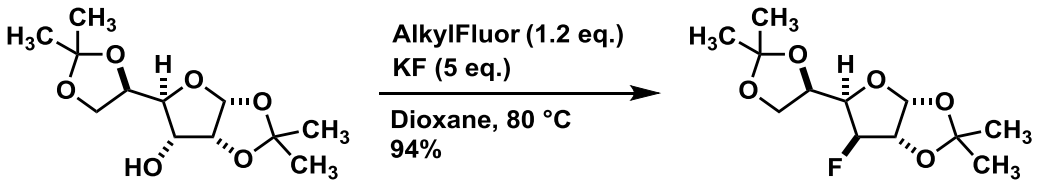
^{1}H NMR (500 MHz, C_6D_6, 23 ºC, δ): 7.69–7.61 (m, 3 H), 7.46 (d, J = 2.0 Hz, 1 H), 7.27 (dd, J = 8.2, 2.4 Hz, 1 H), 7.09–7.05 (m, 2 H), 7.00–6.94 (m, 3 H), 6.10 (ddd, J = 48.1, 7.0, 2.4 Hz, 1 H), 2.86–2.65 (m, 2 H), 2.62–2.36 (m, 4 H), 1.39–1.22 (m, 8 H), 0.90 (t, J = 7.3 Hz, 6 H)

^{13}C NMR (125 MHz, C_6D_6, 23 ºC, δ): 141.9, 138.9, 136.8 (d, J_{CF} = 21.1 Hz), 136.1, 135.1, 135.0, 135.0, 134.8, 134.3, 133.7, 133.3, 130.8, 129.3, 128.8, 128.3, 128.2, 128.0, 126.2 (d, J_{CF} = 13.4 Hz), 125.0 (d, J_{CF} = 2.0 Hz), 124.0, 121.2, 92.6 (d, J_{CF} = 176.4 Hz), 59.7 (d, J_{CF} = 22.1 Hz), 54.6, 29.5, 20.9, 14.3

^{19}F NMR (470 MHz, C_6D_6, 23 ºC, δ): –179.8 (ddd, J = 49.7, 31.7, 22.2 Hz)

HRMS-FIA (m/z) calc'd for $C_{30}H_{32}Cl_3FN$ $[M+H]^+$, 530.1579; found, 530.1585

3-Fluoro-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (9)



According to general procedure A, 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (52.1 mg, 0.200 mmol, 1.00 equiv.), potassium fluoride (58.1 mg, 1.00 mmol, 5.00 equiv.), and AlkylFluor (118.7 mg, 0.240 mmol, 1.20 equiv.) were heated in dioxane (3.0 mL) at 80 °C for 22 hours. The reaction was cooled to room temperature and concentrated *in vacuo*, and the residue was purified by flash column chromatography on silica eluting with hexanes/ethyl acetate (9:1 v/v), to afford the title compound as a colorless oil (49.4 mg, 94%).

R_f = 0.30 (hexanes/ethyl acetate 9:1 v/v, CAM stain)

NMR Spectroscopy:

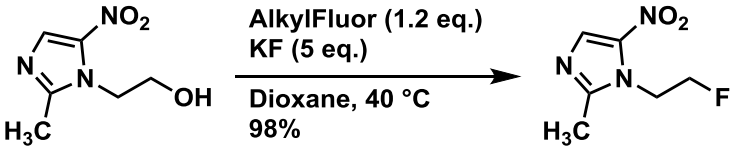
^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 5.95 (d, *J* = 3.4 Hz, 1 H), 5.01 (dd, *J* = 49.9, 2.5 Hz, 1 H), 4.70 (dd, *J* = 10.8, 3.4 Hz, 1 H), 4.32–4.25 (m, 1 H), 4.16–4.06 (m, 2 H), 4.03 (dd, *J* = 8.8, 4.9 Hz, 1 H), 1.50 (s, 3 H), 1.45 (s, 3 H), 1.36 (s, 3 H), 1.32 (s, 3 H)

^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 112.6, 109.7, 94.0 (d, J_{CF} = 184.1 Hz), 82.7 (d, J_{CF} = 32.6 Hz), 80.8 (d, J_{CF} = 19.2 Hz), 72.1 (d, J_{CF} = 7.7 Hz), 67.3, 27.0, 26.9, 26.4, 25.3

^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC, δ): –207.6 (ddd, *J* = 49.6, 29.1, 10.5 Hz)

HRMS-FIA (m/z) calc'd for $C_{12}H_{19}FNaO_5$ $[M+Na]^+$, 285.1109; found, 285.1121

1-(2-Fluoroethyl)-2-methyl-5-nitro-1*H*-imidazole (10)



According to general procedure A, metronidazole (34.2 mg, 0.200 mmol, 1.00 equiv.), potassium fluoride (58.1 mg, 1.00 mmol, 5.00 equiv.), and AlkylFluor (118.7 mg, 0.240 mmol, 1.20 equiv.) were heated in dioxane (3.0 mL) at 40 °C for 17 hours. The reaction was cooled to room temperature and concentrated *in vacuo*, and the residue was purified by flash column chromatography on silica eluting with hexanes/ethyl acetate (4:1 v/v) to ethyl acetate, to afford the title compound as a colorless oil (33.8 mg, 98%).

R_f = 0.34 (ethyl acetate, $KMnO_4$ stain)

NMR Spectroscopy:

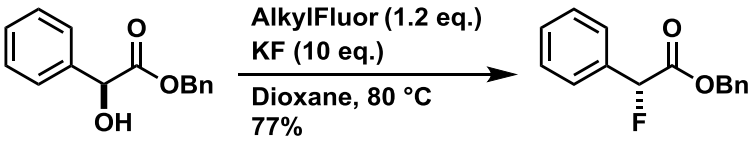
^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.00 (s, 1 H), 4.78 (dt, *J* = 47.0, 4.4 Hz, 2 H), 4.63 (dt, *J* = 26.4, 4.4 Hz, 2 H), 2.52 (s, 3 H)

^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 151.8, 133.4, 82.3 (d, J_{CF} = 171.7 Hz), 46.9 (d, J_{CF} = 20.1 Hz), 14.5

^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC, δ): –224.0 (tt, J = 47.2, 25.7 Hz)

HRMS-FIA (m/z) calc'd for $C_6H_9FN_3O_2$ $[M+H]^+$, 174.0673; found, 174.0676

Benzyl (*R*)-2-fluoro-2-phenylacetate (11)



According to general procedure A, benzyl (*S*)-mandelate (48.6 mg, 0.200 mmol, 1.00 equiv.), potassium fluoride (116.2 mg, 2.00 mmol, 10.0 equiv.), and AlkylFluor (118.7 mg, 0.240 mmol, 1.20 equiv.) were heated in dioxane (3.0 mL) at 80 °C for 18 hours. The reaction was cooled to room temperature and concentrated *in vacuo*, and the residue was purified by flash column chromatography on silica eluting with hexanes/ether (8:1 v/v), to afford the title compound as a colorless oil (37.8 mg, 77%).

R_f = 0.48 (hexanes/ether 5:1 v/v, CAM stain)

NMR Spectroscopy:

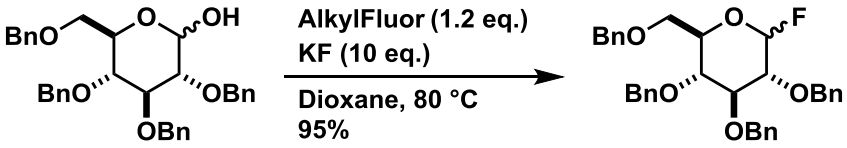
^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.44–7.49 (m, 2 H), 7.38–7.43 (m, 3 H), 7.31–7.36 (m, 3 H), 7.25–7.29 (m, 2 H), 5.83 (d, J = 47.8 Hz, 1 H), 5.26 (d, J = 12.7 Hz, 1 H), 5.18 (d, J = 12.7 Hz, 1 H)

^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 168.5 (d, J_{CF} = 27.8 Hz), 135.1, 134.2 (d, J_{CF} = 20.6 Hz), 129.8 (d, J_{CF} = 1.4 Hz), 128.9, 128.7, 128.6, 128.3, 128.9 (d, J_{CF} = 6.2 Hz), 89.5 (d, J_{CF} = 186.0 Hz), 67.4

^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC, δ): –179.9 (d, J = 47.6 Hz)

HRMS-FIA (m/z) calc'd for $C_{15}H_{13}FNaO_2$ $[M+Na]^+$, 267.0792; found, 267.0824

2,3,4,6-Tetra-*O*-benzyl-D-glucopyranosyl fluoride (12)



α:β = 15:85

According to general procedure A, 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (54.1 mg, 0.100 mmol, 1.00 equiv.), potassium fluoride (58.1 mg, 1.00 mmol, 10.0 equiv.), and AlkylFluor (59.3 mg, 0.120 mmol, 1.20 equiv.) were heated in dioxane (3.0 mL) at 80 °C for 21 hours. The reaction was cooled to room temperature and concentrated *in vacuo*, and the residue was purified by flash column chromatography on silica eluting with benzene/ethyl acetate (30:1 v/v), to afford the title compound as a colorless oil (51.5 mg, 95%, α:β=15:85 by ^{19}F NMR).

R_f = 0.44 (benzene/ethyl acetate 20:1 v/v, CAM stain)

NMR Spectroscopy:

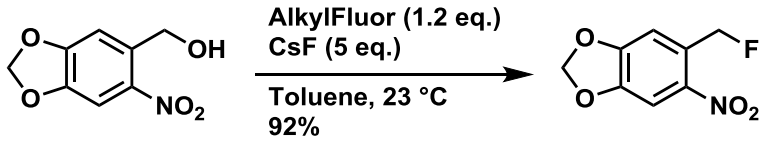
^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.39–7.25 (m, 18 H, α+β), 7.17–7.11 (m, 2 H α+β), 5.56 (dd, *J* = 53.2, 2.6 Hz, 1 H α), 5.26 (dd, *J* = 52.8, 6.7 Hz, 1 H β), 4.96 (d, *J* = 10.9 Hz, 1 H α), 4.90 (d, *J* = 11.0 Hz, 1 H β), 4.87–4.82 (m, 2 H α, 1 H β), 4.82–4.77 (m, 1 H α, 2 H β), 4.71 (d, *J* = 11.0 Hz, 1 H α+β), 4.65–4.58 (m, 1 H α+β), 4.57–4.51 (m, 2 H β, 1 H α), 4.48 (d, *J* = 12.1 Hz, 1 H α), 3.99 (t, *J* = 9.3 Hz, 1 H α), 3.94 (dt, *J* = 10.0, 2.8 Hz, 1 H α), 3.78–3.64 (m, 3 H α, 4 H β), 3.63–3.53 (m, 1 H α, 2 H β)

^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 138.6, 138.4, 138.1, 138.0, 137.9, 137.8, 137.8, 137.8, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 110.0 (d, J_{CF} = 216.0 Hz), 105.7 (d, J_{CF} = 226.8 Hz), 83.6 (d, J_{CF} = 11.3 Hz), 81.6 (d, J_{CF} = 21.6 Hz), 81.5, 79.4 (d, J_{CF} = 24.7 Hz), 77.4, 77.3, 77.2, 77.0, 76.9, 76.7, 75.9, 75.6, 75.3, 75.1, 74.9 (d, J_{CF} = 5.0 Hz), 74.6 (d, J_{CF} = 2.4 Hz), 73.7, 73.6, (d, J_{CF} = 3.6 Hz), 72.8 (d, J_{CF} = 4.1 Hz), 68.5, 67.9

^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC, δ): –138.1 (dd, *J* = 52.9, 11.9 Hz, β), –149.6 (dd, *J* = 52.9, 25.8 Hz, α)

HRMS-FIA (m/z) calc'd for $C_{34}H_{35}FNaO_5$ $[M+Na]^+$, 565.2361; found, 565.2347

6-Nitropiperonyl fluoride (13)



According to general procedure B, 6-nitropiperonyl alcohol (39.4 mg, 0.200 mmol, 1.00 equiv.), cesium fluoride (152 mg, 1.00 mmol, 5.00 equiv.), and AlkylFluor (118.7 mg, 0.240 mmol, 1.20 equiv.) were stirred in toluene (3.0 mL) at 23 °C for 16 hours. The reaction was cooled to room temperature and concentrated *in vacuo*, and the residue was purified by flash column chromatography on silica eluting with hexanes/dichloromethane (1:1 v/v), to afford the title compound as a pale yellow crystalline solid (36.8 mg, 92%).

R_f = 0.44 (hexanes/dichloromethane 1:1 v/v, UV quenching)

NMR Spectroscopy:

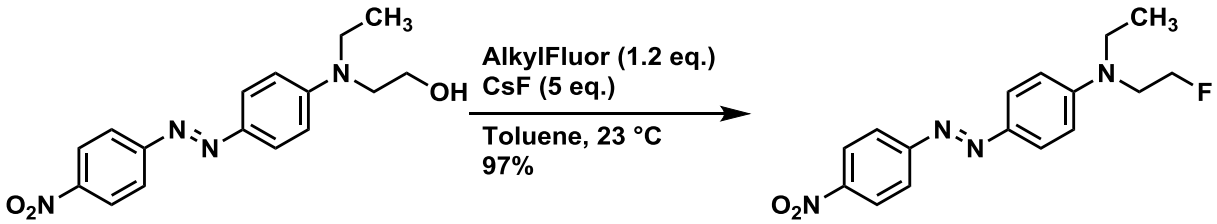
^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.70 (d, *J* = 1.0 Hz, 1 H) 7.20 (q, *J* = 0.9 Hz, 1 H) 6.16 (s, 2 H) 5.80 (dd, *J* = 48.2, 0.9 Hz, 2 H)

^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ: 153.4 (d, J_{CF} = 2.9 Hz), 147.5, 139.8, 132.3 (d, J_{CF} = 19.2 Hz), 105.8 (d, J_{CF} = 21.1 Hz), 105.6, 103.4, 81.7 (d, J_{CF} = 173.1 Hz)

^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC, δ): –216.4 (t, *J* = 47.8 Hz)

HRMS-FIA (m/z) calc'd for $C_8H_6FNaO_4$ $[M+Na]^+$, 222.0173; found, 222.0206

(*E*)-*N*-Ethyl-*N*-(2-fluoroethyl)-4-((4-nitrophenyl)diazenyl)aniline (14)



According to general procedure B, Disperse Red 1 (62.9 mg, 0.200 mmol, 1.00 equiv.), cesium fluoride (152 mg, 1.00 mmol, 5.00 equiv.), and AlkylFluor (118.7 mg, 0.240 mmol, 1.20 equiv.) were stirred in toluene (3.0 mL) at 23 °C for 17 hours. The reaction was cooled to room temperature and concentrated *in vacuo*, and the residue was purified by flash column chromatography on silica eluting with hexanes/dichloromethane (1:1 to 1:3 v/v) to afford the title compound as an intensely crimson solid (61.3 mg, 97%).

R_f = 0.21 (hexanes/dichloromethane 1:1 v/v, UV quenching)

NMR Spectroscopy:

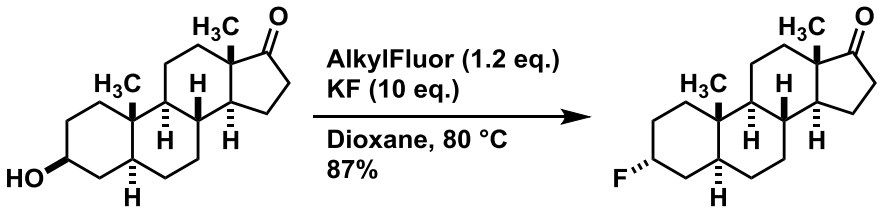
^{1}H NMR (500 MHz, CD_2Cl_2, 23 ºC, δ): 8.34–8.30 (m, 2 H), 7.95–7.92 (m, 2 H), 7.92–7.88 (m, 2 H), 6.82–6.78 (m, 2 H), 4.65 (dt, *J* = 47.1, 5.3 Hz, 2 H), 3.76 (dt, *J* = 24.0, 5.2 Hz, 2 H), 3.57 (q, *J* = 7.1 Hz, 2 H), 1.26 (t, *J* = 7.1 Hz, 3 H)

^{13}C NMR (125 MHz, CD_2Cl_2, 23 ºC, δ): 157.2, 151.8, 147.9, 144.2, 126.5, 125.1, 123.0, 111.9, 82.1 (d, J_{CF} = 170.2 Hz), 50.9 (d, J_{CF} = 21.6 Hz), 46.4, 30.1, 12.3

^{19}F NMR (470 MHz, CD_2Cl_2, 23 ºC, δ): –222.3 (tt, *J* = 47.2, 23.8 Hz)

HRMS-FIA (m/z) calc'd for $C_{16}H_{18}FN_4O_2$ $[M+H]^+$, 317.1408; found, 317.1409

3-Fluoro-3-deoxyandrosterone (15)



According to general procedure A, epiandrosterone (29.0 mg, 0.100 mmol, 1.00 equiv.), potassium fluoride (58.1 mg, 1.00 mmol, 10.0 equiv.), and AlkylFluor (59.3 mg, 0.120 mmol, 1.20 equiv.) were heated in dioxane (3.0 mL) at 80 °C for 17 hours. The reaction was cooled to room temperature and concentrated *in vacuo*, and the residue was purified by flash column chromatography on silica eluting with hexanes/ethyl acetate (12:1 v/v), to afford the title compound as a crystalline colorless solid (25.5 mg, 87%).

R_f = 0.31 (hexanes/ethyl acetate 9:1 v/v, 2,4-DNP stain)

NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 4.81 (d, *J* = 48.4 Hz, 1 H), 2.43 (dd, J=19.6, 8.8 Hz, 1 H), 2.06 (dt, *J* = 19.0, 9.4 Hz, 1 H), 1.99–1.84 (m, 2 H), 1.83–1.75 (m, 2 H), 1.71–1.61 (m, 2 H), 1.61–1.37 (m, 6 H), 1.36–1.17 (m, 7 H), 1.02 (qd, *J* = 12.7, 4.4 Hz, 1 H), 0.85 (s, 3 H), 0.80 (s, 3 H)

^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 221.5, 89.5 (d, J_{CF} = 165.9 Hz), 54.3, 51.6, 47.9, 39.5, 36.0, 35.2, 34.0 (d, J_{CF} = 21.6 Hz), 32.5, 31.7, 30.9, 28.2, 27.2 (d, J_{CF} = 21.6 Hz), 21.9, 20.2, 14.0, 11.3

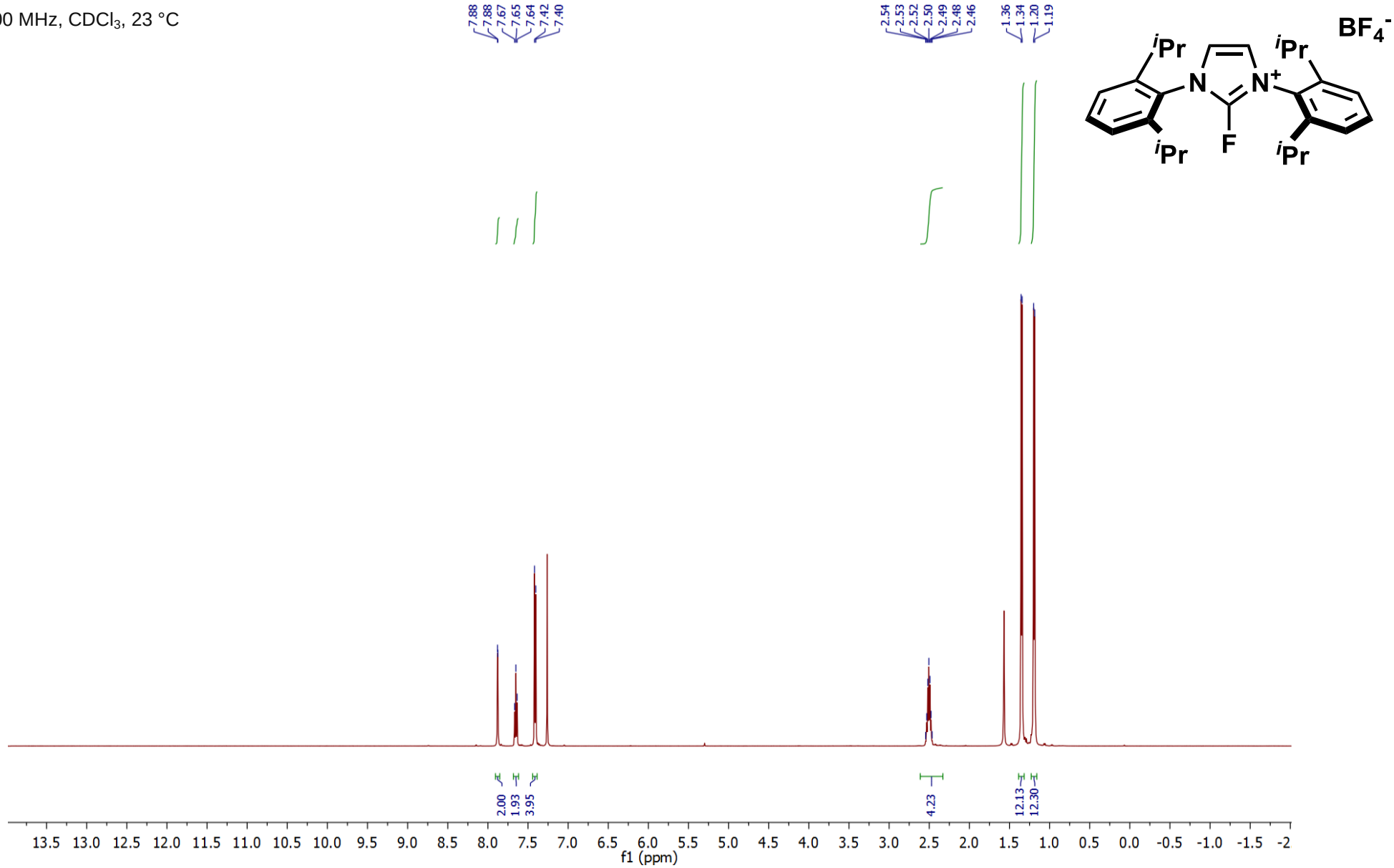
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC, δ): –181.2 (qt, *J* = 47.7, 12.4 Hz)

HRMS-FIA (m/z) calc'd for $C_{19}H_{29}FNaO$ $[M+Na]^+$, 315.2095; found, 315.2101

SPECTROSCOPIC DATA

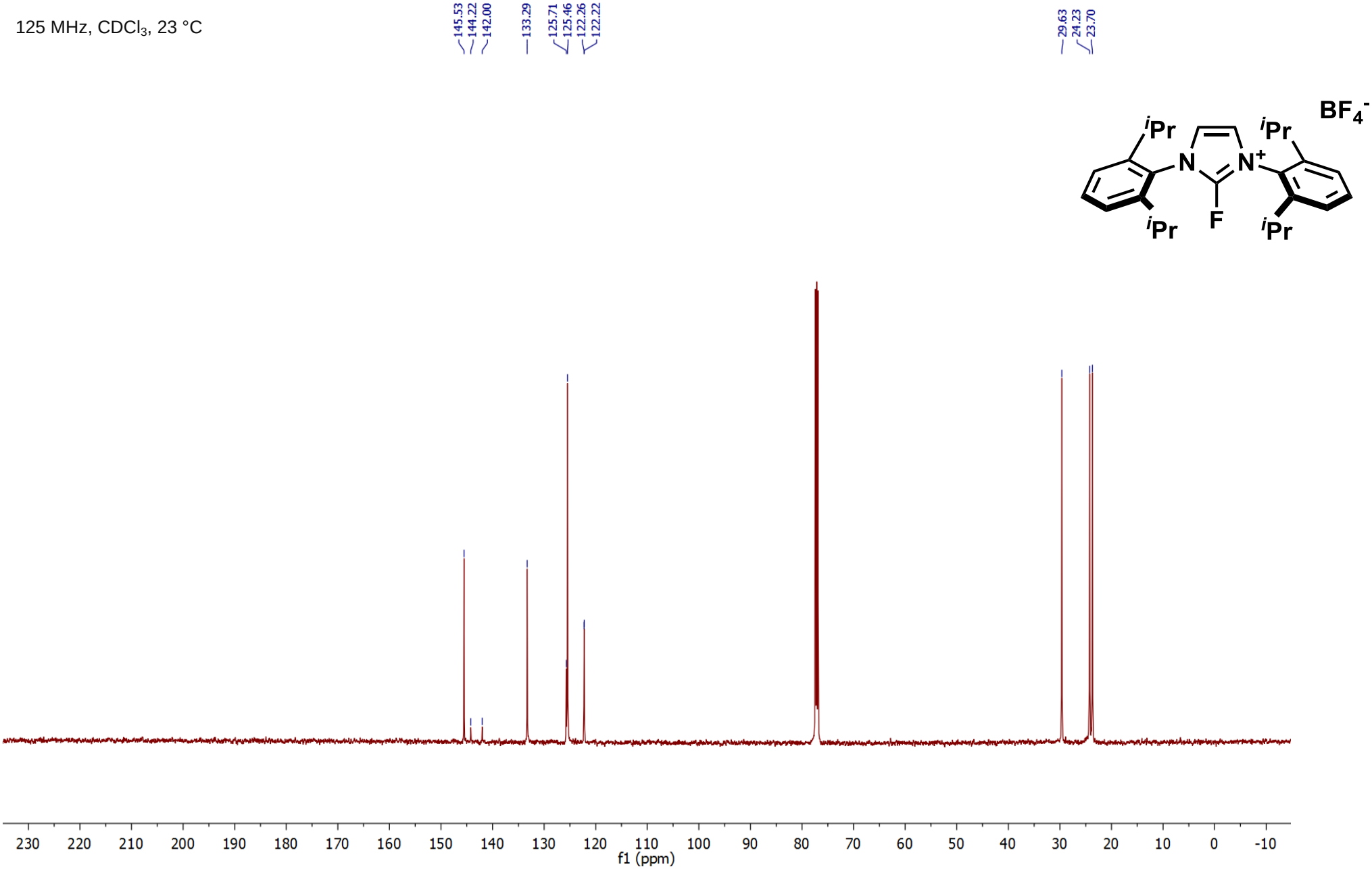
^{1}H NMR spectrum of 1,3-bis(2,6-diisopropylphenyl)-2-fluoroimidazolium tetrafluoroborate (AlkylFluor)

500 MHz, $CDCl_3$, 23 °C



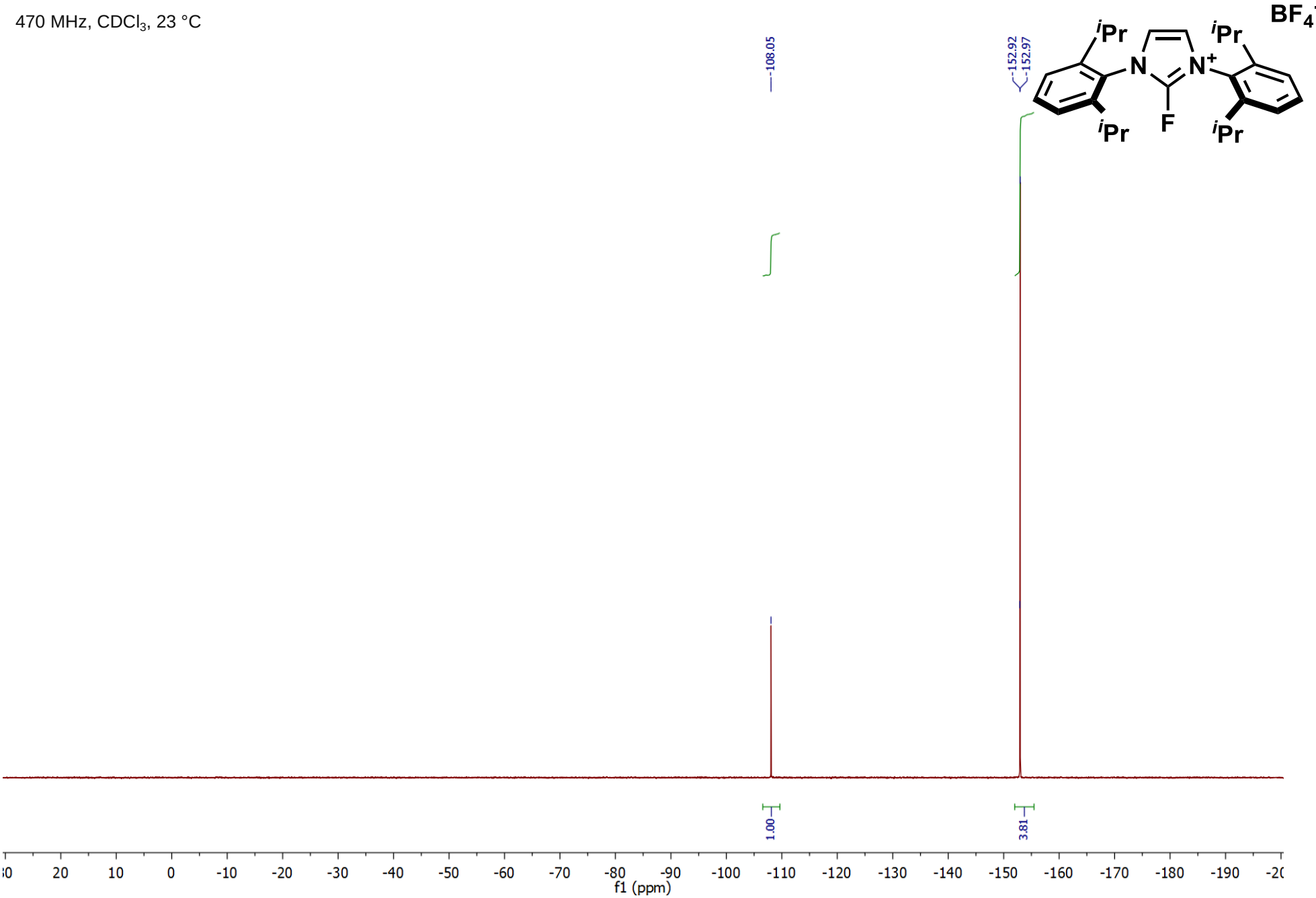
^{13}C NMR spectrum of 1,3-bis(2,6-diisopropylphenyl)-2-fluoroimidazolium tetrafluoroborate (AlkylFluor)

125 MHz, $CDCl_3$, 23 °C



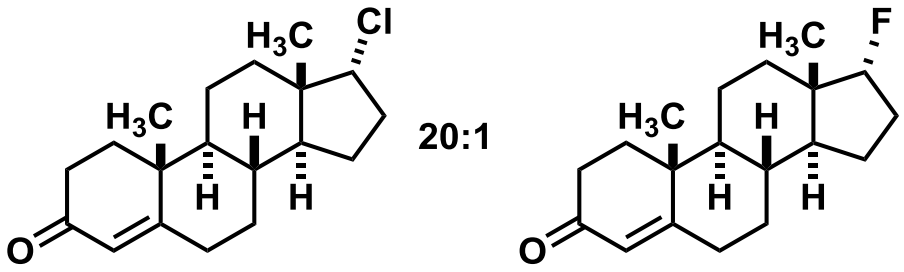
^{19}F NMR spectrum of 1,3-bis(2,6-diisopropylphenyl)-2-fluoroimidazolium tetrafluoroborate (AlkylFluor)

470 MHz, $CDCl_3$, 23 °C



^{1}H NMR spectrum of 17-*epi*-17-chloro-17-deoxytestosterone (S2)

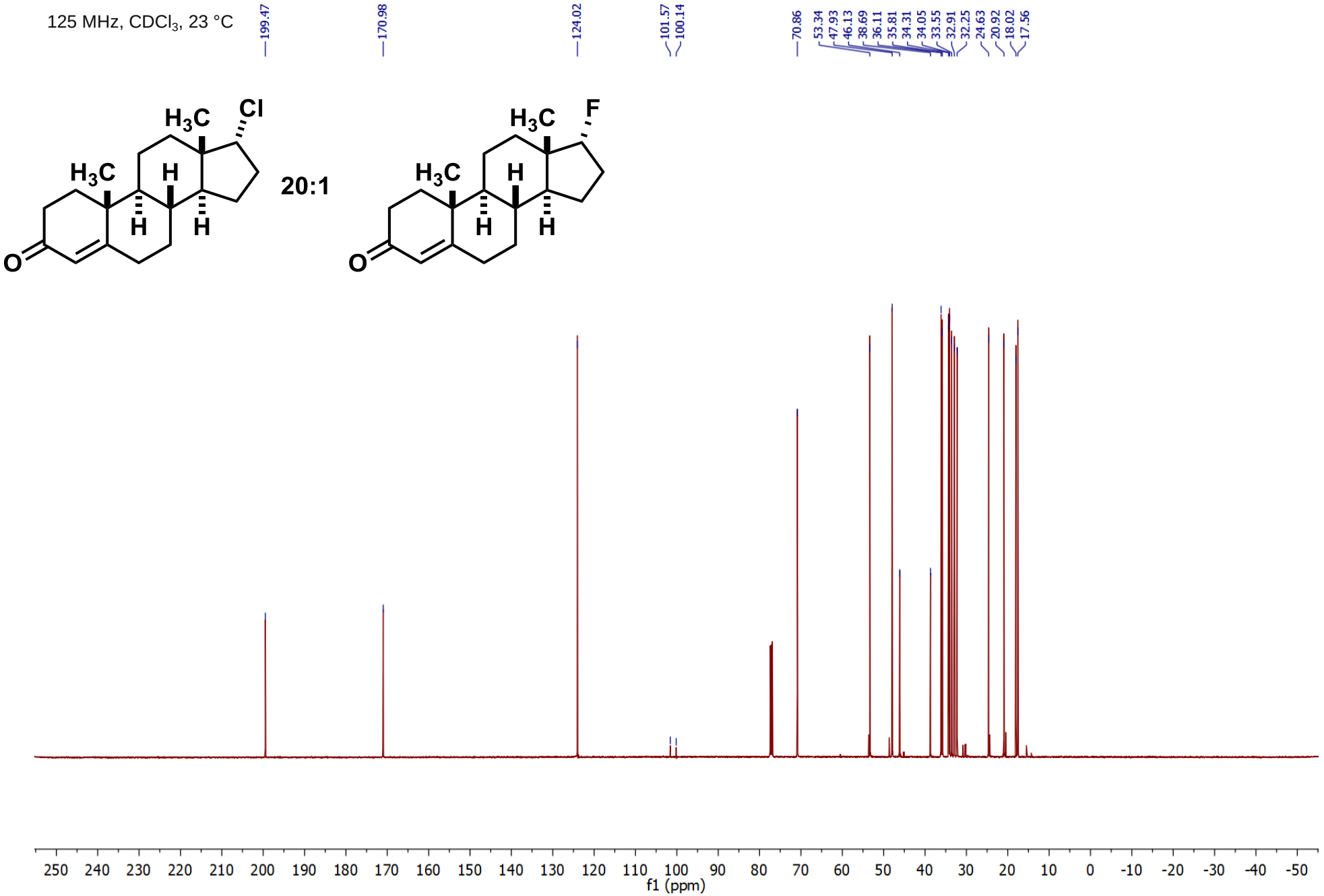
500 MHz, $CDCl_3$, 23 °C



20:1

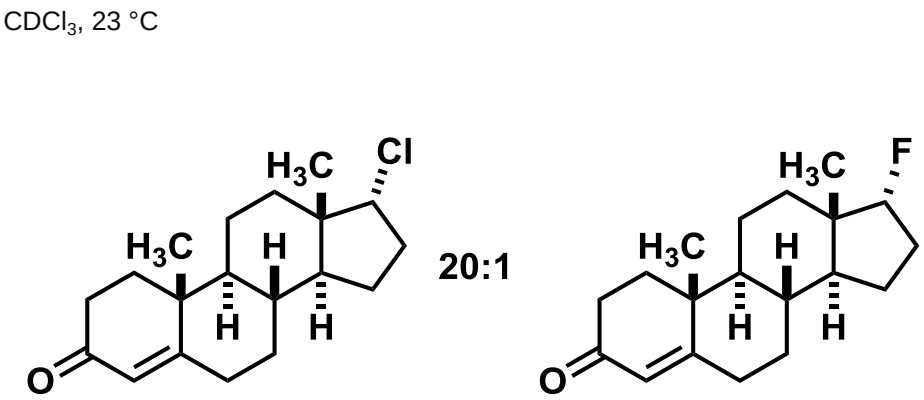
^{13}C NMR spectrum of 17-*epi*-17-chloro-17-deoxytestosterone (S2)

125 MHz, $CDCl_3$, 23 °C



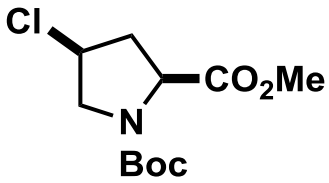
^{19}F NMR spectrum of 17-*epi*-17-chloro-17-deoxytestosterone (S2)

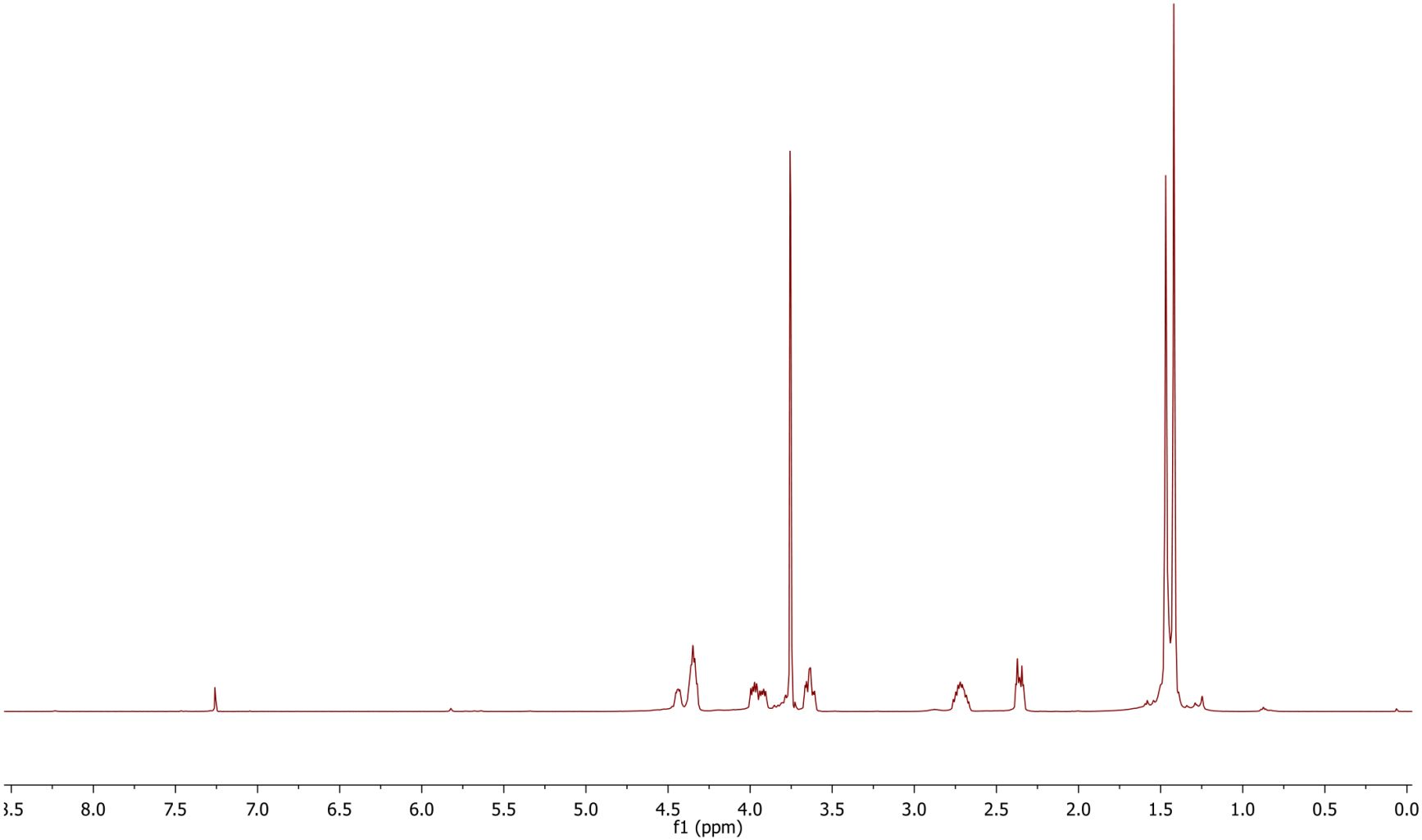
470 MHz, $CDCl_3$, 23 °C



^{1}H NMR spectrum of *N*-boc-*cis*-4-chloro-L-proline methyl ester (S3)

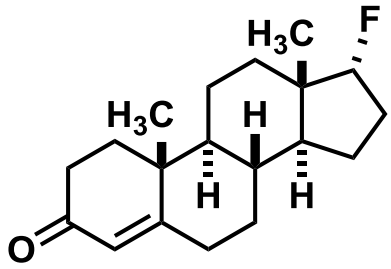
500 MHz, $CDCl_3$, 23 °C





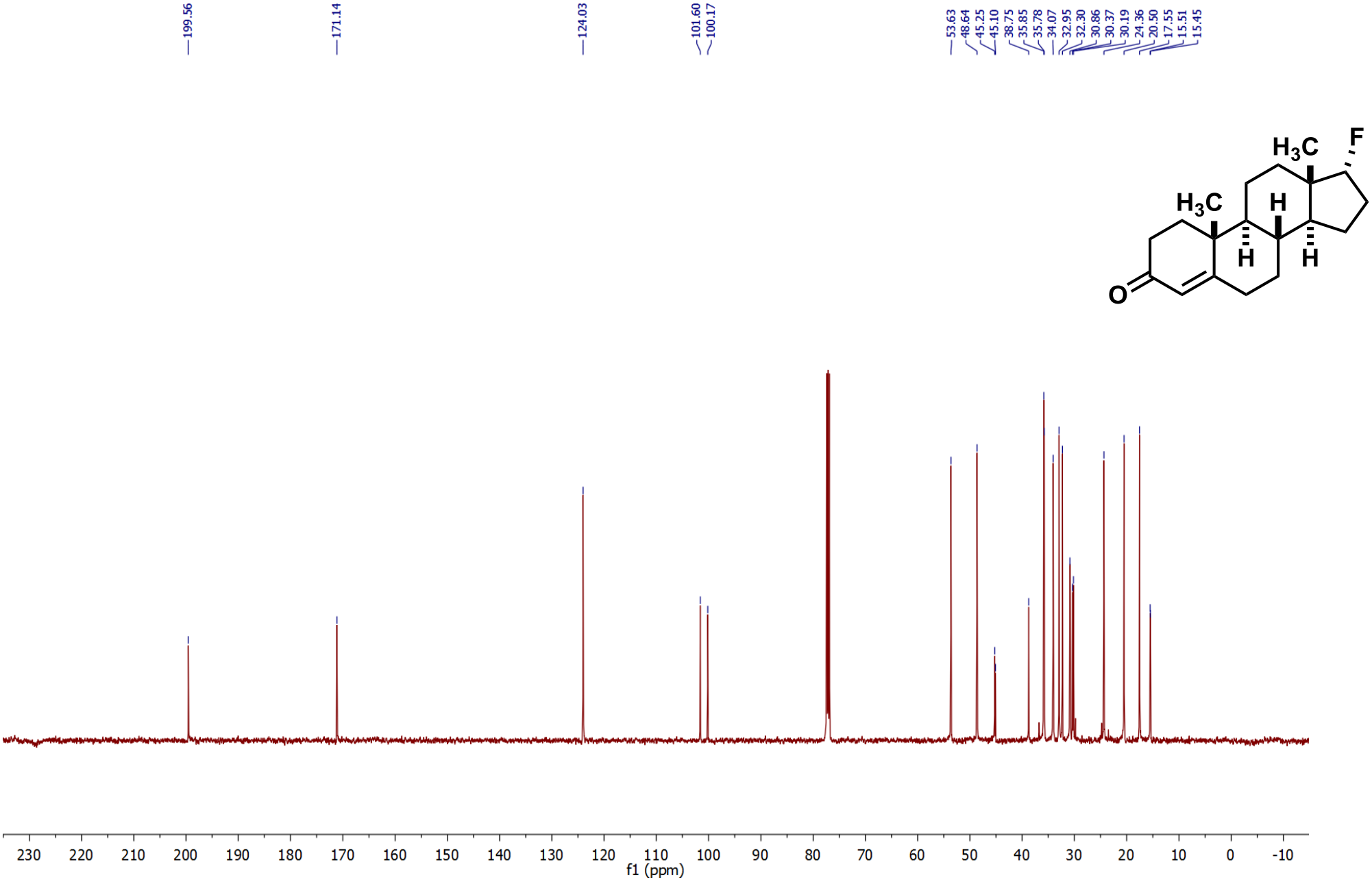
^{1}H NMR spectrum of 17-*epi*-17-fluoro-17-deoxytestosterone (4)

500 MHz, $CDCl_3$, 23 °C



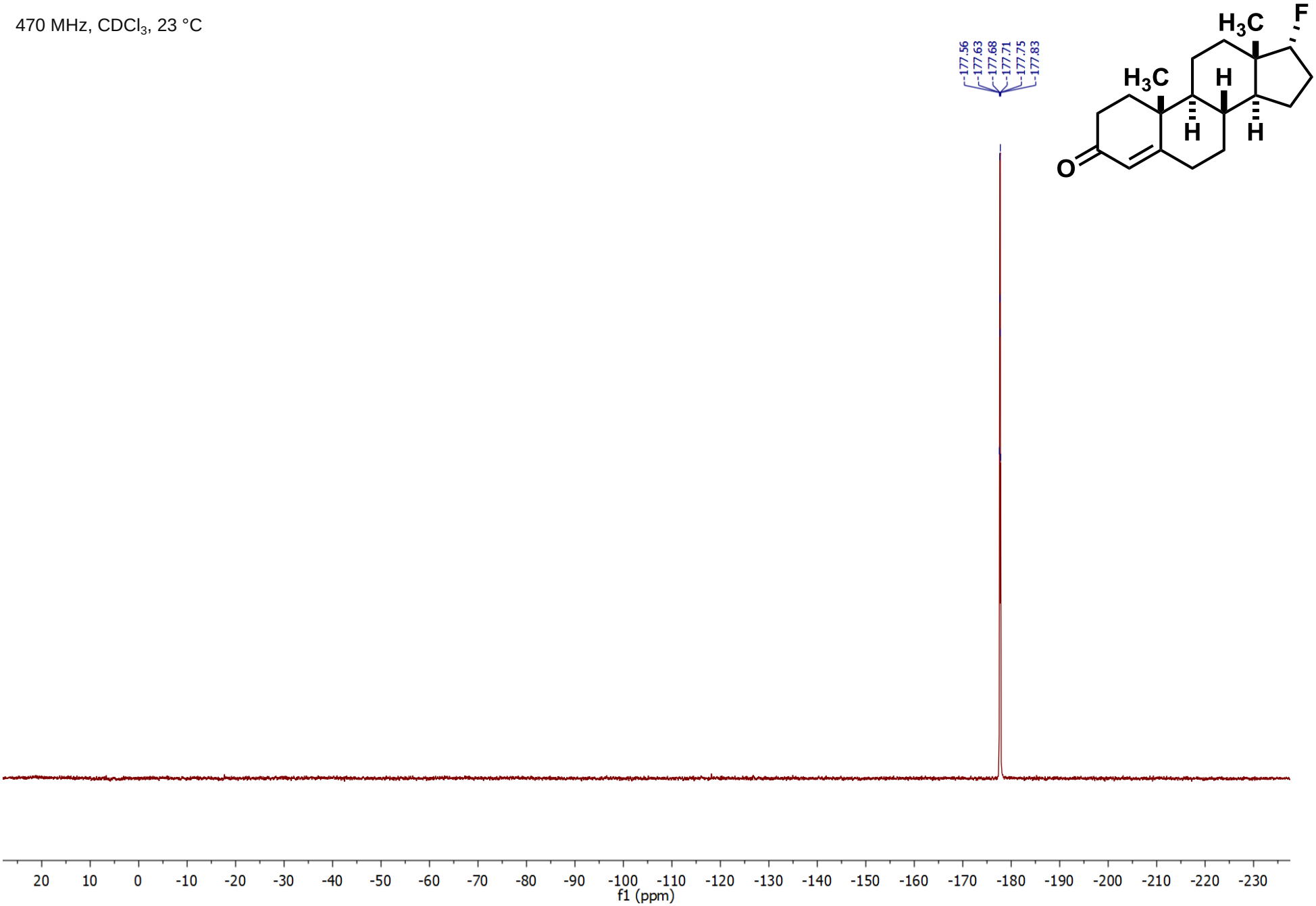
^{13}C NMR spectrum of 17-*epi*-17-fluoro-17-deoxytestosterone (4)

125 MHz, $CDCl_3$, 23 °C



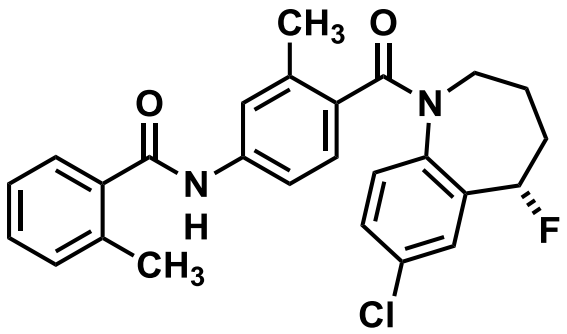
^{19}F NMR spectrum of 17-*epi*-17-fluoro-17-deoxytestosterone (4)

470 MHz, $CDCl_3$, 23 °C



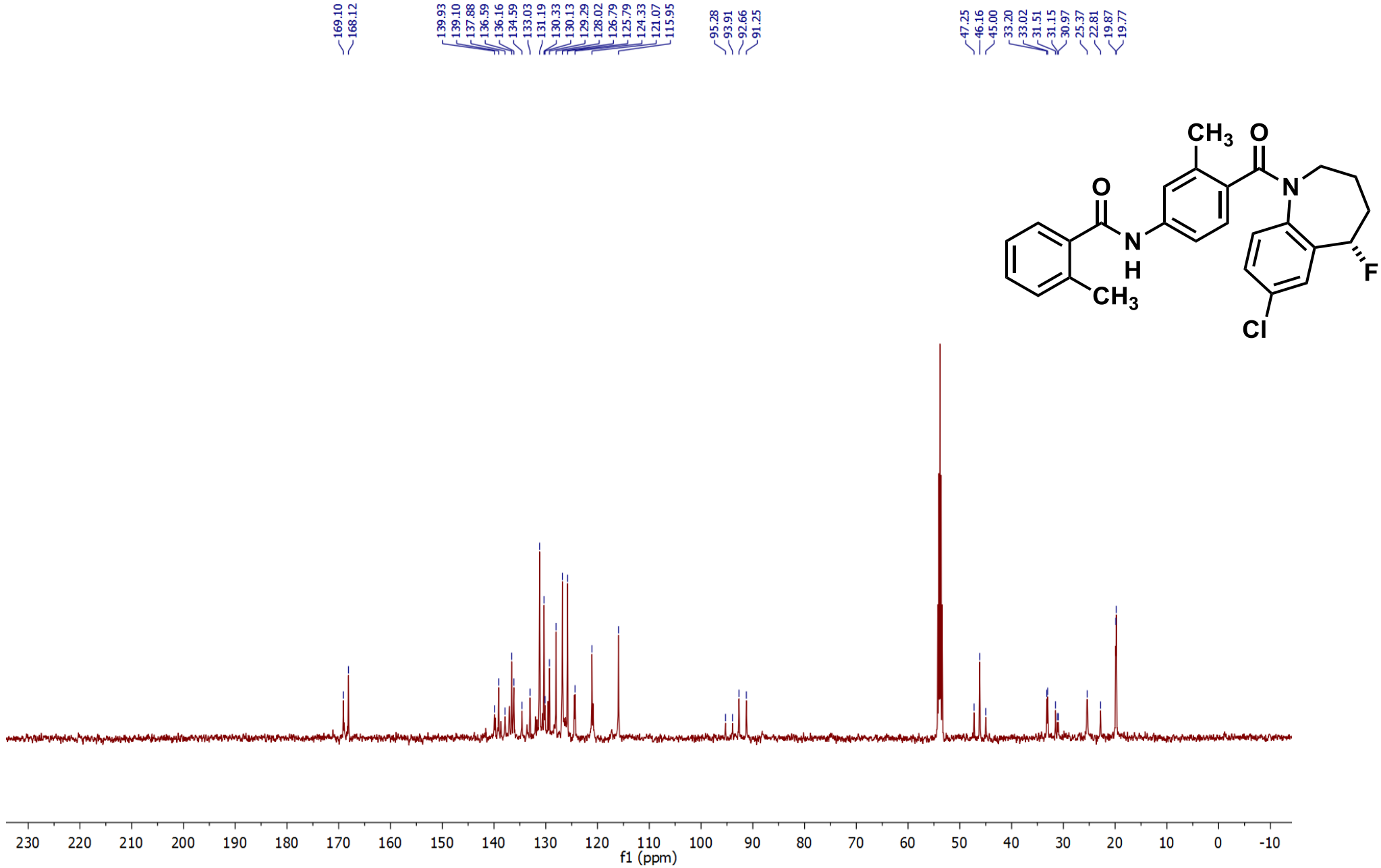
^{1}H NMR spectrum of fluorodeoxytolvaptan (5)

500 MHz, CD_2Cl_2, –20 °C



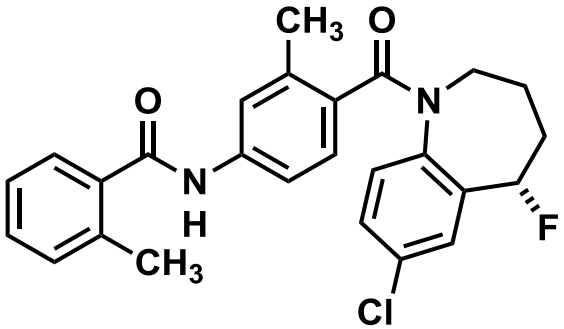
^{13}C NMR spectrum of fluorodeoxytolvaptan (5)

125 MHz, CD_2Cl_2, –20 °C



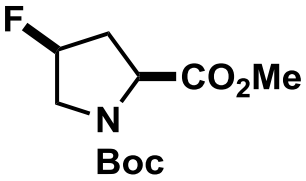
^{19}F NMR spectrum of fluorodeoxytolvaptan (5)

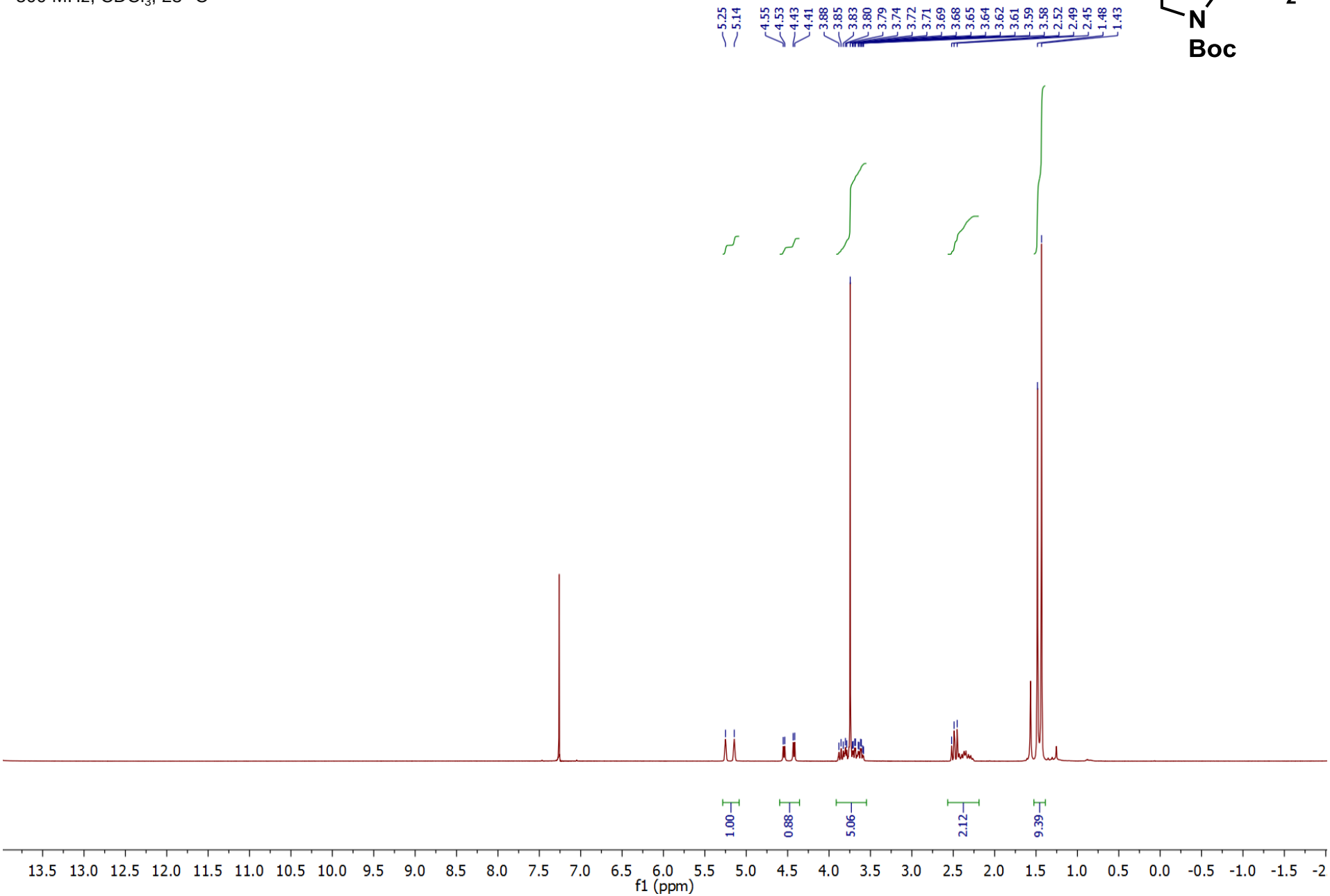
470 MHz, CD_2Cl_2, –20 °C



^{1}H NMR spectrum of *N*-Boc-*cis*-4-fluoro-L-proline methyl ester (6)

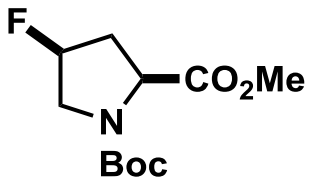
500 MHz, $CDCl_3$, 23 °C

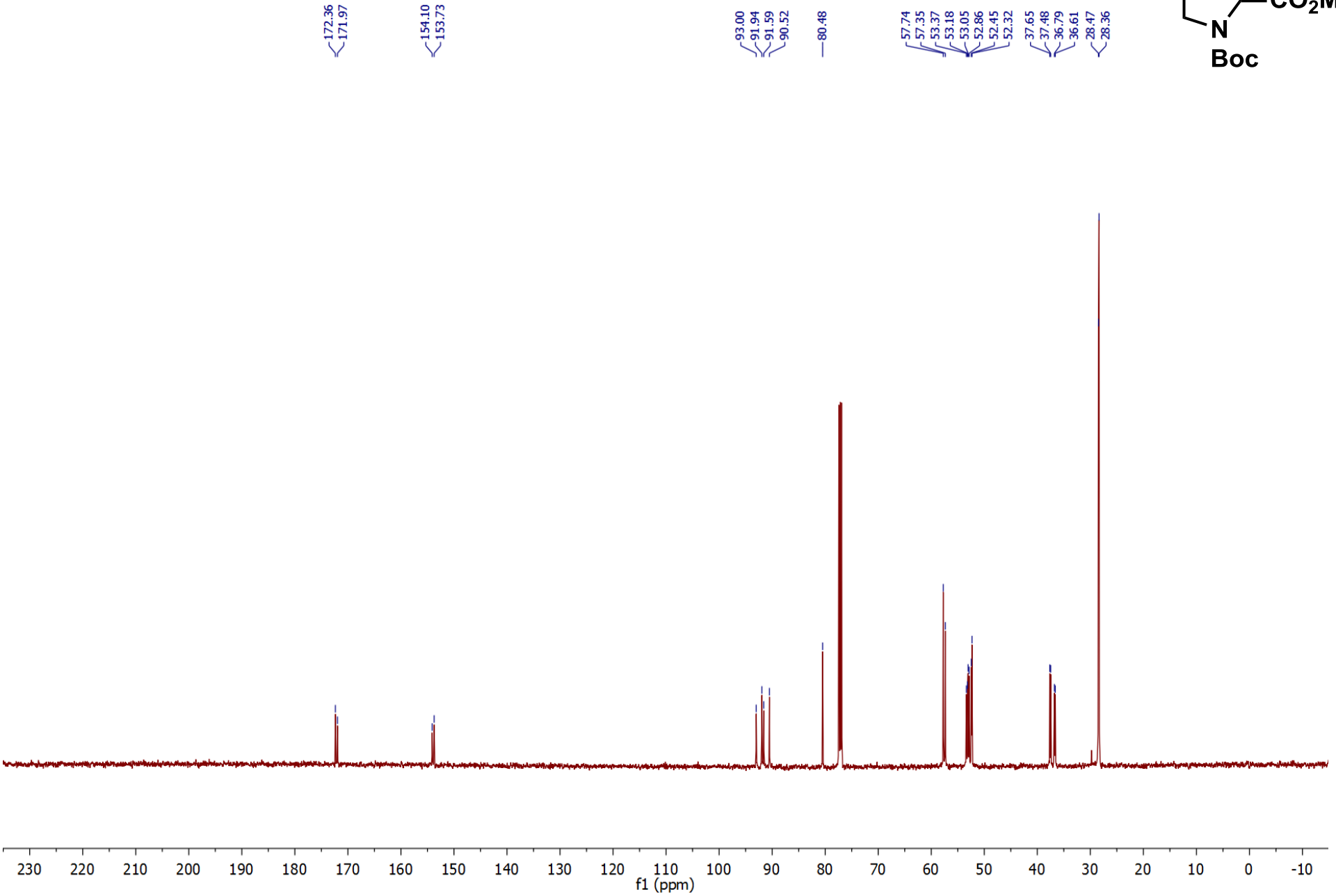




^{13}C NMR spectrum of *N*-Boc-*cis*-4-fluoro-L-proline methyl ester (6)

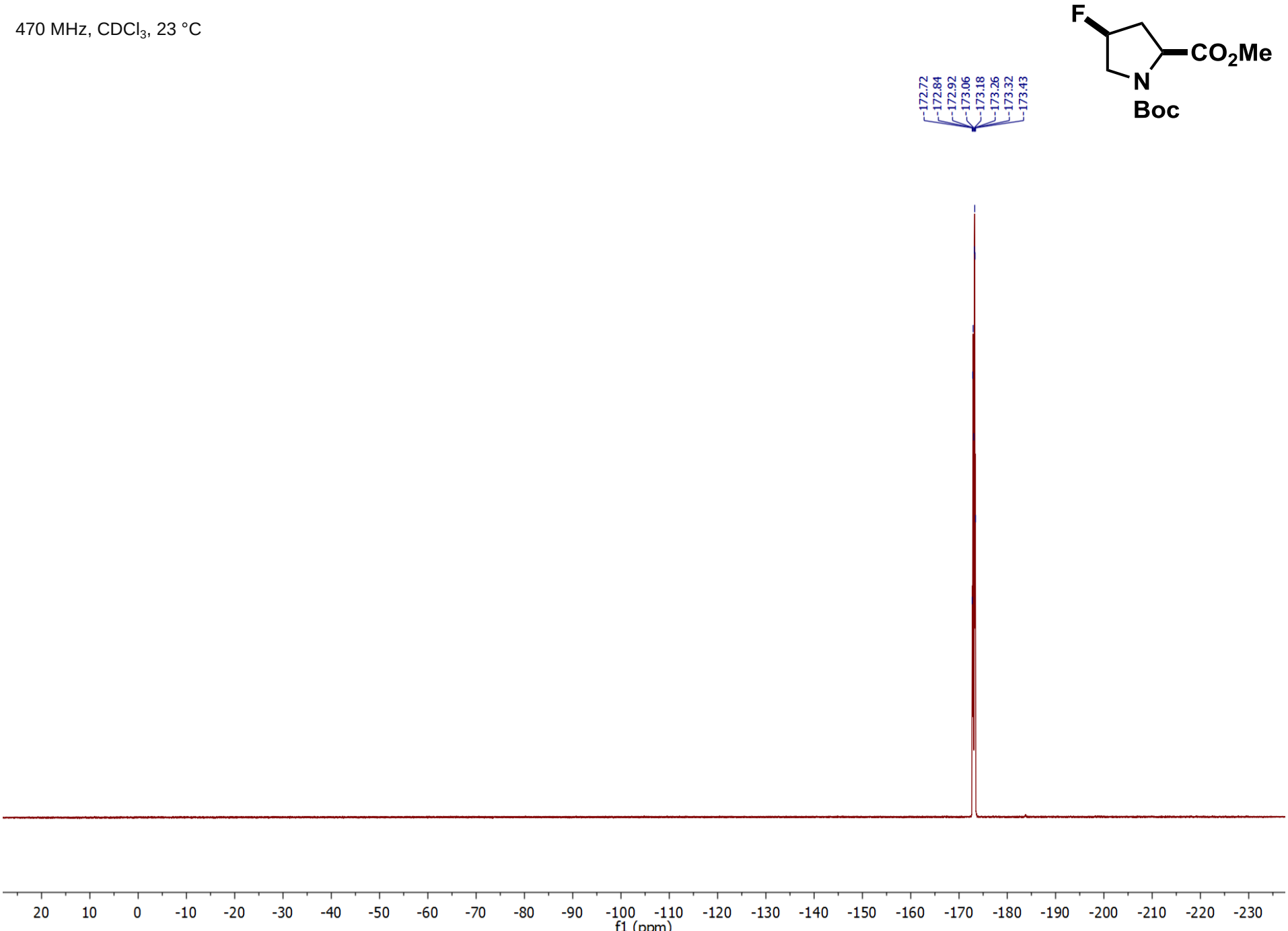
125 MHz, $CDCl_3$, 23 °C





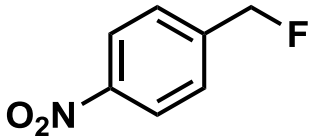
^{19}F NMR spectrum of *N*-Boc-*cis*-4-fluoro-L-proline methyl ester (6)

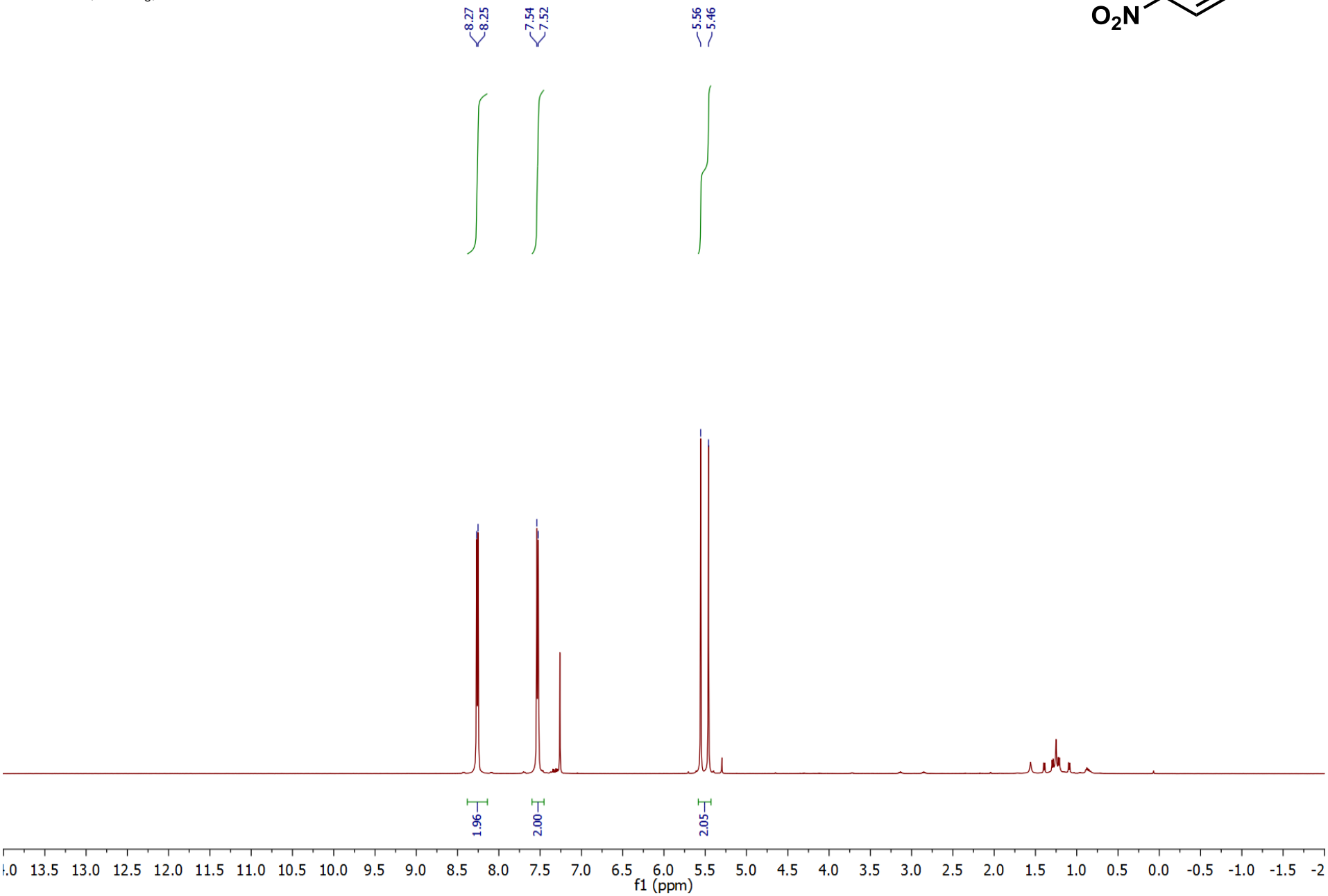
470 MHz, $CDCl_3$, 23 °C



^{1}H NMR spectrum of 4-nitrobenzyl fluoride (7)

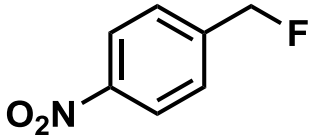
500 MHz, $CDCl_3$, 23 °C





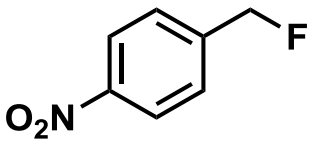
^{13}C NMR spectrum of 4-nitrobenzyl fluoride (7)

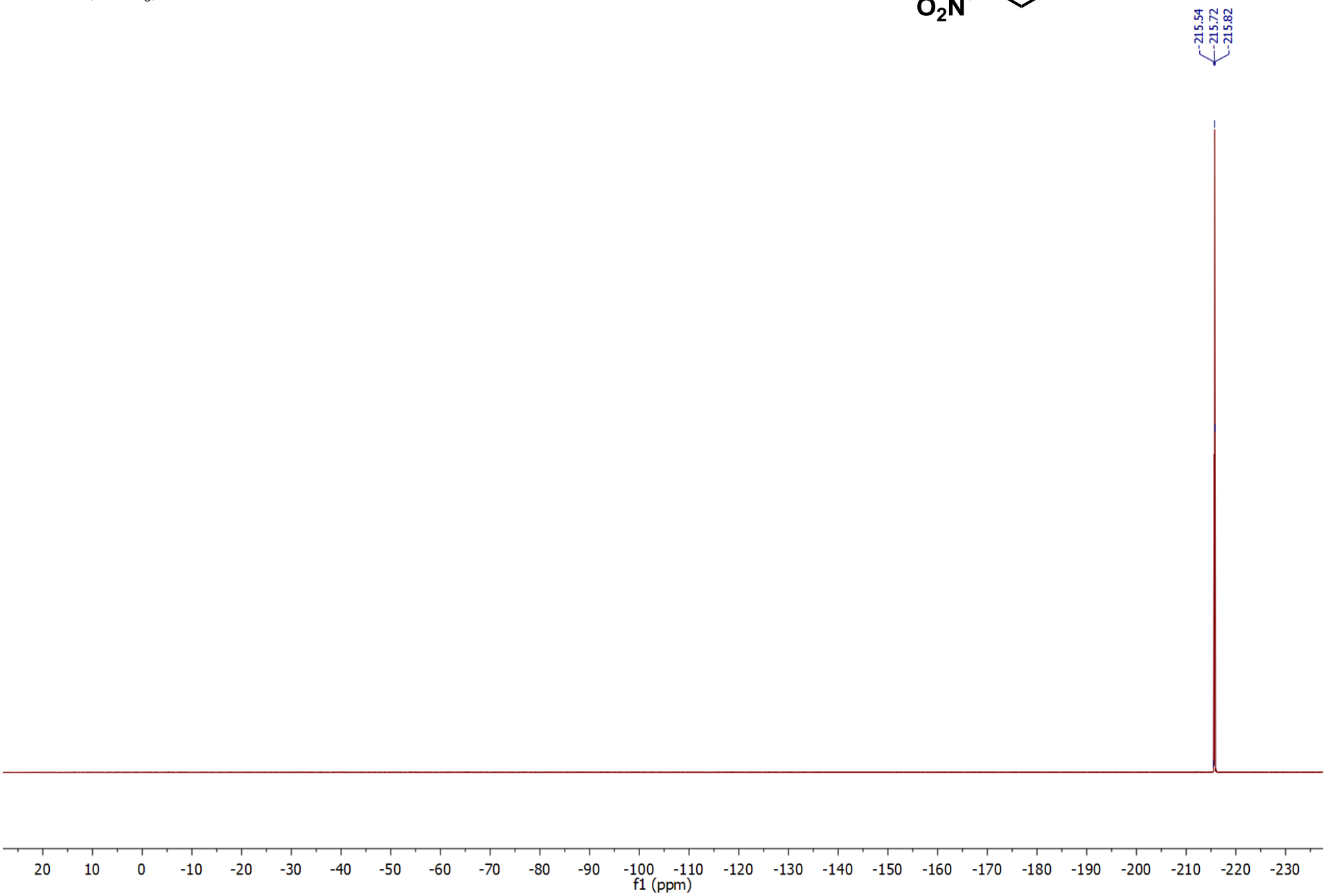
125 MHz, $CDCl_3$, 23 °C



^{19}F NMR spectrum of 4-nitrobenzyl fluoride (7)

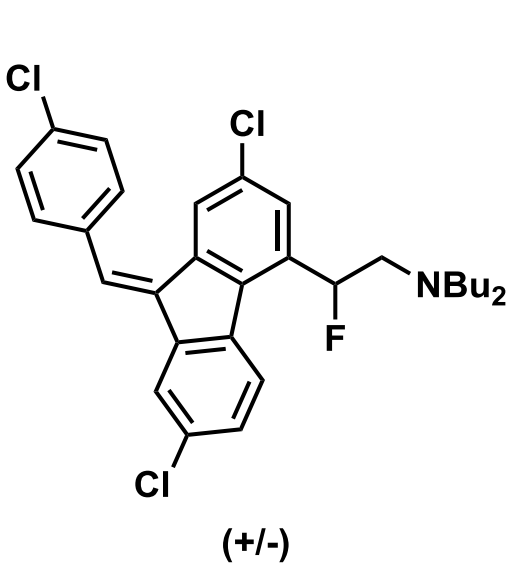
470 MHz, $CDCl_3$, 23 °C





^{1}H NMR spectrum of fluorodeoxylumefantrine (8)

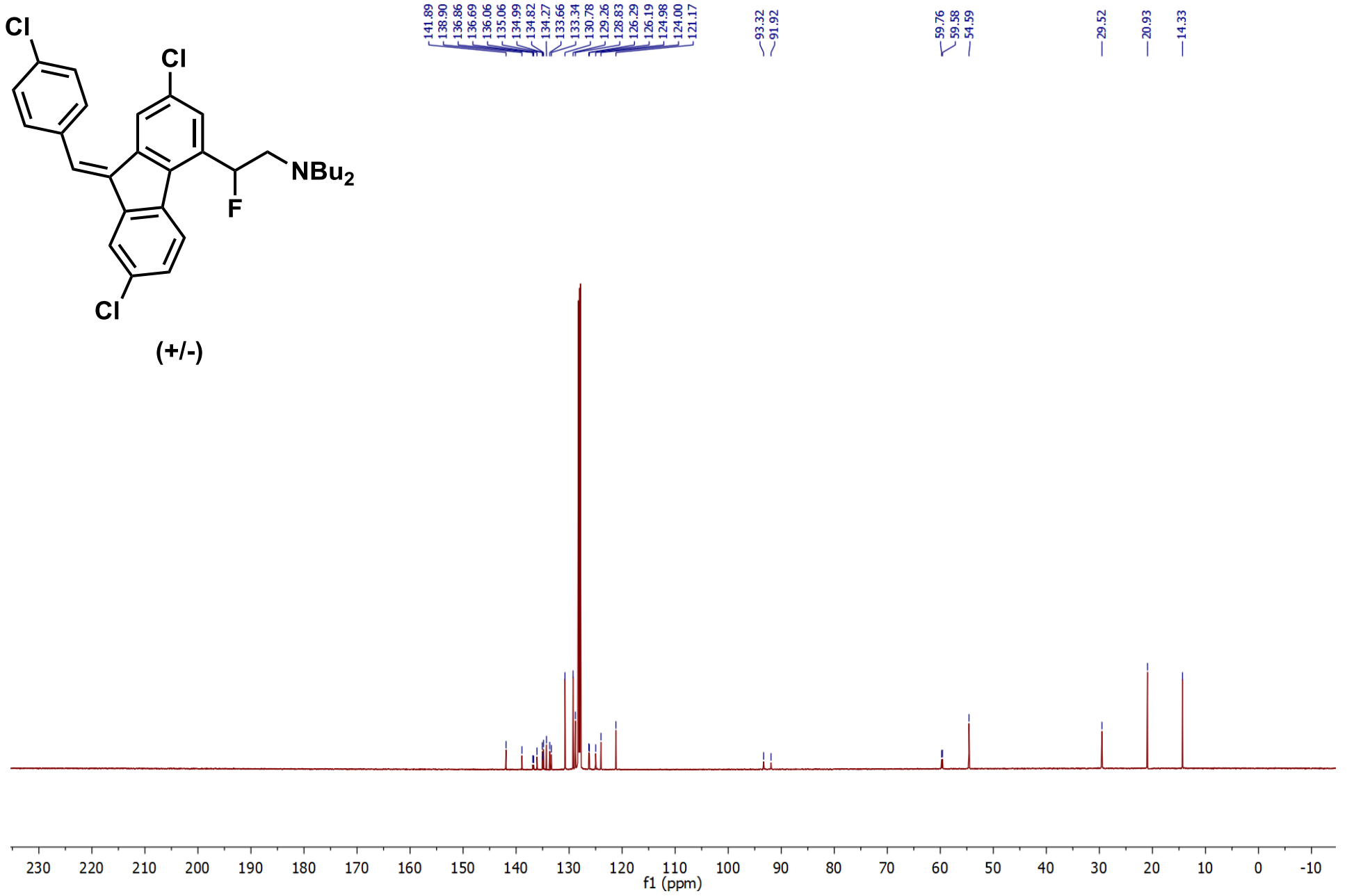
500 MHz, C_6D_6, 23 °C



(+/-)

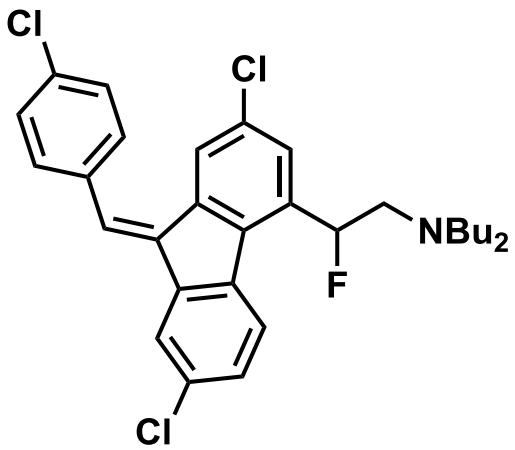
^{13}C NMR spectrum of fluorodeoxylumefantrine (8)

125 MHz, C_6D_6, 23 °C

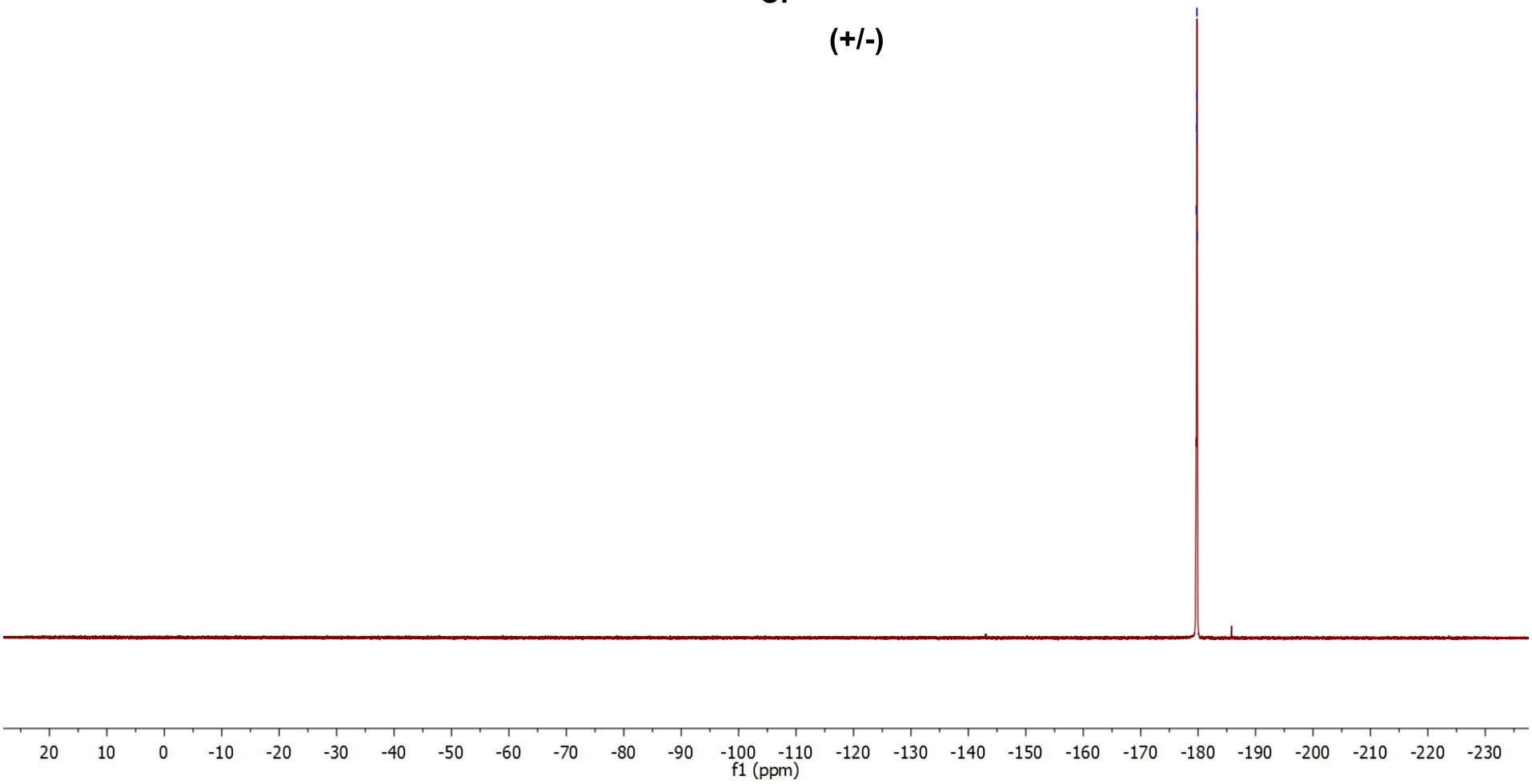


^{19}F NMR spectrum of fluorodeoxylumefantrine (8)

470 MHz, C_6D_6, 23 °C

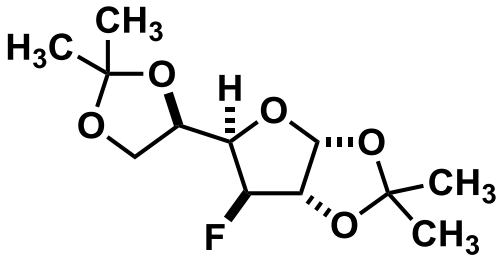


(+/-)



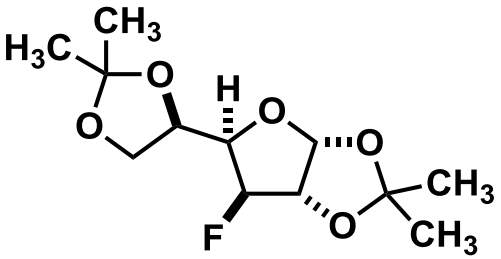
^{1}H NMR spectrum of 3-fluoro-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (9)

500 MHz, $CDCl_3$, 23 °C



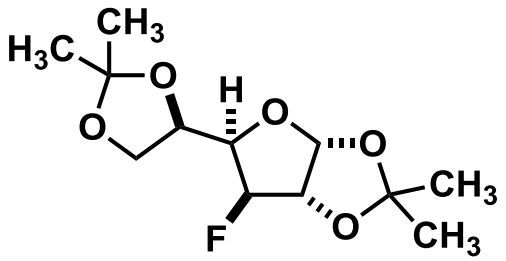
^{13}C NMR spectrum of 3-fluoro-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (9)

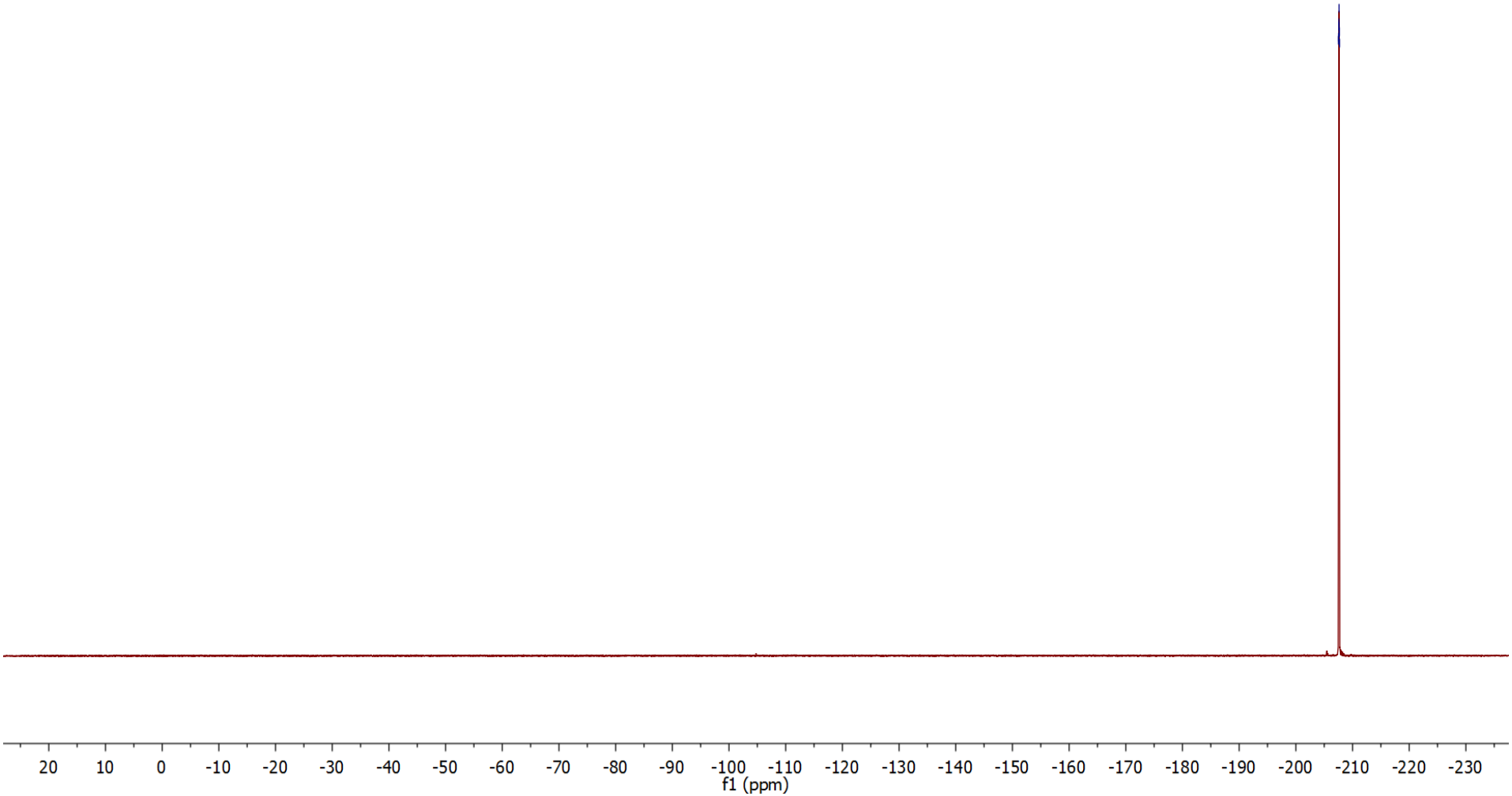
125 MHz, $CDCl_3$, 23 °C



^{19}F NMR spectrum of 3-fluoro-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (9)

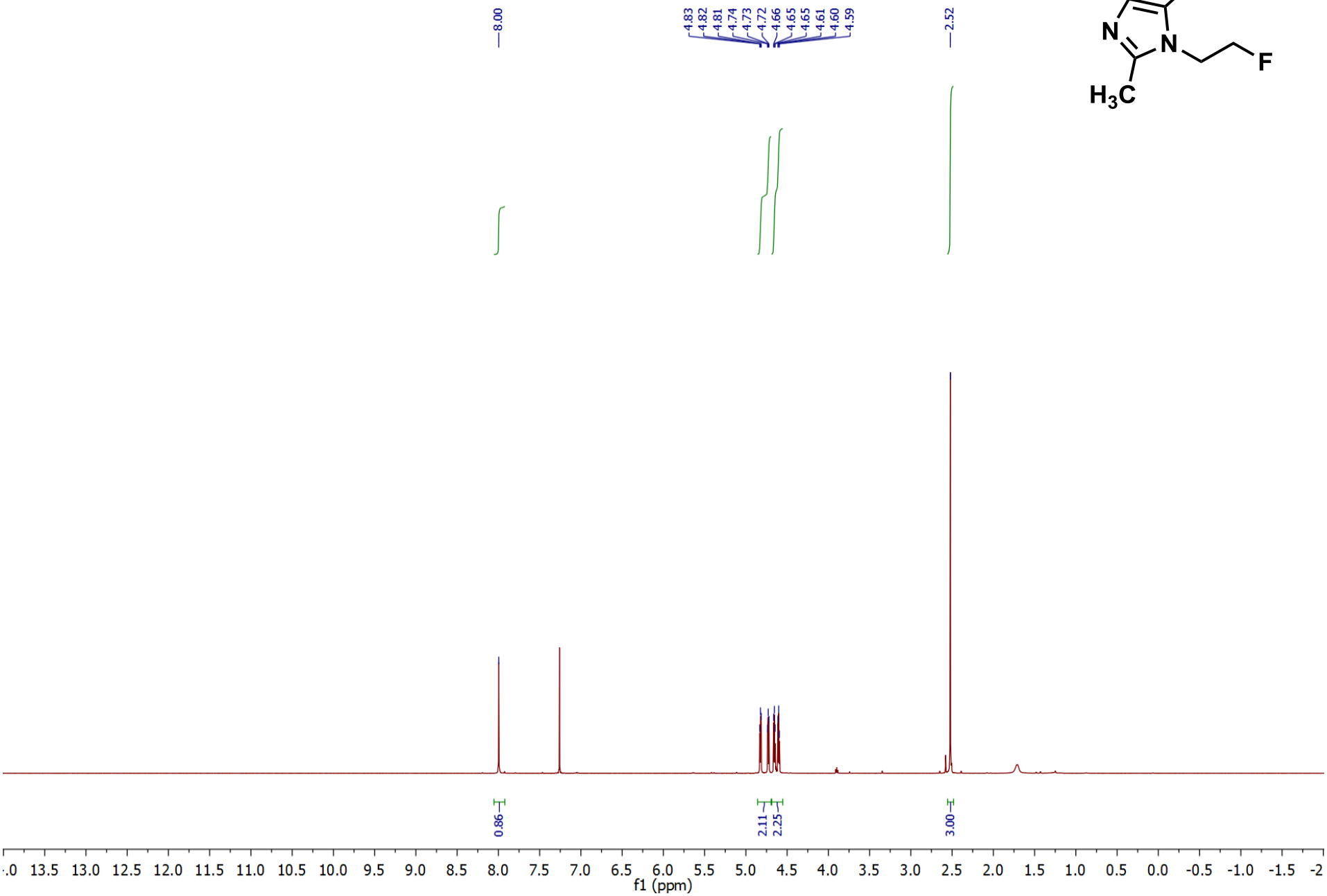
475 MHz, $CDCl_3$, 23 °C





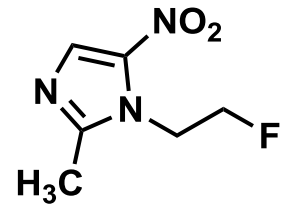
^{1}H NMR spectrum of 1-(2-fluoroethyl)-2-methyl-5-nitro-1*H*-imidazole (10)

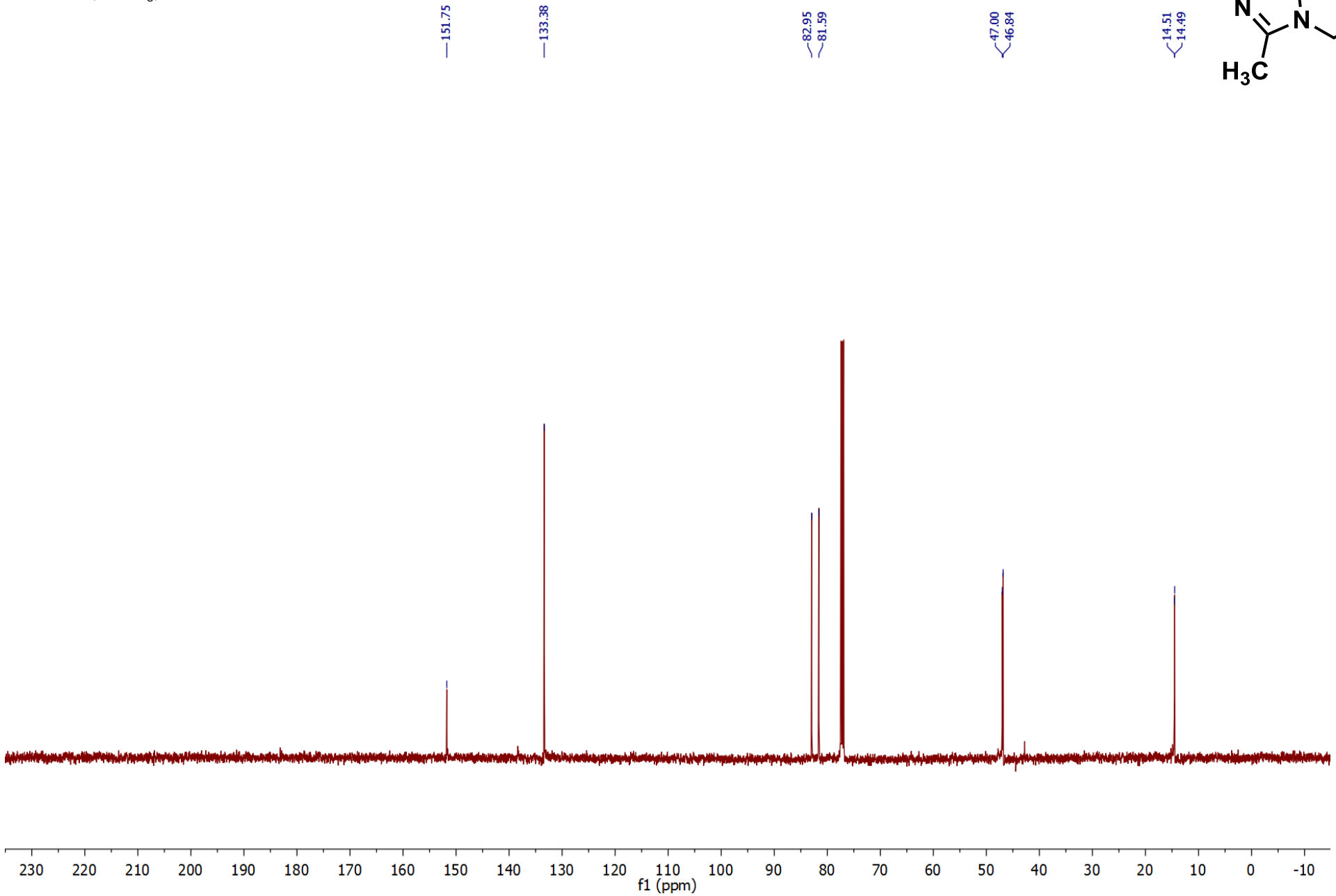
500 MHz, $CDCl_3$, 23 °C



^{13}C NMR spectrum of 1-(2-fluoroethyl)-2-methyl-5-nitro-1*H*-imidazole (10)

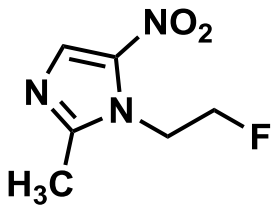
125 MHz, $CDCl_3$, 23 °C

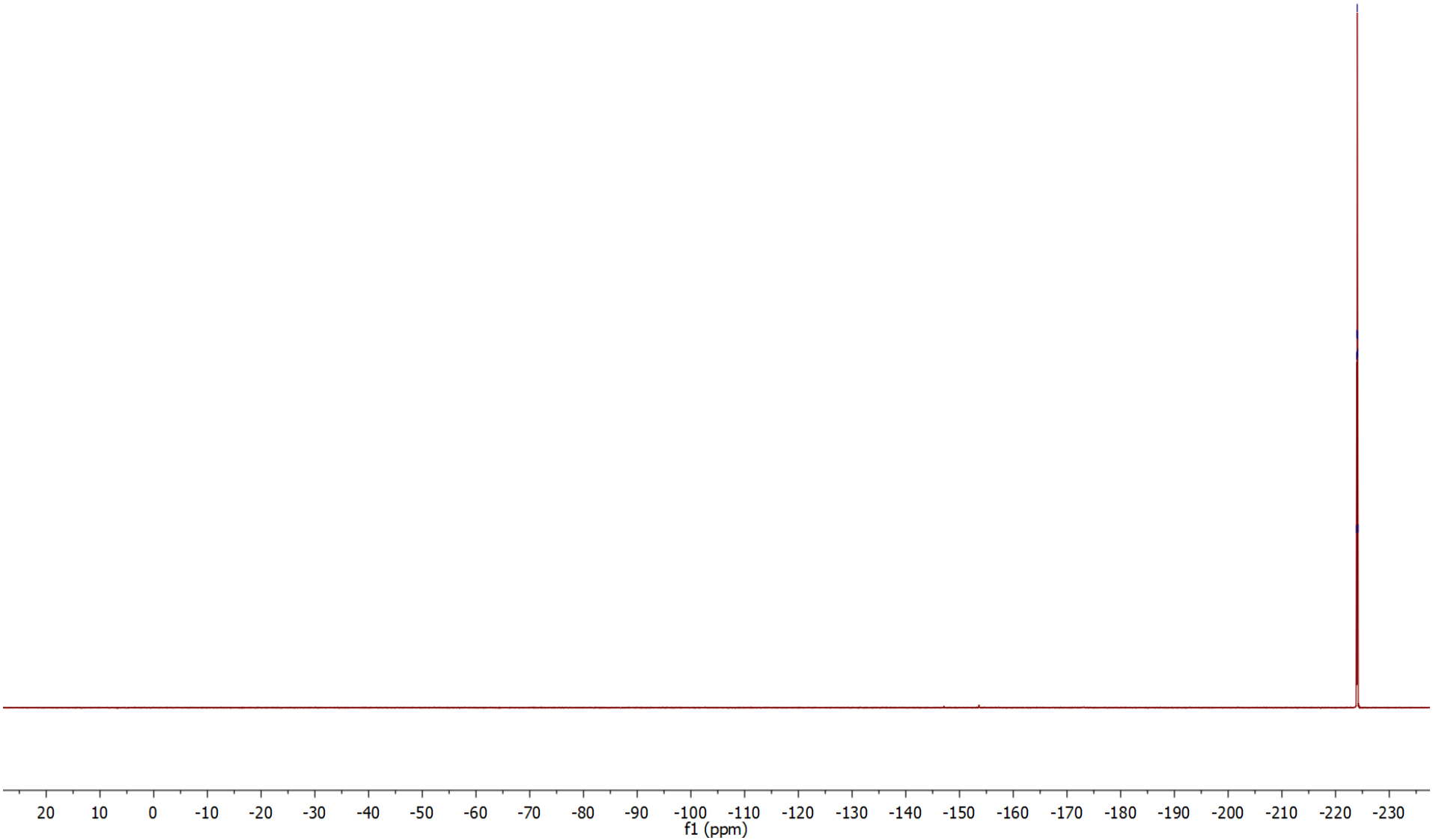




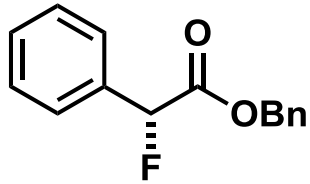
^{19}F NMR spectrum of 1-(2-fluoroethyl)-2-methyl-5-nitro-1*H*-imidazole (10)

470 MHz, $CDCl_3$, 23 °C

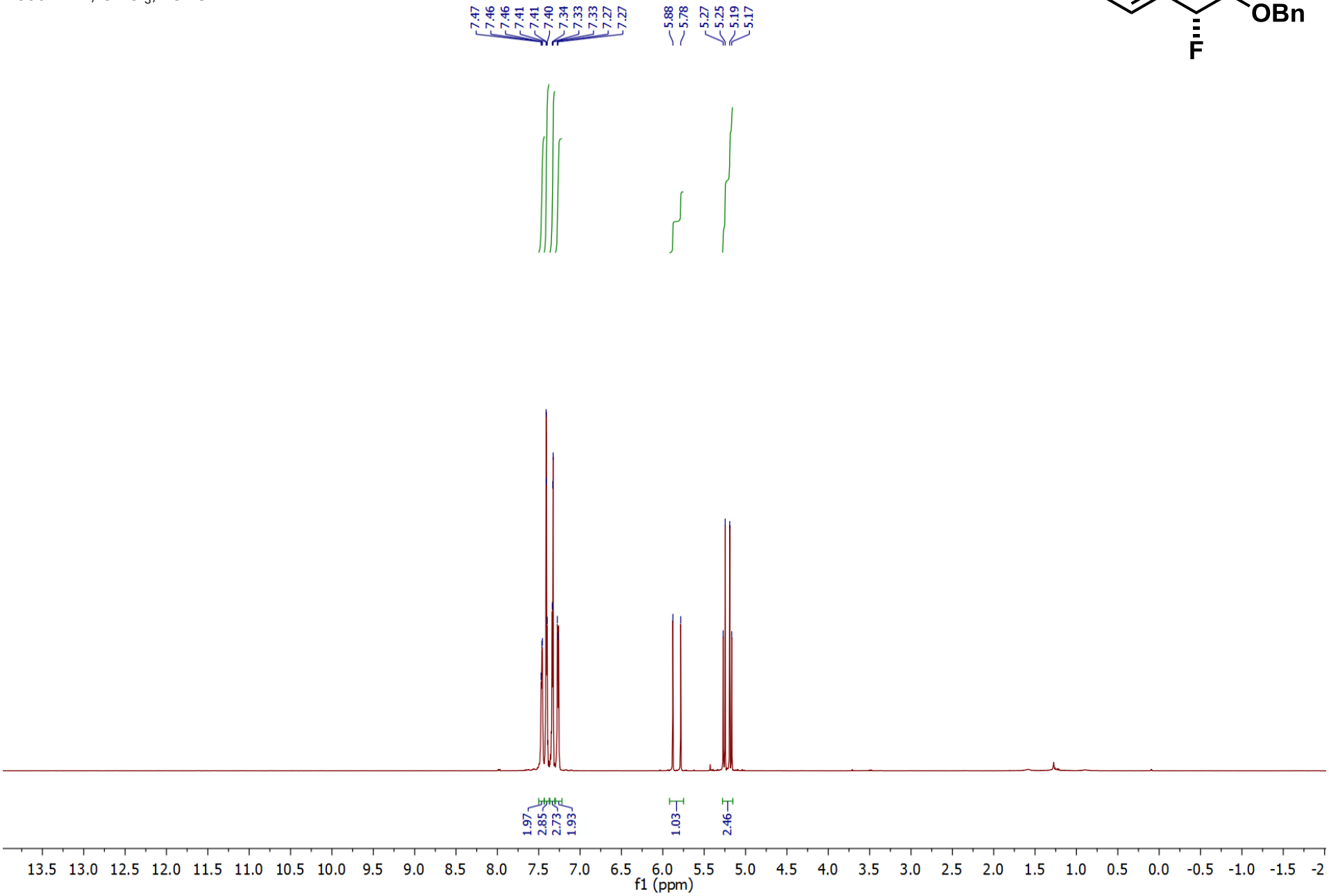




^{1}H NMR spectrum of benzyl (*R*)-2-fluoro-2-phenylacetate (11)

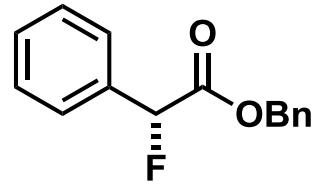


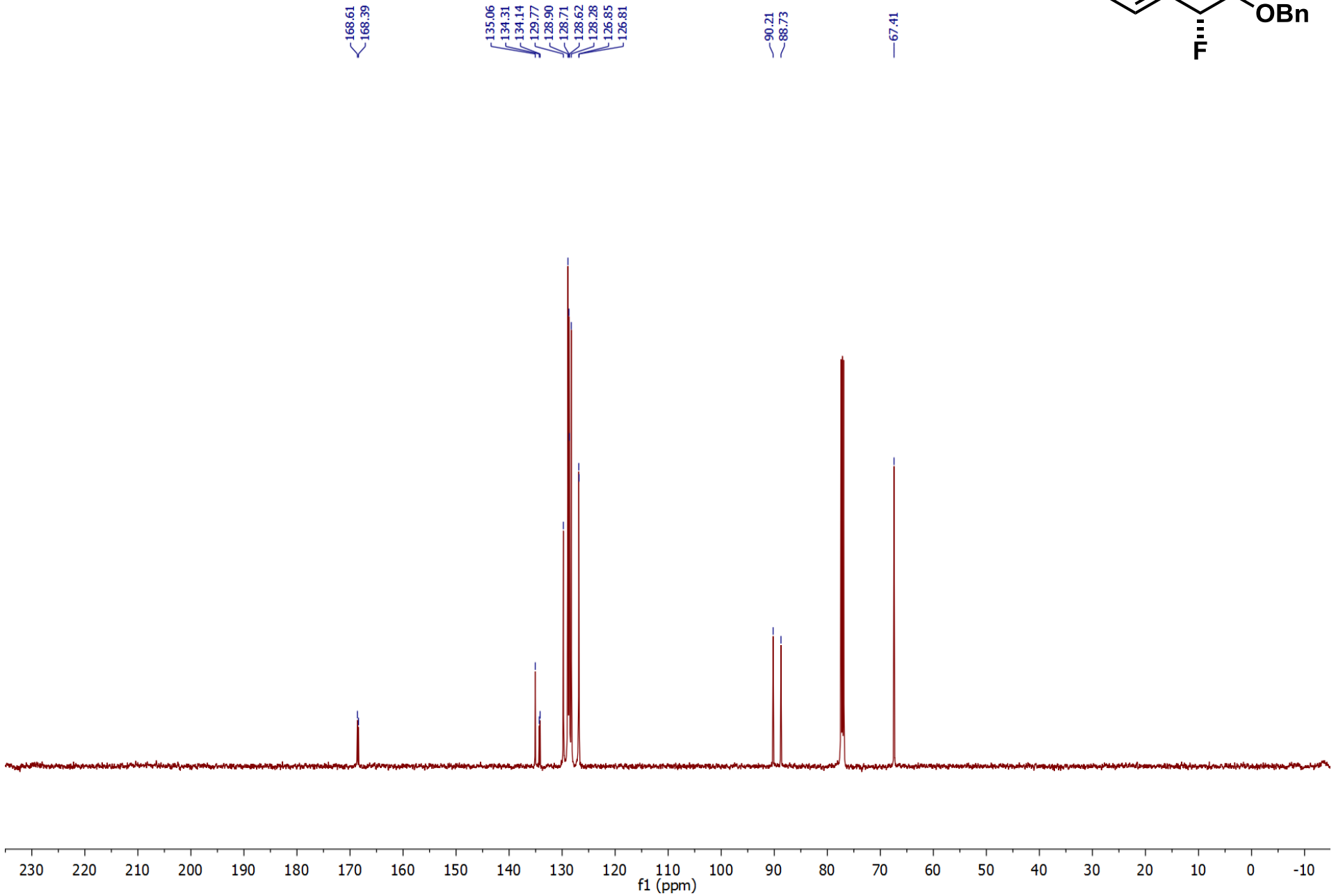
500 MHz, $CDCl_3$, 23 °C



^{13}C NMR spectrum of benzyl (*R*)-2-fluoro-2-phenylacetate (11)

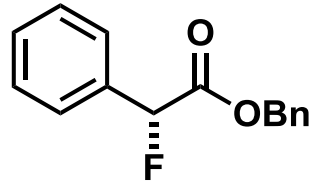
125 MHz, $CDCl_3$, 23 °C

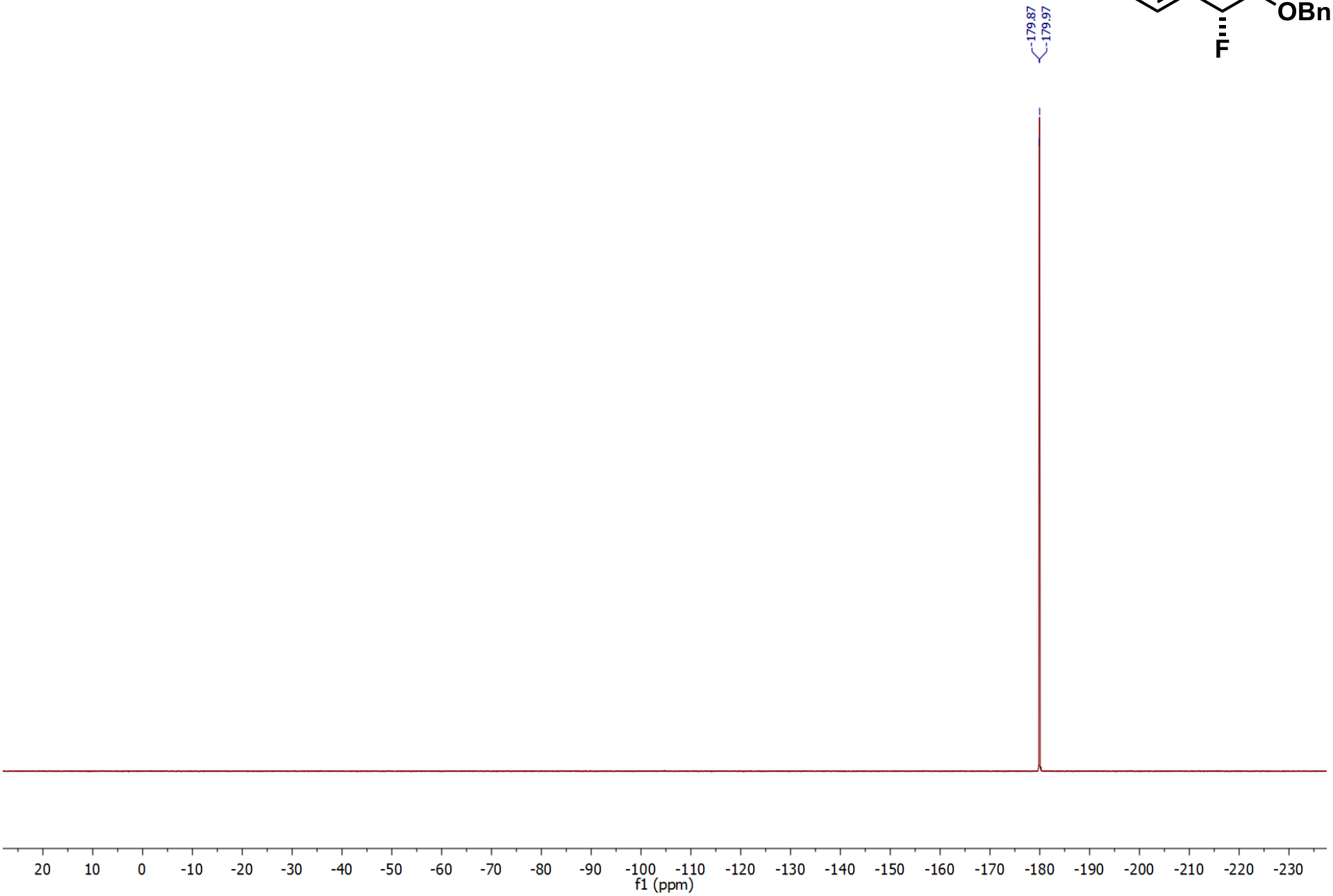




^{19}F NMR spectrum of benzyl (*R*)-2-fluoro-2-phenylacetate (11)

470 MHz, $CDCl_3$, 23 °C

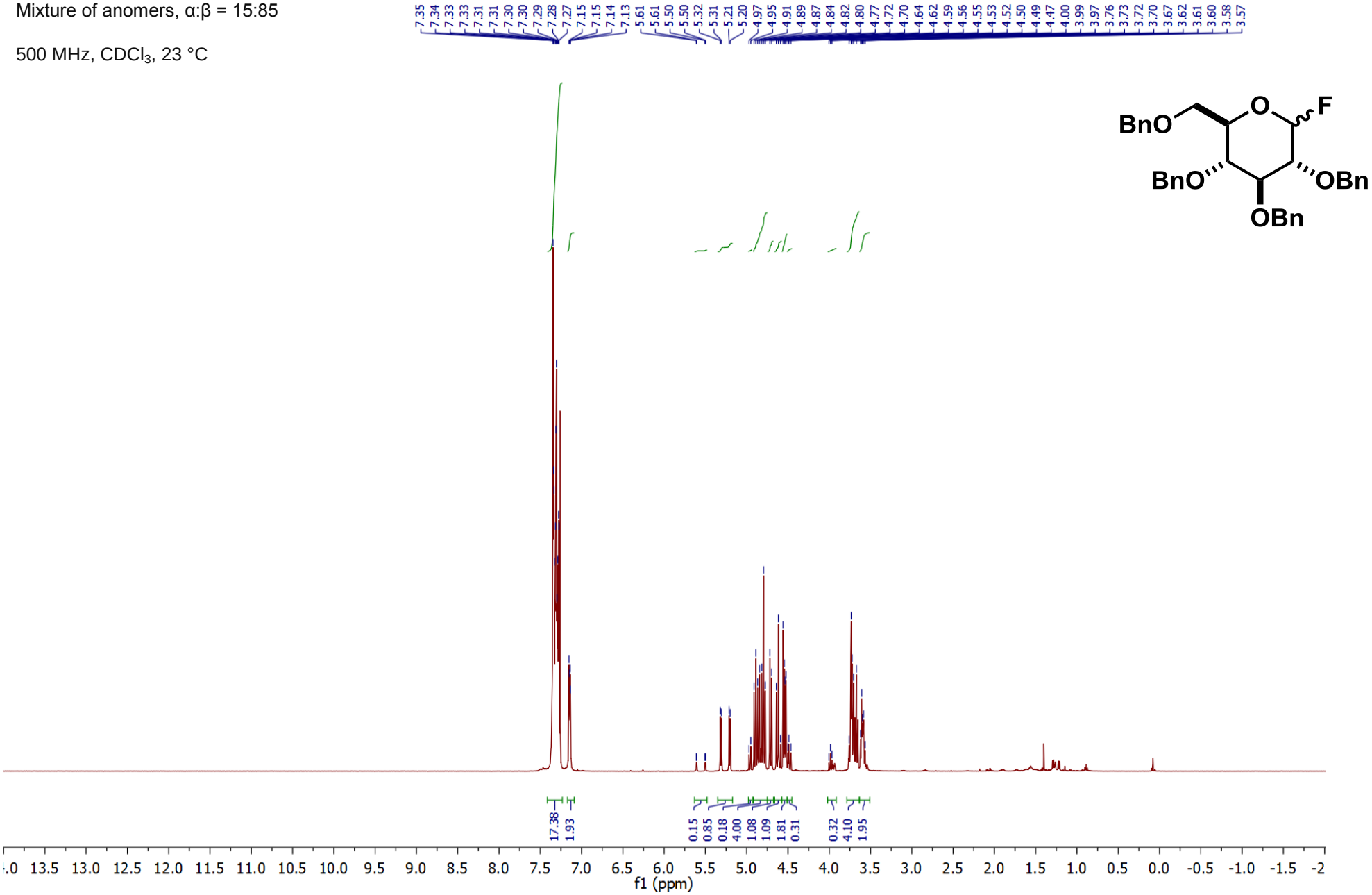




^{1}H spectrum of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl fluoride (12)

Mixture of anomers, α:β = 15:85

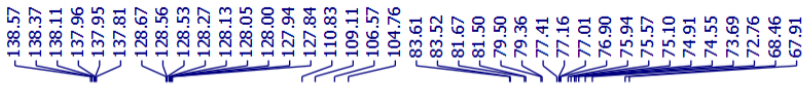
500 MHz, $CDCl_3$, 23 °C

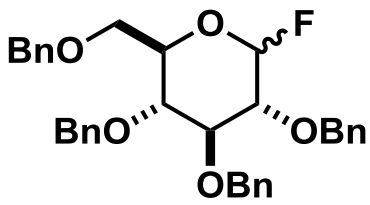


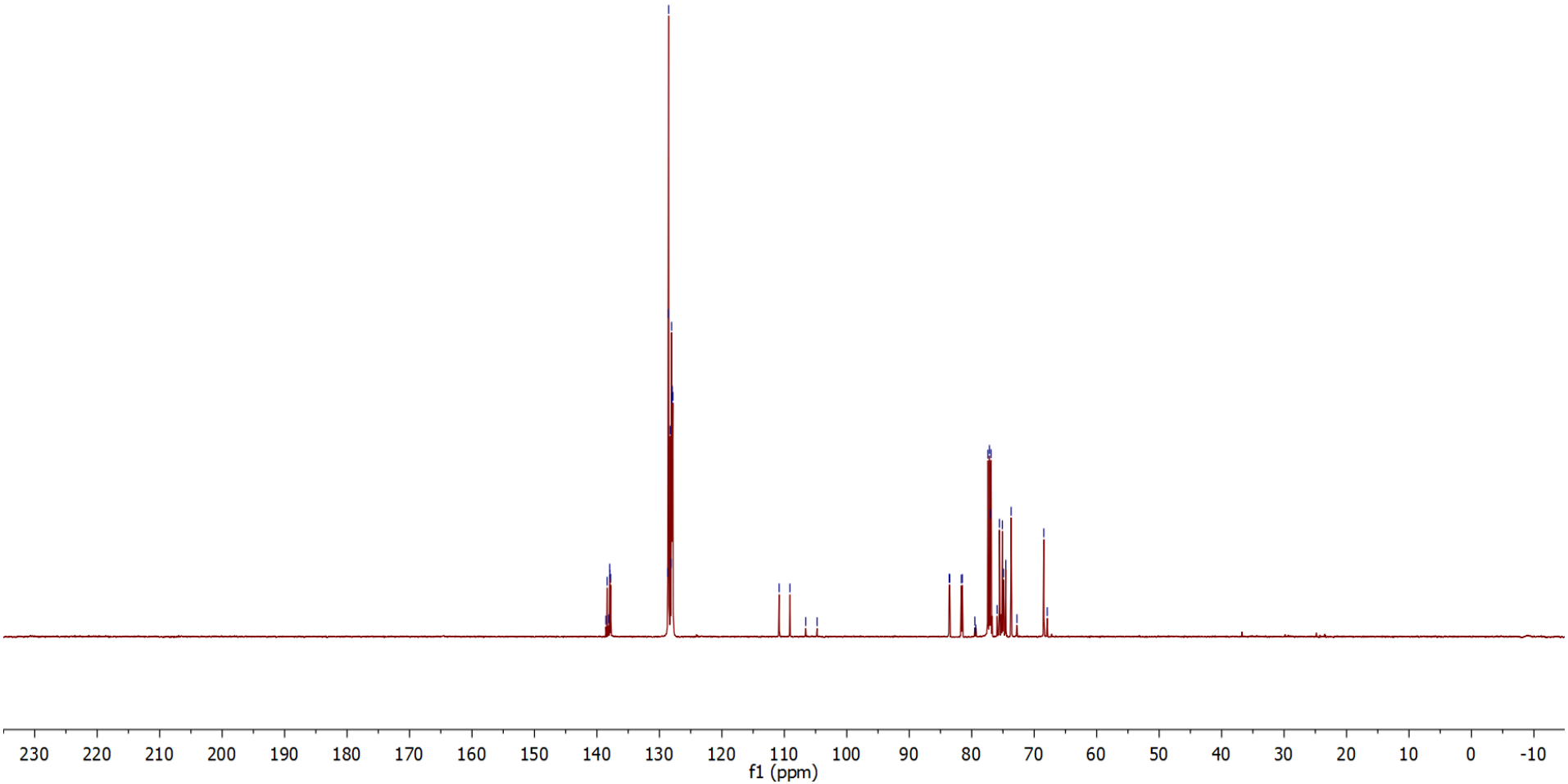
^{13}C spectrum of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl fluoride (12)

Mixture of anomers, α:β = 15:85

125 MHz, $CDCl_3$, 23 °C



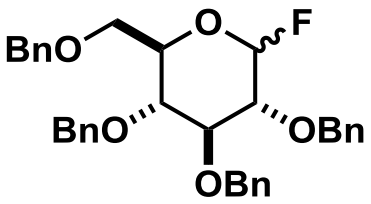




^{19}F spectrum of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl fluoride (12)

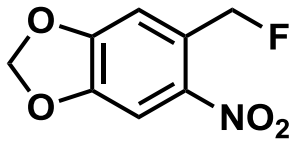
Mixture of anomers, α:β = 15:85

470 MHz, $CDCl_3$, 23 °C



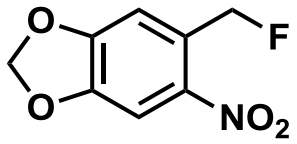
^{1}H NMR spectrum of 6-nitropiperonyl fluoride (13)

500 MHz, $CDCl_3$, 23 °C



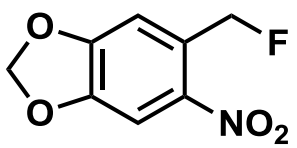
^{13}C NMR spectrum of 6-nitropiperonyl fluoride (13)

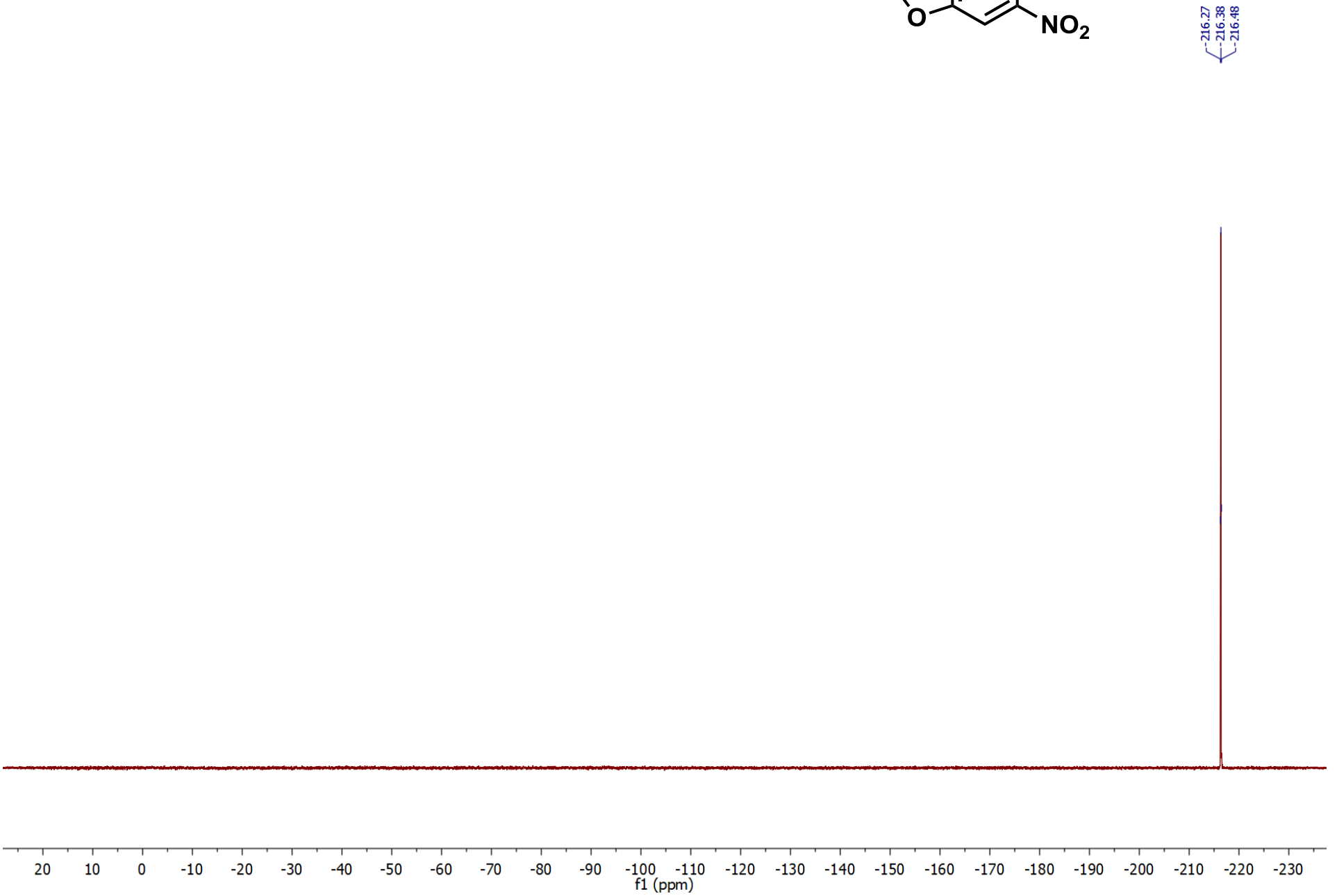
125 MHz, $CDCl_3$, 23 °C



^{19}F NMR spectrum of 6-nitropiperonyl fluoride (13)

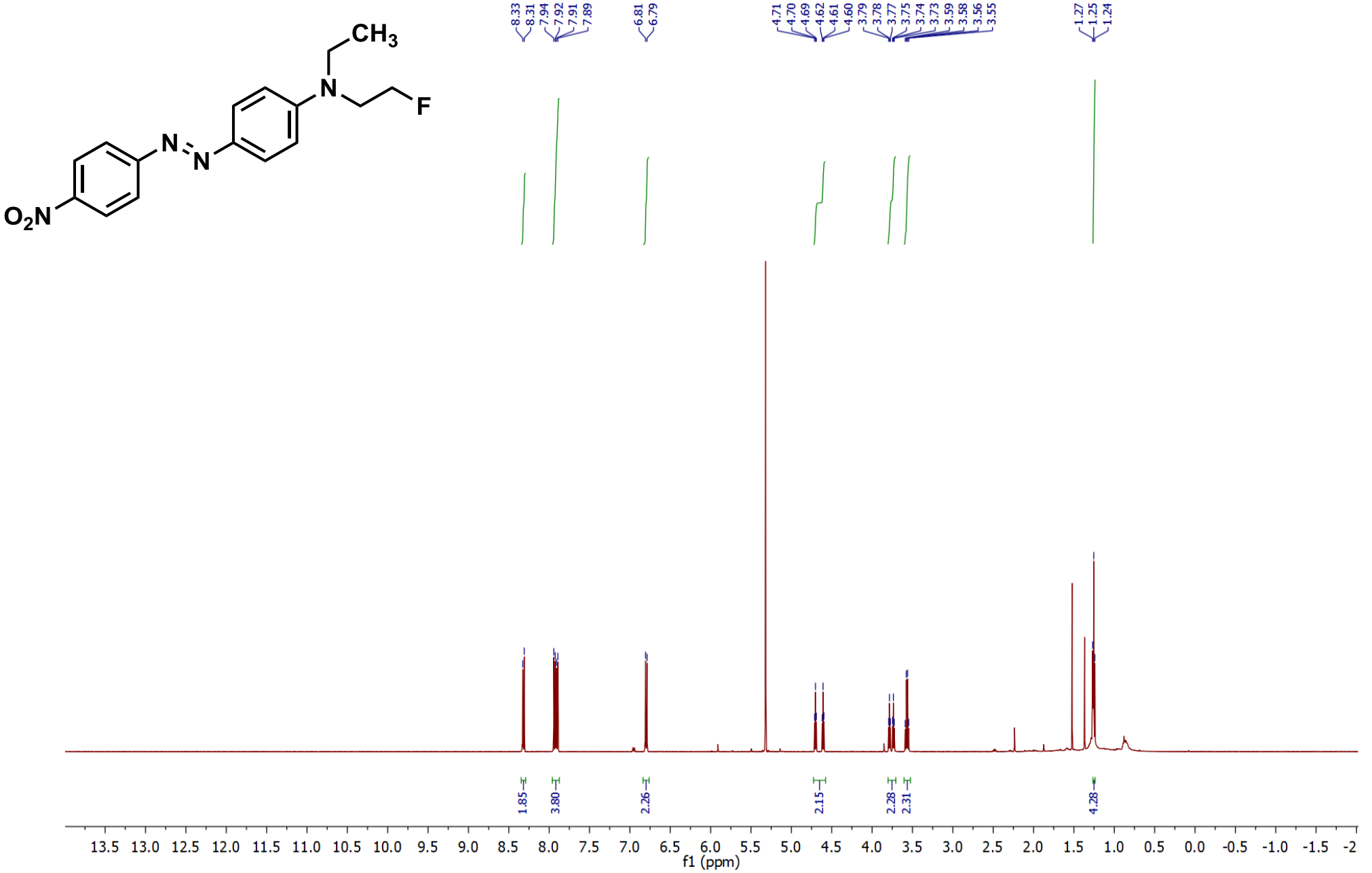
470 MHz, $CDCl_3$, 23 °C





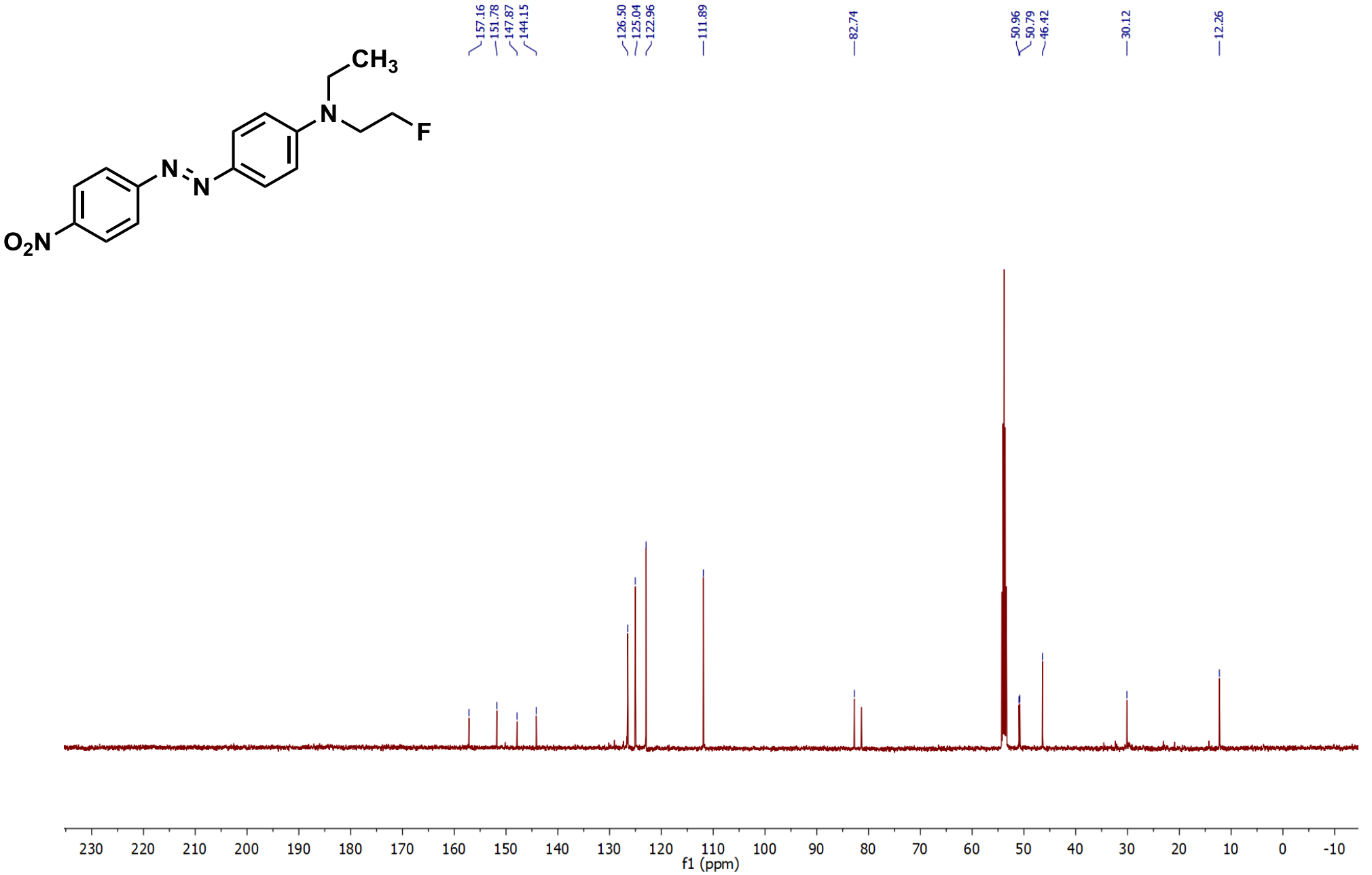
^{1}H NMR spectrum of (*E*)-*N*-ethyl-*N*-(2-fluoroethyl)-4-((4-nitrophenyl)diazenyl)aniline (14)

500 MHz, CD_2Cl_2, 23 °C



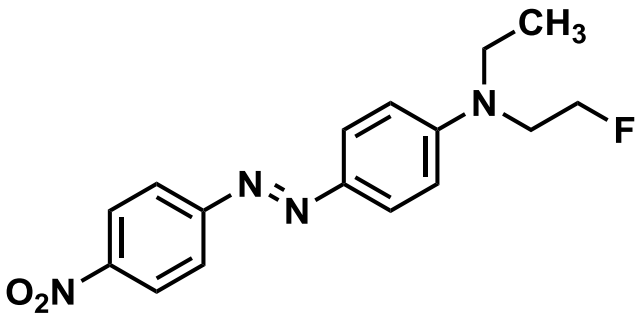
^{13}C NMR spectrum of (*E*)-*N*-ethyl-*N*-(2-fluoroethyl)-4-((4-nitrophenyl)diazenyl)aniline (14)

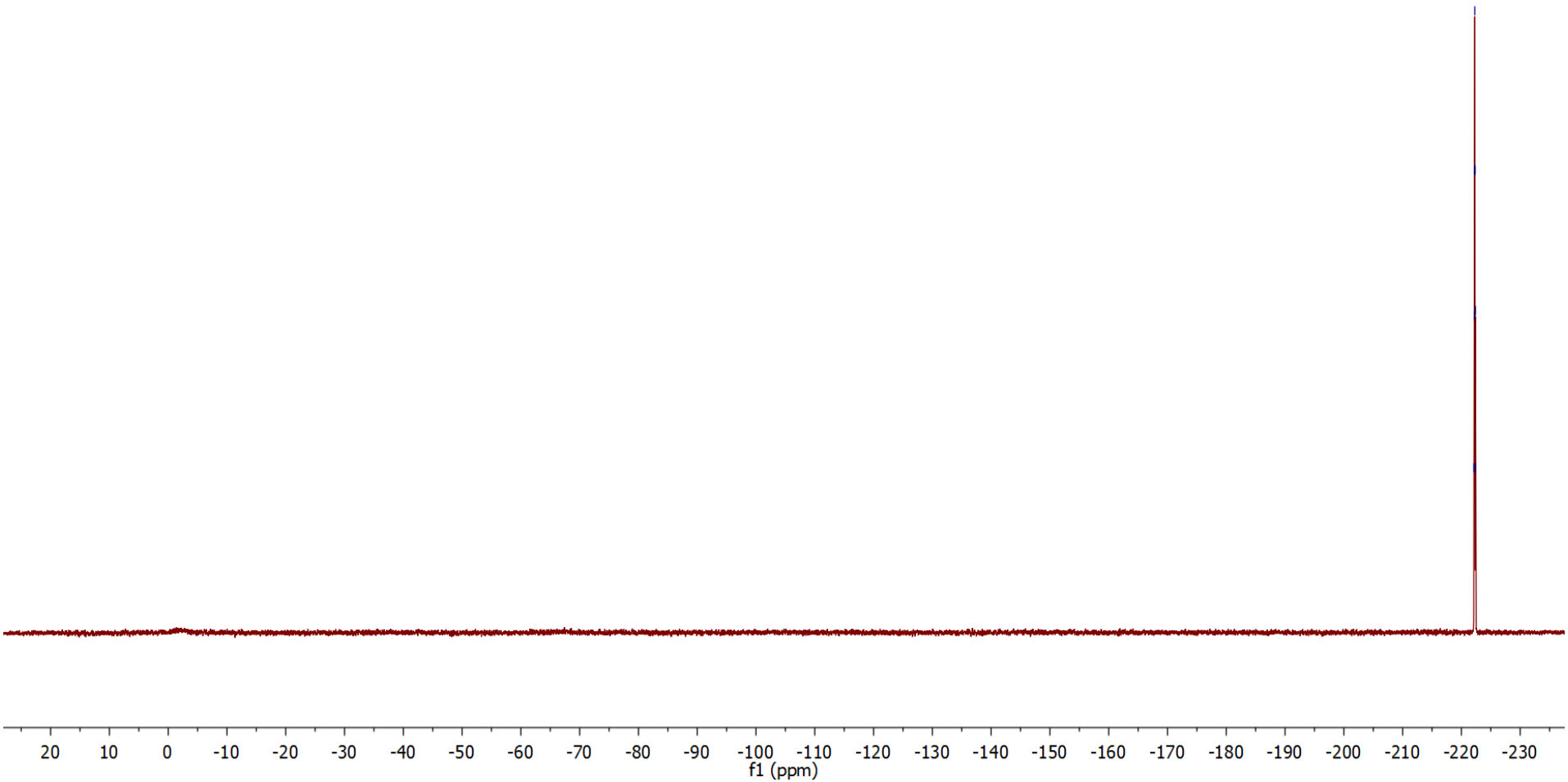
125 MHz, CD_2Cl_2, 23 °C



^{19}F NMR spectrum of (*E*)-*N*-ethyl-*N*-(2-fluoroethyl)-4-((4-nitrophenyl)diazenyl)aniline (14)

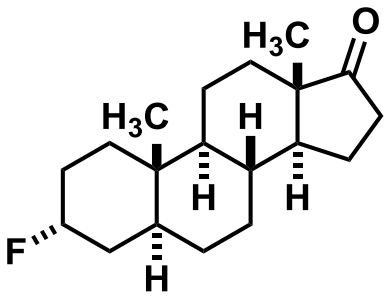
470 MHz, CD_2Cl_2, 23 °C





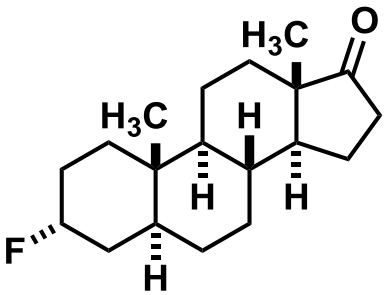
^{1}H NMR spectrum of 3-fluoro-3-deoxyandrosterone (15)

500 MHz, $CDCl_3$, 23 °C



^{13}C NMR spectrum of 3-fluoro-3-deoxyandrosterone (15)

125 MHz, $CDCl_3$, 23 °C



^{19}F NMR spectrum of 3-fluoro-3-deoxyandrosterone (15)

470 MHz, $CDCl_3$, 23 °C