Supporting Information

HFIP-Promoted [^{18}F] Trifluoromethylation via Iodofluorination of *gem*-Difluoroalkenes

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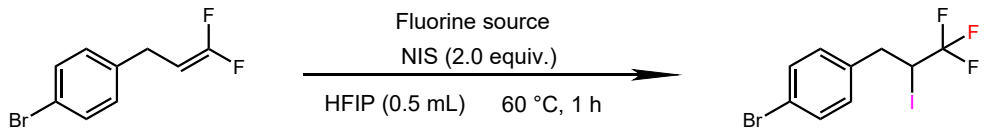
1. General Information

Chemicals were purchased from Leyan (CAS: 920-66-1, Hexafluoroisopropanol, Leyan, Shanghai)， Adamas-beta， Energy Chemical, bidepharm, and Macklin, were used without further purification. The products were purified using a commercial flash chromatography system or a regular glass column. TLC was developed on silica gel 60 F254 glassplates. GC/MS analysis was performed on a Thermo-Fischer Scientific ISQ QD single quadrupole mass spectromerter. ^{1}H, ^{19}F NMR spectra and ^{13}C NMR spectra were recorded on an Agilent AM400 spectrometer and Bruker AM400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were reported in ppm relative to chloroform (1H, δ 7.26; 13C, δ 77.0) and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as internal standard. Chemical shifts (δ) were reported in ppm and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

2. Optimization of Reaction Conditions

Table S1. Screening of fluorine source for the Iodotrifluoromethylation of *gem*-difluoroalkenes.[a]

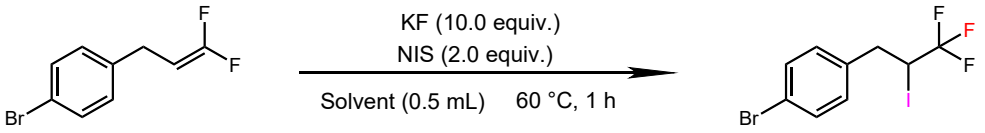


1a **1**

entry	Fluorine source	yield (%)[b]
1	KF	92
2	AgF	55
3	HF	50
4	CsF	20
5	TBAF	62
6	LiF	0
7	NaF	0

[a]Reaction conditions: **1a** (0.05 mmol), NIS (0.1 mmol),HFIP (0.5 mL), 60 ℃, 1 h. [b]Determined by ^{19}F NMR, $PhOCF_3$ as the internal standard.

Table S2. Screening of solvents for the Iodotrifluoromethylation of *gem*-difluoroalkenes.[a]



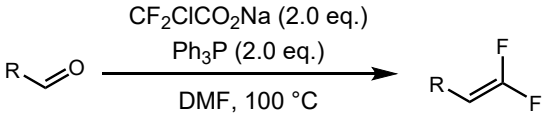
1a **1**

entry	solvent	yield (%)[b]
1	HFIP	92
2	DCM	0
3	HFIP/DCM (1:1)	0
4	HFIP/DCM (95:5)	35
5	TFE	0

[a]Reaction conditions: **1a** (0.05 mmol), NIS (0.1 mmol), KF (0.5 mmol), Solvent (0.5 mL), 60 °C, 1 h. [b]Determined by ^{19}F NMR, $PhOCF_3$ as the internal standard.

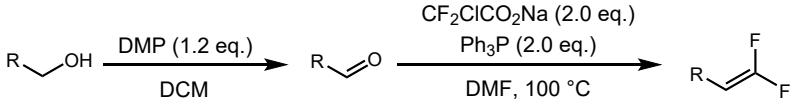
3. Synthesis of *gem*-Difluoroalkenes

General Procedure A



In a 25 mL flask with a stir bar, aldehyde (5 mmol), PPh_3 (2.62 g, 10 mmol) and CF_2ClCO_2Na (1.52 g, 10 mmol) were dissolved in DMF (7 mL). The mixture was vigorously stirred at 100 °C. A large amount of gas was generated. The reaction completed until no gas bubbled (about 30 minutes). The mixture was cooled to 0 °C, and then H_2O_2 (30 wt.% in water) (1.7 mL) was added slowly. The mixture was diluted with DCM and the organic phase was washed with water three times and brine successively, and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure. The residues were purified by column chromatography on silica gel (petroleum ether: EtOAc) to obtain the *gem*-difluoroalkenes[1].

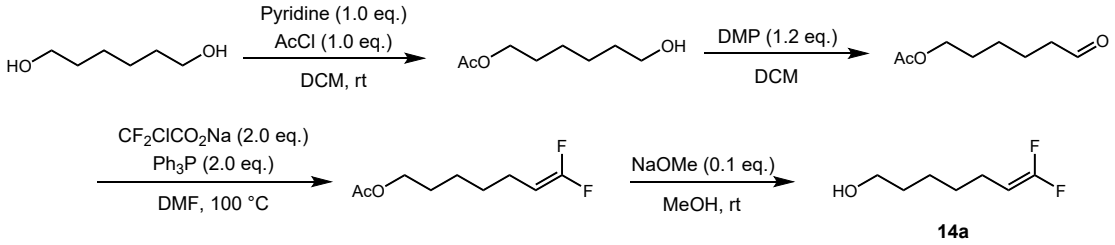
General Procedure B



In a 250 mL flask with a stir bar, primary alcohol (10 mmol) was dissolved in DCM (100 mL). To the solution, DMP (5.09 g, 12 mmol) was added portion wise. The reaction was stirred at room temperature overnight. The suspension was filtered off and concentrated under reduced pressure. The residues were purified by column chromatography on silica gel (petroleum ether: EtOAc) to obtained the aldehydes[2].

In a 25 mL flask with a stir bar, the aldehydes, PPh_3 (2 equiv.) and CF_2ClCO_2Na (2 equiv.) were dissolved in DMF (7 mL). The mixture was vigorously stirred at 100 °C. A large amount of gas was generated. The reaction completed until no gas bubbled (about 30 minutes). The mixture was cooled to 0 °C, and then H_2O_2 (30 wt.% in water) (1.7 mL) was added slowly. The mixture was diluted with DCM and the organic phase was washed with water three times and brine successively, and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure. The residues were purified by column chromatography on silica gel (petroleum ether: EtOAc) to obtain the *gem*-difluoroalkenes[1].

Procedure for Synthesis of 7,7-Difluorohept-6-en-1-ol (14a)[3]



In a 100 mL flask with a stir bar, hexane-1,6-diol (5.91 g, 50 mmol) and pyridine (4.04 mL, 50 mmol) were dissolved in DCM (50 mL). Acetyl chloride (3.56 mL, 50 mmol) was added dropwise at 0 °C. The reaction was stirred at room temperature for 3 h. After completion, the mixture was washed with 1 N HCl twice, water, and brine successively, and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure. The residues were purified by column chromatography on silica gel (petroleum ether: EtOAc = 5:1 to 2:1) to obtain the acetate as a colorless oil (3.04 g, 38 %).

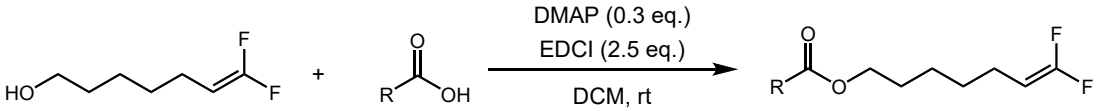
In a 250 mL flask with a stir bar, 6-hydroxyhexyl acetate (3.04 g, 19.0 mmol) was dissolved in DCM (190 mL). To the solution, DMP (9.667 g, 22.8 mmol) was added portion wise. The reaction was stirred at room temperature overnight. The suspension was filtered off and concentrated under reduced pressure. The residues were purified by column chromatography on silica gel (petroleum ether: EtOAc = 5:1) to obtained the aldehyde as a colorless oil (2.39 g, 80 %).

In a 50 mL flask with a stir bar, 6-oxohexyl acetate (2.39 g, 15.1 mmol), PPh_3 (7.93 g, 30.2 mmol) and CF_2ClCO_2Na (4.61 g, 30.2 mmol) were dissolved in DMF (20 mL). The mixture was vigorously stirred at 100 °C. A large amount of gas was generated. The reaction completed until no gas bubbled (about 30 minutes). The mixture was cooled to 0 °C, and then H_2O_2 (30 wt.% in water) (5.1 mL) was added slowly. The mixture was diluted with DCM and the organic phase was washed with water three times and brine successively, and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure. The residues were purified by column chromatography on silica

gel (petroleum ether: EtOAc = 50:1 to 20:1) to obtain the *gem*-difluoroalkene as a pale-yellow oil (1.97 g, 68 %).

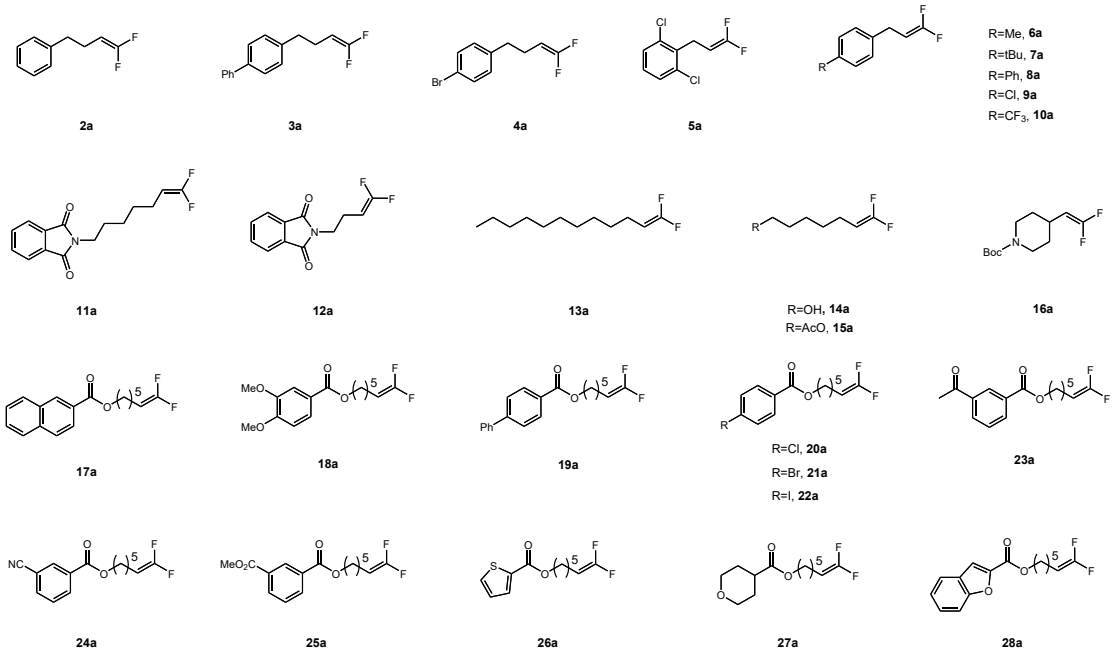
In a 50 mL flask with a stir bar, 7,7-difluorohept-6-en-1-yl acetate (1.97 g, 10.3 mmol) and sodium methoxide (54 mg, 1.0 mmol) were dissolved in MeOH (20 mL). The reaction was stirred at room temperature. After completion (monitored by TLC), the mixture was diluted with EtOAc, and washed with water three times and brine successively, and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure. The residues were purified by column chromatography on silica gel (petroleum ether: EtOAc = 5:1 to 3:1) to obtained the product as a colorless oil (1.14 g, 74 %).

General Procedure C



In a 10 mL flask with a stir bar, 7,7-Difluorohept-6-en-1-ol (1 mmol) was dissolved in DCM (3 mL). To the solution, DMAP (37 mg, 0.3 mmol), EDCI (480 mg, 2.5 mmol) and RCOOH (1.2 mmol) were added portion wise. The reaction was stirred at room temperature overnight. The suspension was filtered off and concentrated under reduced pressure. The residues were purified by column chromatography on silica gel (petroleum ether: EtOAc) to obtain the *gem*-difluoroalkenes.

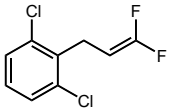
Table S3. substrates scopes of *gem*-difluoroalkenes



The *gem*-difluoroalkenes **1a**[4], **2a**[5], **3a**[6], **4a**[7], **6a**[8], **7a**[4], **8a**[4], **9a**[9], **10a**[9], **11a**[3], **12a**[3], **13a**[6], **14a**[3], **15a**[3] and **16a**[10] are known compounds and were prepared in accordance with references. All spectroscopic data were matched in those reported. The new compound was synthesized according to references

and characterized described below.

1,3-dichloro-2-(3,3-difluoroallyl)benzene (5a)



According to the General Procedure B, **5a** was purified by column chromatography (petroleum ether: EtOAc = 100:1) as a colorless oil (261 mg, 86 %)

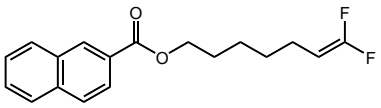
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 8.0 Hz, 1H), 4.31 (dtd, *J* = 24.4, 7.7, 2.4 Hz, 1H), 3.63 (d, *J* = 7.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.9 (dd, *J* = 289.6, 286.1 Hz), 135.5, 128.4, 75.2 (dd, *J* = 25.4, 20.0 Hz), 24.7 (d, *J* = 5.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -88.37 (d, *J* = 42.2 Hz), -88.78 – -89.07 (m).

HRMS (FI): Calculated for $C_9H_6F_2Cl_2$ ([M]$^+$): 221.9809; Found: 221.9813.

7,7-difluorohept-6-en-1-yl 2-naphthoate (17a)



According to the General Procedure C, **17a** was purified by column chromatography (petroleum ether: EtOAc = 50:1) as a colorless oil (261 mg, 86 %)

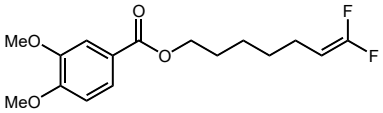
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 8.07 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.7 Hz, 2H), 7.62 – 7.52 (m, 2H), 4.39 (t, *J* = 6.6 Hz, 2H), 4.22 – 4.07 (m, 1H), 2.09 – 1.97 (m, 2H), 1.89 – 1.77 (m, 2H), 1.53 – 1.42 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.0, 161.6 – 151.6 (m), 135.6, 132.6, 131.1, 129.5, 128.3, 128.3, 127.9, 127.8, 126.8, 125.3, 77.9 (t, *J* = 21.1 Hz), 65.1, 28.6, 25.5, 22.6 (d, *J* = 4.0 Hz).

^{19}F NMR (377 MHz, Chloroform-*d*) δ -89.30 (d, *J* = 48.6 Hz), -91.50 – -91.92 (m).

HRMS (FI): Calculated for $C_{18}H_{18}F_2O_2$([M]$^+$). 304.1276; Found: 304.1274.

7,7-difluorohept-6-en-1-yl 3,4-dimethoxybenzoate (18a)



According to the General Procedure C, **18a** was purified by column chromatography (petroleum ether: EtOAc = 20:1) as a colorless oil (295 mg, 94 %)

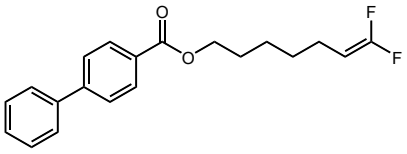
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.53 (d, *J* = 1.9 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.28 (t, *J* = 6.6 Hz, 2H), 4.12 (m, *J* = 25.5, 7.9, 2.6 Hz, 1H), 3.92 (s, 6H), 2.02 – 1.96 (m, 2H), 1.78 – 1.73 (m, 2H), 1.47 – 1.41 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6, 156.4 (t), 153.0, 148.7, 123.6, 123.0, 112.0, 110.3, 77.9 (t, *J* = 21.2 Hz), 64.8, 56.1 (d, *J* = 4.4 Hz), 29.1 (t, *J* = 2.3 Hz), 28.6, 25.4, 22.1 (d, *J* = 4.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -88.59 (d, *J* = 45.0 Hz), -91.27 – -91.87 (m).

HRMS (FI): Calculated for $C_{16}H_{20}F_2O_4$([M]$^+$). 314.1326; Found: 314.1325.

7,7-difluorohept-6-en-1-yl [1,1'-biphenyl]-4-carboxylate (19a)



According to the General Procedure C, **19a** was purified by column chromatography (petroleum ether: EtOAc = 50:1) as a colorless oil (291 mg, 88 %)

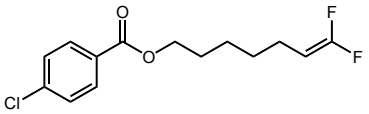
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.70 – 7.62 (m, 4H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.43 – 7.38 (m, 1H), 4.35 (t, *J* = 6.6 Hz, 2H), 4.22 – 4.09 (m, 1H), 2.07 – 2.00 (m, 2H), 1.85 – 1.77 (m, 2H), 1.54 – 1.45 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 159.6 – 153.0 (m), 145.7, 140.1, 130.2, 129.3, 129.0, 128.2, 127.4, 127.6, 77.9 (t, *J* = 21.4 Hz), 65.0, 29.2 (t, *J* = 2.4 Hz), 28.6, 25.5, 22.6 (d, *J* = 3.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -89.32 (d, *J* = 48.7 Hz), -91.50 – -91.94 (m).

HRMS (FI): Calculated for $C_{20}H_{20}F_2O_2$([M]$^+$): 330.1426; Found: 330.1432.

7,7-difluorohept-6-en-1-yl 4-chlorobenzoate (20a)



According to the General Procedure C, **20a** was purified by column chromatography (petroleum ether:EtOAc = 50:1) as a colorless oil (257 mg, 89 %)

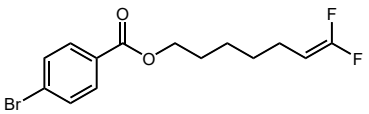
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 4.30 (t, *J* = 6.6 Hz, 2H), 4.19 – 4.05 (m, 1H), 2.04 – 1.95 (m, 2H), 1.81 – 1.73 (m, 2H), 1.48 – 1.41 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 159.7 – 152.8 (m), 139.4, 131.1, 128.8, 77.8 (t, *J* = 21.4 Hz), 65.2, 29.1, 28.5, 25.4, 22.1 (d, *J* = 3.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -89.31 (d, *J* = 48.5 Hz), -91.51 – -92.00 (m).

HRMS (FI): Calculated for $C_{14}H_{15}ClF_2O_2$([M]$^+$): 288.0727; Found: 288.0723.

7,7-difluorohept-6-en-1-yl 4-bromobenzoate (21a)



According to the General Procedure C, **21a** was purified by column chromatography (petroleum ether: EtOAc = 50:1) as a colorless oil (271 mg, 82 %)

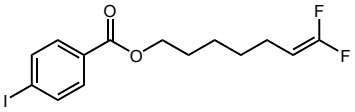
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 4.30 (t, *J* = 6.6 Hz, 2H), 4.19 – 4.06 (m, 1H), 2.04 – 1.96 (m, 2H), 1.79 – 1.72 (m, 2H), 1.48 – 1.40 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.0, 159.4 – 153.4 (m), 131.8, 131.2, 129.4, 128.1, 77.8 (t, *J* = 21.3 Hz), 65.3, 29.1 (t, *J* = 2.5 Hz), 28.5, 25.4, 22.1 (d, *J* = 4.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -89.29 (d, *J* = 48.6 Hz), -91.54 – -91.90 (m).

HRMS (FI): Calculated for $C_{14}H_{15}F_2BrO_2$([M]$^+$): 332.0218; Found: 332.0221.

7,7-difluorohept-6-en-1-yl 4-iodobenzoate (22a)



According to the General Procedure C, **22a** was purified by column chromatography (petroleum ether: EtOAc = 50:1) as a colorless oil (324 mg, 85 %)

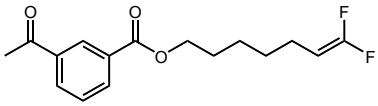
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 4.30 (t, *J* = 6.6 Hz, 2H), 4.18 – 4.05 (m, 1H), 2.03 – 1.96 (m, 2H), 1.80 – 1.72 (m, 2H), 1.49 – 1.39 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 160.6 – 153.1 (m), 137.8, 131.1, 130.0, 100.8, 77.8 (t, *J* = 21.2 Hz), 65.2, 29.1 (t, *J* = 2.5 Hz), 28.5, 25.4, 22.1 (d, *J* = 4.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -89.26 (d, *J* = 48.5 Hz), -91.47 – -91.93 (m).

HRMS (FI): Calculated for $C_{14}H_{15}F_2IO_2$([M]$^+$): 380.0079; Found: 380.0084.

7,7-difluorohept-6-en-1-yl 3-acetylbenzoate (23a)



According to the General Procedure C, **23a** was purified by column chromatography (petroleum ether: EtOAc = 20:1) as a colorless oil (265 mg, 90 %)

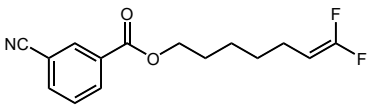
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (t, *J* = 1.7 Hz, 1H), 8.22 (dt, *J* = 7.7, 1.5 Hz, 1H), 8.14 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 4.34 (t, *J* = 6.7 Hz, 2H), 4.19 – 4.06 (m, 1H), 2.65 (s, 3H), 2.05 – 1.97 (m, 2H), 1.83 – 1.76 (m, 2H), 1.49 – 1.40 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.4, 166.0, 156.4 (dd, *J* = 286.6, 284.7 Hz), 137.4, 133.97, 132.4, 131.1, 129.6, 129.0, 77.8 (t, *J* = 21.2 Hz), 65.4, 29.1 (t, *J* = 2.5 Hz), 28.5, 26.8, 25.4, 22.1 (d, *J* = 3.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -89.33 (d, *J* = 49.0 Hz), -91.56 – -91.90 (m).

HRMS (FI): Calculated for $C_{16}H_{18}F_2O_3$([M]$^+$): 296.1219; Found: 296.1226.

7,7-difluorohept-6-en-1-yl 3-cyanobenzoate (24a)



According to the General Procedure C, **24a** was purified by column chromatography (petroleum ether: EtOAc = 20:1) as a colorless oil (257 mg, 82 %)

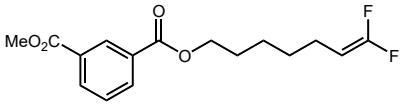
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (t, *J* = 1.7 Hz, 1H), 8.26 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.83 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 4.34 (t, *J* = 6.6 Hz, 2H), 4.19 – 4.06 (m, 1H), 2.05 – 1.96 (m, 2H), 1.83 – 1.74 (m, 2H), 1.49 – 1.41 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.7, 156.4 (t), 136.0, 133.8, 133.3, 131.8, 129.6, 118.1, 113.0, 77.8 (t, *J* = 21.2 Hz), 65.8, 29.8, 29.1 (t, *J* = 2.5 Hz), 25.4, 22.1 (d, *J* = 4.2 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -89.26 (d, *J* = 48.5 Hz), -91.43 – -91.98 (m).

HRMS (FI): Calculated for $C_{15}H_{15}F_2NO_2$([M]$^+$): 279.1076; Found: 279.1072.

7,7-difluorohept-6-en-1-yl methyl isophthalate (25a)



According to the General Procedure C, **25a** was purified by column chromatography (petroleum ether:EtOAc = 20:1) as a colorless oil (287 mg, 92 %)

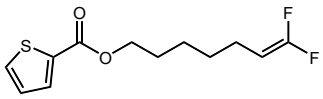
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (t, *J* = 1.8 Hz, 1H), 8.21 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 4.33 (t, *J* = 6.7 Hz, 2H), 4.18 – 4.06 (m, 1H), 3.94 (s, 3H), 2.03 – 1.96 (m, 2H), 1.82 – 1.75 (m, 2H), 1.48 – 1.42 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.4, 165.9, 156.4 (dd, *J* = 286.7, 284.6 Hz), 133.9 (d, *J* = 4.2 Hz), 131.0, 130.8, 130.7, 128.7, 77.9 (t, *J* = 21.1 Hz), 65.4, 52.5, 29.1 (t, *J* = 2.1 Hz), 28.5, 25.4, 22.1 (d, *J* = 4.2 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -88.59 (d, *J* = 45.2 Hz), -91.31 – -91.64 (m).

HRMS (FI): Calculated for $C_{16}H_{18}F_2O_4$([M]$^+$): 312.1175; Found: 312.1171.

7,7-difluorohept-6-en-1-yl thiophene-2-carboxylate (26a)



According to the General Procedure C, **26a** was purified by column chromatography (petroleum ether:EtOAc = 20:1) as a colorless oil (237 mg, 91 %)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.54 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.09 (dd, *J* = 5.0, 3.8 Hz, 1H), 4.28 (t, *J* = 6.6 Hz, 2H), 4.18 – 4.07 (m, 1H), 2.03 – 1.97 (m, 2H), 1.77 – 1.71 (m, 2H), 1.47 – 1.41 (m, 4H).

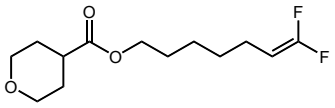
^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.4, 156.4 (dd, *J* = 286.7, 284.5 Hz), 134.1, 133.4, 132.4,

127.8, 77.9 (t, *J* = 21.2 Hz), 65.1, 29.1 (t, *J* = 2.2 Hz), 28.5, 25.4, 22.1 (d, *J* = 4.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -89.38 (d, *J* = 48.7 Hz), -91.63 – -91.93 (m).

HRMS (FI): Calculated for $C_{12}H_{14}F_2O_2S([M]^+)$: 260.0677; Found: 260.0676.

7,7-difluorohept-6-en-1-yl tetrahydro-2H-pyran-4-carboxylate (27a)



According to the General Procedure C, **27a** was purified by column chromatography (petroleum ether:EtOAc = 20:1) as a colorless oil (223 mg, 85 %)

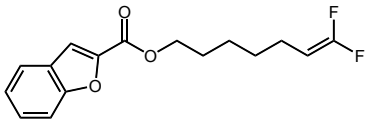
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.15 – 4.02 (m, 3H), 3.93 (dt, *J* = 11.6, 3.6 Hz, 2H), 3.40 (td, *J* = 11.2, 3.0 Hz, 2H), 2.55 – 2.45 (m, 1H), 1.99 – 1.92 (m, 2H), 1.84 – 1.71 (m, 4H), 1.65 – 1.56 (m, 2H), 1.41 – 1.30 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.6, 159.5 – 153.2 (m), 77.8 (t, *J* = 21.1 Hz), 67.2, 64.4, 40.2, 29.0 (t, *J* = 2.3 Hz), 28.7, 28.4, 25.2, 22.1 (d, *J* = 4.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -89.43 (d, *J* = 48.6 Hz), -91.70 – -92.03 (m).

HRMS (FI): Calculated for $C_{13}H_{20}F_2O_3([M]^+)$: 262.1379; Found: 262.1378.

7,7-difluorohept-6-en-1-yl benzofuran-2-carboxylate (28a)



According to the General Procedure C, **28a** was purified by column chromatography (petroleum ether:EtOAc = 20:1) as a colorless oil (268 mg, 91 %)

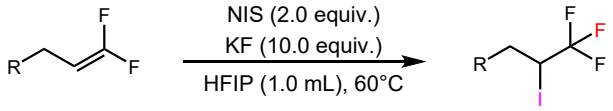
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.9 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.52 (d, *J* = 1.0 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.32 – 7.27 (m, 1H), 4.37 (t, *J* = 6.7 Hz, 2H), 4.19 – 4.07 (m, 1H), 2.04 – 1.97 (m, 2H), 1.83 – 1.75 (m, 2H), 1.48 – 1.41 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.8, 159.4 – 153.3 (m), 155.8, 145.7, 127.7, 127.1, 123.9, 122.9, 113.9, 112.5, 77.8 (t, *J* = 21.4 Hz), 65.4, 29.1 (t, *J* = 2.2 Hz), 28.5, 25.3, 22.1 (d, *J* = 4.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -89.32 (d, *J* = 48.9 Hz), -91.48 – -91.90 (m).

HRMS (FI): Calculated for $C_{16}H_{16}F_2O_3([M]^+)$: 294.1067; Found: 294.1062.

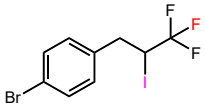
4. General Procedure for Iodotrifluoromethylation of *gem*-Difluoroalkenes.



In a 8 mL vial with a stir bar, NIS (89.6 mg, 0.4 mmol) and KF (118 mg, 2 mmol) were dissolved in HFIP (1.0 mL). The vial was capped under nitrogen atmosphere. To the solution, *gem*-difluoroalkenes (0.2 mmol) was added. The reaction was stirred at 60℃ for 1 h. After completion (monitored by TLC), the mixture was diluted with EtOAc, and washed with water three times and brine successively, and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure. The residues were purified by column chromatography on silica gel (petroleum ether: EtOAc) to obtain the products.

4.1. Characterization for Iodotrifluoromethylation products

1-bromo-4-(3,3,3-trifluoro-2-iodopropyl) benzene (1)



According to the General Procedure for Iodotrifluoromethylation, **1** was purified by column chromatography (petroleum ether: EtOAc = 100:1) as a colorless oil (70 mg, 92%)

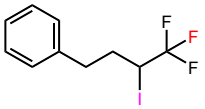
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 4.36 – 4.21 (m, 1H), 3.40 (dd, *J* = 14.8, 3.7 Hz, 1H), 3.04 (dd, *J* = 14.8, 11.2 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 136.0, 132.0, 130.8, 124.5 (q, *J* = 277.3 Hz), 121.7, 38.9, 24.8 (q, *J* = 30.5 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.76 (d, *J* = 8.0 Hz).

HRMS (FI): Calculated for $C_9H_7BrF_3I$([M]$^+$): 377.8722; Found: 377.8721.

(4,4,4-trifluoro-3-iodobutyl) benzene (2)



According to the General Procedure for Iodotrifluoromethylation, **2** was purified by column chromatography (petroleum ether: EtOAc = 100:1) as a colorless oil (41.8 mg, 67%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (t, *J* = 7.2 Hz, 2H), 7.25 – 7.21 (m, 3H), 4.08 – 3.97 (m, 1H), 3.04 – 2.93 (m, 1H), 2.75 – 2.64 (m, 1H), 2.22 – 2.14 (m, 2H).

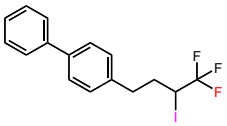
^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.3, 128.9, 128.7, 126.8, 123.3 (q, *J* = 277.2 Hz), 34.6,

34.3, 23.8 (q, J = 31.0 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.74 (d, J = 8.3 Hz).

HRMS (FI): Calculated for $C_{10}H_{10}F_3I$([M]$^+$): 313.9772; Found: 313.9775.

4-(4,4,4-trifluoro-3-iodobutyl)-1,1'-biphenyl (3)



According to the General Procedure for Iodotrifluoromethylation, **3** was purified by column chromatography (petroleum ether: EtOAc = 100:1) as a colorless oil (64.8 mg, 83%)

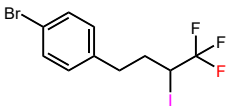
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.55 (m, 4H), 7.46 (t, J = 7.7 Hz, 2H), 7.37 (t, J = 7.3 Hz, 1H), 7.31 (d, J = 8.1 Hz, 2H), 4.16 – 4.03 (m, 1H), 3.09 – 2.99 (m, 1H), 2.81 – 2.71 (m, 1H), 2.27 – 2.19 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.9, 139.8, 138.3, 129.1, 128.9, 127.6, 127.4, 127.2, 124.7(q, J = 276.8 Hz), 34.3 (d, J = 6.8 Hz), 23.8 (q, J = 31.2 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.64 (d, J = 7.9 Hz).

HRMS (FI): Calculated for $C_{16}H_{14}F_3I$([M]$^+$): 390.0095; Found: 390.0093.

1-bromo-4-(4,4,4-trifluoro-3-iodobutyl) benzene (4)



According to the General Procedure for Iodotrifluoromethylation, **4** was purified by column chromatography (petroleum ether: EtOAc = 100:1) as a colorless oil (60.9 mg, 78%)

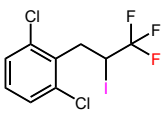
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (dd, J = 6.7, 1.6 Hz, 2H), 7.22 – 7.13 (m, 2H), 4.09 – 3.98 (m, 1H), 2.95 (dt, J = 13.8, 6.7 Hz, 1H), 2.67 (dt, J = 14.1, 8.3 Hz, 1H), 2.21 – 2.12 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.7, 131.7, 130.5, 130.0, 127.3, 126.0 (q, J = 277.8 Hz), 122.9, 34.3 (d, J = 18.1 Hz), 23.3 (q, J = 31.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.69 (d, J = 8.2 Hz).

HRMS (FI): Calculated for $C_{10}H_9BrF_3I$([M]$^+$): 391.8887; Found: 391.8885.

1,3-dichloro-2-(3,3,3-trifluoro-2-iodopropyl) benzene (5)



According to the General Procedure for Iodotrifluoromethylation, **4** was purified by column chromatography (petroleum ether: EtOAc = 100:1) as a colorless oil (67.9 mg, 92%)

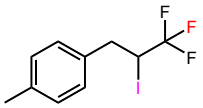
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 4.89 – 4.77 (m, 1H), 3.72 – 3.59 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 136.1, 133.7, 129.4, 128.9, 124.6 (q, *J* = 277.5 Hz), 34.3 (d, *J* = 2.0 Hz), 19.1 (q, *J* = 30.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.71 (d, *J* = 7.8 Hz).

HRMS (FI): Calculated for $C_9H_6F_3ICl_2$([M]$^+$): 367.8838; Found: 367.8841.

1-methyl-4-(3,3,3-trifluoro-2-iodopropyl) benzene (6)



According to the General Procedure for Iodotrifluoromethylation, **6** was purified by column chromatography (petroleum ether: EtOAc = 100:1) as a colorless oil (54.5 mg, 87%)

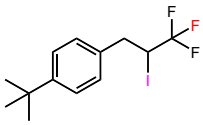
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.06 (m, 4H), 4.38 – 4.22 (m, 1H), 3.40 (dd, *J* = 14.7, 3.8 Hz, 1H), 3.04 (dd, *J* = 14.7, 11.2 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 137.3, 134.1, 129.5, 128.9, 123.52 (q, *J* = 278.1 Hz), 39.0 (d, *J* = 2.0 Hz), 26.0 (q, *J* = 30.0 Hz), 21.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.34 (d, *J* = 7.7 Hz).

HRMS (FI): Calculated for $C_{10}H_{10}F_3I$([M]$^+$): 313.9771; Found: 313.9772.

1-(tert-butyl)-4-(3,3,3-trifluoro-2-iodopropyl) benzene (7)



According to the General Procedure for Iodotrifluoromethylation, **7** was purified by column chromatography (petroleum ether: EtOAc = 100:1) as a colorless oil (51.7 mg, 73%)

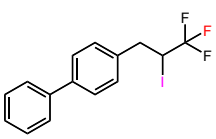
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 4.40 – 4.26 (m, 1H), 3.42 (dd, *J* = 14.8, 3.6 Hz, 1H), 3.06 (dd, *J* = 14.8, 11.1 Hz, 1H), 1.33 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.6, 134.0, 128.7, 125.8 (q, *J* = 277.6 Hz), 125.7, 39.0 (d, *J* = 2.2 Hz), 34.7, 31.5, 25.7 (q, *J* = 30.0 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -69.14 (d, *J* = 9.4 Hz).

HRMS (FI): Calculated for $C_{13}H_{16}F_3I$([M]$^+$): 356.0245; Found: 356.0244.

4-(3,3,3-trifluoro-2-iodopropyl)-1,1'-biphenyl (8)



According to the General Procedure for Iodotrifluoromethylation, **8** was purified by column chromatography (petroleum ether: EtOAc = 100:1) as a colorless oil (61.5 mg, 82%)

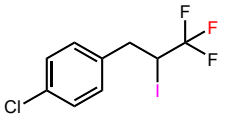
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (t, *J* = 8.2 Hz, 4H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 7.1 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 4.44 – 4.32 (m, 1H), 3.51 (dd, *J* = 14.8, 3.7 Hz, 1H), 3.14 (dd, *J* = 14.7, 11.2 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.7, 140.6, 138.1, 136.1, 129.5, 129.0, 127.6 (d, *J* = 4.5 Hz), 127.2, 124.6 (q, *J* = 277.4 Hz), 39.1, 25.4 (q, *J* = 30.3 Hz).

^{19}F NMR (470 MHz, Chloroform-*d*) δ -68.68 (d, *J* = 7.1 Hz).

HRMS (FI): Calculated for $C_{15}H_{12}F_3I([M]^+)$: 375.9930; Found: 375.9933.

1-chloro-4-(3,3,3-trifluoro-2-iodopropyl) benzene (9)



According to the General Procedure for Iodotrifluoromethylation, **9** was purified by column chromatography (petroleum ether: EtOAc = 100:1) as a colorless oil (55.2 mg, 83%)

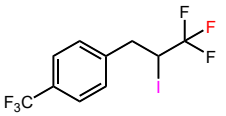
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 4.35 – 4.25 (m, 1H), 3.42 (dd, *J* = 14.8, 3.7 Hz, 1H), 3.06 (dd, *J* = 14.8, 11.2 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 135.5, 133.6, 130.5, 129.1, 125.6 (q, *J* = 277.6 Hz), 38.8, 25.0 (q, *J* = 30.5 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.53 (d, *J* = 7.9 Hz).

HRMS (FI): Calculated for $C_9H_7F_3ICl([M]^+)$: 333.9228; Found: 333.9232.

1-(3,3,3-trifluoro-2-iodopropyl)-4-(trifluoromethyl) benzene (10)



According to the General Procedure for Iodotrifluoromethylation, **10** was purified by column chromatography (petroleum ether: EtOAc = 100:1) as a colorless oil (62.3 mg, 87%)

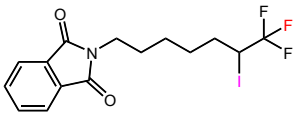
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.39 – 4.28 (m, 1H), 3.52 (dd, *J* = 14.8, 3.8 Hz, 1H), 3.16 (dd, *J* = 14.7, 11.2 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.0, 130.1 (q, *J* = 32.8 Hz), 129.5, 125.86 (q, *J* = 3.9, 3.4 Hz), 125.57 (q, *J* = 278.0 Hz), 39.2, 24.1 (q, *J* = 30.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.98, -68.24 (d, *J* = 7.6 Hz).

HRMS (FI): Calculated for $C_{10}H_7F_6I$: 367.9495; Found: 367.9492.

2-(7,7,7-trifluoro-6-iodoheptyl) isoindoline-1,3-dione (11)



According to the General Procedure for Iodotrifluoromethylation, **11** was purified by column chromatography (petroleum ether: EtOAc = 20:1) as a yellow oil (68.5 mg, 81%)

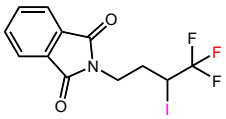
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.16 – 4.07 (m, 1H), 3.68 (t, *J* = 7.2 Hz, 2H), 1.82 (t, *J* = 8.2 Hz, 2H), 1.73 – 1.64 (m, 3H), 1.46 – 1.36 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 134.1, 132.2, 124.59 (q, *J* = 276.7 Hz), 123.3, 37.8, 32.7, 28.7, 28.4, 25.9, 24.2 (q, *J* = 31.1 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.90 (d, *J* = 7.7 Hz).

HRMS (FI): Calculated for $C_{15}H_{15}F_3INO_2$([M]$^+$): 425.0097; Found: 425.0093.

2-(4,4,4-trifluoro-3-iodobutyl) isoindoline-1,3-dione (12)



According to the General Procedure for Iodotrifluoromethylation, **12** was purified by column chromatography (petroleum ether: EtOAc = 20:1) as a yellow oil (62.5 mg, 81%)

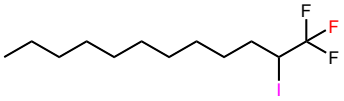
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.83 (m, 2H), 7.77 – 7.73 (m, 2H), 4.26 – 4.15 (m, 1H), 3.95 (dt, *J* = 13.4, 6.6 Hz, 1H), 3.84 (dt, *J* = 14.0, 7.2 Hz, 1H), 2.43 – 2.35 (m, 1H), 2.30 – 2.19 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.3, 134.4, 132.0, 124.4 (q, *J* = 276.4 Hz), 123.7, 37.4, 32.3, 19.6 (q, *J* = 32.2 Hz).

^{19}F NMR (470 MHz, Chloroform-*d*) δ -69.10 (d, *J* = 8.7 Hz).

HRMS (FI): Calculated for $C_{12}H_9F_3INO_2$([M]$^+$): 382.9625; Found: 382.9621.

1,1,1-trifluoro-2-iodododecane (13)



According to the General Procedure for Iodotrifluoromethylation, **13** was purified by column chromatography (petroleum ether: EtOAc = 100:1) as a colorless oil (60.7 mg, 87%)

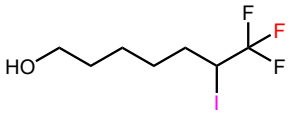
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.20 – 4.07 (m, 1H), 1.84 (q, *J* = 7.3 Hz, 2H), 1.41 – 1.20 (m, 16H), 0.93 – 0.82 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 124.7 (q, *J* = 276.3 Hz), 32.8, 32.0, 29.7 (d, *J* = 4.6 Hz), 29.4 (d, *J* = 4.8 Hz), 29.1, 28.6, 24.7 (q, *J* = 30.7 Hz), 22.8, 14.3.

^{19}F NMR (377 MHz, Chloroform-*d*) δ -68.92 (d, *J* = 8.0 Hz).

HRMS (FI): Calculated for $C_{12}H_{22}F_3I([M]^+)$: 350.0717; Found: 350.0716.

1,1,1-trifluoro-2-iodo-7-methyloctane (14)



According to the General Procedure for Iodotrifluoromethylation, **14** was purified by column chromatography (petroleum ether: EtOAc = 10:1) as a colorless oil (52.5 mg, 89%)

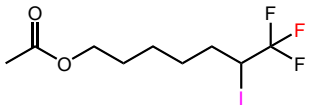
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.26 – 4.03 (m, 1H), 3.66 (t, *J* = 6.5 Hz, 2H), 1.93 – 1.81 (m, 2H), 1.69 – 1.55 (m, 3H), 1.48 – 1.37 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 126.04 (q, *J* = 277.4 Hz), 62.74, 32.76, 32.39, 28.86, 24.80, 24.21 (q, *J* = 31.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.91 (d, *J* = 8.2 Hz).

HRMS (FI): Calculated for $C_7H_{12}F_3IO([M]^+)$: 295.9984; Found: 295.9982.

methyl(prop-1-en-2-yl) (7,7,7-trifluoro-6-iodoheptyl)-l3-oxidane (15)



According to the General Procedure for Iodotrifluoromethylation, **15** was purified by column chromatography (petroleum ether: EtOAc = 100:1) as a colorless oil (63.4 mg, 94%)

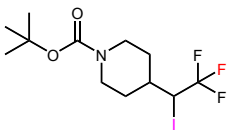
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.19 – 4.09 (m, 1H), 4.05 (t, *J* = 6.6 Hz, 2H), 2.04 (s, 3H), 1.89 – 1.80 (m, 2H), 1.69 – 1.59 (m, 3H), 1.46 – 1.34 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.3, 126.0 (q, *J* = 277.8 Hz), 64.3, 32.7, 28.7, 28.4, 25.0, 24.2 (q, *J* = 30.9 Hz), 21.1.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.94 (d, *J* = 8.3 Hz).

HRMS (FI): Calculated for $C_9H_{14}F_3IO_2([M]^+)$: 337.9987; Found: 337.9985.

***tert*-butyl 4-(2,2,2-trifluoro-1-iodoethyl) piperidine-1-carboxylate (16)**



According to the General Procedure for Iodotrifluoromethylation, **16** was purified by column chromatography (petroleum ether: EtOAc = 20:1) as a colorless oil (44.2 mg, 56%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.19 (dd, *J* = 19.4, 10.3 Hz, 3H), 2.76 (s, 2H), 1.75 (d, *J* =

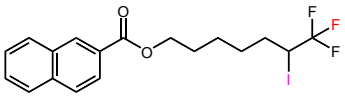
10.6 Hz, 1H), 1.52 (s, 2H), 1.44 (s, 9H), 1.35 (d, *J* = 9.7 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.7, 124.4 (q, *J* = 278.0 Hz), 79.9, 37.2, 32.4 (q, *J* = 29.4 Hz), 31.8, 30.5, 28.5.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.71 (d, *J* = 7.7 Hz).

HRMS (FI): Calculated for $C_{12}H_{19}F_3INO_2$([M]$^+$): 393.0410; Found: 393.0408.

7,7,7-trifluoro-6-iodoheptyl 2-naphthoate (17)



According to the General Procedure for Iodotrifluoromethylation, **17** was purified by column chromatography (petroleum ether: EtOAc = 50:1) as a colorless oil (67.4 mg, 75%)

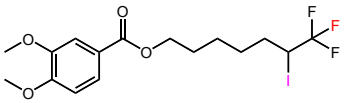
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.62 (s, 1H), 8.07 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.89 (dd, *J* = 8.4, 2.8 Hz, 2H), 7.63 – 7.52 (m, 2H), 4.40 (t, *J* = 6.5 Hz, 2H), 4.22 – 4.11 (m, 1H), 1.95 – 1.83 (m, 4H), 1.78 – 1.70 (m, 1H), 1.62 – 1.46 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 135.6, 132.6, 131.1, 129.4, 128.3 (d, *J* = 8.6 Hz), 127.9, 127.6, 126.8, 124.6 (q, *J* = 276.7 Hz), 125.3, 64.9, 32.7, 28.9, 28.6, 25.2, 24.2 (q, *J* = 31.1 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.82 (d, *J* = 8.2 Hz).

HRMS (FI): Calculated for $C_{18}H_{18}F_3IO_2$([M]$^+$): 450.0298; Found: 450.0302.

7,7,7-trifluoro-6-iodoheptyl 3,4-dimethoxybenzoate (18)



According to the General Procedure for Iodotrifluoromethylation, **18** was purified by column chromatography (petroleum ether: EtOAc = 20:1) as a colorless oil (74.6 mg, 81%)

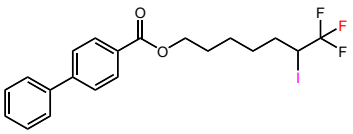
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 4.29 (t, *J* = 6.6 Hz, 2H), 4.20 – 4.06 (m, 1H), 3.92 (s, 6H), 1.89 – 1.75 (m, 4H), 1.71 – 1.62 (m, 1H), 1.55 – 1.39 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.5, 153.0, 148.7, 124.6 (q, *J* = 276.8 Hz), 123.6, 122.9, 112.0, 110.27, 64.6, 56.1, 32.7, 28.8, 28.6, 25.1, 24.2 (q, *J* = 30.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.89 (d, *J* = 8.2 Hz).

HRMS (FI): Calculated for $C_{16}H_{20}F_3IO_4$([M]$^+$): 460.0357; Found: 460.0355.

7,7,7-trifluoro-6-iodoheptyl [1,1'-biphenyl]-4-carboxylate (19)



According to the General Procedure for Iodotrifluoromethylation, **19** was purified by column chromatography (petroleum ether: EtOAc = 50:1) as a colorless oil (79.8 mg, 84%)

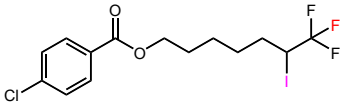
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.71 – 7.60 (m, 4H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.44 – 7.36 (m, 1H), 4.36 (t, *J* = 6.5 Hz, 2H), 4.22 – 4.11 (m, 1H), 1.94 – 1.79 (m, 4H), 1.75 – 1.66 (m, 1H), 1.60 – 1.42 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 145.8, 140.1, 130.2, 129.2, 129.1, 128.3, 127.4, 127.2, 124.6 (q, *J* = 276.7 Hz), 64.8, 32.7, 28.9, 28.6, 25.2, 24.3 (q, *J* = 31.0 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.84 (d, *J* = 8.2 Hz).

HRMS (FI): Calculated for $C_{20}H_{20}F_3IO_2$([M]$^+$): 476.0455; Found: 476.0458.

7,7,7-trifluoro-6-iodoheptyl 4-chlorobenzoate (20)



According to the General Procedure for Iodotrifluoromethylation, **20** was purified by column chromatography (petroleum ether: EtOAc = 100:1) as a colorless oil (79.9 mg, 92%)

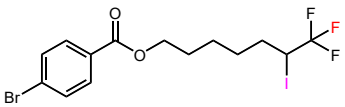
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.93 (m, 2H), 7.45 – 7.39 (m, 2H), 4.32 (t, *J* = 6.5 Hz, 2H), 4.21 – 4.09 (m, 1H), 1.92 – 1.78 (m, 4H), 1.75 – 1.66 (m, 1H), 1.56 – 1.42 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 139.5, 131.1, 128.9, 124.6 (q, *J* = 276.7 Hz), 65.1, 32.7, 28.9, 28.5, 25.2, 24.2 (q, *J* = 30.9 Hz).

^{19}F NMR (377 MHz, Chloroform-*d*) δ -68.88 (d, *J* = 8.3 Hz).

HRMS (FI): Calculated for $C_{14}H_{15}ClF_3IO_2$([M]$^+$): 433.9755; Found: 433.9752.

7,7,7-trifluoro-6-iodoheptyl 4-bromobenzoate (21)



According to the General Procedure for Iodotrifluoromethylation, **21** was purified by column chromatography (petroleum ether: EtOAc = 100:1) as a colorless oil (78.6 mg, 82%)

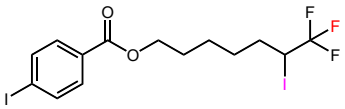
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.86 (m, 2H), 7.61 – 7.55 (m, 2H), 4.32 (t, *J* = 6.5 Hz, 2H), 4.20 – 4.08 (m, 1H), 1.91 – 1.77 (m, 4H), 1.71 – 1.65 (m, 1H), 1.55 – 1.40 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.0, 131.8, 131.2, 129.3, 128.2, 124.6 (q, *J* = 276.5 Hz), 65.1, 32.7, 28.8, 28.5, 25.2, 24.2 (q, *J* = 30.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.86 (d, *J* = 7.0 Hz).

HRMS (FI): Calculated for $C_{14}H_{15}F_3BrIO_2$([M]$^+$): 477.9247; Found: 477.9247.

7,7,7-trifluoro-6-iodoheptyl 4-iodobenzoate (22)



According to the General Procedure for Iodotrifluoromethylation, **22** was purified by column chromatography (petroleum ether: EtOAc = 100:1) as a colorless oil (85.1 mg, 81%)

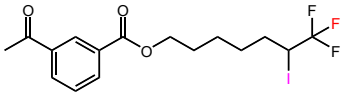
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H), 4.31 (t, *J* = 6.5 Hz, 2H), 4.20 – 4.08 (m, 1H), 1.91 – 1.76 (m, 4H), 1.71 – 1.64 (m, 1H), 1.55 – 1.41 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 137.9, 131.1, 129.9, 124.6 (q, *J* = 276.8 Hz), 100.8, 65.1, 32.7, 28.8, 28.5, 25.2, 24.2 (q, *J* = 31.0 Hz).

^{19}F NMR (377 MHz, Chloroform-*d*) δ -68.86 (d, *J* = 8.2 Hz).

HRMS (FI): Calculated for $C_{14}H_{15}F_3I_2O_2$([M]$^+$): 525.9108; Found: 525.9105.

7,7,7-trifluoro-6-iodoheptyl 3-acetylbenzoate (23)



According to the General Procedure for Iodotrifluoromethylation, **23** was purified by column chromatography (petroleum ether: EtOAc = 20:1) as a colorless oil (64.3 mg, 73%)

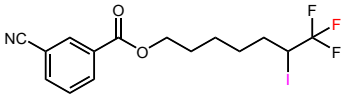
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (t, *J* = 1.8 Hz, 1H), 8.24 (dt, *J* = 7.8, 1.5 Hz, 1H), 8.16 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 4.37 (t, *J* = 6.6 Hz, 2H), 4.20 – 4.10 (m, 1H), 2.66 (s, 3H), 1.93 – 1.79 (m, 4H), 1.76 – 1.66 (m, 1H), 1.56 – 1.42 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.5, 166.0, 137.5, 134.0, 132.5, 131.0, 129.7, 129.0, 124.6 (q, *J* = 277.8 Hz), 65.3, 32.8, 28.9, 28.6, 26.9, 25.2, 24.2 (q, *J* = 30.9 Hz).

^{19}F NMR (377 MHz, Chloroform-*d*) δ -68.89 (d, *J* = 8.1 Hz).

HRMS (FI): Calculated for $C_{16}H_{18}F_3IO_3$([M]$^+$): 442.0247; Found: 442.0246.

7,7,7-trifluoro-6-iodoheptyl 3-cyanobenzoate (24)



According to the General Procedure for Iodotrifluoromethylation, **24** was purified by column chromatography (petroleum ether: EtOAc = 20:1) as a colorless oil (79.1 mg, 93%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (t, *J* = 1.4 Hz, 1H), 8.27 (dt, *J* = 8.0, 1.5 Hz, 1H), 7.84

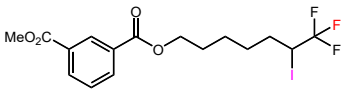
(dt, *J* = 7.7, 1.4 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 4.37 (t, *J* = 6.6 Hz, 2H), 4.21 – 4.09 (m, 1H), 1.94 – 1.79 (m, 4H), 1.75 – 1.66 (m, 1H), 1.57 – 1.43 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.8, 136.1, 133.8, 133.4, 131.7, 129.6, 124.6 (q, *J* = 276.8 Hz), 118.1, 113.1, 65.6, 32.7, 28.9, 28.5, 25.2, 24.1 (q, *J* = 30.9 Hz).

^{19}F NMR (377 MHz, Chloroform-*d*) δ -68.87 (d, *J* = 8.2 Hz).

HRMS (FI): Calculated for $C_{15}H_{15}F_3INO_2$([M]$^+$): 425.0094; Found: 425.0101.

methyl (7,7,7-trifluoro-6-iodoheptyl) isophthalate (25)



According to the General Procedure for Iodotrifluoromethylation, **25** was purified by column chromatography (petroleum ether: EtOAc = 20:1) as a colorless oil (81.7 mg, 89%)

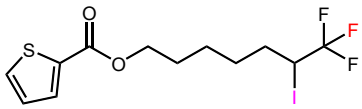
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (t, *J* = 1.8 Hz, 1H), 8.22 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.54 (t, *J* = 7.8 Hz, 1H), 4.36 (t, *J* = 6.6 Hz, 2H), 4.22 – 4.08 (m, 1H), 3.95 (s, 3H), 1.94 – 1.76 (m, 4H), 1.74 – 1.65 (m, 1H), 1.56 – 1.40 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.41, 165.91, 133.94, 130.78 (t, *J* = 8.7 Hz), 128.77, 123.26 (q, *J* = 278.8 Hz), 65.19, 52.54, 32.72, 28.85, 28.53, 25.18, 24.20 (q, *J* = 30.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.90 (d, *J* = 8.3 Hz).

HRMS (FI): Calculated for $C_{16}H_{18}F_3IO_4$([M]$^+$): 458.0196; Found: 458.0195.

7,7,7-trifluoro-6-iodoheptyl thiophene-2-carboxylate (26)



According to the General Procedure for Iodotrifluoromethylation, **26** was purified by column chromatography (petroleum ether: EtOAc = 50:1) as a colorless oil (65.0 mg, 80%)

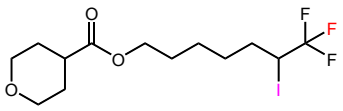
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.55 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.10 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.30 (t, *J* = 6.5 Hz, 2H), 4.20 – 4.08 (m, 1H), 1.91 – 1.75 (m, 4H), 1.72 – 1.64 (m, 1H), 1.55 – 1.39 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.38, 133.95, 133.50, 132.45, 127.88, 126.01 (q, *J* =277.8 Hz), 64.93, 32.71, 28.79, 28.51, 25.11, 24.20 (q, *J* = 30.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.71 (d, *J* = 7.8 Hz).

HRMS (FI): Calculated for $C_{12}H_{14}F_3IO_2S$([M]$^+$): 405.9706; Found: 405.9710.

7,7,7-trifluoro-6-iodoheptyl tetrahydro-2H-pyran-4-carboxylate (27)



According to the General Procedure for Iodotrifluoromethylation, **27** was purified by column chromatography (petroleum ether: EtOAc = 50:1) as a colorless oil (70.2 mg, 86%)

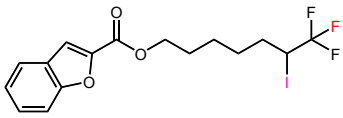
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.18 – 4.11 (m, 1H), 4.09 (t, *J* = 6.5 Hz, 2H), 3.96 (dt, *J* = 11.6, 3.6 Hz, 2H), 3.42 (td, *J* = 11.2, 3.0 Hz, 2H), 2.58 – 2.48 (m, 1H), 1.87 – 1.80 (m, 4H), 1.79 – 1.71 (m, 2H), 1.70 – 1.61 (m, 3H), 1.48 – 1.33 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.66, 126.00 (q, *J* = 277.8 Hz), 67.23, 64.35, 40.29, 32.73, 28.79 (d, *J* = 3.6 Hz), 28.43, 25.09, 24.17 (q, *J* = 30.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.71 (d, *J* = 7.8 Hz).

HRMS (FI): Calculated for $C_{13}H_{20}F_3IO_3$([M]$^+$): 408.0407; Found: 408.0405.

7,7,7-trifluoro-6-iodoheptyl benzofuran-2-carboxylate (28)



According to the General Procedure for Iodotrifluoromethylation, **28** was purified by column chromatography (petroleum ether: EtOAc = 50:1) as a colorless oil (79.1 mg, 90%)

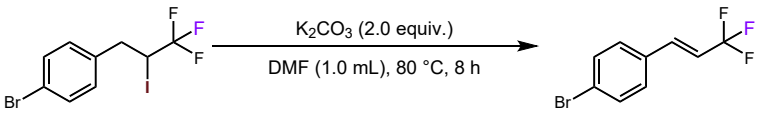
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.7 Hz, 1H), 7.60 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.53 (d, *J* = 1.0 Hz, 1H), 7.45 (td, *J* = 8.5, 7.8, 1.3 Hz, 1H), 7.31 (td, *J* = 7.6, 7.2, 1.0 Hz, 1H), 4.39 (t, *J* = 6.6 Hz, 2H), 4.21 – 4.09 (m, 1H), 1.93 – 1.80 (m, 4H), 1.73 – 1.67 (m, 1H), 1.57 – 1.43 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.8, 155.8, 145.6, 127.8, 127.0, 124.6 (q, *J* = 276.6 Hz), 123.9, 122.9, 114.1, 112.5, 65.3, 32.7 (d, *J* = 2.1 Hz), 28.8, 28.5, 25.1, 24.2 (q, *J* = 30.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.71 (d, *J* = 7.8 Hz).

HRMS (FI): Calculated for $C_{16}H_{16}F_3IO_3$([M]$^+$): 440.0095; Found: 440.0094.

4.2. Conversion of Iodotrifluoromethyl products



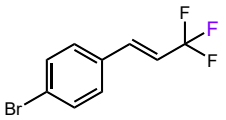
1 **29**

73% yield

Into an 8 mL screw-thread vial equipped with a stir bar were added K_2CO_3 (0.4 mmol, 2.0 equiv.), followed by DMF (1.0 mL). Finally, compound **1** (0.2 mmol, 1.0 equiv.) was added, and the reaction mixture was stirred at 80 °C for 8 hours. Upon completion, the mixture was extracted three times with ethyl acetate and saturated brine. The combined organic layers were dried over

anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography (eluting with neat petroleum ether) to afford the desired product **aa** in 73% yield.

(*E*)-1-bromo-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (29)



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.09 (dd, *J* = 16.2, 2.3 Hz, 1H), 6.20 (dq, *J* = 16.1, 6.4 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 136.7 (q, *J* = 6.7 Hz), 132.5, 132.3, 129.1, 124.4, 123.6 (q, *J* = 269.0 Hz), 116.7 (q, *J* = 34.1 Hz).

^{19}F NMR (470 MHz, Chloroform-*d*) δ -63.47 (d, *J* = 6.8 Hz).

HRMS (FI): Calculated for $C_9H_6BrF_3$([M]$^+$): 249.9595; Found: 249.9599.

4.3. Proposed mechanism

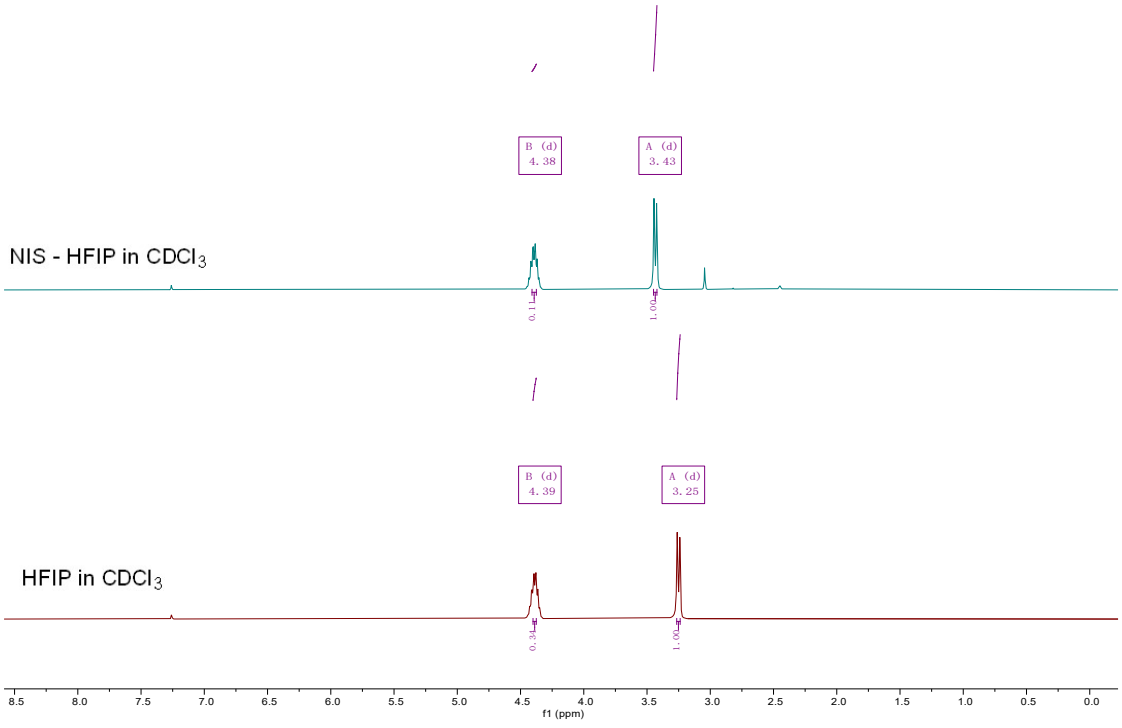


Figure S1. ^{1}H NMR for NIS and HFIP

To verify the interaction between HFIP and NIS, we referred to our group's previous studies[11] and investigated the interaction using nuclear magnetic resonance (NMR) spectroscopy. In $CDCl_3$, the CH_2 signal of NIS appeared at 3.03 ppm. The OH signal of HFIP in $CDCl_3$ was observed at 3.25 ppm, and the CH signal at 4.39 ppm. Upon the addition of NIS to HFIP, the OH signal of HFIP

exhibited a slight downfield shift from 3.25 ppm to 3.43 ppm, indicating the presence of hydrogen-bonding interactions between HFIP and NIS.

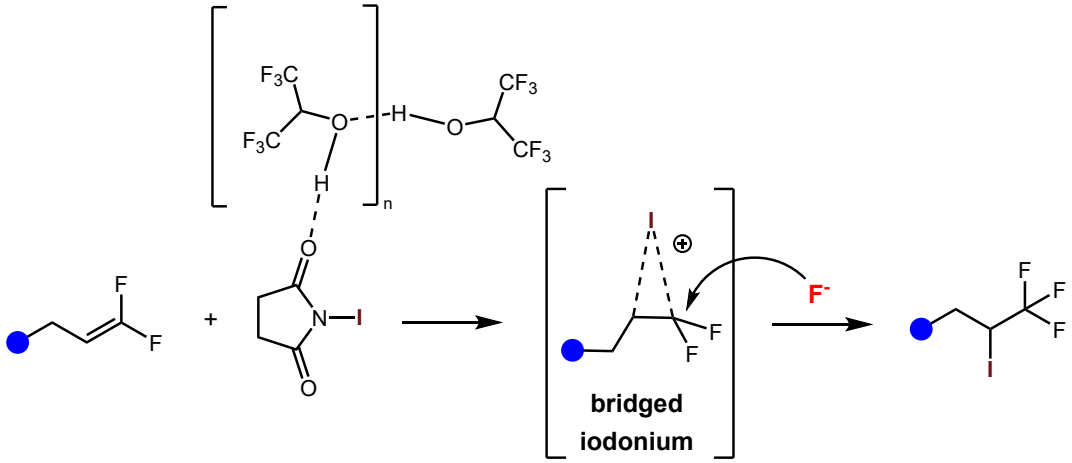


Figure S2. Proposed mechanistic scheme

We investigated the mechanism of this transformation and proposed a plausible pathway based on literature precedents of alkene iodofluorination[12]. Initially, the strong hydrogen-bond donor solvent HFIP activates NIS through hydrogen bonding with the succinimide carbonyl groups, facilitating the formation of an electrophilic iodine species. This species reacts with the gem-difluoroalkene to generate a bridged iodonium ion intermediate.Subsequently, the nucleophilic attack by the fluoride ion (from KF) occurs. Due to the strong electron-withdrawing effect of the two fluorine atoms, the difluoromethylene carbon exhibits significantly higher electrophilicity compared to the internal vinylic carbon. This electronic bias renders the bridged iodonium ion highly unsymmetrical, directing the nucleophilic fluoride to attack the more electrophilic CF_2H position. This directed attack accounts for the excellent regioselectivity and the efficient formation of the target iodo-functionalized product.

5. Radio-synthesis of [^{18}F] Iodotrifluoromethylation products

5.1. General Information

^{18}F-H_2O was received from Fudan University Shanghai Cancer Center. No-carrier-added [^{18}F] fluoride was produced by the ^{18}O (p, n)^{18}F nuclear reaction in a Siemens RDS-112 cyclotron (Siemens CTI RDS Eclips ST, Knoxville, TN) at 11 MeV using a 1 mL tantalum target with havar foil. QMA-light Sep-Paks cartridges were purchased from Waters Corporation and were preconditioned with 10 mL of 0.5 M aqueous KOTf solution, followed by 10 mL of water before use. The crude radiolabeled product was separated by HPLC on an UltiMate 3000 system (Thermo Fisher Scientific, USA) equipped with a Bioscan Flow-Count radio HPLC detector (Eckert & Ziegler) under the following conditions: Agilent Eclipse SB C18, 5 μm, 9.4 × 250 mm, acetonitrile

in phosphate buffer as mobile phase, the flow rate at 2.5 mL/min, UV wavelength at 254 nm and 220 nm. The data were recorded and processed using a Chromatography Data System (Thermo Fisher Scientific, USA) to determine the radiochemical conversion. The activities of [^{18}F] radiolabeled samples were determined using a radioisotope dose calibrator CRC-55tR (Capintec Inc.).

5.2. Preparation of [^{18}F] Radiolabeling Reagents

[^{18}F] KF

For a typical run, [^{18}F] Fluoride (3.0–3.5 GBq) produced by cyclotron was trapped on a Sep-PAK®light QMA cartridge (pre-rinse with 10 mL ethanol and 10 mL water for activation). It was then eluted with 0.3 mL aqueous potassium triflate (KOTf, 3–4 mg) into a small vessel to yield [^{18}F]KF solution.The solution was dried with three cycles of azeotropic drying with MeCN (3 x 1 mL) under a flow of N_2 at 110 ℃ and redissolved in HFIP.

[^{18}F] KF/$K_{2.2.2}$

For a typical run, [^{18}F] Fluoride (3.0 – 3.5 GBq) produced by cyclotron was trapped on a Sep-PAK®light QMA cartridge (pre-rinse with 10 mL ethanol and 10 mL water for activation) and then was released with a 0.3 mL of the aqueous solution of a K_2CO_3 (3 - 4 mg) into a small vessel, followed by the addition of 1 mL of acetonitrile containing kryptofix 222($K_{2.2.2}$, 16 mg) to get [^{18}F]KF/$K_{2.2.2}$ solution. The solution was dried with three cycles of azeotropic drying with MeCN (3 x 1 mL) under a flow of N_2 at 110 ℃ and redissolved in HFIP.

[^{18}F] TBAF

[^{18}F]Fluoride (1.0 – 1.4 GBq) produced by cyclotron was trapped into a Sep-PAK®light QMA cartridge (pre-rinse with 10 mL ethanol and 10 mL water for activation) and then was released with 1.0 mL of the solution (0.5 mL $TBAHCO_3$ solution (0.075 M in water) and 0.5 mL acetonitrile), followed by the addition of 1 mL of acetonitrile to get [^{18}F]TBAF solution. The solution was dried with three cycles of azeotropic drying with MeCN (3 x 1 mL) under a flow of N_2 at 110 ℃ and redissolved in HFIP.

[^{18}F] AgF

For a typical run, [^{18}F] Fluoride (3.0–3.5 GBq) produced by cyclotron was trapped on a Sep-PAK®light QMA cartridge (pre-rinse with 10 mL ethanol and 10 mL water for activation). It was

then eluted with 0.3 mL aqueous potassium triflate (AgOTf, 3–4 mg) into a small vessel to yield [^{18}F]KF solution.The solution was dried with three cycles of azeotropic drying with MeCN (3 x 1 mL) under a flow of N_2 at 110 °C and redissolved in HFIP.

[^{18}F] CsF

For a typical run, [^{18}F] Fluoride (3.0–3.5 GBq) produced by cyclotron was trapped on a Sep-PAK®light QMA cartridge (pre-rinse with 10 mL ethanol and 10 mL water for activation). It was then eluted with 0.3 mL aqueous potassium triflate (Cs_2CO_3, 3–4 mg) into a small vessel to yield [^{18}F]KF solution.The solution was dried with three cycles of azeotropic drying with MeCN (3 x 1 mL) under a flow of N_2 at 110 °C and redissolved in HFIP.

5.3. Determinations of RCC and RCY

TLC RCC

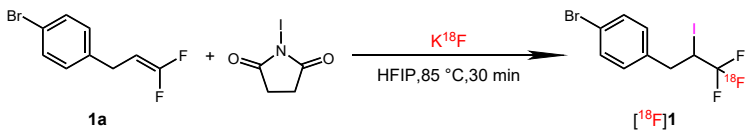
After the radiolabeling reaction, a single drop of the reaction mixture was spotted on the TLC plate. Then, the plate was developed by a mixture of hexane and ethyl acetate (1:1). The TLC analysis was performed using a Bioscan Mini-Scan TLC Scanner (Ekert and Ziegler). The TLC RCC yield was calculated by integrating the free ^{18}F ion and the corresponding product.

Isolation yield (RCY)

100 - 200 μL of the crude reaction mixture (typically 18.5-33.3 MBq) for radio-HPLC analysis. The fraction was collected by an automatic fraction collector. The activity injected into the HPLC was measured (denoted as A), and the injection time was recorded. The fraction corresponding to the radiolabeled product was collected, and the activity was measured (this activity was denoted by B). The decay-corrected RCY was calculated by dividing the decay-corrected B by A. The activities of [^{18}F] radiolabeled samples were determined using a radioisotope dose calibrator CRC-55tR (Capintec Inc.)

5.4. Optimization of Radiofluorination Conditions[a]

Table S4. Screening of Radiofluorination Conditions of *gem*-difluoroalkenes.[a]



Entry	[^{18}F]Fluoride	Solvent	Temp./°C	RCY/% [b]
1	[^{18}F]KF	HFIP	85	35
2	[^{18}F]KF-$K_{2,2,2}$	HFIP	85	29
3	[^{18}F]TBAF	HFIP	85	32
4	[^{18}F]CsF	HFIP	85	12
5	[^{18}F]AgF	HFIP	85	16
6	[^{18}F]KF	TFE	85	0
7	[^{18}F]KF	MeCN	85	0
8	[^{18}F]KF	HFIP	60	24
9	[^{18}F]KF	HFIP	rt	8

[a] Unless otherwise noted, The reaction was carried out with **1a** (0.05 mmol), NIS (0.1 mmol), K^{18}F (5-10 mCi) and in HFIP (0.5 mL) at 85 °C for 30 min. [b] radiochemical yields (RCYs) were determined after radio HPLC isolation.

5.5. Molar activity calculation

The molar activity of **[^{18}F] 1** was determined as follows. A higher dose of radiolabeling reaction was conducted and purified by a semi-prep HPLC column (Agilent Eclipse SB-C18, 5 μm, 9.4 × 250 mm). 100 μL of the isolated solution was analyzed by HPLC under the following conditions: Agilent Eclipse XDB-C18, 5 μm, 4.6 × 250 mm, 70% acetonitrile in as mobile phase, the flow rate at 2.5 mL/min, UV wavelength at 254 and 220 nm. The injected activity was determined in a Capintec dose calibrator. The area of the UV peak (254 nm) corresponding to **[^{18}F] 1** (tR ~11 min) was determined. The mass of **1** in the sample was then determined by linear regression analysis against a standard curve generated from the injection of identical volumes of solutions of known concentration of **1**. Division of the radioactivity for **[^{18}F] 1** (GBq) by the molar of the product (mol) gives the end of synthesis (EOS) molar activity (Ci/mmol).

For 1.85 MBq of purified compound **[^{18}F] 1**, UV absorbance (at 254 nm) of 1.70 was measured, corresponding to 0.474 μg for an average molar activity of 14.8 ± 0.5 GBq/μmol (n = 3) at the end of synthesis (EOS).

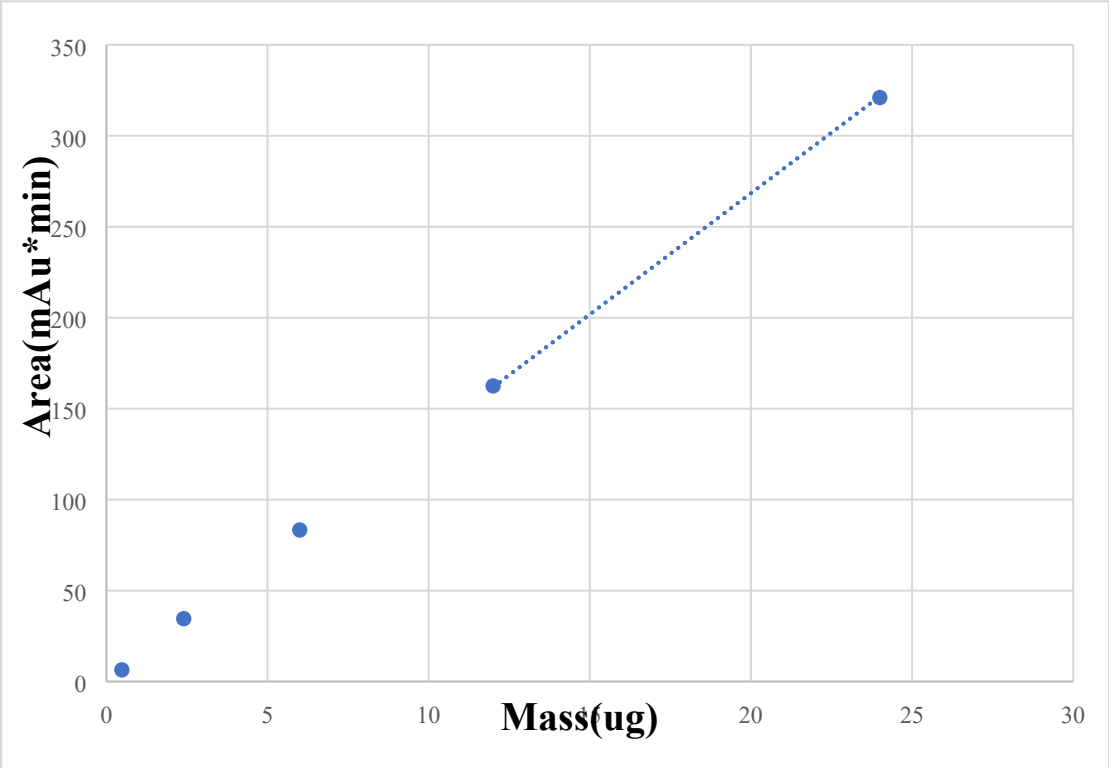
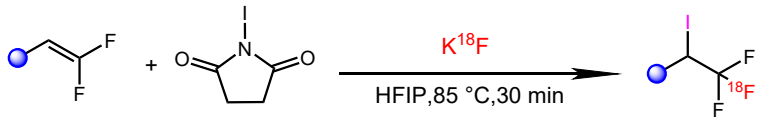


Figure S3. Calibration curve for **[^{18}F]1**

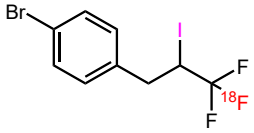
5.6. General procedure for the radio-fluorination



A precursor **1a** (0.05 mmol) dissolved in 300 μL HFIP was added to the reaction vial. Then 200 μL K^{18}F solution (200 - 300 MBq) was transferred to the reaction vial. The reaction was kept at 85 ℃ for 30 min. After the radiolabeling reaction, one drop of the reaction mixture was dotted on the TLC plate. Then, the plate was developed by a mixture of hexane and ethyl acetate (1:1). The TLC analysis was performed using a Bioscan Mini-Scan TLC Scanner (Ekert and Ziegler) to get the RCC yield. If needed, the reaction solution was injected into HPLC for further analysis to get the RCY yield.

5.7. Analysis and characterization for [^{18}F] Trifluoromethyl Iodides

[^{18}F]1-bromo-4-(3,3,3-trifluoro-2-iodopropyl) benzene ([^{18}F]1)



isolation HPLC condition (Agilent Eclipse SB C18, 5 μm, 9.4 × 250 mm, MeCN/ phosphate buffer = 70/30, flow rate = 2.5 mL/min, λ = 254 nm).

analytical HPLC condition (Agilent InfinityLab Poroshell 120 EC-C18, 4.6 x 50 mm, 2.7 μm, MeCN/ phosphate buffer = 70/30, flow rate =1.0 mL/min, λ = 254 nm)

TLC RCC Yield = 65 ± 5 % (n = 5), RCY Yield = 35 ± 4 % (n = 5).

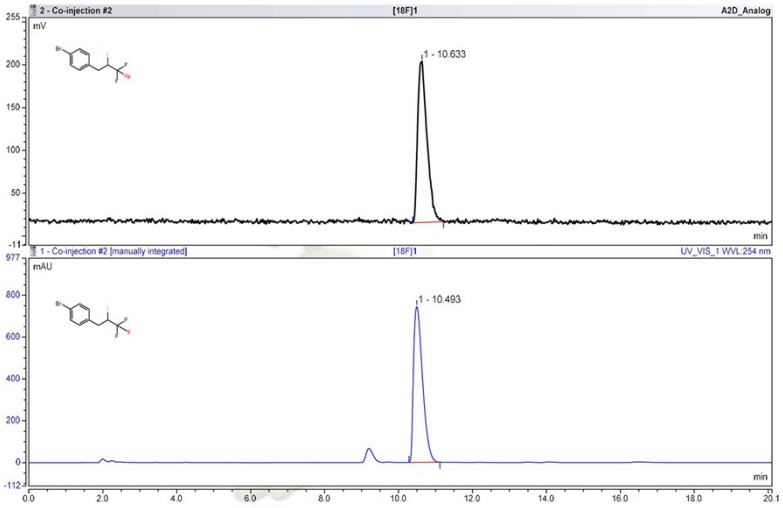
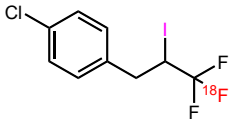


Figure S4 Co-injection of **[^{18}F]1**

[^{18}F]1-chloro-4-(3,3,3-trifluoro-2-iodopropyl)benzene ([^{18}F]2)



isolation HPLC condition (Agilent Eclipse SB C18, 5 μm, 9.4 × 250 mm, MeCN/ phosphate buffer = 70/30, flow rate = 2.5 mL/min, λ = 254 nm).

analytical HPLC condition (Agilent InfinityLab Poroshell 120 EC-C18, 4.6 x 50 mm, 2.7 μm, MeCN/ phosphate buffer = 70/30, flow rate =1.0 mL/min, λ = 254 nm)

TLC RCC Yield = 50 ± 5 % (n = 3), RCY Yield = 31 ± 3 % (n = 3).

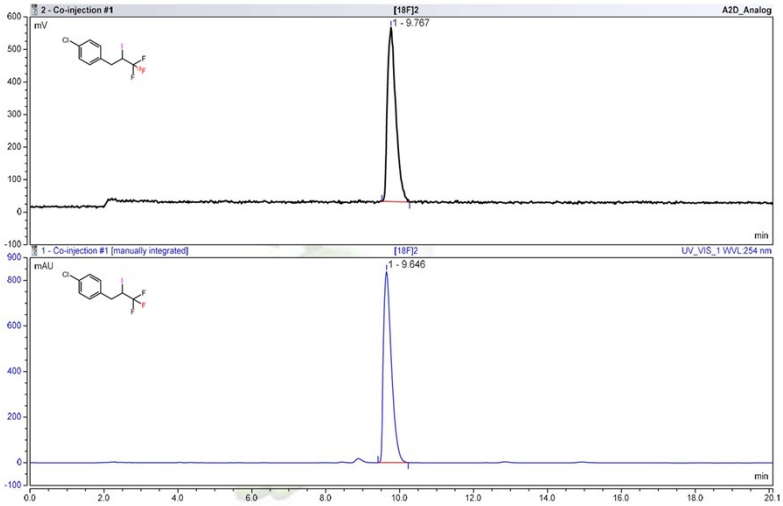
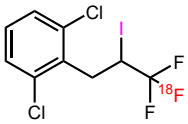


Figure S5 Co-injection of **[^{18}F]2**

[^{18}F]1,3-dichloro-2-(3,3,3-trifluoro-2-iodopropyl)benzene ([^{18}F]3)



isolation HPLC condition (Agilent Eclipse SB C18, 5 µm, 9.4 × 250 mm, MeCN/ phosphate buffer = 70/30, flow rate = 2.5 mL/min, λ = 254 nm).

analytical HPLC condition (Agilent InfinityLab Poroshell 120 EC-C18, 4.6 x 50 mm, 2.7 µm, MeCN/ phosphate buffer = 70/30, flow rate =1.0 mL/min, λ = 254 nm)

TLC RCC Yield = 39 ± 5 % (n = 6), RCY Yield = 27 ± 8 % (n = 6).

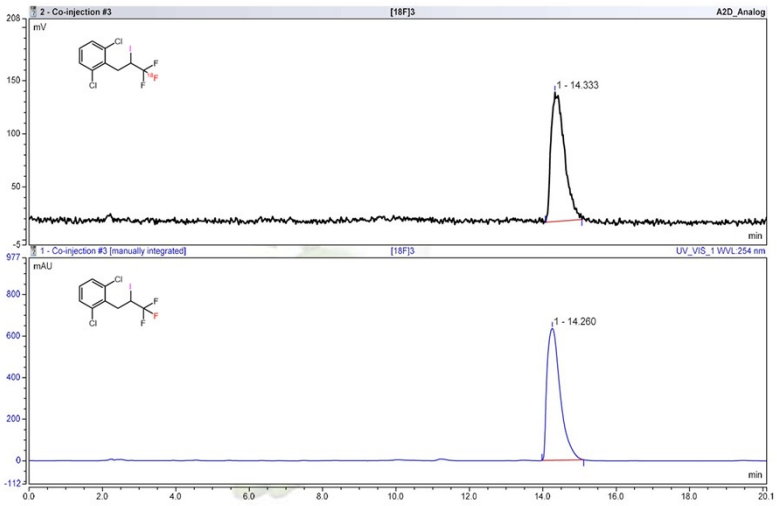
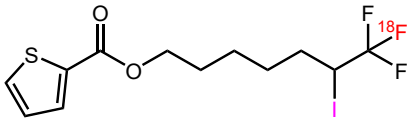


Figure S6 Co-injection of **[^{18}F]3**

[^{18}F]7,7,7-trifluoro-6-iodoheptyl thiophene-2-carboxylate ([^{18}F]4)



isolation HPLC condition (Agilent Eclipse SB C18, 5 µm, 9.4 × 250 mm, MeCN/ phosphate buffer = 70/30, flow rate = 2.5 mL/min, λ = 254 nm).

analytical HPLC condition (Agilent InfinityLab Poroshell 120 EC-C18, 4.6 x 50 mm, 2.7 µm, MeCN/ phosphate buffer = 70/30, flow rate =1.0 mL/min, λ = 254 nm)

TLC RCC Yield = 58 ± 5 % (n = 3), RCY Yield = 32 ± 6 % (n = 3).

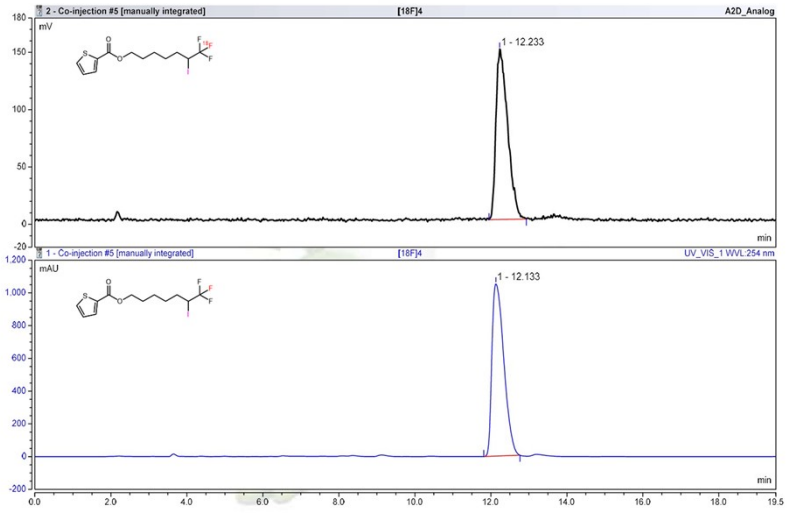
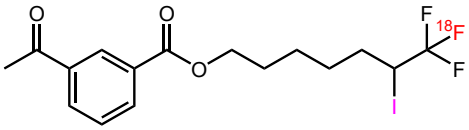


Figure S7 Co-injection of **[^{18}F]4**

[^{18}F]7,7,7-trifluoro-6-iodoheptyl 3-acetylbenzoate ([^{18}F]5)



isolation HPLC condition (Agilent Eclipse SB C18, 5 µm, 9.4 × 250 mm, MeCN/ phosphate buffer = 70/30, flow rate = 2.5 mL/min, λ = 254 nm).

analytical HPLC condition (Agilent InfinityLab Poroshell 120 EC-C18, 4.6 x 50 mm, 2.7 µm, MeCN/ phosphate buffer = 70/30, flow rate =1.0 mL/min, λ = 254 nm)

TLC RCC Yield = 80 ± 5 % (n = 3), RCY Yield = 43 ± 4 % (n = 3).

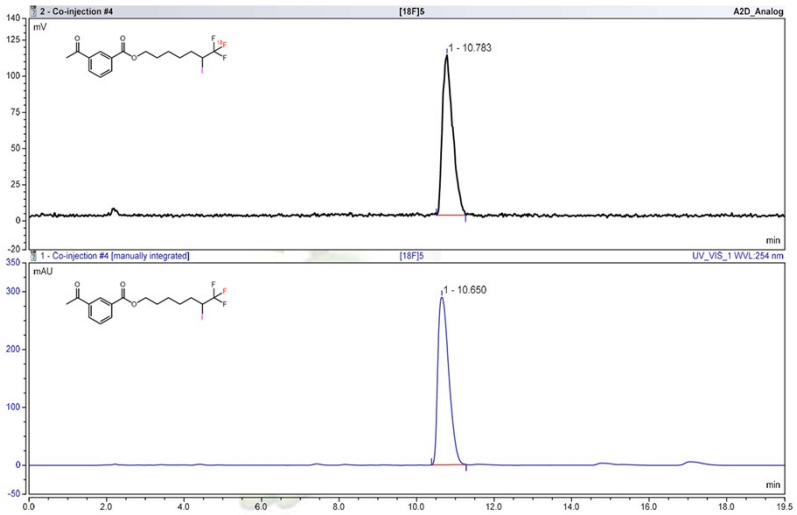
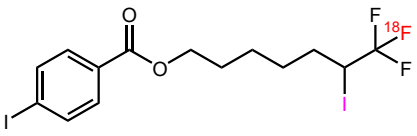


Figure S8 Co-injection of **[^{18}F]5**

[^{18}F]7,7,7-trifluoro-6-iodoheptyl 4-iodobenzoate ([^{18}F]6)



isolation HPLC condition (Agilent Eclipse SB C18, 5 µm, 9.4 × 250 mm, MeCN/ 0.1 M ammonium formate buffer = 85/15, flow rate = 2.5 mL/min, λ = 254 nm).

analytical HPLC condition (Agilent InfinityLab Poroshell 120 EC-C18, 4.6 x 50 mm, 2.7 µm, MeCN/ 0.1 M ammonium formate buffer = 85/15, flow rate =1.0 mL/min, λ = 254 nm)

TLC RCC Yield = 93 ± 5 % (n = 3), RCY Yield = 67 ± 5 % (n = 3).

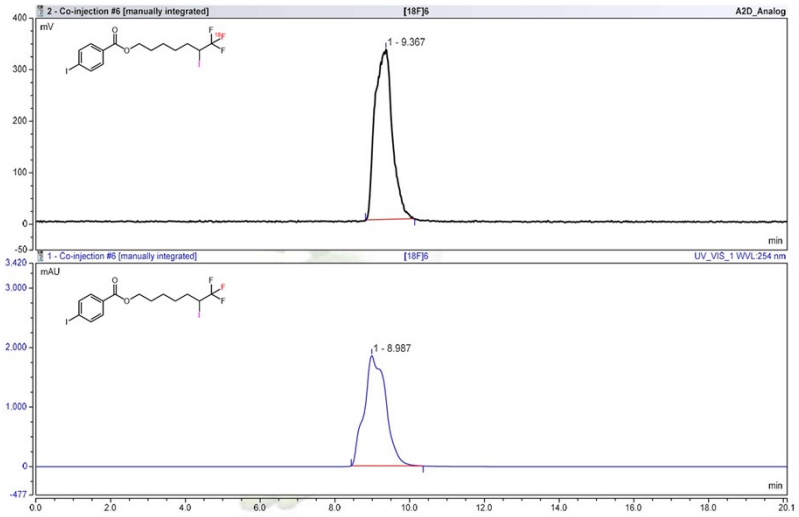
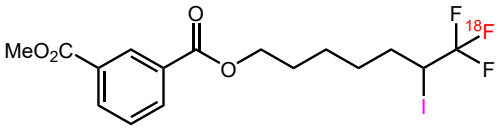


Figure S9 Co-injection of **[^{18}F]6**

[^{18}F]methyl (7,7,7-trifluoro-6-iodoheptyl) isophthalate ([^{18}F]7)



isolation HPLC condition (Agilent Eclipse SB C18, 5 µm, 9.4 × 250 mm, MeCN/ phosphate buffer = 70/30, flow rate = 2.5 mL/min, λ = 254 nm).

analytical HPLC condition (Agilent InfinityLab Poroshell 120 EC-C18, 4.6 x 50 mm, 2.7 µm, MeCN/ phosphate buffer = 70/30, flow rate =1.0 mL/min, λ = 254 nm)

TLC RCC Yield = 86 ± 5 % (n = 3), RCY Yield = 46 ± 3 % (n = 3).

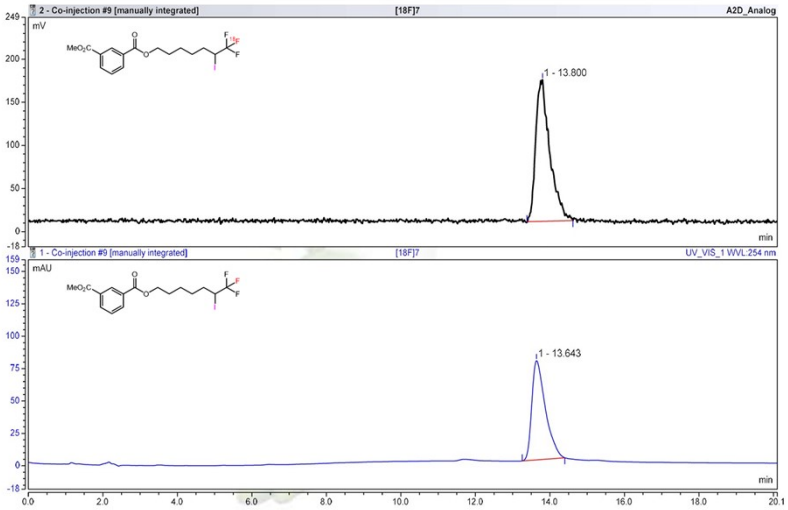
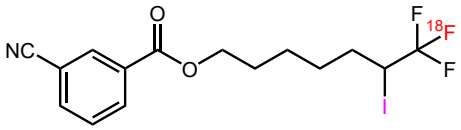


Figure S10 Co-injection of **[^{18}F]7**

[^{18}F]7,7,7-trifluoro-6-iodoheptyl 3-cyanobenzoate ([^{18}F]8)



isolation HPLC condition (Agilent Eclipse SB C18, 5 µm, 9.4 × 250 mm, MeCN/ phosphate buffer = 70/30, flow rate = 2.5 mL/min, λ = 254 nm).

analytical HPLC condition (Agilent InfinityLab Poroshell 120 EC-C18, 4.6 x 50 mm, 2.7 µm, MeCN/ phosphate buffer = 70/30, flow rate =1.0 mL/min, λ = 254 nm)

TLC RCC Yield = 96 ± 4 % (n = 3), RCY Yield = 58 ± 7 % (n = 3).

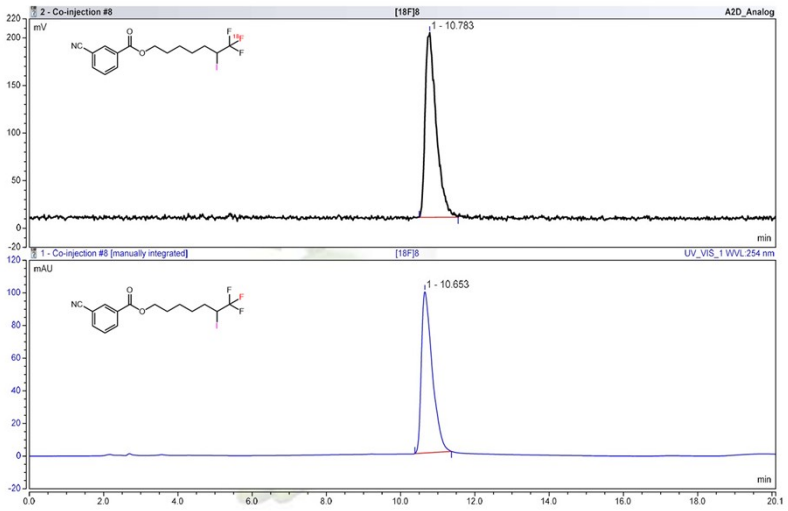
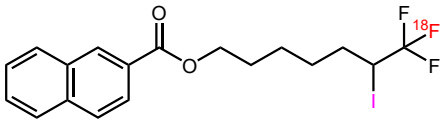


Figure S11 Co-injection of **[^{18}F]8**

[^{18}F]7,7,7-trifluoro-6-iodoheptyl 2-naphthoate ([^{18}F]9)



isolation HPLC condition (Agilent Eclipse SB C18, 5 μm, 9.4 × 250 mm, MeCN/ 0.1 M ammonium formate buffer = 85/15, flow rate = 2.5 mL/min, λ = 254 nm).

analytical HPLC condition (Agilent InfinityLab Poroshell 120 EC-C18, 4.6 x 50 mm, 2.7 μm, MeCN/ 0.1 M ammonium formate buffer = 85/15, flow rate =1.0 mL/min, λ = 254 nm)

TLC RCC Yield = 98 ± 2 % (n = 3), RCY Yield = 61 ± 5 % (n = 3).

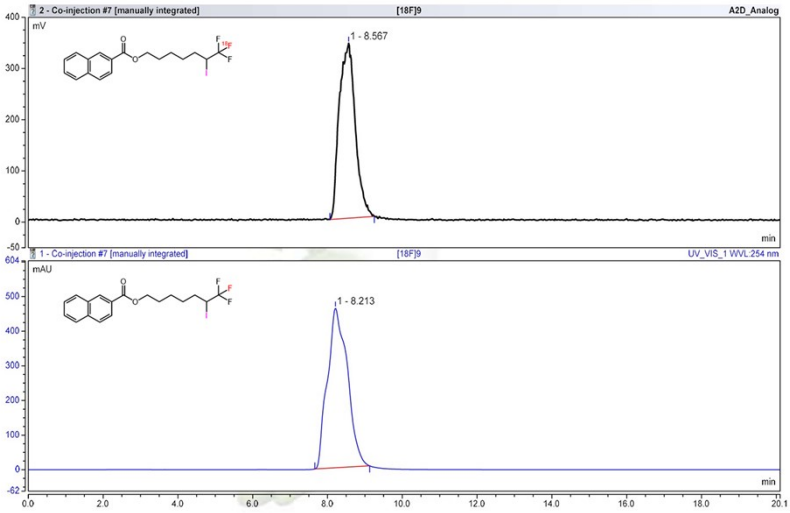
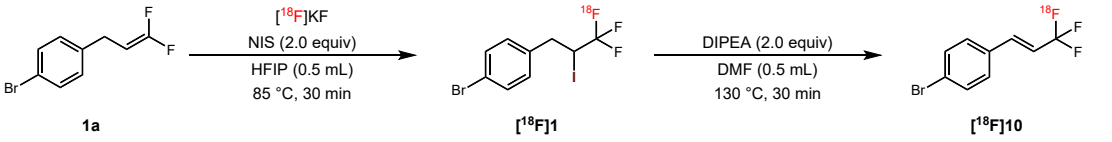


Figure S12 Co-injection of **[^{18}F]9**

5.8. Conversion of [^{18}F]Trifluoromethyl Iodides.



1a **[^{18}F]1** **[^{18}F]10**

19 ± 2 % (n = 3)
RCY of 2 step radiolabeling

Step 1: NIS (0.1 mmol, 2.0 equiv.) was added to an oven-dried 5 mL screw-cap vial, followed by the addition of 0.3 mL of HFIP under stirring to ensure complete dissolution. The gem-difluoroalkene substrate **1a** was then added, and finally, 0.2 mL of a solution of no-carrier-added [^{18}F]KF in HFIP was introduced. The reaction mixture was stirred at 85 °C for 30 minutes. Upon completion, an aliquot of the reaction mixture was withdrawn and analyzed by analytical HPLC.

Step 2: The vial was left open, and the solvent HFIP was evaporated to dryness at 85 °C. After the solvent was completely removed, 0.5 mL of DMF was added, followed by DIPEA (12 μL, 2.0 equiv.). The mixture was then stirred at 130 °C for 30 min. Upon completion of the reaction, an aliquot was withdrawn and analyzed by analytical HPLC to confirm full conversion. Finally, the reaction mixture was subjected to preparative HPLC for isolation.

Isolation HPLC condition (Agilent Eclipse SB C18, 5 μm, 9.4 × 250 mm, MeCN/ 0.1% TFA in

water, flow rate = 2.5 mL/min, λ = 254 nm).

Analytical HPLC condition (Agilent InfinityLab Poroshell 120 EC-C18, 4.6 x 50 mm, 2.7 µm, MeCN/ 0.1% TFA in water, flow rate =1.0 mL/min, λ = 254 nm)

Gradient elution was performed with acetonitrile(phase A) and 0.1% TFA in water (phase B) using the following program: 0-4.5 min, 5% A, 4.5-6.0 min, 5-30% A, 6.0-14 min, 30-60% A, 14-16 min, 60-90% A, 16-23 min, 90% A .

Based on the analytical HPLC analysis of **Step 1**, the product was identified as **[^{18}F]1**, with a RCC of 61 %.

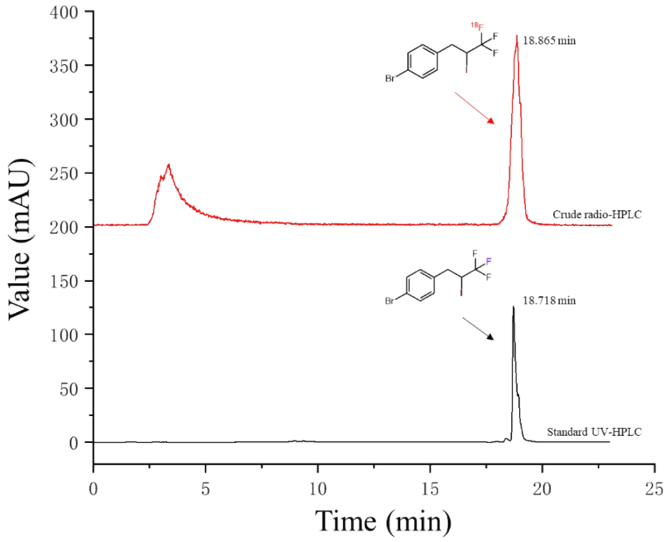


Figure S13 Analytical radio-HPLC chromatogram of **Step 1**.

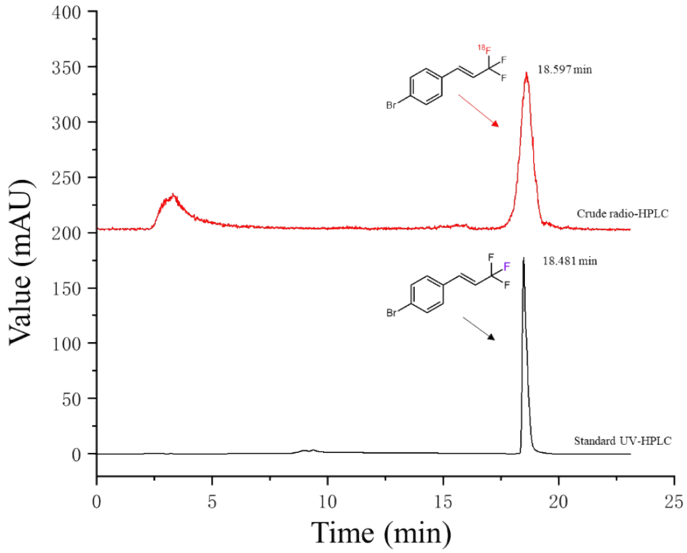


Figure S14 Analytical radio-HPLC chromatogram of **Step 2**

Based on the analytical HPLC analysis of **Step 2**, the product was identified as **[^{18}F]10**. Comparative analysis with the analytical HPLC chromatogram of **Step 1** revealed that **[^{18}F]1** was almost completely converted. This is because our analytical HPLC system is equipped with an external radioactivity detector, and the retention time of the radioactivity signal is delayed by approximately 0.1 min relative to that of the UV signal.

We have developed a two-step, one-pot radiosynthesis strategy for the preparation of [^{18}F]CF_3-labeled alkenes, achieving a two-step radiochemical yield of 19 ± 2% (n = 3). This result demonstrates that the C–I bond not only serves as a transient intermediate to enable the incorporation of the [^{18}F]CF_3 moiety but can also be efficiently eliminated to afford iodine-free tracers. This strategy effectively circumvents the potential negative impacts of the iodine atom on the biological performance of the resulting radiopharmaceuticals.

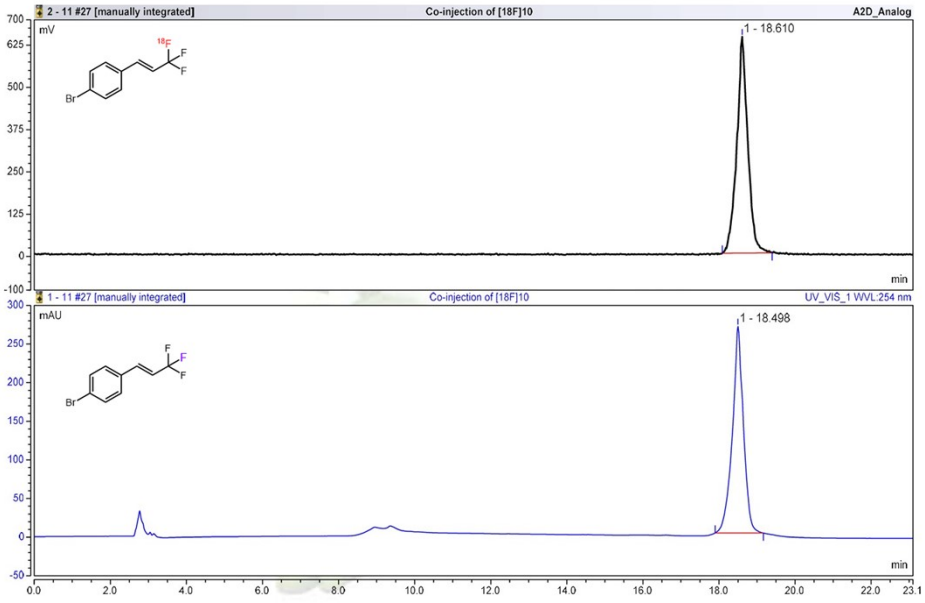
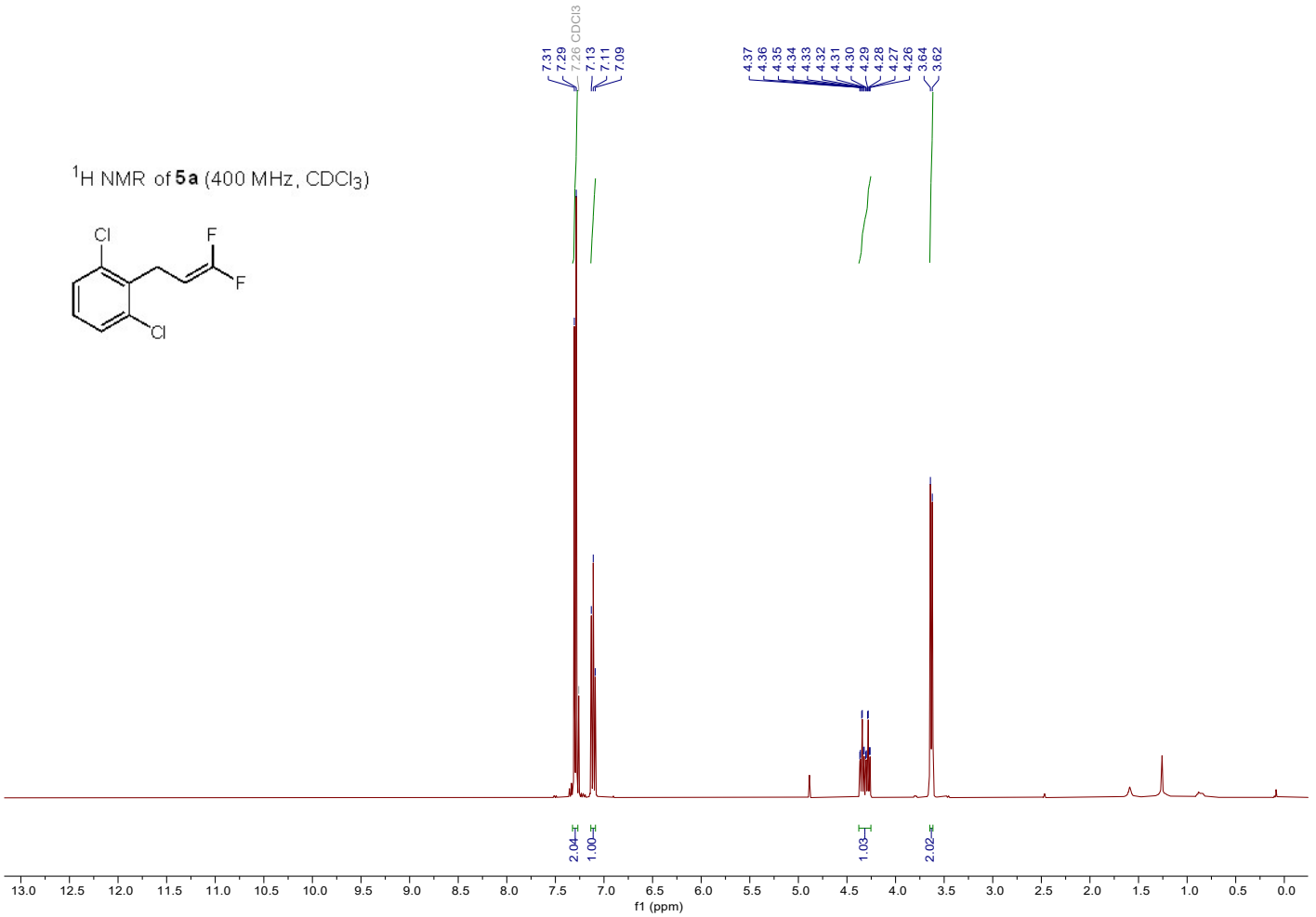
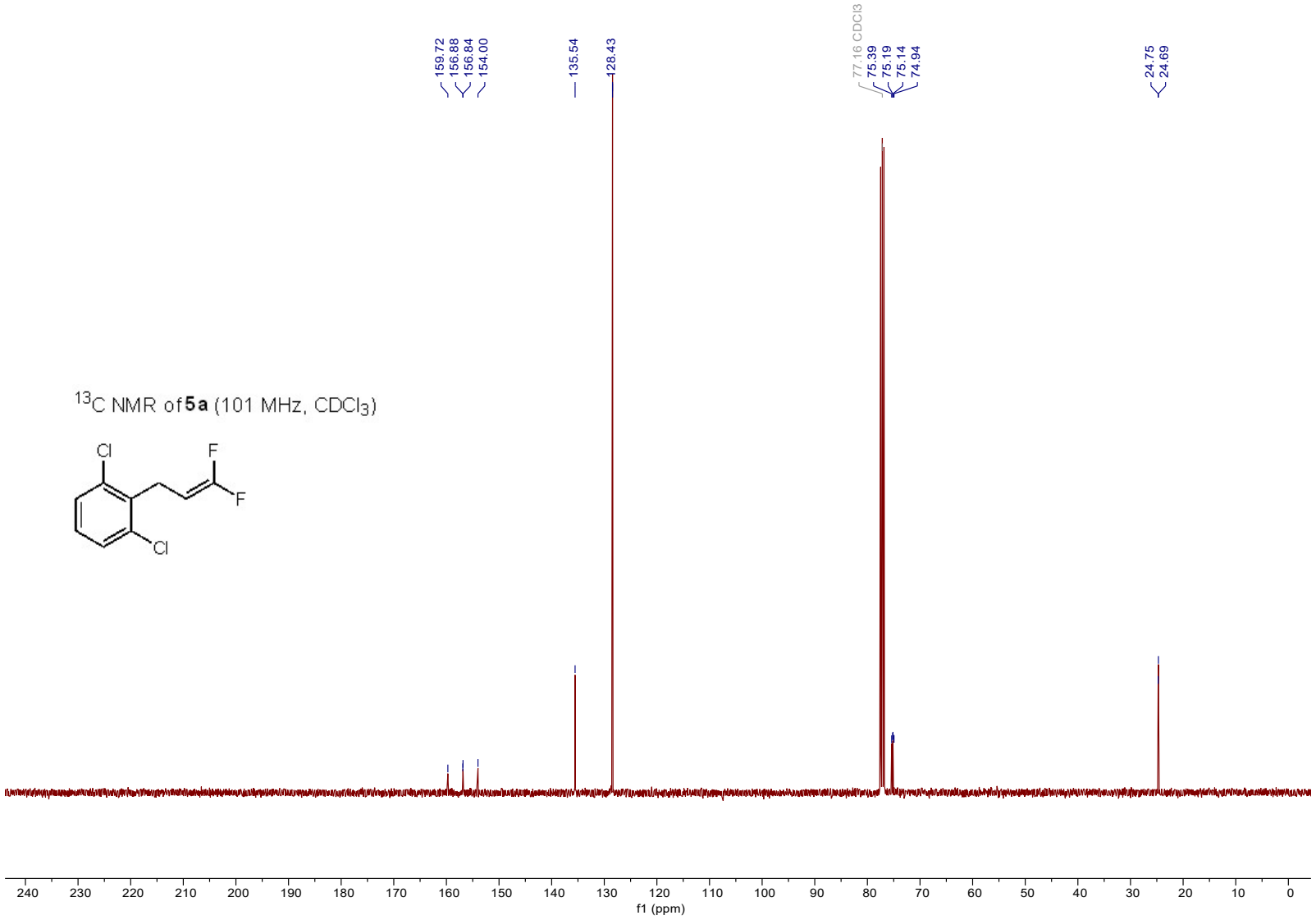
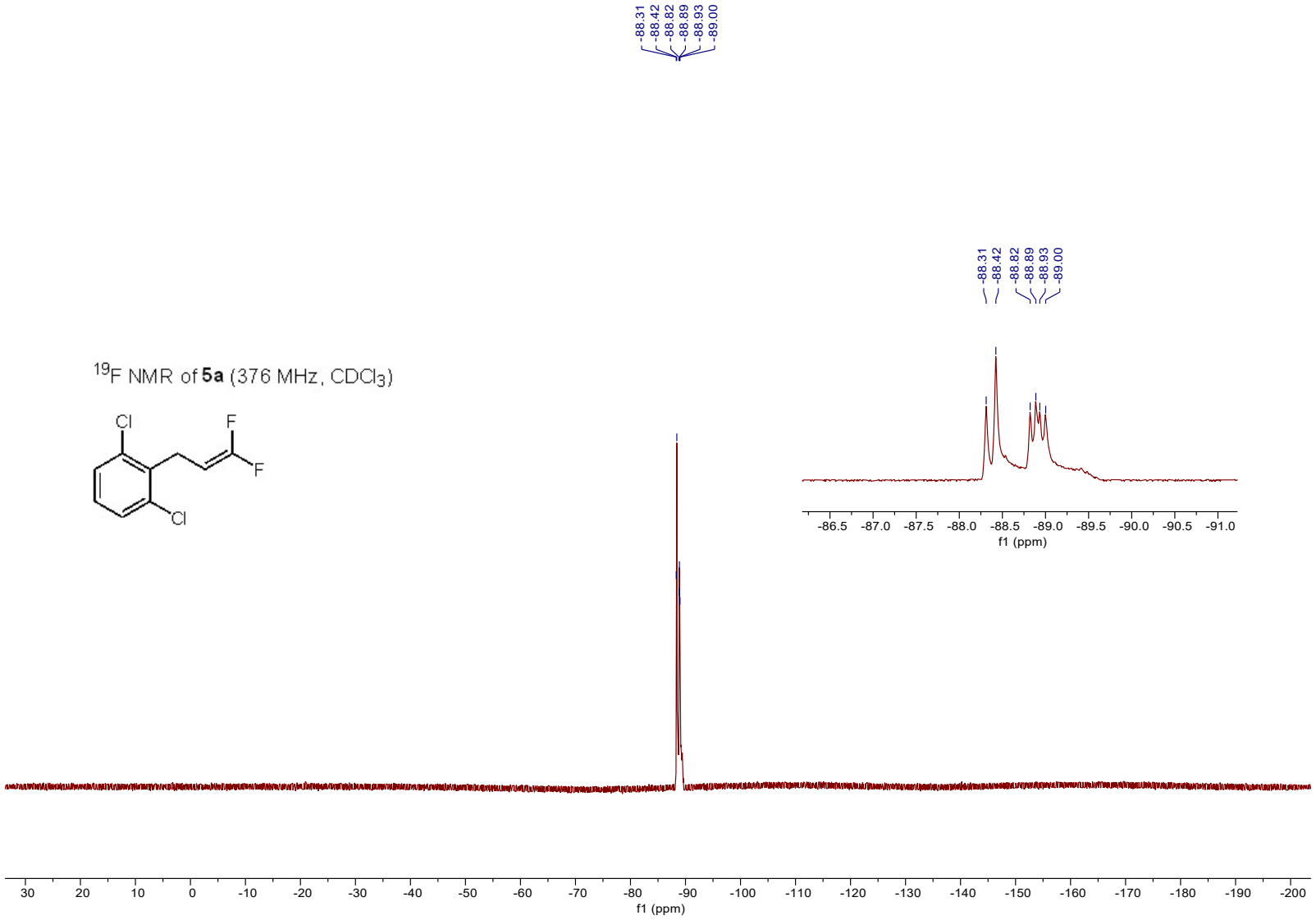


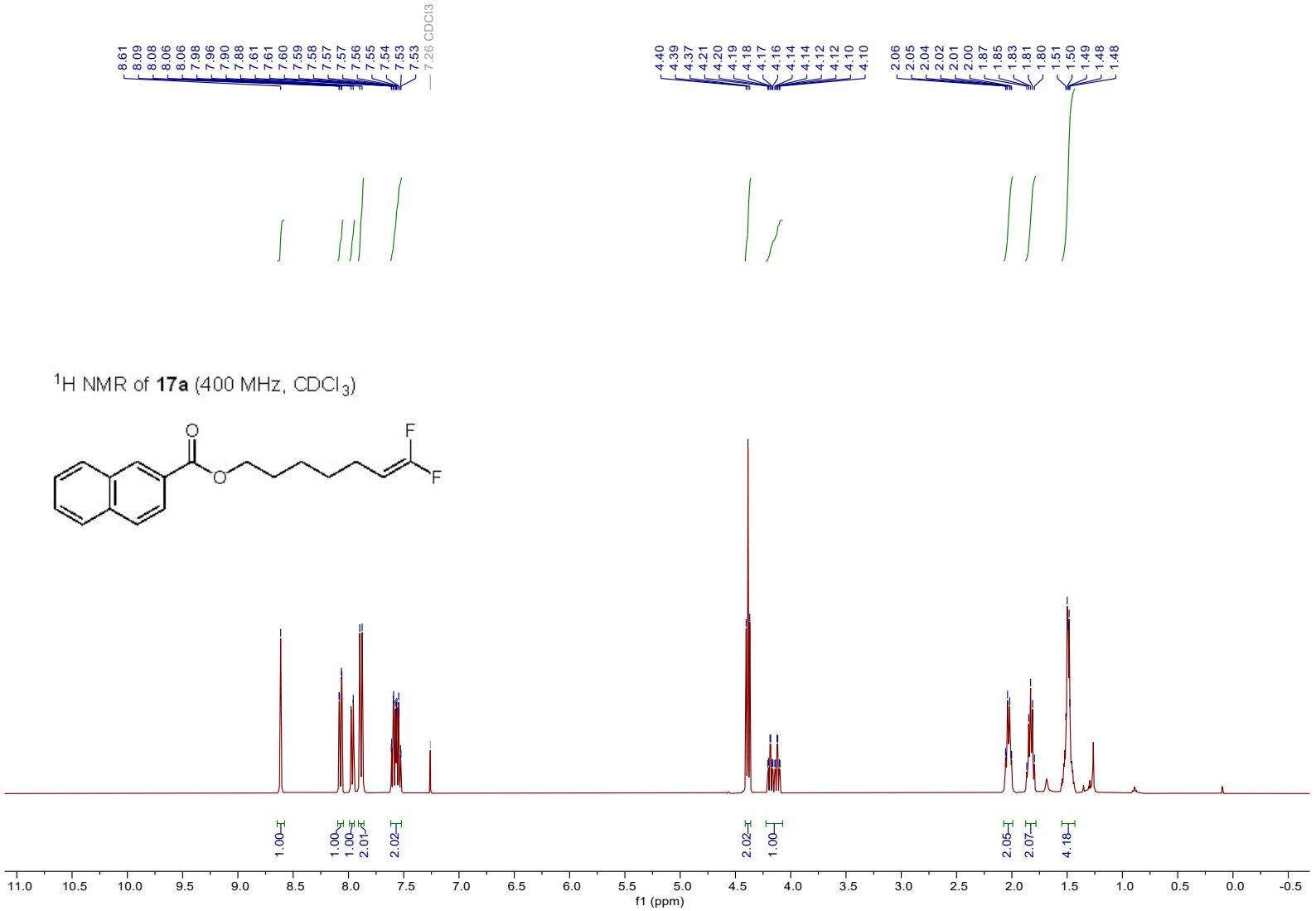
Figure S15 : Co-injection of **[^{18}F]10**

6. NMR Spectra

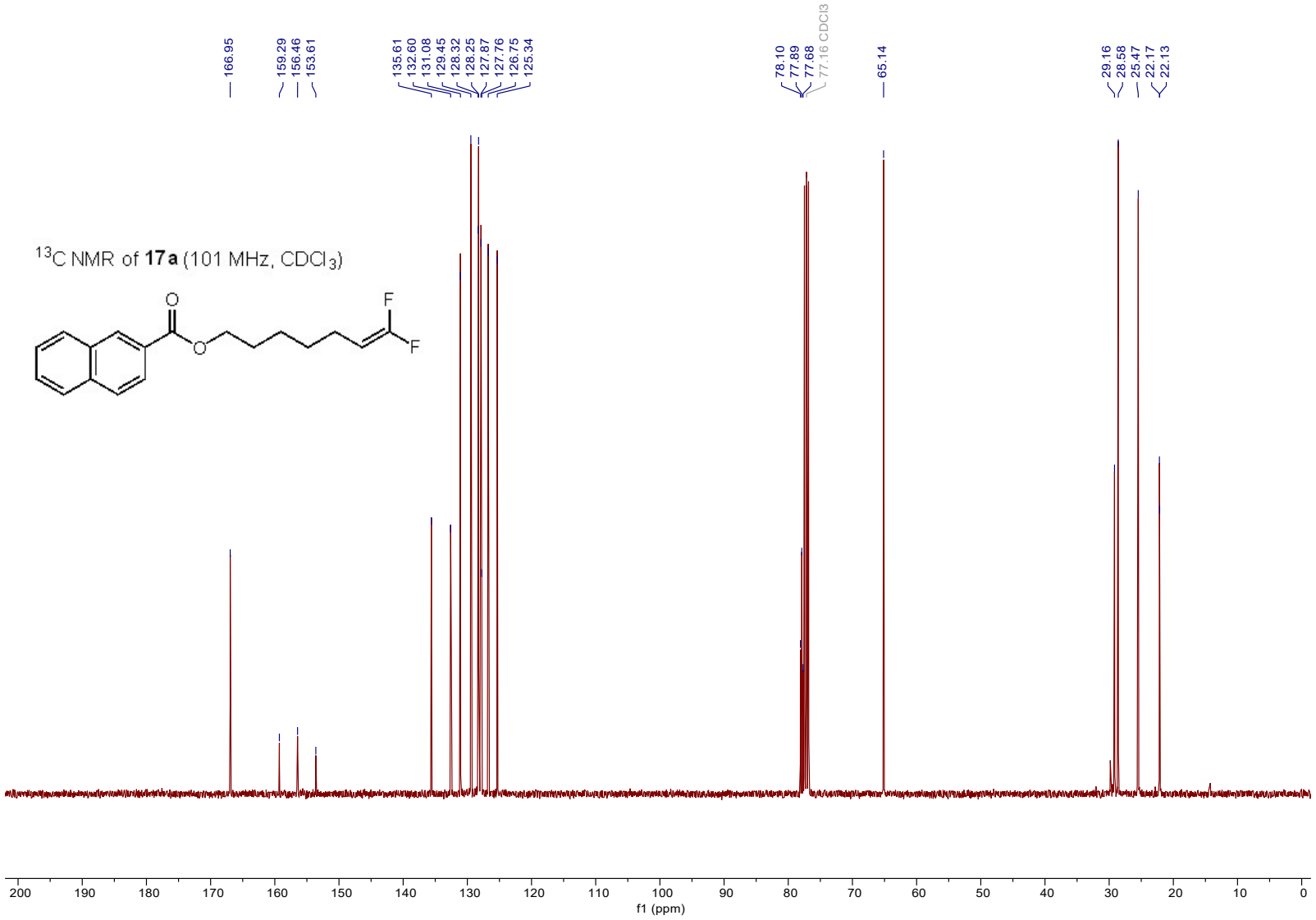


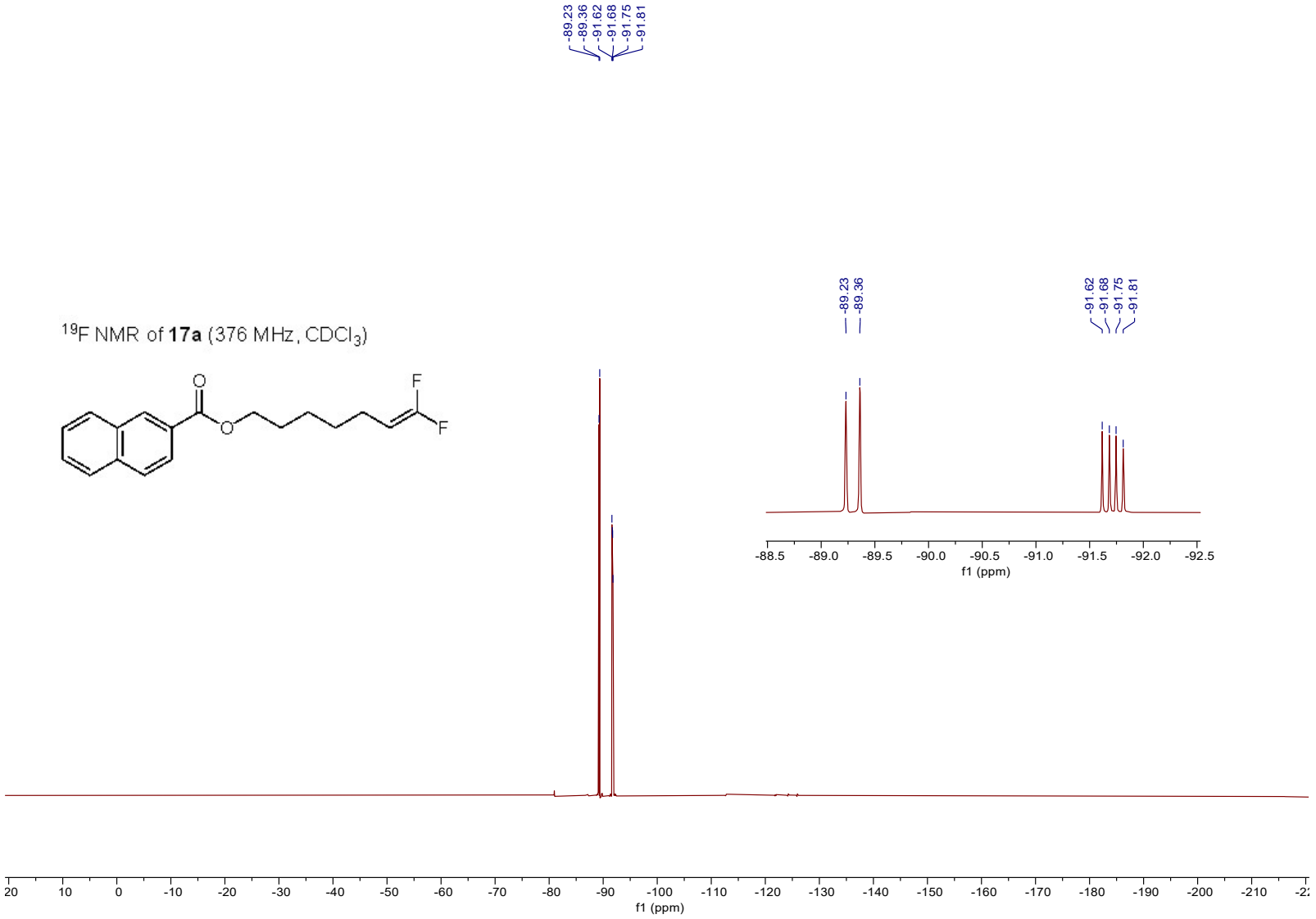

159.72
156.88
156.84
154.00
135.54
128.43
77.16 CDCl3
75.39
75.19
75.14
74.94
24.75
24.69
13C NMR of 5a (101 MHz, CDCl3)
Cl
F
F
Cl
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

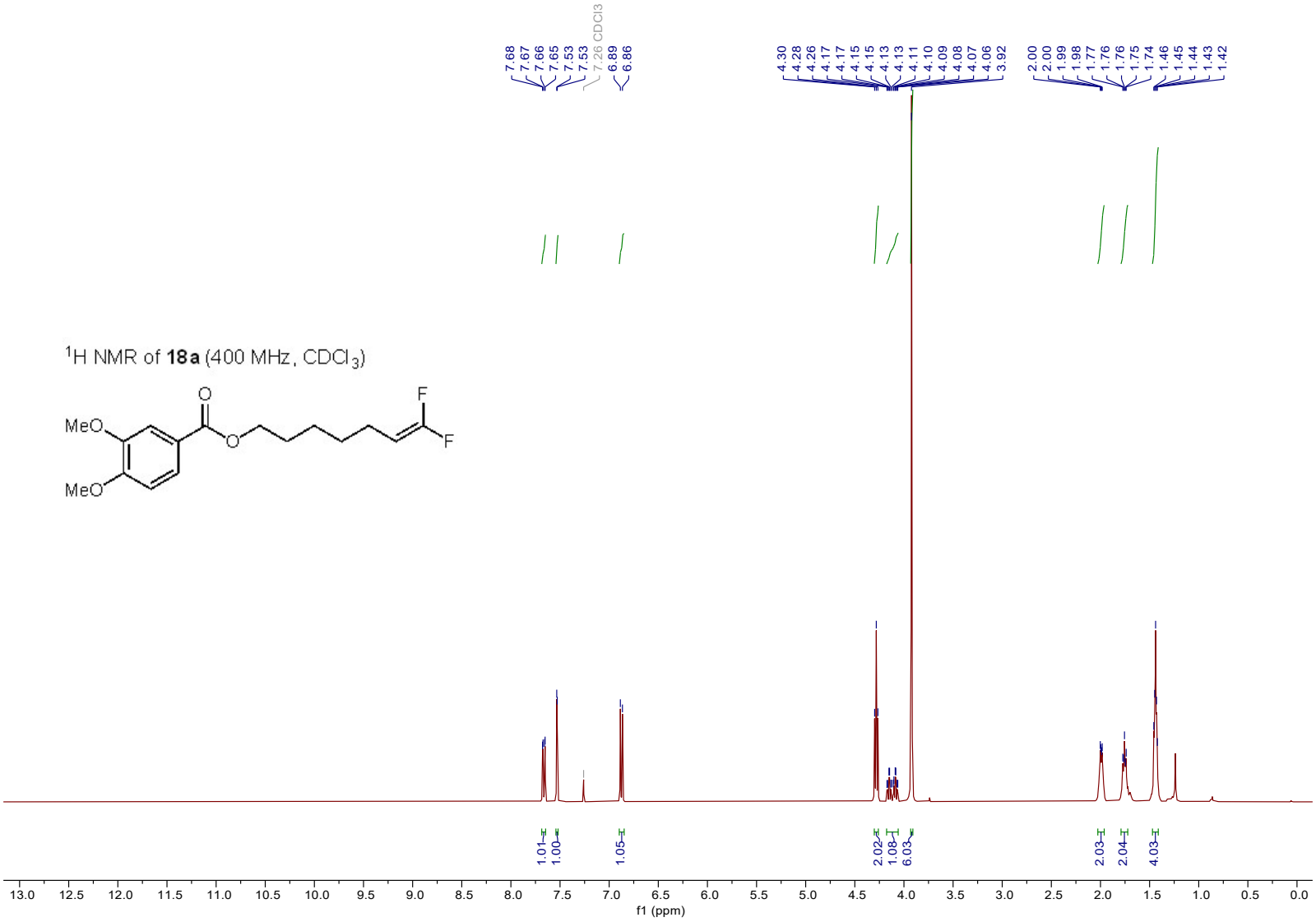

-88.31
-88.42
-88.82
-88.89
-88.93
-89.00
19F NMR of 5a (376 MHz, CDCl3)
Cl
F
F
Cl
-88.31
-88.42
-88.82
-88.89
-88.93
-89.00
-86.5 -87.0 -87.5 -88.0 -88.5 -89.0 -89.5 -90.0 -90.5 -91.0
f1 (ppm)
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

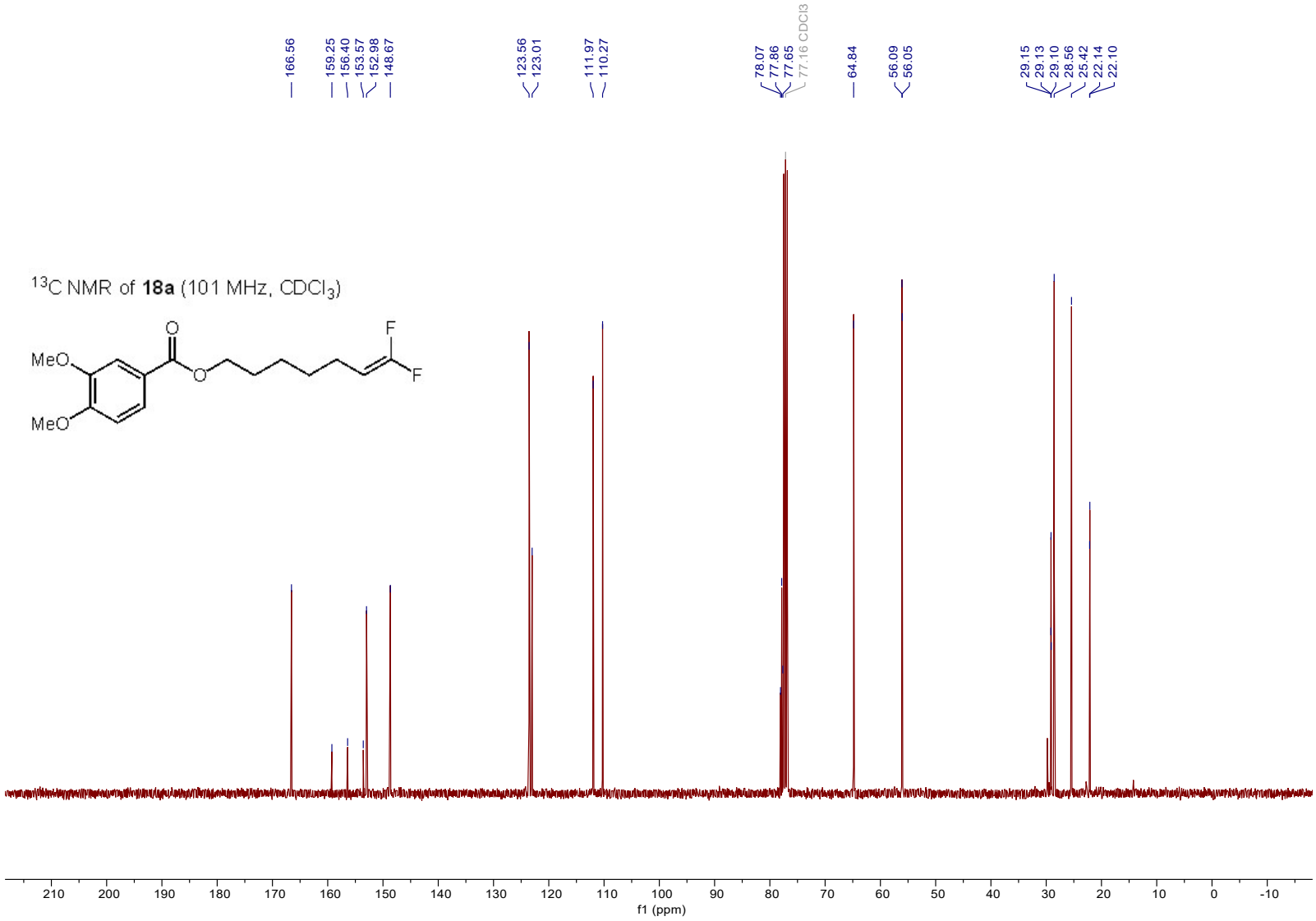


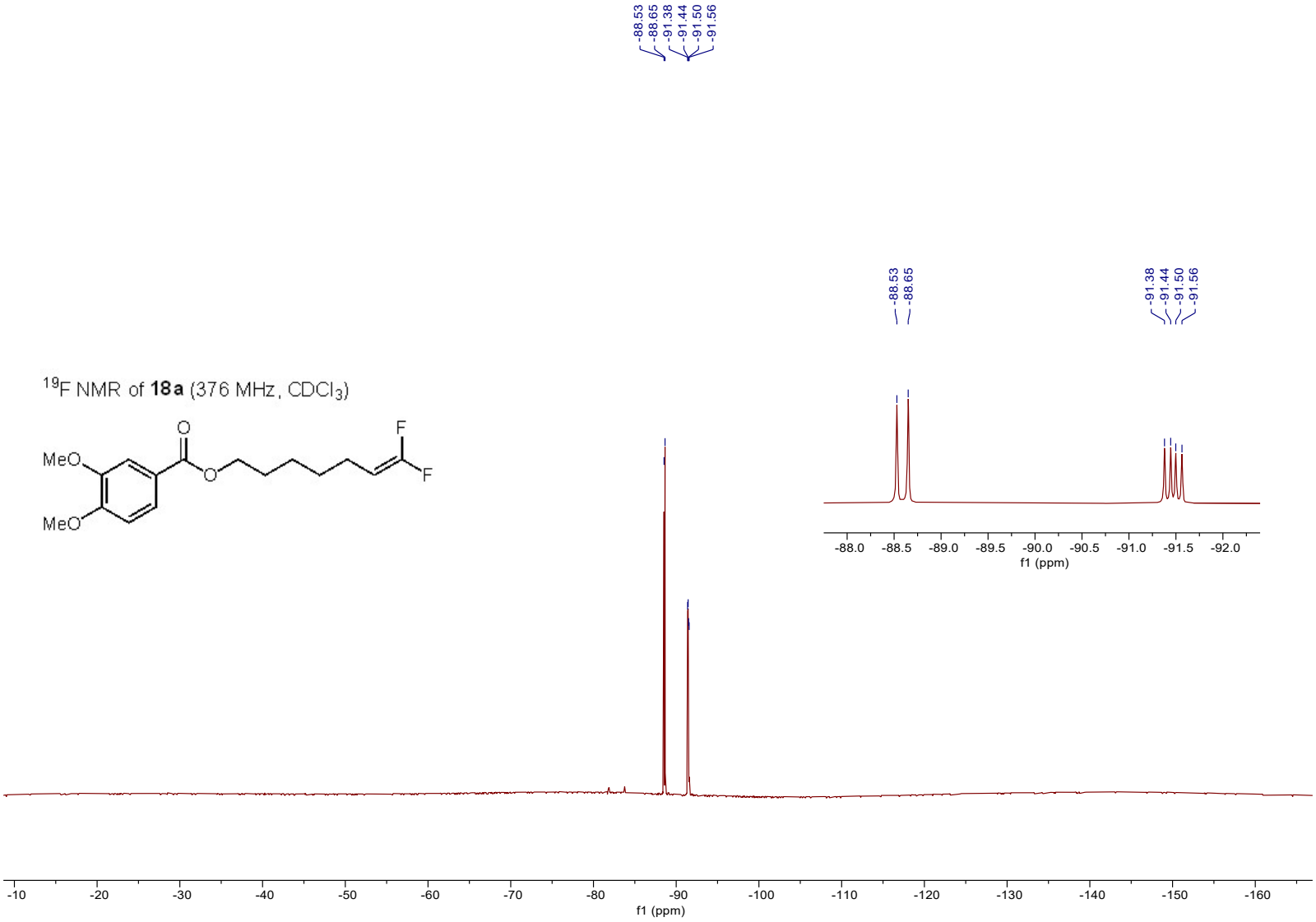
^{1}H NMR of **17a** (400 MHz, $CDCl_3$)

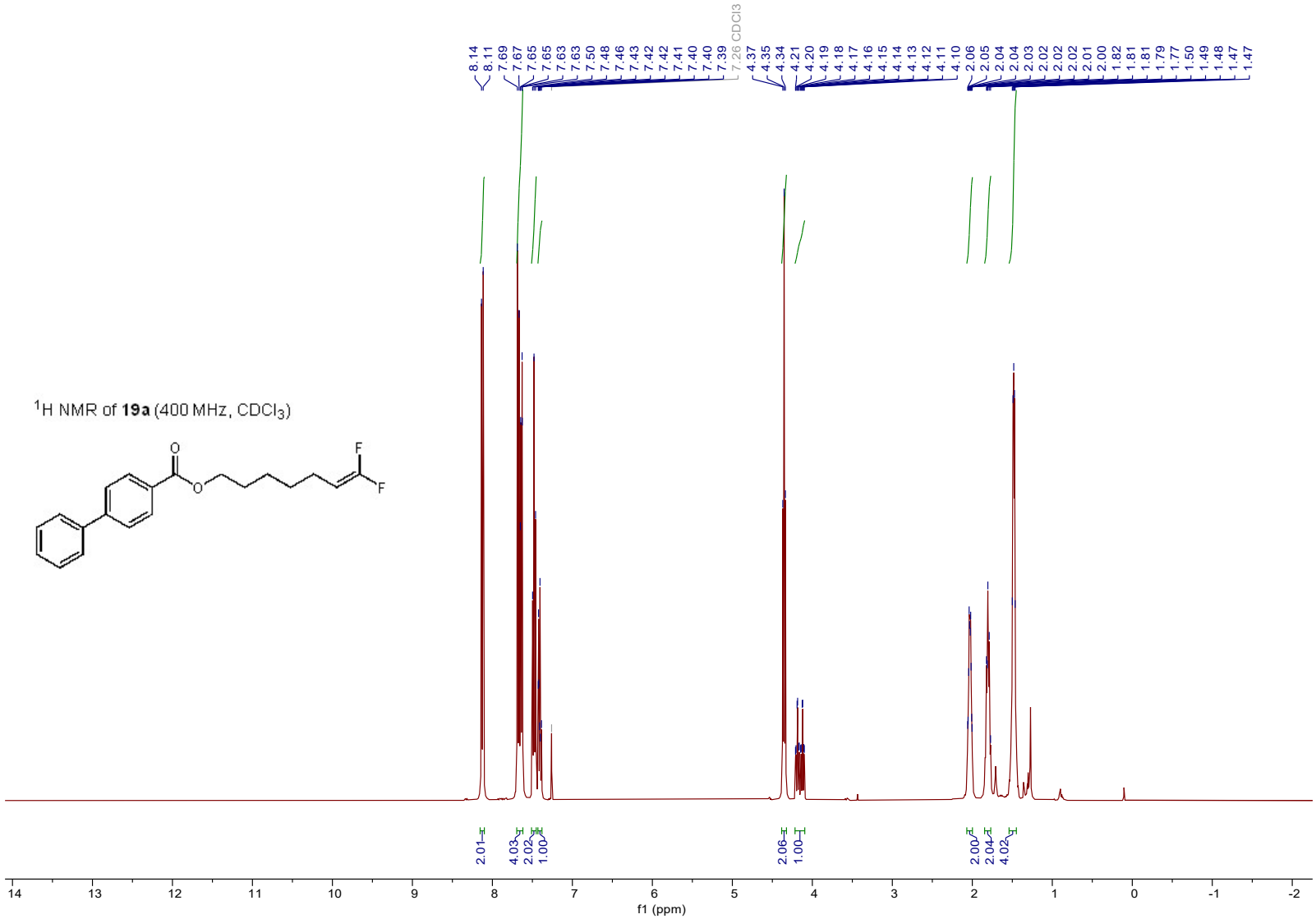

166.95
159.29
156.46
153.61
135.61
132.60
131.08
129.45
128.32
128.25
127.87
127.76
126.75
125.34
78.10
77.89
77.68
77.16 CDCl3
65.14
29.16
28.58
25.47
22.17
22.13
13C NMR of 17a (101 MHz, CDCl3)
O
O
F
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

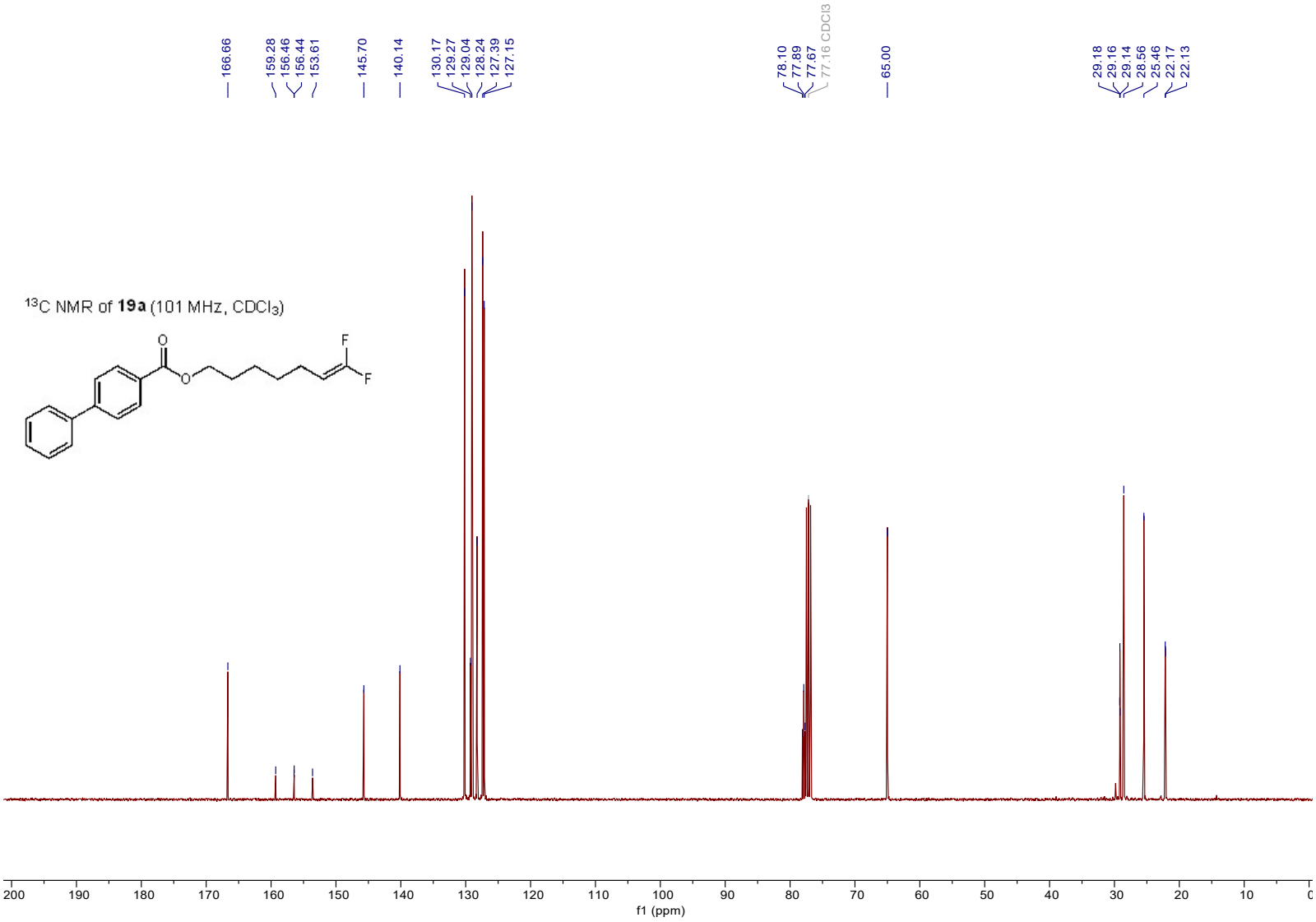

-89.23
-89.36
-91.62
-91.68
-91.75
-91.81
19F NMR of 17a (376 MHz, CDCl3)
O
O
F
F
-89.23
-89.36
-91.62
-91.68
-91.75
-91.81
-88.5
-89.0
-89.5
-90.0
-90.5
-91.0
-91.5
-92.0
-92.5
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

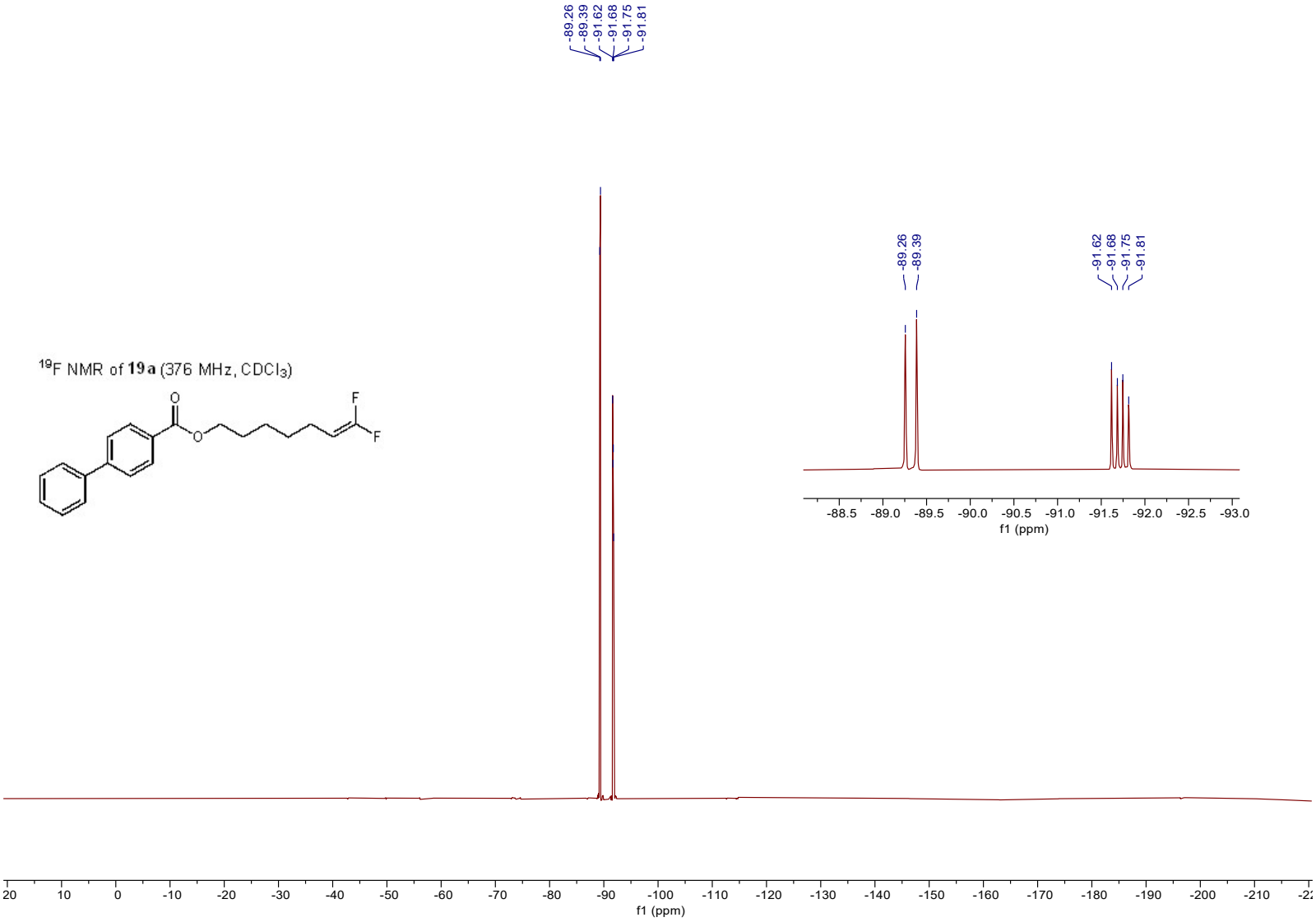

^{1}H NMR of **18a** (400 MHz, $CDCl_3$)
MeO
MeO
O
O
F
F
7.68
7.67
7.66
7.65
7.53
7.53
7.26 CDCl3
6.89
6.86
4.30
4.28
4.26
4.17
4.17
4.15
4.15
4.13
4.13
4.11
4.10
4.09
4.08
4.07
4.06
3.92
2.00
2.00
1.99
1.98
1.77
1.76
1.76
1.75
1.74
1.46
1.45
1.44
1.43
1.42
1.01
1.00
1.05
2.02
1.08
6.03
2.03
2.04
4.03
13.0 12.5 12.0 11.5 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
f1 (ppm)

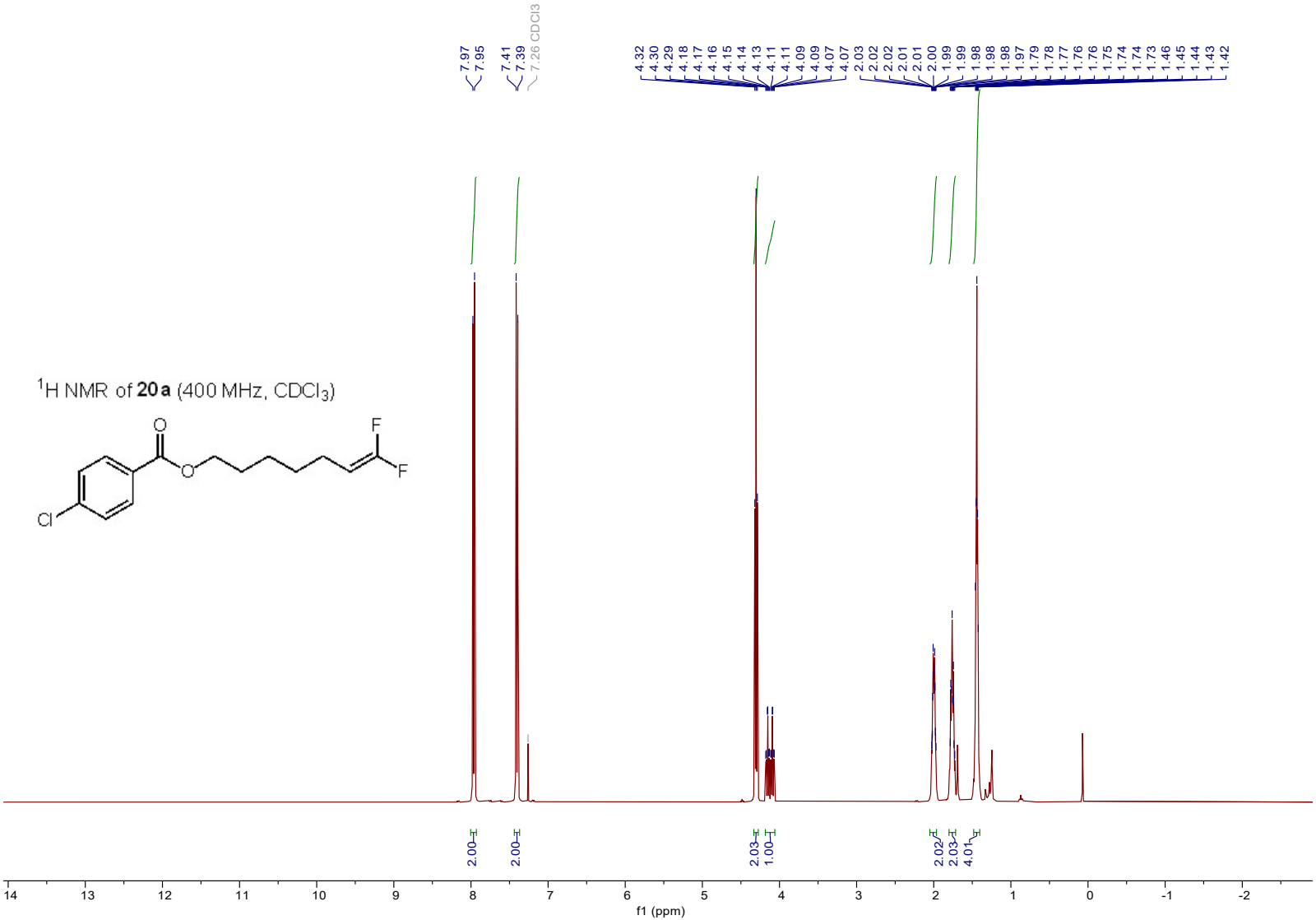

166.56
159.25
156.40
153.57
152.98
148.67
123.56
123.01
111.97
110.27
78.07
77.86
77.65
77.16 CDCl3
64.84
56.09
56.05
29.15
29.13
29.10
28.56
25.42
22.14
22.10
13C NMR of 18a (101 MHz, CDCl3)
MeO
MeO
O
O
F
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

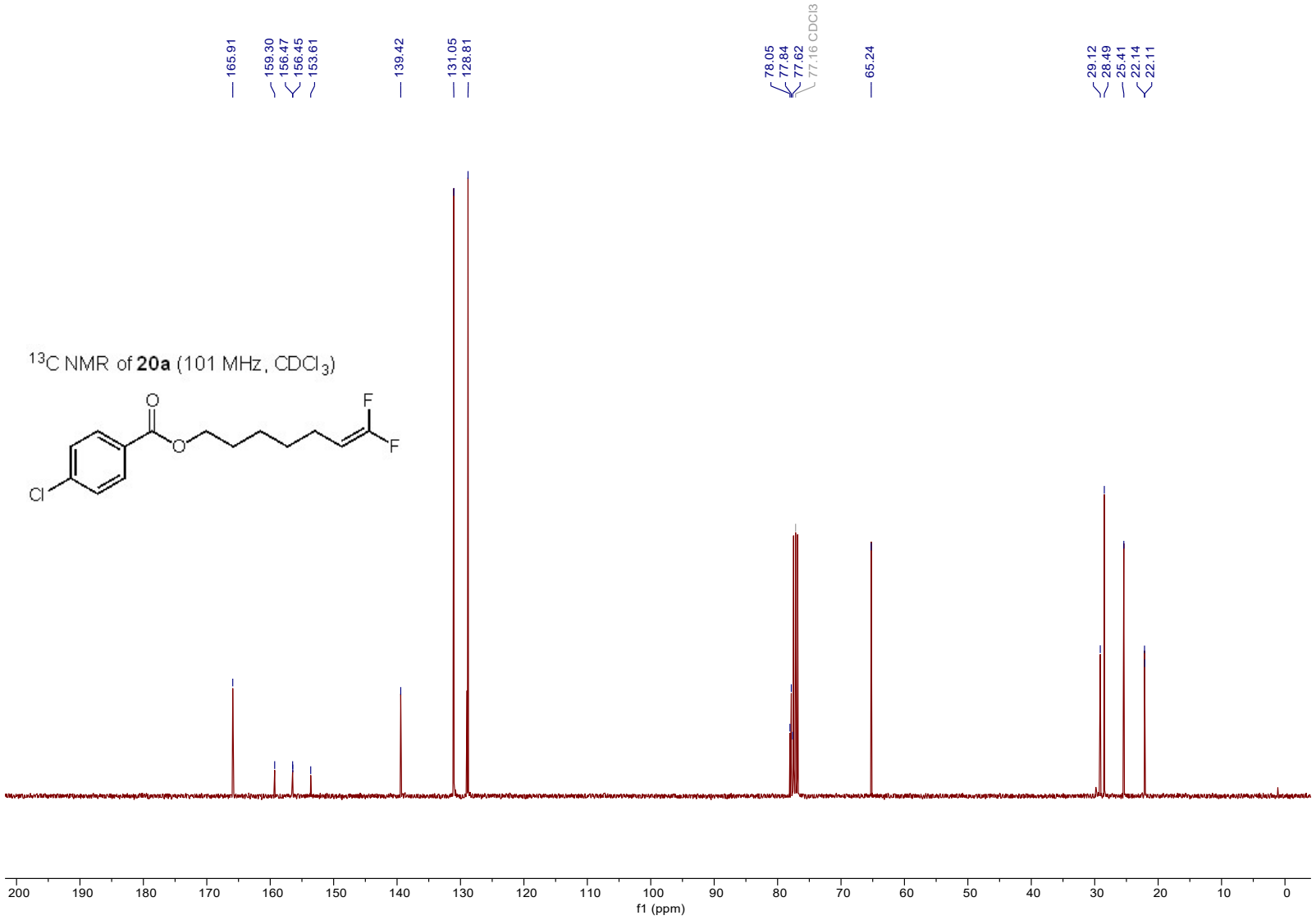

-88.53
-88.65
-91.38
-91.44
-91.50
-91.56
^{19}F NMR of **18a** (376 MHz, $CDCl_3$)
MeO
MeO
O
O
F
F
-88.53
-88.65
-91.38
-91.44
-91.50
-91.56
-88.0 -88.5 -89.0 -89.5 -90.0 -90.5 -91.0 -91.5 -92.0
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

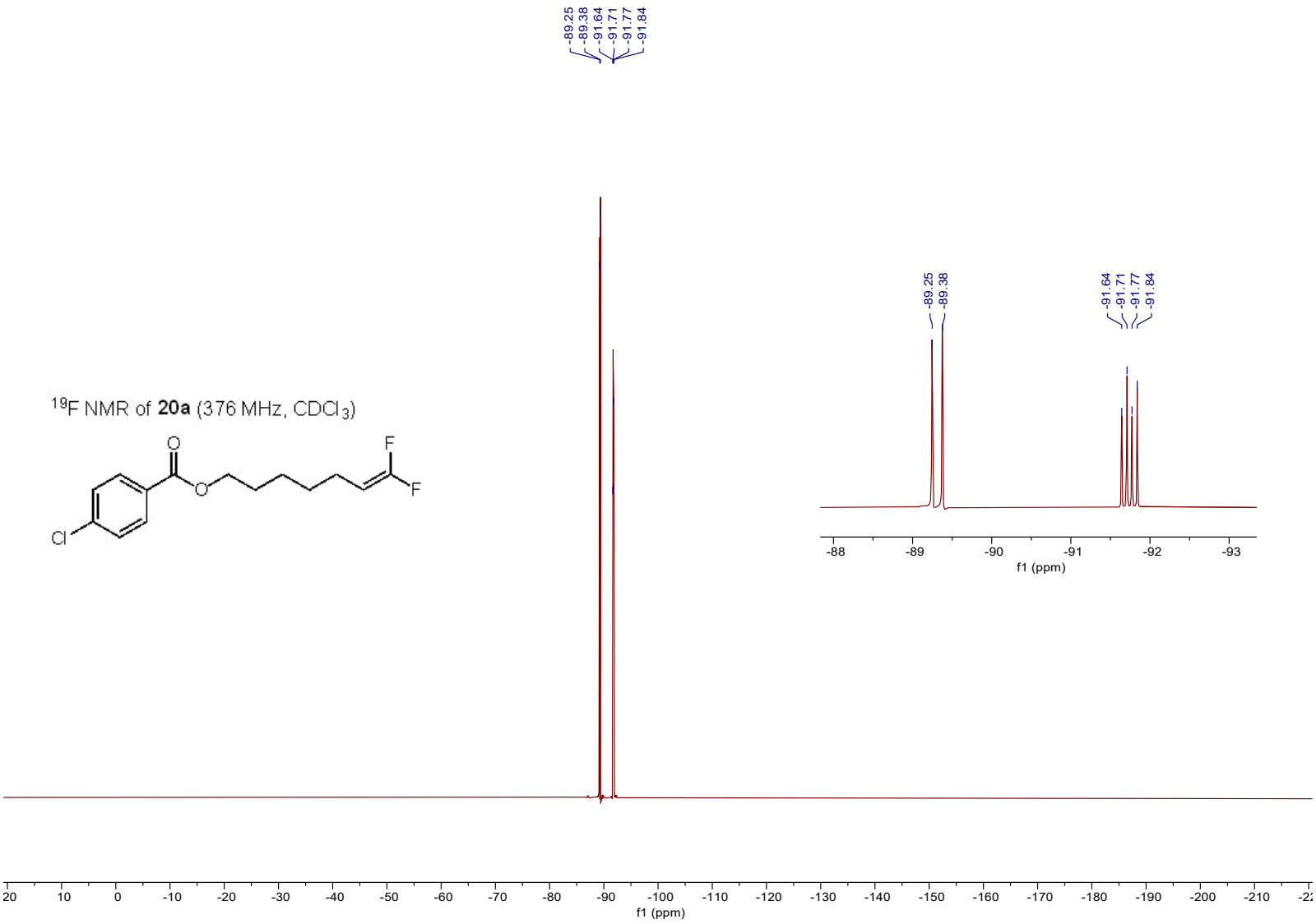

^{1}H NMR of **19a** (400 MHz, $CDCl_3$)
O
O
F
F
8.14
8.11
7.69
7.67
7.65
7.65
7.63
7.63
7.50
7.48
7.46
7.43
7.42
7.42
7.41
7.40
7.40
7.39
7.26 CDCl3
4.37
4.35
4.34
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.14
4.13
4.12
4.11
4.10
2.06
2.05
2.04
2.04
2.03
2.02
2.02
2.02
2.01
2.00
1.82
1.81
1.81
1.79
1.77
1.50
1.49
1.48
1.47
1.47
2.01
4.03
2.02
1.00
2.06
1.00
2.00
2.04
4.02
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

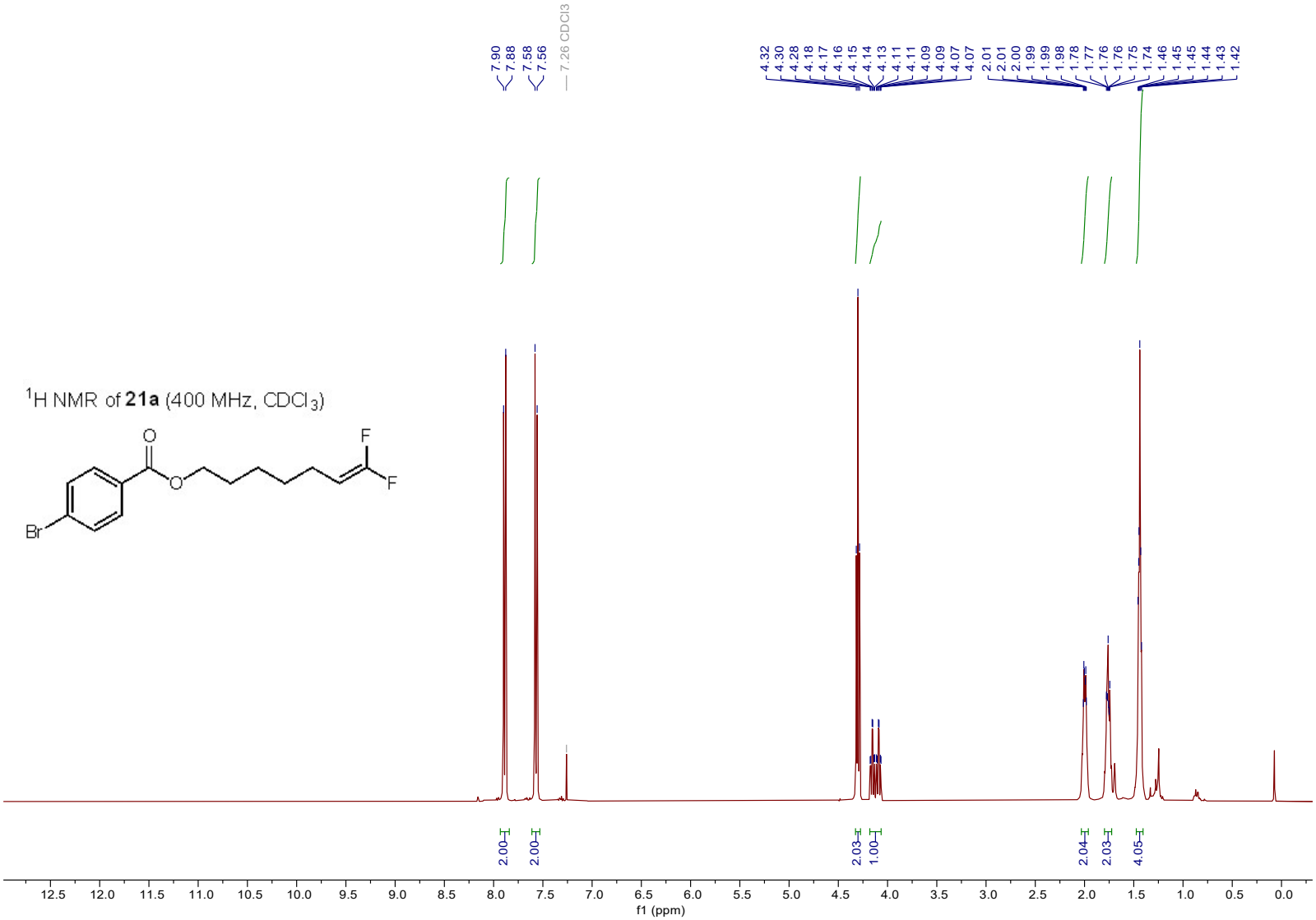

166.66
159.28
156.46
156.44
153.61
145.70
140.14
130.17
129.27
129.04
128.24
127.39
127.15
78.10
77.89
77.67
77.16 CDCl3
65.00
29.18
29.16
29.14
28.56
25.46
22.17
22.13
13C NMR of 19a (101 MHz, CDCl3)
O
O
F
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

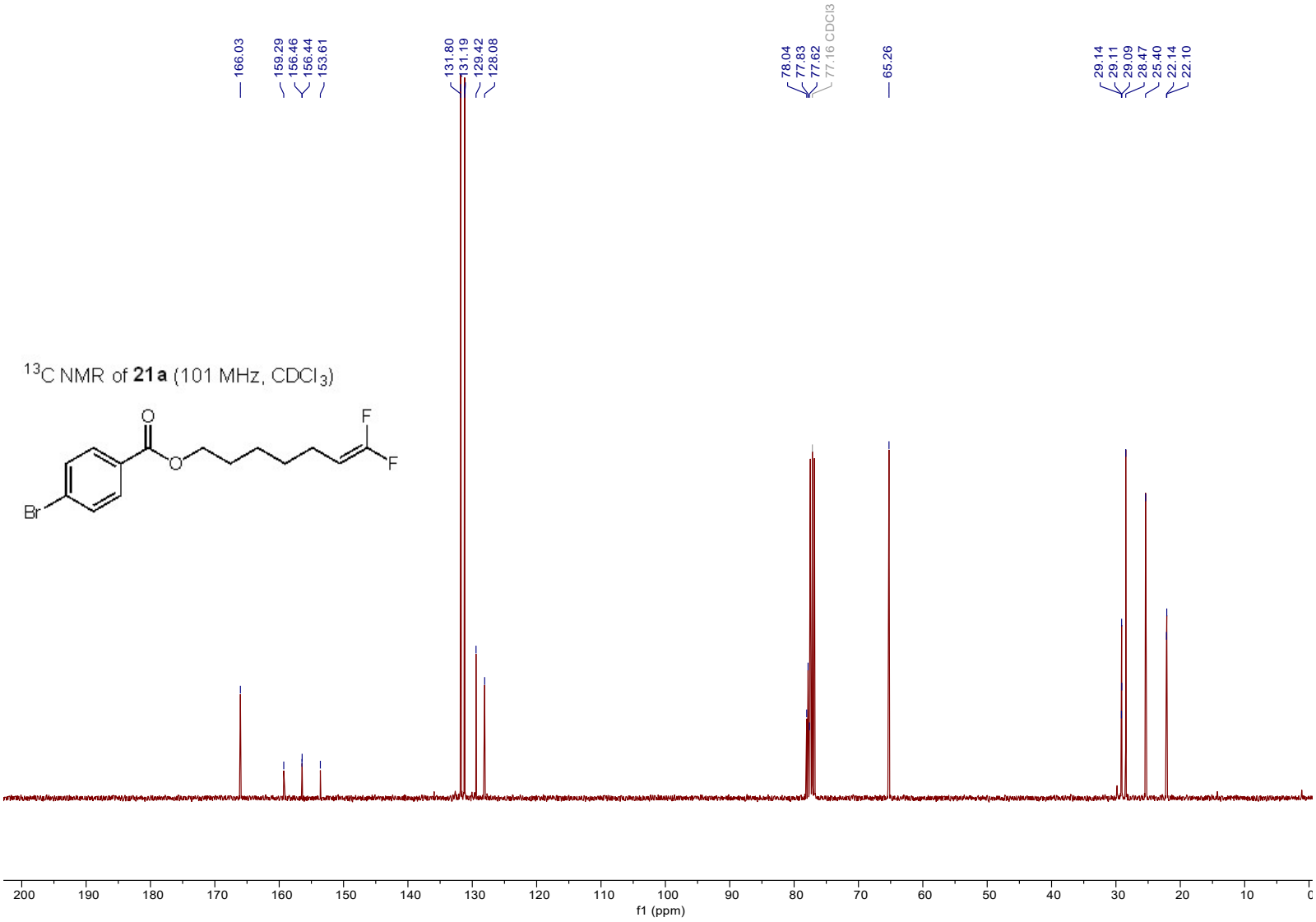

-89.26
-89.39
-91.62
-91.68
-91.75
-91.81
19F NMR of 19a (376 MHz, CDCl3)
O
O
F
F
-89.26
-89.39
-91.62
-91.68
-91.75
-91.81
-88.5 -89.0 -89.5 -90.0 -90.5 -91.0 -91.5 -92.0 -92.5 -93.0
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

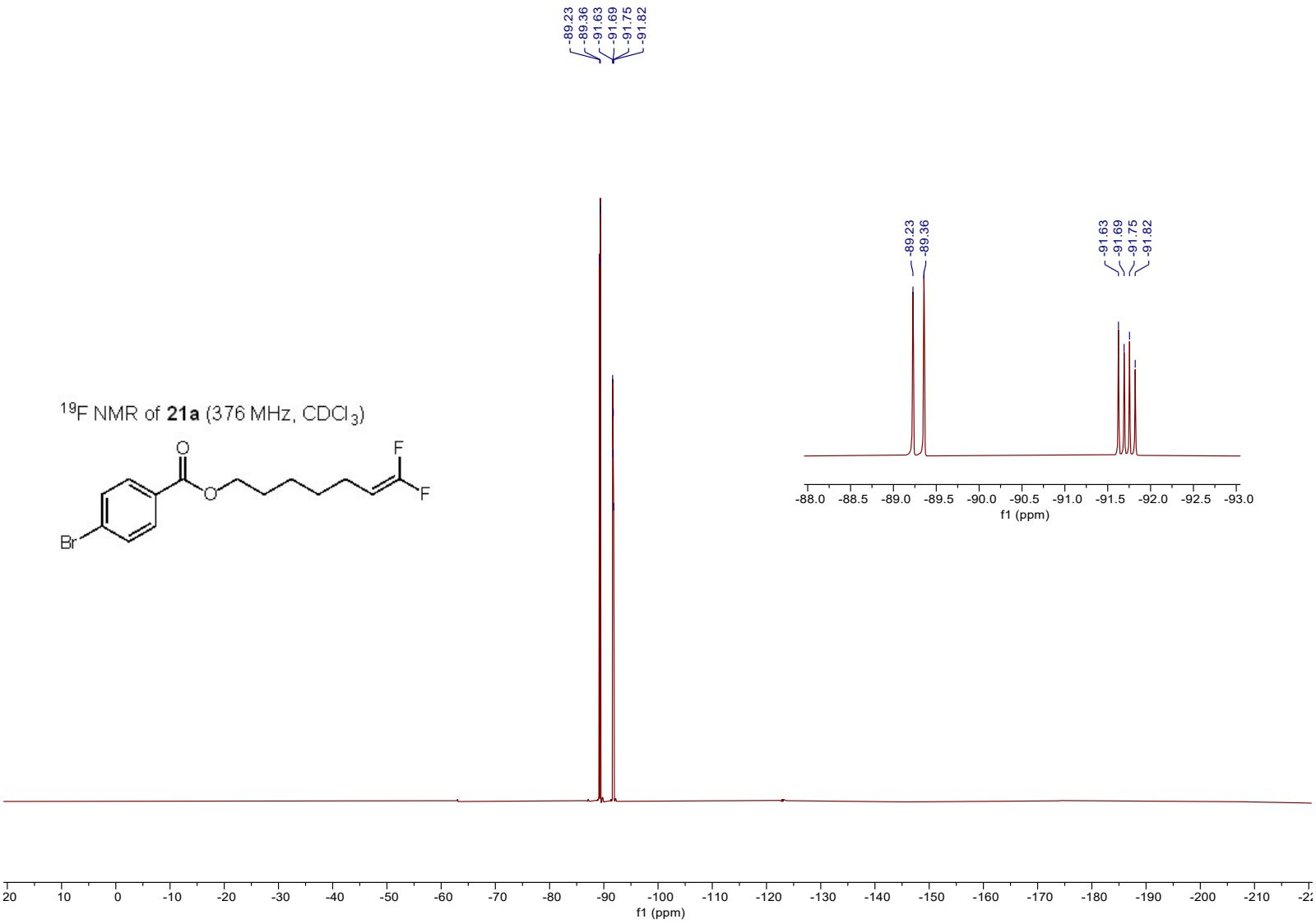

^{1}H NMR of **20a** (400 MHz, $CDCl_3$)
O
O
F
F
Cl
7.97
7.95
7.41
7.39
7.26 CDCl3
4.32
4.30
4.29
4.18
4.17
4.16
4.15
4.14
4.13
4.11
4.11
4.09
4.09
4.07
4.07
2.03
2.02
2.02
2.01
2.01
2.00
1.99
1.99
1.98
1.98
1.98
1.97
1.79
1.78
1.77
1.76
1.76
1.75
1.74
1.74
1.73
1.46
1.45
1.44
1.43
1.42
2.00
2.00
2.03
1.00
2.02
2.03
4.01
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

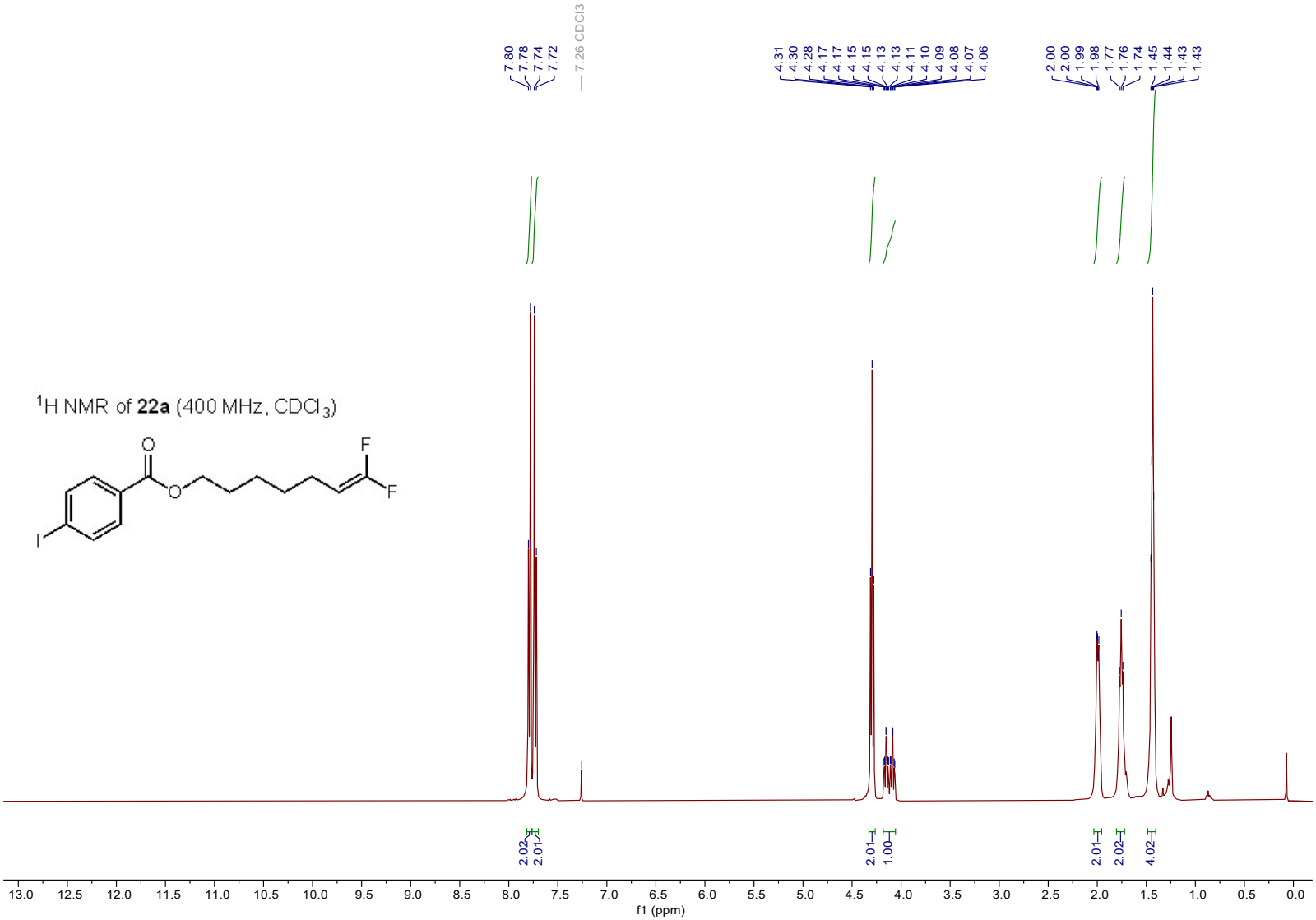

165.91
159.30
156.47
156.45
153.61
139.42
131.05
128.81
78.05
77.84
77.62
77.16 CDCl3
65.24
29.12
28.49
25.41
22.14
22.11
13C NMR of 20a (101 MHz, CDCl3)
O
O
F
F
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

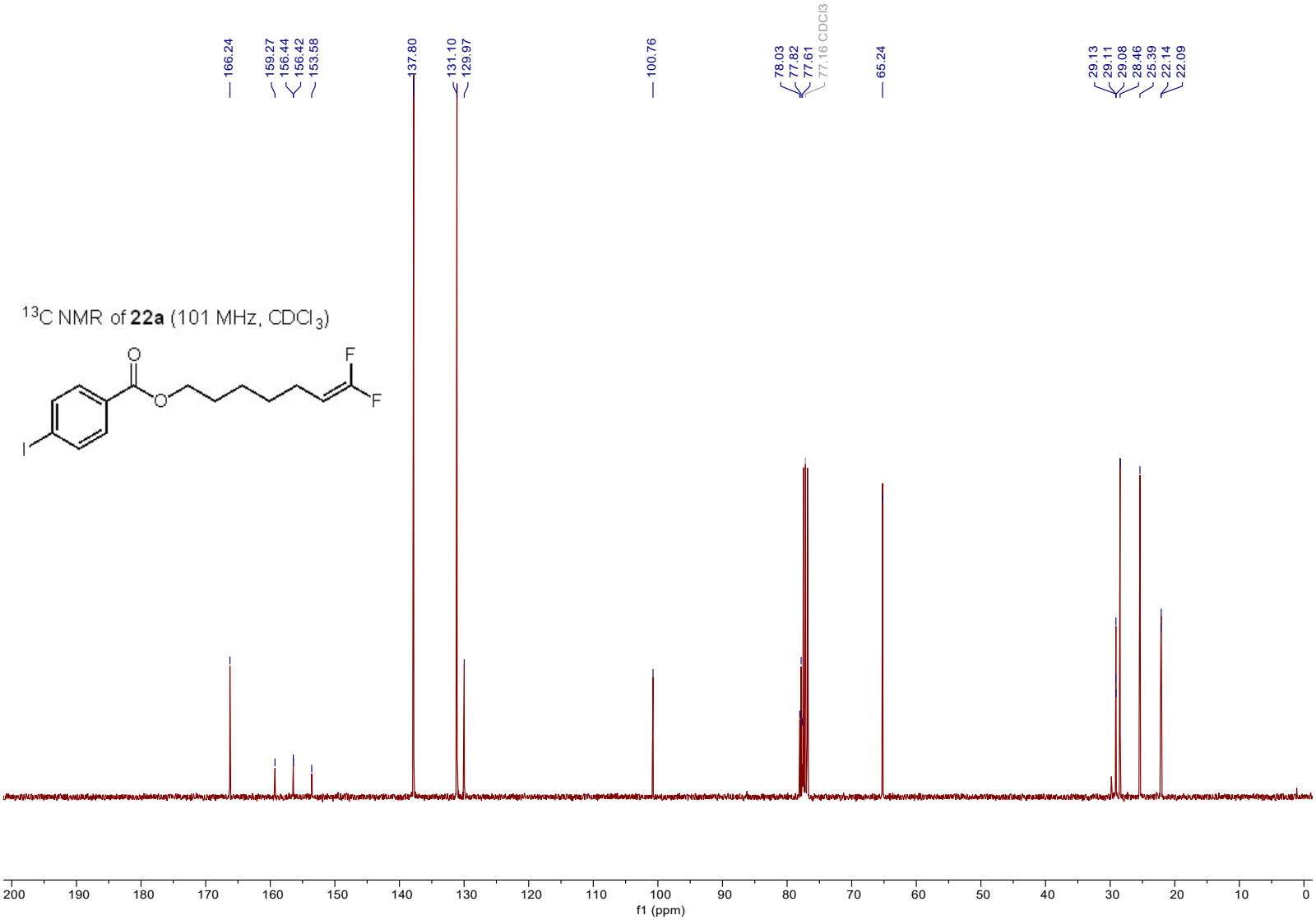

-89.25
-89.38
-91.64
-91.71
-91.77
-91.84
19F NMR of 20a (376 MHz, CDCl3)
O
O
F
F
Cl
-89.25
-89.38
-91.64
-91.71
-91.77
-91.84
-88
-89
-90
-91
-92
-93
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

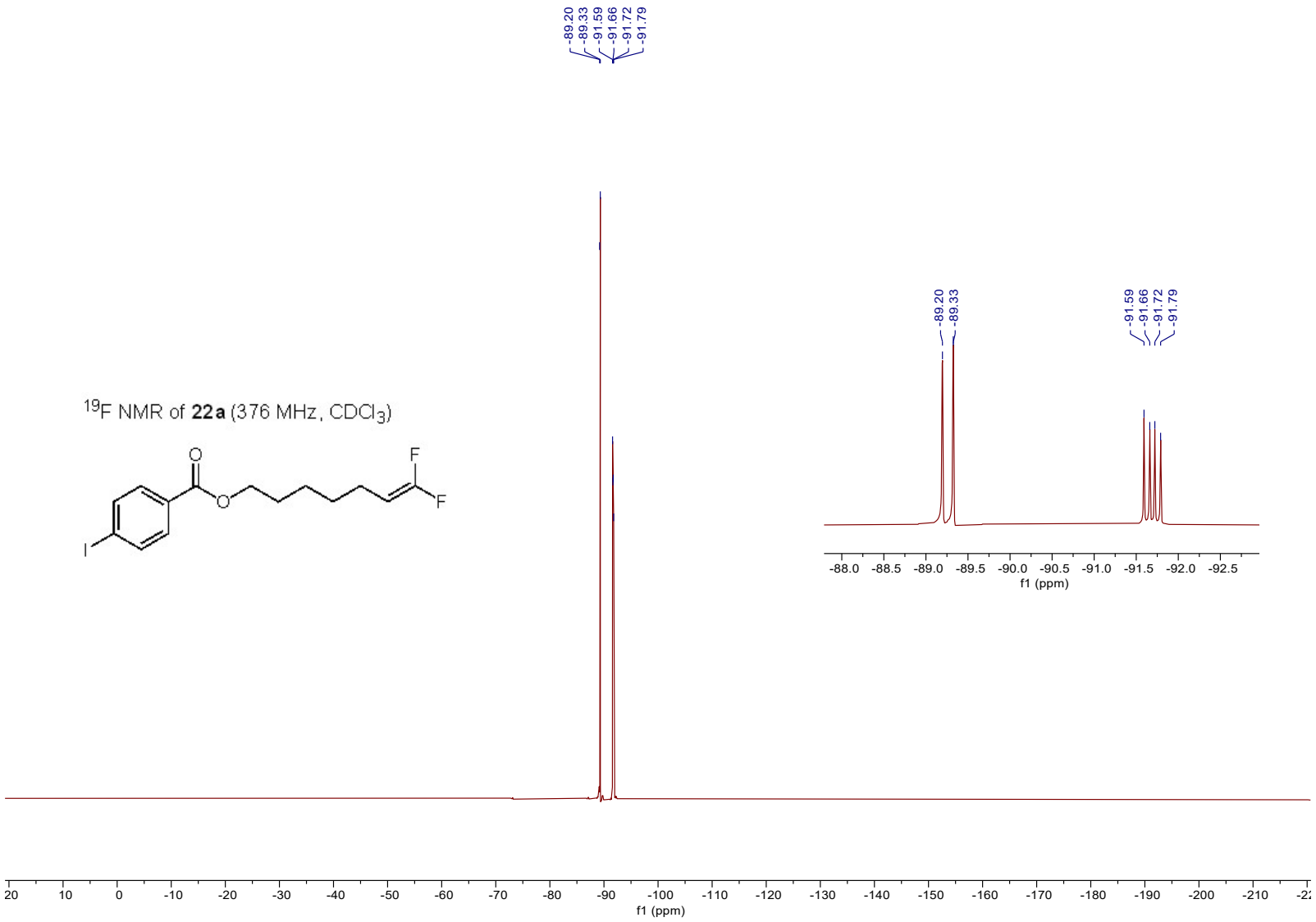

^{1}H NMR of **21a** (400 MHz, $CDCl_3$)
O
F
O
F
Br
7.90
7.88
7.58
7.56
7.26 CDCl3
4.32
4.30
4.28
4.18
4.17
4.16
4.15
4.14
4.13
4.11
4.11
4.09
4.09
4.07
4.07
2.01
2.01
2.00
1.99
1.99
1.98
1.78
1.77
1.76
1.76
1.75
1.74
1.46
1.45
1.45
1.44
1.43
1.42
2.00
2.00
2.03
1.00
2.04
2.03
4.05
12.5 12.0 11.5 11.0 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
f1 (ppm)

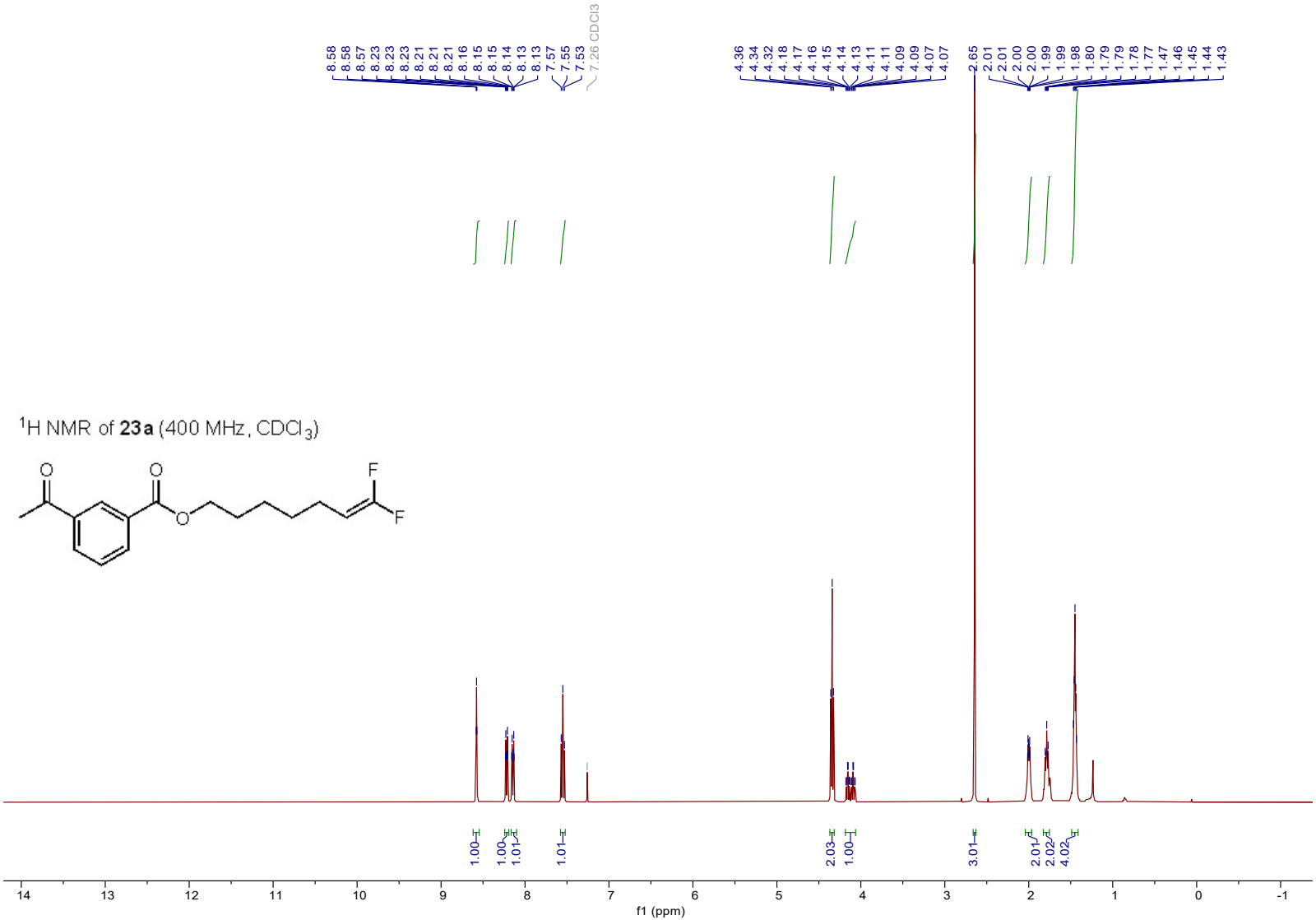

166.03
159.29
156.46
156.44
153.61
131.80
131.19
129.42
128.08
78.04
77.83
77.62
77.16 CDCl3
65.26
29.14
29.11
29.09
28.47
25.40
22.14
22.10
13C NMR of 21a (101 MHz, CDCl3)
O
O
F
F
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

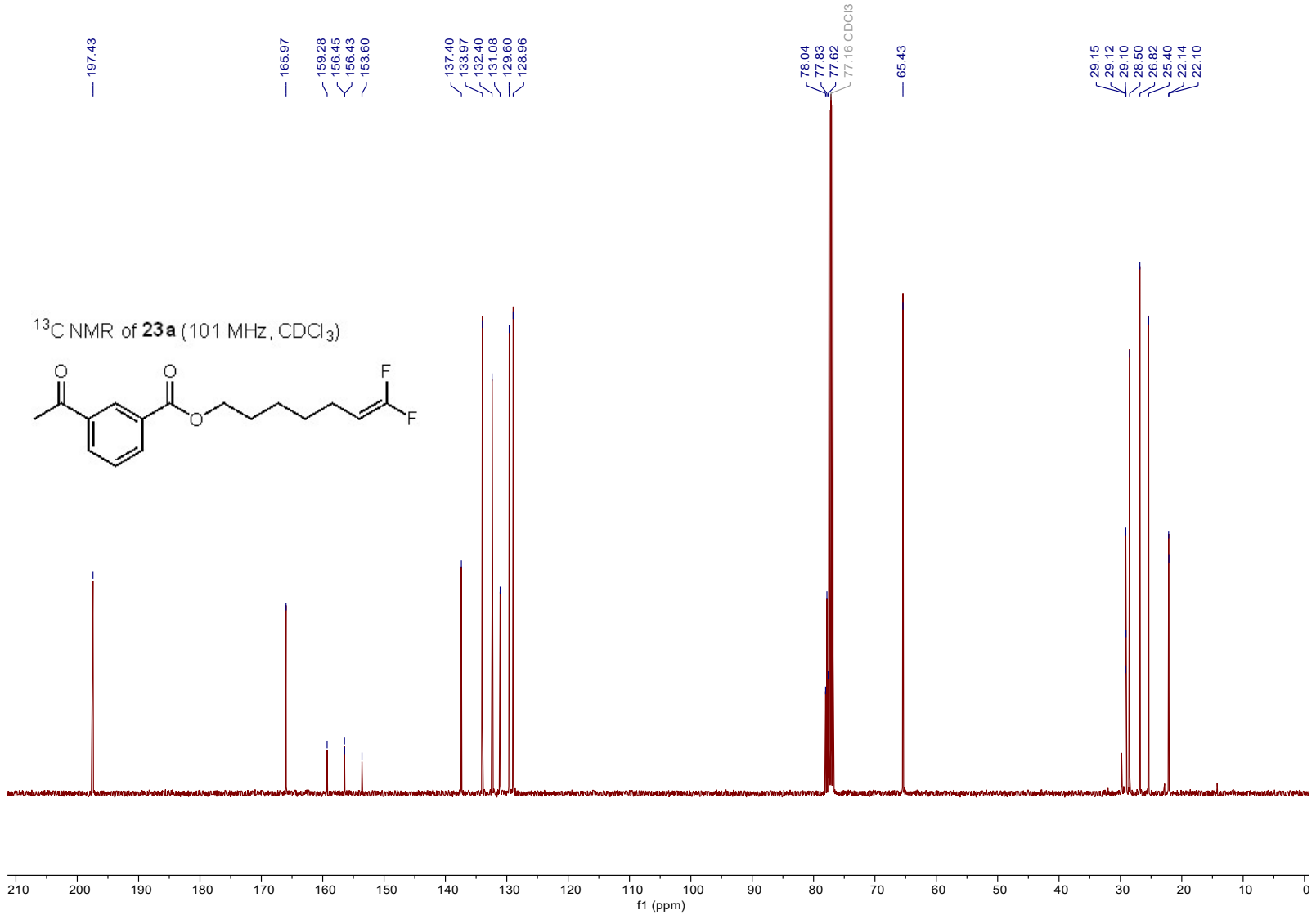

-89.23
-89.36
-91.63
-91.69
-91.75
-91.82
^{19}F NMR of **21a** (376 MHz, $CDCl_3$)
O
O
F
F
Br
-89.23
-89.36
-91.63
-91.69
-91.75
-91.82
-88.0 -88.5 -89.0 -89.5 -90.0 -90.5 -91.0 -91.5 -92.0 -92.5 -93.0
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

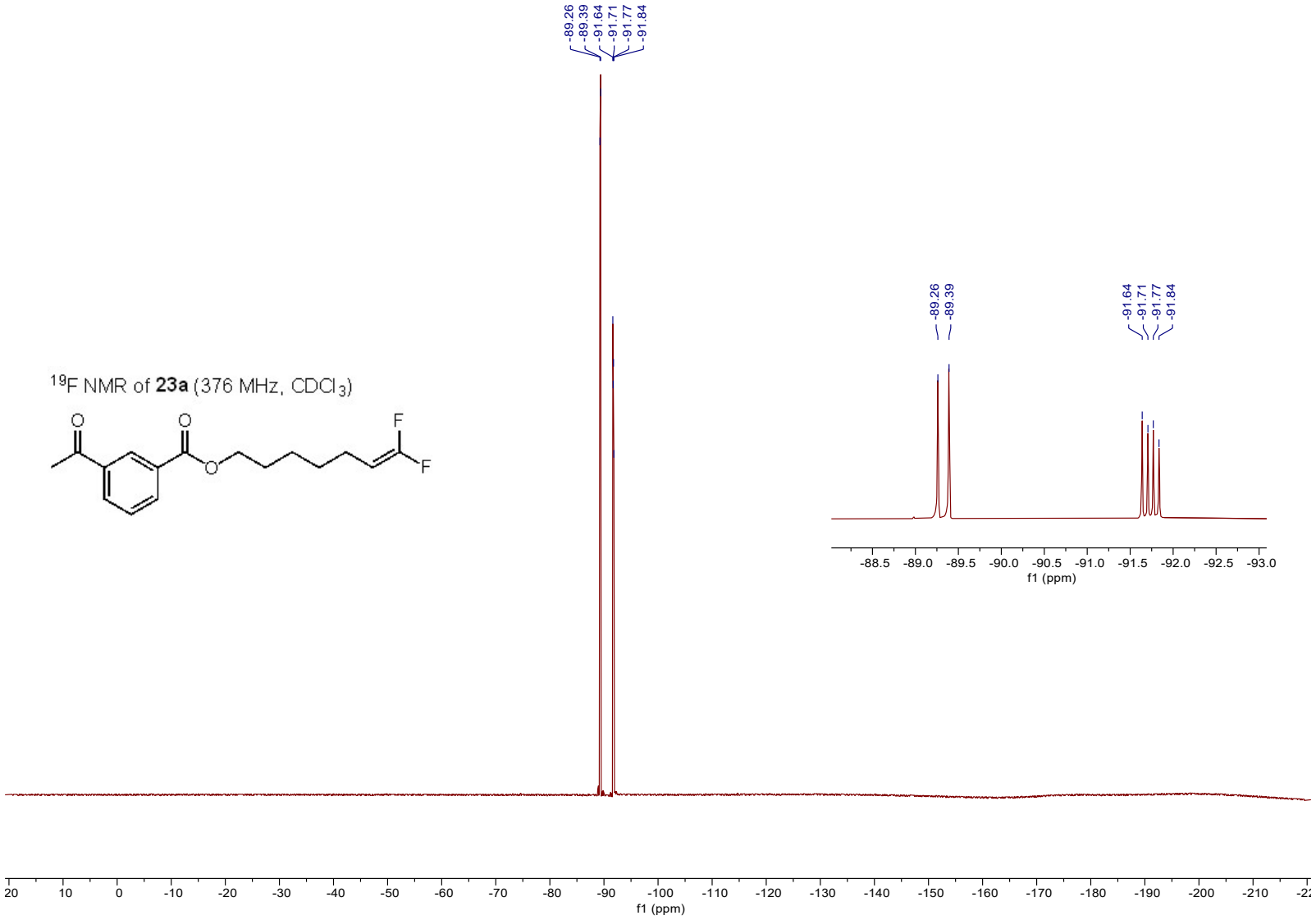

^{1}H NMR of **22a** (400 MHz, $CDCl_3$)
7.80
7.78
7.74
7.72
7.26 CDCl3
4.31
4.30
4.28
4.17
4.17
4.15
4.15
4.13
4.13
4.11
4.10
4.09
4.08
4.07
4.06
2.00
2.00
1.99
1.98
1.77
1.76
1.74
1.45
1.44
1.43
1.43
2.02
2.01
2.01
1.00
2.01
2.02
4.02
f1 (ppm)

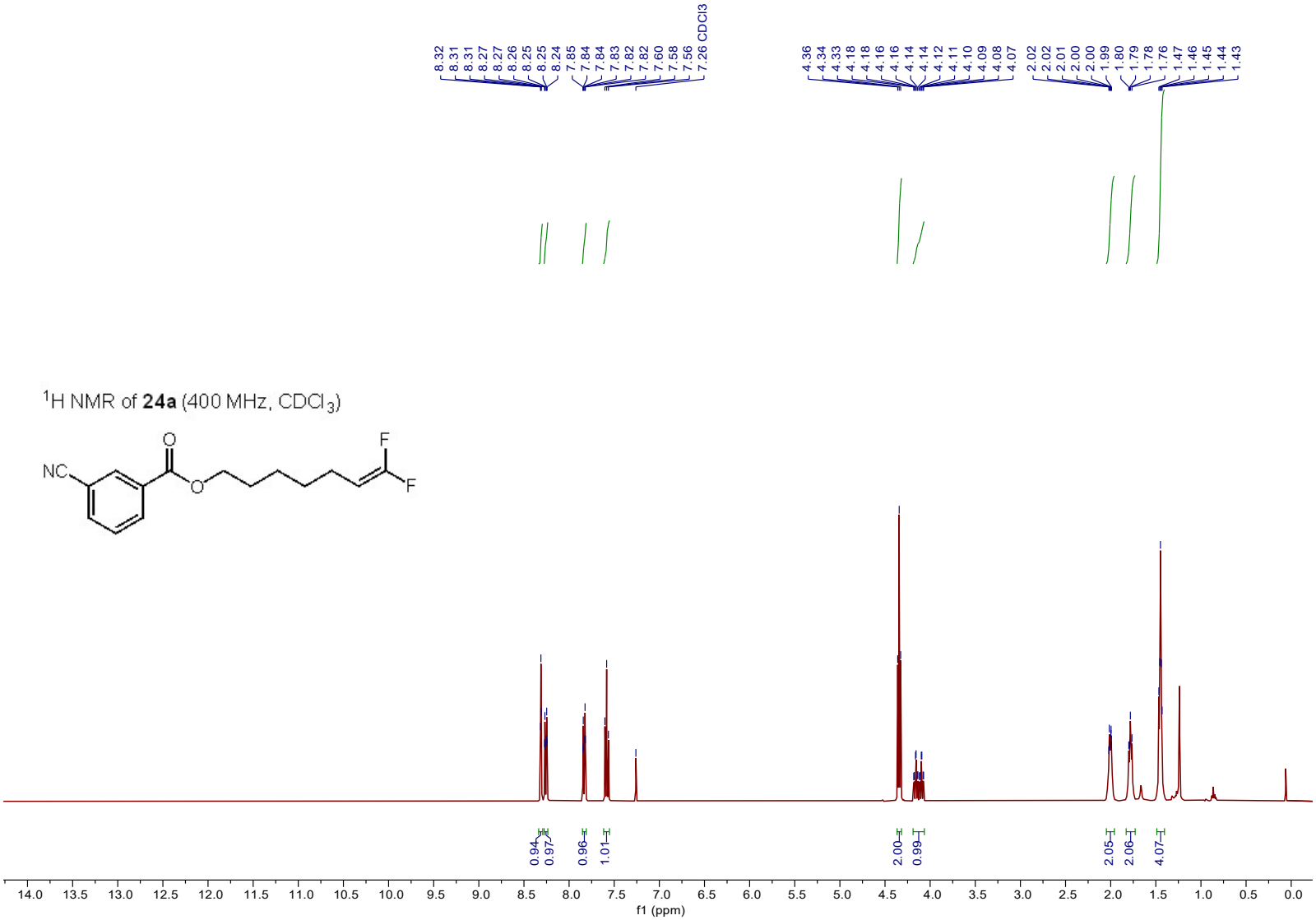

166.24
159.27
156.44
156.42
153.58
137.80
131.10
129.97
100.76
78.03
77.82
77.61
77.16 CDCl3
65.24
29.13
29.11
29.08
28.46
25.39
22.14
22.09
13C NMR of 22a (101 MHz, CDCl3)
O
O
F
F
I
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

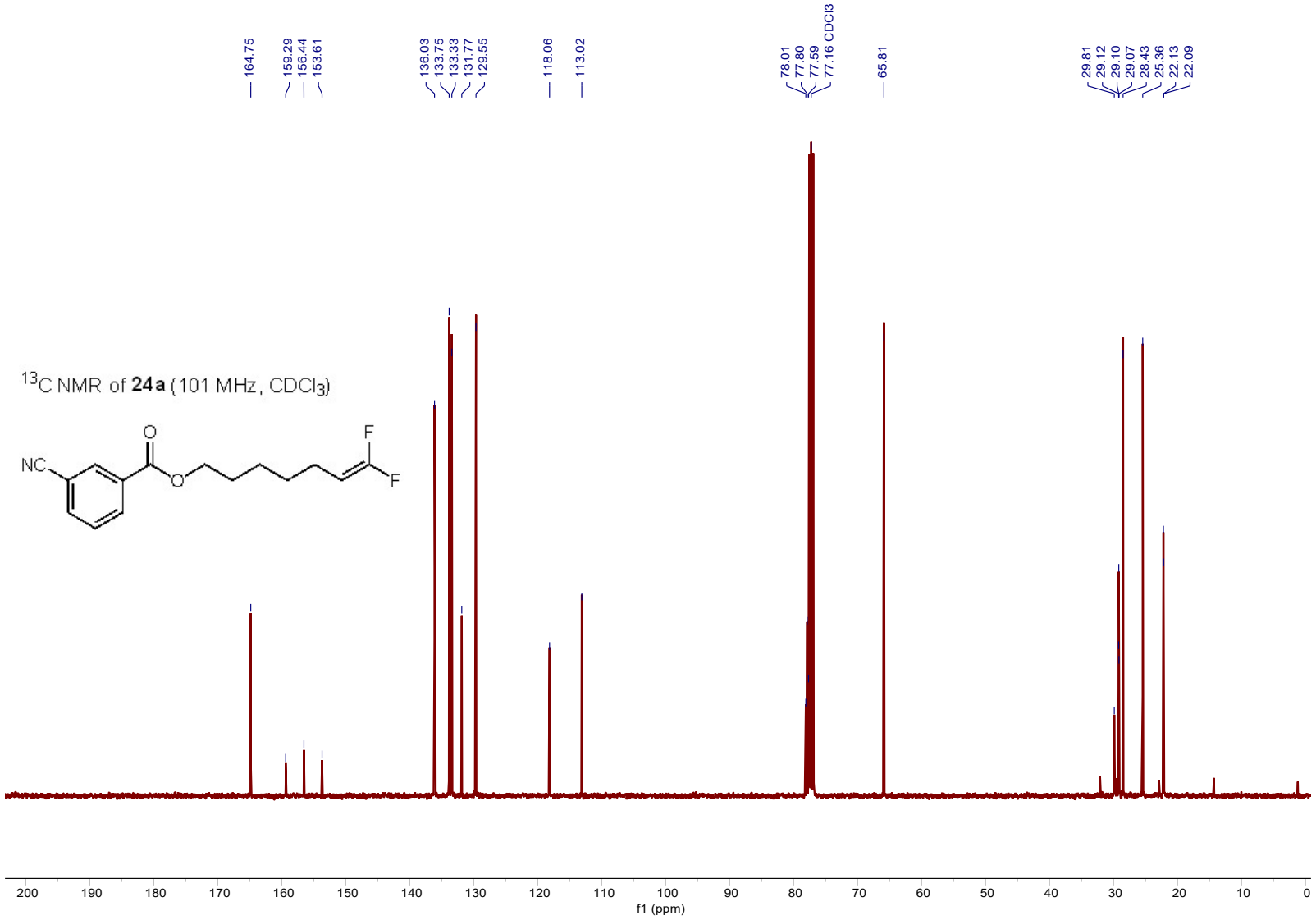

-89.20
-89.33
-91.59
-91.66
-91.72
-91.79
19F NMR of 22a (376 MHz, CDCl3)
O
O
F
F
I
-89.20
-89.33
-91.59
-91.66
-91.72
-91.79
-88.0 -88.5 -89.0 -89.5 -90.0 -90.5 -91.0 -91.5 -92.0 -92.5
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

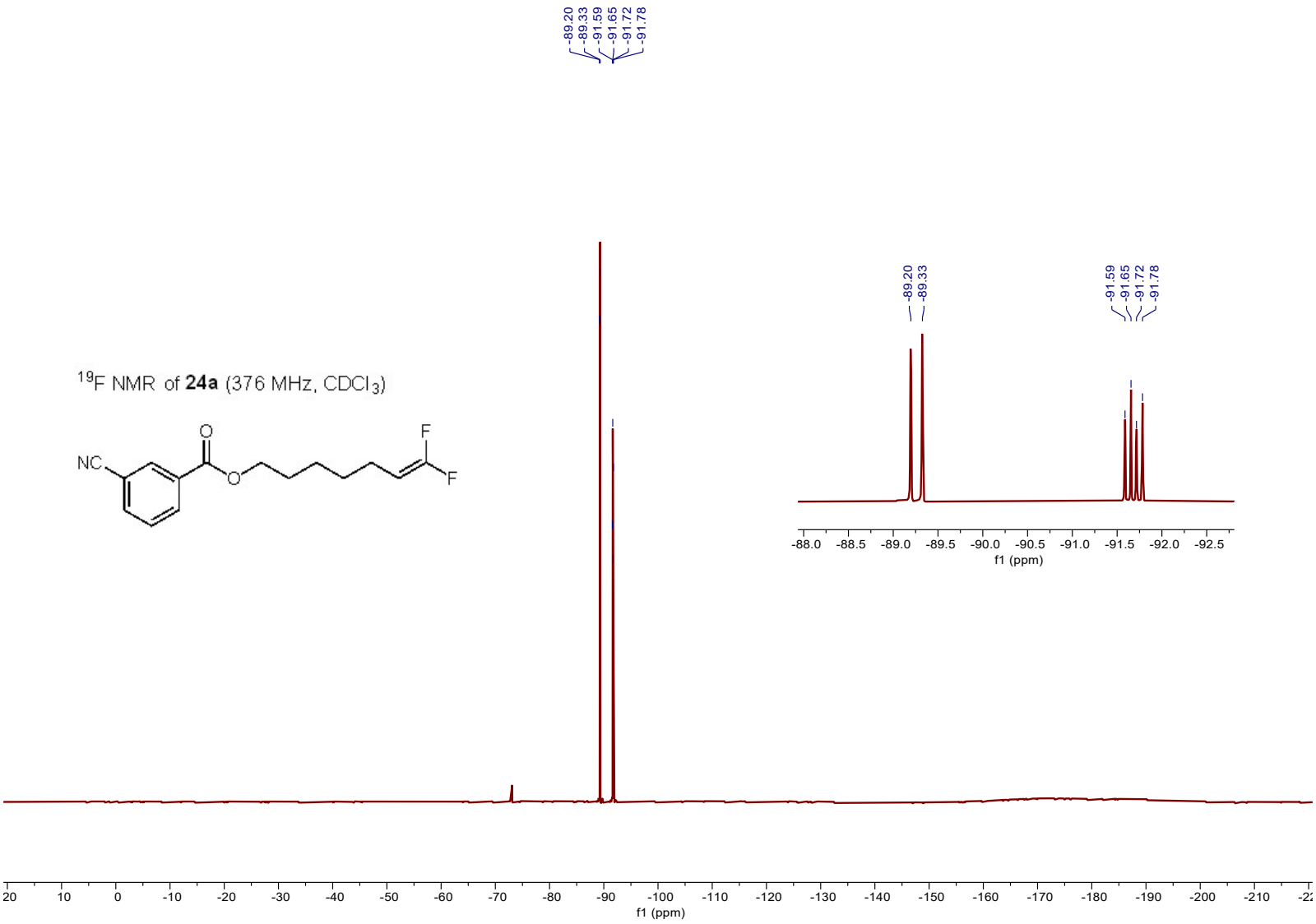

8.58
8.58
8.57
8.23
8.23
8.23
8.21
8.21
8.21
8.16
8.15
8.15
8.14
8.13
8.13
7.57
7.55
7.53
7.26 CDCl3
4.36
4.34
4.32
4.18
4.17
4.16
4.15
4.14
4.13
4.11
4.11
4.09
4.09
4.07
4.07
2.65
2.01
2.01
2.00
2.00
1.99
1.99
1.98
1.80
1.79
1.79
1.78
1.77
1.47
1.46
1.45
1.44
1.43
1H NMR of 23a (400 MHz, CDCl3)
O
O
O
F
F
1.00
1.00
1.01
1.01
2.03
1.00
3.01
2.01
2.02
4.02
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

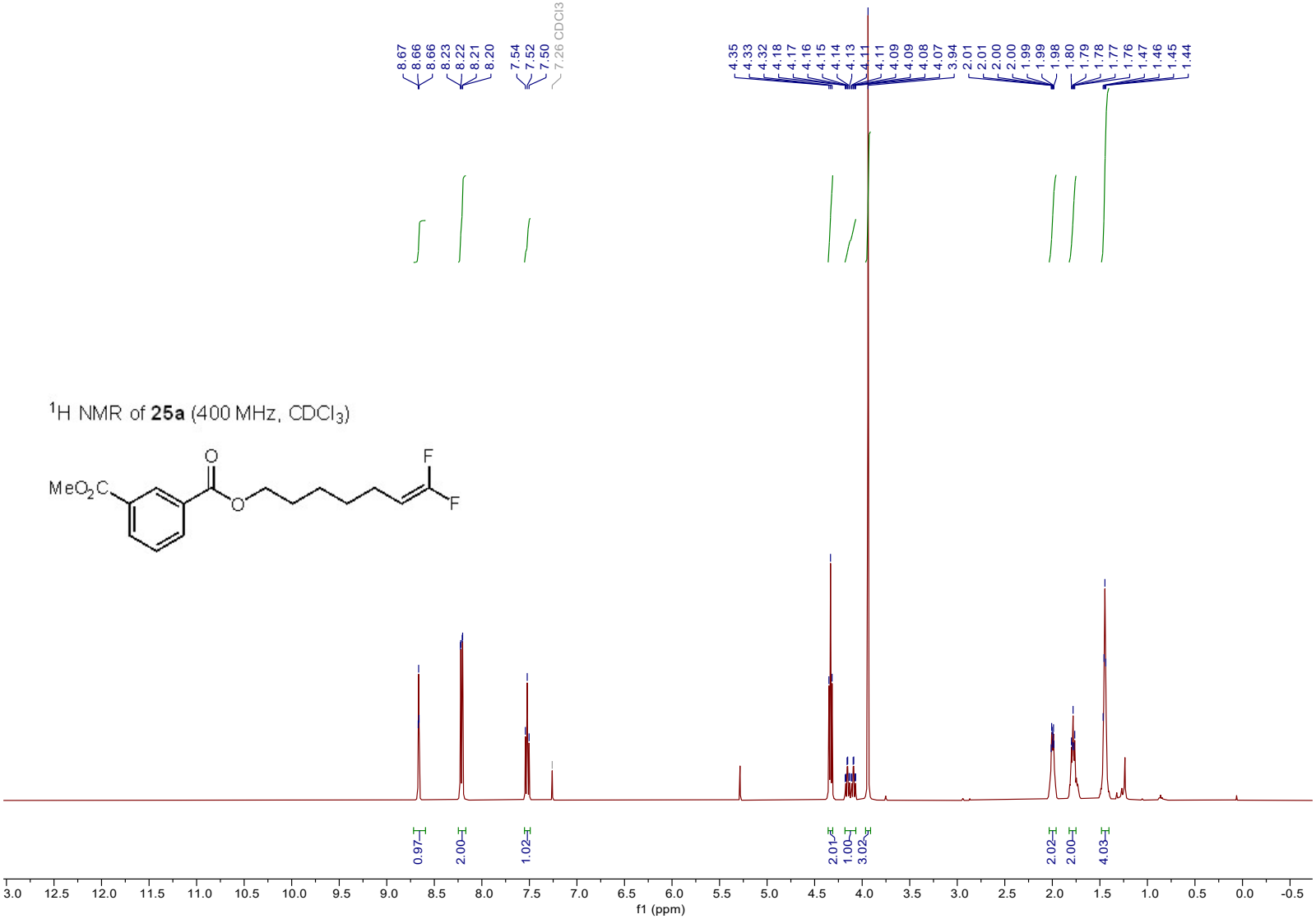

197.43
165.97
159.28
156.45
156.43
153.60
137.40
133.97
132.40
131.08
129.60
128.96
78.04
77.83
77.62
77.16 CDCl3
65.43
29.15
29.12
29.10
28.50
26.82
25.40
22.14
22.10
13C NMR of 23a (101 MHz, CDCl3)
O
O
F
O
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-89.26
-89.39
-91.64
-91.71
-91.77
-91.84
19F NMR of 23a (376 MHz, CDCl3)
O
O
F
F
O
-89.26
-89.39
-91.64
-91.71
-91.77
-91.84
-88.5 -89.0 -89.5 -90.0 -90.5 -91.0 -91.5 -92.0 -92.5 -93.0
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

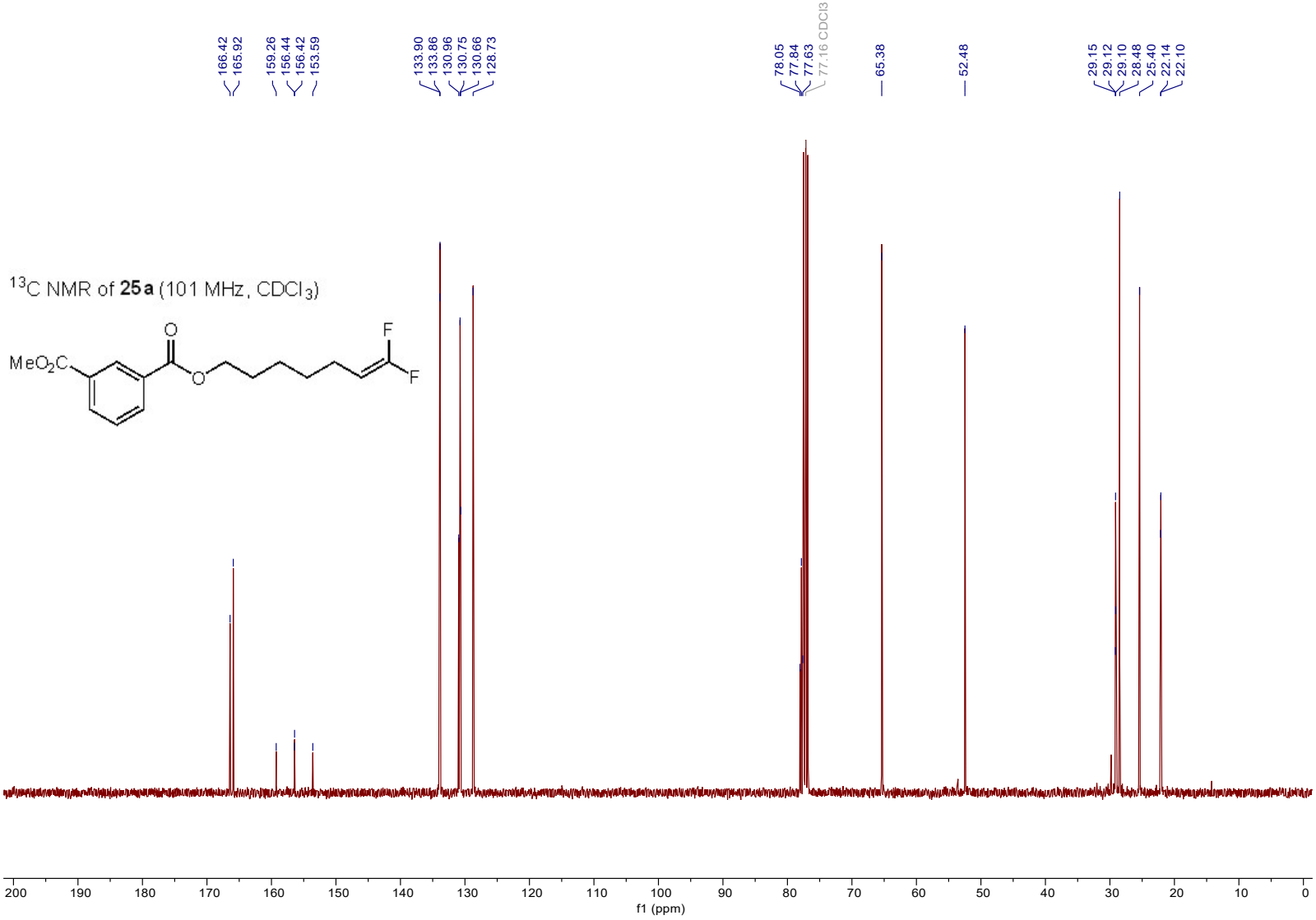

8.32
8.31
8.31
8.27
8.27
8.26
8.25
8.25
8.24
7.85
7.84
7.84
7.83
7.82
7.82
7.60
7.58
7.56
7.26 CDCl3
4.36
4.34
4.33
4.18
4.18
4.16
4.16
4.14
4.14
4.12
4.11
4.10
4.09
4.08
4.07
2.02
2.02
2.01
2.00
2.00
1.99
1.80
1.79
1.78
1.76
1.47
1.46
1.45
1.44
1.43
^{1}H NMR of **24a** (400 MHz, $CDCl_3$)
NC
O
O
F
F
0.94
0.97
0.96
1.01
2.00
0.99
2.05
2.06
4.07
14.0 13.5 13.0 12.5 12.0 11.5 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
f1 (ppm)

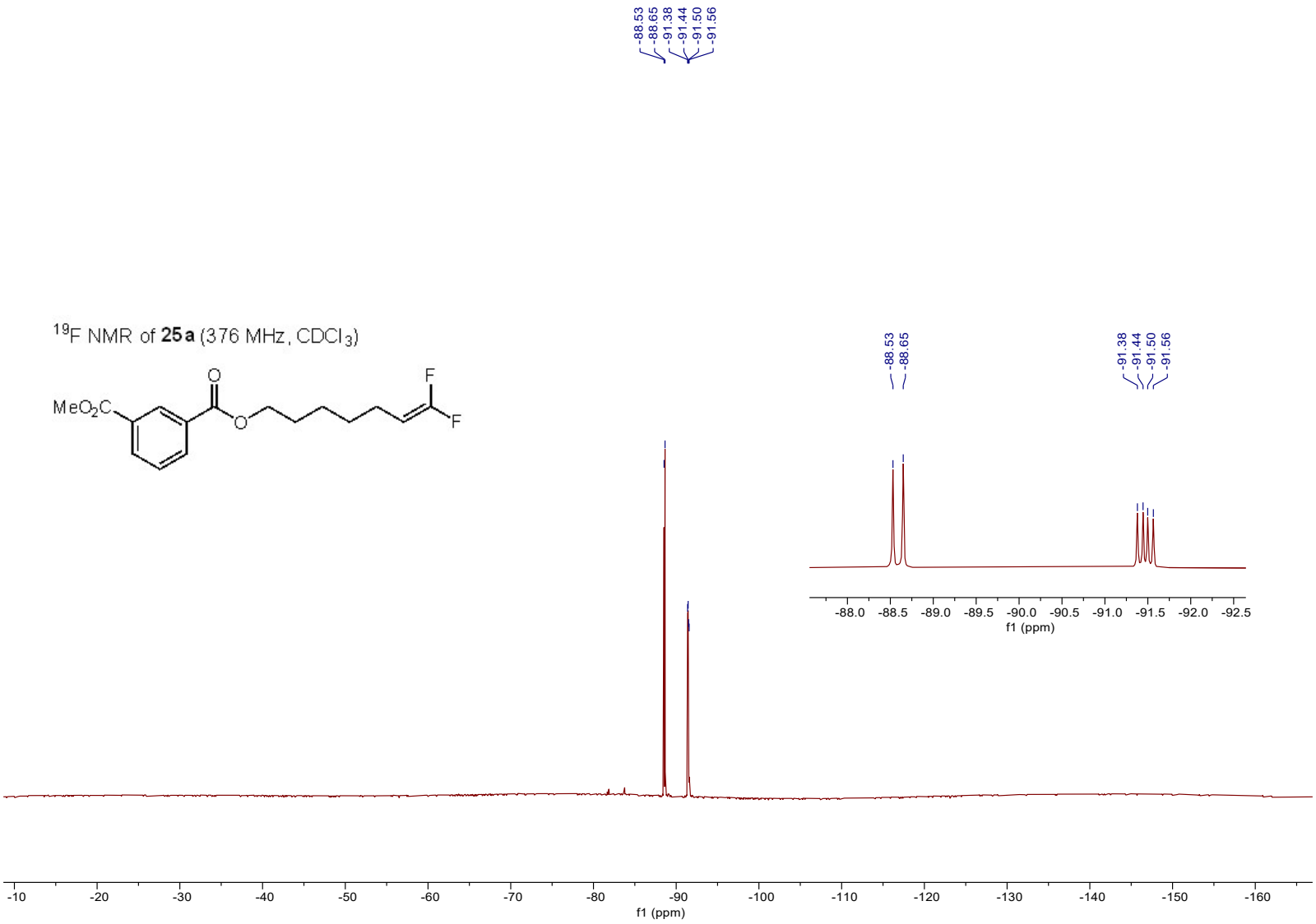

164.75
159.29
156.44
153.61
136.03
133.75
133.33
131.77
129.55
118.06
113.02
78.01
77.80
77.59
77.16 CDCl3
65.81
29.81
29.12
29.10
29.07
28.43
25.36
22.13
22.09
13C NMR of 24a (101 MHz, CDCl3)
NC
O
O
F
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

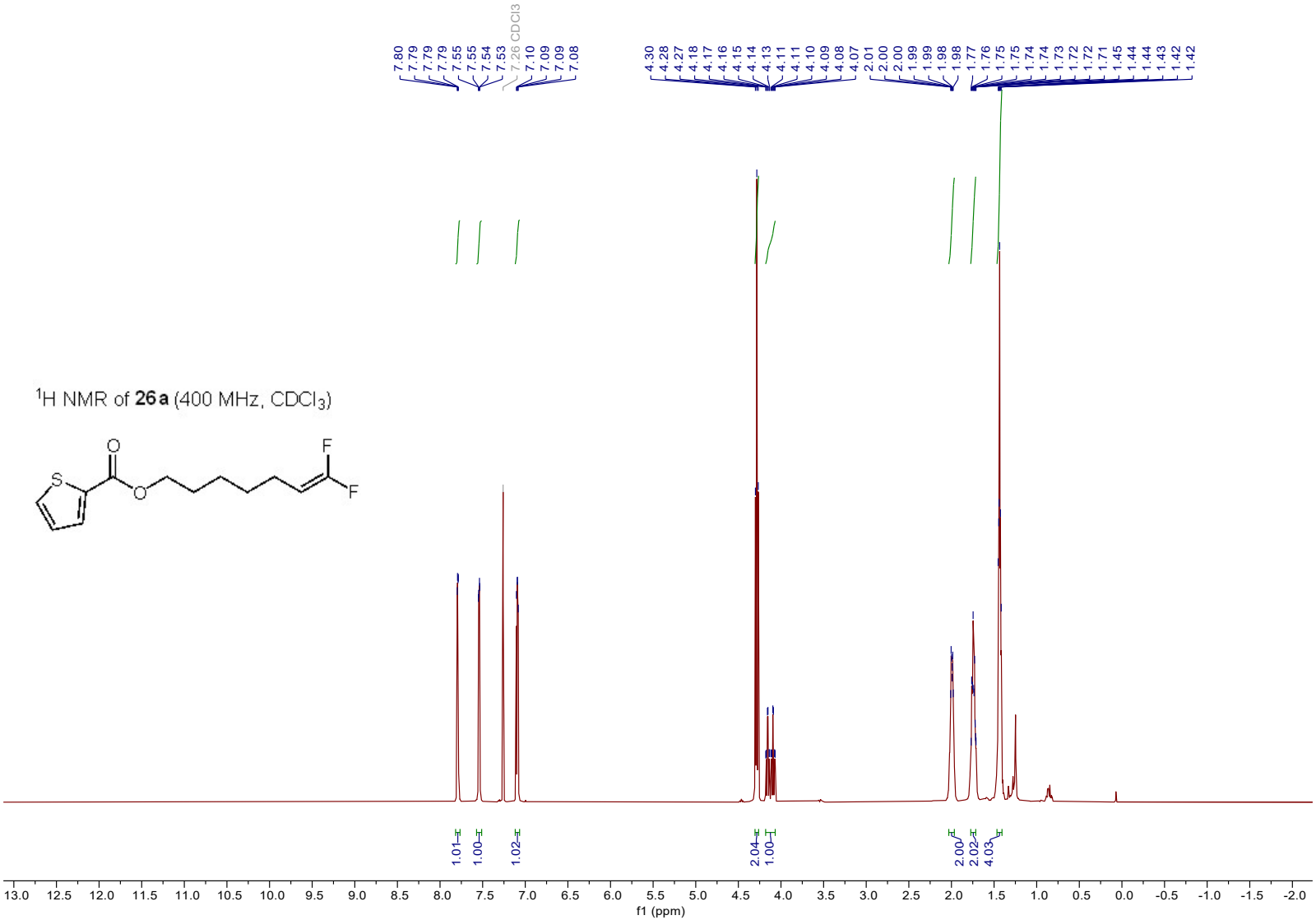

-89.20
-89.33
-91.59
-91.65
-91.72
-91.78
19F NMR of 24a (376 MHz, CDCl3)
NC
O
O
F
F
-89.20
-89.33
-91.59
-91.65
-91.72
-91.78
-88.0 -88.5 -89.0 -89.5 -90.0 -90.5 -91.0 -91.5 -92.0 -92.5
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

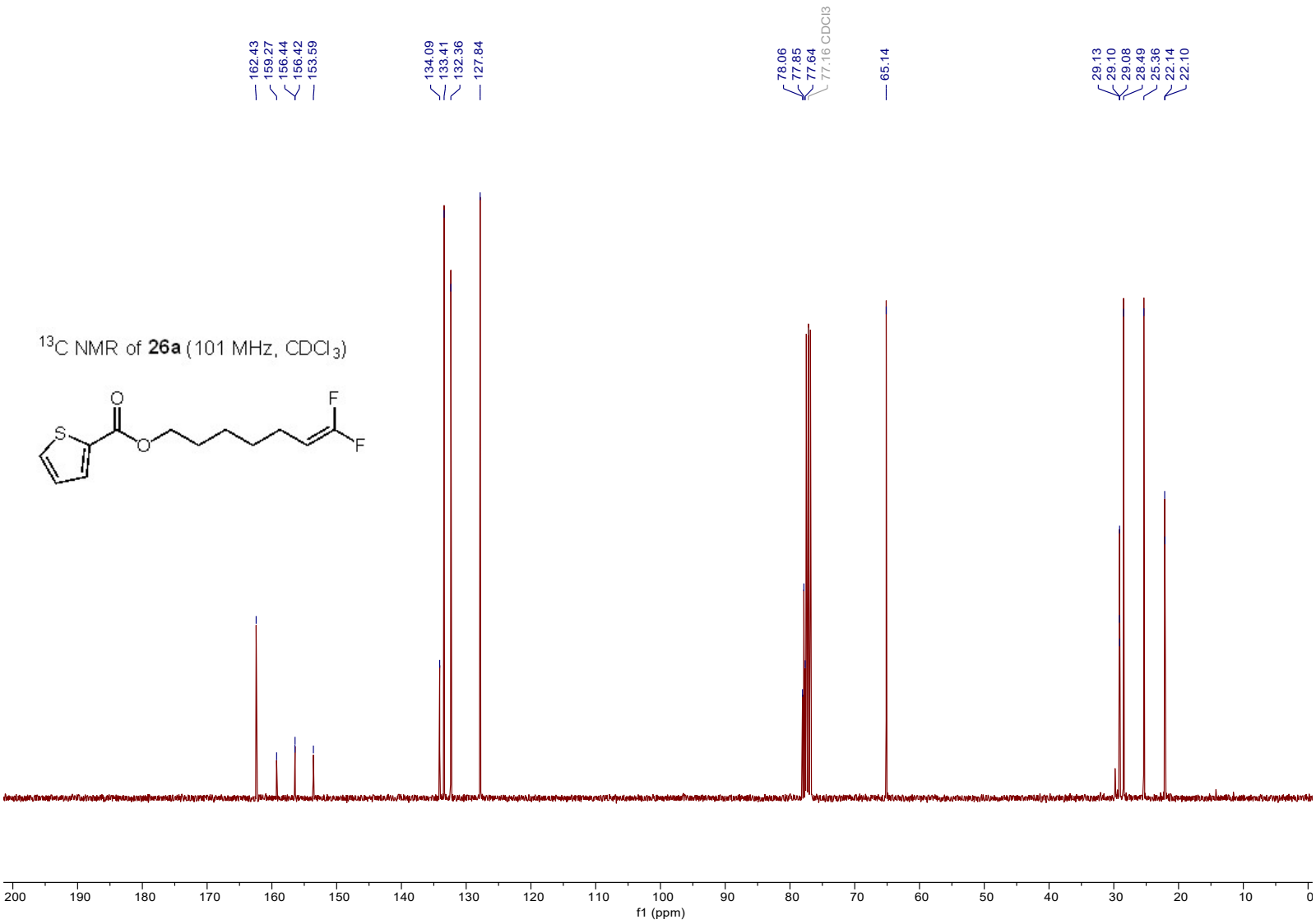


^{1}H NMR of **25a** (400 MHz, $CDCl_3$)

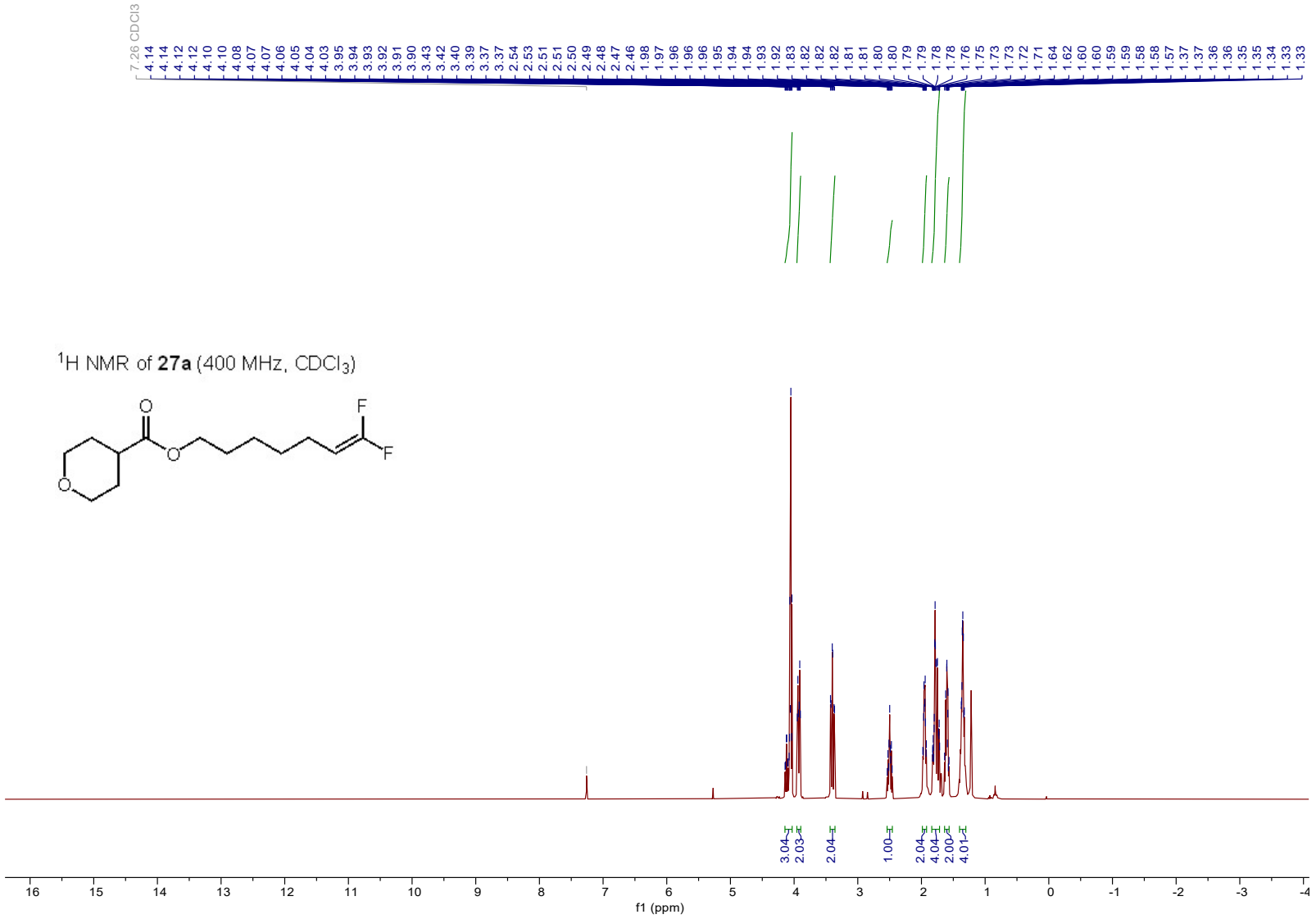

166.42
165.92
159.26
156.44
156.42
153.59
133.90
133.86
130.96
130.75
130.66
128.73
78.05
77.84
77.63
77.16 CDCl3
65.38
52.48
29.15
29.12
29.10
28.48
25.40
22.14
22.10
13C NMR of 25a (101 MHz, CDCl3)
MeO2C
O
O
F
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

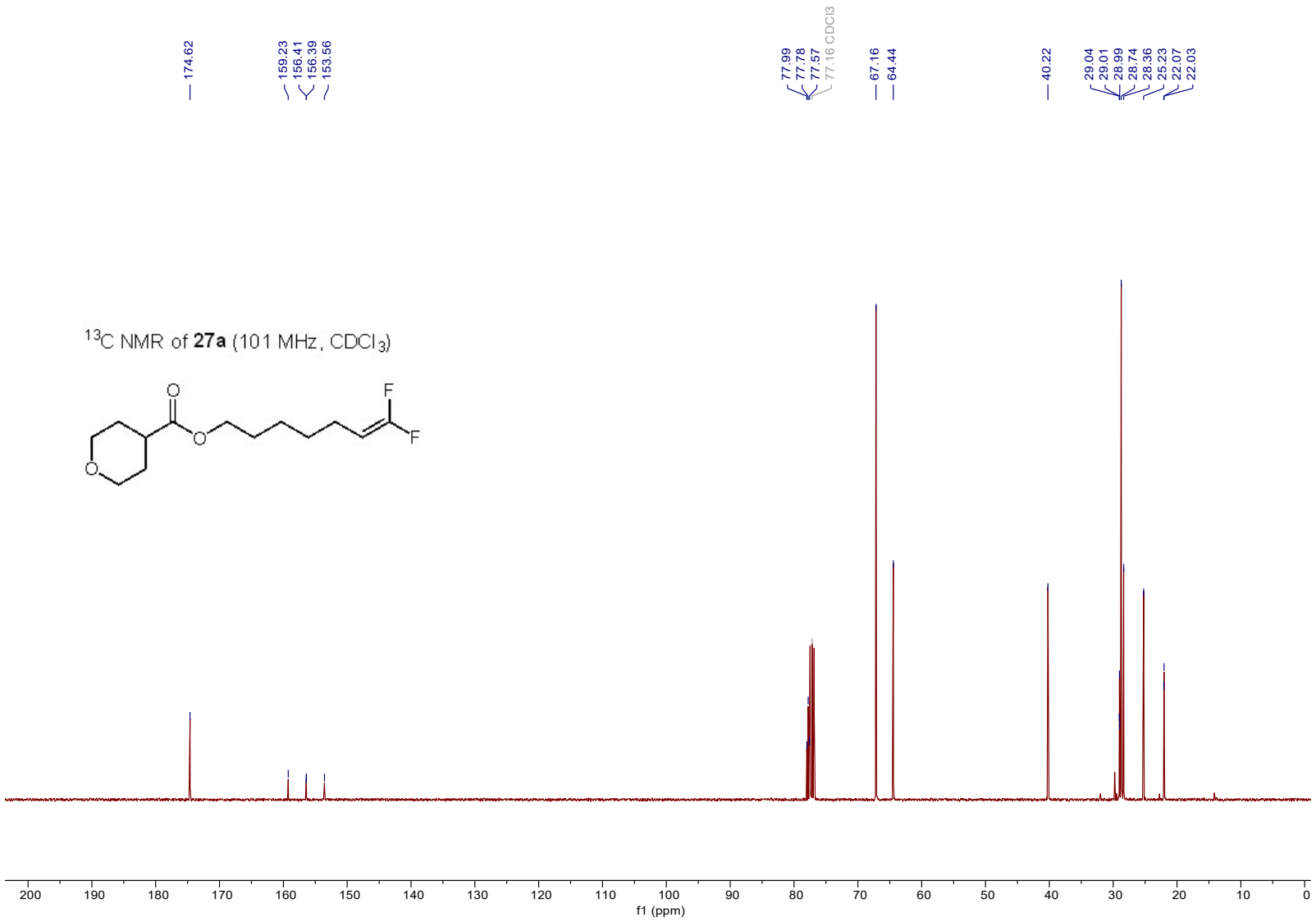

-88.53
-88.65
-91.38
-91.44
-91.50
-91.56
19F NMR of 25a (376 MHz, CDCl3)
MeO2C
O
O
F
F
-88.53
-88.65
-91.38
-91.44
-91.50
-91.56
-88.0 -88.5 -89.0 -89.5 -90.0 -90.5 -91.0 -91.5 -92.0 -92.5
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

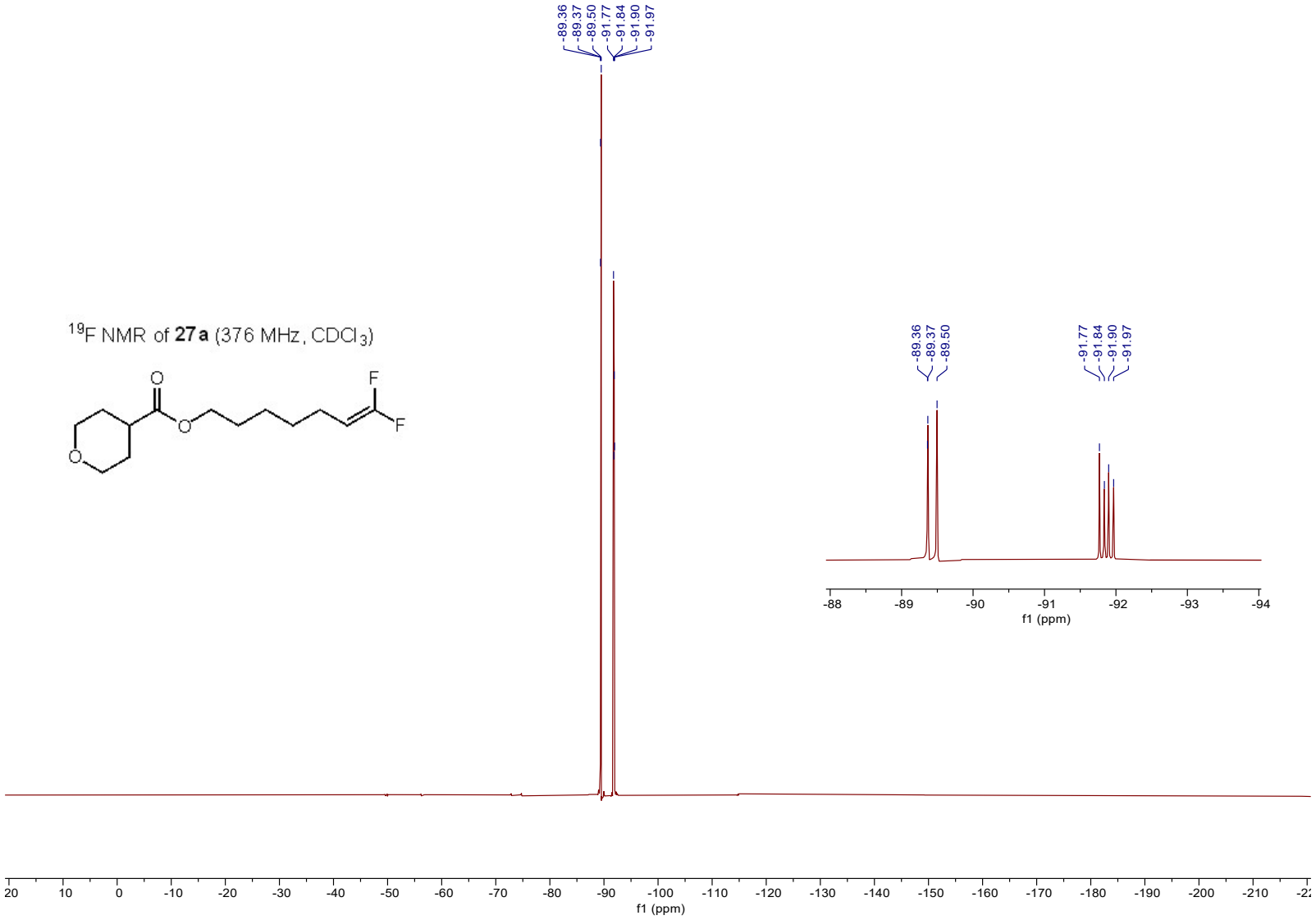

^{1}H NMR of **26a** (400 MHz, $CDCl_3$)
O
F
S
O
F
7.80
7.79
7.79
7.79
7.55
7.55
7.54
7.53
7.26 CDCl3
7.10
7.09
7.09
7.08
4.30
4.28
4.27
4.18
4.17
4.16
4.15
4.14
4.13
4.11
4.11
4.10
4.09
4.08
4.07
2.01
2.00
2.00
1.99
1.99
1.98
1.98
1.77
1.76
1.75
1.75
1.74
1.74
1.73
1.72
1.72
1.71
1.45
1.44
1.44
1.43
1.42
1.42
1.01
1.00
1.02
2.04
1.00
2.00
2.02
4.03
13.0 12.5 12.0 11.5 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 -1.0 -1.5 -2.0
f1 (ppm)

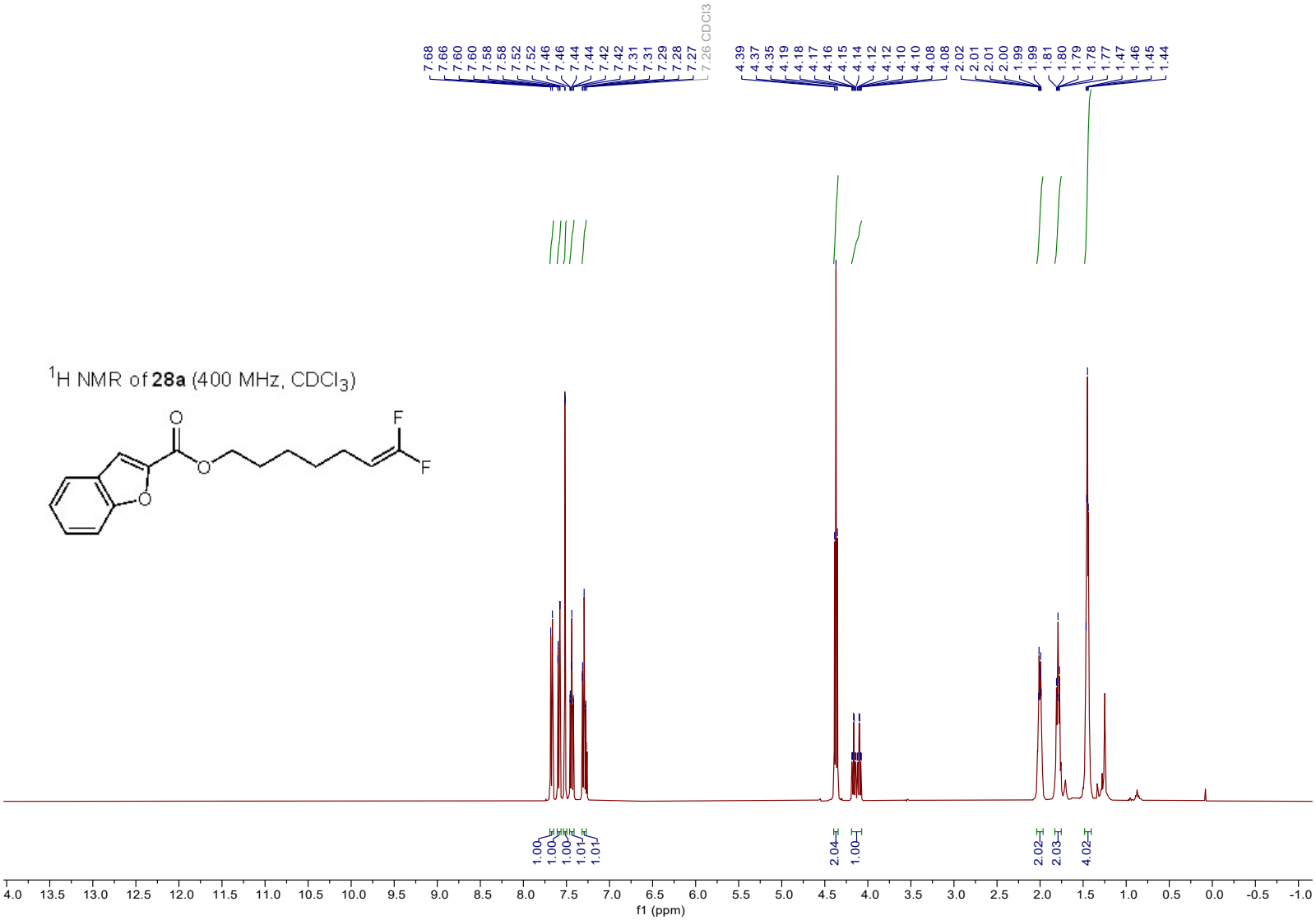

162.43
159.27
156.44
156.42
153.59
134.09
133.41
132.36
127.84
78.06
77.85
77.64
77.16 CDCl3
65.14
29.13
29.10
29.08
28.49
25.36
22.14
22.10
13C NMR of 26a (101 MHz, CDCl3)
O
F
S
O
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

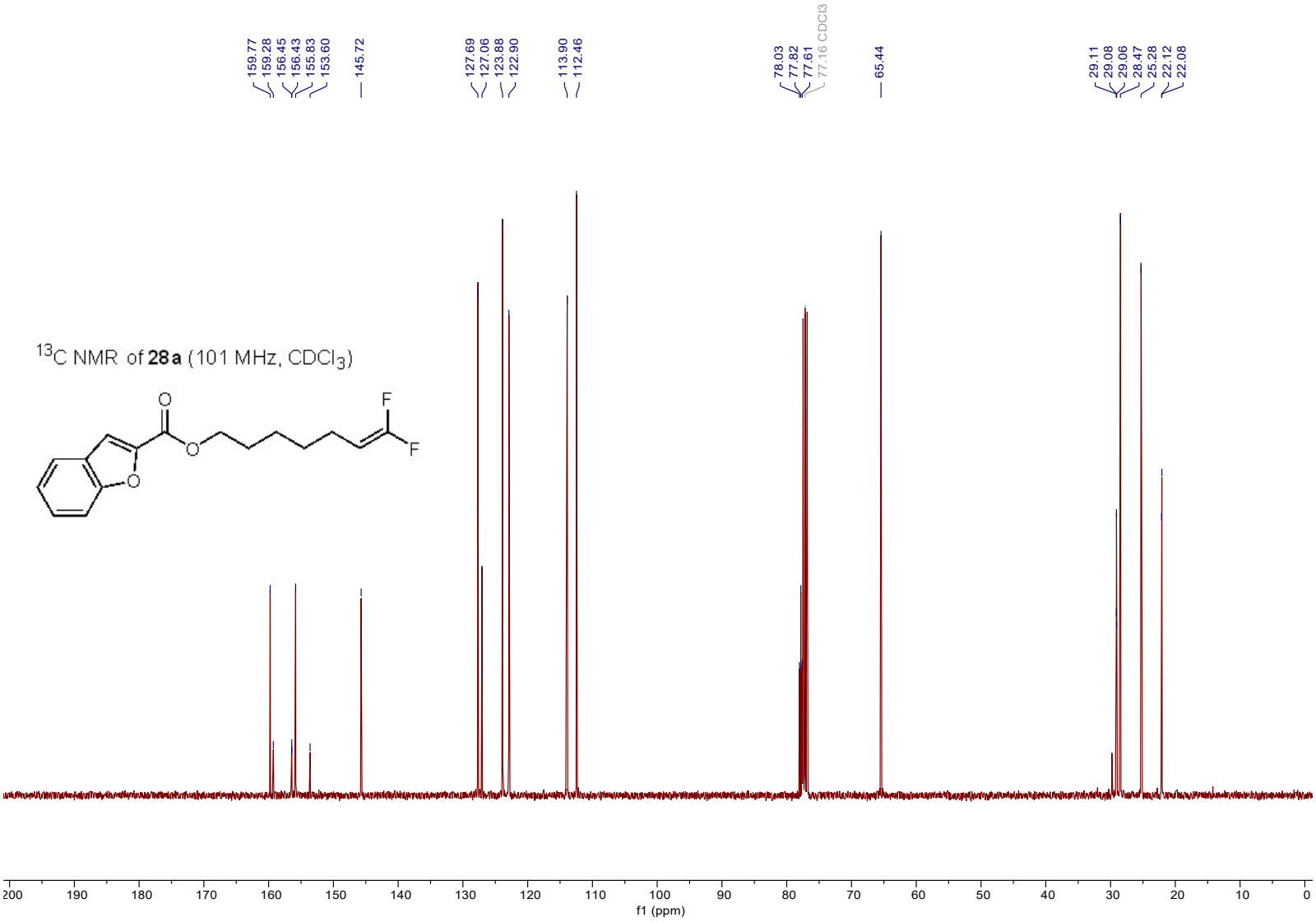

-89.31
-89.44
-91.68
-91.75
-91.81
-91.88
19F NMR of 26a (376 MHz, CDCl3)
O
F
S
O
F
-89.31
-89.44
-91.68
-91.75
-91.81
-91.88
-88.0 -88.5 -89.0 -89.5 -90.0 -90.5 -91.0 -91.5 -92.0 -92.5 -93.0
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

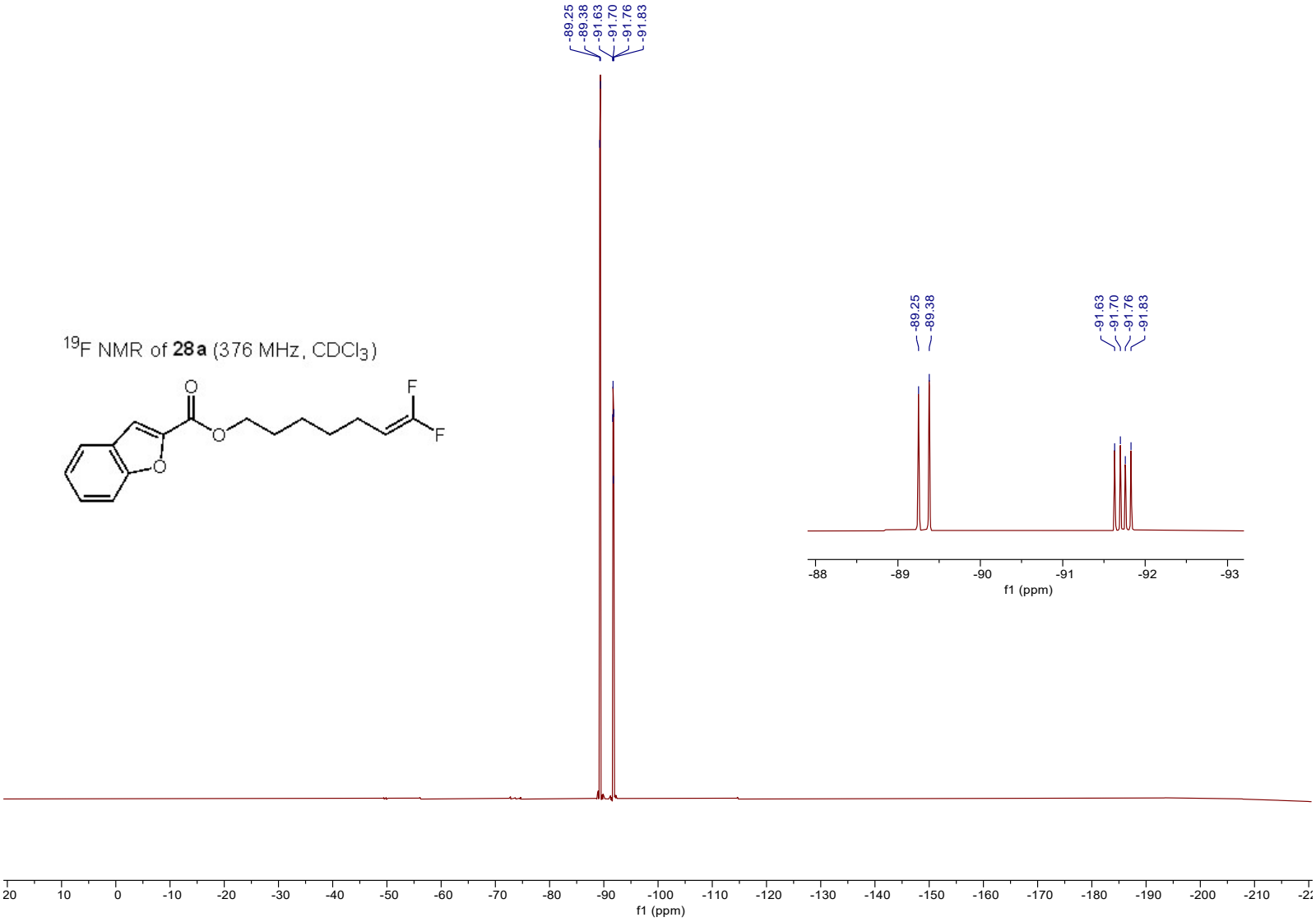

7.26 CDCl3
4.14 4.14 4.12 4.12 4.10 4.08 4.07 4.07 4.06 4.05 4.04 4.03 3.95 3.94 3.93 3.92 3.91 3.90 3.43 3.42 3.40 3.39 3.37 3.37 2.54 2.53 2.51 2.51 2.50 2.49 2.48 2.47 2.46 1.98 1.97 1.96 1.96 1.96 1.95 1.94 1.94 1.93 1.92 1.83 1.82 1.82 1.82 1.81 1.81 1.80 1.80 1.79 1.79 1.78 1.78 1.76 1.75 1.73 1.73 1.72 1.71 1.64 1.62 1.60 1.60 1.59 1.59 1.58 1.58 1.57 1.37 1.37 1.36 1.36 1.35 1.35 1.34 1.33 1.33
^{1}H NMR of **27a** (400 MHz, $CDCl_3$)
O
F
O
F
O
3.04
2.03
2.04
1.00
2.04
4.04
2.00
4.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

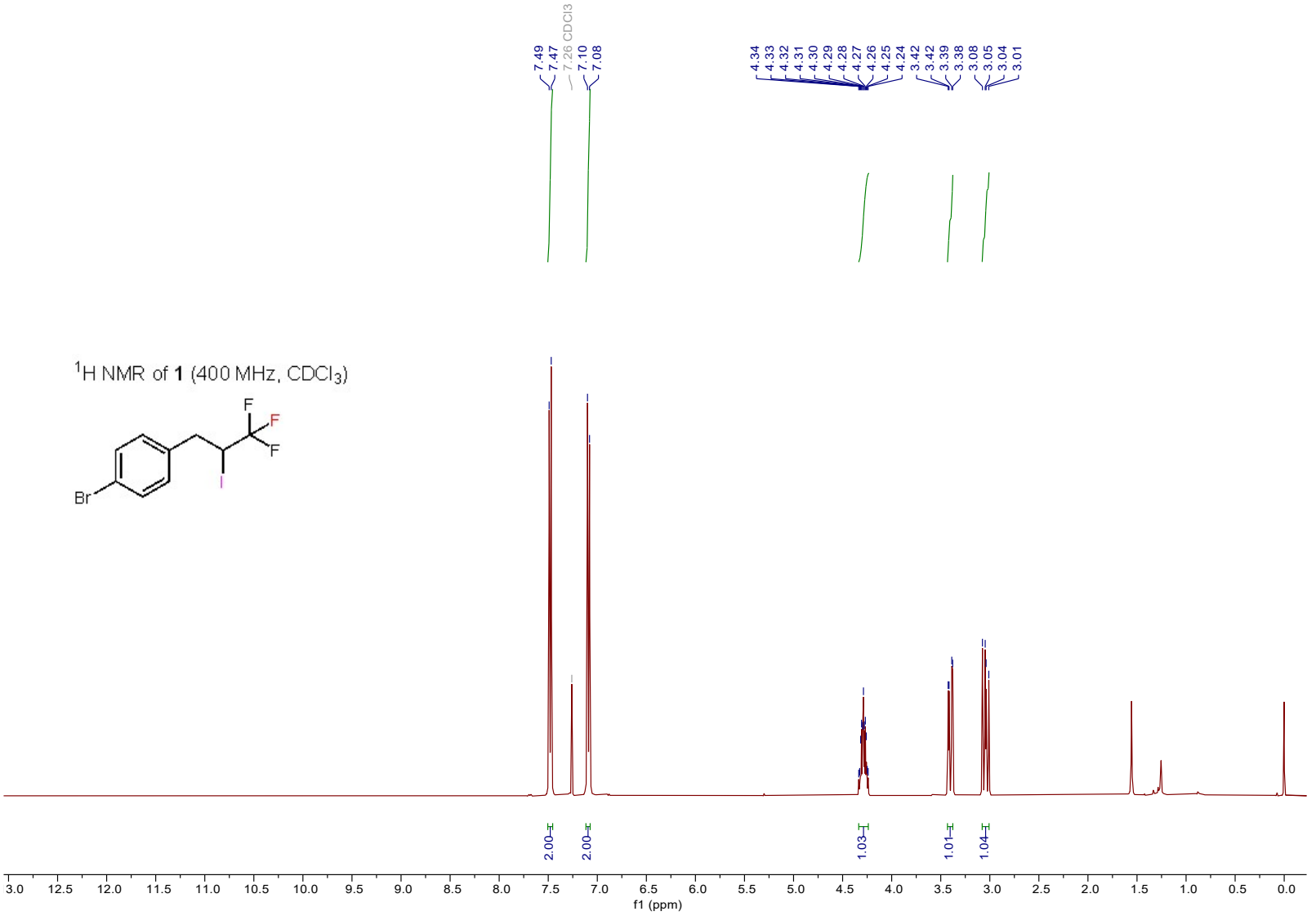

174.62
159.23
156.41
156.39
153.56
77.99
77.78
77.57
77.16 CDCl3
67.16
64.44
40.22
29.04
29.01
28.99
28.74
28.36
25.23
22.07
22.03
13C NMR of 27a (101 MHz, CDCl3)
O
F
O
O
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

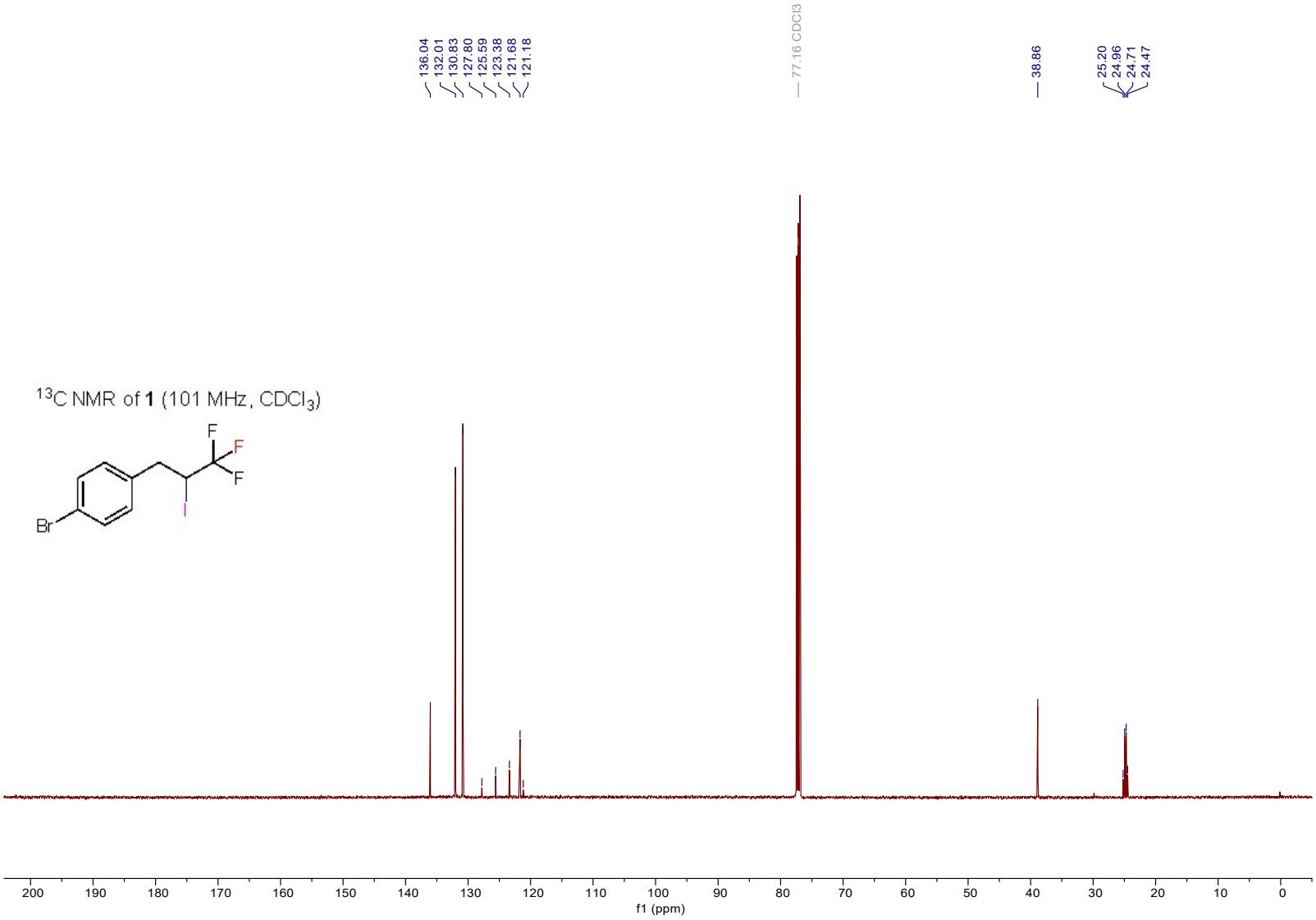

-89.36
-89.37
-89.50
-91.77
-91.84
-91.90
-91.97
19F NMR of 27a (376 MHz, CDCl3)
O
F
O
O
F
-89.36
-89.37
-89.50
-91.77
-91.84
-91.90
-91.97
-88
-89
-90
-91
-92
-93
-94
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

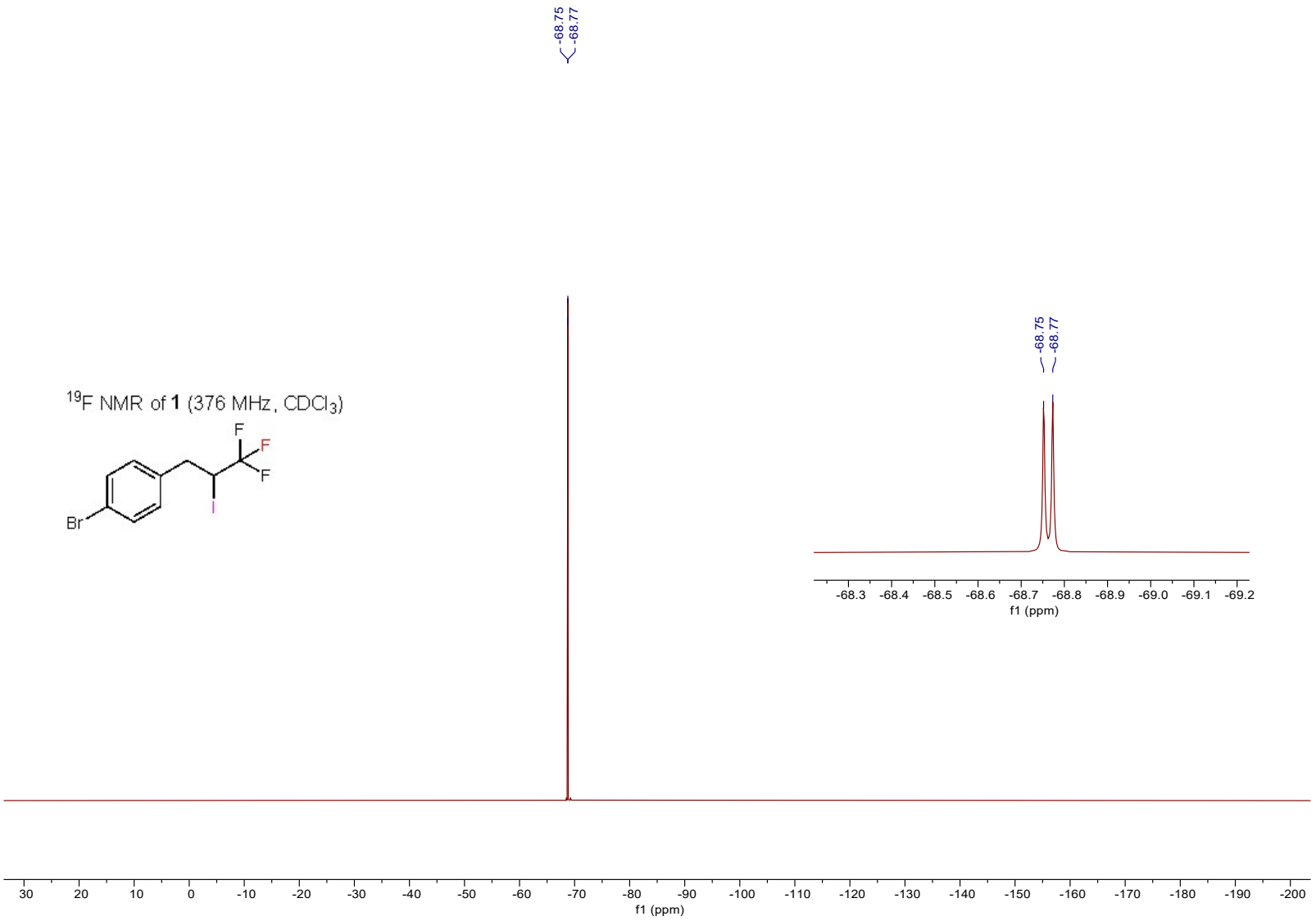

^{1}H NMR of **28a** (400 MHz, $CDCl_3$)
O
O
O
F
F
7.68
7.66
7.60
7.60
7.58
7.58
7.52
7.52
7.46
7.46
7.44
7.44
7.42
7.42
7.31
7.31
7.29
7.28
7.27
7.26 CDCl3
4.39
4.37
4.35
4.19
4.18
4.17
4.16
4.15
4.14
4.12
4.12
4.10
4.10
4.08
4.08
2.02
2.01
2.01
2.00
1.99
1.99
1.81
1.80
1.79
1.78
1.77
1.47
1.46
1.45
1.44
1.00
1.00
1.00
1.01
1.01
2.04
1.00
2.02
2.03
4.02
f1 (ppm)

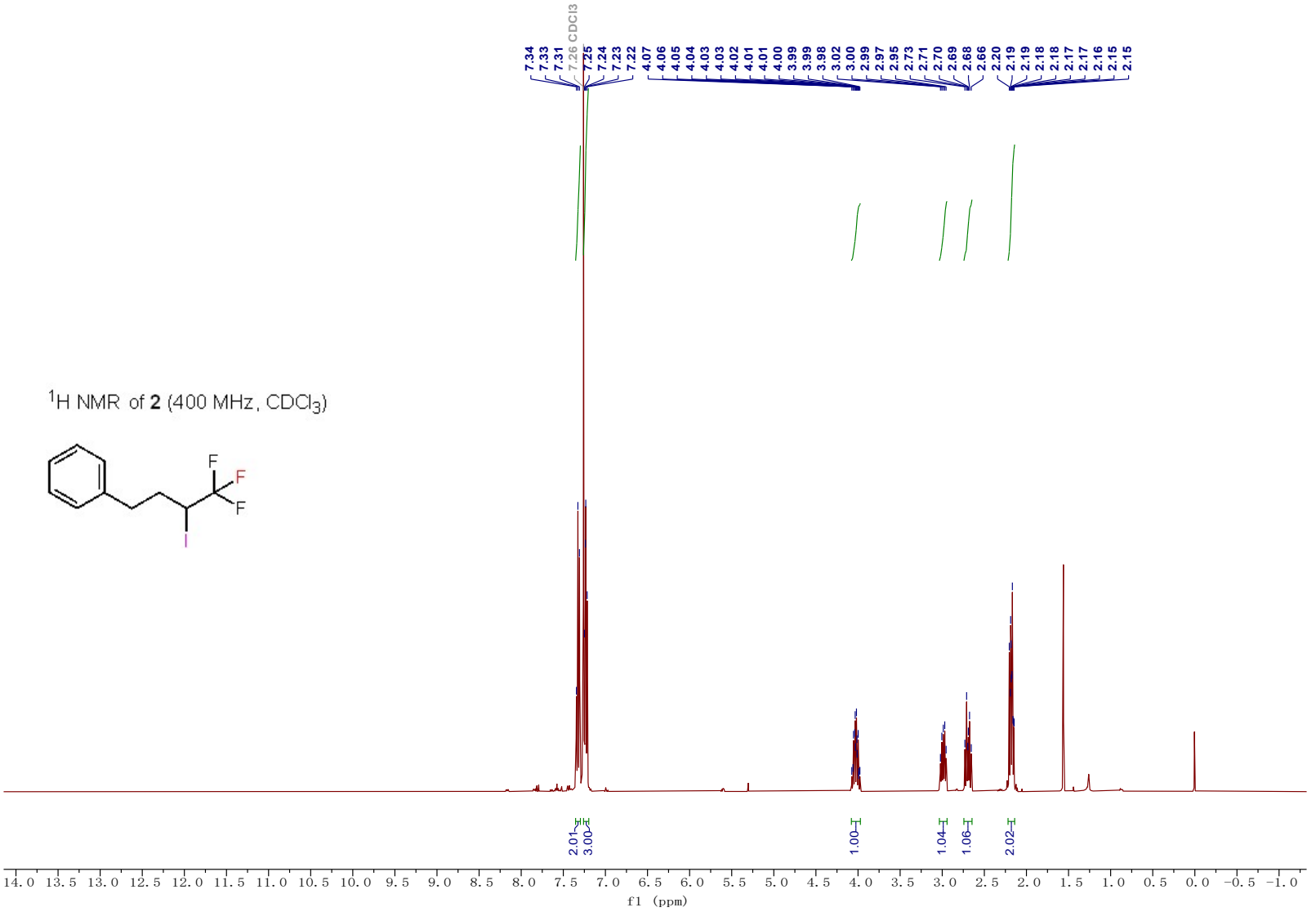

159.77
159.28
156.45
156.43
155.83
153.60
145.72
127.69
127.06
123.88
122.90
113.90
112.46
78.03
77.82
77.61
77.16 CDCl3
65.44
29.11
29.08
29.06
28.47
25.28
22.12
22.08
13C NMR of 28a (101 MHz, CDCl3)
O
O
O
F
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

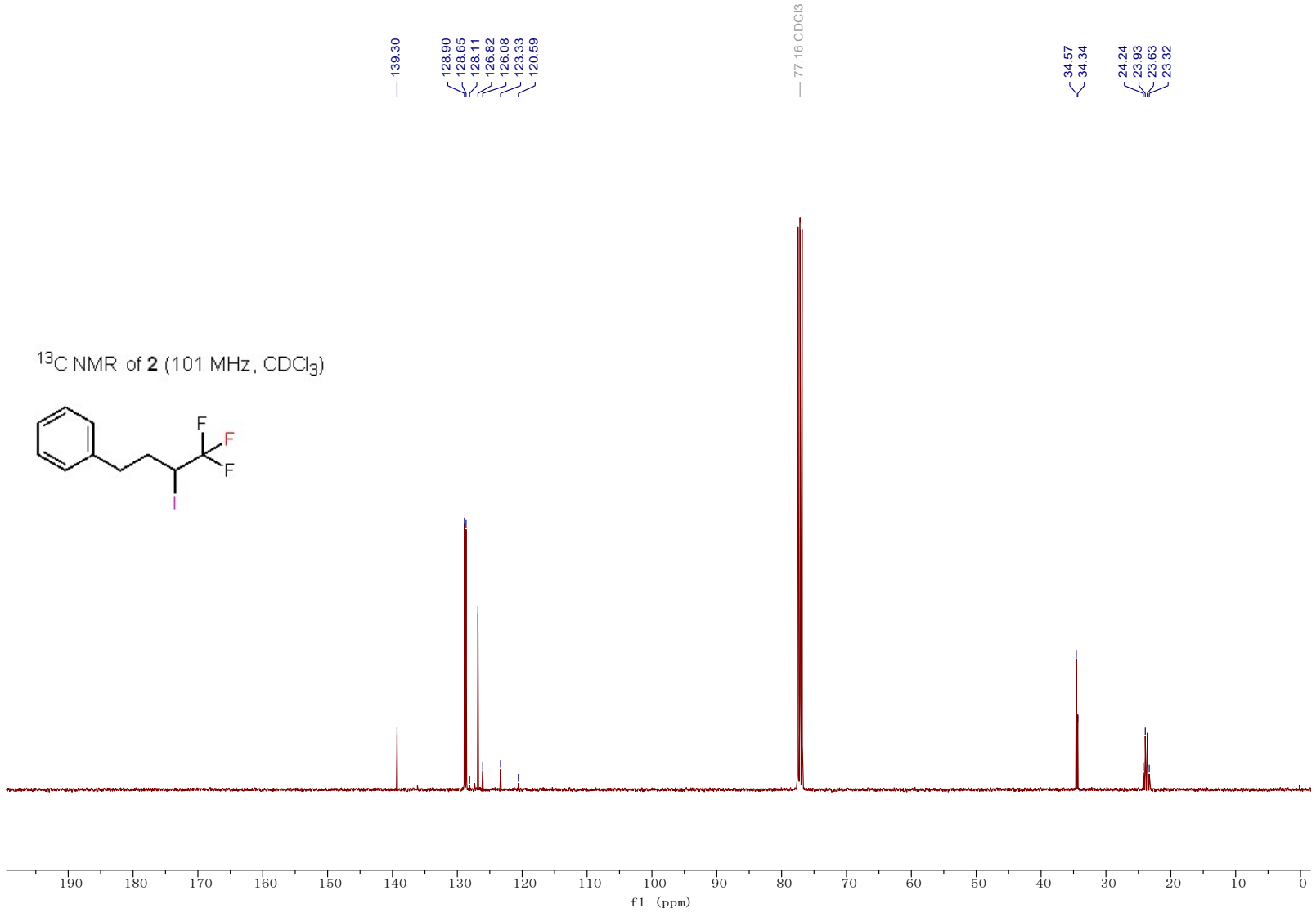

-89.25
-89.38
-91.63
-91.70
-91.76
-91.83
19F NMR of 28a (376 MHz, CDCl3)
O
O
O
F
F
-89.25
-89.38
-91.63
-91.70
-91.76
-91.83
-88
-89
-90
-91
-92
-93
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

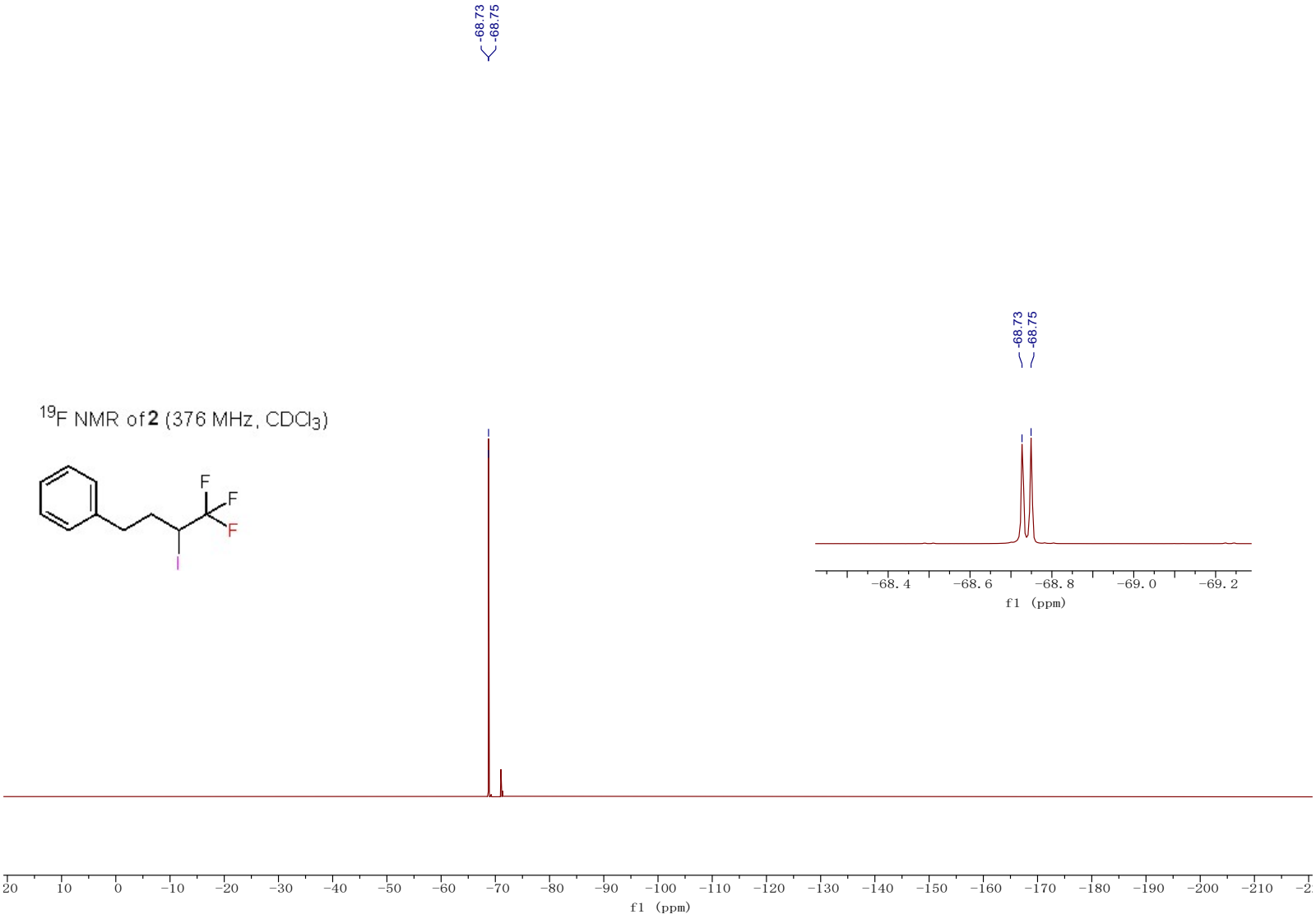

7.49
7.47
7.26 CDCl3
7.10
7.08
4.34
4.33
4.32
4.31
4.30
4.29
4.28
4.27
4.26
4.25
4.24
3.42
3.42
3.39
3.38
3.08
3.05
3.04
3.01
1H NMR of 1 (400 MHz, CDCl3)
F
F
F
Br
I
2.00
2.00
1.03
1.01
1.04
3.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

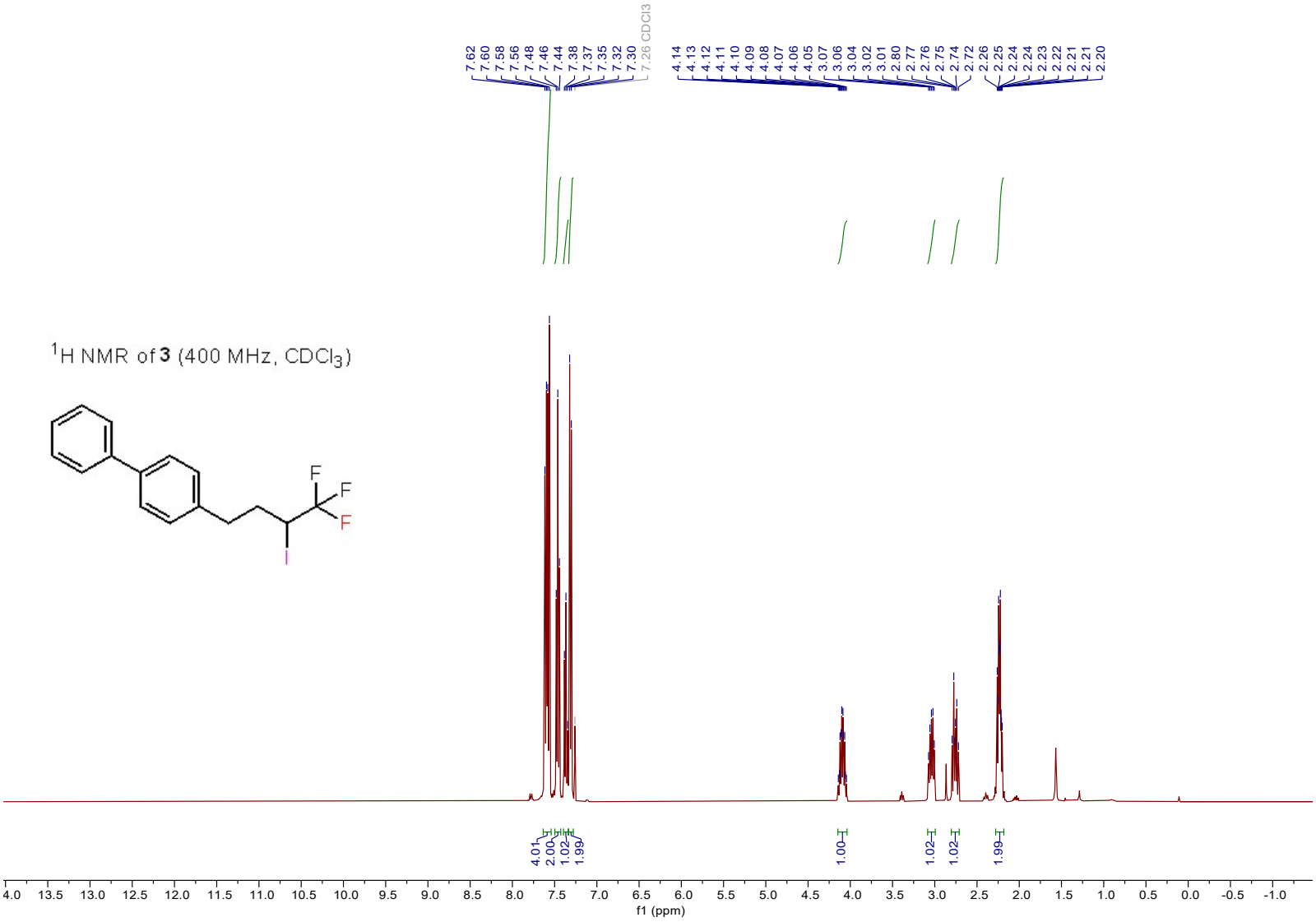

136.04
132.01
130.83
127.80
125.59
123.38
121.68
121.18
77.16 CDCl3
38.86
25.20
24.96
24.71
24.47
13C NMR of 1 (101 MHz, CDCl3)
F
F
F
Br
I
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

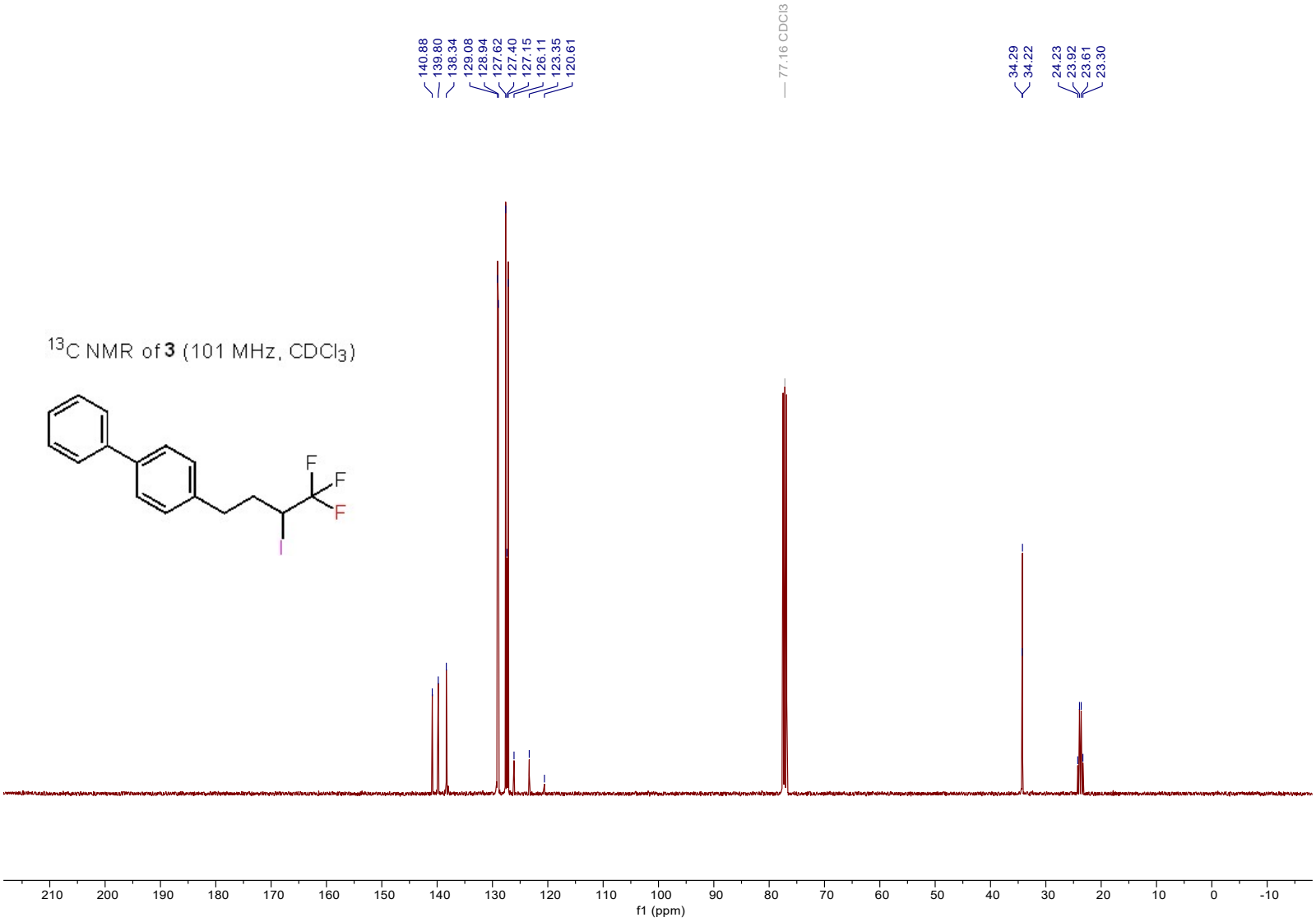

-68.75
-68.77
19F NMR of 1 (376 MHz, CDCl3)
F
F
F
Br
I
-68.75
-68.77
-68.3 -68.4 -68.5 -68.6 -68.7 -68.8 -68.9 -69.0 -69.1 -69.2
f1 (ppm)
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


^{1}H NMR of **2** (400 MHz, $CDCl_3$)
F
F
F
I
7.34
7.33
7.31
7.26 CDCl3
7.25
7.24
7.23
7.22
4.07
4.06
4.05
4.04
4.03
4.03
4.02
4.01
4.01
4.00
3.99
3.99
3.98
3.02
3.00
2.99
2.97
2.95
2.73
2.71
2.70
2.69
2.68
2.66
2.20
2.19
2.19
2.18
2.18
2.17
2.17
2.16
2.15
2.15
2.01
3.00
1.00
1.04
1.06
2.02
14.0 13.5 13.0 12.5 12.0 11.5 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 −1.0
f1 (ppm)

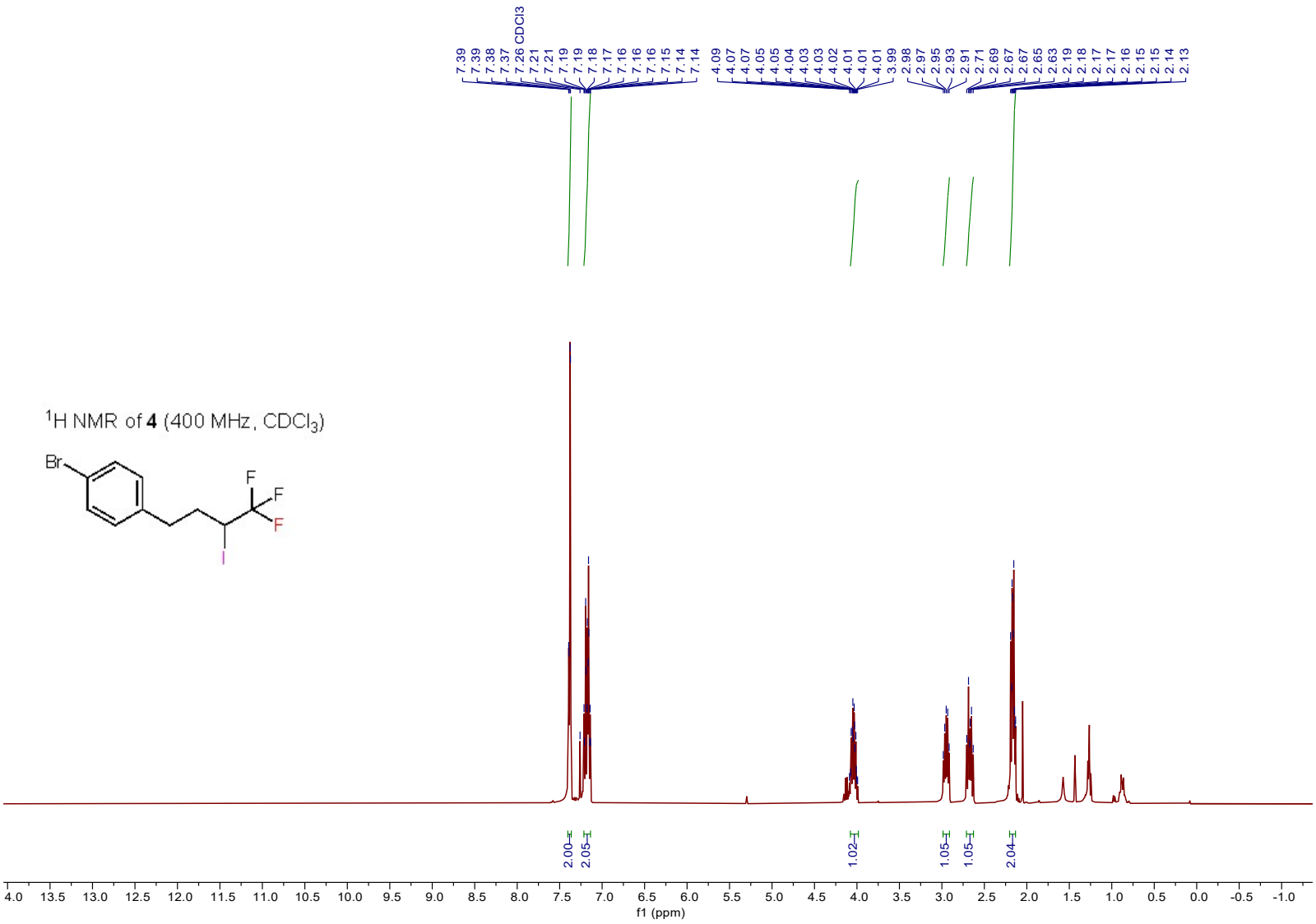

139.30
128.90
128.65
128.11
126.82
126.08
123.33
120.59
77.16 CDCl3
34.57
34.34
24.24
23.93
23.63
23.32
13C NMR of 2 (101 MHz, CDCl3)
F
F
F
I
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

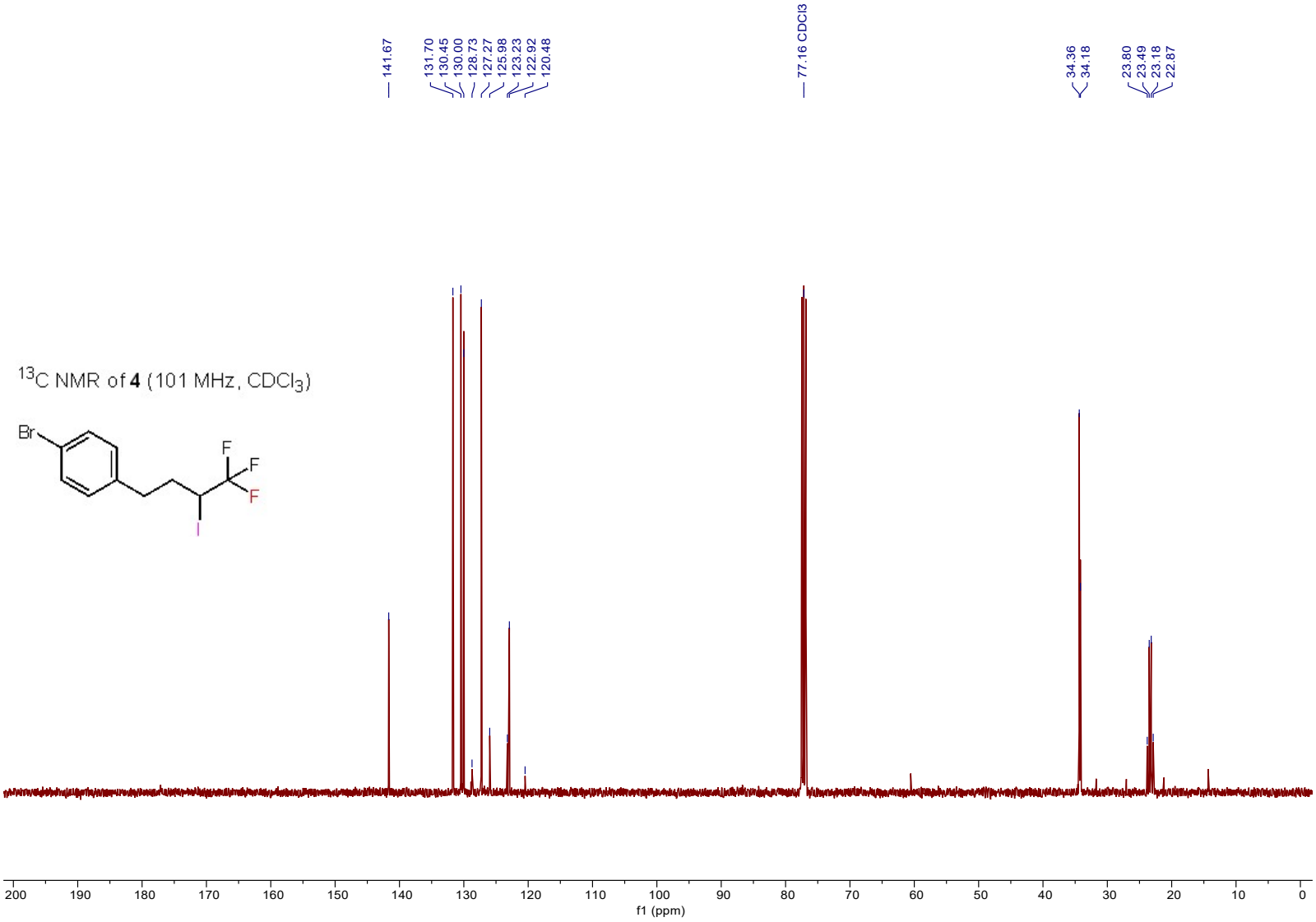

-68.73
-68.75
19F NMR of 2 (376 MHz, CDCl3)
F
F
F
I
-68.73
-68.75
-68.4
-68.6
-68.8
-69.0
-69.2
f1 (ppm)
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

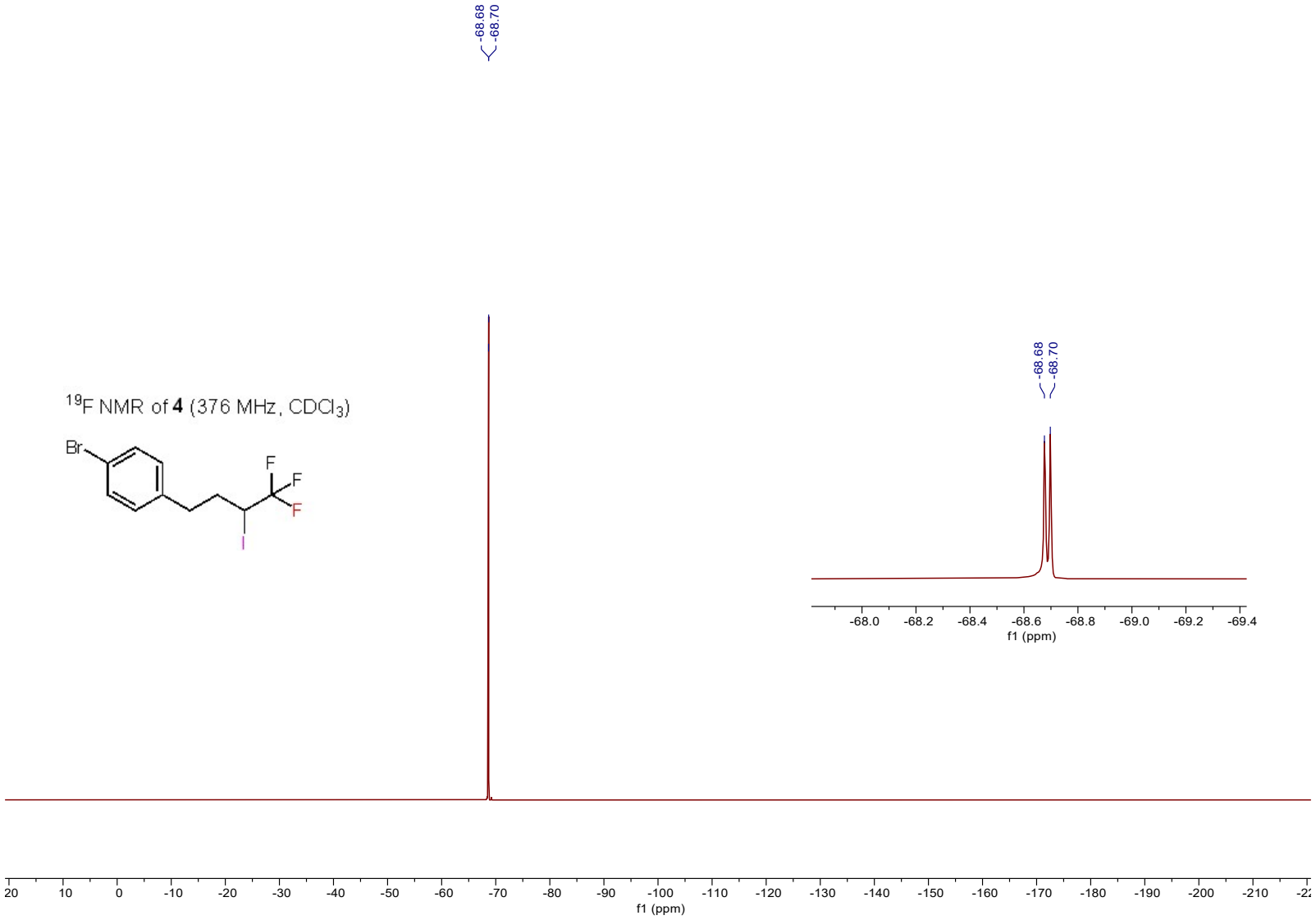

7.62
7.60
7.58
7.56
7.48
7.46
7.44
7.38
7.37
7.35
7.32
7.30
7.26 CDCl3
4.14
4.13
4.12
4.11
4.10
4.09
4.08
4.07
4.06
4.05
3.07
3.06
3.04
3.02
3.01
2.80
2.77
2.76
2.75
2.74
2.72
2.26
2.25
2.24
2.24
2.23
2.22
2.21
2.21
2.20
1H NMR of 3 (400 MHz, CDCl3)
F
F
F
I
4.01
2.00
1.02
1.99
1.00
1.02
1.02
1.99
f1 (ppm)

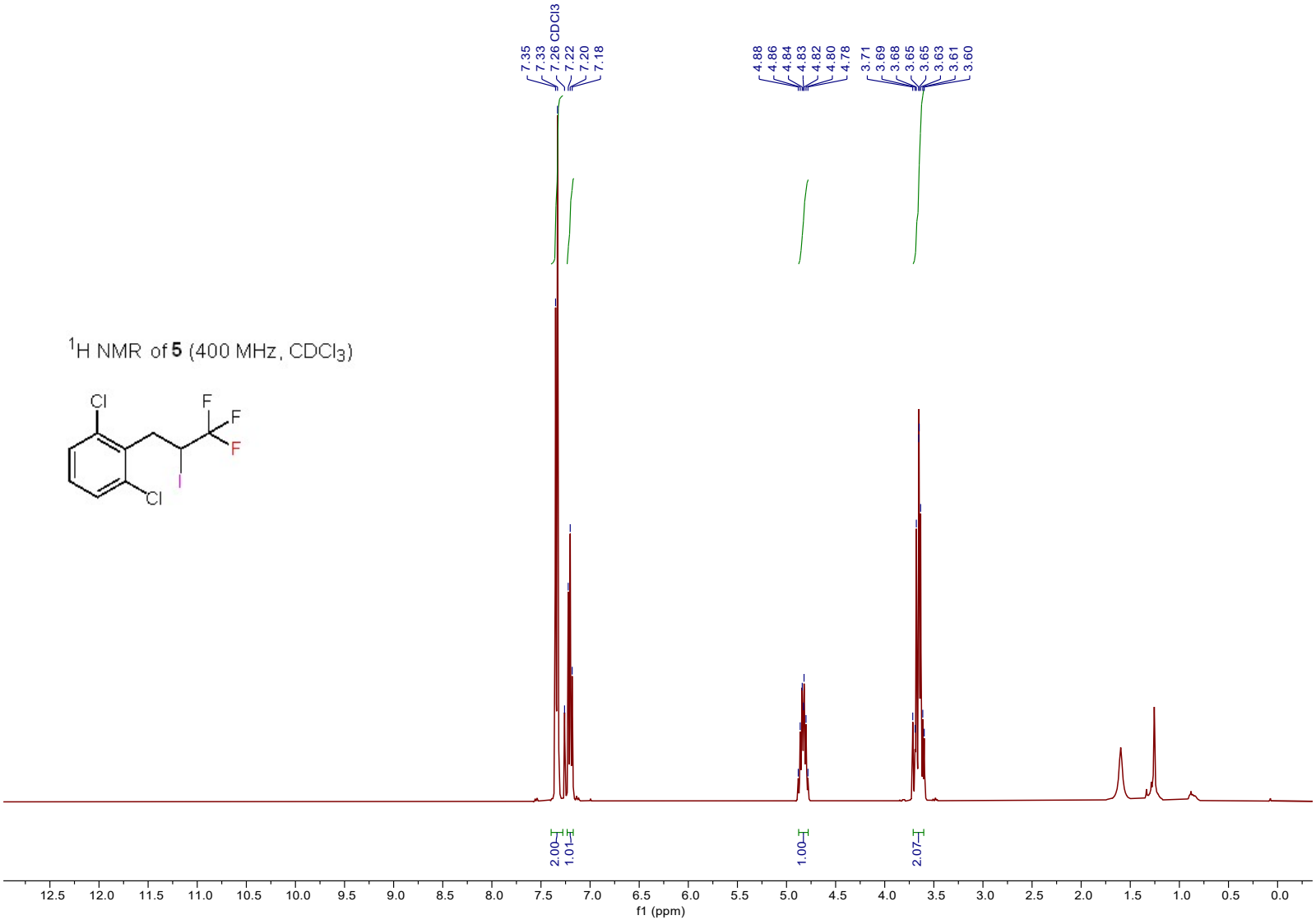

140.88
139.80
138.34
129.08
128.94
127.62
127.40
127.15
126.11
123.35
120.61
77.16 CDCl3
34.29
34.22
24.23
23.92
23.61
23.30
13C NMR of 3 (101 MHz, CDCl3)
F
F
F
I
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

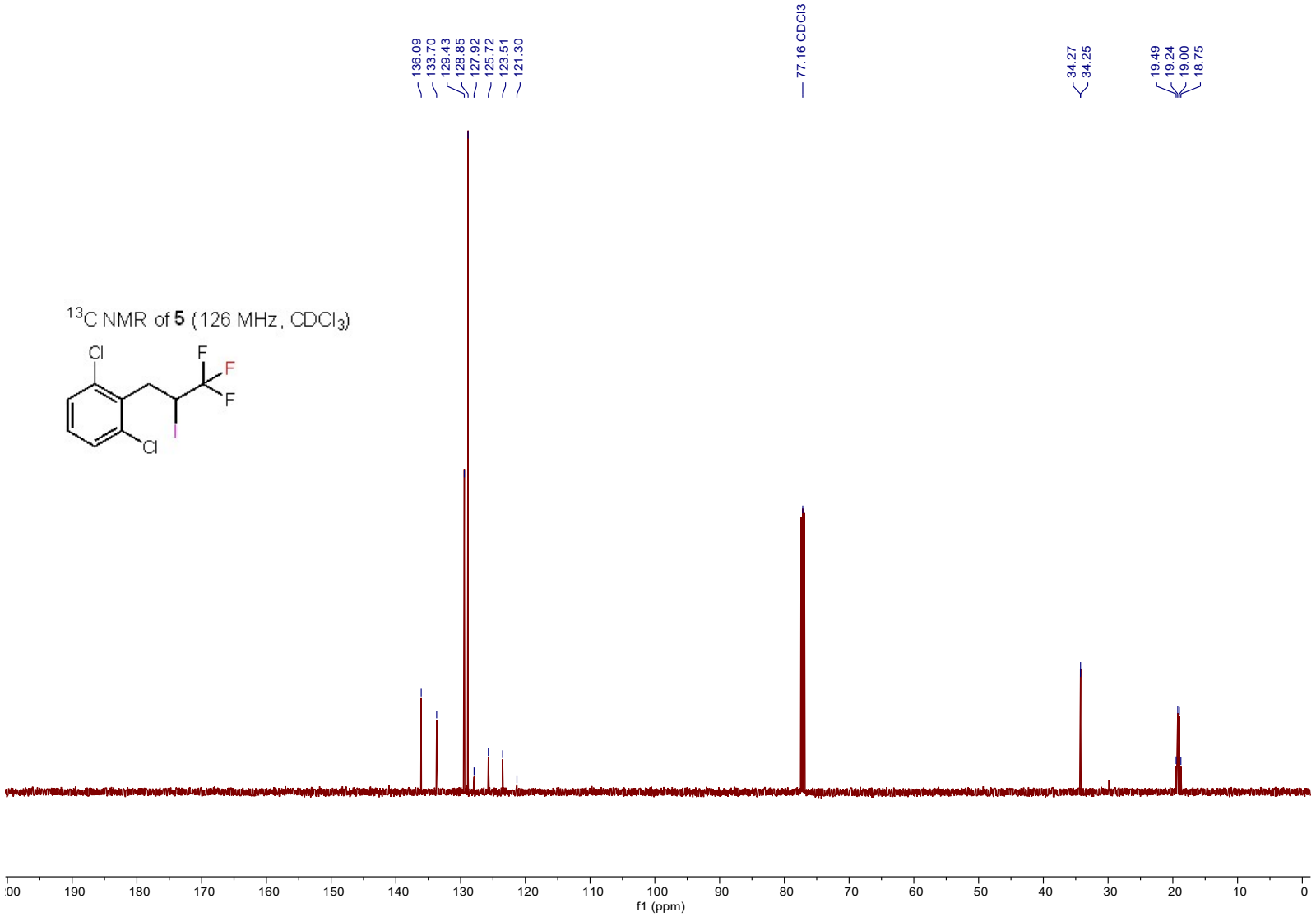

-68.63
-68.65
19F NMR of 3 (376 MHz, CDCl3)
F
F
F
I
-68.63
-68.65
-68.2 -68.3 -68.4 -68.5 -68.6 -68.7 -68.8 -68.9 -69.0
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

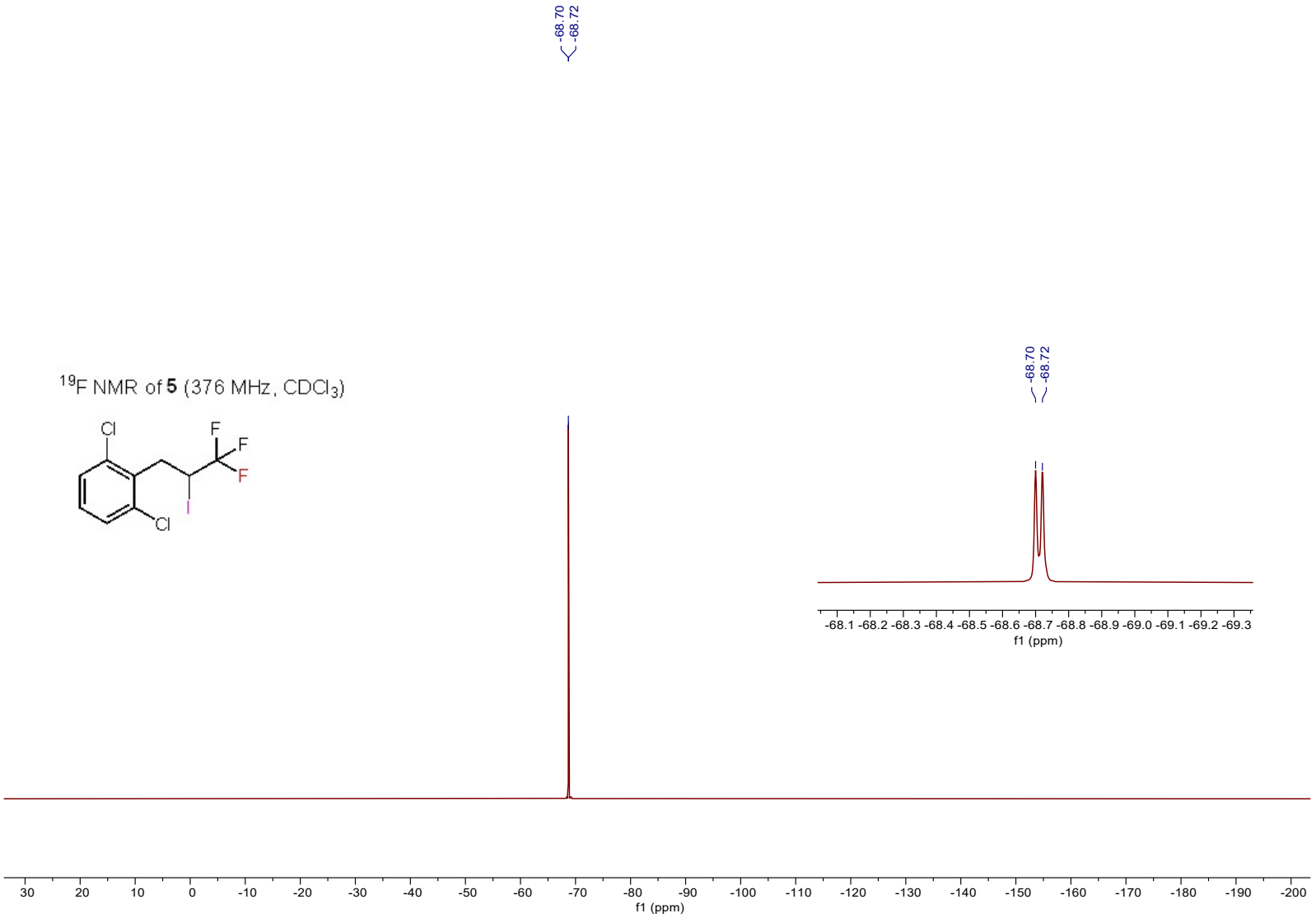

7.39
7.39
7.38
7.37
7.26 CDCl3
7.21
7.19
7.19
7.18
7.17
7.16
7.16
7.16
7.15
7.14
7.14
4.09
4.07
4.07
4.05
4.04
4.03
4.03
4.02
4.01
4.01
4.01
3.99
2.98
2.97
2.95
2.93
2.91
2.71
2.69
2.67
2.67
2.65
2.63
2.19
2.18
2.17
2.17
2.16
2.15
2.15
2.14
2.13
1H NMR of 4 (400 MHz, CDCl3)
Br
F
F
F
I
2.00
2.05
1.02
1.05
1.05
2.04
4.0
13.5
13.0
12.5
12.0
11.5
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
-1.0
f1 (ppm)

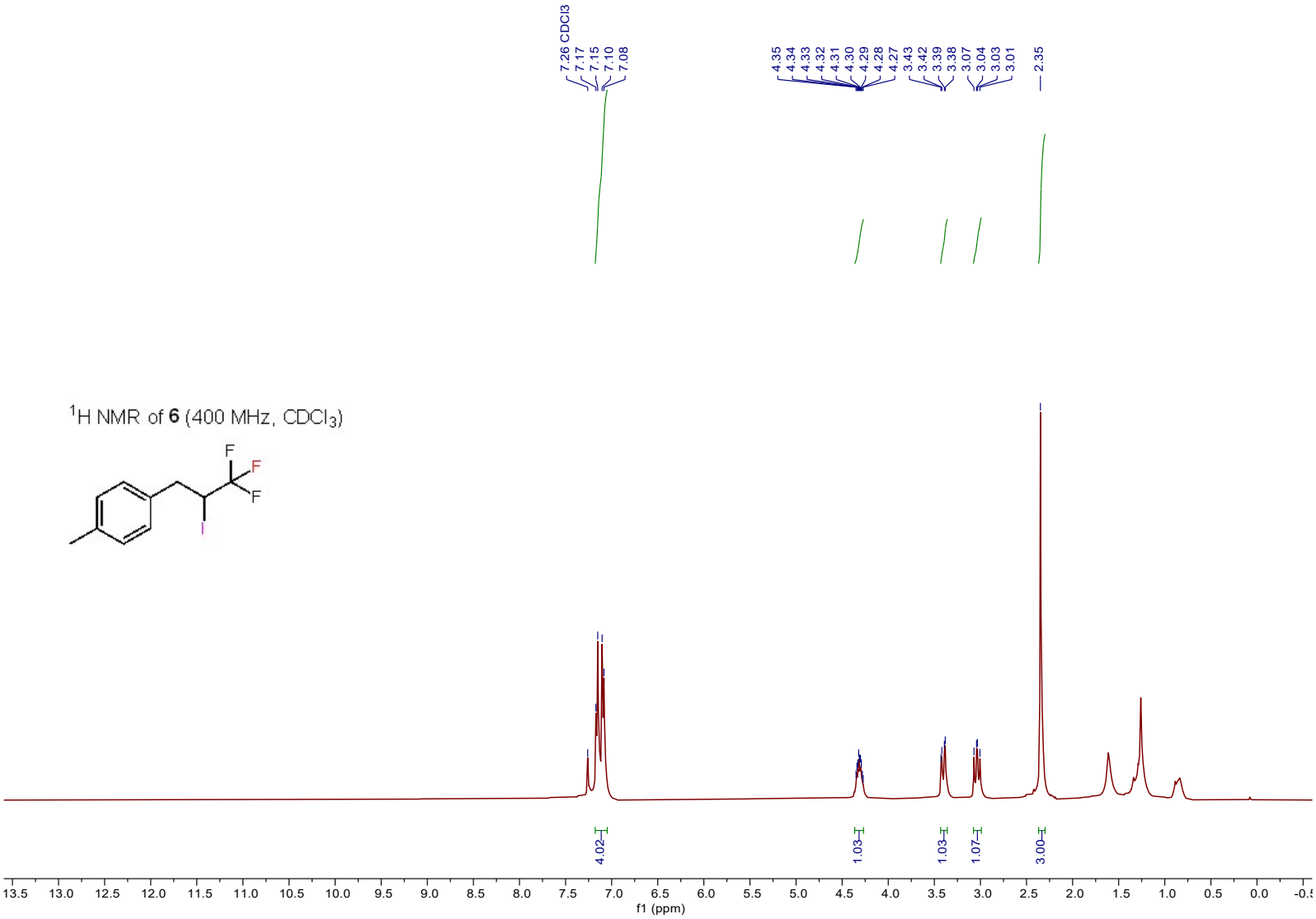

141.67
131.70
130.45
130.00
128.73
127.27
125.98
123.23
122.92
120.48
77.16 CDCl3
34.36
34.18
23.80
23.49
23.18
22.87
13C NMR of 4 (101 MHz, CDCl3)
Br
F
F
F
I
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

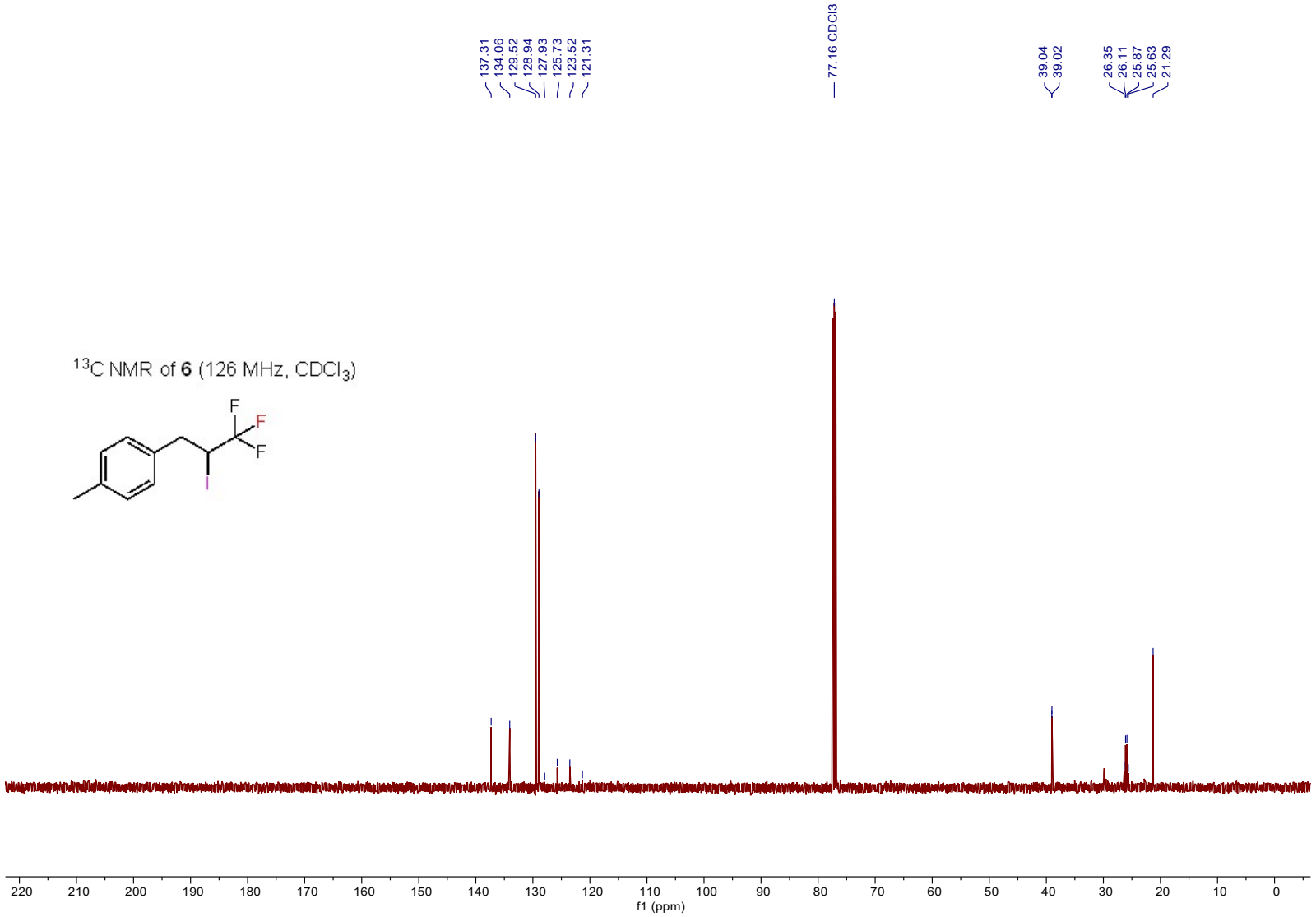

-68.68
-68.70
^{19}F NMR of **4** (376 MHz, $CDCl_3$)
Br
F
F
F
I
-68.68
-68.70
-68.0
-68.2
-68.4
-68.6
-68.8
-69.0
-69.2
-69.4
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

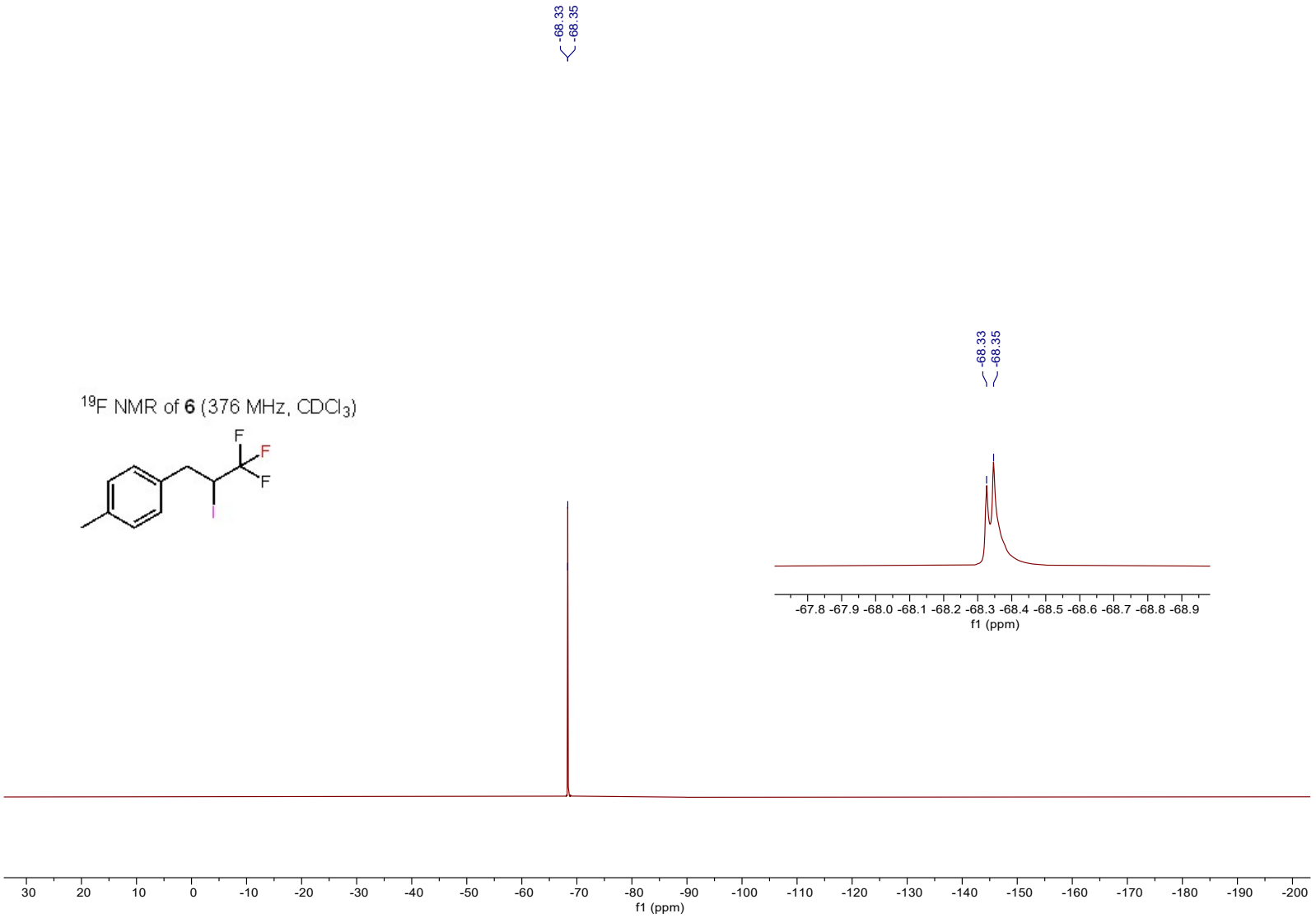

7.35
7.33
7.26 CDCl3
7.22
7.20
7.18
4.88
4.86
4.84
4.83
4.82
4.80
4.78
3.71
3.69
3.68
3.65
3.65
3.63
3.61
3.60
1H NMR of 5 (400 MHz, CDCl3)
Cl
F
F
F
I
Cl
2.00
1.01
1.00
2.07
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

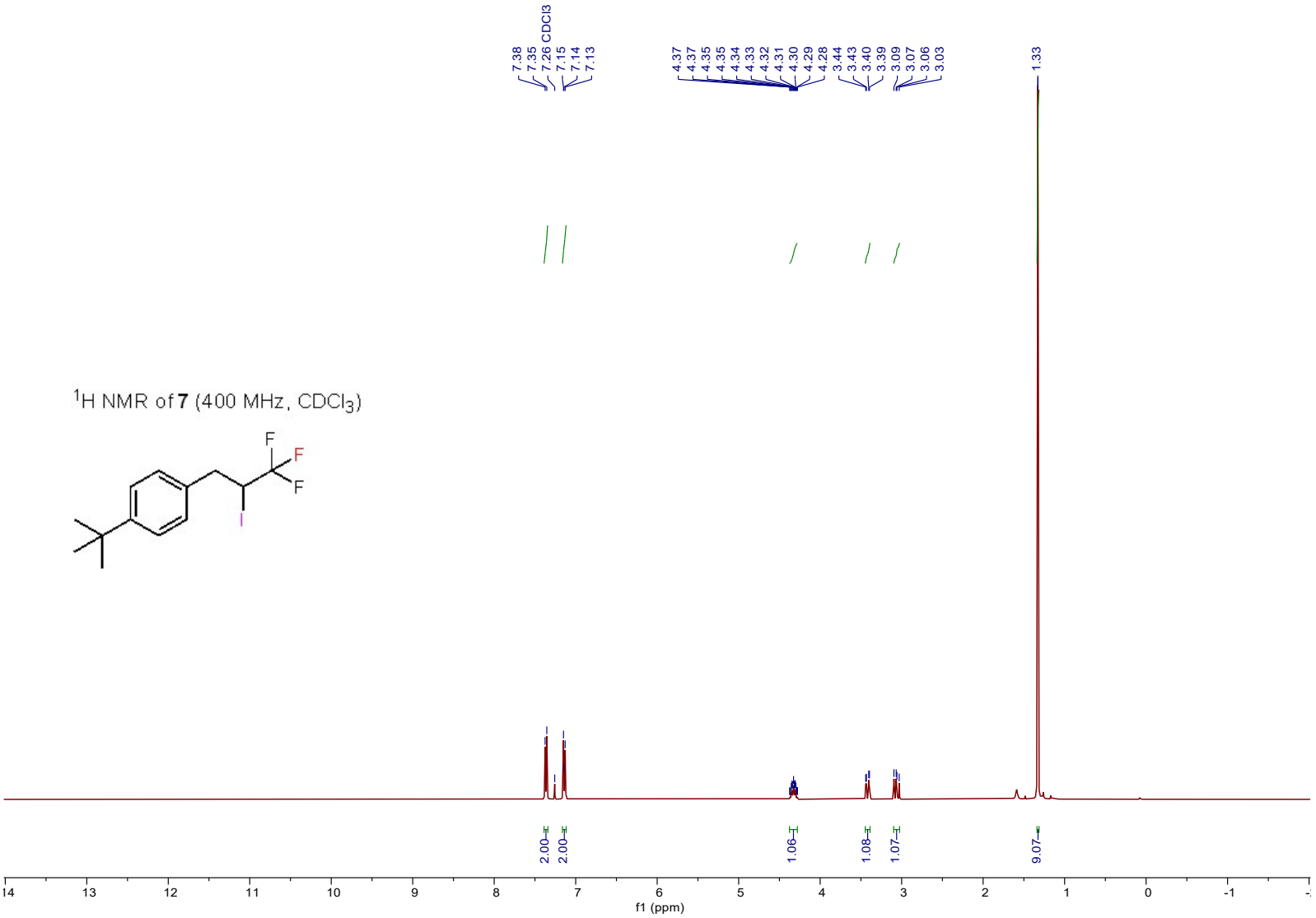

136.09
133.70
129.43
128.85
127.92
125.72
123.51
121.30
77.16 CDCl3
34.27
34.25
19.49
19.24
19.00
18.75
13C NMR of 5 (126 MHz, CDCl3)
Cl
F
F
F
I
Cl
f1 (ppm)


-68.70
-68.72
^{19}F NMR of **5** (376 MHz, $CDCl_3$)
Cl
F
F
F
I
Cl
-68.70
-68.72
-68.1 -68.2 -68.3 -68.4 -68.5 -68.6 -68.7 -68.8 -68.9 -69.0 -69.1 -69.2 -69.3
f1 (ppm)
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

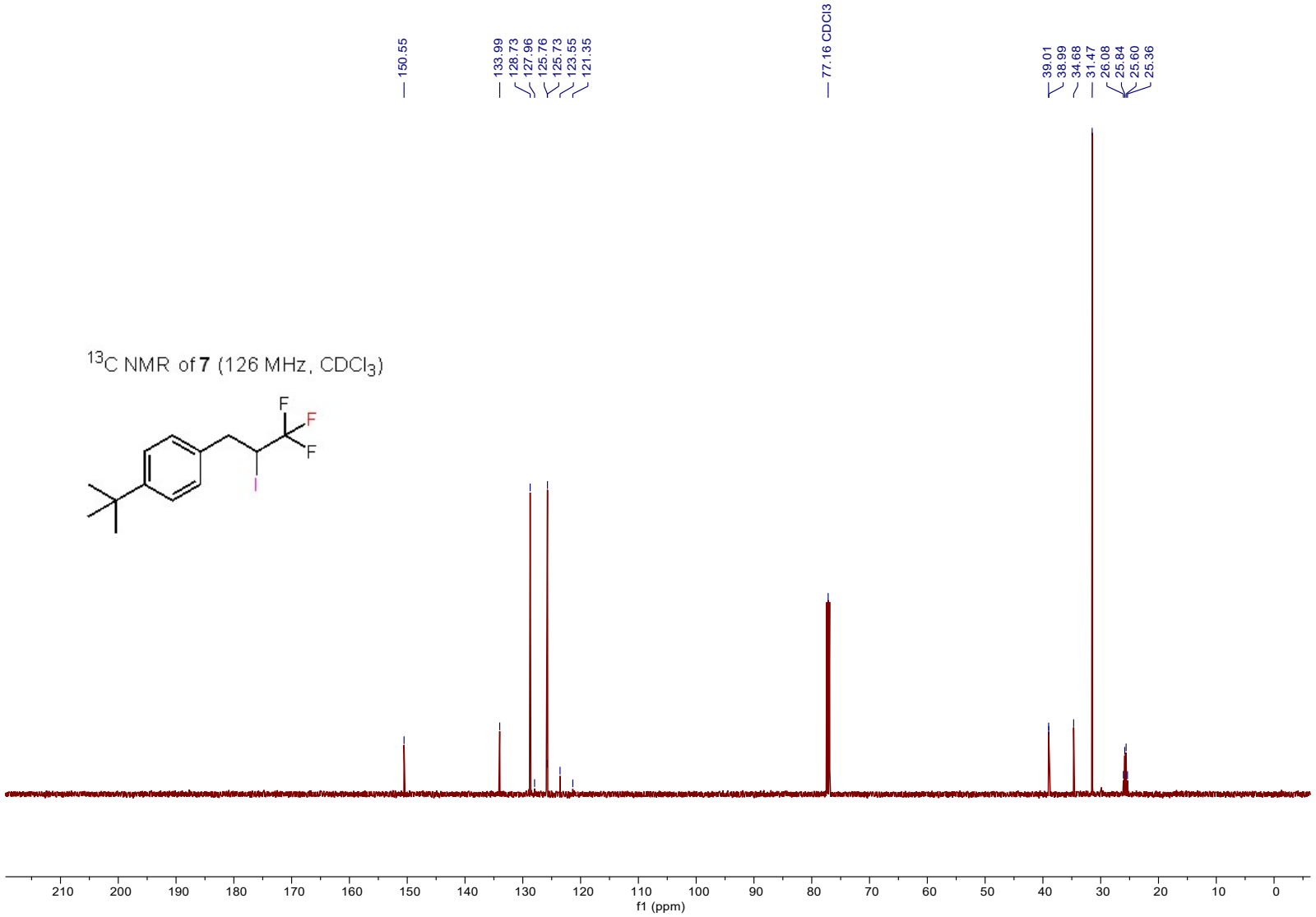

7.26 CDCl3
7.17
7.15
7.10
7.08
4.35
4.34
4.33
4.32
4.31
4.30
4.29
4.28
4.27
3.43
3.42
3.39
3.38
3.07
3.04
3.03
3.01
2.35
1H NMR of 6 (400 MHz, CDCl3)
F
F
F
I
4.02
1.03
1.03
1.07
3.00
f1 (ppm)

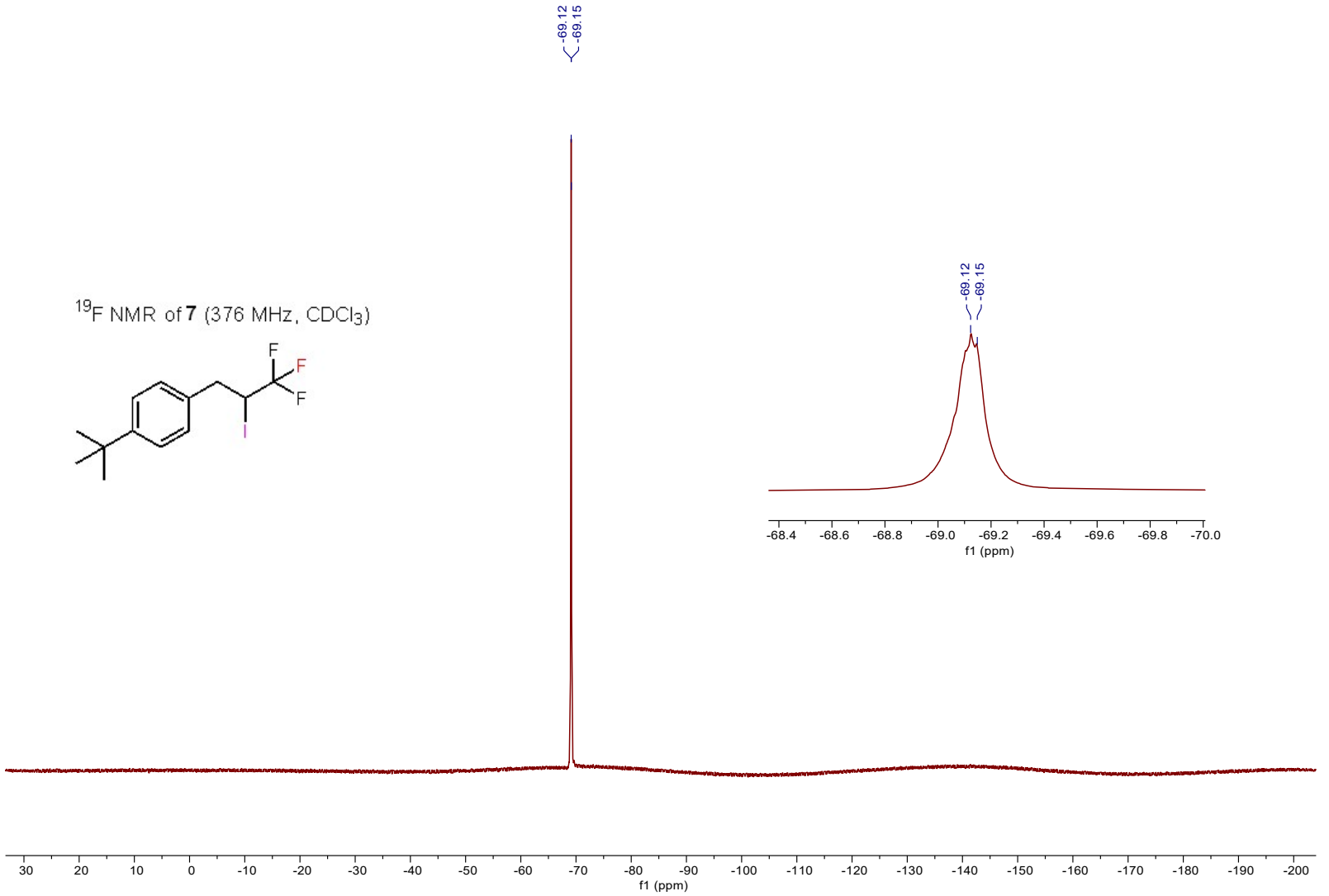

137.31
134.06
129.52
128.94
127.93
125.73
123.52
121.31
77.16 CDCl3
39.04
39.02
26.35
26.11
25.87
25.63
21.29
13C NMR of 6 (126 MHz, CDCl3)
F
F
F
I
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

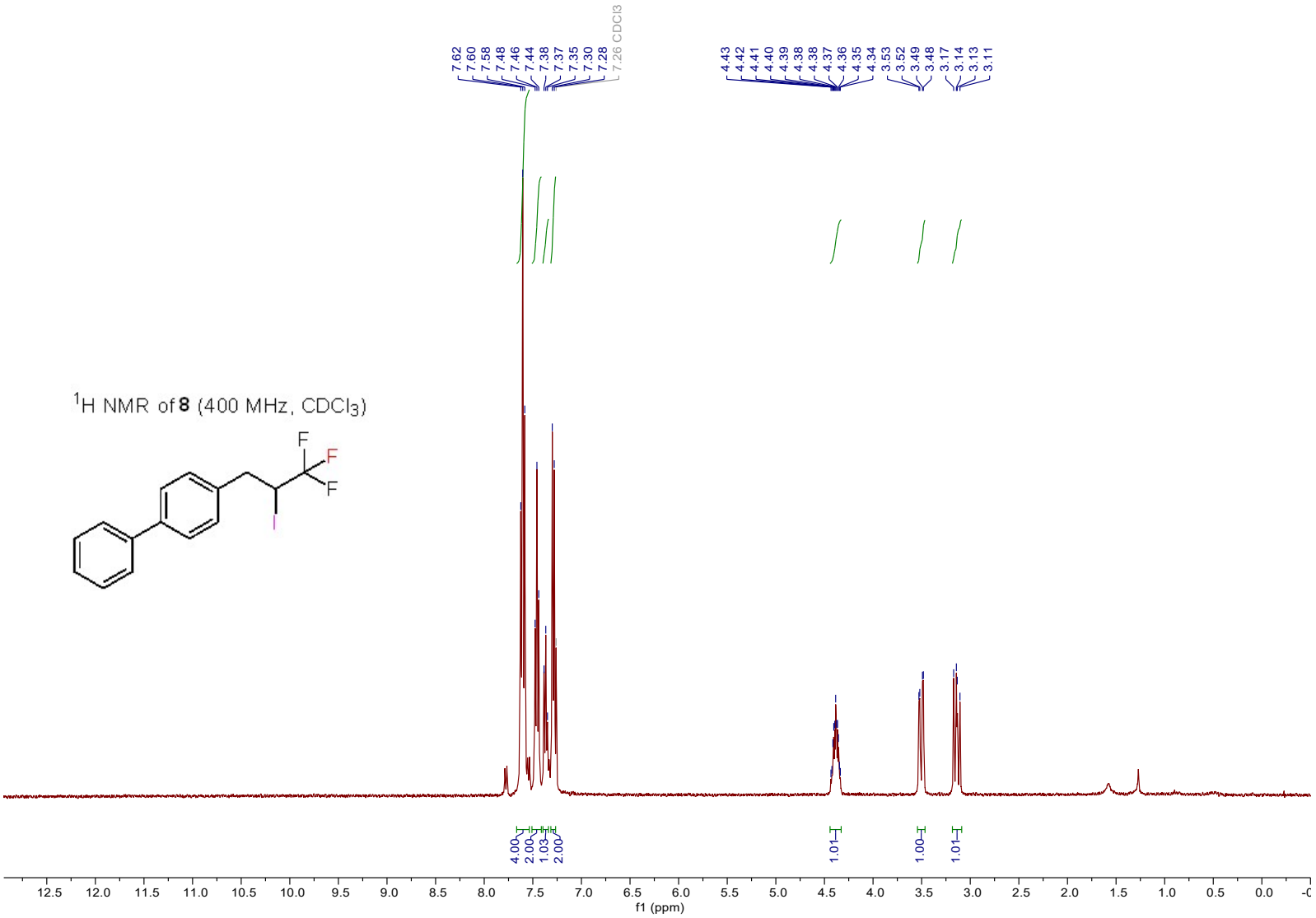

-68.33
-68.35
19F NMR of 6 (376 MHz, CDCl3)
F
F
F
I
-68.33
-68.35
-67.8 -67.9 -68.0 -68.1 -68.2 -68.3 -68.4 -68.5 -68.6 -68.7 -68.8 -68.9
f1 (ppm)
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

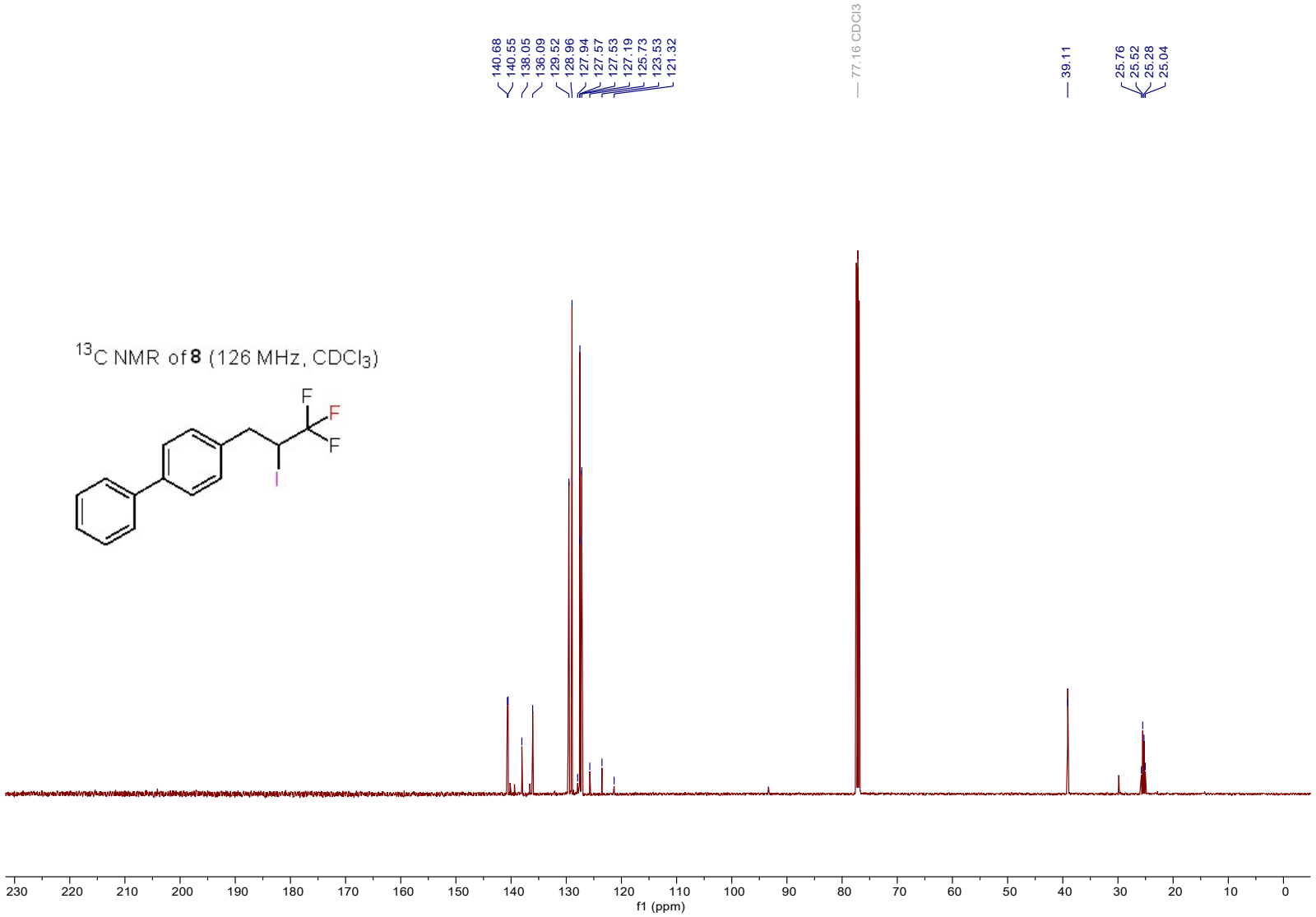


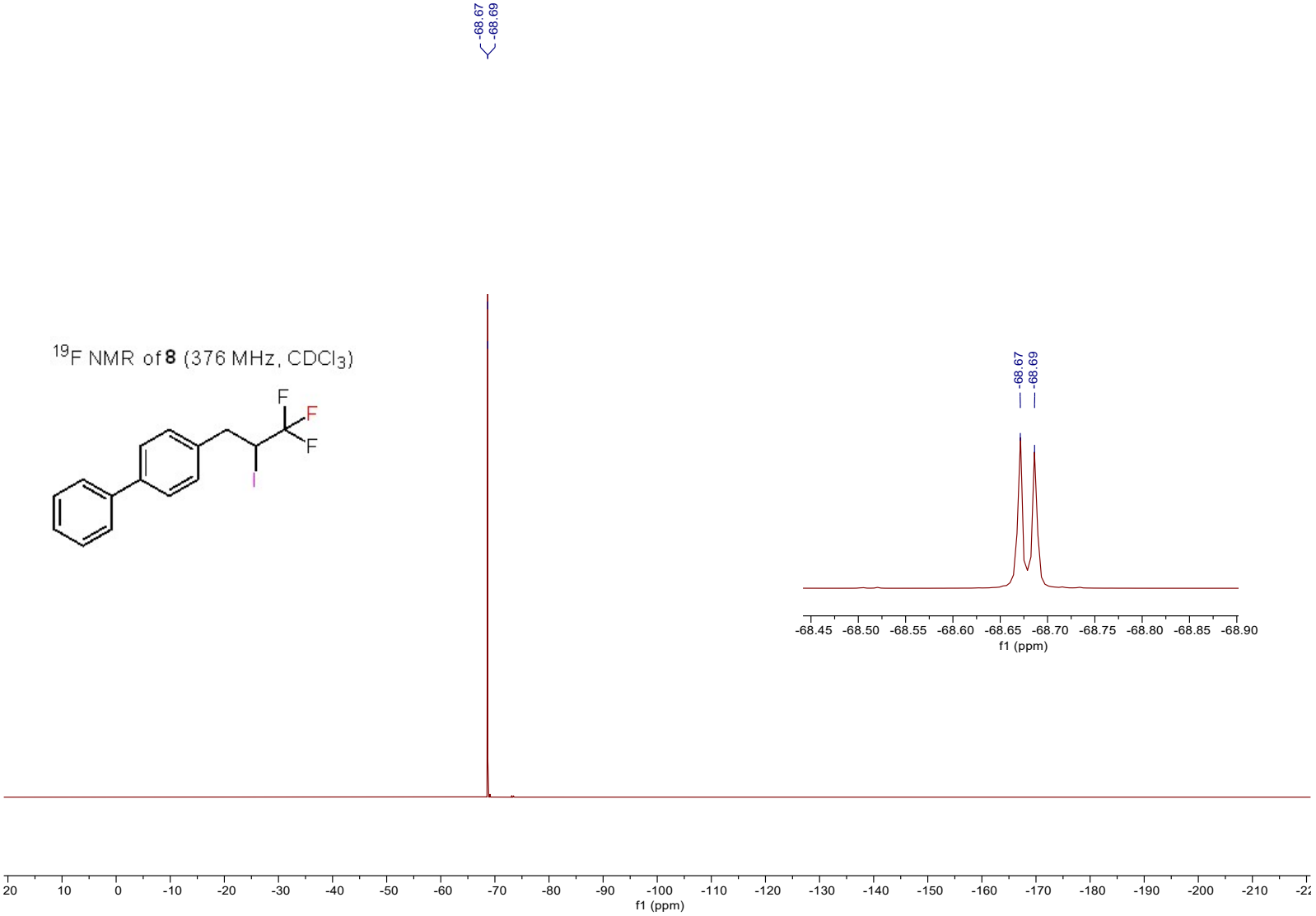
^{1}H NMR of **7** (400 MHz, $CDCl_3$)

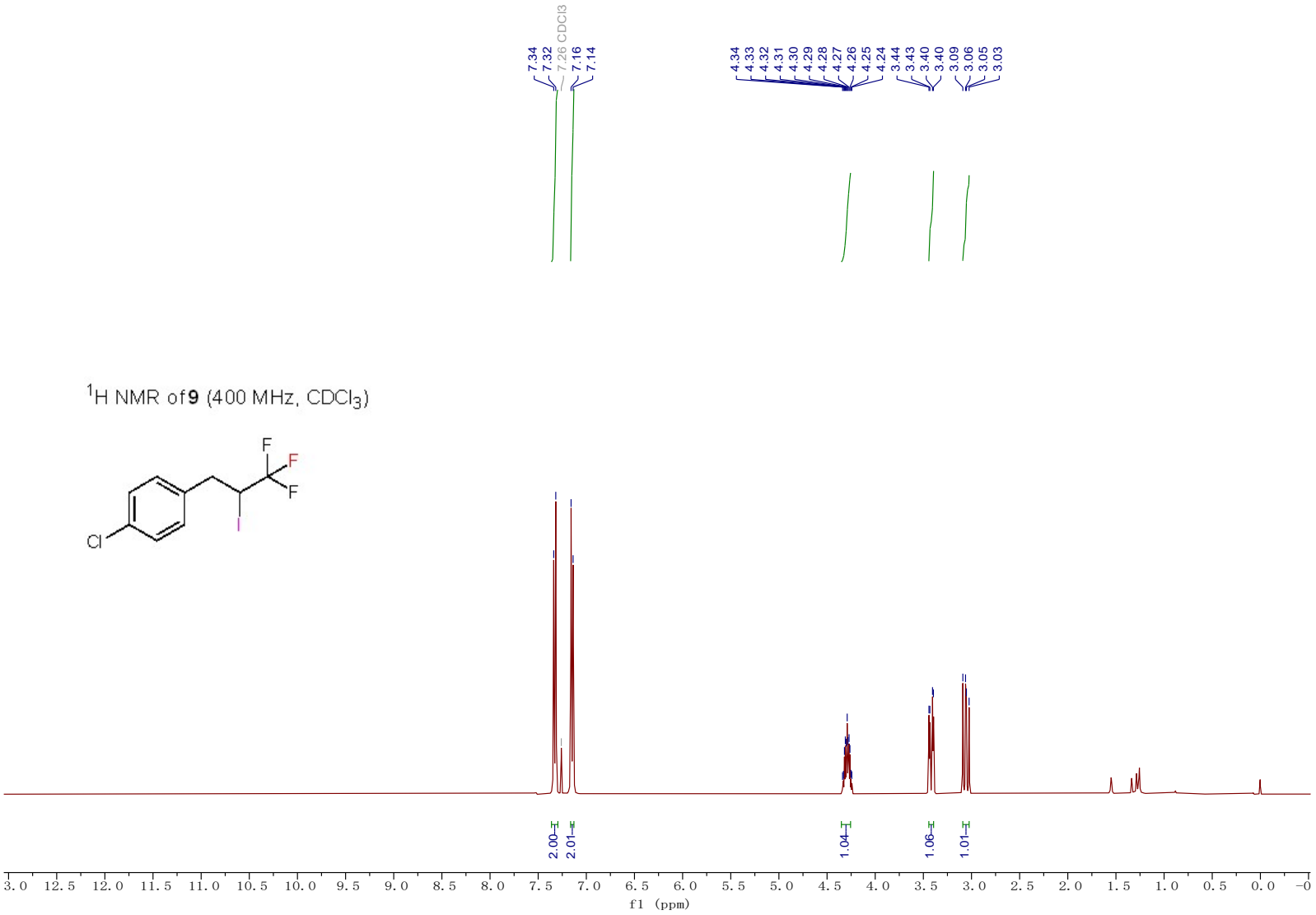

150.55
133.99
128.73
127.96
125.76
125.73
123.55
121.35
77.16 CDCl3
39.01
38.99
34.68
31.47
26.08
25.84
25.60
25.36
13C NMR of 7 (126 MHz, CDCl3)
F
F
F
I
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

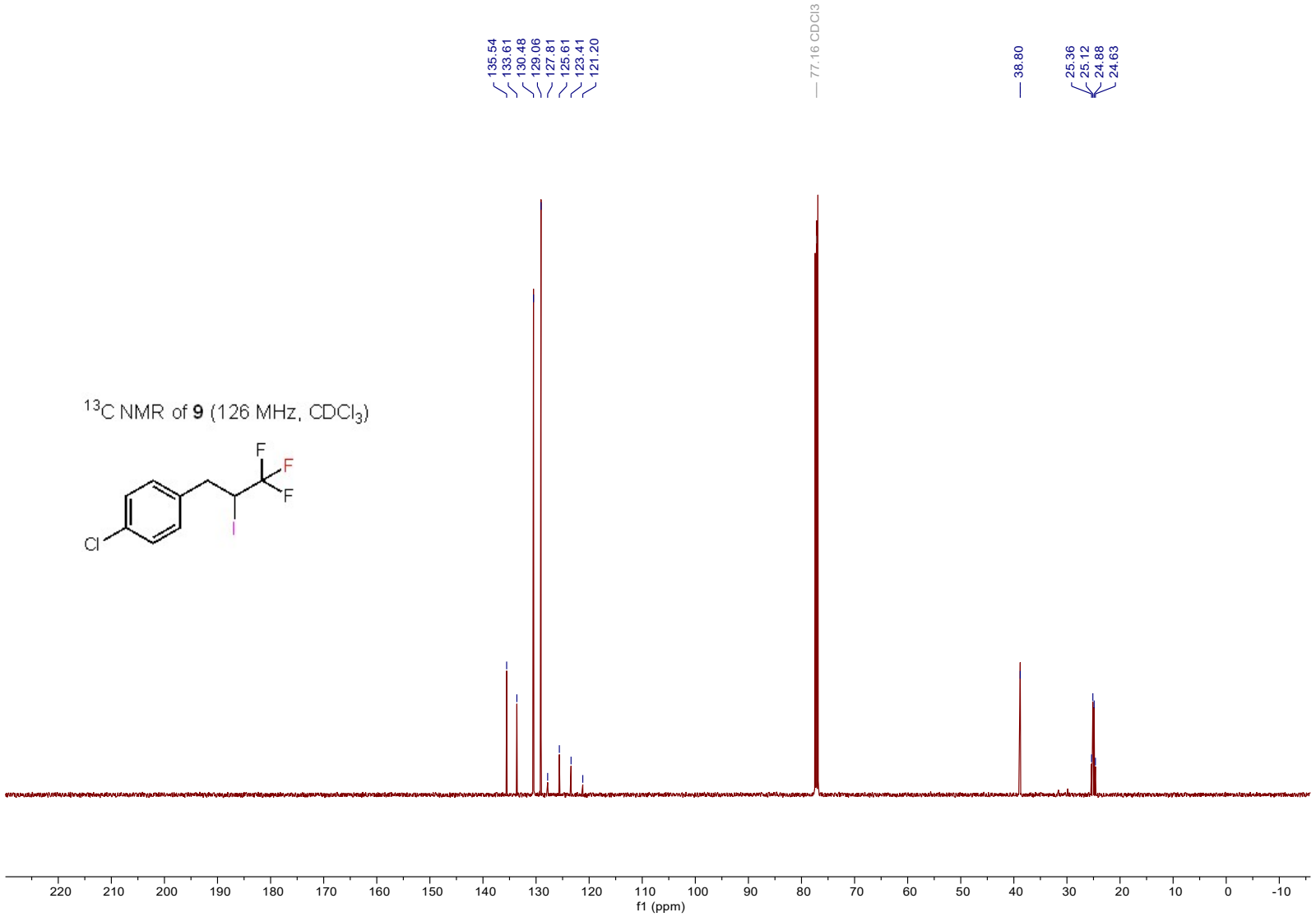

-69.12
-69.15
19F NMR of 7 (376 MHz, CDCl3)
F
F
F
I
-69.12
-69.15
-68.4
-68.6
-68.8
-69.0
-69.2
-69.4
-69.6
-69.8
-70.0
f1 (ppm)
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

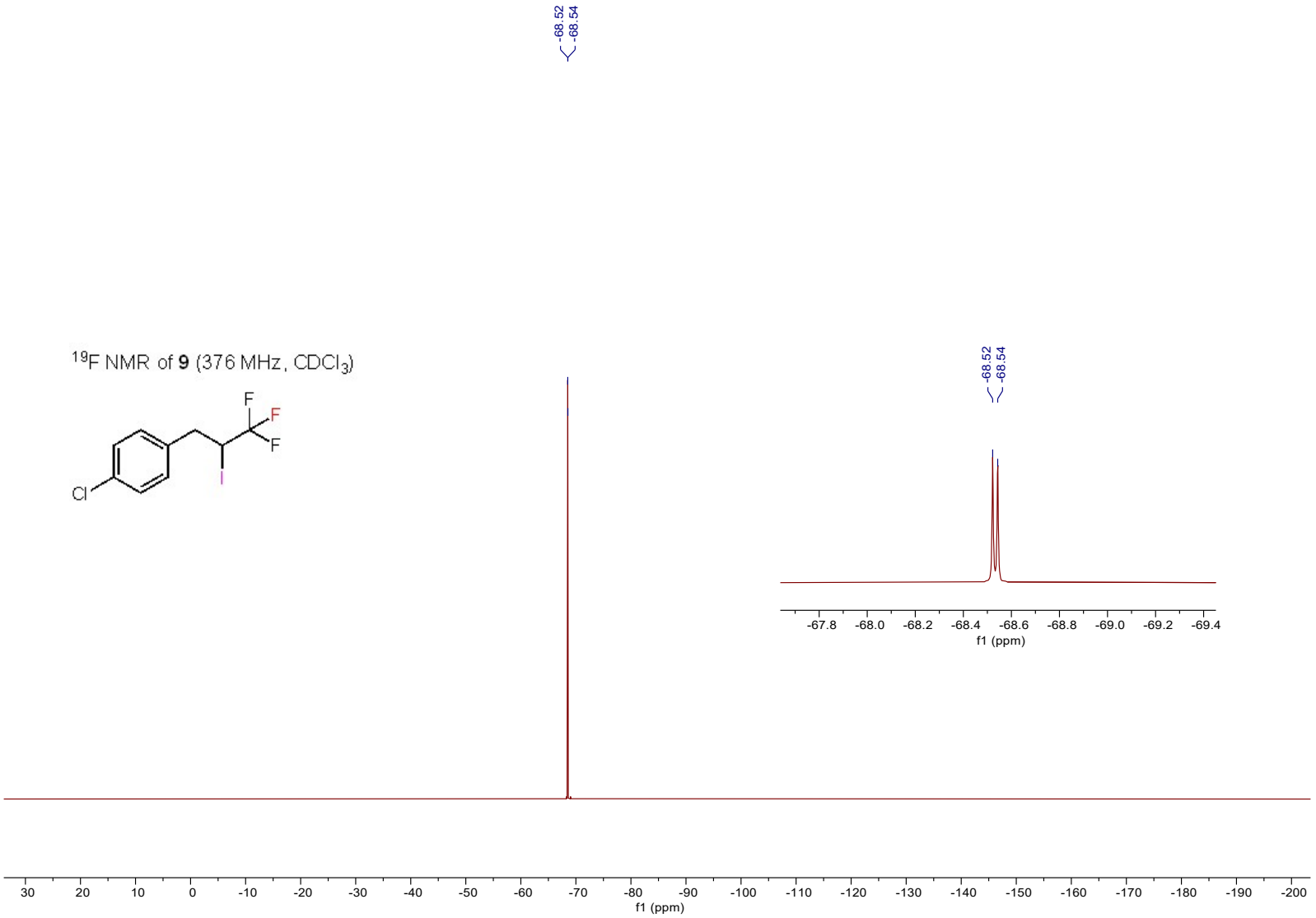

7.62
7.60
7.58
7.48
7.46
7.44
7.38
7.37
7.35
7.30
7.28
7.26 CDCl3
4.43
4.42
4.41
4.40
4.39
4.38
4.38
4.37
4.36
4.35
4.34
3.53
3.52
3.49
3.48
3.17
3.14
3.13
3.11
1H NMR of 8 (400 MHz, CDCl3)
F
F
F
I
4.00
2.00
1.03
2.00
1.01
1.00
1.01
f1 (ppm)

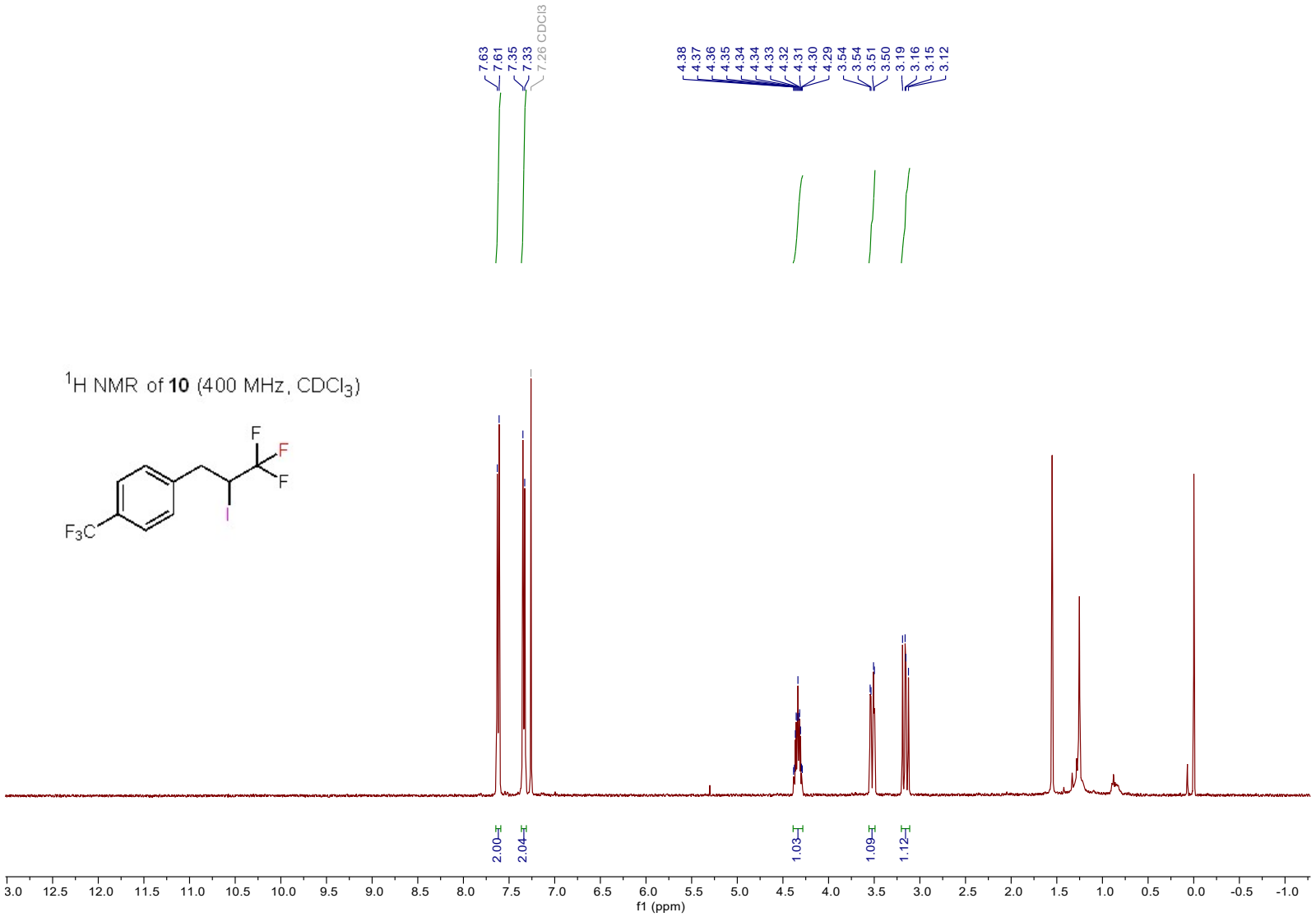

140.68
140.55
138.05
136.09
129.52
128.96
127.94
127.57
127.53
127.19
125.73
123.53
121.32
77.16 CDCl3
39.11
25.76
25.52
25.28
25.04
13C NMR of 8 (126 MHz, CDCl3)
F
F
F
I
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

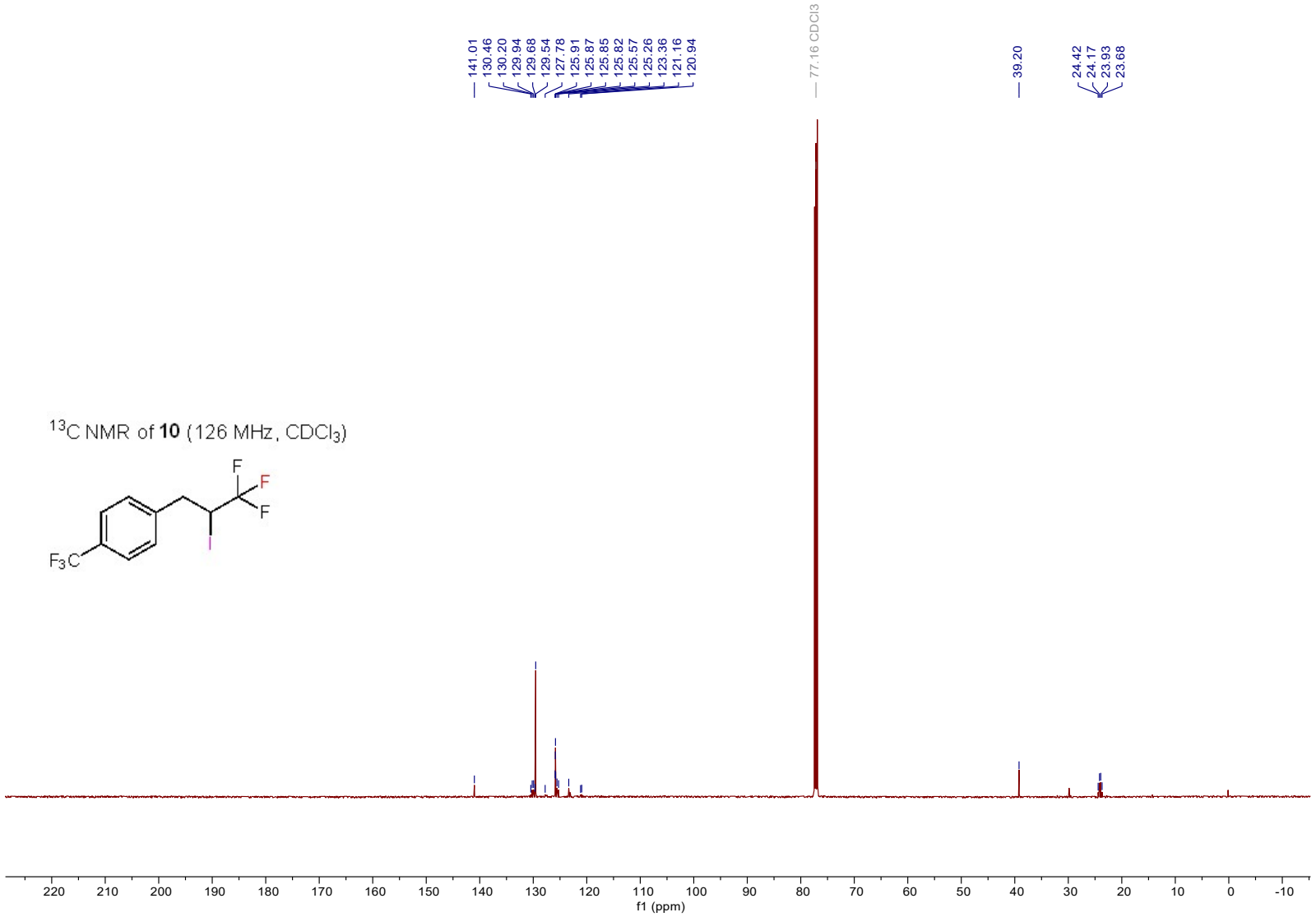

-68.67
-68.69
19F NMR of 8 (376 MHz, CDCl3)
F
F
F
I
-68.67
-68.69
-68.45 -68.50 -68.55 -68.60 -68.65 -68.70 -68.75 -68.80 -68.85 -68.90
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.34
7.32
7.26 CDCl3
7.16
7.14
4.34
4.33
4.32
4.31
4.30
4.29
4.28
4.27
4.26
4.25
4.24
3.44
3.43
3.40
3.40
3.09
3.06
3.05
3.03
1H NMR of9 (400 MHz, CDCl3)
F
F
F
I
Cl
2.00
2.01
1.04
1.06
1.01
f1 (ppm)

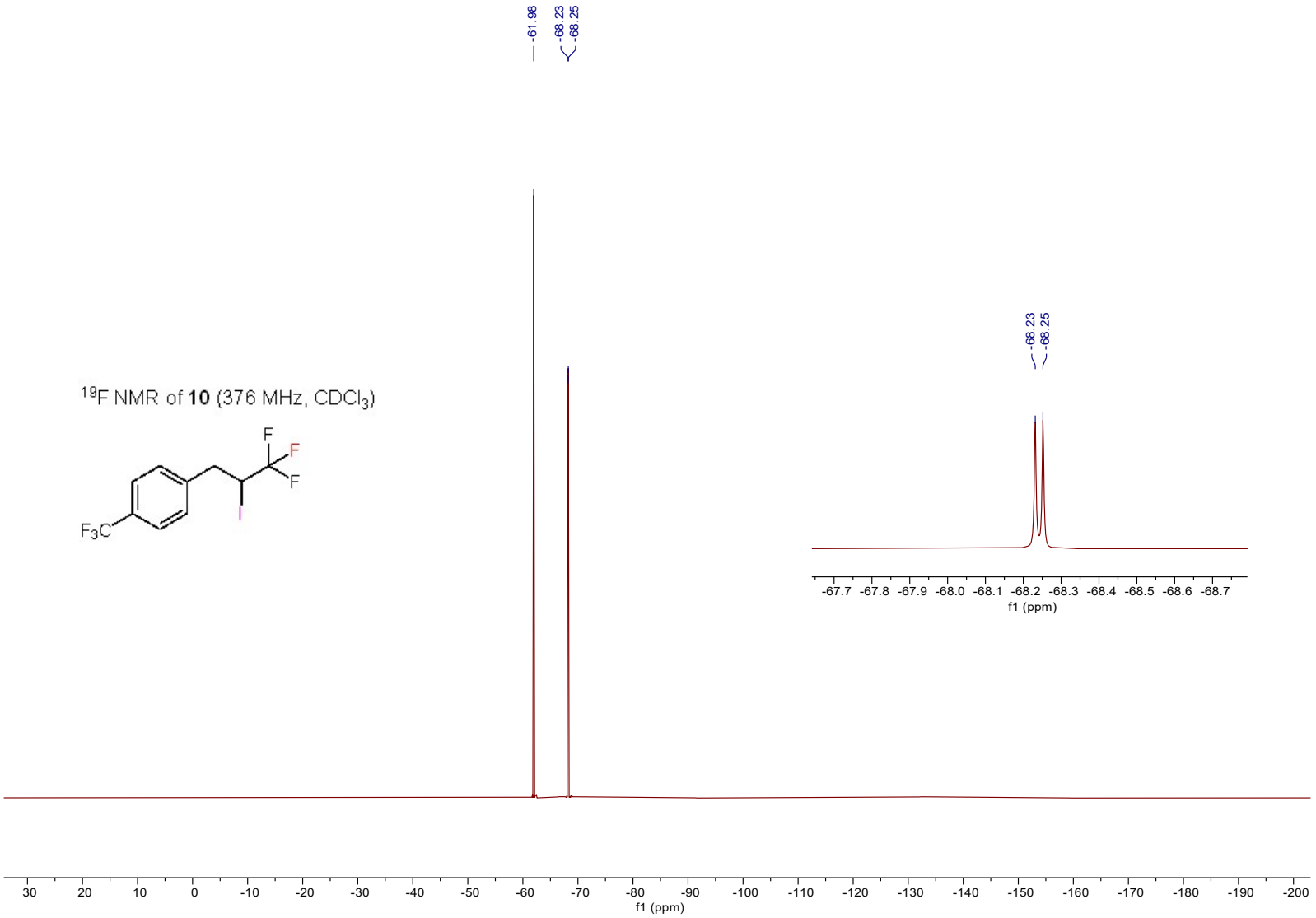

135.54
133.61
130.48
129.06
127.81
125.61
123.41
121.20
77.16 CDCl3
38.80
25.36
25.12
24.88
24.63
13C NMR of 9 (126 MHz, CDCl3)
F
F
F
I
Cl
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

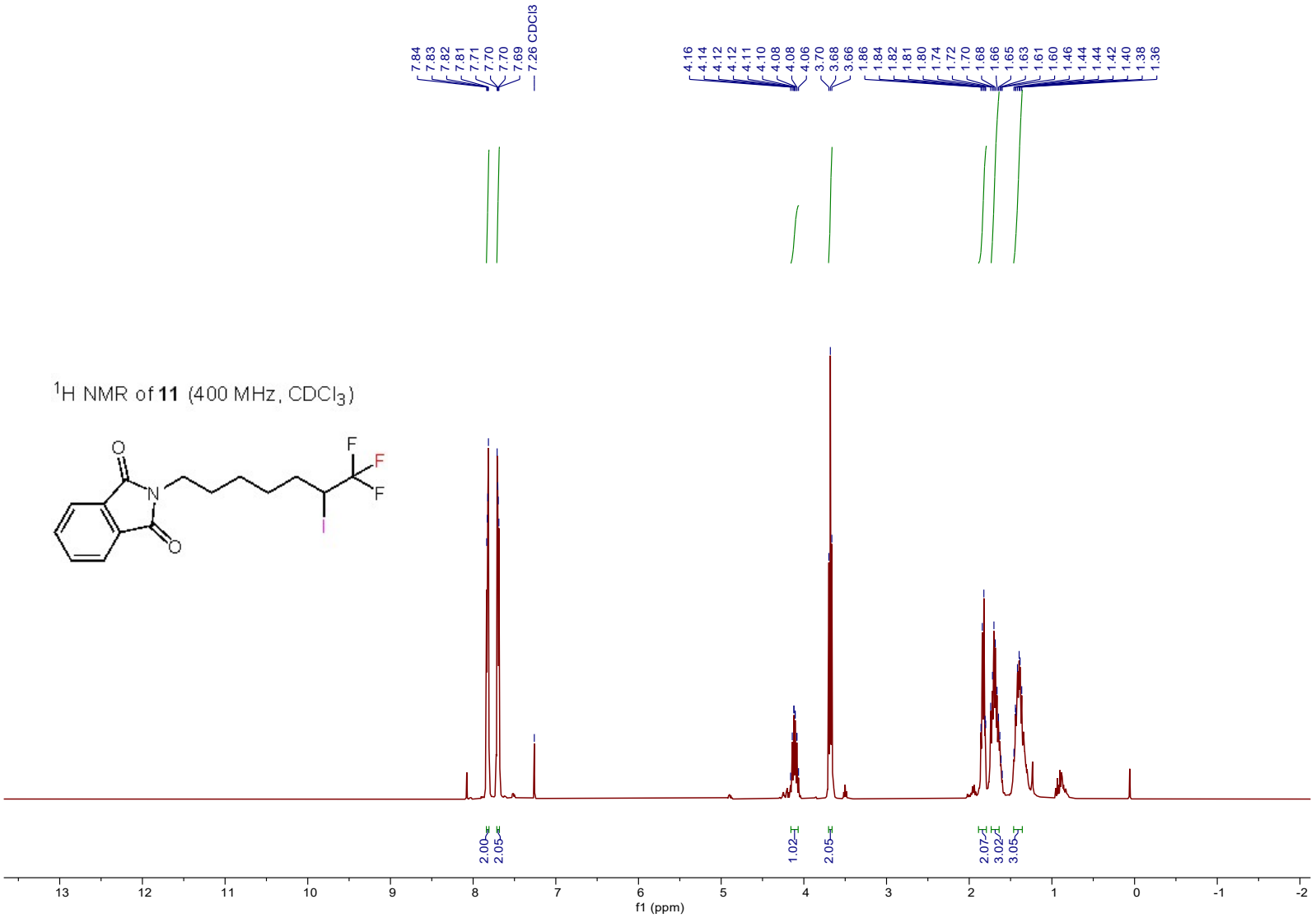

-68.52
-68.54
19F NMR of 9 (376 MHz, CDCl3)
F
F
F
Cl
I
-68.52
-68.54
-67.8
-68.0
-68.2
-68.4
-68.6
-68.8
-69.0
-69.2
-69.4
f1 (ppm)
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

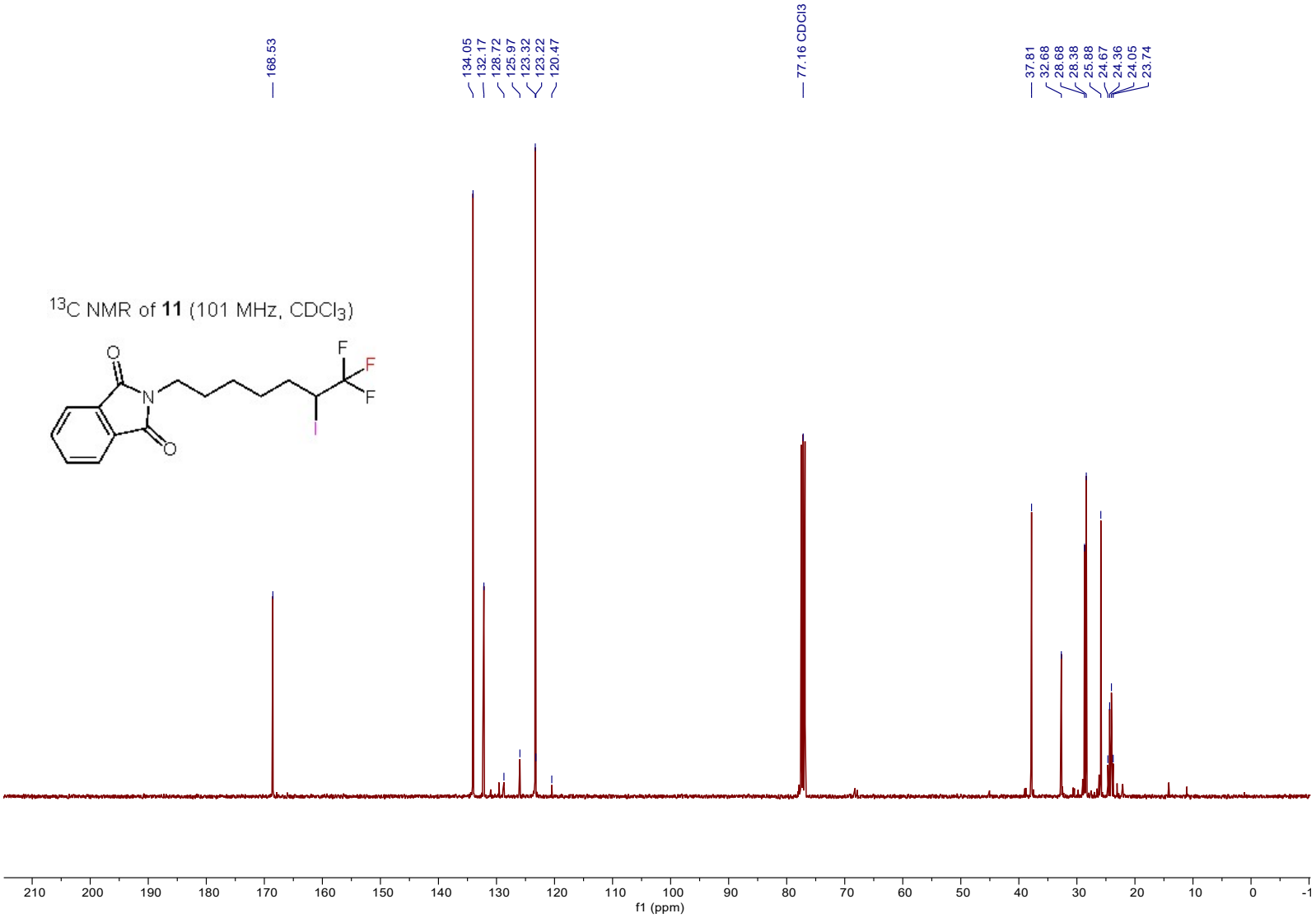

7.63
7.61
7.35
7.33
7.26 CDCl3
4.38
4.37
4.36
4.35
4.34
4.34
4.33
4.32
4.31
4.30
4.29
3.54
3.54
3.51
3.50
3.19
3.16
3.15
3.12
1H NMR of 10 (400 MHz, CDCl3)
F
F
F
F3C
I
2.00
2.04
1.03
1.09
1.12
3.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

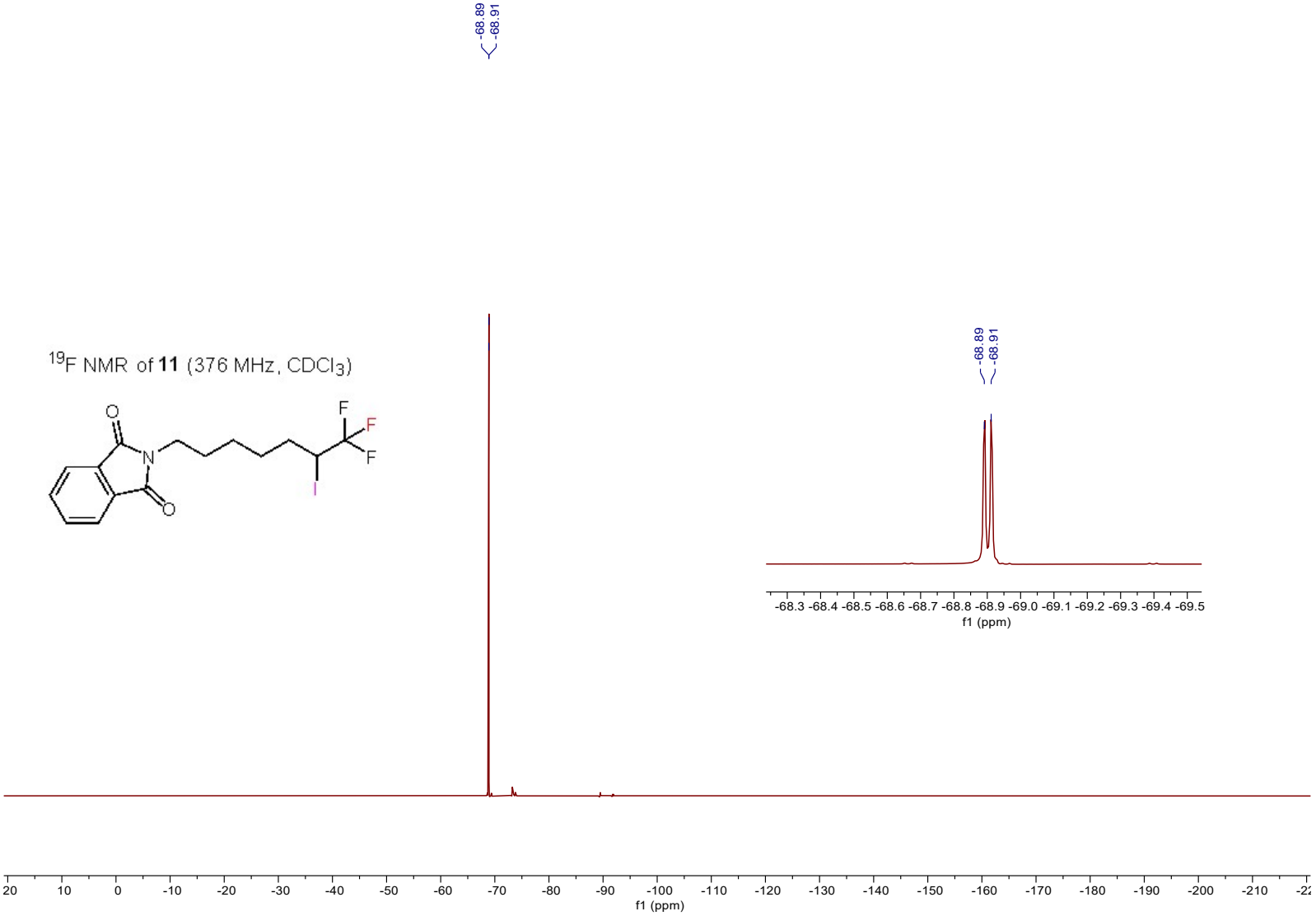


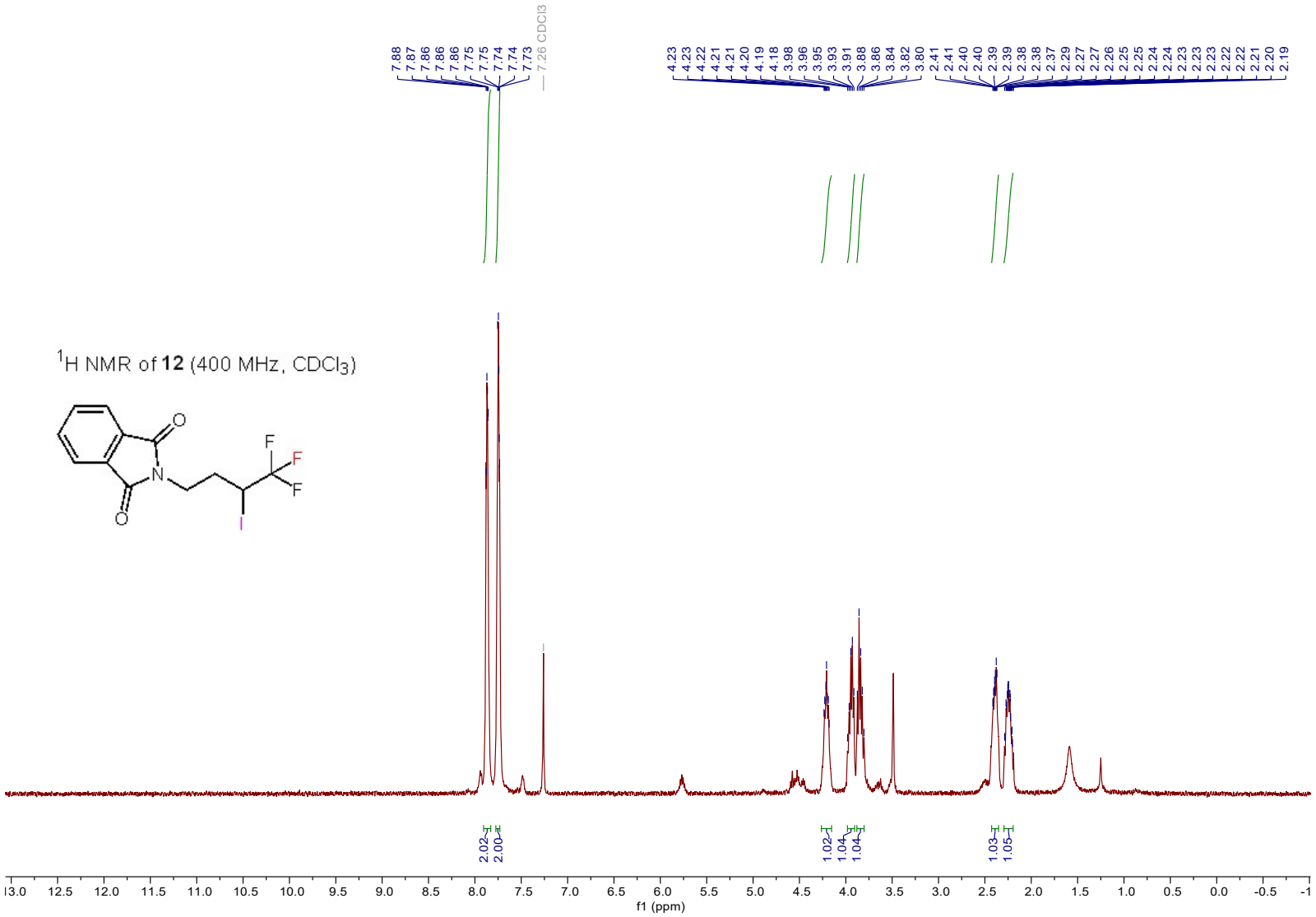
^{13}C NMR of **10** (126 MHz, $CDCl_3$)

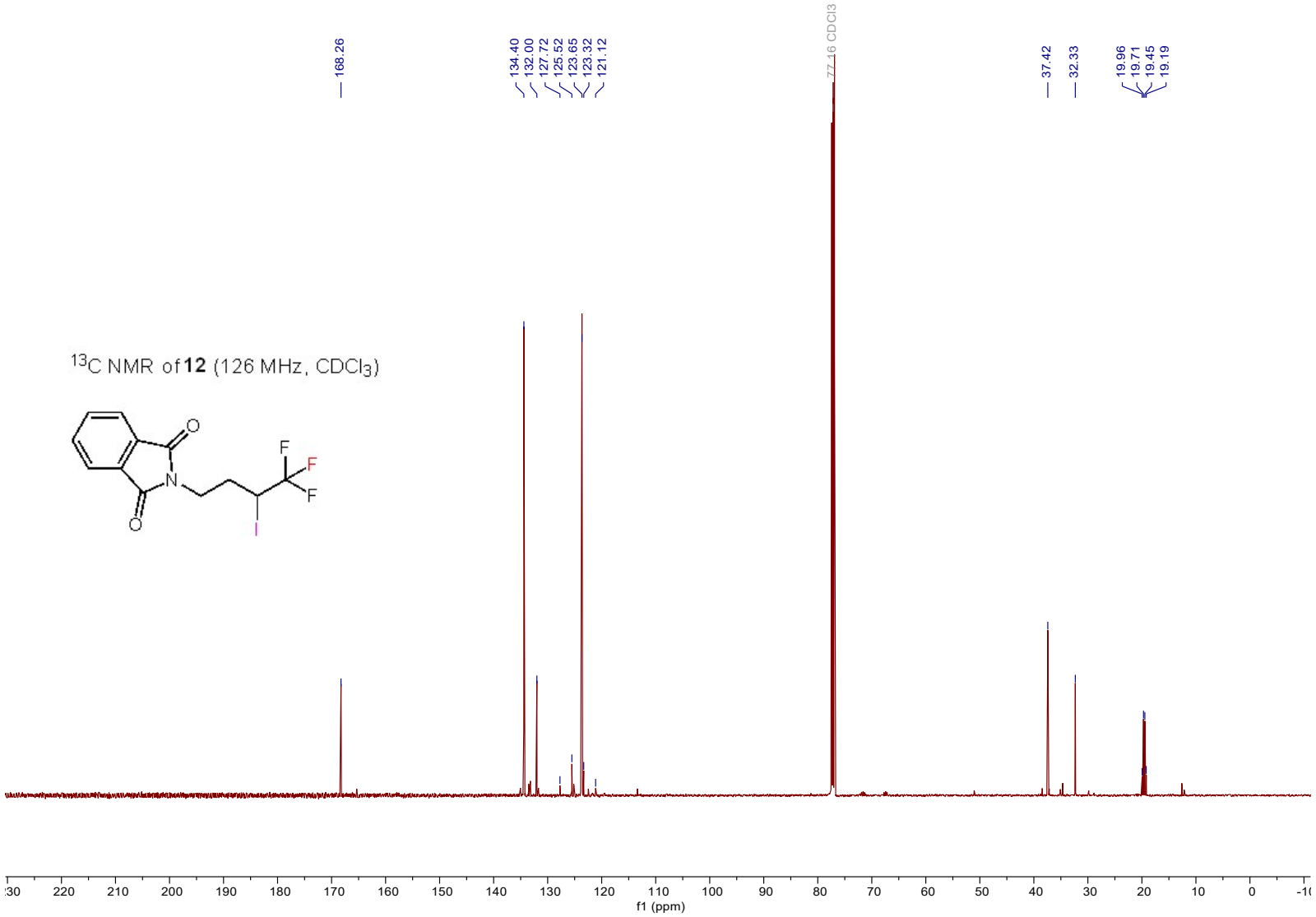

-61.98
-68.23
-68.25
^{19}F NMR of **10** (376 MHz, $CDCl_3$)
F
F
F
I
F_3C
-68.23
-68.25
-67.7 -67.8 -67.9 -68.0 -68.1 -68.2 -68.3 -68.4 -68.5 -68.6 -68.7
f1 (ppm)
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

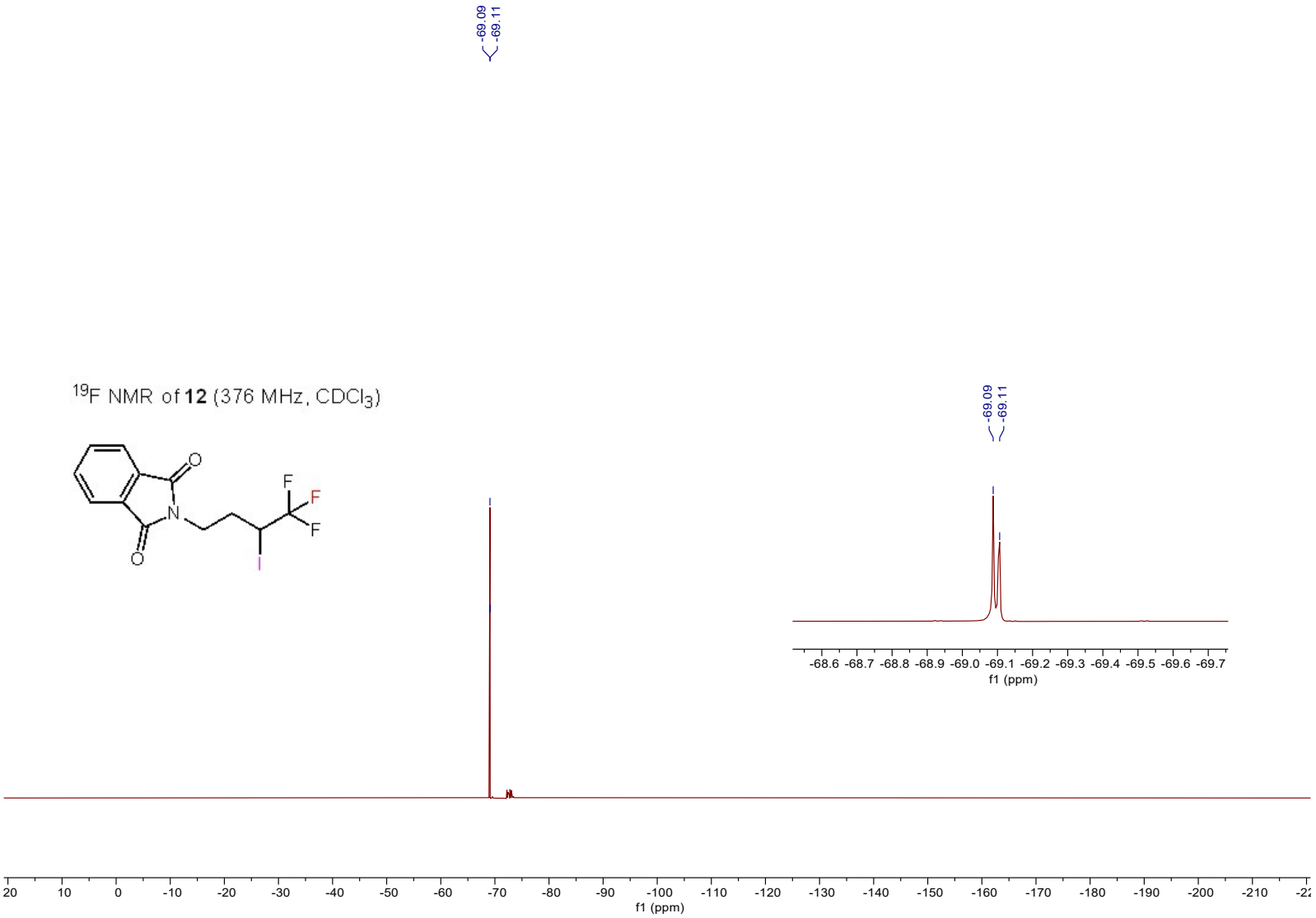

7.84
7.83
7.82
7.81
7.71
7.70
7.70
7.69
7.26 CDCl3
4.16
4.14
4.12
4.12
4.11
4.10
4.08
4.08
4.06
3.70
3.68
3.66
1.86
1.84
1.82
1.81
1.80
1.74
1.72
1.70
1.68
1.66
1.65
1.63
1.61
1.60
1.46
1.44
1.44
1.42
1.40
1.38
1.36
1H NMR of 11 (400 MHz, CDCl3)
O
N
O
F
F
F
I
2.00
2.05
1.02
2.05
2.07
3.02
3.05
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

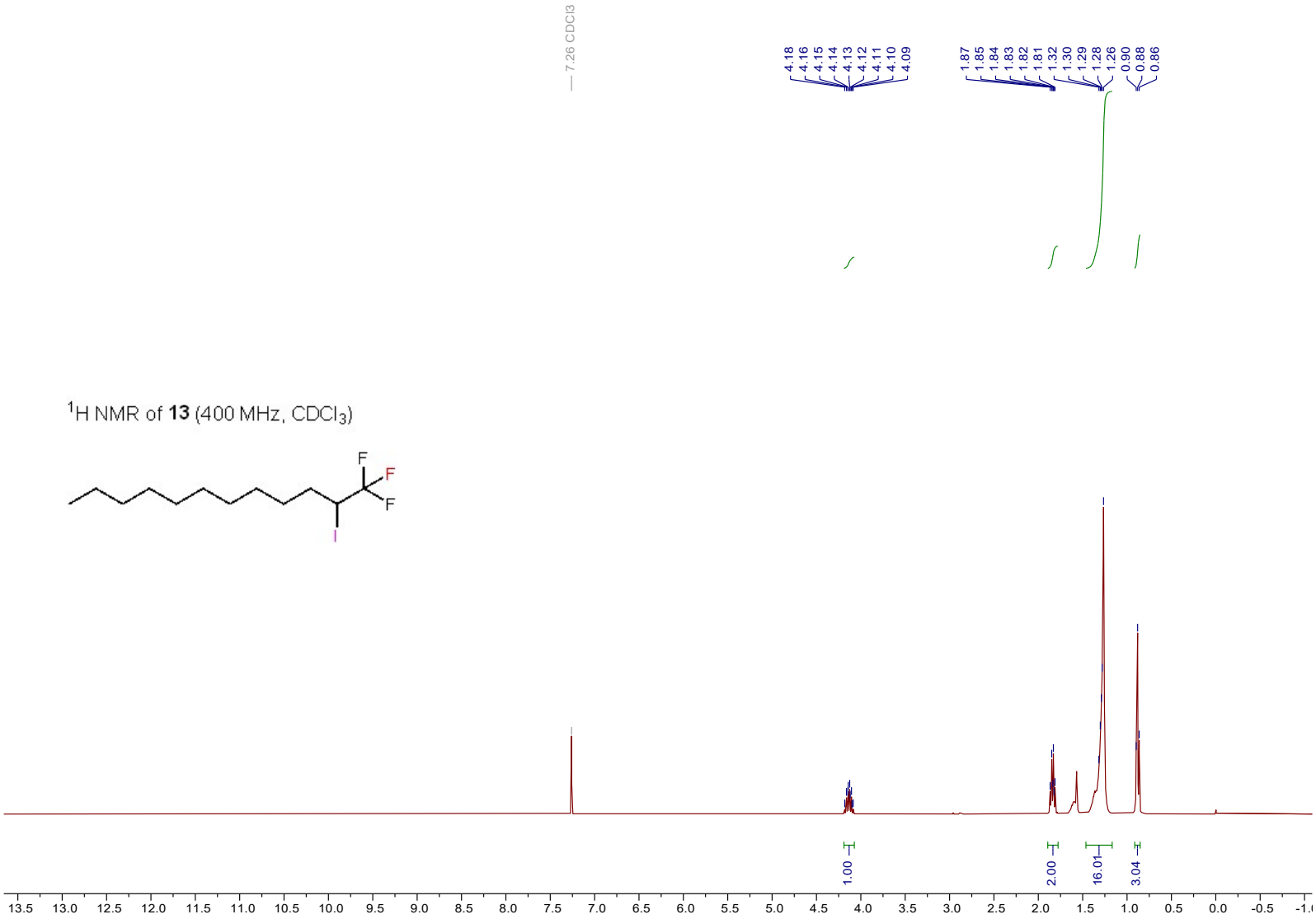

168.53
134.05
132.17
128.72
125.97
123.32
123.22
120.47
77.16 CDCl3
37.81
32.68
28.68
28.38
25.88
24.67
24.36
24.05
23.74
13C NMR of 11 (101 MHz, CDCl3)
O
N
O
F
F
F
I
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

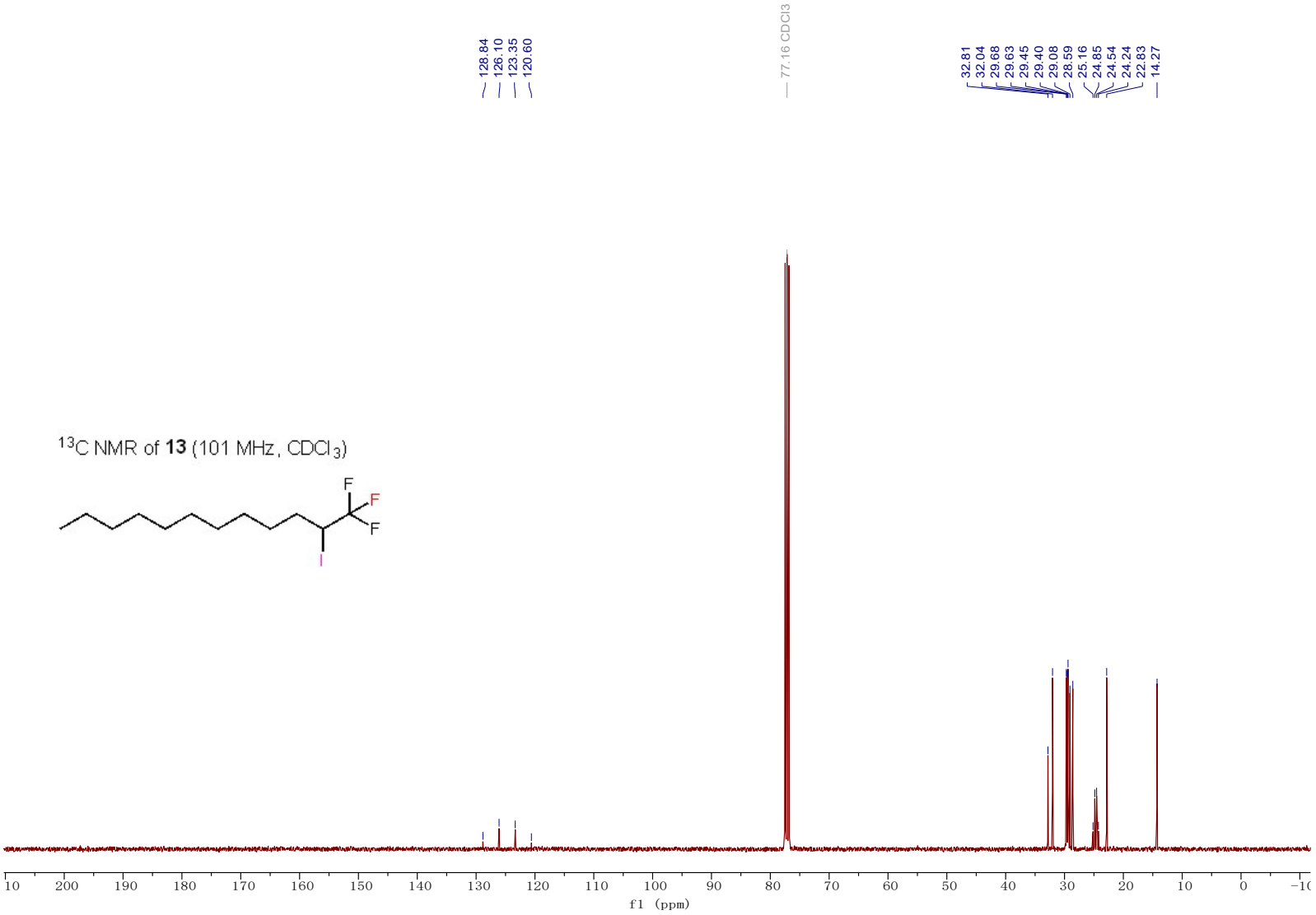

-68.89
-68.91
19F NMR of 11 (376 MHz, CDCl3)
O
N
O
F
F
F
I
-68.89
-68.91
-68.3 -68.4 -68.5 -68.6 -68.7 -68.8 -68.9 -69.0 -69.1 -69.2 -69.3 -69.4 -69.5
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

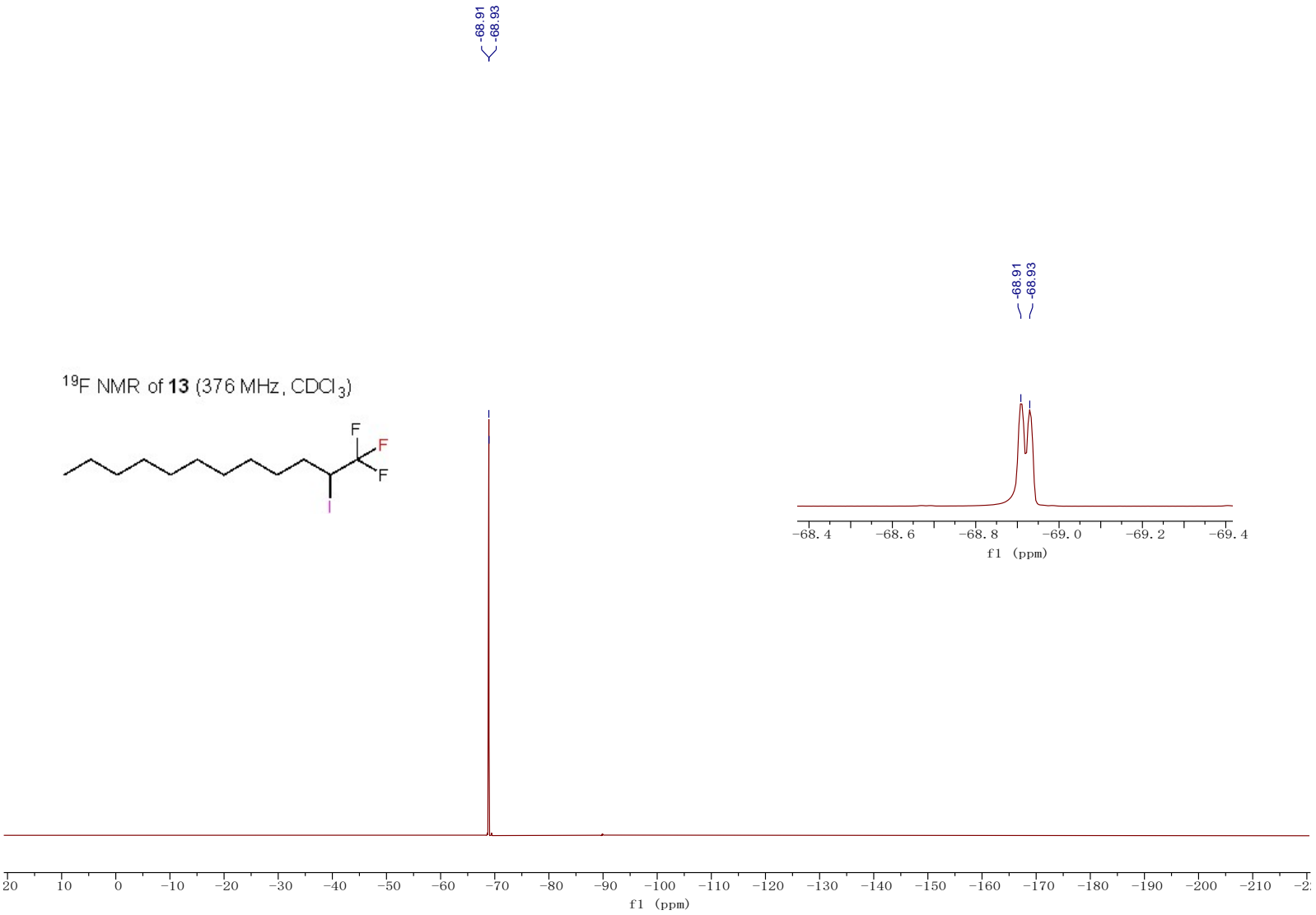

7.88
7.87
7.86
7.86
7.86
7.75
7.75
7.74
7.74
7.73
7.26 CDCl3
4.23
4.23
4.22
4.21
4.21
4.20
4.19
4.18
3.98
3.96
3.95
3.93
3.91
3.88
3.86
3.84
3.82
3.80
2.41
2.41
2.40
2.40
2.39
2.39
2.38
2.38
2.37
2.29
2.27
2.27
2.26
2.25
2.25
2.24
2.24
2.23
2.23
2.22
2.22
2.21
2.20
2.19
1H NMR of 12 (400 MHz, CDCl3)
O
O
N
F
F
F
I
2.02
2.00
1.02
1.04
1.04
1.03
1.05
13.0 12.5 12.0 11.5 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)

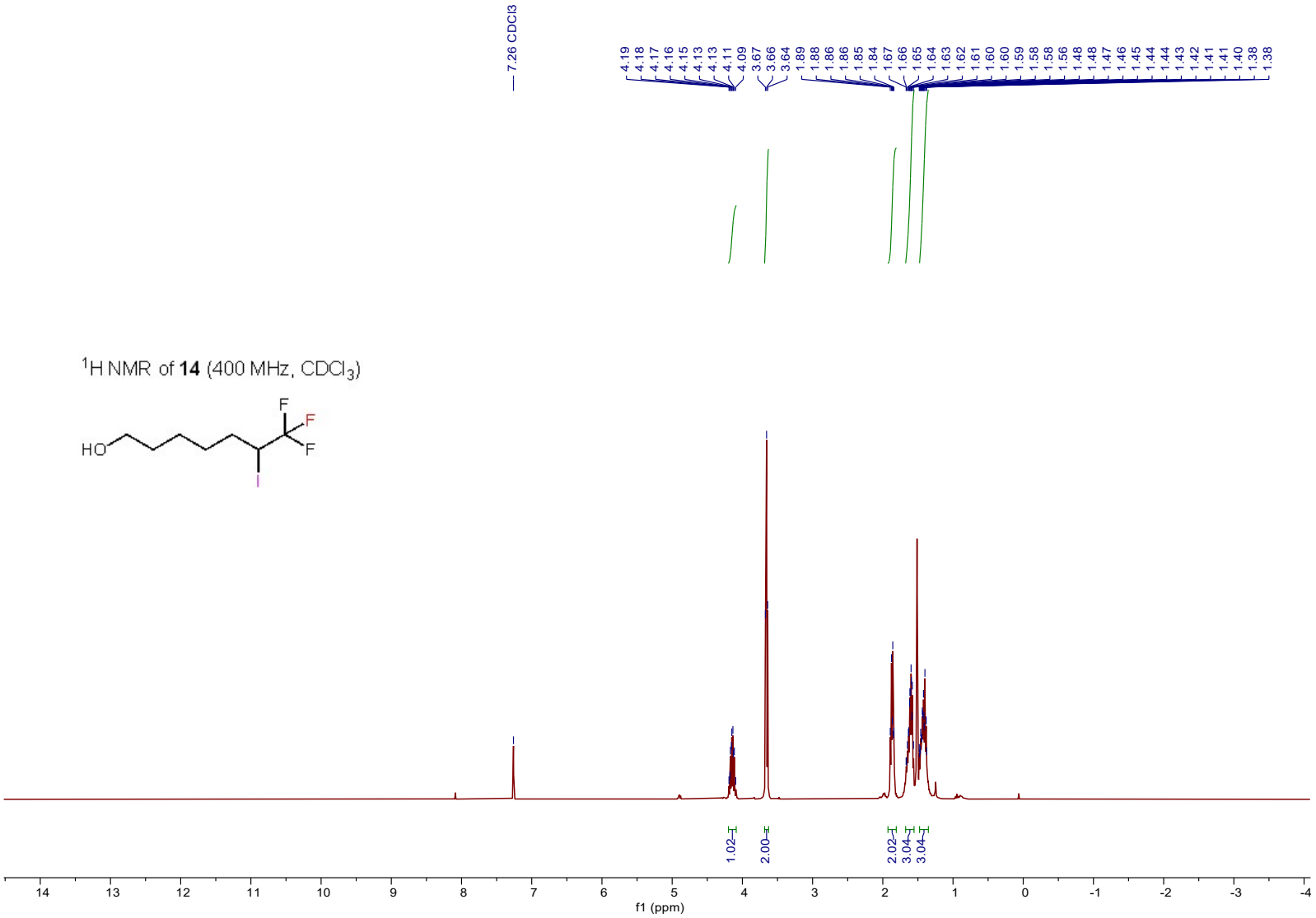

168.26
134.40
132.00
127.72
125.52
123.65
123.32
121.12
77.16 CDCl3
37.42
32.33
19.96
19.71
19.45
19.19
13C NMR of 12 (126 MHz, CDCl3)
O
N
O
F
F
F
I
f1 (ppm)


-69.09
-69.11
19F NMR of 12 (376 MHz, CDCl3)
O
N
O
F
F
F
I
-69.09
-69.11
-68.6 -68.7 -68.8 -68.9 -69.0 -69.1 -69.2 -69.3 -69.4 -69.5 -69.6 -69.7
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

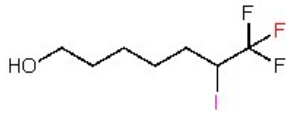

7.26 CDCl3
4.18
4.16
4.15
4.14
4.13
4.12
4.11
4.10
4.09
1.87
1.85
1.84
1.83
1.82
1.81
1.32
1.30
1.29
1.28
1.26
0.90
0.88
0.86
1H NMR of 13 (400 MHz, CDCl3)
F
F
F
I
1.00
2.00
16.01
3.04
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

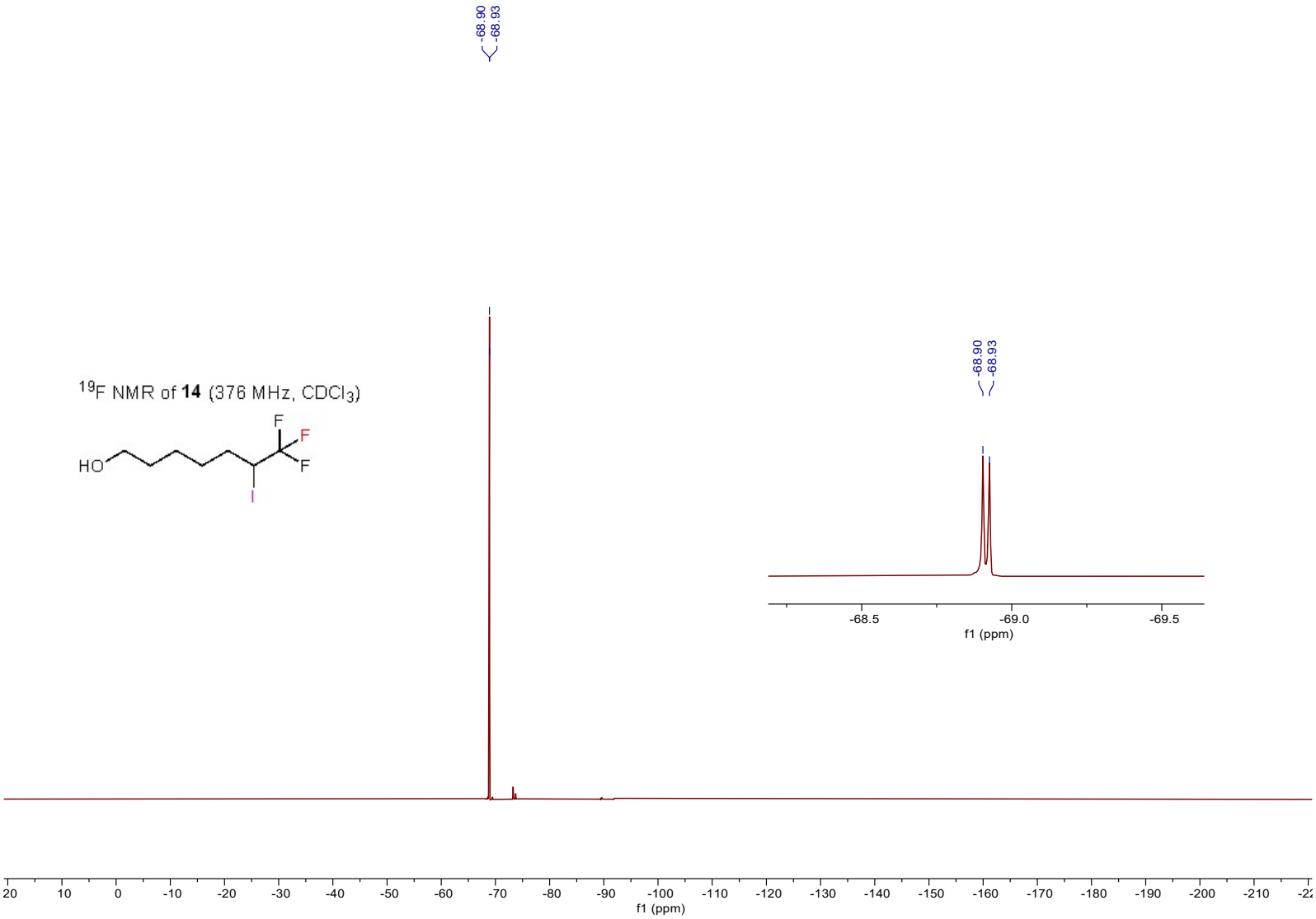

128.84
126.10
123.35
120.60
77.16 CDCl3
32.81
32.04
29.68
29.63
29.45
29.40
29.08
28.59
25.16
24.85
24.54
24.24
22.83
14.27
13C NMR of 13 (101 MHz, CDCl3)
F
F
F
I
f1 (ppm)

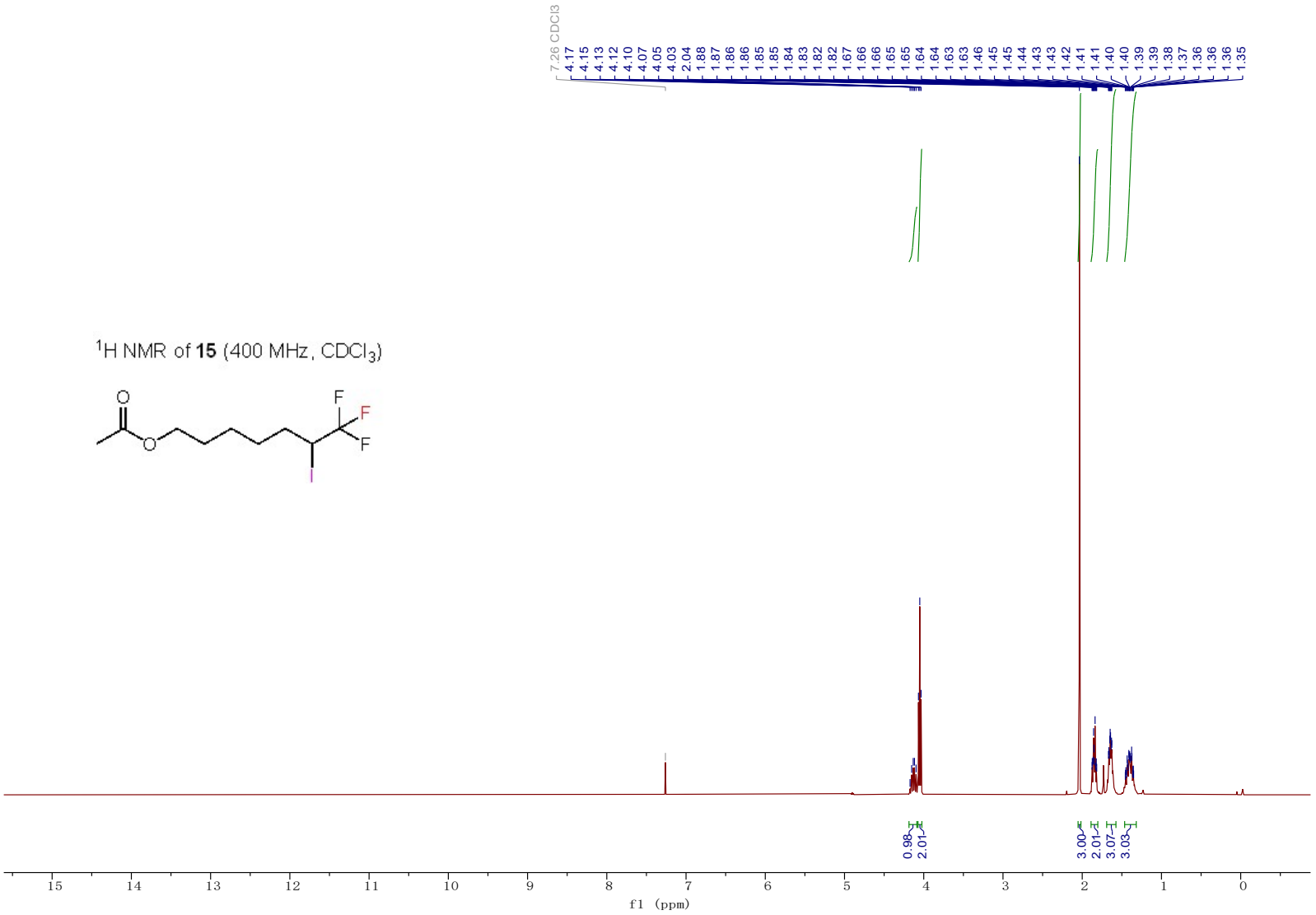

-68.91
-68.93
19F NMR of 13 (376 MHz, CDCl3)
F
F
F
I
-68.91
-68.93
-68.4
-68.6
-68.8
-69.0
-69.2
-69.4
f1 (ppm)
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

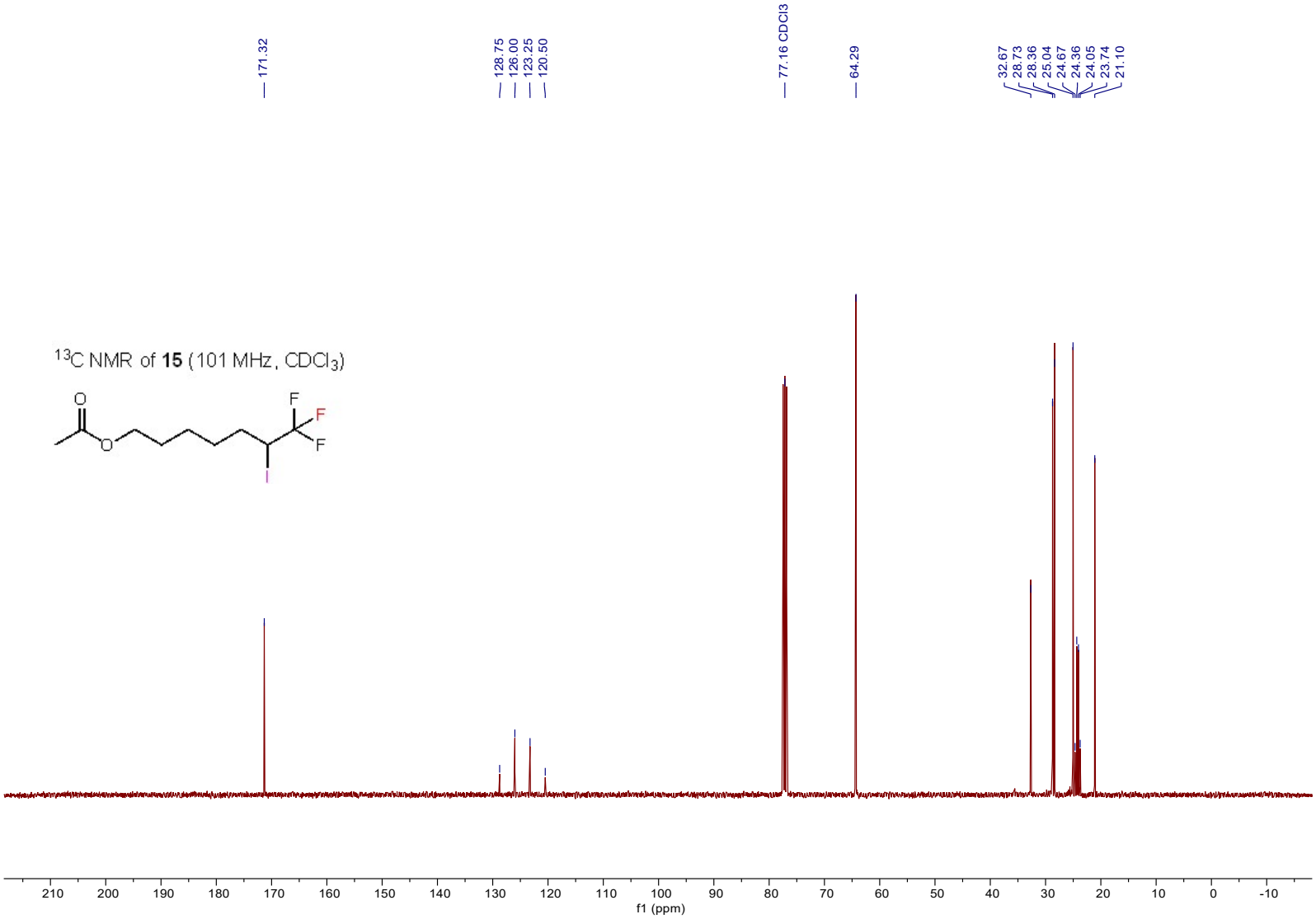

7.26 CDCl3
4.19
4.18
4.17
4.16
4.15
4.13
4.13
4.11
4.09
3.67
3.66
3.64
1.89
1.88
1.86
1.86
1.85
1.84
1.67
1.66
1.65
1.64
1.63
1.62
1.61
1.60
1.60
1.59
1.58
1.58
1.56
1.48
1.48
1.47
1.46
1.45
1.44
1.44
1.43
1.42
1.41
1.41
1.40
1.38
1.38
1H NMR of 14 (400 MHz, CDCl3)
HO
F
F
F
I
1.02
2.00
2.02
3.04
3.04
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

^{13}C NMR of **14** (101 MHz, $CDCl_3$)

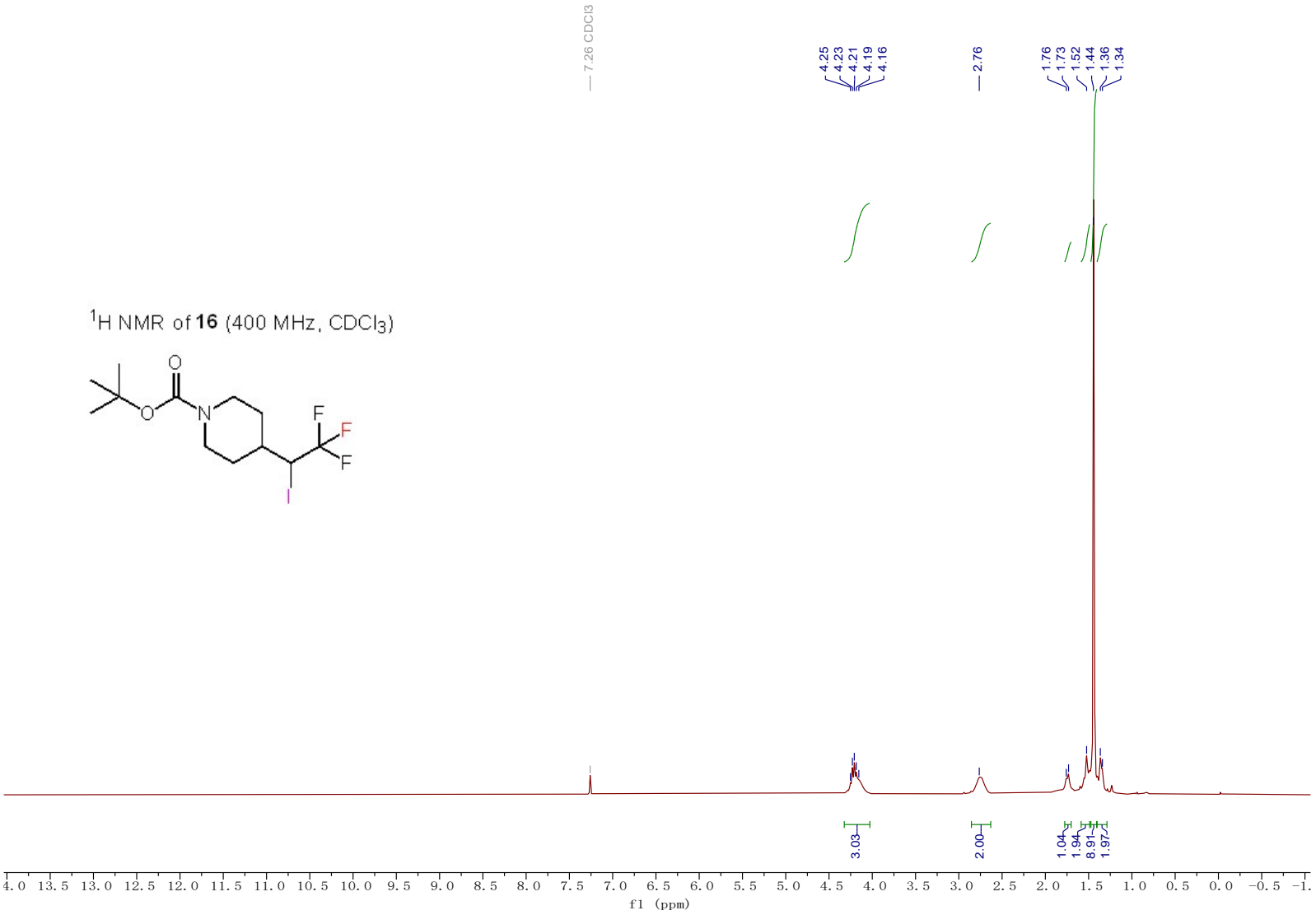


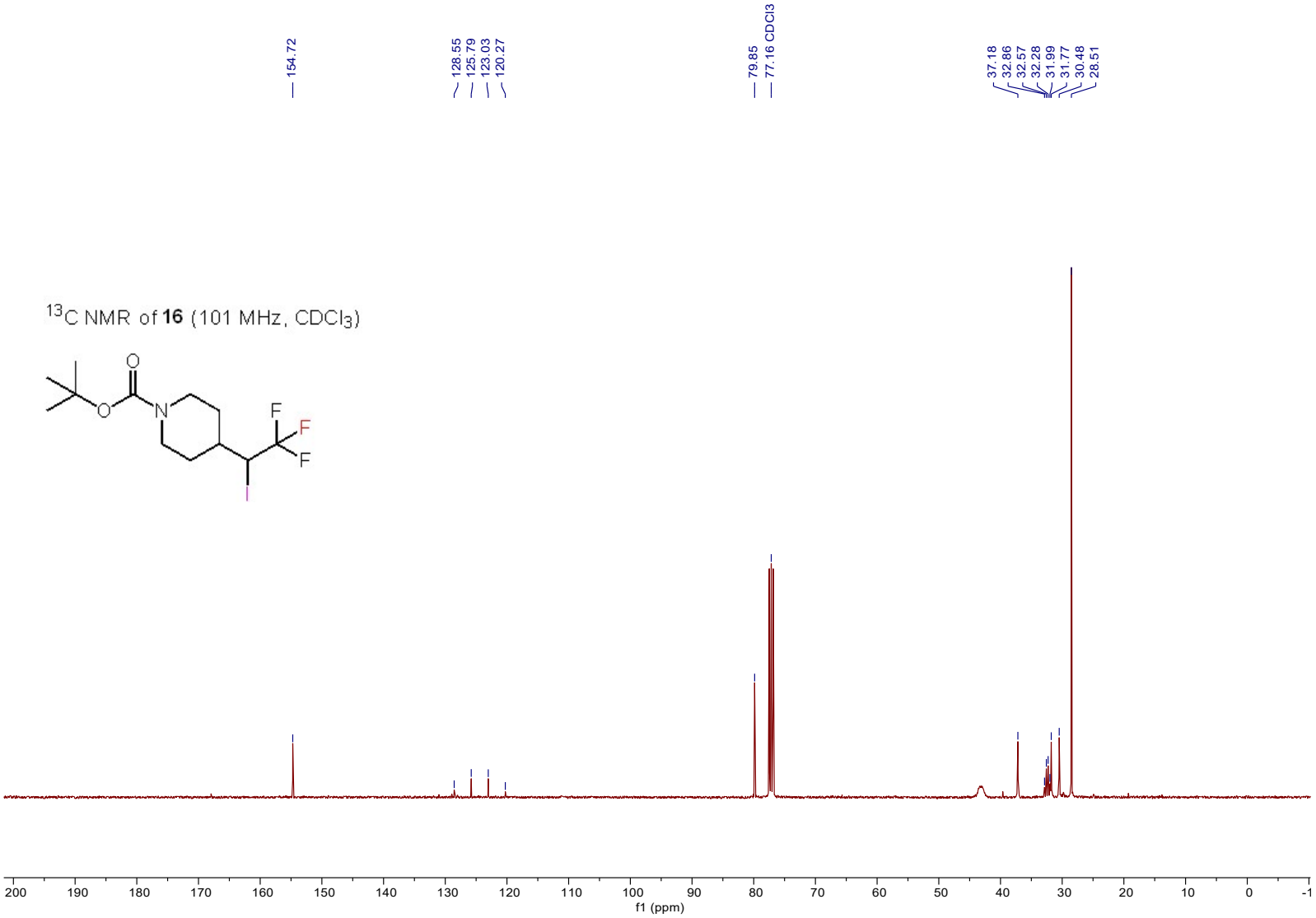

-68.90
-68.93
19F NMR of 14 (376 MHz, CDCl3)
HO
F
F
F
I
-68.90
-68.93
-68.5
-69.0
-69.5
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


^{1}H NMR of **15** (400 MHz, $CDCl_3$)
O
O
F
F
F
I
7.26 CDCl3
4.17
4.15
4.13
4.12
4.10
4.07
4.05
4.03
2.04
1.88
1.87
1.86
1.86
1.85
1.85
1.84
1.83
1.82
1.82
1.67
1.66
1.66
1.65
1.65
1.64
1.64
1.63
1.63
1.46
1.45
1.45
1.44
1.43
1.43
1.42
1.41
1.41
1.40
1.40
1.39
1.39
1.38
1.37
1.36
1.36
1.35
0.98
2.01
3.00
2.01
3.07
3.03
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

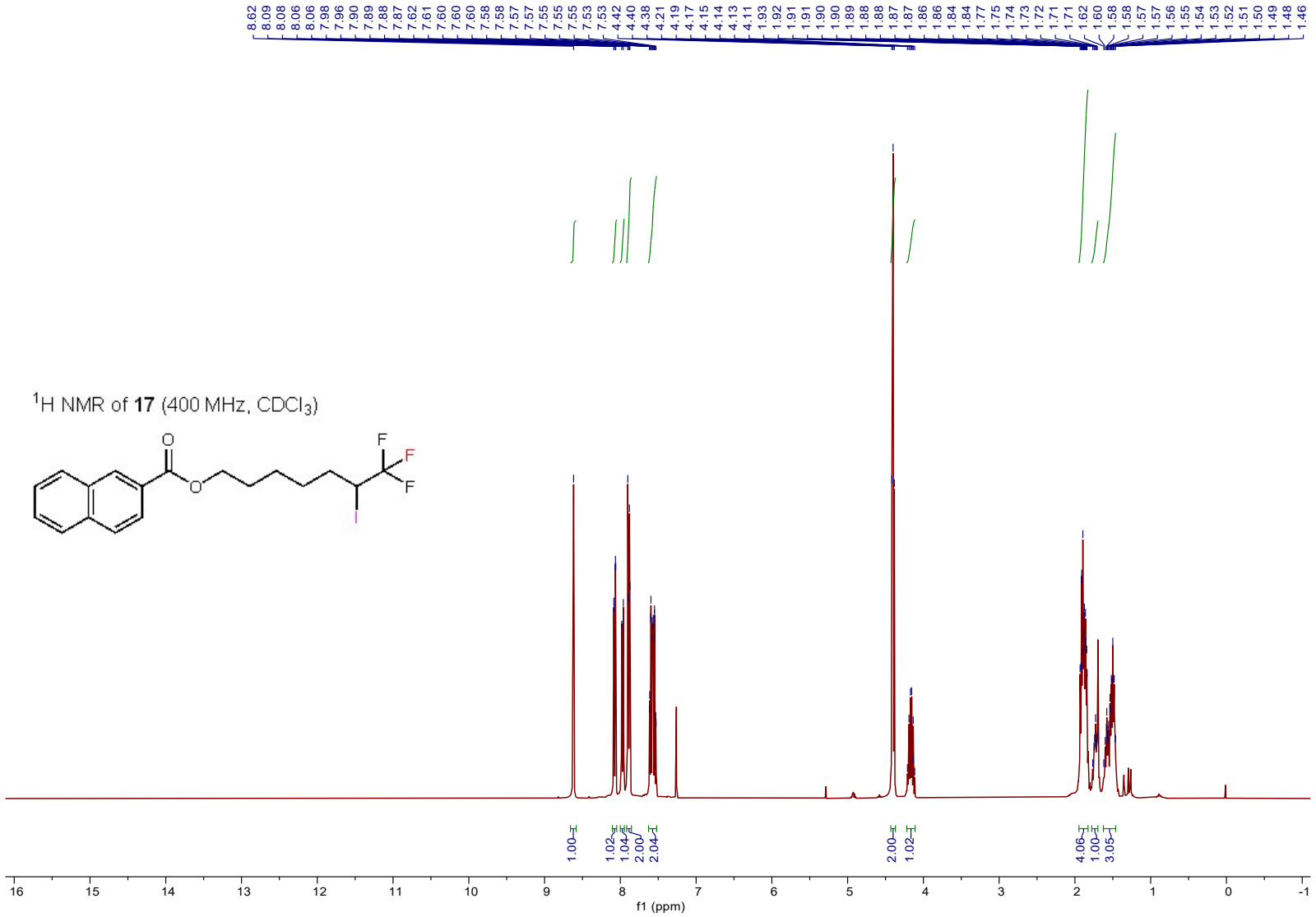

171.32
128.75
126.00
123.25
120.50
77.16 CDCl3
64.29
32.67
28.73
28.36
25.04
24.67
24.36
24.05
23.74
21.10
13C NMR of 15 (101 MHz, CDCl3)
O
O
F
F
F
I
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

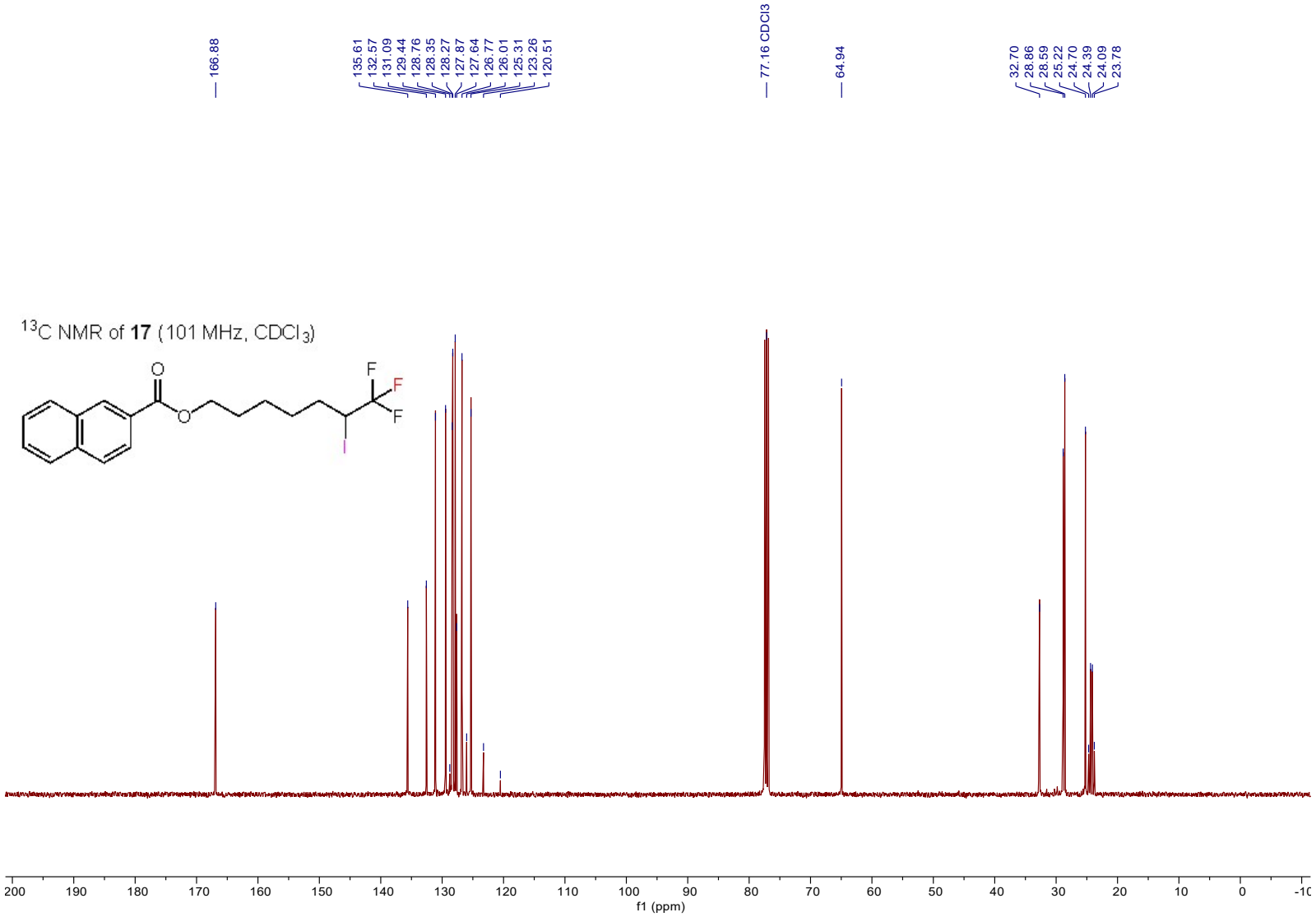

-68.92
-68.95
^{19}F NMR of **15** (376 MHz, $CDCl_3$)
O
O
F
F
F
I
-68.92
-68.95
-68.0 -68.2 -68.4 -68.6 -68.8 -69.0 -69.2 -69.4 -69.6 -69.8 -70.0
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

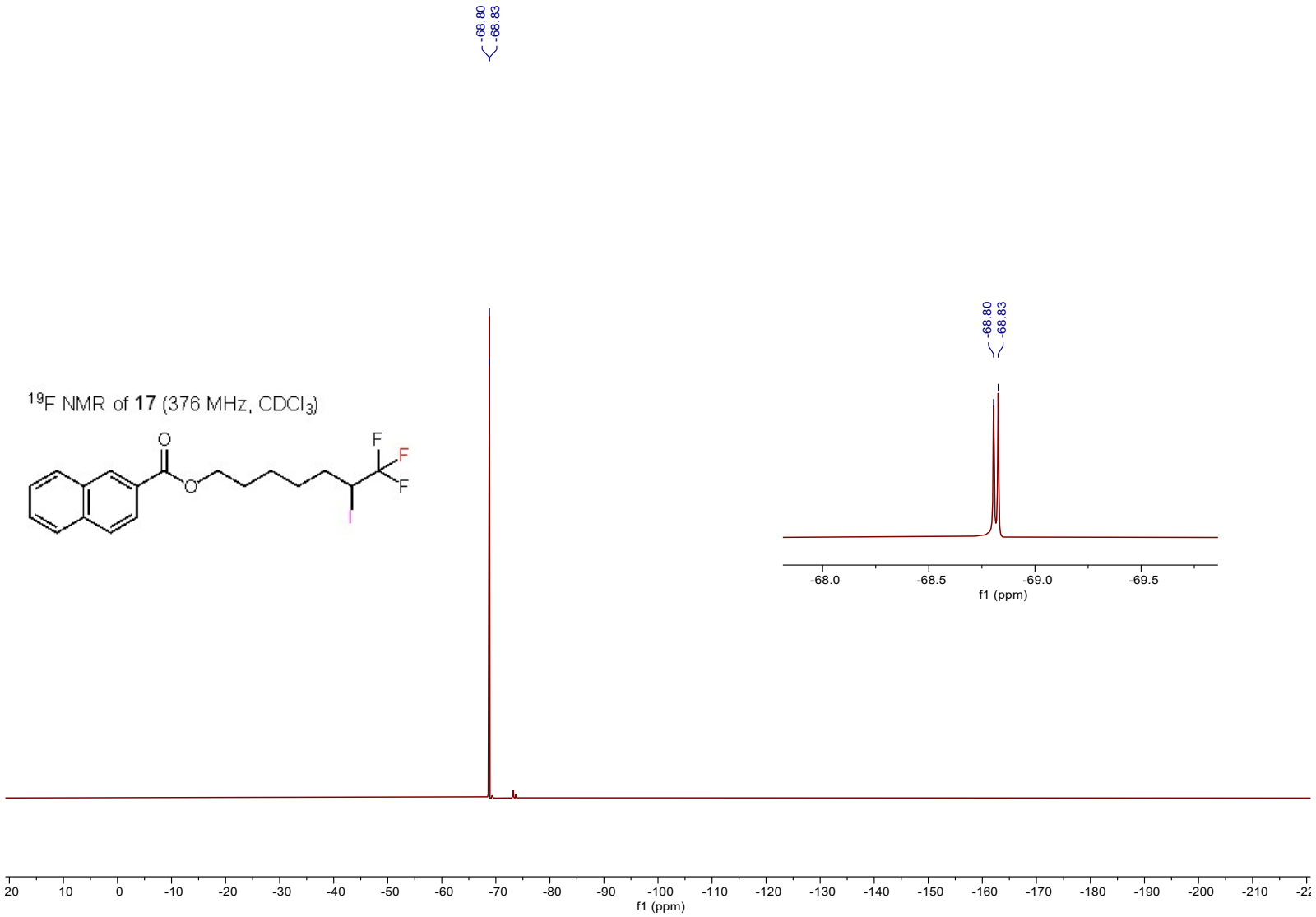

^{1}H NMR of **16** (400 MHz, $CDCl_3$)
7.26 CDCl3
4.25
4.23
4.21
4.19
4.16
2.76
1.76
1.73
1.52
1.44
1.36
1.34
3.03
2.00
1.04
1.94
8.91
1.97
f1 (ppm)

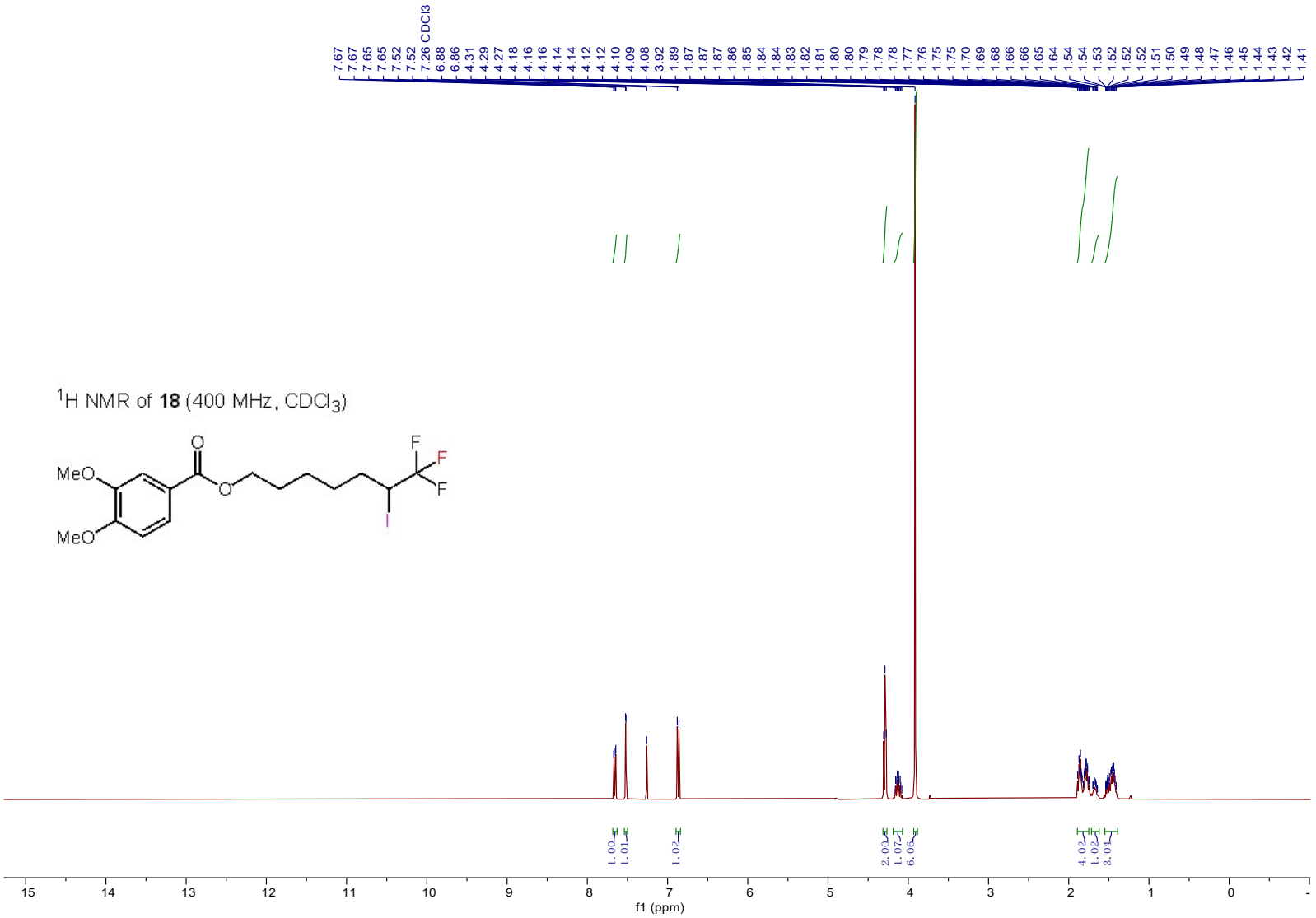

154.72
128.55
125.79
123.03
120.27
79.85
77.16 CDCl3
37.18
32.86
32.57
32.28
31.99
31.77
30.48
28.51
13C NMR of 16 (101 MHz, CDCl3)
O
O
N
F
F
F
I
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

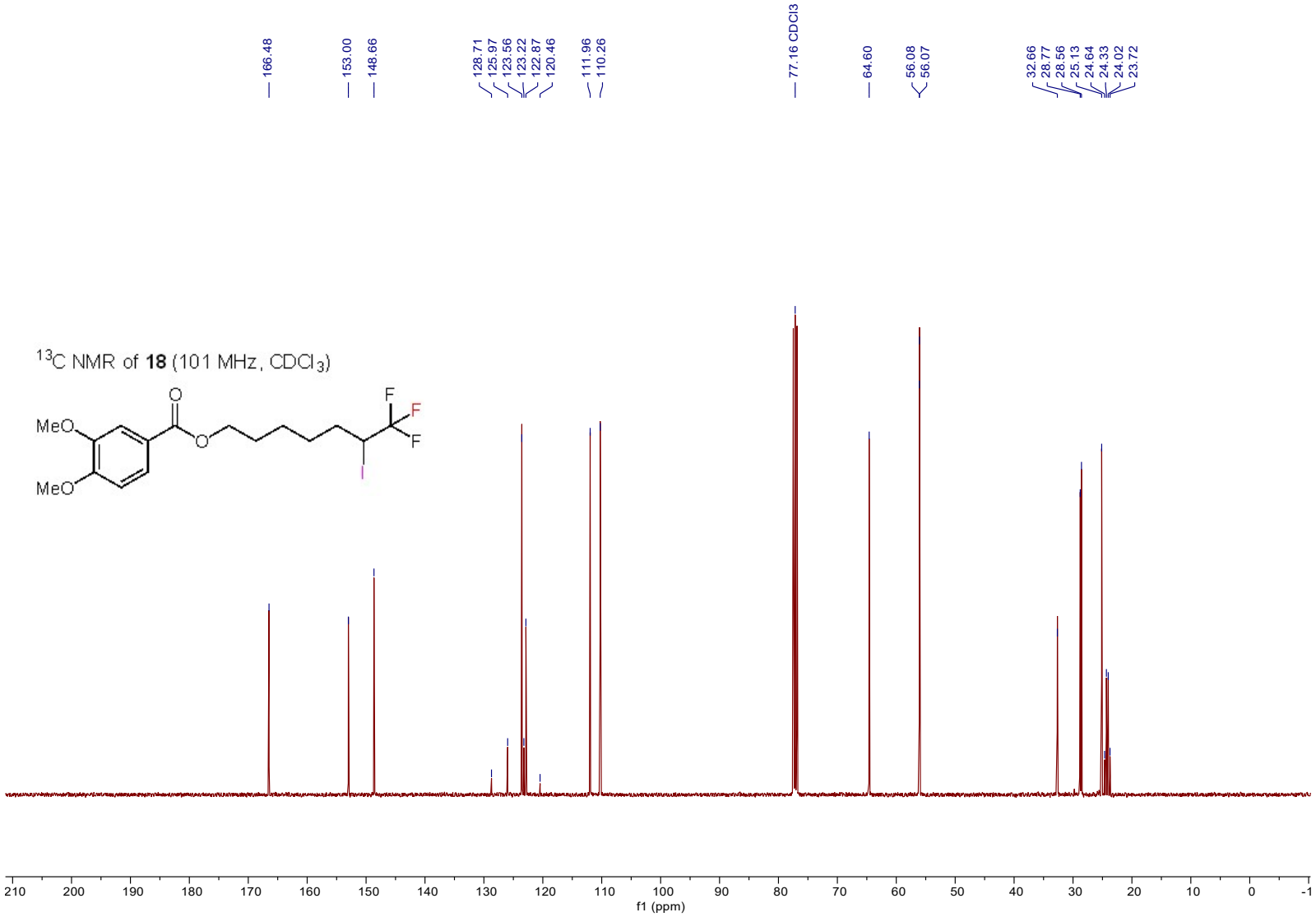

-68.70
-68.72
19F NMR of 16 (376 MHz, CDCl3)
O
O
N
F
F
F
I
-68.70
-68.72
-68.1 -68.2 -68.3 -68.4 -68.5 -68.6 -68.7 -68.8 -68.9 -69.0 -69.1 -69.2 -69.3
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)


^{1}H NMR of **17** (400 MHz, $CDCl_3$)
O
O
F
F
F
I
8.62 8.09 8.08 8.06 8.06 7.98 7.96 7.90 7.89 7.88 7.87 7.62 7.61 7.60 7.60 7.60 7.58 7.58 7.57 7.57 7.55 7.55 7.55 7.53 7.53 4.42 4.40 4.38 4.21 4.19 4.17 4.15 4.14 4.13 4.11 1.93 1.92 1.91 1.91 1.90 1.90 1.89 1.88 1.88 1.87 1.87 1.86 1.86 1.84 1.84 1.77 1.75 1.74 1.73 1.72 1.71 1.71 1.62 1.60 1.58 1.58 1.57 1.57 1.56 1.55 1.54 1.53 1.52 1.51 1.50 1.49 1.48 1.46
1.00 1.02 1.04 2.00 2.04 2.00 1.02 4.06 1.00 3.05
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

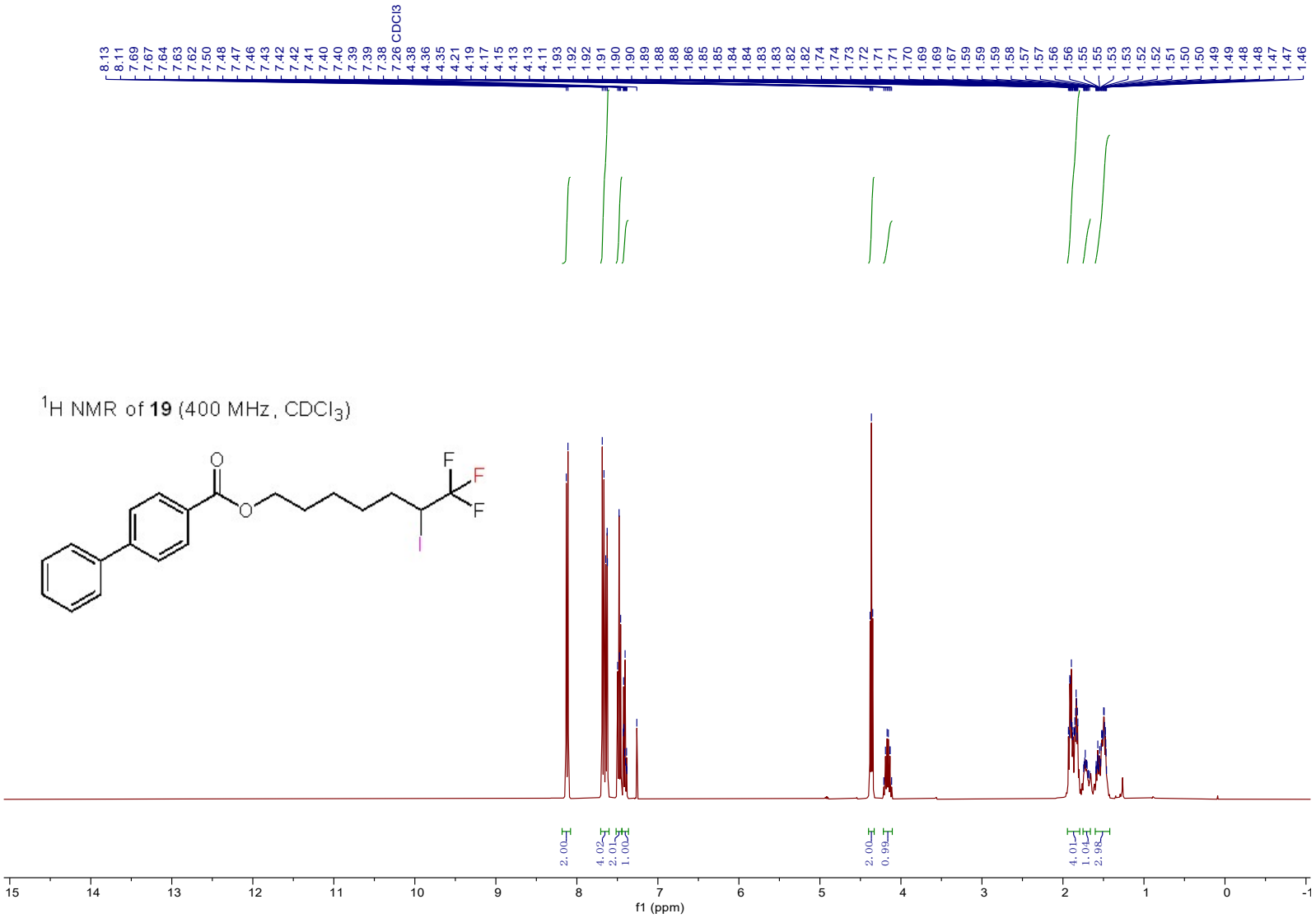

166.88
135.61
132.57
131.09
129.44
128.76
128.35
128.27
127.87
127.64
126.77
126.01
125.31
123.26
120.51
77.16 CDCl3
64.94
32.70
28.86
28.59
25.22
24.70
24.39
24.09
23.78
13C NMR of 17 (101 MHz, CDCl3)
O
O
F
F
F
I
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

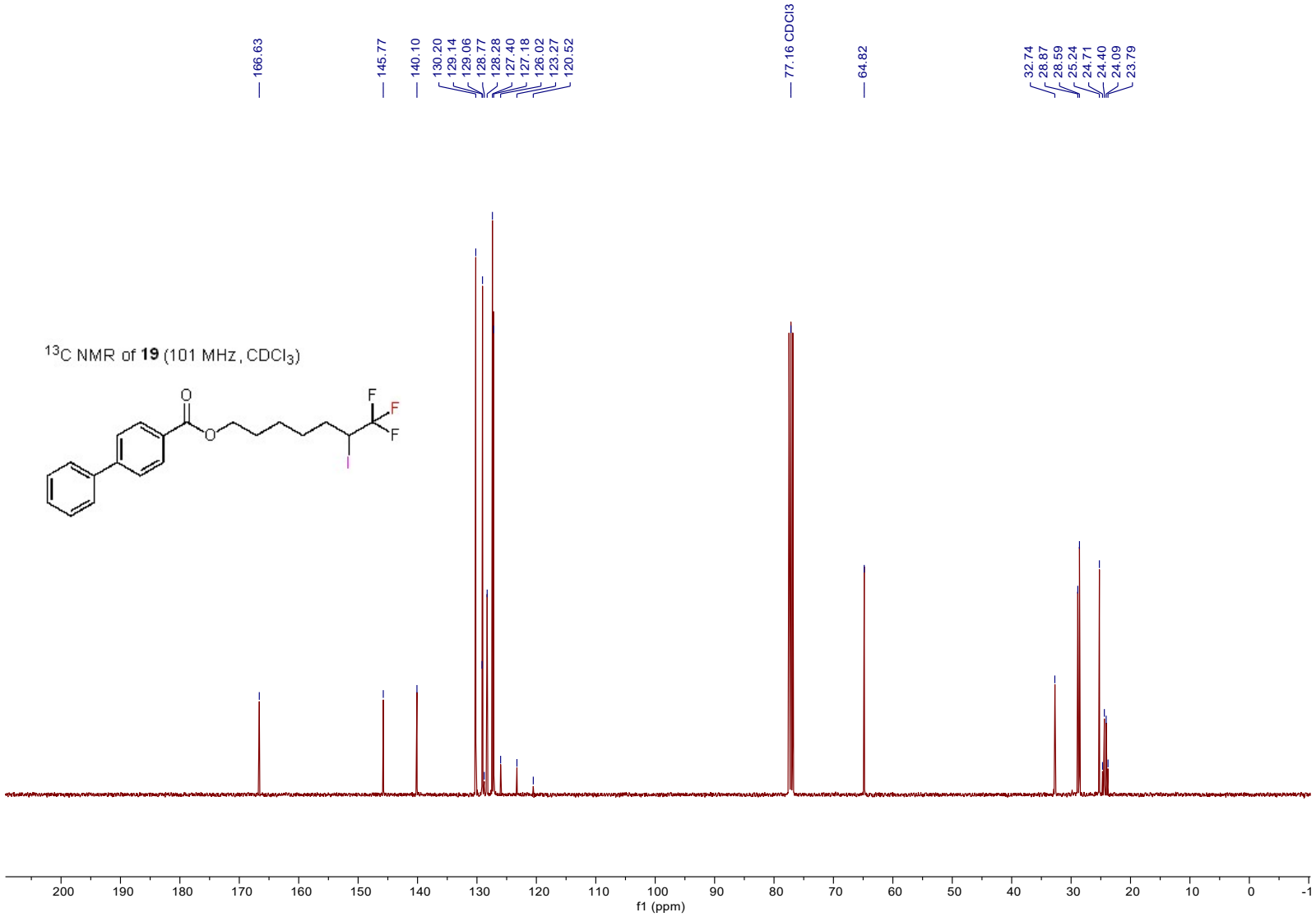

-68.80
-68.83
^{19}F NMR of **17** (376 MHz, $CDCl_3$)
O
O
F
F
F
I
-68.80
-68.83
-68.0
-68.5
-69.0
-69.5
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

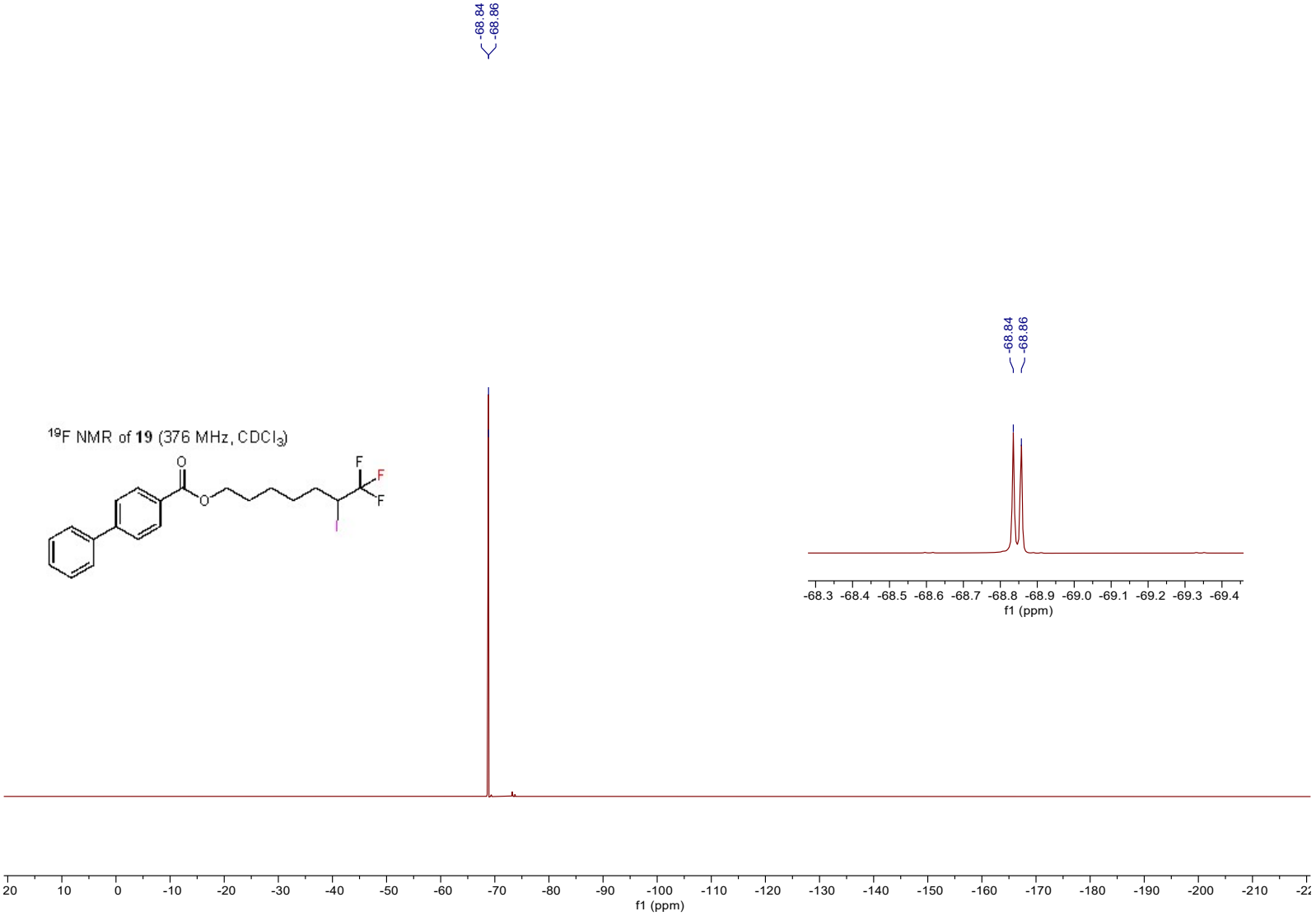

^{1}H NMR of **18** (400 MHz, $CDCl_3$)
MeO
MeO
O
O
F
F
F
I
7.67
7.67
7.65
7.65
7.52
7.52
7.26 CDCl3
6.88
6.86
4.31
4.29
4.27
4.18
4.16
4.16
4.14
4.14
4.12
4.12
4.10
4.09
4.08
3.92
1.89
1.87
1.87
1.87
1.86
1.85
1.84
1.84
1.83
1.82
1.81
1.80
1.80
1.79
1.78
1.78
1.77
1.76
1.75
1.75
1.70
1.69
1.68
1.66
1.66
1.65
1.64
1.54
1.54
1.53
1.52
1.52
1.52
1.51
1.50
1.49
1.48
1.47
1.46
1.45
1.44
1.43
1.42
1.41
1.00
1.01
1.02
2.00
1.07
6.06
4.02
1.02
3.04
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

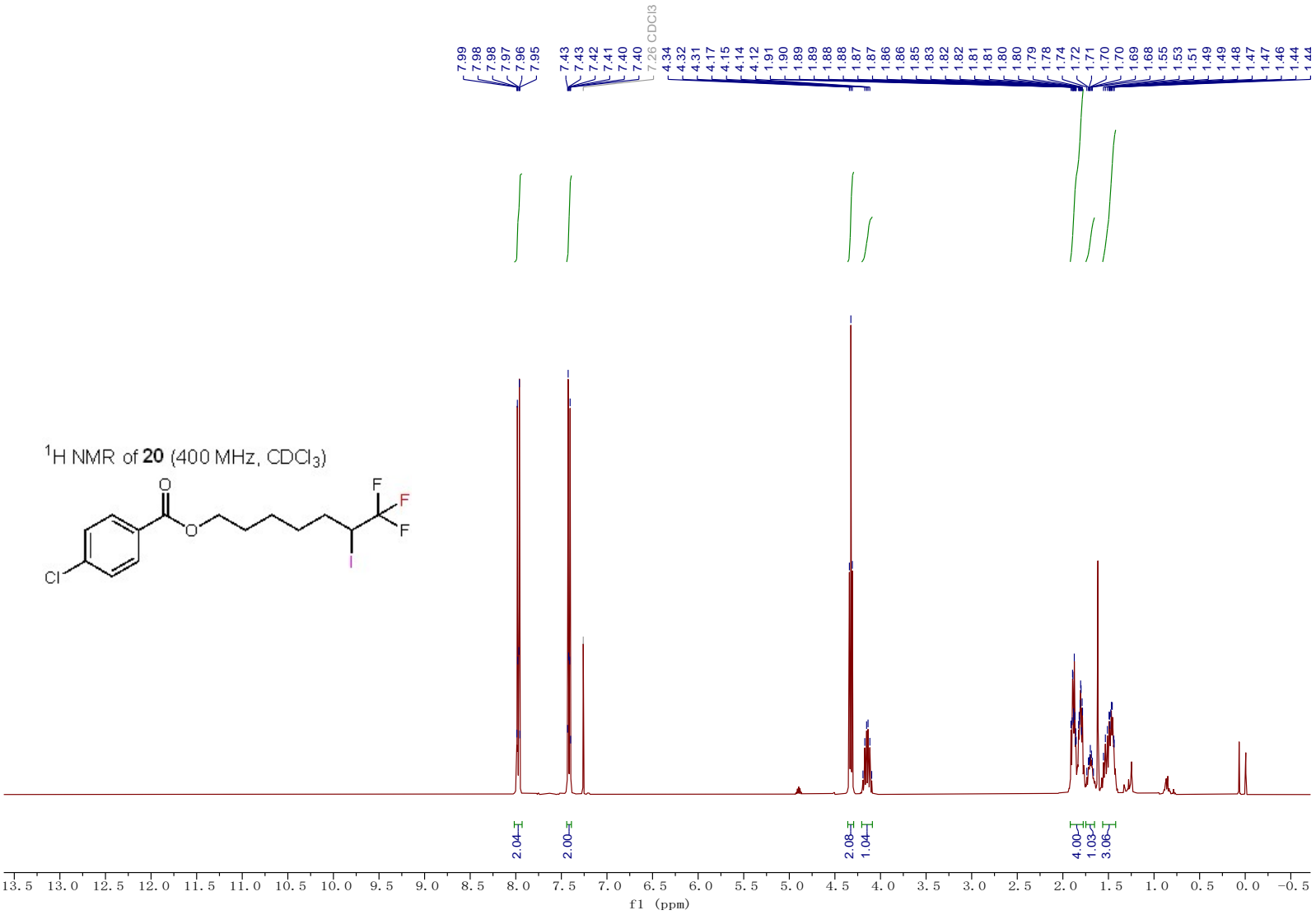

166.48
153.00
148.66
128.71
125.97
123.56
123.22
122.87
120.46
111.96
110.26
77.16 CDCl3
64.60
56.08
56.07
32.66
28.77
28.56
25.13
24.64
24.33
24.02
23.72
13C NMR of 18 (101 MHz, CDCl3)
MeO
MeO
O
O
F
F
F
I
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

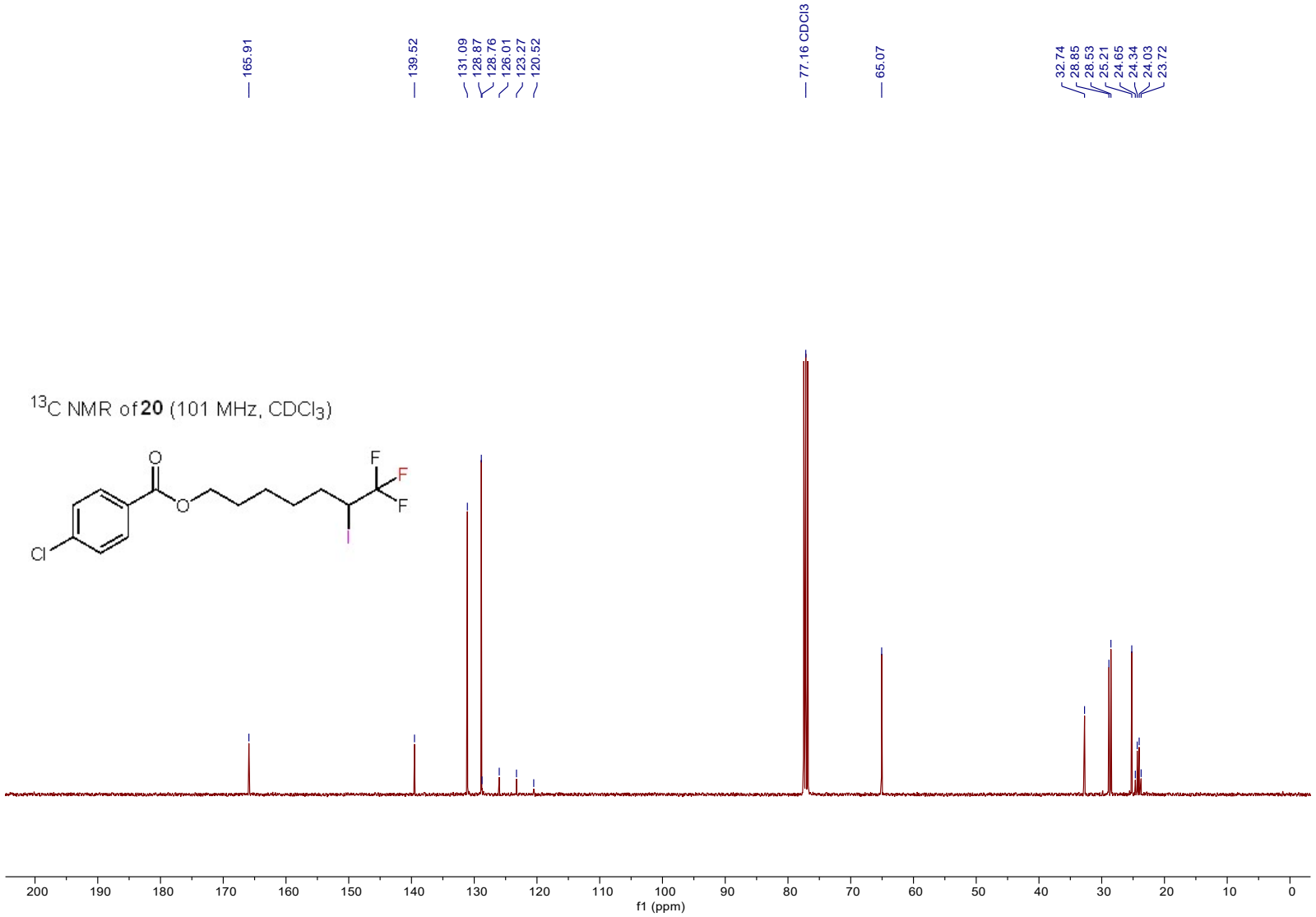

-68.88
-68.90
19F NMR of 18 (376 MHz, CDCl3)
MeO
MeO
O
O
F
F
F
I
-68.88
-68.90
-67.8 -68.0 -68.2 -68.4 -68.6 -68.8 -69.0 -69.2 -69.4 -69.6 -69.8
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


^{1}H NMR of **19** (400 MHz, $CDCl_3$)
O
O
F
F
F
I
8.13 8.11 7.69 7.67 7.64 7.63 7.62 7.50 7.48 7.47 7.46 7.43 7.42 7.42 7.41 7.40 7.40 7.39 7.39 7.38 7.26 CDCl3 4.38 4.36 4.35 4.21 4.19 4.17 4.15 4.13 4.13 4.11 1.93 1.92 1.92 1.91 1.90 1.90 1.89 1.88 1.88 1.86 1.85 1.85 1.84 1.84 1.83 1.83 1.82 1.82 1.74 1.74 1.73 1.72 1.71 1.71 1.70 1.69 1.69 1.67 1.59 1.59 1.59 1.58 1.57 1.57 1.56 1.56 1.55 1.55 1.53 1.53 1.52 1.52 1.51 1.50 1.50 1.49 1.49 1.48 1.48 1.47 1.47 1.46
2.00
4.02
2.01
1.00
2.00
0.99
4.01
1.04
2.98
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

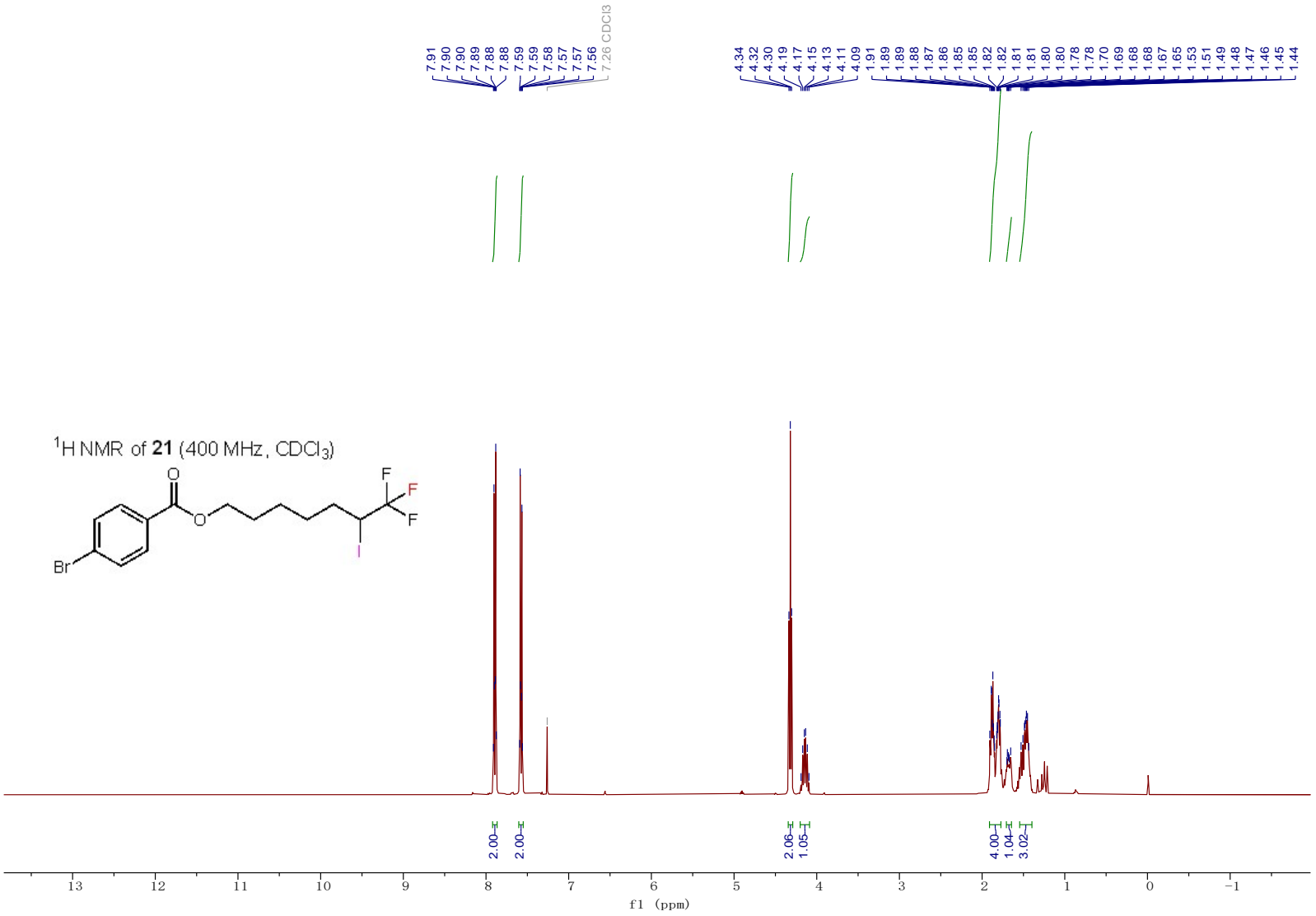

166.63
145.77
140.10
130.20
129.14
129.06
128.77
128.28
127.40
127.18
126.02
123.27
120.52
77.16 CDCl3
64.82
32.74
28.87
28.59
25.24
24.71
24.40
24.09
23.79
13C NMR of 19 (101 MHz, CDCl3)
O
O
F
F
F
I
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

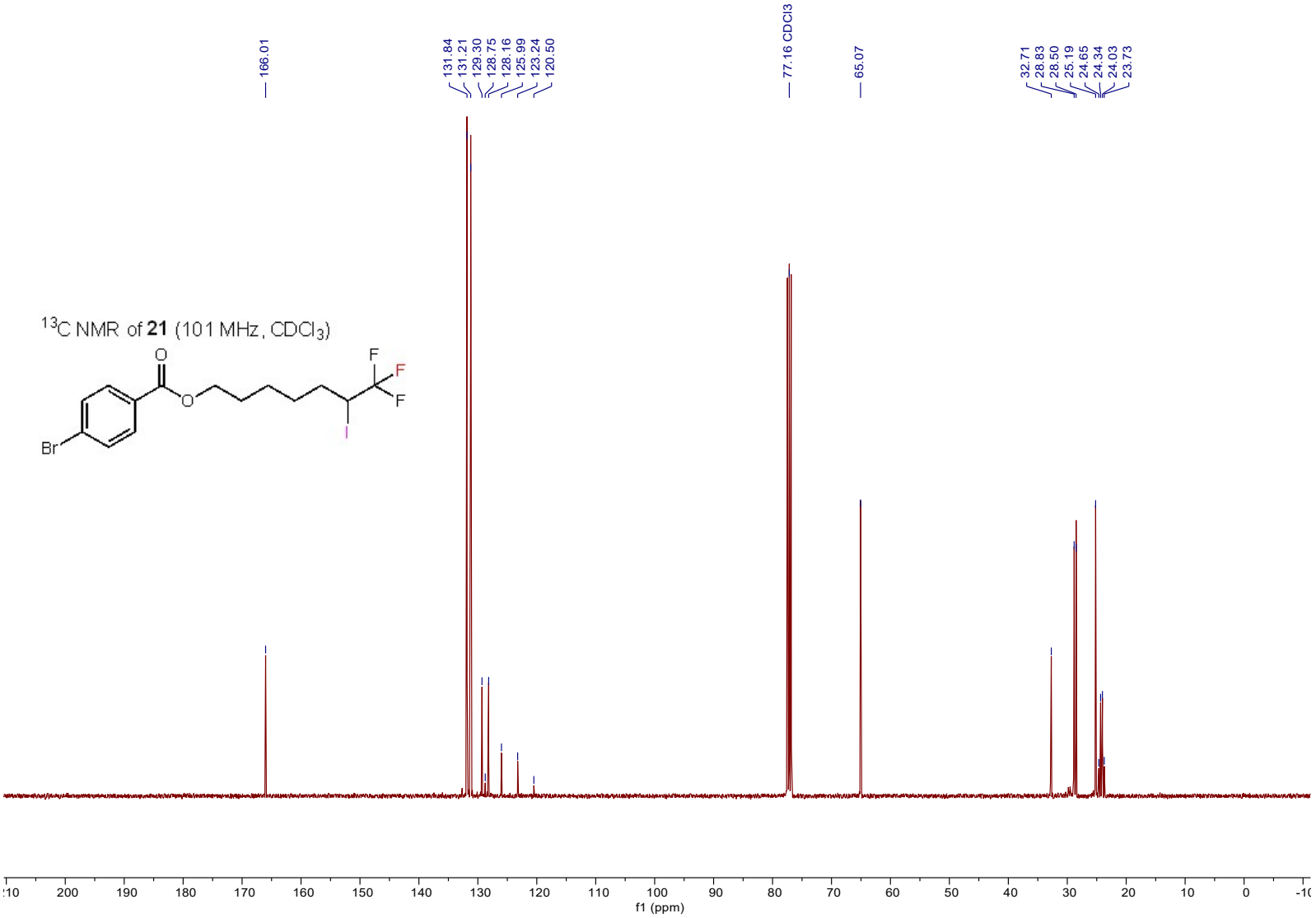

-68.84
-68.86
^{19}F NMR of **19** (376 MHz, $CDCl_3$)
O
O
F
F
F
I
-68.84
-68.86
-68.3 -68.4 -68.5 -68.6 -68.7 -68.8 -68.9 -69.0 -69.1 -69.2 -69.3 -69.4
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


^{1}H NMR of **20** (400 MHz, $CDCl_3$)
O
O
F
F
F
Cl
I
7.99
7.98
7.98
7.97
7.96
7.95
7.43
7.43
7.42
7.41
7.40
7.40
7.26 CDCl3
4.34
4.32
4.31
4.17
4.15
4.14
4.12
1.91
1.90
1.89
1.89
1.88
1.88
1.87
1.87
1.86
1.86
1.85
1.83
1.82
1.82
1.81
1.81
1.80
1.80
1.79
1.78
1.74
1.72
1.71
1.70
1.70
1.69
1.68
1.55
1.53
1.51
1.49
1.49
1.48
1.47
1.47
1.46
1.44
1.44
2.04
2.00
2.08
1.04
4.00
1.03
3.06
13.5 13.0 12.5 12.0 11.5 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
f1 (ppm)

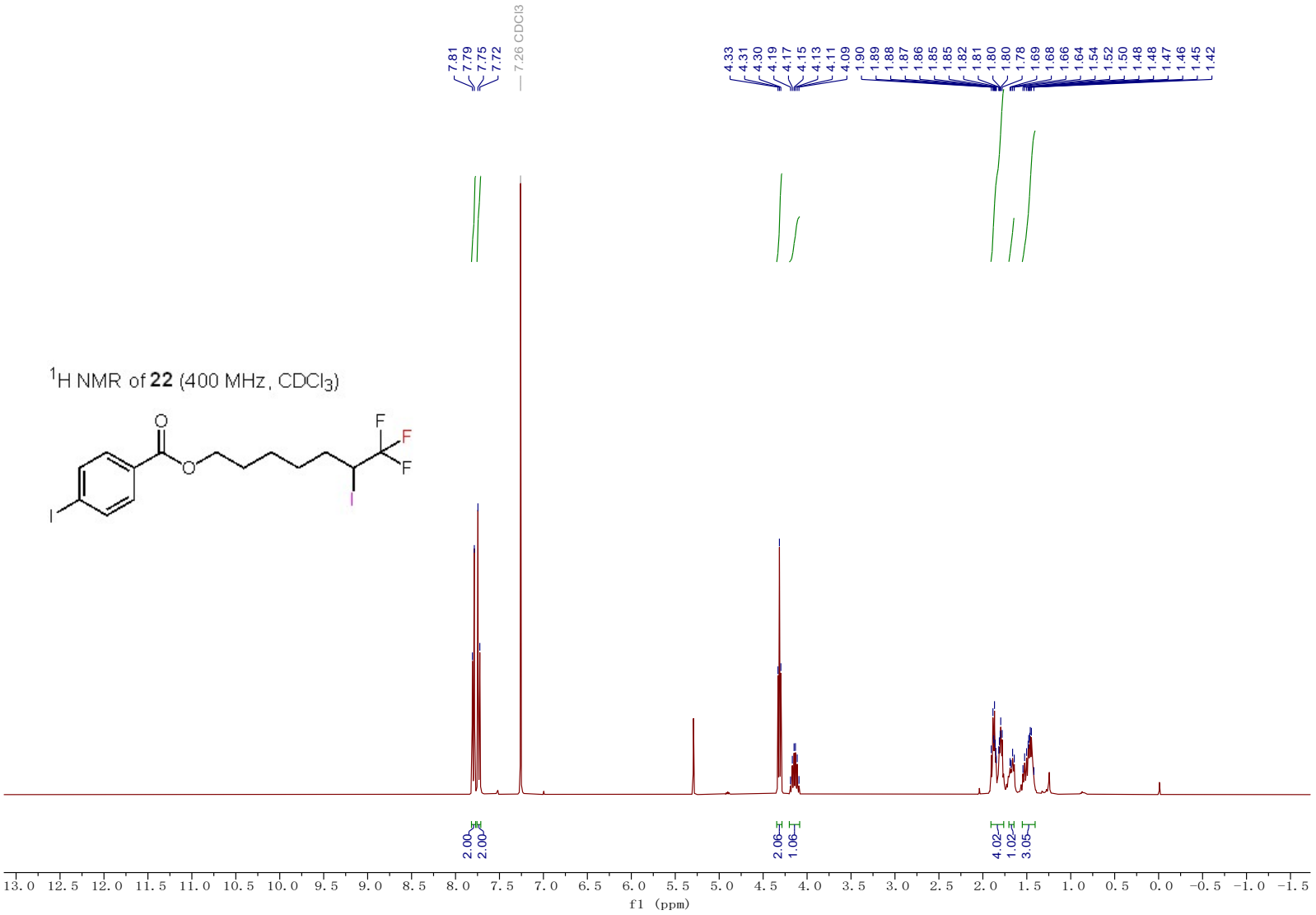

165.91
139.52
131.09
128.87
128.76
126.01
123.27
120.52
77.16 CDCl3
65.07
32.74
28.85
28.53
25.21
24.65
24.34
24.03
23.72
13C NMR of 20 (101 MHz, CDCl3)
O
O
F
F
F
Cl
I
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

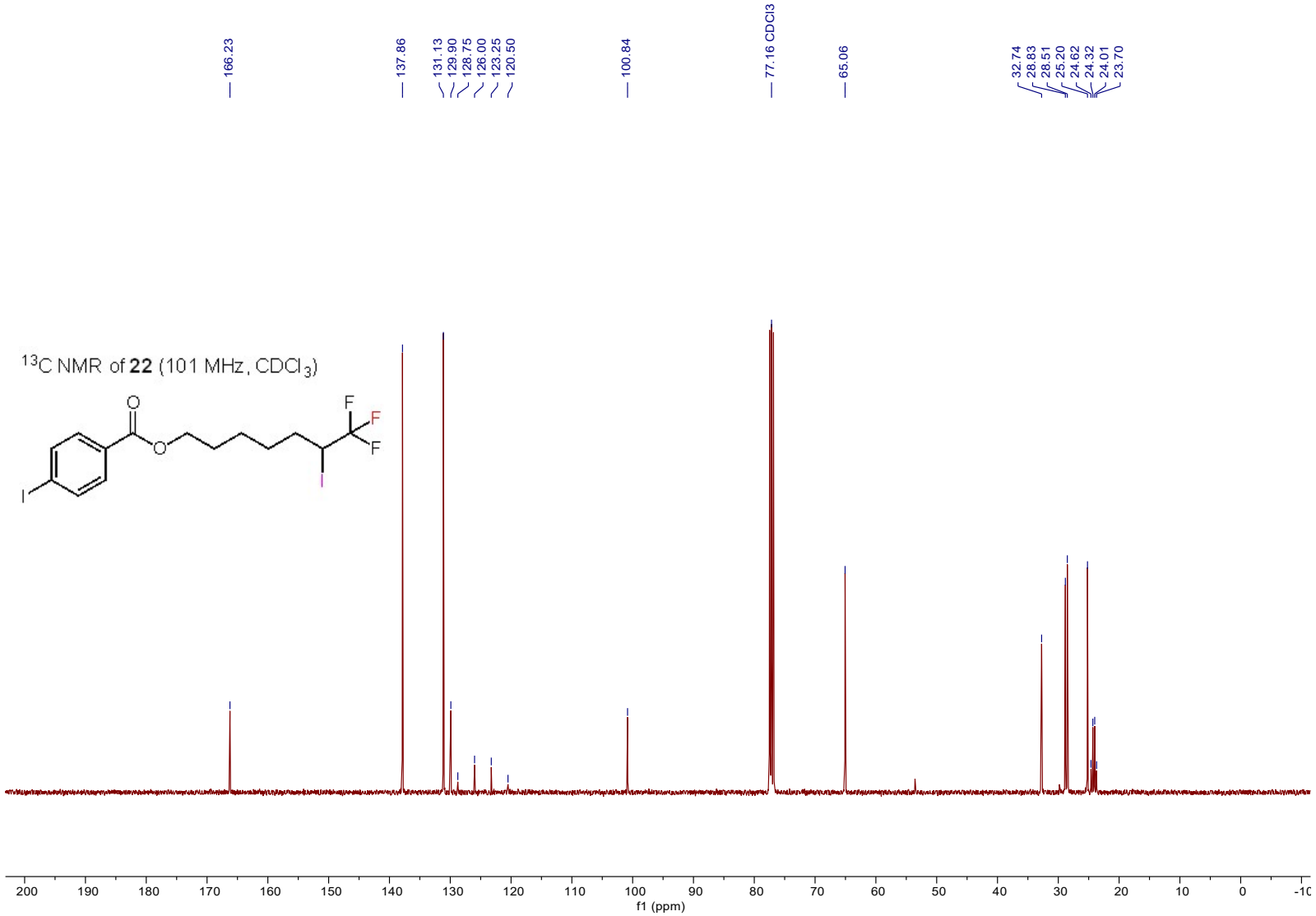

-68.88
-68.90
^{19}F NMR of **20** (376 MHz, $CDCl_3$)
O
O
F
F
F
Cl
I
-68.88
-68.90
-68.5 -68.6 -68.7 -68.8 -68.9 -69.0 -69.1 -69.2 -69.3 -69.4 -69.5
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

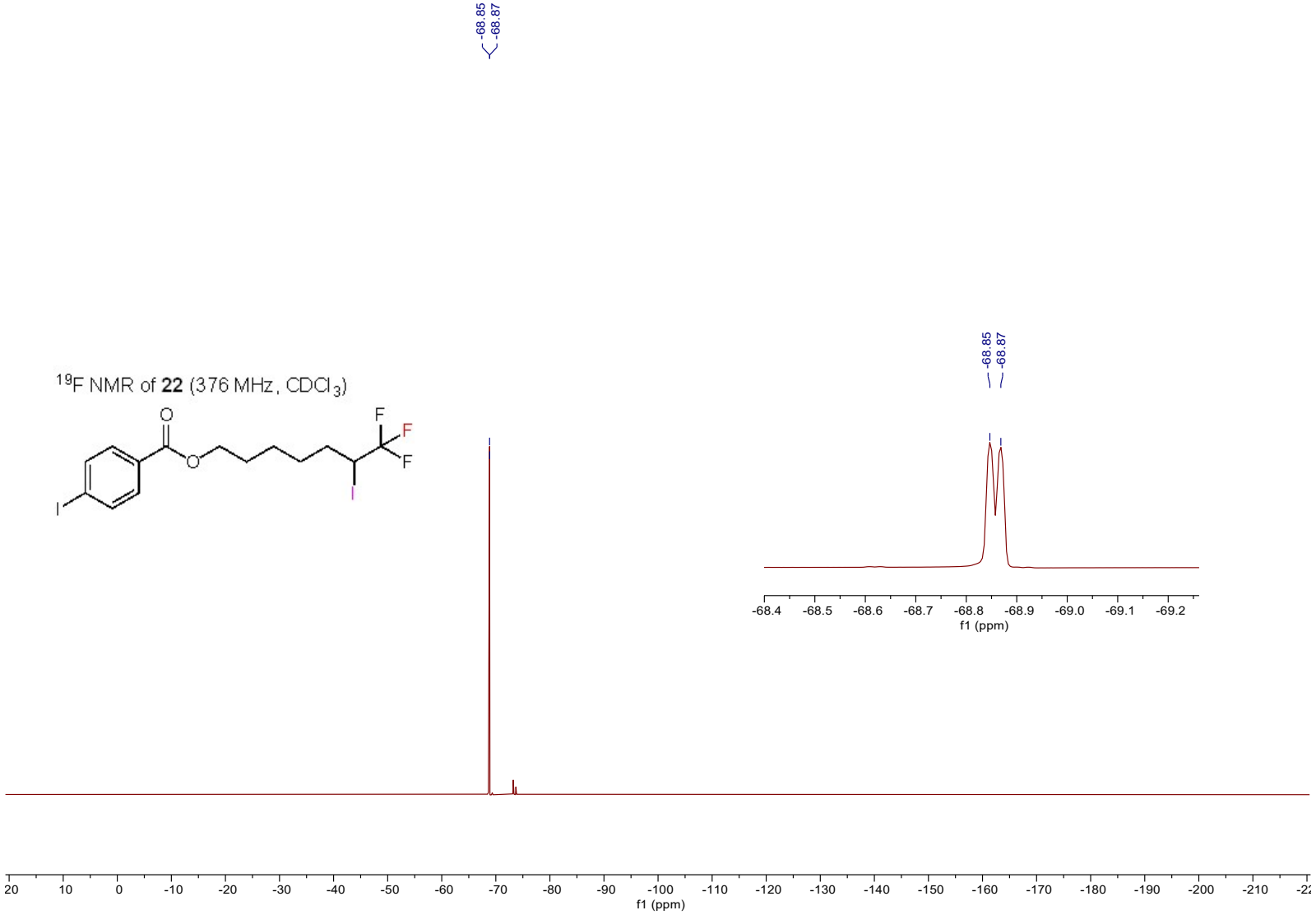

7.91
7.90
7.90
7.89
7.88
7.88
7.59
7.59
7.58
7.57
7.57
7.56
7.26 CDCl3
4.34
4.32
4.30
4.19
4.17
4.15
4.13
4.11
4.09
1.91
1.89
1.89
1.88
1.87
1.86
1.85
1.85
1.82
1.82
1.81
1.81
1.80
1.80
1.78
1.78
1.70
1.69
1.68
1.68
1.67
1.65
1.53
1.51
1.49
1.48
1.47
1.46
1.45
1.44
1H NMR of 21 (400 MHz, CDCl3)
O
O
F
F
F
Br
I
2.00
2.00
2.06
1.05
4.00
1.04
3.02
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

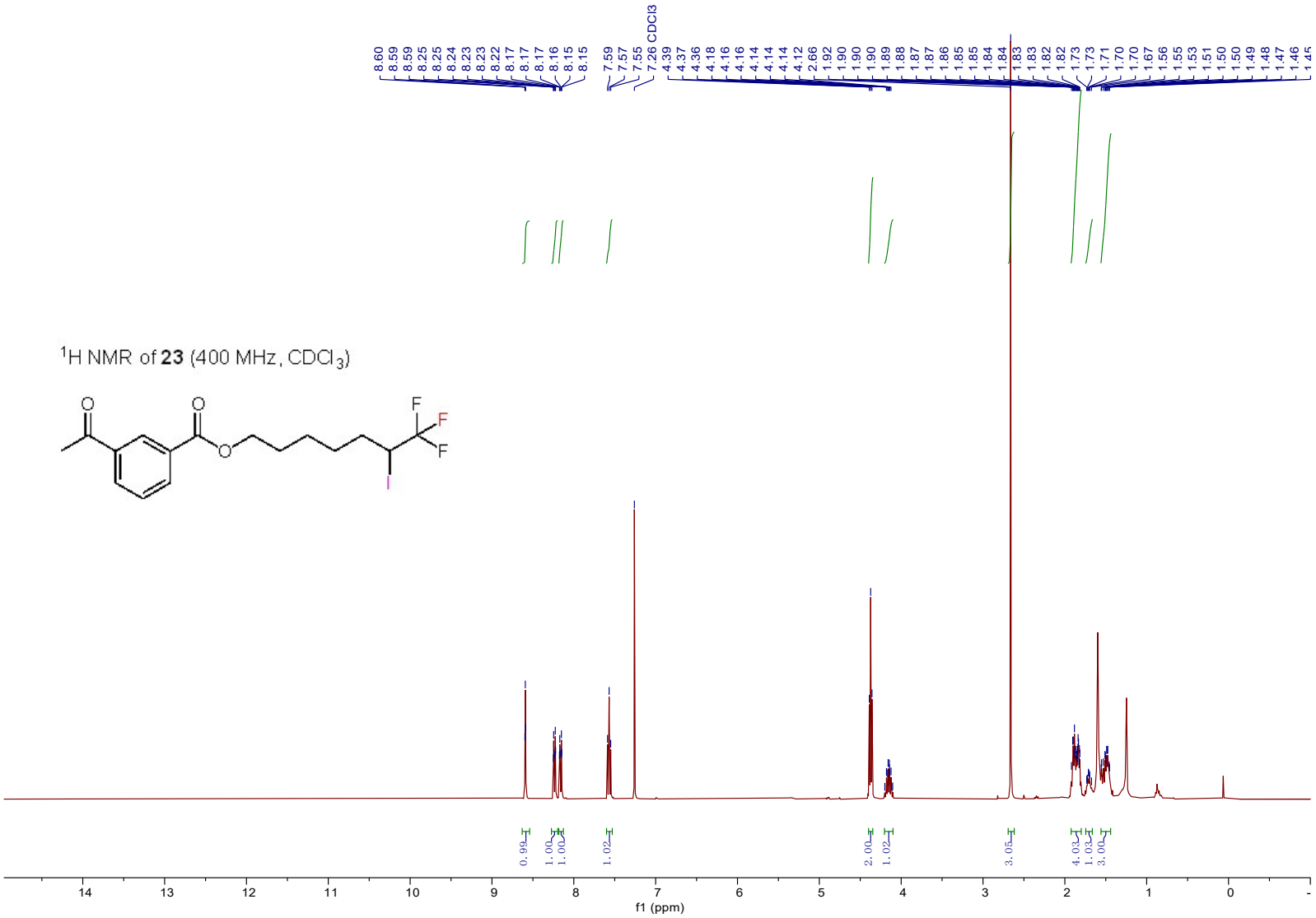

166.01
131.84
131.21
129.30
128.75
128.16
125.99
123.24
120.50
77.16 CDCl3
65.07
32.71
28.83
28.50
25.19
24.65
24.34
24.03
23.73
13C NMR of 21 (101 MHz, CDCl3)
O
O
F
F
F
I
Br
f1 (ppm)

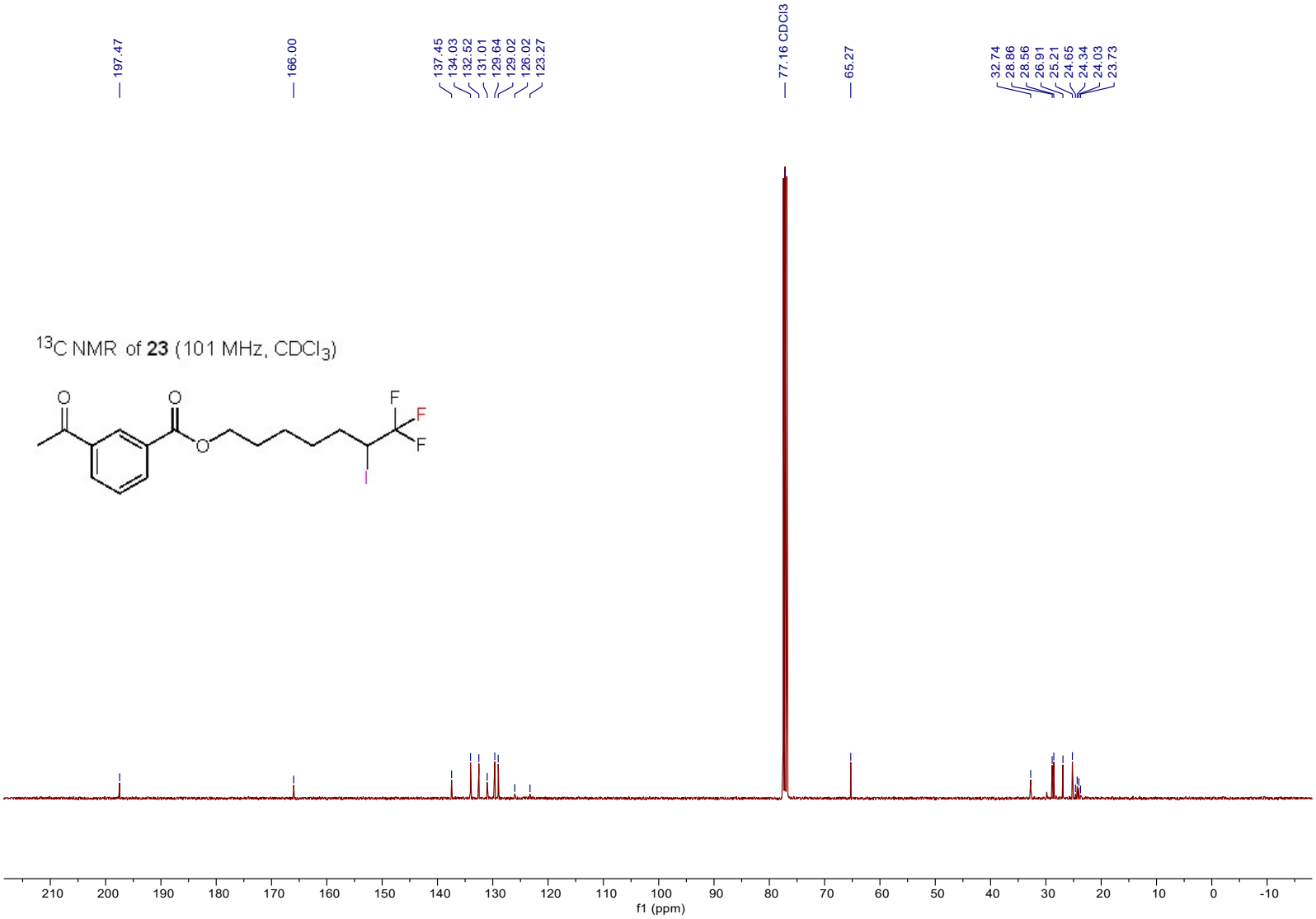

-68.85
-68.87
19F NMR of 21 (376 MHz, CDCl3)
O
O
F
F
F
Br
I
-68.85
-68.87
-68.4 -68.5 -68.6 -68.7 -68.8 -68.9 -69.0 -69.1 -69.2 -69.3 -69.4
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

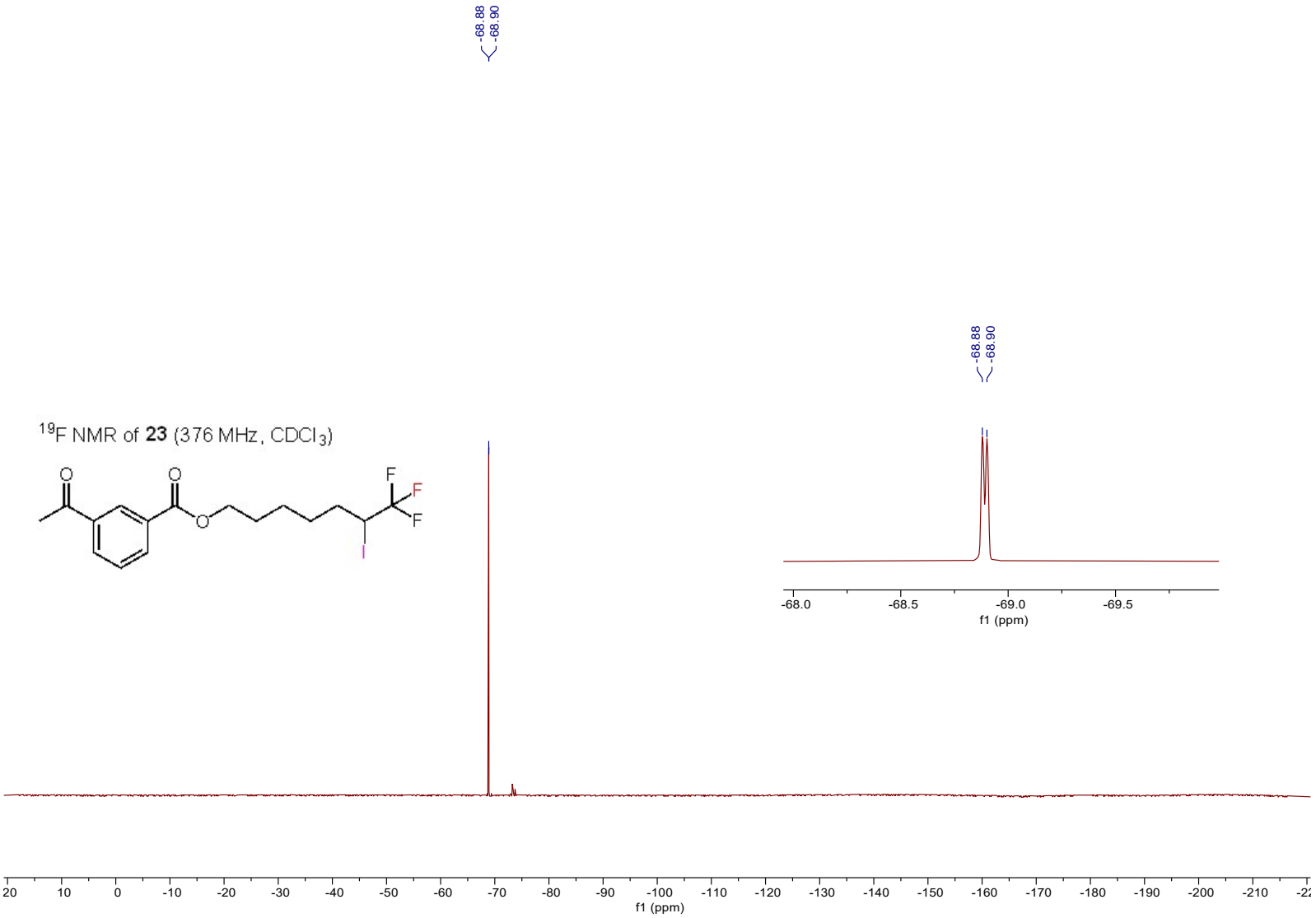

1H NMR of 22 (400 MHz, CDCl3)
7.81
7.79
7.75
7.72
7.26 CDCl3
4.33
4.31
4.30
4.19
4.17
4.15
4.13
4.11
4.09
1.90
1.89
1.88
1.87
1.86
1.85
1.85
1.82
1.81
1.80
1.80
1.78
1.69
1.68
1.66
1.64
1.54
1.52
1.50
1.48
1.48
1.47
1.46
1.45
1.42
2.00
2.00
2.06
1.06
4.02
1.02
3.05
f1 (ppm)

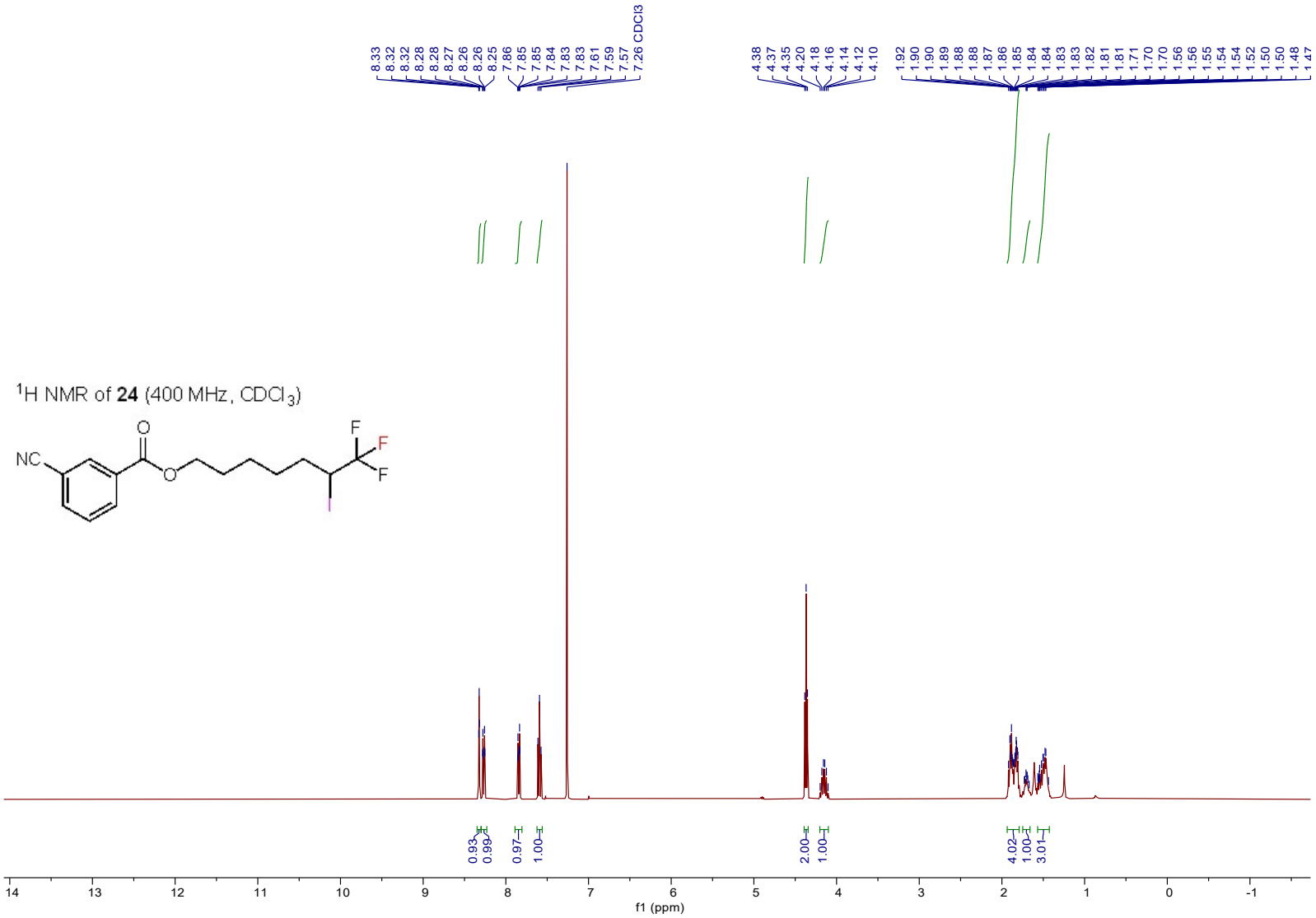

166.23
137.86
131.13
129.90
128.75
126.00
123.25
120.50
100.84
77.16 CDCl3
65.06
32.74
28.83
28.51
25.20
24.62
24.32
24.01
23.70
13C NMR of 22 (101 MHz, CDCl3)
O
O
F
F
F
I
I
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

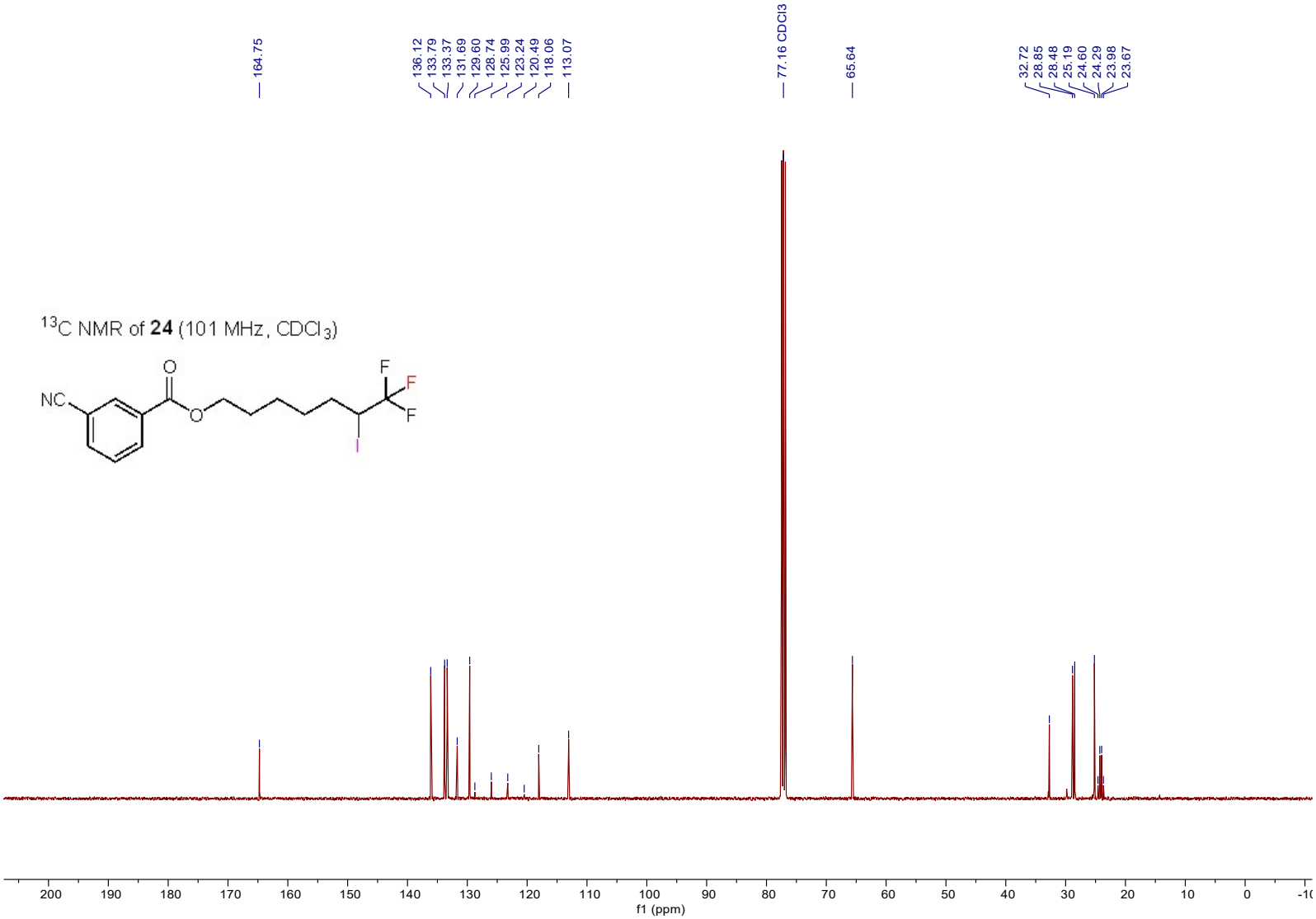

-68.85
-68.87
19F NMR of 22 (376 MHz, CDCl3)
O
O
F
F
F
I
I
-68.85
-68.87
-68.4
-68.5
-68.6
-68.7
-68.8
-68.9
-69.0
-69.1
-69.2
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

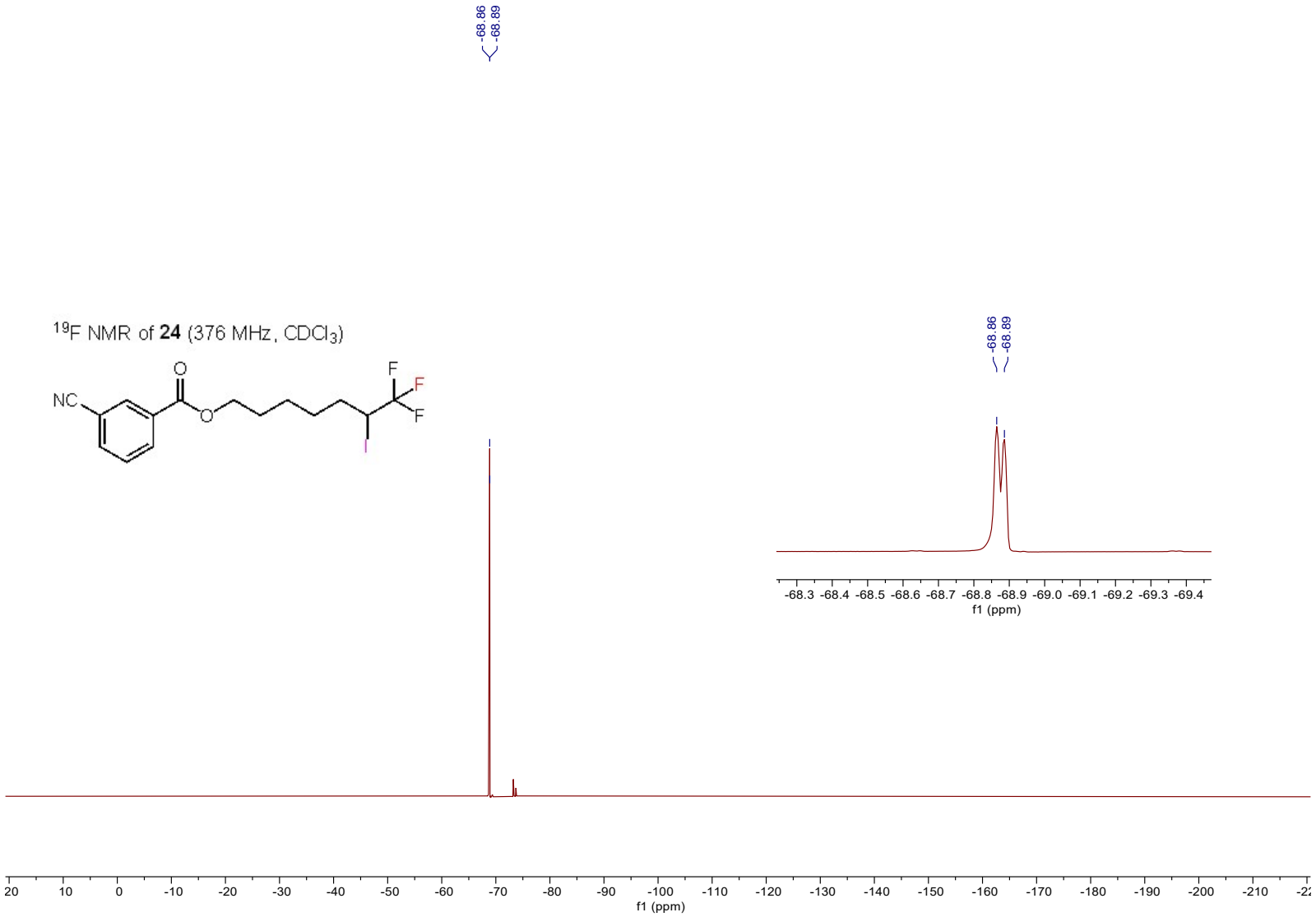

1H NMR of 23 (400 MHz, CDCl3)
O
O
O
F
F
F
I
8.60
8.59
8.59
8.25
8.25
8.24
8.23
8.23
8.22
8.17
8.17
8.17
8.16
8.15
8.15
7.59
7.57
7.55
7.26 CDCl3
4.39
4.37
4.36
4.18
4.16
4.16
4.14
4.14
4.14
4.12
2.66
1.92
1.90
1.90
1.90
1.89
1.88
1.87
1.87
1.86
1.85
1.85
1.84
1.84
1.83
1.83
1.82
1.82
1.73
1.73
1.71
1.70
1.70
1.67
1.56
1.55
1.53
1.51
1.50
1.50
1.49
1.48
1.47
1.46
1.45
0.99
1.00
1.00
1.02
2.00
1.02
3.05
4.03
1.03
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

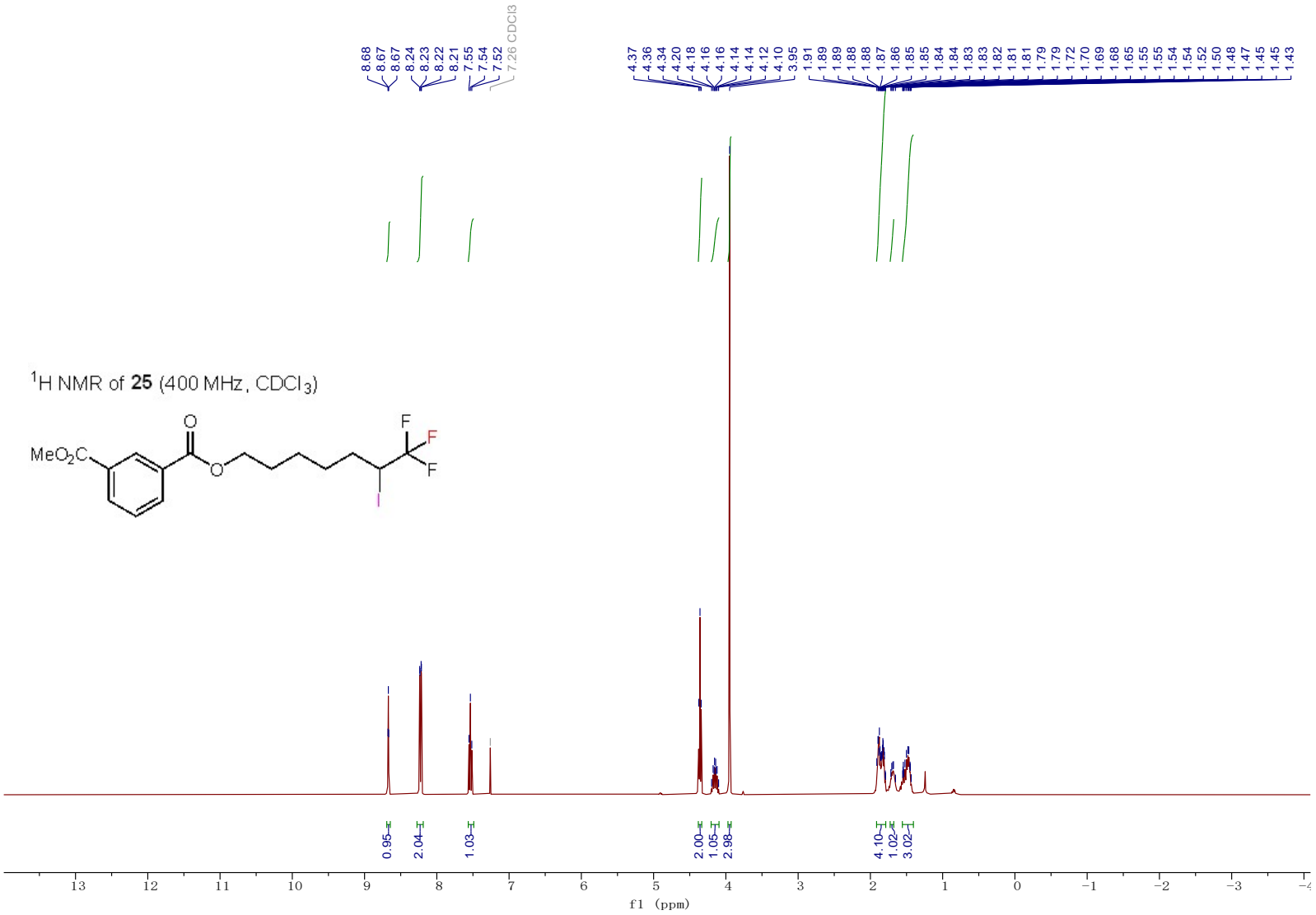

197.47
166.00
137.45
134.03
132.52
131.01
129.64
129.02
126.02
123.27
77.16 CDCl3
65.27
32.74
28.86
28.56
26.91
25.21
24.65
24.34
24.03
23.73
13C NMR of 23 (101 MHz, CDCl3)
O
O
O
F
F
F
I
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

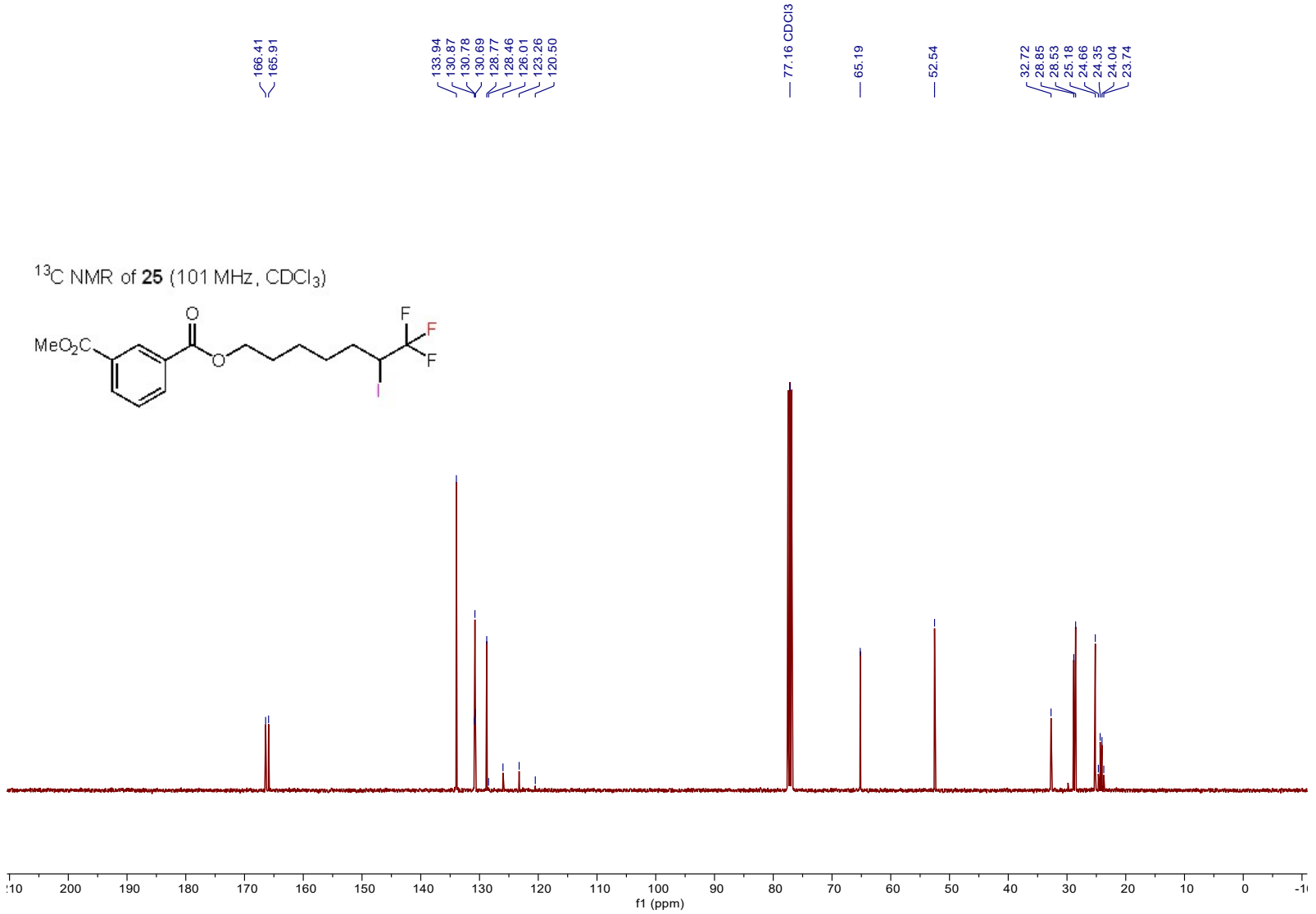

-68.88
-68.90
19F NMR of 23 (376 MHz, CDCl3)
O
O
O
F
F
F
I
-68.88
-68.90
-68.0
-68.5
-69.0
-69.5
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

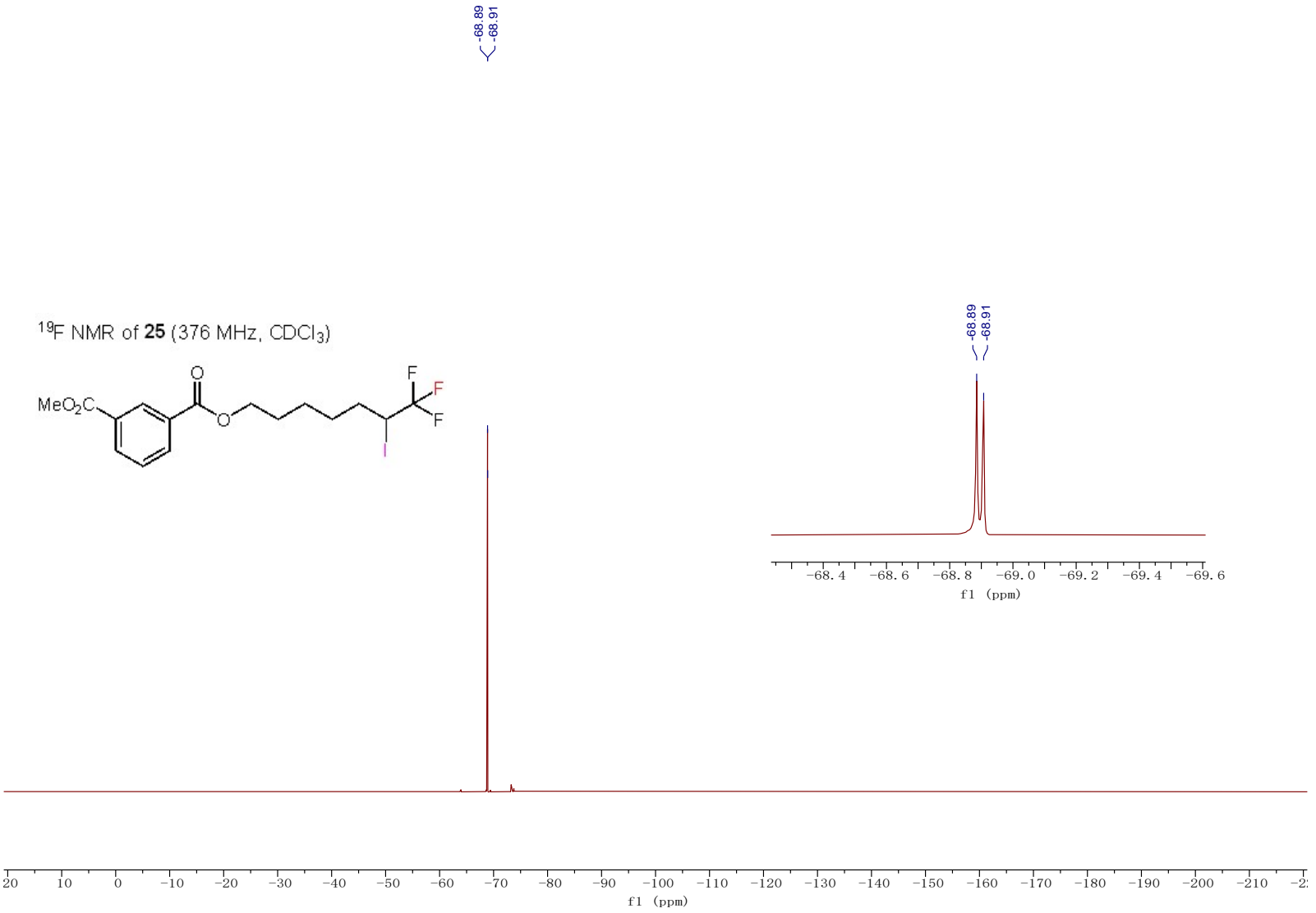

8.33
8.32
8.32
8.28
8.28
8.27
8.26
8.26
8.25
7.86
7.85
7.85
7.84
7.83
7.83
7.61
7.59
7.57
7.26 CDCl3
4.38
4.37
4.35
4.20
4.18
4.16
4.14
4.12
4.10
1.92
1.90
1.90
1.89
1.88
1.88
1.87
1.86
1.85
1.84
1.84
1.83
1.83
1.82
1.81
1.81
1.71
1.70
1.70
1.56
1.56
1.55
1.54
1.54
1.52
1.50
1.50
1.48
1.47
1H NMR of 24 (400 MHz, CDCl3)
NC
O
O
F
F
F
0.93
0.99
0.97
1.00
2.00
1.00
4.02
1.00
3.01
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

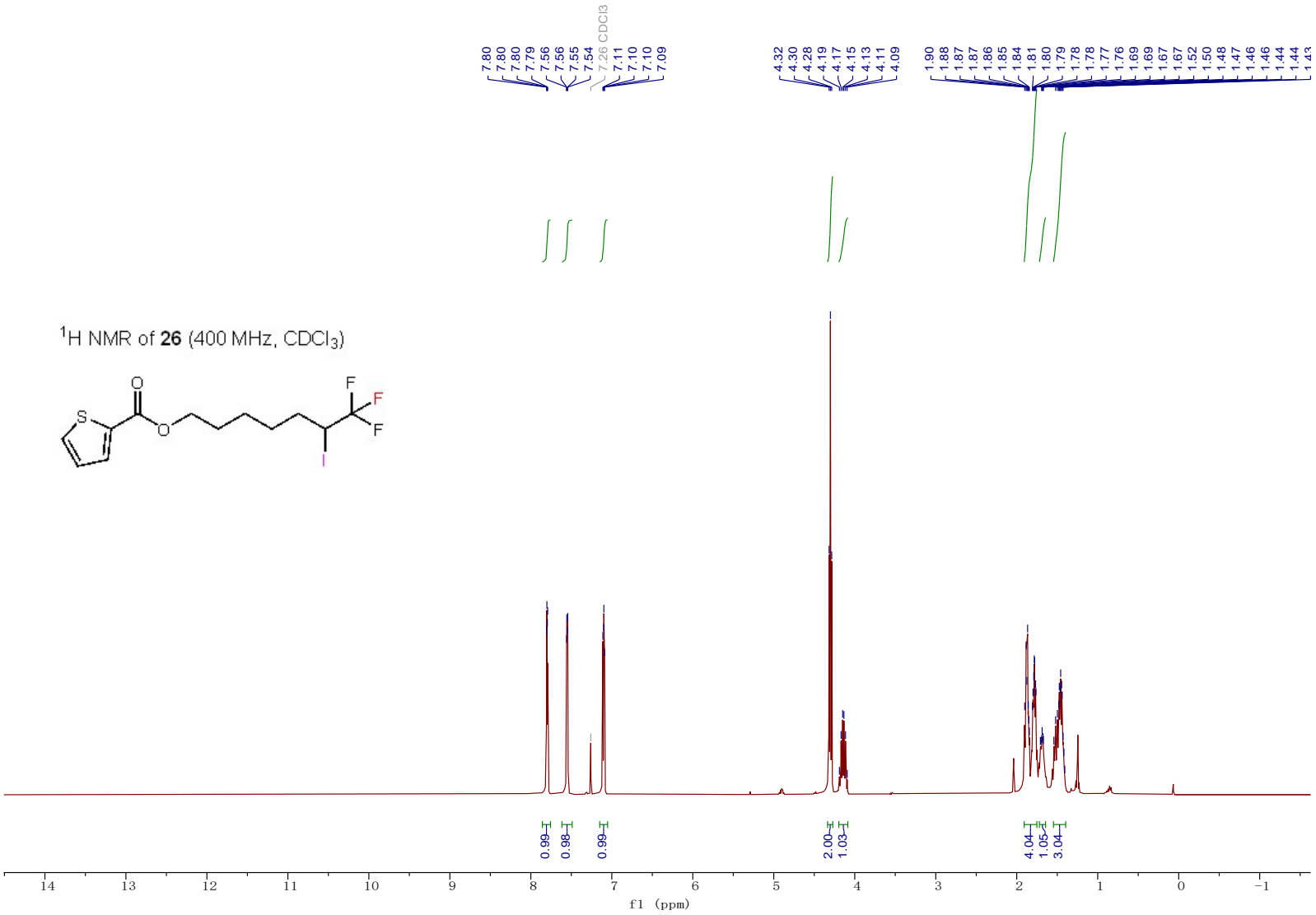

164.75
136.12
133.79
133.37
131.69
129.60
128.74
125.99
123.24
120.49
118.06
113.07
77.16 CDCl3
65.64
32.72
28.85
28.48
25.19
24.60
24.29
23.98
23.67
13C NMR of 24 (101 MHz, CDCl3)
NC
O
O
F
F
F
I
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-68.86
-68.89
19F NMR of 24 (376 MHz, CDCl3)
NC
O
O
F
F
F
I
-68.86
-68.89
-68.3 -68.4 -68.5 -68.6 -68.7 -68.8 -68.9 -69.0 -69.1 -69.2 -69.3 -69.4
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

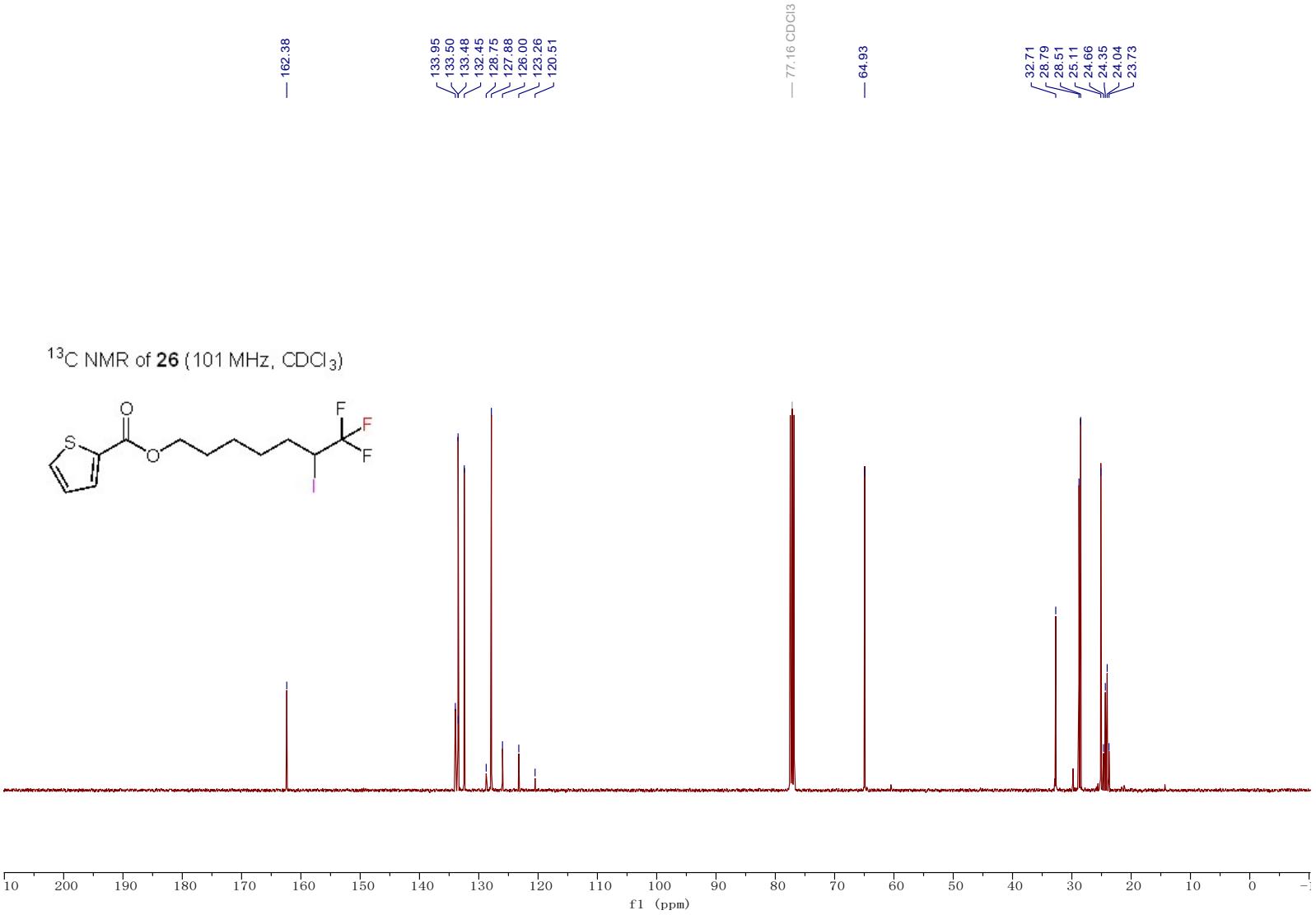

1H NMR of 25 (400 MHz, CDCl3)
MeO2C
O
O
F
F
F
I
8.68
8.67
8.67
8.24
8.23
8.22
8.21
7.55
7.54
7.52
7.26 CDCl3
4.37
4.36
4.34
4.20
4.18
4.16
4.16
4.14
4.14
4.12
4.10
3.95
1.91
1.89
1.89
1.88
1.88
1.87
1.86
1.85
1.85
1.84
1.84
1.83
1.83
1.82
1.81
1.81
1.79
1.79
1.72
1.70
1.69
1.68
1.65
1.55
1.55
1.54
1.54
1.52
1.50
1.48
1.47
1.45
1.45
1.43
0.95
2.04
1.03
2.00
1.05
2.98
4.10
1.02
3.02
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)

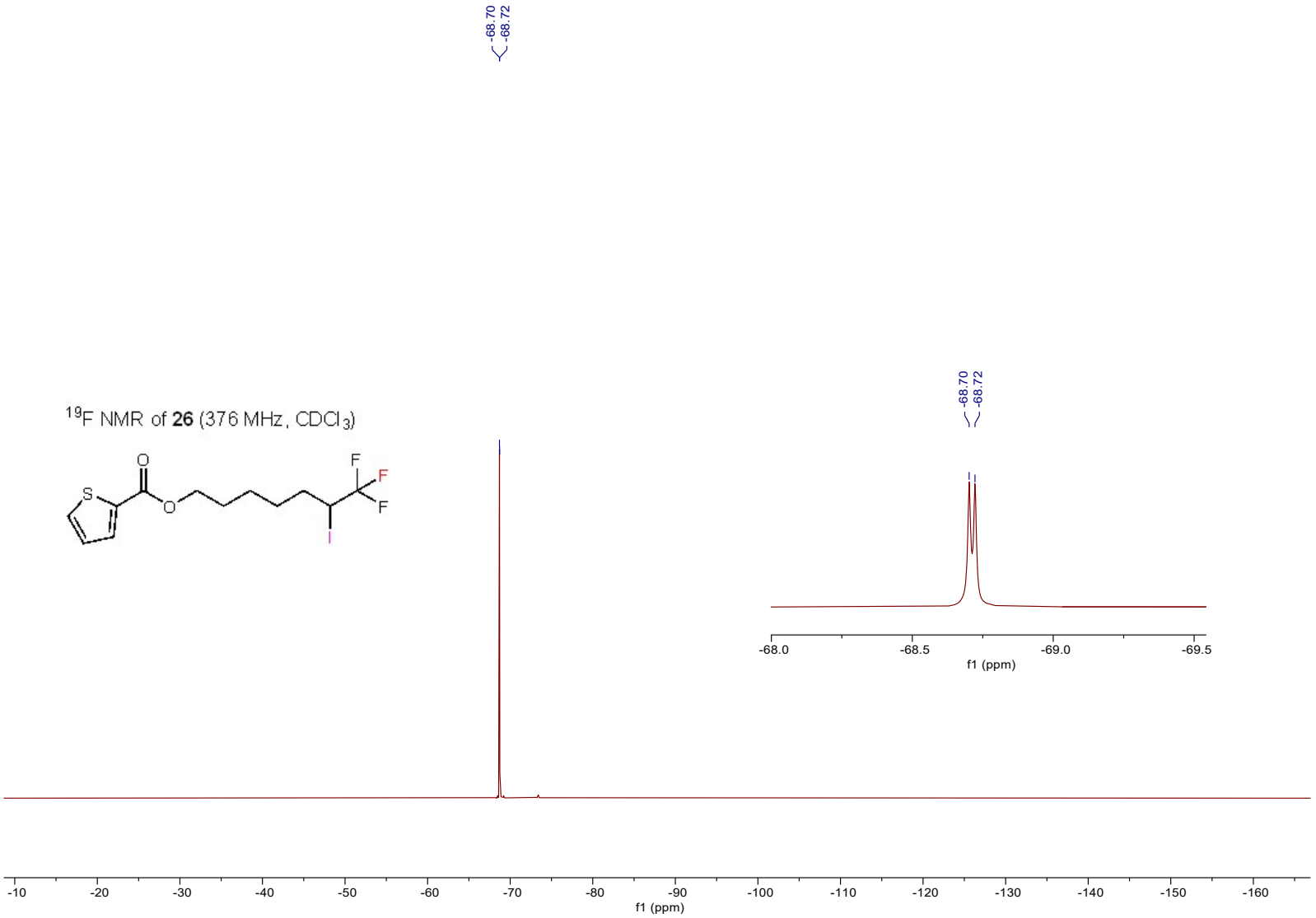

166.41
165.91
133.94
130.87
130.78
130.69
128.77
128.46
126.01
123.26
120.50
77.16 CDCl3
65.19
52.54
32.72
28.85
28.53
25.18
24.66
24.35
24.04
23.74
13C NMR of 25 (101 MHz, CDCl3)
MeO2C
O
O
F
F
F
I
f1 (ppm)

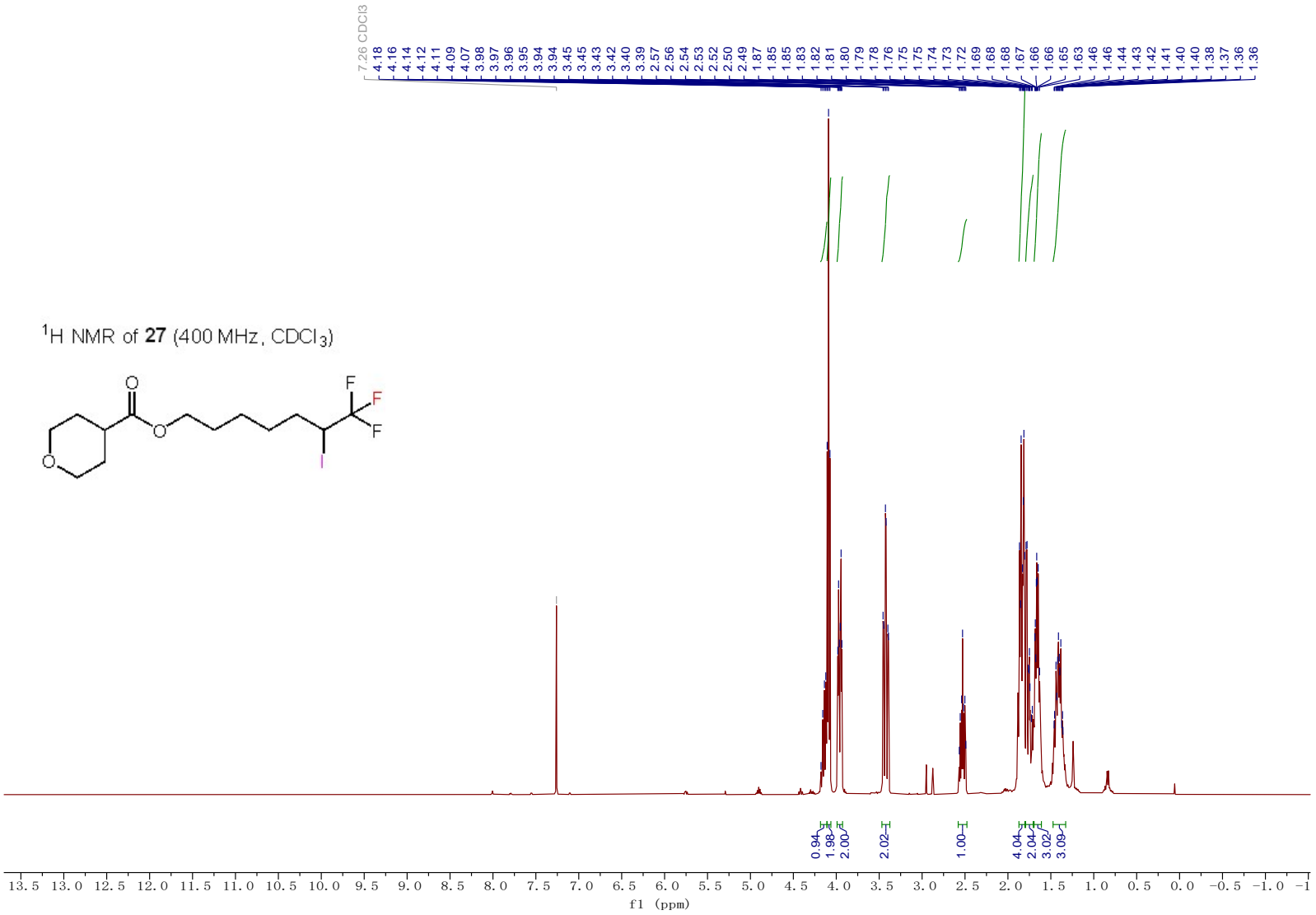

-68.89
-68.91
19F NMR of 25 (376 MHz, CDCl3)
MeO2C
O
O
F
F
F
I
-68.89
-68.91
-68.4
-68.6
-68.8
-69.0
-69.2
-69.4
-69.6
f1 (ppm)
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

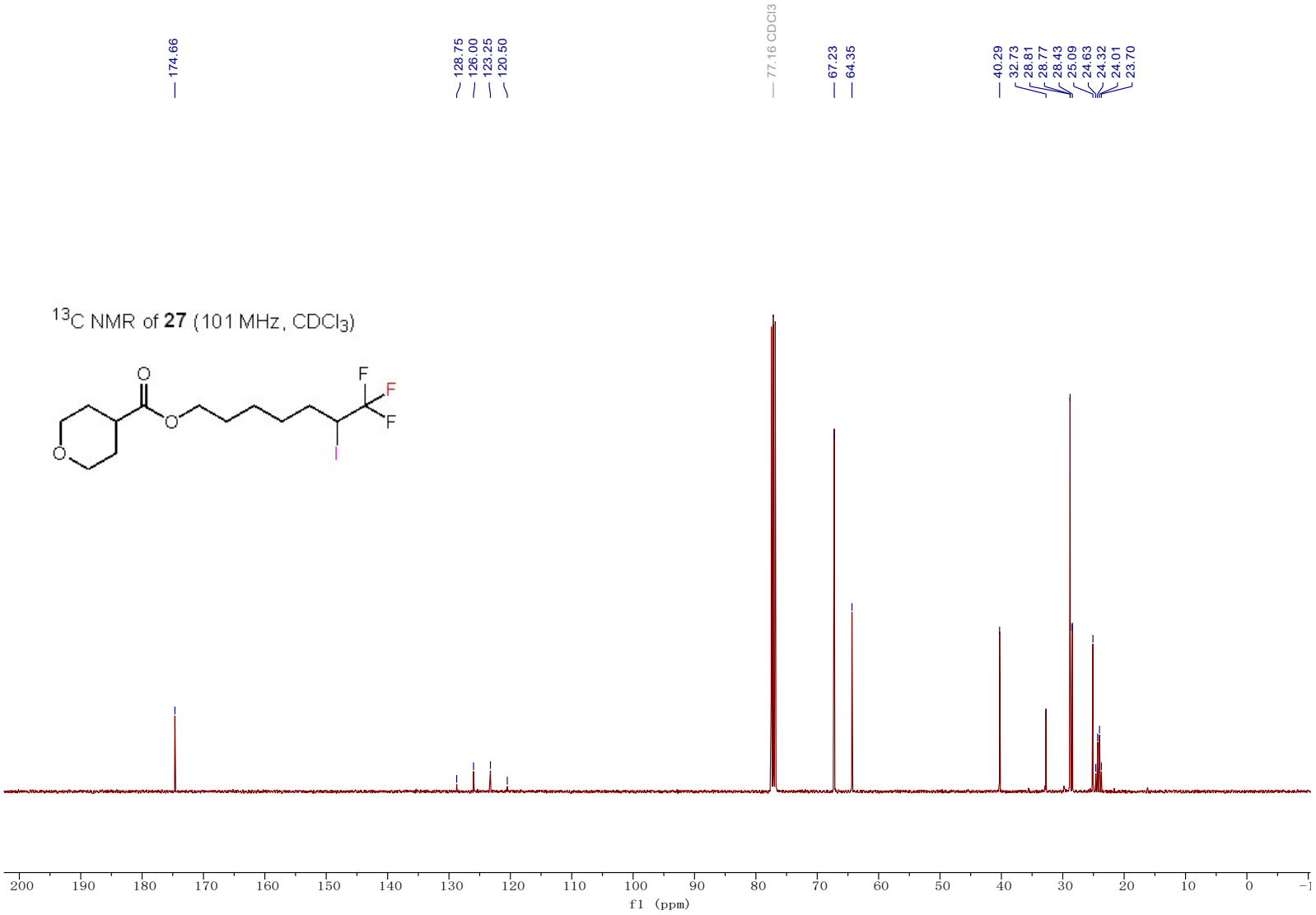


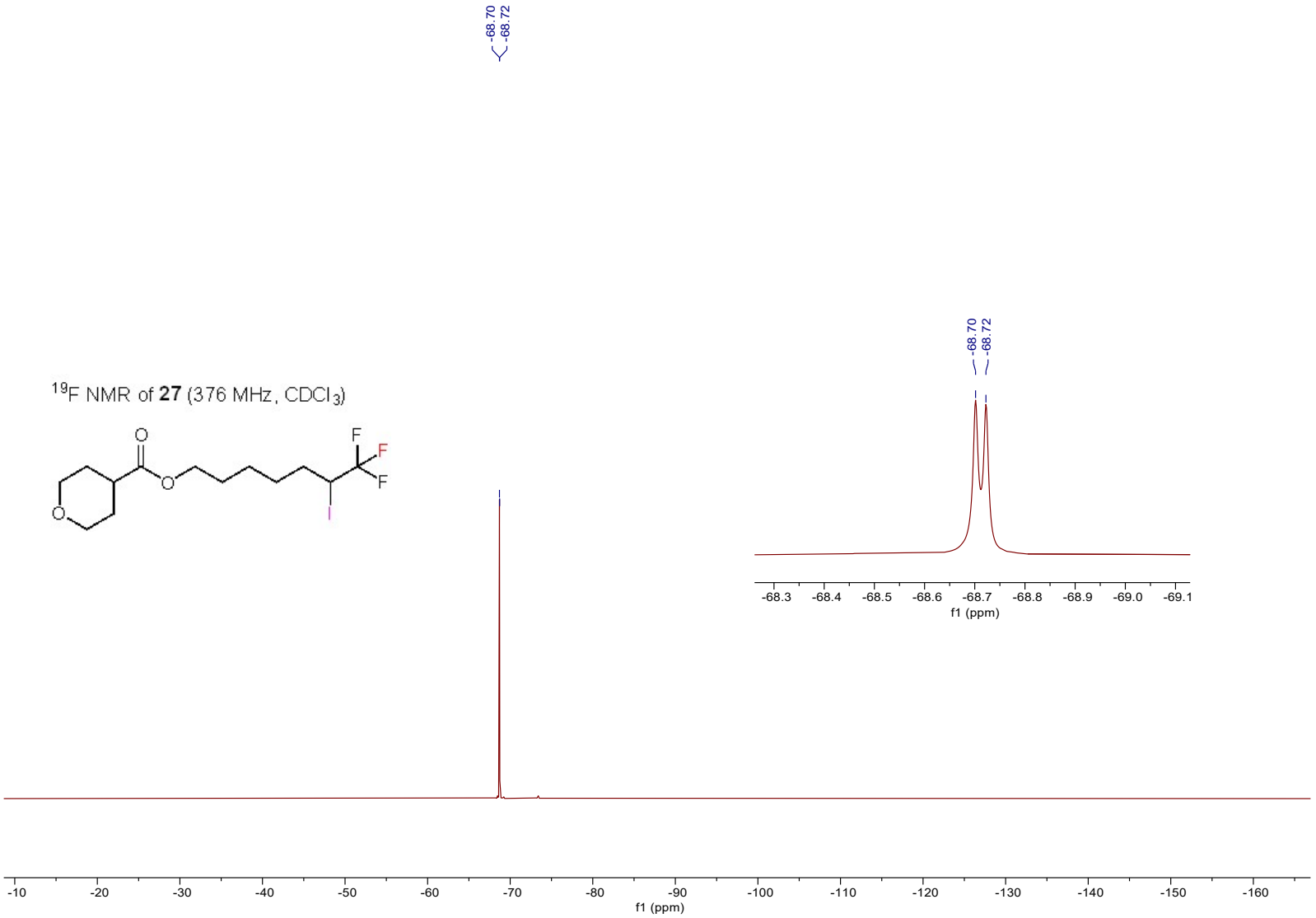
^{1}H NMR of **26** (400 MHz, $CDCl_3$)

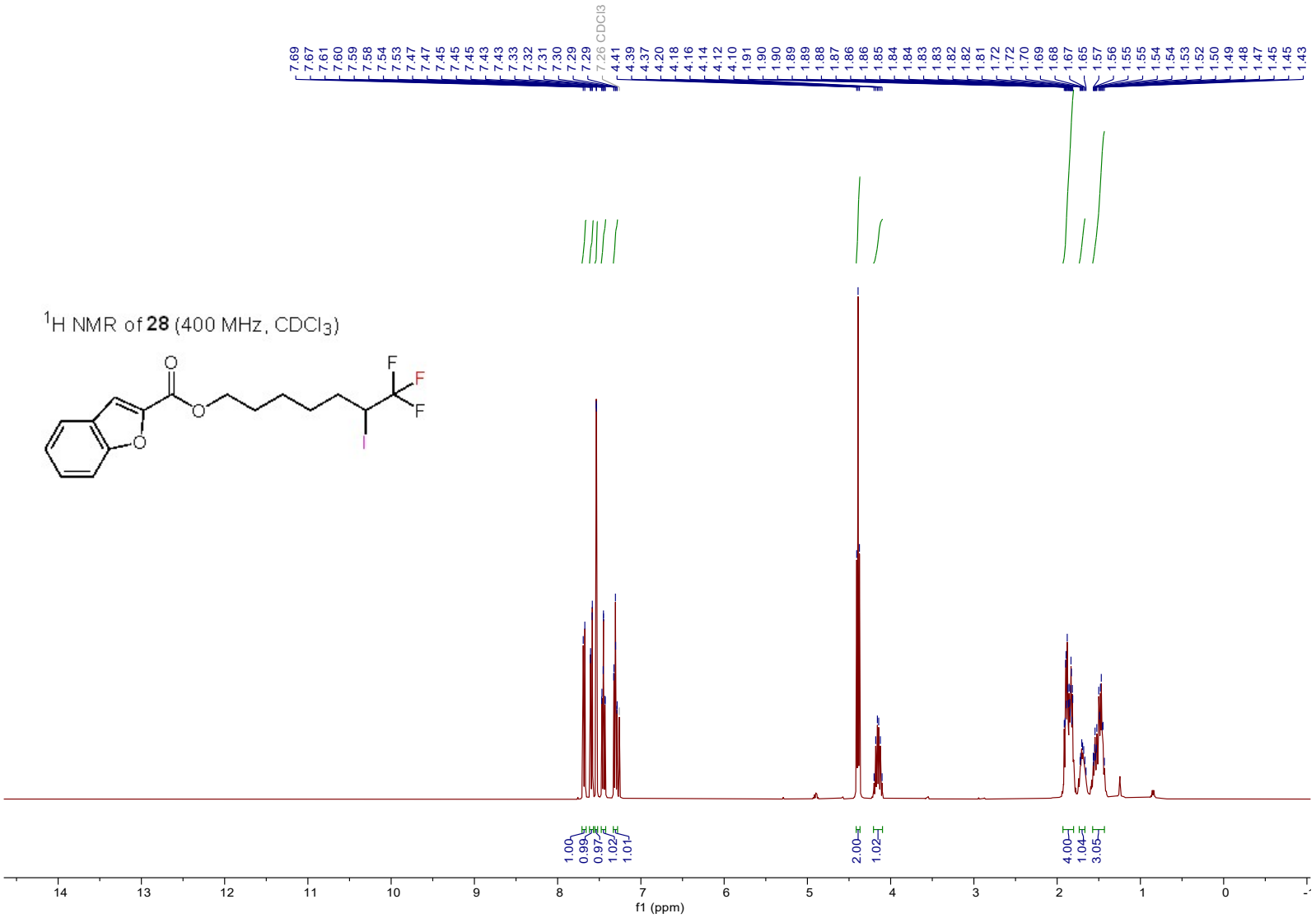

162.38
133.95
133.50
133.48
132.45
128.75
127.88
126.00
123.26
120.51
77.16 CDCl3
64.93
32.71
28.79
28.51
25.11
24.66
24.35
24.04
23.73
13C NMR of 26 (101 MHz, CDCl3)
O
S
O
F
F
F
I
f1 (ppm)

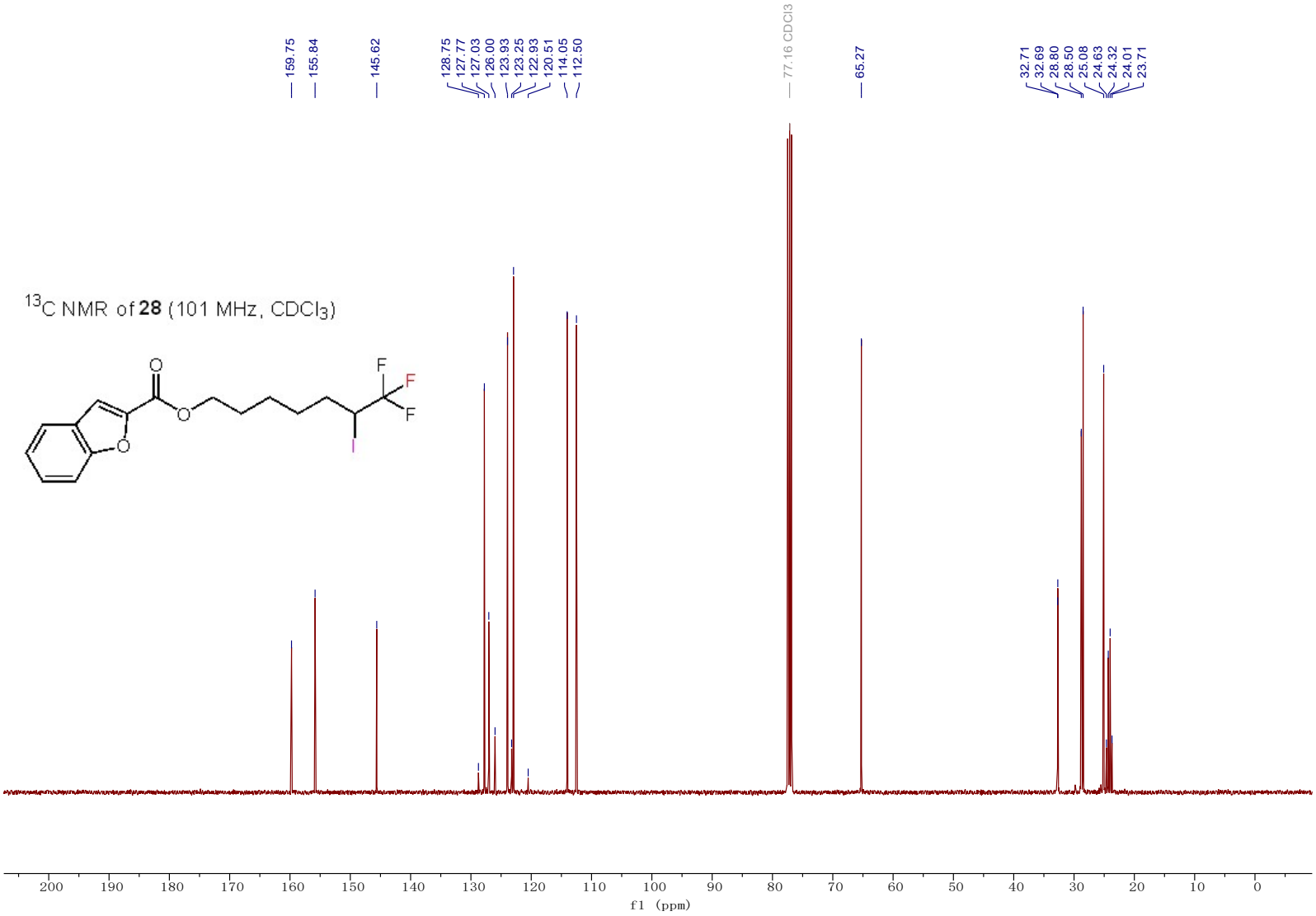

-68.70
-68.72
^{19}F NMR of **26** (376 MHz, $CDCl_3$)
O
S
O
F
F
F
I
-68.70
-68.72
-68.0
-68.5
-69.0
-69.5
f1 (ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

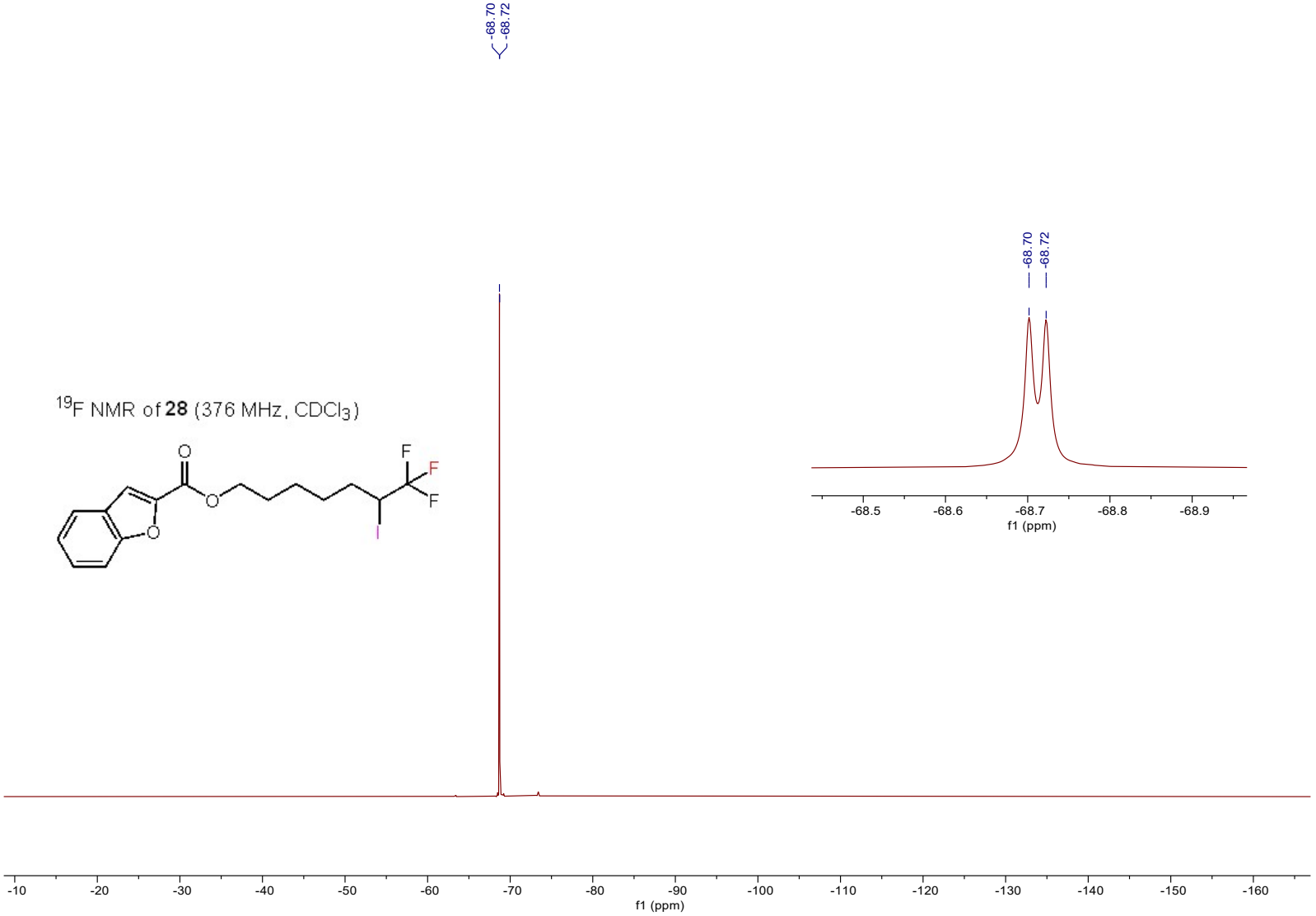

^{1}H NMR of **27** (400 MHz, $CDCl_3$)
O
O
O
F
F
F
I
7.26 CDCl3
4.18 4.16 4.14 4.12 4.11 4.09 4.07 3.98 3.97 3.96 3.95 3.94 3.94 3.45 3.45 3.43 3.42 3.40 3.39 2.57 2.56 2.54 2.53 2.52 2.50 2.49 1.87 1.85 1.85 1.83 1.82 1.81 1.80 1.79 1.78 1.76 1.75 1.75 1.74 1.73 1.72 1.69 1.68 1.68 1.67 1.66 1.66 1.65 1.63 1.46 1.46 1.44 1.43 1.42 1.41 1.40 1.40 1.38 1.37 1.36 1.36
0.94 1.98 2.00 2.02 1.00 4.04 2.04 3.02 3.09
13.5 13.0 12.5 12.0 11.5 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 −1.0 −1
f1 (ppm)

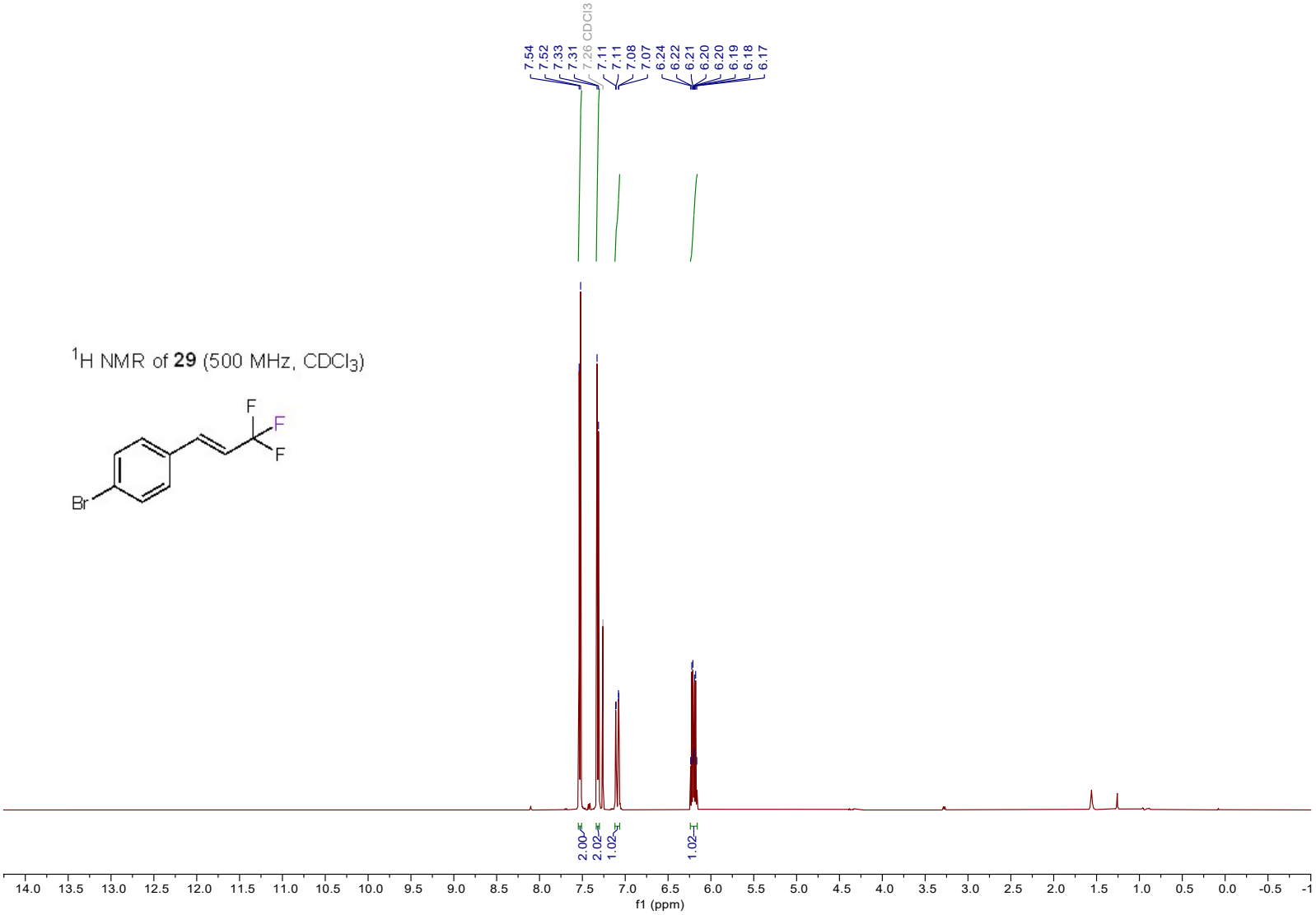

174.66
128.75
126.00
123.25
120.50
77.16 CDCl3
67.23
64.35
40.29
32.73
28.81
28.77
28.43
25.09
24.63
24.32
24.01
23.70
13C NMR of 27 (101 MHz, CDCl3)
O
O
O
F
F
F
I
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

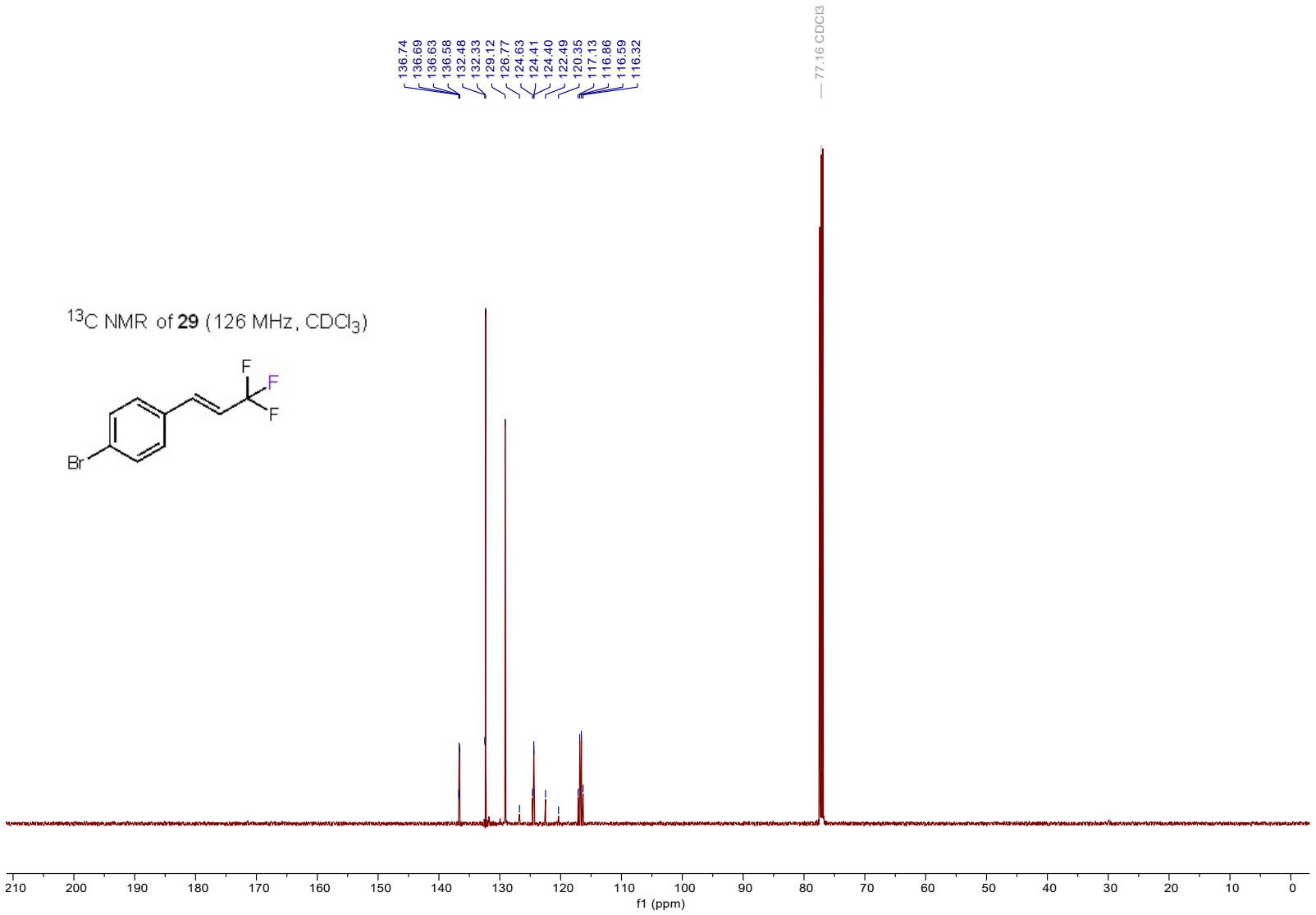

-68.70
-68.72
^{19}F NMR of **27** (376 MHz, $CDCl_3$)
O
O
O
F
F
F
I
-68.70
-68.72
-68.3
-68.4
-68.5
-68.6
-68.7
-68.8
-68.9
-69.0
-69.1
f1 (ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

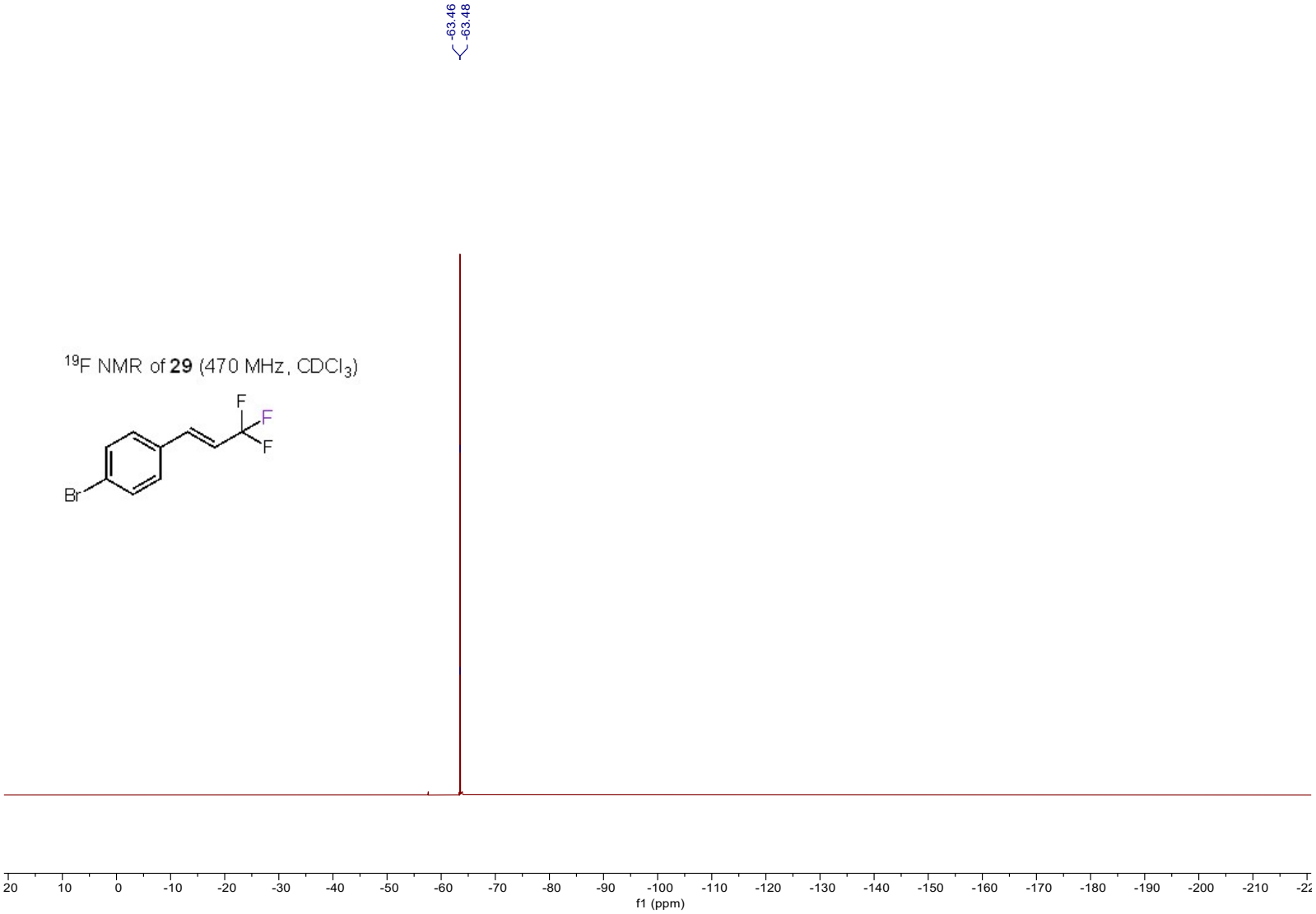

^{1}H NMR of **28** (400 MHz, $CDCl_3$)
O
O
O
F
F
F
I
7.69 7.67 7.61 7.60 7.59 7.58 7.54 7.53 7.47 7.47 7.45 7.45 7.45 7.43 7.43 7.33 7.32 7.31 7.30 7.29 7.29 7.26 CDCl3
4.41 4.39 4.37 4.20 4.18 4.16 4.14 4.12 4.10 1.91 1.90 1.90 1.89 1.89 1.88 1.87 1.86 1.86 1.85 1.84 1.84 1.83 1.83 1.82 1.82 1.81 1.72 1.72 1.70 1.69 1.68 1.67 1.65 1.57 1.56 1.55 1.55 1.54 1.54 1.53 1.52 1.50 1.49 1.48 1.47 1.45 1.45 1.43
1.00 0.99 0.97 1.02 1.01
2.00 1.02
4.00 1.04 3.05
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


159.75
155.84
145.62
128.75
127.77
127.03
126.00
123.93
123.25
122.93
120.51
114.05
112.50
77.16 CDCl3
65.27
32.71
32.69
28.80
28.50
25.08
24.63
24.32
24.01
23.71
13C NMR of 28 (101 MHz, CDCl3)
O
O
O
F
F
F
I
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-68.70
-68.72
19F NMR of 28 (376 MHz, CDCl3)
O
O
O
F
F
F
I
-68.70
-68.72
-68.5
-68.6
-68.7
-68.8
-68.9
f1 (ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)


7.54
7.52
7.33
7.31
7.26 CDCl3
7.11
7.11
7.08
7.07
6.24
6.22
6.21
6.20
6.20
6.19
6.18
6.17
1H NMR of 29 (500 MHz, CDCl3)
F
F
F
Br
2.00
2.02
1.02
1.02
14.0 13.5 13.0 12.5 12.0 11.5 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)


136.74
136.69
136.63
136.58
132.48
132.33
129.12
126.77
124.63
124.41
124.40
122.49
120.35
117.13
116.86
116.59
116.32
77.16 CDCl3
13C NMR of 29 (126 MHz, CDCl3)
F
F
F
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-63.46
-63.48
19F NMR of 29 (470 MHz, CDCl3)
F
F
F
Br
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

7. References

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