SUPPORTING INFORMATION

Copper-Catalyzed Three-Component Aminofluorination of Alkenes and 1,3-Dienes: Direct Entry to Diverse *β*-Fluoro Alkylamines

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1. General Methods

General Procedures

Round-bottom flasks and stir bars were dried either with a propane torch or in an oven at 140 °C overnight and cooled/stored in a desiccator filled with Drierite. Optimization and substrate screens were performed in 10-mL FEP Tubes without prior drying, and a Teflon-coated micro stir bar. All other reactions were performed in round-bottom flasks with rubber septa and Teflon-coated stir bars. Plastic syringes were used for the transfer of pure solvents, while glass pipets were used for transfer of crude reaction mixtures. Analytical thin-layer chromatography (TLC) was performed using aluminum plates coated with a 0.25 mm layer of 230–400 mesh silica gel with fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light and treatment with mainly vanillin or phosphomolybdic acid (PMA) stain. Organic solutions were concentrated under reduced pressure using a rotary evaporator and flash chromatography performed using 60 Å silica gel and HPLC-grade solvents.

Materials

Commercial reagents and anhydrous solvents were used as received. Specific anhydrous solvents (CH_2Cl_2, Toluene, Dioxane, and THF) were obtained from the Innovative Technologies solvent purification system. Commercially available substrates were purchased in >95% purity and used without further purification.

Instrumentation

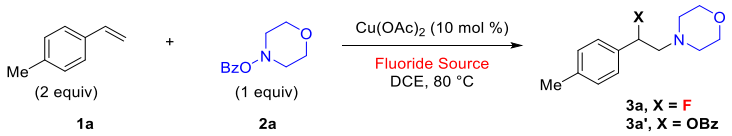
Nuclear magnetic resonance spectra were recorded on either a Varian 400 MHz spectrometer or Bruker 500 MHz spectrometer at room temperature. Chemical shifts for ^1H NMR are reported in parts per million (ppm, δ) and referenced to residual protium in $CDCl_3$ (δ 7.26). NMR values are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad), coupling constant (Hz), and integration. Infrared spectroscopic data are reported in wavenumbers (cm^{-1}) with selected peaks shown. High-resolution mass spectra were obtained using a liquid chromatography-electrospray ionization and time-of-flight mass spectrometer. The X-ray single crystal data and refinement was obtained from UNC Chapel Hill department of chemistry X-ray Core Laboratory.

2. Optimization Screens for Alkene Aminofluorination Reaction Conditions

General procedure 1(GP1) for optimization screening

To a 10-mL FEP tube with Teflon-coated micro stir bar was added *O*-benzoylhydroxylamine and copper catalyst. Solvent (1.0 mL), 4-methylstyrene, and fluorinating reagent were sequentially added via syringe. The mixture was then stirred and heated at the indicated temperature until the consumption of *O*-benzoylhydroxylamine, verified by TLC analysis. The resulting reaction mixture was cooled to room temperature and quenched by the addition of Et_3N (0.5 mL). The solution was then diluted with ethyl acetate to a final volume of 5.0 mL and filtered through a plug of activated, neutral Al_2O_3 (Brockman grade I, 58–60Å). The filtrate was concentrated under reduced pressure, providing the crude reaction mixture. The crude reaction mixture was either purified by silica column chromatography or added to $CDCl_3$ (0.5 mL) with CH_2Br_2 (0.1 mmol) as a quantitative internal standard for NMR analysis.

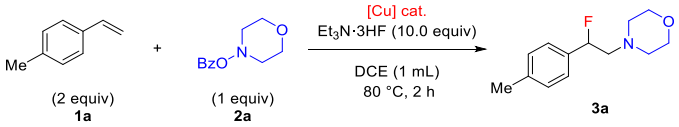
Table S1. Screening of fluoride sources.[a]



Entry	Fluoride source	Fluoride (equiv)	**3a** (%)[b]	**3a'** (%)[b]
1	$Py(HF)_x$	2.0	0	0
2	AgF	2.0	0	0
3	CsF	2.0	0	11
4	TBAF	2.0	0	0
5	$Et_3N{\cdot}3HF$	2.0	40	6
6	**$Et_3N{\cdot}3HF$**	**10.0**	**50 (50)[c]**	**trace**

[a]Reaction conditions: **1a** (2.0 equiv), **2a** (0.2 mmol, 1.0 equiv), fluoride source (2 or 10 equiv), $Cu(OAc)_2$ (10 mol %), DCE (1.0 mL), 80 °C, 2 h. [b]Yields determined by ^1H NMR spectroscopy with CH_2Br_2 as a quantitative internal standard. [c]Isolated yield.

Table S2. Screening of copper catalysts.[a]

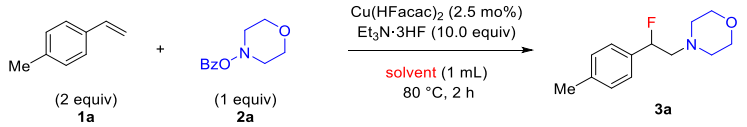


Entry	[Cu] cat.	**3a** (%)[b]
1	$[Cu(OTf)]_2PhMe$	50
2	Cu(OAc)	50
3	$CuCl_2$	40
4	CuCl	44
5	$Cu(eh)_2$	60
6	$Cu(MeCN)_4PF_6$	52
7	**IPrCuCl**	**62 (68%)[c]**
8	CuF_2	54
9	CuBr	52
10	CuI	12
11	CuCN	30
12	CuTC	52
13	$Cu(PhCO_2)_2$	52
14	$Cu(NO_2)_2{\bullet}3H_2O$	40
15	CuSCN	52
16	$CuSO_4$	54
17	$CuSO_4{\bullet}5H_2O$	50
18	CuO	68 (67)[c]

19	CuO_2	58
20	$Cu(OTf)_2$	54
21	$CuBr_2$	42
22	$Cu(MeCN)BF_4$	54
23	$Cu(OAc)_2$	48 (47)[c]
24	$Cu(OAc)_2$	50 (50)[c]
25	$Cu(TFA)_2$	59
26	$Cu(OPiv)_2$	65
27	**$Cu(acac)_2$**	**76 (76)[c]**
28	**$Cu(HFacac)_2$**	**81 (83)[c]**
29	**$Cu(HFacac)_2$ (2.5 mol %)**	**82 (83)[c]**

[a] Reaction conditions: **1a** (2.0 equiv), **2a** (0.2 mmol, 1.0 equiv), fluoride source (10 equiv), copper cat. (2.5–10 mol %), DCE (1.0 mL), 80 °C, 2 h. [b]Yields determined by ^{1}H NMR spectroscopy with CH_2Br_2 as a quantitative internal standard. [c]Isolated yields.

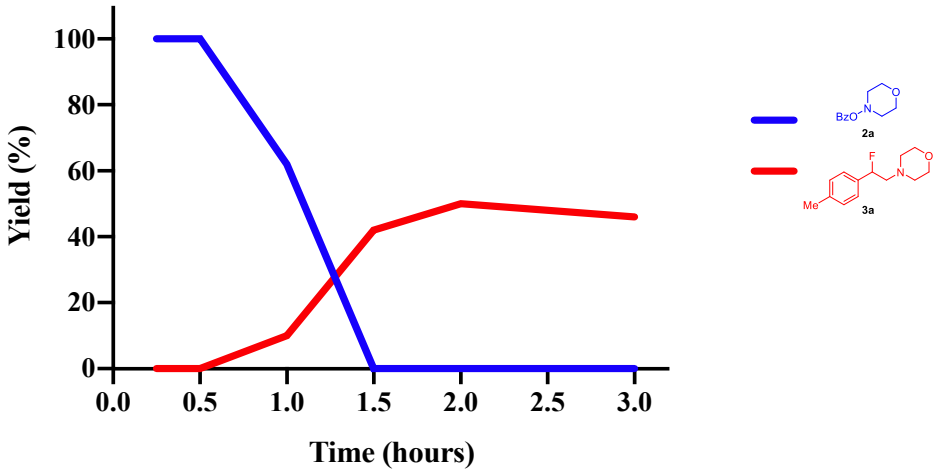
Table S3. Screening of solvents.[a]



Entry	Solvent	**3a** (%)[b]
1	DME	30
2	1,4-Dioxane	46
3	THF	24
4	Toluene	20
5	**DCE**	**83**
6	MeCN	40

[a]Reaction conditions: **1a** (2.0 equiv), **2a** (0.2 mmol, 1.0 equiv), Et_3N•3HF (10 equiv), solvent (1.0 mL), 80 °C, 2 h. [b]Yields determined by ^{1}H NMR spectroscopy with CH_2Br_2 as a quantitative internal standard.

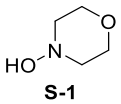
Reaction progress and completion time testing



To determine reaction progress and completion time of the above transformation, seven reactions with 4-methylstyrene **1a** (0.2 mmol scale) and *O*-benzyl hydroxymorpholine **2a** were subject to **GP1**, and quenched at 0.25, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 h, respectively. Crude NMR yields using CH_2Br_2 as a quantitative internal standard were used to generate the above graph, which indicates complete consumption of the hydroxylamine occurs within 1.5 h and the formation of the product finishes within 2.0 h.

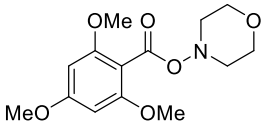
3. Preparation of Starting Materials

3.1. Preparation of hydroxylamine derivatives and compound characterizations.



S-1

Morpholin-4-ol (S-1). To a 250-mL round-bottom flask was added NaOMe (1.59 g, 28 mmol, 1.4 equiv) and MeOH (70 mL). In a separate 100-mL round-bottom flask was added *O*-benzoyl-*N*-hydroxylmorpholine **2a** (4.14 g, 20 mmol, 1.0 equiv) and Et_2O (60 mL). The dissolved hydroxylamine ester was then added via syringe to the solution of NaOMe. The mixture was allowed to stir for 1 h, and then directly dried *in vacuo*. The crude mixture was purified by flash column chromatography (30% ethyl acetate–hexanes to 40% ethyl acetate–hexanes) to afford morpholin-4-ol (**S-1)** as colorless oil (1.33 g, 69%). Spectroscopic data match the commercially available *N*-hydroxylamine (CAS 5765-63-9).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (br, 1H), 3.91 (d, J = 12.0 Hz, 2H), 3.76–3.47 (m, 2H), 3.14 (d, J = 11.0 Hz, 2H), 2.72 (td, J = 11.0, 3.2 Hz, 2H).



B

Morpholino 2,4,6-trimethoxybenzoate (B). To a 100-mL round-bottom flask was added 2,4,6-trimethoxybenzoic acid (0.849 g, 4.0 mmol, 1.0 equiv), CH_2Cl_2 (10 mL), oxalyl chloride (406 µL,

4.8 mmol, 1.2 equiv), and dimethylformamide (0.2 mL). Upon the discontinuation of gas evolution, the mixture was directly concentrated under reduced pressure. The mixture was next diluted with CH_2Cl_2 (10 mL), and morpholin-4-ol (433 mg, 4.2 mmol, 1.05 equiv) was added over 5 min, followed by the addition of triethylamine (585 μL, 4.2 mmol, 1.05 equiv). Upon consumption of acid starting material (monitored by TLC), the reaction was quenched through the addition of saturated aqueous NH_4Cl (10 mL) and H_2O (20 mL). The organic layers were separated, and washed with saturated aqueous NH_4Cl (10 mL × 3), saturated aqueous $NaHCO_3$ (10 mL × 3), H_2O (10 mL × 3), and brine (10 mL × 2). The organic layer was dried over Na_2SO_4, and filtered. The filtrate was concentrated *in vacuo*. Purification by flash column chromatography (20% ethyl acetate–hexanes to 60% ethyl acetate–hexanes) gave **B** as a white solid (493 mg, 42%). Spectroscopic data matched the reported literature.[1]

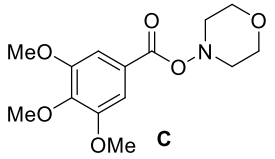
$\mathbf{R}_f$ = 0.33 (10% MeOH, 40% ethyl acetate, 50% hexanes).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.08 (s, 2H), 3.98–3.75 (m, 13H), 3.44 (d, *J* = 9.3 Hz, 2H), 3.04–2.90 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 162.9, 158.9, 104.3, 90.6, 65.8, 56.8, 55.9, 55.4.

FTIR (thin film): cm^{-1} 2965, 2845, 1748, 1607, 1590, 1458, 1243, 1228, 1129, 1039.

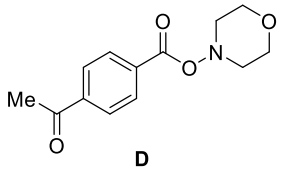
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{20}NO_6^+$ 298.1285; found: 298.1287.



C

Morpholino 3,4,5-trimethoxybenzoate (C). To a 100-mL round-bottom flask was added 3,4,5-trimethoxybenzoic acid (1.02 g, 4.8 mmol, 1.2 equiv), CH_2Cl_2 (15 mL), and 1,1'-carbonyldiimidazole (778 mg, 4.8 mmol, 1.2 equiv). The mixture was allowed to stir overnight, until the formation of CO_2 gas halted. Morpholin-4-ol (413 mg, 4.0 mmol, 1.0 equiv) was next added in CH_2Cl_2 (5 mL). The mixture was allowed to stir until the consumption of hydroxylamine (monitored by TLC). The solvent was removed *in vacuo*. The crude mixture was diluted with ethyl acetate (10 mL) and H_2O (10 mL). The organic layer was separated, washed with H_2O (10 mL × 2), saturated aqueous NH_4Cl (10 mL × 3), brine (10 mL × 2), dried over Na_2SO_4, and filtered. The filtrate was concentrated *in vacuo* to afford the crude product. Purification by flash column chromatography (40% ethyl acetate–hexanes to 50% ethyl acetate–hexanes) gave **C** as a white solid (716 mg, 60%). Spectroscopic data matched the reported literature.[2]

^{1}H NMR (400 MHz, CDCl3): δ 7.25 (s, 2H), 4.02–3.78 (m, 13H), 3.52–3.39 (m, 2H), 3.11–2.96 (m, 2H).



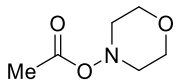
D

Morpholino 4-acetylbenzoate (D). To a 100-mL round-bottom flask was added 4-acetylbenzoic acid (0.657 g, 4.0 mmol, 1.0 equiv), CH_2Cl_2 (10 mL), oxalyl chloride (406 μL, 4.8 mmol, 1.2 equiv), and dimethylformamide (0.2 mL). Upon the discontinuation of gas evolution, the mixture was directly concentrated under reduced pressure. The mixture was next diluted with CH_2Cl_2 (10 mL), and morpholin-4-ol (433 mg, 4.2 mmol, 1.05 equiv) was added over 5 min, followed by the addition of triethylamine (585 μL, 4.2 mmol, 1.05 equiv). Upon consumption of acid starting material (monitored by TLC), the reaction was quenched by the addition of saturated aqueous NH_4Cl (10 mL) and H_2O (20 mL). The separated organic layer was washed with saturated aqueous NH_4Cl (10 mL ×3), saturated aqueous $NaHCO_3$ (10 mL ×3), H_2O (10 mL ×3), and brine (10 mL ×2), dried over Na_2SO_4, and filtered. The

filtrate was concentrated *in vacuo*. Purification by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl acetate–hexanes) gave **D** as a white solid (545 mg, 55%).
$\mathbf{R}_f$ = 0.18 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 2H), 4.08–3.72 (m, 4H), 3.57–3.34 (m, 2H), 3.14–2.90 (m, 2H), 2.65 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 197.3, 163.7, 140.4, 132.9, 129.7, 128.2, 65.8, 57.0, 26.8.
FTIR (thin film): cm^{-1} 2967, 2900, 2858, 1737, 1685, 1404, 1240, 1100, 1083, 857, 763.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}NO_4^+$ 250.1074; found: 250.1077.

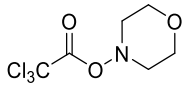
General procedure 2 (GP2) for the preparation of hydroxylamine starting materials E, F and G.

To a 15-mL round-bottom flask was added morpholin-4-ol (433 mg, 4.2 mmol, 1.05 equiv), dimethylaminopyridine (9.0 mg, 0.075 mmol, 0.019 equiv), freshly distilled CH_2Cl_2 (2 mL), and triethylamine (0.59 mL, 4.2 mmol, 1.05 equiv). To the reaction flask at 0 °C was added the solution of acyl chloride (4.0 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL). The mixture was allowed to stir at room temperature for 30 min, until the consumption of acyl chloride (monitored by TLC). The reaction mixture was then washed with aqueous solution of HCl (1 M, 5 mL x 2). The separated organic layer was dried over Na_2SO_4, filtered, and the filtrate was concentrated in *vacuo*. Purification by column chromatography (5% MeOH, 30% ethyl acetate, 65% hexanes unless otherwise noted) generated the desired product.



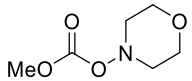
E

Morpholino acetate (E) Preparation *via* **GP2** gave **E** as a light-yellow oil (375 mg, 65%).
$\mathbf{R}_f$ = 0.34 (50% Ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.85 (d, *J* = 10.9 Hz, 2H), 3.77–3.65 (br. m, 2H), 3.23 (d, *J* = 9.6 Hz, 2H), 2.87–2.76 (br. m, 2H), 1.99 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.8, 65.6, 56.7, 19.5.
FTIR (thin film): cm^{-1} 1756, 1210, 1102, 1003, 891, 857.
HRMS (ESI) m/z: $[M+ Na]^+$ Calcd for $C_6H_{11}NO_3Na^+$ 168.0631; found: 168.0628.



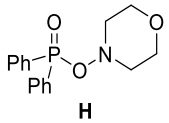
F

Morpholino 2,2,2-trichloroacetate (F). Preparation *via* **GP2** and purification by column chromatography (20% ethyl acetate-hexenes) gave **F** as a yellow solid (726 mg, 73%).
$\mathbf{R}_f$ = 0.34 (50% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.97 (d, *J* = 11.9 Hz, 2H), 3.82–3.72 (br. m, 2H), 3.43 (d, *J* = 9.9 Hz, 2H), 3.11–3.01 (br. m, 2H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 160.0, 88.9, 65.6, 56.8.
FTIR (thin film): cm^{-1} 1777, 1460, 1267, 1194, 1098, 962, 865, 812, 674.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_6H_9{}^{35}Cl_3NO_3^+$ 247.9643; found: 247.9643.



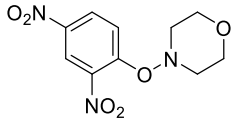
G

Methyl morpholino carbonate (G). Preparation *via* **GP2** gave **G** as a light-yellow oil (496 mg, 77%).
$\mathbf{R}_f$ = 0.48 (50% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.91 (d, *J* = 11.3 Hz, 2H), 3.80 (s, 3H), 3.77–3.70 (br. m, 2H), 3.34 (d, *J* = 9.7 Hz, 2H), 3.00–2.85 (br. m, 2H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.8, 65.6, 56.8, 54.9.
FTIR (thin film): cm^{-1} 1767, 1440, 1268, 1229, 1100, 1052, 860.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_6H_{12}NO_4^+$ 162.0761; found: 162.0761.



H

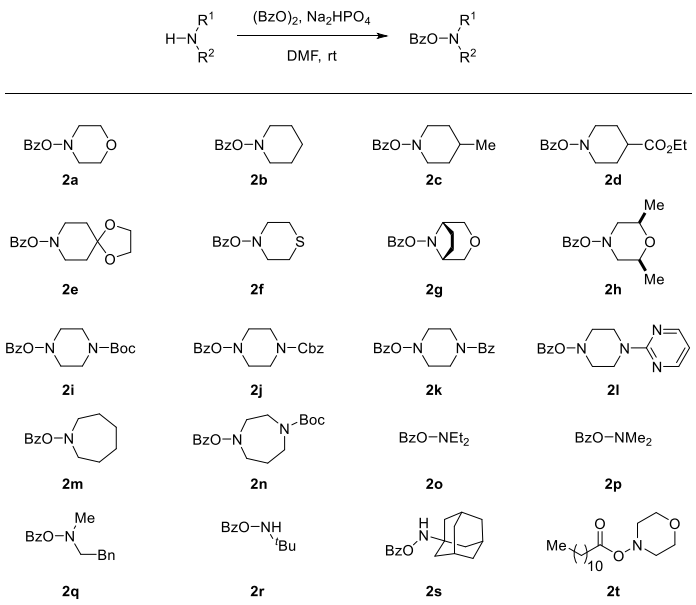
Morpholino diphenylphosphinate (H). H was synthesized following a previously reported method with modification.[3] To a 10-mL round-bottom flask added morpholin-4-ol (412 mg, 4.0 mmol, 1.0 equiv), triethylamine (1.39 mL, 10 mmol, 2.5 equiv) and CH_2Cl_2 (0.5 mL). To the reaction flask at 0 °C, was added diphenylphosphinyl chloride (1.92 mL, 4.8 mmol, 1.2 equiv). The reaction mixture was allowed to stir at room temperature, until the consumption of morpholin-4-ol. Solvents were then removed under reduced pressure. To the residue, was added diethyl ether (10 mL) and decanted for four times. The combined extracts were filtered through a silica/celite pad and concentrated in *vacuo* to give **H** as a white solid (308 mg, 1.01 mmol, 25%).
$\mathbf{R}_f$ = 0.13 (50% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.55–7.50 (m, 2H), 7.47–7.41 (m, 4H), 3.82 (d, *J* = 11.8 Hz, 2H), 3.58–3.50 (br. m, 2H), 3.25 (d, *J* = 10.3 Hz, 2H), 3.04–2.96 (br. m, 2H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 132.2 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.9 (d, $J_{C\text{-}P}$ = 9.9 Hz), 130.7 (d, $J_{C\text{-}P}$ = 135.3 Hz), 128.31 (d, $J_{C\text{-}P}$ = 12.9 Hz), 65.8, 58.7 (d, $J_{C\text{-}P}$ = 2.7 Hz).
^{31}P NMR ($CDCl_3$, 202 MHz): δ 33.63–33.36 (m).
FTIR (thin film): cm^{-1} 1438, 1227, 1128, 1020, 866, 787, 726, 693, 546, 530.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}NO_3P^+$ 304.1097; found: 304.1092.



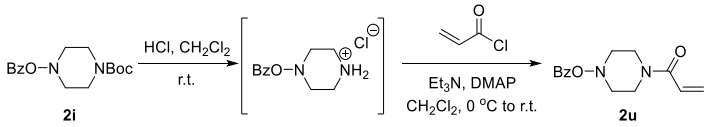
I

4-(2,4-Dinitrophenoxy)morpholine (I). Prepared following a previously reported method.[4] Spectroscopic data were in agreement.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.41 (d, *J* = 9.3 Hz, 1H), 7.90 (d, *J* = 9.3 Hz, 1H), 4.06 (d, *J* = 11.4 Hz, 2H), 3.75 (t, *J* = 11.4 Hz, 2H), 3.33 (d, *J* = 10.3 Hz, 2H), 3.16 (t, *J* = 10.3 Hz, 2H).

O-Benzoylhydroxylamines below were synthesized according to the literature procedure.[5]



4-Acryloylpiperazin-1-yl benzoate (2u)



To a 25-mL round-bottom flask was added *tert*-butyl 4-(benzoyloxy)piperazine-1-carboxylate **2i** (306 mg, 1.0 mmol, 1.0 equiv), CH_2Cl_2 (4.0 mL), the solution of HCl in dioxane (4M, 2 mL, 8.0 mmol, 8.0 equiv). The reaction mixture was allowed to stir at room temperature for 8 h, and then concentrated under reduced pressure. The crude solid was used for the next step without further purification.

To a solution of the crude residue in CH_2Cl_2 (4 mL) at 0 ^oC, was added trimethylamine (202 mg, 2.0 mmol, 2.0 equiv), DMAP (2.4 mg, 0.02 mmol, 0.02 equiv), and acryloyl chloride (91 mg, 1.0 mmol, 1.0 equiv). Then mixture was allowed to warm to room temperature and stir overnight. The mixture was diluted with CH_2Cl_2 (20 mL). The organic layer was washed with water (10 mL × 2) and the brine (10 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash column chromatography (30% ethyl acetate–hexanes to 50% ethyl acetate–hexanes) gave **2u** as a colorless oil (225 mg, 87% over two steps).

$\mathbf{R_f}$ = 0.10 (50% ethyl acetate–hexanes).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.97 (t, *J* = 19.7 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 6.58 (dd, *J* = 16.8, 10.6 Hz, 1H), 6.33 (dd, *J* = 16.8, 1.8 Hz, 1H), 5.74 (dd, *J* = 10.6, 1.8 Hz, 1H), 4.67–4.38 (m, 1H), 4.22–3.82 (m, 1H), 3.70–3.57 (m, 1H), 3.57–3.44 (m, 2H), 3.42–3.25 (m, 1H), 3.09–2.58 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.4, 164.5, 133.4, 129.5, 128.9, 128.6, 128.5, 127.0, 56.1, 55.7, 43.9, 40.3.

FTIR (thin film): cm^{-1} 1736, 1647, 1613, 1438, 1246, 1085, 1019, 709.

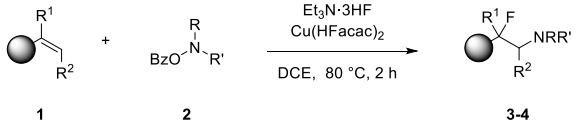
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{16}N_2O_3Na^+$ 283.1053; found: 283.1047.

3.2. Preparation of olefin substrates and compound characterization.

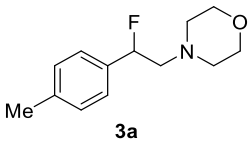
Olefins (**1a**–**1q and 1u**–**1z**) were purchased from commercial sources and used directly without further purification. **1r**–**1s**,[6] and **1t**[7] are known alkenes.

4. Scope of alkenes and compound characterization data

General procedure 3 (GP3) for alkene aminofluorination reactions

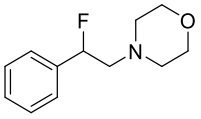


To a 10-mL FEP tube with Teflon-coated micro stir bar was added *O*-benzoylhydroxylamine **2** (0.2 mmol, 1.0 equiv) and $Cu(HFacac)_2$ (2.4 mg, 2.5 mol%). DCE (1.0 mL), alkene **1** (0.4 mmol, 2.0 equiv), and Et_3N•3HF (322 mg, 2 mmol, 10 equiv) were sequentially added. The mixture was allowed to stir at 80 °C for 2 h until the consumption of *O*-benzoylhydroxylamine (verified by TLC, 20% ethyl acetate–hexanes). The resulting reaction mixture was cooled to room temperature and quenched through the addition of Et_3N (0.5 mL). The solution was then diluted with ethyl acetate to a final volume of 5.0 mL and filtered through a plug of activated, neutral Al_2O_3 (Brockman grade I, 58–60Å). The filtrate was concentrated under reduced pressure, providing the crude reaction mixture. The crude reaction mixture was purified by silica column chromatography.



3a

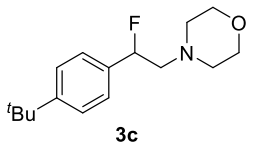
4-(2-Fluoro-2-(*p*-tolyl)ethyl)morpholine (3a). Synthesized using **GP3** from **1a** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl acetate–hexanes), as a pale-yellow oil (37.3 mg, 83%).
$\mathbf{R_f}$ = 0.14 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 5.62 (ddd, *J* = 48.9, 8.8, 2.4 Hz, 1H), 3.77–3.72 (m, 4H), 2.91 (ddd, *J* = 17.1, 14.2, 8.8 Hz, 1H), 2.68–2.53 (m, 5H), 2.36 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 135.7 (d, $J_{C\text{-}F}$ = 20.0 Hz), 129.1, 125.6, 92.6 (d, $J_{C\text{-}F}$ = 173.0 Hz), 66.9, 64.9 (d, $J_{C\text{-}F}$ = 23.4 Hz), 54.1, 21.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ -175.11.
FTIR (thin film): cm^{-1} 2955, 2854, 2808, 1453, 1138, 1115, 1008, 869, 816, 536.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}FNO^+$ 224.1445; found: 224.1451.



3b

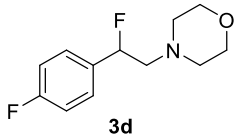
4-(2-Fluoro-2-phenylethyl)morpholine (3b). Synthesized using **GP3** from **1b** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl acetate–hexanes), as a pale oil (27.2 mg, 65%).
$\mathbf{R_f}$ = 0.12 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.22 (m, 5H), 5.60 (ddd, *J* = 48.9, 8.8, 2.3 Hz, 1H), 3.69 (t, *J* = 4.7 Hz, 4H), 2.98–2.72 (m, 1H), 2.67–2.58 (m, 1H), 2.58–2.41 (m, 4H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7 (d, $J_{C\text{-}F}$ = 20.6 Hz), 128.5, 128.5, 125.6 (d, $J_{C\text{-}F}$ = 6.9 Hz), 92.6 (d, $J_{C\text{-}F}$ = 173.7 Hz), 66.9, 64.9 (d, $J_{C\text{-}F}$ = 23.1 Hz), 54.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ -176.90.

FTIR (thin film): cm^{-1} 2956, 2854, 2809, 1495, 1452, 1115, 1008, 914, 727, 698.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{17}FNO^+$ 210.1289; found: 210.1291.



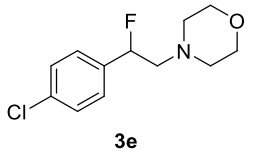
3c

4-(2-(4-(*tert*-Butyl)phenyl)-2-fluoroethyl)morpholine (3c). Synthesized using **GP3** from **1c** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl acetate–hexanes), as a pale-yellow oil (39.2 mg, 74%).
$\mathbf{R}_f$ = 0.20 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 5.58 (ddd, J = 49.1, 9.0, 2.1 Hz, 1H), 3.69 (t, J = 4.7 Hz, 4H), 2.95–2.76 (m, 1H), 2.67–2.58 (m, 1H), 2.58–2.43 (m, 4H), 1.24 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 151.6, 135.6 (d, $J_{C\text{-}F}$ = 20.1 Hz), 125.4, 125.3 (d, $J_{C\text{-}F}$ = 6.5 Hz), 92.5 (d, $J_{C\text{-}F}$ = 172.8 Hz), 66.9, 64.8 (d, $J_{C\text{-}F}$ = 23.1 Hz), 54.0, 34.6, 31.3.
^{19}F NMR (471 MHz, $CDCl_3$) δ -175.11.
FTIR (thin film): cm^{-1} 2960, 2858, 2809, 1453, 1269, 1117, 1009, 870, 835, 71.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{25}FNO^+$ 266.1915; found: 266.1914.



3d

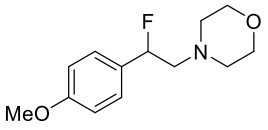
4-(2-Fluoro-2-(4-fluorophenyl)ethyl)morpholine (3d). Synthesized using **GP3** from **1d** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl acetate–hexanes), as a pale oil (29.1 mg, 63%).
$\mathbf{R}_f$ = 0.10 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, J = 8.0, 5.6 Hz, 2H), 7.08–7.03 (m, 2H), 5.62 (ddd, J = 48.5, 8.6, 2.8 Hz, 1H), 3.79–3.66 (m, 4H), 2.89 (ddd, J = 17.3, 14.2, 8.6 Hz, 1H), 2.67–2.54 (m, 5H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7 (dd, $J_{C\text{-}F}$ = 247.0, 2.1 Hz), 134.6 (dd, $J_{C\text{-}F}$ = 20.6, 3.2 Hz), 127.4 (dd, $J_{C\text{-}F}$ = 8.1, 6.9 Hz), 115.4 (d, $J_{C\text{-}F}$ = 21.6 Hz), 92.1 (d, $J_{C\text{-}F}$ = 173.8 Hz), 66.9, 64.8 (d, $J_{C\text{-}F}$ = 23.4 Hz), 54.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ -113.32, -175.06.
FTIR (thin film): cm^{-1} 2957, 2855, 2810, 1605, 1511, 1454, 1222, 1115, 1009, 834, 539.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{16}F_2NO^+$ 228.1195; found: 228.1201.



3e

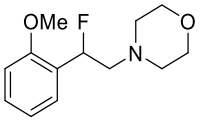
4-(2-(4-Chlorophenyl)-2-fluoroethyl)morpholine (3e). Synthesized using **GP3** from **1e** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl acetate–hexanes), as a pale oil (22.9 mg, 47%).
$\mathbf{R}_f$ = 0.12 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 5.47 (ddd, J = 48.5, 8.5,

2.6 Hz, 1H), 3.56–3.61 (t, J = 4.5 Hz, 4H), 2.72 (ddd, J = 17.6, 14.2, 8.5 Hz, 1H), 2.61–2.31 (m, 5H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 137.2 (d, $J_{C\text{-}F}$ = 20.4 Hz), 134.3, 128.7, 126.9, 92.0 (d, $J_{C\text{-}F}$ = 174.4 Hz), 66.9 , 64.7 (d, $J_{C\text{-}F}$ = 23.3 Hz), 54.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ -177.29.
FTIR (thin film): cm^{-1} 2956, 2854, 2809, 1493, 1453, 1115, 1091, 1010, 880, 824, 719, 537.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{16}ClFNO^+$ 244.0899; found: 244.0906.



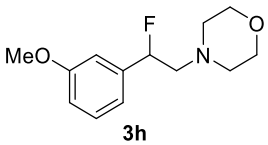
3f

4-(2-Fluoro-2-(4-methoxyphenyl)ethyl)morpholine (3f). Synthesized using **GP3** from **1f** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl acetate–hexanes), as a yellow oil (38.0 mg, 79%).
$\mathbf{R}_f$ = 0.10 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 5.60 (ddd, J = 48.7, 8.8, 2.7 Hz, 1H), 3.81 (s, 3H), 3.72–3.76 (t, J = 4.5 Hz, 4H), 2.92 (ddd, J = 16.7, 14.1, 8.8 Hz, 1H), 2.73–2.46 (m, 5H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 130.8 (d, $J_{C\text{-}F}$ = 20.3 Hz), 127.1 (d, $J_{C\text{-}F}$ = 6.2 Hz), 113.9, 92.4 (d, J = 172.3 Hz), 66.9, 64.7 (d, $J_{C\text{-}F}$ = 24.0 Hz), 55.3, 54.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ -172.14.
FTIR (thin film): cm^{-1} 2956, 2853, 2810, 1613, 1515, 1248, 1116, 1033, 832.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}FNO_2^+$ 240.1394; found: 240.1400.



3g

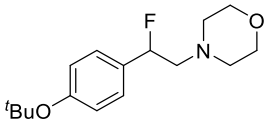
4-(2-Fluoro-2-(2-methoxyphenyl)ethyl)morpholine (3g). Synthesized using **GP3** from **1g** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl acetate–hexanes), as a yellow oil (26.3 mg, 55%).
$\mathbf{R}_f$ = 0.12 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 7.5 Hz, 1H), 7.34–7.27 (m, 1H), 7.02–6.97 (m, 1H), 6.87 (d, J = 8.0 Hz, 1H), 6.04 (ddd, J = 49.1, 8.8, 1.8 Hz, 1H), 3.83 (s, 3H), 3.76 (t, J = 4.6 Hz, 4H), 2.80 (ddd, J = 19.3, 14.2, 8.8 Hz, 1H), 2.72–2.55 (m, 5H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 155.3 (d, $J_{C\text{-}F}$ = 5.6 Hz), 129.2 (d, $J_{C\text{-}F}$ = 1.4 Hz), 127.3, 125.9 (d, $J_{C\text{-}F}$ = 9.6 Hz), 120.6, 110.2, 87.9 (d, $J_{C\text{-}F}$ = 171.9 Hz), 67.0 (2C), 63.8 (d, $J_{C\text{-}F}$ = 22.5 Hz), 55.3, 54.0.
^{19}F NMR (471 MHz, $CDCl_3$) δ -185.00.
FTIR (thin film): cm^{-1} 2955, 2853, 1601, 1586, 1490, 1454, 1288, 1267, 1116, 1034, 869, 783, 698.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}FNO_2^+$ 240.1394; found: 240.1400.



3h

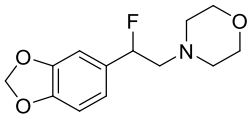
4-(2-Fluoro-2-(3-methoxyphenyl)ethyl)morpholine (3h). Synthesized using **GP3** from **1h** and *O*-

benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl acetate–hexanes), as a pale oil (28.6 mg, 60%).
$\mathbf{R}_f$ = 0.10 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.26 (m, 1H), 6.92–6.84 (m, 3H), 5.63 (ddd, J = 49.0, 8.8, 2.5 Hz, 1H), 3.82 (s, 3H), 3.77–3.73 (m, 4H), 2.90 (ddd, J = 17.6, 14.3, 8.8 Hz, 1H), 2.72–2.53 (m, 5H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 140.3 (d, $J_{C\text{-}F}$ = 20.0 Hz), 129.6, 117.7, 113.9 (d, $J_{C\text{-}F}$ = 1.4 Hz), 111.1 (d, $J_{C\text{-}F}$ = 7.5 Hz), 92.5 (d, $J_{C\text{-}F}$ = 174.4 Hz), 66.9, 64.9 (d, $J_{C\text{-}F}$ = 22.9 Hz), 55.2, 54.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ -177.08.
FTIR (thin film): cm^{-1} 2956, 2853, 2807, 1603, 1493, 1241, 1116, 1031, 754.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}FNO_2^+$ 240.1394; found: 240.1401.



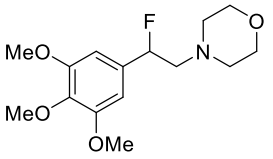
3i

4-(2-(4-(*tert*-Butoxy)phenyl)-2-fluoroethyl)morpholine (3i). Synthesized using **GP3** from **1i** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl acetate–hexanes), as a yellow oil (40.0 mg, 71%).
$\mathbf{R}_f$ = 0.13 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 5.61 (ddd, J = 48.8, 8.9, 2.5 Hz, 1H), 3.77–3.70 (m, 4H), 2.92 (ddd, J = 17.0, 14.2, 8.9 Hz, 1H), 2.70–2.53 (m, 5H), 1.35 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7 (d, $J_{C\text{-}F}$ = 2.1 Hz), 133.4 (d, $J_{C\text{-}F}$ = 20.2 Hz), 126.4 (d, $J_{C\text{-}F}$ = 6.4 Hz, 2C), 124.0, 92.5 (d, $J_{C\text{-}F}$ = 172.6 Hz), 78.7, 67.0, 64.8 (d, $J_{C\text{-}F}$ = 23.5 Hz), 54.1, 28.8.
^{19}F NMR (471 MHz, $CDCl_3$) δ -173.54.
FTIR (thin film): cm^{-1} 2974, 2854, 2808, 1719, 1508, 1365, 1236, 1160, 1116, 895, 853, 549.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{25}FNO_2^+$ 282.1864; found: 282.1869.



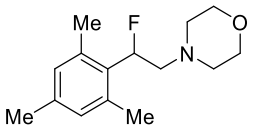
3j

4-(2-(Benzo[*d*][1,3]dioxol-5-yl)-2-fluoroethyl)morpholine (3j). Synthesized using **GP3** from **1j** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (20% ethyl acetate–hexanes to 50% ethyl acetate–hexanes), as a pale-yellow oil (35.8 mg, 71%).
$\mathbf{R}_f$ = 0.14 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.78 (s, 1H), 6.73 (d, J = 0.7 Hz, 2H), 5.90 (s, 2H), 5.48 (ddd, J = 48.5, 8.7, 2.6 Hz, 1H), 3.72–3.56 (m, 4H), 2.89–2.72 (m, 1H), 2.61–2.58 (m, 1H), 2.58–2.42 (m, 4H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 132.6 (d, $J_{C\text{-}F}$ = 20.4 Hz), 119.5 (d, $J_{C\text{-}F}$ = 7.3 Hz), 108.2, 106.3 (d, $J_{C\text{-}F}$ = 6.5 Hz), 101.2, 92.5 (d, $J_{C\text{-}F}$ = 173.7 Hz), 66.9, 64.8 (d, $J_{C\text{-}F}$ = 24.0 Hz), 54.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ -171.98.
FTIR (thin film): cm^{-1} 2894, 2855, 2812, 1717, 1490, 1444, 1247, 1115, 1036, 931, 870, 716.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}FNO_3^+$ 254.1187; found: 254.1189.



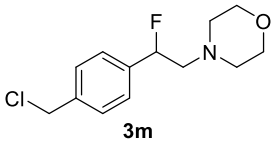
3k

4-(2-Fluoro-2-(3,4,5-trimethoxyphenyl)ethyl)morpholine (3k). Synthesized using **GP3** from **1k** and *O*-benzoylhydroxylmorpholine **2a**. IPrCuCl (5 mol %) was used instead of the $Cu(HFacac)_2$. Isolated by flash column chromatography (25% ethyl acetate–hexanes to 50% ethyl acetate–hexanes), as a pale-yellow oil (27.0 mg, 45%).
$\mathbf{R}_f$ = 0.20 (50% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.56 (s, 2H), 5.59 (ddd, J = 48.7, 8.6, 2.2 Hz, 1H), 3.87 (s, 6H), 3.84 (s, 3H), 3.78–3.72 (m, 4H), 2.98–2.81 (m, 1H), 2.73–2.65 (m, 1H), 2.65–2.50 (m, 4H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 153.4, 138.0, 134.4 (d, $J_{C\text{-}F}$ = 20.4 Hz), 102.6 (d, $J_{C\text{-}F}$ = 7.2 Hz), 92.9 (d, $J_{C\text{-}F}$ = 174.5 Hz), 66.9, 64.9 (d, $J_{C\text{-}F}$ = 23.2 Hz), 60.9, 56.2, 54.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ -174.42.
FTIR (thin film): cm^{-1} 2939, 2841, 1591, 1454, 1236, 1117, 1007, 870, 705.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{23}FNO_4^+$ 300.1606; found: 300.1600.



3l

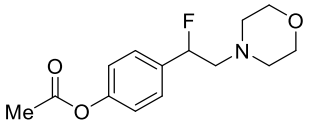
4-(2-Fluoro-2-mesitylethyl)morpholine (3l). Synthesized using **GP3** from **1l** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 20% ethyl acetate–hexanes), as a pale oil (25.6 mg, 51%).
$\mathbf{R}_f$ = 0.14 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (s, 2H), 6.03 (ddd, J = 48.4, 9.3, 2.7 Hz, 1H), 3.78–3.74 (m, 4H), 3.15 (td, J = 14.4, 9.3 Hz, 1H), 2.67–2.57 (m, 4H), 2.50 (ddd, J = 33.1, 14.4, 2.7 Hz, 1H), 2.38–2.34 (m, 6H), 2.26 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7, 135.7 (d, $J_{C\text{-}F}$ = 3.6 Hz), 131.4 (d, $J_{C\text{-}F}$ = 17.8 Hz), 129.9, 90.7 (d, $J_{C\text{-}F}$ = 172.9 Hz), 66.9, 62.2 (d, $J_{C\text{-}F}$ = 22.7 Hz), 54.1, 20.8, 20.4, 20.4.
^{19}F NMR (471 MHz, $CDCl_3$) δ -181.57.
FTIR (thin film): cm^{-1} 2959, 2854, 2809, 1678, 1612, 1452, 1142, 1116, 1050, 1007, 871, 852, 731, 572.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{23}FNO^+$ 252.1758; found: 252.1765.



3m

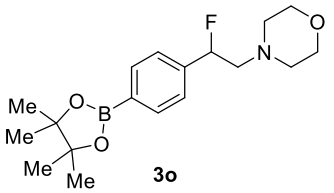
4-(2-(4-(Chloromethyl)phenyl)-2-fluoroethyl)morpholine (3m). Synthesized using **GP3** from **1m** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl actate–hexanes), as a yellow oil (26.8 mg, 52%).
$\mathbf{R}_f$ = 0.16 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 5.67 (ddd, J = 48.7, 8.7, 2.6 Hz, 1H), 4.58 (s, 2H), 3.76–3.74 (m, 4H), 2.89 (ddd, J = 17.4, 14.2, 8.7 Hz, 1H), 2.76–2.54 (m, 5H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9 (d, $J_{C\text{-}F}$ = 20.1 Hz), 137.7, 128.7, 125.9 (d, $J_{C\text{-}F}$ = 7.0 Hz), 92.2 (d,

$J_{C\text{-}F}$ = 174.3 Hz), 66.8, 64.8 (d, $J_{C\text{-}F}$ = 23.0 Hz), 54.0, 45.7.
^{19}F NMR (471 MHz, $CDCl_3$) δ -177.64.
FTIR (thin film): cm^{-1} 2984, 2843, 2801, 1493, 1350, 1123, 1056, 968, 867, 813, 727.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{18}ClFNO^+$ 258.1056; found: 258.1061.



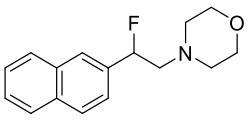
3n

4-(1-Fluoro-2-morpholinoethyl)phenyl acetate (3n). Synthesized using **GP3** from **1n** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (30% ethyl acetate–hexanes to 50% ethyl acetate–hexanes), as a pale oil (27.0 mg, 50%).
$\mathbf{R}_f$ = 0.11 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 5.65 (ddd, *J* = 48.6, 8.7, 2.3 Hz, 1H), 3.76–3.74 (m, 4H), 2.89 (ddd, *J* = 17.4, 14.2, 8.7 Hz, 1H), 2.72–2.53 (m, 5H), 2.30 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 150.6, 136.3 (d, $J_{C\text{-}F}$ = 20.4 Hz), 126.7, 121.7, 92.2 (d, $J_{C\text{-}F}$ = 174.2 Hz), 66.9, 64.8 (d, $J_{C\text{-}F}$ = 23.1 Hz), 54.1, 21.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ -176.30.
FTIR (thin film): cm^{-1} 2929, 2854, 1755, 1509, 1369, 1191, 1116, 1009, 911, 882, 869.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}FNO_3^+$ 268.1344; found: 268.1350.



3o

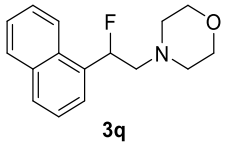
4-(2-Fluoro-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethyl)morpholine (3o). Synthesized using **GP3** from **1o** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl acetate–hexanes), as a pale-yellow oil (40.2 mg, 60%).
$\mathbf{R}_f$ = 0.20 (33% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 5.67 (ddd, *J* = 48.9, 8.6, 2.2 Hz, 1H), 3.82–3.61 (m, 4H), 3.00–2.83 (m, 1H), 2.72–2.64 (m, 1H), 2.64–2.45 (m, 4H), 1.34 (s, 12H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7 (d, $J_{C\text{-}F}$ = 20.1 Hz), 134.9, 128.3 (d, $J_{C\text{-}F}$ = 11.6 Hz), 124.7 (d, $J_{C\text{-}F}$ = 7.1 Hz), 92.5 (d, $J_{C\text{-}F}$ = 174.5 Hz), 83.9, 66.9, 64.8 (d, $J_{C\text{-}F}$ = 22.9 Hz), 54.0, 24.8.
^{19}F NMR (471 MHz, $CDCl_3$) δ -178.83.
FTIR (thin film): cm^{-1} 2976, 2854, 2808, 1614, 1357, 1142, 1009, 857, 658.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{28}[^{11}B]FNO_3^+$ 336.2141; found: 336.2140.



3p

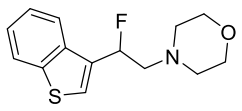
4-(2-Fluoro-2-(naphthalen-2-yl)ethyl)morpholine (3p). Synthesized using **GP3** from **1p** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to

30% ethyl acetate–hexanes), as a pale-yellow oil (32.2 mg, 62%).
$\mathbf{R}_f$ = 0.30 (50% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, J = 9.3, 5.1 Hz, 3H), 7.82 (s, 1H), 7.56–7.47 (m, 2H), 7.45 (d, J = 8.6 Hz, 1H), 5.83 (ddd, J = 48.8, 8.6, 2.4 Hz, 1H), 3.84–3.66 (m, 4H), 3.14–2.88 (m, 1H), 2.81–2.67 (m, 1H), 2.67–2.55 (m, 4H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 136.1 (d, $J_{C\text{-}F}$ = 19.6 Hz), 133.3, 133.1, 128.4, 128.1, 127.8, 126.5, 126.4, 124.8 (d, $J_{C\text{-}F}$ = 8.1 Hz), 123.2 (d, $J_{C\text{-}F}$ = 5.7 Hz), 92.8 (d, $J_{C\text{-}F}$ = 173.9 Hz), 66.9, 64.9 (d, $J_{C\text{-}F}$ = 23.1 Hz), 54.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ -176.57.
FTIR (thin film): cm^{-1} 2937, 2865, 2816, 1717, 1274, 1110, 1011, 872, 824, 741.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}FNO^+$ 260.1445; found: 260.1439.



3q

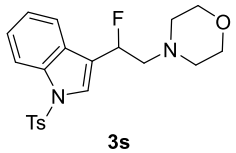
4-(2-Fluoro-2-(naphthalen-1-yl)ethyl)morpholine (3q). Synthesized using **GP3** from **1q** and *O*-benzoylhydroxylmorpholine **2a**. IPrCuCl (5 mol %) was used instead of the $Cu(HFacac)_2$. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 40% ethyl acetate–hexanes), as a pale oil (34.4 mg, 66%).
$\mathbf{R}_f$ = 0.30 (50% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 8.2 Hz, 1H), 7.89 (dd, J = 8.0, 1.6 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.59–7.47 (m, 3H), 6.42 (ddd, J = 48.4, 8.7, 2.1 Hz, 1H), 3.82–3.78 (t, J = 4.5 Hz, 4H), 3.02 (ddd, J = 19.0, 14.6, 8.7 Hz, 1H), 2.86 (ddd, J = 36.0, 14.6, 2.1 Hz, 1H), 2.78–2.58 (m, 4H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 134.4 (d, $J_{C\text{-}F}$ = 18.7 Hz), 133.6, 129.6 (d, $J_{C\text{-}F}$ = 4.1 Hz), 129.0, 128.8 (d, $J_{C\text{-}F}$ = 1.3 Hz), 126.5, 125.8, 125.3, 123.2 (d, $J_{C\text{-}F}$ = 11.2 Hz), 122.6, 91.0 (d, $J_{C\text{-}F}$ = 174.2 Hz), 67.0, 64.6 (d, J = 22.7 Hz), 54.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ -180.07.
FTIR (thin film): cm^{-1} 3050, 2955, 2853, 2809, 1675, 1452, 1137, 1009, 798, 775.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}FNO^+$ 260.1445; found: 260.1449.



3r

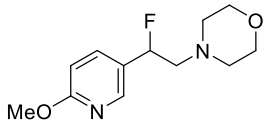
4-(2-(Benzo[*b*]thiophen-3-yl)-2-fluoroethyl)morpholine (3r). Synthesized using **GP3** from **1r** and *O*-benzoylhydroxylmorpholine **2a**. IPrCuCl (5 mol %) was used instead of the $Cu(HFacac)_2$. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl acetate–hexanes), as a pale-yellow oil (23.9 mg, 45%).
$\mathbf{R}_f$ = 0.25 (50% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 7.4 Hz, 1H), 7.83 (d, J = 7.4 Hz, 1H), 7.50 (s, 1H), 7.45–7.33 (m, 2H), 6.04 (ddd, J = 48.1, 8.2, 1.7 Hz, 1H), 3.86–3.70 (m, 4H), 3.20–3.00 (m, 1H), 2.98–2.80 (m, 1H), 2.72–2.56 (m, 4H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 140.6, 136.7, 133.6 (d, $J_{C\text{-}F}$ = 21.2 Hz), 124.7, 124.4, 123.9 (d, $J_{C\text{-}F}$ = 8.5 Hz), 123.0, 121.9, 89.0 (d, $J_{C\text{-}F}$ = 172.3 Hz), 66.9, 63.2 (d, $J_{C\text{-}F}$ = 22.9 Hz), 54.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -175.77.
FTIR (thin film): cm^{-1} 2923, 2854, 1597, 1447, 1371, 1175, 1118, 977, 748, 576.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}FNOS^+$ 266.1009; found: 266.1010.



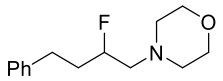
3s

4-(2-Fluoro-2-(1-tosyl-1*H*-indol-3-yl)ethyl)morpholine (3s). Synthesized using **GP3** from **1s** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (20% ethyl acetate–hexanes to 40% ethyl acetate–hexanes), as a pale-yellow oil (26.2 mg, 33%).
$\mathbf{R}_f$ = 0.20 (50% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 2.4 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.27–7.21 (m, 3H), 5.91 (dd, *J* = 48.4, 6.6 Hz, 1H), 5.91 (dd, *J* = 48.4, 6.6 Hz, 1H), 3.75 (t, *J* = 4.5 Hz, 5H), 3.09 (ddd, *J* = 17.9, 14.2, 8.2 Hz, 1H), 2.86 (dd, *J* = 30.2, 14.2 Hz, 1H), 2.74–2.49 (m, 4H), 2.35 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3, 135.2, 135.1, 130.0, 128.4, 128.3, 126.9, 125.2, 123.7 (d, $J_{C\text{-}F}$ = 9.2 Hz), 123.5, 120.1, 113.8, 87.2 (d, $J_{C\text{-}F}$ = 169.6 Hz), 66.9, 62.8 (d, $J_{C\text{-}F}$ = 22.9 Hz), 54.1, 21.6.
^{19}F NMR (471 MHz, $CDCl_3$) δ -175.43 .
FTIR (thin film): cm^{-1} 2924, 2853, 2811, 1673, 1138, 1428, 1115, 1008, 866, 760, 733.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{24}FN_2O_3S^+$ 403.1486; found: 403.1489.



3t

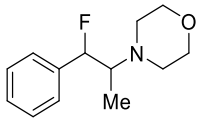
4-(2-Fluoro-2-(6-methoxypyridin-3-yl)ethyl)morpholine (3t). Synthesized using **GP3** from **1t** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl acetate–hexanes), as a pale-yellow oil (31.7 mg, 66%).
$\mathbf{R}_f$ = 0.14 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.59 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.76 (d, *J* = 8.6 Hz, 1H), 5.61 (ddd, *J* = 48.0, 8.3, 3.0 Hz, 1H), 3.94 (s, 3H), 3.73 (t, *J* = 4.7 Hz, 4H), 2.93 (ddd, *J* = 17.1, 14.1, 8.3 Hz, 1H), 2.74–2.46 (m, 1H), 2.74–2.46 (m, 4H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5 (d, $J_{C\text{-}F}$ = 1.4 Hz), 144.9 (d, $J_{C\text{-}F}$ = 7.3 Hz), 136.4 (d, $J_{C\text{-}F}$ = 5.0 Hz), 127.0 (d, $J_{C\text{-}F}$ = 20.8 Hz), 111.0, 90.6 (d, $J_{C\text{-}F}$ = 172.7 Hz), 66.9, 64.1 (d, $J_{C\text{-}F}$ = 24.0 Hz), 54.1, 53.6.
^{19}F NMR (471 MHz, $CDCl_3$) δ -174.28.
FTIR (thin film): cm^{-1} 2948, 2853, 1609, 1495, 1392, 1286, 1116, 1022, 869, 832.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{18}FN_2O_2^+$ 241.1347; found: 241.1342.



3u

4-(2-Fluoro-4-phenylbutyl)morpholine (3u). Synthesized using **GP3** from **1u** and *O*-benzoylhydroxylmorpholine **2a**. IPrCuCl (5 mol %) was used instead of the $Cu(HFacac)_2$. Isolated by flash column chromatography (20% ethyl acetate–hexanes to 50% ethyl acetate–hexanes), as a pale oil (5.5 mg, 12%).
$\mathbf{R}_f$ = 0.10 (50% ethyl acetate–hexanes).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.27 (m, 2H), 7.23–7.18 (m, 3H), 4.81–4.52 (m, 1H), 3.75–3.58 (m, 4H), 2.88–2.78 (m, 1H), 2.75–2.68 (m, 1H), 2.68–2.58 (m, 1H), 2.55–2.41 (m, 5H), 2.07–1.95 (m, 1H), 1.95–1.78 (m, 1H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 141.2, 128.5, 128.8, 126.1, 91.5 (d, $J_{C\text{-}F}$ = 170.0 Hz), 66.9, 62.8 (d, $J_{C\text{-}F}$ = 20.5 Hz), 54.3, 35.2 (d, $J_{C\text{-}F}$ = 20.8 Hz), 31.2 (d, $J_{C\text{-}F}$ = 4.6 Hz).
^{19}F NMR (471 MHz, $CDCl_3$) δ -182.13.
FTIR (thin film): cm^{-1} 2952, 2853, 1717, 1453, 1273, 1116, 1035, 867, 699.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{21}FNO^+$ 238.1602; found: 238.1600.



3v

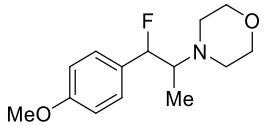
4-(1-Fluoro-1-phenylpropan-2-yl)morpholine (3v). Synthesized using **GP3** from (*E*)-**1v** and *O*-benzoylhydroxylmorpholine **2a**. ^{1}H-NMR analysis of the crude reaction mixture indicated a diastereomeric ratio (dr) of 2.5:1. Isolated as a mixture of two diastereomers by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl acetate–hexanes), as a pale-yellow oil (32.2 mg, 60%).
Synthesized using **GP3** from (*Z*)-**1v** and *O*-benzoylhydroxylmorpholine **2a**. ^{1}H-NMR analysis of the crude reaction mixture indicated a diastereomeric ratio (dr) of 1.8:1. Isolated as a mixture of two diastereomers by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl acetate–hexanes), as a pale-yellow oil (25.0 mg, 56%).
$\mathbf{R}_f$ = 0.20 (33% ethyl acetate–hexanes).

Major isomer (3v-I): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.29 (m, 5H), 5.36 (dd, *J* = 47.9, 8.3 Hz, 1H), 3.72 (t, *J* = 4.0 Hz, 4H), 3.13–2.92 (m, 1H), 2.80–2.58 (m, 4H), 0.84 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5 (d, *J* = 20.1 Hz), 128.5 (d, *J* = 2.0 Hz), 128.3, 126.7 (d, *J* = 6.4 Hz), 95.8 (d, *J* = 176.5 Hz), 67.6, 63.5 (d, *J* = 21.8 Hz), 49.6, 11.2 (d, *J* = 6.2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -175.16.
FTIR (thin film): cm^{-1} 2955, 2851, 1720, 1451, 1267, 1114, 999, 751, 699.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}FNO^+$ 224.1445; found: 224.1447.
The relative stereochemistry of major isomer **3v-I** has been determined by X-ray analysis. More information of the X-ray analysis is provided on S283.

Minor isomer (3v-II): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39–7.34 (m, 2H), 7.30 (3, *J* = 6.6 Hz, 3H), 5.72 (dd, *J* = 48.1, 2.2 Hz, 1H), 3.71 (t, *J* = 4.5 Hz, 4H), 2.83 (dqd, *J* = 13.4, 6.8, 2.2 Hz, 1H), 2.73–2.57 (m, 4H), 1.04 (dd, *J* = 6.8, 1.1 Hz, 3H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 139.5 (d, *J* = 20.7 Hz), 128.2, 127.7, 125.1 (d, *J* = 8.5 Hz), 94.7 (d, *J* = 178.7 Hz), 67.5, 64.9 (d, *J* = 22.0 Hz), 49.9, 7.6 (d, *J* = 6.7 Hz).
^{19}F NMR (471 MHz, $CDCl_3$) δ -193.68.
FTIR (thin film): cm^{-1} 2924, 2853, 1669, 1450, 1254, 1199, 1117, 955, 984, 720, 699.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}FNO^+$ 224.1445; found: 224.1448.



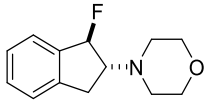
3w

4-(1-Fluoro-1-(4-methoxyphenyl)propan-2-yl)morpholine (3w). Synthesized using **GP3** from **1w** and *O*-benzoylhydroxylmorpholine **2a**. ^{1}H-NMR analysis of the crude reaction mixture indicated a diastereomeric ratio (dr) of 1.8:1. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 15% ethyl acetate–hexanes), as a pale-yellow oil (26.8 mg, 53%).

Minor isomer (3w-I): $\mathbf{R}_f$ = 0.40 (33% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 5.30 (dd, J = 47.3, 8.1 Hz, 1H), 3.82 (s, 3H), 3.73 (t, J = 4.4 Hz, 3H), 3.09–2.98 (m, 1H), 2.78–2.64 (m, 4H), 0.82 (d, J = 6.9 Hz, 3H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 159.8 (d, $J_{C\text{-}F}$ = 1.8 Hz), 130.6 (d, $J_{C\text{-}F}$ = 20.7 Hz), 128.1 (d, $J_{C\text{-}F}$ = 5.7 Hz), 113.8, 95.4 (d, $J_{C\text{-}F}$ = 175.9 Hz), 67.5, 63.5 (d, $J_{C\text{-}F}$ = 22.1 Hz), 55.3, 49.6, 11.3 (d, $J_{C\text{-}F}$ = 5.8 Hz).
^{19}F NMR (471 MHz, $CDCl_3$) δ -170.96.
FTIR (thin film): cm^{-1} 2933, 2851, 1613, 1514, 1249, 1115, 1033, 996, 831.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{21}FNO_2^+$ 254.1551; found: 254.1545.

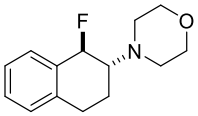
Major isomer (3w-II): $\mathbf{R}_f$ = 0.35 (33% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.5 Hz, 2H), 5.64 (d, J = 47.3 Hz, 1H), 3.81 (s, 3H), 3.70 (t, J = 4.5 Hz, 4H), 2.88–2.74 (m, 1H), 2.74–2.54 (m, 4H), 1.06 (d, J = 6.6 Hz, 3H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 159.2, 126.6 (d, $J_{C\text{-}F}$ = 8.2 Hz), 113.6, 94.8 (d, $J_{C\text{-}F}$ = 177.1 Hz), 67.4, 64.8 (d, $J_{C\text{-}F}$ = 22.9 Hz), 55.3, 49.9, 7.8.
^{19}F NMR (471 MHz, $CDCl_3$) δ -189.81.
FTIR (thin film): cm^{-1} 2924, 2852, 1613, 1514, 1453, 1247, 1115, 1033, 981, 828.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{21}FNO_2^+$ 254.1551; found: 254.1548.

The assignments of relative stereochemistry of two diastereomers **3w-I** and **3w-II** are based on the ^{1}H, ^{13}C, and ^{19}F-NMR analysis in comparison to **3v-I** and **3v-II**.



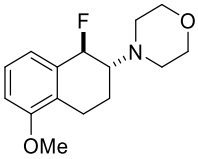
3x

4-(1-Fluoro-2,3-dihydro-1*H*-inden-2-yl)morpholine (3x). Synthesized using **GP3** from **1x** and *O*-benzoylhydroxylmorpholine **2a**. ^{1}H-NMR analysis of the crude reaction mixture indicated a diastereomeric ratio (dr) of 10:1. Isolated as a mixture of two diastereomers by flash column chromatography (10% ethyl acetate–hexanes to 20% ethyl acetate–hexanes), as a pale-yellow oil (26.5 mg, 60%).
$\mathbf{R}_f$ = 0.20 (33% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 7.1 Hz, 1H), 7.34–7.25 (m, 2H), 7.22 (d, J = 7.2 Hz, 1H), 6.00 (dd, J = 57.7, 5.5 Hz, 1H), 3.79 (t, J = 4.7 Hz, 4H), 3.35–3.09 (m, 2H), 2.90–2.76 (m, 1H), 2.72 (s, 2H), 2.65–2.56 (m, 2H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 139.5 (d, $J_{C\text{-}F}$ = 5.3 Hz), 139.0 (d, $J_{C\text{-}F}$ = 20.5 Hz), 129.4 (d, $J_{C\text{-}F}$ = 2.3 Hz), 127.3 (d, $J_{C\text{-}F}$ = 1.8 Hz), 124.8, 124.6, 99.0 (d, $J_{C\text{-}F}$ = 179.9 Hz), 73.3 (d, $J_{C\text{-}F}$ = 17.4 Hz), 66.9, 52.4, 34.2 (d, $J_{C\text{-}F}$ = 5.6 Hz).
^{19}F NMR (471 MHz, $CDCl_3$) δ -170.49 (major), -180.50 (minor).
FTIR (thin film): cm^{-1} 2949, 2850, 1483, 1356, 1146, 1115, 1001, 896, 751, 664.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}FNO^+$ 222.1289; found: 222.1295.



3y

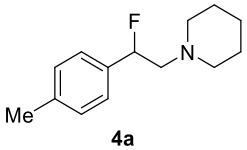
4-(1-Fluoro-1,2,3,4-tetrahydronaphthalen-2-yl)morpholine (3y). Synthesized using **GP3** from **1y** and morpholino dodecanoate **2t**. Only one diastereomer (dr >20:1) was observed by ^{1}H-NMR analysis of the crude reaction mixture. Isolated by flash column chromatography (5% ethyl acetate–hexanes to 15% ethyl acetate–hexanes), as a pale-yellow oil (24.5 mg, 52%).
$\mathbf{R_f}$ = 0.30 (20% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 4.0 Hz, 1H), 7.25 (dd, *J* = 5.7, 3.5 Hz, 2H), 7.12 (d, *J* = 4.0 Hz, 1H), 5.71 (dd, *J* = 52.7, 7.9 Hz, 1H), 3.76 (t, *J* = 4.3 Hz, 4H), 3.04–2.92 (m, 1H), 2.90–2.84 (m, 2H), 2.83–2.71 (m, 4H), 2.12 (ddt, *J* = 12.2, 8.0, 4.2 Hz, 1H), 1.76 (ddd, *J* = 24.5, 12.2, 8.0 Hz, 1H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 137.0 (d, $J_{C\text{-}F}$ = 3.6 Hz), 134.4 (d, $J_{C\text{-}F}$ = 17.7 Hz), 128.4, 128.4 (d, $J_{C\text{-}F}$ = 5.7 Hz), 128.2, 126.5, 89.8 (d, $J_{C\text{-}F}$ = 173.4 Hz), 67.3, 65.1 (d, $J_{C\text{-}F}$ = 17.4 Hz), 50.1, 28.5, 23.4 (d, $J_{C\text{-}F}$ = 6.7 Hz).
^{19}F NMR (471 MHz, $CDCl_3$) δ -167.52.
FTIR (thin film): cm^{-1} 2923, 2852, 1734, 1454, 1251, 1117, 1012, 746.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}FNO^+$ 236.1445; found: 236.1442.



3z

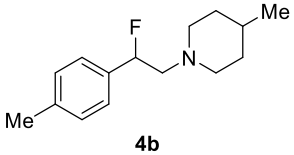
4-(1-Fluoro-5-methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)morpholine (3z). Synthesized using **GP3** from **1z** and *O*-benzoylhydroxylmorpholine **2a**. Only one diastereomer (dr >20:1) was observed by ^{1}H-NMR analysis of the crude reaction mixture. Isolated by flash column chromatography (5% ethyl acetate–hexanes to 12% ethyl acetate–hexanes), as a pale-yellow oil (28.6 mg, 54%).
$\mathbf{R_f}$ = 0.20 (20% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 5.68 (dd, *J* = 52.5, 8.0 Hz, 1H), 3.82 (s, 3H), 3.75 (t, *J* = 4.6 Hz, 4H), 2.97–2.83 (m, 2H), 2.81–2.68 (m, 4H), 2.64–2.51 (m, 1H), 2.18–2.05 (m, 1H), 1.77–1.63 (m, 1H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 156.5, 136.0 (d, $J_{C\text{-}F}$ = 18.3 Hz), 127.0, 126.0 (d, $J_{C\text{-}F}$ = 3.7 Hz), 120.0 (d, $J_{C\text{-}F}$ = 8.0 Hz), 109.3, 89.7 (d, $J_{C\text{-}F}$ = 173.8 Hz), 67.5, 64.3 (d, $J_{C\text{-}F}$ = 17.1 Hz), 55.4, 50.1, 22.6 (d, $J_{C\text{-}F}$ = 1.4 Hz), 22.5 (d, $J_{C\text{-}F}$ =2.3 Hz).
^{19}F NMR (471 MHz, $CDCl_3$) δ -168.61.
FTIR (thin film): cm^{-1} 2951, 2855, 1587, 1473, 1263, 1111, 1069, 941, 790, 746.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{21}FNO_2^+$ 266.1551; found: 266.1550.

5. Scope of amines and compound characterization data



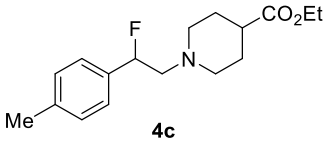
4a

1-(2-Fluoro-2-(*p*-tolyl)ethyl)piperidine (4a). Synthesized using **GP3** from **1a** and *O*-benzoylhydroxylpiperidine **2b**. Isolated by flash column chromatography (5% ethyl acetate–hexanes to 10% ethyl acetate–hexanes), as a pale oil (21.0 mg, 47%).
$\mathbf{R}_f$ = 0.30 (20% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 5.64 (ddd, J = 49.0, 8.9, 2.0 Hz, 1H), 3.01–2.79 (m, 1H), 2.70–2.56 (m, 1H), 2.56–2.45 (m, 4H), 2.35 (s, 3H), 1.70–1.52 (m, 4H), 1.51–1.37 (m, 2H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 138.1 (d, $J_{C\text{-}F}$ = 1.6 Hz), 136.3 (d, $J_{C\text{-}F}$ = 20.2 Hz), 129.1, 125.6 (d, $J_{C\text{-}F}$ = 6.6 Hz), 92.6 (d, $J_{C\text{-}F}$ = 172.8 Hz), 65.5 (d, $J_{C\text{-}F}$ = 23.4 Hz), 55.0, 26.0, 24.2, 21.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -174.77.
FTIR (thin film): cm^{-1} 2932, 2853, 1516, 1452, 1300, 1121, 1017, 880, 814, 759.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{21}FN^+$ 222.1653; found: 222.1657.



4b

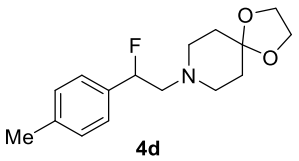
1-(2-Fluoro-2-(*p*-tolyl)ethyl)-4-methylpiperidine (4b). Synthesized using **GP3** from **1a** and *O*-benzoyl-4-methyl-hydroxylpiperidine **2c**. Isolated by flash column chromatography (5% ethyl acetate–hexanes to 10% ethyl acetate–hexanes), as a pale oil (15.3 mg, 32%).
$\mathbf{R}_f$ = 0.20 (10% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 5.63 (ddd, J = 49.0, 8.9, 2.2 Hz, 1H), 3.08–3.01 (m, 1H), 3.00–2.95 (m, 1H), 2.90 (ddd, J = 17.3, 14.3, 9.0 Hz, 1H), 2.59 (ddd, J = 35.3, 14.3, 2.4 Hz, 1H), 2.35 (s, 3H), 2.19–2.06 (m, 2H), 1.72–1.58 (m, 2H), 1.45–1.23 (m, 3H), 0.93 (d, J = 6.1 Hz, 3H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 138.1 (d, $J_{C\text{-}F}$ = 1.4 Hz), 136.3 (d, $J_{C\text{-}F}$ = 20.0 Hz), 129.1, 125.6 (d, $J_{C\text{-}F}$ = 6.6 Hz), 92.7 (d, $J_{C\text{-}F}$ = 172.8 Hz), 65.1 (d, $J_{C\text{-}F}$ = 23.3 Hz), 54.6, 54.3, 34.3, 30.6, 21.9, 21.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -174.83.
FTIR (thin film): cm^{-1} 2947, 2922, 2869, 1721, 1454, 1269, 1125, 1041, 978, 811.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{23}FN^+$ 236.1809; found: 236.1807.



4c

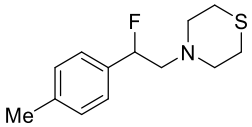
Ethyl 1-(2-fluoro-2-(*p*-tolyl)ethyl)piperidine-4-carboxylate (4c). Synthesized using **GP3** from **1a** and *O*-benzoyl-4-ethyloxycarbonylhydroxylpiperidine **2d**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl acetate–hexanes), as a pale oil (35.2 mg, 60%).
$\mathbf{R}_f$ = 0.27 (50% ethyl aceteate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 5.61 (ddd, J = 48.8, 8.7, 2.5 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.03 (d, J = 11.4 Hz, 1H), 2.95 (d, J = 11.4 Hz, 1H), 2.90 (ddd, J = 17.2, 14.3, 8.7 Hz, 1H), 2.61 (ddd, J = 34.0, 14.3, 2.5 Hz, 1H), 2.35 (s, 3H), 2.29–2.17 (m, 3H), 1.95–1.88 (m, 2H), 1.87–1.75 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 175.1, 138.2 (d, $J_{C\text{-}F}$ = 1.9 Hz), 136.0 (d, $J_{C\text{-}F}$ = 20.1 Hz), 129.1, 125.5 (d, $J_{C\text{-}F}$ = 6.7 Hz), 92.7 (d, $J_{C\text{-}F}$ = 172.9 Hz), 64.7 (d, $J_{C\text{-}F}$ = 23.6 Hz), 60.3, 53.4, 53.4, 40.9, 28.3, 21.2, 14.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -174.99.
FTIR (thin film): cm^{-1} 2944, 2803, 1729, 1515, 1448, 1284, 1181, 1047, 816, 527.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{25}FNO_2^+$ 294.1864; found: 294.1869.



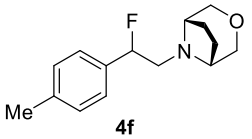
4d

8-(2-Fluoro-2-(*p*-tolyl)ethyl)-1,4-dioxa-8-azaspiro[4.5]decane (4d). Synthesized using **GP3** from **1a** and 1,4-dioxa-8-azaspiro[4.5]decan-8-yl benzoate **2e**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 33% ethyl acetate–hexanes), as a colorless oil (27.7 mg, 50%).
$\mathbf{R}_f$ = 0.20 (33% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.23 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 5.61 (ddd, J = 49.6, 8.9, 2.3 Hz, 1H), 3.96 (s, 4H), 2.95 (ddd, J = 17.2, 14.3, 8.9 Hz, 1H), 2.70 (br s, 4H), 2.66–2.57 (m, 1H), 2.35 (s, 3H), 1.84–1.75 (m, 4H).
^{13}C NMR ($CDCl_3$, 125 MHZ): δ 138.2 (d, $J_{C\text{-}F}$ = 1.6 Hz), 136.0 (d, $J_{C\text{-}F}$ = 19.9 Hz), 129.1, 125.5 (d, $J_{C\text{-}F}$ = 6.5 Hz,), 107.0, 92.7 (d, $J_{C\text{-}F}$ = 172.9 Hz), 64.2, 64.2 (d, $J_{C\text{-}F}$ = 23.6 Hz), 51.8, 34.8, 21.2.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -175.35
FTIR (thin film): cm^{-1} 1143, 1094, 1039, 964, 946, 915, 818.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{23}FNO_2^+$ 280.1707; found: 280.1714.



4e

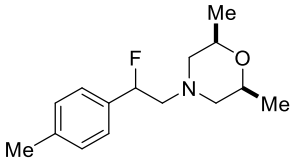
4-(2-Fluoro-2-(*p*-tolyl)ethyl)thiomorpholine (4e). Synthesized using **GP3** from **1a** and *O*-benzoylhydroxylthiomorpholine **2f**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 15% ethyl acetate–hexanes), as a pale oil (33.1 mg, 69%).
$\mathbf{R}_f$ = 0.10 (10% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 5.60 (ddd, J = 48.7, 8.5, 2.3 Hz, 1H), 3.02–2.89 (m, 1H), 2.89–2.83 (m, 4H), 2.75–2.69 (m, 4H), 2.69–2.58 (m, 1H), 2.36 (s, 3H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 138.3 (d, $J_{C\text{-}F}$ = 1.7 Hz), 135.8 (d, $J_{C\text{-}F}$ = 20.1 Hz), 129.2, 125.6 (d, $J_{C\text{-}F}$ = 6.5 Hz), 92.5 (d, $J_{C\text{-}F}$ = 173.2 Hz), 65.2 (d, $J_{C\text{-}F}$ = 23.8 Hz), 55.4, 28.0, 21.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -175.19.
FTIR (thin film): cm^{-1} 2920, 2808, 1719, 1516, 1454, 1273, 1131, 1040, 957, 815, 755.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}FNS^+$ 240.1217; found: 240.1220.



4f

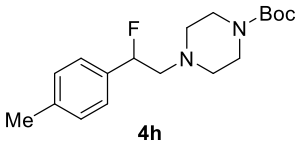
8-(2-Fluoro-2-phenylethyl)-3-oxa-8-azabicyclo[3.2.1]octane (4f). Synthesized using **GP3** from **1a** and 3-oxa-8-azabicyclo[3.2.1]octan-8-yl benzoate **2g**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 20% ethyl acetate–hexanes), as a pale-yellow oil (26.0 mg, 52%).
$\mathbf{R}_f$ = 0.10 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 5.57 (ddd, J = 48.4, 8.1, 3.1 Hz, 1H), 3.76 (dd, J = 14.4, 10.4 Hz, 2H), 3.49 (ddd, J = 12.6, 10.4, 1.9 Hz, 2H), 3.28–3.24 (m, 1H), 3.00–2.93 (m, 1H), 2.81 (ddd, J = 17.9, 14.1, 8.1 Hz, 1H), 2.51 (ddd, J = 31.7, 14.1, 3.1 Hz, 1H), 2.36 (s,

3H), 1.98–1.78 (m, 4H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 138.2 (d, $J_{C\text{-}F}$ = 1.9 Hz), 136.0 (d, $J_{C\text{-}F}$ = 20.1 Hz), 129.0, 125.7 (d, $J_{C\text{-}F}$ = 6.7 Hz), 94.8 (d, $J_{C\text{-}F}$ = 172.0 Hz), 73.1, 73.1, 62.1, 61.8 (d, $J_{C\text{-}F}$ = 2.2 Hz), 60.3 (d, $J_{C\text{-}F}$ = 23.7 Hz), 25.1, 24.8, 21.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -176.73.
FTIR (thin film): cm^{-1} 2946, 2855, 1516, 1182, 1132, 1008, 981, 883, 816, 641, 543.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{21}FNO^+$ 250.1602; found: 250.1608.



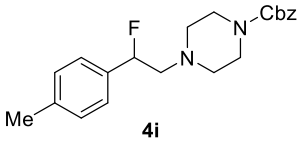
4g

4-(2-Fluoro-2-(*p*-tolyl)ethyl)-2,6-dimethylmorpholine (4g). Synthesized using **GP3** from **1a** and *O*-benzoyl-2,6-dimethyl-hydroxylmorpholine **2h**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 15% ethyl acetate–hexanes), as a pale oil (43.1 mg, 86%).
$\mathbf{R}_f$ = 0.10 (10% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.63 (ddd, *J* = 49.0, 8.9, 2.1 Hz, 1H), 3.84–3.53 (m, 2H), 2.92 (d, *J* = 9.2 Hz, 1H), 2.91 – 2.84 (m, 1H), 2.81 (d, *J* = 10.6 Hz, 1H), 2.59 (ddd, *J* = 34.9, 14.2, 2.1 Hz, 1H), 2.36 (s, 3H), 1.92 (dt, *J* = 17.8, 10.6 Hz, 2H), 1.18 (d, *J* = 2.7 Hz, 3H), 1.16 (d, *J* = 2.7 Hz, 3H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 138.3 (d, $J_{C\text{-}F}$ = 1.7 Hz), 135.8 (d, $J_{C\text{-}F}$ = 19.9 Hz), 129.2, 125.6 (d, $J_{C\text{-}F}$ = 6.7 Hz), 92.6 (d, $J_{C\text{-}F}$ = 172.9 Hz), 71.7, 71.6, 64.6 (d, $J_{C\text{-}F}$ = 23.1 Hz), 60.1, 59.6, 21.2, 19.2, 19.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ -175.17.
FTIR (thin film): cm^{-1} 2972, 2864, 1516, 1454, 1323, 1142, 1083, 1027, 885, 812, 712.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{23}FNO^+$ 252.1758; found: 252.1753.



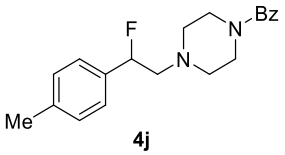
4h

***tert*-Butyl 4-(2-fluoro-2-(*p*-tolyl)ethyl)piperazine-1-carboxylate (4h).** Synthesized using **GP3** from **1a** and *O*-benzoyl-4-*tert*-butoxycarbonyl-hydroxylpiperazine **2i**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 30% ethyl acetate–hexanes), as a pale oil (39.9 mg, 62%).
$\mathbf{R}_f$ = 0.25 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.59 (ddd, *J* = 48.8, 8.8, 2.3 Hz, 1H), 3.47–3.44 (m, 4H), 2.87 (ddd, *J* = 17.1, 14.3, 8.8 Hz, 1H), 2.62–2.43 (m, 5H), 2.27 (s, 3H), 1.39 (s, 9H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 154.7, 138.3, 135.7 (d, $J_{C\text{-}F}$ = 20.0 Hz), 129.1, 125.5 (d, $J_{C\text{-}F}$ = 6.59 Hz), 92.63 (d, $J_{C\text{-}F}$ = 173.0 Hz), 79.6, 64.5 (d, $J_{C\text{-}F}$ = 23.5 Hz), 53.4, 28.6, 21.4.
^{19}F NMR (471 MHz, $CDCl_3$) δ -175.12
FTIR (thin film): cm^{-1} 2975, 2928, 2860, 2811, 1693, 1455, 1419, 1365, 1243, 1170, 1125, 1004, 816.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{25}FNO_2^+$ 294.1864; found: 294.1869.



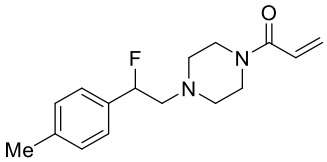
4i

2-(4-(2-Fluoro-2-(*p*-tolyl)ethyl)piperazin-1-yl)-1-phenyl-2-ethan-1-one (4i). Synthesized using **GP3** from **1a** and *O*-benzoyl-4-benzyloxycarbonyl-hydroxylpiperazine **2j**. Isolated by flash column chromatography (12% ethyl acetate–hexanes to 20% ethyl acetate–hexanes), as a yellow oil (54.1 mg, 76%).
$\mathbf{R}_f$ = 0.38 (50% ethyl aceteate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39–7.30 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.61 (ddd, *J* = 48.8, 8.8, 2.3 Hz, 1H), 5.14 (s, 2H), 3.75–3.45 (m, 4H), 2.93 (ddd, *J* = 17.0, 14.3, 8.8 Hz, 1H), 2.71–2.62 (m, 1H), 2.61–2.57 (m, 4H), 2.36 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHZ): δ 155.2, 138.4, 136.7, 135.6 (d, $J_{C\text{-}F}$ = 20.1 Hz), 129.2, 128.4, 128.0, 127.9, 125.5 (d, $J_{C\text{-}F}$ = 6.7 Hz), 92.6 (d, $J_{C\text{-}F}$ = 173.3 Hz), 67.1, 64.4 (d, $J_{C\text{-}F}$ = 23.6 Hz), 53.3, 43.8, 21.1.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -175.15.
FTIR (thin film): cm^{-1} 1696, 1455, 1428, 1235, 1123, 1003, 762, 697.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{26}FN_2O_2^+$ 357.1973; found: 357.1977.



4j

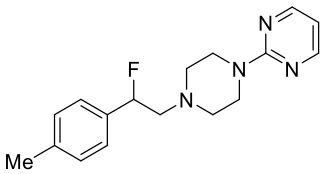
(4-(2-Fluoro-2-(*p*-tolyl)ethyl)piperazin-1-yl)(phenyl)methanone (4j). Synthesized using **GP3** from **1a** and *O*-benzoyl-4-benzoylhydroxylpiperazine **2k**. Isolated by flash column chromatography (20% ethyl acetate–hexanes to 50% ethyl acetate–hexanes), as a yellow oil. (45.1 mg, 69%).
$\mathbf{R}_f$ = 0.40 (50% ethyl aceteate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 5H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.62 (ddd, *J* = 48.8, 8.7, 2.3 Hz, 1H), 3.82 (br, 2H), 3.46 (br, 2H), 2.94 (ddd, *J* = 17.0, 14.3, 8.7 Hz, 1H), 2.79–2.46 (m, 5H), 2.35 (s, 3H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 170.3, 138.4 (d, $J_{C\text{-}F}$ = 1.8 Hz), 135.7, 135.5 (d, $J_{C\text{-}F}$ = 20.0 Hz), 129.6, 129.2, 128.4, 127.0, 125.5 (d, $J_{C\text{-}F}$ = 6.6 Hz), 92.6 (d, $J_{C\text{-}F}$ = 173.2 Hz), 64.2 (d, $J_{C\text{-}F}$ = 23.6 Hz), 53.8, 53.3, 47.6, 42.1, 21.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ -175.16.
FTIR (thin film): cm^{-1} 1648, 1414, 1406, 1215, 1114, 754, 598.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{24}FN_2O^+$ 327.1867; found: 327.1872.



4k

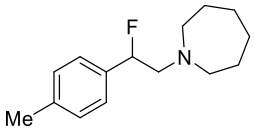
1-(4-(2-Fluoro-2-(*p*-tolyl)ethyl)piperazin-1-yl)prop-2-en-1-one (4k). Synthesized using **GP3** from **1a** and 4-acryloylpiperazin-1-yl benzoate **2u**. Isolated by flash column chromatography (30% ethyl acetate–hexanes to 50% ethyl acetate–hexanes), as a pale oil (27.0 mg, 49%).
$\mathbf{R}_f$ = 0.10 (50% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.56 (dd, *J* = 16.8, 10.6

Hz, 1H), 6.28 (dd, J = 16.8, 1.5 Hz, 1H), 5.69 (dd, J = 10.6, 1.5 Hz, 1H), 5.59 (ddd, J = 49.0, 8.9, 2.1 Hz, 1H), 3.88–3.50 (m, 4H), 3.04–2.85 (m, 1H), 2.75–2.66 (m, 1H), 2.66–2.50 (m, 4H), 2.35 (s, 3H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 165.3, 138.5 (d, $J_{C\text{-}F}$ = 1.2 Hz), 135.5 (d, $J_{C\text{-}F}$ = 20.2 Hz), 129.2, 127.9, 127.4, 125.6 (d, $J_{C\text{-}F}$ = 6.5 Hz), 64.2 (d, $J_{C\text{-}F}$ = 23.7 Hz), 53.8, 53.2, 45.8, 41.9, 21.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -175.16.
FTIR (thin film): cm^{-1} 2922, 2857, 1642, 1612, 1439, 1233, 1147, 1001, 818, 790, 717.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{22}FN_2O^+$ 277.1711; found: 277.1711.



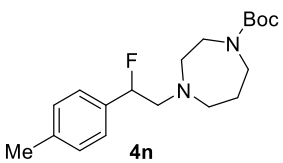
4l

2-(4-(2-Fluoro-2-(*p*-tolyl)ethyl)piperazin-1-yl)pyrimidine (4l). Synthesized using **GP3** from **1a** and 4-(pyrimidin-2-yl)piperazin-1-yl benzoate **2l**. Isolated by flash column chromatography (20% ethyl acetate–hexanes to 33% ethyl acetate–hexanes), as a pale oil (28.2 mg, 47%).
$\mathbf{R_f}$ = 0.10 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, J = 4.7 Hz, 2H), 7.25 (d, J = 7.8 Hz, 2H), 7.19 (d, J = 7.8 Hz, 2H), 6.48 (t, J = 4.7 Hz, 1H), 5.67 (ddd, J = 48.6, 8.3, 1.2 Hz, 1H), 3.87 (t, J = 4.9 Hz, 4H), 3.03–2.88 (m, 1H), 2.74 – 2.58 (m, 1H), 2.74 – 2.58 (m, 4H), 2.36 (s, 3H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 161.7, 161.5, 157.7, 138.4 (d, $J_{C\text{-}F}$ = 1.5 Hz), 135.8 (d, $J_{C\text{-}F}$ = 19.8 Hz), 129.2, 125.6 (d, $J_{C\text{-}F}$ = 6.5 Hz), 109.9, 92.7 (d, $J_{C\text{-}F}$ = 173.0 Hz), 64.7 (d, $J_{C\text{-}F}$ = 23.4 Hz), 53.5, 43.7, 21.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -175.11.
FTIR (thin film): cm^{-1} 2938, 2852, 1583, 1545, 1497, 1358, 1257, 982, 796.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{22}FN_4^+$ 301.1823; found: 301.1816.



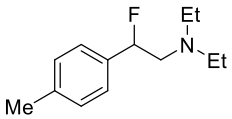
4m

1-(2-Fluoro-2-(p-tolyl)ethyl)azepane (4m). Synthesized using **GP3** from **1a** and *O*-benzoylhydroxylazepane **2m**. Isolated by flash column chromatography (hexanes–dichloromethane–ethyl acetate = 15:1:1, v/v/v), as a pale oil (15.1 mg, 32%).
$\mathbf{R_f}$ = 0.10 (10% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 5.57 (ddd, J = 48.8, 8.4, 2.6 Hz, 1H), 3.11–3.01 (m, 1H), 2.88–2.74 (m, 1H), 2.88–2.74 (m, 4H), 2.35 (s, 3H), 1.71–1.54 (m, 8H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 138.0 (d, $J_{C\text{-}F}$ = 1.5 Hz), 136.4 (d, $J_{C\text{-}F}$ = 20.0 Hz), 129.1, 125.6 (d, $J_{C\text{-}F}$ = 6.9 Hz), 93.2 (d, $J_{C\text{-}F}$ = 172.8 Hz), 63.7 (d, $J_{C\text{-}F}$ = 23.6 Hz), 55.8, 28.0, 27.1, 21.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -176.95.
FTIR (thin film): cm^{-1} 2923, 2853, 1721, 1451, 1356, 1269, 1135, 1014, 814.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{23}FN^+$ 236.1809; found: 236.1808.



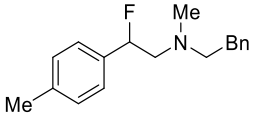
4n

***tert*-Butyl 4-(2-fluoro-2-(*p*-tolyl)ethyl)-1,4-diazepane-1-carboxylatez (4n).** Synthesized using **GP3** from **1a** and *tert*-butyl 4-(benzoyloxy)-1,4-diazepane-1-carboxylate **2n**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 20% ethyl acetate–hexanes), as a colorless oil (26.9 mg, 40%).
$\mathbf{R_f}$ = 0.27 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 5.54 (ddd, *J* = 48.6, 8.3, 2.2 Hz, 1H), 3.52–3.39 (m, 4H), 3.04 (ddd, *J* = 16.6, 14.5, 8.3 Hz, 1H), 2.86–2.72 (m, 5H), 2.35 (s, 3H), 1.86–1.76 (m, 2H), 1.45 (s, 9H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 155.6, 155.4, 138.2 (d, $J_{C\text{-}F}$ = 7.0 Hz), 135.9 (d, $J_{C\text{-}F}$ = 19.9 Hz), 129.1, 125.5 (d, $J_{C\text{-}F}$ = 6.6 Hz), 93.2 (d, $J_{C\text{-}F}$ = 173.0 Hz), 93.2 (d, $J_{C\text{-}F}$ = 173.4 Hz), 79.2, 76.7, 63.2, 63.0, 56.3, 56.1, 55.2, 55.0, 46.9, 46.4, 46.0, 45.1, 28.5, 27.9, 27.7, 21.1. (Mixture of *cis*- and *trans*-amide rotamers).
^{19}F NMR (471 MHz, $CDCl_3$) δ -176.75, -176.95. (The product gives two sets of ^{19}FNMR signals, owing to the presence of N-Boc rotamers around the amide.).
FTIR (thin film): cm^{-1} 2930, 1688, 1460, 1411, 1157, 903, 726.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{30}FN_2O_2^+$ 337.2286; found: 337.2289.



4o

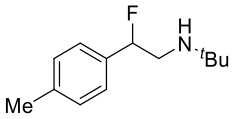
***N*,*N*-diethyl-2-fluoro-2-(*p*-tolyl)ethan-1-amine (4o).** Synthesized using **GP3** from **1a** and *O*-benzoylhydroxyldiethylamine **2o**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 20% ethyl acetate–hexanes), as a pale oil (9.0 mg, 21%).
$\mathbf{R_f}$ = 0.20 (30% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 5.55 (ddd, *J* = 48.6, 8.7, 2.5 Hz, 1H), 2.98 (ddd, *J* = 16.8, 14.7, 8.7 Hz, 1H), 2.77–2.69 (m, 1H), 2.69–2.62 (m, 4H), 2.35 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 138.1 (d, $J_{C\text{-}F}$ = 1.5 Hz), 136.3 (d, $J_{C\text{-}F}$ = 20.5 Hz), 129.1, 125.6 (d, $J_{C\text{-}F}$ = 6.5 Hz), 93.4 (d, $J_{C\text{-}F}$ = 172.9 Hz), 59.4 (d, $J_{C\text{-}F}$ = 23.9 Hz), 47.8, 21.2, 11.8.
^{19}F NMR (471 MHz, $CDCl_3$) δ -177.06.
FTIR (thin film): cm^{-1} 2970, 2927, 1720, 1450, 1270, 1111, 1069, 816, 711.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{21}FN^+$ 210.1653; found: 210.1650.



4p

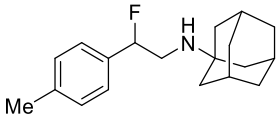
2-Fluoro-*N*-methyl-*N*-phenethyl-2-(*p*-tolyl)ethan-1-amine (4p). Synthesized using **GP3** from **1a** and *O*-benzoyl-*N*-benzyl-*N*-methylhydroxylamine **2q**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 20% ethyl acetate–hexanes), as a pale oil (29.8 mg, 55%).
$\mathbf{R_f}$ = 0.10 (20% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.27 (m, 2H), 7.23 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 7.25–7.17 (m, 3H), 5.59 (ddd, J = 48.7, 8.6, 2.8 Hz, 1H), 3.01 (ddd, J = 16.6, 14.3, 8.6 Hz, 1H), 2.86–2.64 (m,4H), 2.78–2.64 (m, 1H), 2.48 (s, 3H), 2.36 (s, 3H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 140.3, 138.2 (d, $J_{C\text{-}F}$ = 1.7 Hz), 136.0 (d, $J_{C\text{-}F}$ = 19.8 Hz), 129.2, 128.7, 128.4, 126.0, 125.6 (d, $J_{C\text{-}F}$ = 6.5 Hz), 92.9 (d, $J_{C\text{-}F}$ = 172.9 Hz), 63.5 (d, $J_{C\text{-}F}$ = 23.9 Hz), 59.9, 42.9, 33.8, 21.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -176.41.
FTIR (thin film): cm^{-1} 2924, 2851, 1453, 1122, 1030, 813, 746, 698.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{23}FN^+$ 272.1809; found: 272.1802.



4q

***N*-(2-Fluoro-2-(*p*-tolyl)ethyl)-2-methylpropan-2-amine (4q).** Synthesized using **GP3** from **1a** and *O*-benzoyl-*N*-(*tert*-butyl)hydroxylamine **2r**. Isolated by flash column chromatography (6% ethyl acetate–hexanes to 12% ethyl acetate–hexanes), as a pale oil (11.2 mg, 26%).
R_f = 0.10 (12% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 5.51 (ddd, *J* = 48.9, 9.0, 3.0 Hz, 1H), 3.08 (ddd, *J* = 15.3, 12.5, 9.1 Hz, 1H), 2.80 (ddd, *J* = 33.3, 12.5, 3.2 Hz, 1H), 2.36 (s, 3H), 1.12 (s, 9H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 138.4 (d, $J_{C\text{-}F}$ = 1.7 Hz), 135.7 (d, $J_{C\text{-}F}$ = 19.6 Hz), 129.2, 125.7 (d, $J_{C\text{-}F}$ = 6.5 Hz), 95.0 (d, $J_{C\text{-}F}$ = 170.1 Hz), 50.3, 49.2 (d, $J_{C\text{-}F}$ = 24.1 Hz), 28.9, 21.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -180.14.
FTIR (thin film): cm^{-1} 2962, 2924, 1721, 1514, 1361, 1231, 1111, 1014, 815.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{21}FN^+$ 210.1653; found: 210.1659.

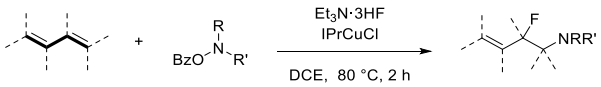


4r

***N*-(2-Fluoro-2-(*p*-tolyl)ethyl)adamantan-1-amine (4r).** Synthesized using **GP3** from **1a** and *N*-(adamantan-1-yl)-*O*-benzoylhydroxylamine **2s**. Isolated by flash column chromatography (5% ethyl acetate–hexanes to 12% ethyl acetate–hexanes), as a pale oil (20.4 mg, 36%).
R_f = 0.15 (12% ethyl acetate–hexanes).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.49 (ddd, *J* = 49.0, 9.0, 3.2 Hz, 1H), 3.12 (ddd, *J* = 15.3, 12.5, 9.1 Hz, 1H), 2.82 (ddd, *J* = 33.4, 12.5, 3.2 Hz, 1H), 2.36 (s, 3H), 2.07 (s, 3H), 1.66 (d, *J* = 12.1 Hz, 6H), 1.63 – 1.56 (m, 6H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 138.4 (d, $J_{C\text{-}F}$ = 1.8 Hz), 135.8 (d, $J_{C\text{-}F}$ = 19.6 Hz), 129.2, 125.7 (d, $J_{C\text{-}F}$ = 6.5 Hz), 95.2 (d, $J_{C\text{-}F}$ = 170.0 Hz), 50.3, 47.1 (d, $J_{C\text{-}F}$ = 24.3 Hz), 42.8, 36.7, 29.6, 21.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -180.02.
FTIR (thin film): cm^{-1} 2901, 2846, 1515, 1450, 1356, 1310, 1151, 1111, 1033, 814.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{27}FN^+$ 288.2122; found: 288.2123.

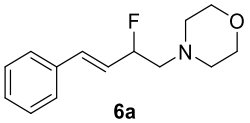
6. Aminofluorination of 1,3-dienes and compound characterization data

General procedure 4 (GP4) for aminofluorination of 1,3-dienes



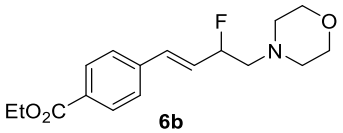
5 **2** **6**
1,2-products

To a 10-mL FEP tube with Teflon-coated micro stir bar was added *O*-benzoylhydroxylamine **2** (0.2 mmol, 1.0 equiv) and IPrCuCl (4.9 mg, 5 mol %). DCE (1.0 mL), 1,3-diene **5** (0.4 mmol, 2.0 equiv) and Et_3N•3HF (322 mg, 2 mmol, 10 equiv) were sequentially added. The mixture was allowed to stir at 80 °C for 2 h until the consumption of *O*-benzoylhydroxylamine (verified by TLC analysis, 20% ethyl acetate–hexanes). The resulting reaction mixture was cooled to room temperature and quenched through the addition of Et_3N (0.5 mL). The solution was then diluted with ethyl acetate to a final volume of 5.0 mL and filtered through a plug of activated, neutral Al_2O_3 (Brockman grade I, 58–60Å). The filtrate was concentrated under reduced pressure, providing the crude reaction mixture. The crude reaction mixture was purified by silica column chromatography.



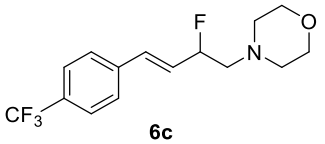
6a

(*E*)-4-(2-Fluoro-4-phenylbut-3-en-1-yl)morpholine (6a). Synthesized using **GP4** from **5a** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (12% ethyl acetate–hexanes to 20% ethyl acetate–hexanes), as a pale oil (21.2 mg, 45%).
$\mathbf{R}_f$ = 0.20 (30% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 6.70 (dd, *J* = 16.0, 3.3 Hz, 1H), 6.24 (ddd, *J* = 16.0, 13.3, 6.5 Hz, 1H), 5.40–5.11 (m, 1H), 3.75 (t, 4H), 2.79 (ddd, *J* = 18.3, 14.0, 8.0 Hz, 1H), 2.72–2.45 (m, 1H), 2.63–2.45 (m, 4H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 135.9 (d, $J_{C\text{-}F}$ = 1.4 Hz), 133.1 (d, $J_{C\text{-}F}$ = 11.5 Hz), 128.7, 128.3, 126.7, 125.5 (d, $J_{C\text{-}F}$ = 18.4 Hz), 91.7 (d, $J_{C\text{-}F}$ = 170.0 Hz), 66.9, 63.1 (d, *J* = 22.6 Hz), 54.2.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -174.38.
FTIR (thin film): cm^{-1} 1635, 1451, 1279, 1117, 1010, 745, 695.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}FNO^+$ 236.1445; found: 236.1446.



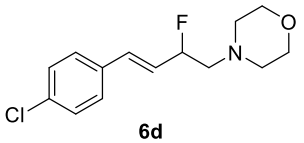
6b

Ethyl (*E*)-4-(3-fluoro-4-morpholinobut-1-en-1-yl)benzoate (6b). Synthesized using **GP4** from **5b** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (20% ethyl acetate–hexanes to 30% ethyl acetate–hexanes), as a yellowish oil (29.0 mg, 47%).
$\mathbf{R}_f$ = 0.25 (50% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 6.73 (d, *J* = 16.0 Hz, 1H), 6.35 (ddd, *J* = 16.0, 13.4, 6.4 Hz, 1H), 5.41–5.19 (m, 1H),4.37 (q, *J* = 7.1 Hz, 2H), 3.74 (t, *J* = 4.4 Hz, 4H), 2.79 (ddd, *J* = 18.7, 14.1, 7.9 Hz, 1H), 2.73–2.63 (m, 1H), 2.58–2.49 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 166.2, 140.2, 131.7 (d, $J_{C\text{-}F}$ = 11.8 Hz), 130.0, 129.9, 128.0 (d, $J_{C\text{-}F}$ = 18.4 Hz), 126.5, 91.3 (d, $J_{C\text{-}F}$ = 171.5 Hz), 66.9, 62.9 (d, $J_{C\text{-}F}$ = 22.2 Hz), 61.0, 54.1, 14.3.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -176.56.
FTIR (thin film): cm^{-1} 2958, 2854, 1711, 1607, 1453, 1272, 1106, 1018, 868, 762.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}FNO_3^+$ 308.1657; found: 308.1660.



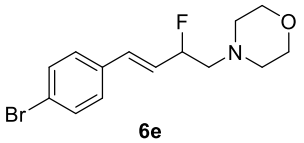
6c

(*E*)-4-(2-fluoro-4-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)morpholine (6c). Synthesized using **GP4** from **5c** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (12% ethyl acetate–hexanes to 25% ethyl acetate–hexanes), as a yellowish oil (22.6 mg, 38%).
$\mathbf{R}_f$ = 0.30 (50% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 6.73 (dd, *J* = 16.0, 1.9 Hz, 1H), 6.34 (ddd, *J* = 18.8, 15.4, 5.9 Hz, 1H), 5.45–5.10 (m, 1H), 3.75 (t, *J* = 4.5 Hz, 4H), 2.79 (ddd, *J* = 18.8, 14.0, 7.8 Hz, 1H), 2.71–2.61 (m, 1H), 2.64–2.56 (m, 4H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 139.5, 131.2 (d, $J_{C\text{-}F}$ = 11.9 Hz), 130.0 (q, $J_{C\text{-}F}$ = 32.7 Hz), 128.3 (d, $J_{C\text{-}F}$ = 18.4 Hz), 126.8, 125.6 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.1 (q, $J_{C\text{-}F}$ = 271.9 Hz), 91.2 (d, $J_{C\text{-}F}$ = 171.7 Hz), 66.9, 62.9 (d, $J_{C\text{-}F}$ = 22.2 Hz), 54.1.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -62.61, -176.98.
FTIR (thin film): cm^{-1} 2856, 2814, 1616, 1454, 1323, 1164, 1115, 1066, 1015, 868.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}F_4NO^+$ 304.1319; found: 304.1321.



6d

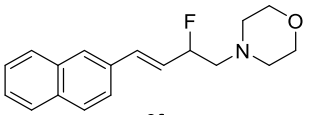
(*E*)-4-(4-(4-Chlorophenyl)-2-fluorobut-3-en-1-yl)morpholine (6d). Synthesized using **GP4** from **5d** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 25% ethyl acetate–hexanes), as a yellowish oil (26.3 mg, 49%).
$\mathbf{R}_f$ = 0.21 (30% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.65 (dd, *J* = 16.0, 2.6 Hz, 1H), 6.22 (ddd, *J* = 16.0, 13.7, 6.3 Hz, 1H), 5.37–5.03 (m, 1H), 3.74 (t, *J* = 4.6 Hz, 4H), 2.78 (ddd, *J* = 18.5, 14.0, 7.9 Hz, 1H), 2.69–2.59 (m, 1H), 2.63–2.53 (m, 4H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 134.5, 134.0, 131.7 (d, $J_{C\text{-}F}$ = 11.8 Hz), 128.9, 127.9, 126.2 (d, $J_{C\text{-}F}$ = 18.4 Hz), 91.5 (d, $J_{C\text{-}F}$ = 170.7 Hz), 66.9, 63.0 (d, $J_{C\text{-}F}$ = 22.2 Hz), 54.2.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -175.22.
FTIR (thin film): cm^{-1} 2855, 2811, 1491, 1453, 1115, 1089, 1011, 968, 869, 719.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{18}ClFNO^+$ 270.1056; found: 270.1055.



6e

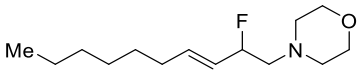
(*E*)-4-(4-(4-Bromophenyl)-2-fluorobut-3-en-1-yl)morpholine (6e). Synthesized using **GP4** from **5e** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 25% ethyl acetate–hexanes), as a yellowish solid (30.4 mg, 48%).
$\mathbf{R}_f$ = 0.22 (30% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 6.63 (dd, *J* = 16.0, 2.9 Hz, 1H), 6.23 (ddd, *J* = 16.0, 13.9, 6.3 Hz, 1H), 5.36–5.09 (m, 1H), 3.74 (t, *J* =4.5 Hz, 4H), 2.77 (ddd, *J* = 18.5, 14.0, 7.9 Hz, 1H), 2.67–2.58 (m, 1H), 2.64 –2.39 (m, 4H).

^{13}C NMR (125 MHZ, $CDCl_3$) δ 134.9, 131.8, 131.7 (d, $J_{C\text{-}F}$ = 12.0 Hz), 128.2, 126.3 (d, $J_{C\text{-}F}$ = 18.4 Hz), 122.1, 91.5 (d, $J_{C\text{-}F}$ = 170.8 Hz), 66.9, 63.0 (d, $J_{C\text{-}F}$ = 22.5 Hz), 54.2.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -175.42.
FTIR (thin film): cm^{-1} 2957, 2854, 1487, 1453, 1115, 1071, 1008, 967, 868, 712.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{18}BrFNO^+$ 314.0550; found: 314.0550.

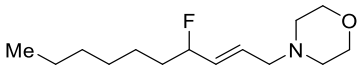


6f

(*E*)-4-(2-Fluoro-4-(naphthalen-2-yl)but-3-en-1-yl)morpholine (6f). Synthesized using **GP4** from **5f** and *O*-benzoylhydroxylmorpholine **2a**. Isolated by flash column chromatography (12% ethyl acetate–hexanes to 20% ethyl acetate–hexanes), as a yellowish oil (18.4 mg, 33%).
R_f = 0.20 (30% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.85–7.78 (m, 3H), 7.76 (s, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.51–7.43 (m, 2H), 6.88 (dd, *J* = 15.9, 3.0 Hz, 1H), 6.36 (ddd, *J* = 15.9, 13.5, 6.4 Hz, 1H), 5.56–5.26 (m, 1H), 3.80 (t, *J* = 4.4 Hz, 4H), 2.87 (ddd, *J* = 18.1, 14.1, 8.0 Hz, 1H), 2.8 –2.69 (m, 1H), 2.76 –2.60 (m, 4H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 133.5, 133.4 (d, $J_{C\text{-}F}$ = 11.6 Hz), 133.3, 133.3, 128.4, 128.1, 127.7, 127.2, 126.4, 126.3, 125.4 (d, $J_{C\text{-}F}$ = 18.9 Hz), 123.4, 91.5 (d, $J_{C\text{-}F}$ = 170.2 Hz),66.6, 62.9 (d, $J_{C\text{-}F}$ = 22.4 Hz), 54.0.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -174.02.
FTIR (thin film): cm^{-1} 2924, 2853, 1716, 1596, 1452, 1271, 1115, 1009, 966, 867, 746.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{21}FNO^+$ 286.1602; found: 286.1600.



6g



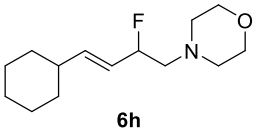
7g

(*E*)-4-(2-fluorodec-3-en-1-yl)morpholine (6g) and (*E*)-4-(4-fluorodec-2-en-1-yl)morpholine (7g). Synthesized using **GP4** from **5g** and *O*-benzoylhydroxylmorpholine **2a**. ^{1}H-NMR analysis of the crude reaction mixture indicated the formation of 1,2-product **6g** and 1,4-product **7g** in a ratio of 7:1.

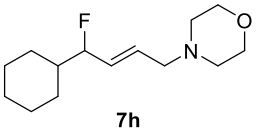
1,2-Product **6g** was isolated by flash column chromatography (5% ethyl acetate–hexanes to 10% ethyl acetate–hexanes) as a yellowish oil (17.1 mg, 35%).
R_f = 0.20 (13% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.89–5.75 (m, 1H), 5.61–5.45 (m, 1H), 5.05 (dt, *J* = 14.8, 6.5 Hz, 1H), 3.82–3.65 (t, *J* = 4.6, 4H), 2.69 (ddd, *J* = 17.7, 14.0, 8.2 Hz, 1H), 2.61–2.51 (m, 4H), 2.57–2.41 (m, 1H), 2.11–2.00 (m, 2H), 1.44–1.33 (m, 2H), 1.3 –1.18 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 136.3 (d, $J_{C\text{-}F}$ = 11.1 Hz), 126.4 (d, $J_{C\text{-}F}$ = 18.7 Hz), 91.9 (d, $J_{C\text{-}F}$ = 167.3 Hz), 66.9, 63.2 (d, $J_{C\text{-}F}$ = 22.8 Hz), 54.1, 32.2 (d, $J_{C\text{-}F}$ = 1.2 Hz), 31.7, 28.8 (d, $J_{C\text{-}F}$ = 2.5 Hz), 22.6, 14.1.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -171.31.
FTIR (thin film): cm^{-1} 2925, 2854, 1672, 1454, 1294, 1119, 1009, 968, 869.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{27}FNO^+$ 244.2071; found: 244.2073.

1,4-Product **7g** was isolated by flash column chromatography (10% ethyl acetate–hexanes to 25% ethyl acetate–hexanes) as a yellowish oil (3.4 mg, 7%).
R_f = 0.15 (20% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.82–5.75 (m, 1H), 5.74–5.65 (m, 1H), 4.86 (ddd, *J* = 48.8, 12.8, 6.3 Hz,

1H), 3.72 (t, J = 4.6 Hz, 4H), 3.01 (dd, J = 5.8, 3.6 Hz, 2H), 2.54–2.30 (m, 4H), 1.77–1.67 (m, 1H), 1.64–1.57 (m, 1H), 1.37–1.24 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 132.6 (d, $J_{C\text{-}F}$ = 20.4 Hz), 129.6 (d, $J_{C\text{-}F}$ = 10.5 Hz), 93.2 (d, $J_{C\text{-}F}$ = 165.2 Hz), 66.9, 60.5, 53.5, 35.4 (d, $J_{C\text{-}F}$ = 22.5 Hz), 31.7, 29.0, 24.7 (d, $J_{C\text{-}F}$ = 4.5 Hz), 22.5, 14.1.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -172.83.
FTIR (thin film): cm^{-1} 2927, 2855, 1677, 1454, 1118, 1004, 974, 867.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{27}FNO^+$ 244.2071; found: 244.2073.



6h

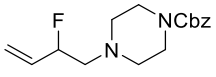


7h

(*E*)-4-(4-Cyclohexyl-2-fluorobut-3-en-1-yl)morpholine (6h) and (*E*)-4-(4-Cyclohexyl-4-fluorobut-2-en-1-yl)morpholine (7h). Synthesized using **GP4** from **5h** and *O*-benzoylhydroxylmorpholine **2a**. ^{1}H-NMR analysis of the crude reaction mixture indicated the formation of 1,2-product **6h** and 1,4-product **7h** in a ratio of 8:1.

1,2-Product **6h** was isolated by flash column chromatography (5% ethyl acetate–hexanes to 10% ethyl acetate–hexanes) as a yellowish oil (21.4 mg, 44%).
R_f = 0.20 (10% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.76 (ddd, J = 15.5, 6.0, 4.5 Hz, 1H), 5.47 (dddd, J = 15.6, 11.0, 7.1, 1.3 Hz, 1H), 5.15–4.80 (m, 1H), 3.73 (t, J = 4.5Hz, 4H), 2.69 (ddd, J = 17.6, 14.0, 8.3 Hz, 1H), 2.55 (t, J = 4.5 Hz, 4H), 2.48 (ddd, J = 31.9, 14.0, 2.7 Hz, 1H), 2.10–1.87 (m, 1H), 1.80–1.59 (m, 5H), 1.34–1.21 (m, 2H), 1.20–1.12 (m, 1H), 1.12–1.01 (m, 2H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 141.6 (d, J = 10.8 Hz), 123.9 (d, $J_{C\text{-}F}$ = 19.0 Hz), 92.1 (d, $J_{C\text{-}F}$ = 167.4 Hz), 66.9, 63.3 (d, $J_{C\text{-}F}$ = 22.8 Hz), 54.1, 40.3, 32.5 (d, $J_{C\text{-}F}$ = 1.8 Hz), 32.4 (d, $J_{C\text{-}F}$ = 1.8 Hz), 26.1, 25.9.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -171.47.
FTIR (thin film): cm^{-1} 2923, 2851, 2810, 1620, 1450, 1293, 1140, 1118, 1009, 969, 869.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{25}FNO^+$ 242.1915; found: 242.1915.

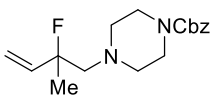
1,4-Product **7h** was isolated by flash column chromatography (10% ethyl acetate–hexanes to 25% ethyl acetate–hexanes) as a yellowish oil (2.4 mg, 5%).
R_f = 0.10 (20% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.85–5.57 (m, 2H), 4.58 (dt, J = 48.5, 6.6 Hz, 1H), 3.72 (t, J = 4.6 Hz, 4H), 3.11–2.85 (m, 2H), 2.44 (s, 4H), 1.86 (d, J = 12.8 Hz, 1H), 1.81–1.72 (m, 2H), 1.67 (d, J = 12.2 Hz, 1H), 1.60–1.49 (m, 1H), 1.30–1.09 (m, 4H), 1.07–0.94 (m, 2H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 131.1 (d, J = 20.3 Hz), 130.7 (d, J = 12.2 Hz), 97.2 (d, J = 167.7 Hz), 66.9, 60.6, 53.5, 42.3 (d, J = 21.1 Hz), 28.2 (d, J = 4.5 Hz), 27.9 (d, J = 5.1 Hz), 26.3, 25.8, 25.7.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -178.48.
FTIR (thin film): cm^{-1} 2923, 2851, 1718, 1450, 1269, 1117, 1069, 969, 869.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{25}FNO^+$ 242.1915; found: 242.1914.



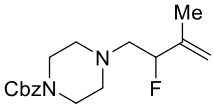
6i

Benzyl 4-(2-fluorobut-3-en-1-yl)piperazine-1-carboxylate (6i). Synthesized using **GP4** from **5i** and *O*-benzoyl-4-benzyloxycarbonyl-hydroxylpiperazine **2i**. Isolated by flash column chromatography (12% ethyl acetate–hexanes to 25% ethyl acetate–hexanes), as a colorless oil (30.0 mg, 51%).

$\mathbf{R}_f$ = 0.50 (50% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.44–7.29 (m, 5H), 5.99–5.77 (m, 1H), 5.44–5.32 (m, 1H), 5.27 (d, J = 10.7 Hz, 1H), 5.13 (s, 2H), 5.16–5.00 (m, 1H), 3.66–3.47 (m, 4H), 2.70 (ddd, J = 18.7, 14.2, 8.0 Hz, 1H), 2.61–2.50 (m, 1H), 2.58– 2.41(m, 4H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 155.2, 136.7, 134.6 (d, $J_{C\text{-}F}$ = 19.3 Hz), 128.5, 128.0, 127.9, 117.6 (d, $J_{C\text{-}F}$ = 11.8 Hz), 91.6 (d, $J_{C\text{-}F}$ = 170.9 Hz), 67.1, 62.4 (d, $J_{C\text{-}F}$ = 21.9 Hz), 53.3, 43.8.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -178.96.
FTIR (thin film): cm^{-1} 2924, 2814, 1696, 1426, 1234, 1121, 1001, 933, 696.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{22}FN_2O_2^+$ 293.1660; found: 293.1662.



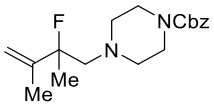
6j



6j'

Benzyl 4-(2-fluoro-2-methylbut-3-en-1-yl)piperazine-1-carboxylate (6j) and benzyl 4-(2-fluoro-3-methylbut-3-en-1-yl)piperazine-1-carboxylate (6j'). Synthesized using **GP4** from **5j** and *O*-benzoyl-4-benzyloxycarbonyl-hydroxylpiperazine **2j**. ^{1}H-NMR analysis of the crude reaction mixture indicated the formation of two 1,2-products **6j** and **6j'** in a ratio of 10:1.

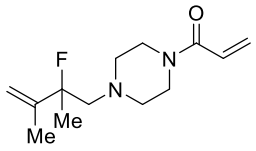
1,2-Product **6j** was isolated by flash column chromatography (2.5% 1,4-dioxane–hexanes), as a colorless oil (27.5 mg, 45%).
$\mathbf{R}_f$ = 0.10 (10% 1,4-dioxane–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45–7.21 (m, 5H), 5.94 (td, J = 17.6, 11.0 Hz, 1H), 5.30 (d, J = 17.4 Hz, 1H), 5.15 (d, J = 11.1 Hz, 1H), 5.13 (s, 2H), 3.49 (t, J = 5.0 Hz, 4H), 2.59–2.33 (m, 2H), 2.59–2.33 (m, 4H), 1.44 (d, J = 21.6 Hz, 3H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 155.3, 139.7 (d, $J_{C\text{-}F}$ = 22.2 Hz), 136.8, 128.5, 128.0, 127.9, 114.0 (d, $J_{C\text{-}F}$ = 11.1 Hz), 96.8 (d, $J_{C\text{-}F}$ = 171.4 Hz), 67.1, 65.7 (d, $J_{C\text{-}F}$ = 22.3 Hz), 54.1, 54.1, 43.9, 23.4 (d, $J_{C\text{-}F}$ = 24.8 Hz).
^{19}F NMR ($CDCl_3$, 471 MHz): δ -147.99.
FTIR (thin film): cm^{-1} 2926, 2858, 2810, 1698, 1427, 1362, 1242, 1123, 1007, 920, 752.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{24}FN_2O_2^+$ 307.1816; found: 307.1816.
Minor product **6j'** was unable to be obtained as a pure product.



6k

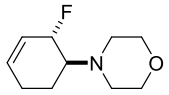
Benzyl 4-(2-fluoro-2,3-dimethylbut-3-en-1-yl)piperazine-1-carboxylate (6k). Synthesized using **GP4** from **5k** and *O*-benzoyl-4-benzyloxycarbonyl-hydroxylpiperazine **2j**. Isolated by flash column chromatography (2.5% 1,4-dioxane–hexanes to 3.3% 1,4-dioxane–hexanes), as a colorless oil (27.0 mg, 42%).
$\mathbf{R}_f$ = 0.15 (10% 1,4-dioxane–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46–7.26 (m, 5H), 5.13 (s, 2H), 5.01 (s, 1H), 4.89 (s, 1H), 3.51 (s, 4H), 2.82–2.34 (m, 2H), 2.82–2.34 (m, 4H), 1.77 (s, 3H), 1.46 (d, J = 22.2 Hz, 3H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 155.2, 146.3 (d, $J_{C\text{-}F}$ = 19.9 Hz), 136.8, 128.5, 128.0, 127.9, 110.7 (d, $J_{C\text{-}F}$ = 11.4 Hz), 99.0 (d, $J_{C\text{-}F}$ = 174.4 Hz), 67.1, 64.4 (d, $J_{C\text{-}F}$ = 22.1 Hz), 54.0 (d, $J_{C\text{-}F}$ = 2.0 Hz), 43.7, 23.2 (d, $J_{C\text{-}F}$ = 25.4 Hz), 19.3 (d, $J_{C\text{-}F}$ = 5.5 Hz).
^{19}F NMR ($CDCl_3$, 471 MHz): δ -146.45.

FTIR (thin film): cm^{-1} 2938, 2861, 2810, 1698, 1427, 1237, 1119, 1094, 1008, 905, 734.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{26}FN_2O_2^+$ 321.1973; found: 321.1973.



6l

1-(4-(2-Fluoro-2,3-dimethylbut-3-en-1-yl)piperazin-1-yl)prop-2-en-1-one (6l). Synthesized using **GP4** from **5k** and 4-acryloylpiperazin-1-yl benzoate **2u**. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 20% ethyl acetate–hexanes), as a pale oil (21.2 mg, 44%).
$\mathbf{R_f}$ = 0.35 (25% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.54 (dd, *J* = 16.8, 10.6 Hz, 1H), 6.27 (dd, *J* = 16.8, 1.9 Hz, 1H), 5.67 (dd, *J* = 10.6, 1.9 Hz, 1H), 5.00 (s, 1H), 4.88 (dd, *J* = 2.3, 1.5 Hz, 1H), 3.59 (d, *J* = 71.1 Hz, 4H), 2.76–2.37 (m, 2H), 2.76–2.37 (m, 4H), 1.77 (s, 3H), 1.45 (d, *J* = 22.2 Hz, 3H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 165.3, 146.4 (d, $J_{C\text{-}F}$ = 20.1 Hz), 127.7, 127.5, 110.5 (d, $J_{C\text{-}F}$ = 11.4 Hz), 99.2 (d, $J_{C\text{-}F}$ = 174.1 Hz), 64.4 (d, $J_{C\text{-}F}$ = 22.0 Hz), 54.3 (d, $J_{C\text{-}F}$ = 41.0 Hz), 45.9, 42.1, 23.3 (d, $J_{C\text{-}F}$ = 25.6 Hz), 19.3 (d, $J_{C\text{-}F}$ = 5.4 Hz).
^{19}F NMR ($CDCl_3$, 471 MHz): δ -146.57.
FTIR (thin film): cm^{-1} 2982, 2924, 2809, 1648, 1613, 1439, 1238, 1129, 1007, 905, 791.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{22}FN_2O^+$ 241.1711; found: 241.1707.

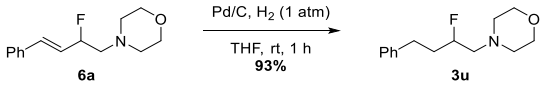


6m

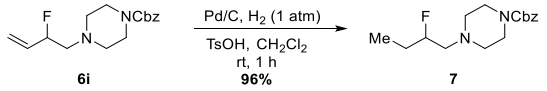
***trans*-4-(2-Fluorocyclohex-3-en-1-yl)morpholine (6m).** Synthesized using **GP4** from **5m** and *O*-benzoylhydroxylmorpholine **2a**. Only *trans*-isomer was observed (dr >20:1) by ^{1}H-NMR analysis of the crude reaction mixture. Isolated by flash column chromatography (12% ethyl acetate–hexanes to 25% ethyl acetate–hexanes), as a colorless oil (16.5 mg, 45%).
$\mathbf{R_f}$ = 0.20 (50% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.87 (dd, *J* = 9.7, 2.5 Hz, 1H), 5.76–5.64 (m, 1H), 5.28–5.11 (m, 1H), 3.73 (t, *J* = 4.5 Hz, 4H), 2.81–2.57 (m, 1H), 2.81–2.57 (m, 4H), 2.23–2.09 (m, 2H), 1.92 (dd, *J* = 8.9, 4.5 Hz, 1H), 1.59–1.47 (m, 1H).
^{13}C NMR (125 MHZ, $CDCl_3$) δ 131.5 (d, $J_{C\text{-}F}$ = 9.5 Hz), 126.3 (d, $J_{C\text{-}F}$ = 21.6 Hz), 88.7 (d, $J_{C\text{-}F}$ = 166.2 Hz), 67.5, 64.4 (d, $J_{C\text{-}F}$ = 16.1 Hz), 49.9, 25.4 (d, $J_{C\text{-}F}$ = 2.9 Hz), 23.1 (d, $J_{C\text{-}F}$ = 7.4 Hz).
^{19}F NMR ($CDCl_3$, 471 MHz): δ -172.49.
FTIR (thin film): cm^{-1} 2924, 2852, 1717, 1451, 1268, 1116, 1015, 901, 854, 732.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{17}FNO^+$ 186.1289; found: 186.1287.

7. Synthetic applications

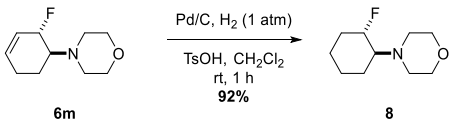
7.1. Transformations of *β*-fluoro homoallylic amines to alkyl-substituted *β*-fluoroalkylamines



4-(2-Fluoro-4-phenylbutyl)morpholine (3u). To a stirring solution of (*E*)-4-(2-fluoro-4-phenylbut-3-en-1-yl)morpholine **6a** (23.5 mg, 0.1 mmol, 1 equiv) in THF (2.0 mL) was added Pd/C (10% on activated carbon, 4 mg) at room temperature. After the inner atmosphere of the flask was changed to hydrogen by a hydrogen balloon (1atm), the resulting mixture was allowed to stir at room temperature for 1 h. Upon the completion consumption of **6a** (monitored by LC-MS analysis), the reaction was stopped immediately and filtered. The solvent was removed under reduced pressure. The resulting residue was purified by silica gel chromatography (40% ethyl acetate–hexanes), giving **3u** as yellow oil (22.1 mg, 93%).
$\mathbf{R}_f$ = 0.10 (33% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32–7.27 (m, 2H), 7.23–7.18 (m, 3H), 4.81–4.52 (m, 1H), 3.75–3.58 (m, 4H), 2.88–2.78 (m, 1H), 2.75–2.68 (m, 1H), 2.68–2.58 (m, 1H), 2.55–2.41 (m, 5H), 2.07–1.95 (m, 1H), 1.95–1.78 (m, 1H).
^{13}C NMR ($CDCl_3$, 125 MHZ): δ 141.2, 128.5, 128.8, 126.1, 91.5 (d, $J_{C\text{-}F}$ = 170.0 Hz), 66.9, 62.8 (d, $J_{C\text{-}F}$ = 20.5 Hz), 54.3, 35.2 (d, $J_{C\text{-}F}$ = 20.8 Hz), 31.2 (d, $J_{C\text{-}F}$ = 4.6 Hz).
^{19}F NMR ($CDCl_3$, 471 MHz): δ -182.13.
FTIR (thin film): cm^{-1} 2952, 2853, 1717, 1453, 1273, 1116, 1035, 867, 699.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{21}FNO^+$ 238.1602; found: 238.1600.



Benzyl 4-(2-fluorobutyl)piperazine-1-carboxylate (7). To a stirring solution of benzyl 4-(2-fluorobut-3-en-1-yl)piperazine-1-carboxylate **6i** (29.2 mg, 0.1 mmol, 1 equiv) in CH_2Cl_2 (2.0 mL) was added Pd/C (10% on activated carbon, 4 mg) and $TsOH{\cdot}H_2O$ (19 mg, 0.1 mmol, 1.0 equiv) at room temperature. After the inner atmosphere of the flask was changed to hydrogen by a hydrogen balloon (1atm), the resulting mixture was allowed to stir at room temperature for 1 h. Upon the completion consumption of **6i** (monitored by LC-MS analysis), the reaction was stopped immediately and filtered through a plug of activated, neutral Al_2O_3 (Brockman grade I, 58–60Å). The solvent was removed under reduced pressure. The resulting residue was purified by silica gel chromatography (30% ethyl acetate–hexanes), giving **7** as yellow oil (28.2 mg, 96%).
$\mathbf{R}_f$ = 0.15 (20% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.50–7.26 (m, 5H), 5.13 (s, 2H), 4.59 (dtdd, *J* = 50.0, 7.5, 5.0, 2.6 Hz, 1H), 3.53 (t, *J* = 4.5 Hz, 4H), 2.62 (ddd, *J* = 19.1, 14.0, 7.6 Hz, 1H), 2.55–2.33 (m, 1H), 2.55–2.33 (m, 4H), 1.77–1.47 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR ($CDCl_3$, 125 MHZ): δ 155.2, 136.8, 128.5, 128.0, 127.9, 93.6 (d, $J_{C\text{-}F}$ = 170.0 Hz), 67.1, 62.1 (d, $J_{C\text{-}F}$ = 20.8 Hz), 53.5, 43.8, 26.6 (d, $J_{C\text{-}F}$ = 21.3 Hz), 9.3 (d, $J_{C\text{-}F}$ = 6.1 Hz).
^{19}F NMR ($CDCl_3$, 471 MHz): δ -181.26.
FTIR (thin film): cm^{-1} 2935, 2812, 1697, 1426, 1233, 1119, 997, 854, 763, 697.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{24}FN_2O_2^+$ 295.1916; found: 295.1816.



4-(2-Fluorocyclohexyl)morpholine (8). To a stirring solution of 4-(2-fluorocyclohex-3-en-1-

yl)morpholine **6m** (18.5 mg, 0.1 mmol, 1 equiv) in CH_2Cl_2 (2.0 mL) was added Pd/C (10% on activated carbon, 4 mg) and $TsOH{\cdot}H_2O$ (19 mg, 0.1 mmol, 1.0 equiv) at room temperature. After the inner atmosphere of the flask was changed to hydrogen by a hydrogen balloon (1atm), the resulting mixture was allowed to stir at room temperature for 1 h. Upon the completion consumption of **6m** (monitored by LC-MS analysis), the reaction was stopped immediately and filtered through a plug of activated, neutral Al_2O_3 (Brockman grade I, 58–60Å). The solvent was removed under reduced pressure. The resulting residue was purified by silica gel chromatography (50% ethyl acetate–hexanes), giving **8** as yellow oil (17.2 mg, 92%).

$\mathbf{R_f}$ = 0.20 (50% ethyl acetate–hexanes).

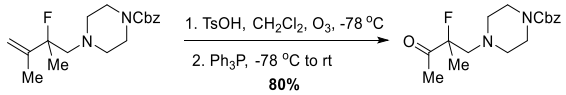
^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.52 (dtd, *J* = 50.3, 10.1, 4.8 Hz, 1H), 3.71 (t, *J* = 4.4 Hz, 4H), 2.69 (t, *J* = 4.4 Hz, 4H), 2.50 (dddd, 13.6 Hz, 11.3 Hz, 4.8 Hz, 2.2 Hz, 1H), 2.20–2.00 (m, 1H), 1.95–1.81 (m, 1H), 1.78–1.65 (m, 2H), 1.53–1.38 (m, 1H), 1.33–1.12 (m, 1H), 1.33–1.12 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHZ): δ 92.0 (d, $J_{C\text{-}F}$ = 177.3 Hz), 67.7, 67.2 (d, $J_{C\text{-}F}$ = 15.3 Hz), 49.8, 32.3 (d, $J_{C\text{-}F}$ = 18.0 Hz), 26.1 (d, $J_{C\text{-}F}$ = 8.3 Hz), 24.7 (d, $J_{C\text{-}F}$ = 1.8 Hz), 23.8 (d, $J_{C\text{-}F}$ = 11.2 Hz).

^{19}F NMR ($CDCl_3$, 471 MHz): δ -174.21.

FTIR (thin film): cm^{-1} 2933, 2854, 1451, 1266, 1116, 1012, 940, 868, 848, 665.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{19}FNO^+$ 188.1445; found: 188.1444.



6k **9**

Benzyl 4-(2-fluoro-2-methyl-3-oxobutyl)piperazine-1-carboxylate (9). A solution of benzyl 4-(2-fluoro-2,3-dimethylbut-3-en-1-yl)piperazine-1-carboxylate **6k** (32.0 mg, 0.10 mmol, 1.0 equiv) and $TsOH{\cdot}H_2O$ (28.5 mg, 0.15 mmol, 1.5 equiv) in CH_2Cl_2 was cooled to -78 °C. Ozone was then bubbled through until the solution turned light blue after 10 min. Then triphenylphosphine (39.3, 0.15 mmol, 1.5 equiv) was added. The reaction mixture was allowed to slowly warm up to room temperature and to stir for another 8 h. To the reaction mixture was added water (4 mL) and extracted with dichloromethane (8 mL × 3). The combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The crude reaction mixture was purified by silica column chromatography (50% ethyl acetate–hexanes), giving **9** as yellow oil (25.8 mg, 80%).

$\mathbf{R_f}$ = 0.20 (25% ethyl acetate–hexanes).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40–7.28 (m, 5H), 5.11 (s, 2H), 2.79 (dd, *J* = 33.5, 14.4 Hz, 1H), 2.62 (dd, *J* = 15.6, 14.4 Hz, 1H), 2.69–2.54 (m, 2H), 2.49–2.33 (m, 2H), 2.28 (d, *J* = 5.3 Hz, 3H), 1.35 (d, *J* = 21.5 Hz, 3H).

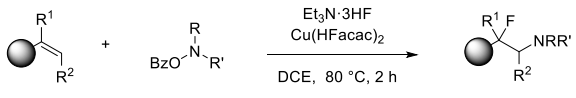
^{13}C NMR ($CDCl_3$, 125 MHZ): δ 210.9 (d, $J_{C\text{-}F}$ = 30.2 Hz), 155.2, 136.7, 128.5, 128.0, 127.9, 102.7 (d, $J_{C\text{-}F}$ = 184.9 Hz), 67.1, 63.9 (d, $J_{C\text{-}F}$ = 19.3 Hz), 54.2 (d, $J_{C\text{-}F}$ = 2.4 Hz), 44.0, 26.7, 20.8 (d, $J_{C\text{-}F}$ = 23.9 Hz).

^{19}F NMR ($CDCl_3$, 471 MHz): δ -156.11.

FTIR (thin film): cm^{-1} 2860, 2810, 1697, 1425, 1358, 1236, 1098, 1008, 849, 734, 696.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{24}FN_2O_3^+$ 323.1766; found: 323.1764.

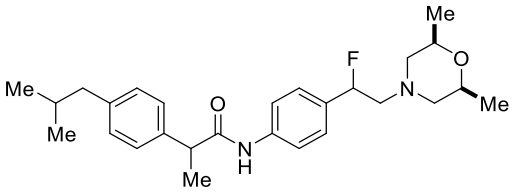
7.2. Synthesis of the bioactive β-fluoro alkylamine compounds



1 **2** **10**

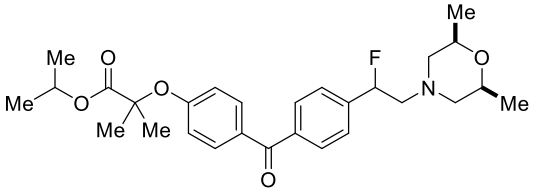
General procedure 3 (GP3) for alkene aminofluorination reactions.

To a 10-mL FEP tube with Teflon-coated micro stir bar was added *O*-benzoylhydroxylamine **2** (0.2 mmol, 1.0 equiv) and $Cu(HFacac)_2$ (2.4 mg, 2.5 mol%). DCE (1.0 mL), alkene **1** (0.4 mmol, 2.0 equiv), and Et_3N•3HF (322 mg, 2 mmol, 10 equiv) were sequentially added. The mixture was allowed to stir at 80 °C for 2 h until the consumption of *O*-benzoylhydroxylamine (verified by TLC, 20% ethyl acetate–hexanes). The resulting reaction mixture was cooled to room temperature and quenched through the addition of Et_3N (0.5 mL). The solution was then diluted with ethyl acetate to a final volume of 5.0 mL and filtered through a plug of activated, neutral Al_2O_3 (Brockman grade I, 58–60Å). The filtrate was concentrated under reduced pressure, providing the crude reaction mixture. The crude reaction mixture was purified by silica column chromatography.



10a

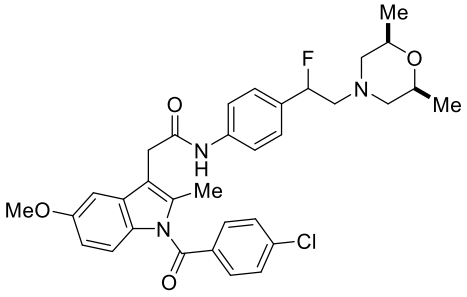
***N*-(4-(2-(2,6-Dimethylmorpholino)-1-fluoroethyl)phenyl)-2-(4-isobutylphenyl)propanamide (10a).** Synthesized using **GP3** from **1aa** and *O*-benzoyl-2,6-dimethyl-hydroxylmorpholine **2h**. ^{19}F-NMR analysis of the crude reaction mixture indicated a diastereomeric ratio (dr) of 1:1.
Isolated by flash column chromatography (20% ethyl acetate–hexanes to 33% ethyl acetate–hexanes), as a yellowish oil (55.5 mg, 63%).
$\mathbf{R}_f$ = 0.10 (33% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.59 (ddd, *J* = 48.6, 8.5, 1.7 Hz, 1H), 3.78–3.65 (m, 2H), 3.78–3.65 (m, 1H), 2.90 (d, *J* = 11.3 Hz, 1H), 2.87–2.81 (m, 1H), 2.79 (d, *J* = 10.4 Hz, 1H), 2.57 (dd, *J* = 33.8, 14.5 Hz, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.97–1.79 (m, 2H), 1.97–1.79 (m, 1H), 1.58 (d, *J* = 7.1 Hz, 3H), 1.16 (d, *J* = 4.1 Hz, 3H), 1.15 (d, *J* = 4.1 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR ($CDCl_3$, 125 MHZ): δ 172.7, 141.2, 138.1, 137.9, 134.4 (d, $J_{C\text{-}F}$ = 20.3 Hz), 129.9, 127.4, 126.3 (d, $J_{C\text{-}F}$ = 6.6 Hz), 119.6, 92.2 (d, $J_{C\text{-}F}$ = 173.6 Hz), 71.6, 64.4 (d, $J_{C\text{-}F}$ = 23.5 Hz), 59.9, 59.6, 47.8, 45.0, 30.2, 22.4, 19.2, 19.1, 18.5.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -175.18, -175.20.
FTIR (thin film): cm^{-1} 2969, 2632, 2868, 1663, 1601, 1516, 1454, 1411, 1248, 1083, 885, 840, 735.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{38}FN_2O_2^+$ 441.2912; found: 441.2912.



10b

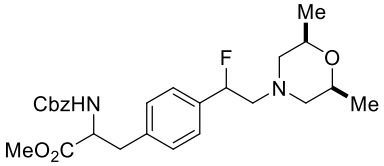
Isopropyl 2-(4-(4-(2-(2,6-dimethylmorpholino)-1-fluoroethyl)benzoyl)phenoxy)-2-methylpropanoate (10b). Synthesized using **GP3** from **1ab** and *O*-benzoyl-2,6-dimethyl-hydroxylmorpholine **2h**. Isolated by flash column chromatography (20% ethyl acetate–hexanes to 40% ethyl acetate–hexanes), as a yellowish oil (37.0 mg, 38%).
$\mathbf{R}_f$ = 0.20 (33% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.76 (d, *J* = 4.1 Hz, 2H), 7.74 (d, *J* = 4.1 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H),

6.86 (d, J = 8.1 Hz, 2H), 5.73 (ddd, J = 48.9, 8.5, 2.3 Hz, 1H), 5.19–4.95 (m, 1H), 3.79–3.58 (m, 2H), 2.89 (ddd, J = 22.5, 14.4, 8.5 Hz, 2H), 2.81 (d, J = 10.9 Hz, 1H), 2.66 (ddd, J = 33.6, 14.4, 2.3 Hz, 1H), 1.95 (dd, J = 23.4, 10.8 Hz, 2H), 1.66 (s, 6H), 1.20 (d, J = 6.3 Hz, 6H), 1.18 (d, J = 3.1 Hz, 3H), 1.17 (d, J = 3.1 Hz, 3H).
^{13}C NMR ($CDCl_3$, 125 MHZ): δ 195.0, 173.1, 159.7, 142.7 (d, $J_{C\text{-}F}$ = 20.0 Hz), 138.2, 132.0, 130.4, 129.9, 125.2 (d, $J_{C\text{-}F}$ = 7.3 Hz), 117.2, 92.2 (d, $J_{C\text{-}F}$ = 175.4 Hz), 79.4, 71.7, 69.4, 64.4 (d, $J_{C\text{-}F}$ = 22.5 Hz), 60.0, 59.7, 25.4, 21.5, 19.2, 19.1.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -179.49.
FTIR (thin film): cm^{-1} 2978, 2933, 2807, 1729, 1653, 1598, 1249, 1144, 1102, 929, 854, 767.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{37}FNO_5^+$ 486.2650; found: 486.2645.



10c

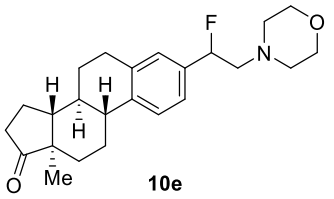
2-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)-*N*-(4-(2-(2,6-dimethylmorpholino)-1-fluoroethyl)phenyl)acetamide (10c). Synthesized using **GP3** from **1ac** and *O*-benzoyl-2,6-dimethyl-hydroxylmorpholine **2h** from the reaction on 0.1 mmol scale. Isolated by flash column chromatography (33% ethyl acetate–hexanes to 70% ethyl acetate–hexanes), as a yellowish oil (38.3 mg, 65%).
$\mathbf{R}_f$ = 0.20 (67% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.67 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 7.43–7.33 (m, 2H), 7.38 (br, 1H), 7.30–7.16 (m, 2H), 6.94 (s, 1H), 6.87 (d, J = 7.3 Hz, 1H), 6.71 (d, J = 7.3 Hz, 1H), 5.59 (dd, J = 48.6, 7.5 Hz, 1H), 3.80 (s, 3H), 3.80 (s, 2H), 3.76–3.64 (m, 2H), 2.88 (d, J = 10.7 Hz, 1H), 2.85–2.80 (m, 1H), 2.77 (d, J = 11.1 Hz, 1H), 2.64–2.49 (m, 1H), 2.44 (s, 3H), 1.97–1.83 (m, 2H), 1.16 (d, J = 3.3 Hz, 3H), 1.15 (d, J = 3.3 Hz, 3H).
^{13}C NMR ($CDCl_3$, 125 MHZ): δ 168.4, 168.3, 156.4, 139.7, 137.6, 136.7, 135.1, 134.9, 133.5, 131.2, 131.0, 130.1, 129.3, 126.3 (d, $J_{C\text{-}F}$ = 6.6 Hz), 120.1, 115.2, 112.5, 112.2, 100.8, 92.2 (d, $J_{C\text{-}F}$ = 173.7 Hz), 71.6, 64.4 (d, $J_{C\text{-}F}$ = 23.4 Hz), 60.0, 59.6, 55.8, 33.4, 19.2, 19.1, 13.4.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -175.59.
FTIR (thin film): cm^{-1} 3294, 2929, 2855, 1679, 1603, 1477, 1357, 1322, 1144, 1087, 836, 754.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{33}H_{36}ClFN_3O_4^+$ 592.2373; found: 592.2372.



10d

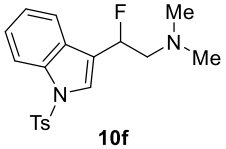
Methyl 2-(((benzyloxy)carbonyl)amino)-3-(4-(2-(2,6-dimethylmorpholino)-1-fluoroethyl)phenyl) propanoate (10d). Synthesized using **GP3** from **1ad** and *O*-benzoyl-2,6-dimethyl-hydroxylmorpholine **2h**. ^{19}F-NMR analysis of the crude reaction mixture indicated a diastereomeric ratio (dr) of 1:1. Isolated by flash column chromatography (20% ethyl acetate–hexanes to 33% ethyl acetate–hexanes), as a yellowish oil (56.8 mg, 60%).
$\mathbf{R}_f$ = 0.25 (50% ethyl acetate–hexanes).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39–7.29 (m, 5H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 5.62 (ddd, *J* = 48.8, 8.7, 1.9 Hz, 1H), 5.22 (d, *J* = 6.8 Hz, 1H), 5.13–5.01 (m, 2H), 4.66 (dd, *J* = 13.5, 5.8 Hz, 1H), 3.83–3.61 (m, 2H), 3.72 (s, 3H), 3.21–3.02 (m, 2H), 2.90 (d, *J* = 11.0 Hz, 1H), 2.88–2.82 (m, 1H), 2.79 (d, *J* = 11.0 Hz, 1H), 2.57 (dd, *J* = 34.8, 14.3 Hz, 1H), 1.97–1.85 (m, 2H), 1.17 (d, *J* = 2.5 Hz, 3H), 1.16 (d, *J* = 2.5 Hz, 3H).
^{13}C NMR ($CDCl_3$, 125 MHZ): δ 171.8, 155.6, 137.7 (d, $J_{C\text{-}F}$ = 20.1 Hz), 136.2, 136.1, 129.5, 128.6, 128.3, 128.1, 125.8 (d, $J_{C\text{-}F}$ = 6.7 Hz), 92.4 (d, $J_{C\text{-}F}$ = 173.7 Hz), 71.7, 71.6, 67.0, 64.5 (d, $J_{C\text{-}F}$ = 23.0 Hz), 60.1, 59.6, 54.7, 52.4, 37.9, 37.8, 19.2, 19.1.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -176.68, -176.68.
FTIR (thin film): cm^{-1} 3330, 2970, 2870, 1718, 1514, 1454, 1212, 1112, 886, 736, 698.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{34}FN_2O_5^+$ 473.2446; found: 473.2445.



10e

3-(1-Fluoro-2-morpholinoethyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a] phenanthren-17-one (10e). Synthesized using **GP3** from **1ae** and *O*-benzoylhydroxylmorpholine **2a**. Run the reaction at (0.1 mmol) scale. ^{19}F-NMR analysis of the crude reaction mixture indicated a diastereomeric ratio (dr) of 1:1. Isolated by flash column chromatography (10% ethyl acetate–hexanes to 40% ethyl acetate–hexanes), as a yellowish oil (33.6 mg, 87%).
$\mathbf{R}_f$ = 0.25 (50% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30 (d, *J* = 8.1 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 7.08 (s, 1H), 5.61 (ddd, *J* = 49.1, 8.9, 1.8 Hz, 1H), 3.75 (t, *J* = 4.6 Hz, 4H), 2.99–2.86 (m, 2H), 2.99–2.86 (m, 1H), 2.69–2.56 (m, 1H), 2.69–2.56 (m, 4H), 2.51 (dd, *J* = 18.1, 8.9 Hz, 1H), 2.41 (dd, *J* = 18.1, 10.1 Hz, 1H), 2.36–2.25 (m, 1H), 2.20–2.09 (m, 1H), 2.10–2.00 (m, 2H), 2.00–1.93 (m, 1H), 1.68–1.57 (m, 2H), 1.57–1.40 (m, 4H), 0.91 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHZ): δ 220.7, 140.3, 140.2, 136.8, 136.3 (d, $J_{C\text{-}F}$ = 19.7 Hz), 136.1 (d, $J_{C\text{-}F}$ = 19.7 Hz), 126.3 (d, $J_{C\text{-}F}$ = 6.5 Hz), 126.2 (d, $J_{C\text{-}F}$ = 6.5 Hz), 125.6, 125.5, 123.1, 123.0, 92.6 (d, $J_{C\text{-}F}$ = 173.2 Hz), 92.5 (d, $J_{C\text{-}F}$ = 173.2 Hz), 67.0, 65.0 (d, $J_{C\text{-}F}$ = 23.5 Hz), 64.9 (d, $J_{C\text{-}F}$ = 23.5 Hz), 54.1, 50.5, 48.0, 44.4, 38.2, 38.1, 35.9, 31.6, 29.5, 29.4, 26.3, 25.7, 21.6, 13.9.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -175.26, -175.53.
FTIR (thin film): cm^{-1} 2929, 2855, 1736, 1453, 1257, 1116, 1008, 869, 734.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{33}FNO_2^+$ 386.2490; found: 386.2489.

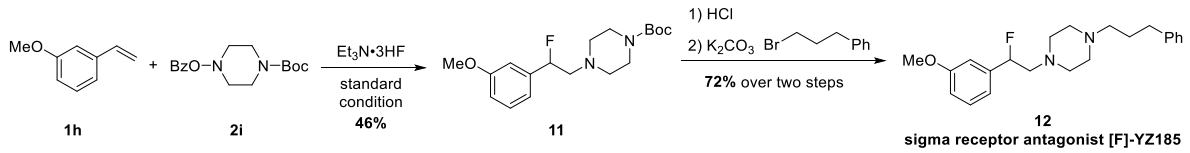


10f

2-Fluoro-*N*,*N*-dimethyl-2-(1-tosyl-1*H*-indol-3-yl)ethan-1-amine (10f). Synthesized using **GP3** from **1af** and *O*-benzoyl-*N*,*N*-dimethylhydroxylamine **2p**. Isolated by flash column chromatography (20% ethyl acetate–hexanes to 50% ethyl acetate–hexanes), as a yellowish oil (20.9 mg, 26%).
$\mathbf{R}_f$ = 0.20 (50% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.97 (d, *J* = 8.3 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 2.3 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 5.85 (ddd, *J* = 48.4, 8.5, 2.2 Hz, 1H), 3.05 (ddd, *J* = 17.0, 14.0, 8.6 Hz, 1H), 2.76 (ddd, *J* = 32.1, 14.0, 2.5 Hz,

1H), 2.40 (s, 6H), 2.35 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHZ): δ 145.2, 135.1 (d, J_{C-F} = 9.0 Hz), 130.0, 128.4 (d, J_{C-F} = 2.7 Hz), 126.9, 125.1, 123.7 (d, J_{C-F} = 9.3 Hz), 123.4, 120.2, 120.1, 120.0, 113.8, 87.3 (d, J_{C-F} = 169.8 Hz), 63.5 (d, J_{C-F} = 22.8 Hz), 46.0, 21.6.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -176.88.
FTIR (thin film): cm^{-1} 2923, 2853, 1596, 1446, 1370, 1172, 1019, 974, 746.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{22}FN_2O_2S^+$ 361.1381; found: 361.1377.

7.3. Synthesis of the sigma receptor antagonist derivative [F]-YZ185



To a 10-mL FEP tube with Teflon-coated micro stir bar was added *O*-benzoyl-4-*tert*-butoxycarbonyl-hydroxylpiperazine **2i** (0.2 mmol, 1.0 equiv) and $Cu(HFacac)_2$ (2.4 mg, 2.5 mol%). DCE (1.0 mL), 1-methoxy-3-vinylbenzene **1h** (0.4 mmol, 2.0 equiv), and Et_3N•3HF (322 mg, 2 mmol, 10 equiv) were sequentially added. The mixture was then stirred at 80 °C for 2 h until the consumption of *O*-benzoylhydroxylamine, verified by TLC (20% ethyl acetate–hexanes) analysis. The resulting reaction mixture was cooled to room temperature and quenched through the addition of Et_3N (0.5 mL). The solution was then diluted with ethyl acetate to a final volume of 5.0 mL and filtered through a plug of activated, neutral Al_2O_3 (Brockman grade I, 58–60Å). The filtrate was concentrated under reduced pressure, providing the crude reaction mixture. The crude reaction mixture was purified by silica column chromatography (50% ethyl acetate–hexanes), giving **11** as yellowish oil (30.7 mg, 46%).

tert-Butyl 4-(2-fluoro-2-(3-methoxyphenyl)ethyl)piperazine-1-carboxylate (11).

R_f = 0.15 (25% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.28 (t, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 2H), 6.78 (s, 1H), 5.62 (ddd, *J* = 48.9, 8.7, 2.2 Hz, 1H), 3.81 (s, 3H), 3.47 (t, *J* = 4.6 Hz, 4H), 2.91 (ddd, *J* = 17.6, 14.3, 8.7 Hz, 1H), 2.65 (ddd, *J* = 34.3, 14.3, 2.5 Hz, 1H), 2.60–2.49 (m, 4H), 1.46 (s, 9H).
^{13}C NMR ($CDCl_3$, 125 MHZ): δ 159.7, 154.7, 140.3 (d, J_{C-F} = 19.8 Hz), 129.6, 117.7 (d, J_{C-F} = 7.1 Hz), 113.9, 111.1 (d, J_{C-F} = 7.8 Hz), 92.6 (d, J_{C-F} = 174.6 Hz), 79.7, 64.6 (d, J_{C-F} = 23.0 Hz), 55.3, 53.4, 28.4.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -177.09.
FTIR (thin film): cm^{-1} 2933, 1692, 1421, 1365, 1245, 1169, 1125, 1004, 868, 779, 698.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{28}FN_2O_3^+$ 339.2079; found: 339.2076.

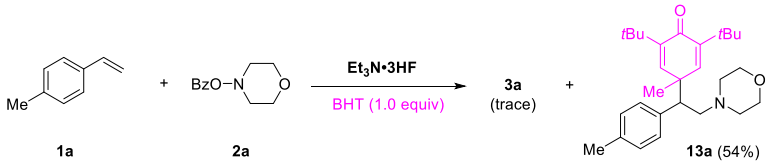
To a 25-mL round-bottom flask was added *tert*-butyl 4-(2-fluoro-2-(3-methoxyphenyl)ethyl)piperazine-1-carboxylate **11** (33.8 mg, 0.1 mmol, 1.0 equiv), 1,4-dioxane (2.0 mL), HCl in 1,4-dioxane (4 M, 0.2 mL, 0.8 mmol, 8.0 equiv). The reaction was allowed to stir at room temperature for 8 h, and then concentrated under reduced pressure. The crude solid was used for the next step without further purification.

To a solution of the crude residue in DMSO (2 mL), was added potassium carbonate (27.6 mg, 0.2 mmol, 2.0 equiv), 1-bromo-3-phenylpropane (23.9 mg, 0.12 mmol, 1.2 equiv). The mixture was allowed to stir at room temperature for overnight. The reaction was quenched by the addition of water (2 mL). The mixture was extracted with ethyl acetate (5 mL × 3). The combined organic layers were washed with water (10 mL × 2) and the brine (10 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash column chromatography (30% ethyl acetate–hexanes to 50% ethyl acetate–hexanes) gave **12** as colorless oil (25.6 mg, 72% over two steps).

1-(2-Fluoro-2-(3-methoxyphenyl)ethyl)-4-(3-phenylpropyl)piperazine (12).
$\mathbf{R_f}$ = 0.15 (50% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.28 (dd, *J* = 8.5, 7.0 Hz, 3H), 7.19 (d, *J* = 7.1 Hz, 3H), 6.94–6.80 (m, 3H), 5.62 (ddd, *J* = 49.1, 8.8, 1.9 Hz, 1H), 3.81 (s, 3H), 2.91 (ddd, *J* = 17.6, 14.3, 8.9 Hz, 1H), 2.78–2.46 (m, 1H), 2.78–2.46 (m, 8H), 2.78–2.46 (m, 2H), 2.45–2.34 (m, 2H), 1.84 (q, *J* = 7.7 Hz, 2H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.7, 142.1, 140.5 (d, $J_{C\text{-}F}$ = 19.7 Hz), 129.6, 128.4, 128.3, 125.8, 117.8 (d, $J_{C\text{-}F}$ = 6.7 Hz), 113.9, 111.1 (d, $J_{C\text{-}F}$ = 7.5 Hz), 92.6 (d, $J_{C\text{-}F}$ = 174.4 Hz), 64.6 (d, $J_{C\text{-}F}$ = 22.8 Hz), 58.0, 55.3, 53.6, 53.1, 33.7, 28.5.
^{19}F NMR ($CDCl_3$, 471 MHz): δ -177.01.
FTIR (thin film): cm^{-1} 2934, 2809, 1699, 1602, 1493, 1454, 1267, 1158, 1030, 784, 748.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{30}FN_2O^+$ 357.2337; found: 357.2337.

8. Mechanism studies

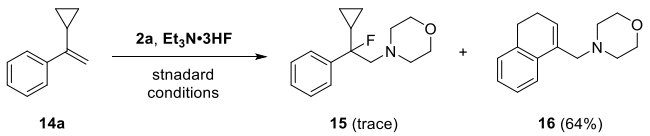
8.1. Control experiment in the presence of 2,6-di-tert-butyl-4-methylphenol (BHT)



To a 10-mL FEP tube with Teflon-coated micro stir bar was added *O*-benzoylhydroxylmorpholine **2a** (41.4 mg, 0.2 mmol, 1.0 equiv), 2,6-di-tert-butyl-4-methylphenol (BHT, 44.1 mg, 0.2 mmol, 1.0 equiv) and $Cu(HFacac)_2$ (2.4 mg, 2.5 mol %). DCE (1.0 mL), 4-methylstyrene **1a** (0.4 mmol, 2.0 equiv) and Et_3N•3HF (322 mg, 2 mmol, 10 equiv) were sequentially added. The mixture was allowed to stir at 80 °C for 2 h until the consumption of *O*-benzoylhydroxylamine (verified by TLC, 20% ethyl acetate–hexanes). The resulting reaction mixture was cooled to room temperature and quenched through the addition of Et_3N (0.5 mL). The solution was then diluted with ethyl acetate to a final volume of 5.0 mL and filtered through a plug of activated, neutral Al_2O_3 (Brockman grade I, 58–60Å). The filtrate was concentrated under reduced pressure, providing the crude reaction mixture. The crude reaction mixture was purified by silica column chromatography (20% ethyl acetate–hexanes), giving **13a** as yellow oil (46.1 mg, 54%).

2,6-Di-*tert*-butyl-4-methyl-4-(2-morpholino-1-(*p*-tolyl)ethyl)cyclohexa-2,5-dien-1-one (13a).
$\mathbf{R_f}$ = 0.31 (33% ethyl acetate–hexanes).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.08 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.56 (d, *J* = 2.8 Hz, 1H), 6.43 (d, *J* = 2.8 Hz, 1H), 3.61–3.50 (m, 4H), 2.92 (dd, *J* = 8.1, 4.5 Hz, 1H), 2.53 (dd, *J* = 12.9, 8.1 Hz, 1H), 2.48 (dd, *J* = 12.9, 4.5 Hz, 1H), 2.32 (s, 3H), 2.28–2.24 (m, 4H), 1.26 (s, 9H), 1.15 (s, 9H), 1.07 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHZ): δ 186.3, 146.5, 146.4, 144.3, 137.3, 136.4, 129.2, 128.5, 66.9, 60.1, 53.9, 52.5, 42.4, 34.9, 34.8, 29.5, 29.4, 25.2, 21.0.
FTIR (thin film): cm^{-1} 1656, 1637, 1456, 1362, 1249, 1118, 910, 868, 734.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{42}NO_2^+$ 424.3210; found: 424.3215.

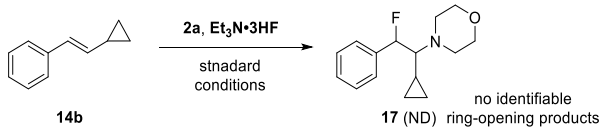
8.2. Radical clock experiments



To a 10-mL FEP tube with Teflon-coated micro stir bar was added *O*-benzoylhydroxylmorpholine **2a** (41.4 mg, 0.2 mmol, 1.0 equiv) and $Cu(HFacac)_2$ (2.4 mg, 2.5 mol %). DCE (1.0 mL), (1-cyclopropylvinyl)benzene **14a** (0.4 mmol, 2.0 equiv), and Et_3N•3HF (322 mg, 2 mmol, 10 equiv) were sequentially added. The mixture was allowed to stir at 80 °C for 2 h until the consumption of *O*-benzoylhydroxylamine (verified by TLC, 20% ethyl acetate–hexanes). The resulting reaction mixture was cooled to room temperature and quenched through the addition of Et_3N (0.5 mL). The solution was then diluted with ethyl acetate to a final volume of 5.0 mL and filtered through a plug of activated, neutral Al_2O_3 (Brockman grade I, 58–60Å). The filtrate was concentrated under reduced pressure, providing the crude reaction mixture. The crude reaction mixture was purified by silica column chromatography (10% ethyl acetate–hexanes), giving **16** as clear oil (29.4 mg, 64%)

4-((3,4-Dihydronaphthalen-1-yl)methyl)morpholine (16).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.22–7.11 (m, 3H), 6.02 (t, *J* = 4.2 Hz, 1H), 3.75–3.66 (m, 4H), 3.30 (s, 2H), 2.76 (t, *J* = 8.0 Hz, 2H), 2.48 (br s, 4H), 2.35–2.26 (m, 2H). Spectroscopic data match a previous report.[8]



To a 10-mL FEP tube with Teflon-coated micro stir bar was added *O*-benzoylhydroxylmorpholine **2a** (41.4 mg, 0.2 mmol, 1.0 equiv) and $Cu(HFacac)_2$ (2.4 mg, 2.5 mol %). DCE (1.0 mL), (*E*)-(2-cyclopropylvinyl)benzene **14b** (0.4 mmol, 2.0 equiv), and Et_3N•3HF (322 mg, 2 mmol, 10 equiv) were sequentially added. The mixture was allowed to stir at 80 °C for 2 h until the consumption of *O*-benzoylhydroxylamine (verified by TLC, 20% ethyl acetate–hexanes). The resulting reaction mixture was cooled to room temperature and quenched through the addition of Et_3N (0.5 mL). The solution was then diluted with ethyl acetate to a final volume of 5.0 mL and filtered through a plug of activated, neutral Al_2O_3 (Brockman grade I, 58–60Å). The filtrate was concentrated under reduced pressure, providing the crude reaction mixture. The crude reaction mixture was analyzed by LC-MS, ^{1}H NMR and ^{19}F NMR spectrometry, none of which shows identifiable ring-opening product **17**.

9. References

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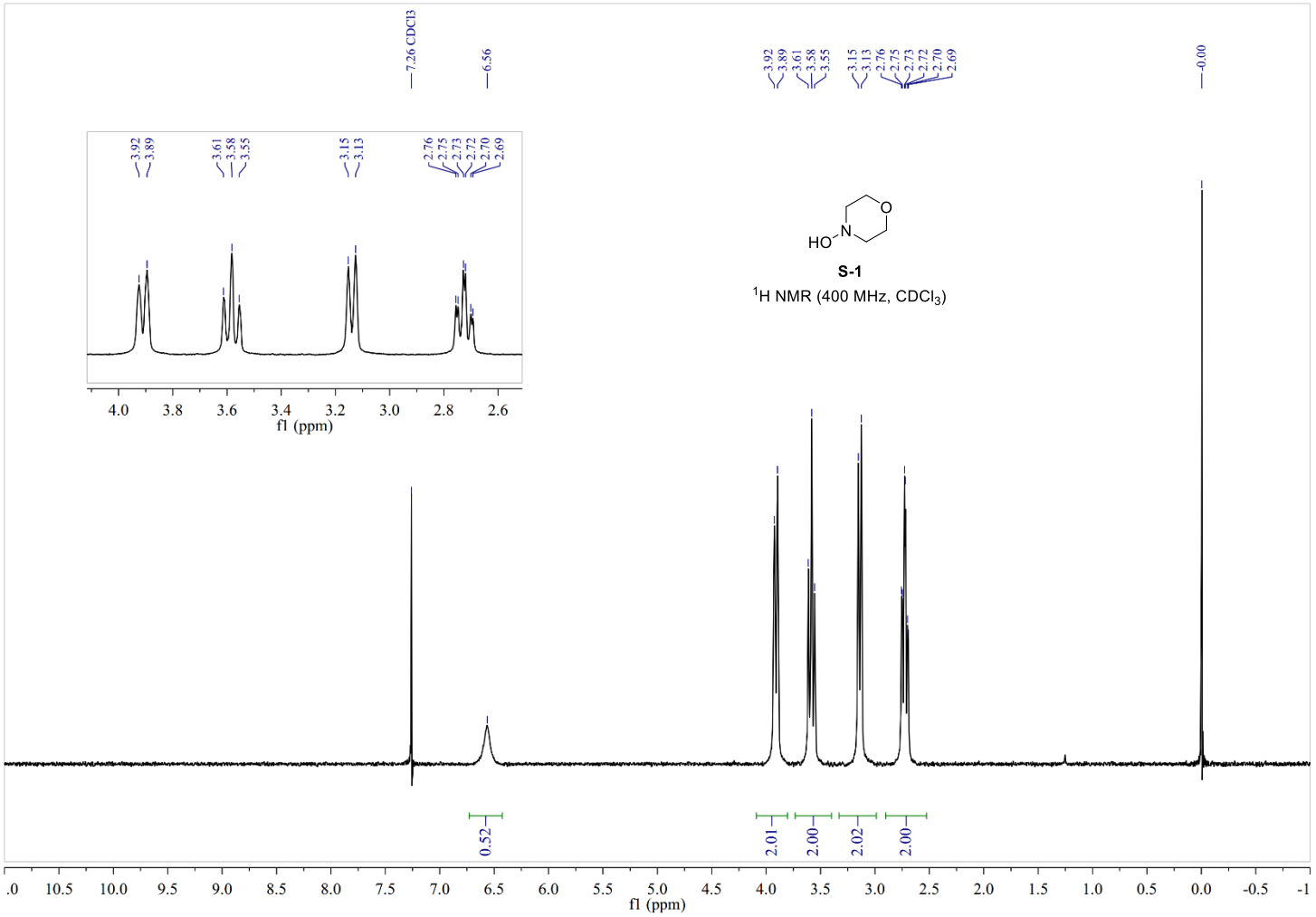
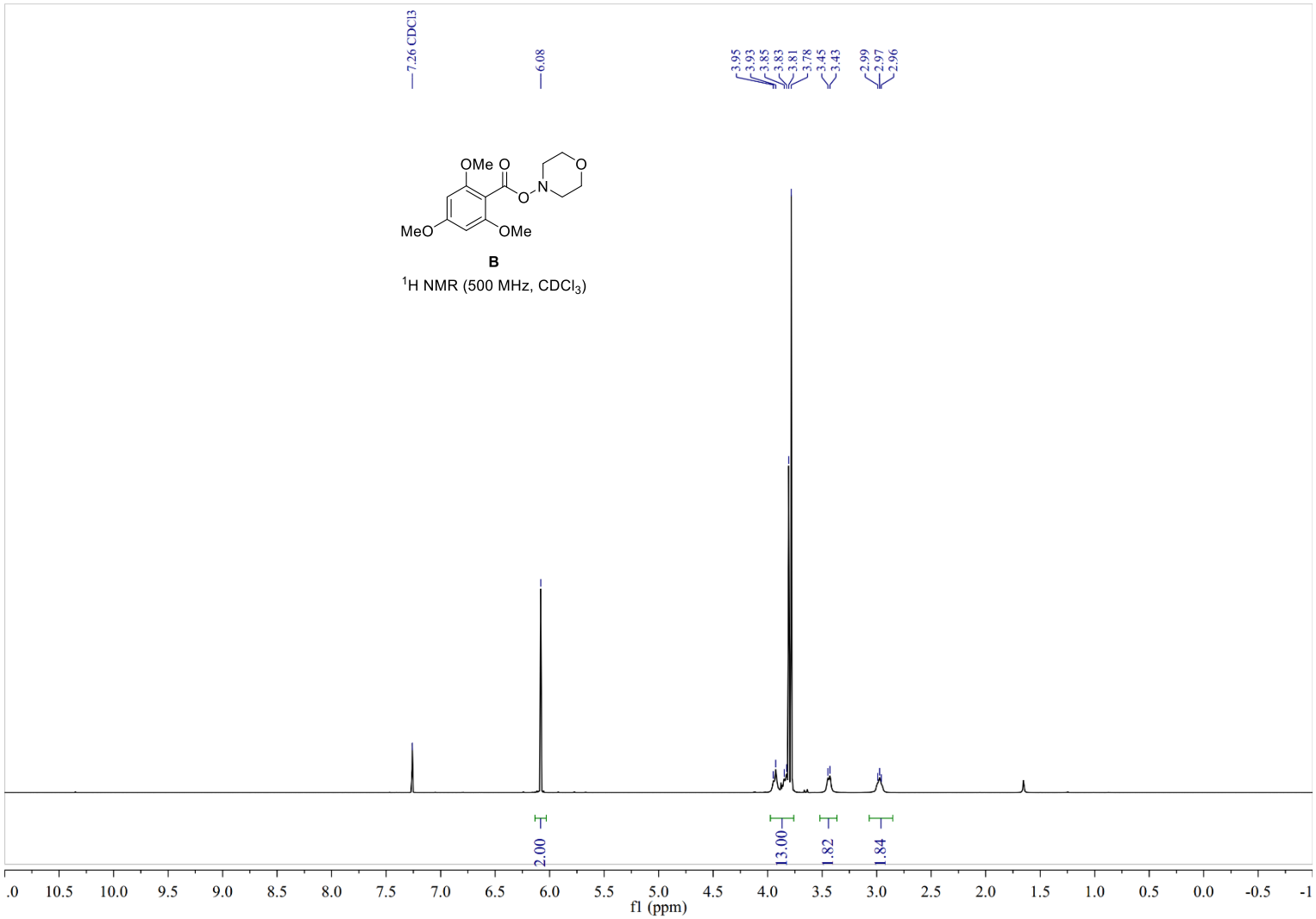
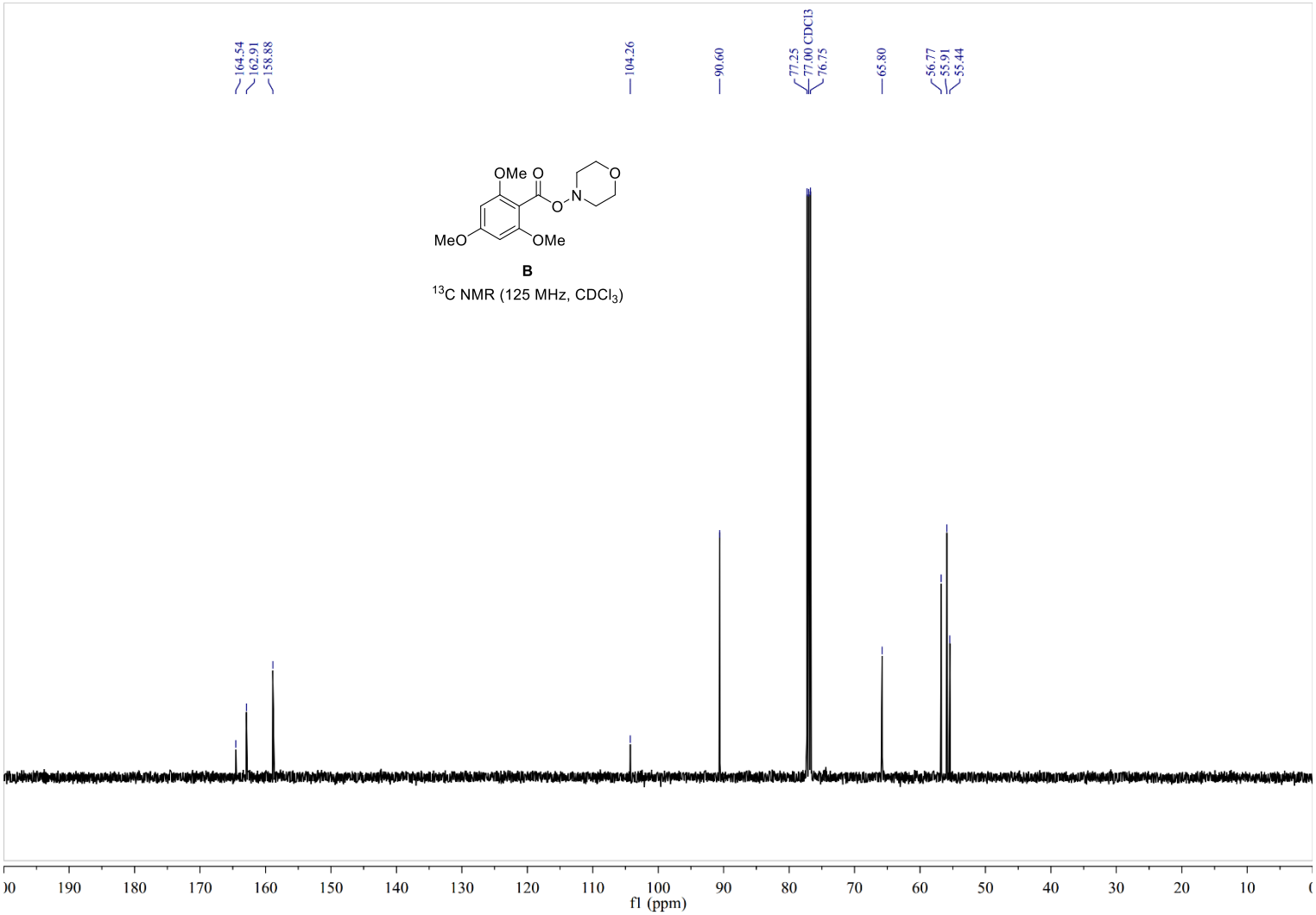
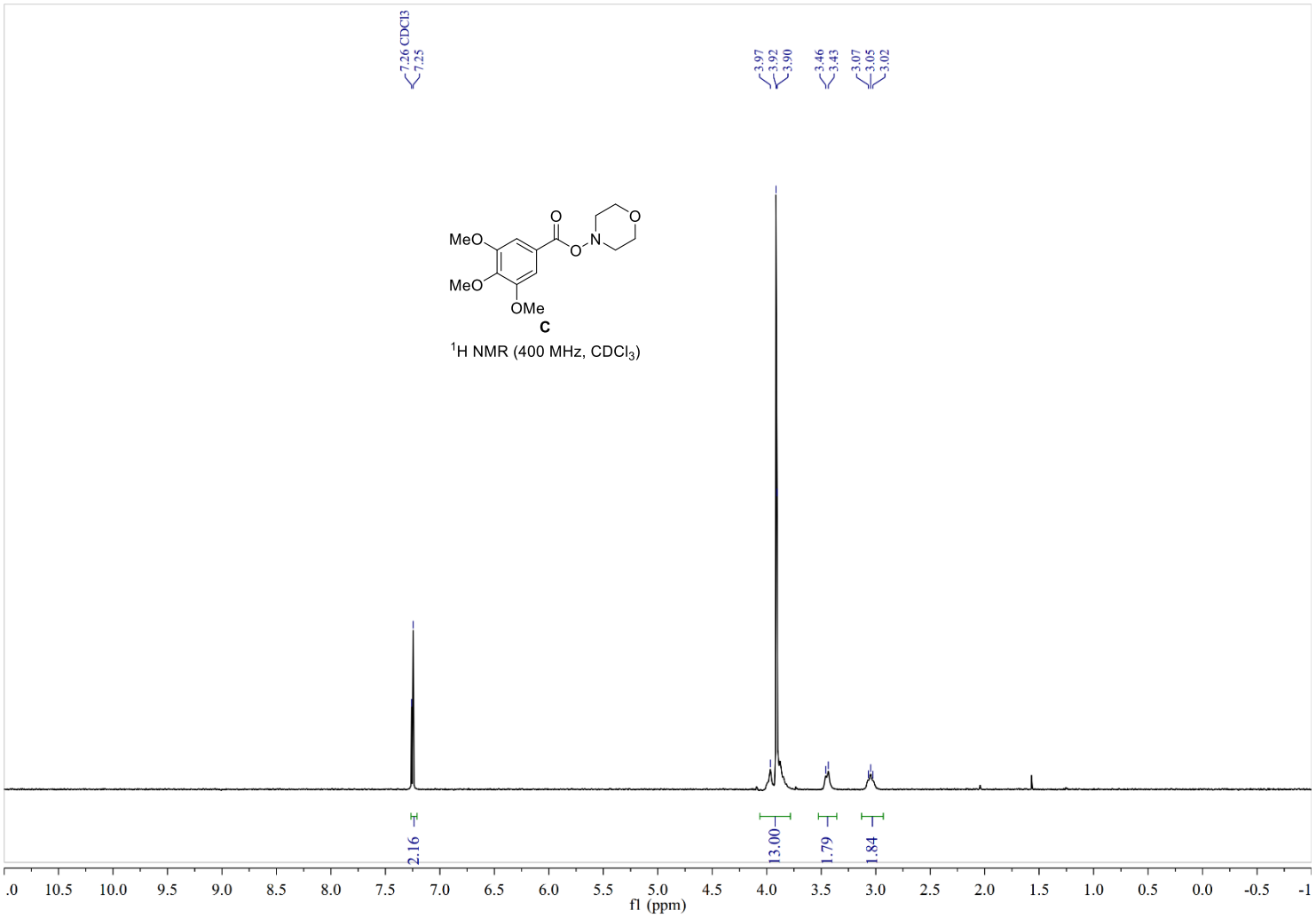
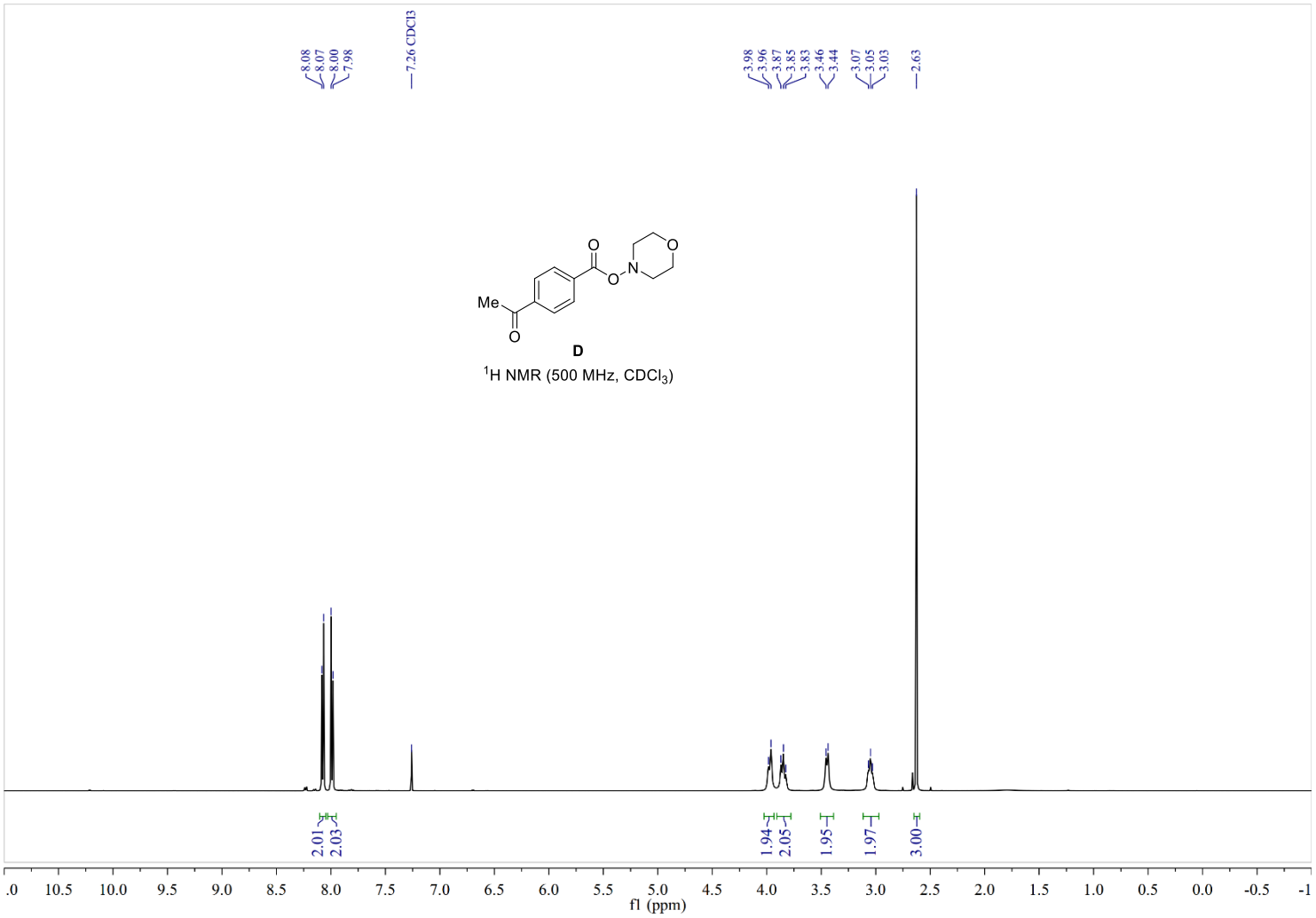
10. Copies of the NMR Spectra




7.26 CDCl3
6.08
3.95
3.93
3.85
3.83
3.81
3.78
3.45
3.43
2.99
2.97
2.96
OMe O
O
N
O
MeO
OMe
B
1H NMR (500 MHz, CDCl3)
2.00
13.00
1.82
1.84
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


164.54
162.91
158.88
104.26
90.60
77.25
77.00 CDCl3
76.75
65.80
56.77
55.91
55.44
OMe O
O
N
O
MeO
OMe
B
13C NMR (125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.26 CDCl3
7.25
3.97
3.92
3.90
3.46
3.43
3.07
3.05
3.02
MeO
MeO
OMe
O
O
N
O
C
1H NMR (400 MHz, CDCl3)
2.16
13.00
1.79
1.84
f1 (ppm)


8.08
8.07
8.00
7.98
7.26 CDCl3
3.98
3.96
3.87
3.85
3.83
3.46
3.44
3.07
3.05
3.03
2.63
Me
O
O
N
O
O
D
1H NMR (500 MHz, CDCl3)
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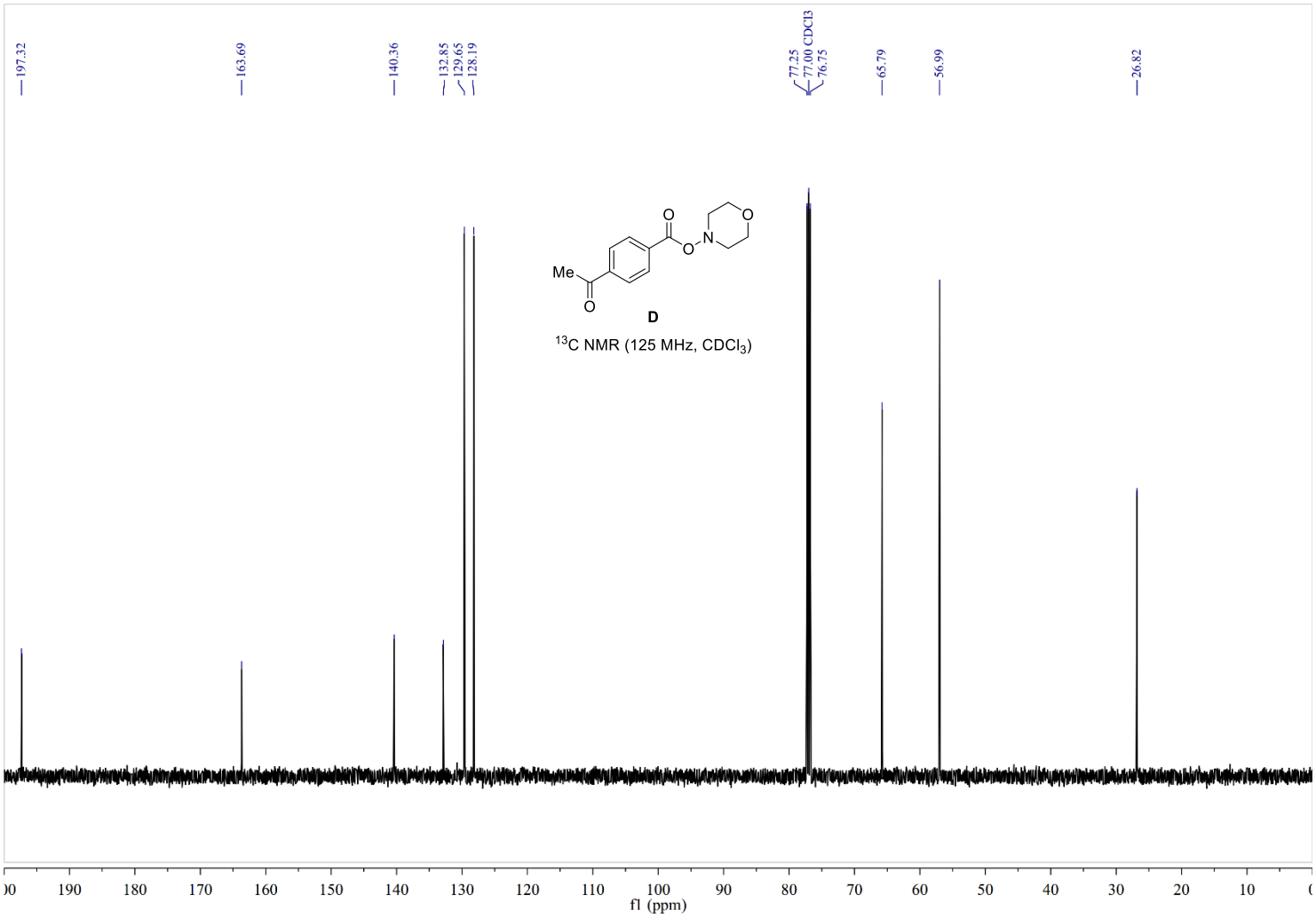
2.03
1.94
2.05
1.95
1.97
3.00
f1 (ppm)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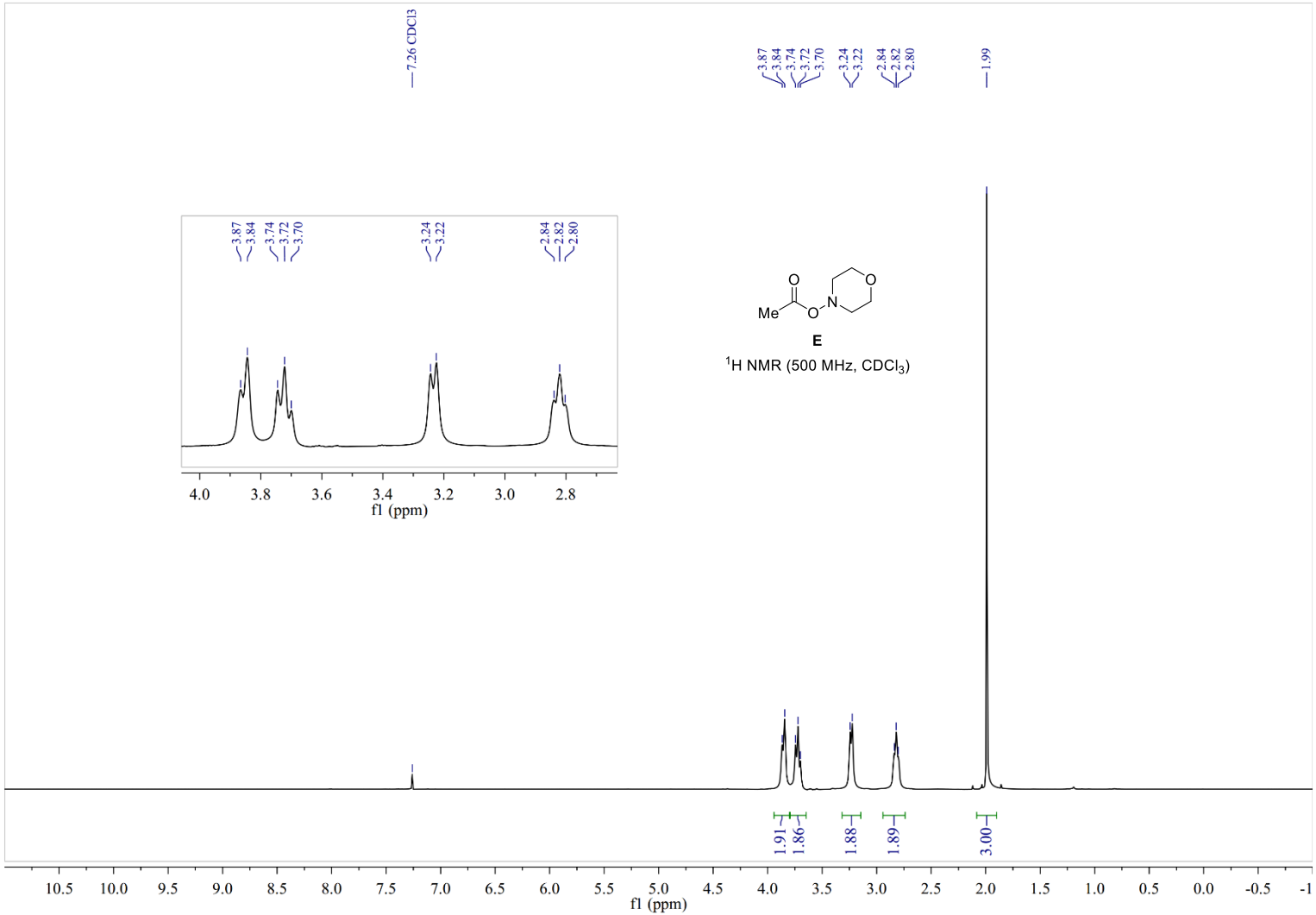
163.69
140.36
132.85
129.65
128.19
77.25
77.00 CDCl3
76.75
65.79
56.99
26.82
Me
O
O
O
N
O
D
13C NMR (125 MHz, CDCl3)
f1 (ppm)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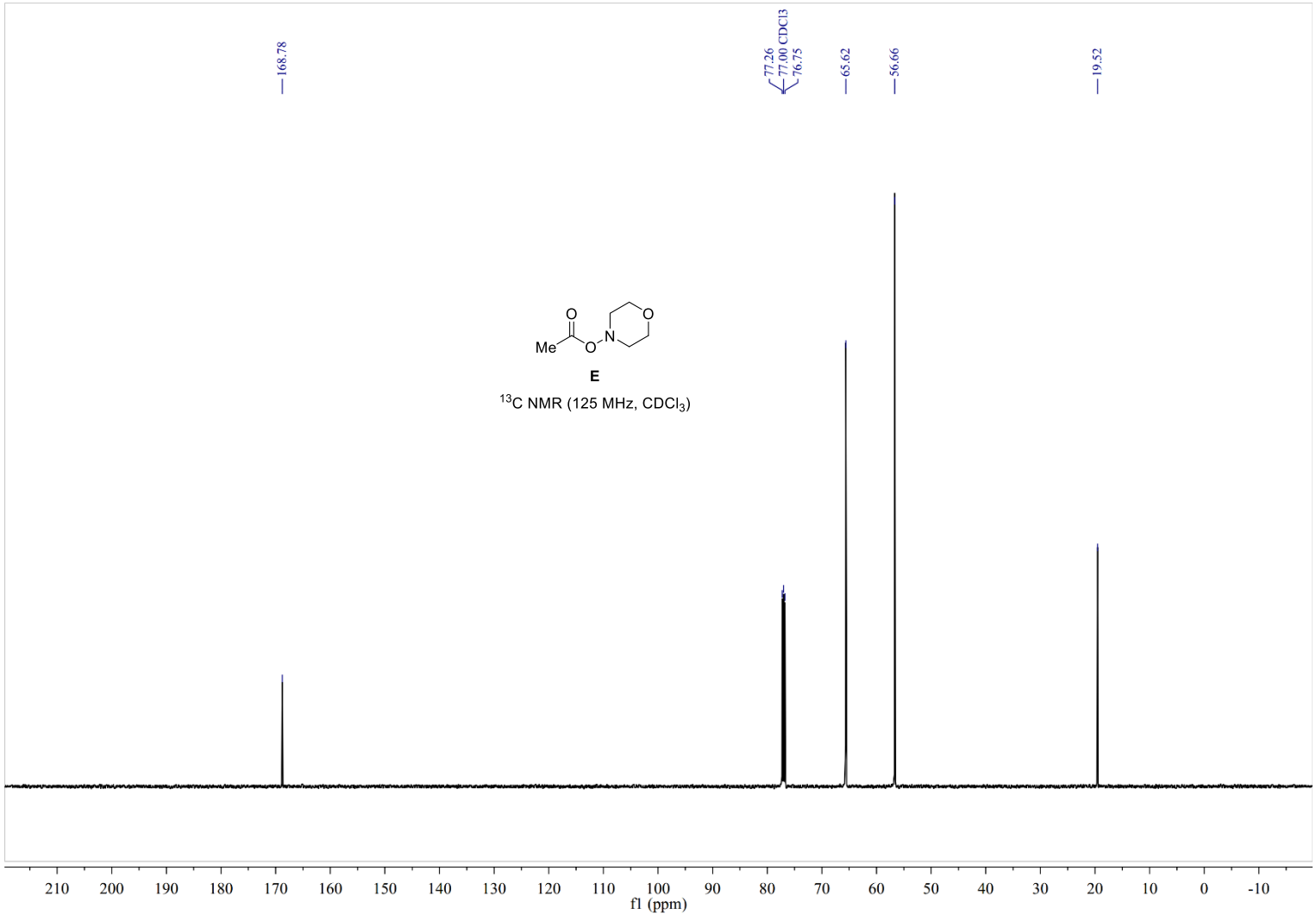
3.87
3.84
3.74
3.72
3.70
3.24
3.22
2.84
2.82
2.80
1.99
Me
O
O
N
O
E
1H NMR (500 MHz, CDCl3)
1.91
1.86
1.88
1.89
3.00
f1 (ppm)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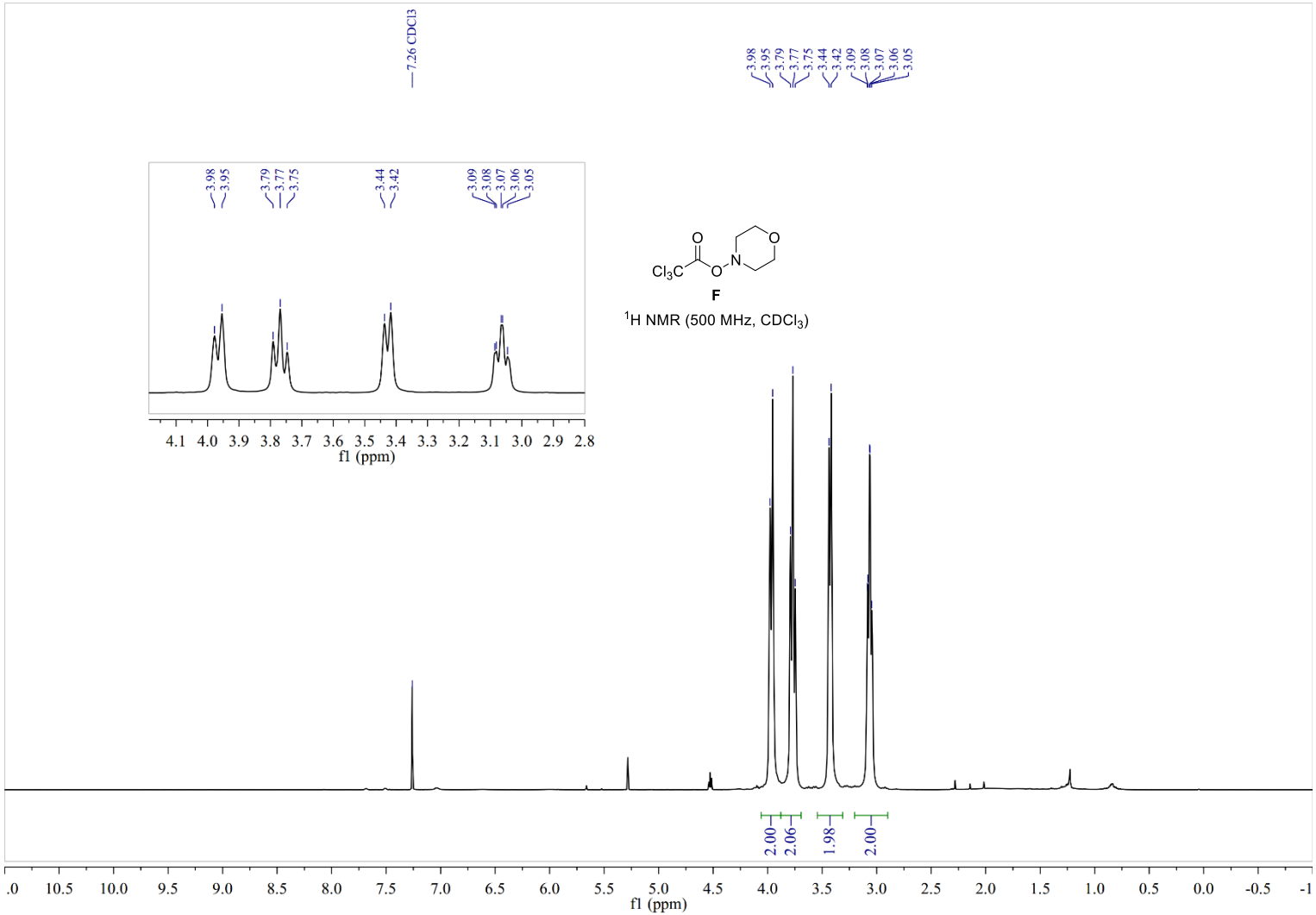
77.26
77.00 CDCl3
76.75
65.62
56.66
19.52
Me
O
O
N
O
E
13C NMR (125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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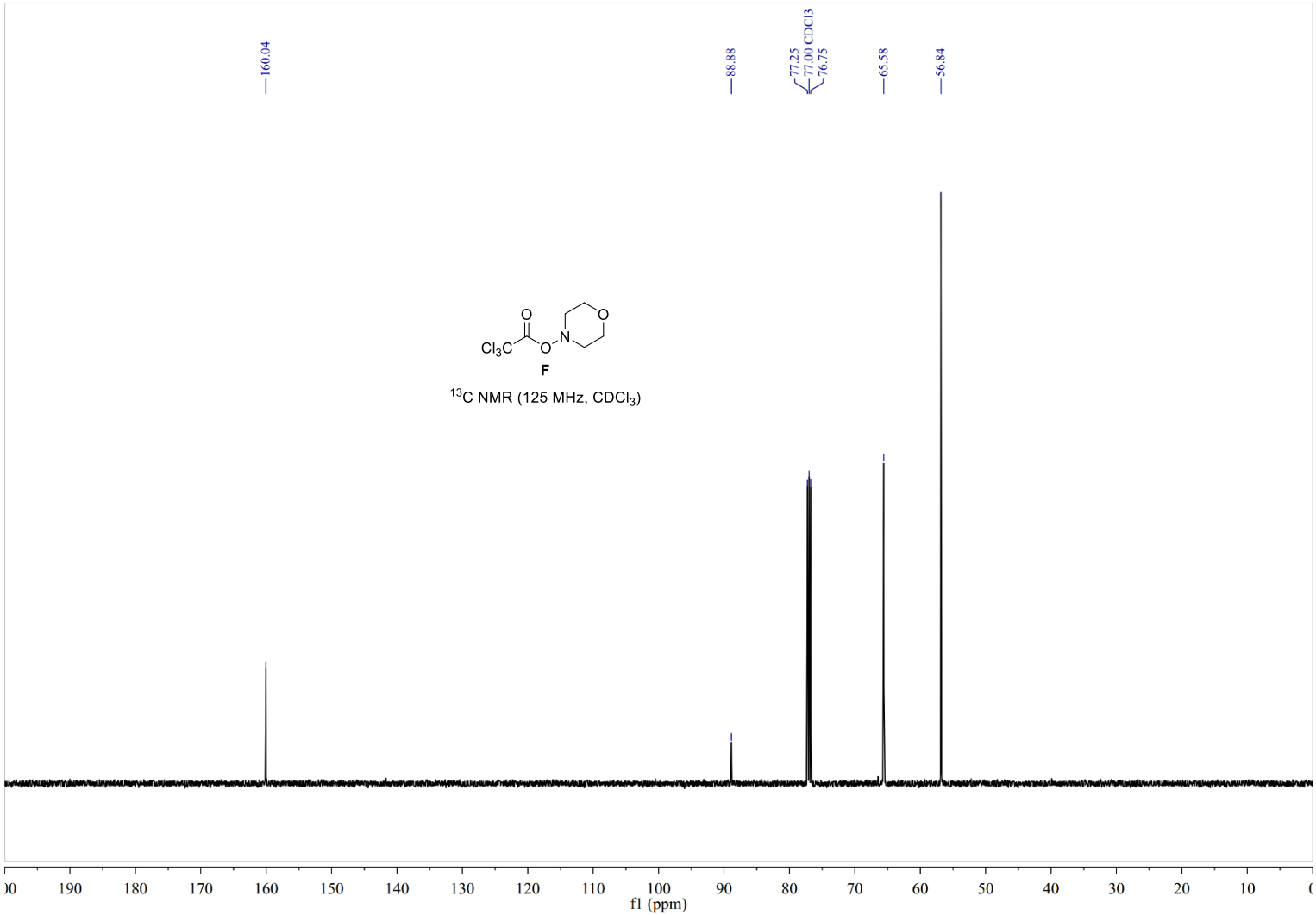
3.98
3.95
3.79
3.77
3.75
3.44
3.42
3.09
3.08
3.07
3.06
3.05
F
1H NMR (500 MHz, CDCl3)
2.00
2.06
1.98
2.00
f1 (ppm)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88.88
77.25
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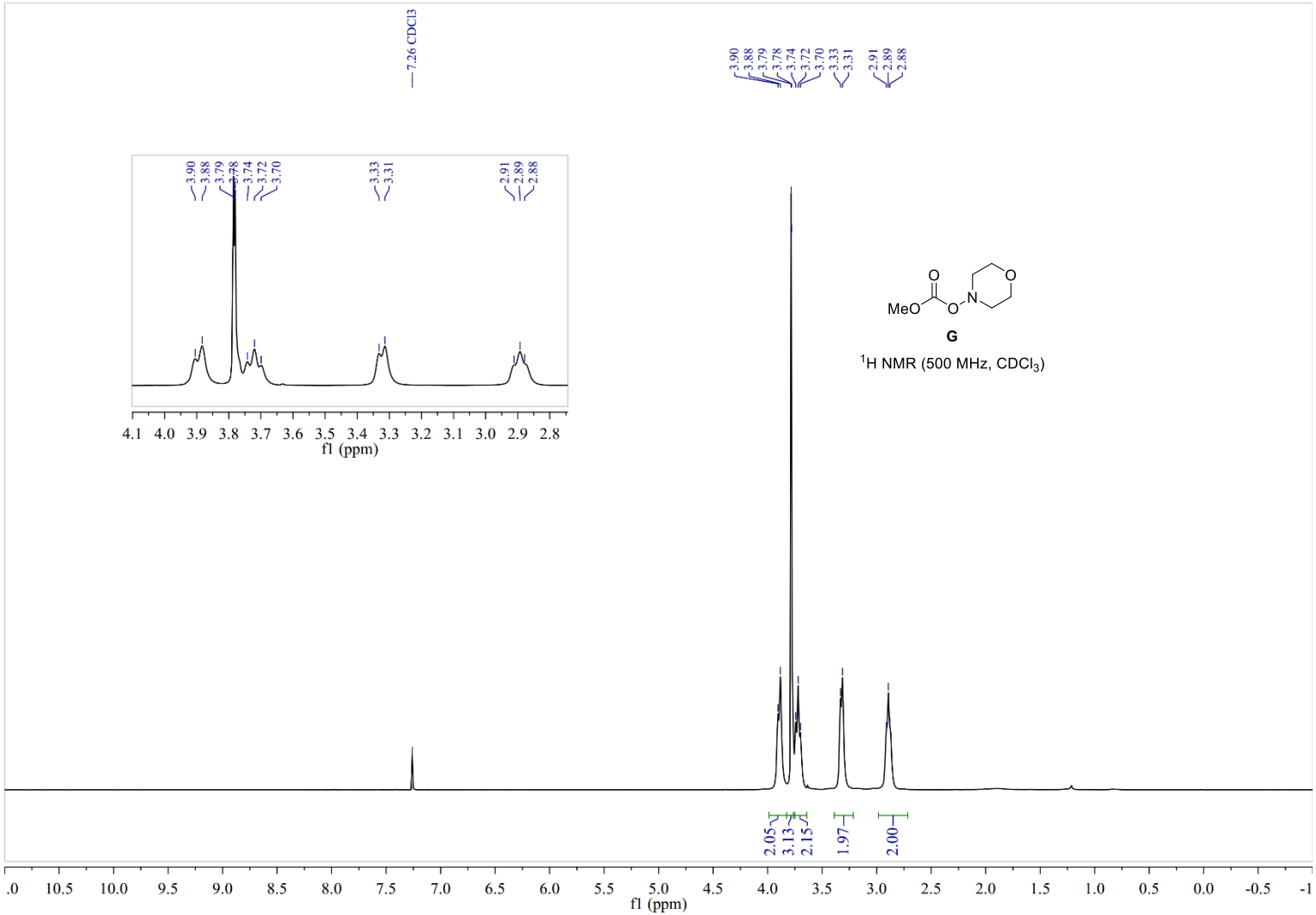
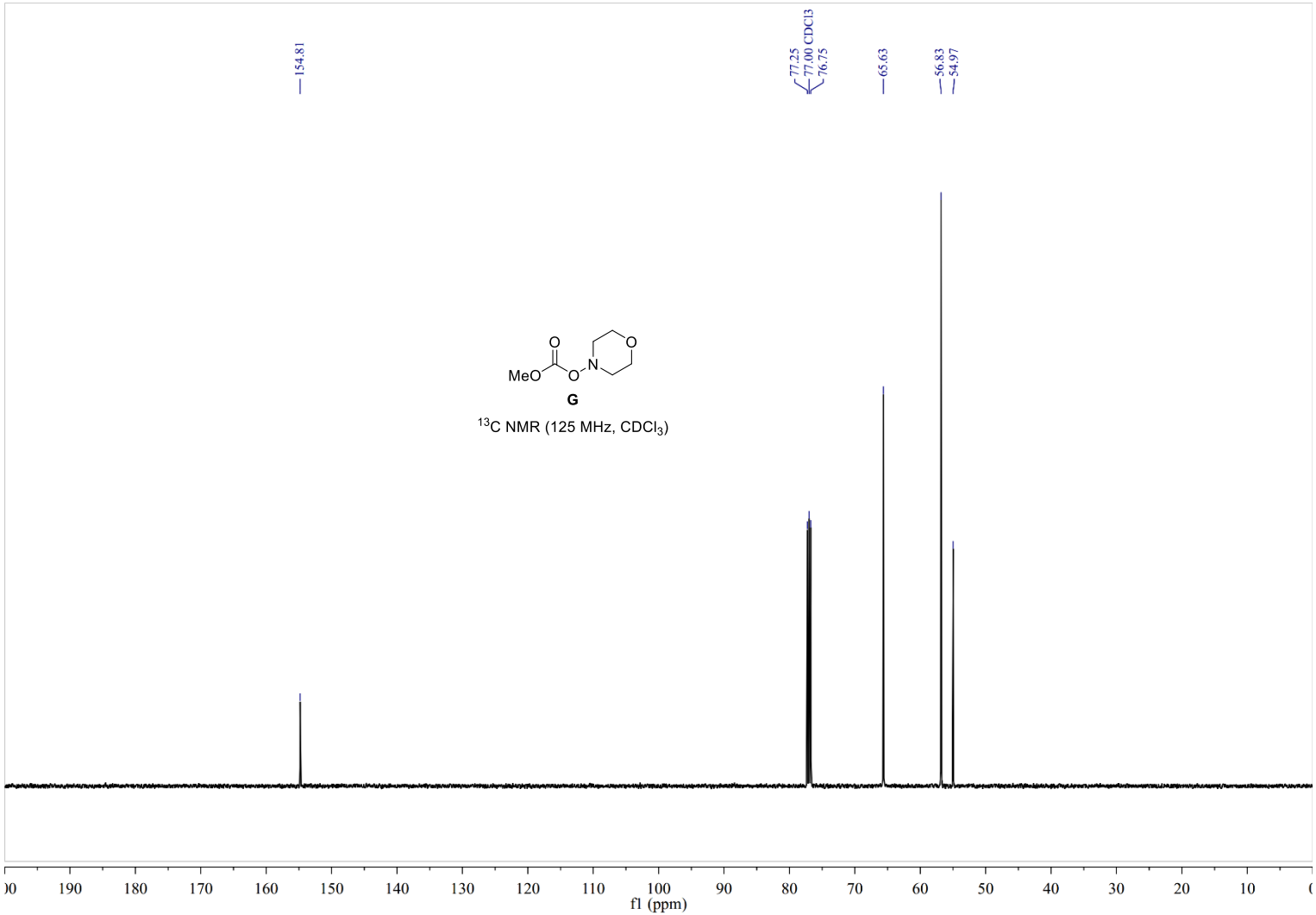
65.58
56.84
O
O
N
O
Cl3C
F
13C NMR (125 MHz, CDCl3)
f1 (ppm)


7.26 CDCl3
3.90
3.88
3.79
3.78
3.74
3.72
3.70
3.33
3.31
2.91
2.89
2.88
MeO
O
N
G
1H NMR (500 MHz, CDCl3)
2.05
3.13
2.15
1.97
2.00
f1 (ppm)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77.25
77.00 CDCl3
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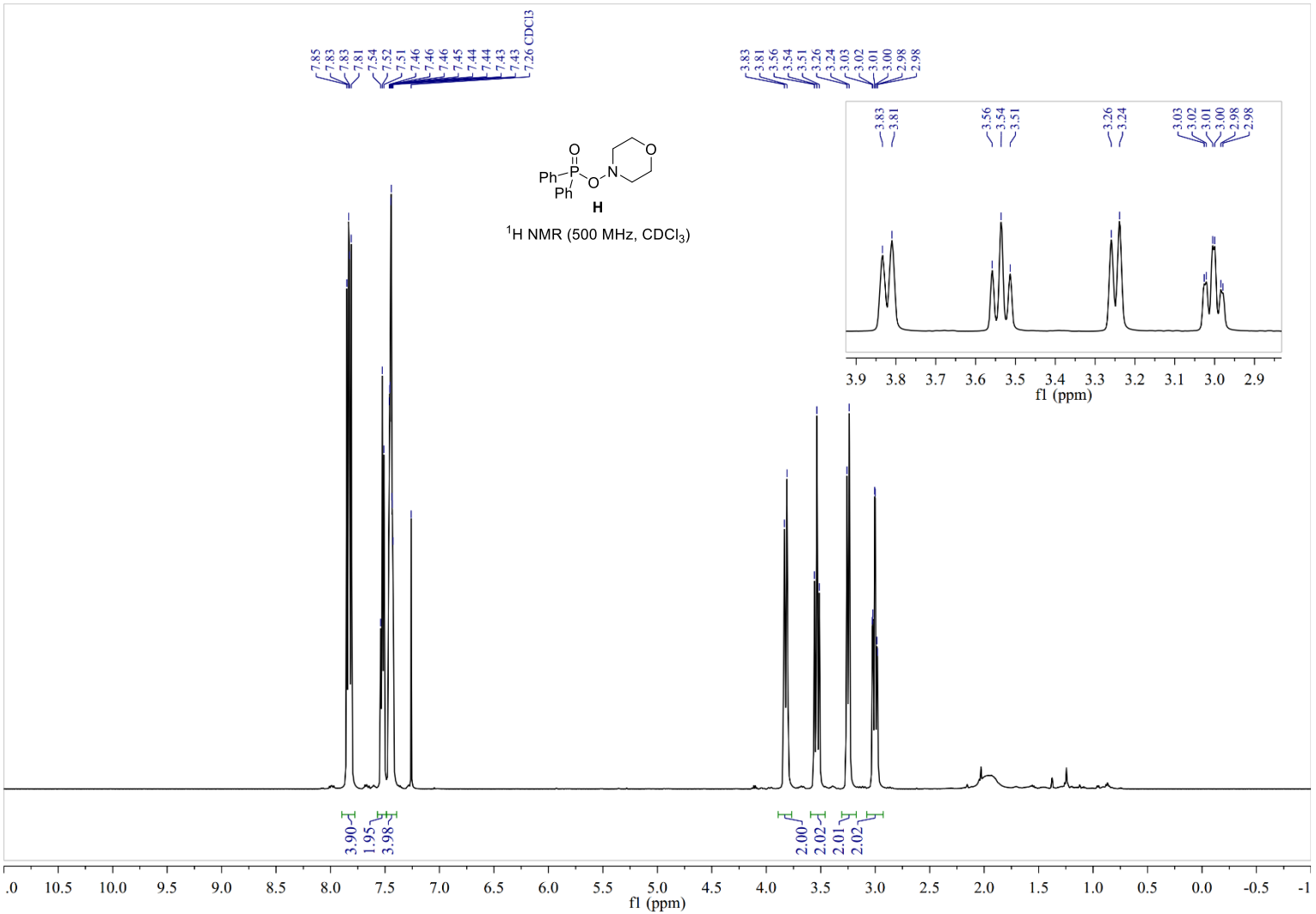
O
O
N
O
G
13C NMR (125 MHz, CDCl3)
f1 (ppm)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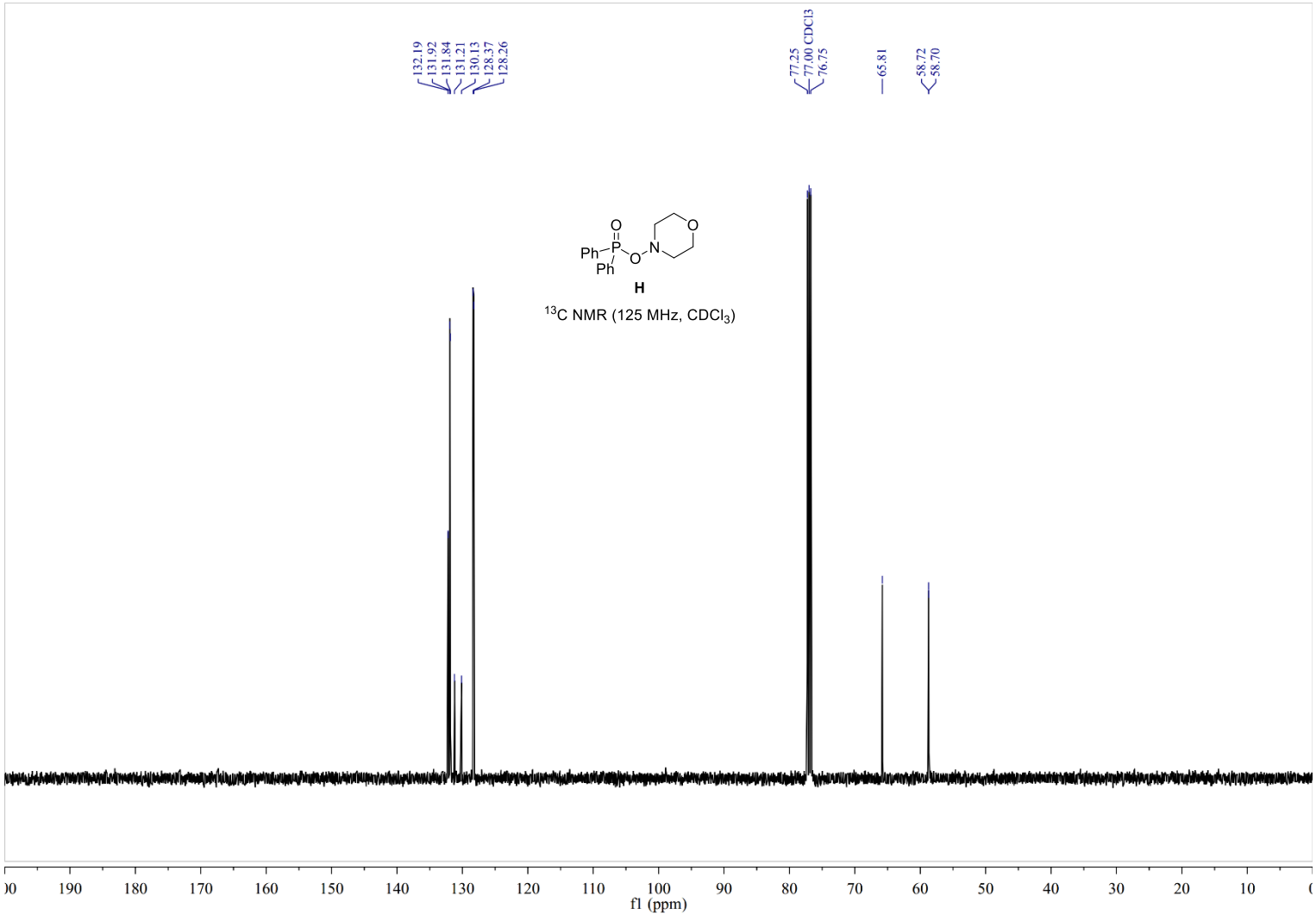
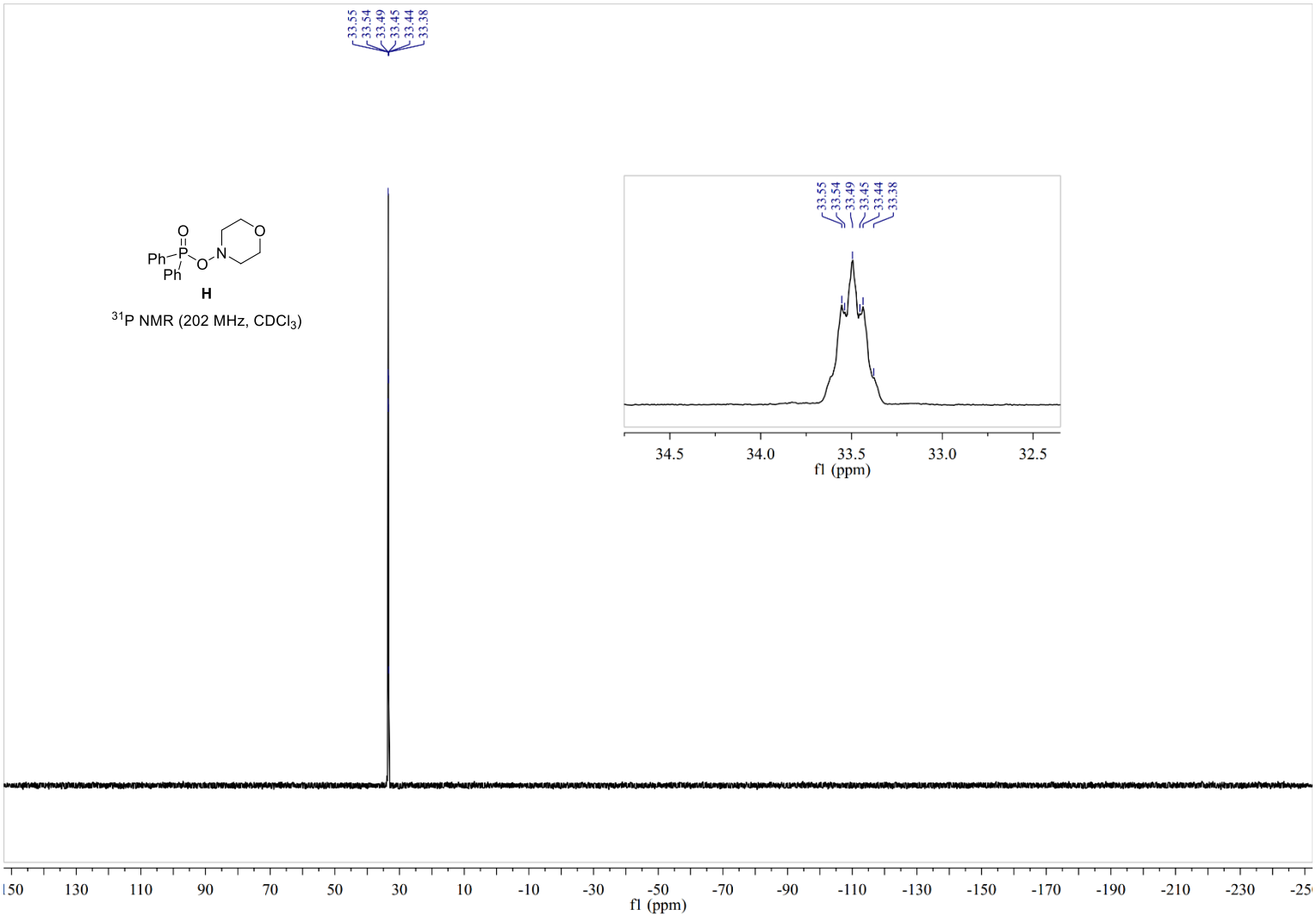
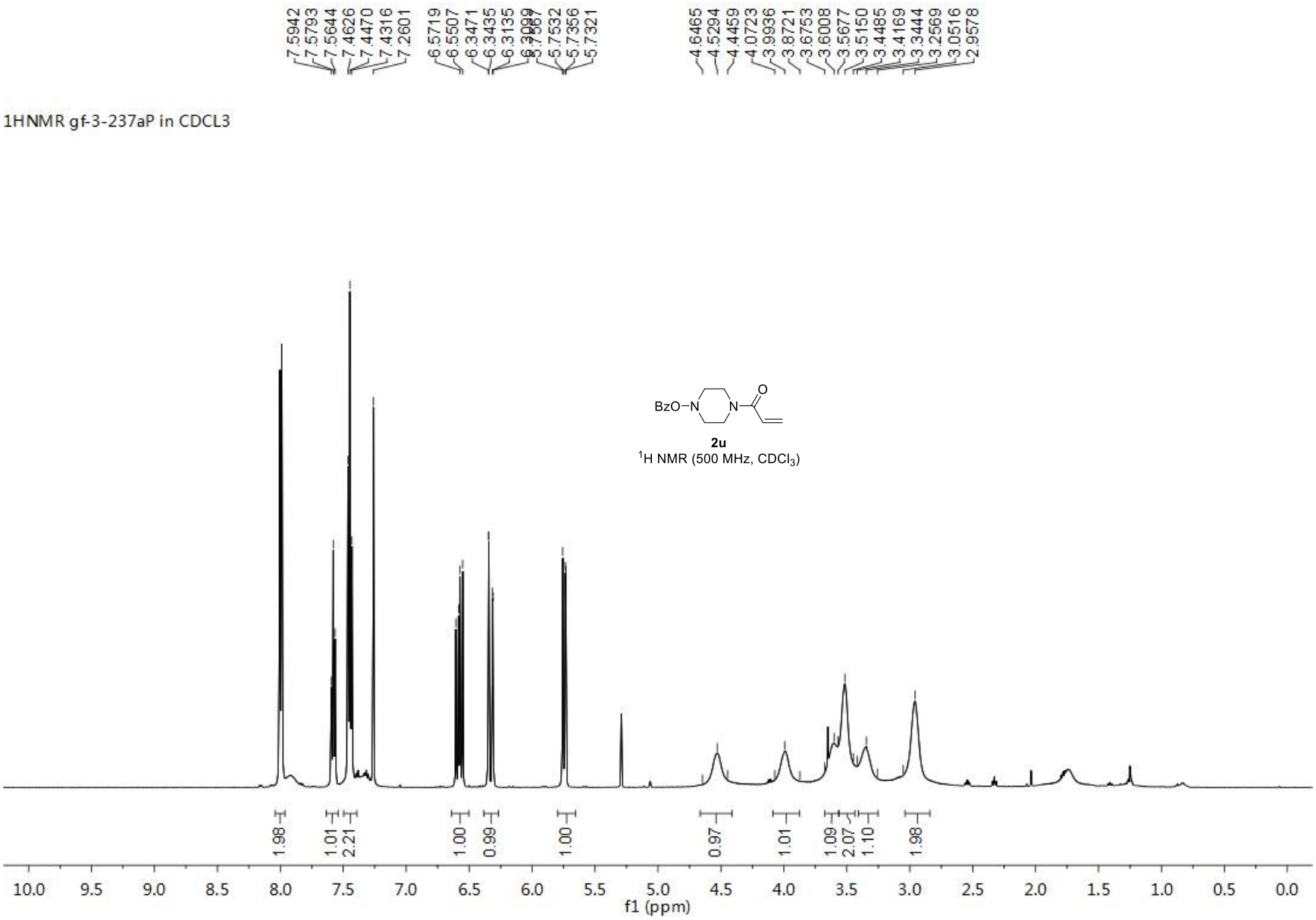
7.83
7.83
7.81
7.54
7.52
7.51
7.46
7.46
7.46
7.45
7.44
7.44
7.43
7.43
7.26 CDCl3
3.83
3.81
3.56
3.54
3.51
3.26
3.24
3.03
3.02
3.01
3.00
2.98
2.98
Ph
Ph
O
P
O
N
O
H
1H NMR (500 MHz, CDCl3)
3.90
1.95
3.98
2.00
2.02
2.01
2.02
f1 (ppm)


132.19
131.92
131.84
131.21
130.13
128.37
128.26
77.25
77.00 CDCl3
76.75
65.81
58.72
58.70
O
Ph
P
O
N
O
Ph
H
13C NMR (125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


33.55
33.54
33.49
33.45
33.44
33.38
O
O
Ph
P
O
N
Ph
H
31P NMR (202 MHz, CDCl3)
34.5
34.0
33.5
33.0
32.5
f1 (ppm)
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)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7.5644
7.4626
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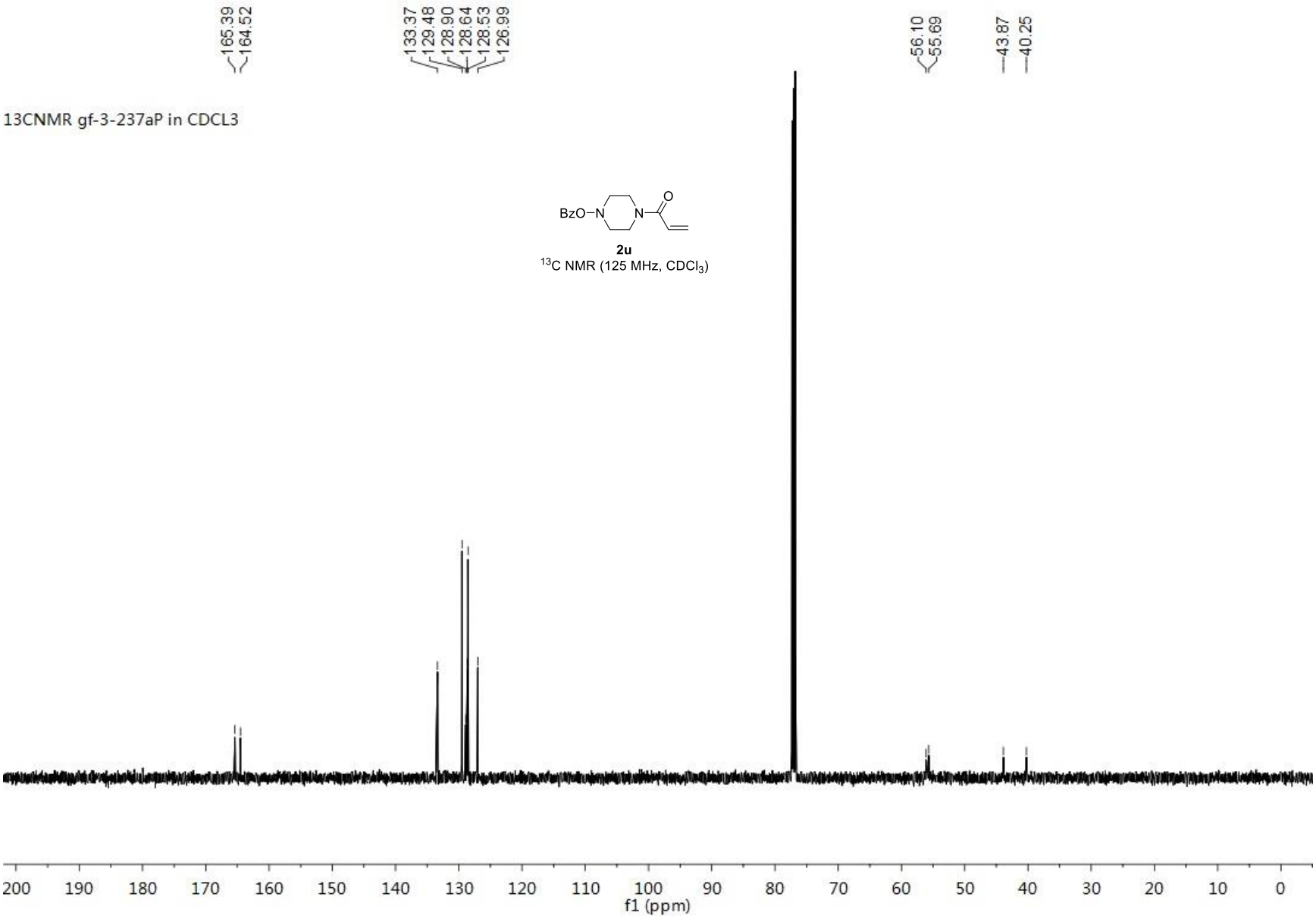
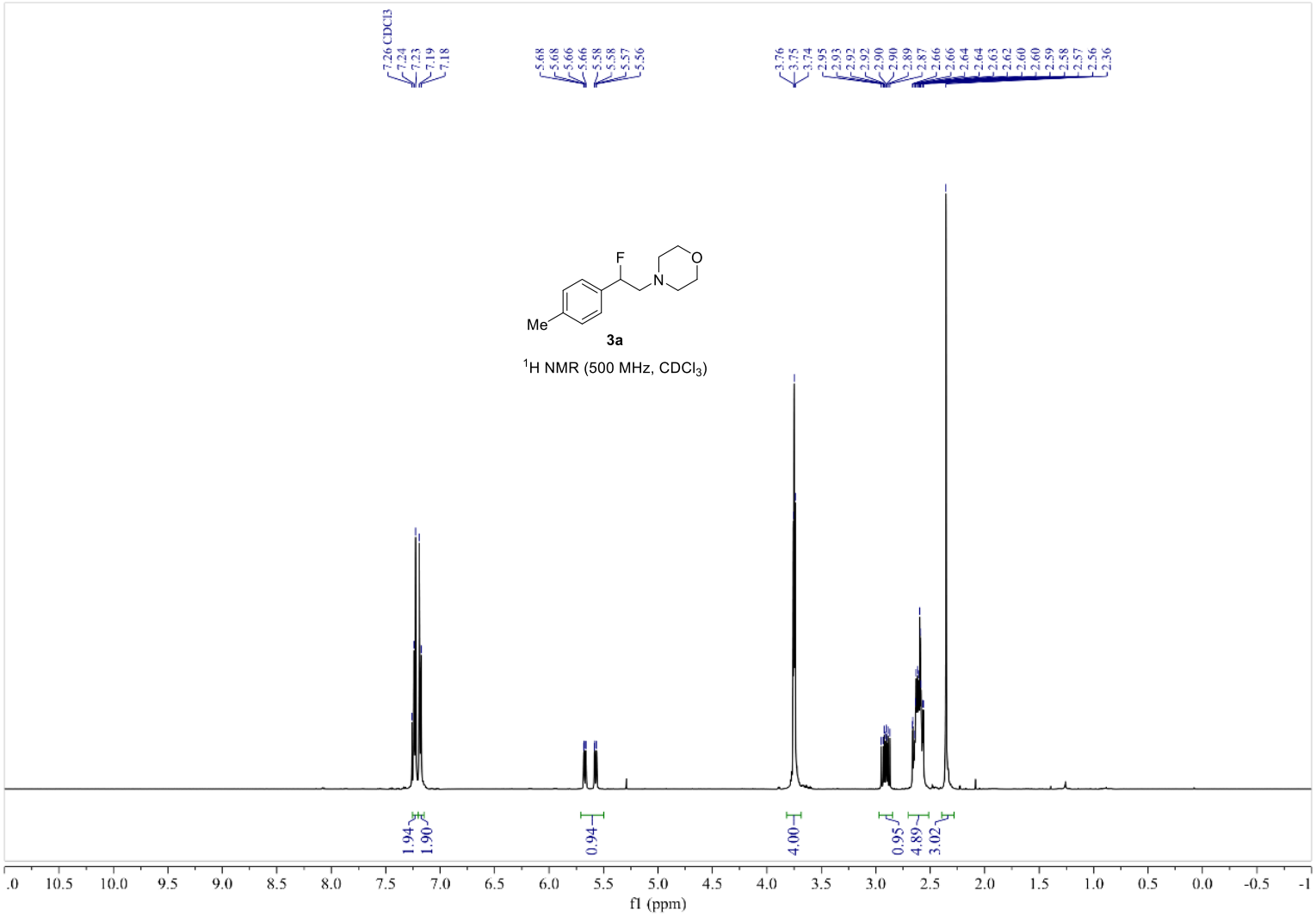
7.2601
6.5719
6.5507
6.3471
6.3435
6.3135
5.7532
5.7356
5.7321
4.6465
4.5294
4.4459
4.0723
3.9936
3.8721
3.6753
3.6008
3.5677
3.5150
3.4485
3.4169
3.3444
3.2569
3.0516
2.9578
1HNMR gf-3-237aP in CDCL3
BzO
N
N
O
2u
1H NMR (500 MHz, CDCl3)
1.98
1.01
2.21
1.00
0.99
1.00
0.97
1.01
1.09
2.07
1.10
1.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.39
164.52
133.37
129.48
128.90
128.64
128.53
126.99
56.10
55.69
43.87
40.25
13CNMR gf-3-237aP in CDCL3
BzO–N
N
O
2u
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26 CDCl3
7.24
7.23
7.19
7.18
5.68
5.68
5.66
5.66
5.58
5.58
5.57
5.56
3.76
3.75
3.74
2.95
2.93
2.92
2.92
2.90
2.90
2.89
2.87
2.66
2.66
2.64
2.64
2.63
2.62
2.60
2.60
2.59
2.58
2.57
2.56
2.36
F
O
N
Me
3a
1H NMR (500 MHz, CDCl3)
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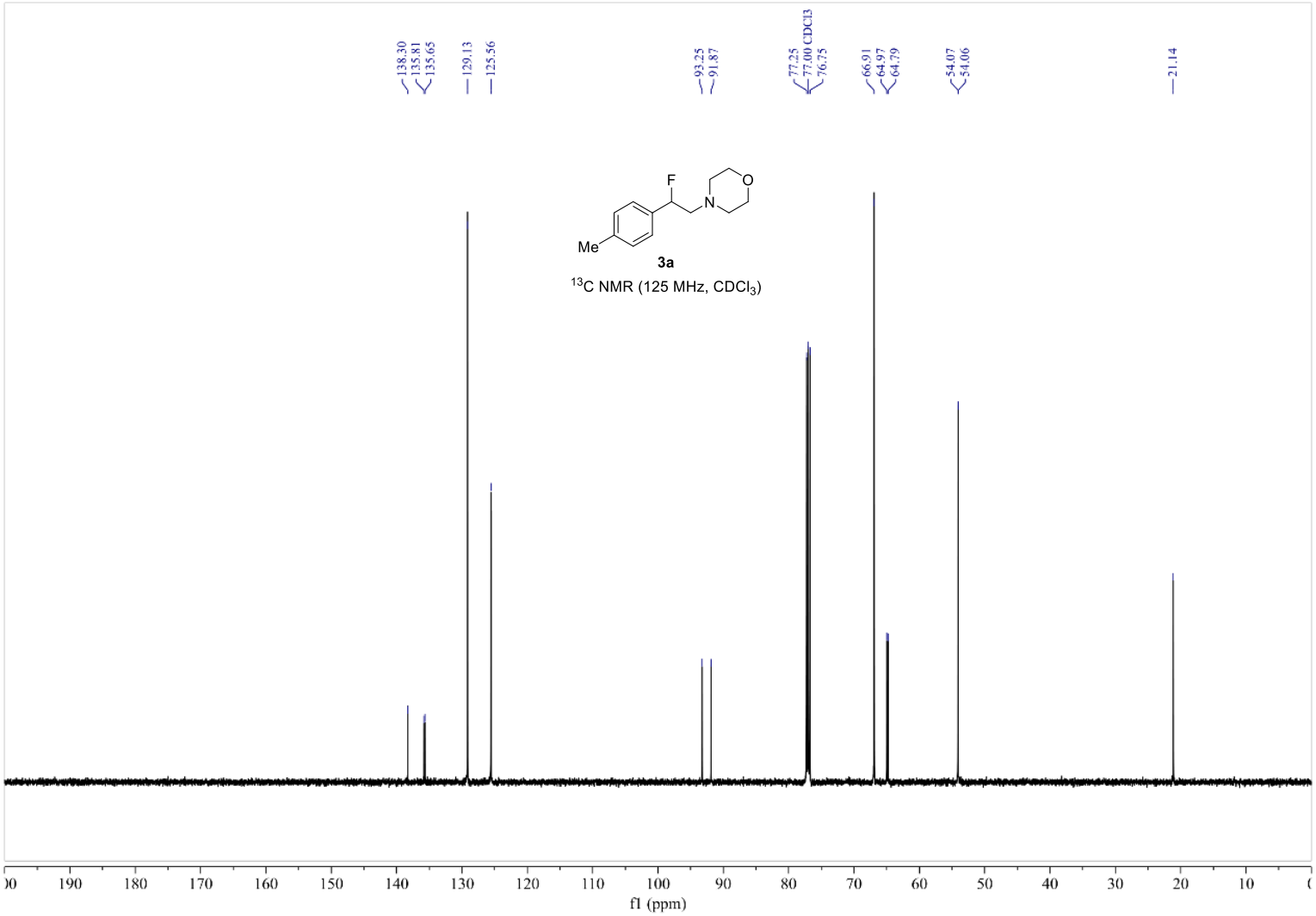
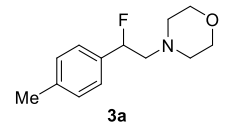
0.94
4.00
0.95
4.89
3.02
f1 (ppm)


138.30
135.81
135.65
129.13
125.56
93.25
91.87
77.25
77.00 CDCl3
76.75
66.91
64.97
64.79
54.07
54.06
21.14
F
O
N
Me
3a
13C NMR (125 MHz, CDCl3)
f1 (ppm)

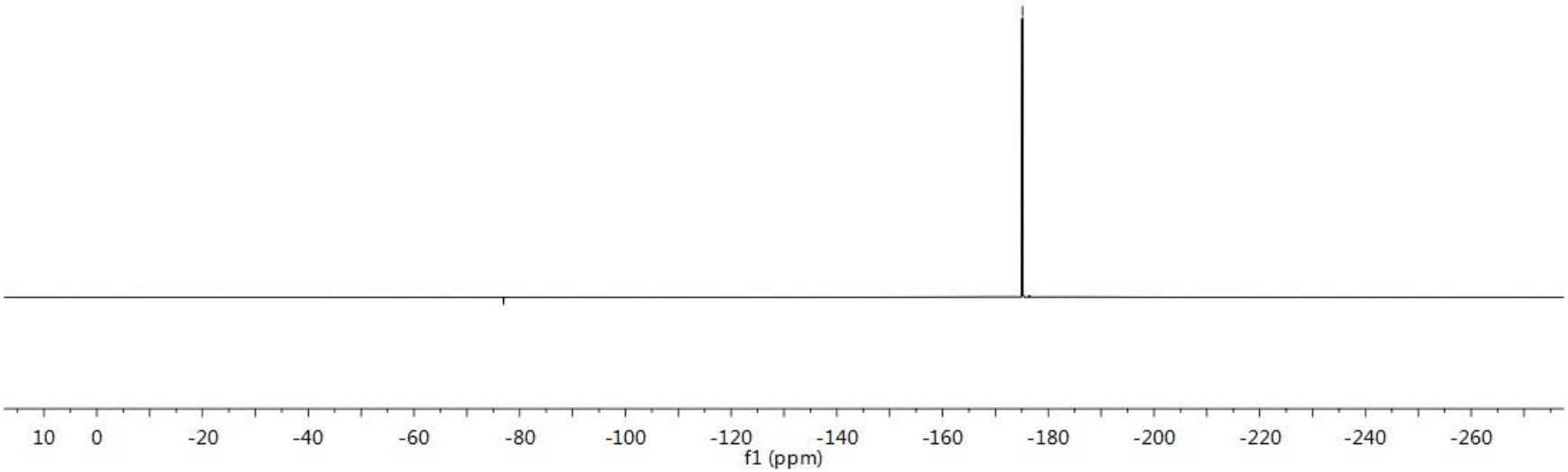
19F NMR gf-3-32a P in CDCl3

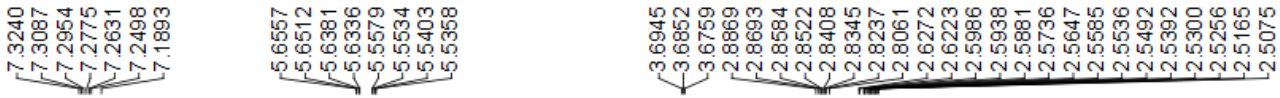
-175.1088



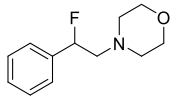
3a

^{19}F NMR (471 MHz, $CDCl_3$)



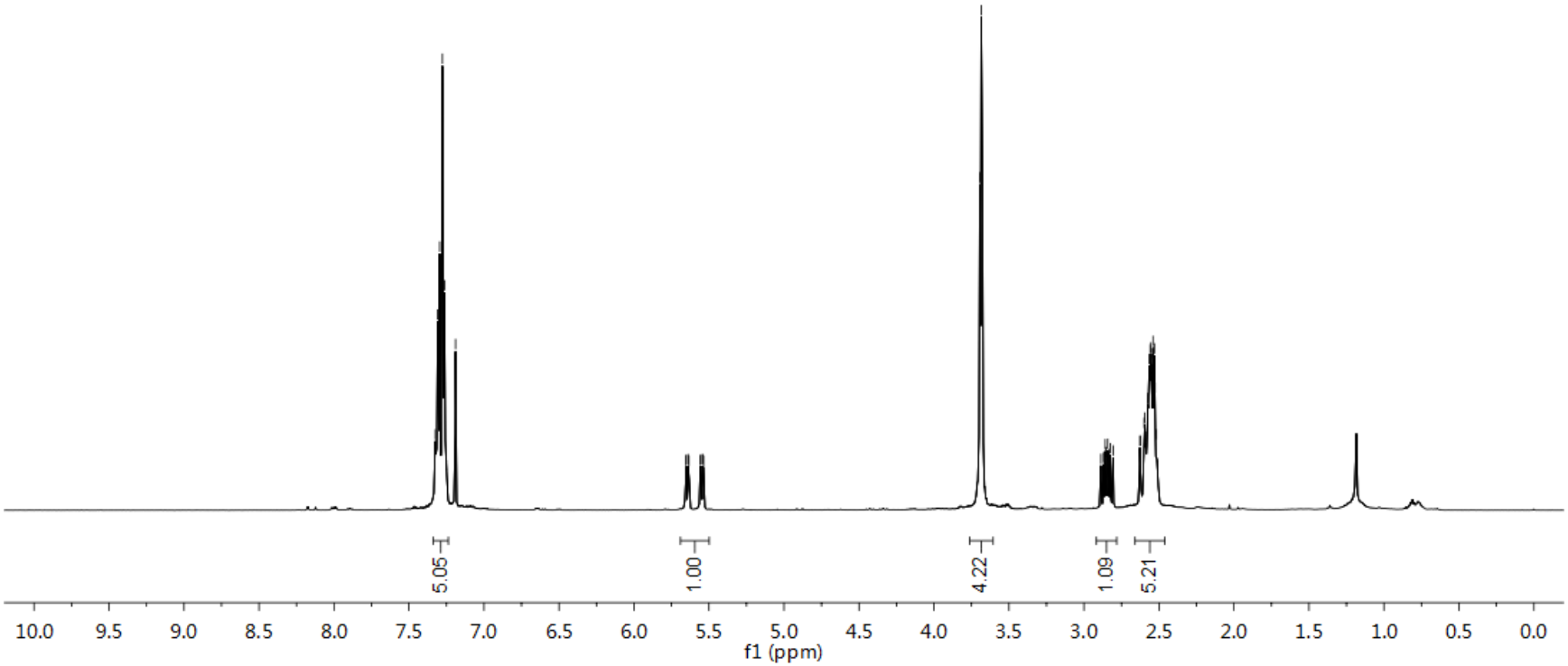


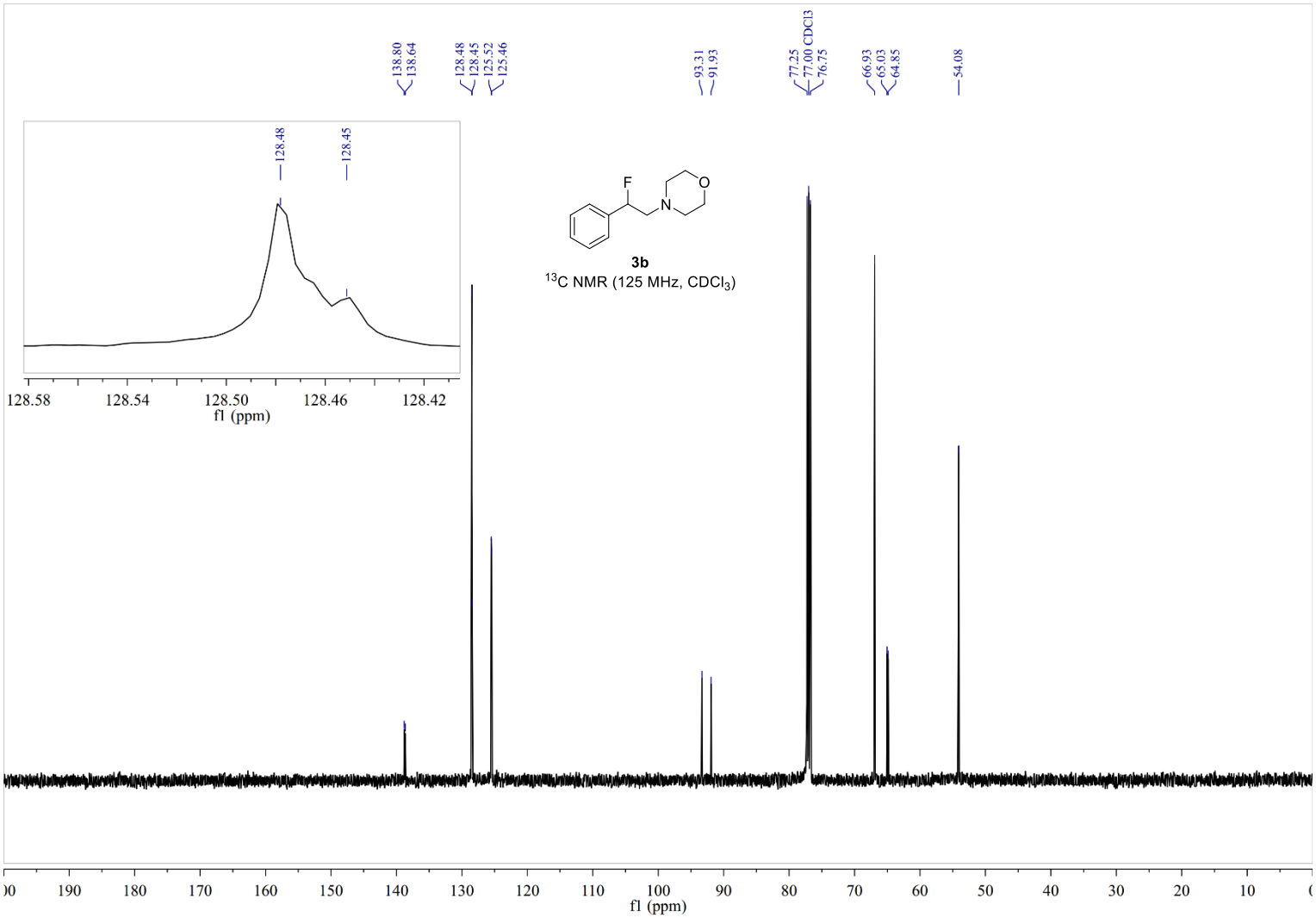
1HNMR gf-ck-II-56aP in CDCl3



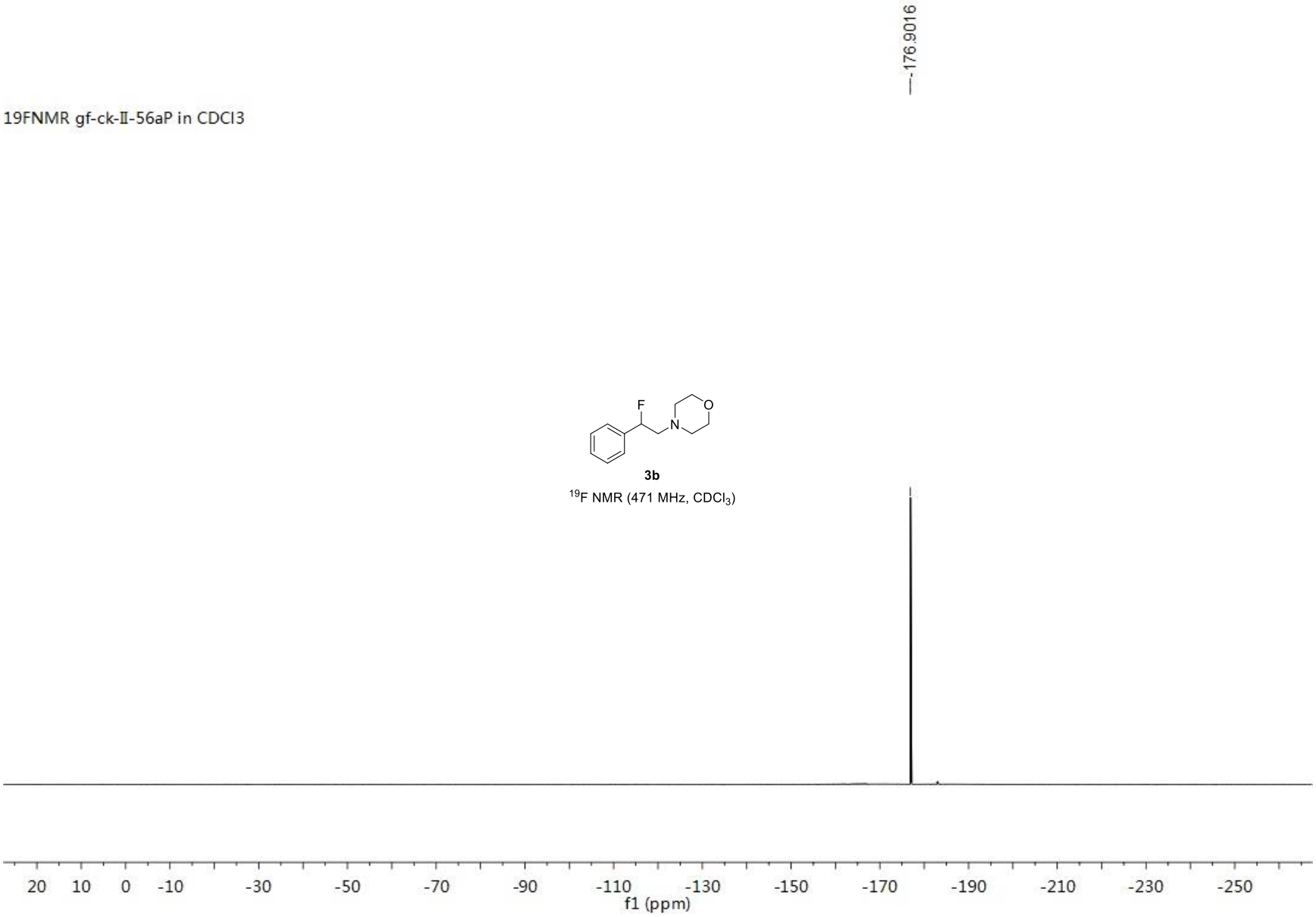
3b

^{1}H NMR (500 MHz, $CDCl_3$)



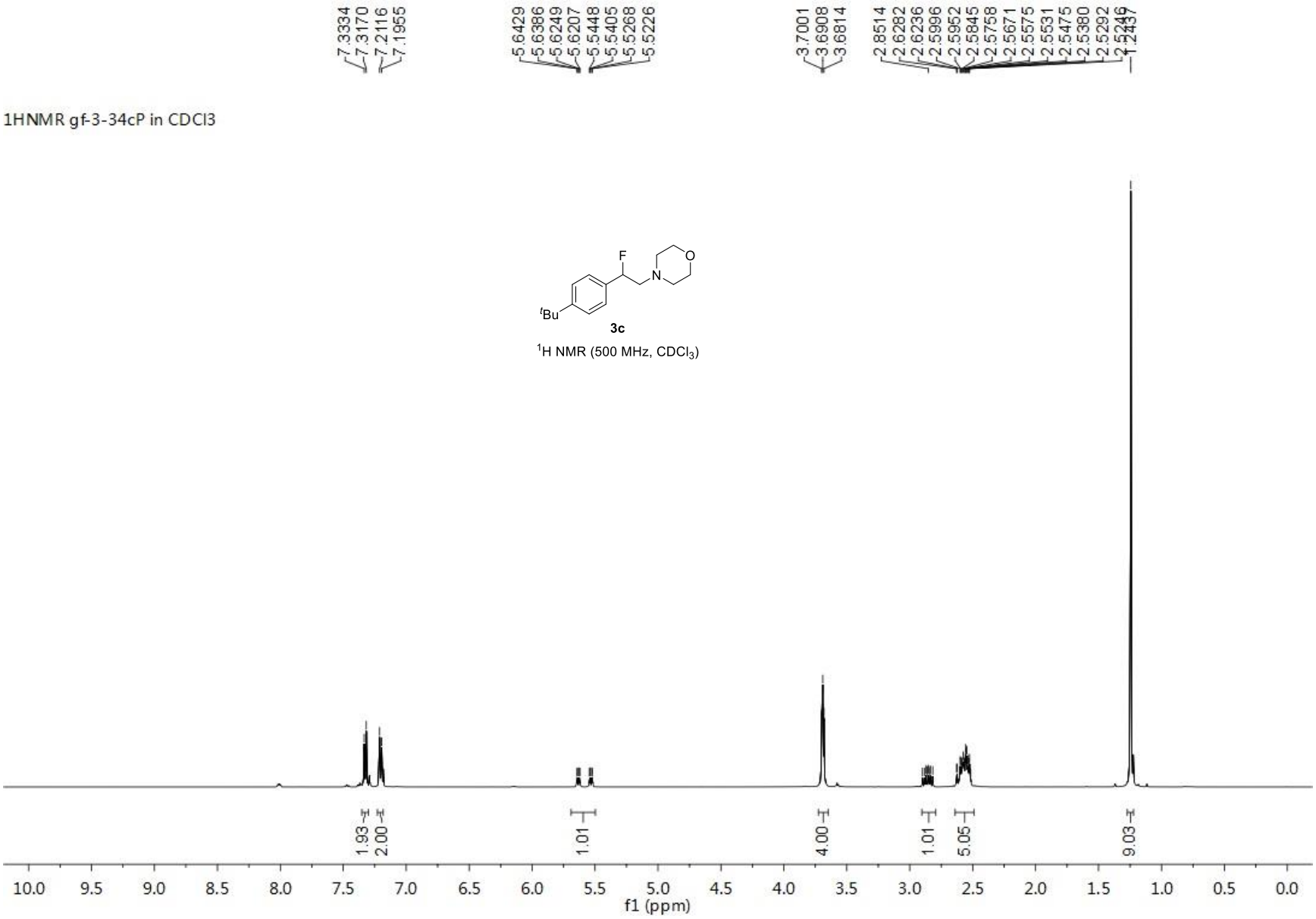

138.80
138.64
128.48
128.45
125.52
125.46
93.31
91.93
77.25
77.00 CDCl3
76.75
66.93
65.03
64.85
54.08
128.48
128.45
128.58
128.54
128.50
128.46
128.42
f1 (ppm)
F
O
N
3b
13C NMR (125 MHz, CDCl3)
f1 (ppm)

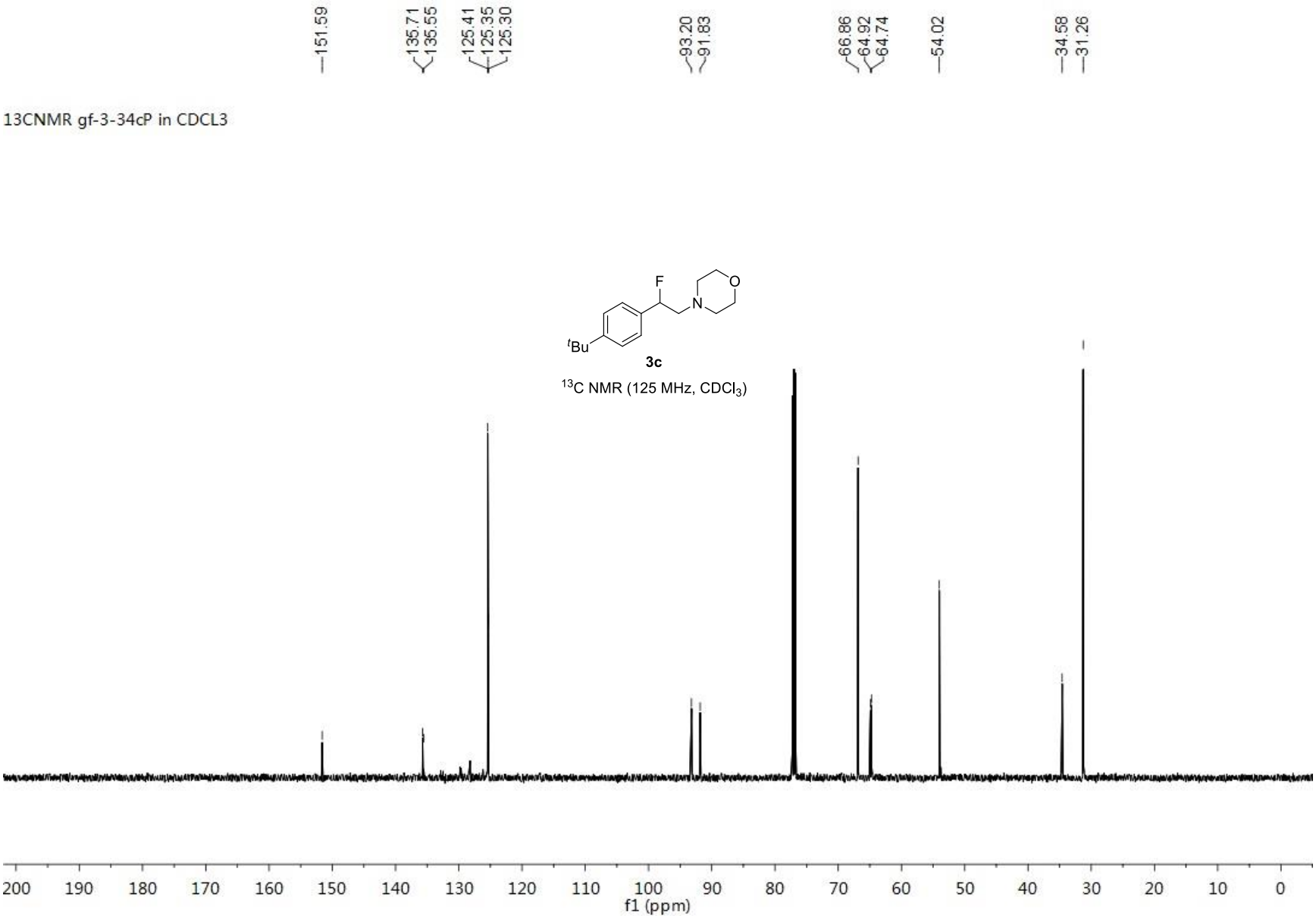
19FNMR gf-ck-Ⅱ-56aP in CDCl3



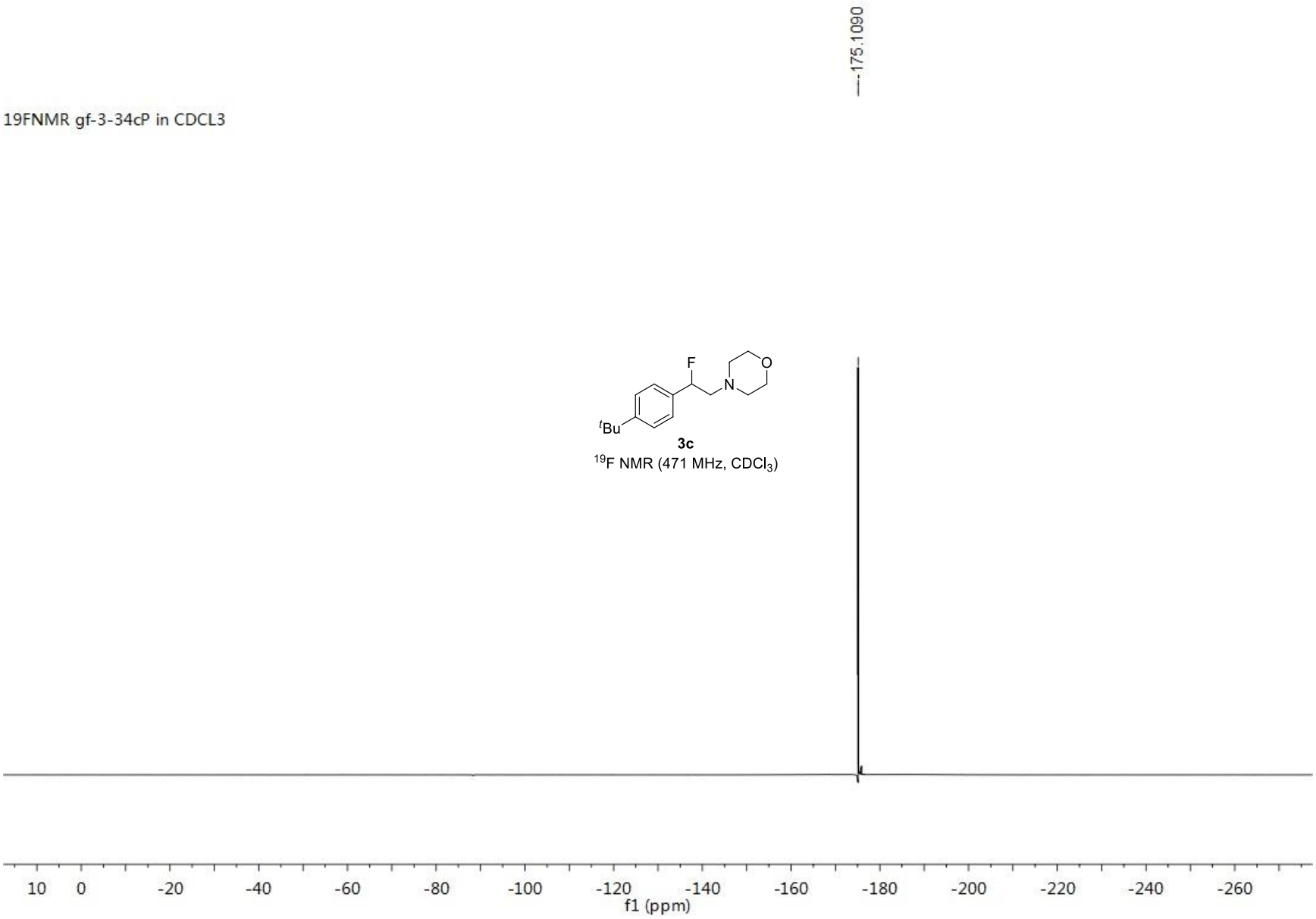
3b

^{19}F NMR (471 MHz, $CDCl_3$)


7.3334
7.3170
7.2116
7.1955
5.6429
5.6386
5.6249
5.6207
5.5448
5.5405
5.5268
5.5226
3.7001
3.6908
3.6814
2.8514
2.6282
2.6236
2.5996
2.5952
2.5845
2.5758
2.5671
2.5575
2.5531
2.5475
2.5380
2.5292
1.2437
1HNMR gf-3-34cP in CDCl3
F
O
N
tBu
3c
1H NMR (500 MHz, CDCl3)
1.93
2.00
1.01
4.00
1.01
5.05
9.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

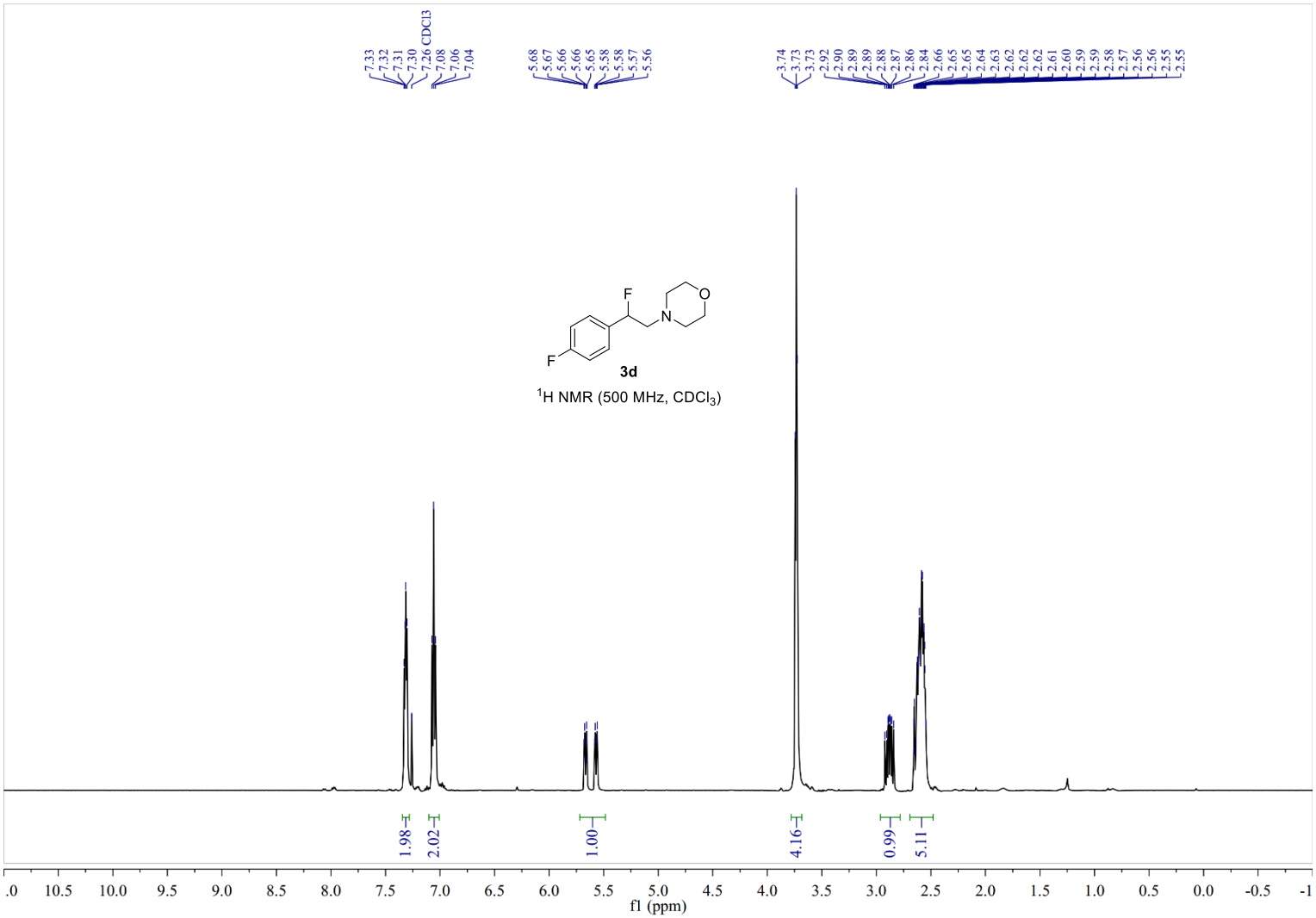

151.59
135.71
135.55
125.41
125.35
125.30
93.20
91.83
66.86
64.92
64.74
54.02
34.58
31.26
13CNMR gf-3-34cP in CDCL3
F
O
N
tBu
3c
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

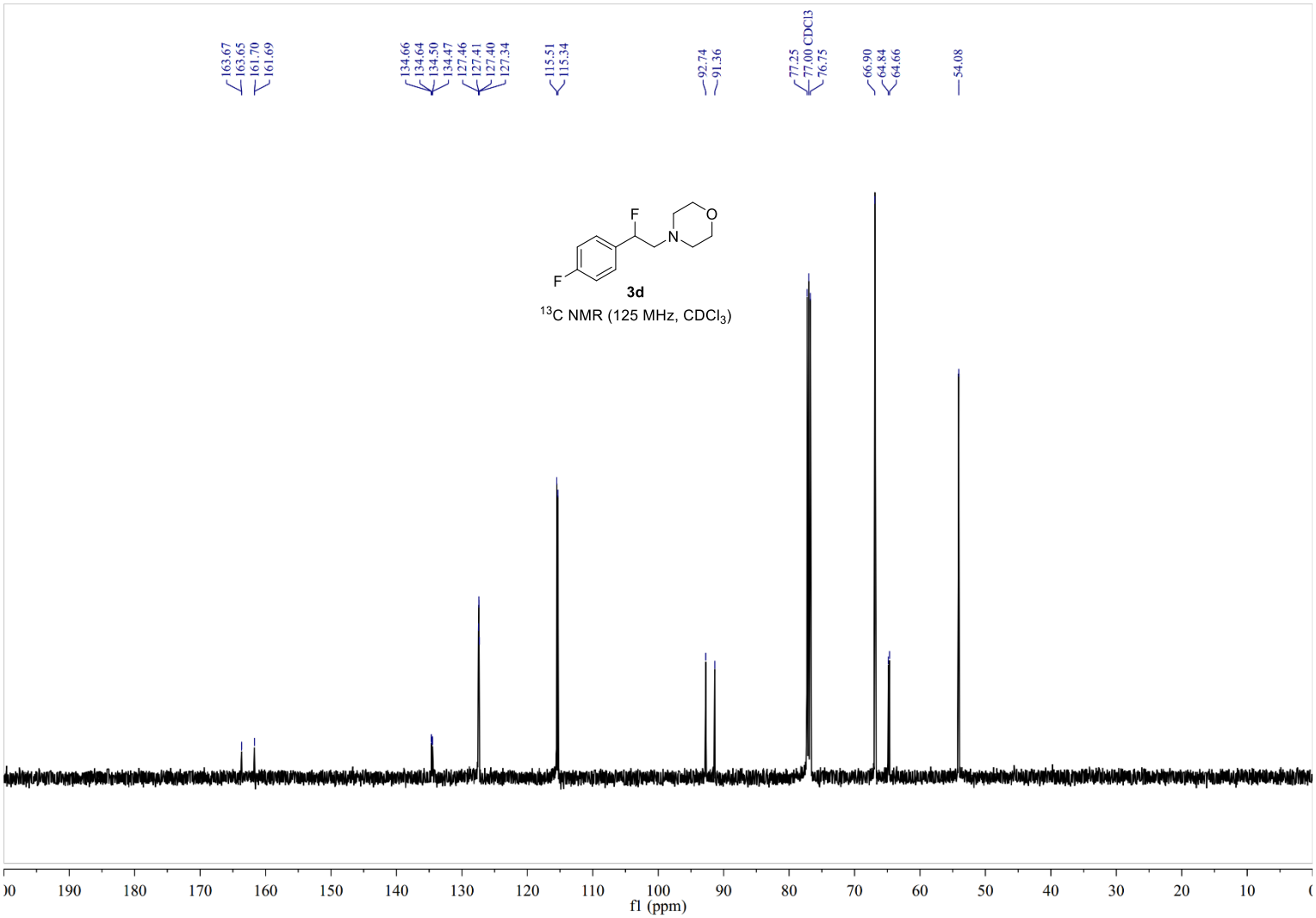
19FNMR gf-3-34cP in CDCL3

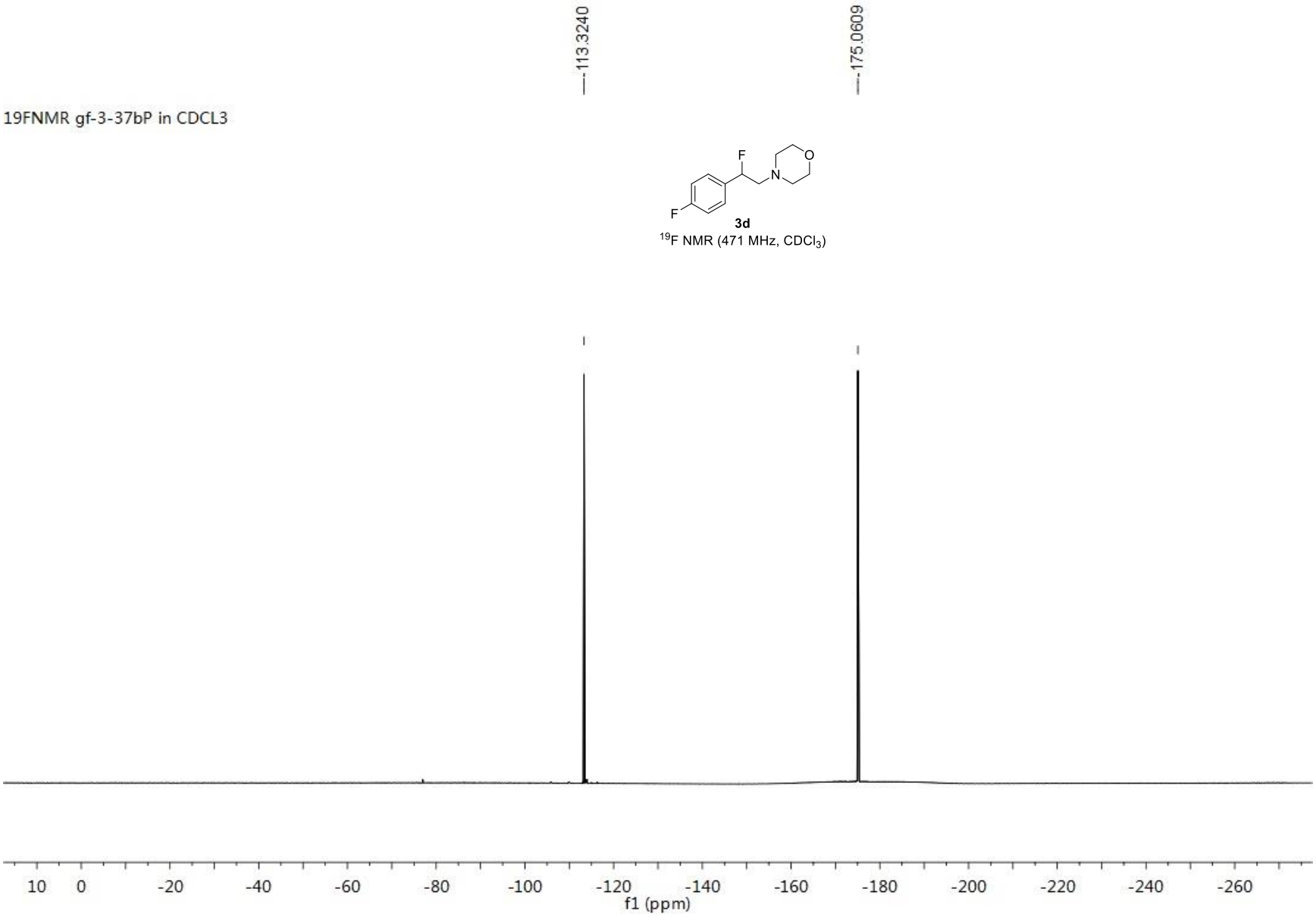


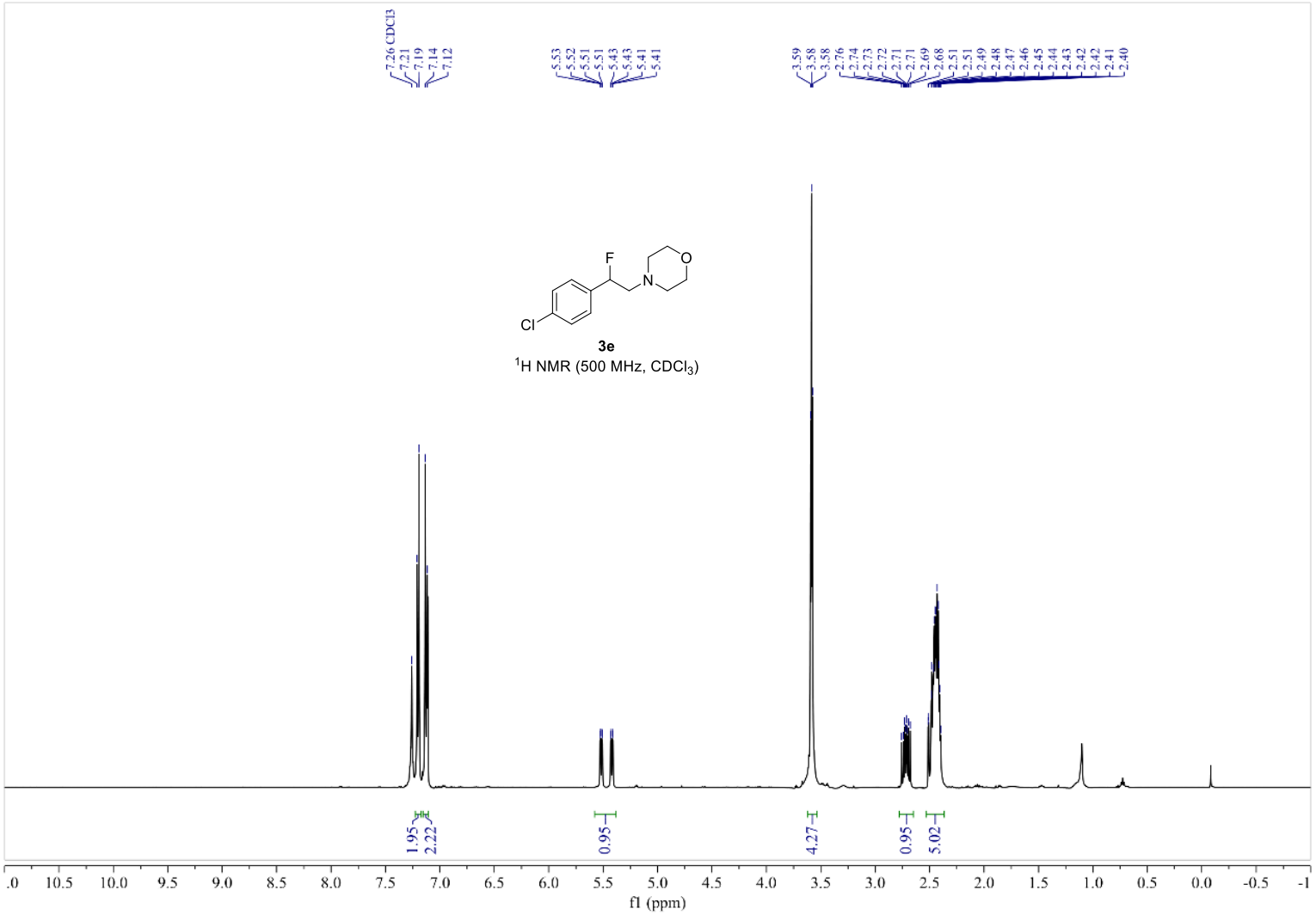
3c

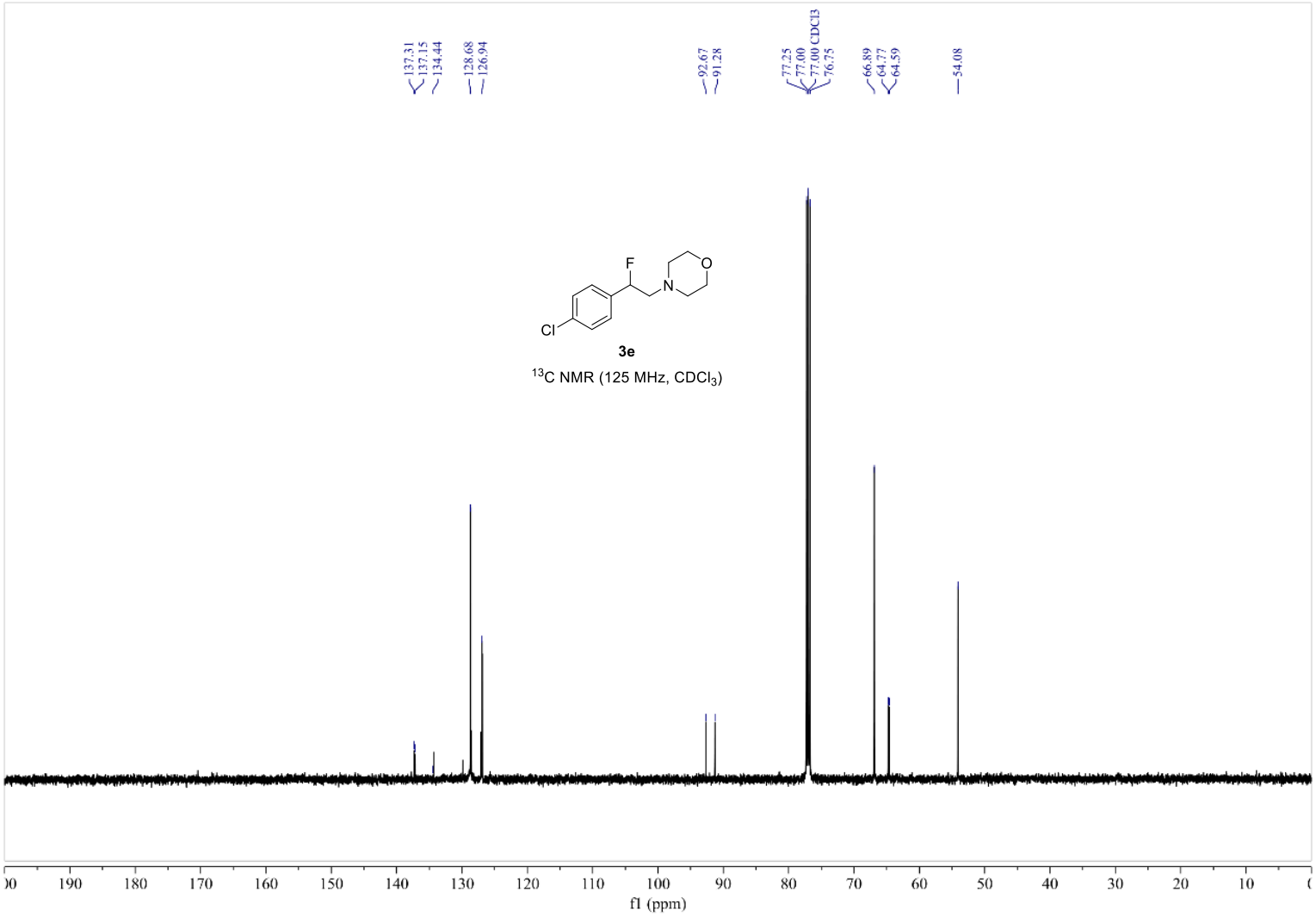
^{19}F NMR (471 MHz, $CDCl_3$)


7.33
7.32
7.31
7.30
7.26 CDCl3
7.08
7.06
7.04
5.68
5.67
5.66
5.66
5.65
5.58
5.58
5.57
5.56
3.74
3.73
3.73
2.92
2.90
2.89
2.89
2.88
2.87
2.86
2.84
2.66
2.65
2.65
2.64
2.63
2.62
2.62
2.62
2.61
2.60
2.59
2.59
2.58
2.57
2.56
2.56
2.55
2.55
F
O
N
F
3d
1H NMR (500 MHz, CDCl3)
1.98
2.02
1.00
4.16
0.99
5.11
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

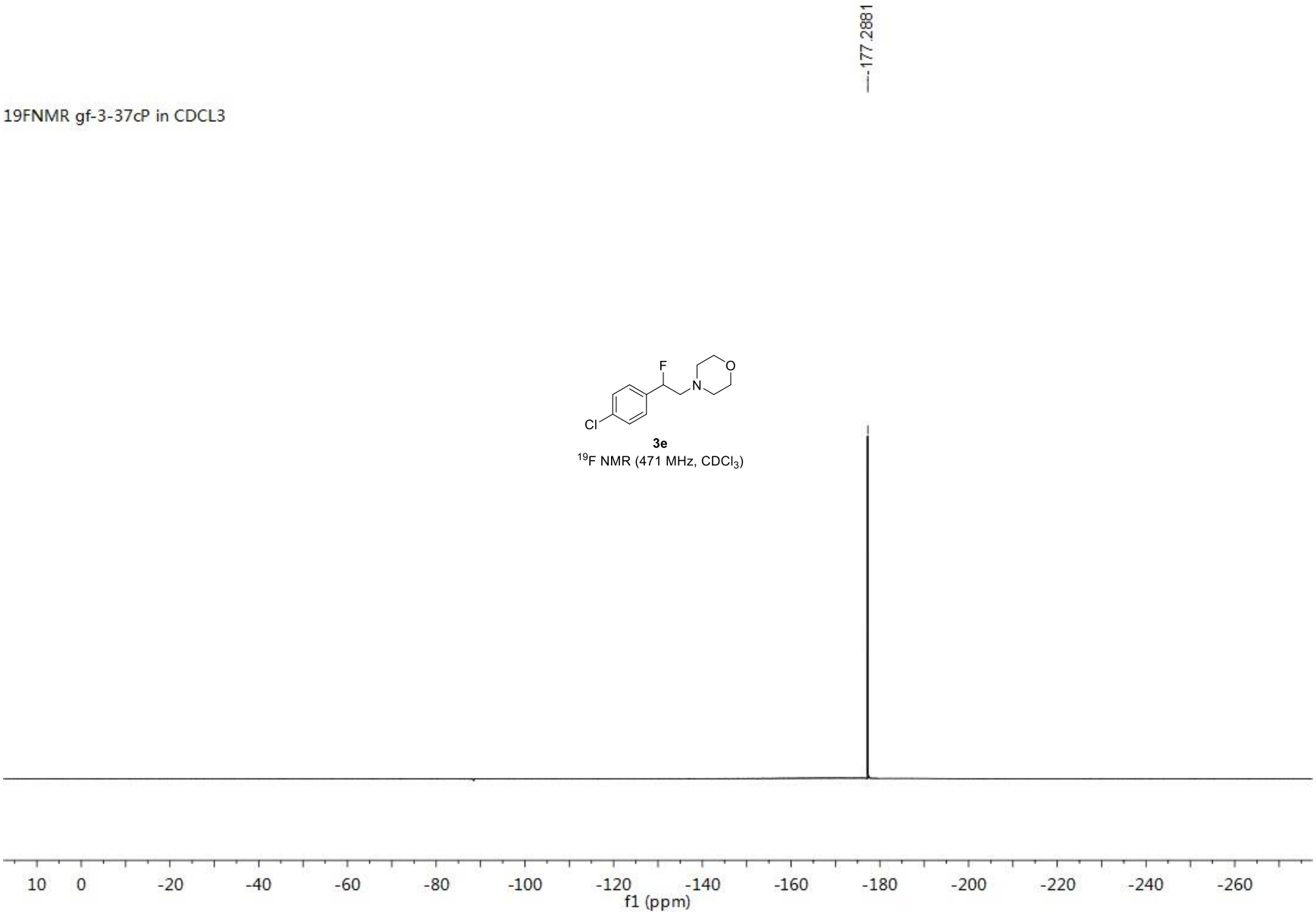

163.67
163.65
161.70
161.69
134.66
134.64
134.50
134.47
127.46
127.41
127.40
127.34
115.51
115.34
92.74
91.36
77.25
77.00 CDCl3
76.75
66.90
64.84
64.66
54.08
F
O
N
F
3d
13C NMR (125 MHz, CDCl3)
f1 (ppm)


-113.3240
-175.0609
19FNMR gf-3-37bP in CDCL3
F
O
N
F
3d
^{19}F NMR (471 MHz, $CDCl_3$)
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
f1 (ppm)


7.26 CDCl3
7.21
7.19
7.14
7.12
5.53
5.52
5.51
5.51
5.43
5.43
5.41
5.41
3.59
3.58
3.58
2.76
2.74
2.73
2.72
2.71
2.71
2.69
2.68
2.51
2.51
2.49
2.48
2.47
2.46
2.45
2.44
2.43
2.42
2.42
2.41
2.40
F
O
N
Cl
3e
1H NMR (500 MHz, CDCl3)
1.95
2.22
0.95
4.27
0.95
5.02
f1 (ppm)

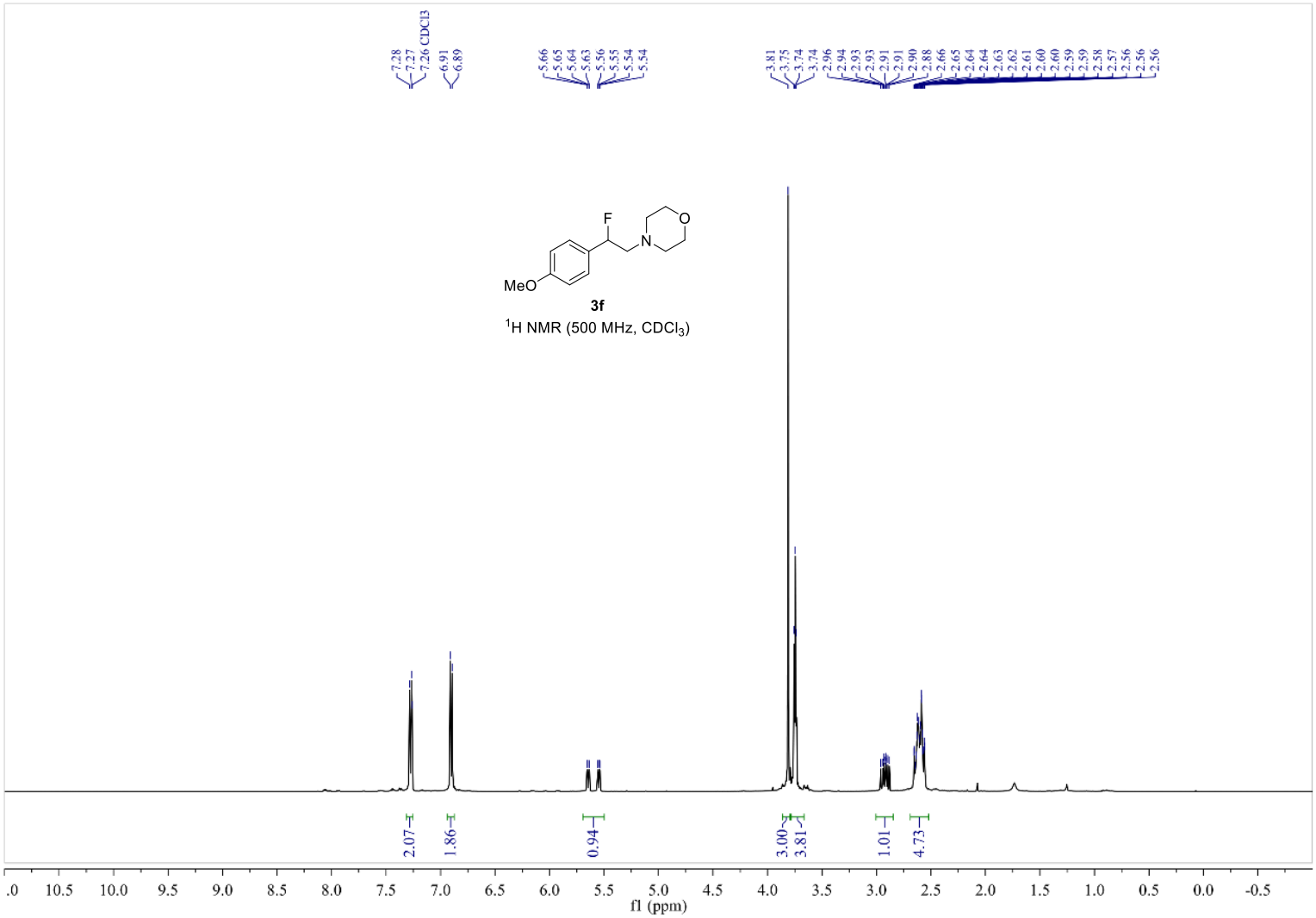

137.31
137.15
134.44
128.68
126.94
92.67
91.28
77.25
77.00
77.00 CDCl3
76.75
66.89
64.77
64.59
54.08
F
O
N
Cl
3e
13C NMR (125 MHz, CDCl3)
f1 (ppm)

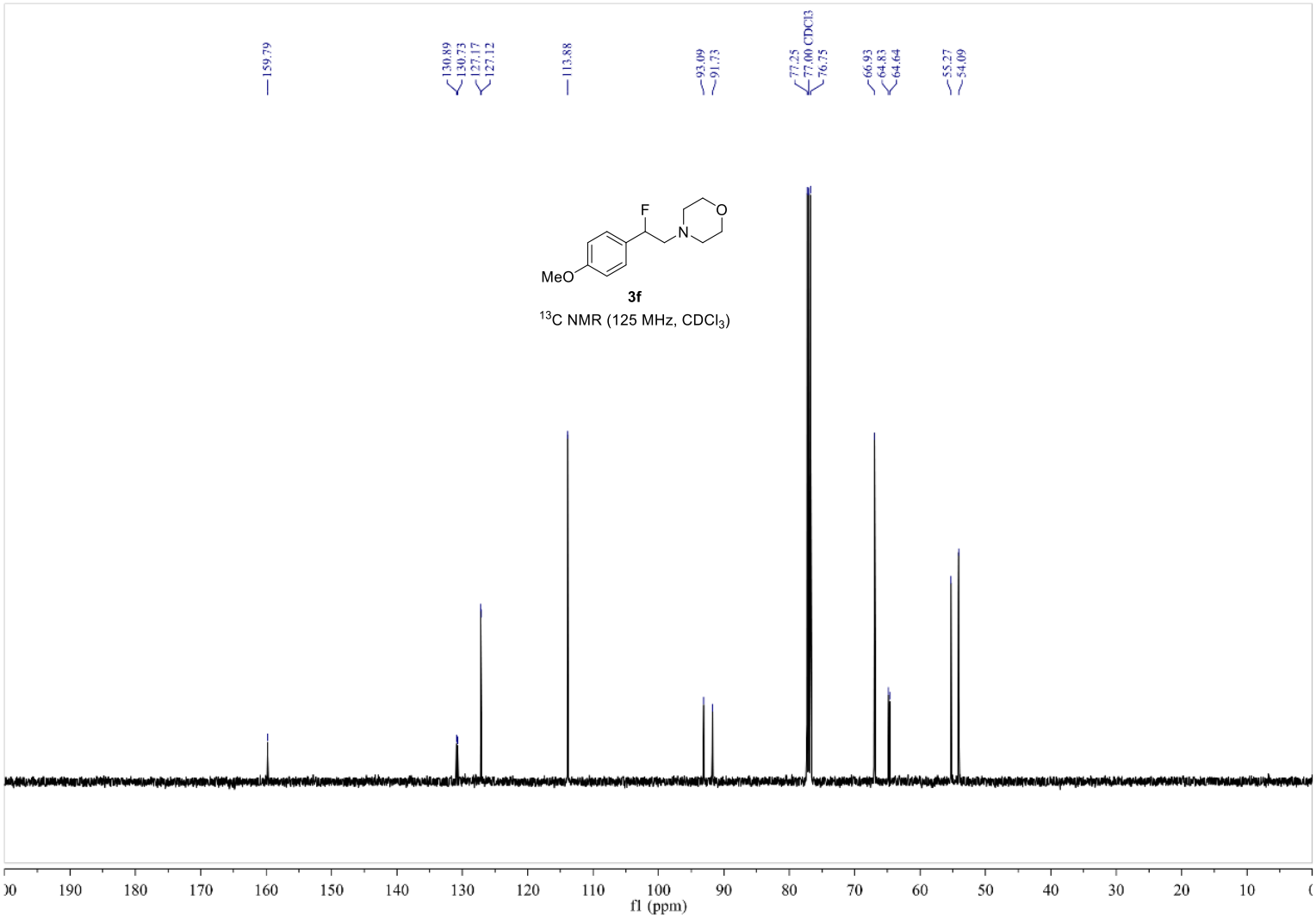
19FNMR gf-3-37cP in CDCL3



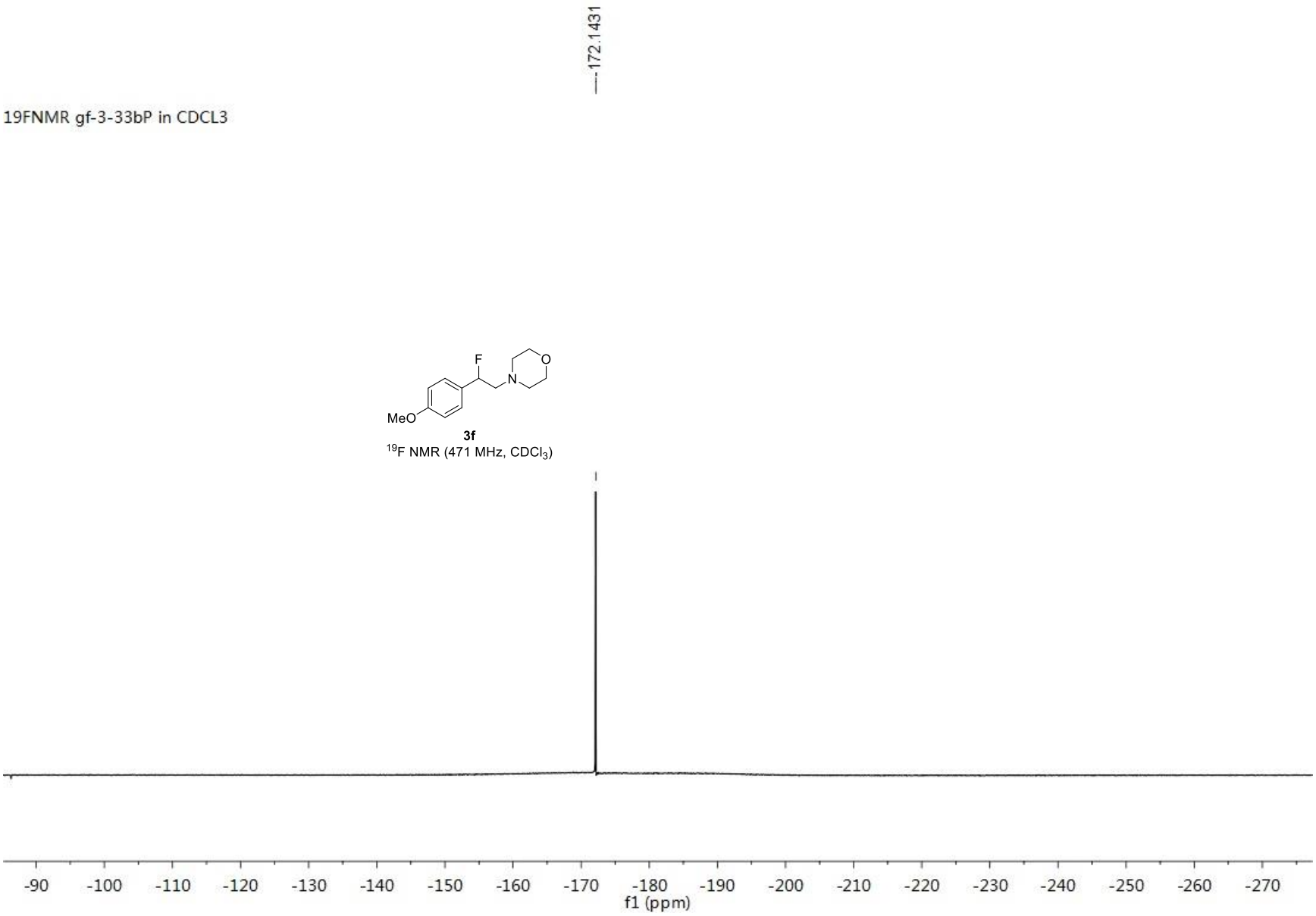
3e

^{19}F NMR (471 MHz, $CDCl_3$)


7.28
7.27
7.26 CDCl3
6.91
6.89
5.66
5.65
5.64
5.63
5.56
5.55
5.54
5.54
3.81
3.75
3.74
3.74
2.96
2.94
2.93
2.93
2.91
2.91
2.90
2.88
2.66
2.65
2.64
2.64
2.63
2.62
2.61
2.60
2.60
2.59
2.59
2.58
2.57
2.56
2.56
2.56
F
O
N
MeO
3f
1H NMR (500 MHz, CDCl3)
2.07
1.86
0.94
3.00
3.81
1.01
4.73
f1 (ppm)

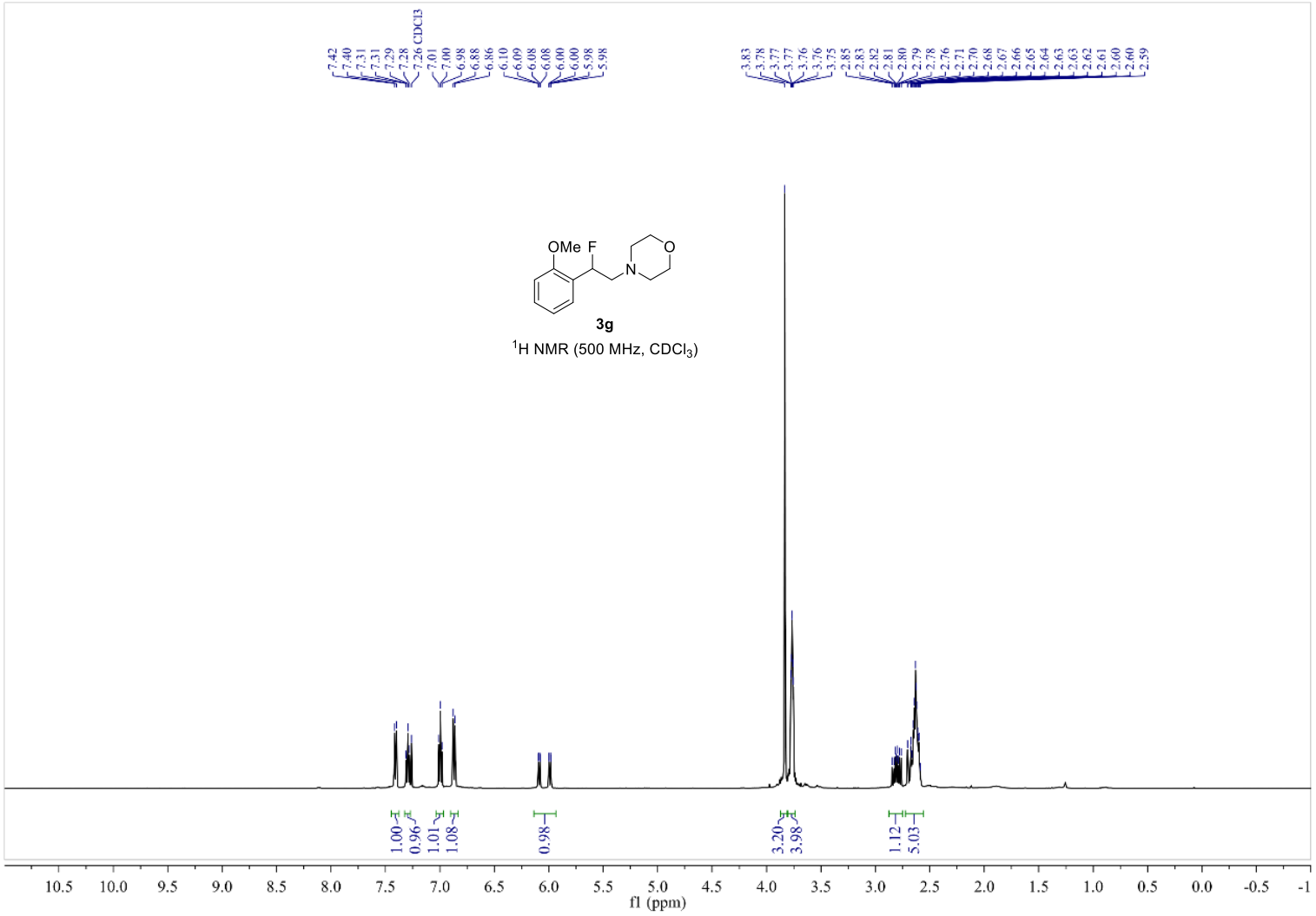

159.79
130.89
130.73
127.17
127.12
113.88
93.09
91.73
77.25
77.00 CDCl3
76.75
66.93
64.83
64.64
55.27
54.09
F
O
N
MeO
3f
13C NMR (125 MHz, CDCl3)
f1 (ppm)

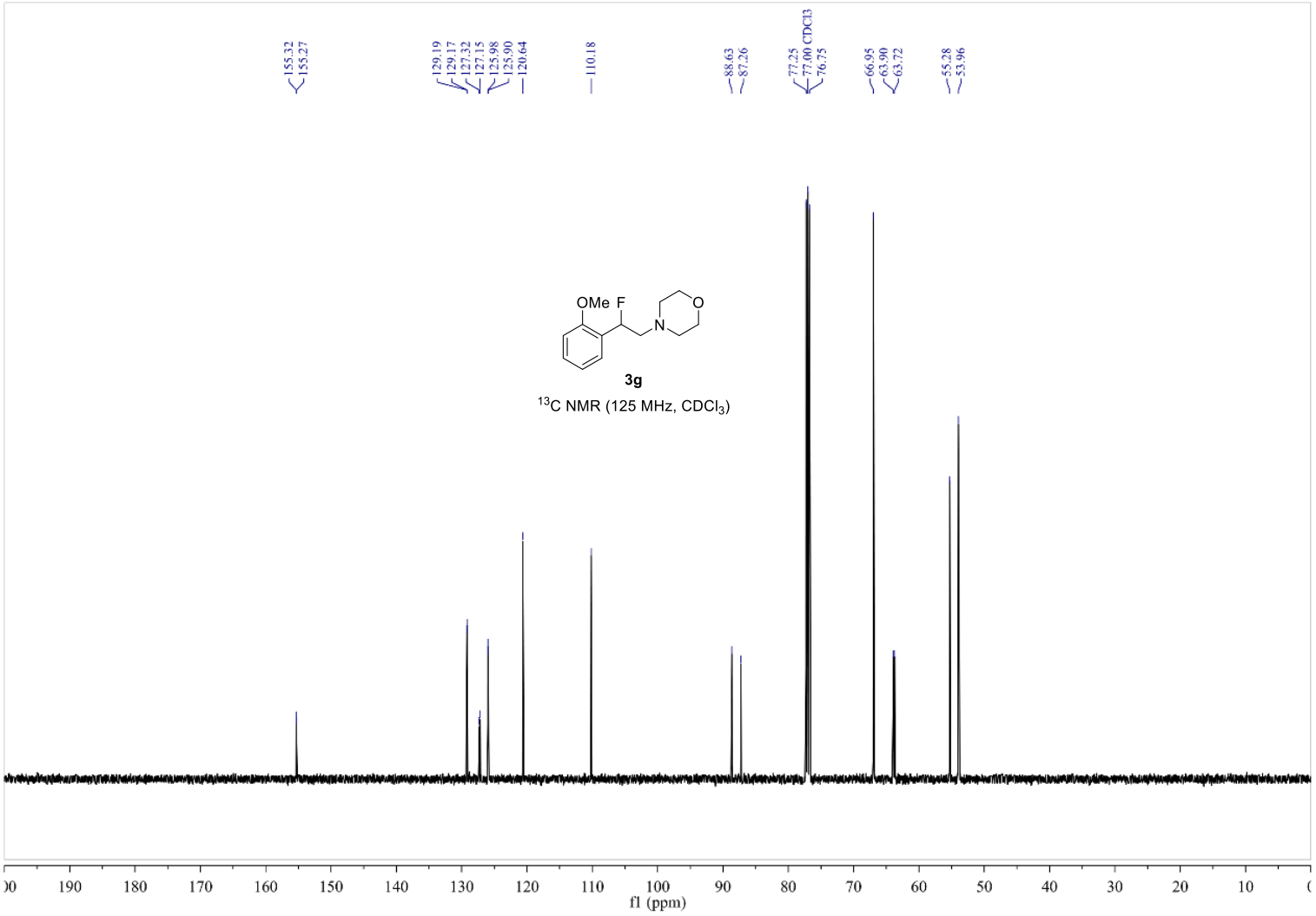
19FNMR gf-3-33bP in CDCL3



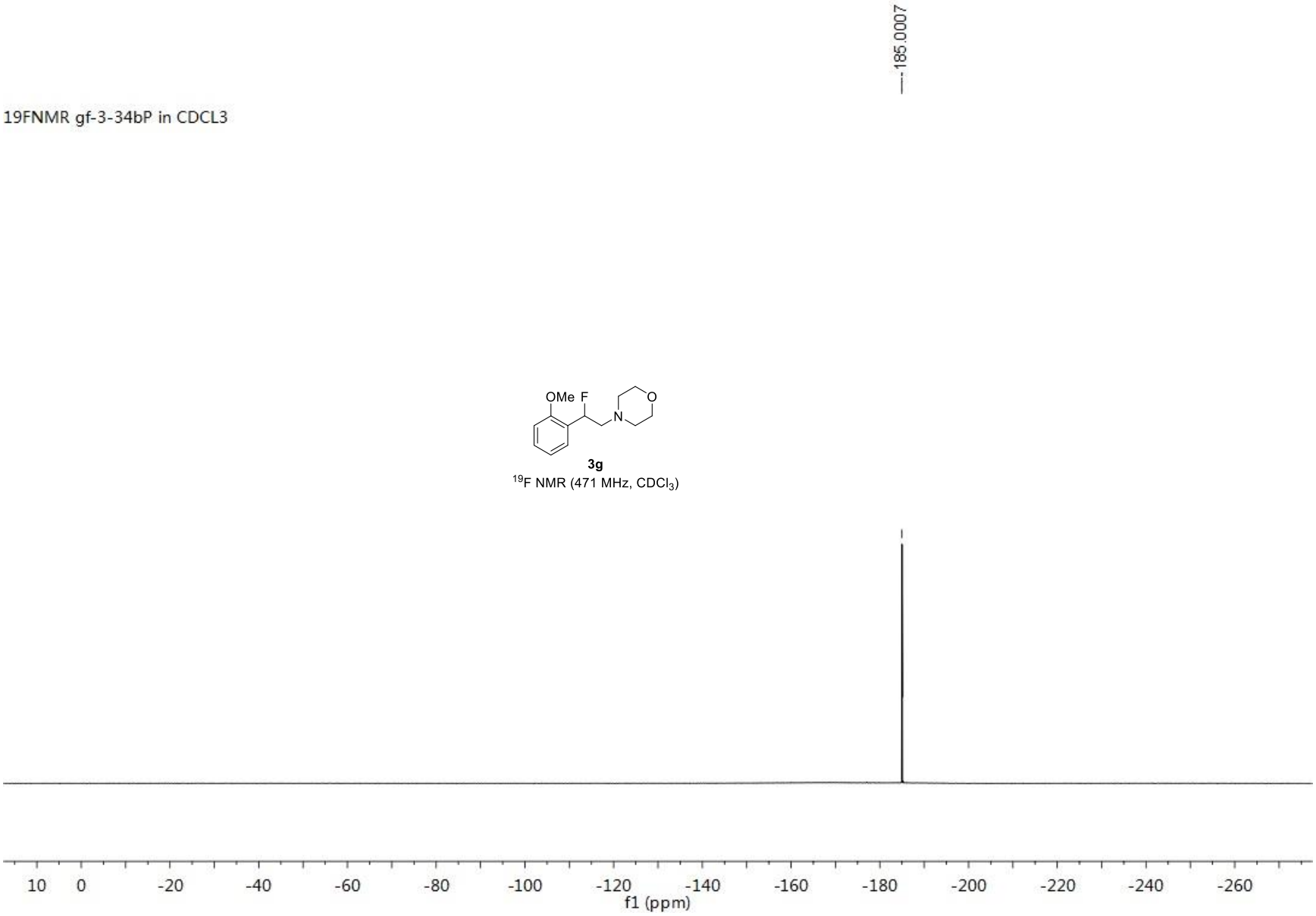
3f

^{19}F NMR (471 MHz, $CDCl_3$)


7.42
7.40
7.31
7.31
7.29
7.28
7.26 CDCl3
7.01
7.00
6.98
6.88
6.86
6.10
6.09
6.08
6.08
6.00
6.00
5.98
5.98
3.83
3.78
3.77
3.77
3.76
3.76
3.75
2.85
2.83
2.82
2.81
2.80
2.79
2.78
2.76
2.71
2.70
2.68
2.67
2.66
2.65
2.64
2.63
2.63
2.62
2.61
2.60
2.60
2.59
OMe F
O
N
3g
1H NMR (500 MHz, CDCl3)
1.00
0.96
1.01
1.08
0.98
3.20
3.98
1.12
5.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

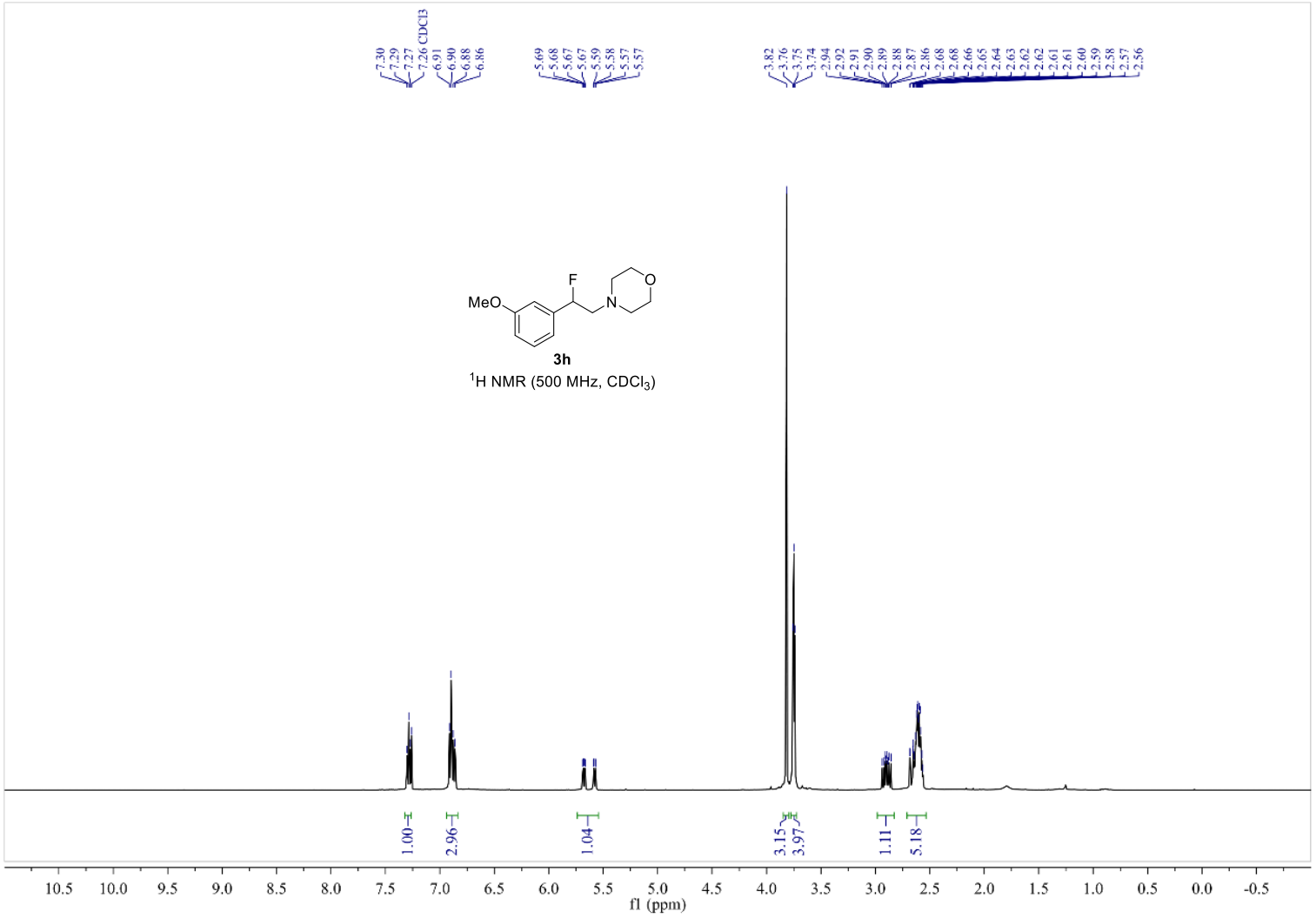

155.32
155.27
129.19
129.17
127.32
127.15
125.98
125.90
120.64
110.18
88.63
87.26
77.25
77.00 CDCl3
76.75
66.95
63.90
63.72
55.28
53.96
OMe F
O
N
3g
13C NMR (125 MHz, CDCl3)
f1 (ppm)

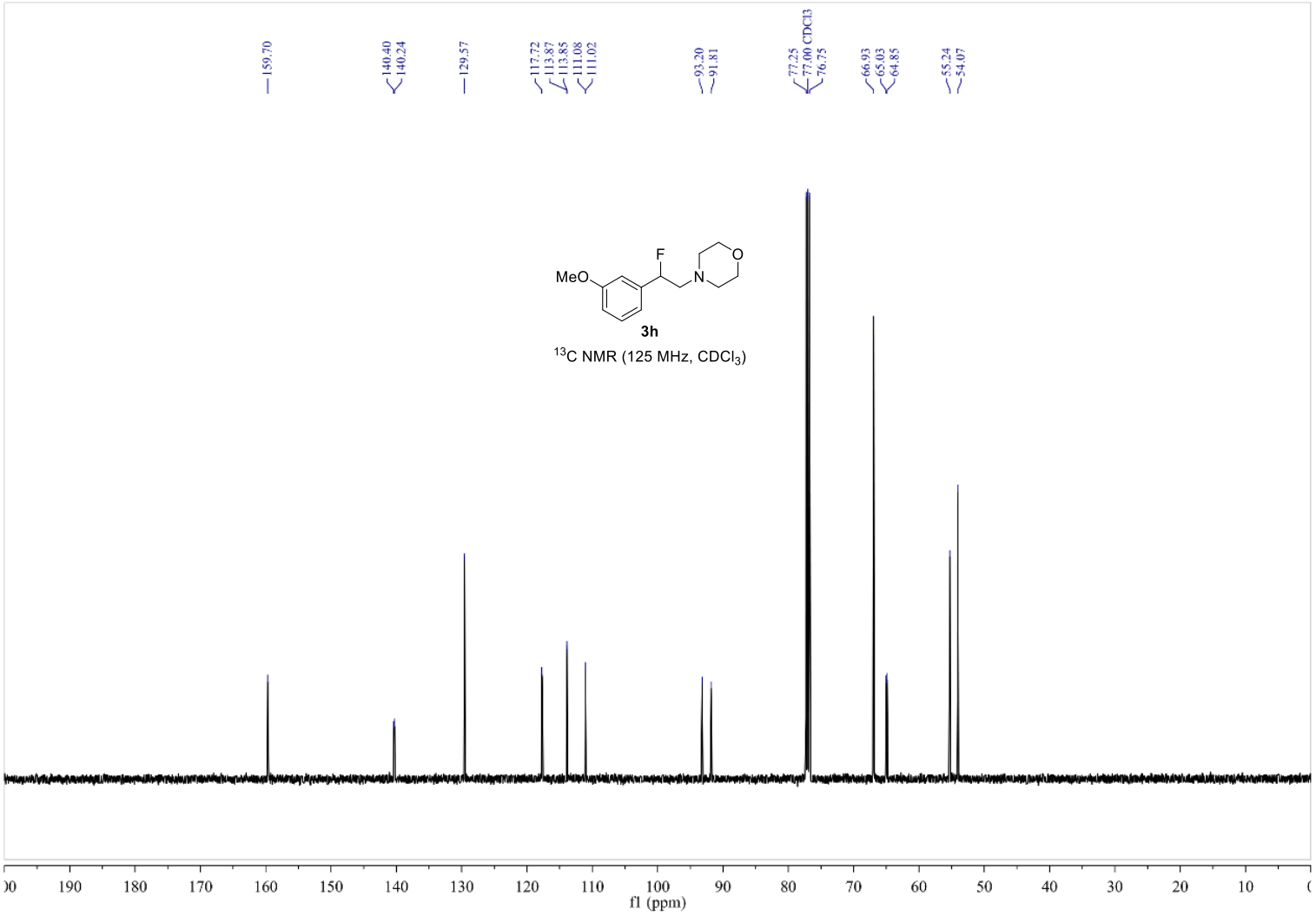
19FNMR gf-3-34bP in CDCL3



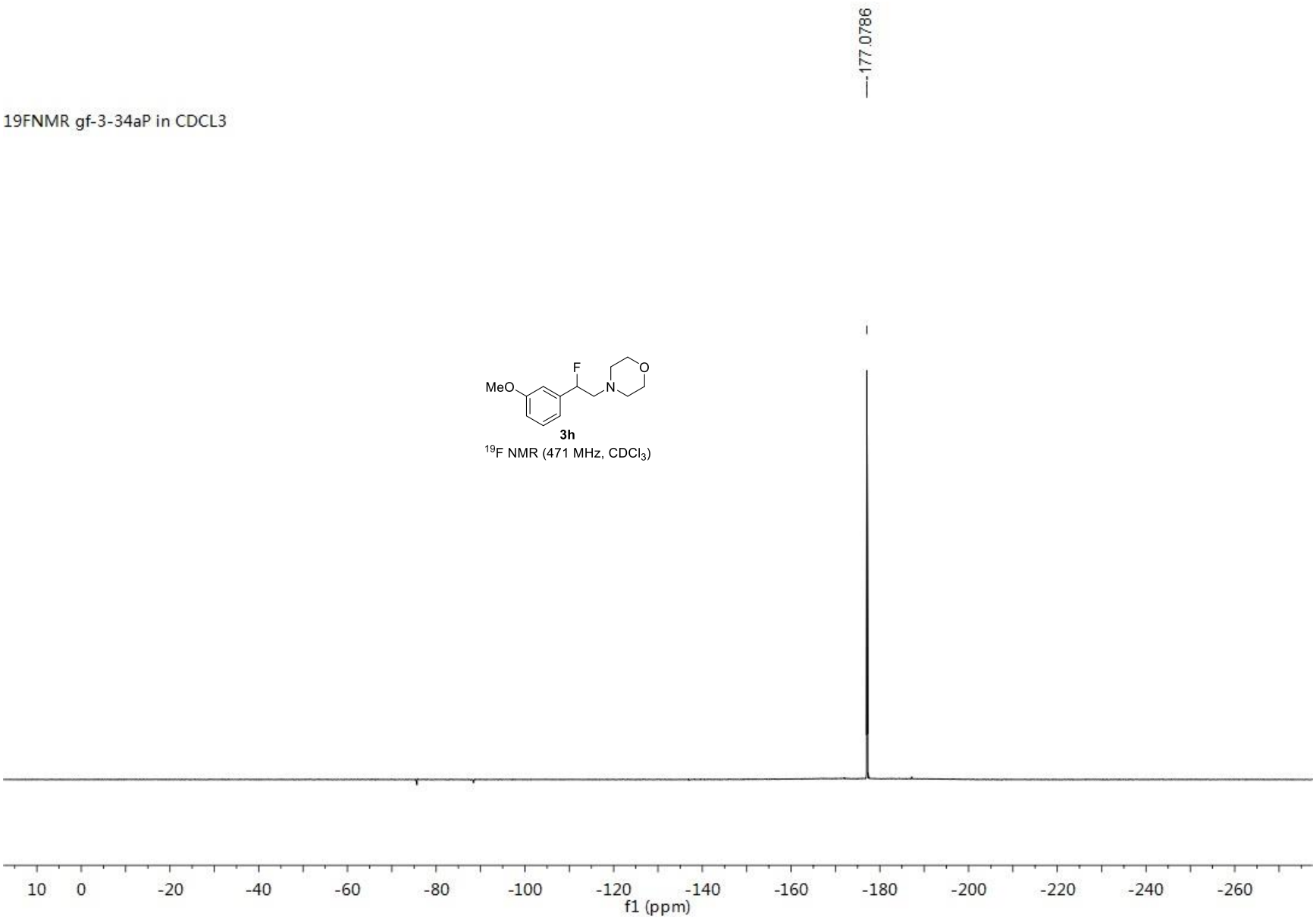
3g

^{19}F NMR (471 MHz, $CDCl_3$)


7.30
7.29
7.27
7.26 CDCl3
6.91
6.90
6.88
6.86
5.69
5.68
5.67
5.67
5.59
5.58
5.57
5.57
3.82
3.76
3.75
3.74
2.94
2.92
2.91
2.90
2.89
2.88
2.87
2.86
2.68
2.68
2.66
2.65
2.64
2.63
2.62
2.62
2.61
2.61
2.60
2.59
2.58
2.57
2.56
F
O
MeO
N
3h
1H NMR (500 MHz, CDCl3)
1.00
2.96
1.04
3.15
3.97
1.11
5.18
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

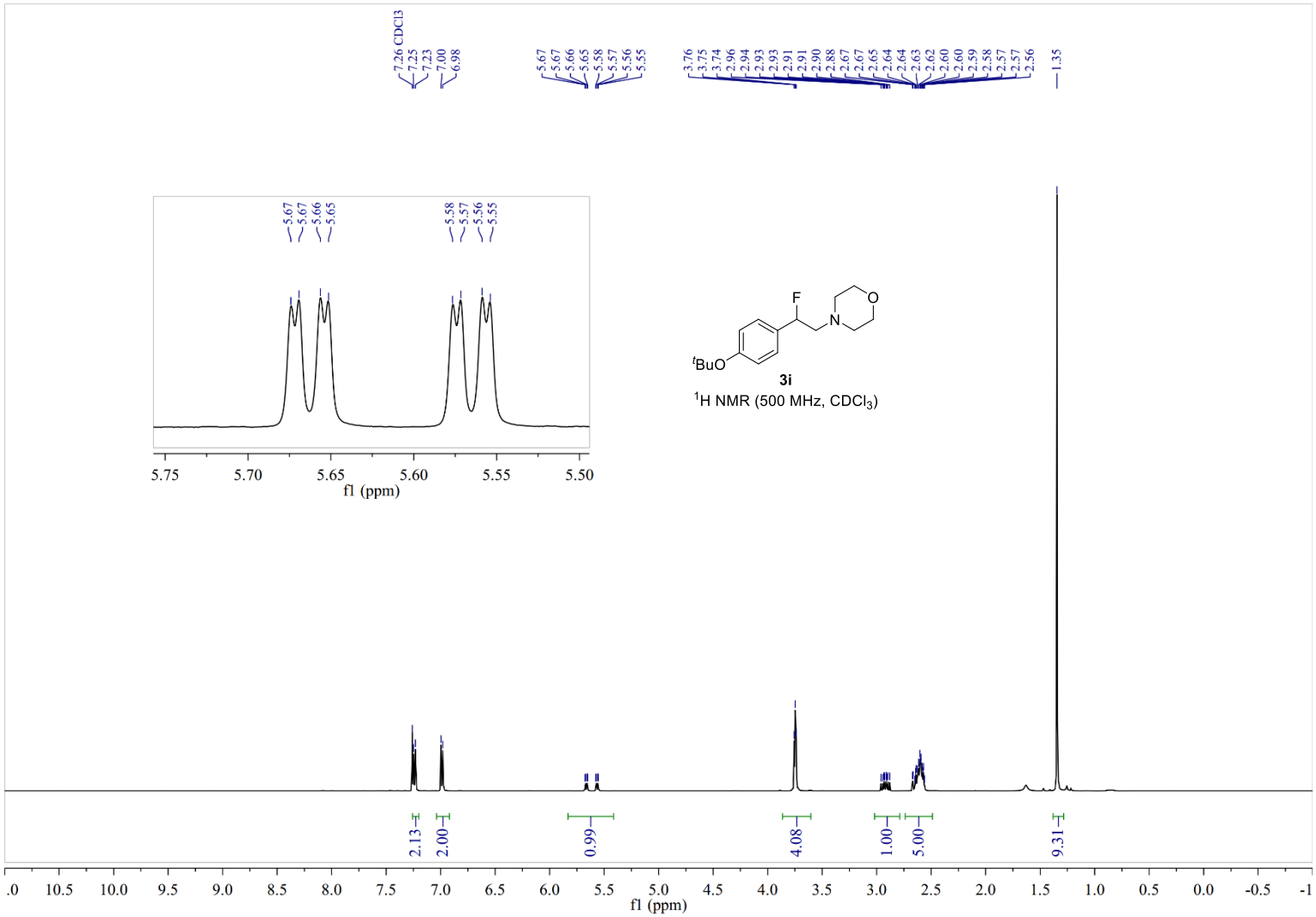

159.70
140.40
140.24
129.57
117.72
113.87
113.85
111.08
111.02
93.20
91.81
77.25
77.00 CDCl3
76.75
66.93
65.03
64.85
55.24
54.07
F
O
MeO
N
3h
13C NMR (125 MHz, CDCl3)
f1 (ppm)

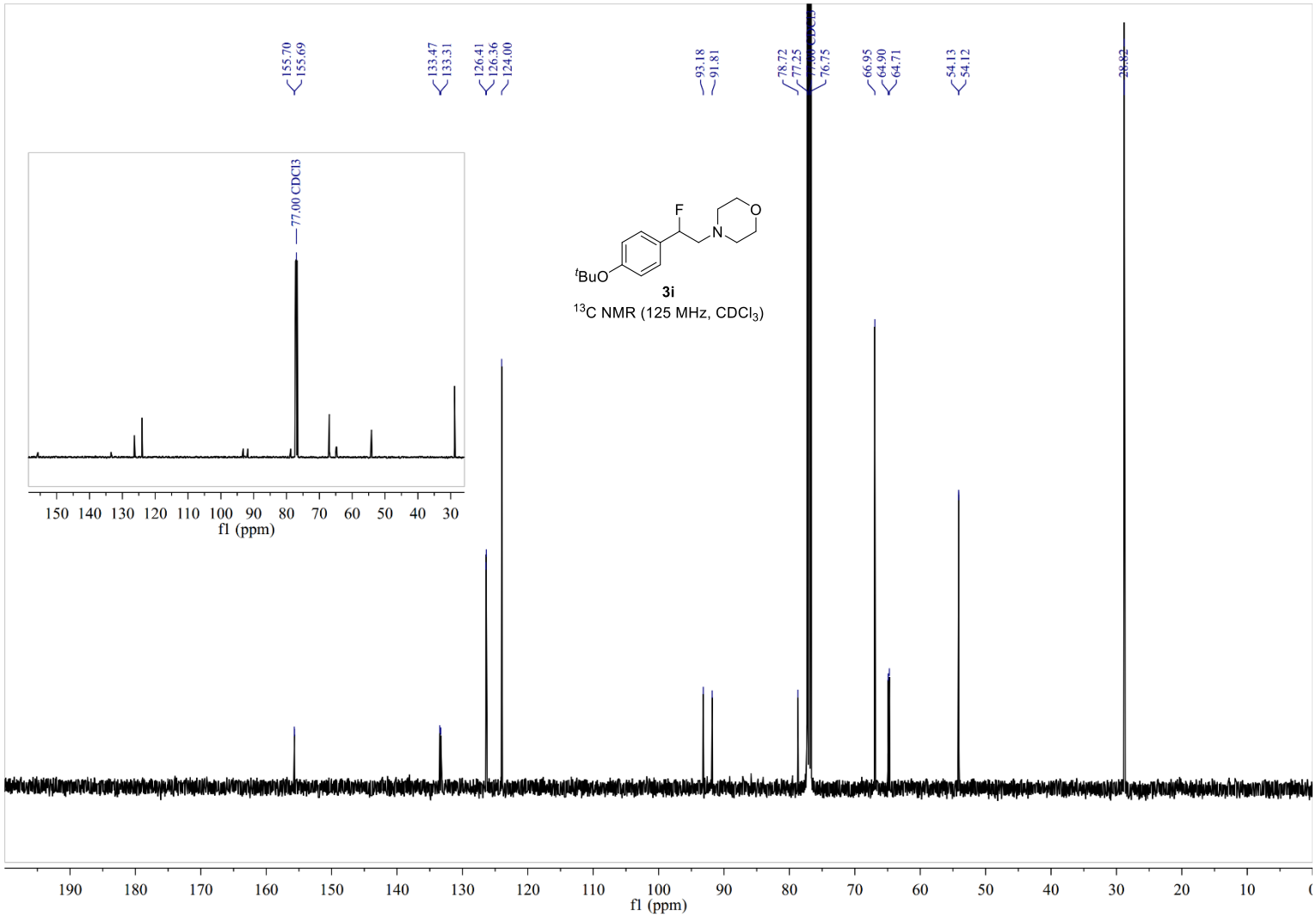
19FNMR gf-3-34aP in CDCL3



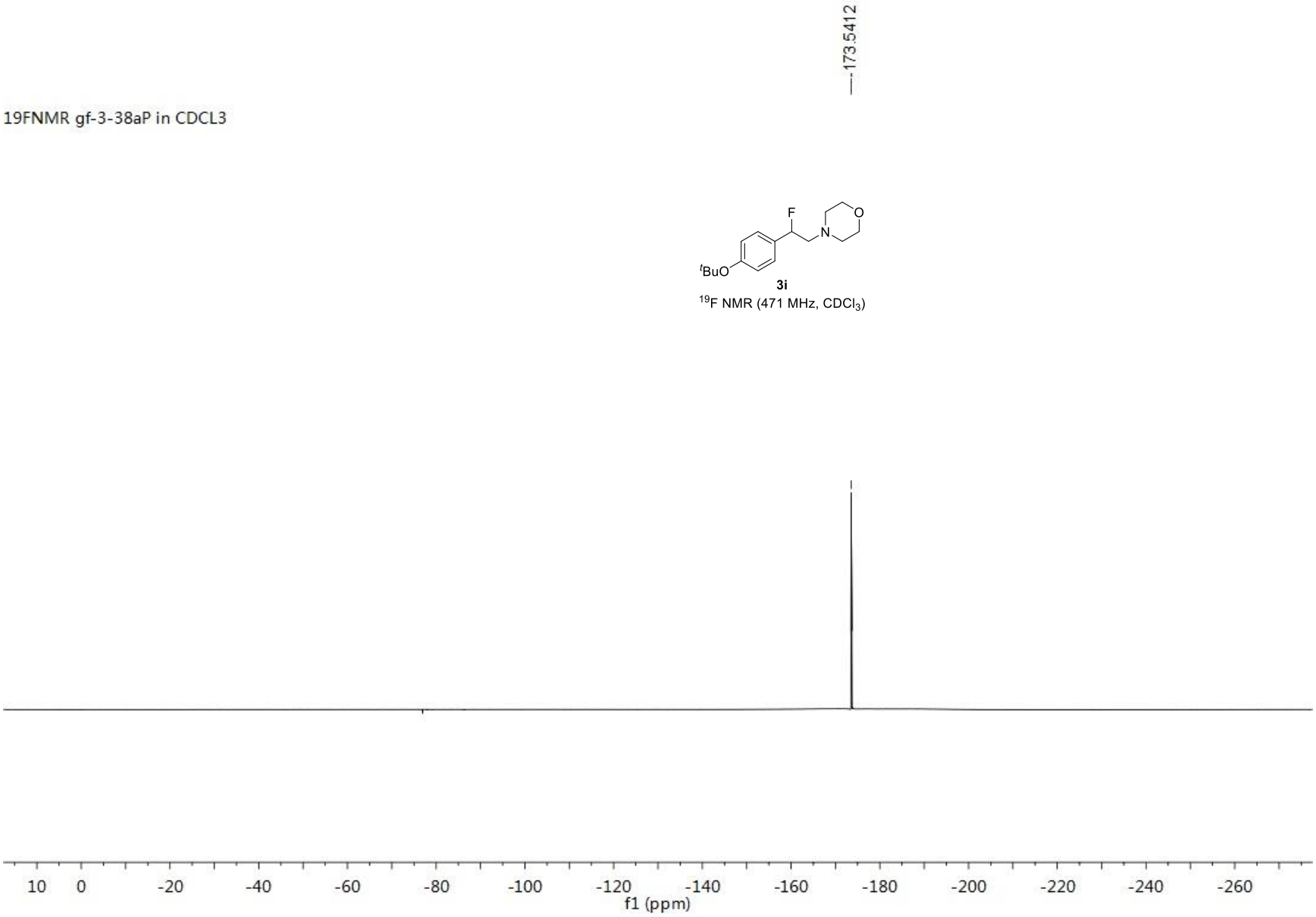
3h

^{19}F NMR (471 MHz, $CDCl_3$)


7.26 CDCl3
7.25
7.23
7.00
6.98
5.67
5.67
5.66
5.65
5.58
5.57
5.56
5.55
3.76
3.75
3.74
2.96
2.94
2.93
2.93
2.91
2.91
2.90
2.88
2.67
2.67
2.65
2.64
2.64
2.63
2.62
2.60
2.60
2.59
2.58
2.57
2.57
2.56
1.35
F
O
N
tBuO
3i
1H NMR (500 MHz, CDCl3)
fl (ppm)
2.13
2.00
0.99
4.08
1.00
5.00
9.31
fl (ppm)


155.70
155.69
133.47
133.31
126.41
126.36
124.00
93.18
91.81
78.72
77.25
76.75
66.95
64.90
64.71
54.13
54.12
28.82
77.00 CDCl3
F
O
N
tBuO
3i
13C NMR (125 MHz, CDCl3)
150 140 130 120 110 100 90 80 70 60 50 40 30
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

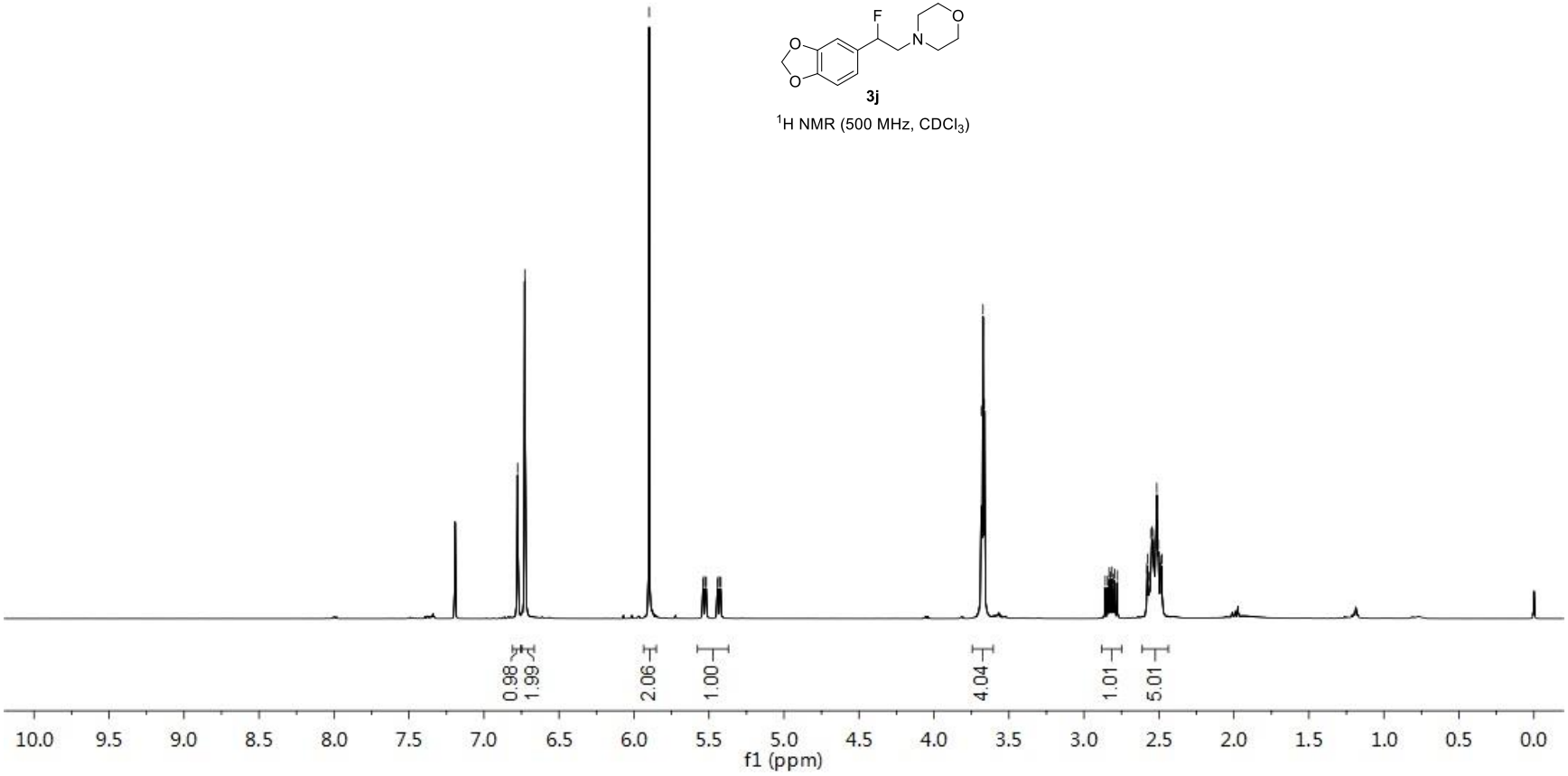
19FNMR gf-3-38aP in CDCL3



3i

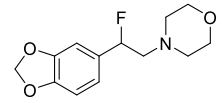
^{19}F NMR (471 MHz, $CDCl_3$)

1HNMR gf-3-39cP in CDCL3



147.86
132.66
132.50
119.56
119.50
108.23
106.32
106.27
101.23
93.23
91.84
66.94
64.90
64.71
54.11

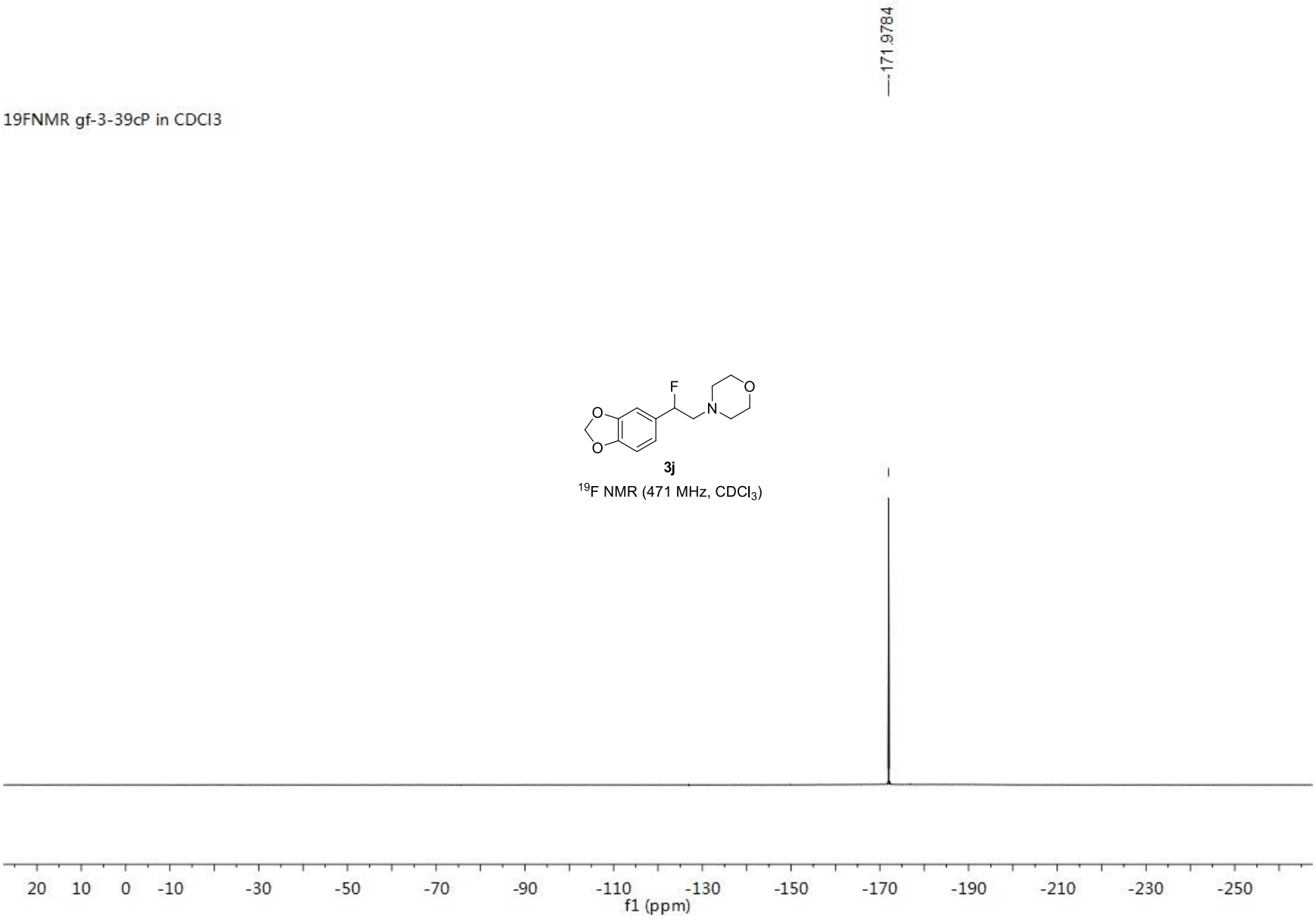
13CNMR gf-3-39cP in CDCL3



3j

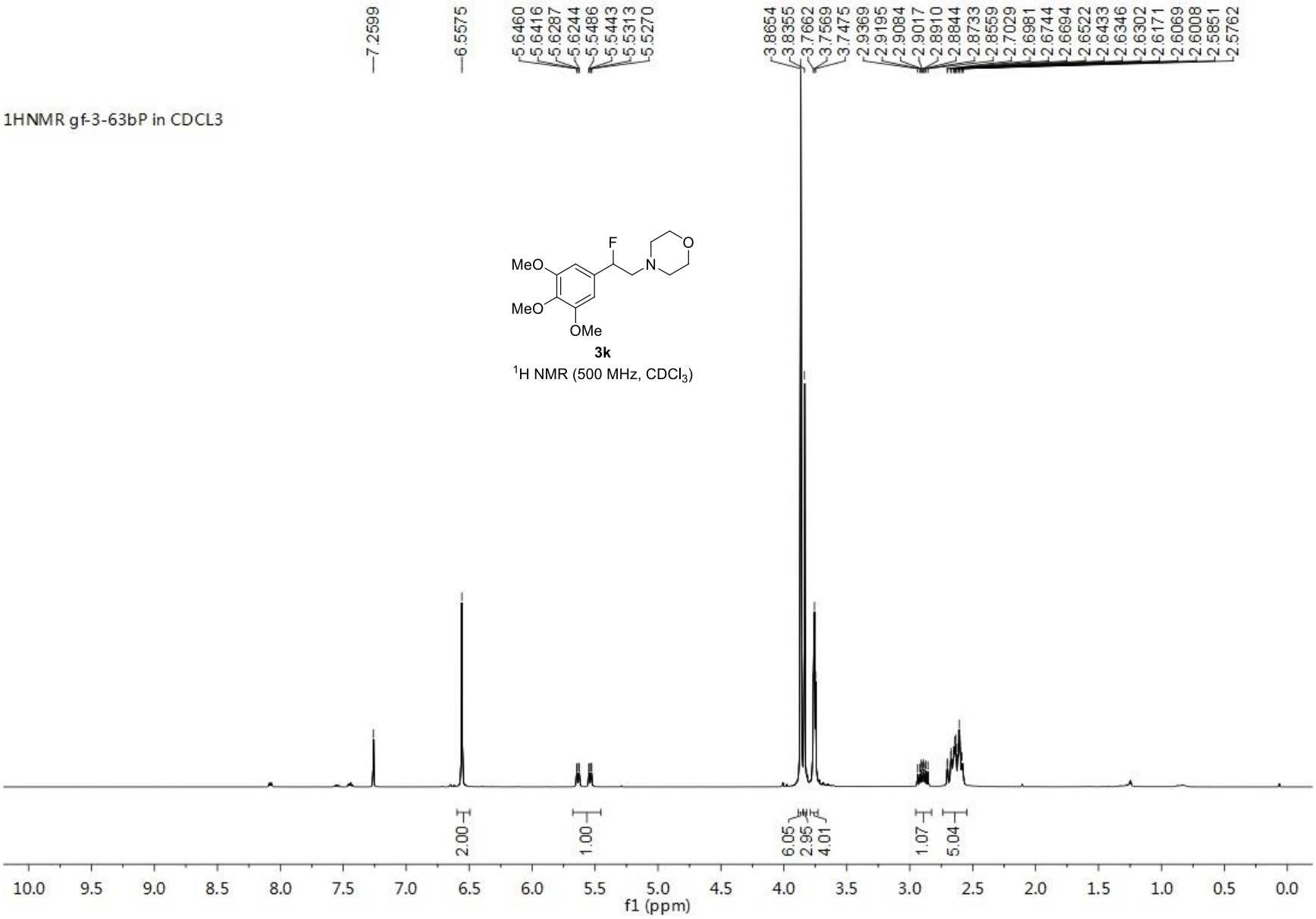
^{13}C NMR (125 MHz, $CDCl_3$)

19FNMR gf-3-39cP in CDCl3



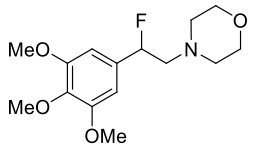
3j

^{19}F NMR (471 MHz, $CDCl_3$)


1HNMR gf-3-63bP in CDCL3
7.2599
6.5575
5.6460
5.6416
5.6287
5.6244
5.5486
5.5443
5.5313
5.5270
3.8654
3.8355
3.7662
3.7569
3.7475
2.9369
2.9195
2.9084
2.9017
2.8910
2.8844
2.8733
2.8559
2.7029
2.6981
2.6744
2.6694
2.6522
2.6433
2.6346
2.6302
2.6171
2.6069
2.6008
2.5851
2.5762
MeO
MeO
OMe
F
N
O
3k
1H NMR (500 MHz, CDCl3)
2.00
1.00
6.05
2.95
4.01
1.07
5.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

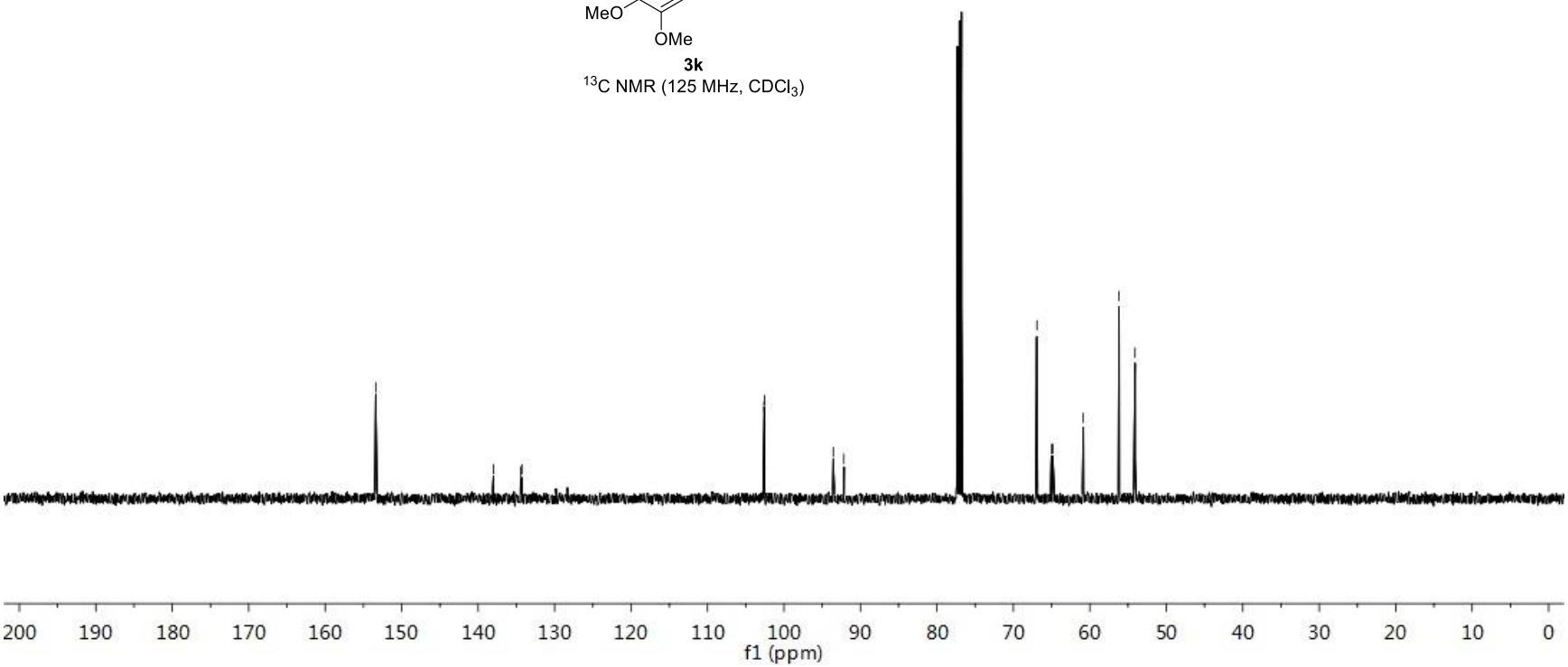
153.39
138.00
134.43
134.27
102.61
102.56
93.55
92.17
66.93
65.03
64.85
60.86
56.17
54.09

13CNMR gf-3-63bP in CDCL3

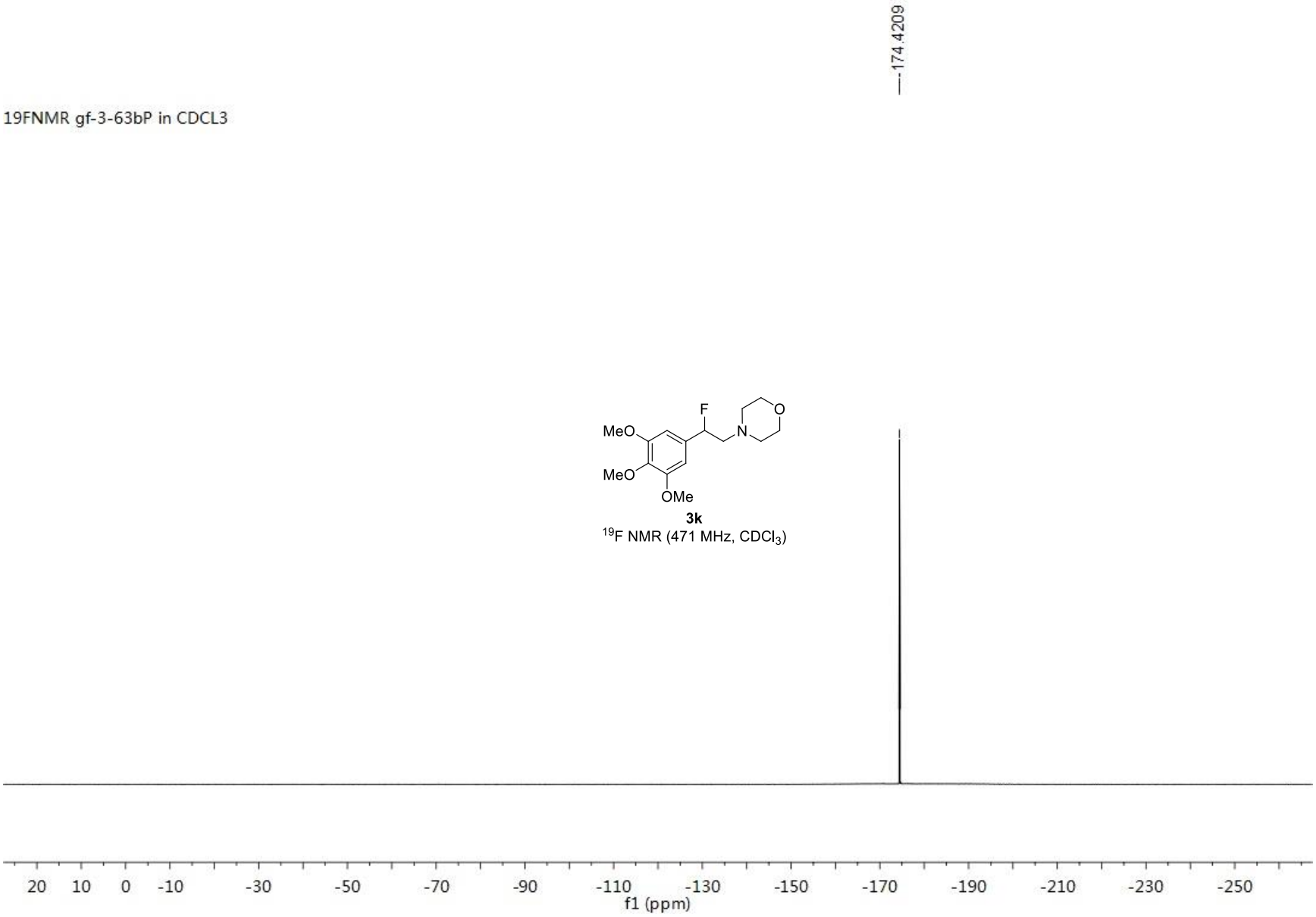


3k

^{13}C NMR (125 MHz, $CDCl_3$)

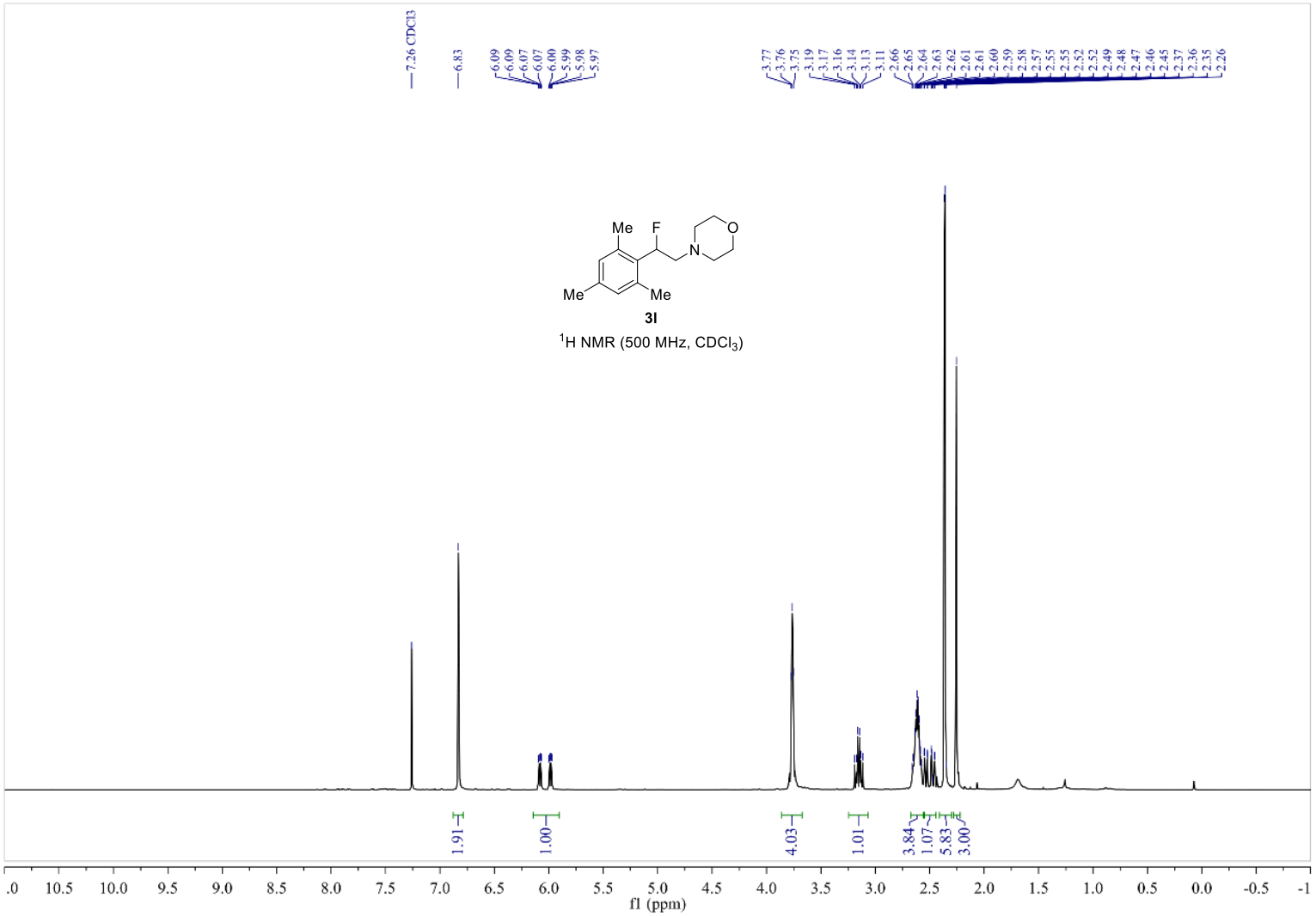


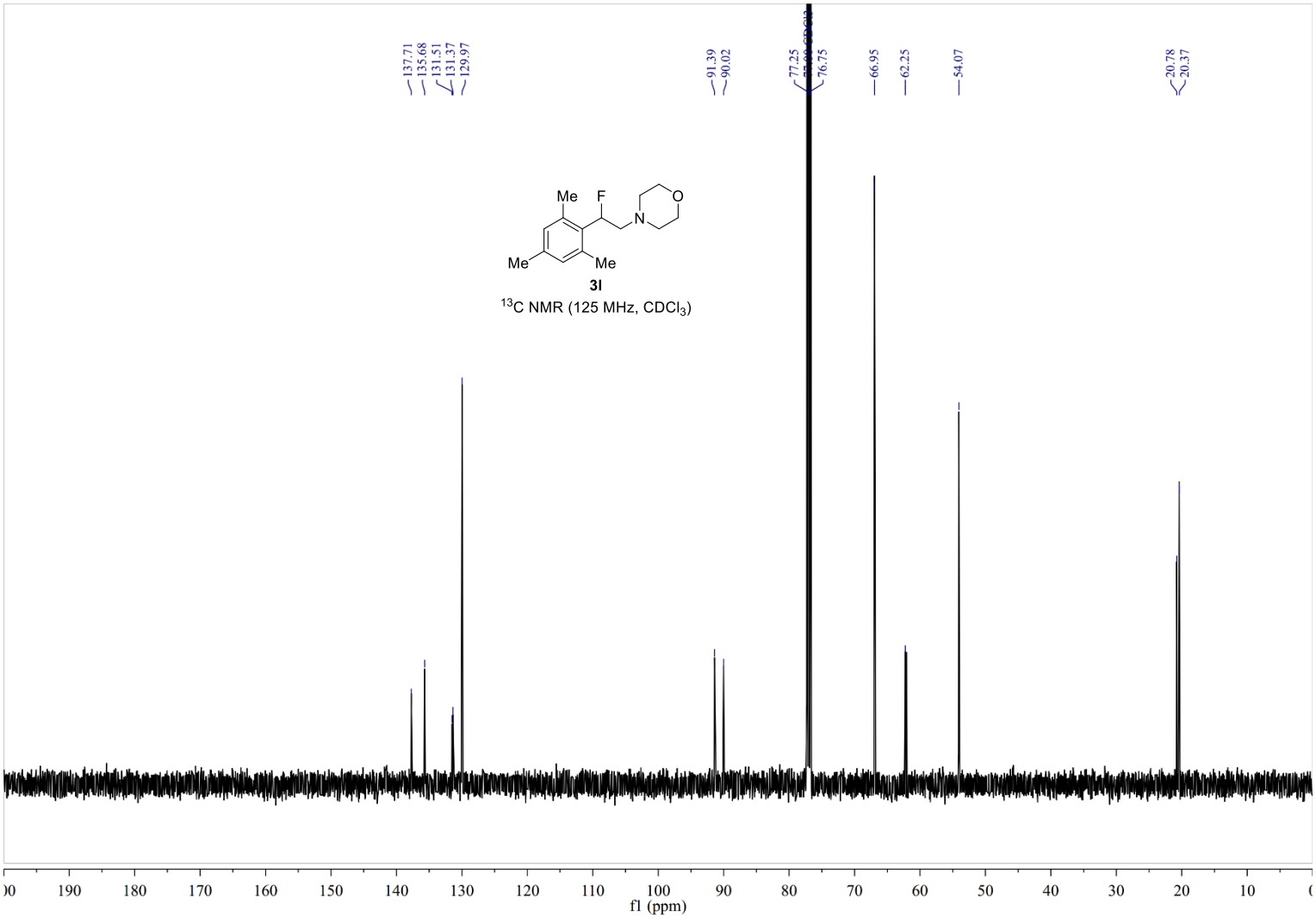
19FNMR gf-3-63bP in CDCL3



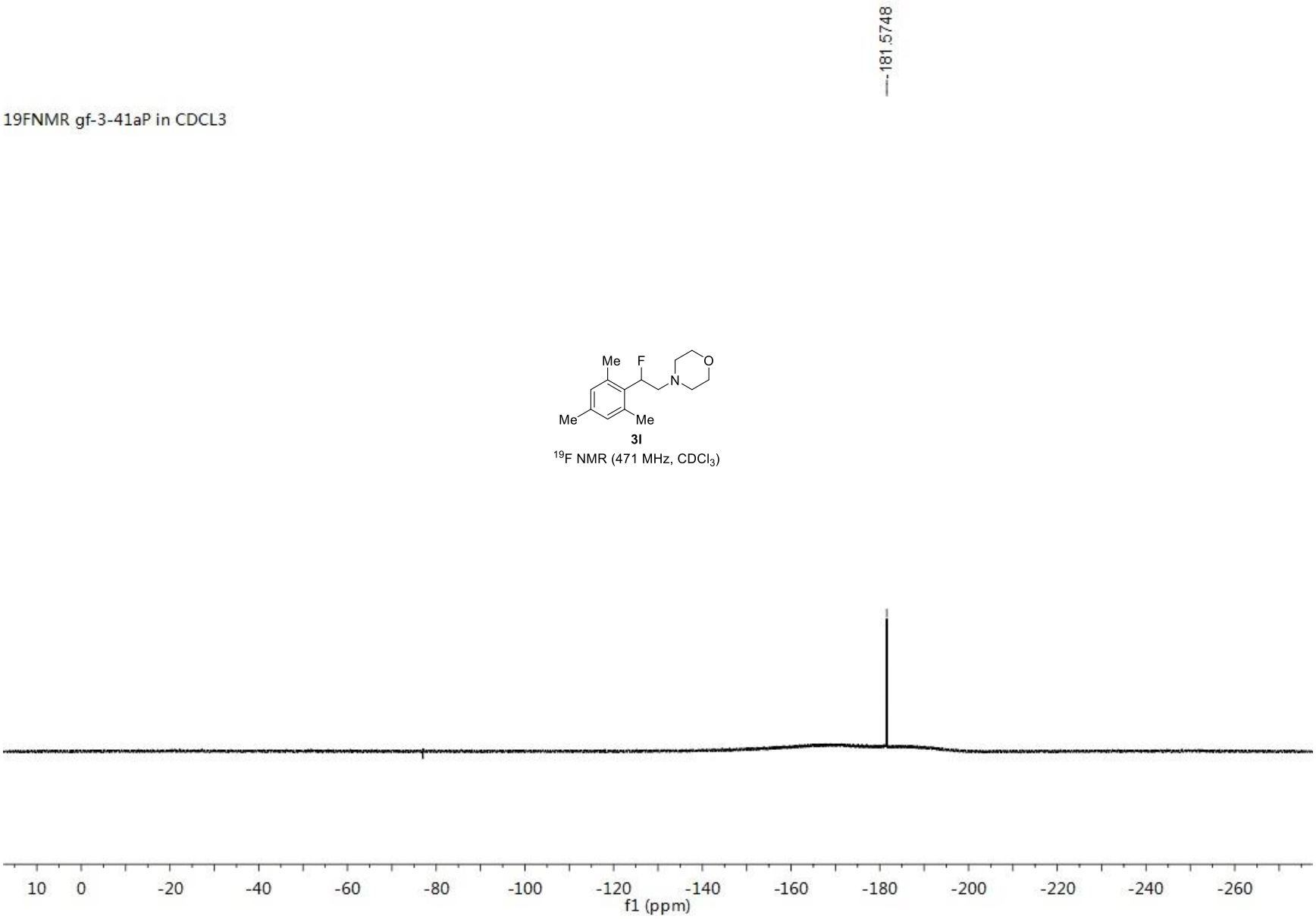
3k

^{19}F NMR (471 MHz, $CDCl_3$)


7.26 CDCl3
6.83
6.09
6.09
6.07
6.07
6.00
5.99
5.98
5.97
3.77
3.76
3.75
3.19
3.17
3.16
3.14
3.13
3.11
2.66
2.65
2.64
2.63
2.62
2.61
2.61
2.60
2.59
2.58
2.57
2.55
2.55
2.52
2.52
2.49
2.48
2.47
2.46
2.45
2.37
2.36
2.35
2.26
Me
F
O
N
Me
Me
3l
1H NMR (500 MHz, CDCl3)
1.91
1.00
4.03
1.01
3.84
1.07
5.83
3.00
fl (ppm)

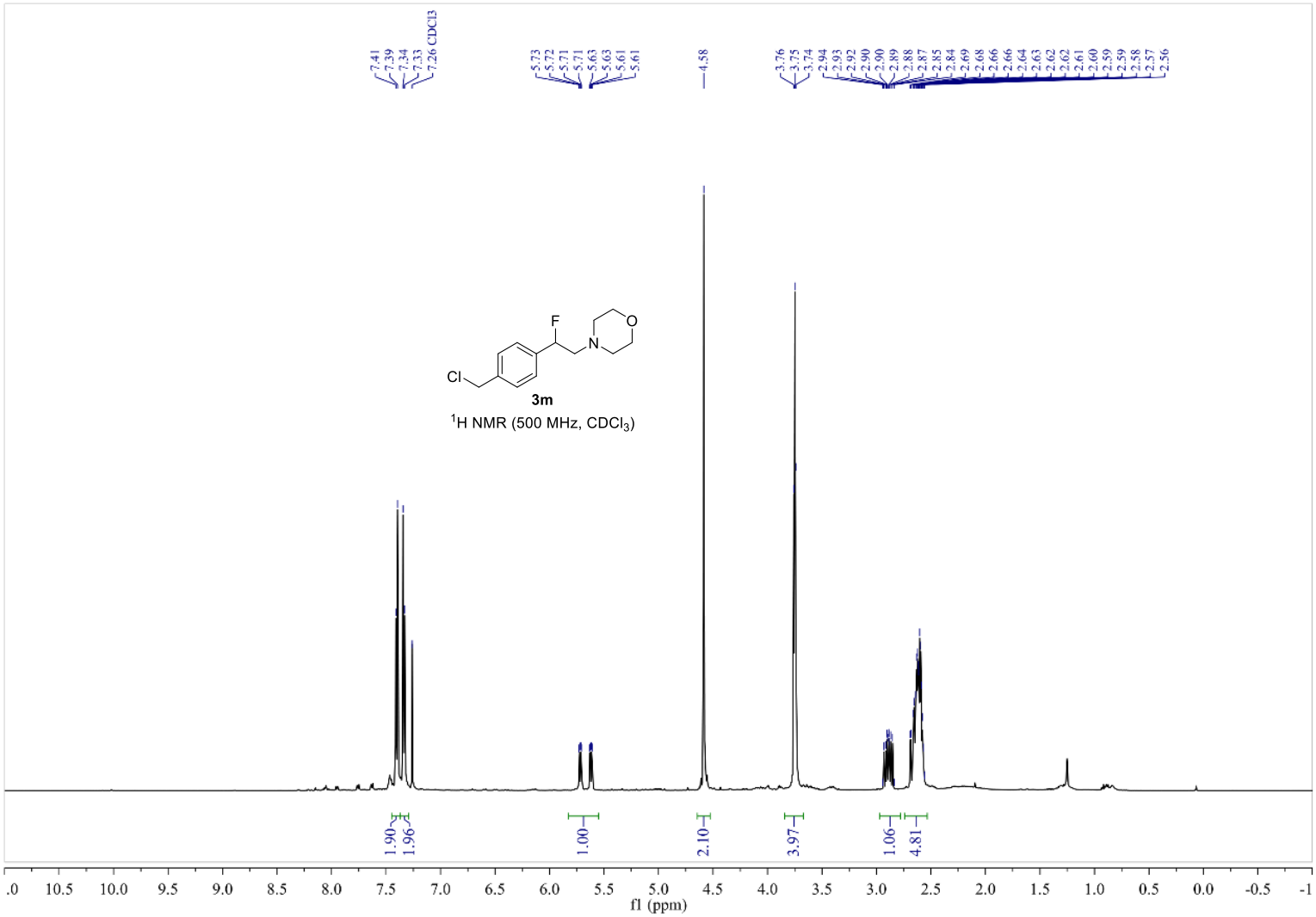

137.71
135.68
131.51
131.37
129.97
91.39
90.02
77.25
76.75
66.95
62.25
54.07
20.78
20.37
Me
F
O
N
Me
Me
3l
13C NMR (125 MHz, CDCl3)
f1 (ppm)

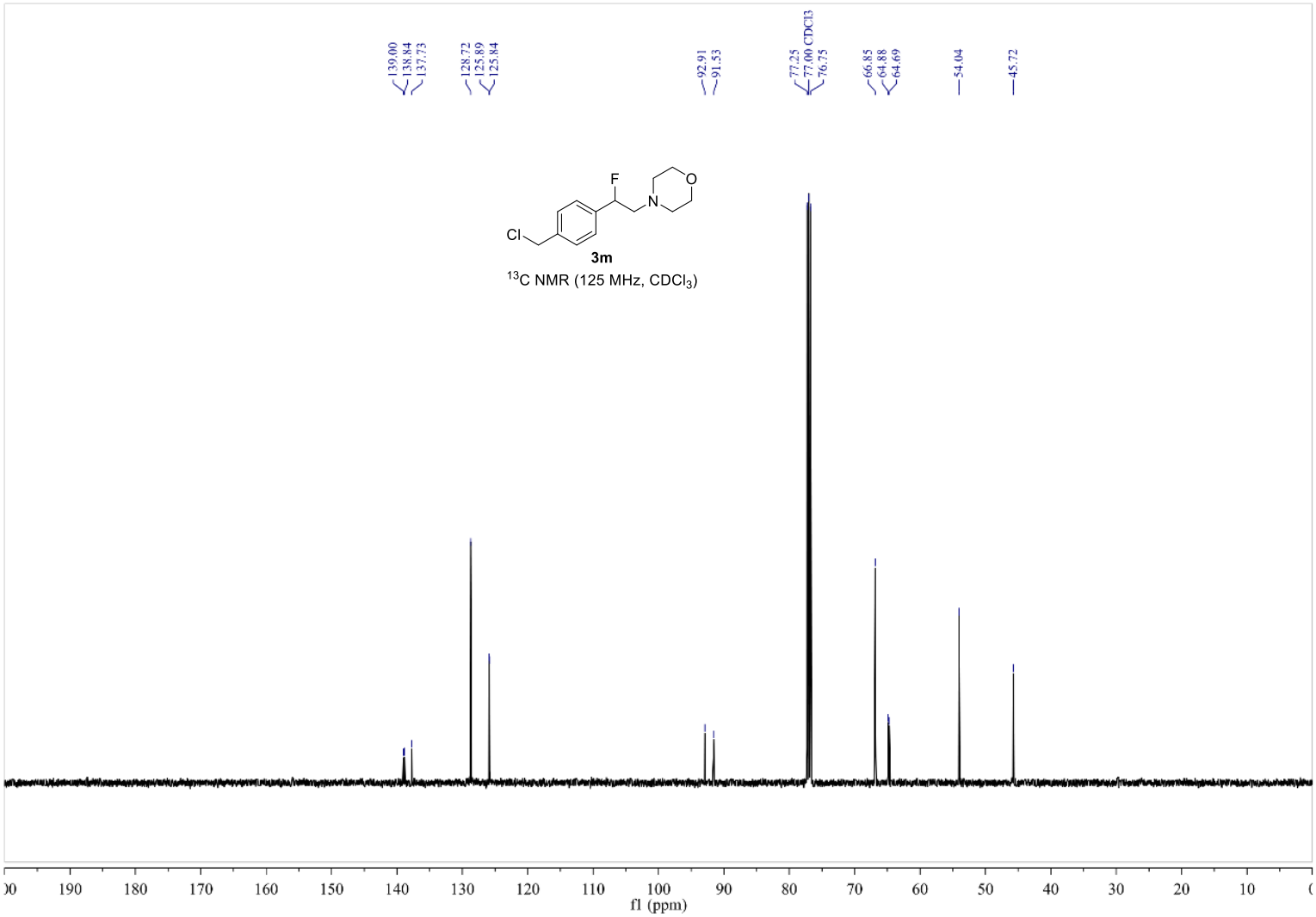
19FNMR gf-3-41aP in CDCL3



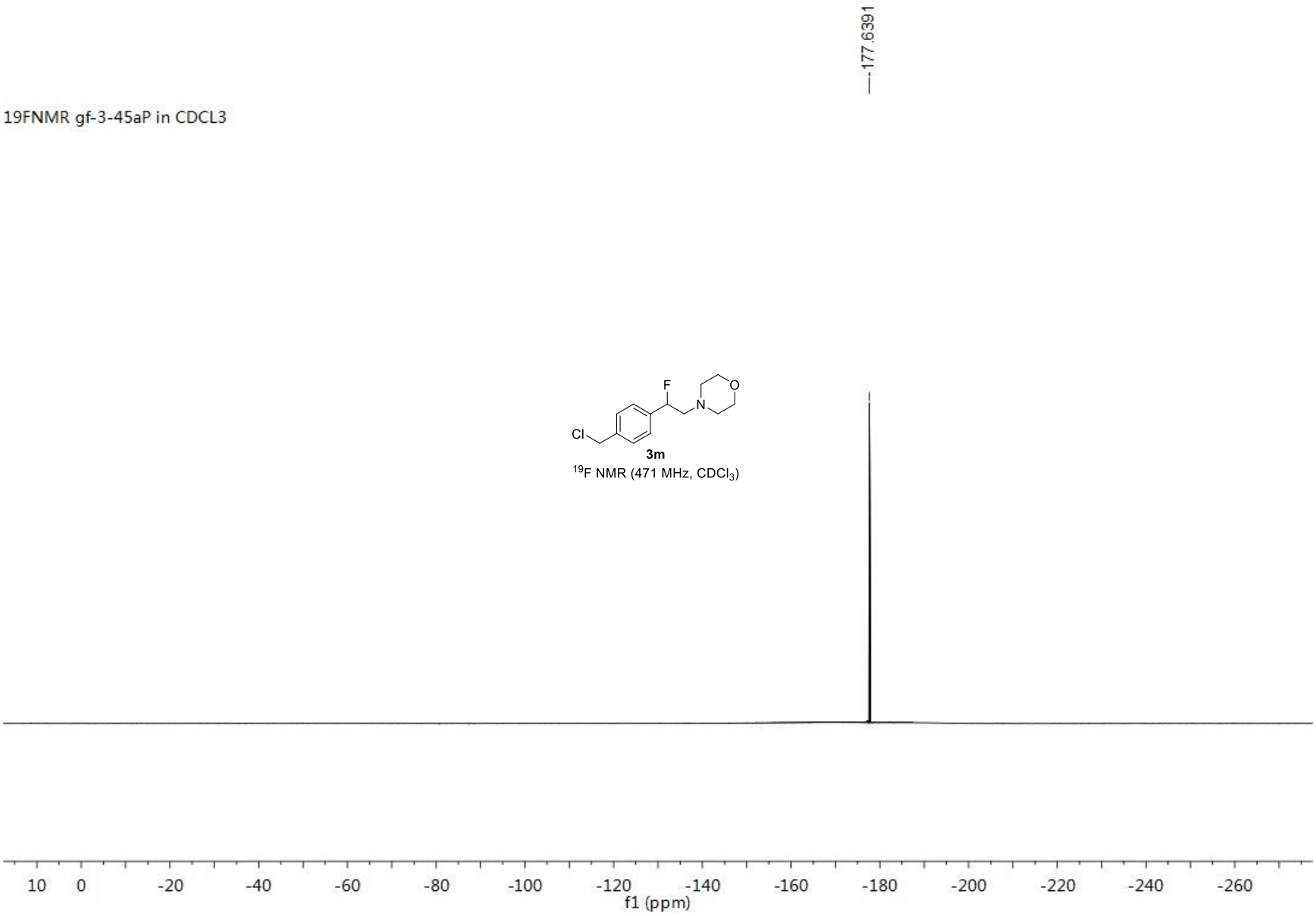
3l

^{19}F NMR (471 MHz, $CDCl_3$)


7.41
7.39
7.34
7.33
7.26 CDCl3
5.73
5.72
5.71
5.71
5.63
5.63
5.61
5.61
4.58
3.76
3.75
3.74
2.94
2.93
2.92
2.90
2.90
2.89
2.88
2.87
2.85
2.84
2.69
2.68
2.66
2.66
2.64
2.63
2.62
2.62
2.61
2.60
2.59
2.59
2.58
2.57
2.56
F
O
N
Cl
3m
1H NMR (500 MHz, CDCl3)
1.90
1.96
1.00
2.10
3.97
1.06
4.81
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

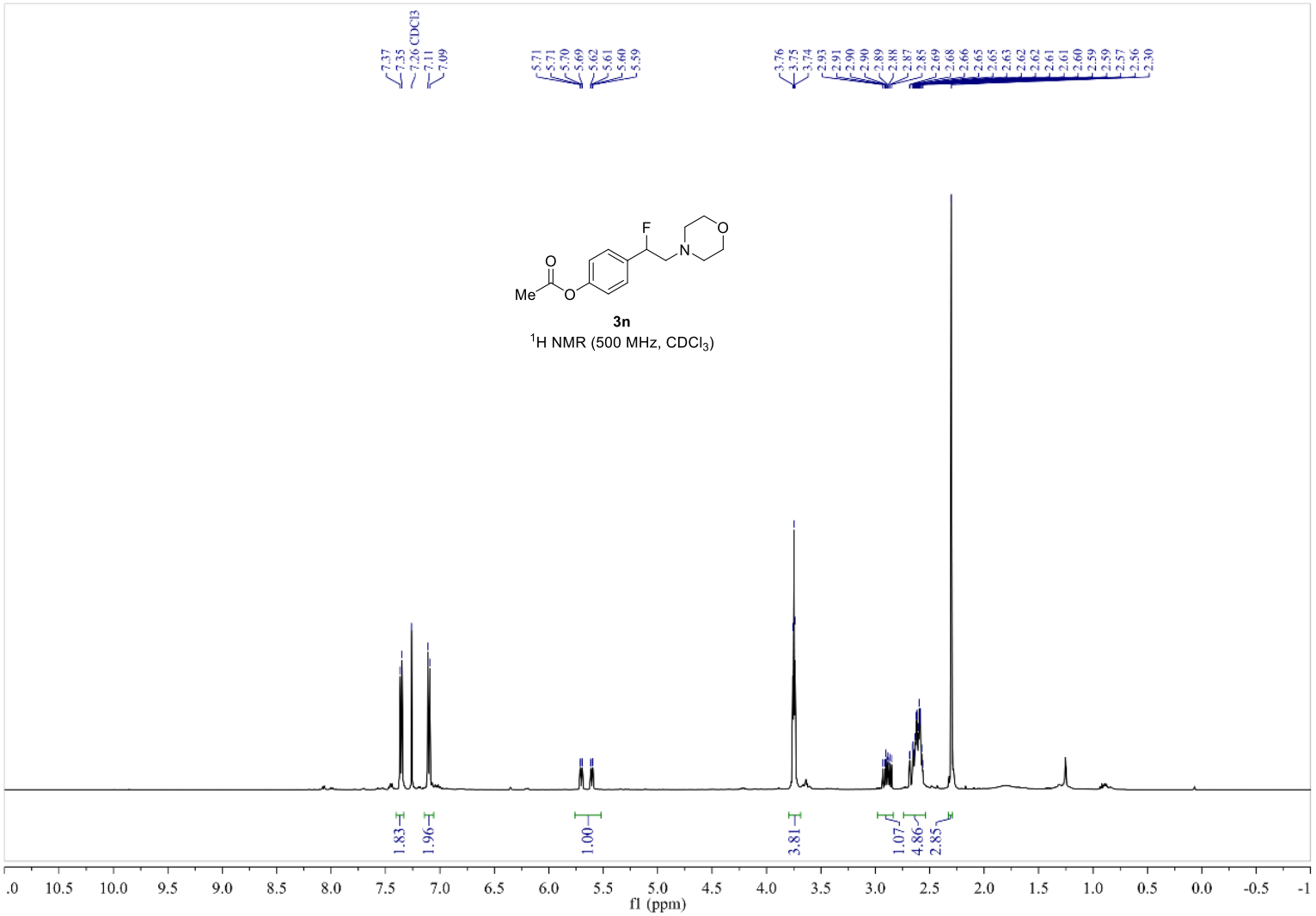

139.00
138.84
137.73
128.72
125.89
125.84
92.91
91.53
77.25
77.00 CDCl3
76.75
66.85
64.88
64.69
54.04
45.72
F
O
N
Cl
3m
13C NMR (125 MHz, CDCl3)
f1 (ppm)

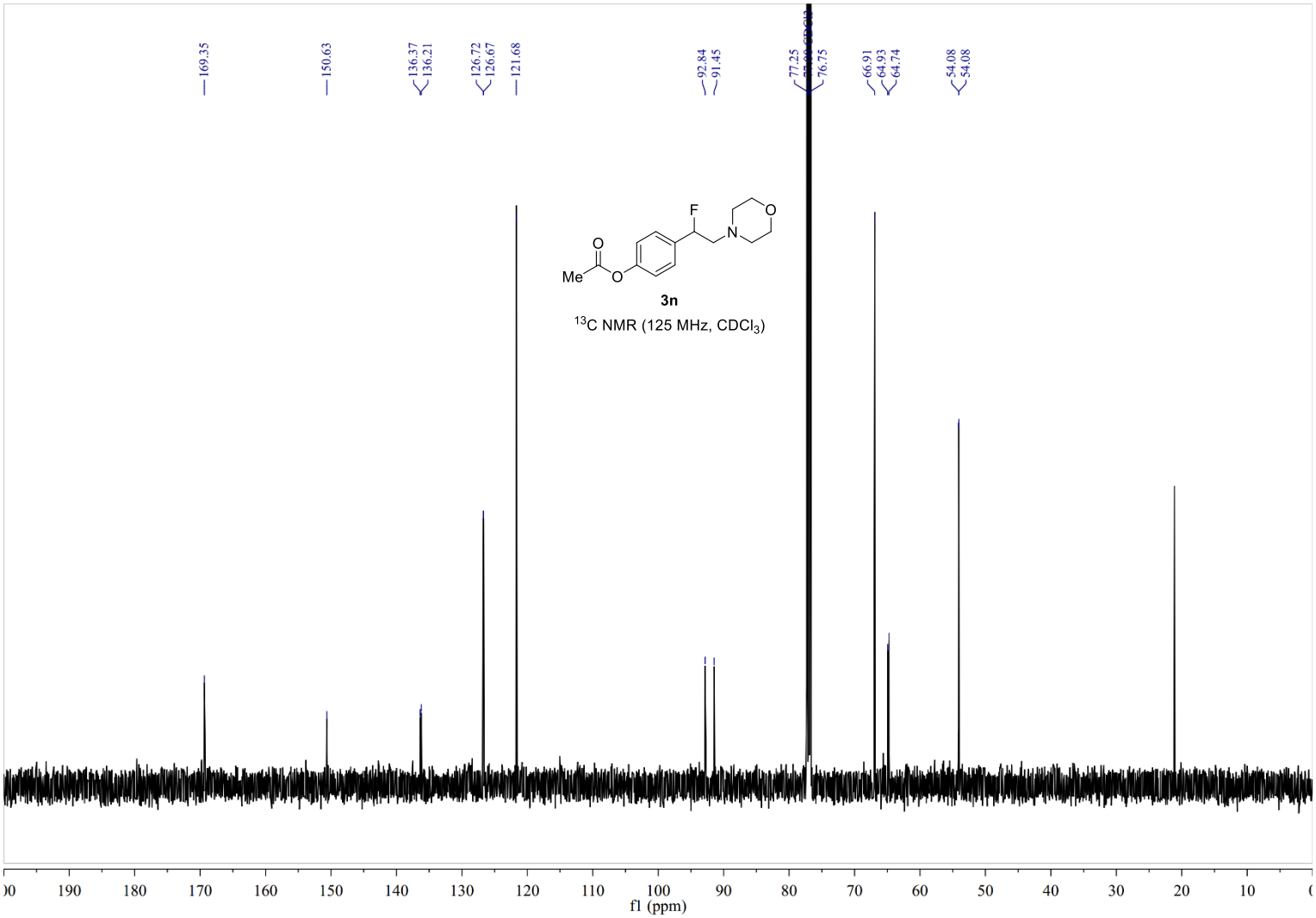
19FNMR gf-3-45aP in CDCL3



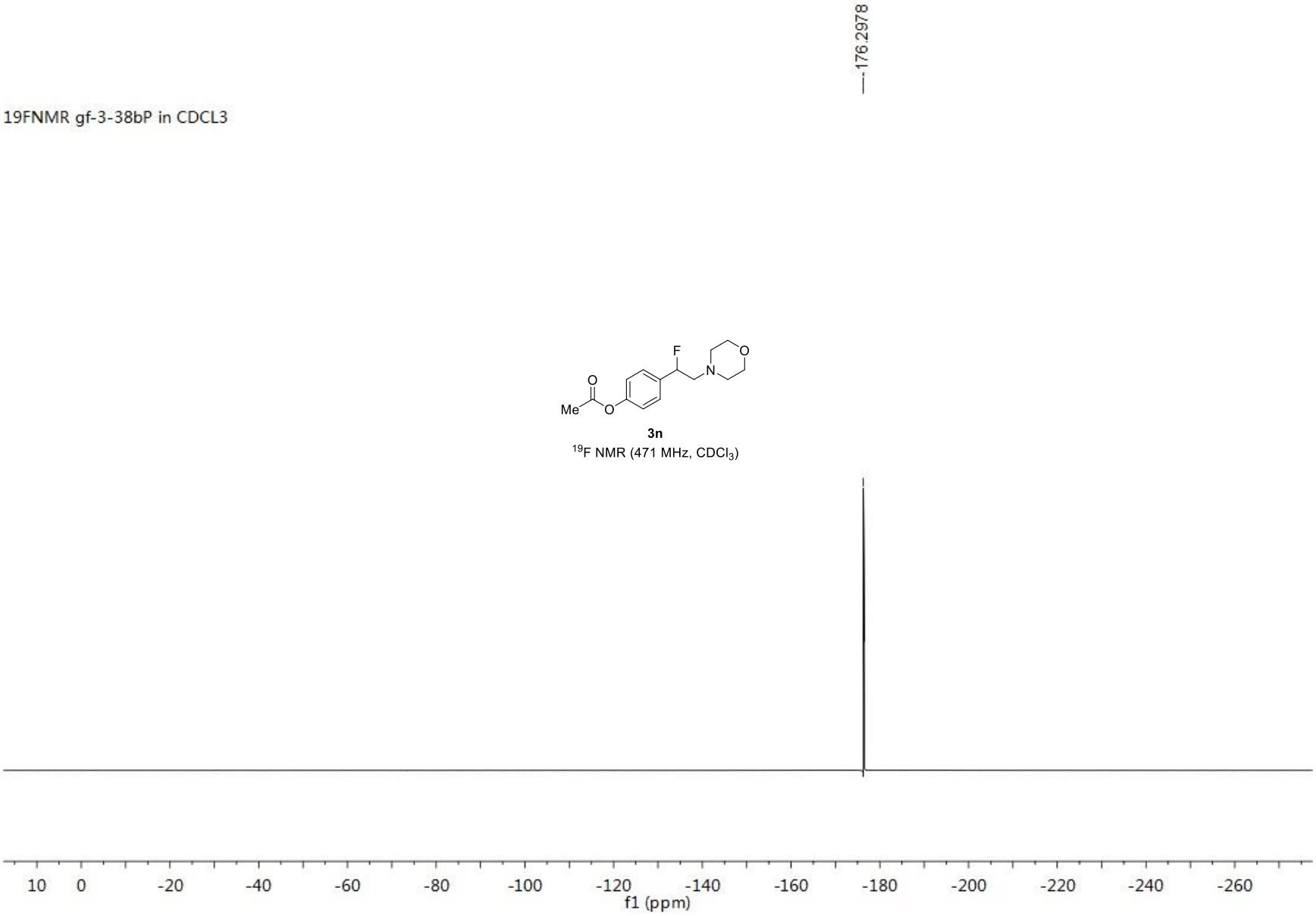
3m

^{19}F NMR (471 MHz, $CDCl_3$)


7.37
7.35
7.26 CDCl3
7.11
7.09
5.71
5.71
5.70
5.69
5.62
5.61
5.60
5.59
3.76
3.75
3.74
2.93
2.91
2.90
2.90
2.89
2.88
2.87
2.85
2.69
2.68
2.66
2.65
2.65
2.63
2.62
2.62
2.61
2.61
2.60
2.59
2.59
2.57
2.56
2.30
F
O
N
O
Me
O
3n
1H NMR (500 MHz, CDCl3)
1.83
1.96
1.00
3.81
1.07
4.86
2.85
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


169.35
150.63
136.37
136.21
126.72
126.67
121.68
92.84
91.45
77.25
76.75
66.91
64.93
64.74
54.08
54.08
F
O
N
O
Me
O
3n
13C NMR (125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

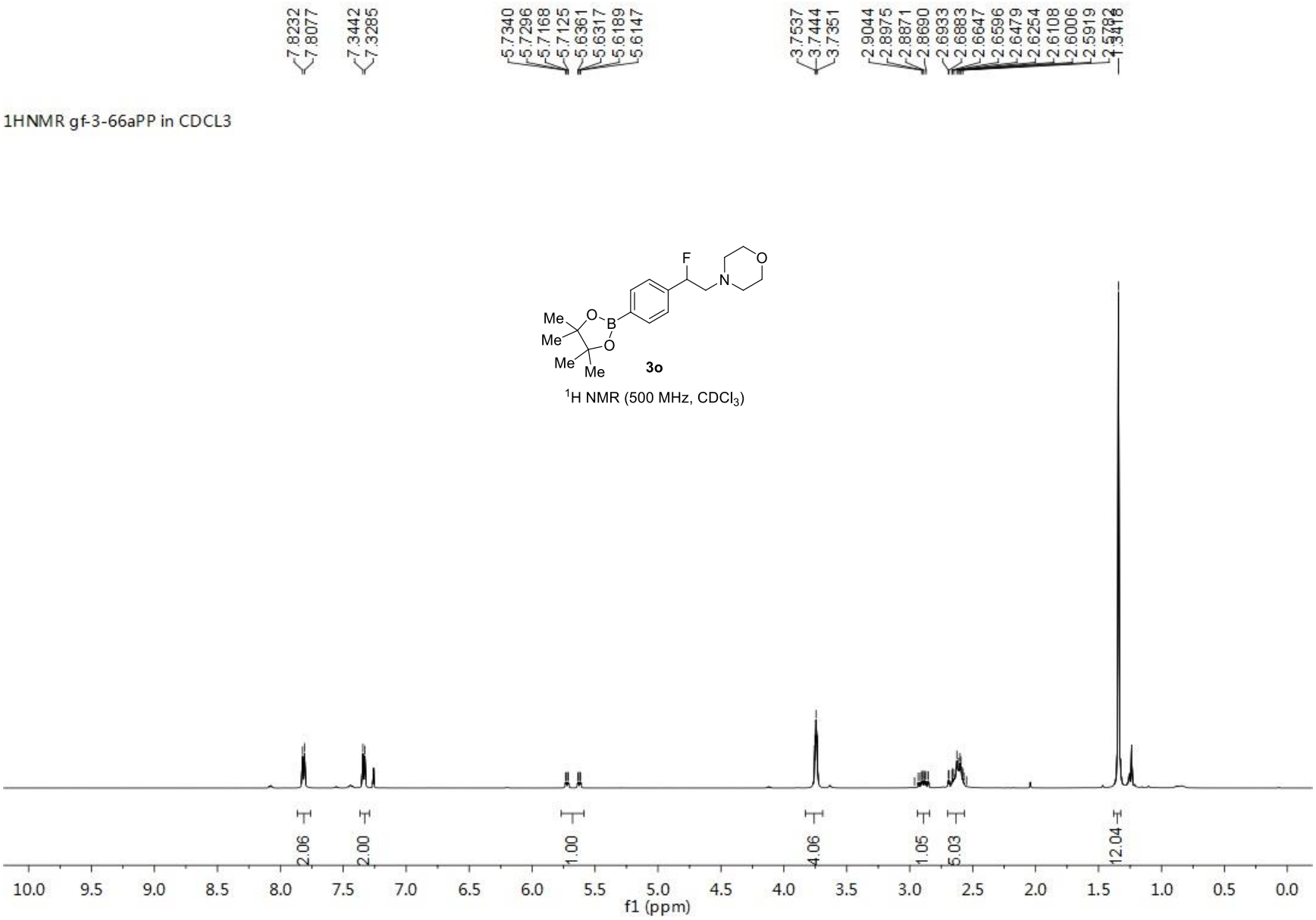
19FNMR gf-3-38bP in CDCL3

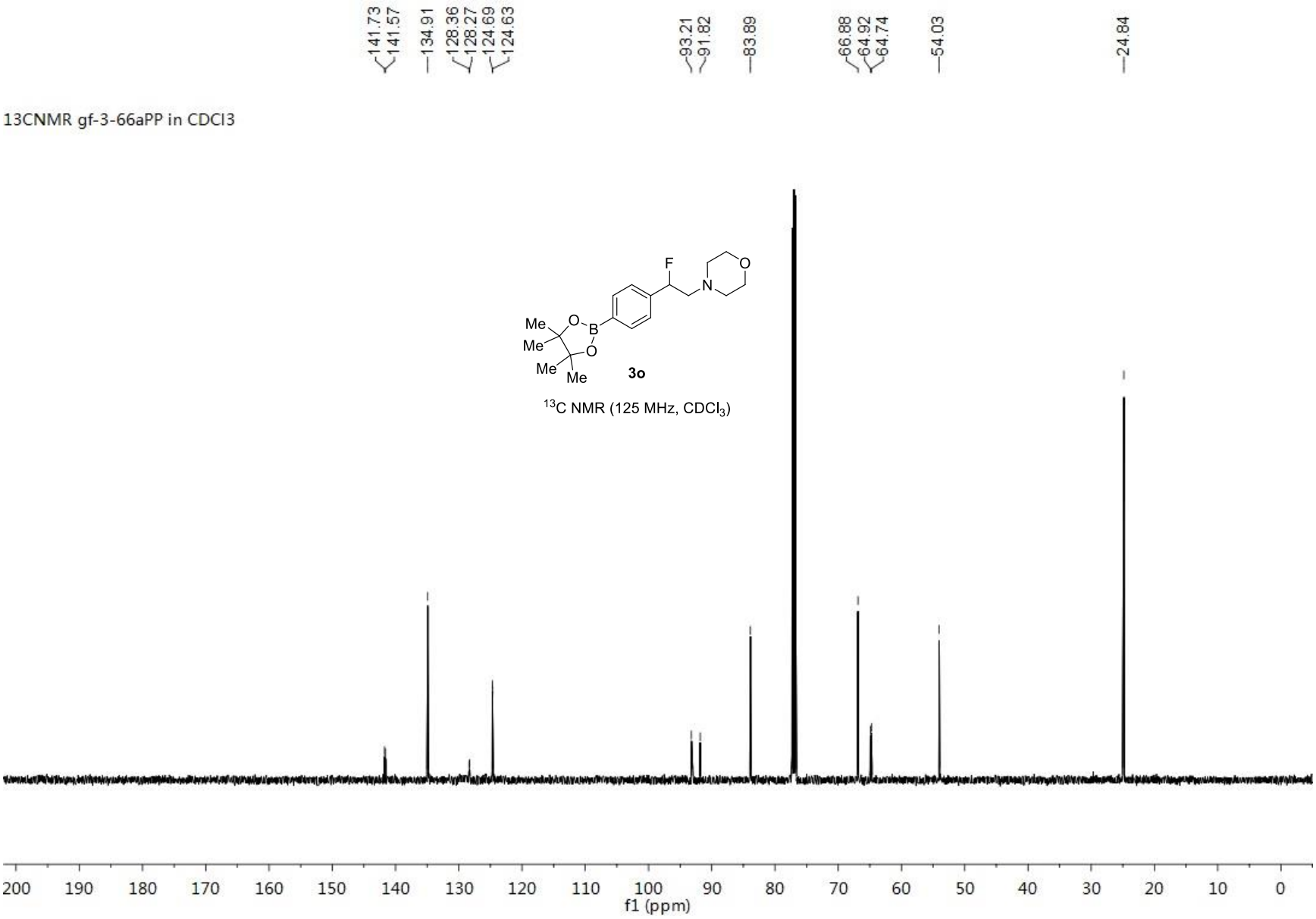


3n

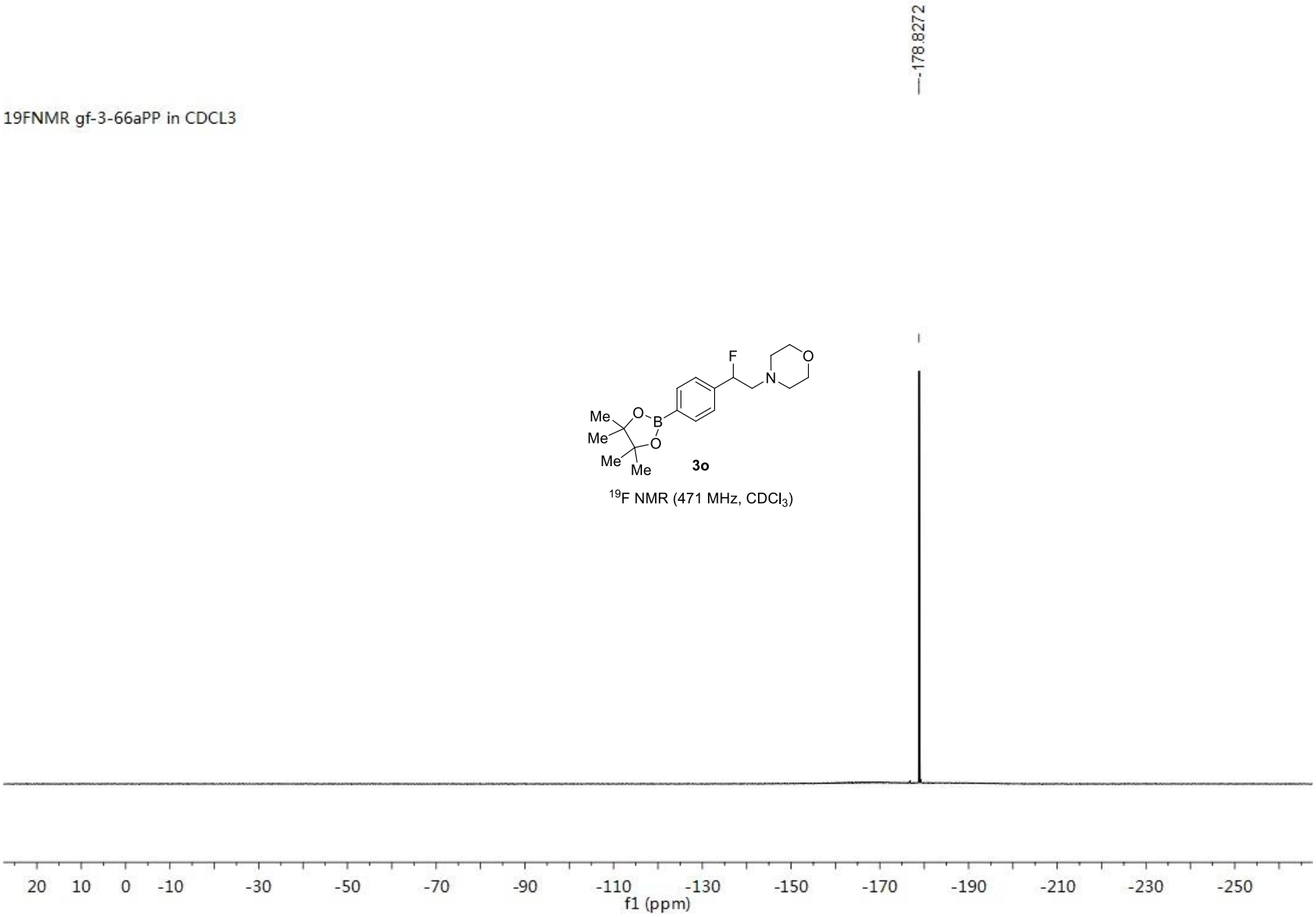
^{19}F NMR (471 MHz, $CDCl_3$)

1HNMR gf-3-66aPP in CDCL3




141.73
141.57
134.91
128.36
128.27
124.69
124.63
93.21
91.82
83.89
66.88
64.92
64.74
54.03
24.84
13CNMR gf-3-66aPP in CDCl3
F
O
N
Me
O
B
Me
O
Me
Me
3o
^{13}C NMR (125 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

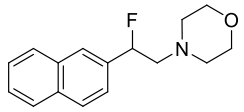
19FNMR gf-3-66aPP in CDCL3



3o

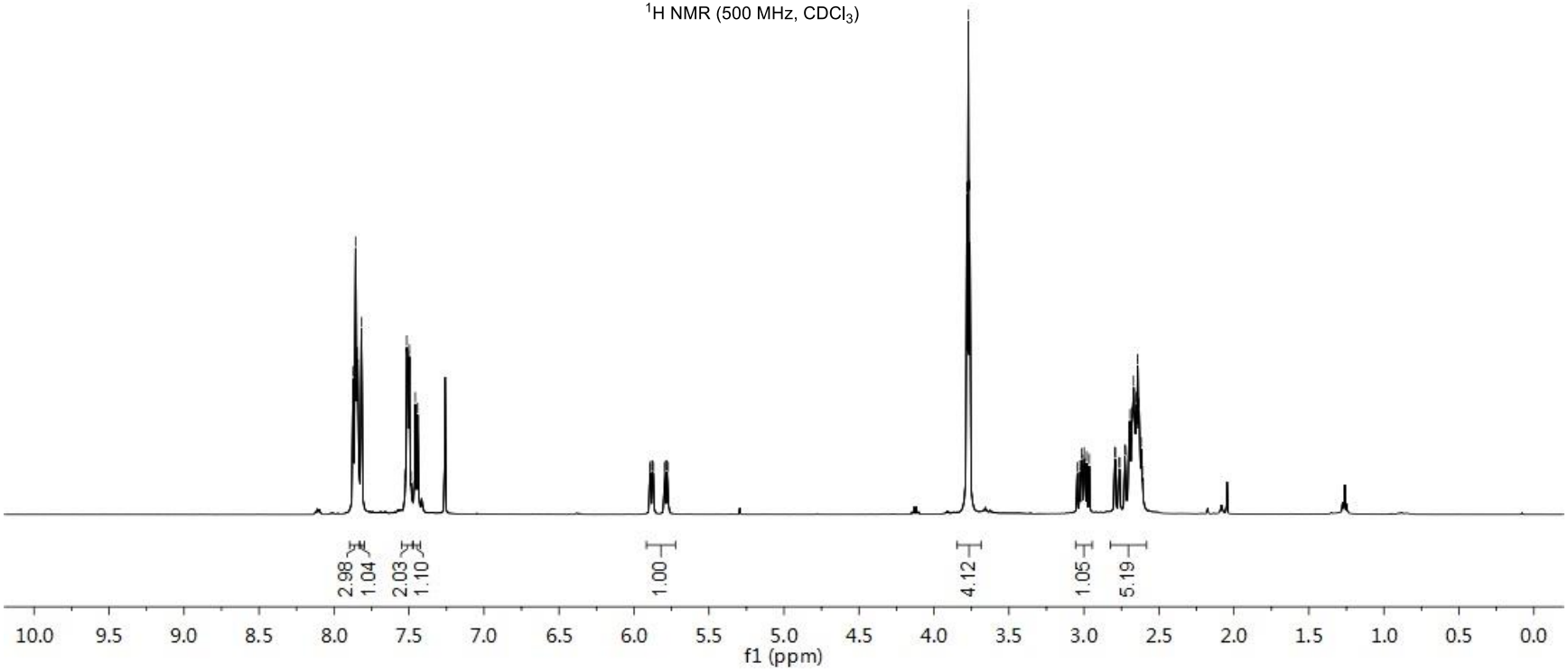
^{19}F NMR (471 MHz, $CDCl_3$)

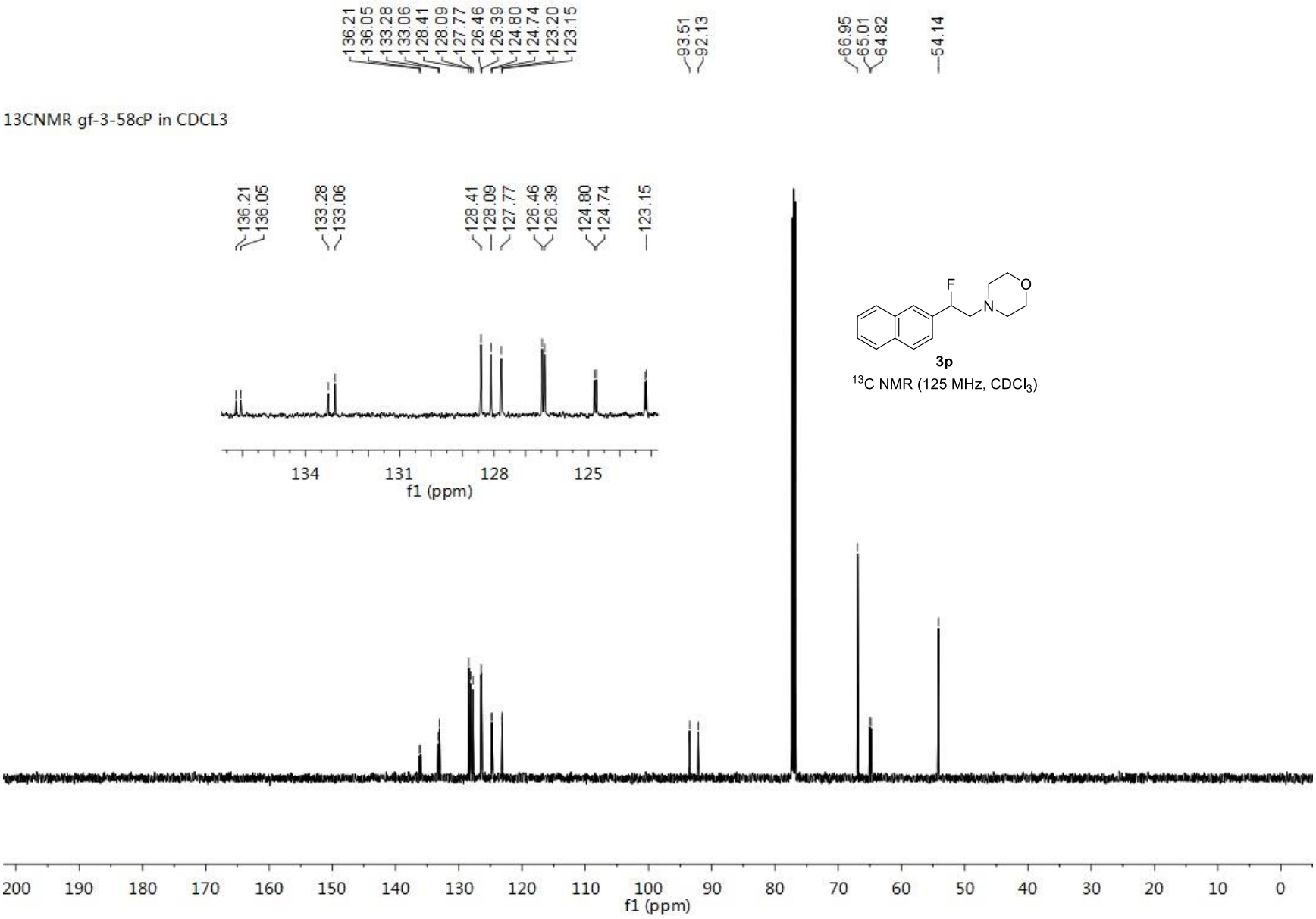
1HNMR gf-3-58cP in CDCL3

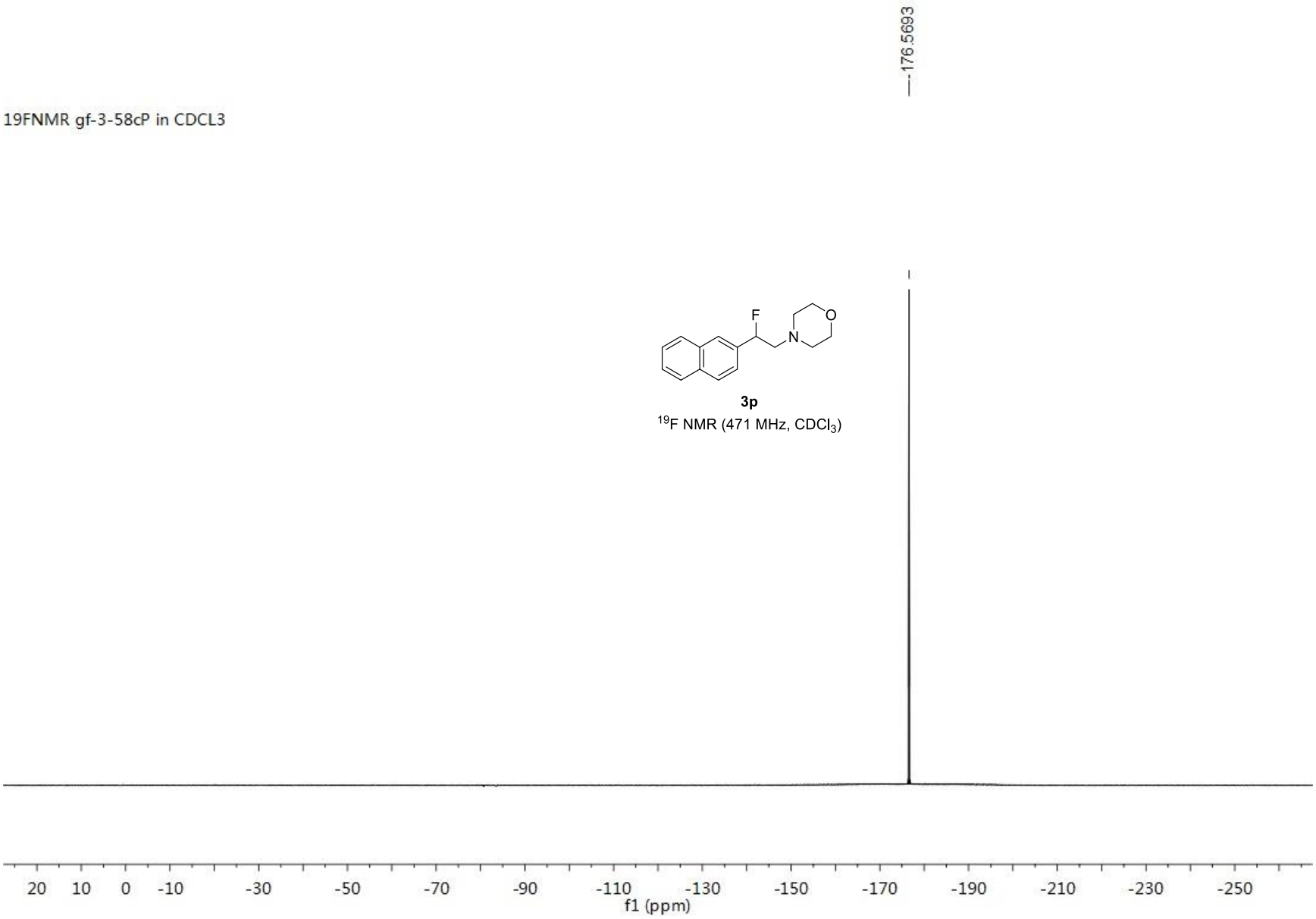


3p

^{1}H NMR (500 MHz, $CDCl_3$)

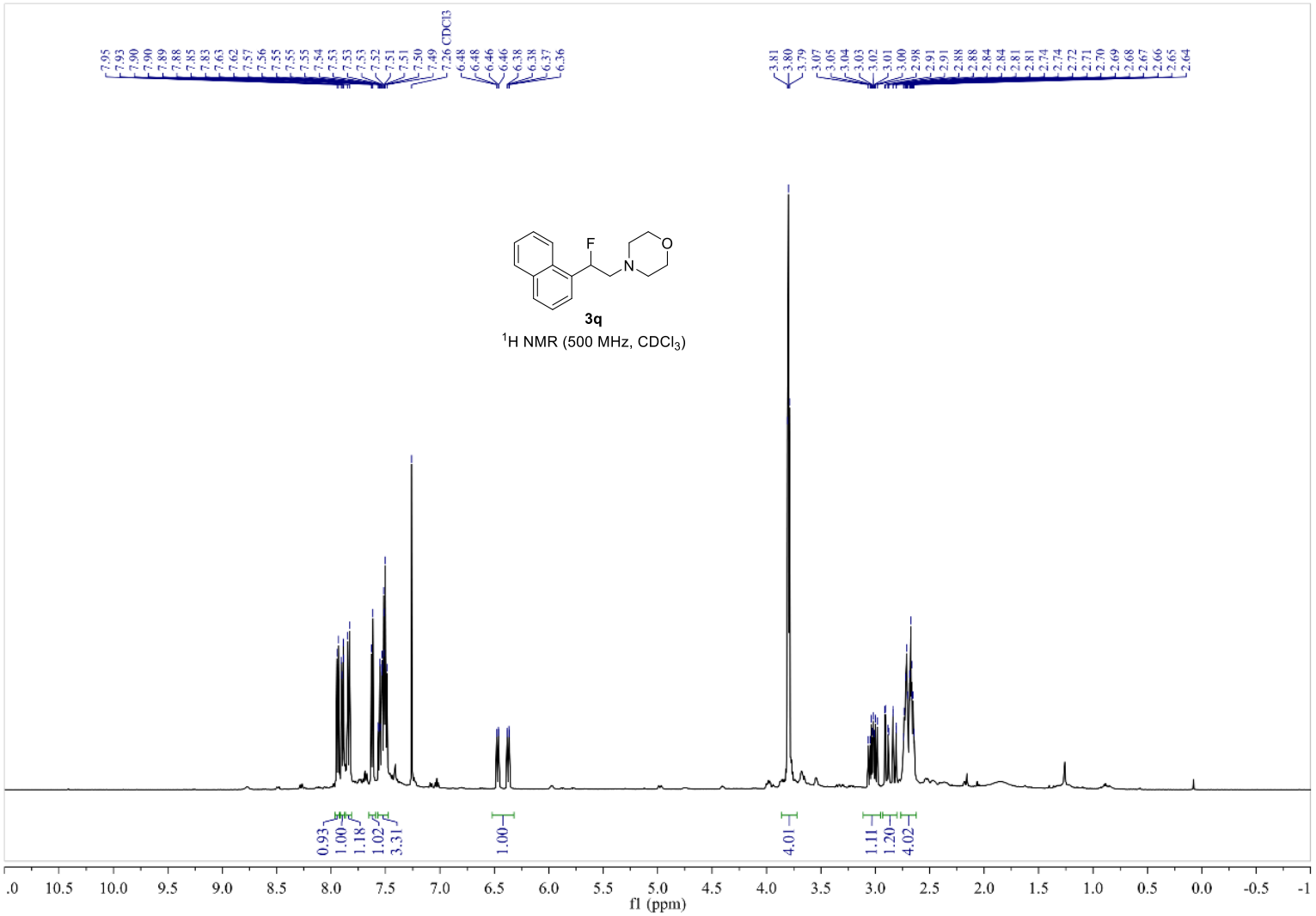


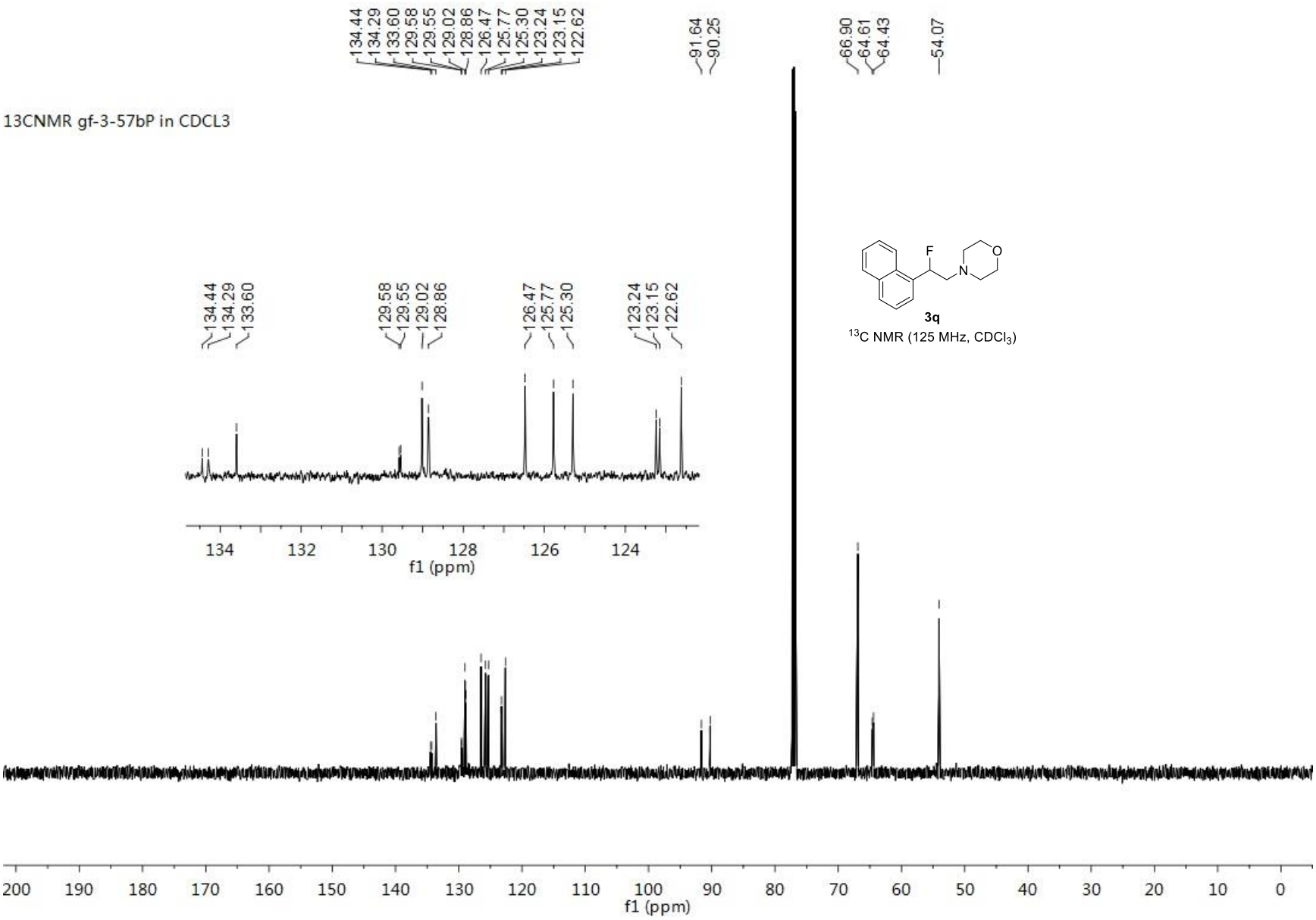

136.21
136.05
133.28
133.06
128.41
128.09
127.77
126.46
126.39
124.80
124.74
123.20
123.15
93.51
92.13
66.95
65.01
64.82
54.14
13CNMR gf-3-58cP in CDCL3
F
O
N
3p
^{13}C NMR (125 MHz, $CDCl_3$)
134
131
128
125
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



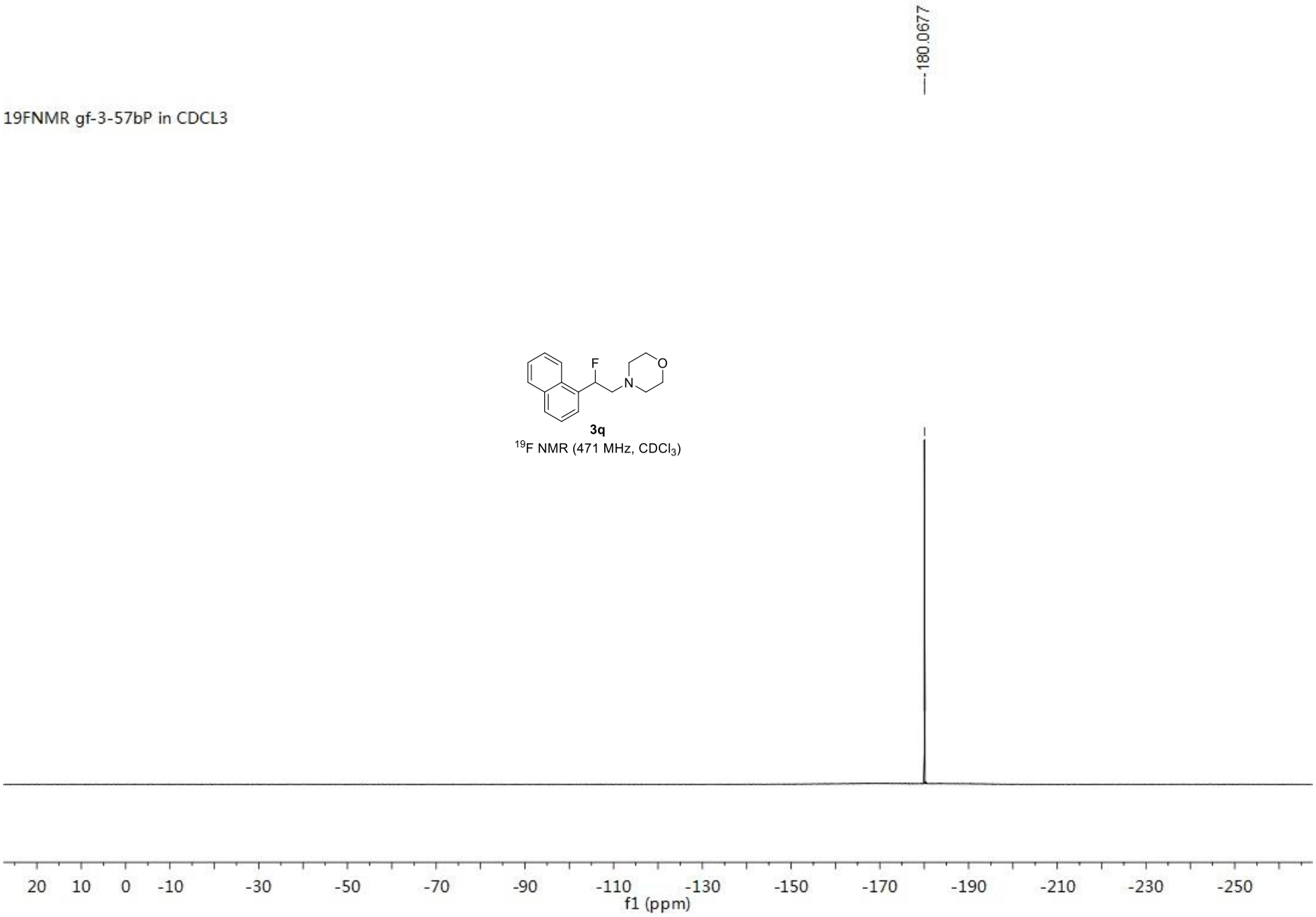
3p

^{19}F NMR (471 MHz, $CDCl_3$)


7.95
7.93
7.90
7.90
7.89
7.88
7.85
7.83
7.63
7.62
7.57
7.56
7.55
7.55
7.55
7.54
7.53
7.53
7.53
7.52
7.51
7.51
7.50
7.49
7.26 CDCl3
6.48
6.48
6.46
6.46
6.38
6.38
6.37
6.36
3.81
3.80
3.79
3.07
3.05
3.04
3.03
3.02
3.01
3.00
2.98
2.91
2.91
2.88
2.88
2.84
2.84
2.81
2.81
2.74
2.74
2.72
2.71
2.70
2.69
2.68
2.67
2.66
2.65
2.64
F
O
N
3q
1H NMR (500 MHz, CDCl3)
0.93
1.00
1.18
1.02
3.31
1.00
4.01
1.11
1.20
4.02
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


13CNMR gf-3-57bP in CDCL3
134.44
134.29
133.60
129.58
129.55
129.02
128.86
126.47
125.77
125.30
123.24
123.15
122.62
91.64
90.25
66.90
64.61
64.43
54.07
F
O
N
3q
^{13}C NMR (125 MHz, CDCl$_3$)
f1 (ppm)
f1 (ppm)

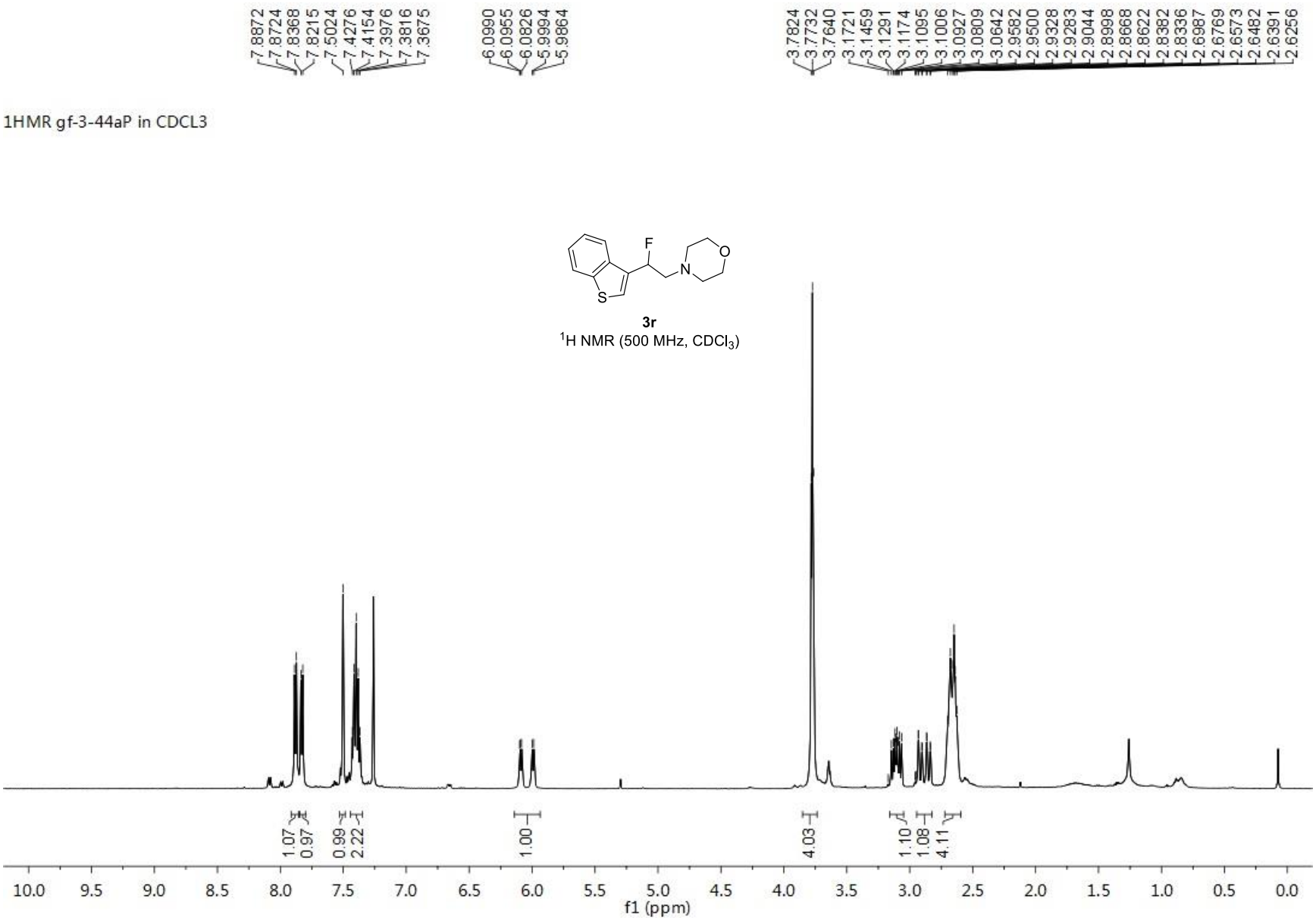
19FNMR gf-3-57bP in CDCL3

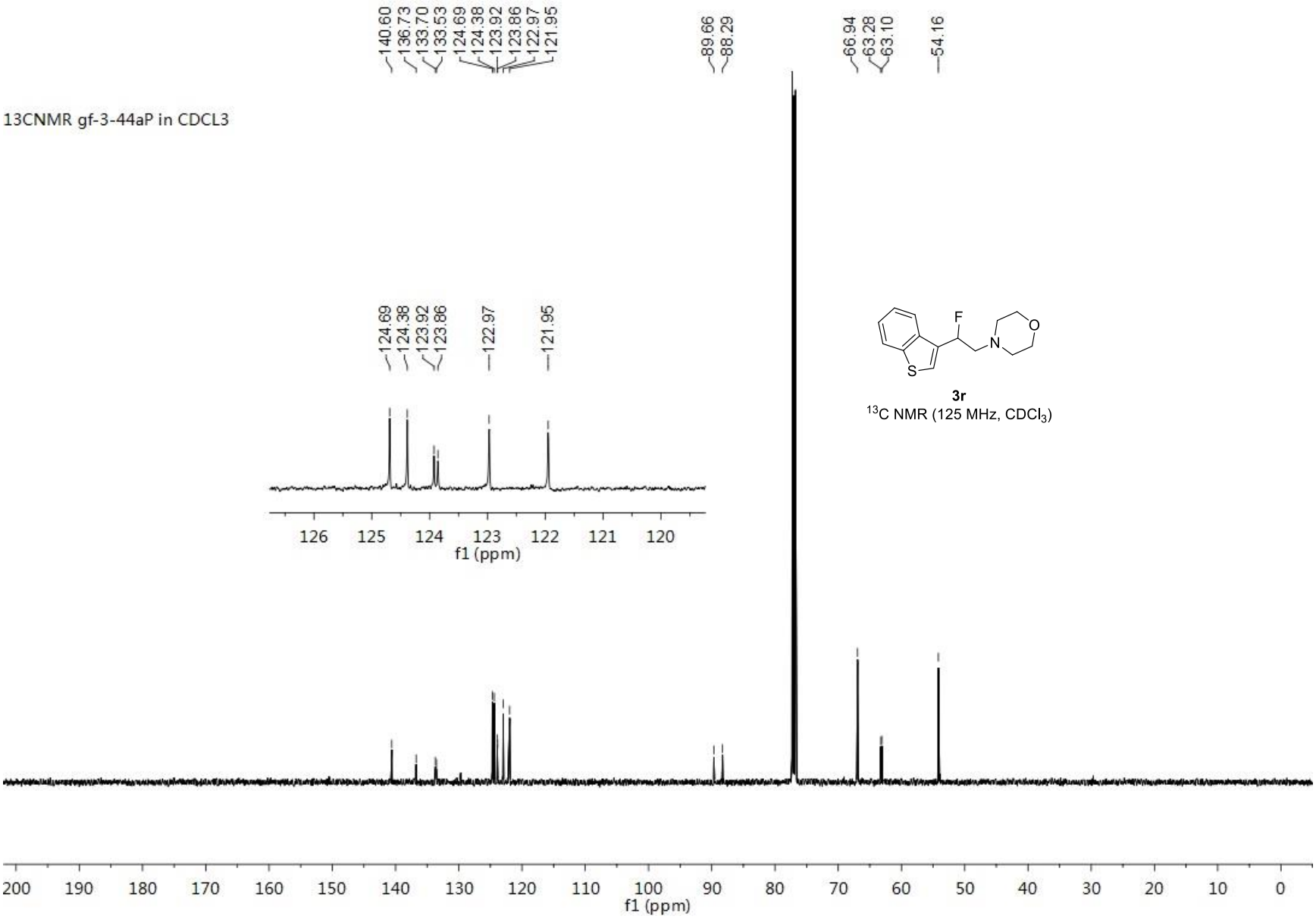


3q

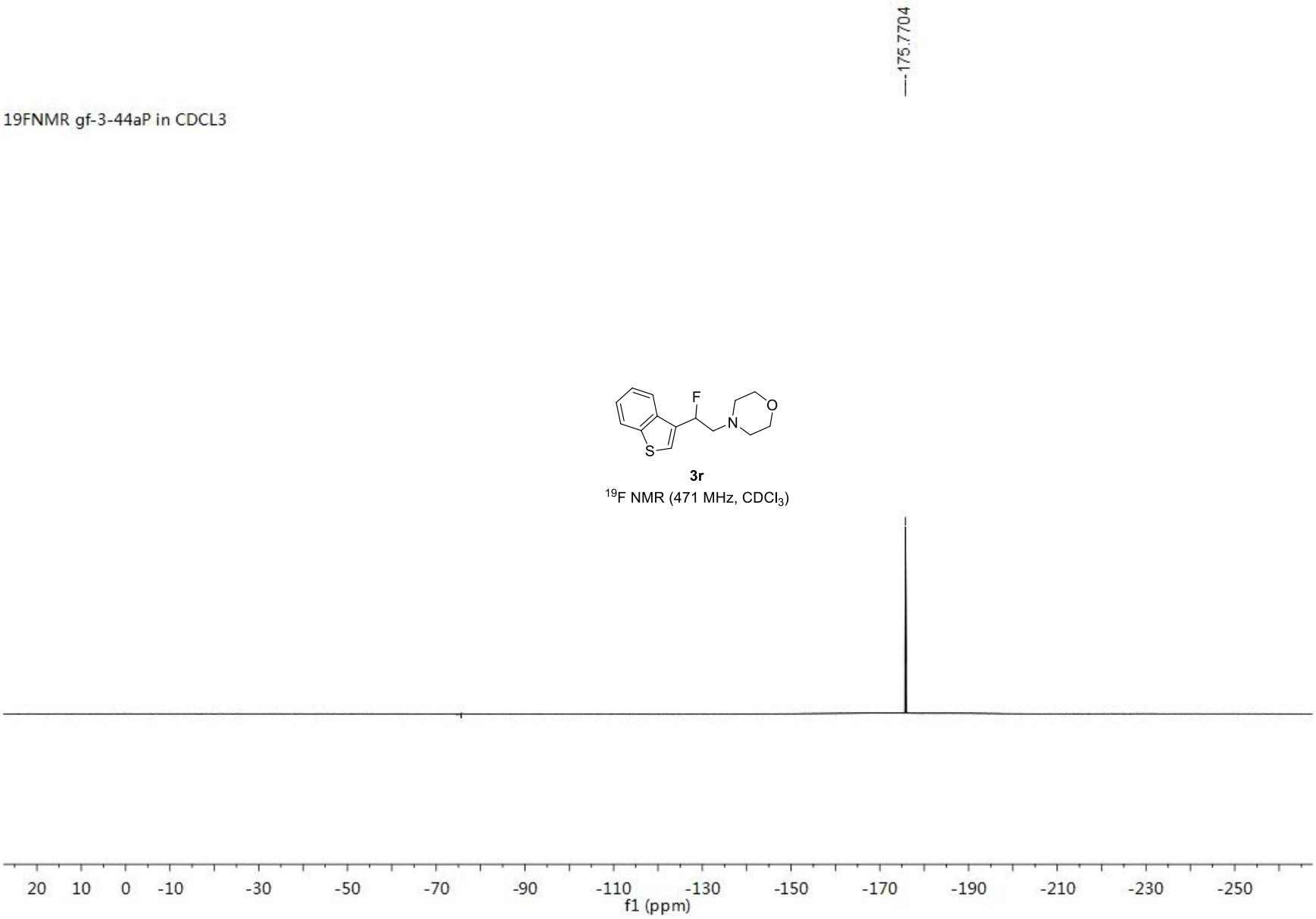
^{19}F NMR (471 MHz, $CDCl_3$)

1HMR gf-3-44aP in CDCL3




13CNMR gf-3-44aP in CDCL3
140.60
136.73
133.70
133.53
124.69
124.38
123.92
123.86
122.97
121.95
89.66
88.29
66.94
63.28
63.10
54.16
F
O
N
S
3r
13C NMR (125 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

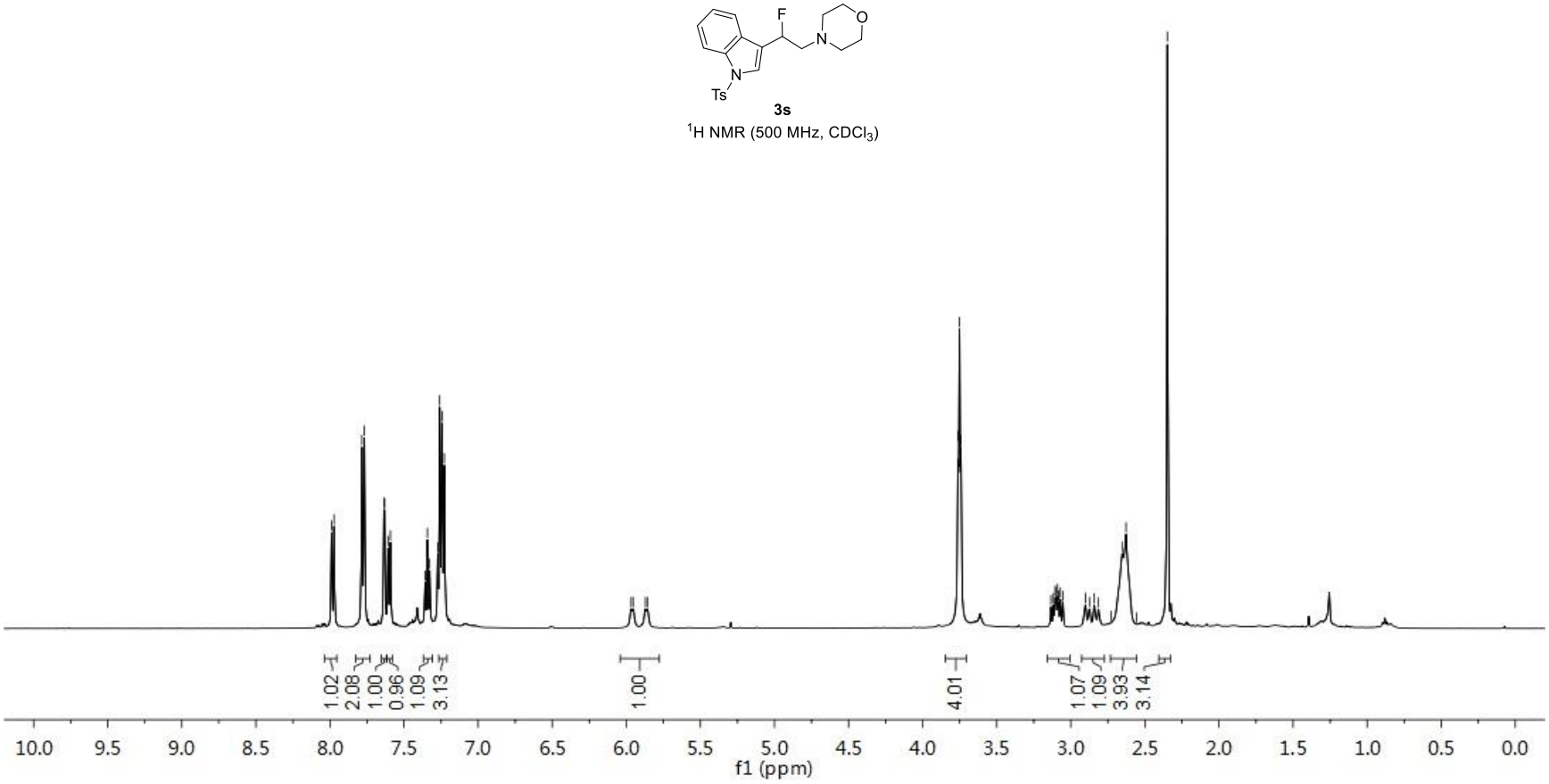
19FNMR gf-3-44aP in CDCL3

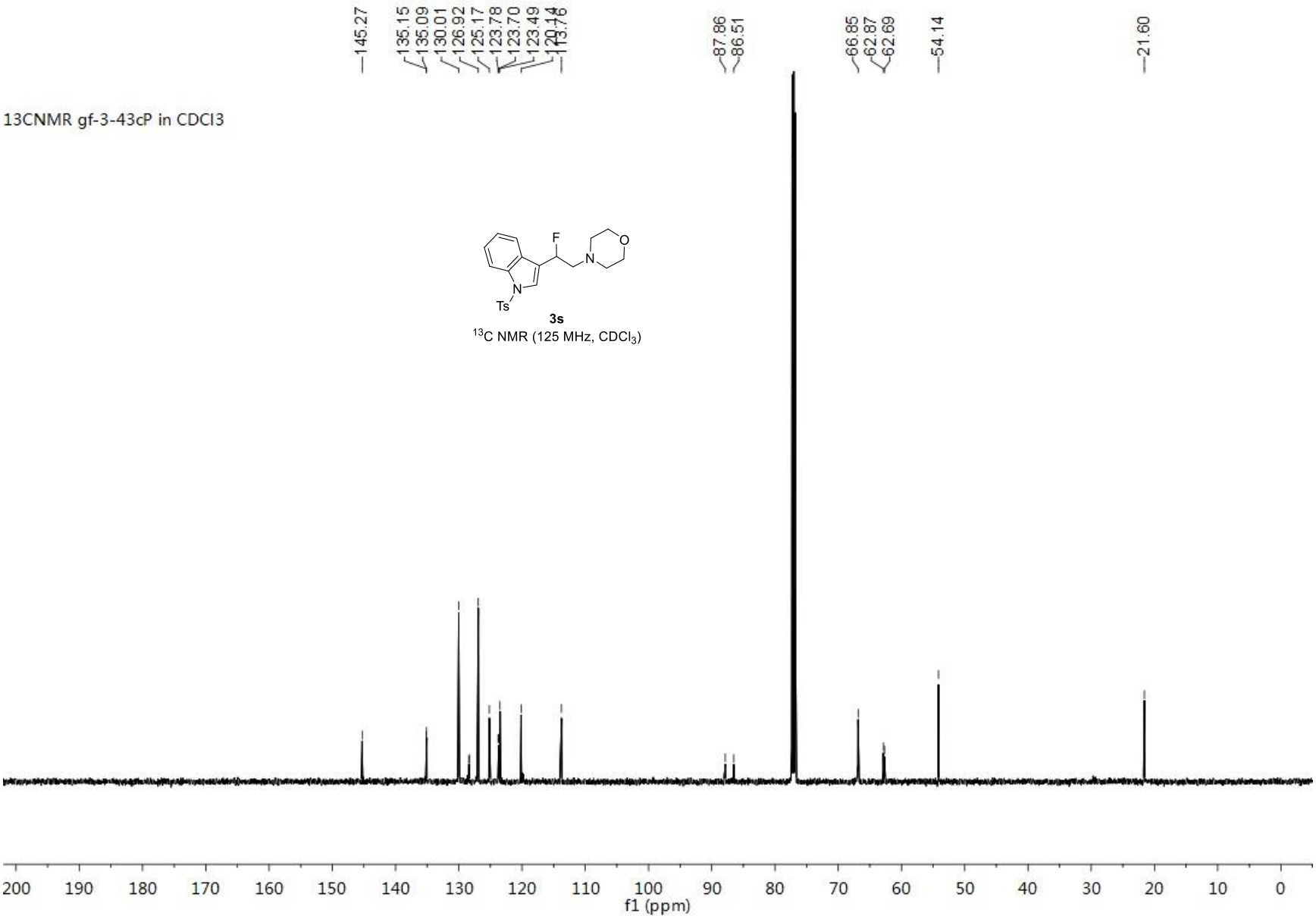


3r

^{19}F NMR (471 MHz, $CDCl_3$)

1HNMR gf-3-43cP in CDCL3

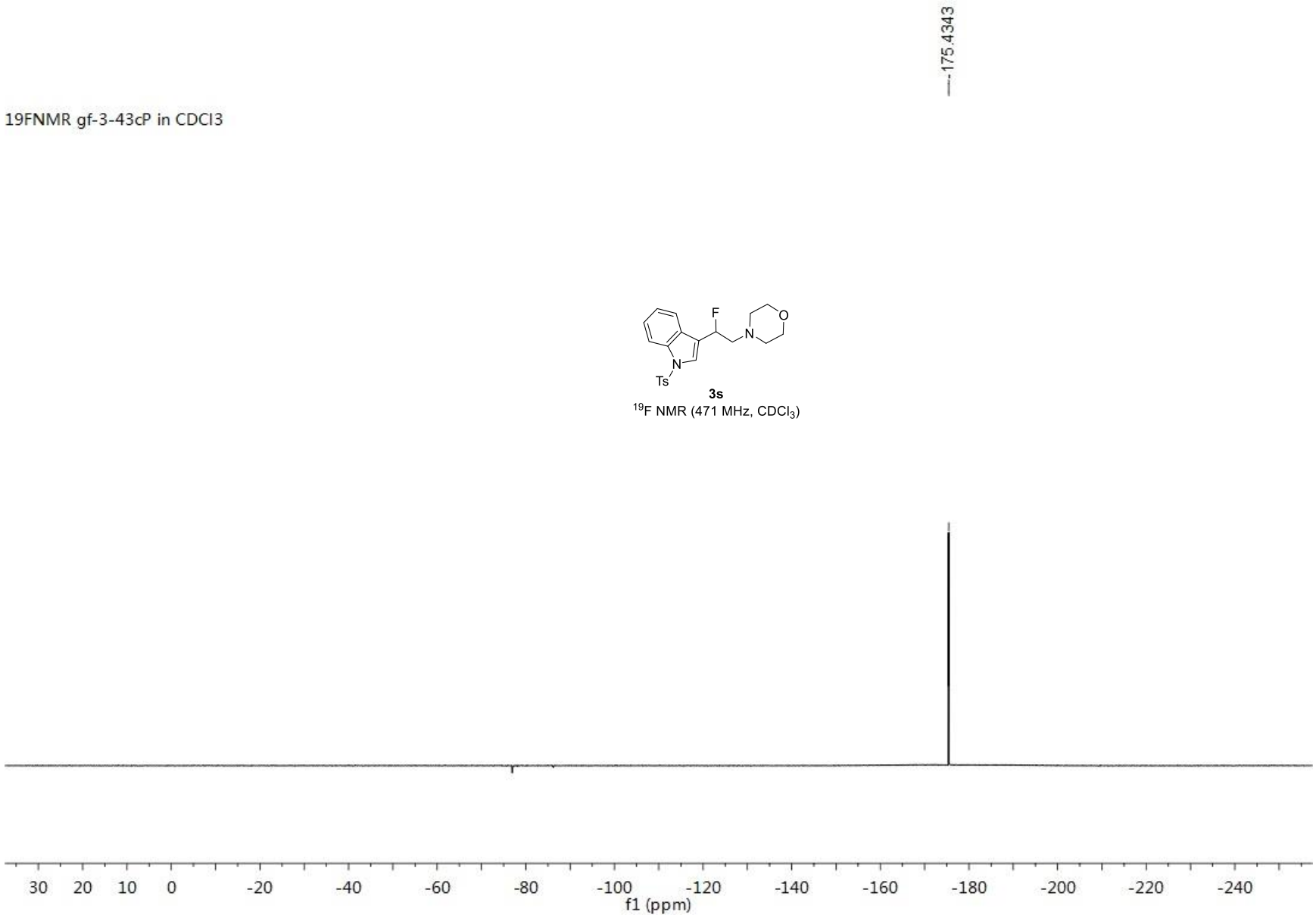




3s

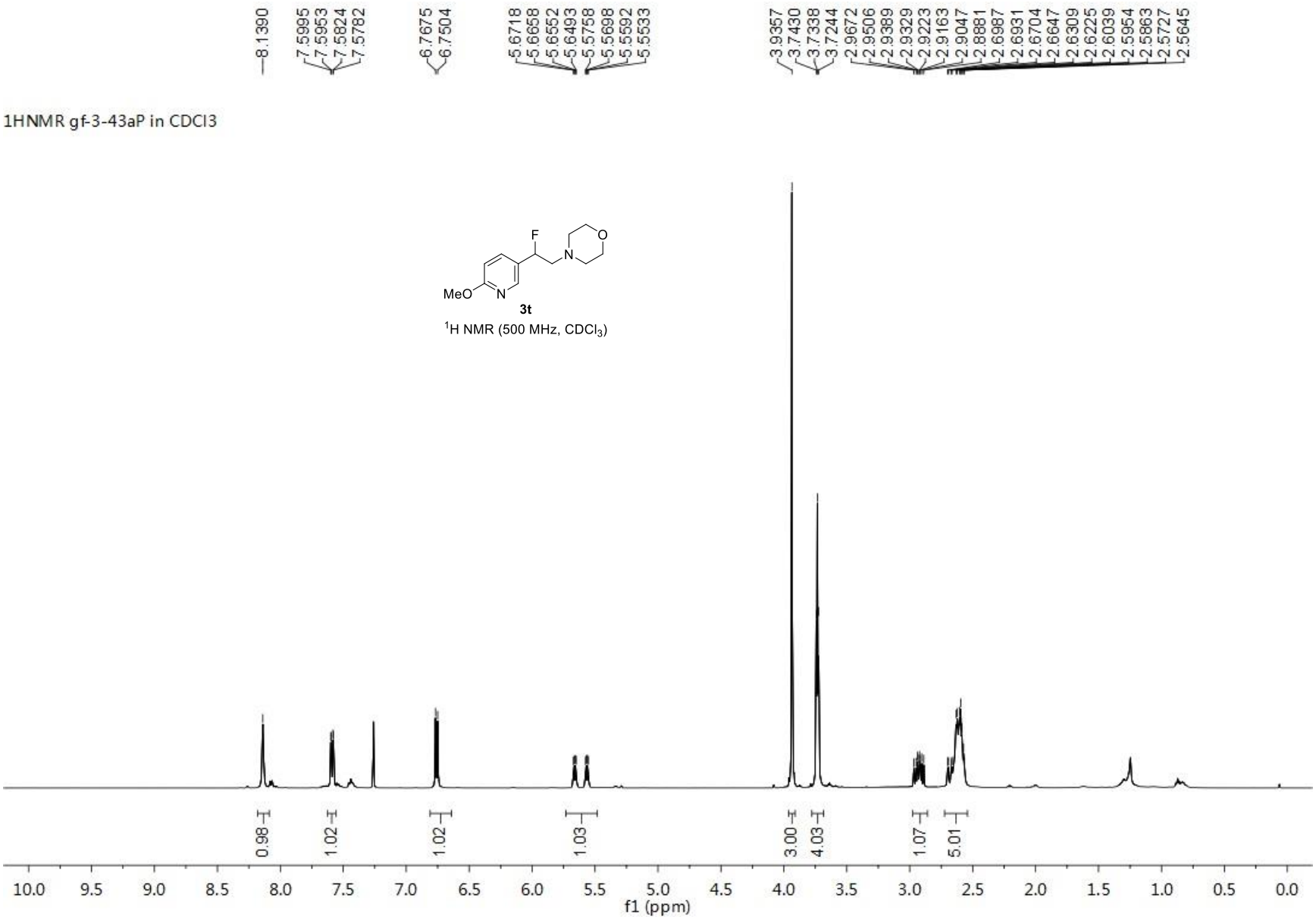
^{13}C NMR (125 MHz, $CDCl_3$)

19FNMR gf-3-43cP in CDCl3



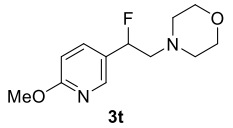
3s

^{19}F NMR (471 MHz, $CDCl_3$)


8.1390
7.5995
7.5953
7.5824
7.5782
6.7675
6.7504
5.6718
5.6658
5.6552
5.6493
5.5758
5.5698
5.5592
5.5533
3.9357
3.7430
3.7338
3.7244
2.9672
2.9506
2.9389
2.9329
2.9223
2.9163
2.9047
2.8881
2.6987
2.6931
2.6704
2.6647
2.6309
2.6225
2.6039
2.5954
2.5863
2.5727
2.5645
1HNMR gf-3-43aP in CDCl3
F
O
N
MeO
N
3t
1H NMR (500 MHz, CDCl3)
0.98
1.02
1.02
1.03
3.00
4.03
1.07
5.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

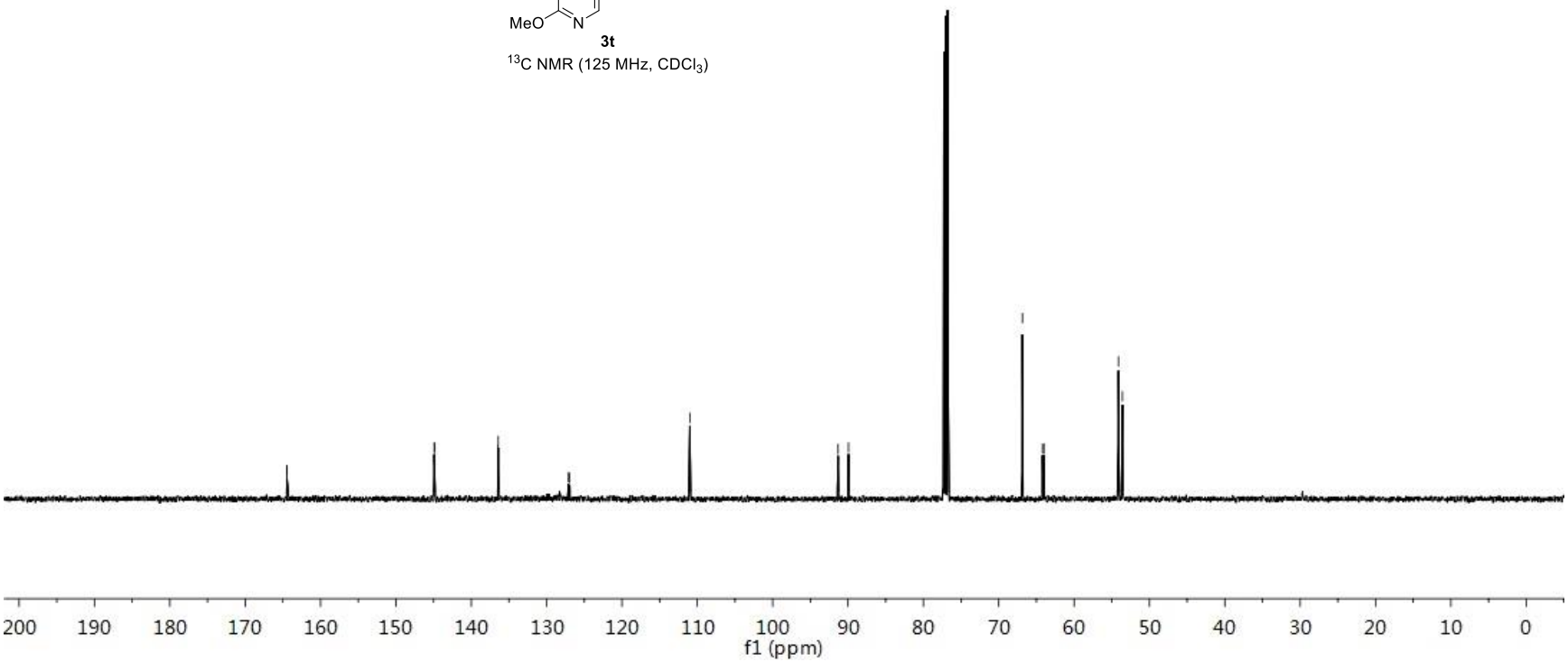
164.48
164.47
144.92
144.86
136.46
136.42
127.10
126.93
110.99
91.31
89.94
66.86
64.20
64.01
54.11
53.59

13CNMR gf-3-43aP in CDCl3

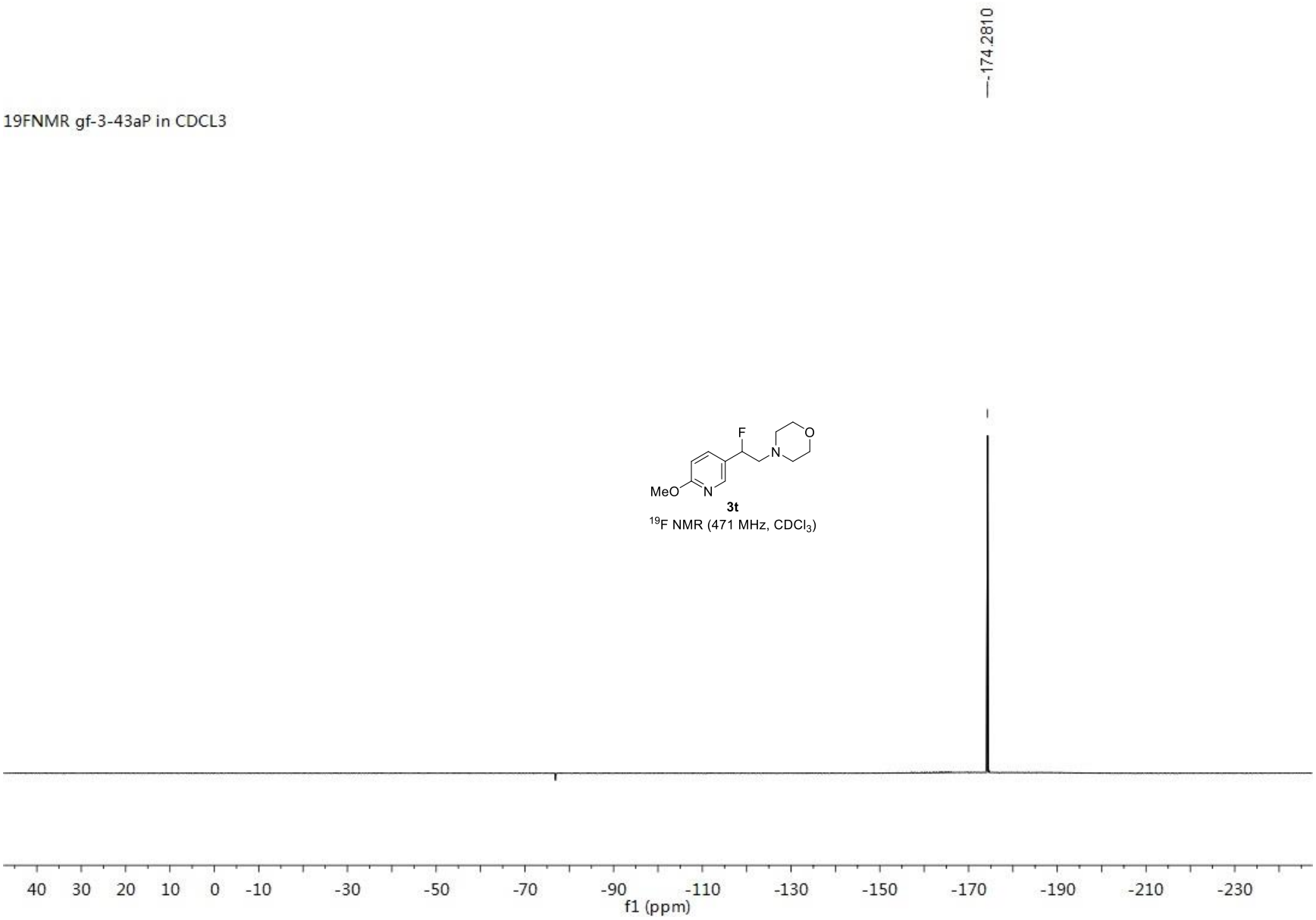


3t

^{13}C NMR (125 MHz, $CDCl_3$)

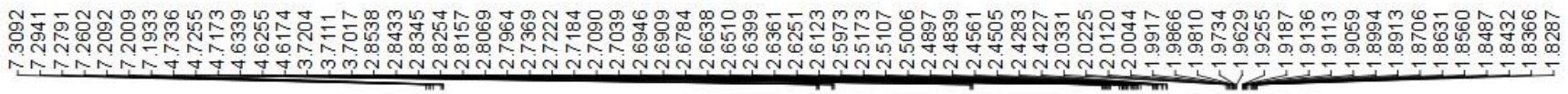


19FNMR gf-3-43aP in CDCL3

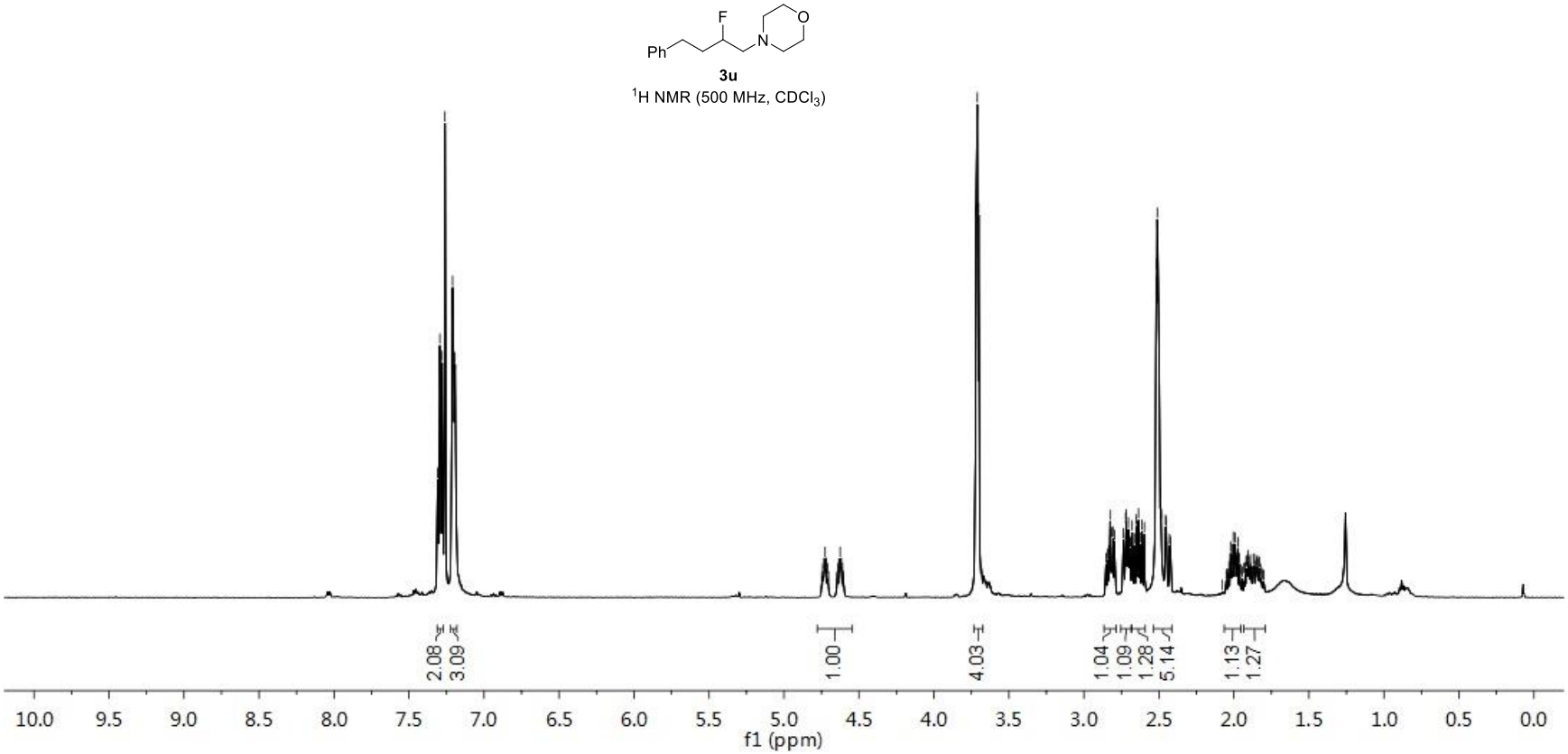


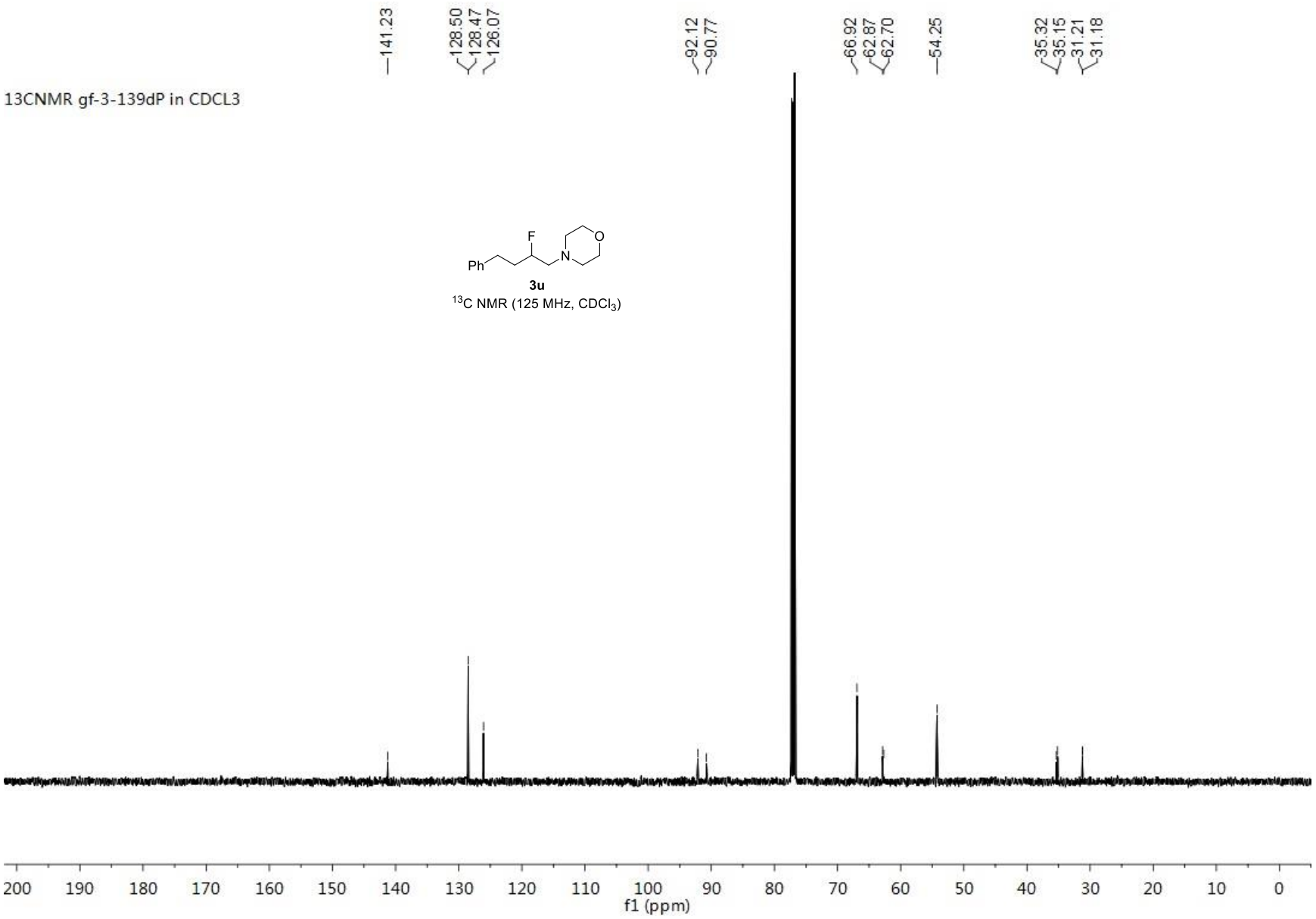
3t

^{19}F NMR (471 MHz, $CDCl_3$)

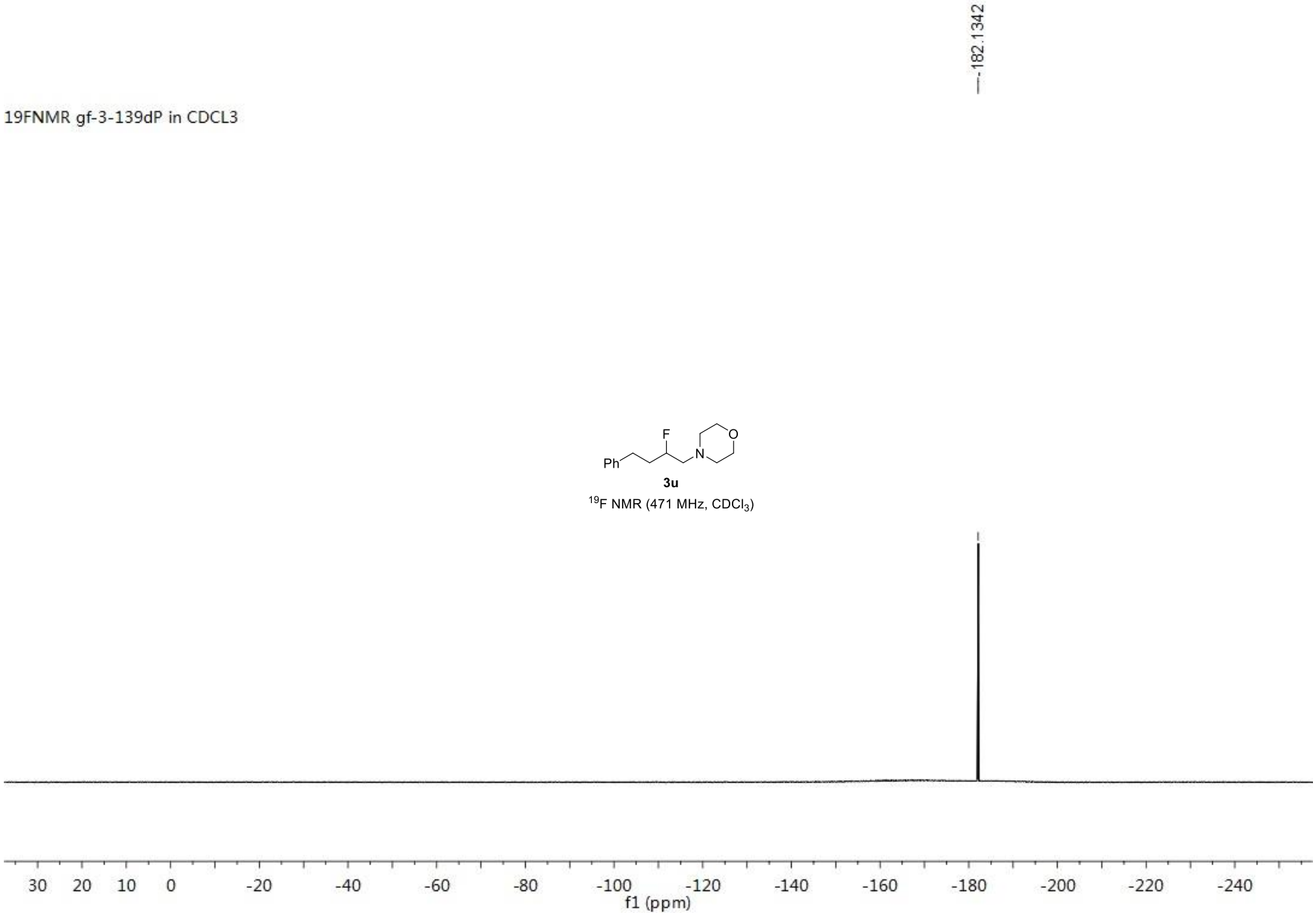


1HNMR gf-3-139dP in CDCL3



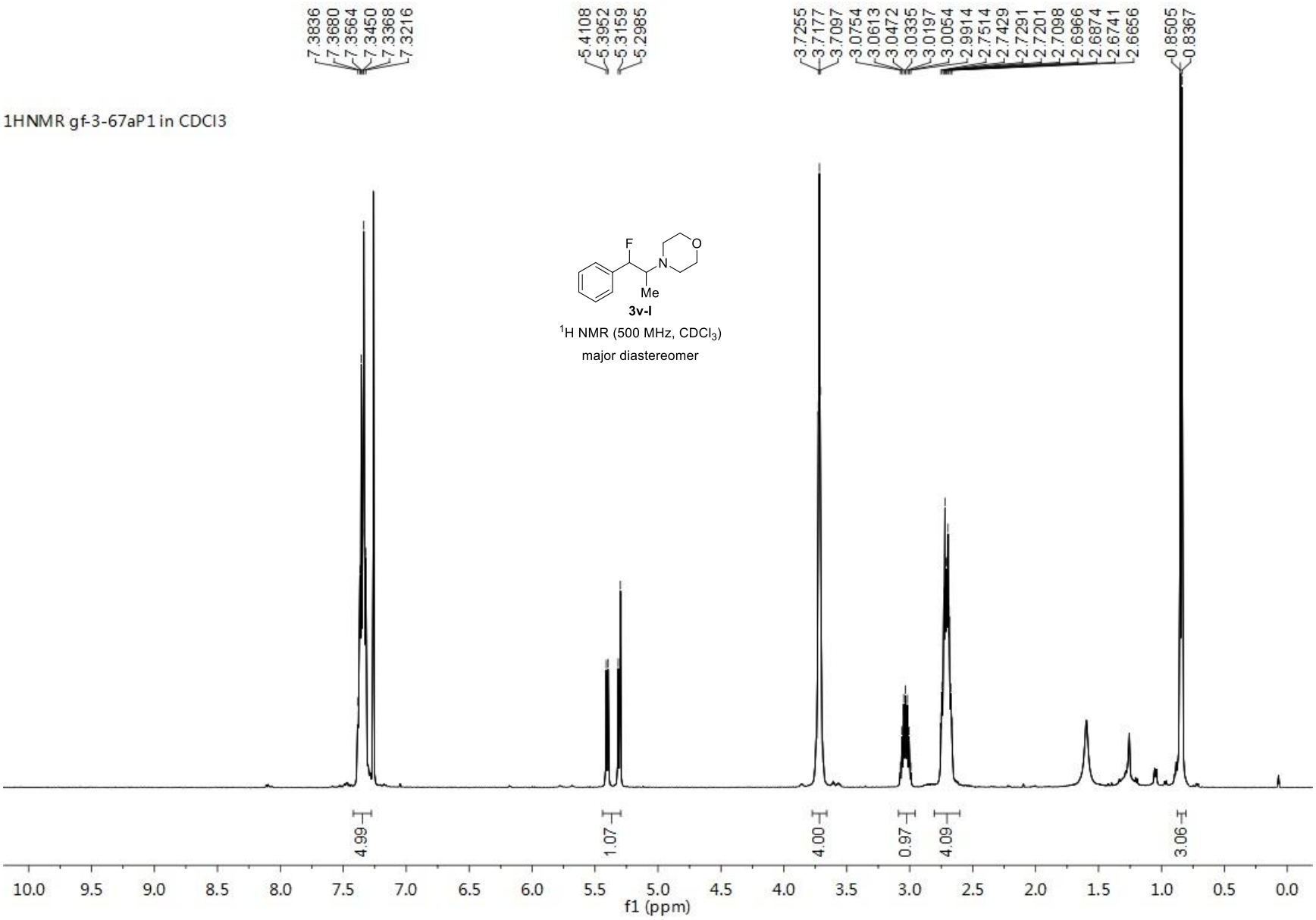

13CNMR gf-3-139dP in CDCL3
141.23
128.50
128.47
126.07
92.12
90.77
66.92
62.87
62.70
54.25
35.32
35.15
31.21
31.18
F
O
N
Ph
3u
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

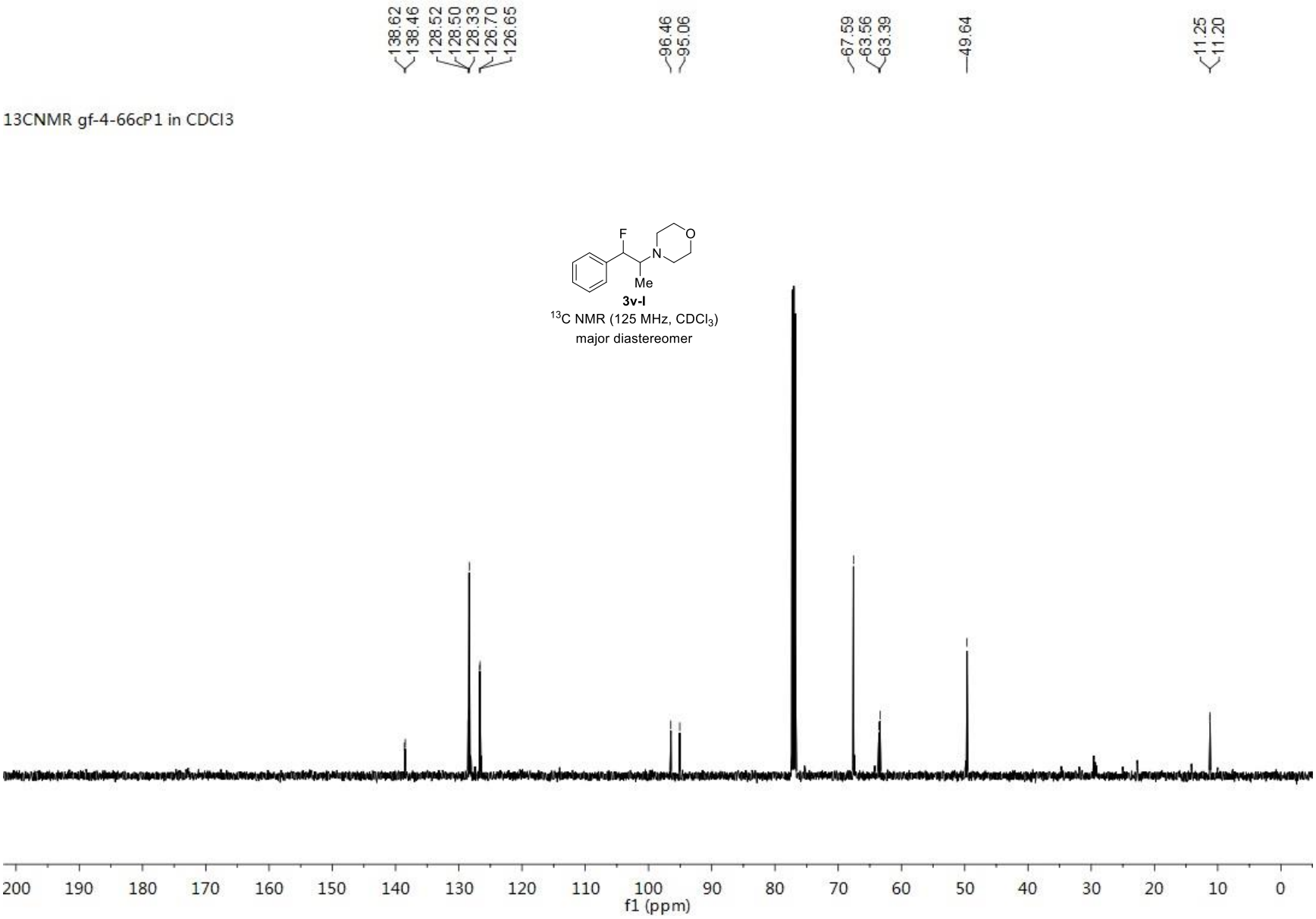
19FNMR gf-3-139dP in CDCL3



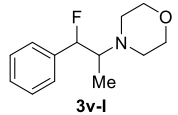
3u

^{19}F NMR (471 MHz, $CDCl_3$)


1HNMR gf-3-67aP1 in CDCl3
7.3836
7.3680
7.3564
7.3450
7.3368
7.3216
5.4108
5.3952
5.3159
5.2985
3.7255
3.7177
3.7097
3.0754
3.0613
3.0472
3.0335
3.0197
3.0054
2.9914
2.7514
2.7429
2.7291
2.7201
2.7098
2.6966
2.6874
2.6741
2.6656
0.8505
0.8367
F
O
N
Me
3v-l
1H NMR (500 MHz, CDCl3)
major diastereomer
4.99
1.07
4.00
0.97
4.09
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


138.62
138.46
128.52
128.50
128.33
126.70
126.65
96.46
95.06
67.59
63.56
63.39
49.64
11.25
11.20
13CNMR gf-4-66cP1 in CDCl3
F
O
N
Me
3v-l
13C NMR (125 MHz, CDCl3)
major diastereomer
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

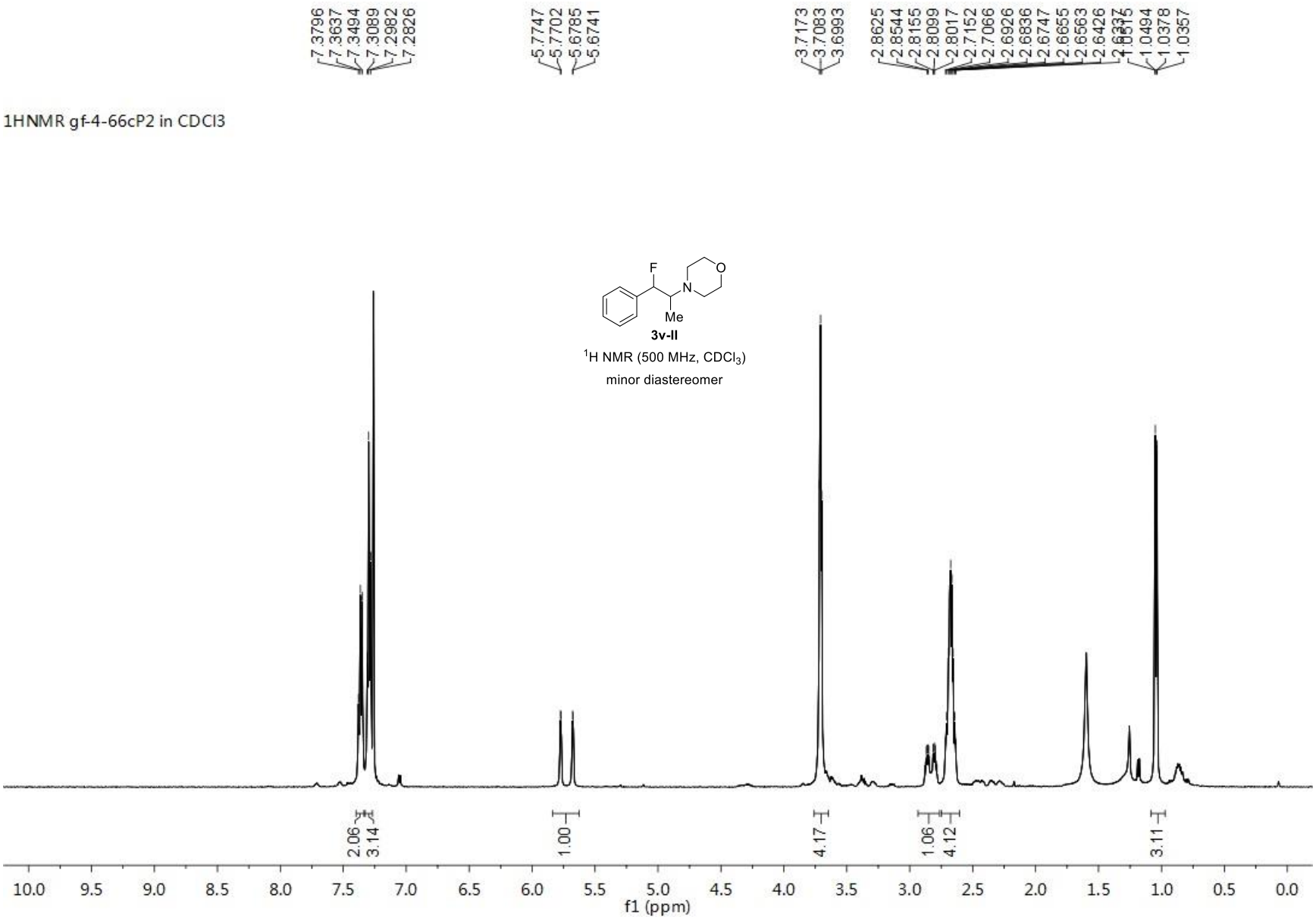
19FNMR gf-3-67aP1 in CDCl3

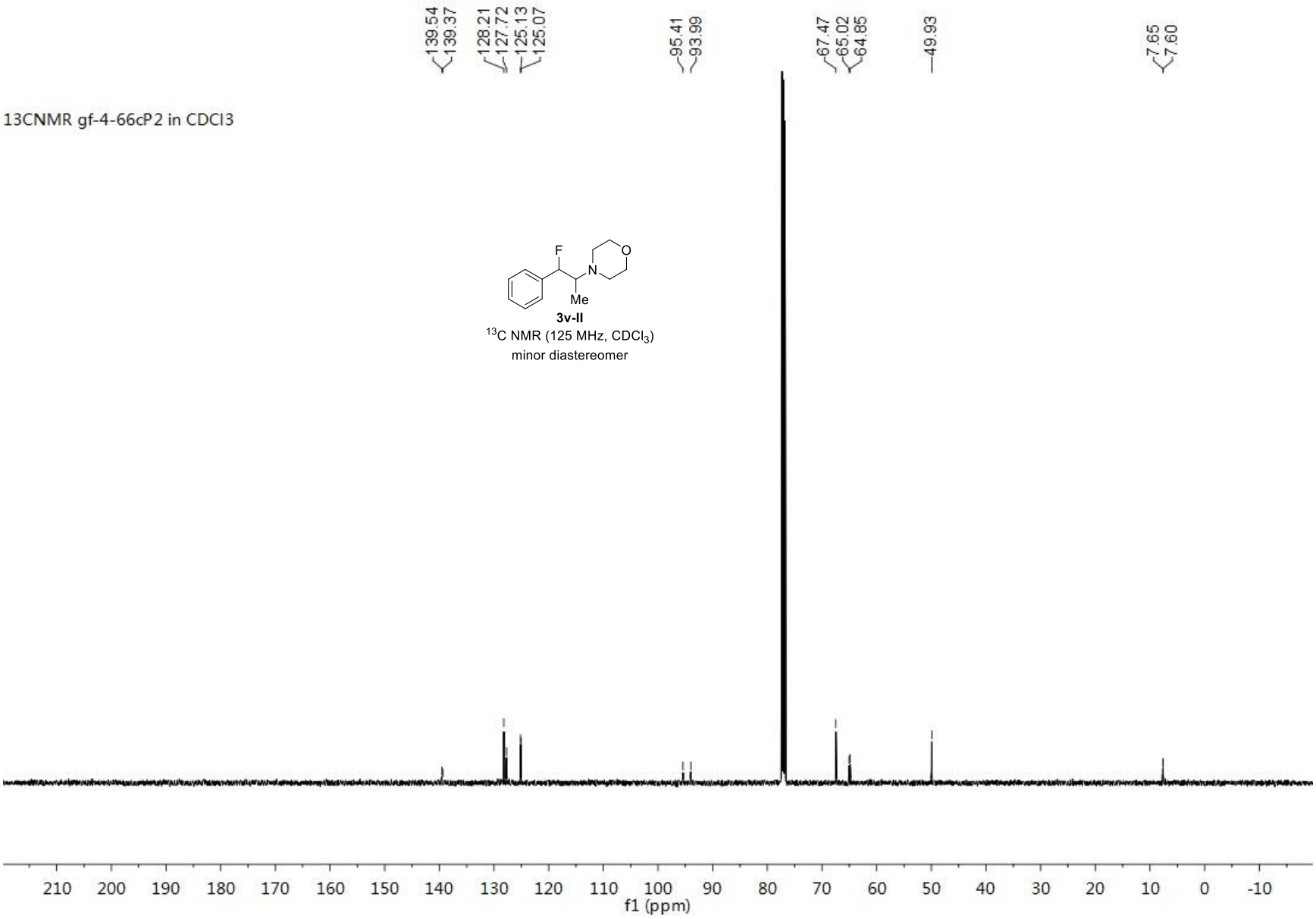


3v-l

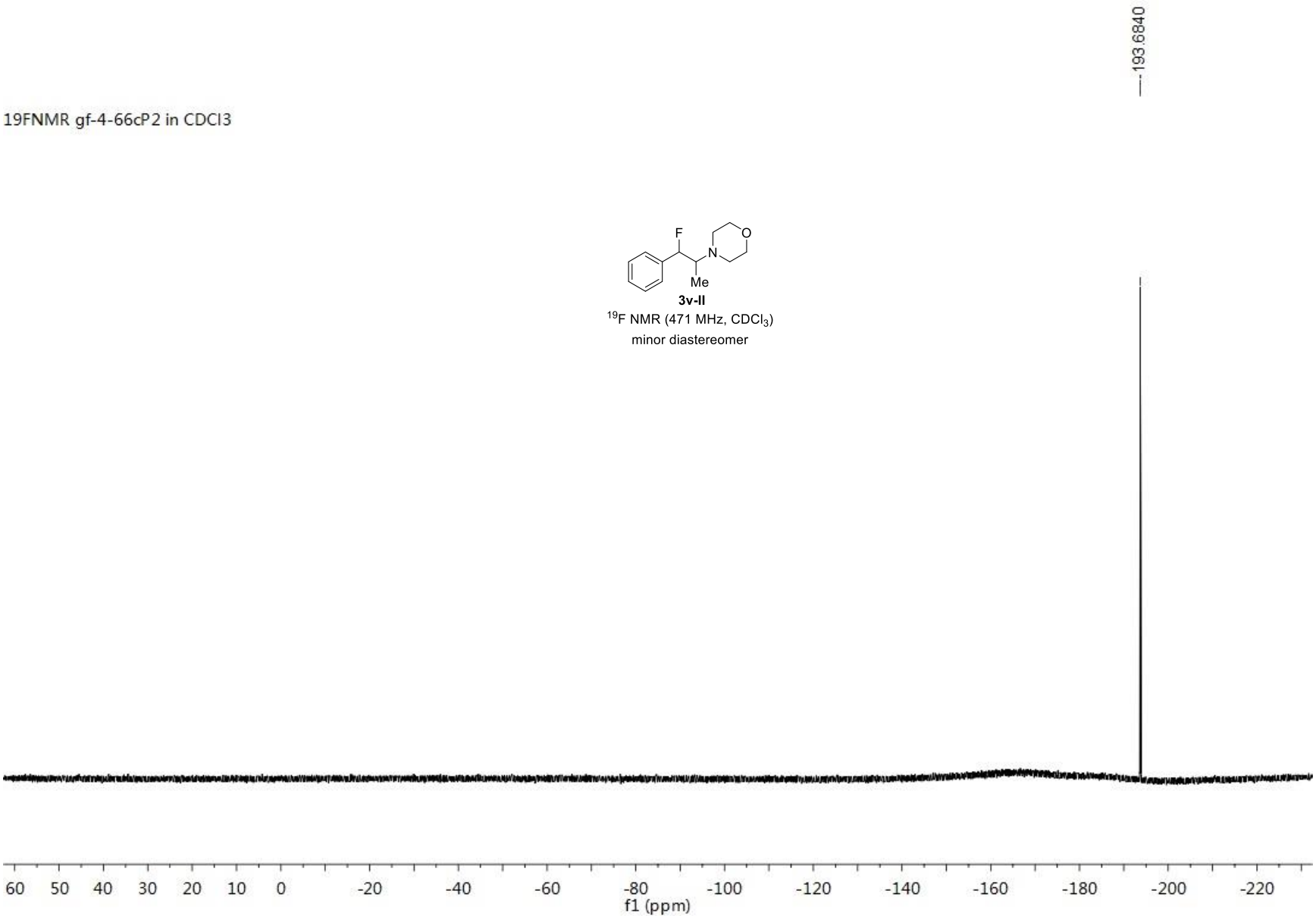
^{19}F NMR (471 MHz, $CDCl_3$)

major diastereomer


7.3796
7.3637
7.3494
7.3089
7.2982
7.2826
5.7747
5.7702
5.6785
5.6741
3.7173
3.7083
3.6993
2.8625
2.8544
2.8155
2.8099
2.8017
2.7152
2.7066
2.6926
2.6836
2.6747
2.6655
2.6563
2.6426
1.0494
1.0378
1.0357
1HNMR gf-4-66cP2 in CDCl3
F
O
N
Me
3v-II
1H NMR (500 MHz, CDCl3)
minor diastereomer
2.06
3.14
1.00
4.17
1.06
4.12
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


139.54
139.37
128.21
127.72
125.13
125.07
95.41
93.99
67.47
65.02
64.85
49.93
7.65
7.60
13CNMR gf-4-66cP2 in CDCl3
F
O
N
Me
3v-II
13C NMR (125 MHz, CDCl3)
minor diastereomer
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

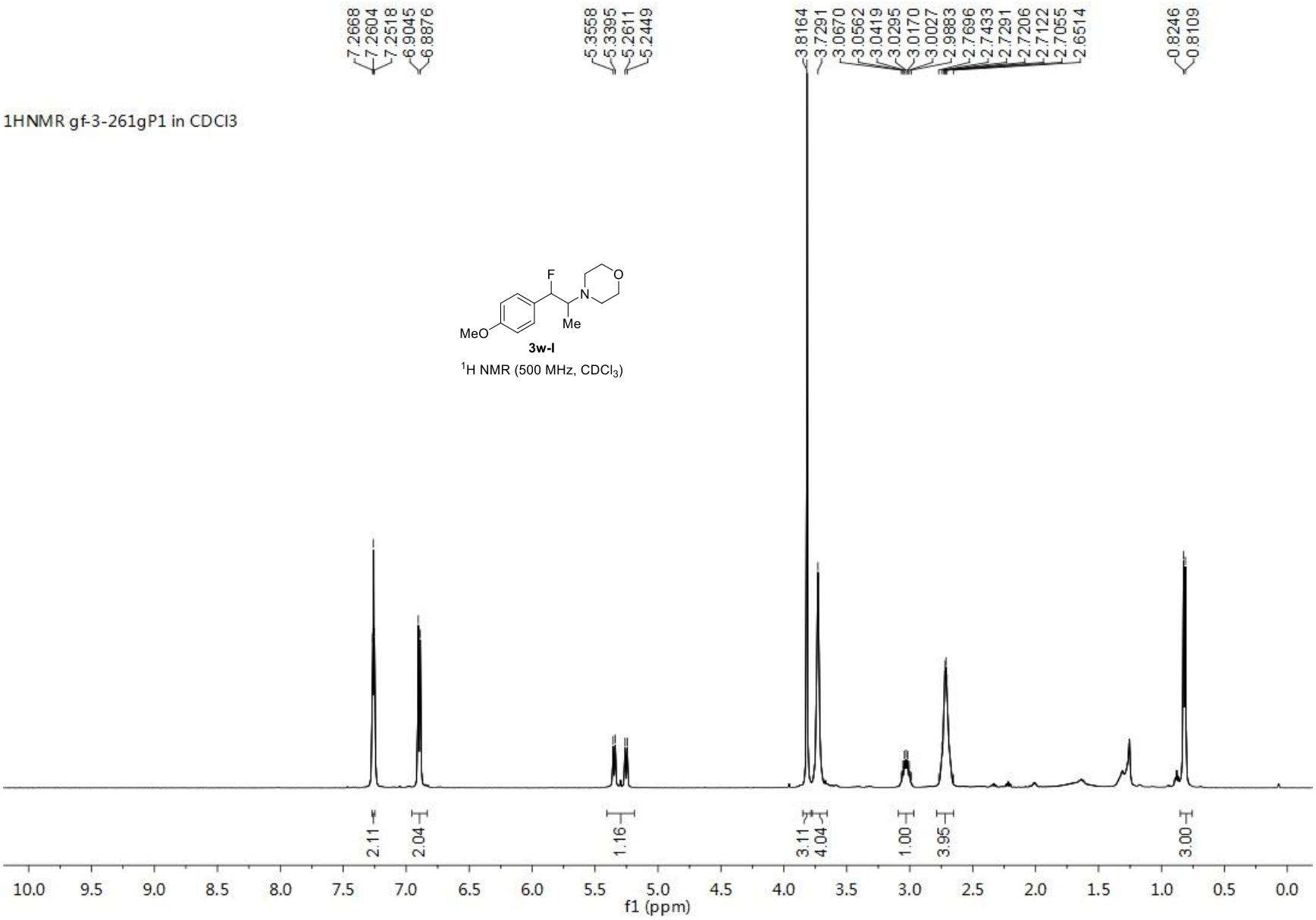
19FNMR gf-4-66cP2 in CDCl3

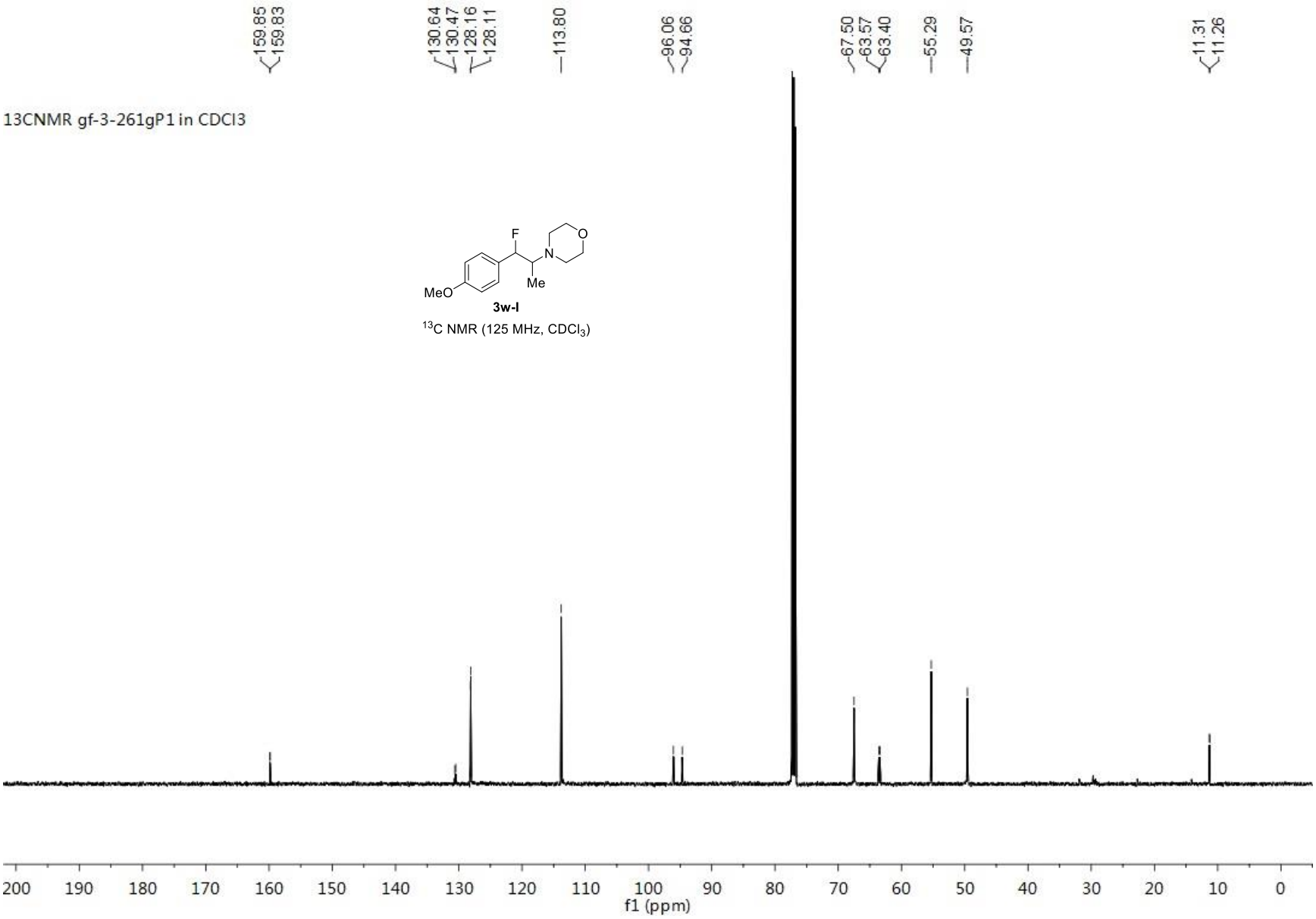


3v-II

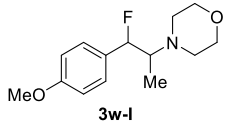
^{19}F NMR (471 MHz, $CDCl_3$)

minor diastereomer


1HNMR gf-3-261gP1 in CDCl3
7.2668
7.2604
7.2518
6.9045
6.8876
5.3558
5.3395
5.2611
5.2449
3.8164
3.7291
3.0670
3.0562
3.0419
3.0295
3.0170
3.0027
2.9883
2.7696
2.7433
2.7291
2.7206
2.7122
2.7055
2.6514
0.8246
0.8109
F
O
N
Me
MeO
3w-l
1H NMR (500 MHz, CDCl3)
2.11
2.04
1.16
3.11
4.04
1.00
3.95
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


159.85
159.83
130.64
130.47
128.16
128.11
113.80
96.06
94.66
67.50
63.57
63.40
55.29
49.57
11.31
11.26
13CNMR gf-3-261gP1 in CDCl3
F
O
N
Me
MeO
3w-l
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

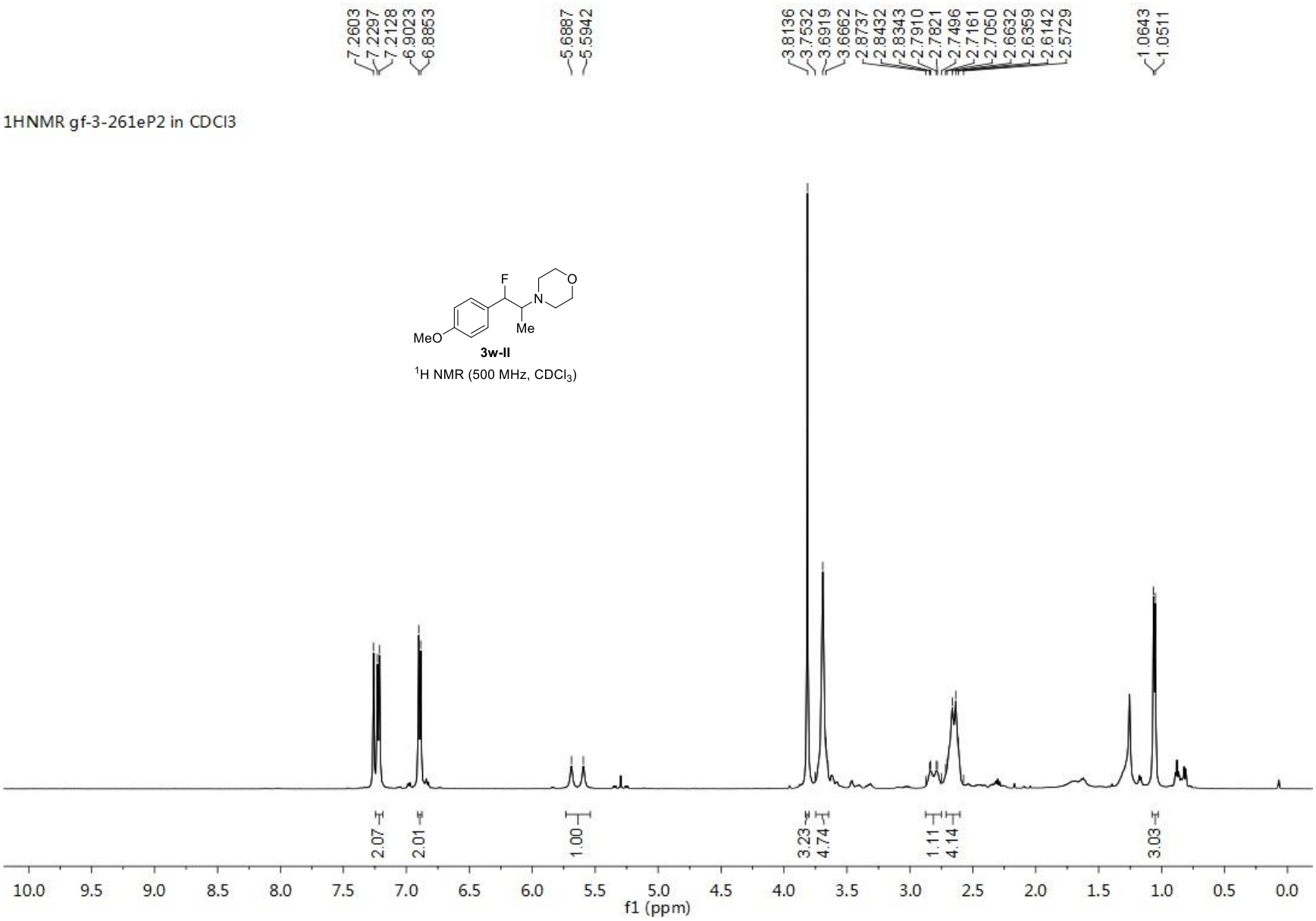
19FNMR gf-3-261gP1 in CDCl3

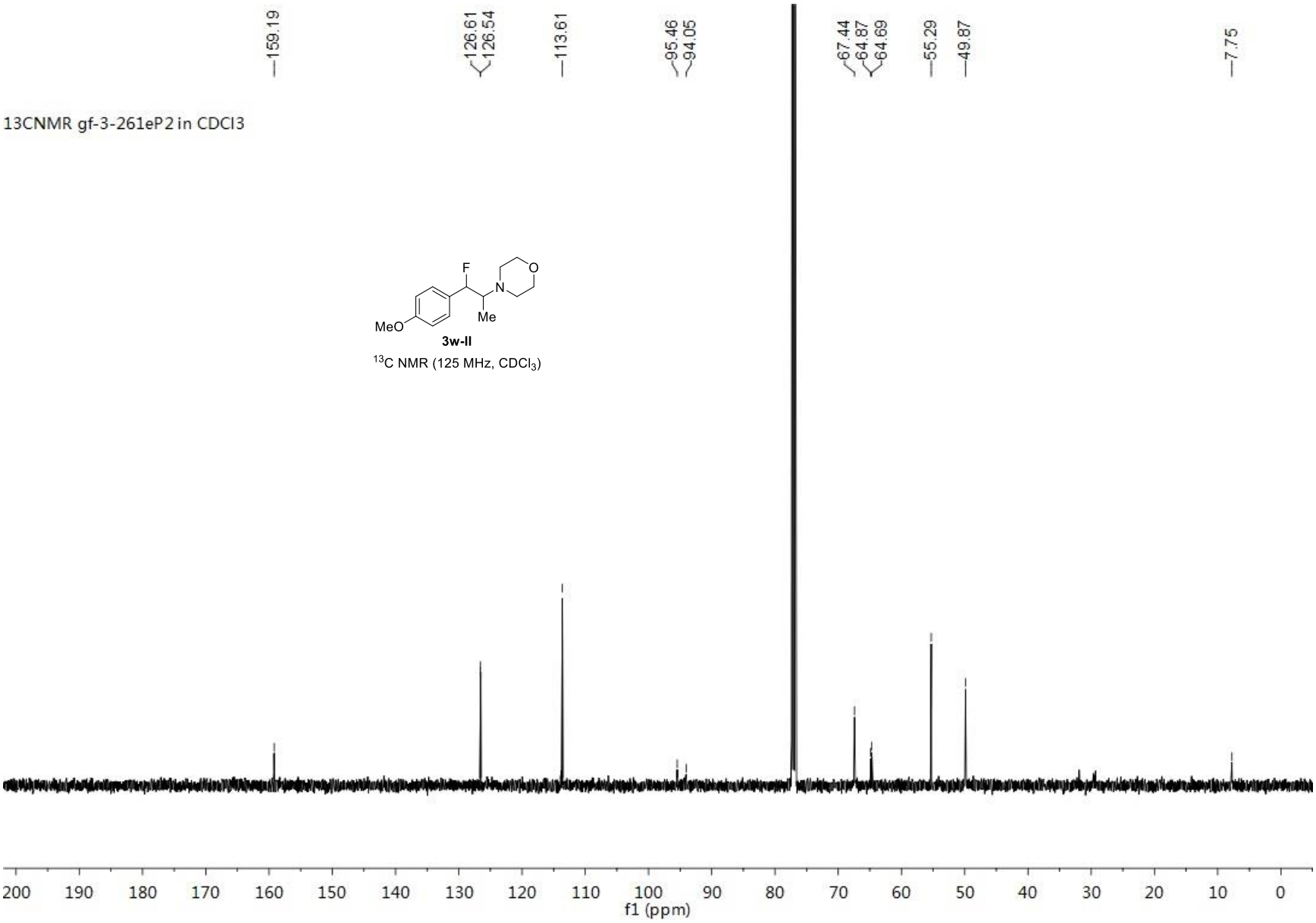


3w-l

^{19}F NMR (471 MHz, $CDCl_3$)

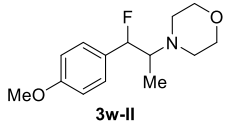
1HNMR gf-3-261eP2 in CDCl3




159.19
126.61
126.54
113.61
95.46
94.05
67.44
64.87
64.69
55.29
49.87
7.75
13CNMR gf-3-261eP2 in CDCl3
F
O
N
Me
MeO
3w-II
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

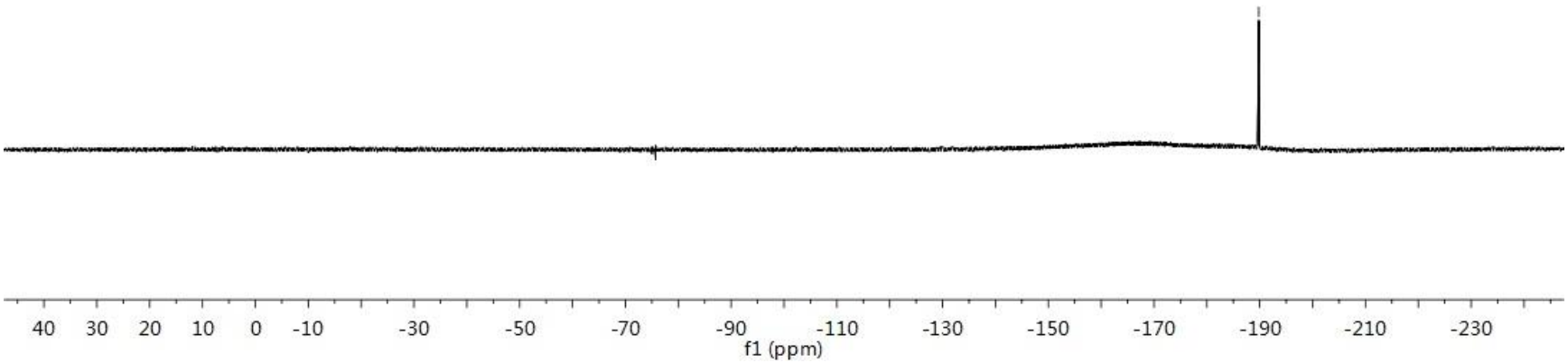
19FNMR gf-3-261aP in CDCl3

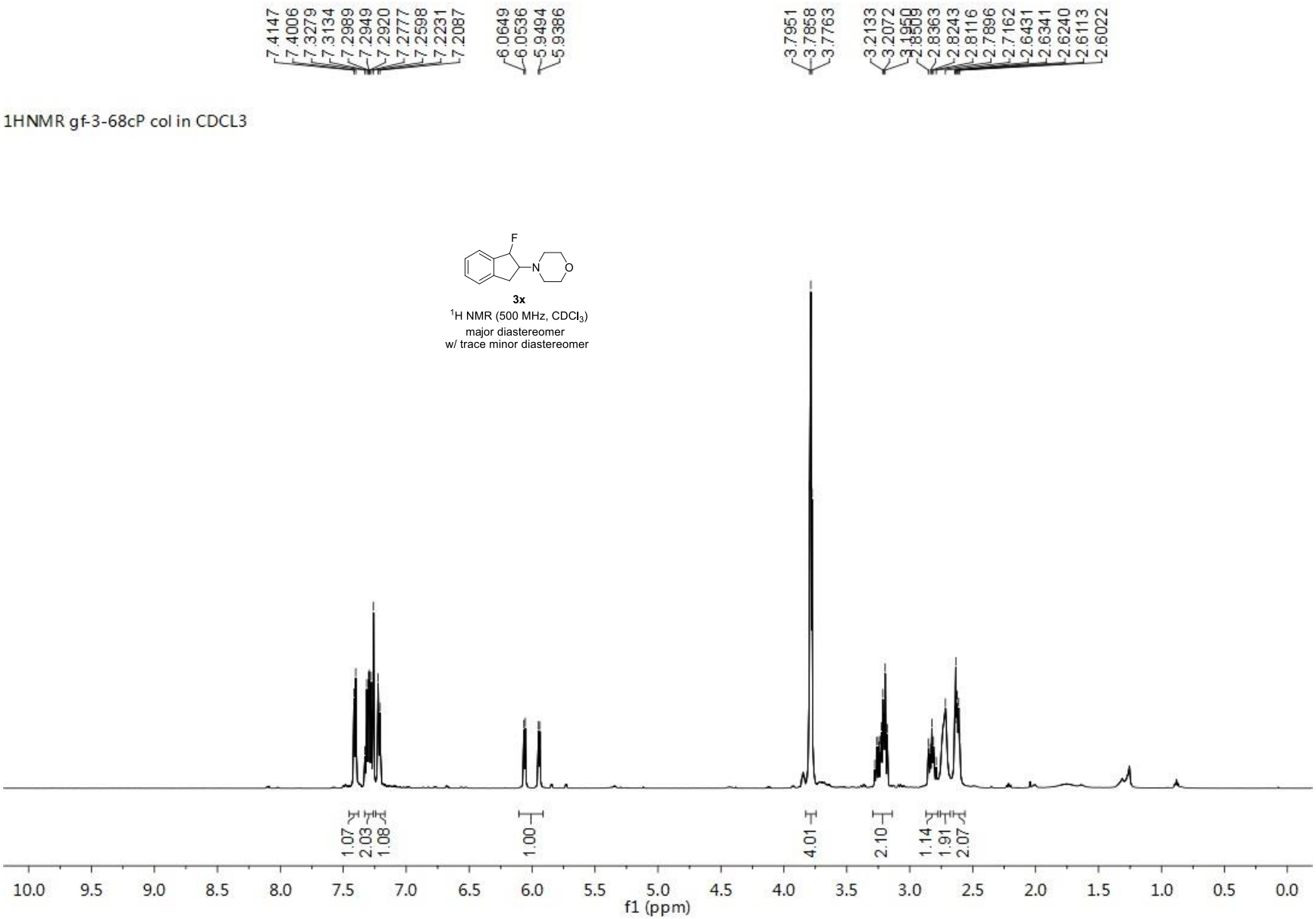
-189.8105



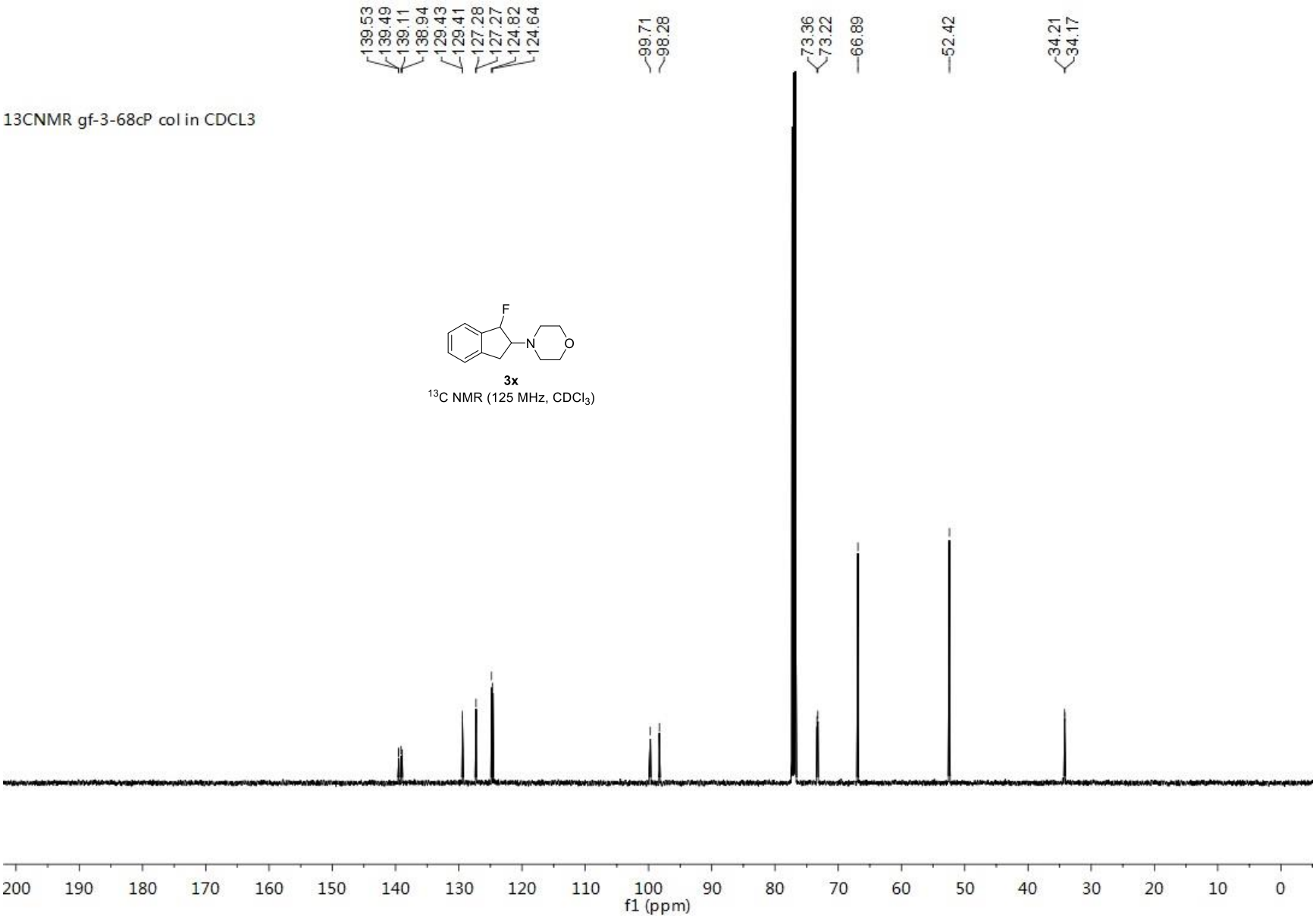
3w-II

^{19}F NMR (471 MHz, $CDCl_3$)





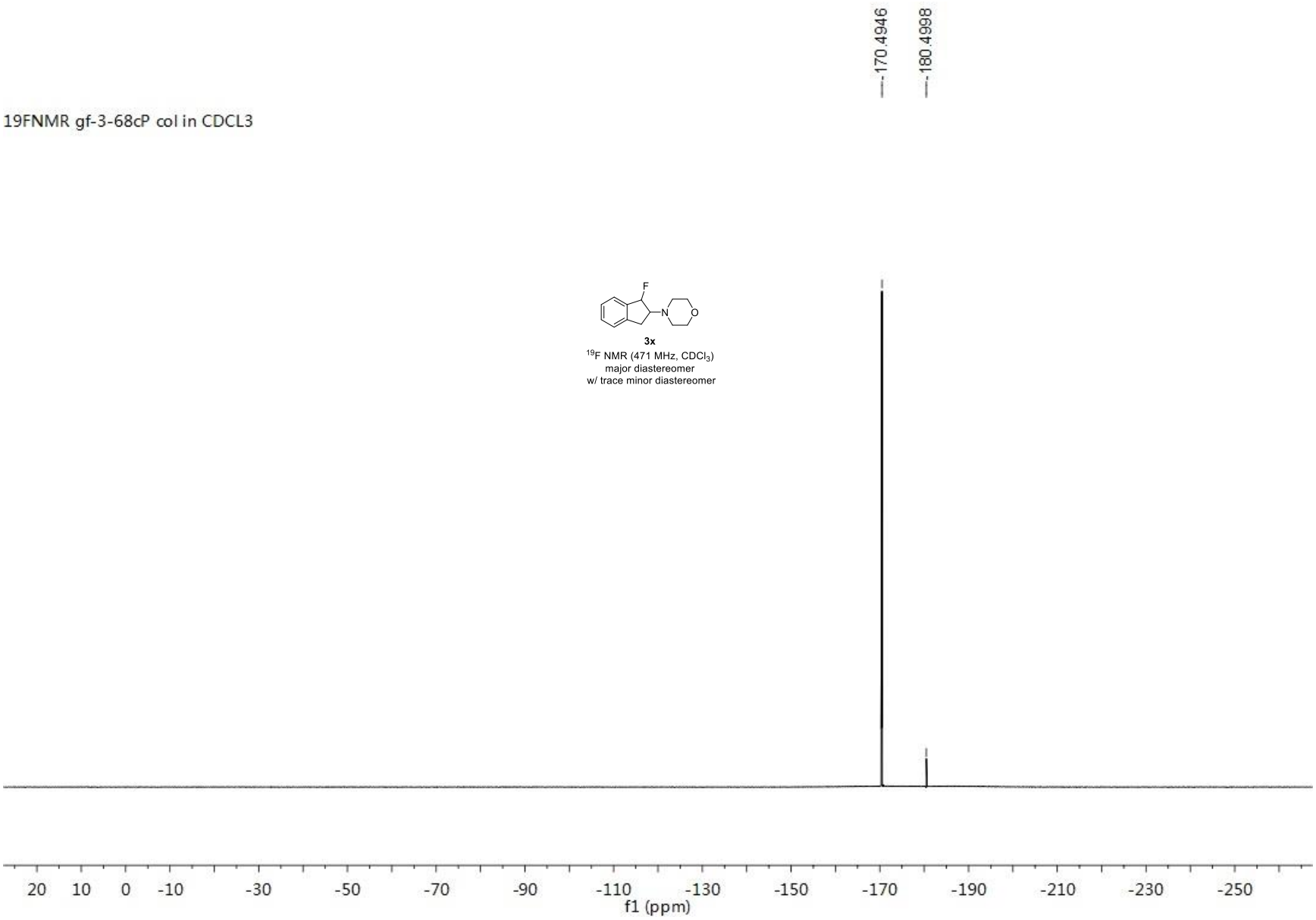
major diastereomer w/ trace minor diastereomer



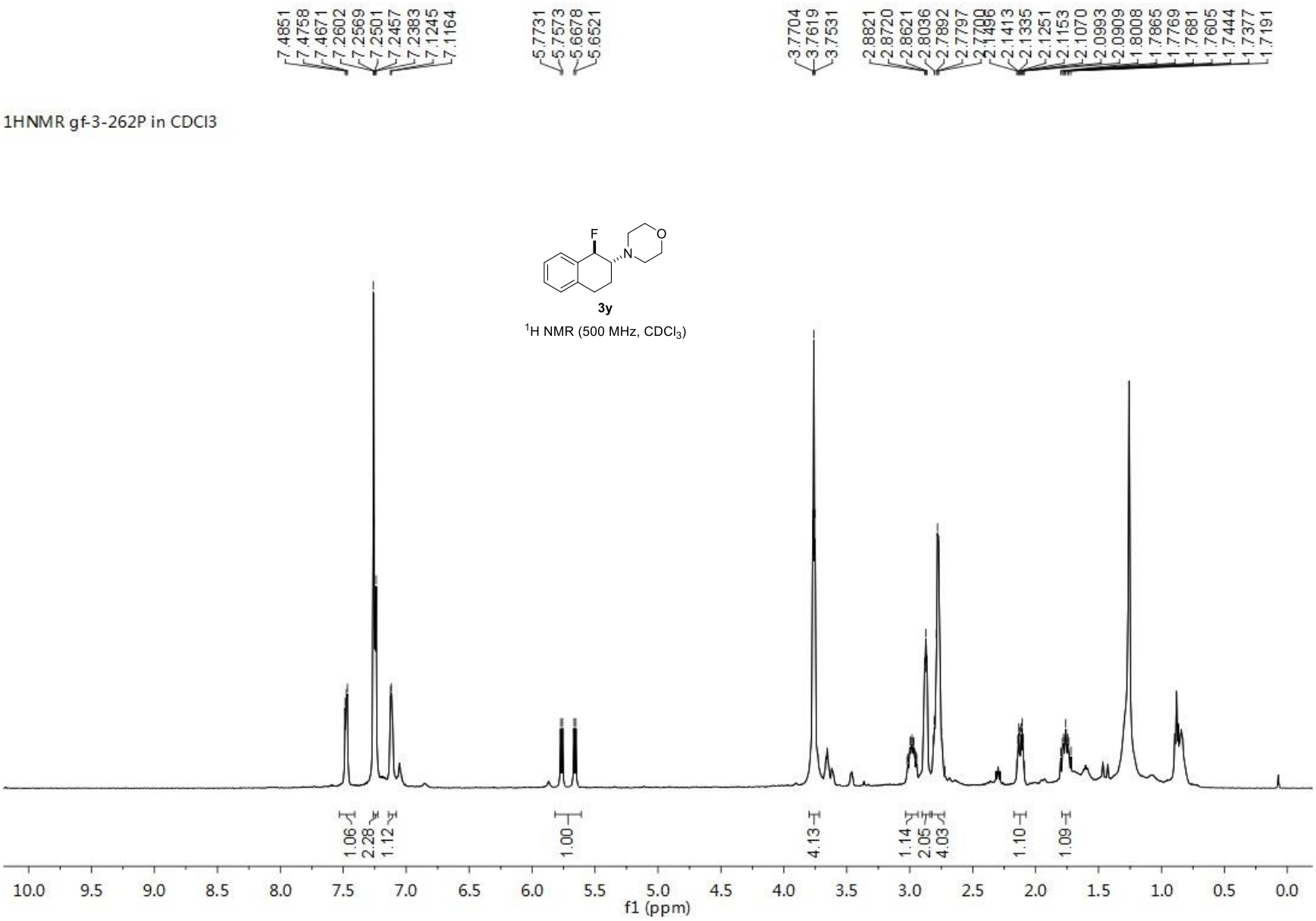
3x

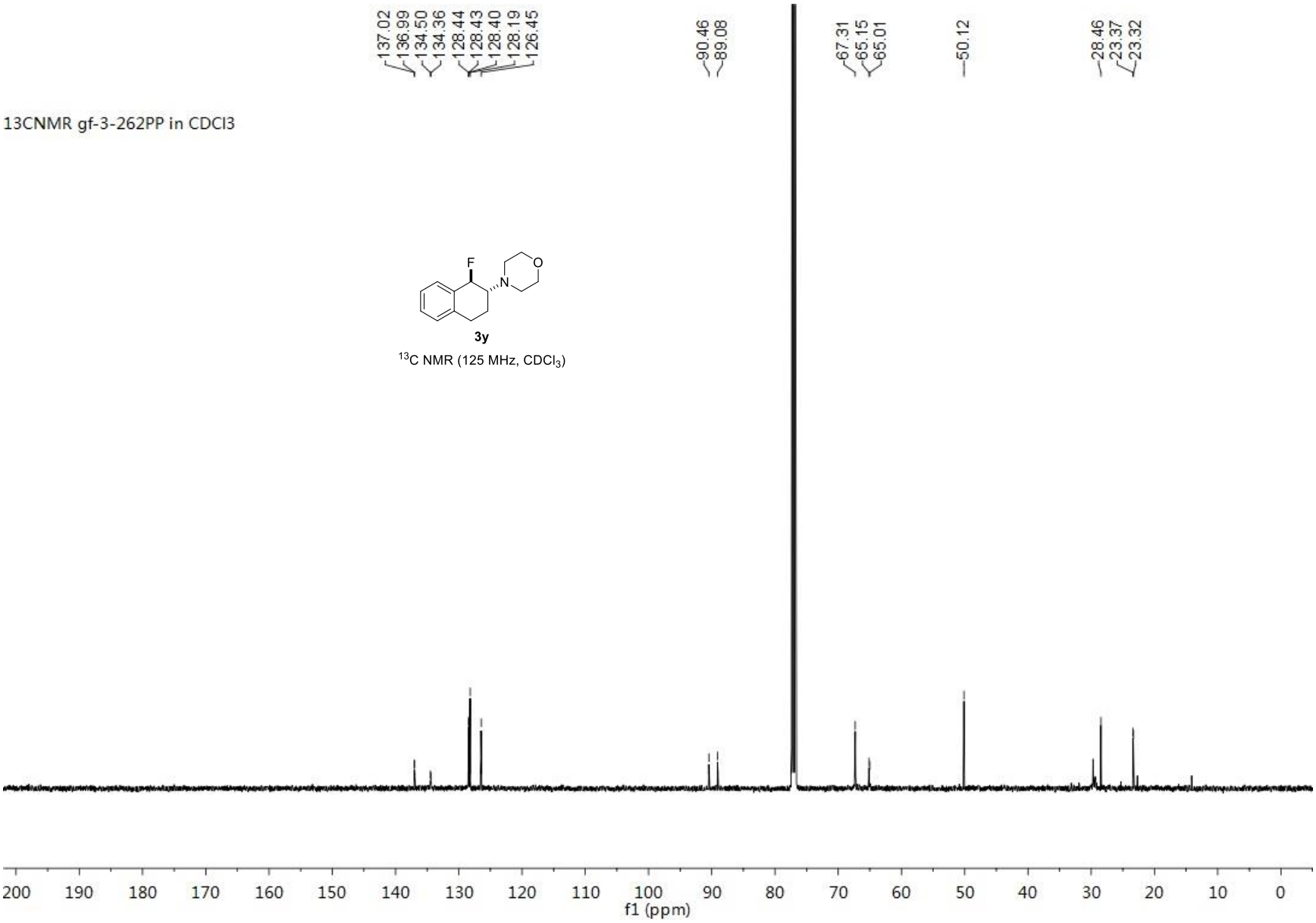
^{13}C NMR (125 MHz, $CDCl_3$)

19FNMR gf-3-68cP col in CDCL3



1HNMR gf-3-262P in CDCl3

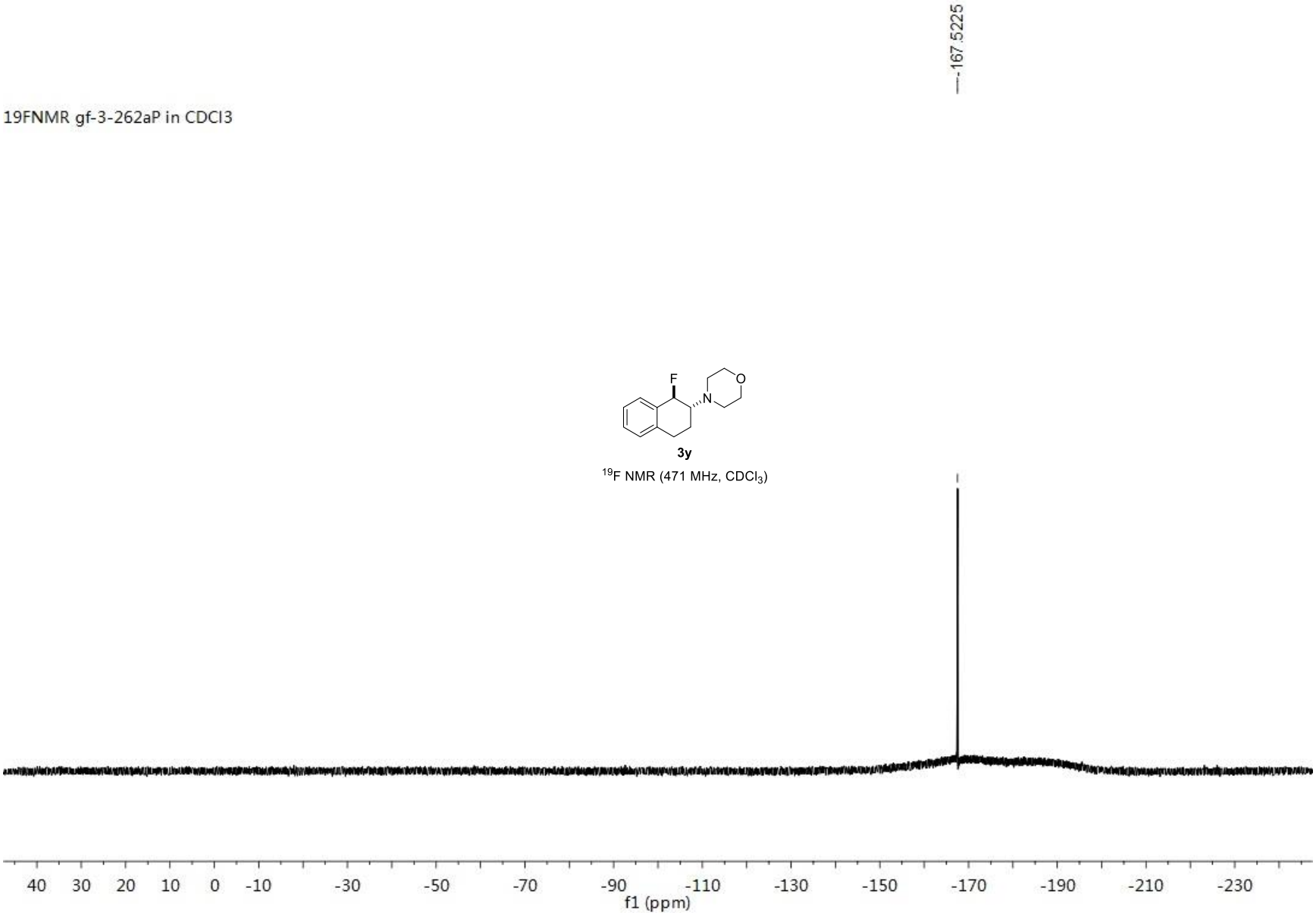




3y

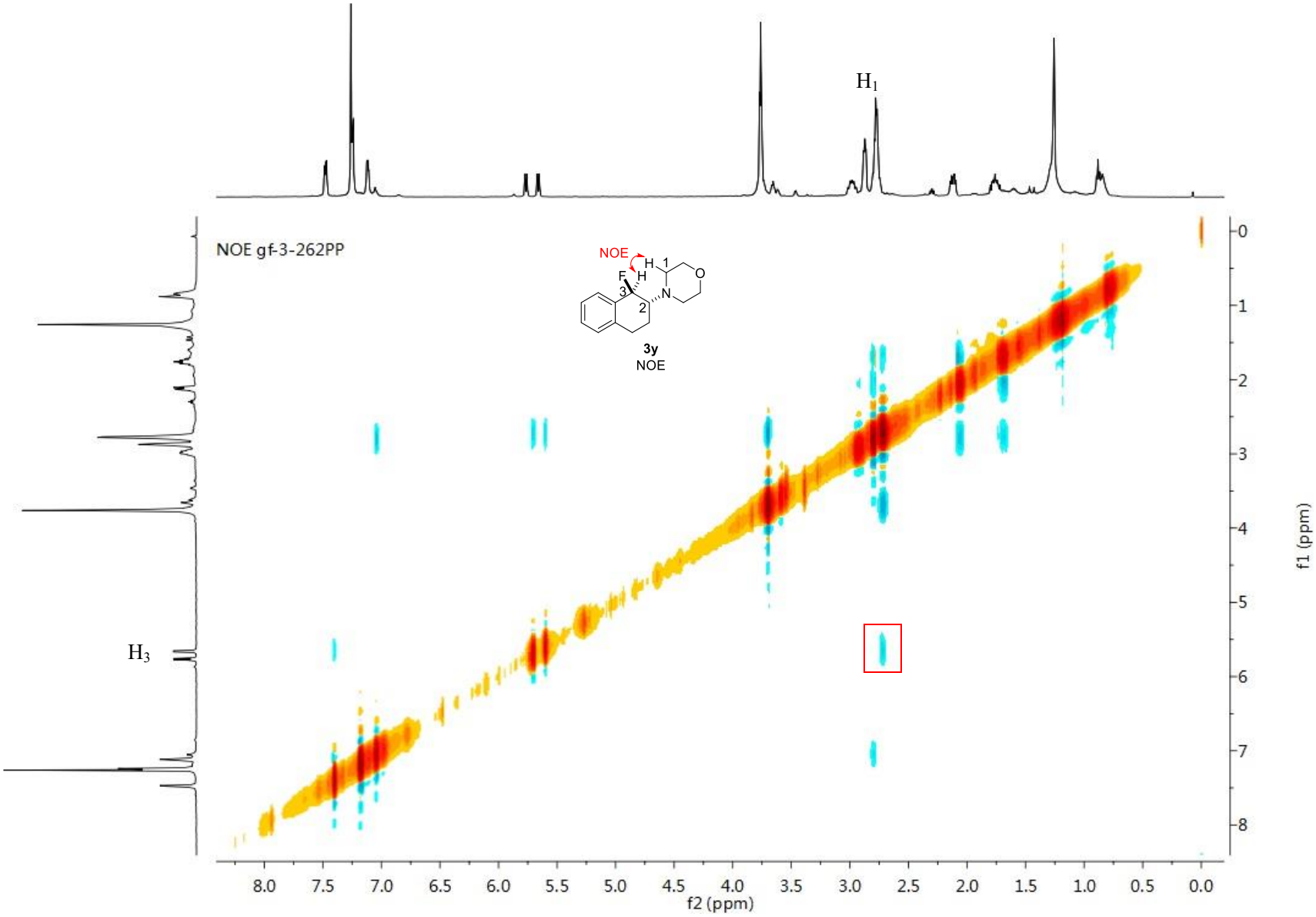
^{13}C NMR (125 MHz, $CDCl_3$)

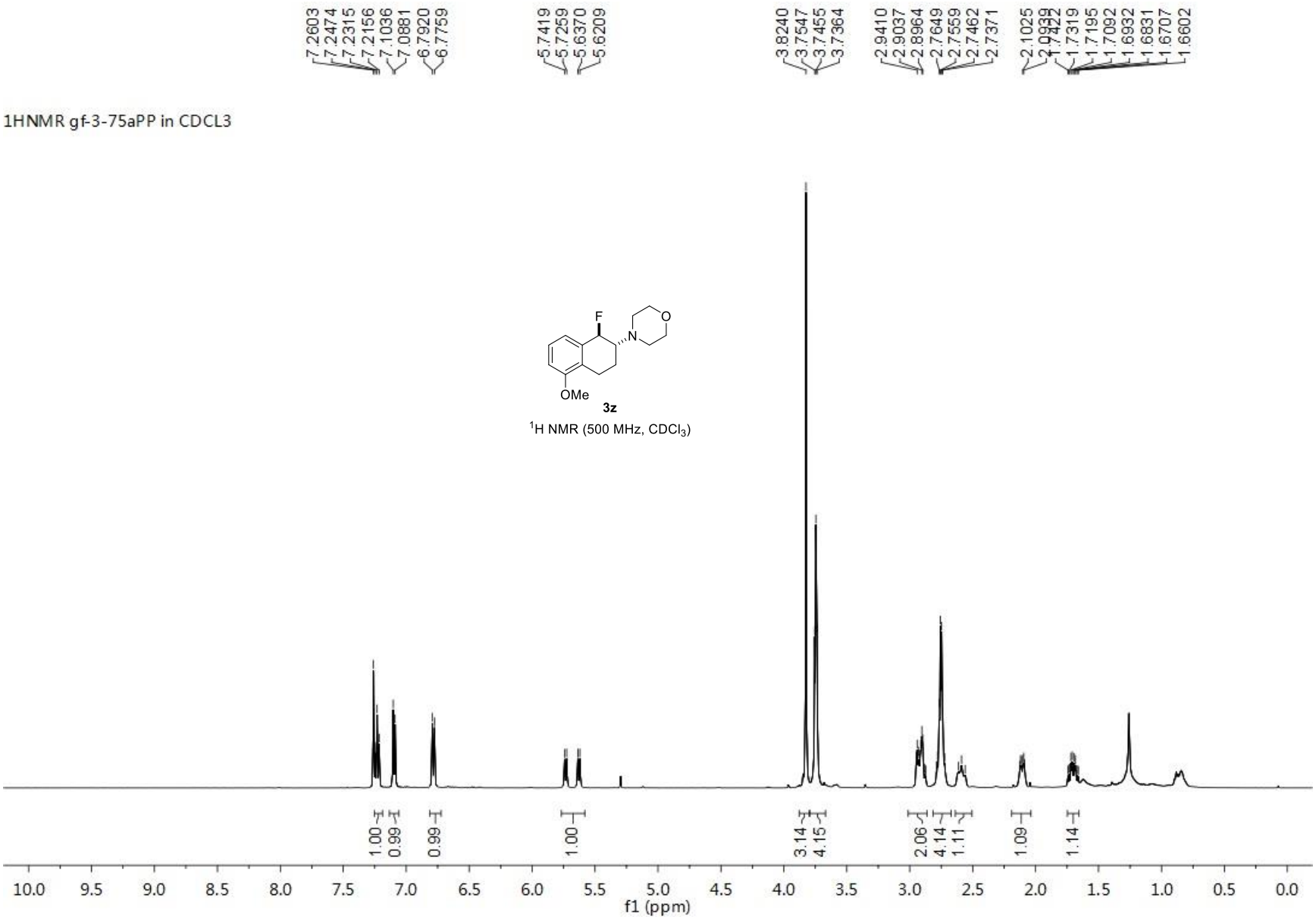
19FNMR gf-3-262aP in CDCl3

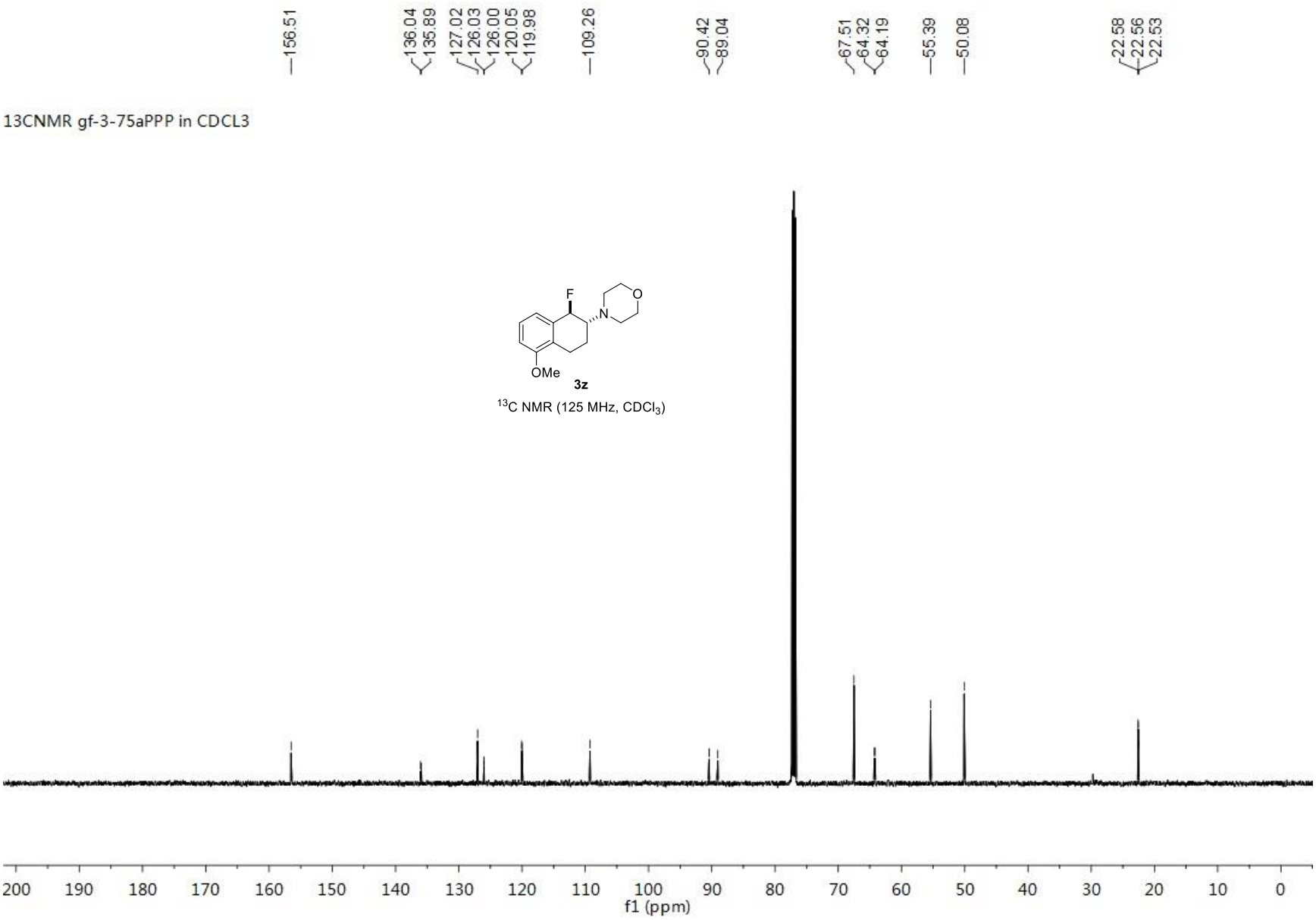


3y

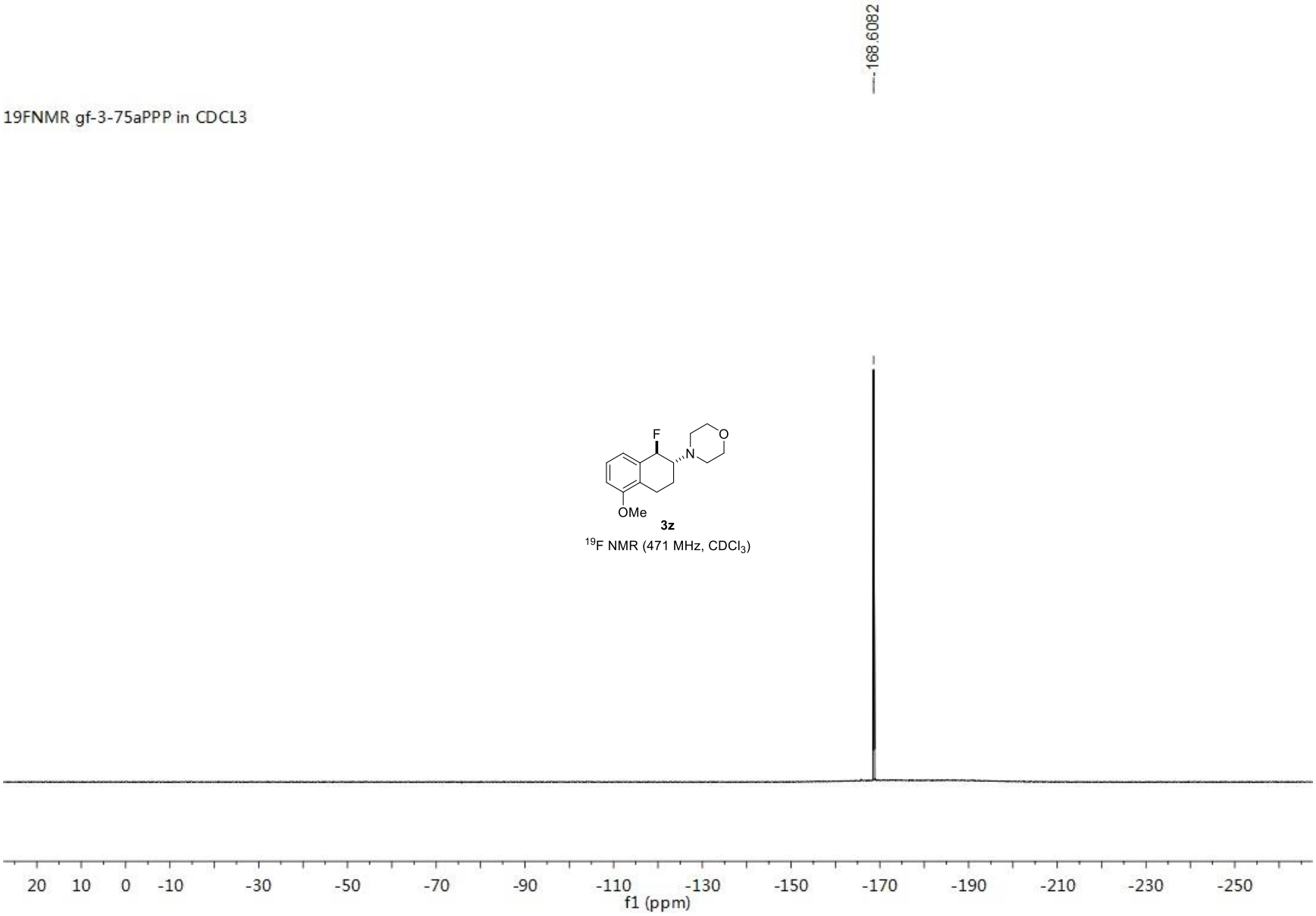
^{19}F NMR (471 MHz, $CDCl_3$)


H1
NOE gf-3-262PP
NOE
H
1
F
H
3
N
O
2
3y
NOE
H3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)


7.2603
7.2474
7.2315
7.2156
7.1036
7.0881
6.7920
6.7759
5.7419
5.7259
5.6370
5.6209
3.8240
3.7547
3.7455
3.7364
2.9410
2.9037
2.8964
2.7649
2.7559
2.7462
2.7371
2.1025
1.7319
1.7195
1.7092
1.6932
1.6831
1.6707
1.6602
1HNMR gf-3-75aPP in CDCL3
F
O
N
OMe
3z
1H NMR (500 MHz, CDCl3)
1.00
0.99
0.99
1.00
3.14
4.15
2.06
4.14
1.11
1.09
1.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


156.51
136.04
135.89
127.02
126.03
126.00
120.05
119.98
109.26
90.42
89.04
67.51
64.32
64.19
55.39
50.08
22.58
22.56
22.53
13CNMR gf-3-75aPPP in CDCL3
F
O
N
OMe
3z
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

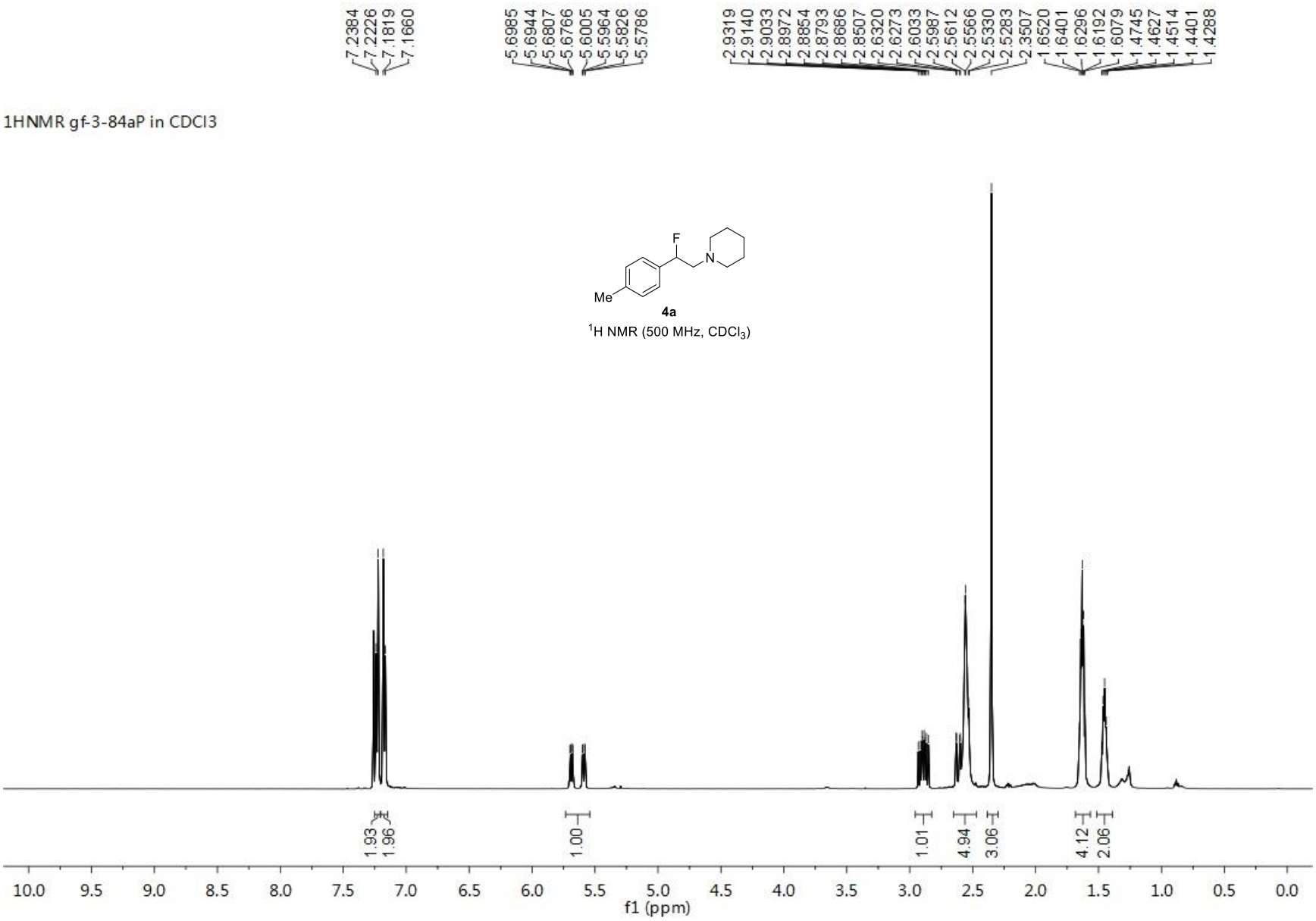
19FNMR gf-3-75aPPP in CDCL3

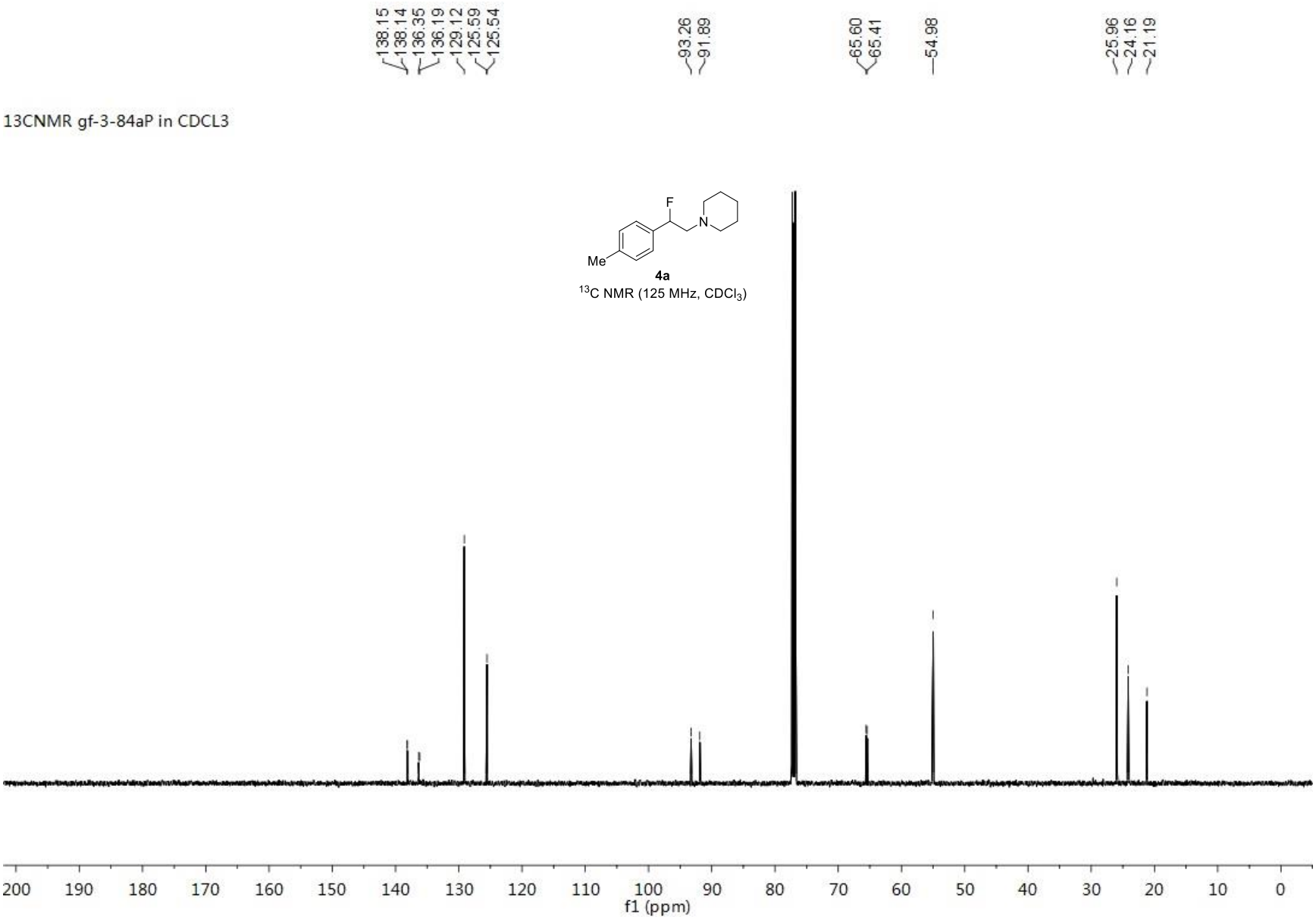


3z

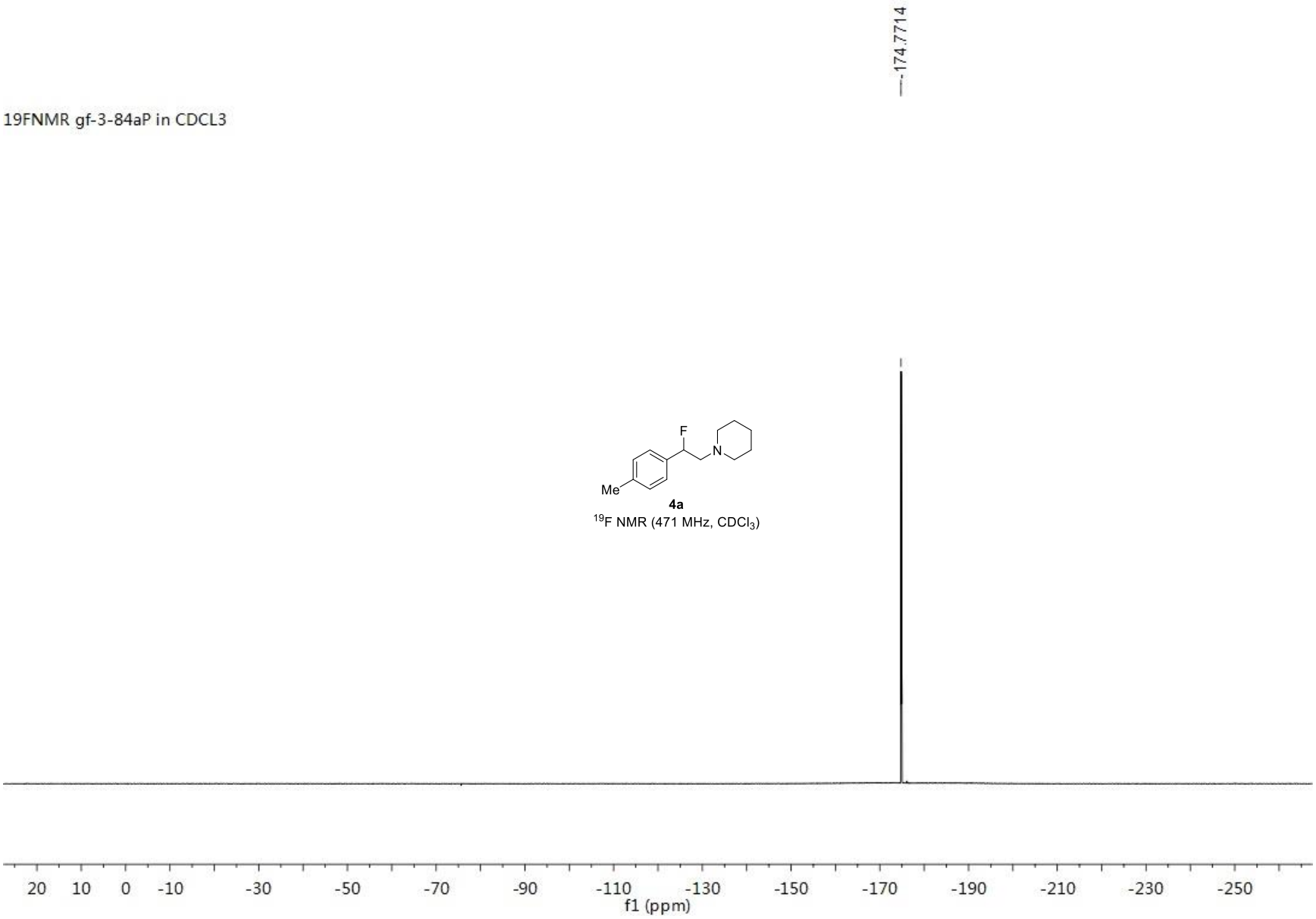
^{19}F NMR (471 MHz, $CDCl_3$)

1HNMR gf-3-84aP in CDCl3



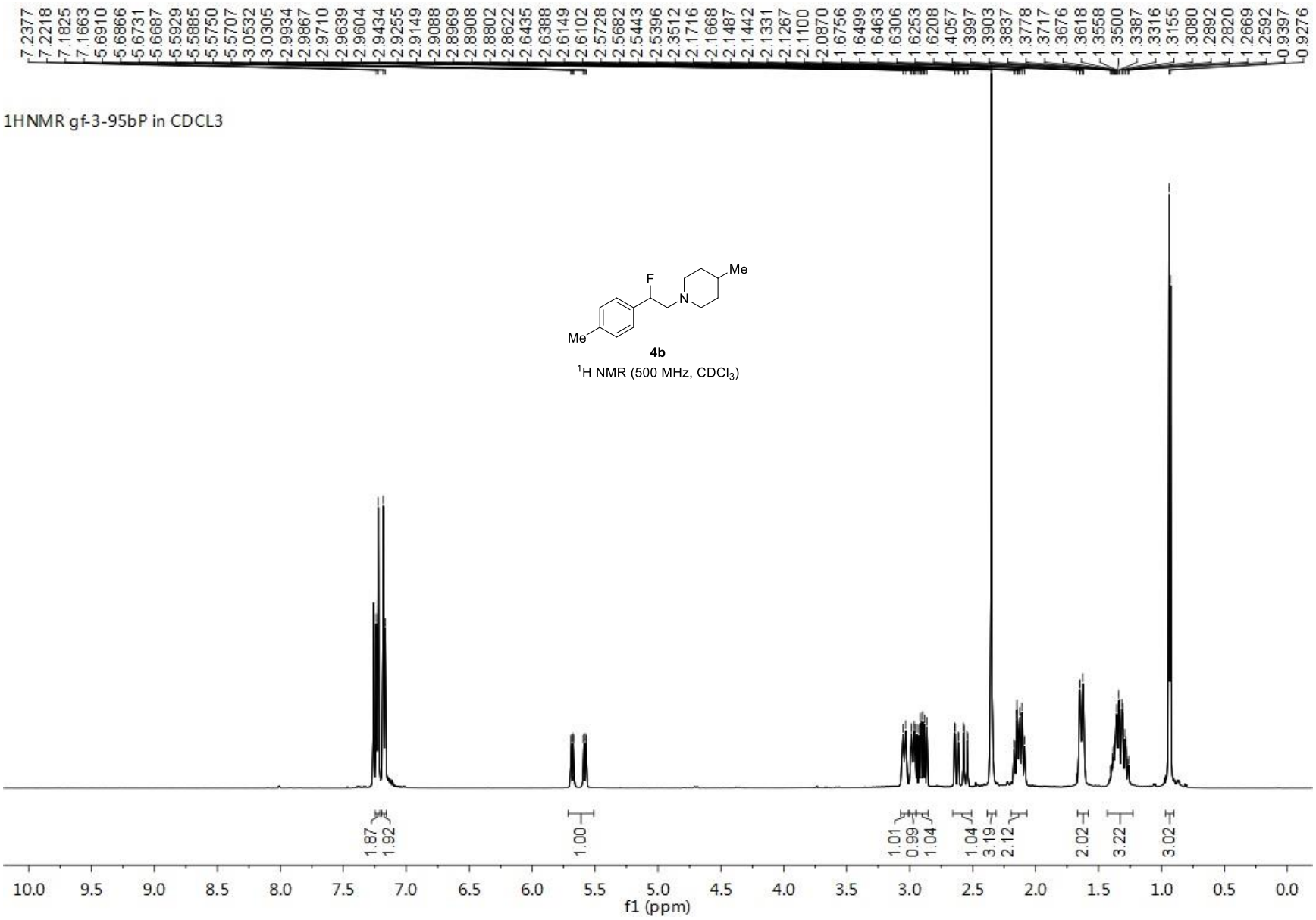

138.15
138.14
136.35
136.19
129.12
125.59
125.54
93.26
91.89
65.60
65.41
54.98
25.96
24.16
21.19
13CNMR gf-3-84aP in CDCL3
F
N
Me
4a
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

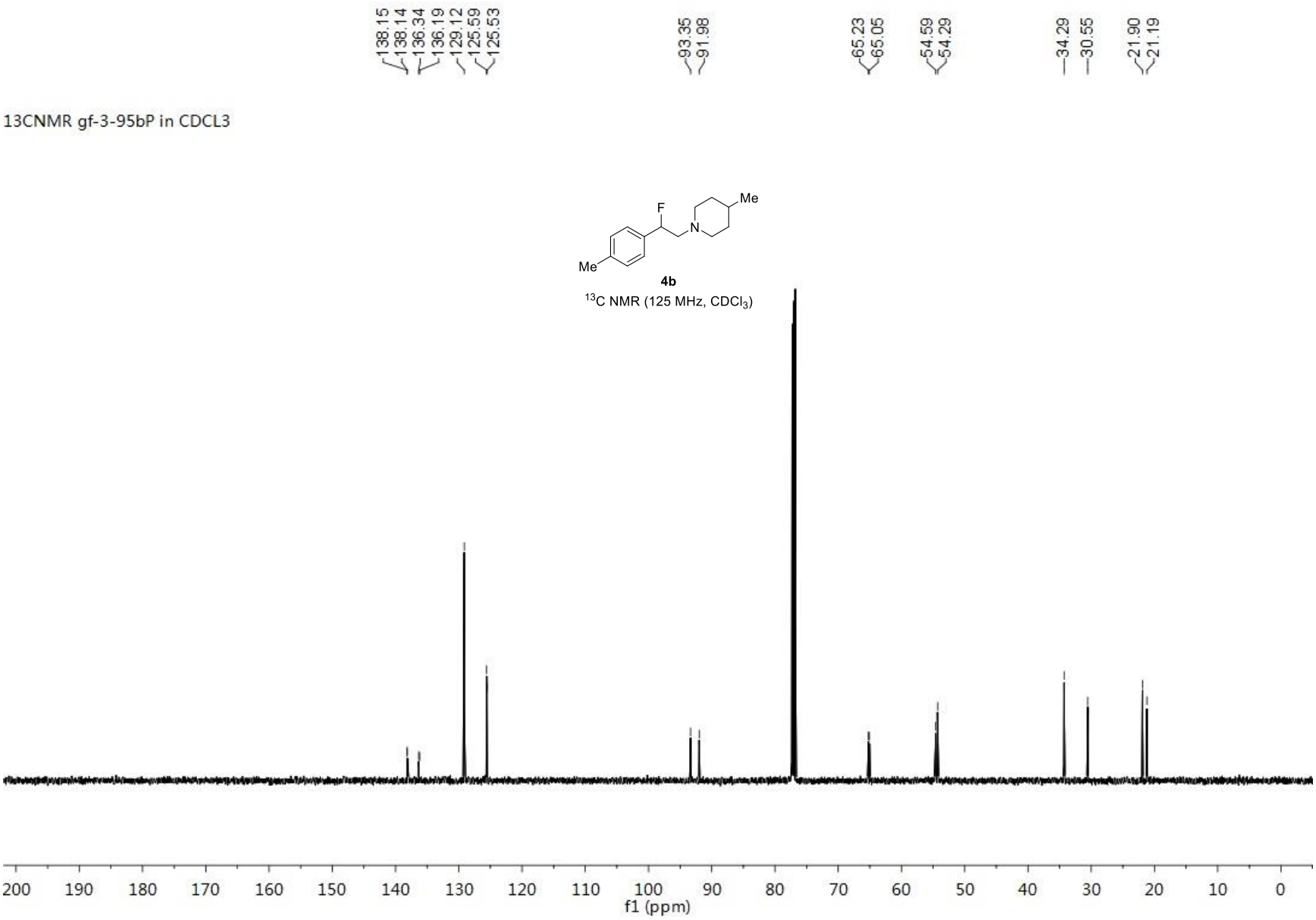
19FNMR gf-3-84aP in CDCL3



4a

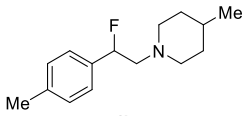
^{19}F NMR (471 MHz, $CDCl_3$)


1HNMR gf-3-95bP in CDCL3
F
N
Me
Me
4b
1H NMR (500 MHz, CDCl3)
f1 (ppm)


138.15
138.14
136.34
136.19
129.12
125.59
125.53
93.35
91.98
65.23
65.05
54.59
54.29
34.29
30.55
21.90
21.19
13CNMR gf-3-95bP in CDCL3
F
N
Me
Me
4b
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

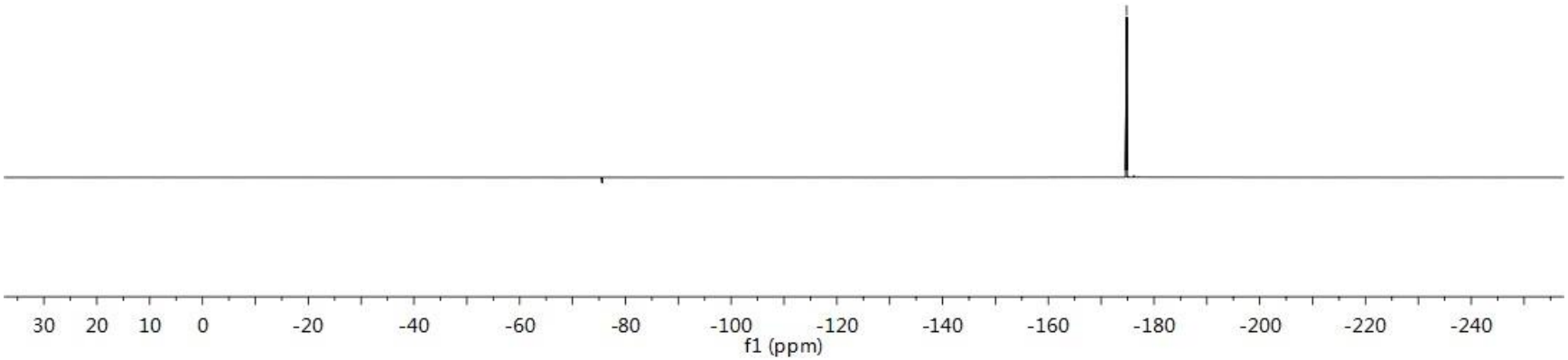
-174.8311

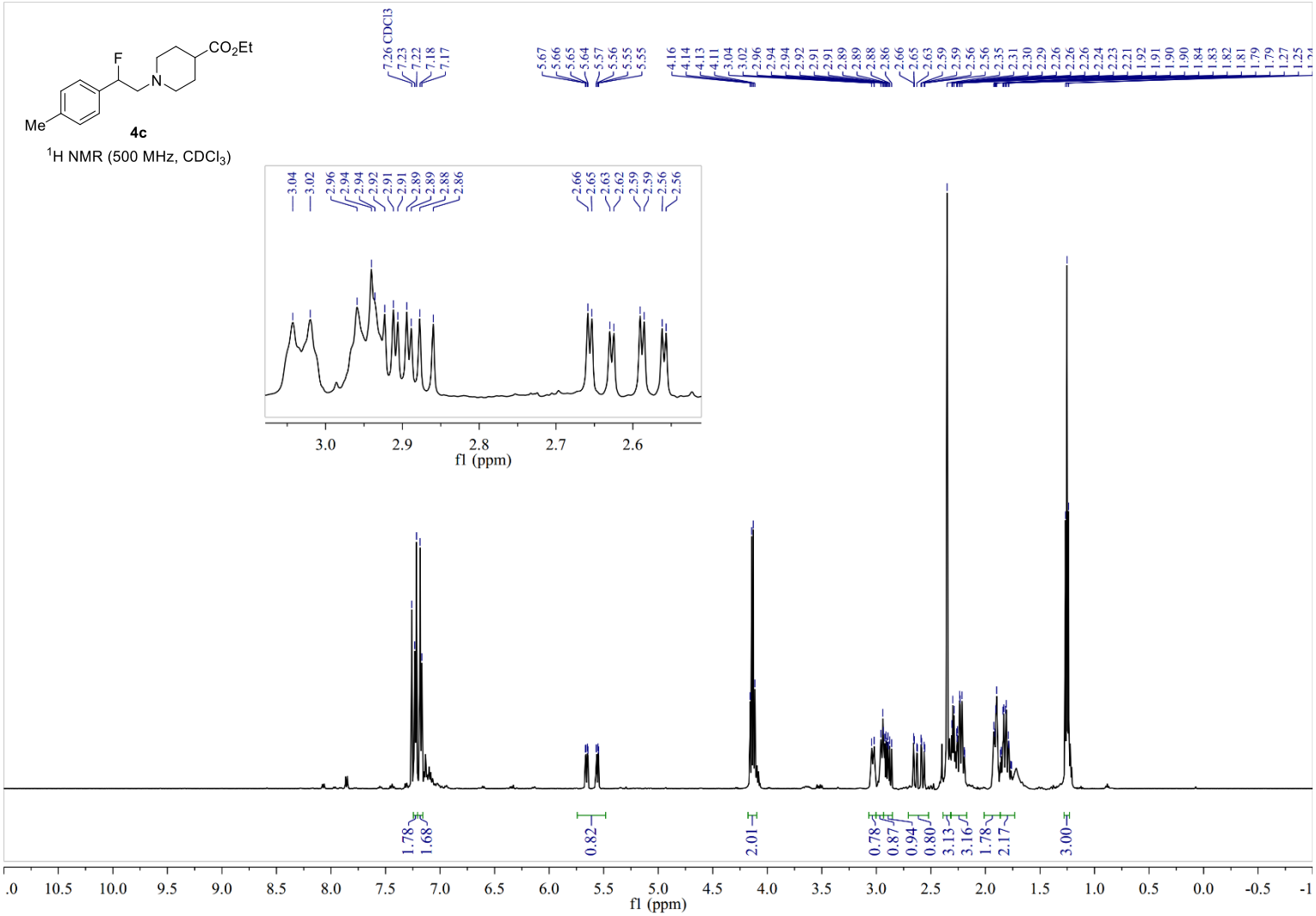
19FNMR gf-3-95bP in CDCL3

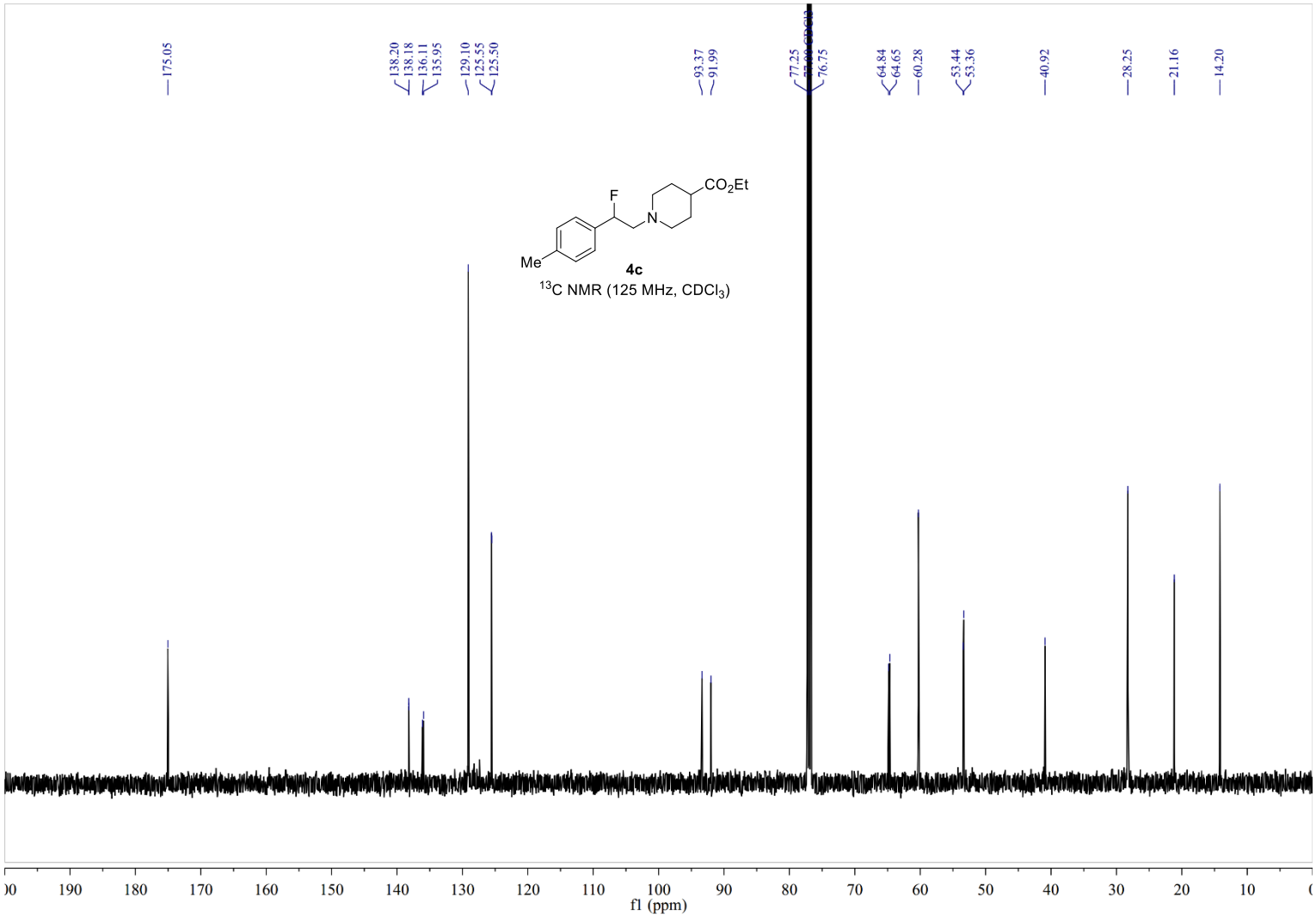


4b

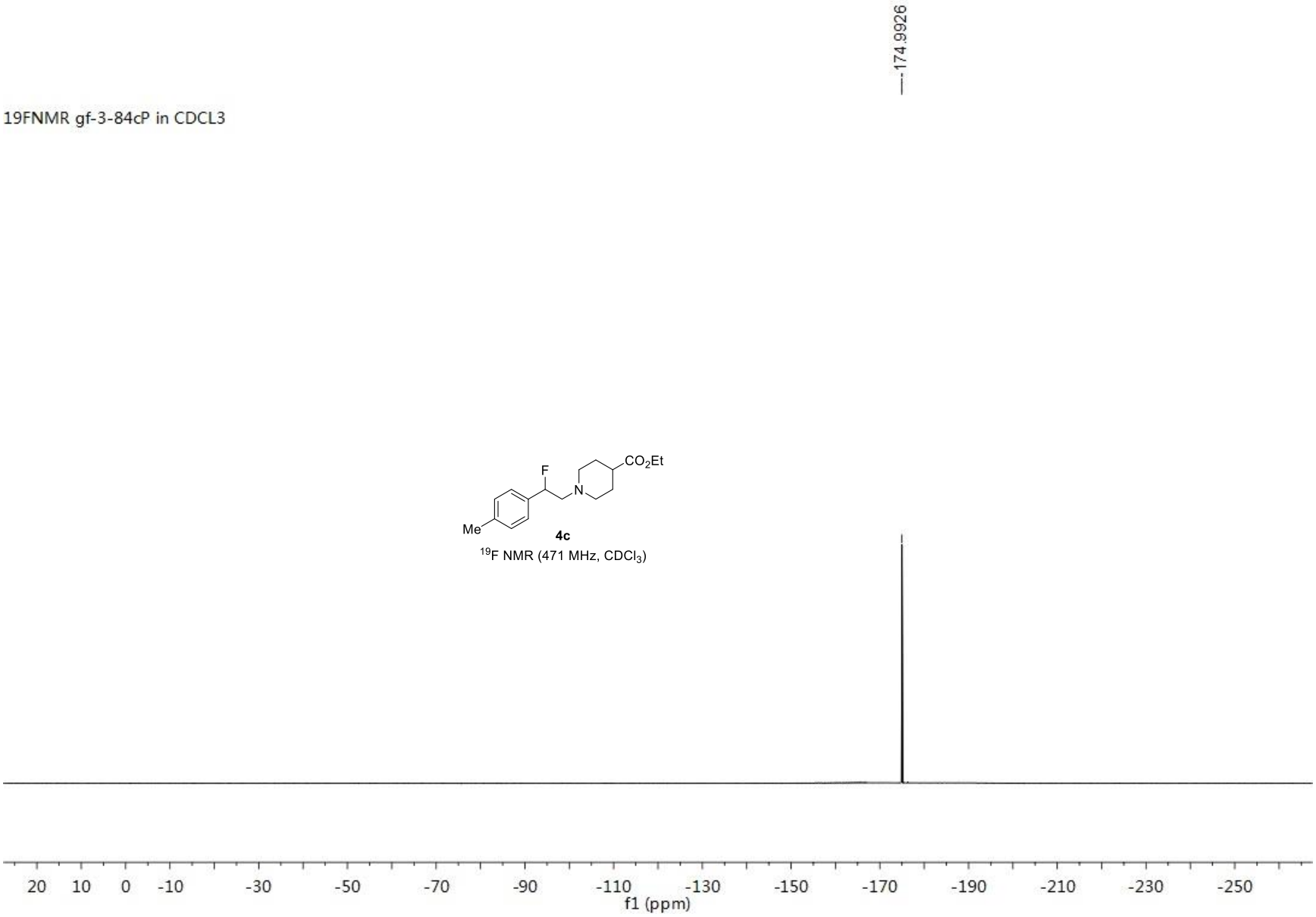
^{19}F NMR (471 MHz, $CDCl_3$)




CO2Et
F
N
Me
4c
1H NMR (500 MHz, CDCl3)
7.26 CDCl3
fl (ppm)
1.78
1.68
0.82
2.01
0.78
0.87
0.94
0.80
3.13
3.16
1.78
2.17
3.00

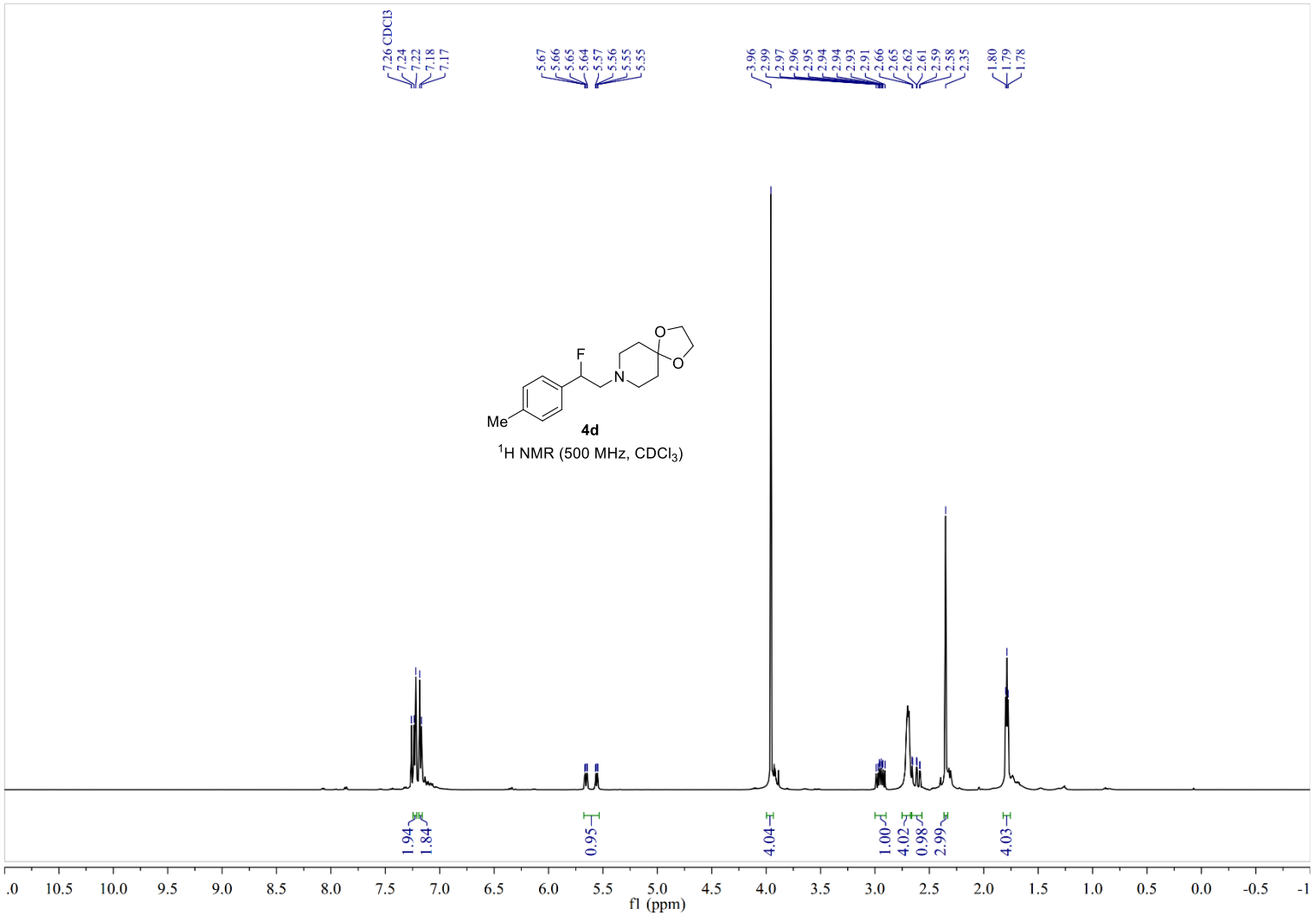

175.05
138.20
138.18
136.11
135.95
129.10
125.55
125.50
93.37
91.99
77.25
76.75
64.84
64.65
60.28
53.44
53.36
40.92
28.25
21.16
14.20
F
CO2Et
N
Me
4c
13C NMR (125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

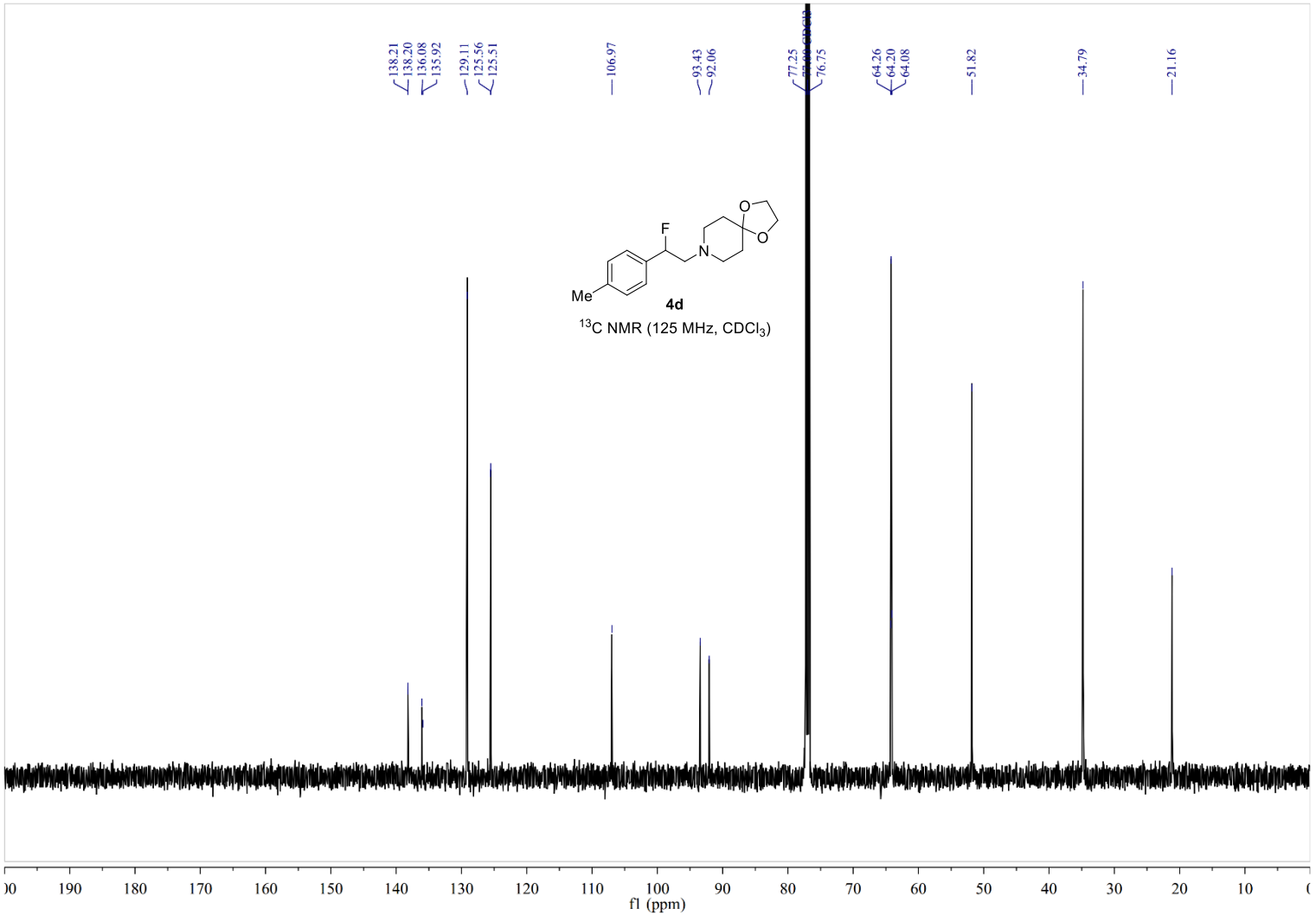
19FNMR gf-3-84cP in CDCL3



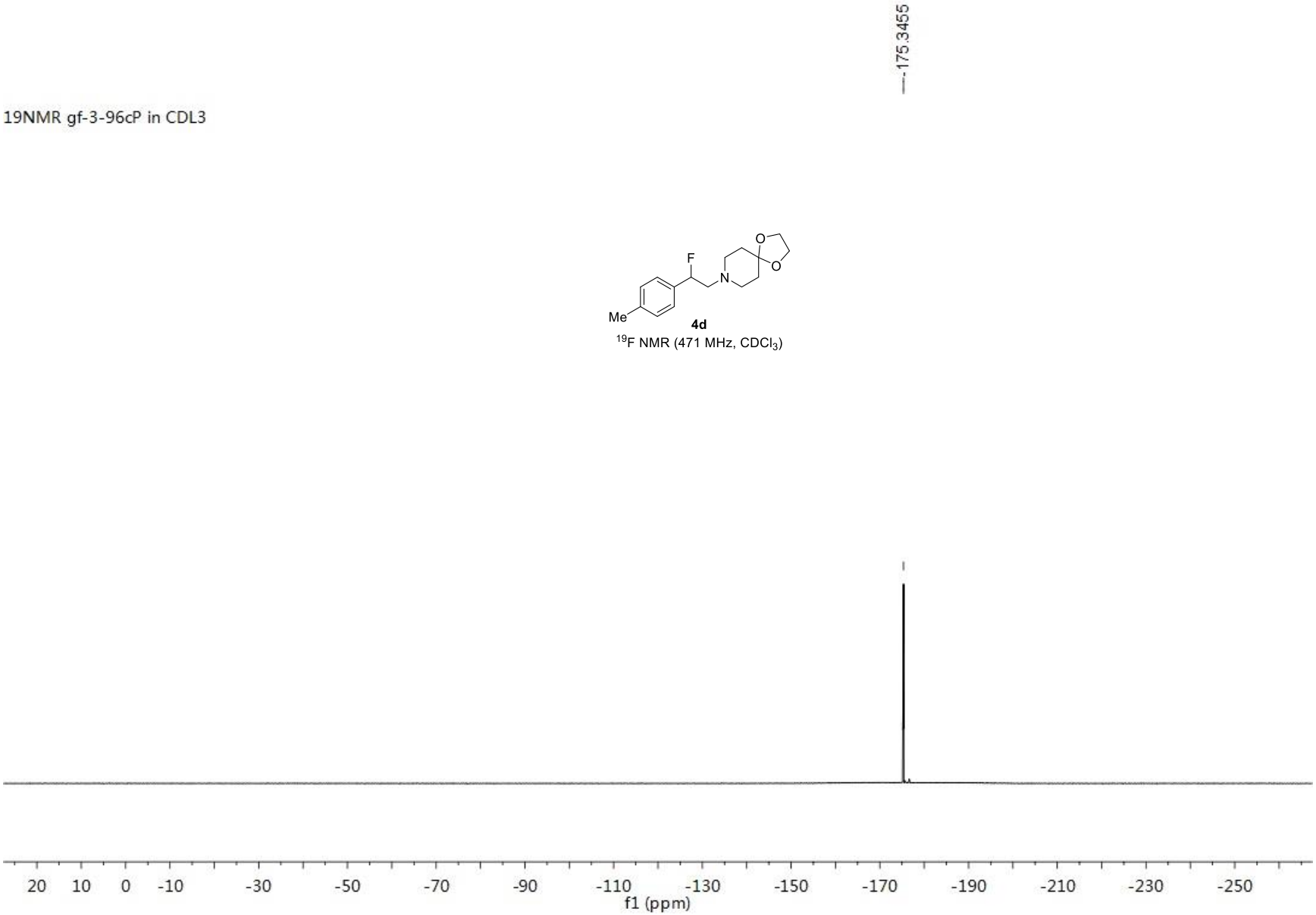
4c

^{19}F NMR (471 MHz, $CDCl_3$)


7.26 CDCl3
7.24
7.22
7.18
7.17
5.67
5.66
5.65
5.64
5.57
5.56
5.55
5.55
3.96
2.99
2.97
2.96
2.95
2.94
2.94
2.93
2.91
2.66
2.65
2.62
2.61
2.59
2.58
2.35
1.80
1.79
1.78
F
N
O
O
Me
4d
1H NMR (500 MHz, CDCl3)
1.94
1.84
0.95
4.04
1.00
4.02
0.98
2.99
4.03
f1 (ppm)

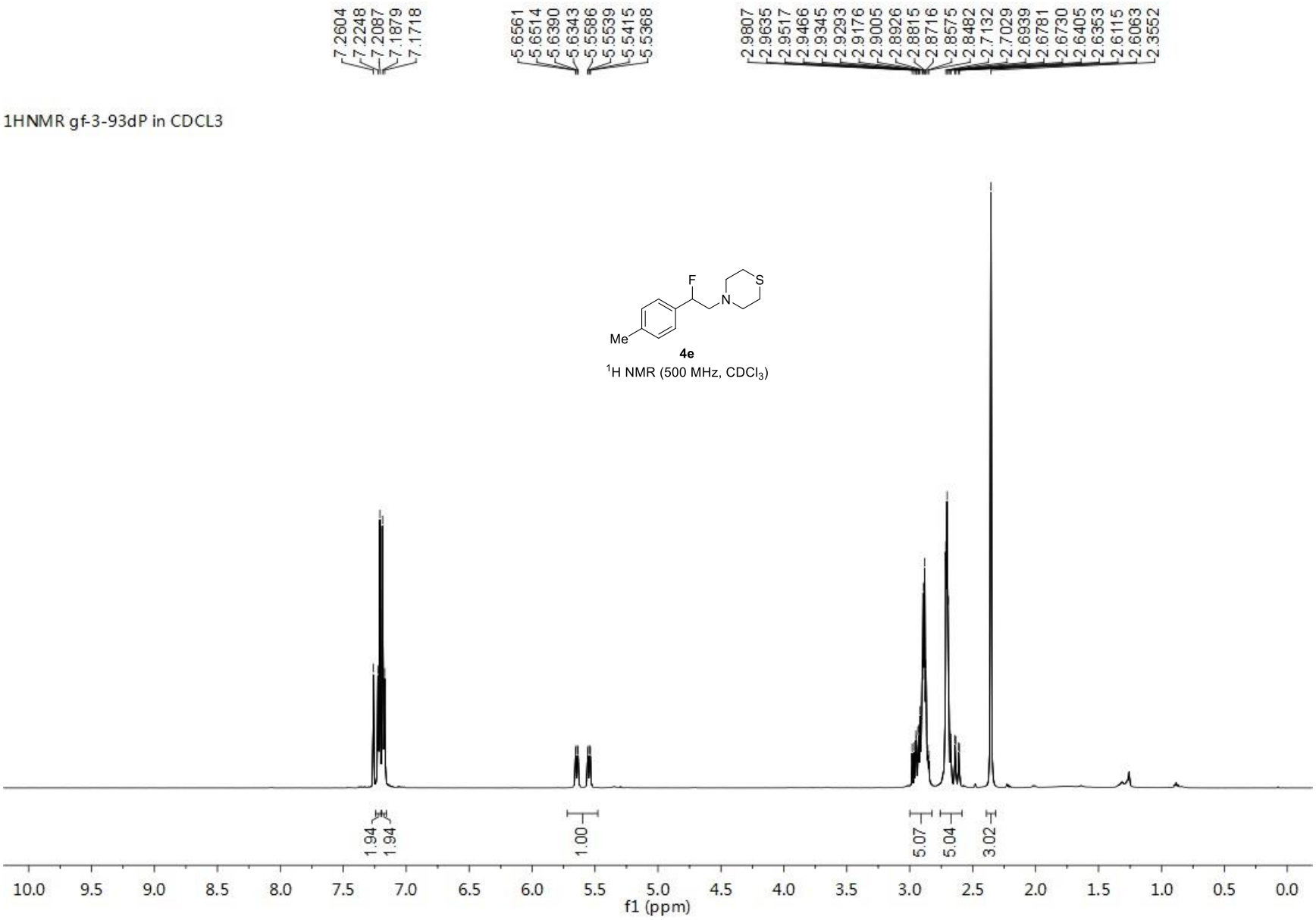

138.21
138.20
136.08
135.92
129.11
125.56
125.51
106.97
93.43
92.06
77.25
76.75
64.26
64.20
64.08
51.82
34.79
21.16
F
N
O
O
Me
4d
13C NMR (125 MHz, CDCl3)
f1 (ppm)

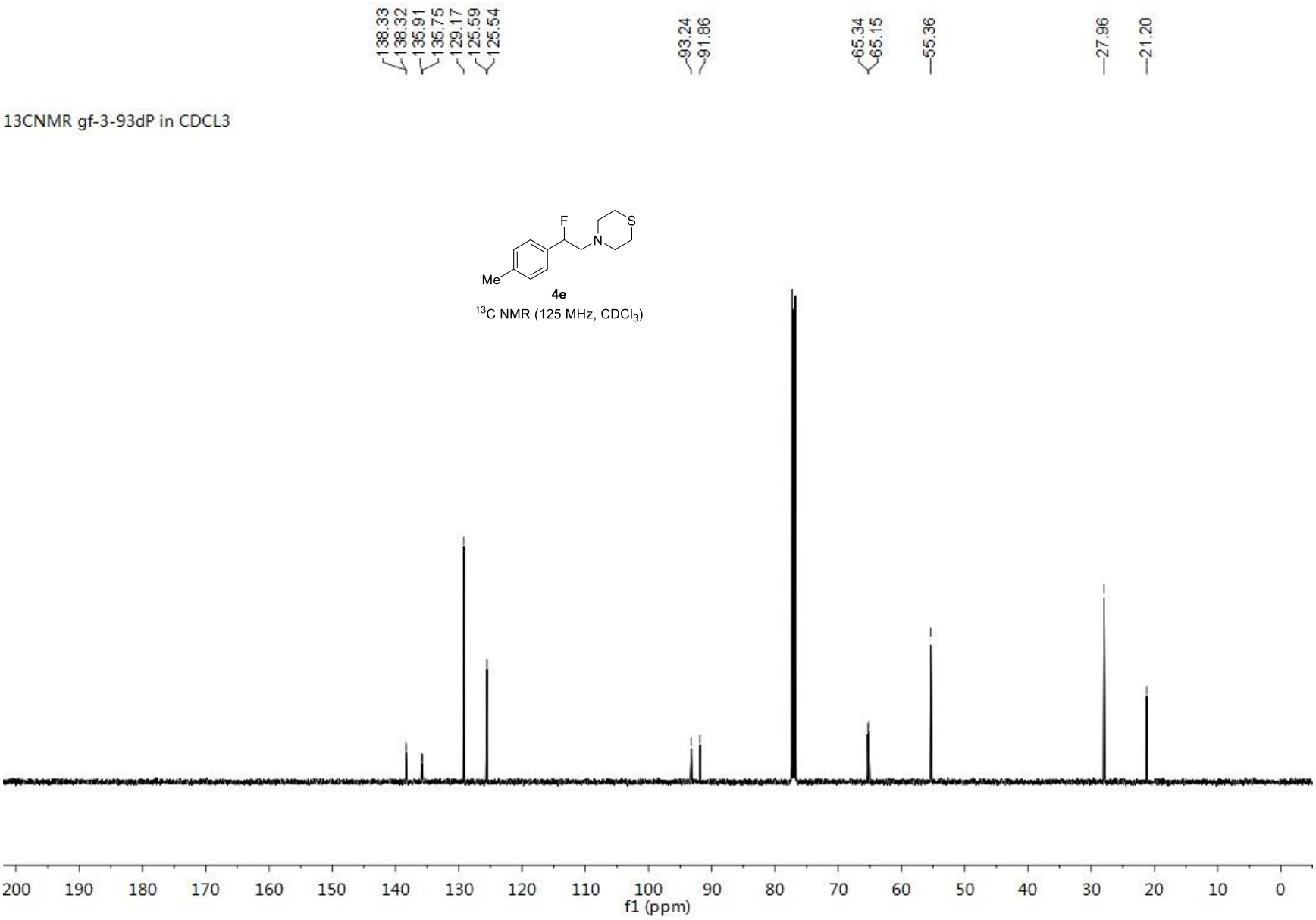
19NMR gf-3-96cP in CDL3



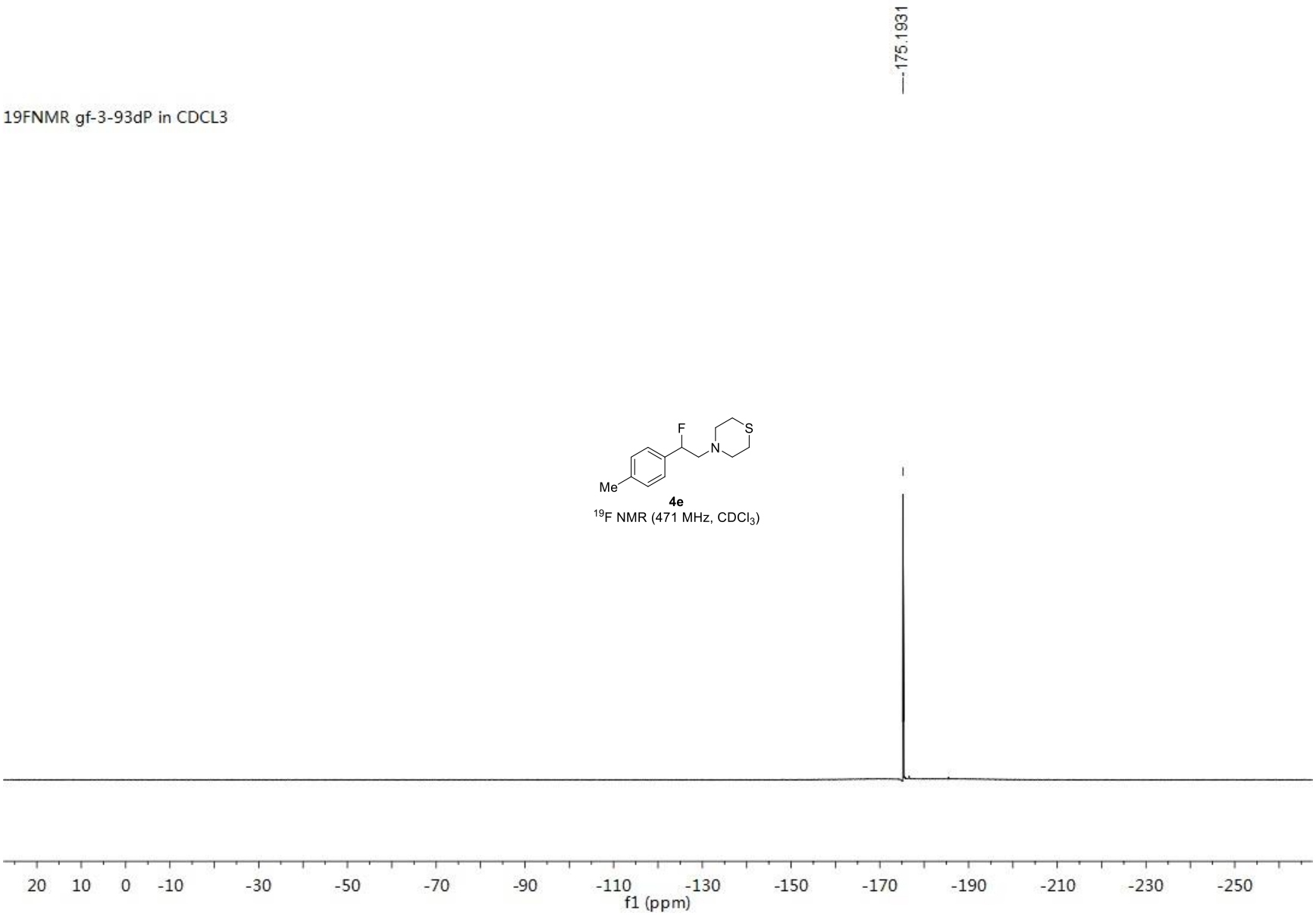
4d

^{19}F NMR (471 MHz, $CDCl_3$)


7.2604
7.2248
7.2087
7.1879
7.1718
5.6561
5.6514
5.6390
5.6343
5.5586
5.5539
5.5415
5.5368
2.9807
2.9635
2.9517
2.9466
2.9345
2.9293
2.9176
2.9005
2.8926
2.8815
2.8716
2.8575
2.8482
2.7132
2.7029
2.6939
2.6781
2.6730
2.6405
2.6353
2.6115
2.6063
2.3552
1HNMR gf-3-93dP in CDCL3
F
S
N
Me
4e
1H NMR (500 MHz, CDCl3)
1.94
1.94
1.00
5.07
5.04
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

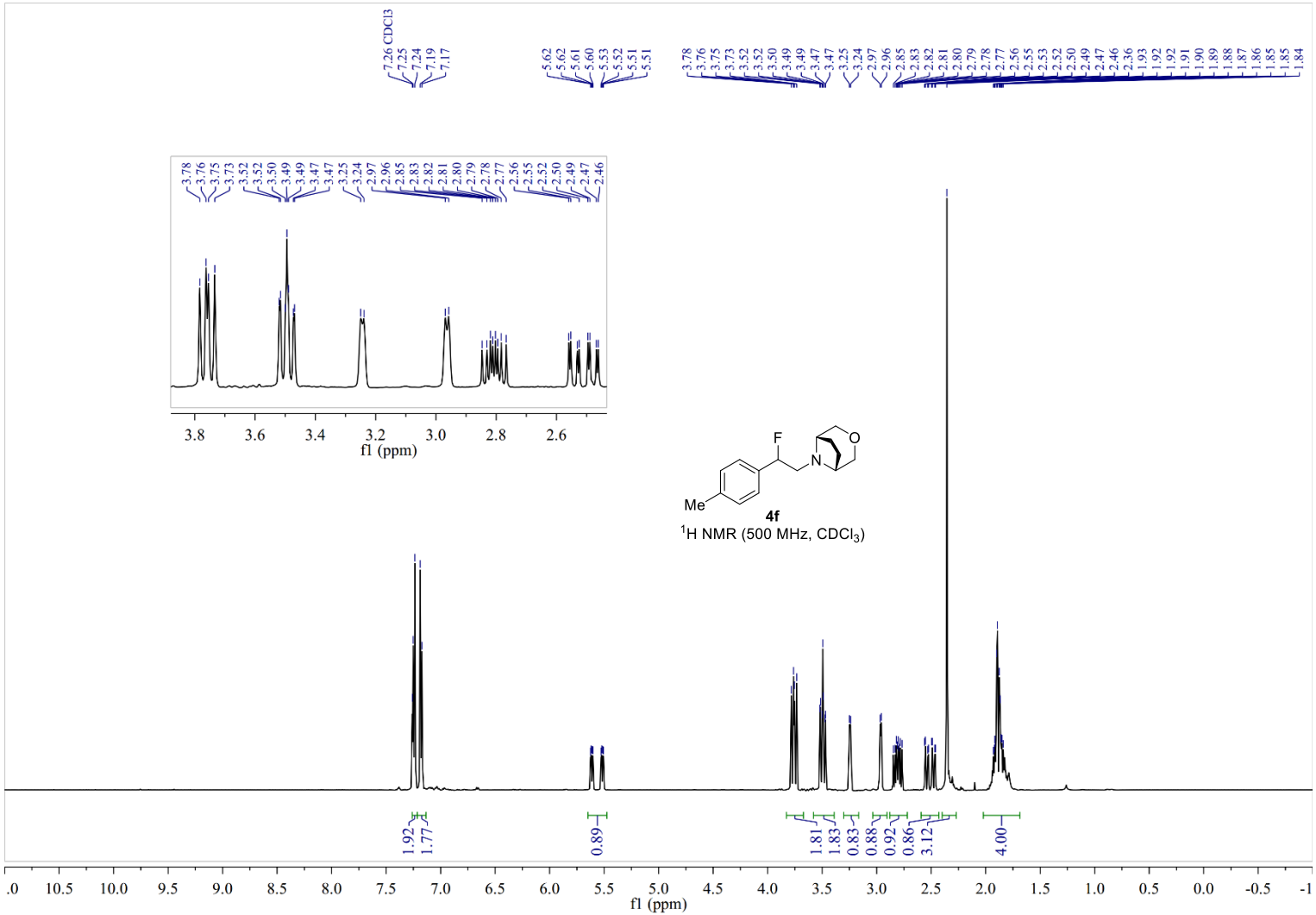

138.33
138.32
135.91
135.75
129.17
125.59
125.54
93.24
91.86
65.34
65.15
55.36
27.96
21.20
13CNMR gf-3-93dP in CDCL3
F
S
N
Me
4e
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

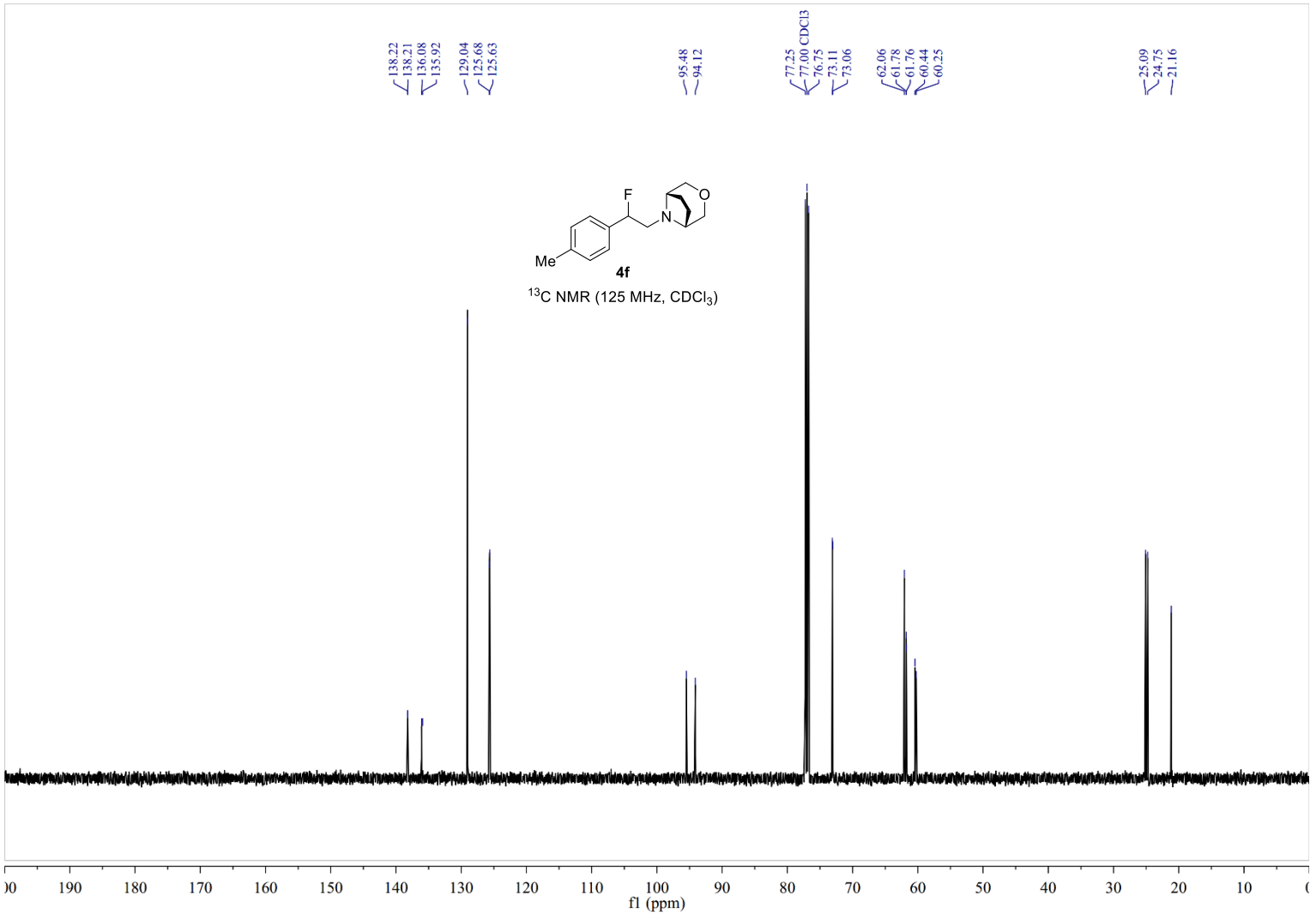
19FNMR gf-3-93dP in CDCL3



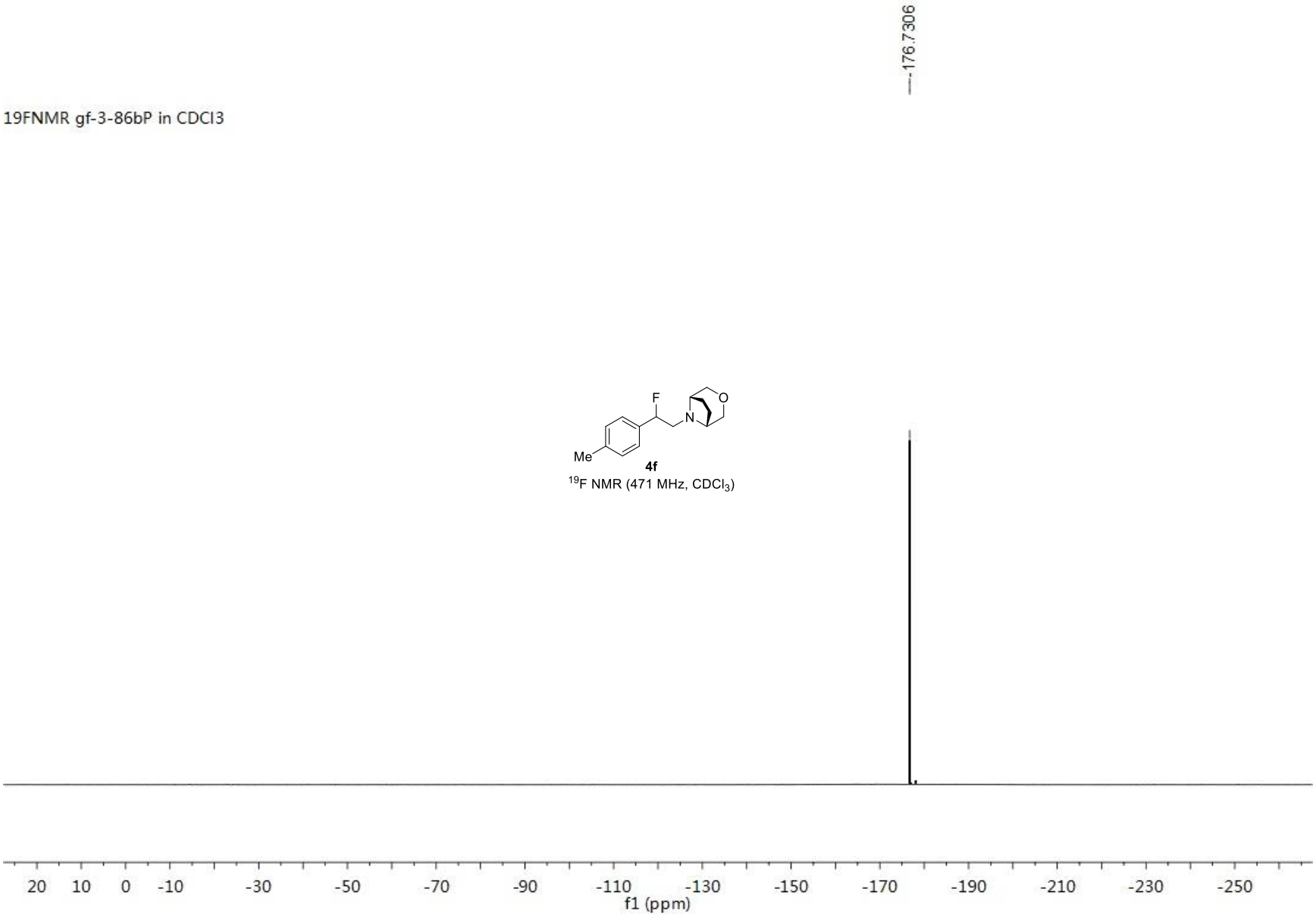
4e

^{19}F NMR (471 MHz, $CDCl_3$)


7.26 CDCl3
7.25
7.24
7.19
7.17
5.62
5.62
5.61
5.60
5.53
5.52
5.51
5.51
3.78
3.76
3.75
3.73
3.52
3.52
3.50
3.49
3.49
3.47
3.47
3.25
3.24
2.97
2.96
2.85
2.83
2.82
2.81
2.80
2.79
2.78
2.77
2.56
2.55
2.53
2.52
2.50
2.49
2.47
2.46
2.36
1.93
1.92
1.92
1.91
1.90
1.89
1.88
1.87
1.86
1.85
1.85
1.84
f1 (ppm)
F
O
N
Me
4f
1H NMR (500 MHz, CDCl3)
1.92
1.77
0.89
1.81
1.83
0.83
0.88
0.92
0.86
3.12
4.00
f1 (ppm)


138.22
138.21
136.08
135.92
129.04
125.68
125.63
95.48
94.12
77.25
77.00 CDCl3
76.75
73.11
73.06
62.06
61.78
61.76
60.44
60.25
25.09
24.75
21.16
F
O
N
Me
4f
13C NMR (125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

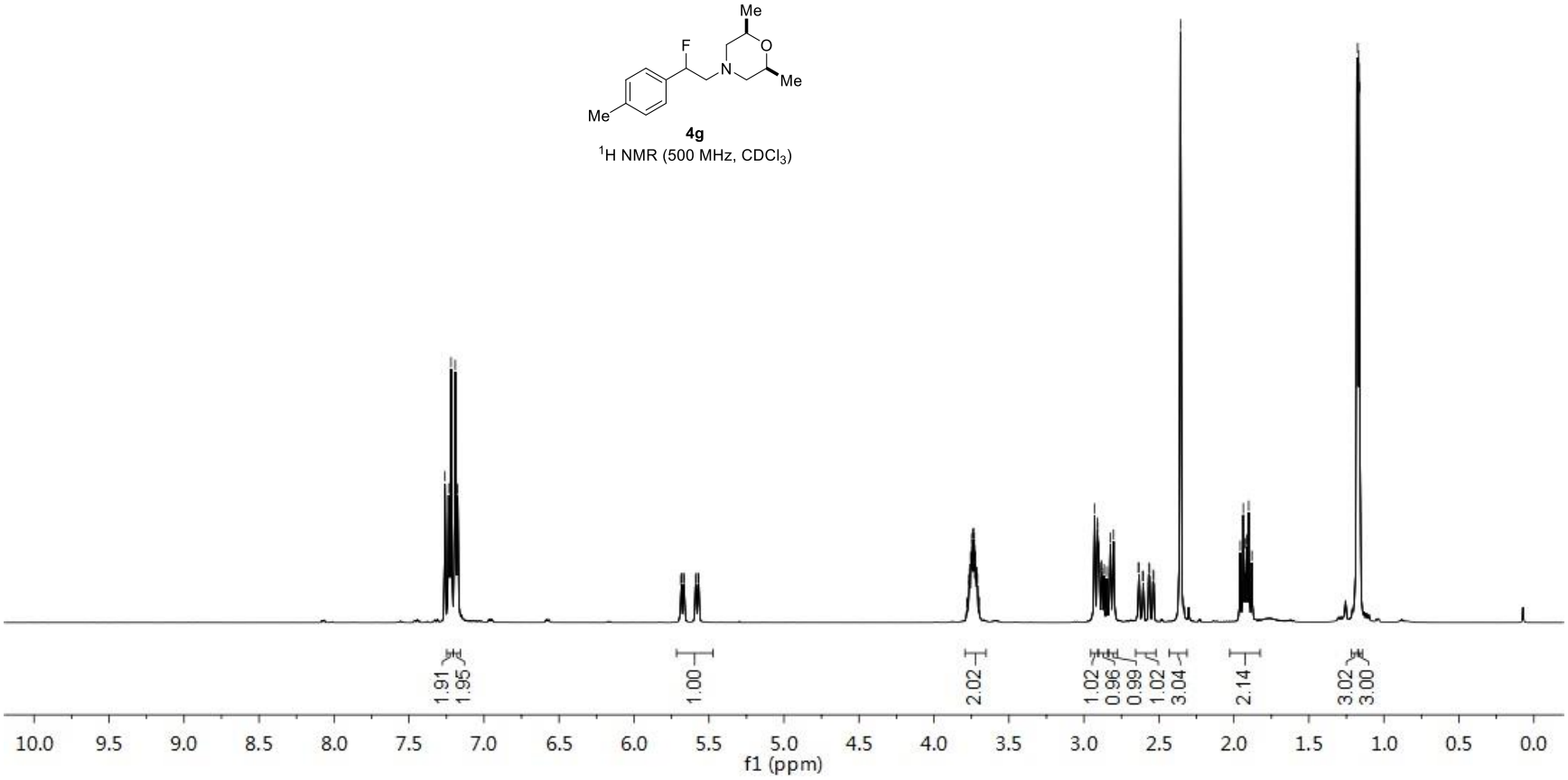
19FNMR gf-3-86bP in CDCl3

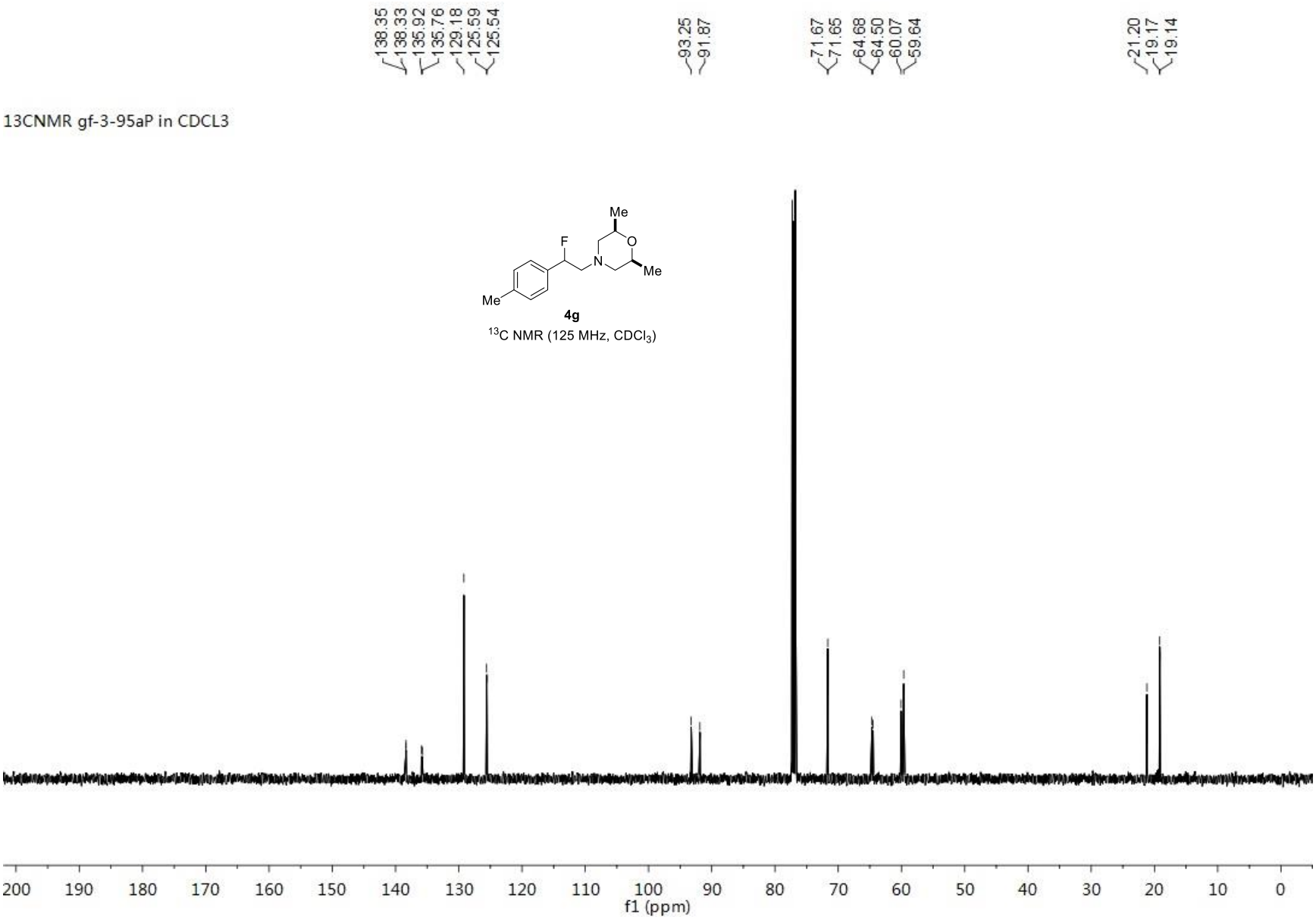


4f

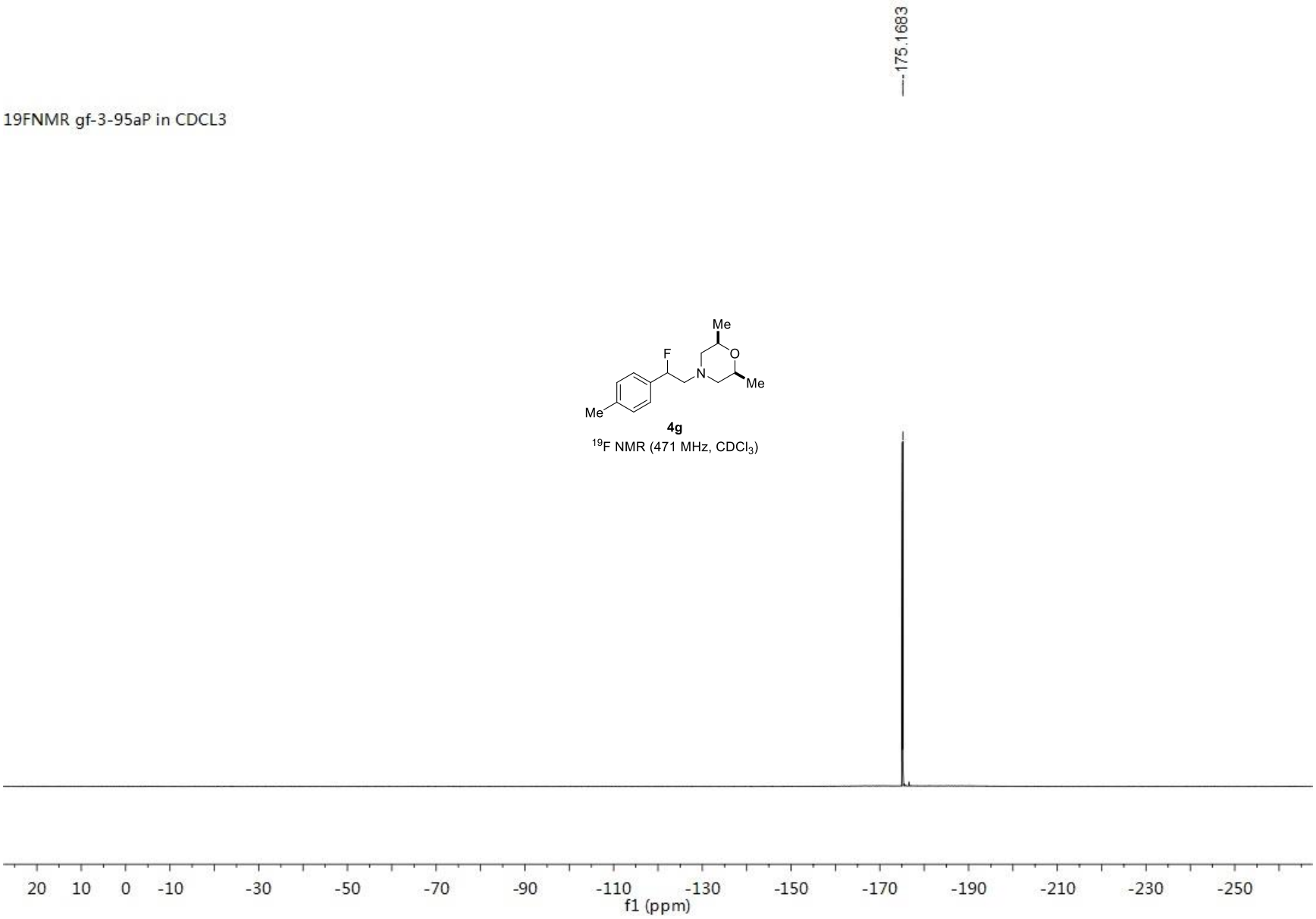
^{19}F NMR (471 MHz, $CDCl_3$)

1HNMR gf-3-95aP in CDCL3



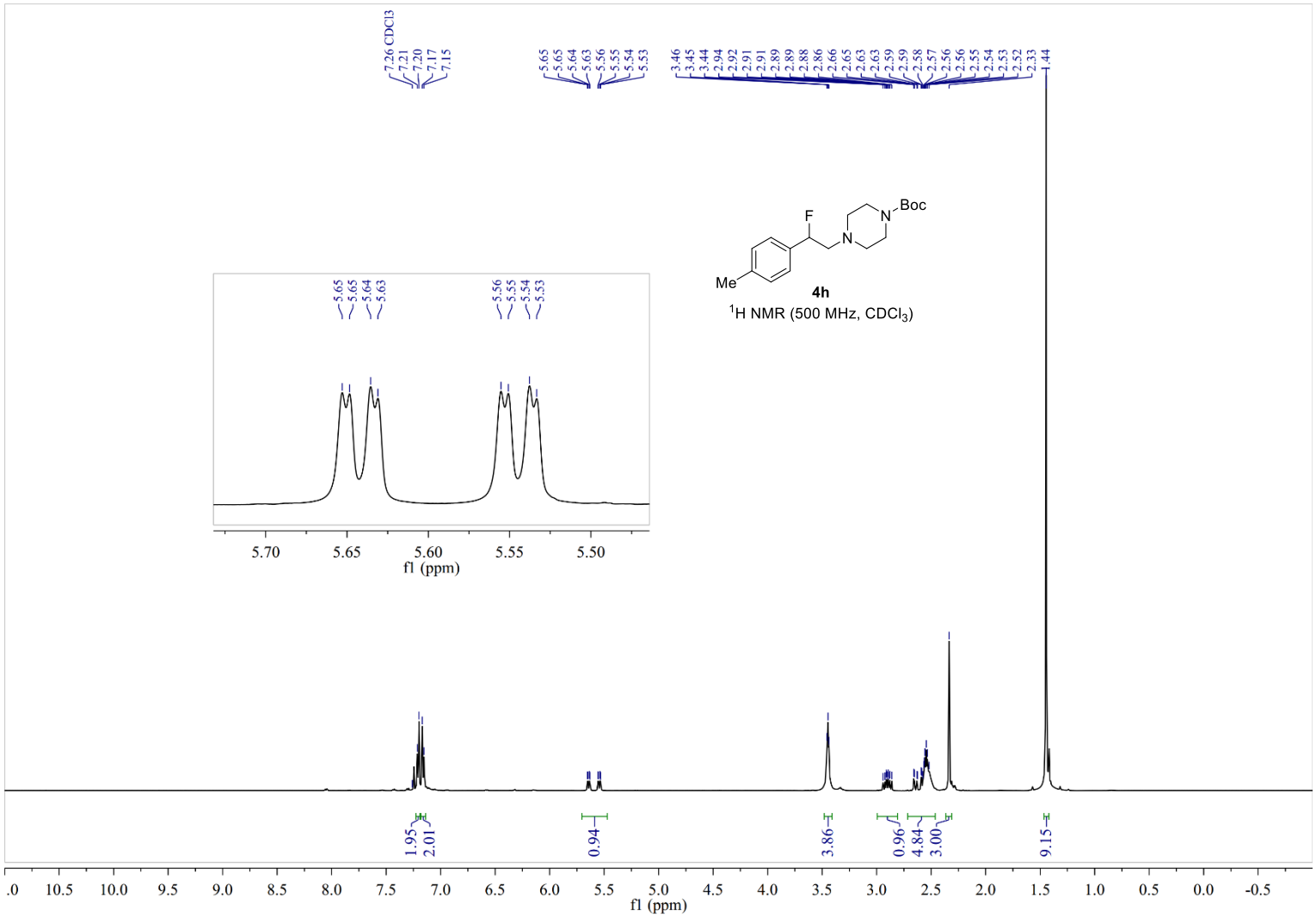

138.35
138.33
135.92
135.76
129.18
125.59
125.54
93.25
91.87
71.67
71.65
64.68
64.50
60.07
59.64
21.20
19.17
19.14
13CNMR gf-3-95aP in CDCL3
Me
F
O
N
Me
Me
4g
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

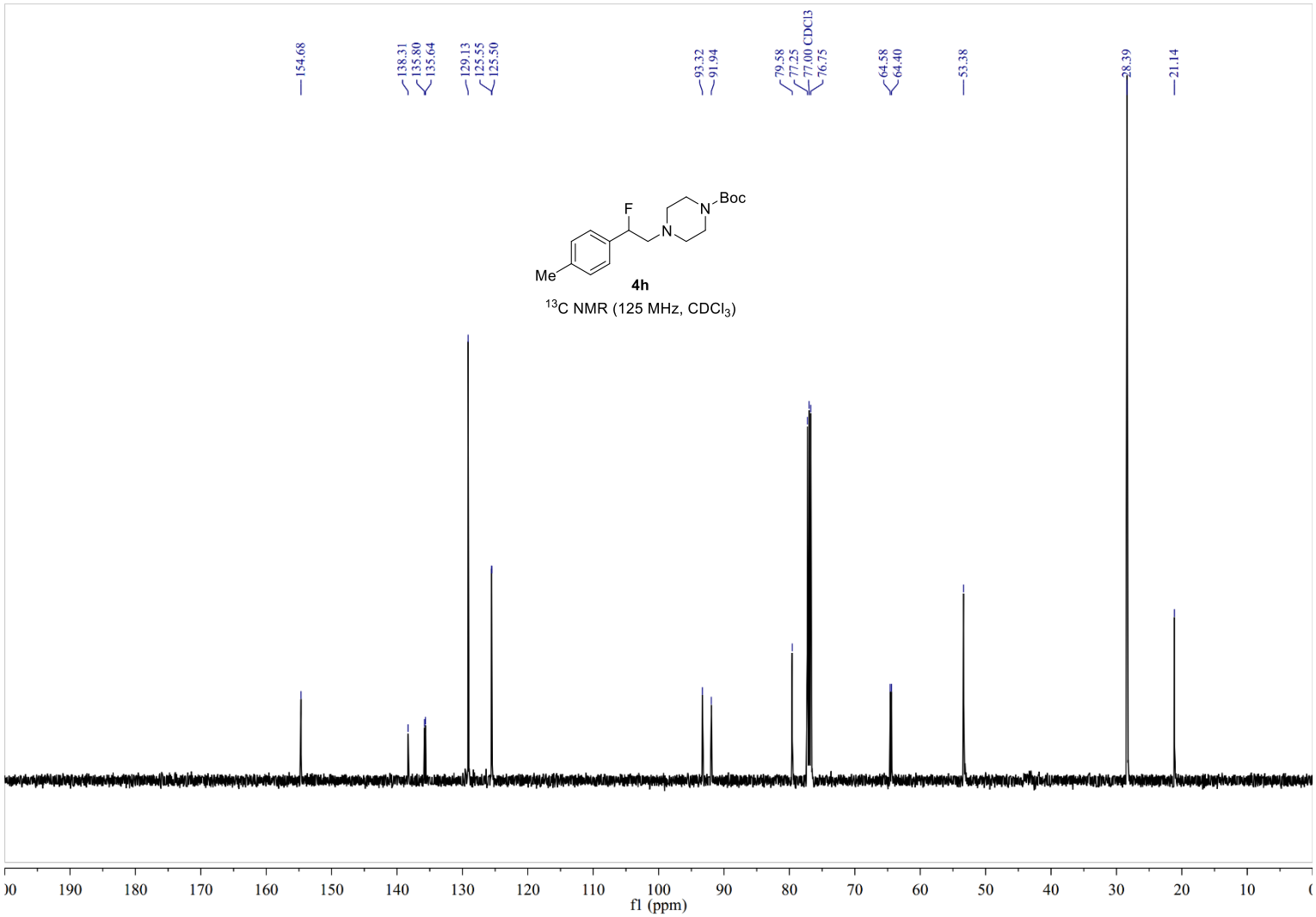
19FNMR gf-3-95aP in CDCL3



4g

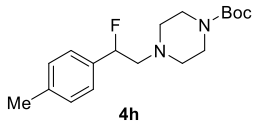
^{19}F NMR (471 MHz, $CDCl_3$)


7.26 CDCl3
7.21
7.20
7.17
7.15
5.65
5.65
5.64
5.63
5.56
5.55
5.54
5.53
3.46
3.45
3.44
2.94
2.92
2.91
2.91
2.89
2.89
2.88
2.86
2.66
2.65
2.63
2.63
2.59
2.59
2.58
2.57
2.56
2.56
2.55
2.54
2.53
2.52
2.33
1.44
F
N
N
Boc
Me
4h
1H NMR (500 MHz, CDCl3)
5.70
5.65
5.60
5.55
5.50
f1 (ppm)
1.95
2.01
0.94
3.86
0.96
4.84
3.00
9.15
f1 (ppm)


154.68
138.31
135.80
135.64
129.13
125.55
125.50
93.32
91.94
79.58
77.25
77.00 CDCl3
76.75
64.58
64.40
53.38
28.39
21.14
F
N
N
Boc
Me
4h
13C NMR (125 MHz, CDCl3)
f1 (ppm)

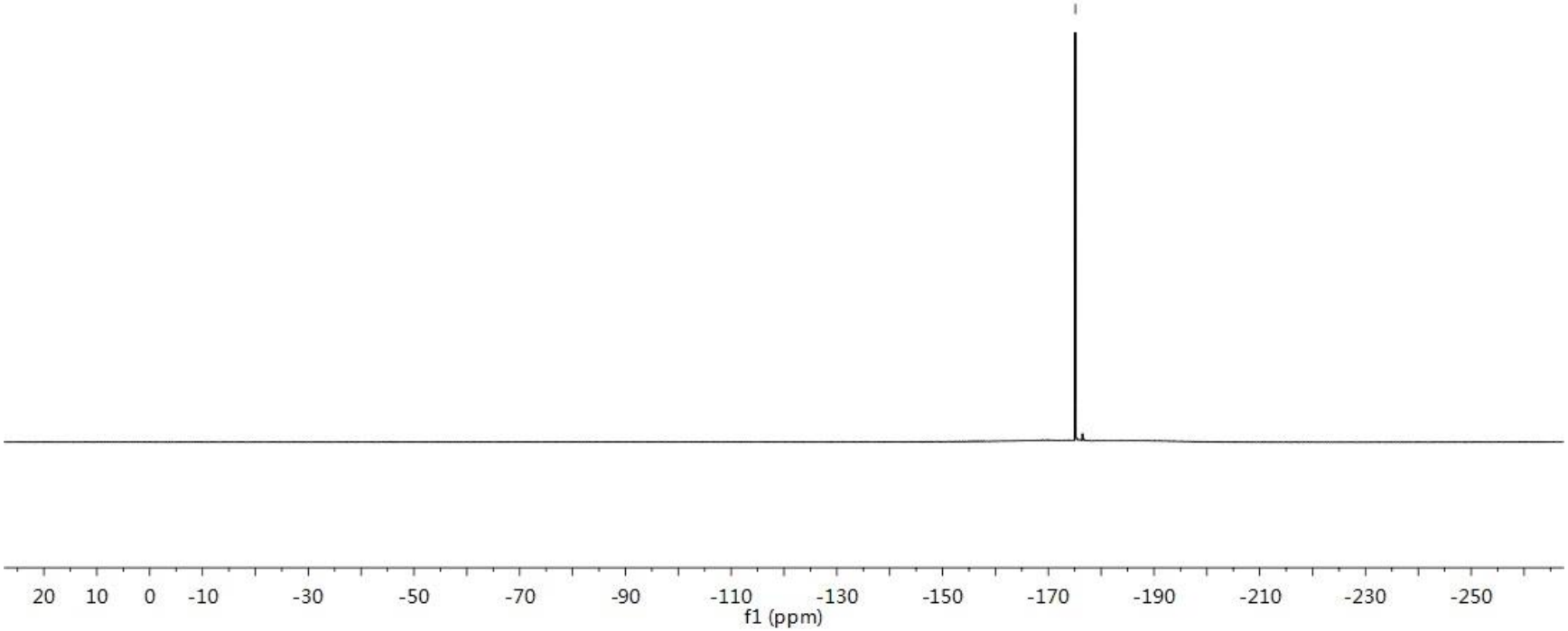
19FNMR gf-3-86dP in CDCL3

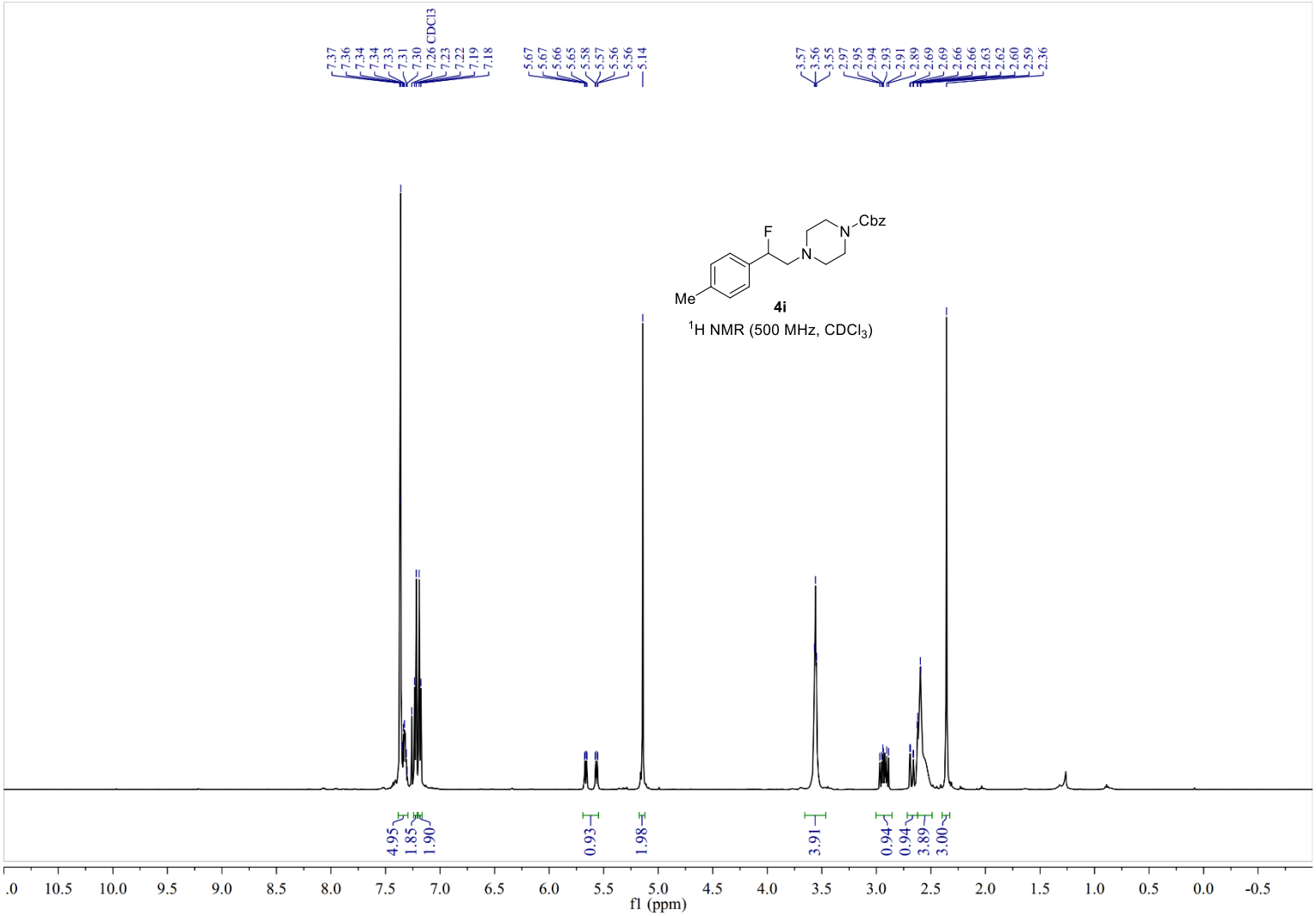
-175.1202

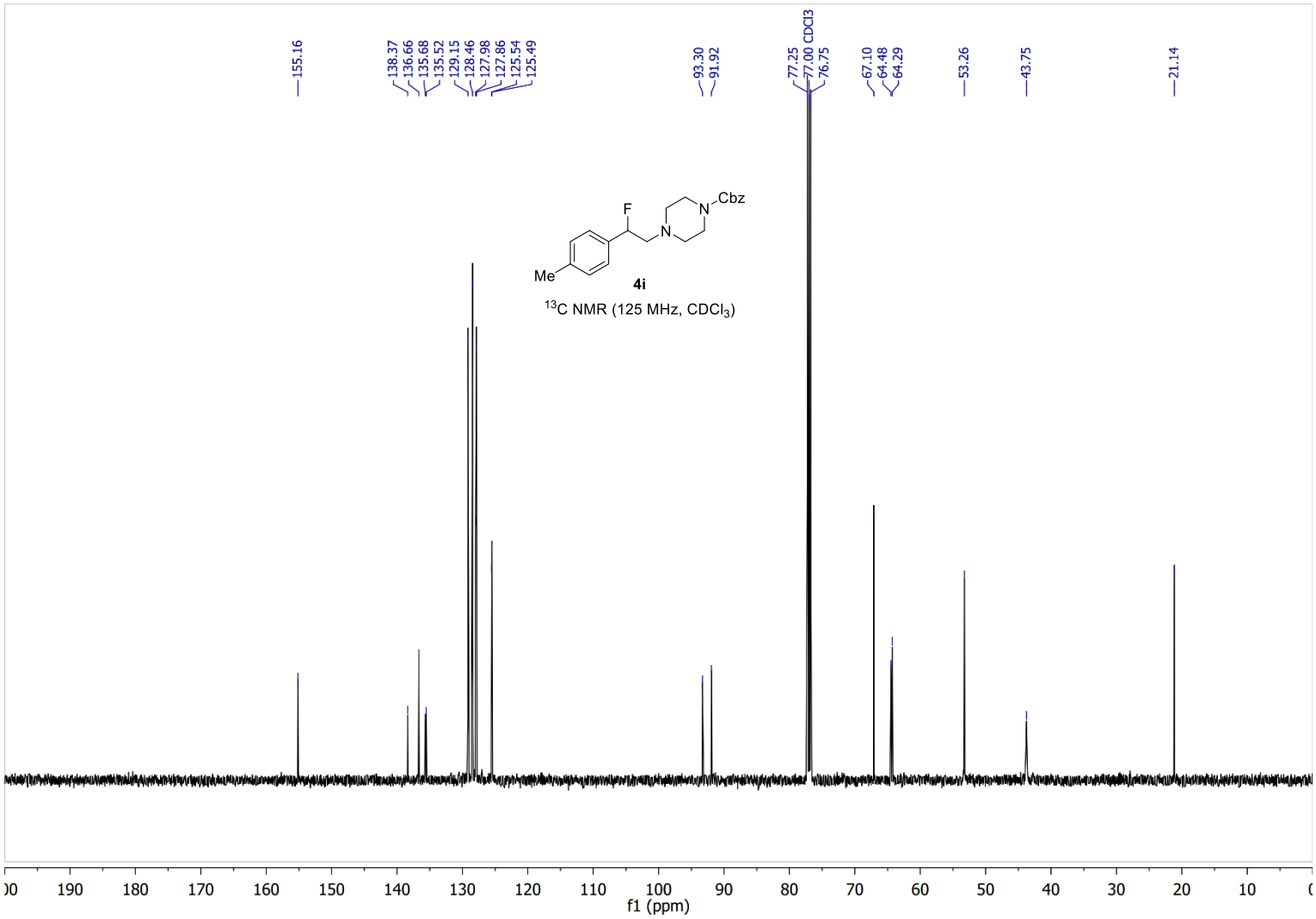


4h

^{19}F NMR (471 MHz, $CDCl_3$)

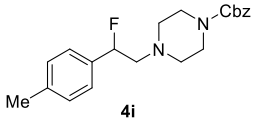



7.37
7.36
7.34
7.34
7.33
7.31
7.30
7.26 CDCl3
7.23
7.22
7.19
7.18
5.67
5.67
5.66
5.65
5.58
5.57
5.56
5.56
5.14
3.57
3.56
3.55
2.97
2.95
2.94
2.93
2.91
2.89
2.69
2.69
2.66
2.66
2.63
2.62
2.60
2.59
2.36
F
N
N
Cbz
Me
4i
1H NMR (500 MHz, CDCl3)
4.95
1.85
1.90
0.93
1.98
3.91
0.94
0.94
3.89
3.00
f1 (ppm)


155.16
138.37
136.66
135.68
135.52
129.15
128.46
127.98
127.86
125.54
125.49
93.30
91.92
77.25
77.00 CDCl3
76.75
67.10
64.48
64.29
53.26
43.75
21.14
F
N
N
Cbz
Me
4i
13C NMR (125 MHz, CDCl3)
f1 (ppm)

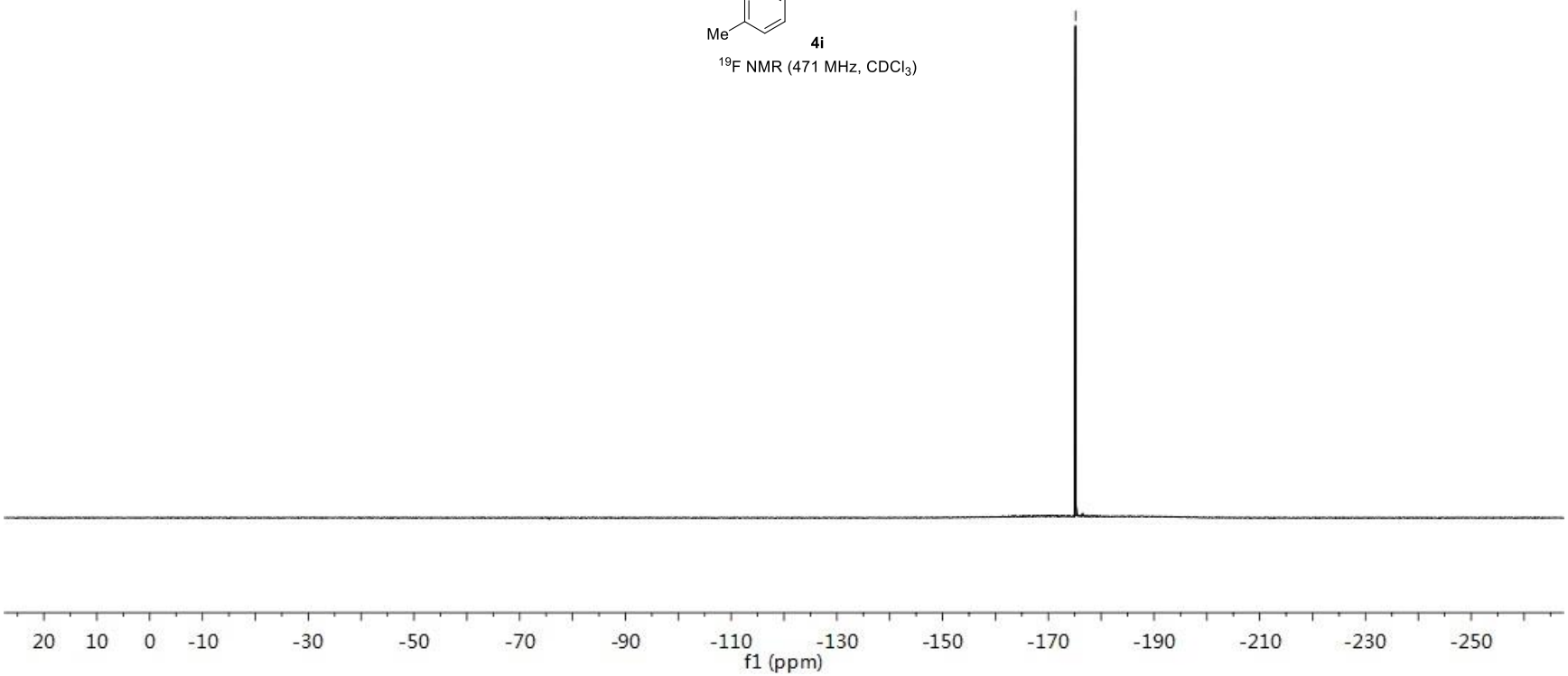
19FNRM gf-3-84bPP in CDCL3

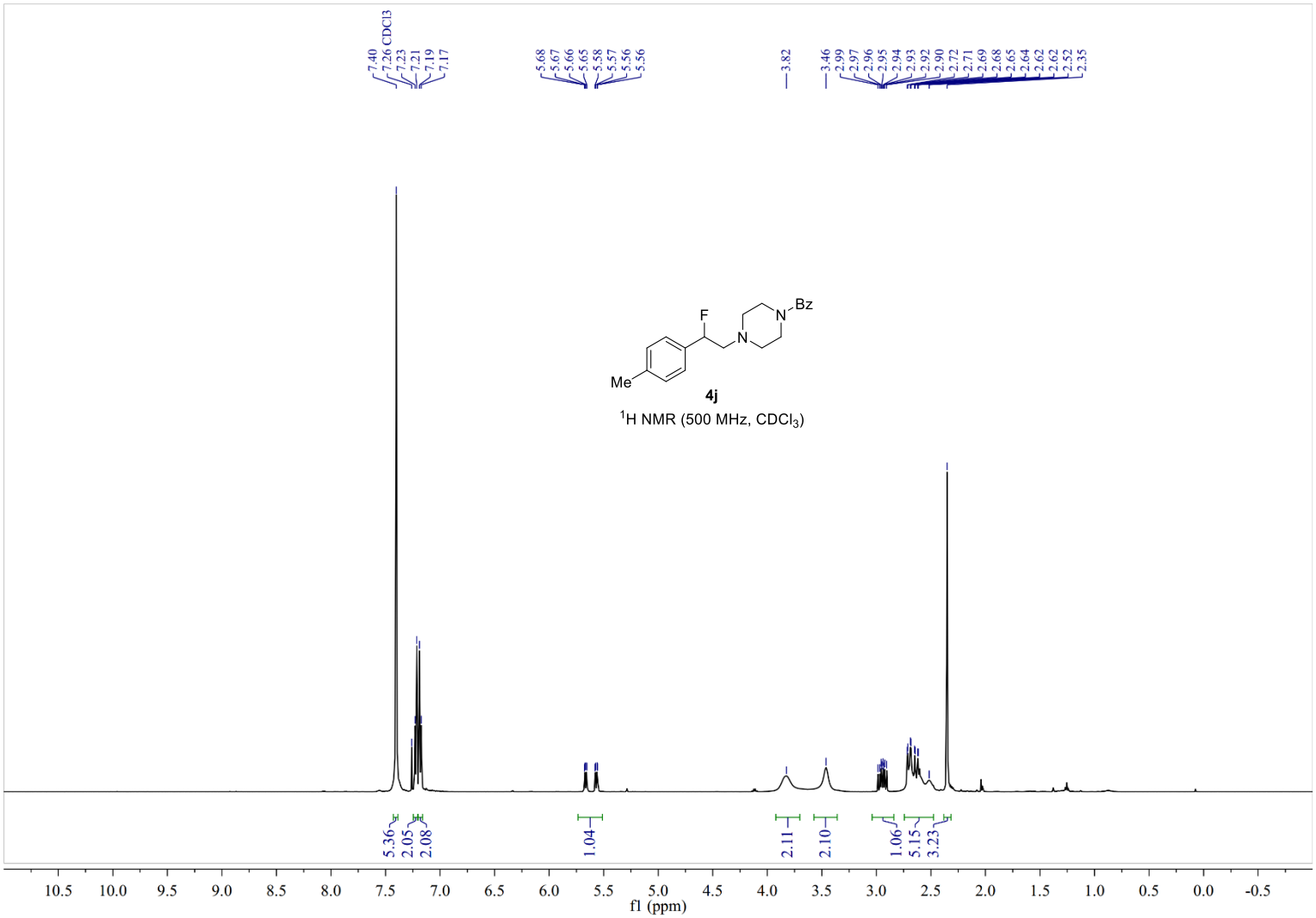
-175.1542

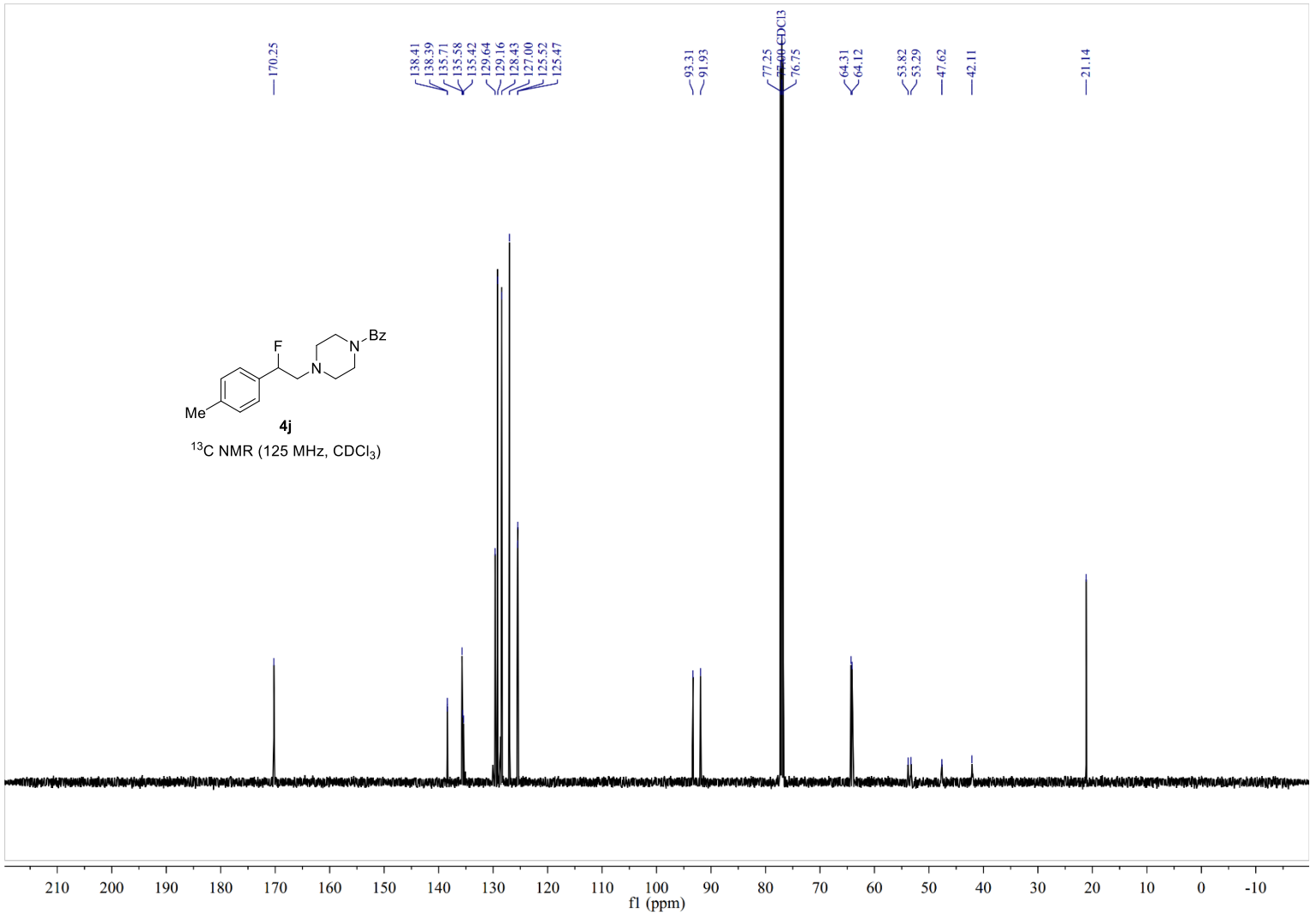


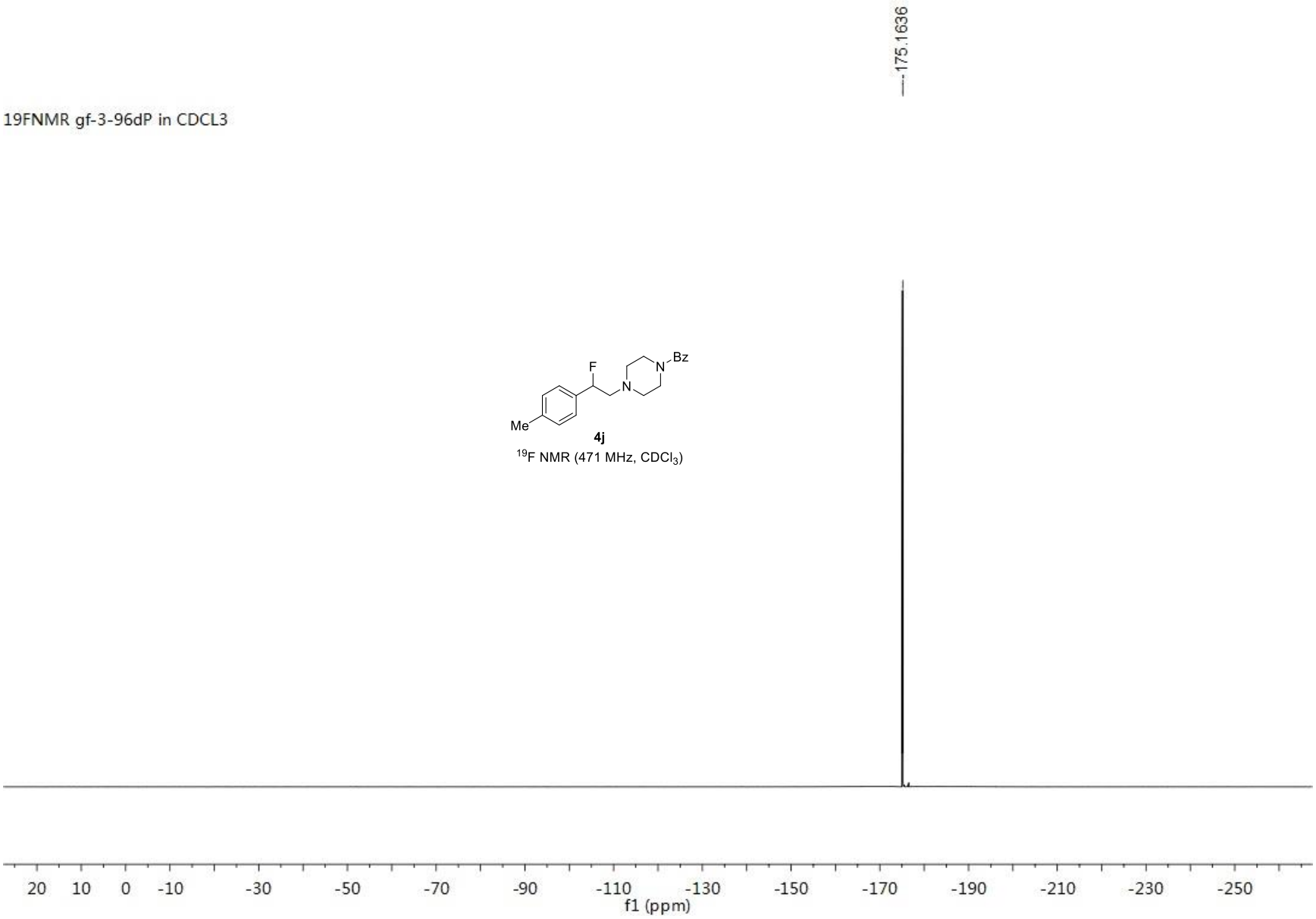
4i

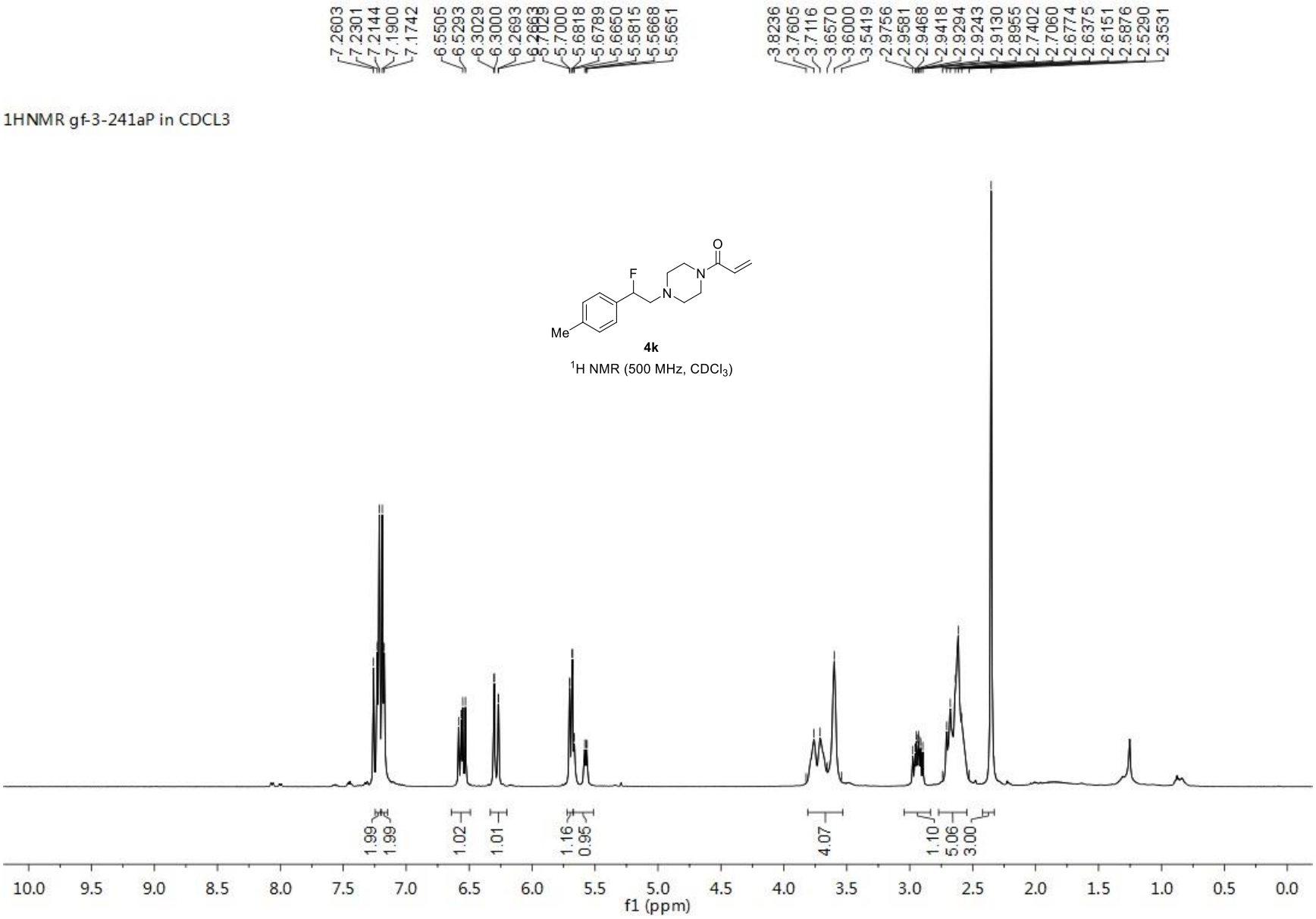
^{19}F NMR (471 MHz, $CDCl_3$)

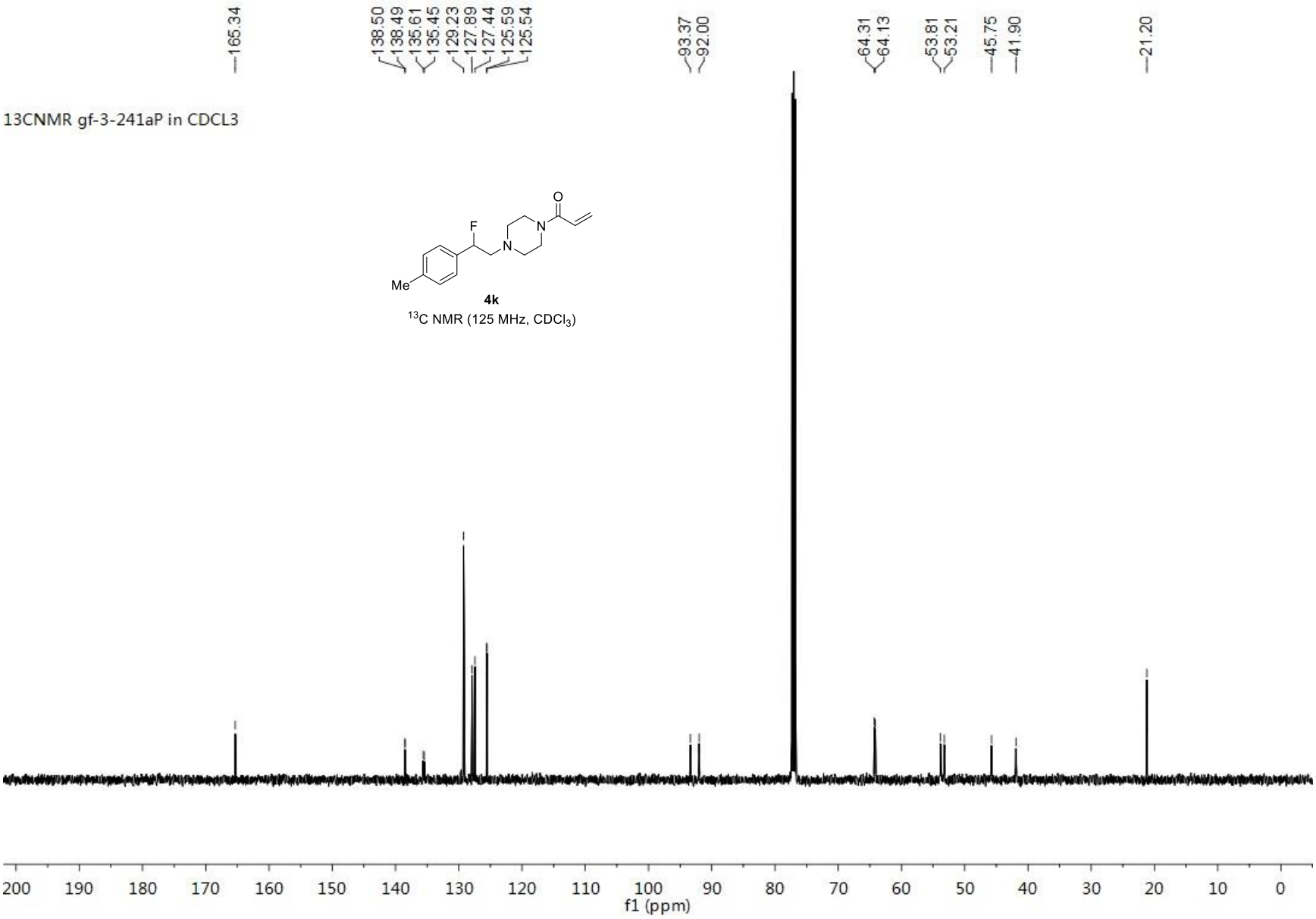



7.40
7.26 CDCl3
7.23
7.21
7.19
7.17
5.68
5.67
5.66
5.65
5.58
5.57
5.56
5.56
3.82
3.46
2.99
2.97
2.96
2.95
2.94
2.93
2.92
2.90
2.72
2.71
2.69
2.68
2.65
2.64
2.62
2.62
2.52
2.35
F
N
N
Bz
Me
4j
1H NMR (500 MHz, CDCl3)
5.36
2.05
2.08
1.04
2.11
2.10
1.06
5.15
3.23
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

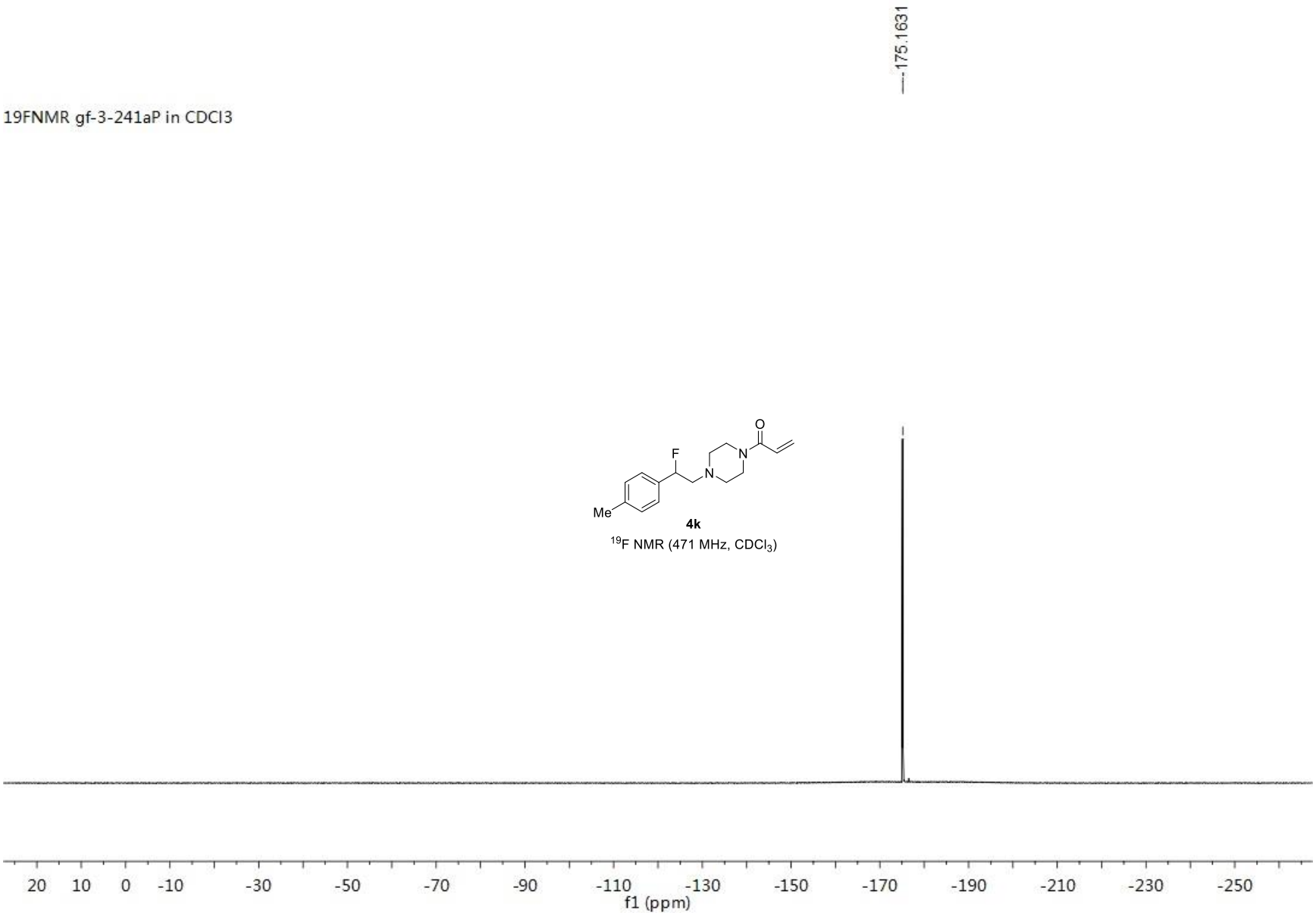

170.25
138.41
138.39
135.71
135.58
135.42
129.64
129.16
128.43
127.00
125.52
125.47
93.31
91.93
77.25
76.75
64.31
64.12
53.82
53.29
47.62
42.11
21.14
F
N
N
Bz
Me
4j
13C NMR (125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-175.1636
19FNMR gf-3-96dP in CDCL3
F
N
N
Bz
Me
4j
^{19}F NMR (471 MHz, $CDCl_3$)
20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250
f1 (ppm)


7.2603
7.2301
7.2144
7.1900
7.1742
6.5505
6.5293
6.3029
6.3000
6.2693
6.2663
5.7000
5.6818
5.6789
5.6650
5.5815
5.5668
5.5651
3.8236
3.7605
3.7116
3.6570
3.6000
3.5419
2.9756
2.9581
2.9468
2.9418
2.9294
2.9243
2.9130
2.8955
2.7402
2.7060
2.6774
2.6375
2.6151
2.5876
2.5290
2.3531
1HNMR gf-3-241aP in CDCL3
F
N
N
O
Me
4k
1H NMR (500 MHz, CDCl3)
1.99
1.99
1.02
1.01
1.16
0.95
4.07
1.10
5.06
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

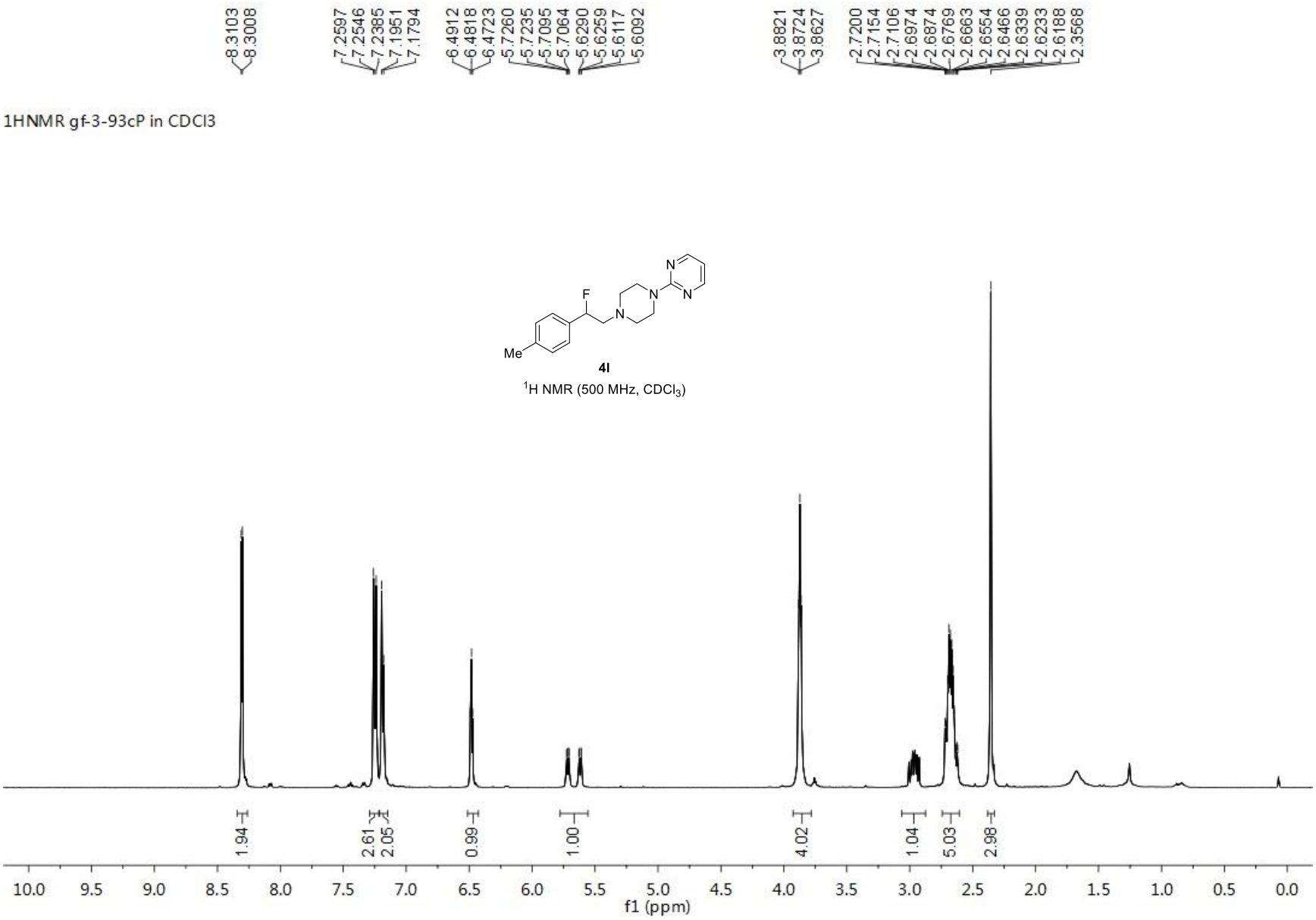

165.34
138.50
138.49
135.61
135.45
129.23
127.89
127.44
125.59
125.54
93.37
92.00
64.31
64.13
53.81
53.21
45.75
41.90
21.20
13CNMR gf-3-241aP in CDCL3
F
N
N
O
Me
4k
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

19FNMR gf-3-241aP in CDCl3



4k

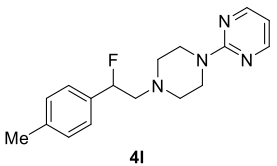
^{19}F NMR (471 MHz, $CDCl_3$)


8.3103
8.3008
7.2597
7.2546
7.2385
7.1951
7.1794
6.4912
6.4818
6.4723
5.7260
5.7235
5.7095
5.7064
5.6290
5.6259
5.6117
5.6092
3.8821
3.8724
3.8627
2.7200
2.7154
2.7106
2.6974
2.6874
2.6769
2.6663
2.6554
2.6466
2.6339
2.6233
2.6188
2.3568
1HNMR gf-3-93cP in CDCl3
F
N
N
N
N
Me
4l
1H NMR (500 MHz, CDCl3)
1.94
2.61
2.05
0.99
1.00
4.02
1.04
5.03
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

v

161.69
157.73
138.37
138.36
135.90
135.75
129.20
125.63
125.58
109.89
93.38
92.00
64.75
64.57
53.54
43.68
21.20

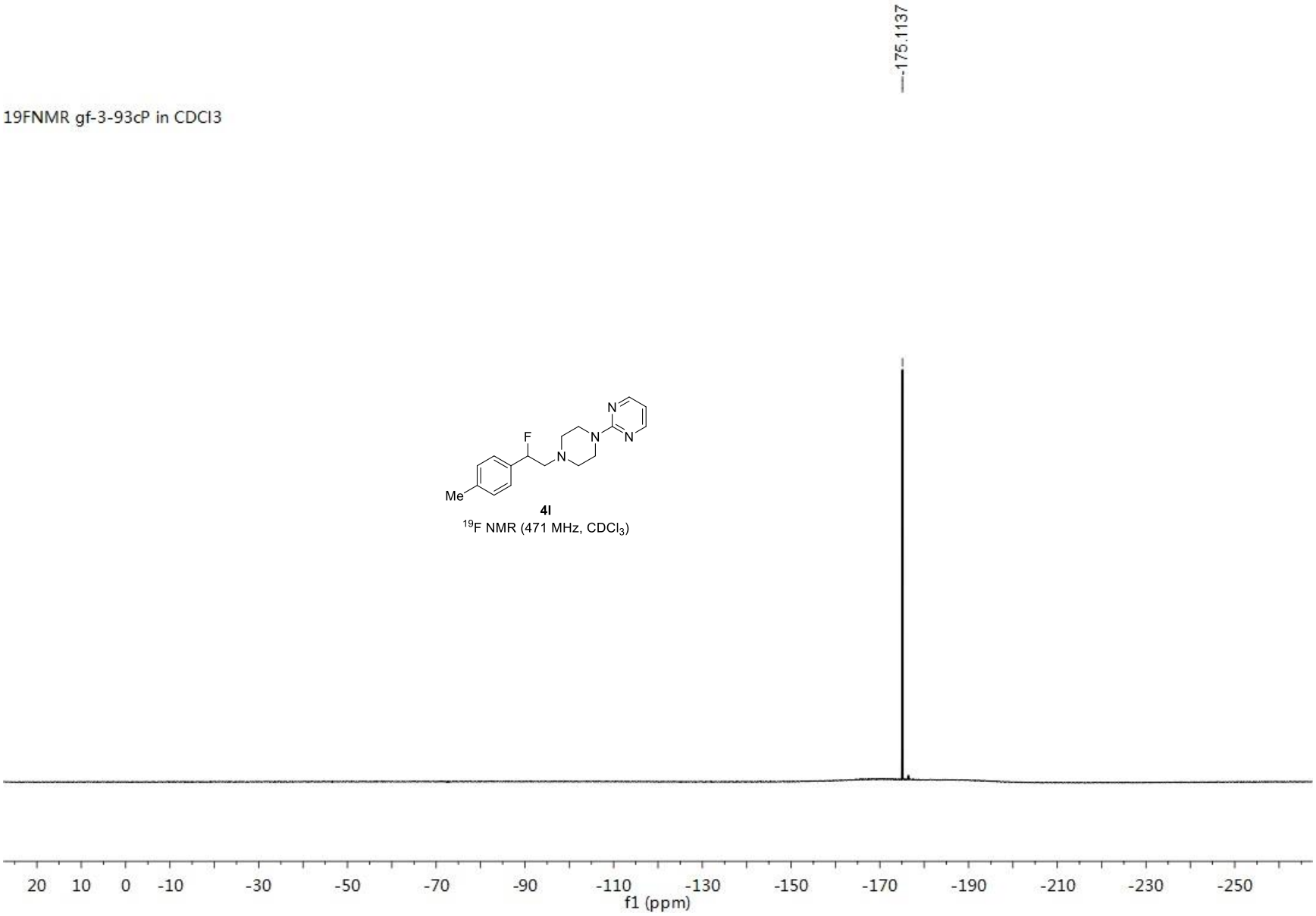
13CNMR gf-3-93cP in CDCl3



4l

^{13}C NMR (125 MHz, $CDCl_3$)

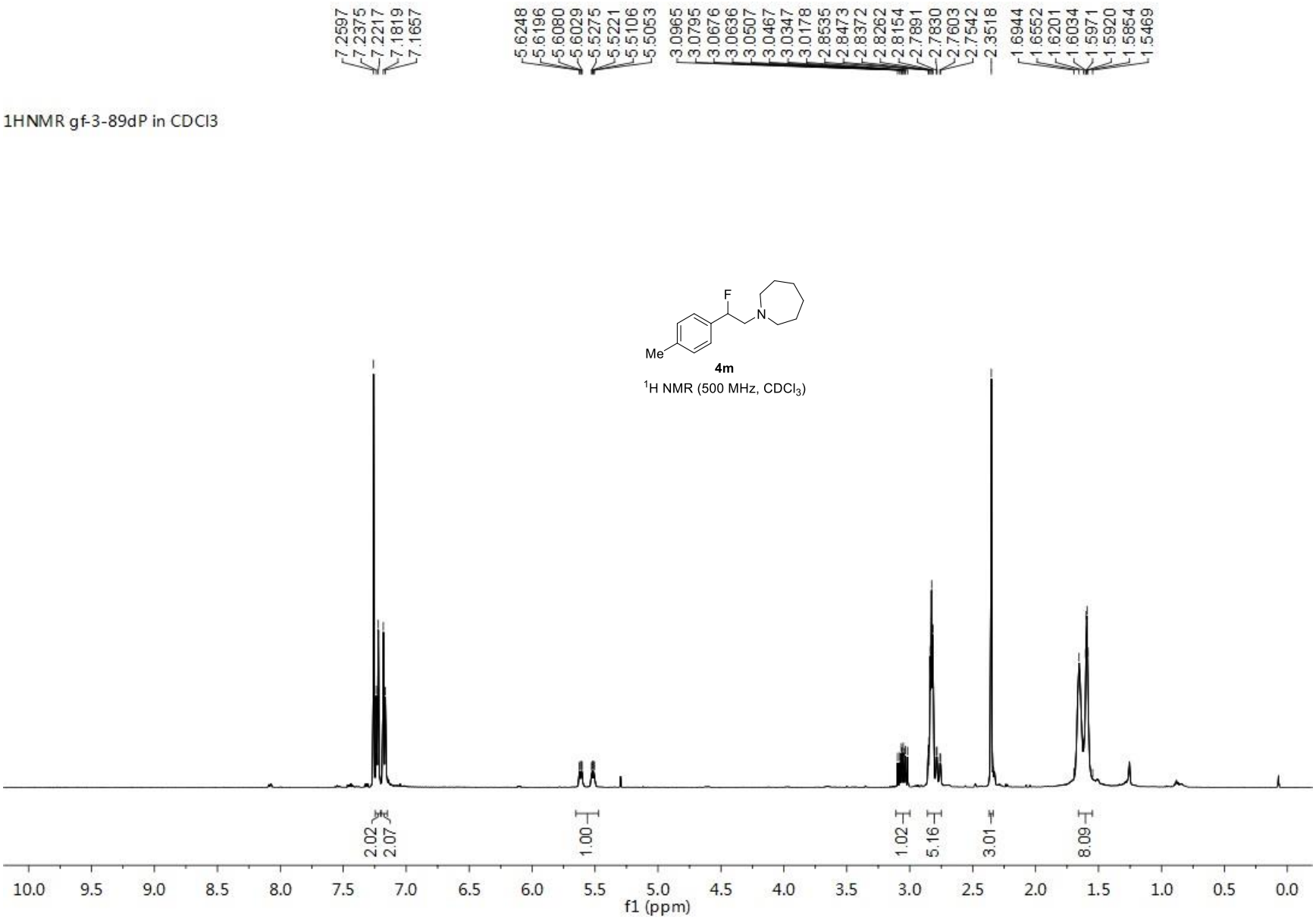
19FNMR gf-3-93cP in CDCl3

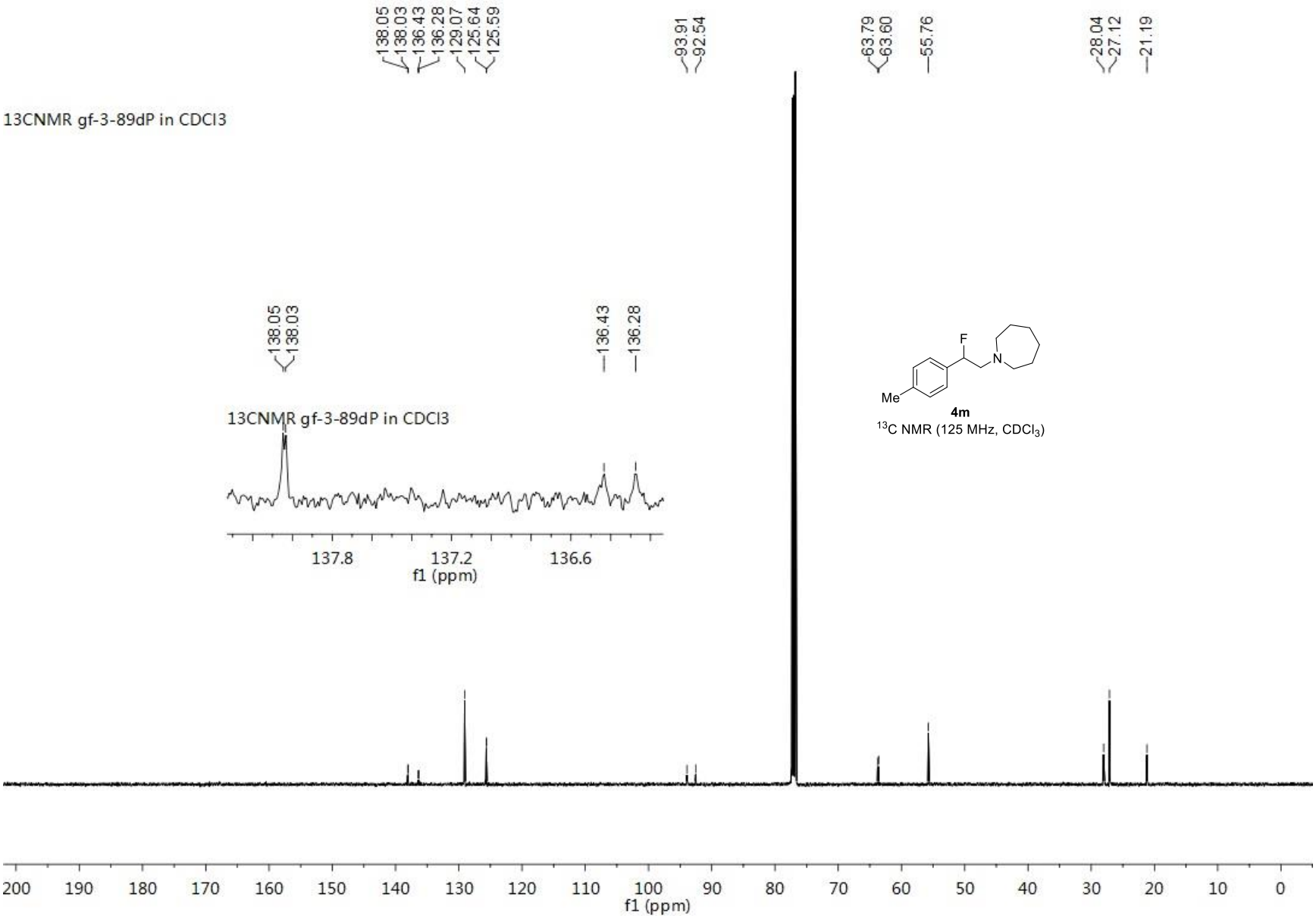


4l

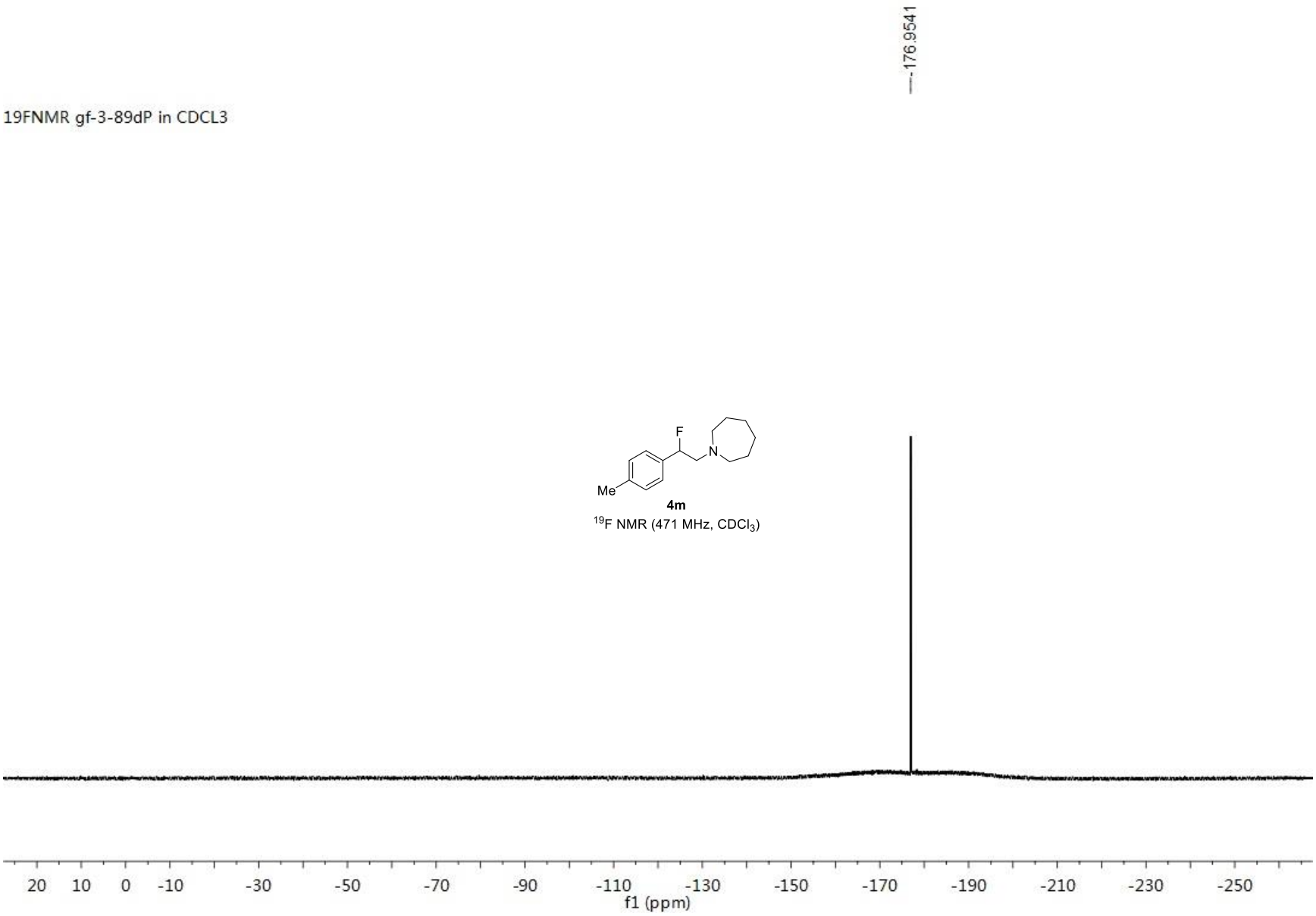
^{19}F NMR (471 MHz, $CDCl_3$)

1HNMR gf-3-89dP in CDCl3



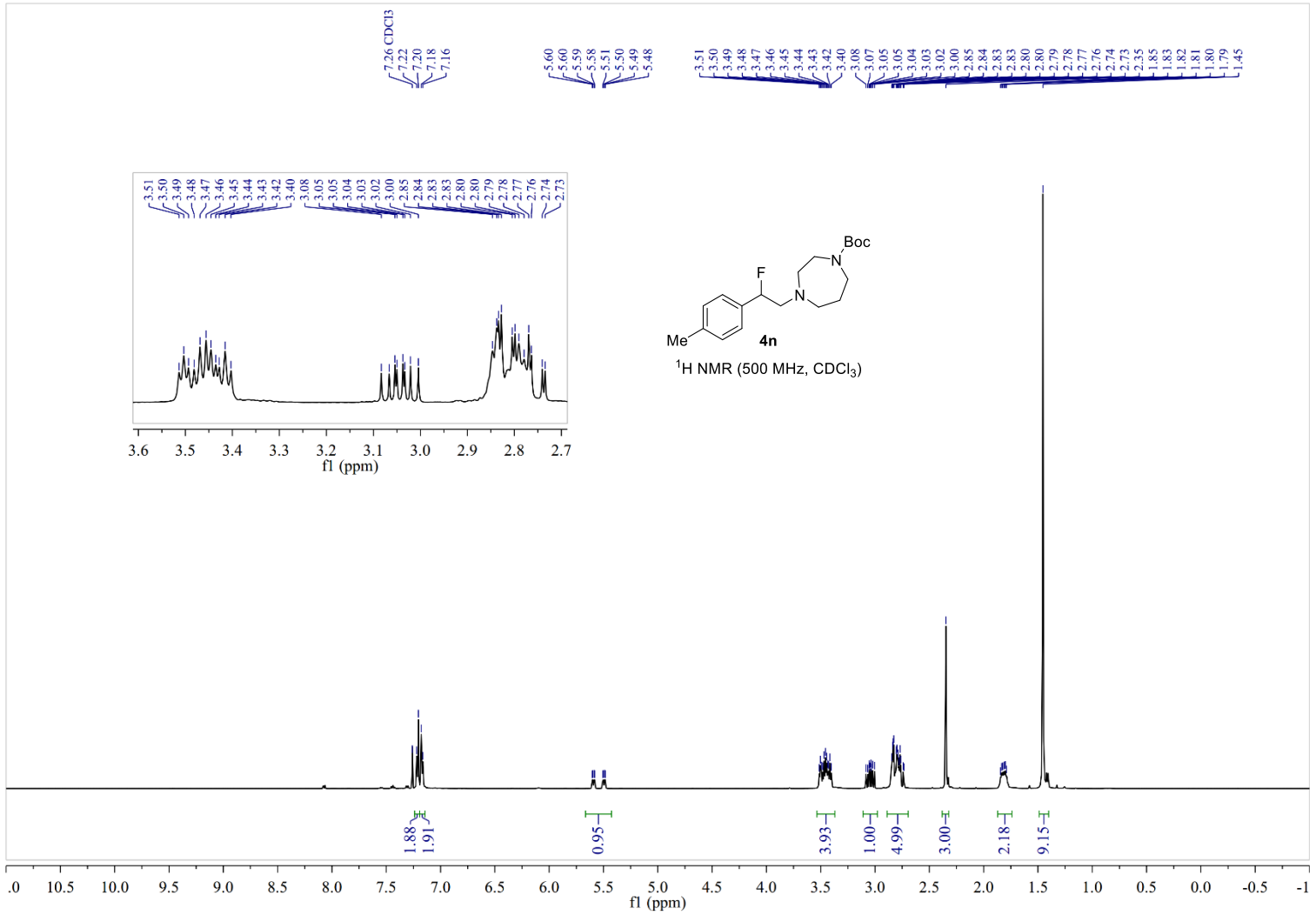

13CNMR gf-3-89dP in CDCl3
138.05
138.03
136.43
136.28
129.07
125.64
125.59
93.91
92.54
63.79
63.60
55.76
28.04
27.12
21.19
13CNMR gf-3-89dP in CDCl3
137.8
137.2
136.6
f1 (ppm)
F
N
Me
4m
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

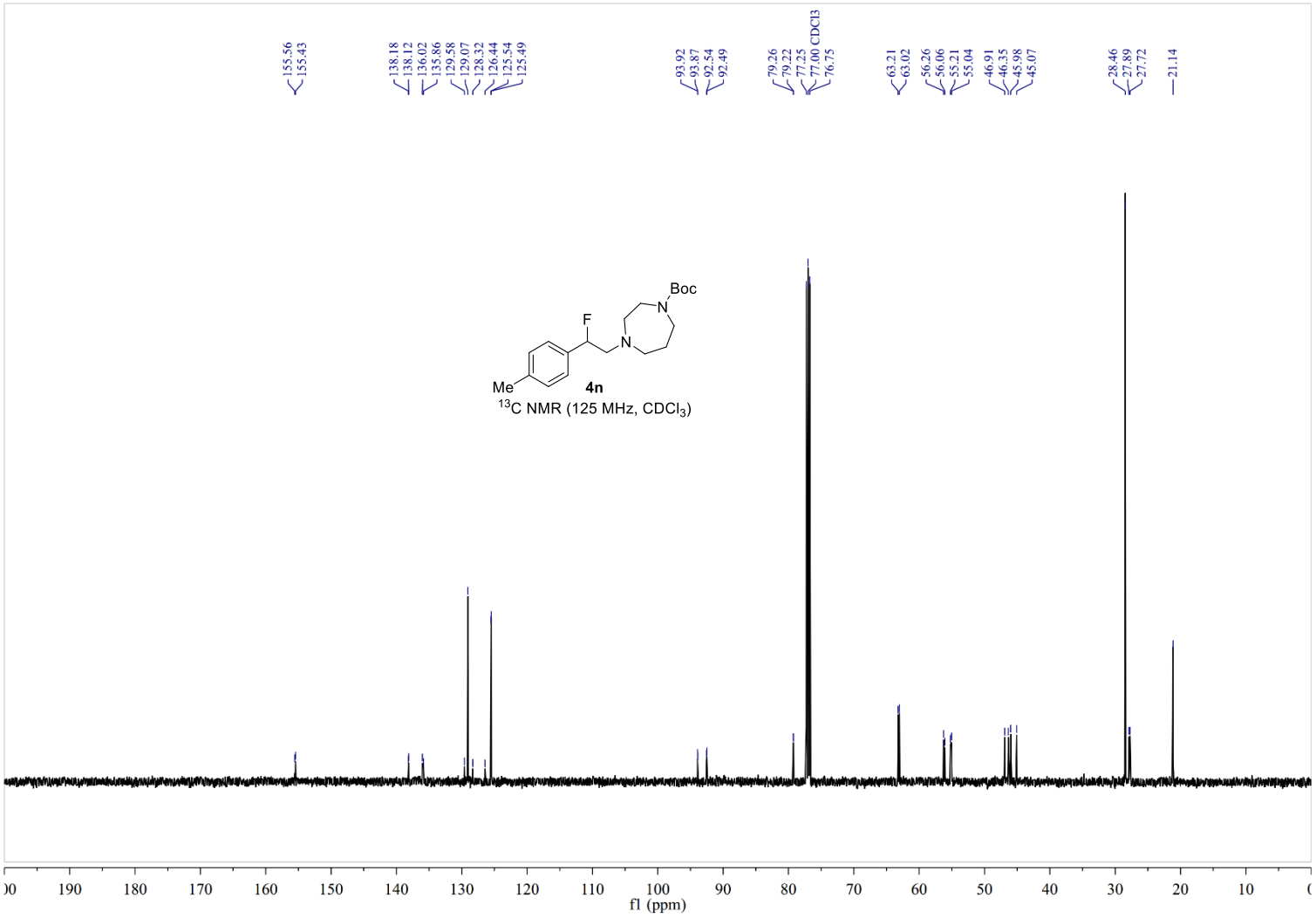
19FNMR gf-3-89dP in CDCL3



4m

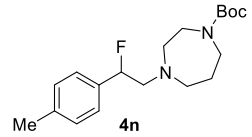
^{19}F NMR (471 MHz, $CDCl_3$)


Boc
F
N
N
Me
4n
^{1}H NMR (500 MHz, $CDCl_3$)
fl (ppm)


155.56
155.43
138.18
138.12
136.02
135.86
129.58
129.07
128.32
126.44
125.54
125.49
93.92
93.87
92.54
92.49
79.26
79.22
77.25
77.00 CDCl3
76.75
63.21
63.02
56.26
56.06
55.21
55.04
46.91
46.35
45.98
45.07
28.46
27.89
27.72
21.14
Boc
N
F
N
Me
4n
13C NMR (125 MHz, CDCl3)
f1 (ppm)

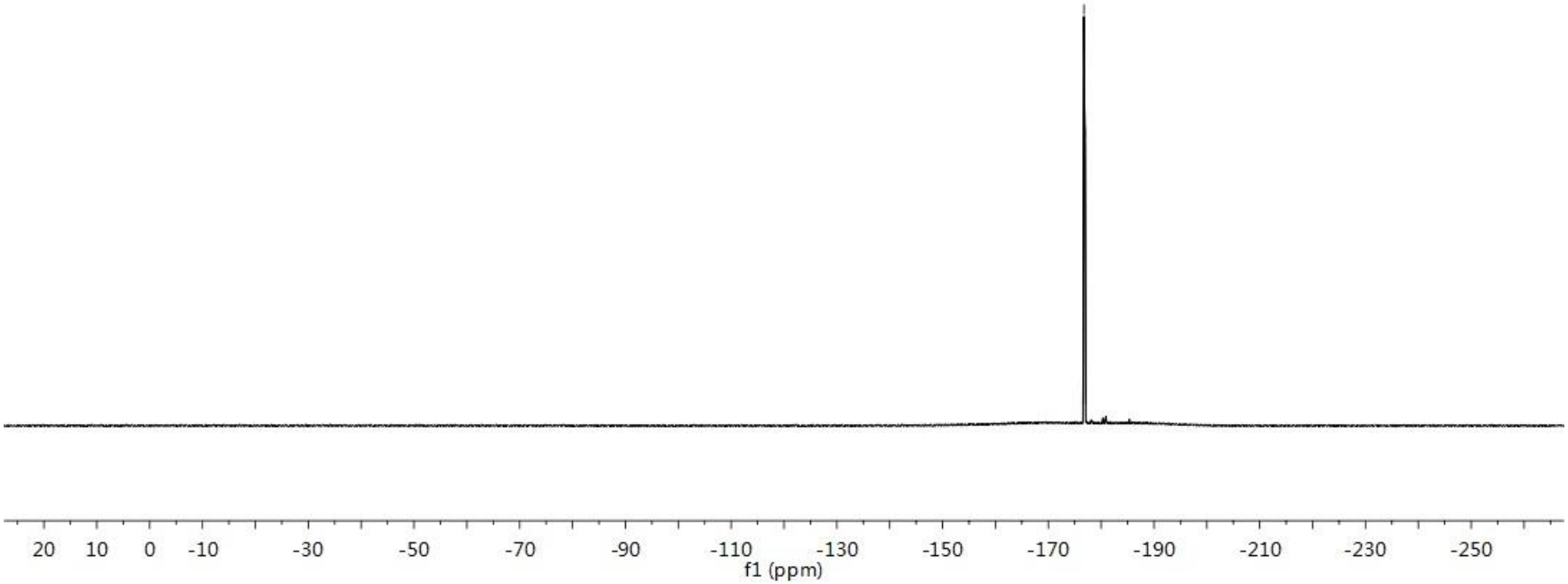
-176.7485
-176.9494

19FNMR gf-ck-Ⅱ-96dP in CDCl3



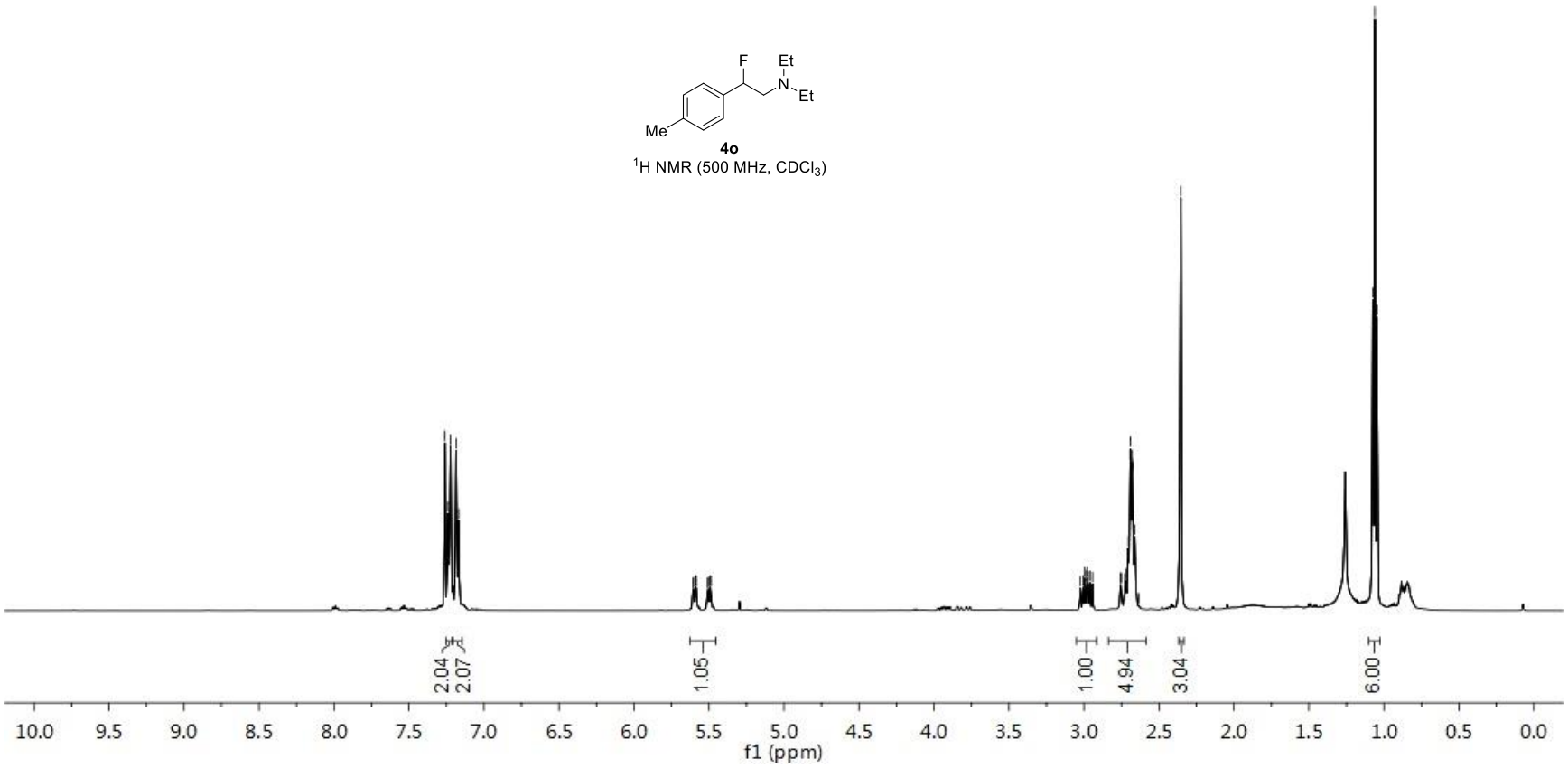
4n

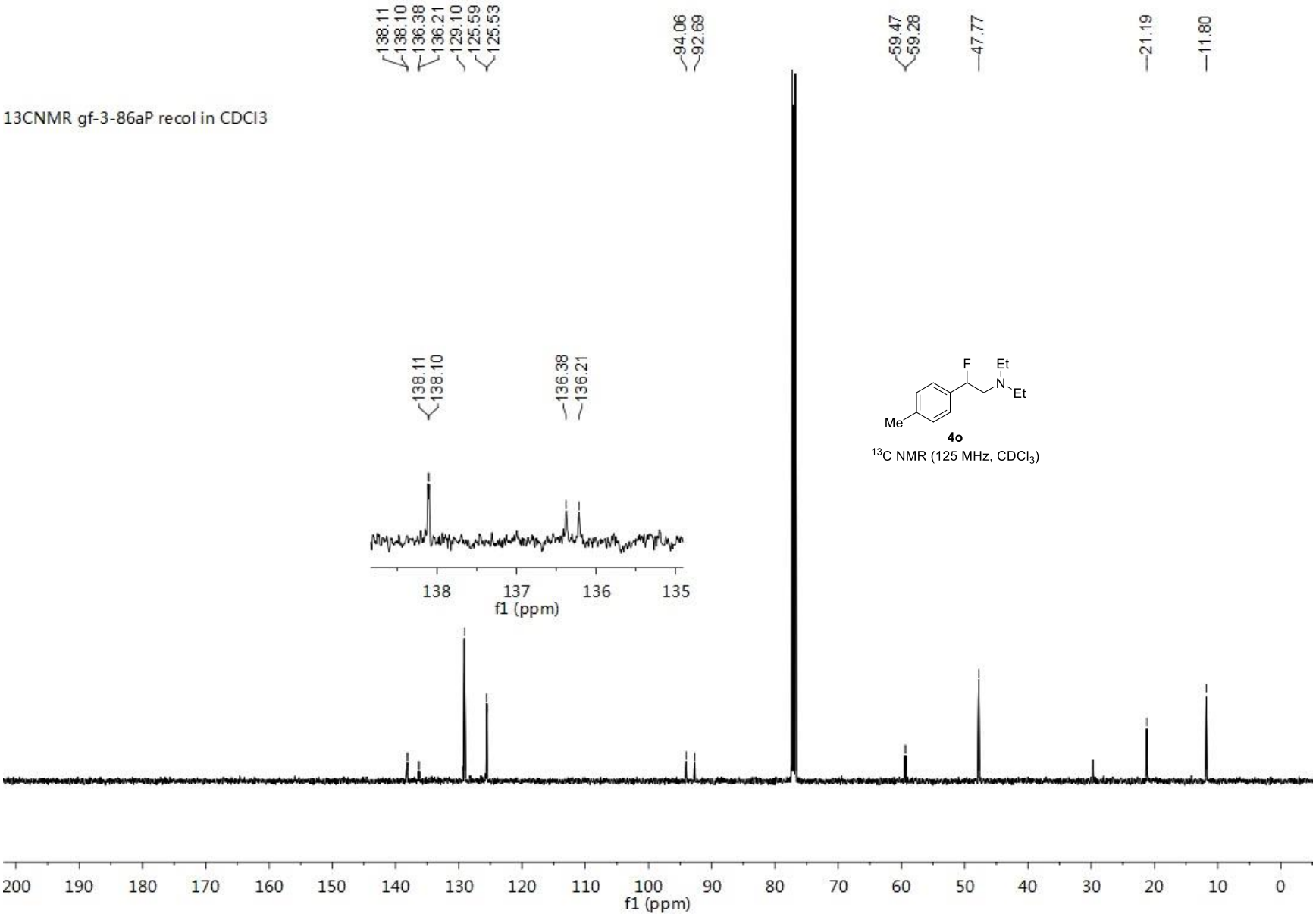
^{19}F NMR (471 MHz, $CDCl_3$)

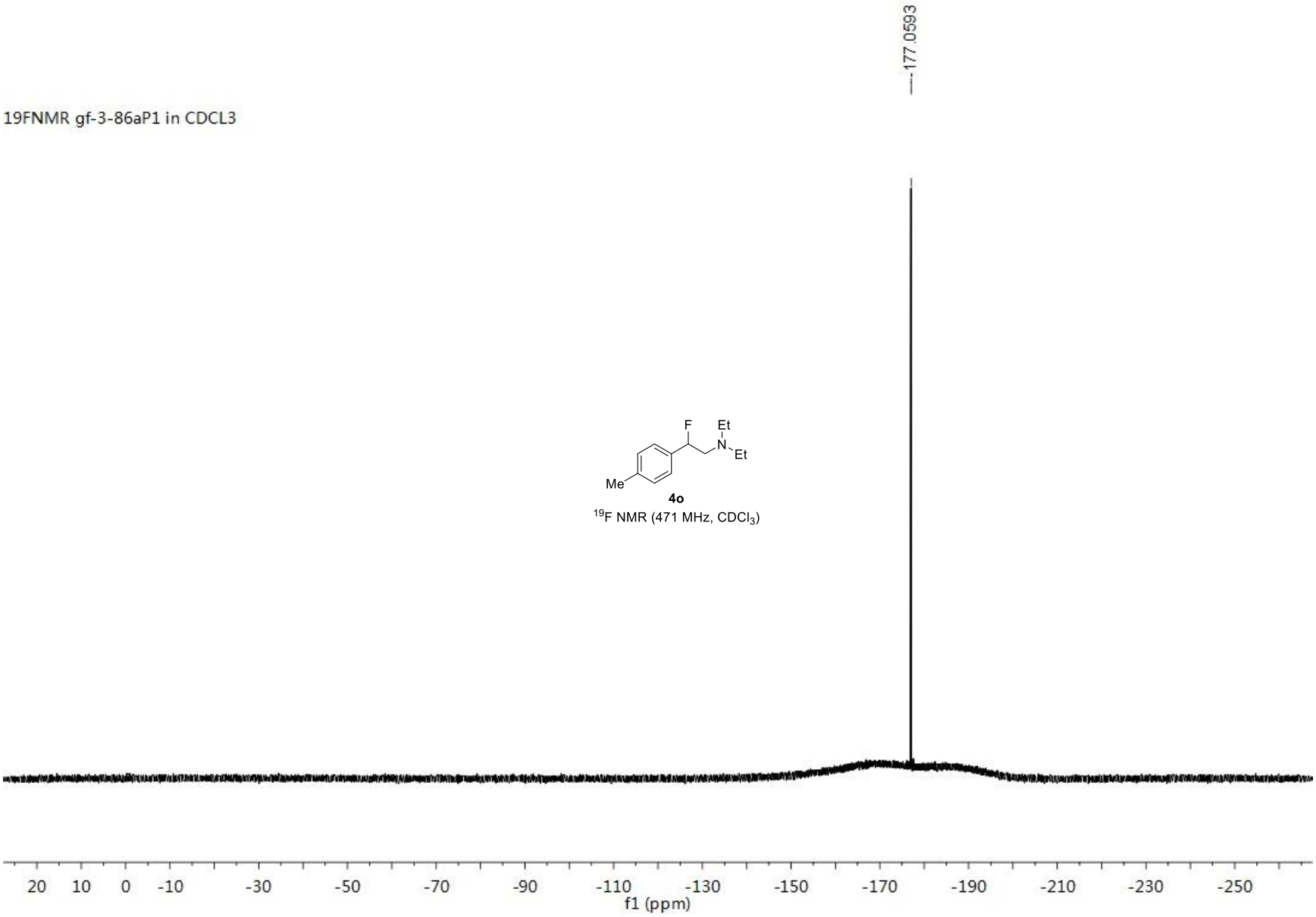


7.2602
7.2393
7.2236
7.1862
7.1704
5.6065
5.6014
5.5890
5.5842
5.5091
5.5041
5.4917
5.4869
3.0232
3.0059
2.9938
2.9897
2.9765
2.9724
2.9602
2.9429
2.7558
2.7503
2.7264
2.7204
2.7031
2.6922
2.6890
2.6783
2.6750
2.6606
2.6344
2.3540
1.0745
1.0602
1.0460

1HNMR gf-3-86aP recol in CDCL3

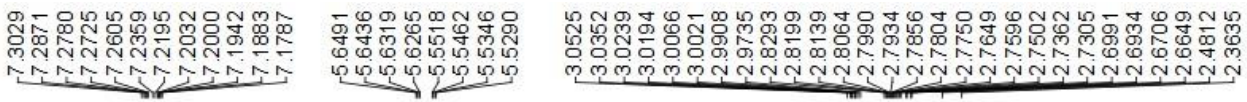



13CNMR gf-3-86aP recol in CDCl3
138.11
138.10
136.38
136.21
129.10
125.59
125.53
94.06
92.69
59.47
59.28
47.77
21.19
11.80
f1 (ppm)
F
Et
N
Et
Me
4o
13C NMR (125 MHz, CDCl3)

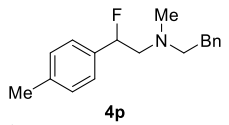


4o

^{19}F NMR (471 MHz, $CDCl_3$)

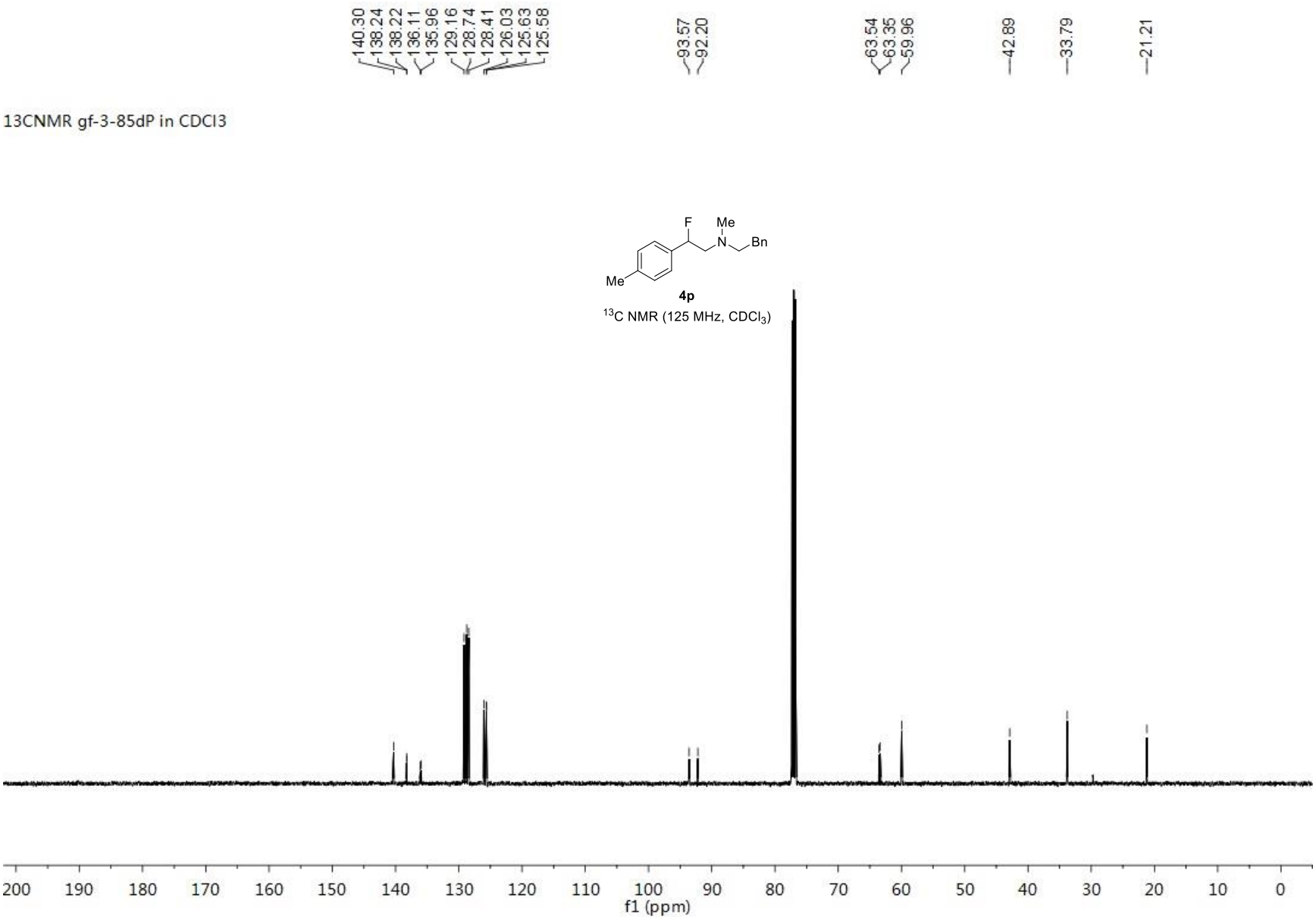


1HNMR gf-3-85dP in CDCL3



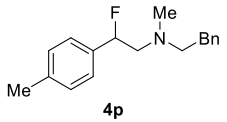
4p

^{1}H NMR (500 MHz, $CDCl_3$)


140.30
138.24
138.22
136.11
135.96
129.16
128.74
128.41
126.03
125.63
125.58
93.57
92.20
63.54
63.35
59.96
42.89
33.79
21.21
13CNMR gf-3-85dP in CDCl3
F
Me
N
Bn
Me
4p
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

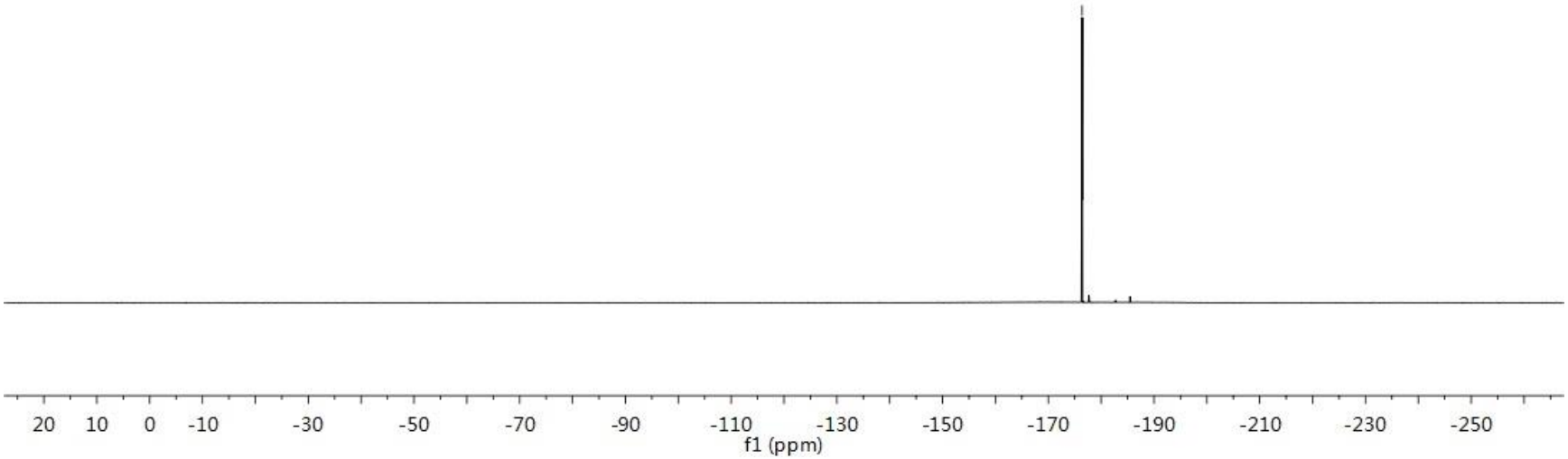
19FNMR gf-3-85dP in CDCl3

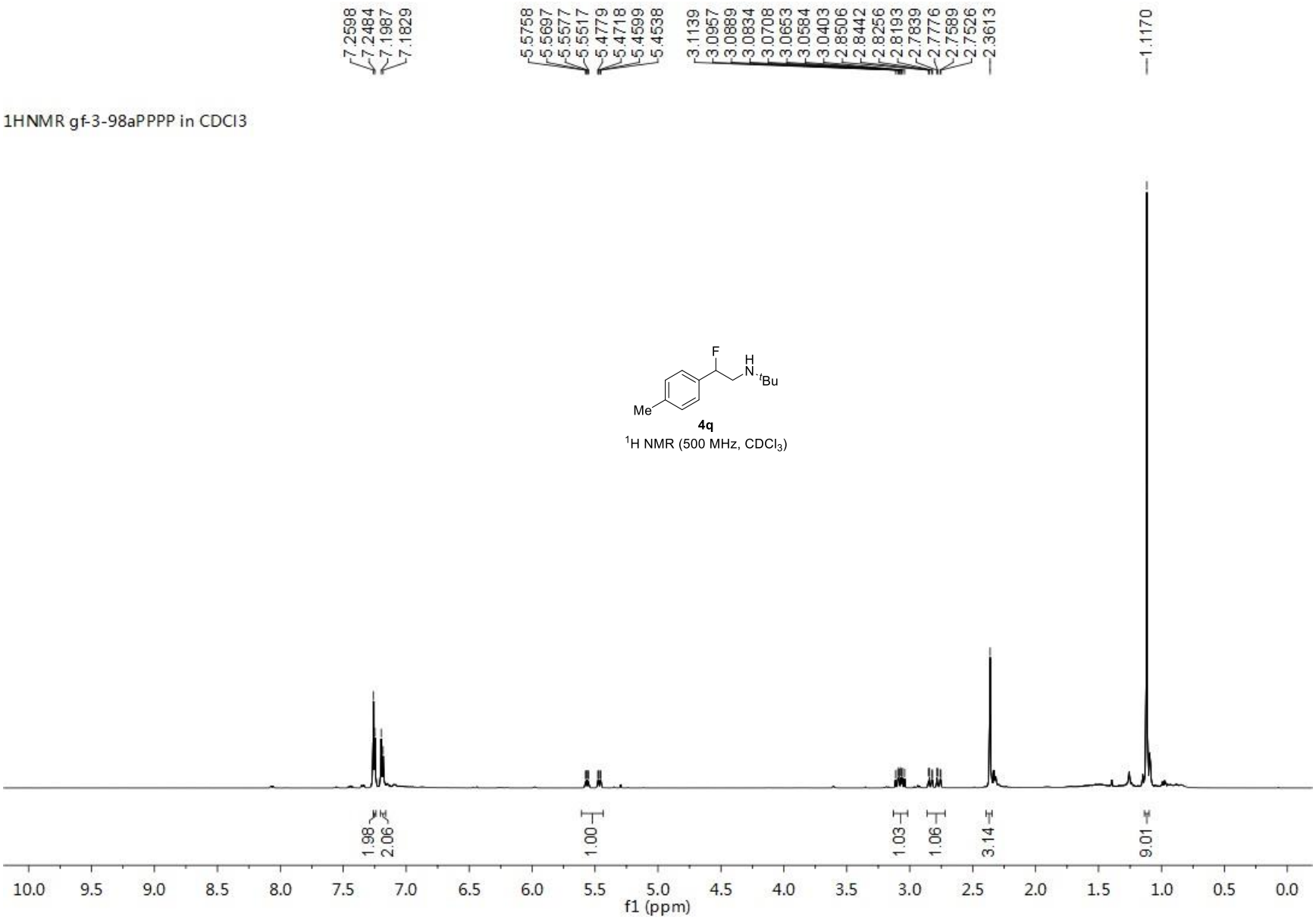
-176.4063

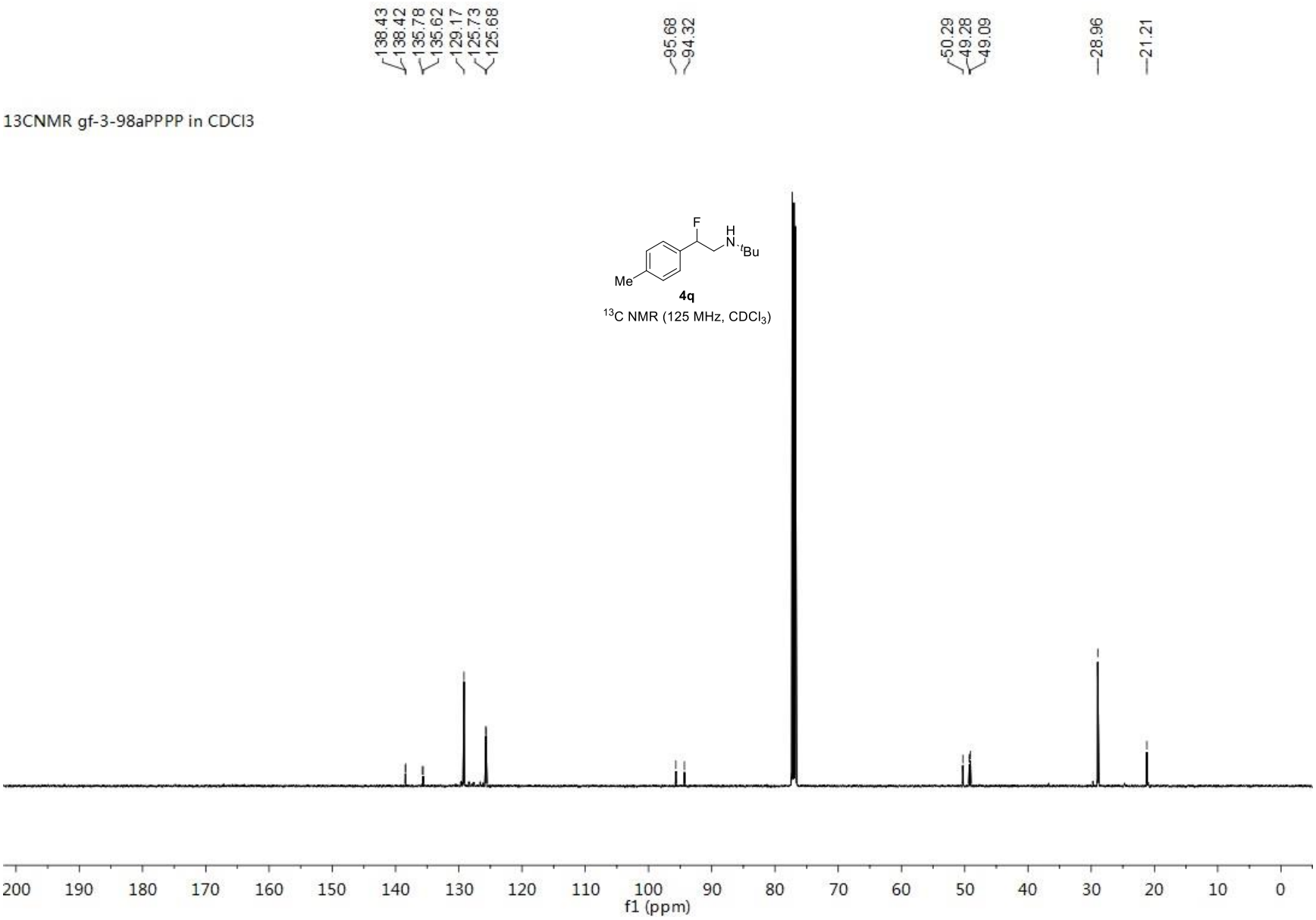


4p

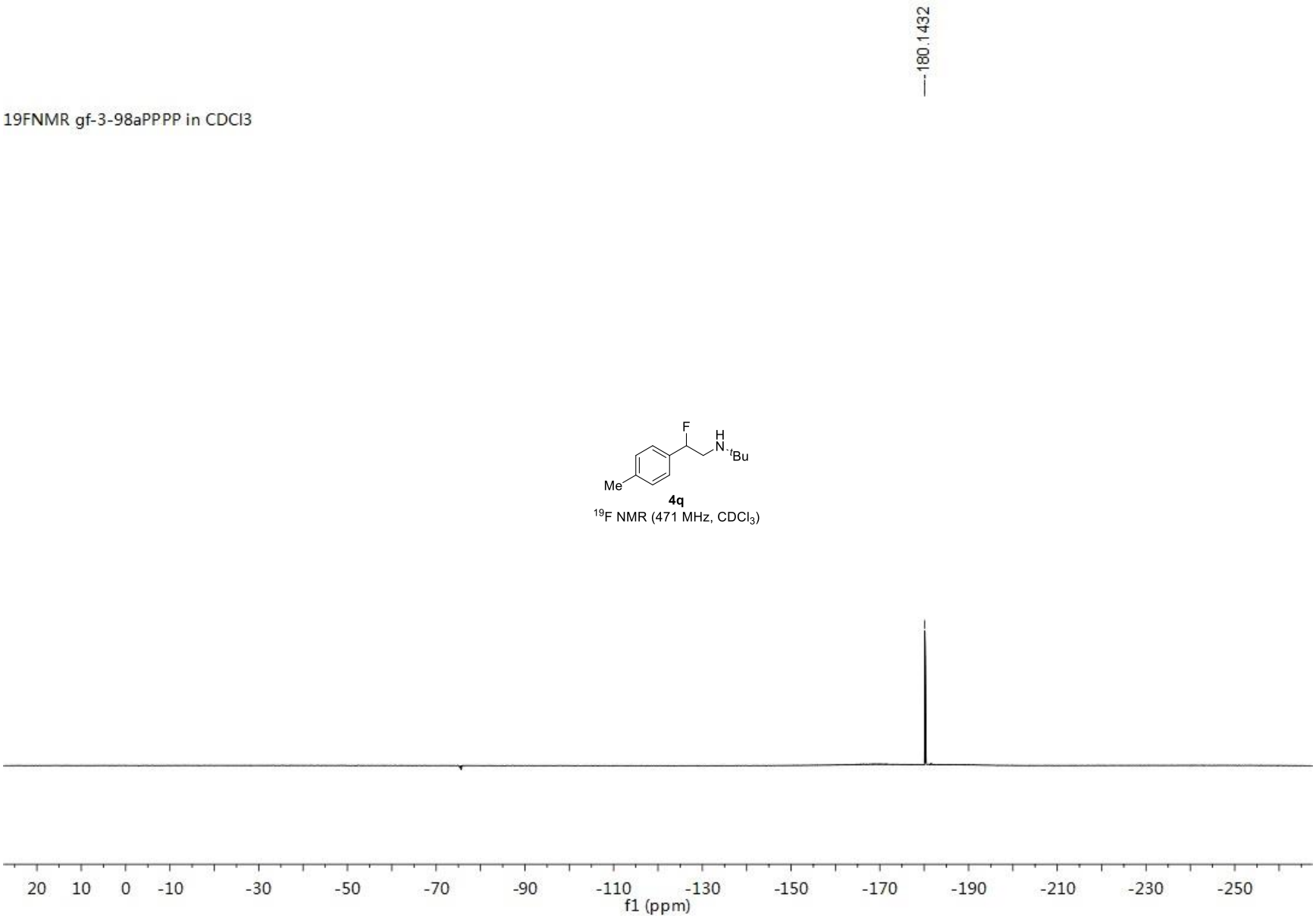
^{19}F NMR (471 MHz, $CDCl_3$)




7.2598
7.2484
7.1987
7.1829
5.5758
5.5697
5.5577
5.5517
5.4779
5.4718
5.4599
5.4538
3.1139
3.0957
3.0889
3.0834
3.0708
3.0653
3.0584
3.0403
2.8506
2.8442
2.8256
2.8193
2.7839
2.7776
2.7589
2.7526
2.3613
1.1170
1HNMR gf-3-98aPPPP in CDCl3
F
H
N
tBu
Me
4q
1H NMR (500 MHz, CDCl3)
1.98
2.06
1.00
1.03
1.06
3.14
9.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


138.43
138.42
135.78
135.62
129.17
125.73
125.68
95.68
94.32
50.29
49.28
49.09
28.96
21.21
13CNMR gf-3-98aPPPP in CDCl3
F
H
N
tBu
Me
4q
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

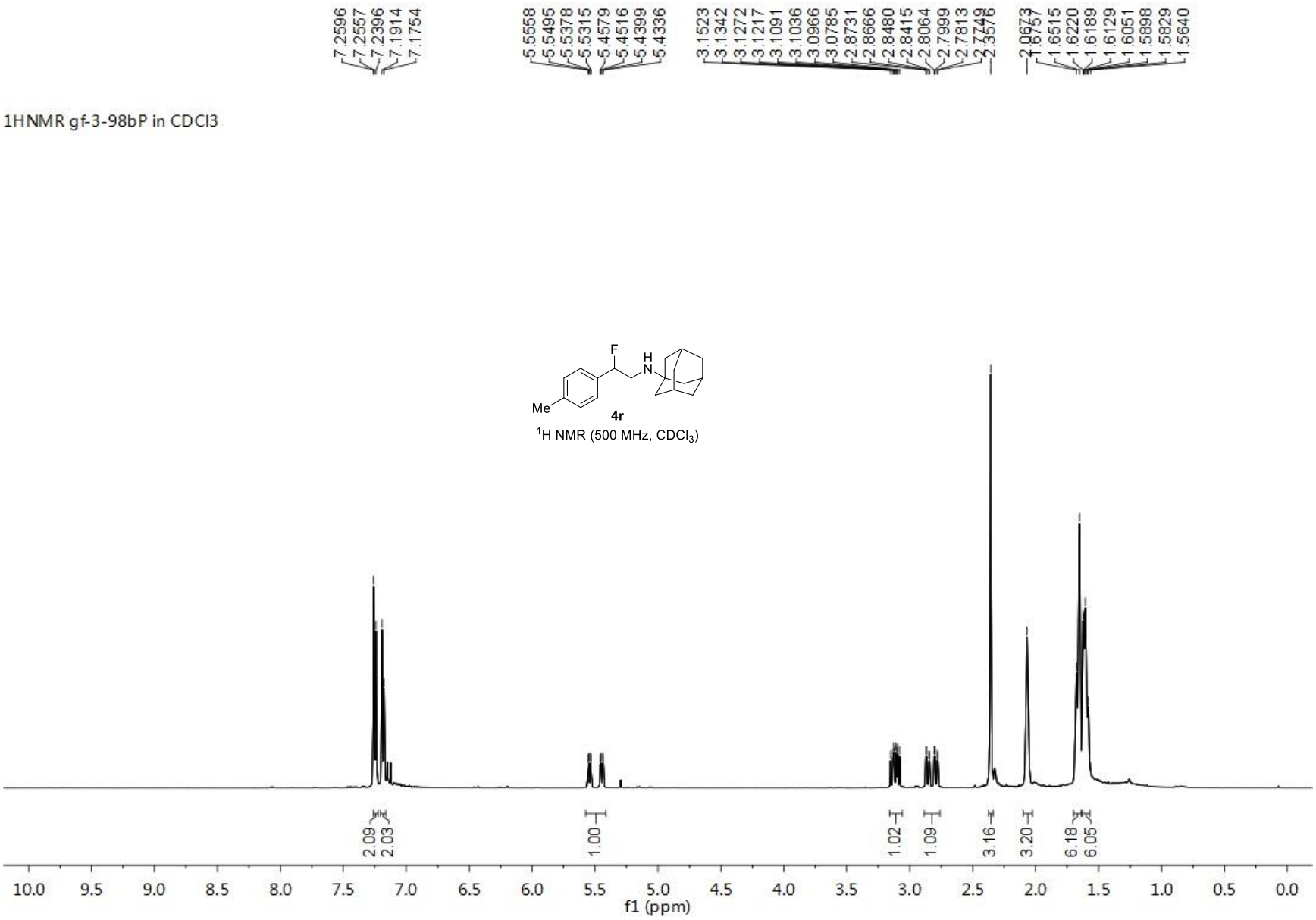
19FNMR gf-3-98aPPPP in CDCl3

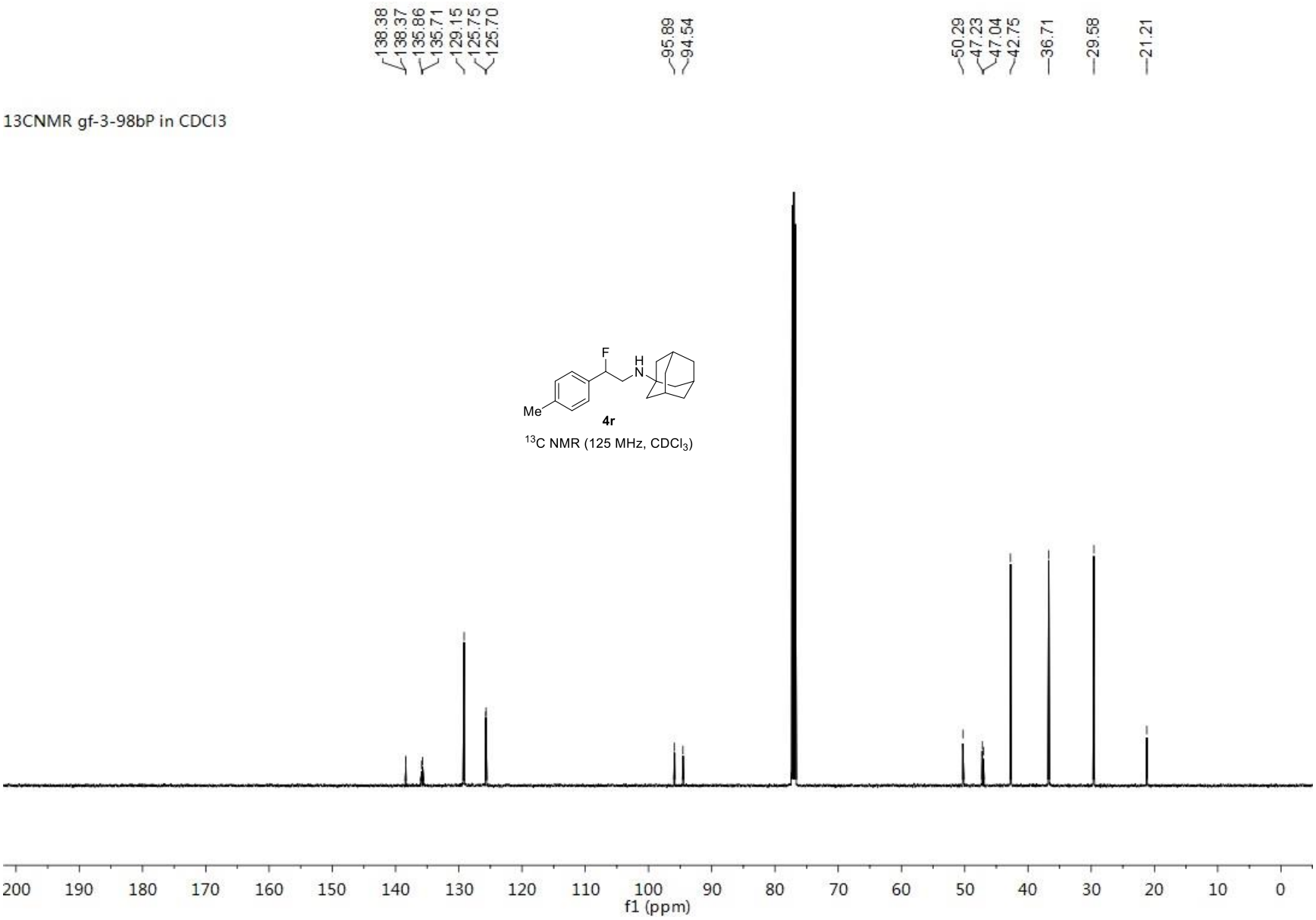


4q

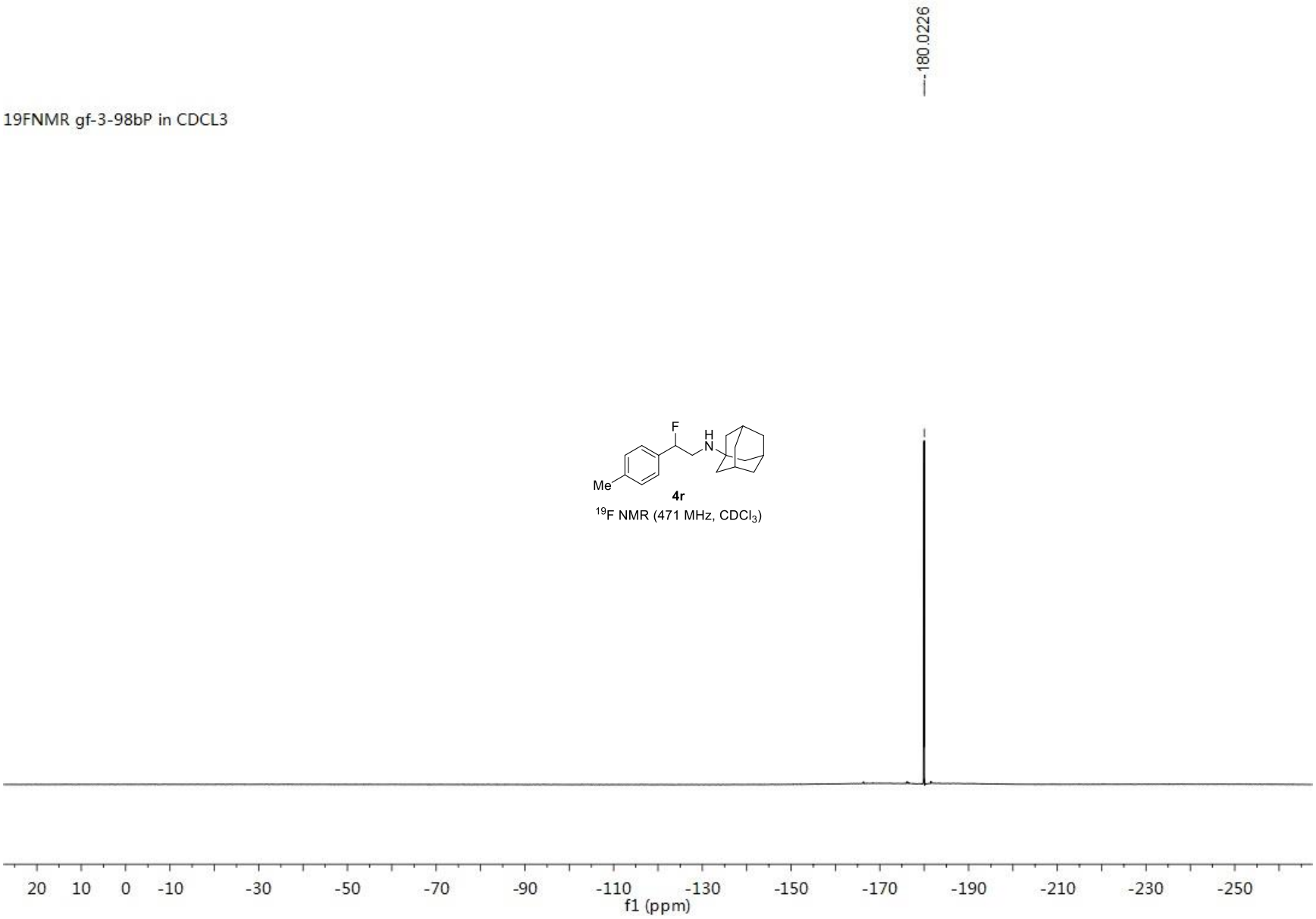
^{19}F NMR (471 MHz, $CDCl_3$)

1HNMR gf-3-98bP in CDCl3




138.38
138.37
135.86
135.71
129.15
125.75
125.70
95.89
94.54
50.29
47.23
47.04
42.75
36.71
29.58
21.21
13CNMR gf-3-98bP in CDCl3
F
H
N
Me
4r
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

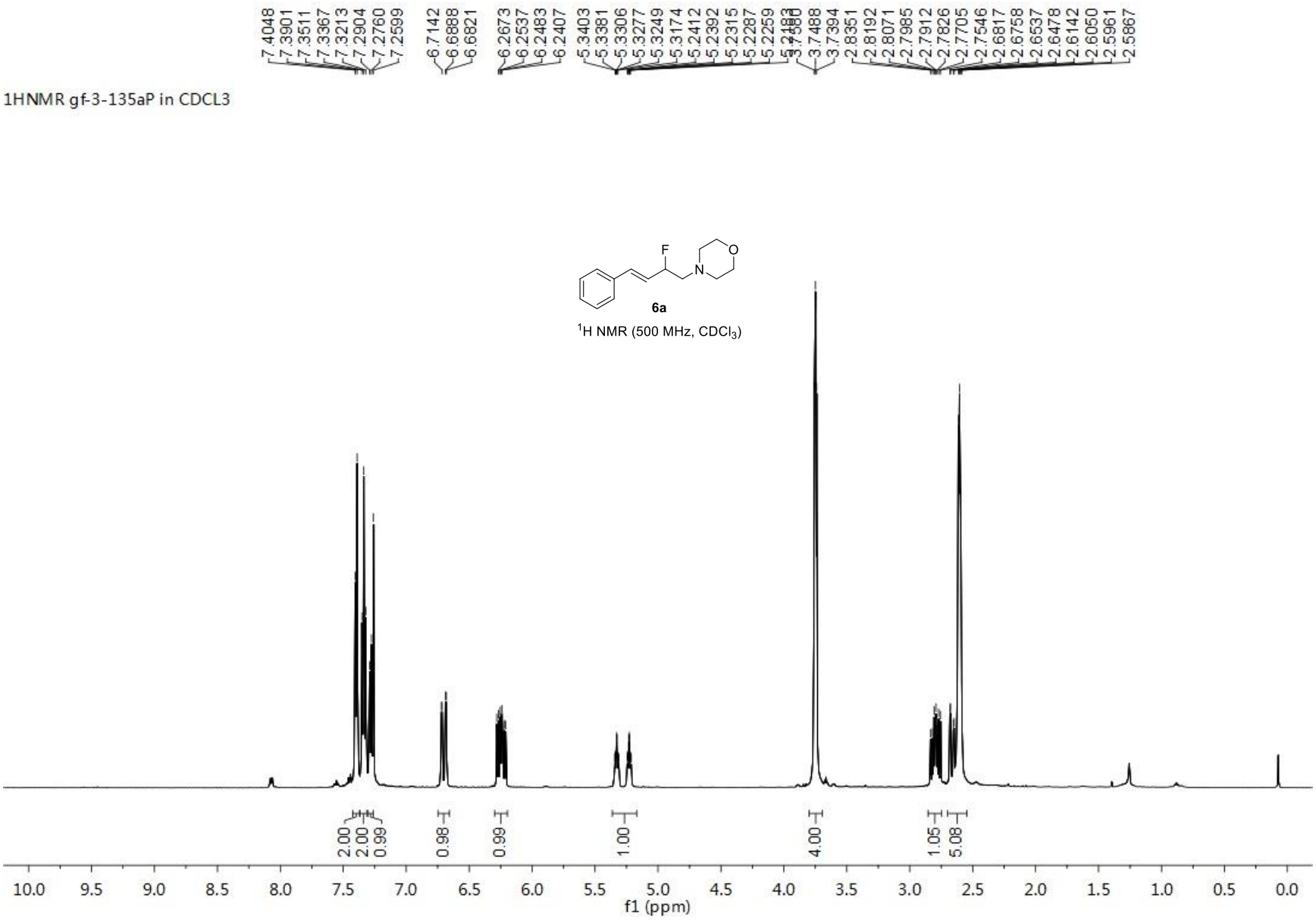
19FNMR gf-3-98bP in CDCL3

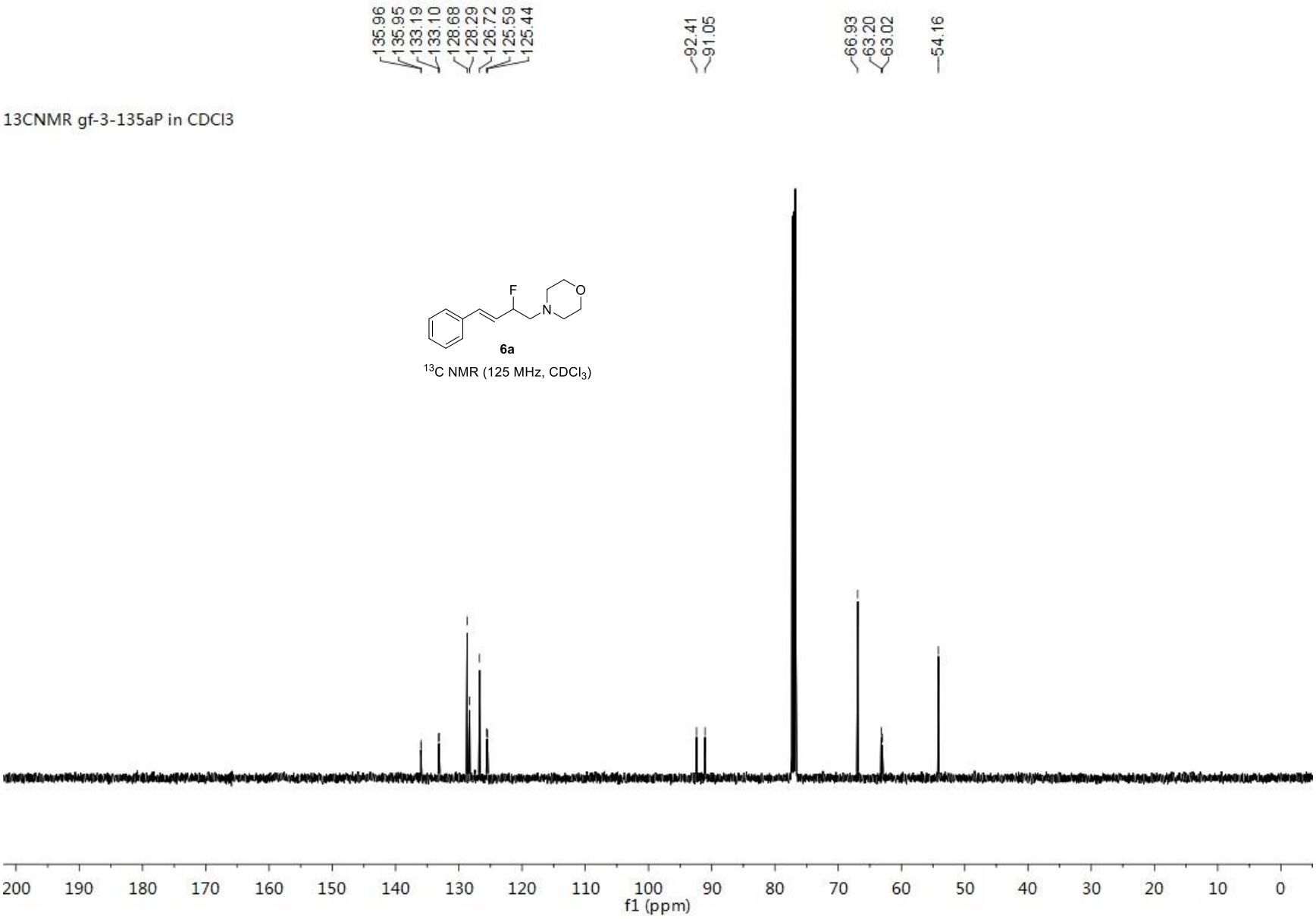


4r

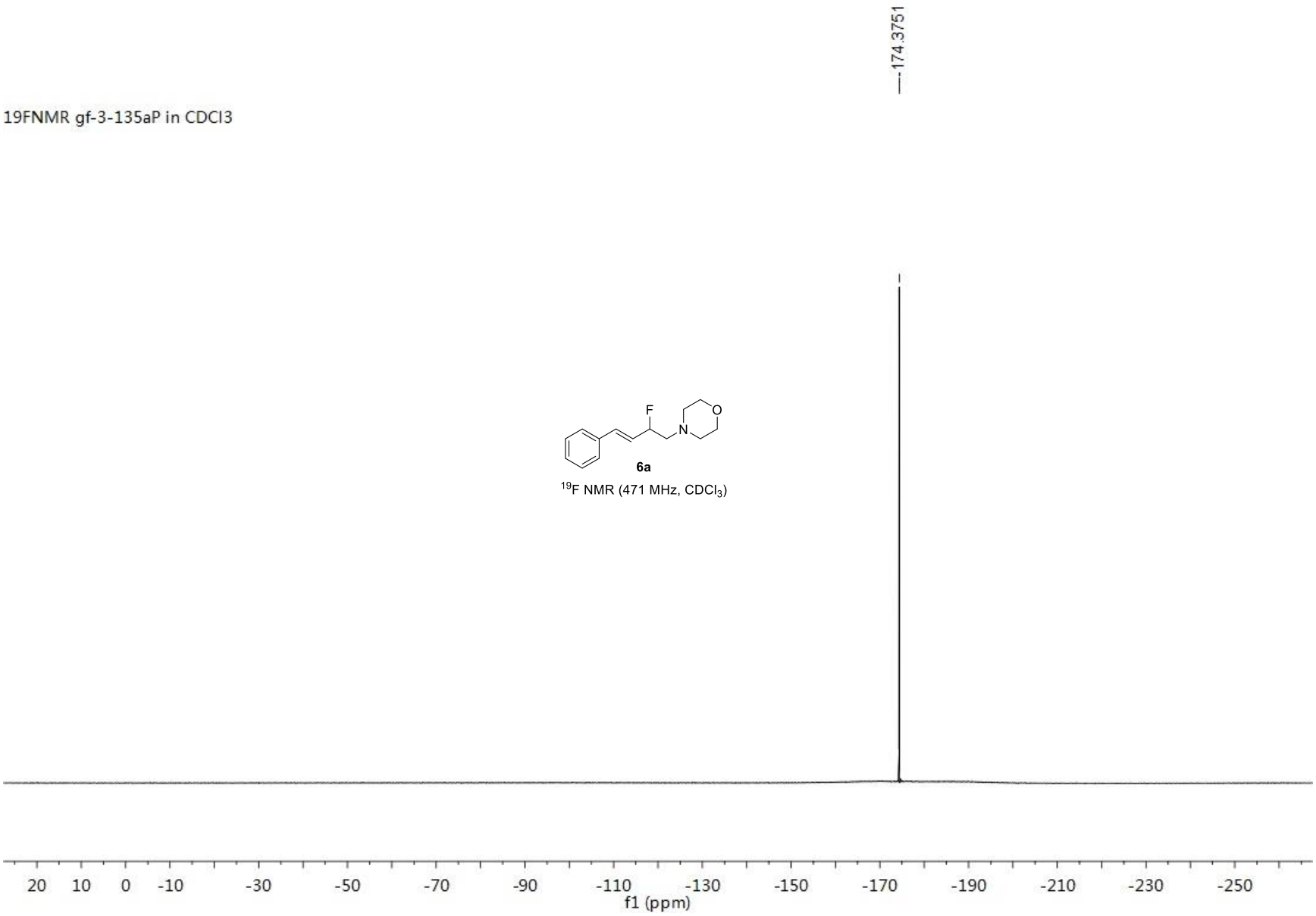
^{19}F NMR (471 MHz, $CDCl_3$)

1HNMR gf-3-135aP in CDCL3



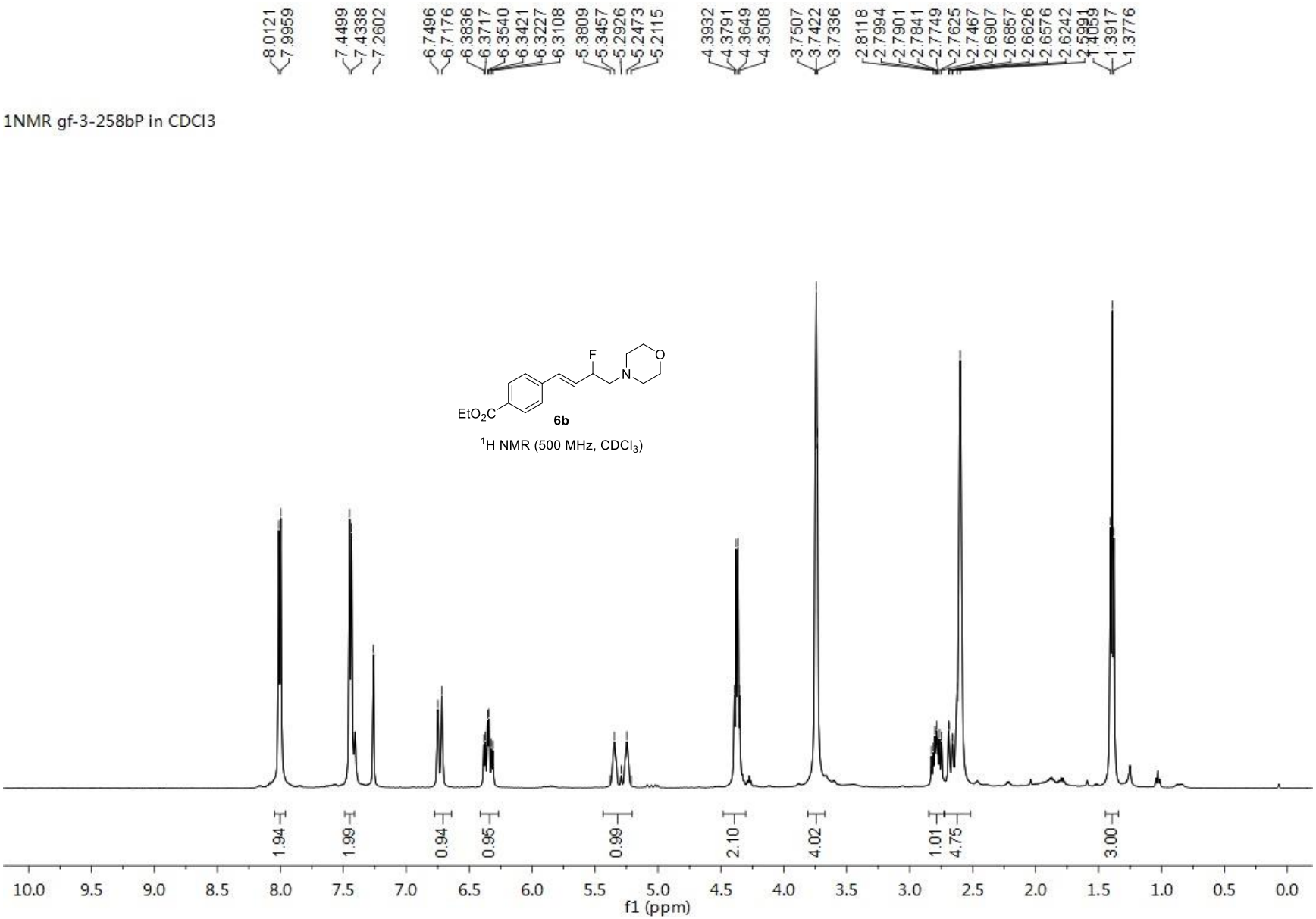

135.96
135.95
133.19
133.10
128.68
128.29
126.72
125.59
125.44
92.41
91.05
66.93
63.20
63.02
54.16
13CNMR gf-3-135aP in CDCl3
F
O
N
6a
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

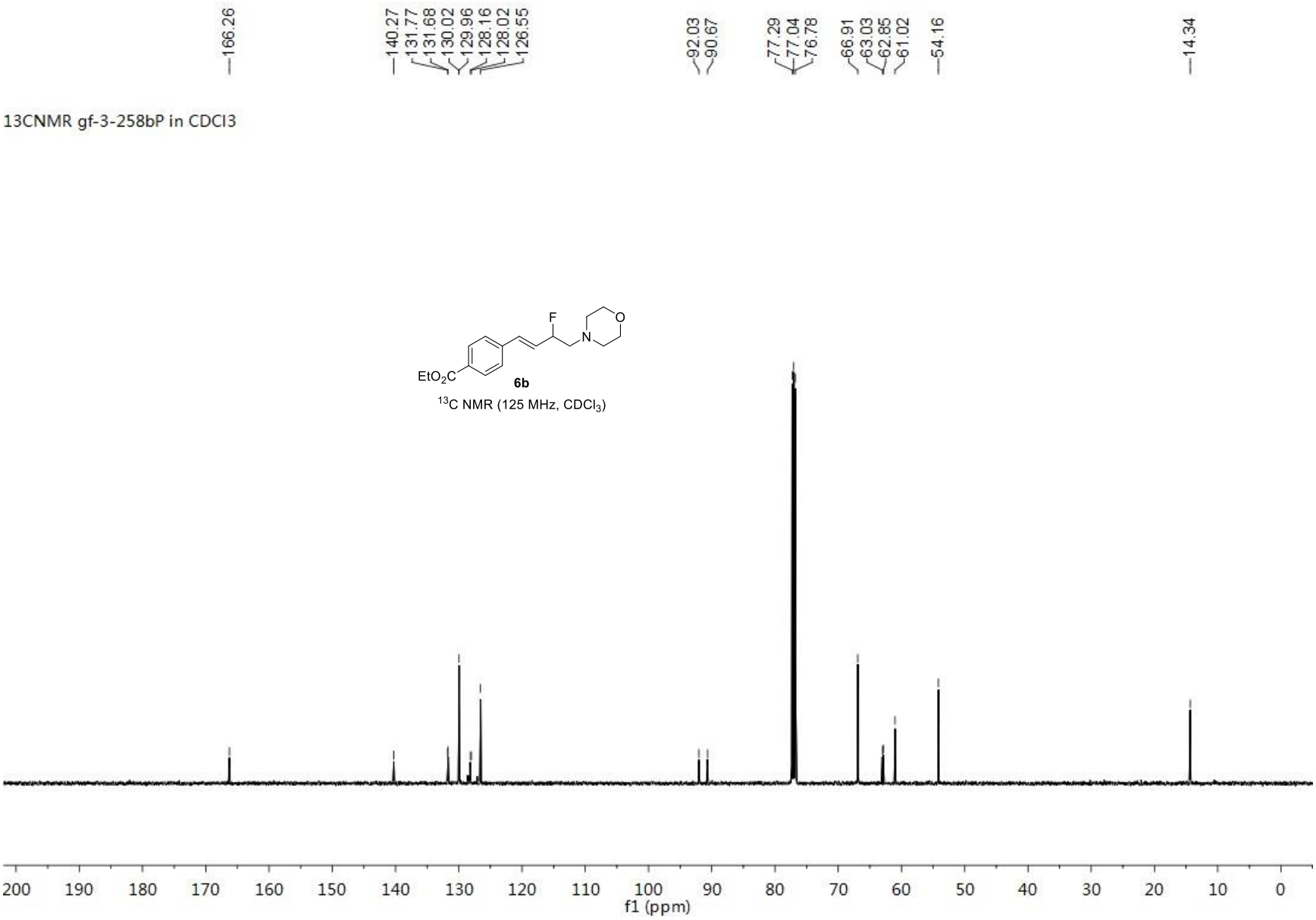
19FNMR gf-3-135aP in CDCl3



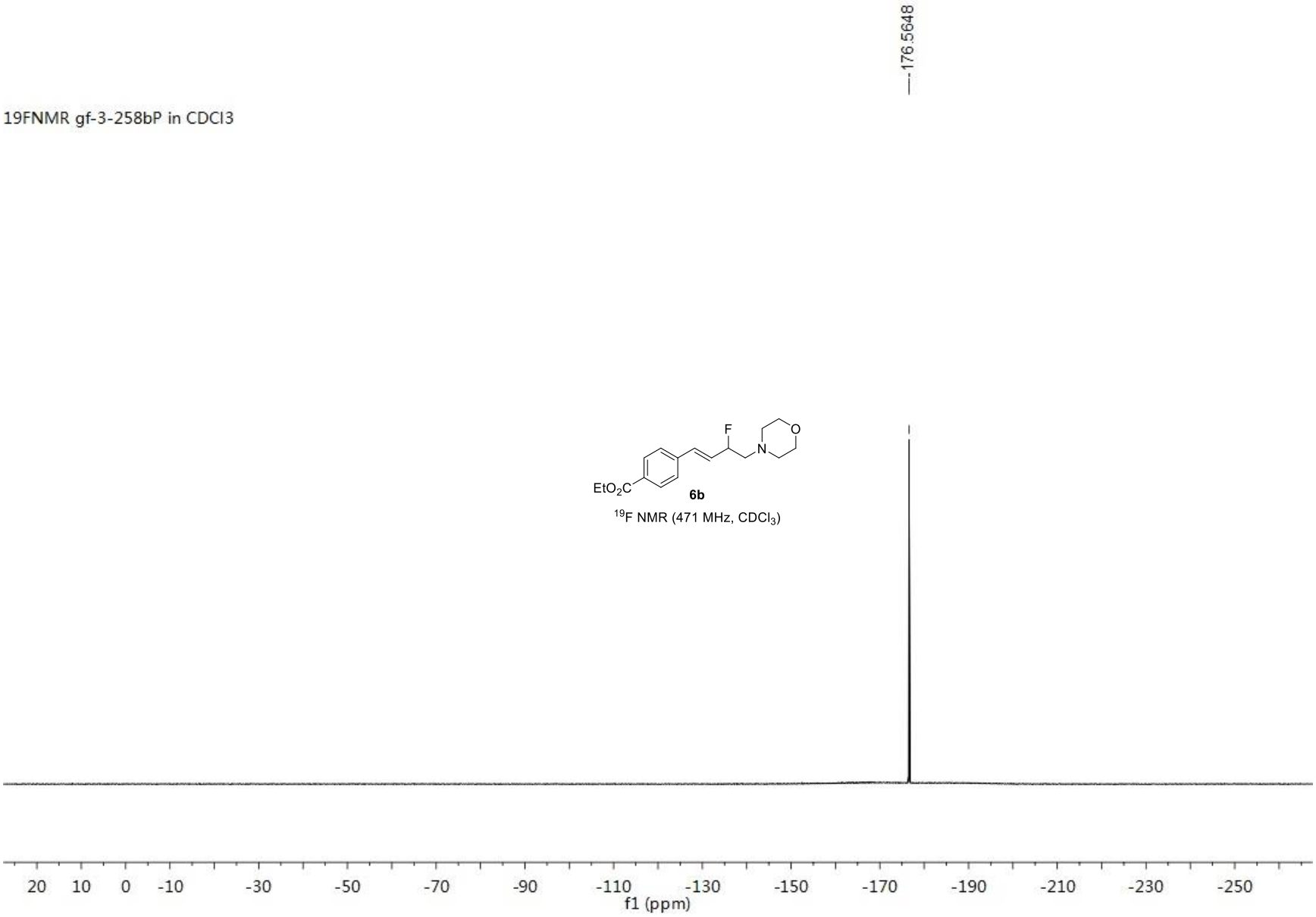
6a

^{19}F NMR (471 MHz, $CDCl_3$)


8.0121
7.9959
7.4499
7.4338
7.2602
6.7496
6.7176
6.3836
6.3717
6.3540
6.3421
6.3227
6.3108
5.3809
5.3457
5.2926
5.2473
5.2115
4.3932
4.3791
4.3649
4.3508
3.7507
3.7422
3.7336
2.8118
2.7994
2.7901
2.7841
2.7749
2.7625
2.7467
2.6907
2.6857
2.6626
2.6576
2.6242
1.4059
1.3917
1.3776
1NMR gf-3-258bP in CDCl3
F
O
N
EtO2C
6b
1H NMR (500 MHz, CDCl3)
1.94
1.99
0.94
0.95
0.99
2.10
4.02
1.01
4.75
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.26
140.27
131.77
131.68
130.02
129.96
128.16
128.02
126.55
92.03
90.67
77.29
77.04
76.78
66.91
63.03
62.85
61.02
54.16
14.34
13CNMR gf-3-258bP in CDCl3
F
O
N
EtO2C
6b
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

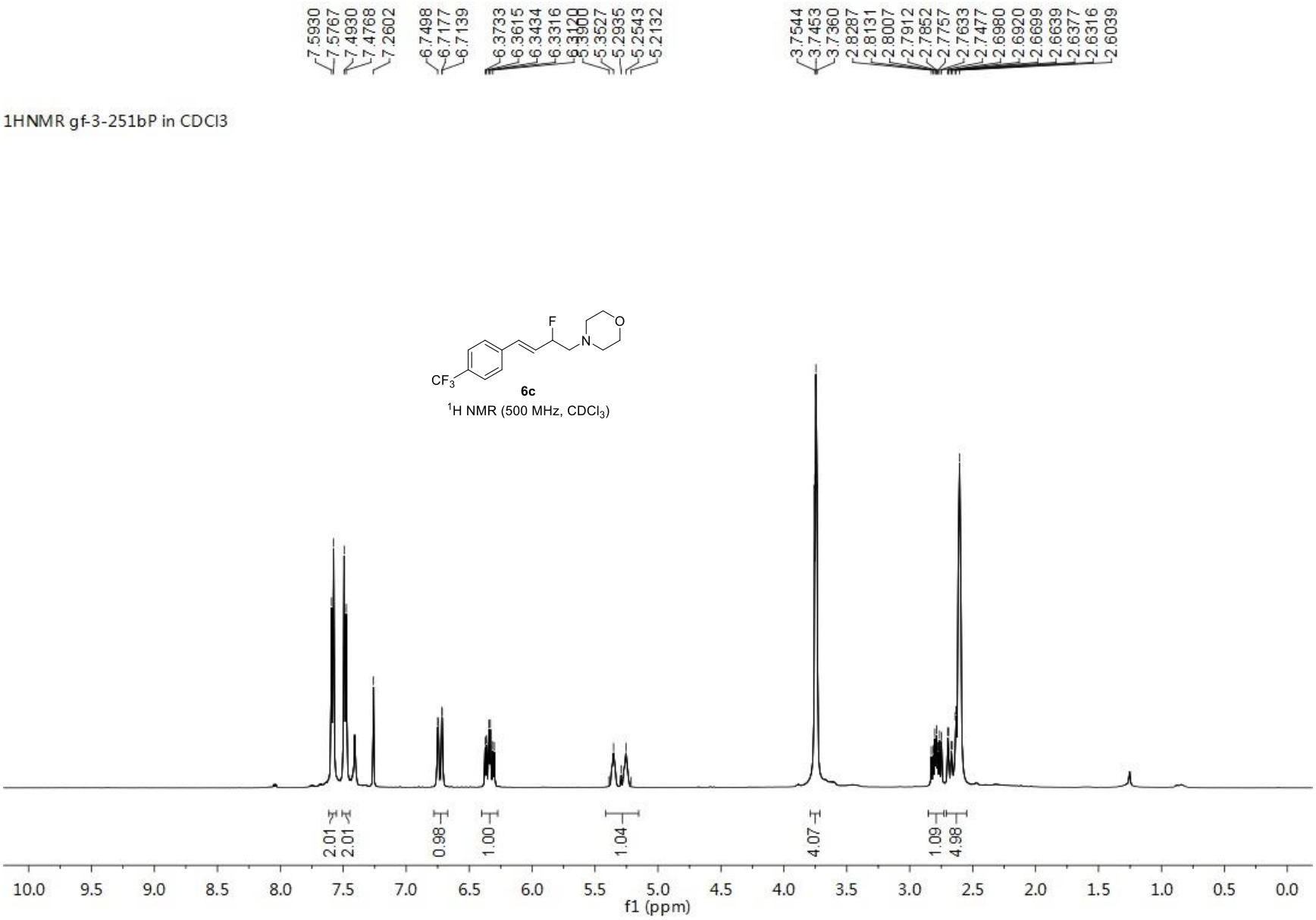
19FNMR gf-3-258bP in CDCl3

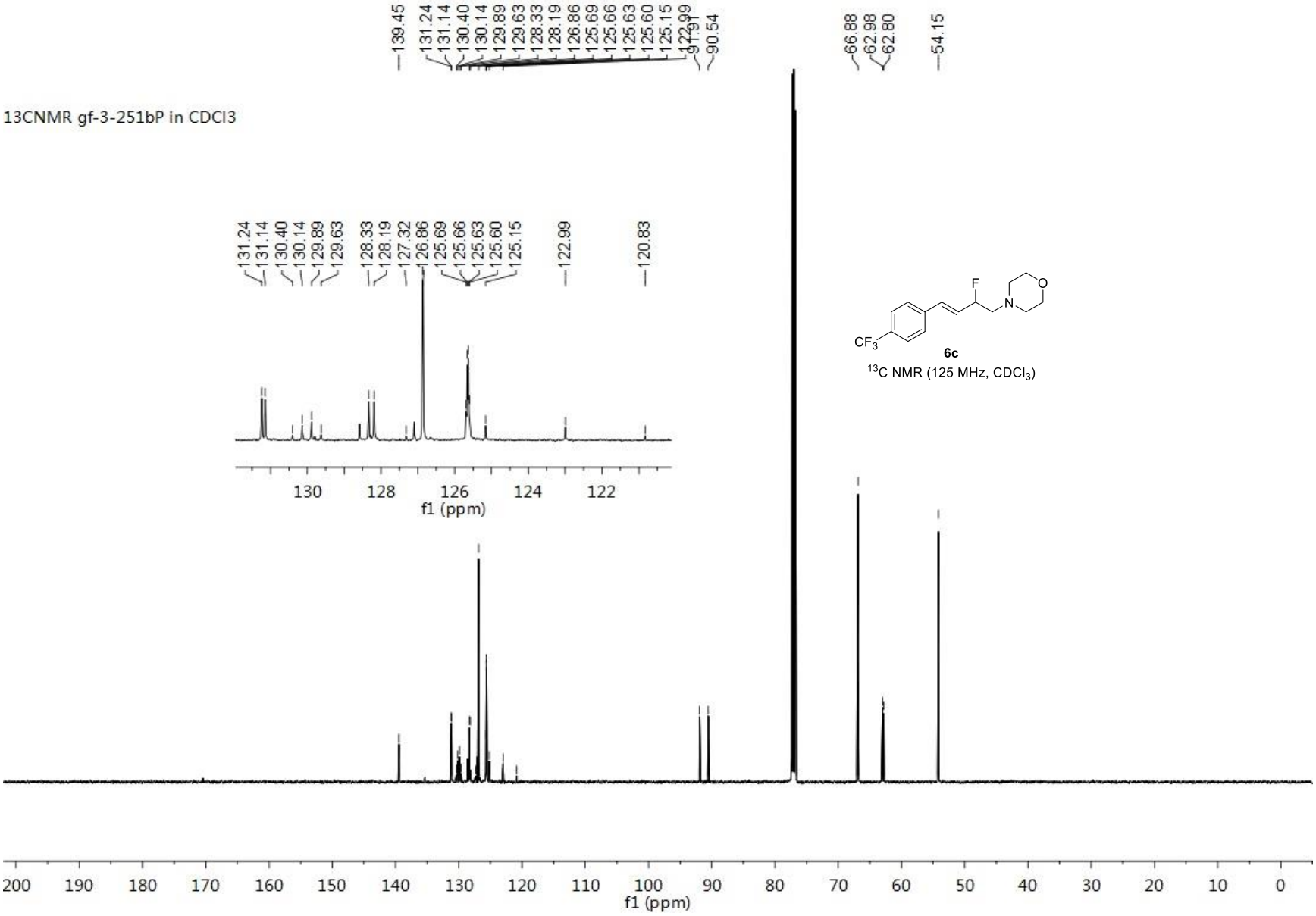


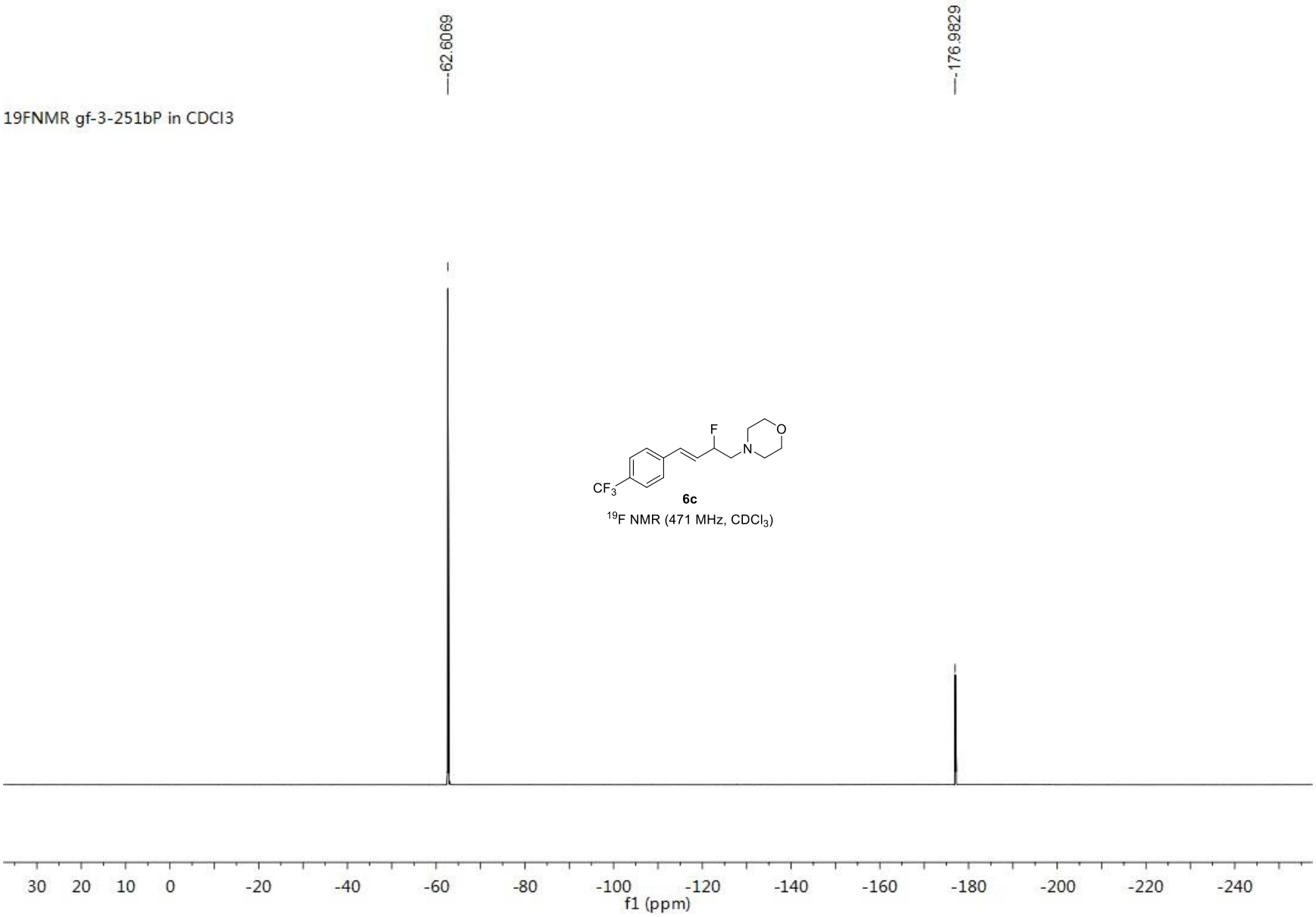
6b

^{19}F NMR (471 MHz, $CDCl_3$)

1HNMR gf-3-251bP in CDCl3

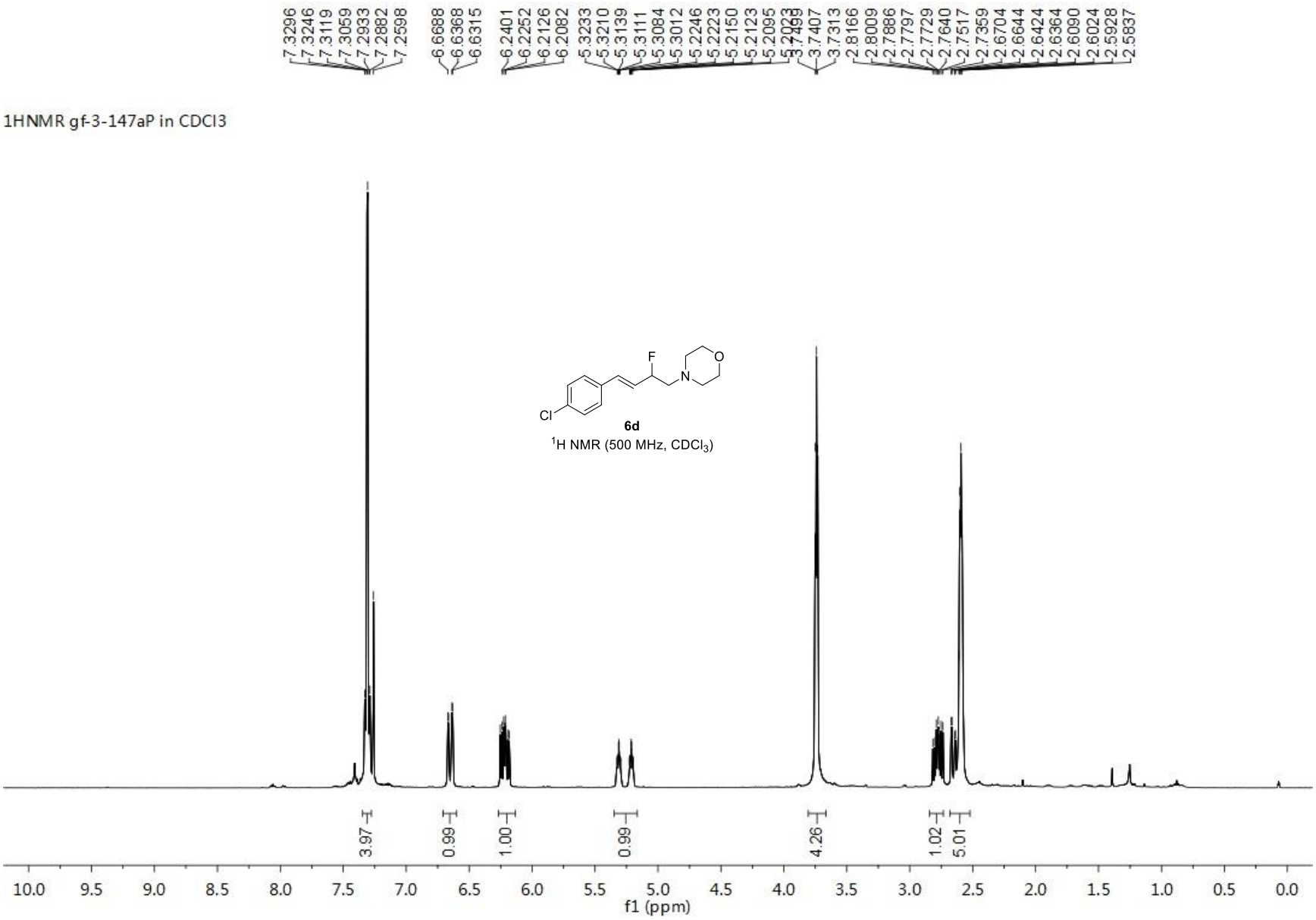


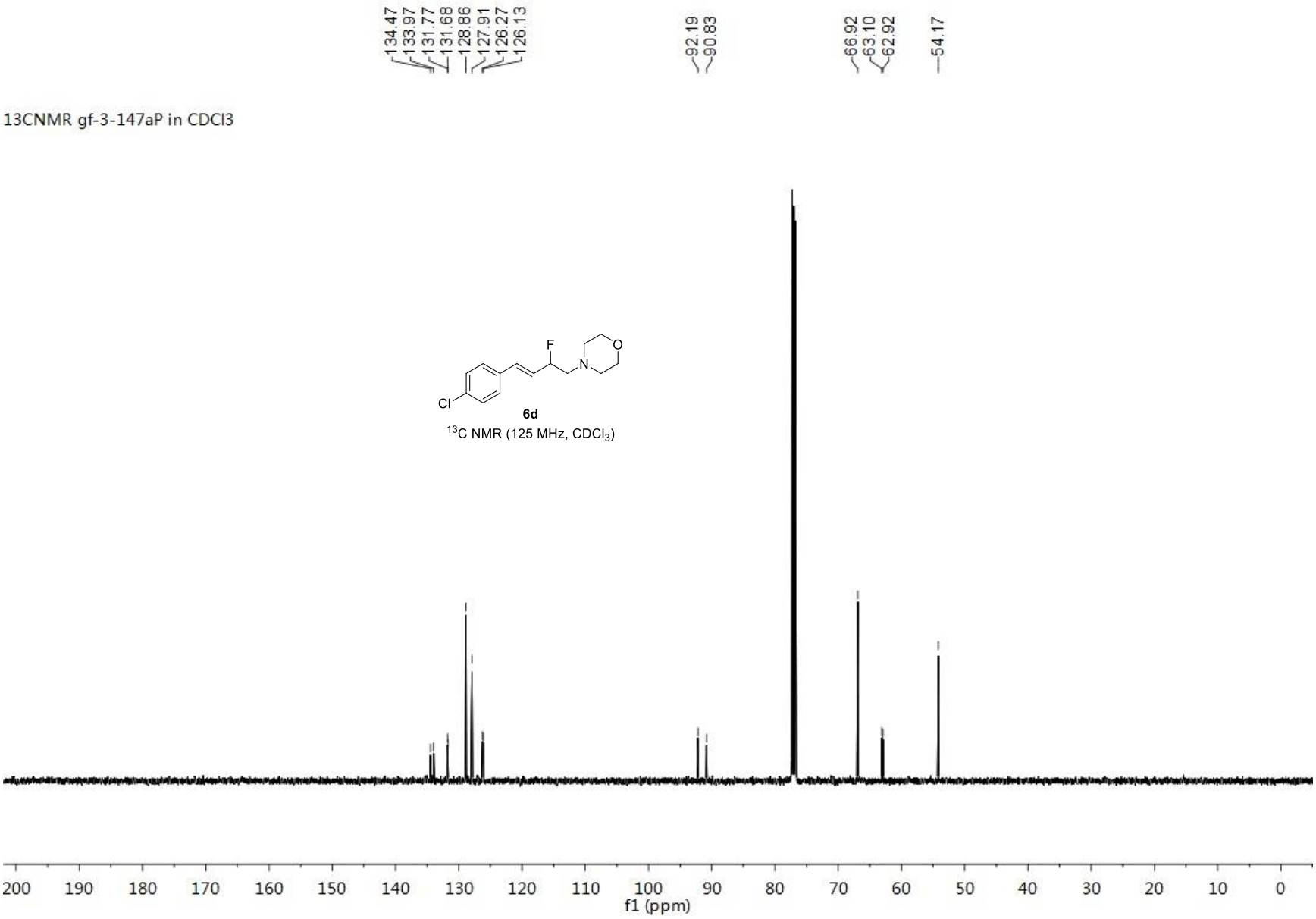

13CNMR gf-3-251bP in CDCl3
139.45
131.24
131.14
130.40
130.14
129.89
129.63
128.33
128.19
126.86
125.69
125.66
125.63
125.60
125.15
122.99
91.91
90.54
66.88
62.98
62.80
54.15
131.24
131.14
130.40
130.14
129.89
129.63
128.33
128.19
127.32
126.86
125.69
125.66
125.63
125.60
125.15
122.99
120.83
130
128
126
124
122
f1 (ppm)
F
O
N
CF3
6c
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



6c

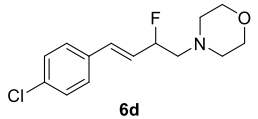
^{19}F NMR (471 MHz, $CDCl_3$)


7.3296
7.3246
7.3119
7.3059
7.2933
7.2882
7.2598
6.6688
6.6368
6.6315
6.2401
6.2252
6.2126
6.2082
5.3233
5.3210
5.3139
5.3111
5.3084
5.3012
5.2246
5.2223
5.2150
5.2123
5.2095
3.7407
3.7313
2.8166
2.8009
2.7886
2.7797
2.7729
2.7640
2.7517
2.7359
2.6704
2.6644
2.6424
2.6364
2.6090
2.6024
2.5928
2.5837
1HNMR gf-3-147aP in CDCl3
F
O
N
Cl
6d
1H NMR (500 MHz, CDCl3)
3.97
0.99
1.00
0.99
4.26
1.02
5.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


134.47
133.97
131.77
131.68
128.86
127.91
126.27
126.13
92.19
90.83
66.92
63.10
62.92
54.17
13CNMR gf-3-147aP in CDCl3
F
O
N
Cl
6d
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

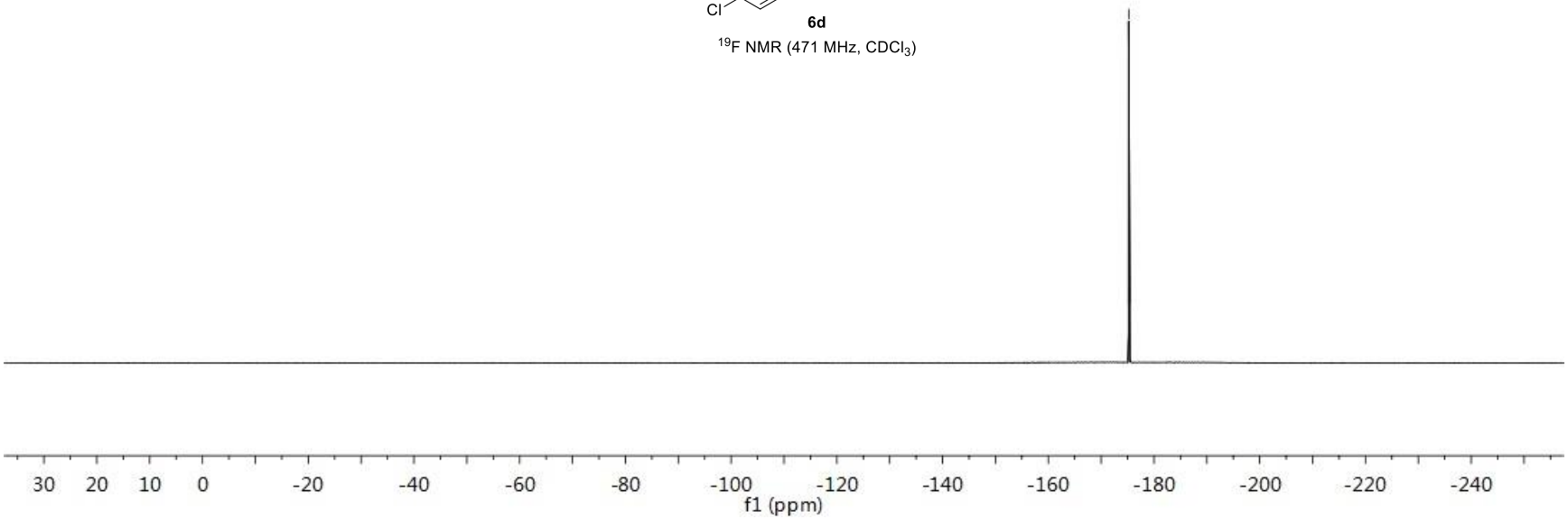
19FNMR gf-3-147aP in CDCl3

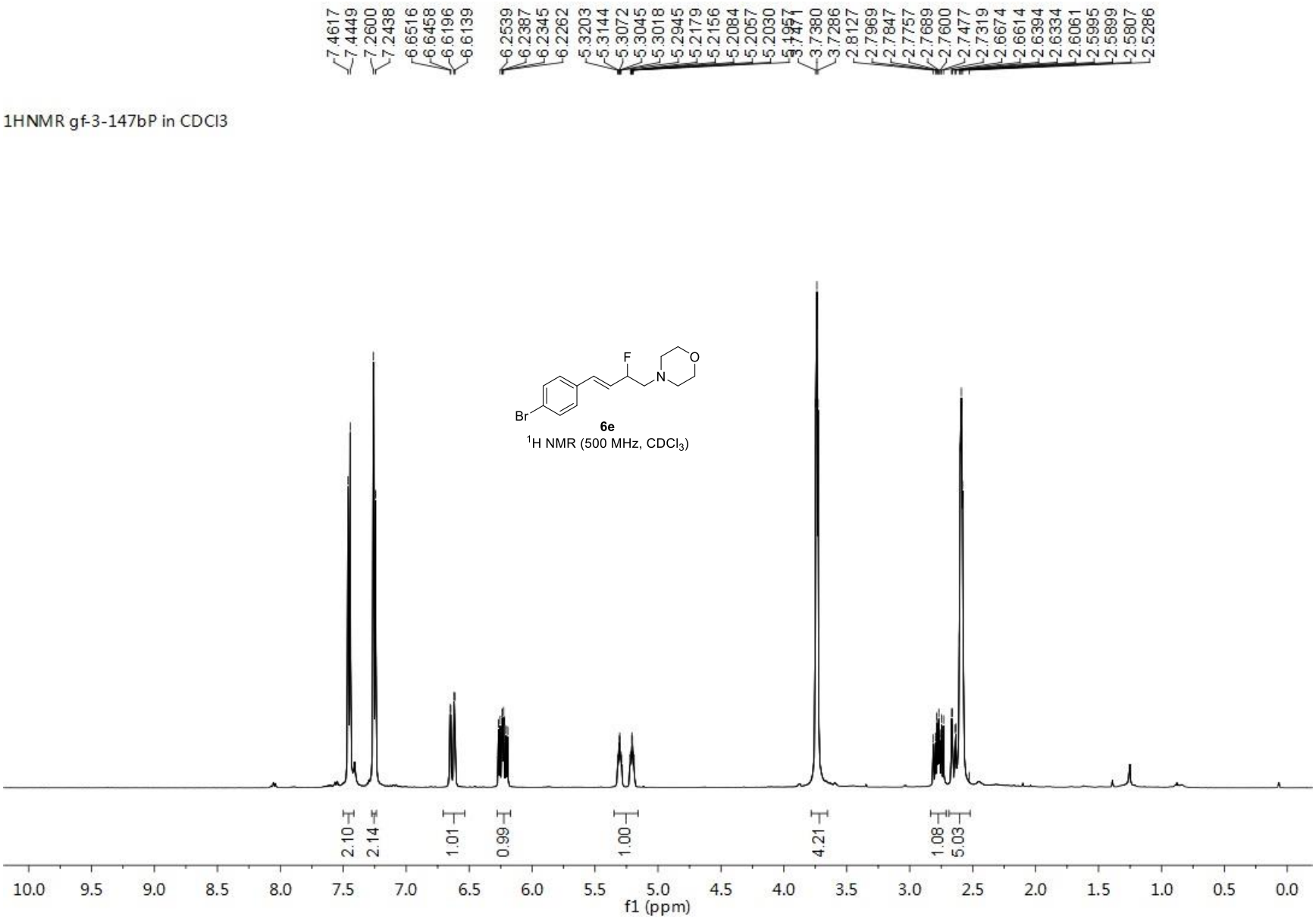
-175.2228

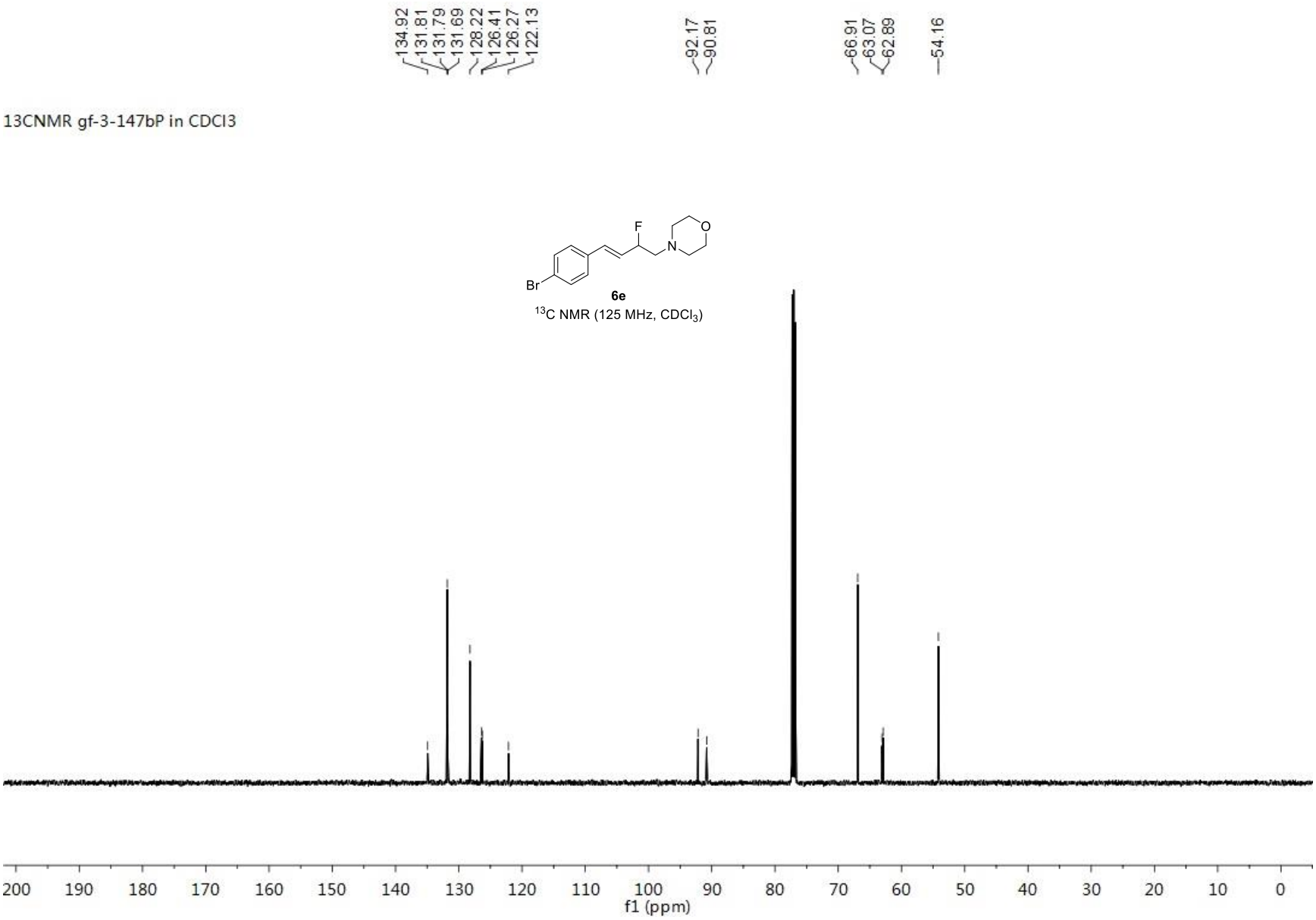


6d

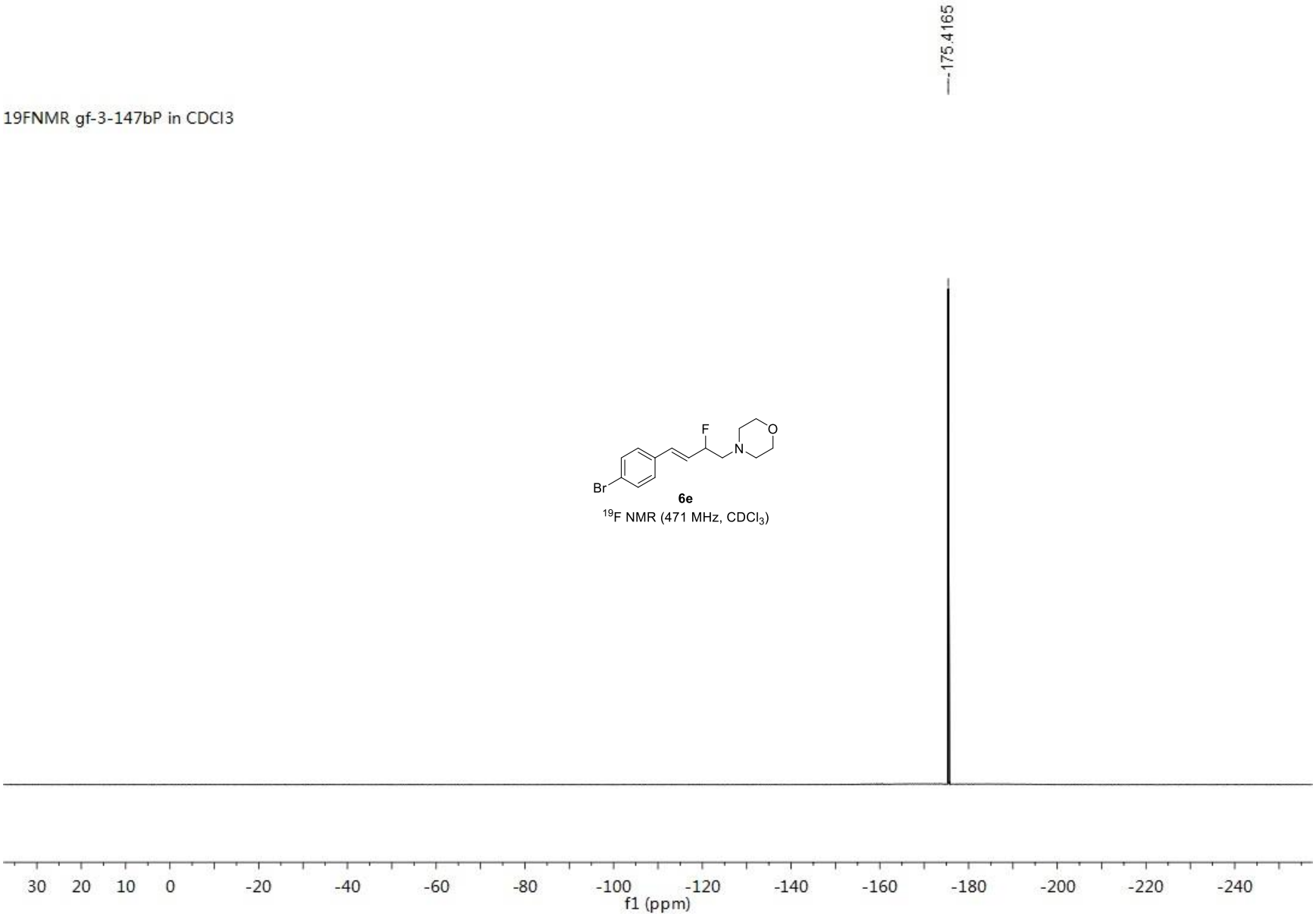
^{19}F NMR (471 MHz, $CDCl_3$)




7.4617
7.4449
7.2600
7.2438
6.6516
6.6458
6.6196
6.6139
6.2539
6.2387
6.2345
6.2262
5.3203
5.3144
5.3072
5.3045
5.3018
5.2945
5.2179
5.2156
5.2084
5.2057
5.2030
3.7380
3.7286
2.8127
2.7969
2.7847
2.7757
2.7689
2.7600
2.7477
2.7319
2.6674
2.6614
2.6394
2.6334
2.6061
2.5995
2.5899
2.5807
2.5286
1HNMR gf-3-147bP in CDCl3
F
O
N
Br
6e
1H NMR (500 MHz, CDCl3)
2.10
2.14
1.01
0.99
1.00
4.21
1.08
5.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

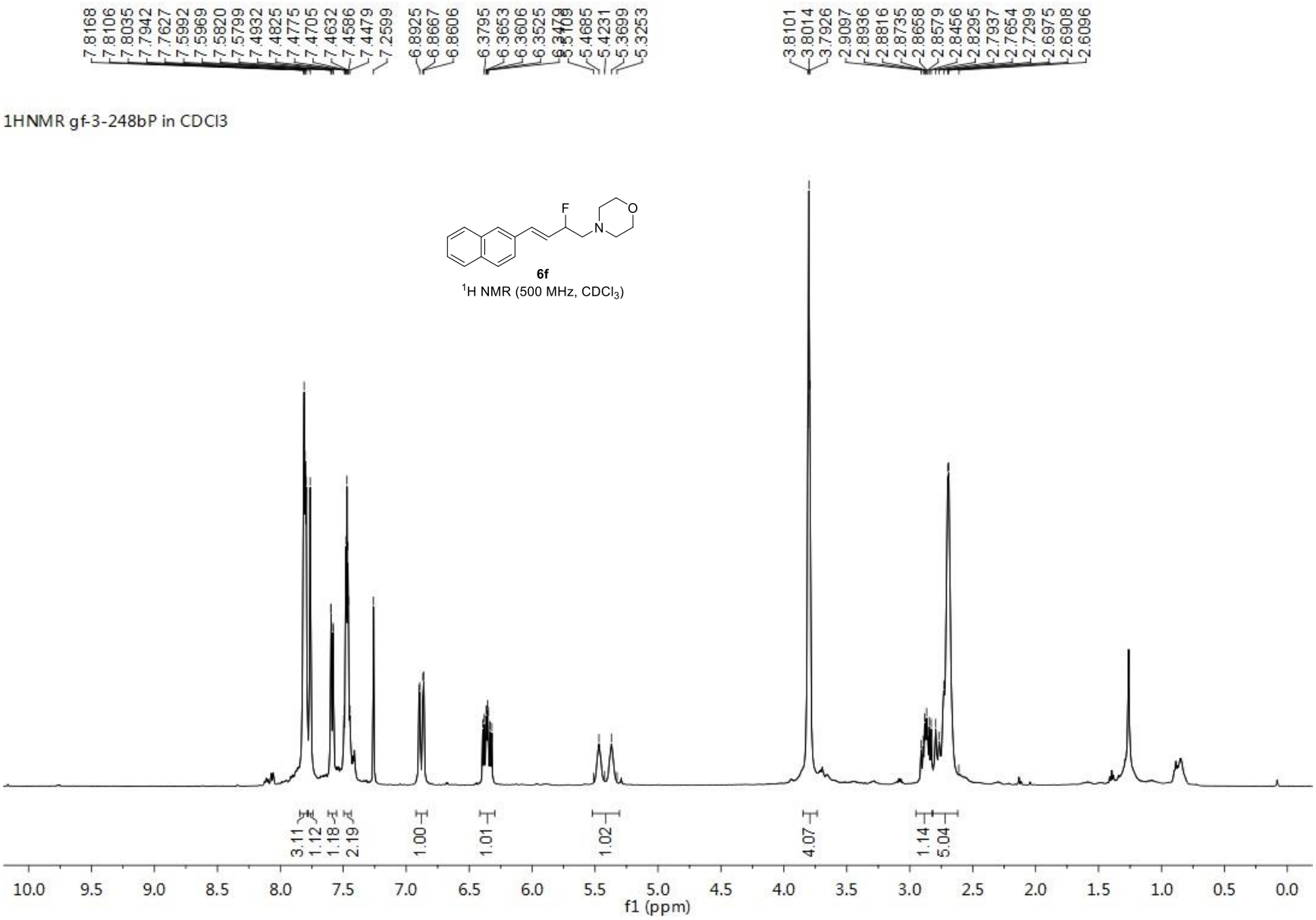

134.92
131.81
131.79
131.69
128.22
126.41
126.27
122.13
92.17
90.81
66.91
63.07
62.89
54.16
13CNMR gf-3-147bP in CDCl3
F
O
N
Br
6e
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

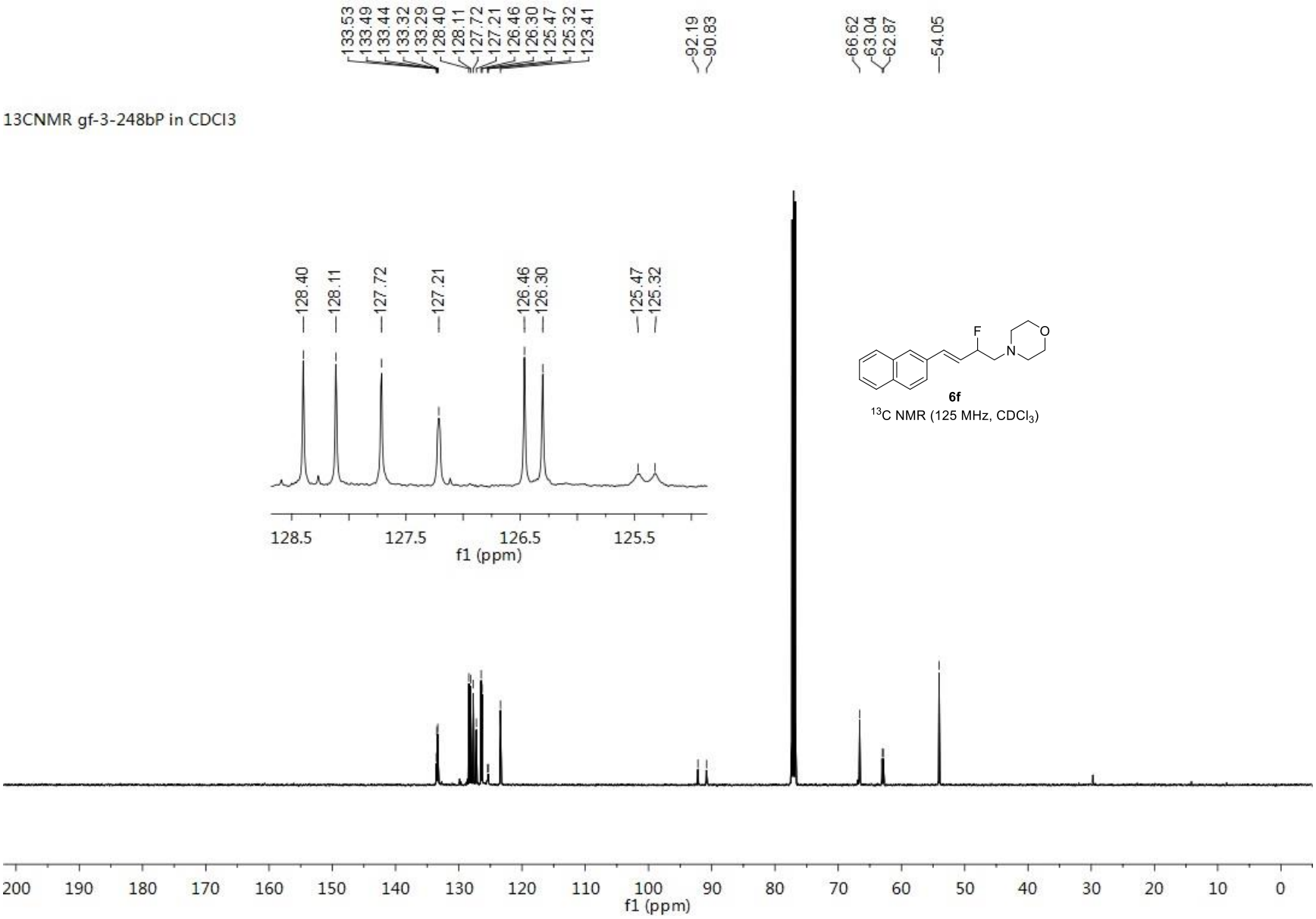
19FNMR gf-3-147bP in CDCl3



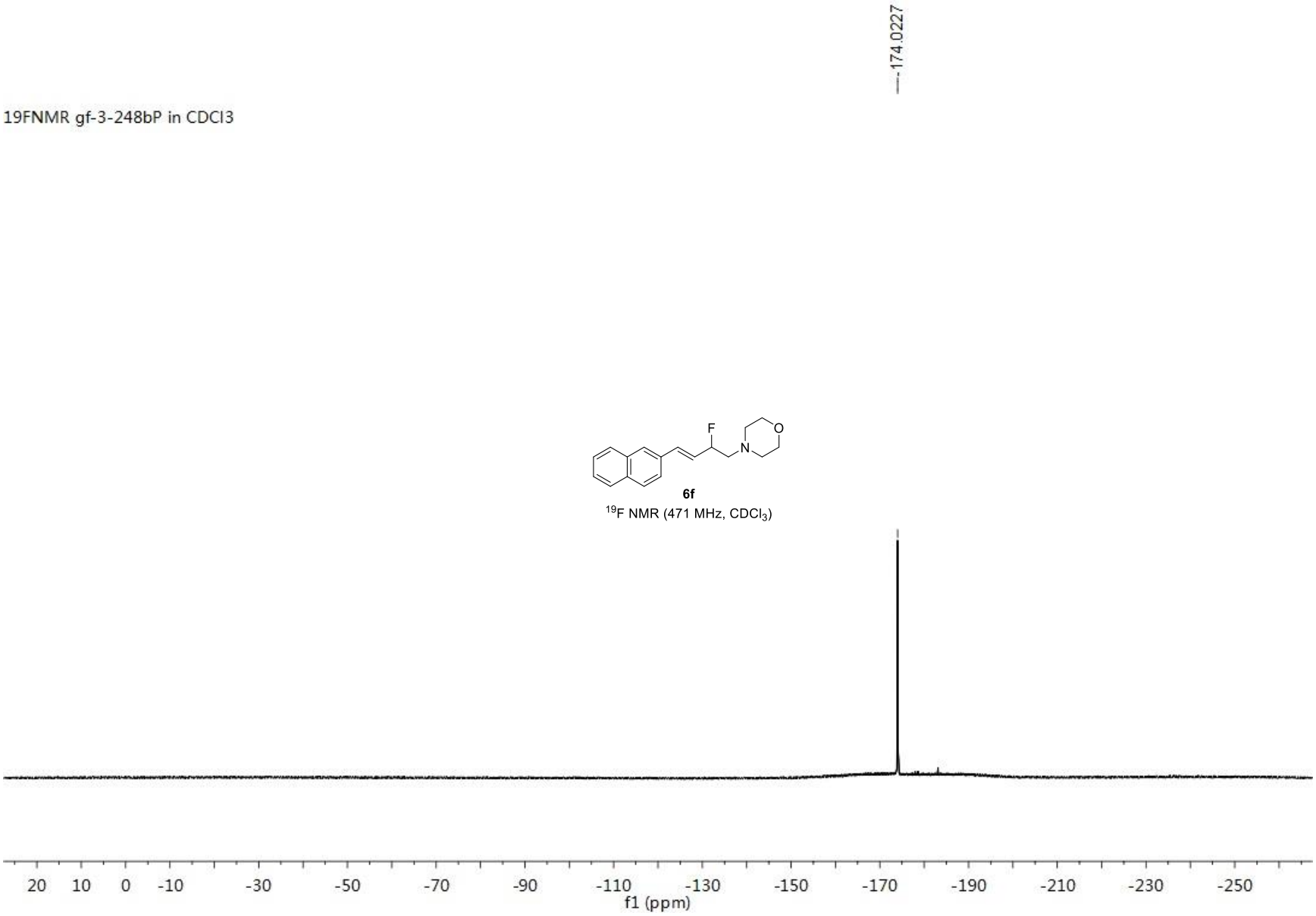
6e

^{19}F NMR (471 MHz, $CDCl_3$)


7.8168
7.8106
7.8035
7.7942
7.7627
7.5992
7.5969
7.5820
7.5799
7.4932
7.4825
7.4775
7.4705
7.4632
7.4586
7.4479
7.2599
6.8925
6.8667
6.8606
6.3795
6.3653
6.3606
6.3525
5.4685
5.4231
5.3699
5.3253
3.8101
3.8014
3.7926
2.9097
2.8936
2.8816
2.8735
2.8658
2.8579
2.8456
2.8295
2.7937
2.7654
2.7299
2.6975
2.6908
2.6096
1HNMR gf-3-248bP in CDCl3
F
N
O
6f
1H NMR (500 MHz, CDCl3)
3.11
1.12
1.18
2.19
1.00
1.01
1.02
4.07
1.14
5.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

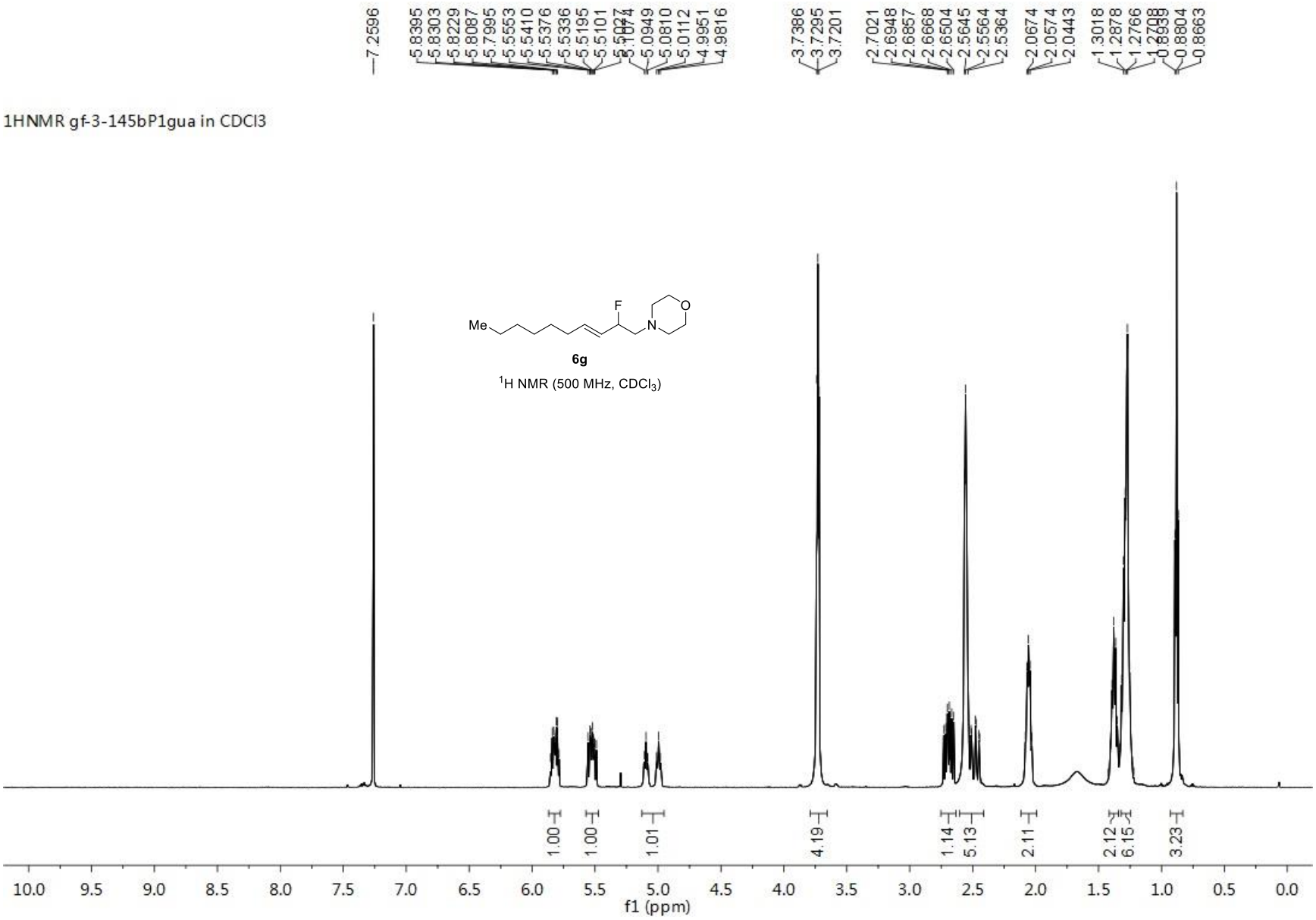

133.53
133.49
133.44
133.32
133.29
128.40
128.11
127.72
127.21
126.46
126.30
125.47
125.32
123.41
92.19
90.83
66.62
63.04
62.87
54.05
13CNMR gf-3-248bP in CDCl3
128.40
128.11
127.72
127.21
126.46
126.30
125.47
125.32
128.5
127.5
126.5
125.5
f1 (ppm)
F
O
N
6f
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

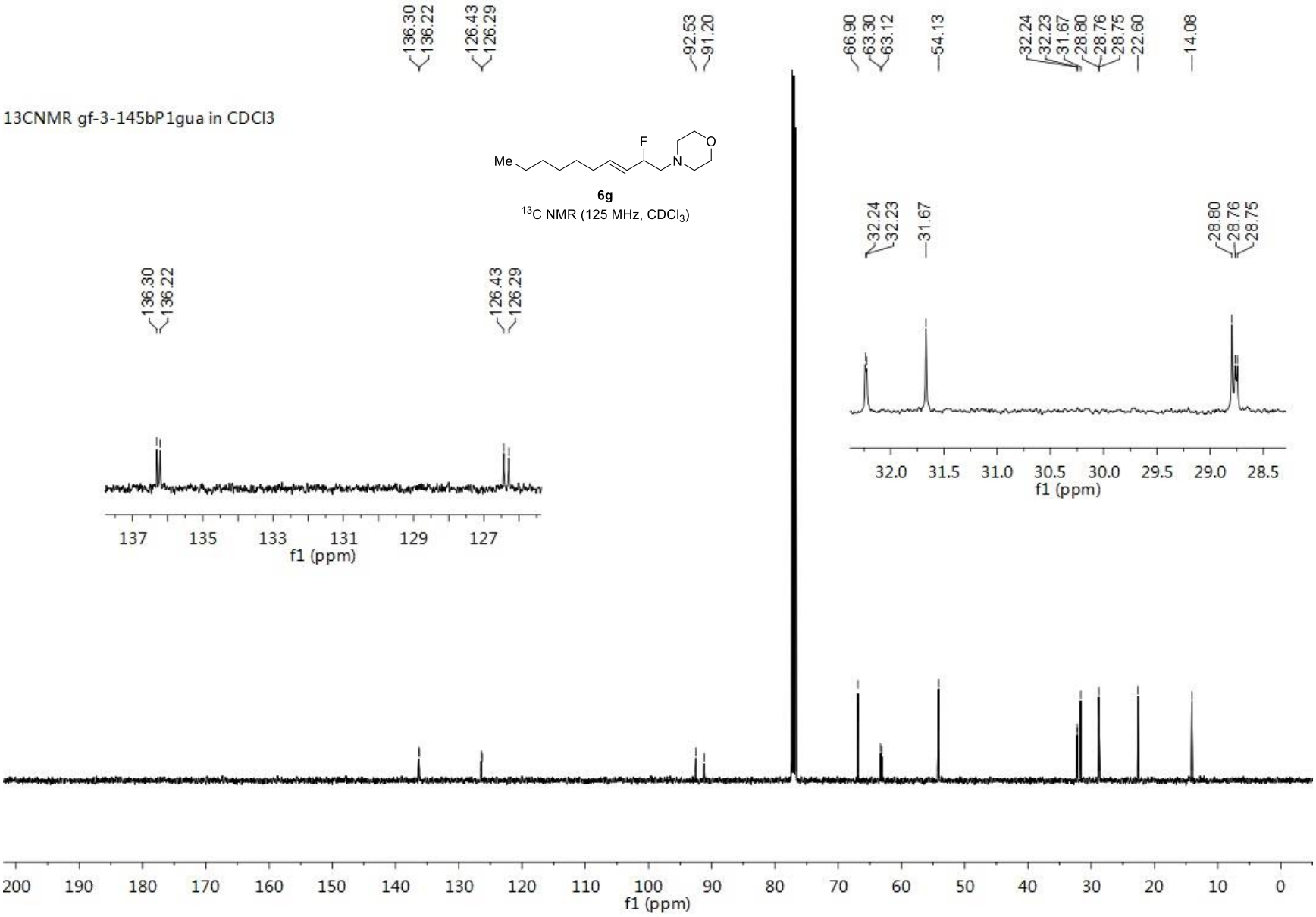
19FNMR gf-3-248bP in CDCl3



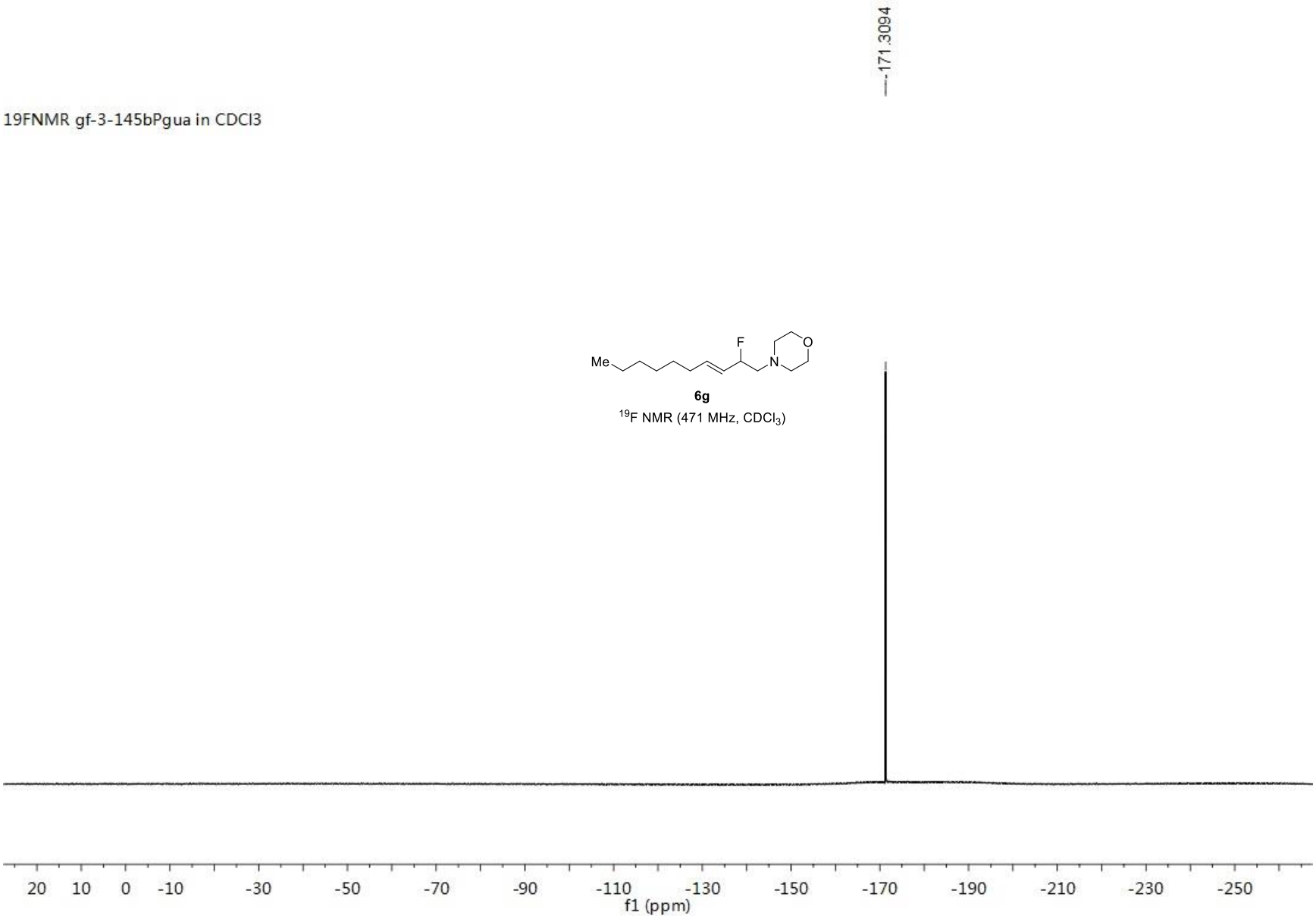
6f

^{19}F NMR (471 MHz, $CDCl_3$)


7.2596
5.8395
5.8303
5.8229
5.8087
5.7995
5.5553
5.5410
5.5376
5.5336
5.5195
5.5101
5.0949
5.0810
5.0112
4.9951
4.9816
3.7386
3.7295
3.7201
2.7021
2.6948
2.6857
2.6668
2.6504
2.5645
2.5564
2.5364
2.0674
2.0574
2.0443
1.3018
1.2878
1.2766
0.8939
0.8804
0.8663
1HNMR gf-3-145bP1gua in CDCl3
Me
F
N
O
6g
1H NMR (500 MHz, CDCl3)
1.00
1.00
1.01
4.19
1.14
5.13
2.11
2.12
6.15
3.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

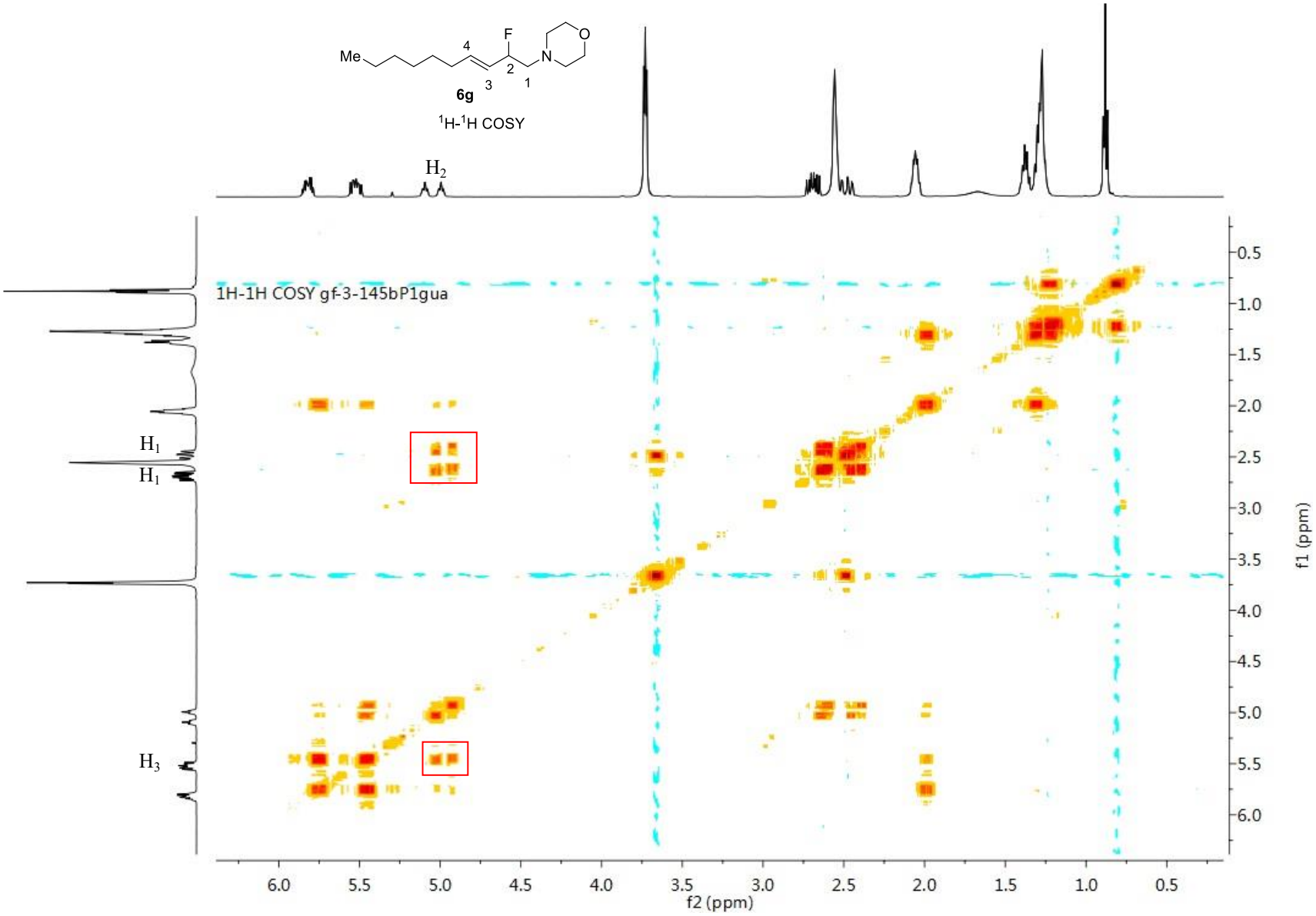

13CNMR gf-3-145bP1gua in CDCl3
136.30
136.22
126.43
126.29
92.53
91.20
66.90
63.30
63.12
54.13
32.24
32.23
31.67
28.80
28.76
28.75
22.60
14.08
Me
F
O
N
6g
13C NMR (125 MHz, CDCl3)
f1 (ppm)

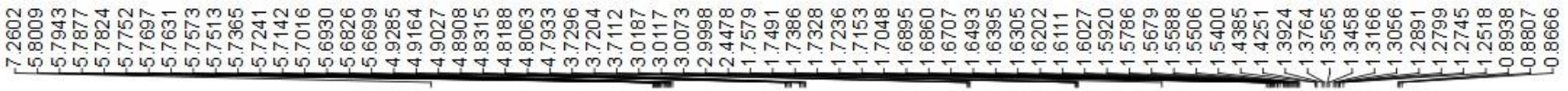
19FNMR gf-3-145bPgua in CDCl3



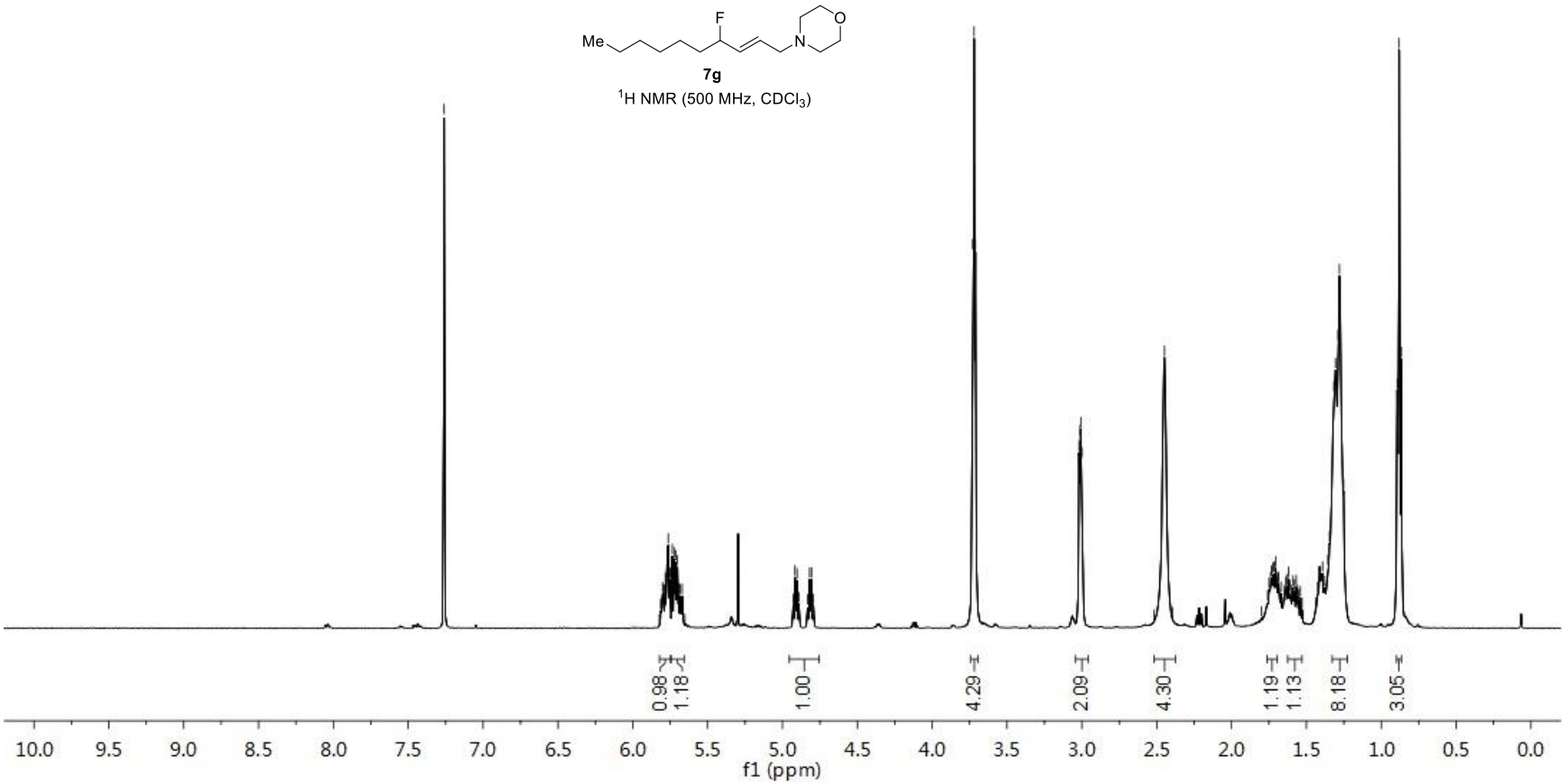
6g

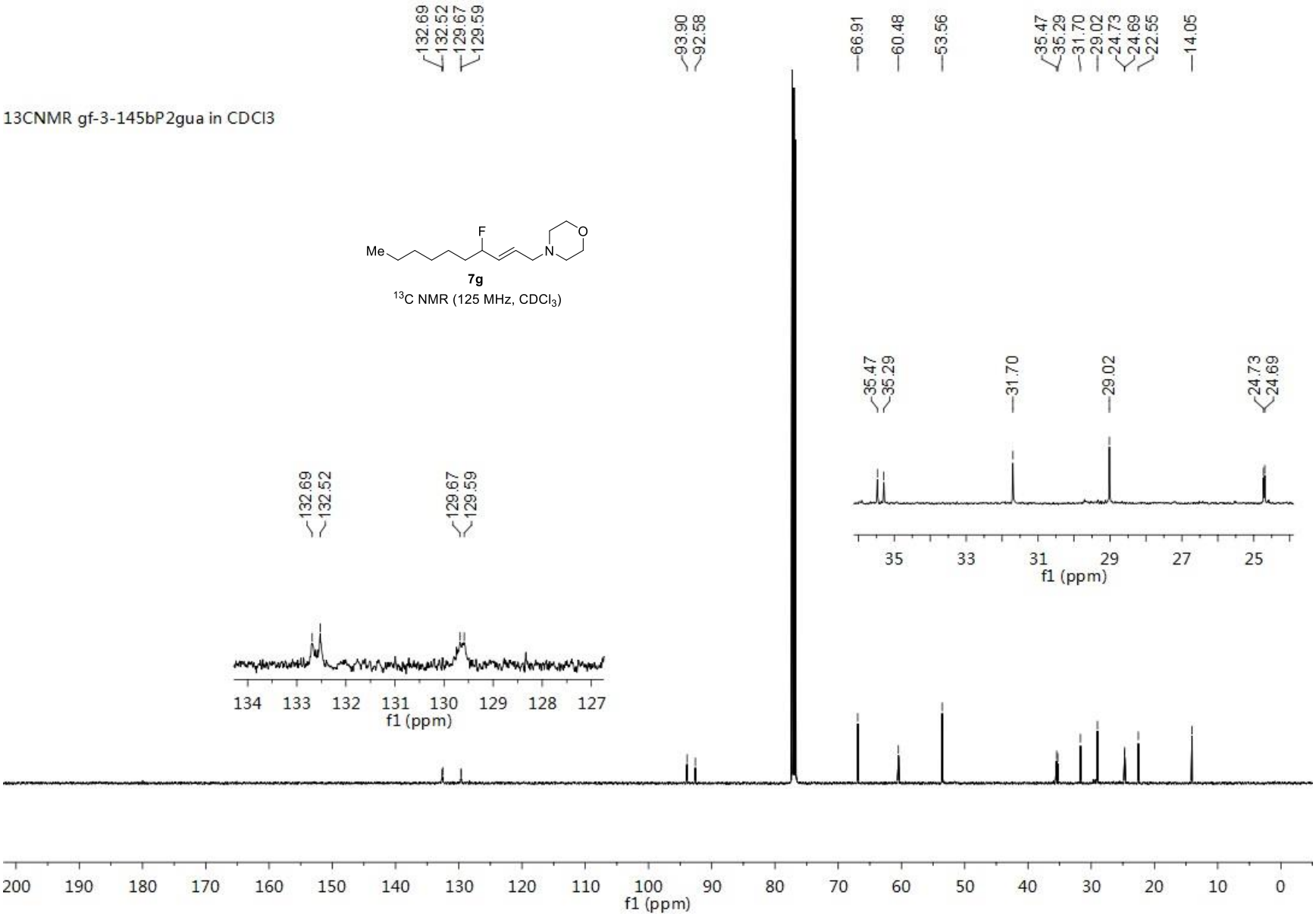
^{19}F NMR (471 MHz, $CDCl_3$)


Me
4
F
O
2
N
3
1
6g
^{1}H-^{1}H COSY
H$_2$
1H-1H COSY gf-3-145bP1gua
H$_1$
H$_1$
H$_3$
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
f1 (ppm)

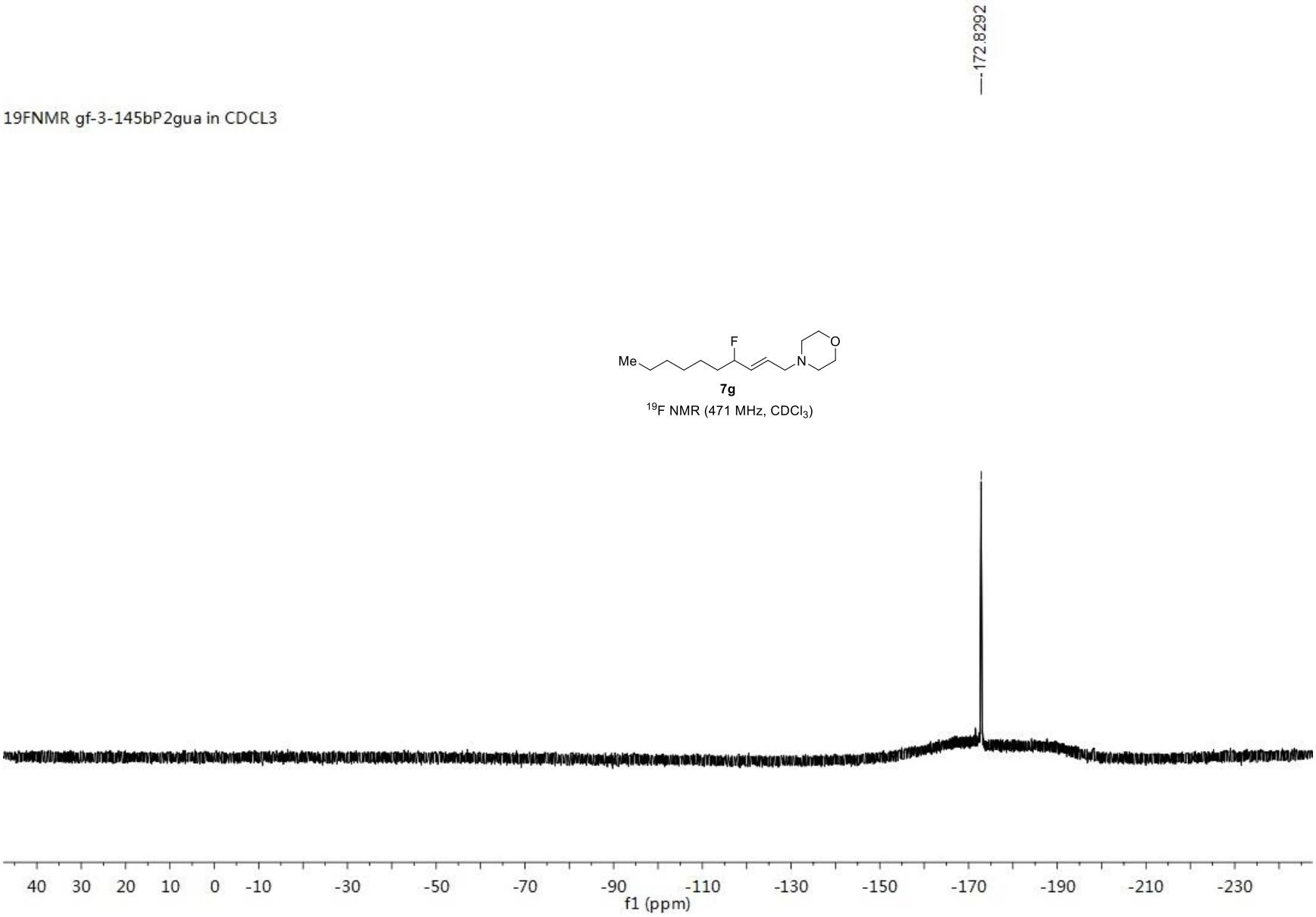


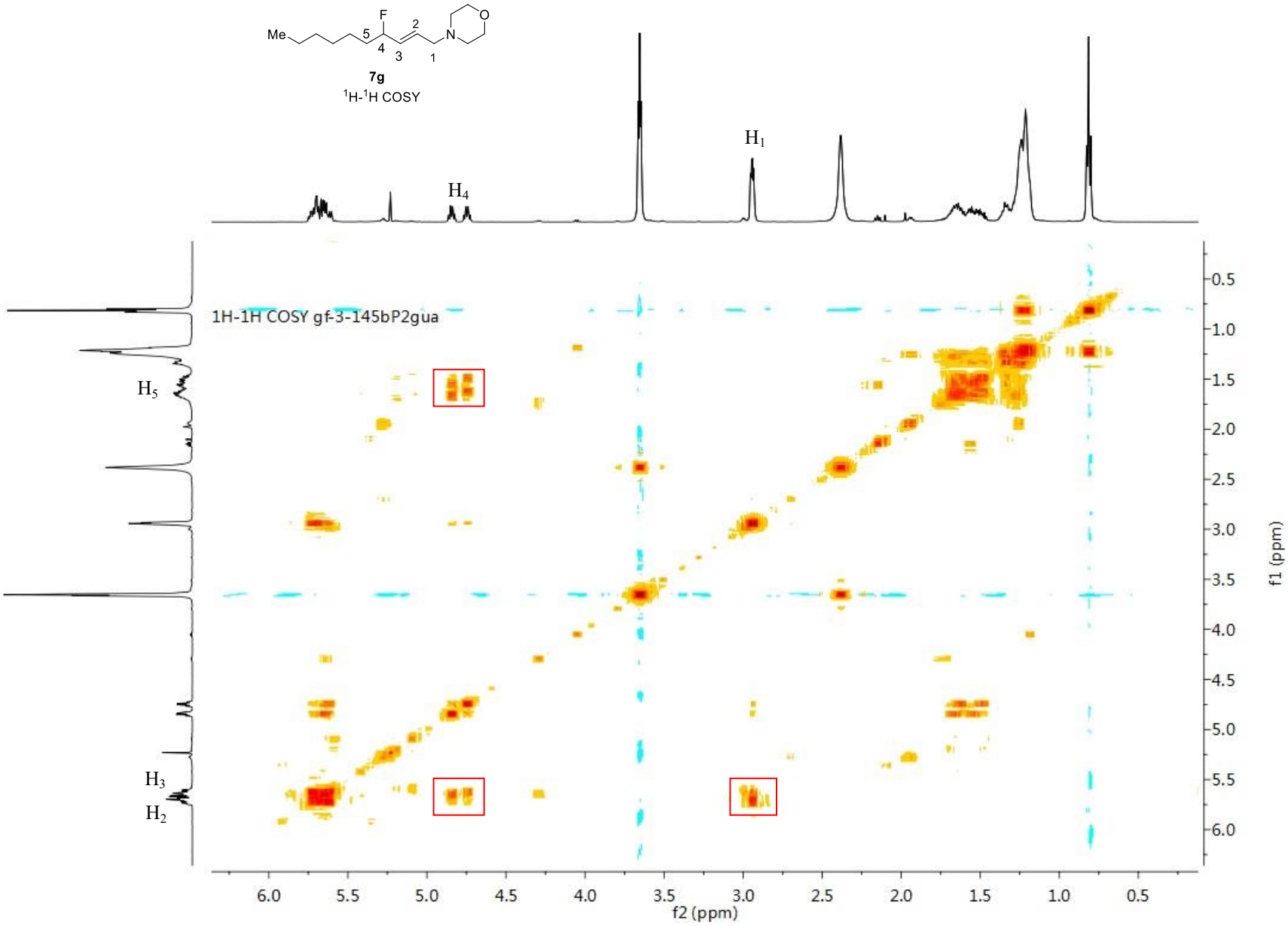
1HNMR gf-3-145bP2 in CDCl3

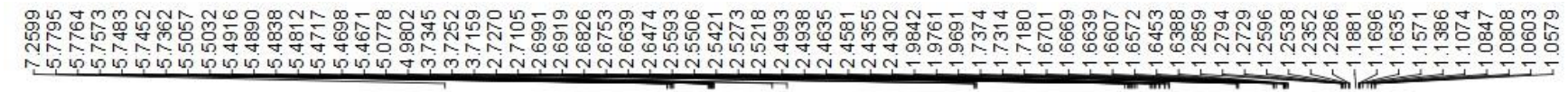



13CNMR gf-3-145bP2gua in CDCl3
132.69
132.52
129.67
129.59
93.90
92.58
66.91
60.48
53.56
35.47
35.29
31.70
29.02
24.73
24.69
22.55
14.05
Me
F
N
O
7g
13C NMR (125 MHz, CDCl3)
f1 (ppm)

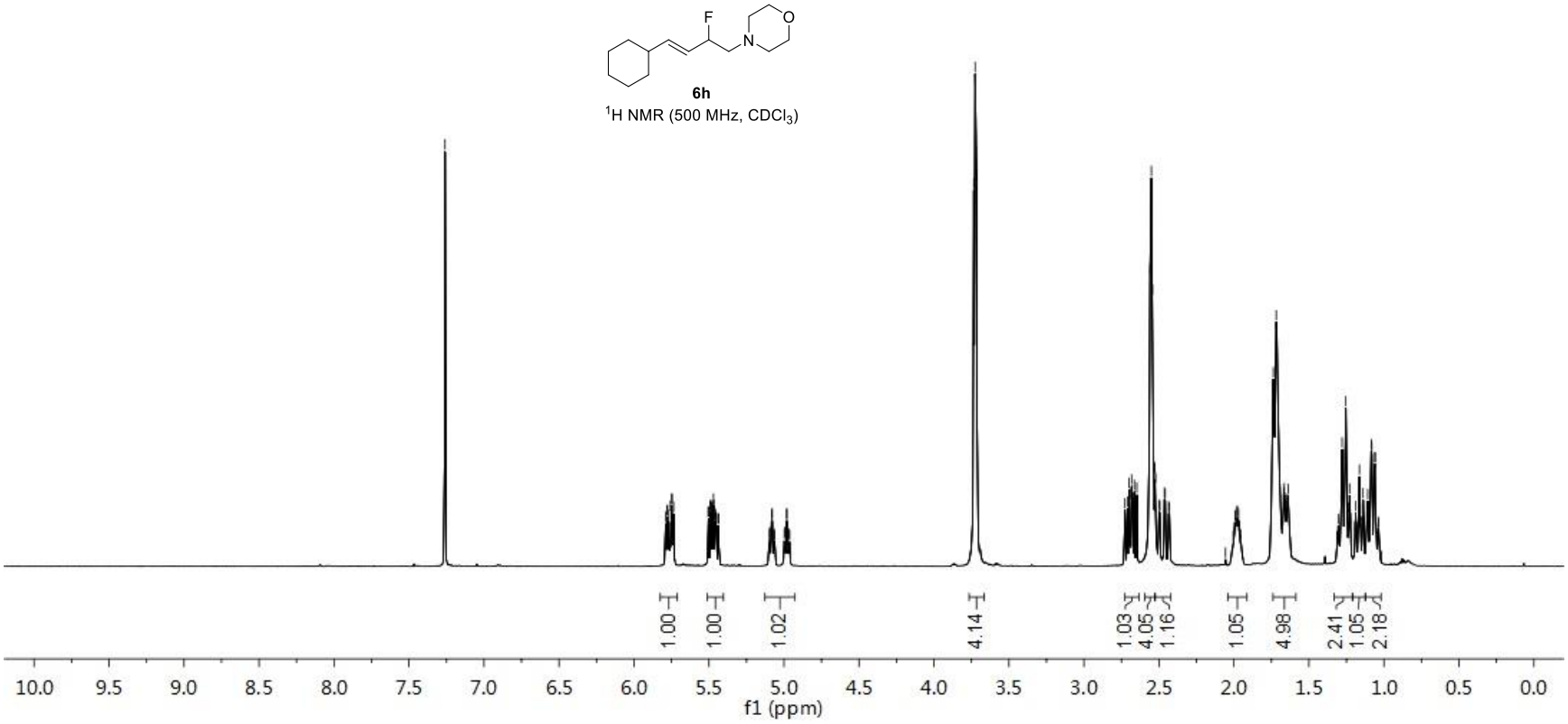
19FNMR gf-3-145bP2gua in CDCL3

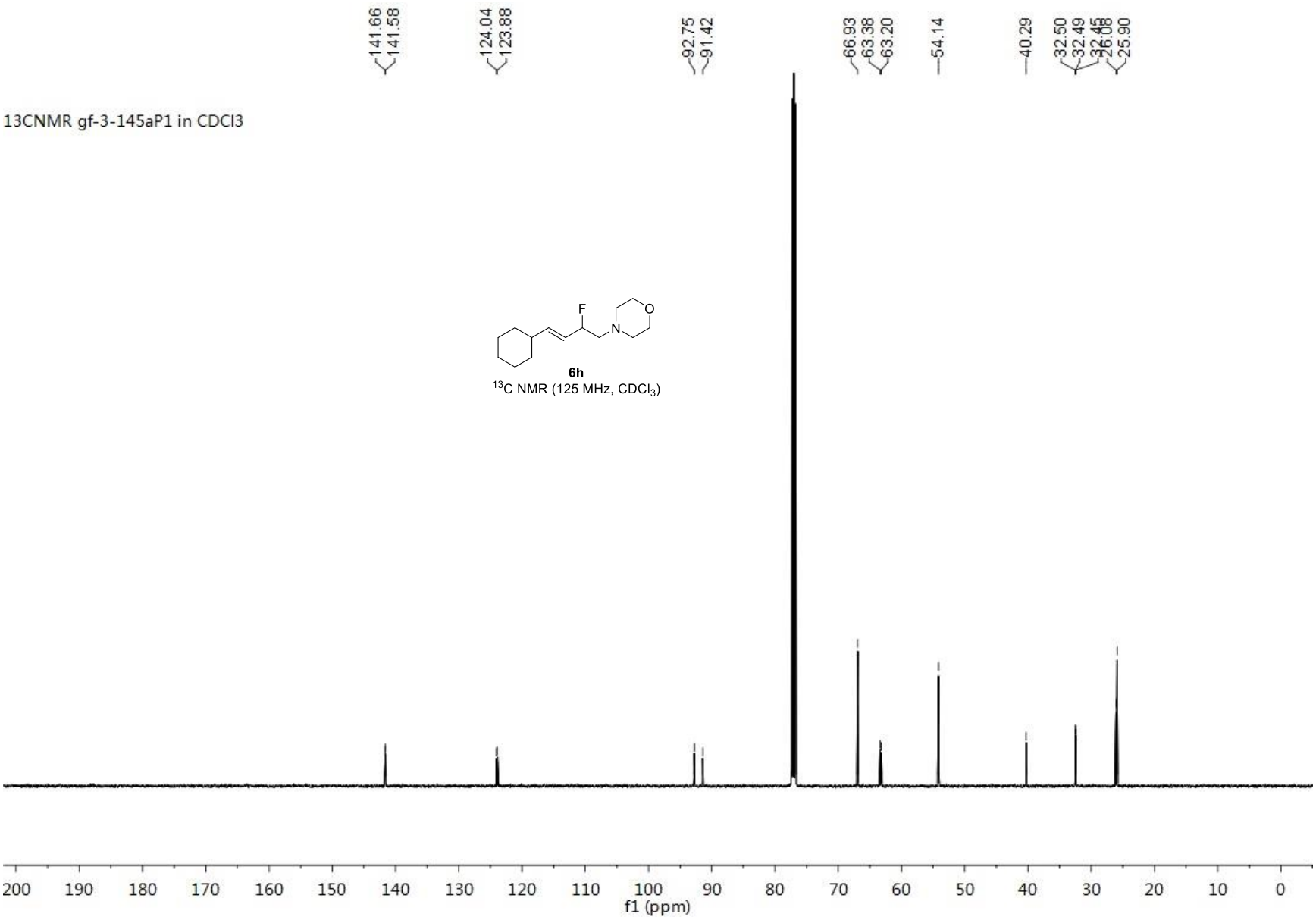



F
Me
5
4
3
2
1
N
O
7g
^{1}H-^{1}H COSY
H$_1$
H$_4$
H$_5$
H$_3$
H$_2$
1H-1H COSY gf-3-145bP2gua
f2 (ppm)
f1 (ppm)

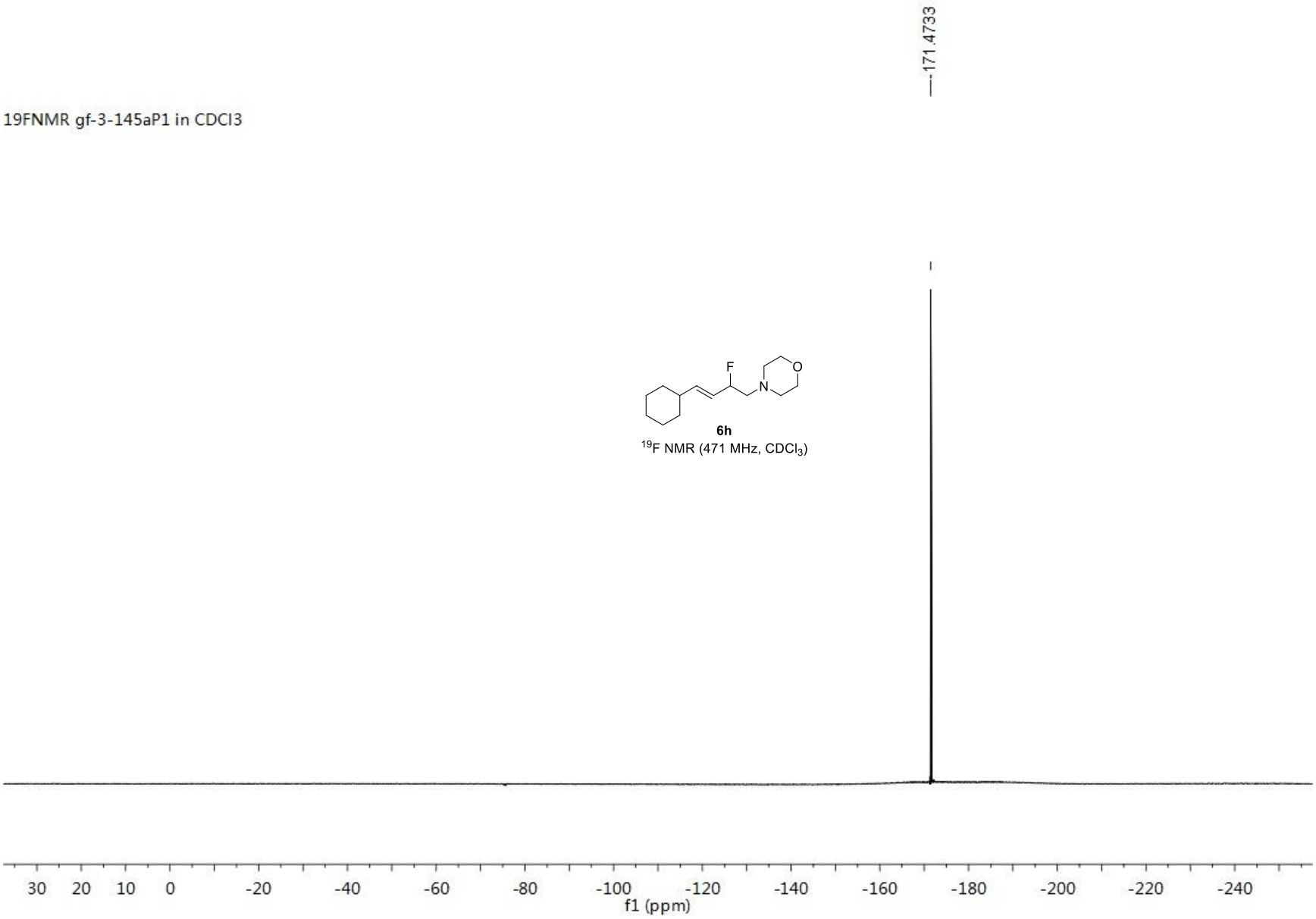


1HNMR gf-3-145aP1 in CDCl3



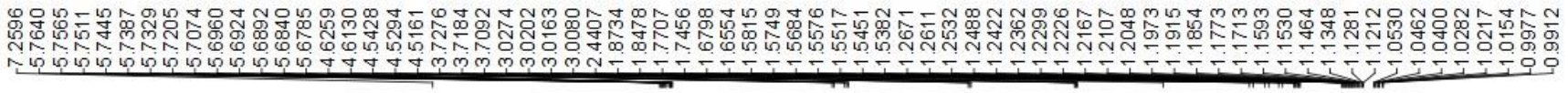

141.66
141.58
124.04
123.88
92.75
91.42
66.93
63.38
63.20
54.14
40.29
32.50
32.49
32.45
26.08
25.90
13CNMR gf-3-145aP1 in CDCl3
F
N
O
6h
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

19FNMR gf-3-145aP1 in CDCl3

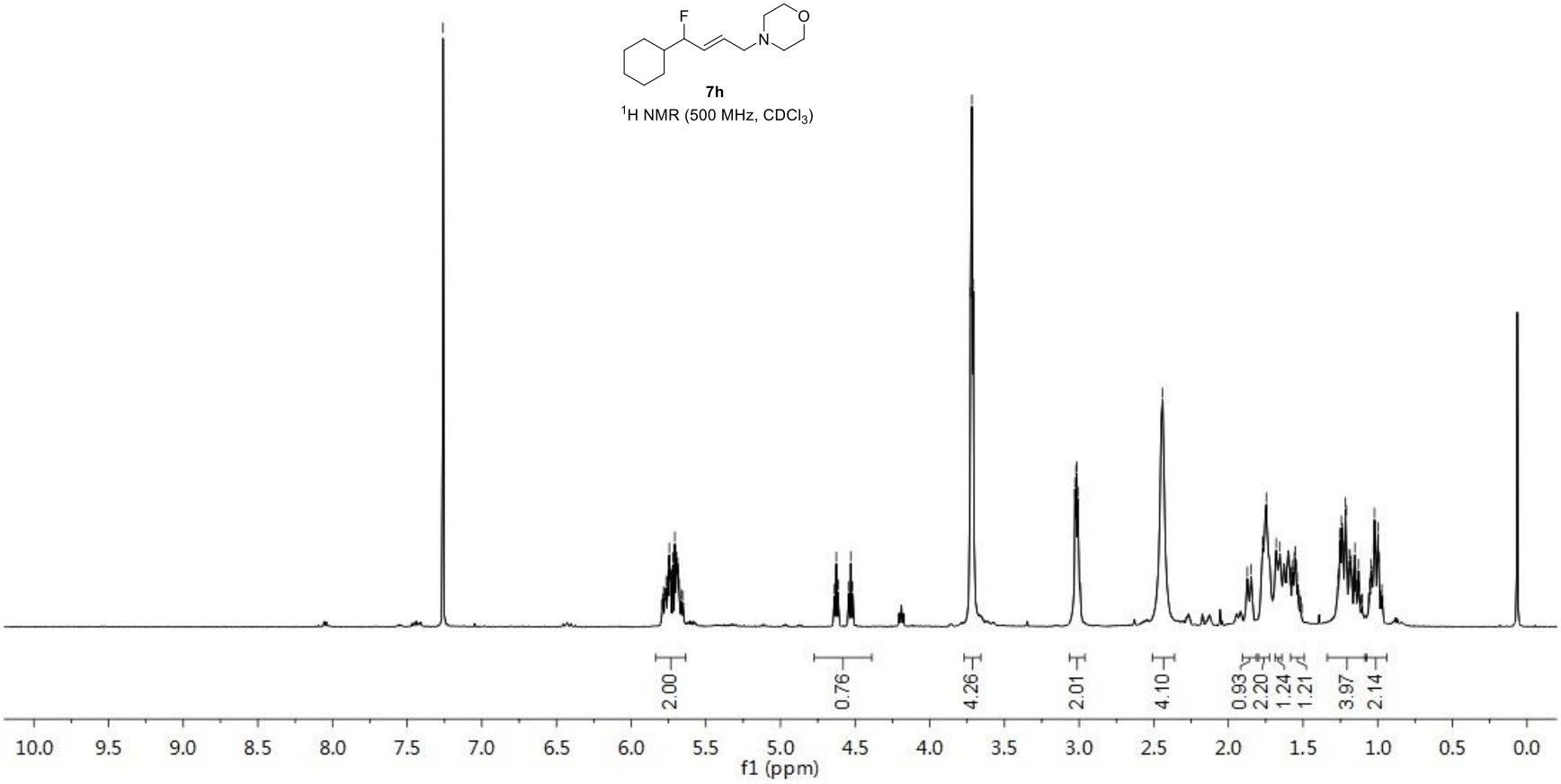


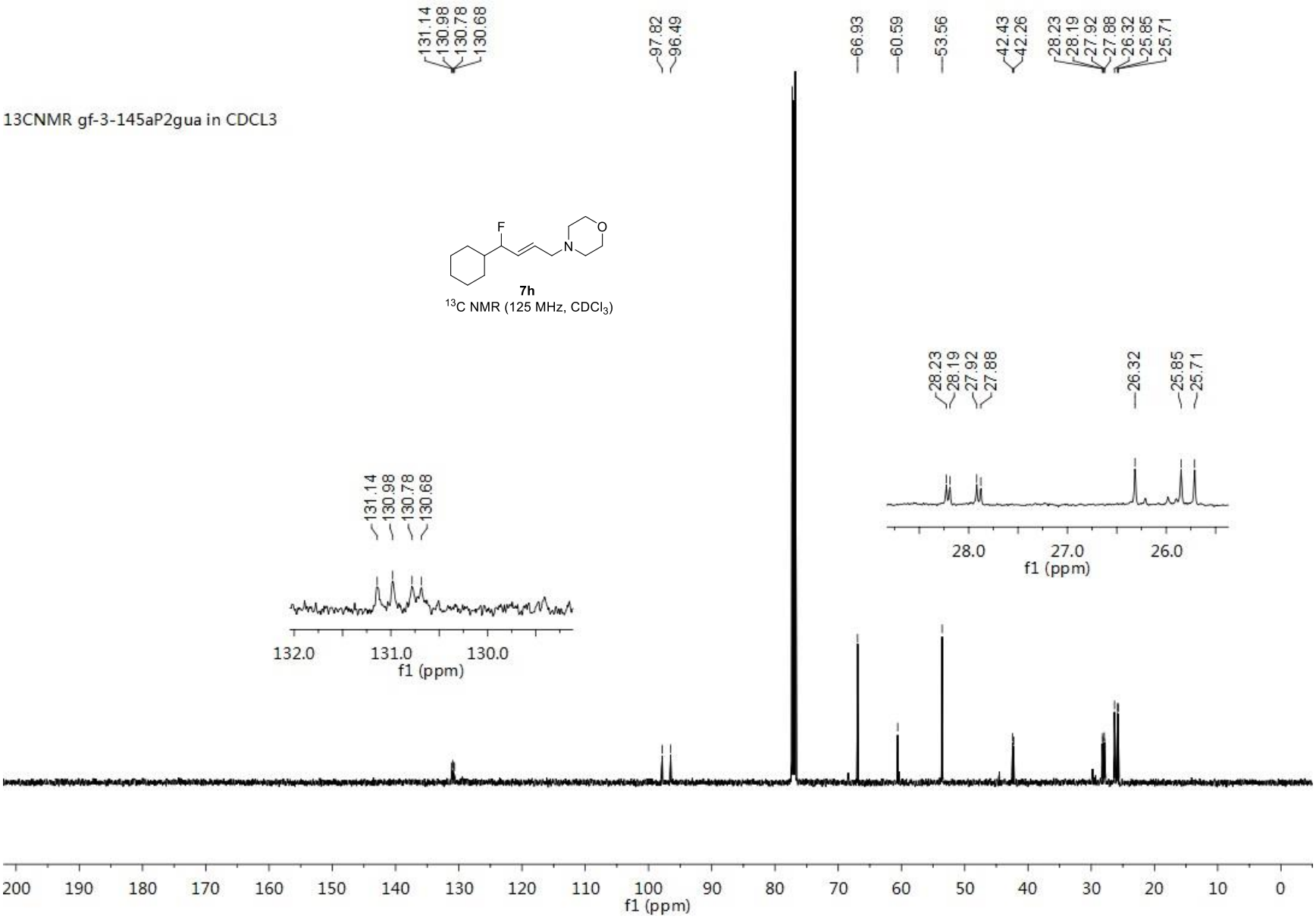
6h

^{19}F NMR (471 MHz, $CDCl_3$)



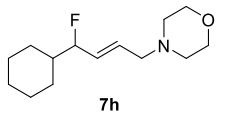
1HNMR gf-3-145aP2 in CDCl3




13CNMR gf-3-145aP2gua in CDCL3
131.14
130.98
130.78
130.68
97.82
96.49
66.93
60.59
53.56
42.43
42.26
28.23
28.19
27.92
27.88
26.32
25.85
25.71
F
O
N
7h
13C NMR (125 MHz, CDCl3)
132.0
131.0
130.0
f1 (ppm)
28.0
27.0
26.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

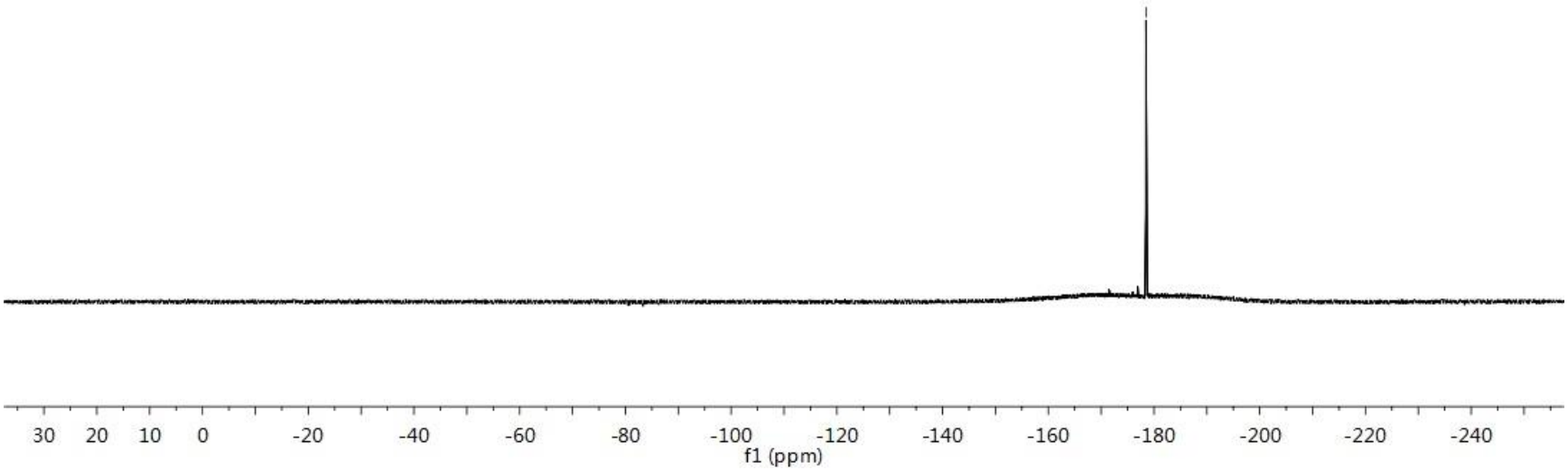
19FNMR gf-3-145aP2 in CDCl3

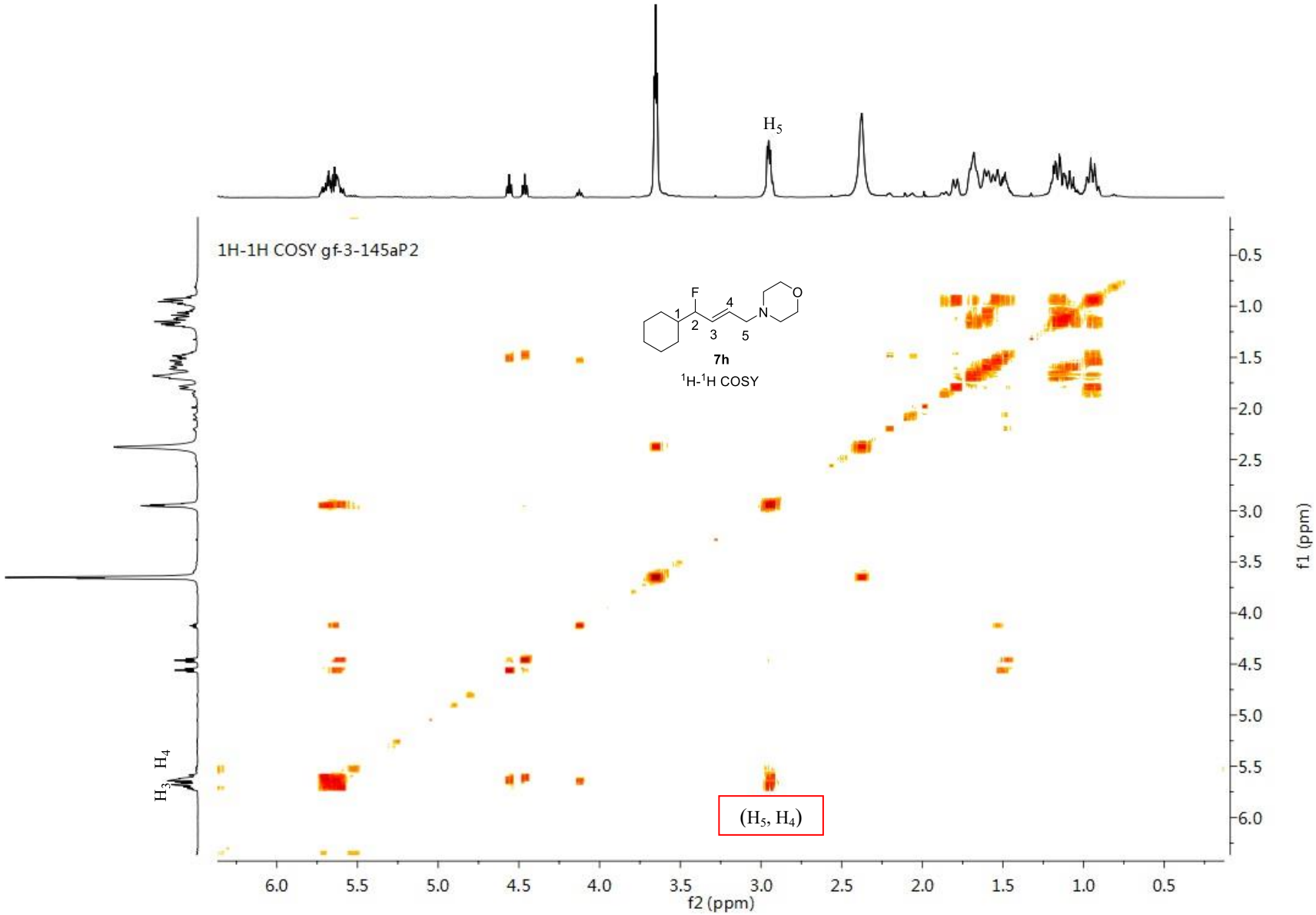
-178.4836

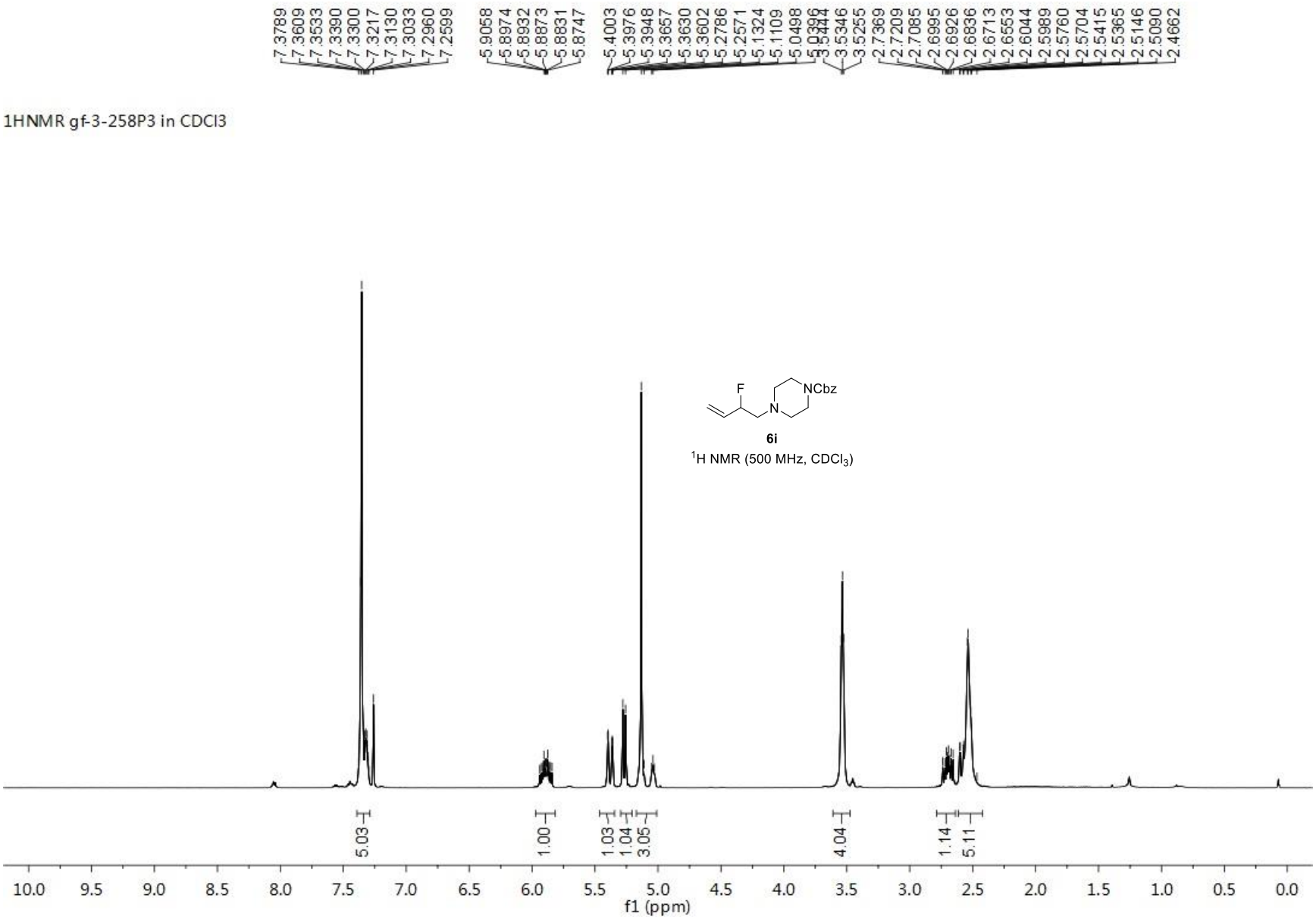


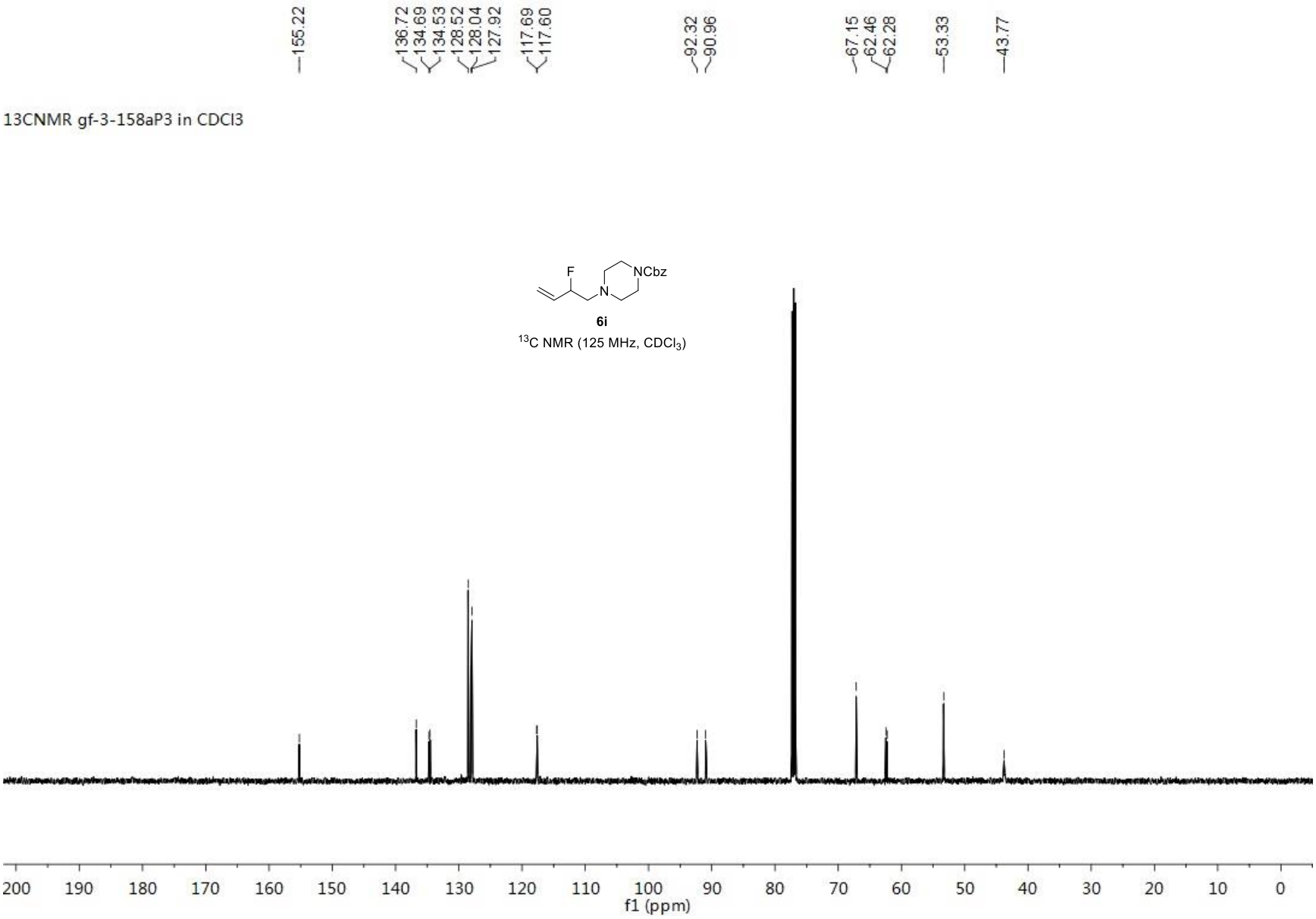
7h

^{19}F NMR (471 MHz, $CDCl_3$)



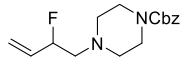

1H-1H COSY gf-3-145aP2
H5
H3, H4
(H5, H4)
7h
1H-1H COSY
f2 (ppm)
f1 (ppm)


7.3789
7.3609
7.3533
7.3390
7.3300
7.3217
7.3130
7.3033
7.2960
7.2599
5.9058
5.8974
5.8932
5.8873
5.8831
5.8747
5.4003
5.3976
5.3948
5.3657
5.3630
5.3602
5.2786
5.2571
5.1324
5.1109
5.0498
3.5346
3.5255
2.7369
2.7209
2.7085
2.6995
2.6926
2.6836
2.6713
2.6553
2.6044
2.5989
2.5760
2.5704
2.5415
2.5365
2.5146
2.5090
2.4662
1HNMR gf-3-258P3 in CDCl3
F
NCbz
N
6i
1H NMR (500 MHz, CDCl3)
5.03
1.00
1.03
1.04
3.05
4.04
1.14
5.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


155.22
136.72
134.69
134.53
128.52
128.04
127.92
117.69
117.60
92.32
90.96
67.15
62.46
62.28
53.33
43.77
13CNMR gf-3-158aP3 in CDCl3
F
N
NCbz
6i
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

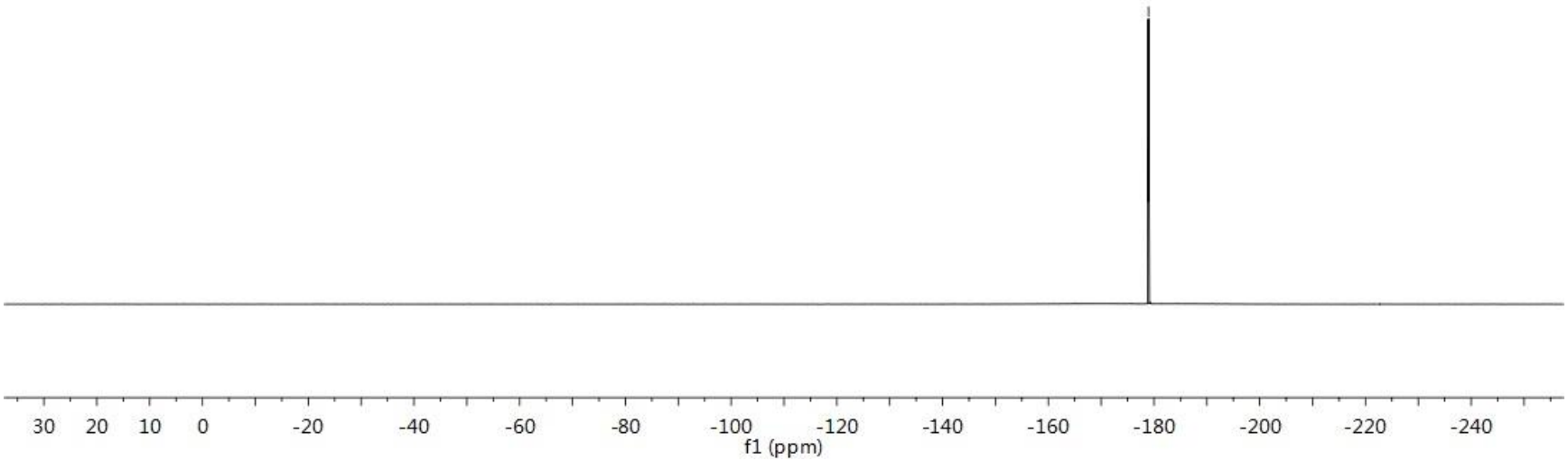
19FNMR gf-3-158aP3 in CDCl3

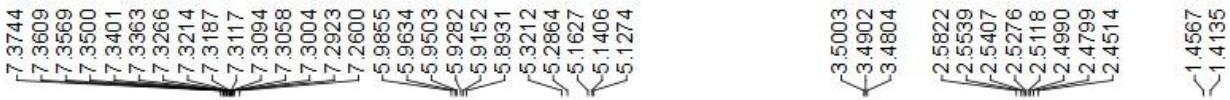
-178.9649



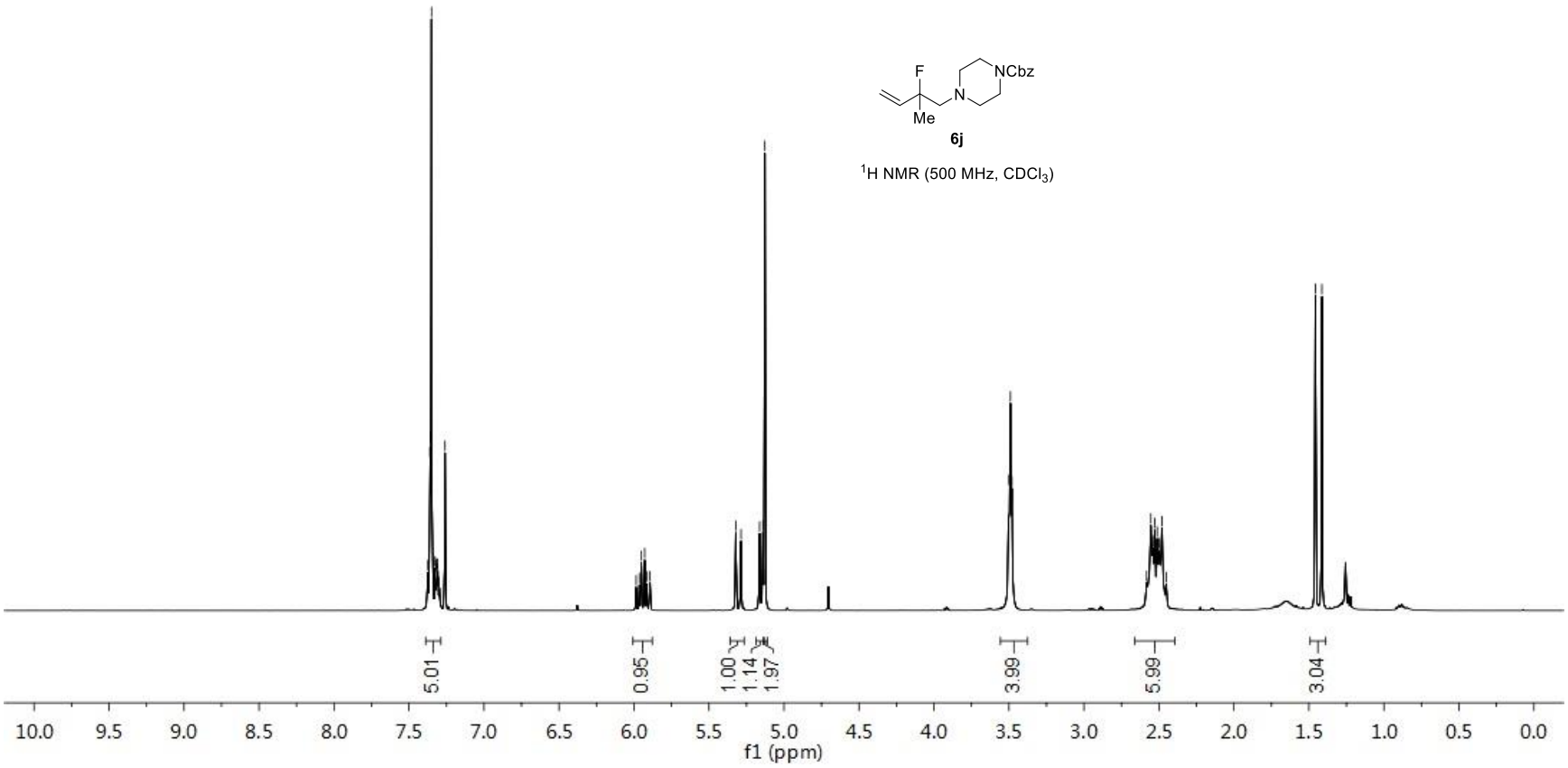
6i

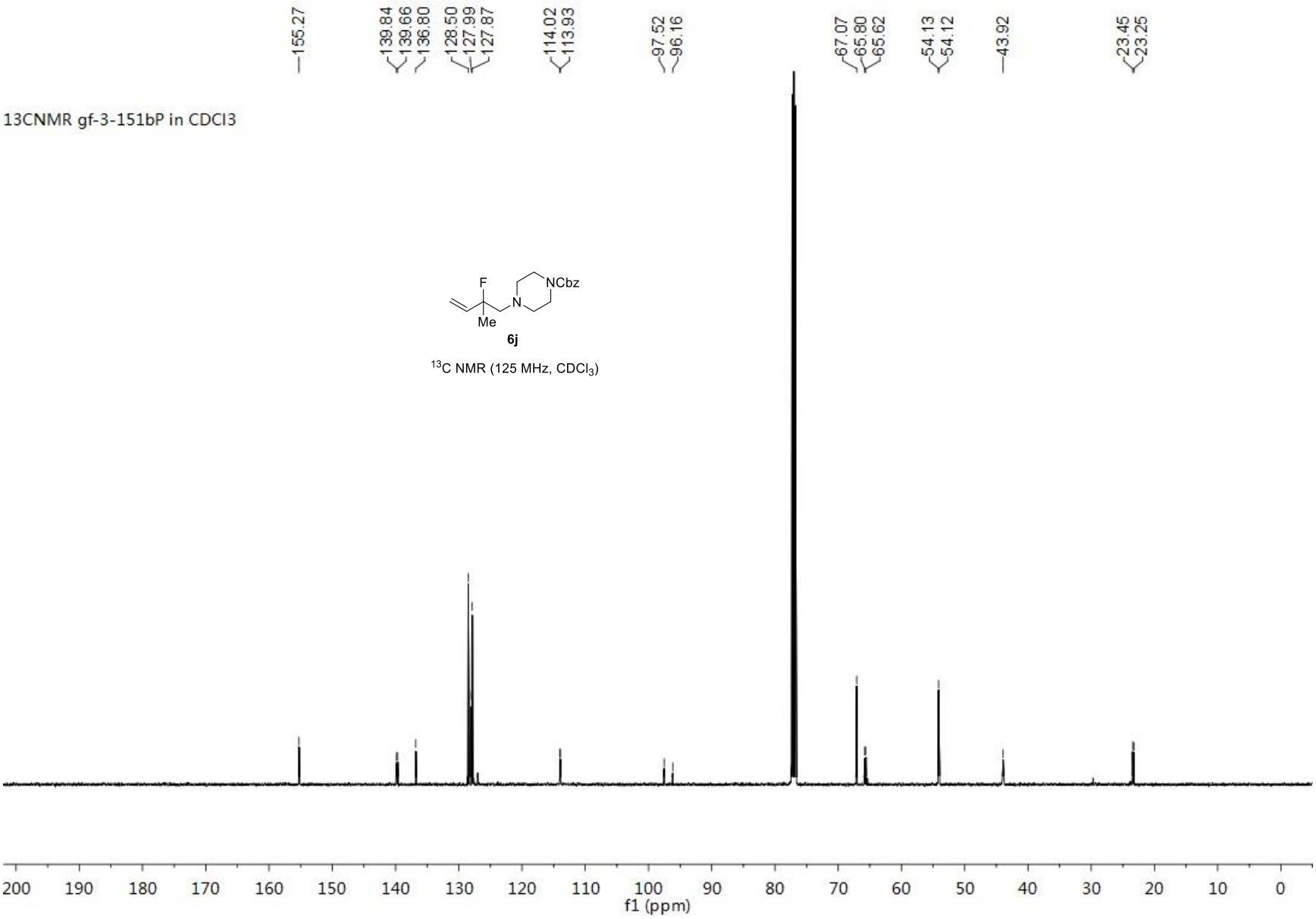
^{19}F NMR (471 MHz, $CDCl_3$)





1HNMR gf-3-151bP in CDCl3



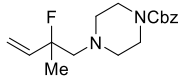


6j

^{13}C NMR (125 MHz, $CDCl_3$)

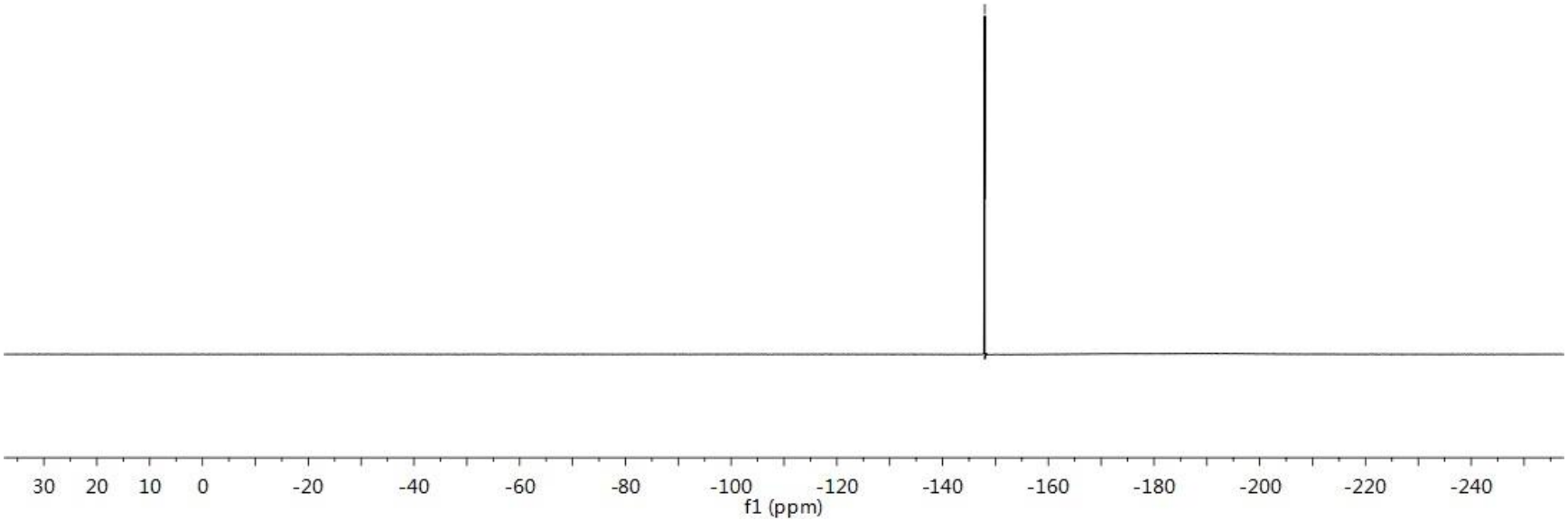
19FNMR gf-3-151bP1 in CDCl3

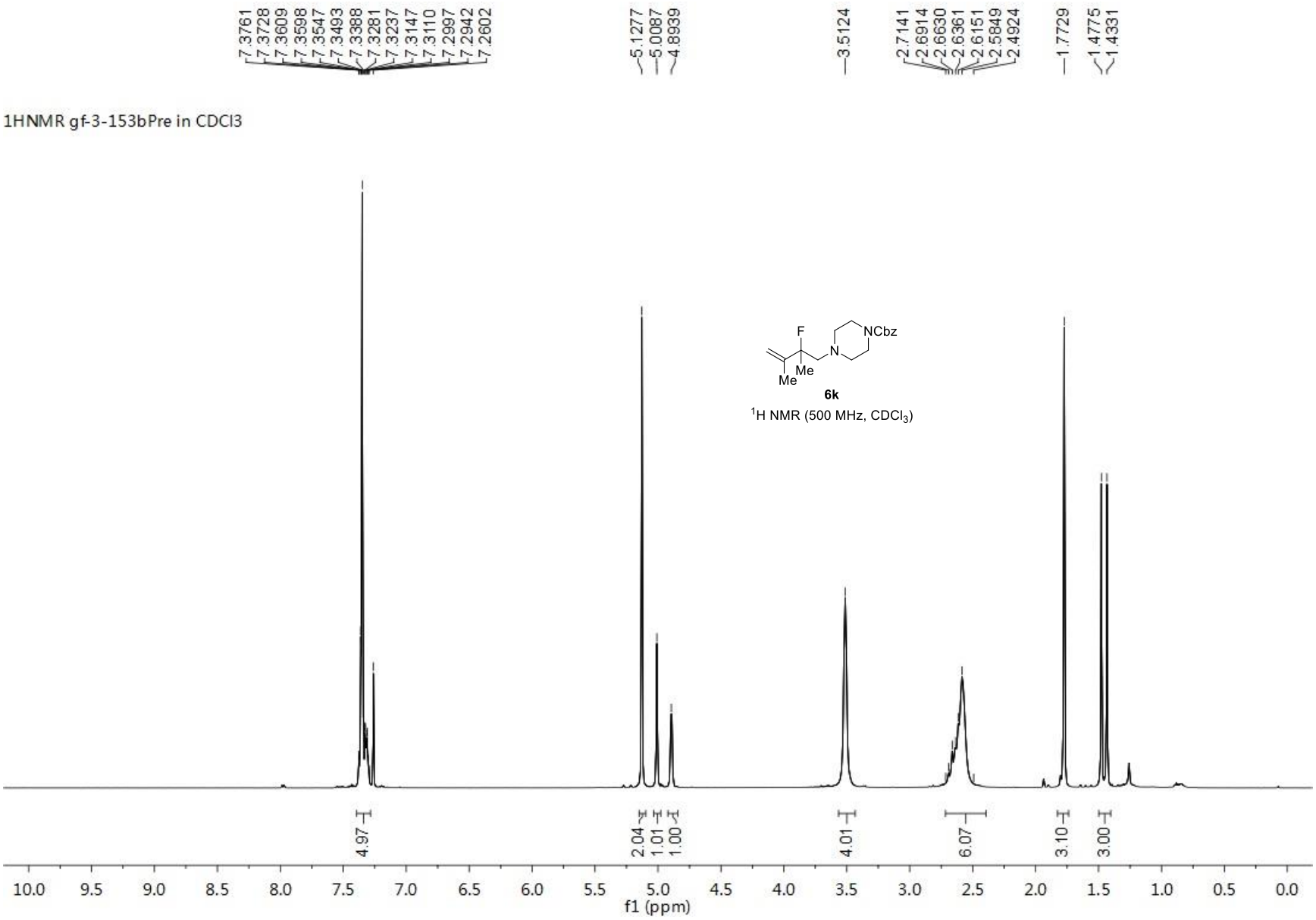
-147.9854

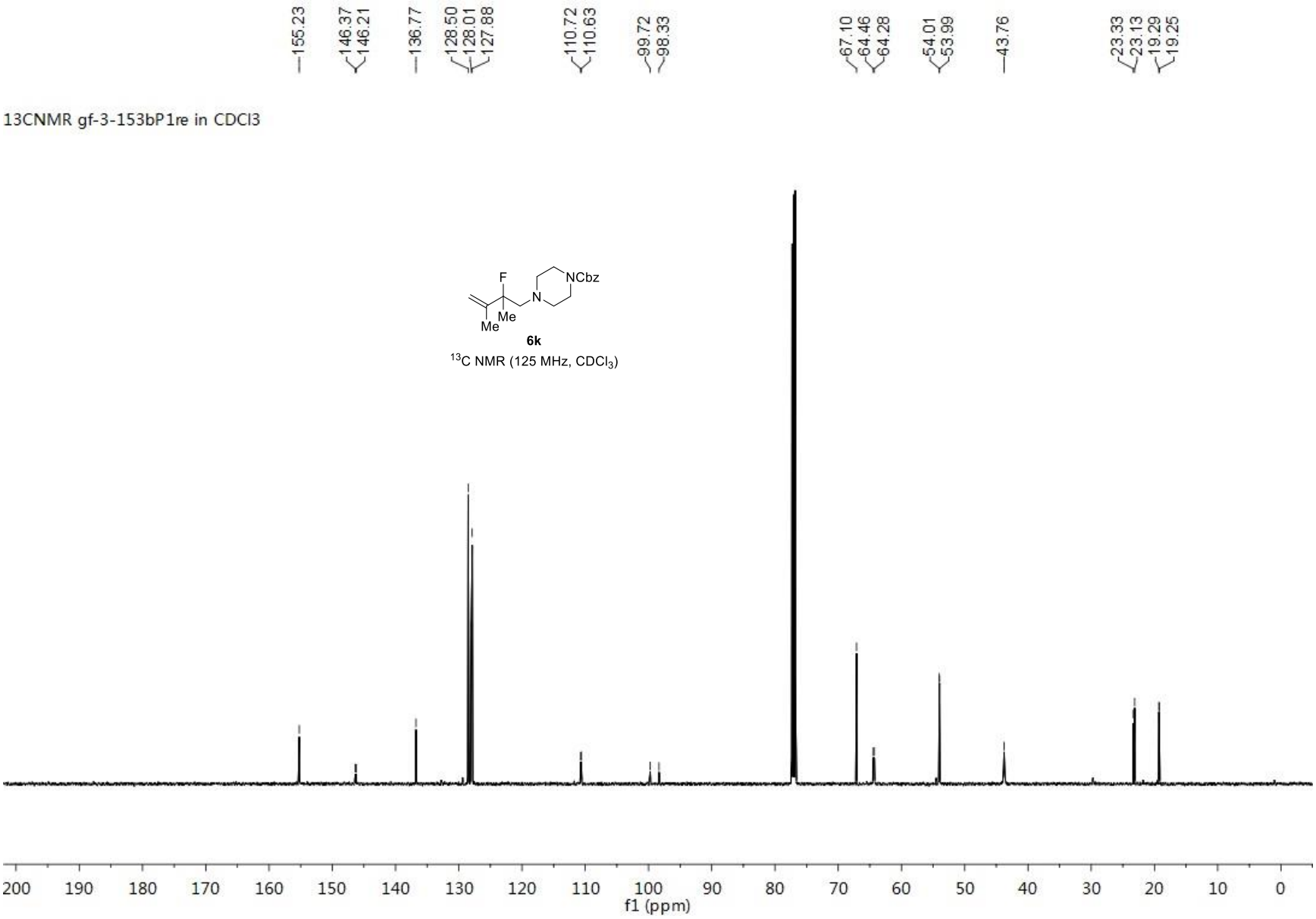


6j

^{19}F NMR (471 MHz, $CDCl_3$)

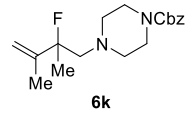



7.3761
7.3728
7.3609
7.3598
7.3547
7.3493
7.3388
7.3281
7.3237
7.3147
7.3110
7.2997
7.2942
7.2602
5.1277
5.0087
4.8939
3.5124
2.7141
2.6914
2.6630
2.6361
2.6151
2.5849
2.4924
1.7729
1.4775
1.4331
1HNMR gf-3-153bPre in CDCl3
F
NCbz
N
Me
Me
6k
1H NMR (500 MHz, CDCl3)
4.97
2.04
1.01
1.00
4.01
6.07
3.10
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


155.23
146.37
146.21
136.77
128.50
128.01
127.88
110.72
110.63
99.72
98.33
67.10
64.46
64.28
54.01
53.99
43.76
23.33
23.13
19.29
19.25
13CNMR gf-3-153bP1re in CDCl3
F
NCbz
N
Me
Me
6k
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

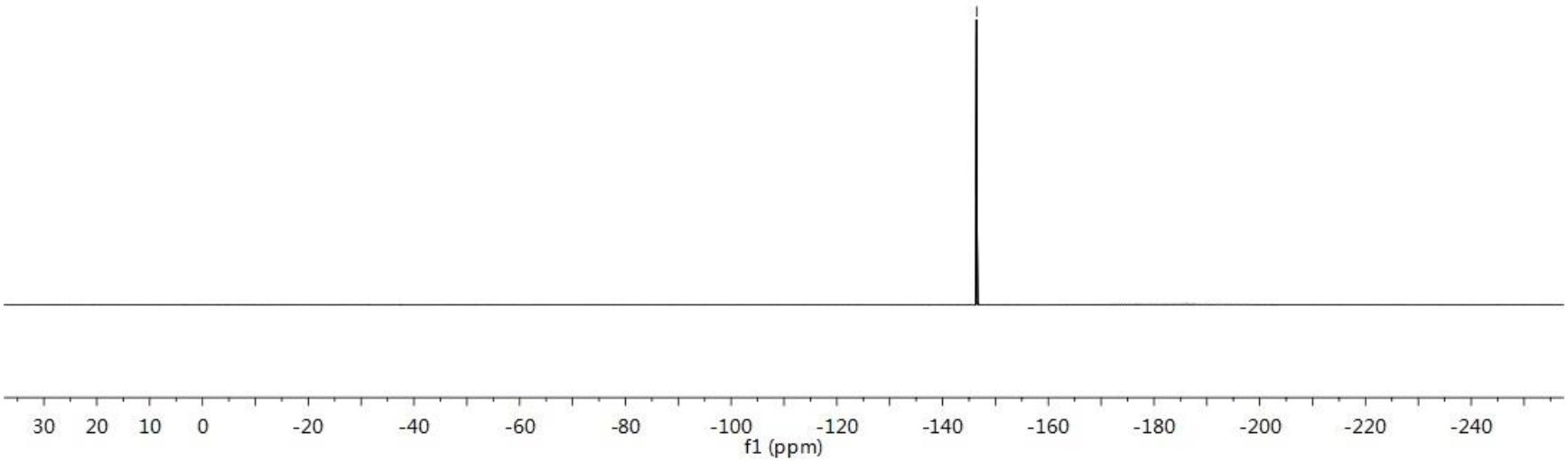
19FNMR gf-3-153bP1 in CDCl3

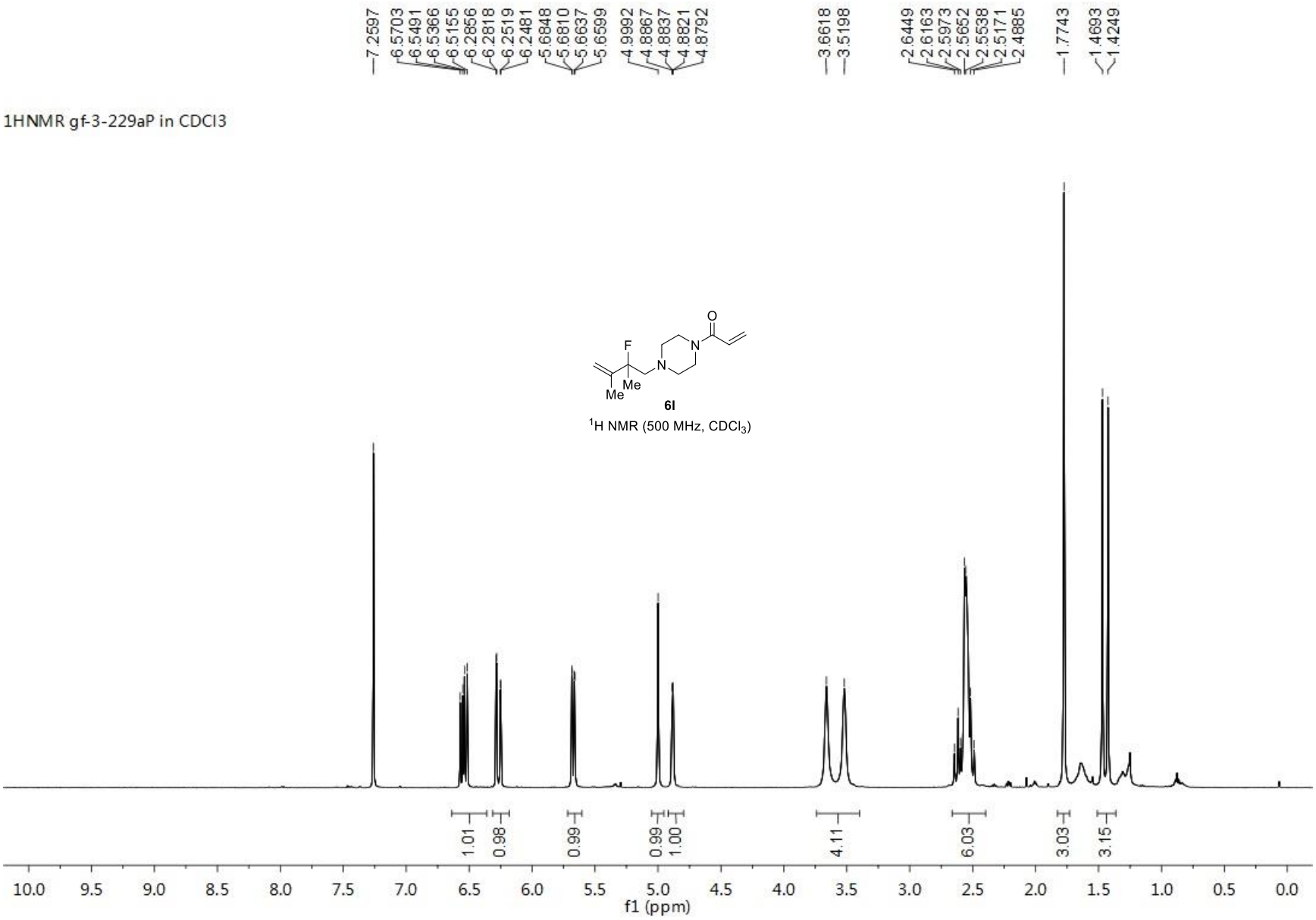
-146.4459



6k

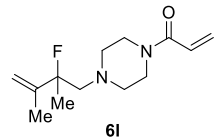
^{19}F NMR (471 MHz, $CDCl_3$)




7.2597
6.5703
6.5491
6.5366
6.5155
6.2856
6.2818
6.2519
6.2481
5.6848
5.6810
5.6637
5.6599
4.9992
4.8867
4.8837
4.8821
4.8792
3.6618
3.5198
2.6449
2.6163
2.5973
2.5652
2.5538
2.5171
2.4885
1.7743
1.4693
1.4249
1HNMR gf-3-229aP in CDCl3
F
N
N
O
Me
Me
6l
1H NMR (500 MHz, CDCl3)
1.01
0.98
0.99
0.99
1.00
4.11
6.03
3.03
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

165.31
146.47
146.31
127.67
127.54
110.56
110.47
99.88
98.49
64.43
64.26
54.41
54.09
45.89
42.10
23.35
23.15
19.32
19.28

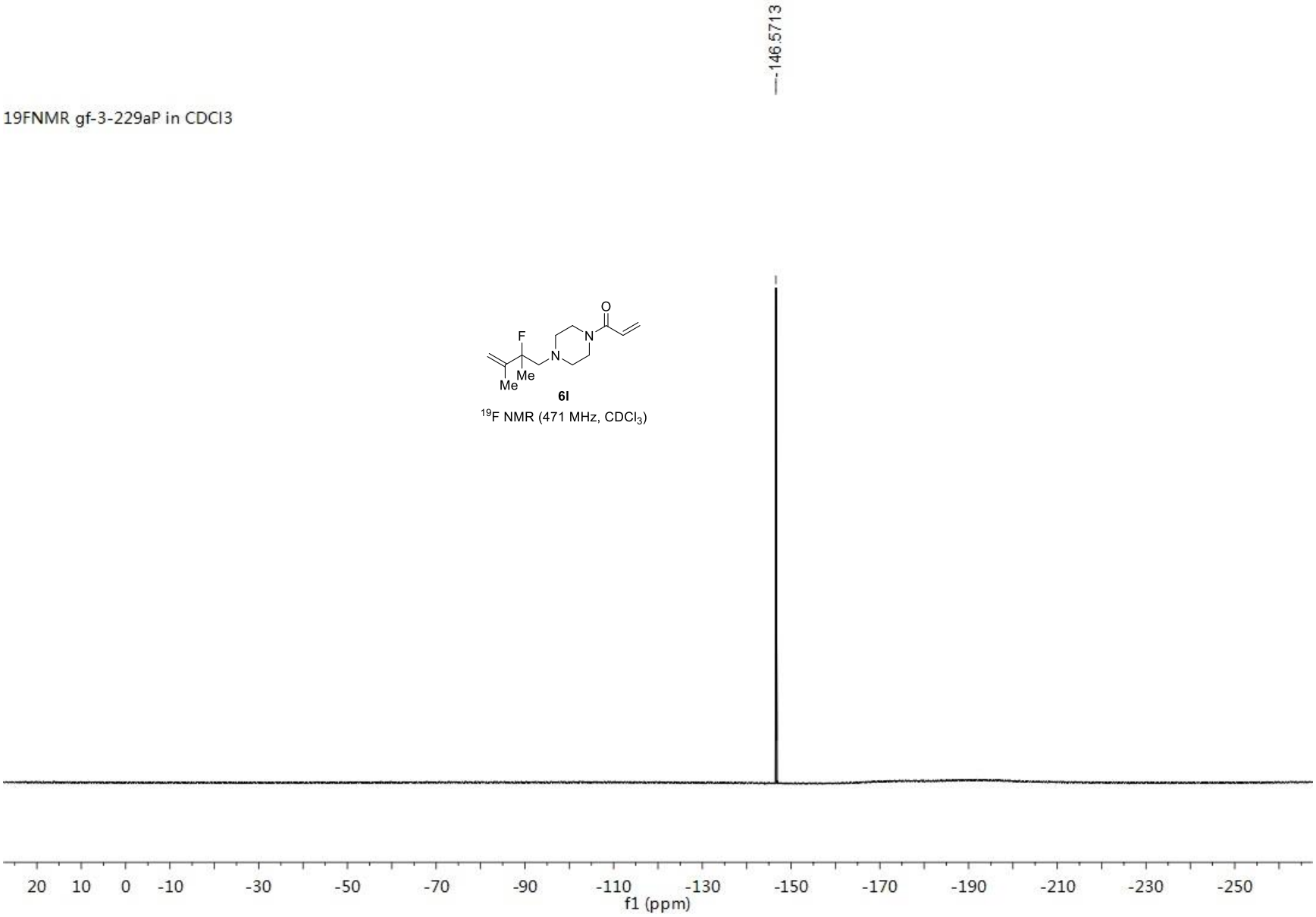
13CNMR gf-3-229PP in CDCl3



6l

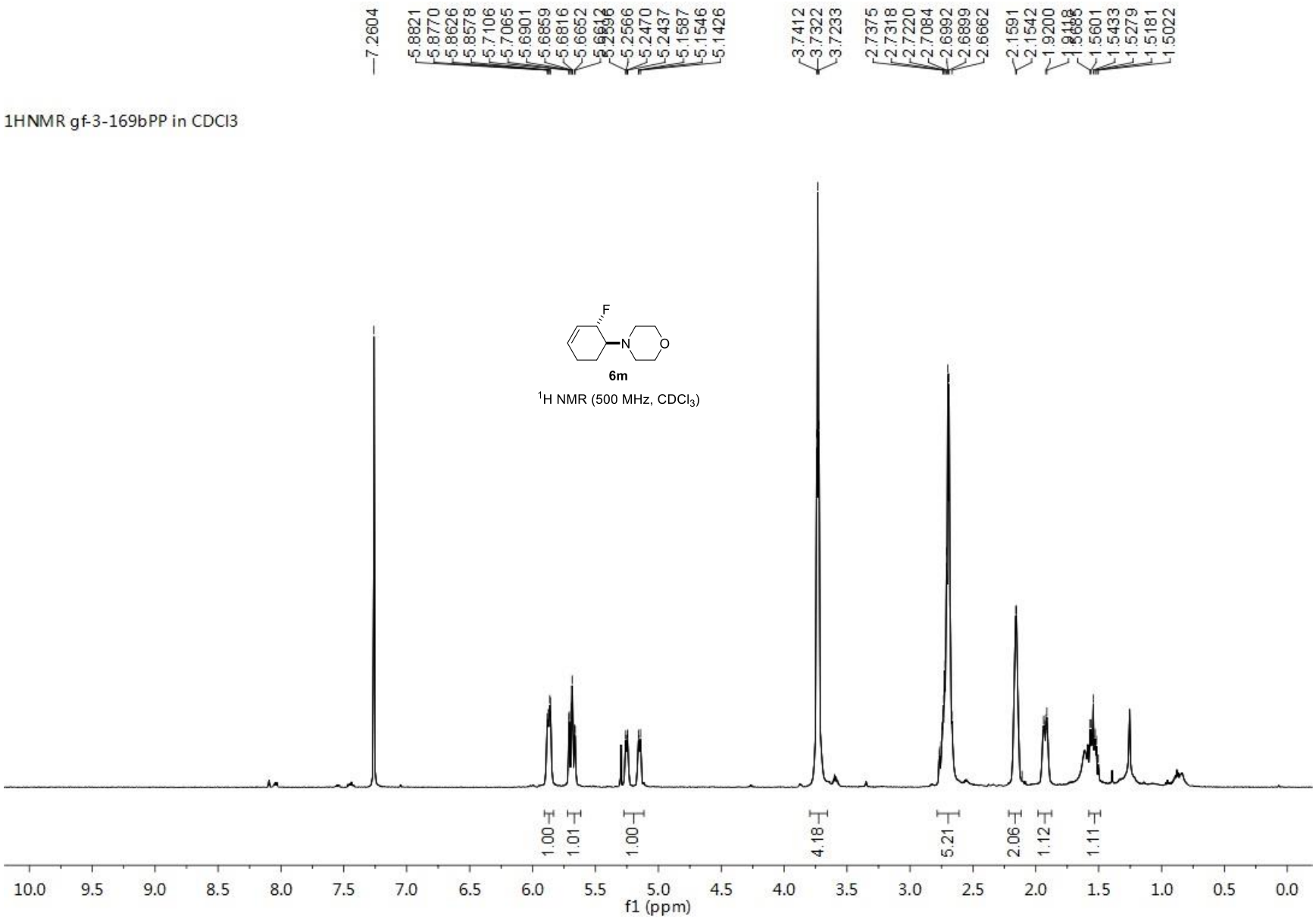
^{13}C NMR (125 MHz, $CDCl_3$)

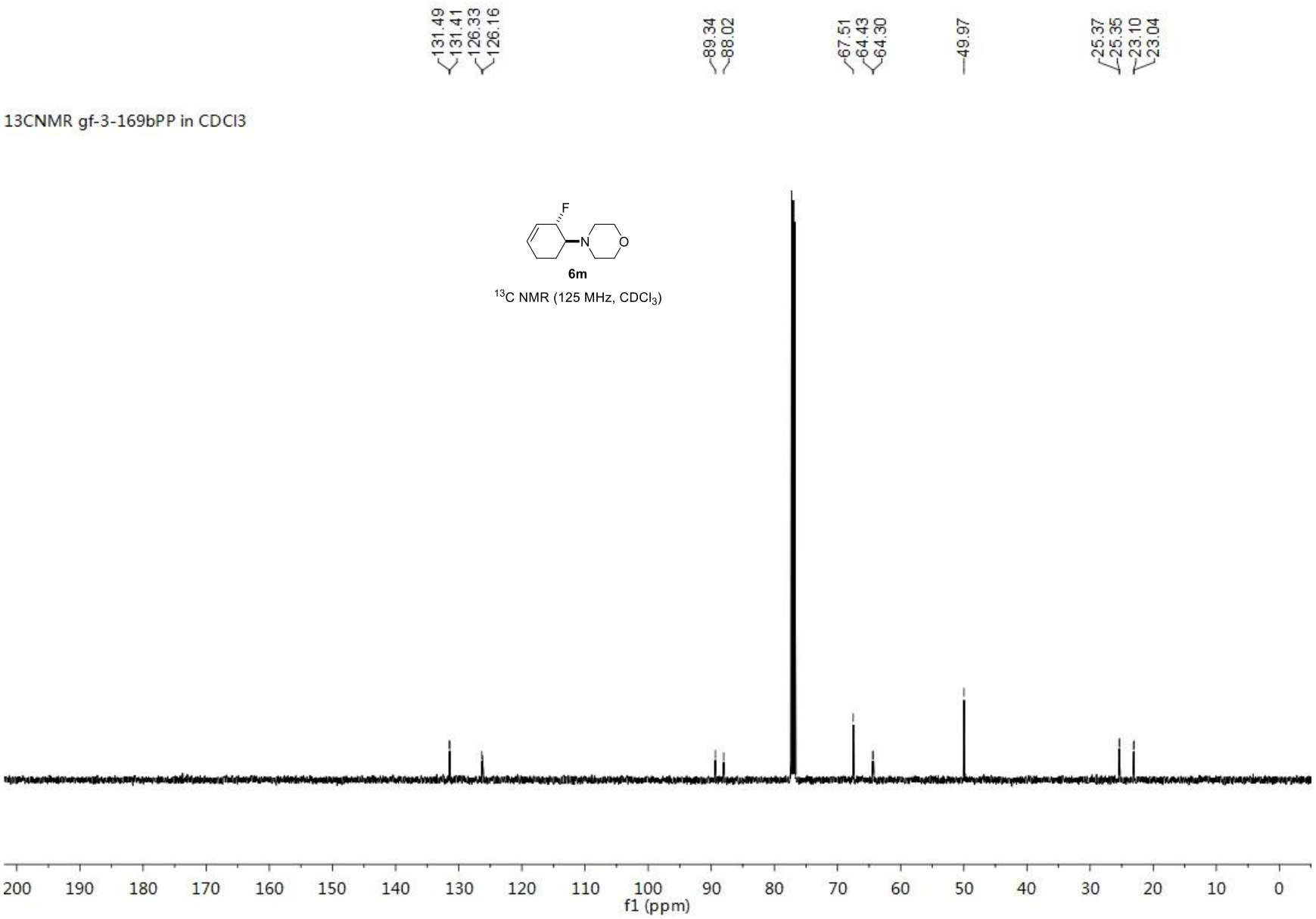
19FNMR gf-3-229aP in CDCl3



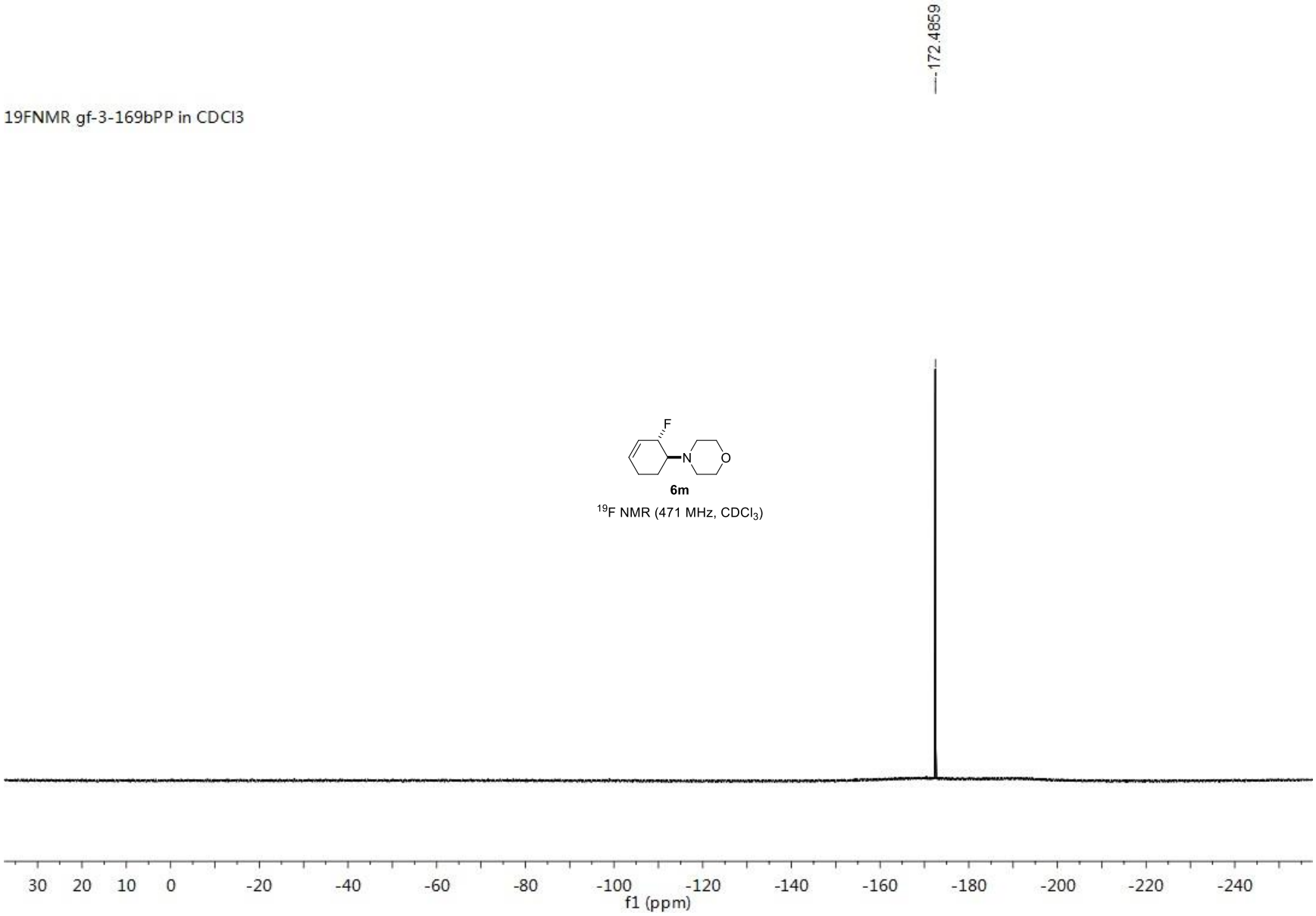
6l

^{19}F NMR (471 MHz, $CDCl_3$)


7.2604
5.8821
5.8770
5.8626
5.8578
5.7106
5.7065
5.6901
5.6859
5.6816
5.6652
5.2566
5.2470
5.2437
5.1587
5.1546
5.1426
3.7412
3.7322
3.7233
2.7375
2.7318
2.7220
2.7084
2.6992
2.6899
2.6662
2.1591
2.1542
1.9200
1.5601
1.5433
1.5279
1.5181
1.5022
1HNMR gf-3-169bPP in CDCl3
F
N
O
6m
1H NMR (500 MHz, CDCl3)
1.00
1.01
1.00
4.18
5.21
2.06
1.12
1.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

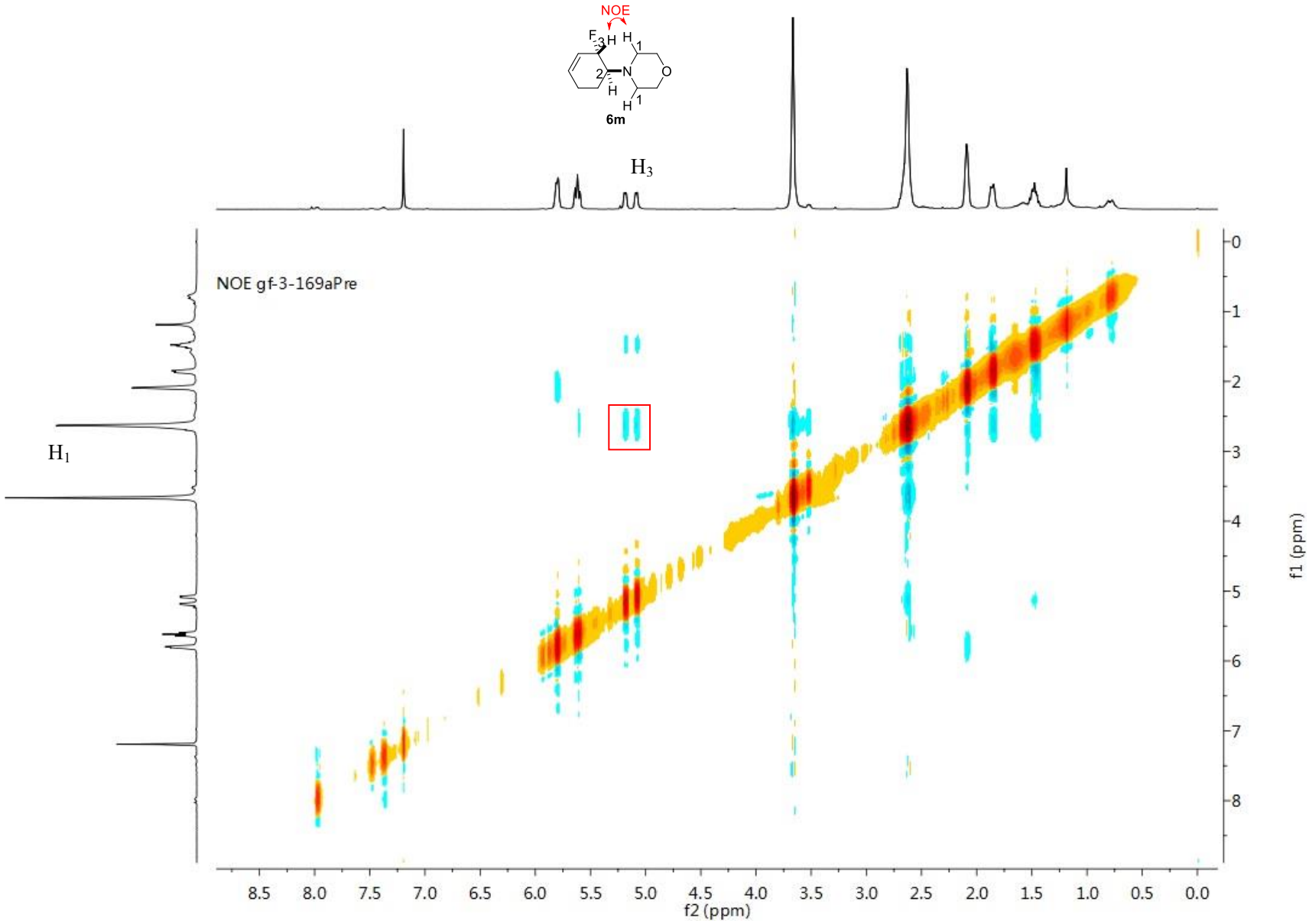

131.49
131.41
126.33
126.16
89.34
88.02
67.51
64.43
64.30
49.97
25.37
25.35
23.10
23.04
13CNMR gf-3-169bPP in CDCl3
F
N
O
6m
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

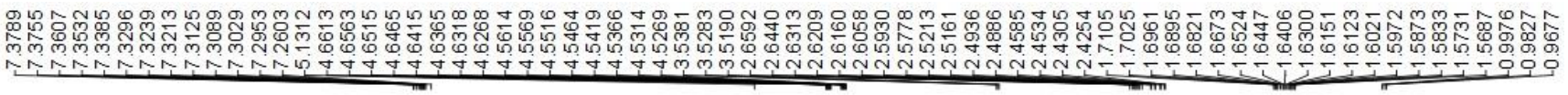
19FNMR gf-3-169bPP in CDCl3



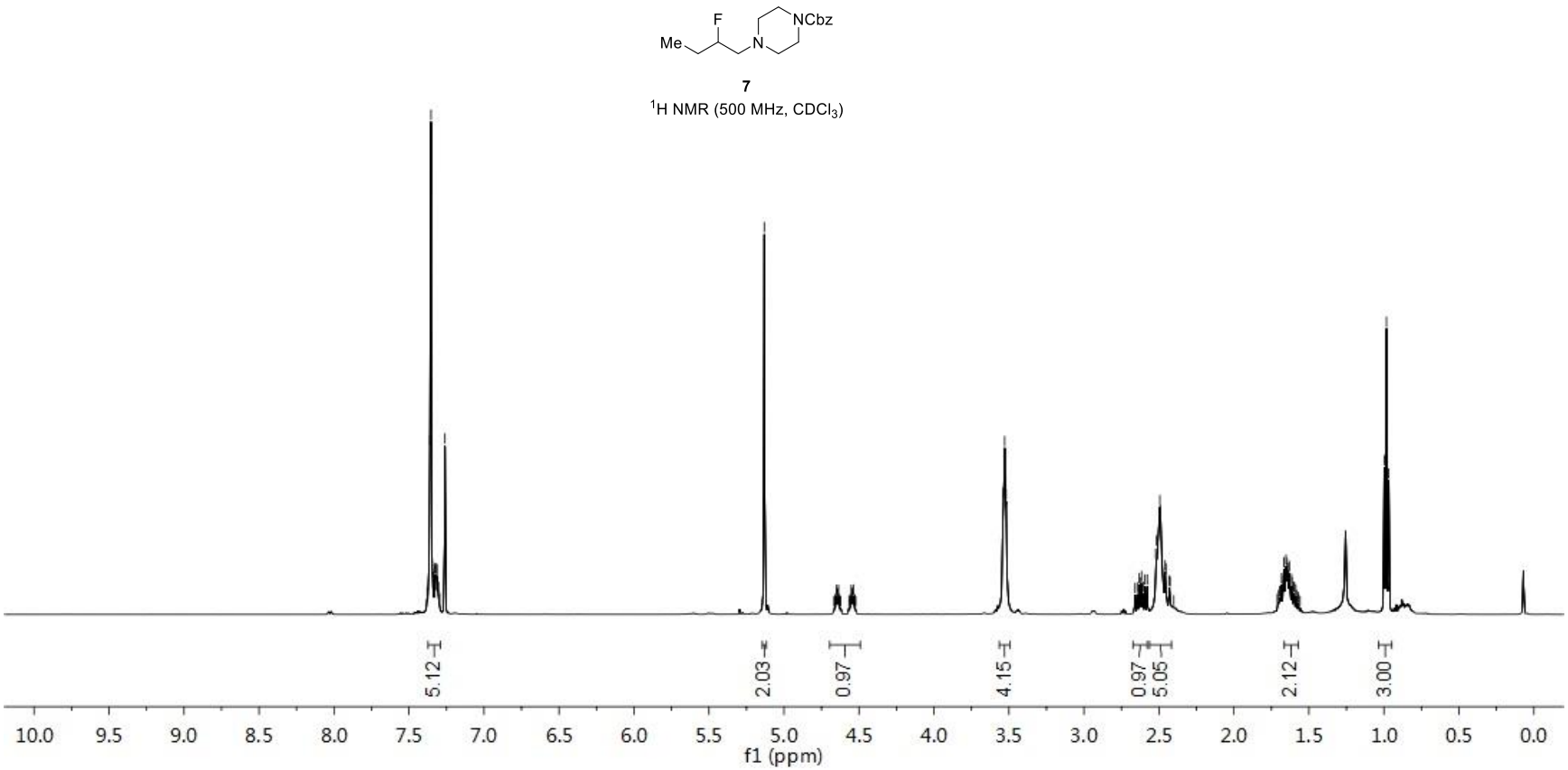
6m

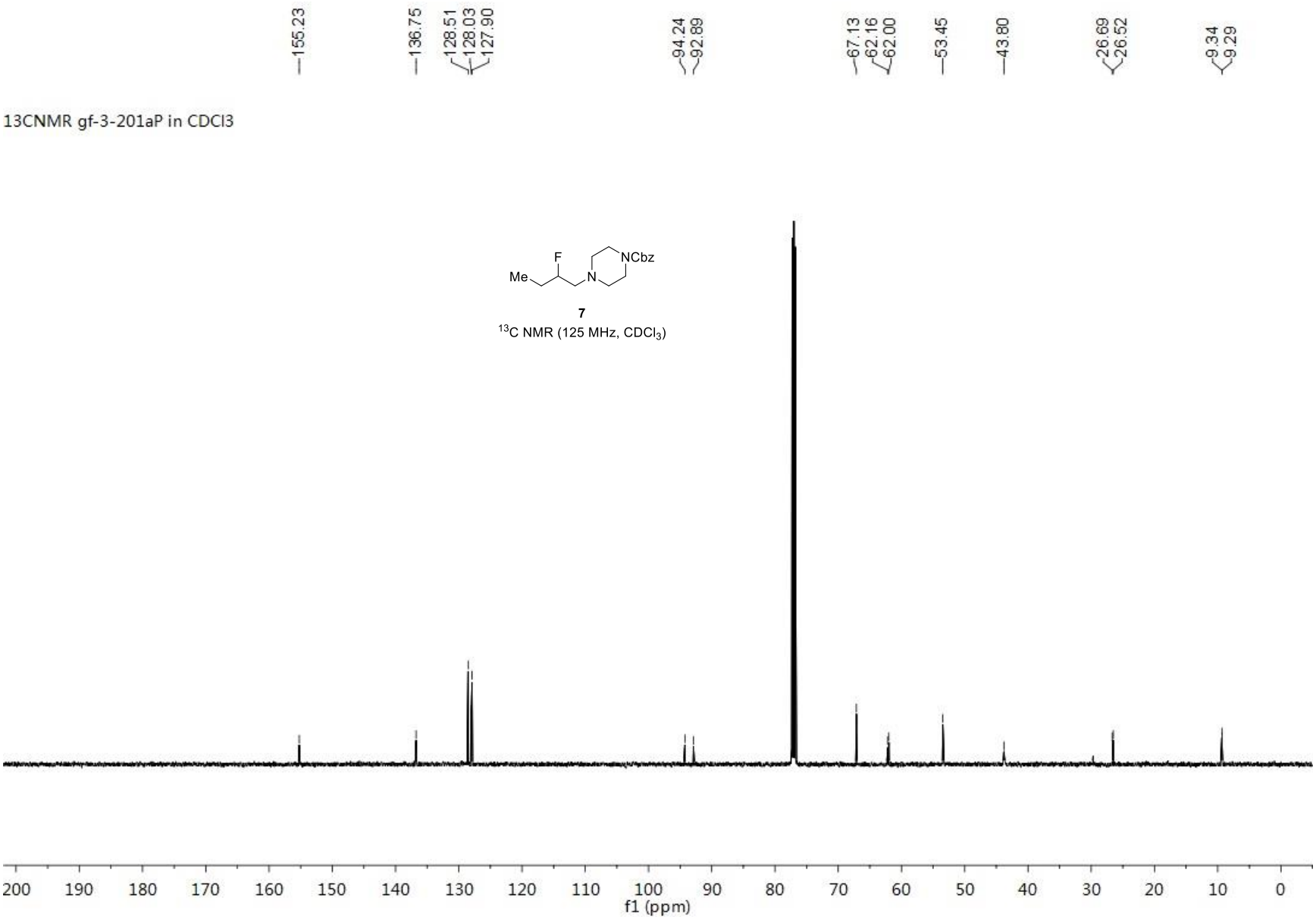
^{19}F NMR (471 MHz, $CDCl_3$)


NOE
F
3
H
H
1
2
N
O
H
H
1
6m
H3
NOE gf-3-169aPre
H1
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

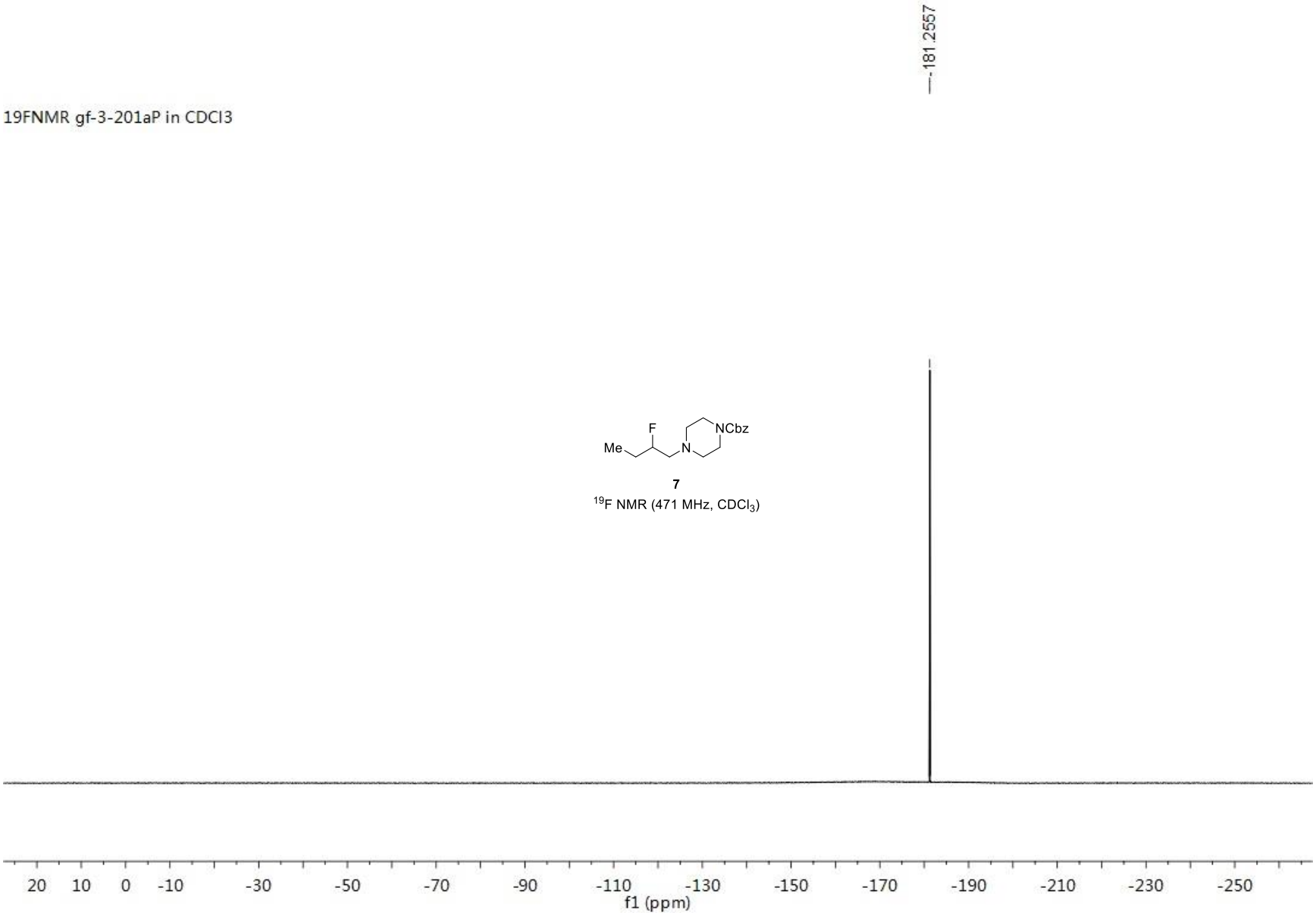


1HNMR gf-3-201aP in CDCl3



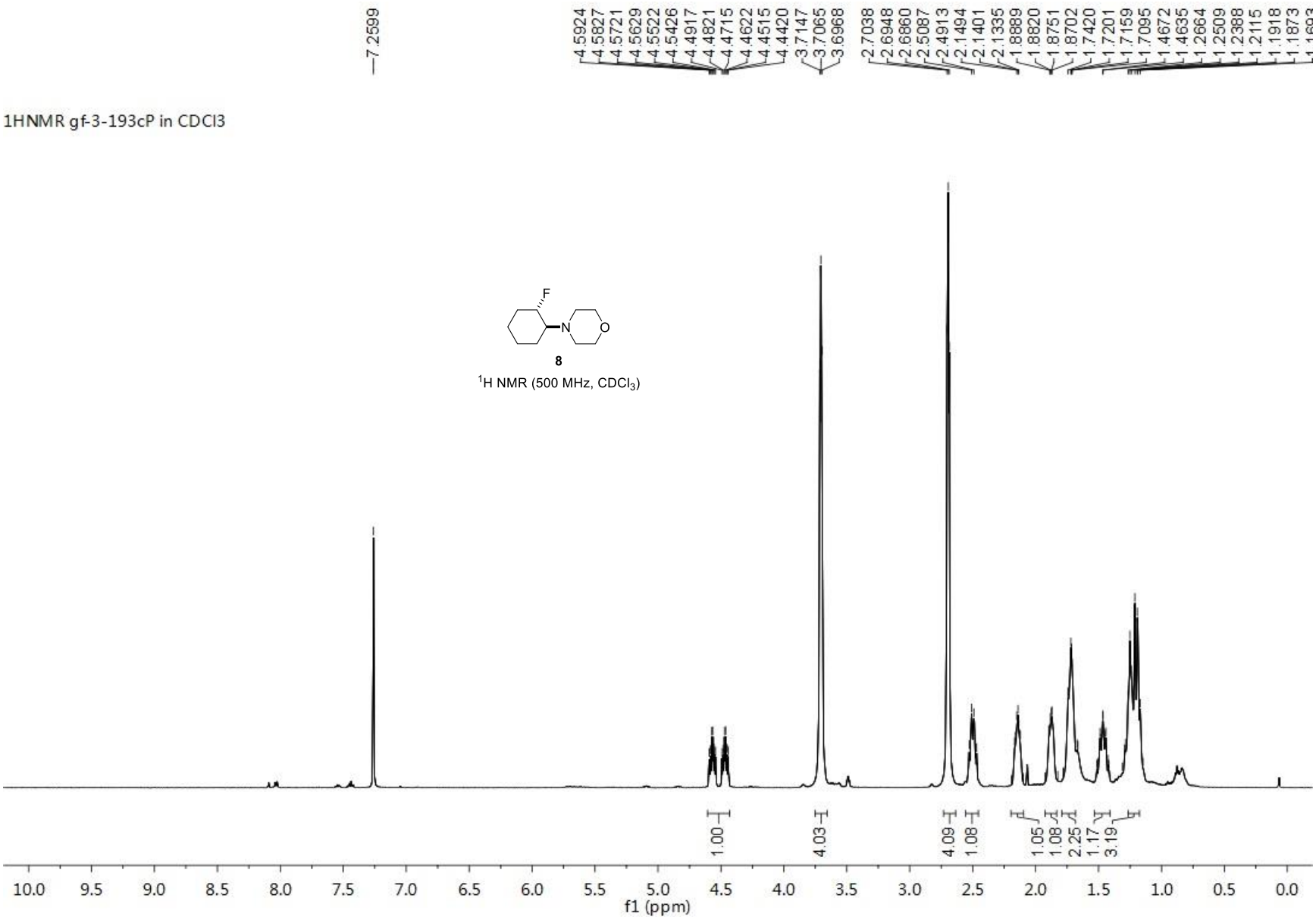

155.23
136.75
128.51
128.03
127.90
94.24
92.89
67.13
62.16
62.00
53.45
43.80
26.69
26.52
9.34
9.29
13CNMR gf-3-201aP in CDCl3
F
NCbz
Me
N
7
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

19FNMR gf-3-201aP in CDCl3

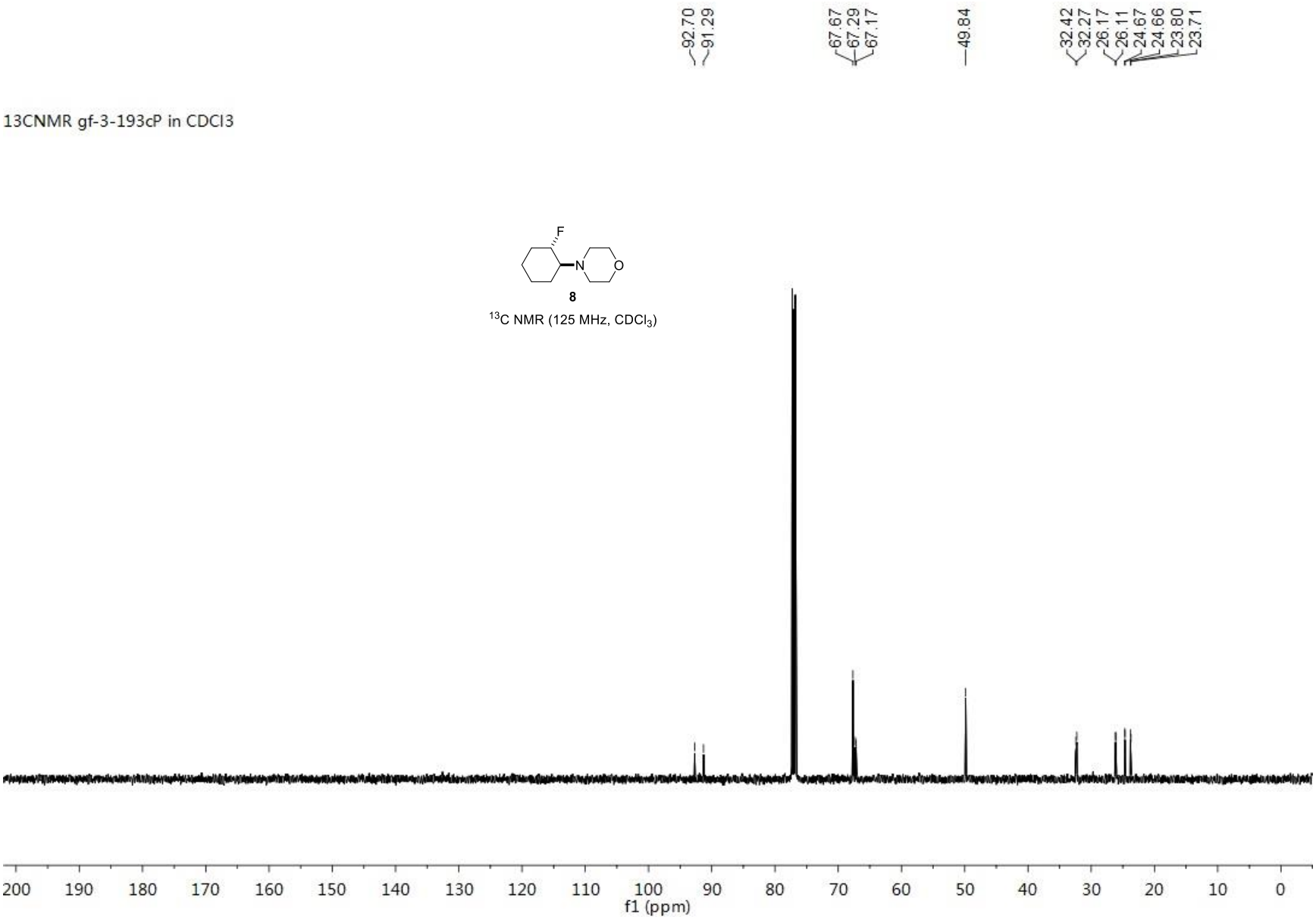


7

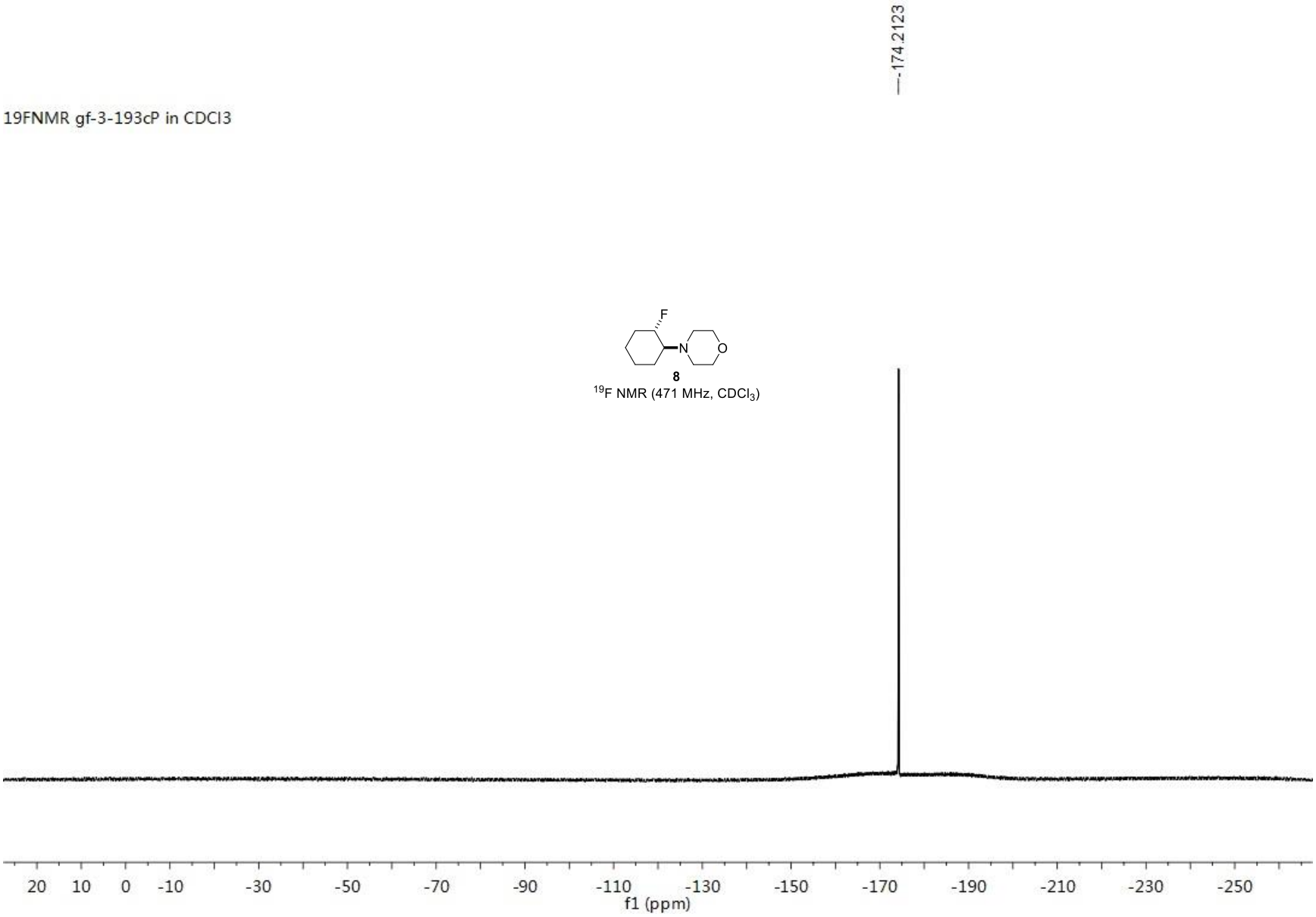
^{19}F NMR (471 MHz, $CDCl_3$)


7.2599
4.5924
4.5827
4.5721
4.5629
4.5522
4.5426
4.4917
4.4821
4.4715
4.4622
4.4515
4.4420
3.7147
3.7065
3.6968
2.7038
2.6948
2.6860
2.5087
2.4913
2.1494
2.1401
2.1335
1.8889
1.8820
1.8751
1.8702
1.7420
1.7201
1.7159
1.7095
1.4672
1.4635
1.2664
1.2509
1.2388
1.2115
1.1918
1.1873
1HNMR gf-3-193cP in CDCl3
F
N
O
8
1H NMR (500 MHz, CDCl3)
1.00
4.03
4.09
1.08
1.05
1.08
2.25
1.17
3.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

13CNMR gf-3-193cP in CDCl3



19FNMR gf-3-193cP in CDCl3



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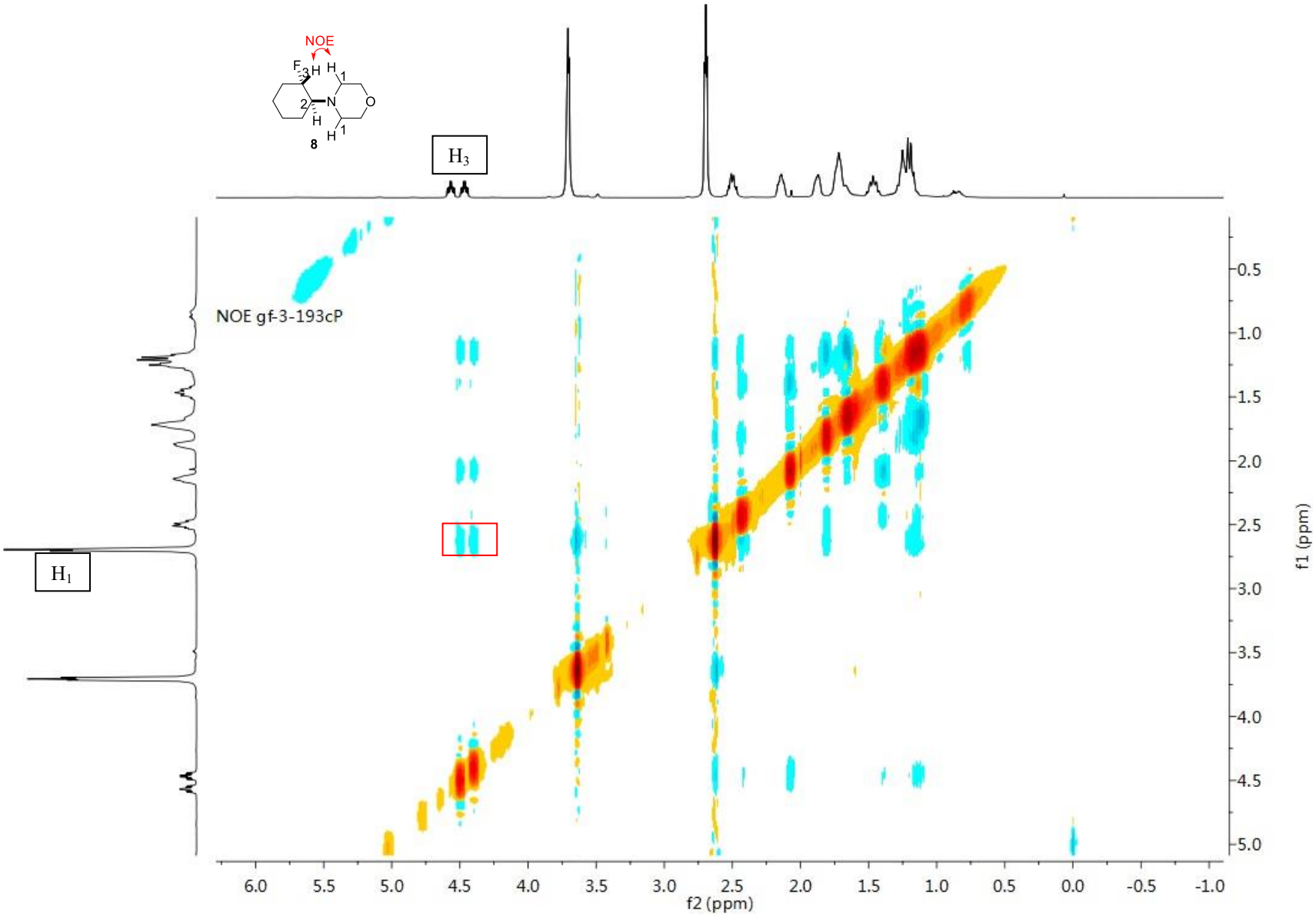
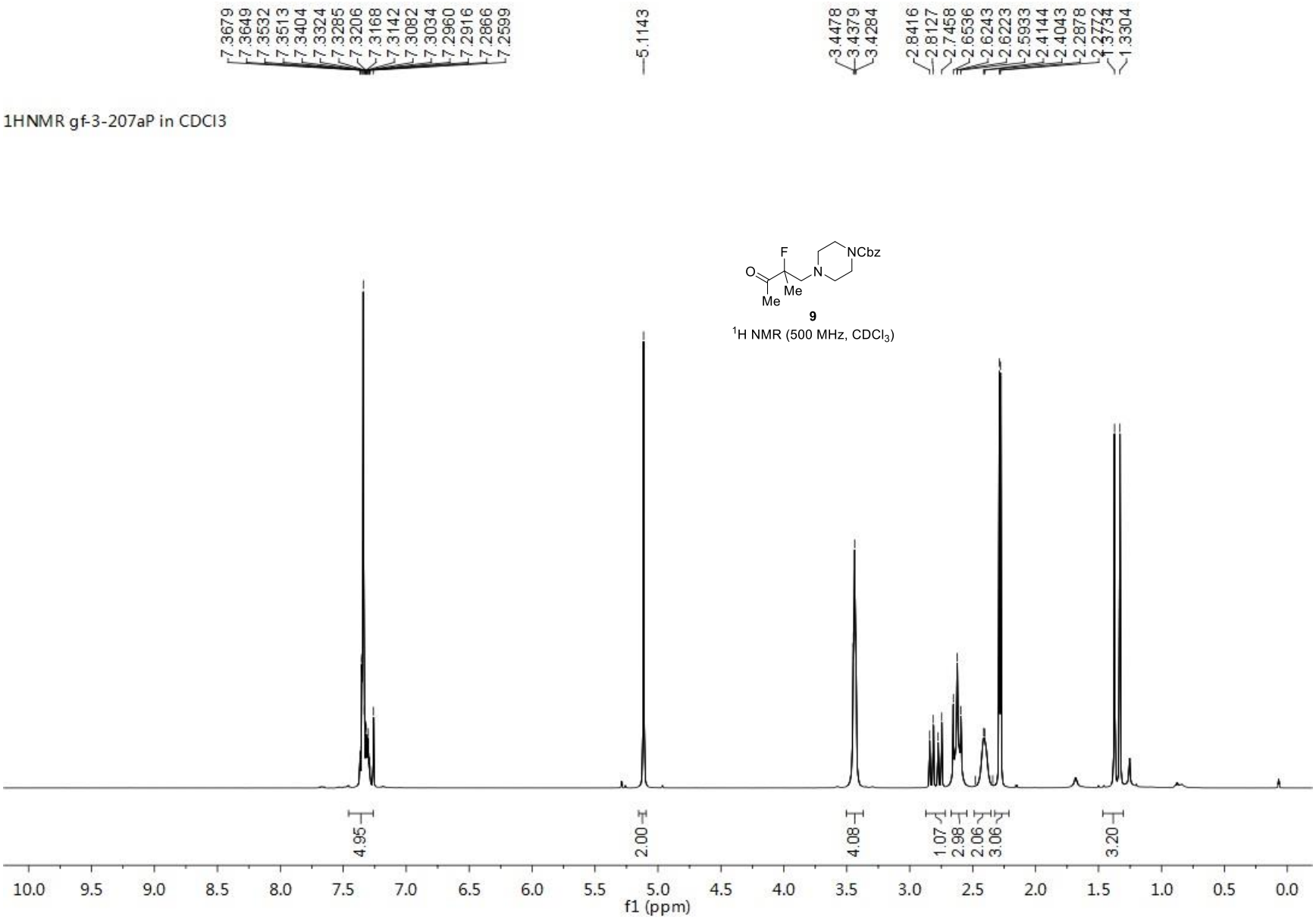
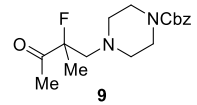
^{19}F NMR (471 MHz, $CDCl_3$)


NOE
H3
H1
8
H3
H1
NOE gf-3-193cP
f2 (ppm)
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0


7.3679
7.3649
7.3532
7.3513
7.3404
7.3324
7.3285
7.3206
7.3168
7.3142
7.3082
7.3034
7.2960
7.2916
7.2866
7.2599
5.1143
3.4478
3.4379
3.4284
2.8416
2.8127
2.7458
2.6536
2.6243
2.6223
2.5933
2.4144
2.4043
2.2878
2.2772
1.3734
1.3304
1HNMR gf-3-207aP in CDCl3
F
NCbz
O
N
Me
Me
9
1H NMR (500 MHz, CDCl3)
4.95
2.00
4.08
1.07
2.98
2.06
3.06
3.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

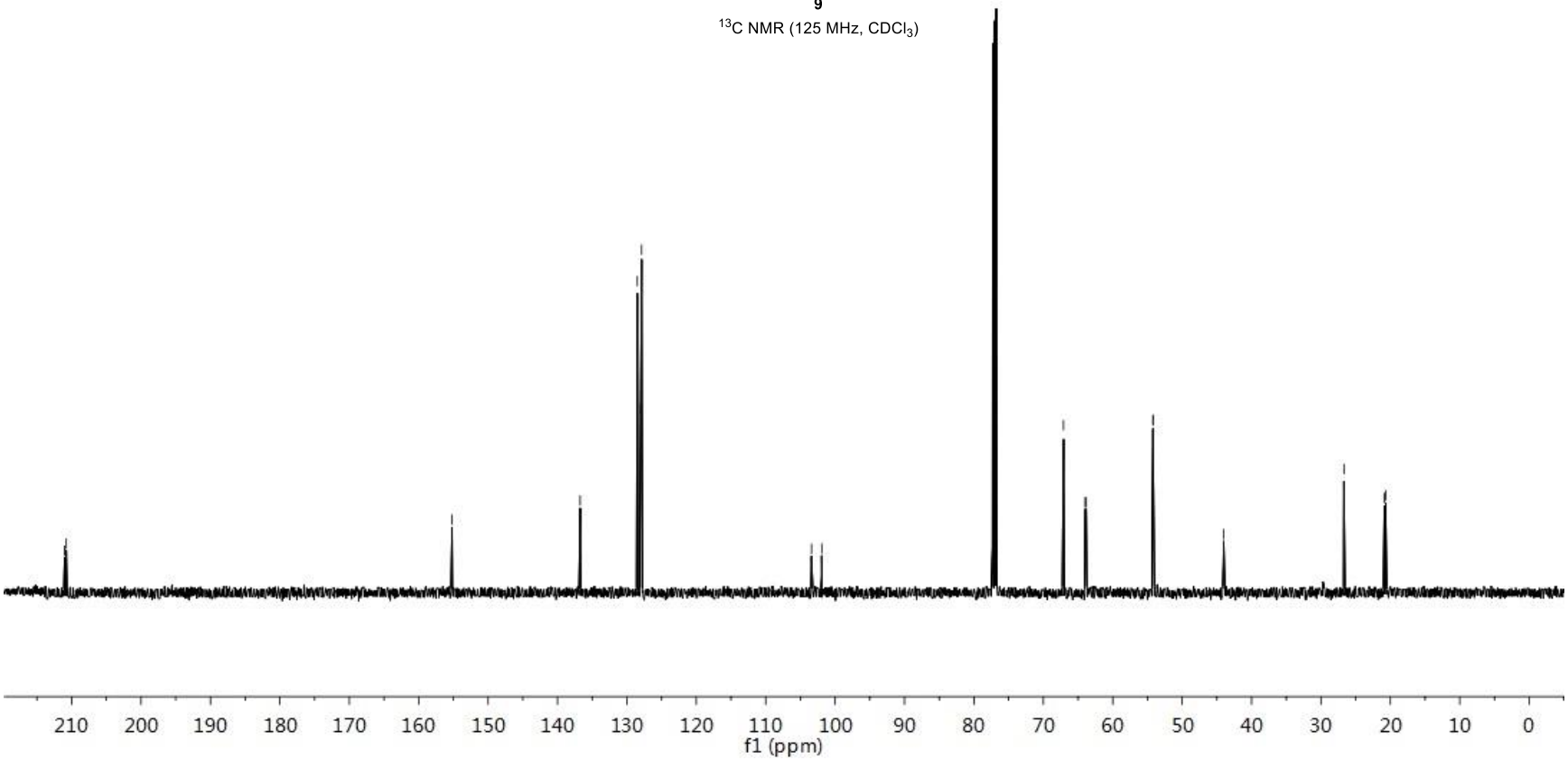
211.02
210.78
155.20
136.74
128.50
128.02
127.88
103.40
101.93
67.10
63.98
63.82
54.20
54.19
44.01
26.69
20.87
20.68

13CNMR gf-3-207aP in CDCl3

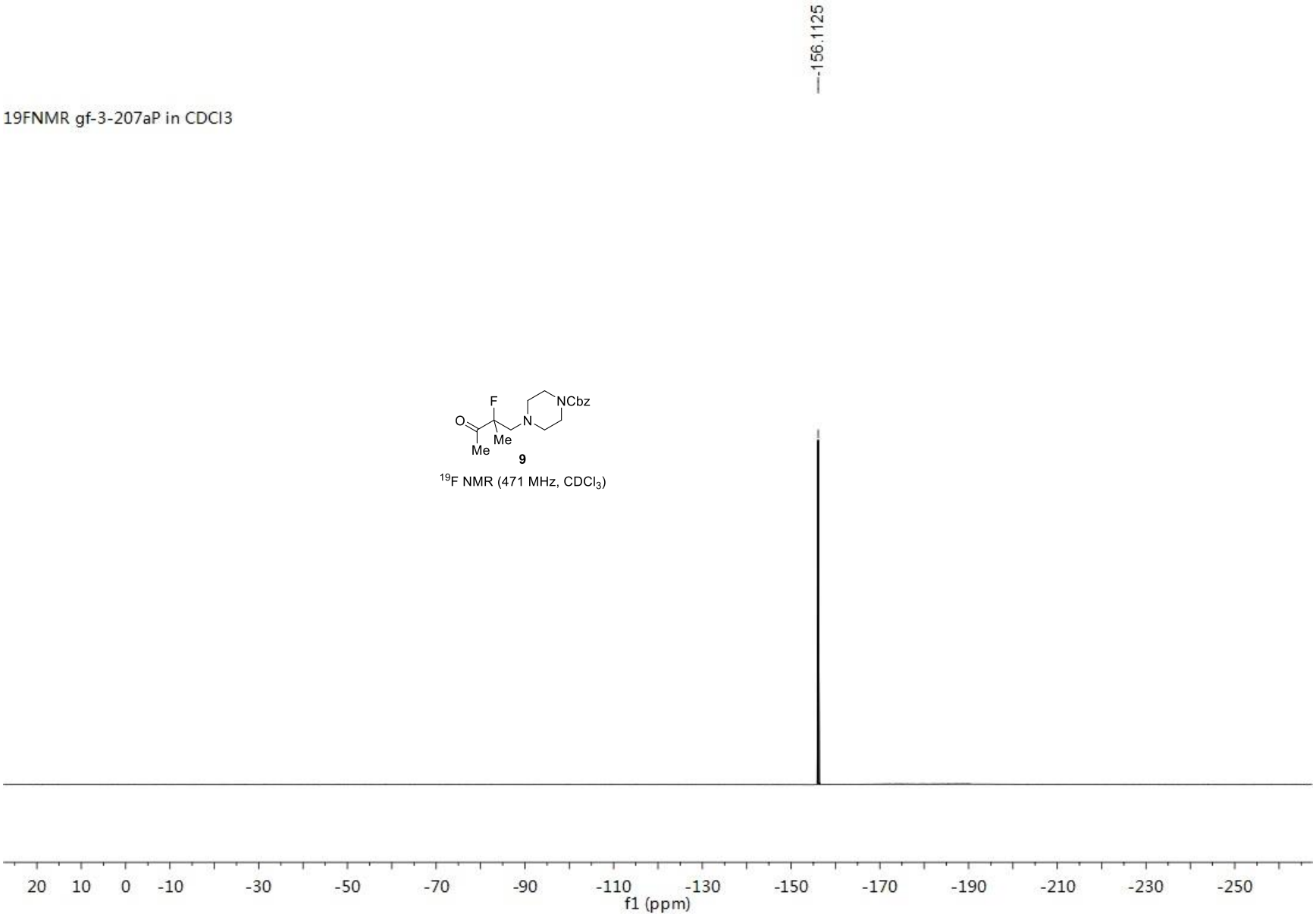


9

^{13}C NMR (125 MHz, $CDCl_3$)



19FNMR gf-3-207aP in CDCl3

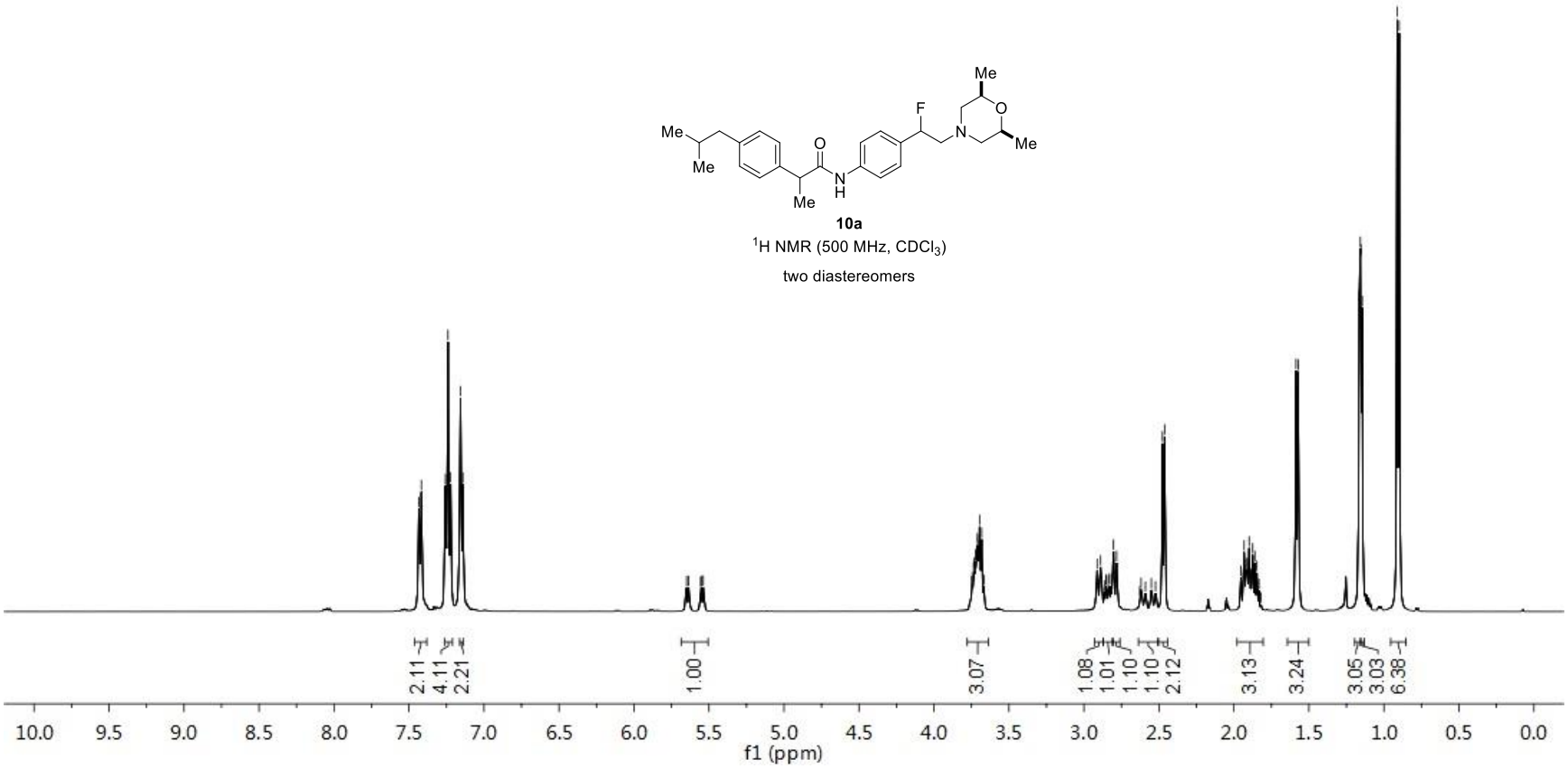


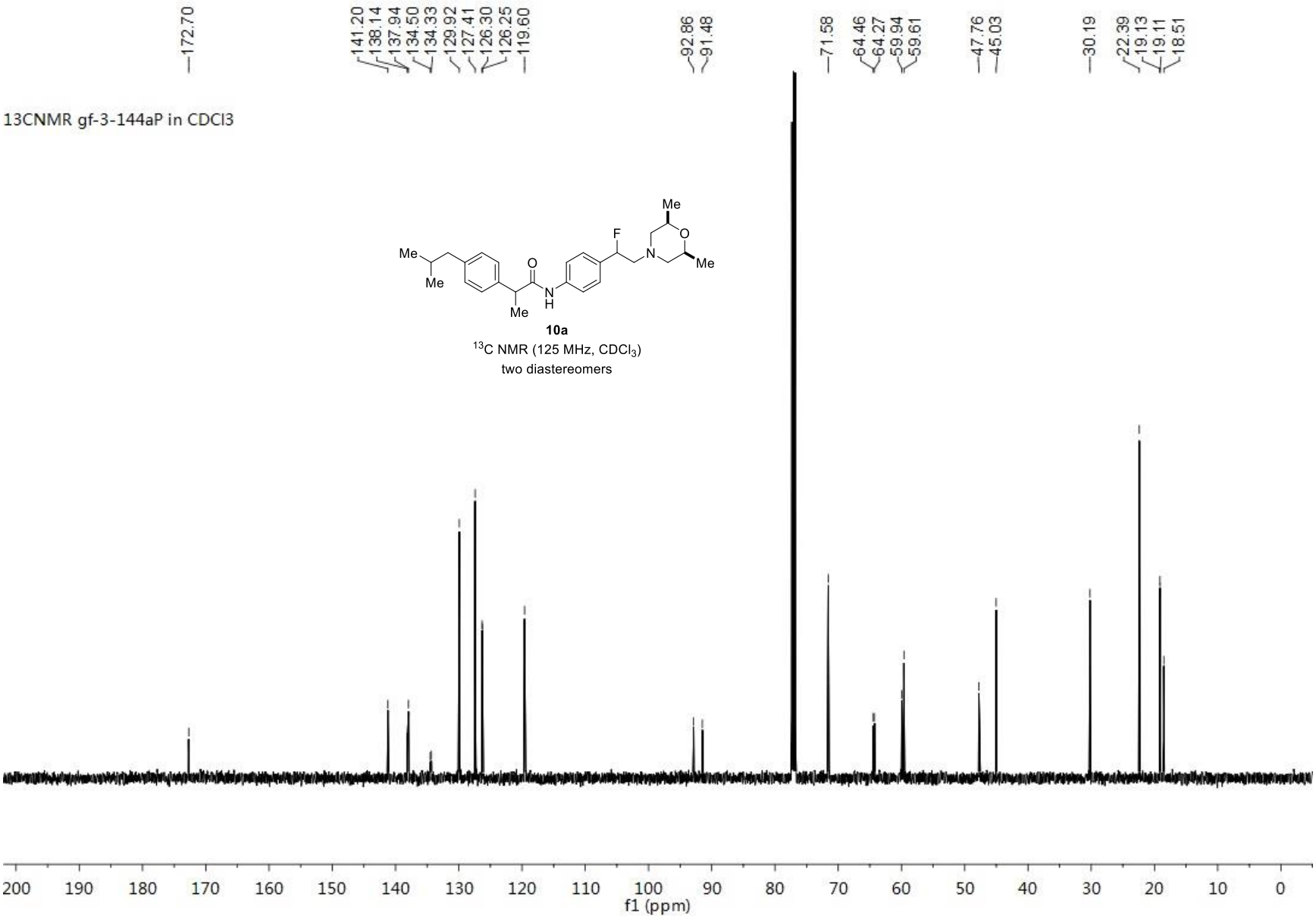
9

^{19}F NMR (471 MHz, $CDCl_3$)

7.4341
7.4175
7.2602
7.2567
7.2400
7.2223
7.1568
7.1408
5.6490
5.6353
5.5551
5.5517
5.5380
3.7488
3.7447
3.7361
3.7315
3.7237
3.7170
3.7108
3.7062
3.7032
3.6958
3.6814
3.6673
2.9118
2.8892
2.8350
2.8029
2.7821
2.4763
2.4620
1.9322
1.8987
1.8747
1.5864
1.5721
1.1571
1.1529
1.1447
0.9115
0.8982

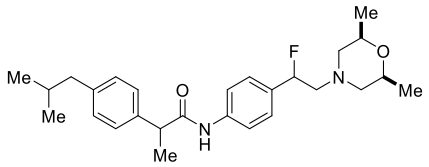
1HNMR gf-3-144aP in CDCl3




172.70
141.20
138.14
137.94
134.50
134.33
129.92
127.41
126.30
126.25
119.60
92.86
91.48
71.58
64.46
64.27
59.94
59.61
47.76
45.03
30.19
22.39
19.13
19.11
18.51
13CNMR gf-3-144aP in CDCl3
Me
F
O
N
Me
Me
O
N
H
Me
Me
10a
13C NMR (125 MHz, CDCl3)
two diastereomers
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

19FNMR gf-3-144aP in CDCl3

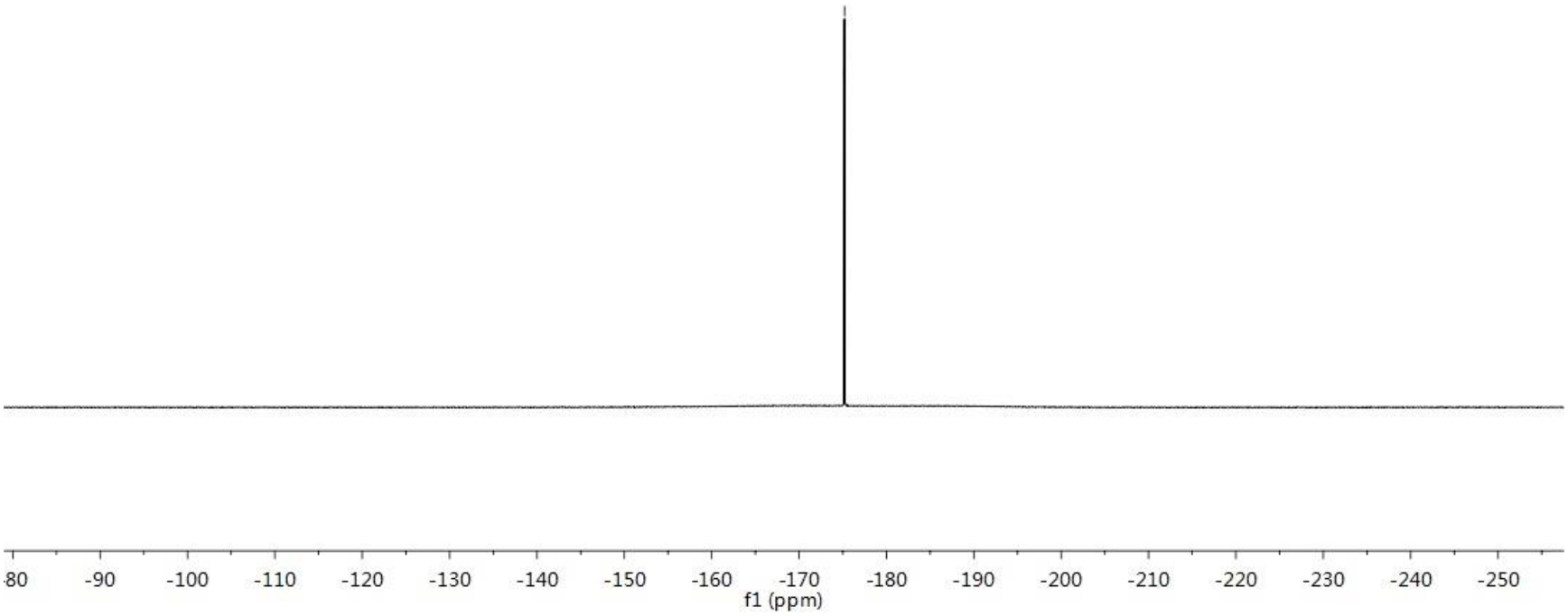
-175.1791
-175.2007

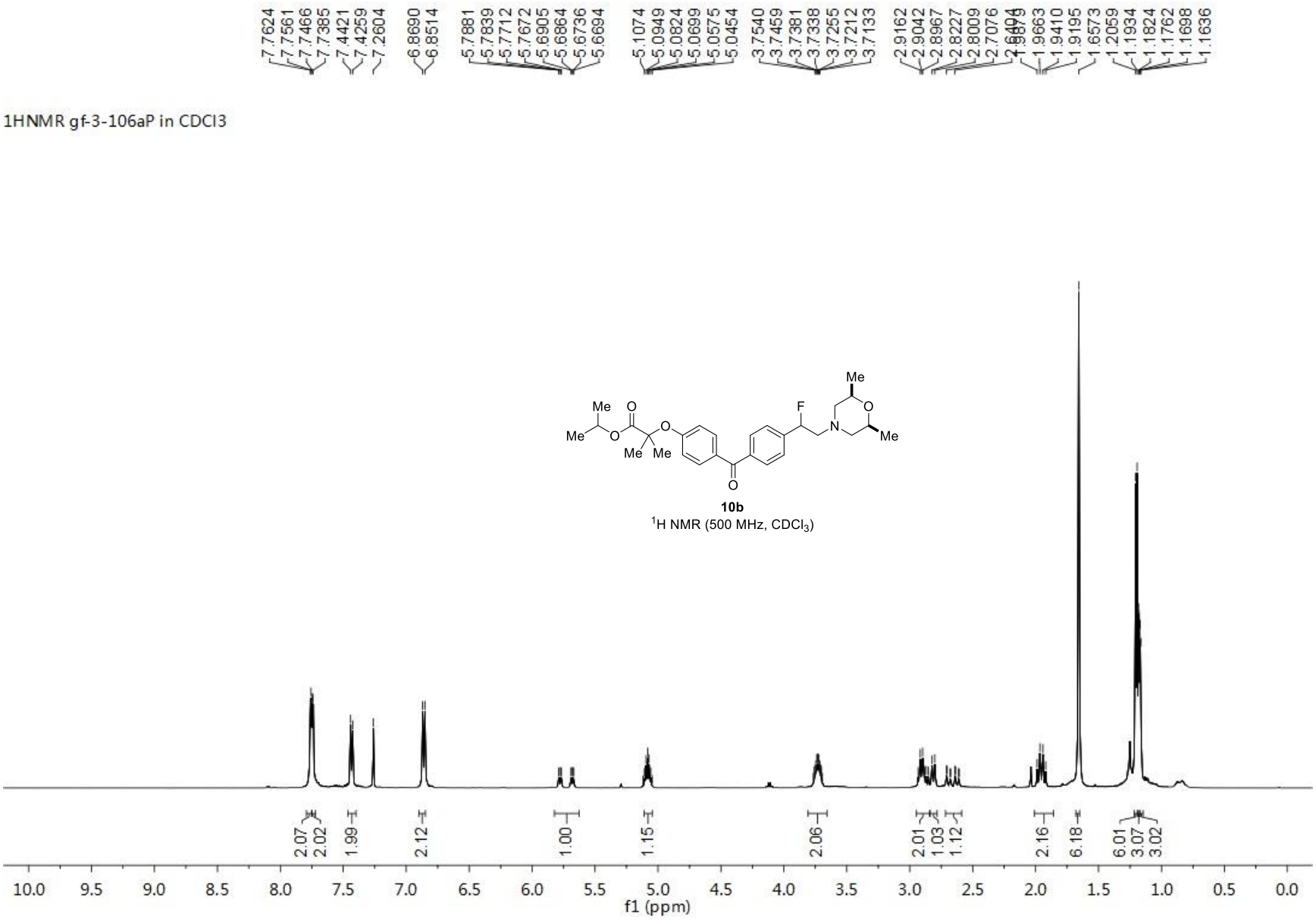


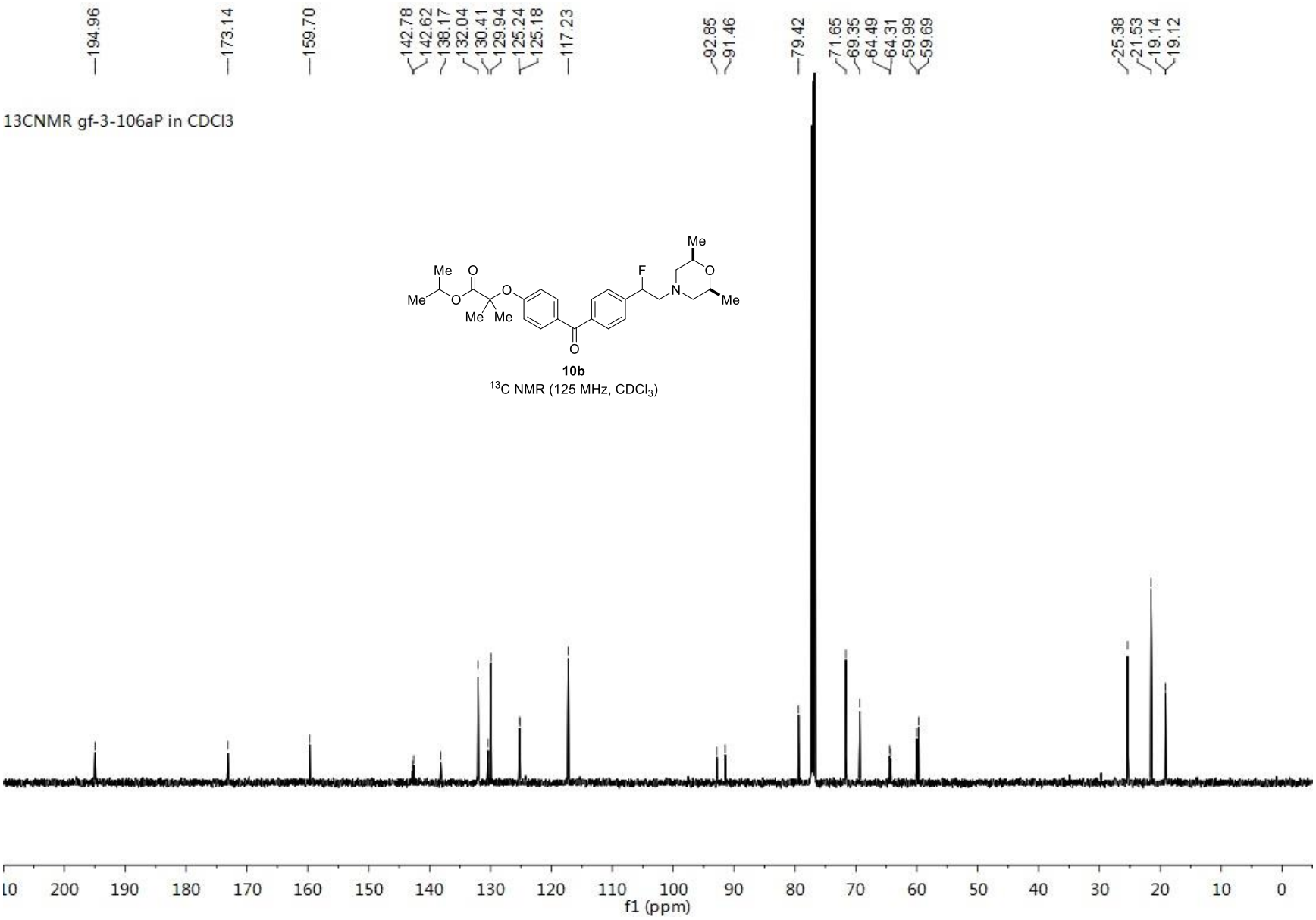
10a

^{19}F NMR (471 MHz, $CDCl_3$)

two diastereomers




7.7624
7.7561
7.7466
7.7385
7.4421
7.4259
7.2604
6.8690
6.8514
5.7881
5.7839
5.7712
5.7672
5.6905
5.6864
5.6736
5.6694
5.1074
5.0949
5.0824
5.0699
5.0575
5.0454
3.7540
3.7459
3.7381
3.7338
3.7255
3.7212
3.7133
2.9162
2.9042
2.8967
2.8227
2.8009
2.7076
1.9663
1.9410
1.9195
1.6573
1.2059
1.1934
1.1824
1.1762
1.1698
1.1636
1HNMR gf-3-106aP in CDCl3
Me
Me
O
O
Me
Me
O
Me
F
N
O
Me
O
10b
1H NMR (500 MHz, CDCl3)
2.07
2.02
1.99
2.12
1.00
1.15
2.06
2.01
1.03
1.12
2.16
6.18
6.01
3.07
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

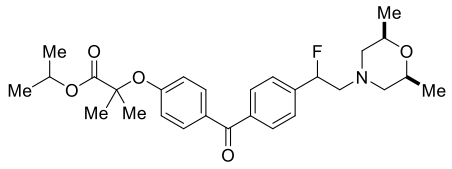


10b

^{13}C NMR (125 MHz, $CDCl_3$)

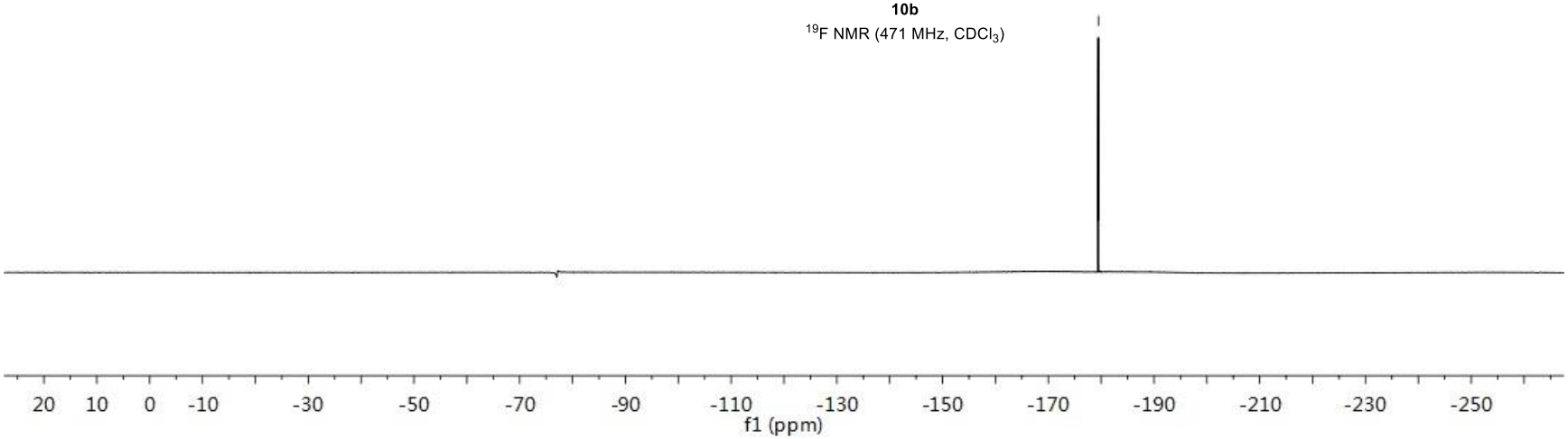
19FNMR gf-3-106aP in CDCl3

-179.4938

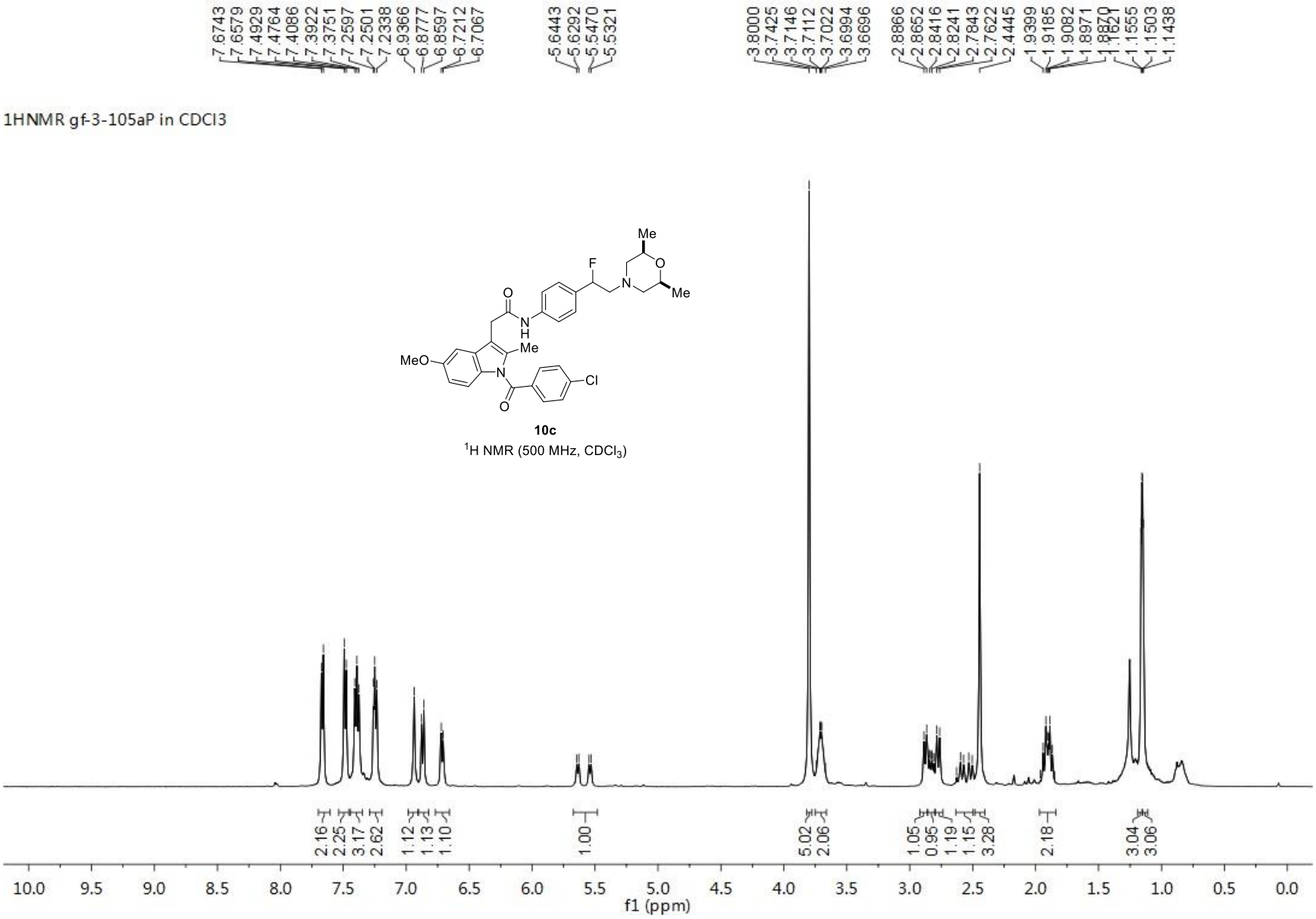


10b

^{19}F NMR (471 MHz, $CDCl_3$)

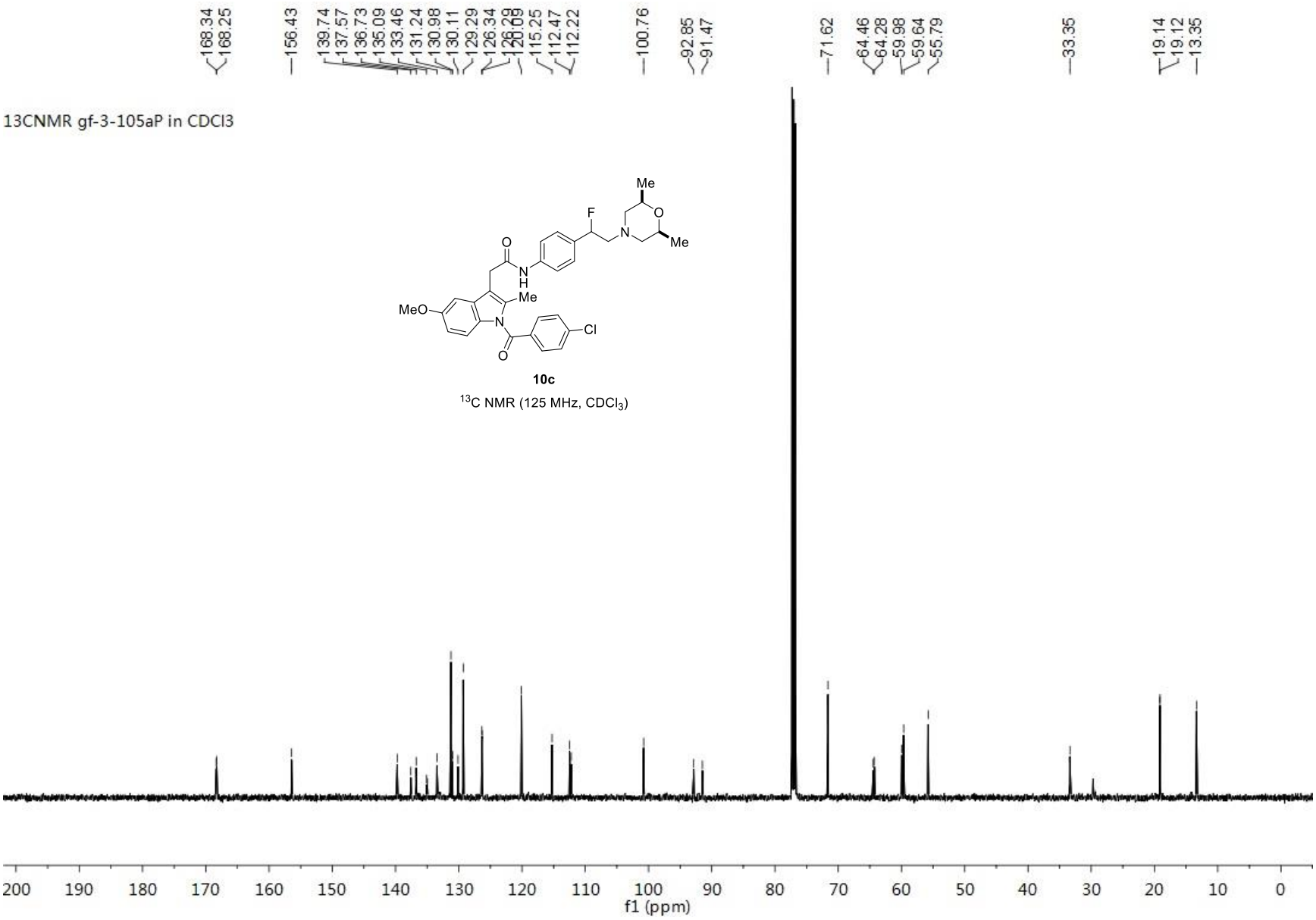


1HNMR gf-3-105aP in CDCl3



10c

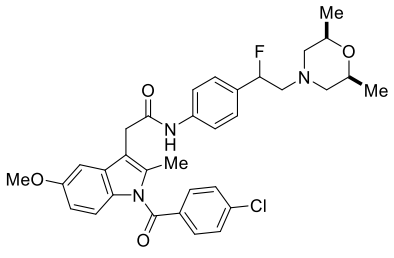
^{1}H NMR (500 MHz, $CDCl_3$)



10c

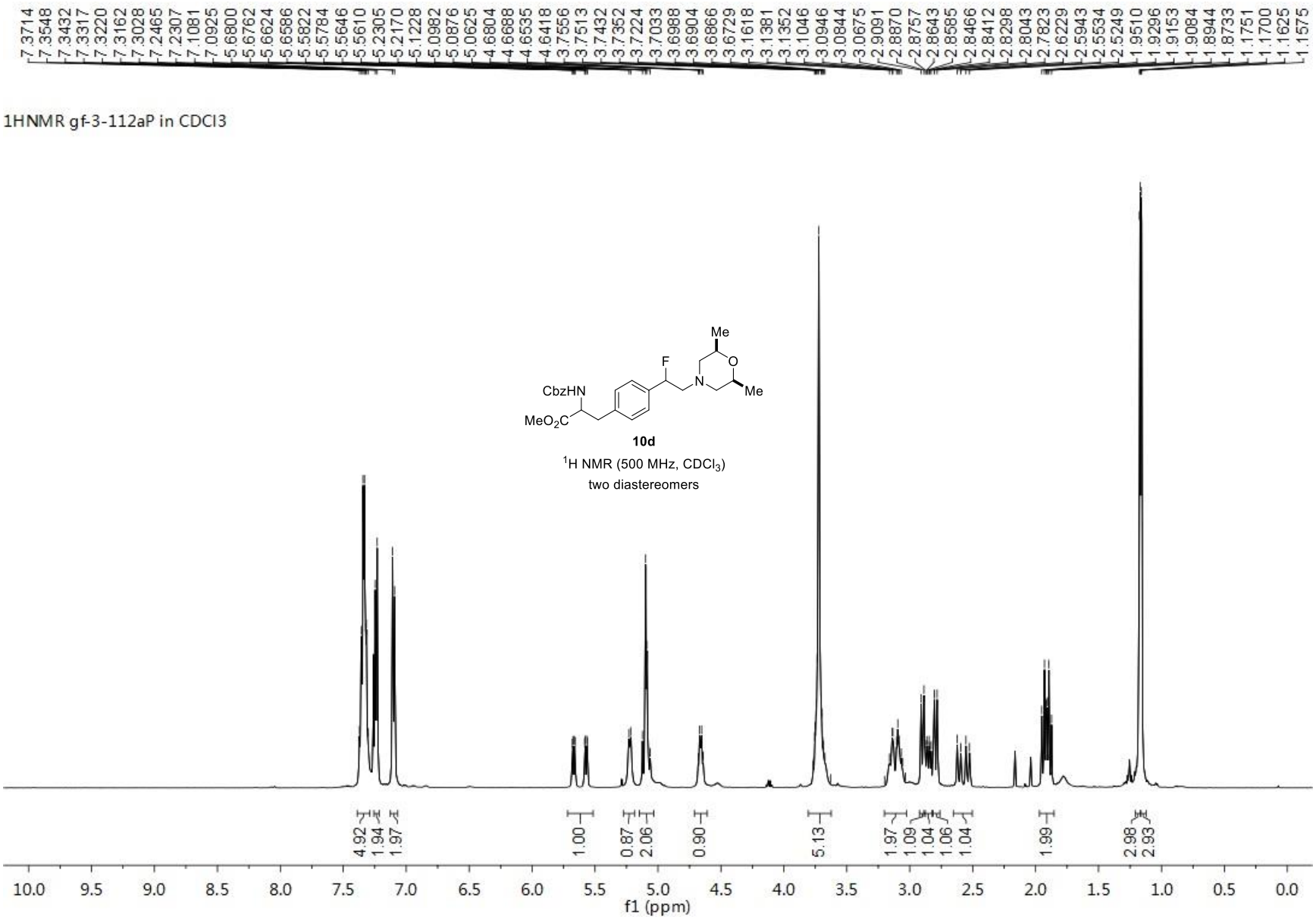
^{13}C NMR (125 MHz, $CDCl_3$)

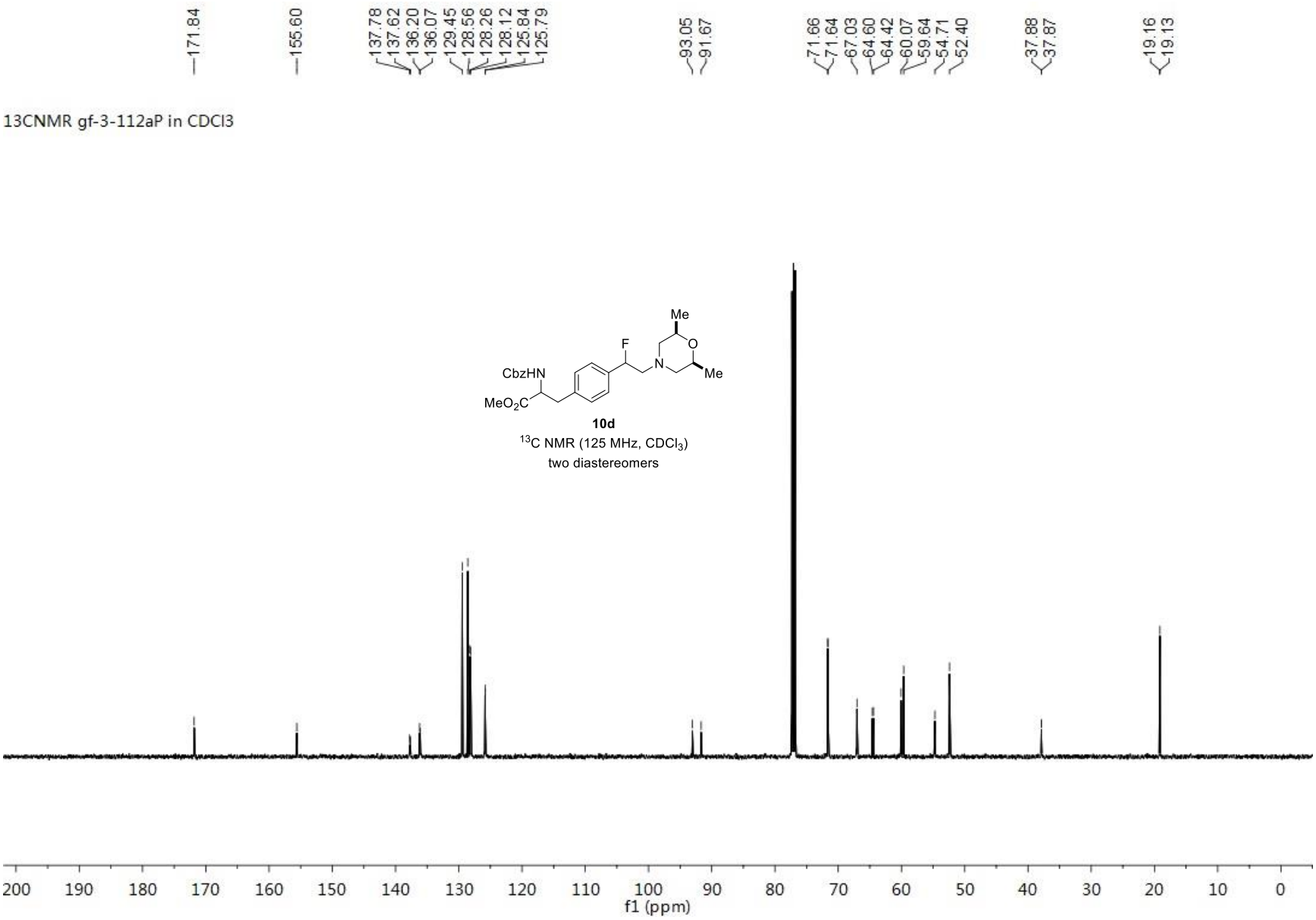
19FNMR gf-3-105aP in CDCl3



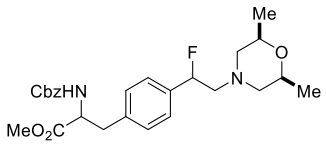
10c

^{19}F NMR (471 MHz, $CDCl_3$)


7.3714
7.3548
7.3432
7.3317
7.3220
7.3162
7.3028
7.2465
7.2307
7.1081
7.0925
5.6800
5.6762
5.6624
5.6586
5.5822
5.5784
5.5646
5.5610
5.2305
5.2170
5.1228
5.0982
5.0876
5.0625
4.6804
4.6688
4.6535
4.6418
3.7556
3.7513
3.7432
3.7352
3.7224
3.7033
3.6988
3.6904
3.6866
3.6729
3.1618
3.1381
3.1352
3.1046
3.0946
3.0844
3.0675
2.9091
2.8870
2.8757
2.8643
2.8585
2.8466
2.8412
2.8298
2.8043
2.7823
2.6229
2.5943
2.5534
2.5249
1.9510
1.9296
1.9153
1.9084
1.8944
1.8733
1.1751
1.1700
1.1625
1.1575
1HNMR gf-3-112aP in CDCl3
Me
F
O
N
Me
CbzHN
MeO2C
10d
1H NMR (500 MHz, CDCl3)
two diastereomers
4.92
1.94
1.97
1.00
0.87
2.06
0.90
5.13
1.97
1.09
1.04
1.06
1.04
1.99
2.98
2.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


171.84
155.60
137.78
137.62
136.20
136.07
129.45
128.56
128.26
128.12
125.84
125.79
93.05
91.67
71.66
71.64
67.03
64.60
64.42
60.07
59.64
54.71
52.40
37.88
37.87
19.16
19.13
13CNMR gf-3-112aP in CDCl3
Me
F
O
N
Me
CbzHN
MeO2C
10d
13C NMR (125 MHz, CDCl3)
two diastereomers
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

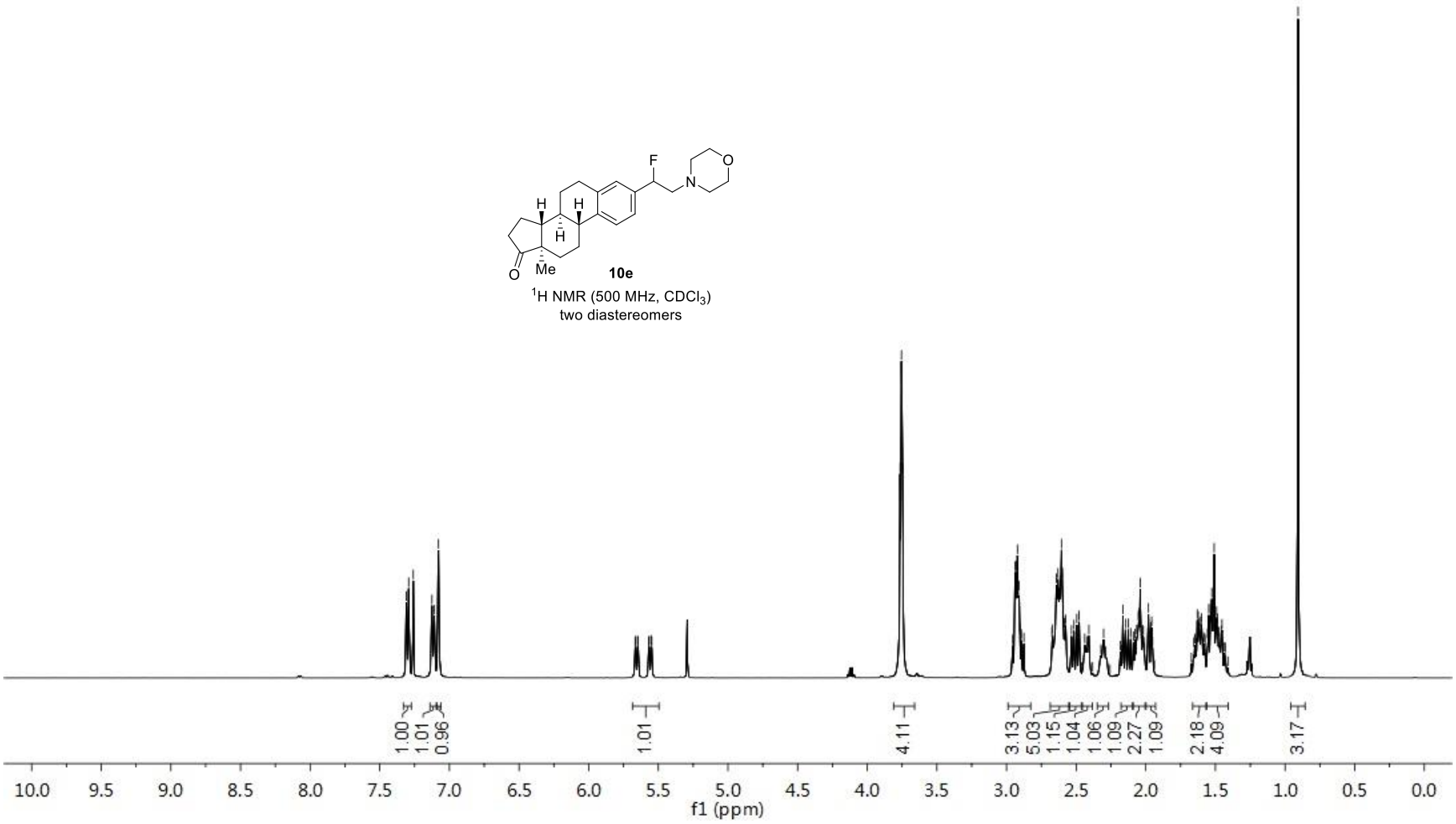
19FNMR gf-3-112aP in CDCl3

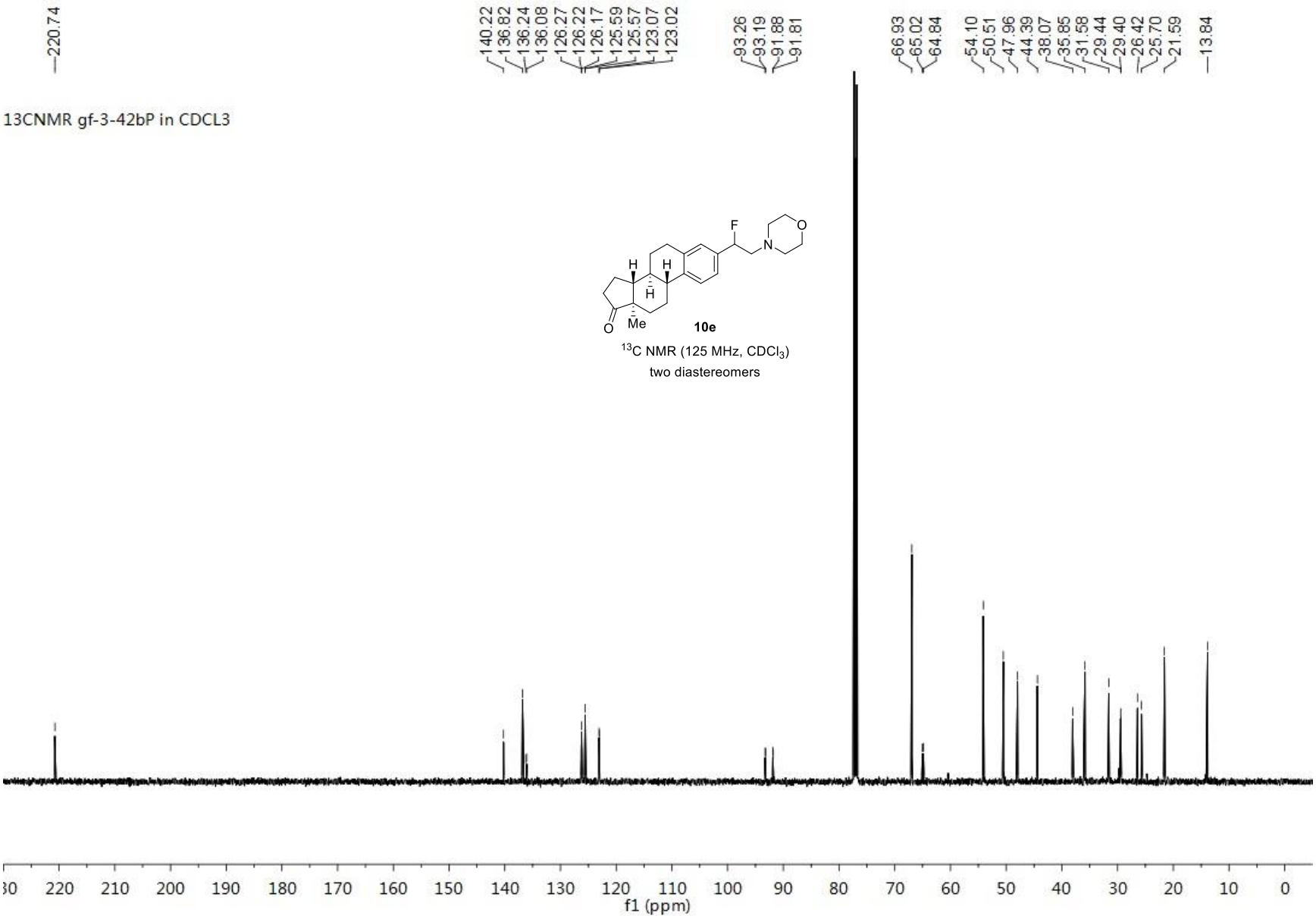


10d

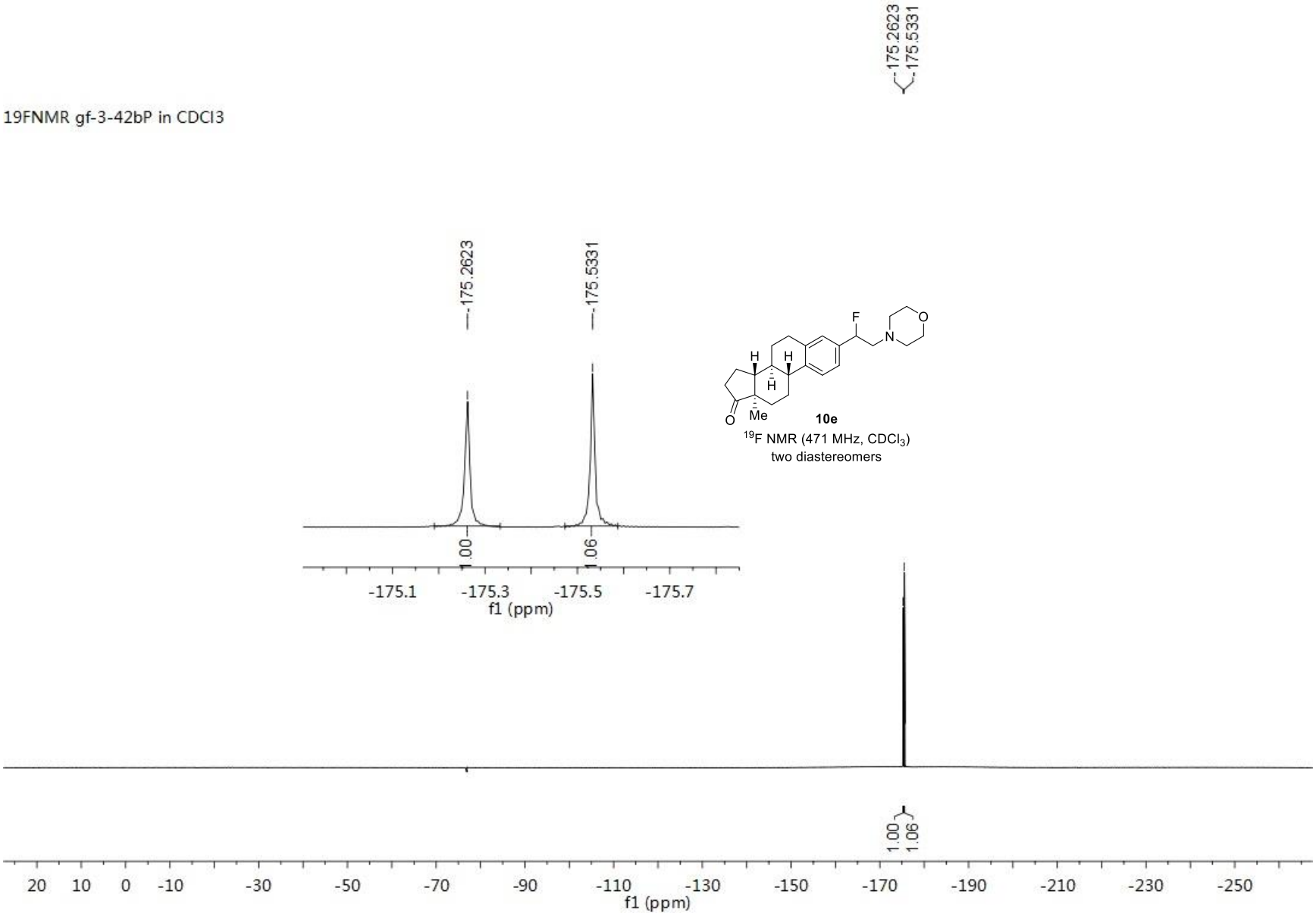
^{19}F NMR (471 MHz, $CDCl_3$)
two diastereomers

1HNMR gf-3-42bP in CDCl3




220.74
140.22
136.82
136.24
136.08
126.27
126.22
126.17
125.59
125.57
123.07
123.02
93.26
93.19
91.88
91.81
66.93
65.02
64.84
54.10
50.51
47.96
44.39
38.07
35.85
31.58
29.44
29.40
26.42
25.70
21.59
13.84
13CNMR gf-3-42bP in CDCL3
F
O
N
H
H
H
Me
O
10e
13C NMR (125 MHz, CDCl3)
two diastereomers
f1 (ppm)

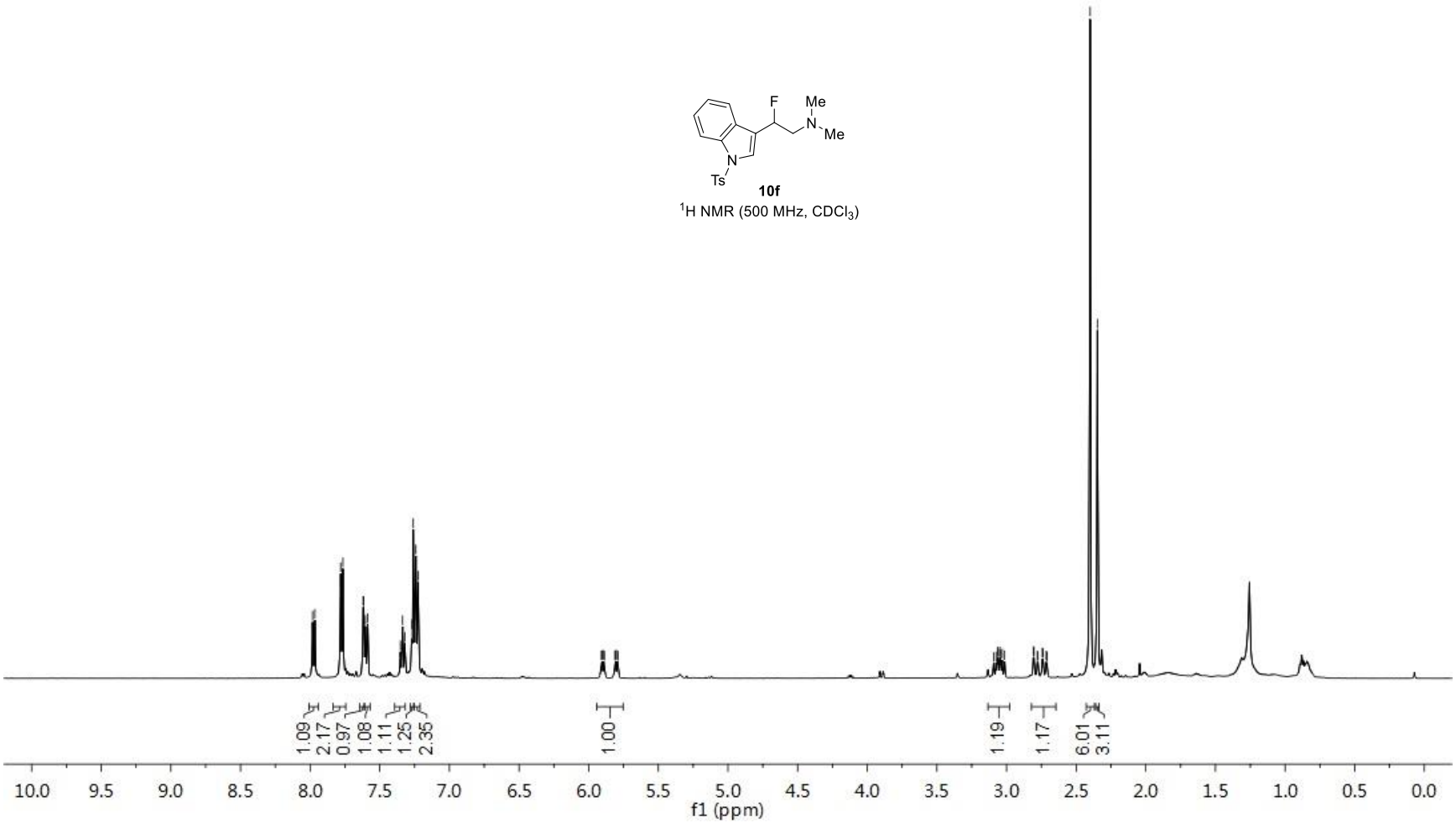
19FNMR gf-3-42bP in CDCl3

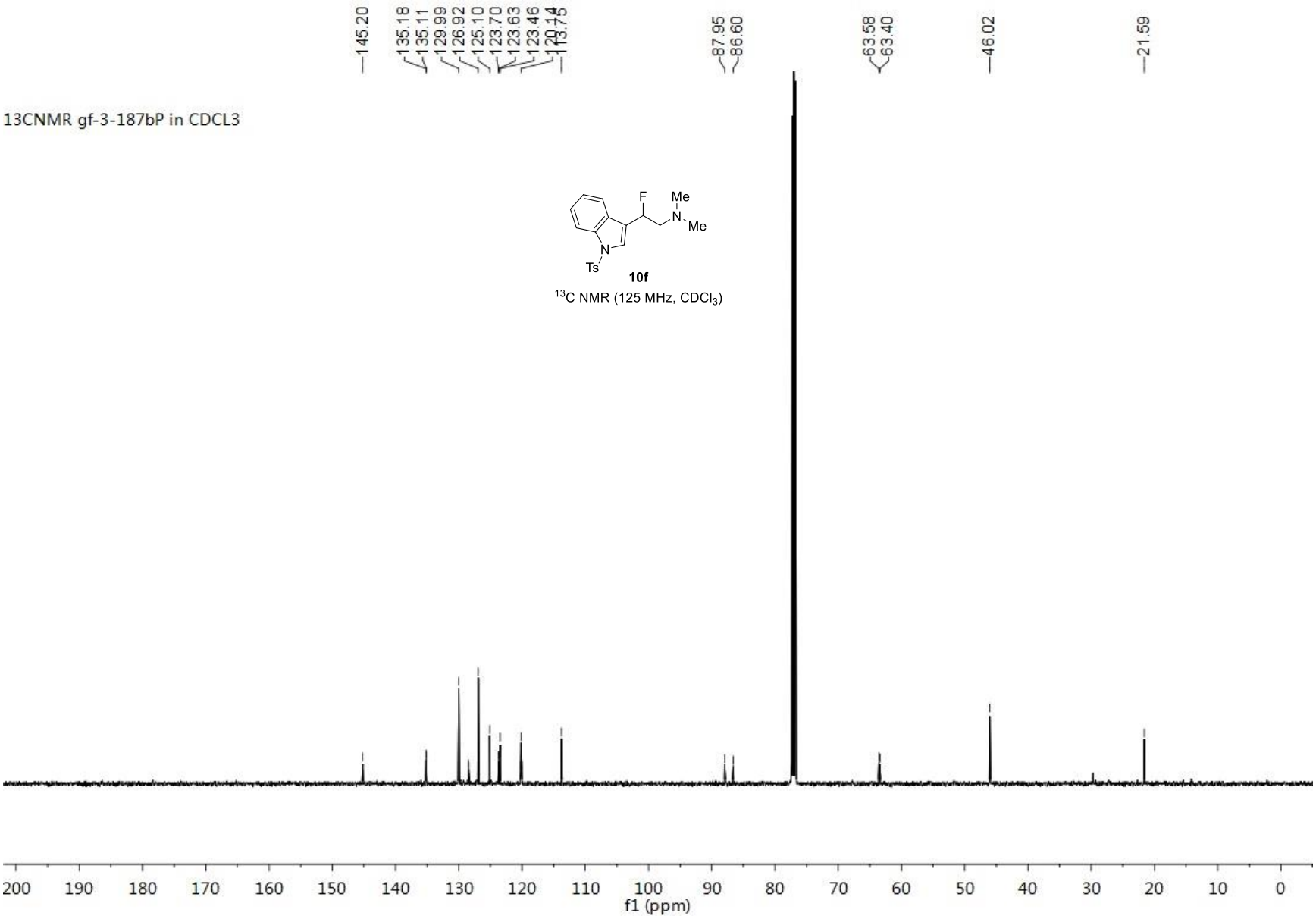


7.9827
7.9661
7.7812
7.7647
7.6198
7.6153
7.6026
7.5869
7.3515
7.3362
7.3209
7.2690
7.2598
7.2549
7.2407
7.2249
5.9090
5.9047
5.8921
5.8876
5.8121
5.8077
5.7952
5.7907

3.0928
3.0755
3.0647
3.0589
3.0476
3.0417
3.0308
3.0136
2.8073
2.8022
2.7793
2.7743
2.7431
2.7380
2.7151
2.7101
2.3998
2.3475

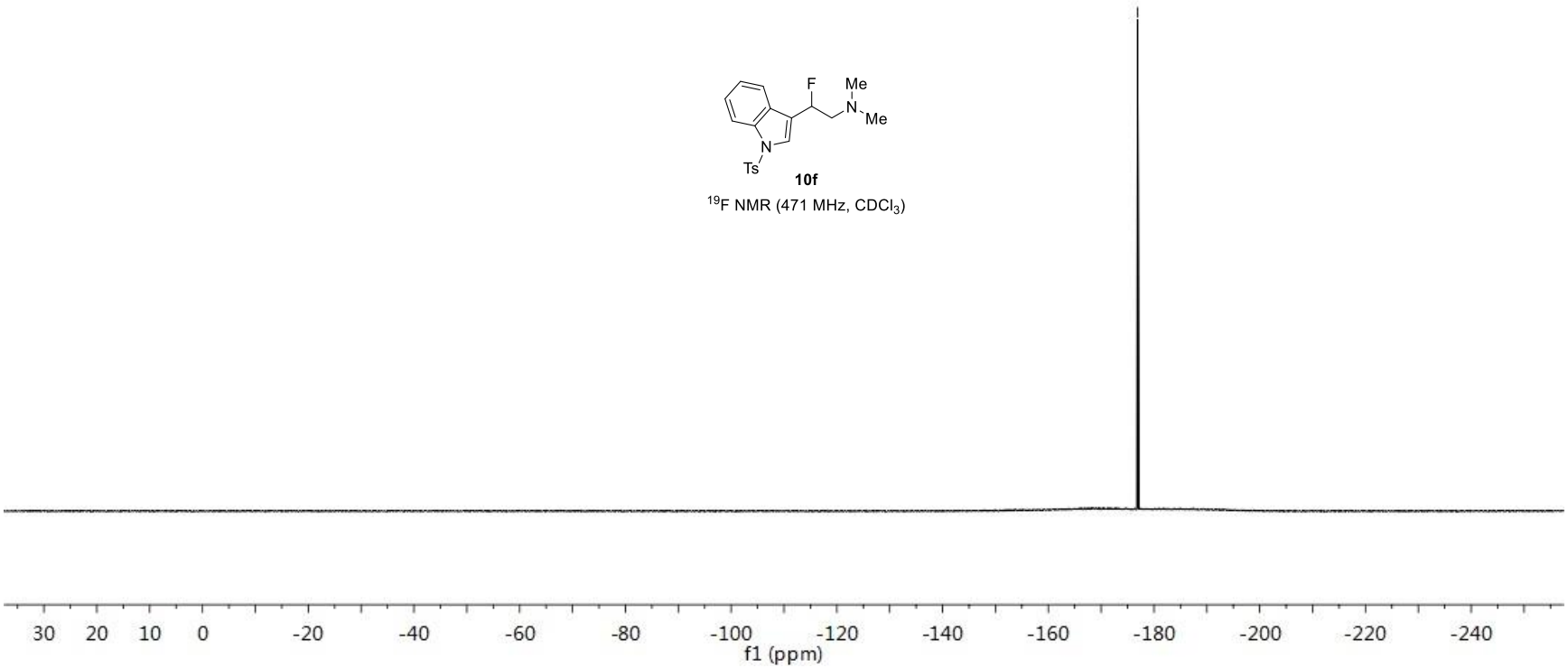
1HNMR gf-3-187bP in CDCl3




145.20
135.18
135.11
129.99
126.92
125.10
123.70
123.63
123.46
120.14
113.75
87.95
86.60
63.58
63.40
46.02
21.59
13CNMR gf-3-187bP in CDCL3
F
Me
N
Me
N
Ts
10f
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

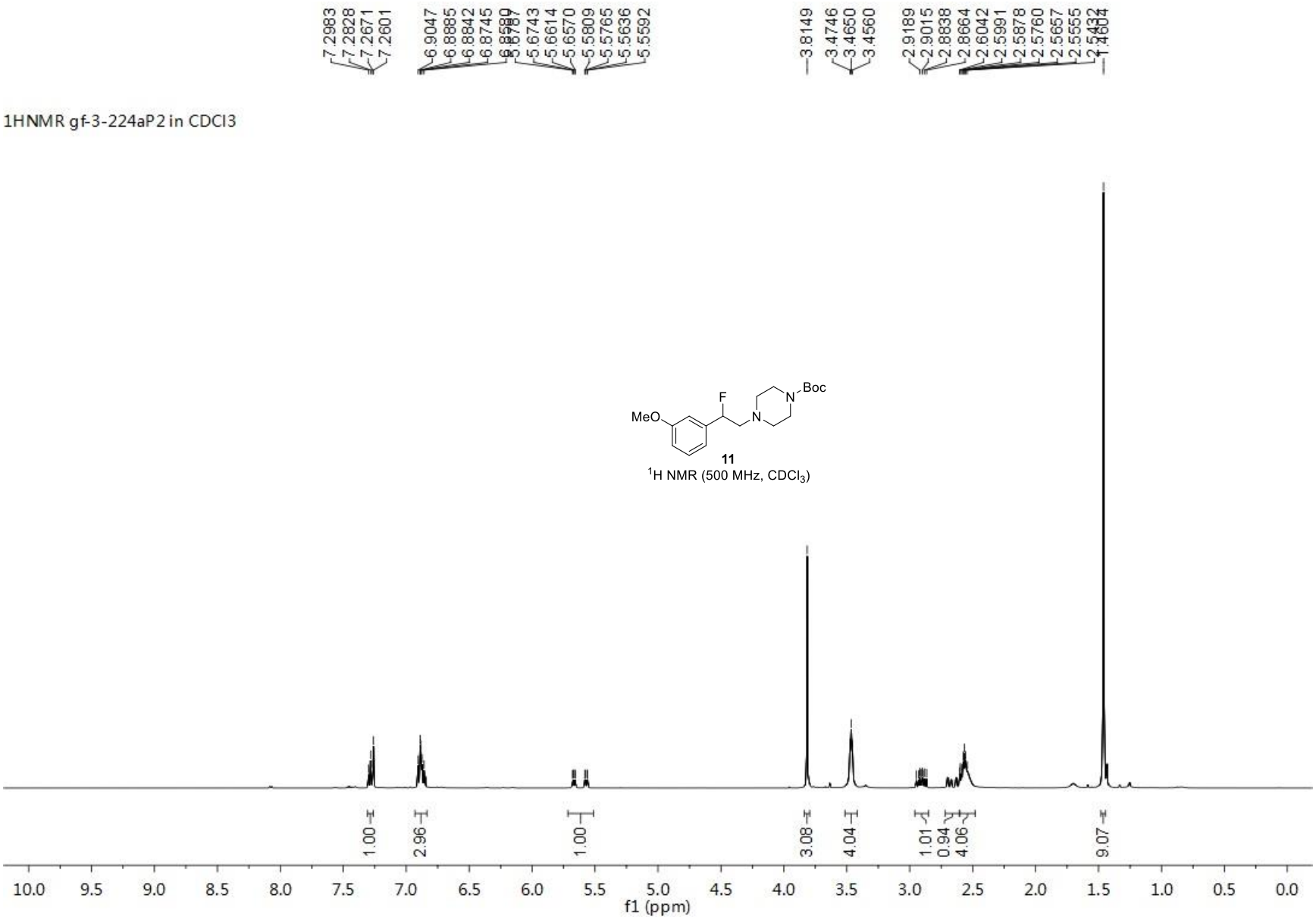
19FNMR gf-3-187bP in CDCl3

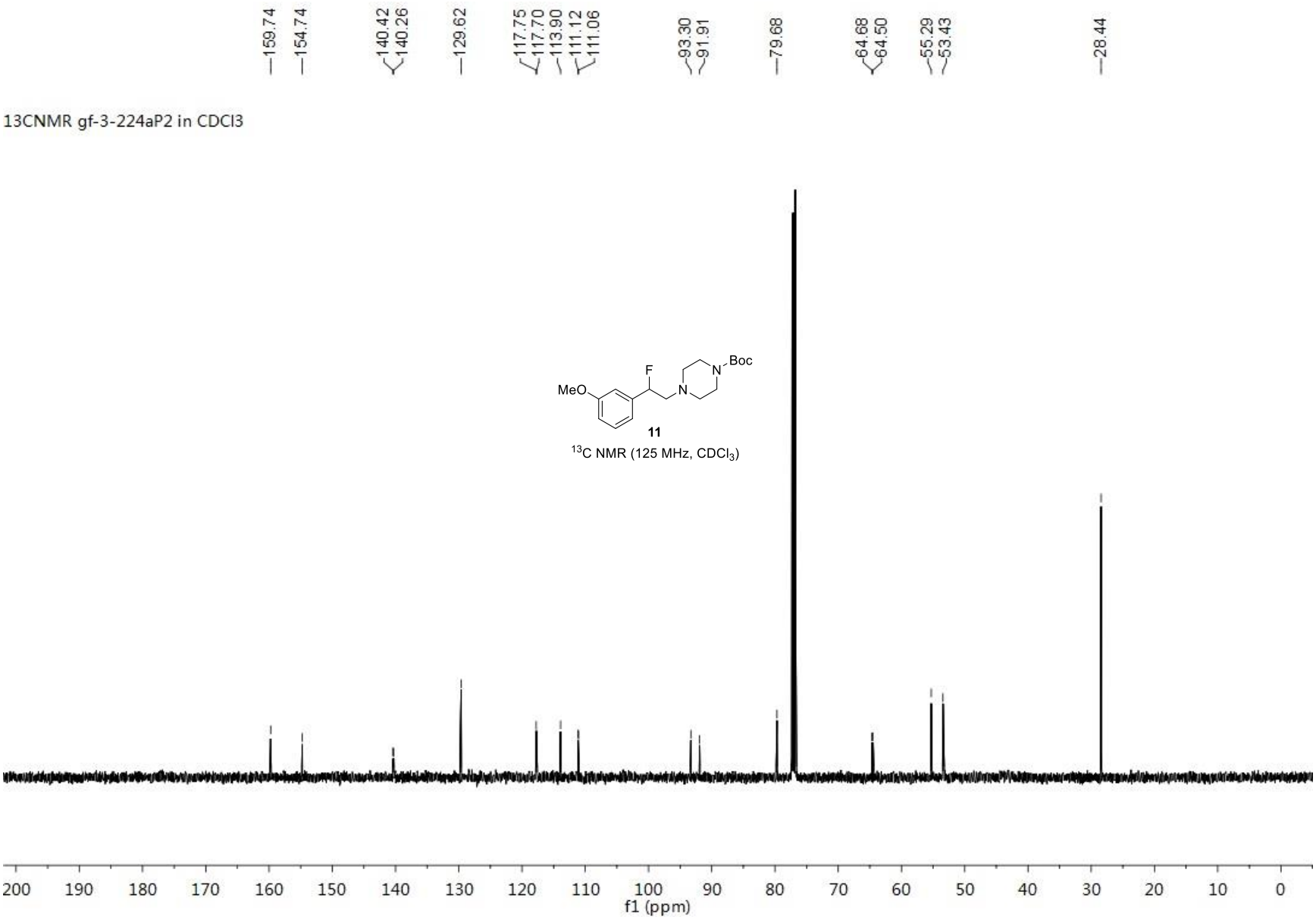
-176.8845



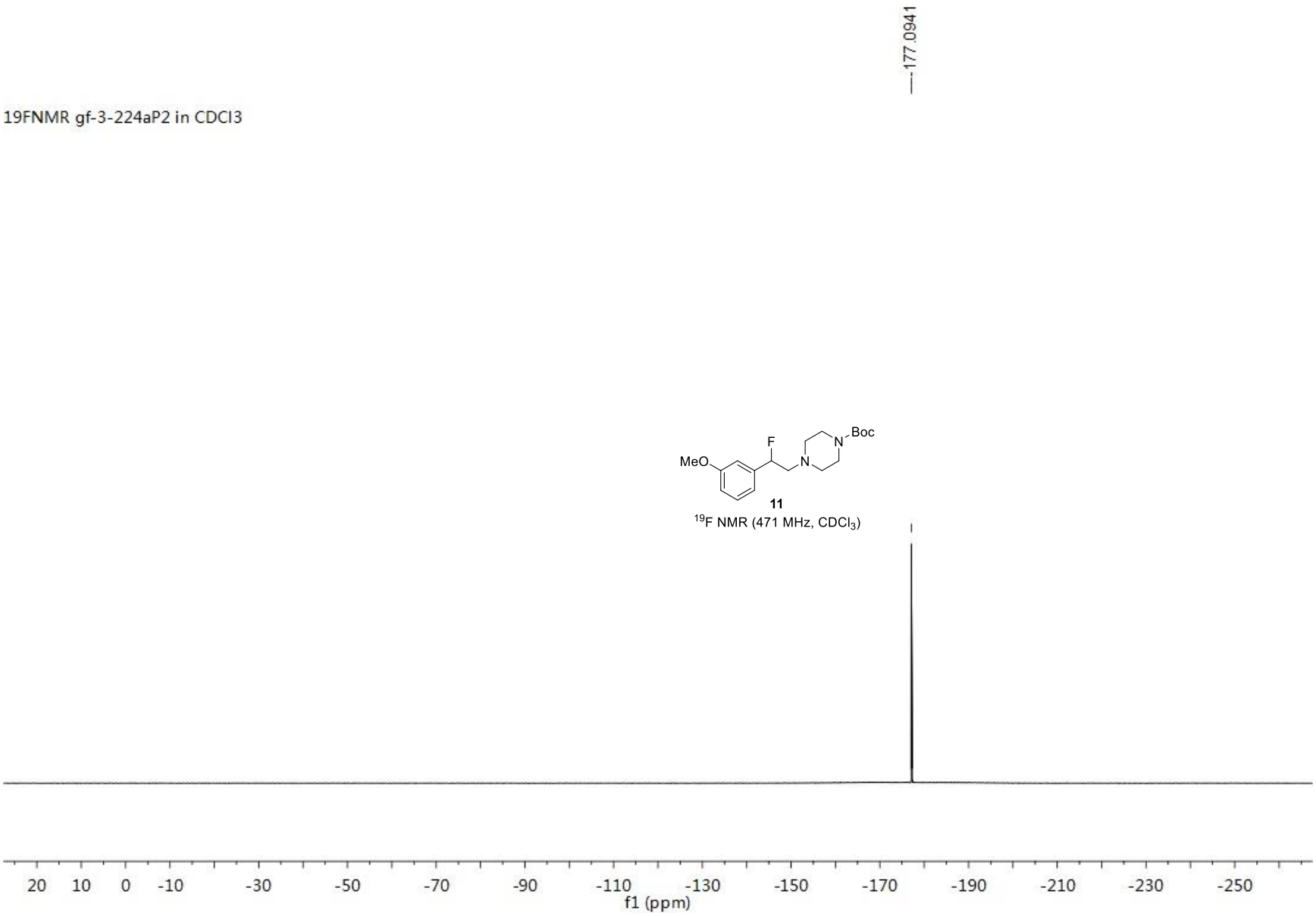
10f

^{19}F NMR (471 MHz, $CDCl_3$)


7.2983
7.2828
7.2671
7.2601
6.9047
6.8885
6.8842
6.8745
6.8587
6.8787
5.6743
5.6614
5.6570
5.5809
5.5765
5.5636
5.5592
3.8149
3.4746
3.4650
3.4560
2.9189
2.9015
2.8838
2.8664
2.6042
2.5991
2.5878
2.5760
2.5657
2.5555
2.5432
1.4604
1HNMR gf-3-224aP2 in CDCl3
MeO
F
N
N
Boc
11
1H NMR (500 MHz, CDCl3)
1.00
2.96
1.00
3.08
4.04
1.01
0.94
4.06
9.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

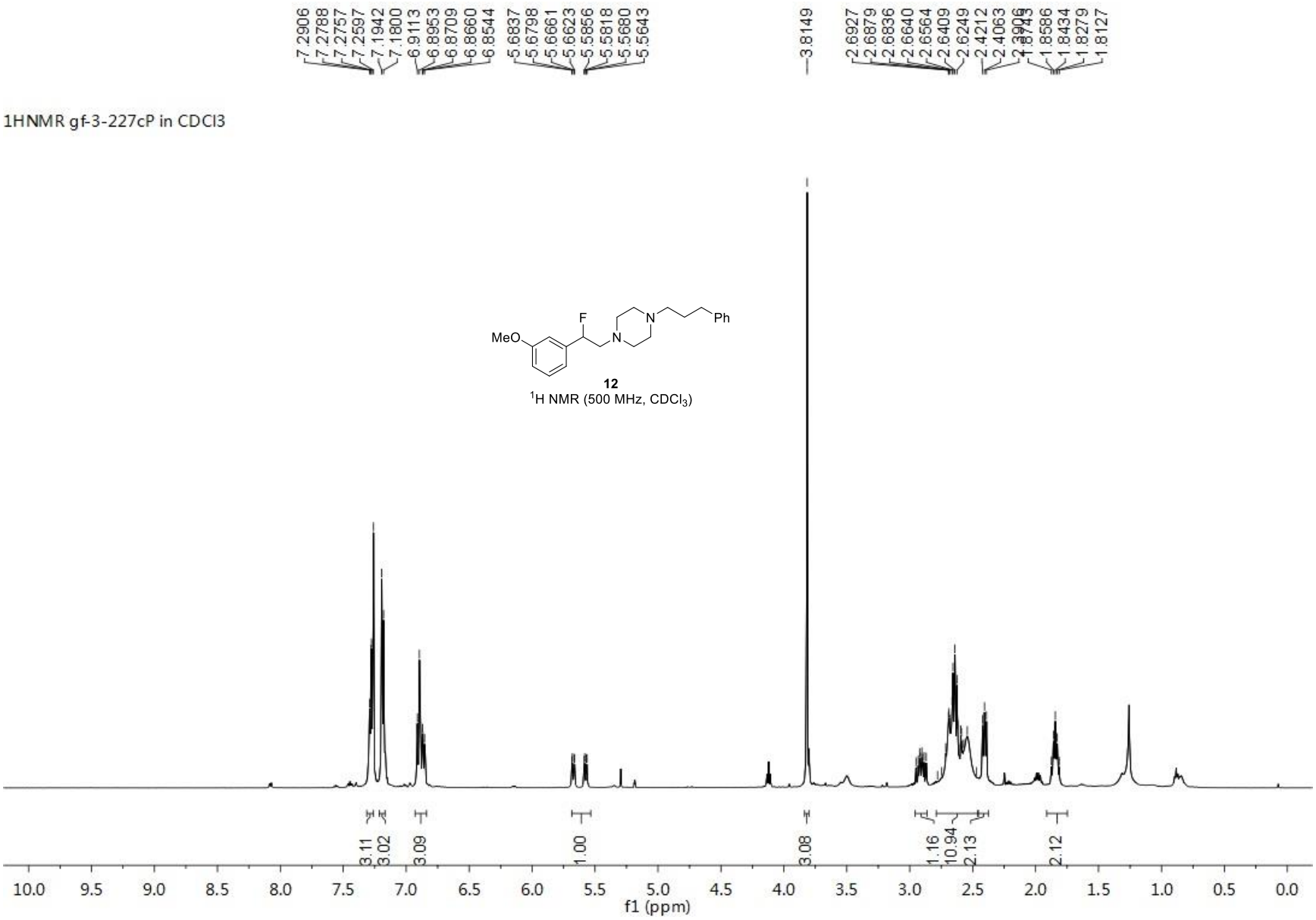

159.74
154.74
140.42
140.26
129.62
117.75
117.70
113.90
111.12
111.06
93.30
91.91
79.68
64.68
64.50
55.29
53.43
28.44
13CNMR gf-3-224aP2 in CDCl3
MeO
F
N
N
Boc
11
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

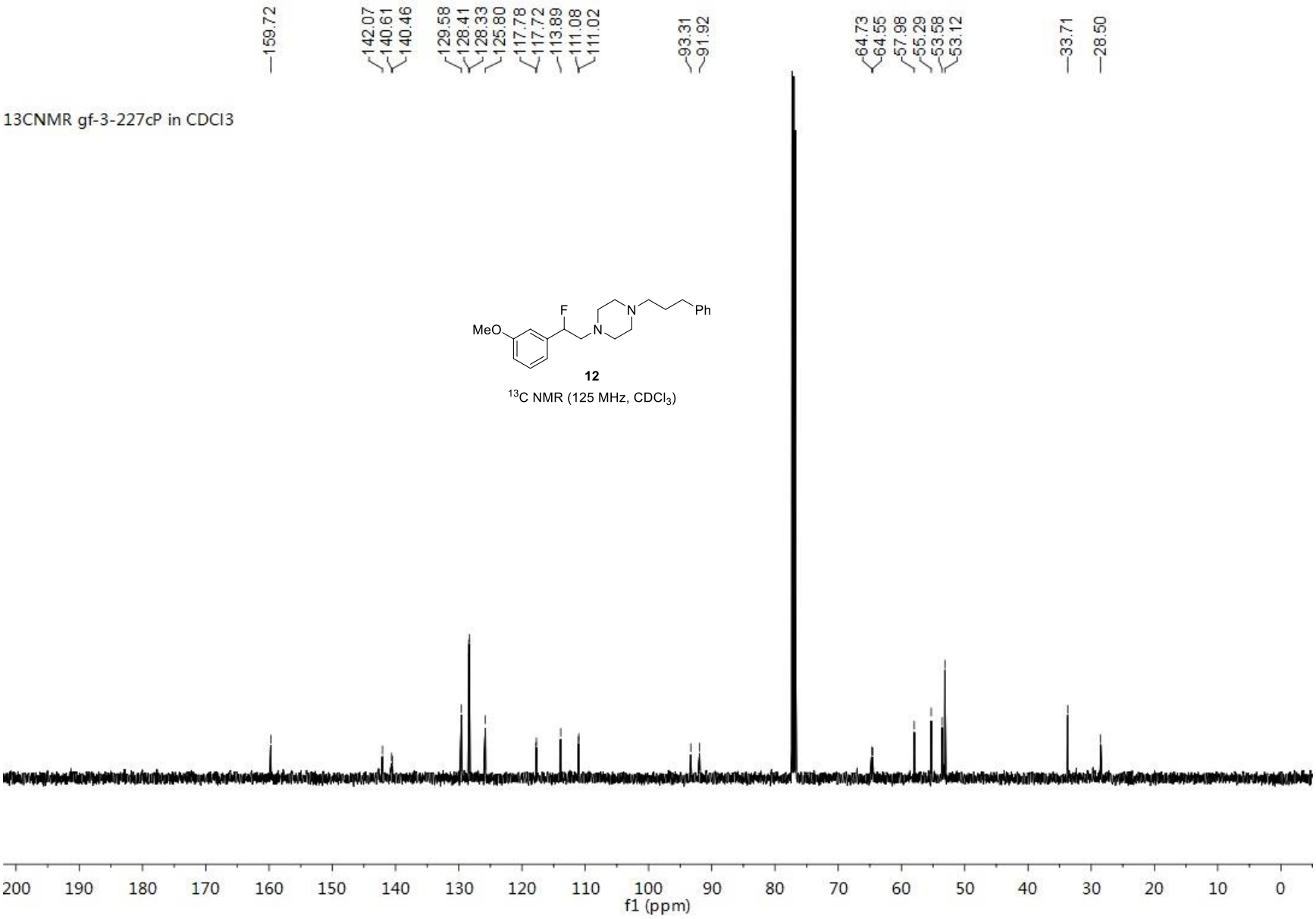
19FNMR gf-3-224aP2 in CDCl3



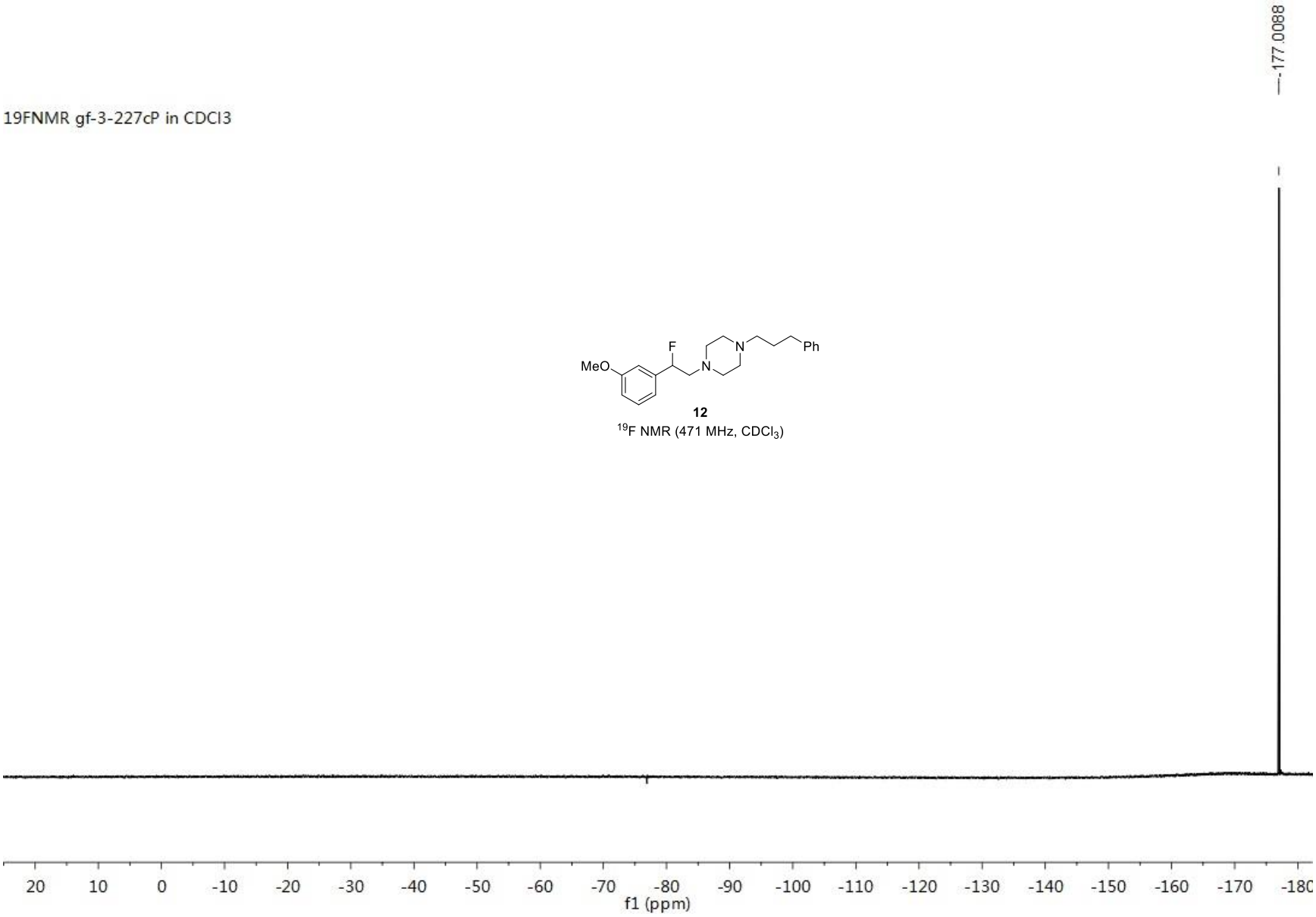
11

^{19}F NMR (471 MHz, $CDCl_3$)


7.2906
7.2788
7.2757
7.2597
7.1942
7.1800
6.9113
6.8953
6.8709
6.8660
6.8544
5.6837
5.6798
5.6661
5.6623
5.5856
5.5818
5.5680
5.5643
3.8149
2.6927
2.6879
2.6836
2.6640
2.6564
2.6409
2.6249
2.4212
2.4063
1.8586
1.8434
1.8279
1.8127
1HNMR gf-3-227cP in CDCl3
MeO
F
N
N
Ph
12
1H NMR (500 MHz, CDCl3)
3.11
3.02
3.09
1.00
3.08
1.16
10.94
2.13
2.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

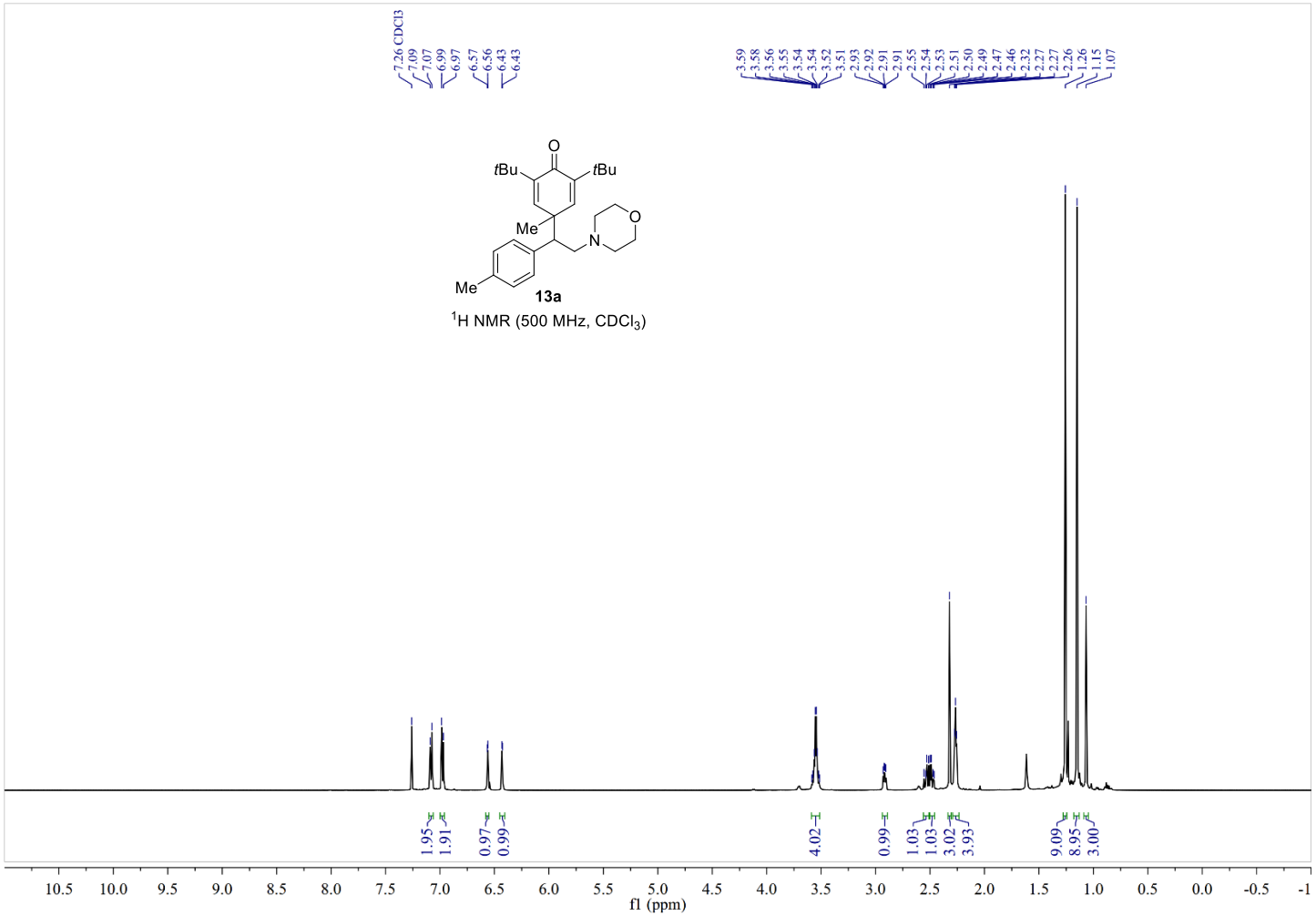

159.72
142.07
140.61
140.46
129.58
128.41
128.33
125.80
117.78
117.72
113.89
111.08
111.02
93.31
91.92
64.73
64.55
57.98
55.29
53.58
53.12
33.71
28.50
13CNMR gf-3-227cP in CDCl3
MeO
F
N
N
Ph
12
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

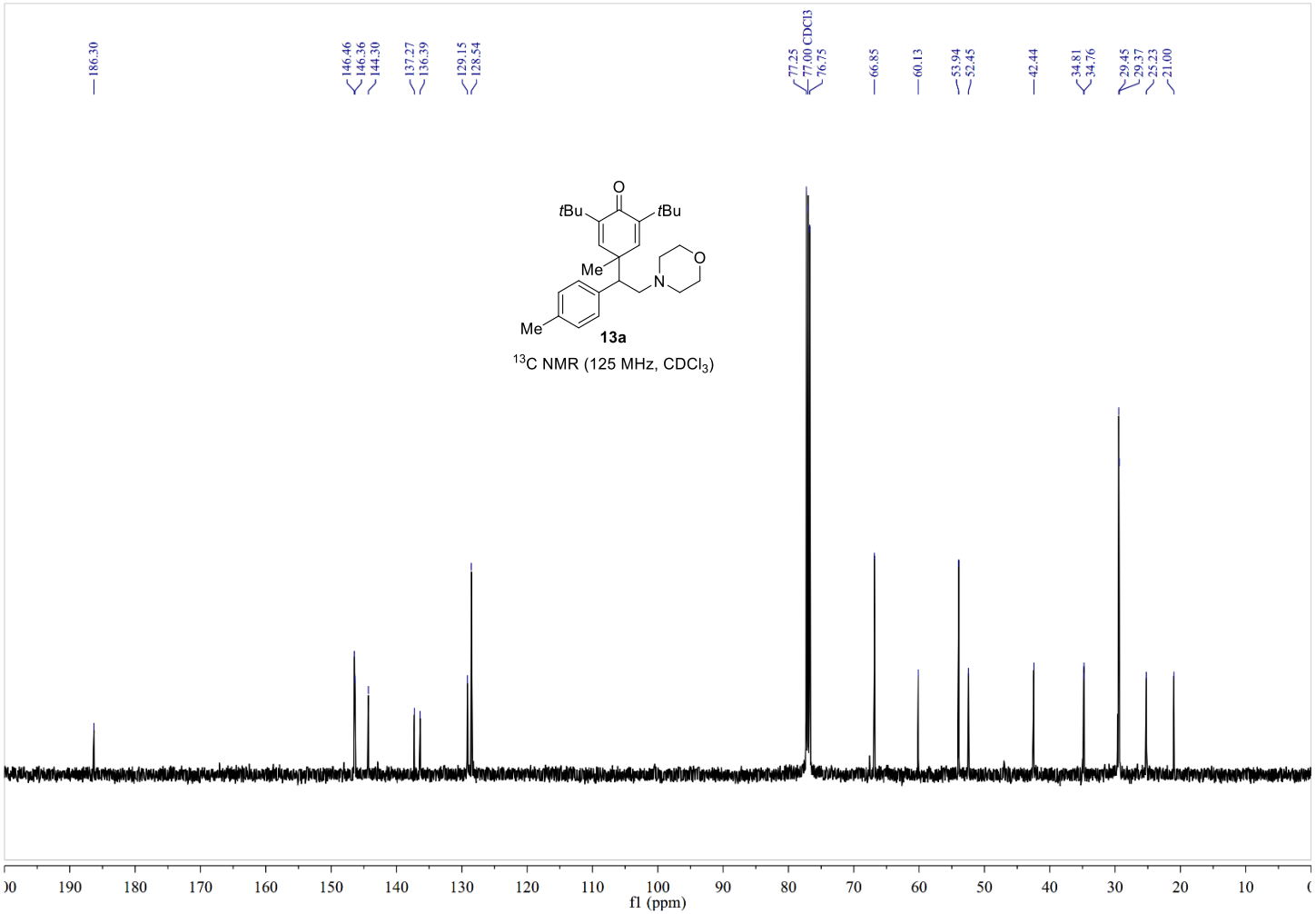
19FNMR gf-3-227cP in CDCl3



12

^{19}F NMR (471 MHz, $CDCl_3$)

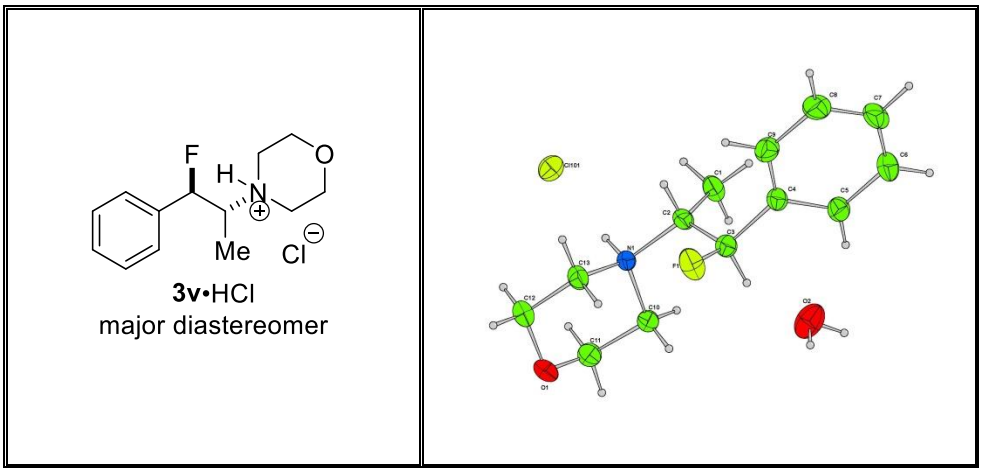

7.26 CDCl3
7.09
7.07
6.99
6.97
6.57
6.56
6.43
6.43
3.59
3.58
3.56
3.55
3.54
3.54
3.52
3.51
2.93
2.92
2.91
2.91
2.55
2.54
2.53
2.51
2.50
2.49
2.47
2.46
2.32
2.27
2.27
2.26
1.26
1.15
1.07
O
tBu
tBu
Me
N
O
Me
13a
1H NMR (500 MHz, CDCl3)
1.95
1.91
0.97
0.99
4.02
0.99
1.03
1.03
3.02
3.93
9.09
8.95
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


186.30
146.46
146.36
144.30
137.27
136.39
129.15
128.54
77.25
77.00 CDCl3
76.75
66.85
60.13
53.94
52.45
42.44
34.81
34.76
29.45
29.37
25.23
21.00
O
tBu
tBu
Me
N
O
Me
13a
13C NMR (125 MHz, CDCl3)
f1 (ppm)

11. X-ray crystallography information

The major single diastereomer of compound **3v**•HCl was recrystallized twice in dichloromethane and hexanes. Then, a crystal of was slowly grown from dichloromethane, ethyl acetate and *n*-hexane, which is suitable for X-ray diffraction analysis. The chemical structure was showed as follows, CCDC number is 2210154. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc. com.ac.uk/data_request/cif.

Crystal structure report for 22097 (**3v**•HCl–major single diastereomer)



The sample was submitted by Guangshou Feng (research group of Wang, Department of Chemistry, Duke University). A colorless crystal (approximate dimensions 0.230 x 0.100 x 0.040 mm^3) was placed onto the tip of MiTeGen and mounted on a Bruker D8 VENTURE diffractometer and measured at 150 K.

Table 1. Crystal data and structure refinement for 22097.

Empirical formula	C13 H20.50 Cl1 F1.00 N1 O1.75	
Formula weight	273.26	
Crystal color, shape, size	colorless block fragment, 0.230 x 0.100 x 0.040 mm^3	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, C2/c	
Unit cell dimensions	a = 22.792(2) Å	a= 90°.
	b = 11.6050(13) Å	b= 111.875(3)°.
	c = 23.759(3) Å	g = 90°.
Volume	5831.8(10) $Å^3$	
Z	16	
Density (calculated)	1.245 Mg/m^3	
Absorption coefficient	0.266 mm^{-1}	
F(000)	2328	

Data collection	
Diffractometer	Bruker D8 VENTURE, Bruker
Theta range for data collection	2.002 to 25.697°.
Index ranges	-27<=h<=26, -14<=k<=14, -28<=l<=28
Reflections collected	84262
Independent reflections	5542 [R(int) = 0.192]
Observed Reflections	3473
Completeness to theta = 25.697°	99.7 %
Solution and Refinement	
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.99 and 0.97
Solution	Intrinsic phasing methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = [s^2Fo^2 + AP^2 + BP]^{-1}$, with
	$P = (Fo^2 + 2\,Fc^2)/3$, A = 0.115, B = 12.240
Data / restraints / parameters	5542 / 183 / 414
Goodness-of-fit on F^2	0.9871
Final R indices [I>2sigma(I)]	R1 = 0.0752, wR2 = 0.2076
R indices (all data)	R1 = 0.1109, wR2 = 0.2320
Largest diff. peak and hole	1.21 and -1.20 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 22097. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl1	2371(1)	4325(1)	4342(1)	57
Cl101	4124(1)	8189(1)	2817(1)	66
F1	4143(2)	4872(2)	4548(1)	86
F101	4538(4)	4343(5)	5999(5)	42
F201	4444(2)	4427(4)	5808(3)	47
O1	3365(2)	8662(3)	4296(2)	93
O2	2054(2)	4746(5)	2935(2)	105
O101	4450(2)	796(3)	5456(2)	70
O102	5000	3638(5)	7500	88
N1	3723(1)	6803(3)	3708(1)	46
N101	3685(1)	2456(2)	5755(1)	42
C1	3526(2)	5372(3)	2882(2)	65
C2	3818(1)	5581(2)	3535(1)	54
C3	3752(1)	4666(2)	3935(1)	57
C4	3936(1)	3478(2)	3791(2)	56

C5	3415(2)	2767(3)	3456(2)	64
C6	3534(2)	1683(3)	3270(2)	76
C7	4140(2)	1340(3)	3400(2)	83
C8	4632(2)	2034(4)	3720(3)	88
C9	4520(2)	3120(3)	3910(2)	71
C10	3044(2)	7002(4)	3639(2)	62
C11	2956(3)	8271(4)	3722(3)	82
C12	4006(3)	8519(5)	4355(3)	79
C13	4153(2)	7268(4)	4305(2)	63
C101	2871(4)	3805(4)	5812(5)	73
C102	3530(1)	3640(2)	5925(2)	60
C103	3877(2)	4598(4)	5814(2)	42
C104	3843(2)	5707(2)	6155(1)	52
C105	3445(8)	6608(9)	5760(3)	53
C106	3443(8)	7690(8)	5995(4)	55
C107	3745(7)	7871(8)	6589(4)	53
C108	4118(8)	7010(10)	6961(4)	54
C109	4169(9)	5924(9)	6714(4)	49
C110	3744(2)	2416(4)	5151(2)	52
C111	3885(3)	1218(4)	5006(2)	67
C112	4362(2)	729(4)	6017(2)	64
C113	4247(2)	1899(4)	6224(2)	50
C201	3058(3)	3632(4)	6200(3)	48
C203	4047(1)	4444(3)	6157(1)	48
C205	3520(5)	6320(5)	5672(2)	60
C206	3367(5)	7469(6)	5736(3)	68
C207	3572(4)	7969(5)	6305(3)	62
C208	3923(5)	7369(6)	6799(3)	65
C209	4060(6)	6220(5)	6742(2)	58

Table 3. Bond lengths [Å] and angles [°] for 22097.

H1-N1	0.884(19)	H2-N101	0.883(19)
H3-O2	0.83(2)	H4-O2	0.83(2)
H5-O102	0.841(14)	F1-C3	1.417(4)
F101-C103	1.436(9)	F201-C203	1.438(6)
O1-C11	1.410(7)	O1-C12	1.424(6)
O101-C111	1.420(6)	O101-C112	1.423(6)
N1-C2	1.515(4)	N1-C10	1.512(5)
N1-C13	1.493(5)	N101-C102	1.511(4)
N101-C110	1.492(5)	N101-C113	1.496(5)
C1-C2	1.461(5)	C1-H11	0.950
C1-H12	0.950	C1-H13	0.950
C2-C3	1.470(4)	C2-H21	0.950
C3-C4	1.517(3)	C3-H31	0.950
C4-C5	1.421(4)	C4-C9	1.320(4)
C5-C6	1.393(5)	C5-H51	0.950
C6-C7	1.359(5)	C6-H61	0.950
C7-C8	1.360(5)	C7-H71	0.950
C8-C9	1.396(5)	C8-H81	0.950
C9-H91	0.950	C10-C11	1.509(7)
C10-H101	0.950	C10-H102	0.950
C11-H111	0.950	C11-H112	0.950
C12-C13	1.505(7)	C12-H121	0.950
C12-H122	0.950	C13-H131	0.950
C13-H132	0.950	C101-C102	1.437(9)
C101-H1011	0.950	C101-H1012	0.950
C101-H1013	0.950	C102-C103	1.443(5)
C102-H1021	0.950	C102-C201	1.452(5)
C102-C203	1.441(4)	C102-H1022	0.950
C103-C104	1.537(4)	C103-C104	1.537(4)
C103-H1032	0.950	C104-C105	1.471(7)
C104-C109	1.282(7)	C104-C203	1.537(4)
C104-C205	1.316(6)	C104-C209	1.427(6)
C105-C106	1.375(7)	C105-H1051	0.950
C106-C107	1.336(8)	C106-H1061	0.950
C107-C108	1.395(8)	C107-H1071	0.950
C108-C109	1.414(7)	C108-H1081	0.950
C109-H1091	0.950	C110-C111	1.496(6)
C110-H1101	0.950	C110-H1102	0.950
C111-H1111	0.950	C111-H1112	0.950
C112-C113	1.499(6)	C112-H1121	0.950
C112-H1122	0.950	C113-H1131	0.950

C113-H1132	0.950	C201-H2011	0.950
C201-H2012	0.950	C201-H2013	0.950
C203-H2031	0.950	C205-C206	1.401(6)
C205-H2051	0.950	C206-C207	1.381(6)
C206-H2061	0.950	C207-C208	1.342(6)
C207-H2071	0.950	C208-C209	1.387(6)
C208-H2081	0.950	C209-H2091	0.950

C11-O1-C12	110.0(4)	H4-O2-H3	97(8)
C111-O101-C112	108.6(3)	H5-O102-H5#1	114(11)
H1-N1-C2	105.1(15)	H1-N1-C10	105.5(15)
C2-N1-C10	111.0(3)	H1-N1-C13	105.8(15)
C2-N1-C13	119.1(3)	C10-N1-C13	109.3(3)
H2-N101-C102	106.4(15)	H2-N101-C110	106.5(15)
C102-N101-C110	113.5(3)	H2-N101-C113	105.1(15)
C102-N101-C113	114.5(3)	C110-N101-C113	110.1(3)
C2-C1-H11	109.2	C2-C1-H12	109.9
H11-C1-H12	109.5	C2-C1-H13	109.3
H11-C1-H13	109.5	H12-C1-H13	109.5
N1-C2-C1	112.83(10)	N1-C2-C3	116.15(9)
C1-C2-C3	116.76(10)	N1-C2-H21	102.9
C1-C2-H21	102.9	C3-C2-H21	102.5
C2-C3-F1	111.47(10)	C2-C3-C4	114.01(10)
F1-C3-C4	105.31(10)	C2-C3-H31	108.3
F1-C3-H31	108.8	C4-C3-H31	108.8
C3-C4-C5	114.23(8)	C3-C4-C9	125.34(8)
C5-C4-C9	120.21(8)	C4-C5-C6	118.78(9)
C4-C5-H51	119.8	C6-C5-H51	121.4
C5-C6-C7	119.60(9)	C5-C6-H61	119.9
C7-C6-H61	120.5	C6-C7-C8	120.75(9)
C6-C7-H71	119.8	C8-C7-H71	119.4
C7-C8-C9	120.17(9)	C7-C8-H81	119.9
C9-C8-H81	119.8	C8-C9-C4	120.48(9)
C8-C9-H91	119.8	C4-C9-H91	119.7
N1-C10-C11	108.4(4)	N1-C10-H101	109.6
C11-C10-H101	109.1	N1-C10-H102	109.8
C11-C10-H102	110.5	H101-C10-H102	109.5
C10-C11-O1	111.6(5)	C10-C11-H111	108.3
O1-C11-H111	107.8	C10-C11-H112	110.1
O1-C11-H112	109.5	H111-C11-H112	109.5
O1-C12-C13	110.8(4)	O1-C12-H121	108.7

C13-C12-H121	109.5	O1-C12-H122	109.1
C13-C12-H122	109.3	H121-C12-H122	109.5
C12-C13-N1	109.6(4)	C12-C13-H131	109.7
N1-C13-H131	109.5	C12-C13-H132	109.5
N1-C13-H132	108.9	H131-C13-H132	109.5
H1011-C101-H1012	109.5	H1011-C101-H1013	109.5
H1012-C101-H1013	109.5	N101-C102-C101	113.76(10)
N101-C102-C103	117.01(9)	C101-C102-C103	117.93(10)
N101-C102-H1021	103.3	C101-C102-H1021	96.9
C103-C102-H1021	103.6	N101-C102-C201	113.59(10)
N101-C102-C203	116.90(9)	C201-C102-C203	117.92(10)
N101-C102-H1022	101.4	C201-C102-H1022	102.2
C203-C102-H1022	100.8	C102-C103-C104	114.27(10)
F101-C103-C104	105.34(10)	F101-C103-H1032	107.2
C104-C103-H1032	108.2	C103-C104-C105	113.58(10)
C103-C104-C109	125.87(10)	C105-C104-C109	120.17(10)
C203-C104-C205	126.05(8)	C203-C104-C209	113.60(8)
C205-C104-C209	120.30(8)	C104-C105-C106	119.03(10)
C104-C105-H1051	119.5	C106-C105-H1051	121.4
C105-C106-C107	119.60(10)	C105-C106-H1061	119.7
C107-C106-H1061	120.7	C106-C107-C108	120.70(10)
C106-C107-H1071	119.8	C108-C107-H1071	119.5
C107-C108-C109	119.95(10)	C107-C108-H1081	120.0
C109-C108-H1081	120.0	C108-C109-C104	120.05(10)
C108-C109-H1091	119.9	C104-C109-H1091	120.0
N101-C110-C111	110.8(4)	N101-C110-H1101	109.2
C111-C110-H1101	108.8	N101-C110-H1102	109.0
C111-C110-H1102	109.7	H1101-C110-H1102	109.5
C110-C111-O101	111.0(4)	C110-C111-H1111	108.9
O101-C111-H1111	108.9	C110-C111-H1112	109.1
O101-C111-H1112	109.4	H1111-C111-H1112	109.5
O101-C112-C113	111.1(4)	O101-C112-H1121	109.6
C113-C112-H1121	110.2	O101-C112-H1122	108.6
C113-C112-H1122	107.7	H1121-C112-H1122	109.5
C112-C113-N101	110.6(3)	C112-C113-H1131	110.2
N101-C113-H1131	109.6	C112-C113-H1132	108.0
N101-C113-H1132	108.9	H1131-C113-H1132	109.5
H2011-C201-H2012	109.5	H2011-C201-H2013	109.5
H2012-C201-H2013	109.5	C104-C203-C102	114.41(10)
C104-C203-F201	105.39(10)	C104-C203-H2031	108.3
F201-C203-H2031	110.3	C104-C205-C206	120.03(9)
C104-C205-H2051	120.0	C206-C205-H2051	120.0
C205-C206-C207	119.94(9)	C205-C206-H2061	120.0

C207-C206-H2061	120.1	C206-C207-C208	120.74(9)
C206-C207-H2071	119.4	C208-C207-H2071	119.8
C207-C208-C209	119.74(9)	C207-C208-H2081	120.4
C209-C208-H2081	119.9	C104-C209-C208	119.15(9)
C104-C209-H2091	119.6	C208-C209-H2091	121.2

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+3/2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 22097. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl1	46(1)	54(1)	68(1)	4(1)	16(1)	-5(1)
Cl101	69(1)	67(1)	64(1)	15(1)	26(1)	-1(1)
F1	137(3)	60(2)	57(2)	1(1)	34(2)	-6(2)
F101	35(4)	44(5)	43(6)	-3(4)	8(4)	-2(3)
F201	45(3)	47(3)	52(4)	-4(2)	22(3)	-2(2)
O1	116(3)	61(2)	134(4)	-35(2)	84(3)	-9(2)
O2	85(3)	133(4)	83(3)	13(3)	15(2)	-30(3)
O101	65(2)	56(2)	97(3)	-12(2)	40(2)	12(2)
O102	99(4)	78(4)	64(3)	0	4(3)	0
N1	54(2)	36(2)	54(2)	-2(2)	28(2)	-2(2)
N101	37(2)	34(2)	58(2)	-4(2)	20(2)	-1(1)
C1	92(3)	48(3)	55(3)	-6(2)	29(3)	-5(2)
C2	69(3)	39(2)	63(3)	-4(2)	36(2)	1(2)
C3	70(3)	47(3)	63(3)	0(2)	34(2)	-4(2)
C4	71(3)	39(2)	65(3)	3(2)	35(2)	-2(2)
C5	66(3)	44(3)	87(3)	3(2)	33(3)	4(2)
C6	89(4)	47(3)	89(4)	-5(3)	30(3)	-5(3)
C7	124(5)	40(3)	107(4)	4(3)	67(4)	13(3)
C8	88(4)	56(3)	140(5)	16(3)	65(4)	25(3)
C9	60(3)	58(3)	100(4)	6(3)	36(3)	3(2)
C10	57(2)	49(3)	90(3)	-9(2)	37(2)	-1(2)
C11	78(3)	50(3)	137(5)	-8(3)	63(4)	3(3)
C12	92(4)	60(3)	92(4)	-27(3)	43(3)	-17(3)
C13	76(3)	54(3)	62(3)	-14(2)	29(2)	-12(2)
C101	62(6)	64(5)	89(6)	-10(6)	23(5)	-8(5)
C102	59(2)	42(2)	93(3)	-8(2)	43(2)	0(2)
C103	46(4)	37(4)	50(5)	0(4)	27(4)	1(4)
C104	58(2)	36(2)	73(3)	-6(2)	36(2)	-6(2)
C105	64(6)	43(5)	58(5)	1(5)	28(5)	13(6)
C106	68(5)	53(6)	48(7)	7(6)	27(7)	2(6)
C107	67(7)	41(5)	50(6)	4(5)	21(5)	13(4)
C108	73(10)	36(6)	48(6)	9(5)	16(5)	17(6)
C109	58(7)	32(6)	58(5)	-1(5)	24(5)	18(6)
C110	56(2)	45(2)	47(2)	-4(2)	11(2)	3(2)
C111	88(3)	51(3)	65(3)	-15(2)	32(3)	-2(3)
C112	53(2)	42(3)	83(3)	6(2)	11(2)	7(2)
C113	51(2)	46(2)	47(2)	3(2)	13(2)	0(2)
C201	51(3)	42(3)	65(4)	-14(3)	38(3)	-4(3)

C203	56(4)	42(3)	50(4)	-6(3)	24(3)	-4(3)
C205	74(5)	52(5)	64(4)	-8(4)	37(4)	1(4)
C206	74(5)	56(5)	71(6)	19(5)	24(5)	4(4)
C207	73(6)	45(4)	71(5)	-1(4)	30(5)	7(4)
C208	79(7)	51(5)	64(5)	-2(4)	24(4)	6(5)
C209	74(6)	35(5)	69(4)	-4(3)	33(4)	6(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 22097.

	x	y	z	U(eq)
H1	3782(11)	7243(19)	3430(10)	68(2)
H2	3362(10)	2009(19)	5728(10)	63(2)
H3	2100(40)	4610(80)	3290(16)	158(2)
H4	1720(20)	4370(70)	2770(40)	158(2)
H5	5190(30)	3240(60)	7320(30)	131(2)
H11	3601	4597	2800	80
H12	3702	5877	2672	80
H13	3084	5503	2751	80
H21	4258	5558	3609	65
H31	3324	4647	3902	69
H51	2996	3032	3368	79
H61	3191	1194	3049	93
H71	4223	616	3258	97
H81	5054	1766	3828	103
H91	4865	3611	4122	86
H101	2956	6581	3942	75
H102	2768	6755	3249	75
H111	3054	8683	3423	100
H112	2530	8421	3675	100
H121	4274	8807	4739	100
H122	4076	8942	4043	100
H131	4580	7190	4339	74
H132	4091	6844	4621	74
H1011	2798	4564	5922	94
H1012	2707	3262	6015	94
H1013	2667	3709	5386	94
H1021	3673	3608	6355	72
H1022	3303	3964	5537	72
H1032	3723	4765	5393	56
H1051	3185	6426	5353	70
H1061	3223	8300	5734	73
H1071	3706	8594	6759	68
H1081	4350	7163	7378	68
H1091	4441	5352	6963	63
H1101	4079	2909	5157	61
H1102	3359	2674	4850	61
H1111	3544	728	4988	79
H1112	3929	1219	4623	79

H1121	4722	384	6315	77
H1122	3999	271	5961	77
H1131	4182	1840	6595	59
H1132	4610	2359	6283	59
H2011	2977	4399	6290	61
H2012	3212	3194	6564	61
H2013	2679	3296	5928	61
H2031	4281	4224	6565	62
H2051	3385	5979	5281	78
H2061	3125	7904	5389	88
H2071	3468	8749	6344	79
H2081	4072	7724	7187	79
H2091	4298	5773	7087	72

Table 6. Torsion angles [°] for 22097.

C112-O101-C111-C110	63.3(5)	C111-O101-C112-C113	-63.1(5)
C110-N101-C102-C201	137.7(4)	C110-N101-C102-C203	-79.7(4)
C113-N101-C102-C201	-94.8(4)	C113-N101-C102-C203	47.9(4)
C102-N101-C110-C111	-178.9(4)	C113-N101-C110-C111	51.2(5)
C102-N101-C113-C112	179.8(3)	C110-N101-C113-C112	-50.9(4)
C12-O1-C11-C10	62.2(6)	C11-O1-C12-C13	-61.3(6)
C201-C102-C203-F201	-174.8(4)	N101-C102-C203-F201	44.2(4)
N101-C102-C203-C104	163.8(3)	C201-C102-C203-C104	-55.2(4)
C209-C104-C203-F201	-116.9(7)	C209-C104-C203-C102	119.9(6)
C205-C104-C203-C102	-62.6(7)	C209-C104-C205-C206	-2.5(14)
C203-C104-C209-C208	178.1(9)	C203-C104-C205-C206	-179.8(7)
C205-C104-C203-F201	60.5(8)	C205-C104-C209-C208	0.5(15)
N101-C110-C111-O101	-58.2(6)	O101-C112-C113-N101	57.6(5)
C104-C205-C206-C207	2.0(16)	C205-C206-C207-C208	0.7(16)
C206-C207-C208-C209	-2.7(16)	C207-C208-C209-C104	2.1(17)
C10-N1-C2-C1	71.5(4)	C10-N1-C2-C3	-67.1(4)
C13-N1-C2-C1	-160.2(4)	C13-N1-C2-C3	61.2(4)
C2-N1-C10-C11	-171.3(4)	C13-N1-C10-C11	55.4(5)
C2-N1-C13-C12	175.2(4)	C10-N1-C13-C12	-55.8(5)
N1-C2-C3-F1	-53.3(4)	N1-C2-C3-C4	-172.4(3)
C1-C2-C3-F1	169.7(3)	C1-C2-C3-C4	50.6(4)
F1-C3-C4-C5	136.7(3)	F1-C3-C4-C9	-48.8(4)
C2-C3-C4-C5	-100.8(3)	C2-C3-C4-C9	73.8(4)
C3-C4-C5-C6	176.3(3)	C9-C4-C5-C6	1.4(6)
C3-C4-C9-C8	-175.6(4)	C5-C4-C9-C8	-1.3(6)
C4-C5-C6-C7	-1.4(6)	C5-C6-C7-C8	1.3(7)
C6-C7-C8-C9	-1.2(8)	C7-C8-C9-C4	1.2(8)
N1-C10-C11-O1	-59.1(6)	O1-C12-C13-N1	58.7(6)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+3/2