Supporting Information

Visible Light Induced Hydroxyfluoroalkylation of Quinoxalin-2(1*H*)-ones with *N*-Trifluoroethoxyphthalimide under Catalyst-free Conditions

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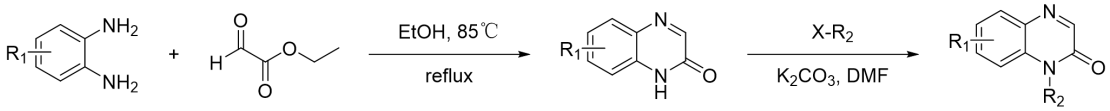
1. General information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon with magnetic stirring. The raw materials for preparation are selected from commercial suppliers and can be used without further purification. For chromatography, 200-300 mesh silica gel (Shanxi, China) was employed. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were acquired at 400, 100, and 376 MHz using an ARX 400 spectrometer. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. Chemical shifts are reported in ppm using tetramethylsilane (TMS) as internal standard. High resolution mass spectra were obtained on a Bruker SCION 436-GC SQ mass spectrometer or on a Bruker Apex IV FTMS spectrometer.The light-induced reactions were conducted utilizing a standard LED lamp equipped with Thirty-three light-emitting diodes (220 V, 1 × 21 W, 1 × 12 W 440-450 nm). The distance between the light source and the irradiation vessel was 2-3 cm.

2. Experimental procedures

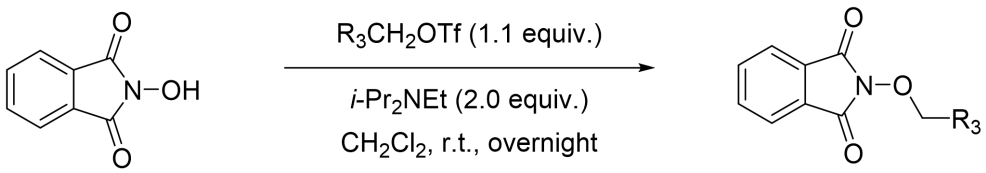
2.1. General procedure for the synthesis of substrates 1a-1w[1]



Ethyl 2-oxoacetate (50% in toluene, 4.5 g, 22.0 mmol, 1.1 equiv.) was added to a suspension of o-arylenediamine (20.0 mmol, 1.0 equiv.) in ethanol (40 mL, 0.5 M). The reaction mixture was stirred and refluxed in an oil bath for 1 h, then stirred at room temperature for 16 h. Upon completion (as monitored by TLC), the precipitate was filtered and washed with ethanol, then dried to give quinoxalinone. For alkylation, the corresponding halogenoalkane (16 mmol, 1.6 equiv.) was added to a suspension of quinoxalinone (10 mmol, 1.0 equiv.) and potassium carbonate (12 mmol, 1.2 equiv.) in DMF (20.0 mL, 0.5 M). The mixture was stirred at room temperature for 16 h. Upon completion (as monitored by TLC), the reaction mixture was washed with saturated solution of ammonium chloride (5.0 mL), ethyl acetate (10.0 mL) and water (10.0 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 × 10.0 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and

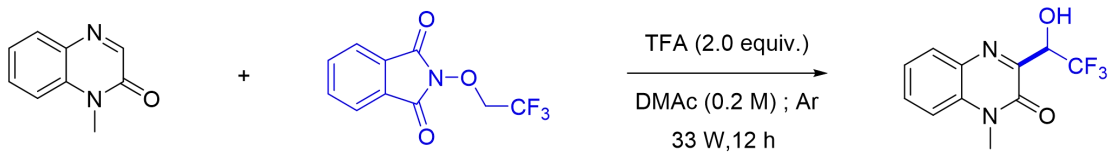
concentrated under reduced pressure. The resulting organic residue was purified by flash chromatography column over silica gel (SiO_2) to afford the alkylated quinoxalinone.The synthesis steps of **1a-1b** follow the above steps.

2.2. General procedure for the synthesis of substrates 2a,2b[2]



Under a argon atmosphere, to a solution of *N*-hydroxyphthalimide (3.2 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) at room temperature was added *i*-Pr_2NEt (6.4 mmol, 2.0 equiv.) followed by Trifluoromethanesulfonate (3.5 mmol, 1.1 equiv.) and the solution stirred overnight. The reaction was quenched with water (30 mL) and extracted into CH_2Cl_2 (3 × 40 mL). The organic extracts were combined and washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (20% EtOAc/PE) to afford the alkoxylated phthalimide.

2.3. General procedure for the synthesis of substrates 3a-3w

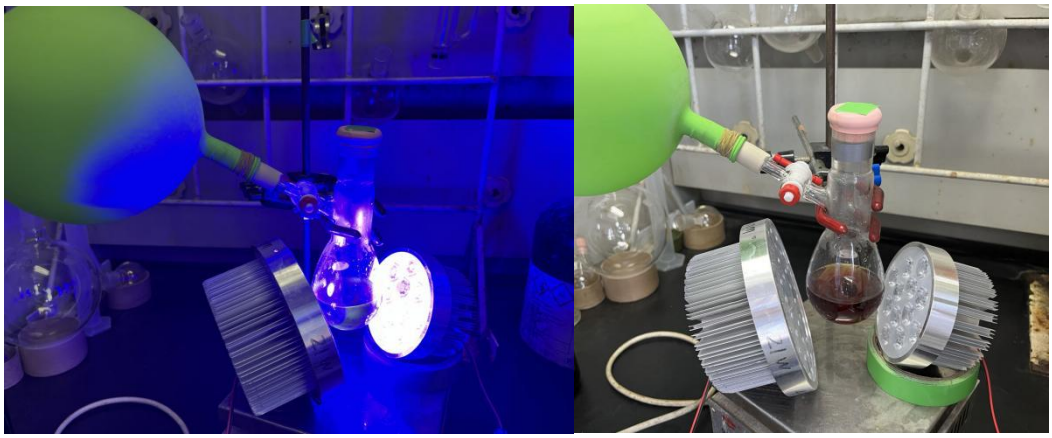


1a **2a** **3a**

Taking the synthesis of **3a** as an example: *N*-methylquinoxalin-2(1*H*)-one **1a** (48.1 mg, 0.3 mmol) and *N*-trifluoroethoxyphthalimide **2a** (147.1 mg, 2.0 equiv.) were added to a 10 mL dry Schlenk tube with a magnetic stirrer, and then the air in the bottle was pumped out and refilled with argon three times. After sealing, TFA (45.94 μL, 2.0 equiv.) and dry dimethylacetamide solvent (0.2 M) were added to the syringe. The reaction mixture was stirred at 33 W blue LED (440 nm) for 12 hours. After completion, the reaction mixture was neutralized with saturated $NaHCO_3$ solution and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4.The solvent was evaporated under reduced pressure, and the crude mixture was purified by column chromatography using silica gel (230−400 mesh size) and petroleum ether/EtOAc as the eluent. The synthesis steps of **3b-3w** follow the above steps.

3. Large-Scale Reaction

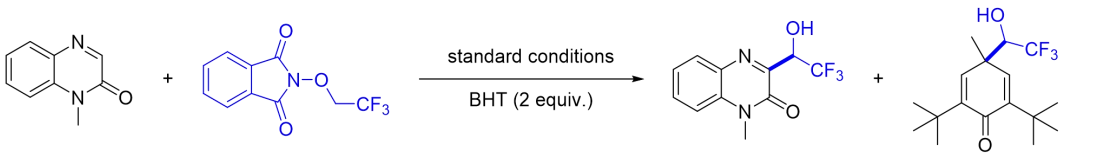
N-methylquinoxalin-2(1*H*)-one **1a** (1.28 g, 8.0 mmol) and *N*-trifluoroethoxyphthalimide **2a** (3.92 g, 2.0 equiv.) were added to a 50 mL dry Schlenk tube with a magnetic stirrer. Then the air in the bottle was pumped out and filled with argon three times. After sealing, TFA (1.18 mL, 2.0 equiv.) and dry dimethylacetamide solvent (40 mL) were added to the syringe. The reaction mixture was stirred at 33 W blue LED (440 nm) for 36 hours.After completion, the reaction mixture was neutralized with saturated $NaHCO_3$ solution and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure, and then purified by silica gel (PE : EA = 4 : 1) column. The corresponding product **3a** was white solid (1.7g, 82%).



Supplementary figure 1. The setup for the blue LEDs-driven large-scale reaction

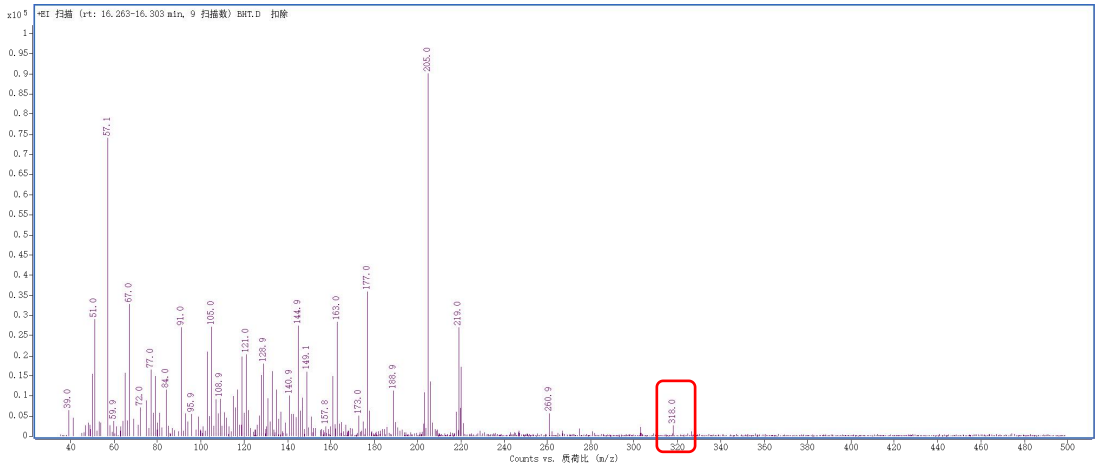
4. Mechanistic studies

4.1. Radical-Quenching Experiments



N-methylquinoxaline-2 (1*H*) -one **1a** (32.03 mg, 0.2 mmol), *N*-trifluoroethoxyphthalimide **2a** (98.06 mg, 2.0 equiv.), BHT (88.14 mg, 2.0 equiv.) were added to a dry Schrenk tube with a magnetic stirrer, and then the air in the bottle was pumped out and refilled three times with argon.

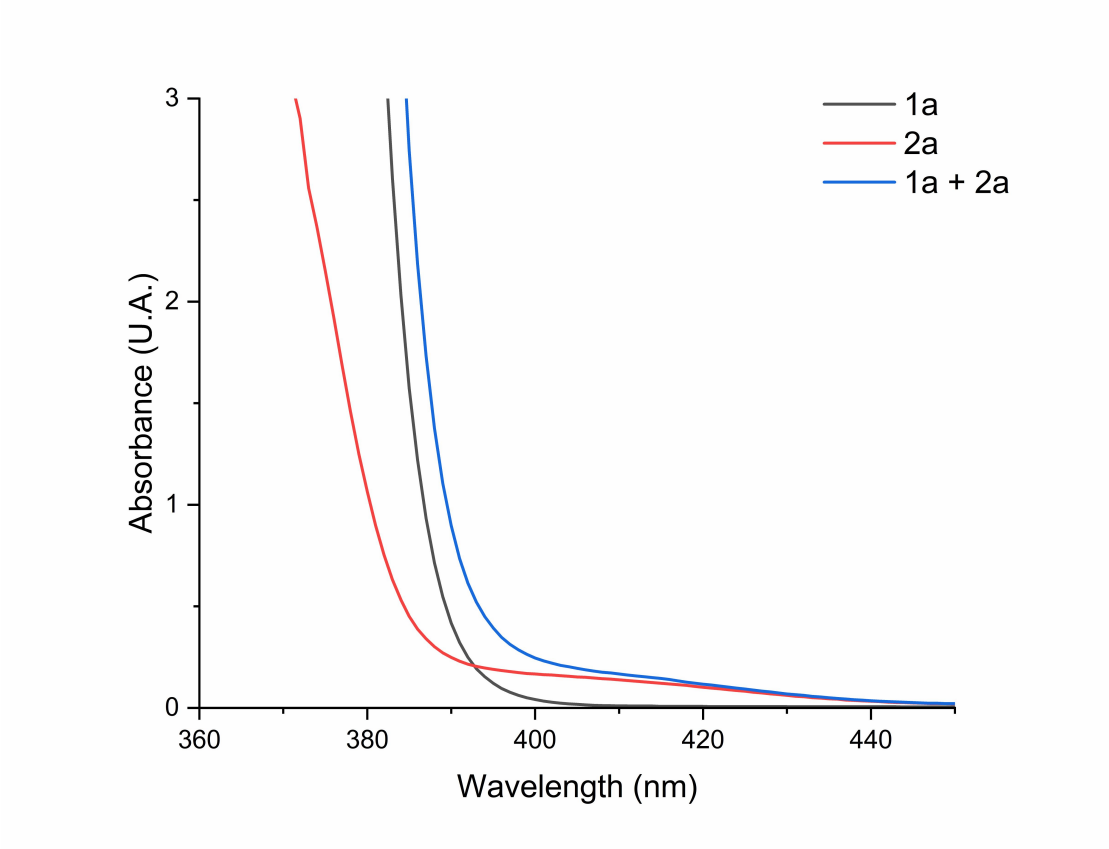
After sealing, TFA (29.7 μL, 2.0 equiv) and dry dimethylacetamide solvent (0.2 M) were added to the syringe. The reaction mixture was stirred for 12 h under a 33 W blue LED (440 nm). After irradiation, 0.5 mL of the reaction mixture was extracted with a syringe, quenched with water, and the organic layer was collected and analyzed by NMR using 1,3,5-Trimethoxybenzene as an internal standard. No product **3a** was detected. and BHT-trapped complex **4** was detected by GC-MS analysis. GC-MS found:318 m/z.



Supplementary figure 2. Result of BHT experiment.

4.2. UV/Vis absorbance studies

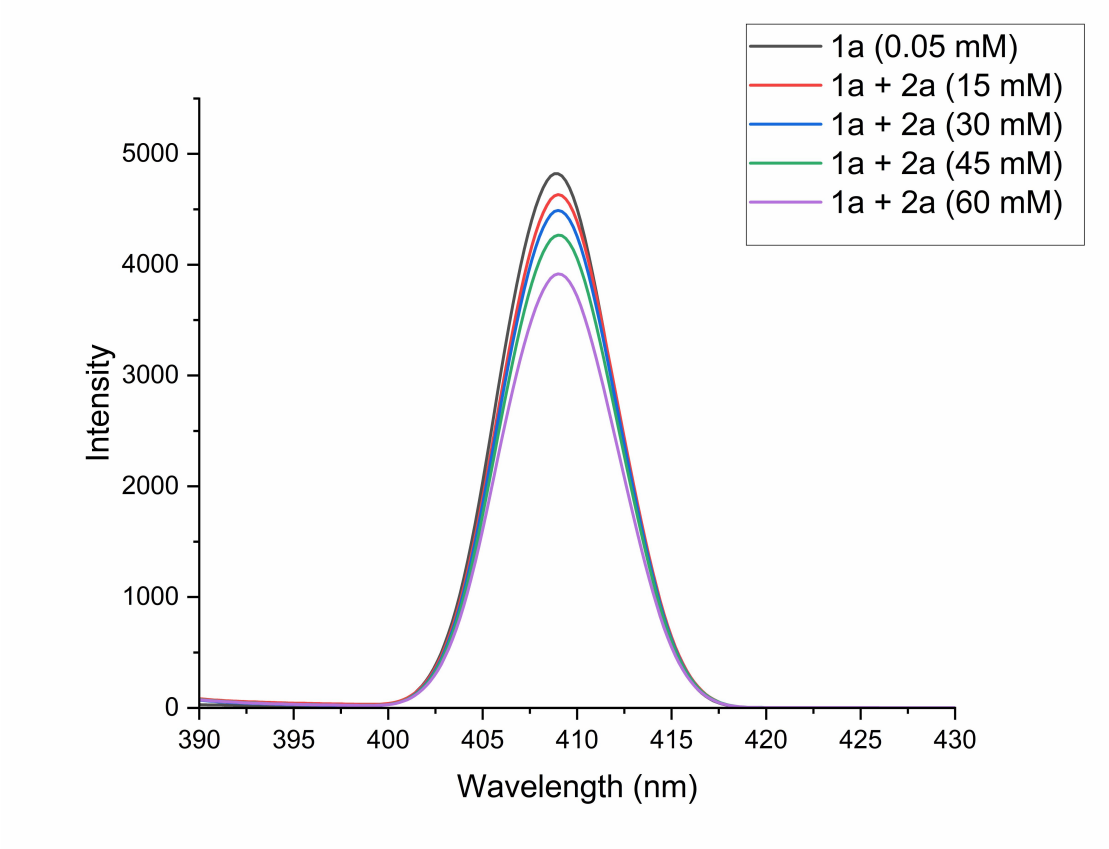
A 10 mL stock solution of each *N*-methylquinoxalin-2(1*H*)-one **1a** (0.01 M), N-trifluoroethoxyphthalimide **2a** (0.3 M), and mixture of **1a** (0.01 M), **2a** (0.3 M) in DMAc to confirm the presence of EDA interactions in this reagent system. during this period ,The maximum absorption of the solution has a strong shift, indicating the formation of an electron donor-acceptor complex.



Supplementary figure 3. Absorption Spectra of **1a** (0.01 M), **2a** (0.3 M), and their EDA complex.

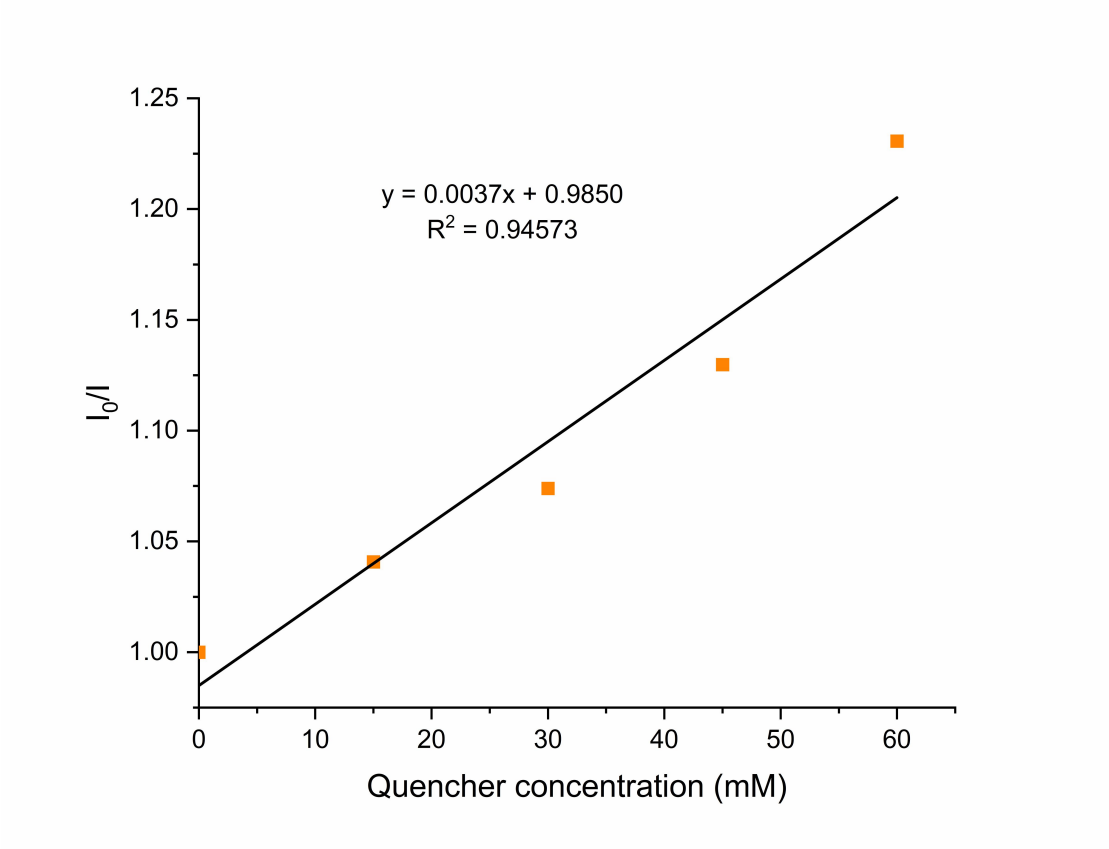
4.3. Fluorescence quenching studies

Fluorescence quenching experiment without photocatalyst. Emission intensities were recorded using an F-7000 Fluorescence Spectrophotometer. First, the emission intensity of **1a** solutions was observed at 380 nm. The solutions were irradiated at 410 nm (Maximum absorption wavelength of **1a**) and fluorescence was measured from 350 nm to 600 nm. The solution of **1a** (1 mM, 10 mL) and **2a** (600 mM, 10 mL) were prepared in glovebox. In each quenching experiment, Add 10 µL **1a** solution and 0 µL, 50 µL, 100 µL, 150 µL, 200 µL **2a** solution respectively in the quartz cuvette, then diluted the solution to 2 mL.



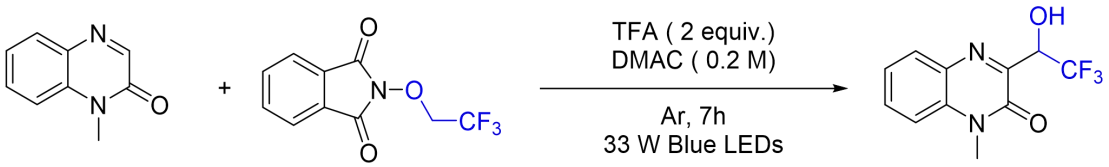
Supplementary figure 4. Fluorescence spectrum of **1a** + **2a**.

An indeed fluorescence quenching phenomenon of **1a** under various concentrations of **2a** was demonstrated in a curve of [I_0/I] vs C [**2a**], as shown in Stern-Volmer plots (Supplementary figure 5).



Supplementary figure 5. Stern-Volmer Luminescence Quenching Analysis of **1a** + **2a**.

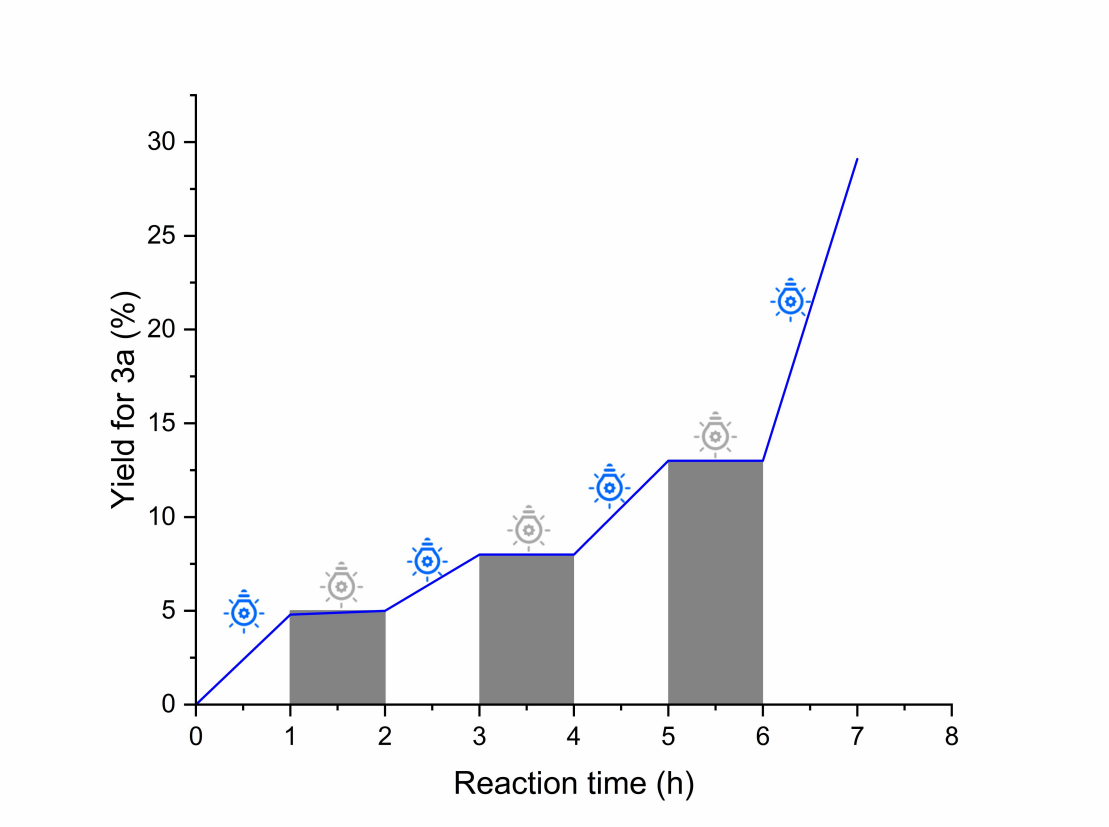
4.4. Light on/off experiment



1a 2a 3a

N-Methylquinoxaline-2 (1*H*) -one **1a** (48.1 mg, 0.3 mmol) and *N*-trifluoroethoxyphthalimide **2a** (147.1 mg, 2.0 equiv.) were added to a dry Schlenk tube with a magnetic stirrer. Subsequently, the air in the bottle was pumped out and filled with argon three times. After sealing, TFA (45.94 μ L, 2.0 equiv.) and dimethylacetamide solvent (0.2 M) were added to the syringe. The reaction mixture was stirred at room temperature for 7 h under 33 W blue LED (440 nm). The yield of the product was determined by ^{1}H NMR (1,3,5-trimethoxybenzene as internal standard). The reaction profile is shown below (Fig.6), indicating that continuous light irradiation is essential to promote the reaction.

Entry	Time (h)	Light Source	Yield
1	1	On	4.8
2	2	Off	5
3	3	On	8
4	4	Off	8
5	5	On	13
6	6	Off	13
7	7	On	29



Supplementary figure 6. Light on/off experiment.

4.5. Quantum Yield Experiment

According to the previous literature procedure[3], the photo flux of the 33 W 440 nm LED lamp was first determined by standard ferrioxalate actinometry.

Preparation of 0.15 M solution of ferrioxalate (0.15 M):

Potassium ferrioxalate trihydrate (736.9 mg) was dissolved in H_2SO_4 aq. (10 mL, 0.2M).

Preparation of buffered solution (0.15 M):

1, 10- phenanthroline (540.6 mg, 3.0 mmol), NaOAc (1.23 g, 15.0 mmol) were dissolved in H_2SO_4 aq. (20 mL, 0.2M).

To two 8 mL vials added ferrioxalate solution (1 mL) respectively and irradiated one of the vials with an LED lamp (33W, 440 nm) while the other kept in dark. After 30 s, buffered solution (3 mL) and H_2SO_4 aq. (2 mL, 0.2M) were added immediately to both vials. The resulting mixtures were kept in dark for another 1 h to allow the formed ferrous ions completely coordinate to the phenanthroline. Then, 25 μL of each resulting mixture was transferred to a cuvette (l = 10 mm) and diluted with H_2SO_4 aq. (2 mL, 0.2 M). The absorbance at 510 nm was measured by UV-Vis spectrometry. The photo flux was measured as following equivlent (eq.1).

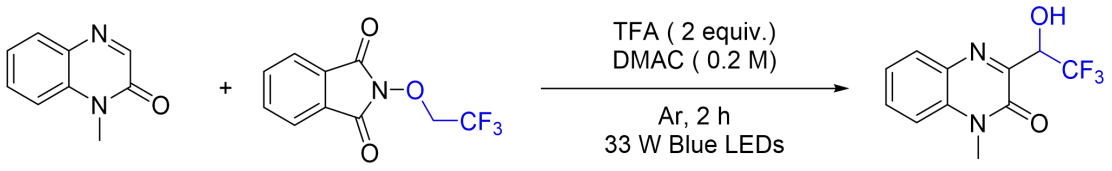
$$mol\ Fe^{2+} = \frac{V \times \Delta A\ (510\ nm)}{l \times \varepsilon} \qquad (eq\ 1)$$

Where V is the total volume (0.486 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.0 cm), and ε is the molar absorptivity at 510 nm (11,100 L·mol-1·cm-1). The photon flux can be calculated using eq 2.

$$photo\ flux = \frac{mol\ Fe^{2+}}{\Phi \times t \times f} \qquad (eq\ 2)$$

$$f = 1 - 10^{-A(440\ nm)} \qquad (eq\ 3)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (approximate 1.000 for a 0.15 M solution at λ = 440 nm), t is the time (30 s), and f is the fraction of light absorbed at λ = 440 nm (0.2655, A= 0.134). The photon flux was calculated to be 1.6844 × 10-4 einstein.



1a 2a 3a

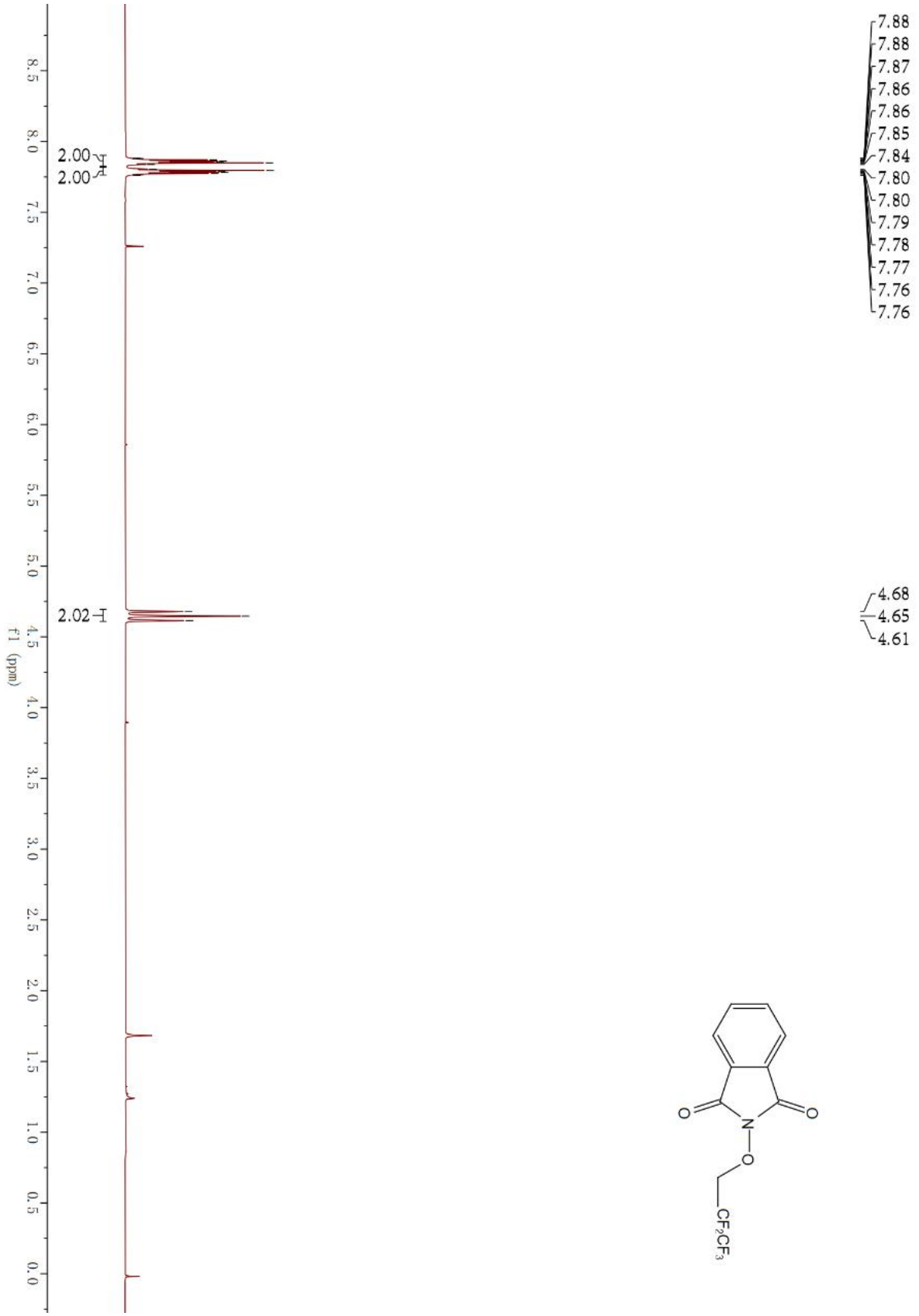
N-methylquinoxalin-2(1*H*)-one **1a** (0.3 mmol, 48.1 mg, 1 equiv.), 2-(2,2,2-trifluoroethoxy) isoindoline-1,3-dione **2a** (0.6 mmol, 147.1 mg, 2 equiv.), trifluoroacetic acid (0.6 mmol, 40 μL, 2 equiv.) in DMAc were added in a pre-dried 10 ml Schlenk tube under Ar atmosphere. The reaction was carried out under an atmosphere of Argon gas and was stirred under LED lamp (33 W, 440 nm) for 2 h. The measured yield is 26.2% after stirred for 2 h, which indicated that the quantum yield was 0.0902 using the eq 4 below.

$$\emptyset = \frac{mol\ product}{photo\ flux \times t \times f} \qquad (eq\ 4)$$

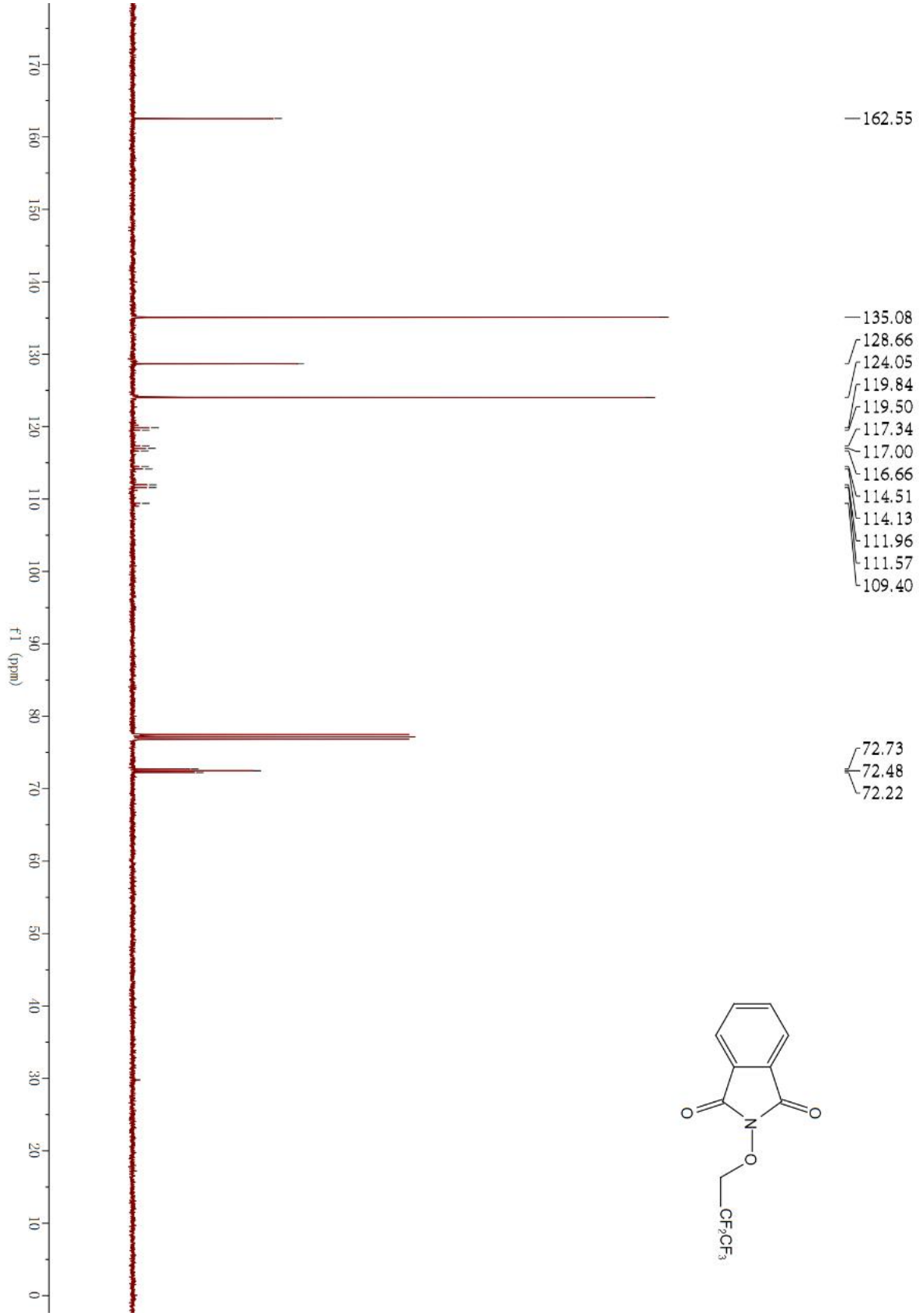
Where mol product is 0.0786 mmol, t is the time (7200s), and *f* is the fraction of light absorbed at λ = 440 nm (0.7188, A= 0.551).

5. Copies of ^{1}H, ^{13}C, and ^{19}F NMR Spectra for the Products

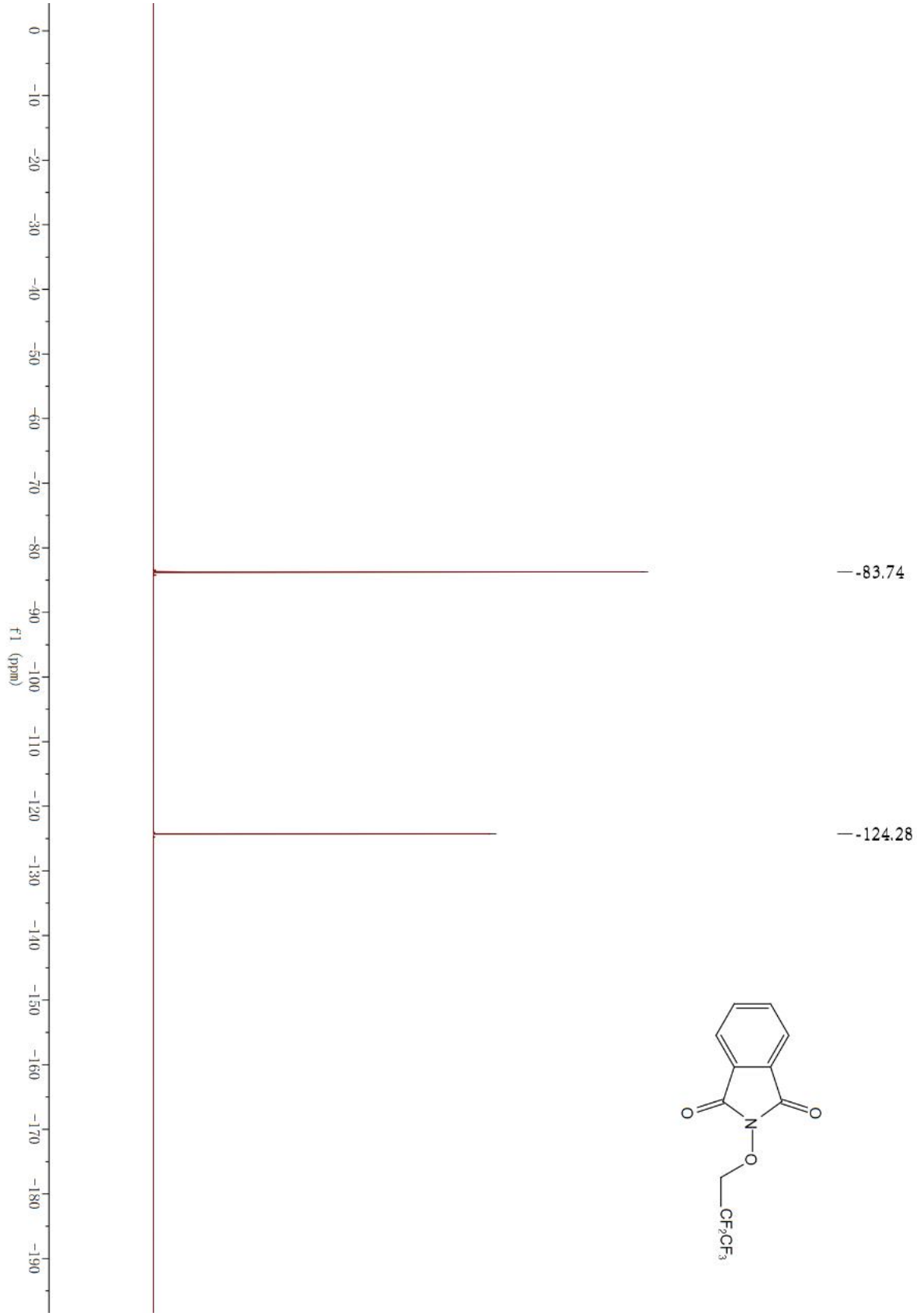
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2b**



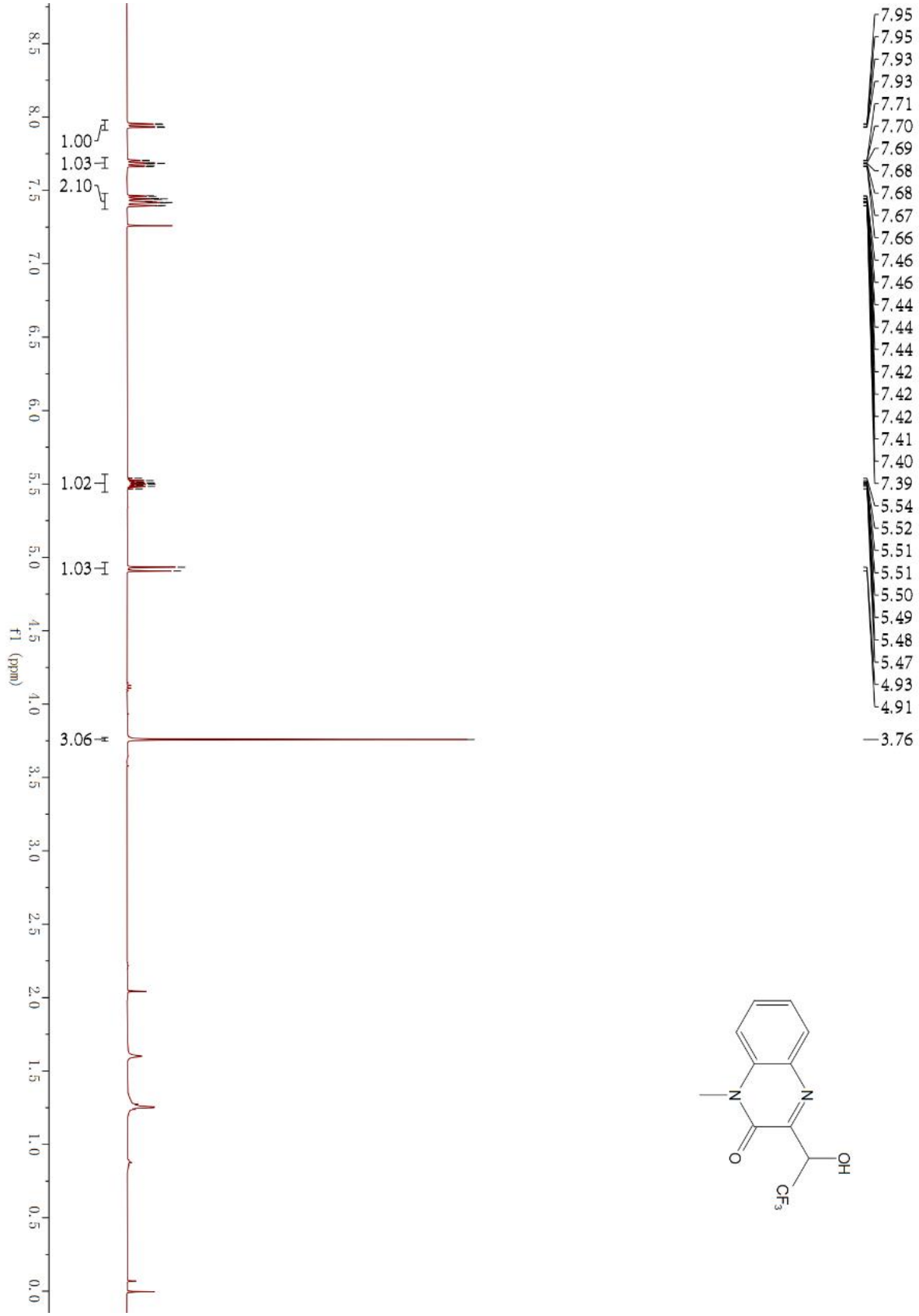
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2b**



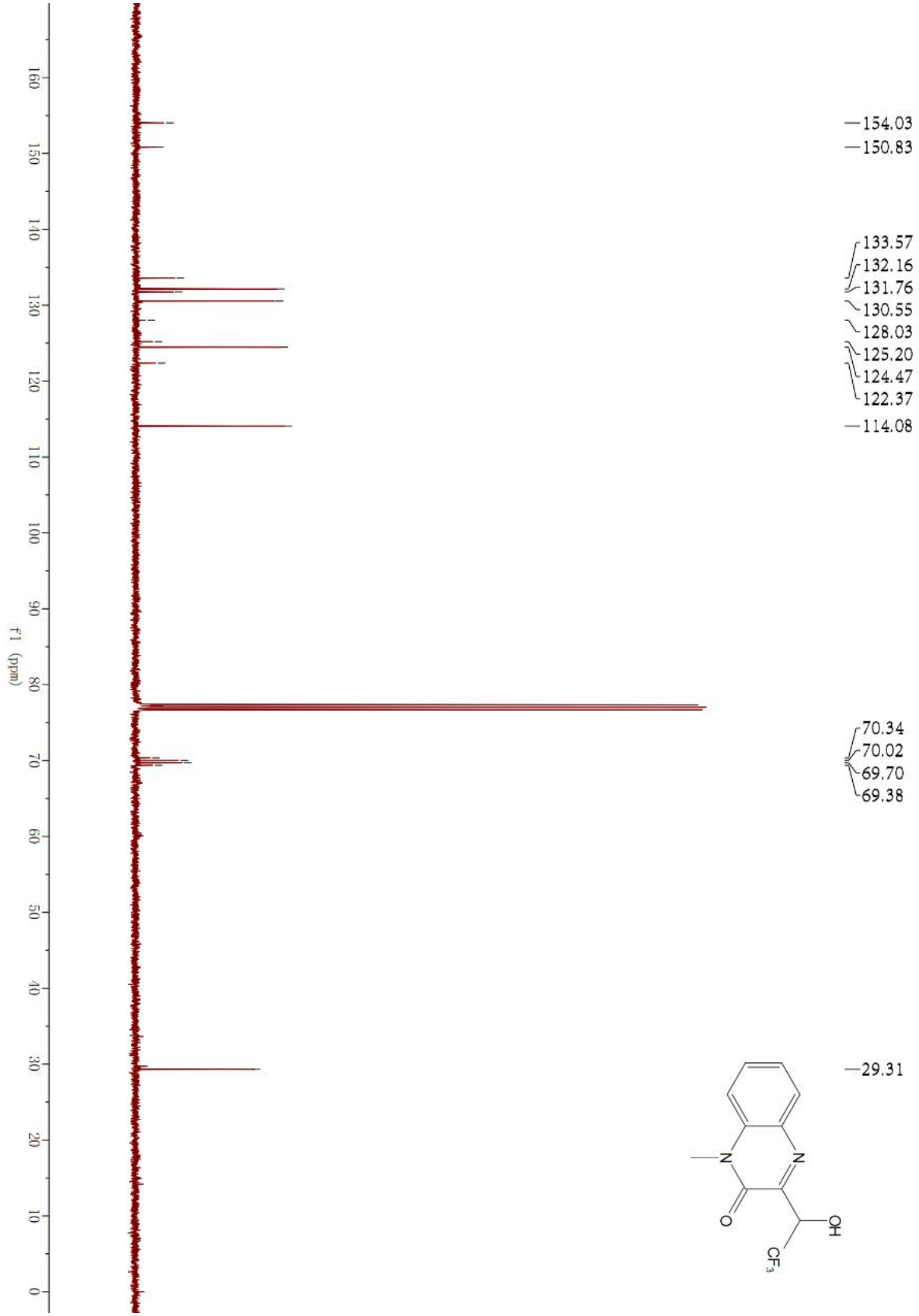
^{19}F NMR (376 MHz, $CDCl_3$) of compound **2b**



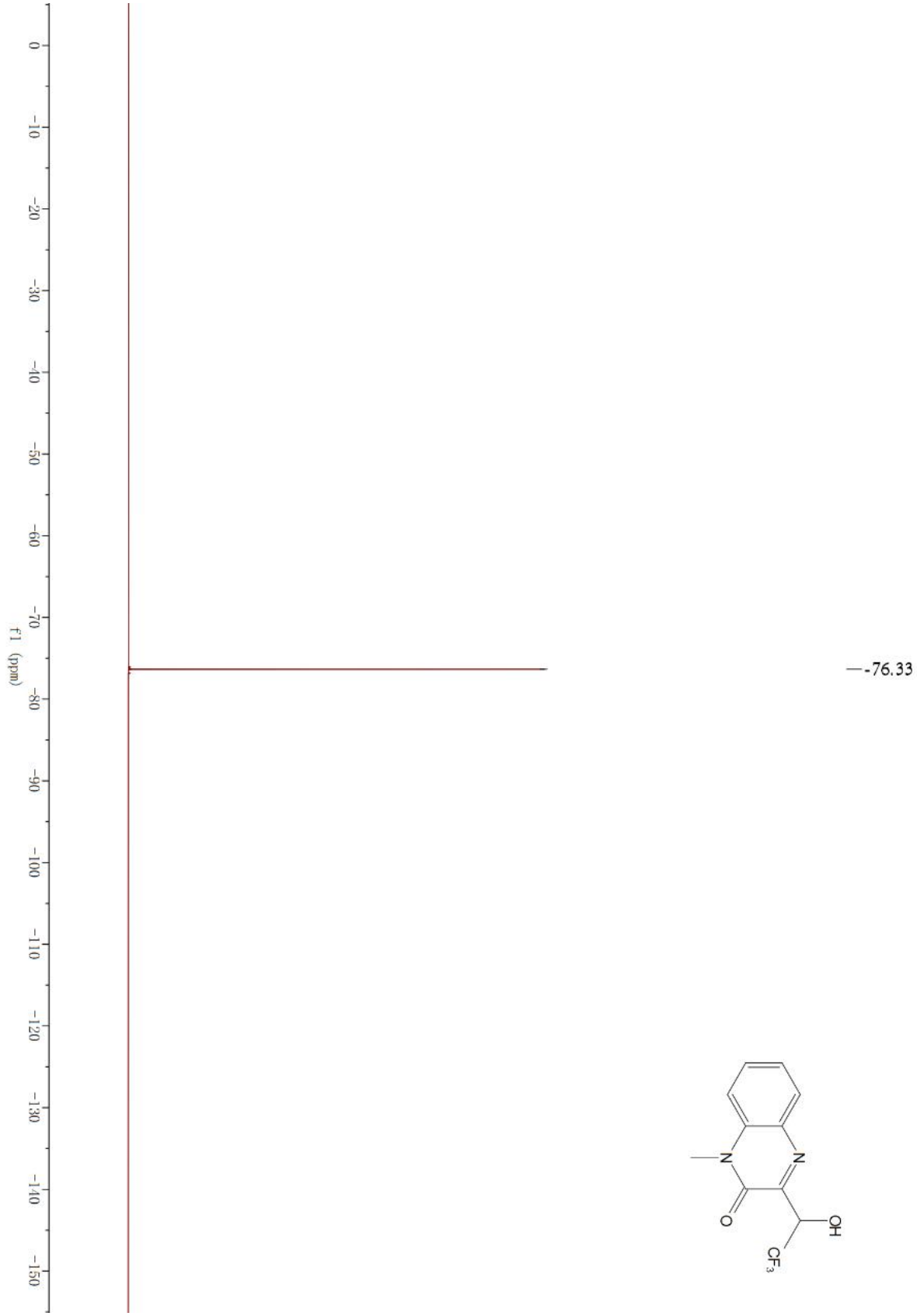
^{1}H NMR (400 MHz, $CDCl_3$) of compound compound **3a**



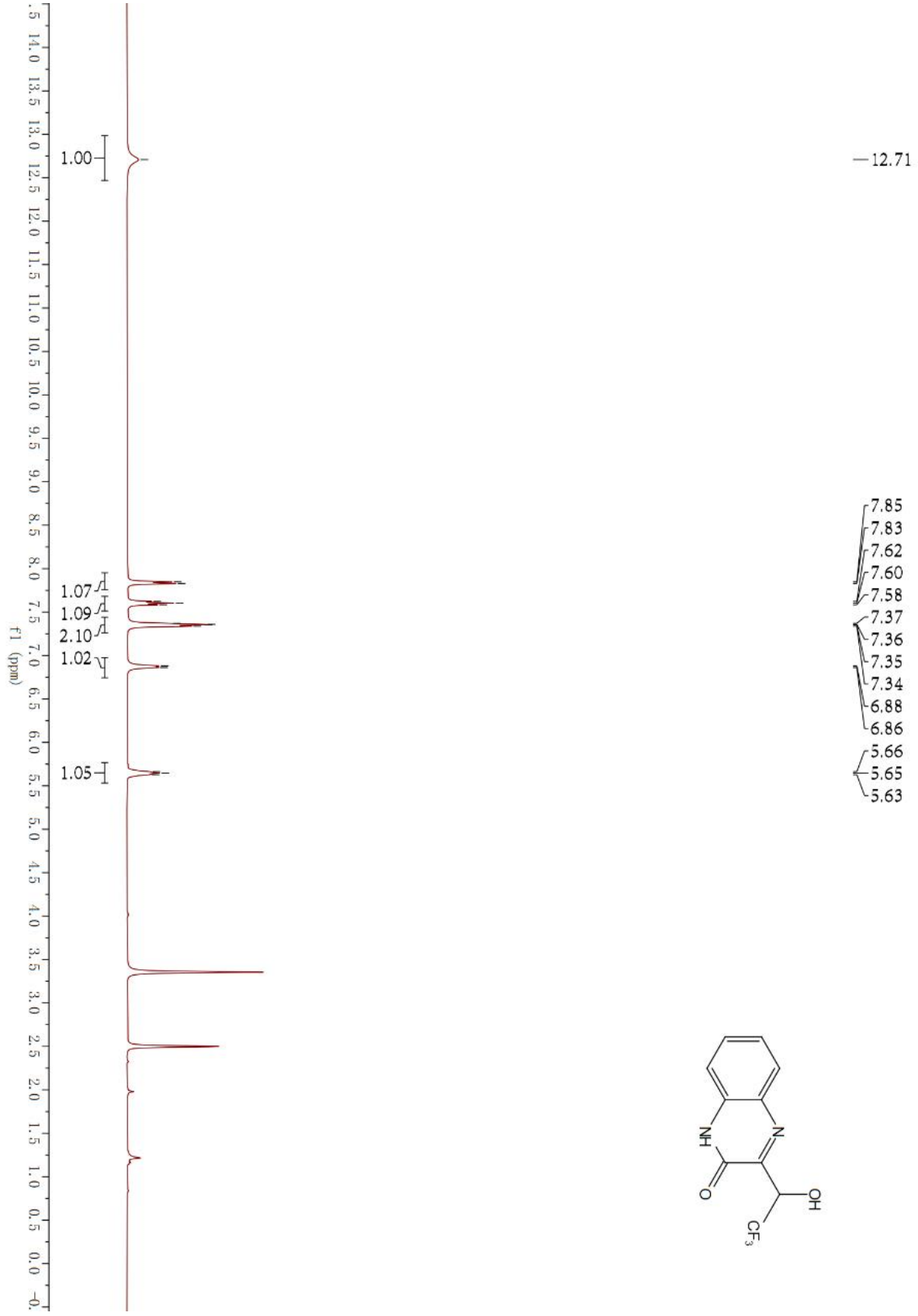
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3a**



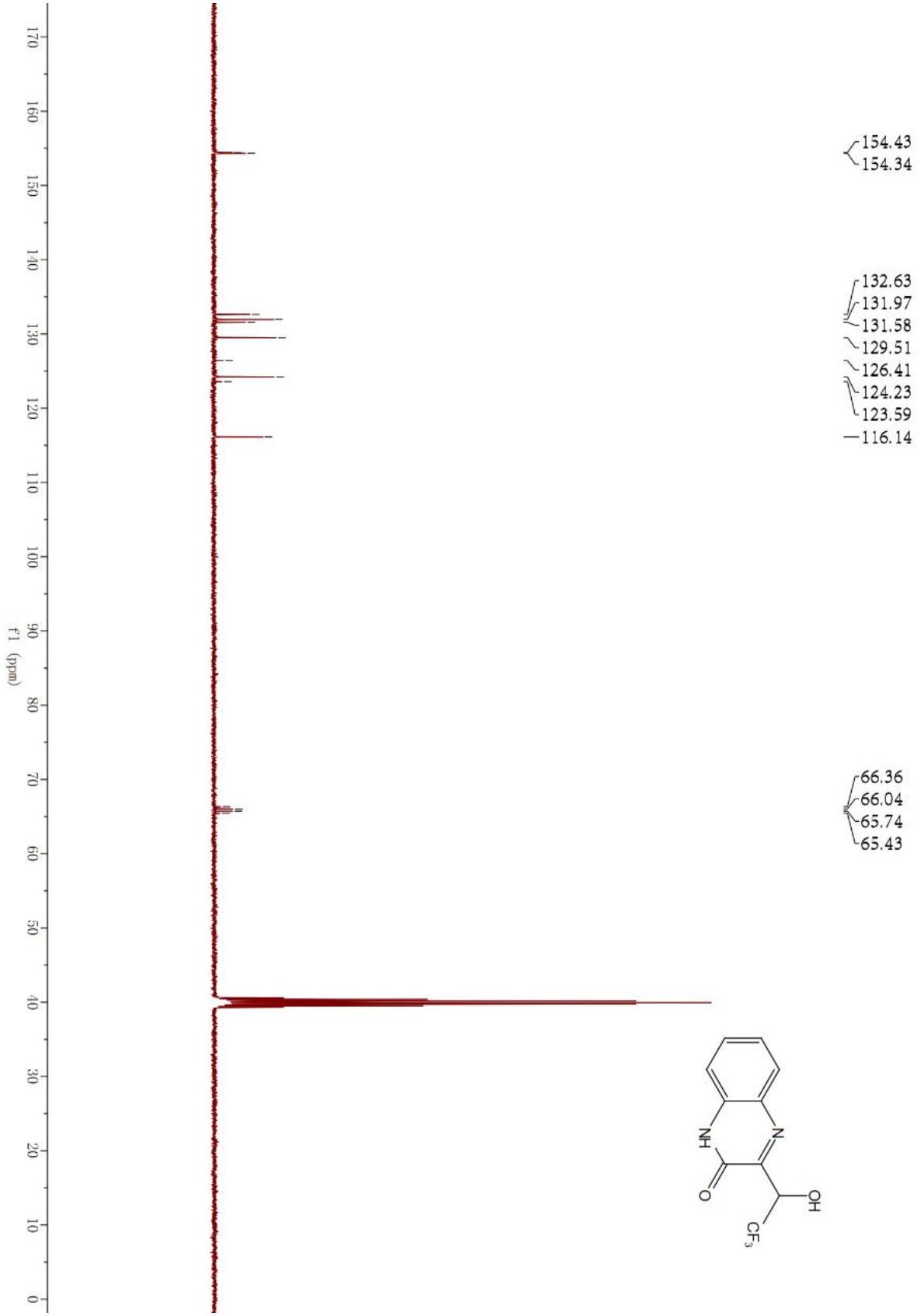
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3a**



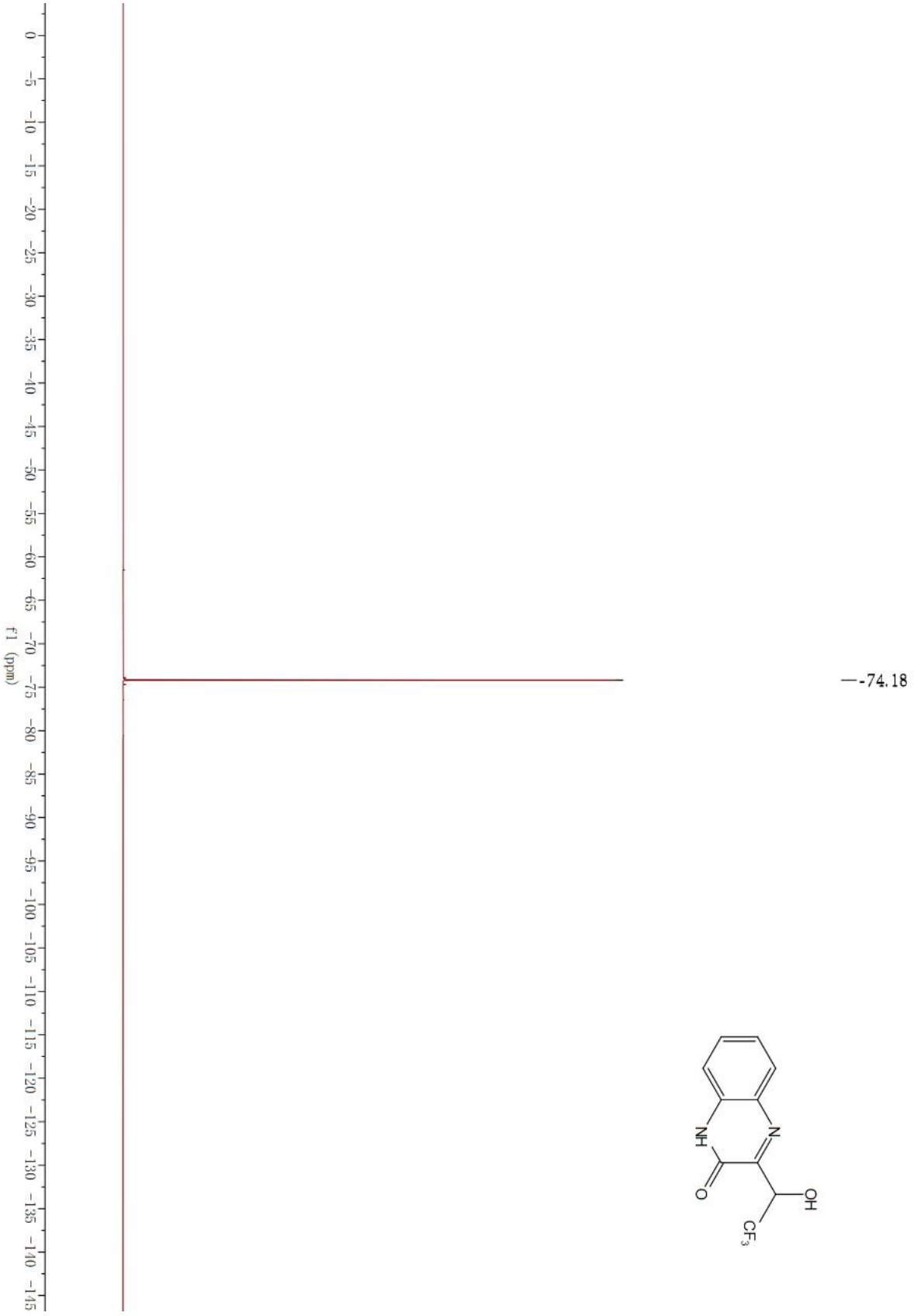
^{1}H NMR (400 MHz, DMSO-d6) of compound **3b**



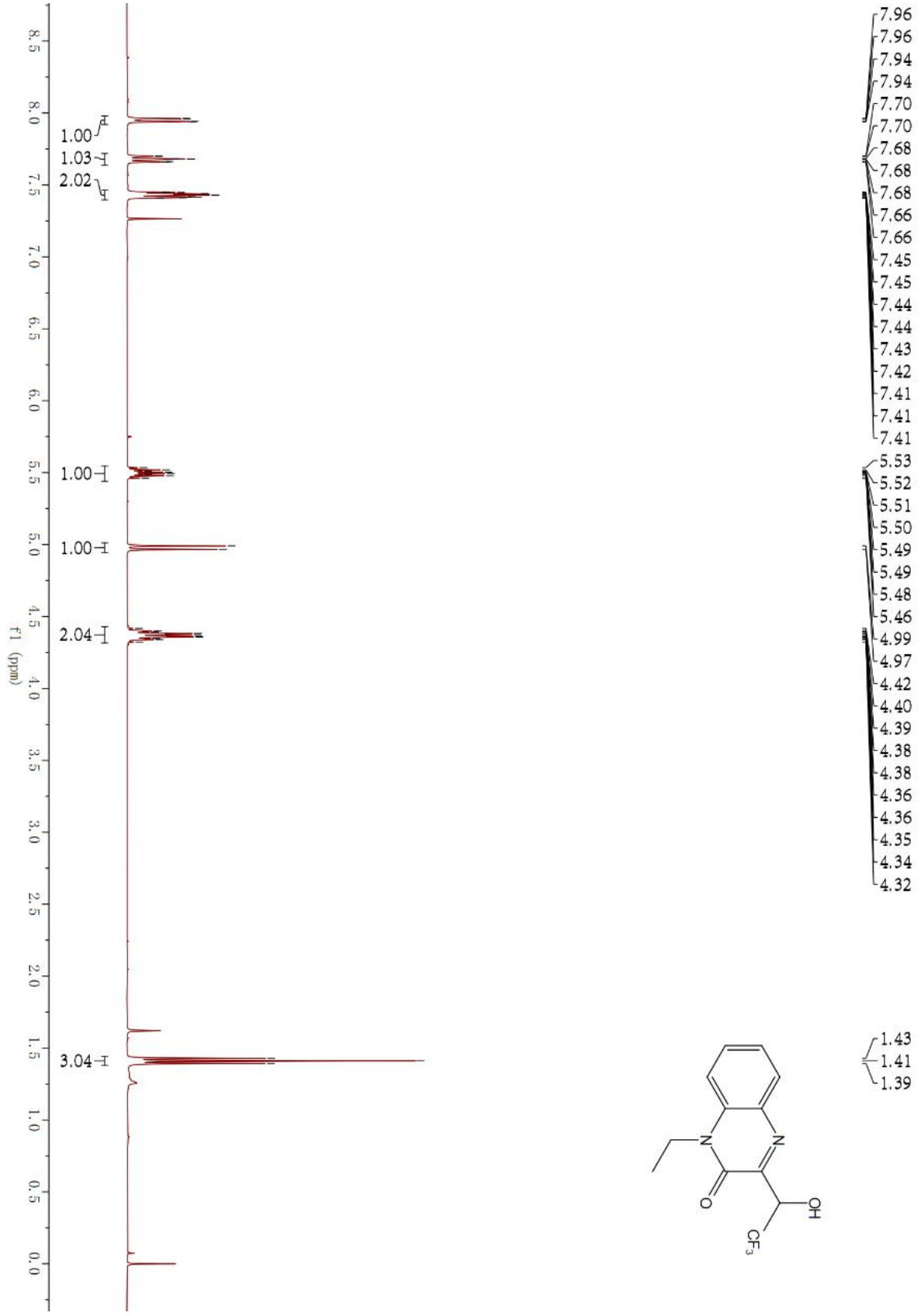
^{13}C NMR (100 MHz, DMSO-d6) of compound **3a**



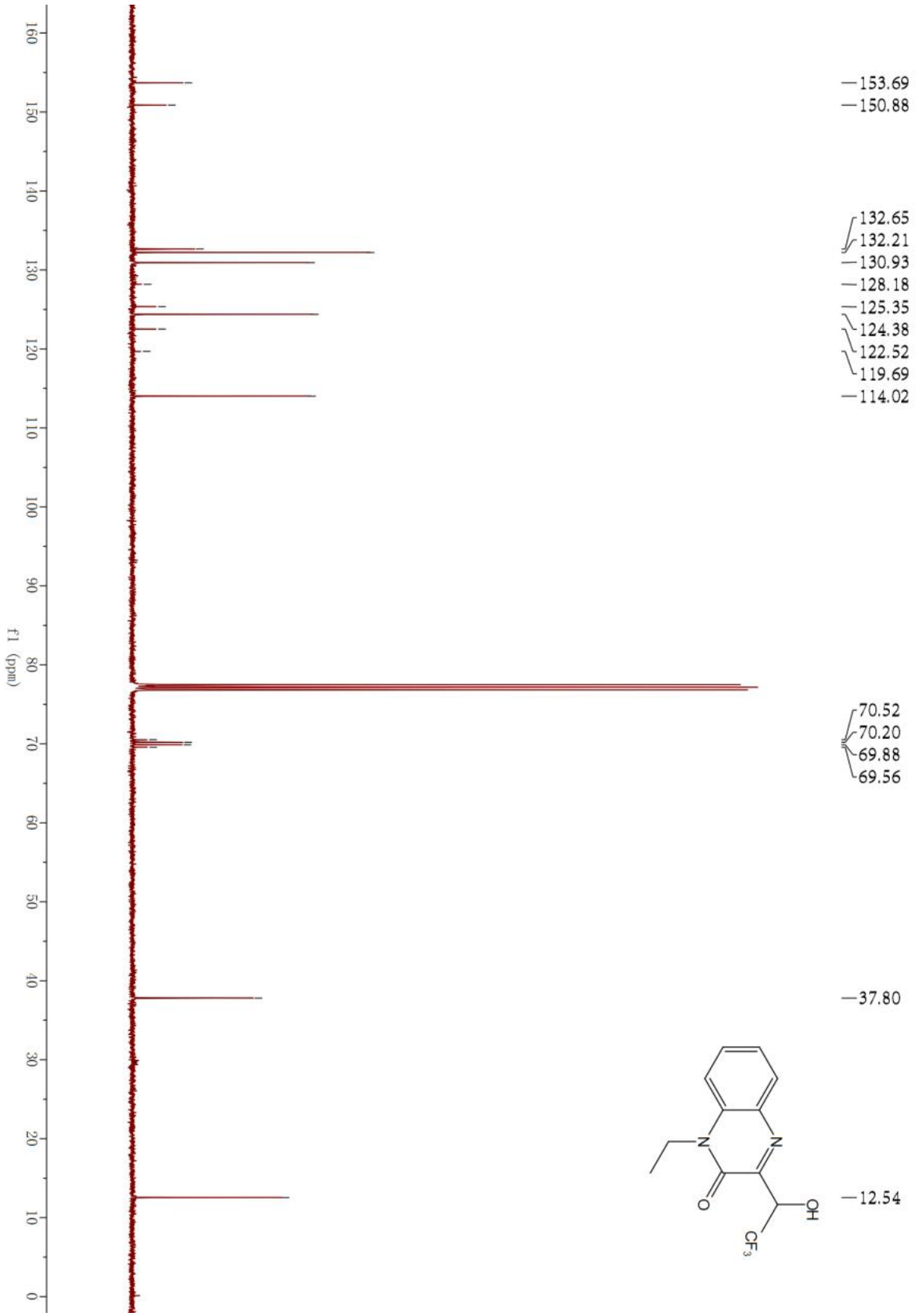
^{19}F NMR (376 MHz, DMSO-d6) of compound **3b**



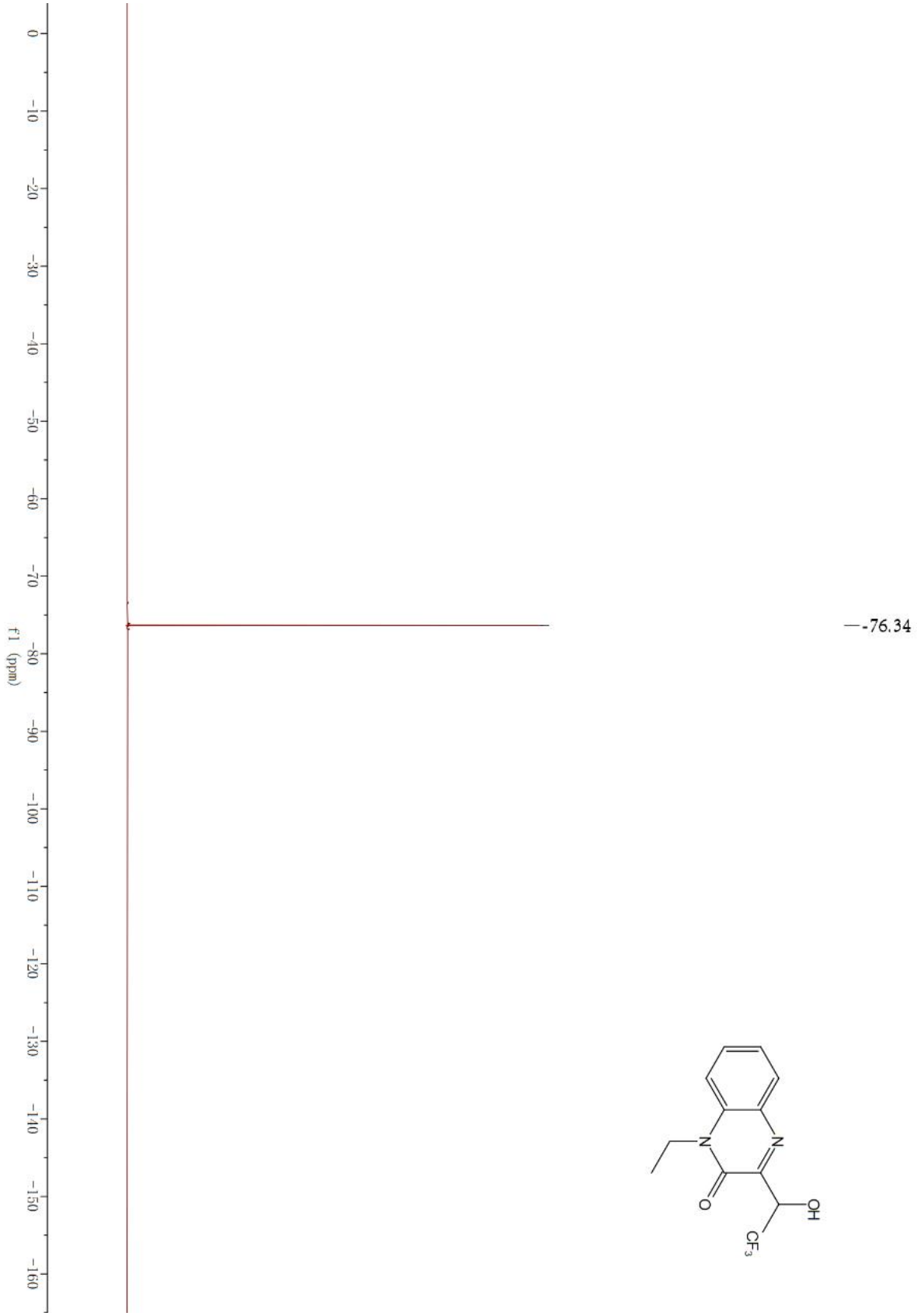
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3c**



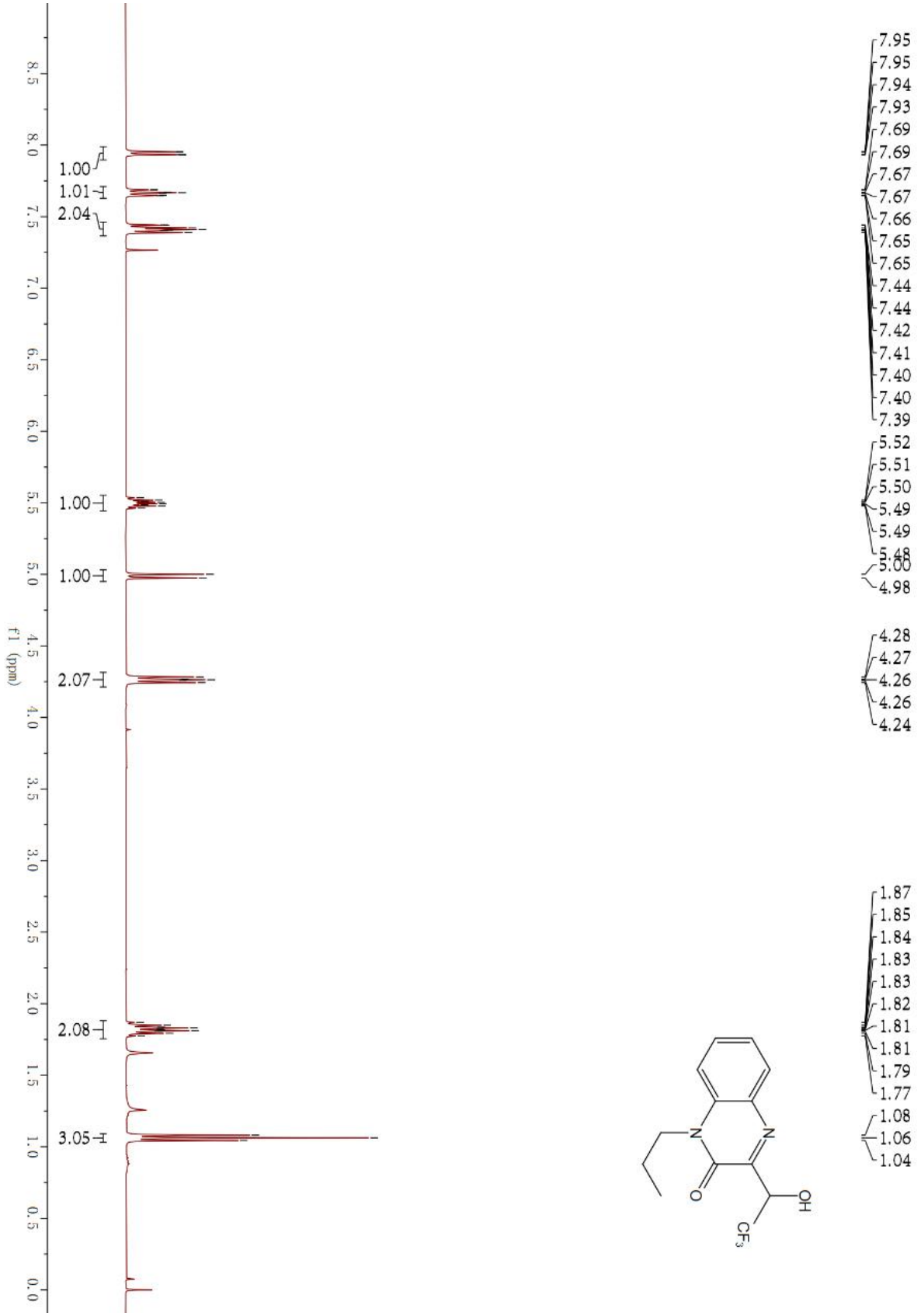
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3c**



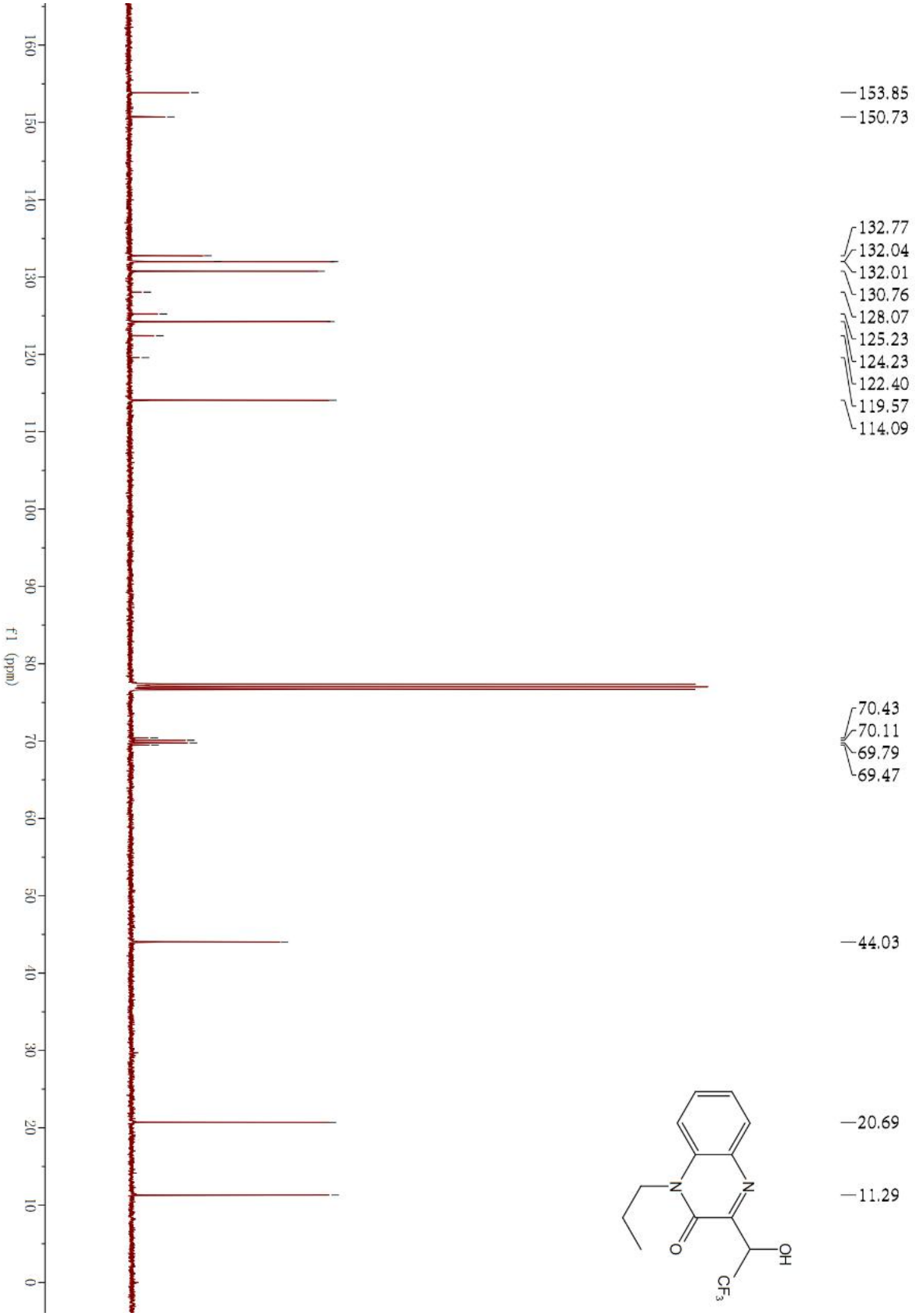
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3c**



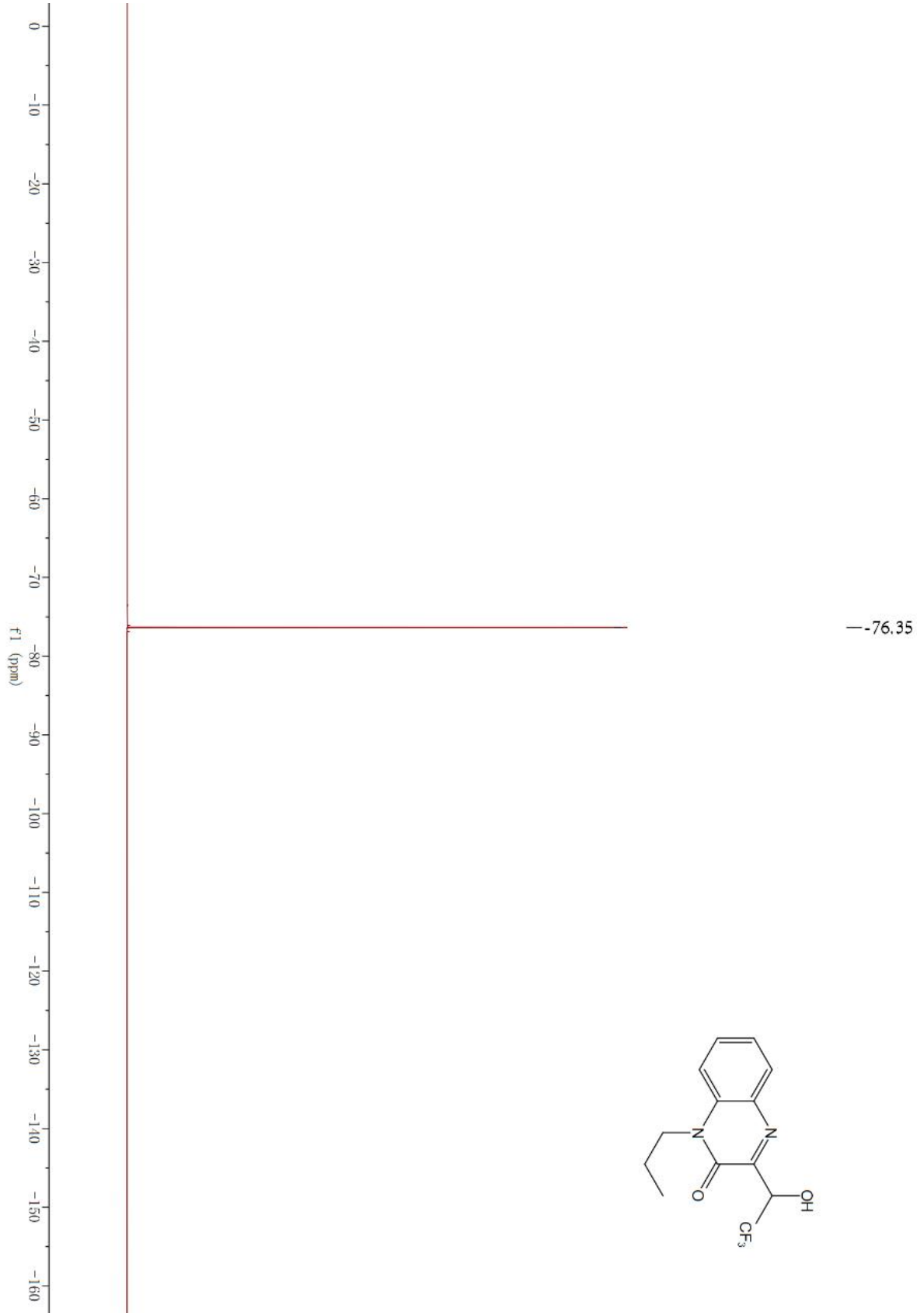
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d**



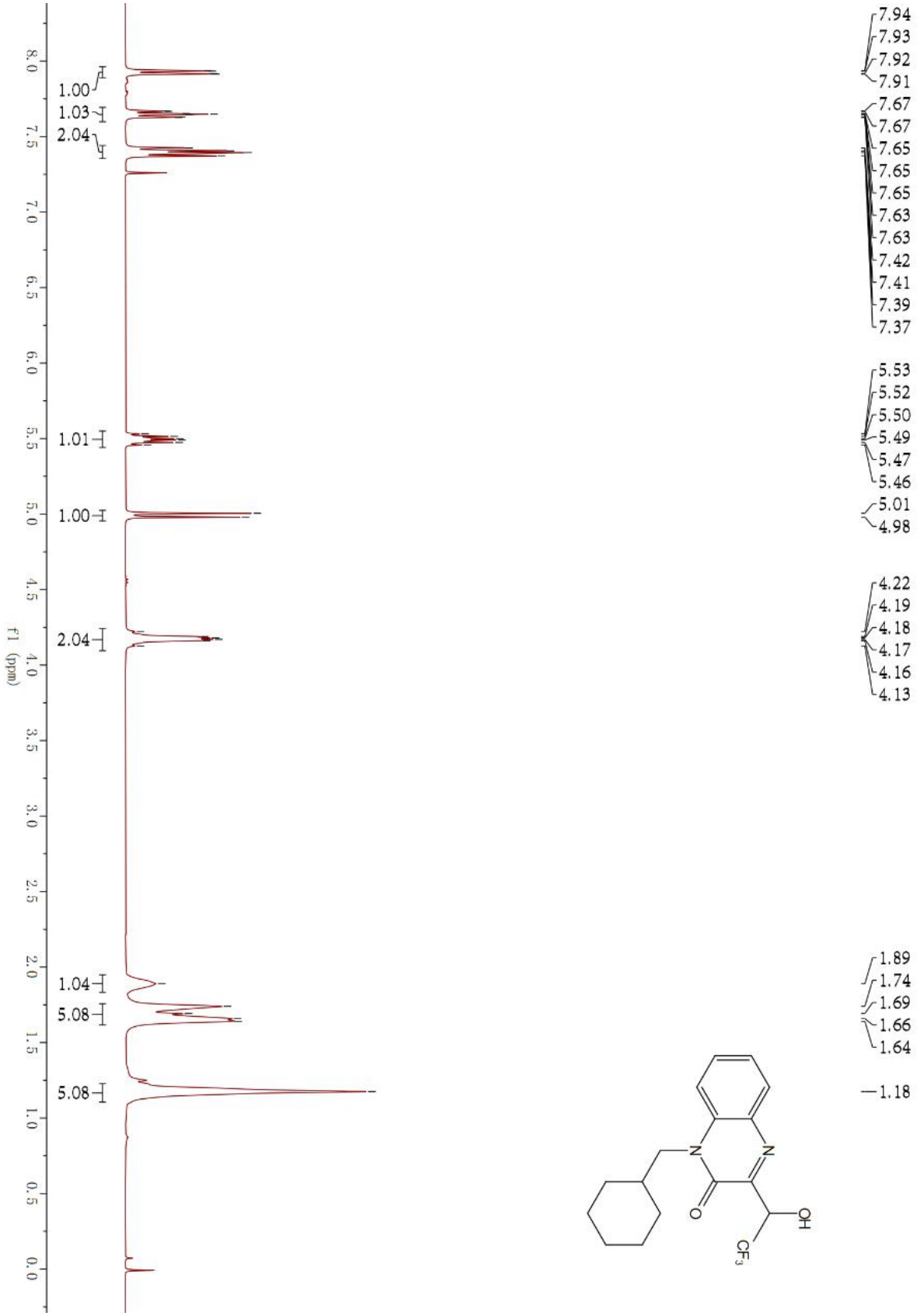
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3d**



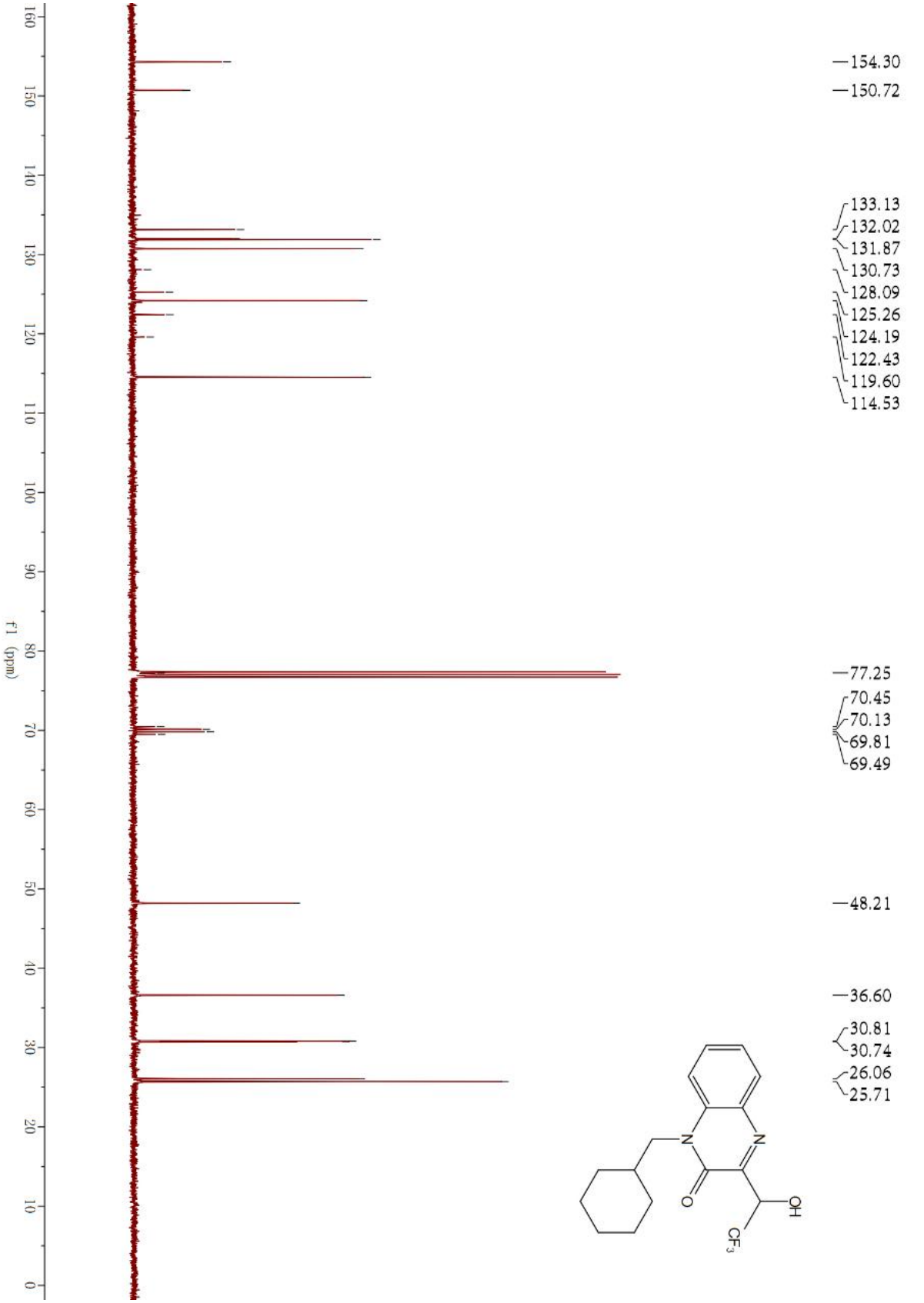
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3d**



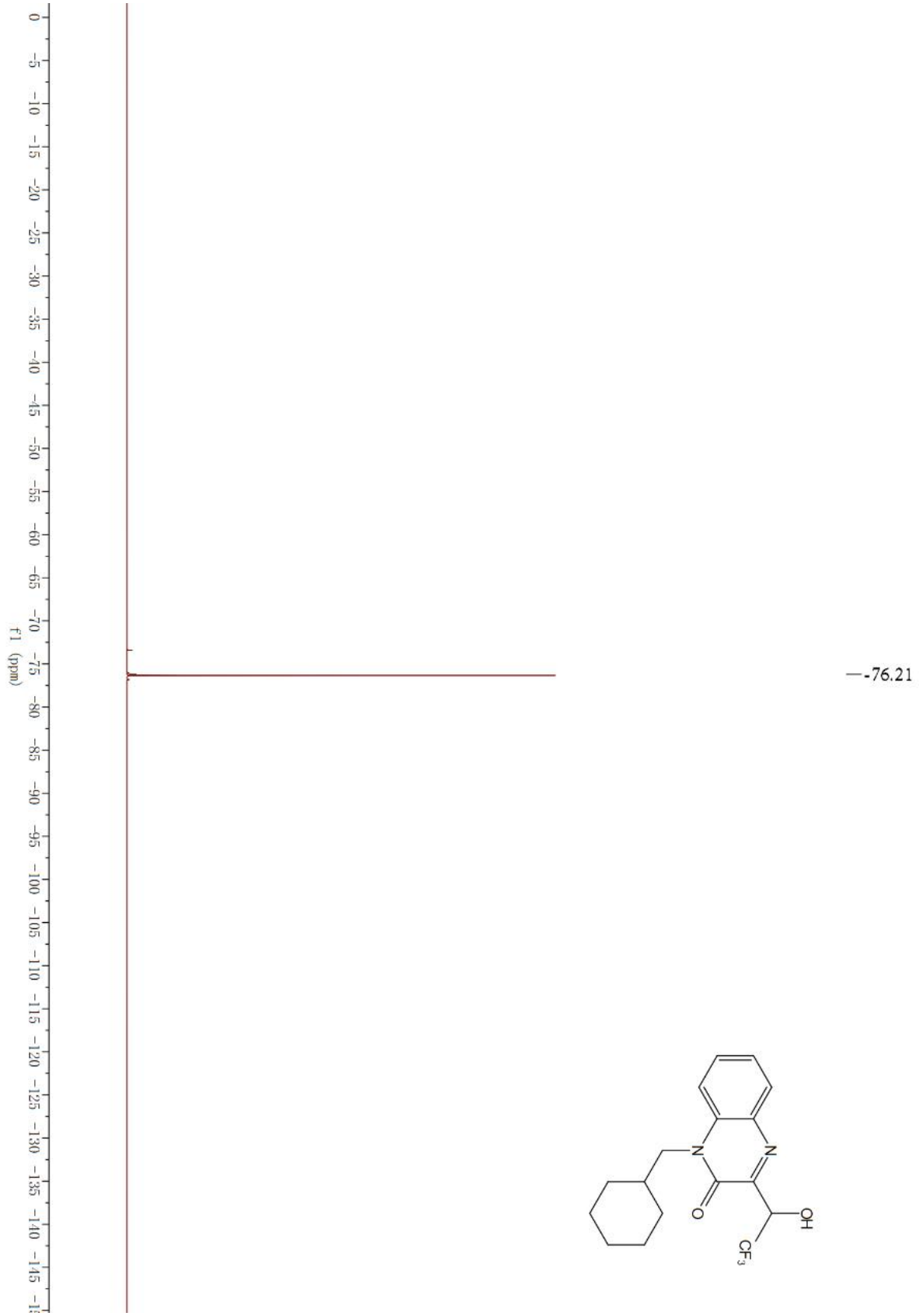
^{1}H NMR (400 MHz, $CDCl_3$) of compound**3e**



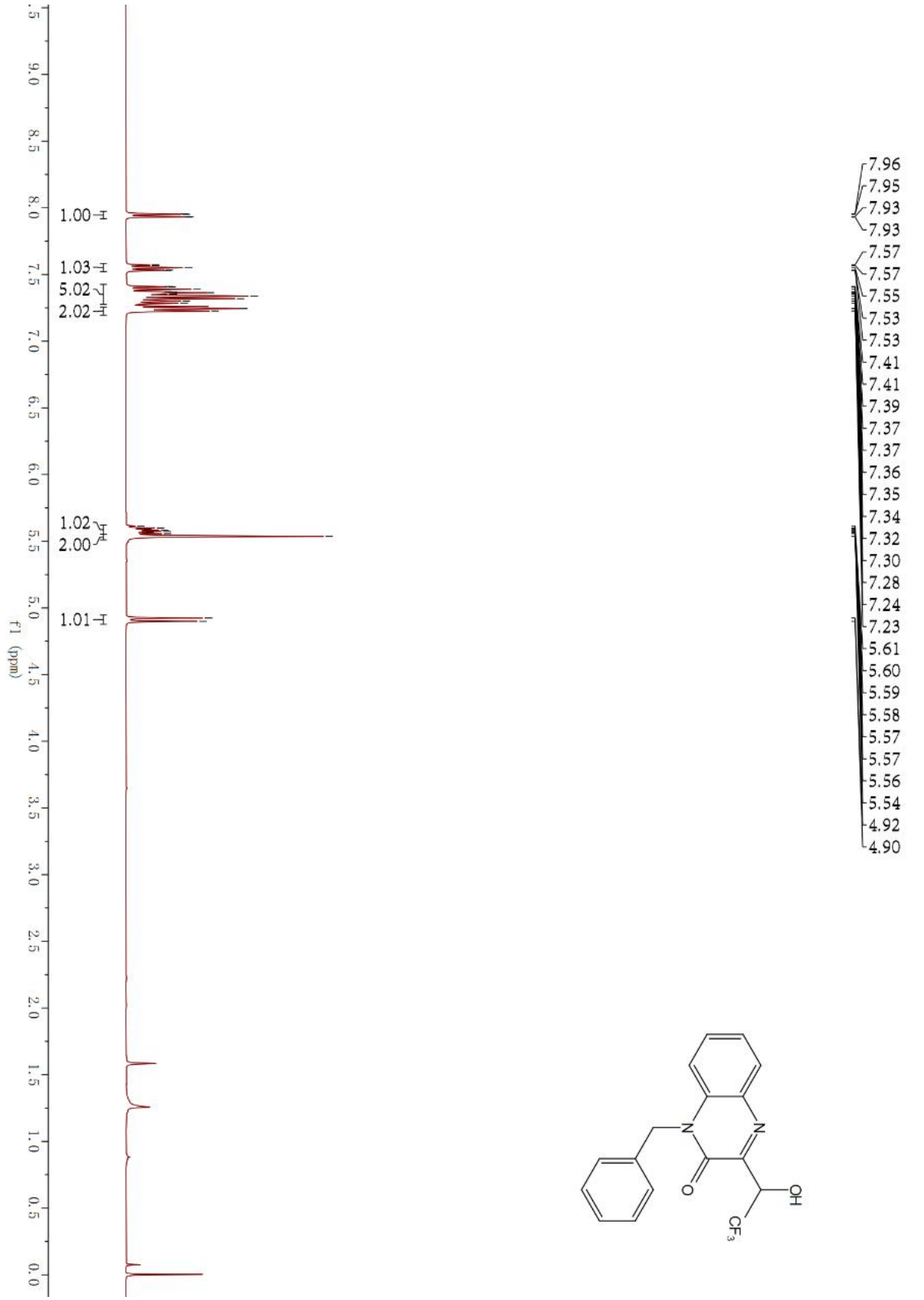
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3e**



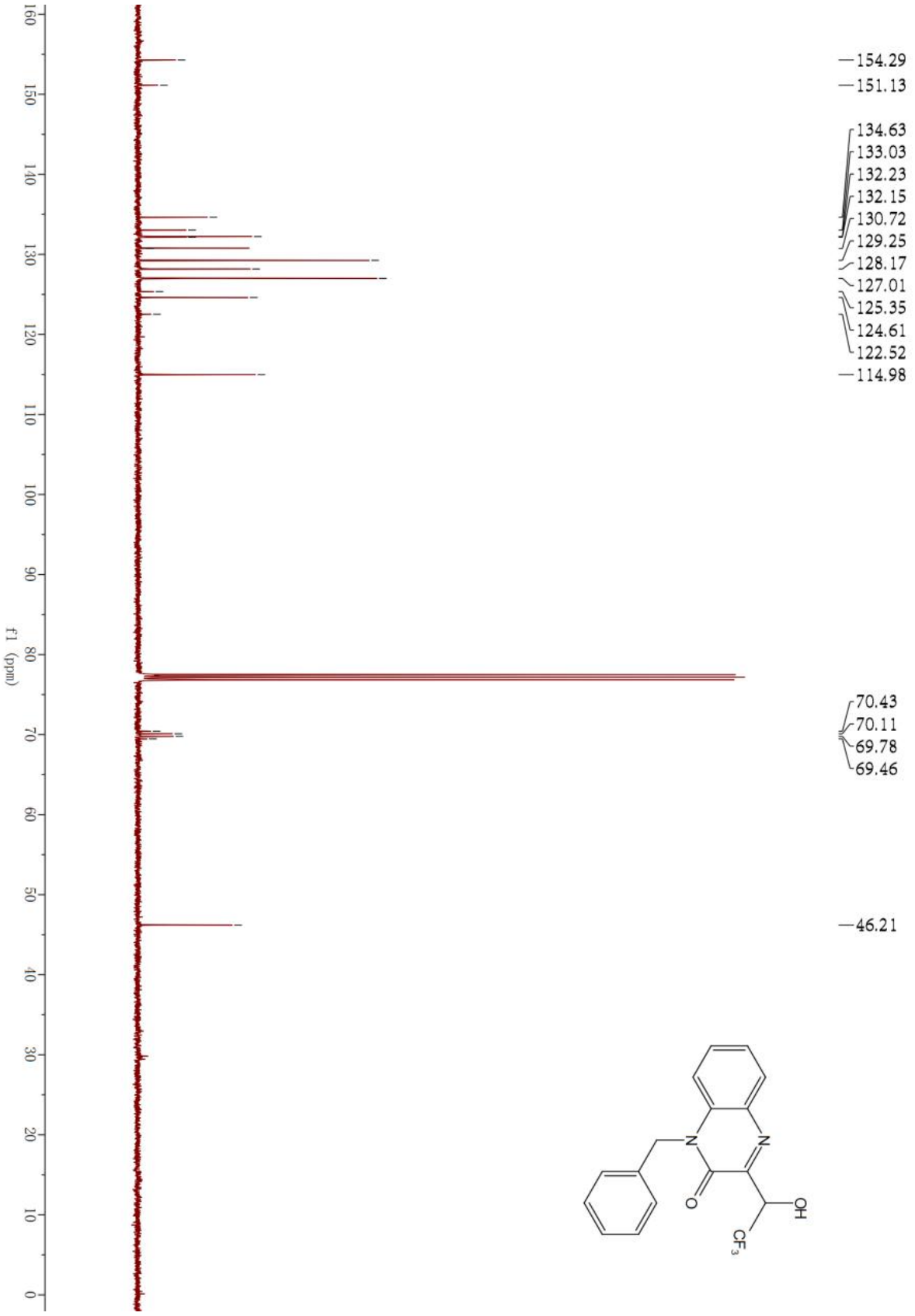
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3e**



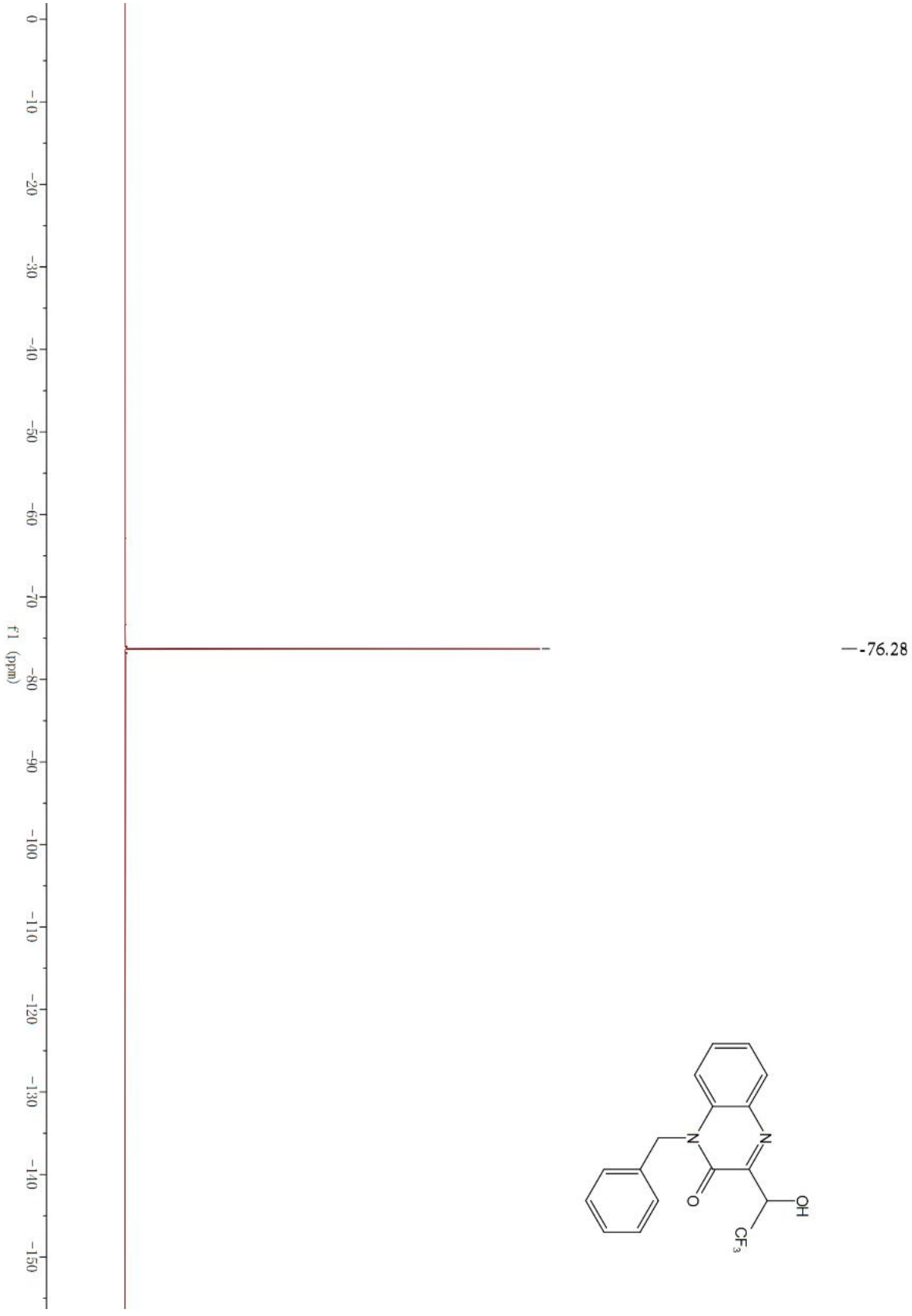
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3f**



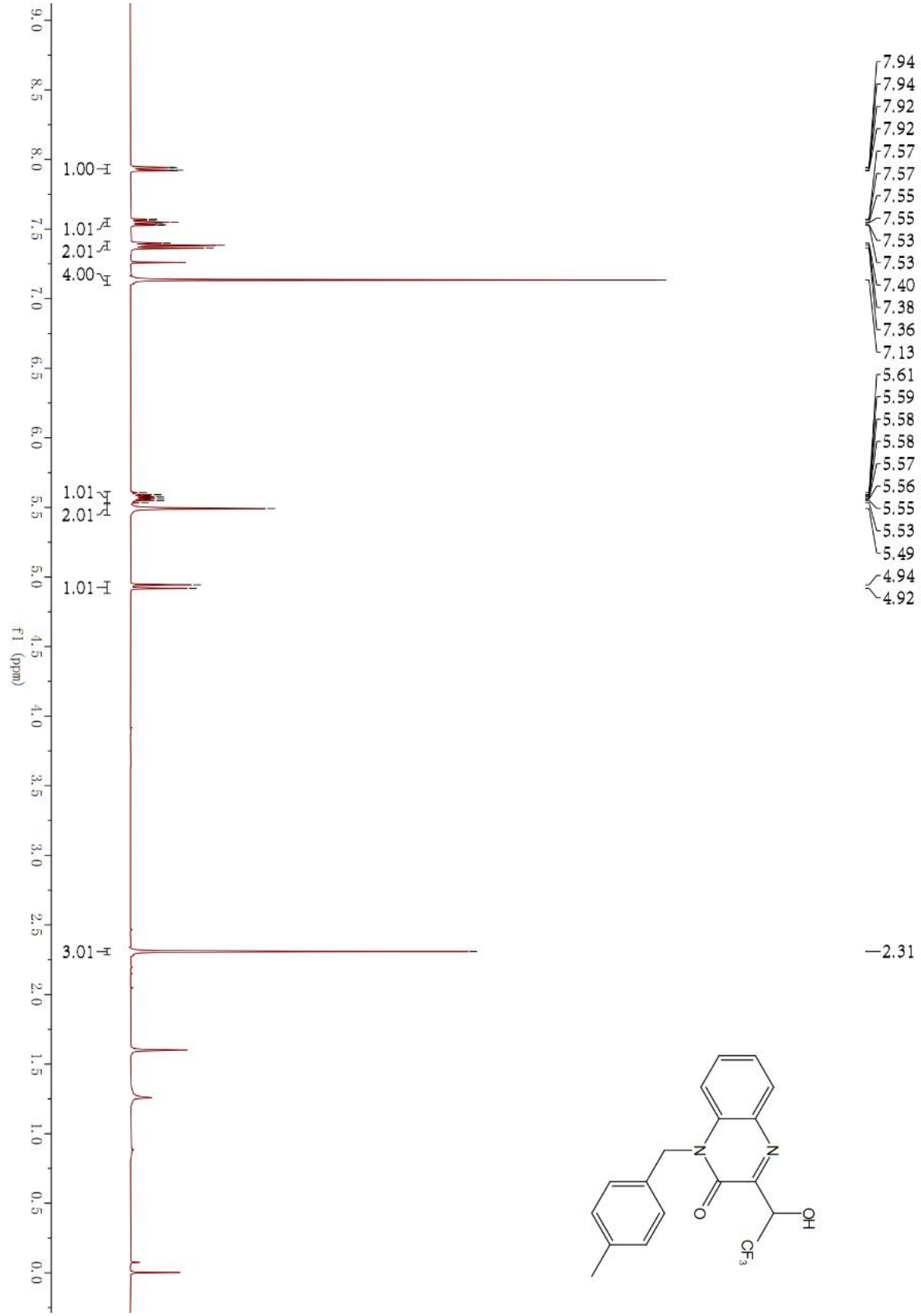
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3f**



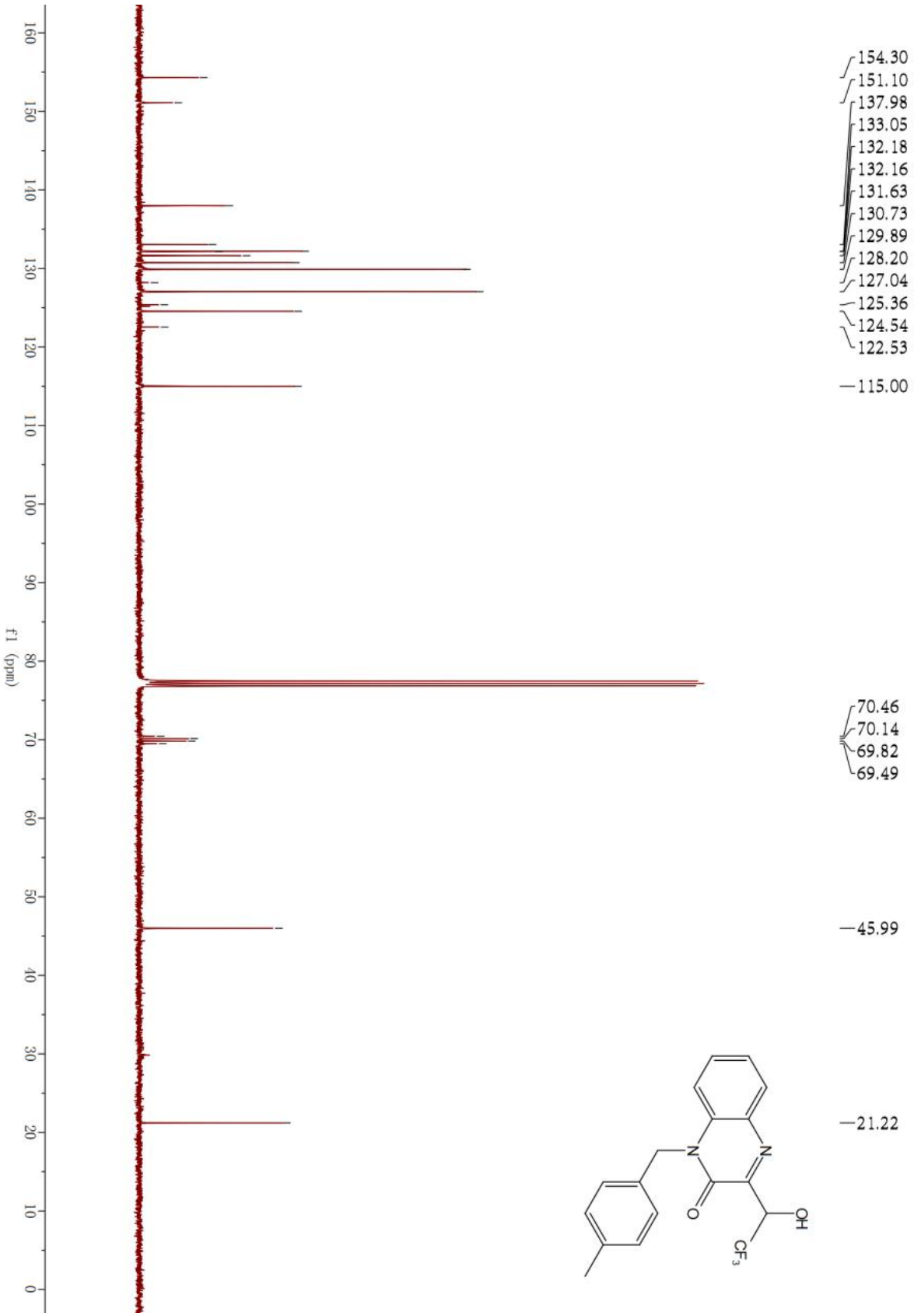
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3f**



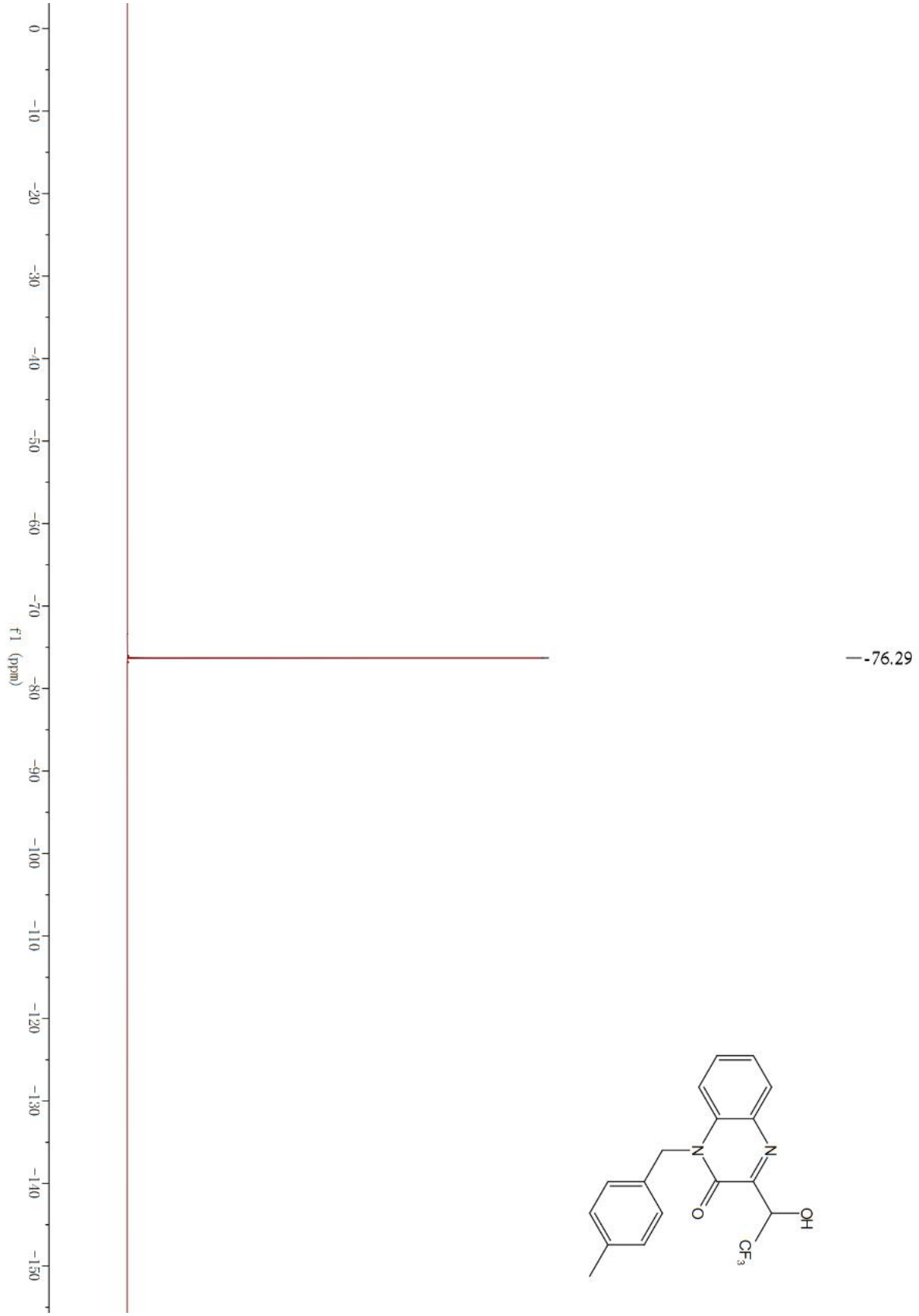
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g**



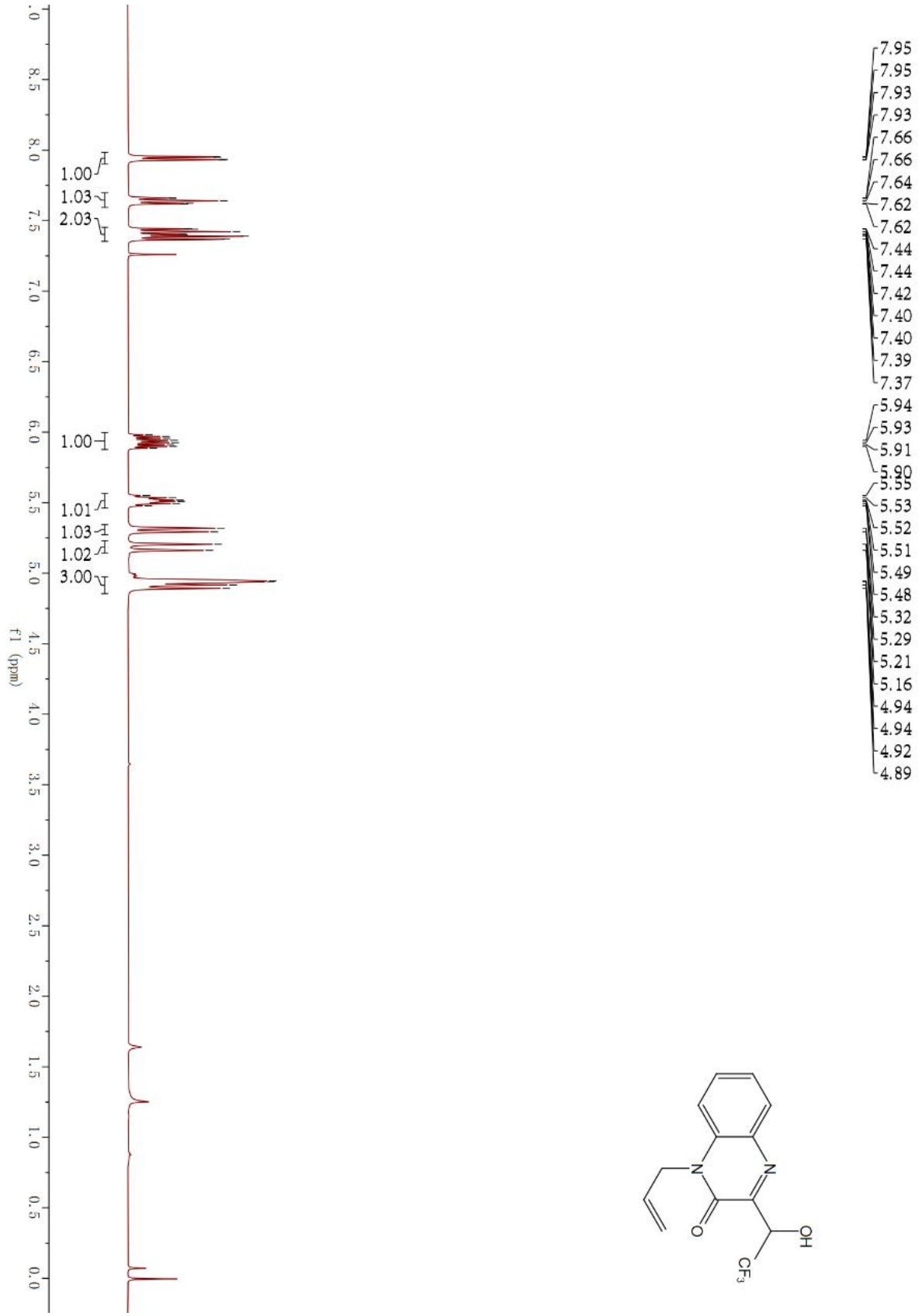
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3g**



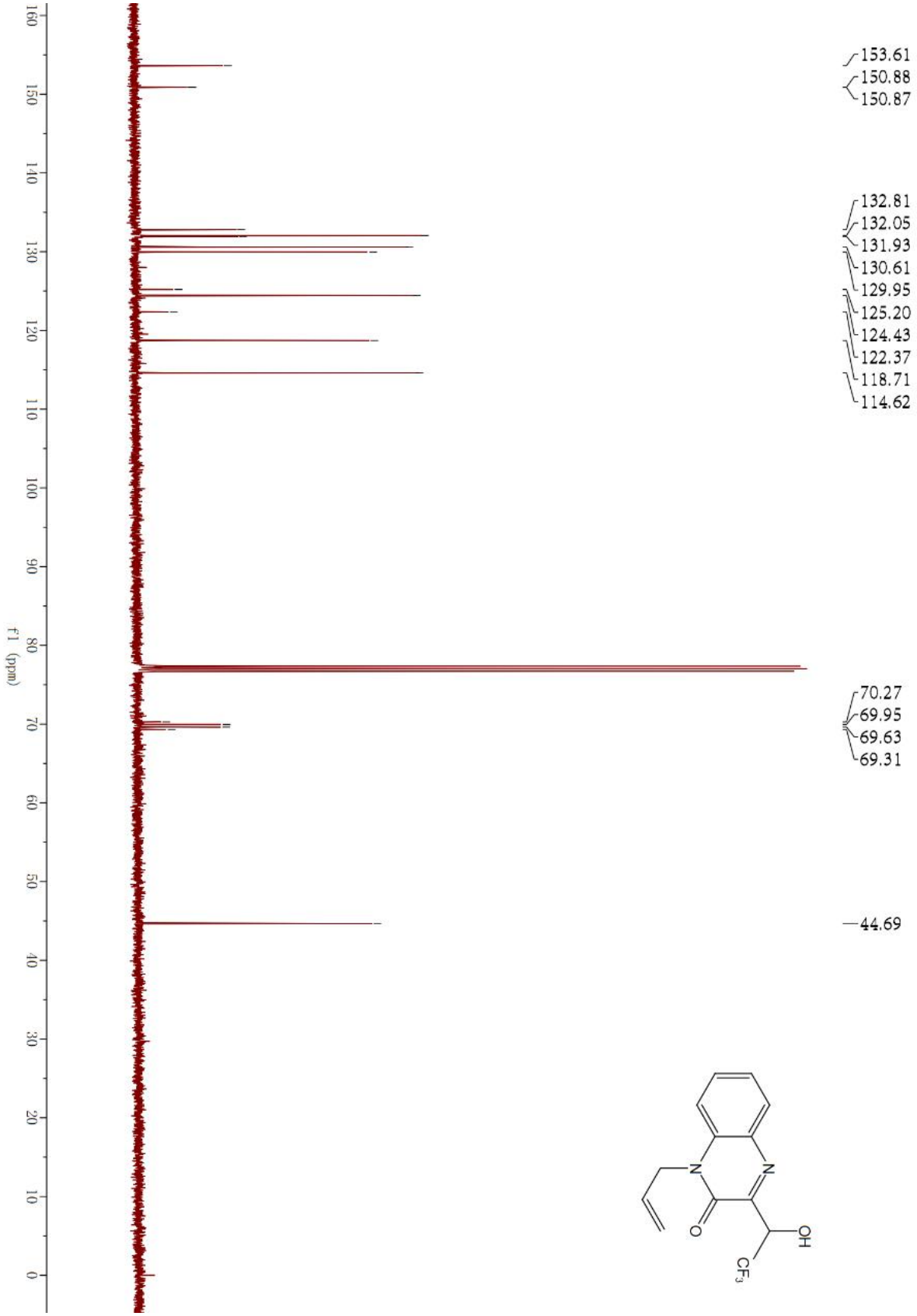
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3g**



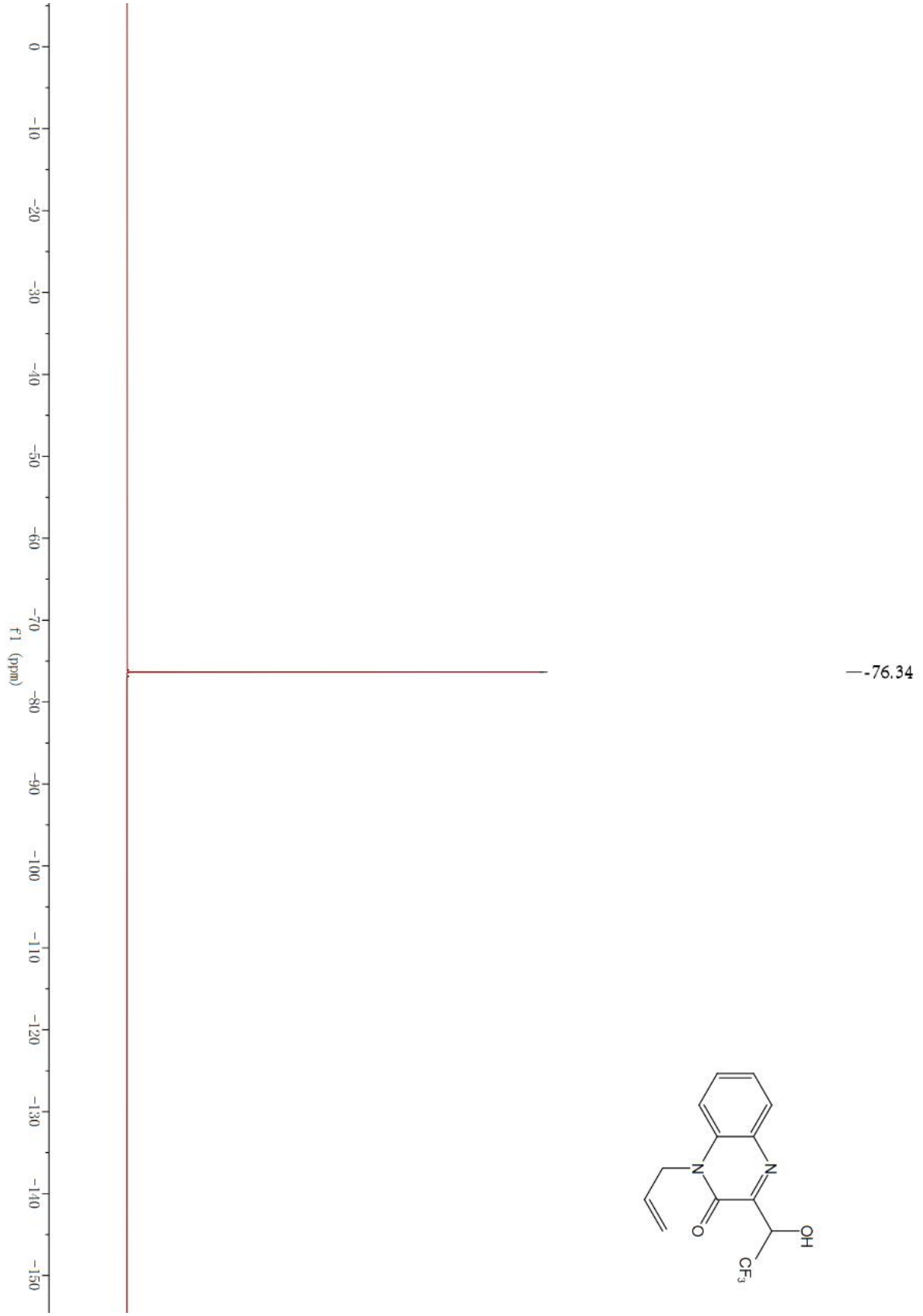
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h**



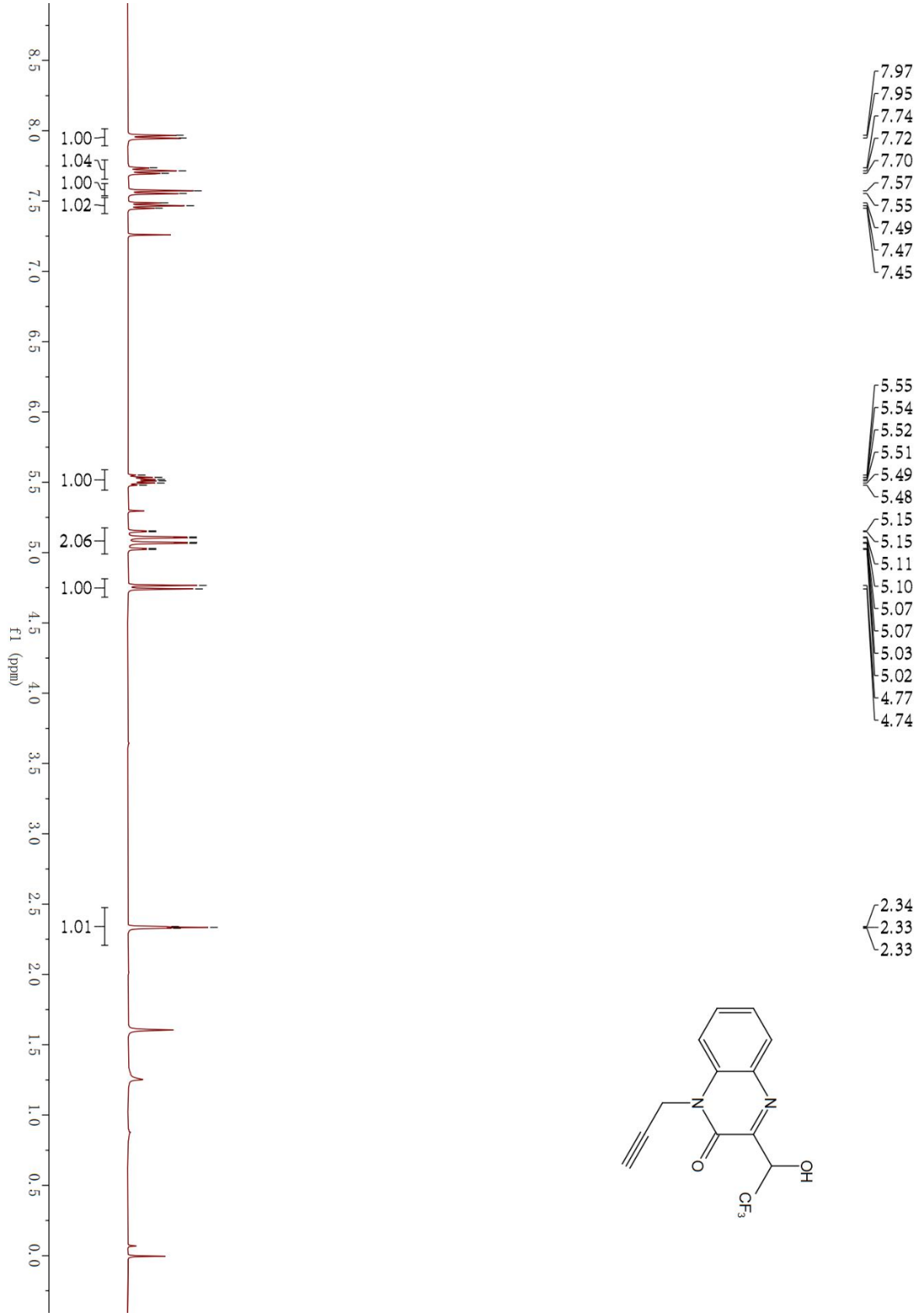
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3h**



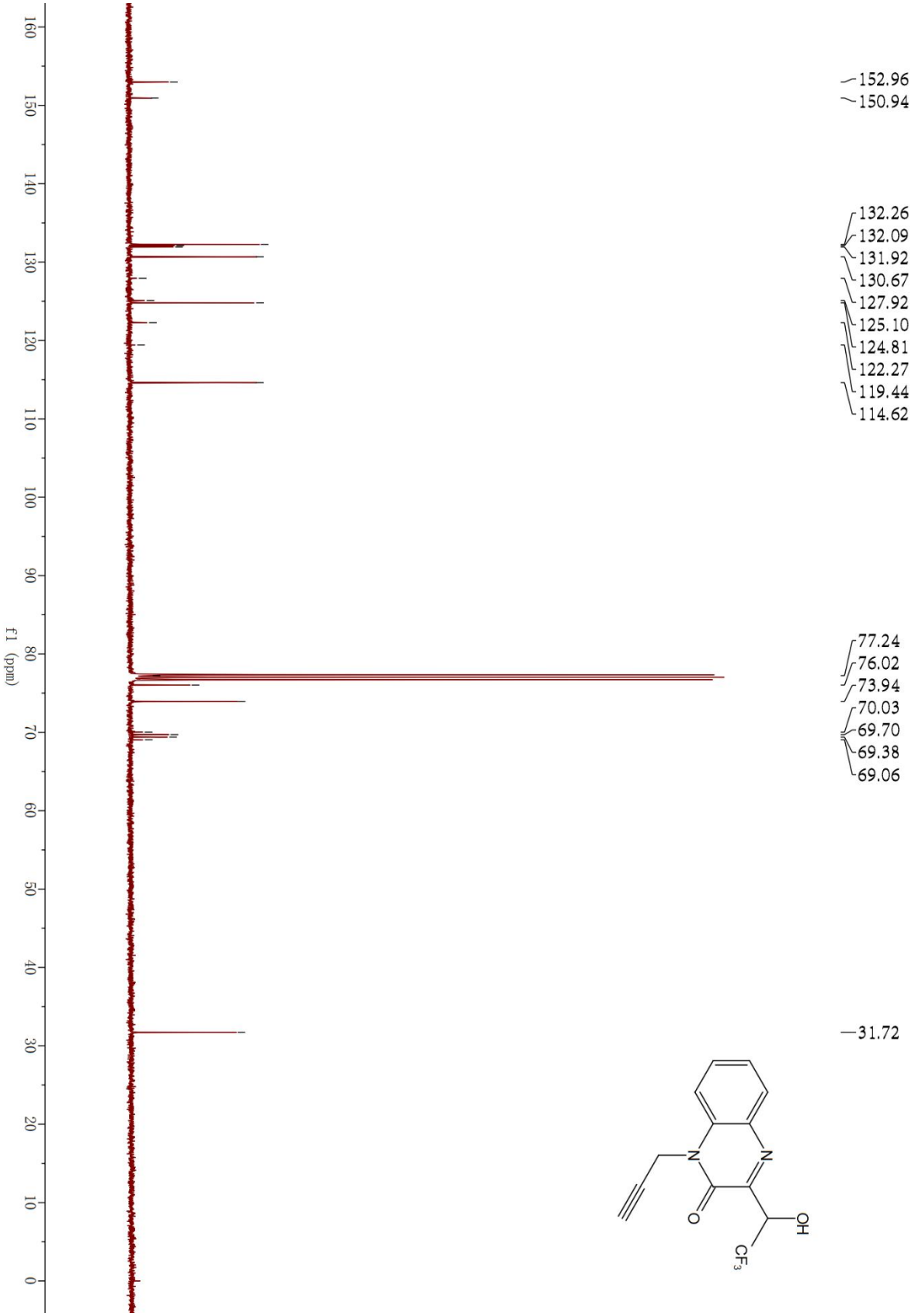
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3h**



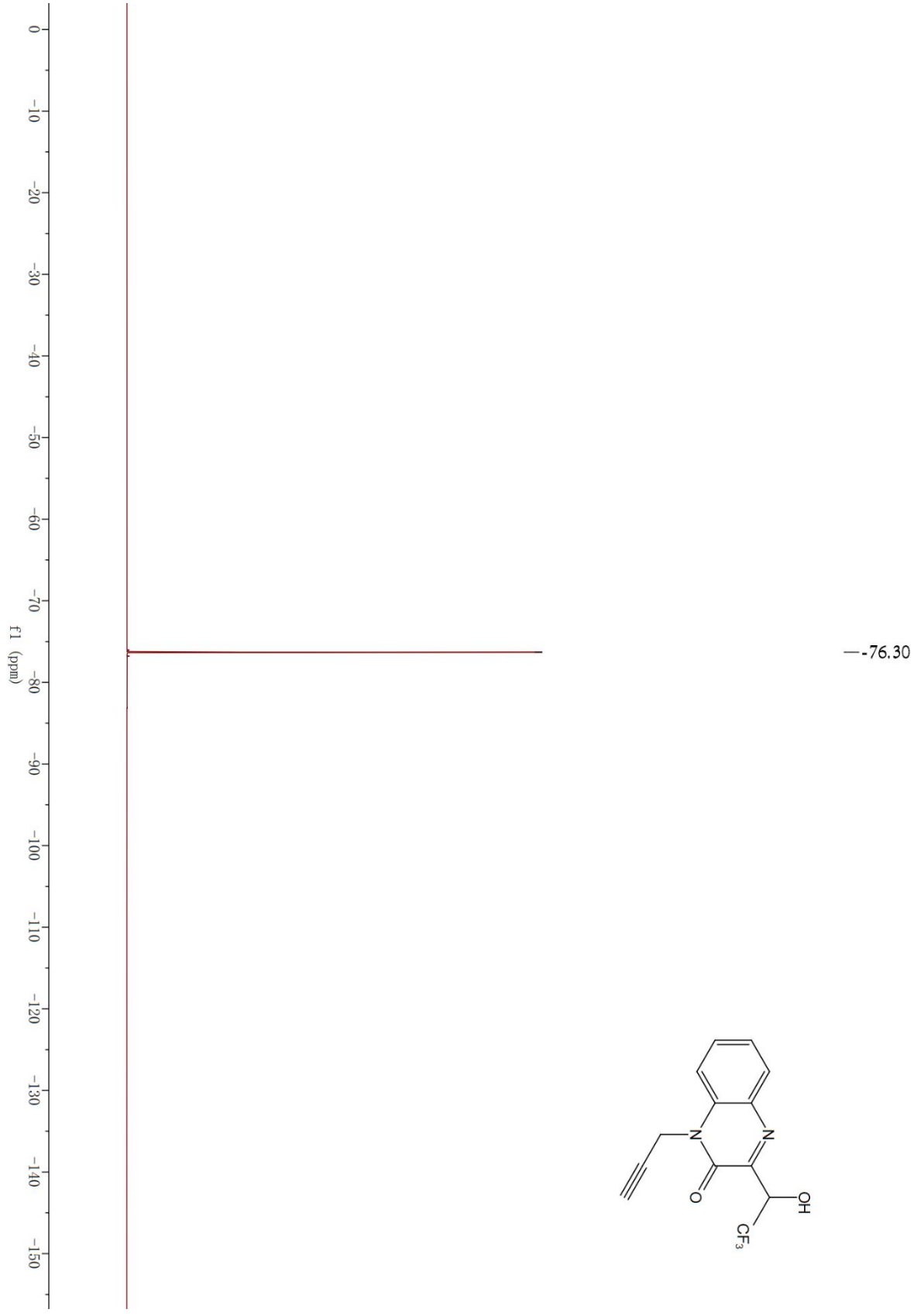
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i**



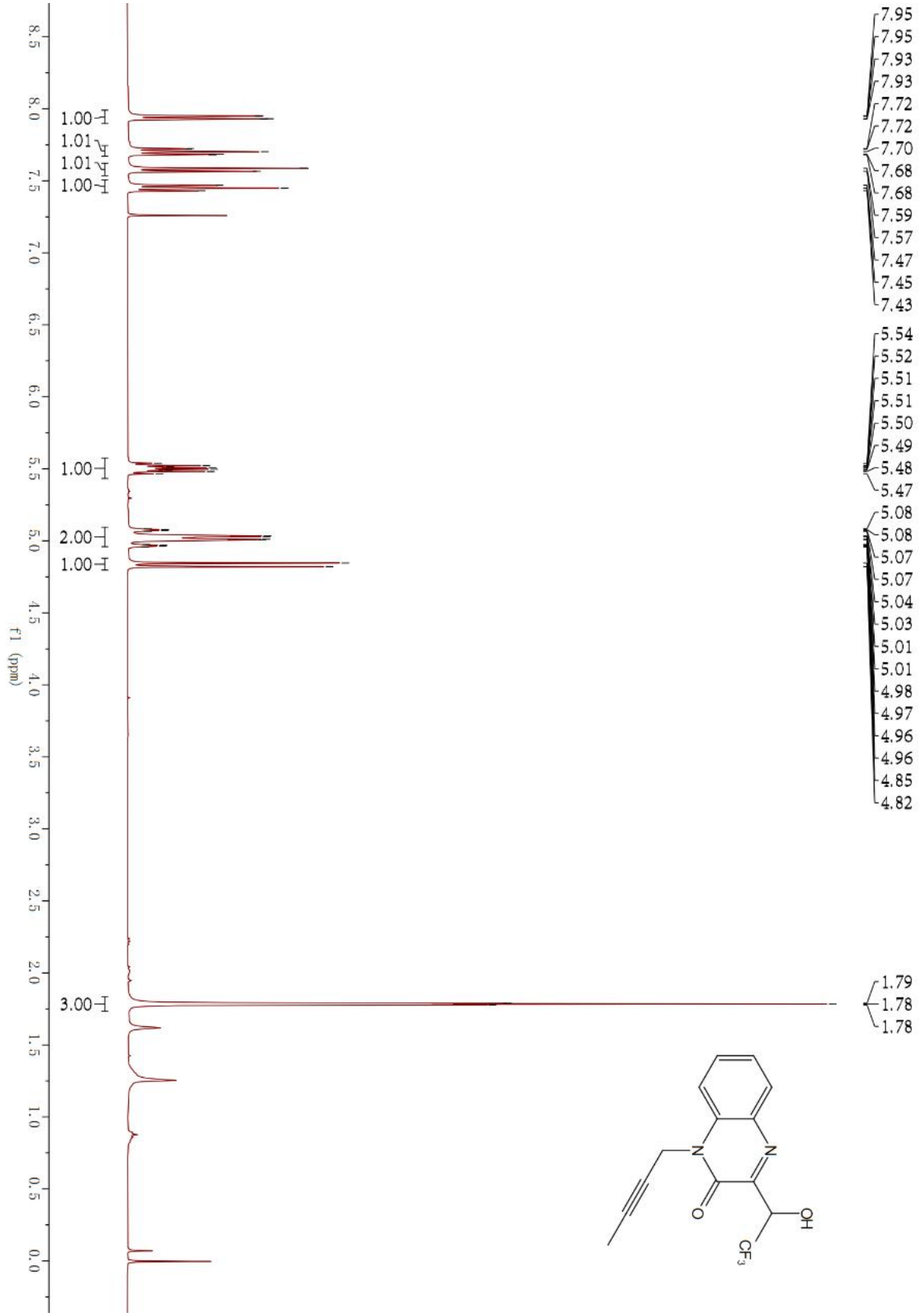
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3i**



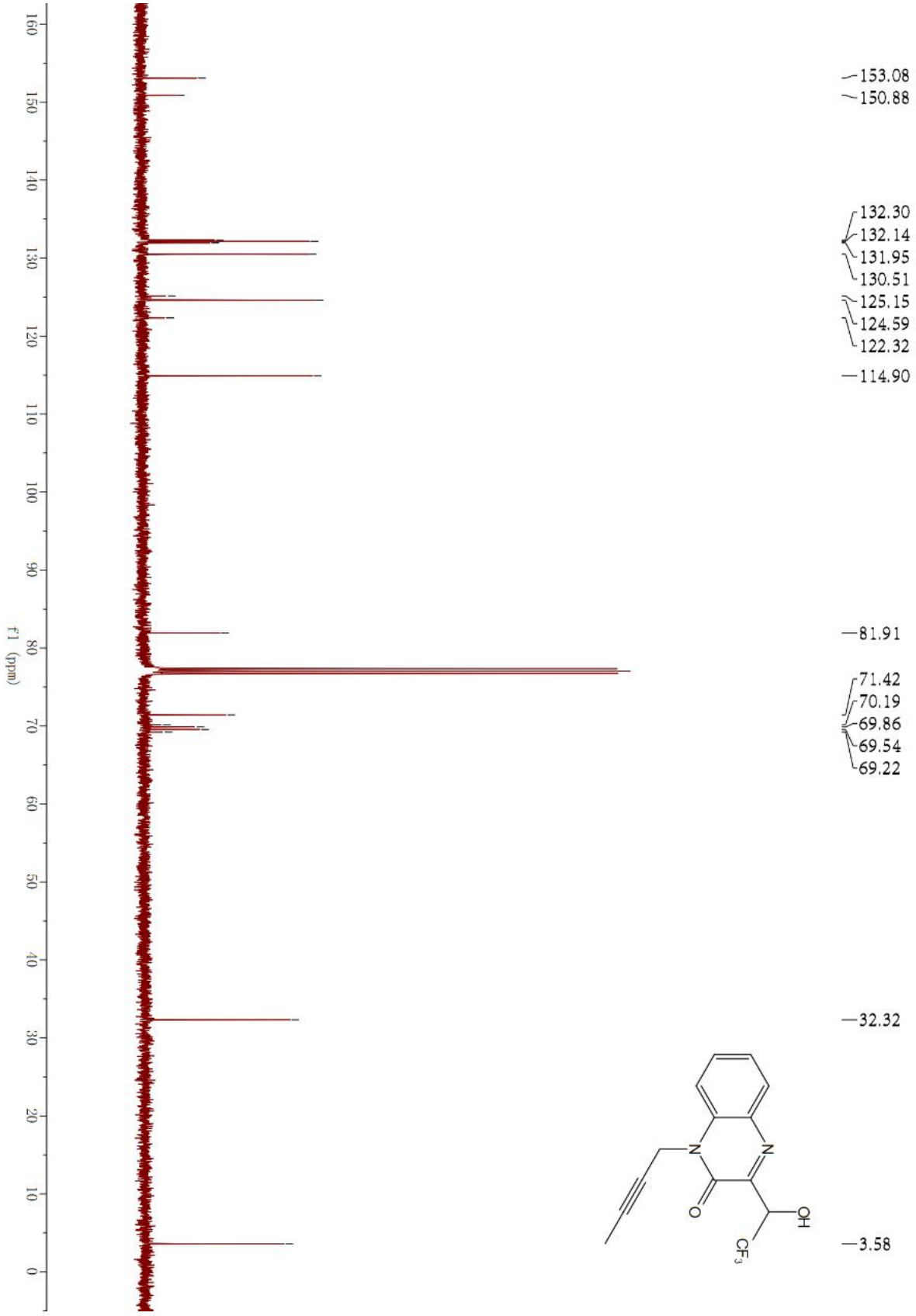
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3i**



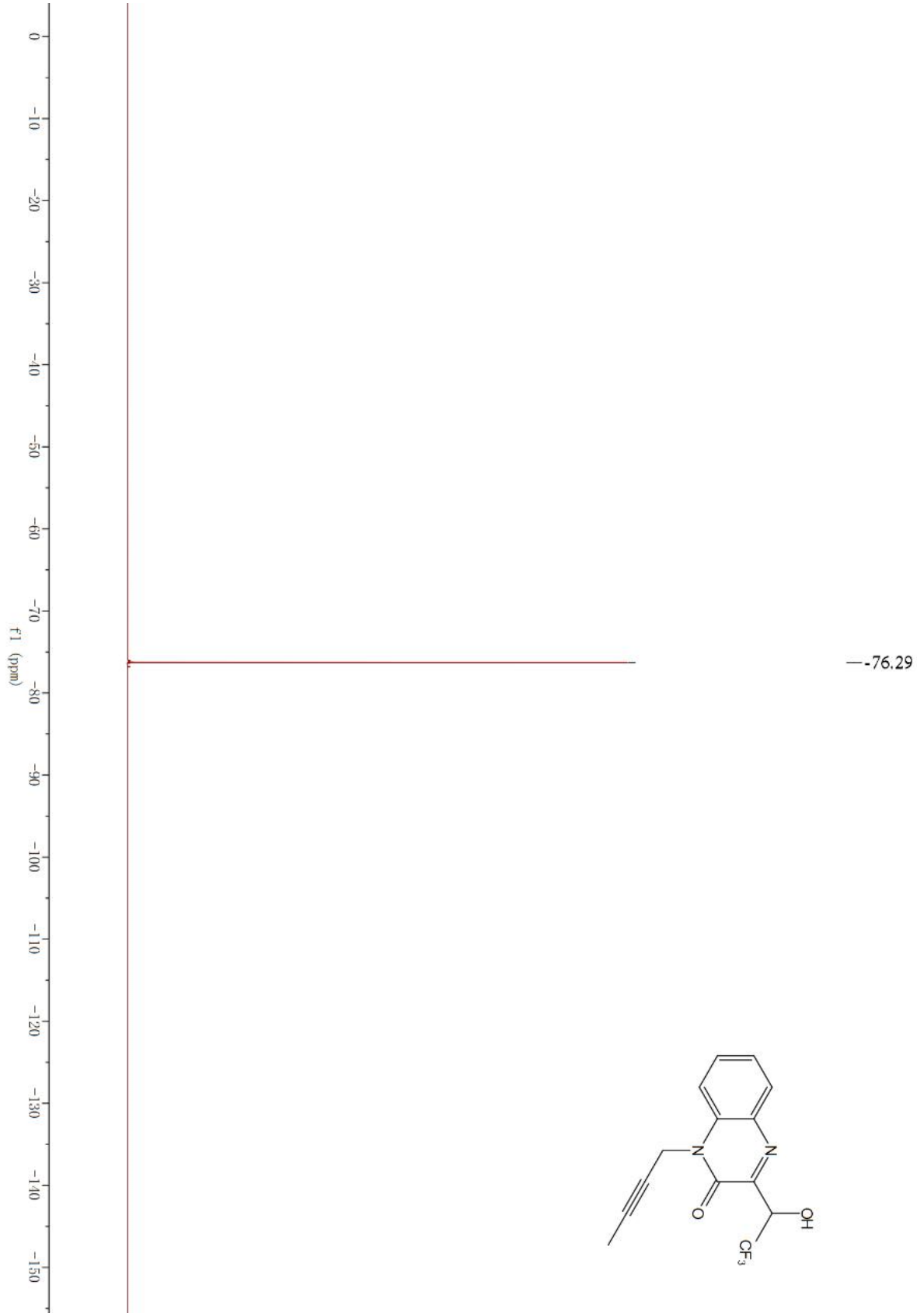
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3j**



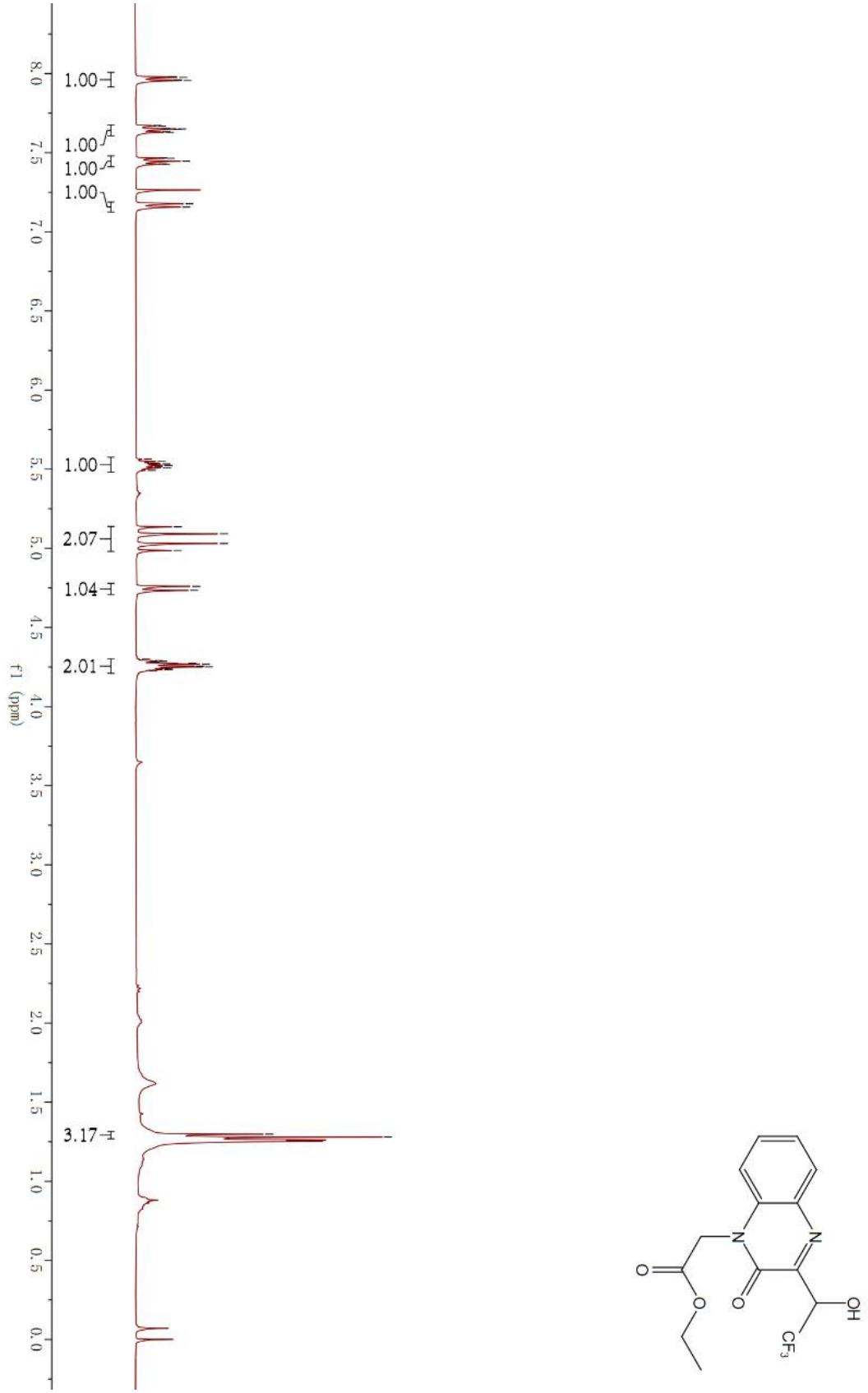
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3j**



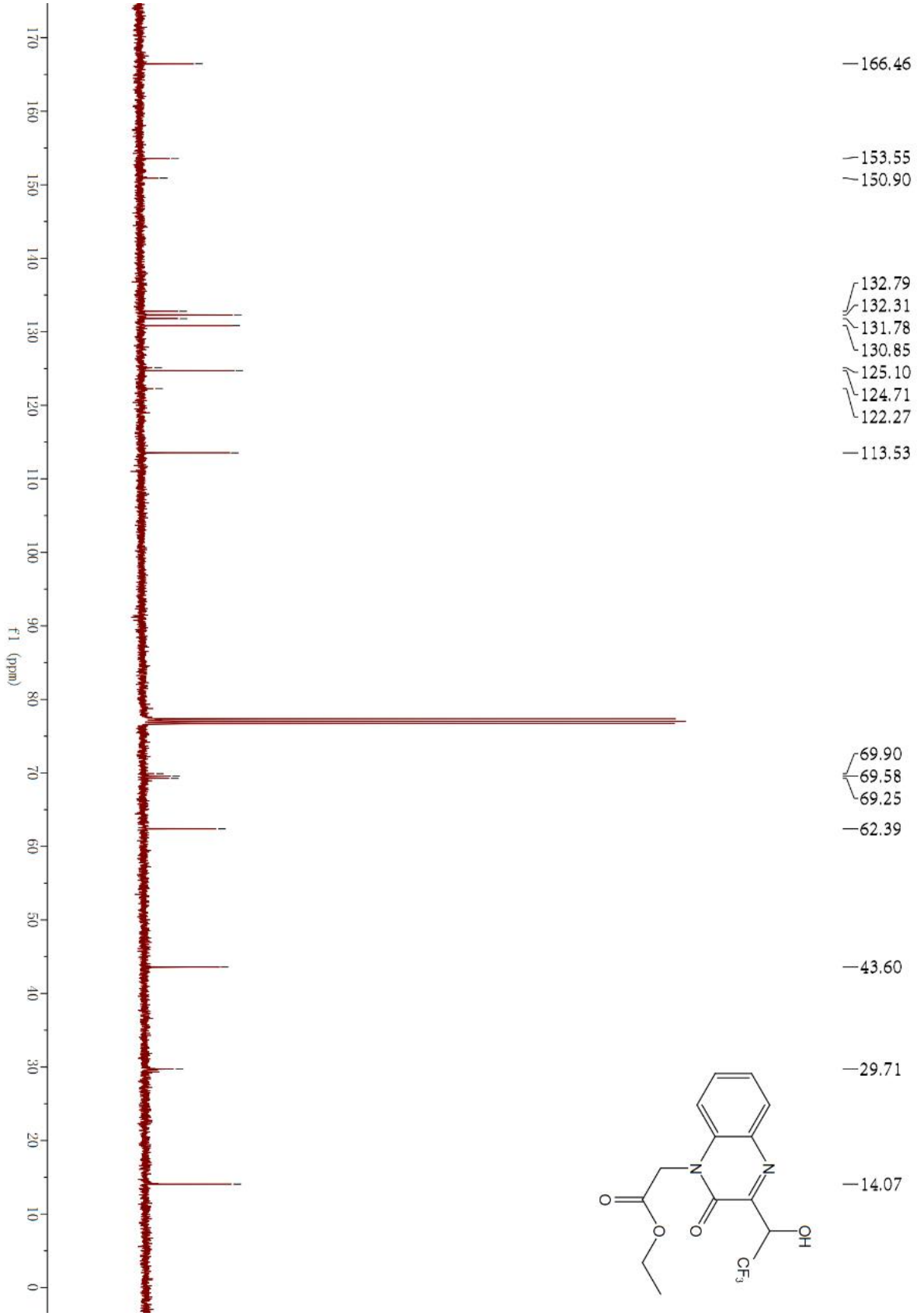
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3j**



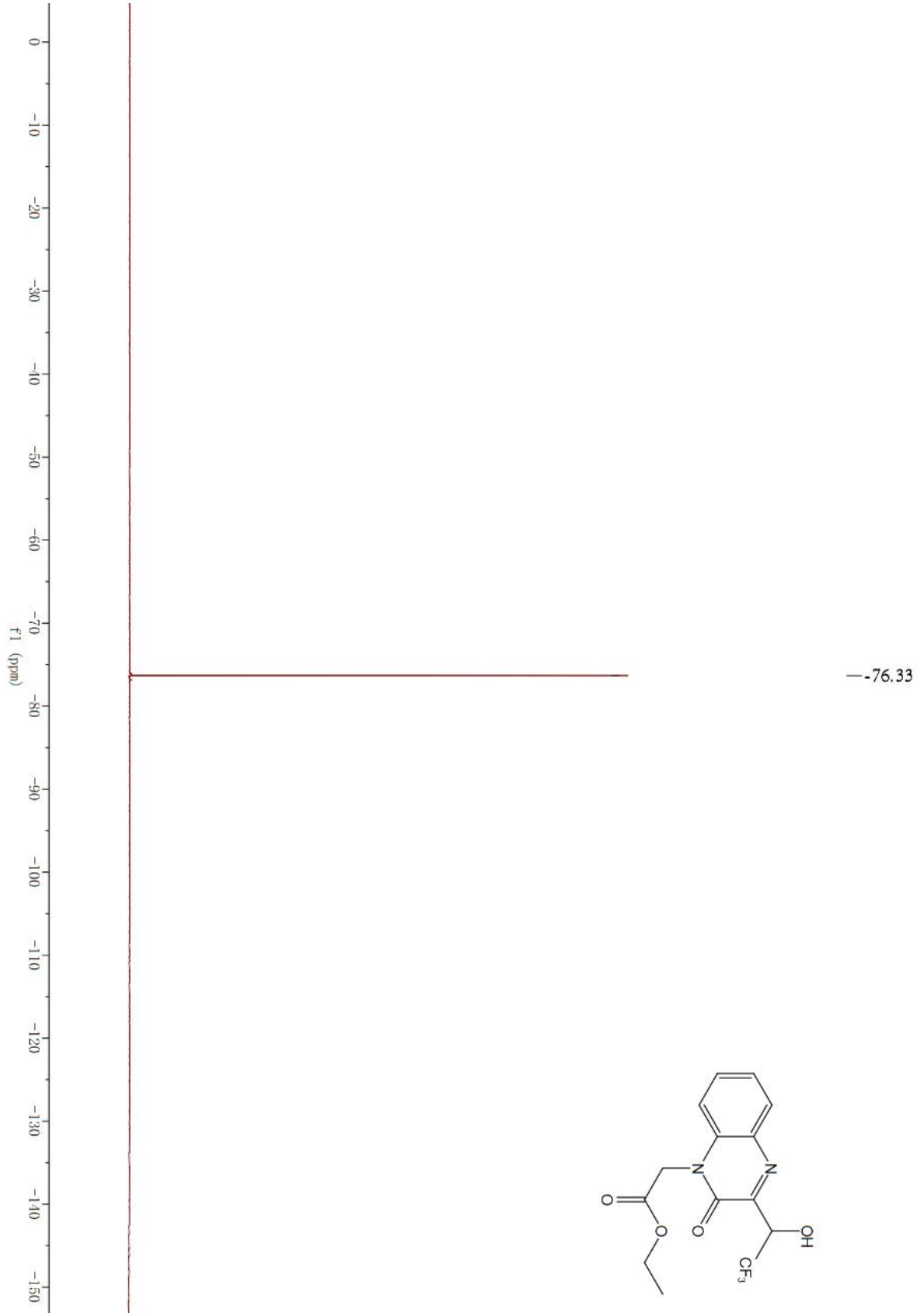
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3k**



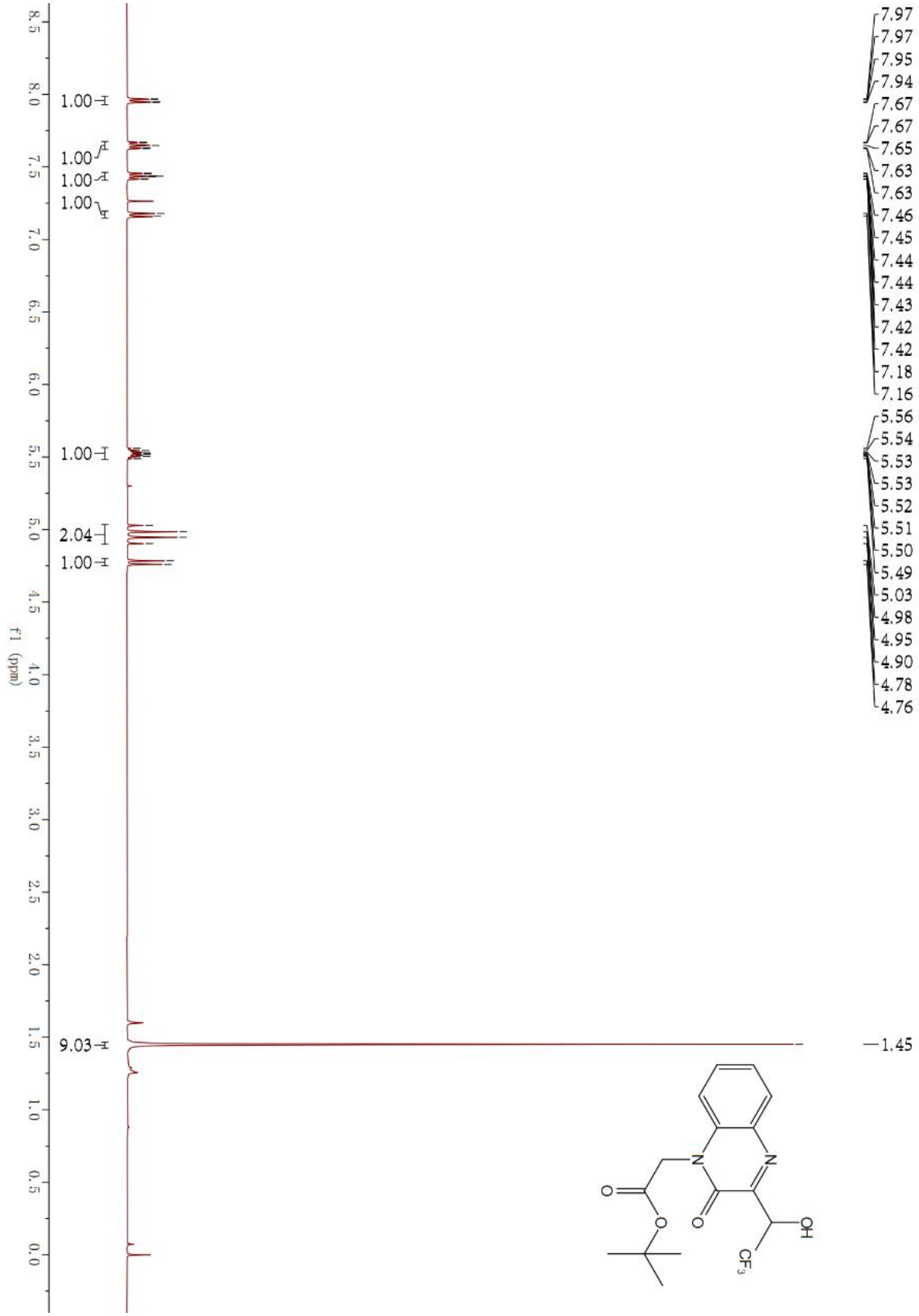
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3k**



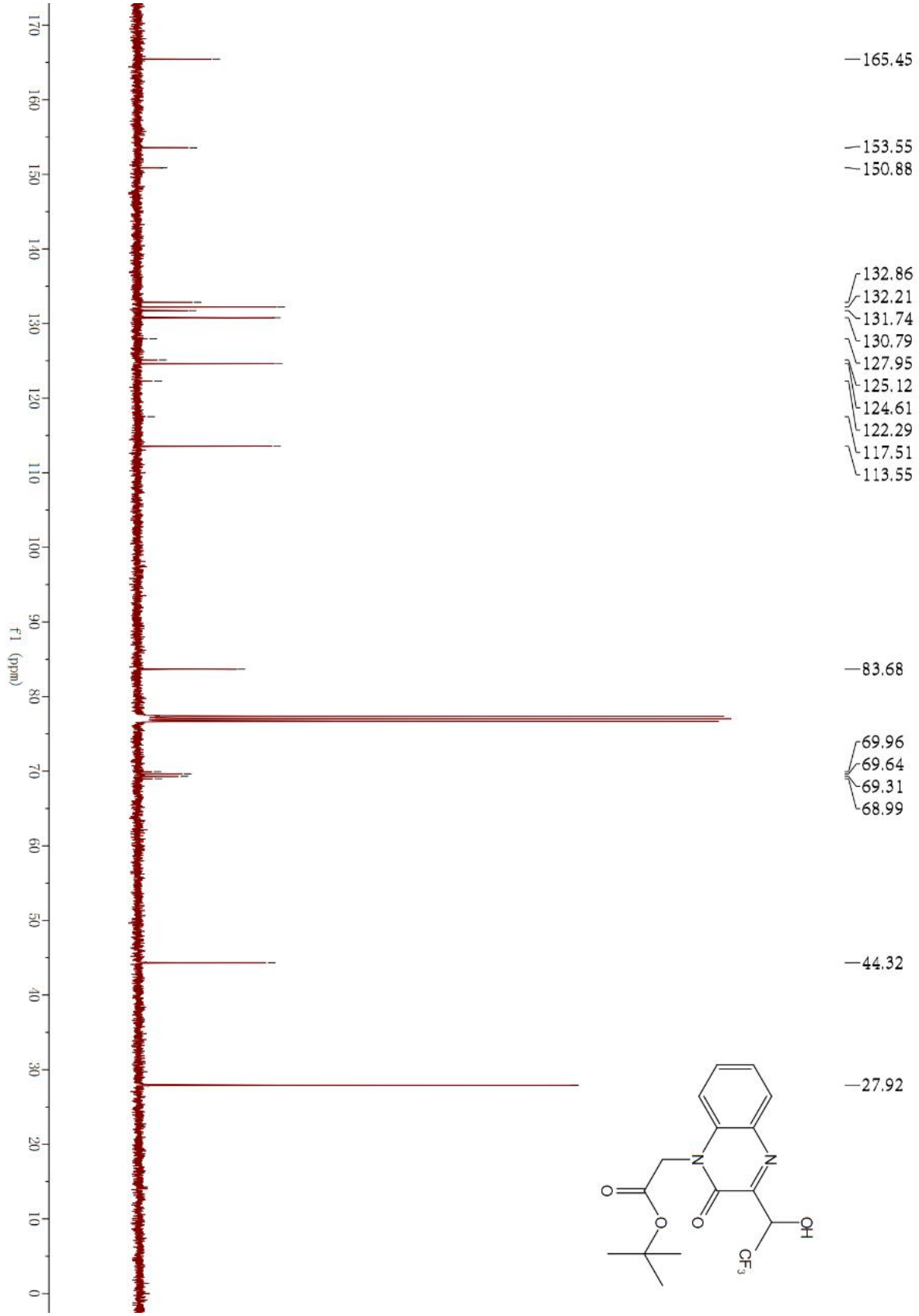
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3k**



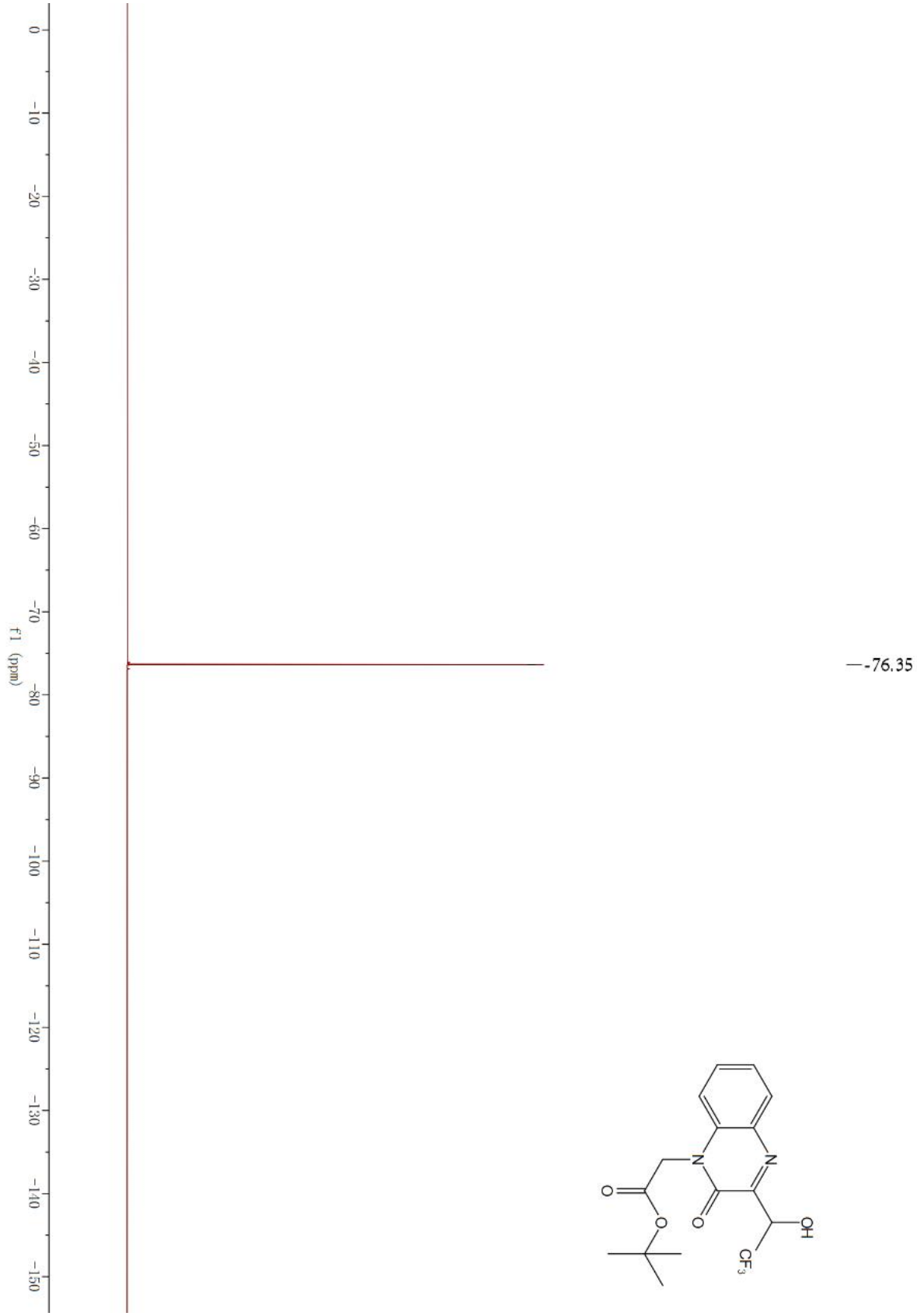
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3l**



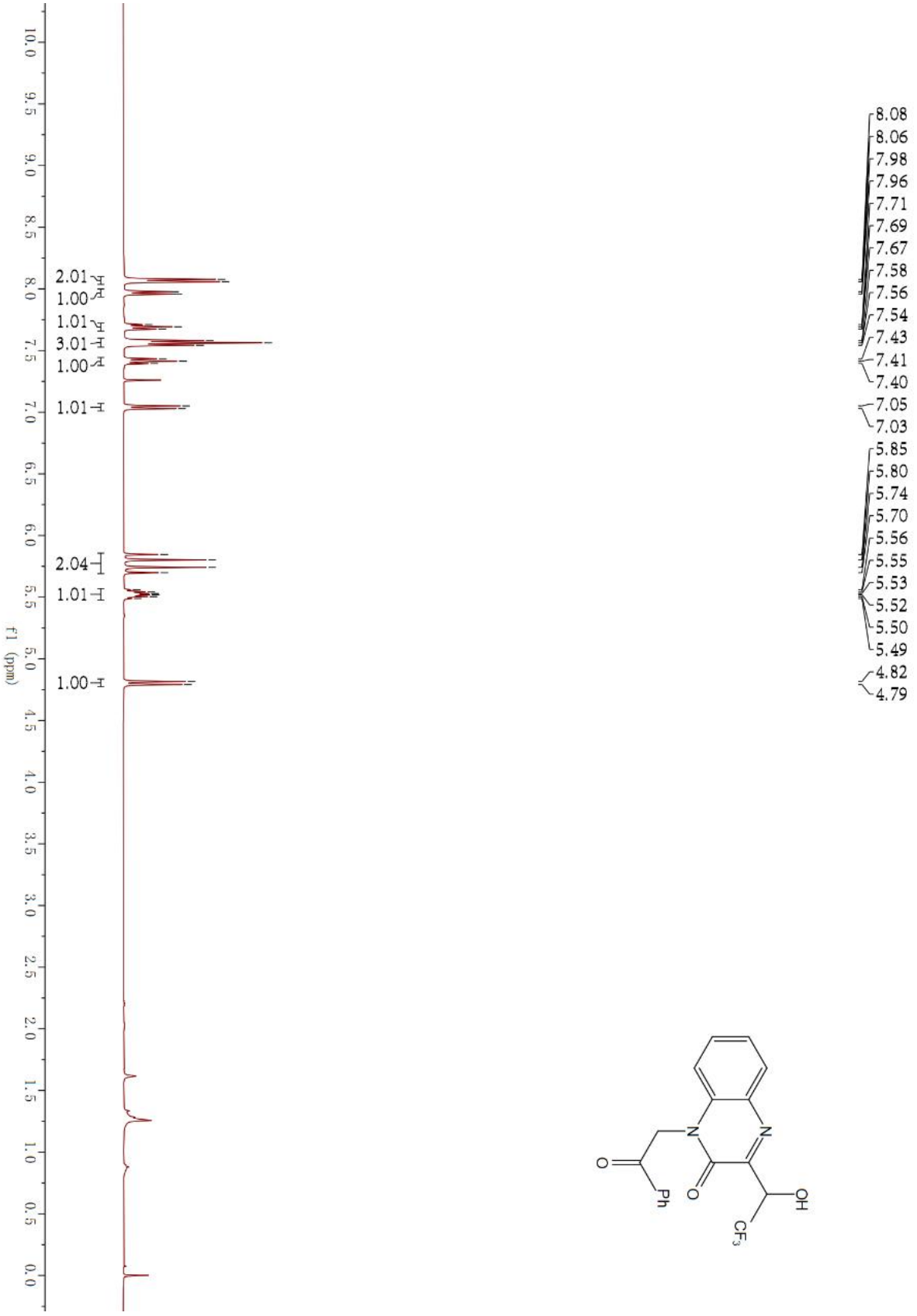
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3l**



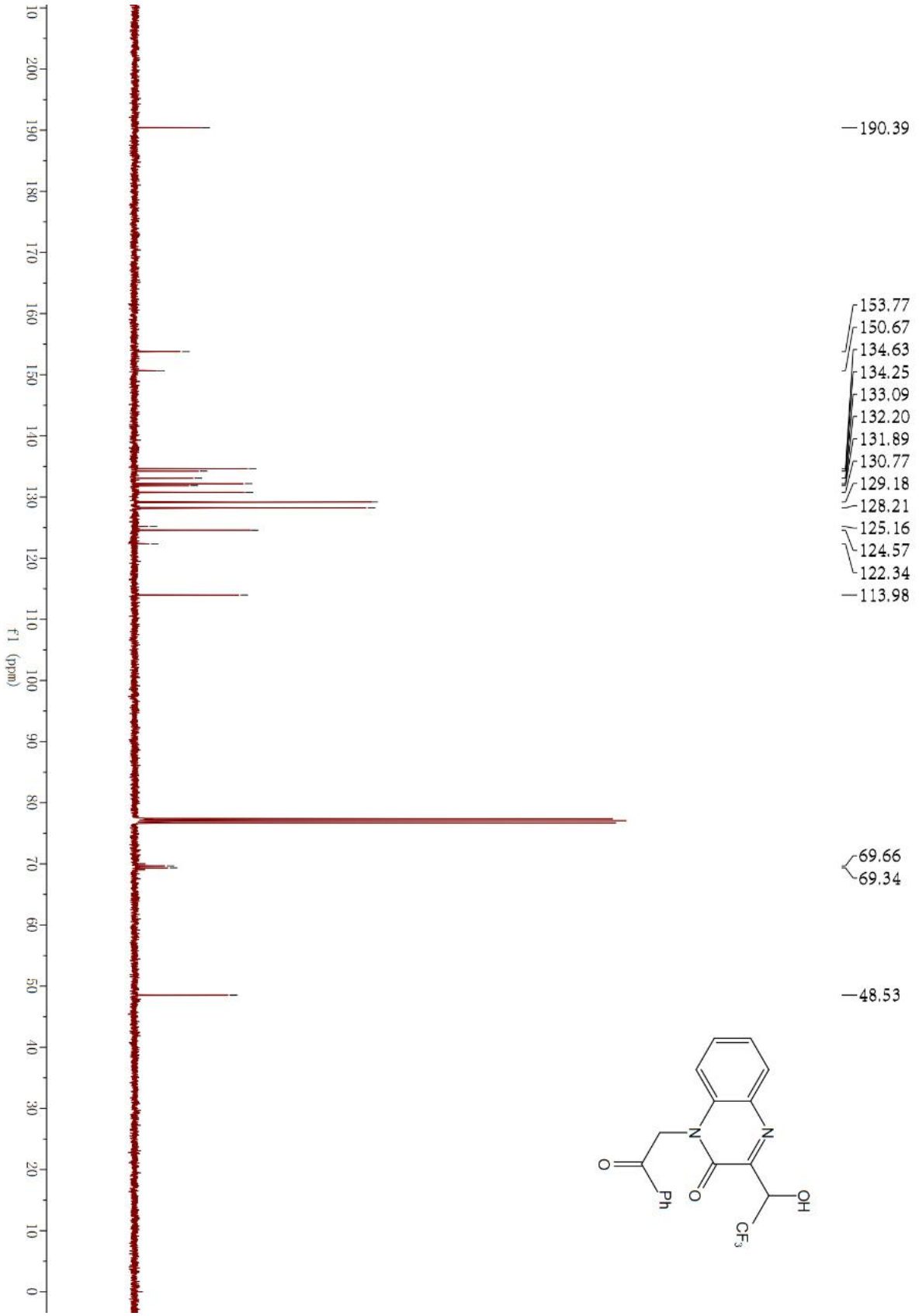
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3l**



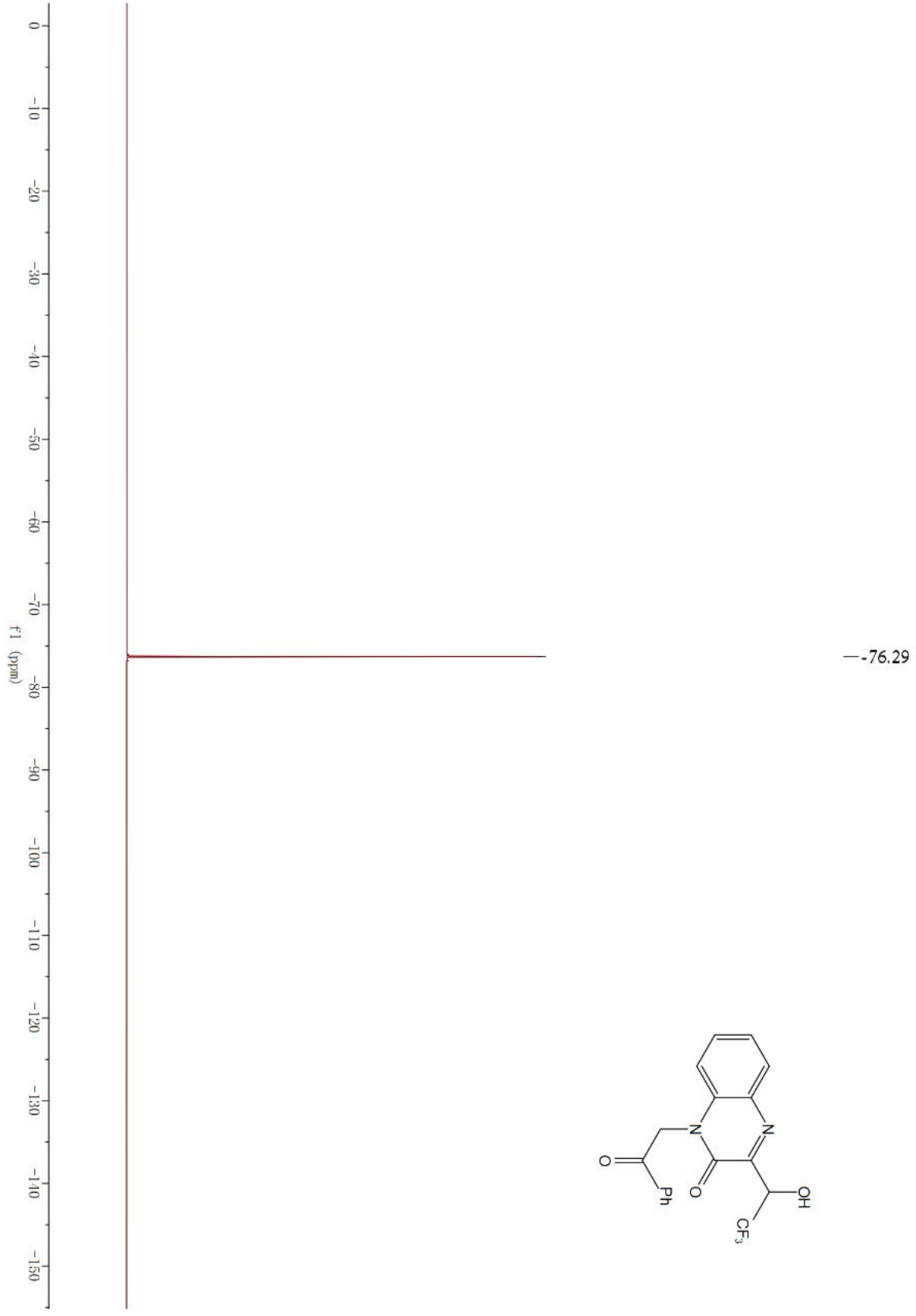
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3m**



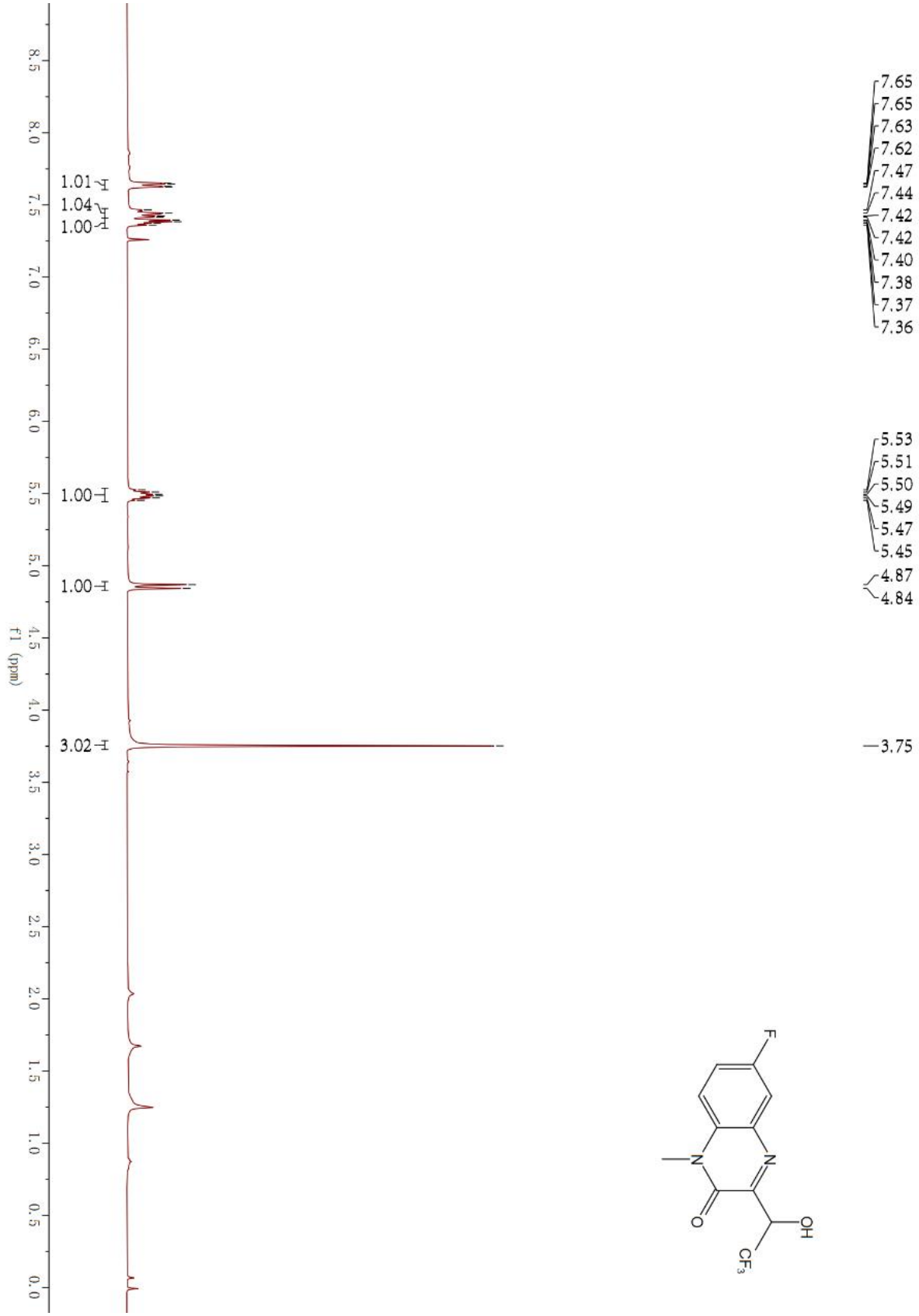
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3m**



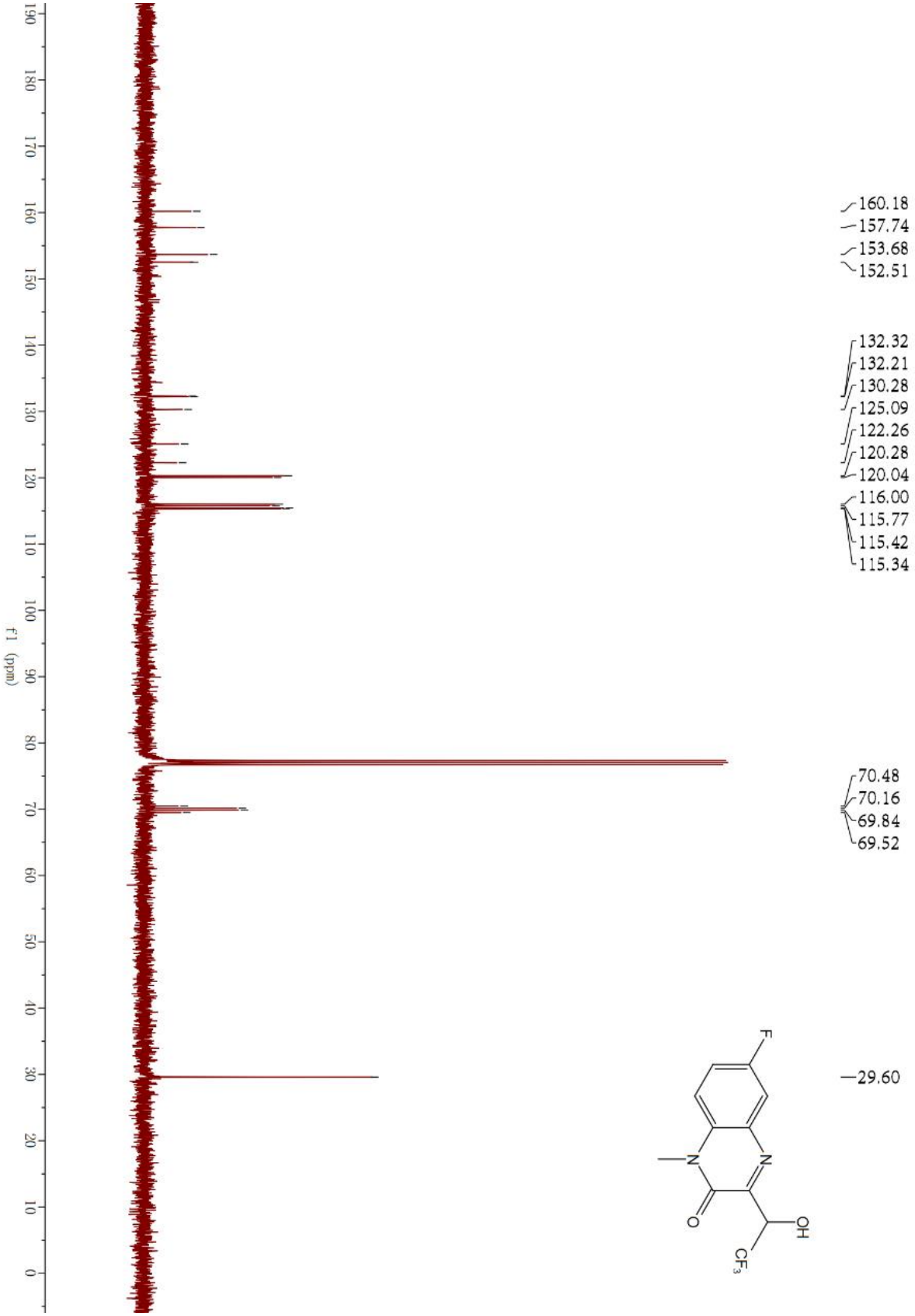
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3m**



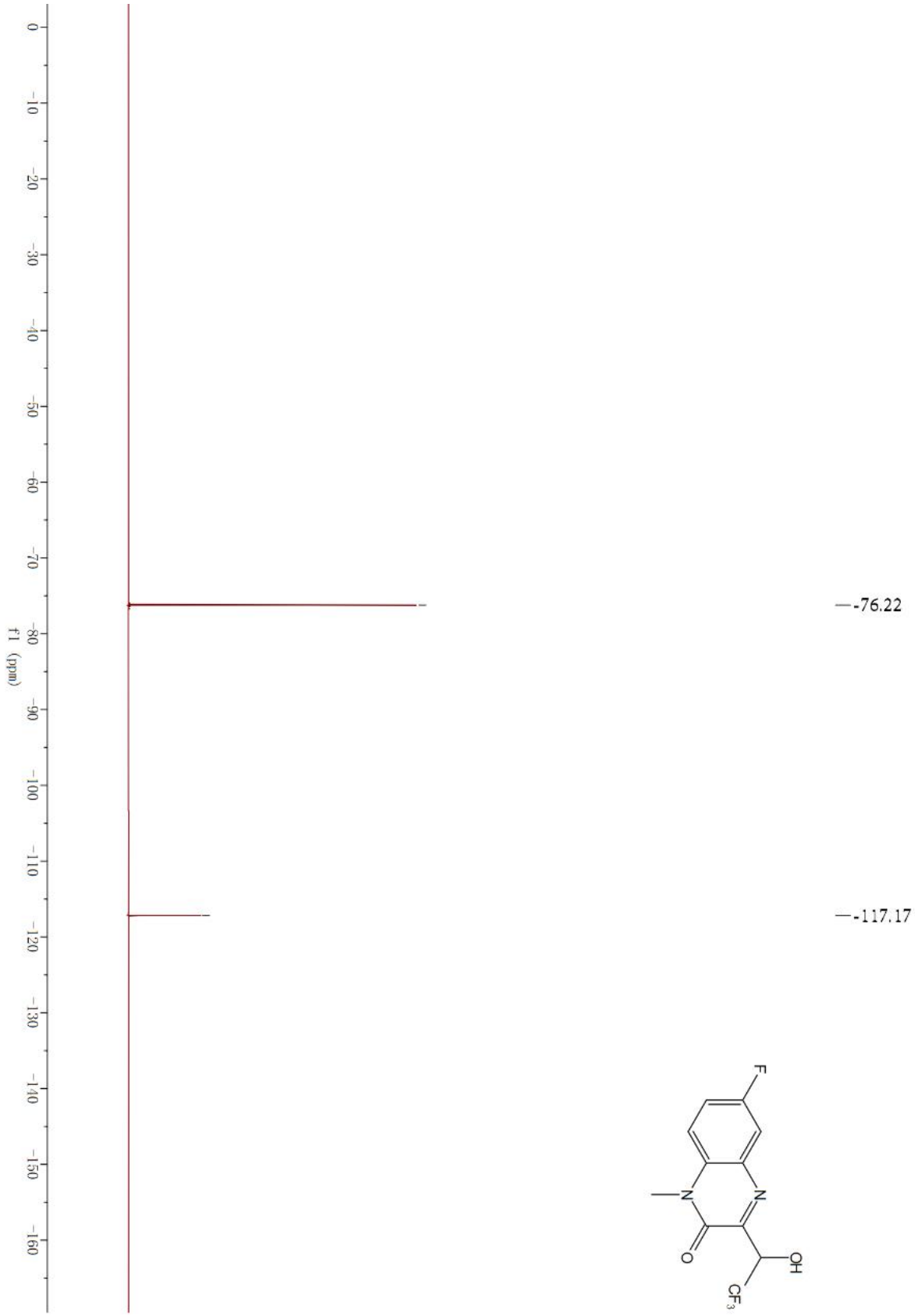
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3n**



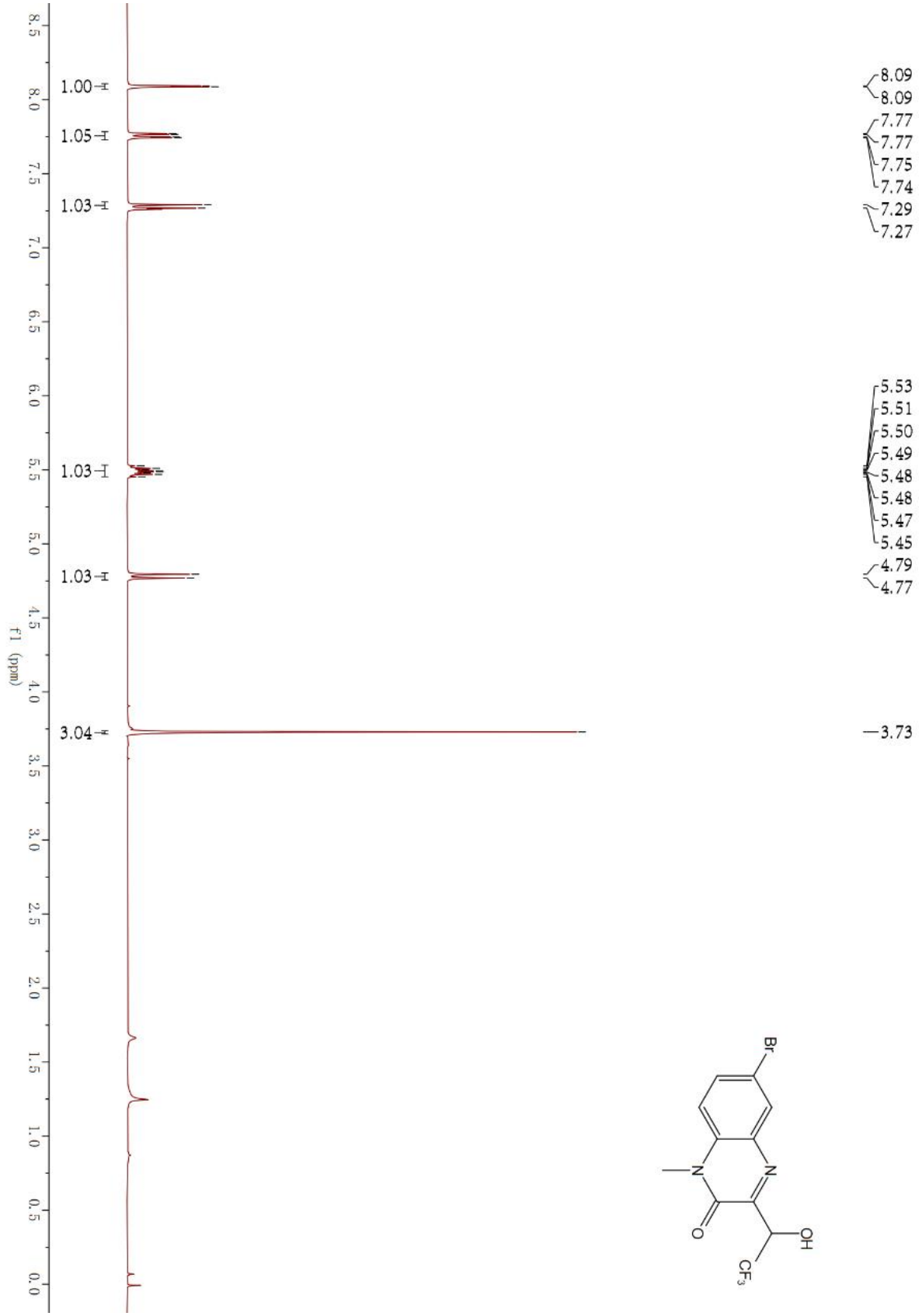
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3n**



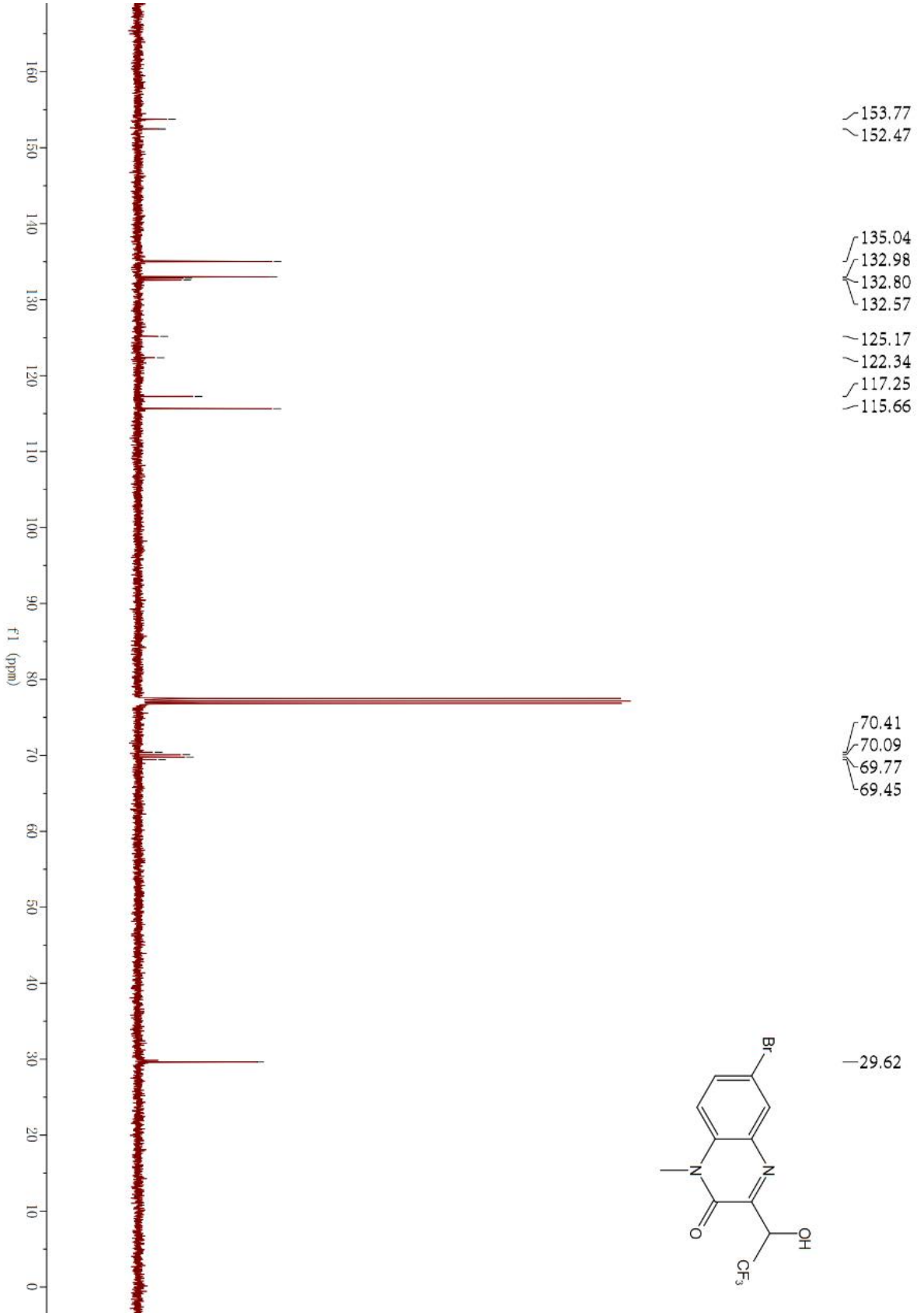
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3n**



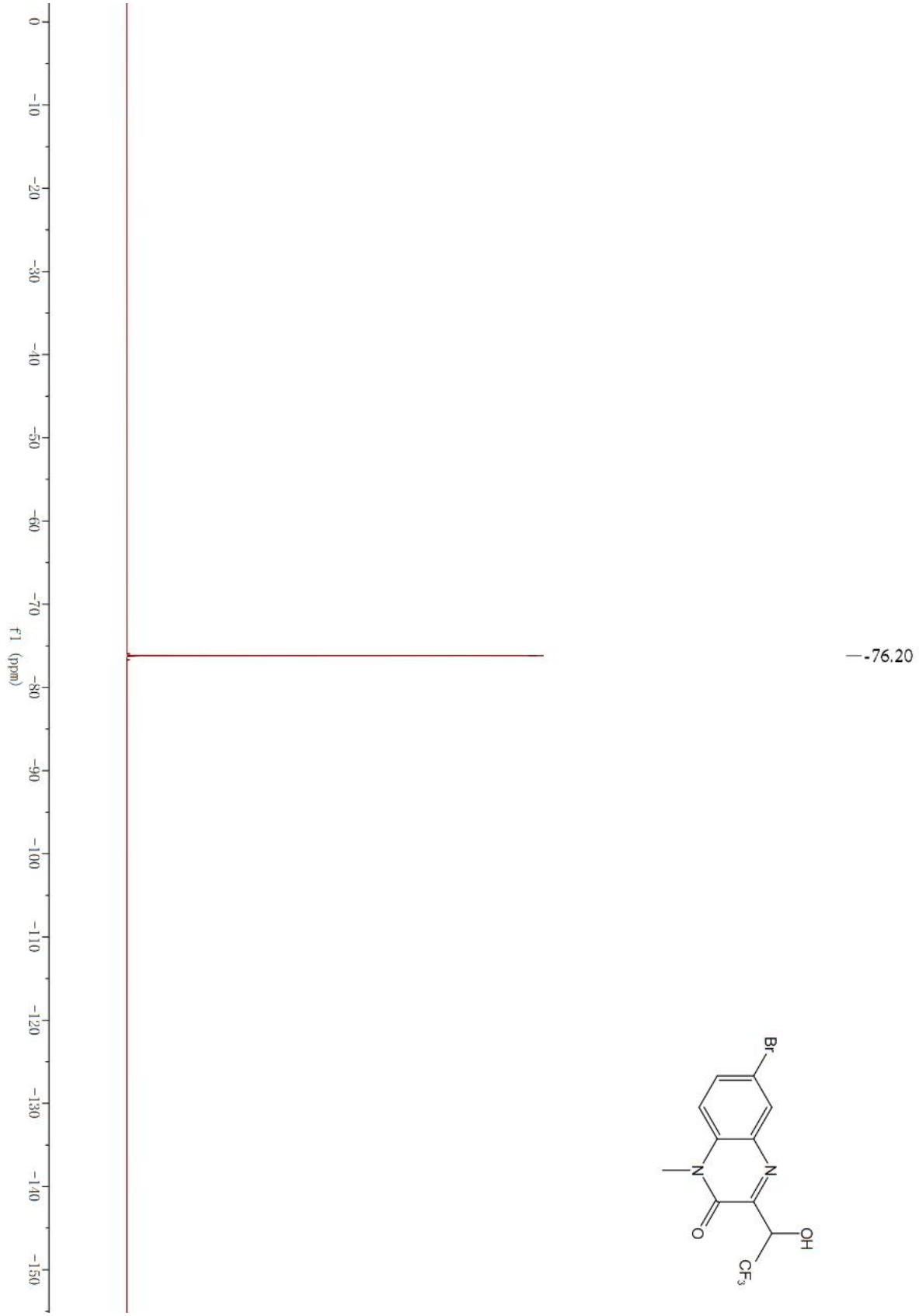
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3o**



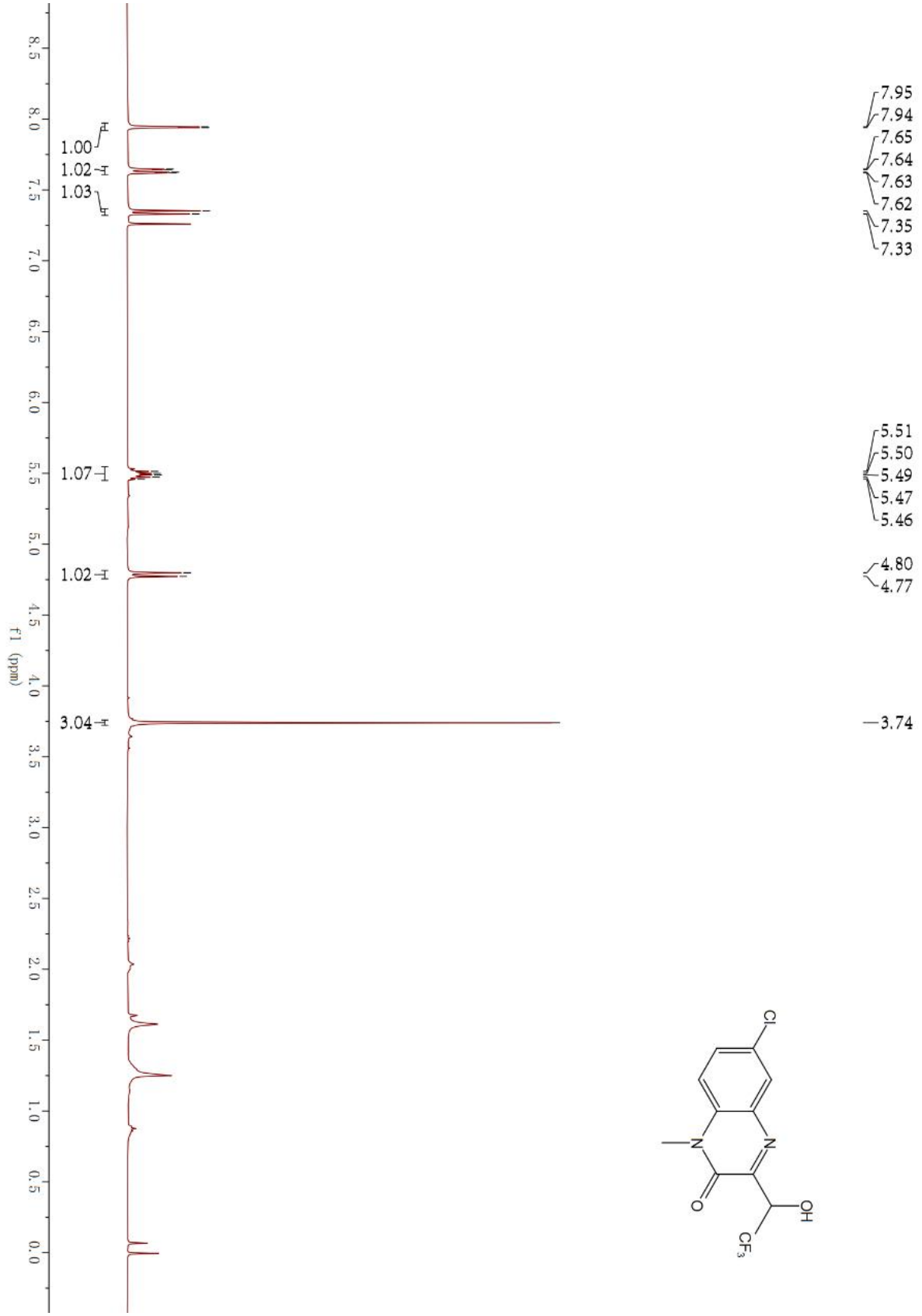
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3o**



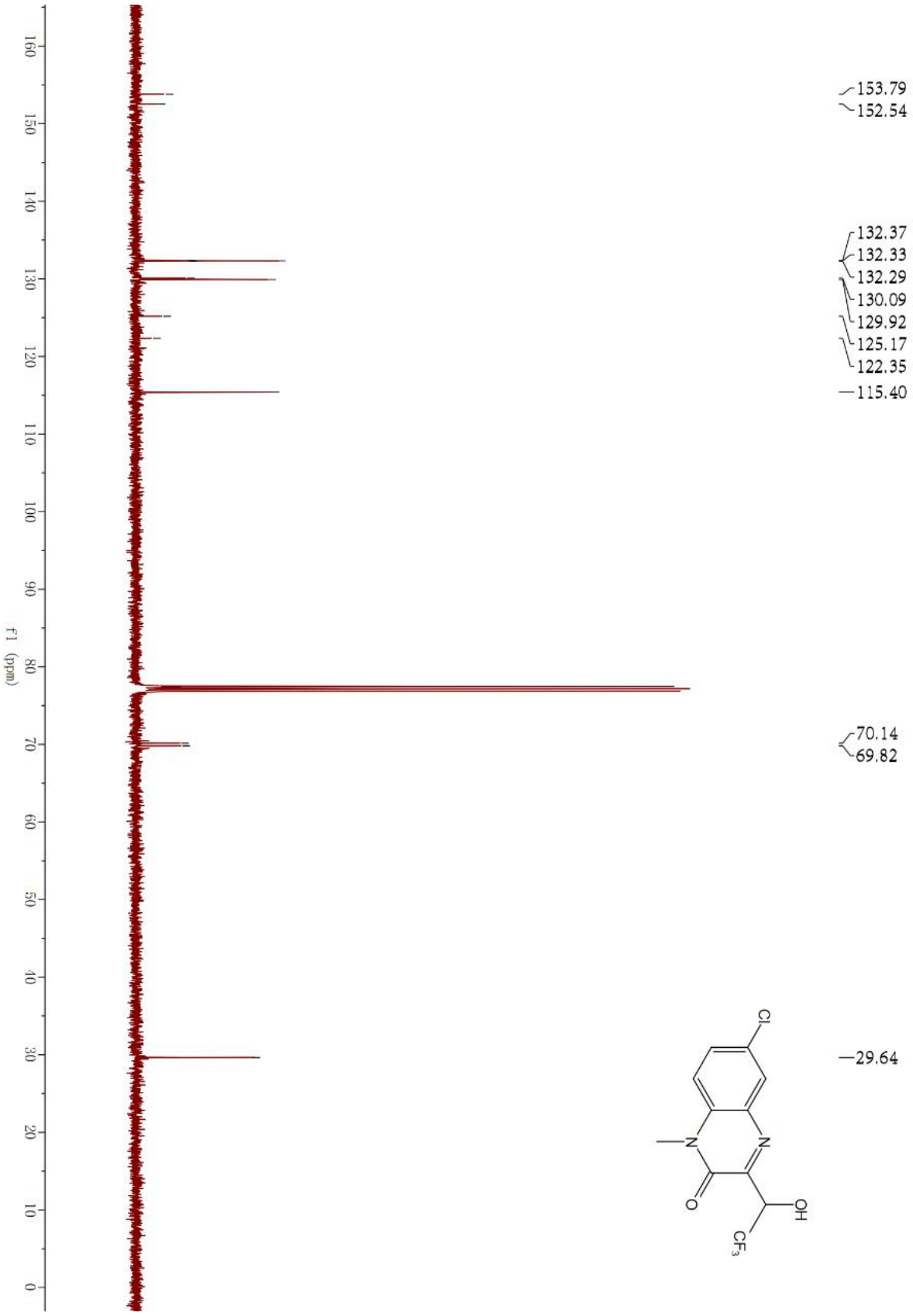
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3o**



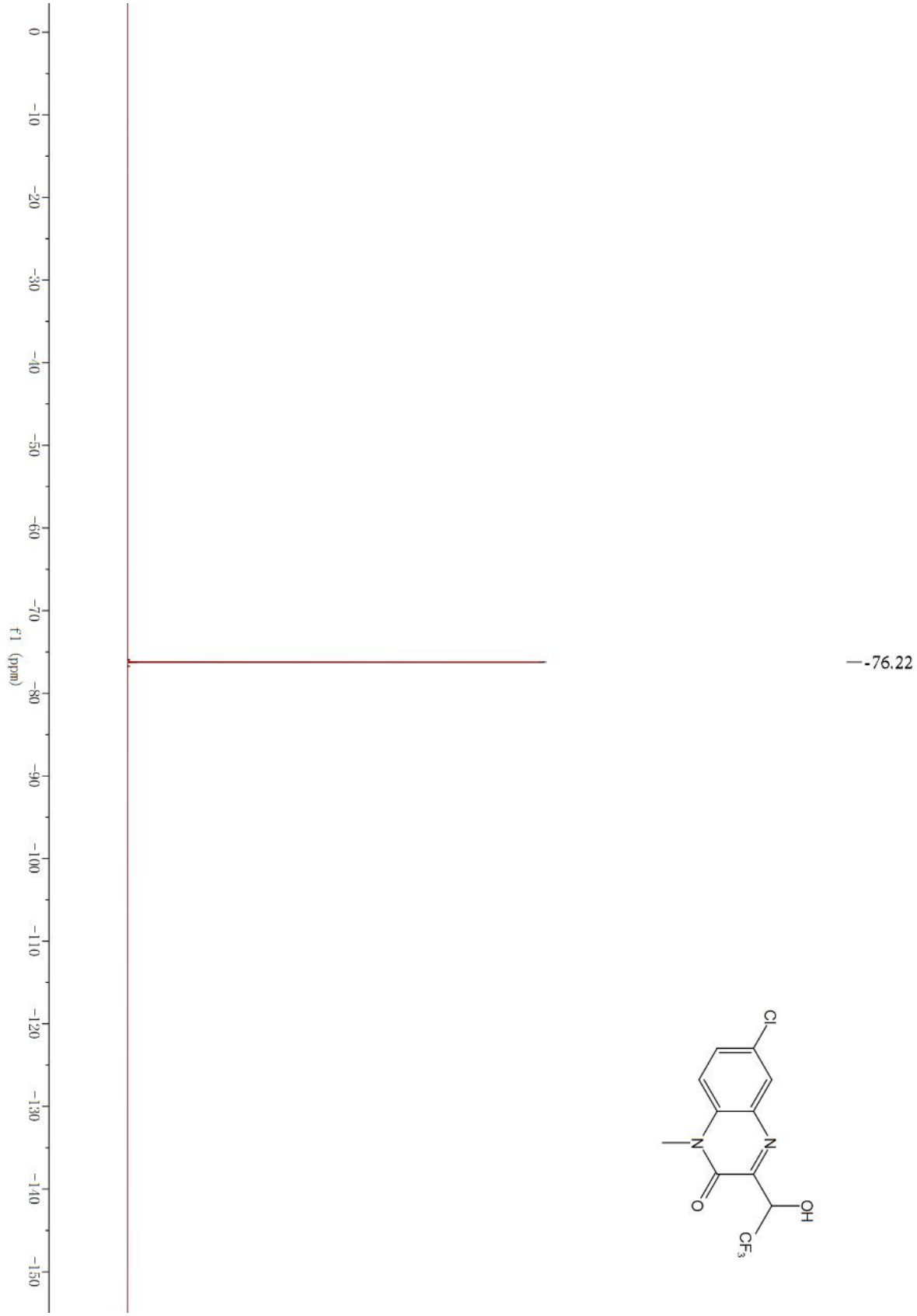
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3p**



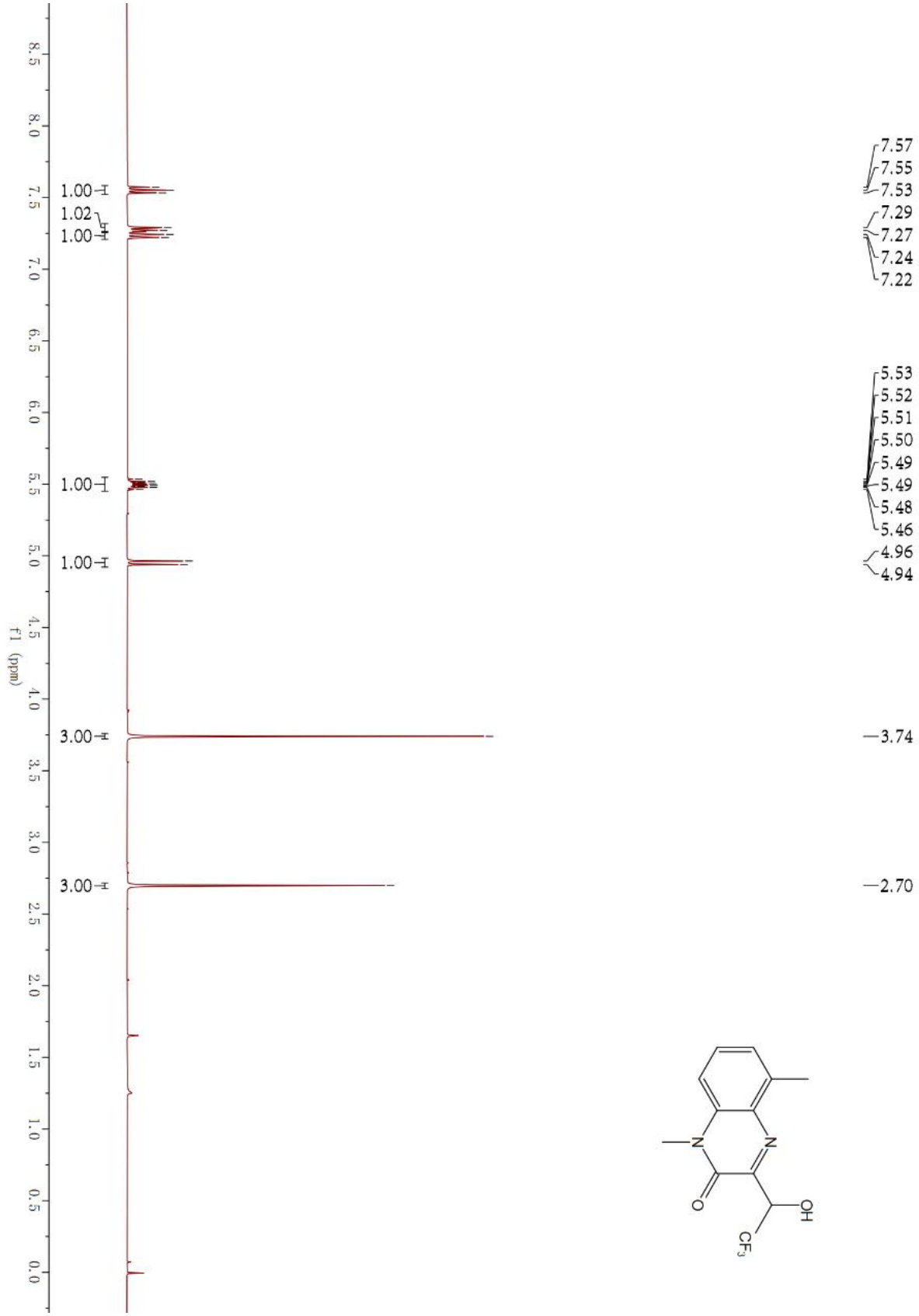
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3p**



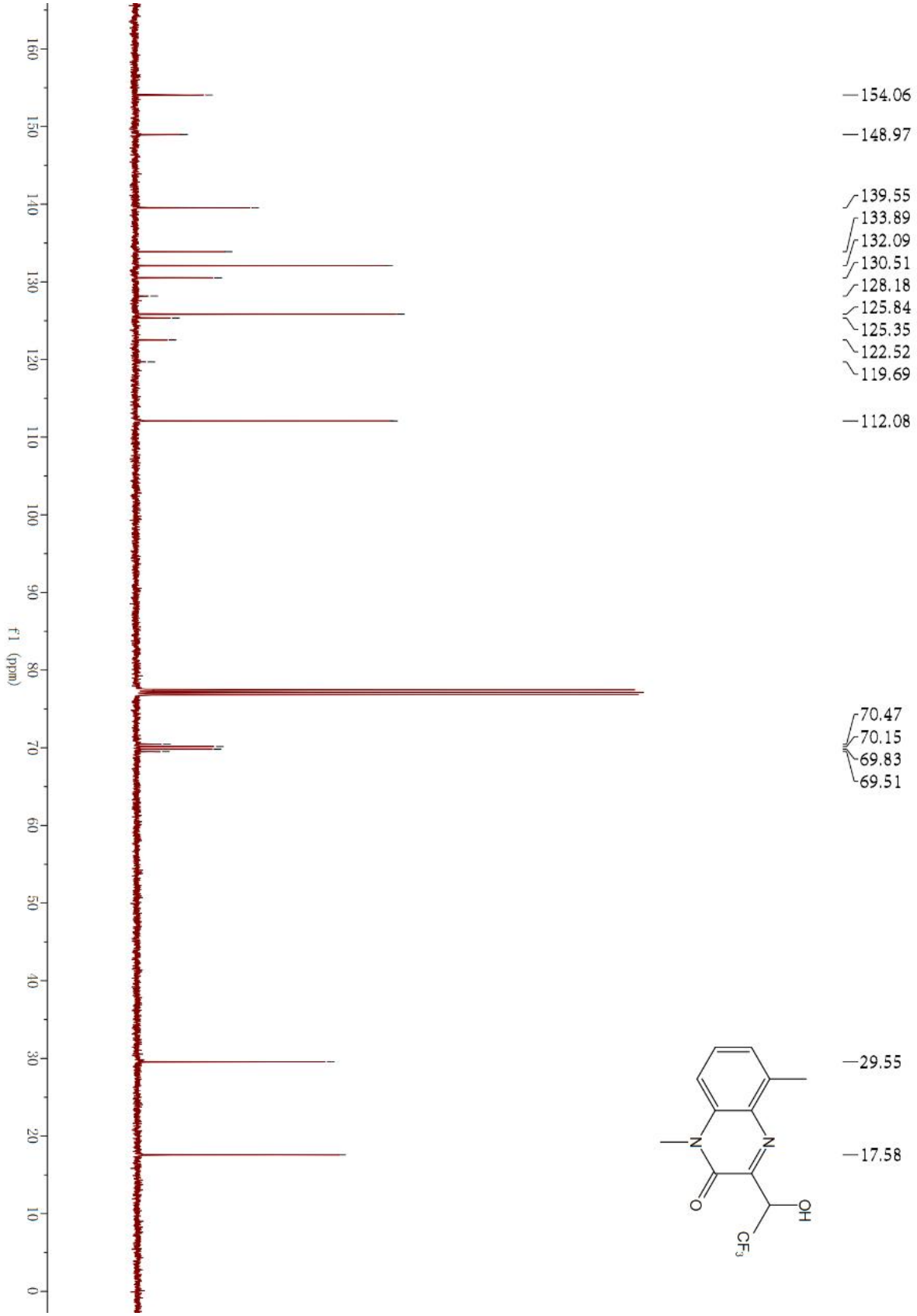
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3p**



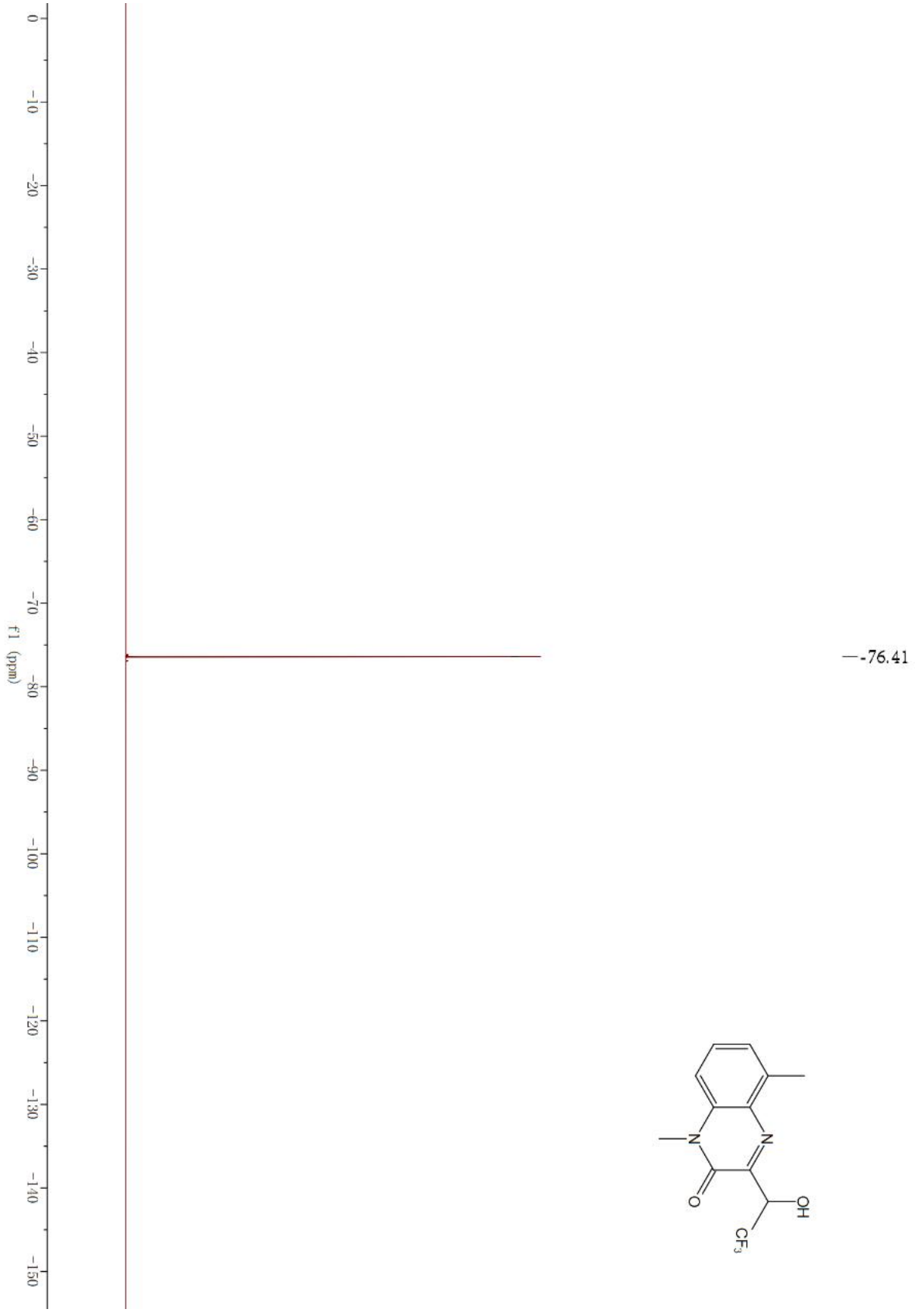
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3q**



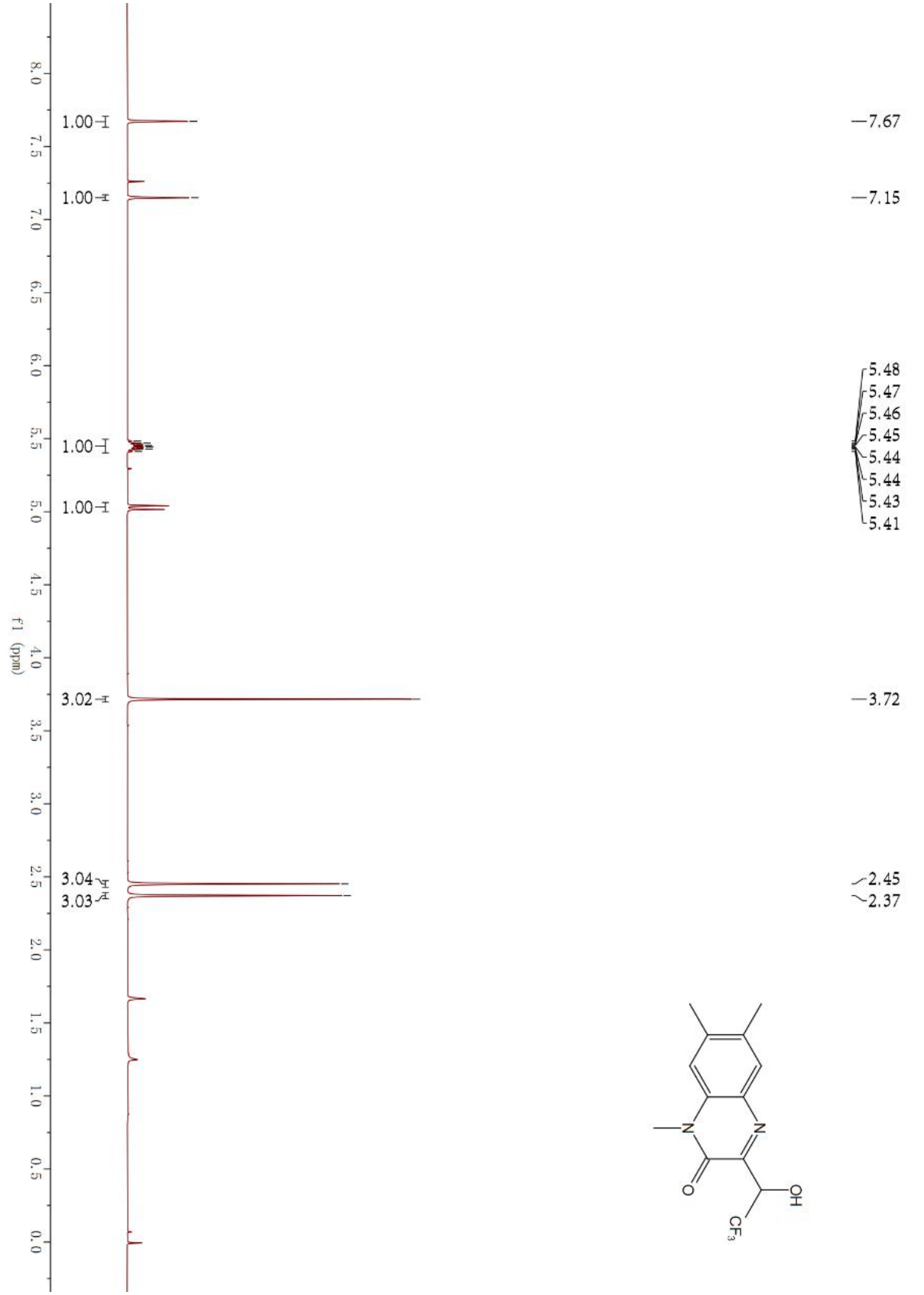
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3q**



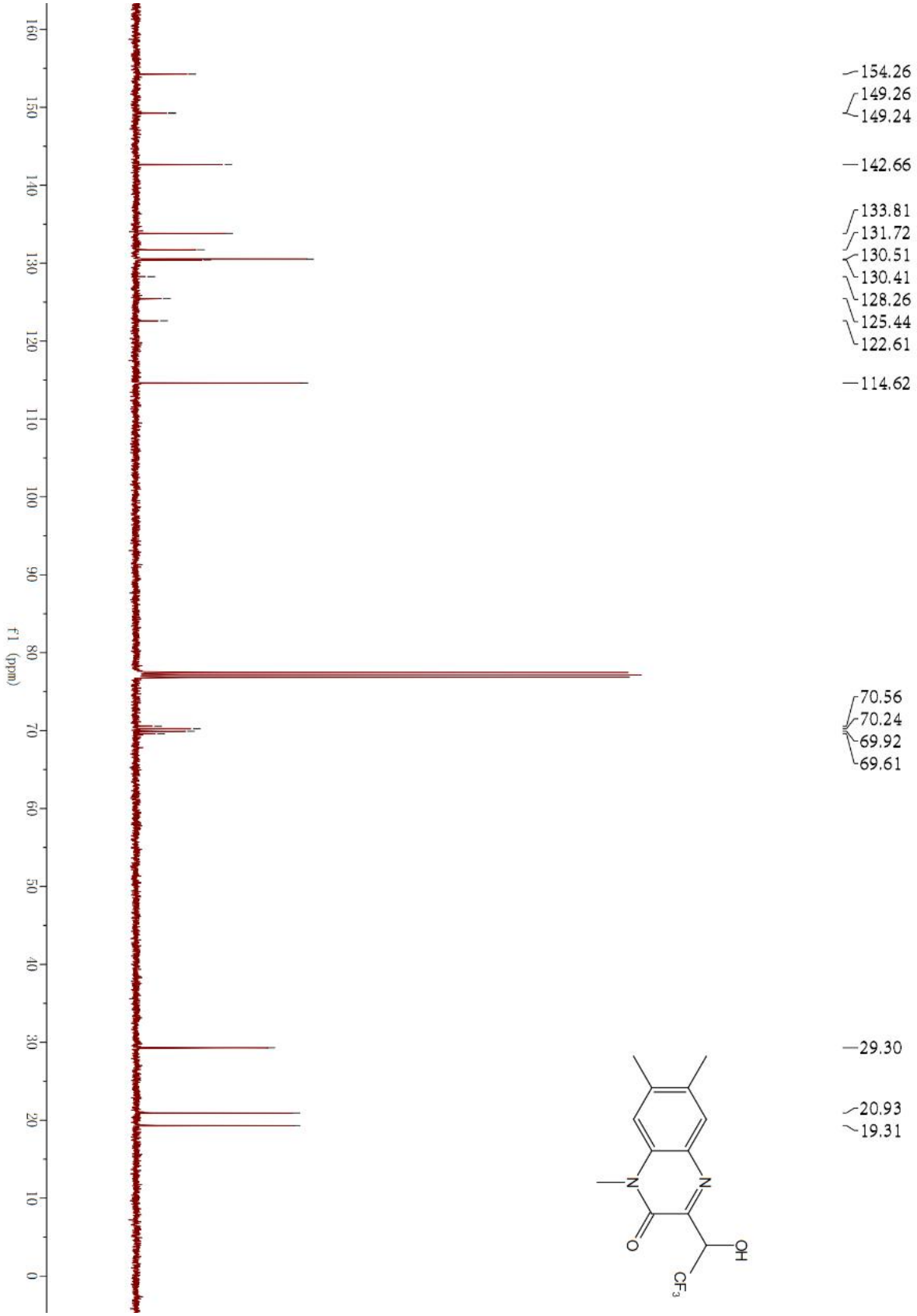
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3q**



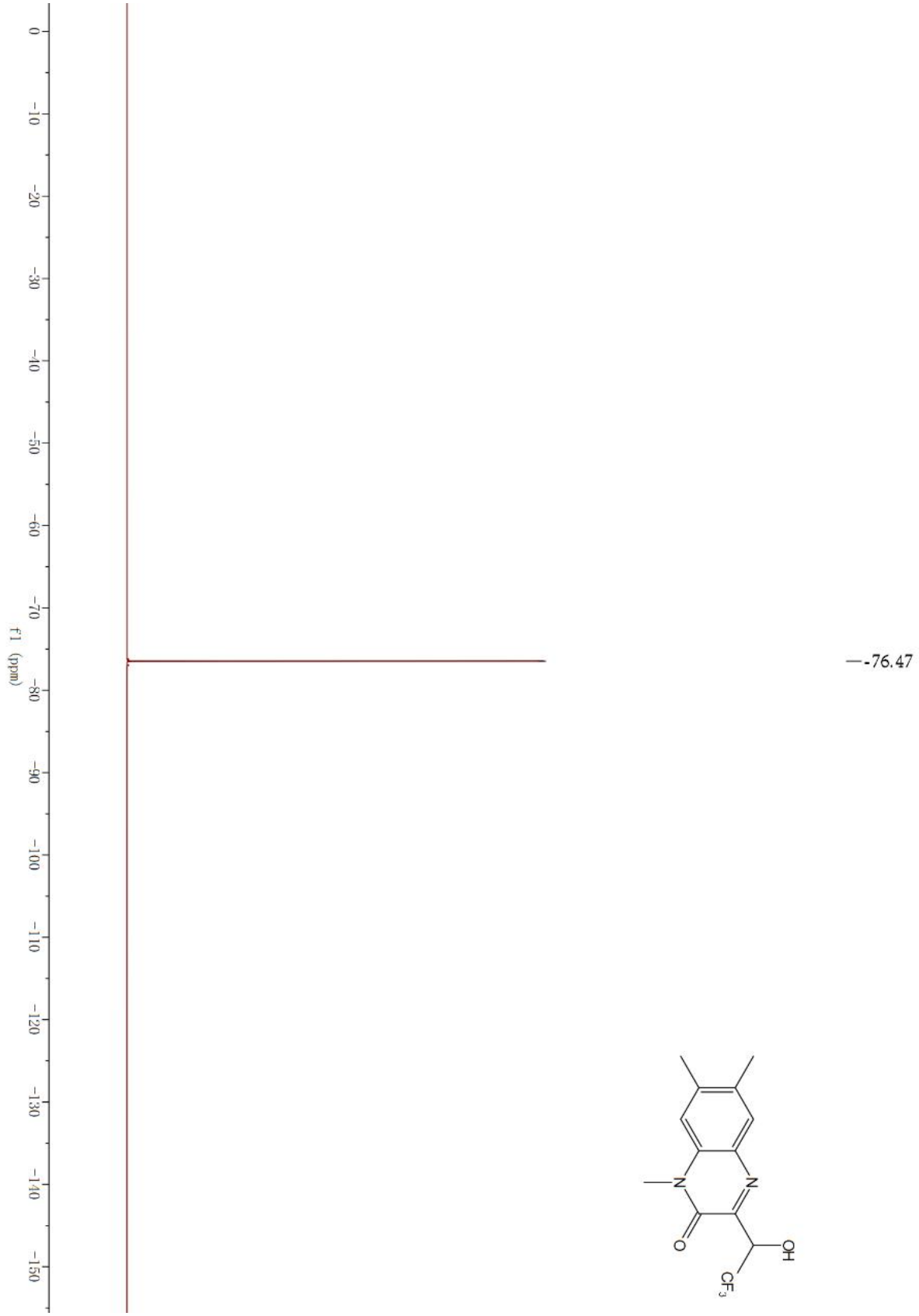
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3r**



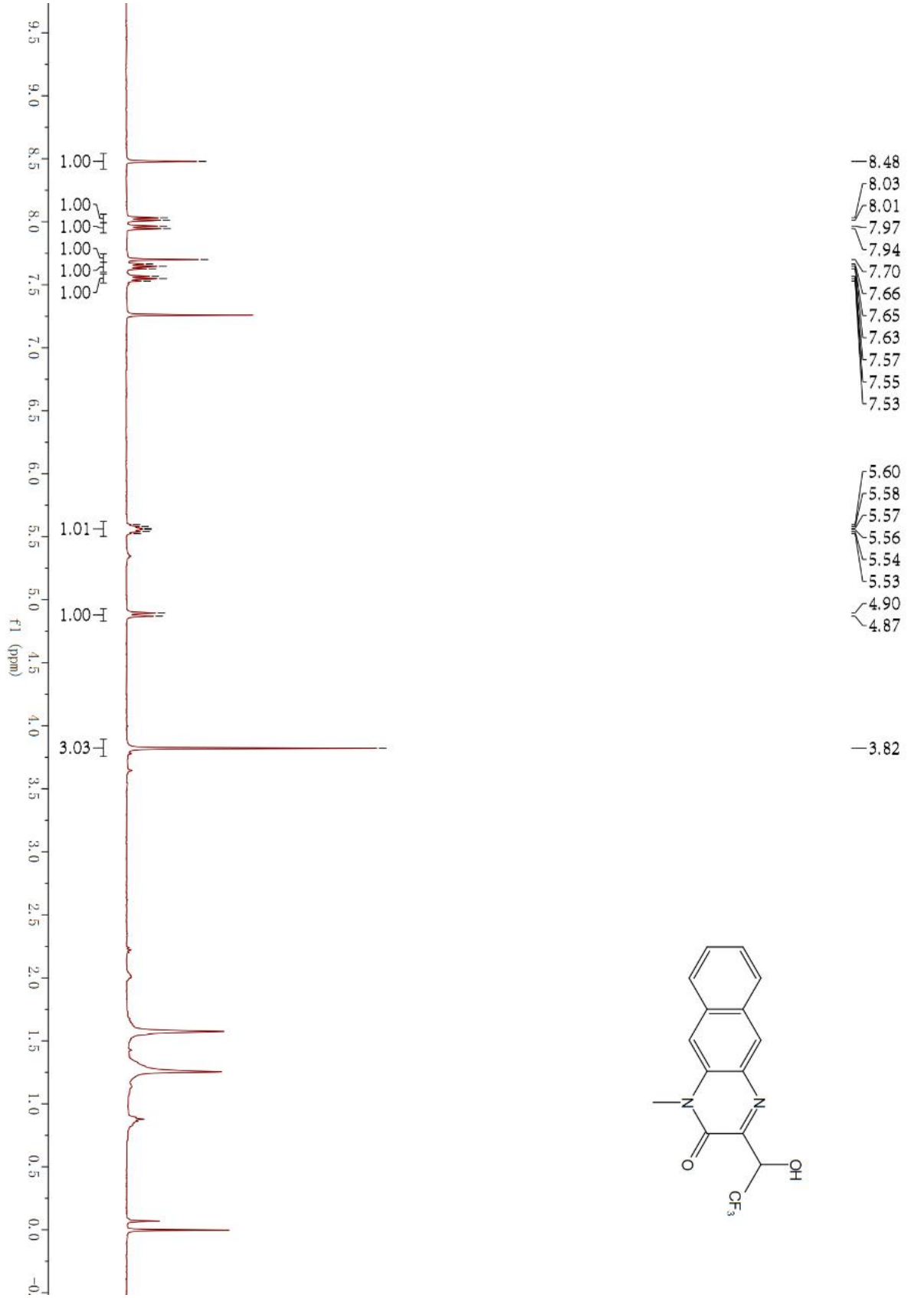
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3r**



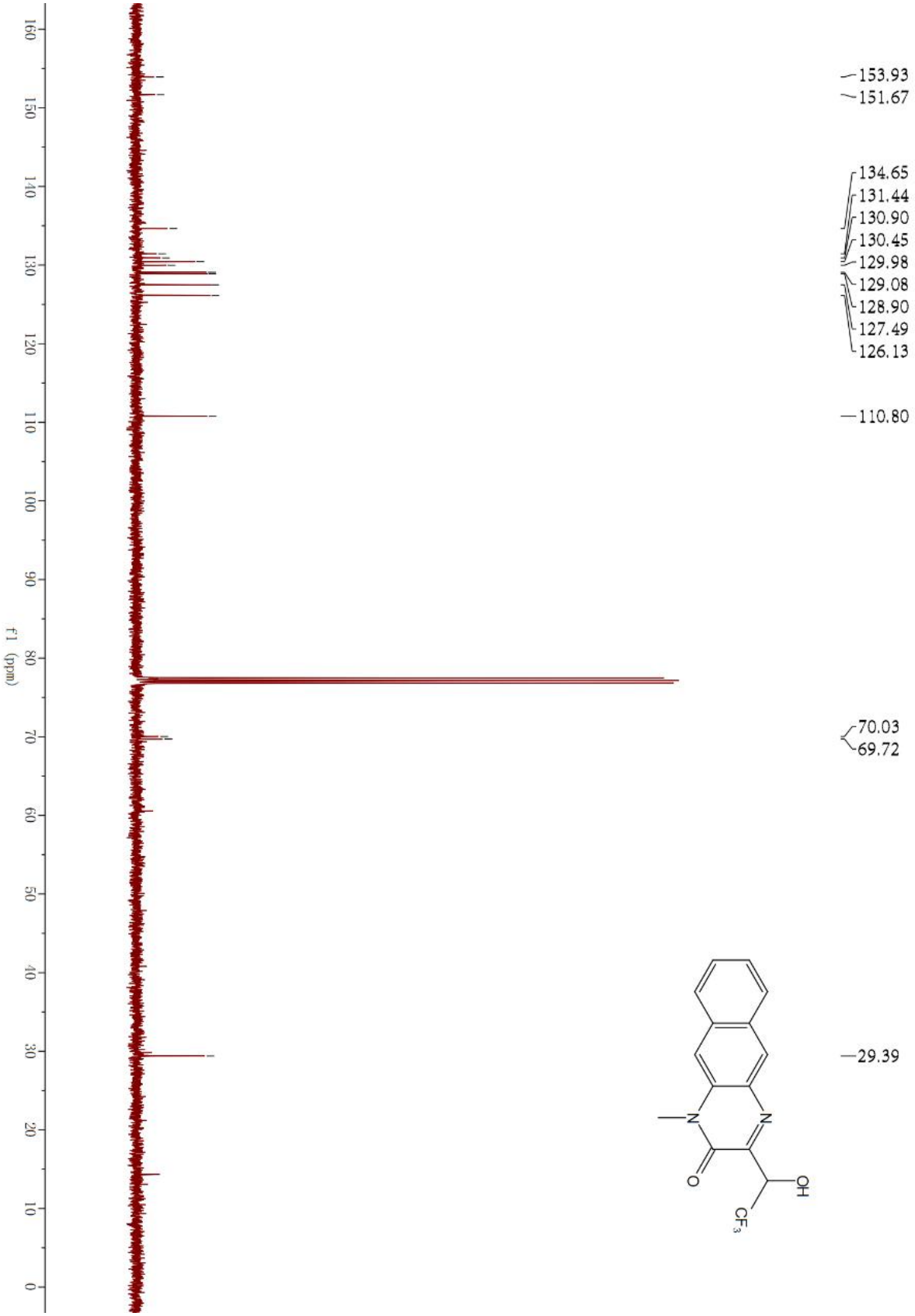
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3r**



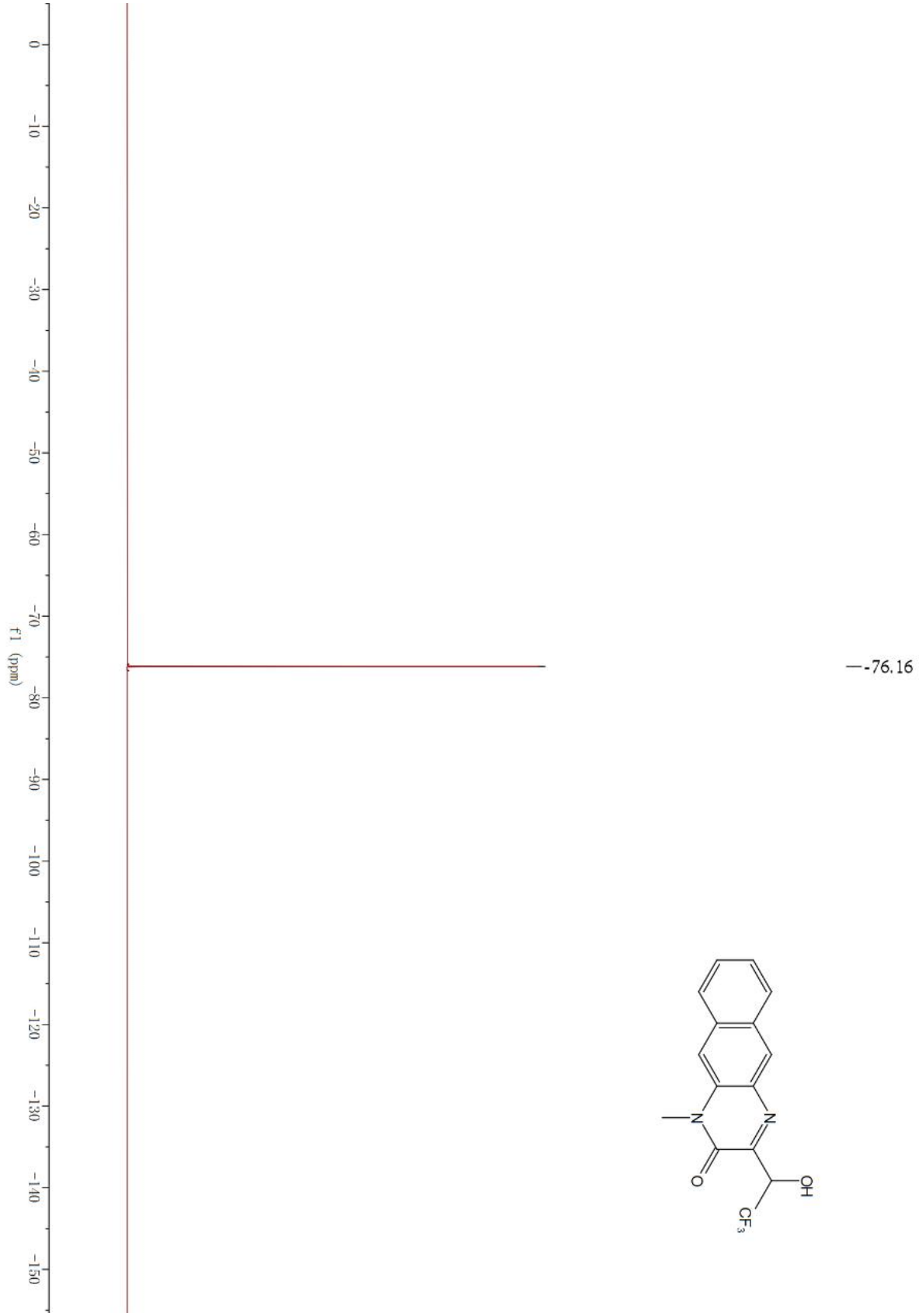
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3s**



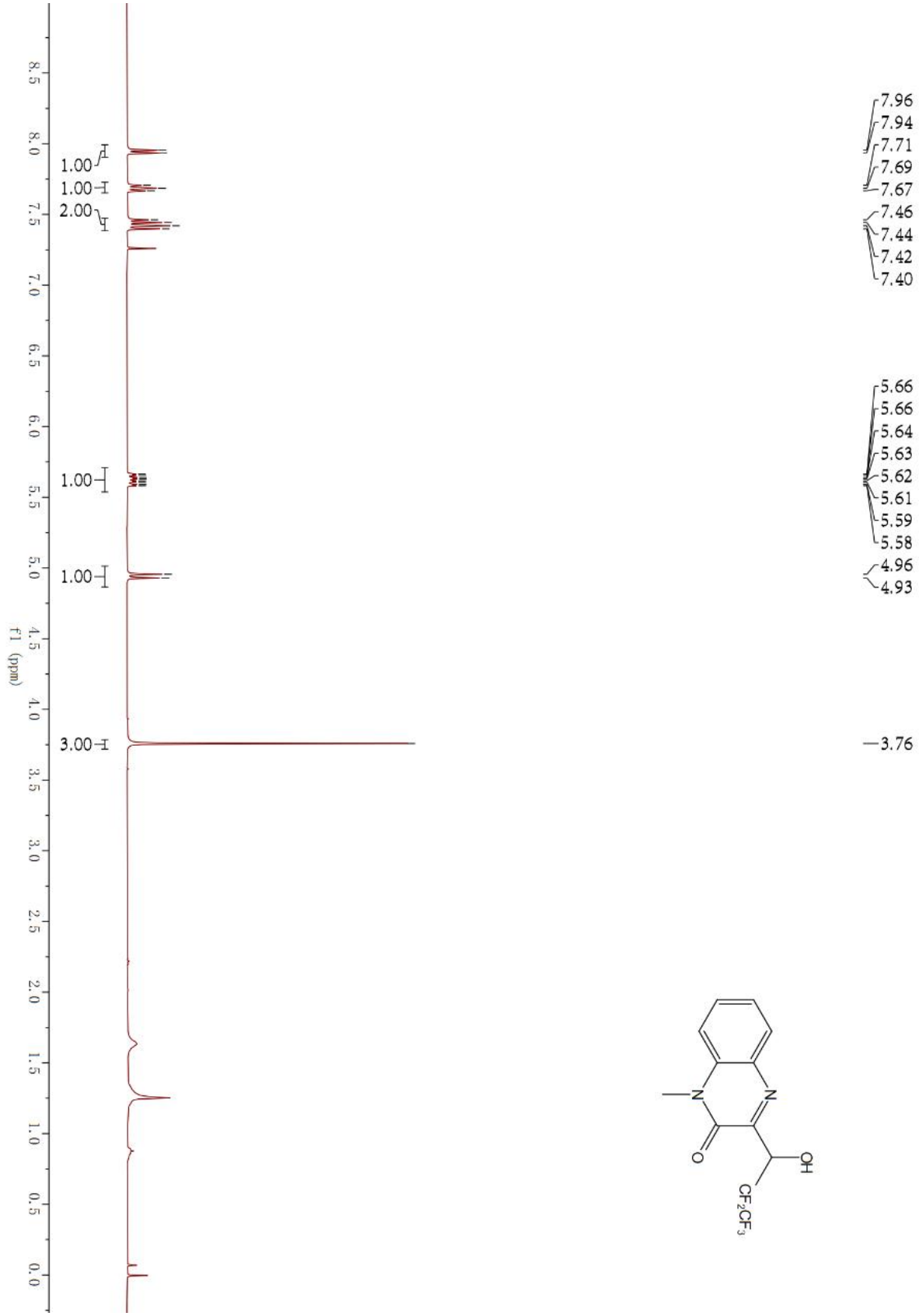
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3s**



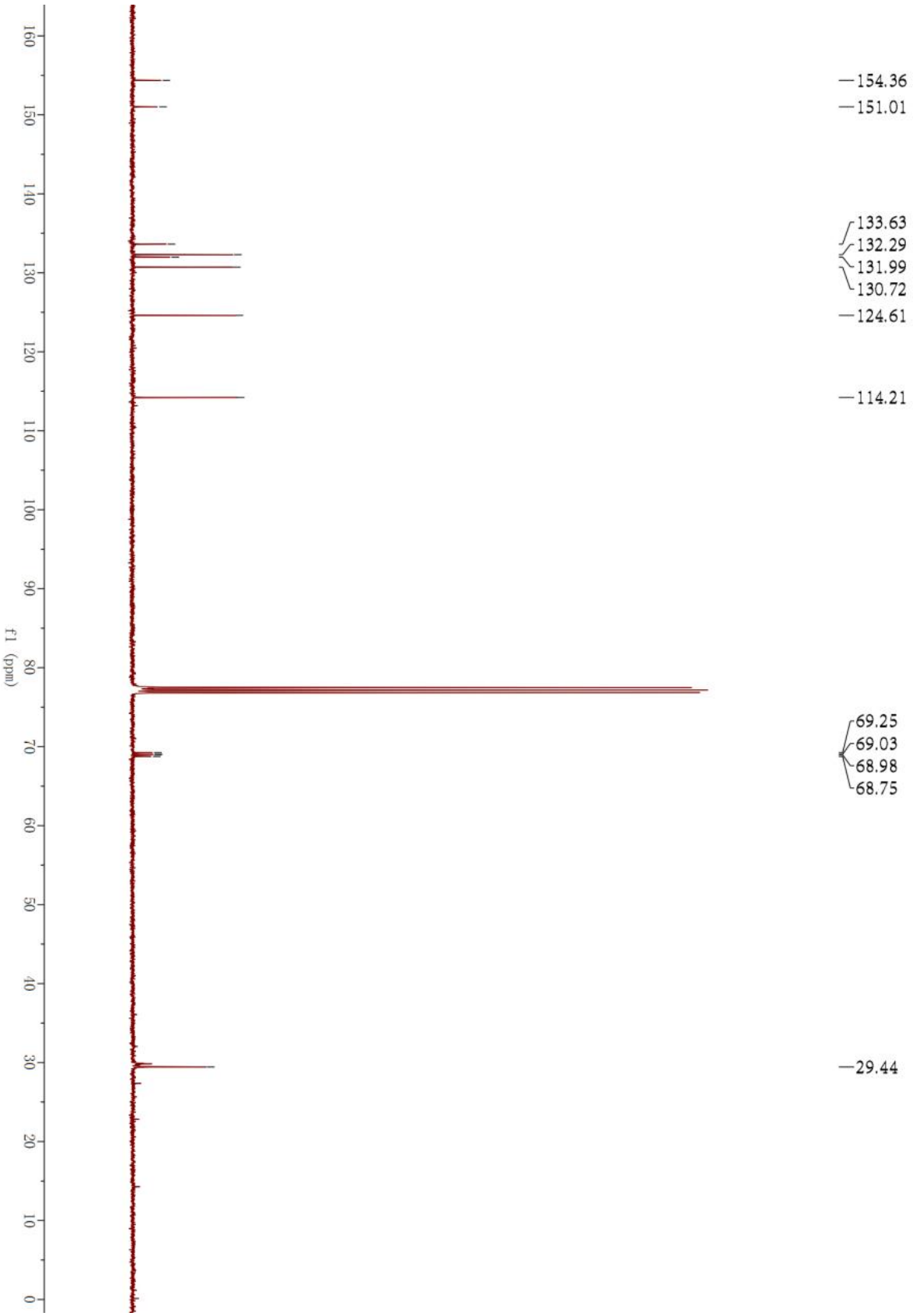
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3s**



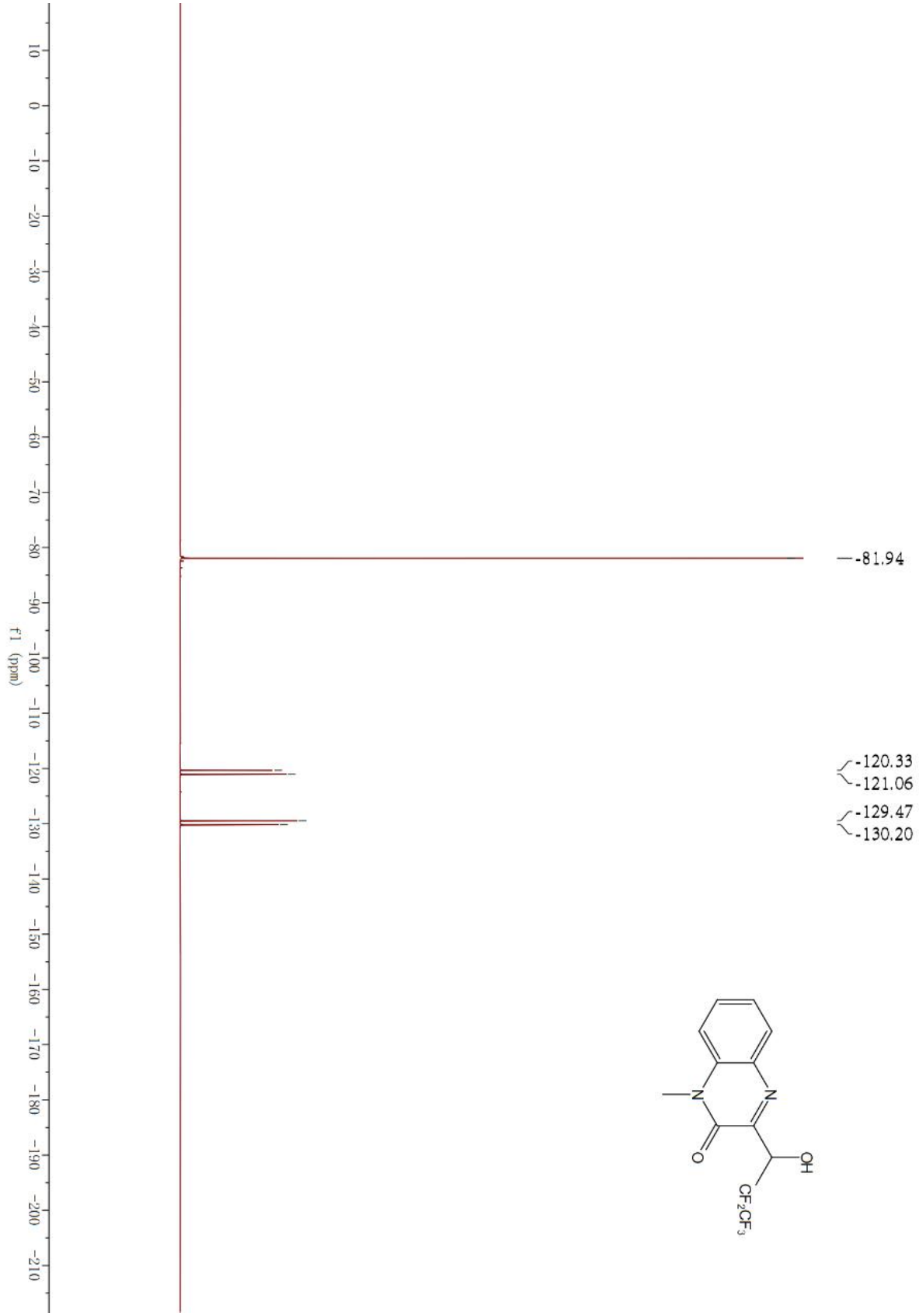
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3t**



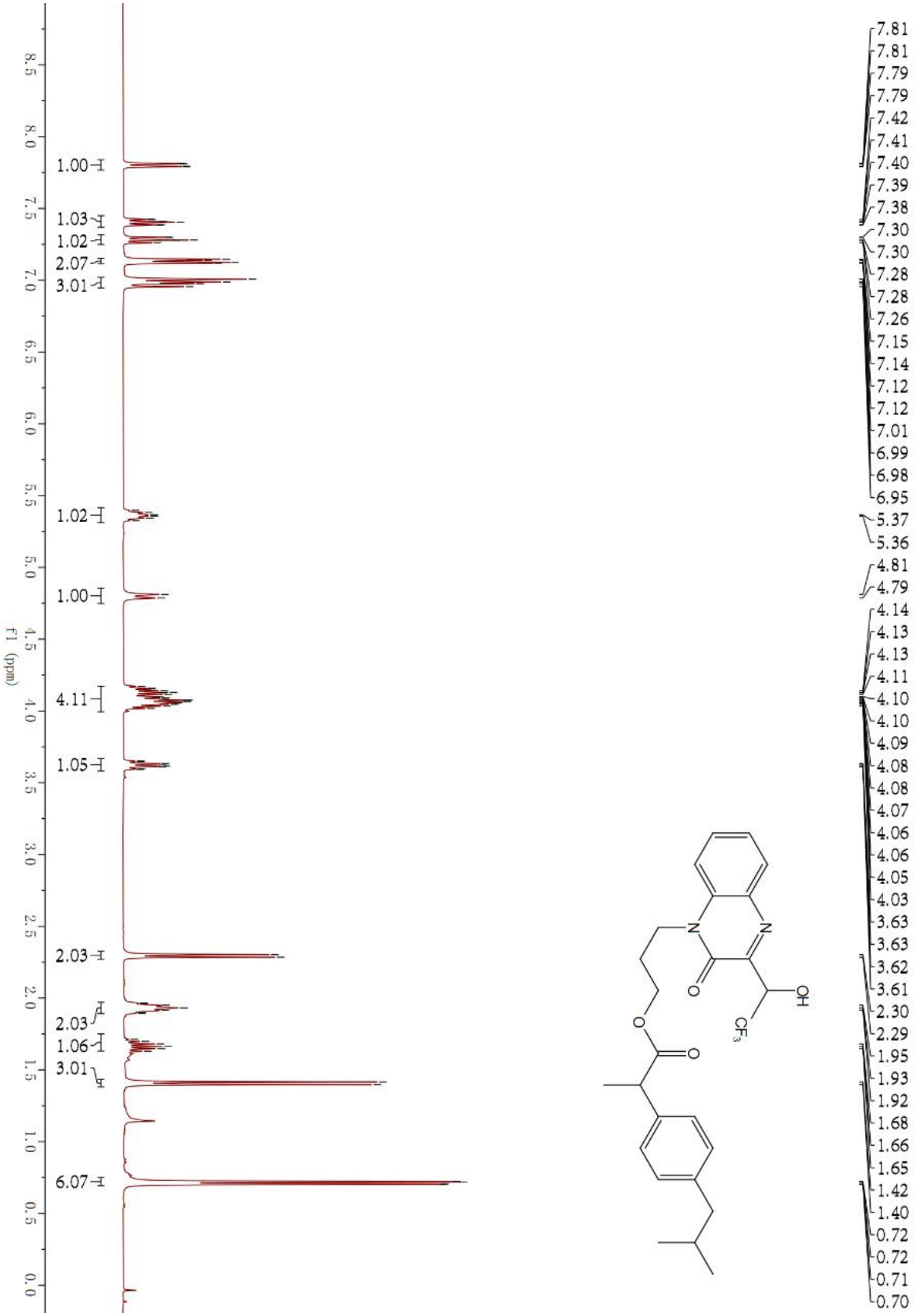
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3t**



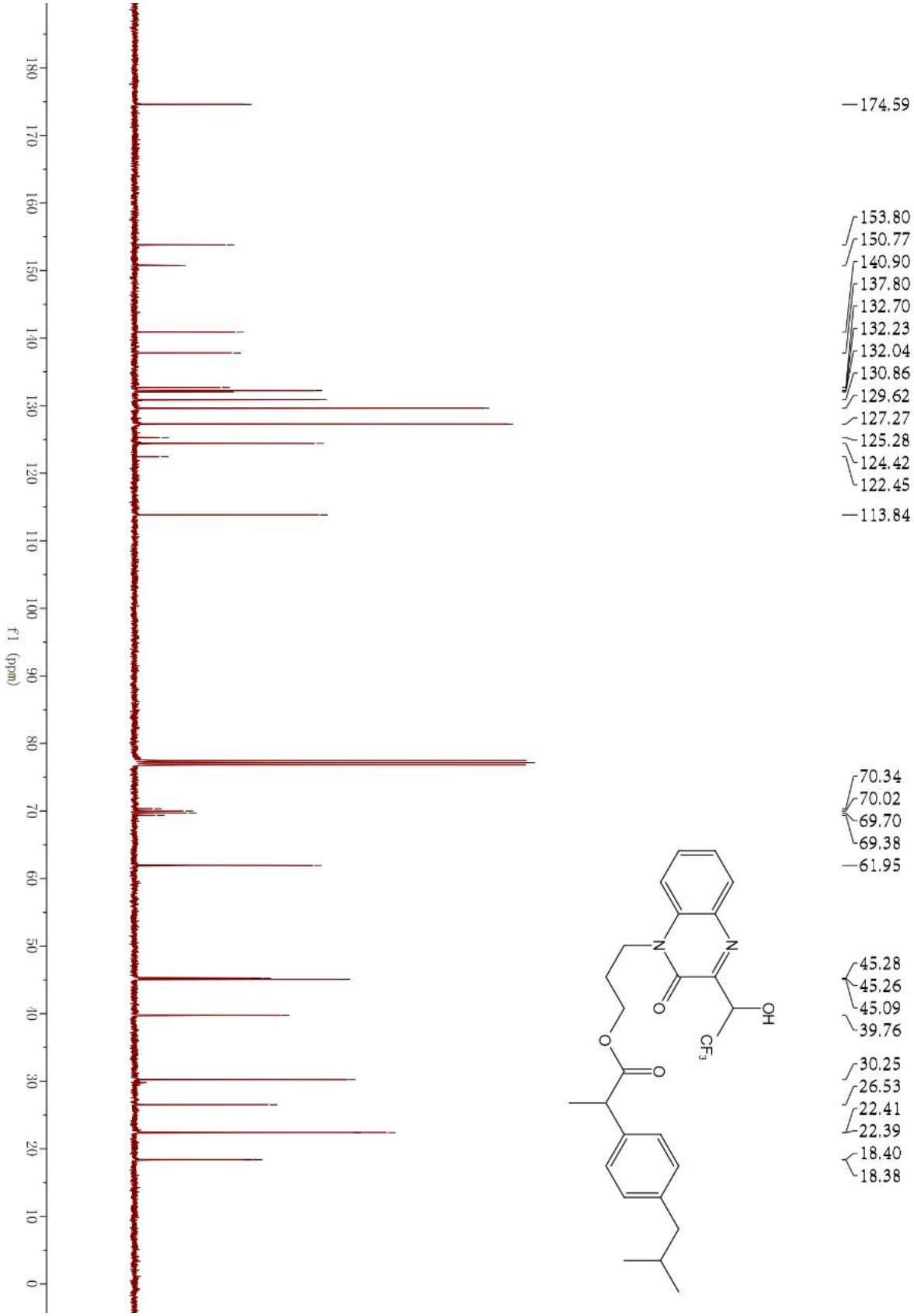
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3t**



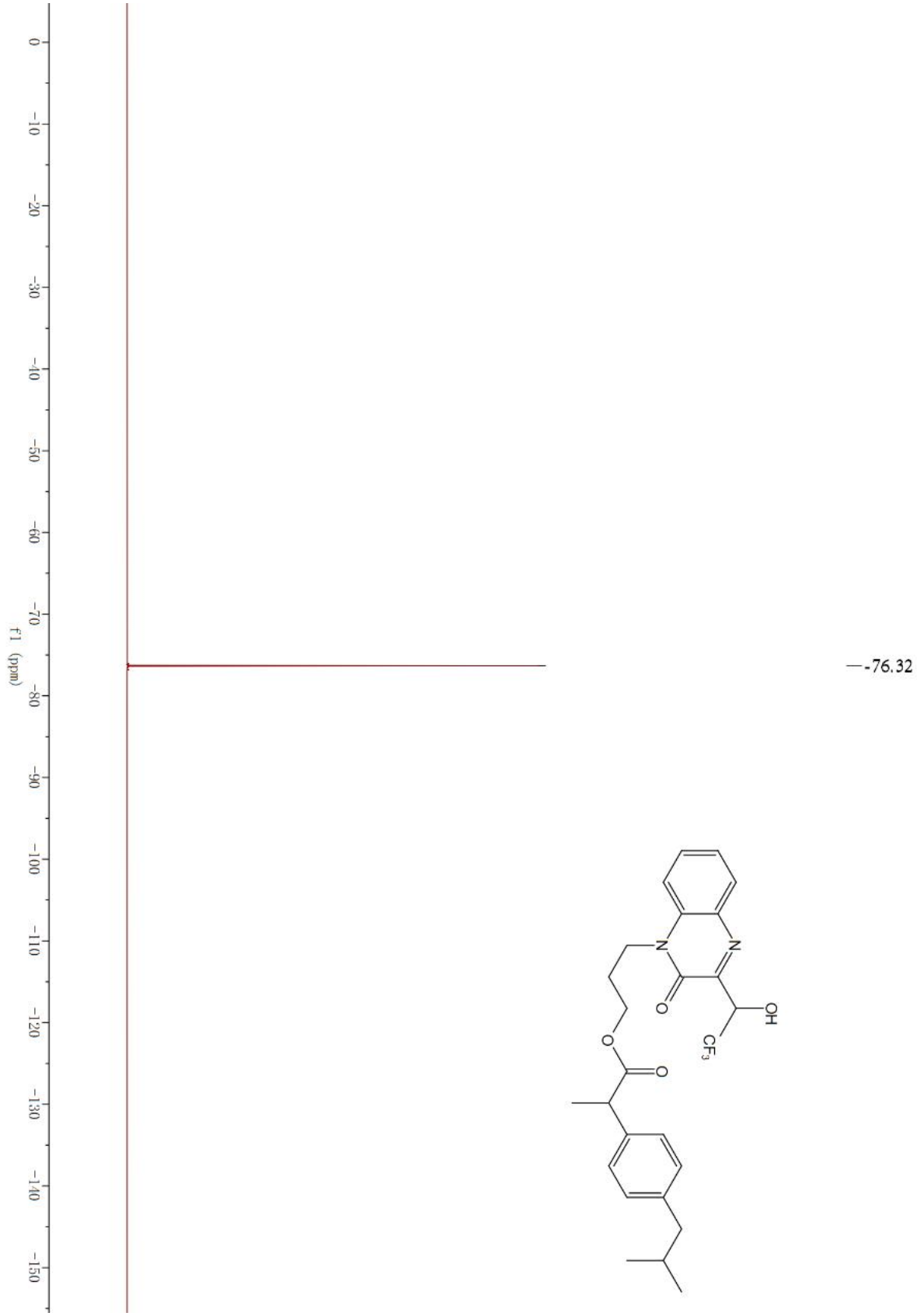
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3u**



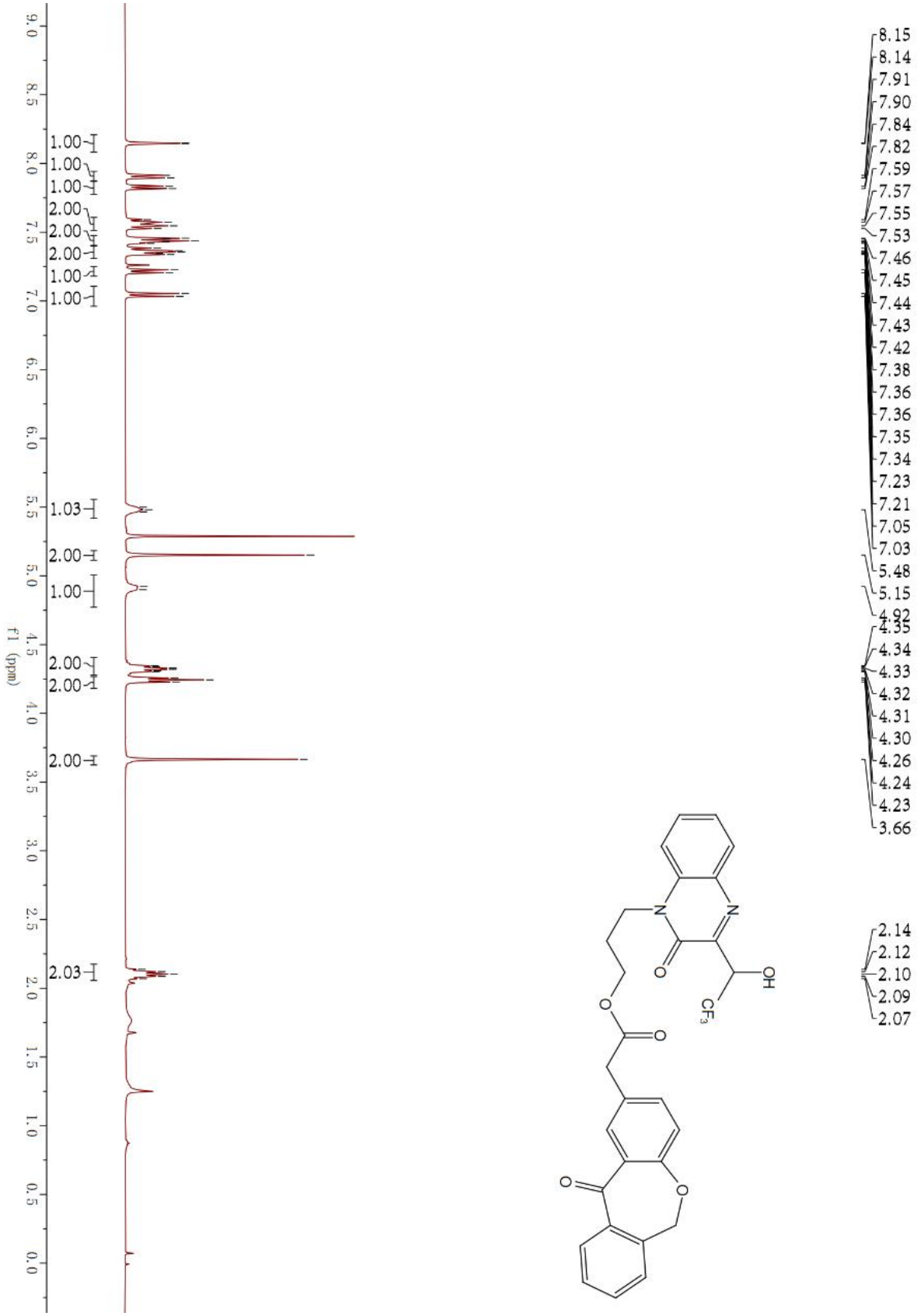
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3u**



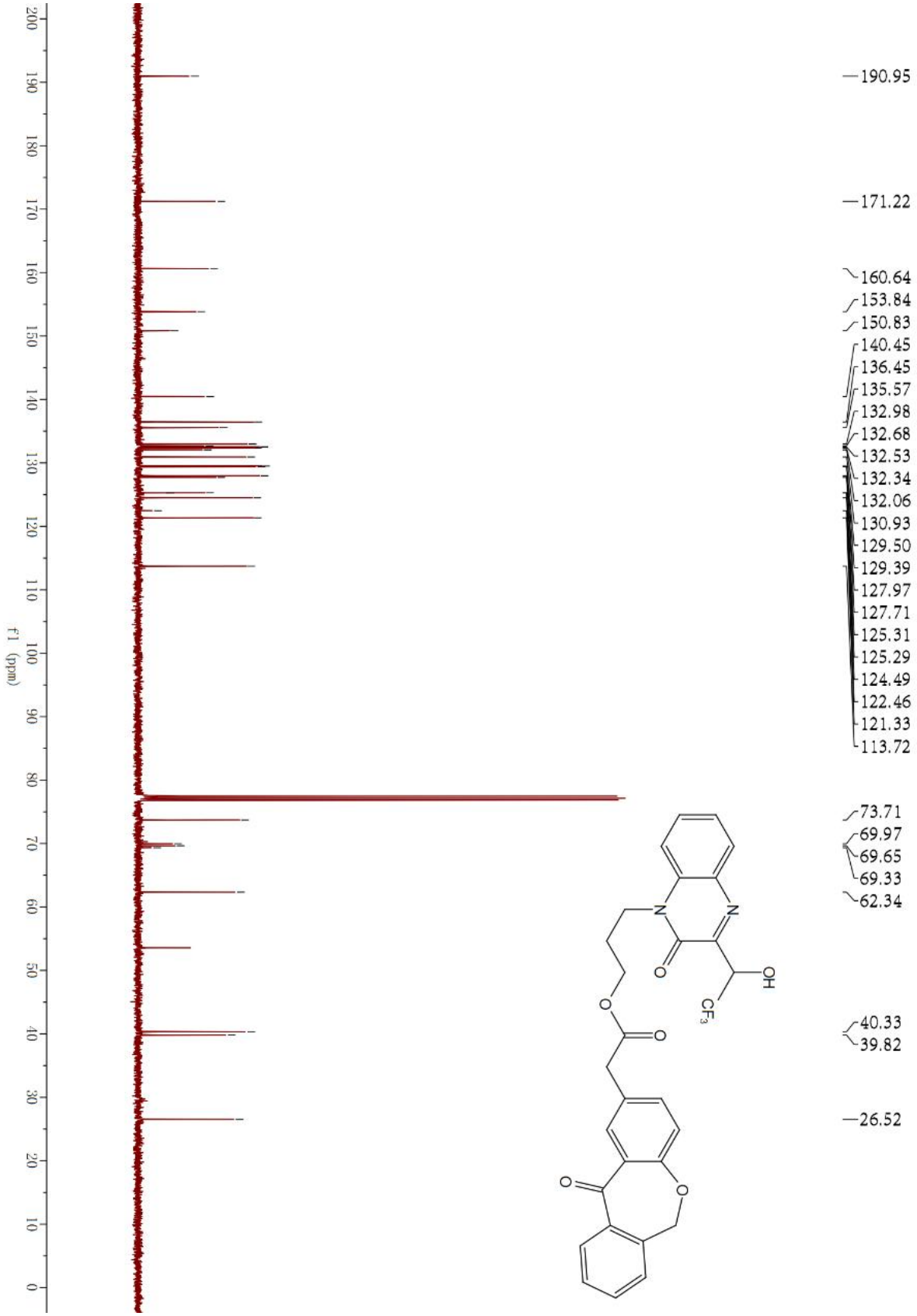
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3u**



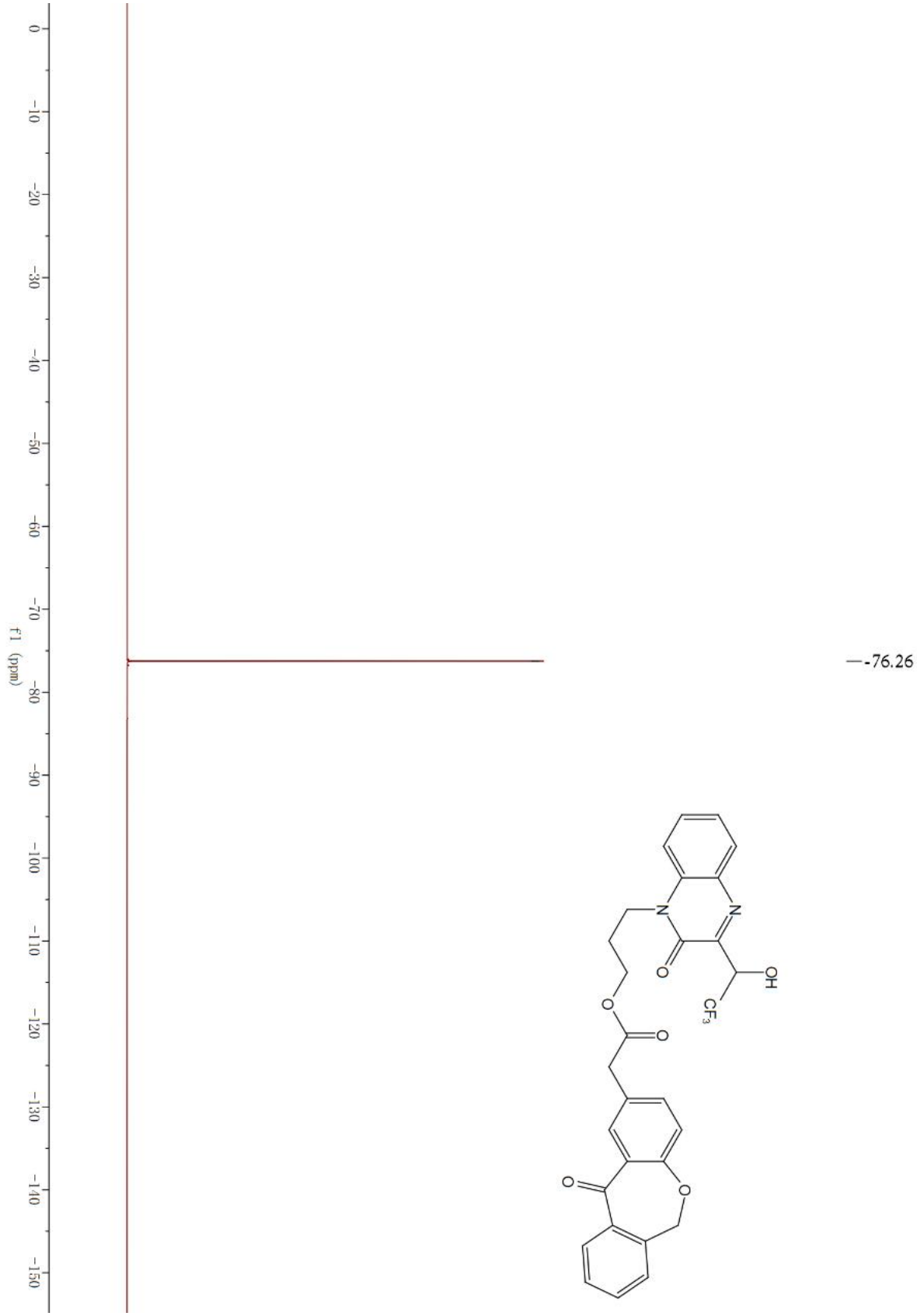
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3v**



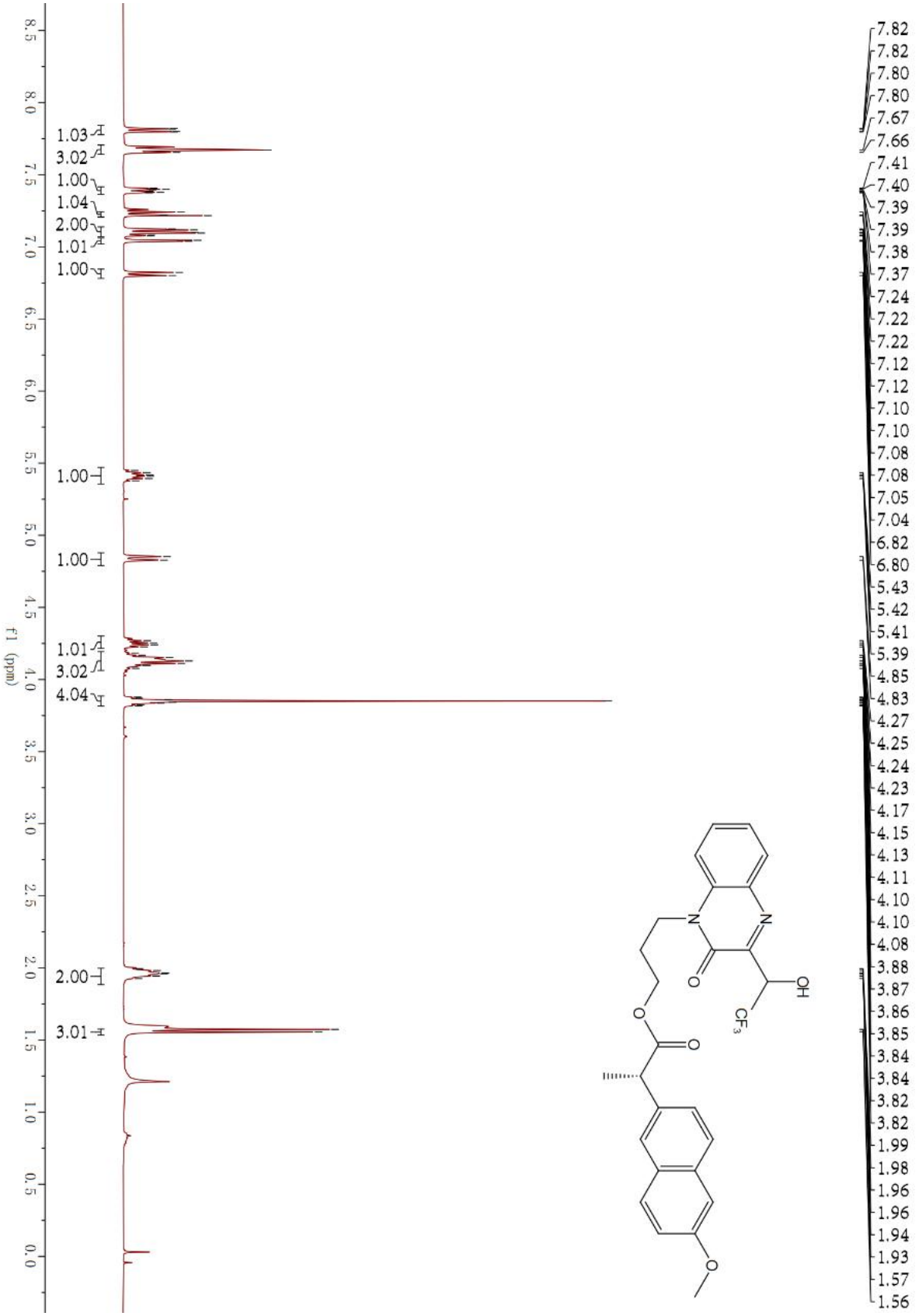
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3v**



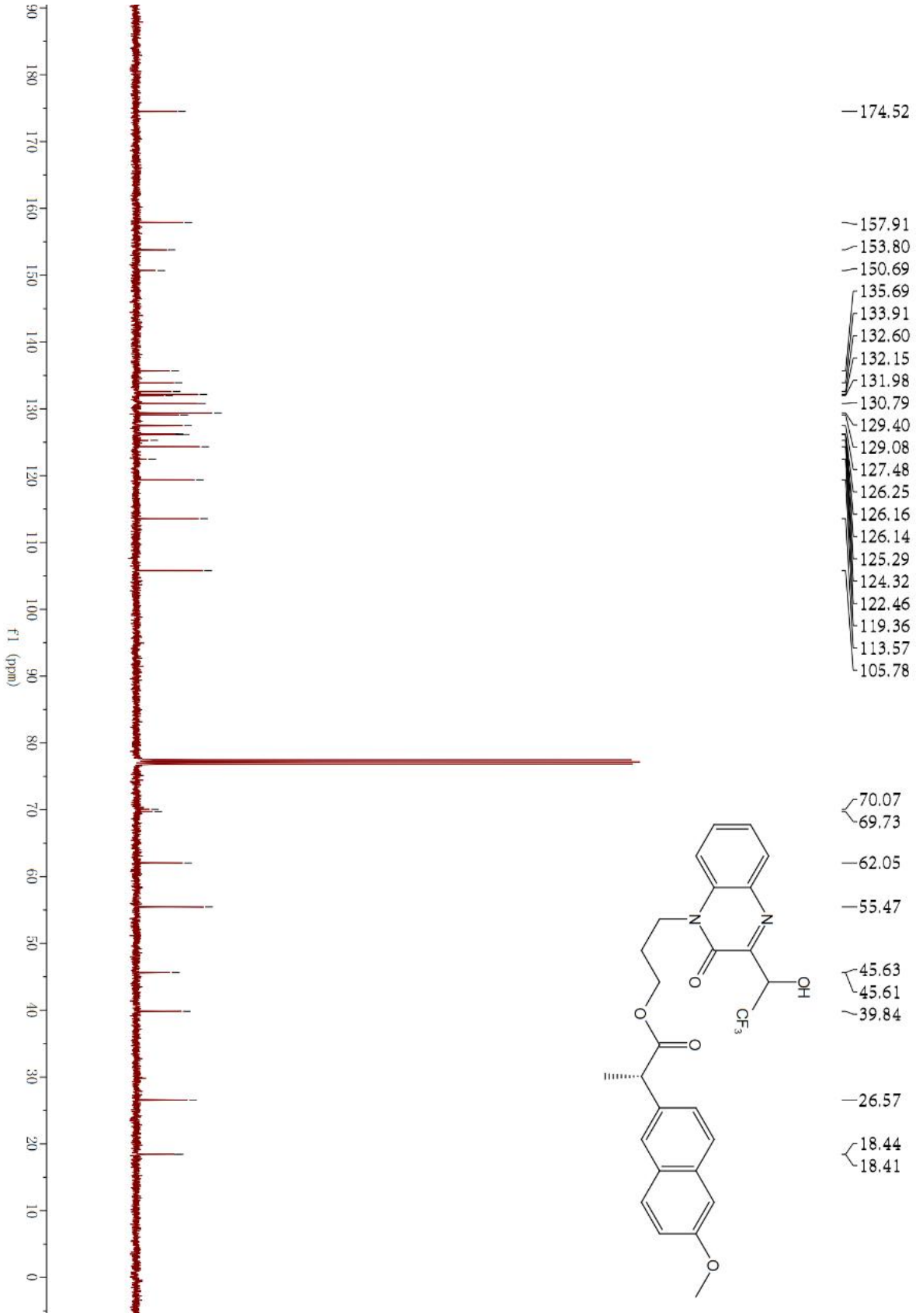
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3v**



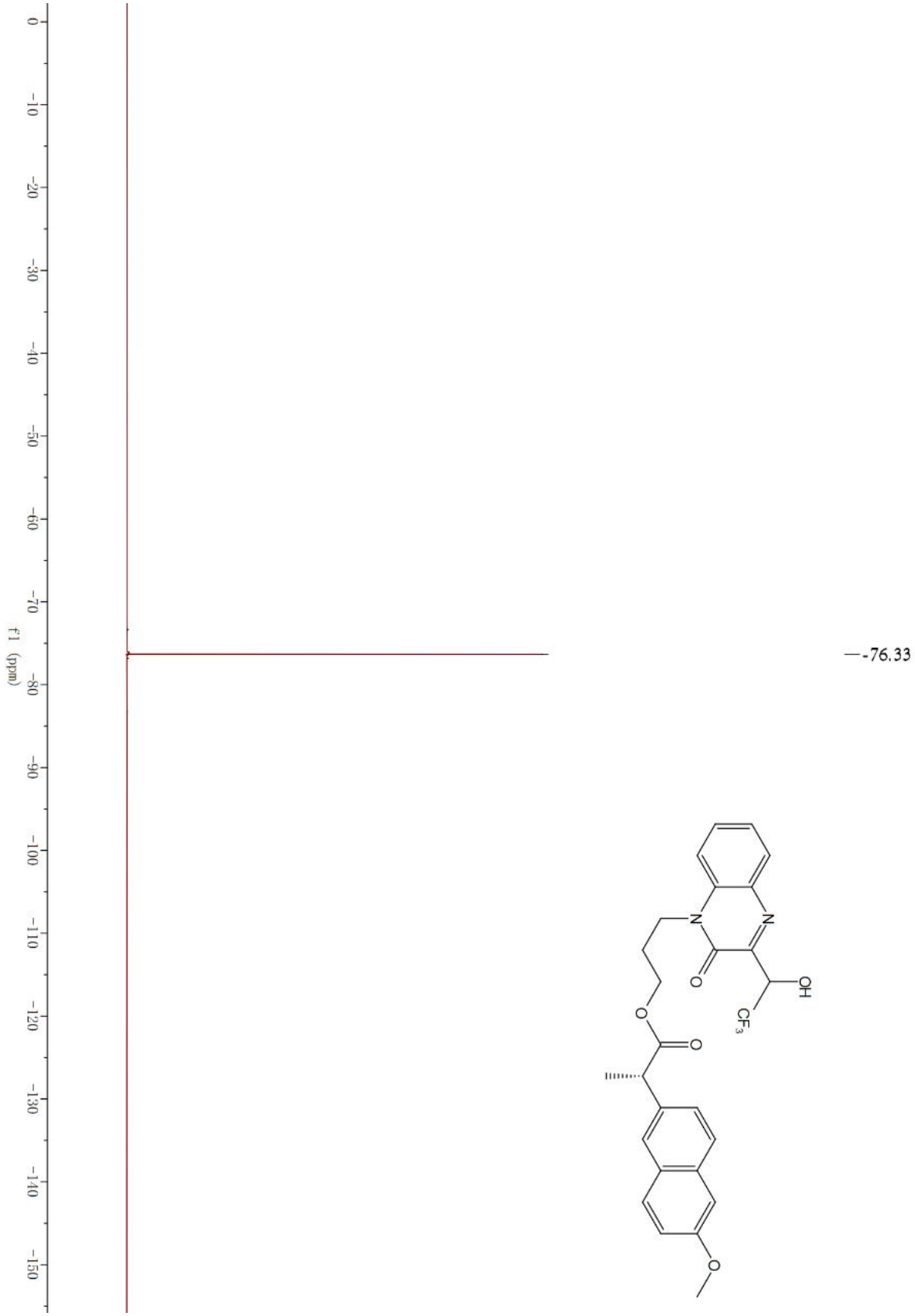
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3w**



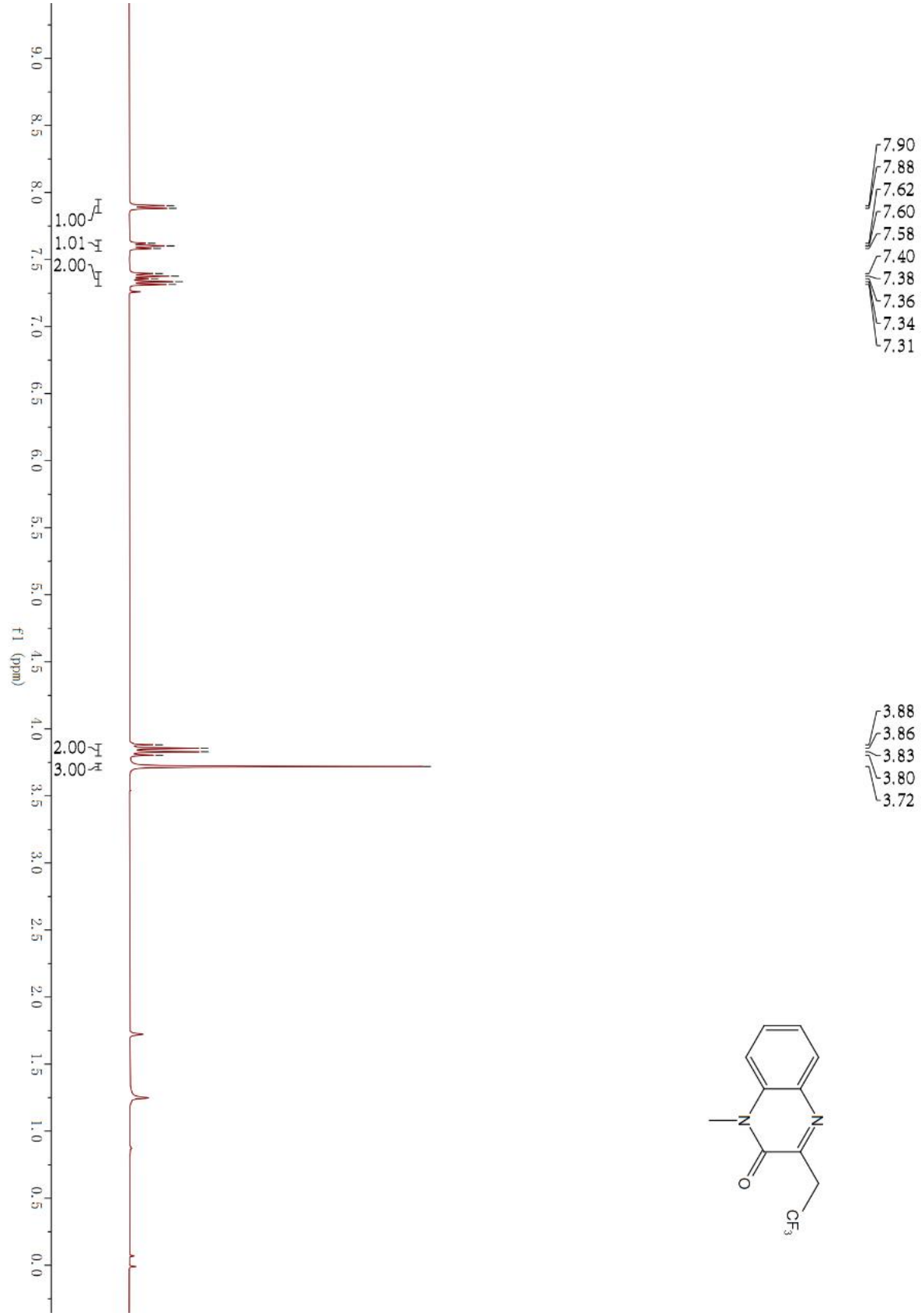
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3w**



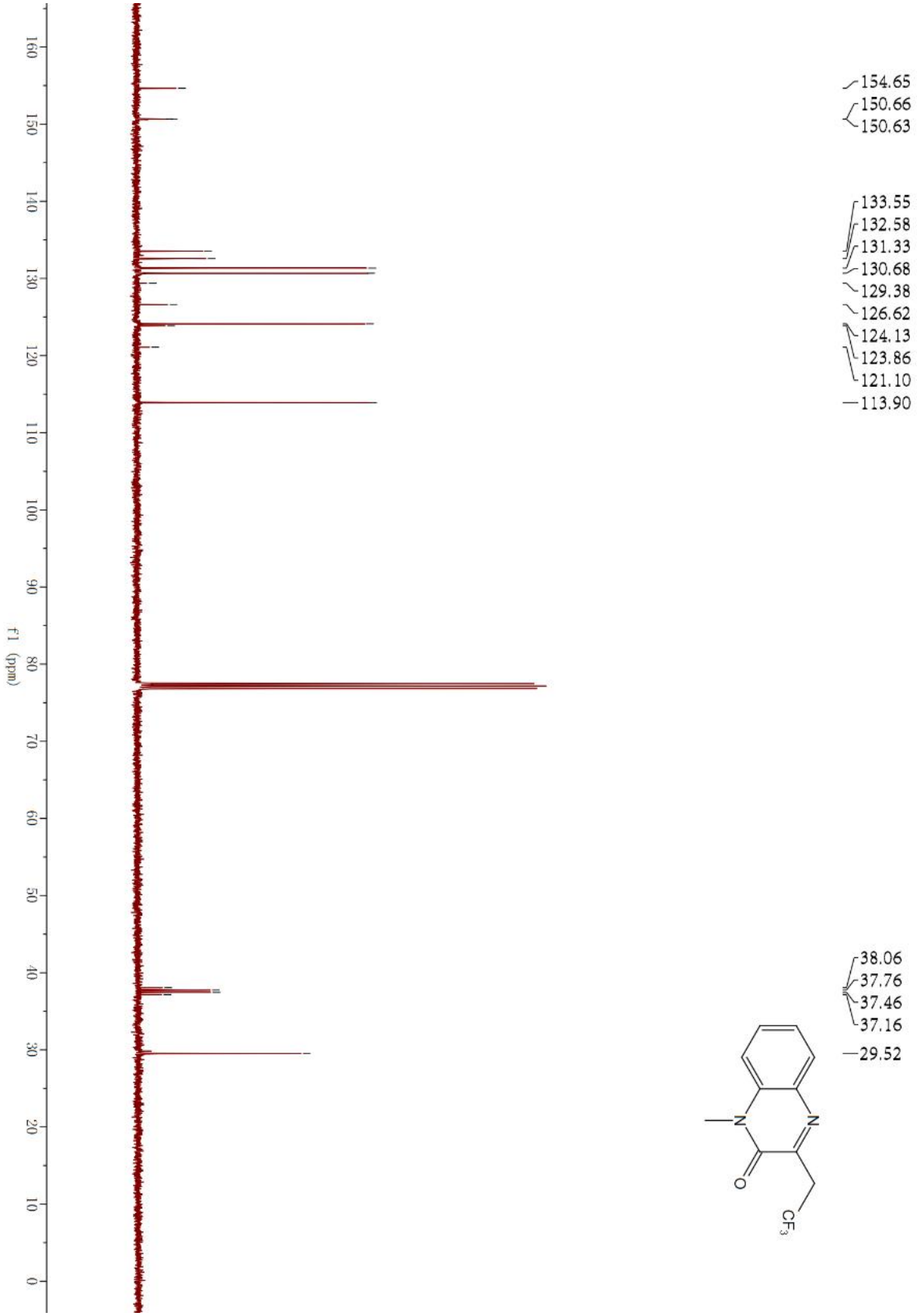
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3w**



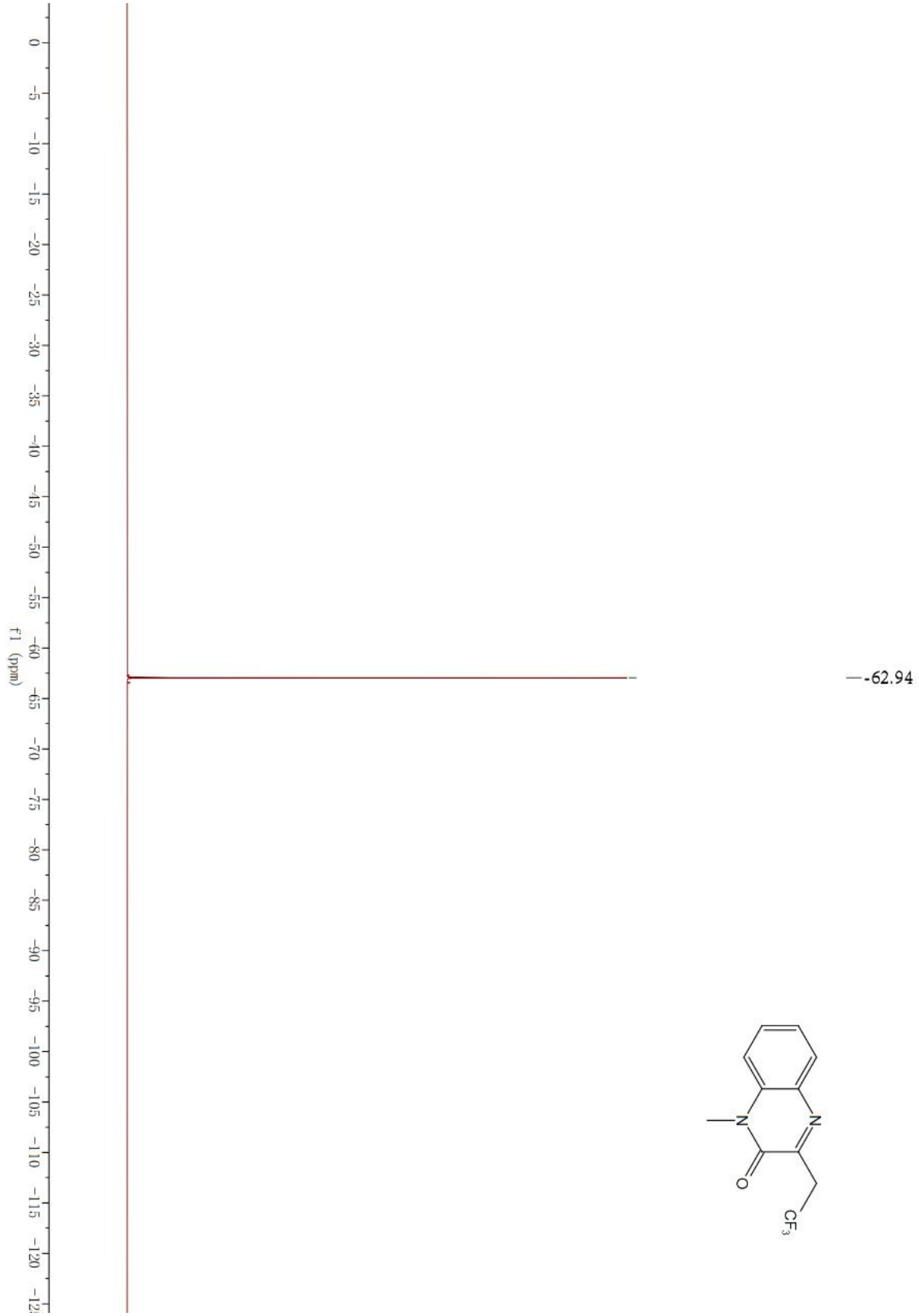
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5**



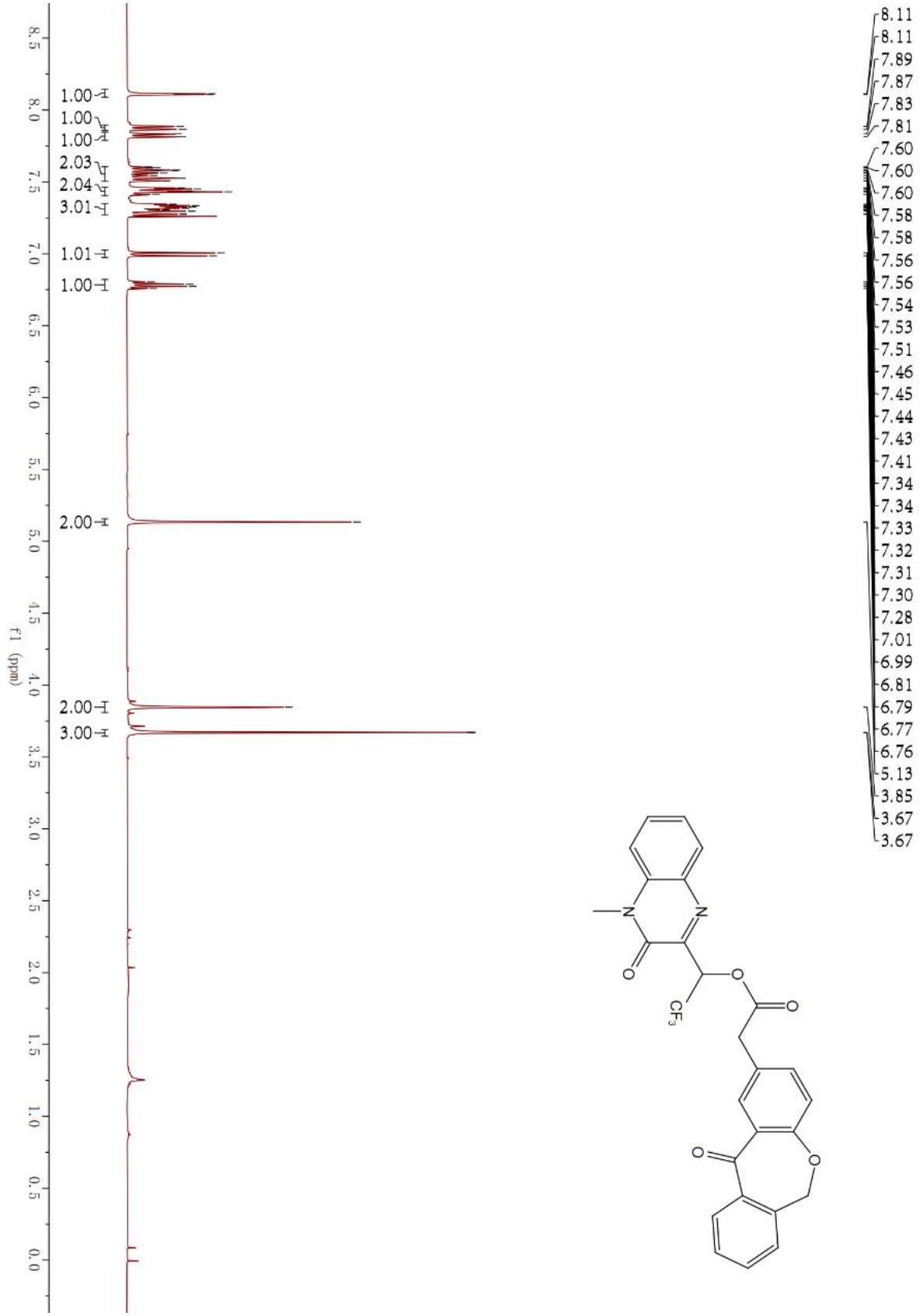
^{13}C NMR (100 MHz, $CDCl_3$) of compound **5**



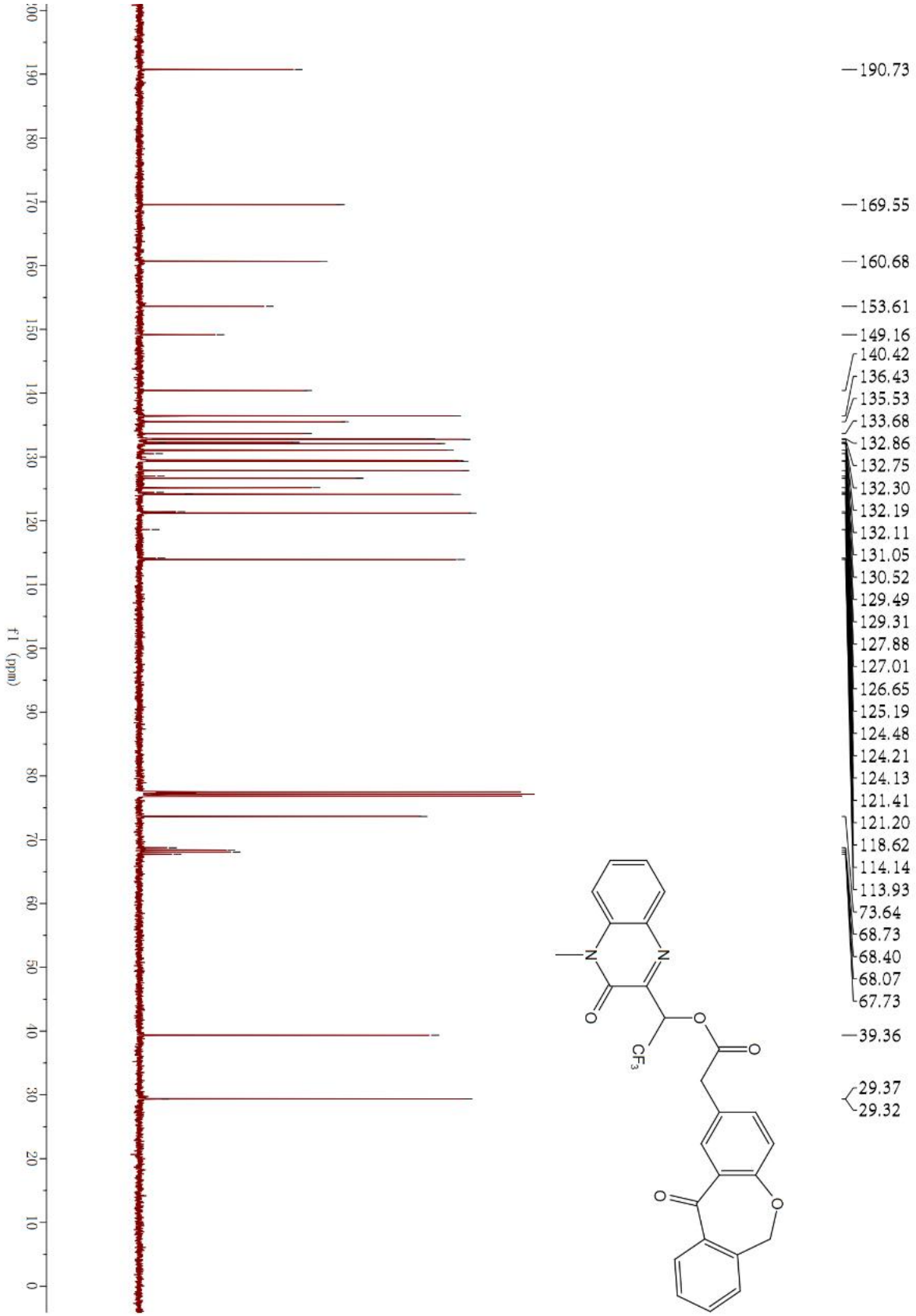
^{19}F NMR (376 MHz, $CDCl_3$) of compound **5**



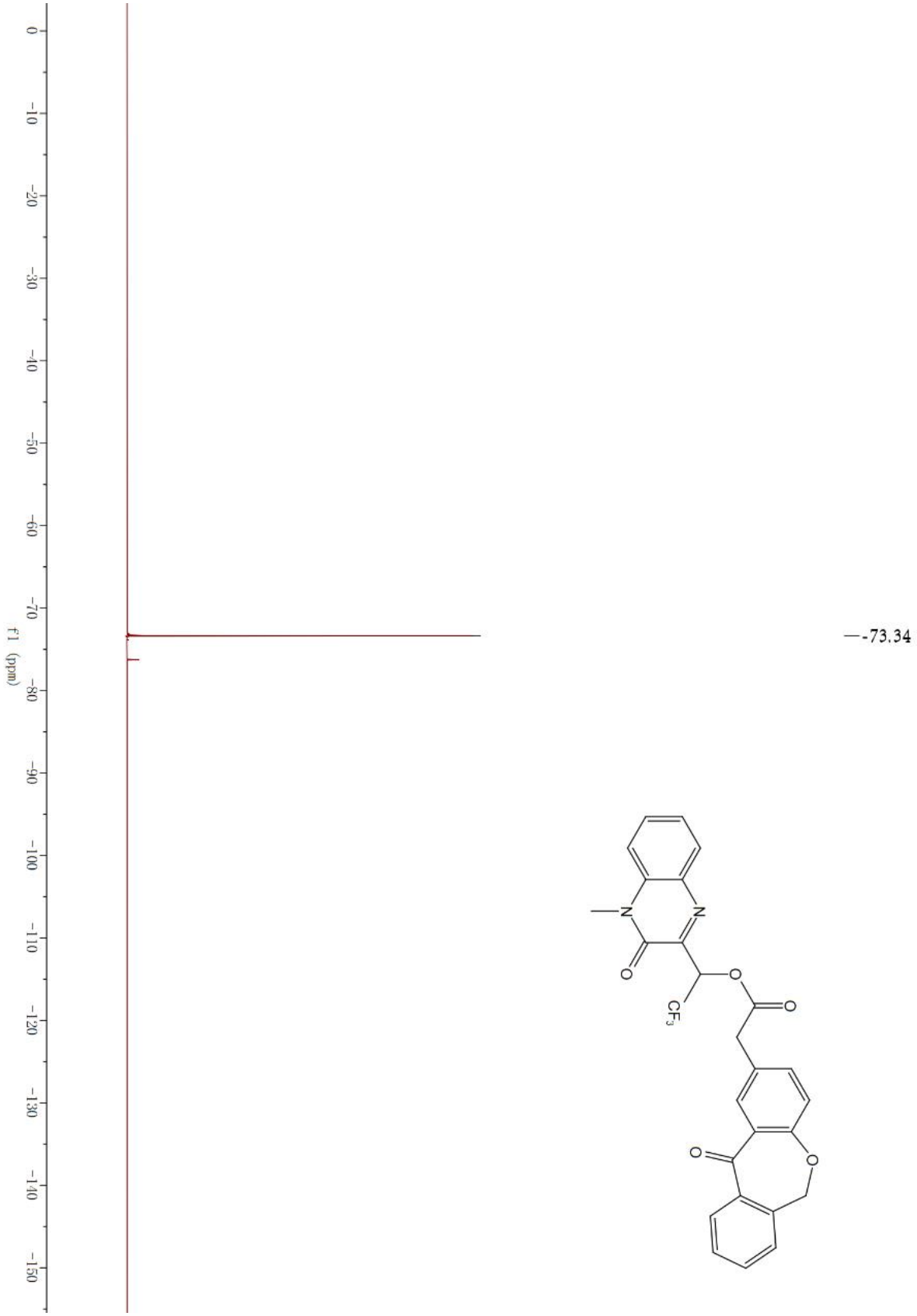
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **7**



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



6. References

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