Supporting Information

Nickel-Catalyzed Hydrodefluorination/ Deuterodefluorination of CF_3-Alkenes with Formic Acid

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1. General information

All NMR spectra were acquired on Bruker AV 400 MHz NMR spectrometers. ^{1}H NMR chemical shifts were recorded relative to $SiMe_4$ (δ 0.00). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a *J* value ifn Hz. ^{13}C NMR chemical shifts were recorded relative to solvent resonance ($CDCl_3$: δ 77.16). Gas chromatography (GC) analysis was performed on a Shimadzu GC-2030 instrument with GC column SH-Rxi-5ms. GC/MS analysis was performed using Agilent J&W GC column HP-INNOWAX on Agilent triple quadrupole gas chromatography-mass spectrometry 7890B-7000D. High resolution mass spectral analyses (HRMS) were recorded on a Bruck micro-TOF mass spectrometer using electrospray ionization (ESI), positive ion mode.

All air-sensitive compounds were handled under an atmosphere of argon or in a nitrogen-filled glovebox. Glassware was dried at 120 °C for at least 3 h before use. Tetrahydrofuran (THF) were dried over molecular sieve and stored in a glove box. Unless noted otherwise, commercially available chemicals were used as received without purification. Flash column chromatographies were performed using the indicated solvent system on silica gel (200–300 mesh).

2. Hydrodefluorination of CF_3-alkenes

(1) Condition optimization.

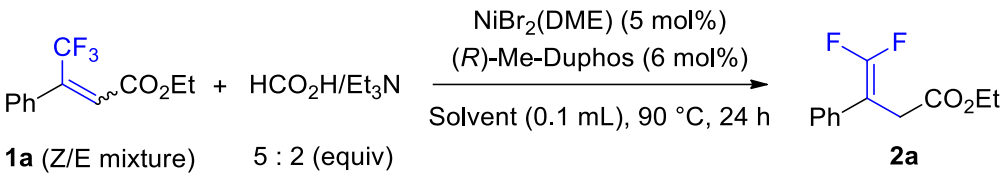
A general procedure for condition optimization: In a nitrogen-filled glove box, Ni salt (0.005 mmol), Ligand (0.006 mmol) and dry solvent (0.1 mL) were charged into a 10-mL Schlenk tube. After stirring for 15 min, internal standard $C_{12}H_{26}$ (10 μL), Hydrogen donor and CF_3-alkenes **1a** (24.4 mg, 0.1 mmol) were added. The Schlenk tube was sealed and the reaction mixture was stirred in a metal sand bath maintained at 90 °C for 24 h. After cooled to room temperature, the reaction mixture was filtered by a short silica gel column plug and determined the yield of **2a** by GC analysis.

Table S1. The effect of nickel salts

1a (Z/E mixture) 5 : 2 (equiv) **2a**

Entry	Ni salts	2a Yield(%)
1	**$NiBr_2$(DME)**	**34**
2	$NiCl_2$(DME)	28
3	$Ni(acac)_2$	25
4	$Ni(OTf)_2$	18
5	$Ni(OAc)•4H_2O$	29
6	$Ni(OAc)_2$	19

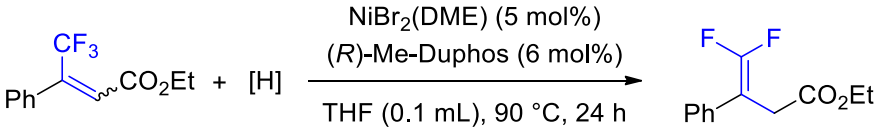
Table S2. The effect of solvents



1a (Z/E mixture) 5 : 2 (equiv) **2a**

Entry	Solvent	2a Yield(%)
1	Toluene	50
2	*i*-PrOH	47
3	1,4-dioxane	39
4	**THF**	**57**
5	DMSO	24

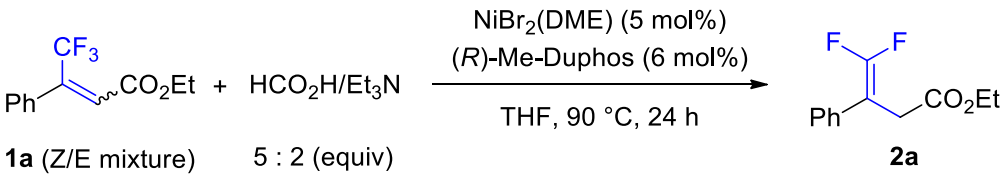
Table S3. The effect of hydrogen donor



1a (Z/E mixture) **2a**

Entry	Hydrogen donor	2a Yield(%)
1	$PhSiH_3$ (1.0 eq.)	5
2	HCOOH/Et_3N (5:4)	23
3	HCOOH/Et_3N (5:1)	51
4	**HCOOH/Et_3N (5:2)**	**57**
5	$LiBH(Et)_3$ (1.5 eq.)	0
6	HCOONa (2.0 eq.)	0

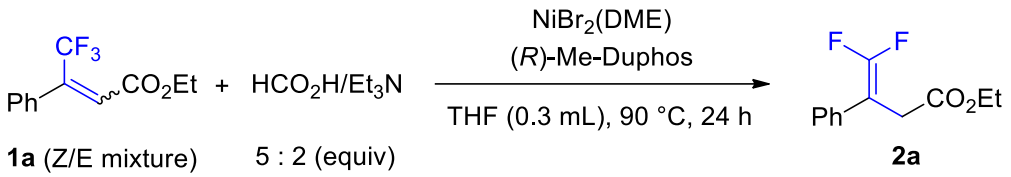
Table S4. The effect of concentration



1a (Z/E mixture) 5 : 2 (equiv) **2a**

Entry	System concentration	2a Yield(%)
1	THF (0.2 mL, *c* = 0.25 M)	59
2	**THF (0.3 mL, *c* = 0.17 M)**	**74**
3	THF (0.4 mL, *c* = 0.12 M)	70

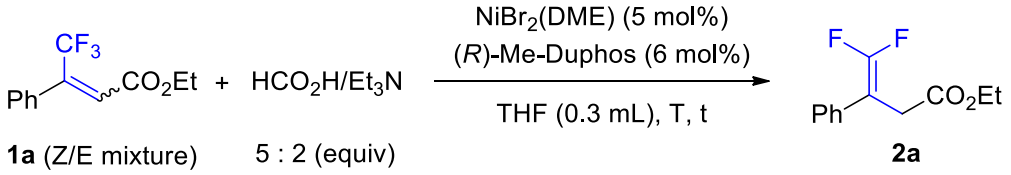
Table S5. The effect of catalyst amount



1a (Z/E mixture) 5 : 2 (equiv) **2a**

Entry	$NiBr_2$(DME) (mmol%)	(*R*)-Me-Duphos (mmol%)	2a Yield(%)
1	**10**	**10**	**93**
2	5	6	74
3	3	4	22
4	1	2	10

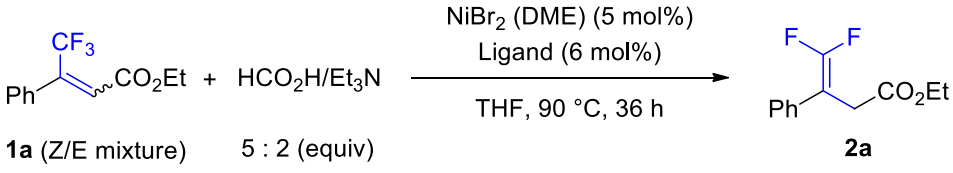
Table S6. The effect of time and temperature



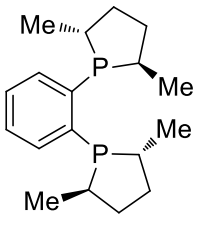
1a (Z/E mixture) 5 : 2 (equiv) **2a**

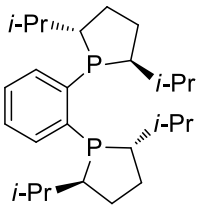
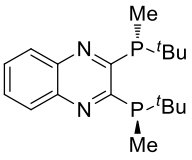
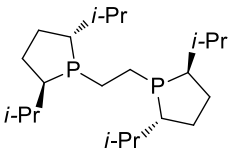
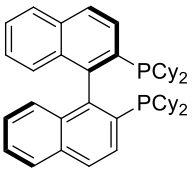
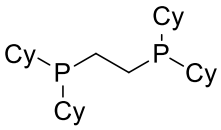
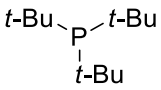
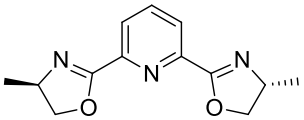
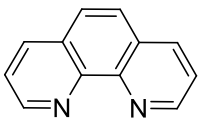
Entry	T (℃), t (h)	2a Yield(%)
1	100 ℃, 24h	82
2	**90 ℃, 36 h**	**90**

Table S7. The effect of ligands

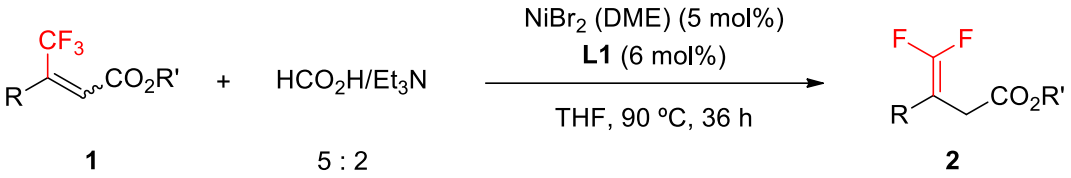


1a (Z/E mixture) 5 : 2 (equiv) **2a**

Entry	Ligand	2a Yield(%)
1	 **L1**, (*R,R*)-Me-DuPhos	**90**

2	 **L2**, (*R,R*)-*i*-Pr-DuPhos	14
3	 **L3,** (*R,R*)-QuinoxP*	72
4	 **L4**, (*R,R*)-*i*-*P*r-BPE	18
5	 **L5,** (*R*)-Cy-BINAP	0
6	 **L6**	0
7	 **L7**	0
8	 **L8**	0
9	 **L9**	0

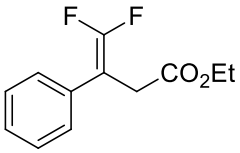
(2) A general procedure for the hydrodefluorination of CF_3-alkenes 1a:



1 **2**

In a nitrogen-filled glove box, $NiBr_2$(DME) (0.005 mmol), (*R*)-Me-Duphos (0.006 mmol) and dry THF (0.3 mL) were charged into a 10-mL Schlenk tube. After stirring for 15 min, Et_3N (28 μL, 0.5 mmol), HCO_2H (20 μL, 0.2 mmol), and CF_3-alkenes **1a** (24.4 mg, 0.1 mmol) were added. The Schlenk tube was sealed and the reaction mixture was stirred in a metal sand bath maintained at 90 °C for 36 h. After cooled to room temperature, the reaction was quenched by 2 mL of dilute HCl (1.0 M). The reaction mixture was extracted 3 times by EA and dried by anhydrous Na_2SO_4. Solvent was removed and the residue was purified by silica gel column chromatography using EA/Hexanes as eluent to give the alkylation product.

(3) Analytical data for alkylation products:



Ethyl 4,4-difluoro-3-phenylbut-3-enoate (2a) [852561-60-5]

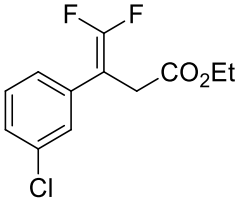
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 90%. The NMR data of 2a are consistent with the data reported in the literature (X.-Q. Chu, L.-W. Sun, Y.-L. Chen, J.-W. Chen, X. Ying, M. Ma, Z.-L. Shen, *Green Chem.,* 2022, **24**, 2777-2782).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.19 (m, 5H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.39 (t, *J* = 2.2 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.30 (dd, *J* = 4.0, 2.9 Hz), 154.96 (dd, *J* = 292.1, 289.1 Hz), 133.20 (t, *J* = 3.9 Hz), 128.65, 128.01 (t, *J* = 3.0 Hz), 127.69, 87.33 (dd, *J* = 21.3, 17.7 Hz), 61.24, 34.05 (d, *J* = 2.3 Hz), 14.20.

^{19}F NMR (376 MHz, $CDCl_3$) δ -87.91 (d, *J* = 35.5 Hz, 1F), -89.19 (d, *J* = 34.9 Hz, 1F).

GC-MS (EI): calculated for $C_{12}H_{12}F_2O_2$ $[M\text{-}H]^+$: 225.1, found: 225.1.



Ethyl 3-(3-chlorophenyl)-4,4-difluorobut-3-enoate (2b)

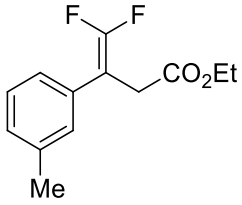
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 86%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.13 (m, 4H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.30 (t, *J* = 2.2 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.98 (dd, *J* = 3.9, 2.7 Hz), 155.12 (dd, *J* = 294.9, 247.5 Hz,), 135.04 (t, *J* = 4.0), 134.58, 129.90, 128.20 (t, *J* = 3.8 Hz), 127.90, 126.22 (t, *J* = 3.9 Hz), 86.69 (dd, *J* = 22.8, 17.5 Hz), 61.40, 33.82 (d, *J* = 2.3 Hz), 14.22.

^{19}F NMR (376 MHz, $CDCl_3$) δ -86.58 (d, *J* = 32.4 Hz, 1F), -87.66 (d, *J* = 32.3 Hz, 1F).

HRMS (ESI): calculated for $C_{12}H_{11}ClF_2O_2$ $[M+Na]^+$: 283.0313, found: 283.0324.



Ethyl 4,4-difluoro-3-(m-tolyl)but-3-enoate (2c)

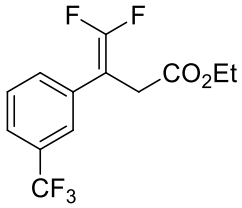
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 79%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.14 (m, 1H), 7.04 (dd, *J* = 17.7, 9.0 Hz, 3H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.30 (t, *J* = 2.1 Hz, 2H), 2.28 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.35, 154.94 (dd, *J* = 292.1, 288.7 Hz), 138.25, 133.12 (t, *J* = 3.8 Hz), 128.72 (t, *J* = 3.3 Hz), 128.53, 128.49, 125.09 (t, *J* = 3.5 Hz), 87.34 (dd, *J* = 21.3, 17.9 Hz), 61.21, 34.10 (d, *J* = 2.4 Hz), 21.58, 14.22.

^{19}F NMR (376 MHz, $CDCl_3$) δ -88.15 (d, *J* = 35.8 Hz, 1F), -89.25 (d, *J* = 35.8 Hz, 1F).

HRMS (ESI): calculated for $C_{13}H_{14}F_2O_2$ $[M+Na]^+$: 263.0860, found: 263.0876.



Ethyl 4,4-difluoro-3-(3-(trifluoromethyl)phenyl)but-3-enoate (2d)

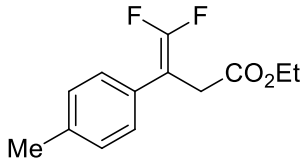
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 78%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.30 (m, 4H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.34 (t, *J* = 2.2 Hz, 2H), 1.13 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.91 (dd, *J* = 4.2, 2.7 Hz), 155.22 (dd, *J* = 293.4, 290.5 Hz), 134.15 (t, *J* = 4.1 Hz), 131.43, 131.17 (q, *J* = 32.4 Hz), 129.21, 124.87 (dd, *J* = 7.4, 3.7 Hz), 124.53 (dd, *J* = 7.4, 3.7 Hz), 124.05 (q, *J* = 272.4 Hz), 86.77 (dd, *J* = 22.6, 17.4 Hz), 61.46, 33.82 (d, *J* = 2.1 Hz), 14.14.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.81 (s, 3F), -86.34 (d, *J* = 32.1 Hz, 1F), -87.75 (d, *J* = 32.3 Hz, 1F).

HRMS (ESI): calculated for $C_{13}H_{11}F_5O_2$ $[M+Na]^+$: 317.0577, found: 317.0583.



Ethyl 4,4-difluoro-3-(p-tolyl)but-3-enoate (2e)

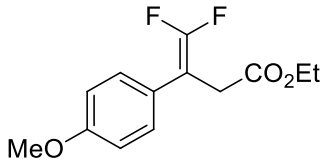
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 85%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.37 (t, *J* = 2.2 Hz, 2H), 2.34 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.37 (dd, *J* = 4.1, 2.8 Hz), 154.87 (dd, *J* = 291.7, 288.7 Hz), 137.49, 130.18 (t, *J* = 3.8 Hz), 129.36, 127.85 (t, *J* = 3.5 Hz), 87.14 (dd, *J* = 21.3, 17.9 Hz), 61.20, 34.06 (d, *J* = 2.4 Hz), 21.26, 14.22.

^{19}F NMR (376 MHz, $CDCl_3$) δ -88.46 (d, *J* = 36.6 Hz, 1F), -89.55 (d, *J* = 36.5 Hz, 1F).

HRMS (ESI): calculated for $C_{13}H_{14}F_2O_2$ $[M+Na]^+$: 263.0860, found: 263.0866.



Ethyl 4,4-difluoro-3-(4-methoxyphenyl)but-3-enoate (2f) [2797146-95-1]

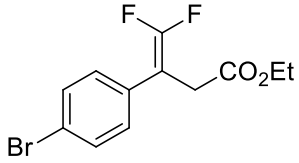
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 66%. The NMR data of **2f** are consistent with the data reported in the literature (J. Yang, S. Ponra, X. Li, B. B. C. Peters, L. Massaro, T. Zhou, P. G. Andersson, *Chem. Sci.,* 2022, **13**, 8590-8596).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.36 (t, *J* = 2.0 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.42 (dd, *J* = 4.1, 2.8 Hz), 159.03, 154.78 (dd, *J* = 291.1, 288.5 Hz), 129.21 (t, *J* = 3.5 Hz), 125.35 (t, *J* = 3.8 Hz), 114.11, 86.83 (dd, *J* = 21.6, 18.2 Hz), 61.21, 55.39, 34.18 (d, *J* = 2.5 Hz), 14.24.

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.15 (d, *J* = 38.2 Hz, 1F), -90.20 (d, *J* = 38.2 Hz, 1F).

GC-MS (EI): calculated for $C_{13}H_{14}F_2O_3$ $[M-H]^+$: 255.1, found: 255.1.



Ethyl 3-(4-bromophenyl)-4,4-difluorobut-3-enoate (2g)

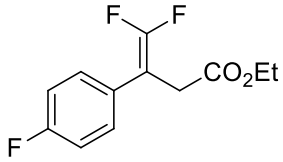
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 77%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.36 (s, 2H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.03, 154.90 (dd, *J* = 292.9, 289.9 Hz), 132.15 (t, *J* = 4.0 Hz), 131.84, 129.66 (t, *J* = 3.6 Hz), 121.74, 86.73 (dd, *J* = 22.3, 17.5 Hz), 61.36, 33.80 (d, *J* = 2.3 Hz), 14.21.

^{19}F NMR (376 MHz, $CDCl_3$) δ -87.01 (d, *J* = 33.4 Hz, 1F), -88.20 (d, *J* = 33.6 Hz, 1F).

HRMS (ESI): calculated for $C_{12}H_{11}BrF_2O_2$ $[M+Na]^+$: 326.9808, found: 326.9774.



Ethyl 4,4-difluoro-3-(4-fluorophenyl)but-3-enoate (2h)

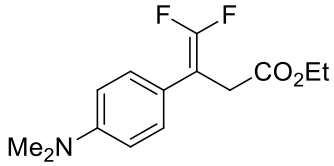
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 47%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 8.2, 5.5 Hz, 2H), 7.04 (t, *J* = 8.7 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.36 (t, *J* = 2.1 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.17 (dd, *J* = 4.2, 2.8 Hz), 154.91 (dd, *J* = 290.5, 289.4 Hz), 130.26 – 129.55 (m), 128.32 (d, *J* = 7.8 Hz), 115.79, 115.57, 86.61 (dd, *J* = 23.0, 19.0 Hz), 61.33, 34.14 (d, *J* = 2.2 Hz), 14.22.

^{19}F NMR (376 MHz, $CDCl_3$) δ -88.14 (dd, *J* = 35.8, 2.3 Hz, 1F), -89.32 (d, *J* = 36.1 Hz, 1F), -113.44 – -115.24 (m, 1F).

HRMS (ESI): calculated for $C_{12}H_{11}F_3O_2$ $[M+Na]^+$: 267.0609, found: 267.0607.



Ethyl 3-(4-(dimethylamino)phenyl)-4,4-difluorobut-3-enoate (2i)

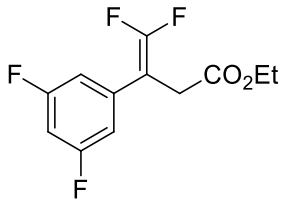
The product was isolated by flash chromatography (EA/hexanes 1/10-1/1) as yellow oily liquid. Yield: 58%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.2 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.35 (t, *J* = 2.0 Hz, 2H), 2.95 (s, 6H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.67, 154.67 (dd, *J* = 290.7, 287.7 Hz), 149.80, 128.67 (t, *J* = 3.6 Hz), 120.71, 112.44, 86.94 (dd, *J* = 21.2, 18.0 Hz), 61.12, 40.57, 34.12 (d, *J* = 2.6 Hz), 14.26.

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.01 (d, *J* = 40.5 Hz, 1F), -90.97 (d, *J* = 40.5 Hz, 1F).

HRMS (ESI): calculated for $C_{14}H_{17}F_2NO_2$ $[M+Na]^+$: 292.1125, found: 292.1125.



Ethyl 3-(3,5-difluorophenyl)-4,4-difluorobut-3-enoate (2j)

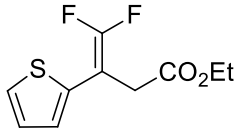
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 40%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 – 6.84 (m, 2H), 6.74 (tt, *J* = 8.8, 2.2 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.36 (t, *J* = 2.2 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.78 (dd, *J* = 4.0, 2.8 Hz), 164.35 (d, *J* = 13.2 Hz), 161.88 (d, *J* = 13.3 Hz), 155.32 (dd, *J* = 294.9, 290.8 Hz), 111.61 – 110.40 (m), 103.52, 103.27, 103.02, 86.48 (dd, *J* = 22.7, 20.3 Hz), 61.54, 33.54 (d, *J* = 1.7 Hz), 14.21.

^{19}F NMR (376 MHz, $CDCl_3$) δ -70.20 (s, 1F), -85.04 (d, *J* = 29.2 Hz, 1F), -85.92 (d, *J* = 29.3 Hz, 1F), -109.43 (s, 1F).

HRMS (ESI): calculated for $C_{12}H_{10}F_4O_2$ $[M+Na]^+$: 285.0515, found: 285.0516.



Ethyl 3-(3,5-difluorophenyl)-4,4-difluorobut-3-enoate (2k)

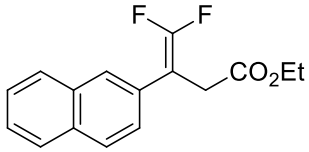
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 68%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.06 – 6.95 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.42 (t, *J* = 2.0 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.92 (dd, *J* = 3.9, 2.9 Hz), 154.84 (dd, *J* = 295.8, 289.8 Hz), 135.15 (d, *J* = 2.9 Hz), 135.08 (d, *J* = 3.0 Hz), 127.20, 125.89 – 124.77 (m), 83.97 (dd, *J* = 26.0, 18.1 Hz), 61.45, 33.83 (d, *J* = 2.9 Hz), 14.24.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.02 (d, *J* = 28.7 Hz, 1F), -89.10 (d, *J* = 28.8 Hz, 1F).

HRMS (ESI): calculated for $C_{10}H_{10}F_2O_2S$ $[M+Na]^+$: 255.0268, found: 255.0268.



Ethyl 4,4-difluoro-3-(naphthalen-2-yl)but-3-enoate (2l)

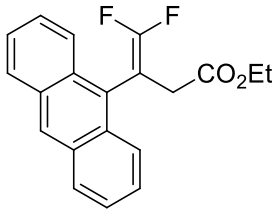
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 58%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.72 (m, 4H), 7.54 – 7.37 (m, 3H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.50 (t, *J* = 1.9 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.31 (dd, *J* = 4.0, 2.9 Hz), 155.19 (dd, *J* = 292.7, 289.4 Hz), 133.34, 132.67, 130.63 (t, *J* = 3.9 Hz), 128.31, 128.15, 127.72, 127.17 (t, *J* = 3.6 Hz), 126.49, 126.43, 125.81 (dd, *J* = 4.3, 2.8 Hz), 87.51 (dd, *J* = 21.7, 17.6 Hz), 61.29, 34.17 (d, *J* = 2.4 Hz), 14.23.

^{19}F NMR (376 MHz, $CDCl_3$) δ -87.34 (d, *J* = 34.7 Hz, 1F), -88.75 (d, *J* = 34.4 Hz, 1F).

HRMS (ESI): calculated for $C_{16}H_{14}F_2O_2$ $[M+Na]^+$: 299.0860, found: 299.0859.



Ethyl 3-(anthracen-9-yl)-4,4-difluorobut-3-enoate (2m)

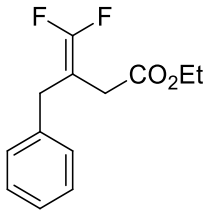
The product was isolated by flash chromatography (EA/hexanes 1/20-1/1) as yellow oily liquid. Yield: 55%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.13 (d, *J* = 8.7 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.50 (dddd, *J* = 9.4, 7.8, 6.5, 1.2 Hz, 4H), 3.98 (q, *J* = 7.1 Hz, 2H), 3.55 (t, *J* = 2.2 Hz, 2H), 1.03 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.89, 154.86 (dd, *J* = 293.9, 288.5 Hz), 131.64, 130.22 (d, *J* = 2.3 Hz), 129.01, 128.27, 126.69 (dd, *J* = 4.2, 1.3 Hz), 126.45, 125.52, 125.43, 82.78 (dd, *J* = 23.6, 22.0 Hz), 61.23, 35.97 (d, *J* = 2.1 Hz), 13.98.

^{19}F NMR (376 MHz, $CDCl_3$) δ -84.90 (d, *J* = 32.0 Hz, 1F), -87.52 (d, *J* = 31.8 Hz, 1F).

HRMS (ESI): calculated for $C_{20}H_{16}F_2O_2$ $[M+Na]^+$: 349.1016, found: 349.0989.



Ethyl 3-benzyl-4,4-difluorobut-3-enoate (2n)

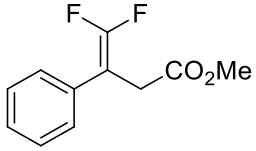
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 72%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.10 (m, 5H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.42 (s, 2H), 2.87 (t, *J* = 1.9 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.41 (dd, *J* = 4.2, 2.8 Hz), 154.80 (dd, *J* = 286.6, 285.0 Hz), 137.79 (t, *J* = 3.0 Hz), 128.93, 128.72, 126.84, 84.39 (dd, *J* = 22.0, 17.1 Hz), 61.06, 32.73 (d, *J* = 1.4 Hz), 31.55 (d, *J* = 2.8 Hz), 14.24.

^{19}F NMR (376 MHz, $CDCl_3$) δ -93.28 (d, *J* = 47.1 Hz, 1F), -93.92 (d, *J* = 47.1 Hz, 1F).

HRMS (ESI): calculated for $C_{13}H_{14}F_2O_2$ $[M+Na]^+$: 263.0860, found: 263.0862.



Methyl 4,4-difluoro-3-phenylbut-3-enoate (2o)

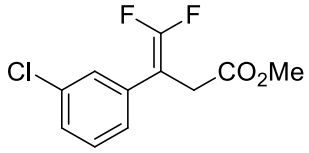
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 94%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.26 (m, 5H), 3.67 (s, 3H), 3.40 (t, *J* = 2.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.78, 155.01 (dd, *J* = 292.8, 289.2 Hz), 133.12 (t, *J* = 3.8 Hz), 128.69, 127.97 (t, *J* = 3.6 Hz), 127.74, 87.22 (dd, *J* = 21.3, 17.9 Hz), 52.32, 33.79 (d, *J* = 2.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -87.69 (d, *J* = 34.8 Hz, 1F), -88.92 (d, *J* = 34.8 Hz, 1F).

HRMS (ESI): calculated for $C_{11}H_{10}F_2O_2$ $[M+Na]^+$: 235.0547, found: 235.0550.



Methyl 3-(3-chlorophenyl)-4,4-difluorobut-3-enoate (2p)

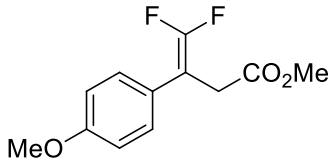
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 73%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.13 (m, 5H), 3.69 (s, 3H), 3.39 (t, *J* = 2.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.49 (dd, *J* = 4.1, 3.0 Hz), 155.15 (dd, *J* = 293.4, 290.1 Hz), 134.93 (t, *J* = 4.0 Hz), 134.60, 129.94, 128.14 (t, *J* = 3.0 Hz), 127.95, 126.16 (t, *J* = 3.5 Hz), 86.54 (dd, *J* = 22.6, 17.6 Hz), 52.49, 33.55 (d, *J* = 2.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -86.33 (d, *J* = 31.9 Hz, 1F), -87.43 (d, *J* = 31.9 Hz, 1F).

HRMS (ESI): calculated for $C_{12}H_{11}ClF_2O_2$ $[M+Na]^+$: 269.0157, found: 269.0160.



Methyl 4,4-difluoro-3-(4-methoxyphenyl)but-3-enoate (2q)

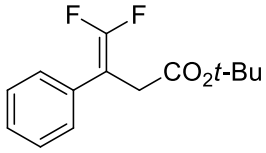
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 71%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 2H), 6.95 – 6.88 (m, 2H), 3.83 (s, 3H), 3.70 (s, 3H), 3.40 (t, *J* = 2.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.88 (dd, *J* = 4.1, 2.9 Hz), 159.07, 154.81 (dd, *J* = 291.1, 288.6 Hz), 129.16 (t, *J* = 3.6 Hz), 125.26 (t, *J* = 3.7 Hz), 114.16, 86.72 (dd, *J* = 21.4, 18.2 Hz), 55.38, 52.29, 33.92 (d, *J* = 2.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -88.94 (d, *J* = 37.8 Hz, 1F), -89.96 (d, *J* = 37.8 Hz, 1F).

HRMS (ESI): calculated for $C_{12}H_{12}F_2O_3$ $[M+Na]^+$: 265.0653, found: 265.0655.



***tert*-Butyl 4,4-difluoro-3-phenylbut-3-enoate (2r)**

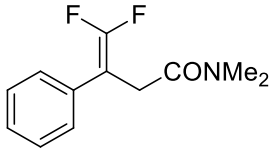
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 56%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 5H), 3.31 (t, *J* = 2.2 Hz, 2H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.47, 154.84 (dd, *J* = 290.8, 289.7 Hz), 128.57, 128.02 (t, *J* = 4.0 Hz), 127.57, 100.13, 89.16 (dd, *J* = 20.0, 18.8 Hz), 81.46, 35.24 (d, *J* = 2.7 Hz), 28.01.

^{19}F NMR (376 MHz, $CDCl_3$) δ -88.42 (d, *J* = 36.2 Hz, 1F), -89.84 (d, *J* = 36.2 Hz, 1F).

HRMS (ESI): calculated for $C_{14}H_{16}F_2O_2$ $[M+Na]^+$: 277.1016, found: 277.1014.



4,4-Difluoro-N,N-dimethyl-3-phenylbut-3-enamide (2s) [849104-36-5]

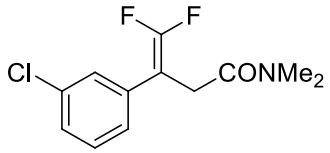
The product was isolated by flash chromatography (EA/hexanes 1/20-1/1) as yellow oily liquid. Yield: 51%. The NMR data of **2s** are consistent with the data reported in the literature (C.-R. Cao, S. Ou, M. Jiang, J.-T. Liu, *Tetrahedron Lett.,* 2017, **58**, 482-485.)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 5H), 3.41 (t, *J* = 2.1 Hz, 2H), 3.03 (s, 3H), 2.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.06, 154.71 (dd, *J* = 291.4, 287.8 Hz), 133.75 (t, *J* = 4.0 Hz), 128.58, 128.27 (t, *J* = 3.3 Hz), 127.57, 87.97 (dd, *J* = 22.6, 18.8 Hz), 37.38, 35.91, 33.46 (d, *J* = 2.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.09 (d, *J* = 38.3 Hz, 1F), -90.02 (d, *J* = 38.2 Hz, 1F).

GC-MS (EI): calculated for $C_{12}H_{13}F_2NO$ $[M-H]^+$: 224.1, found: 224.0.



3-(3-Chlorophenyl)-4,4-difluoro-N,N-dimethylbut-3-enamide (2t)

The product was isolated by flash chromatography (EA/hexanes 1/20-1/1) as yellow oily liquid. Yield: 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 4H), 3.39 (s, 2H), 3.05 (s, 3H), 2.95 (s, 3H).

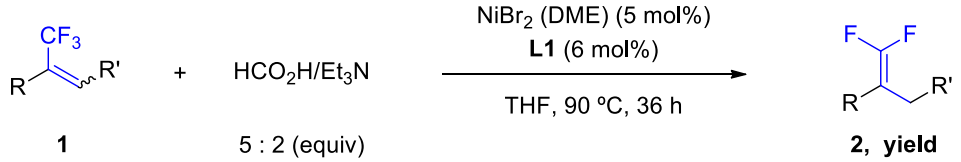
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.72, 154.89 (dd, *J* = 292.4, 288.7 Hz), 135.69 (t, *J* = 3.0 Hz), 134.42, 129.81, 128.33 (t, *J* = 3.6 Hz), 127.74, 126.57 (t, *J* = 3.3 Hz), 87.50 (dd, *J* = 22.3, 17.4 Hz), 37.37, 35.93, 33.15 (d, *J* = 2.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -87.77 (d, *J* = 35.4 Hz, 1F), -88.61 (d, *J* = 35.8 Hz, 1F).

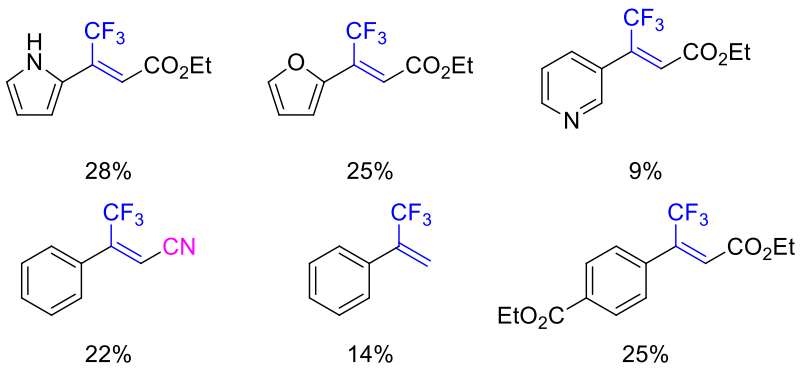
HRMS (ESI): calculated for $C_{12}H_{12}ClF_2NO$ $[M+Na]^+$: 282.0473, found: 282.0475.

(4) Unsuccessful substrates

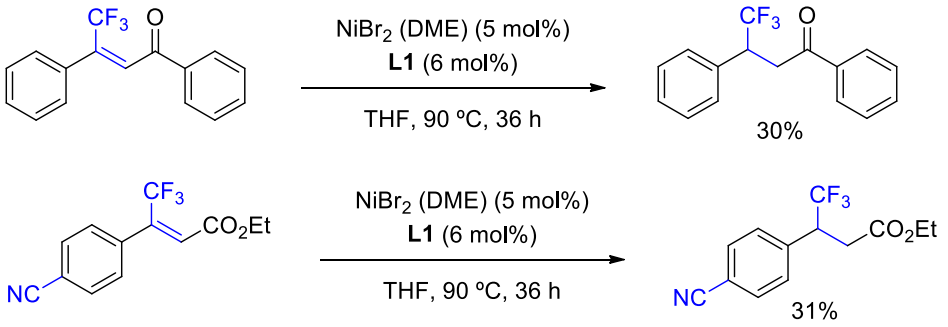
(1) substrates with low conversions and yields



1 **2, yield**



(2) substates underwent hydrogenation reaction



(3) tetra-substituted substrate underwent multiple defluorination

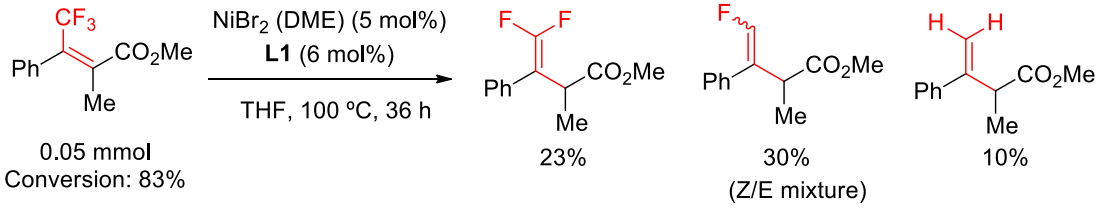
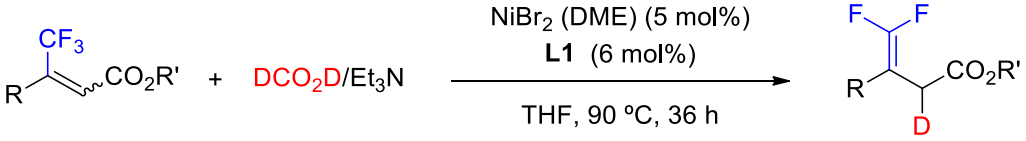


Figure S1 Unsuccessful substrates

3. Deuterodefluorination of CF_3-alkenes

(1) A general procedure for the Deuterodefluorination of CF_3-alkenes 1a:

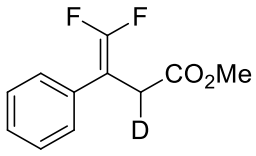


1 **3**

In a nitrogen-filled glove box, $NiBr_2$(DME) (0.005 mmol), (R)-Me-Duphos (0.006 mmol) and dry THF (0.3 mL) were charged into a 10-mL Schlenk tube. After stirring for 15 min, Et_3N (28 μL, 0.5 mmol), DCO_2D (19 μL, 0.2 mmol), and CF_3-alkenes **1a** (24.4 mg, 0.1 mmol) were added. The Schlenk

tube was sealed and the reaction mixture was stirred in a metal sand bath maintained at 90 °C for 36 h. After cooled to room temperature, the reaction was quenched by 2 mL of dilute HCl (1.0 M). The reaction mixture was extracted 3 times by EA and dried by anhydrous Na_2SO_4. Solvent was removed and the residue was purified by silica gel column chromatography using EA/Hexanes as eluent to give the alkenylation product.

(2) Analytical data for products：



Methyl 4,4-difluoro-3-phenylbut-3-enoate-2-D (3a)

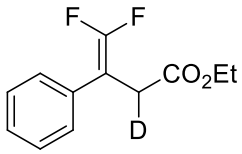
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 77% (1.28 D).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.19 (m, 5H), 3.67 (s, 3H), 3.39 (pseudomultiplet, 0.72H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.78, 155.08 (dd, *J* = 276.9, 273.7 Hz), 133.09 (t, *J* = 2.9 Hz), 128.69, 127.96 (t, *J* = 3.5 Hz), 127.73, 87.17 (dd, *J* = 21.7, 17.6 Hz), 52.31, 33.55 (t, $J_{C\text{-}D}$ = 20.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -87.69 (d, *J* = 35.3 Hz, 1F), -88.90 (d, *J* = 34.8 Hz, 1F).

HRMS (ESI): calculated for $C_{11}H_9DF_2O_2$ $[M+Na]^+$: 236.0610, found: 236.0607.



Ethyl 4,4-difluoro-3-phenylbut-3-enoate-2-D (3b)

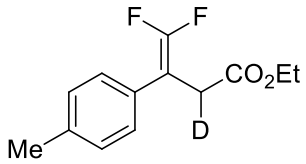
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 75% (1.33 D).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 5H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.49 – 3.22 (pseudomultiplet, 0.67H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.27, 154.96 (dd, *J* = 292.2, 289.2 Hz), 133.17 (t, *J* = 3.7 Hz), 128.62, 127.99 (t, *J* = 3.5 Hz), 127.67, 87.30 (dd, *J* = 21.4, 17.7 Hz), 61.20, 33.78 (t, $J_{C\text{-}D}$ = 19.2 Hz), 14.16.

^{19}F NMR (376 MHz, $CDCl_3$) δ -87.97 (dd, *J* = 35.7, 5.7 Hz, 1F), -89.18 (dd, *J* = 35.5, 6.4 Hz, 1F).

HRMS (ESI): calculated for $C_{12}H_{11}DF_2O_2$ $[M+Na]^+$: 250.0766, found: 250.0775.



Ethyl 4,4-difluoro-3-(p-tolyl)but-3-enoate-2-D (3c)

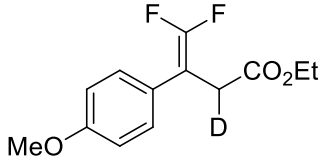
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 74% (1.18 D).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 7.5 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.32 – 3.24 (pseudomultiplet, 0.82H), 2.26 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.40, 154.85 (dd, *J* = 291.9, 288.8 Hz), 137.48, 129.36, 127.82 (t, *J* = 3.5 Hz), 87.07 (dd, *J* = 21.6, 18.3 Hz), 61.20, 33.79 (t, $J_{C\text{-}D}$ = 18.2 Hz), 21.27, 14.22.

^{19}F NMR (376 MHz, $CDCl_3$) δ -88.51 (d, *J* = 36.4 Hz, 1F), -89.55 (d, *J* = 36.2 Hz, 1F).

HRMS (ESI): calculated for $C_{13}H_{13}DF_2O_2$ $[M+Na]^+$: 264.0923, found: 264.0918.



Ethyl 4,4-difluoro-3-(4-methoxyphenyl)but-3-enoate-2-D (3d)

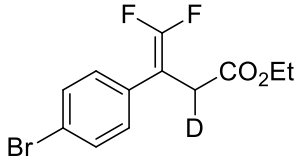
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 51% (1.16 D).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 8.9, 0.9 Hz, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 3.31 – 3.22 (pseudomultiplet, 0.84H), 1.13 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.43, 159.01, 154.77 (dd, *J* = 290.7, 288.5 Hz), 129.21 (d, *J* = 3.4 Hz), 125.32 (t, *J* = 3.6 Hz), 114.10, 86.77 (dd, *J* = 21.6, 17.9 Hz), 61.20, 55.39, 33.90 (t, $J_{C\text{-}D}$ = 20.2 Hz), 14.23.

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.18 (d, *J* = 38.0 Hz, 1F), -90.19 (d, *J* = 37.5 Hz, 1F).

HRMS (ESI): calculated for $C_{13}H_{13}DF_2O_3$ $[M+Na]^+$: 280.0872, found: 280.0871.



Ethyl 3-(4-bromophenyl)-4,4-difluorobut-3-enoate-2-D (3e)

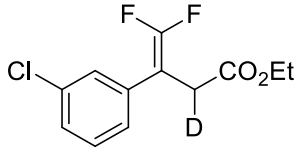
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 60% (1.25 D).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.38 – 3.34 (pseudomultiplet, 0.75H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.05, 154.90 (dd, *J* = 292.8, 290.0 Hz), 132.13 (t, *J* = 3.5 Hz), 131.84, 129.65 (t, *J* = 3.6 Hz), 121.74, 86.67 (dd, *J* = 22.5, 17.6 Hz), 61.35, 33.56 (t, $J_{C\text{-}D}$= 25.3 Hz), 14.21.

^{19}F NMR (376 MHz, $CDCl_3$) δ -87.01 (d, *J* = 33.3 Hz, 1F), -88.17 (d, *J* = 33.3 Hz, 1F).

HRMS (ESI): calculated for $C_{12}H_{10}DBrF_2O_2$ $[M+Na]^+$: 327.9871, found: 327.9872.



Ethyl 3-(3-chlorophenyl)-4,4-difluorobut-3-enoate-2-D (3f)

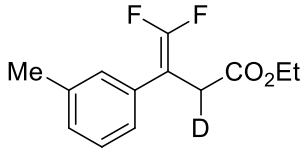
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 66% (1.46 D).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.13 (m, 4H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.35 – 3.23 (pseudomultiplet, 0.54H), 1.14 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.98, 155.12 (dd, *J* = 293.3, 290.2 Hz), 135.01, 134.57, 129.89, 128.18 (t, *J* = 3.7 Hz), 127.89, 126.21 (t, *J* = 3.5 Hz), 86.64 (dd, *J* = 22.5, 17.6 Hz), 61.38, 33.54 (t, $J_{C\text{-}D}$ = 21.2 Hz), 14.20.

^{19}F NMR (376 MHz, $CDCl_3$) δ -86.61 (dd, *J* = 32.0, 4.1 Hz, 1F), -87.64 (dd, *J* = 32.3, 7.9 Hz, 1F).

HRMS (ESI): calculated for $C_{12}H_{10}DClF_2O_2$ $[M+Na]^+$: 284.0376, found: 284.0374.



Ethyl 4,4-difluoro-3-(*m*-tolyl)but-3-enoate-2-D (3g)

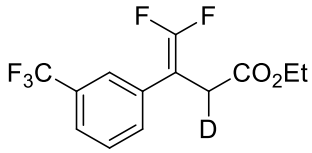
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 61% (1.21 D).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.03 (m, 4H), 4.12 (dd, *J* = 14.2, 7.1 Hz, 2H), 3.36 (pseudomultiplet, 0.79H), 2.35 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.36, 154.93 (dd, *J* = 291.9, 289.0 Hz), 138.25, 133.09 (t, *J* = 3.6 Hz), 128.71 (t, *J* = 3.4 Hz), 128.52, 128.49, 125.08 (t, *J* = 3.5 Hz), 87.28 (dd, *J* = 21.3, 17.9 Hz), 61.20, 33.85 (t, $J_{C\text{-}D}$ = 18.2 Hz), 21.58, 14.22.

^{19}F NMR (376 MHz, $CDCl_3$) δ -88.16 (d, *J* = 35.8 Hz, 1F), -89.24 (d, *J* = 35.8 Hz, 1F).

HRMS (ESI): calculated for $C_{13}H_{13}DF_2O_2$ $[M+Na]^+$: 264.0923, found: 264.0926.



Ethyl 4,4-difluoro-3-(3-(trifluoromethyl)phenyl)but-3-enoate-2-D (3h)

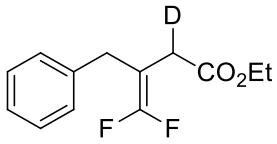
The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 63% (1.58 D).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.32 (m, 4H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.36 – 3.27 (pseudomultiplet, 0.42H), 1.13 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.92, 155.22 (dd, *J* = 293.2, 290.8 Hz), 134.10, 131.41, 131.17 (q, *J* = 32.5 Hz), 129.21, 124.85 (dd, *J* = 7.4, 3.7 Hz), 124.53 (q, *J* = 3.6 Hz), 124.05 (q, *J* = 272.3 Hz), 86.68 (dd, *J* = 25.0, 19.7 Hz), 61.44, 33.57 (t, $J_{C\text{-}D}$ = 20.2 Hz), 14.14.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.82 (s, 1F), -86.37 (d, *J* = 32.0 Hz, 1F), -87.73 (dd, *J* = 32.0, 8.2 Hz, 1F).

HRMS (ESI): calculated for $C_{13}H_{10}DF_5O_2$ $[M+Na]^+$: 318.0640, found: 318.0650.



Ethyl 3-benzyl-4,4-difluorobut-3-enoate-2-D (3i)

The product was isolated by flash chromatography (EA/hexanes 1/100-1/20) as yellow oily liquid. Yield: 71% (1.00 D).

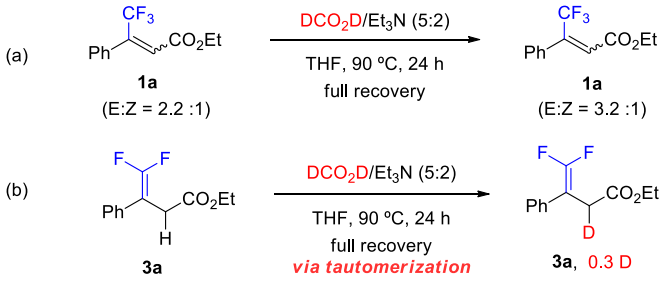
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.05 (m, 5H), 4.01 (q, *J* = 7.1 Hz, 2H), 3.35 (s, 2H), 2.86 – 2.72 (pseudomultiplet, 1.00H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.43, 154.81 (dd, *J* = 286.1, 285.6 Hz), 137.81 (t, *J* = 2.0 Hz), 128.94, 128.73, 126.85, 84.34 (dd, *J* = 22.7, 17.3 Hz), 61.06, 32.69, 31.32 (t, $J_{C\text{-}D}$ = 21.2 Hz), 14.24.

^{19}F NMR (376 MHz, $CDCl_3$) δ -93.29 (dd, *J* = 46.8, 1.5 Hz, 1F), -93.92 (dd, *J* = 46.9, 1.7 Hz, 1F).

HRMS (ESI): calculated for $C_{13}H_{13}DF_2O_2$ $[M+Na]^+$: 264.0923, found: 264.0923.

4. Mechanism studies.



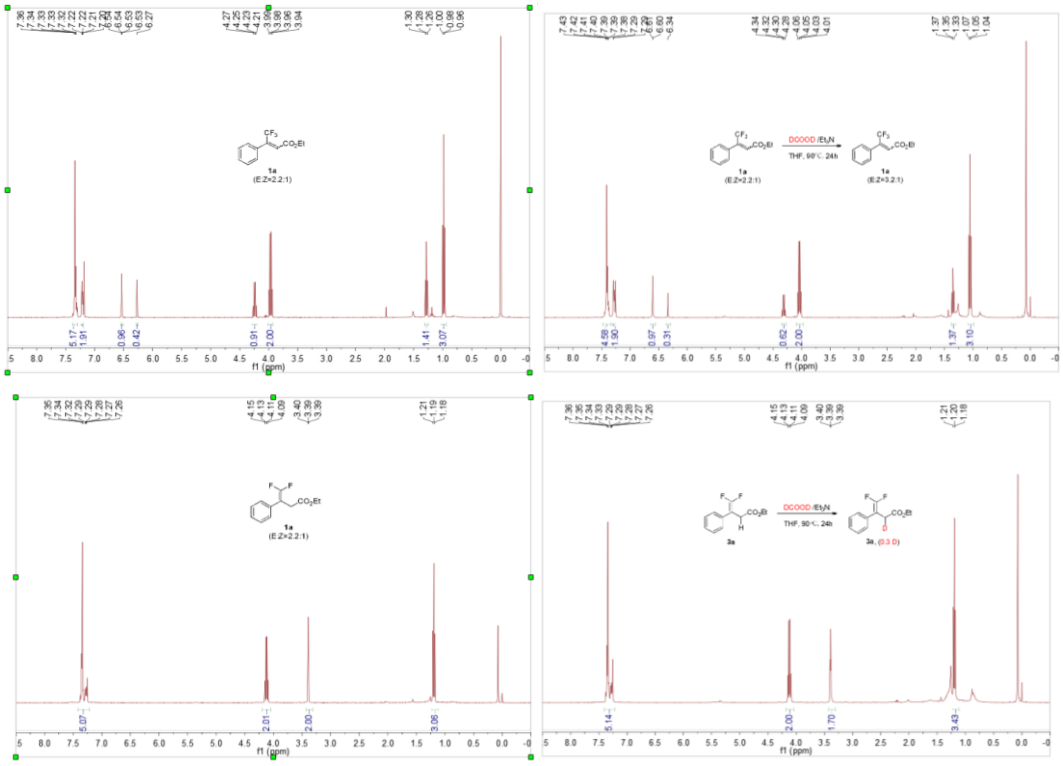


Figure S2 ^{1}H NMR spectra of deuterated compounds

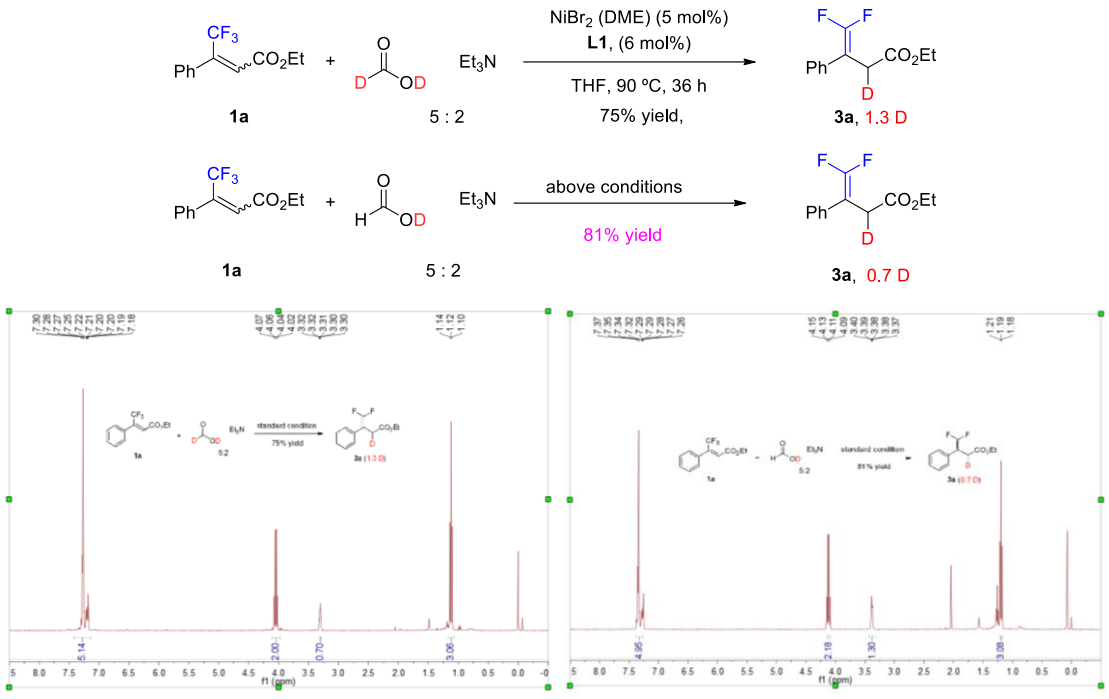


Figure S3 ^{1}H NMR spectra of deuterated compounds

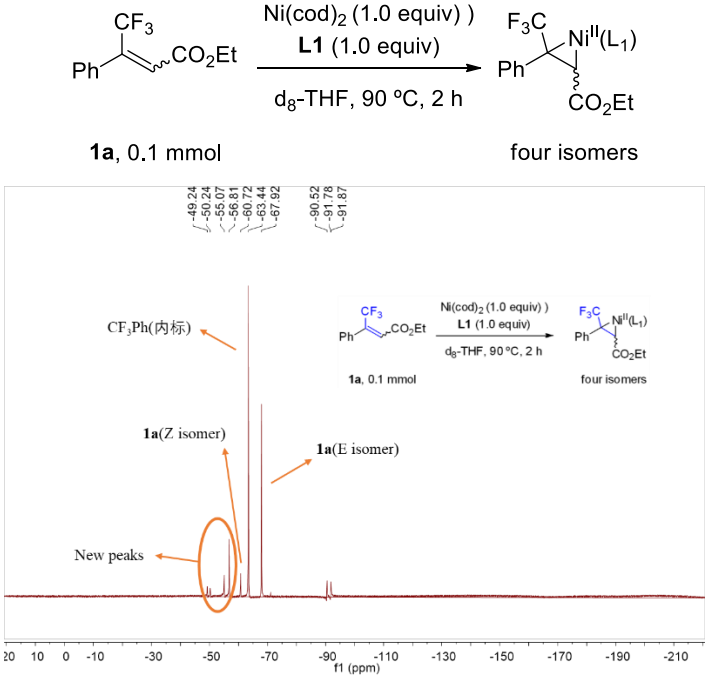
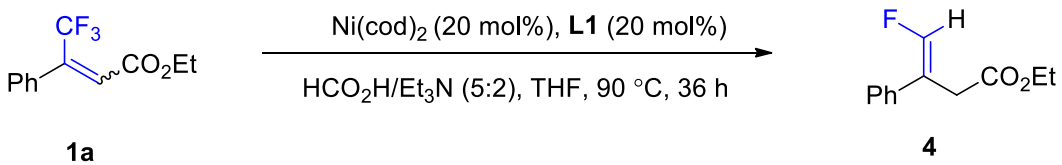


Figure S4 ^{19}F NMR spectra of proposed nickelacyclopropane intermediate

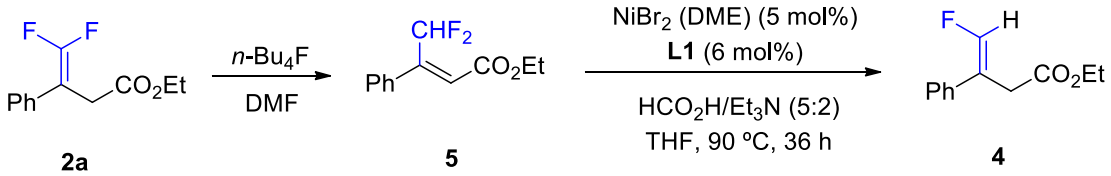
5. Synthesis monofluoroalkene



In a nitrogen-filled glove box, $Ni(cod)_2$ (0.02 mmol), **L1** (0.02 mmol) and dry THF (0.3 mL) were charged into a 10-mL Schlenk tube. After stirring for 15 min, Et_3N (28 μL, 2 equiv), HCO_2H (20 μL, 5 equiv) and **1a** (0.1 mmol) was added. The Schlenk tube was sealed and the reaction mixture was stirred in a metal sand bath maintained at 90 °C for 36 h. After cooled to room temperature, the reaction mixture was subjected to silica gel column chromatography directly using EA/Hexanes as eluent to give the **4** (60 yield %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.27 (m, 5H), 6.95 (d, *J* = 83.8 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.55 (d, *J* = 2.6 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -126.89 (s).



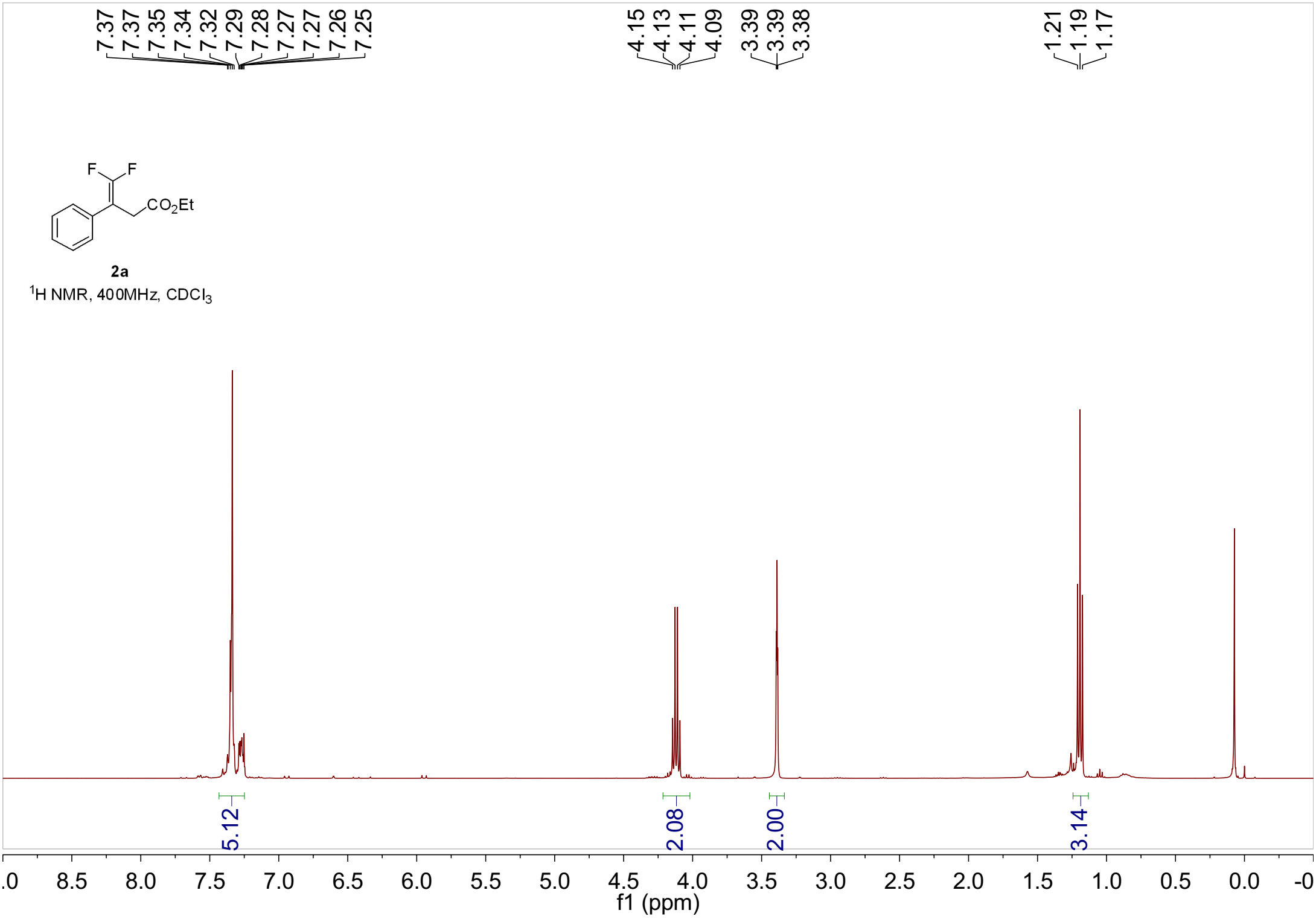
Isomerization of **2a** to **5**. A mixture of **2a** (52 mg, 0.23 mmol) and tetra-*n*-butylammonium fluoride (TBAF) (1.2 equiv, 0.28 mL, 1 M in THF) in DMF (0.46 mL) was stirred at 12-15 °C. After the solution was stirred for 40 min at that temperature, it was quenched with aq. NH_4Cl. Oily materials were extracted with a mixture of hexanes-ethyl acetate, and the extract was dried over $MgSO_4$. On removal of the solvent, the reaction mixture was subjected to silica gel column chromatography directly using EA/Hexanes as eluent to give the **5** (59 yield %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 3H), 7.30 – 7.22 (m, 2H), 6.35 (s, 1H), 6.24 (t, *J* = 55.2Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 1.07 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.28 (s, 1F).

Hydrodefluoronation of **5** to **4**. In a nitrogen-filled glove box, $NiBr_2$ (DME) (0.05 mmol), **L1** (0.06 mmol) and dry THF (0.3 mL) were charged into a 10-mL Schlenk tube. After stirring for 15 min, Et_3N (28 μL, 2 equiv), HCO_2H (20 μL, 5 equiv) and **5** was added. The Schlenk tube was sealed and the reaction mixture was stirred in a metal sand bath maintained at 90 °C for 36 h. After cooled to room temperature, the reaction mixture was subjected to silica gel column chromatography directly using EA/Hexanes as eluent to give the **4** (87 yield %).

6. NMR spectra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7.34
7.32
7.29
7.28
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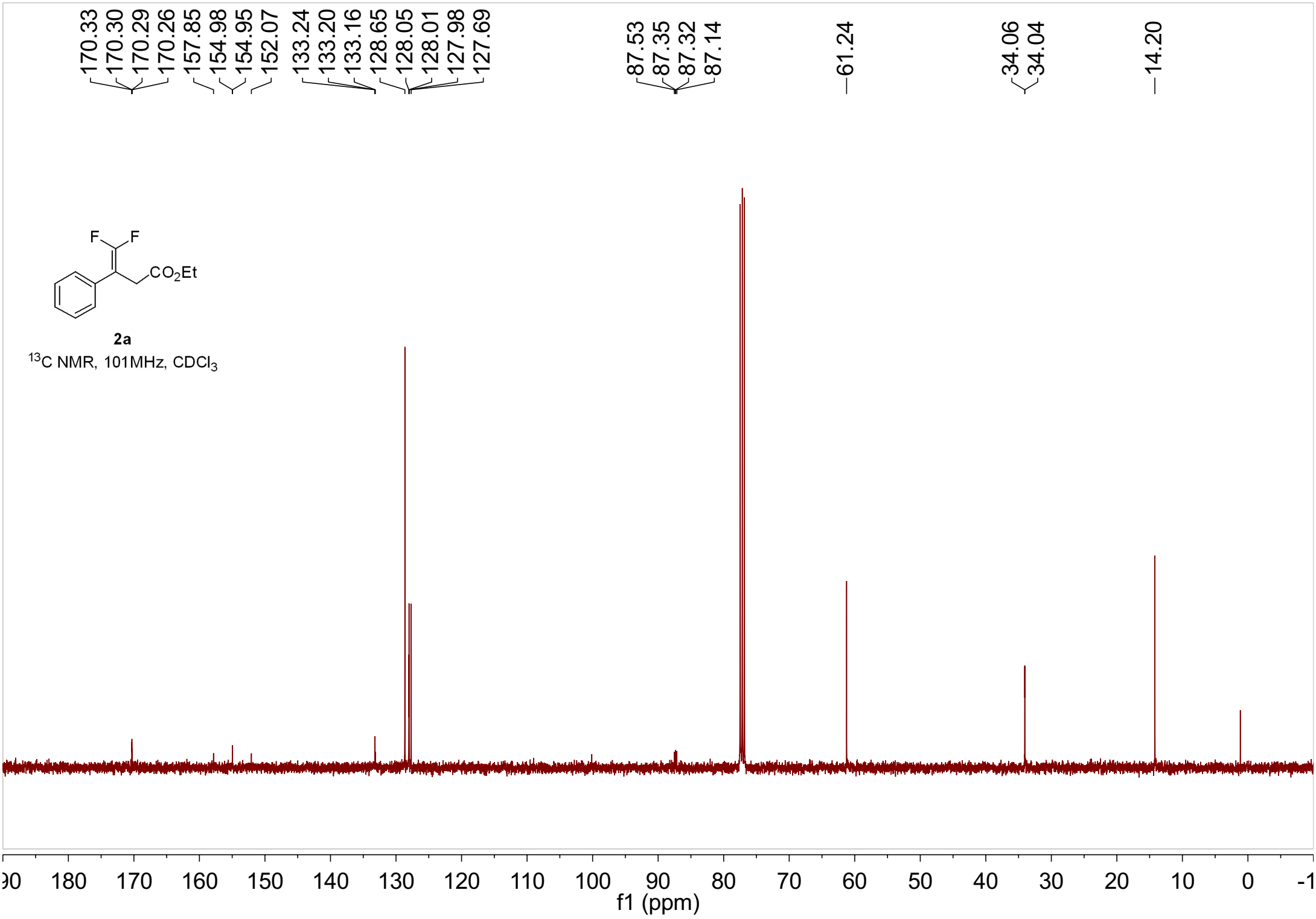
7.26
7.25
4.15
4.13
4.11
4.09
3.39
3.39
3.38
1.21
1.19
1.17
F
F
CO2Et
2a
1H NMR, 400MHz, CDCl3
5.12
2.08
2.00
3.14
f1 (ppm)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170.26
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154.98
154.95
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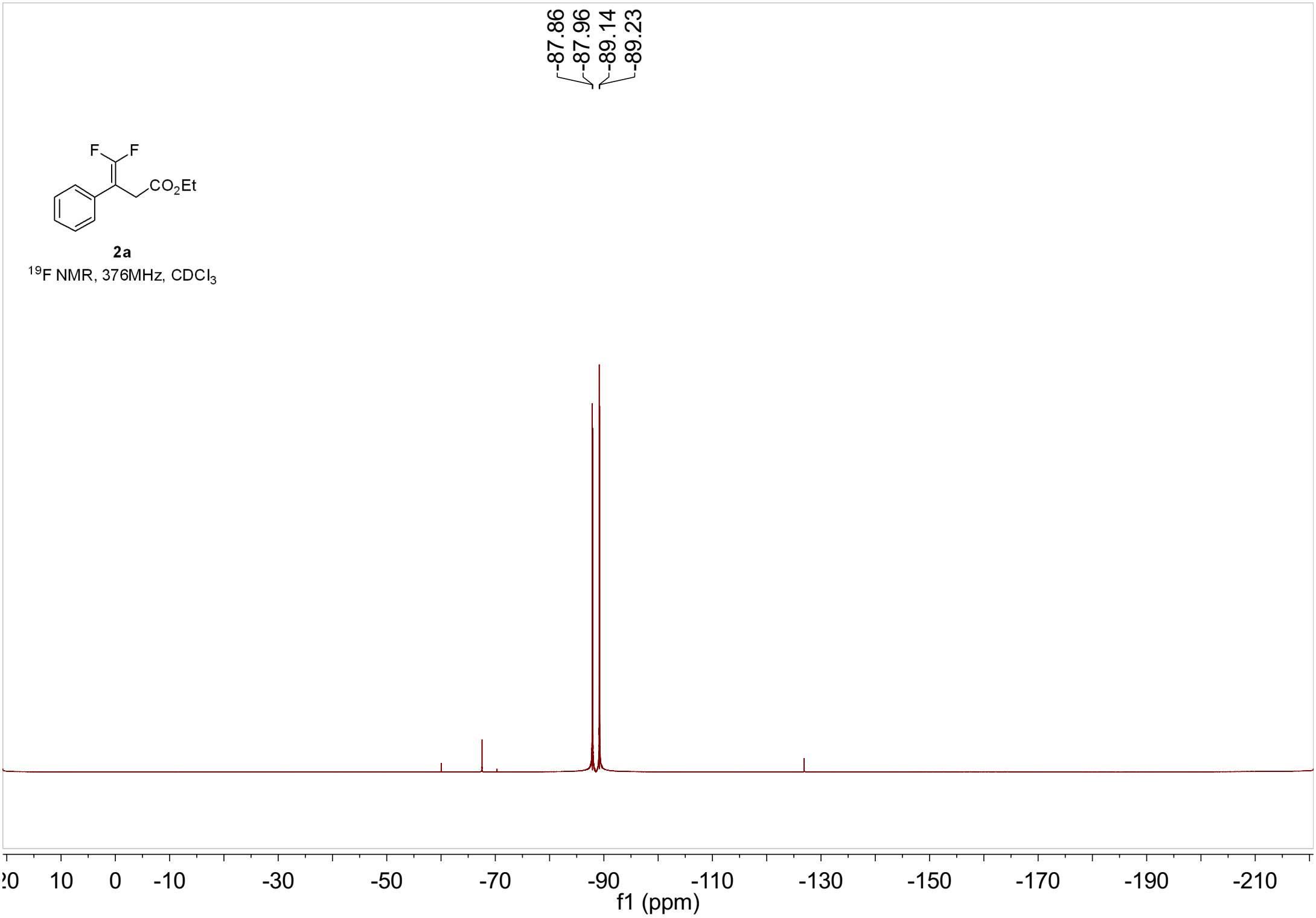
133.20
133.16
128.65
128.05
128.01
127.98
127.69
87.53
87.35
87.32
87.14
61.24
34.06
34.04
14.20
F
F
CO2Et
2a
13C NMR, 101MHz, CDCl3
f1 (ppm)


-87.86
-87.96
-89.14
-89.23
F
F
CO2Et
2a
19F NMR, 376MHz, CDCl3
20
10
0
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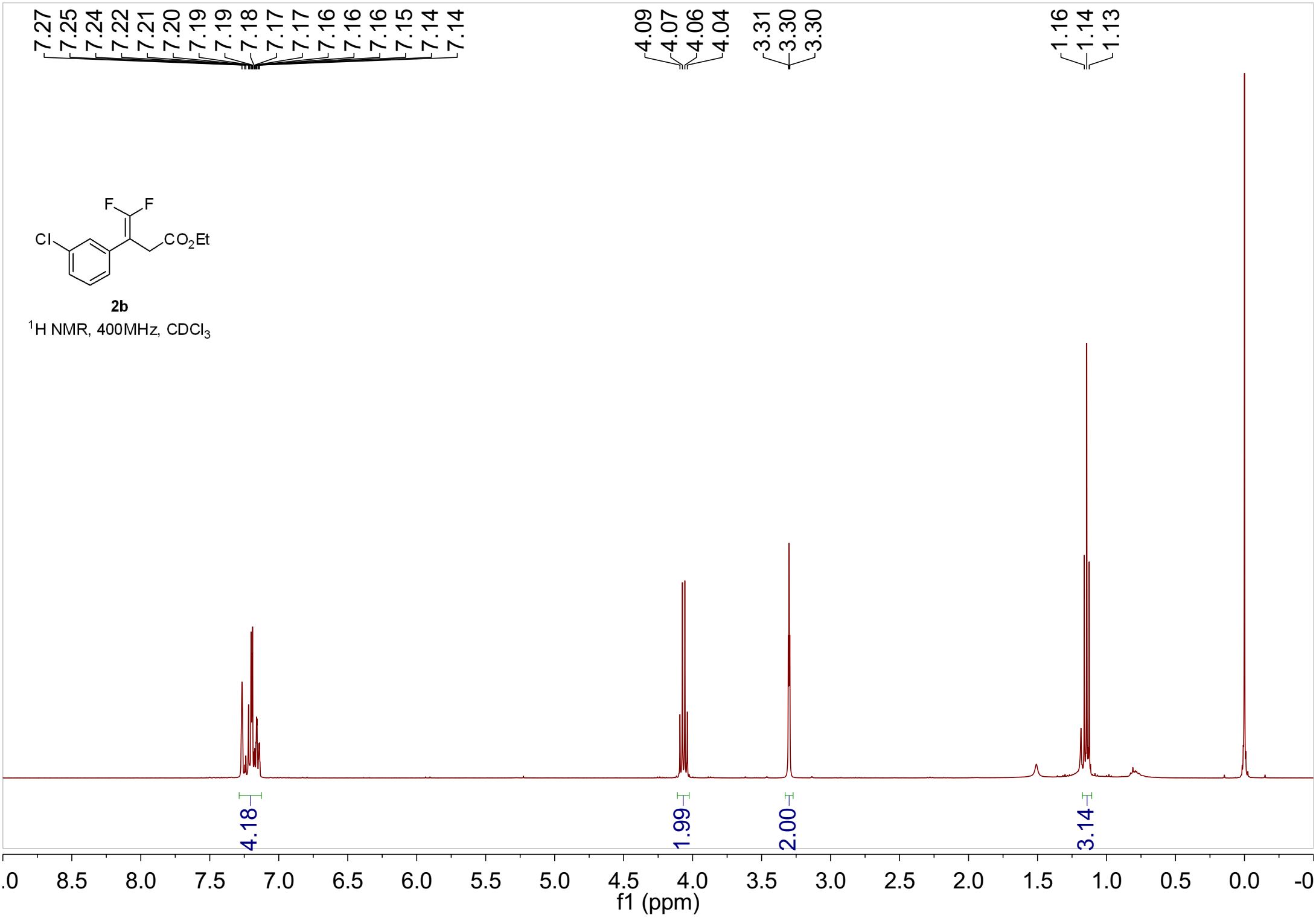
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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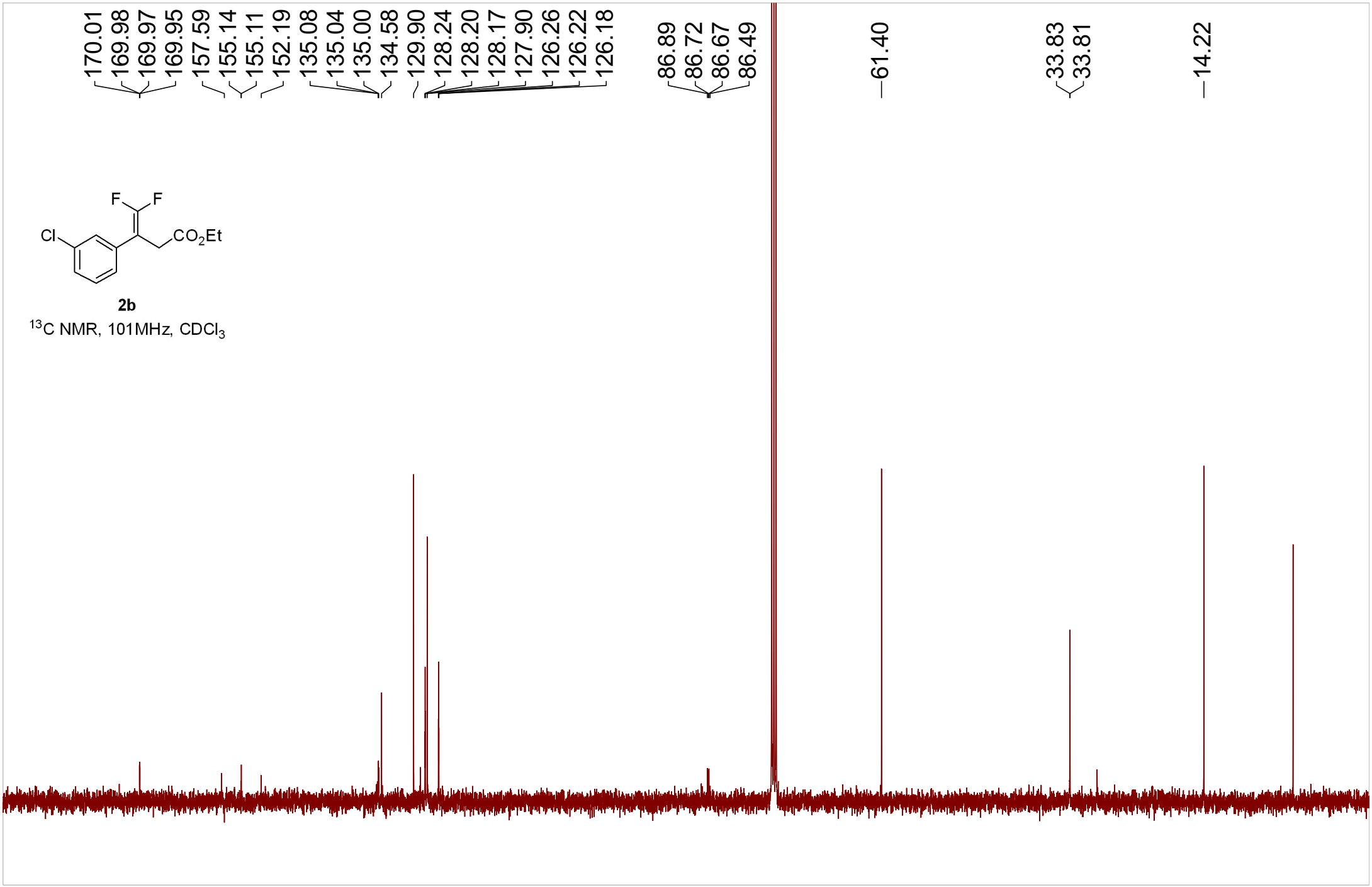
7.16
7.15
7.14
7.14
4.09
4.07
4.06
4.04
3.31
3.30
3.30
1.16
1.14
1.13
F
F
Cl
CO2Et
2b
1H NMR, 400MHz, CDCl3
4.18
1.99
2.00
3.14
f1 (ppm)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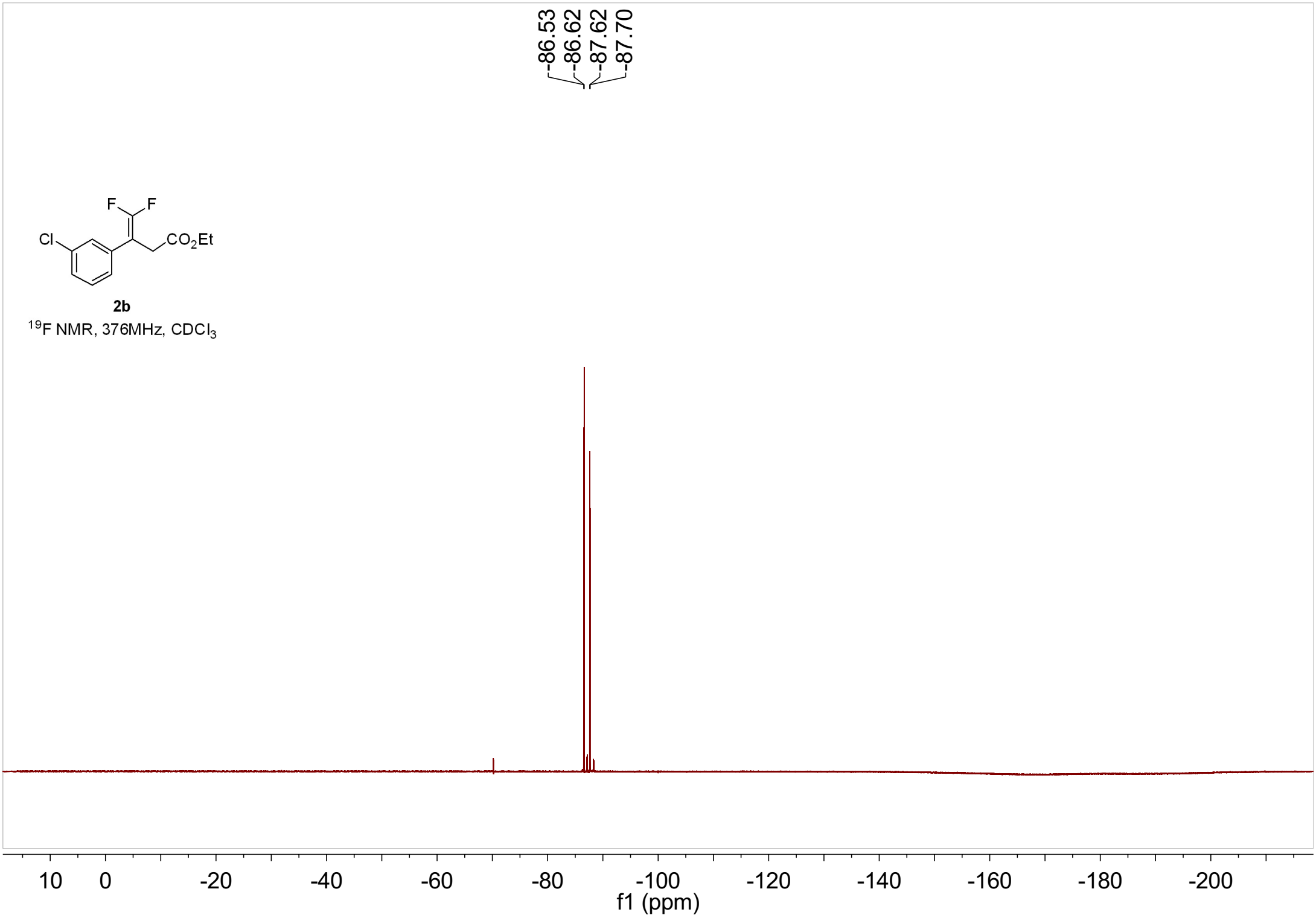
127.90
126.26
126.22
126.18
86.89
86.72
86.67
86.49
61.40
33.83
33.81
14.22
F
F
Cl
CO2Et
2b
13C NMR, 101MHz, CDCl3
f1 (ppm)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-87.62
-87.70
F
F
Cl
CO2Et
2b
19F NMR, 376MHz, CDCl3
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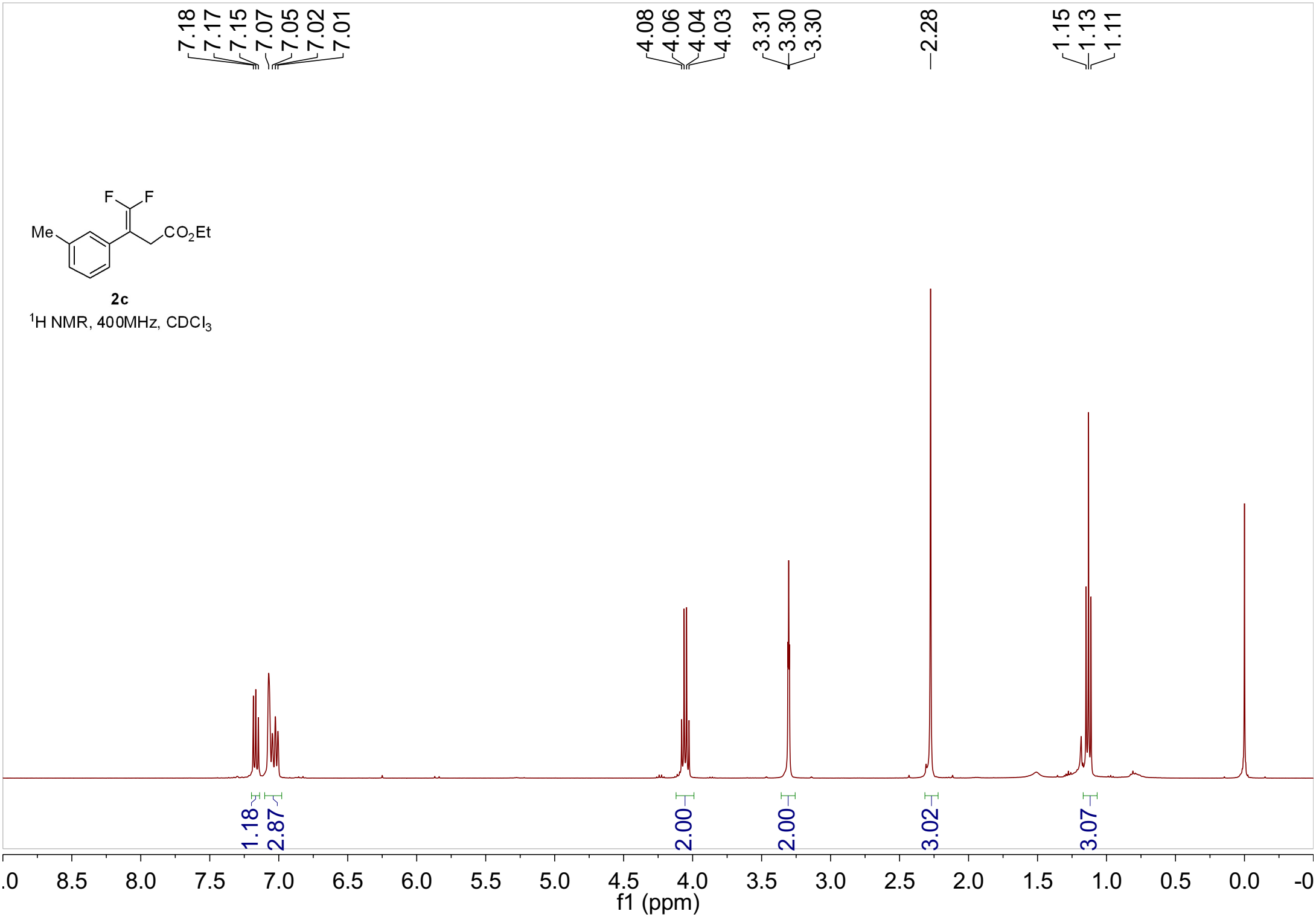
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)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3.30
3.30
2.28
1.15
1.13
1.11
F
F
Me
CO2Et
2c
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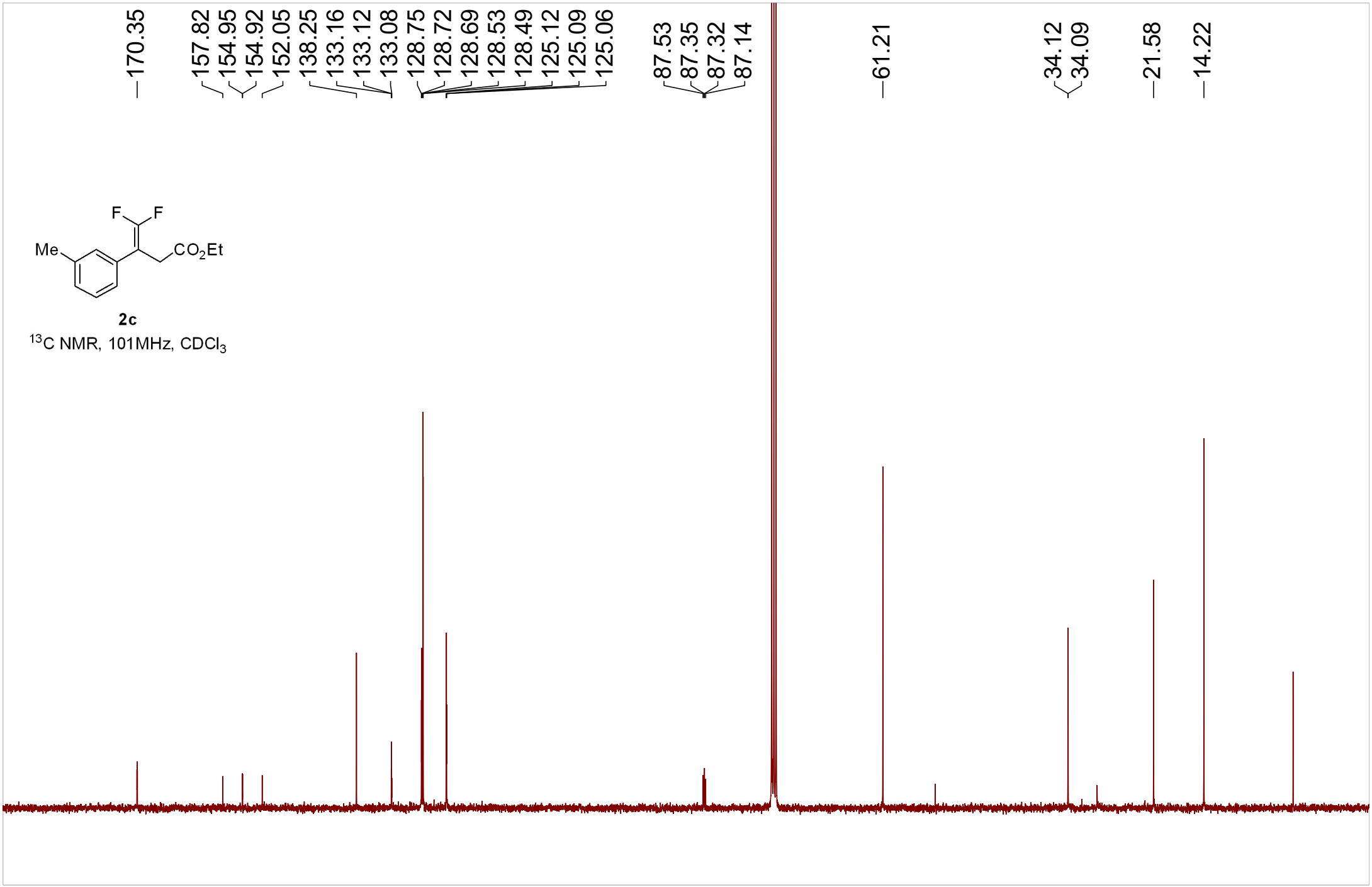
2.87
2.00
2.00
3.02
3.07
f1 (ppm)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128.53
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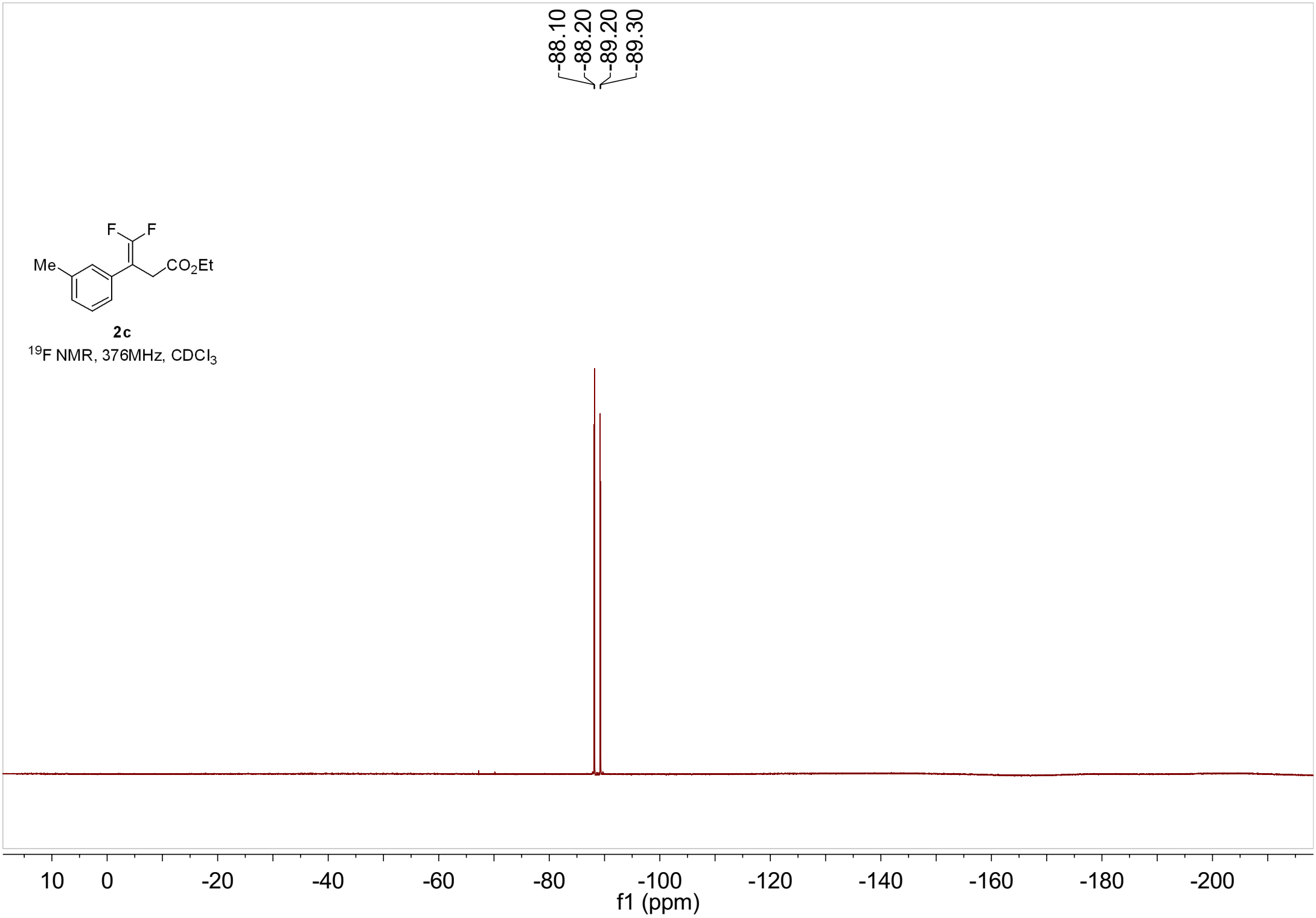
Me
CO2Et
2c
13C NMR, 101MHz, CDCl3
f1 (ppm)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Me
CO2Et
2c
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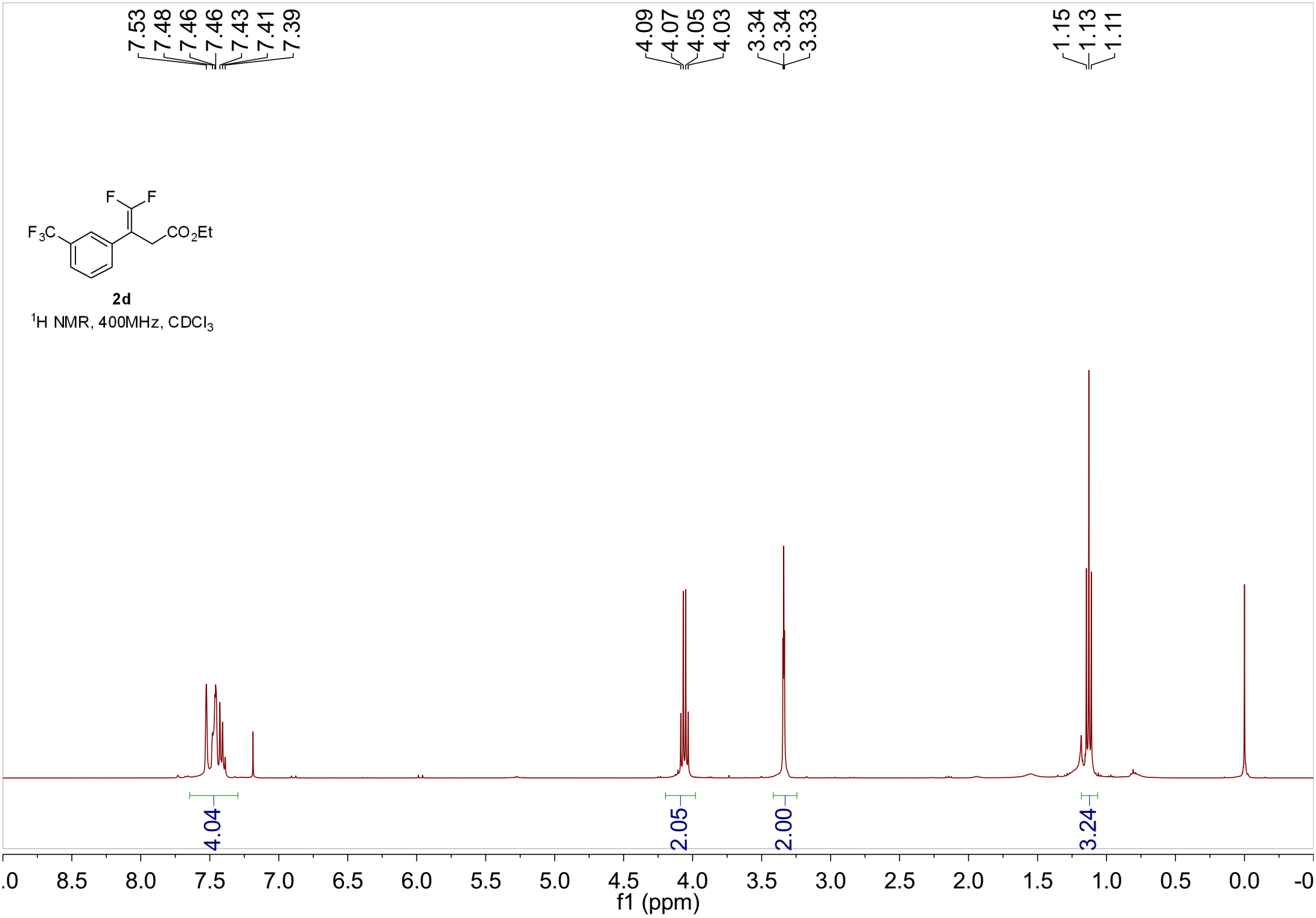
-120
-140
-160
-180
-200
f1 (ppm)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3.34
3.34
3.33
1.15
1.13
1.11
F
F
F3C
CO2Et
2d
1H NMR, 400MHz, CDCl3
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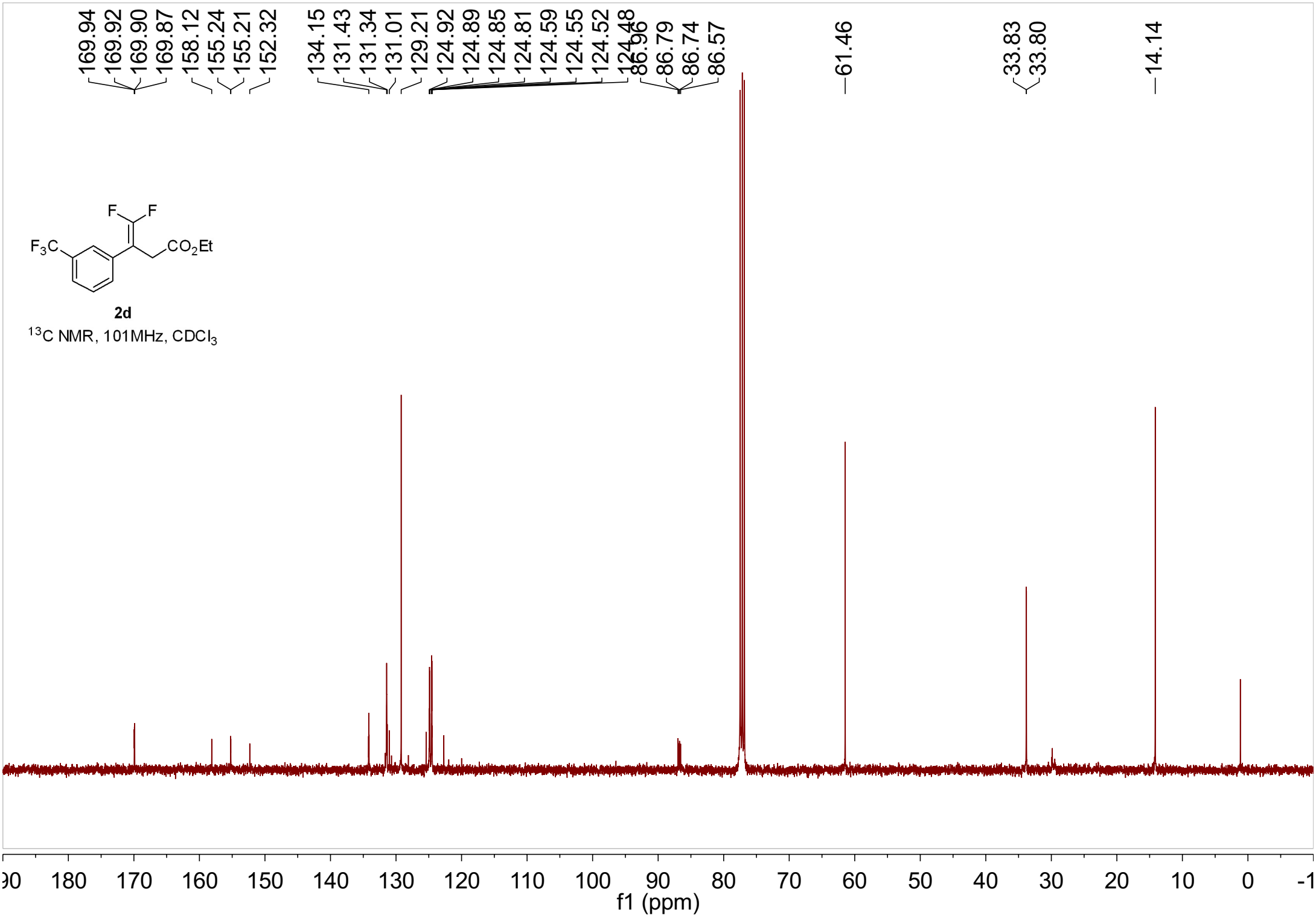
2.05
2.00
3.24
f1 (ppm)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124.81
124.59
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124.52
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86.79
86.74
86.57
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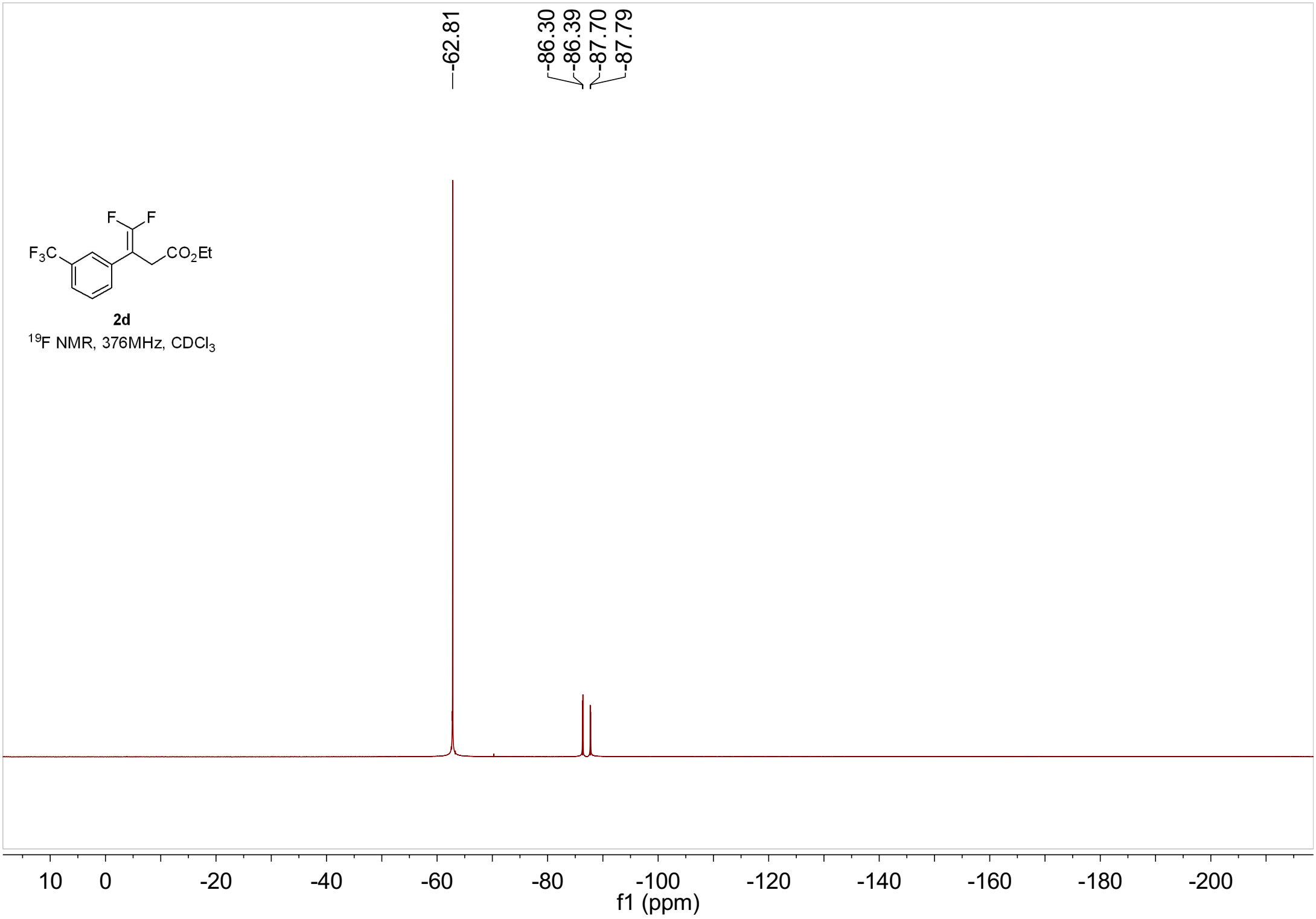
F
F3C
CO2Et
2d
13C NMR, 101MHz, CDCl3
f1 (ppm)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F3C
CO2Et
2d
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-60
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-100
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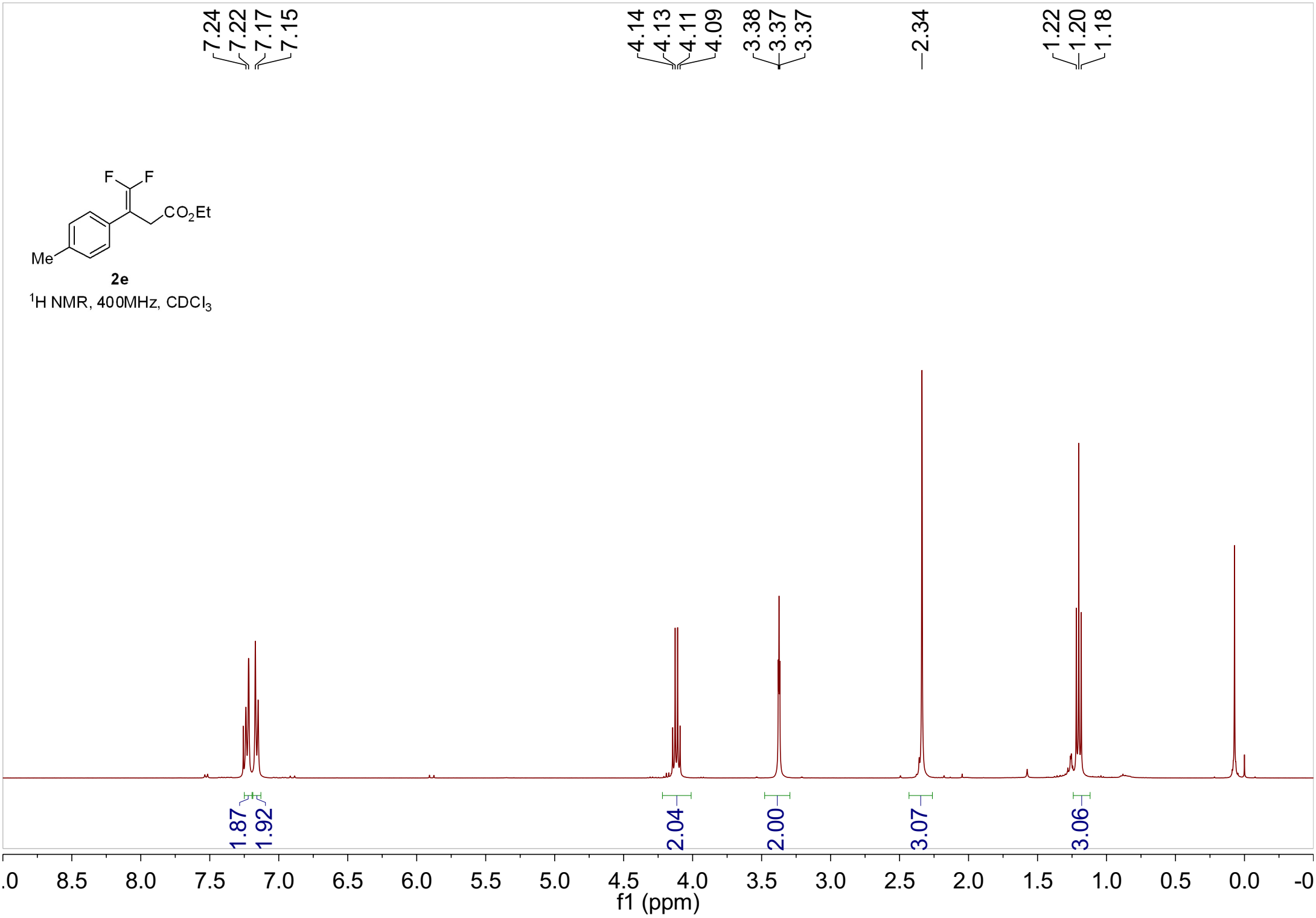
-180
-200
f1 (ppm)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4.09
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3.37
3.37
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1.22
1.20
1.18
F
F
CO2Et
Me
2e
1H NMR, 400MHz, CDCl3
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1.92
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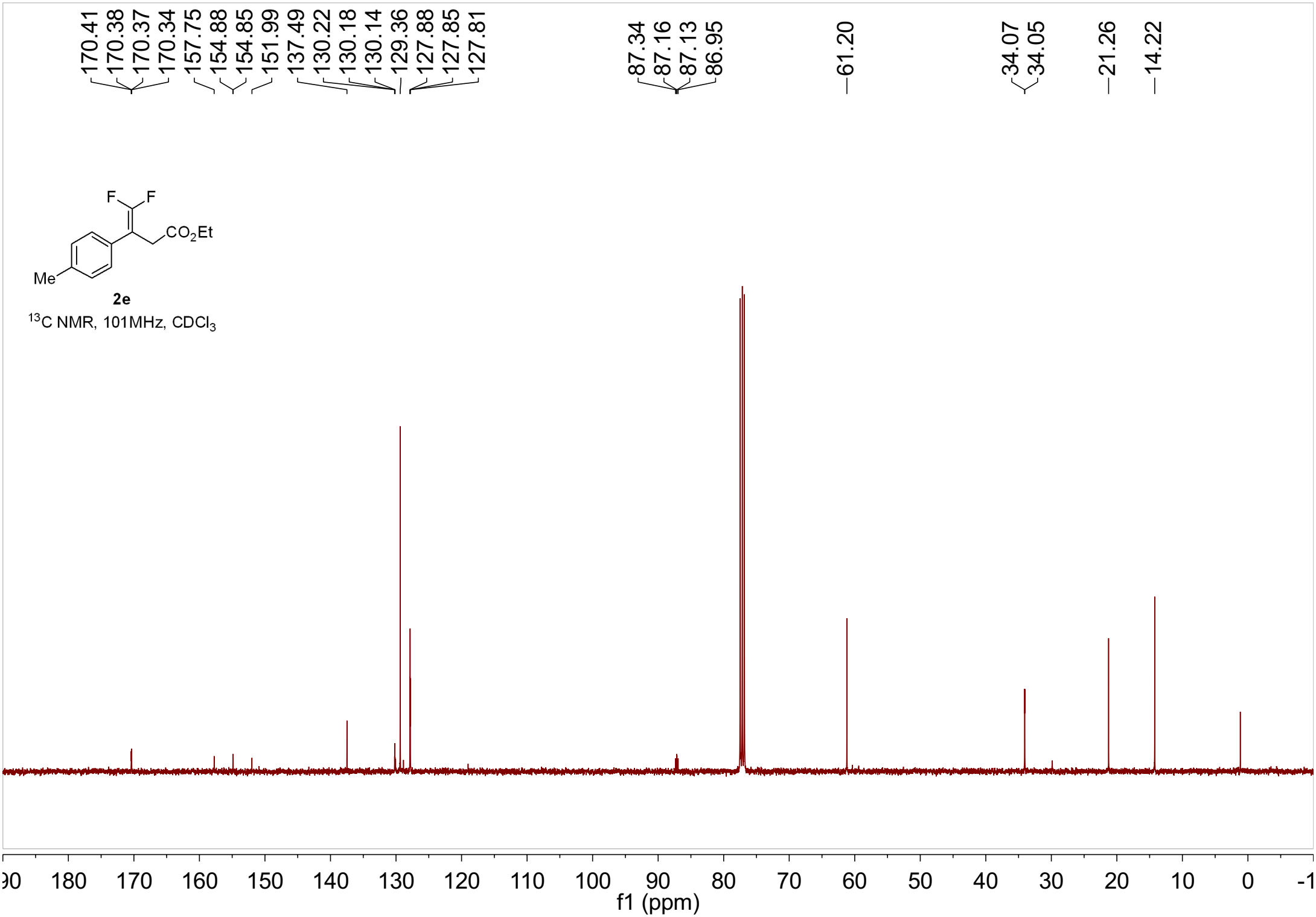
2.00
3.07
3.06
f1 (ppm)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127.85
127.81
87.34
87.16
87.13
86.95
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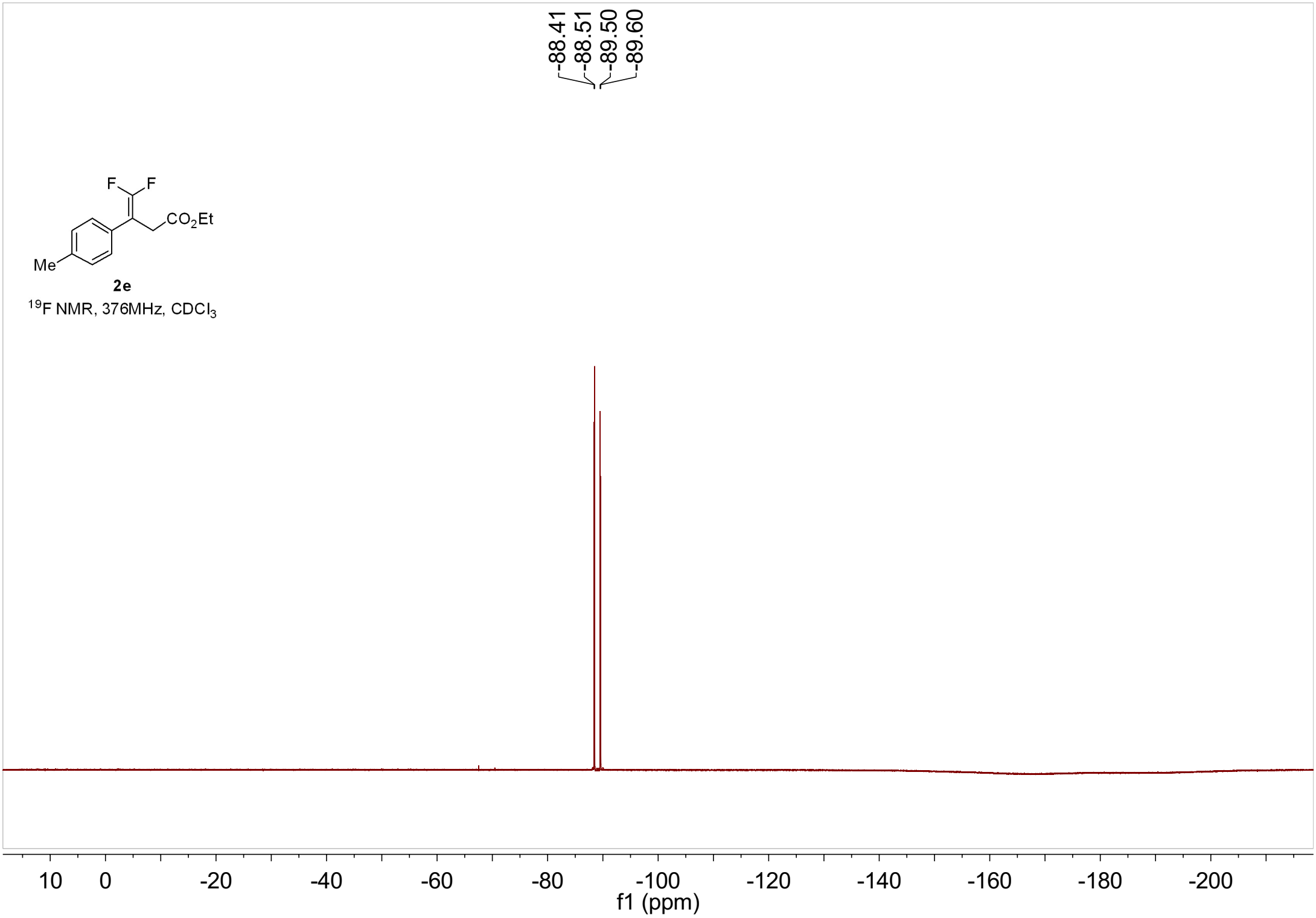
21.26
14.22
F
F
CO2Et
Me
2e
13C NMR, 101MHz, CDCl3
f1 (ppm)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Me
2e
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-140
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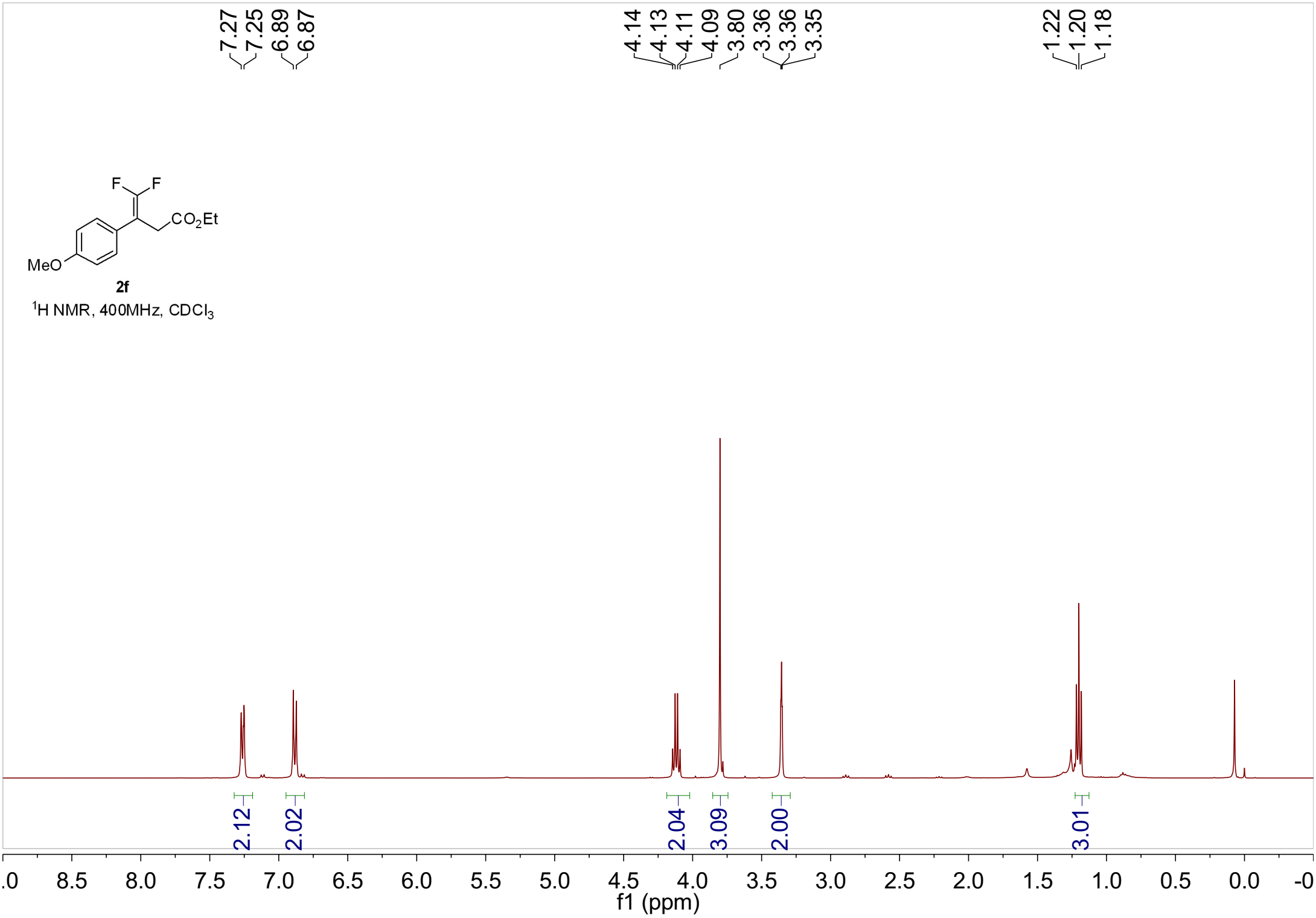
-200
f1 (ppm)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3.36
3.35
1.22
1.20
1.18
F
F
CO2Et
MeO
2f
1H NMR, 400MHz, CDCl3
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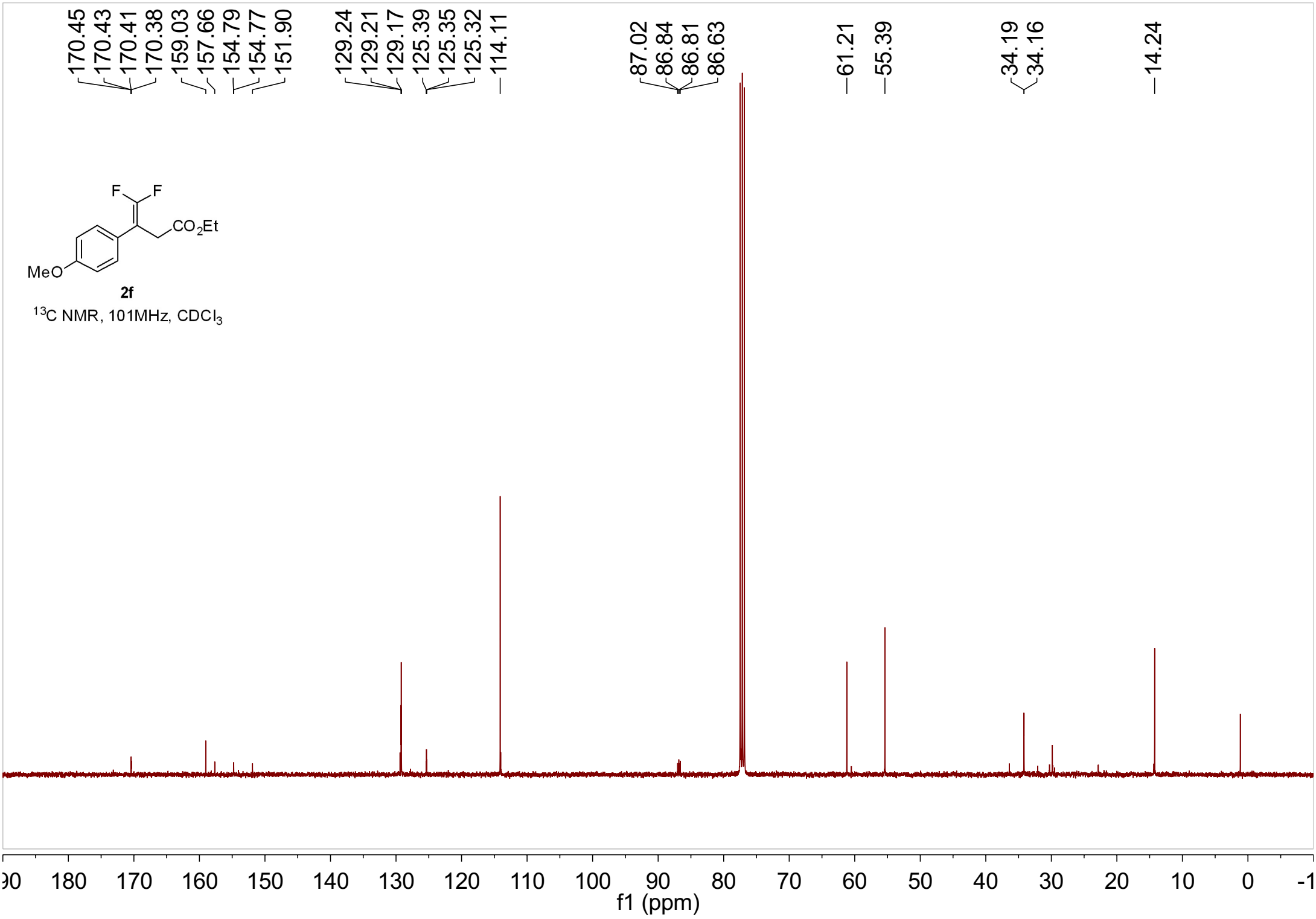
2.04
3.09
2.00
3.01
f1 (ppm)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125.35
125.32
114.11
87.02
86.84
86.81
86.63
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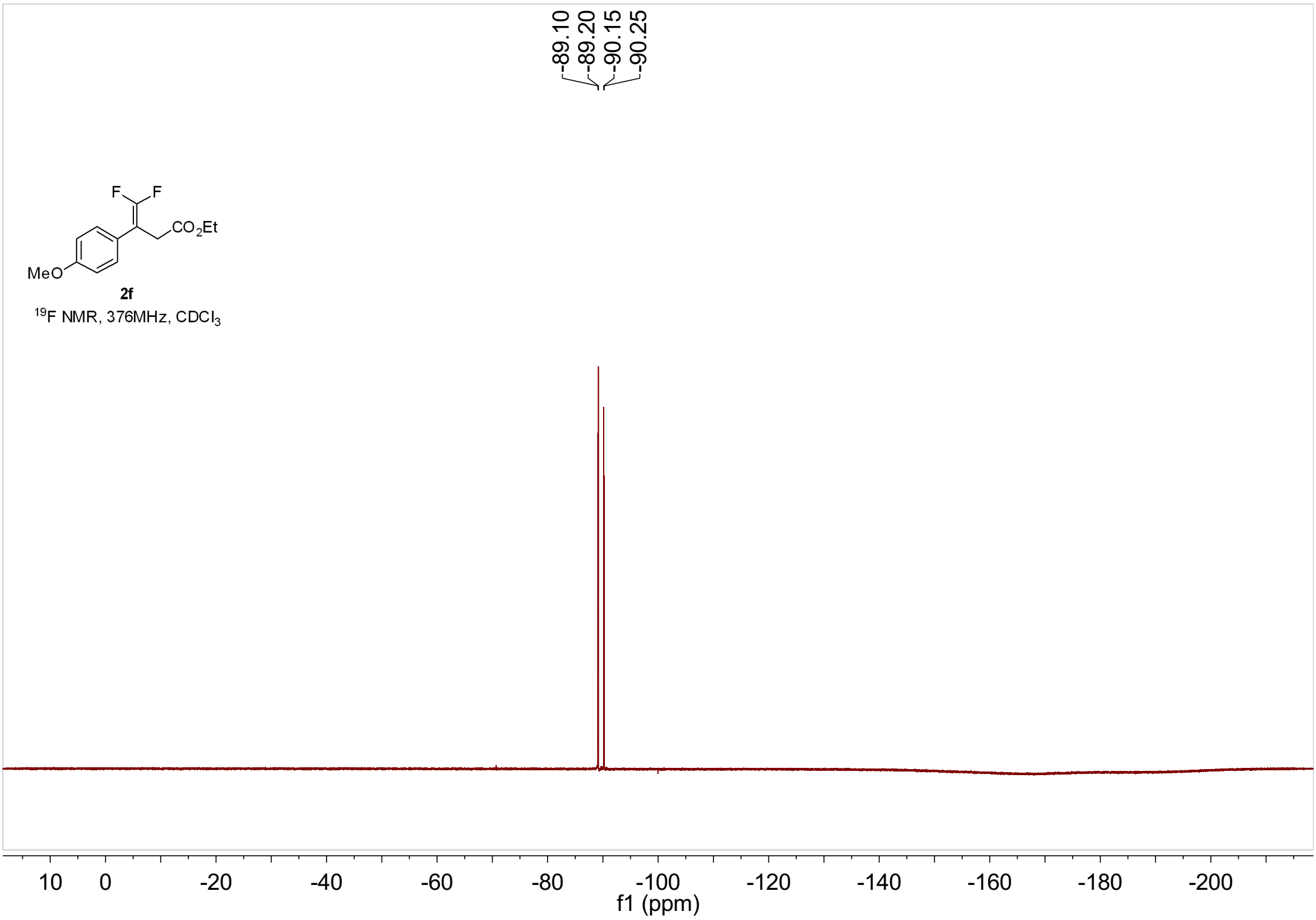
34.16
14.24
F
F
CO2Et
MeO
2f
13C NMR, 101MHz, CDCl3
f1 (ppm)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-89.20
-90.15
-90.25
F
F
CO2Et
MeO
2f
19F NMR, 376MHz, CDCl3
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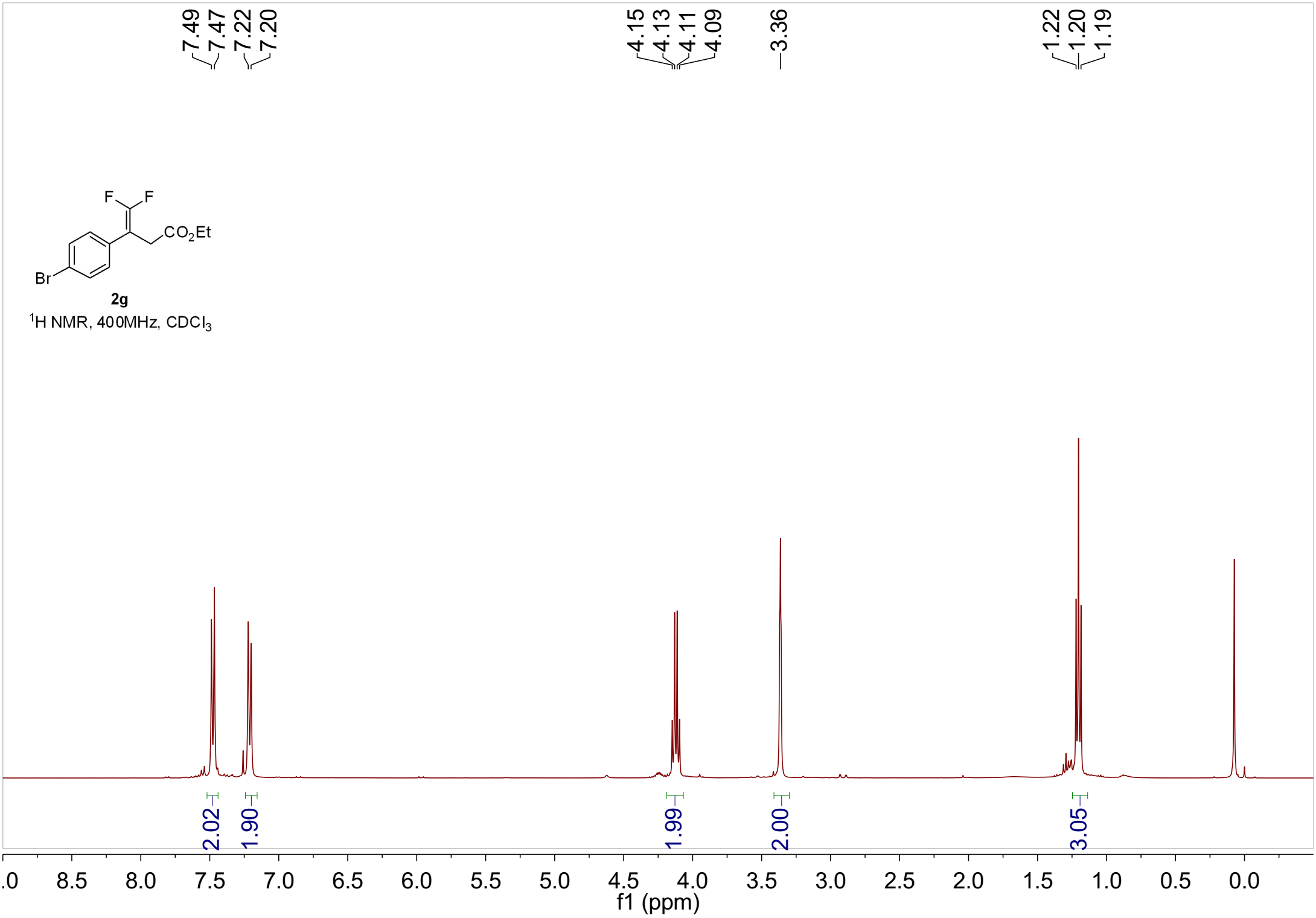
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)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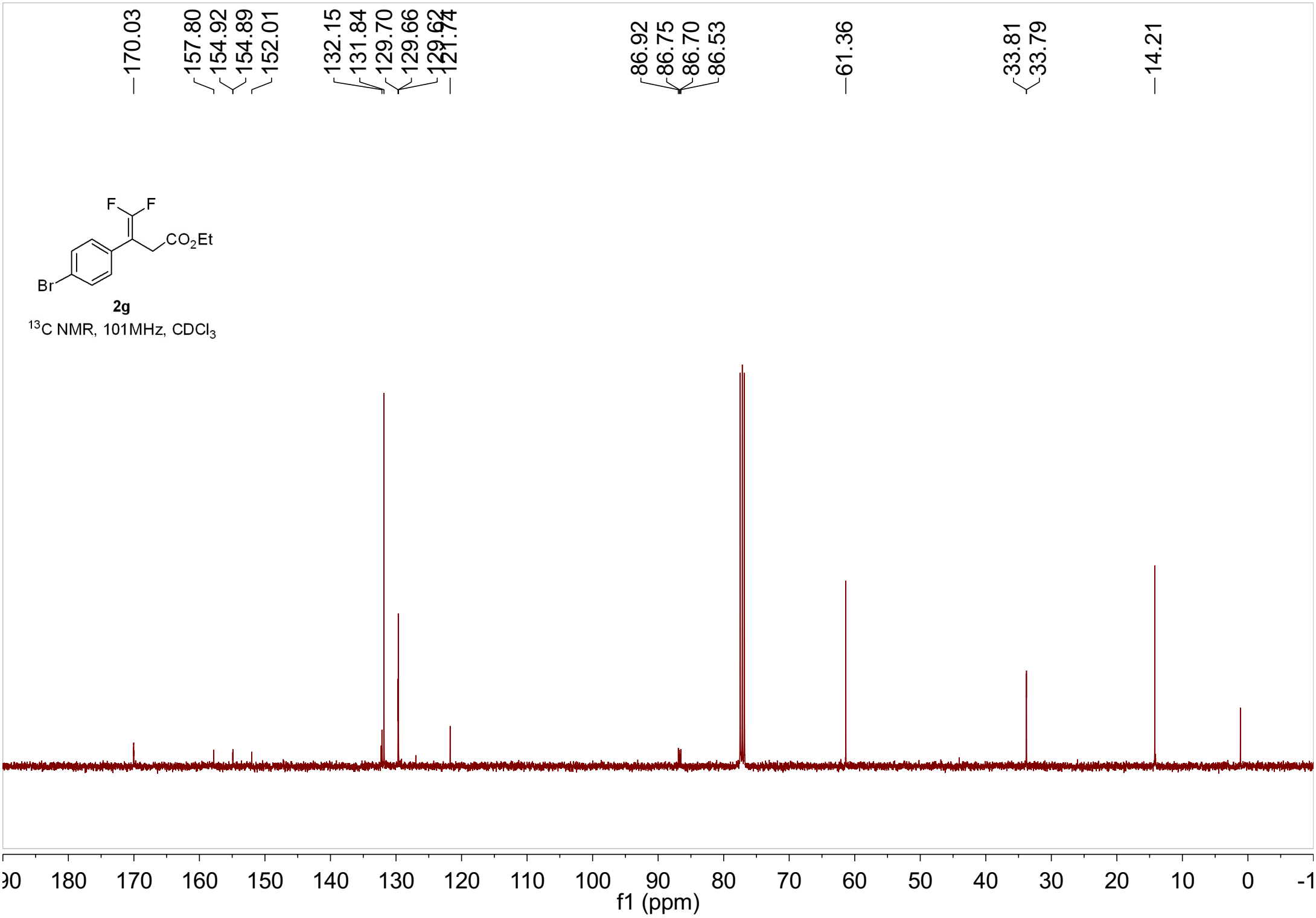
4.13
4.11
4.09
3.36
1.22
1.20
1.19
F
F
CO2Et
Br
2g
1H NMR, 400MHz, CDCl3
2.02
1.90
1.99
2.00
3.05
f1 (ppm)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86.70
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61.36
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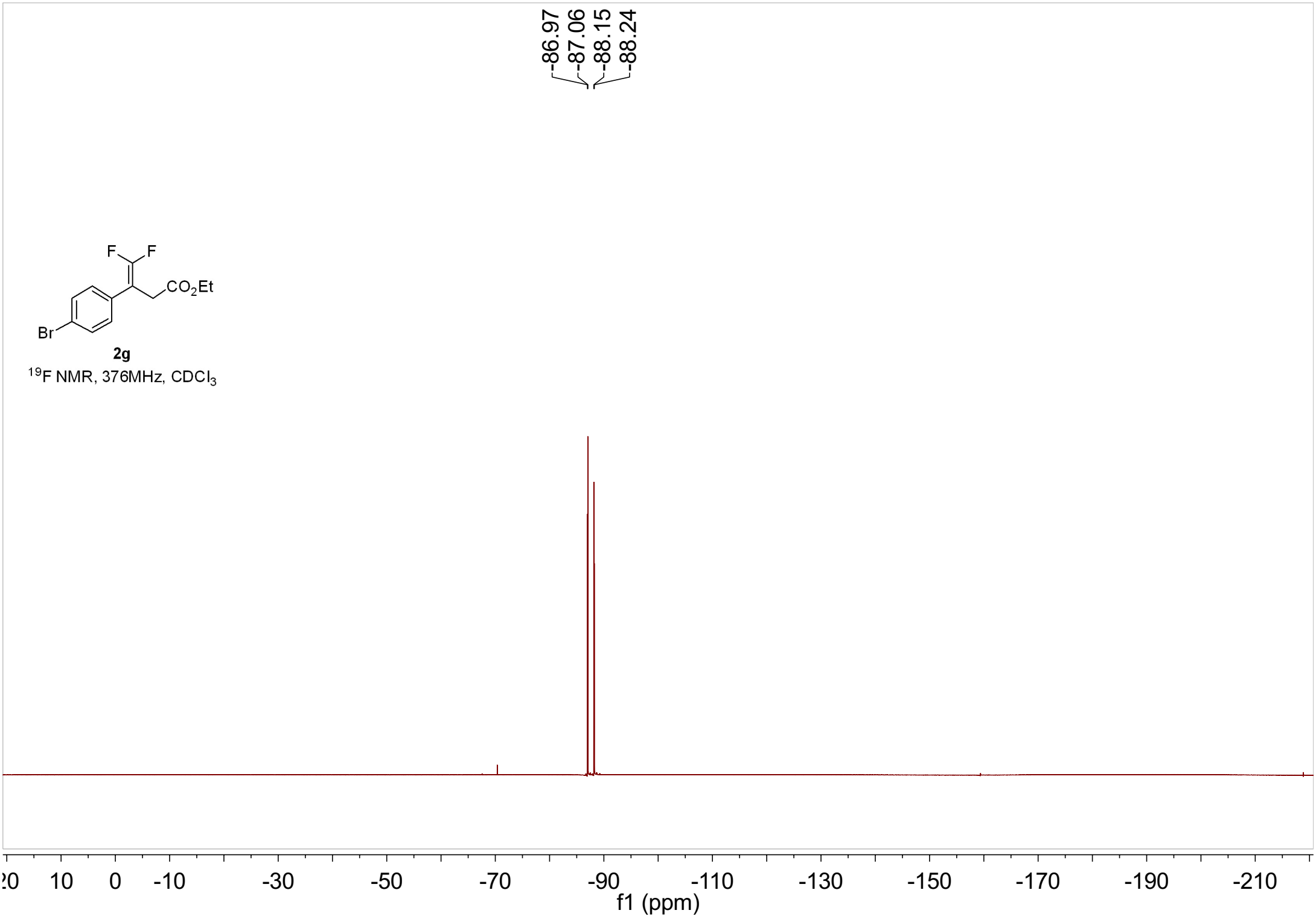
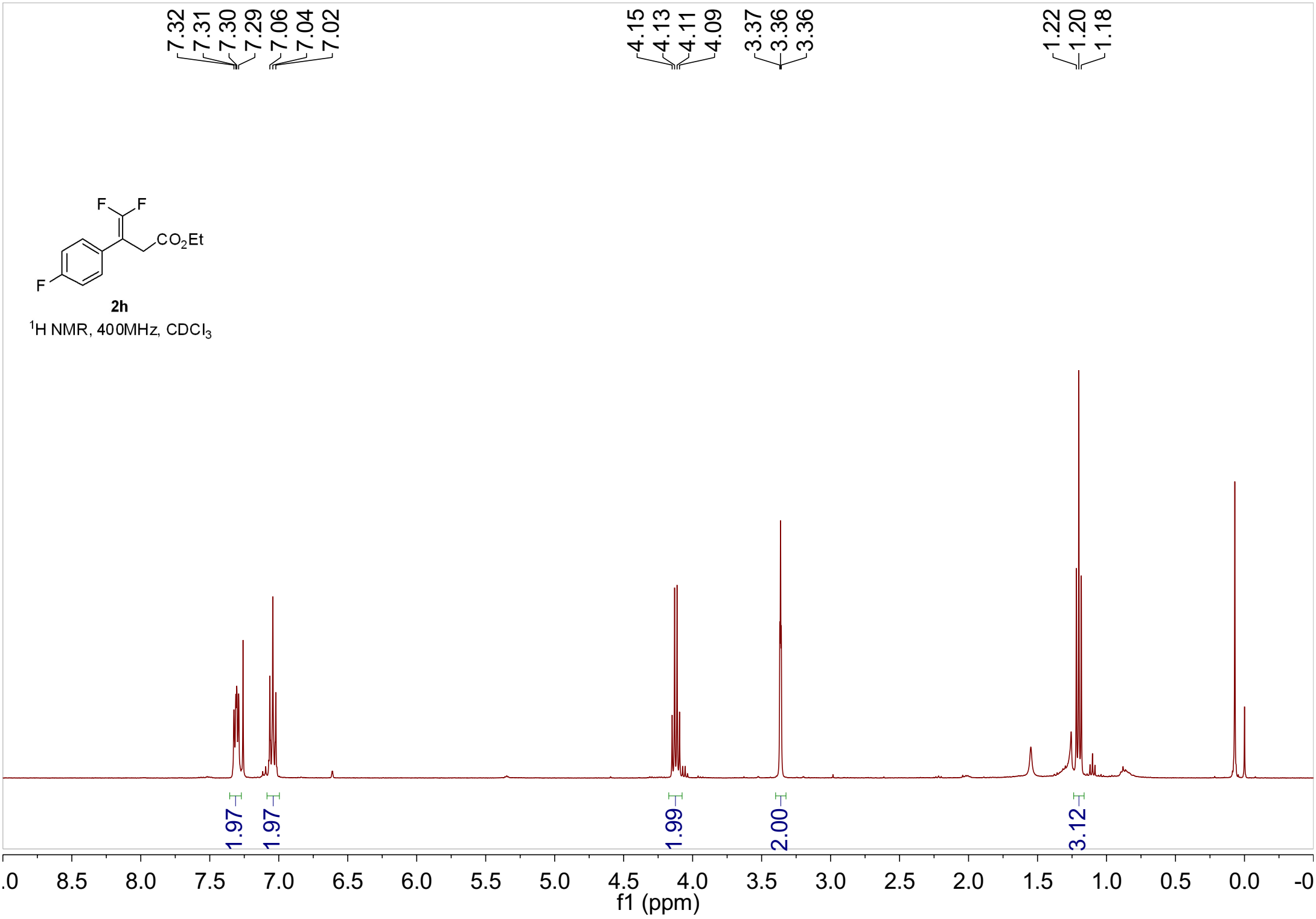
33.79
14.21
F
F
CO2Et
Br
2g
13C NMR, 101MHz, CDCl3
f1 (ppm)


-86.97
-87.06
-88.15
-88.24
F
F
CO2Et
Br
2g
19F NMR, 376MHz, CDCl3
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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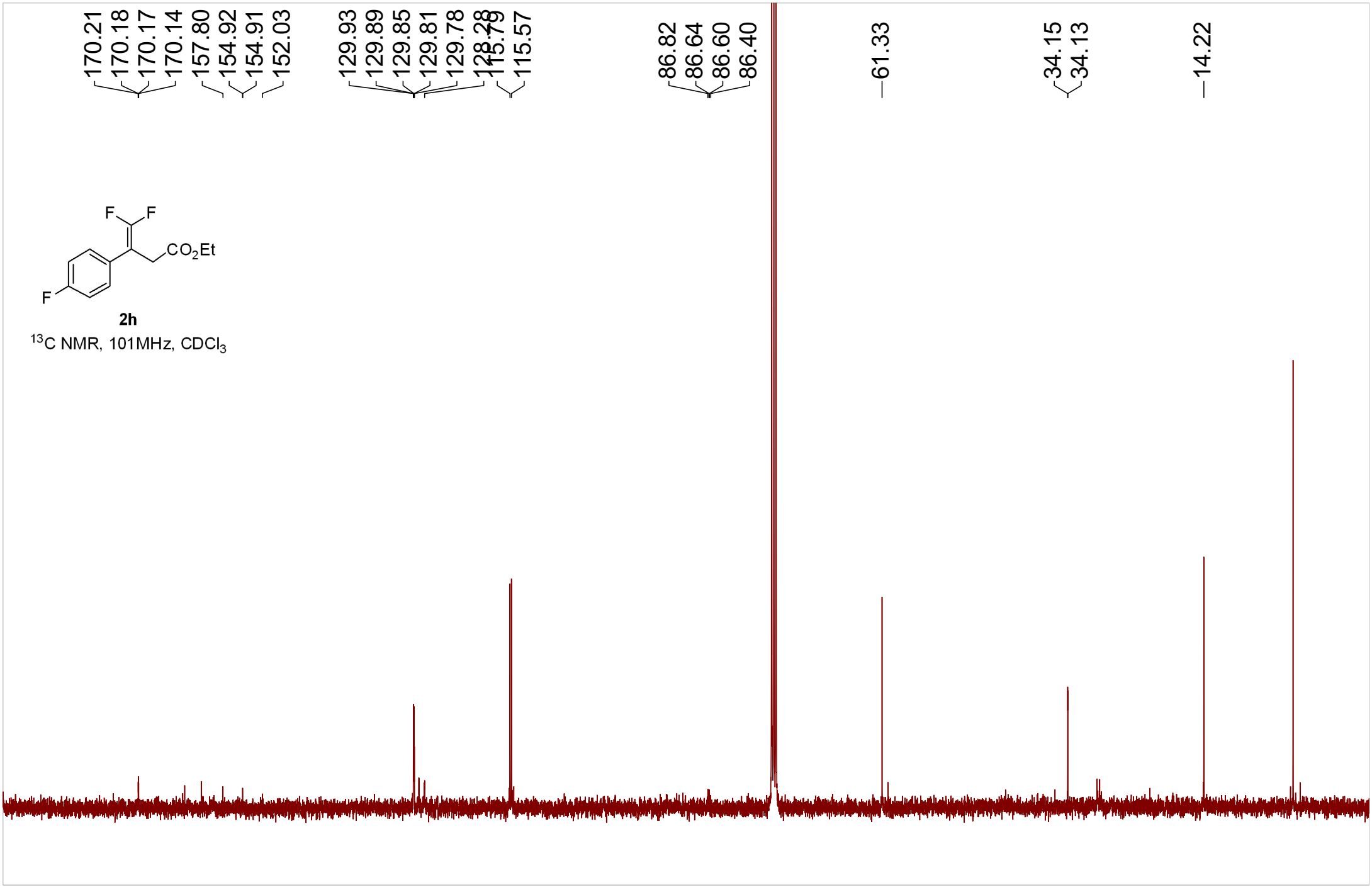
7.02
4.15
4.13
4.11
4.09
3.37
3.36
3.36
1.22
1.20
1.18
F
F
CO2Et
F
2h
1H NMR, 400MHz, CDCl3
1.97
1.97
1.99
2.00
3.12
f1 (ppm)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128.28
115.79
115.57
86.82
86.64
86.60
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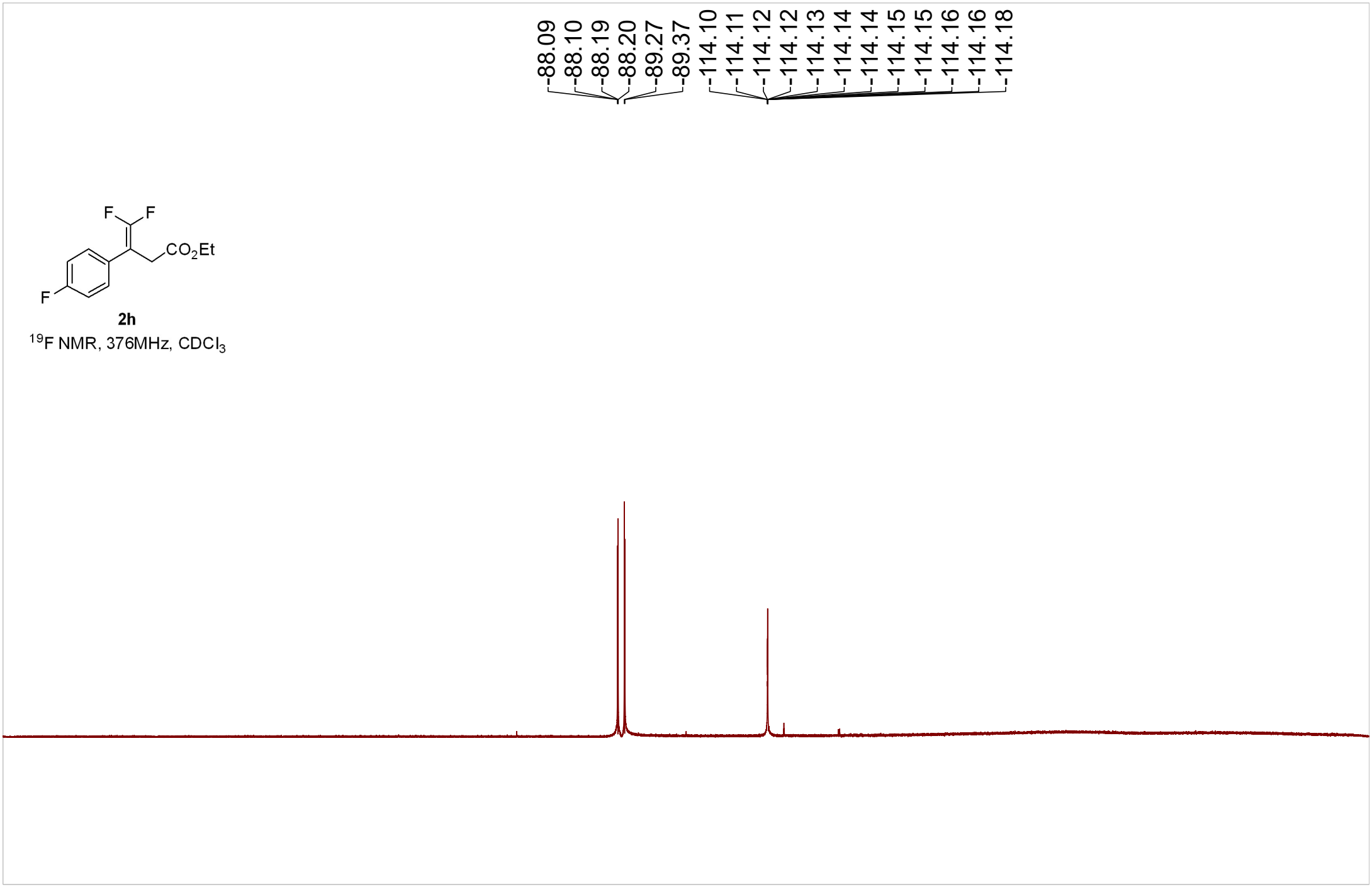
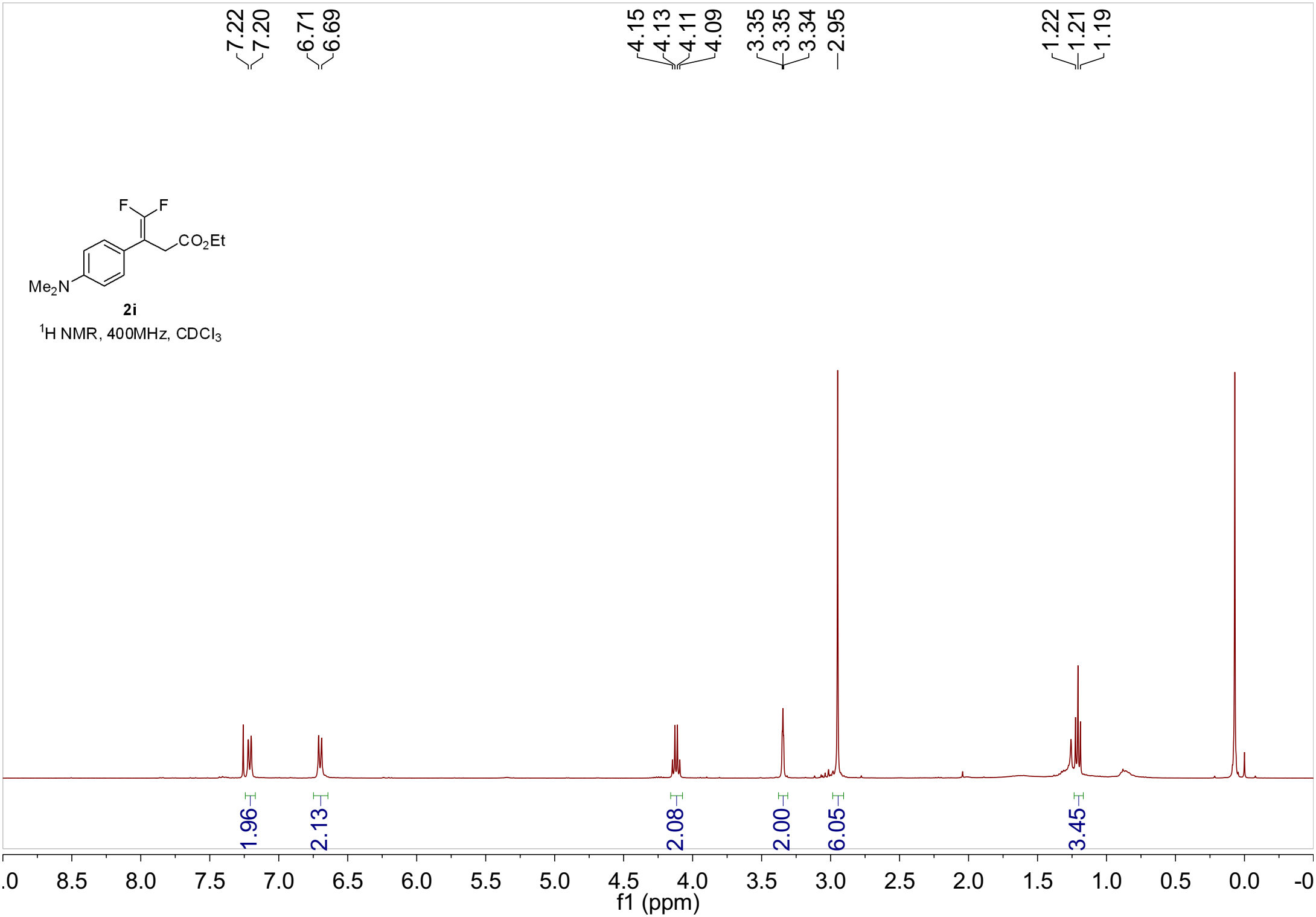
34.15
34.13
14.22
F
F
CO2Et
F
2h
13C NMR, 101MHz, CDCl3
f1 (ppm)



2h

^{19}F NMR, 376MHz, $CDCl_3$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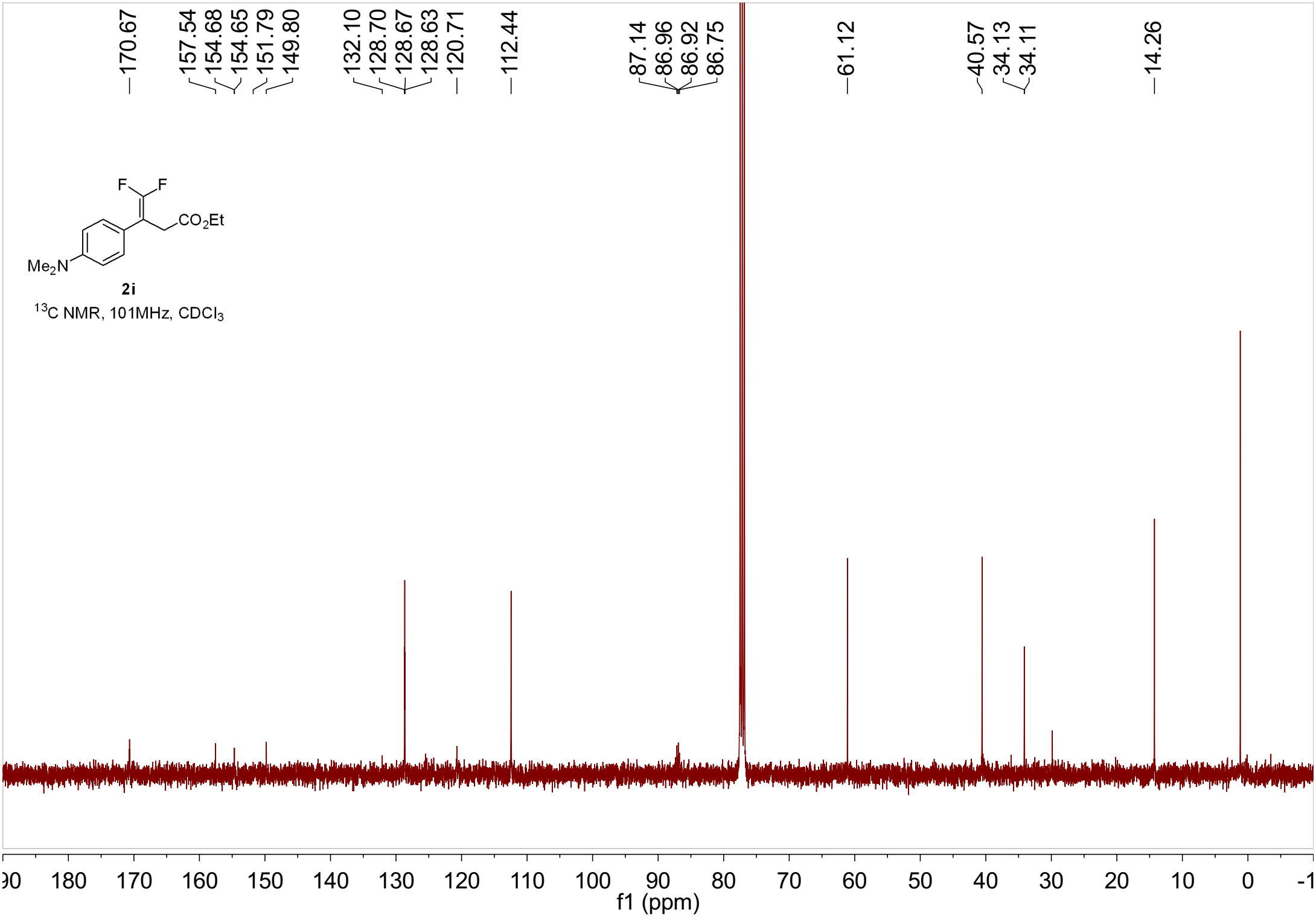
4.11
4.09
3.35
3.35
3.34
2.95
1.22
1.21
1.19
F
F
CO2Et
Me2N
2i
1H NMR, 400MHz, CDCl3
1.96
2.13
2.08
2.00
6.05
3.45
f1 (ppm)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120.71
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87.14
86.96
86.92
86.75
61.12
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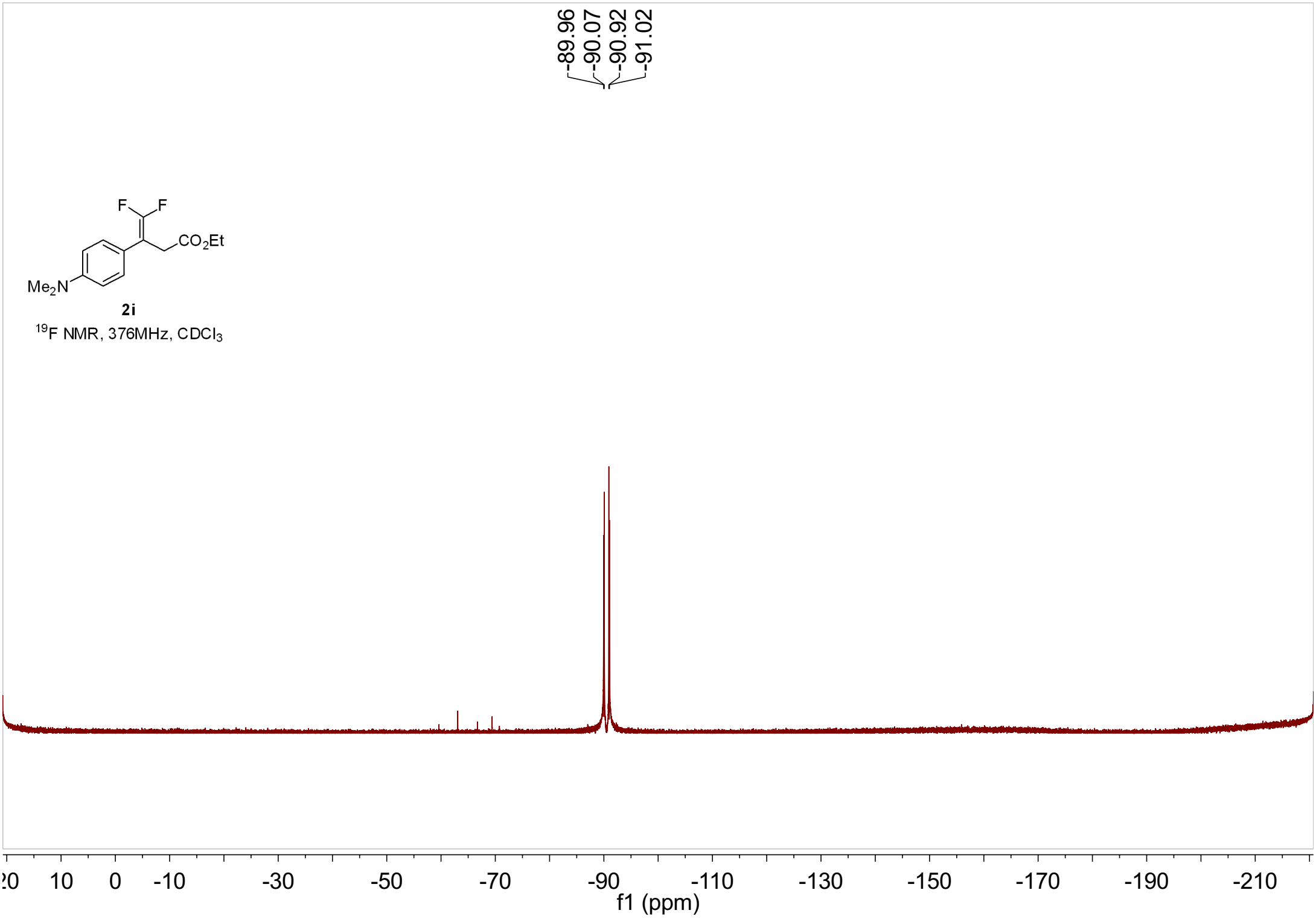
34.11
14.26
F
F
CO2Et
Me2N
2i
13C NMR, 101MHz, CDCl3
f1 (ppm)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-90.07
-90.92
-91.02
F
F
CO2Et
Me2N
2i
19F NMR, 376MHz, CDCl3
10
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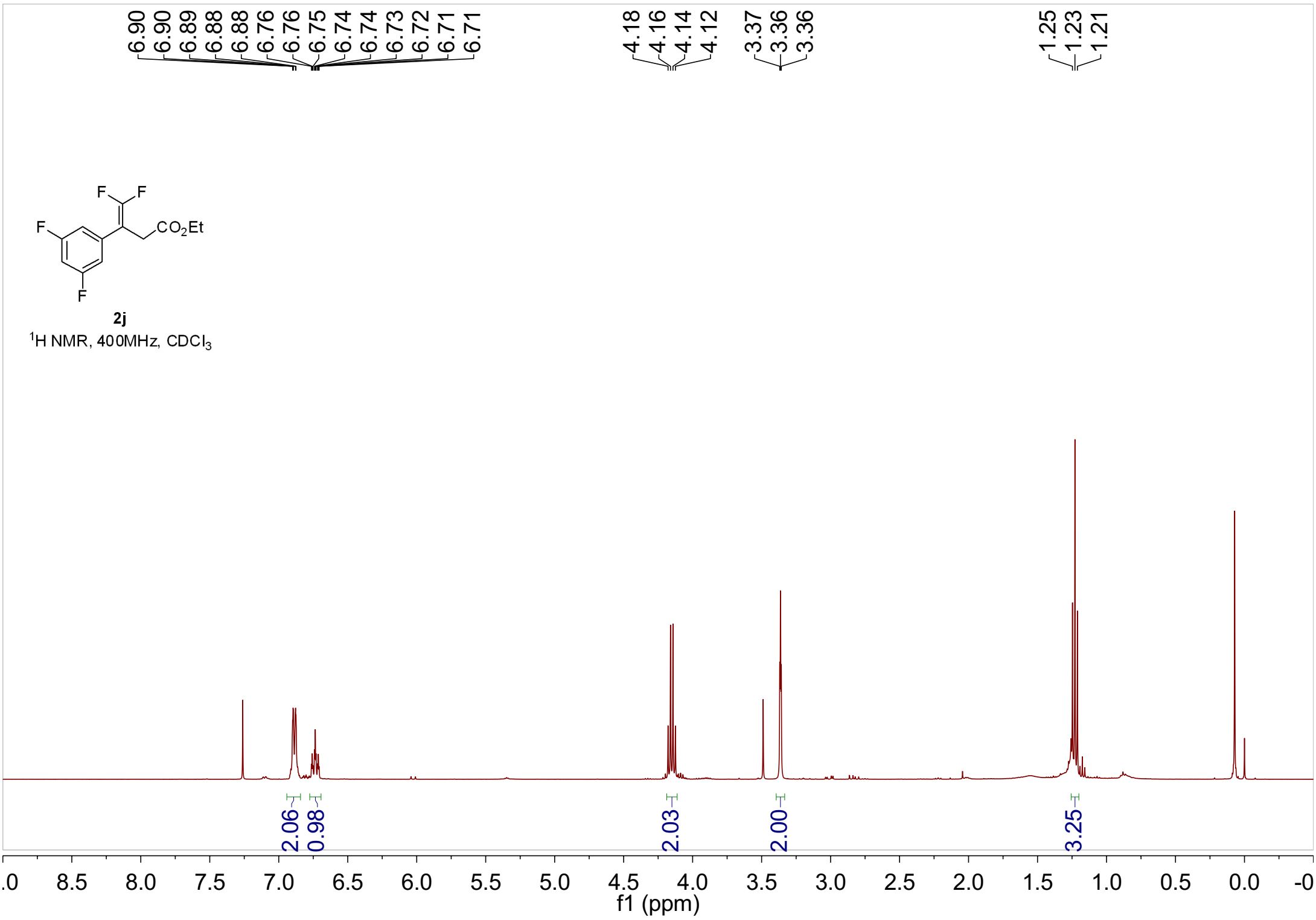
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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6.74
6.73
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6.71
4.18
4.16
4.14
4.12
3.37
3.36
3.36
1.25
1.23
1.21
F
F
F
F
CO2Et
2j
1H NMR, 400MHz, CDCl3
2.06
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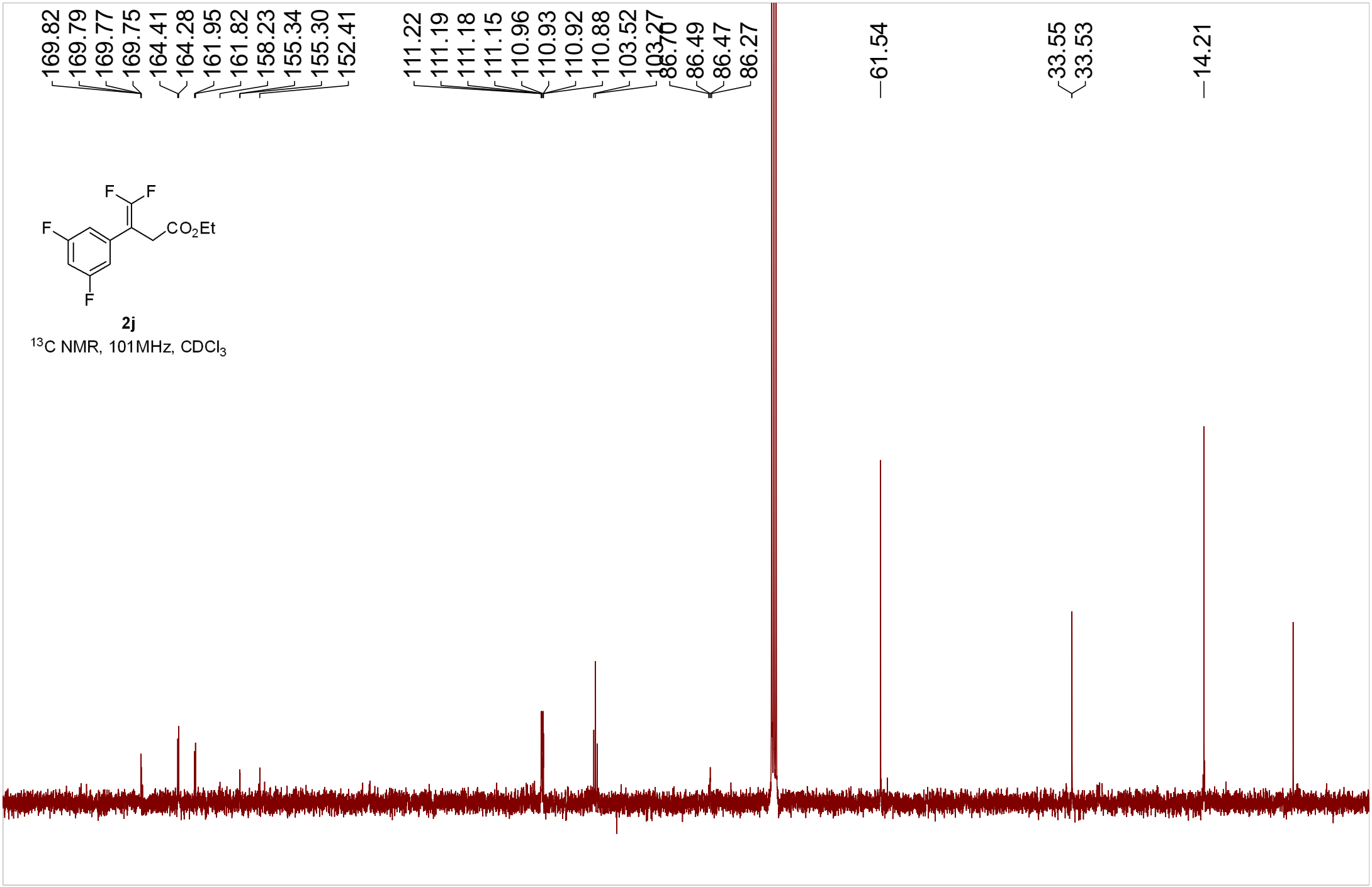
2.03
2.00
3.25
f1 (ppm)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111.19
111.18
111.15
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110.93
110.92
110.88
103.52
103.27
86.70
86.49
86.47
86.27
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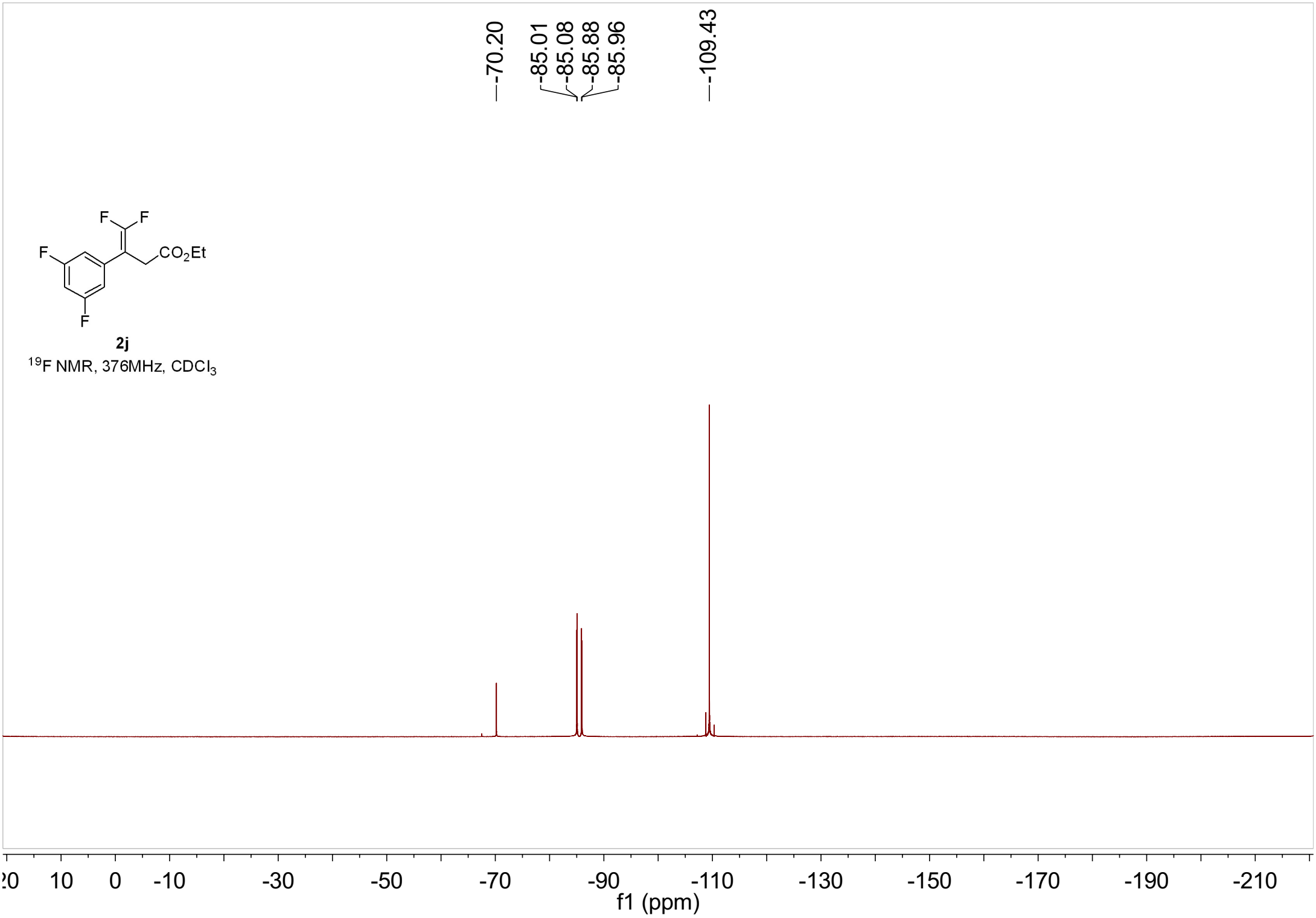
33.55
33.53
14.21
F
F
F
F
CO2Et
2j
13C NMR, 101MHz, CDCl3
f1 (ppm)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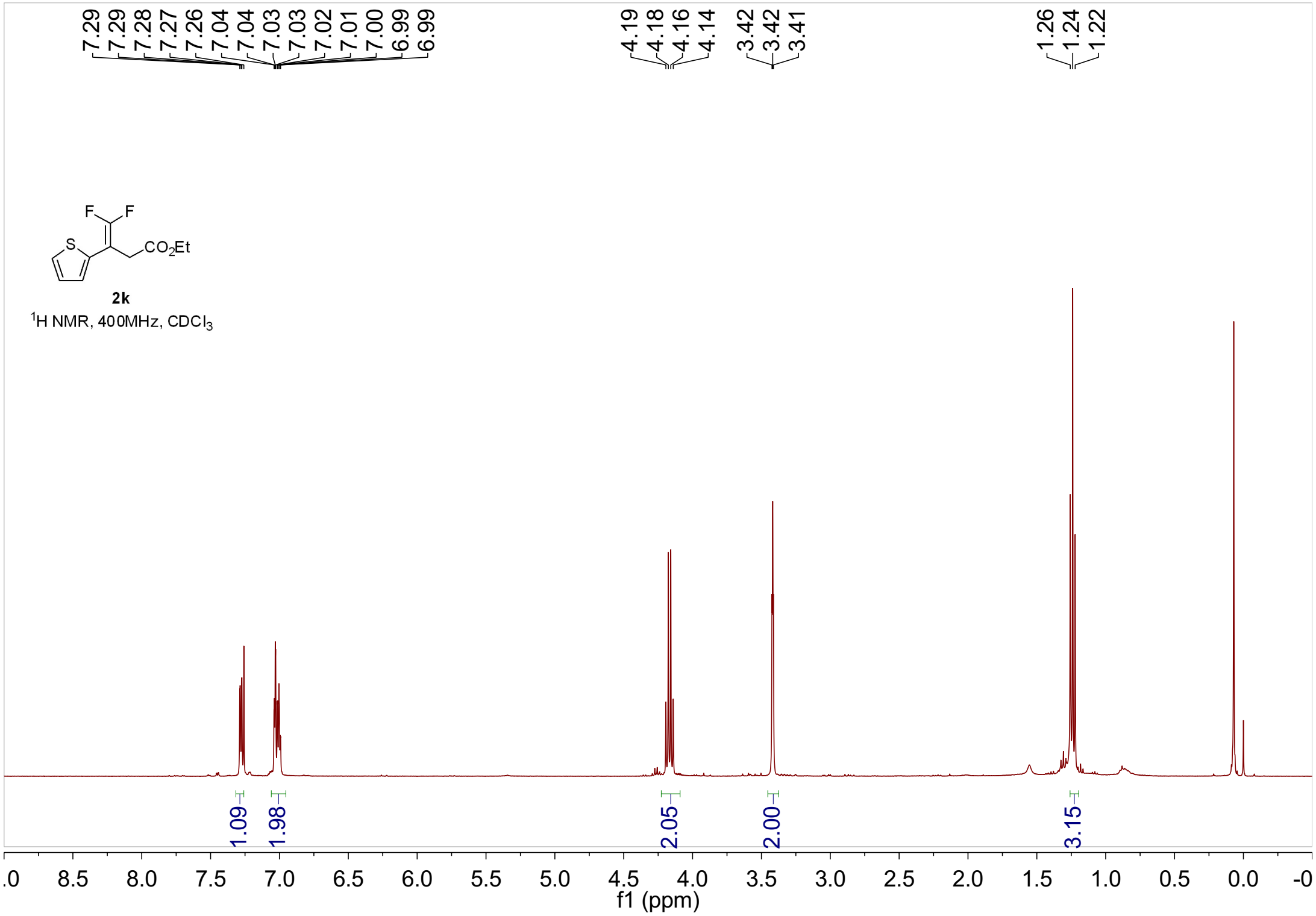
F
F
F
F
CO2Et
2j
19F NMR, 376MHz, CDCl3
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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7.03
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7.02
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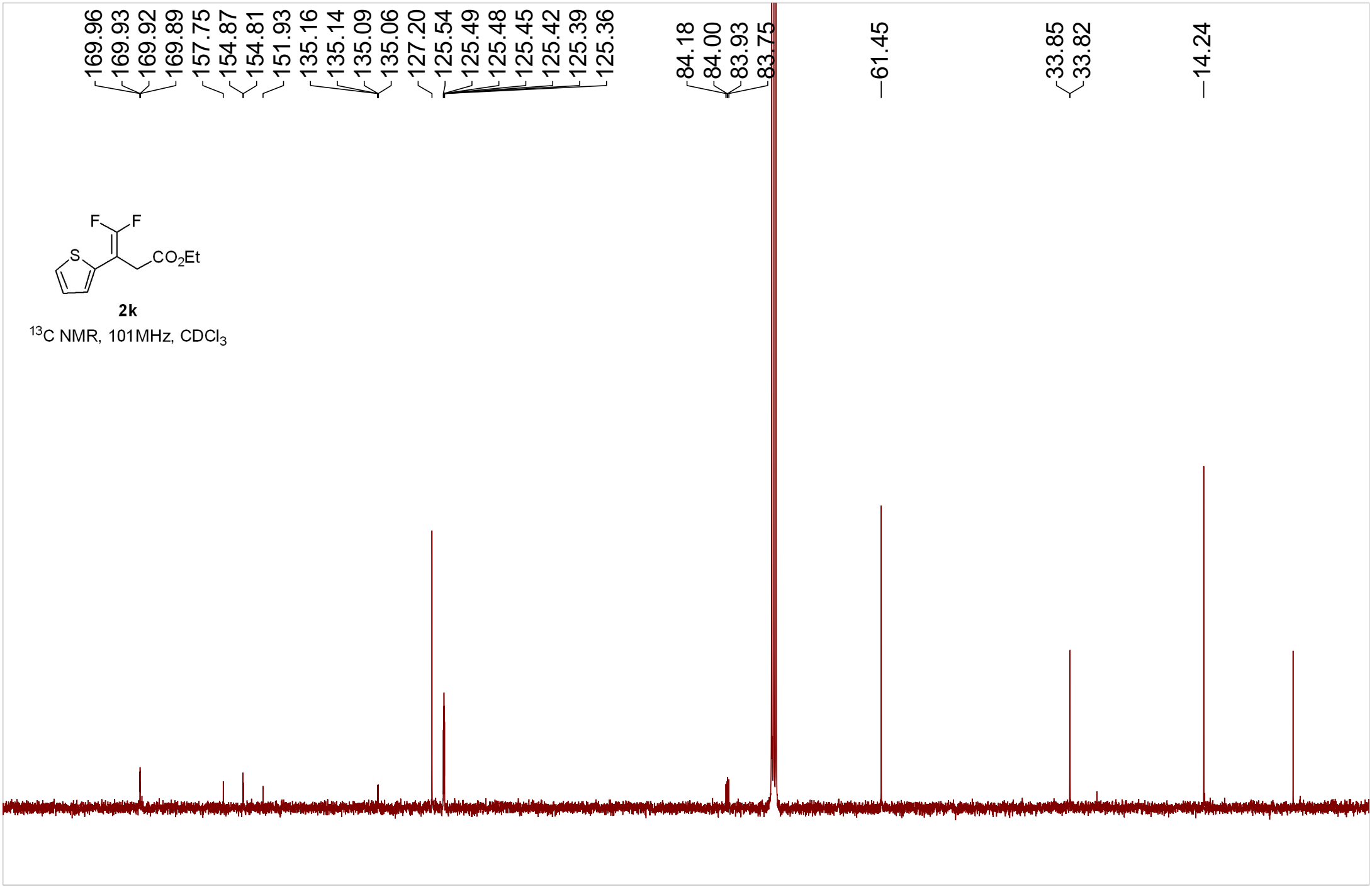
6.99
6.99
4.19
4.18
4.16
4.14
3.42
3.42
3.41
1.26
1.24
1.22
F
F
S
CO2Et
2k
1H NMR, 400MHz, CDCl3
1.09
1.98
2.05
2.00
3.15
f1 (ppm)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125.54
125.49
125.48
125.45
125.42
125.39
125.36
84.18
84.00
83.93
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33.82
14.24
F
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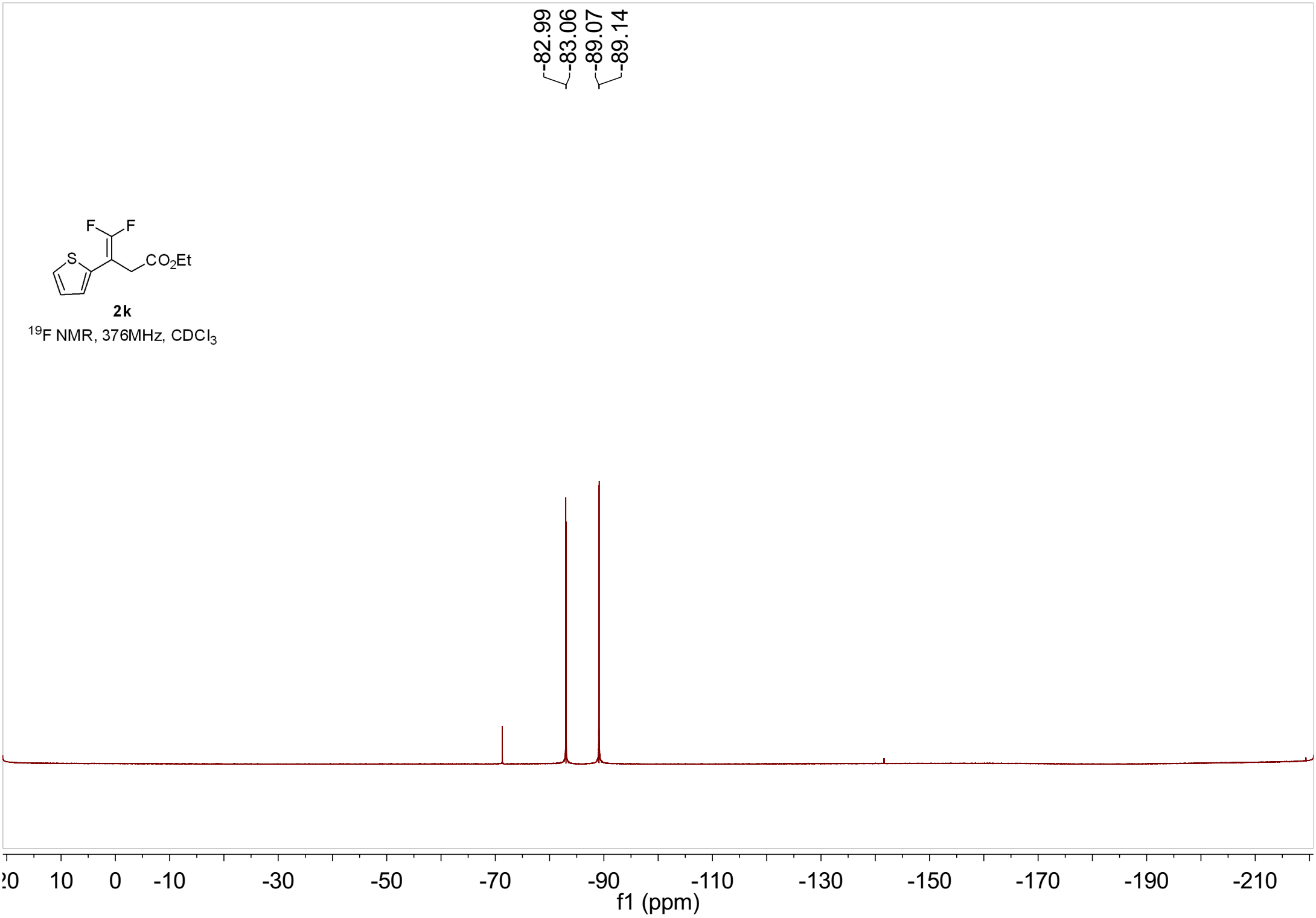
S
CO2Et
2k
13C NMR, 101MHz, CDCl3
f1 (ppm)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F
S
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2k
19F NMR, 376MHz, CDCl3
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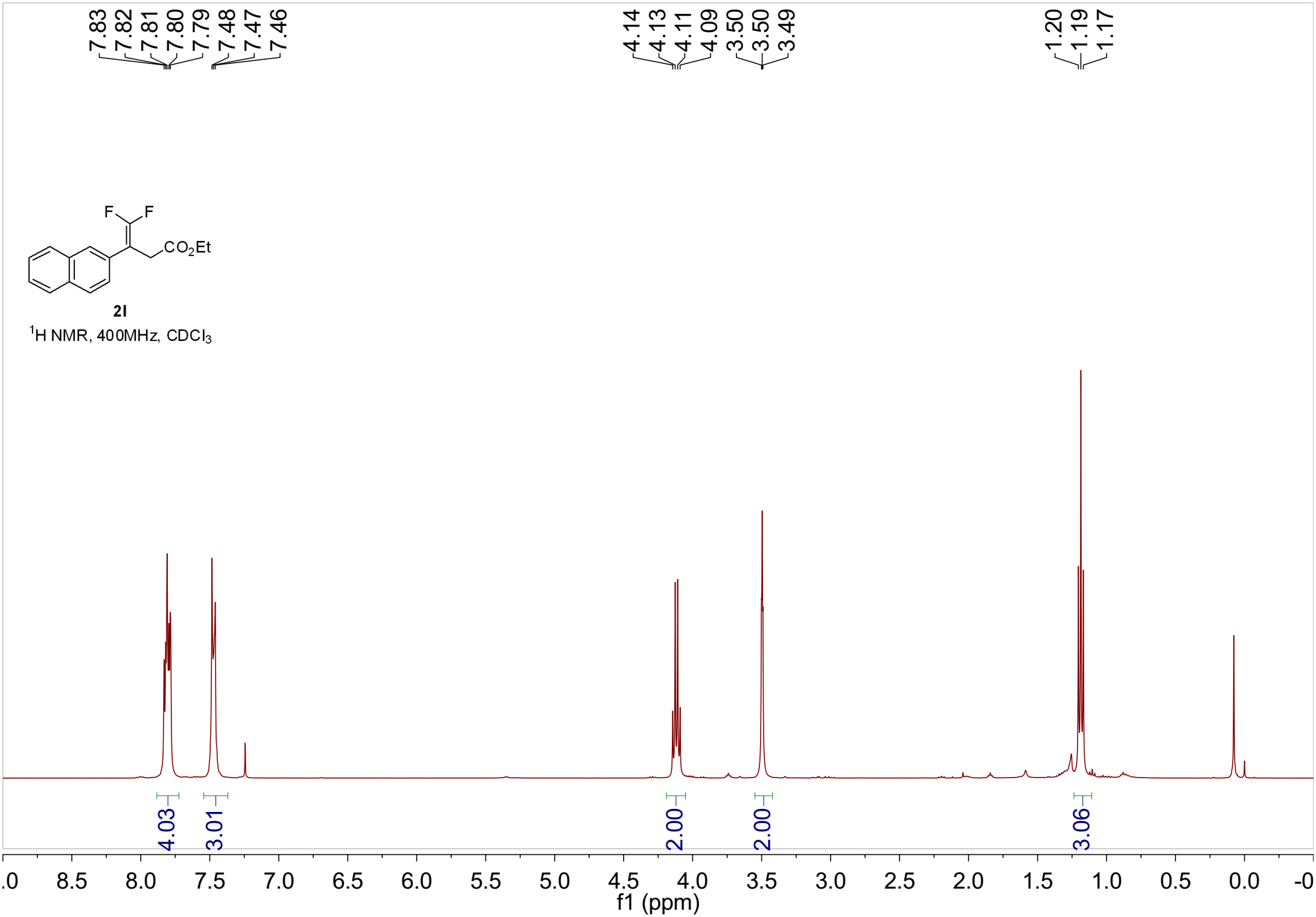
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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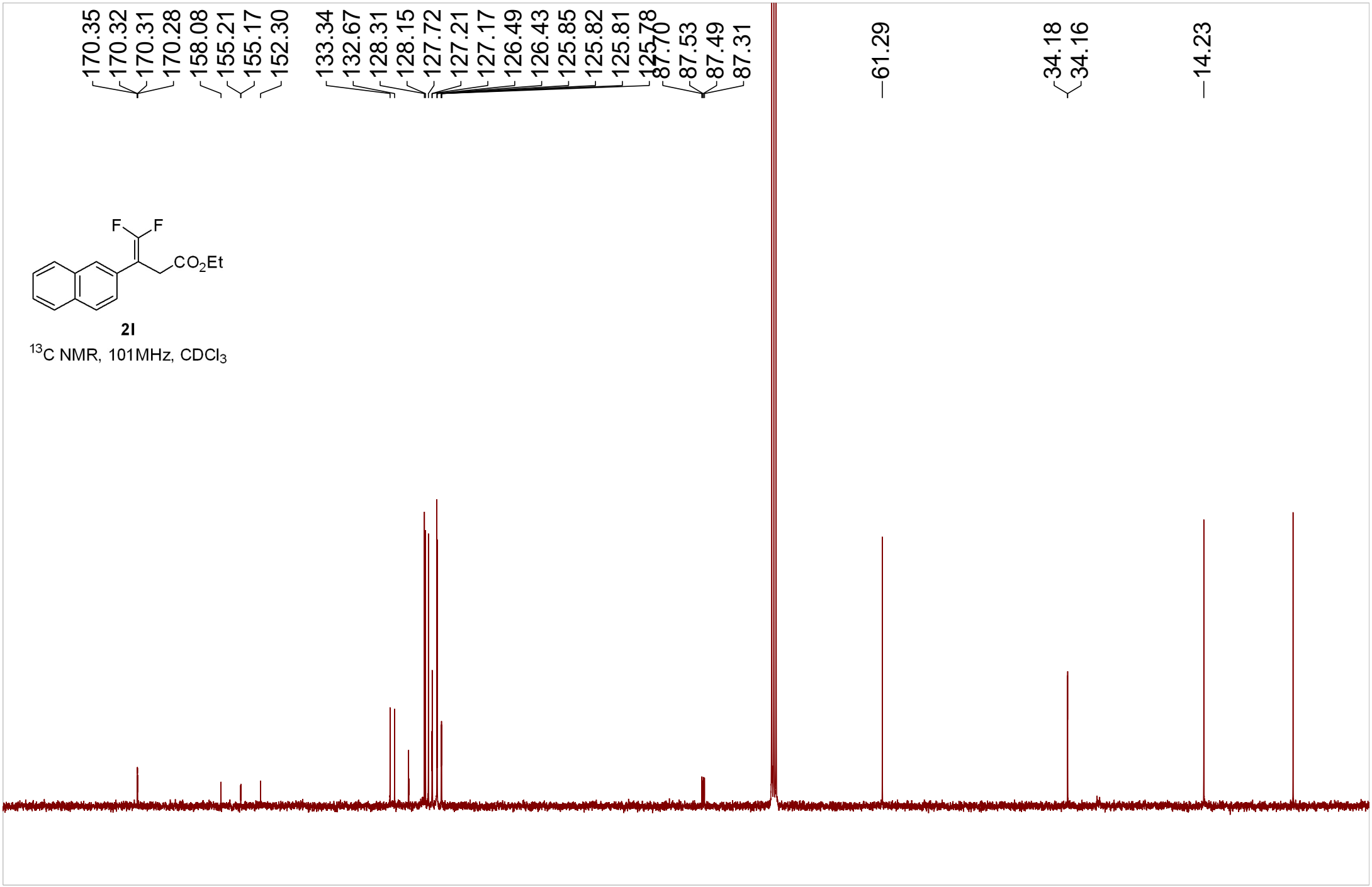
4.13
4.11
4.09
3.50
3.50
3.49
1.20
1.19
1.17
F
F
CO2Et
2l
1H NMR, 400MHz, CDCl3
4.03
3.01
2.00
2.00
3.06
f1 (ppm)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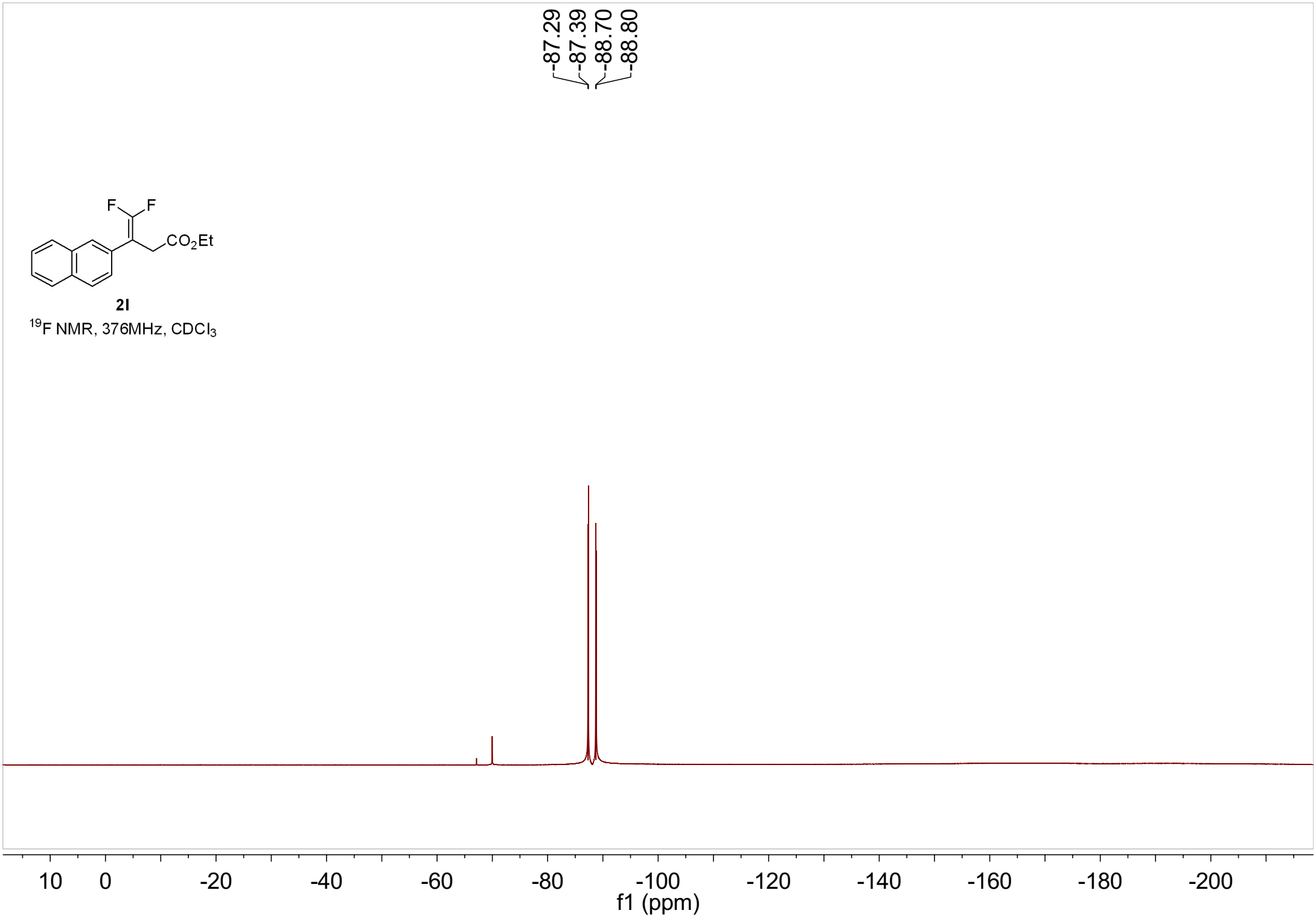
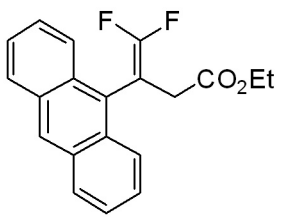
127.21
127.17
126.49
126.43
125.85
125.82
125.81
125.78
87.70
87.53
87.49
87.31
61.29
34.18
34.16
14.23
F
F
CO2Et
2l
13C NMR, 101MHz, CDCl3
f1 (ppm)



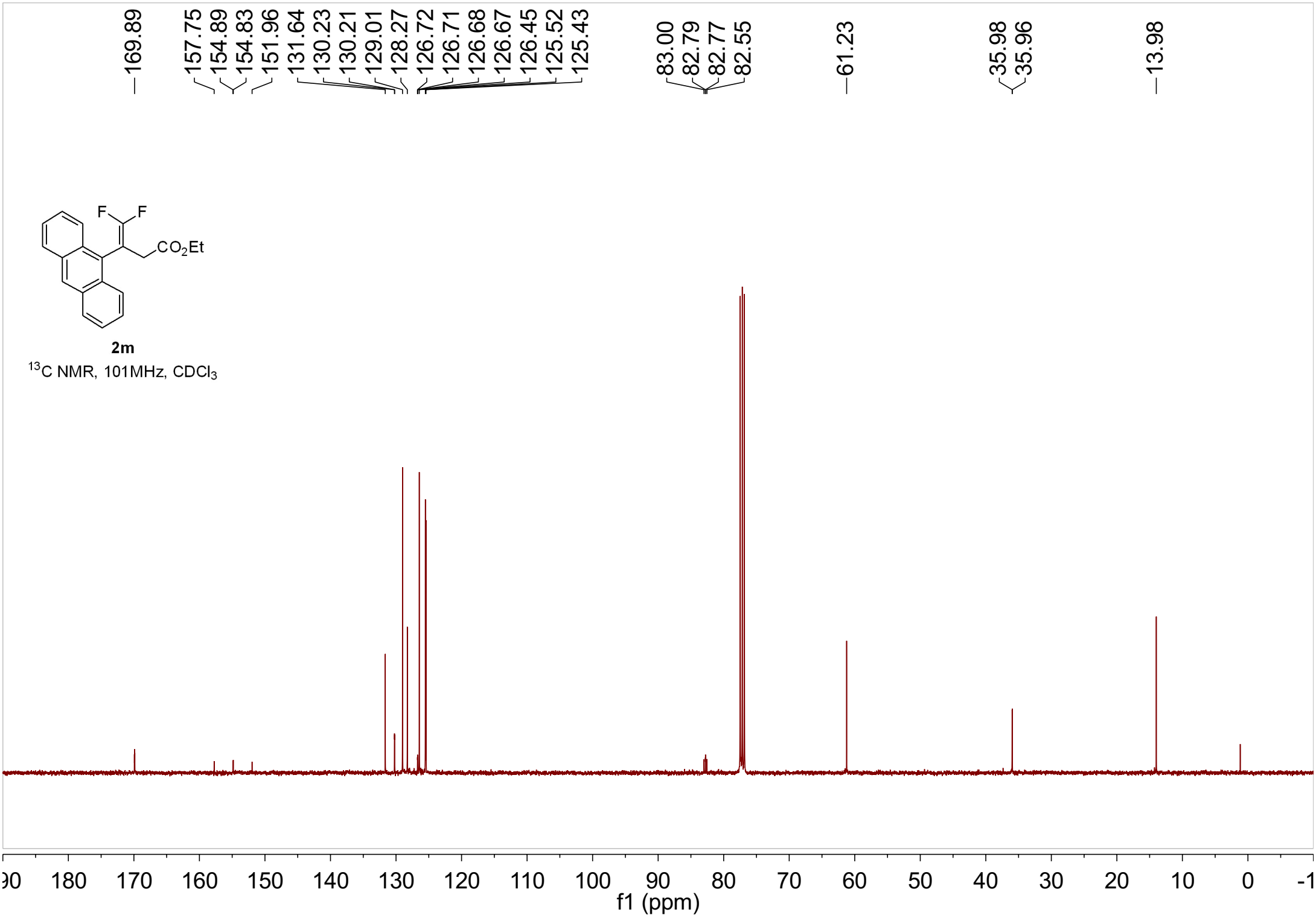
2l

^{19}F NMR, 376MHz, $CDCl_3$



2m

^{1}H NMR, 400MHz, $CDCl_3$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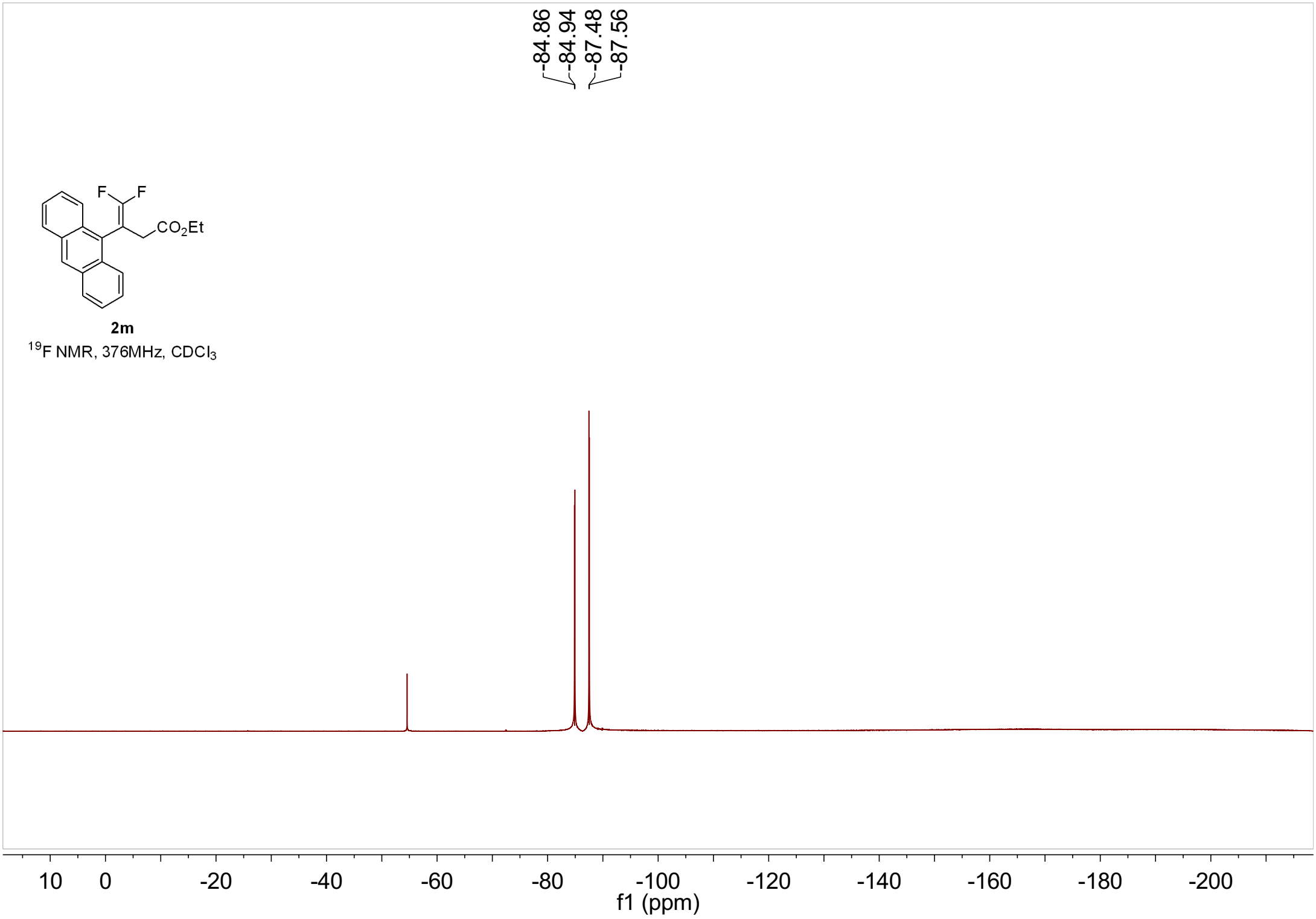
126.68
126.67
126.45
125.52
125.43
83.00
82.79
82.77
82.55
61.23
35.98
35.96
13.98
F
F
CO2Et
2m
13C NMR, 101MHz, CDCl3
f1 (ppm)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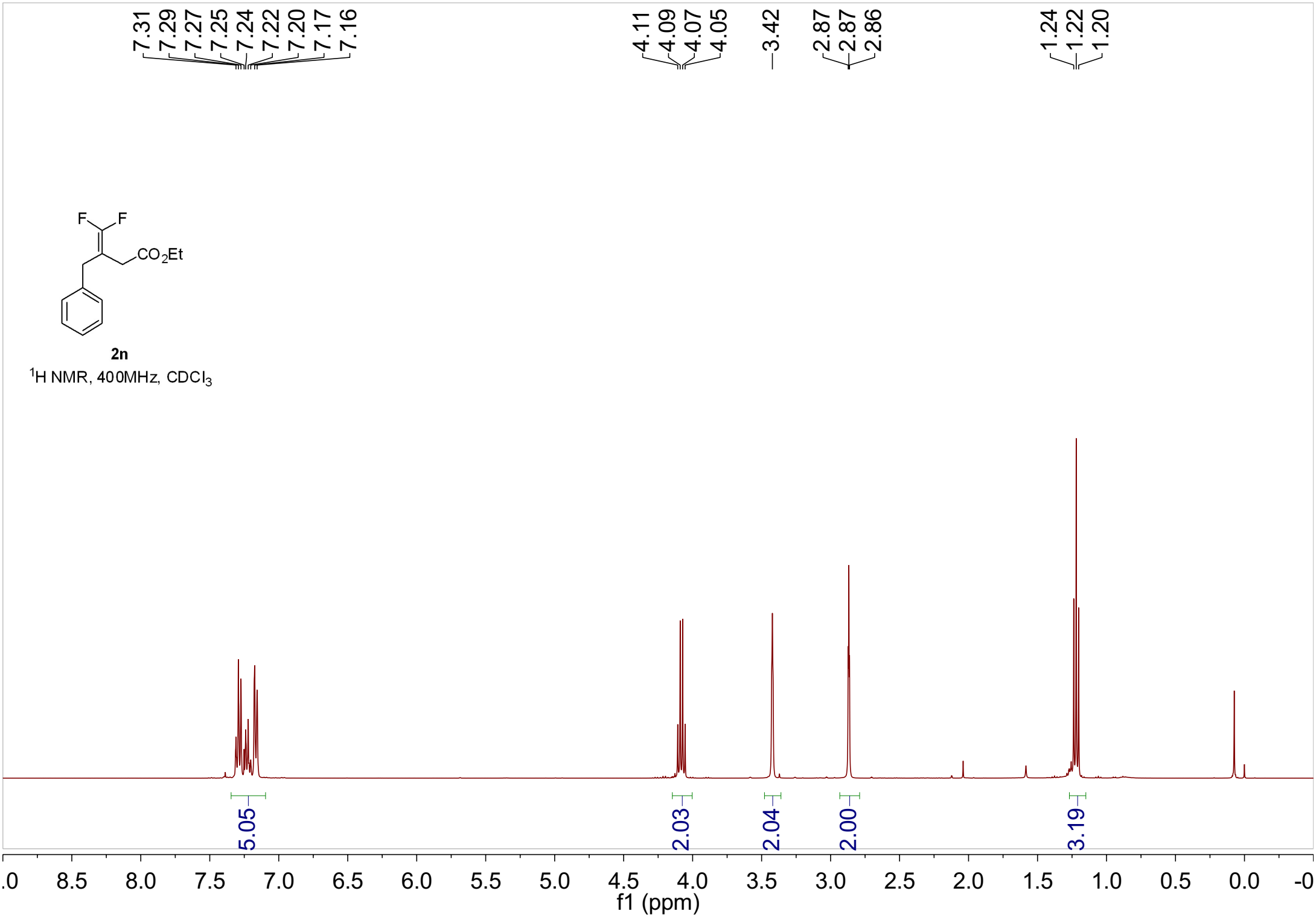
-84.94
-87.48
-87.56
F
F
CO2Et
2m
19F NMR, 376MHz, CDCl3
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)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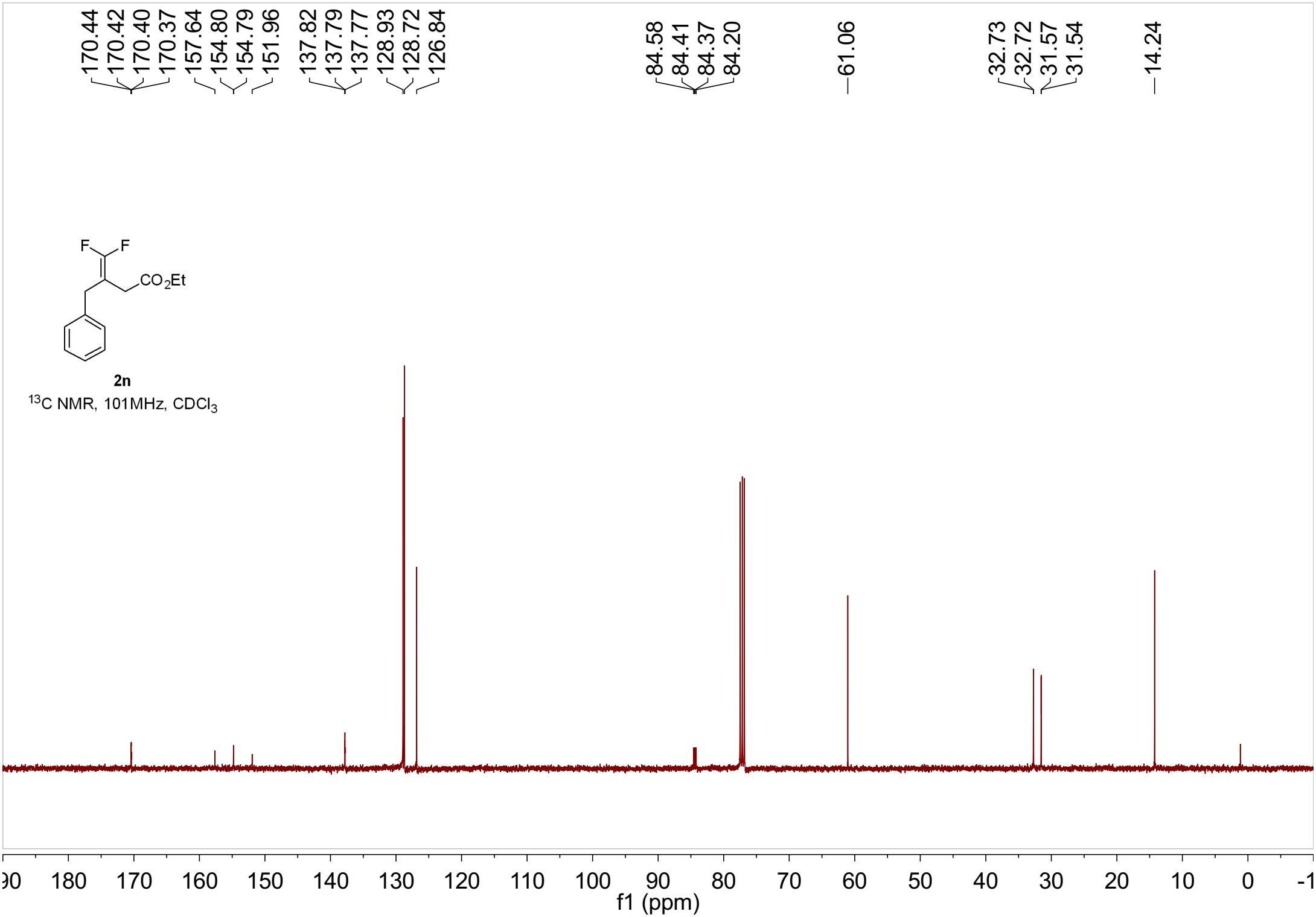
4.05
3.42
2.87
2.87
2.86
1.24
1.22
1.20
F
F
CO2Et
2n
1H NMR, 400MHz, CDCl3
5.05
2.03
2.04
2.00
3.19
f1 (ppm)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84.58
84.41
84.37
84.20
61.06
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31.54
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F
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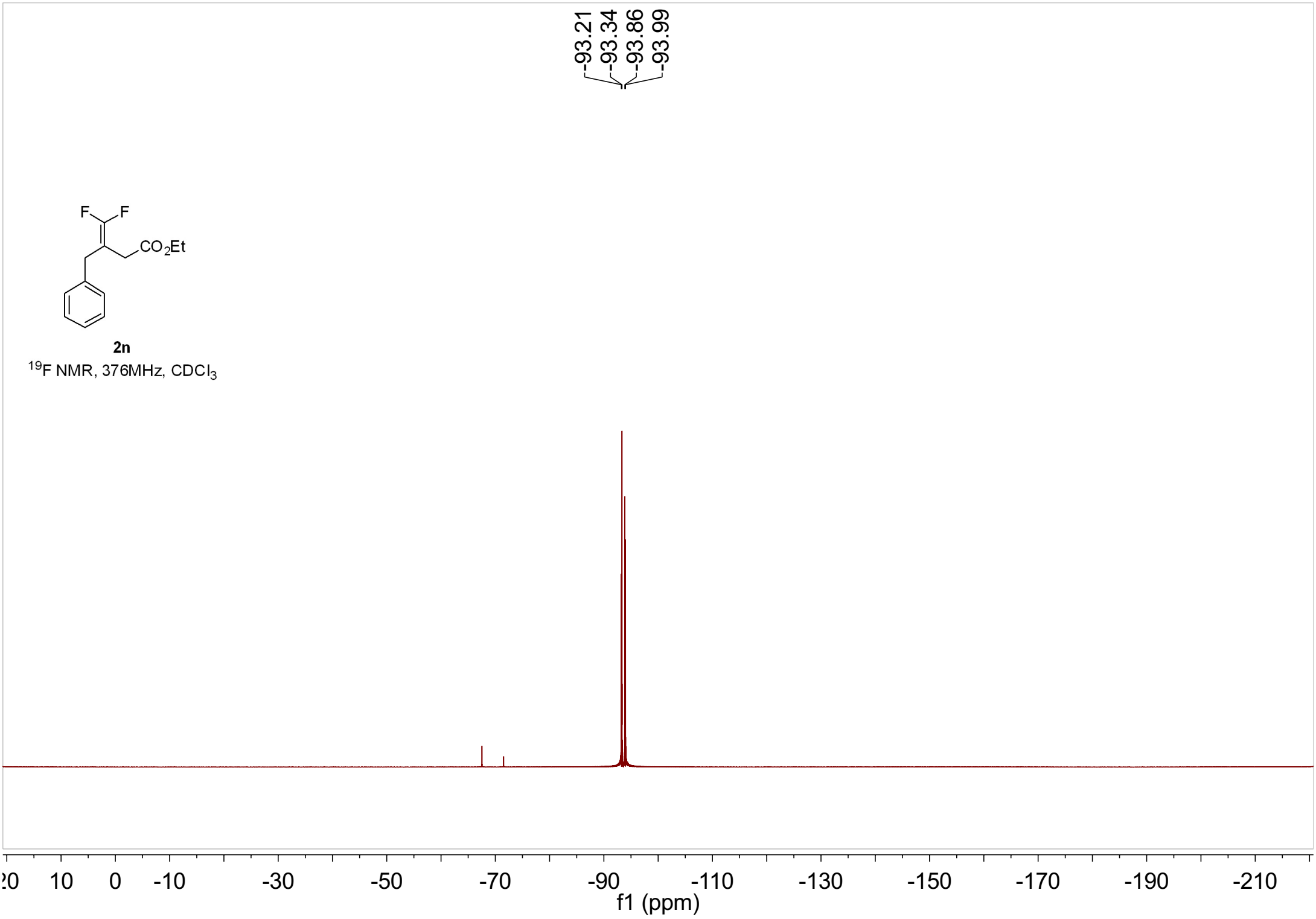
2n
13C NMR, 101MHz, CDCl3
f1 (ppm)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2n
19F NMR, 376MHz, CDCl3
20
10
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-10
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-70
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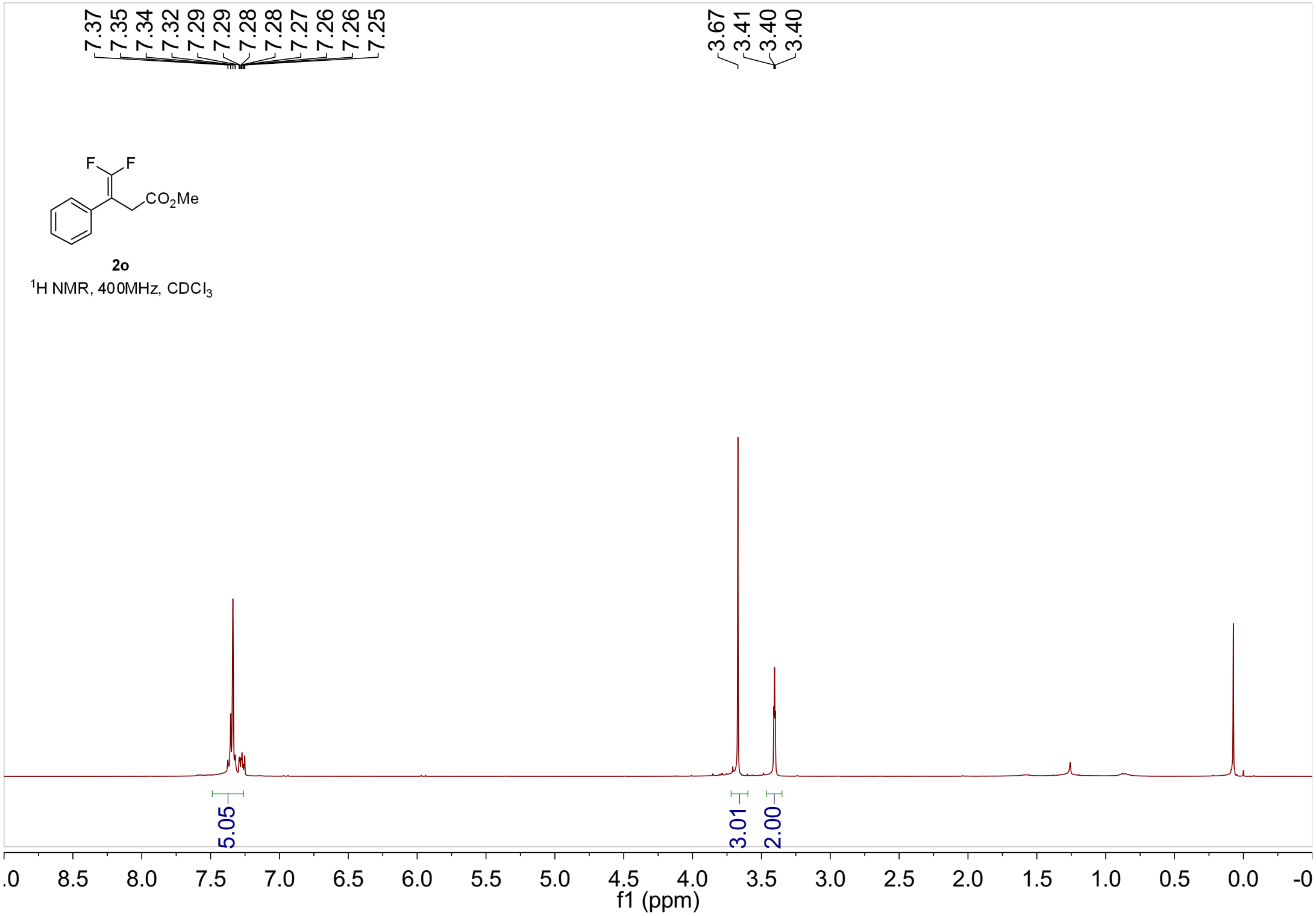
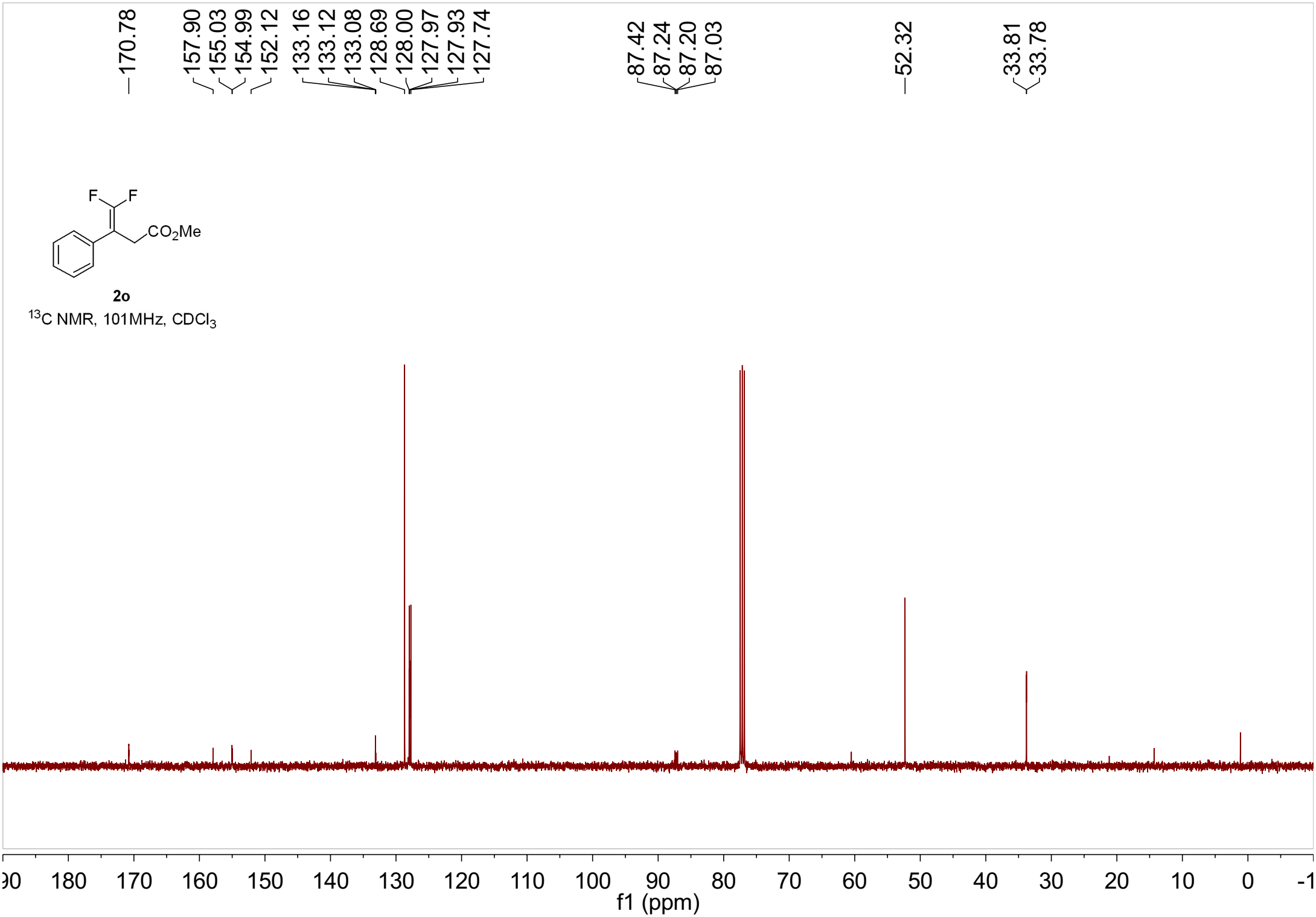
-110
-130
-150
-170
-190
-210
f1 (ppm)



2o

^{1}H NMR, 400MHz, $CDCl_3$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87.24
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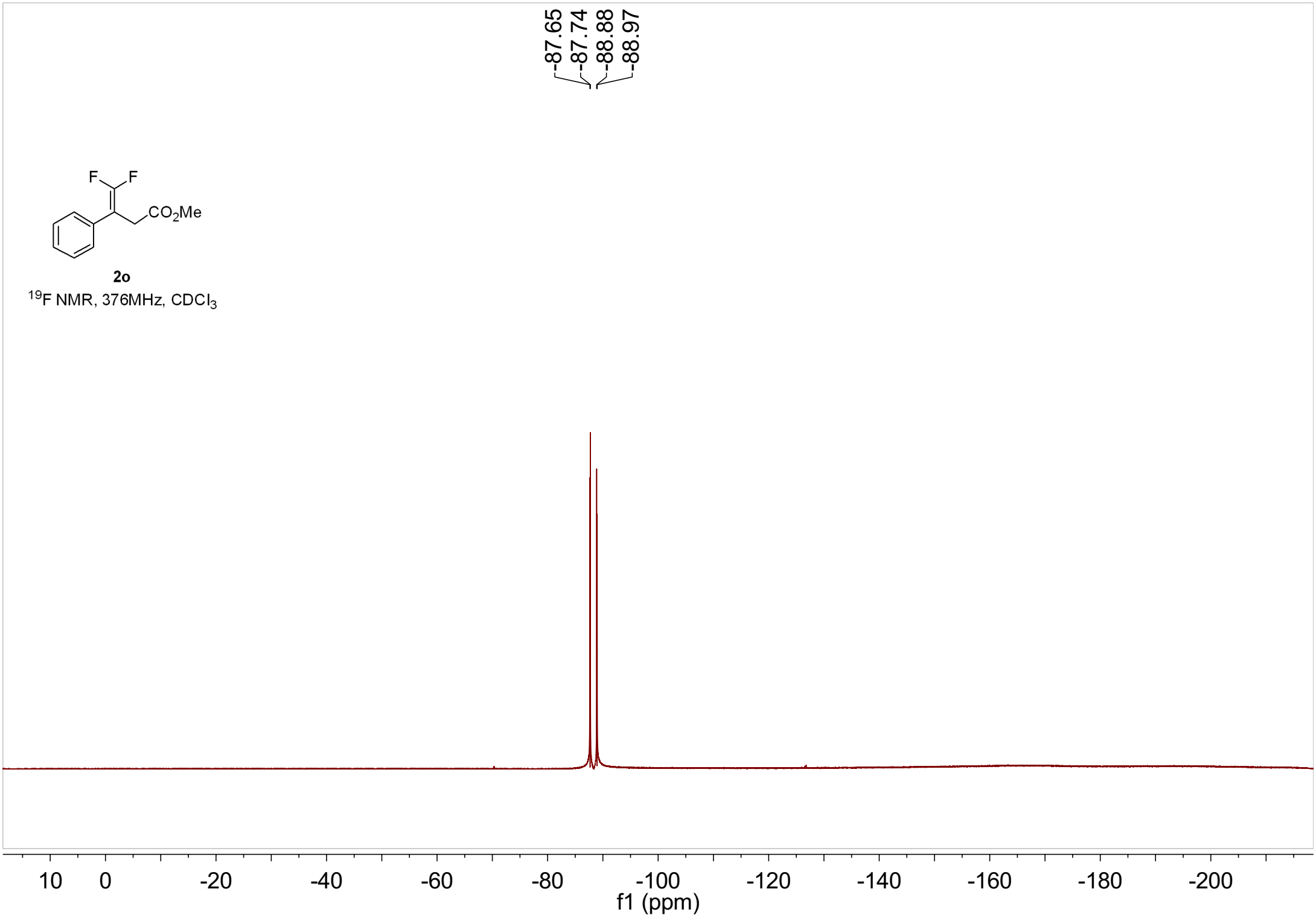
F
CO2Me
2o
13C NMR, 101MHz, CDCl3
f1 (ppm)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F
CO2Me
2o
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0
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-100
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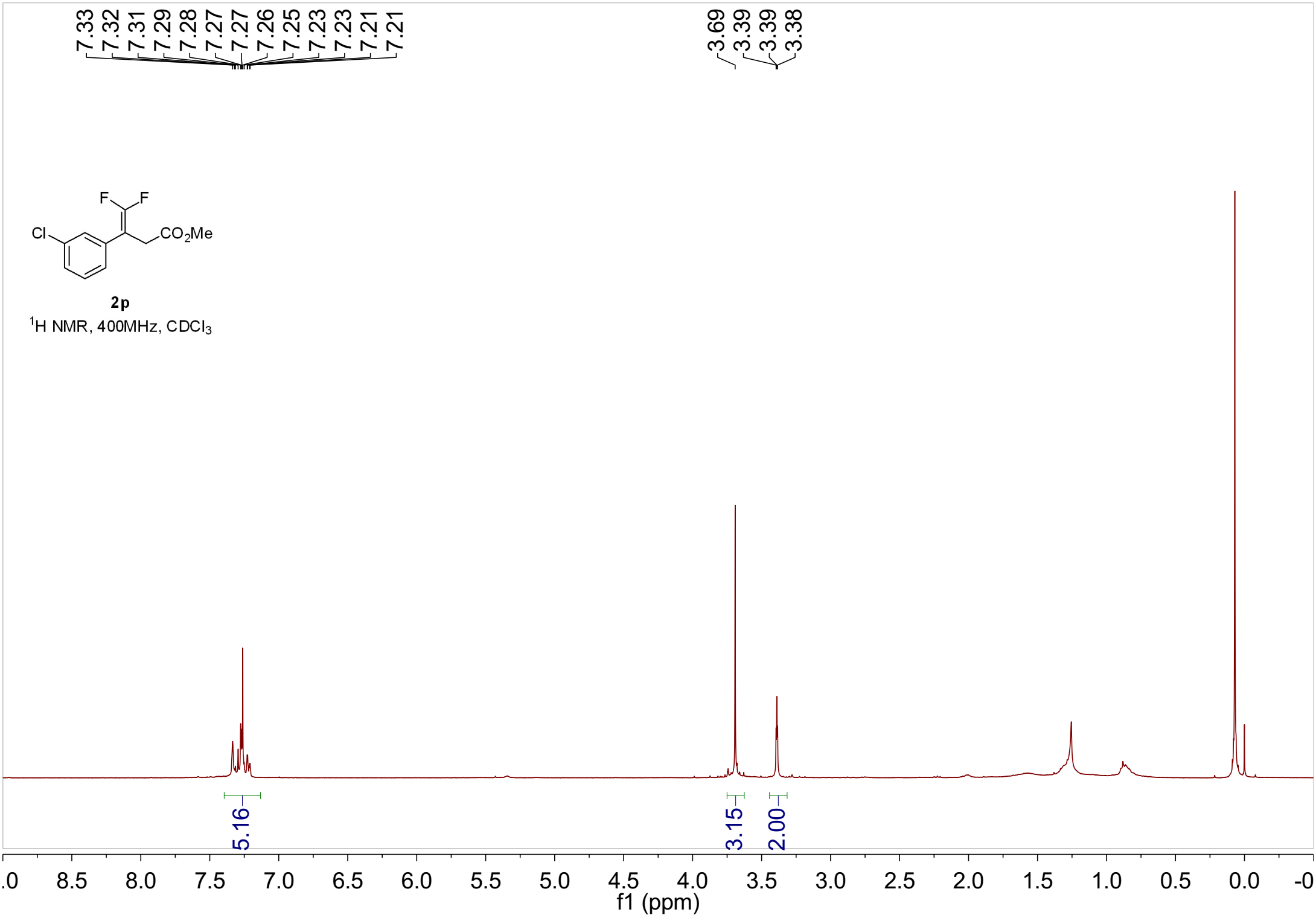
-180
-200
f1 (ppm)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7.21
3.69
3.39
3.39
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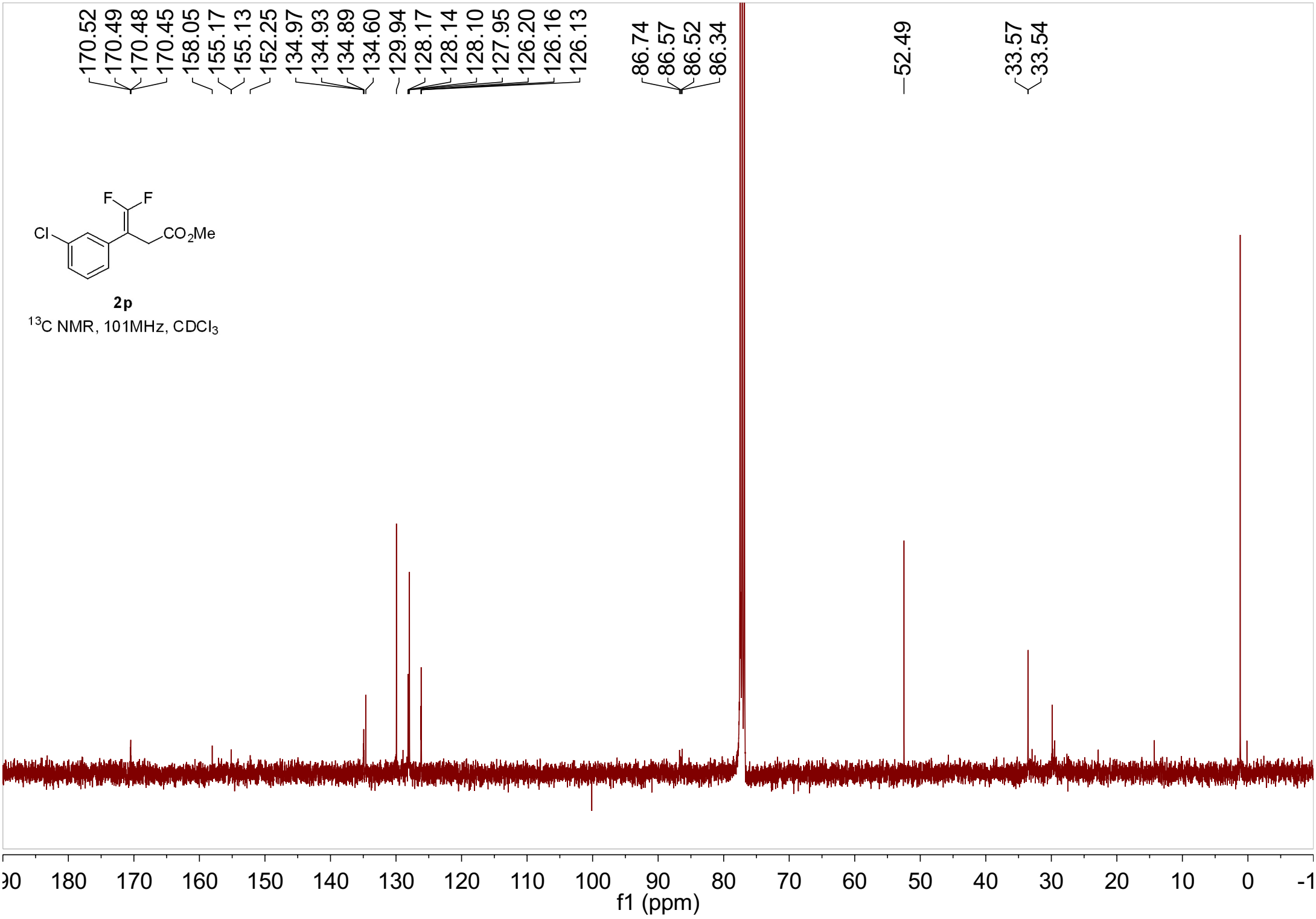
F
Cl
CO2Me
2p
1H NMR, 400MHz, CDCl3
5.16
3.15
2.00
f1 (ppm)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126.16
126.13
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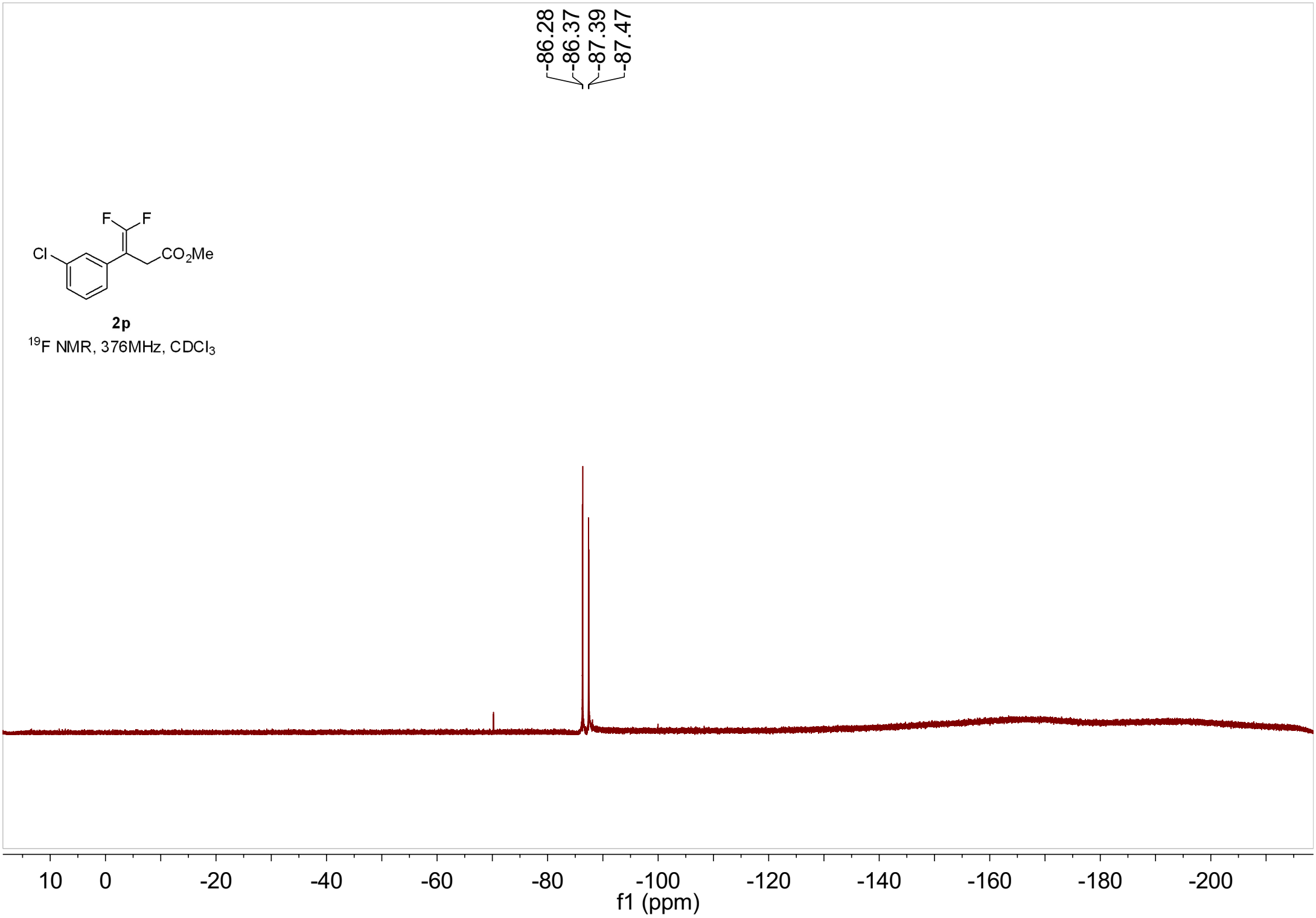
33.54
F
F
Cl
CO2Me
2p
13C NMR, 101MHz, CDCl3
f1 (ppm)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F
Cl
CO2Me
2p
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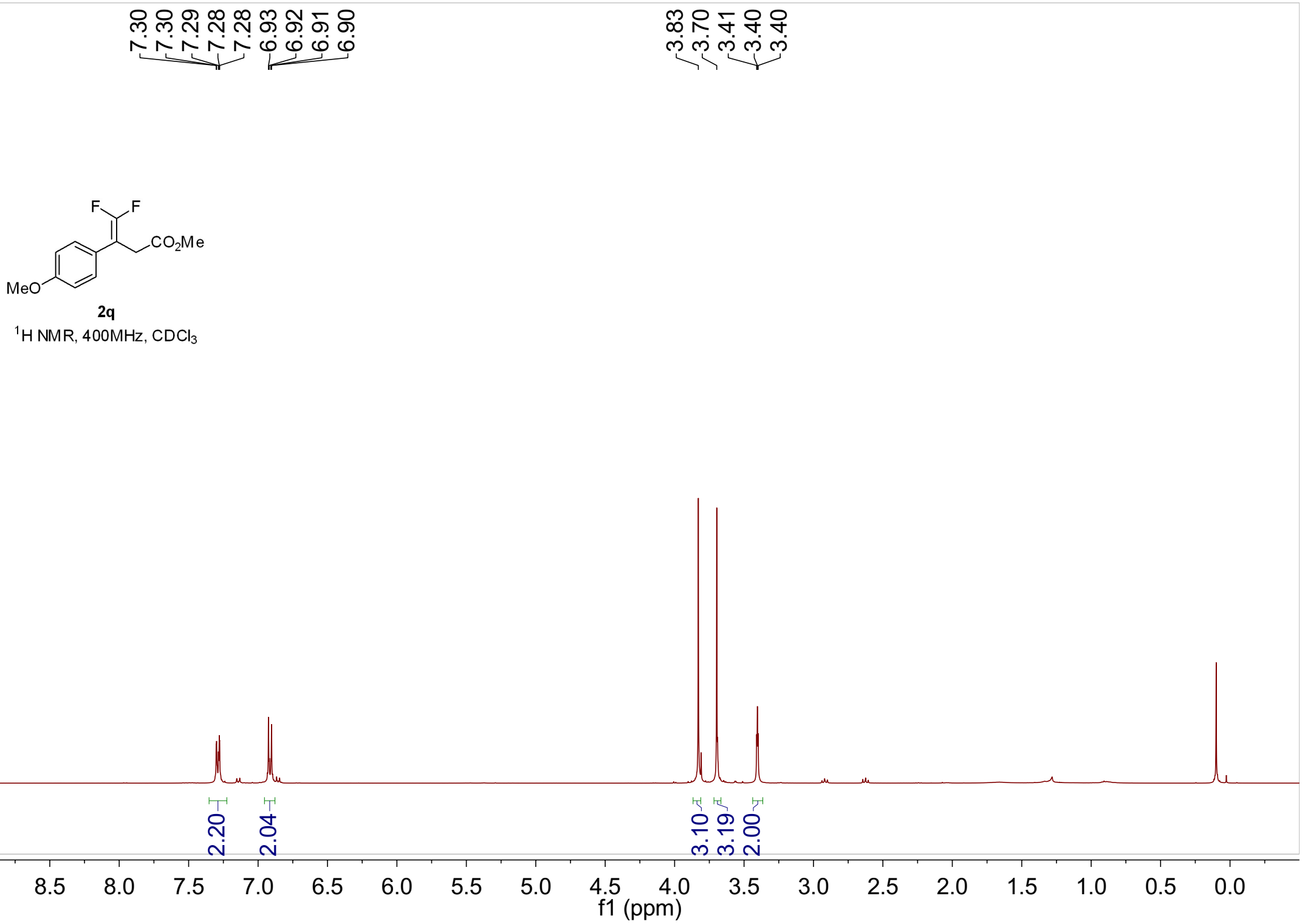
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)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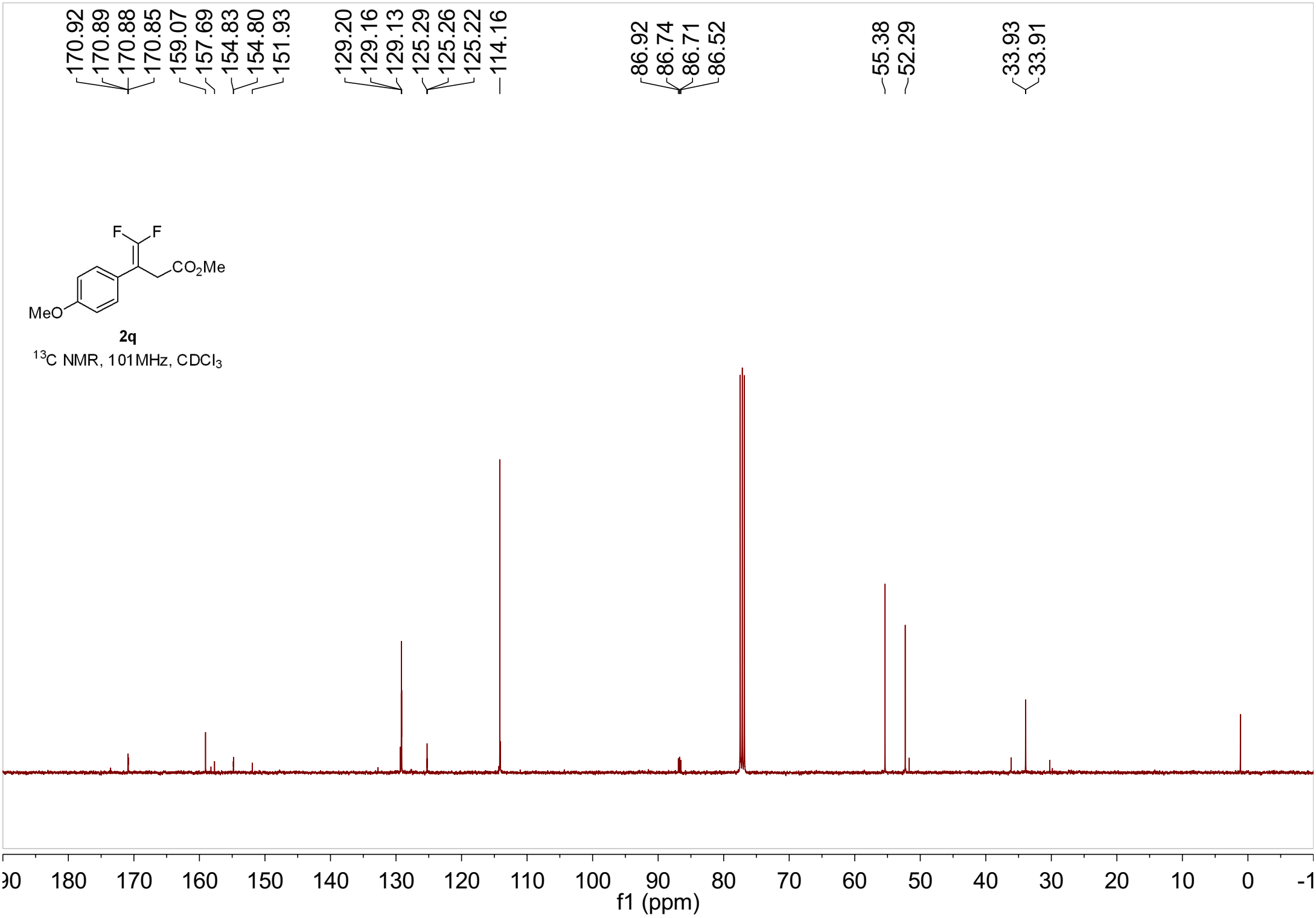
3.83
3.70
3.41
3.40
3.40
F
F
CO2Me
MeO
2q
1H NMR, 400MHz, CDCl3
2.20
2.04
3.10
3.19
2.00
f1 (ppm)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125.26
125.22
114.16
86.92
86.74
86.71
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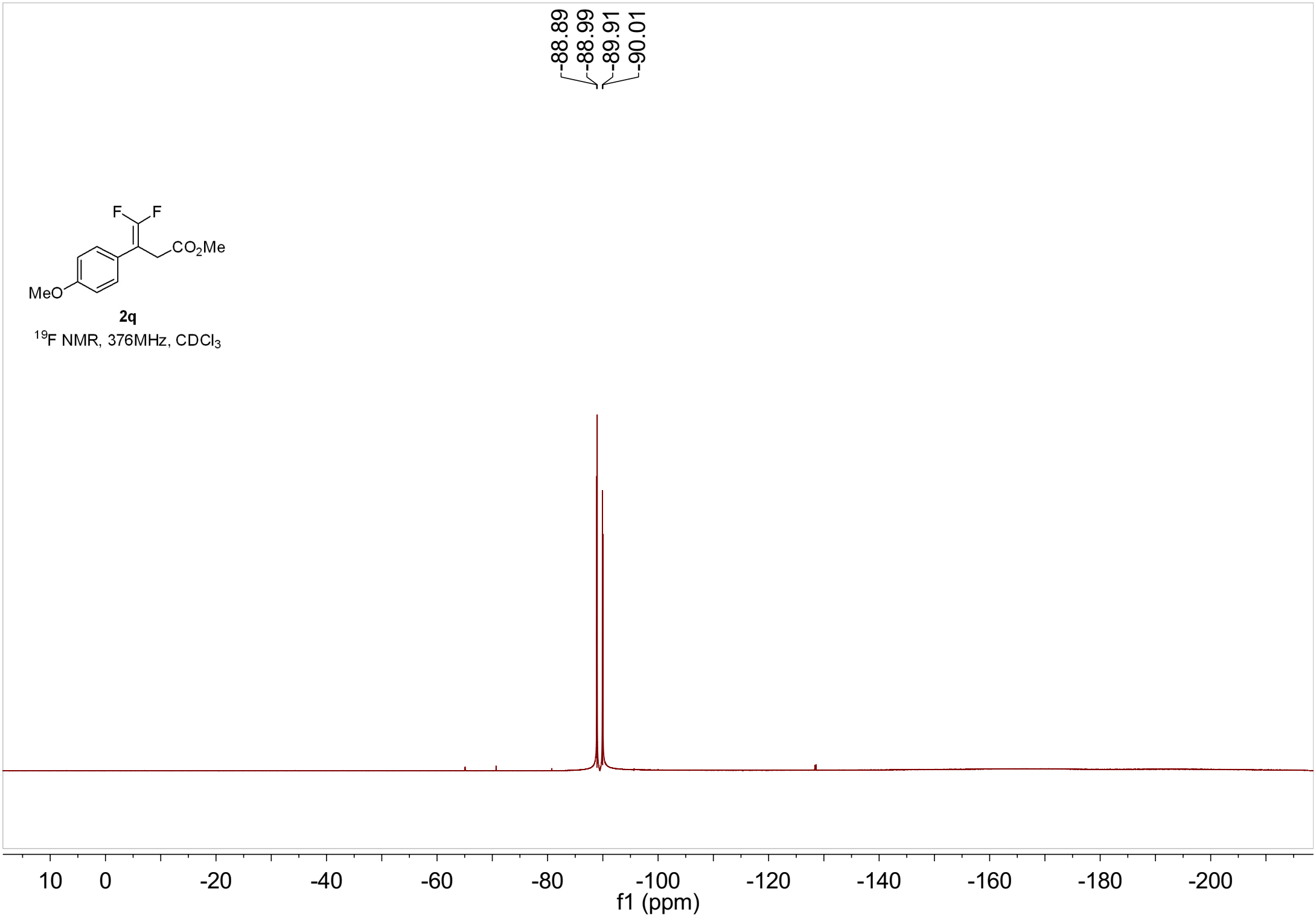
33.93
33.91
F
F
CO2Me
MeO
2q
13C NMR, 101MHz, CDCl3
f1 (ppm)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F
CO2Me
MeO
2q
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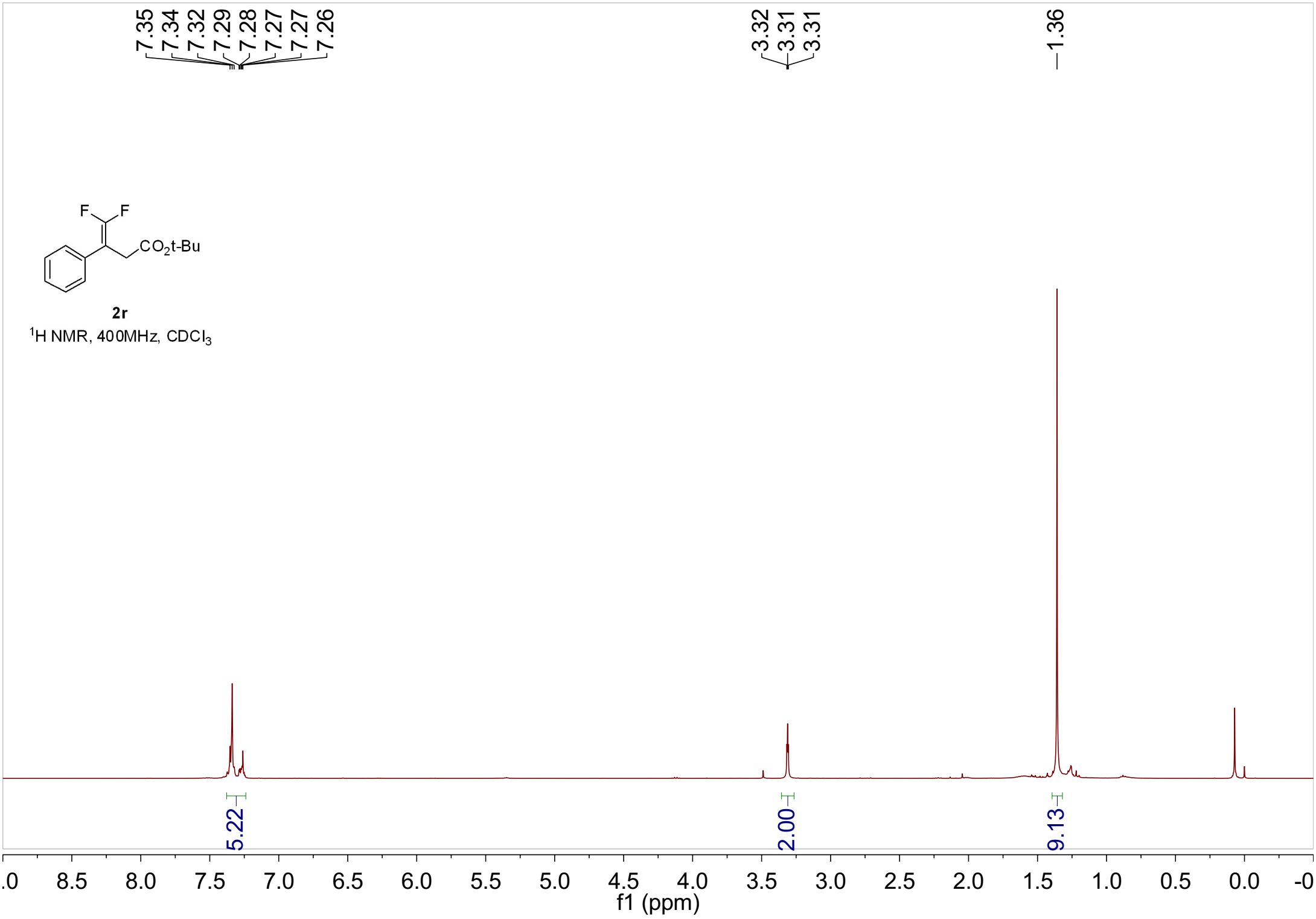
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)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7.34
7.32
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7.27
7.27
7.26
3.32
3.31
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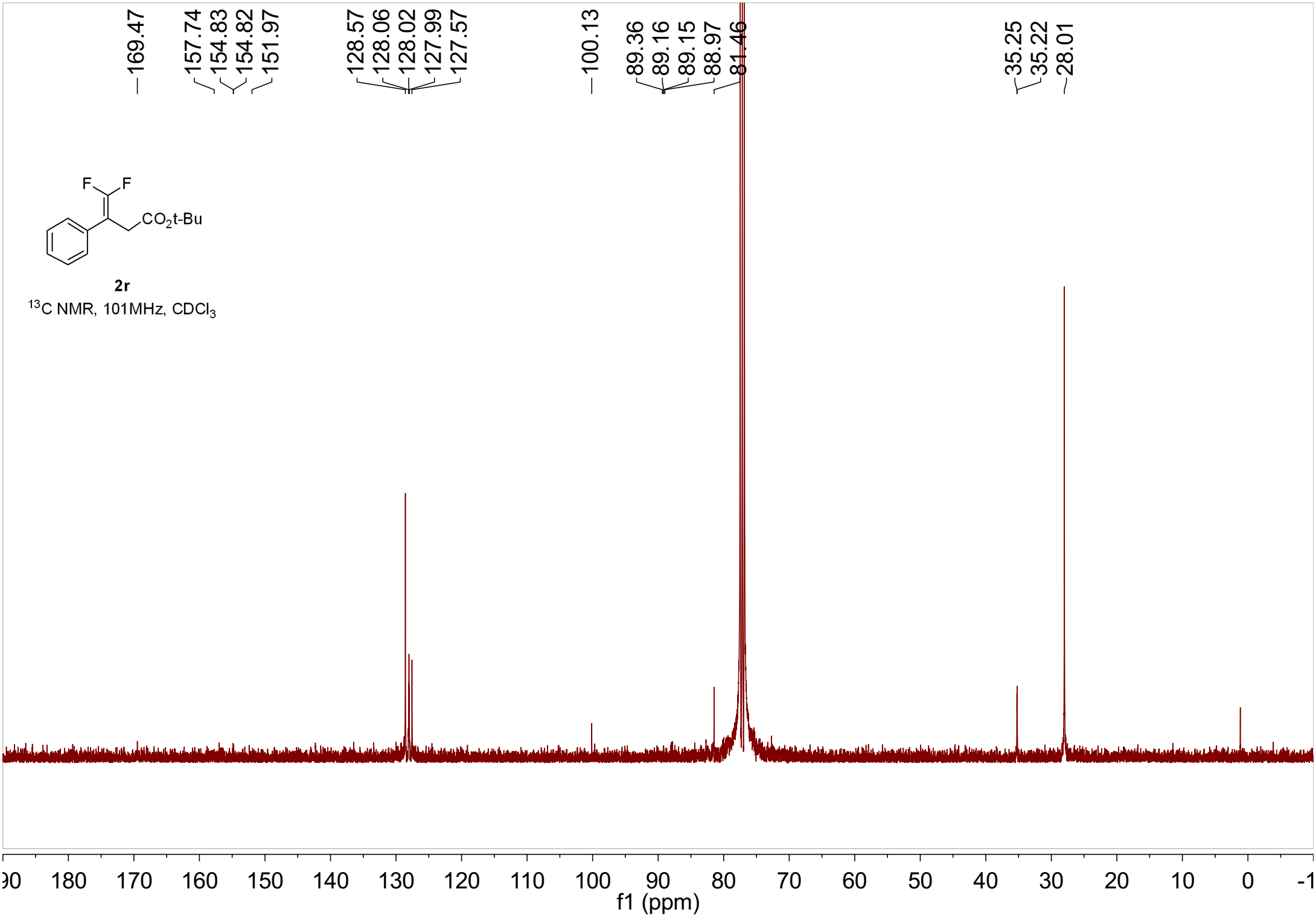
F
F
CO2t-Bu
2r
1H NMR, 400MHz, CDCl3
5.22
2.00
9.13
f1 (ppm)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89.15
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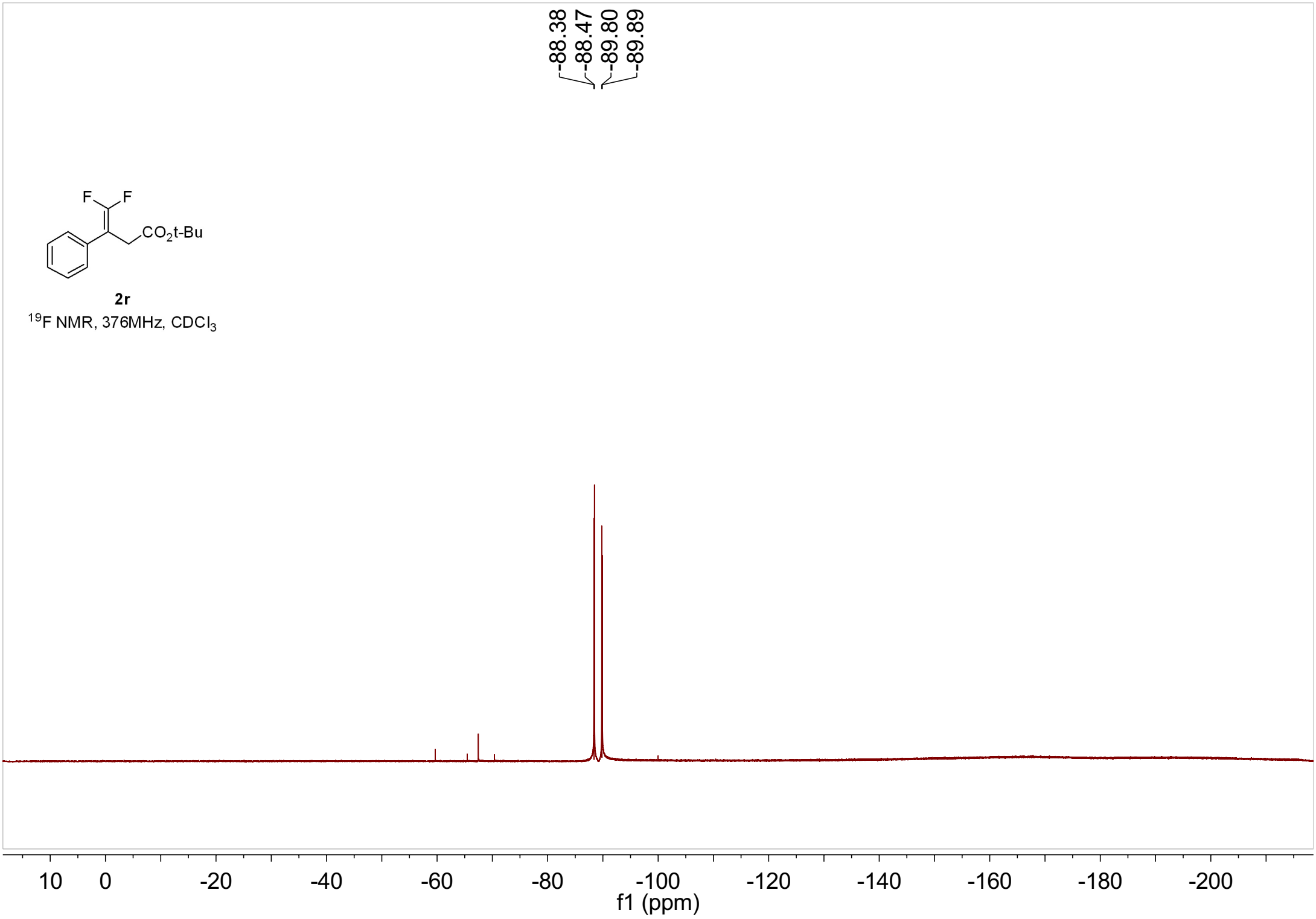
35.22
28.01
F
F
CO2t-Bu
2r
13C NMR, 101MHz, CDCl3
f1 (ppm)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-89.89
F
F
CO2t-Bu
2r
19F NMR, 376MHz, CDCl3
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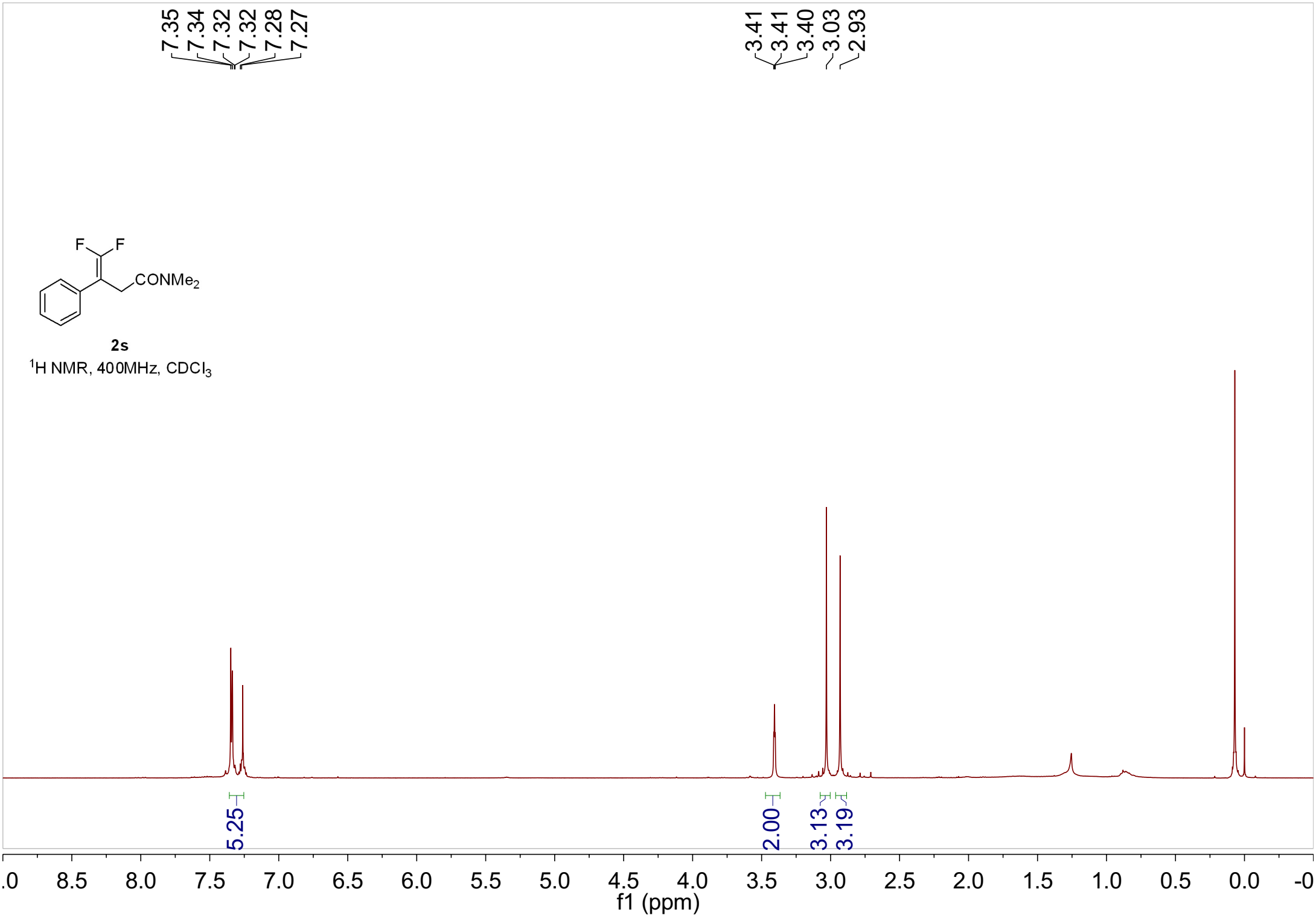
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)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7.28
7.27
3.41
3.41
3.40
3.03
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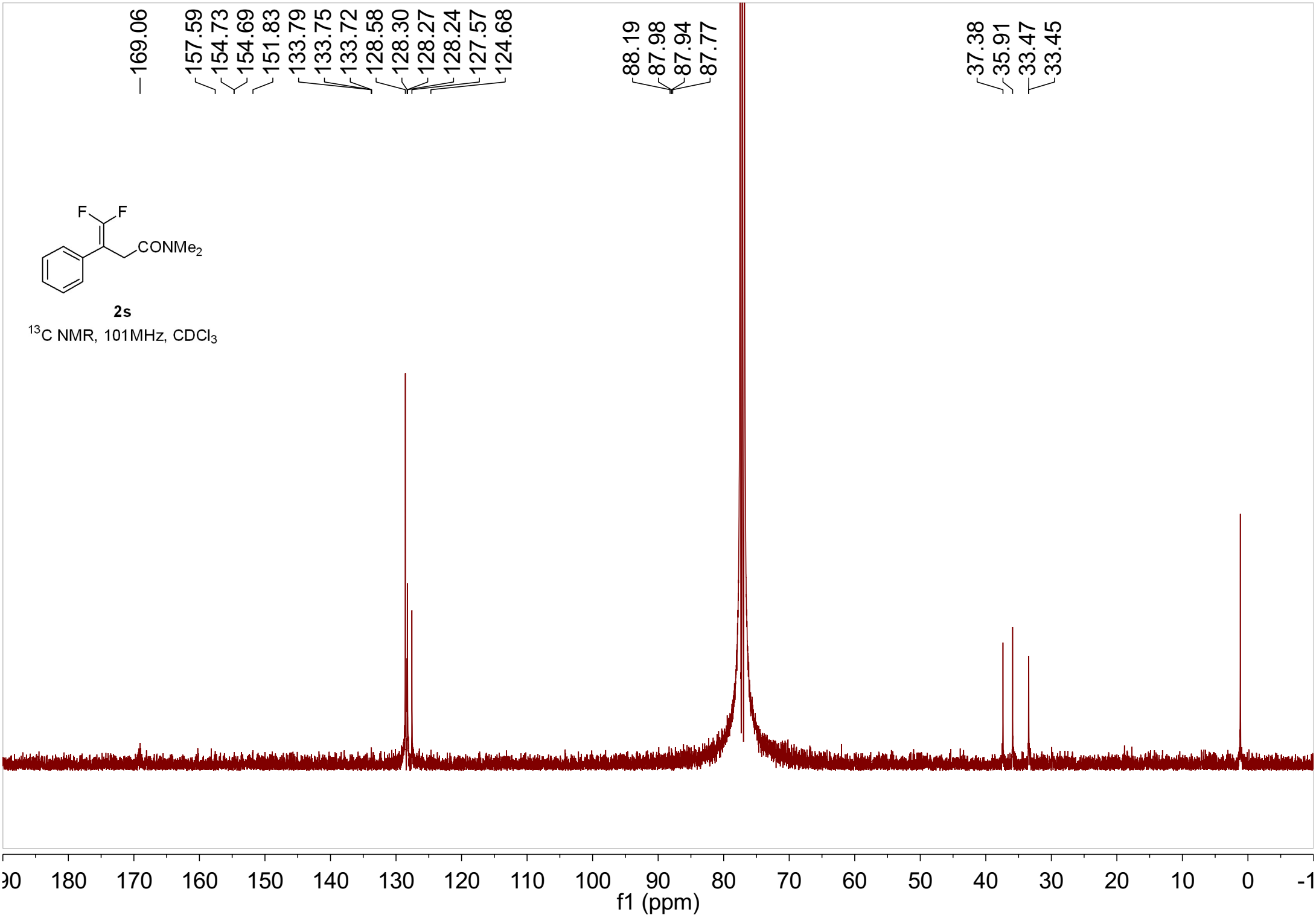
F
F
CONMe2
2s
1H NMR, 400MHz, CDCl3
5.25
2.00
3.13
3.19
f1 (ppm)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124.68
88.19
87.98
87.94
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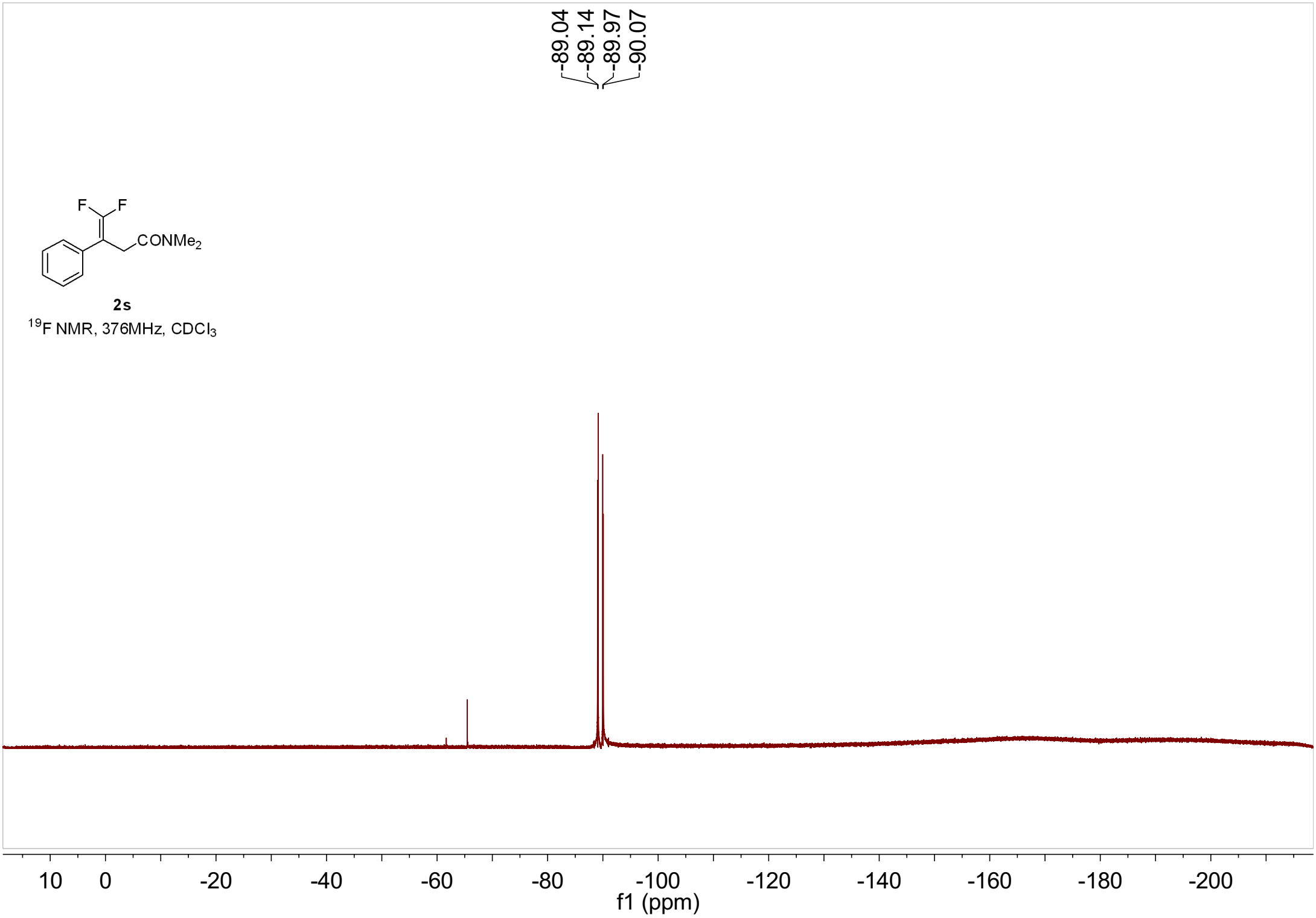
F
CONMe2
2s
13C NMR, 101MHz, CDCl3
f1 (ppm)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F
F
CONMe2
2s
19F NMR, 376MHz, CDCl3
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-60
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-140
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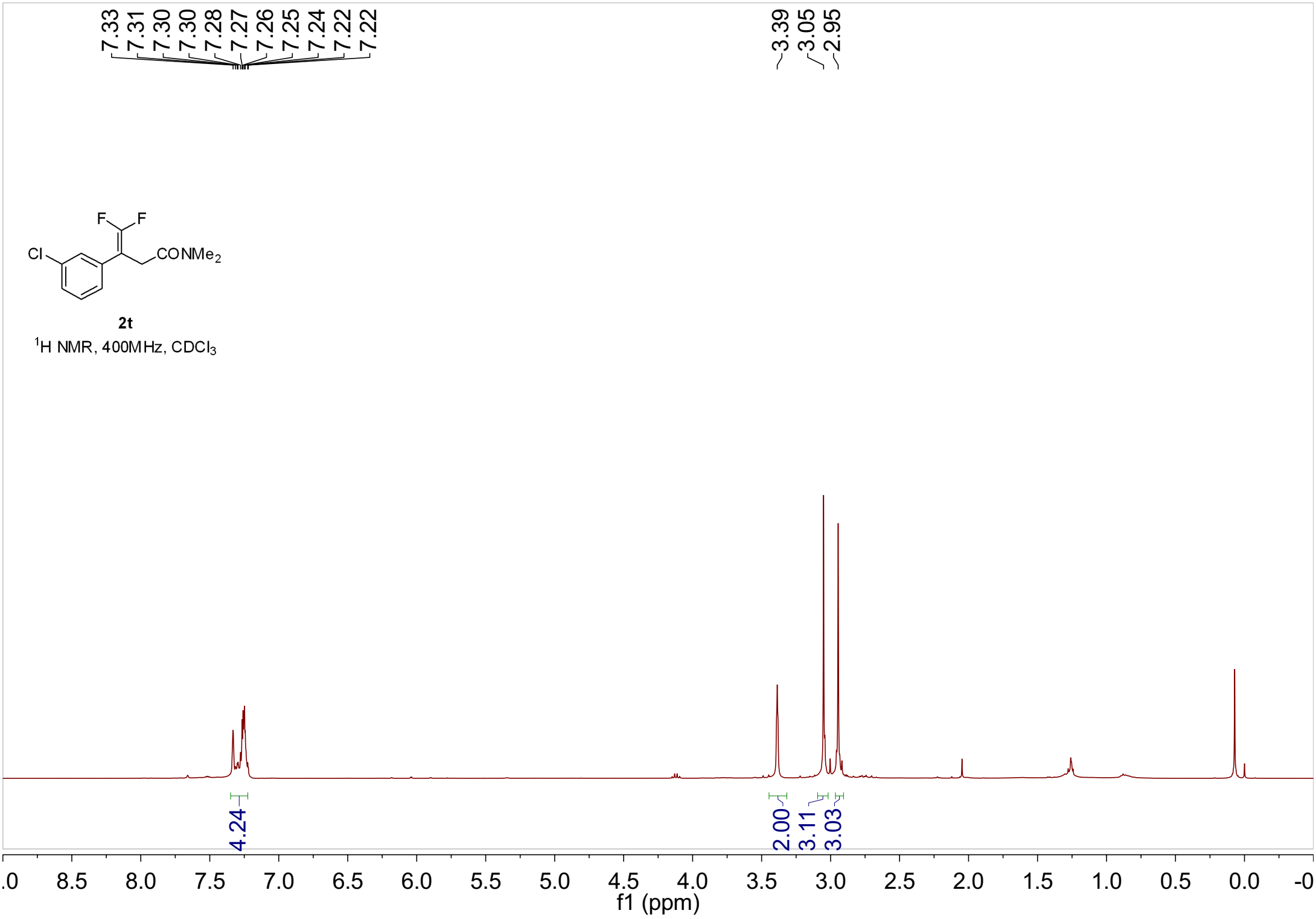
-180
-200
f1 (ppm)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3.39
3.05
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F
F
Cl
CONMe2
2t
1H NMR, 400MHz, CDCl3
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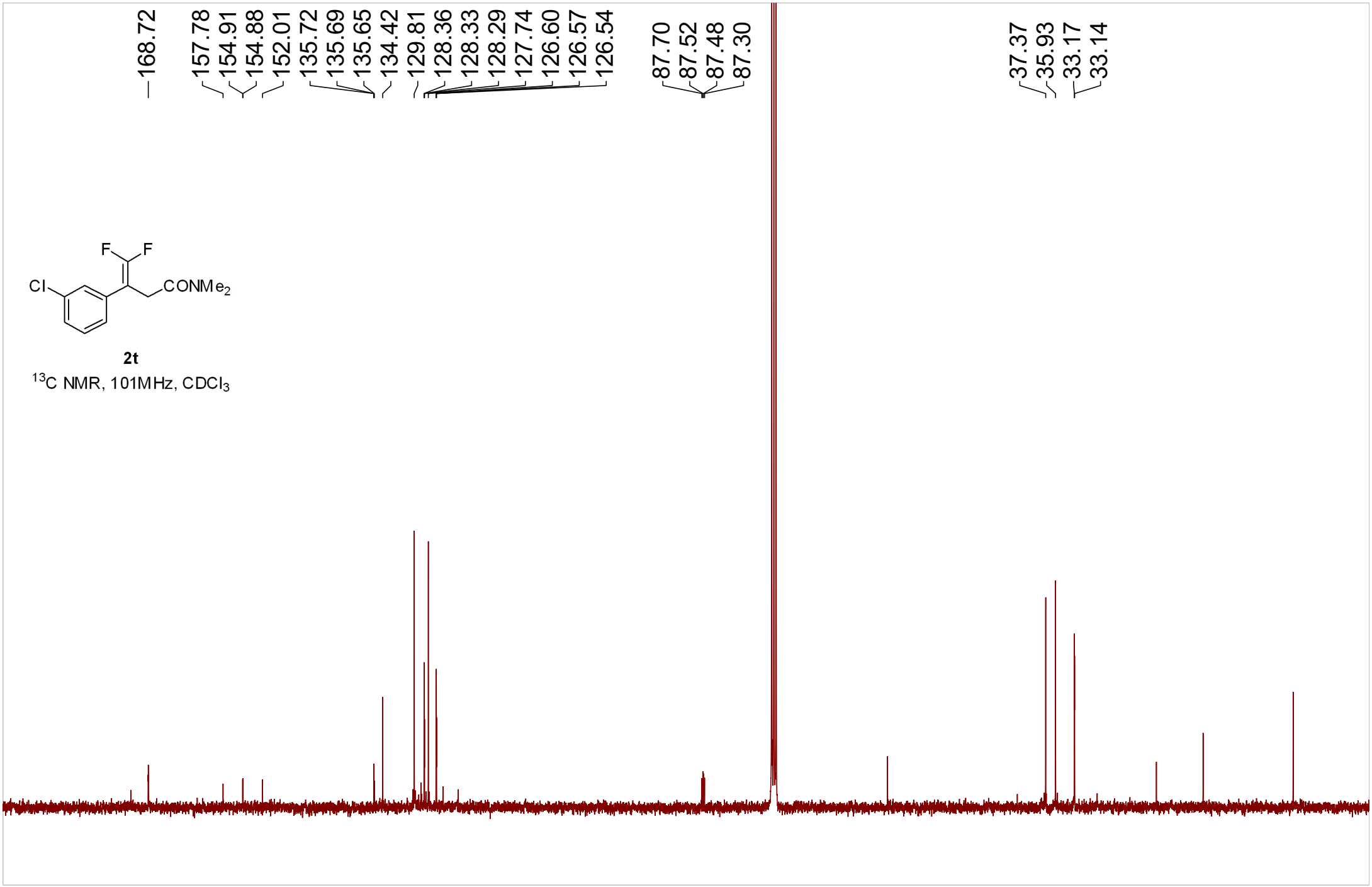
2.00
3.11
3.03
f1 (ppm)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126.60
126.57
126.54
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87.52
87.48
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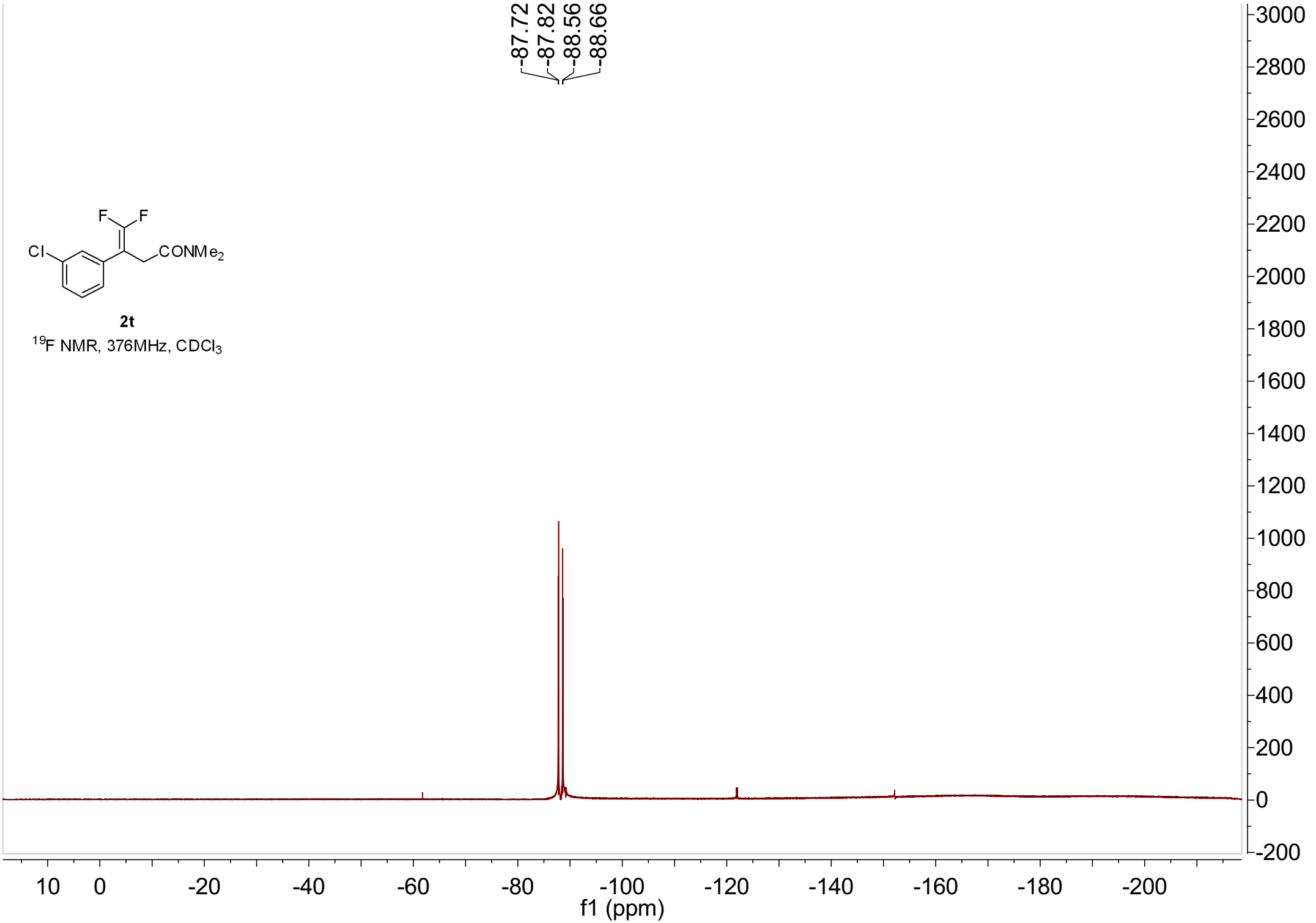
2t
13C NMR, 101MHz, CDCl3
f1 (ppm)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2t
19F NMR, 376MHz, CDCl3
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2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
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-60
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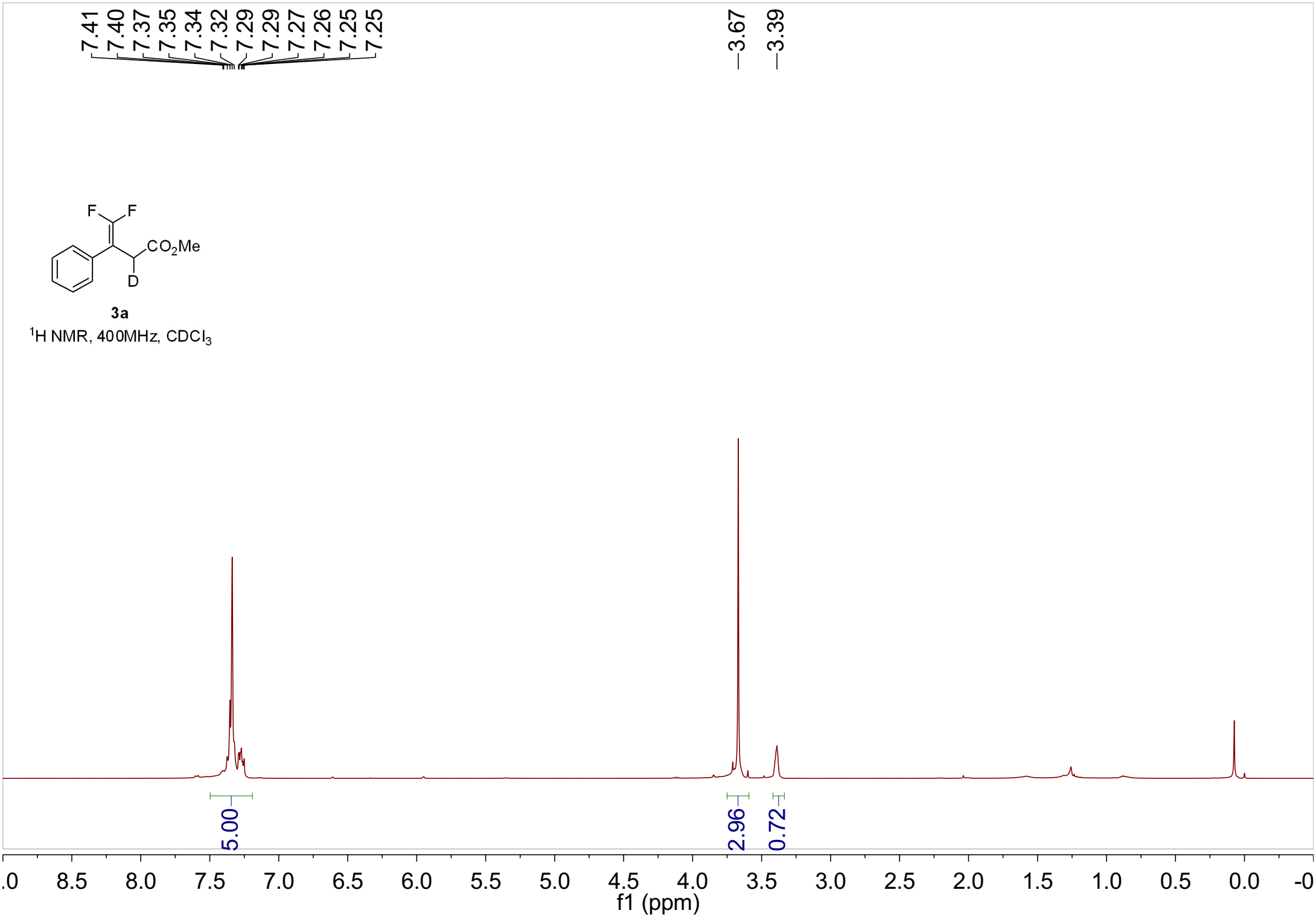
f1 (ppm)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7.25
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F
CO2Me
D
3a
1H NMR, 400MHz, CDCl3
5.00
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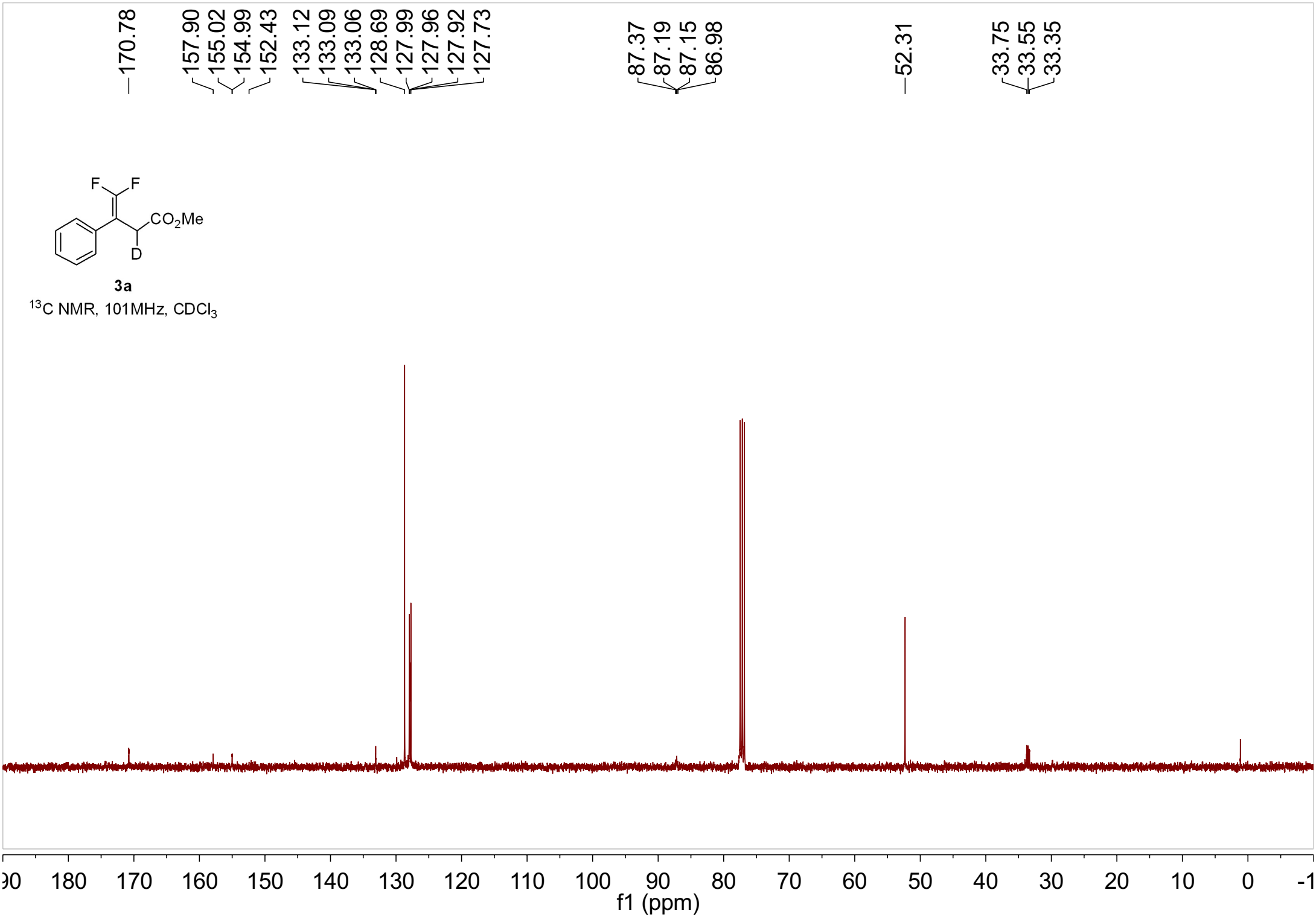
0.72
f1 (ppm)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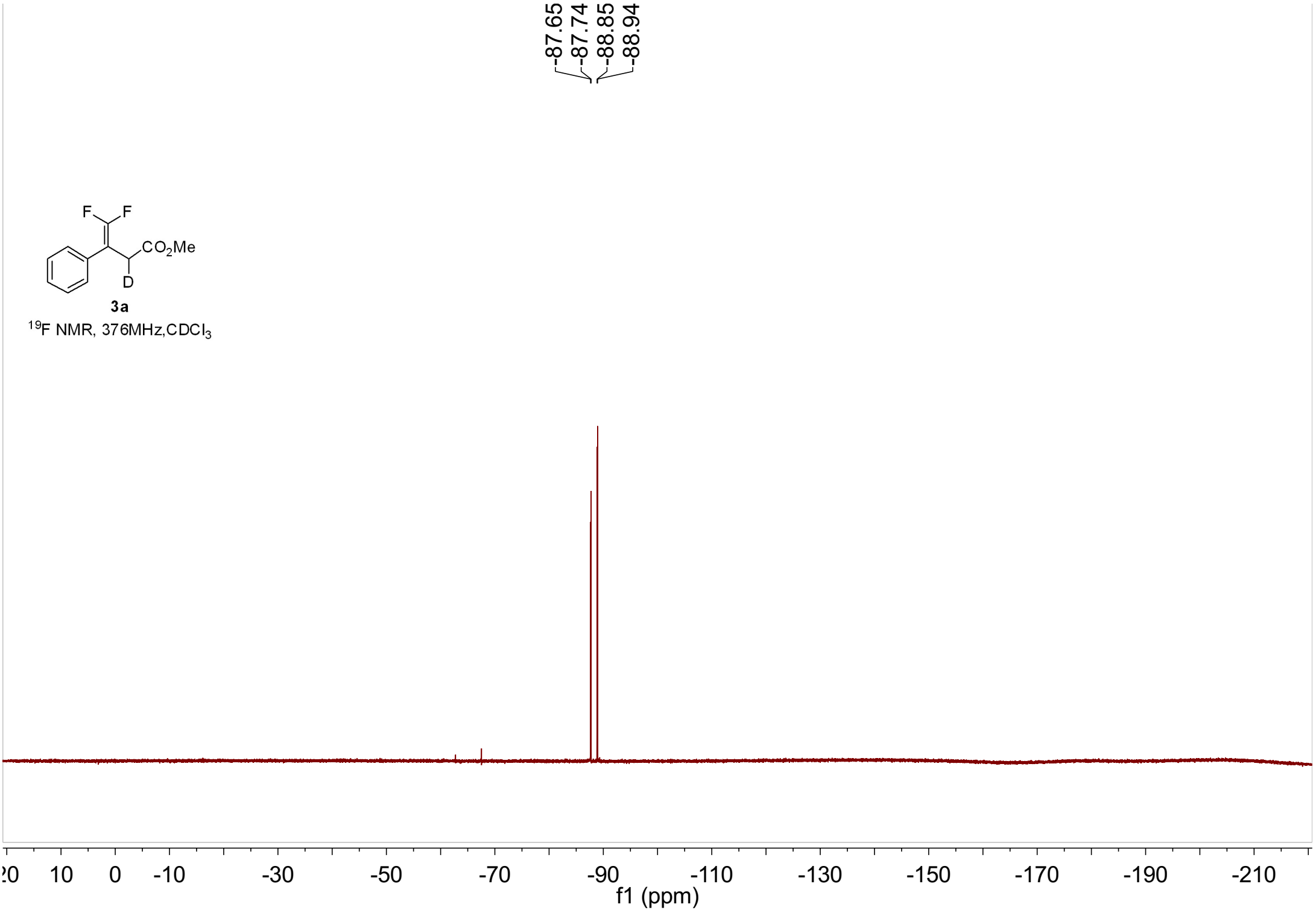
F
F
CO2Me
D
3a
13C NMR, 101MHz, CDCl3
f1 (ppm)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F
F
CO2Me
D
3a
19F NMR, 376MHz,CDCl3
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-70
-90
-110
-130
-150
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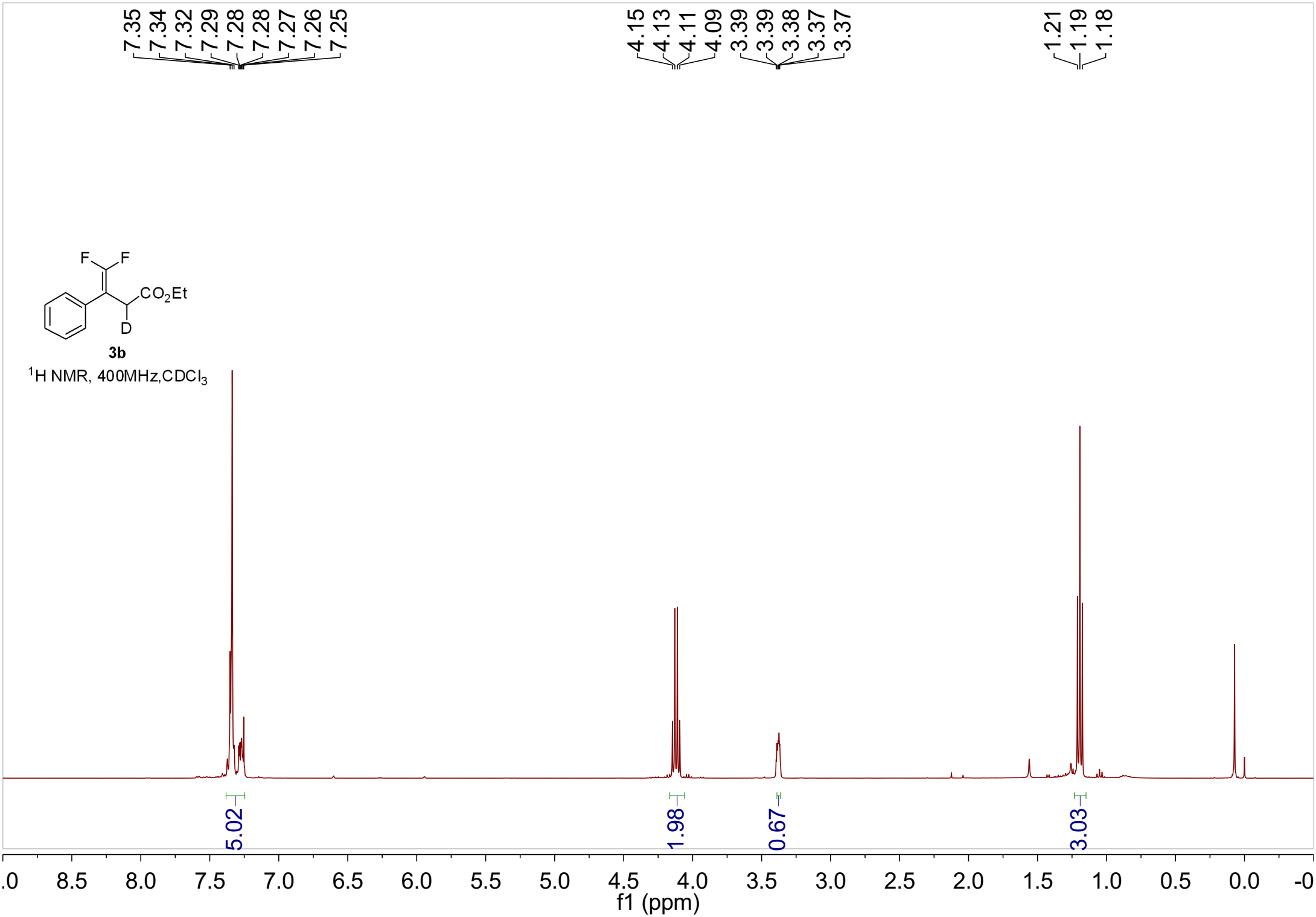
-190
-210
f1 (ppm)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3.38
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3.37
1.21
1.19
1.18
F
F
CO2Et
D
3b
1H NMR, 400MHz,CDCl3
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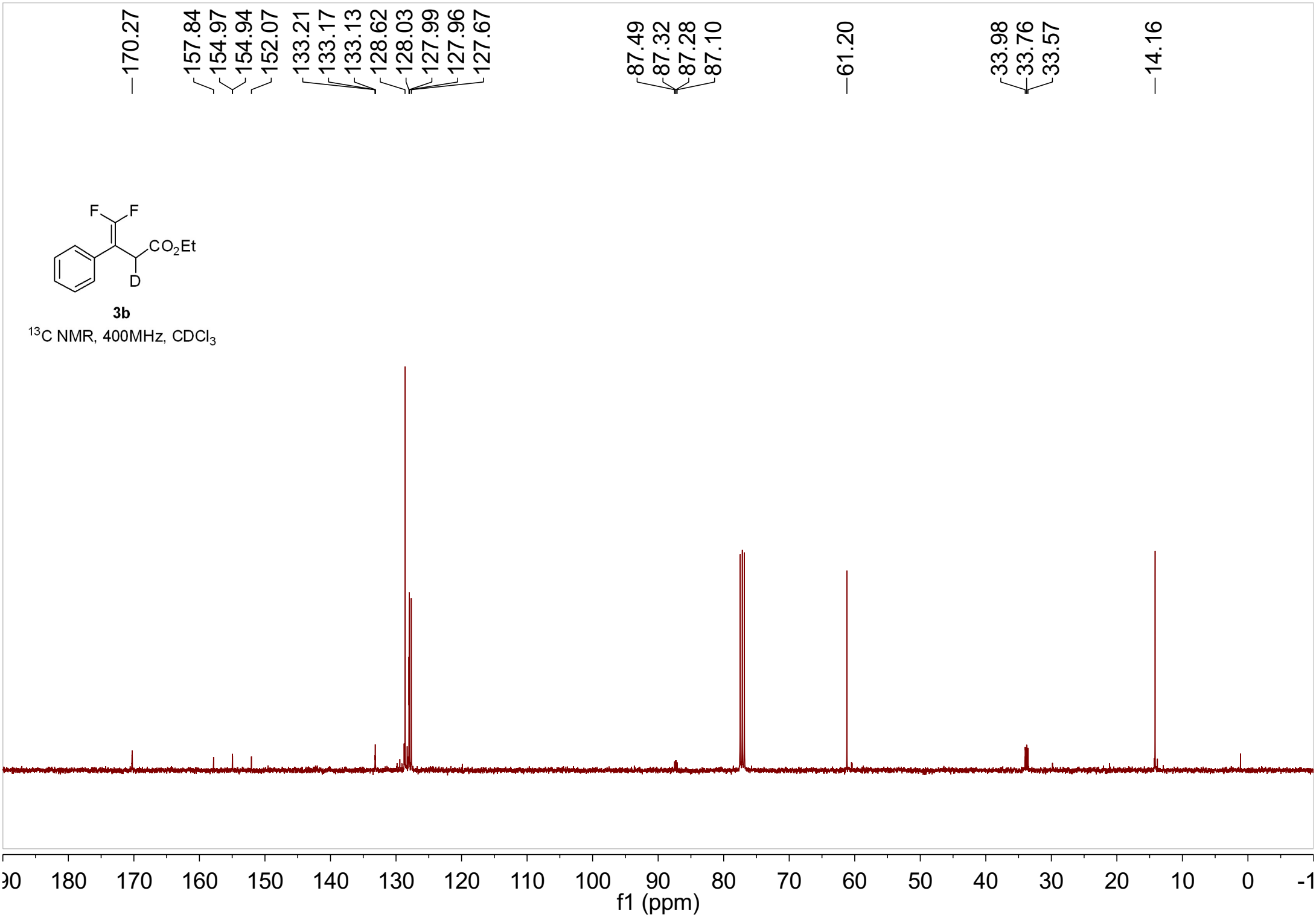
3.03
f1 (ppm)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87.10
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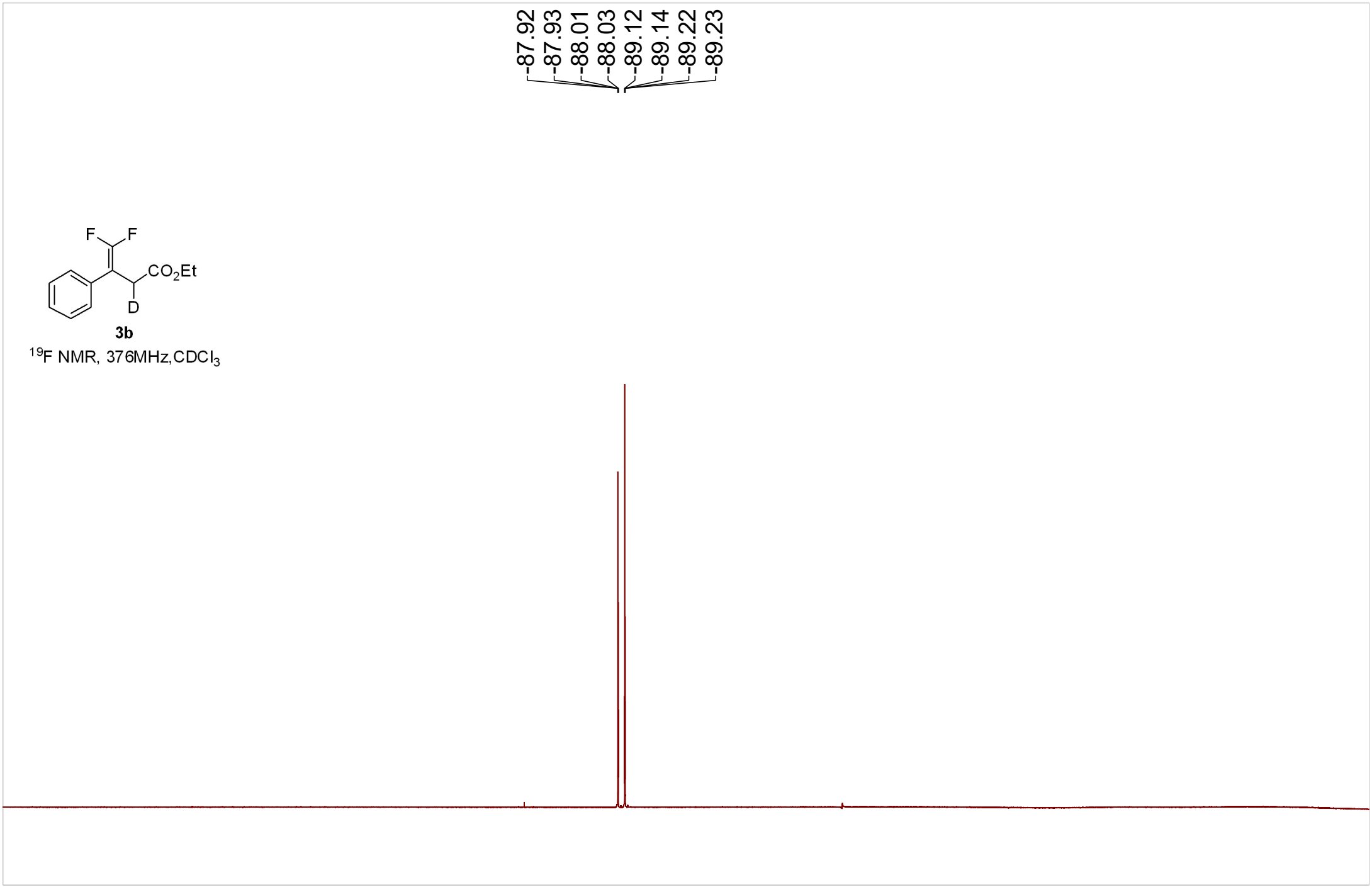
F
F
CO2Et
D
3b
13C NMR, 400MHz, CDCl3
f1 (ppm)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F
F
CO2Et
D
3b
19F NMR, 376MHz,CDCl3
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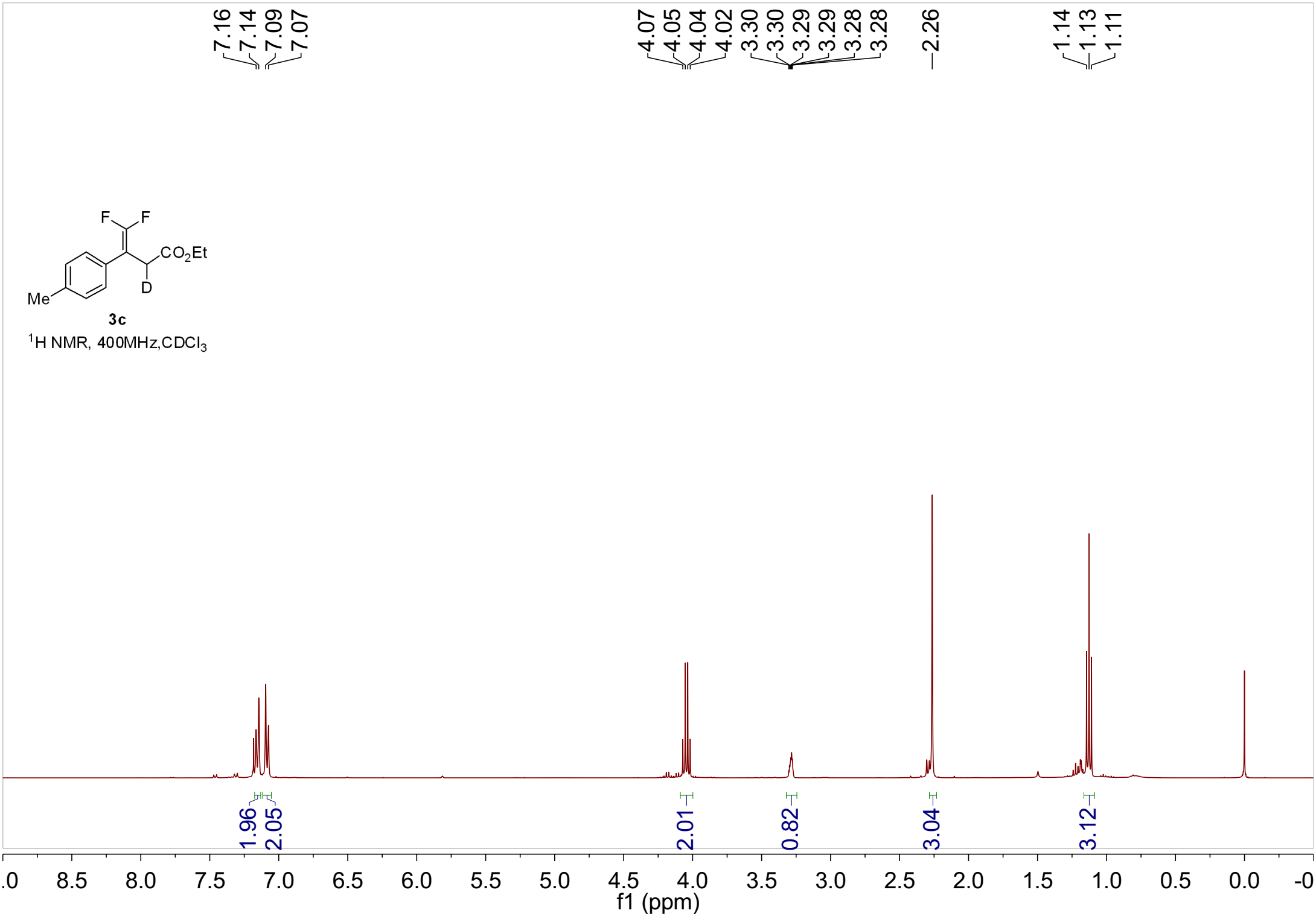
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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4.02
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3.28
2.26
1.14
1.13
1.11
F
F
CO2Et
D
Me
3c
1H NMR, 400MHz,CDCl3
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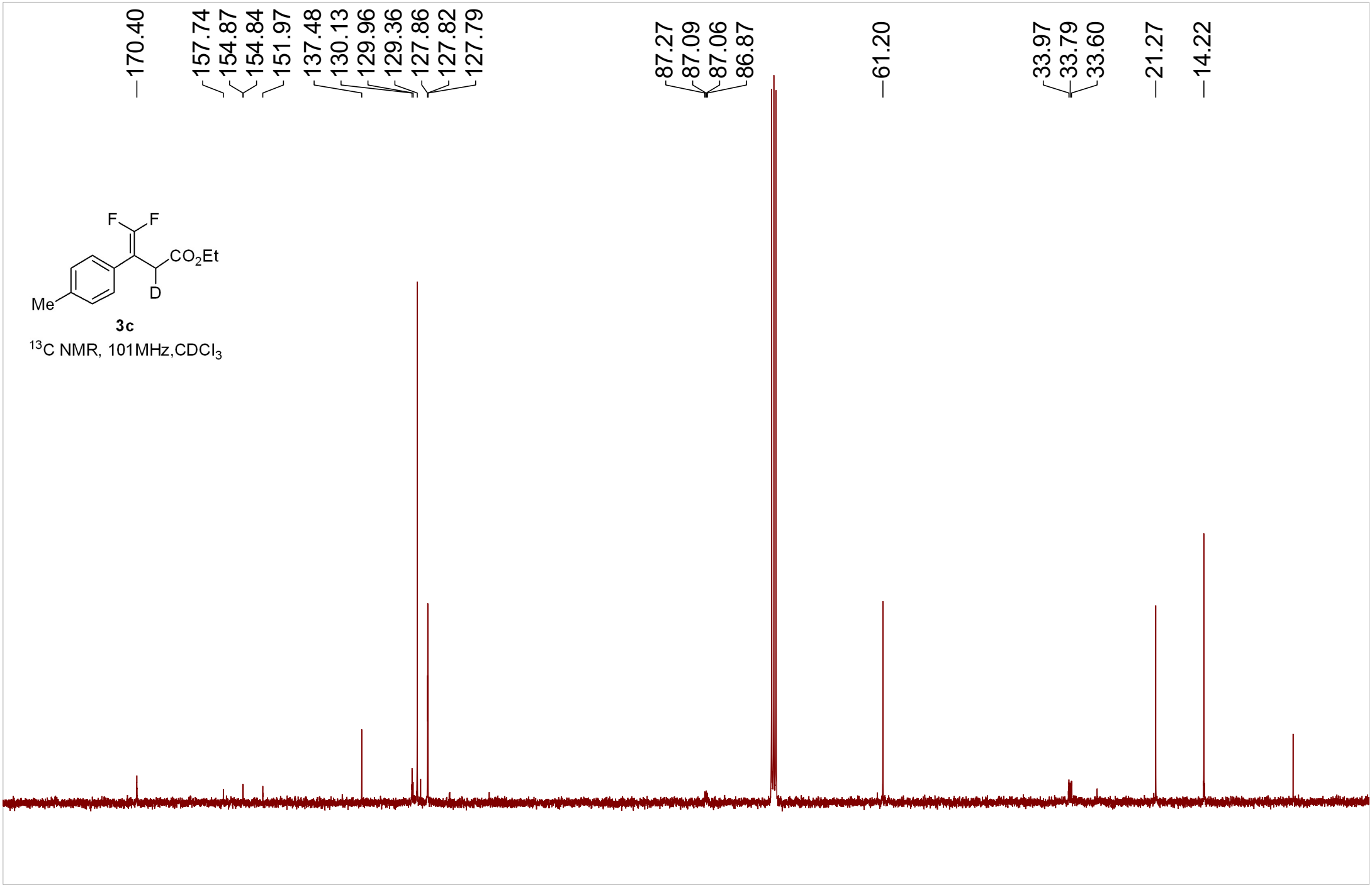
0.82
3.04
3.12
f1 (ppm)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87.06
86.87
61.20
33.97
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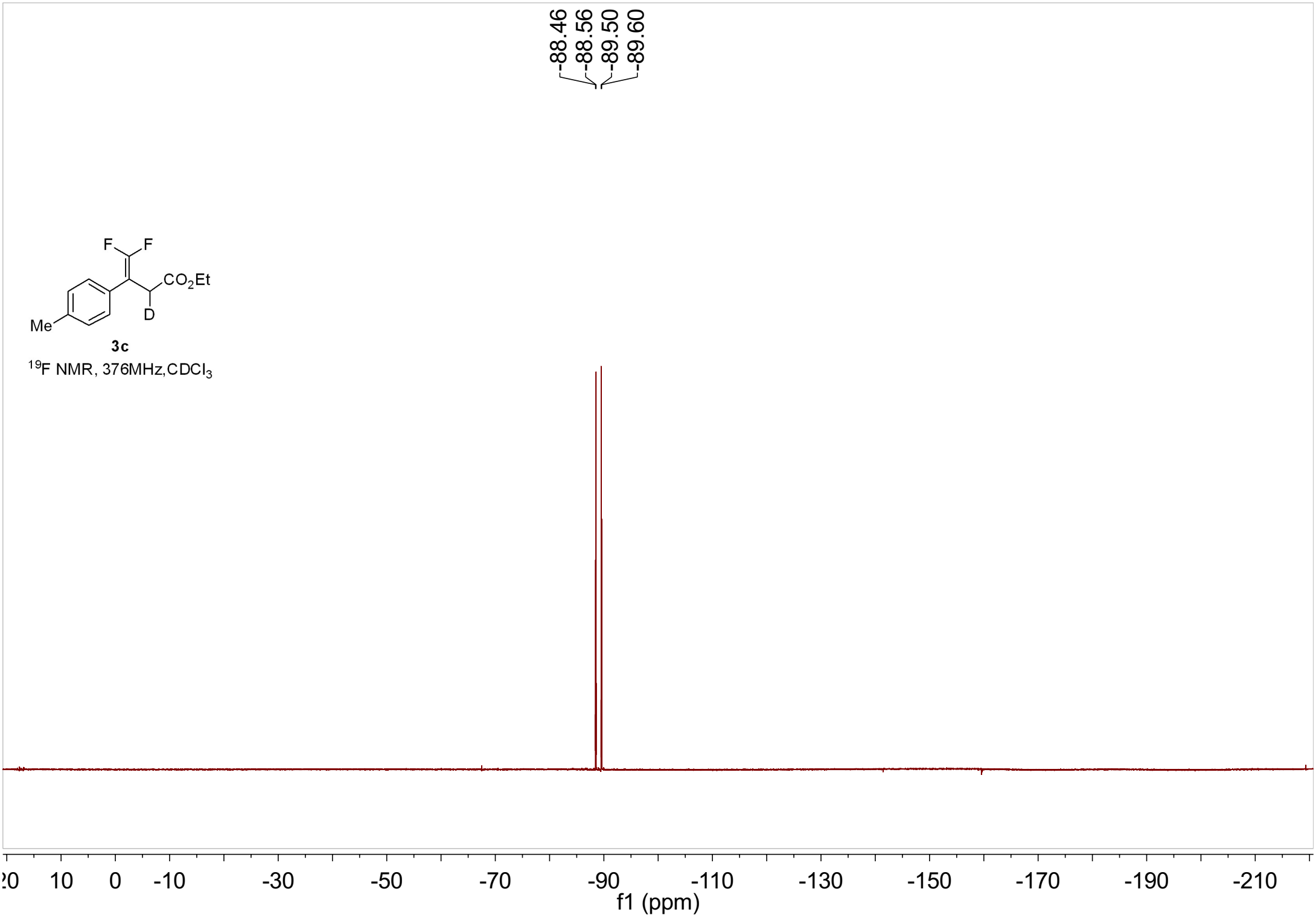
F
CO2Et
D
Me
3c
13C NMR, 101MHz,CDCl3
f1 (ppm)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F
F
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D
Me
3c
19F NMR, 376MHz,CDCl3
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-50
-70
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-110
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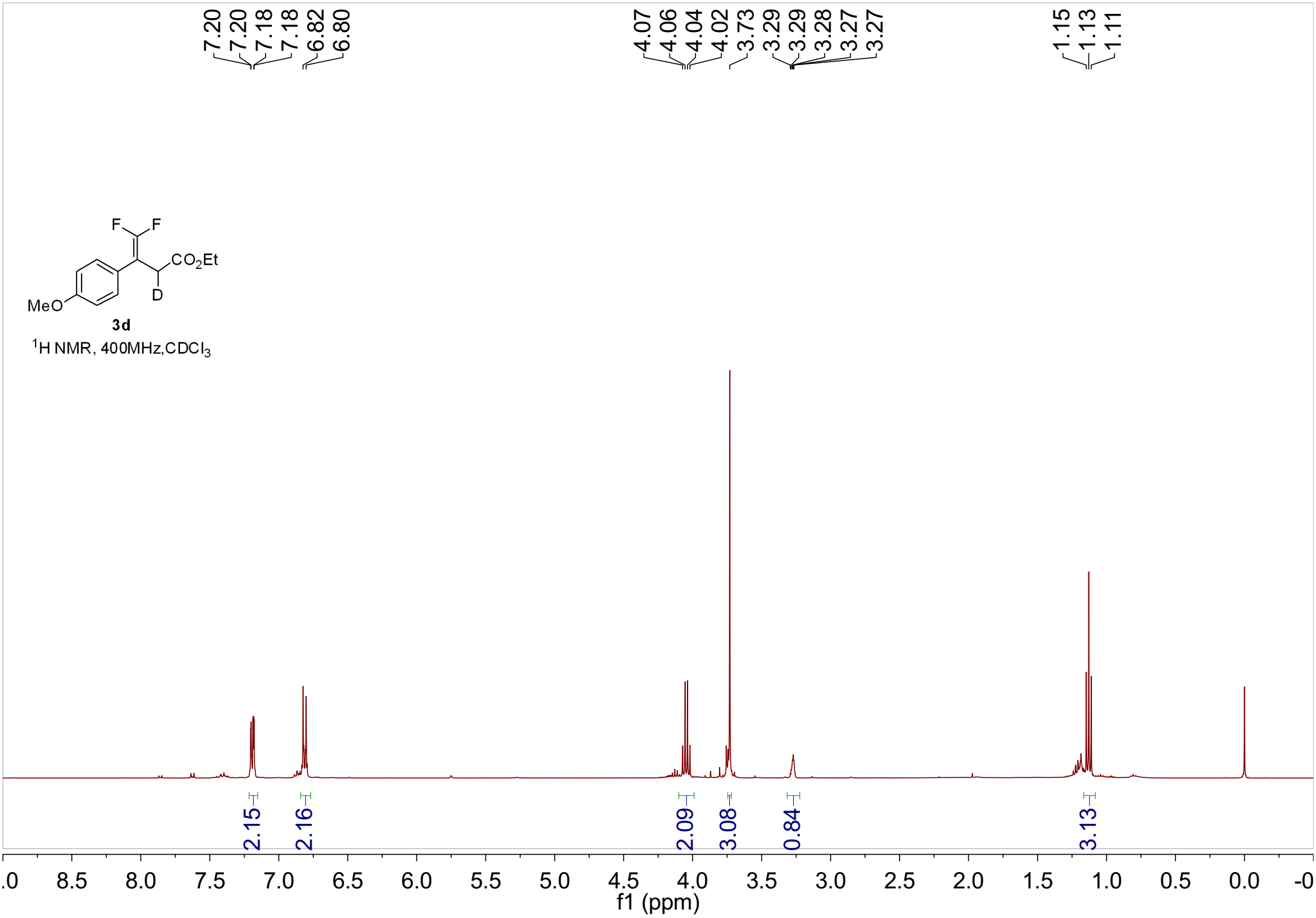
-150
-170
-190
-210
f1 (ppm)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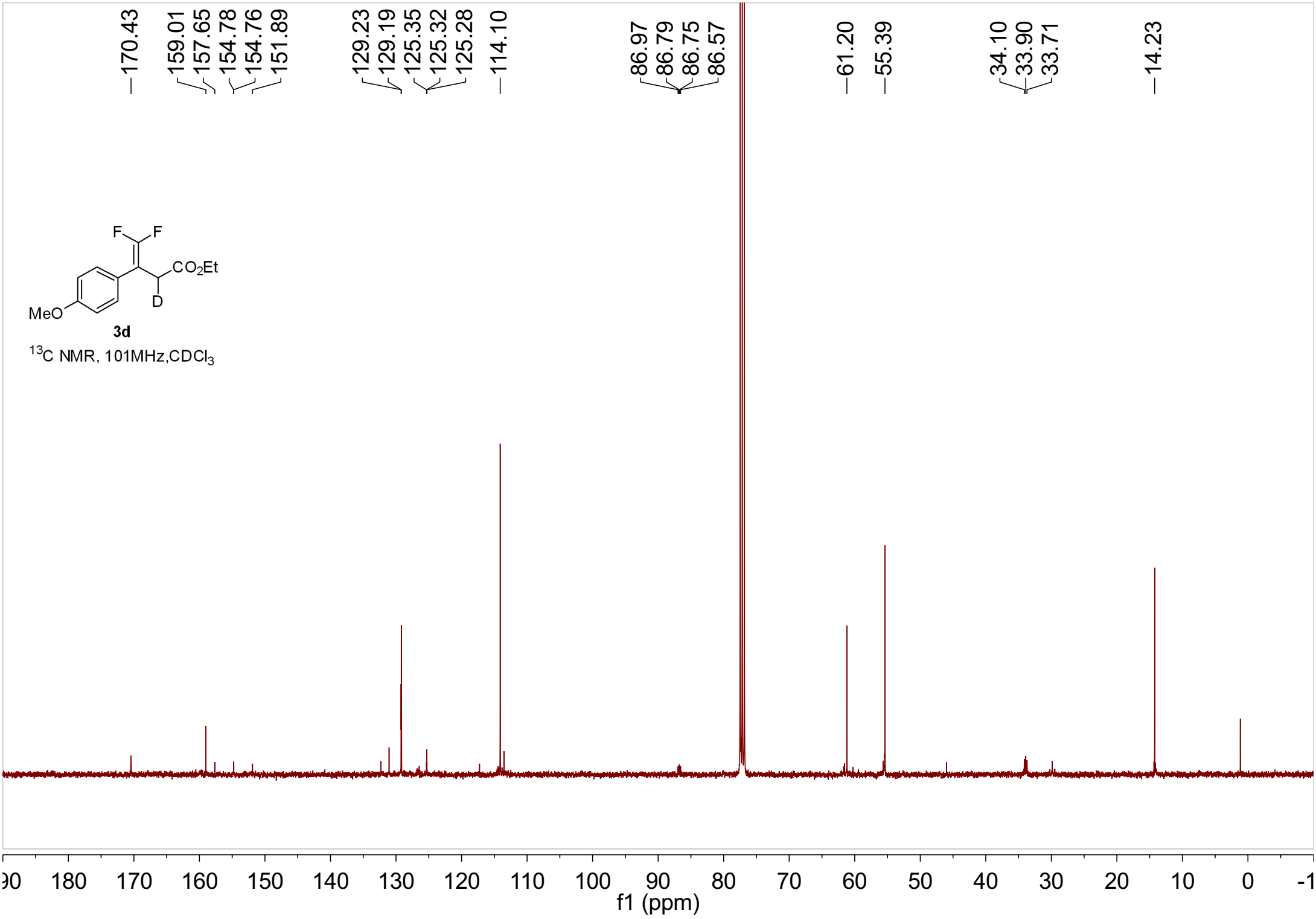
3.29
3.28
3.27
3.27
1.15
1.13
1.11
F
F
CO2Et
D
MeO
3d
1H NMR, 400MHz,CDCl3
2.15
2.16
2.09
3.08
0.84
3.13
f1 (ppm)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129.19
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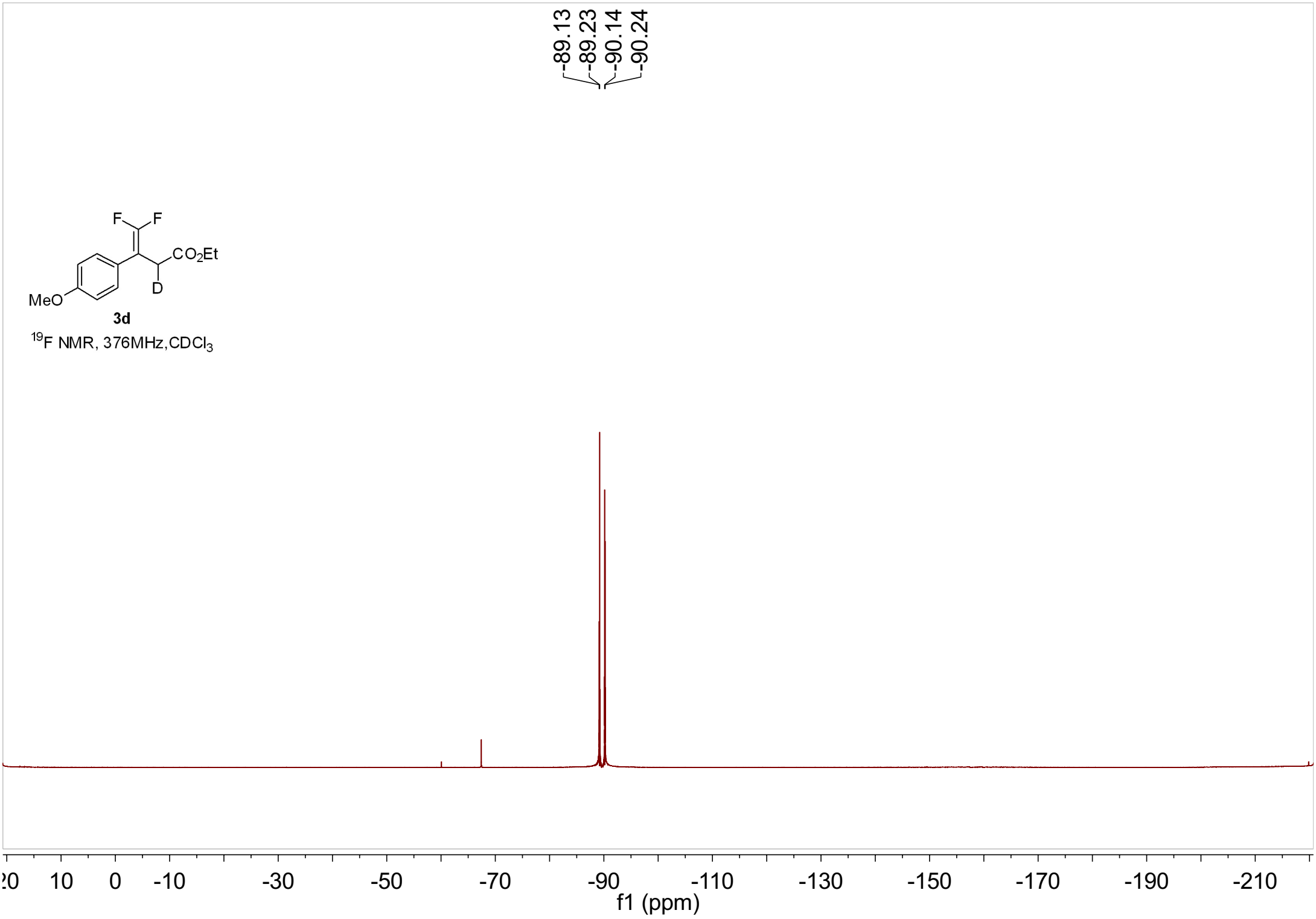
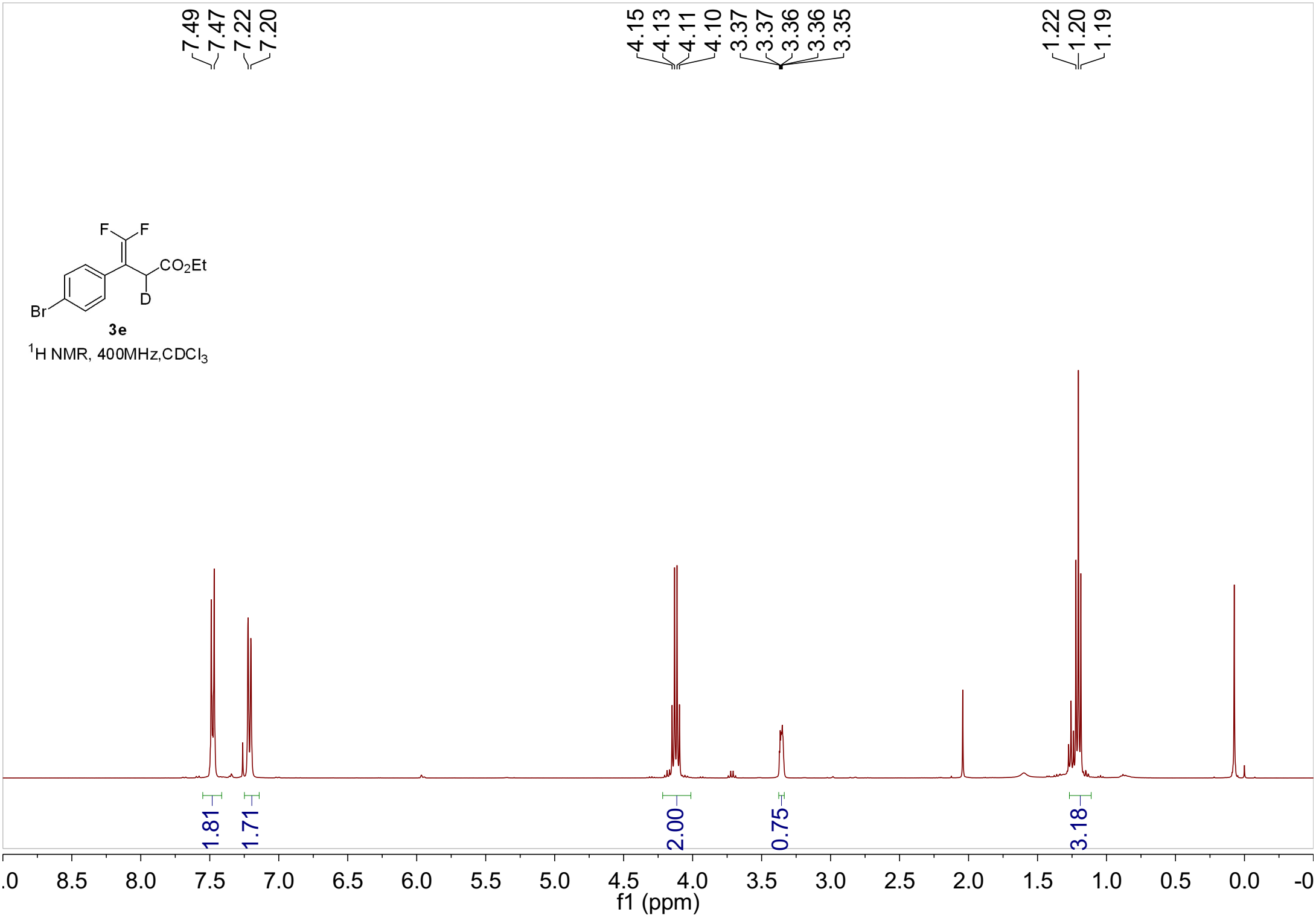
125.32
125.28
114.10
86.97
86.79
86.75
86.57
61.20
55.39
34.10
33.90
33.71
14.23
F
F
CO2Et
D
MeO
3d
13C NMR, 101MHz,CDCl3
f1 (ppm)


-89.13
-89.23
-90.14
-90.24
F
F
CO2Et
D
MeO
3d
19F NMR, 376MHz,CDCl3
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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7.22
7.20
4.15
4.13
4.11
4.10
3.37
3.37
3.36
3.36
3.35
1.22
1.20
1.19
F
F
CO2Et
D
Br
3e
1H NMR, 400MHz,CDCl3
1.81
1.71
2.00
0.75
3.18
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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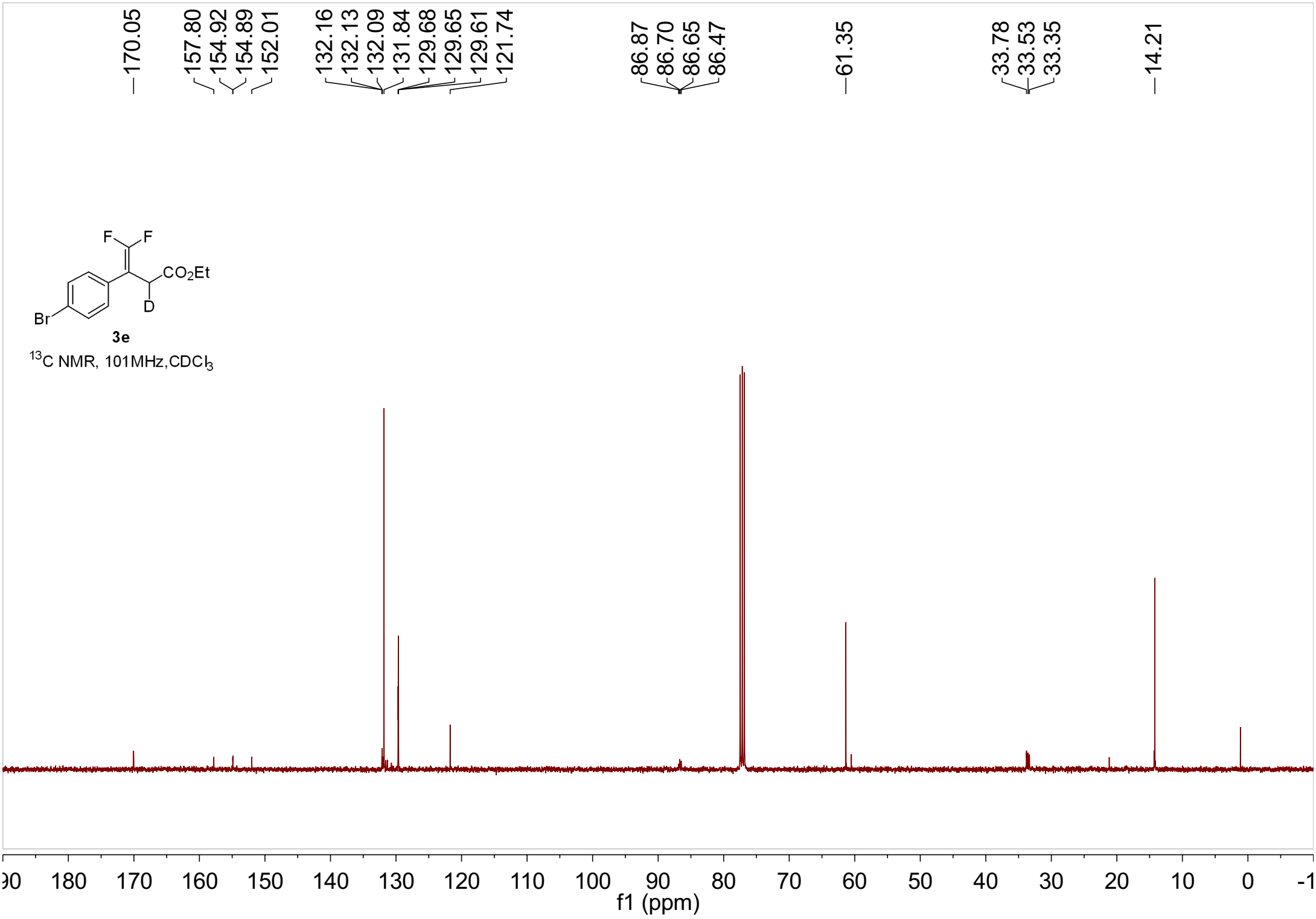
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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152.01
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132.09
131.84
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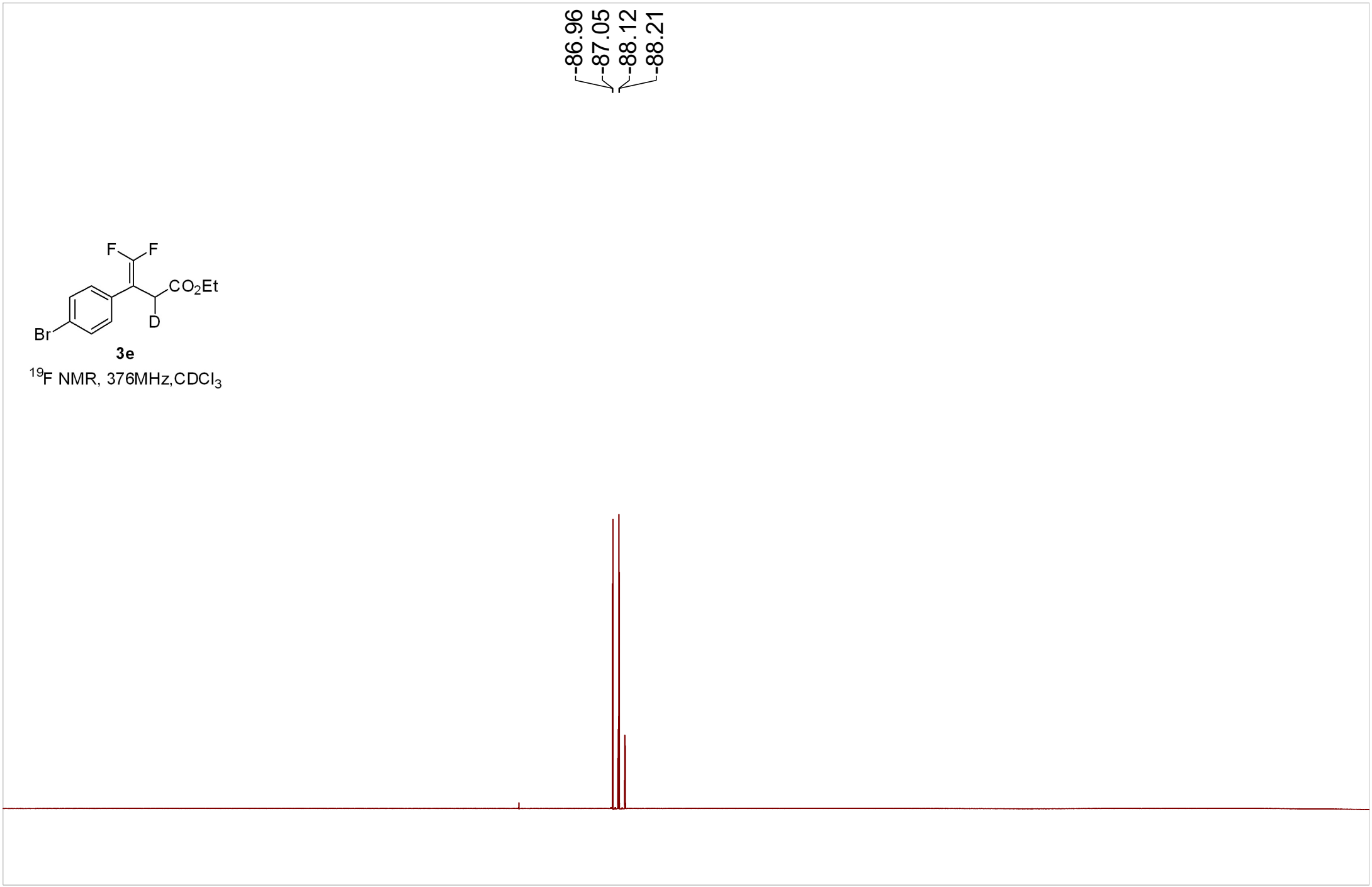
129.65
129.61
121.74
86.87
86.70
86.65
86.47
61.35
33.78
33.53
33.35
14.21
F
F
CO2Et
D
Br
3e
13C NMR, 101MHz,CDCl3
f1 (ppm)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-87.05
-88.12
-88.21
F
F
CO2Et
D
Br
3e
19F NMR, 376MHz,CDCl3
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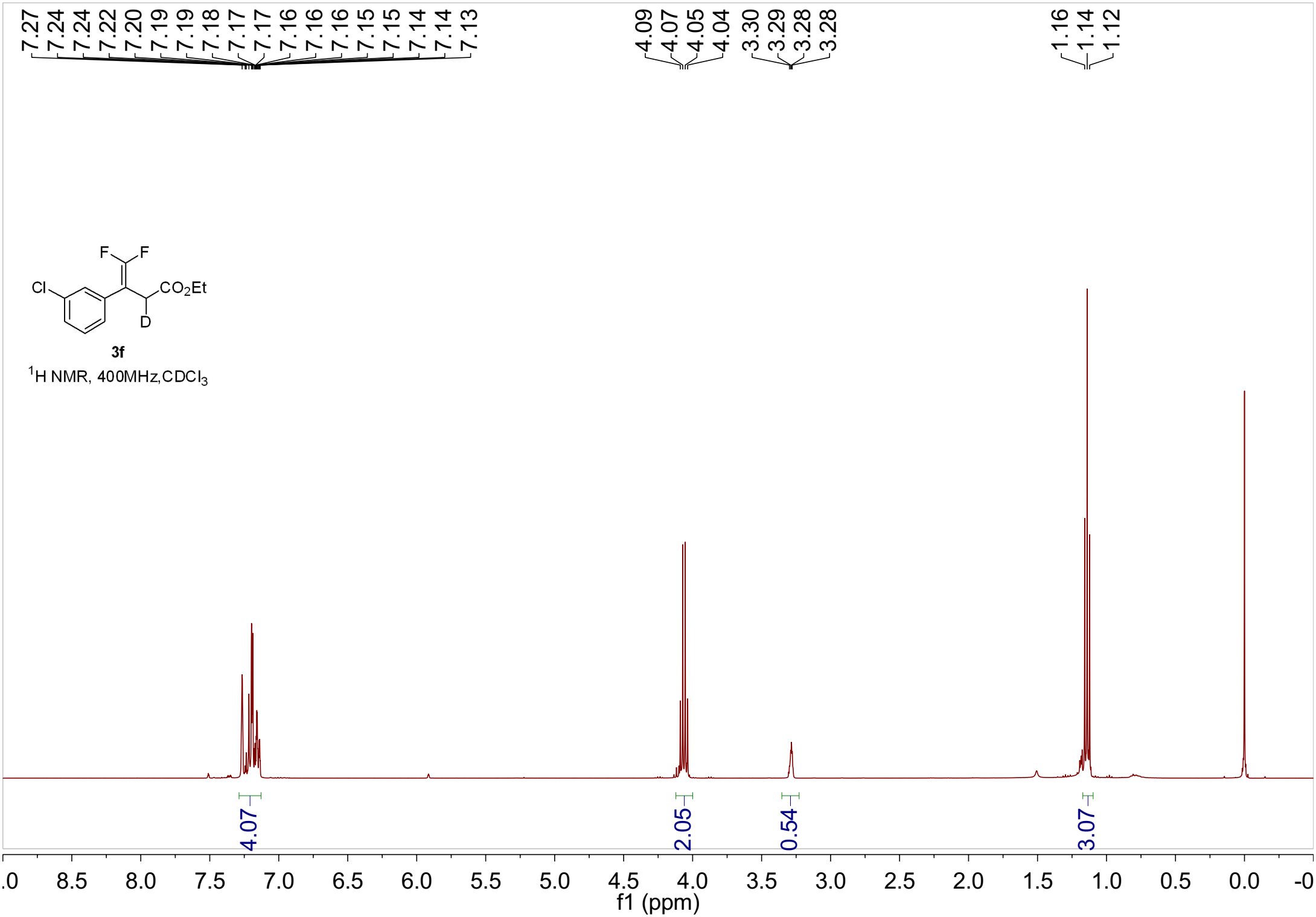
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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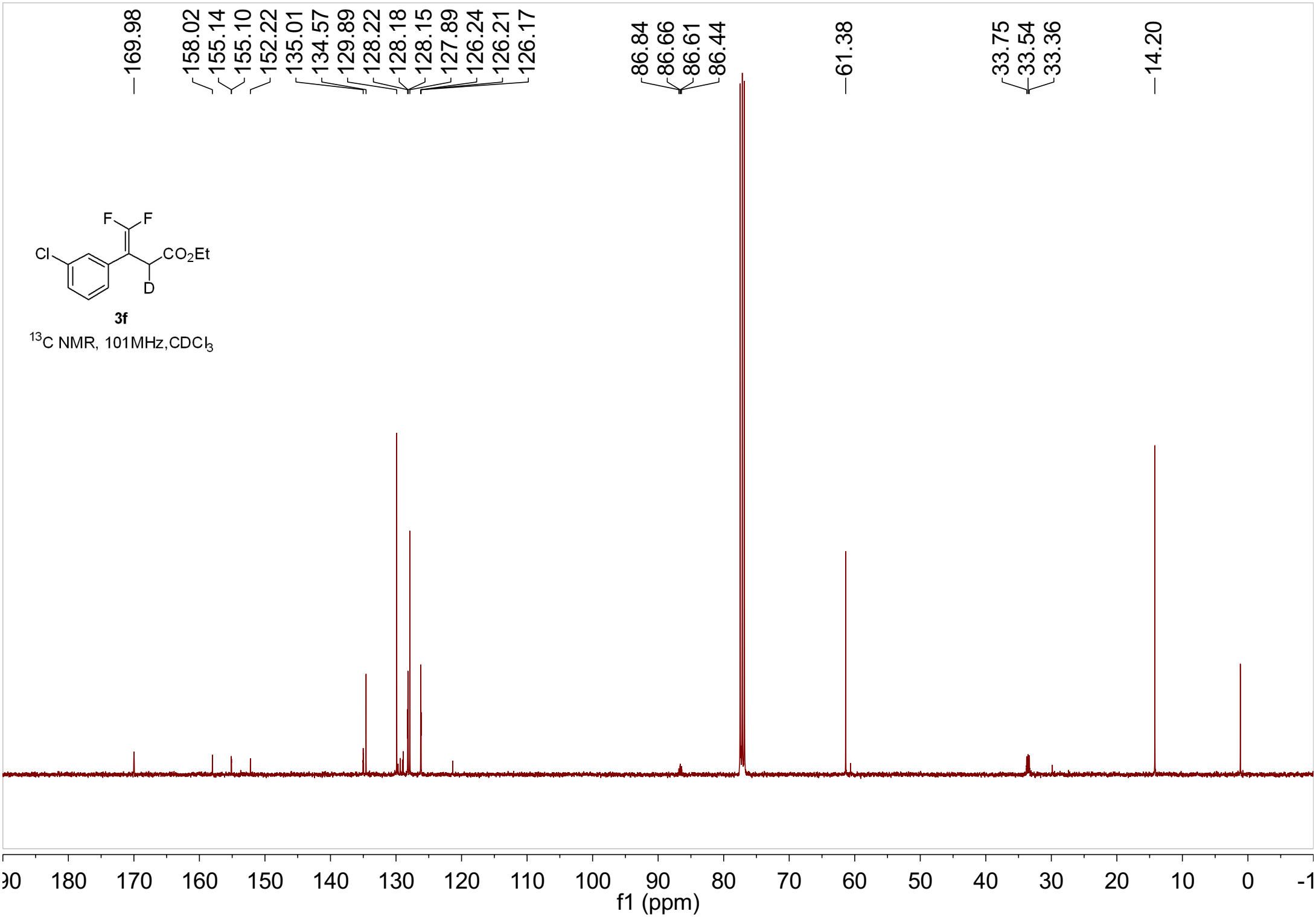
7.16
7.15
7.15
7.14
7.14
7.13
4.09
4.07
4.05
4.04
3.30
3.29
3.28
3.28
1.16
1.14
1.12
F
F
Cl
CO2Et
D
3f
1H NMR, 400MHz,CDCl3
4.07
2.05
0.54
3.07
f1 (ppm)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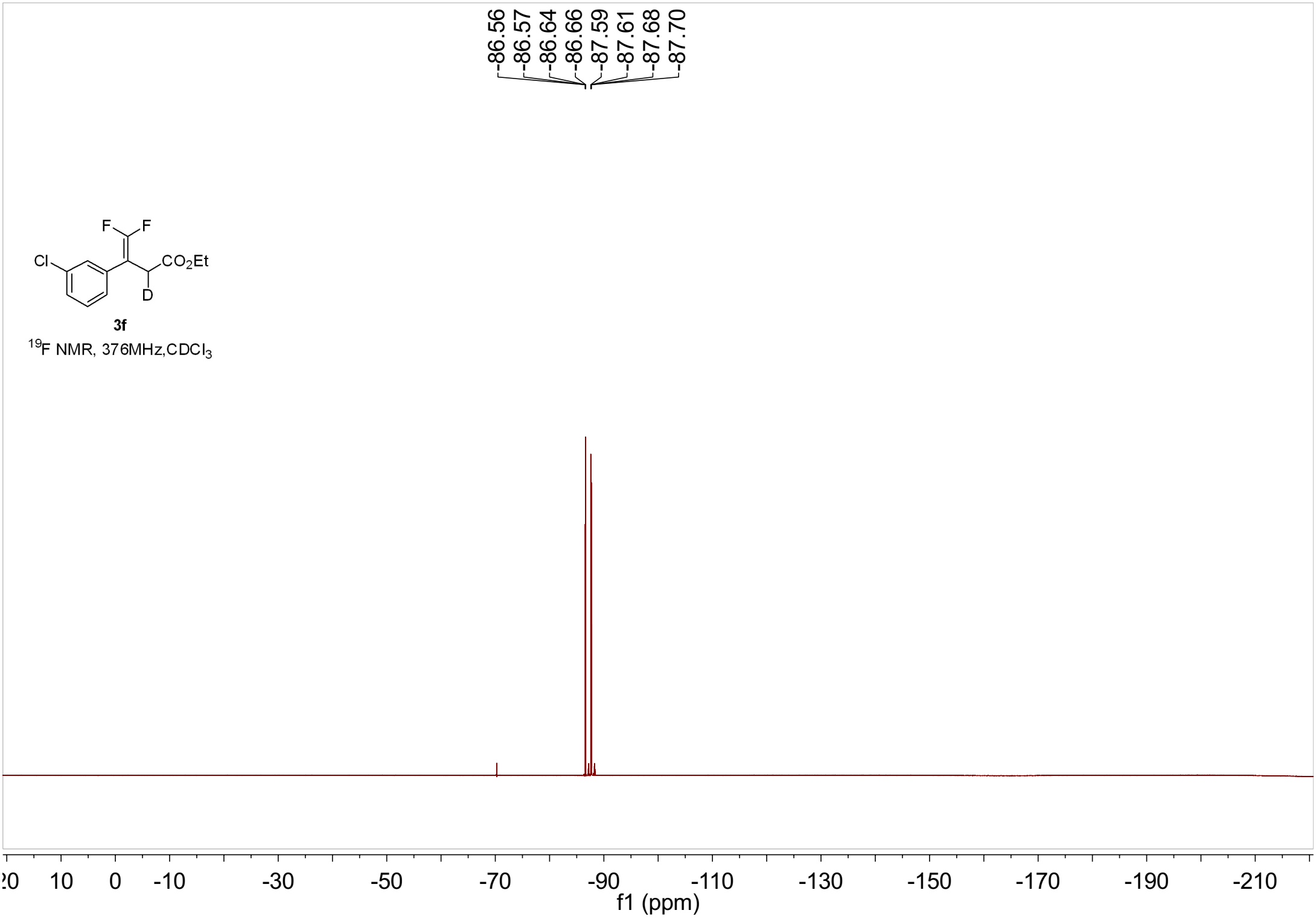
127.89
126.24
126.21
126.17
86.84
86.66
86.61
86.44
61.38
33.75
33.54
33.36
14.20
F
F
Cl
CO2Et
D
3f
13C NMR, 101MHz,CDCl3
f1 (ppm)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-86.57
-86.64
-86.66
-87.59
-87.61
-87.68
-87.70
F
F
Cl
CO2Et
D
3f
19F NMR, 376MHz,CDCl3
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10
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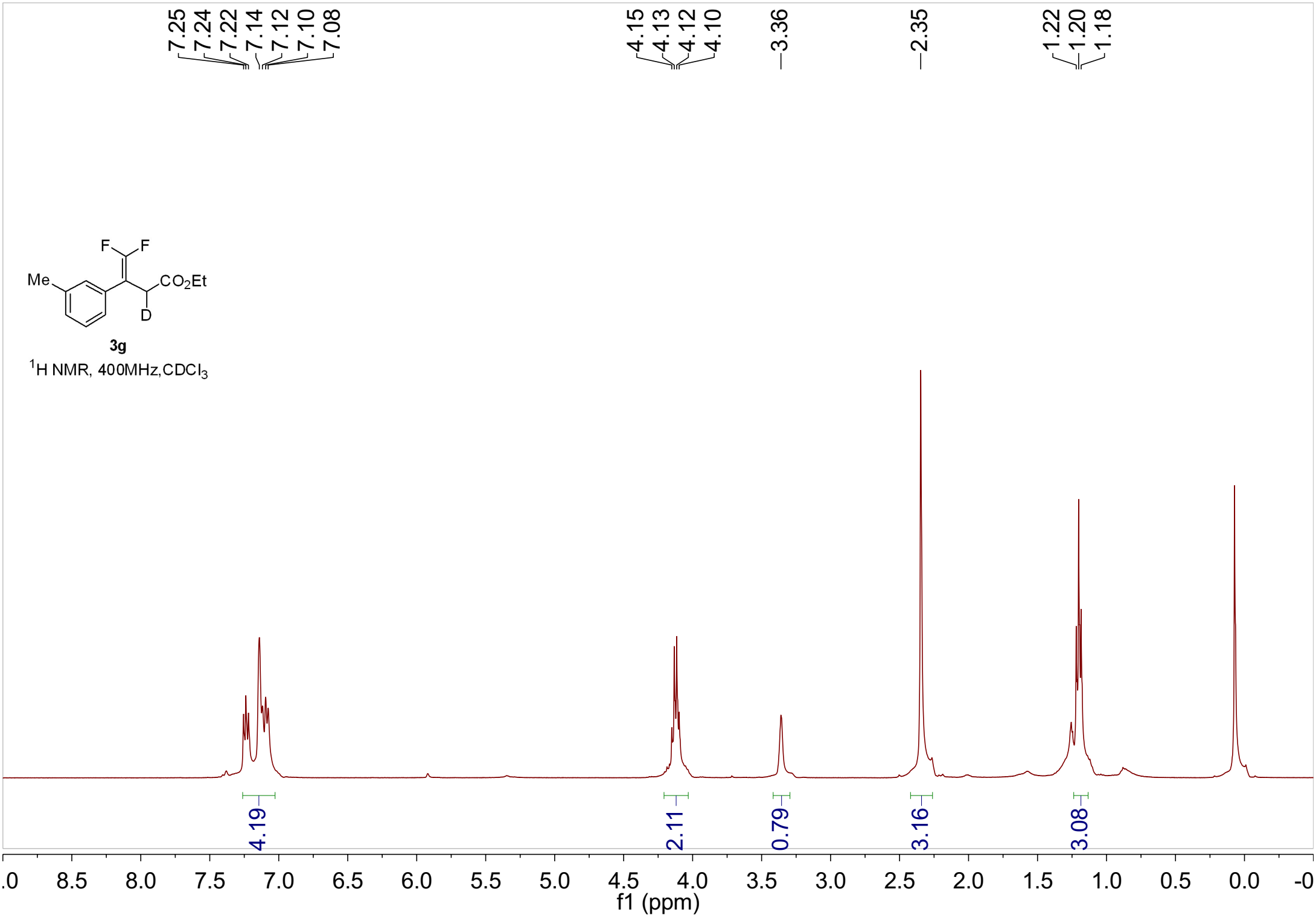
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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7.22
7.14
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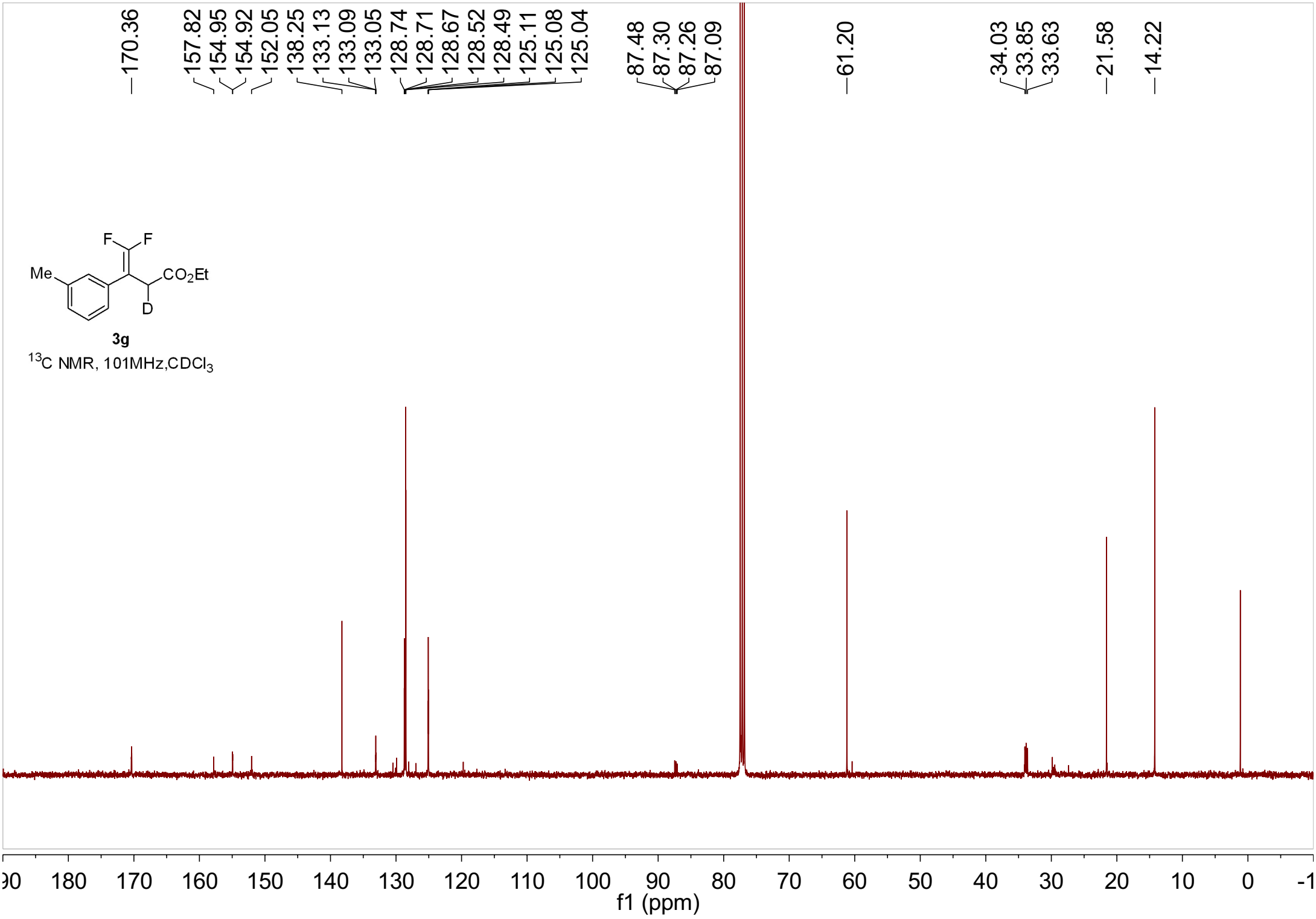
7.10
7.08
4.15
4.13
4.12
4.10
3.36
2.35
1.22
1.20
1.18
F
F
Me
CO2Et
D
3g
1H NMR, 400MHz,CDCl3
4.19
2.11
0.79
3.16
3.08
f1 (ppm)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128.52
128.49
125.11
125.08
125.04
87.48
87.30
87.26
87.09
61.20
34.03
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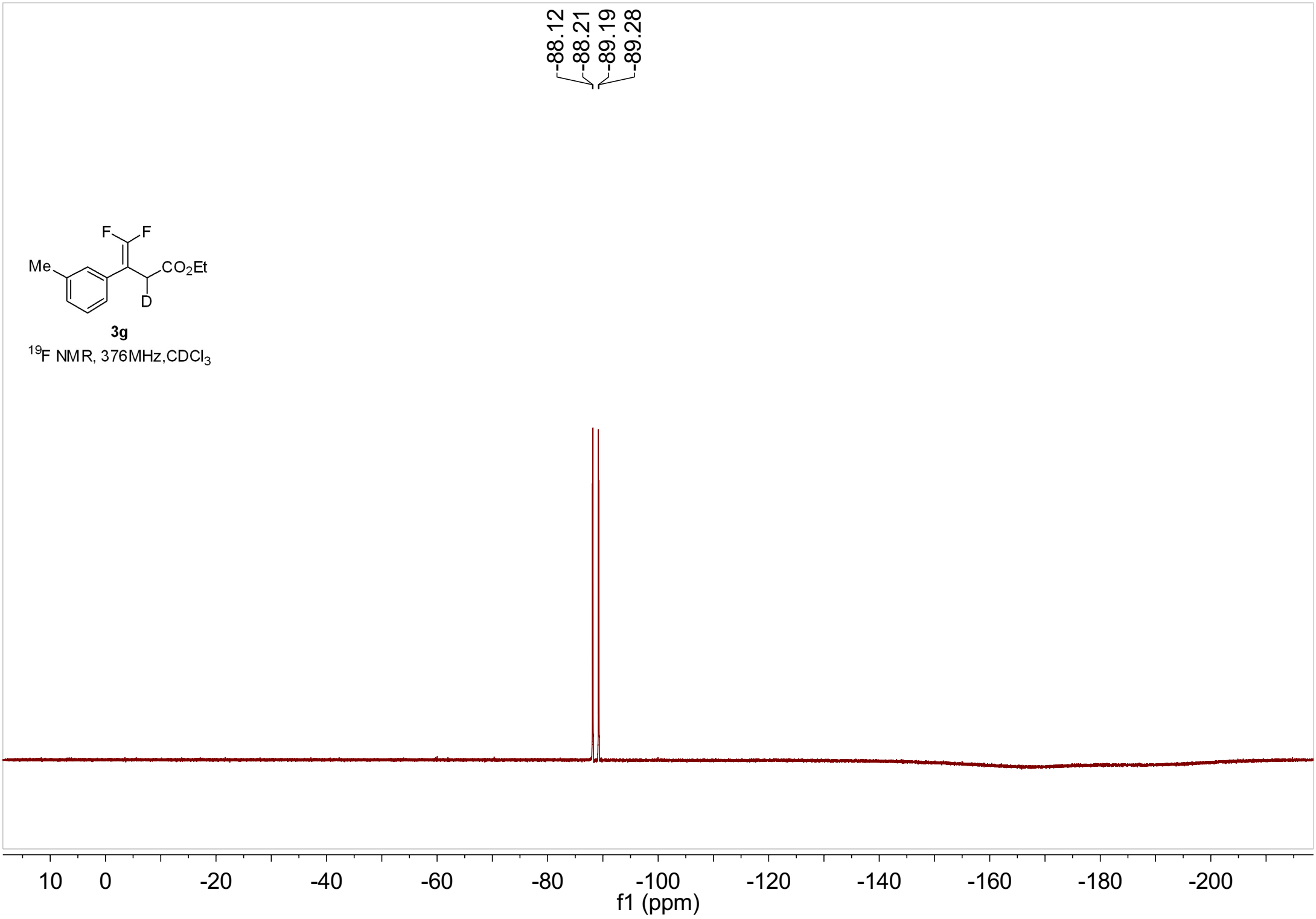
14.22
F
F
Me
CO2Et
D
3g
13C NMR, 101MHz,CDCl3
f1 (ppm)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-88.21
-89.19
-89.28
F
F
Me
CO2Et
D
3g
19F NMR, 376MHz,CDCl3
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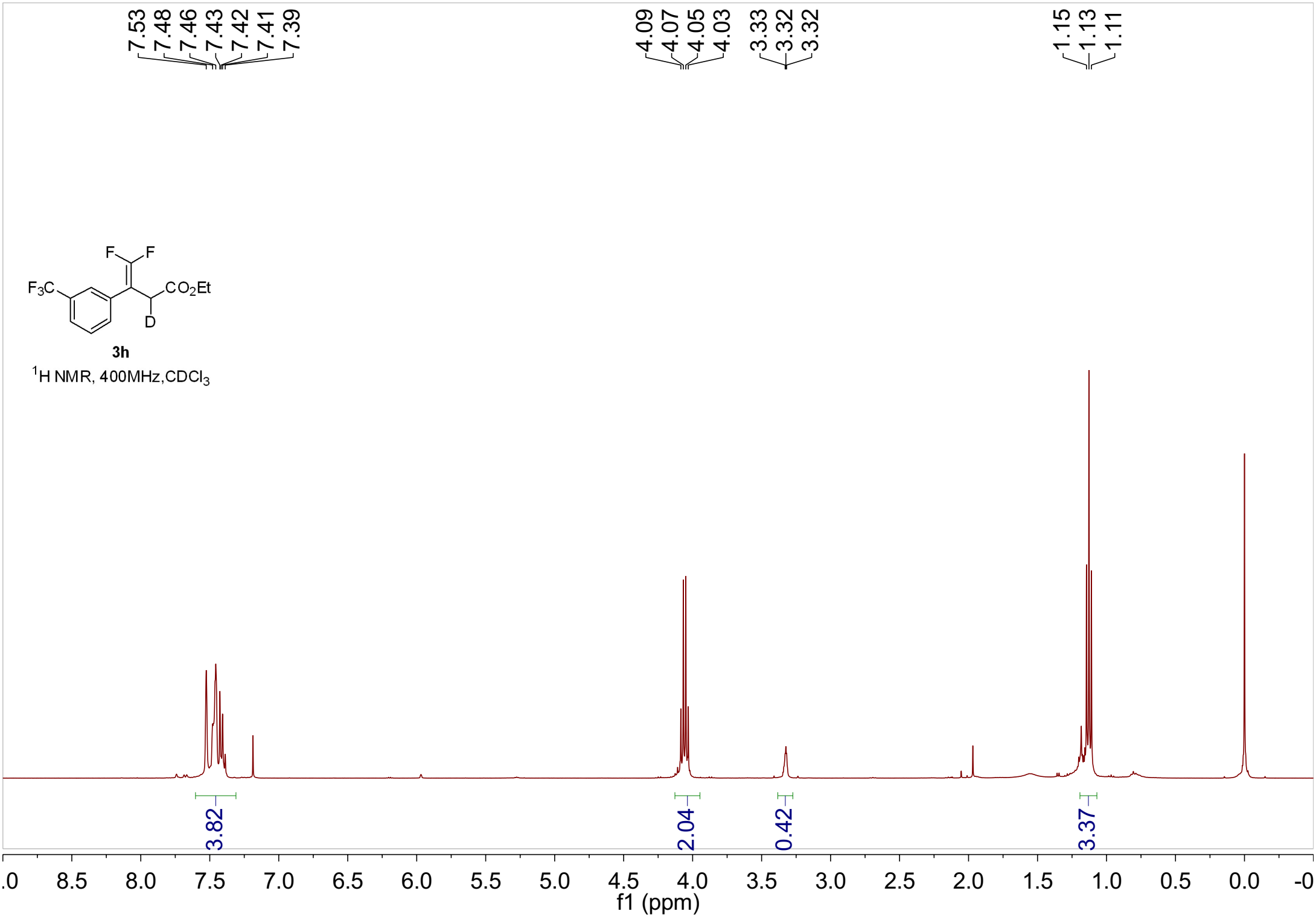
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)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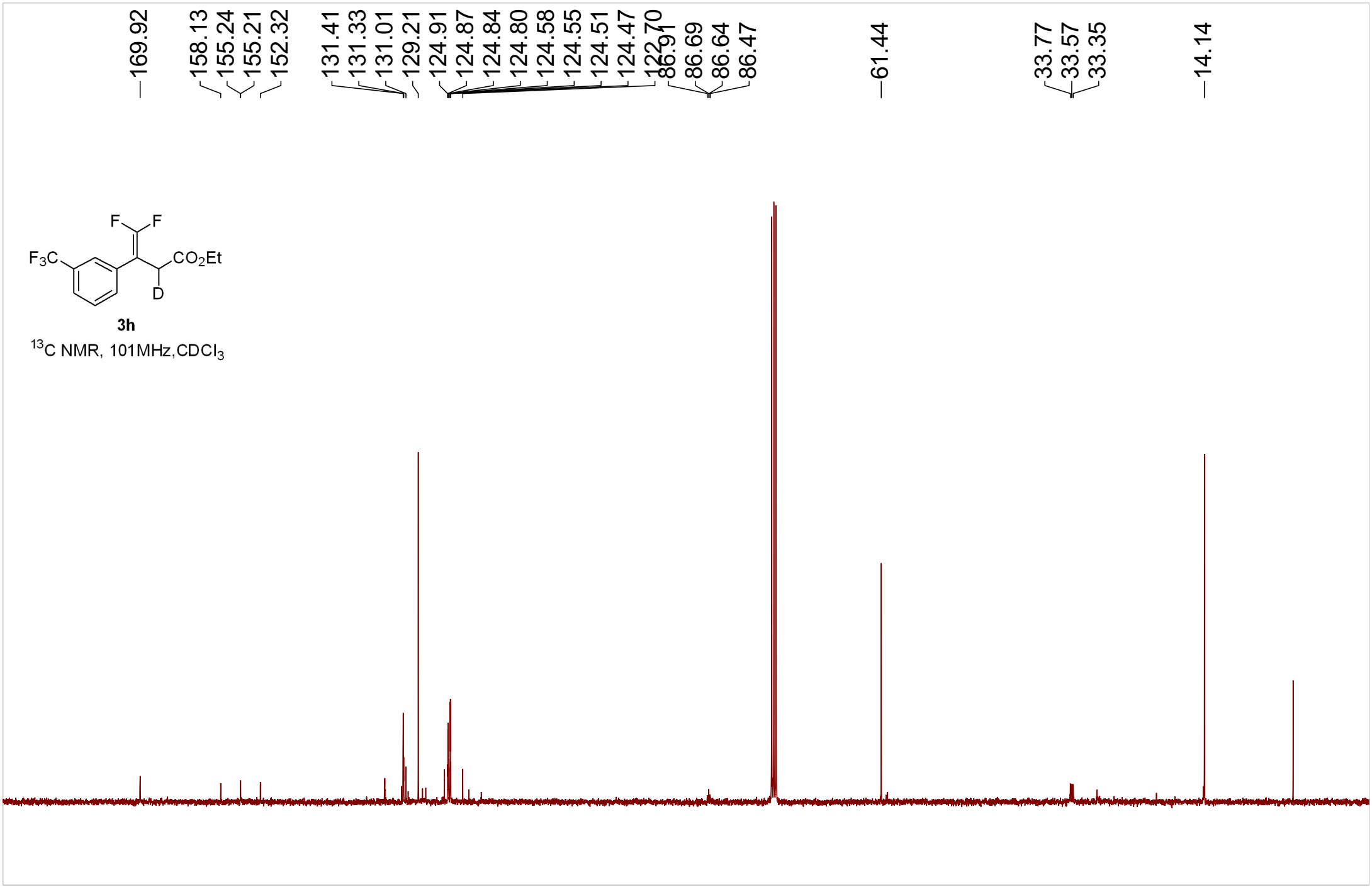
4.07
4.05
4.03
3.33
3.32
3.32
1.15
1.13
1.11
F
F
F3C
CO2Et
D
3h
1H NMR, 400MHz,CDCl3
3.82
2.04
0.42
3.37
f1 (ppm)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124.51
124.47
122.70
86.91
86.69
86.64
86.47
61.44
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33.57
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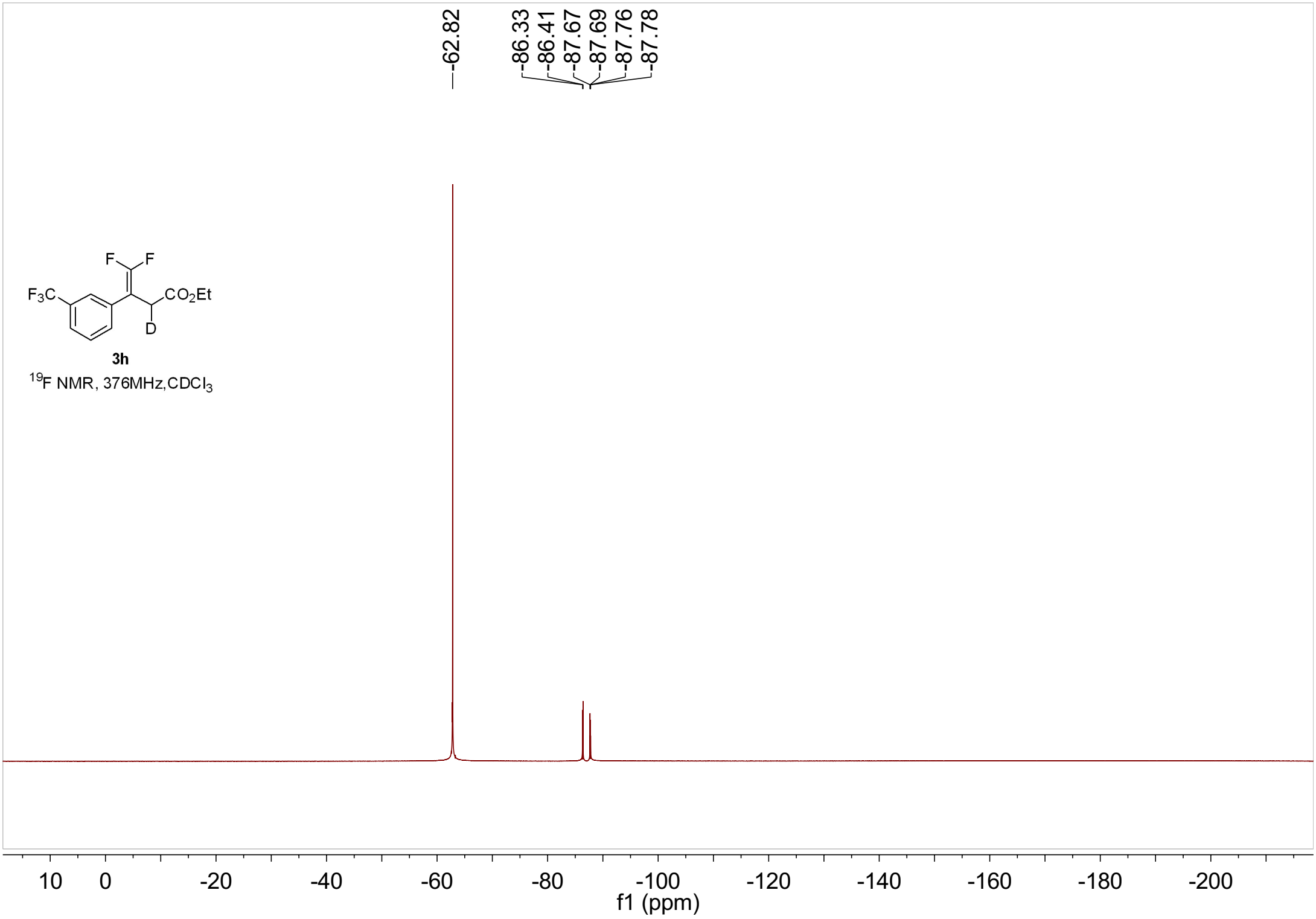
14.14
F
F
F3C
CO2Et
D
3h
13C NMR, 101MHz,CDCl3
f1 (ppm)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-87.78
F
F
F3C
CO2Et
D
3h
19F NMR, 376MHz,CDCl3
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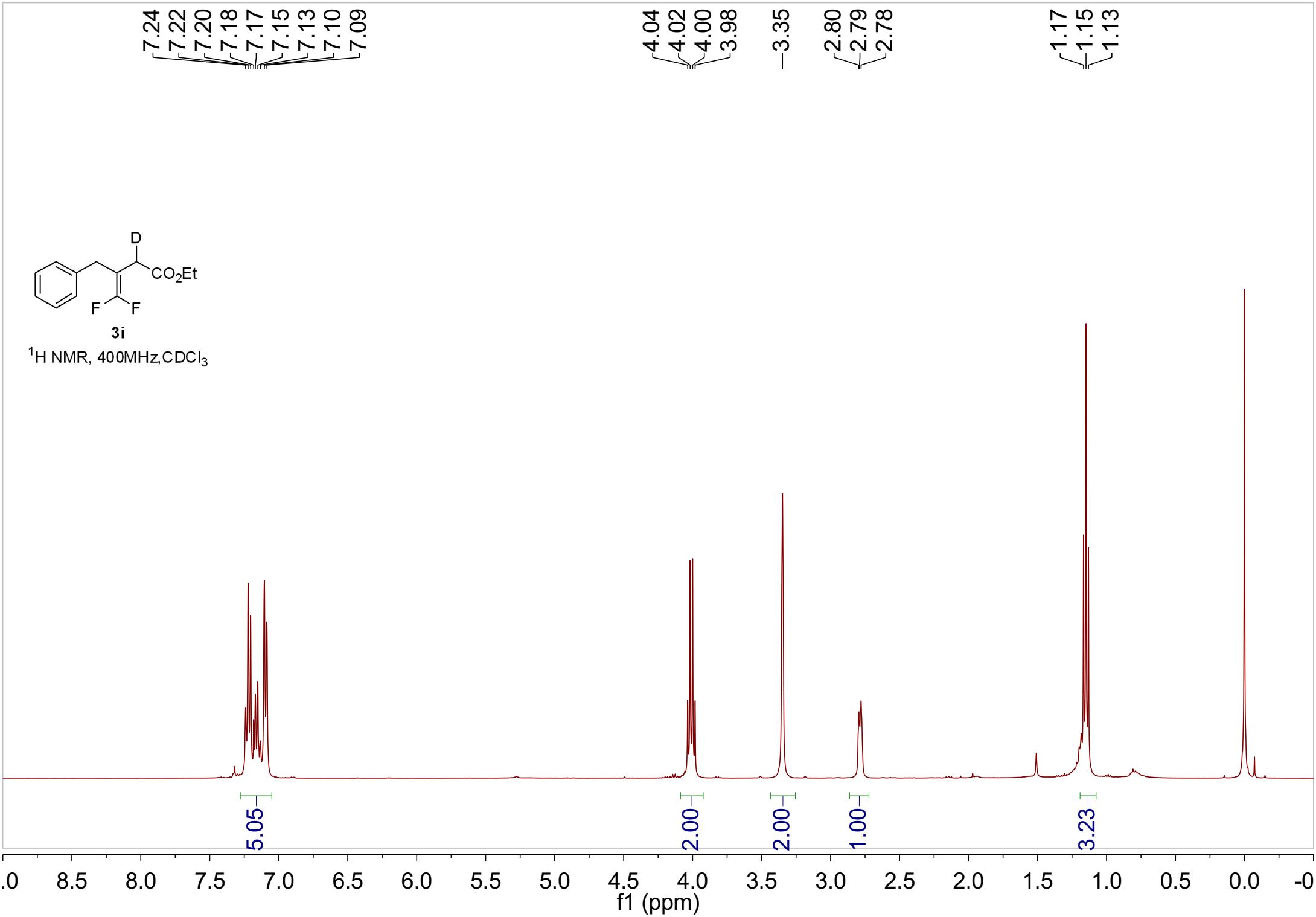
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)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7.13
7.10
7.09
4.04
4.02
4.00
3.98
3.35
2.80
2.79
2.78
1.17
1.15
1.13
D
CO2Et
F
F
3i
1H NMR, 400MHz,CDCl3
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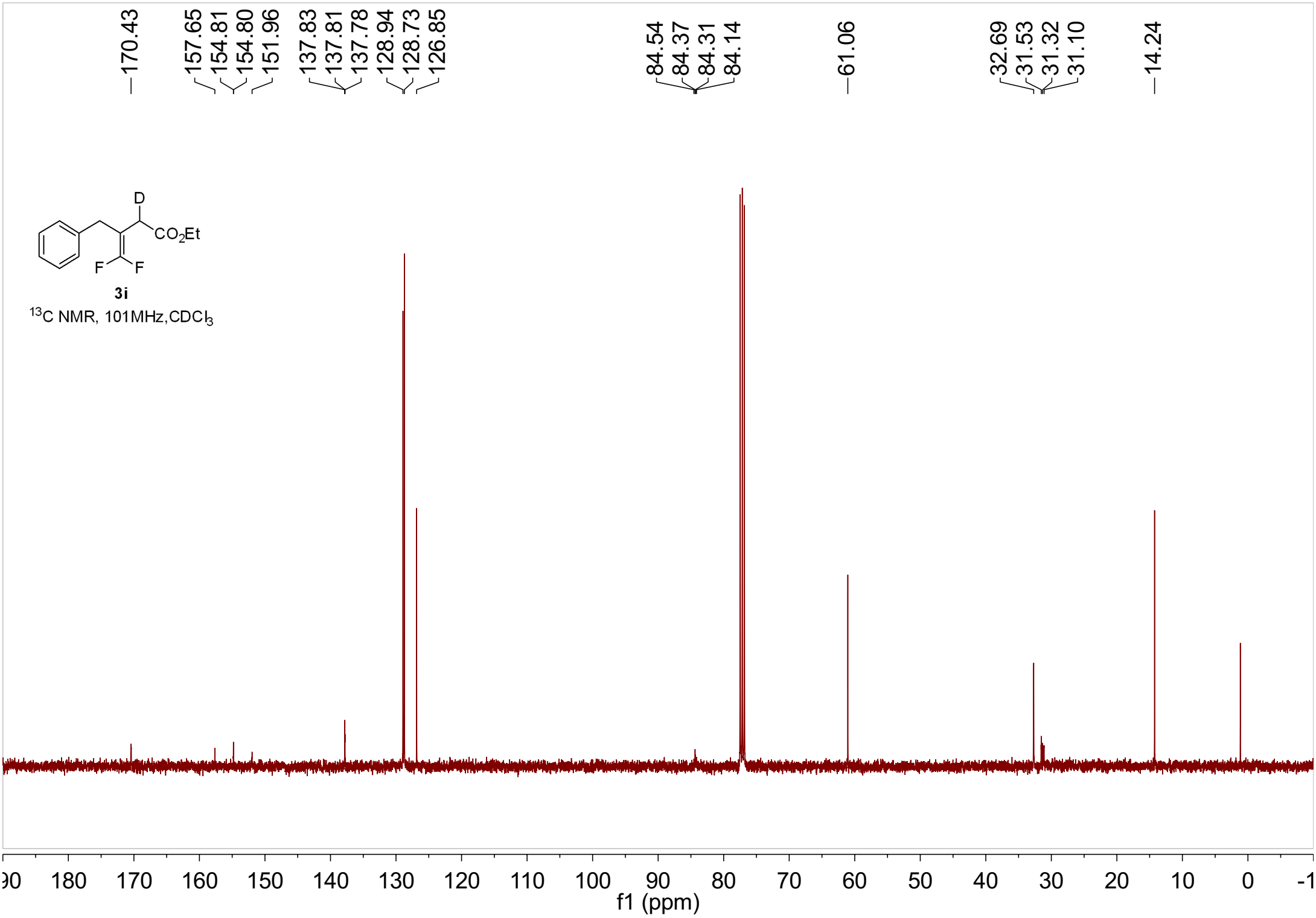
2.00
2.00
1.00
3.23
f1 (ppm)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126.85
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84.37
84.31
84.14
61.06
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31.53
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31.10
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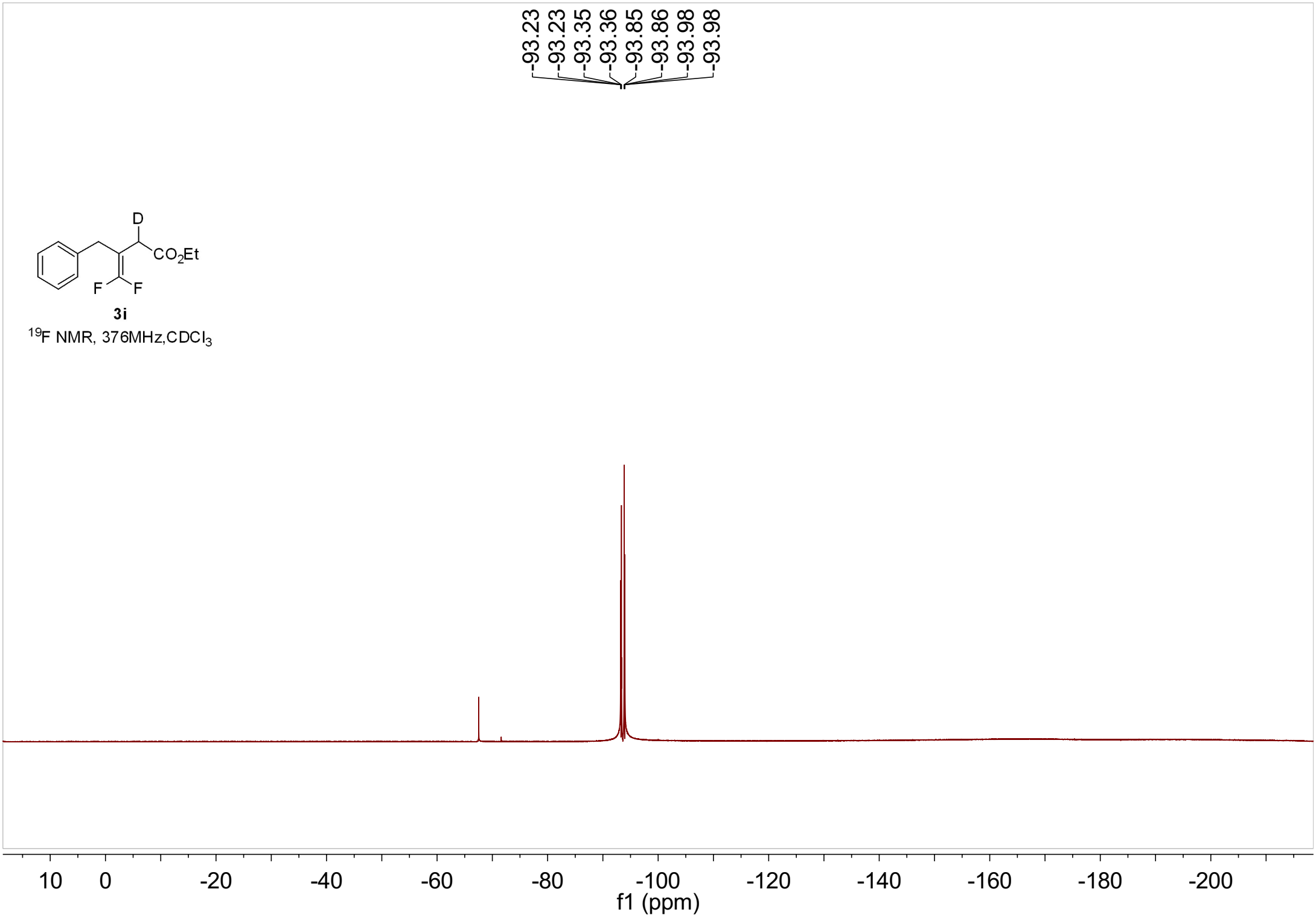
D
CO2Et
F
F
3i
13C NMR, 101MHz,CDCl3
f1 (ppm)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-93.35
-93.36
-93.85
-93.86
-93.98
-93.98
D
CO2Et
F
F
3i
19F NMR, 376MHz,CDCl3
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)