Ni-catalysed Deamidative Fluorination of Amides with Electrophilic Fluorinating Reagent

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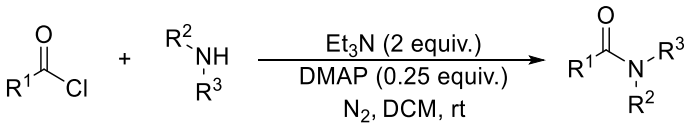
I. General

Unless otherwise stated, all experiments were carried out under N_2 atmosphere. The reagents and solvents were purchased from commercial suppliers and used without further purification unless noted. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker AVANCE III 500 instrument in $CDCl_3$ using TMS as an internal standard, operating at 600 MHz, 400MHz, 151 MHz and 101MHz. respectively. Chemical shifts (δ) are expressed in ppm and coupling constants J are given in Hz. For $CDCl_3$ solution the chemical shifts are reported as parts per million (ppm) to residual protium or carbon of the solvents; $CHCl_3$ δH (7.28 ppm) and $CDCl_3$ δC (77.03 ppm). ^{19}F NMR were recorded on a Bruker AVANCE III or Ascend400. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet. GC experiments were carried out using Agilent 7890B GC. GC-MS experiments that used dodecane as an internal standard were performed with an Agilent 6890N GC system equipped with a 5973N mass-selective detector, high resolution mass spectra (HRMS) were obtained on a Waters GCT Premier TOF MS with EI or CI source, or Agilent 6545 Q-TOF LCMS spectrometer equipped with an ESI source.

II. General procedure for amide synthesis

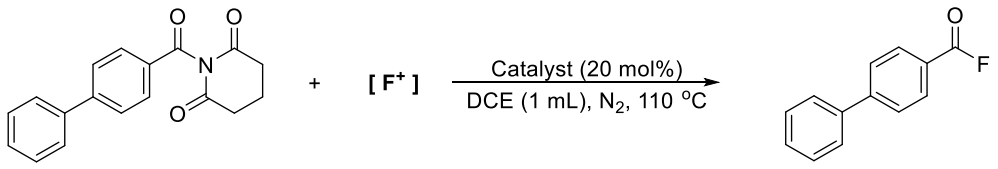


Scheme S1. Synthesis of amides

An oven-dried round-bottomed flask (100 mL) equipped with a stir bar was charged with amine (10 mmol, 1.0 equiv.), triethylamine (typically, 2.0 equiv.), 4-dimethylaminopyridine (typically, 0.25 equiv.) and dichloromethane (typically, 50 mL), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Acyl chloride (typically, 1.1 equiv.) was added dropwise to the reaction mixture with vigorous stirring at 0 °C, and the reaction mixture was stirred overnight at room temperature. After the indicated time, the reaction mixture was diluted with Et_2O (20 mL) and filtered. The organic layer was washed with HCl (1.0 N, 30 mL), brine (30 mL), dried, and concentrated. The residue was purified by recrystallization or chromatography on silica gel to afford the corresponding amides.

III. Screening of the fluorination conditions

Table S1. Screening of the catalysts and fluorinating reagents[a]

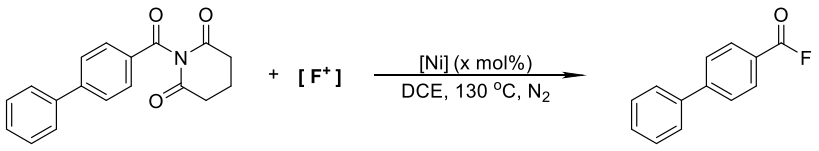


1aa **2a**

Entry	Catalyst	[F^+]	Yield of 2a (%)
1	$Pd(OAc)_2$	NFSI	-
2	$Pd(cod)Cl_2$	NFSI	5
3	$Pd(PPh_3)Cl_2$	NFSI	-
4	$Ni(dppf)Cl_2$	NFSI	70
5	NiI_2	NFSI	76
6	NiF_2	NFSI	-
7	NiF_2	Selectfluor	11
8	$Ni(dppf)Cl_2$	N-Fluoropyridinium tetrafluroborate	-
9	$Ni(dppf)Cl_2$	N-Fluoropyridinium trifluoromethanesulphonate	-
10	**$Ni(dppf)Cl_2$**	**Selectfluor**	**91**

[a]Reaction conditions: **1aa** (0.2 mmol), [F^+] (2.0 equiv.), catalyst (20 mol%), DCE (2 mL), N_2, 110 °C, yield is determined by GC using dodecane as an internal standard.

Table S2. Screening of the temperature and solvents[a]



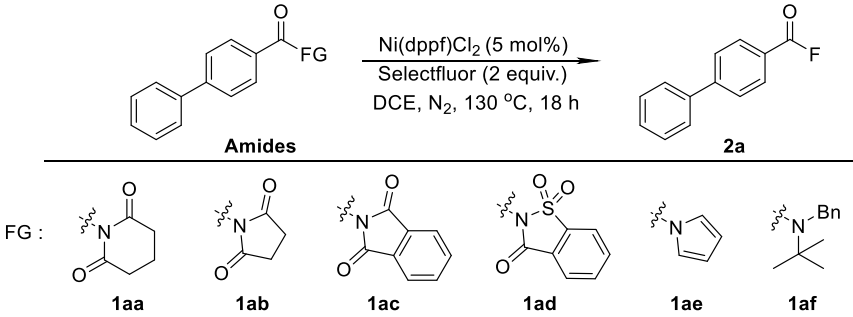
1aa **2a**

Entry	[F^+]	[Ni] (x mol%)	T (°C)	Solvents	Yield of 2a (%)
1	NFSI	$Ni(dppf)Cl_2$ (20 mol%)	110	DCE	70
2	NFSI	NiI_2 (20 mol%)	110	DCE	76
3	NFSI	$Ni(dppf)Cl_2$ (20 mol%)	110	THF	21
4	NFSI	$Ni(dppf)Cl_2$ (20 mol%)	110	HFIP	44
5	NFSI	$Ni(dppf)Cl_2$ (20 mol%)	110	1,4-dioxane	30
6	Selectfluor	$Ni(dppf)Cl_2$ (20 mol%)	110	DCE	91
7	Selectfluor	$Ni(dppf)Cl_2$ (20 mol%)	130	DCE	98
8	**Selectfluor**	**$Ni(dppf)Cl_2$ (5 mol%)**	**130**	**DCE**	**98**
9	Selectfluor	$Ni(dppe)Cl_2$ (5 mol%)	130	DCE	11

10	Selectfluor	$Ni(PPh_3)_2Cl_2$ (5 mol%)	130	DCE	79
11	Selectfluor	$NiCl_2$ (5 mol%)	130	DCE	3
12	Selectfluor	$Ni(COD)_2$ (5 mol%)	130	DCE	50

[a]Reaction conditions: **1aa** (0.2mmol), [F^+] (2.0 equiv.), [Ni] (x mol%), DCE (2 mL), N_2, yield is determined by GC using dodecane as an internal standard.

Table S3. Screening of different amides[a]



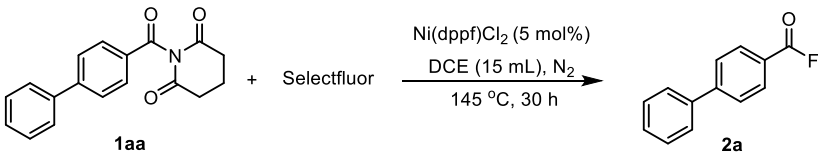
Entry	Amides	Yield of 2a (%)
1	**1aa**	**98**
2	1ab	82
3	1ac	37
4	1ad	52
5	1ae	-
6	1af	-

[a]Reaction conditions: **Amides** (0.2 mmol), selectfluor (2.0 equiv.), $Ni(dppf)Cl_2$ (20 mol%), DCE (2 mL), N_2, 130 °C, yield is determined by GC using dodecane as an internal standard.

IV. Typical experimental procedure for the synthesis of 2

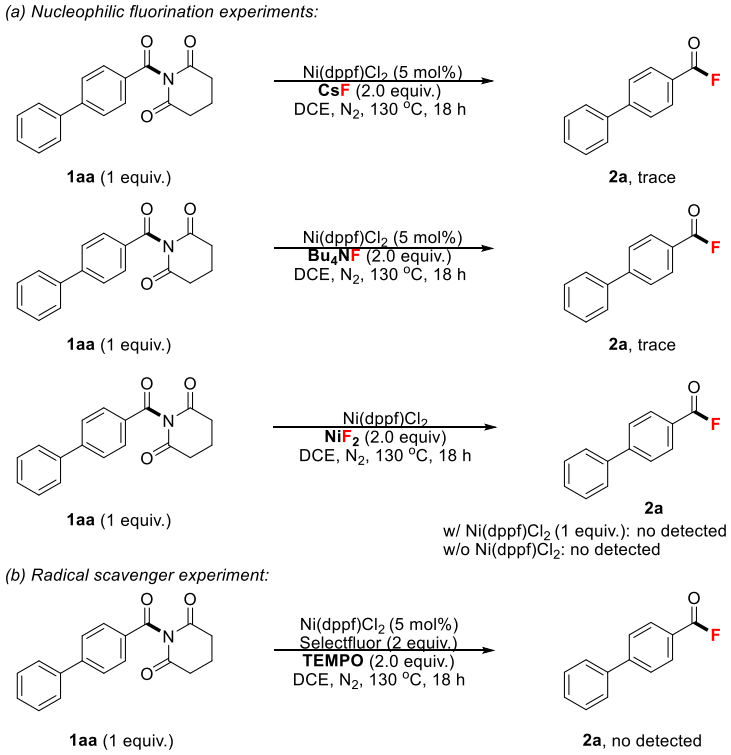
An oven-dried Schlenk tube (25 mL) equipped with a stir bar was charged with benzamide **1** (0.2 mmol), nickel catalyst (5 mol%), Selectfluor (2.0 equiv.), DCE (2 mL), placed under a positive pressure of nitrogen, and subjected to three evacuation/backfilling cycles under high vacuum, and the reaction mixture was stirred for 18 h at 130 °C. After the indicated time, the reaction mixture was diluted with DCM (5 mL), concentrated, and the crude product was purified by chromatography on silica gel to afford the title product **2**.

V. Gram scale-up experiment:



An oven-dried Schlenk tube (50 mL) equipped with a stir bar was charged with benzamide **1aa** (1.0 g, 3.41 mmol, 1.0 equiv.), nickel catalyst (0.116 g, 5 mol%), Selectfluor (6.82 mmol, 2.42g, 2.0 equiv.), DCE (15 mL), placed under a positive pressure of nitrogen, and subjected to three evacuation/backfilling cycles under high vacuum, and the reaction mixture was stirred for 30 h at 145 °C. After the indicated time, the reaction mixture was diluted with DCM (20 mL), concentrated, and the crude product was purified by chromatography on silica gel to afford the title product **2a** (0.53 g, 2.65 mmol, 78%).

VI. Control experiments



Procedures for experiments in (a): An oven-dried Schlenk tube (25 mL) equipped with a stir bar was charged with **1aa** (0.2 mmol), Ni(dppf)Cl_2 (x mol%), fluoride resource (2.0 equiv.), DCE (2 mL), placed under a positive pressure of nitrogen, and subjected to three evacuation/backfilling cycles under high vacuum, and the reaction mixture was stirred for 18 h at 130 °C. After the indicated time, product **2a** status was checked by GC.

Procedures for experiments in (b): An oven-dried Schlenk tube (25 mL) equipped with a stir bar was charged with **1aa** (0.2 mmol), Ni(dppf)Cl_2 (5 mol%), Selectfluor (2.0 equiv.), TEMPO (2.0 equiv.), DCE (2 mL), placed under a positive pressure of nitrogen, and subjected to three evacuation/backfilling cycles under high vacuum, and the reaction mixture was stirred for 18 h at 130 °C. After the indicated time, product **2a** status was checked by GC.

Proposed mechanism: One possible reaction mechanism involving a Ni(0)/Ni(II)/Ni(III)/Ni(I) pathway

was proposed in Figure S1. The Ni(0) species is generated from the reduction of Ni(II) pre-catalyst and is probably the key reactive catalysts to initial the catalytic cycle, which could undergo oxidative addition with N-acylglutarimide to give an Ni(II) adduct **I**. The $1e^-$ oxidation (SET) of Ni(II) complex by Selectfluor would form a high-valent Ni(III) fluoride **II**, which proceeds reductive elimination to furnish the acyl fluoride **2a** and generate a Ni(I) intermediate **III**. Selectfluor radical cation is further reduced by solvent molecules by H atom abstraction. Finally, the unstable Ni(I) species was reduced to the catalytically active Ni(0) species through a SET process of a radical alkyl species.

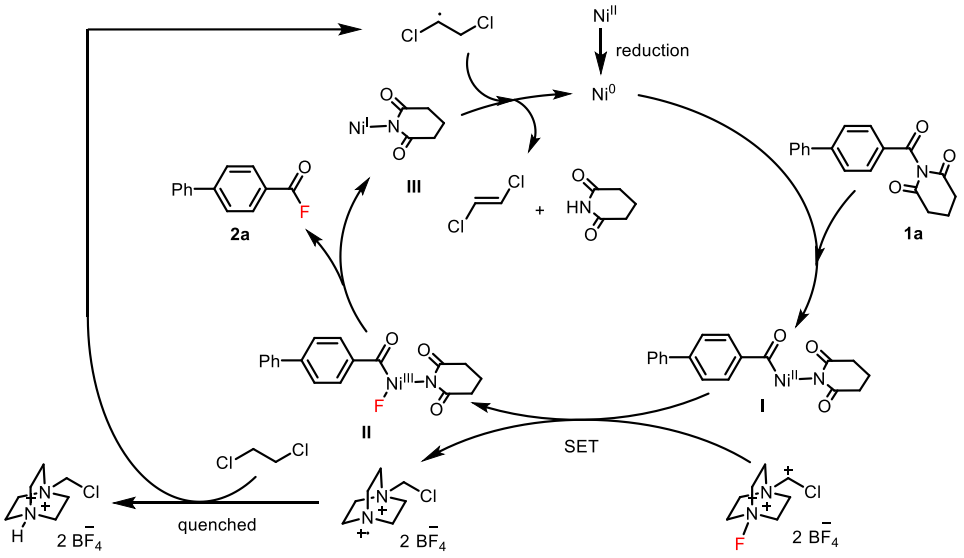


Figure S1. A Possible Ni(0)/Ni(II)/Ni(III)/Ni(I) reaction mechanism.

Another possible reaction mechanism involving a Ni(0)/Ni(I)/Ni(III)/Ni(I) pathway was proposed in Figure S2. In this case, the $1e^-$ oxidation of Ni(0) by Selectfluor takes place prior to the oxidative addition with N-acylglutarimide, providing a Ni(I)-F. This Ni(I) species then undergoes oxidative addition with N-acylglutarimide to give a high-valent Ni(III) adduct **II**, which proceeds reductive elimination to furnish the acyl fluoride **2a** and generate a Ni(I) intermediate **III**. Selectfluor radical cation is further reduced by solvent molecules by H atom abstraction. Finally, the unstable Ni(I) species was reduced to the catalytically active Ni(0) species through a SET process of a radical alkyl species.

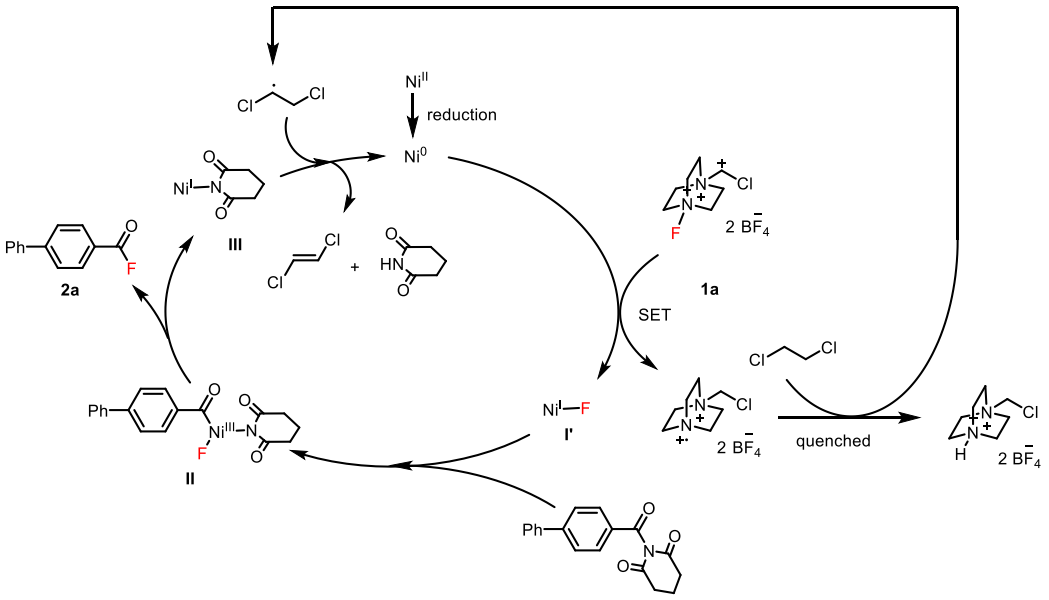


Figure S2. A Possible Ni(0)/Ni(I)/Ni(III)/Ni(I) reaction mechanism.

Besides the pathways involving an oxidative addition elementary step, an alternative one-electron redox Ni(II)/Ni(III) catalytic cycle could not be ruled out. The possible process was proposed in Figure S3. The Ni(II) is not reactive for the oxidative addition of N-acylglutarimide and may coordinate with this substrate to give **I"**. This intermediate undergoes 1e$^-$ oxidation by Selectfluor to give a Ni(III)-coordinated acyliminium species **II'**, which leads to the formation of an acyl fluoride **2a** and generate a Ni(III) species **III'**. This high-valent Ni(III) species is finally reduced to Ni(II) through a SET process of a radical alkyl species.

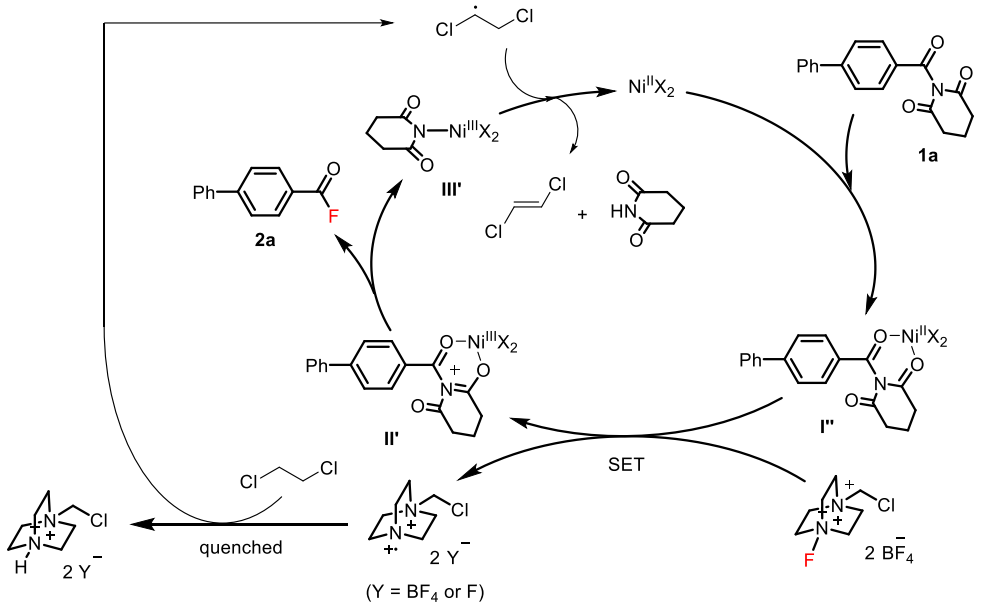
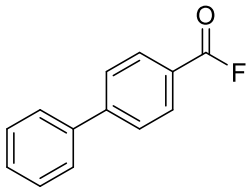


Figure S3. A Possible Ni(II)/Ni(III) reaction mechanism.

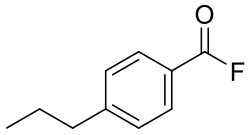
VII.Spectroscopic data of the products

[1,1'-Biphenyl]-4-carbonyl fluoride (2a)



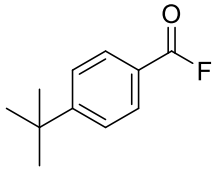
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2a** (34.8 mg, 87% yield) as a white solid.^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.69 – 7.64 (m, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.4 (d, *J* = 343.0 Hz), 148.1, 139.3, 132.0 (d, *J* = 3.8 Hz), 129.1, 128.8, 127.7, 127.4, 123.5 (d, *J* = 61.4 Hz); ^{19}F NMR (565 MHz, Chloroform-*d*) δ 18.13. Spectroscopic data was agreement with the literature.[1]

4-Propylbenzoyl fluoride (2b)



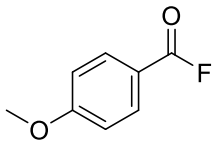
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2b** (27.6 mg, 83% yield) as a colorless liquid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 2.84 – 2.61 (m, 2H), 1.70 (d, *J* = 7.6 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.6 (d, *J* = 342.8 Hz), 151.2, 131.5 (d, *J* = 4.0 Hz), 129.2, 122.3 (d, *J* = 60.8 Hz), 38.2, 24.1, 13.7; ^{19}F NMR (565 MHz, Chloroform-*d*) δ 17.47; HRMS (EI) m/z [M^{+}] Calcd. for $C_{10}H_{11}FO$: 166.0794; Found 166.0787.

4-(tert-Butyl)benzoyl fluoride (2c)



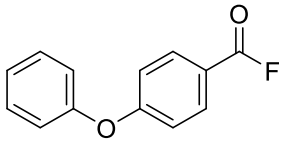
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2d** (30.2 mg, 84% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 1.38 (s, 9H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.5, 157.5 (d, *J* = 342.8 Hz), 131.4 (d, *J* = 3.9 Hz), 126.1, 122.1 (d, *J* = 61.0 Hz), 35.4, 31.0; ^{19}F NMR (565 MHz, Chloroform-*d*) δ 17.64. Spectroscopic data was agreement with the literature.[1]

4-Methoxybenzoyl fluoride (2d)



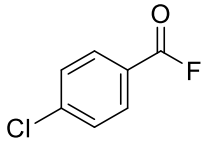
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2c** (21.9 mg, 71% yield) as a colorless liquid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 7.8 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.2, 157.3 (d, *J* = 339.9 Hz), 133.8 (d, *J* = 4.0 Hz), 116.9 (d, *J* = 61.9 Hz), 114.4, 55.7; ^{19}F NMR (565 MHz, Chloroform-*d*) δ 15.97. Spectroscopic data was agreement with the literature.[1]

4-Phenoxybenzoyl fluoride (2e)



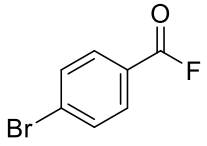
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2e** (32.8 mg, 76% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.9 Hz, 2H), 7.50 – 7.40 (m, 2H), 7.31 – 7.24 (m, 1H), 7.12 (dt, *J* = 7.8, 1.1 Hz, 2H), 7.08 – 7.02 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.1, 157.0 (d, *J* = 340.4 Hz), 154.7, 133.8, 130.3, 125.3, 120.6, 118.5 (d, *J* = 61.3 Hz), 117.4; ^{19}F NMR (565 MHz, Chloroform-*d*) δ 16.78. Spectroscopic data was agreement with the literature.[2]

4-Chlorobenzoyl fluoride (2f)



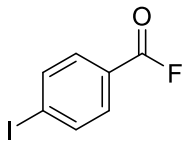
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2f** (24.2 mg, 76% yield) as a colorless liquid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.68 – 7.49 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.6 (d, *J* = 343.4 Hz), 142.2, 132.7 (d, *J* = 3.8 Hz), 129.6, 123.4 (d, *J* = 62.5 Hz); ^{19}F NMR (565 MHz, Chloroform-*d*) δ 18.43. Spectroscopic data was agreement with the literature.[1]

4-Bromobenzoyl fluoride (2g)



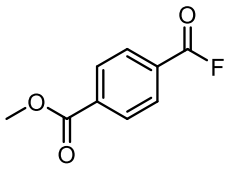
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2g** (33.9 mg, 84% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.73 – 7.69 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.8 (d, *J* = 343.5 Hz), 132.7 (d, *J* = 3.8 Hz), 132.6, 131.0, 123.9 (d, *J* = 62.6 Hz); ^{19}F NMR (565 MHz, Chloroform-*d*) δ 18.43. Spectroscopic data was agreement with the literature.[1]

4-Iodobenzoyl fluoride (2h)



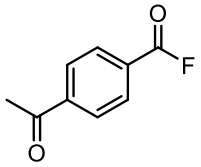
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2h** (36.5 mg, 73% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (d, J = 7.7 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.1 (d, J = 343.9 Hz), 138.6, 132.5 (d, J = 3.8 Hz), 124.4 (d, J = 62.4 Hz), 104.0; ^{19}F NMR (565 MHz, Chloroform-*d*) δ 18.29. Spectroscopic data was agreement with the literature.[3]

Methyl 4-(fluorocarbonyl)benzoate (2i)



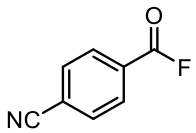
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 10:1) to afford the title compound **2u** (17.5 mg, 48% yield) as a white solid.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 – 8.18 (m, 2H), 8.14 (d, J = 8.5 Hz, 2H), 4.00 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.6, 156.6 (d, J = 345.9 Hz), 136.1, 131.4 (d, J = 3.8 Hz), 130.1, 128.6 (d, J = 61.6 Hz), 52.7. ^{19}F NMR (377 MHz, Chloroform-*d*) δ 20.09. Spectroscopic data was agreement with the literature.[4]

4-Acetylbenzoyl fluoride (2j)



The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 10:1) to afford the title compound **2u** (14.3 mg, 41% yield) as a white solid.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, J = 8.6 Hz, 2H), 8.12 – 8.07 (m, 2H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.9, 156.5 (d, J = 345.7 Hz), 142.0, 131.7 (d, J = 3.8 Hz), 128.7, 128.5 (d, J = 61.7 Hz), 26.9. ^{19}F NMR (377 MHz, Chloroform-*d*)) δ 20.19. Spectroscopic data was agreement with the literature.[5]

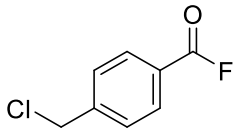
4-Cyanobenzoyl fluoride (2k)



The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 10:1) to afford the title compound **2u** (6.8 mg, 23% yield) as a white solid.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (d, J = 8.4 Hz, 2H), 7.92 – 7.83 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.70 (d, J = 346.1 Hz), 132.80,

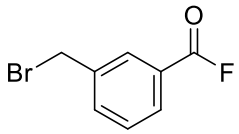
131.80 (d, J = 3.6 Hz), 128.78 (d, J = 63.5 Hz), 118.80, 117.20. ^{19}F NMR (377 MHz, $CDCl_3$) δ 20.22. Spectroscopic data was agreement with the literature.[6]

4-(Chloromethyl)benzoyl fluoride (2l)



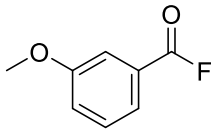
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2i** (20.3 mg, 59% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.07 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 4.66 (s, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.9 (d, J = 344.2 Hz), 144.9, 131.9 (d, J = 3.9 Hz), 129.1, 124.9 (d, J = 61.9 Hz), 44.9; ^{19}F NMR (565 MHz, Chloroform-*d*) δ 18.67; HRMS (EI) m/z [M^+] Calcd. for C_8H_6ClFO: 172.0091; Found 172.0083.

3-(Bromomethyl)benzoyl fluoride (2m)



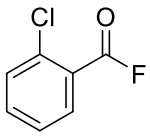
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2j** (28.1 mg, 65% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 8.04 (d, J = 7.8 Hz, 1H), 7.77 (d, J = 7.7 Hz, 1H), 7.57 (t, J = 7.7 Hz, 1H), 4.66 (s, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.9 (d, J = 344.7 Hz), 138.8, 135.3, 131.3 (d, J = 7.5 Hz), 131.3, 129.6, 125.5 (d, J = 61.5 Hz), 44.90; ^{19}F NMR (565 MHz, Chloroform-*d*) δ 18.74; HRMS (EI) m/z [M^+] Calcd. for C_8H_6BrFO: 215.9586; Found 215.9580.

3-Methoxybenzoyl fluoride (2n)



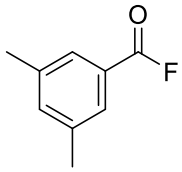
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2k** (22.5 mg, 73% yield) as a colorless liquid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 (dt, J = 7.7, 1.3 Hz, 1H), 7.55 (dd, J = 2.7, 1.6 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.26 (ddd, J = 8.3, 2.7, 1.0 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.0 (d, J = 1.3 Hz), 157.3 (d, J = 344.7 Hz), 130.1, 126.1 (d, J = 61.0 Hz), 123.9 (d, J = 3.5 Hz), 122.1, 115.5 (d, J = 4.3 Hz), 55.6; ^{19}F NMR (565 MHz, Chloroform-*d*) δ 18.60. Spectroscopic data was agreement with the literature.[7]

2-Chlorobenzoyl fluoride (2o)



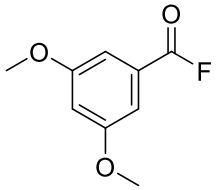
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2l** (22.6 mg, 71% yield) as a colorless liquid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.46 – 7.42 (m, 1H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.5 (d, *J* = 344.5 Hz), 136.9 (d, *J* = 4.4 Hz), 135.4, 133.6 (d, *J* = 2.5 Hz), 132.0 (d, *J* = 3.3 Hz), 127.1, 123.7 (d, *J* = 61.3 Hz); ^{19}F NMR (565 MHz, Chloroform-*d*) δ 32.27. Spectroscopic data was agreement with the literature.[1]

3,5-Dimethylbenzoyl fluoride (2p)



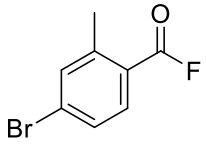
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2m** (18.5mg, 61% yield) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (s, 2H), 7.34 (s, 1H), 2.41 (s, 6H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.8 (d, *J* = 344.4 Hz), 138.9, 137.0, 129.1 (d, *J* = 3.8 Hz), 124.8 (d, *J* = 59.6 Hz), 21.1; ^{19}F NMR (565 MHz, Chloroform-*d*) δ 18.36. Spectroscopic data was agreement with the literature.[8]

3,5-Dimethoxybenzoyl fluoride (2q)



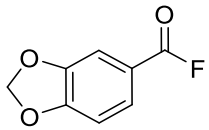
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2n** (30.2 mg, 82% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 2.4 Hz, 2H), 6.77 (s, 1H), 3.86 (s, 6H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.0, 157.3 (d, *J* = 344.6 Hz), 126.5 (d, *J* = 61.3 Hz), 108.8 (d, *J* = 3.6 Hz), 108.0, 55.7; ^{19}F NMR (565 MHz, Chloroform-*d*) δ 18.72. Spectroscopic data was agreement with the literature.[9]

4-Bromo-2-methylbenzoyl fluoride (2r)



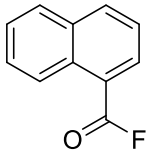
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2o** (30.2 mg, 70% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.4 Hz, 1H), 7.55 (s, 1H), 7.51 (dd, *J* = 8.4, 1.7 Hz, 1H), 2.65 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.1 (d, *J* = 344.9 Hz), 145.5 (d, *J* = 7.1 Hz), 135.2 (d, *J* = 4.0 Hz), 133.7 (d, *J* = 1.9 Hz), 130.1, 129.8, 122.5 (d, *J* = 58.1 Hz), 21.7; ^{19}F NMR (565 MHz, Chloroform-d) δ 29.47; HRMS (EI) [M^+] Calcd. for C_8H_6BrFO: 215.9585; Found 215.9588.

Benzo[d][1,3]dioxole-5-carbonyl fluoride(2s)



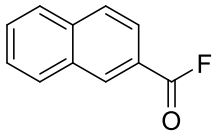
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2p** (30.6 mg, 91% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.69 (dd, J = 8.2, 1.7 Hz, 1H), 7.44 (d, J = 1.7 Hz, 1H), 6.93 (d, J = 8.9 Hz, 1H), 6.12 (s, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.9 (d, J = 340.2 Hz), 153.8, 148.3, 128.2 (d, J = 3.5 Hz), 118.4 (d, J = 62.5 Hz), 110.7 (d, J = 3.9 Hz), 108.6, 102.4; ^{19}F NMR (565 MHz, Chloroform-d) δ 16.40. Spectroscopic data was agreement with the literature.[10]

1-Naphthoyl fluoride (2t)



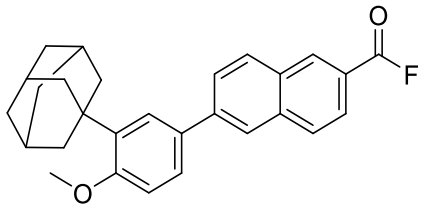
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2q** (17.7 mg, 51% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.05 (d, J = 8.5 Hz, 1H), 8.39 (d, J = 7.1 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.64 (t, J = 7.3 Hz, 1H), 7.59 (t, J = 7.7 Hz, 1H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.4 (d, J = 344.5 Hz), 136.7, 133.9 (d, J = 3.9 Hz), 133.7 (d, J = 2.1 Hz), 132.1 (d, J = 7.1 Hz), 129.2, 129.0, 127.0, 125.2, 124.5, 120.4 (d, J = 55.9 Hz); ^{19}F NMR (565 MHz, Chloroform-*d*) δ 29.95. Spectroscopic data was agreement with the literature.[1]

2-Naphthoyl fluoride (2u)



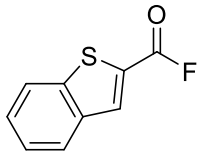
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2r** (26.1 mg, 75% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 8.06 – 8.00 (m, 2H), 8.00 – 7.93 (m, 2H), 7.71 (t, J = 7.2 Hz, 1H), 7.64 (t, J = 7.2 Hz, 1H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.7 (d, J = 343.6 Hz), 136.5, 134.0 (d, J = 3.1 Hz), 132.3, 129.7, 129.7, 129.1, 128.0, 127.4, 125.6 (d, J = 4.1 Hz), 122.0 (d, J = 60.5 Hz); ^{19}F NMR (565 MHz, Chloroform-*d*) δ 18.08. Spectroscopic data was agreement with the literature.[1]

6-(3-(Adamantan-1-yl)-4-methoxyphenyl)-2-naphthoyl fluoride (2v)



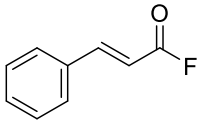
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 3:1) to afford the title compound **2s** (43.9 mg, 53% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 8.10 – 7.99 (m, 4H), 7.89 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.64 (d, *J* = 2.3 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 3H), 2.22 (s, 6H), 2.14 (s, 3H), 1.84 (s, 6H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.2, 157.7 (d, *J* = 343.4 Hz), 142.9, 139.2, 137.0, 133.8 132.1, 131.0, 130.0, 129.1, 127.2, 126.0, 126.0 (d, *J* = 3.4 Hz), 124.8, 121.4 (d, *J* = 60.2 Hz), 112.2, 55.2, 40.6, 37.3, 37.1, 29.1; ^{19}F NMR (565 MHz, Chloroform-*d*) δ 17.67. Spectroscopic data was agreement with the literature.[7]

Benzo[b]thiophene-2-carbonyl fluoride (2w)



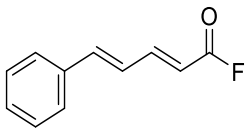
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2t** (23.4 mg, 65% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-d) δ 8.24 (s, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.58 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 7.53 – 7.48 (m, 1H); ^{13}C NMR (151 MHz, Chloroform-d) δ 153.2 (d, *J* = 334.8 Hz), 143.7, 138.2, 135.2, 128.5 (d, *J* = 1.3 Hz), 126.9 (d, *J* = 76.1 Hz), 126.3, 125.6 (d, *J* = 1.3 Hz), 122.9; ^{19}F NMR (565 MHz, Chloroform-*d*) δ 25.14. Spectroscopic data was agreement with the literature.[10]

(E)-3-Phenylacryloyl fluoride (2x)



The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2u** (19.5 mg, 65% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 15.9 Hz, 1H), 7.59 (d, *J* = 6.8 Hz, 2H), 7.47 (m, *J* = 7.0 Hz, 3H), 6.40 (dd, *J* = 15.9, 7.0 Hz, 1H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.1 (d, *J* = 338.4 Hz), 151.4 (d, *J* = 6.0 Hz), 133.2, 131.9, 129.2, 128.8, 112.1 (d, *J* = 67.2 Hz); ^{19}F NMR (565 MHz, Chloroform-*d*) δ 25.62. Spectroscopic data was agreement with the literature.[11]

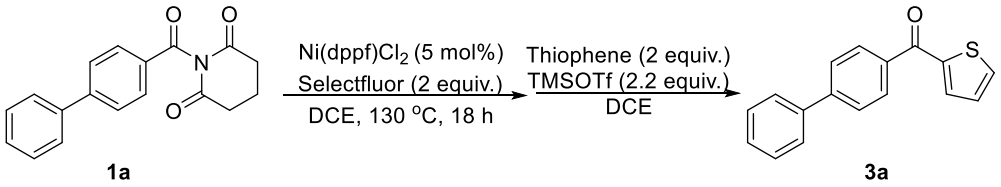
(2E,4E)-5-Phenylpenta-2,4-dienoyl fluoride (2y)



The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 20:1) to afford the title compound **2v** (20.4 mg, 58% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 – 7.58 (m, 1H), 7.53 (d, *J* = 6.5 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 3H), 7.07 (d, *J* = 15.5 Hz, 1H), 6.98 – 6.91 (m, 1H), 5.94 (dd, *J* = 15.0, 7.6 Hz, 1H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.2 (d, *J* = 337.2 Hz), 151.2 (d, *J* = 6.0 Hz), 144.2, 135.3, 130.0, 129.0, 127.7, 125.2, 114.6 (d, *J* = 67.0 Hz); ^{19}F NMR (565 MHz, Chloroform-*d*) δ 24.52. Spectroscopic data was agreement with the literature.[12]

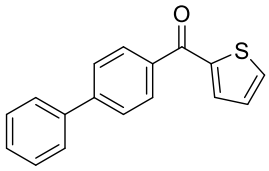
VIII. Synthetic application

Application 1:



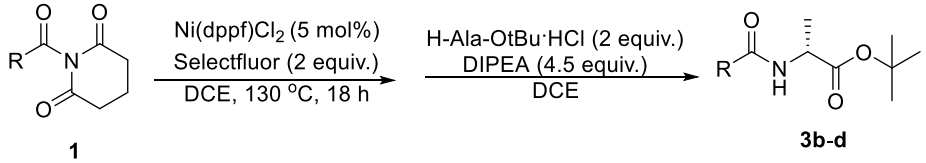
An oven-dried Schlenk tube (25 mL) equipped with a stir bar was charged with benzamide **1a** (0.2 mmol), Ni(dppf)Cl_2 (5 mol%), Selectfluor (2.0 equiv.), DCE (2 mL), placed under a positive pressure of nitrogen, and subjected to three evacuation/backfilling cycles under high vacuum, and the reaction mixture was stirred for 18 h at 130 °C. After the reaction over, add thiophene (2 equiv.) and TMSOTf (2.2 equiv.) to the tube and react for 4 hours. The crude mixture was purified by column chromatography.

[1,1'-Biphenyl]-4-yl(thiophen-2-yl)methanone (3a)



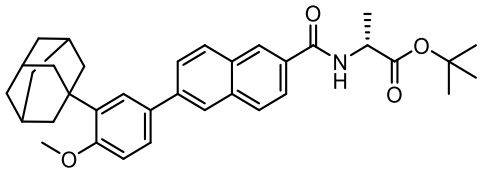
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 5:1) to afford the title compound **3a** (28.0 mg, 63% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.99 (d, J = 8.4 Hz, 2H), 7.79 – 7.71 (m, 4H), 7.70 – 7.66 (m, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.44 (t, J = 7.4 Hz, 1H), 7.21 (dd, J = 4.9, 3.8 Hz, 1H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 187.8, 145.2, 143.7, 140.0, 136.8, 134.7, 134.1, 129.9, 129.0, 128.2, 128.0, 127.3, 127.1. HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd. for $C_{17}H_{12}OSNa$: 287.0501; Found: 287.0502.

Application 2:



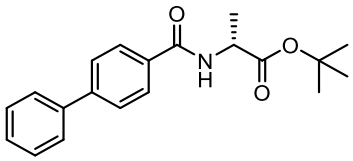
An oven-dried Schlenk tube (25 mL) equipped with a stir bar was charged with benzamide **1a** (0.2 mmol), Ni(dppf)Cl_2 (5 mol%), Selectfluor (2.0 equiv.), DCE (2 mL), placed under a positive pressure of nitrogen, and subjected to three evacuation/backfilling cycles under high vacuum, and the reaction mixture was stirred for 18 h at 130 °C. After the reaction over, add H-Ala-OtBu·HCl (2 equiv.) and DIPEA (4.5 equiv.) to the tube and react for 5 hours. The crude mixture was purified by column chromatography.

Isopropyl (6-(3-(adamantan-1-yl)-4-methoxyphenyl)-2-naphthoyl)-D-alaninate (3b)



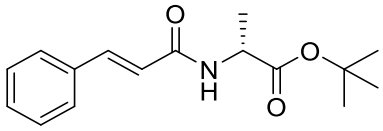
The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 5:1) to afford the title compound **3b** (62.5 mg, 58% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.38 – 8.34 (s, 1H), 8.04 – 8.01 (m, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.90 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.82 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.62 (d, *J* = 2.3 Hz, 1H), 7.56 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 7.1 Hz, 1H), 4.77 (p, *J* = 7.1 Hz, 1H), 3.93 (s, 3H), 2.21 (d, *J* = 3.2 Hz, 6H), 2.07 (s, 3H), 1.83 (d, *J* = 3.7 Hz, 6H), 1.59 (s, 3H), 1.55 (s, 9H);^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.7, 171.2, 166.7, 158.9, 140.9, 139.0, 135.3, 132.7, 131.4, 130.9, 129.3, 128.5, 127.3, 126.6, 126.0, 125.7, 124.7, 123.9, 112.1, 82.3, 55.2, 49.2, 40.6, 37.2, 37.2, 29.1, 28.0, 19.0. HRMS (ESI-TOF) m/z: [M + Na]$^{+}$ Calcd. for $C_{35}H_{41}NO_4Na$ 562.2928; Found: 562.2929.

Isopropyl ([1,1'-biphenyl]-4-carbonyl)-D-alaninate (3c)



The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 5:1) to afford the title compound **3c** (46.8 mg, 72% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 – 7.89 (m, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.66 – 7.62 (m, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.39 (m, 1H), 6.86 (d, *J* = 7.1 Hz, 1H), 4.72 (p, *J* = 7.1 Hz, 1H), 1.53 (d, *J* = 3.7 Hz, 12H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.6, 166.3, 144.4, 140.1, 132.9, 128.9, 128.0, 127.5, 127.2, 82.3, 49.1, 28.0, 19.0. HRMS (ESI-TOF) m/z [M + Na]$^{+}$ Calcd. for $C_{20}H_{23}NO_3Na$: 348.1570; Found: 348.1578.

Isopropyl cinnamoyl-D-alaninate (3d)



3d

The crude mixture was purified by column chromatography (n-Hexane: EtOAc = 5:1) to afford the title compound **3d** (34.1 mg, 62% yield) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 15.6 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.38 (q, *J* = 5.6 Hz, 3H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.34 (d, *J* = 7.3 Hz, 1H), 4.64 (m, *J* = 7.1 Hz, 1H), 1.51 (s, 9H), 1.46 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.5, 165.1, 141.3, 134.8, 129.7, 128.8, 127.8, 120.4, 82.2, 48.8, 28.0, 18.9. HRMS (ESI-TOF) m/z [M + K]$^{+}$ Calcd. for $C_{16}H_{21}NO_3K$: 313,1144; Found: 314.1155.

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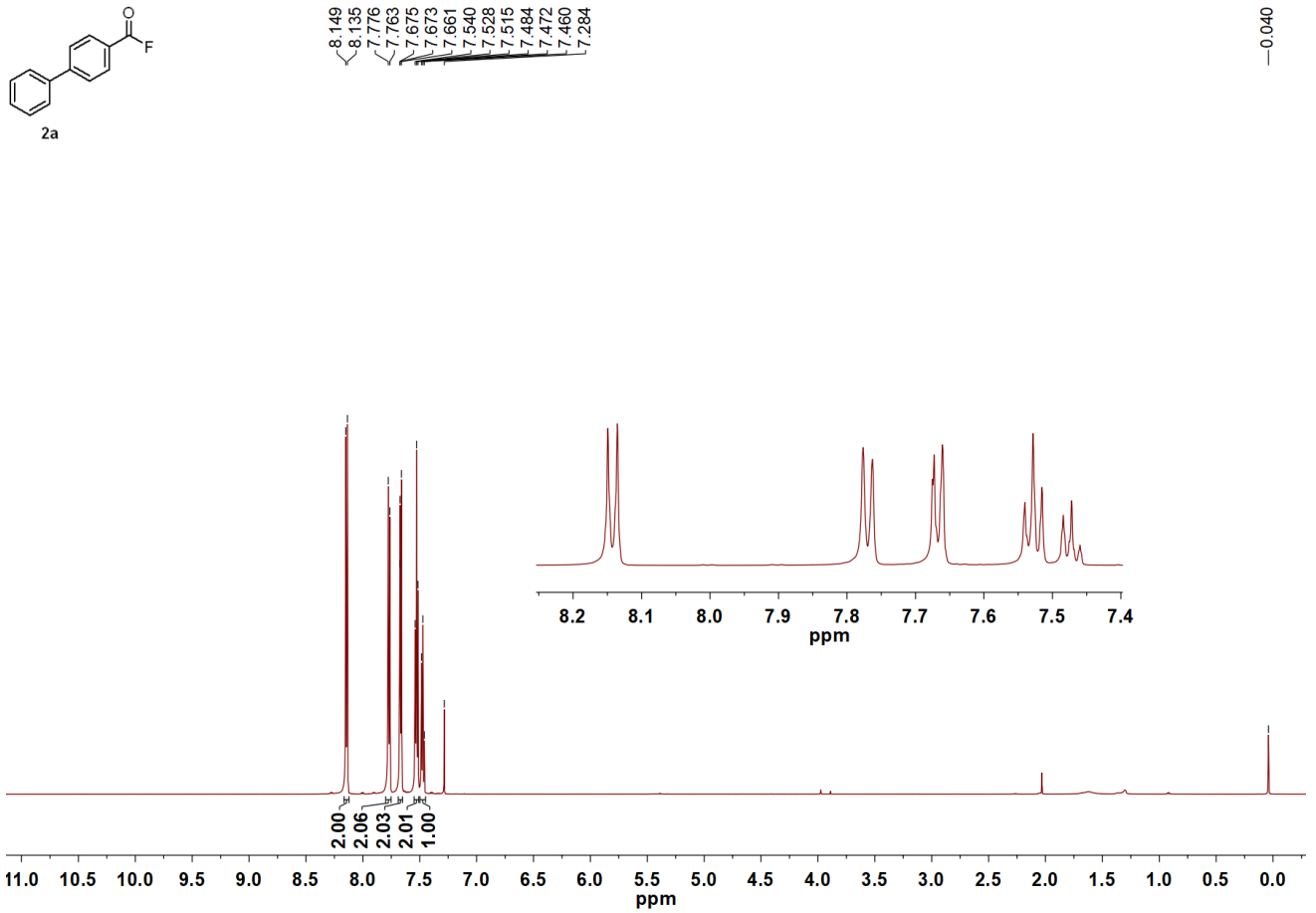
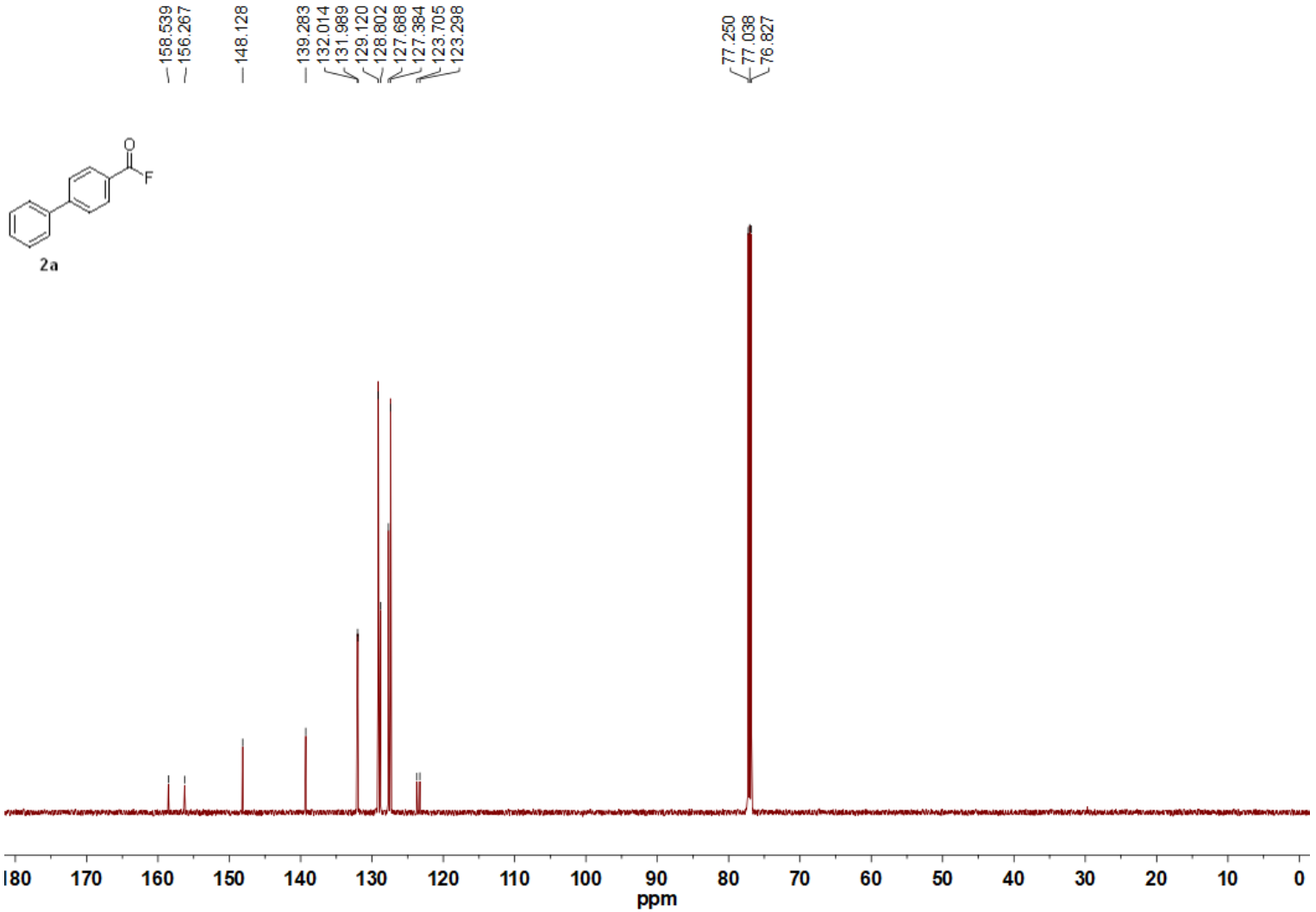
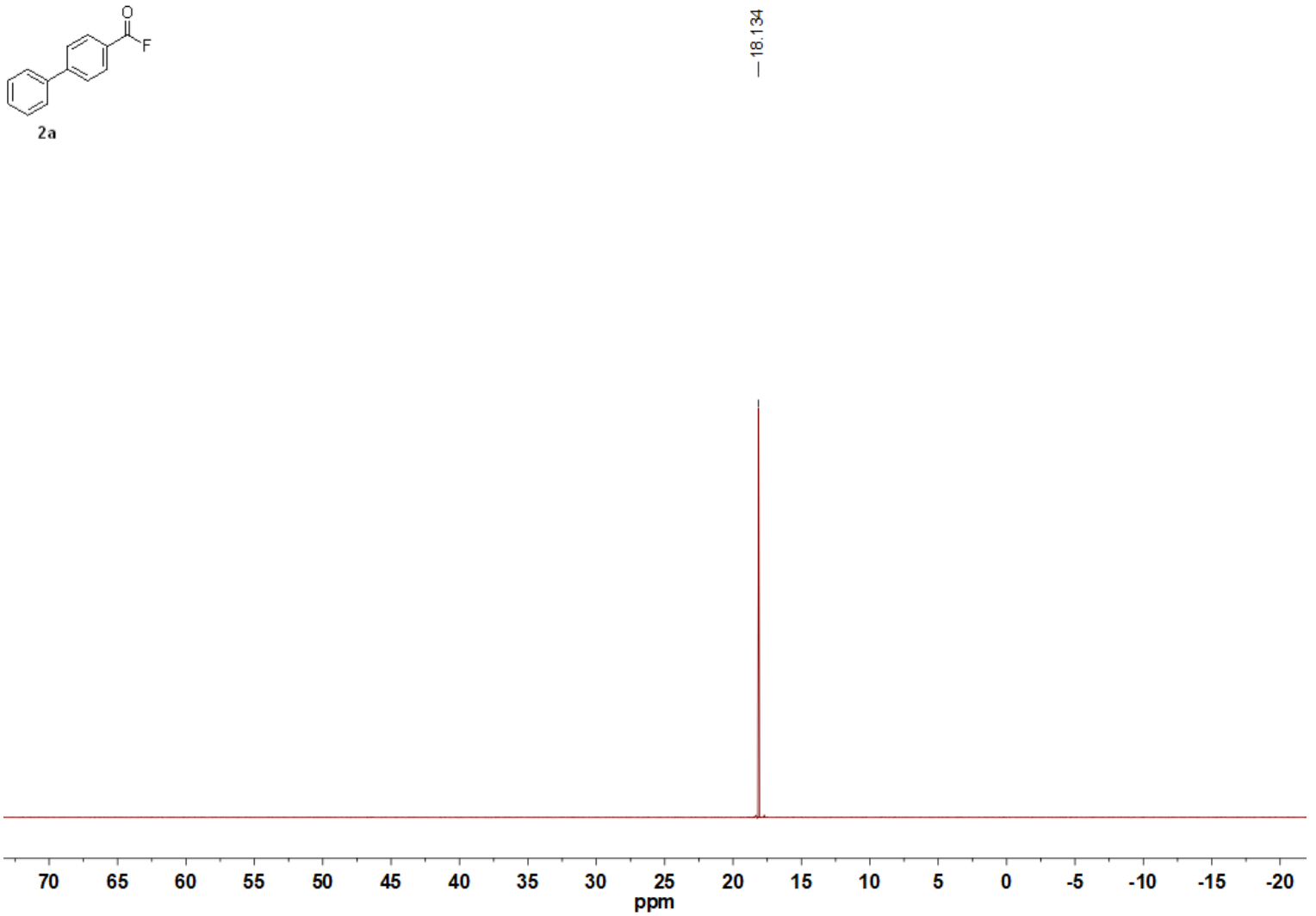
X. NMR Spectra



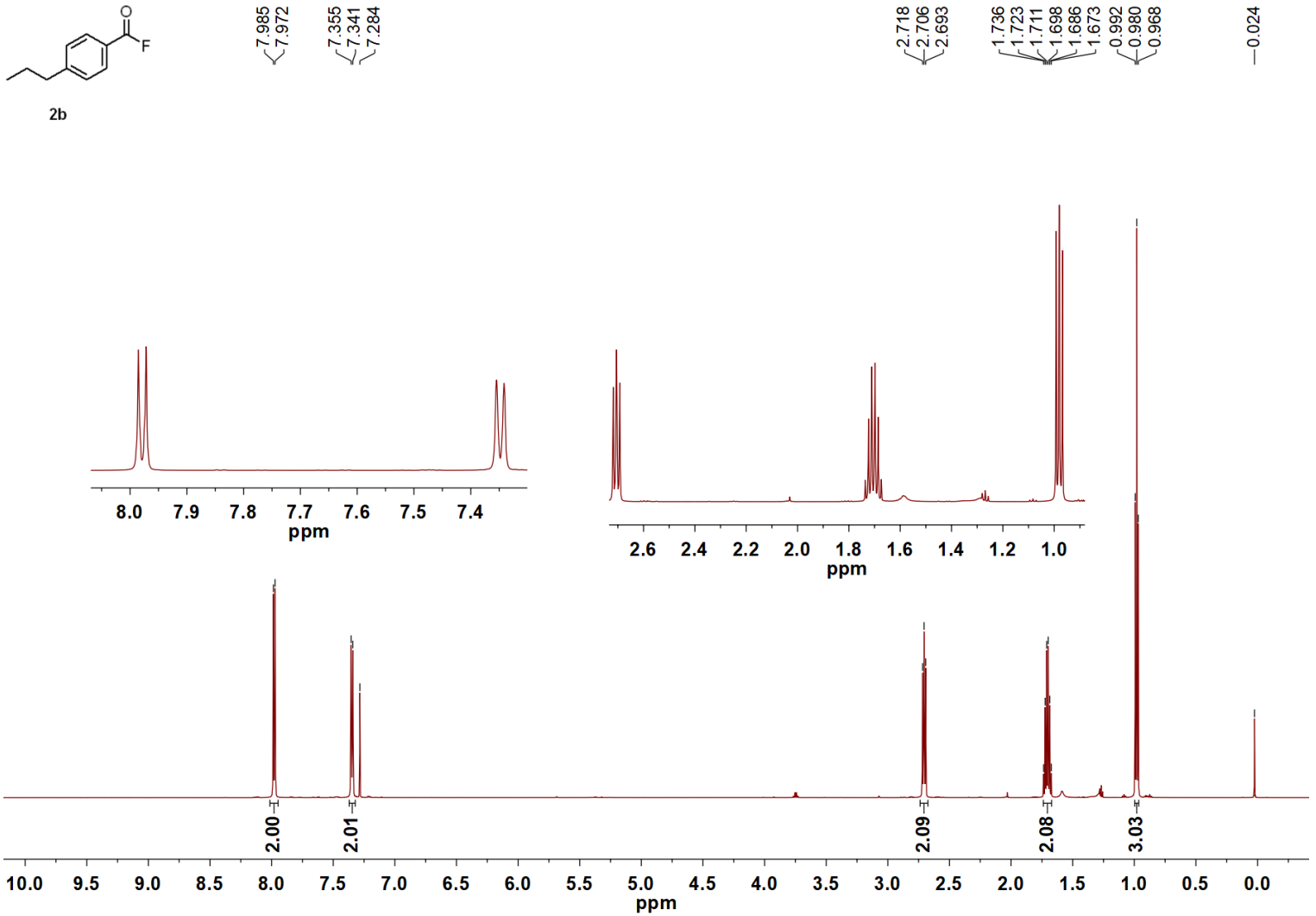
^{1}H NMR Spectrum of 2a (600 MHz, $CDCl_3$)



^{13}C NMR Spectrum of 2a (151 MHz, $CDCl_3$)



^{19}F NMR Spectrum of 2a (565 MHz, $CDCl_3$)



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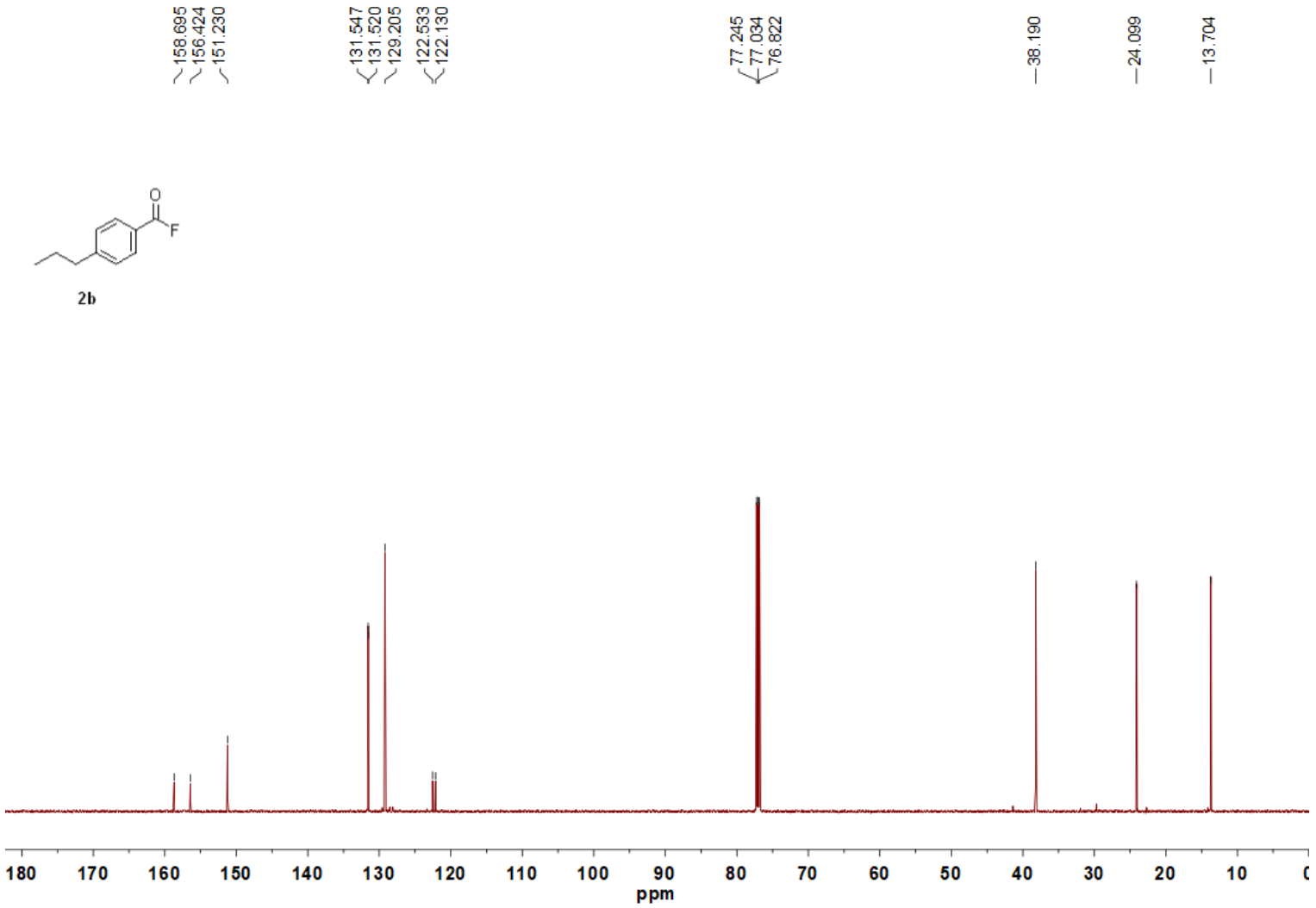

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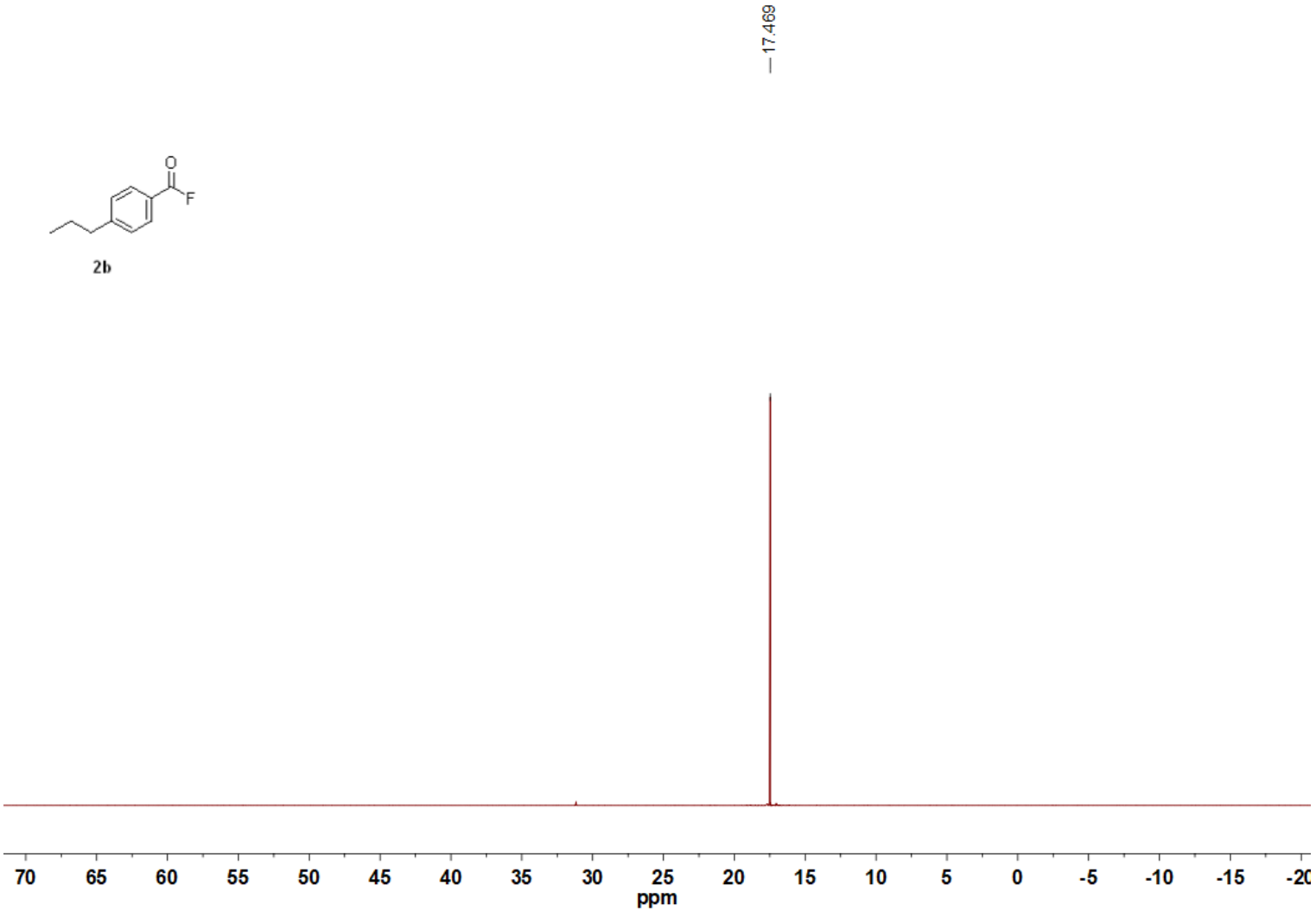
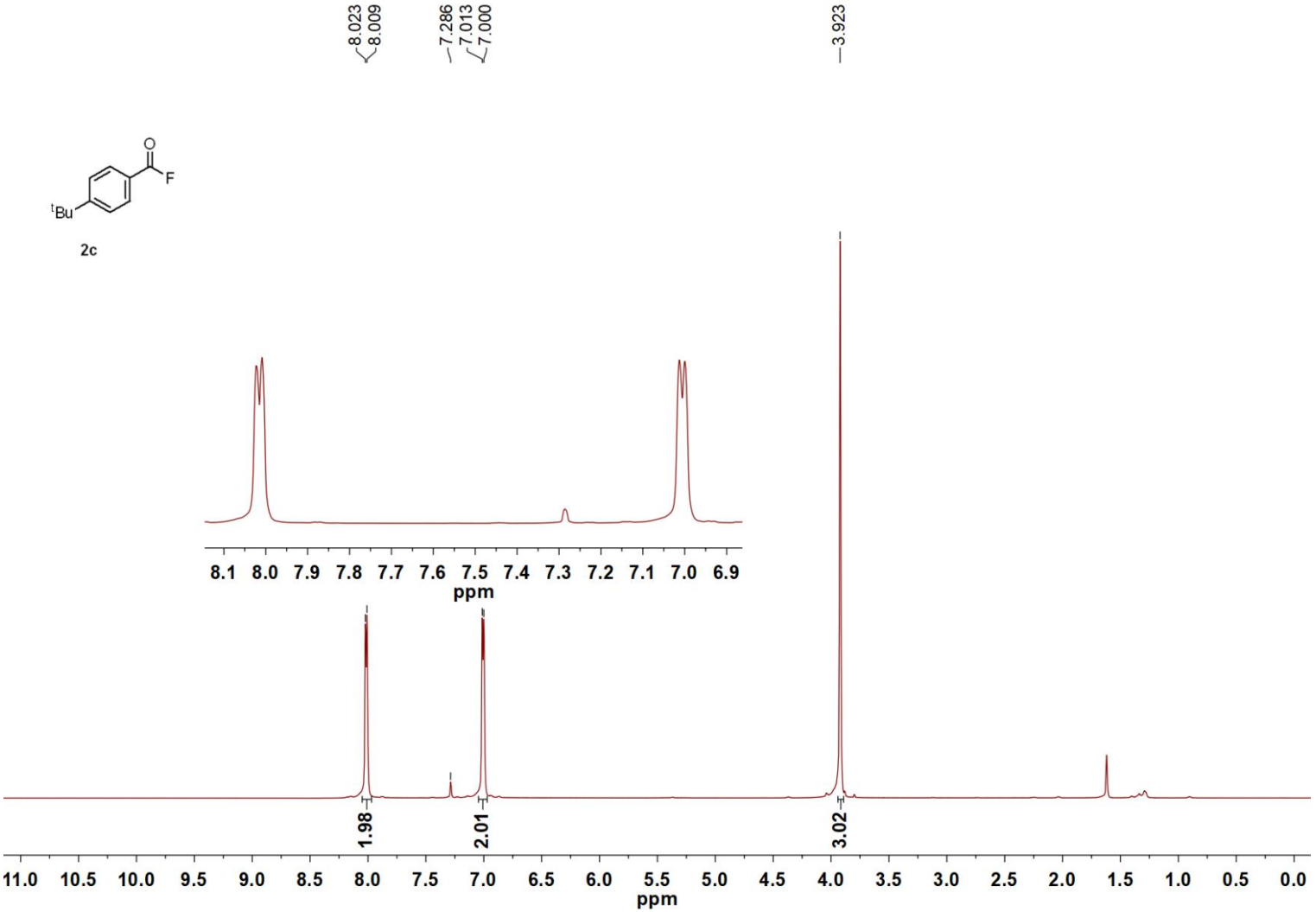


^{19}F NMR Spectrum of 2b (565 MHz, $CDCl_3$)



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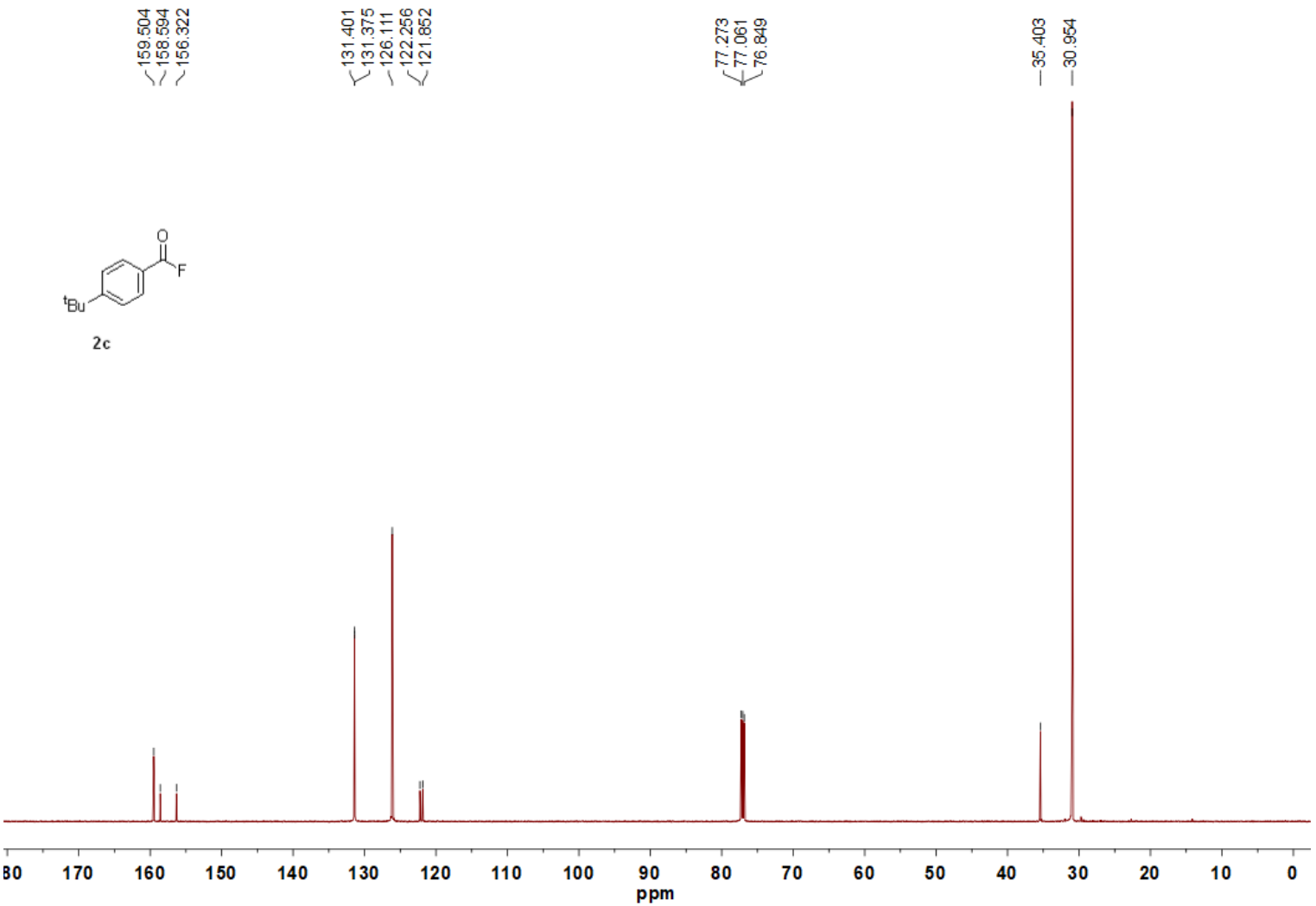

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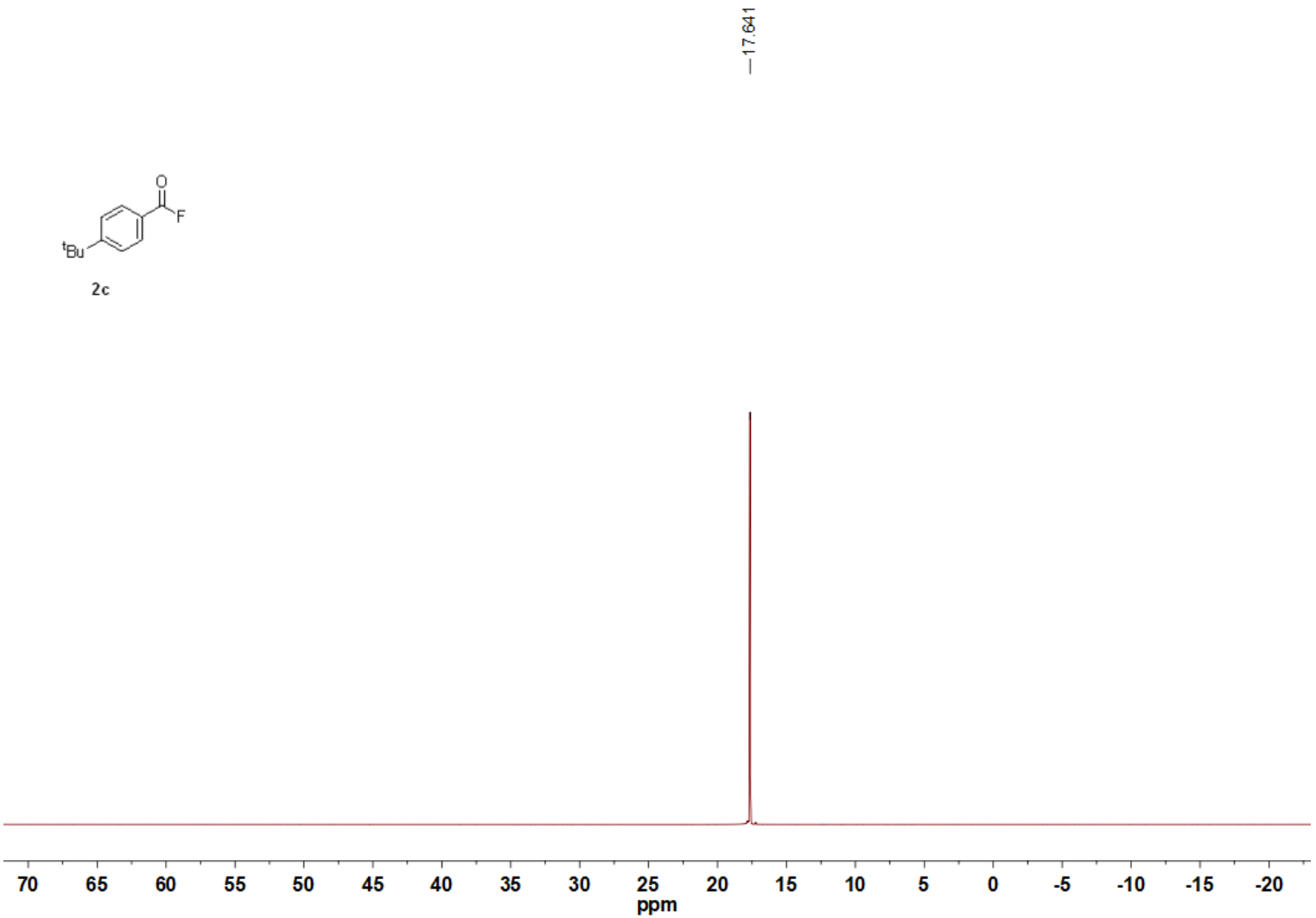

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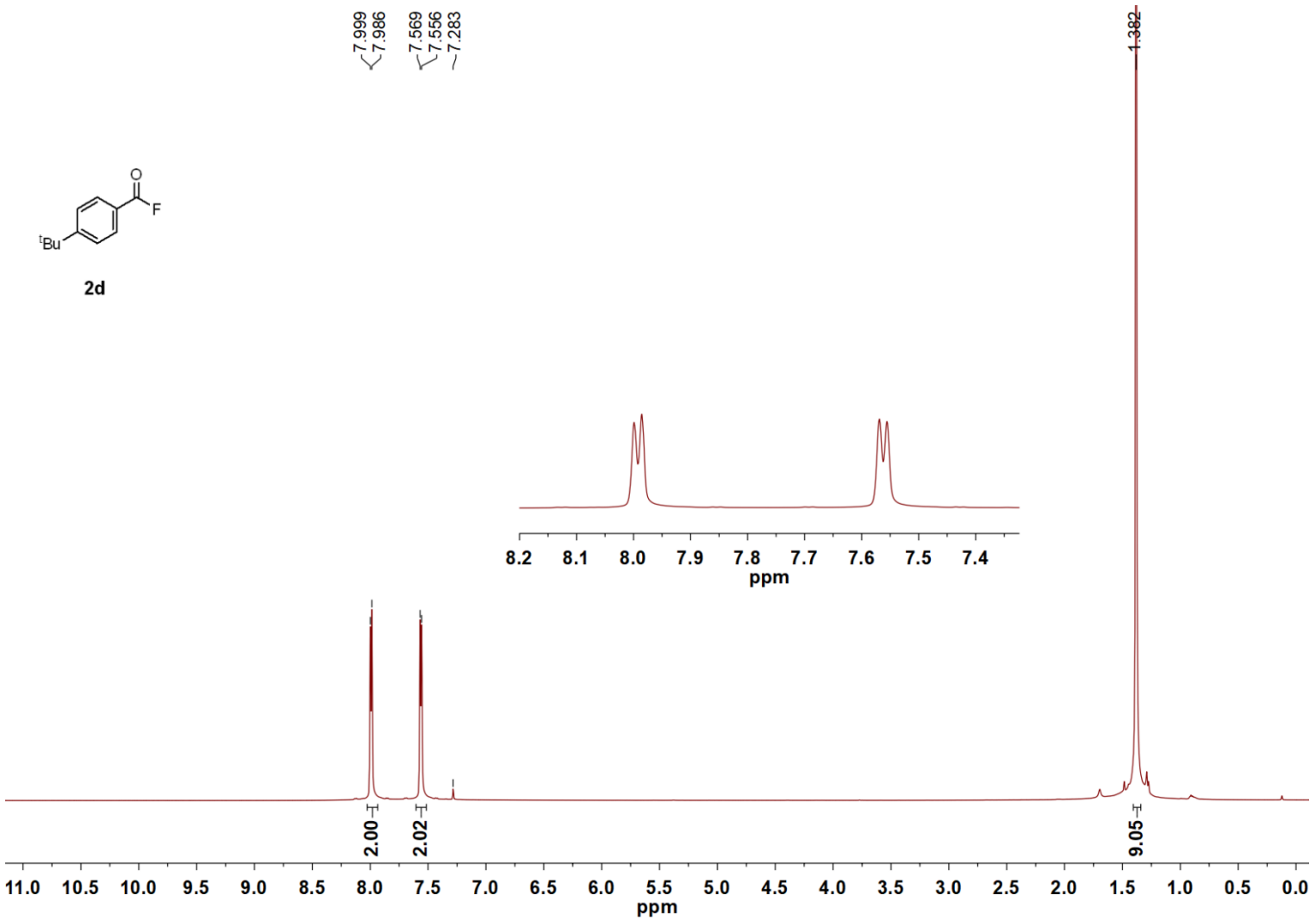

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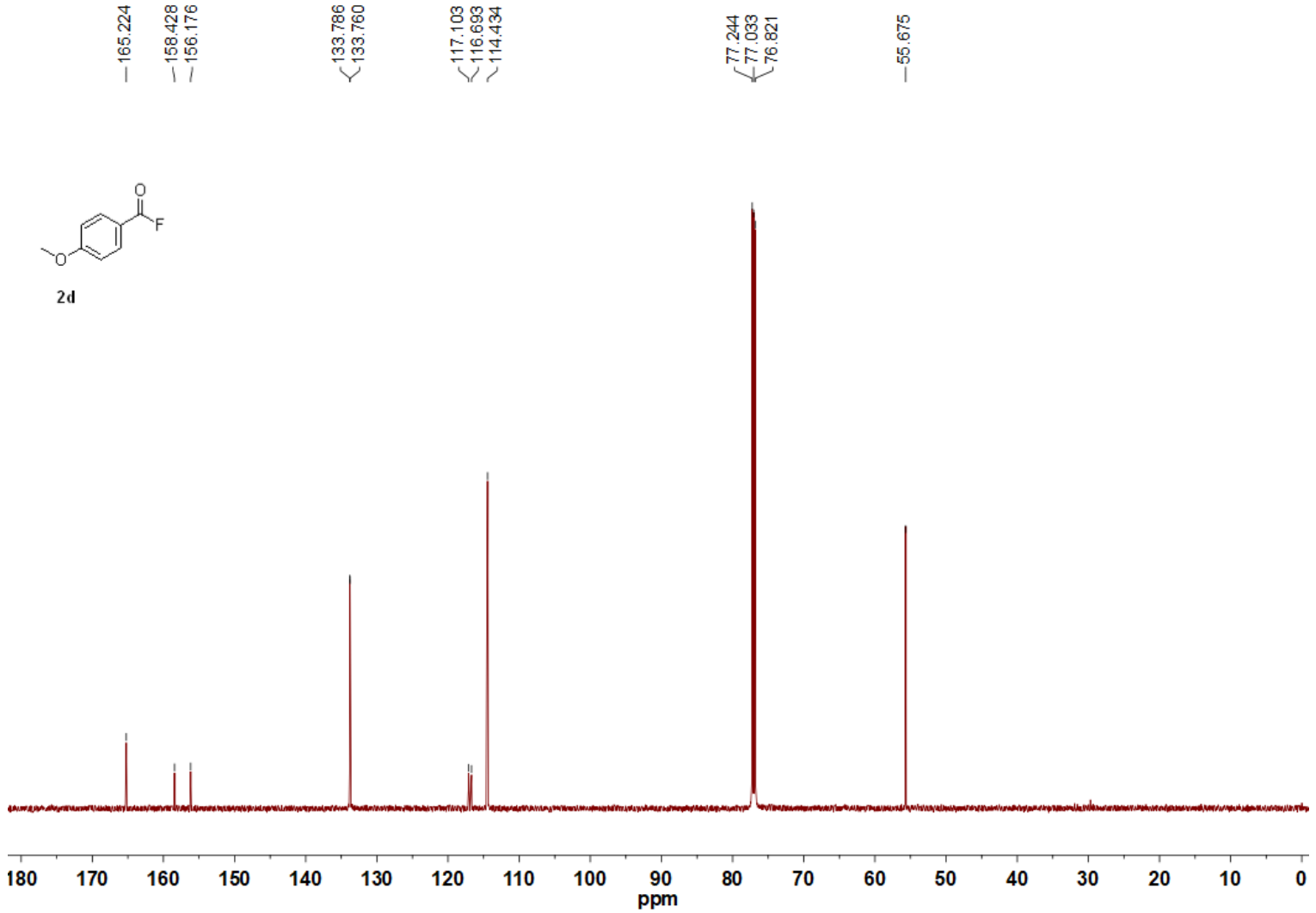

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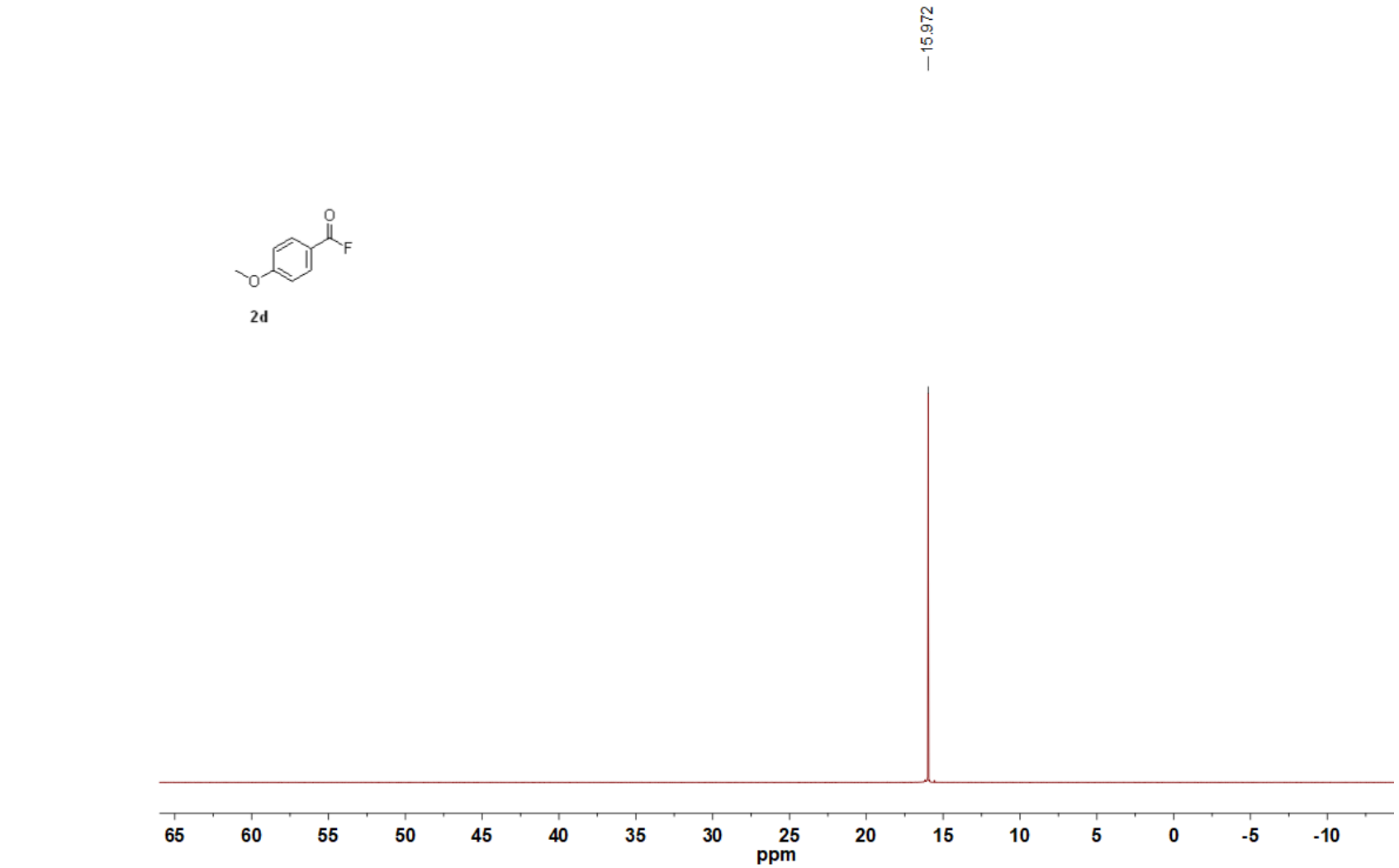

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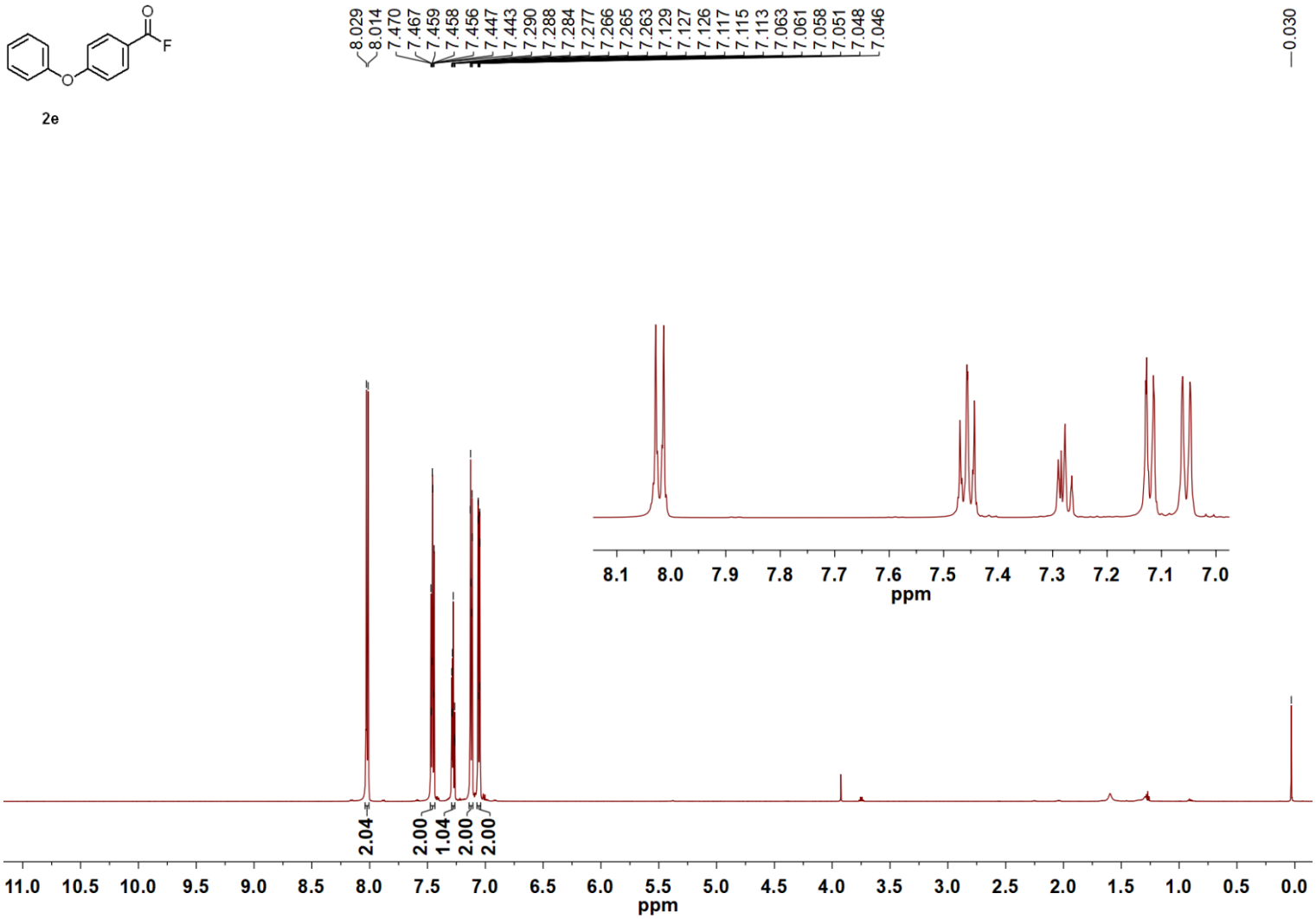

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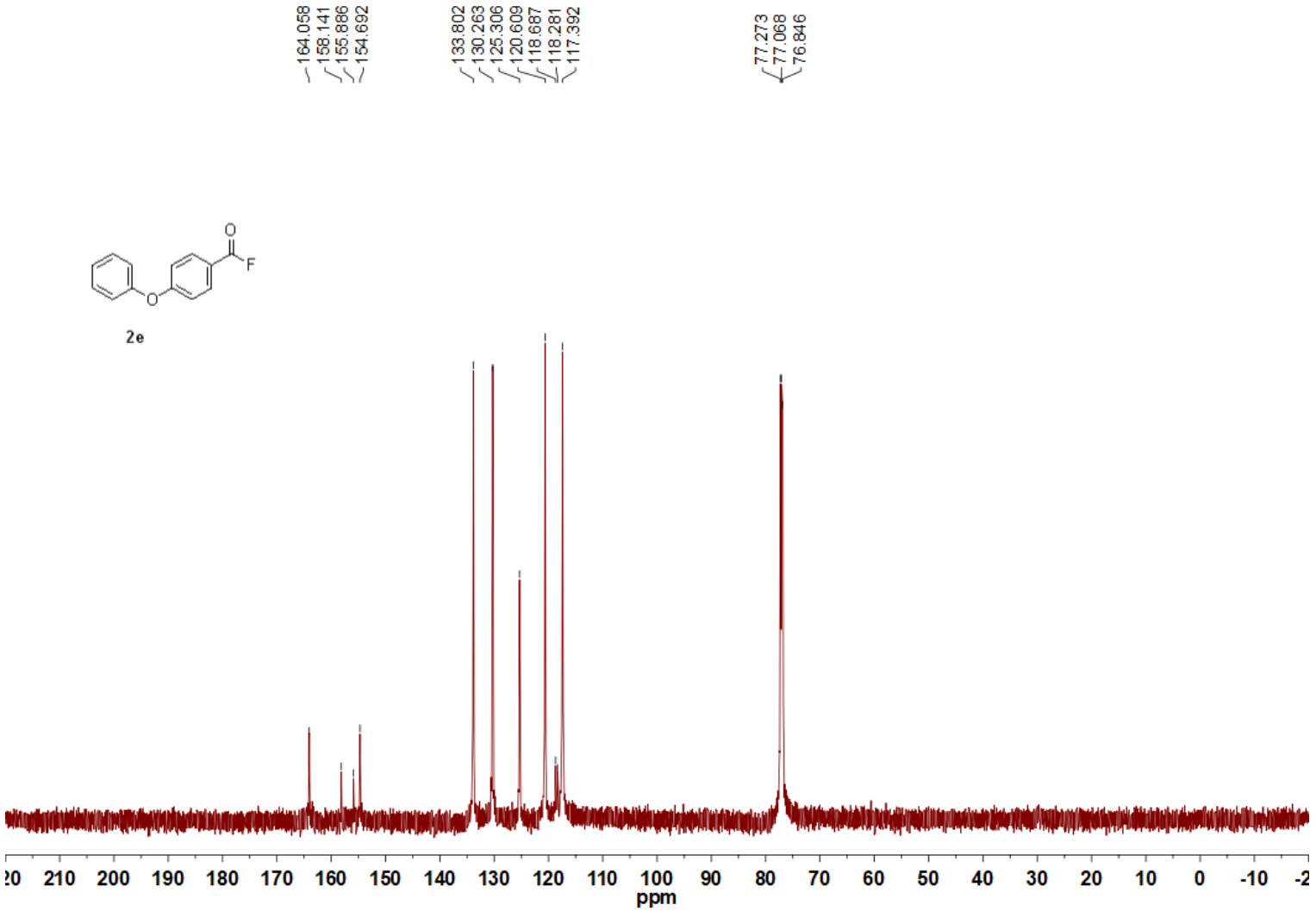

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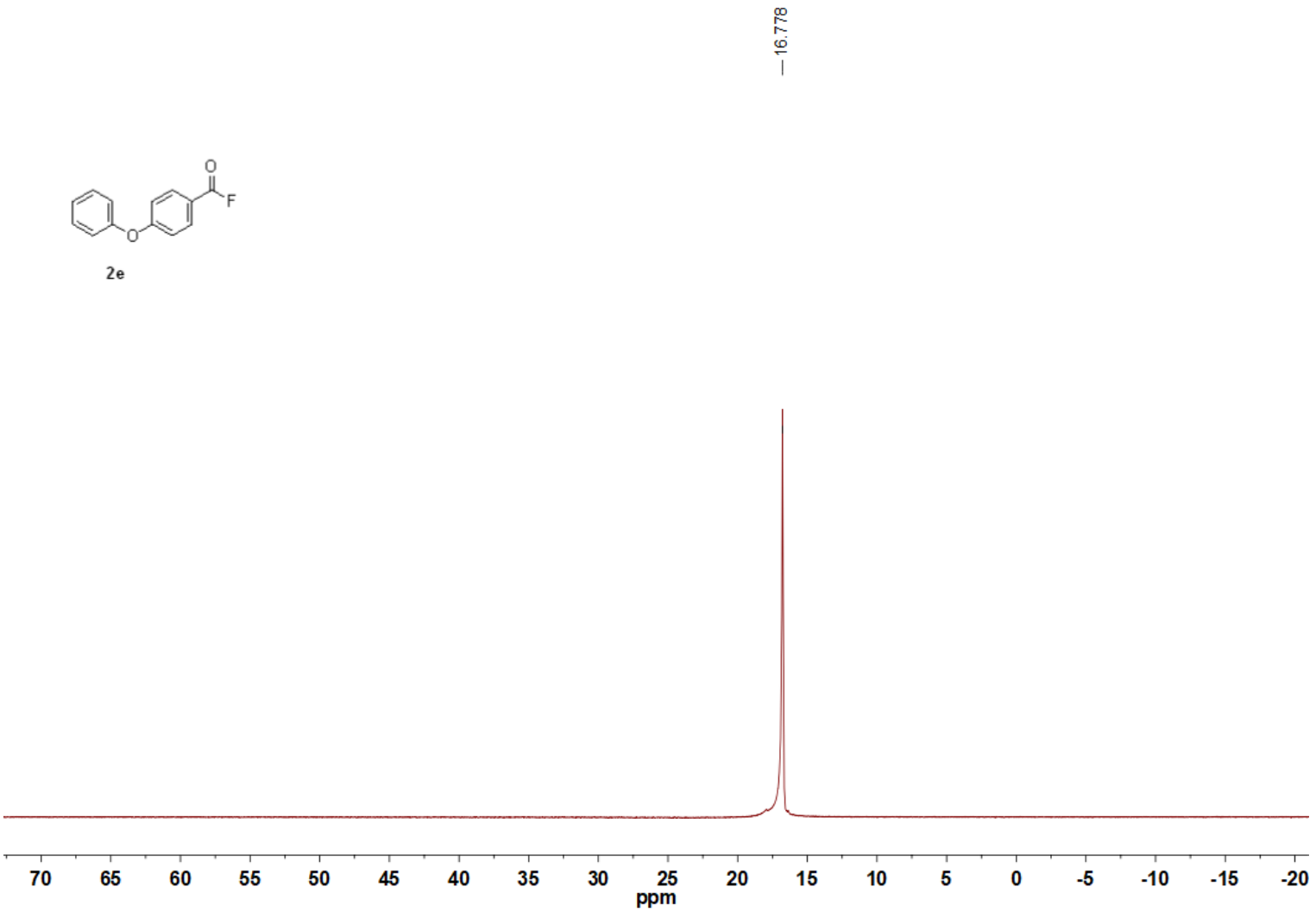
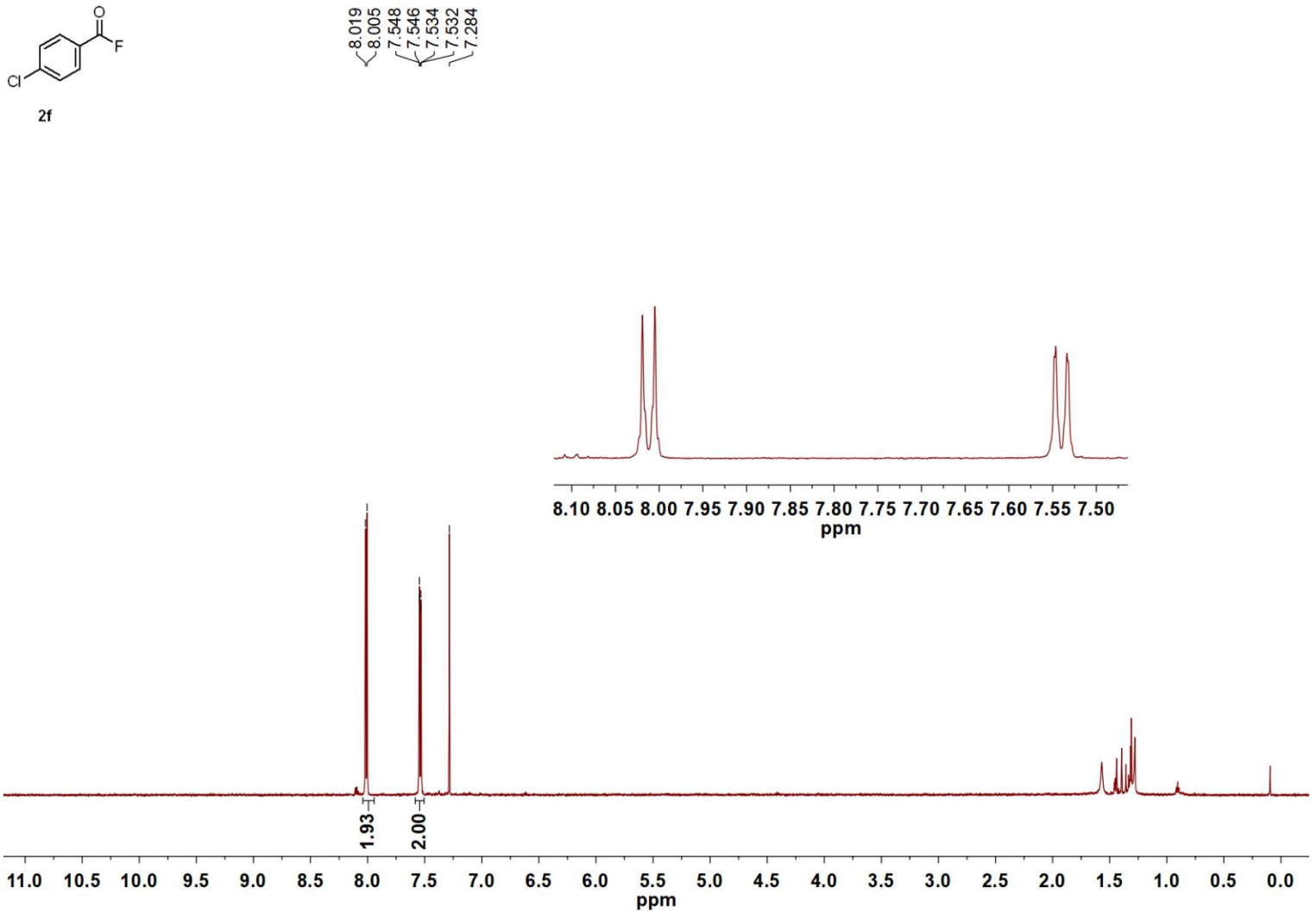


^{19}F NMR Spectrum of 2e (565 MHz, $CDCl_3$)



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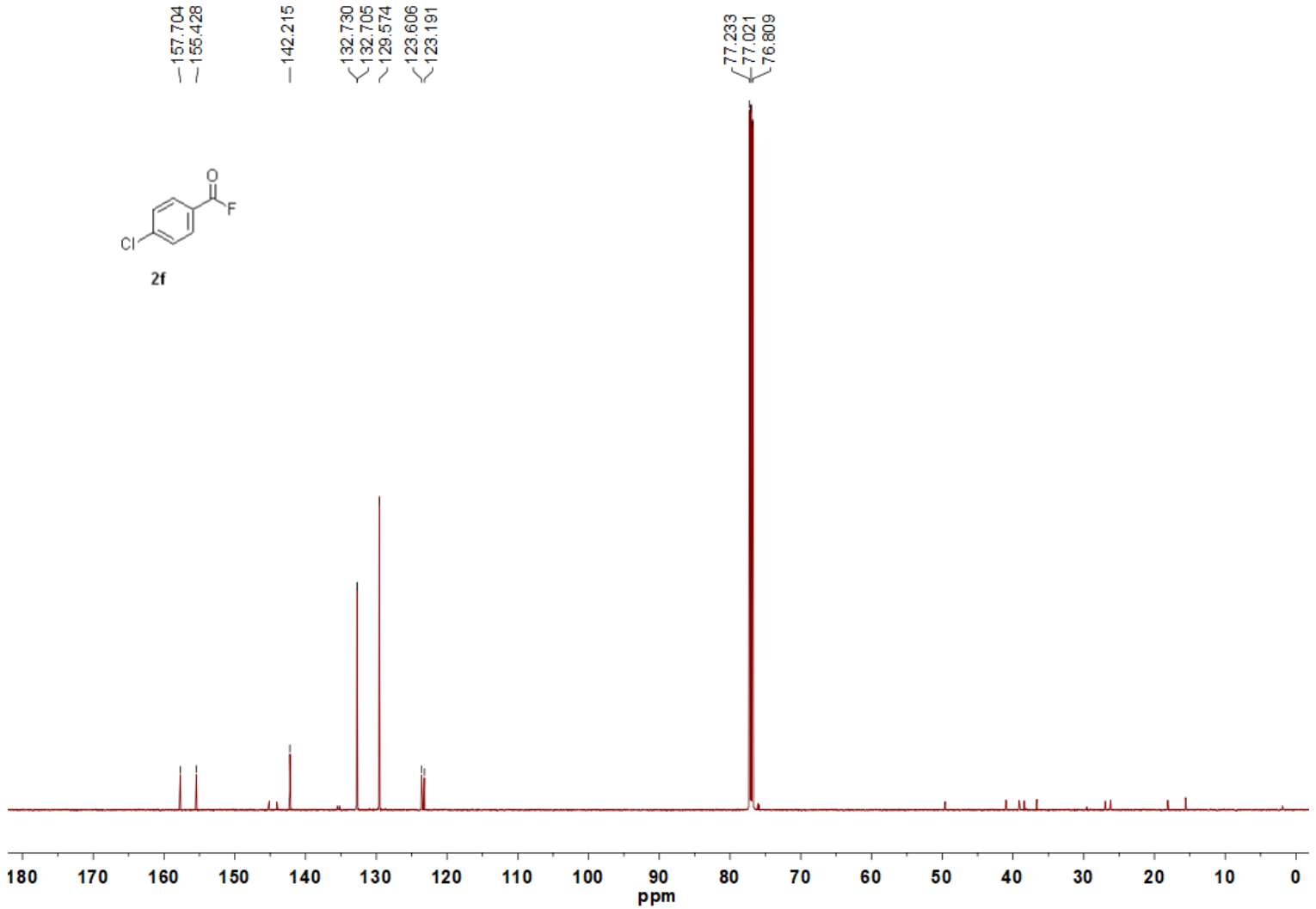

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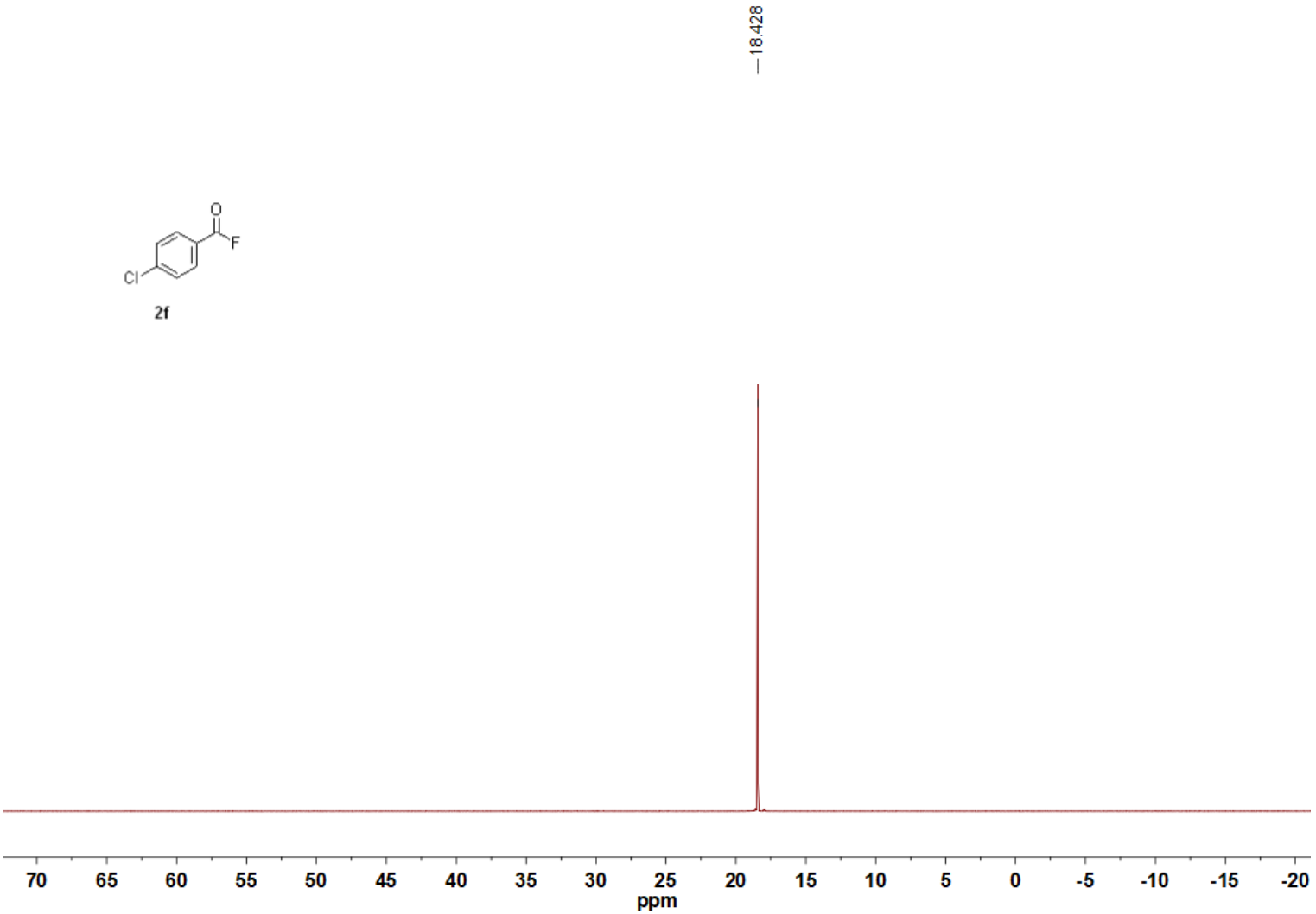

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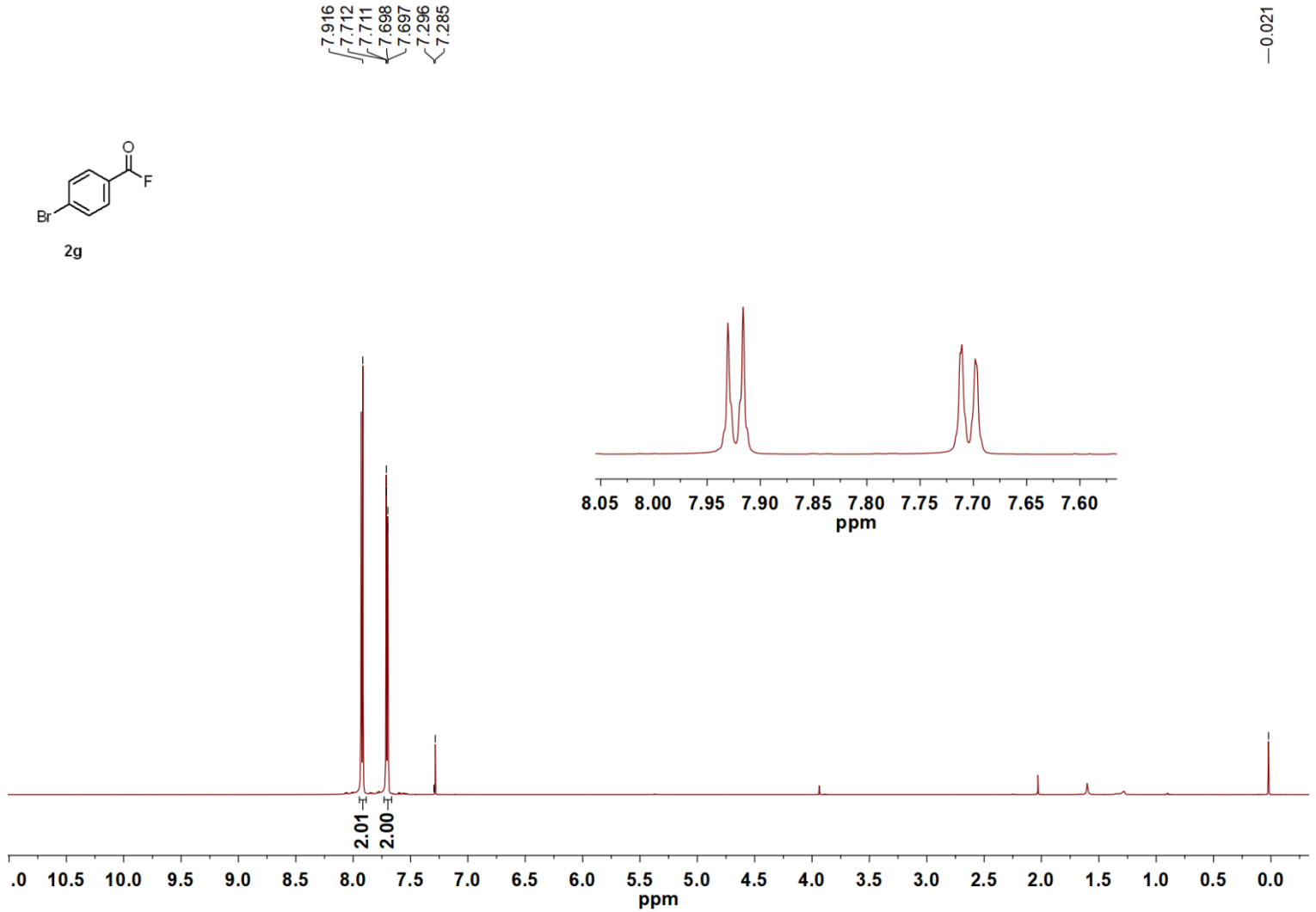

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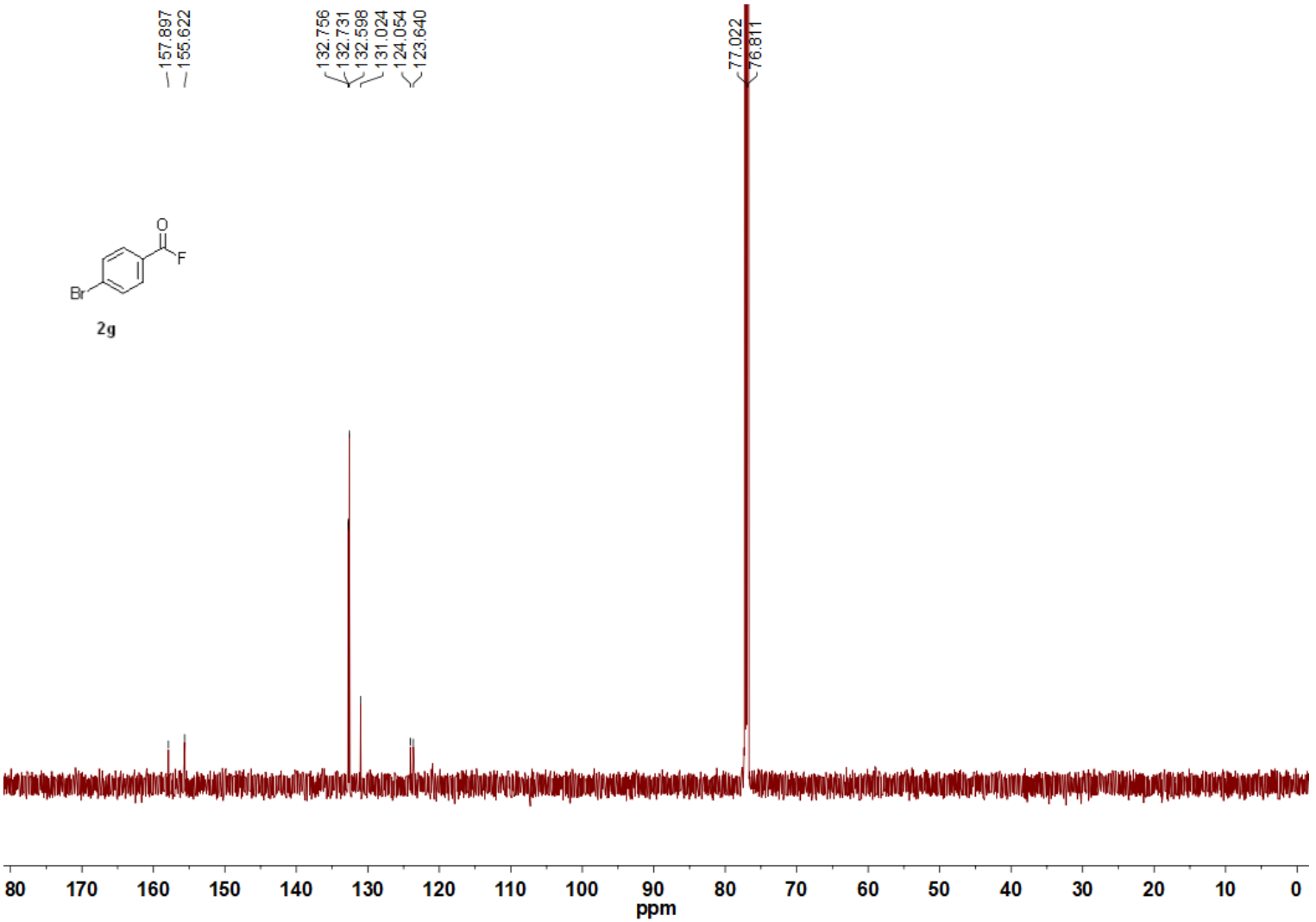

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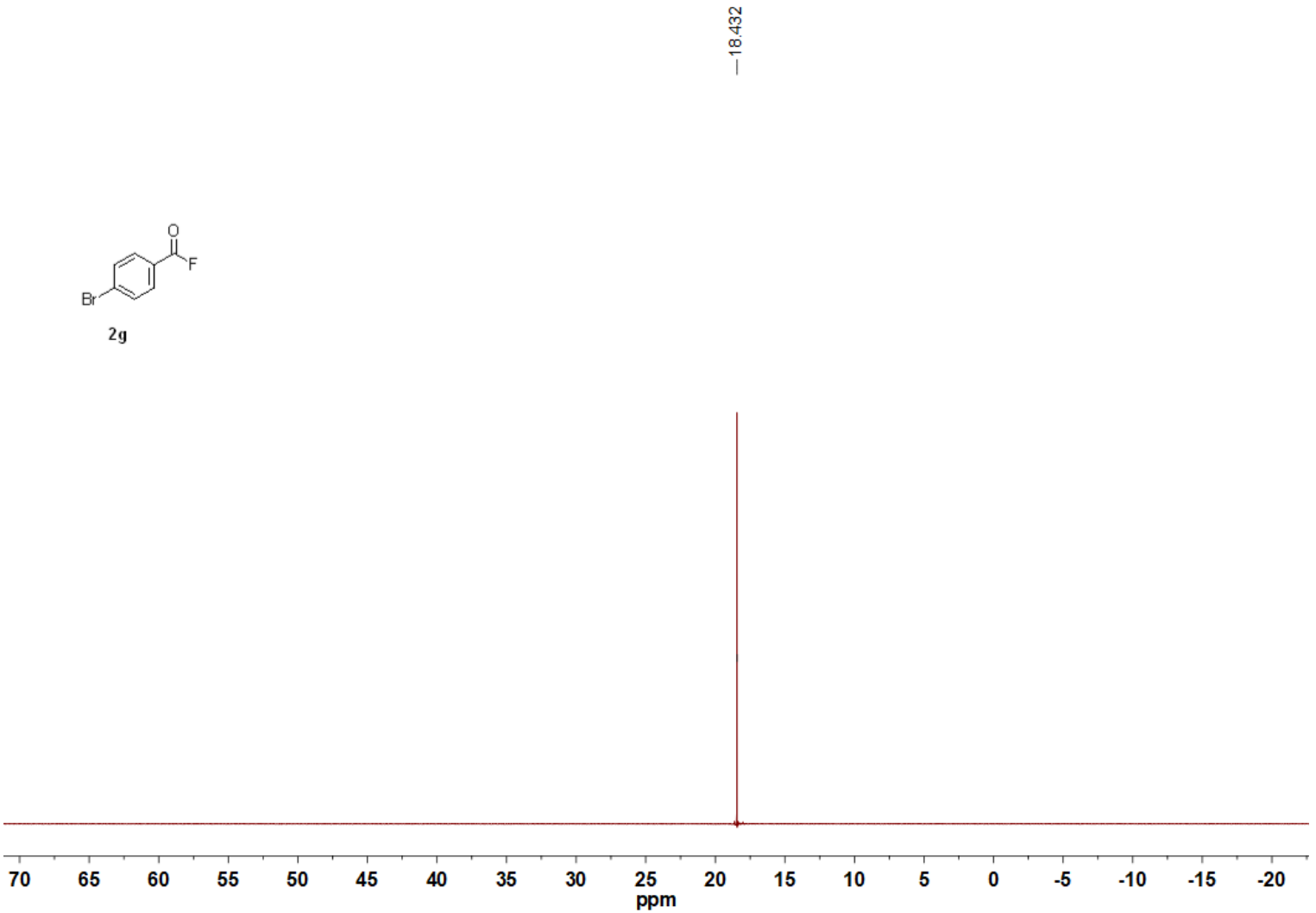

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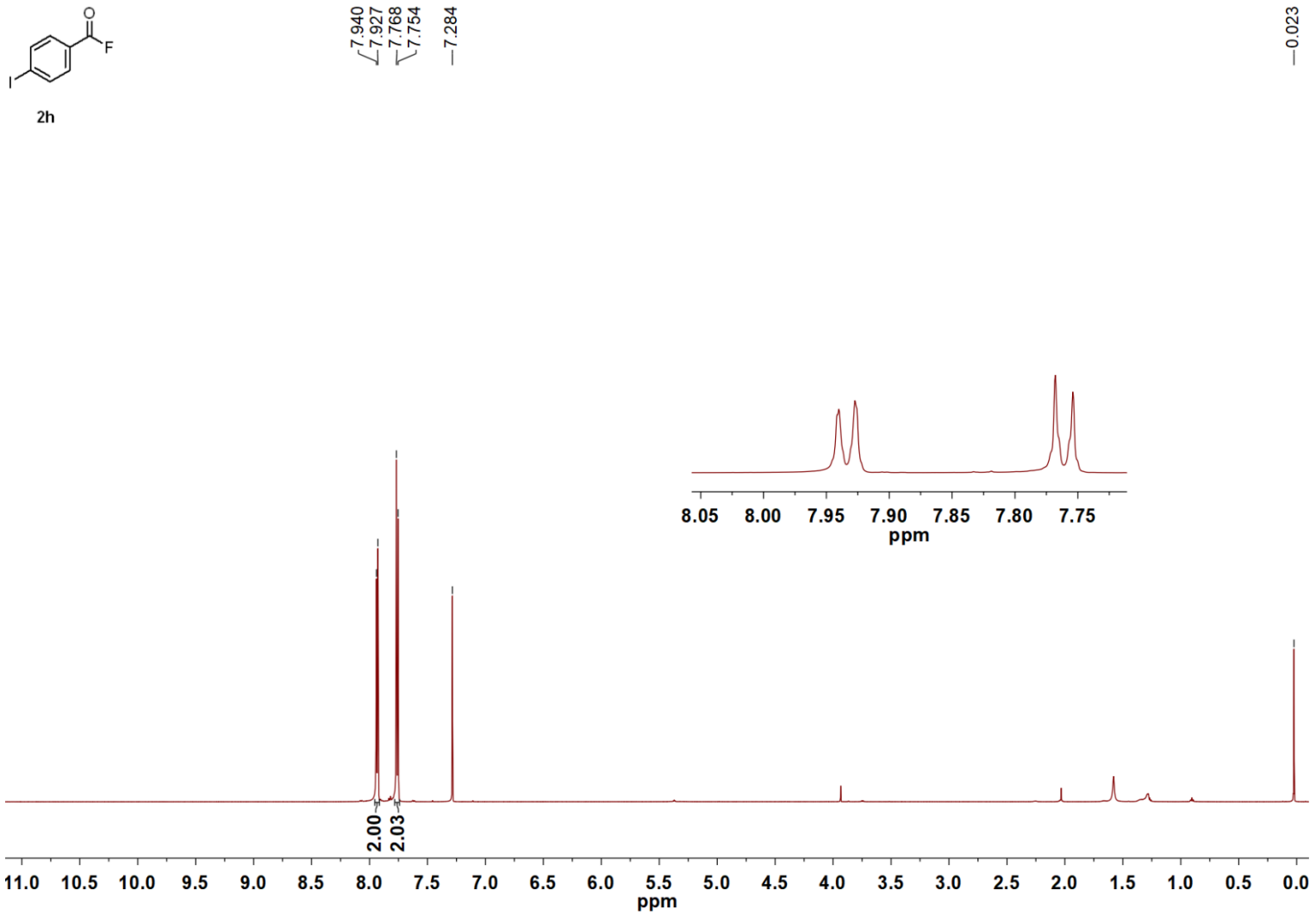
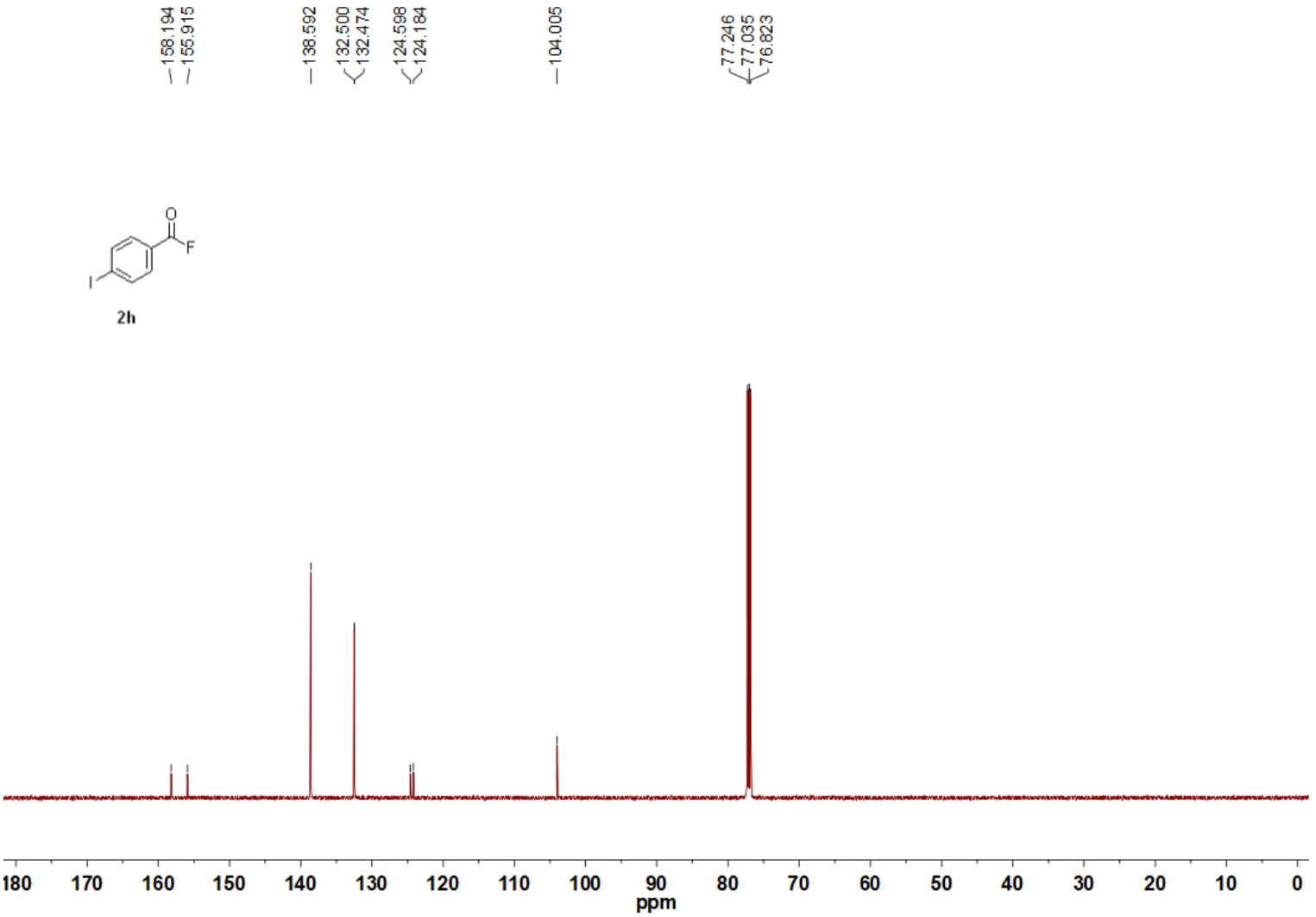
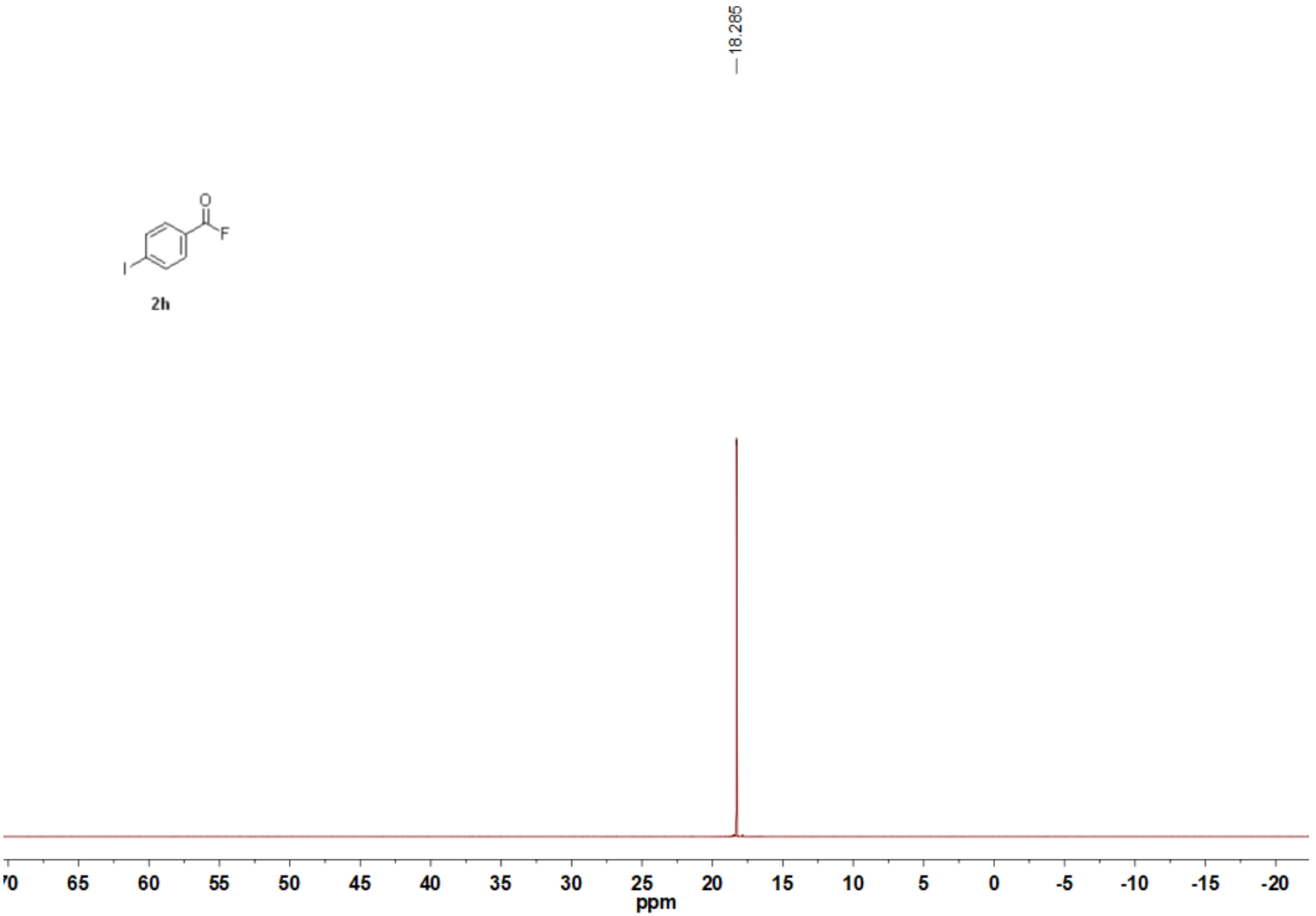


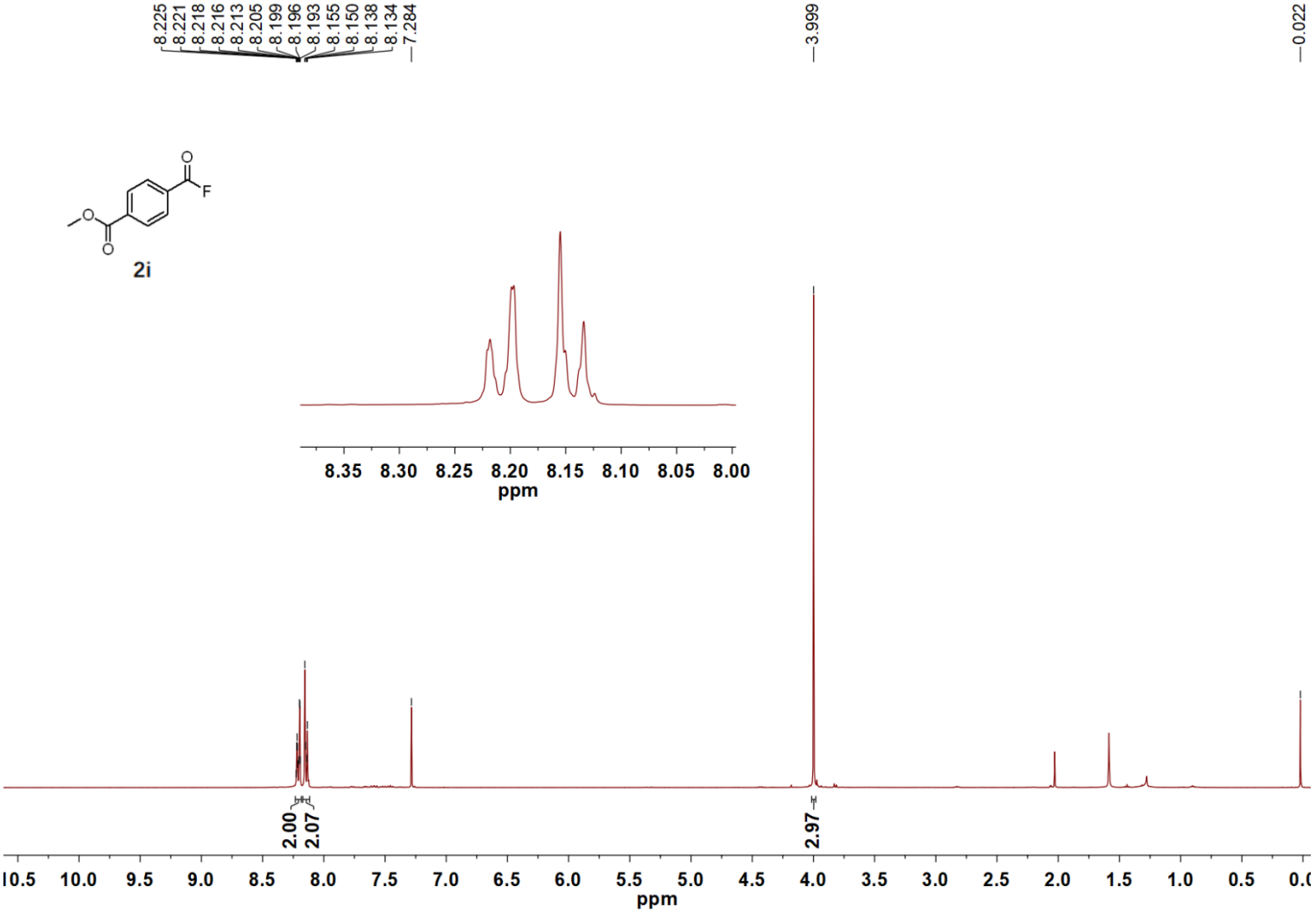
^{1}H NMR Spectrum of 2h (600 MHz, $CDCl_3$)



^{13}C NMR Spectrum of 2h (151 MHz, $CDCl_3$)



^{19}F NMR Spectrum of 2h (565 MHz, $CDCl_3$)



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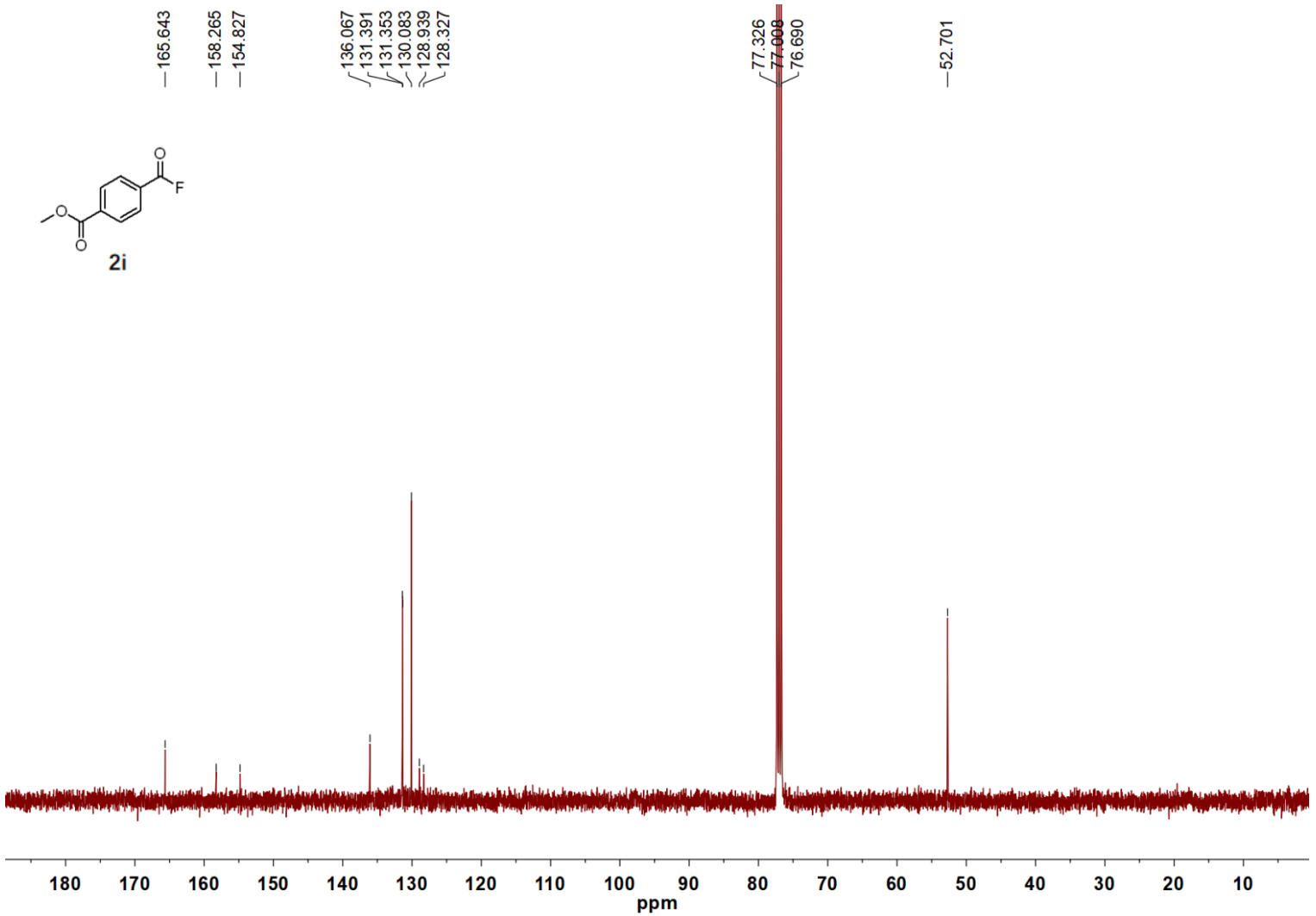
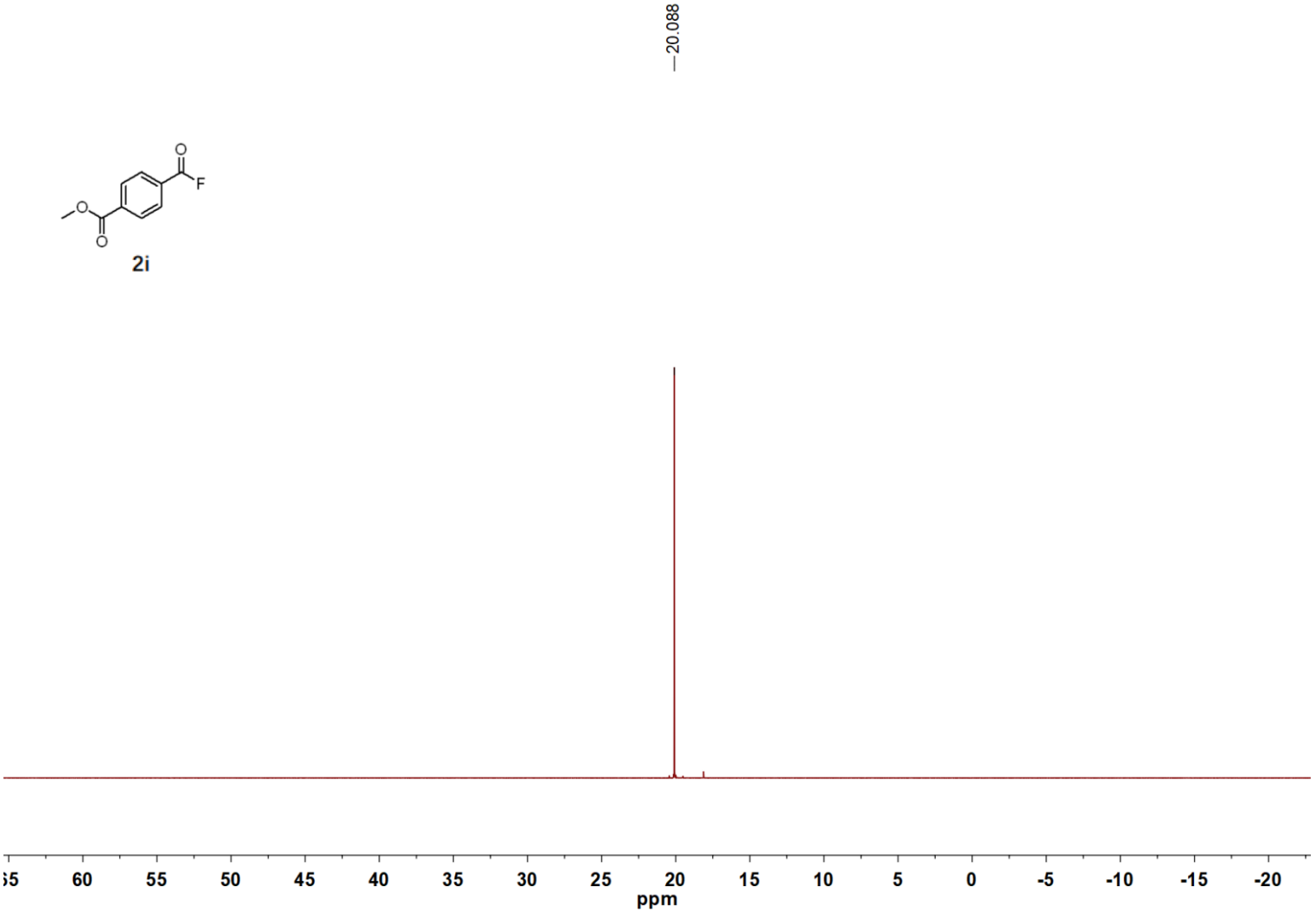
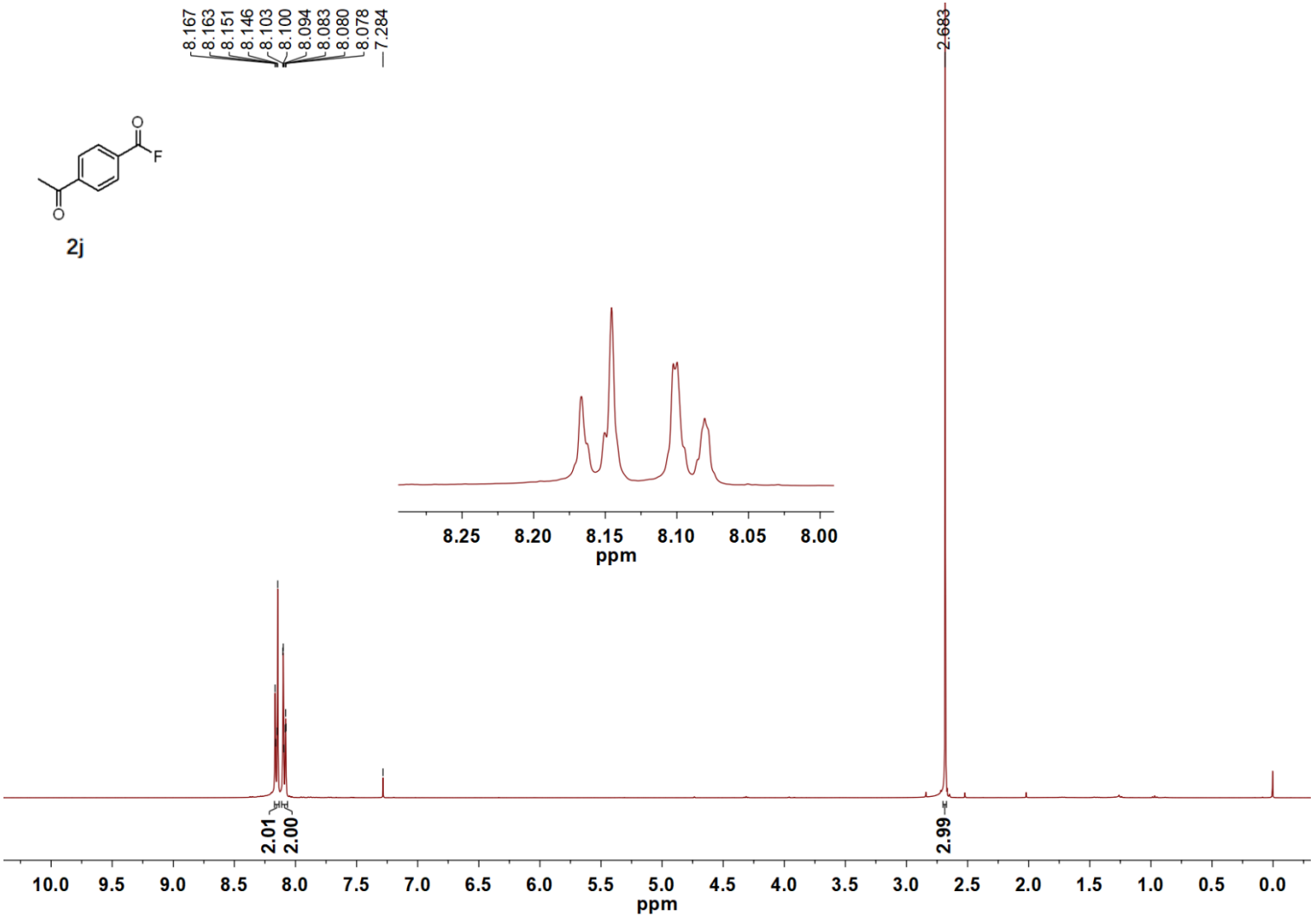


^{13}C NMR Spectrum of 2i (101 MHz, $CDCl_3$)



^{13}F NMR Spectrum of 2i (377 MHz, $CDCl_3$)



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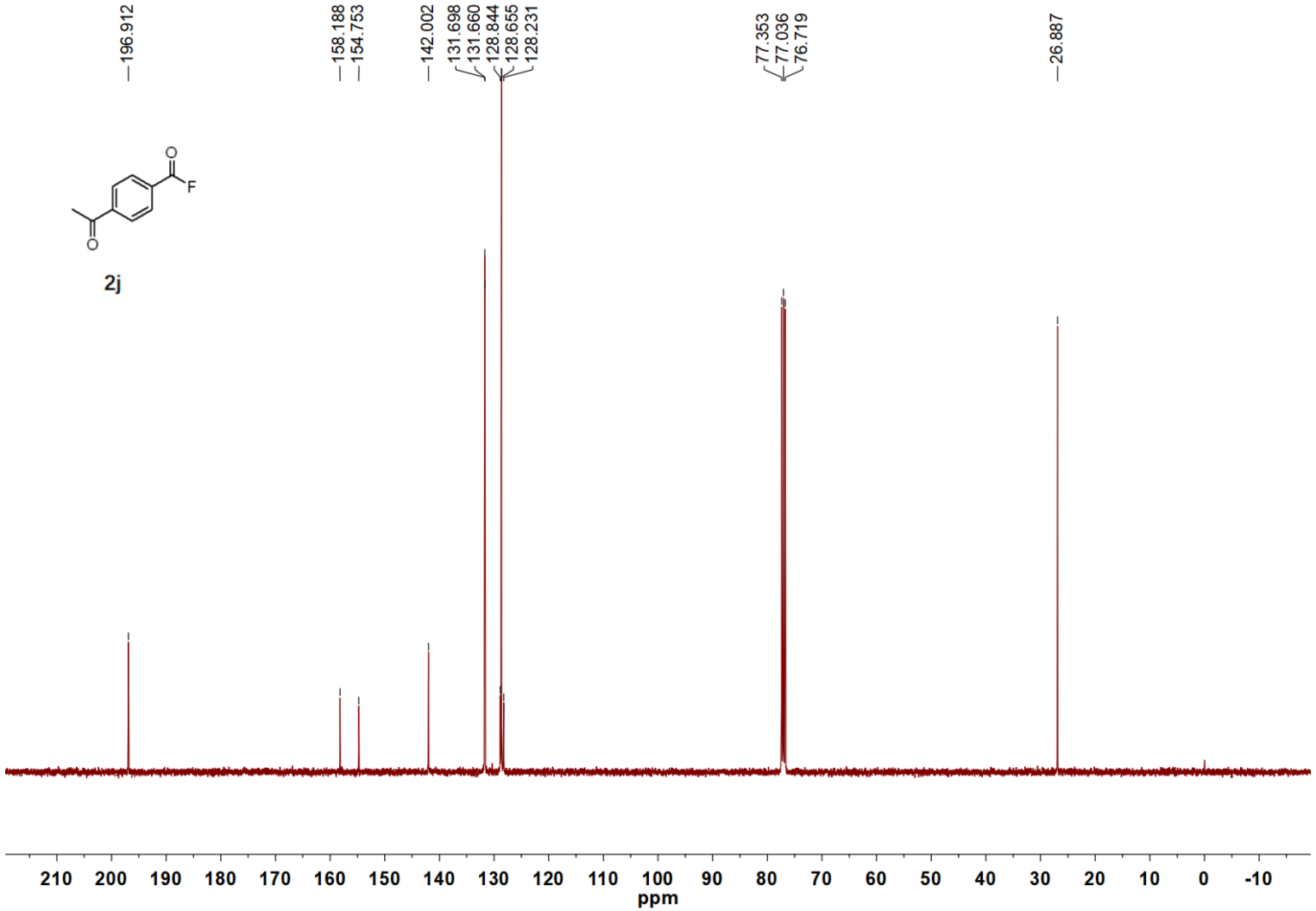
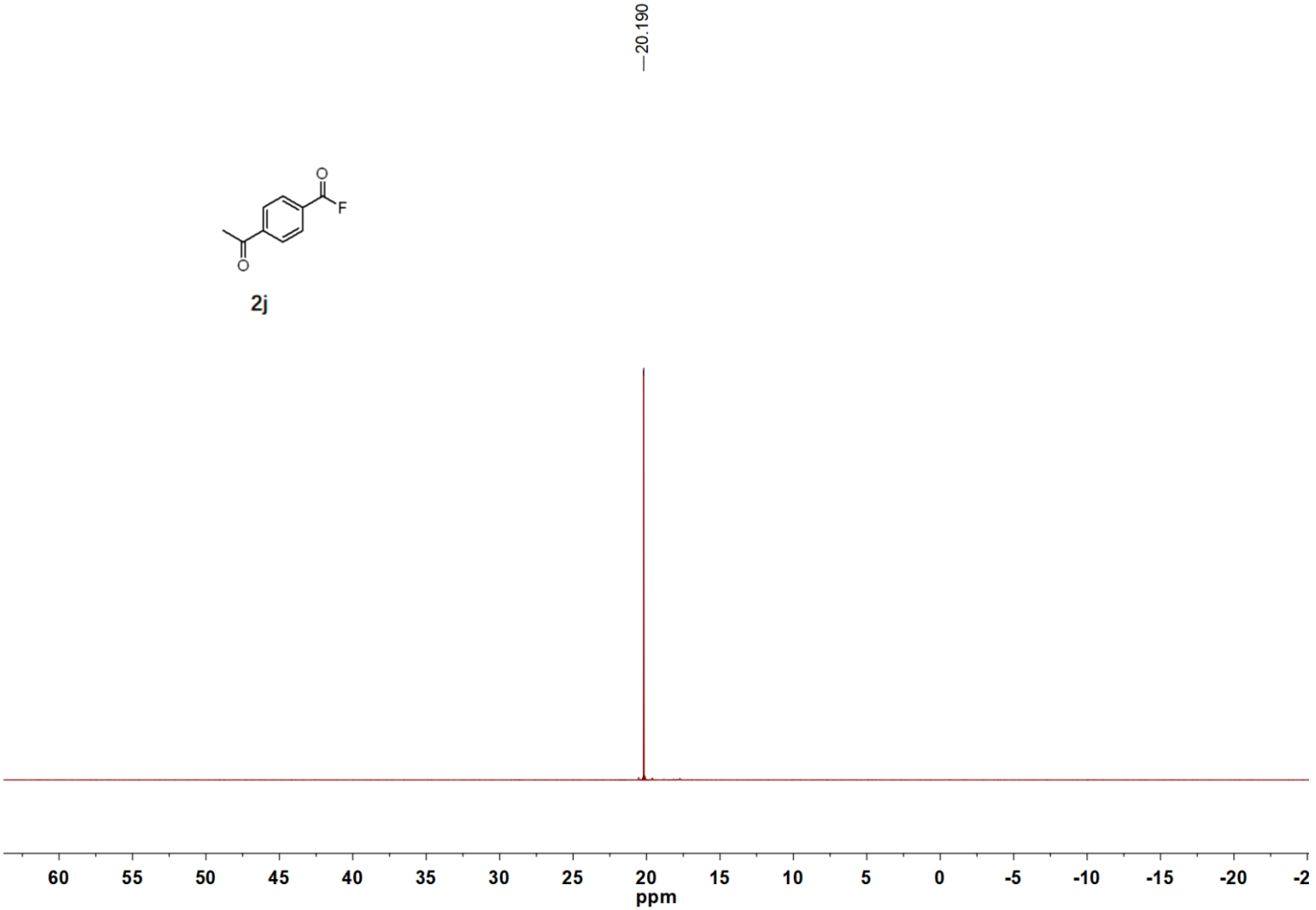


^{13}C NMR Spectrum of 2j (101 MHz, $CDCl_3$)



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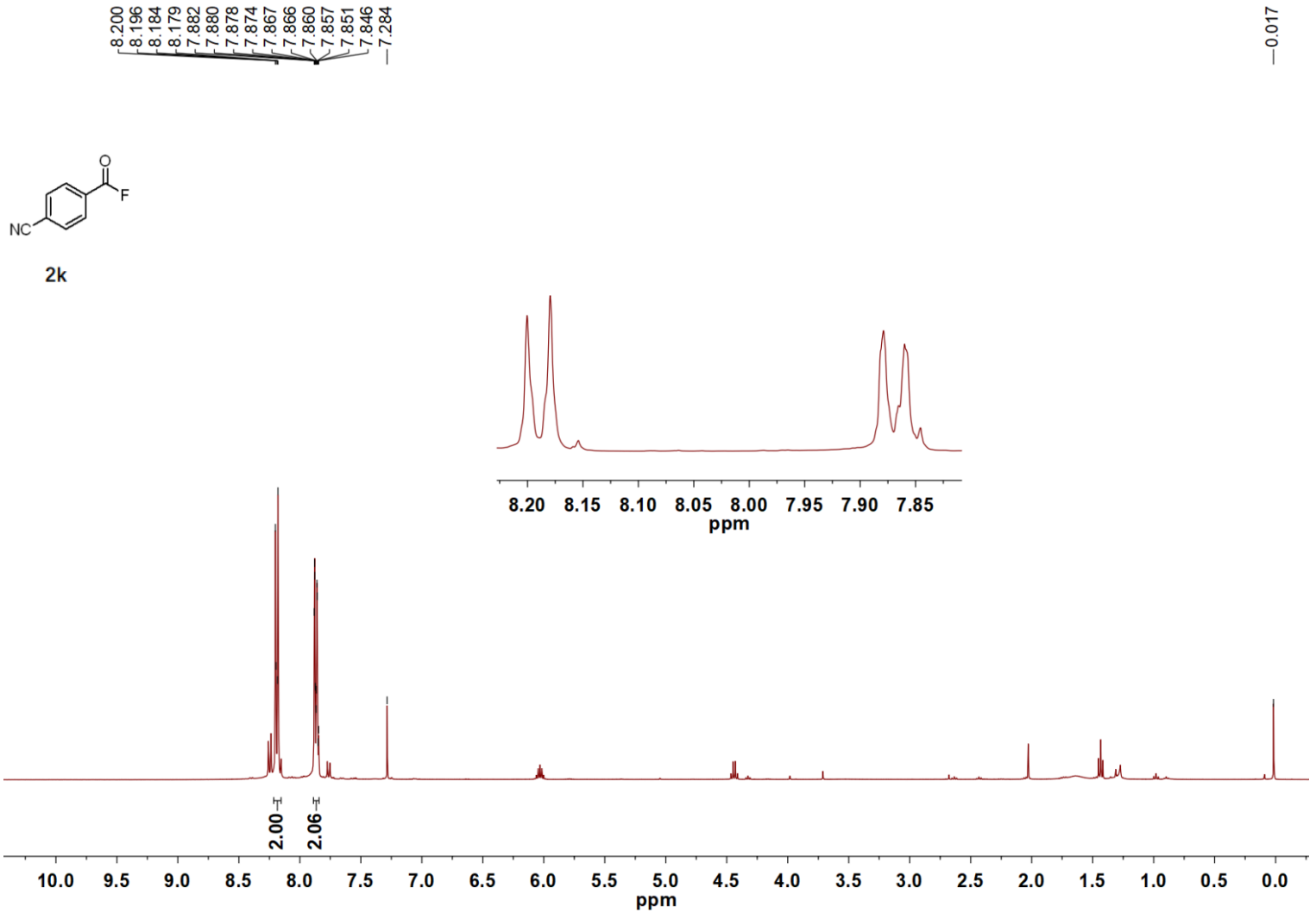

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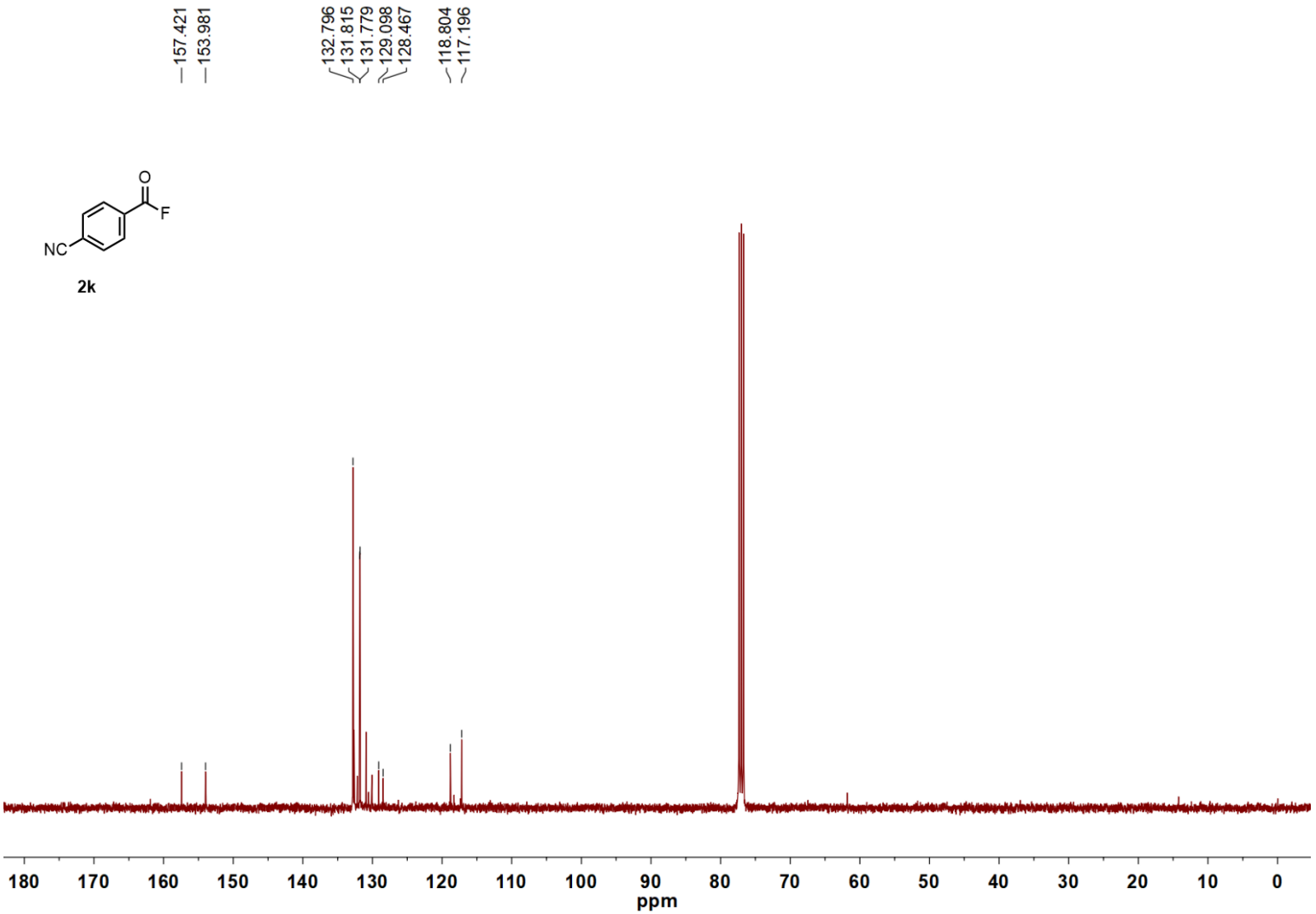

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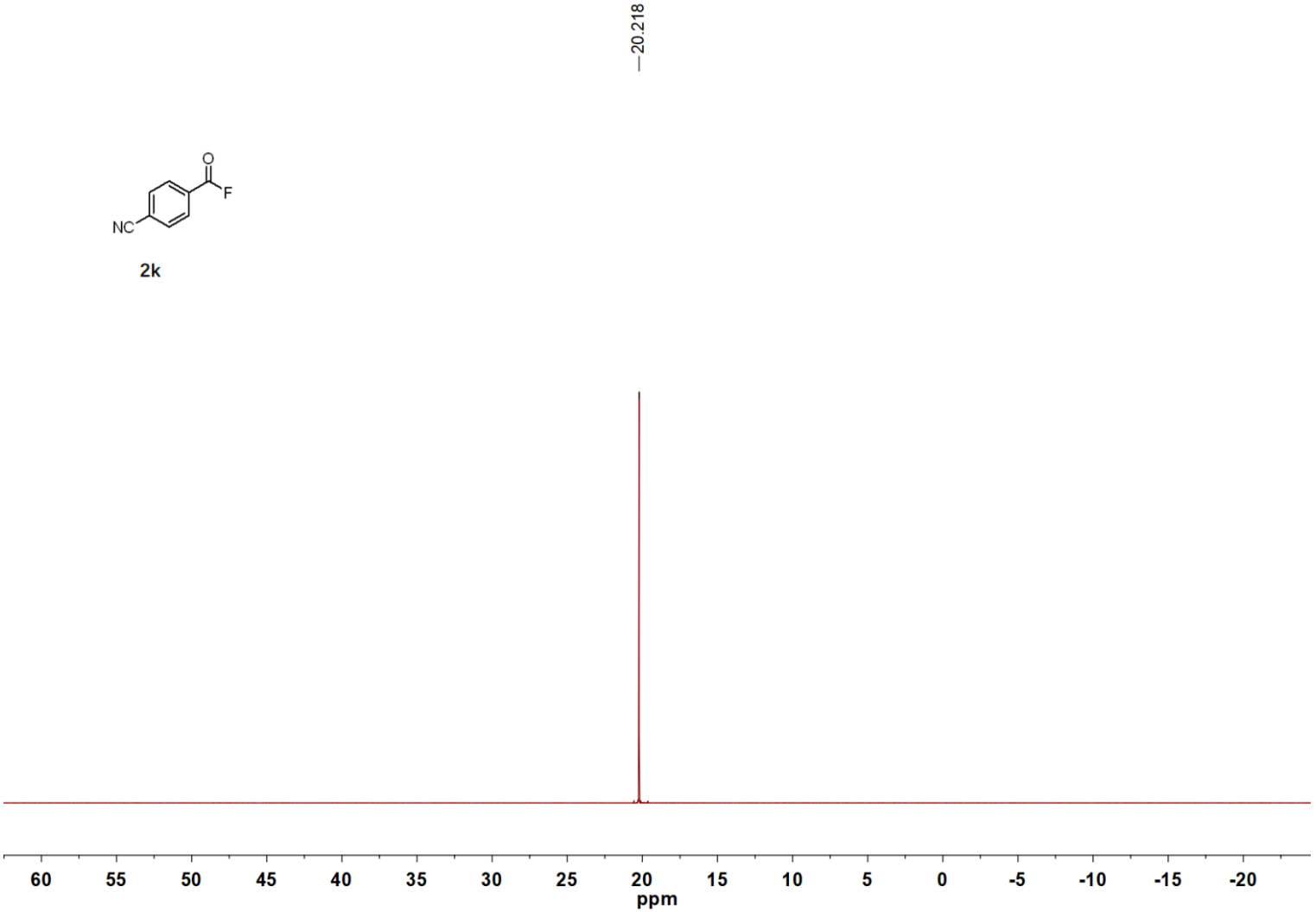

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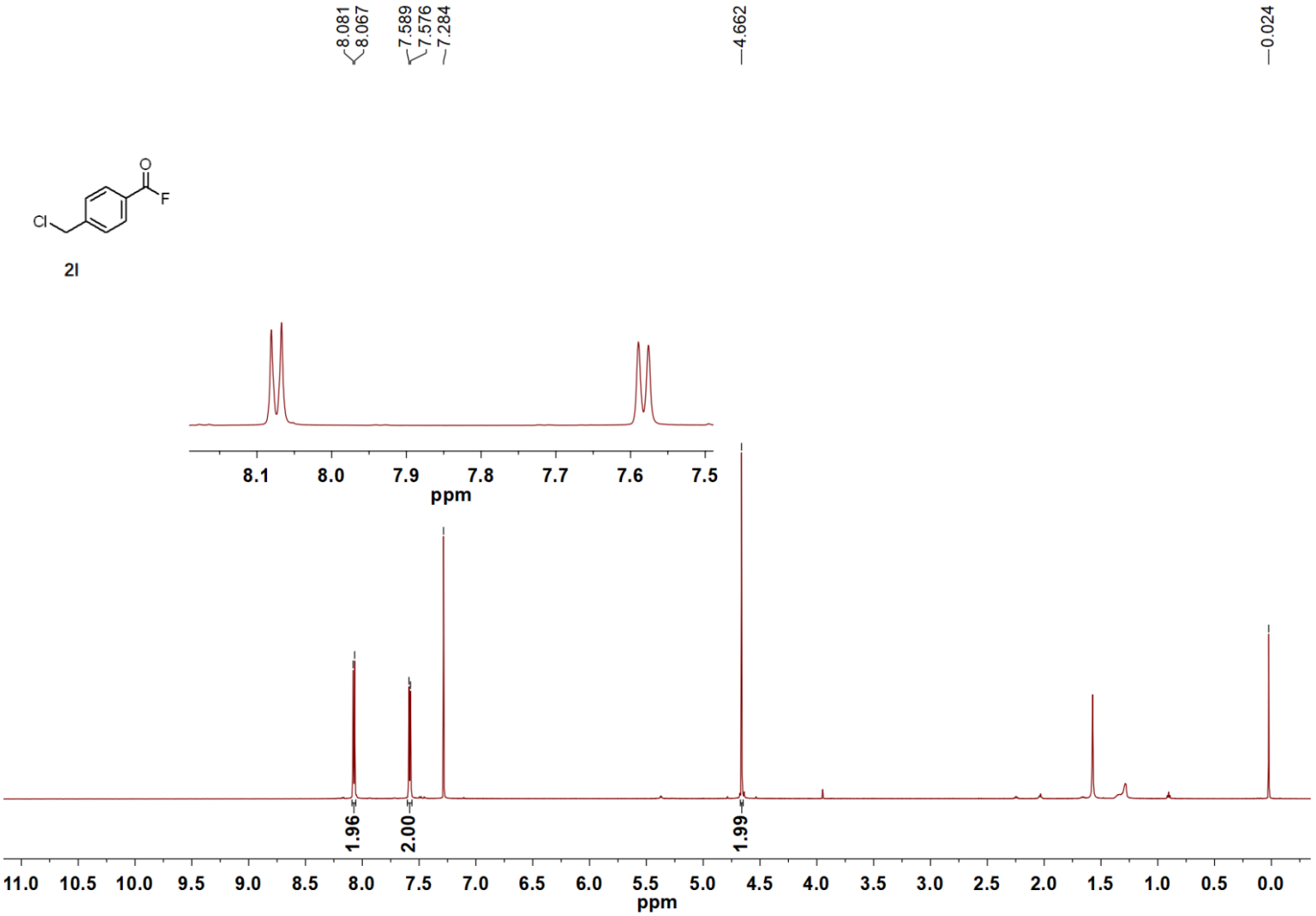
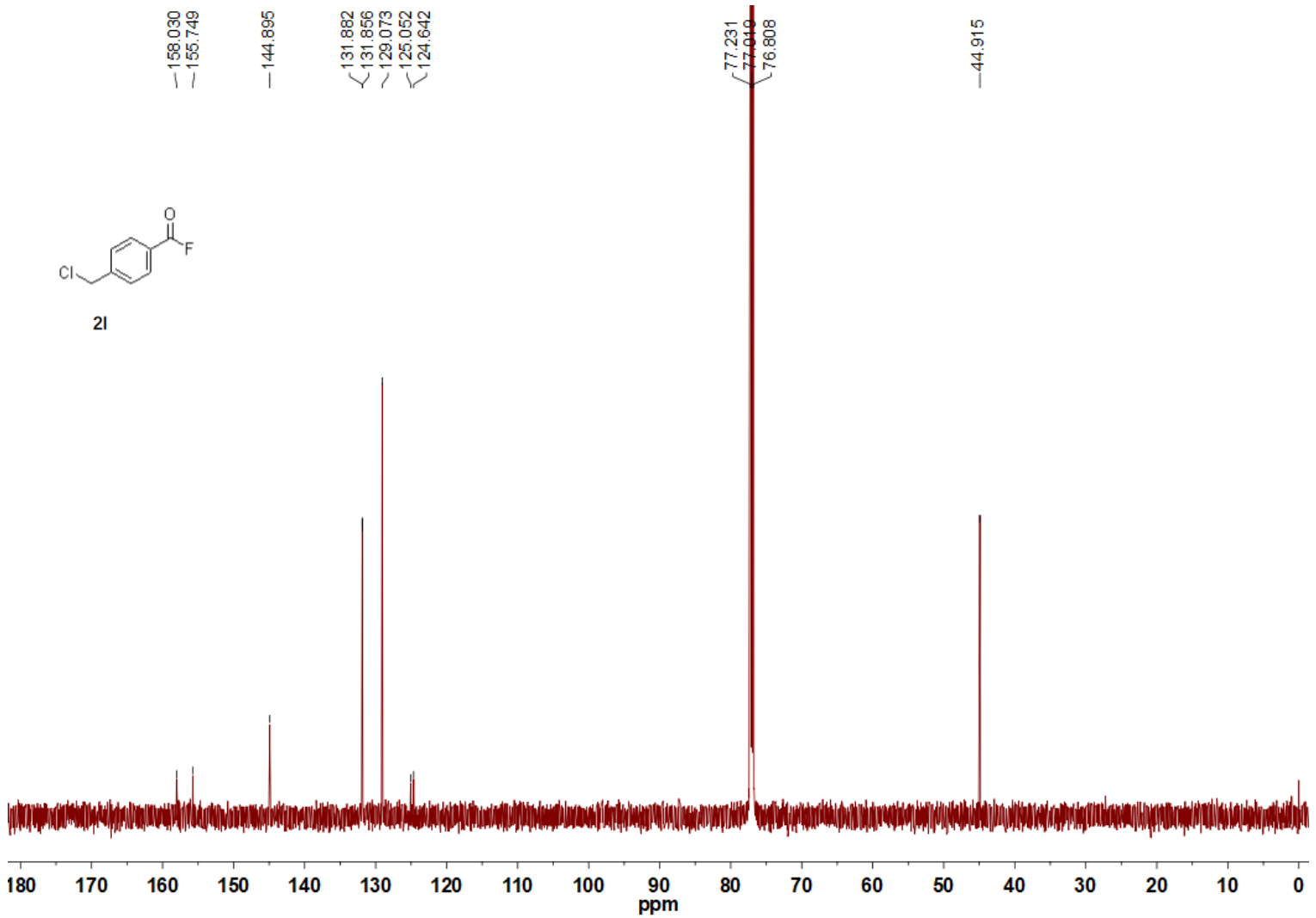
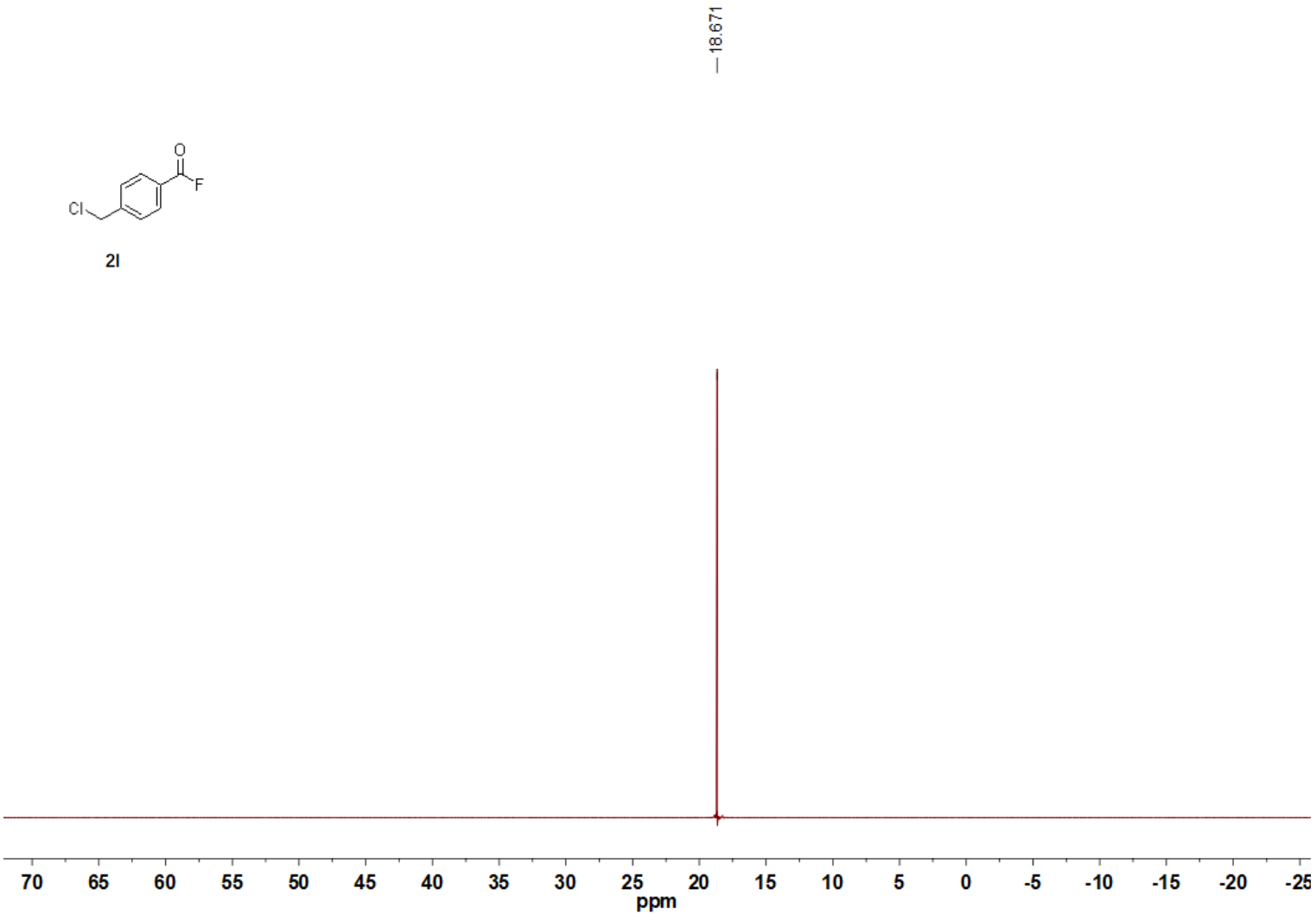


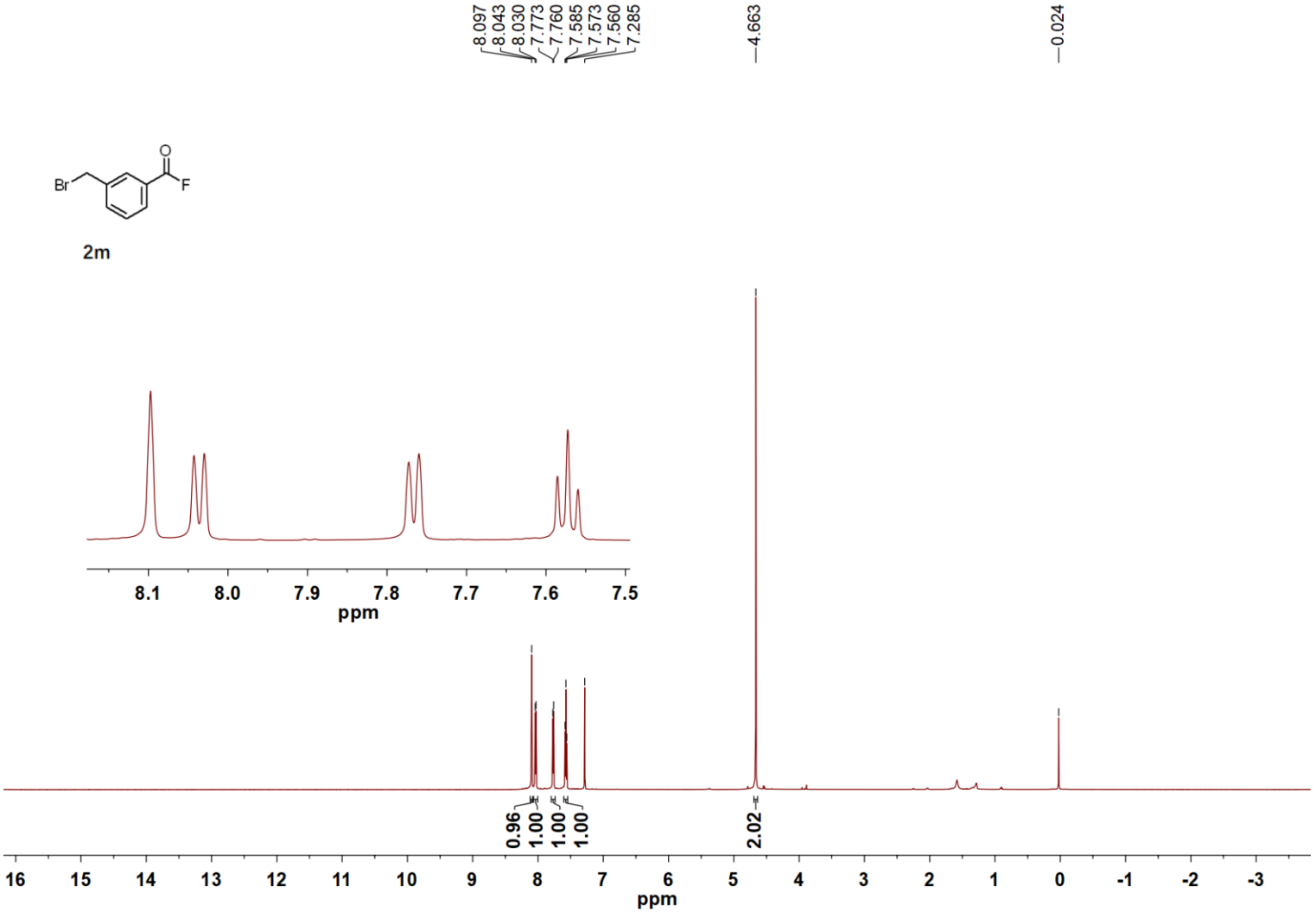
^{1}H NMR Spectrum of 2l (600 MHz, $CDCl_3$)



^{13}C NMR Spectrum of 2l (151 MHz, $CDCl_3$)



^{19}F NMR Spectrum of 2l (565 MHz, $CDCl_3$)



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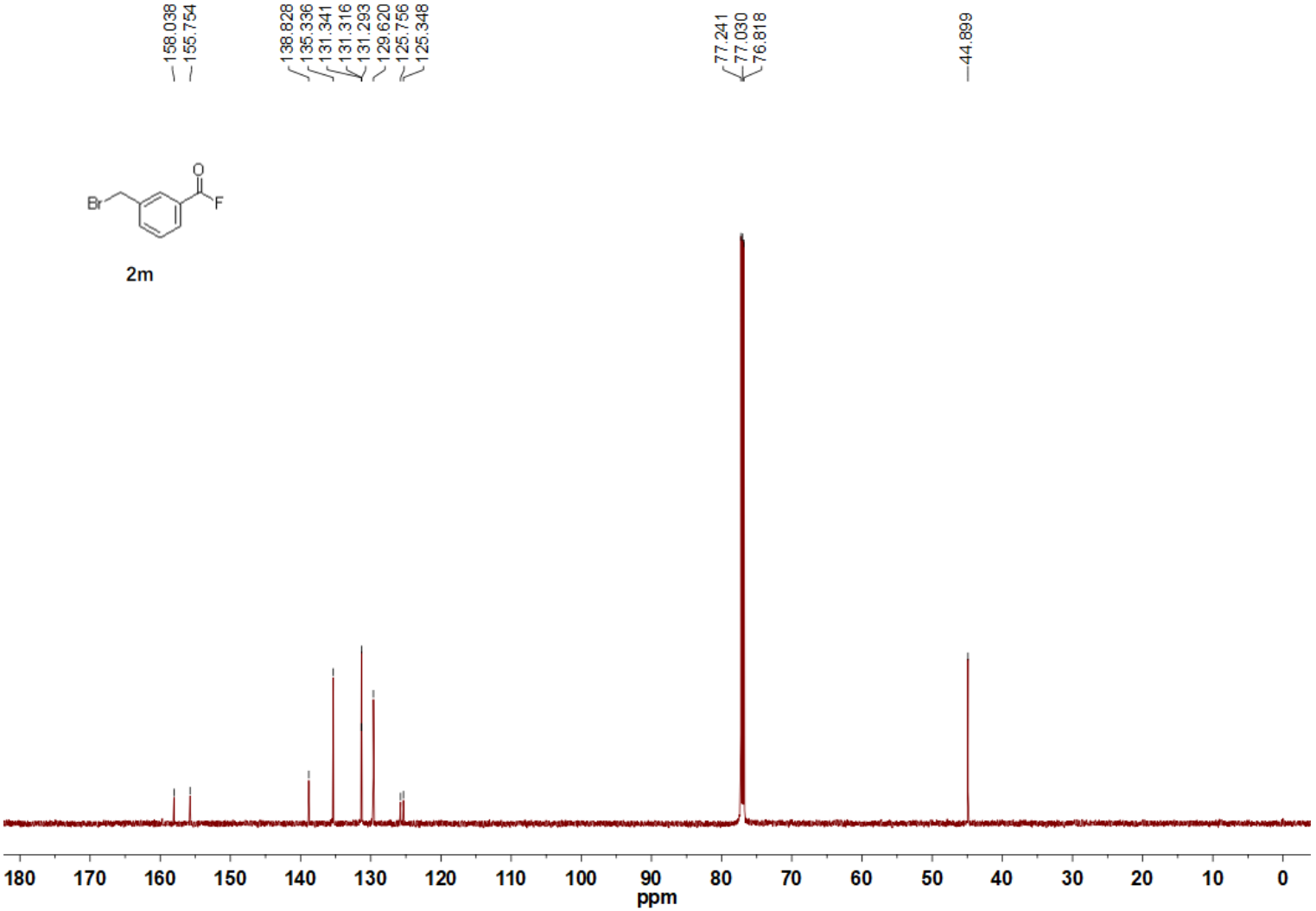
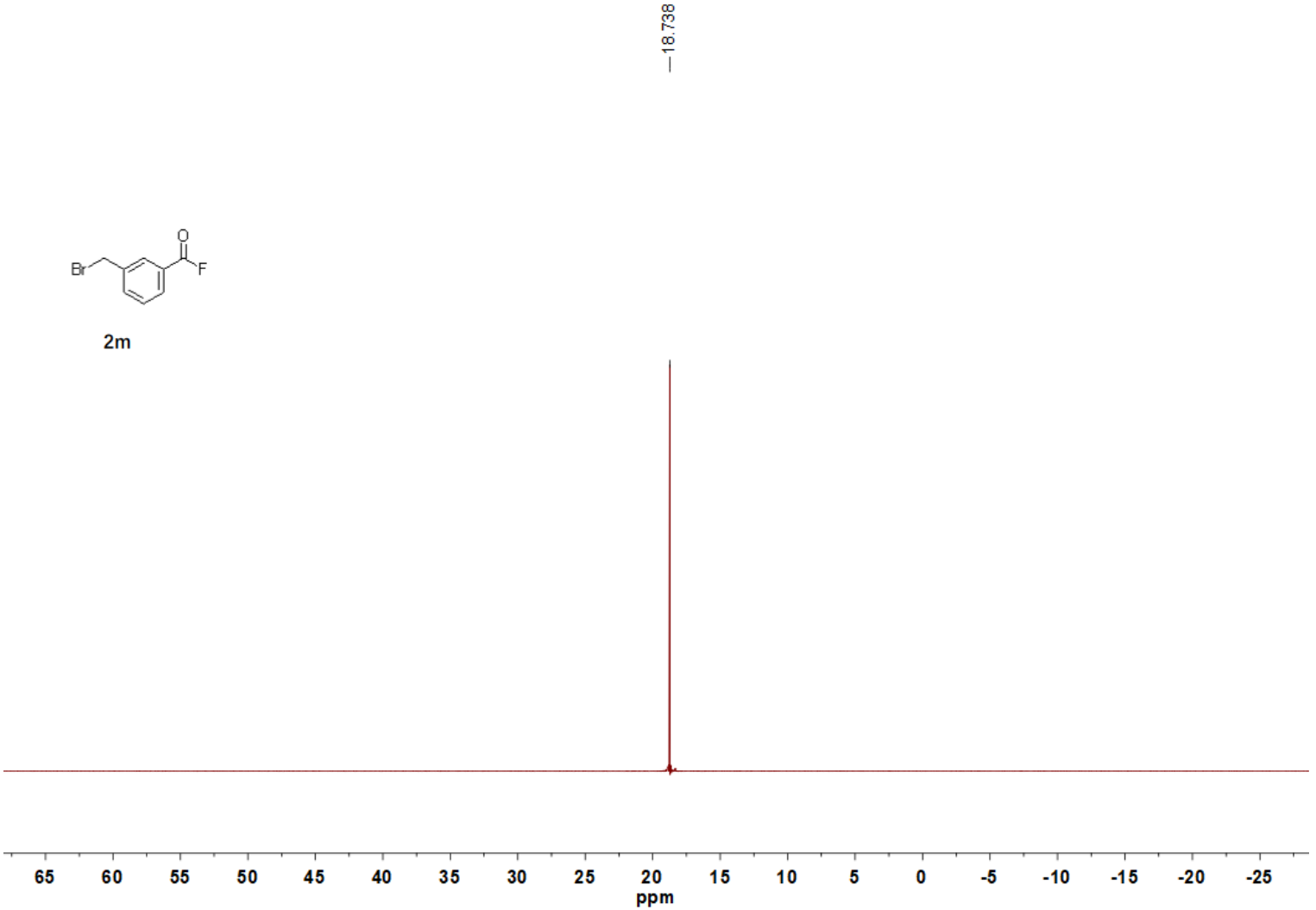


^{13}C NMR Spectrum of 2m (151 MHz, $CDCl_3$)



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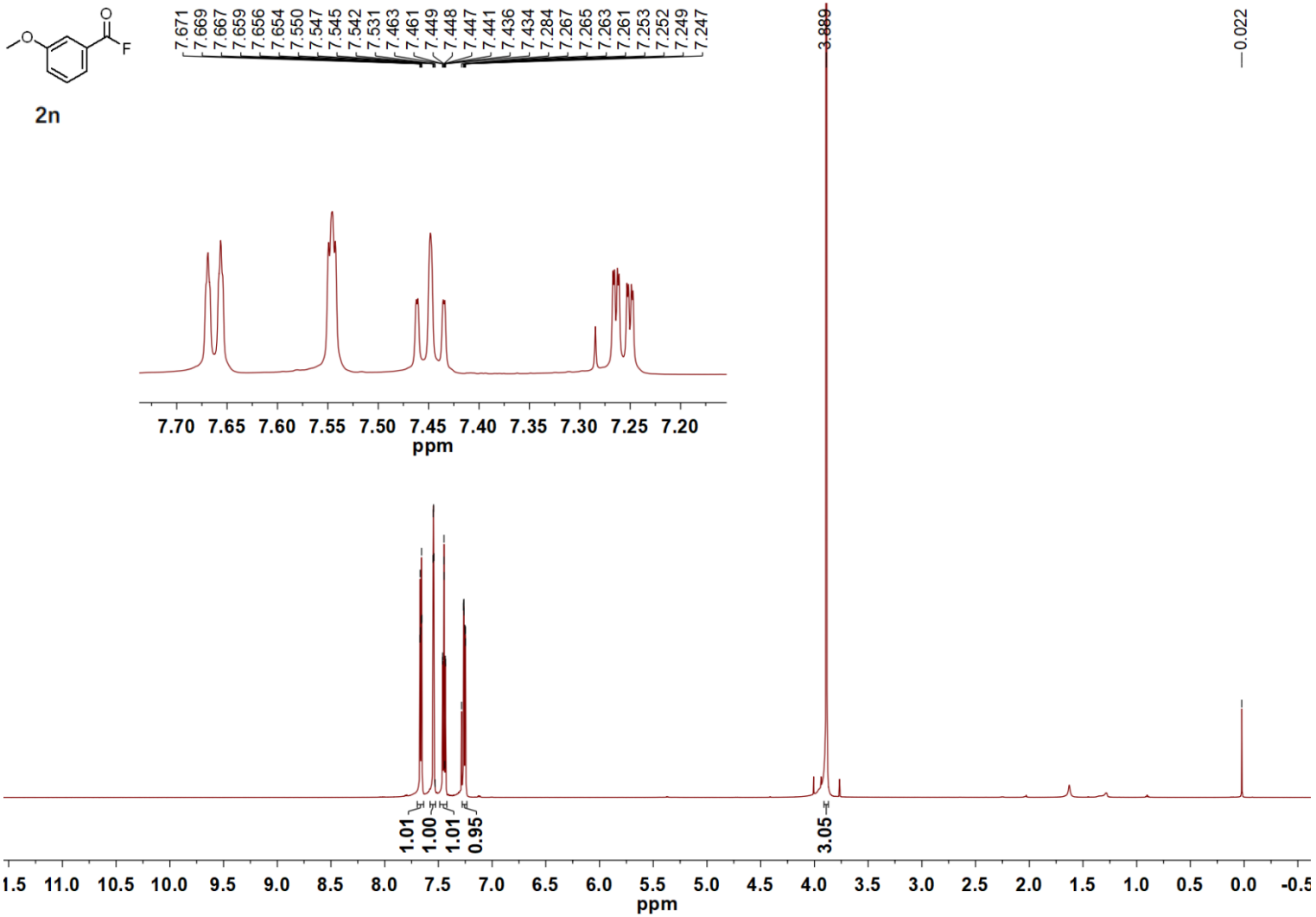

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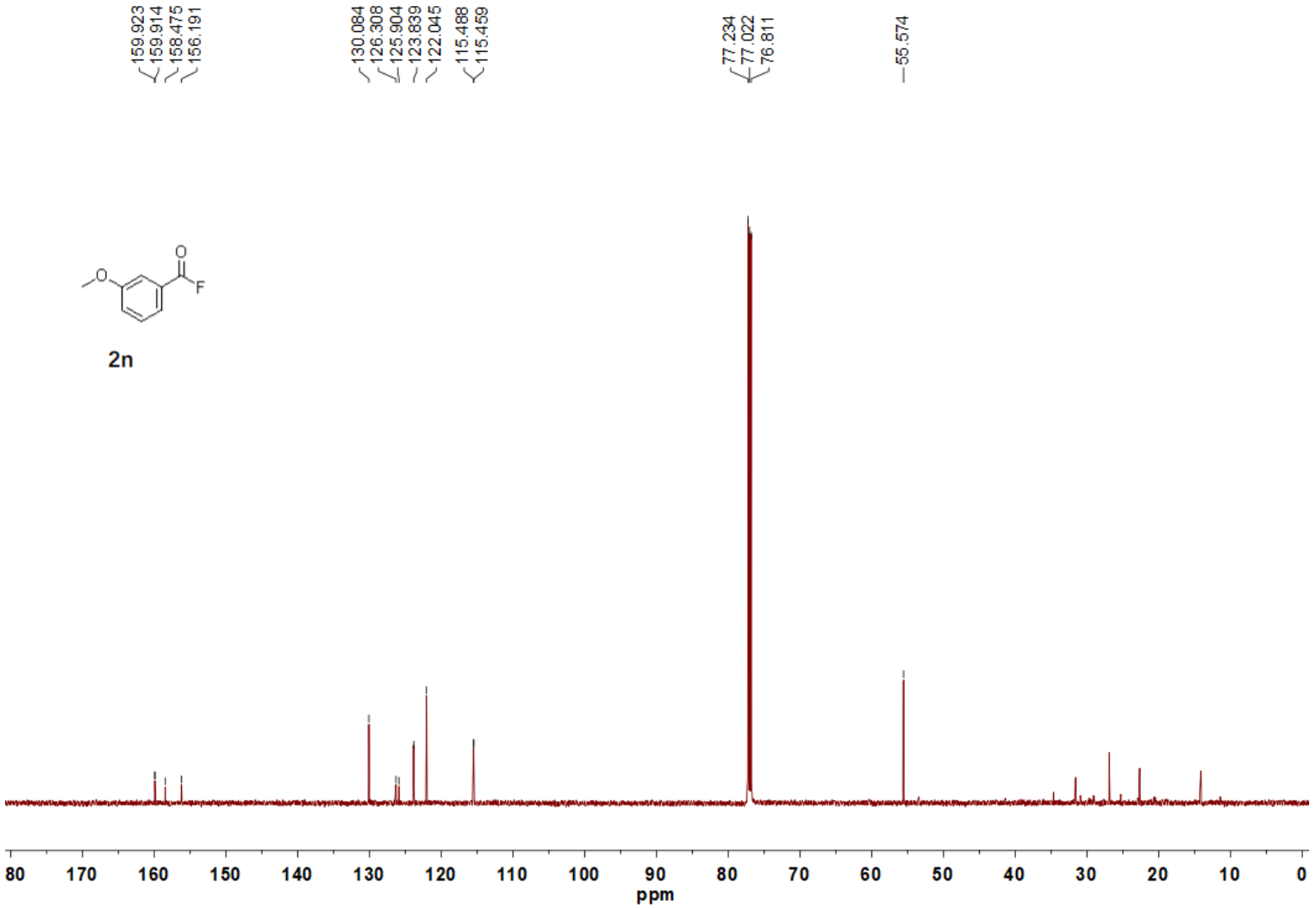

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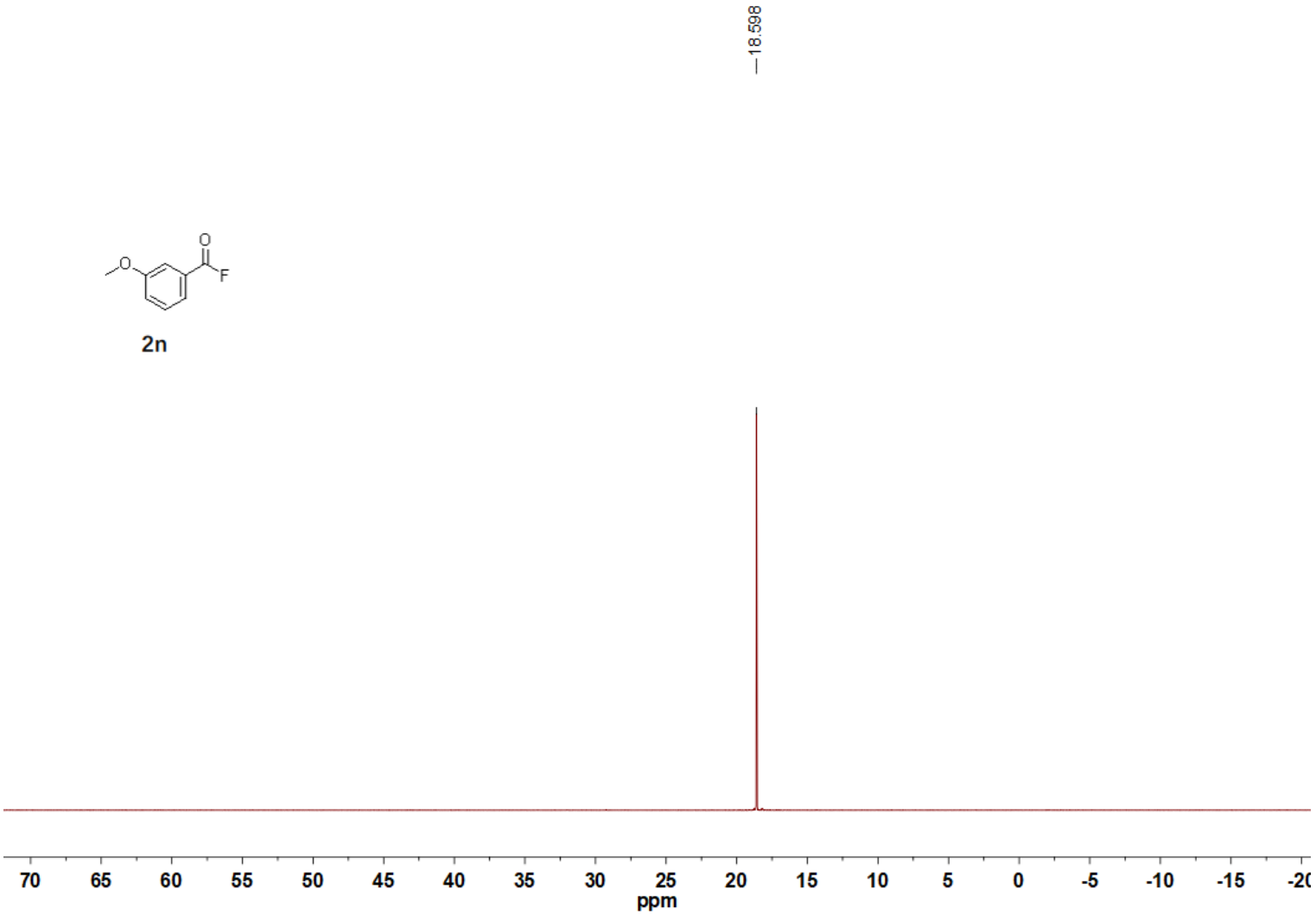

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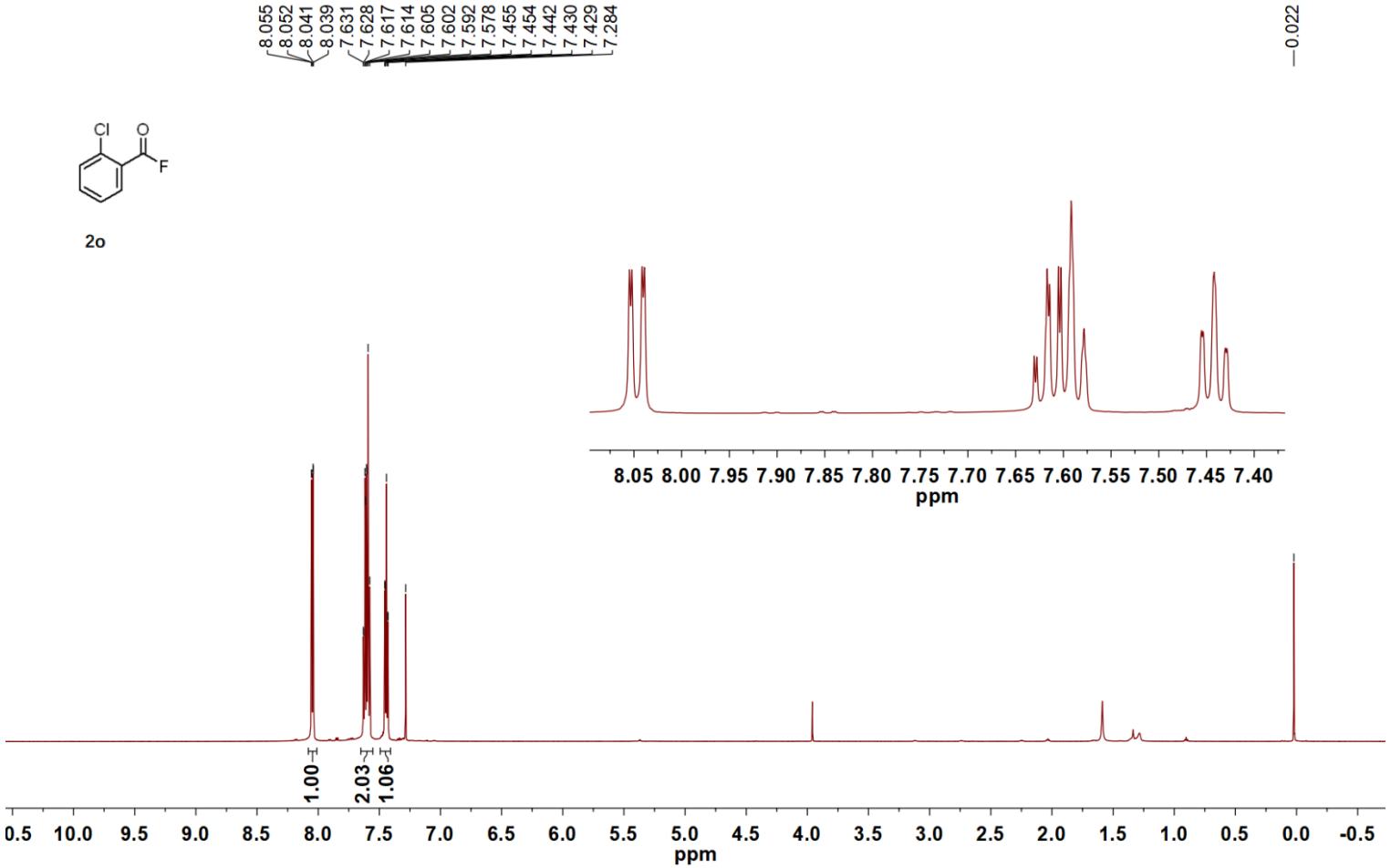

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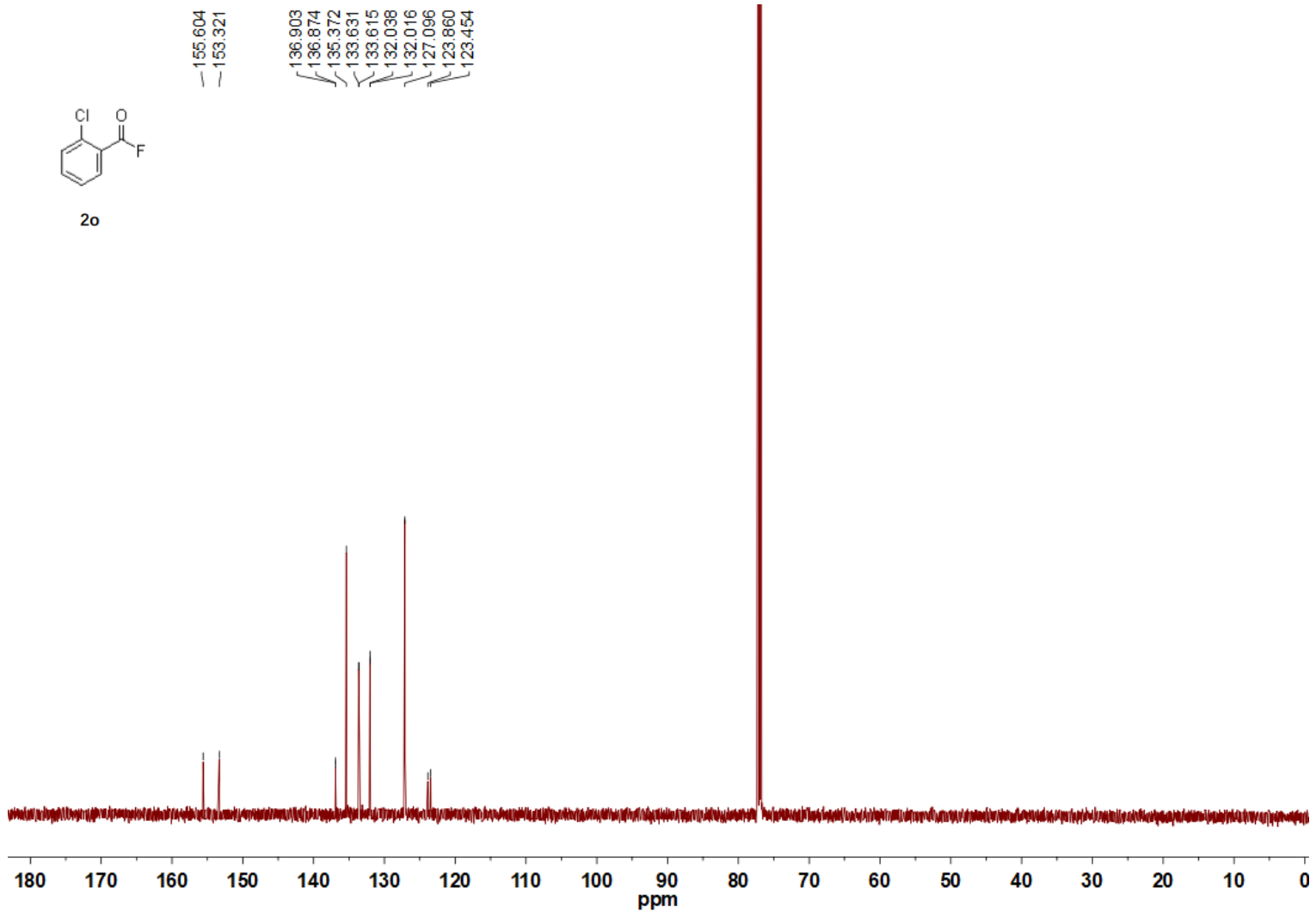
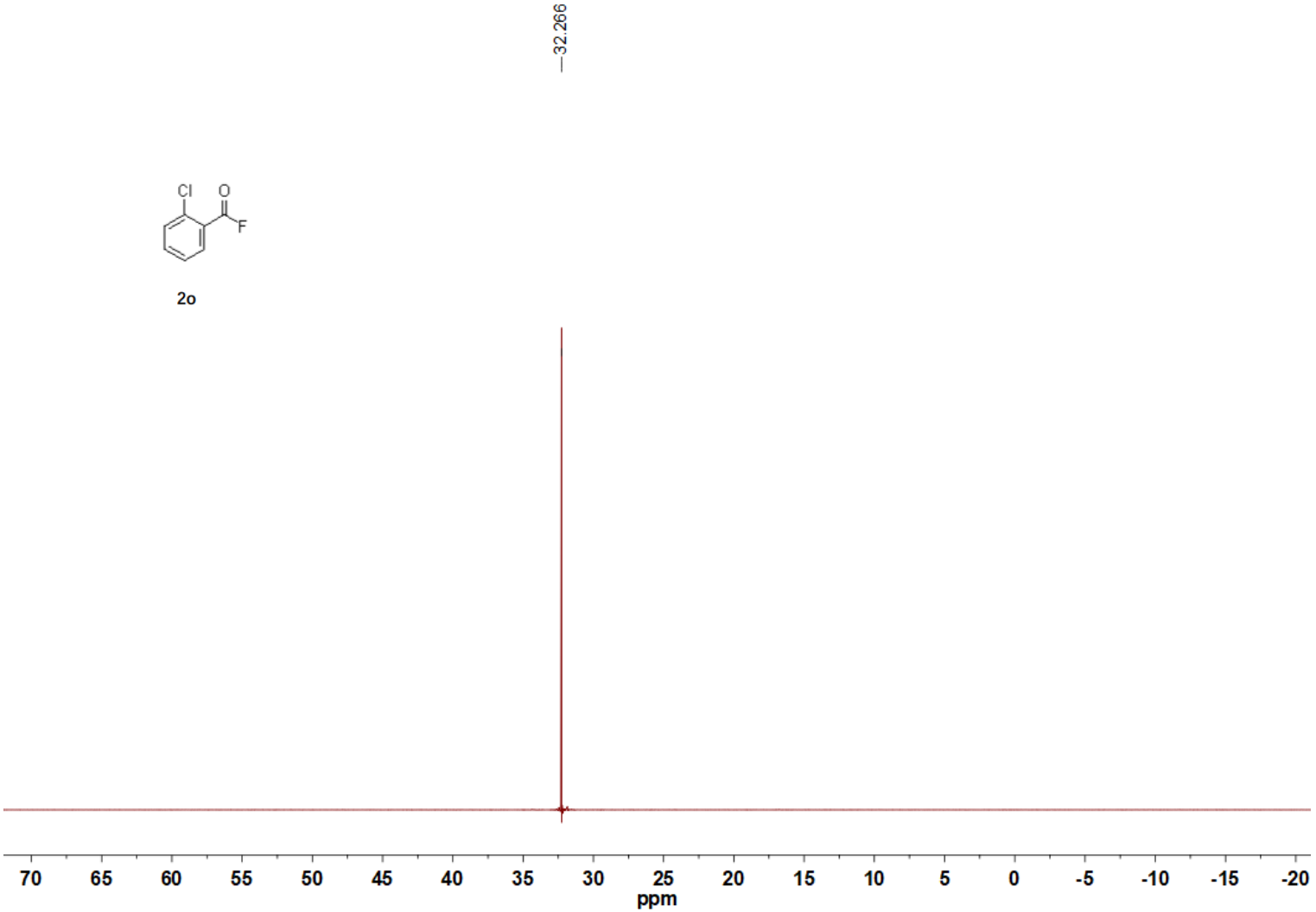
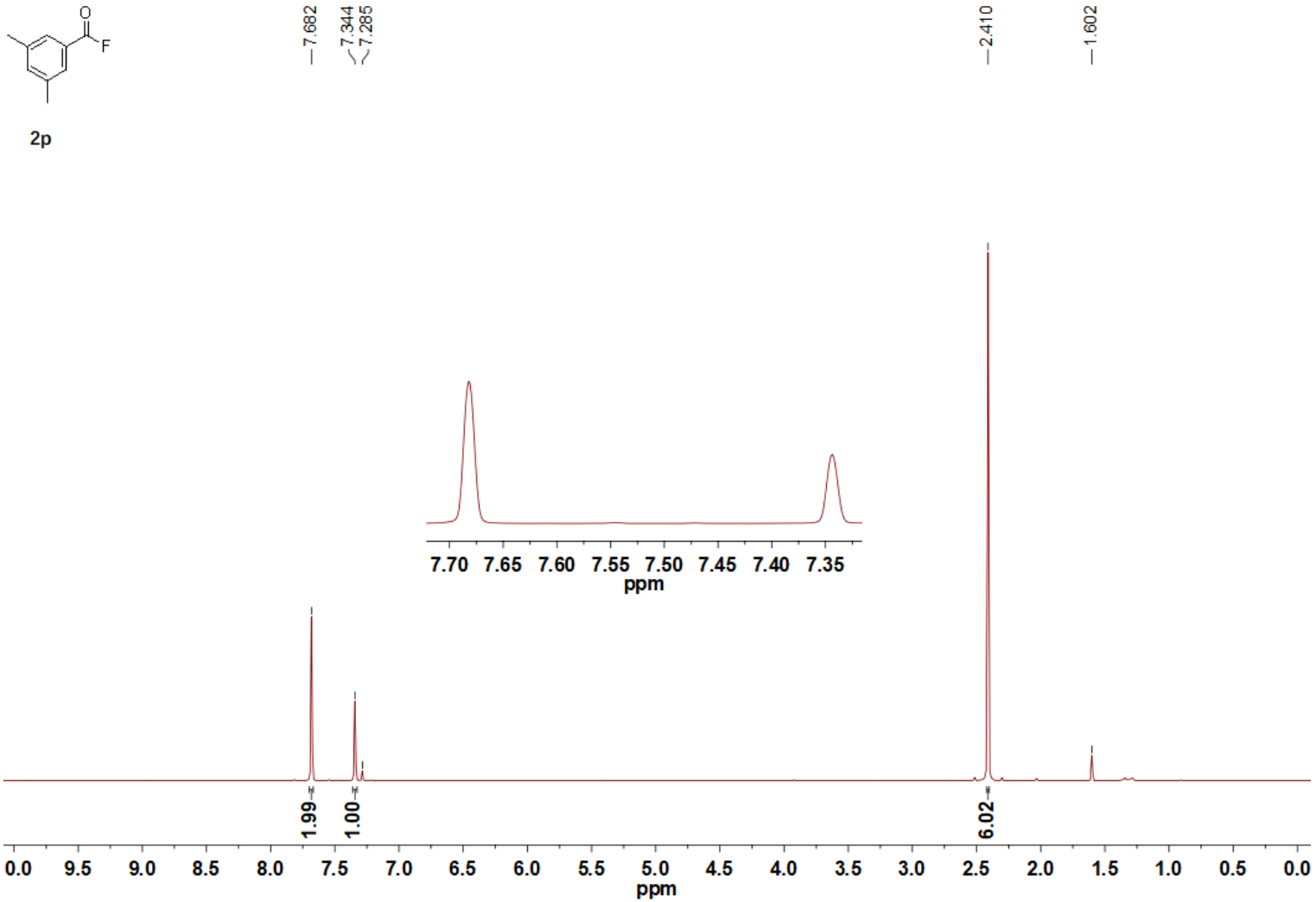


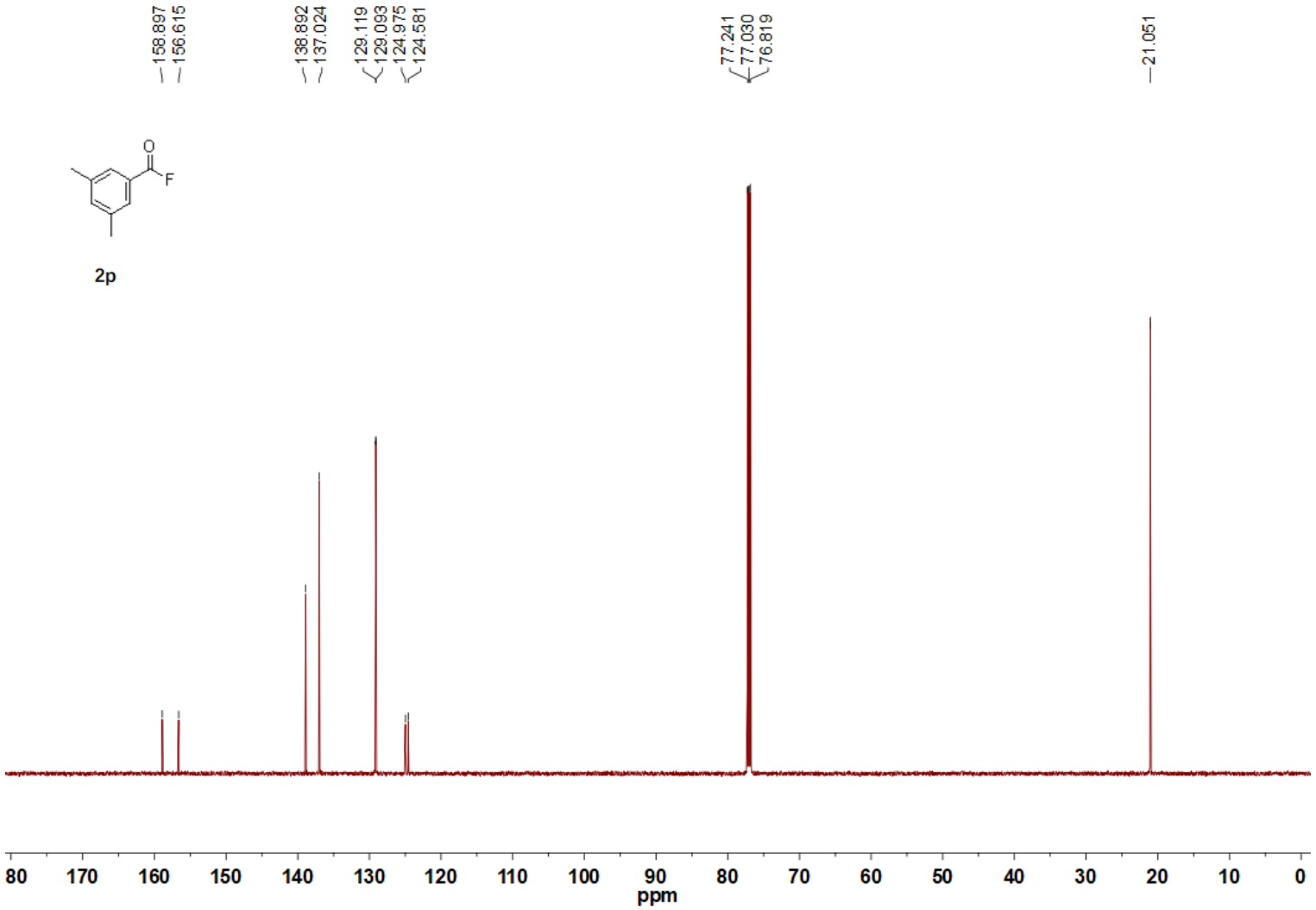
^{13}C NMR Spectrum of 2o (151 MHz, $CDCl_3$)



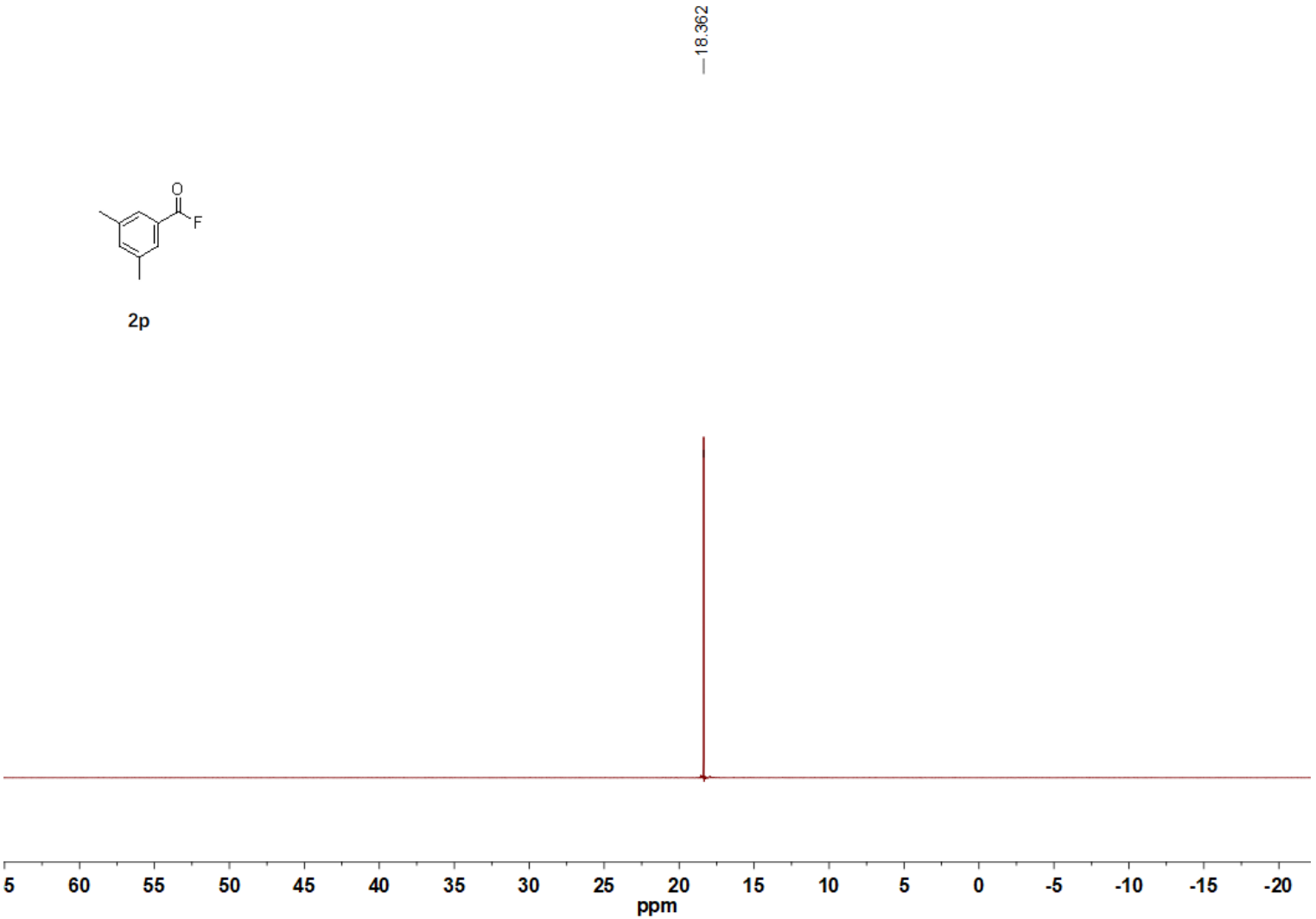
^{19}F NMR Spectrum of 2o (565 MHz, $CDCl_3$)



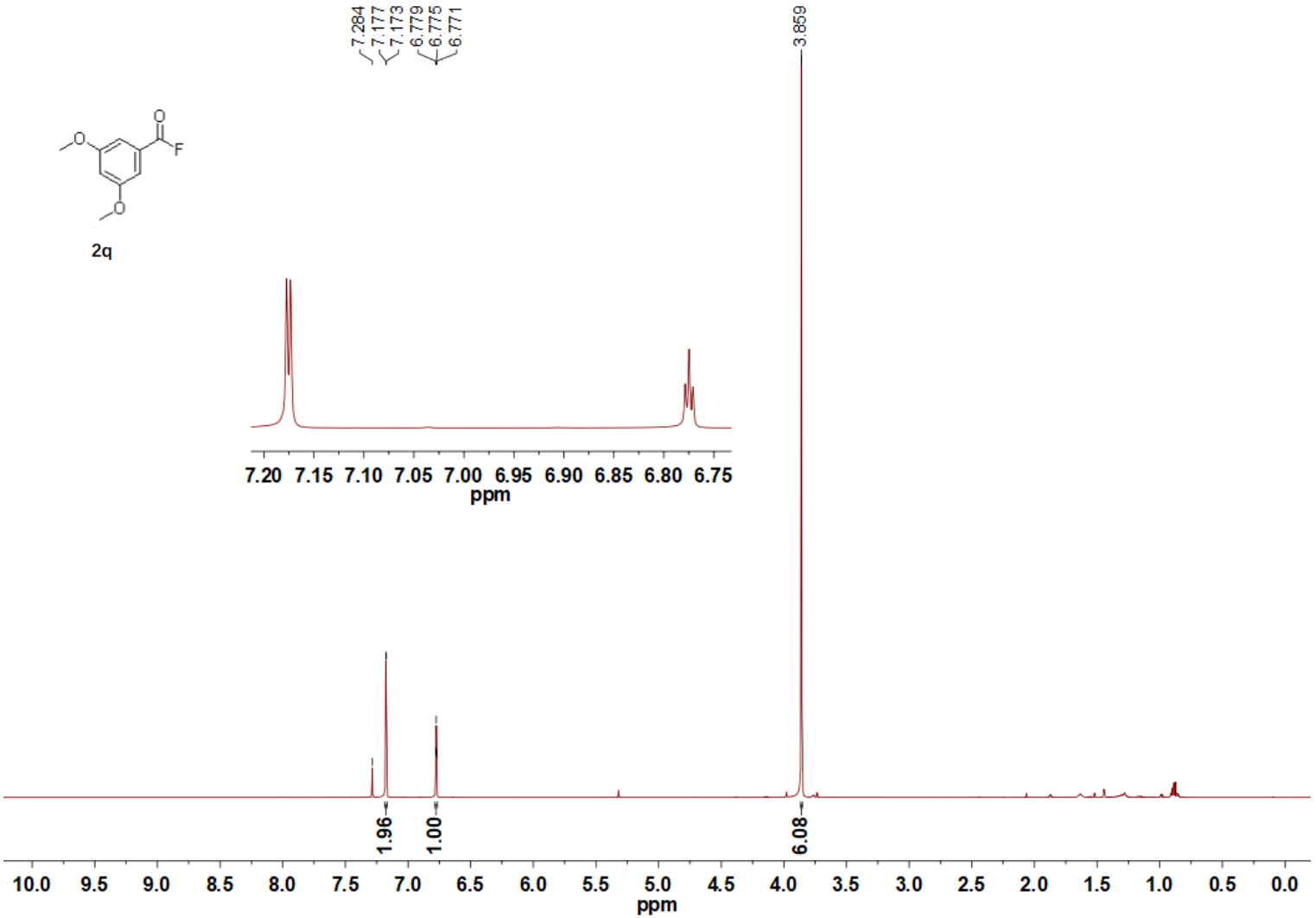
^{1}H NMR Spectrum of 2p (600 MHz, $CDCl_3$)



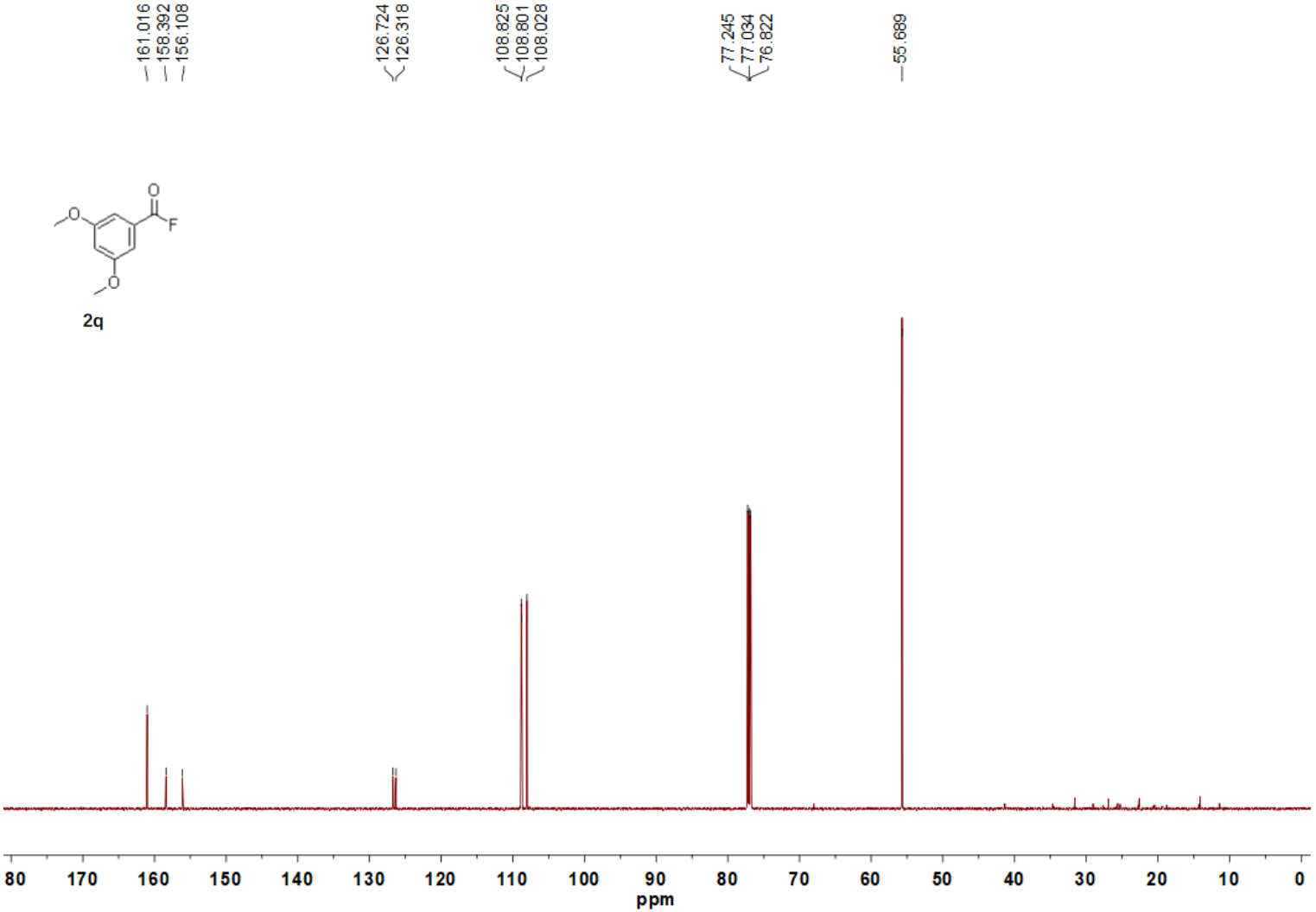
^{13}C NMR Spectrum of 2p (151 MHz, $CDCl_3$)



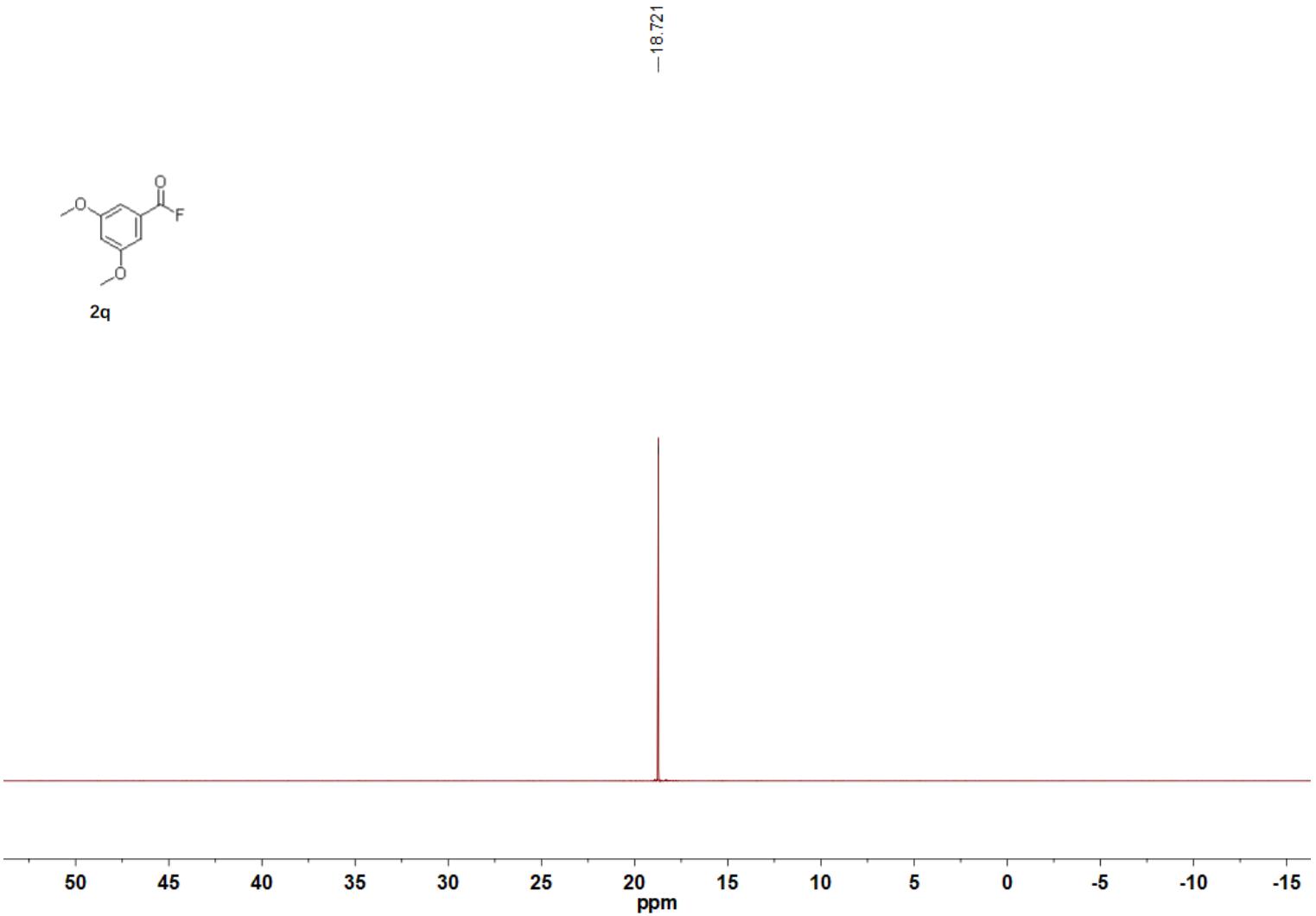
^{19}F NMR Spectrum of 2p (565 MHz, $CDCl_3$)



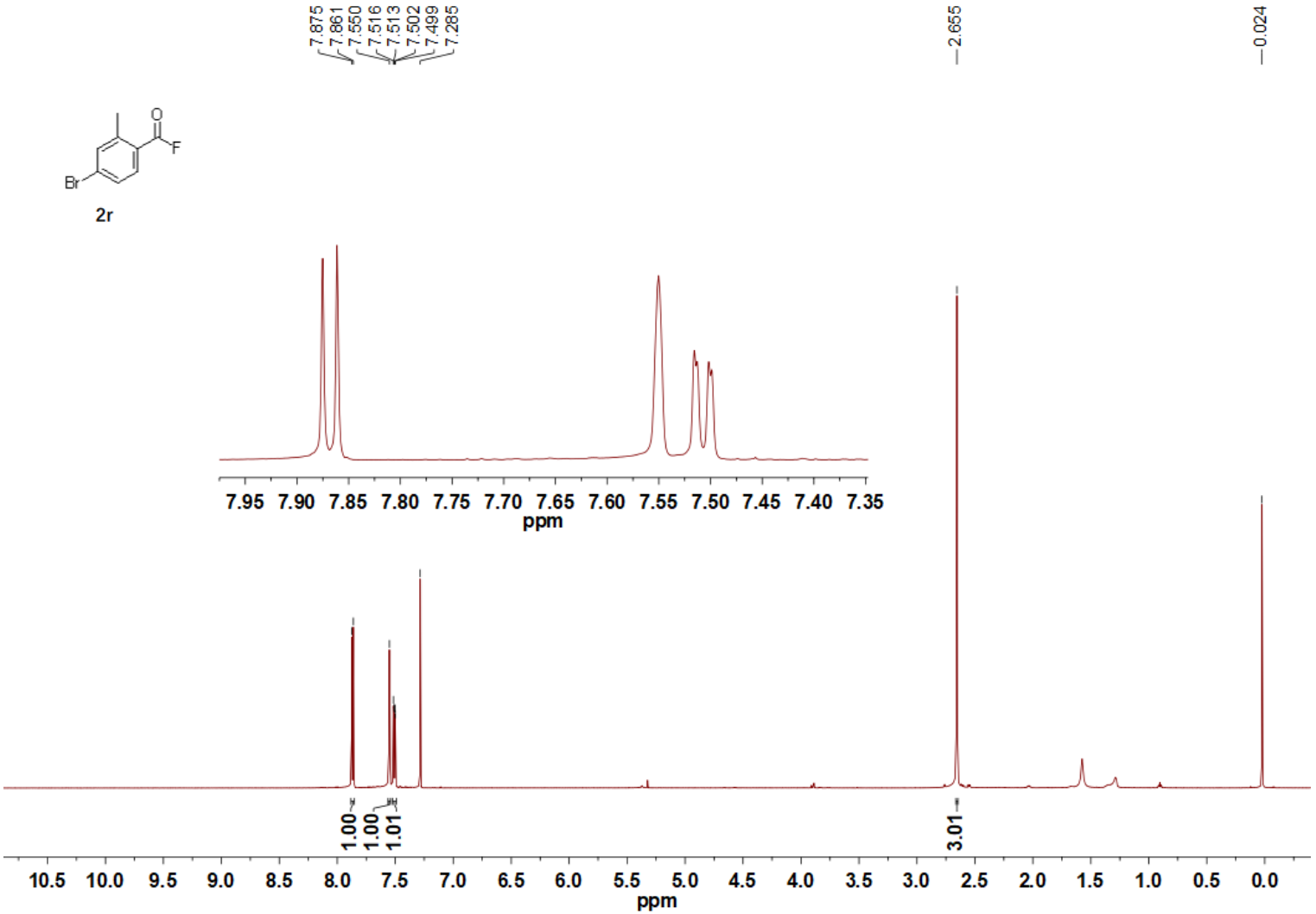
^{1}H NMR Spectrum of 2q (600 MHz, $CDCl_3$)



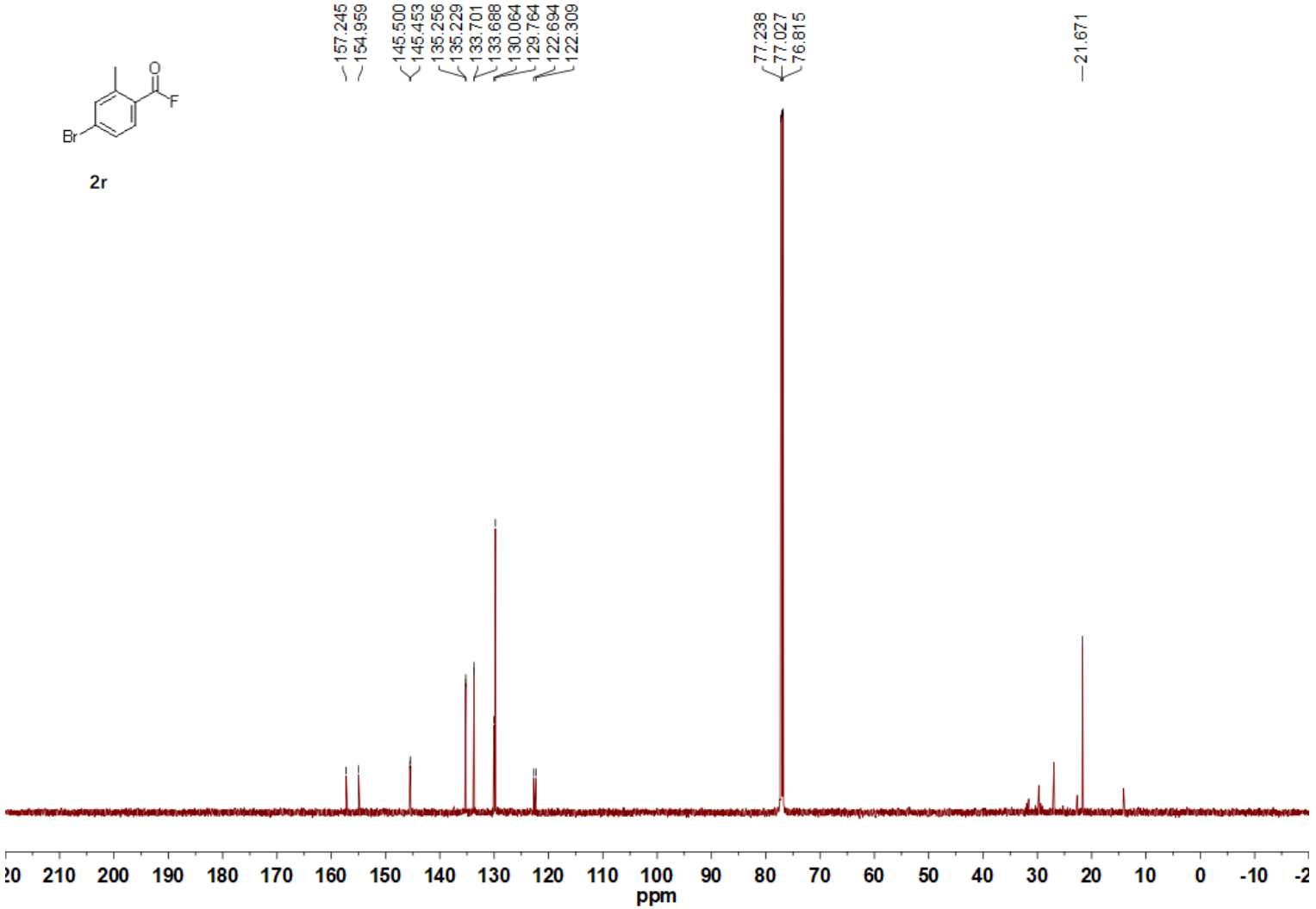
^{13}C NMR Spectrum of 2q (151 MHz, $CDCl_3$)



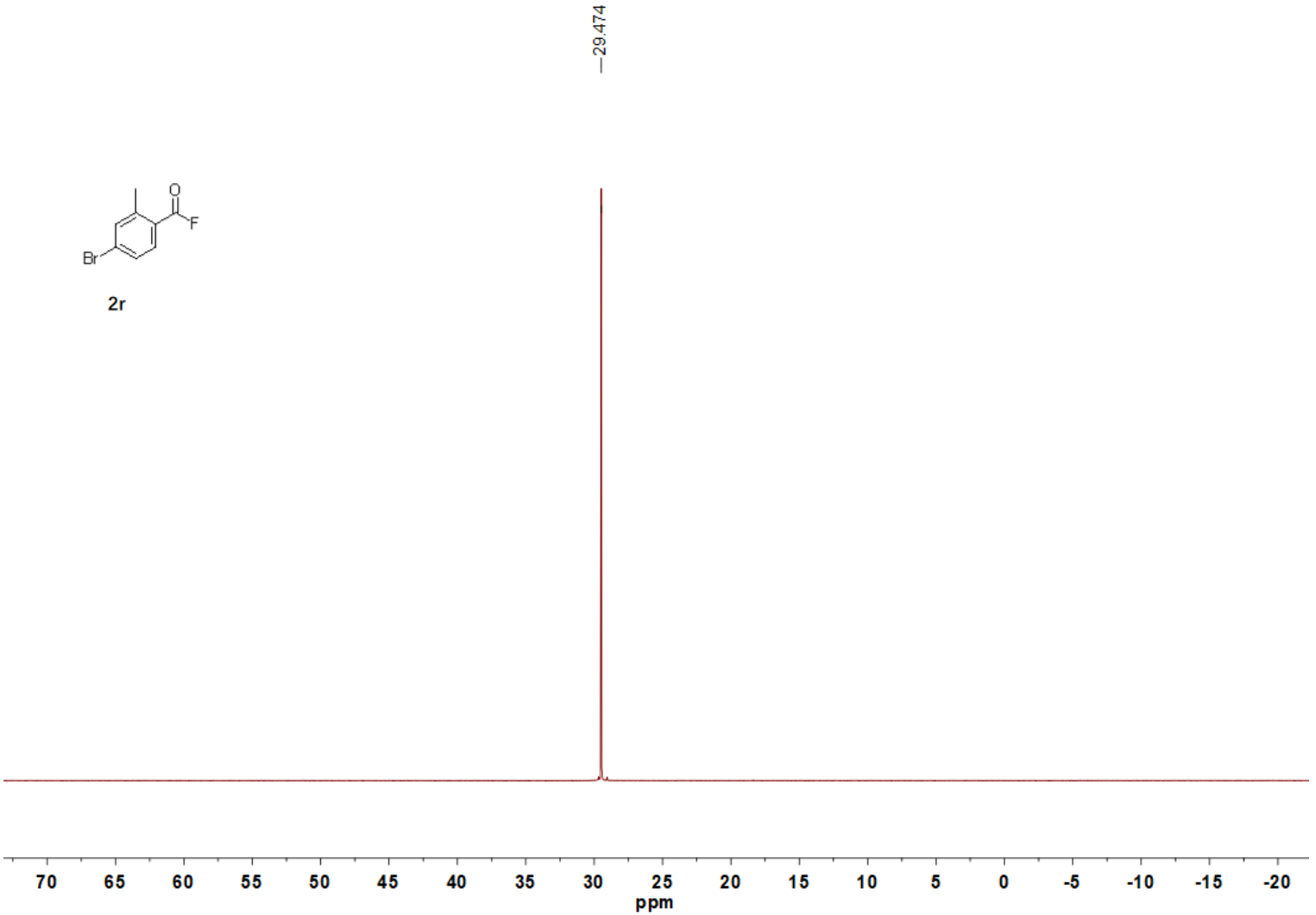
^{19}F NMR Spectrum of 2q (565 MHz, $CDCl_3$)



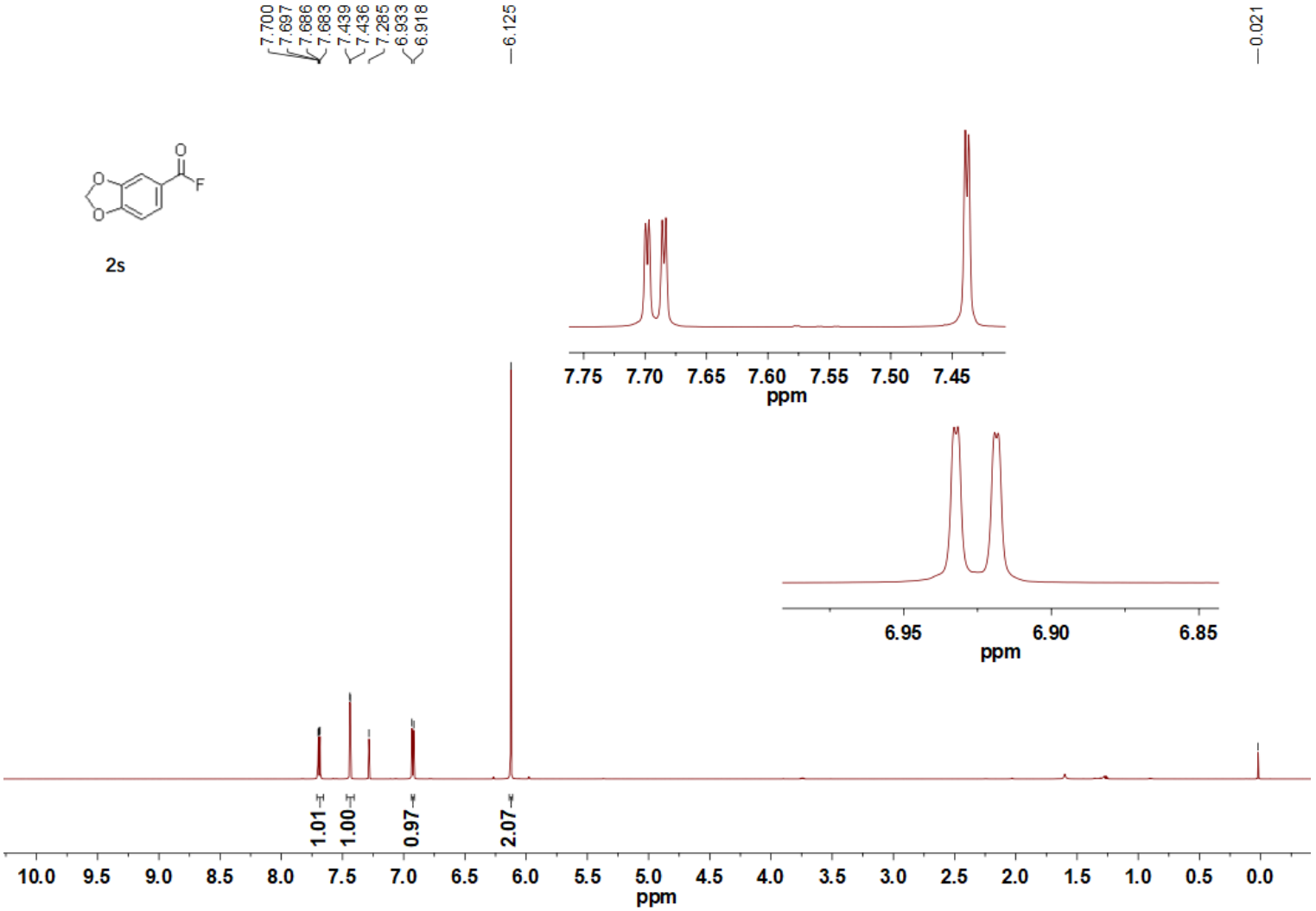
^{1}H NMR Spectrum of 2r (600 MHz, $CDCl_3$)



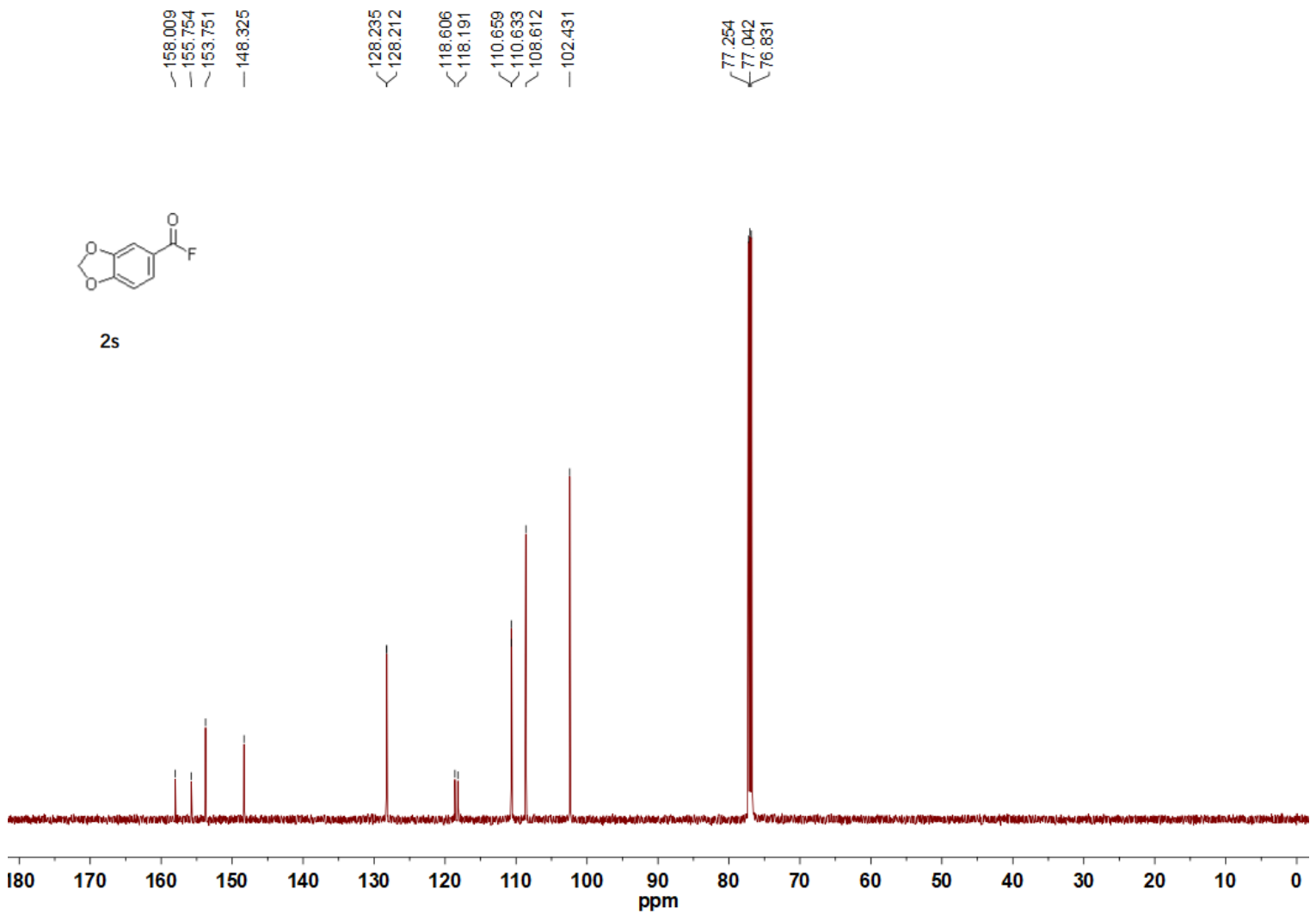
^{13}C NMR Spectrum of 2r (151 MHz, $CDCl_3$)



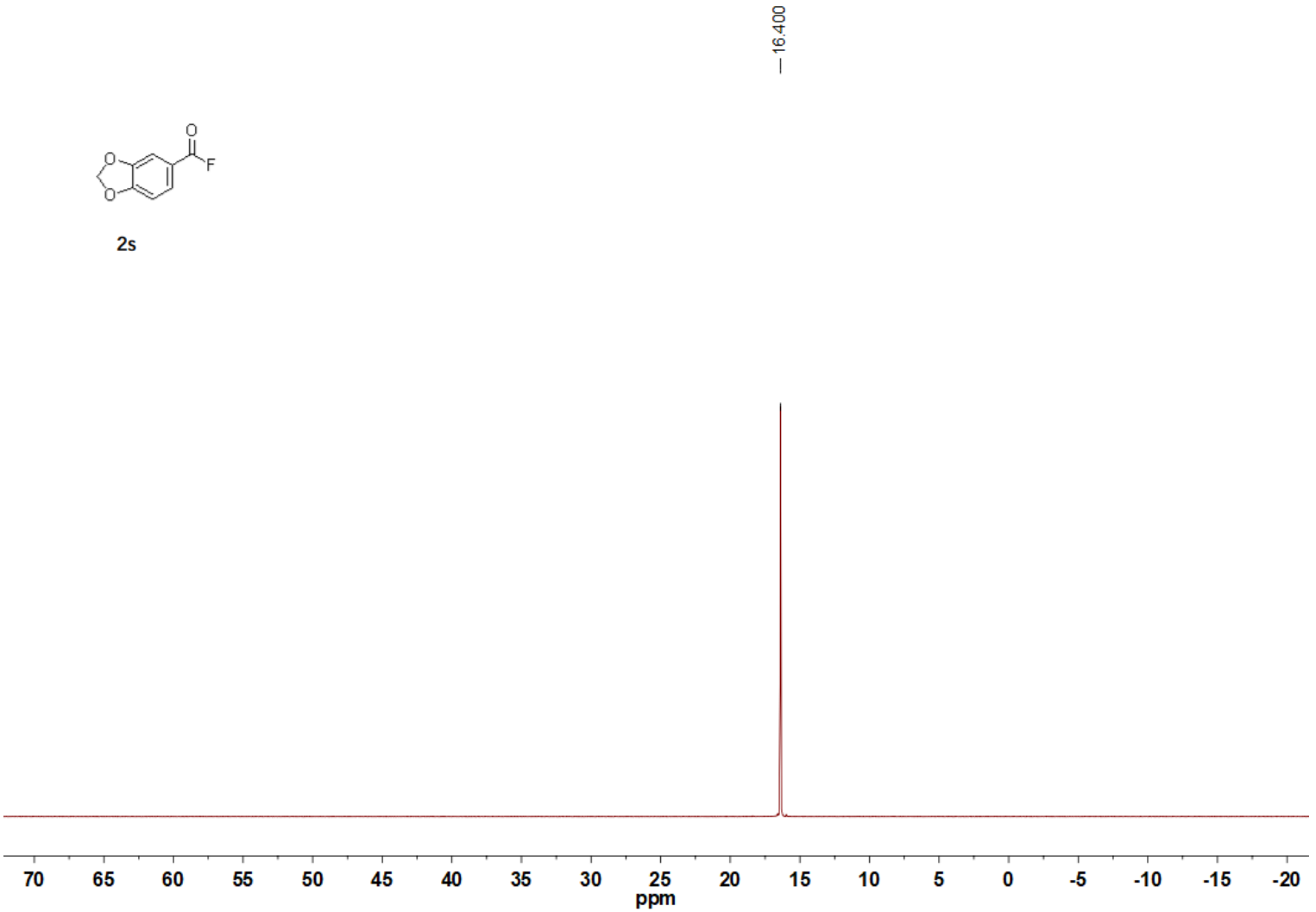
^{19}F NMR Spectrum of 2r (565 MHz, $CDCl_3$)



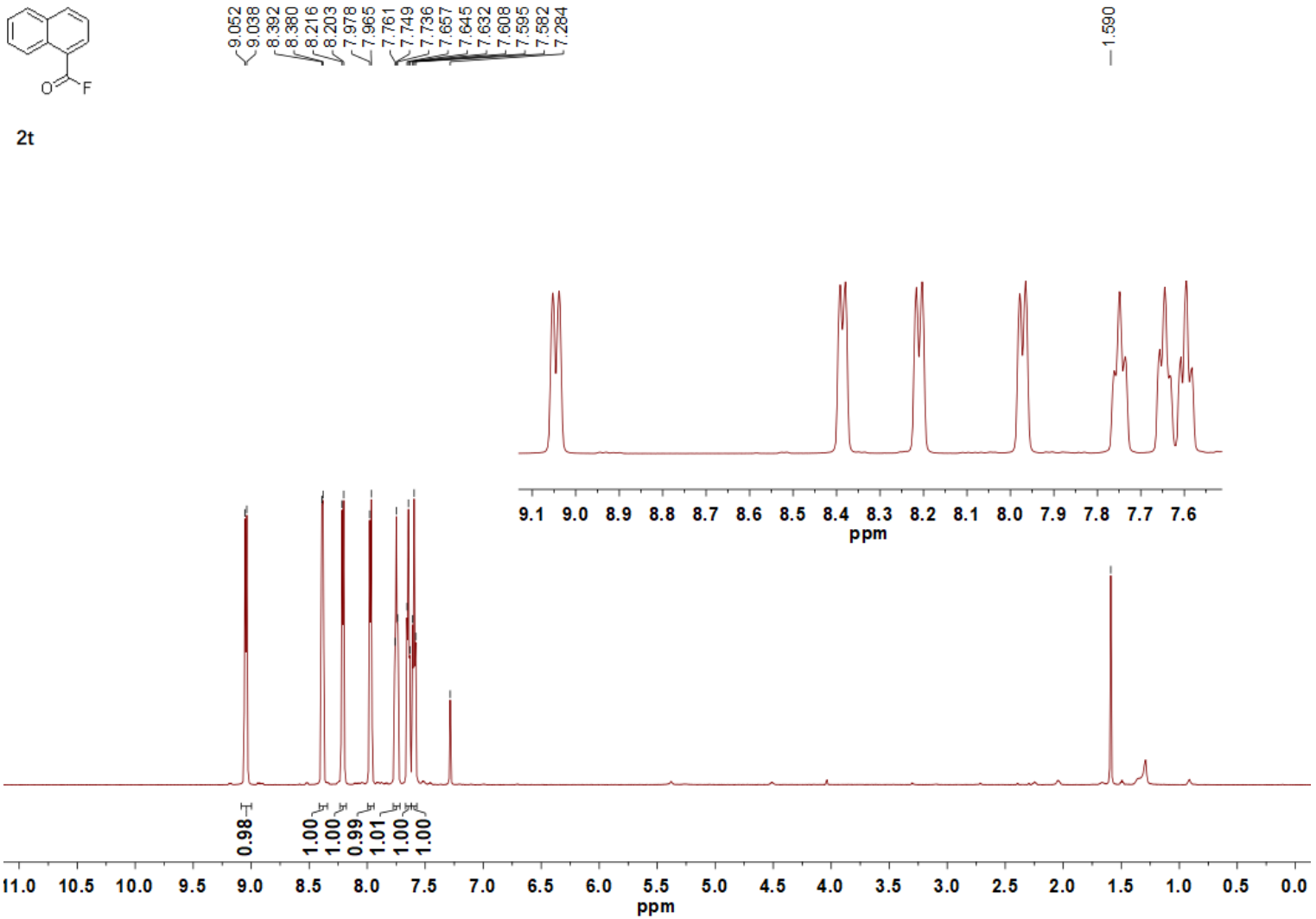
^{1}H NMR Spectrum of 2s (600 MHz, $CDCl_3$)



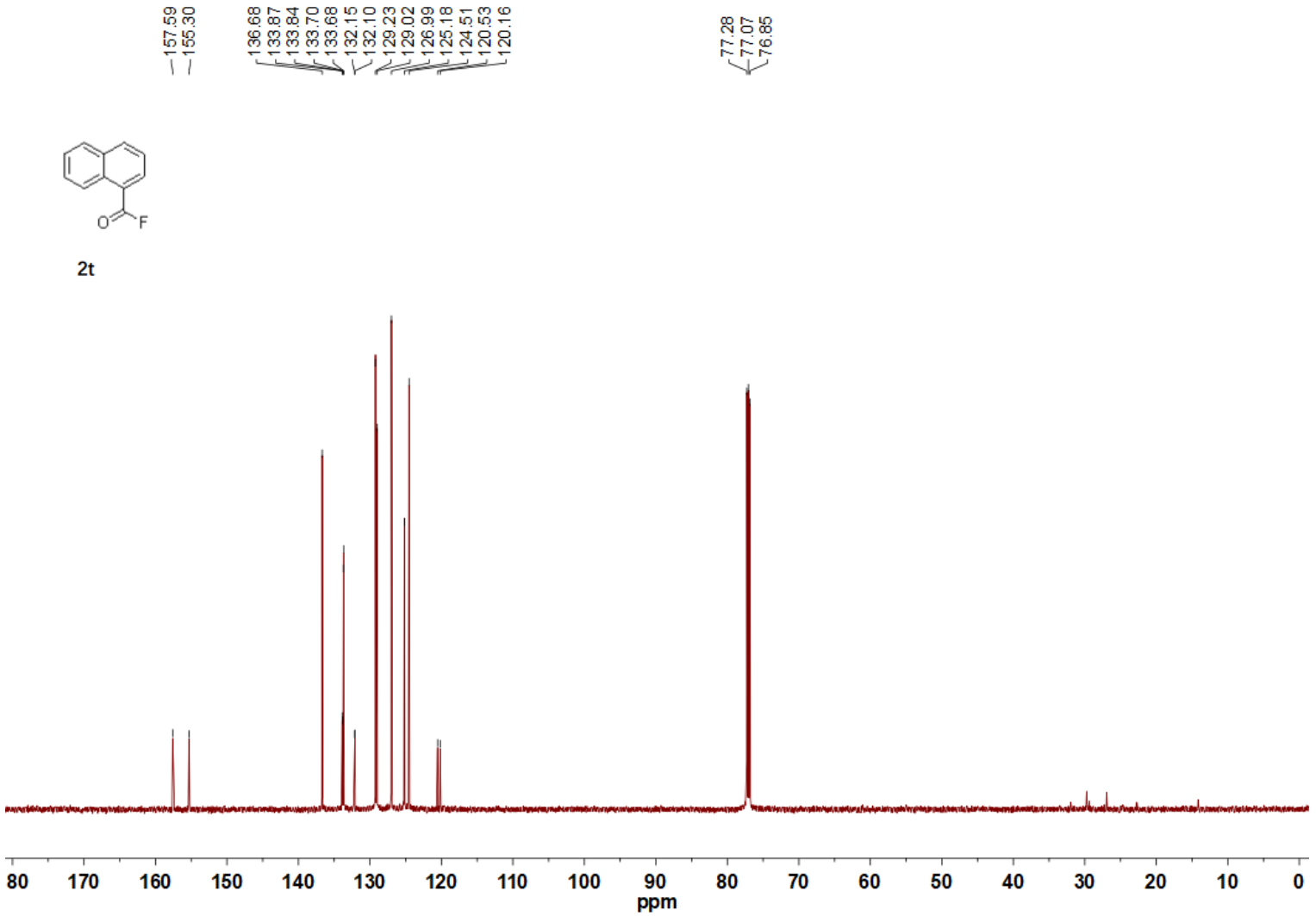
^{13}C NMR Spectrum of 2s (151 MHz, $CDCl_3$)



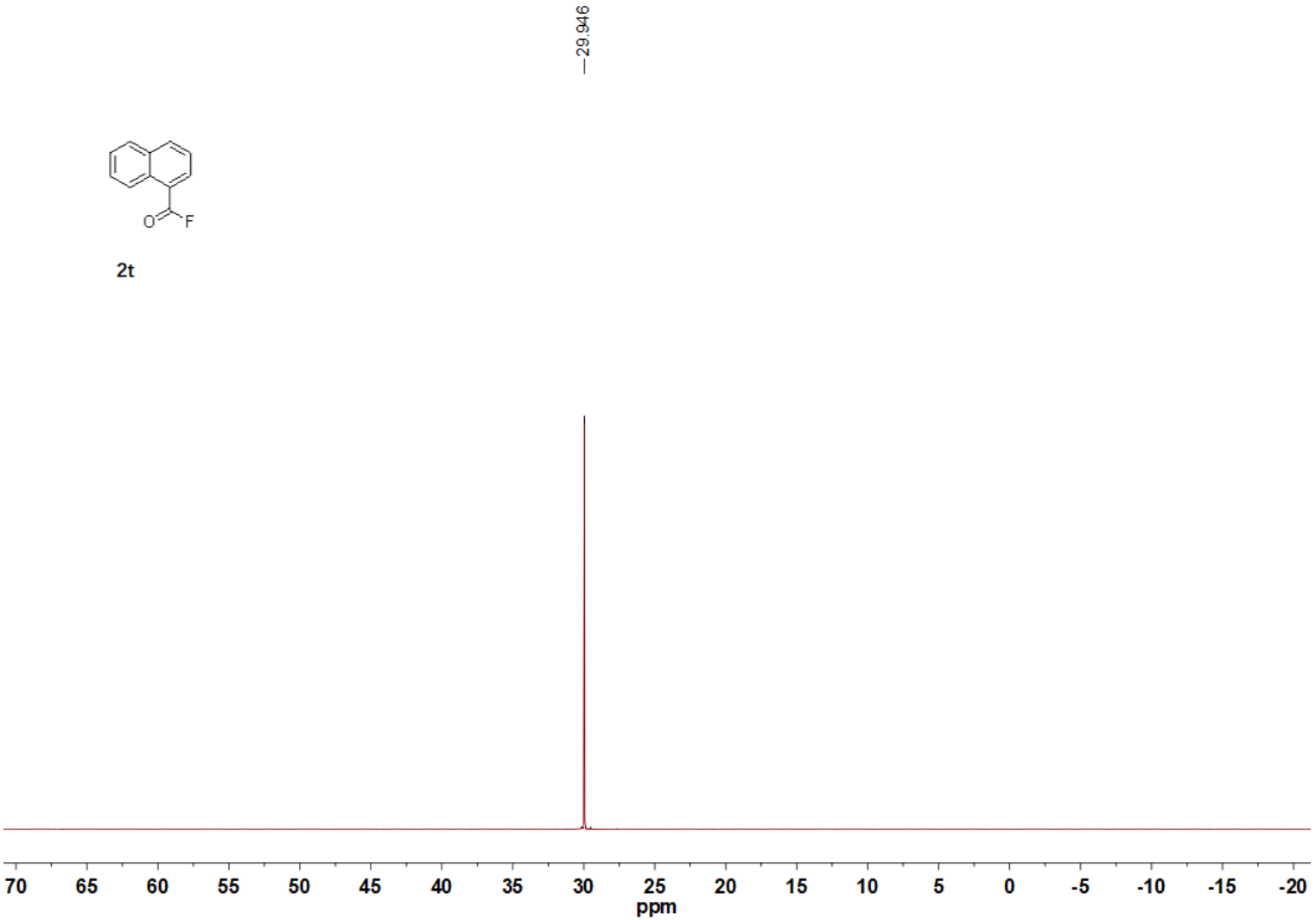
^{19}F NMR Spectrum of 2s (565 MHz, $CDCl_3$)



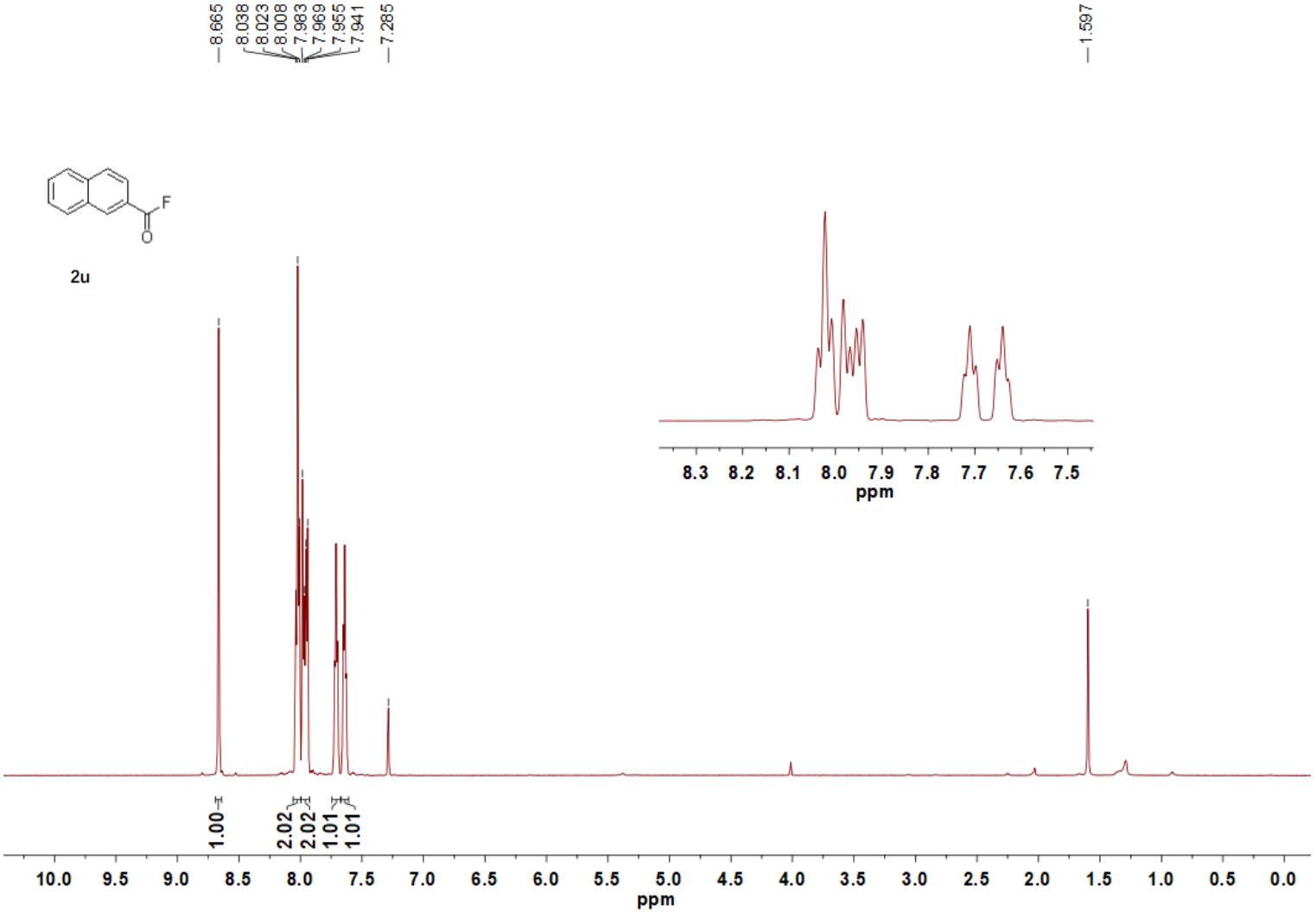
^{1}H NMR Spectrum of 2t (600 MHz, $CDCl_3$)



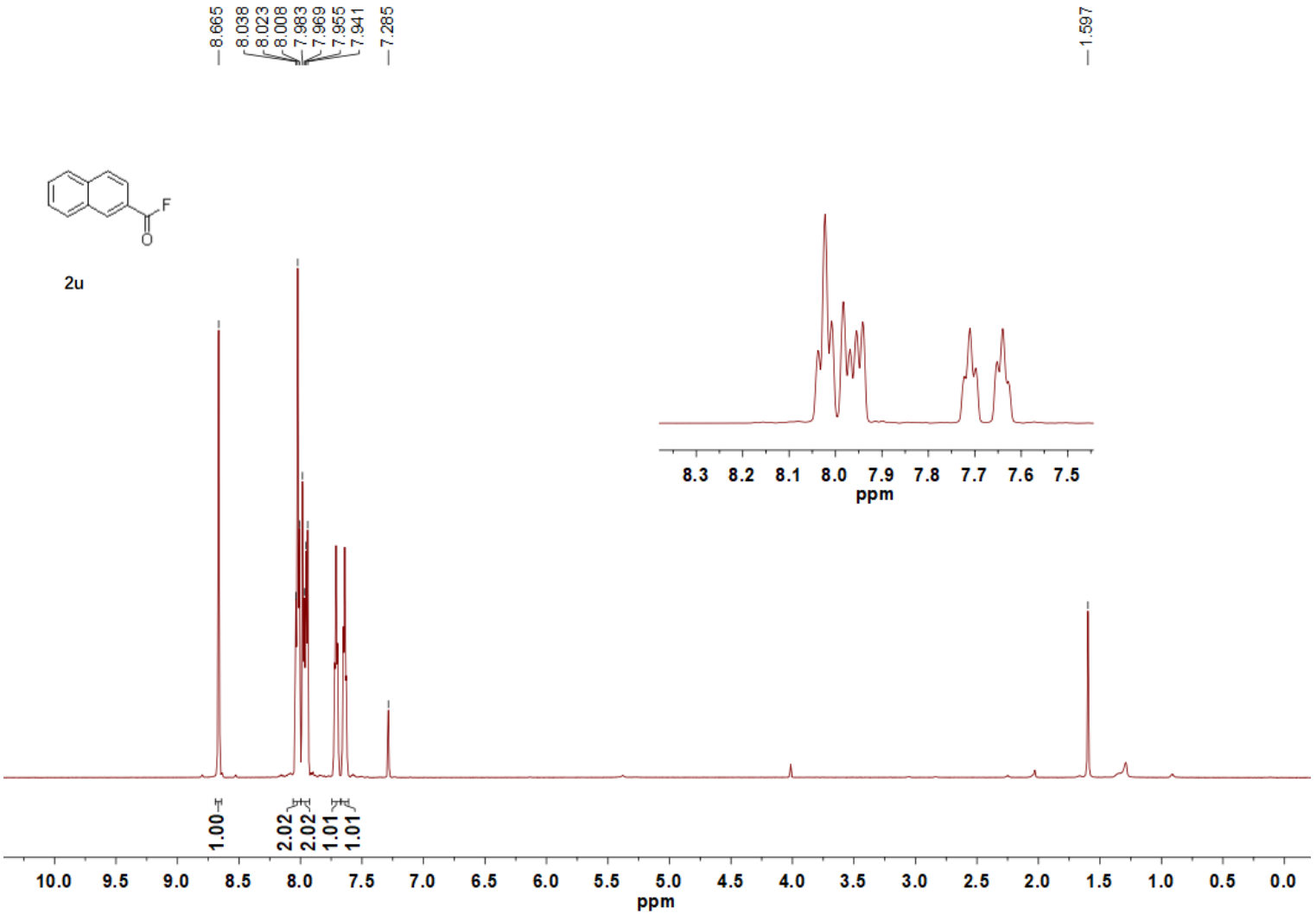
^{13}C NMR Spectrum of 2t (151 MHz, $CDCl_3$)



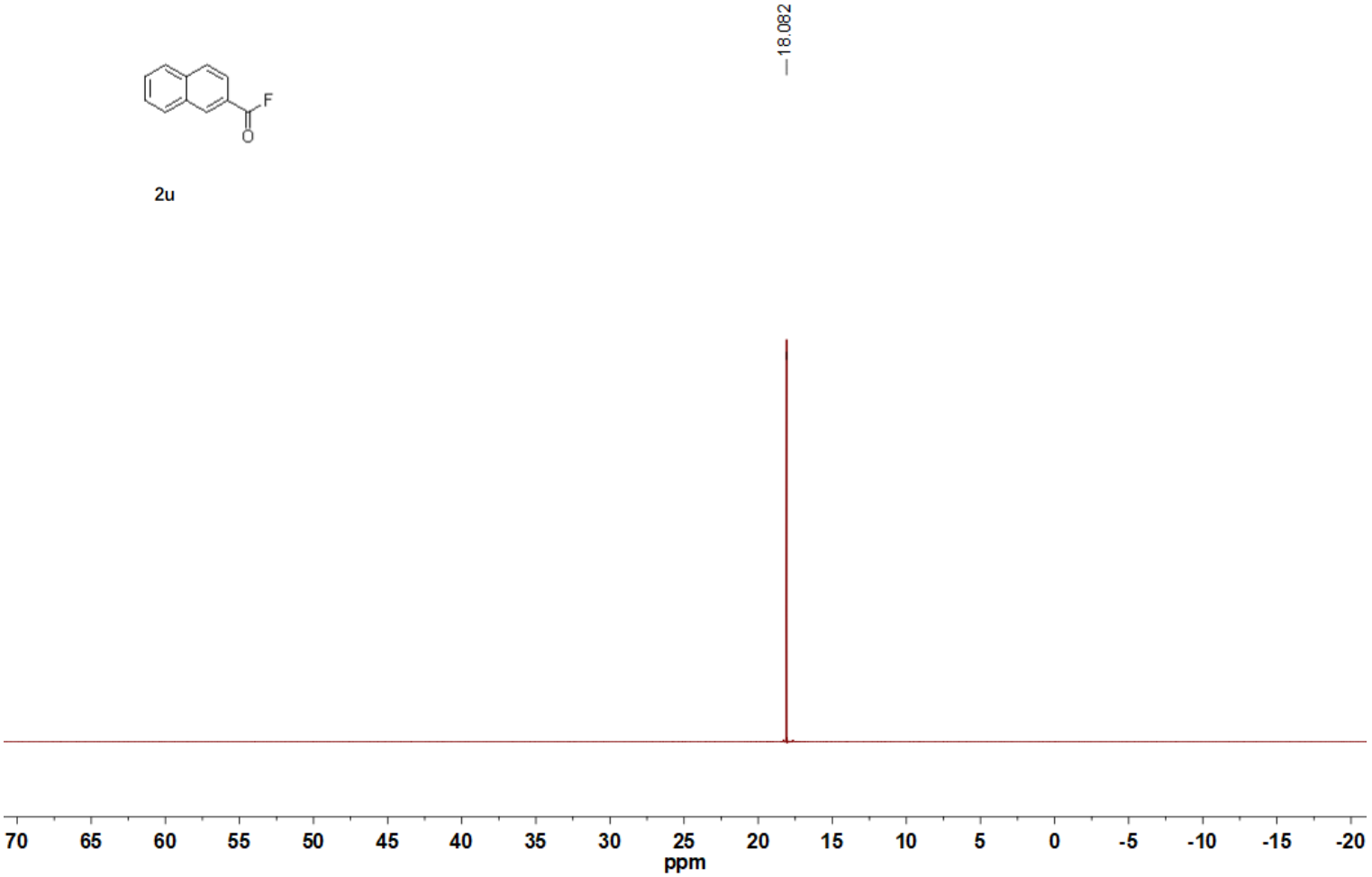
^{19}F NMR Spectrum of 2t (565 MHz, $CDCl_3$)



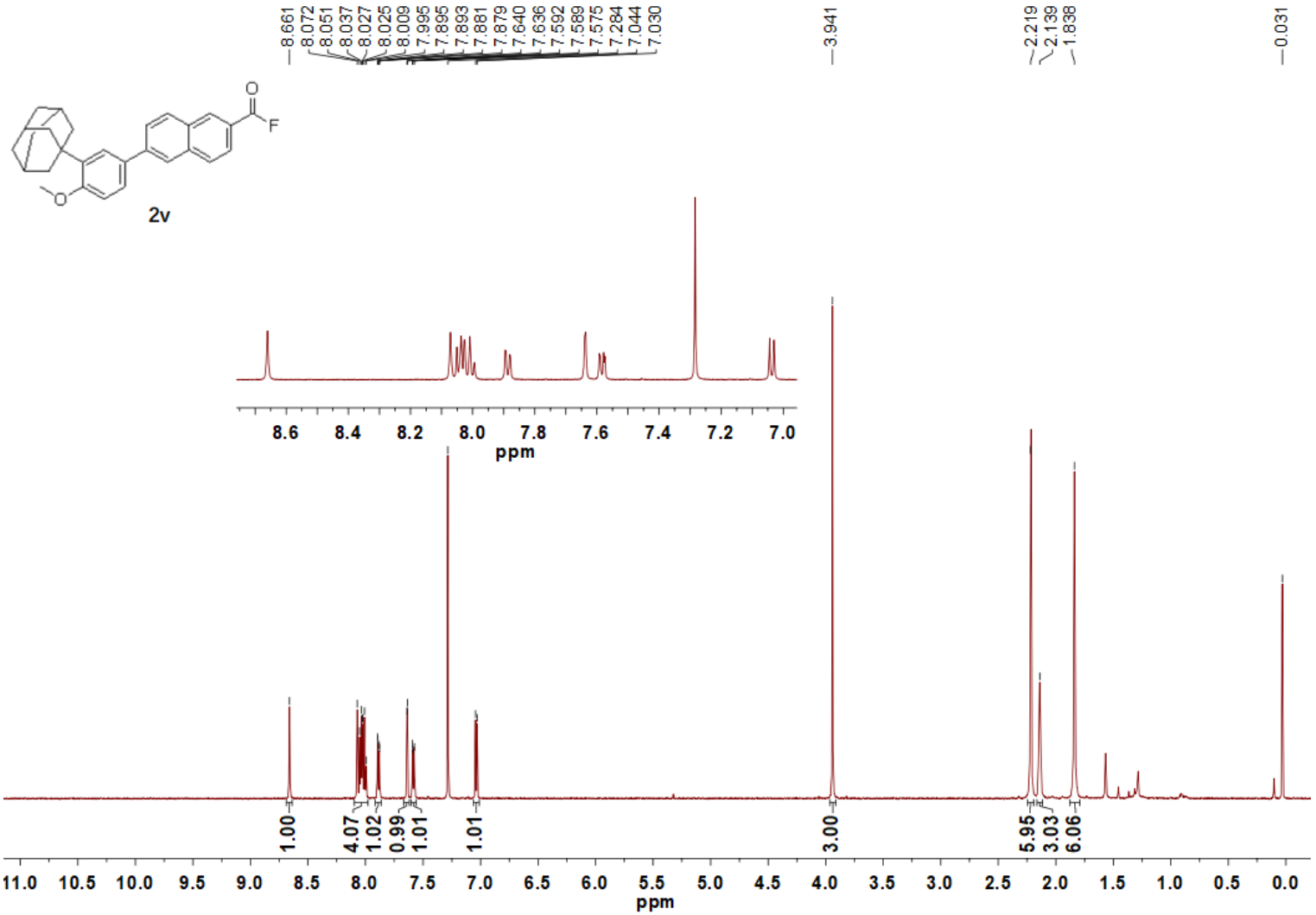
^{1}H NMR Spectrum of 2u (600 MHz, $CDCl_3$)



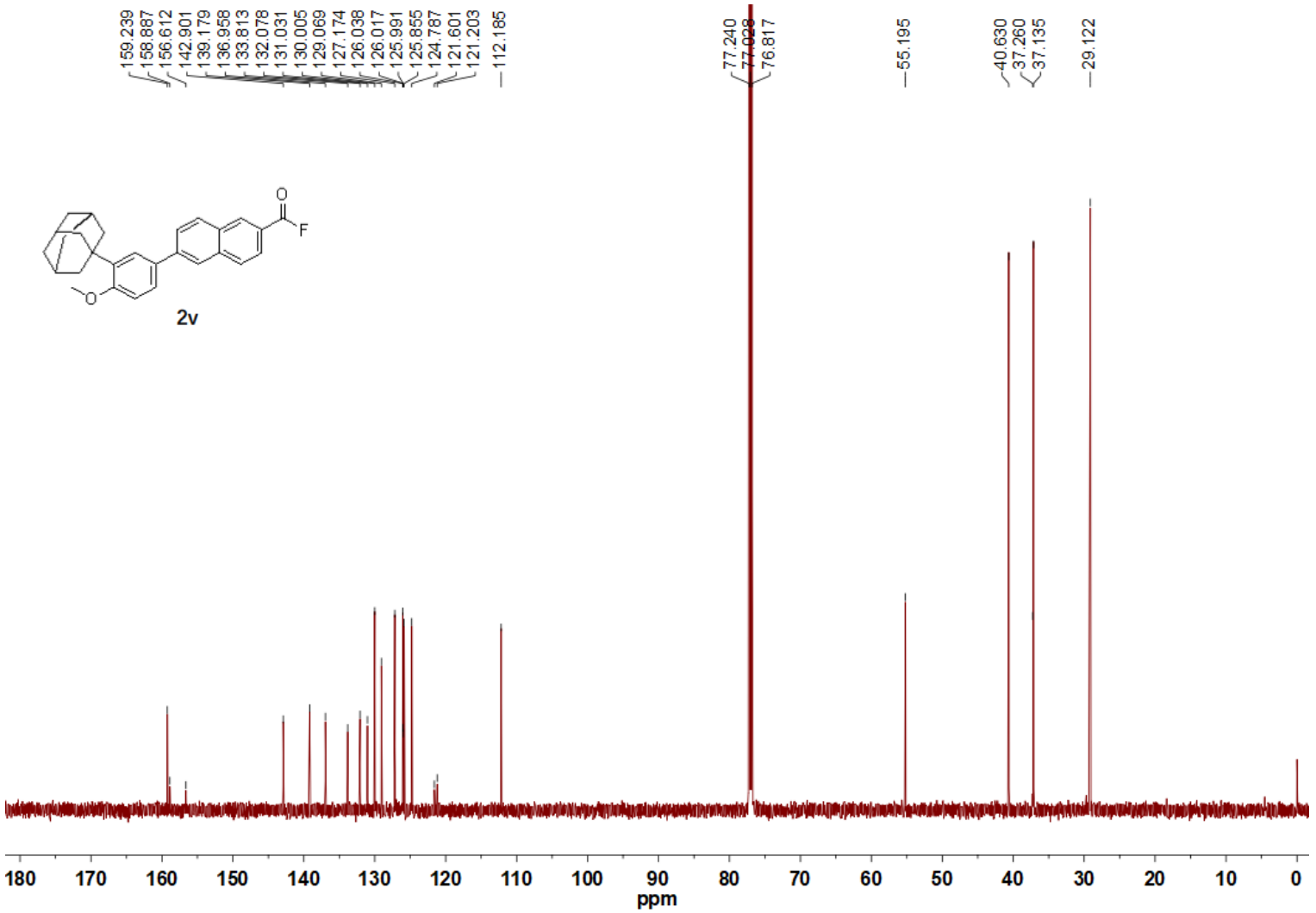
^{13}C NMR Spectrum of 2u (151 MHz, $CDCl_3$)



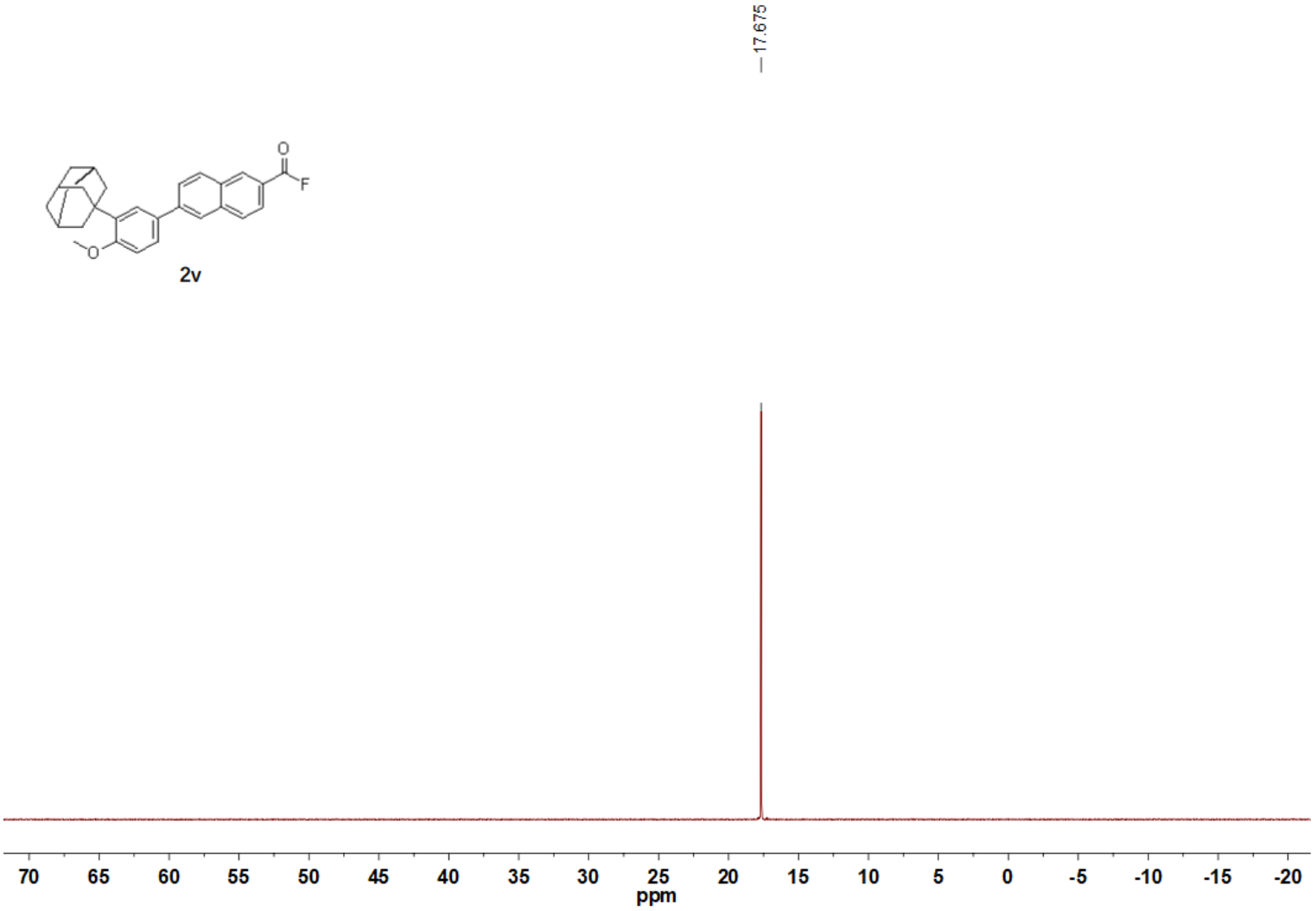
^{19}F NMR Spectrum of 2u (565 MHz, $CDCl_3$)



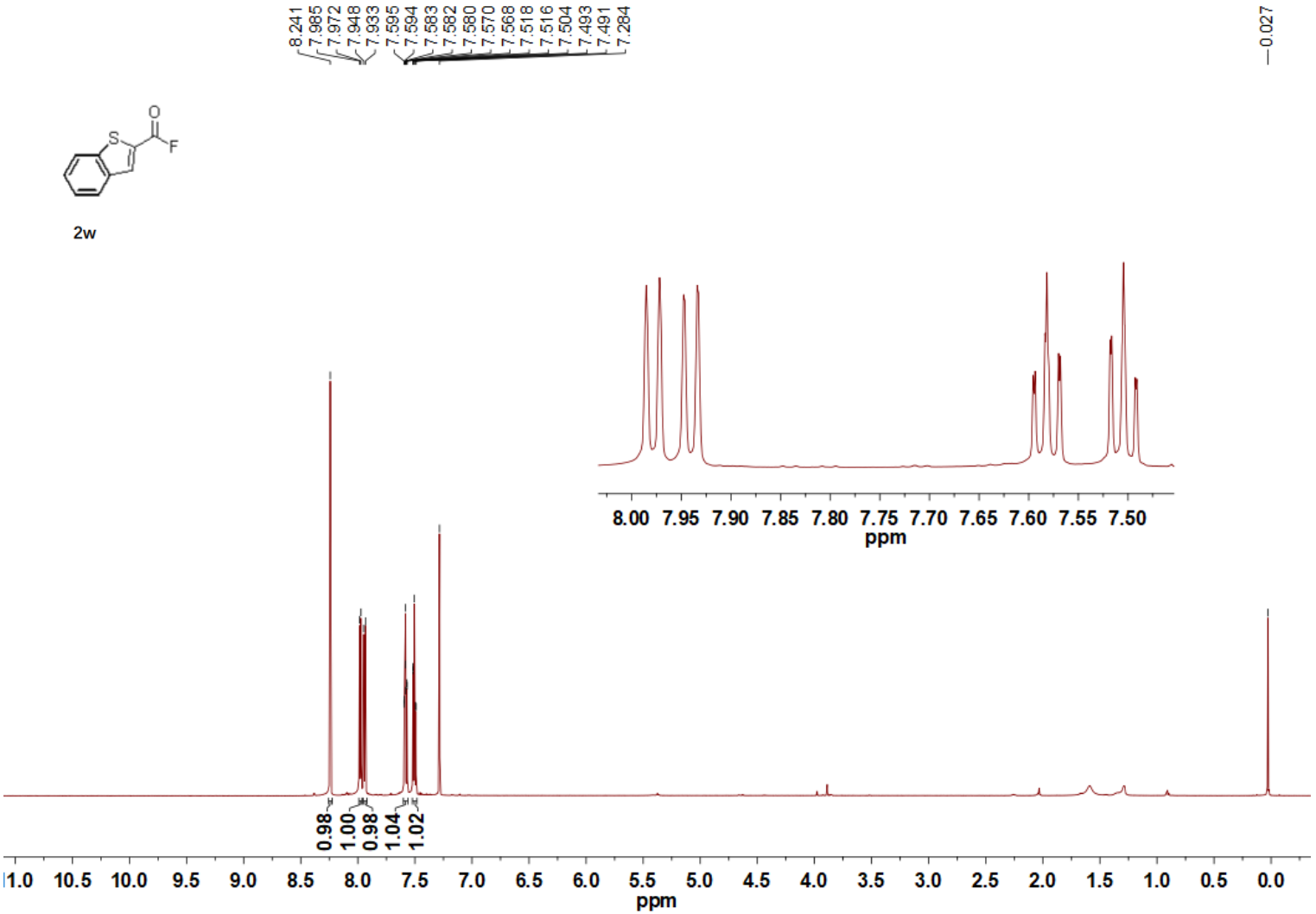
^{1}H NMR Spectrum of 2v (600 MHz, $CDCl_3$)



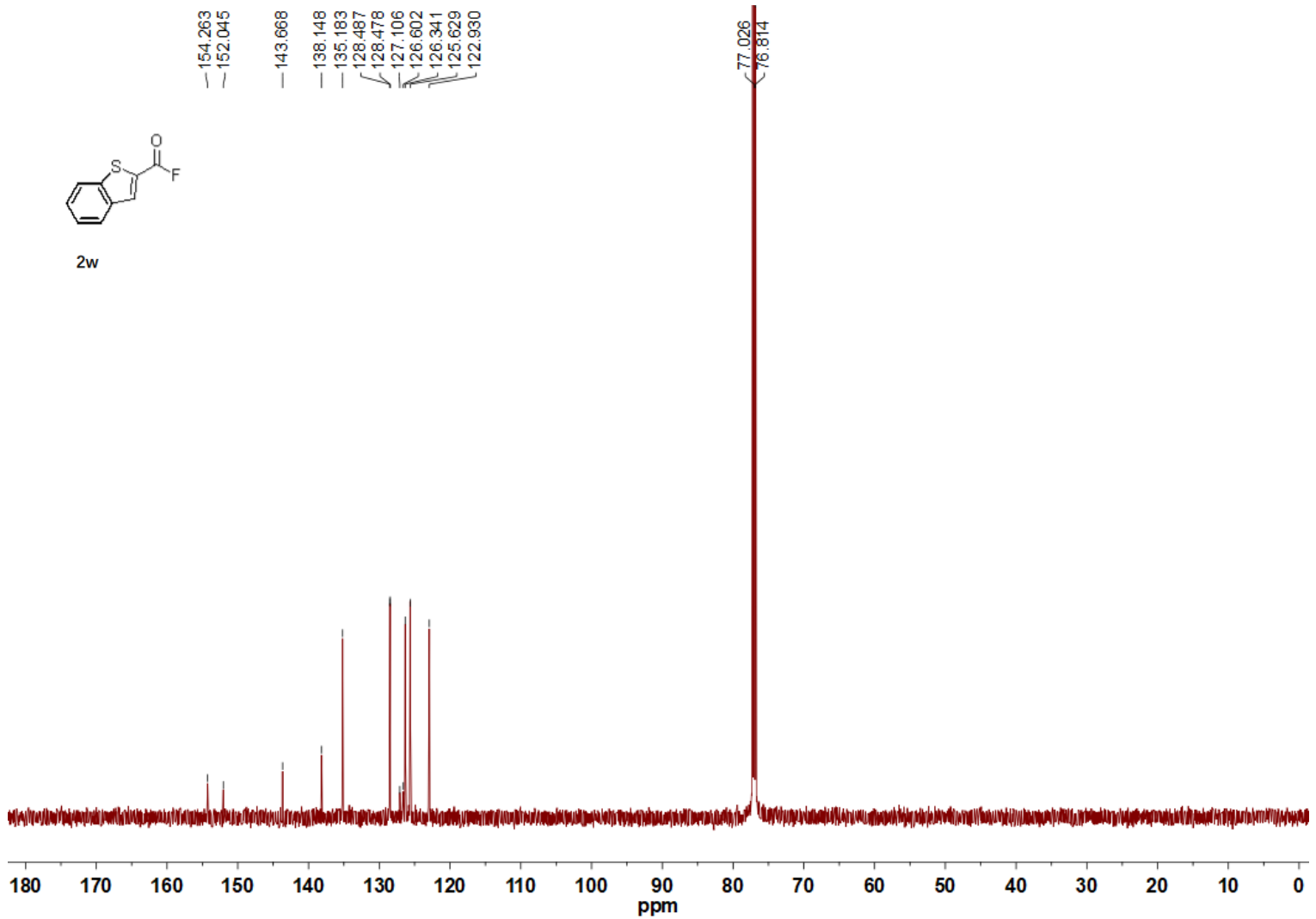
^{13}C NMR Spectrum of 2v (151 MHz, $CDCl_3$)



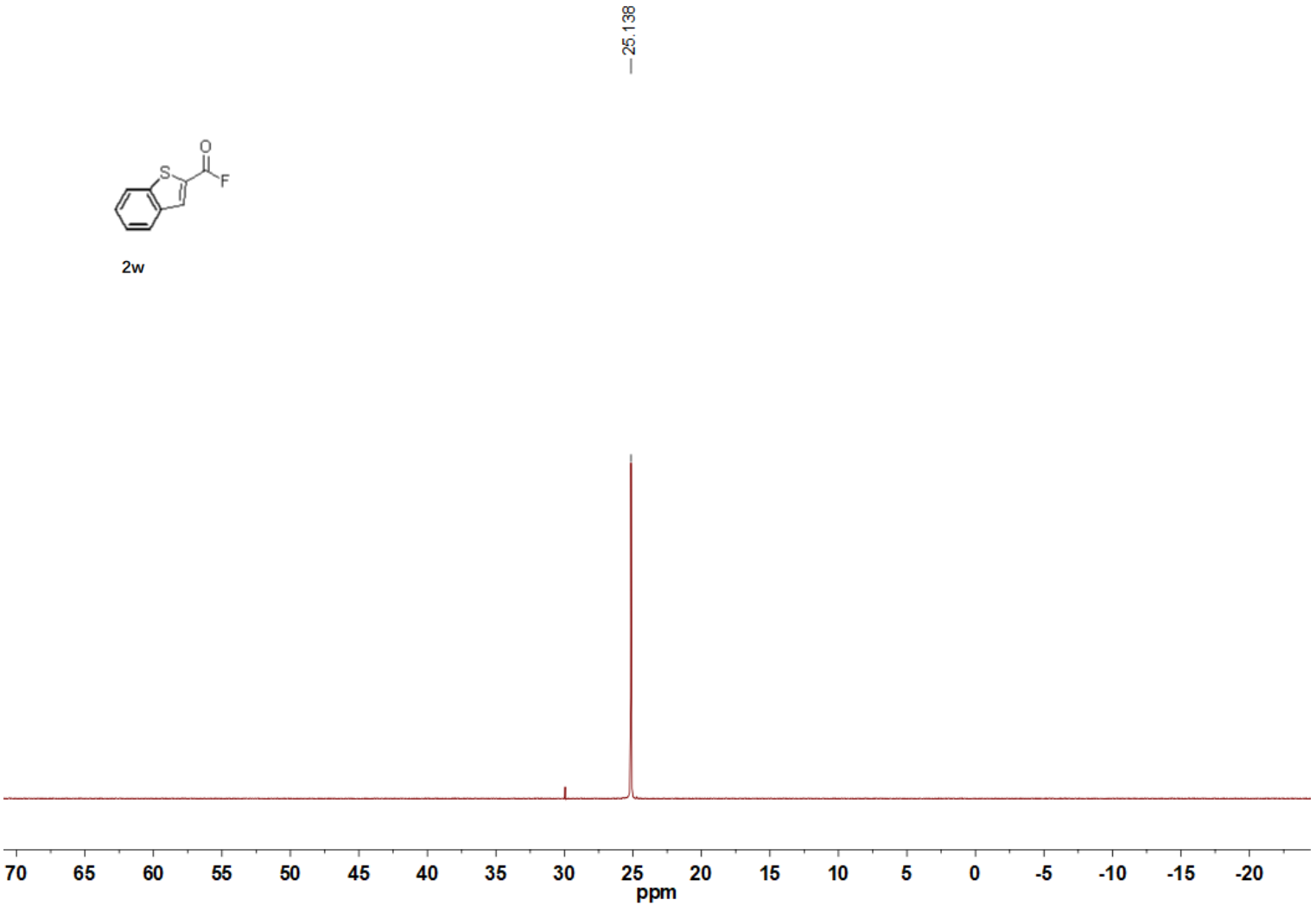
^{13}F NMR Spectrum of 2v (565 MHz, $CDCl_3$)



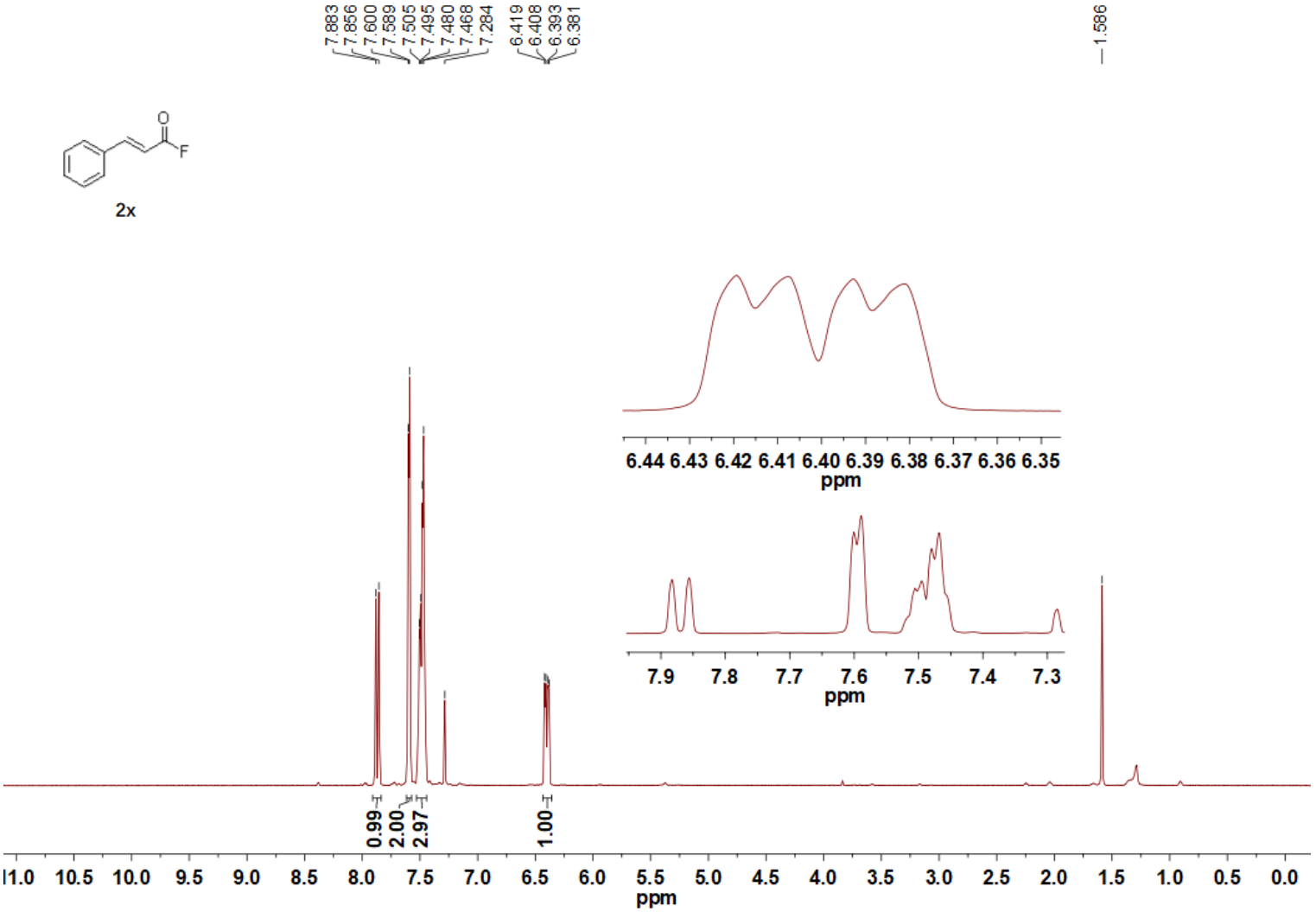
^{1}H NMR Spectrum of 2w (600 MHz, $CDCl_3$)



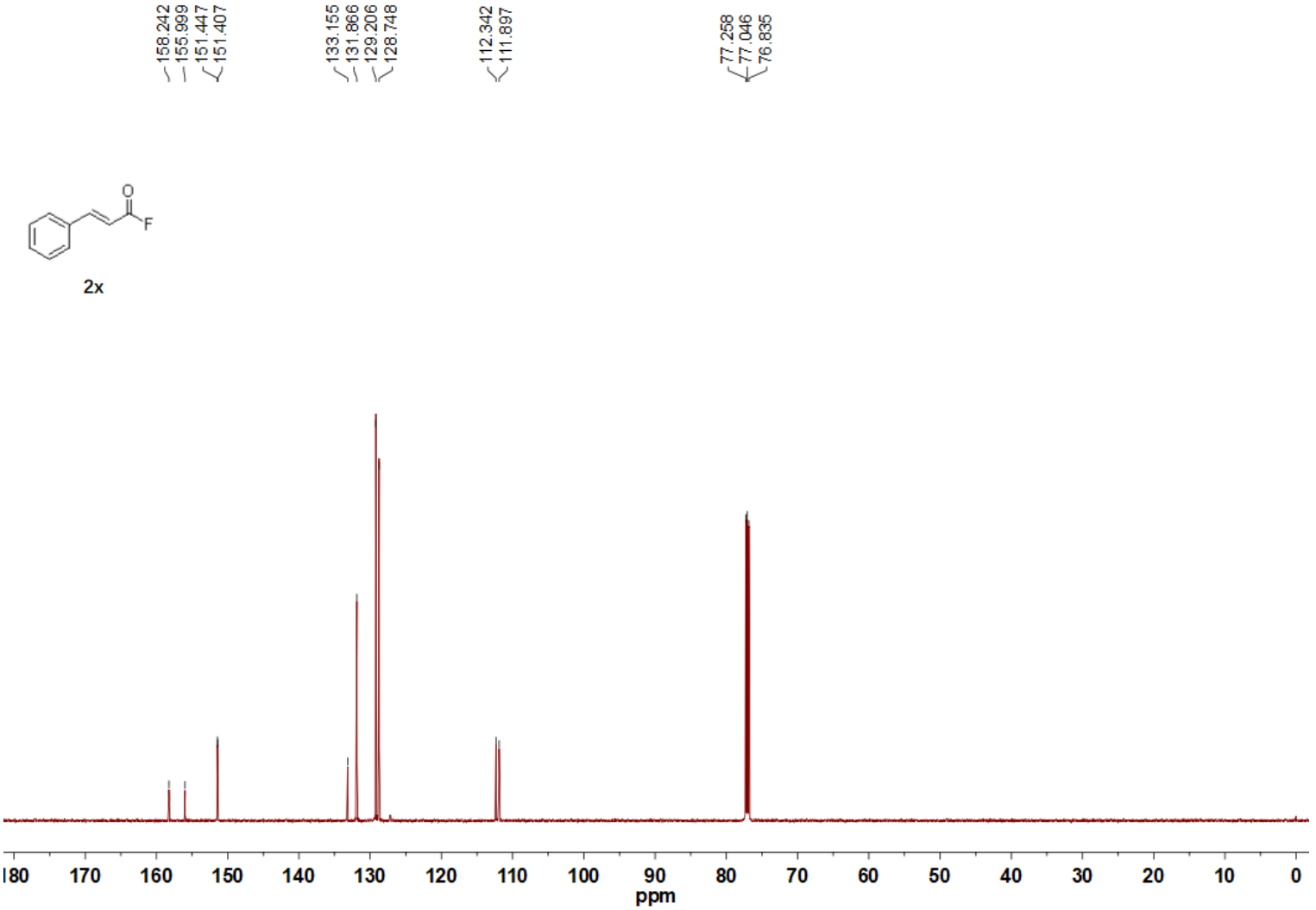
^{13}C NMR Spectrum of 2w (151 MHz, $CDCl_3$)



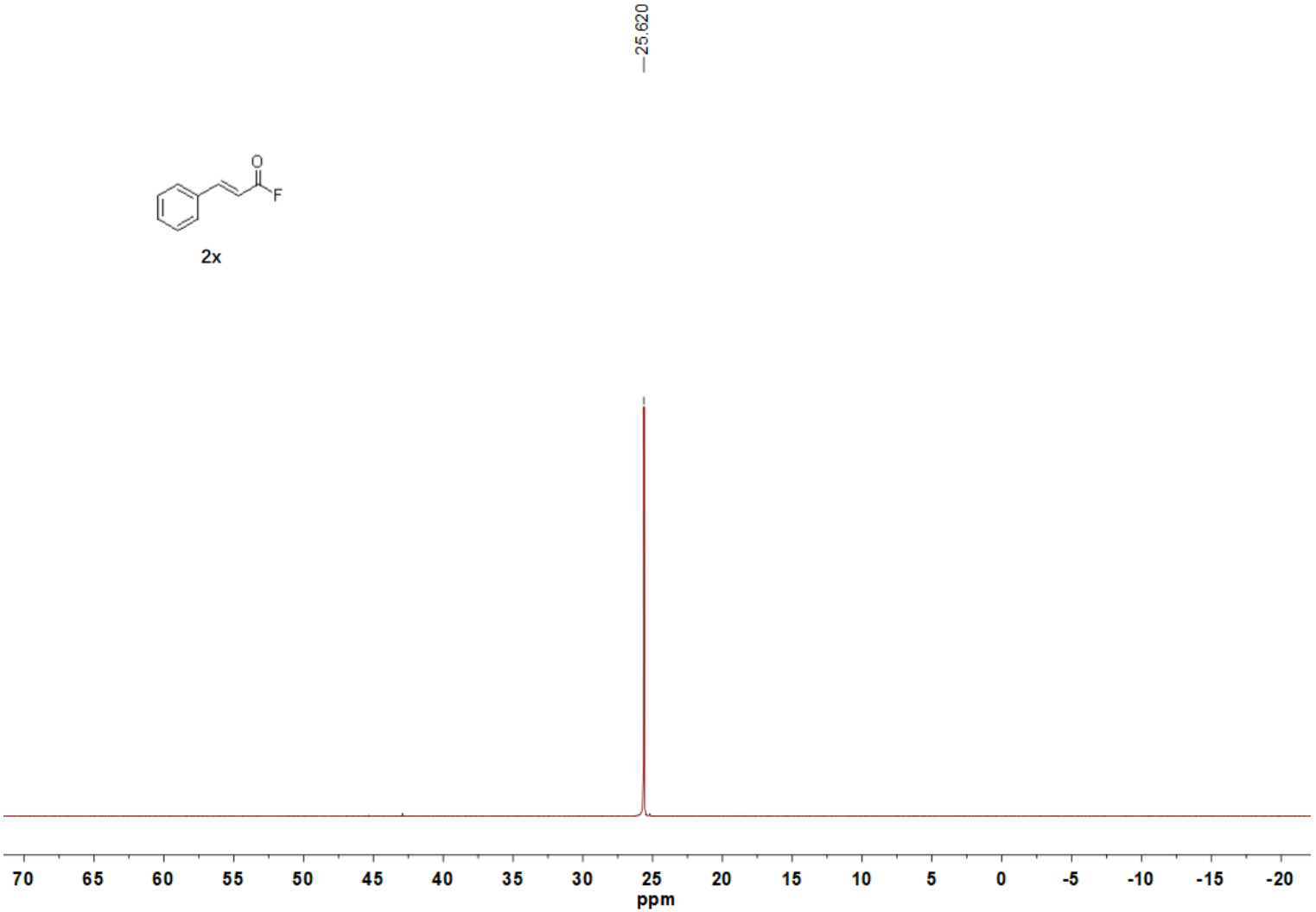
^{19}F NMR Spectrum of 2w (565 MHz, $CDCl_3$)



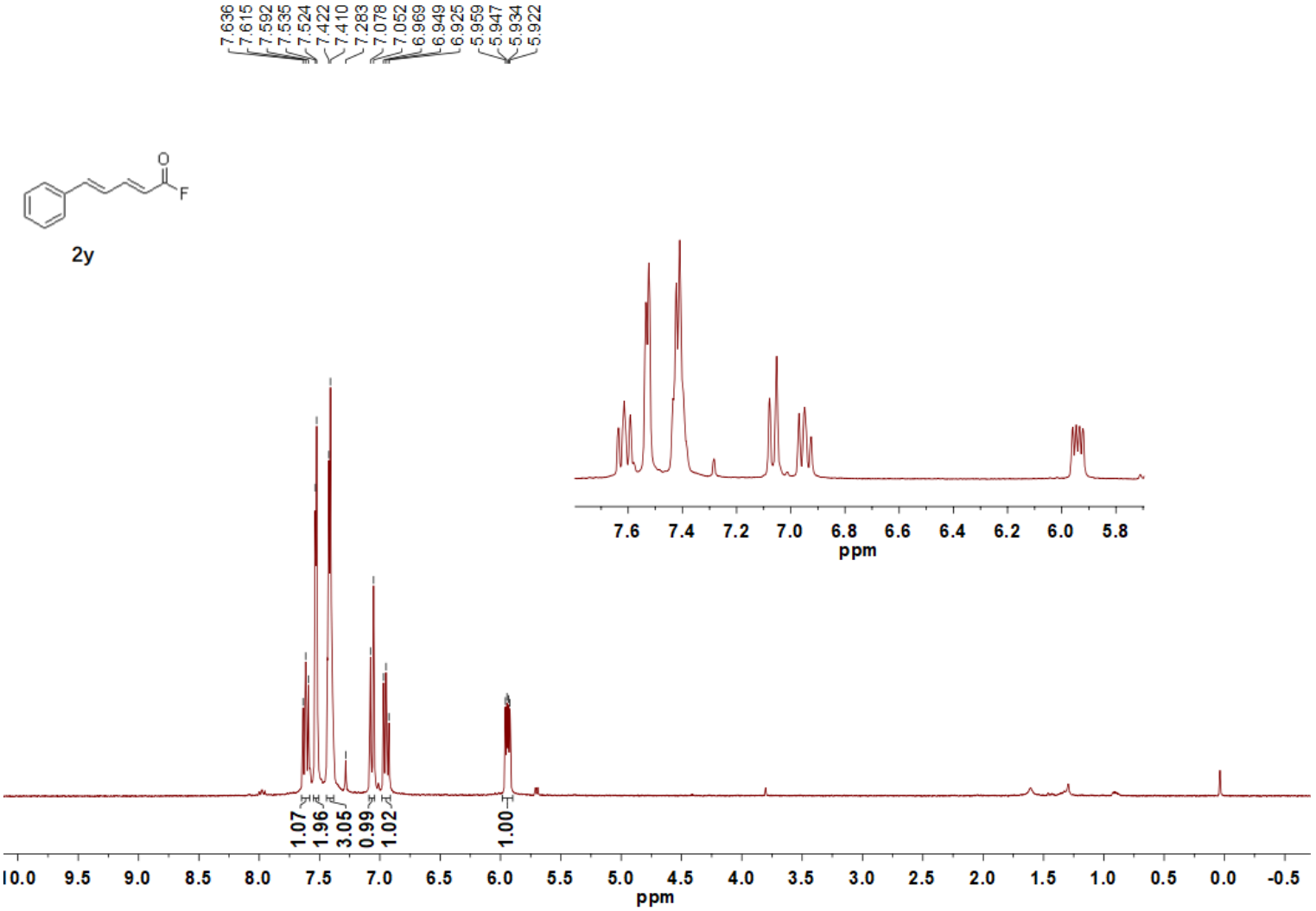
^{1}H NMR Spectrum of 2x (600 MHz, $CDCl_3$)



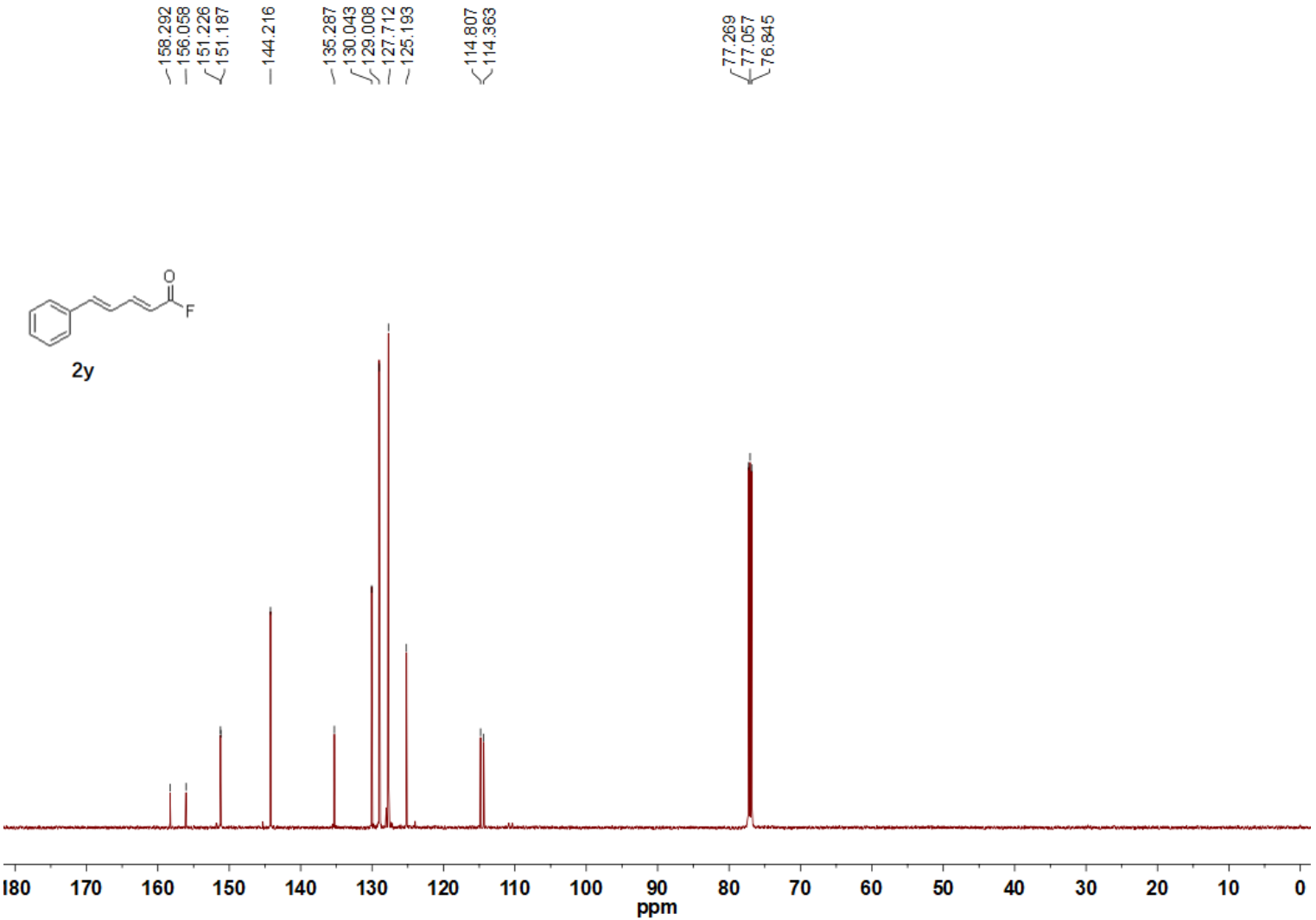
^{13}C NMR Spectrum of 2x (151 MHz, $CDCl_3$)



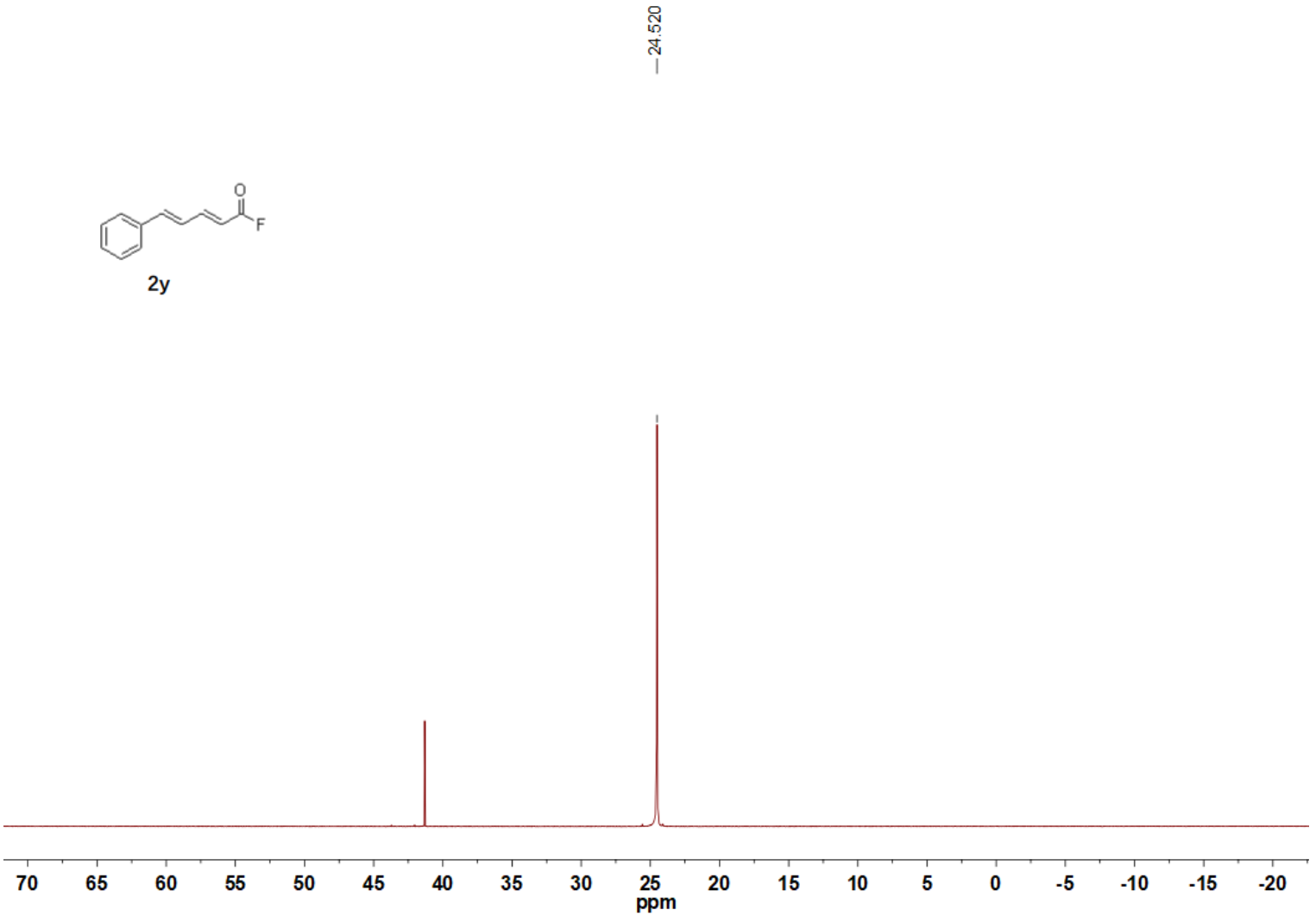
^{19}F NMR Spectrum of 2x (565 MHz, $CDCl_3$)



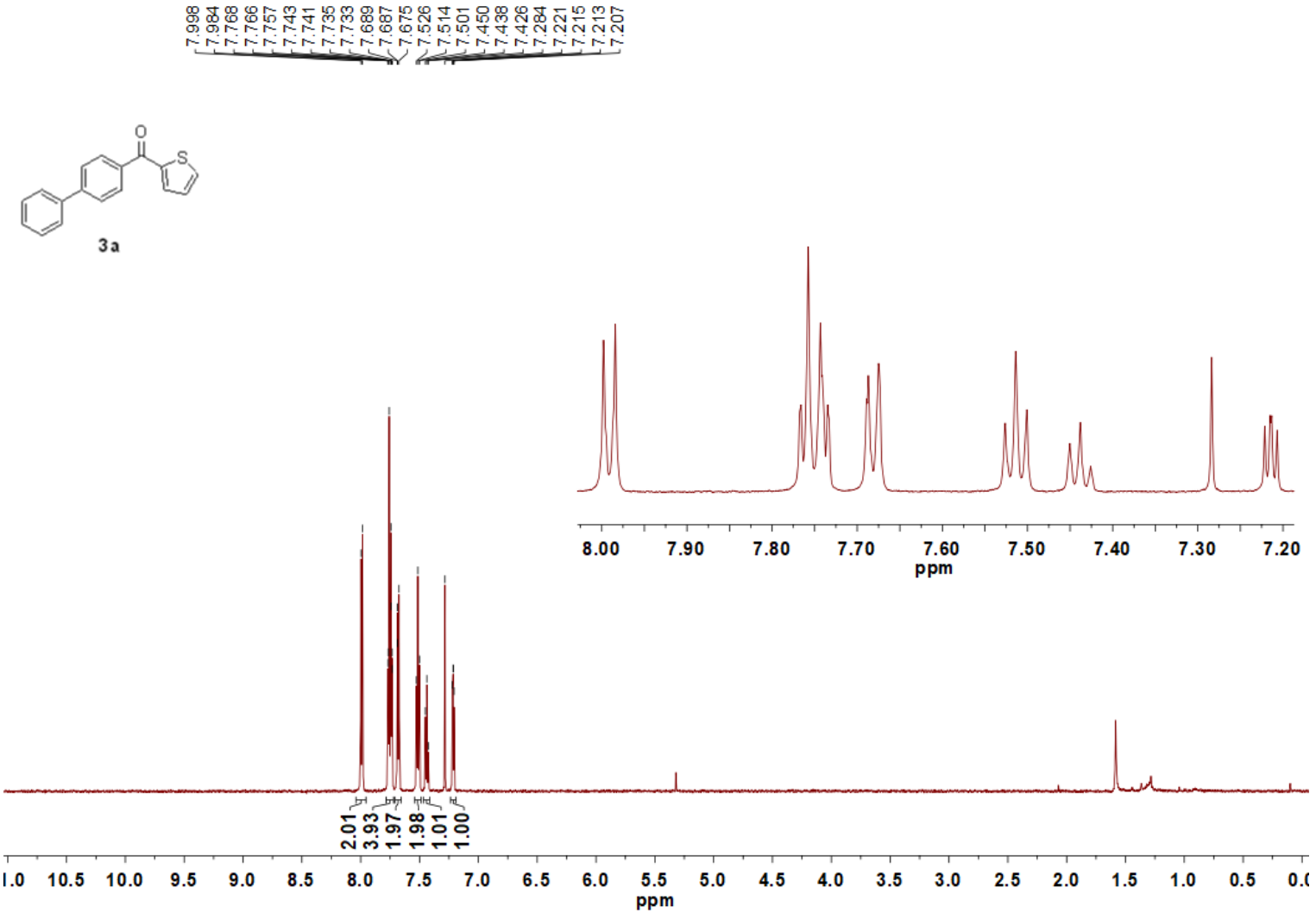
^{1}H NMR Spectrum of 2y (600 MHz, $CDCl_3$)



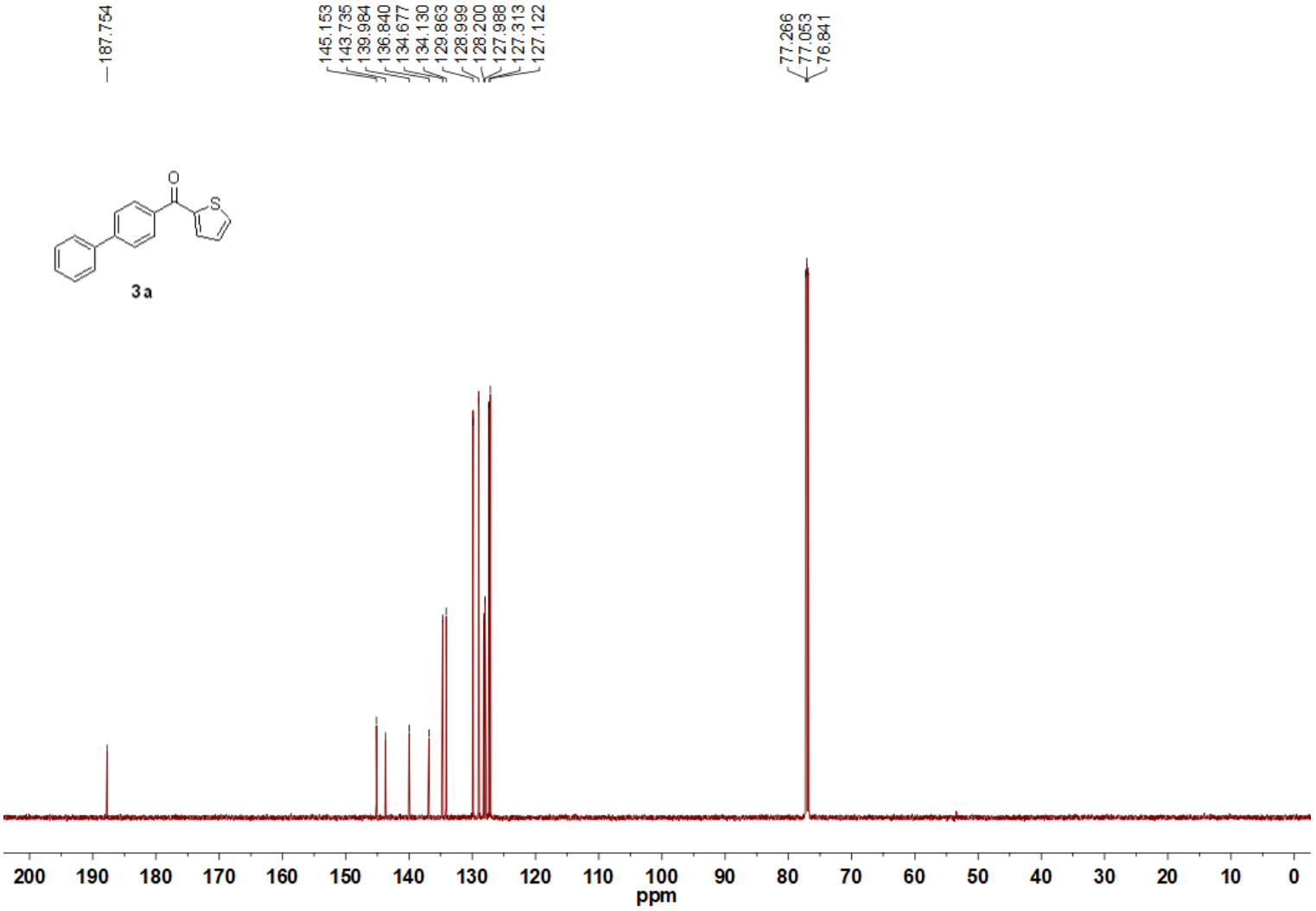
^{13}C NMR Spectrum of 2y (151 MHz, $CDCl_3$)



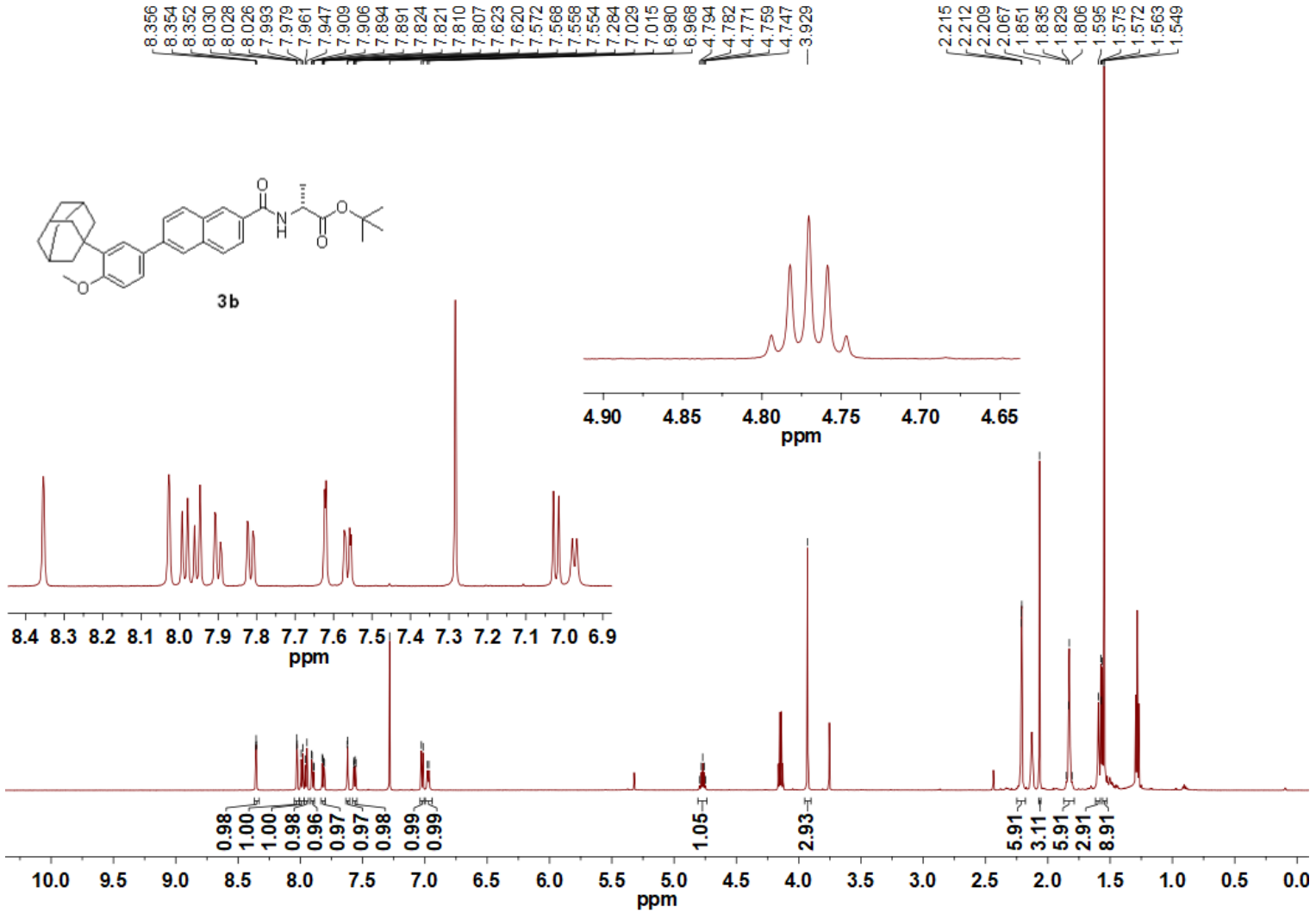
^{19}F NMR Spectrum of 2y (565 MHz, $CDCl_3$)



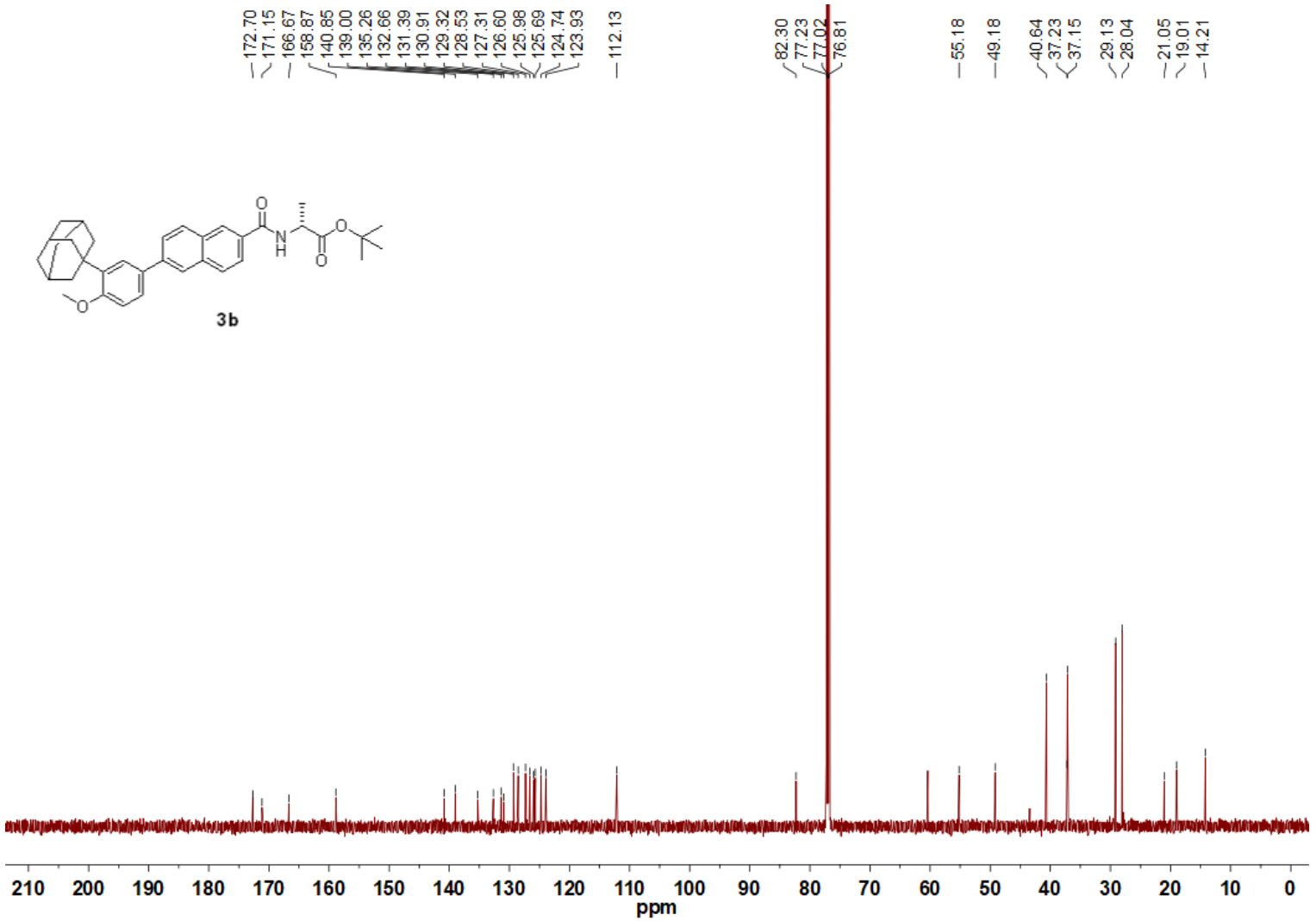
^{1}H NMR Spectrum of 3a (600 MHz, $CDCl_3$)



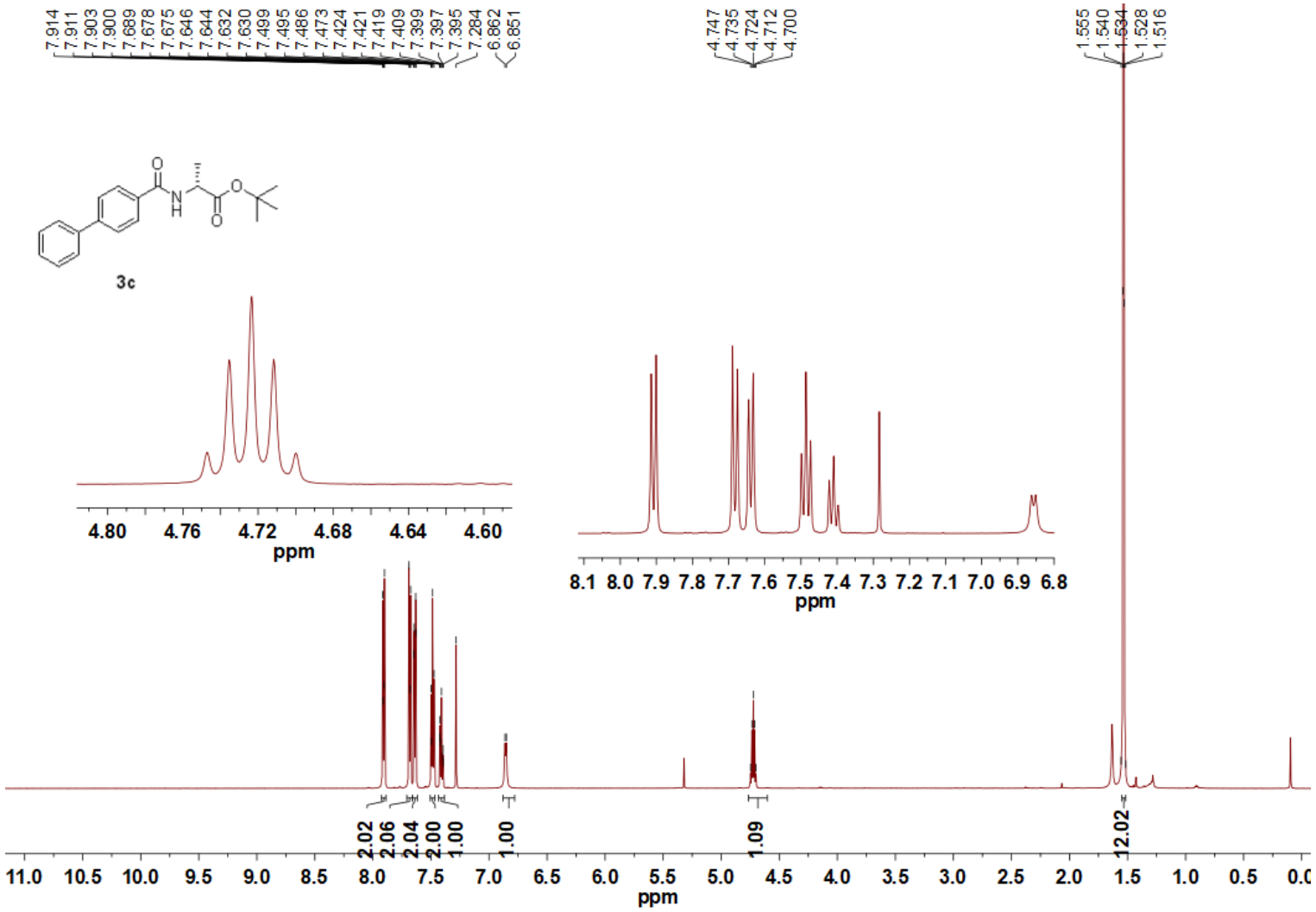
^{13}C NMR Spectrum of 3a (151 MHz, $CDCl_3$)



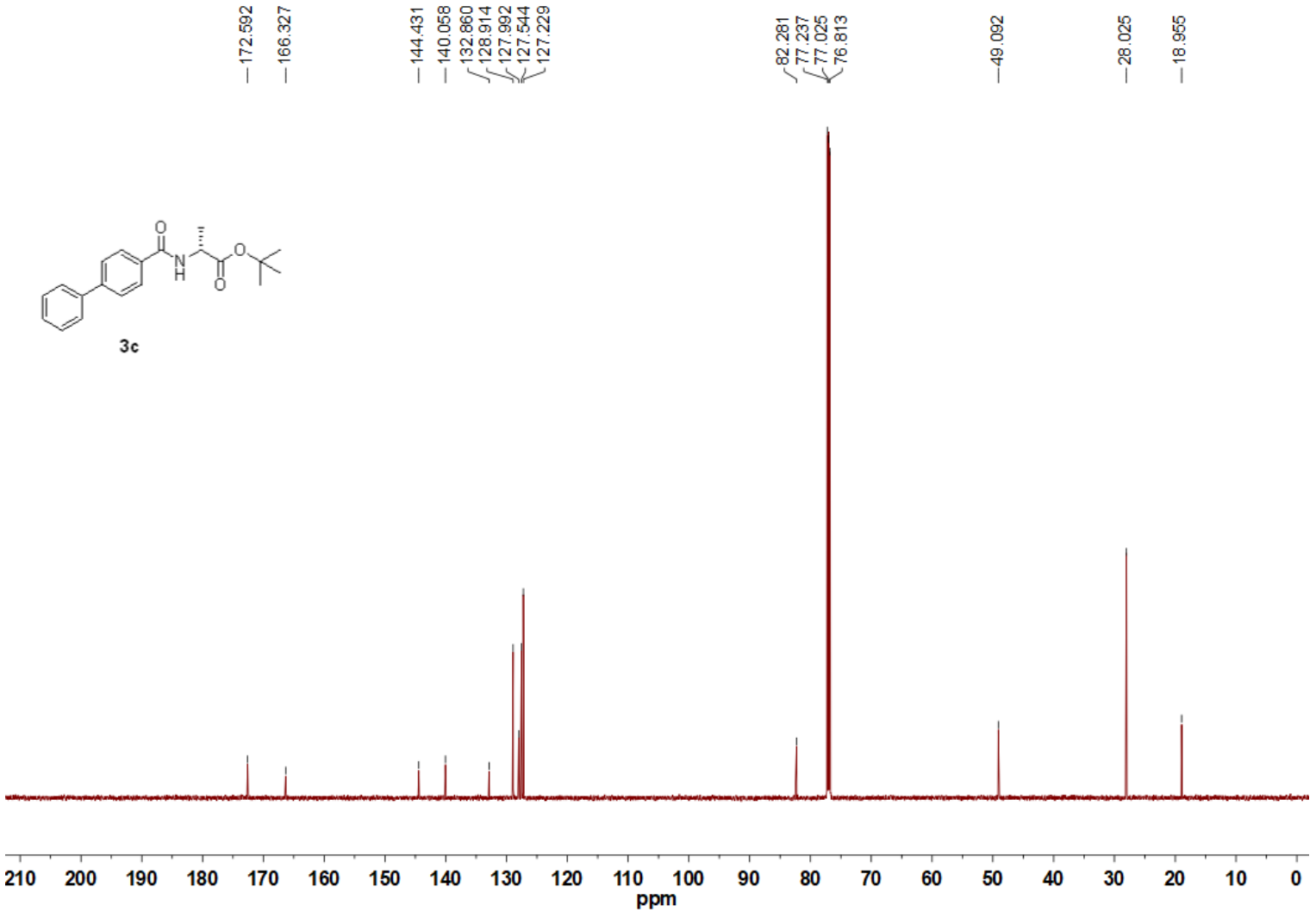
^{1}H NMR Spectrum of 3b (600 MHz, $CDCl_3$)



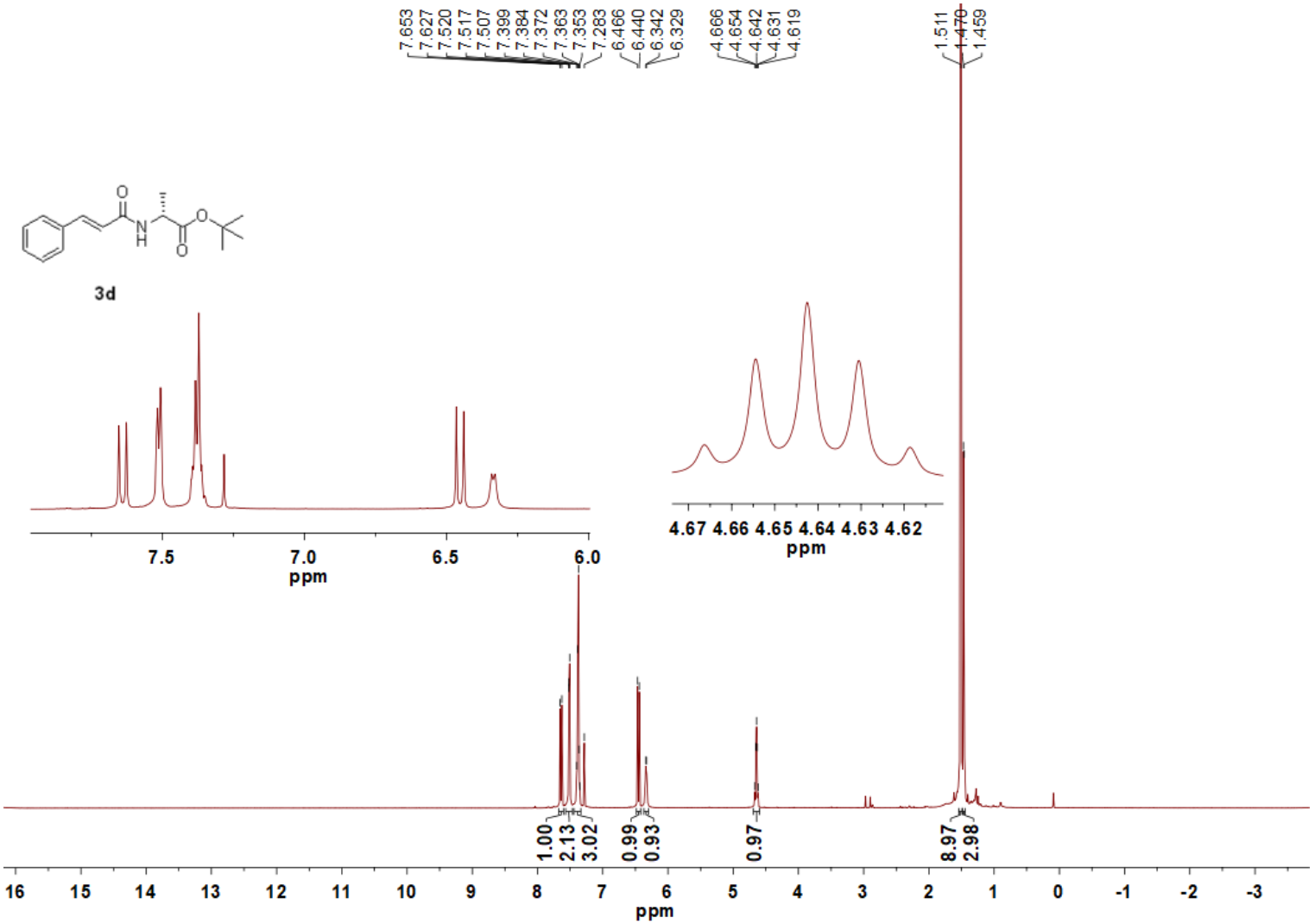
^{13}C NMR Spectrum of 3b (151 MHz, $CDCl_3$)



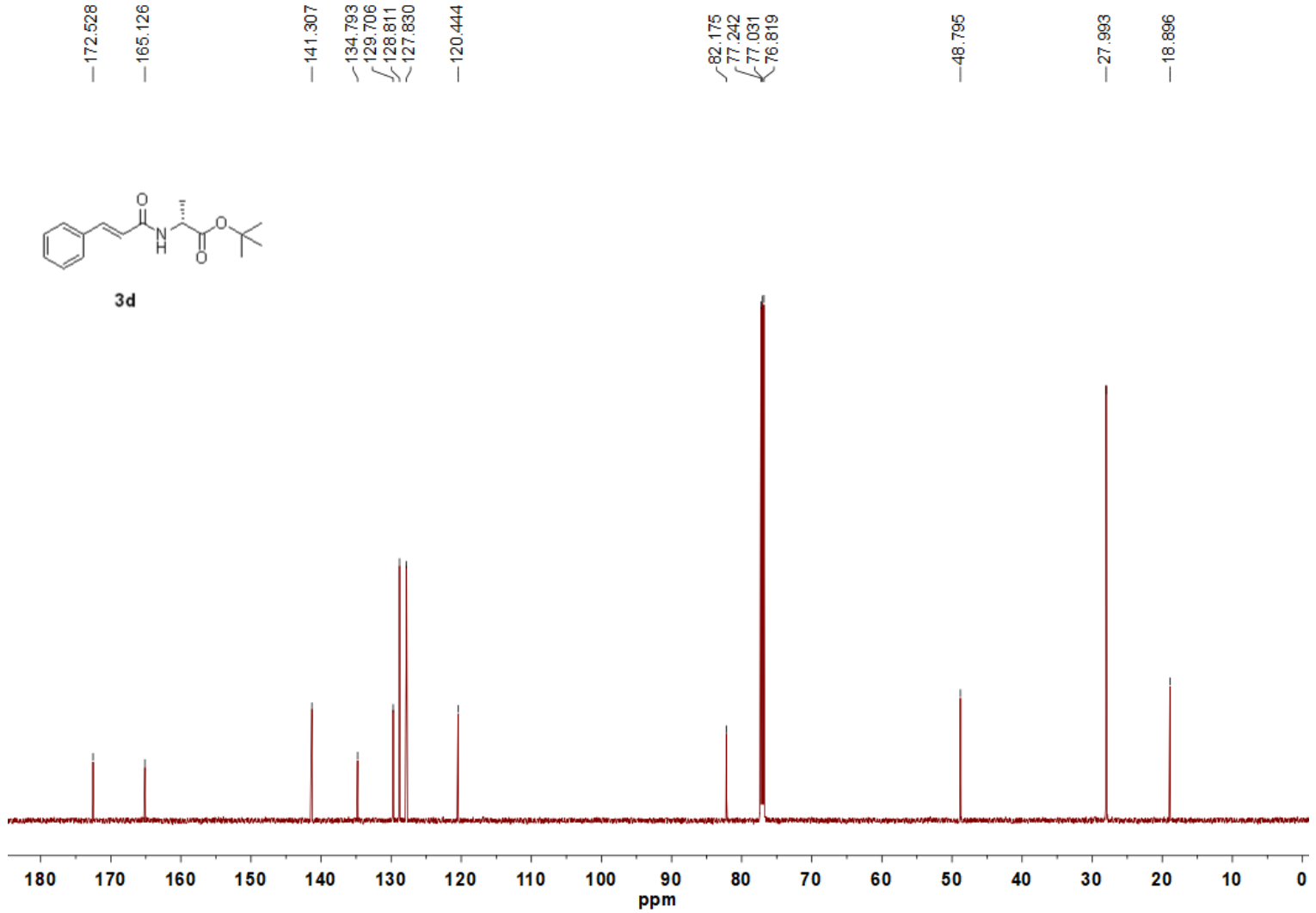
^{1}H NMR Spectrum of 3c (600 MHz, $CDCl_3$)



^{13}C NMR Spectrum of 3c (151 MHz, $CDCl_3$)



^{1}H NMR Spectrum of 3d (600 MHz, $CDCl_3$)



^{13}C NMR Spectrum of 3d (151 MHz, $CDCl_3$)