Supplementary Information (SI) for Organic & Biomolecular Chemistry.

Photoinduced SF_6 degradation for deoxyfluorination of propargyl alcohols

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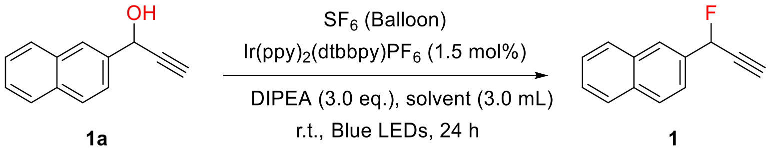
Content

1. General information

All reactions involving air or moisture sensitive reagents were carried out in flame dried glass ware under nitrogen atmosphere using standard Schlenk techniques. Solvents were either freshly distilled or obtained in extra-dry grade from commercial sources, and stored over molecular sieves (3 Å). Diethyl ether (Et_2O) was distilled over sodium/ benzophenone and stored over activated molecular sieves (3 Å). Dichloromethane (CH_2Cl_2) was refluxed over CaH_2 and used as freshly distilled. SF_6 gas (purity ⩾ 99.999%) was purchased from Chengdu Kemelte Special Gas Co., Ltd. The material of vessels for the reactions is borosilicate glass. Blue LED lamps (465 nm) were purchased from Zhongshan Langniu Lighting Technology Co., Ltd. (E27, 15 W) and the Blue LED strips (475 nm, 3 meters, 32 W) were purchased from Inwares Pte Ltd (Singapore). The needle valves, and PFA, HPFA micro tubings were purchased from IDEX Health & Science (Oak Harbor, WA). Column chromatography was performed with silica gel (300-400 mesh). Merck silica gel 60 F254 plates were used for thin layer chromatography (TLC). The NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz (^1H), 101 MHz (^{13}C), 162 MHz (^{31}P) and 376 MHz (^{19}F) in $CDCl_3$ with tetramethylsilane as the internal standard. Chemical shifts (δ) were reported in parts per million (ppm). Splitting patterns were designated as s, singlet; d, doublet; t; dd, doublet of doublets; m, multiplet. All GC analysis was performed on Agilent 8860 GCMS. High-resolution mass spectra were obtained with an AB Triple 5600 mass spectrometer by ESI on a TOF mass analyzer.

2. Detailed optimization of reaction conditions

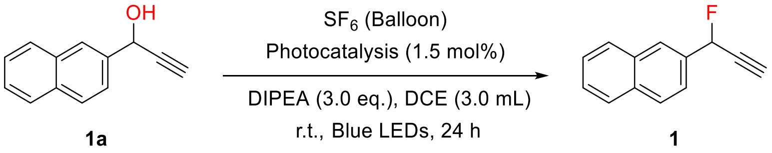
2.1 Screening of solvents



Entry	Solvent (3.0 mL)	Yield of **1** (%)[a]
1	DMF	9%
2	DMSO	0%
3	THF	33%
4	MeCN	18%
5	1,4-dioxane	35%
6	DCE	56%

Table S1 Reaction conditions: 1-(2-naphthyl)-2-propyn-1-ol **1a** (0.3 mmol, 1.0 eq.), $Ir(ppy)_2(dtbbpy)PF_6$ (0.0045 mmol, 1.5 mol%), DIPEA (0.9 mmol, 3.0 eq.), solvent (3.0 mL), 1.0 atm of SF_6 (balloon), 15 W blue LED lamp, r.t. (23 ~ 25 °C), 24 h, [a]Isolated yields are given.

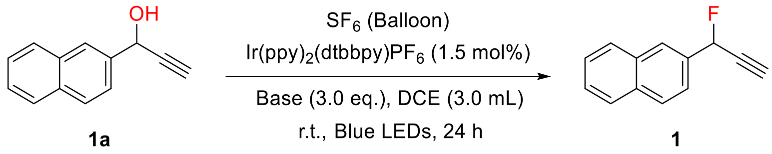
2.2 Screening of photocatalysts



Entry	Photocatalyst (1.5 mol%)	Yield of **1** (%)[a]
1	$Ir(ppy)_2(dtbbpy)PF_6$	56%
2	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	55%
3	$Ir(ppy)_3$	5%
4	Eosin Y	5%
5	$Ru(bpy)_3PF_6$	40%

Table S2 Reaction conditions: 1-(2-naphthyl)-2-propyn-1-ol **1a** (0.3 mmol, 1.0 eq.), photocatalyst (0.0045 mmol, 1.5 mol%), DIPEA (0.9 mmol, 3.0 eq.), DCE (3.0 mL), 1.0 atm of SF_6 (balloon), 15 W blue LED lamp, r.t. (23 ~ 25 °C), 24 h, [a]Isolated yields are given.

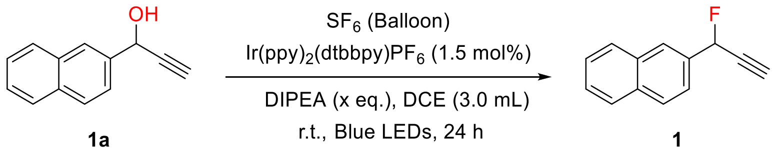
2.3 Screening of base



Entry	Base (3.0 eq.)	Yield of **1** (%)[a]
1	DIPEA	56%
2	Et_3N	48%
3	NCy_2Me	50%

Table S3 Reaction conditions: 1-(2-naphthyl)-2-propyn-1-ol **1a** (0.3 mmol, 1.0 eq.), $Ir(ppy)_2(dtbbpy)PF_6$ (0.0045 mmol, 1.5 mol%), base (0.9 mmol, 3.0 eq.), DCE (3.0 mL), 1.0 atm of SF_6 (balloon), 15 W blue LED lamp, r.t. (23 ~ 25 °C), 24 h, Isolated yields are given.

2.4 Screening of the equivalents of base



Entry	Base (x equiv.)	Yield of **1** (%)[a]
1	3.0 equiv.	55%
2	5.0 equiv.	60%
3	10.0 equiv.	37%

Table S4 Reaction conditions: 1-(2-naphthyl)-2-propyn-1-ol **1a** (0.3 mmol, 1.0 eq.), $Ir(ppy)_2(dtbbpy)PF_6$ (0.0045 mmol, 1.5 mol%), DIPEA (x eq.), DCE (3.0 mL), 1 atm of SF_6 (balloon), 15 W blue LED lamp, r.t. (23 ~ 25 °C), 24 h, [a]Isolated yields are given.

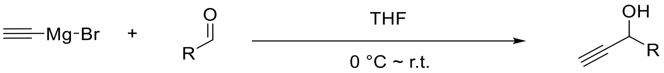
3 Experimental procedures and characterization data of products

3.1 Set-up of general photochemical reactions

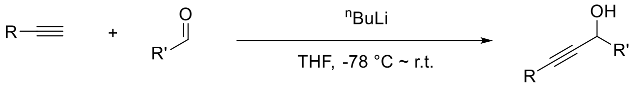
General photochemical reactions were performed within 10.0 mL glass tubes sealed with PTFE caps and irradiated by a blue LED lamp (15 W, 465 nm). The reaction vials were placed at approximately 1.0 ~ 2.5 cm distance away from the LED lamp with a cooling fan to keep the reaction temperature at 23 ~ 25 °C (Figure S1).

Figure S1 General photochemical equipment

3.2 Synthesis of propargyl alcohols



General procedure A: To a 100 mL schlenk tube were added aldehyde (5.0 mmol, 1.0 eq.) and dry THF (10.0 mL), then a solution of ethynyl magnesium bromide (0.5 M in THF, 1.2 eq.) was added dropwise at 0 °C within ten minutes under N_2 atmosphere. After the addition of ethynyl magnesium bromide was finished, the mixture was further stirred at room temperature until complete consumption of starting material as monitored by TLC analysis. Then, a saturated aqueous solution of NH_4Cl (10.0 mL) was added to quench the reaction and H_2O (10.0 mL) was added to dilute. Subsequently, the reaction mixture was extracted using EtOAc (3×10.0 mL) and the organic layer was dried with anhydrous Na_2SO_4, filtrated and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/ethyl acetate = 5/1) to afford the corresponding propargyl alcohols.



General procedure B: To a 100 mL schlenk tube were added alkyne (6.0 mmol, 1.2 eq.) and dry THF (10.0 mL), then a solution of n-butyllithium (2.4 M in hexane, 1.2 eq.) was added dropwise at -78 °C within ten minutes under N_2 atmosphere. After the addition of n-butyllithium was finished and the mixture was further stirred at -78 °C for one hour, aldehyde (5 mmol, 1.0 eq.) was slowly added to the solution. After stirring at low temperature for half an hour, the mixture was further stirred at room temperature until complete consumption of starting material as monitored by TLC analysis. Then, a saturated aqueous solution of NH_4Cl (10 mL) was added to quench the reaction and H_2O (10 mL) was added to dilute. Subsequently, the reaction mixture was extracted using EtOAc (3×10 mL) and the organic layer was dried with anhydrous Na_2SO_4, filtrated and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/ethyl acetate = 5/1) to afford the corresponding propargyl alcohol.

3.3 Synthesis of propargyl fluoride products

To an oven-dried transparent glass tube (10.0 mL) equipped with a magnetic stir bar was added alcohol (0.3 mmol, 1.0 eq.) and $Ir(ppy)_2(dtbbpy)PF_6$ (0.0045 mmol, 1.5 mol%). The tube was sealed and connected to a vacuum line where it was evacuated and back-filled with SF_6 for three times. Then DCE (3.0 mL) and DIPEA (260.8 μL, 5.0 eq. 1.5 mmol) were added under SF_6 flow. During the reaction stirring, the tube was filled with SF_6 constantly through a SF_6 balloon (about 1.20 x 10^{-4} m^3) and irradiated with 15 W blue LED lamp (2.0 ~ 3.0 cm away, with cooling fan to keep the reaction temperature at 23 ~ 25 °C) for 24 hours. Upon completion, the mixture was concentrated in vacuum to remove the solvent thoroughly. After alkalizing the silica gel column (petroleum ether/triethylamine = 100:1 ~ 100:5), the residue was purified by a silica gel flash column chromatography to give the desired product.

SF_6 is known not being able to be described by the ideal gas model due to non-negligible intermolecular interactions. Therefore, the van-der-Waals equation[2] has to be used to calculate the pressure inside of the reaction vessel. The van-der-Waals coefficients were used as reported to be a = 0.7857 Pa m^{-6} mol^{-2} and b = 8.79 · 10^{-5} m^3 mol^{-1}.[3]

$$(V - nb)\left[P - a\left(\frac{n}{V}\right)^2\right] = nRT$$

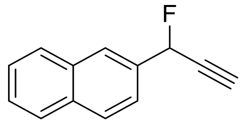
The relevant volume of SF_6 gas were V(transparent glass tube + ballon) - V(liguid) ≈ 127.0 ml under standard conditions (0.50 mmol scale, 1.0 atm). The resulting number of moles was calculated by solving the van-der-Waals equation:

$$n(SF_6) \approx 5.11\ mmol$$

Though it was not showed in this work, the further study on the lowest equivalent of SF_6 are under way to make sure this potent greenhouse gas completely consumed.

3.4 Characterization data of fluorinated products

2-(1-Fluoroprop-2-yn-1-yl)naphthalene (1)



The product purified by flash column chromatography on silica gel (PE/ EA = 100:1) to afford the **1** as a colorless viscous oil (33.1 mg, 60%).

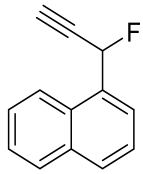
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.94-7.88 (m, 3H), 7.70-7.67 (m, 1H), 7.59-7.53 (m, 2H), 6.26 (dd, *J* = 48.0, 2.0 Hz, 1H), 2.97 (dd, *J* = 5.6, 2.4 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.7 (d, *J* = 2.1 Hz), 133.4 (d, *J* = 21.0 Hz), 132.9 (d, *J* = 1.6 Hz), 128.7 (d, *J* = 1.3 Hz), 128.4 (d, *J* = 1.4 Hz), 127.7 (d, *J* = 1.5 Hz), 126.9 (d, *J* = 1.4 Hz), 126.8 (d, *J* = 5.9 Hz), 126.6, 124.2 (d, *J* = 3.2 Hz), 83.0 (d, *J* = 168.6 Hz), 79.3 (d, *J* = 28.7 Hz), 78.7 (d, *J* = 9.8 Hz) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -157.5 ppm.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{10}F$ 185.0761; Found 185.0752.

1-(1-Fluoroprop-2-yn-1-yl)naphthalene (2)



The product purified by flash column chromatography on silica gel (PE/ EA = 100:1) to afford the **2** as a yellowish oil (33.7 mg, 61%).

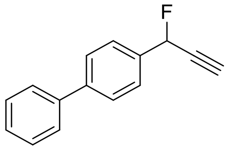
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36-8.34 (m, 1H), 7.98-7.91 (m, 3H), 7.70-7.54 (m, 3H), 6.26-6.73 (m, 1H), 3.07-3.05 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.7, 131.3 (d, *J* = 20.1 Hz), 130.6 (d, *J* = 2.9 Hz), 130.3, 128.7, 126.8, 126.1, 125.9 (d, *J* = 6.7 Hz), 124.9, 123.5, 81.5 (d, *J* = 168.5 Hz), 79.2 (d, *J* = 10.3 Hz), 79.1 (d, *J* = 28.8 Hz) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -159.9 ppm.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{10}F$ 185.0761; Found 185.0754.

4-(1-Fluoroprop-2-yn-1-yl)-1,1'-biphenyl (3)



The product purified by flash column chromatography on silica gel (PE/ EA = 100:1) to afford the **3** as a colorless viscous oil (47.3 mg, 75%).

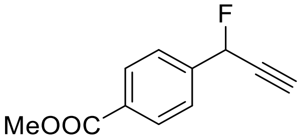
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.66 (m, 6H), 7.55-7.43 (m, 3H), 6.18 (dd, *J* = 50.0, 2.0 Hz, 1H), 2.97 (dd, *J* = 7.2, 2.0 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6 (d, *J* = 3.2 Hz), 140.2 (d, *J* = 1.3 Hz), 135.0 (d, *J* = 21.1 Hz), 128.8, 127.7 (d, *J* = 1.7 Hz), 127.6, 127.4 (d, *J* = 1.8 Hz), 127.1, 82.5 (d, *J* = 168.5 Hz), 79.3 (d, *J* = 28.7 Hz), 78.5 (d, *J* = 9.7 Hz) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -156.9 ppm.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}F$ 211.0918; Found 211.0923.

Ethyl 4-(1-Fluoroprop-2-yn-1-yl)benzoate (4)



The product purified by flash column chromatography on silica gel (PE/ EA = 20:1) to afford the **4** as a colorless viscous oil (26.6 mg, 43%).

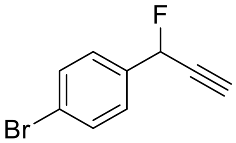
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 6.09 (dd, *J* = 47.2, 2.4 Hz, 1H), 3.91 (s, 3H), 2.92 (dd, *J* = 5.6, 2.0 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 140.6 (d, *J* = 21.0 Hz), 131.1 (d, *J* = 2.5 Hz), 129.9, 126.7 (d, *J* = 4.6 Hz), 82.0 (d, *J* = 170.5 Hz), 79.0 (d, *J* = 10.0 Hz), 78.6 (d, *J* = 27.8 Hz), 52.2 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -162.6 ppm.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_9FO_2Na$ 215.0479; Found 215.0477.

1-Bromo-4-(1-fluoroprop-2-yn-1-yl)benzene (5)



The product purified by flash column chromatography on silica gel (PE/ EA = 100:1) to afford the **5** as a colorless oil (36.3 mg, 57%).

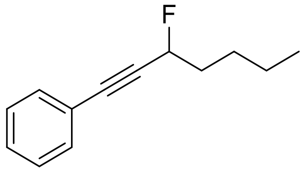
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57-7.55 (m, 2H), 7.44-7.42 (m, 2H), 6.02 (dd, *J* = 48.0, 2.4 Hz, 1H), 2.92 (dd, *J* = 5.6, 2.4 Hz, 1H) ppm.

^{13}C NMR (101 MHz, CDCl$_3$) δ 135.1 (d, *J* = 21.5 Hz), 131.9 (d, *J* = 1.4 Hz), 128.8 (d, *J* = 4.3 Hz), 123.9 (d, *J* = 3.7 Hz), 82.0 (d, *J* = 169.7 Hz), 78.8 (d, *J* = 9.8 Hz), 78.7 (d, *J* = 28.3 Hz) ppm.

^{19}F NMR (376 MHz, CDCl$_3$) δ -158.5 ppm.

HRMS (ESI) m/z: [M + H]$^+$ Calcd for C_9H_7BrF 212.9710; Found 212.9712.

(3-Fluorohept-1-yn-1-yl)benzene (6)



The product purified by flash column chromatography on silica gel (PE/ EA = 100:1) to afford the **6** as a colorless oil (28.5 mg, 50%).

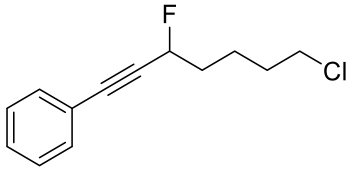
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.48-7.46 (m, 2H), 7.38-7.30 (m, 3H), 5.33 (dt, *J* = 48.8, 6.4 Hz, 1H), 2.05-1.85 (m, 2H), 1.62-1.48 (m, 2H), 1.46-1.35 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, CDCl$_3$) δ 131.8 (d, *J* = 2.9 Hz), 128.8, 128.3, 122.0 (d, *J* = 3.7 Hz), 87.8 (d, *J* = 10.5 Hz), 85.7 (d, *J* = 25.9 Hz), 83.2 (d, *J* = 167.3 Hz), 35.7 (d, *J* = 22.5 Hz), 26.7 (d, *J* = 3.9 Hz), 22.2, 13.9 ppm.

^{19}F NMR (376 MHz, CDCl$_3$) δ -171.6 ppm.

HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{13}H_{16}F$ 191.1231; Found 191.1228.

(7-Chloro-3-fluorohept-1-yn-1-yl)benzene (7)



The product purified by flash column chromatography on silica gel (PE/ EA = 100:1) to afford the **7** as a yellowish oil (32.3 mg, 48%).

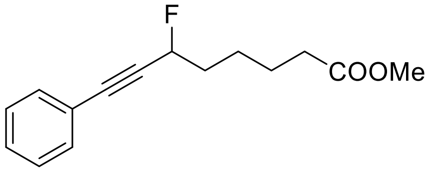
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.51-7.49 (m, 2H), 7.37-7.35 (m, 3H), 5.36 (dt, *J* = 48.8, 6.0 Hz, 1H), 3.58 (t, *J* = 6.4 Hz, 2H), 2.08-1.93 (m, 2H), 1.92-1.84 (m, 2H), 1.81-1.65 (m, 2H) ppm.

^{13}C NMR (101 MHz, CDCl$_3$) δ 131.7 (d, *J* = 2.8 Hz), 128.9, 128.3, 121.7 (d, *J* = 3.7 Hz), 88.0 (d, *J* = 10.3 Hz), 85.2 (d, *J* = 26.1 Hz), 82.7 (d, *J* = 168.1 Hz), 44.5, 35.1 (d, *J* = 23.0 Hz), 31.9, 21.9 (d, *J* = 4.0 Hz) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -171.8 ppm.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{15}ClF$ 225.0841; Found 225.0846.

Methyl 6-fluoro-8-phenyloct-7-ynoate (8)



The product purified by flash column chromatography on silica gel (PE/ EA = 100:1) to afford the **8** as a yellowish oil (23.1 mg, 31%).

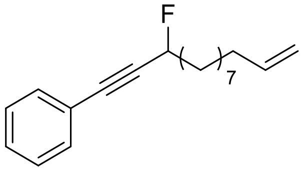
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.43 (m, 2H), 7.35-7.33 (m, 3H), 5.30 (dt, *J* = 48.4, 5.2 Hz, 1H), 3.64 (s, 3H), 2.34 (t, *J* = 7.2 Hz, 2H), 2.03-1.84 (m, 2H), 1.76-1.65 (m, 2H), 1.63-1.49 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 131.6 (d, *J* = 2.8 Hz), 128.8, 128.2, 121.7 (d, *J* = 3.7 Hz), 87.9 (d, *J* = 10.3 Hz), 85.3 (d, *J* = 25.9 Hz), 82.6 (d, *J* = 168.0 Hz), 51.3, 35.5 (d, *J* = 22.9 Hz), 33.6, 24.3, 23.9 (d, *J* = 3.9 Hz) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -172.0 ppm.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{18}FO_2$ 249.1285 Found 249.1282.

(3-Fluorohept-6-en-1-yn-1-yl)benzene (9)



The product purified by flash column chromatography on silica gel (PE/ EA = 100:1) to afford the **9** as a colorless oil (23.7 mg, 42%).

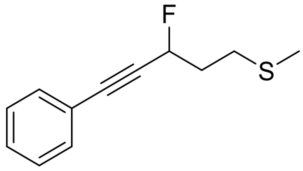
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.49 (m, 2H), 7.36-7.35 (m, 3H), 5.90-5.80 (m, 1H), 5.35 (dt, *J* = 48.4, 6.0 Hz, 1H), 5.06-4.97 (m, 2H), 2.11-2.06 (m, 2H), 2.03-1.87 (m, 2H), 1.64-1.52 (m, 2H), 1.43-1.32 (m, 10H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 131.7 (d, *J* = 2.9 Hz), 128.8, 128.2, 122.0 (d, *J* = 3.7 Hz), 114.1, 87.8 (d, *J* = 10.3 Hz), 85.7 (d, *J* = 25.9 Hz), 83.1 (d, *J* = 167.6 Hz), 36.0 (d, *J* = 22.6 Hz), 33.7, 29.4, 29.3, 29.1, 29.0, 28.9, 24.5 (d, *J* = 3.9 Hz) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -171.6 ppm.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{25}FNa$ 295.1833; Found 295.1831.

(3-Fluoro-5-phenylpent-4-yn-1-yl)(methyl)sulfane (10)



The product purified by flash column chromatography on silica gel (PE/ EA = 100:1) to afford the **10** as a yellowish oil (32.4 mg, 52%).

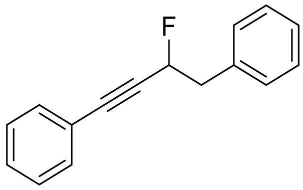
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.48-7.46 (m, 2H), 7.35-7.33 (m, 3H), 5.50 (dt, *J* = 48.4, 5.2 Hz, 1H), 2.79-2.66 (m, 2H), 2.34-2.13 (m, 5H) ppm.

^{13}C NMR (101 MHz, CDCl$_3$) δ 131.7 (d, *J* = 2.9 Hz), 128.9, 128.3, 121.6 (d, *J* = 3.8 Hz), 88.4 (d, *J* = 10.4 Hz), 84.8 (d, *J* = 25.7 Hz), 81.6 (d, *J* = 168.7 Hz), 35.6 (d, *J* = 23.5 Hz), 29.0 (d, *J* = 4.0 Hz), 15.5 ppm.

^{19}F NMR (376 MHz, CDCl$_3$) δ -174.0 ppm.

HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{12}H_{14}FS$ 209.0795; Found 209.0797.

(3-Fluorobut-1-yne-1,4-diyl)dibenzene (11)



The product purified by flash column chromatography on silica gel (PE/ EA = 100:1) to afford the **11** as a colorless oil (30.9 mg, 56%).

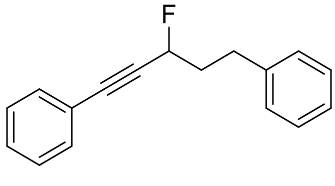
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49-7.36 (m, 10H), 5.53 (dt, *J* = 48.4, 6.0 Hz, 1H), 3.38-3.23 (m, 2H) ppm.

^{13}C NMR (101 MHz, CDCl$_3$) δ 135.4 (d, *J* = 4.4 Hz), 131.8 (d, *J* = 2.8 Hz), 129.7, 128.9, 128.4, 128.3, 127.1, 121.8 (d, *J* = 3.8 Hz), 88.8 (d, *J* = 10.2 Hz), 85.1 (d, *J* = 25.8 Hz), 85.3 (d, *J* = 171.4 Hz), 42.5 (d, *J* = 23.5 Hz) ppm.

^{19}F NMR (376 MHz, CDCl$_3$) δ -169.7 ppm.

HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{16}H_{14}F$ 225.1074; Found 225.1069.

(3-Fluoropent-1-yne-1,5-diyl)dibenzene (12)



The product purified by flash column chromatography on silica gel (PE/ EA = 100:1) to afford the **12** as a colorless oil (34.3 mg, 48%).

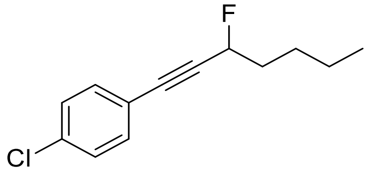
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.59 (m, 2H), 7.45-7.42 (m, 5H), 7.37-7.33 (m, 3H), 5.45 (dt, *J* = 48.8, 6.4 Hz, 1H), 3.08-2.95 (m, 2H), 2.50-2.27 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 131.8 (d, *J* = 2.9 Hz), 128.9, 128.5, 128.4, 128.3, 126.1, 121.8 (d, *J* = 3.7 Hz), 88.2 (d, *J* = 10.4 Hz), 85.3 (d, *J* = 25.6 Hz), 82.2 (d, *J* = 168.3 Hz), 37.6 (d, *J* = 23.1 Hz), 30.7 (d, *J* = 4.0 Hz) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -169.7 ppm.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}F$ 239.1231; Found 239.1239.

1-Chloro-4-(3-fluorohept-1-yn-1-yl)benzene (13)



The product purified by flash column chromatography on silica gel (PE/ EA = 100:1) to afford the **13** as a yellowish oil (36.6 mg, 55%).

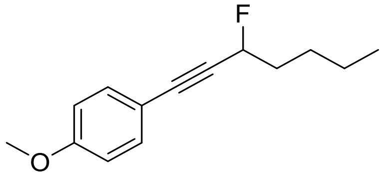
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.38 (m, 2H), 7.31-7.29 (m, 2H), 5.31 (dt, *J* = 48.8, 6.0 Hz, 1H), 2.04-1.84 (m, 2H), 1.61-1.49 (m, 2H), 1.47-1.37 (m, 2H), 0.96 (t, *J* = 7.6 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.9, 133.0 (d, *J* = 2.8 Hz), 128.6, 120.4 (d, *J* = 3.7 Hz), 86.7 (d, *J* = 25.9 Hz), 86.6 (d, *J* = 10.4 Hz), 82.9 (d, *J* = 168.0 Hz), 35.6 (d, *J* = 22.7 Hz), 26.6 (d, *J* = 3.9 Hz), 22.2, 13.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -172.1 ppm.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{15}ClF$ 225.0841; Found 225.0839.

1-(3-Fluorohept-1-yn-1-yl)-4-methoxybenzene (14)



The product purified by flash column chromatography on silica gel (PE/ EA = 100:1) to afford the **14** as a yellowish oil (35.6 mg, 54%).

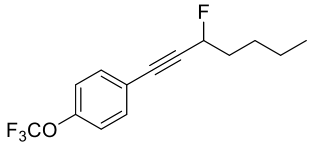
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.39 (m, 2H), 6.86-6.84 (m, 2H), 5.31 (dt, *J* = 48.8, 6.4 Hz, 1H), 3.81 (s, 3H), 2.03-1.83 (m, 2H), 1.59-1.48 (m, 2H), 1.46-1.36 (m, 2H), 0.95 (t, *J* = 7.6 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 160, 133.4 (d, *J* = 2.7 Hz), 113.9, 87.9 (d, *J* = 10.6 Hz), 84.4 (d, *J* = 25.8 Hz), 83.3 (d, *J* = 166.7 Hz), 55.3, 35.8 (d, *J* = 22.7 Hz), 26.7 (d, *J* = 3.8 Hz), 22.2, 13.9 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -170.6 ppm.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{18}FO$ 221.1336 Found 221.1328.

1-(3-Fluorohept-1-yn-1-yl)-4-(trifluoromethoxy) benzene (15)



The product purified by flash column chromatography on silica gel (PE/ EA = 100:1) to afford the **15** as a colorless oil (35.3 mg, 43%).

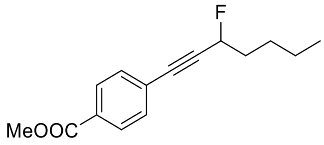
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.48 (m, 2H), 7.19-7.17 (m, 2H), 5.32 (dt, *J* = 48.8, 6.4 Hz, 1H), 2.05-1.85 (m, 2H), 1.62-1.50 (m, 2H), 1.48-1.38 (m, 2H), 0.96 (t, *J* = 7.6, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 133.4 (d, *J* = 2.8 Hz), 120.8, 120.8, 120.4 (q, *J* = 258.9 Hz), 86.6 (d, *J* = 25.8 Hz), 86.3 (d, *J* = 10.3 Hz), 83.0 (d, *J* = 168.0 Hz), 35.9 (d, *J* = 22.5 Hz), 26.7 (d, *J* = 3.9 Hz), 22.2, 13.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.0, -172.5 ppm.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}F_4O$ 275.1054; Found 275.1054.

Methyl 4-(3-fluorohept-1-yn-1-yl) benzoate (16)



The product purified by flash column chromatography on silica gel (PE/ EA = 20:1) to afford the **16** as a colorless oil (36.5 mg, 49%).

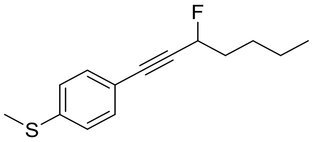
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 2H), 7.49-7.47 (m, 2H), 5.30 (dt, *J* = 48.4, 6.4 Hz, 1H), 3.88 (s, 3H), 2.01-1.81 (m, 2H), 1.56-1.43 (m, 2H), 1.42-1.33 (m, 2H), 0.92 (t, *J* = 7.2, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 131.6 (d, *J* = 2.9 Hz), 130.0, 129.3, 126.5 (d, *J* = 3.7 Hz), 88.5 (d, *J* = 26.0 Hz), 86.8 (d, *J* = 10.3 Hz), 82.8 (d, *J* = 168.4 Hz), 52.1, 35.5 (d, *J* = 22.5 Hz), 26.5 (d, *J* = 3.9 Hz), 22.1, 13.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -172.8 ppm.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{18}FO_2$ 249.1285; Found 249.1285.

(4-(3-Fluorohept-1-yn-1-yl)phenyl)(methyl)sulfane (17)



The product purified by flash column chromatography on silica gel (PE/ EA = 100:1) to afford the **17** as a yellowish oil (36.1 mg, 51%).

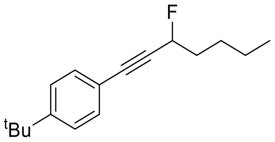
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38-7.35 (m, 2H), 7.18-7.16 (m, 2H), 5.31 (dt, *J* = 48.8, 6.4 Hz, 1H), 2.48 (s, 3H), 2.02-1.83 (m, 2H), 1.58-1.48 (m, 2H), 1.46-1.36 (m, 2H), 0.95 (t, *J* = 7.6, 3H) ppm.

^{13}C NMR (101 MHz, CDCl$_3$) δ 140.2, 132.1 (d, *J* = 2.9 Hz), 125.6, 118.1 (d, *J* = 3.8 Hz), 87.6 (d, *J* = 10.5 Hz), 85.7 (d, *J* = 25.9 Hz), 83.2 (d, *J* = 167.3 Hz), 35.7 (d, *J* = 22.6 Hz), 26.7 (d, *J* = 3.9 Hz), 22.2, 15.2, 13.9 ppm.

^{19}F NMR (376 MHz, CDCl$_3$) δ -171.2 ppm.

HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{14}H_{18}FS$ 237.1108; Found 237.1104.

1-(Tert-butyl)-4-(3-fluorohept-1-yn-1-yl)benzene (18)



The product purified by flash column chromatography on silica gel (PE/ EA = 100:1) to afford the **18** as a colorless oil (36.9 mg, 50%).

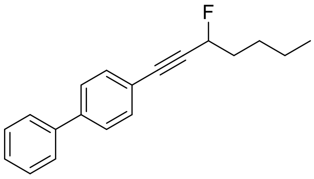
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46-7.37 (m, 4H), 5.35 (dt, *J* = 48.4, 6.4 Hz, 1H), 2.08-1.88 (m, 2H), 1.65-1.51 (m, 2H), 1.49-1.40 (m, 2H), 1.35 (s, 9H), 0.99 (t, *J* = 7.2, 3H) ppm.

^{13}C NMR (101 MHz, CDCl$_3$) δ 152.1, 131.5 (d, *J* = 2.9 Hz), 125.3, 119.0 (d, *J* = 3.7 Hz), 87.9 (d, *J* = 10.3 Hz), 85.1 (d, *J* = 25.9 Hz), 83.2 (d, *J* = 167.3 Hz), 35.8 (d, *J* = 22.6 Hz), 34.7, 31.1, 26.7 (d, *J* = 3.9 Hz), 22.2, 13.9 ppm.

^{19}F NMR (376 MHz, CDCl$_3$) δ -172.0 ppm.

HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{17}H_{24}F$ 247.1857 Found 247.1850.

4-(3-Fluorohept-1-yn-1-yl)-1,1'-biphenyl (19)



The product purified by flash column chromatography on silica gel (PE/ EA = 100:1) to afford the **19** as a colorless viscous oil (41.5 mg, 52%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63-7.55 (m, 6H), 7.49-7.46 (m, 2H), 7.41-7.37 (m, 1H), 5.38 (dt, *J* = 48.8, 6.0 Hz, 1H), 2.10-1.90 (m, 2H), 1.66-1.53 (m, 2H), 1.50-1.39 (m, 2H), 1.00 (t, *J* = 7.2, 3H) ppm.

^{13}C NMR (101 MHz, CDCl$_3$) δ 141.6, 140.1, 132.2 (d, *J* = 2.7 Hz), 128.8, 127.7, 127.0, 126.9, 120.8 (d, *J* = 3.8 Hz), 87.7 (d, *J* = 10.5 Hz), 86.4 (d, *J* = 25.8 Hz), 83.2 (d, *J* = 167.4 Hz), 35.8 (d, *J* = 22.6 Hz), 26.7 (d, *J* = 3.9 Hz), 22.2, 13.9 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -171.4 ppm.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{20}F$ 267.1544; Found 267.1541.

4. Gram-scale synthesis and mechanistic studies

4.1 Set-up of gram-scale photochemical reaction

Gram-scale photochemical reactions were performed under irradiation of three blue LED lamps (15 W × 3, 465 nm). The reaction flask was placed at approximately 3.0 ~ 5.0 cm distance away from the LED lamps with a cooling fan to keep the reaction temperature at 23 ~ 25 °C (Figure S2).

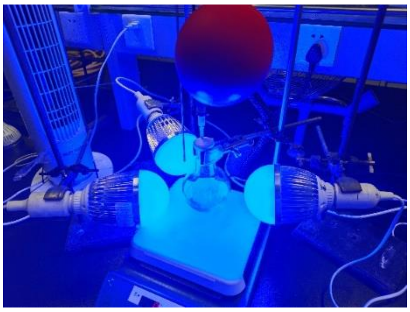
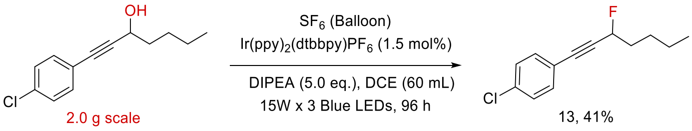


Figure S2 gram-scale photochemical reaction setup

4.2 Procedure for gram-scale synthesis of fluorinated product



To an oven-dried round-bottom flask (100.0 mL) equipped with a magnetic stir bar was added 1-(4-chlorophenyl)hept-1-yn-3-ol (9.0 mmol, 2.0 g, 1.0 eq.) and Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.135 mmol, 123.4 mg, 1.5 mol%). The flask was sealed and connected to a vacuum line where it was evacuated and back-filled with SF$_6$ for three times. Then DCE (60.0 mL) and DIPEA (45.0 mmol, 7.8 mL, 5.0 eq.) were added under SF$_6$ flow. During the reaction stirring, the tube was filled with SF$_6$ constantly through a SF$_6$ balloon and irradiated with three 15 W blue LED lamps (3.0 ~ 5.0 cm away, with cooling fan to keep the reaction temperature at 23 ~ 25 °C) for 96 hours. Upon completion, the mixture was concentrated in vacuum to remove the solvent thoroughly. The residue was purified by a silica gel flash column chromatography to give the desired product 1-chloro-4-(3-fluorohept-1-yn-1-yl) benzene (**13**) 826.8 mg (41% yield).

4.3 Light on-off experiments

According to the synthesis of acetylacetylene fluoride products, create six identical reactions in parallel and place them in the same environment. As shown in Figure S3, blue light irradiation was performed from the beginning of the reaction to 6 hours, after 6 hours of reaction take out one reaction bottle every two hours and intermittent light on and off were performed. During the light off period, the reaction was stirred in a completely black environment.

The yield at each stage was monitored by ^{19}F NMR to investigate the effect of blue light irradiation on the reaction. The experimental results showed that the reaction yield increased under blue light irradiation, indicating the progress of the reaction. However, when the blue light irradiation was stopped, the reaction yield remained basically unchanged, indicating the cessation of the reaction. Proving that blue light illumination is necessary for the occurrence and progression of reactions.

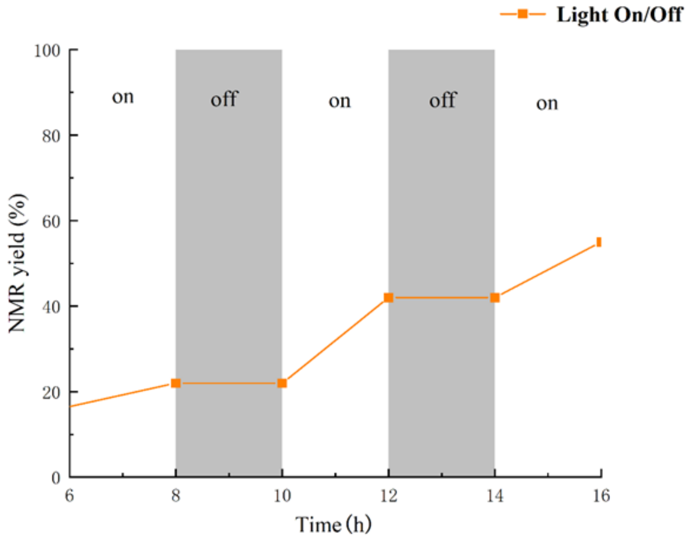
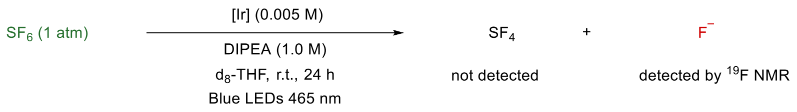


Figure S3 Light on-off experiments

4.4 NMR experiment



To an oven-dried NMR tube was added Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.0025 mmol, 2.3 mg, 0.005 M). The tube was sealed and connected to a vacuum line where it was evacuated and back-filled with SF$_6$ for three times. Then d$_8$-THF (0.5 mL) and DIPEA (0.5 mmol, 84.4 μL, 1.0 M) were added under SF$_6$ flow which was provided by a SF$_6$ balloon. The NMR tube was irradiated with 15 W blue LED lamp (2.0 ~ 3.0 cm away, with cooling fan to keep the reaction temperature at 23 ~ 25 °C) for 20 hours. Upon completion of the reaction, the tube was directly sent to ^{19}F NMR spectrum test (Figure S4).

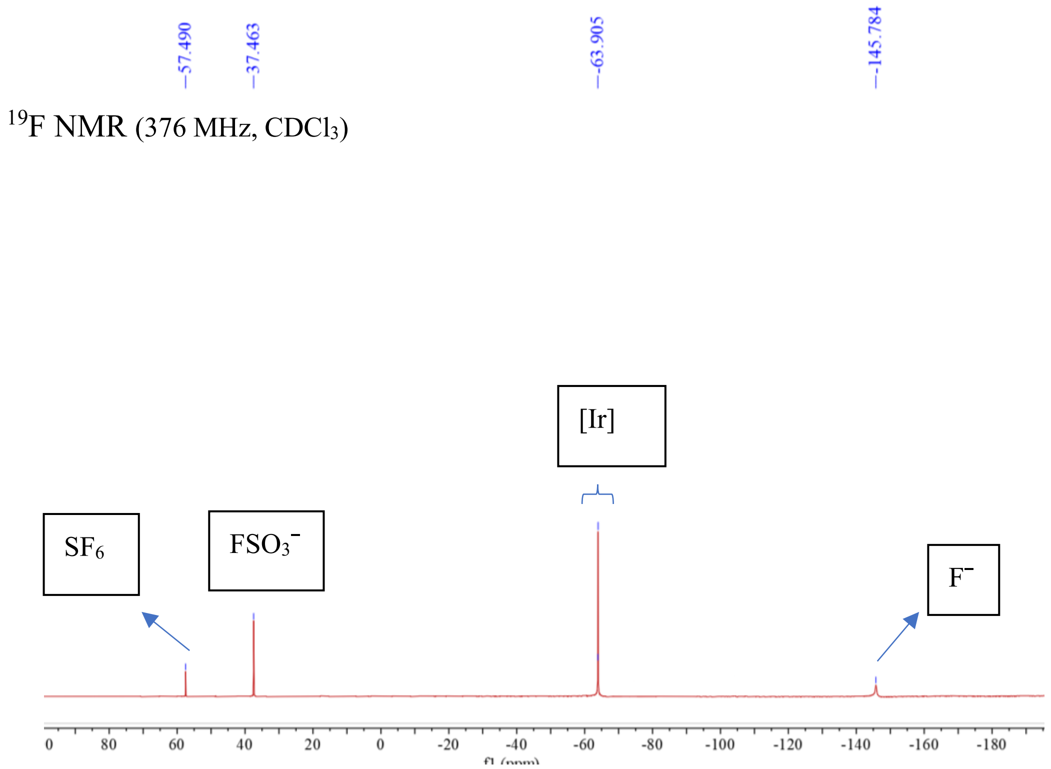
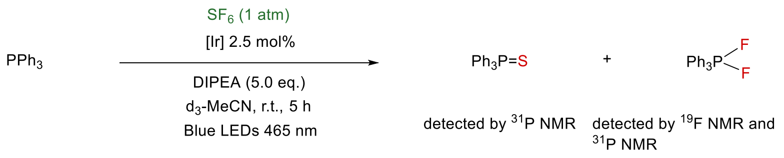


Figure S4 Capture of F$^-$ under photocatalysis condition through ^{19}F NMR spectrum

The ^{19}F NMR signal at -145.8 ppm (br) is assigned to F$^-$ which is origin from SF$_6$ degradation, signal at 57.5 ppm (s) is assigned to gas SF$_6$, and 37.5 ppm (s) to FSO$_3^-$ which is reported by Nagorny[1]. The remaining signals (-63.9 ppm) are assigned to Ir(ppy)$_2$(dtbbpy)PF$_6$.



To an oven-dried NMR tube was added Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.0025 mmol, 2.3 mg, 2.5 mol%). The tube was sealed and connected to a vacuum line where it was evacuated and back-filled with SF$_6$ for three times. Then PPh$_3$ (0.1 mmol, 26.2 mg ,1.0 eq.), d$_3$-MeCN (0.5 mL) and DIPEA (0.5 mmol, 84.4 μL, 5.0 eq.) were added under SF$_6$ flow which was provided by a SF$_6$ balloon. The NMR tube was irradiated with 15 W blue LED lamp (2.0 ~ 3.0 cm away, with cooling fan to keep the reaction temperature at 23 ~ 25 °C) for 5 hours. Upon completion of the reaction, the NMR tube was directly sent to ^{19}F NMR (Figure S5) and ^{31}P NMR (Figure S6) test.

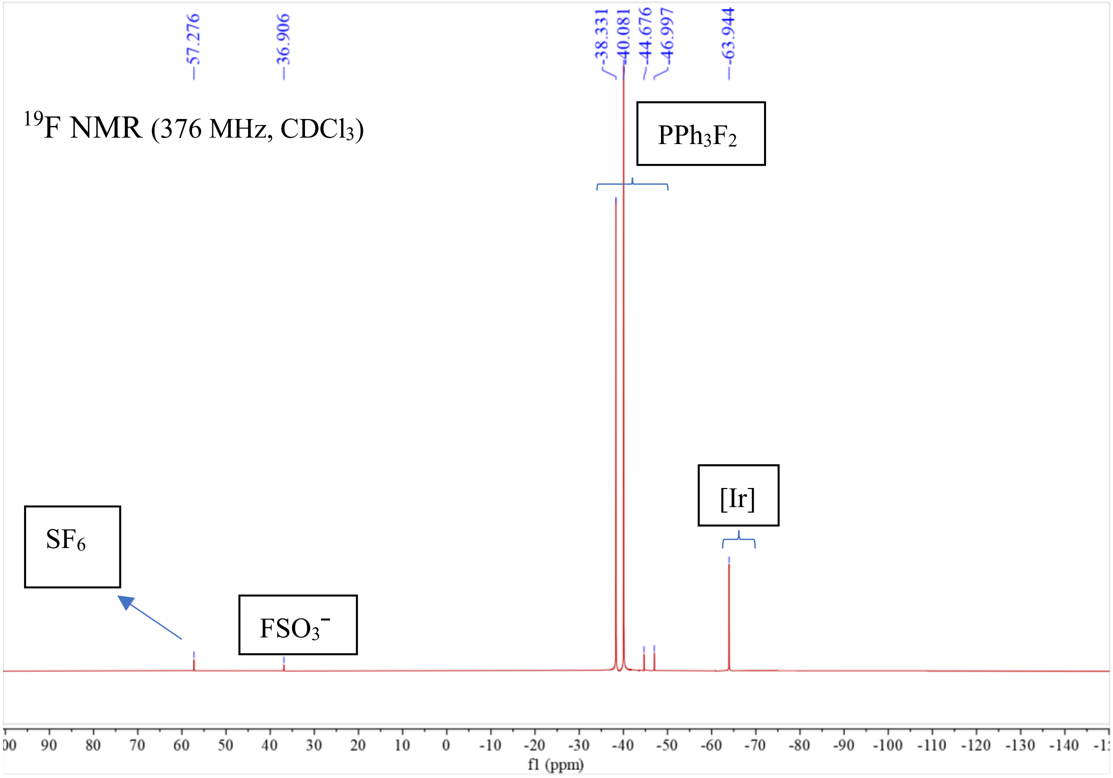


Figure S5 Capture of PPh$_3$F$_2$ under photocatalysis condition through ^{19}F NMR spectrum

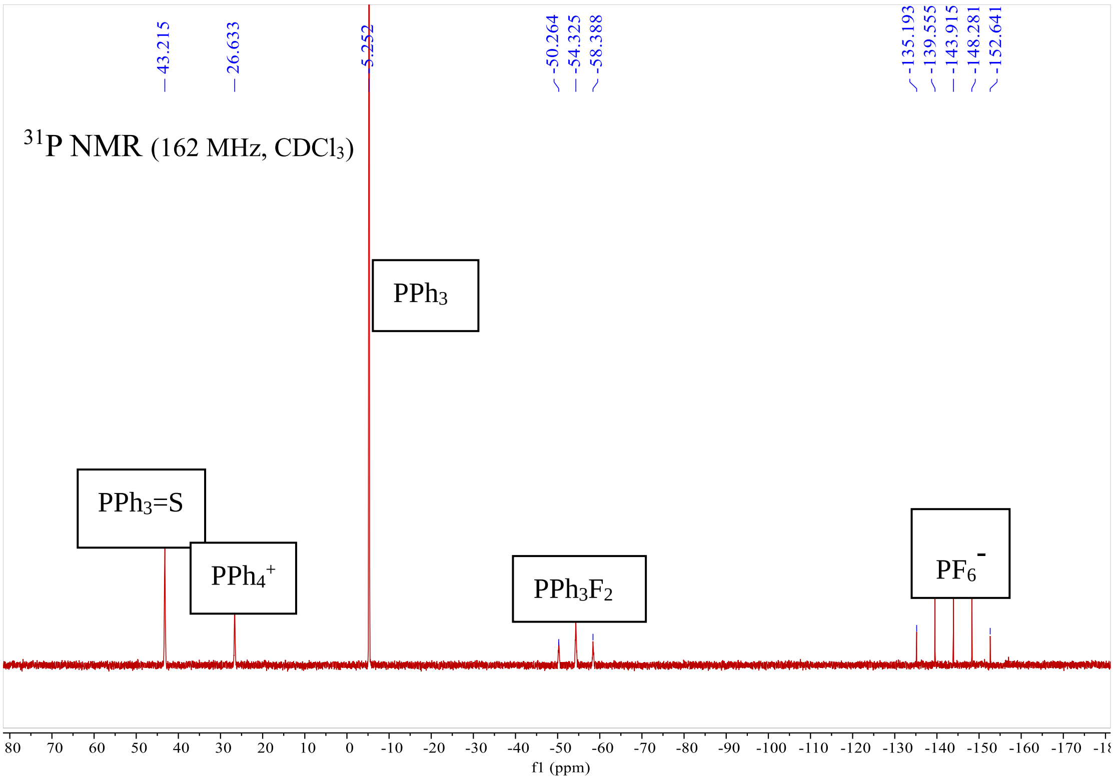
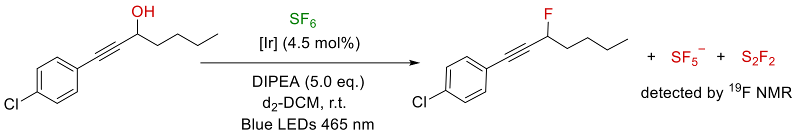


Figure S6 Capture of PPh$_3$F$_2$ and PPh$_3$S under photocatalysis condition through ^{31}P NMR spectrum

The ^{19}F NMR signal at -39.2 ppm (d, J = 658.0 Hz) is assigned to PPh_3F_2, signal at 57.3 ppm (s) is assigned to gas SF_6, and 36.9 ppm (s) to FSO_3^-. The remaining signals (-63.9 ppm) are assigned to $Ir(ppy)_2(dtbbpy)PF_6$.

The ^{31}P NMR signal at 43.2 ppm (m) is assigned to $PPh_3=S$, signal at -54.3 ppm (t, J = 658.0 Hz) is assigned to gas PPh_3F_2, 26.6 ppm (s) to PPh_4^+ and 143.9 (m) are assigned to PF_6^-.



To an oven-dried NMR tube was added $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.0045 mmol, 5.0 mg, 4.5 mol%). The tube was sealed and connected to a vacuum line where it was evacuated and back-filled with SF_6 for three times. Then 1-(4-chlorophenyl)hept-1-yn-3-ol (0.1 mmol, 22.2 mg ,1.0 eq.), d_2-DCM (0.5 mL) and DIPEA (0.5 mmol, 84.4 μL, 5.0 eq.) were added under SF_6 flow which was provided by a SF_6 balloon. The NMR tube was irradiated with 15 W blue LED lamp (2.0 ~ 3.0 cm away, with cooling fan to keep the reaction temperature at 23 ~ 25 °C) for 24 hours. Upon completion of the reaction, the NMR tube was directly sent to ^{19}F NMR (Figure S7) test.

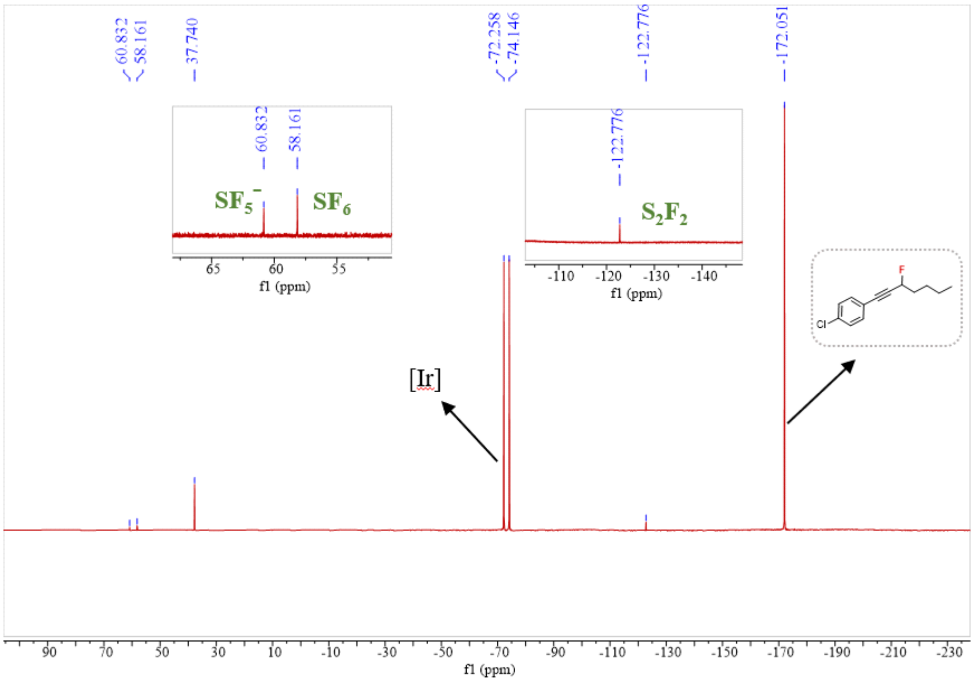
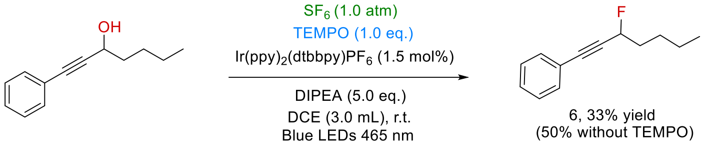


Figure S7 Capture of SF_5^- and S_2F_2 under photocatalysis condition through ^{19}F NMR spectrum

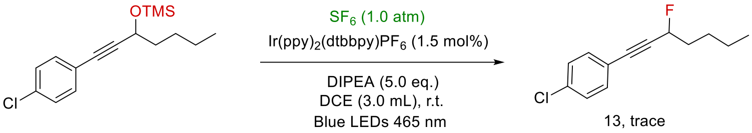
The ^{19}F NMR signal at 60.8 ppm (s) is assigned to SF_5^-, signal at 58.2 ppm (s) is assigned to gas SF_6, , 122.8 ppm (s) is assigned to S_2F_2 and signal at -172.1 ppm (s) is assigned to **13**. The remaining signals (-72.3 ppm and -74.1 ppm) are assigned to $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$.

4.5 Radical trapping experiments



To an oven-dried transparent glass tube (10.0 mL) equipped with a magnetic stir bar was added 1-phenylhept-1-yn-3-ol (0.3 mmol, 56.4 mg, 1.0 eq.), TEMPO (0.3 mol, 48.9 mg, 1.0 eq.) and Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.0045 mmol, 4.1 mg, 1.5 mol%). The tube was sealed and connected to a vacuum line where it was evacuated and back-filled with SF$_6$ for three times. Then DCE (3.0 mL) and DIPEA (1.5 mmol, 253.2 μL, 5.0 eq.) were added under SF$_6$ flow. During the reaction stirring process, the tube was filled with SF$_6$ constantly through a SF$_6$ balloon and irradiated with 15 W blue LED lamp (2.0 ~ 3.0 cm away, with cooling fan to keep the reaction temperature at 23 ~ 25 °C) for 24 hours. Upon completion of the reaction, the mixture was concentrated in vacuum. The residue was purified by a silica gel flash column chromatography to give the desired product (**6**) 18.9 mg (33% yield).

4.6 Controlled experiment



To an oven-dried transparent glass tube (10.0 mL) equipped with a magnetic stir bar was added ((1-(4-chlorophenyl)hept-1-yn-3-yl)oxy)trimethylsilane (0.3 mmol, 88.2 mg, 1.0 eq.) and Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.0045 mmol, 4.1 mg, 1.5 mol%). The tube was sealed and connected to a vacuum line where it was evacuated and back-filled with SF$_6$ for three times. Then DCE (3.0 mL) and DIPEA (1.5 mmol, 253.2 μL, 5.0 eq.) were added under SF$_6$ flow. During the reaction stirring process, the tube was filled with SF$_6$ constantly through a SF$_6$ balloon and irradiated with 15 W blue LED lamp (2.0 ~ 3.0 cm away, with cooling fan to keep the reaction temperature at 23 ~ 25 °C) for 24 hours. Upon completion of the reaction, the mixture was concentrated in vacuum. The yield of **13** was determined by both thin layer chromatography (TLC) and GC-MS with mesitylene as internal standard.

5. References

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[2] J. V. van der Waals, Over de Continuiteit van den Gas- en Vloeistoftoestand. (Dissertation, Leiden, 1873).

[3] R. C. Reid, J.M. Prausnitz, B. E. Poling (Edrs.), *The Properties of Gases and Liquids* (Fourth Edition, McGraw-Hill, New York, 1987)

[4] K. Matsumura, S. Hashiguchi, T. Ikariya, R. Noyori, Asymmetric Transfer Hydrogenation of α, β-Acetylenic Ketones. *J. Am. Chem. Soc.* **1997**, *119*, 8738–8739.

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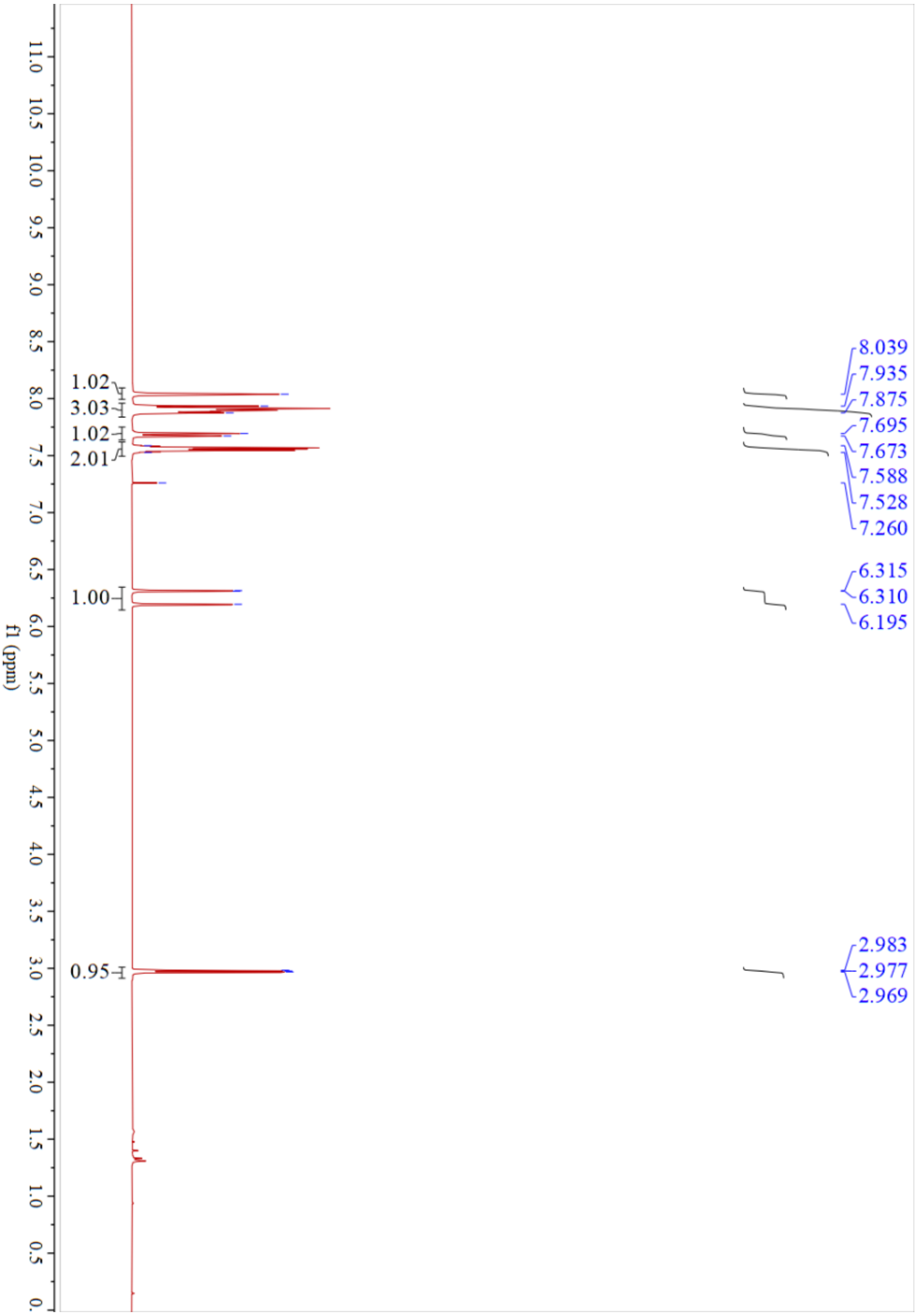
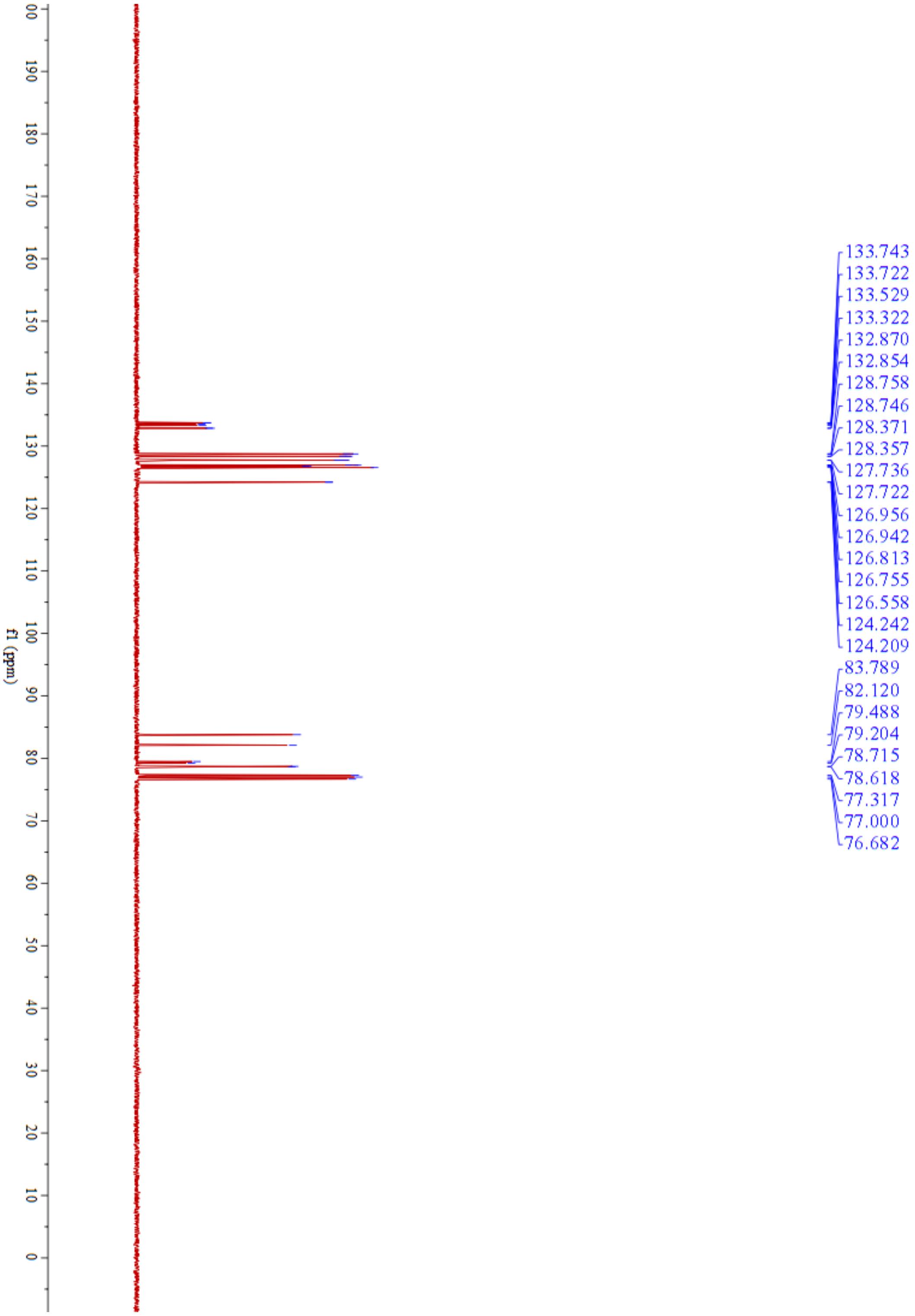
6. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

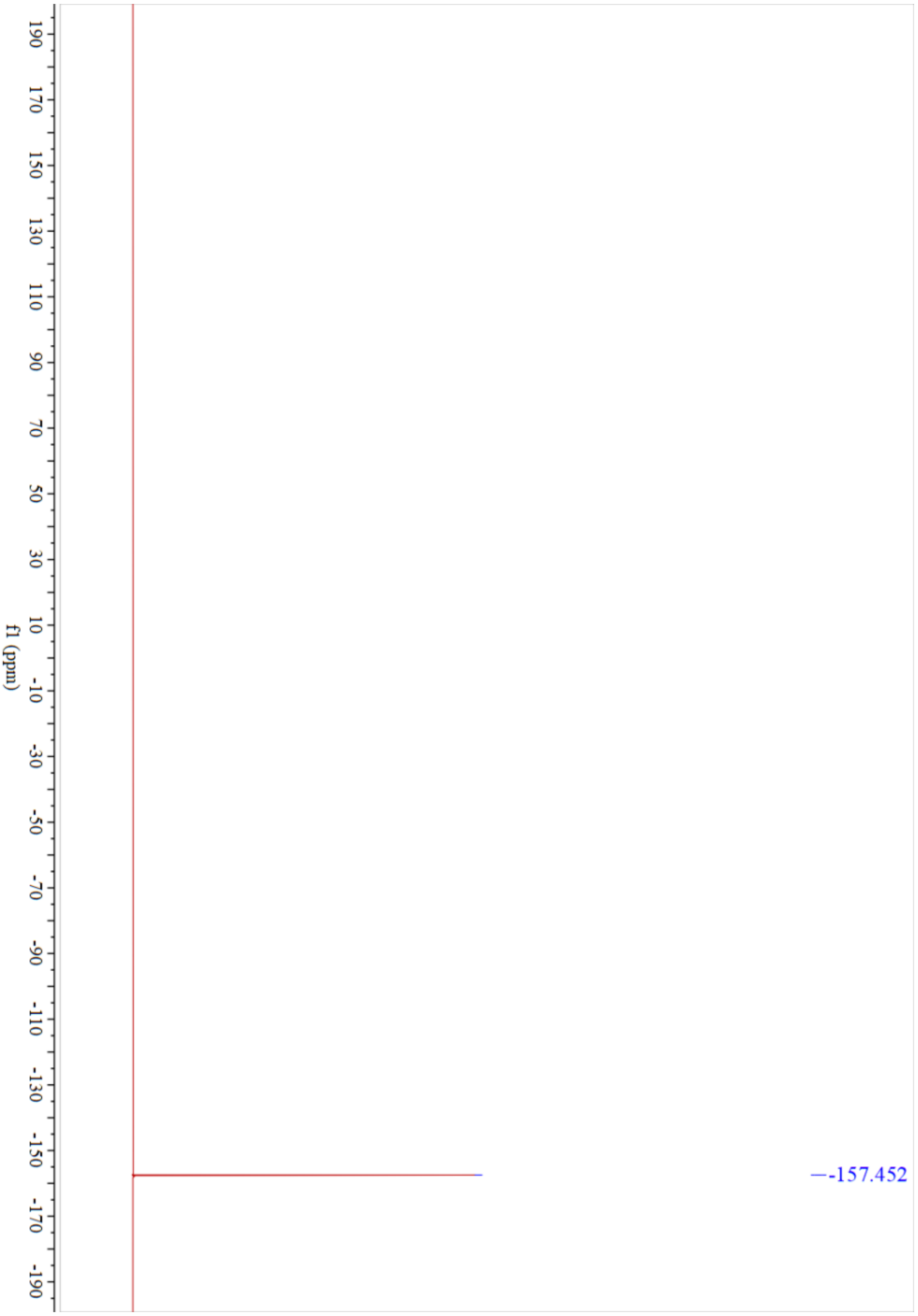
^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **1**



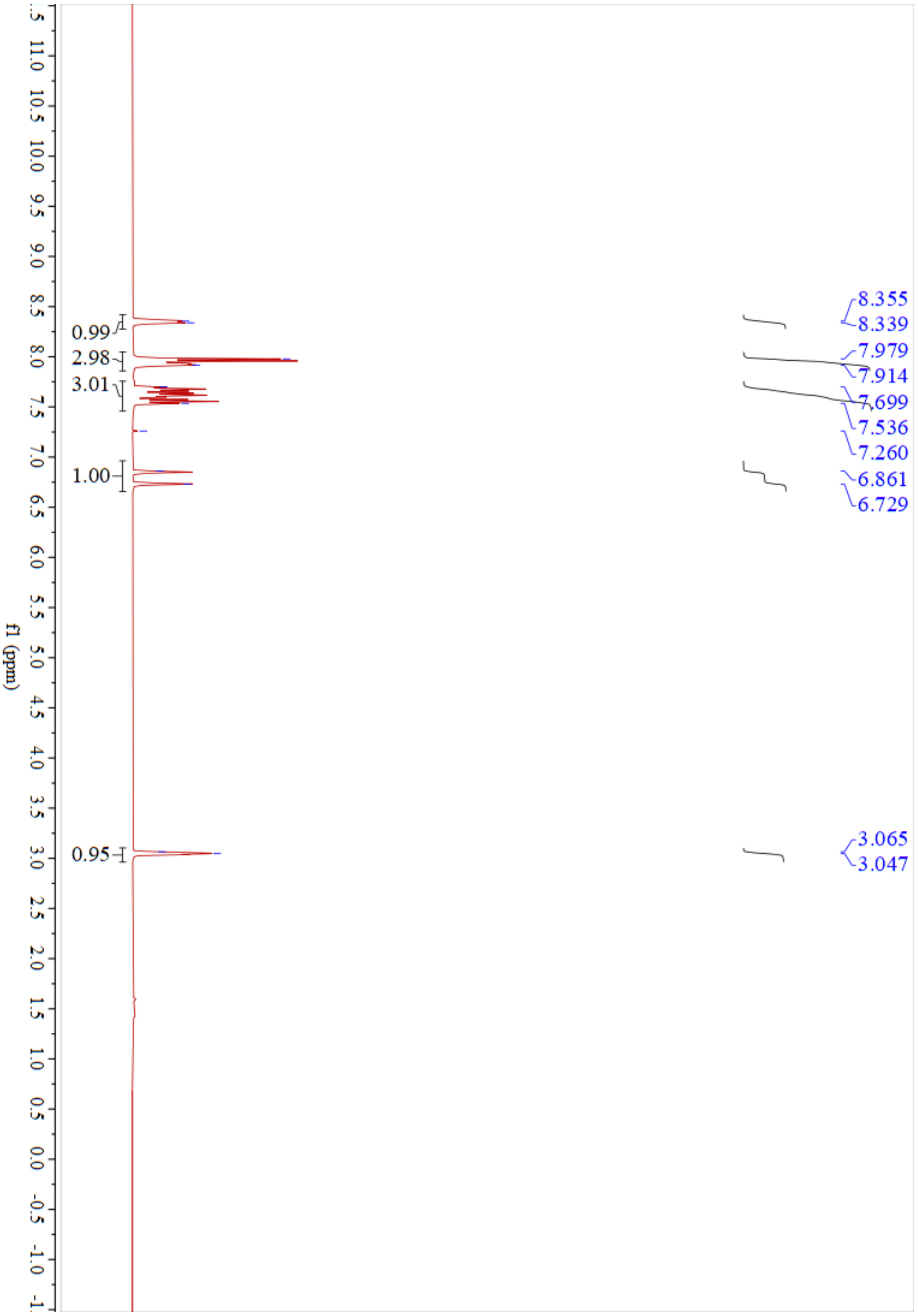
^{13}C **NMR** (101 MHz, CDCl$_3$) spectrum of **1**



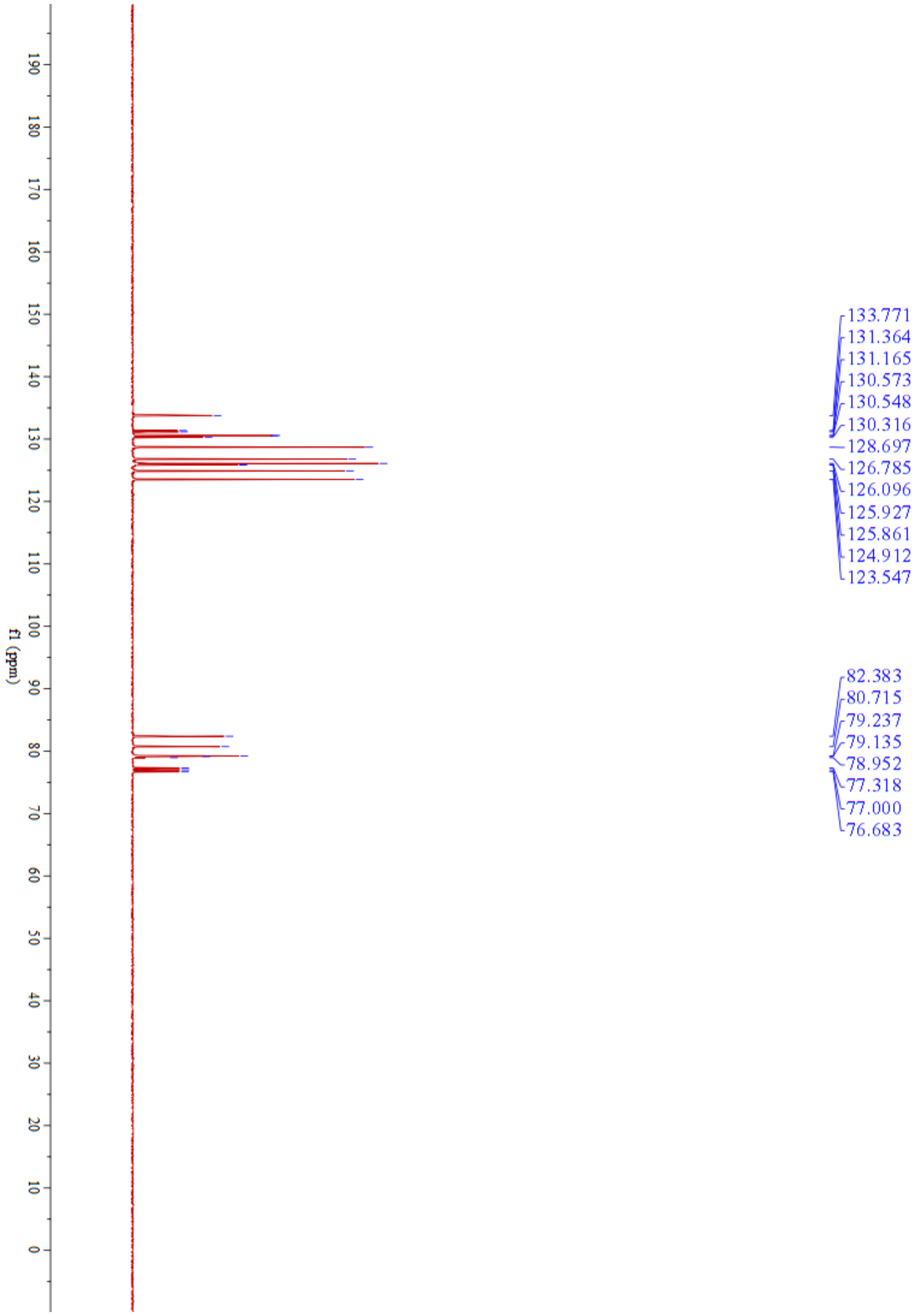
^{19}F NMR (376 MHz, CDCl$_3$) spectrum of **1**



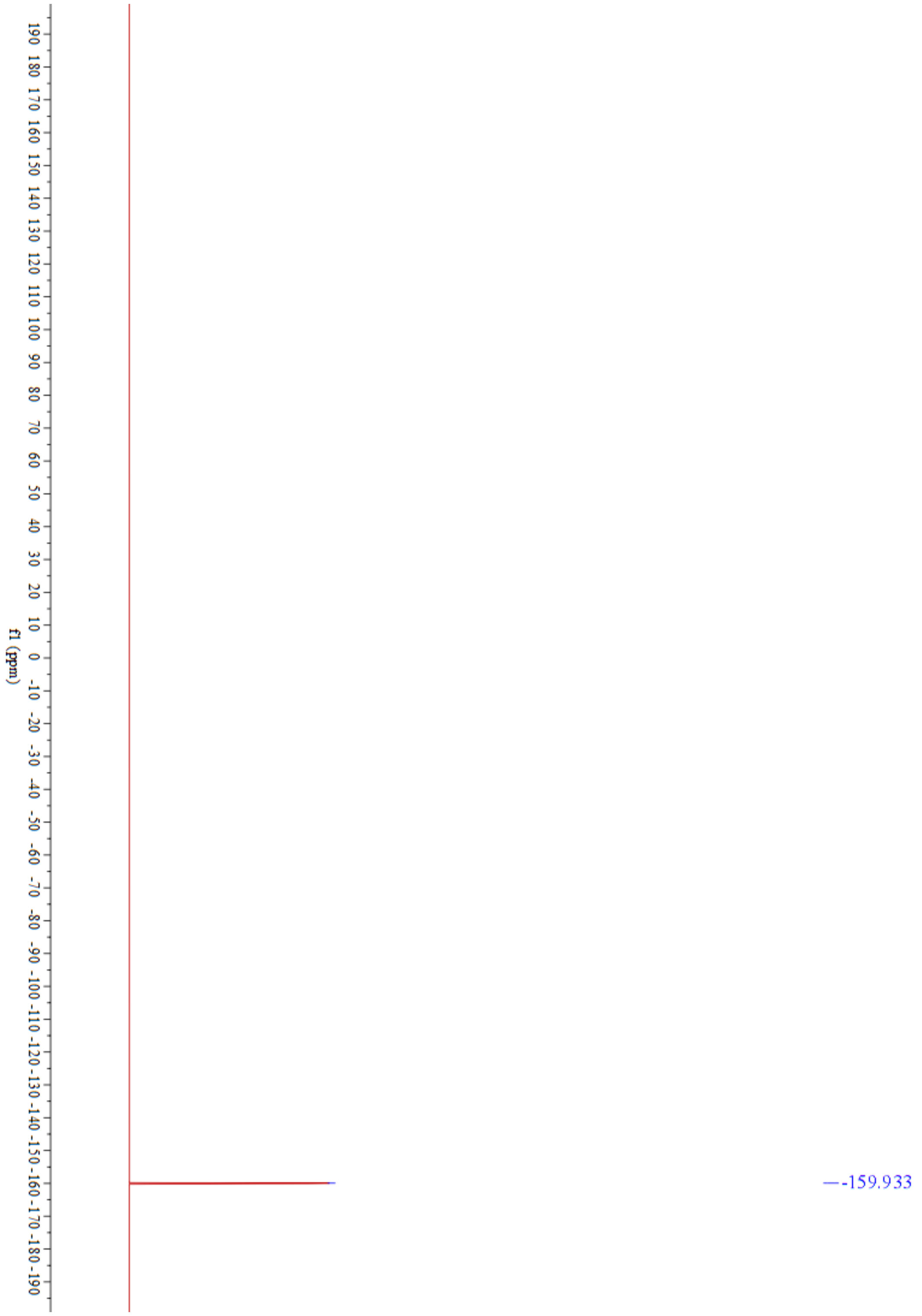
^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **2**



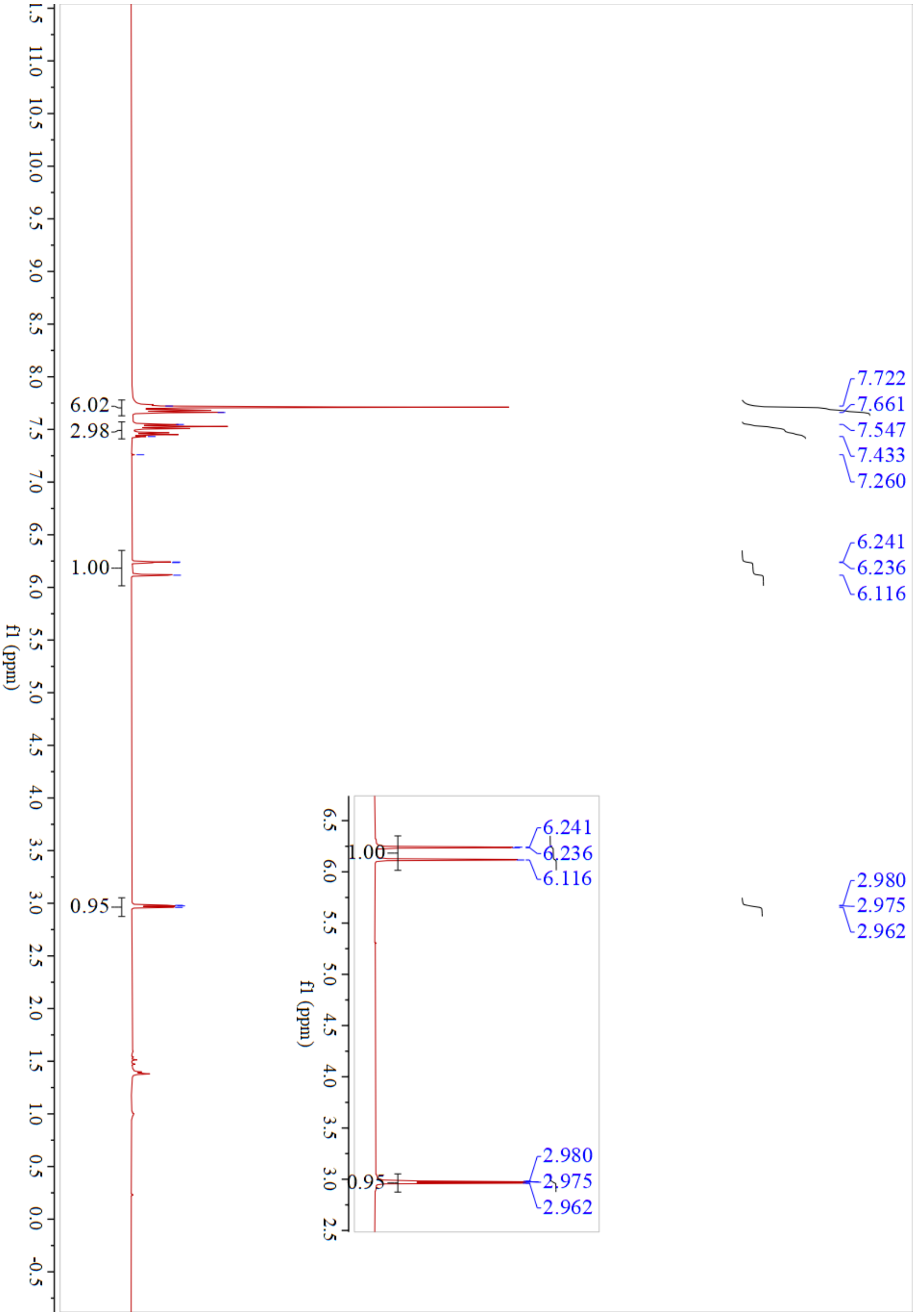
^{13}C NMR (101 MHz, CDCl$_3$) spectrum of **2**



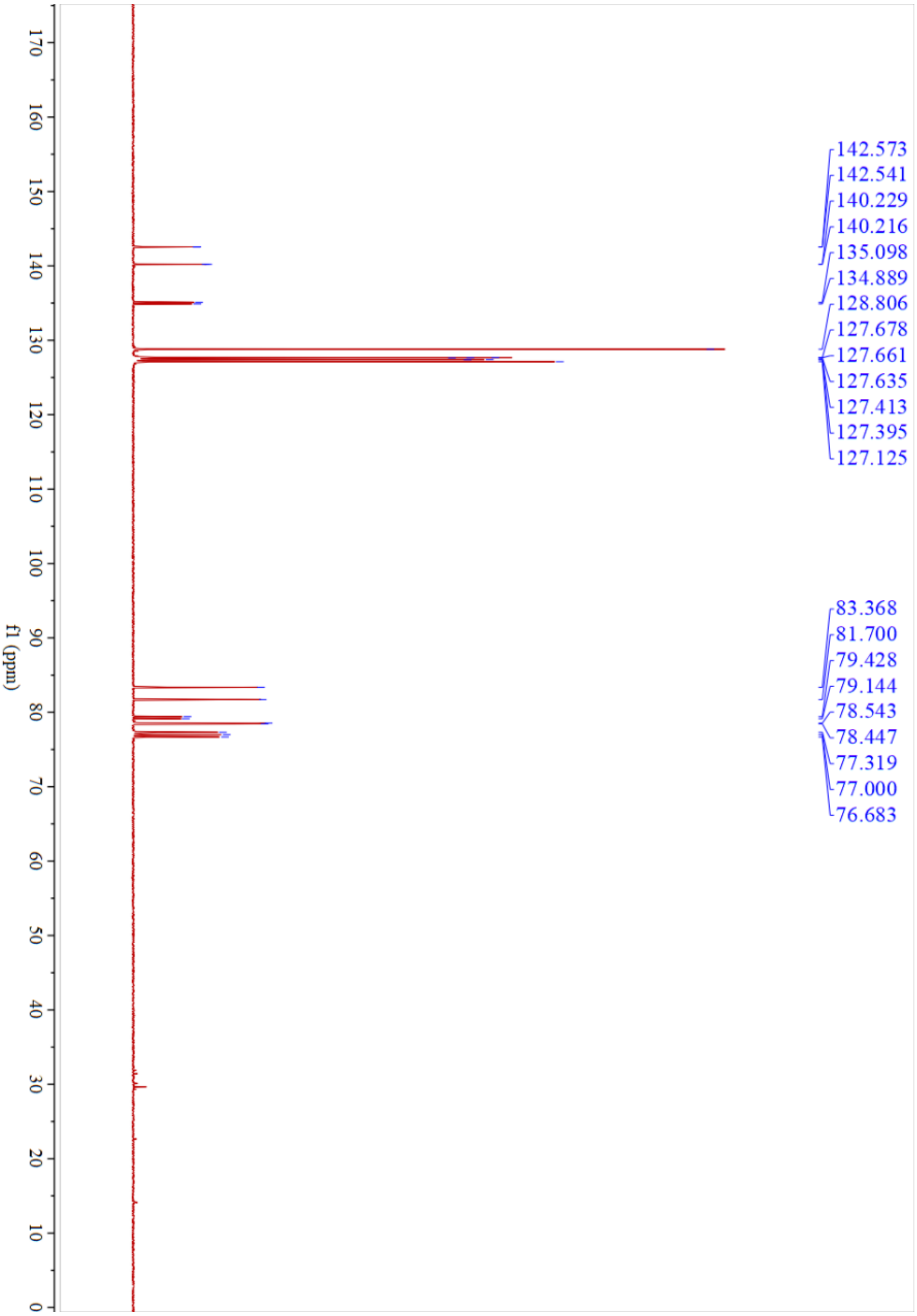
^{19}**F NMR** (376 MHz, $CDCl_3$) spectrum of **2**



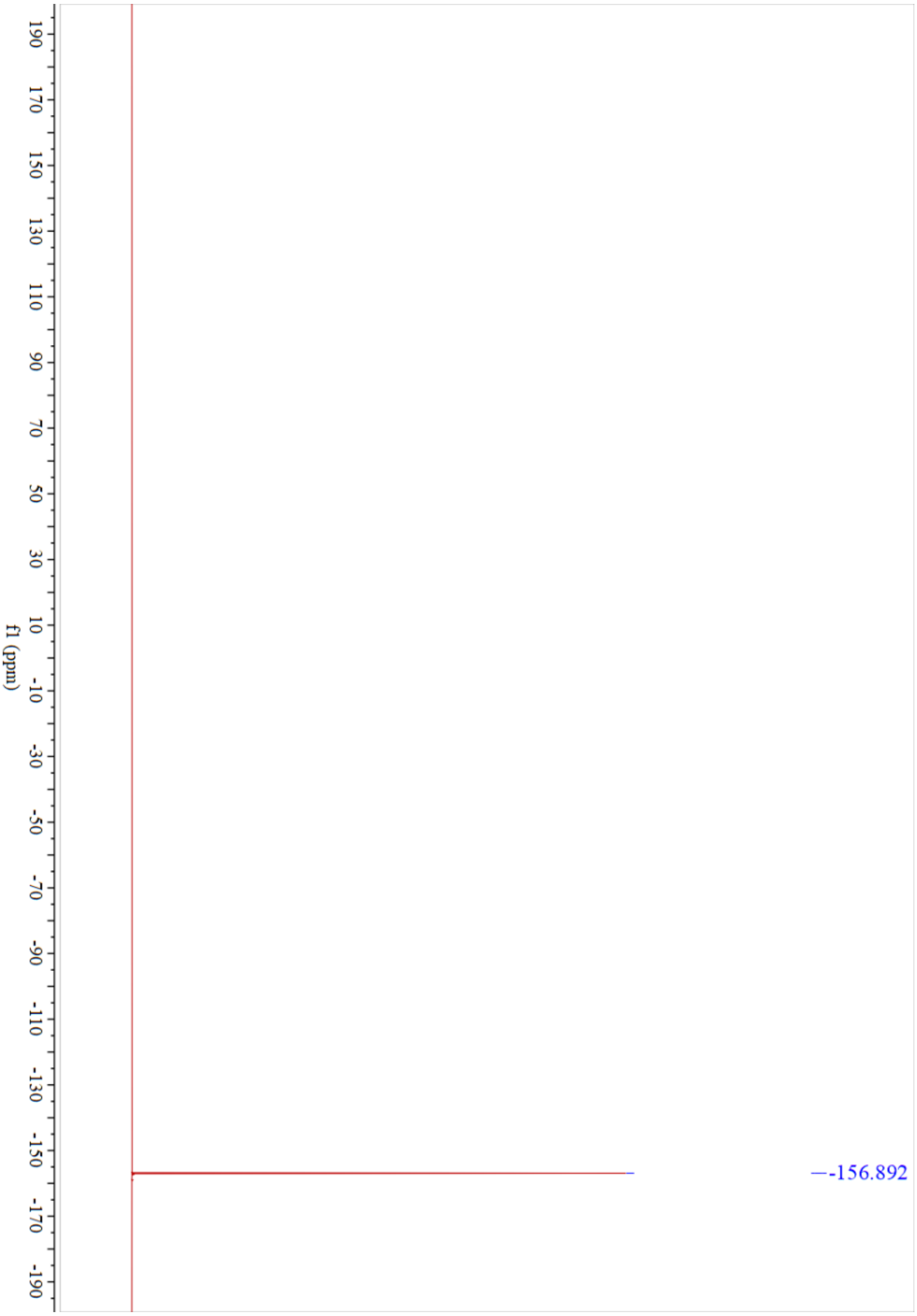
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3**



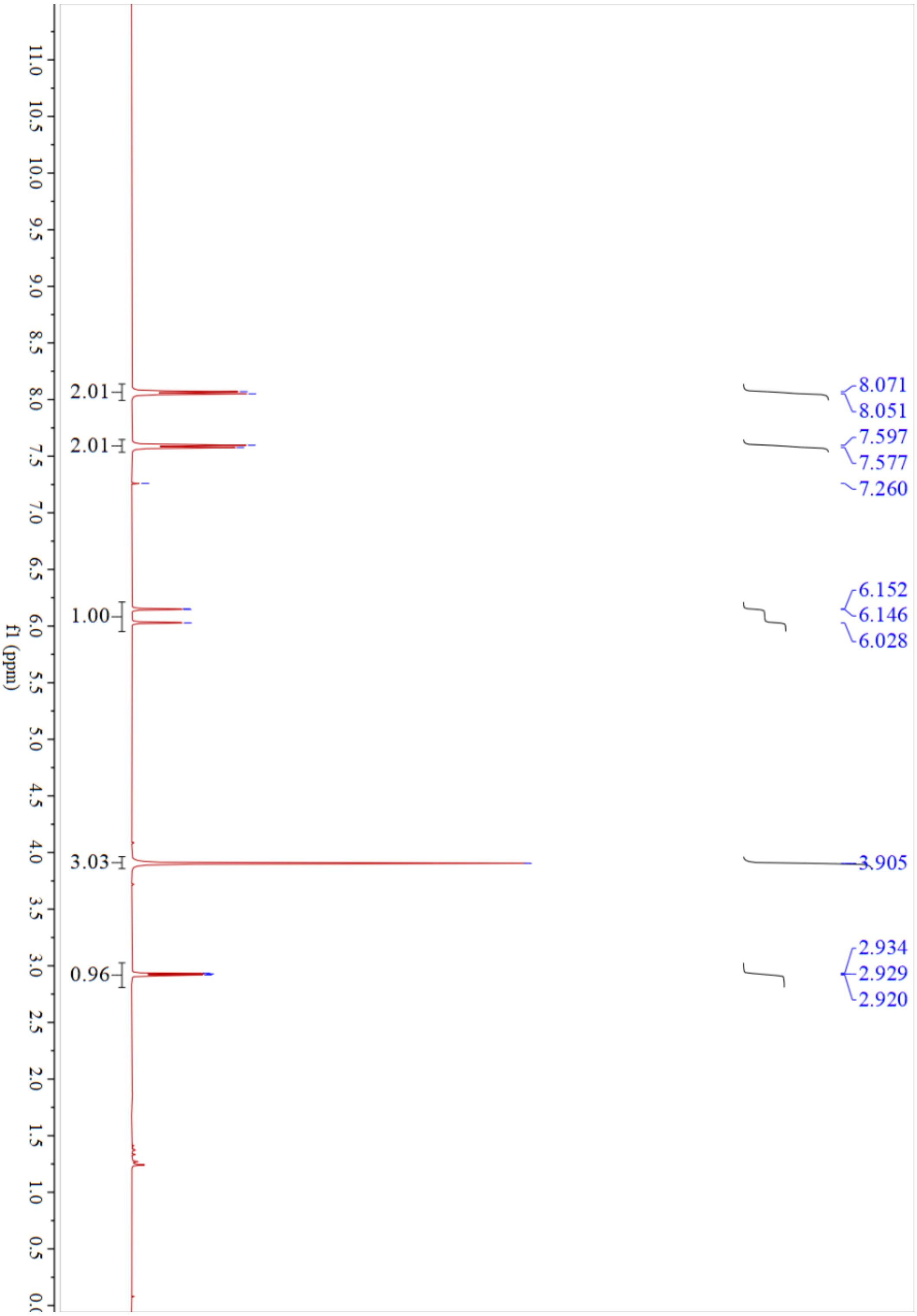
^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **3**



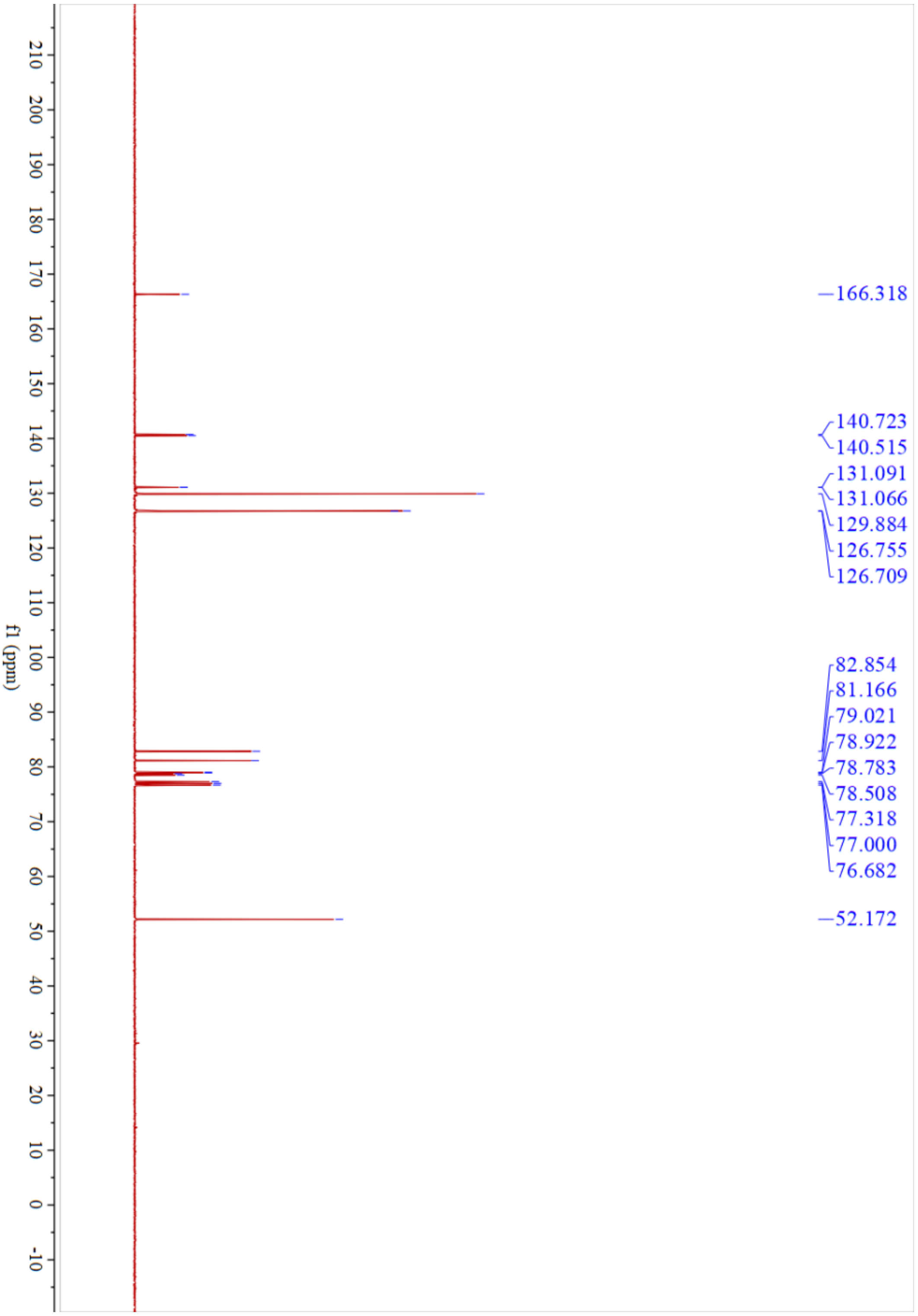
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3**



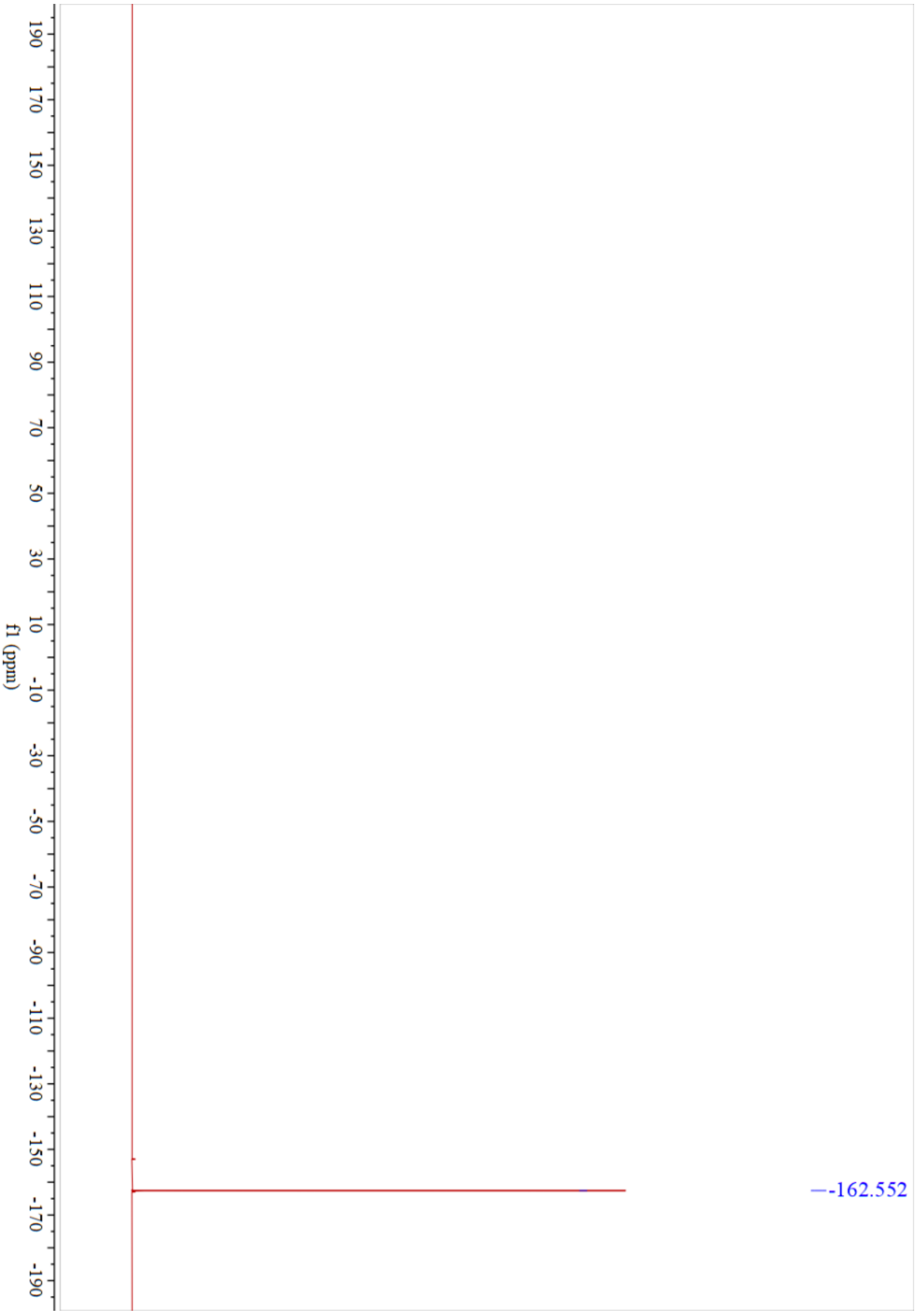
^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **4**



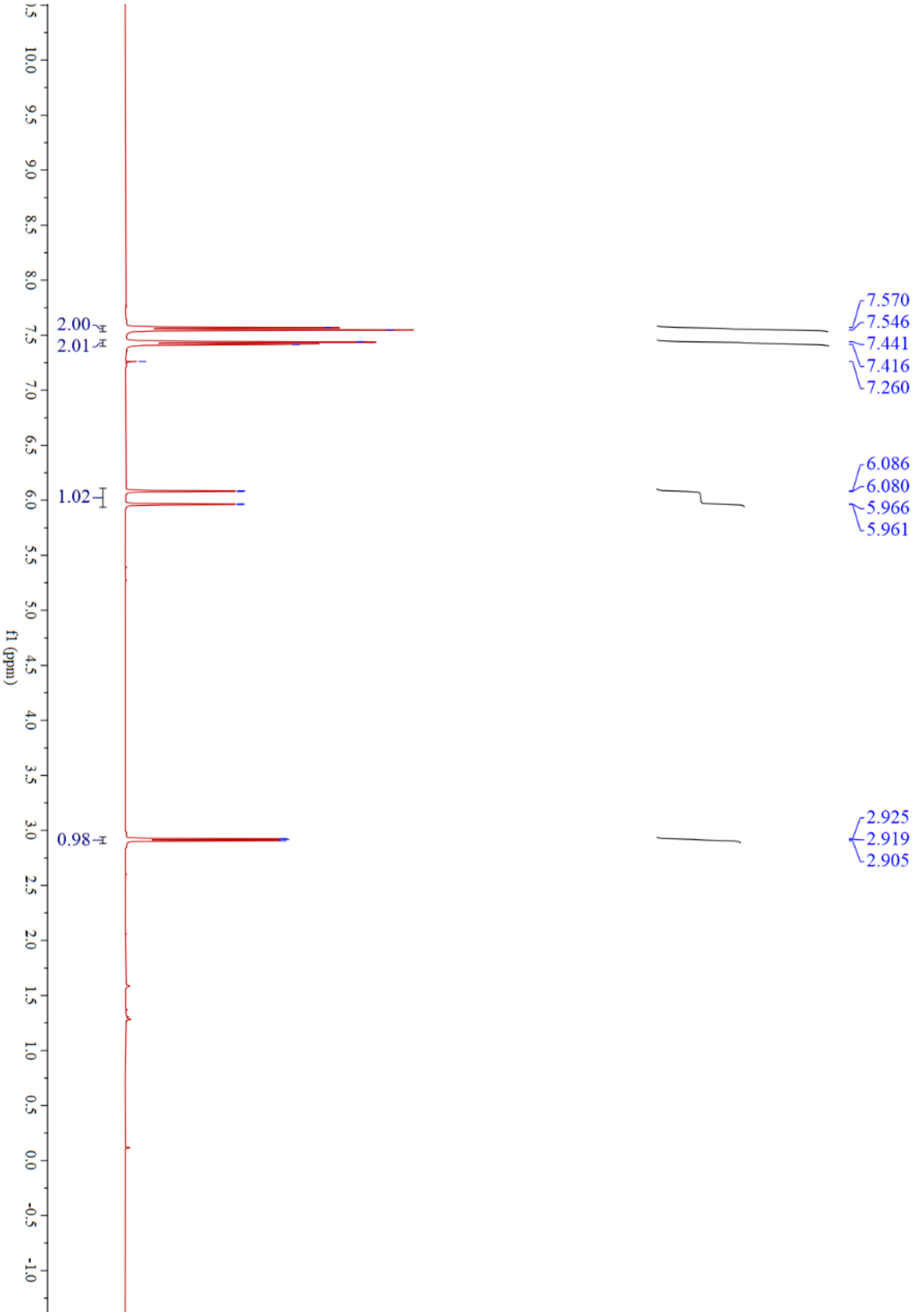
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4**



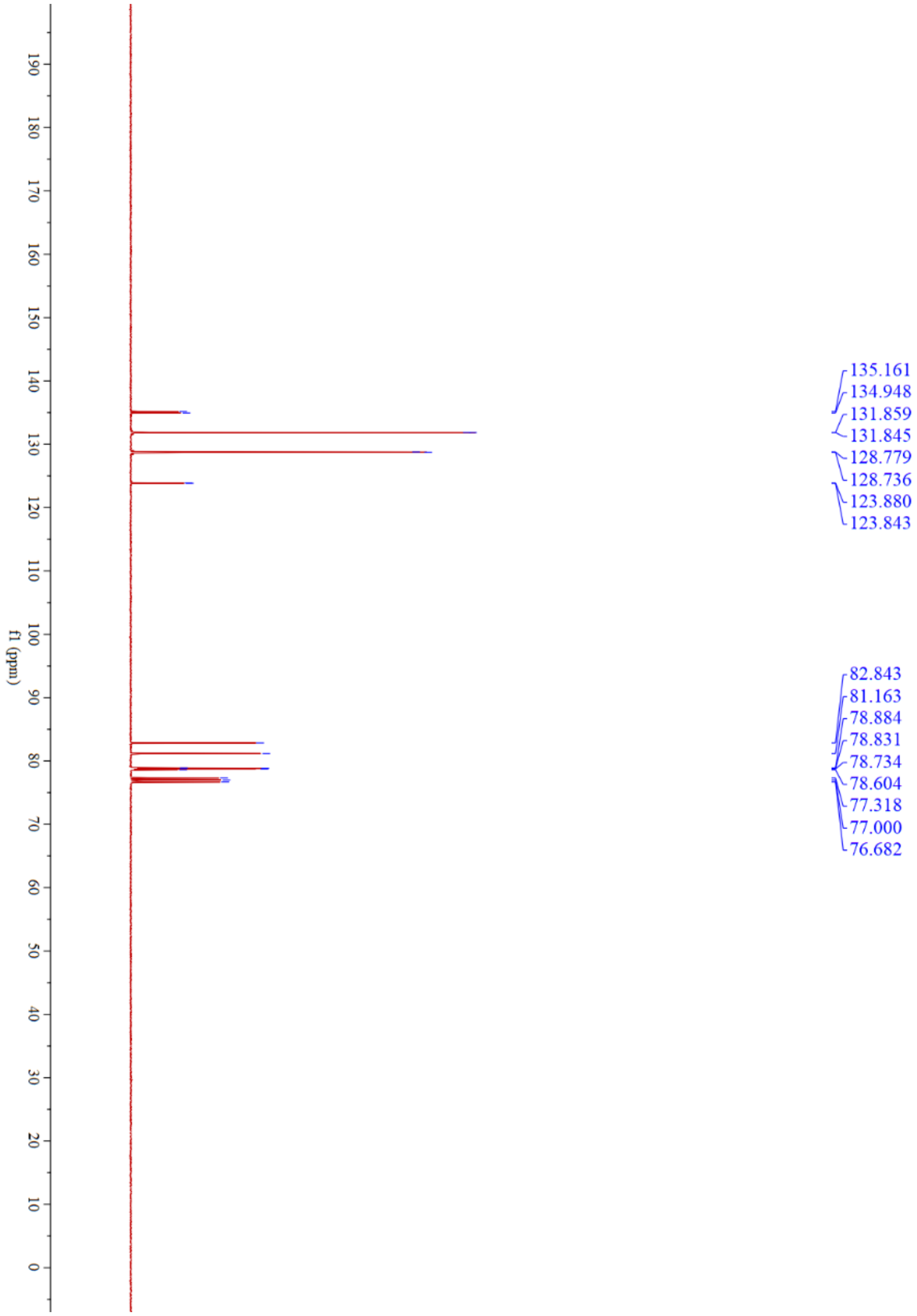
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4**



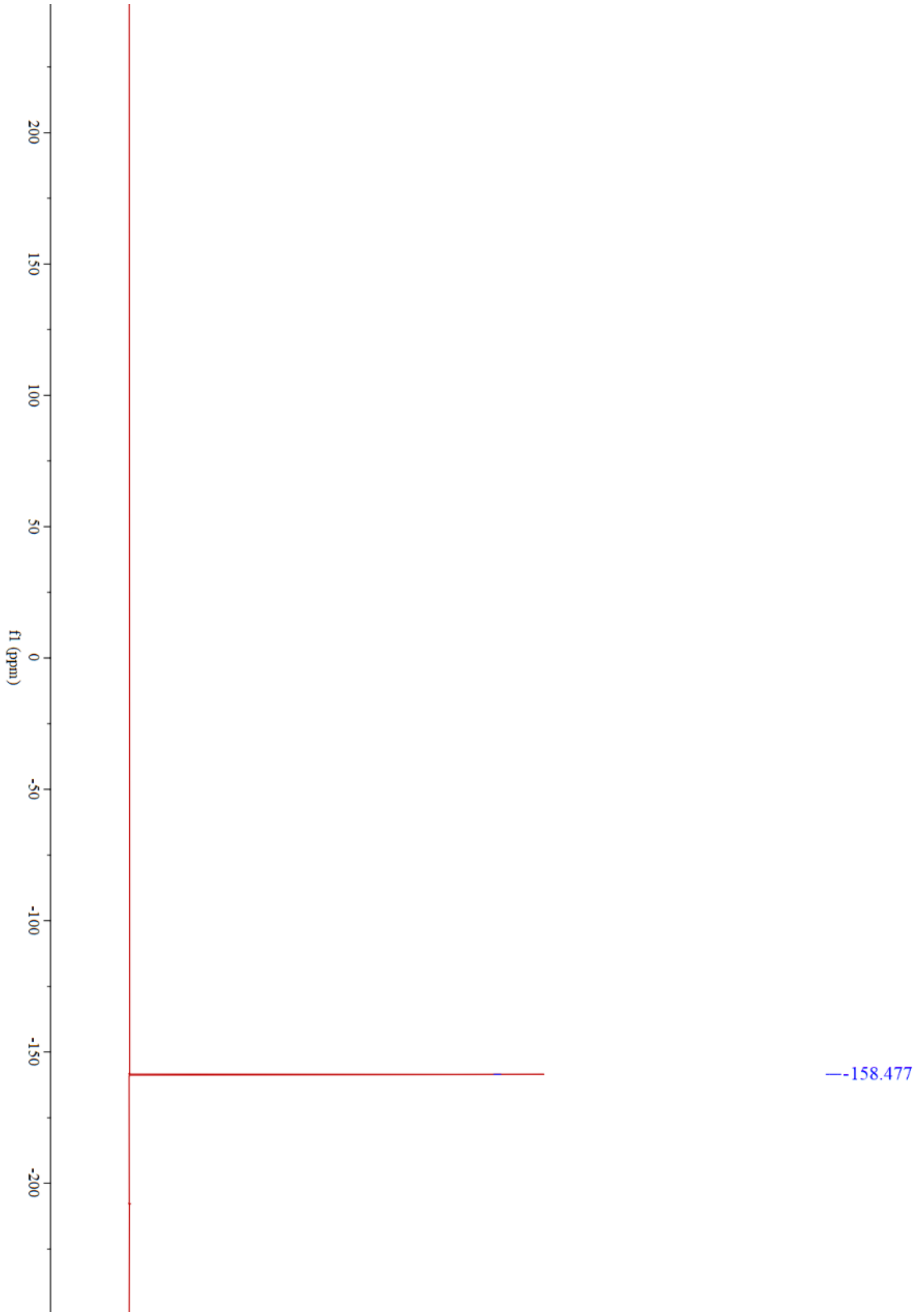
^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **5**



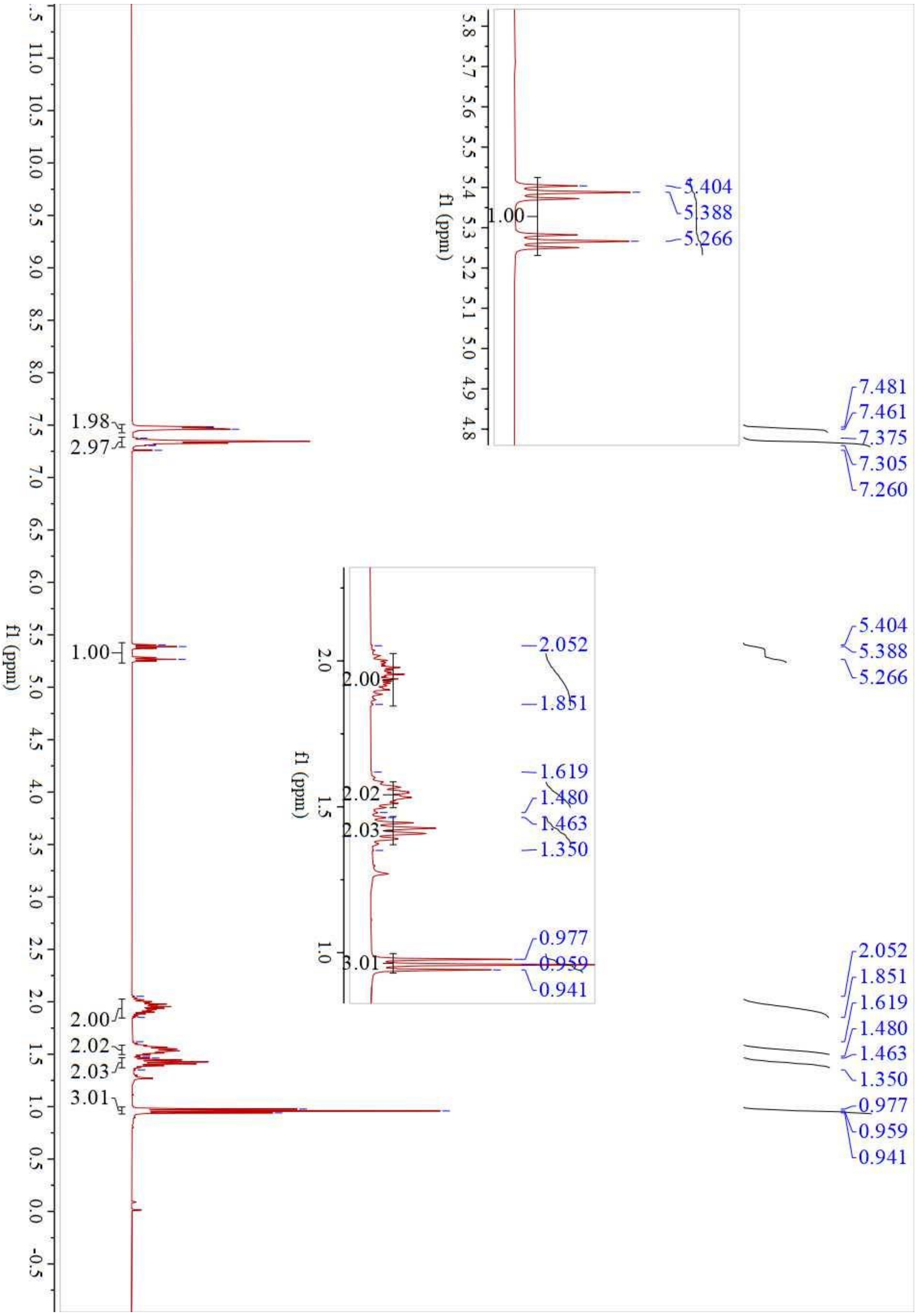
^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **5**



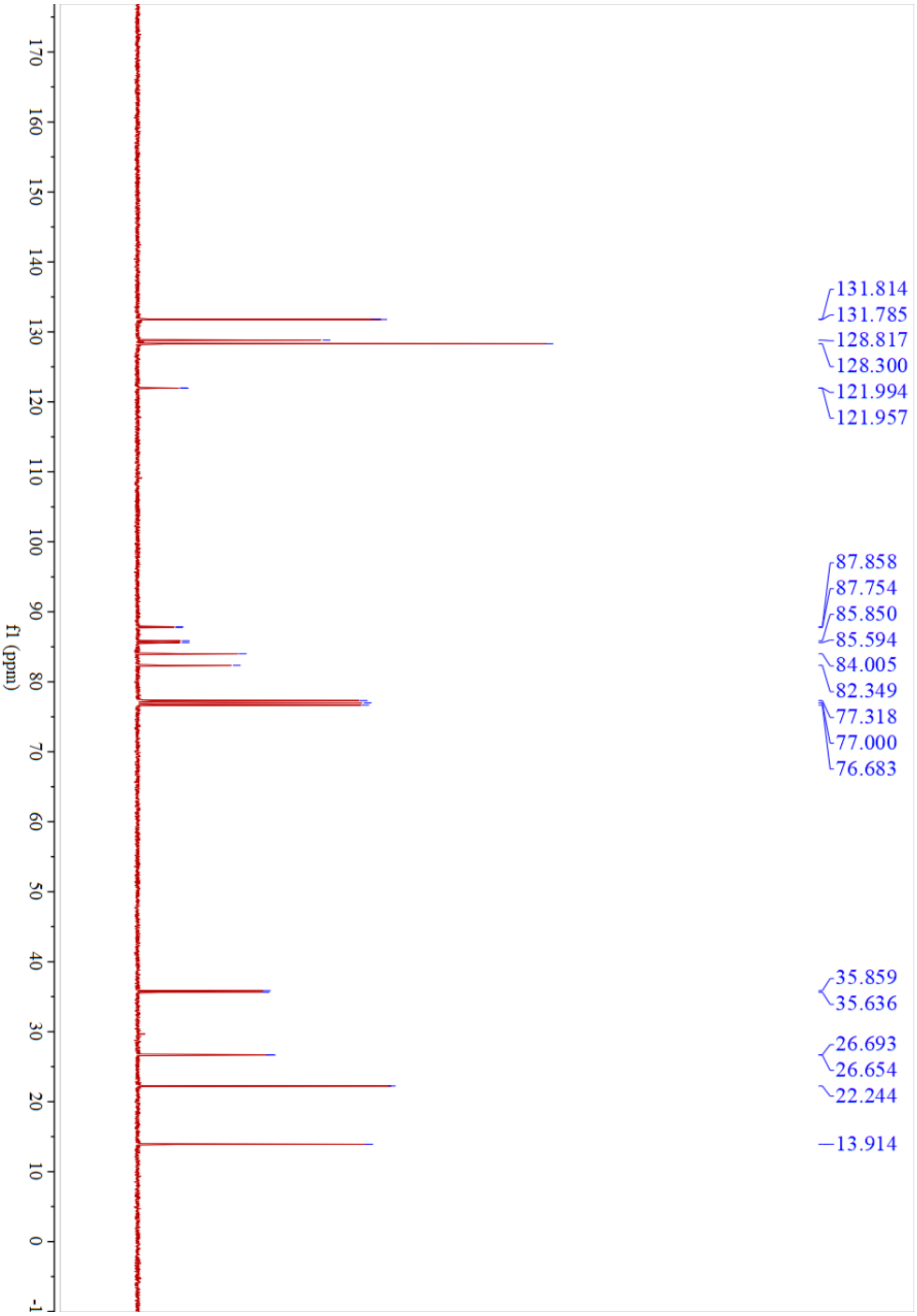
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **5**



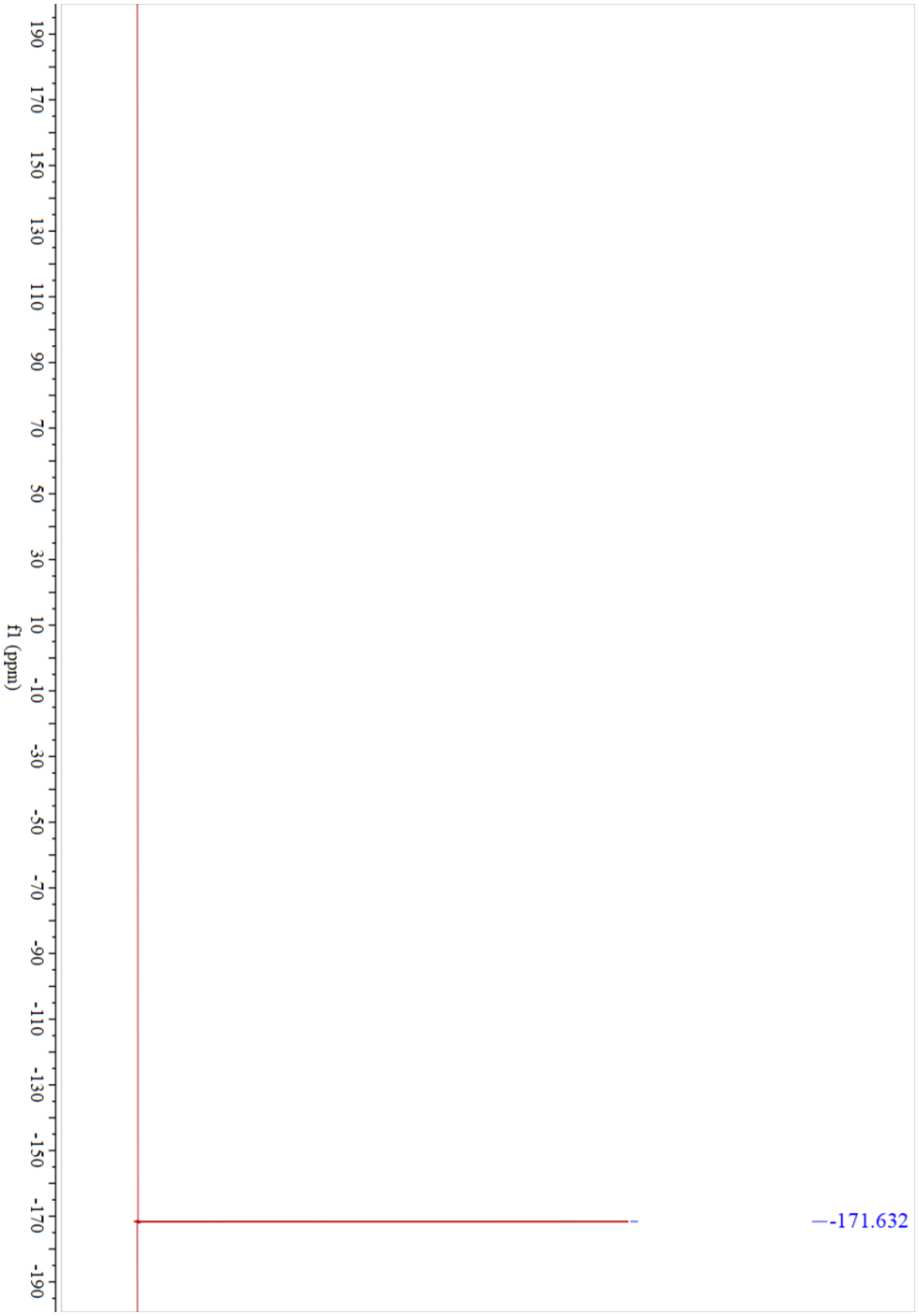
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6**



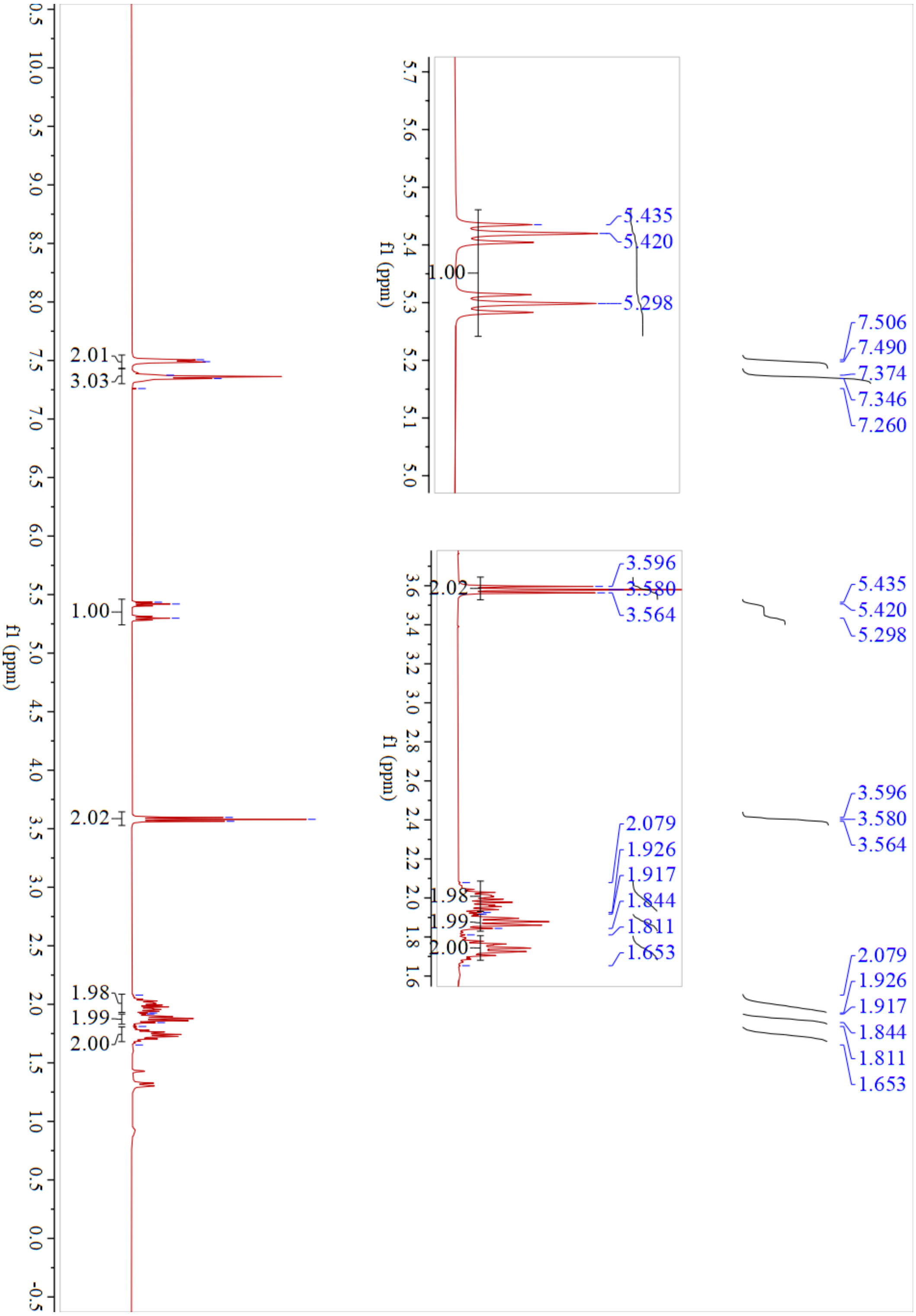
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **6**



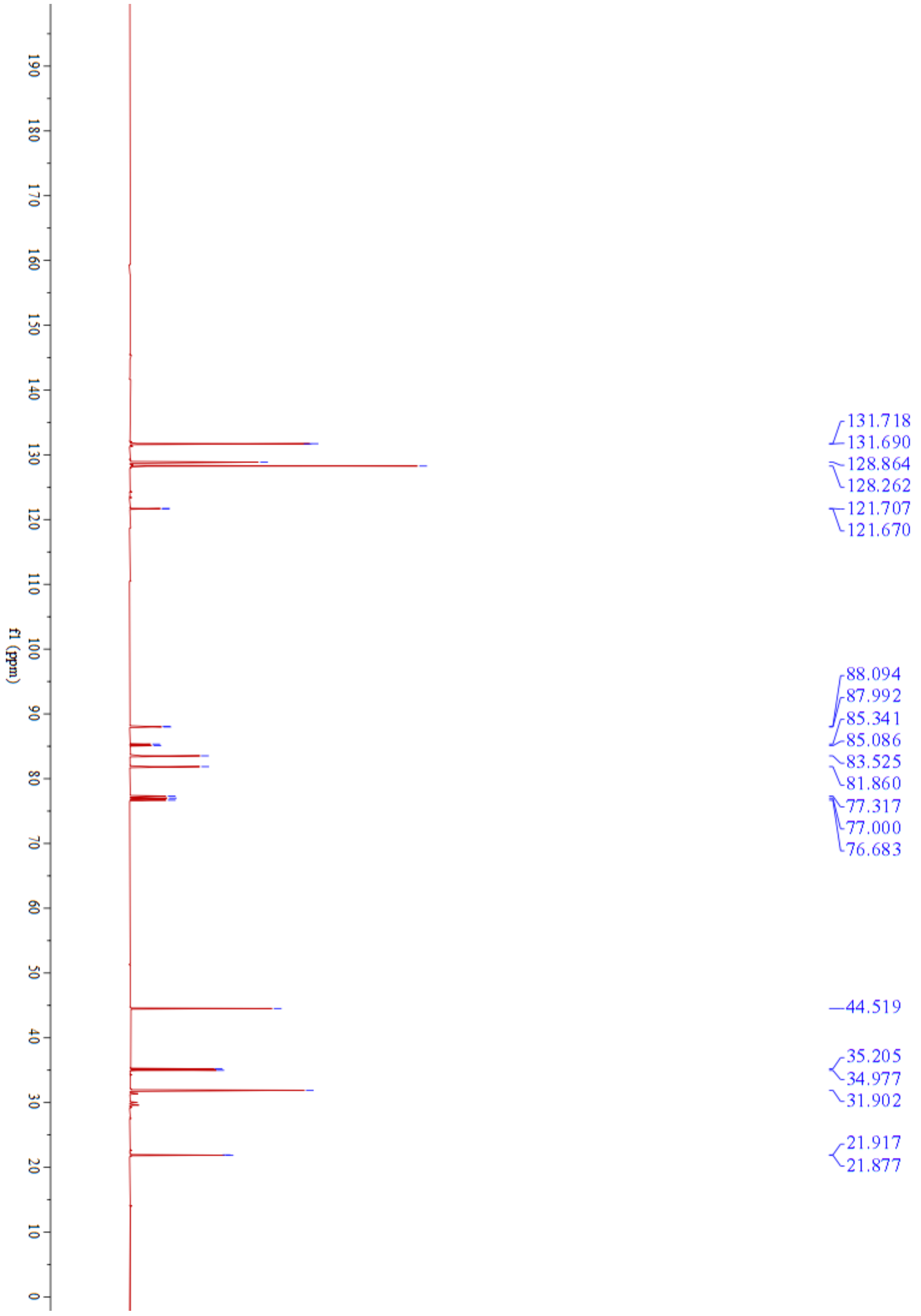
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **6**



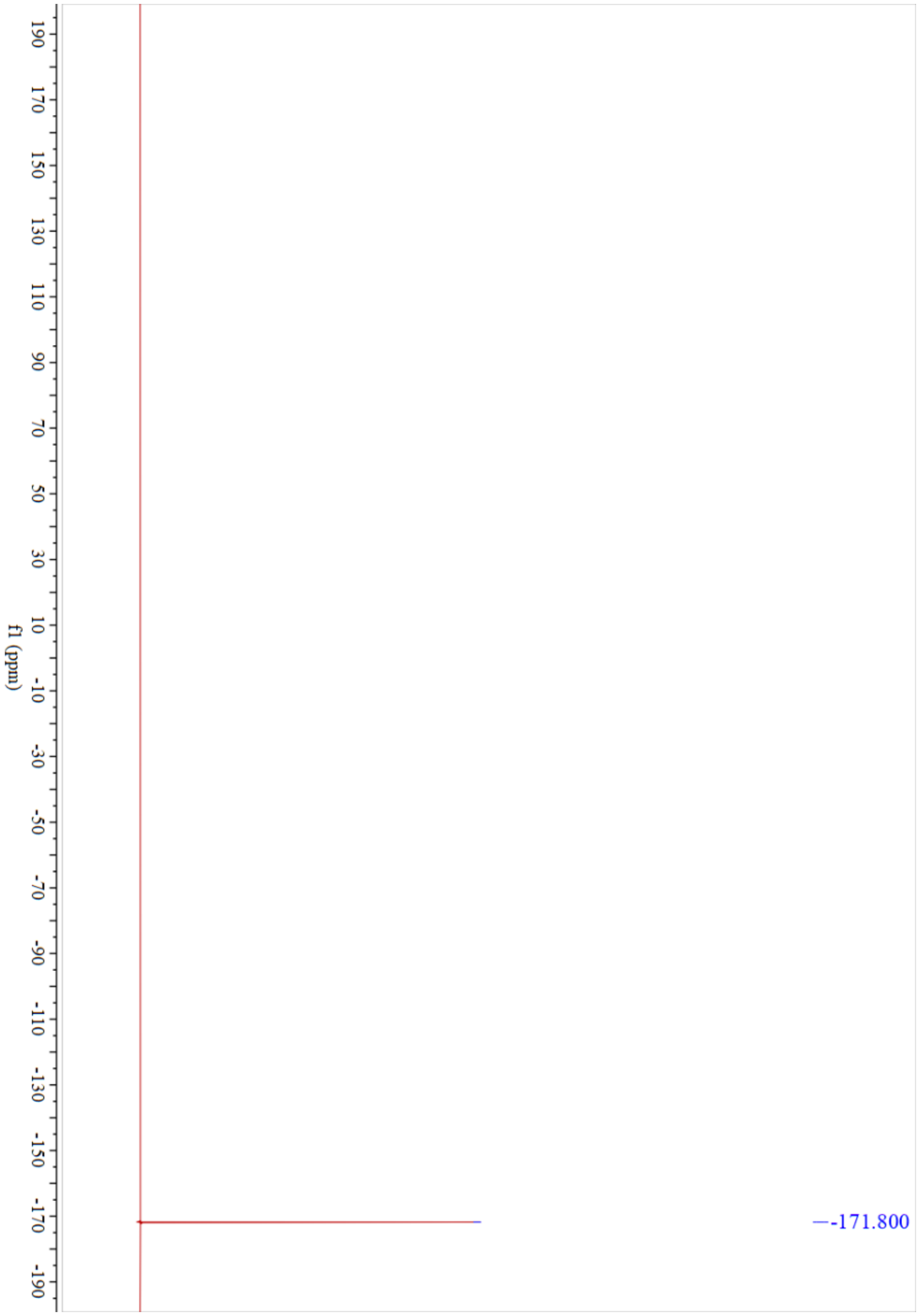
^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **7**



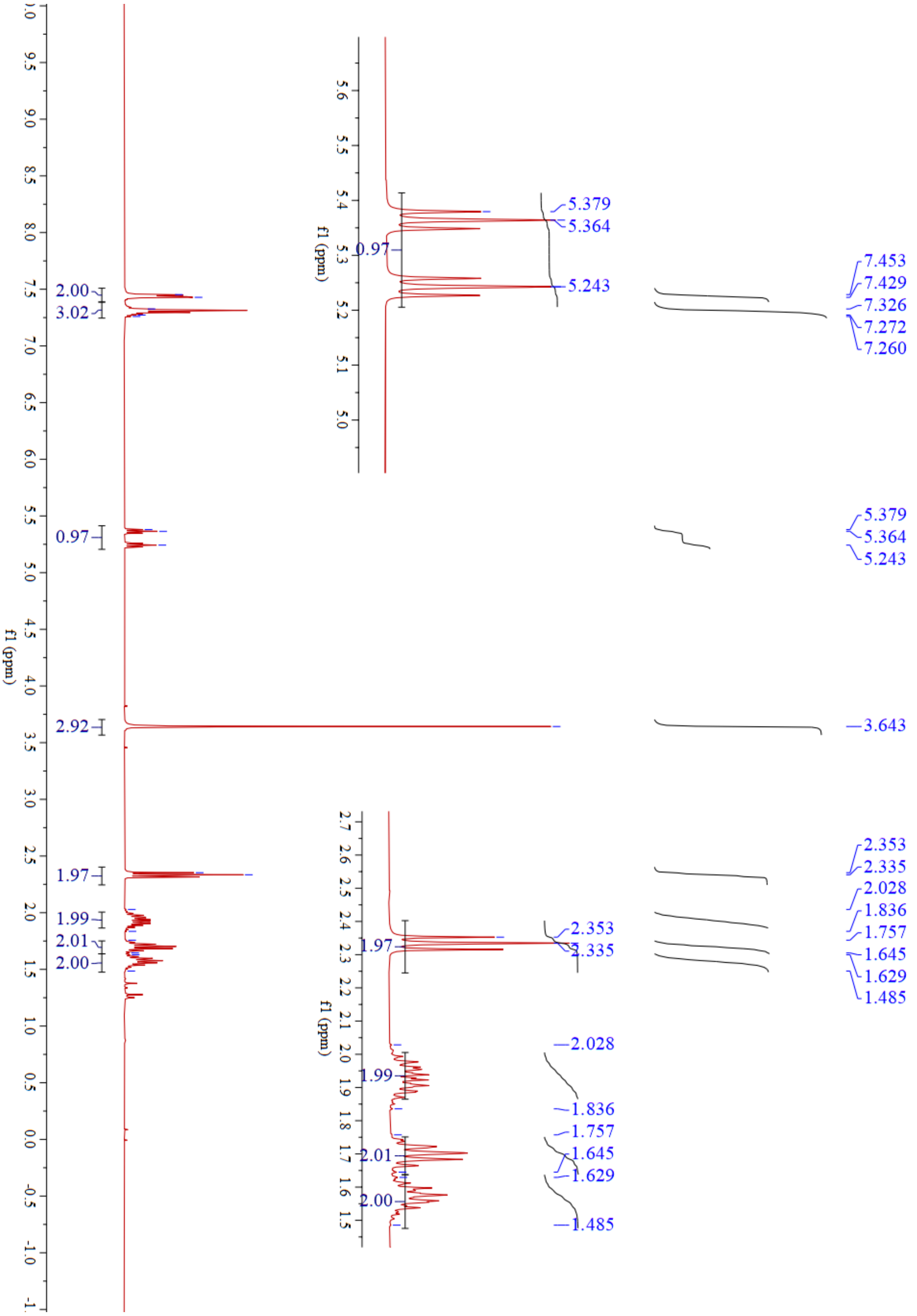
^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **7**



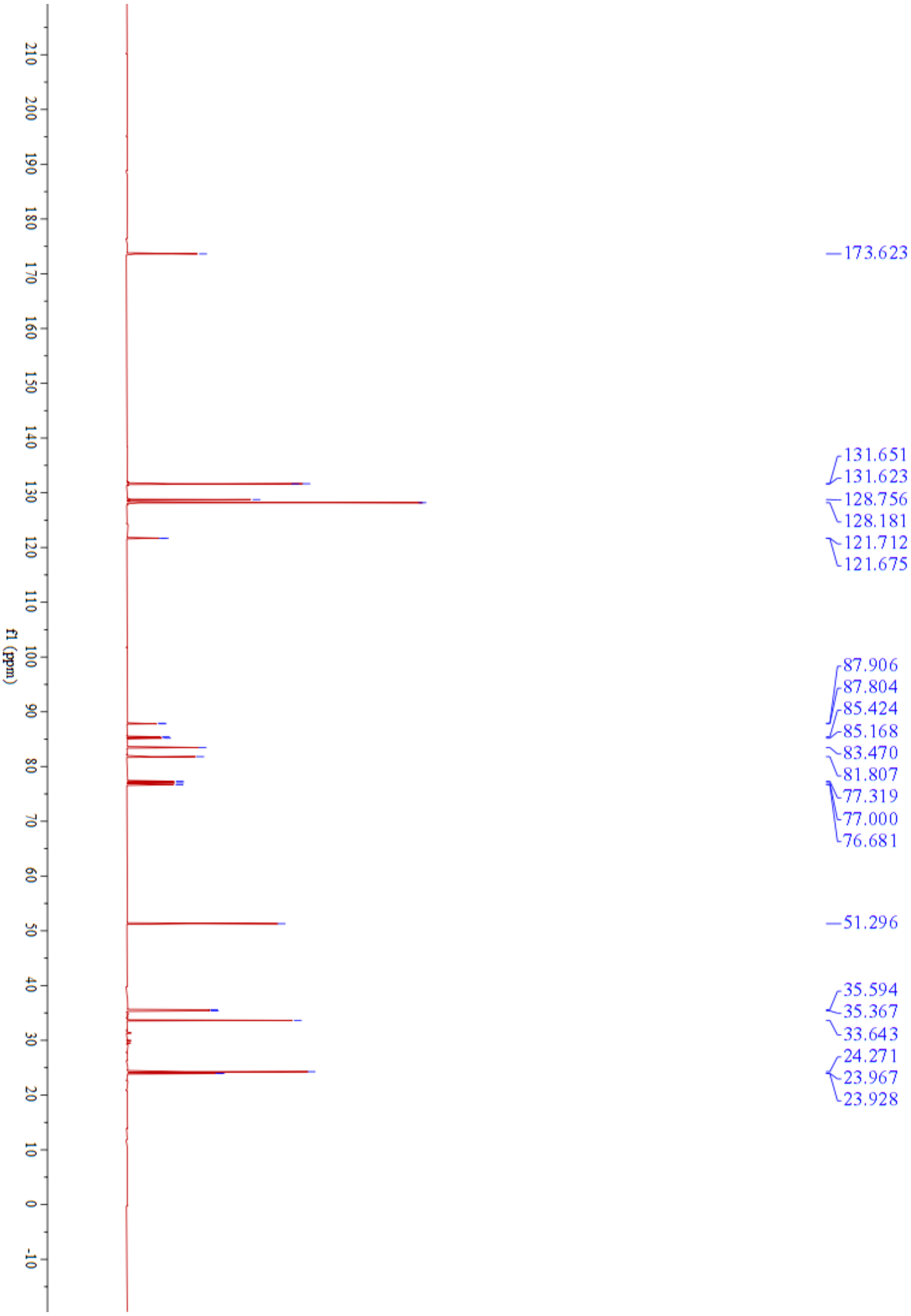
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **7**



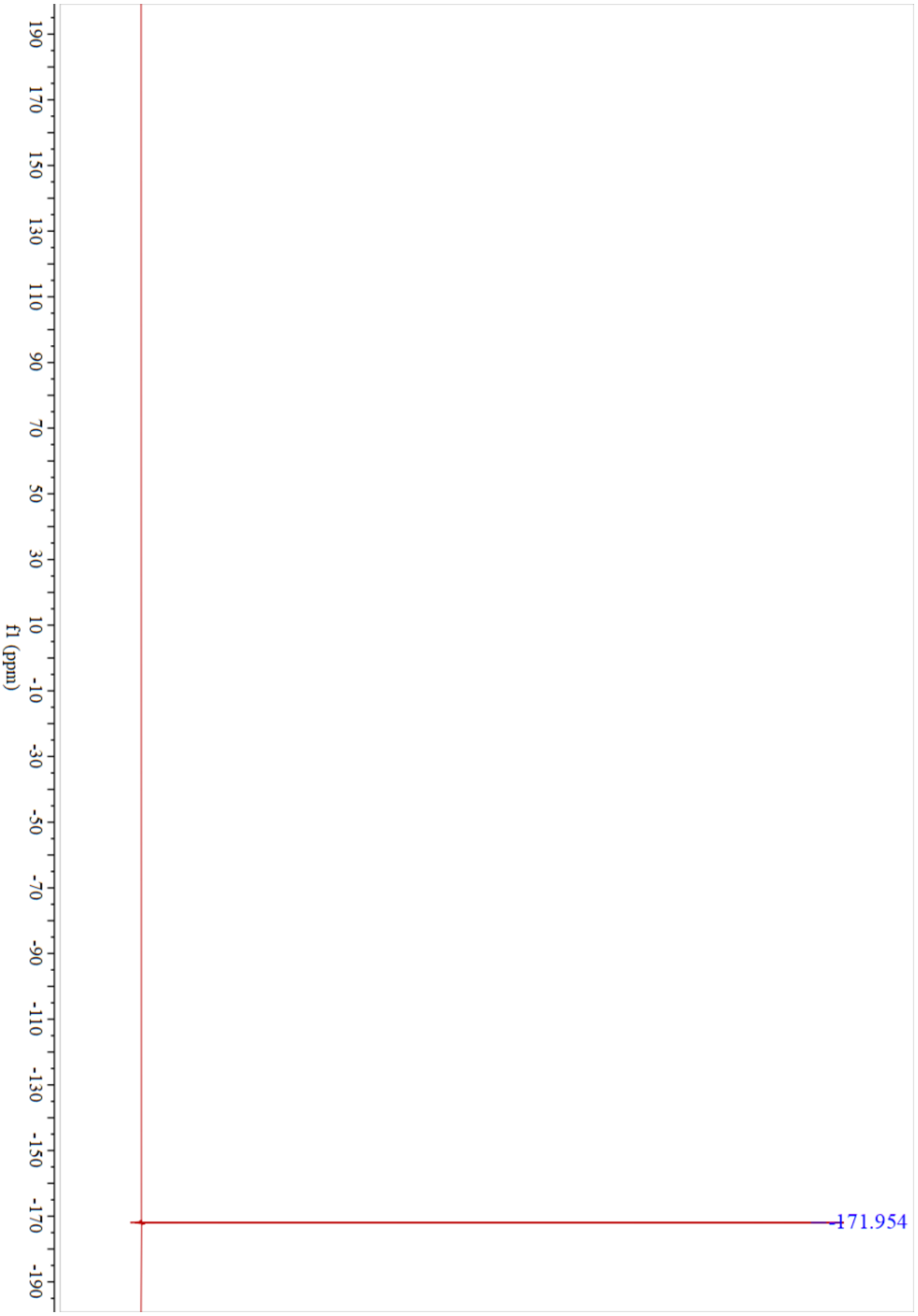
^{1}**H NMR** (400 MHz, CDCl$_3$) spectrum of **8**



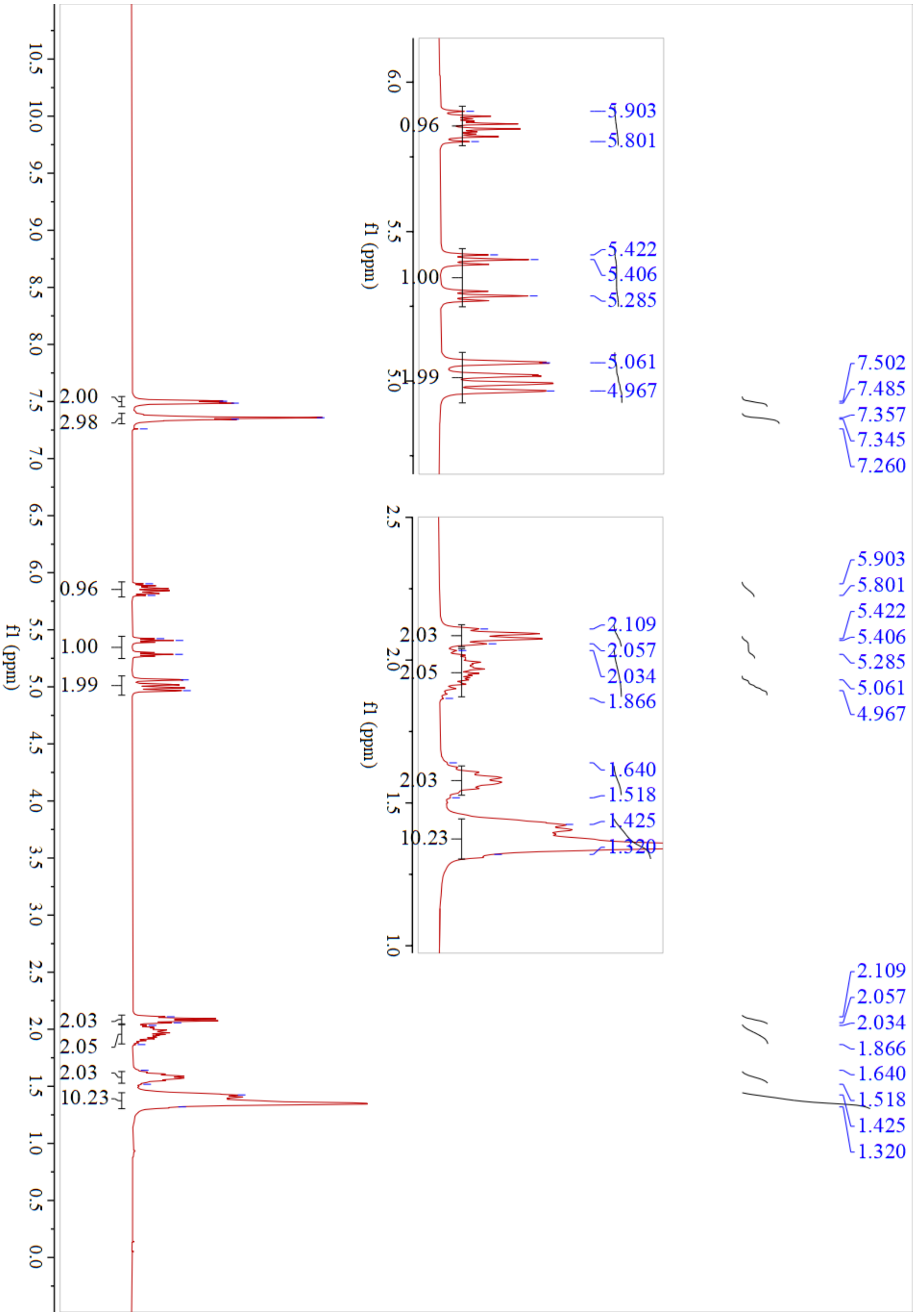
^{13}C NMR (101 MHz, CDCl$_3$) spectrum of **8**



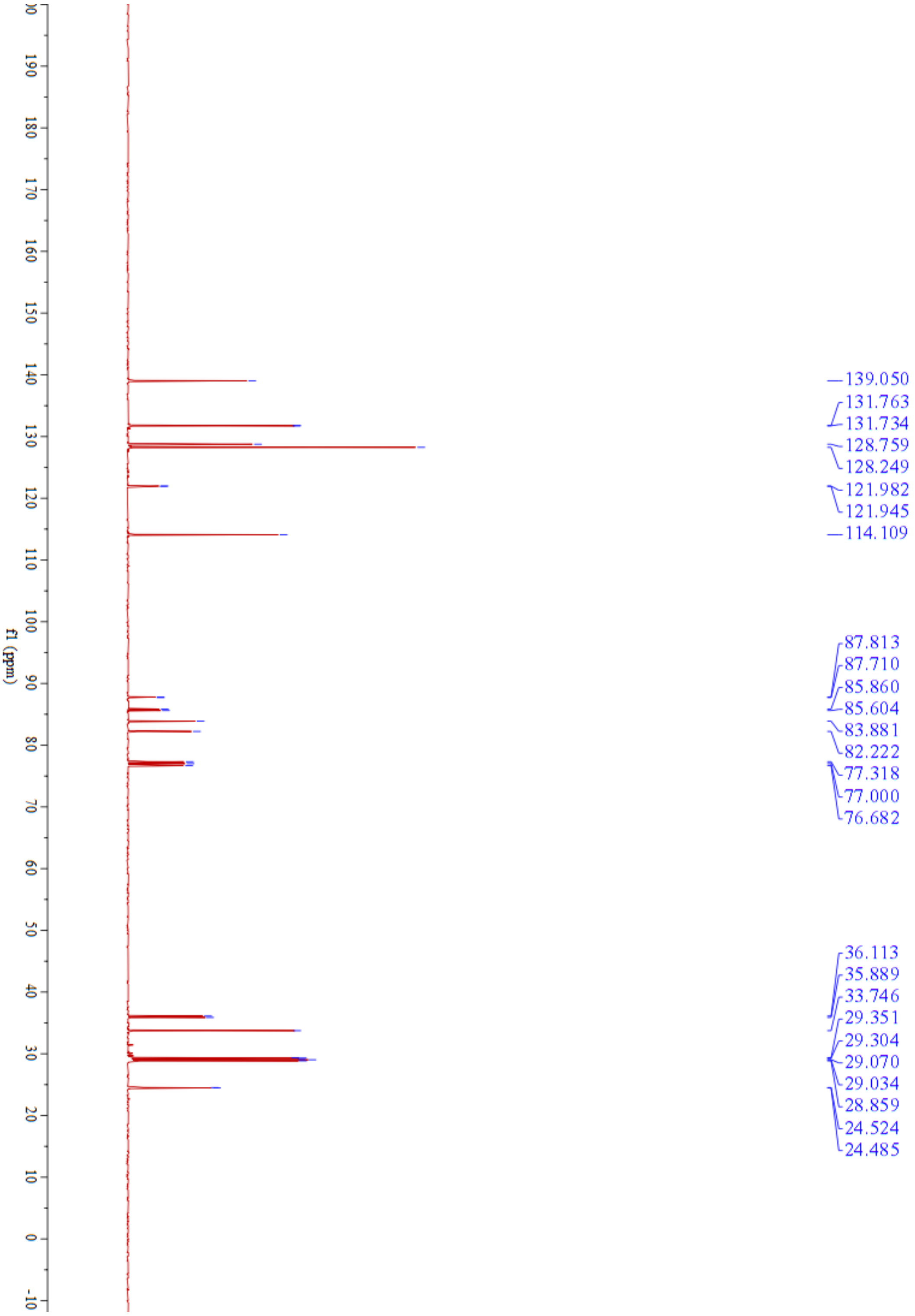
^{19}**F NMR** (376 MHz, $CDCl_3$) spectrum of **8**



^{1}**H NMR** (400 MHz, CDCl$_3$) spectrum of **9**



^{13}**C NMR** (101 MHz, CDCl$_3$) spectrum of **9**



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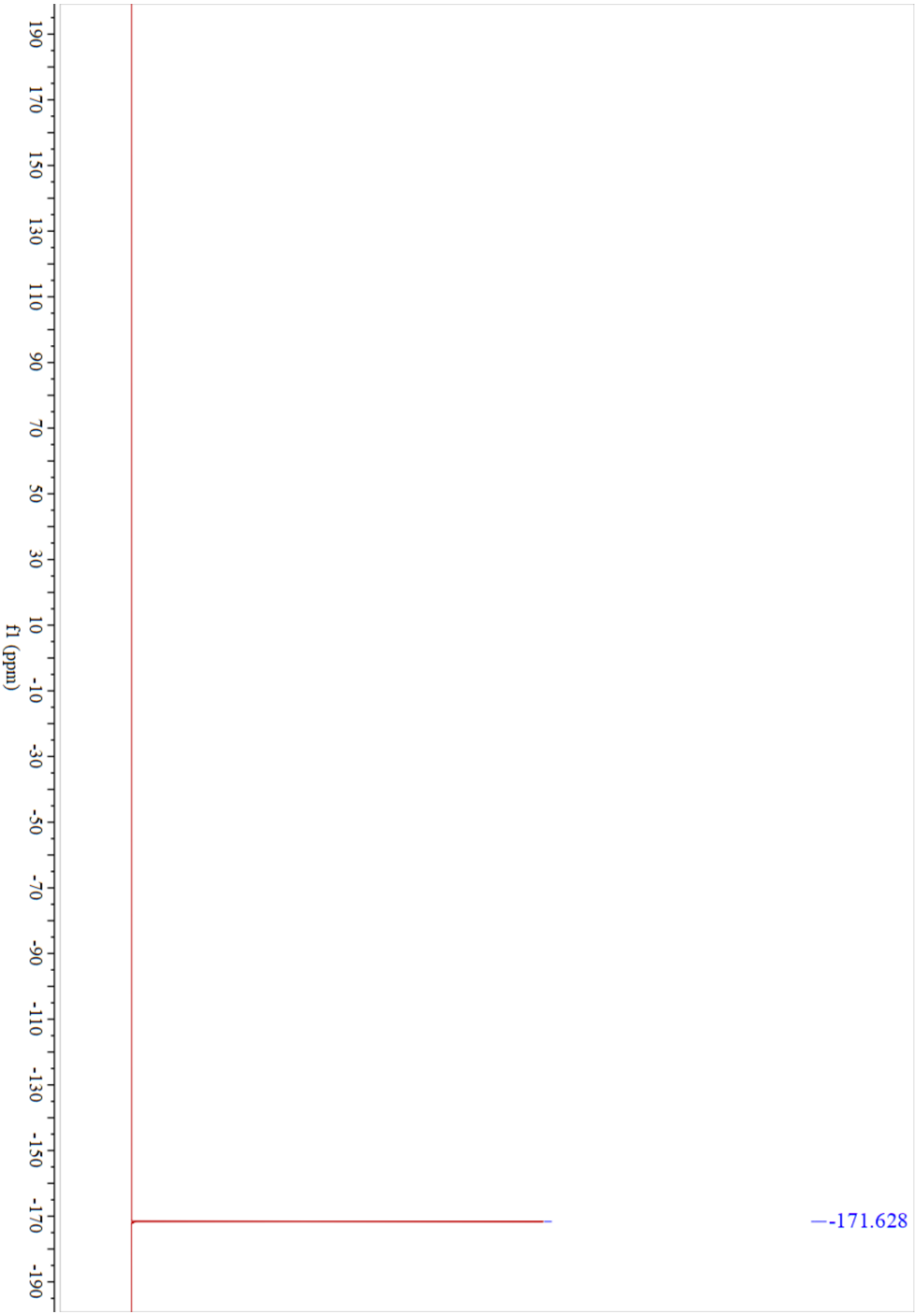

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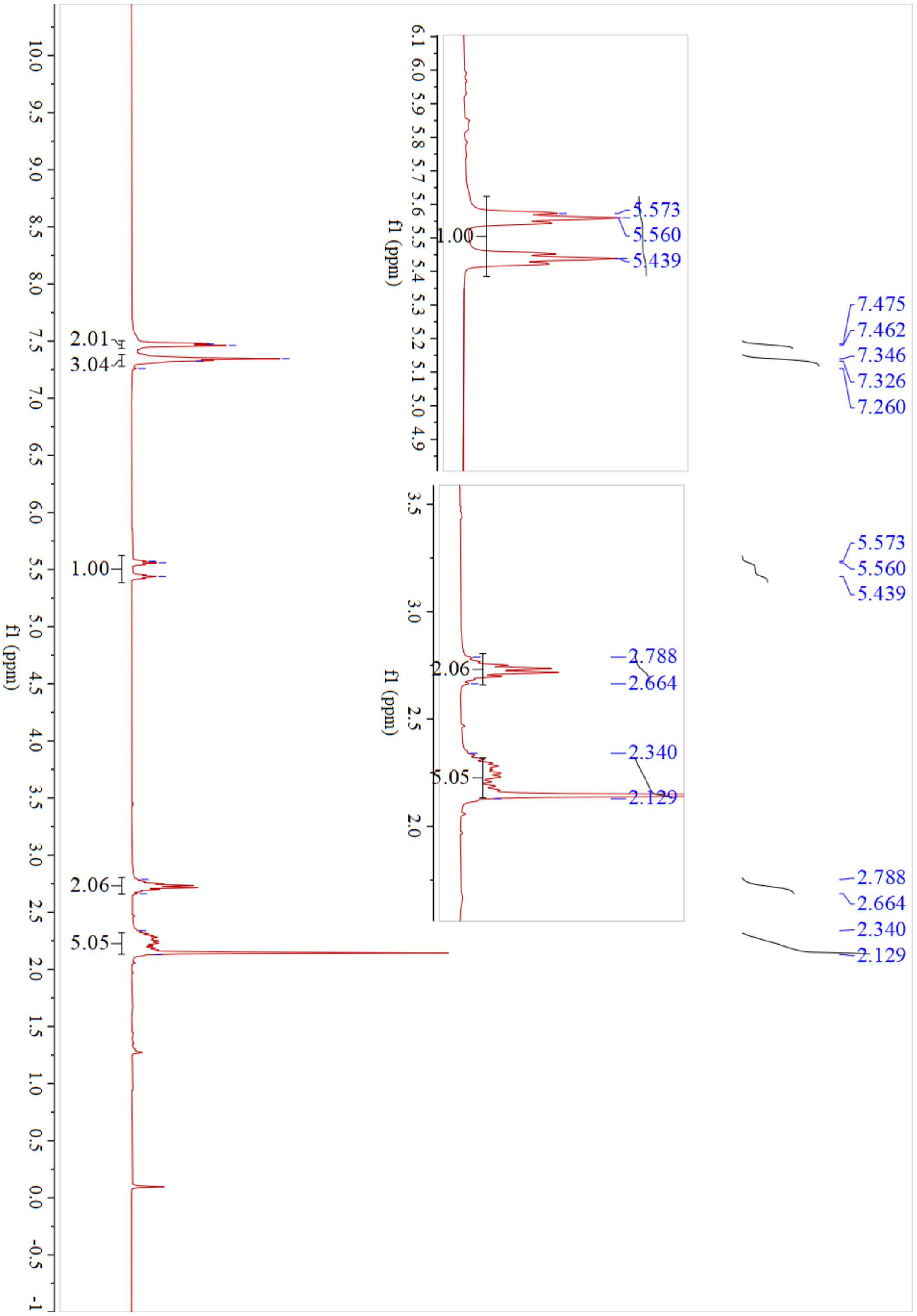
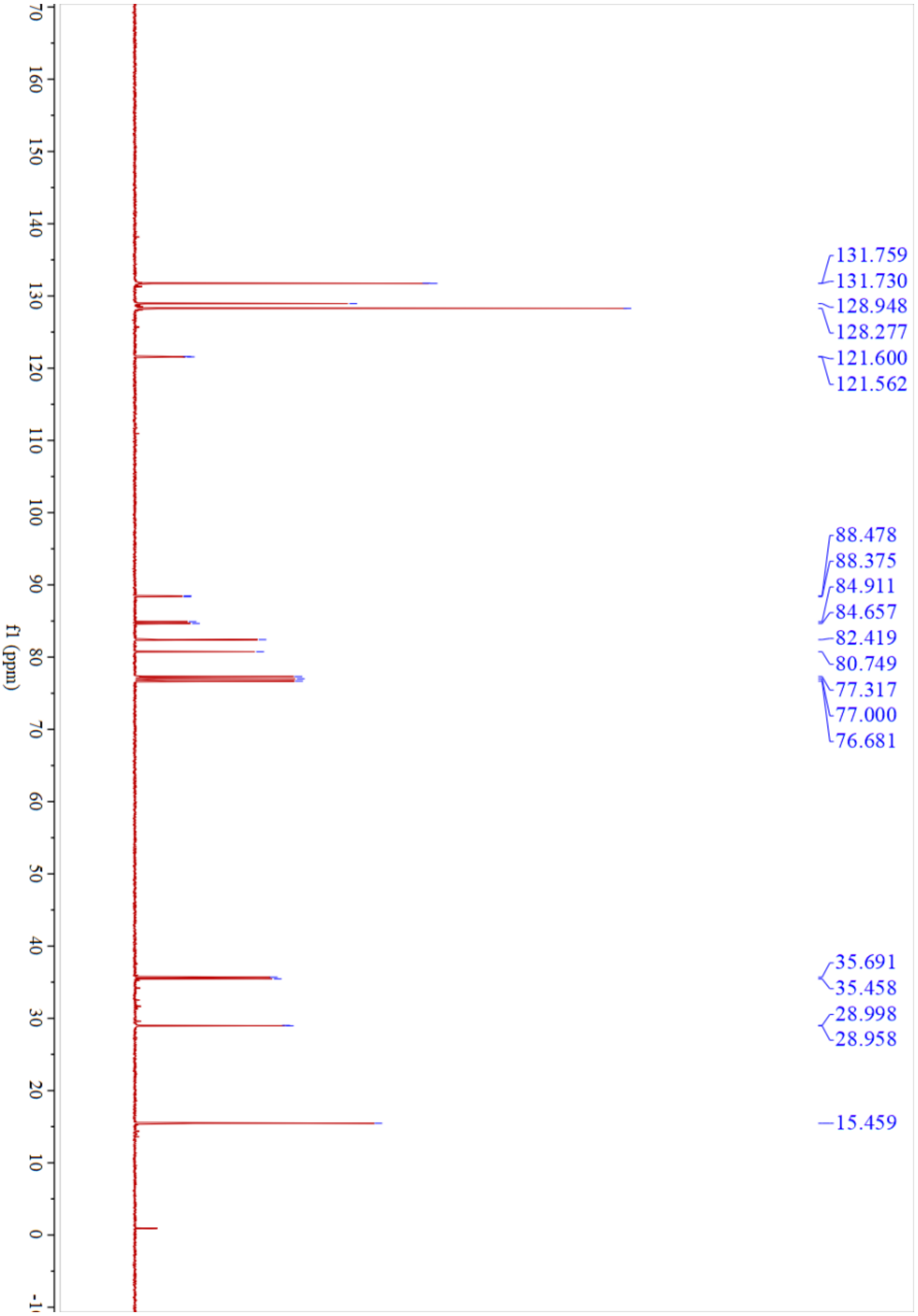
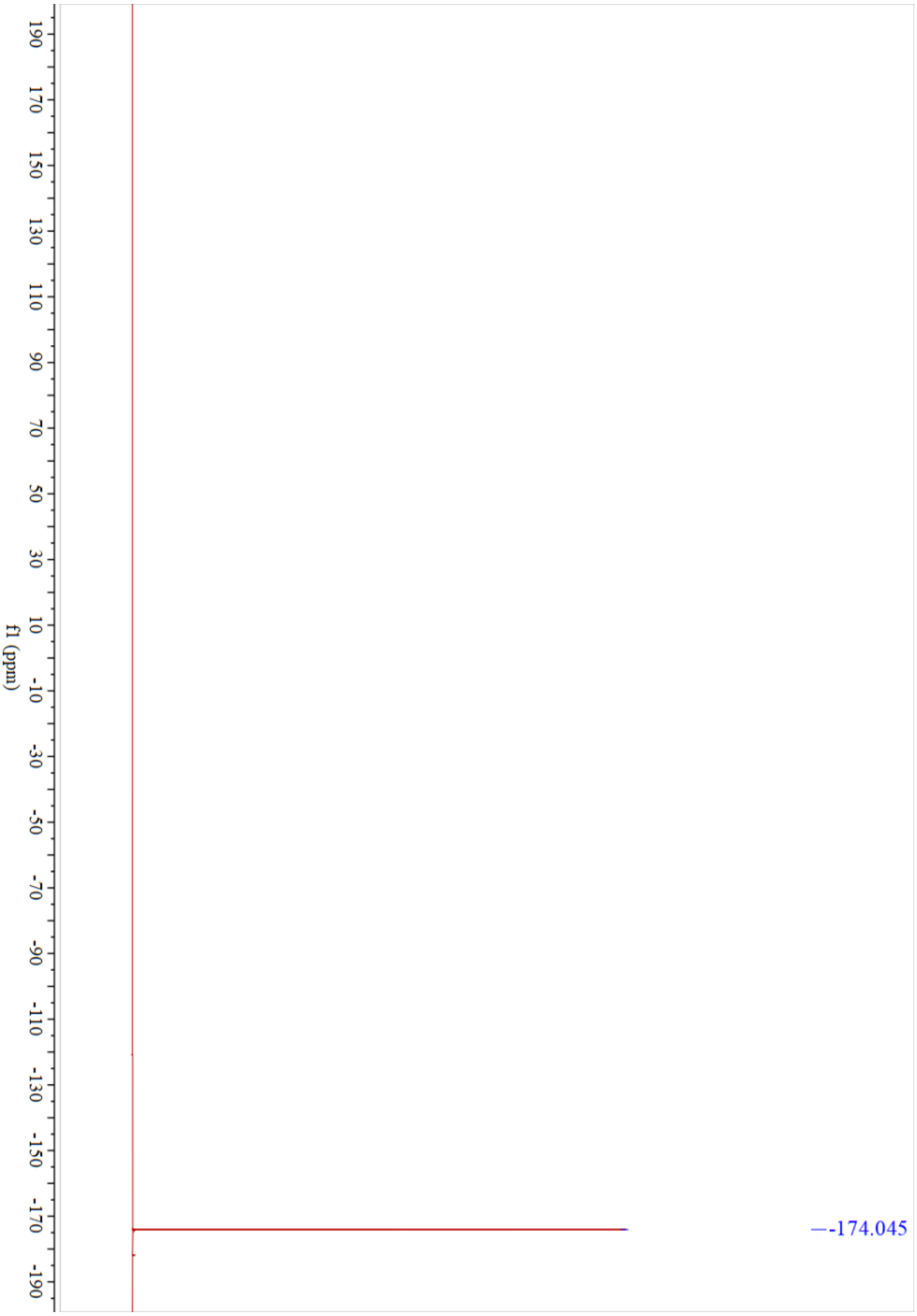


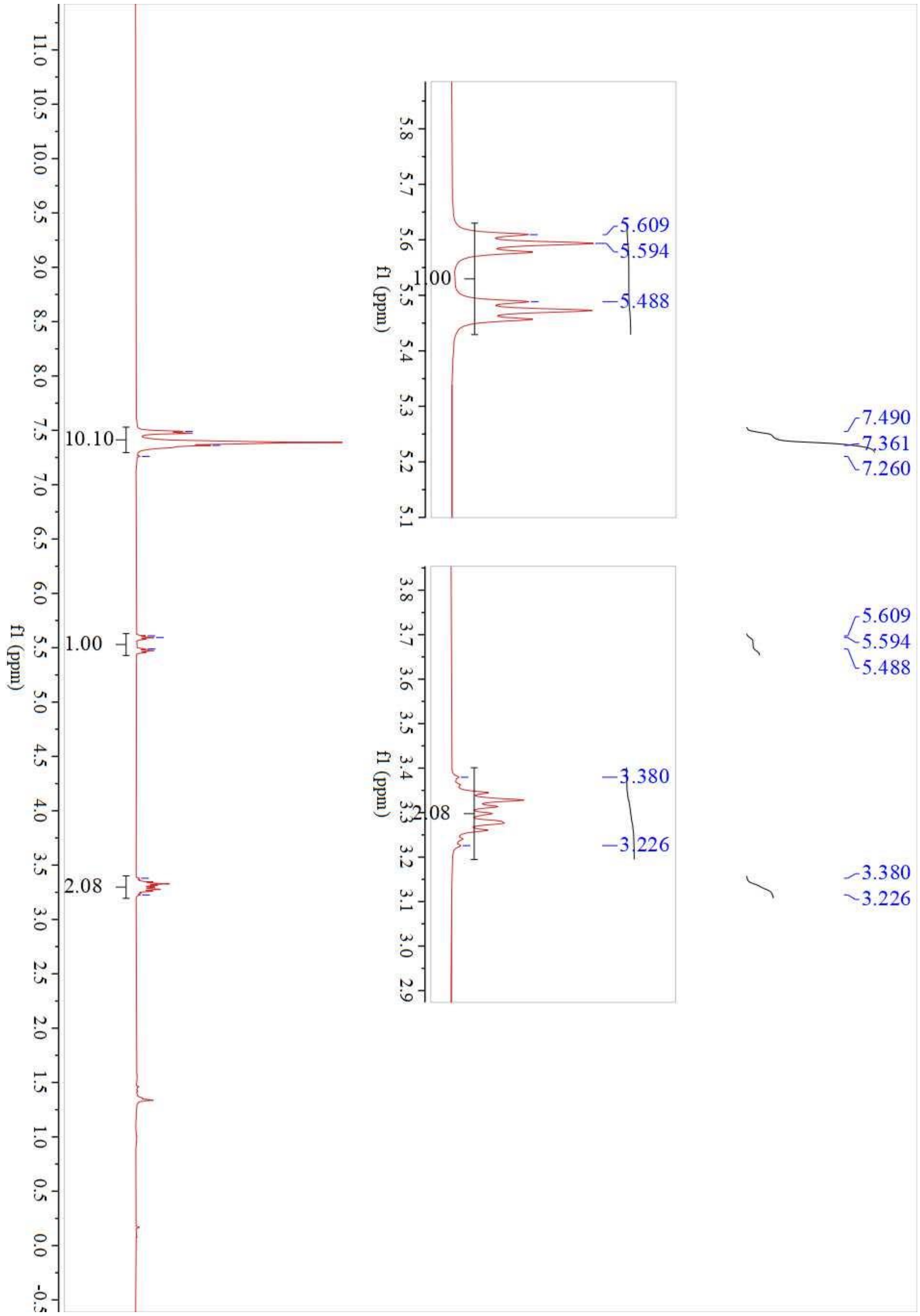
^{13}C NMR (101 MHz, CDCl$_3$) spectrum of **10**



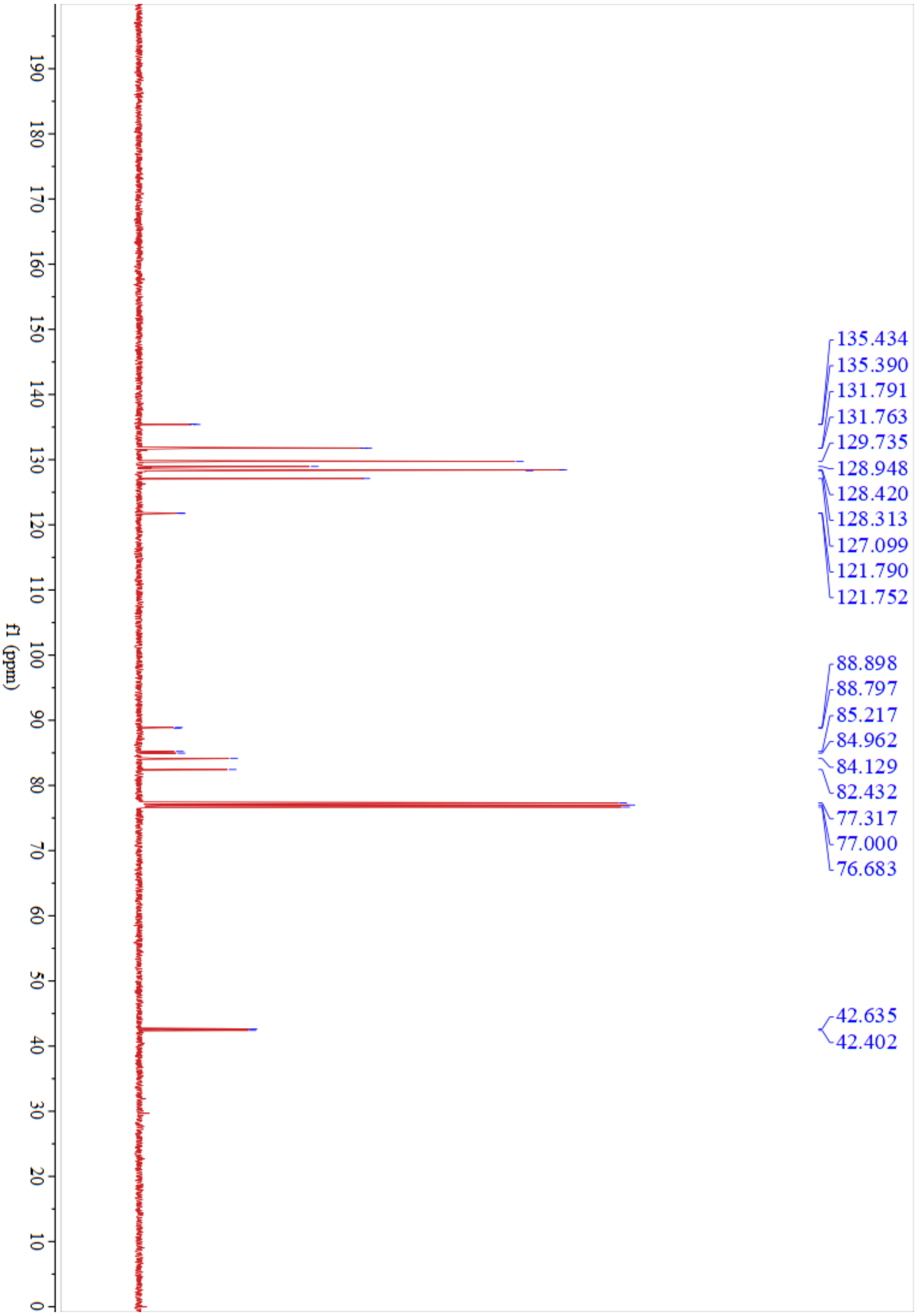
^{19}F NMR (376 MHz, CDCl$_3$) spectrum of **10**



^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **11**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **11**



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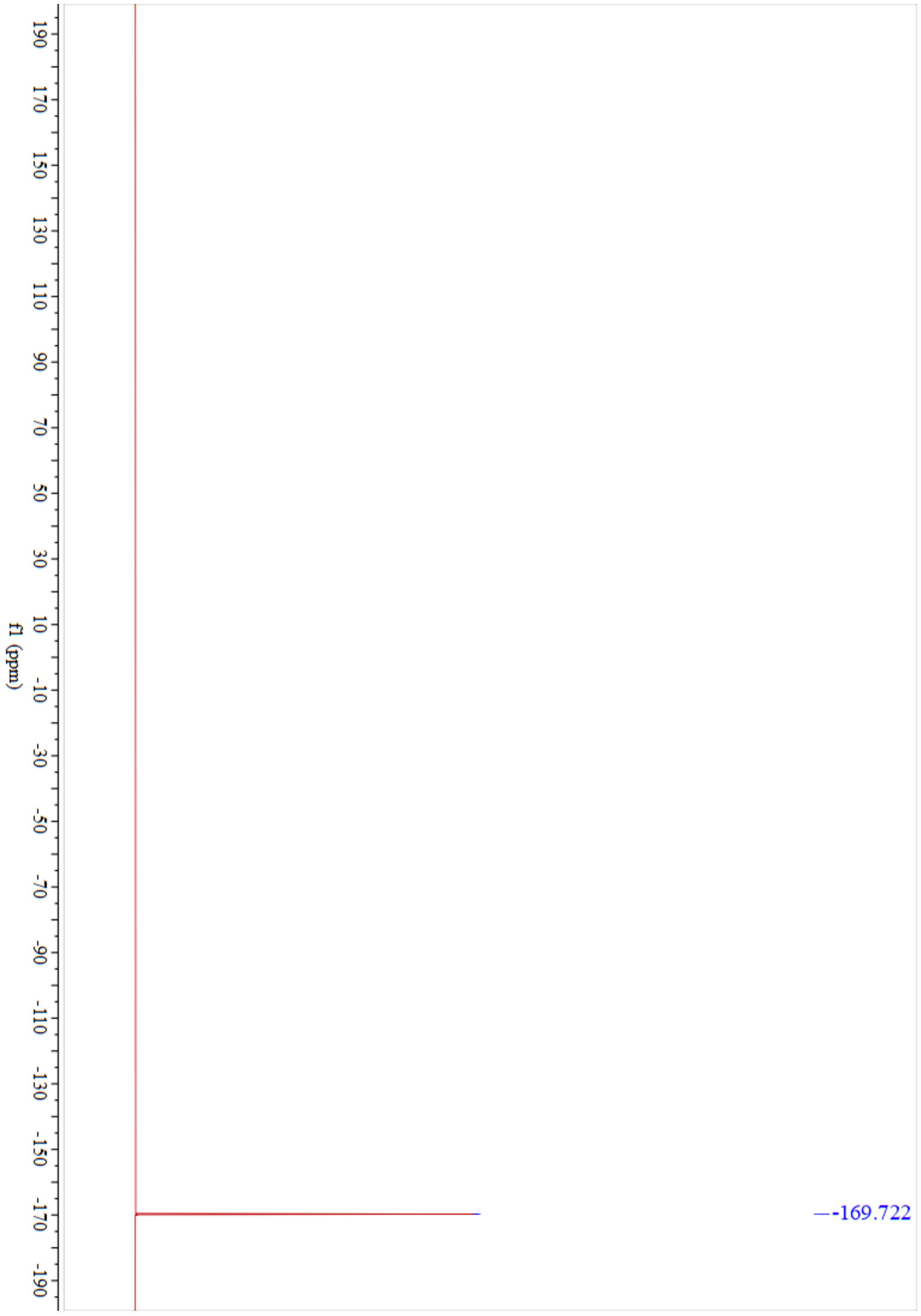
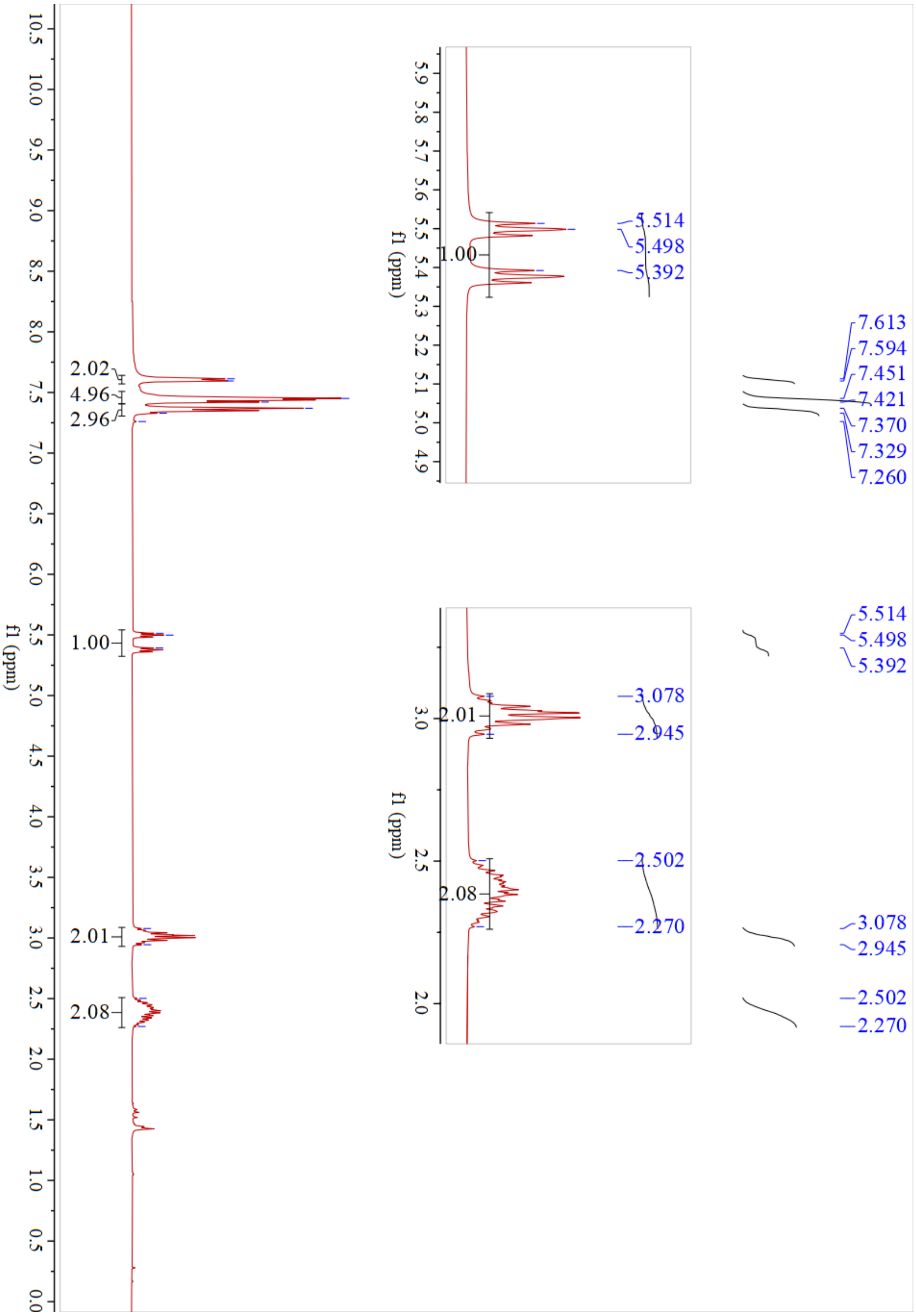
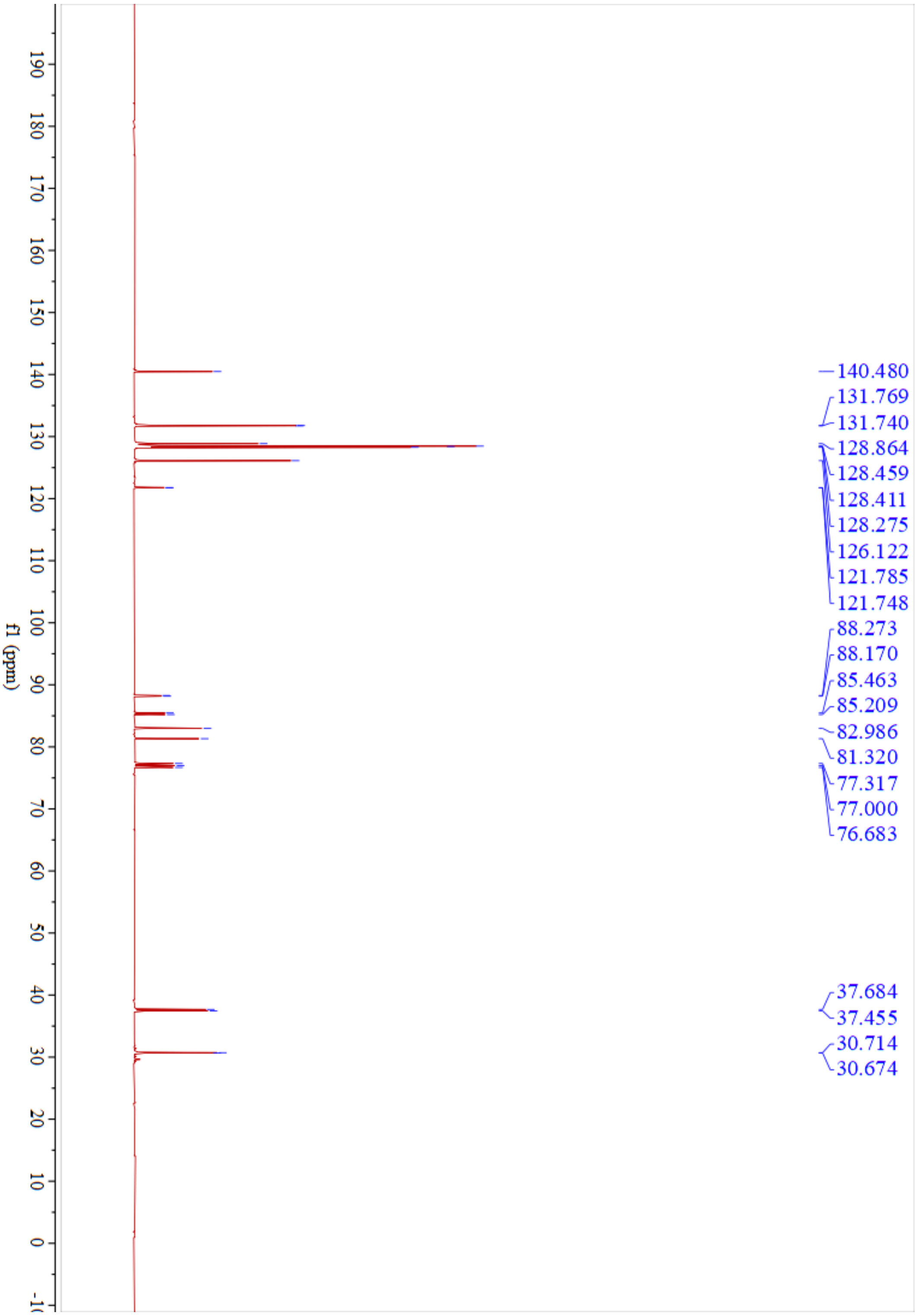


^{1}**H NMR** (400 MHz, CDCl$_3$) spectrum of **12**



^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **12**



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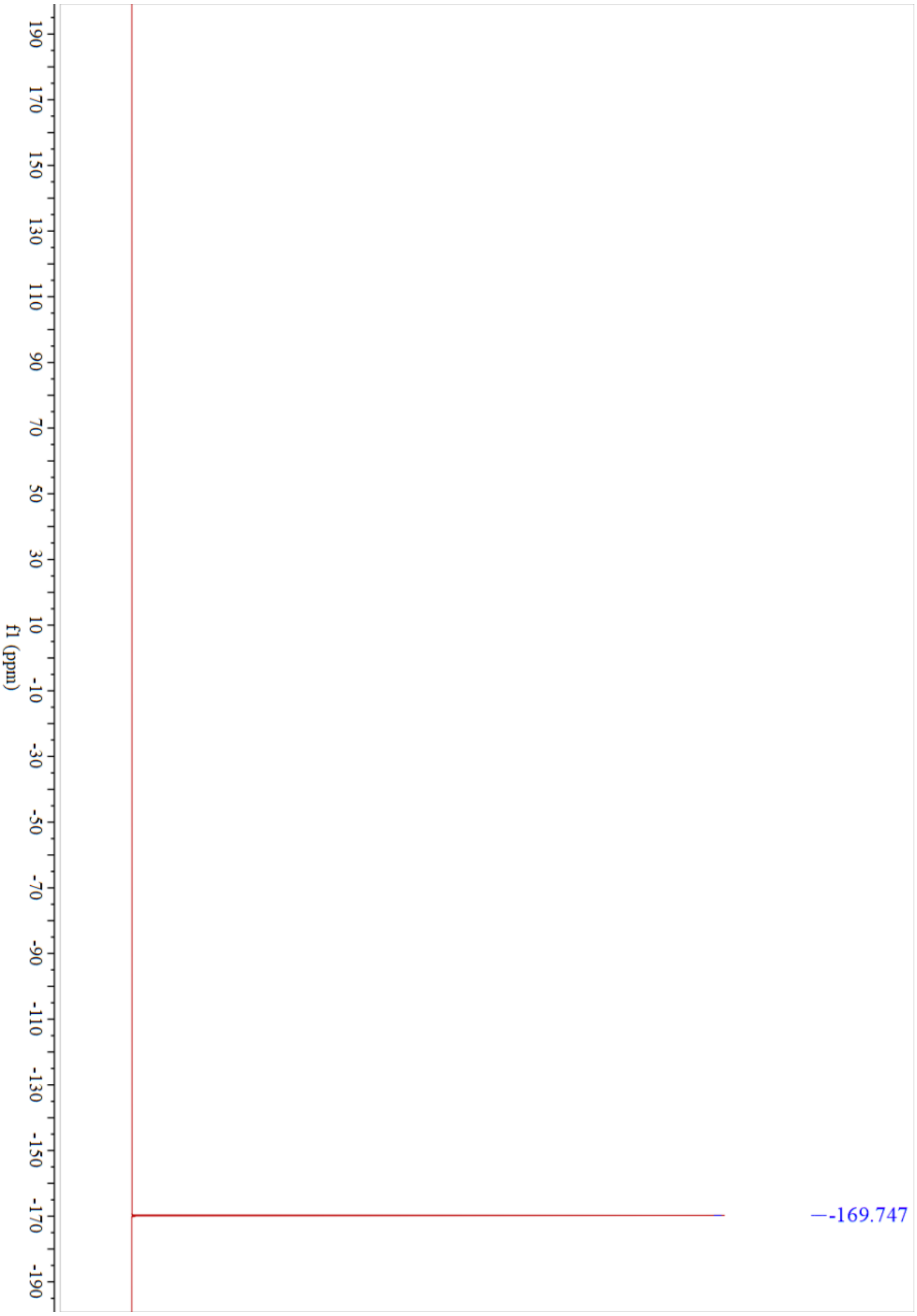

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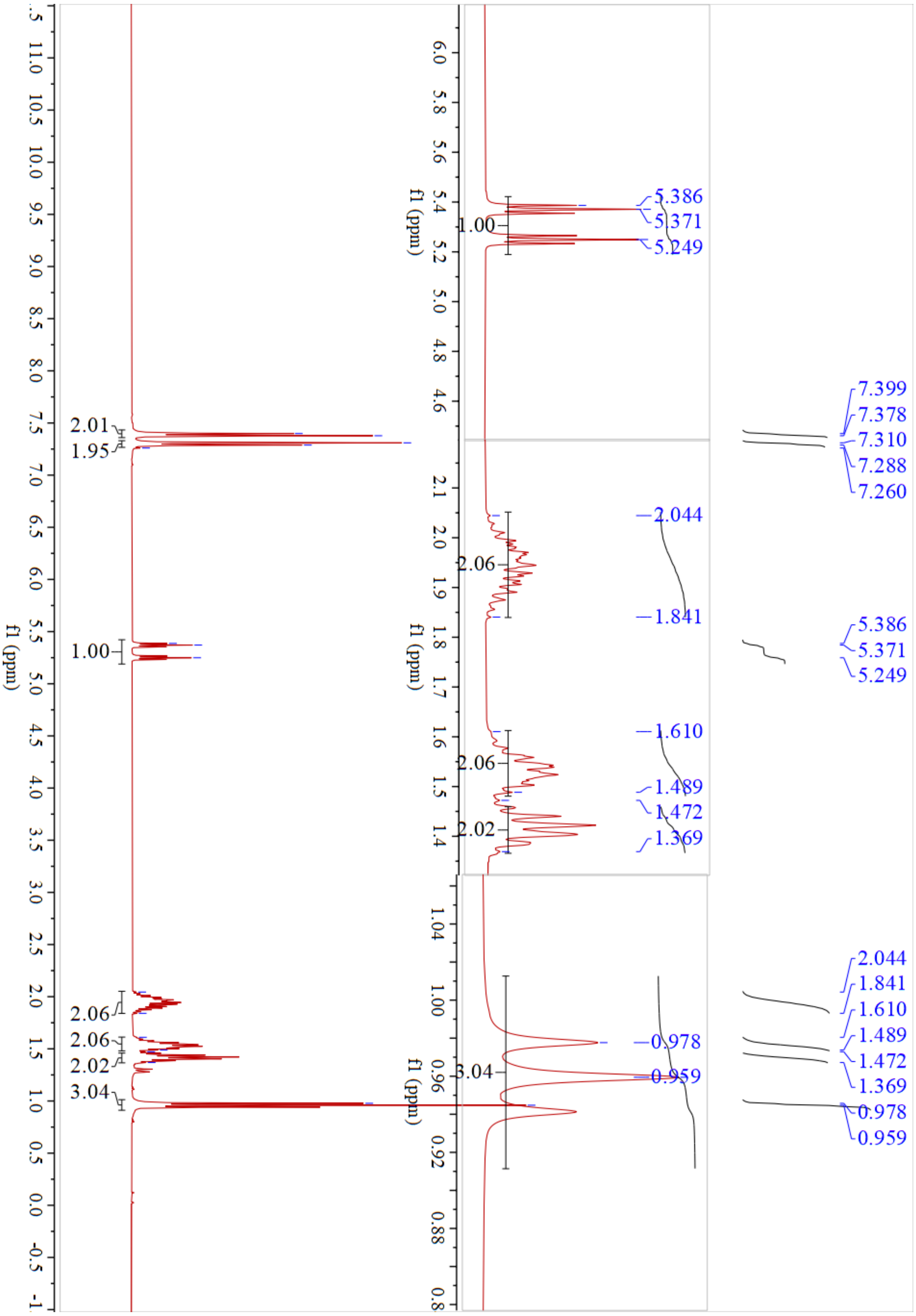

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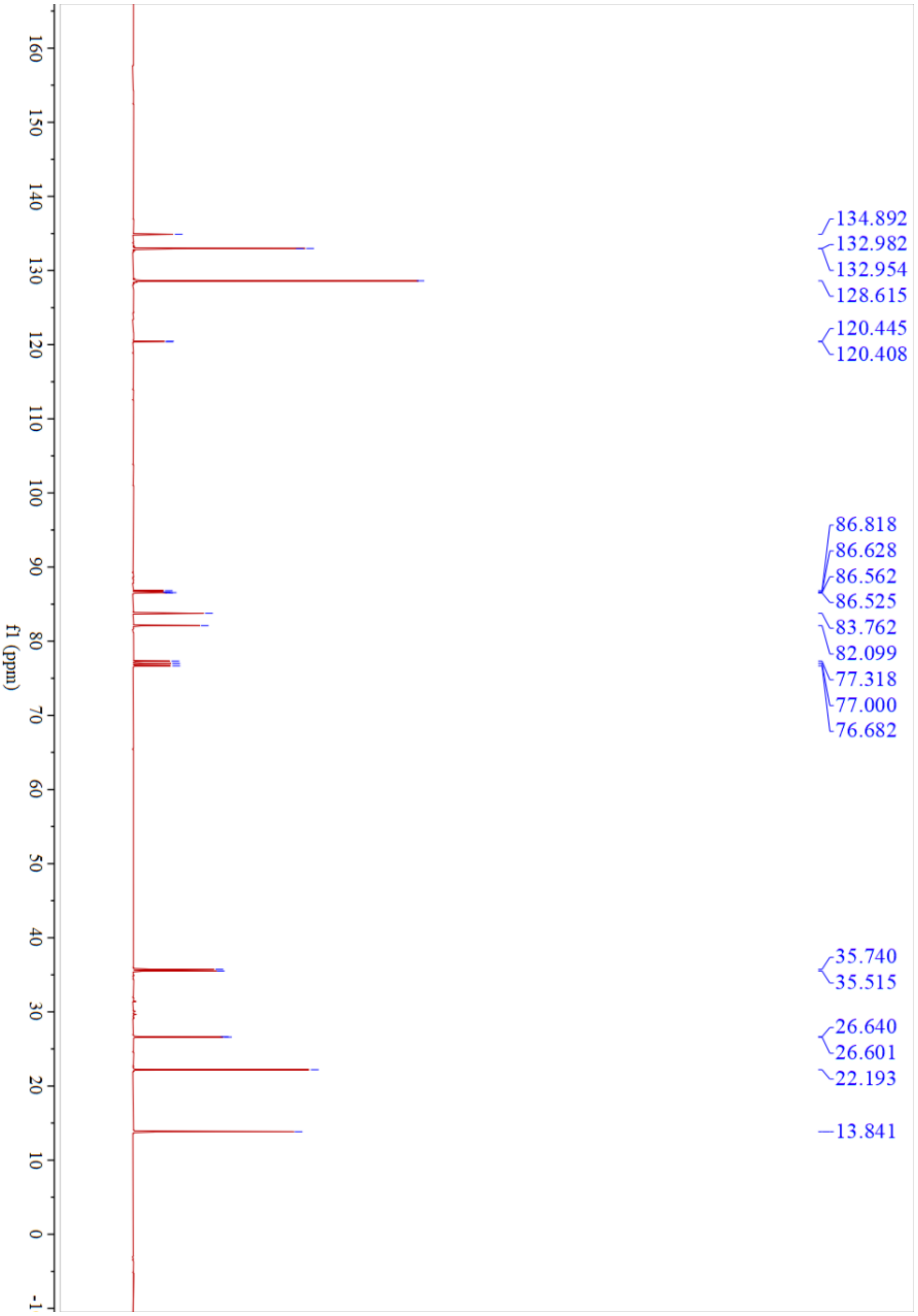

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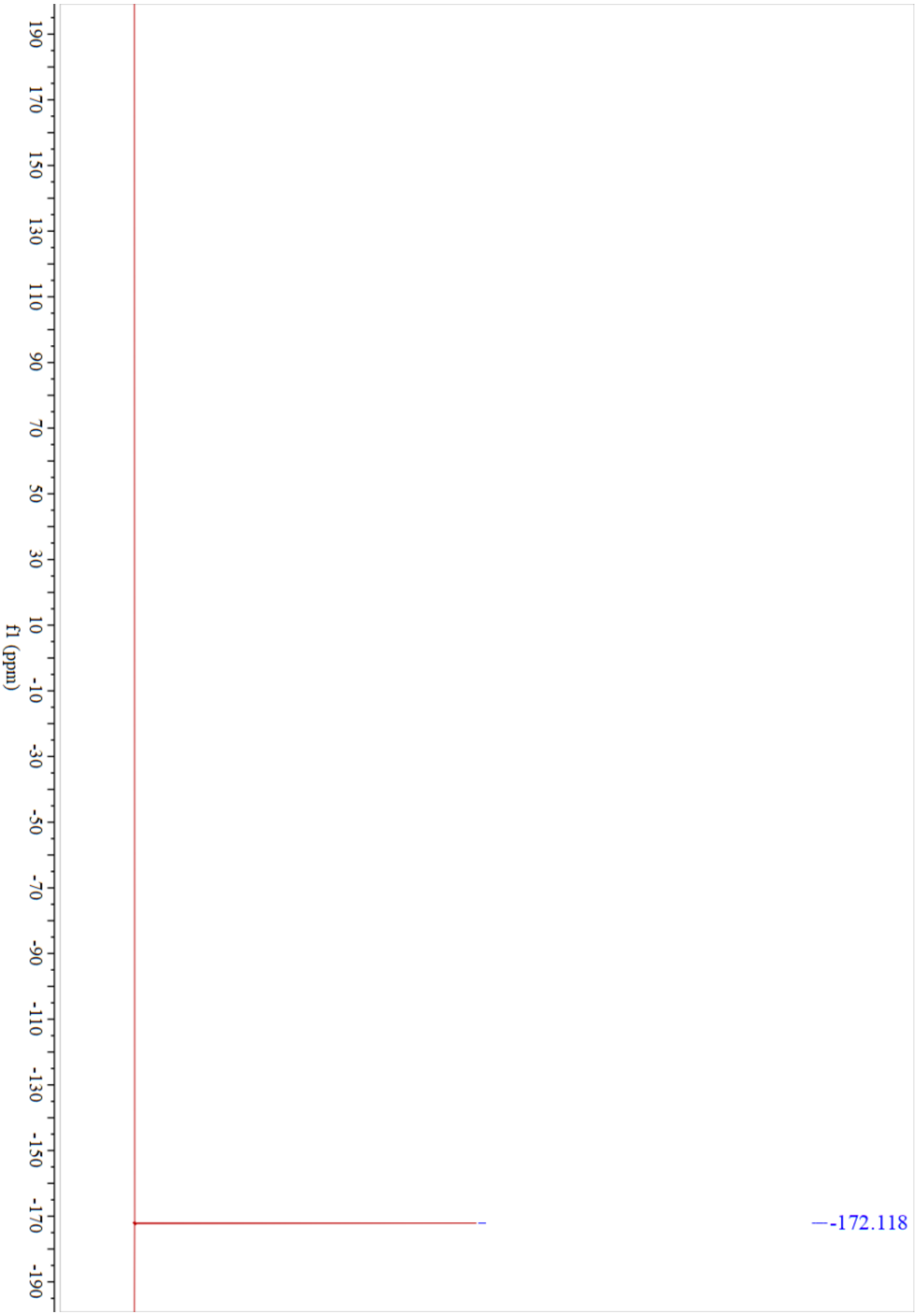

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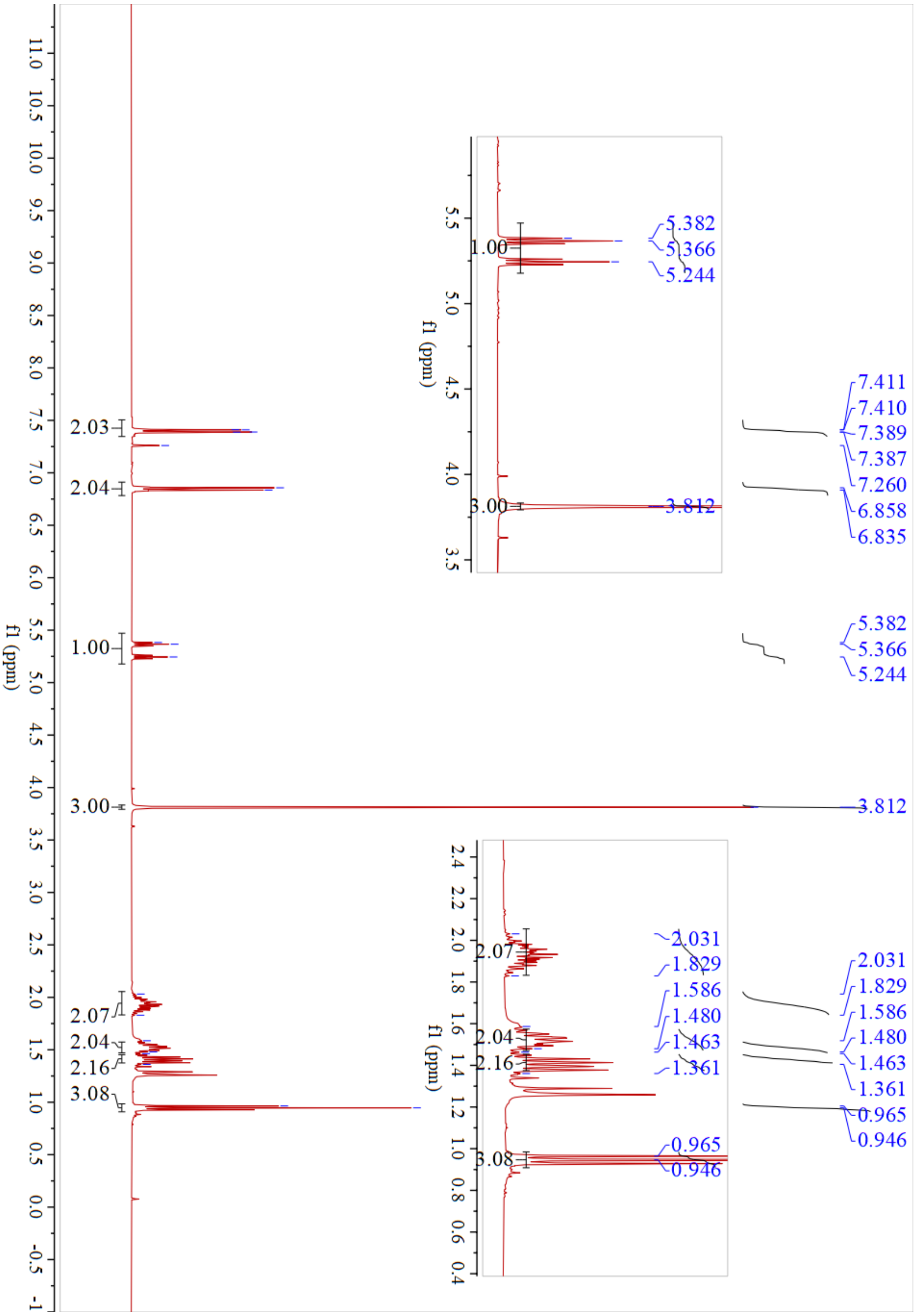

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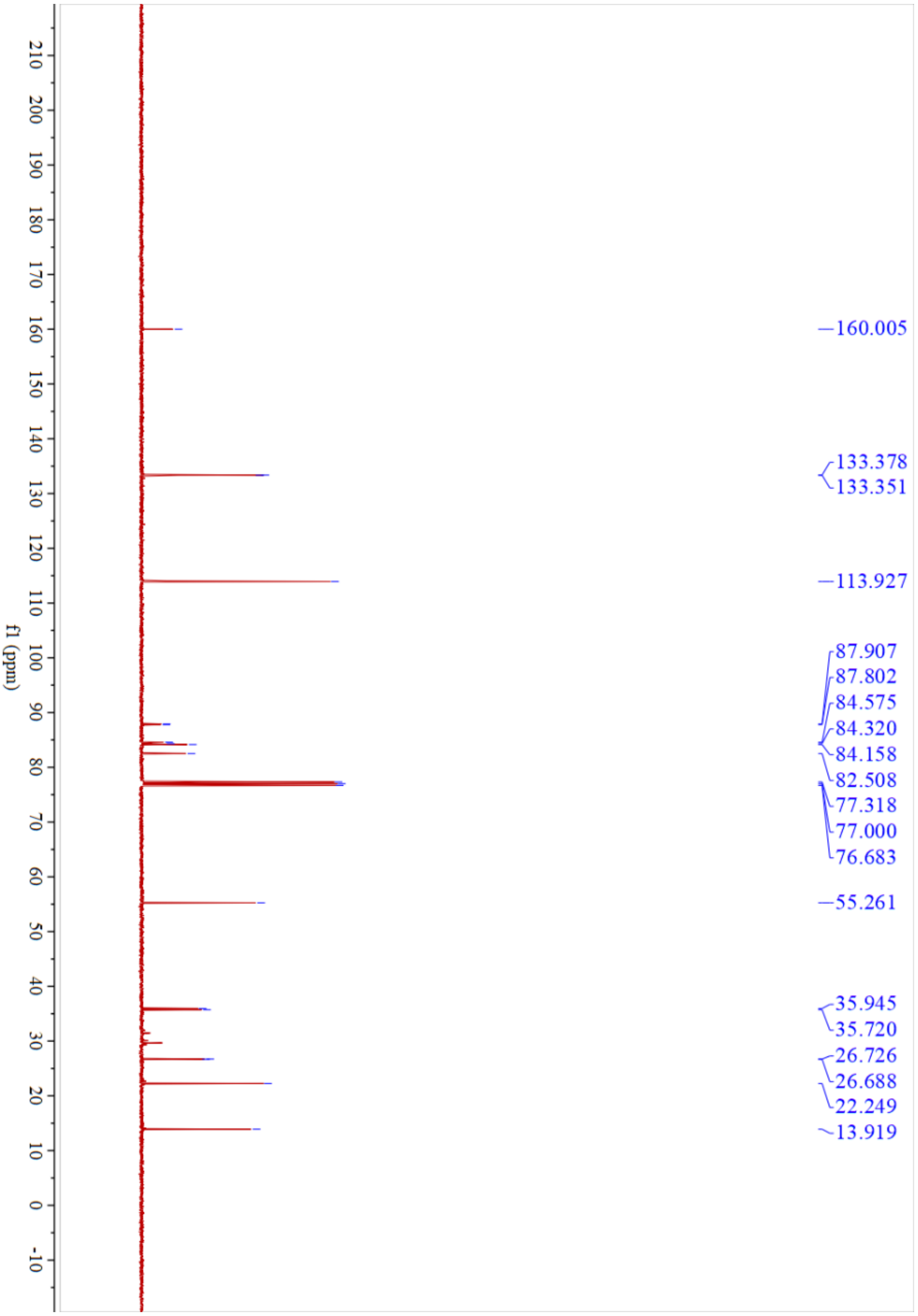

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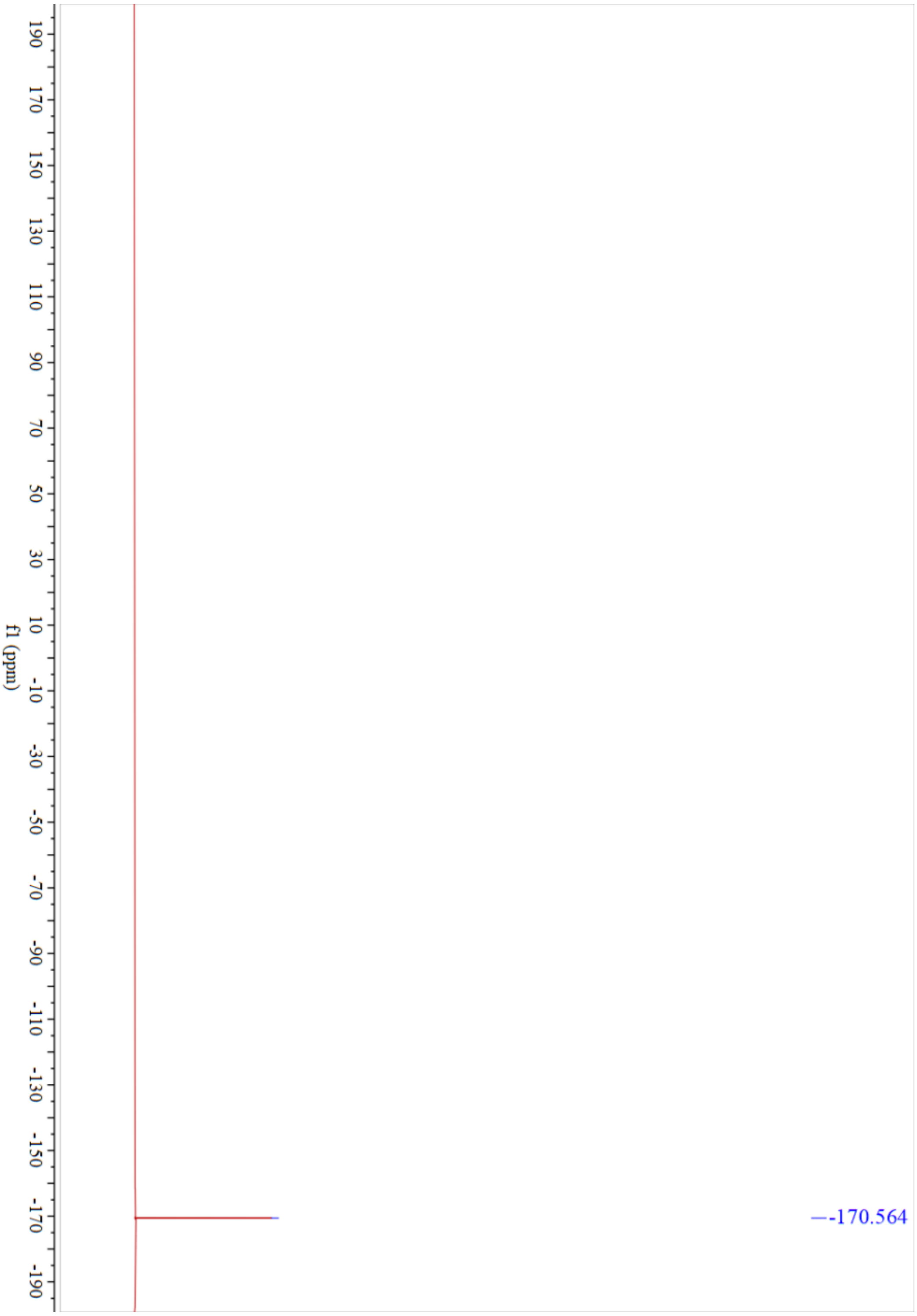

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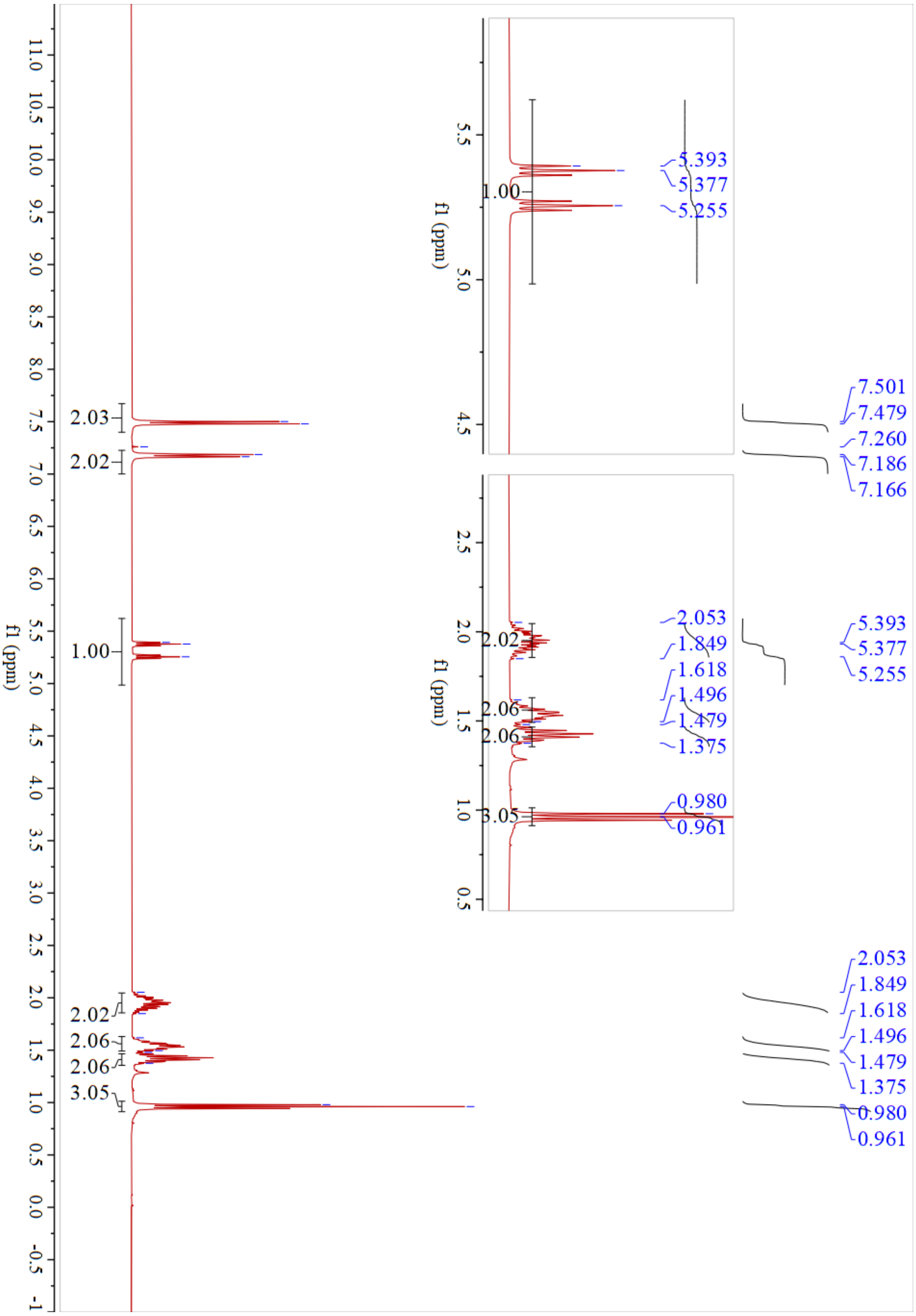

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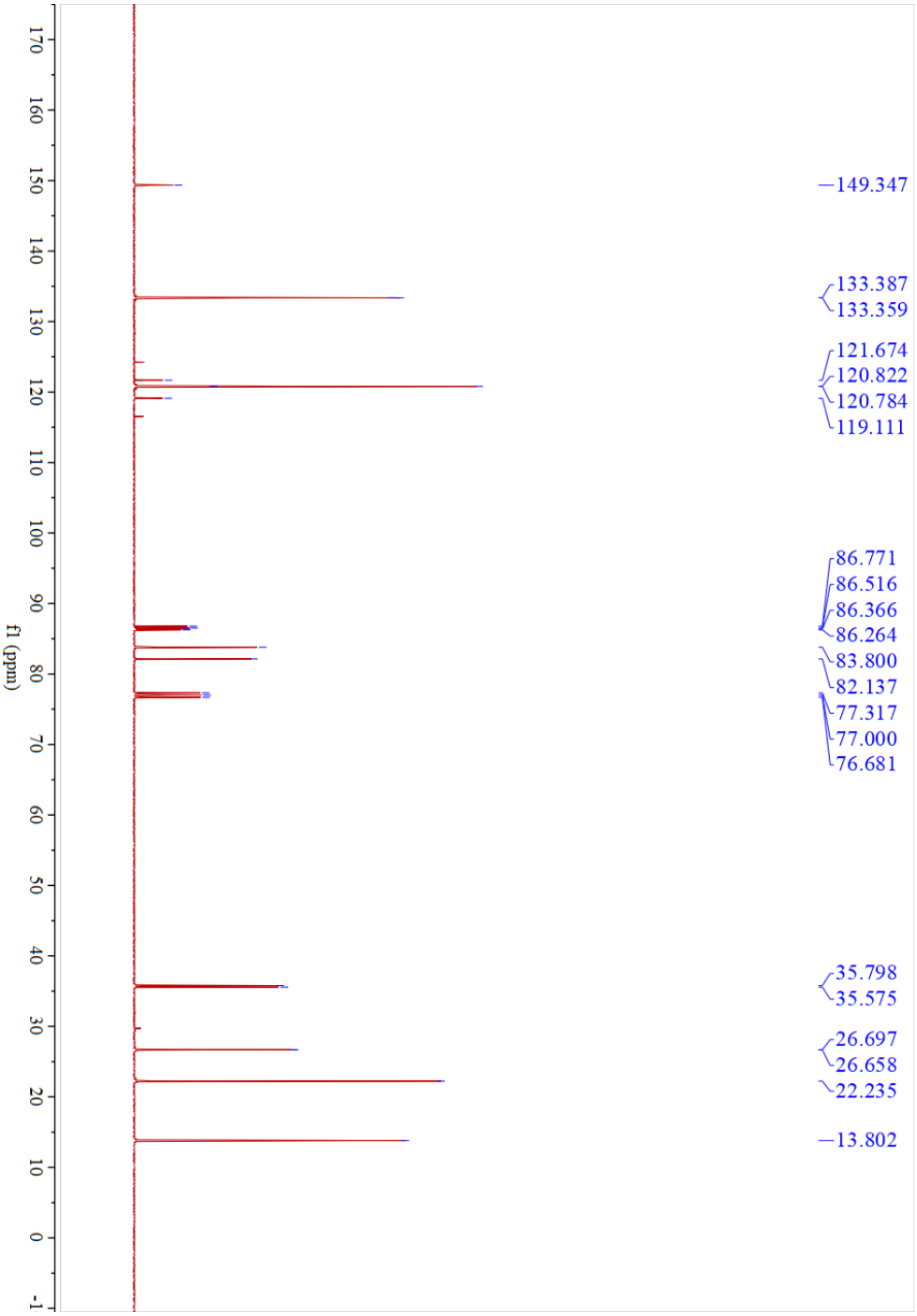

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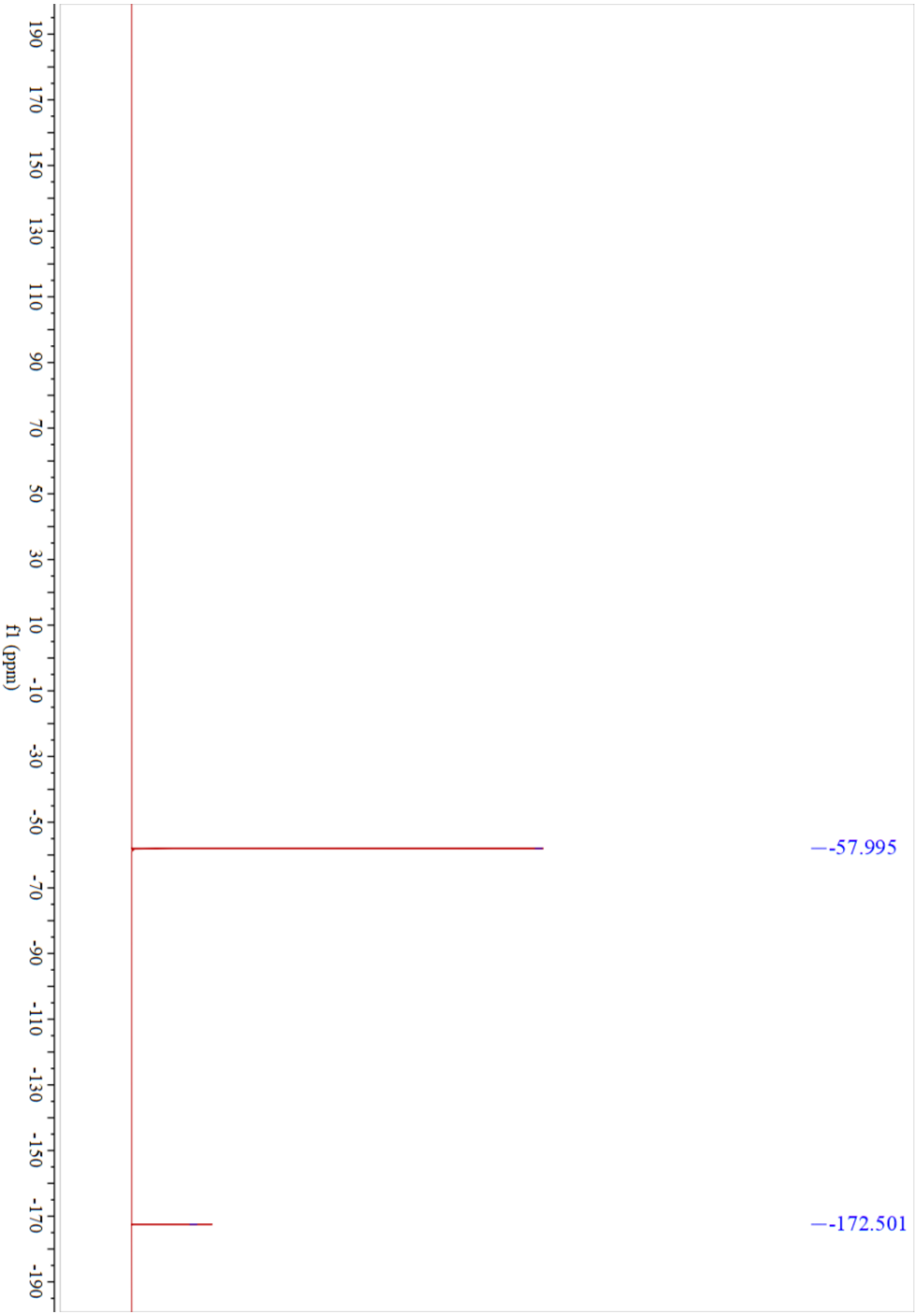
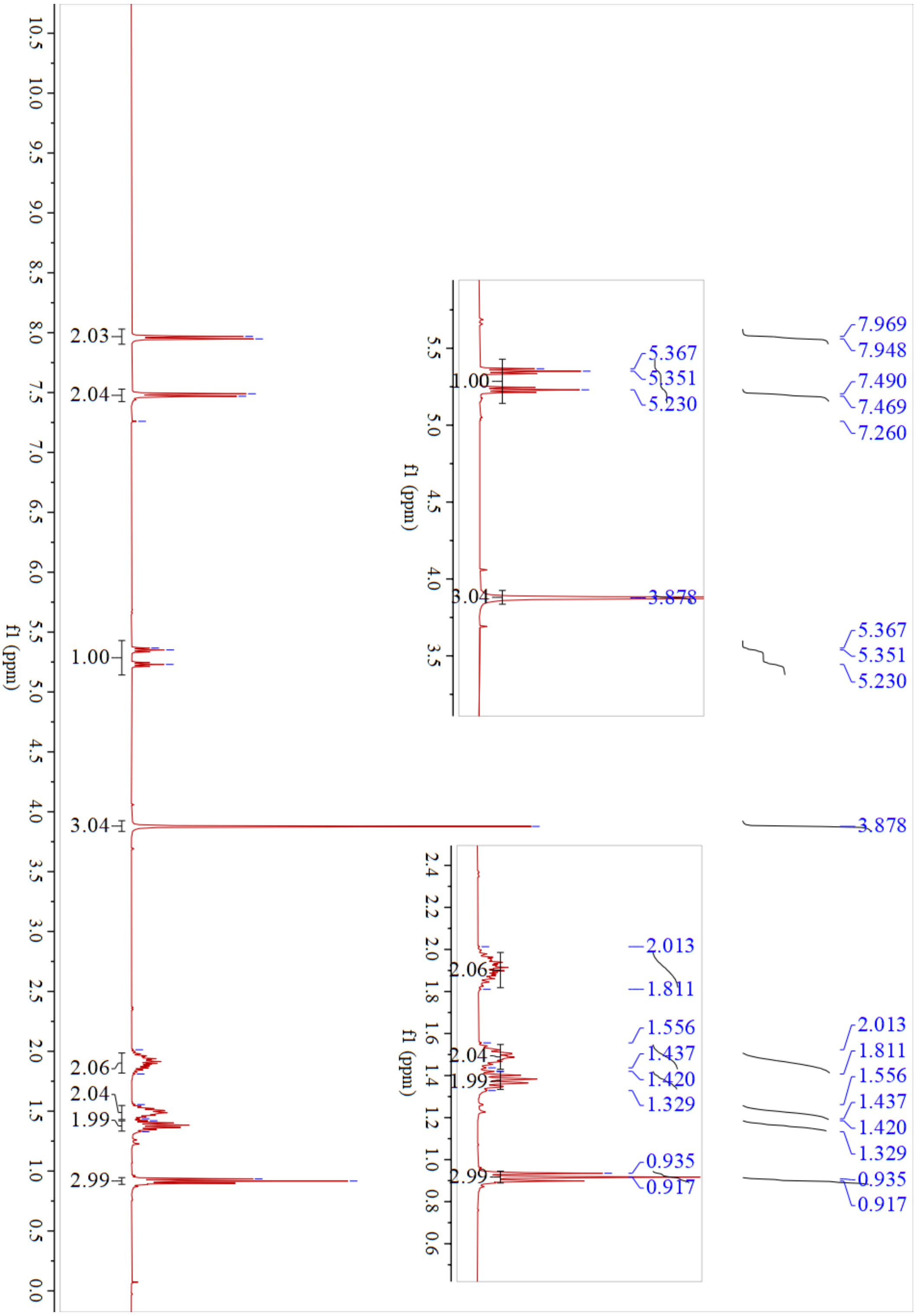
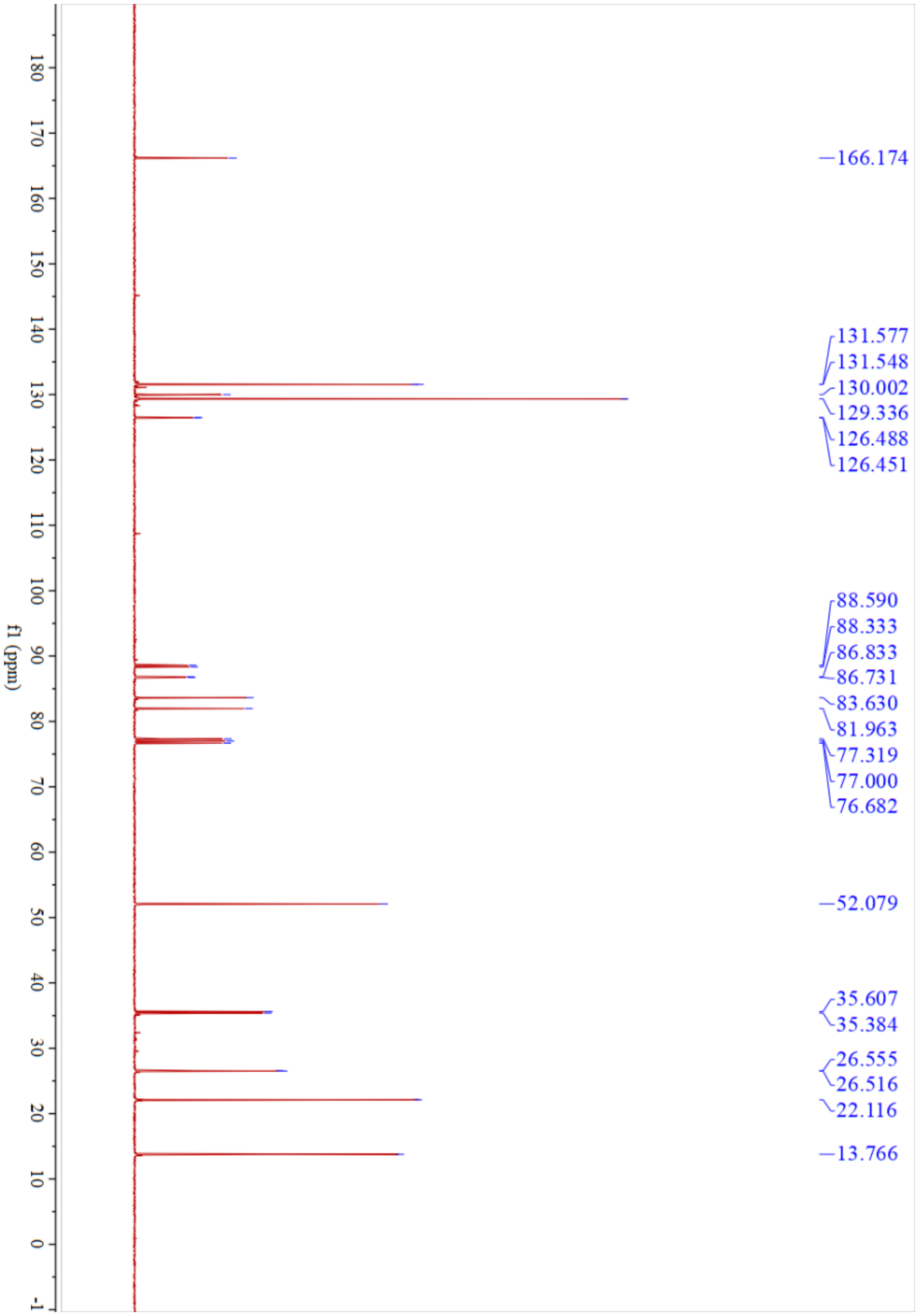


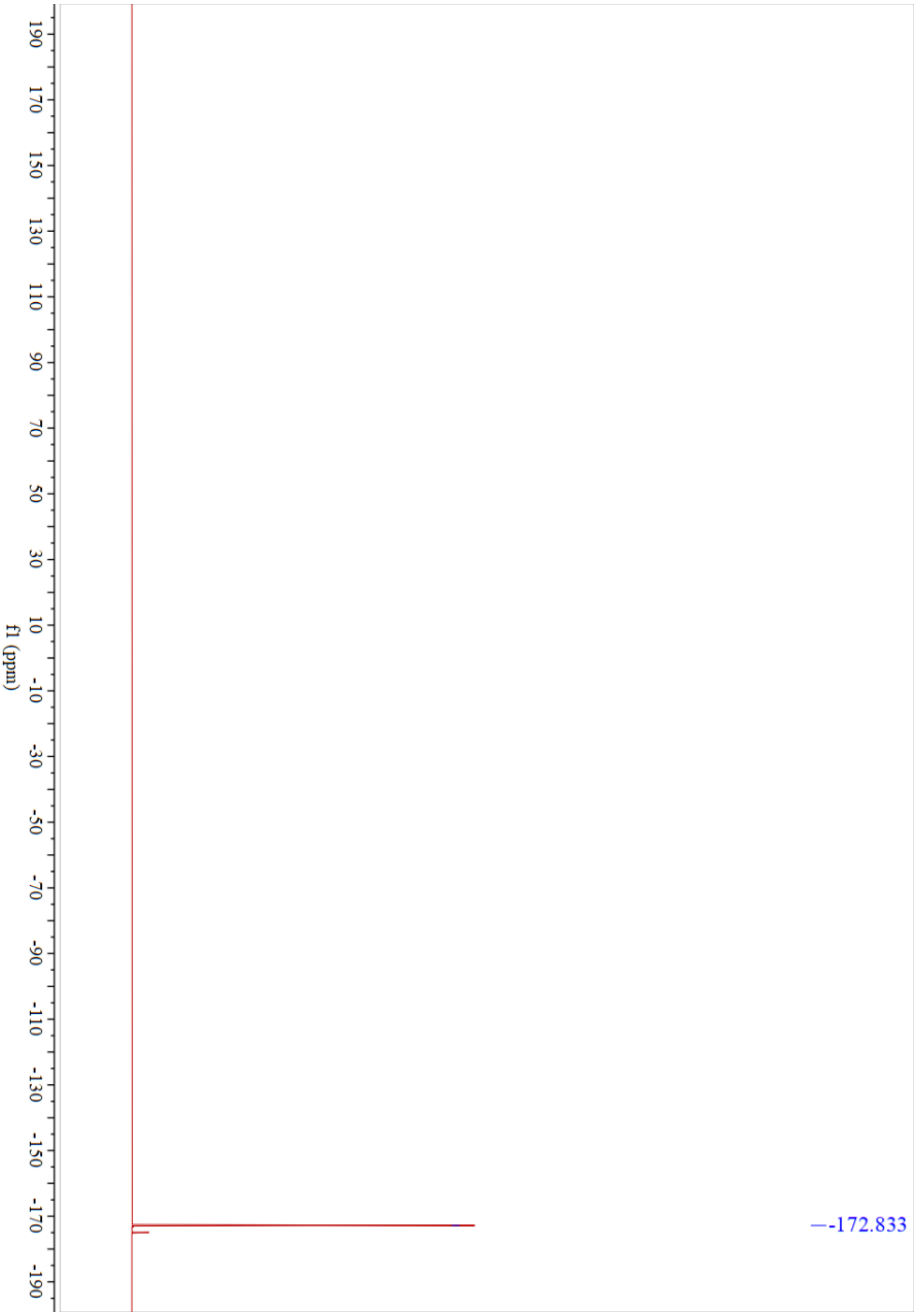
^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **16**



^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **16**



^{19}**F NMR** (376 MHz, $CDCl_3$) spectrum of **16**



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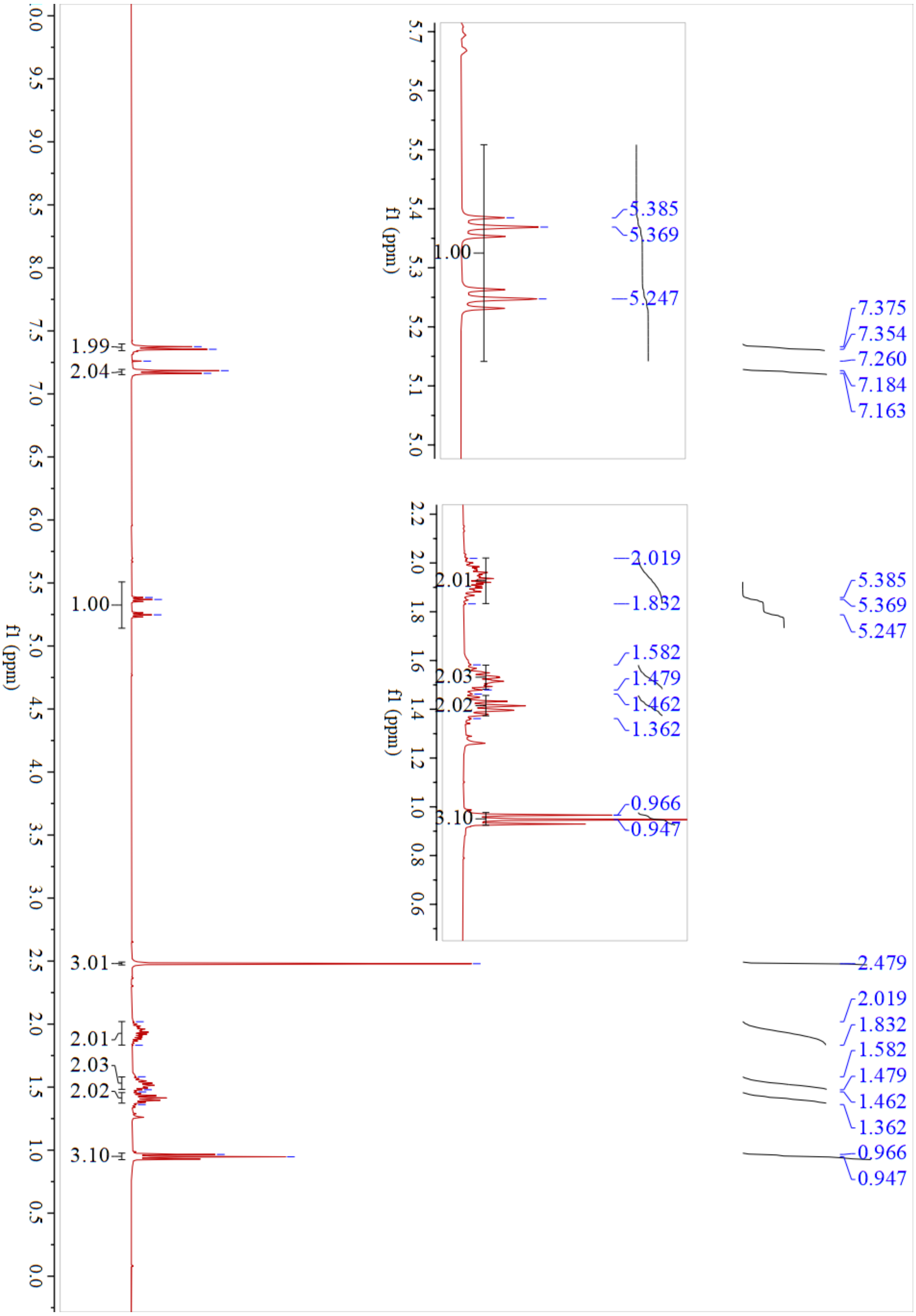
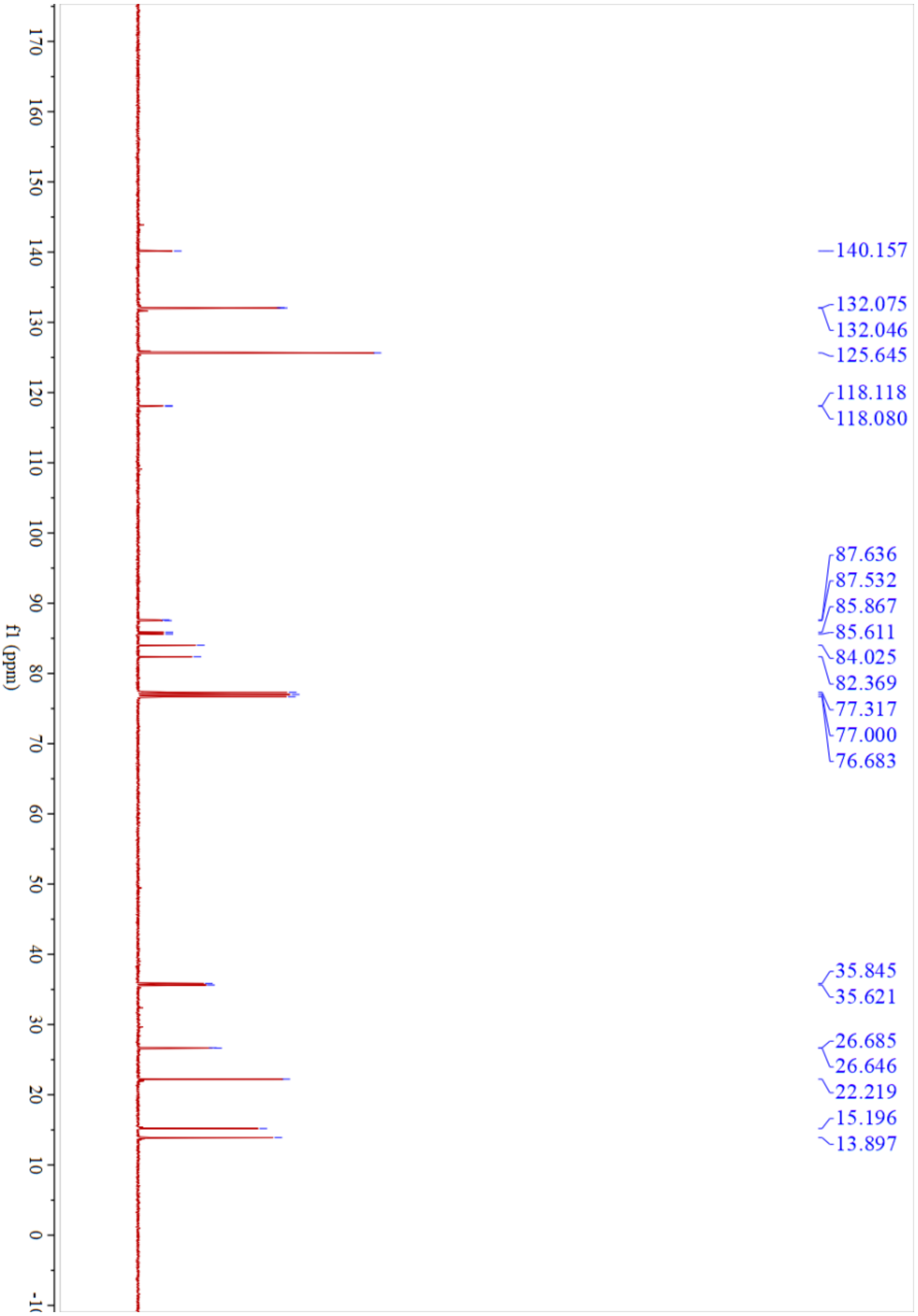
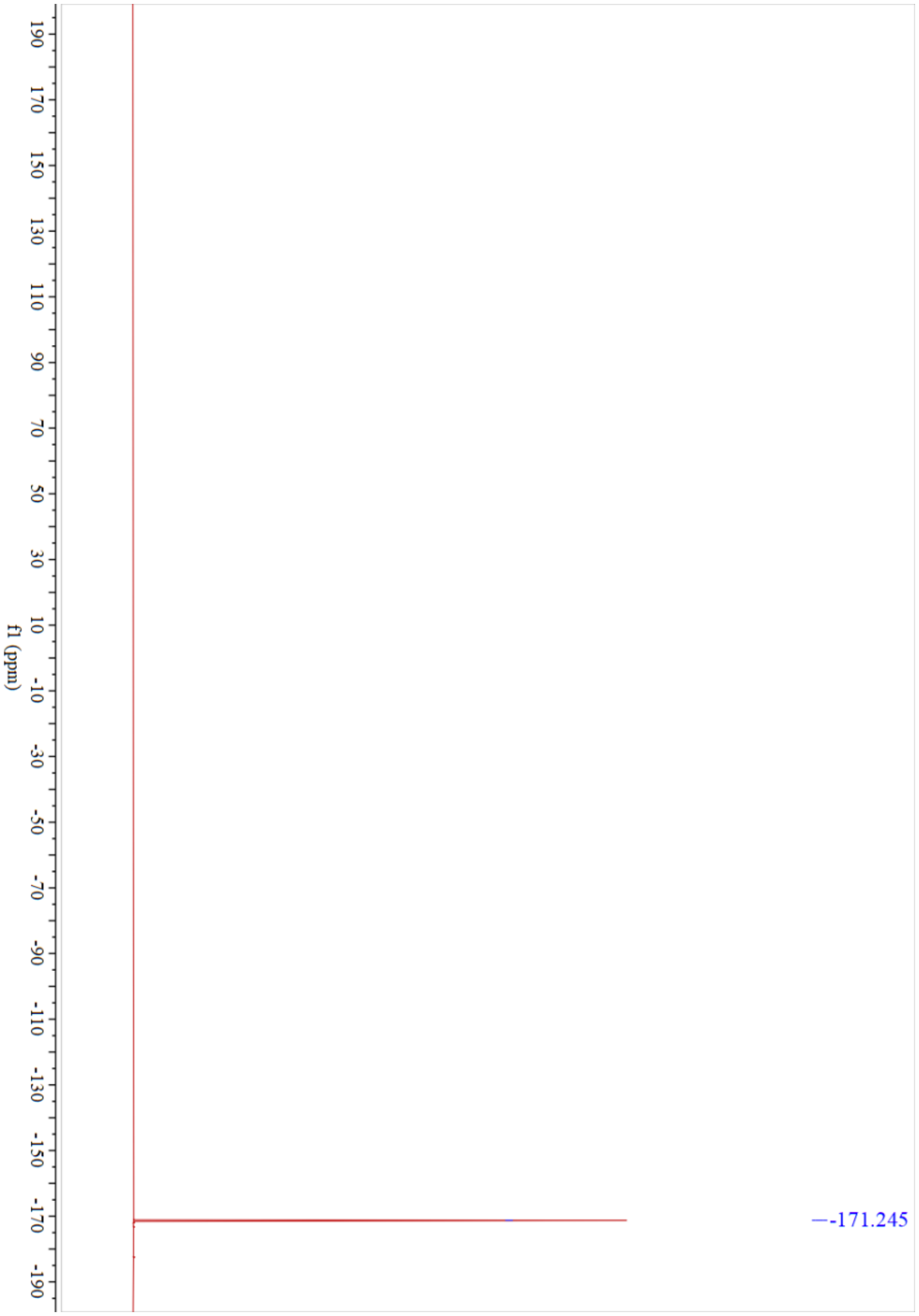


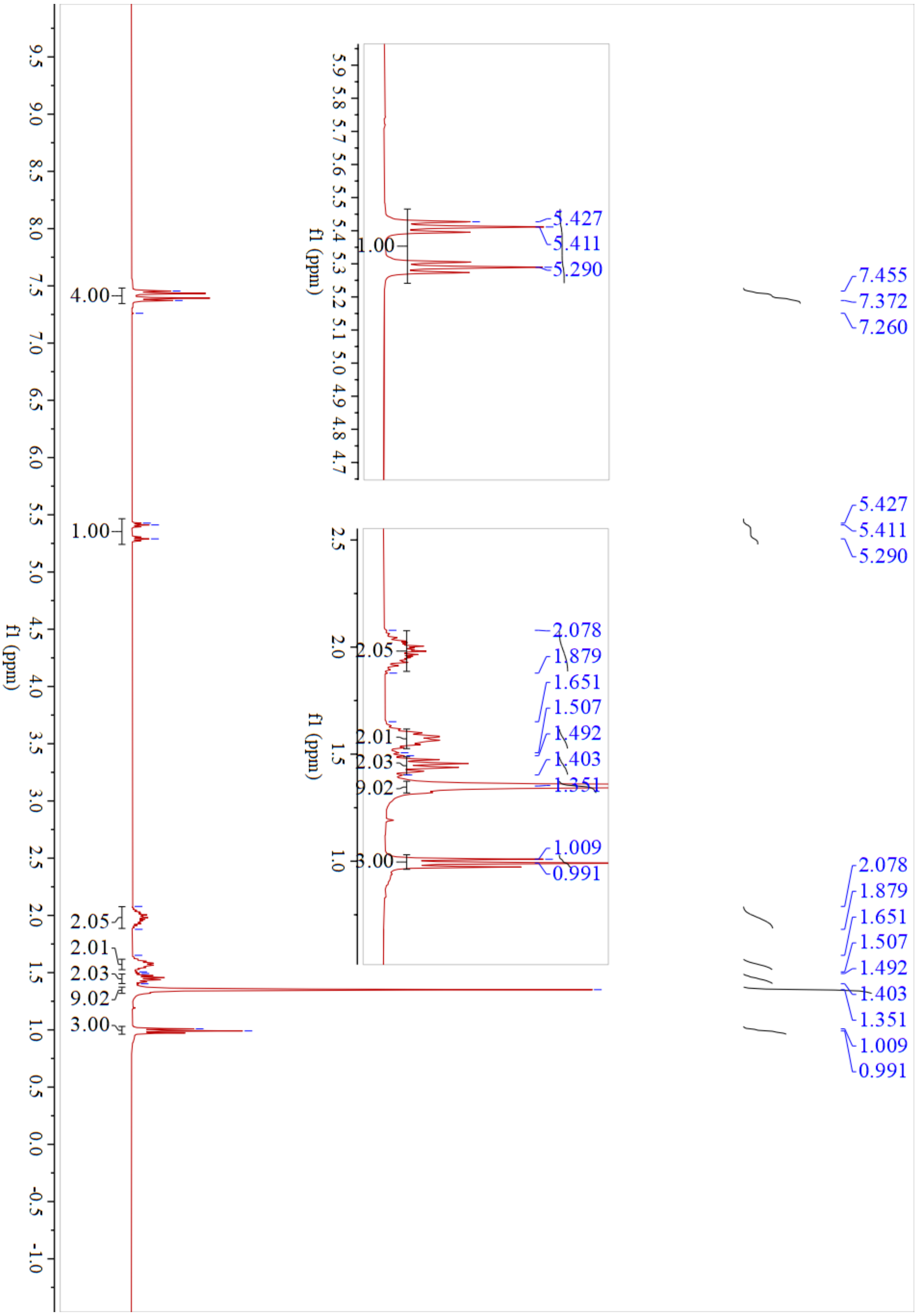
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **17**



^{19}**F NMR** (376 MHz, $CDCl_3$) spectrum of **17**



^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **18**



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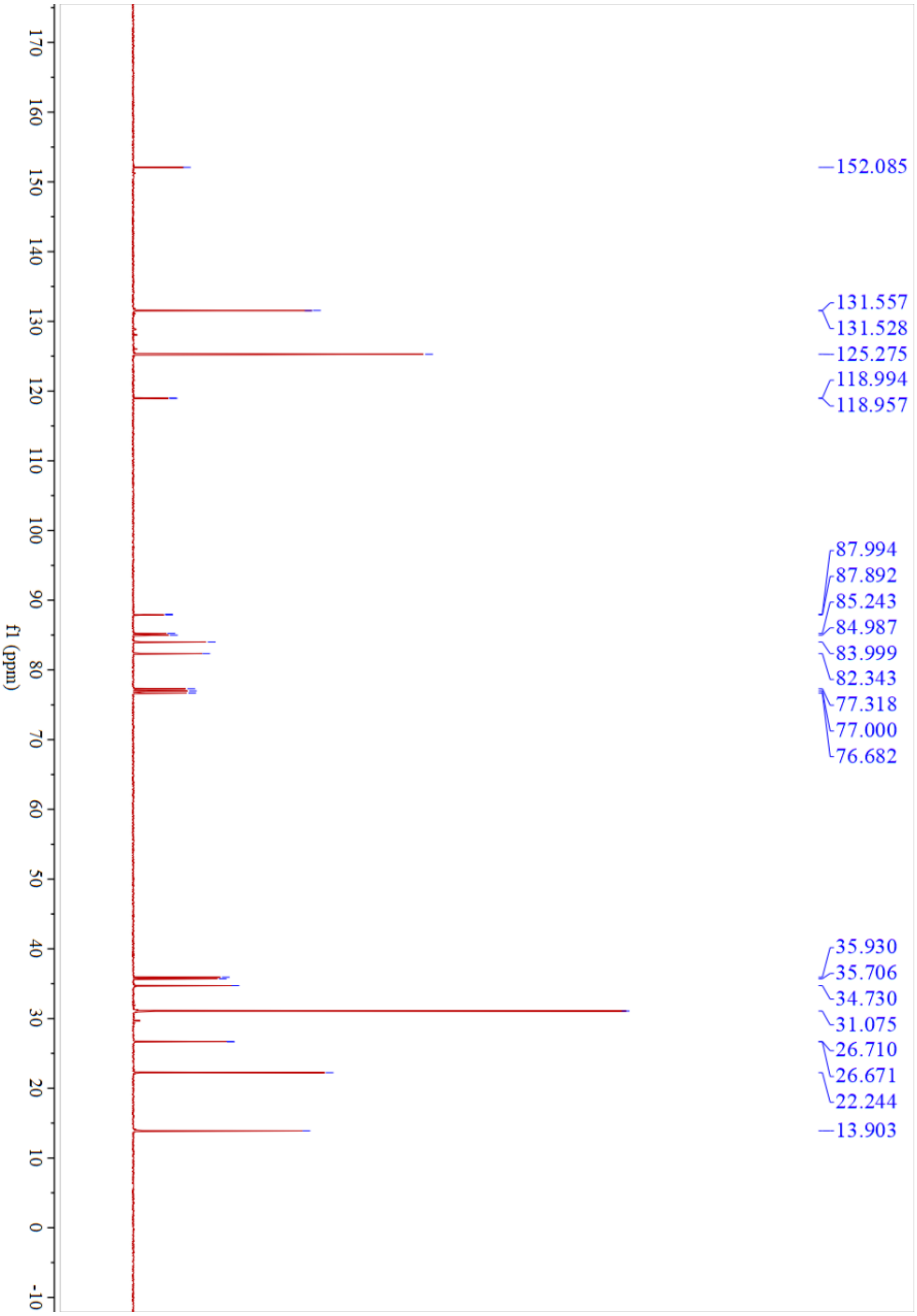

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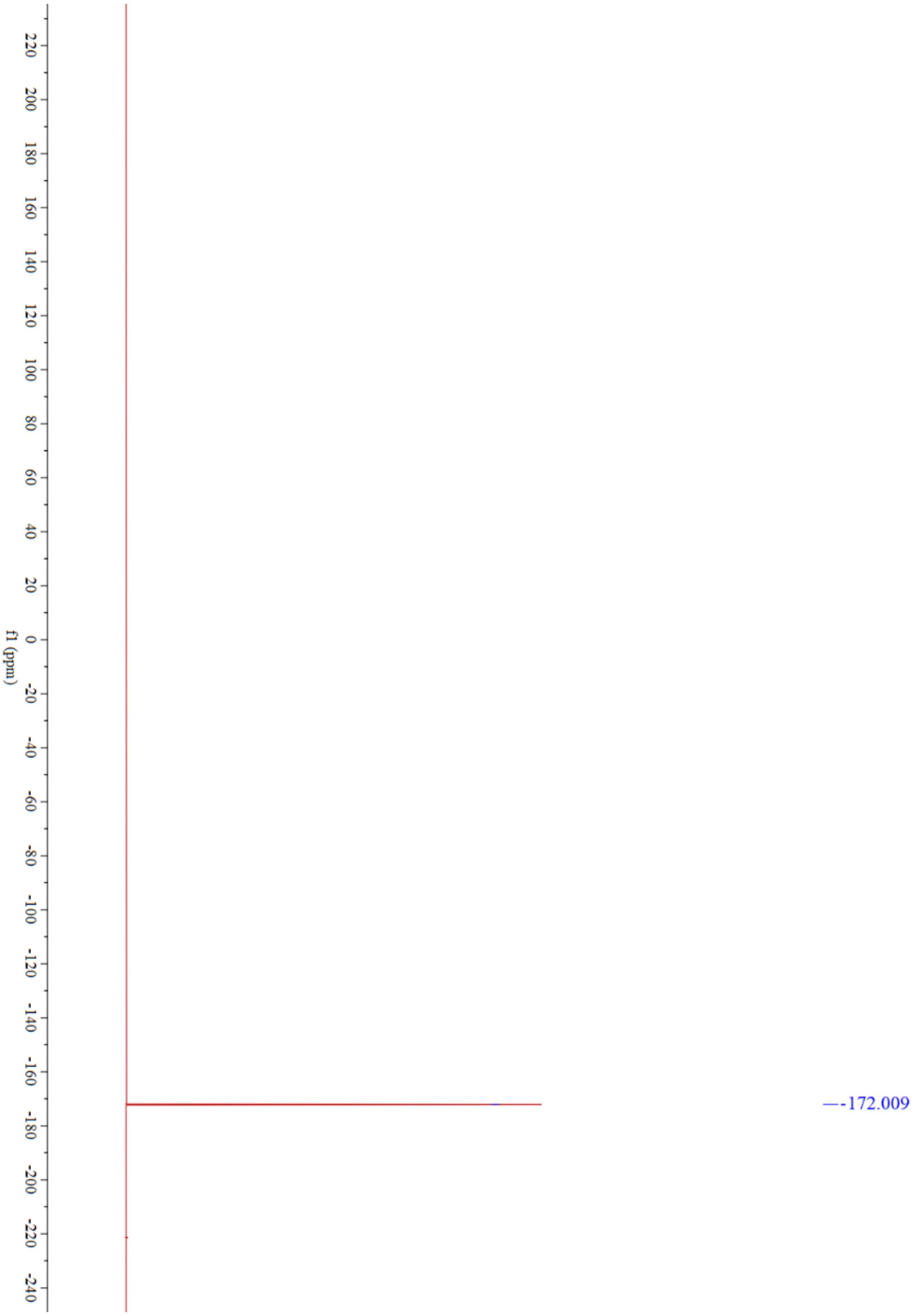
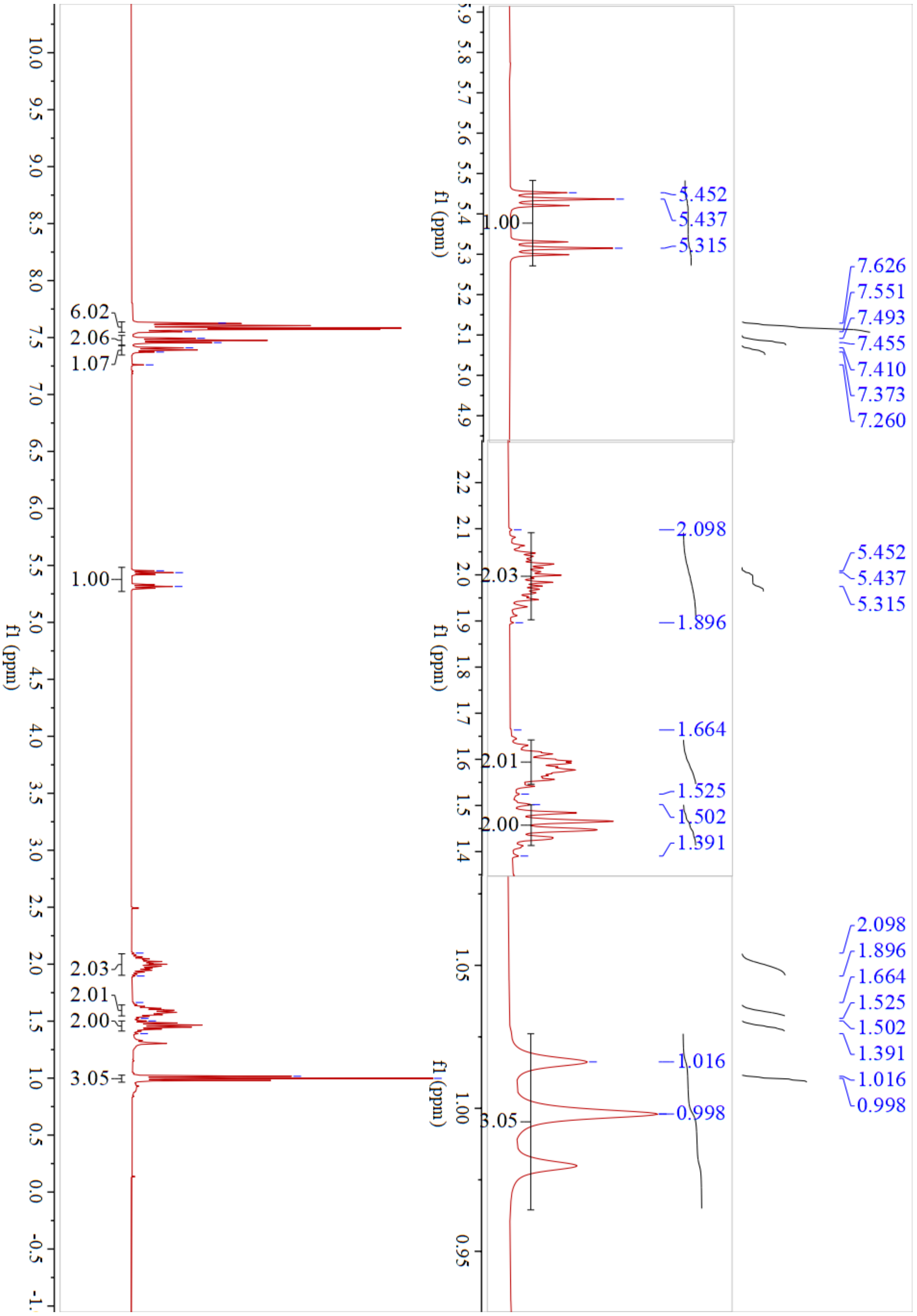


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **19**



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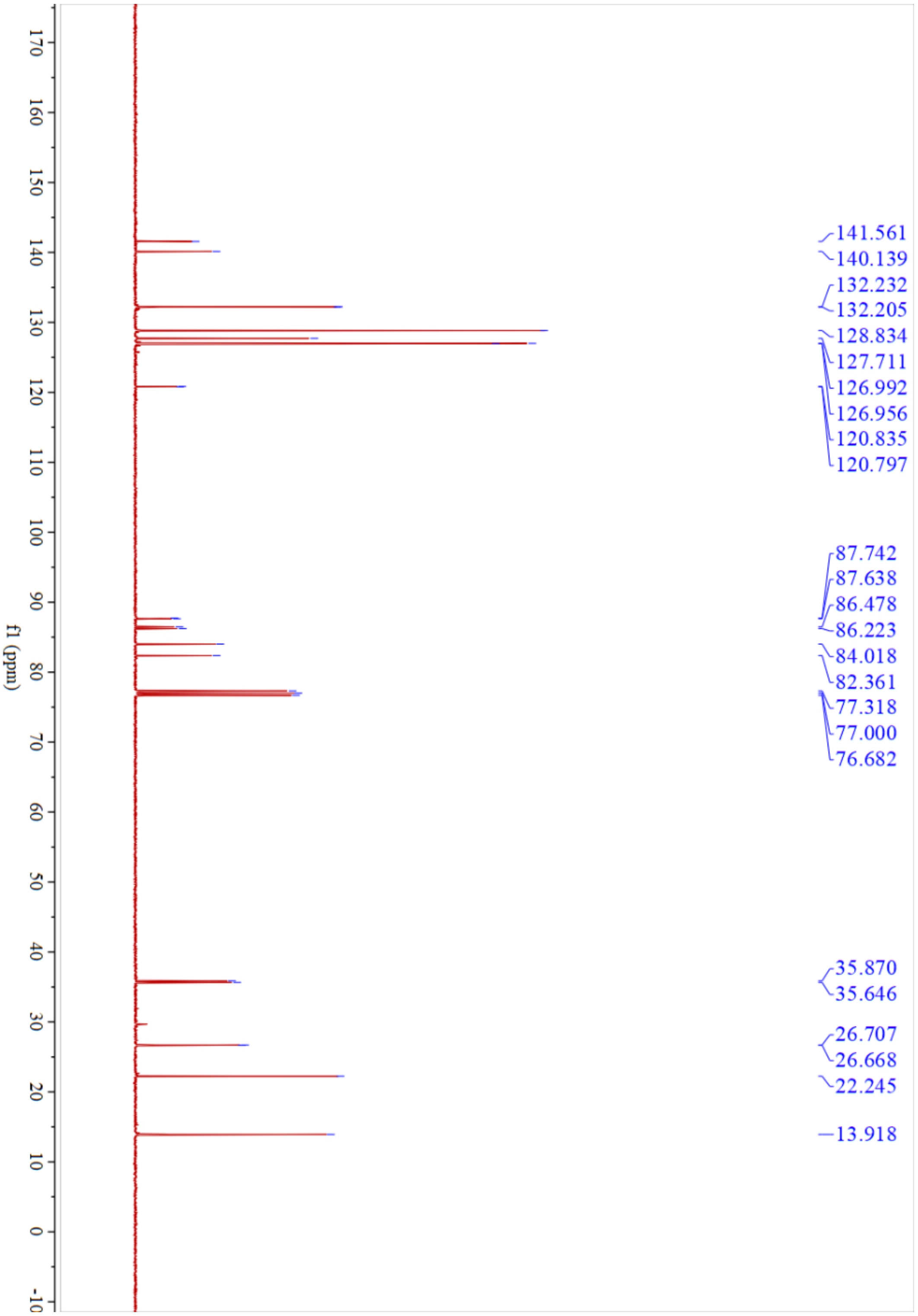

^{19}**F NMR** (376 MHz, $CDCl_3$) spectrum of **19**