Supporting Information for:

Visible-light-promoted C3-H alkoxycarbonylation of quinoxalin-2(1*H*)-ones or coumarins with alkyloxalyl chlorides

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1. General Information

Flash column chromatography was performed using silica gel from Qingdao Haiyang. Anhydrous solvents [tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), toluene，ethyl acetate (EtOAc), acetonitrile (CH_3CN), dimethyl sulfoxide (DMSO), and dichloromethane (DCM)] were purchased from Adamas, Energy Chemicals, or Innochem, and used as received. All commercial reagents were purchased from Bidepharm, Energy Chemical, Aladdin, and Adamas of the highest purity grade. Photosensitizers were purchased from laajoo, Adamas, Alfa, or Aldrich, and used as received.

General Analytical Information

All new compounds were characterized by NMR spectroscopy, high-resolution mass spectroscopy, and melting point (if solids). NMR spectra were recorded on a Bruker Ascend^{TM} 400 spectrometer and were calibrated using TMS or residual deuterated solvent as an internal reference (Chloroform-*d*: 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR). Data were reported as follows: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constants (hertz), and integration. HRMS spectra were recorded on a Waters Acquity UPLC/Xevo TQD MSMS. Melting points (Mp) were recorded on a MP450 melting point apparatus.

Experimental Set-up

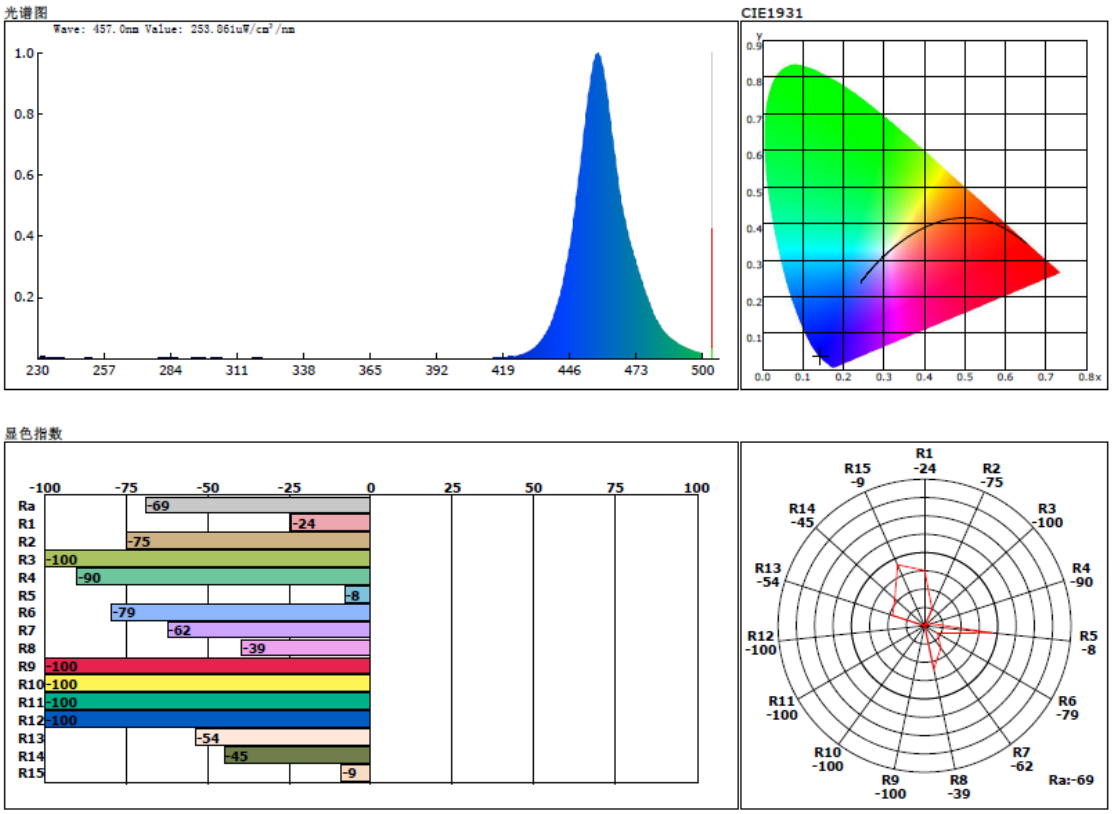


Figure S1 The emission spectra and spectral distribution of the blue LEDs

The Material of the Irradiation Vessel
Manufacturer: GeAo Chemical
Model: 24 W, blue LEDs
Broadband source: λ = 450-460 nm (λ_{max} = 457 nm)
Material of the irradiation vessel: borosilicate reaction tube
Distance from the light source to the irradiation vessel: 3.0 cm
Not use any filters

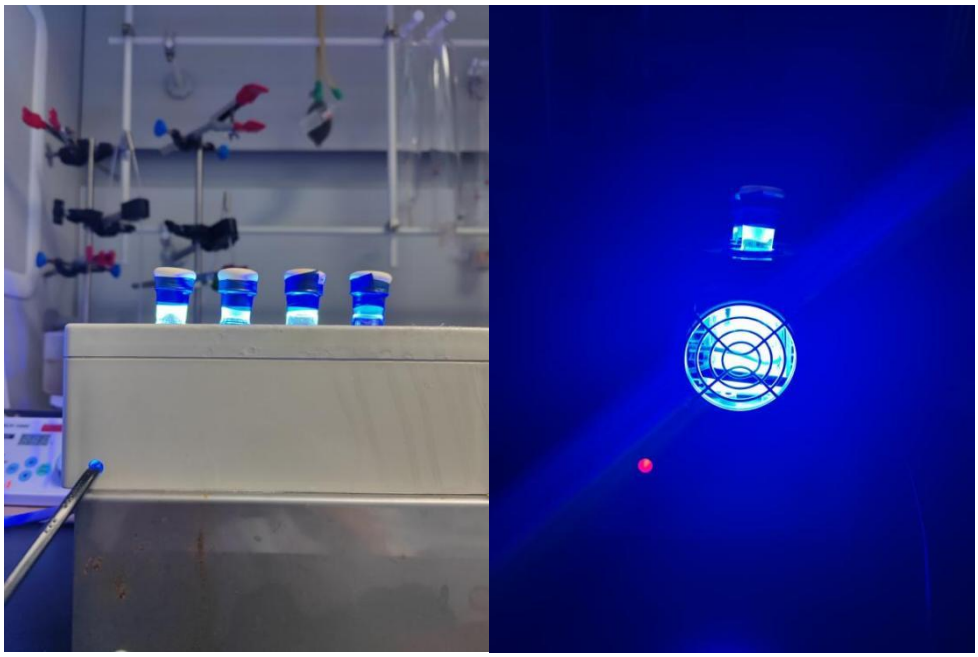
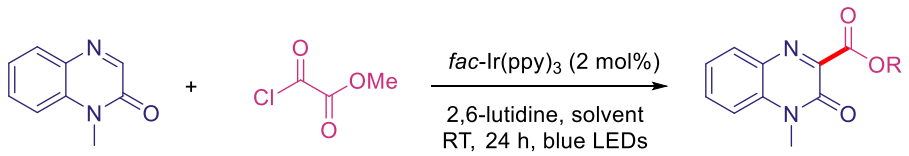


Figure S2 The set-up for the reaction

2. Reaction Optimization

Table S1. Effect of solvents on this reaction[a]



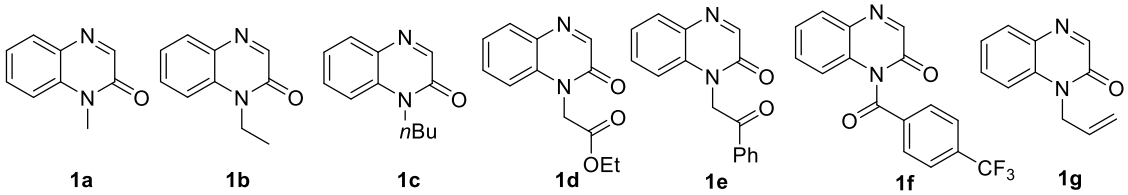
1a **2a** **3**

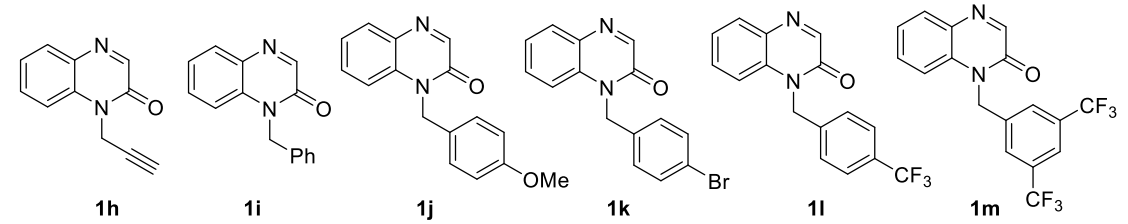
Entry	Solvent	Yield of **3** (%)[b]
1	DCM	16
2	DMF	15
3	THF	16
4	EtOAc	7
5	DMSO	25
7	CH_3CN	60

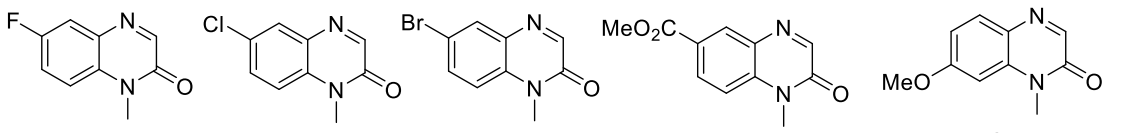
[a] Optimizations were performed on 0.1 mmol scale using **1a** (0.1 mmol, 1.0 equiv.), **2a** (1.0 equiv.), *fac*-Ir(ppy)$_3$ (2 mol%), 2,6-lutidine (1.5 equiv.), solvent (1 mL), 24 W blue LEDs (460 nm), room temperature, nitrogen atmosphere, 24 h. [b] The yield was determined by crude ^{1}H NMR using CH_2Br_2 as internal standard.

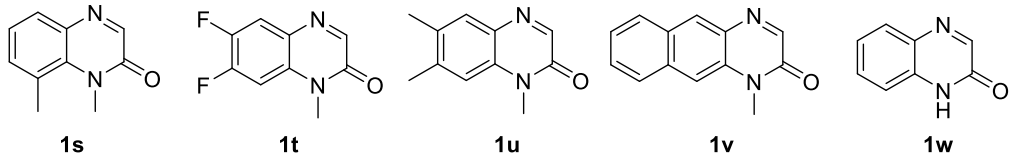
3. Product Synthesis and Characterization

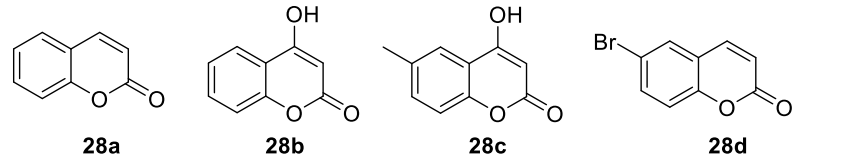
3.1 List of Substrates

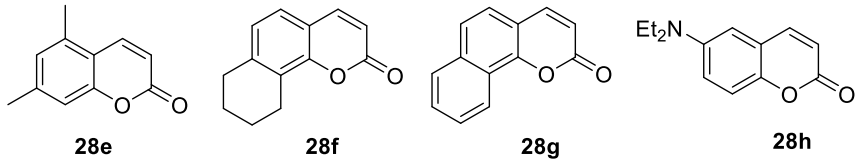


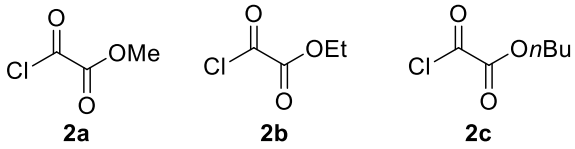


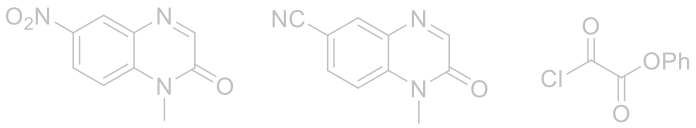






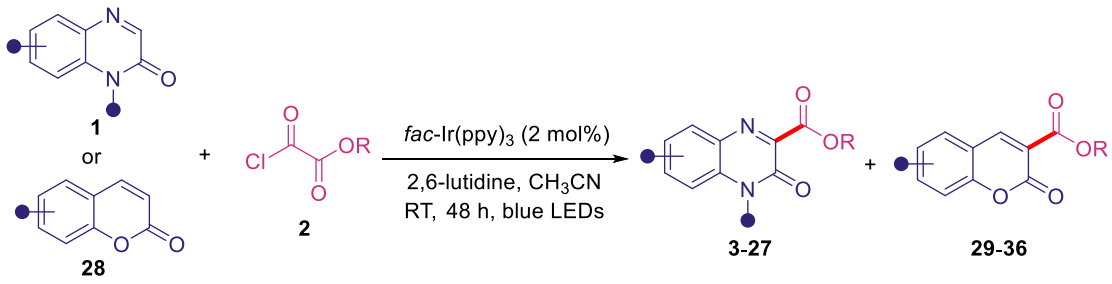






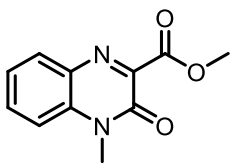
All the quinoxalin-2(1*H*)-ones and coumarins were synthesized according to the reported procedure.[1,2]

3.2 General procedure for the visible-light-promoted C3-H alkoxycarbonylation of quinoxalinones or coumarins



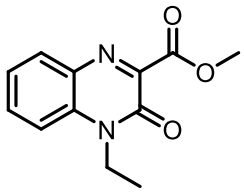
General Procedure:

To an oven-dried quartz tube, quinoxalin-2(1*H*)-one **1** (0.1 mmol, 1.0 equiv.) or coumarin **28** (0.1 mmol, 1.0 equiv.), alkyloxalyl chloride **2** (0.2 mmol, 2.0 equiv.), 2,6-lutidine (0.3 mmol, 3.0 equiv), and *fac*-Ir(ppy)$_3$ (0.002 mmol, 2 mol%) were added in a nitrogen-filled glove-box. CH_3CN (1.0 mL) was added into the tube via a syringe. The tube was sealed with a rubber plug wrapped with plastic film, removed from the glove box. The mixture was irradiated by 24 W 460 nm LEDs at room temperature for 48 h. After removal of solvents, the crude mixture was purified by flash chromatography (petroleum ether/ethyl acetate) to afford the pure products **3-27**, **29-36**.



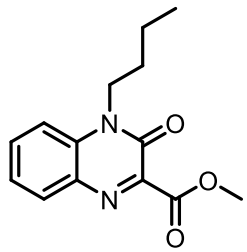
3

Methyl 4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (3).[3] **General Procedure** was used to prepare the desired product **3**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **3** as a yellow solid (14.7 mg, 0.067 mmol, 67%); **Mp:** 134.7-135.0 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.96 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.68 (tt, *J* = 7.3, 1.3 Hz, 1H), 7.53 – 7.35 (m, 2H), 4.03 (s, 3H), 3.74 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 164.1, 152.6, 148.4, 134.2, 132.7, 131.9, 131.4, 124.3, 113.9, 53.2, 29.2. **HRMS (DART-TOF)** calculated for $C_{11}H_{10}N_2O_3Na^+$ $[M+Na]^+$ m/z 241.0584, found 241.0590.



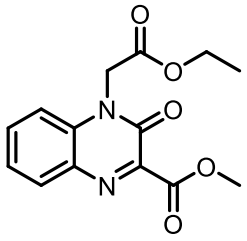
4

Methyl 4-ethyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (4).[3] **General Procedure** was used to prepare the desired product **4**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **4** as a yellow oil (14.7 mg, 0.063 mmol, 63%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.90 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.60 (dd, *J* = 8.7, 7.2 Hz, 1H), 7.33 (dd, *J* = 8.4, 6.5 Hz, 2H), 4.29 (q, *J* = 7.2 Hz, 2H), 3.96 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 164.1, 152.1, 148.5, 133.2, 132.7, 132.2, 131.6, 124.1, 113.8, 53.2, 37.7, 12.3. **HRMS (DART-TOF)** calculated for $C_{12}H_{12}N_2O_3Na^+$ $[M+Na]^+$ m/z 255.0740, found 255.0747.



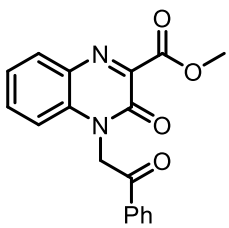
5

Methyl 4-butyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (5). General Procedure was used to prepare the desired product **5**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **5** as a brown oil (14.9 mg, 0.057 mmol, 57%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.89 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.59 (ddd, *J* = 8.7, 7.3, 1.5 Hz, 1H), 7.51 – 7.25 (m, 2H), 4.32 – 4.09 (m, 2H), 3.96 (s, 3H), 1.69 (ddt, *J* = 9.6, 7.9, 3.6 Hz, 2H), 1.43 (q, *J* = 7.5 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 164.2, 152.4, 148.5, 133.5, 132.6, 132.2, 131.6, 124.0, 113.9, 53.2, 42.4, 29.3, 20.3, 13.7. **HRMS (DART-TOF)** calculated for $C_{14}H_{16}N_2O_3Na^+$ $[M+Na]^+$ m/z 283.1053, found 283.1061.



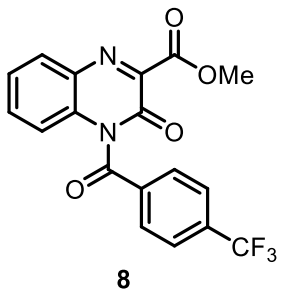
6

Methyl 4-(2-ethoxy-2-oxoethyl)-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (6).[3] **General Procedure** was used to prepare the desired product **6**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **6** as a yellow solid (14.9 mg, 0.051 mmol, 51%); **Mp:** 92.4-92.7 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.9 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.6 (dd, *J* = 8.6, 7.4 Hz, 1H), 7.3 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.1 (dd, *J* = 8.5, 1.2 Hz, 1H), 5.0 (s, 2H), 4.2 (q, *J* = 7.1 Hz, 2H), 4.0 (s, 3H), 1.2 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 166.6, 163.7, 152.1, 148.1, 133.5, 132.9, 132.0, 131.7, 124.6, 113.4, 62.3, 53.3, 43.5, 14.1. **HRMS (DART-TOF)** calculated for $C_{14}H_{14}N_2O_5Na^+$ $[M+Na]^+$ m/z 313.0795, found 313.0804.



7

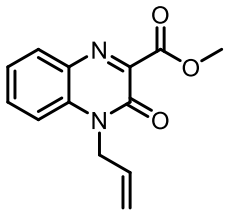
Methyl 3-oxo-4-(2-oxo-2-phenylethyl)-3,4-dihydroquinoxaline-2-carboxylate (7).[3] **General Procedure** was used to prepare the desired product **7**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **7** as a yellow oil (23.6 mg, 0.073 mmol, 73%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.00 (dd, *J* = 8.31, 1.36 Hz, 2H), 7.93 (dd, *J* = 8.09, 1.53 Hz, 1H), 7.66 – 7.58 (m, 1H), 7.49 (td, *J* = 8.30, 3.44 Hz, 3H), 7.36 – 7.27 (m, 1H), 6.94 (dd, *J* = 8.47, 1.10 Hz, 1H), 5.69 (s, 2H), 3.96 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 190.5, 163.8, 152.4, 147.9, 134.5, 134.4, 133.8, 132.8, 132.1, 131.7, 129.1, 128.2, 124.4, 113.9, 53.3, 48.4. **HRMS (DART-TOF)** calculated for $C_{18}H_{14}N_2O_4Na^+$ $[M+Na]^+$ m/z 345.0846, found 345.0852.



8

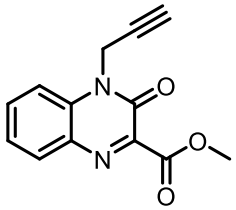
Methyl 3-oxo-4-(4-(trifluoromethyl)benzoyl)-3,4-dihydroquinoxaline-2-carboxylate (8). General Procedure was used to prepare the desired product **8**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (10/1) as eluent afforded **8** as a yellow oil (15.2 mg, 0.04 mmol, 40%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.41 (d, *J* = 8.16 Hz, 2H), 8.39 – 8.31 (m, 1H), 8.13 (dd, *J* = 8.11, 1.62 Hz, 1H), 8.00 – 7.90 (m, 2H), 7.84 (d, *J* = 8.21 Hz, 2H), 3.98 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 163.5, 151.9, 141.5, 140.6, 140.4, 135.8 (q, *J* = 32.8 Hz), 131.1, 131.0, 130.9, 130.5, 130.0, 129.3, 128.7, 125.8 (q, *J* = 3.7 Hz), 123.4 (q, *J* = 272.8 Hz), 53.4. **^{19}F NMR (376 MHz,**

Chloroform-*d*) δ -63.24. **HRMS (DART-TOF)** calculated for $C_{18}H_{12}F_3N_2O_4^+$ $[M+H]^+$ m/z 377.0744, found 377.0747.



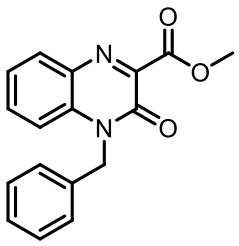
9

Methyl 4-allyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (9).[3] **General Procedure** was used to prepare the desired product **9**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **9** as a brown oil (7.2 mg, 0.029 mmol, 29%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.90 (dd, *J* = 8.05, 1.53 Hz, 1H), 7.57 (dd, *J* = 8.69, 7.30 Hz, 1H), 7.37 – 7.24 (m, 2H), 5.86 (ddt, *J* = 17.23, 10.41, 5.25 Hz, 1H), 5.24 (dq, *J* = 10.32, 1.33 Hz, 1H), 5.15 (dq, *J* = 17.32, 1.49 Hz, 1H), 4.87 (dt, *J* = 5.35, 1.72 Hz, 2H), 3.97 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 164.0, 152.2, 148.5, 133.5, 132.6, 132.1, 131.5, 130.1, 124.2, 118.8, 114.5, 53.2, 44.7. **HRMS (DART-TOF)** calculated for $C_{13}H_{12}N_2O_3Na^+$ $[M+Na]^+$ m/z 267.0740, found 267.0748.



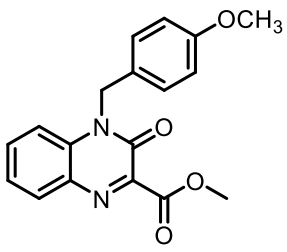
10

Methyl 3-oxo-4-(prop-2-yn-1-yl)-3,4-dihydroquinoxaline-2-carboxylate (10).[3] **General Procedure** was used to prepare the desired product **10**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **10** as a yellow oil (2.3 mg, 0.01 mmol, 10%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.98 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.71 (dd, *J* = 8.7, 7.3 Hz, 1H), 7.53 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.44 (dd, *J* = 8.4, 7.3 Hz, 1H), 5.08 (d, *J* = 2.6 Hz, 2H), 4.04 (s, 3H), 2.31 (s, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 163.7, 151.6, 148.2, 132.8, 132.7, 132.1, 131.5, 124.7, 114.5, 76.2, 73.8, 53.3, 31.6. **HRMS (DART-TOF)** calculated for $C_{13}H_{10}N_2O_3Na^+$ $[M+Na]^+$ m/z 265.0584, found 265.0585.



11

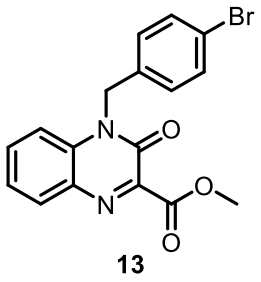
Methyl 4-benzyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (11).[3] **General Procedure** was used to prepare the desired product **11**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **11** as a yellow solid (16.6 mg, 0.056 mmol, 56%); **Mp:** 124.8-125.1 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.89 (dd, *J* = 8.02, 1.52 Hz, 1H), 7.47 (dd, *J* = 8.59, 7.26 Hz, 1H), 7.31 – 7.15 (m, 7H), 5.45 (s, 2H), 3.98 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 164.0, 152.7, 148.6, 134.7, 133.6, 132.7, 132.2, 131.5, 129.0, 128.0, 127.1, 124.3, 114.7, 53.3, 46.1. **HRMS (DART-TOF)** calculated for $C_{17}H_{14}N_2O_3Na^+$ $[M+Na]^+$ m/z 317.0897, found 317.0905.



12

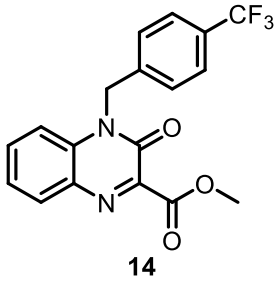
Methyl 4-(4-methoxybenzyl)-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (12). General Procedure was used to prepare the desired product **12**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **12** as a yellow solid (8.9 mg, 0.027 mmol, 27%); **Mp:** 115.8-116.0 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.88 (dd, *J* = 8.04, 1.50 Hz, 1H), 7.49 (dd, *J* = 8.61, 7.16 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.16 (d, *J* = 8.62

Hz, 2H), 6.83 – 6.73 (m, 2H), 5.37 (s, 2H), 3.98 (s, 3H), 3.69 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 164.1, 159.3, 152.7, 148.6, 133.6, 132.6, 132.2, 131.5, 128.6, 126.8, 124.3, 114.7, 114.4, 55.3, 53.3, 45.6. **HRMS (DART-TOF)** calculated for $C_{18}H_{16}N_2O_4Na^+$ $[M+Na]^+$ m/z 347.1002, found 347.0994.



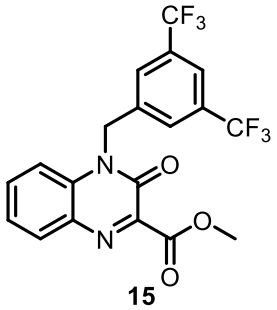
13

Methyl 4-(4-bromobenzyl)-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (13). General Procedure was used to prepare the desired product **13**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **13** as a yellow oil (17.7 mg, 0.047 mmol, 47%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.90 (dd, *J* = 8.03, 1.52 Hz, 1H), 7.49 (dd, *J* = 8.67, 7.29 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.31 (dd, *J* = 8.27, 7.31 Hz, 1H), 7.23 – 7.16 (m, 1H), 7.09 (d, *J* = 8.32 Hz, 2H), 5.39 (s, 2H), 3.98 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 163.9, 152.6, 148.5, 133.7, 133.4, 132.8, 132.2 (2C), 131.6, 128.9, 124.5, 122.0, 114.5, 53.3, 45.6. **HRMS (DART-TOF)** calculated for $C_{17}H_{13}N_2O_3BrNa^+$ $[M+Na]^+$ m/z 395.0002, found 395.0004.



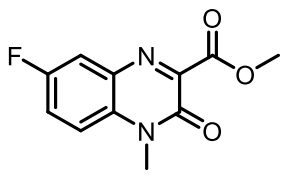
14

Methyl 3-oxo-4-(4-(trifluoromethyl)benzyl)-3,4-dihydroquinoxaline-2-carboxylate (14). General Procedure was used to prepare the desired product **14**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **14** as a yellow solid (17.7 mg, 0.058 mmol, 58%); **Mp:** 123.1-123.6 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.92 (dd, *J* = 8.12, 1.51 Hz, 1H), 7.56 – 7.46 (m, 3H), 7.32 (t, *J* = 7.29 Hz, 3H), 7.22 – 7.11 (m, 1H), 5.49 (s, 2H), 3.99 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 163.8, 152.6, 148.5, 138.7, 133.3, 132.9, 132.2, 131.7, 130.4 (q, *J* = 32.9 Hz), 127.4, 126.1 (q, *J* = 3.8 Hz), 124.6, 123.8 (q, *J* = 272.3 Hz), 114.3, 53.3, 45.7. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -62.72. **HRMS (DART-TOF)** calculated for $C_{18}H_{13}F_3N_2O_3Na^+$ $[M+Na]^+$ m/z 385.0770, found 385.0779.



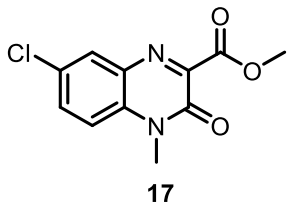
15

Methyl 4-(3,5-bis(trifluoromethyl)benzyl)-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (15). General Procedure was used to prepare the desired product **15**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **15** as a yellow solid (19.4 mg, 0.045 mmol, 45%); **Mp:** 123.1-123.6 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.83 (s, 1H), 7.72 (s, 2H), 7.63 (dd, *J* = 8.7, 7.4 Hz, 1H), 7.50 – 7.39 (m, 1H), 7.25 – 7.16 (m, 1H), 5.60 (s, 2H), 4.06 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 163.6, 152.5, 148.3, 137.5, 133.2, 133.1, 132.6 (q, *J* = 33.8 Hz), 132.2, 132.1, 127.4 (q, *J* = 3.3 Hz), 124.9, 122.9 (q, *J* = 273.2 Hz), 122.3 (q, *J* = 3.3 Hz), 113.8, 53.4, 45.5. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -62.87. **HRMS (DART-TOF)** calculated for $C_{19}H_{12}F_6N_2O_3Na^+$ $[M+Na]^+$ m/z 453.0644, found 453.0654.



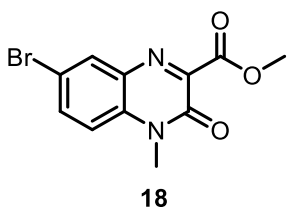
16

Methyl 6-fluoro-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (16).[3] **General Procedure** was used to prepare the desired product **16**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **16** as a yellow oil (9.5 mg, 0.04 mmol, 40%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.59 (dd, *J* = 8.3, 2.9 Hz, 1H), 7.37 (dd, *J* = 9.2, 7.7 Hz, 1H), 7.27 (dd, *J* = 9.2, 4.7 Hz, 1H), 3.97 (s, 3H), 3.67 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 163.8, 158.8 (d, *J* = 245.7 Hz), 152.2, 150.0, 132.4 (d, *J* = 11.4 Hz), 130.9 (d, *J* = 2.1 Hz), 120.6 (d, *J* = 24.2 Hz), 116.5 (d, *J* = 22.7 Hz), 115.1 (d, *J* = 8.7 Hz), 53.3, 29.5. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -117.50 (td, *J* = 7.8, 4.4 Hz). **HRMS (DART-TOF)** calculated for $C_{11}H_9N_2O_3FNa^+$ $[M+Na]^+$ m/z 259.0489, found 259.0496.



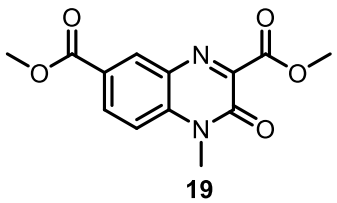
17

Methyl 6-chloro-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (17).[3] **General Procedure** was used to prepare the desired product **17**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **17** as a yellow solid (10.6 mg, 0.041 mmol, 41%); **Mp:** 148.2-149.0 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.87 (d, *J* = 2.4 Hz, 1H), 7.56 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.24 (d, *J* = 9.0 Hz, 1H), 3.96 (s, 3H), 3.65 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 163.7, 152.2, 149.8, 132.8, 132.7, 132.3, 130.5, 129.7, 115.1, 53.3, 29.4. **HRMS (DART-TOF)** calculated for $C_{11}H_9N_2O_3Cl$ Na^+ $[M+Na]^+$ m/z 275.0194, found 275.0194.



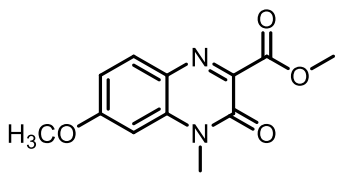
18

Methyl 6-bromo-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (18).[3] **General Procedure** was used to prepare the desired product **18**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **18** as a yellow solid (17.7 mg, 0.06 mmol, 60%); **Mp:** 153.0-153.2 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.87 (d, *J* = 2.4 Hz, 1H), 7.56 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.24 (d, *J* = 9.0 Hz, 1H), 3.96 (s, 3H), 3.65 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 163.7, 152.2, 149.7, 135.4, 133.6, 133.3, 132.6, 116.9, 115.4, 53.3, 29.4. **HRMS (DART-TOF)** calculated for $C_{11}H_9N_2O_3BrNa^+$ $[M+Na]^+$ m/z 318.9689, found 318.9690.



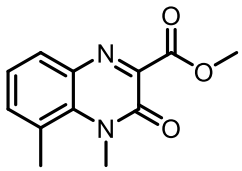
19

Dimethyl 4-methyl-3-oxo-3,4-dihydroquinoxaline-2,6-dicarboxylate (19).[3] **General Procedure** was used to prepare the desired product **19**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **19** as a yellow solid (12.4 mg, 0.045 mmol, 45%); **Mp:** 177.8-178.3 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.56 (d, *J* = 2.0 Hz, 1H), 8.24 (d, *J* = 8.8 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 3.97 (s, 3H), 3.90 (s, 3H), 3.69 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 165.6, 163.6, 152.4, 149.4, 137.2, 133.2, 133.1, 131.2, 126.3, 114.0, 53.3, 52.5, 29.5. **HRMS (DART-TOF)** calculated for $C_{13}H_{12}N_2O_5Na^+$ $[M+Na]^+$ m/z 299.0638, found 299.0639.



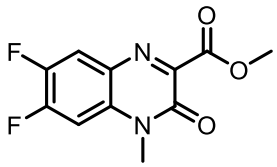
20

Methyl 6-methoxy-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (20). General Procedure was used to prepare the desired product **20**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (15/1) as eluent afforded **20** as a yellow oil (5.0 mg, 0.02 mmol, 20%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.59 (d, *J* = 2.3 Hz, 1H), 6.47 (s, 1H), 6.43 (s, 1H), 3.21 (s, 3H), 3.06 (s, 3H), 2.91 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 164.1, 156.4, 152.3, 148.6, 132.6, 128.6, 122.6, 114.8, 112.0, 55.9, 53.2, 29.4. **HRMS (DART-TOF)** calculated for $C_{12}H_{12}N_2O_4Na^+$ $[M+Na]^+$ m/z 271.0689, found 271.0695.



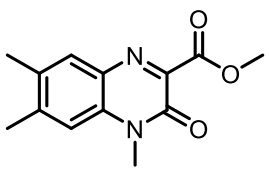
21

Methyl 4,5-dimethyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (21). General Procedure was used to prepare the desired product **21**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **21** as a yellow solid (19.3 mg, 0.083 mmol, 83%); **Mp:** 134.7-135.0 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.46 (dd, *J* = 8.5, 7.5 Hz, 1H), 7.17 (dt, *J* = 7.5, 1.1 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 1H), 3.95 (s, 3H), 3.64 (s, 3H), 2.61 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 164.6, 152.6, 147.0, 140.5, 134.3, 132.3, 130.7, 125.5, 111.7, 53.0, 29.3, 17.5. **HRMS (DART-TOF)** calculated for $C_{12}H_{13}N_2O_3^+$ $[M+H]^+$ m/z 233.0921, found 233.0921.



22

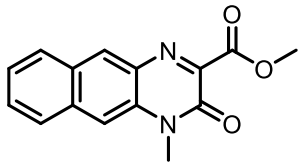
Methyl 6,7-difluoro-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (22). General Procedure was used to prepare the desired product **22**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **22** as a yellow oil (15.0 mg, 0.059 mmol, 59%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.78 (dd, *J* = 9.8, 8.1 Hz, 1H), 7.17 (dd, *J* = 11.0, 6.9 Hz, 1H), 4.03 (s, 3H), 3.69 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 159.9, 157.5, 154.7, 151.6, 133.9 (d, *J* = 11.2 Hz), 129.9 (d, *J* = 2.1 Hz), 118.8 (d, *J* = 24.0 Hz), 115.9 (d, *J* = 22.5 Hz), 114.9 (d, *J* = 8.7 Hz), 53.4, 29.0. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -129.17, -141.68. **HRMS (DART-TOF)** calculated for $C_{11}H_8F_2N_2O_3Na^+$ $[M+Na]^+$ m/z 277.0395, found 277.0401.



23

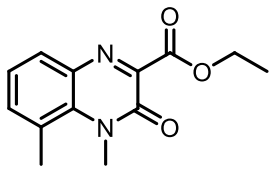
Methyl 4,6,7-trimethyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (23).[3] **General Procedure** was used to prepare the desired product **23**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **23** as a brown oil (14.8 mg, 0.06 mmol, 60%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.63 (s, 1H), 7.05 (s, 1H), 3.95 (s, 3H), 3.64 (s, 3H), 2.38 (s, 3H), 2.29 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 164.3, 152.8, 146.8, 143.4, 133.5, 132.4, 131.3, 130.4, 114.4, 53.1, 29.1, 20.9, 19.2. **HRMS (DART-TOF)** calculated for $C_{13}H_{14}N_2O_3Na^+$ $[M+H]^+$ m/z 269.0897, found 269.0904.

Methyl 4-methyl-3-oxo-3,4-dihydrobenzo[g]quinoxaline-2-carboxylate (24). General Procedure was used to prepare the desired product **24**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **24** as a yellow oil (4.1 mg, 0.015



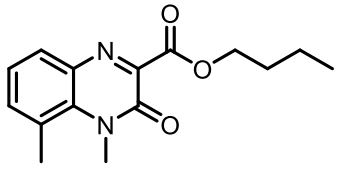
24

mmol, 15%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.43 (s, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.65 – 7.54 (m, 2H), 7.46 (dd, *J* = 8.4, 6.6 Hz, 1H), 3.99 (s, 3H), 3.74 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 164.0, 152.4, 149.3, 134.9, 131.8, 131.4, 131.1, 129.8, 129.1, 129.0, 127.3, 125.9, 110.4, 53.3, 29.2. **HRMS (DART-TOF)** calculated for $C_{15}H_{12}N_2O_3Na^+$ $[M+Na]^+$ m/z 291.0740, found 291.0743.



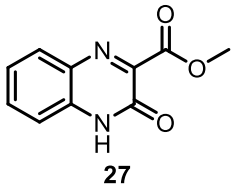
25

Ethyl 4,5-dimethyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (25). General Procedure was used to prepare the desired product **25**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **25** as a yellow oil (8.7 mg, 0.035 mmol, 35%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.53 (dd, *J* = 8.49, 7.45 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.18 (d, *J* = 8.46 Hz, 1H), 4.50 (q, *J* = 7.13 Hz, 2H), 3.72 (s, 3H), 2.69 (s, 3H), 1.44 (t, *J* = 7.14 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 164.3, 152.6, 147.5, 140.5, 134.3, 132.1, 130.8, 125.5, 111.7, 62.3, 29.3, 17.5, 14.2. **HRMS (DART-TOF)** calculated for $C_{13}H_{14}N_2O_3Na^+$ $[M+Na]^+$ m/z 269.0897, found 269.0901.



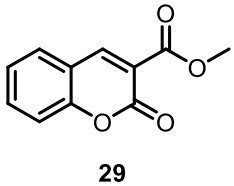
26

Butyl 4,5-dimethyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (26). General Procedure was used to prepare the desired product **26**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **26** as a yellow oil (5.6 mg, 0.02 mmol, 20%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.52 (dd, *J* = 8.44, 7.46 Hz, 1H), 7.24 (d, *J* = 7.54 Hz, 1H), 7.18 (d, *J* = 8.48 Hz, 1H), 4.45 (t, *J* = 6.73 Hz, 2H), 3.71 (s, 3H), 2.69 (s, 3H), 1.86 – 1.72 (m, 2H), 1.49 (dt, *J* = 14.74, 7.45 Hz, 2H), 0.98 (t, *J* = 7.40 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 158.1, 155.1, 148.4, 139.3, 133.4, 132.1, 130.8, 125.1, 111.7, 66.9, 30.3, 28.9, 19.0, 17.6, 13.6. **HRMS (DART-TOF)** calculated for $C_{15}H_{19}N_2O_3^+$ $[M+H]^+$ m/z 275.1390, found 275.1395.



27

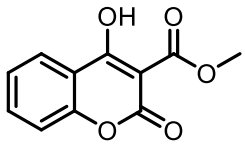
Methyl 3-oxo-3,4-dihydroquinoxaline-2-carboxylate (27). General Procedure was used to prepare the desired product **27**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **27** as a yellow oil (4.1 mg, 0.02 mmol, 20%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.42 (dd, *J* = 8.1, 5.8 Hz, 2H), 4.07 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 163.6, 154.4, 147.7, 133.0, 132.3, 132.1, 130.4, 125.2, 116.4, 53.3. **HRMS (DART-TOF)** calculated for $C_{10}H_8N_2O_3Na^+$ $[M+Na]^+$ m/z 227.0427, found 227.0434.



29

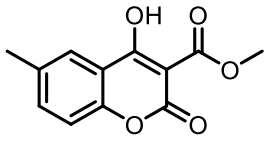
Methyl 2-oxo-2*H*-chromene-3-carboxylate (29). General Procedure was used to prepare the desired product **29**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **29** as a yellow oil (9.6 mg, 0.047 mmol, 47%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.57 (s, 1H), 7.87 – 7.51 (m, 2H), 7.48 – 7.28 (m, 2H),

3.96 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 163.7, 156.7, 155.2, 134.5, 129.6, 124.9, 117.9, 117.9, 116.8, 116.8, 53.0. **HRMS (DART-TOF)** calculated for $C_{11}H_8O_4Na^+$ $[M+Na]^+$ m/z 227.0317, found 227.0315.



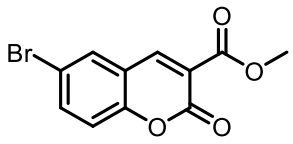
30

Methyl 4-hydroxy-2-oxo-2*H*-chromene-3-carboxylate (30). General Procedure was used to prepare the desired product **30**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **30** as a yellow oil (16.8 mg, 0.076 mmol, 76%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 14.55 (s, 1H), 7.96 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.62 (dd, *J* = 8.8, 7.4 Hz, 1H), 7.32 – 7.22 (m, 2H), 3.97 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 175.6, 172.3, 157.6, 154.5, 135.7, 125.2, 124.4, 117.0, 114.4, 93.0, 53.4. **HRMS (DART-TOF)** calculated for $C_{11}H_8O_5Na^+$ $[M+Na]^+$ m/z 243.0264, found 243.0266.



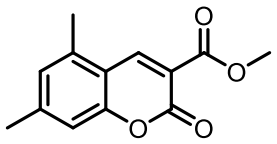
31

Methyl 4-hydroxy-6-methyl-2-oxo-2*H*-chromene-3-carboxylate (31). General Procedure was used to prepare the desired product **31**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **31** as a yellow solid (12.9 mg, 0.055 mmol, 55%); **Mp:**118.3-119.0 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 14.51 (s, 1H), 7.73 (s, 1H), 7.46 – 7.38 (m, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 3.97 (d, *J* = 1.2 Hz, 3H), 2.37 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 175.6, 172.4, 157.8, 152.7, 136.9, 134.2, 124.6, 116.7, 114.1, 92.9, 53.3, 20.8. **HRMS (DART-TOF)** calculated for $C_{12}H_{10}O_5Na^+$ $[M+Na]^+$ m/z 257.0420, found 257.0423.



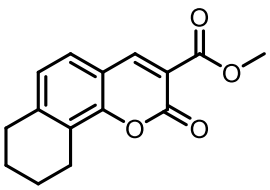
32

Methyl 7-bromo-2-oxo-2*H*-chromene-3-carboxylate (32). General Procedure was used to prepare the desired product **32**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **32** as a yellow oil (9.4 mg, 0.033 mmol, 33%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.45 (s, 1H), 7.48 (s, 1H), 7.41 (s, 2H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 163.5, 155.9, 155.3, 148.4, 130.3, 129.1, 128.5, 120.2, 118.1, 116.8, 53.0. **HRMS (DART-TOF)** calculated for $C_{11}H_7O_4BrNa^+$ $[M+Na]^+$ m/z 304.9420, found 304.9420.



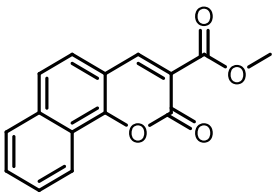
33

Methyl 5,7-dimethyl-2-oxo-2*H*-chromene-3-carboxylate (33). General Procedure was used to prepare the desired product **33**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **33** as a yellow oil (7.0 mg, 0.039 mmol, 39%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.75 (s, 1H), 6.99 (d, *J* = 9.6 Hz, 2H), 3.96 (s, 3H), 2.55 (s, 3H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 164.4, 157.1, 156.2, 146.5, 146.3, 137.9, 127.5, 115.6, 114.9, 114.7, 52.9, 22.1, 18.3. **HRMS (DART-TOF)** calculated for $C_{13}H_{12}O_4Na^+$ $[M+Na]^+$ m/z 255.0628, found 255.0638.



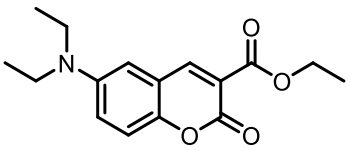
34

Methyl 2-oxo-7,8,9,10-tetrahydro-2*H*-benzo[*h*]chromene-3-carboxylate (34). General Procedure was used to prepare the desired product **34**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **34** as a yellow solid (5.0 mg, 0.02 mmol, 20%); **Mp:** 132.6-132.8 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.45 (s, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 3.88 (s, 3H), 2.83 (dt, *J* = 17.1, 5.6 Hz, 4H), 1.89 – 1.64 (m, 4H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 164.2, 157.2, 153.6, 149.8, 145.9, 126.0, 125.9, 125.7, 116.0, 115.2, 52.8, 30.3, 22.5, 22.3, 21.9. **HRMS (DART-TOF)** calculated for $C_{15}H_{14}O_4Na^+$ $[M+Na]^+$ m/z 281.0784, found 281.0792.



35

Methyl 2-oxo-2*H*-benzo[*h*]chromene-3-carboxylate (35). General Procedure was used to prepare the desired product **35**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **35** as a yellow oil (12.2 mg, 0.048 mmol, 48%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.71 (s, 1H), 8.63 – 8.51 (m, 1H), 7.90 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.72 (d, *J* = 6.0 Hz, 3H), 7.54 (d, *J* = 8.6 Hz, 1H), 3.99 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 164.0, 156.8, 153.7, 150.0, 136.1, 130.1, 128.0, 127.6, 125.0, 124.1, 123.2, 122.6, 116.7, 113.4, 52.9. **HRMS (DART-TOF)** calculated for $C_{15}H_{10}O_4Na^+$ $[M+Na]^+$ m/z 277.0471, found 277.0479.

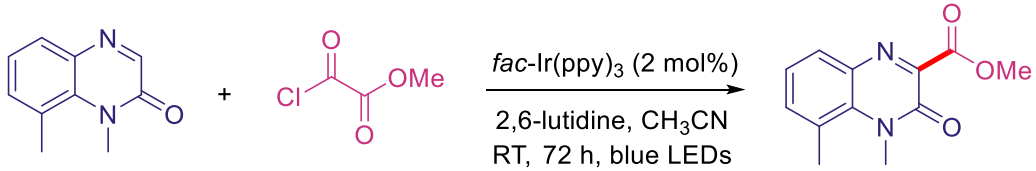


36

Ethyl 6-(diethylamino)-2-oxo-2*H*-chromene-3-carboxylate (36). General Procedure was used to prepare the desired product **36**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **36** as a yellow solid (10.1 mg, 0.035 mmol, 35%); **Mp:** 85.9-86.3 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.42 (d, *J* = 1.47 Hz, 1H), 7.35 (dd, *J* = 8.91, 1.28 Hz, 1H), 6.67 – 6.56 (m, 1H), 6.47 (q, *J* = 2.31 Hz, 1H), 4.66 – 4.18 (m, 2H), 3.77 – 3.05 (m, 4H), 1.39 (td, *J* = 7.17, 1.40 Hz, 3H), 1.23 (td, *J* = 7.15, 1.43 Hz, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 164.3, 158.5, 158.3, 152.9, 149.2, 131.0, 109.5, 109.1, 107.7, 96.8, 61.1, 45.1, 14.4, 12.4. **HRMS (DART-TOF)** calculated for $C_{16}H_{20}NO_4^+$ $[M+H]^+$ m/z 290.1387, found 290.1390

4. Scale-up and Transformation of Product

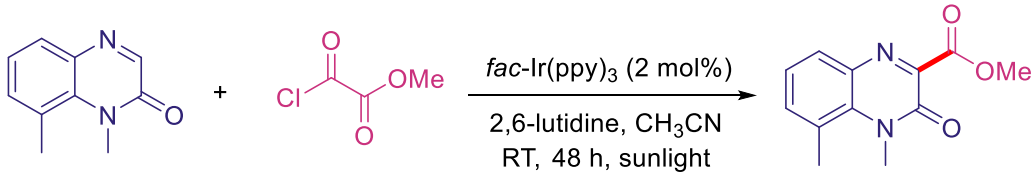
4.1 Scale-up reaction



1s, 1 mmol + **2a**, 2 mmol → **21**, 68% yield

A mixture of 1,8-dimethylquinoxalin-2(1*H*)-one **1s** (1.0 mmol), methyl 2-chloro-2-oxoacetate **2a** (2.0 mmol, 2.0 equiv.), 2,6-lutidine (3.0 mmol, 3.0 equiv), and *fac*-Ir(ppy)$_3$ (0.02 mmol, 2 mol%) and CH_3CN (3 mL) was degassed by three cycles of freeze-pump-thaw. The mixture was irradiated by 24 W 460 nm blue LEDs at room temperature for 72 h. After removal of solvents, the crude mixture was purified by flash chromatography (petroleum ether/ethyl acetate) to afford the pure product **21** (0.158 g, 0.68 mmol, 68%).

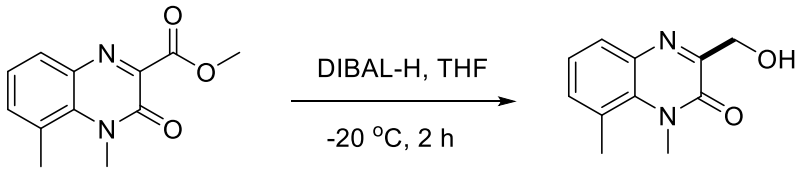
4.2 Sunlight driven experiment



1s, 0.1 mmol **2a**, 0.2 mmol **21**, 46% yield

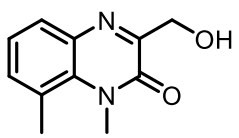
To an oven-dried quartz tube, 1,8-dimethylquinoxalin-2(1*H*)-one **1s** (0.1 mmol), methyl 2-chloro-2-oxoacetate **2a** (0.2 mmol, 2.0 equiv.), 2,6-lutidine (0.3 mmol, 3.0 equiv), and *fac*-Ir(ppy)$_3$ (0.002 mmol, 2 mol%) was added in a nitrogen-filled glove-box. CH_3CN (1 mL) was added into the tube via a syringe. The tube was sealed with a rubber plug wrapped with plastic film, removed from the glove box. The resulting mixture was irradiated by sunlight for 48 h (as an on/off visible light irradiation experiment, the reaction solution was kept in dark place at night). After completion of the reaction, the crude mixture was purified by flash chromatography (petroleum ether/ethyl acetate) to afford the product **21** (0.011 g, 0.046 mmol, 46%).

4.3 Synthetic applications



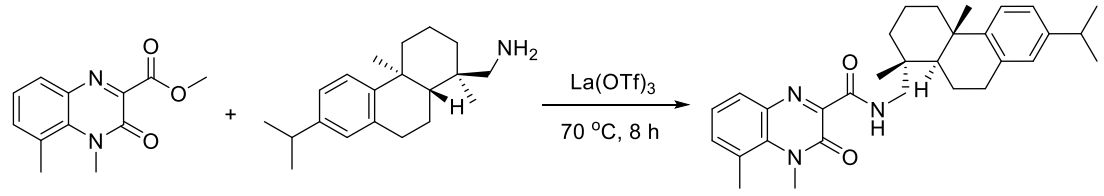
21 **37**, 57% yield

To an oven-dried quartz vial, equipped with a magnetic stirring bar, methyl 4,5-dimethyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate **21** (0.1 mmol) was dissolved in THF. After cooling to -20 °C, DIBAL-H (0.2 mmol, 2.0 equiv.) was slowly added and stirred for 2 h at the same temperature. After completion of reaction, it was quenched by the addition of aqueous 1 N HCl at room temperature and extracted with diethyl ether. The combined organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure to afford the crude product, which was further purified by flash chromatography on silica gel to give the desired product **37** (11.7 mg, 57%).



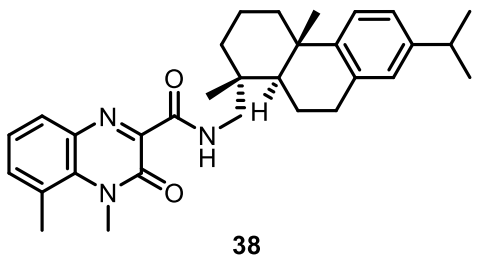
37

3-(Hydroxymethyl)-1,8-dimethylquinoxalin-2(1*H*)-one (37). Chromatographic purification on silica gel using petroleum ether/ethyl acetate (1/1) as eluent afforded **37** as a yellow oil (11.7 mg, 0.057 mmol, 57%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.32 (s, 1H), 7.48 (t, *J* = 7.94 Hz, 1H), 7.20 (dd, *J* = 13.09, 7.92 Hz, 2H), 5.30 (s, 2H), 3.69 (s, 3H), 2.69 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 155.0, 148.4, 139.3, 133.4, 132.1, 130.8, 125.1, 111.7, 53.4, 28.9, 17.6. **HRMS (DART-TOF)** calculated for $C_{11}H_{13}N_2O_2^+$ $[M+H]^+$ m/z 205.0972, found 205.0976.



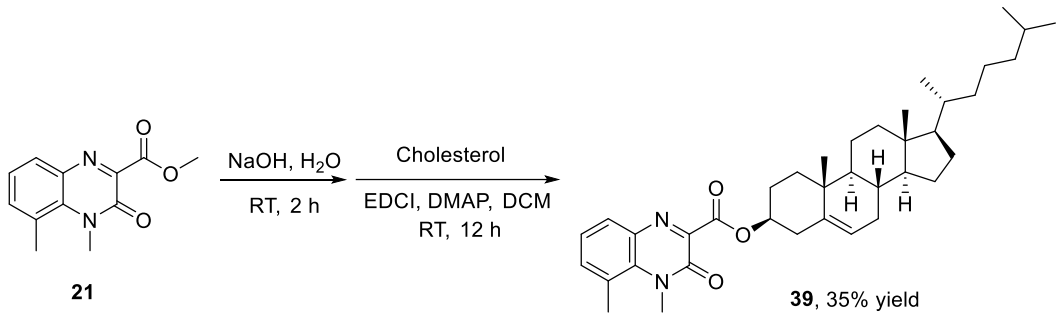
21 dehydroabietylamine **38**, 41% yield

To an oven-dried quartz vial, methyl 4,5-dimethyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate **21** (0.1 mmol) and dehydroabietylamine (0.1 mmol, 1.0 equiv.) were added sequentially. The vial was charged with a stir bar and transferred to a glovebox, where the solids were backfilled with an inert atmosphere. In the glovebox, lanthanum trifluoromethanesulfonate (0.002 mmol, 2.0 mol%) was added into the vial. The vial was sealed with a rubber plug, removed from the glove box, and irradiated and stir at 70 ℃ for 8 h. The crude mixture was diluted with dichloromethane and purified by flash chromatography to afford the pure products **38** (20.1 mg, 41%).



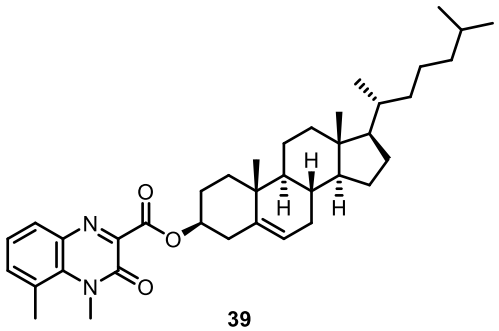
38

***N*-(((*1R*,*4aS*,*10aR*)-7-Isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-4,5-dimethyl-3-oxo-3,4-dihydroquinoxaline-2-carboxamide (38).** Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **38** as a yellow oil (20.1 mg, 0.041 mmol, 41%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.83 (t, *J* = 6.3 Hz, 1H), δ 7.56 (t, *J* = 7.96 Hz, 1H), 7.28 (d, *J* = 7.39 Hz, 1H), 7.18 (dd, *J* = 10.63, 8.28 Hz, 2H), 6.97 (dd, *J* = 8.18, 2.07 Hz, 1H), 6.88 (d, *J* = 2.00 Hz, 1H), 3.74 (s, 3H), 3.57 – 3.34 (m, 2H), 2.97 – 2.87 (m, 2H), 2.80 (s, 3H), 2.28 (dd, *J* = 12.91, 3.71 Hz, 1H), 2.09 – 1.50 (m, 9H), 1.24 (s, 3H), 1.20 (d, *J* = 6.95 Hz, 6H), 1.04 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 162.0, 155.2, 147.2, 145.5, 143.0, 141.7, 135.0, 133.9, 132.8, 131.5, 126.9, 125.9, 124.3, 123.8, 111.6, 50.7, 45.8, 38.4, 37.8, 37.6, 36.6, 33.4, 30.5, 29.7, 25.5, 24.0, 19.1, 18.8, 18.8, 17.7. **HRMS (DART-TOF)** calculated for $C_{31}H_{40}N_3O_2^+$ $[M+H]^+$ m/z 486.3115, found 486.3122.



To a solution of methyl 4,5-dimethyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate **21** (0.2 mmol, 1.0 equiv.) was added NaOH and H_2O. The reaction mixture was stirred at room temperature for 2 h, the reaction mixture was concentrated to a residue in vacuo. The first part of the product was obtained and 0.1 mmol was used in the second part of the reaction.

A solution of 4,5-dimethyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylic acid (21.8 mg, 0.1 mmol), cholesterol (46.4 mg, 0.12 mmol), EDCI (24.9 mg, 0.13 mmol) and DMAP (17.1 mg, 0.14 mmol) in 1 mL CH_2Cl_2 were stirred at room temperature overnight. Until completion of the reaction monitored by TLC, the reaction mixture was quenched with water, extracted with DCM. Combined organic layers were dried over $MgSO_4$, filtered and evaporated under reduced pressure to afford the crude product, which was further purified by flash chromatography on silica gel to give the desired product **39** (20.6 mg, 35%).

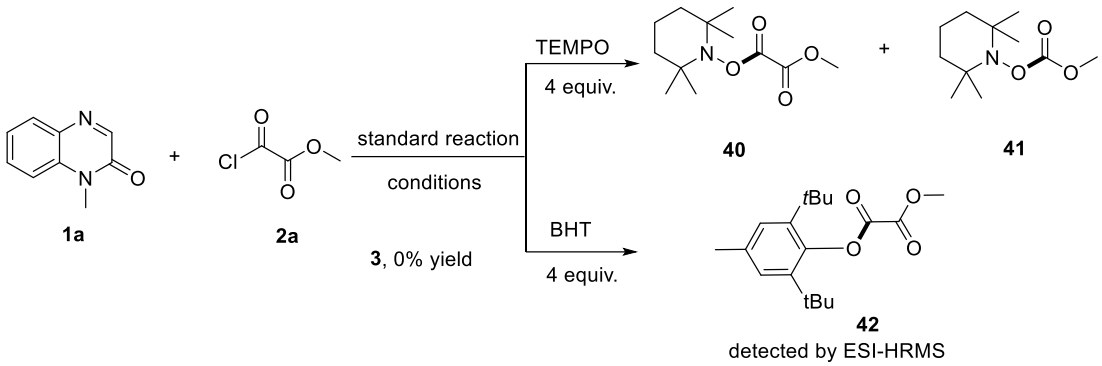


(*3S,8S,9S,10R,13R,14S,17R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4,5-dimethyl-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (39).

Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **39** as a yellow oil (20.6 mg, 0.035 mmol, 35%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.52 (dd, *J* = 8.47, 7.46 Hz, 1H), 7.24 (d, *J* = 7.44 Hz, 1H), 7.17 (d, *J* = 8.45 Hz, 1H), 5.44 (dd, *J* = 4.98, 2.53 Hz, 1H), 5.00 (tq, *J* = 9.80, 4.99 Hz, 1H), 3.71 (s, 3H), 2.69 (s, 3H), 2.63 – 2.45 (m, 2H), 2.37 – 1.70 (m, 13H), 1.43 – 1.28 (m, 8H), 1.05 (s, 3H), 1.01 (s, 3H), 0.92 (dd, *J* = 6.57, 3.30 Hz, 5H), 0.87 (t, *J* = 1.81 Hz, 3H), 0.86 (d, *J* = 1.83 Hz, 3H), 0.69 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ163.9, 152.6, 147.9, 140.4, 139.5, 134.2, 132.0, 130.8, 125.4, 123.0, 121.7, 111.6, 76.2, 71.8, 56.8, 56.7, 56.2, 56.2, 50.2, 50.0, 42.3, 39.8, 39.8, 39.5, 37.9, 37.0, 36.7, 36.2, 35.8, 32.0, 31.9, 31.9, 29.2, 28.2, 28.0, 27.7, 24.3, 23.8, 22.8, 22.6, 21.1, 21.1, 19.4, 19.4, 18.7, 17.5, 11.9. **HRMS (DART-TOF)** calculated for $C_{38}H_{54}N_2O_3Na^+$ $[M+Na]^+$ m/z 609.4027, found 609.4025.

5. Mechanistic Experiments

5.1 Radical Inhibition Experiments



To an oven-dried quartz vial, 1-methylquinoxalin-2(1*H*)-one **1a** (0.1 mmol, 1.0 equiv.), TEMPO (4.0 equiv.), 2,6-lutidine (0.3 mmol, 3.0 equiv.), and *fac*-Ir(ppy)$_3$ (0.002 mmol, 2 mol%) were added sequentially. The vial was charged with a stir bar and transferred to a glovebox, where the solids were backfilled with an inert atmosphere. In the glovebox, methyl 2-chloro-2-oxoacetate **2a** (0.2 mmol, 2.0 equiv.) was added into the vial, followed by CH_3CN (1.0 mL). The vial was sealed with a rubber plug, removed from the glove box, and irradiated and stir by 24 W 460 nm LEDs at room temperature for 48 h. **HRMS (DART-TOF)**: compound **40** calculated for $C_{12}H_{31}NO_4^+$ $[M+H]^+$ m/z 244.1543, found 244.1548. **HRMS (DART-TOF)**: compound **41** calculated for $C_{11}H_{22}NO_3^+$ $[M+H]^+$ m/z 216.1594, found 216.1598.

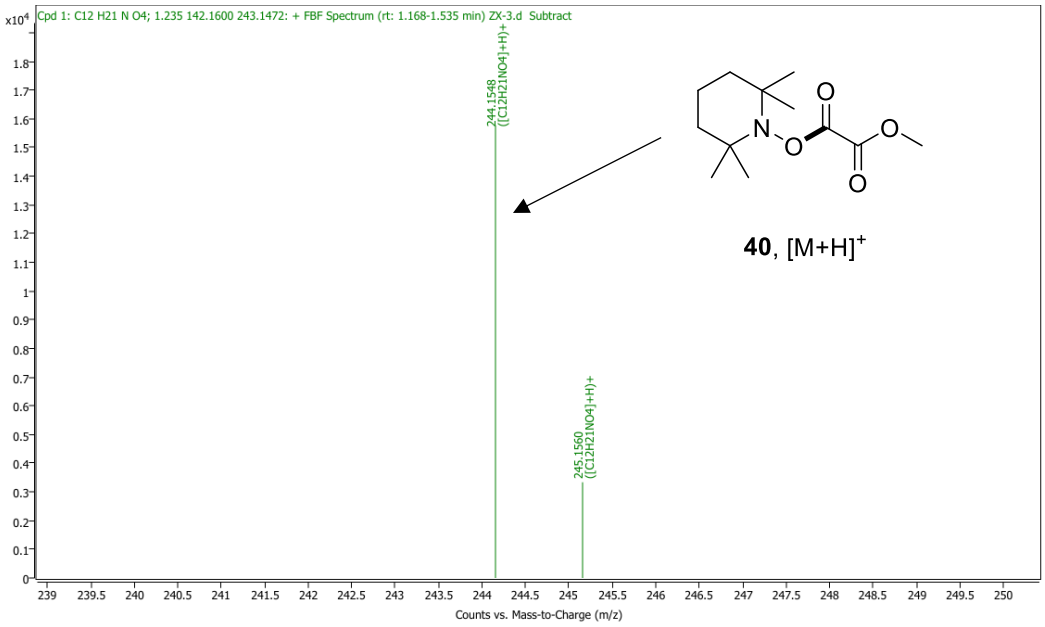


Figure S3 1-Methylquinoxalin-2(1*H*)-one **1a** and methyl 2-chloro-2-oxoacetate **2a** under standard conditions with TEMPO (4.0 equiv.)

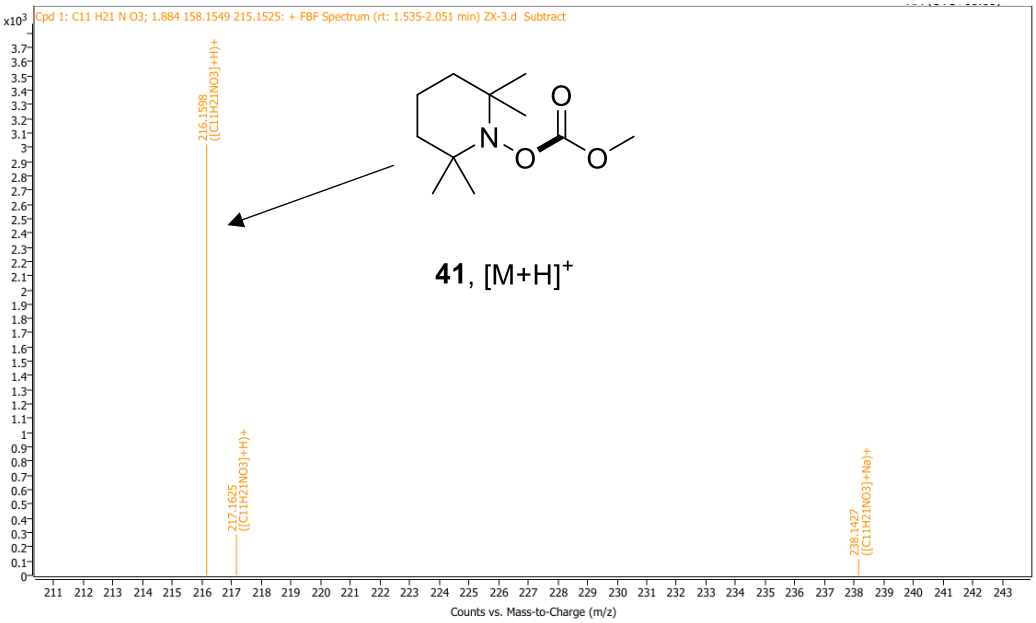


Figure S4 1-Methylquinoxalin-2(1*H*)-one **1a** and methyl 2-chloro-2-oxoacetate **2a** under standard conditions with TEMPO (4.0 equiv.)

To an oven-dried quartz vial, 1-methylquinoxalin-2(1*H*)-one **1a** (0.1 mmol, 1.0 equiv.), BHT (4.0 equiv.), 2,6-lutidine (0.3 mmol, 3.0 equiv.), and *fac*-Ir(ppy)$_3$ (0.002 mmol, 2 mol%) were added sequentially. The vial was charged with a stir bar and transferred to a glovebox, where the solids were backfilled with an inert atmosphere. In the glovebox, methyl 2-chloro-2-oxoacetate **2a** (0.2 mmol, 2.0 equiv.) was added into the vial, followed by CH_3CN (1.0 mL). The vial was sealed with a rubber plug, removed from the glove box, and irradiated and stir by 24 W 460 nm LEDs at room temperature for 48 h. **HRMS (DART-TOF)**: compound **42** calculated for $C_{18}H_{30}NO_4^+$ $[M+NH_4]^+$ m/z 324.2169, found 324.2166.

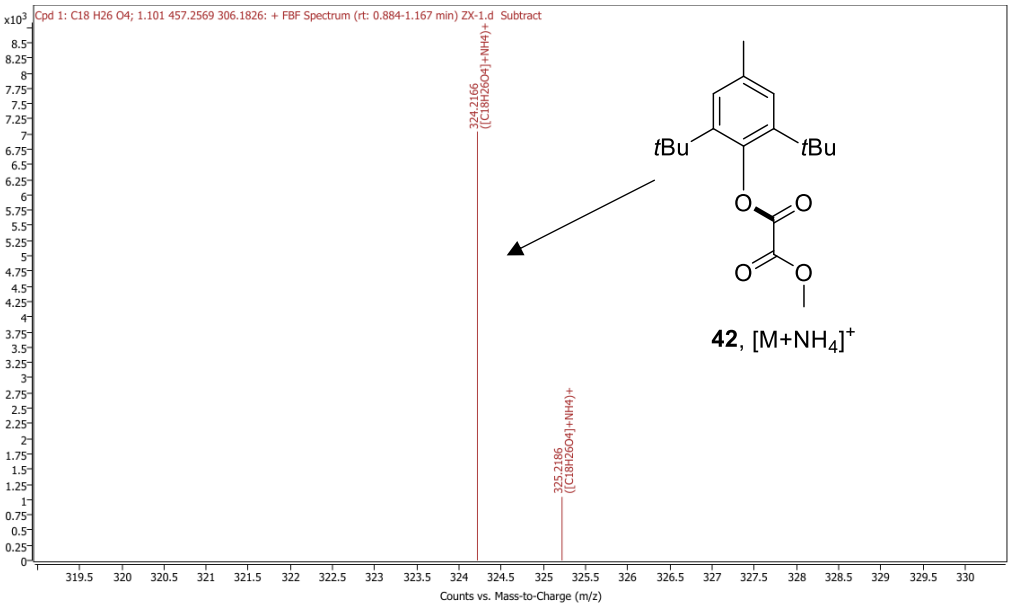


Figure S5 1-Methylquinoxalin-2(1*H*)-one **1a** and methyl 2-chloro-2-oxoacetate **2a** under standard conditions with BHT (4.0 equiv.)

5.2 Stern-Volmer fluorescence quenching experiments

All fluorescence measurements were recorded by a F-4600 FL Spectrophotometer. Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of *fac*-Ir(ppy)$_3$ (5×10^{-6} M in CH_3CN) added with the appropriate amount of a quencher in a screw-top quartz cuvette at room temperature. The substrates from methyl 2-chloro-2-oxoacetate **2a**, **2,6-lutidine**, **2a+2,6-lutidine** were dissolved in CH_3CN (0.1 M), respectively. For each quenching experiment, 5 μL of the stock solution were titrated to a solution (1 mL) of *fac*-Ir(ppy)$_3$ in 10.0 mm quartz cuvette and the fluorescence spectra immediately recorded. I_0 is the luminescence intensity without the quencher, I is the intensity in the presence of the quencher.

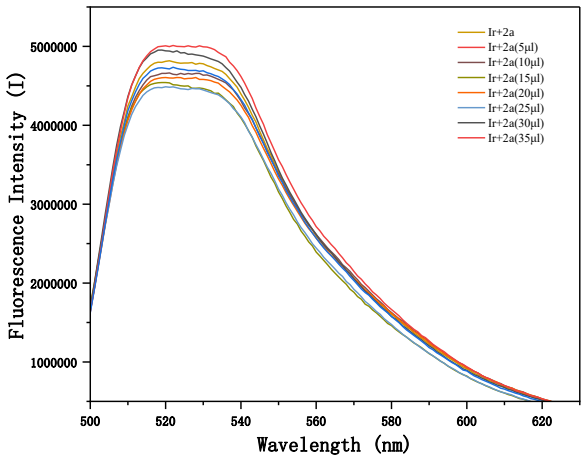


Figure S6 The fluorescence emission spectra of excited *fac*-Ir(ppy)$_3$ with different concentration of **2a** in CH_3CN (excitation wavelength: 360 nm)

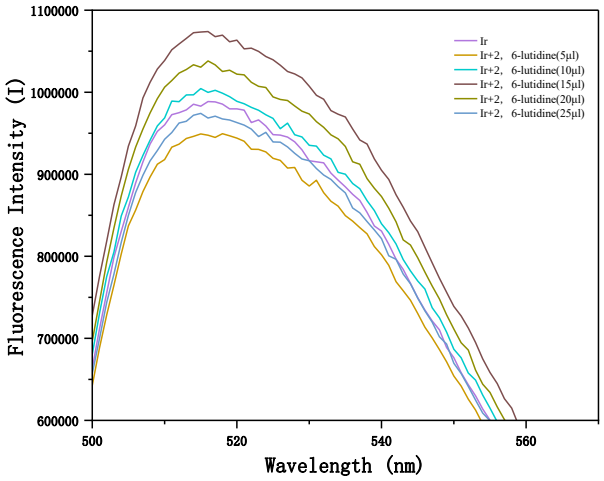


Figure S7 The fluorescence emission spectra of excited *fac*-Ir(ppy)$_3$ with different concentration of 2,6-lutidine in CH_3CN (excitation wavelength: 360 nm)

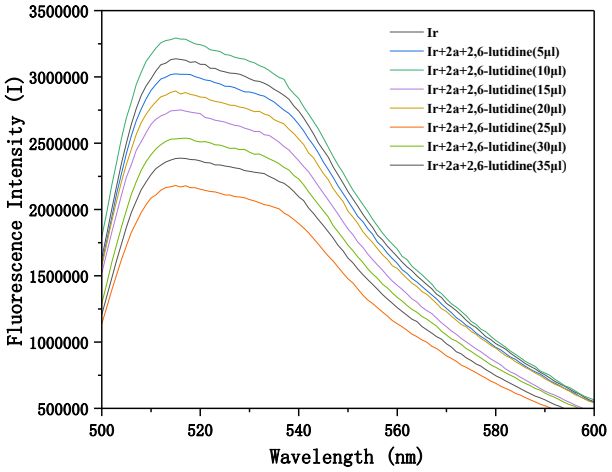


Figure S8 The fluorescence emission spectra of excited *fac*-Ir(ppy)$_3$ with different concentration of **2a**+2,6-lutidine in CH_3CN (excitation wavelength: 360 nm)

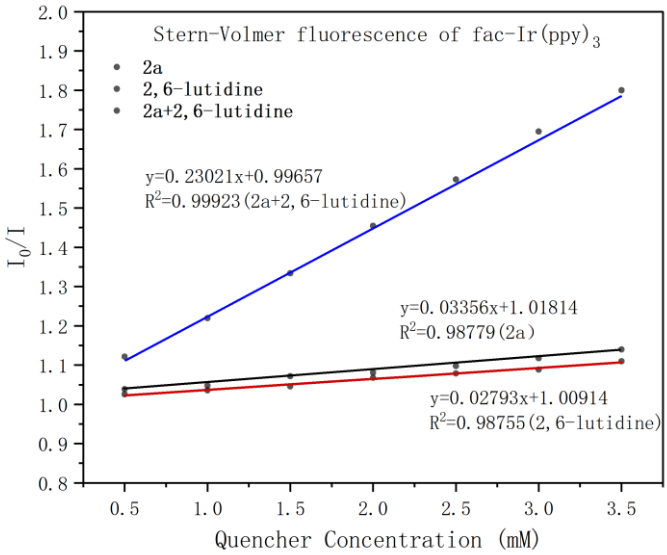


Figure S9 Stern-Volmer fluorescence quenching plot

5.3 Time profile of the transformation with the light ON/OFF over time

The standard reaction was set up on a 0.10 mmol scale according to the general procedure. After being irradiated for 8 h, an aliquot (100 μL) from the reaction mixture was transferred into a nuclear magnetic tube charged with 0.55 mL of $CDCl_3$-d_1. The yield of product was determined by ^{1}H NMR. Then the reaction mixture was stirred for 8 h with light-off. All of the following yields were analyzed in the identical way after a 8 h light on or off.

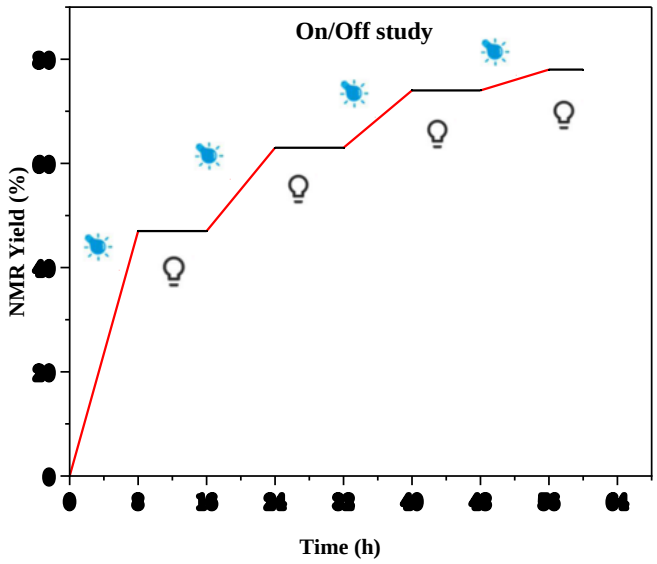


Figure S10 Time profile of the transformation with the light ON/OFF over time

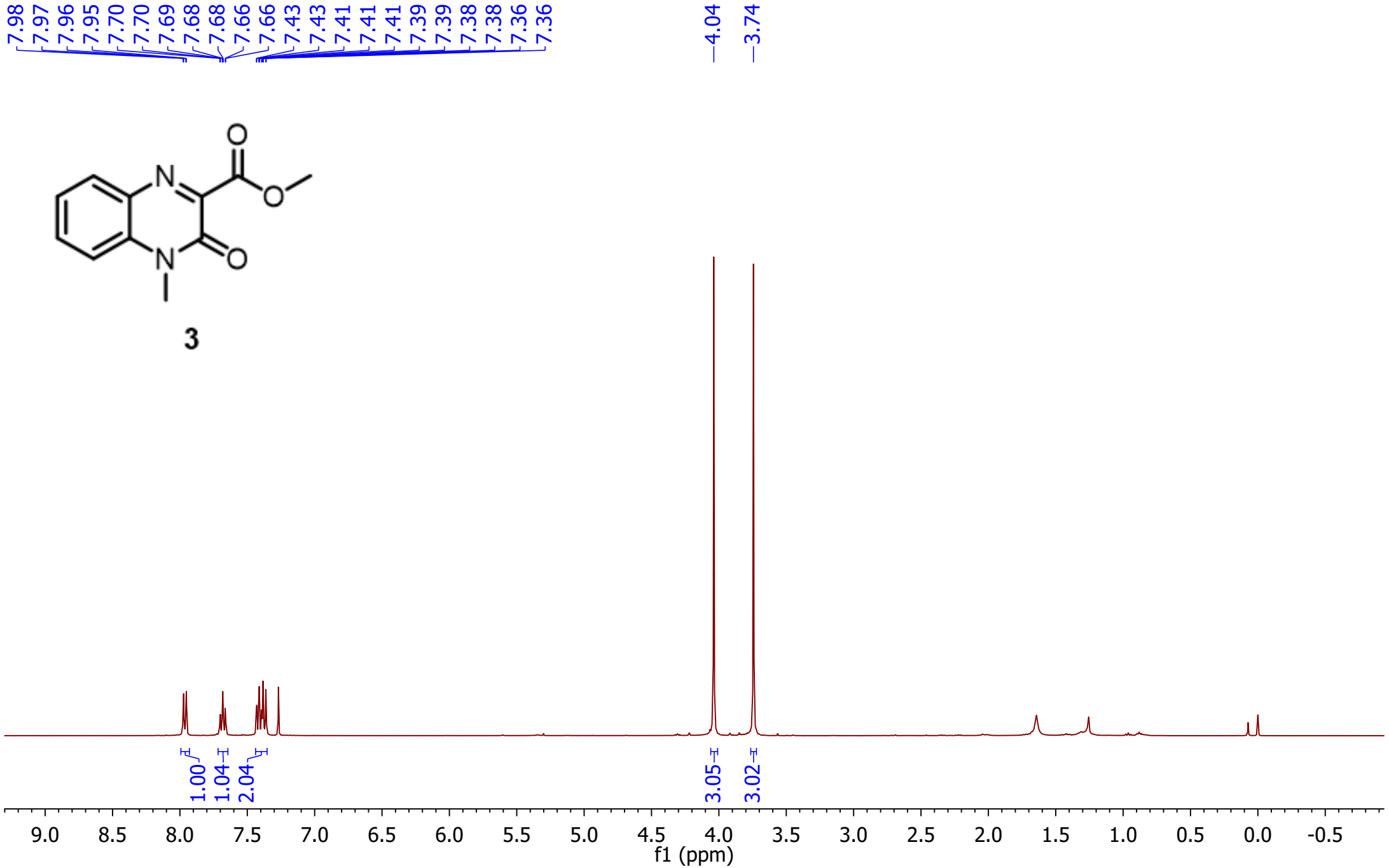
6. References

1. Ghosh, P.; Kwon, N. Y.; Kim, S.; Han, S.; Lee, S. H.; An, W.; Mishra, N. K.; Han, S. B.; Kim, I. S. *Angew. Chem., Int. Ed.* **2021**, *60*, 191.

2. Chen, X.-Y; Li, L.-L.; Pei, C.-C.; Jingya Li, J.-Y.; Zou, D.-P.; Wu, Y.-J.; Wu, Y.-S. *J. Org. Chem.* **2021**, *86*, 2772.

3. Xie, L.; Peng, S.; Fan, T.; Liu, Y.; Sun, M.; Jiang, L.; Wang, X.; Cao, Z.; He, W. *Sci. China Chem.* **2019**, *62*, 460-464.

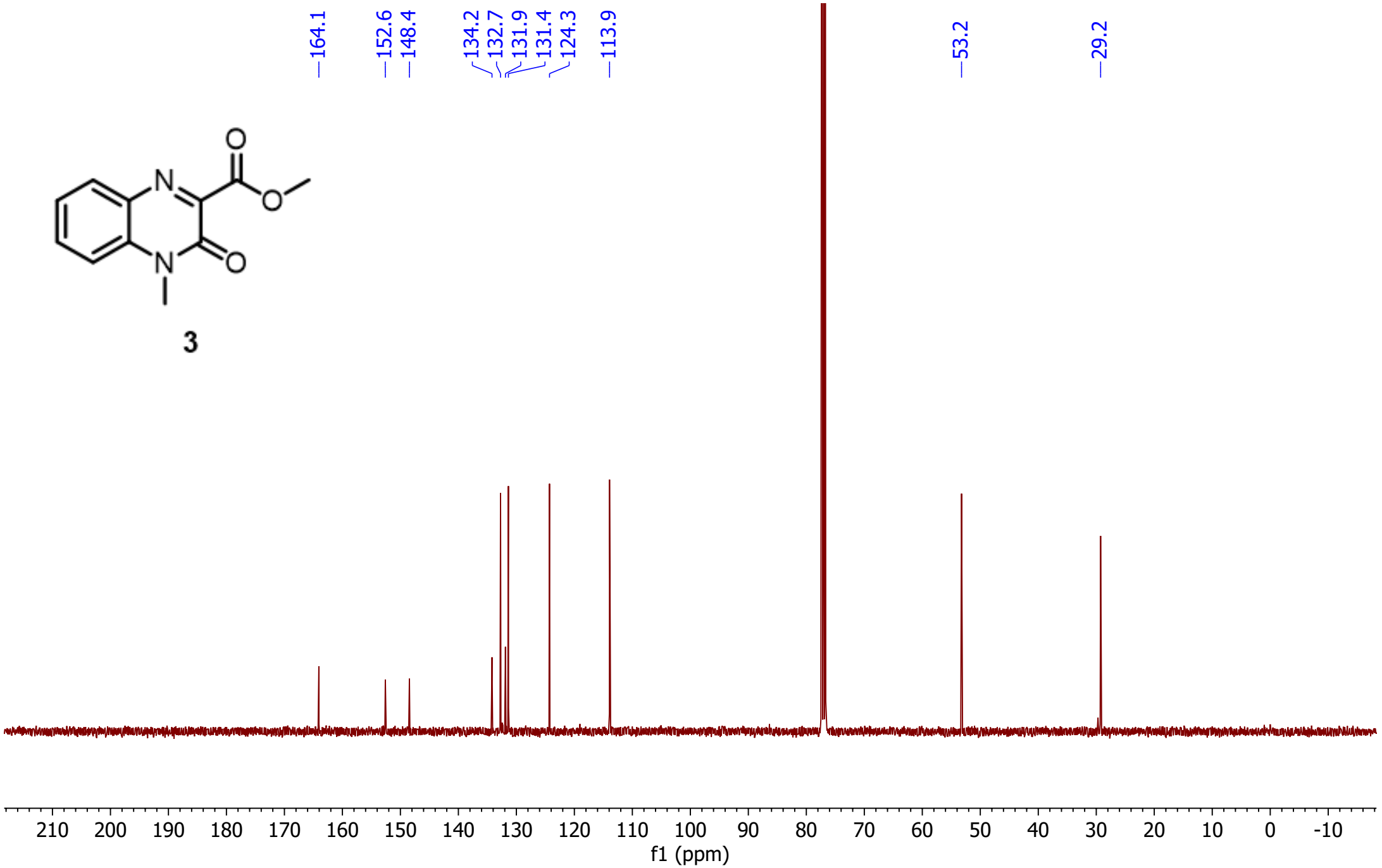
1H (CDCl3, 400 MHz)



3

^{1}H NMR Spectrum of **3**

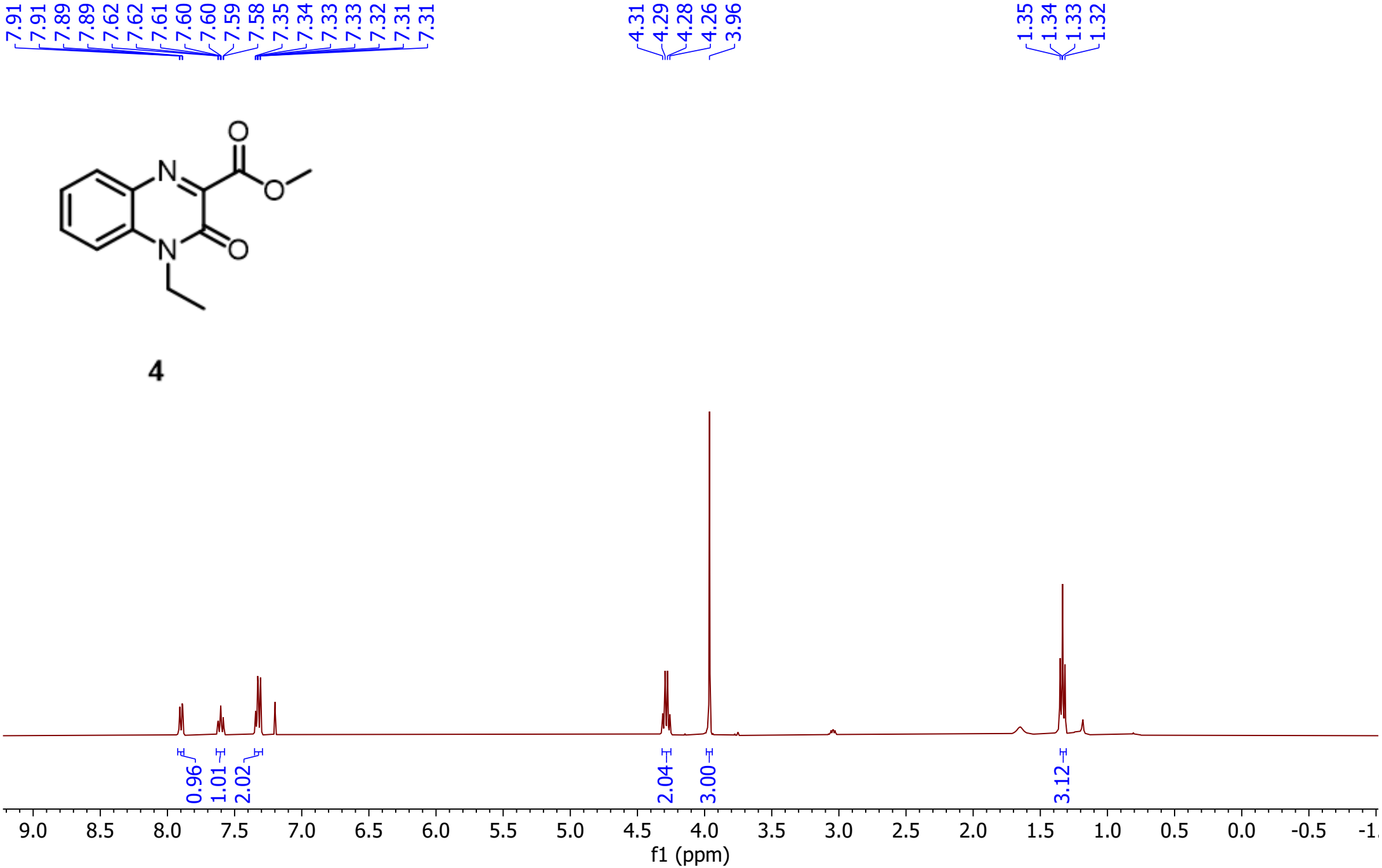
13C (CDCl3, 101 MHz)



3

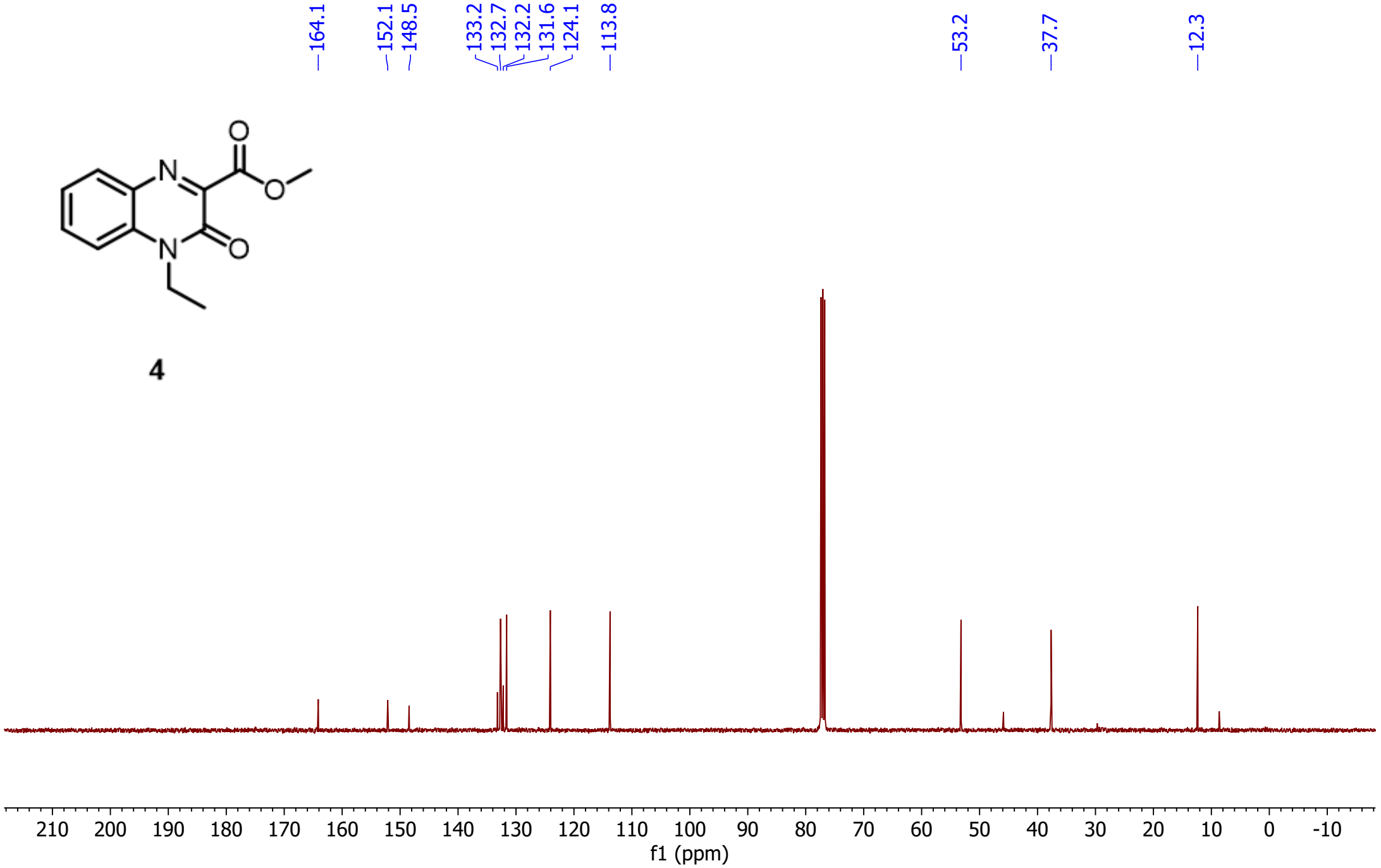
^{13}C NMR Spectrum of **3**

1H (CDCl3, 400 MHz)



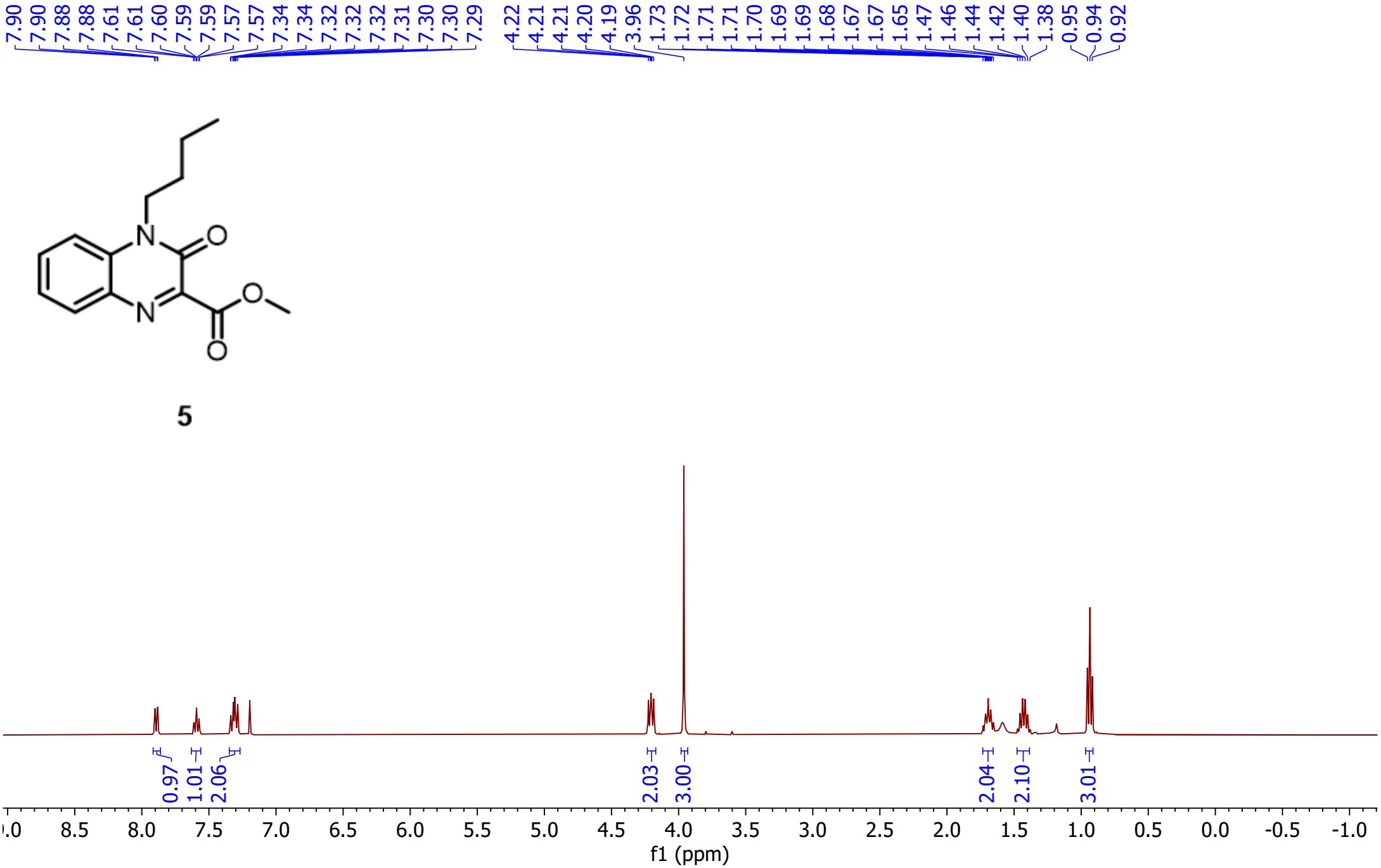
^{1}H NMR Spectrum of **4**

13C (CDCl3, 101 MHz)



^{13}C NMR Spectrum of **4**

1H (CDCl3, 400 MHz)



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^{1}H NMR Spectrum of **5**

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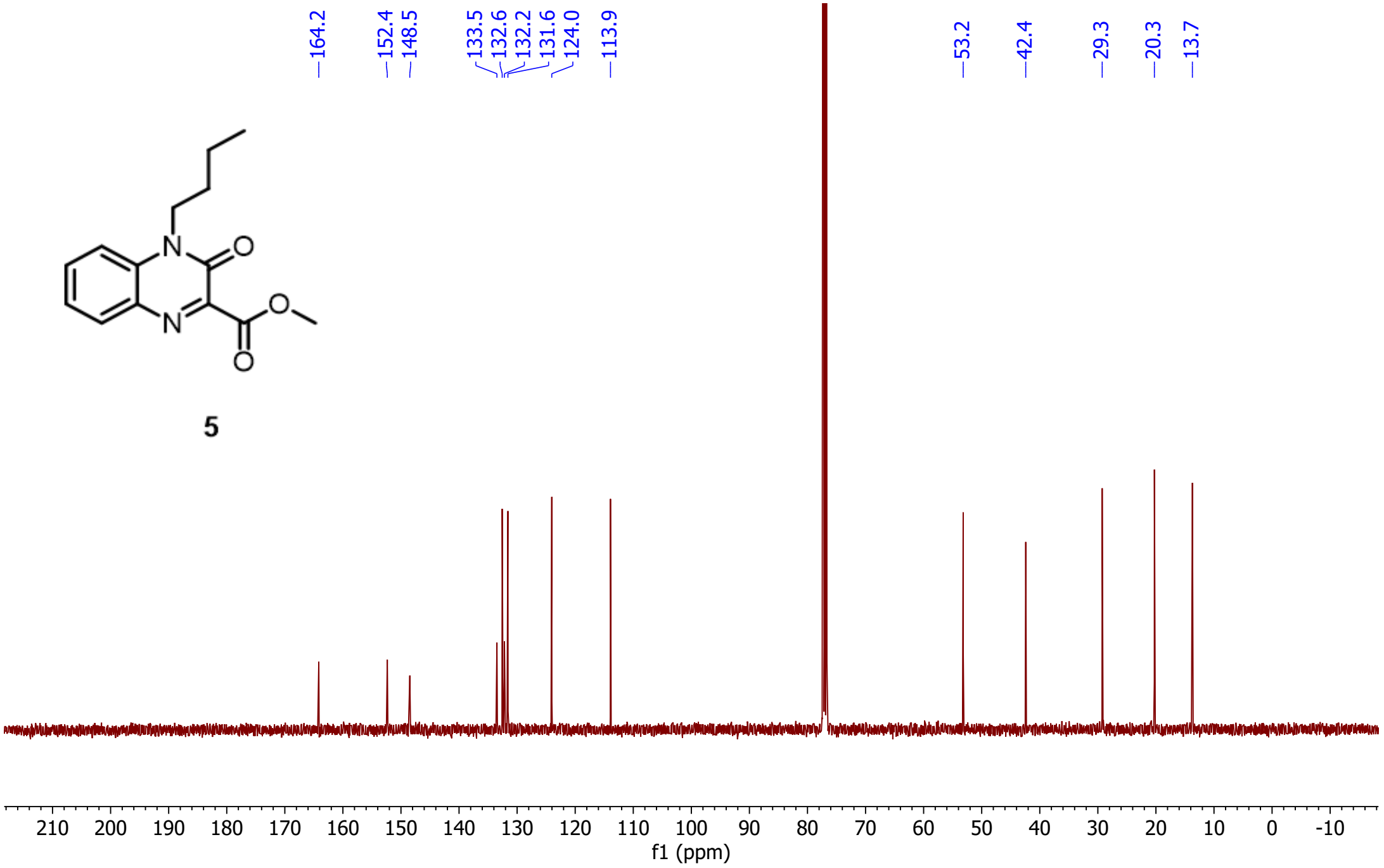
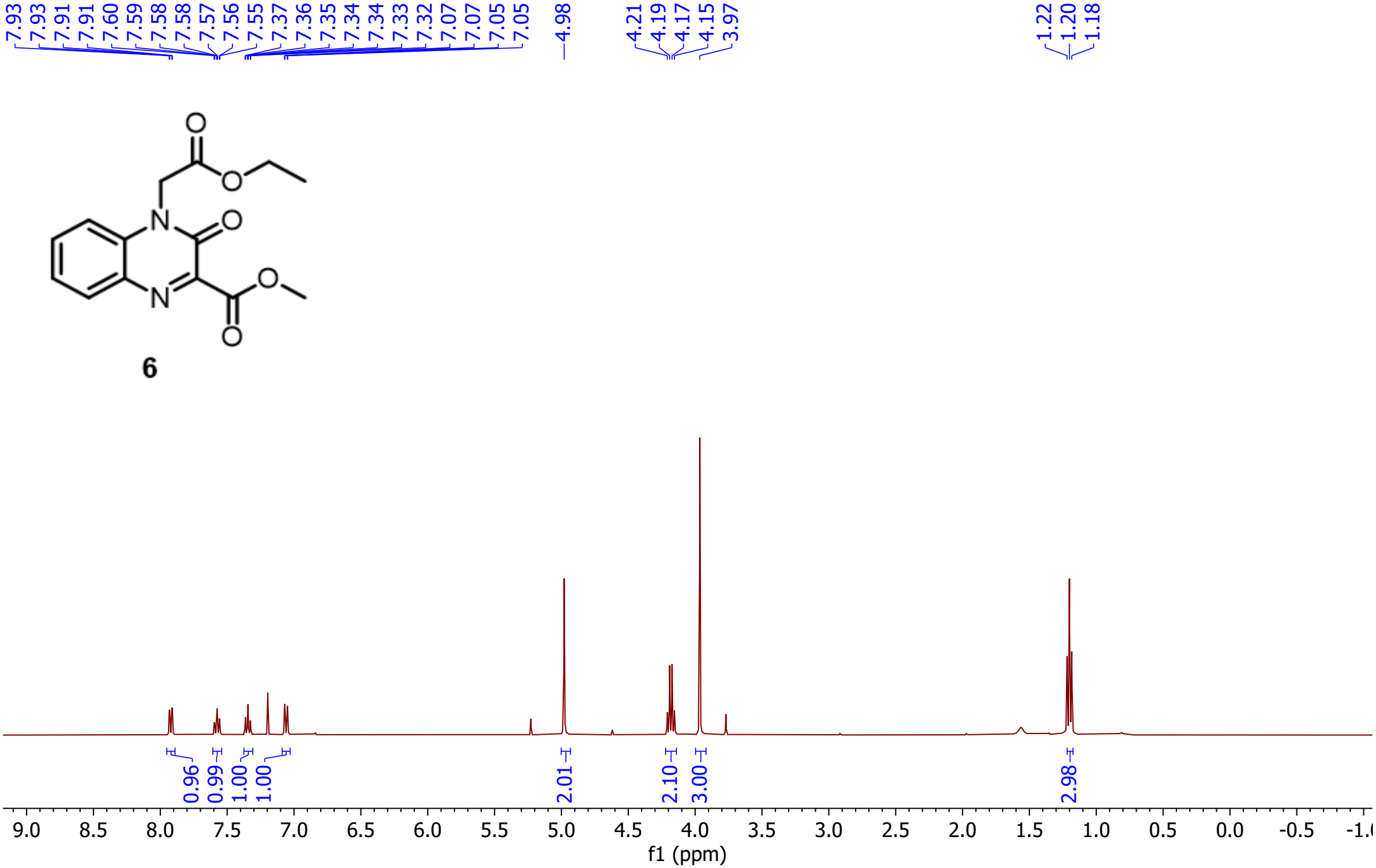


5

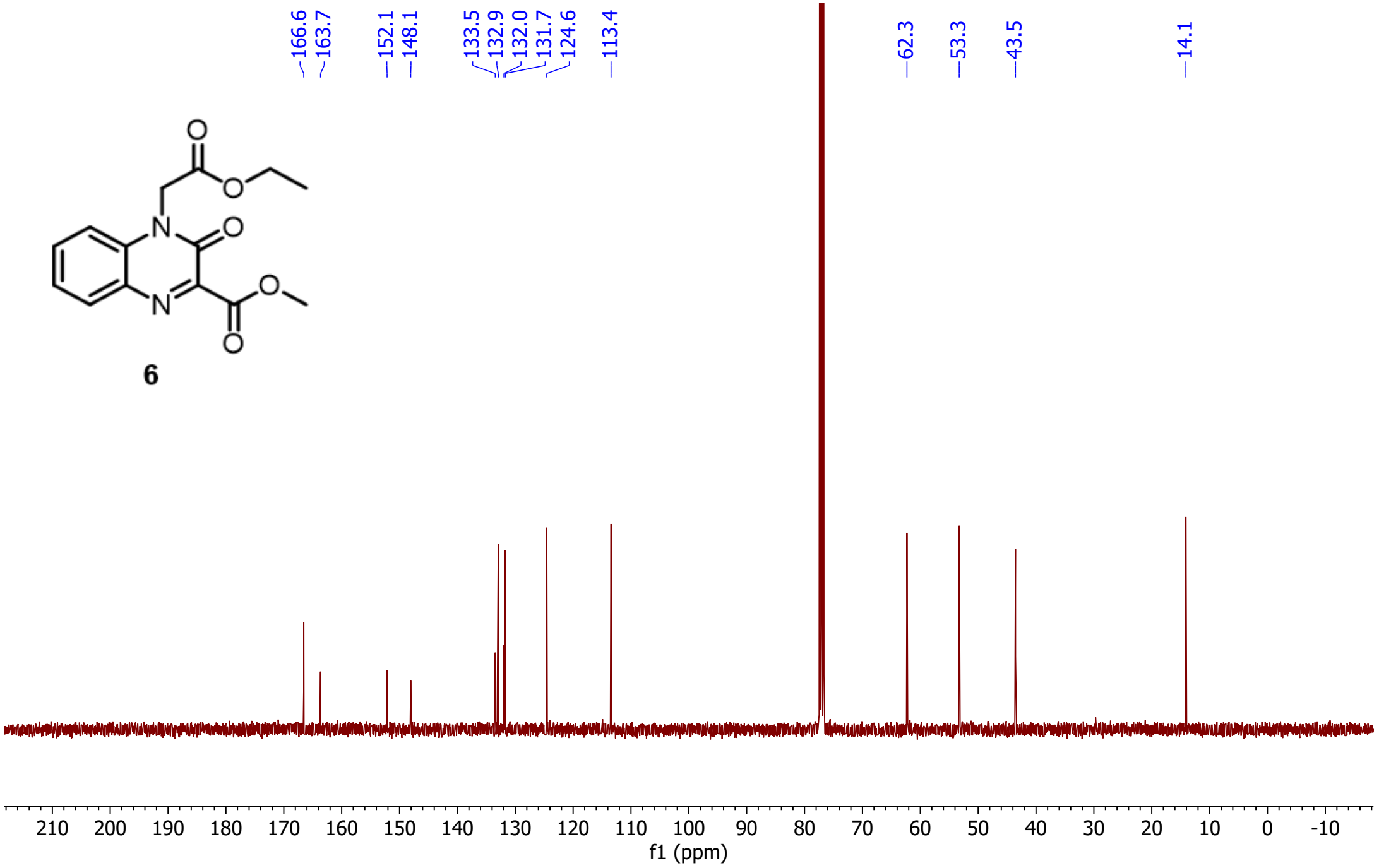
^{13}C NMR Spectrum of **5**

1H (CDCl3, 400 MHz)



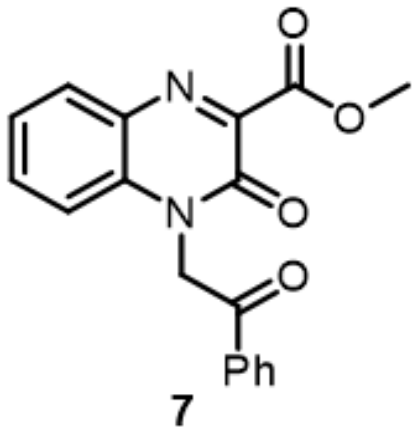
^{1}H NMR Spectrum of **6**

13C (CDCl3, 101 MHz)



^{13}C NMR Spectrum of **6**

1H (CDCl3, 400 MHz)



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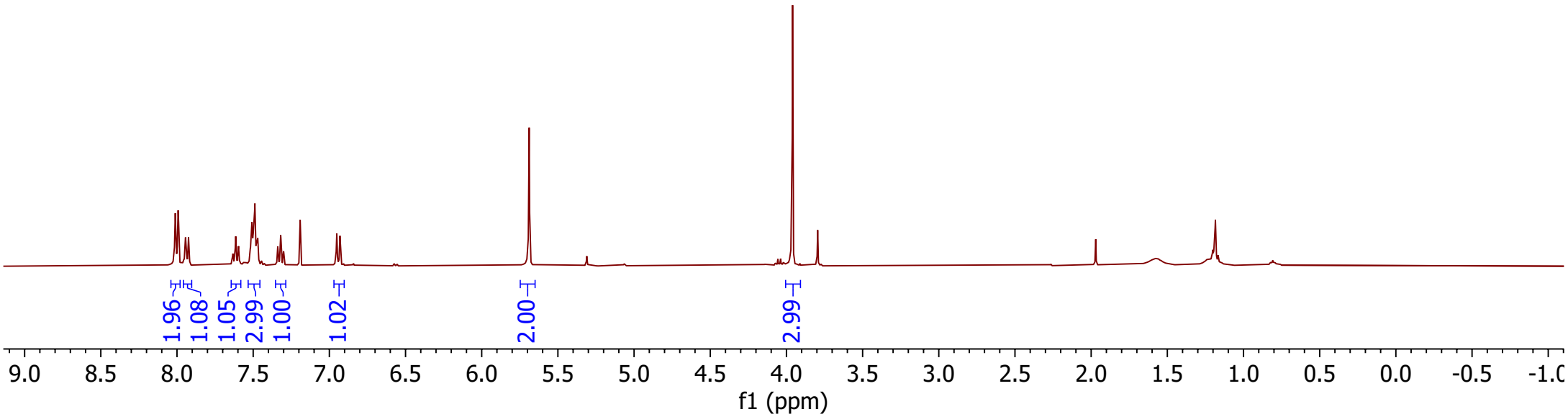
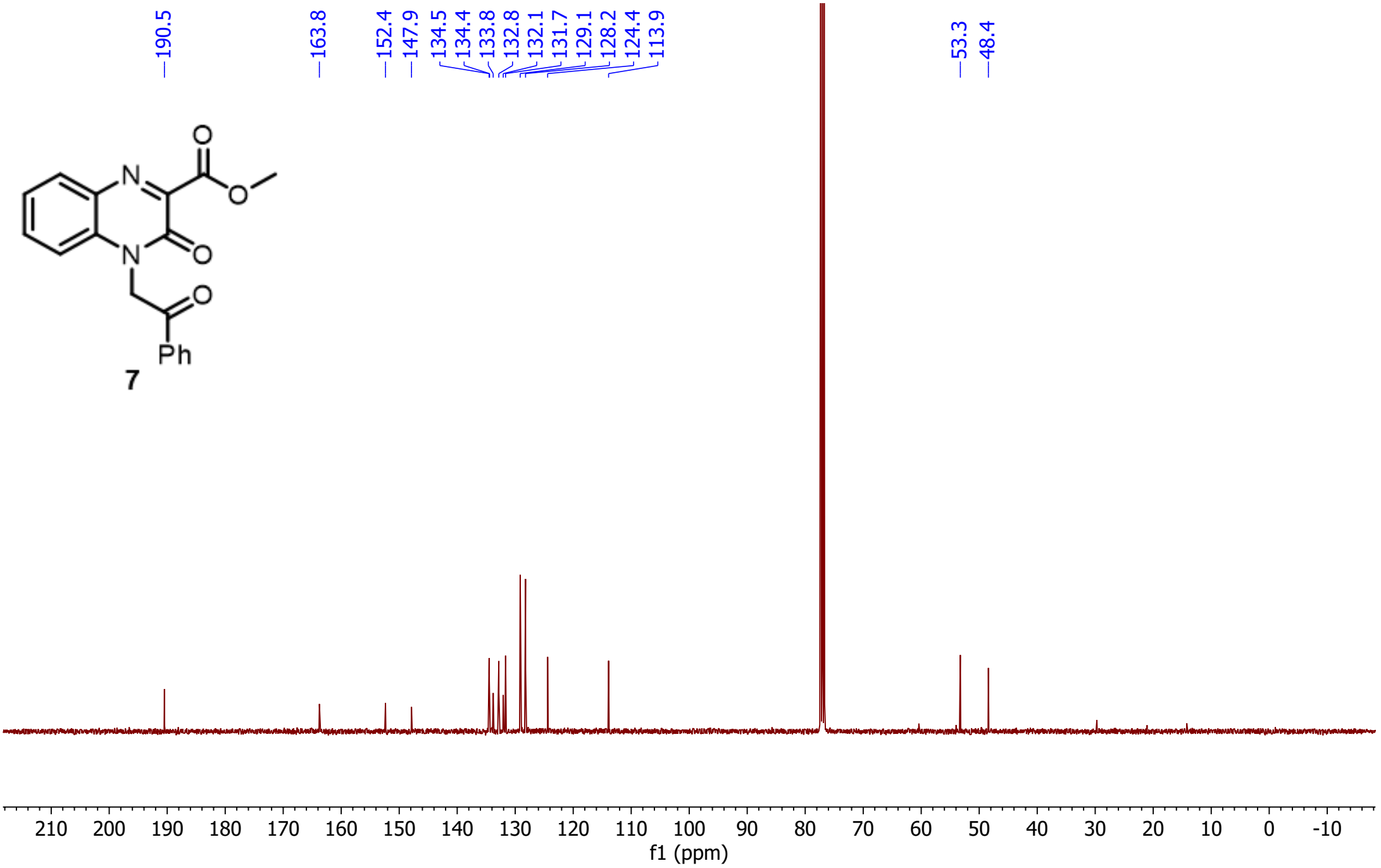


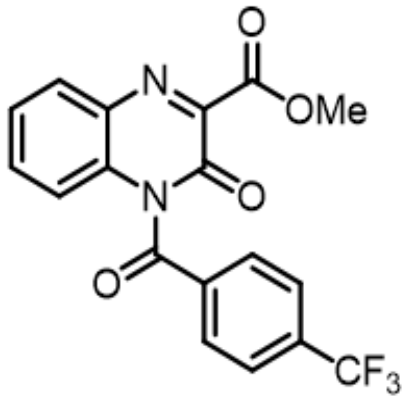
^{1}H NMR Spectrum of **7**

13C (CDCl3, 101 MHz)



^{13}C NMR Spectrum of **7**

1H (CDCl3, 400 MHz)



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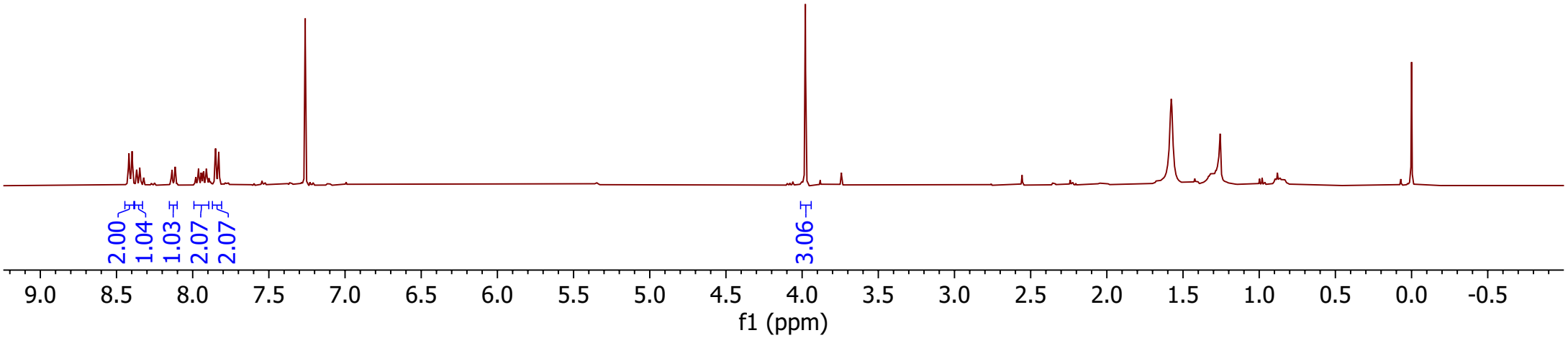
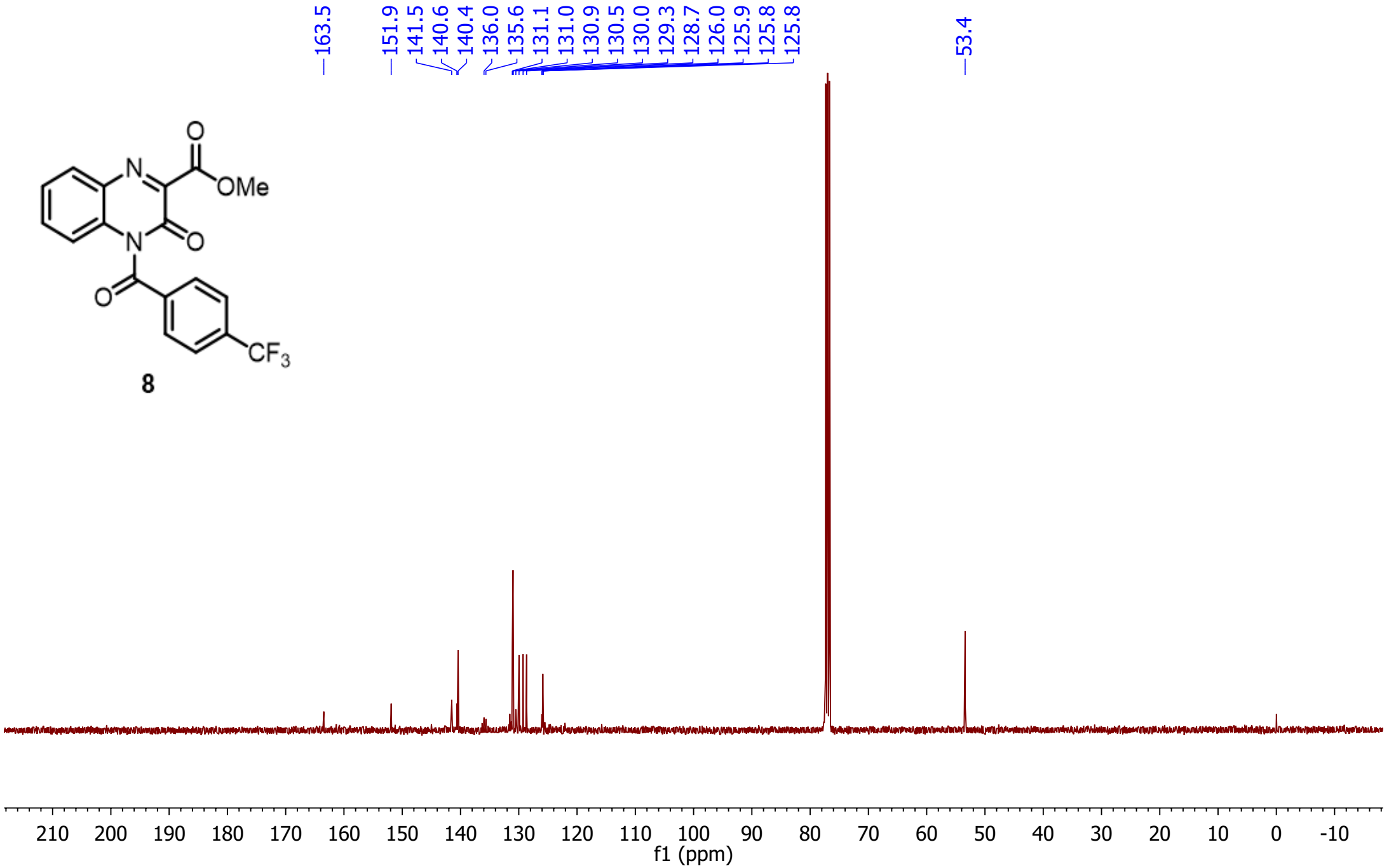


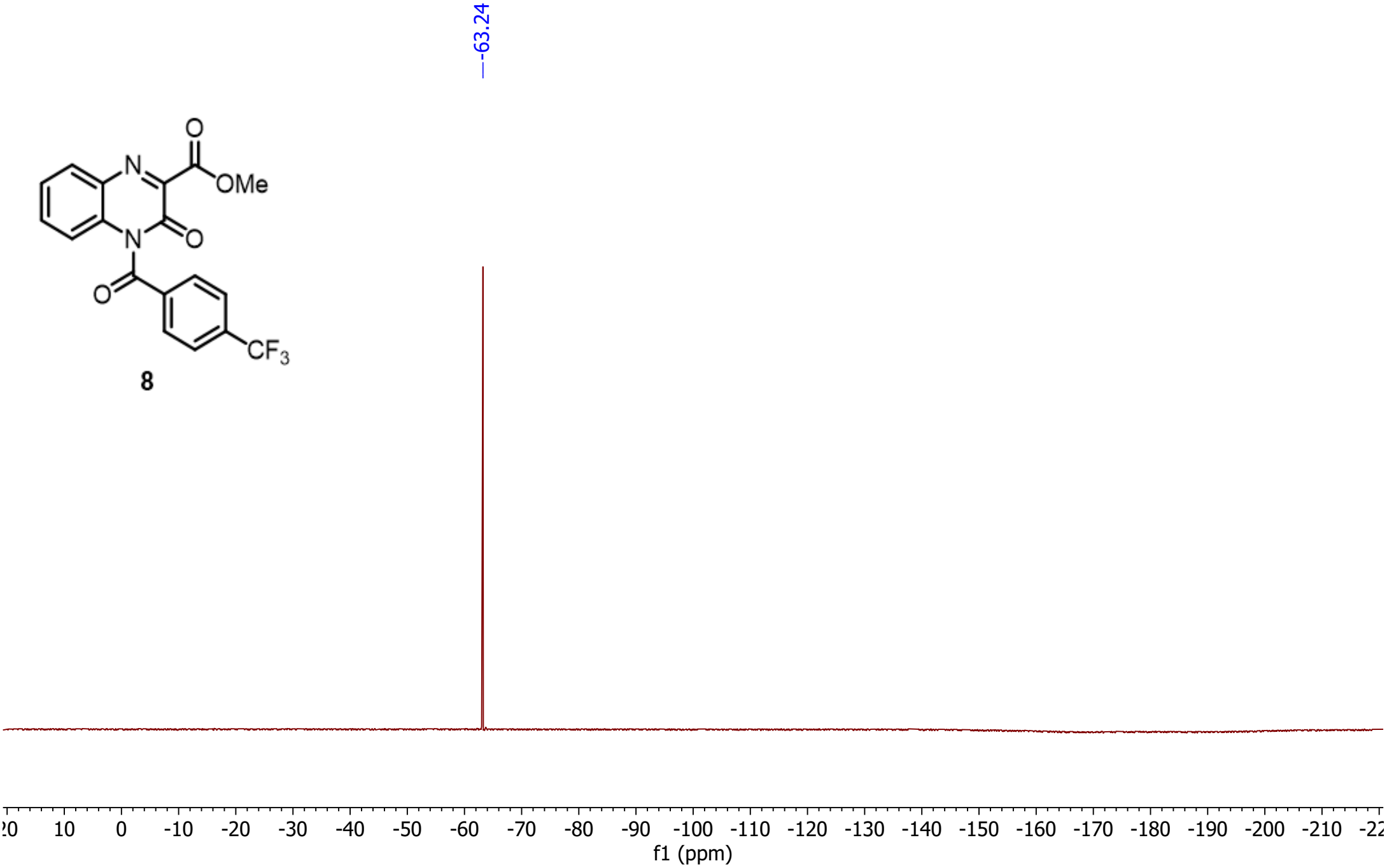
^{1}H NMR Spectrum of **8**

13C (CDCl3, 101 MHz)



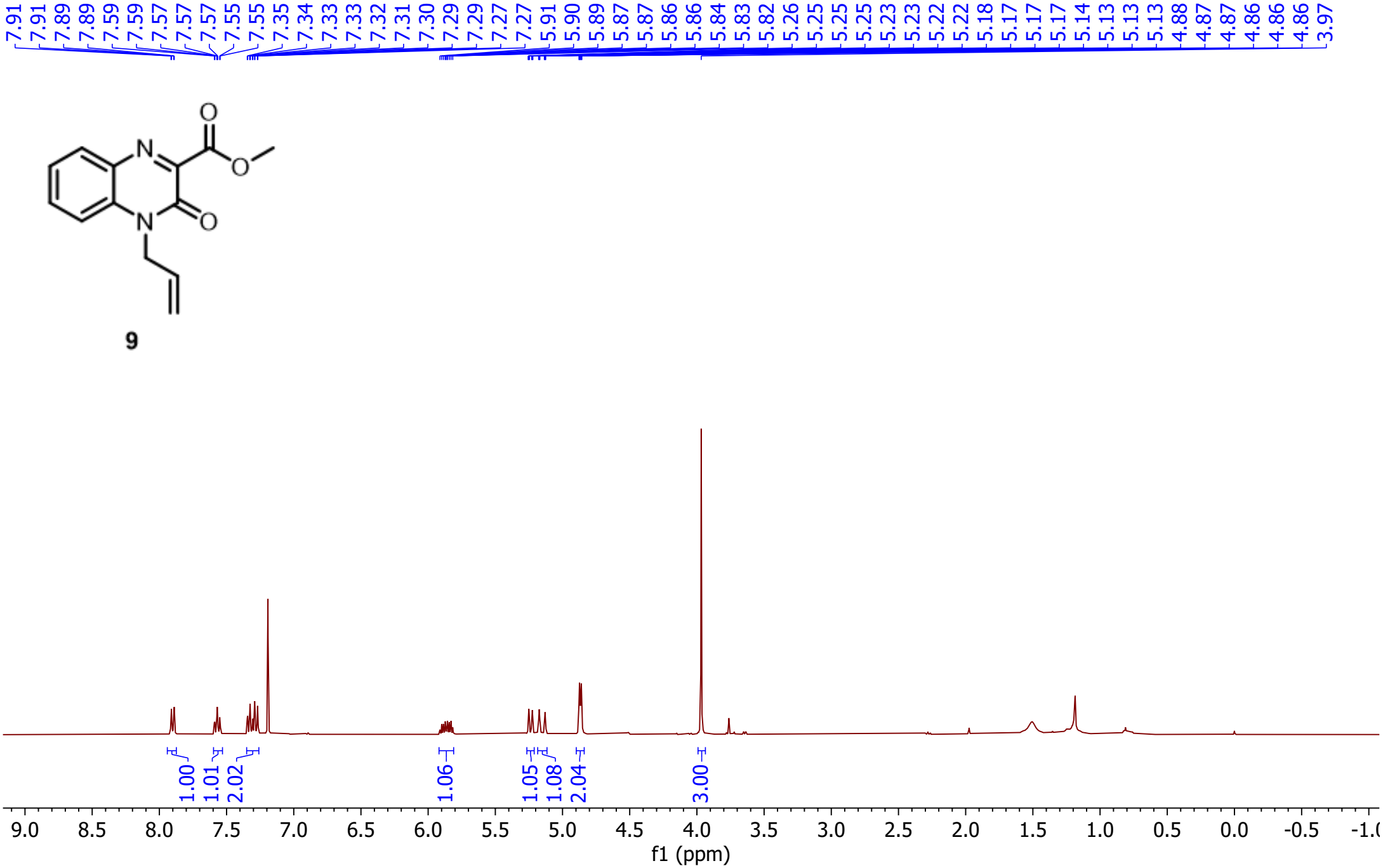
^{13}C NMR Spectrum of **8**

19F (CDCl3, 376 MHz)



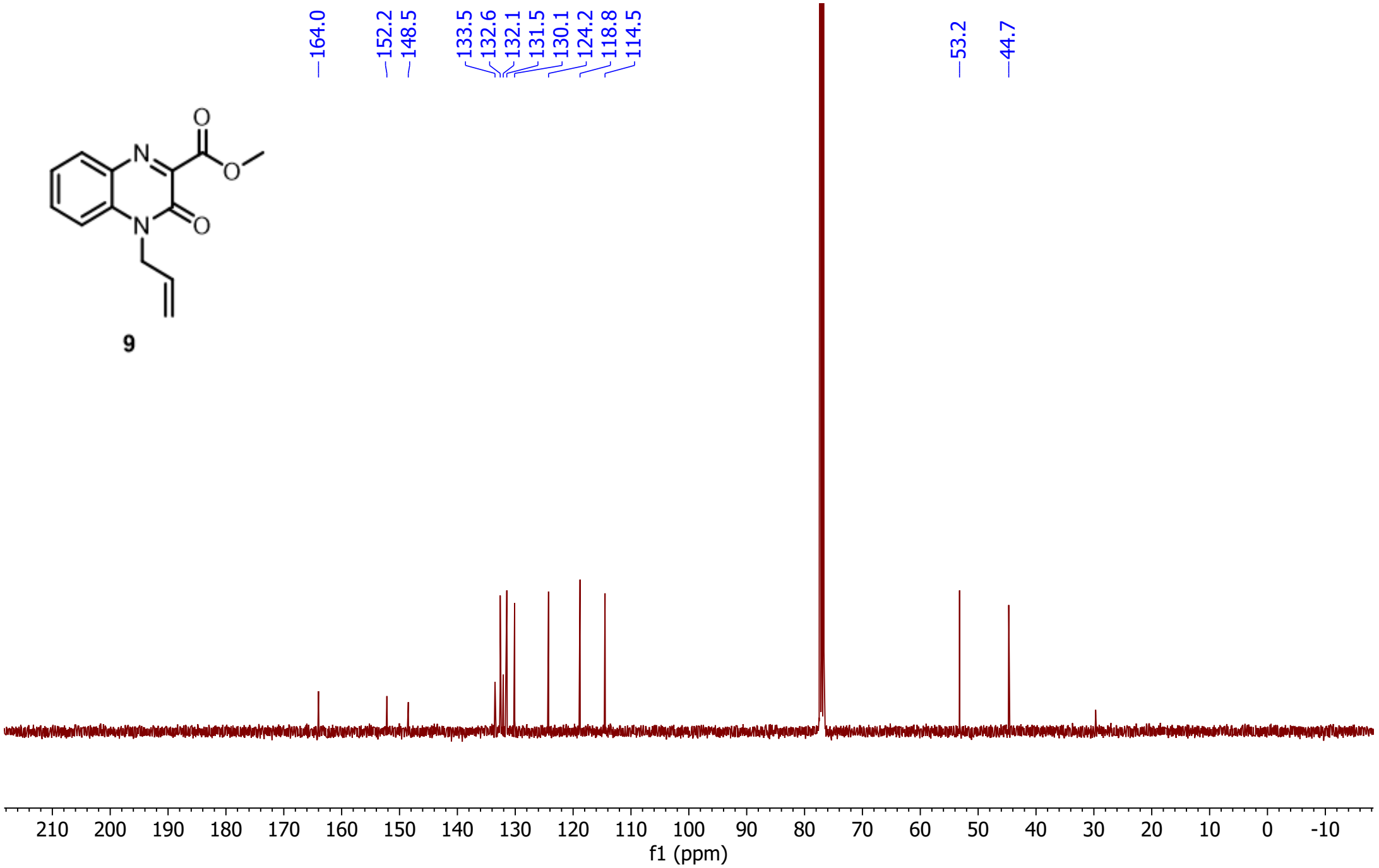
^{19}F NMR Spectrum of **8**

1H (CDCl3, 400 MHz)



^{1}H NMR Spectrum of **9**

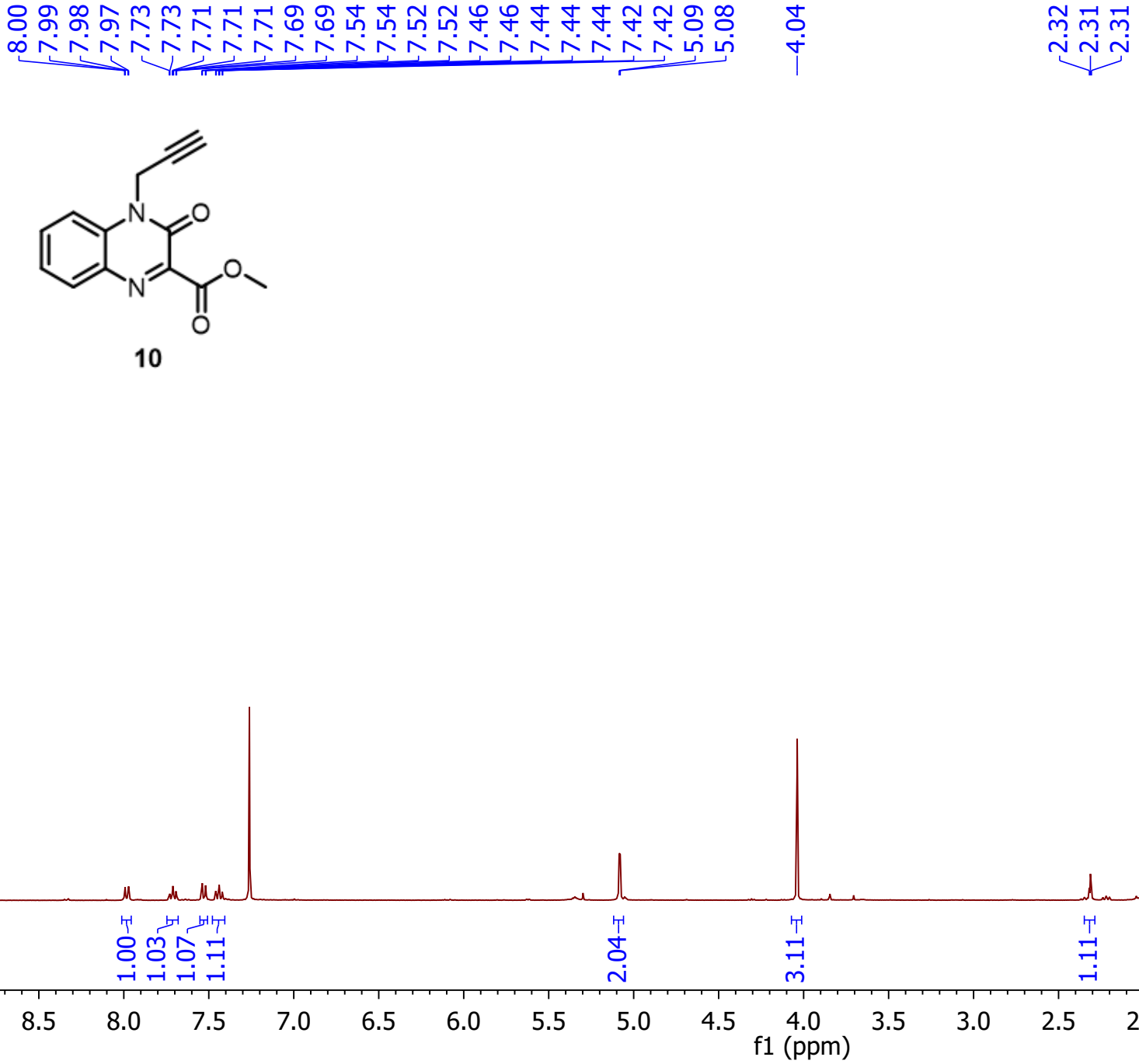
13C (CDCl3, 101 MHz)



9

^{13}C NMR Spectrum of **9**

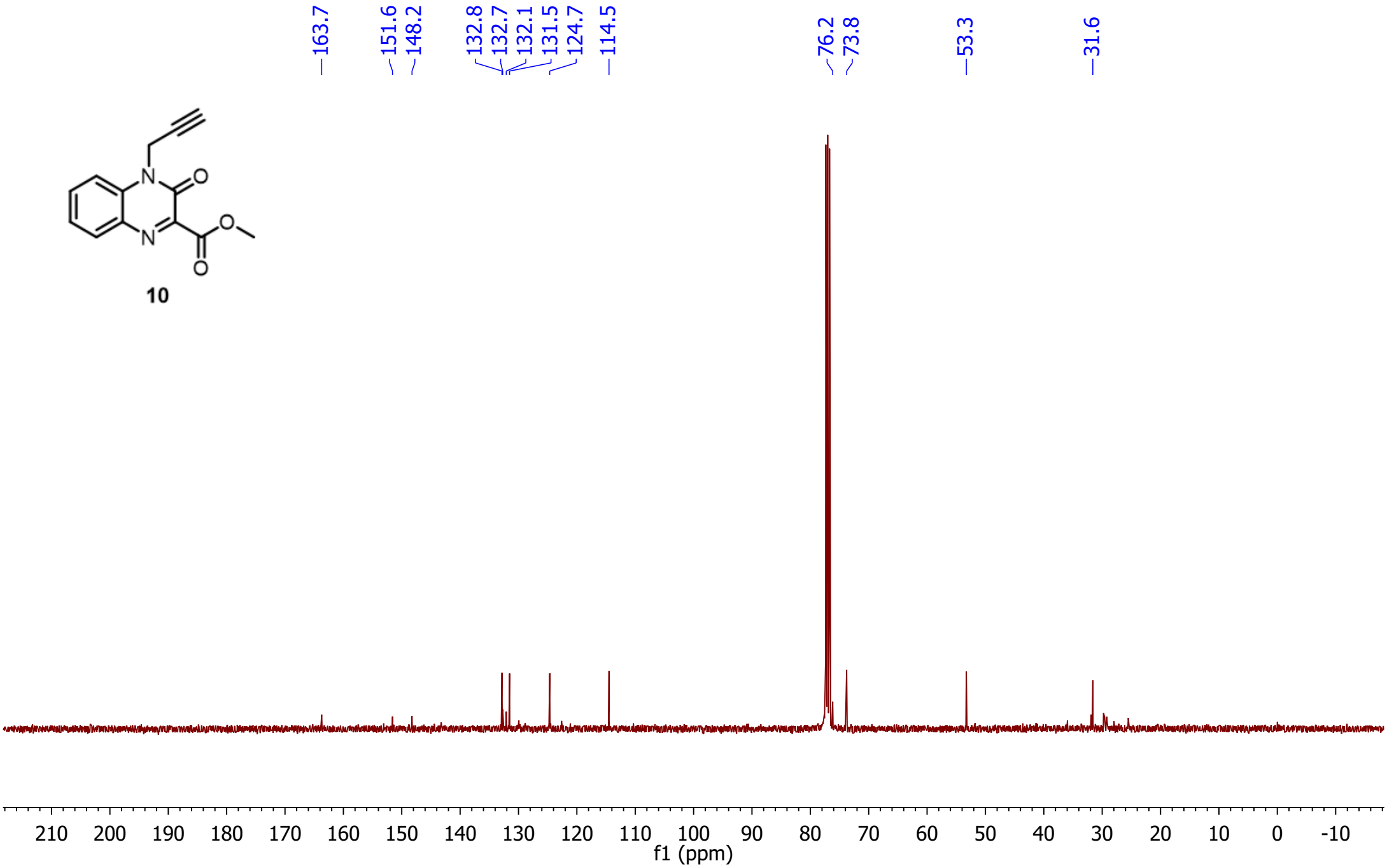
1H (CDCl3, 400 MHz)



10

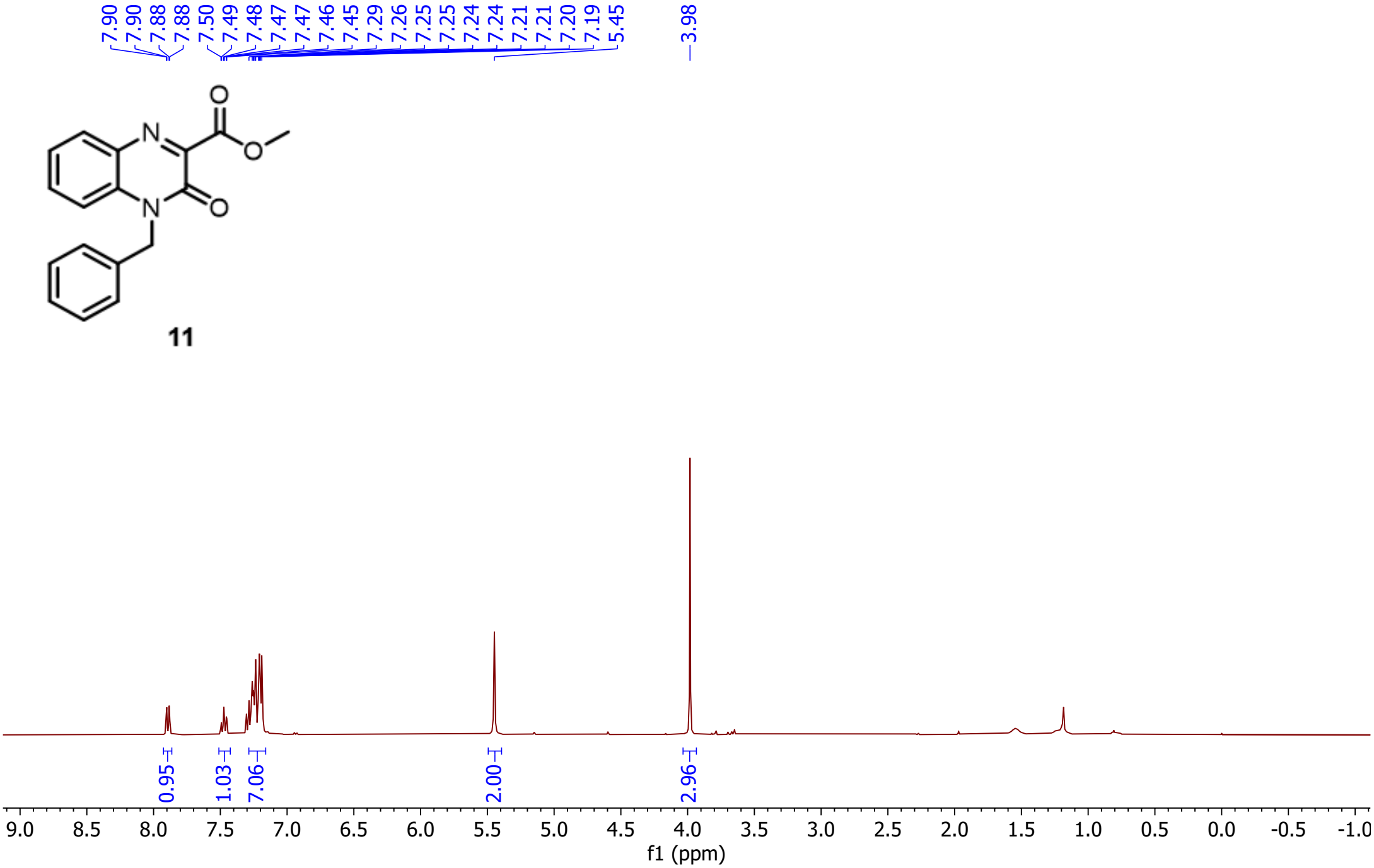
^{1}H NMR Spectrum of **10**

13C (CDCl3, 101 MHz)



^{13}C NMR Spectrum of **10**

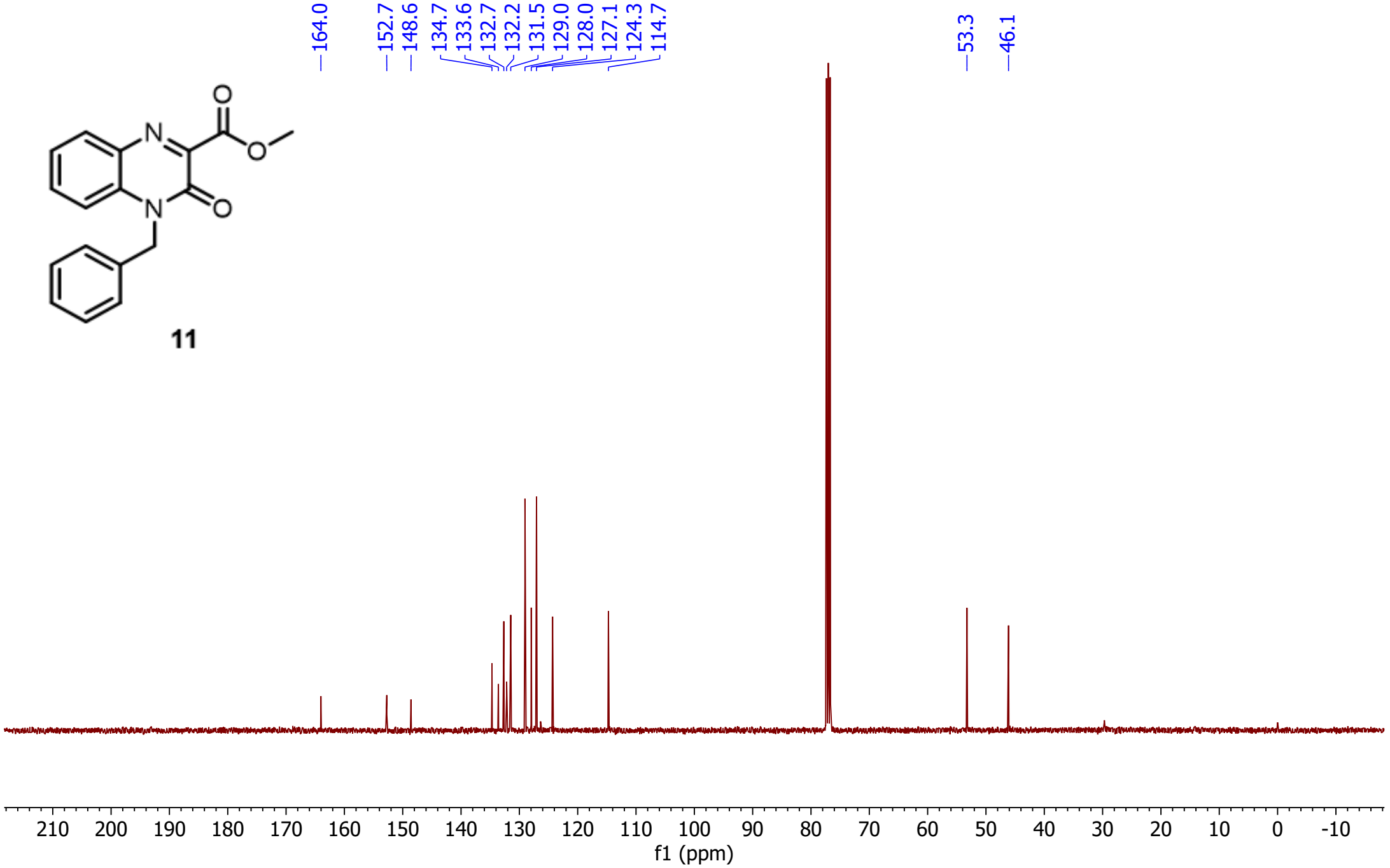
1H (CDCl3, 400 MHz)



11

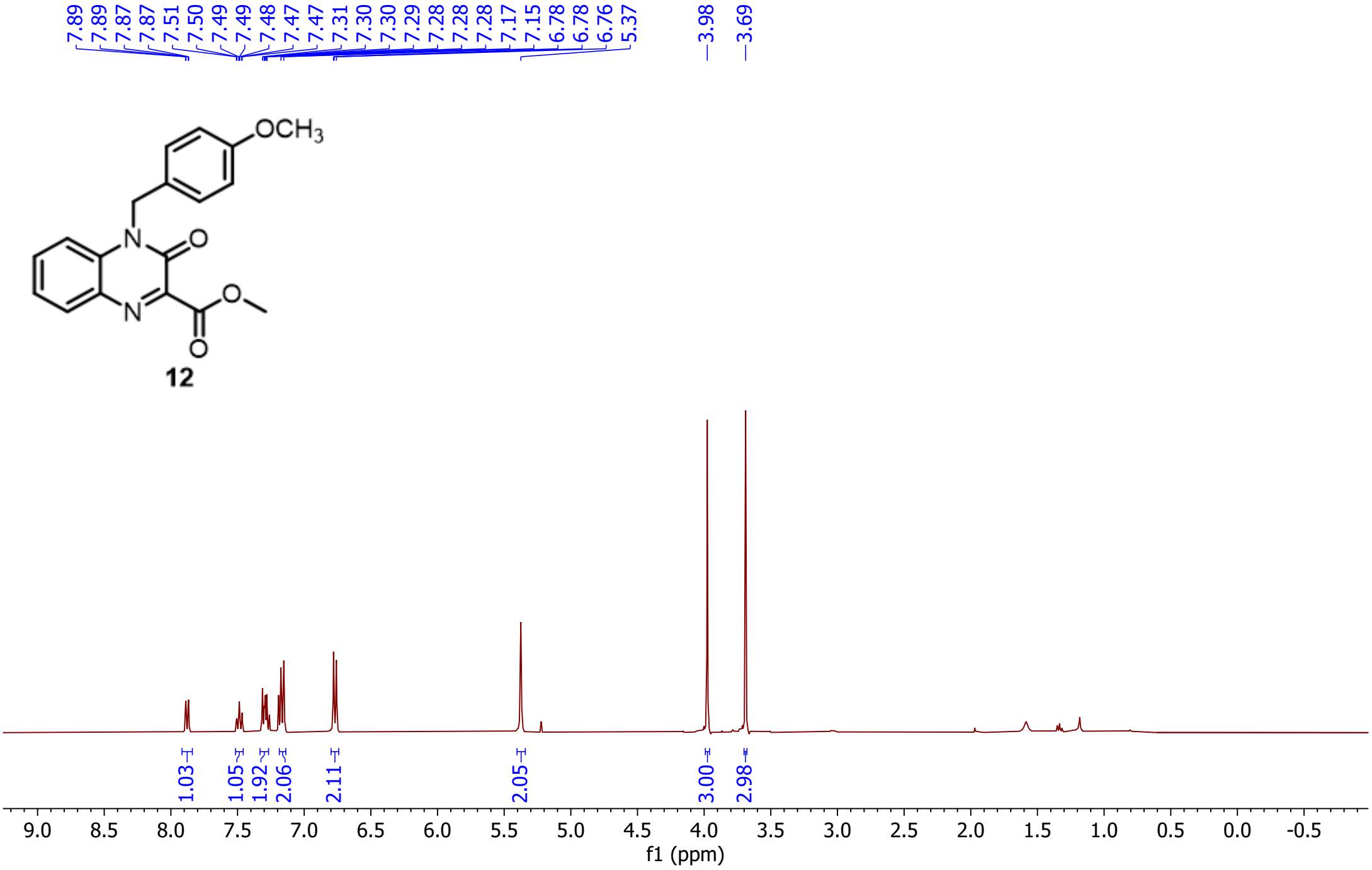
^{1}H NMR Spectrum of **11**

13C (CDCl3, 101 MHz)



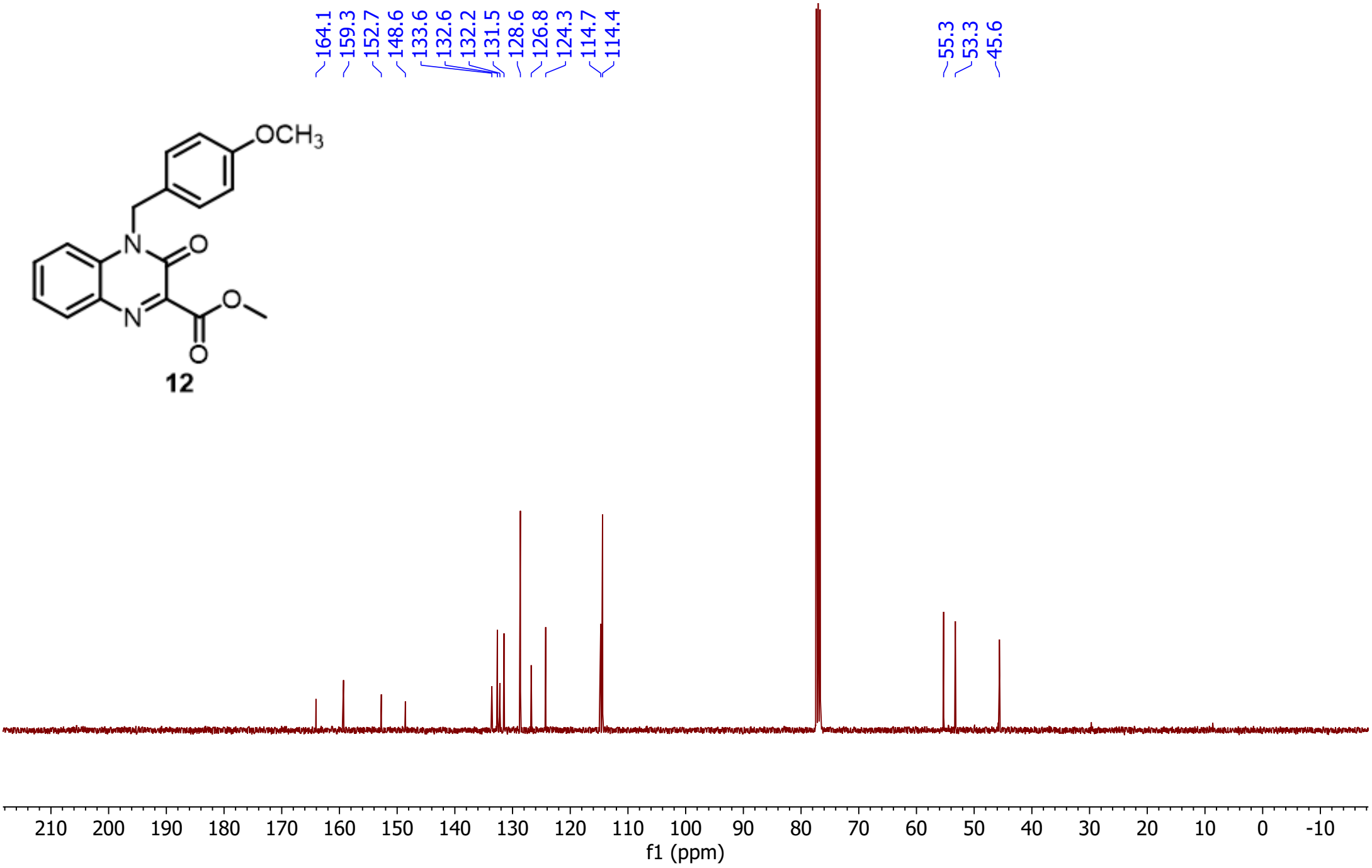
^{13}C NMR Spectrum of **11**

1H (CDCl3, 400 MHz)



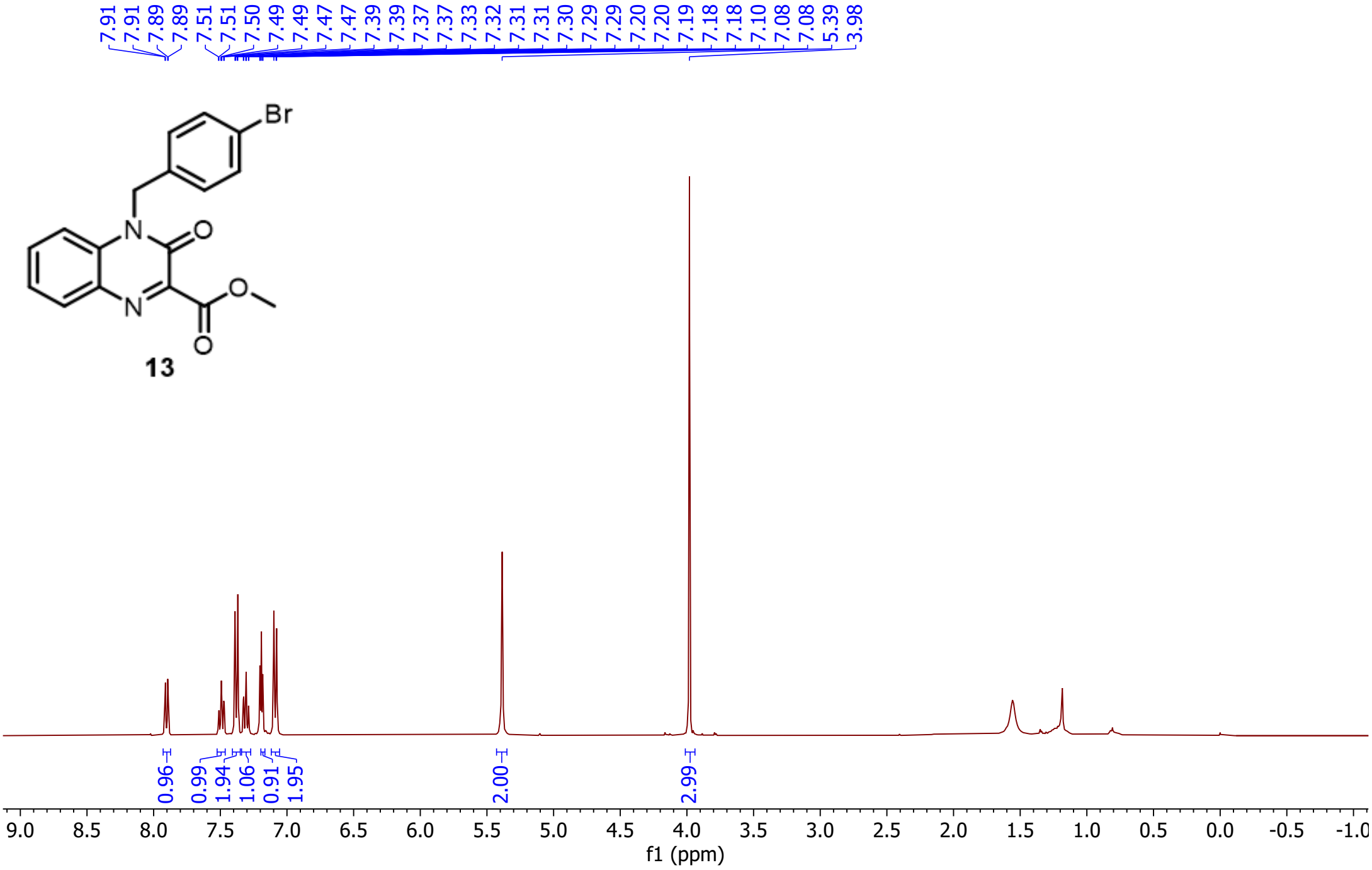
^{1}H NMR Spectrum of **12**

13C (CDCl3, 101 MHz)



^{13}C NMR Spectrum of **12**

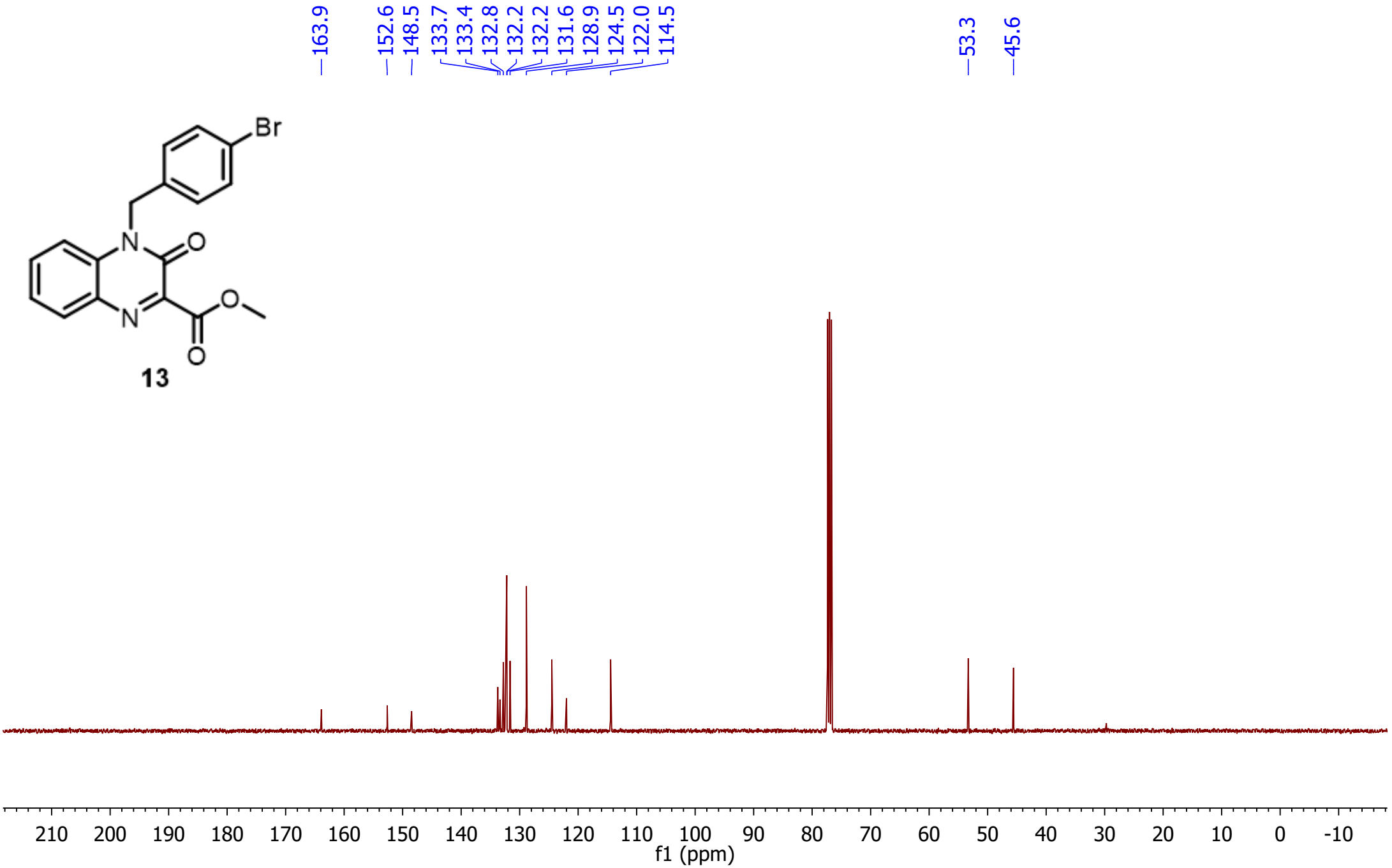
1H (CDCl3, 400 MHz)



13

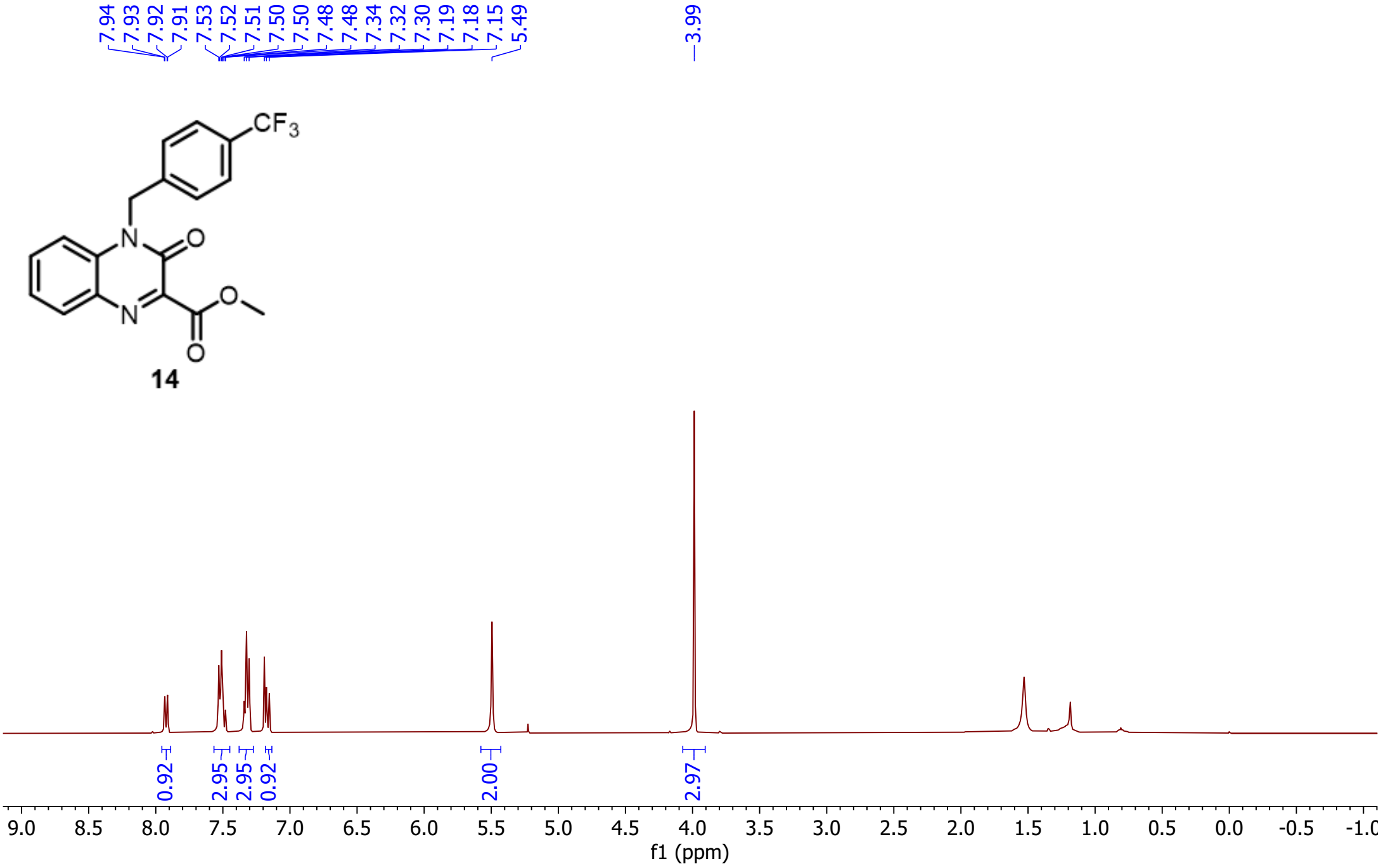
^{1}H NMR Spectrum of **13**

13C (CDCl3, 101 MHz)



^{13}C NMR Spectrum of **13**

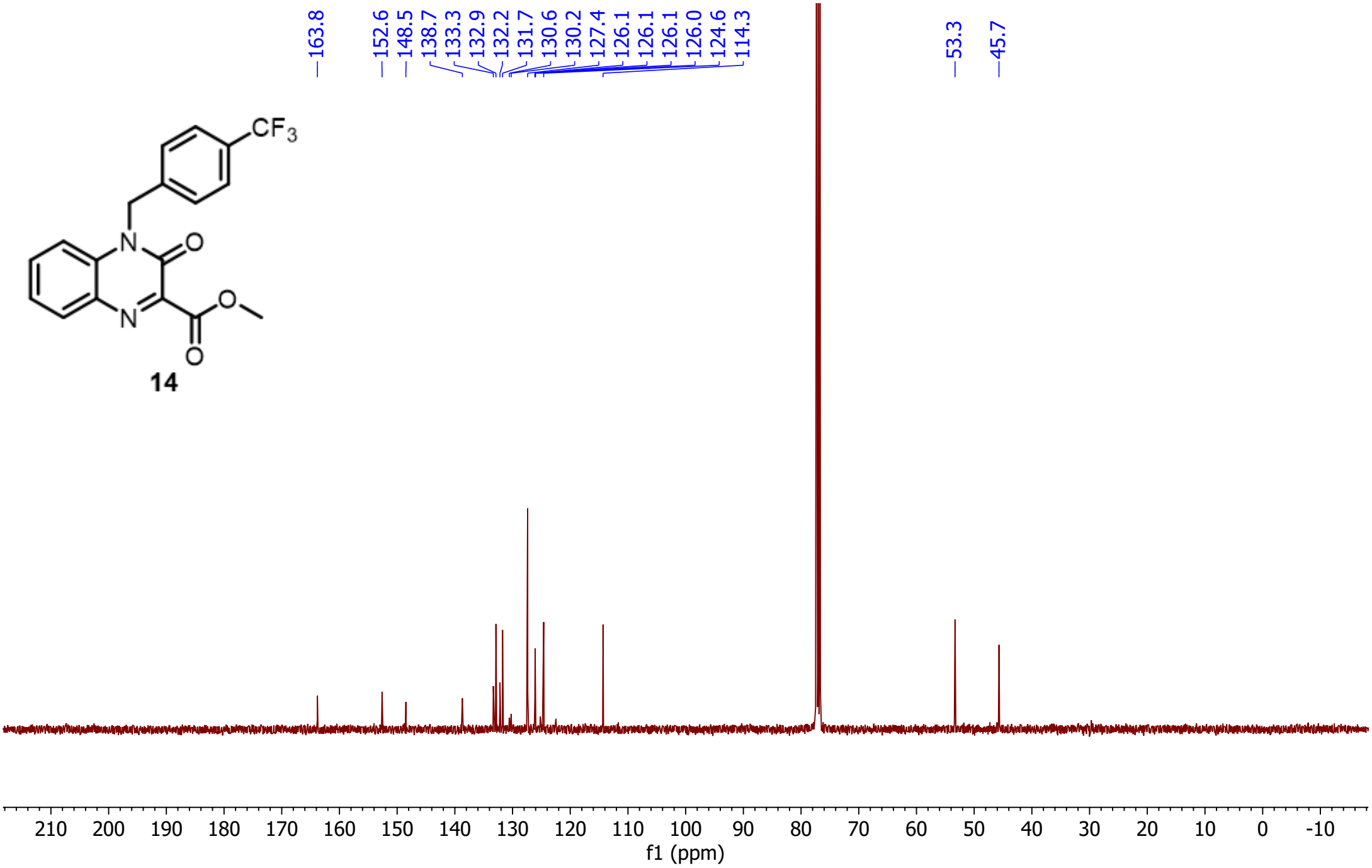
1H (CDCl3, 400 MHz)



14

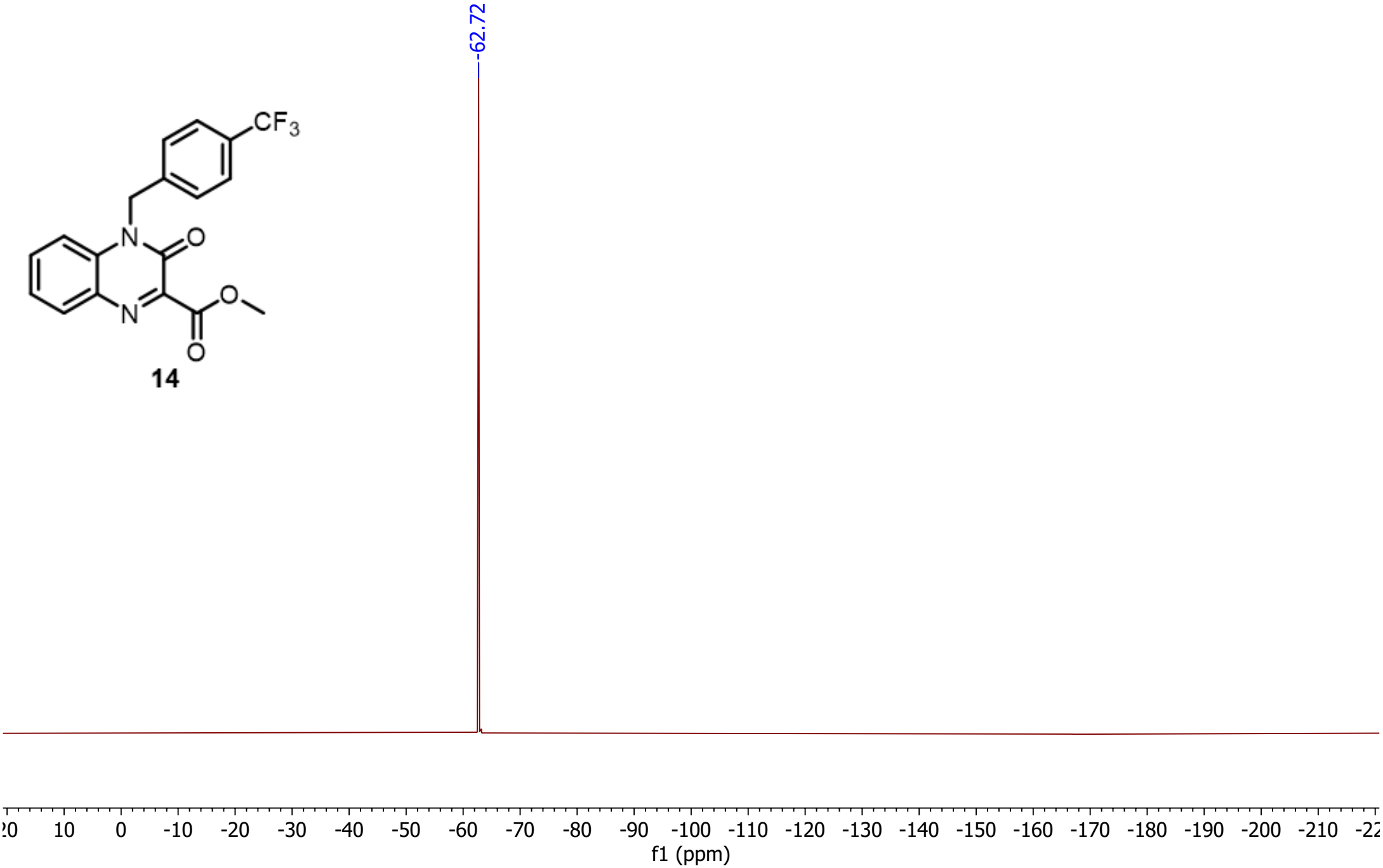
^{1}H NMR Spectrum of **14**

13C (CDCl3, 101 MHz)



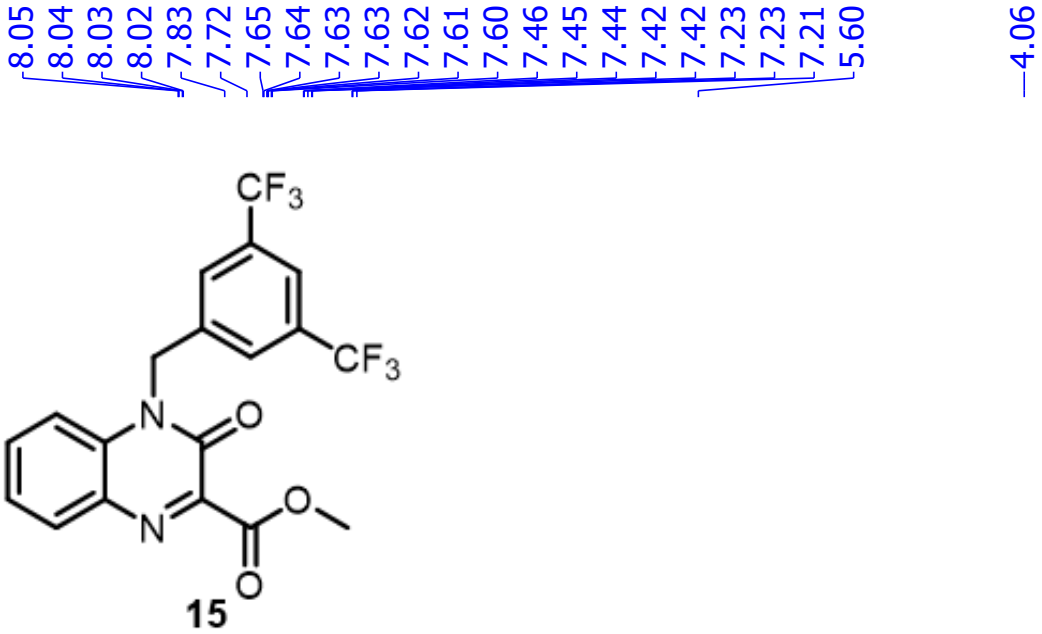
^{13}C NMR Spectrum of **14**

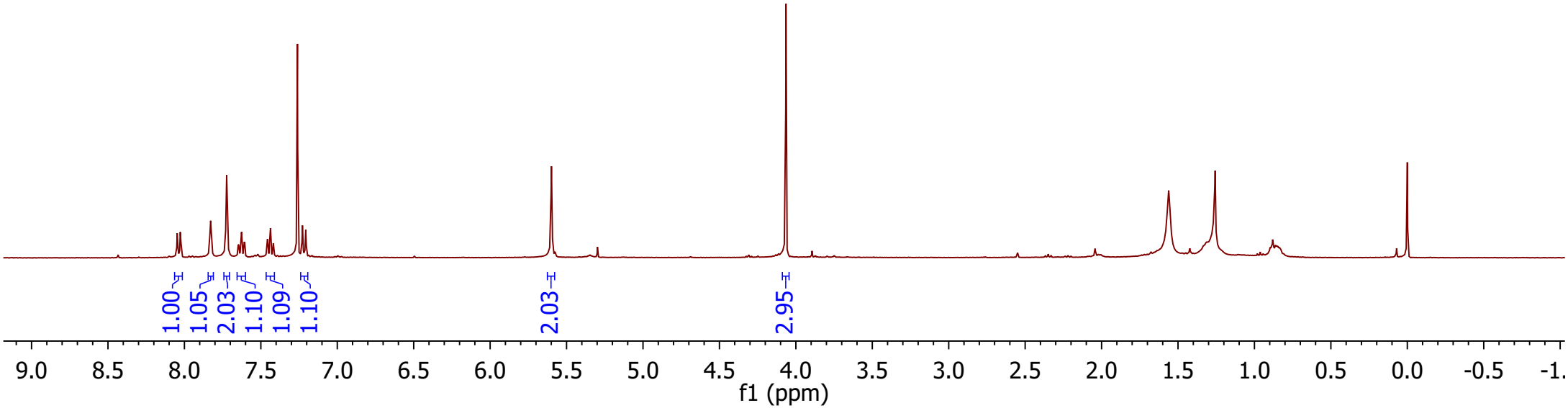
19F (CDCl3, 376 MHz)



^{19}F NMR Spectrum of **14**

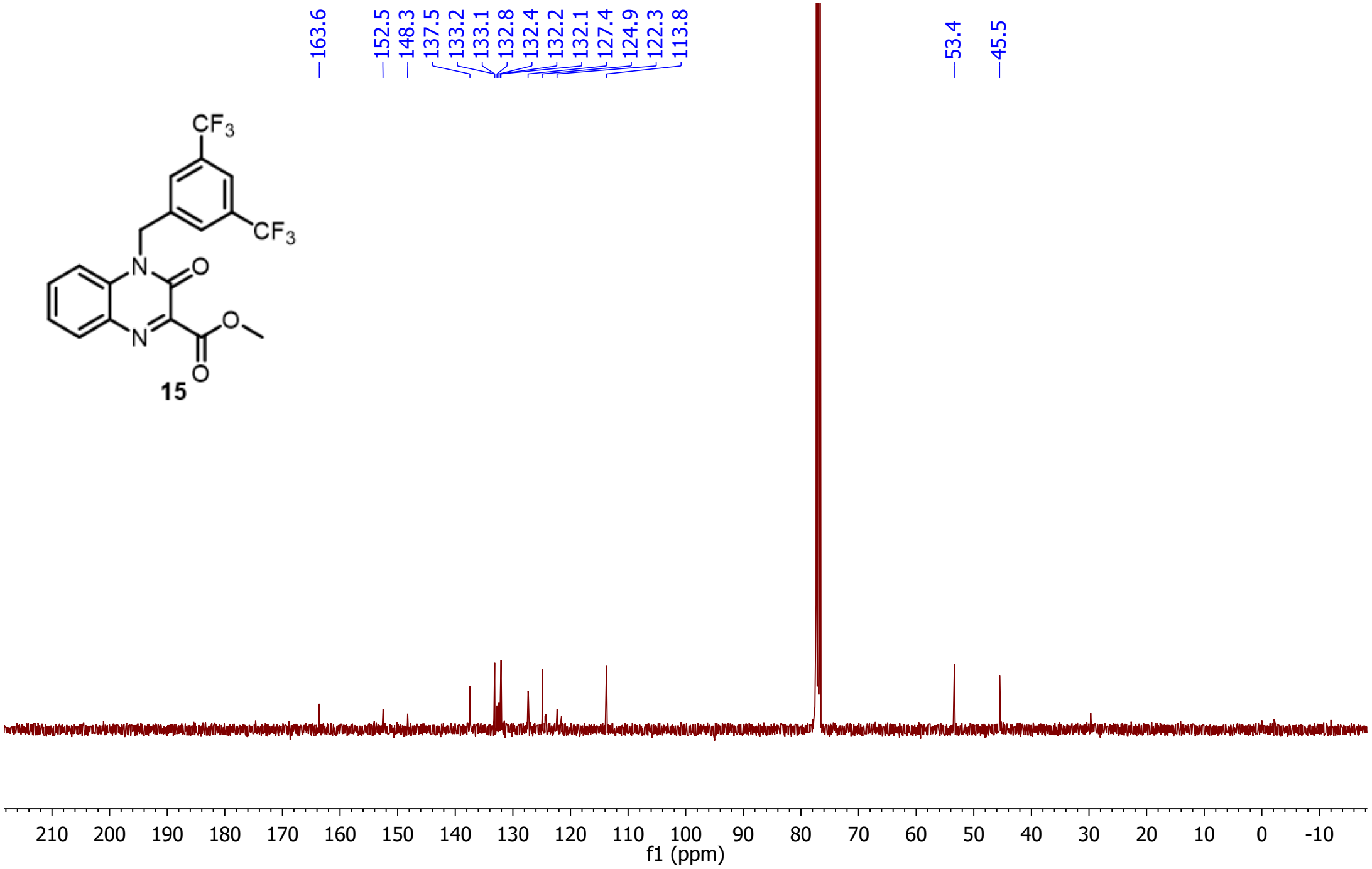
1H (CDCl3, 400 MHz)





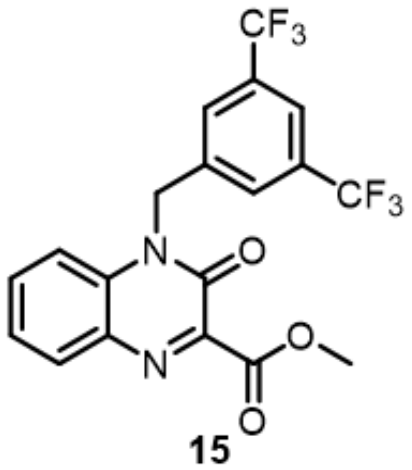
^{1}H NMR Spectrum of **15**

13C (CDCl3, 101 MHz)



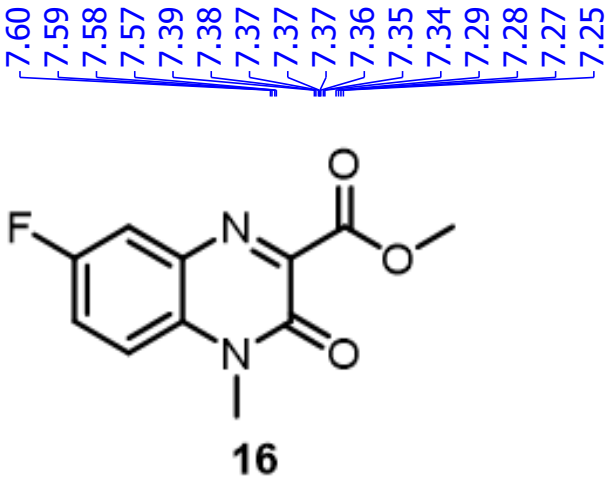
^{13}C NMR Spectrum of **15**

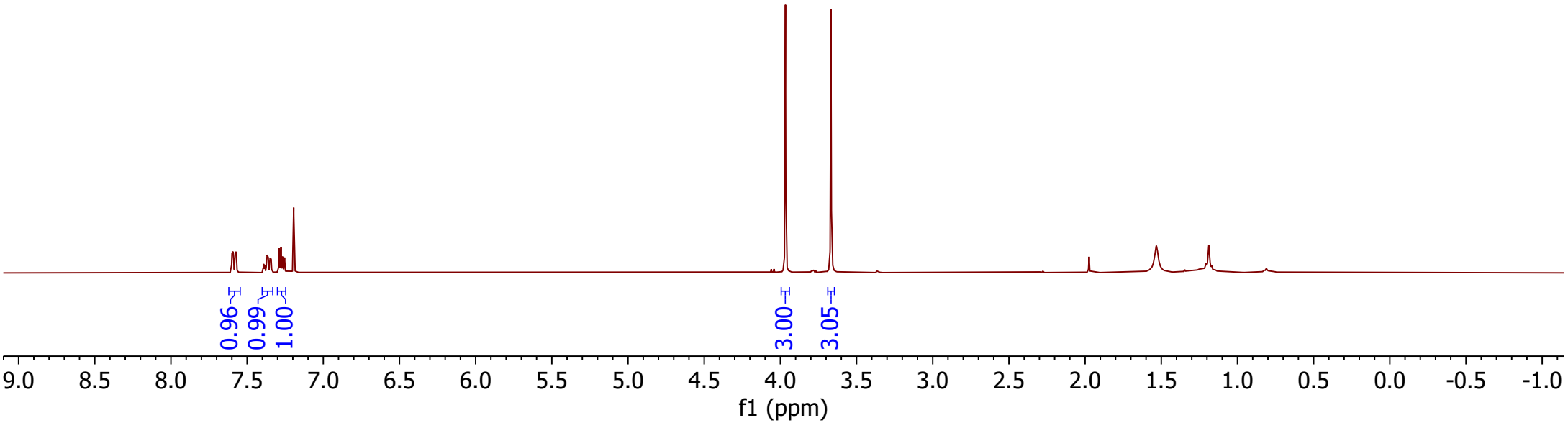
19F (CDCl3, 376 MHz)



^{19}F NMR Spectrum of **15**

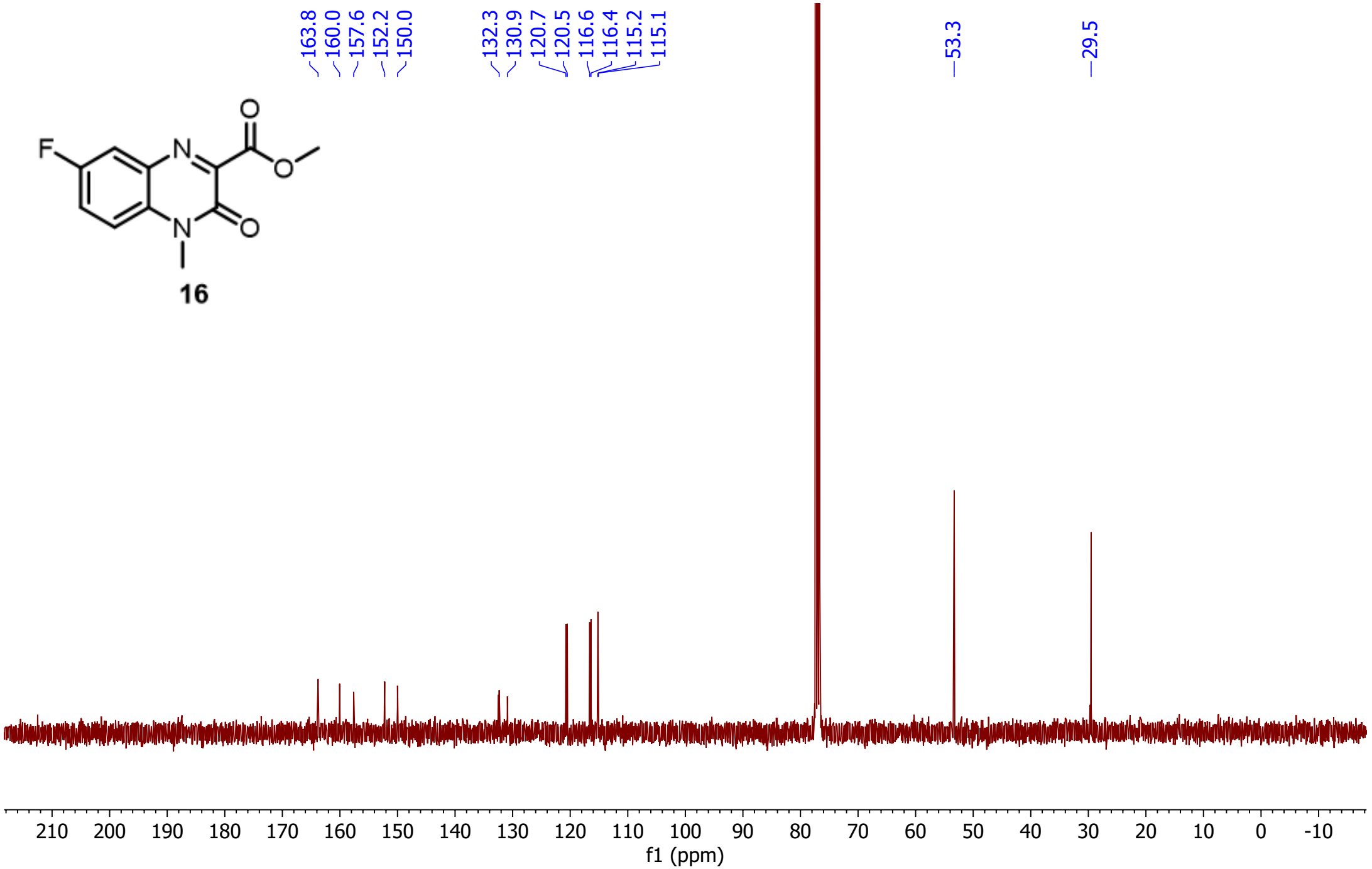
1H (CDCl3, 400 MHz)





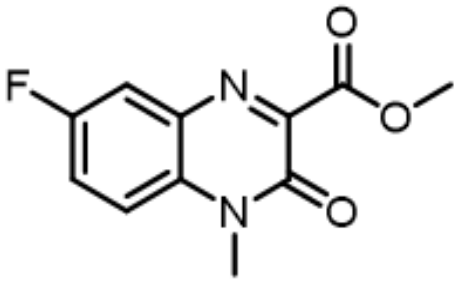
^{1}H NMR Spectrum of **16**

13C (CDCl3, 101 MHz)



^{13}C NMR Spectrum of **16**

19F (CDCl3, 376 MHz)



16

^{19}F NMR Spectrum of **16**

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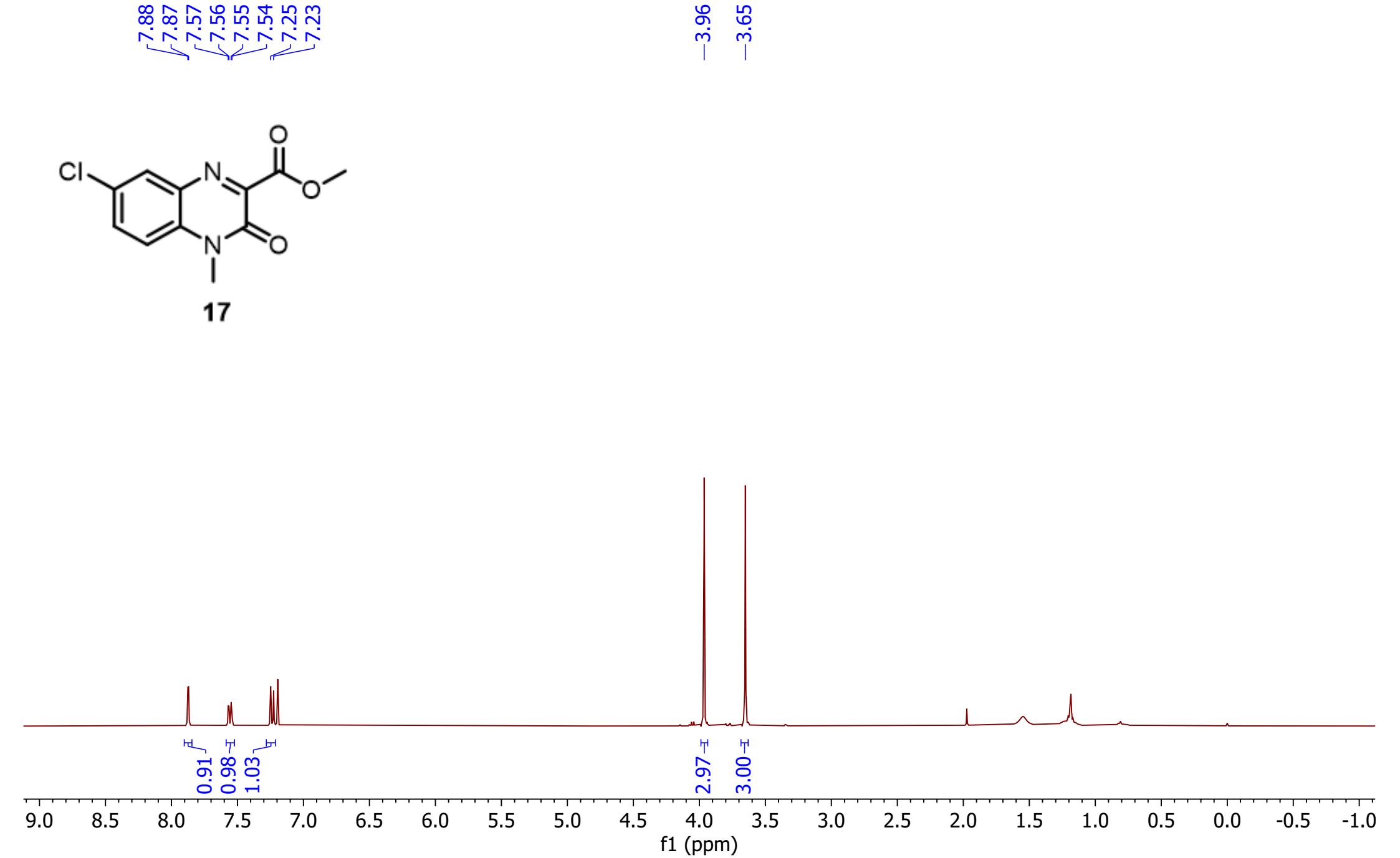

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^{1}H NMR Spectrum of **17**

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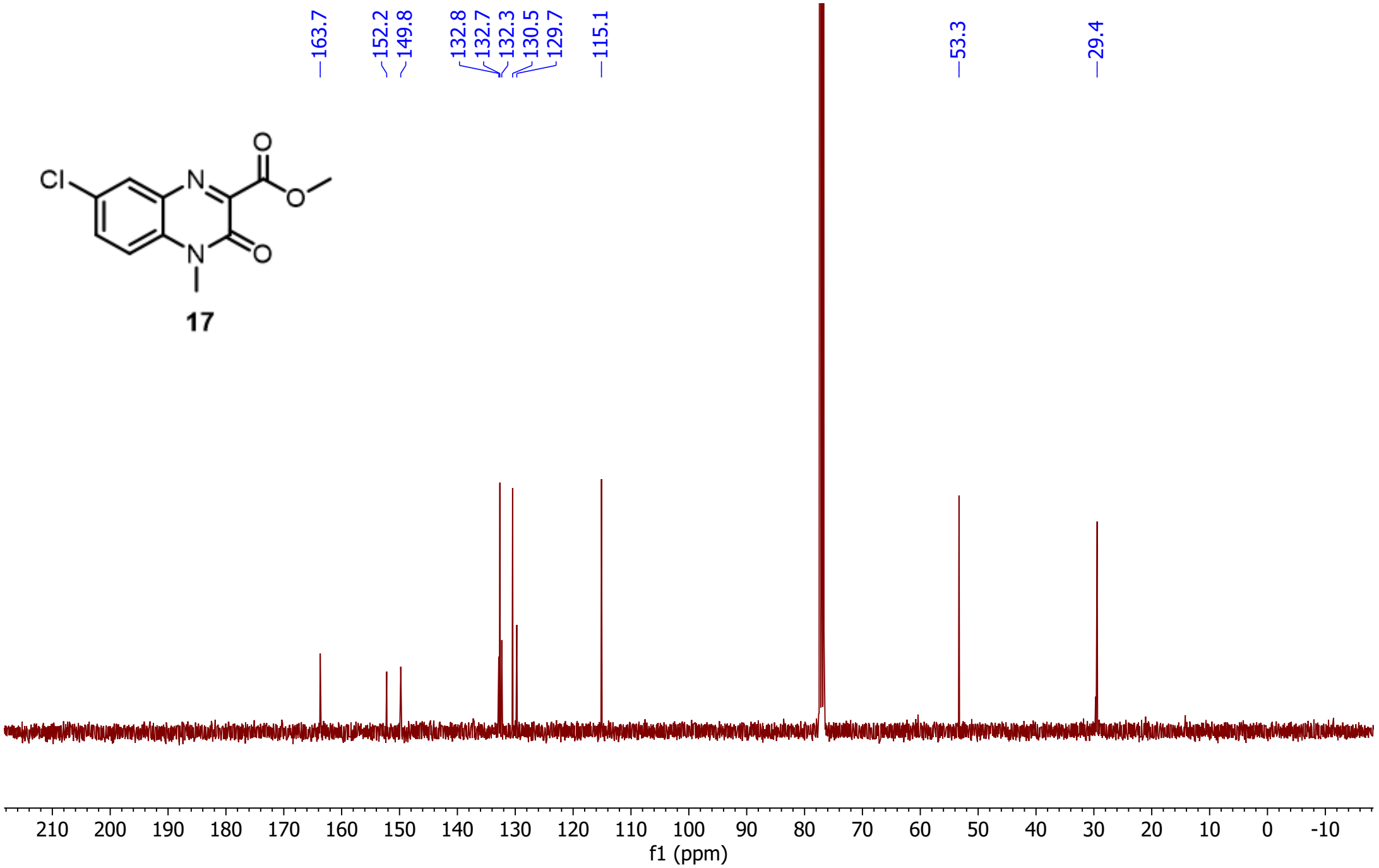
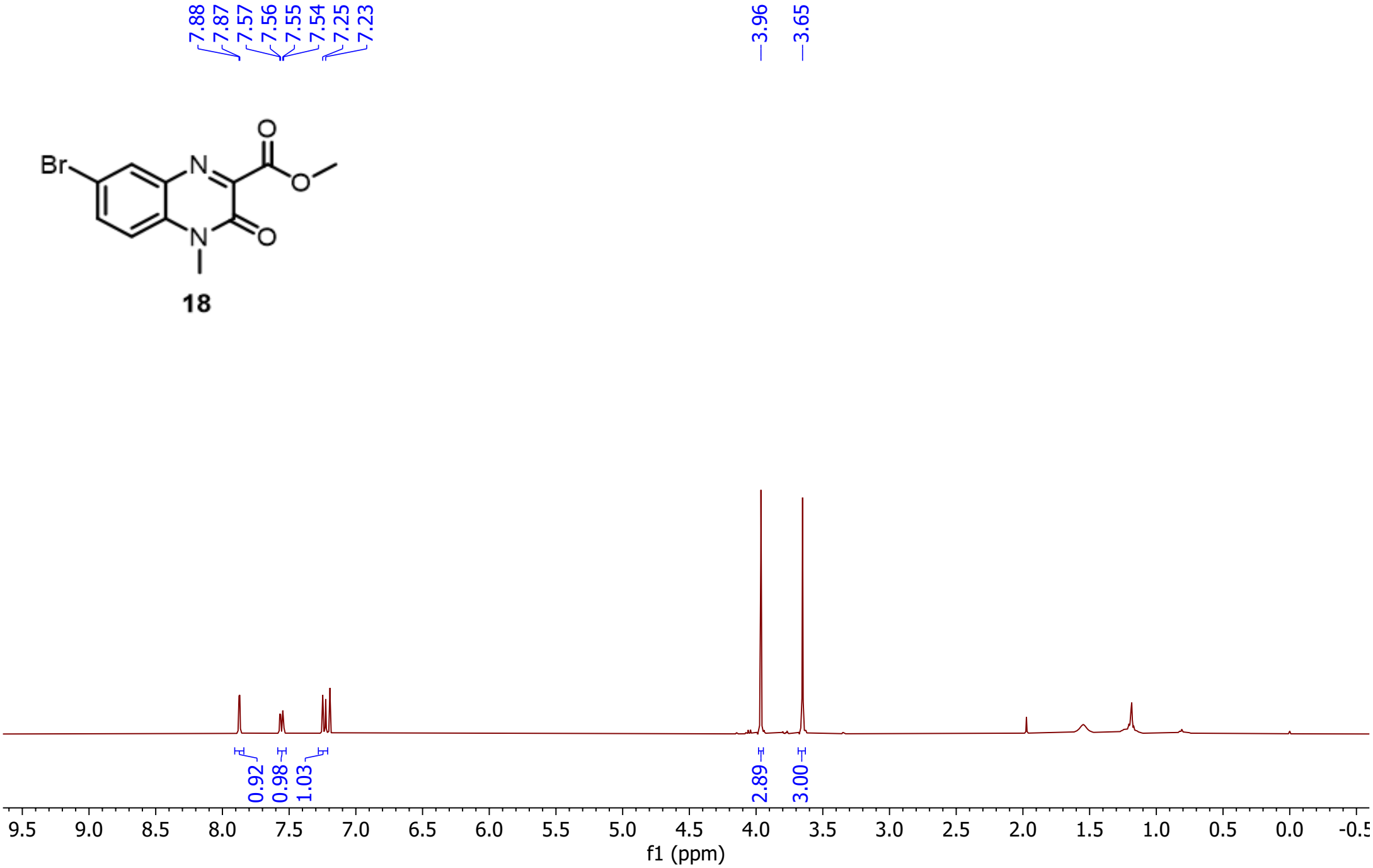


^{13}C NMR Spectrum of **17**

1H (CDCl3, 400 MHz)



^{1}H NMR Spectrum of **18**

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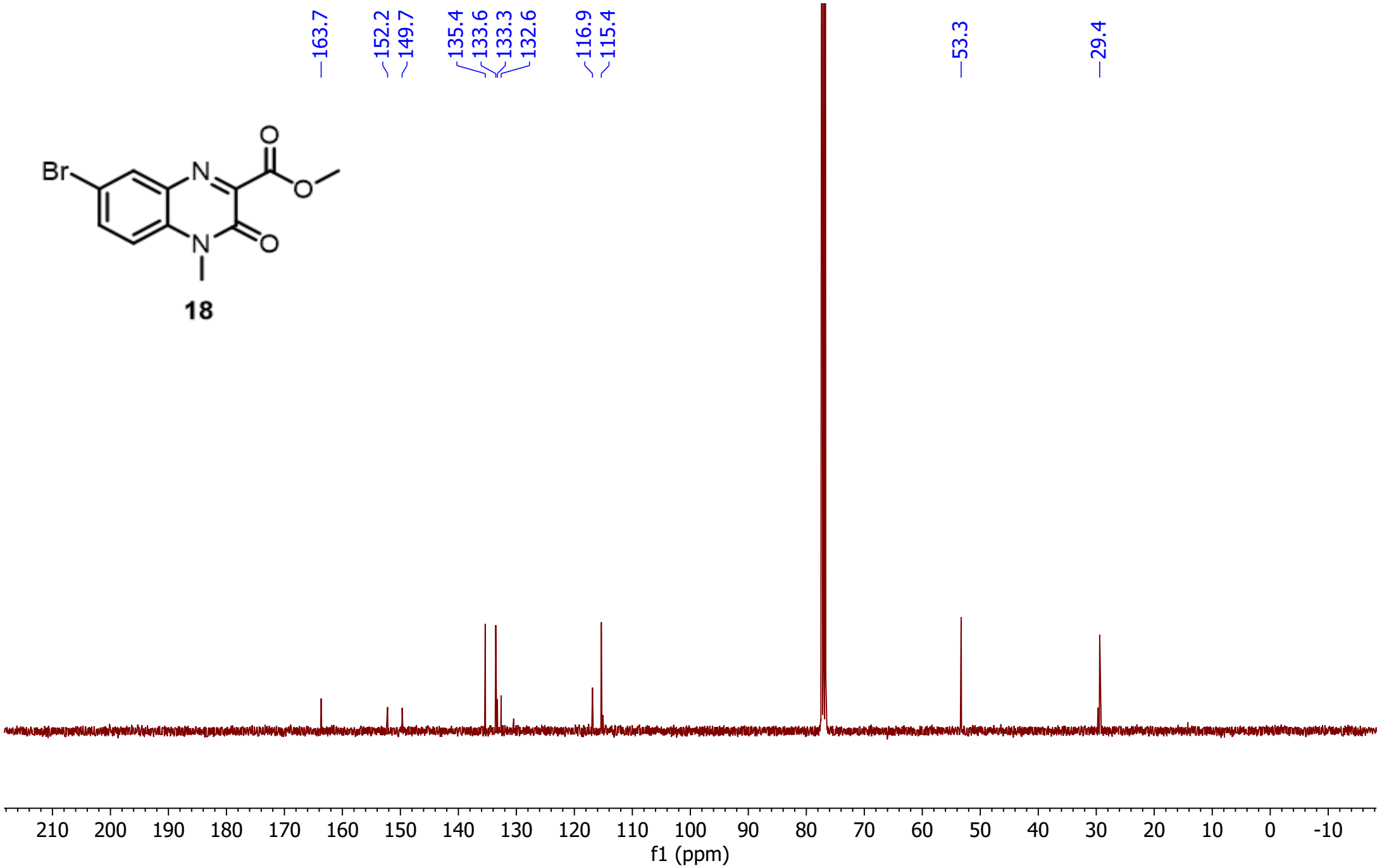

^{13}C NMR Spectrum of **18**

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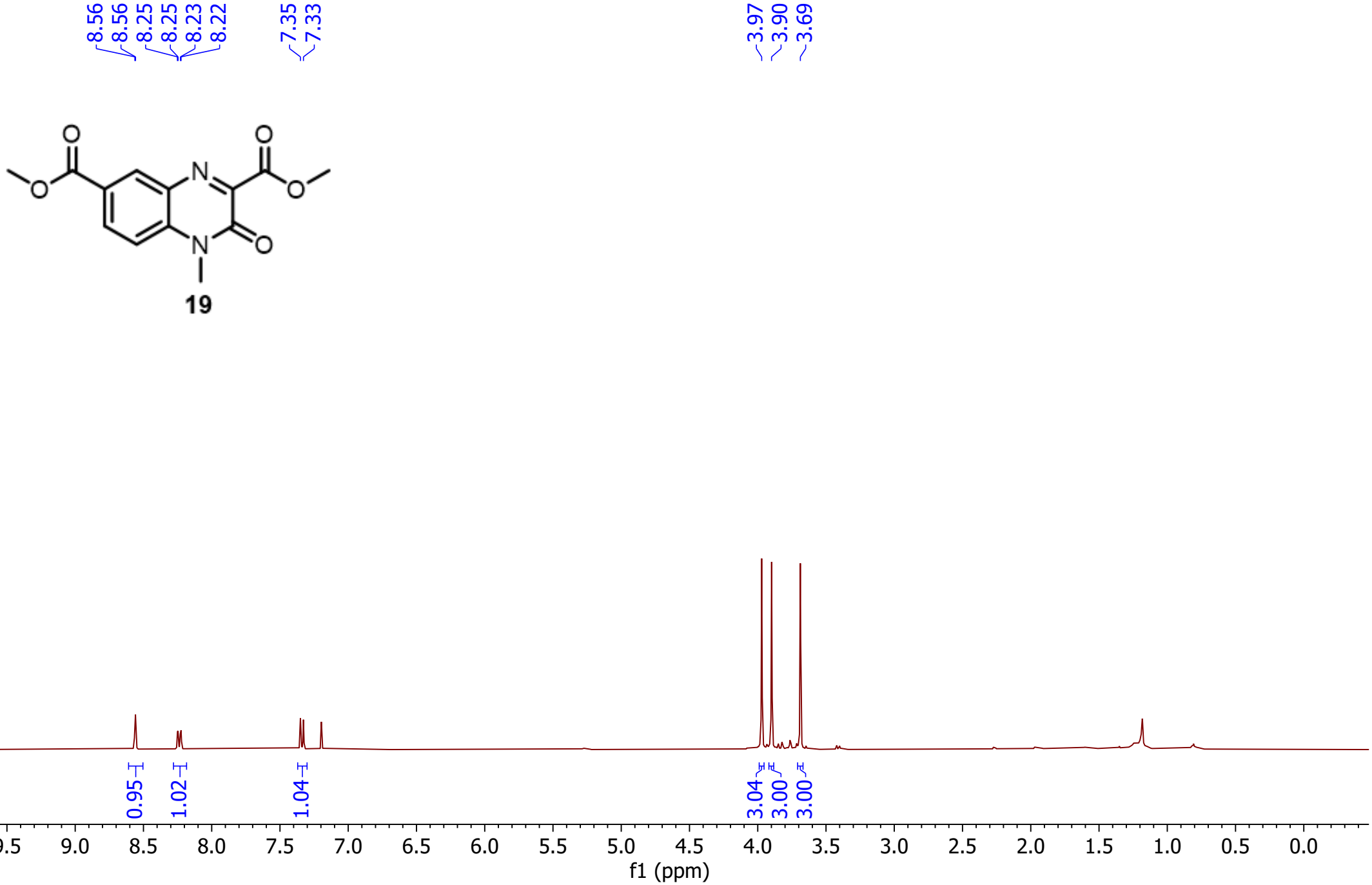
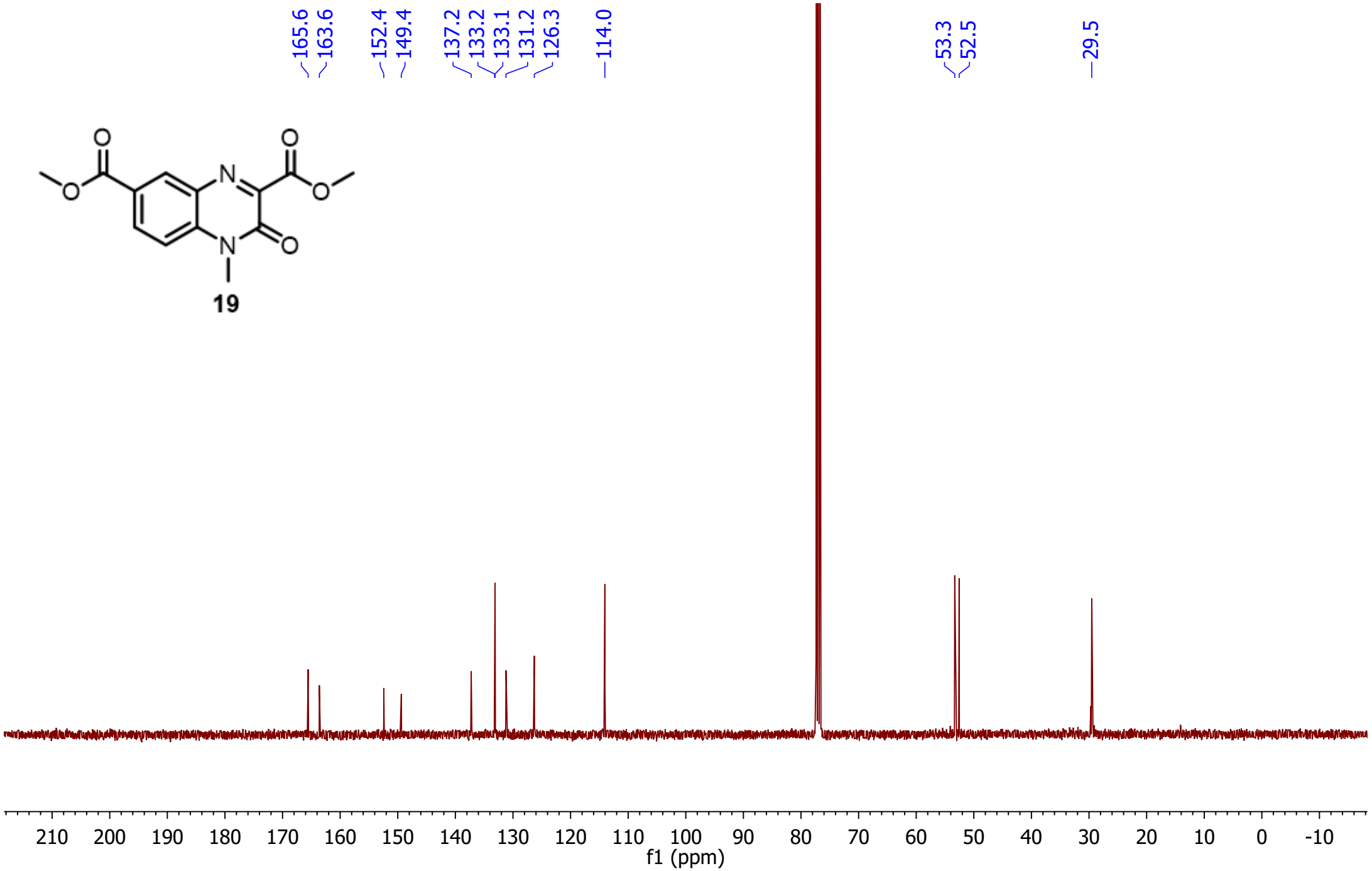


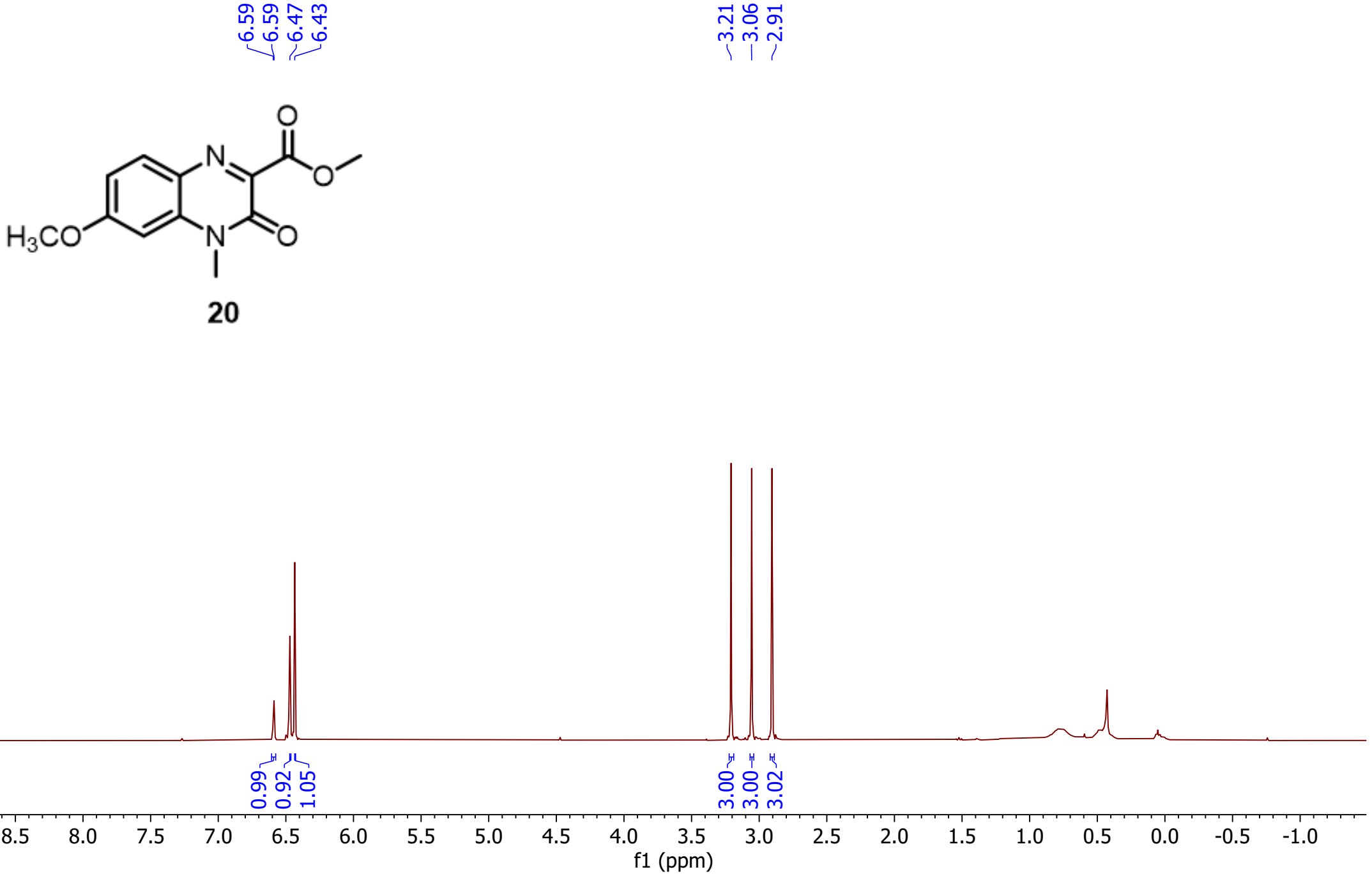
^{1}H NMR Spectrum of **19**

13C (CDCl3, 101 MHz)



^{13}C NMR Spectrum of **19**

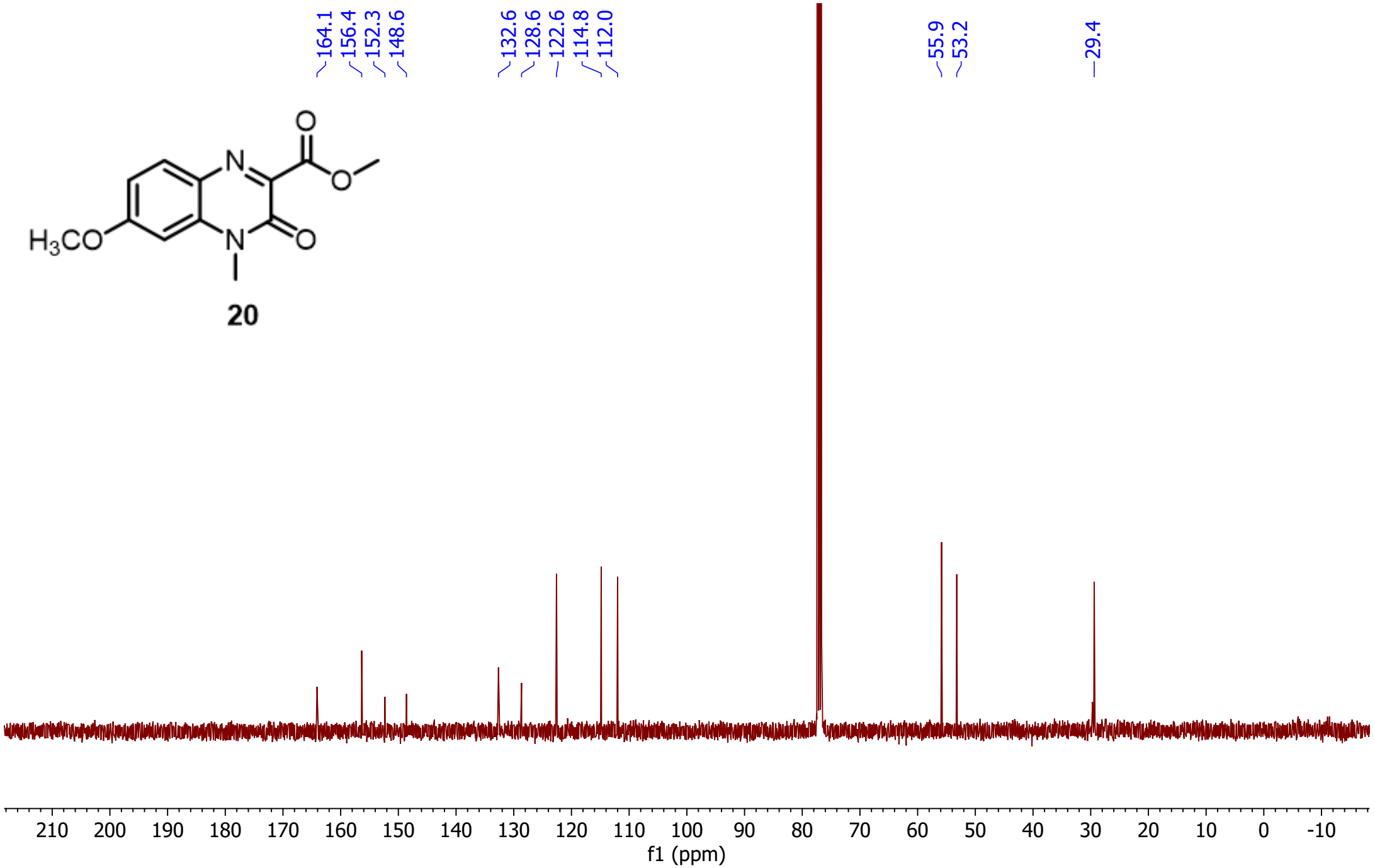
1H (CDCl3, 400 MHz)



20

^{1}H NMR Spectrum of **20**

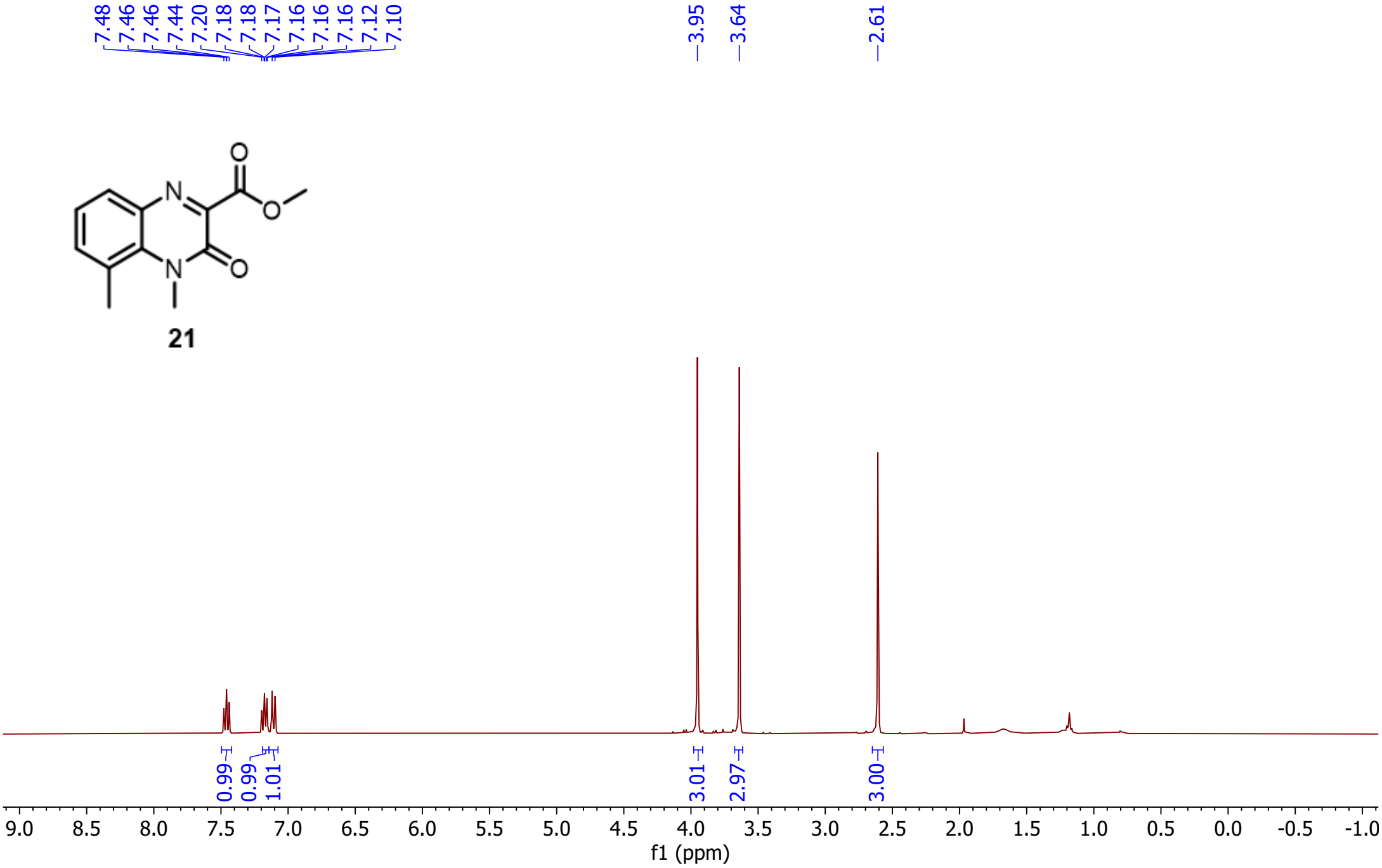
13C (CDCl3, 101 MHz)



20

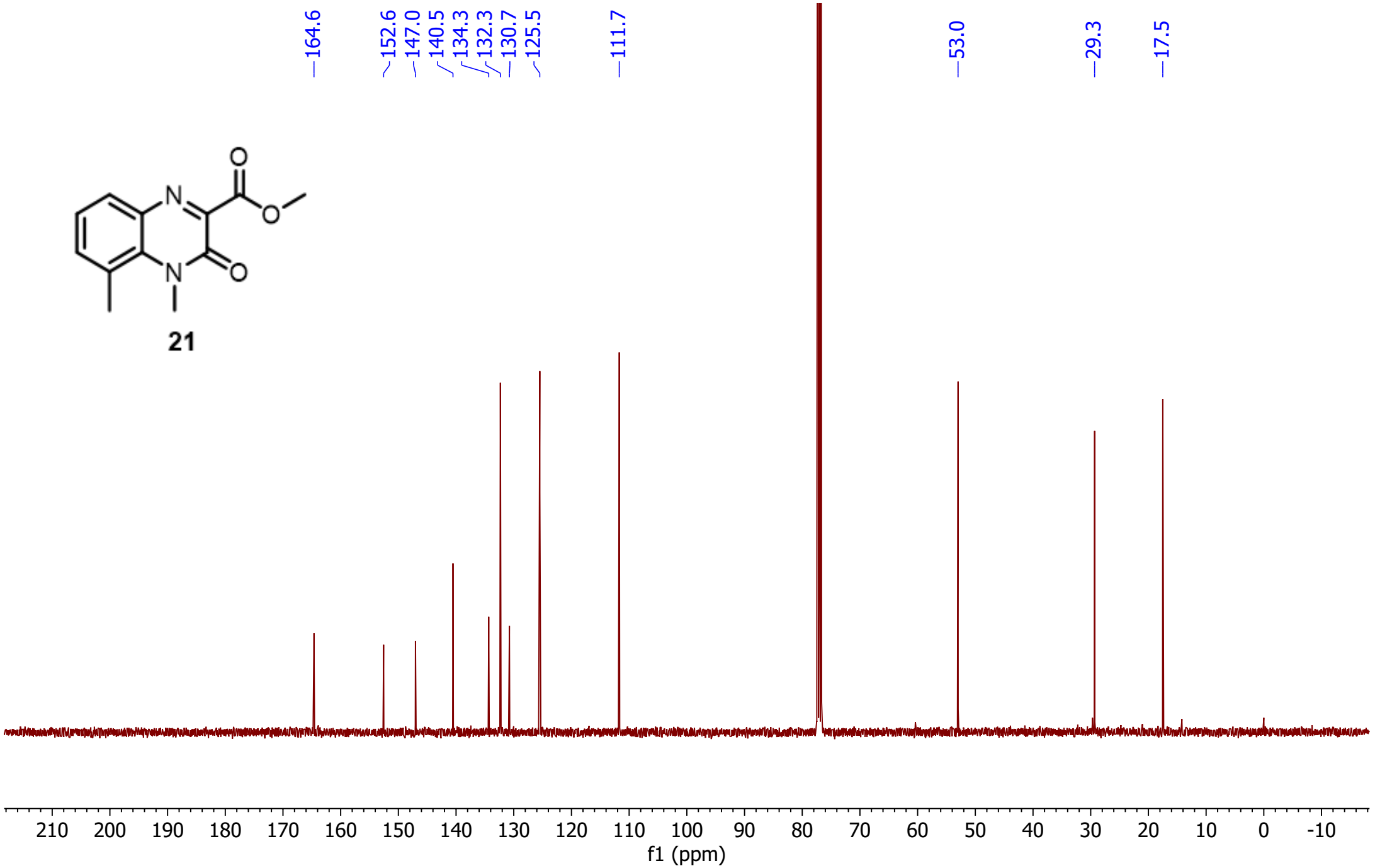
^{13}C NMR Spectrum of **20**

1H (CDCl3, 400 MHz)



^{1}H NMR Spectrum of **21**

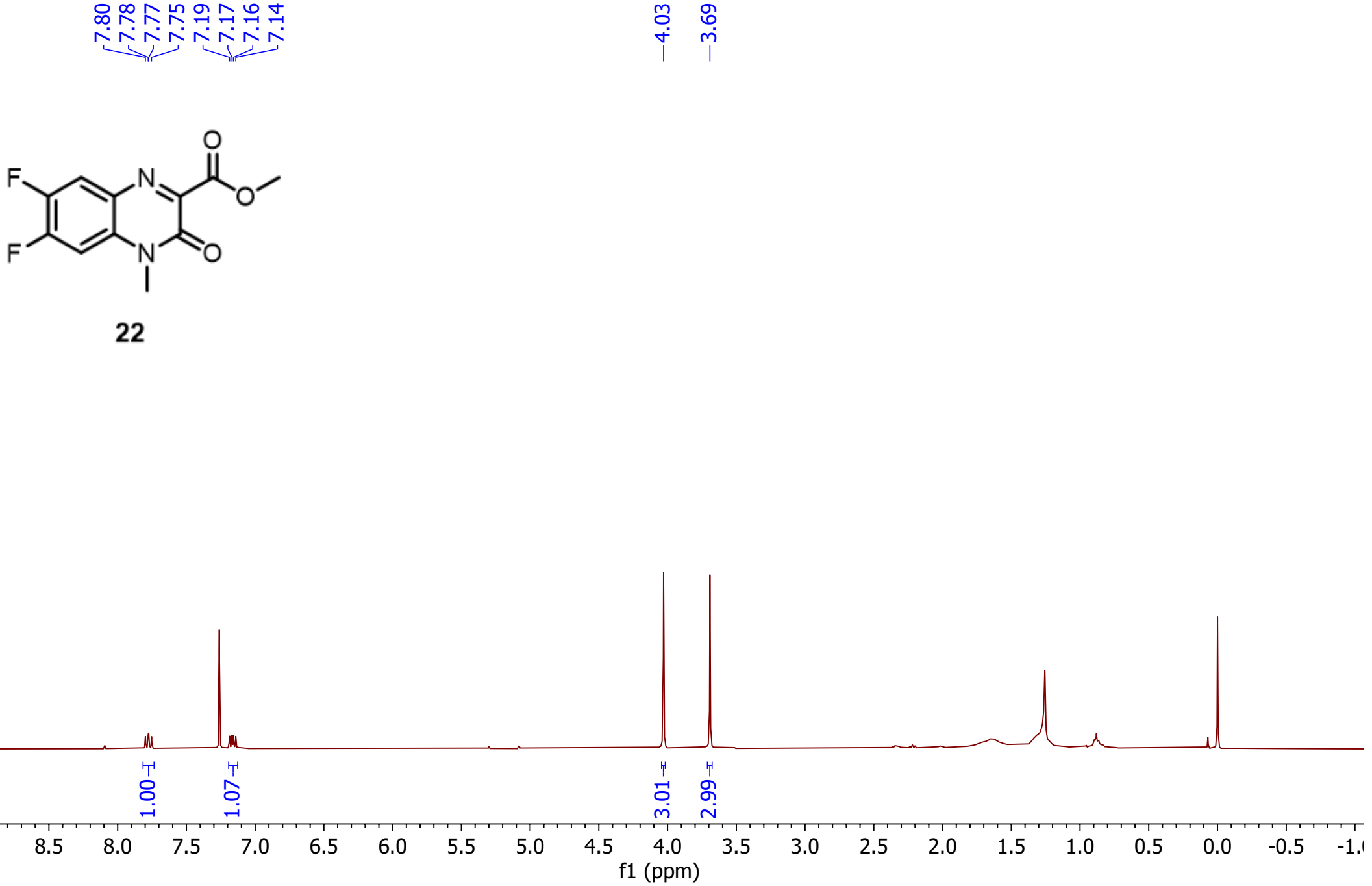
13C (CDCl3, 101 MHz)



21

^{13}C NMR Spectrum of **21**

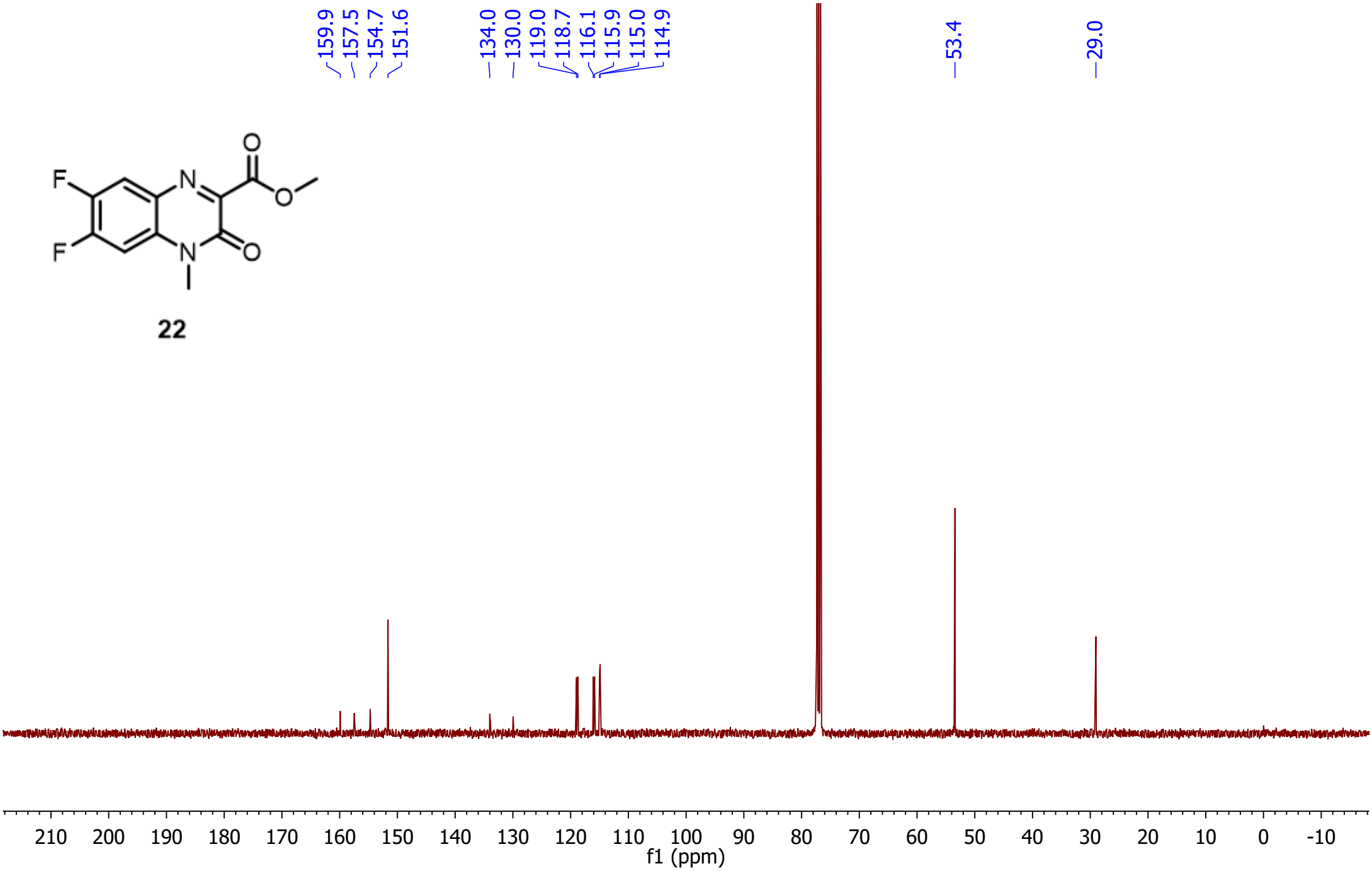
1H (CDCl3, 400 MHz)



22

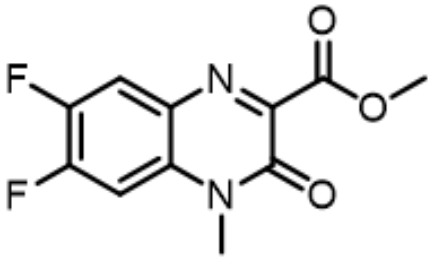
^{1}H NMR Spectrum of **22**

13C (CDCl3, 101 MHz)



^{13}C NMR Spectrum of **22**

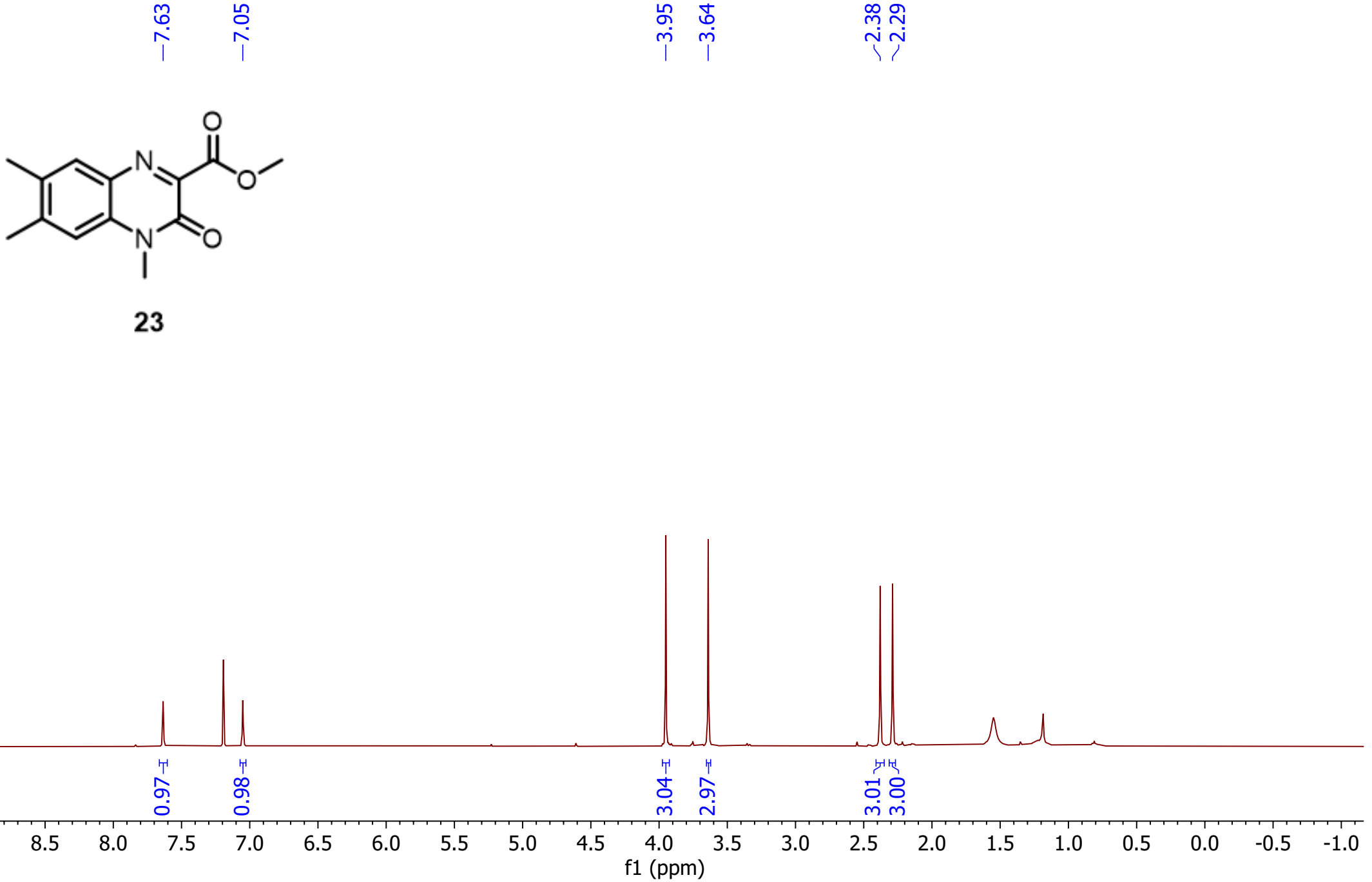
19F (CDCl3, 376 MHz)



22

^{19}F NMR Spectrum of **22**

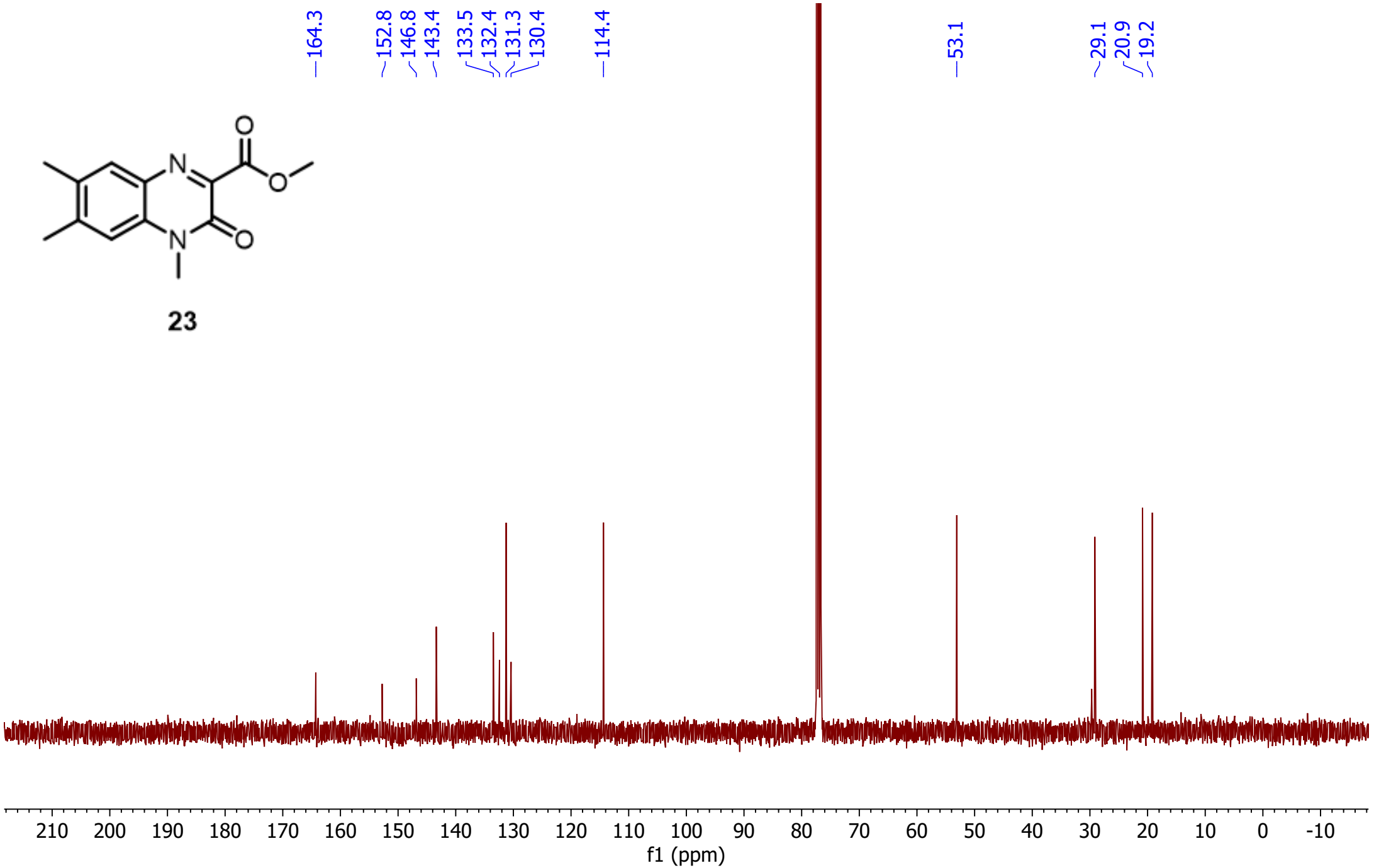
1H (CDCl3, 400 MHz)



23

^{1}H NMR Spectrum of **23**

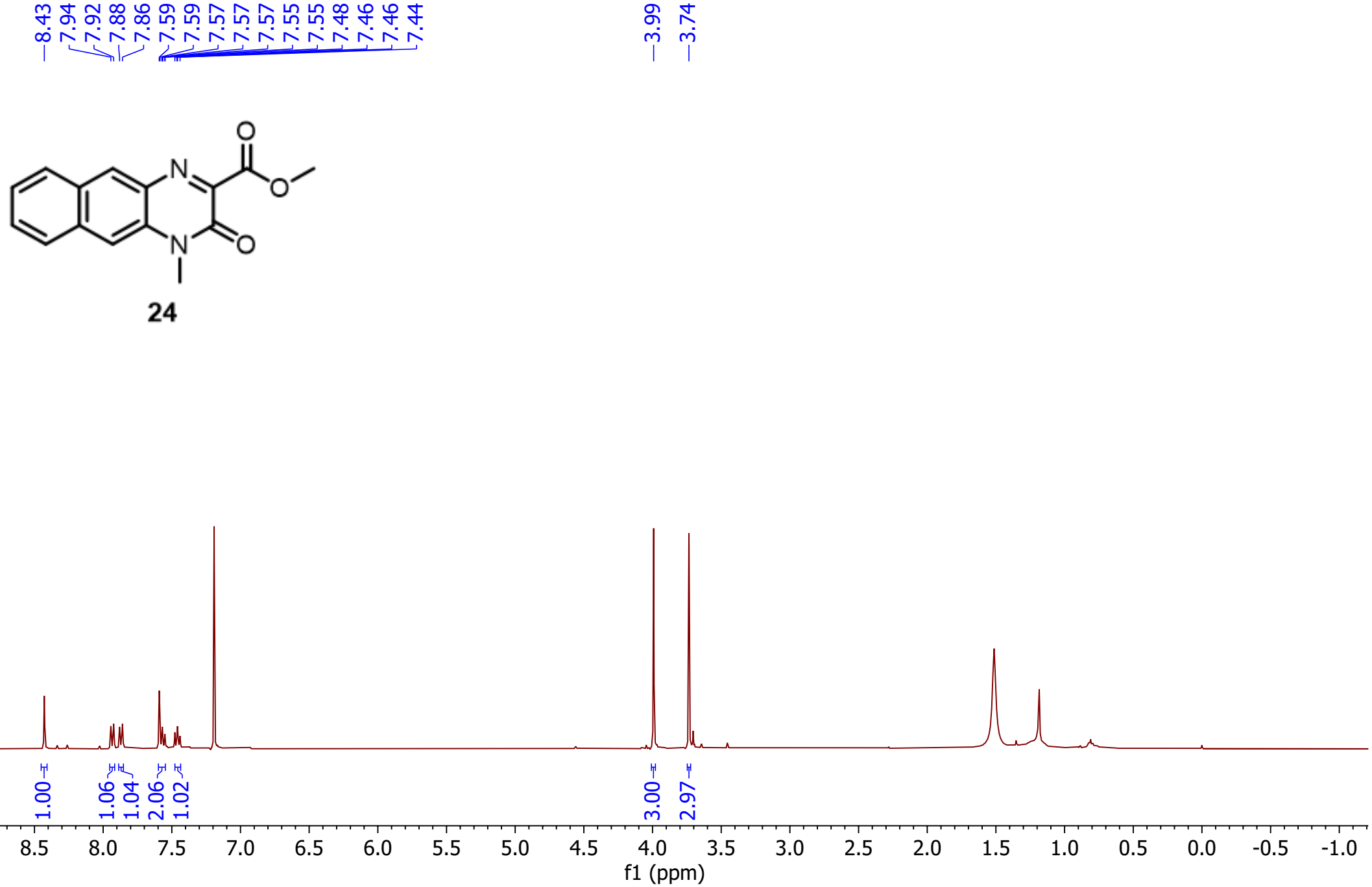
13C (CDCl3, 101 MHz)



23

^{13}C NMR Spectrum of **23**

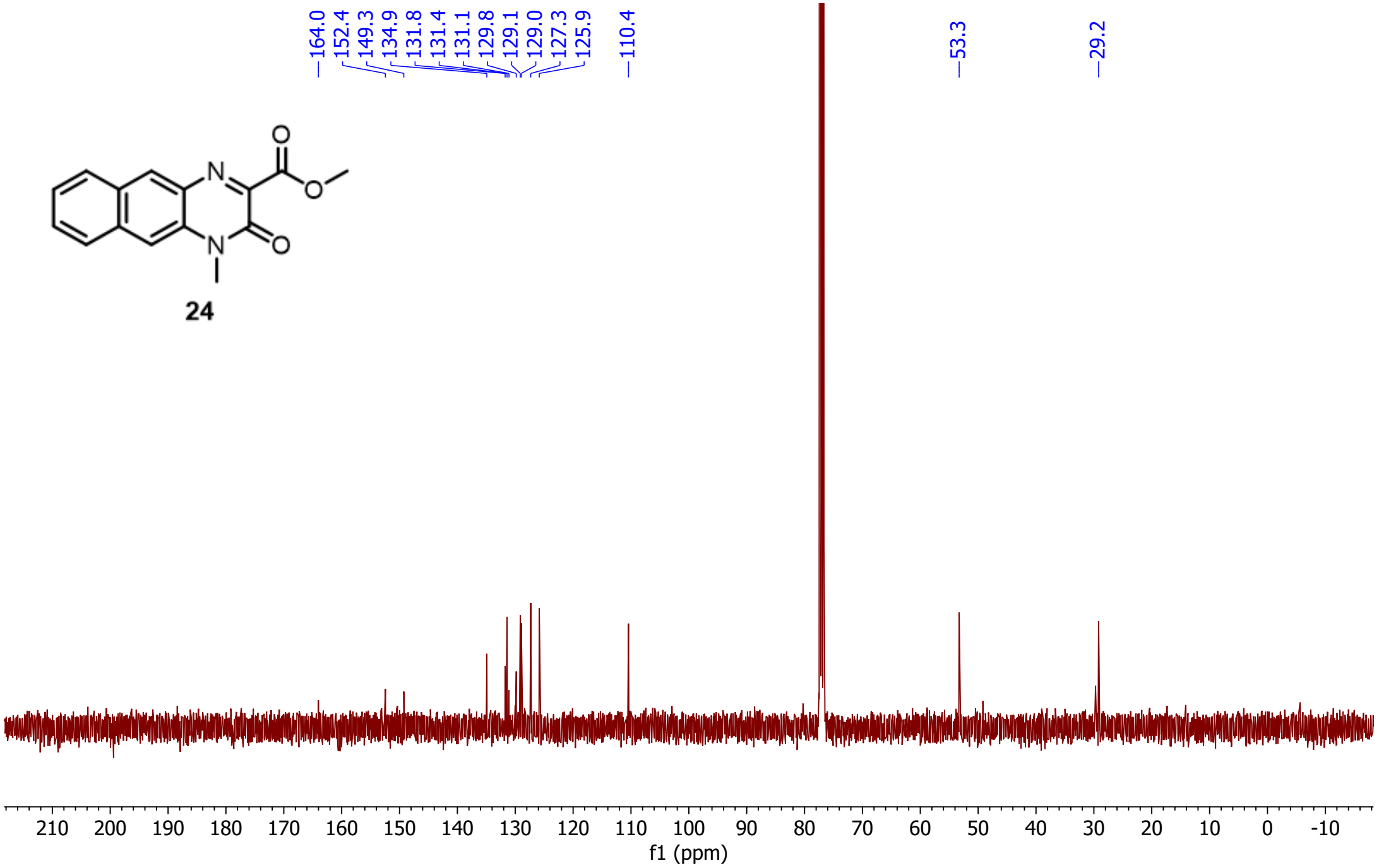
1H (CDCl3, 400 MHz)



24

^{1}H NMR Spectrum of **24**

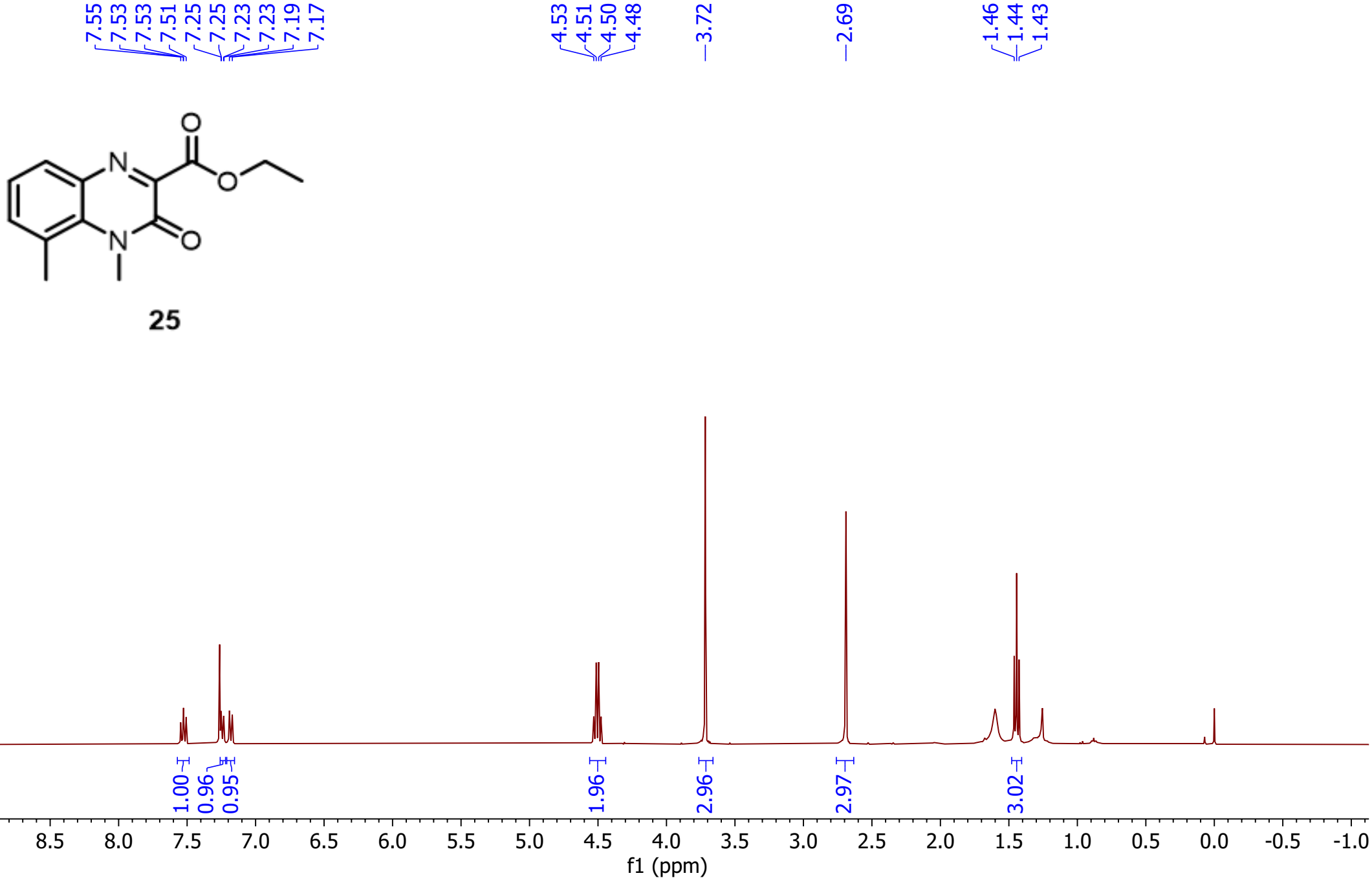
13C (CDCl3, 101 MHz)



24

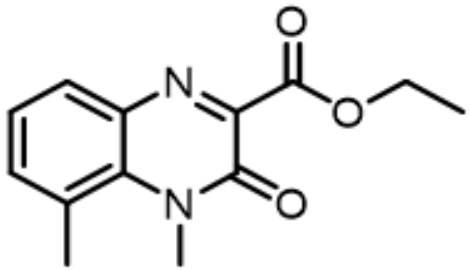
^{13}C NMR Spectrum of **24**

1H (CDCl3, 400 MHz)



^{1}H NMR Spectrum of **25**

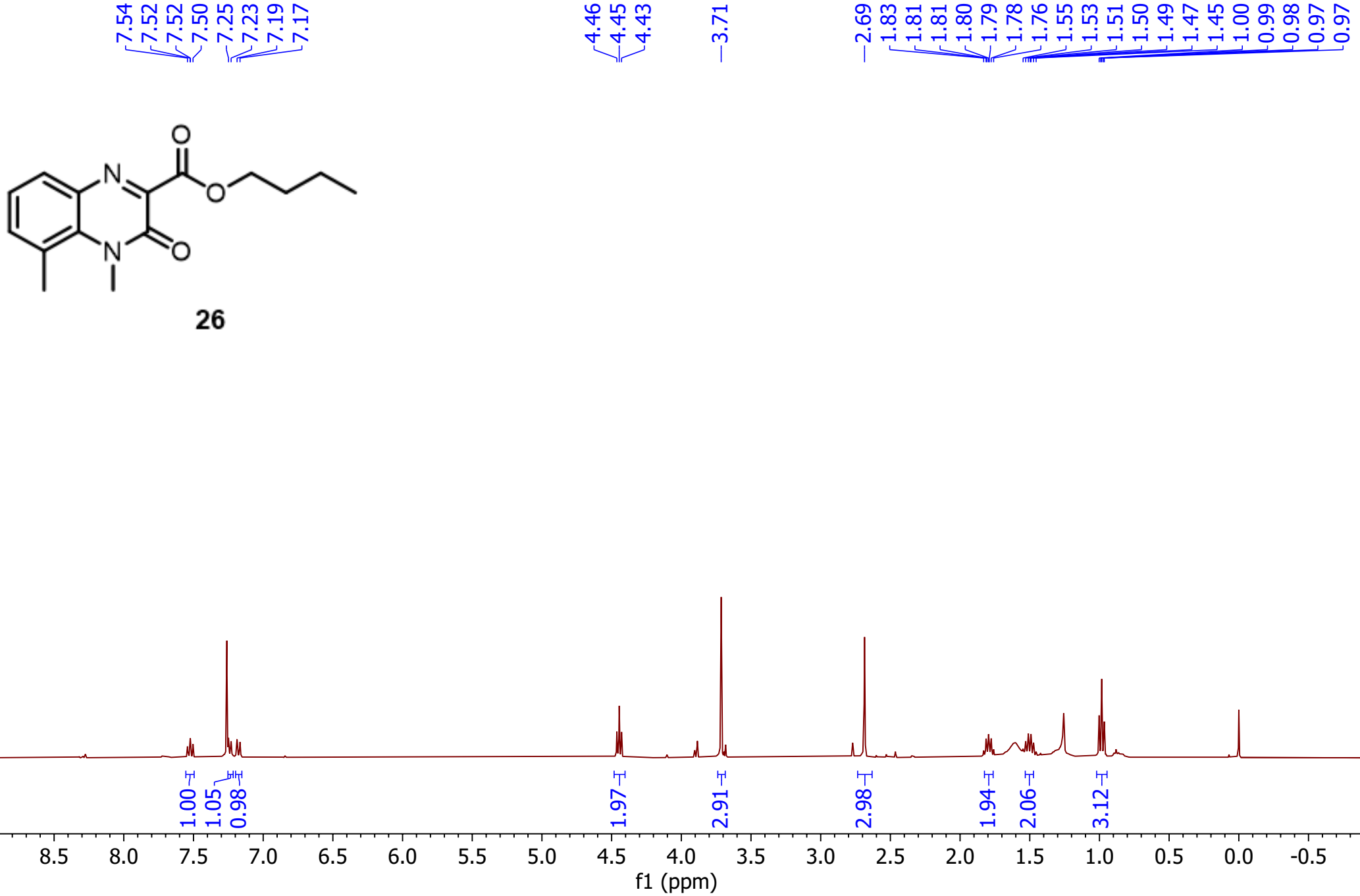
13C (CDCl3, 101 MHz)



25

^{13}C NMR Spectrum of **25**

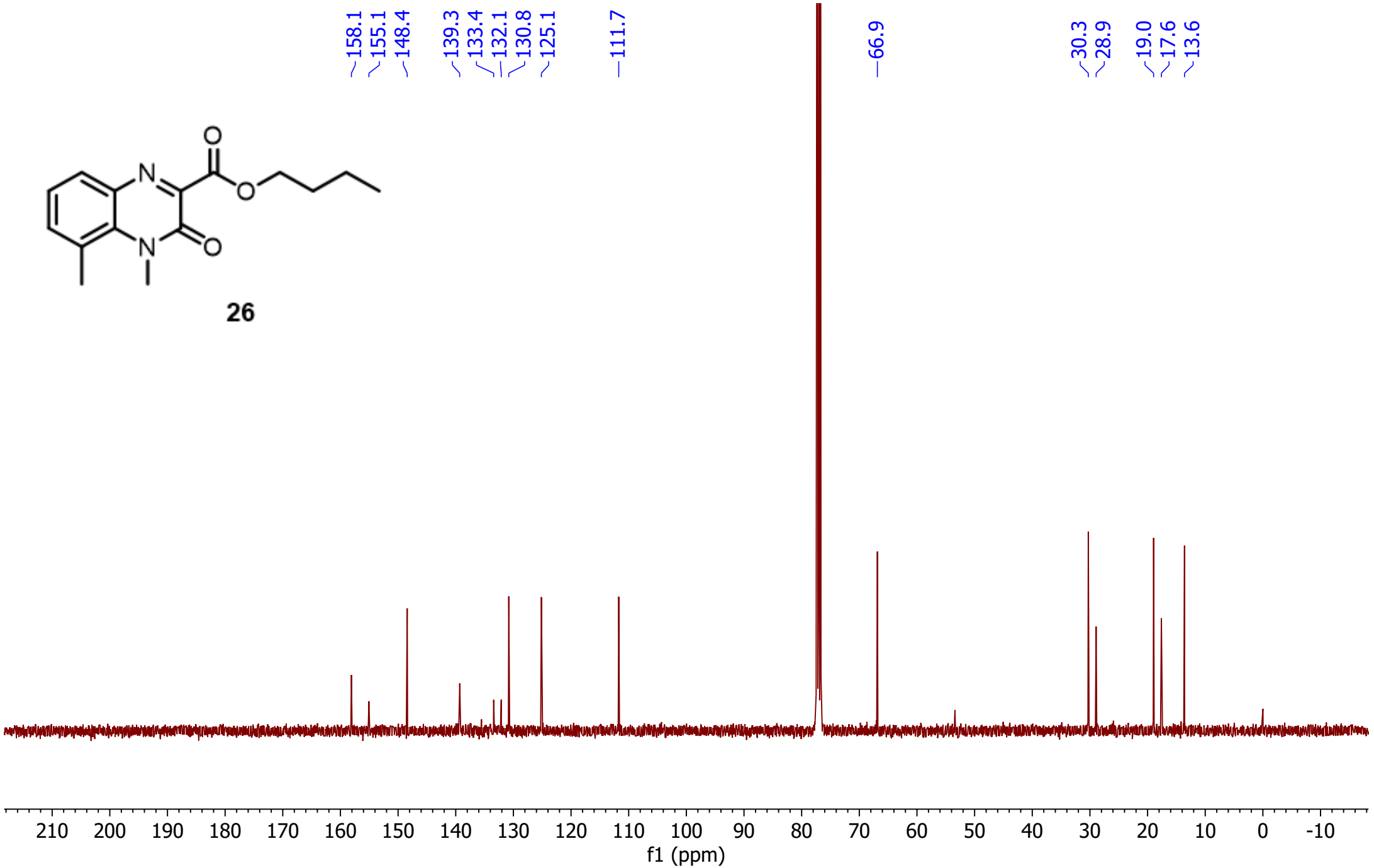
1H (CDCl3, 400 MHz)



26

^{1}H NMR Spectrum of **26**

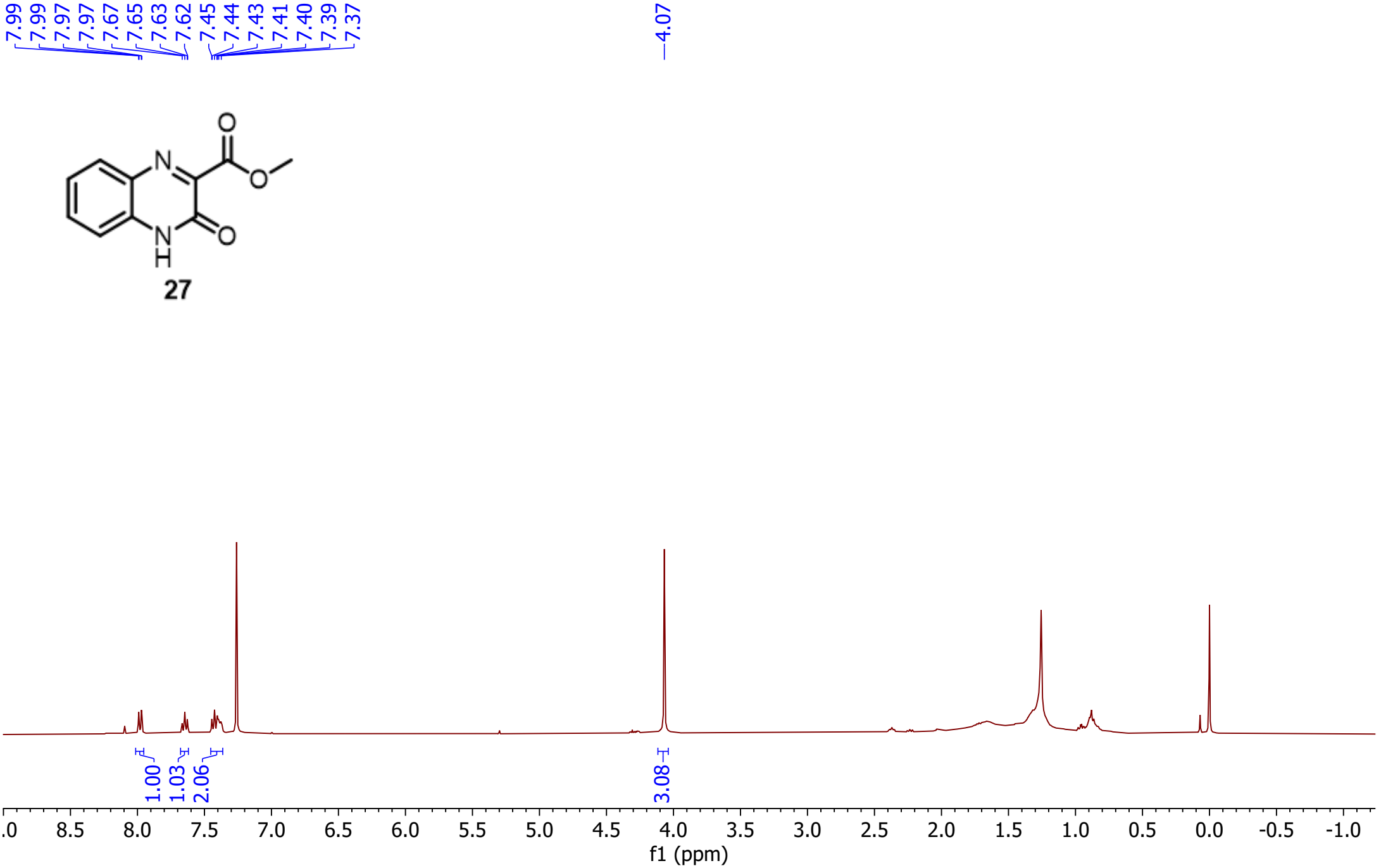
13C (CDCl3, 101 MHz)



26

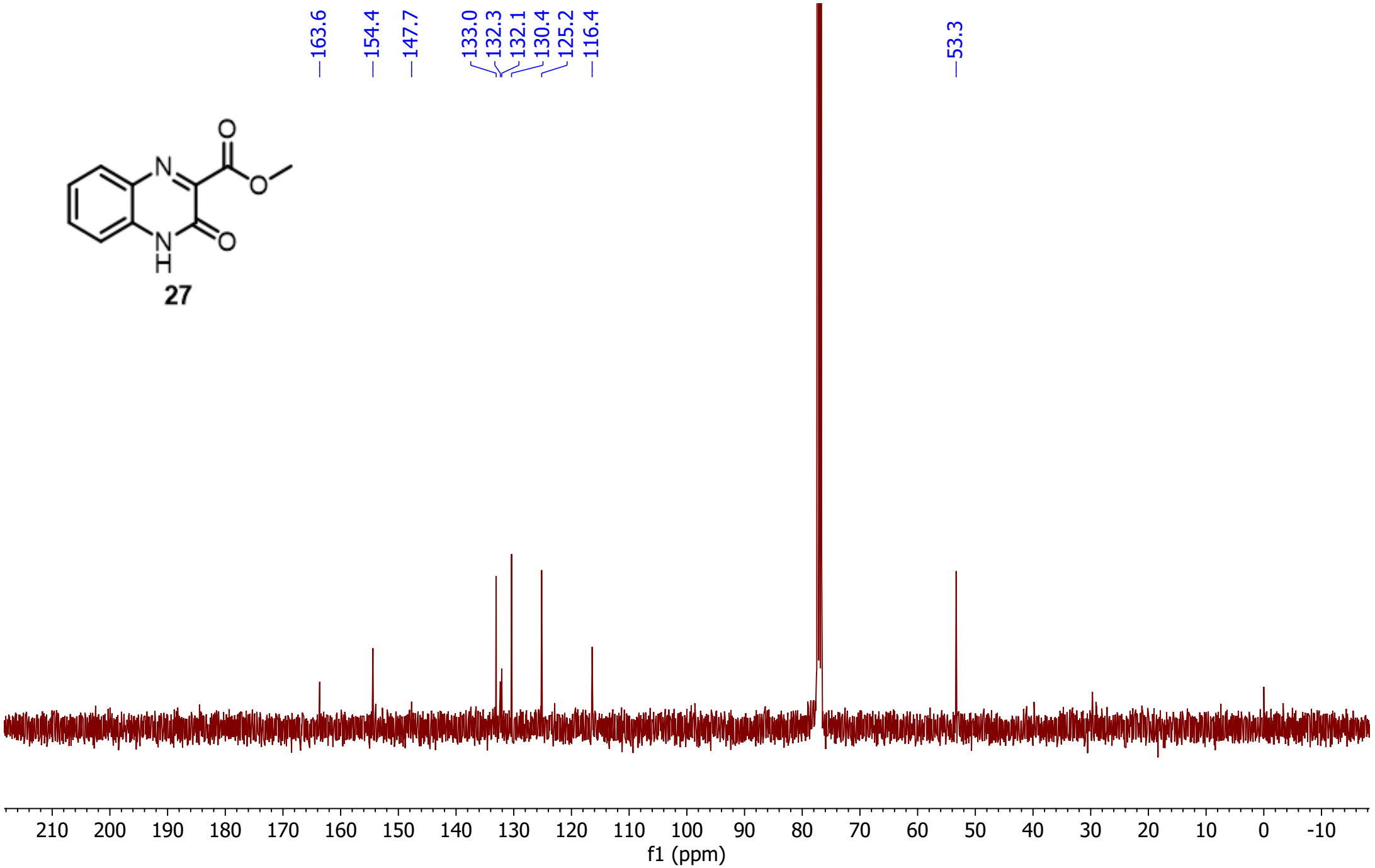
^{13}C NMR Spectrum of **26**

1H (CDCl3, 400 MHz)



^{1}H NMR Spectrum of **27**

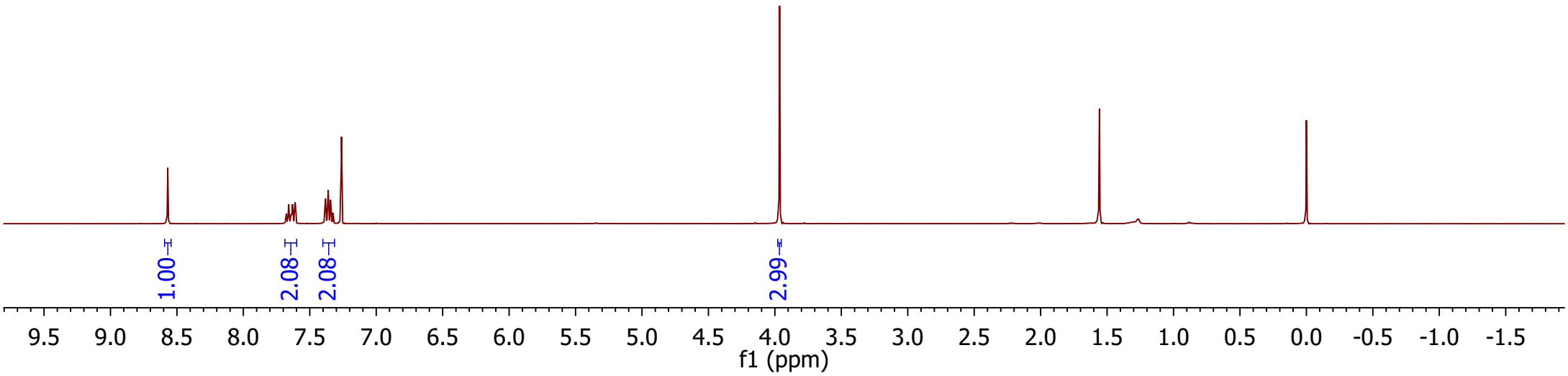
13C (CDCl3, 101 MHz)



^{13}C NMR Spectrum of **27**

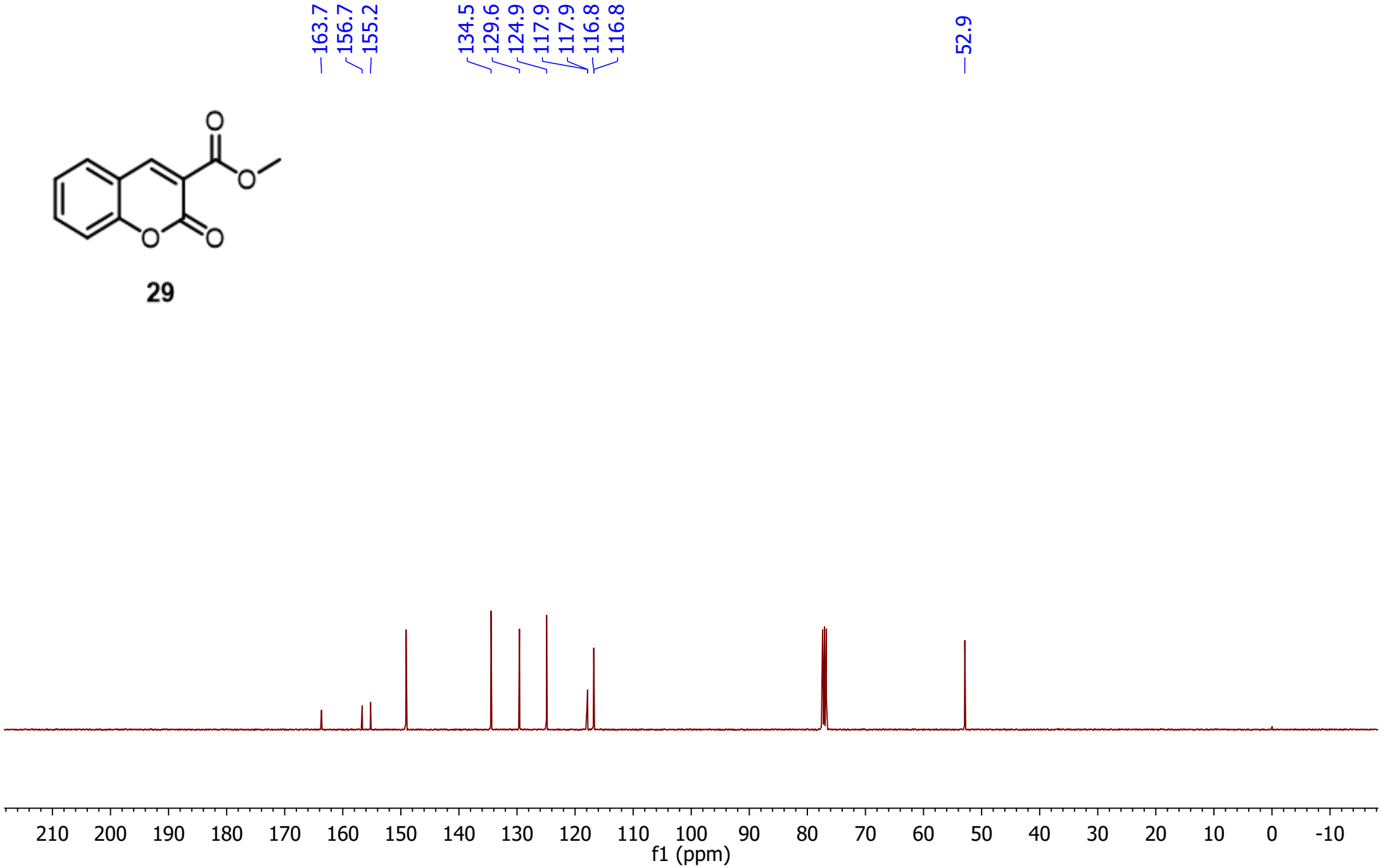
1H (CDCl3, 400 MHz)

29



^{1}H NMR Spectrum of **29**

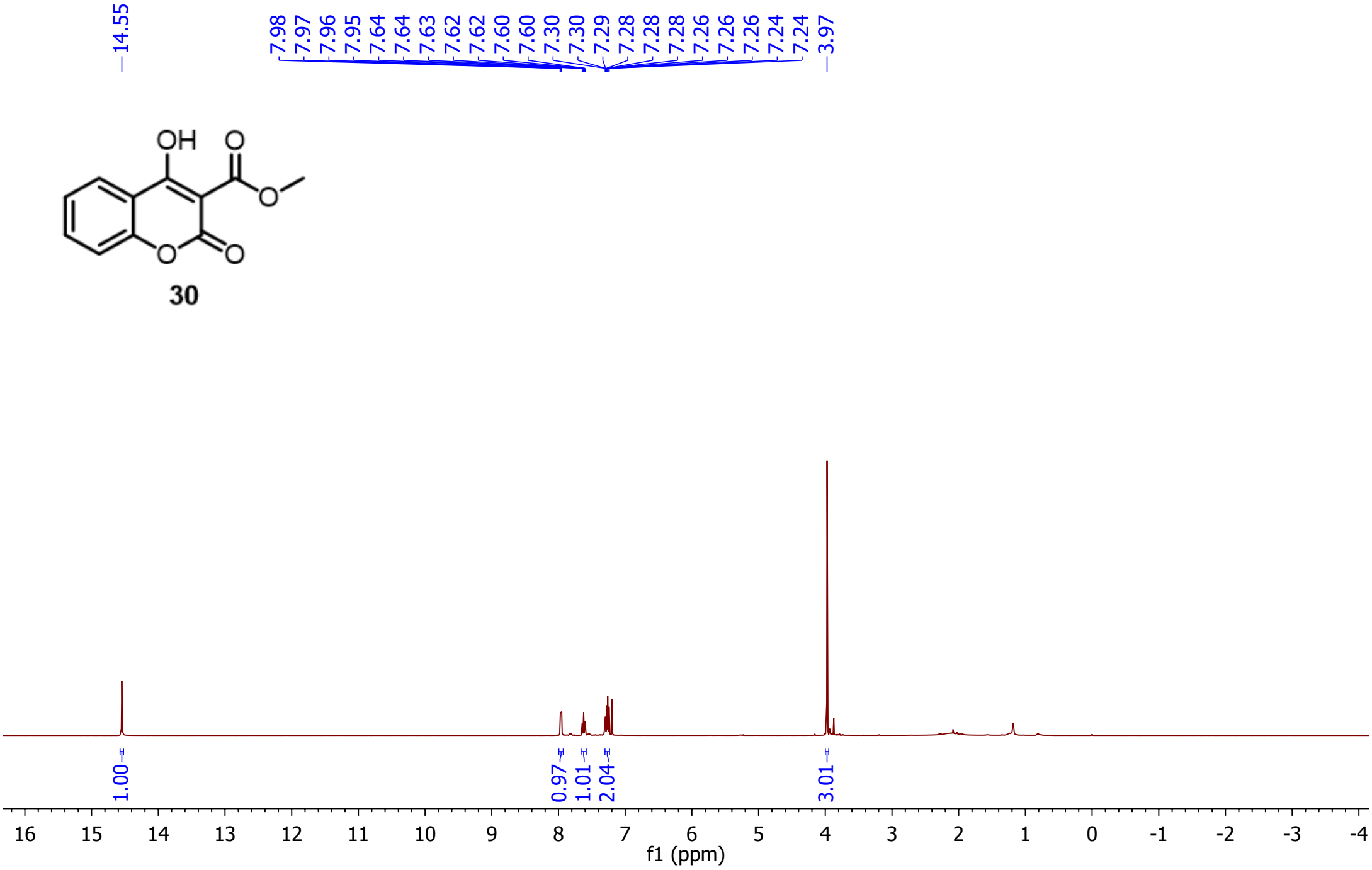
13C (CDCl3, 101 MHz)



29

^{13}C NMR Spectrum of **29**

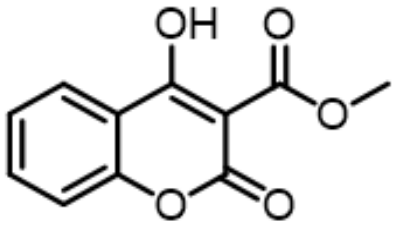
1H (CDCl3, 400 MHz)



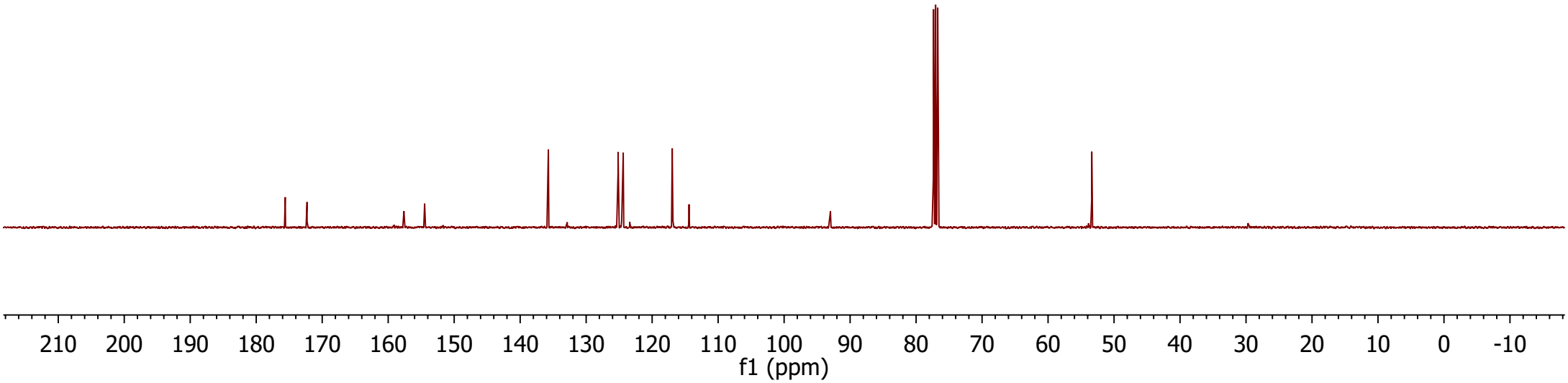
^{1}H NMR Spectrum of **30**

13C (CDCl3, 101 MHz)

175.6
172.3
157.6
154.5
135.7
125.2
124.4
117.0
114.4
93.0
53.4

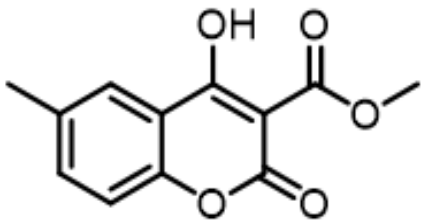


30



^{13}C NMR Spectrum of **30**

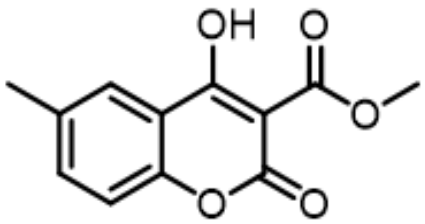
1H (CDCl3, 400 MHz)



31

^{1}H NMR Spectrum of **31**

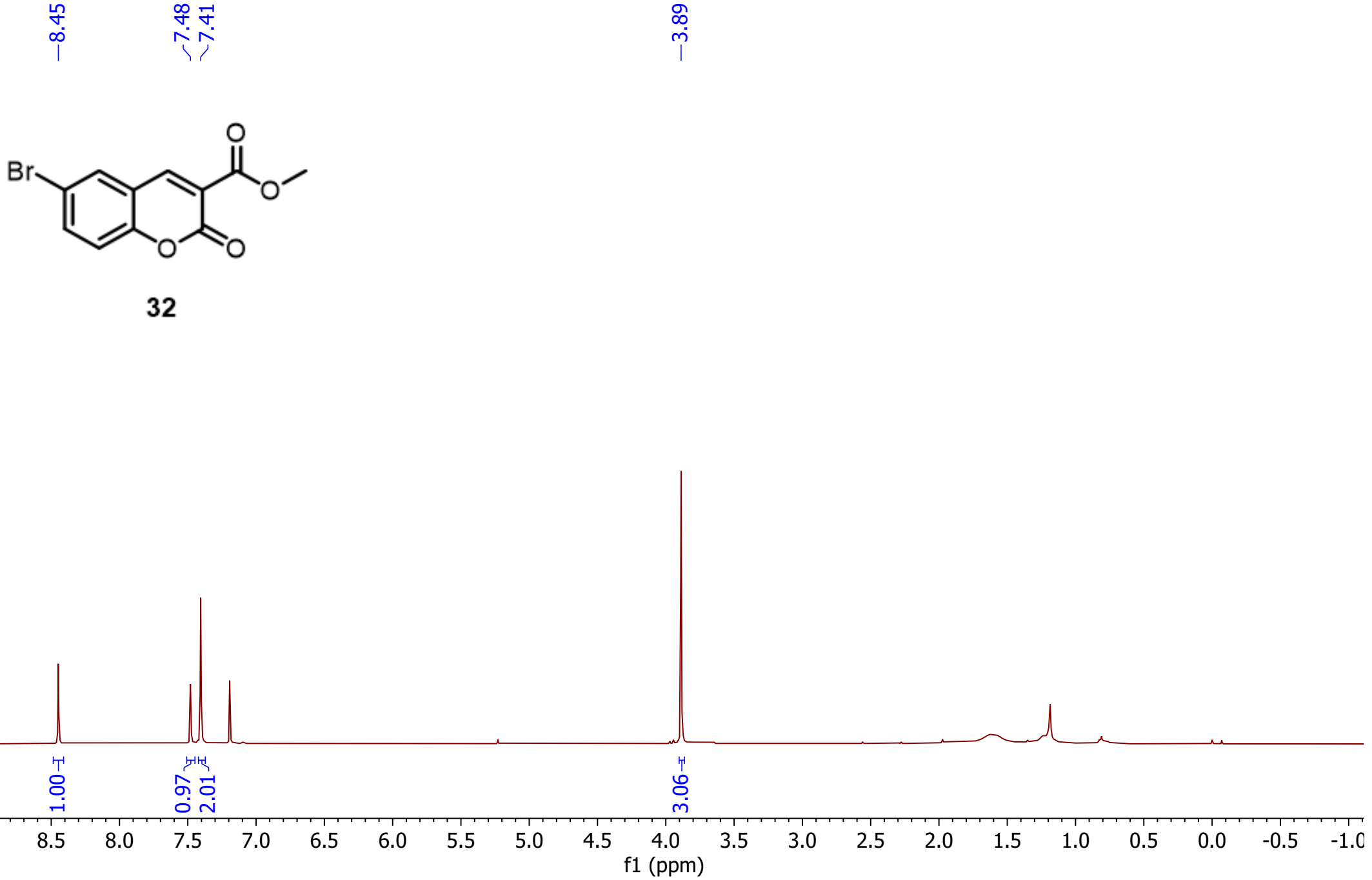
13C (CDCl3, 101 MHz)



31

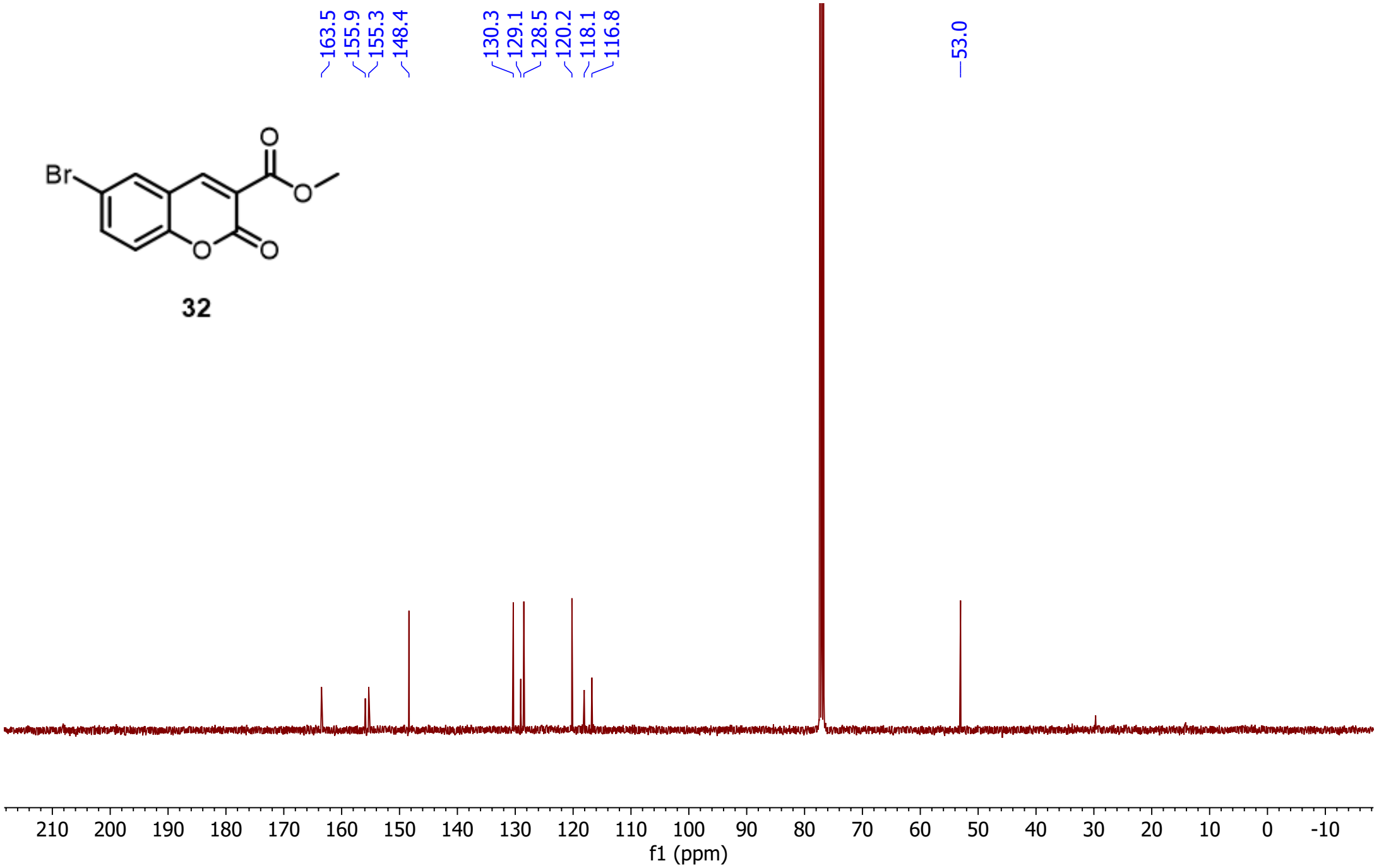
^{13}C NMR Spectrum of **31**

1H (CDCl3, 400 MHz)



^{1}H NMR Spectrum of **32**

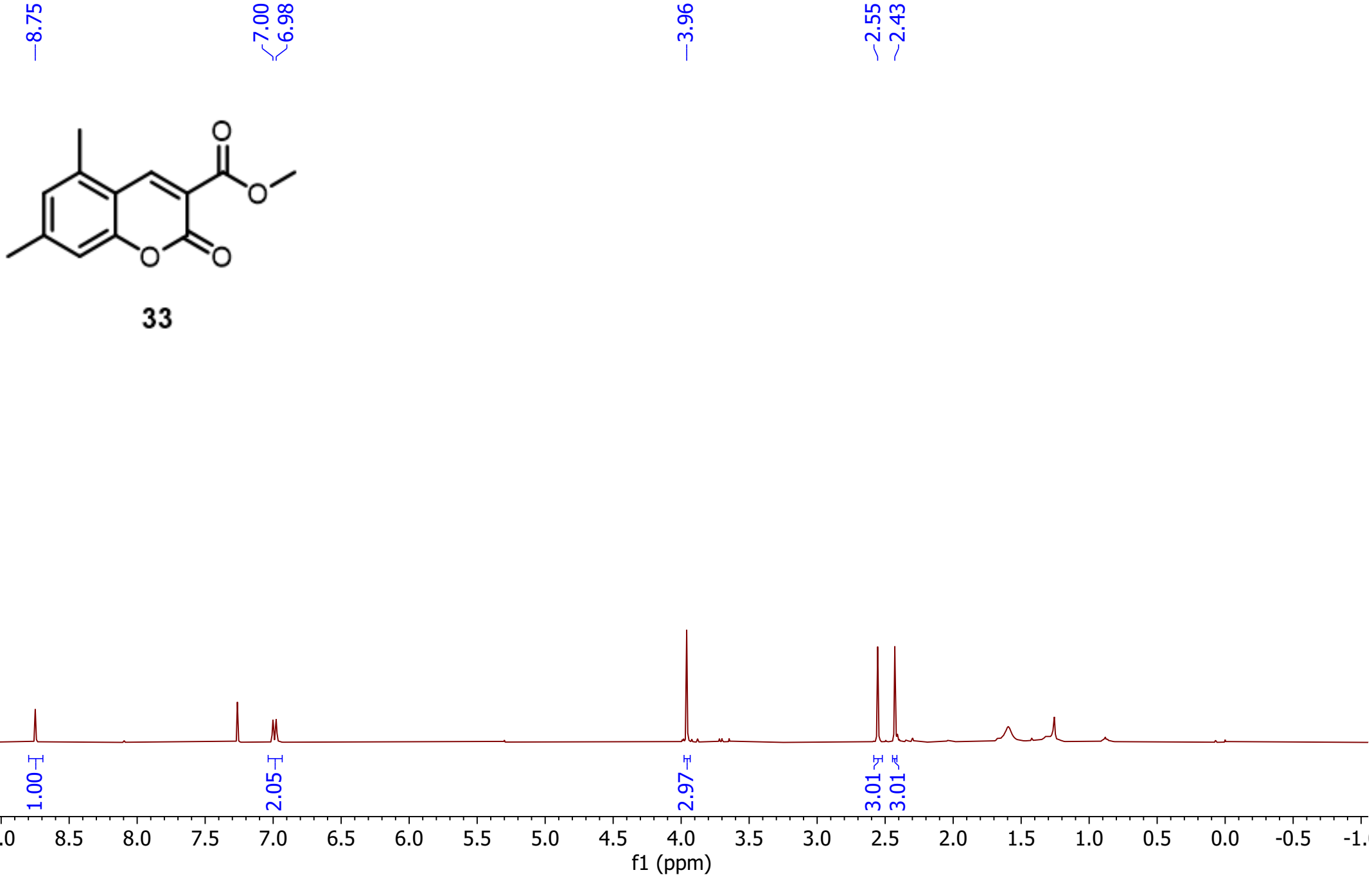
13C (CDCl3, 101 MHz)



32

^{13}C NMR Spectrum of **32**

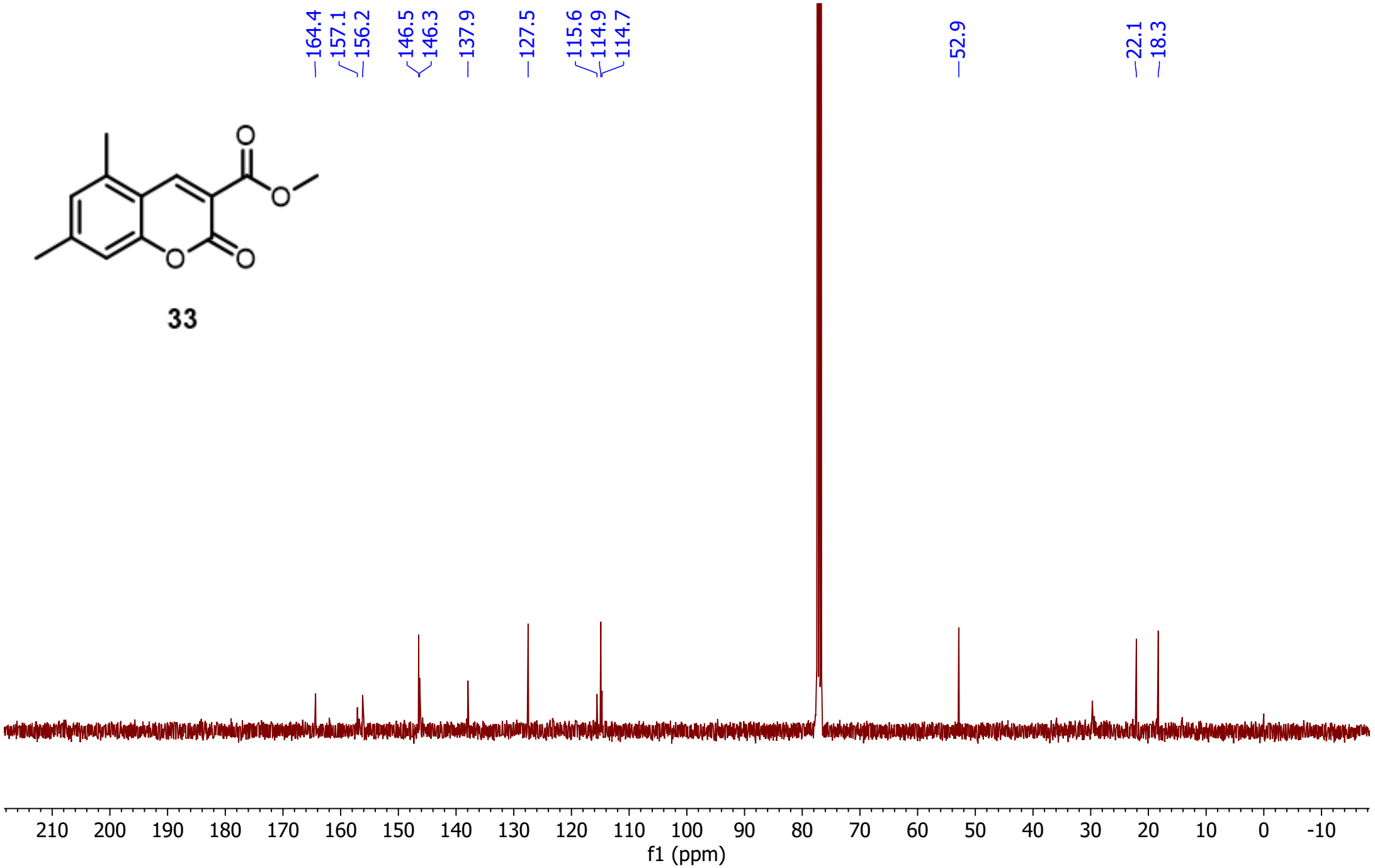
1H (CDCl3, 400 MHz)



33

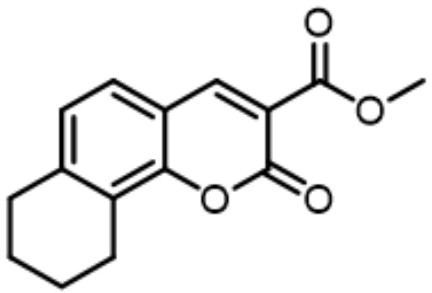
^{1}H NMR Spectrum of **33**

13C (CDCl3, 101 MHz)



^{13}C NMR Spectrum of **33**

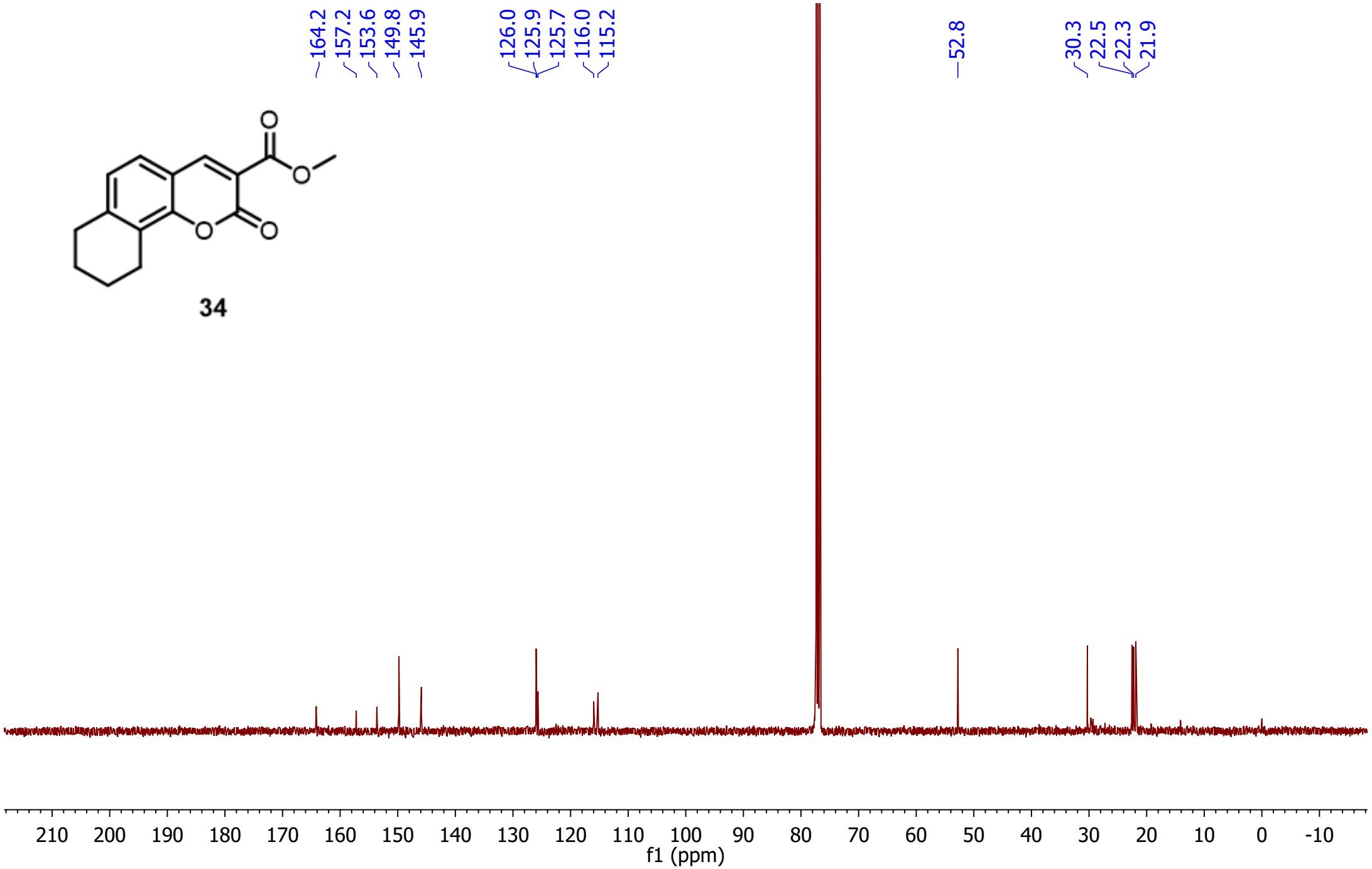
1H (CDCl3, 400 MHz)



34

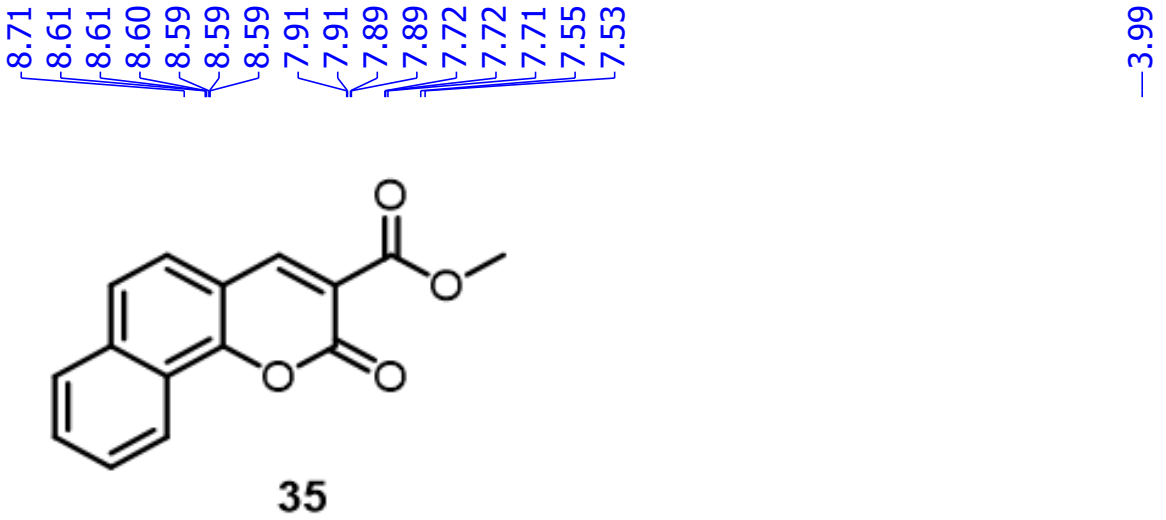
^{1}H NMR Spectrum of **34**

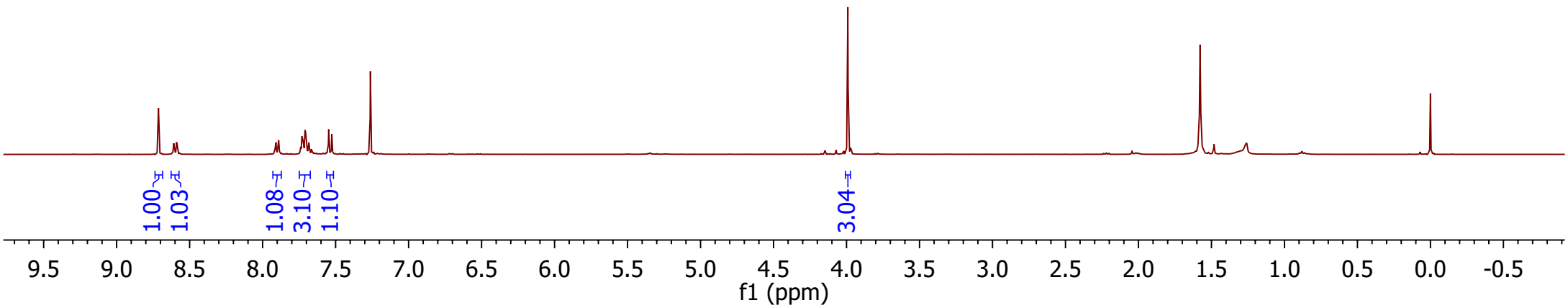
13C (CDCl3, 101 MHz)



^{13}C NMR Spectrum of **34**

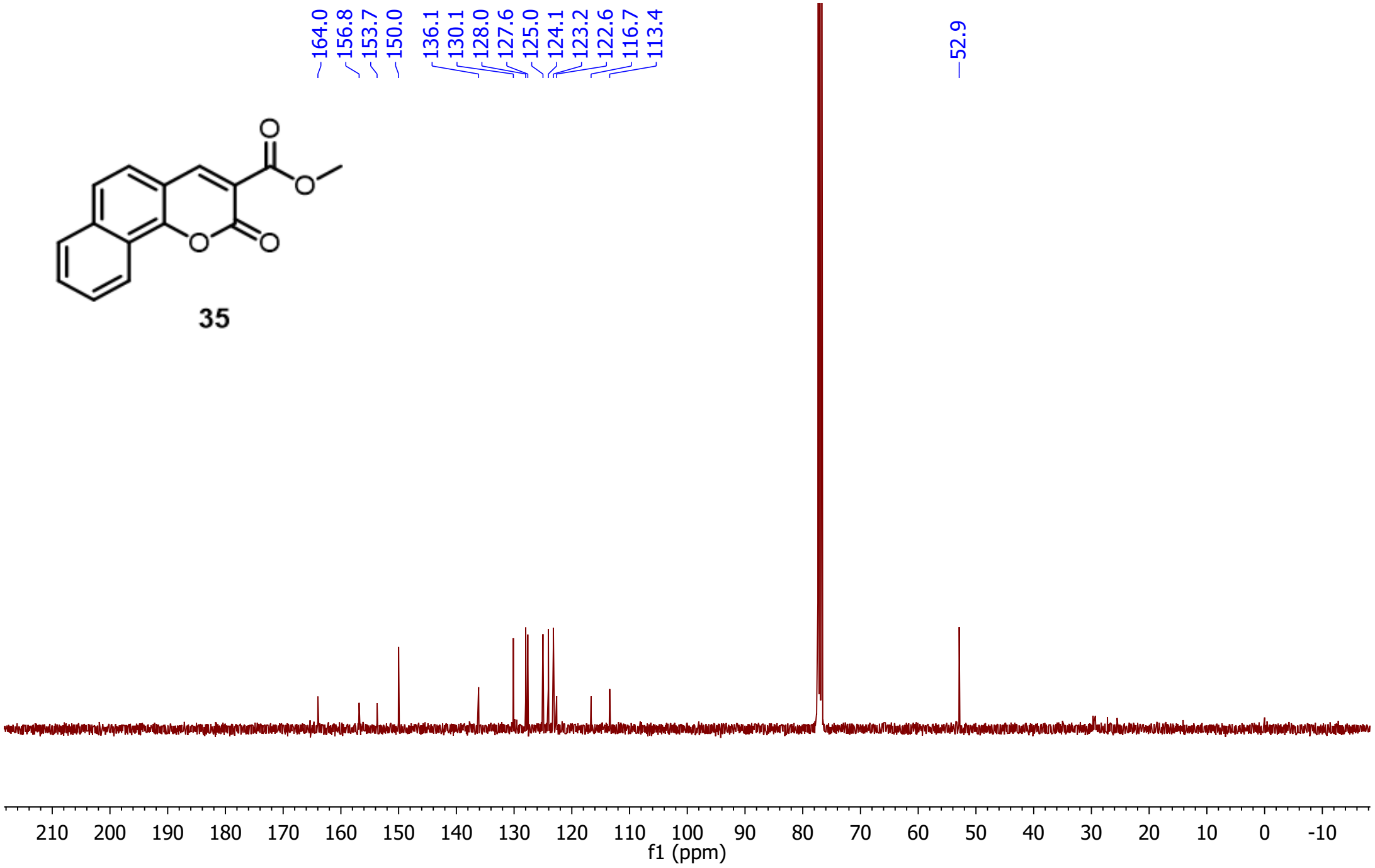
1H (CDCl3, 400 MHz)





^{1}H NMR Spectrum of **35**

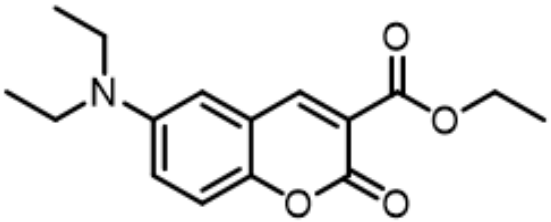
13C (CDCl3, 101 MHz)



35

^{13}C NMR Spectrum of **35**

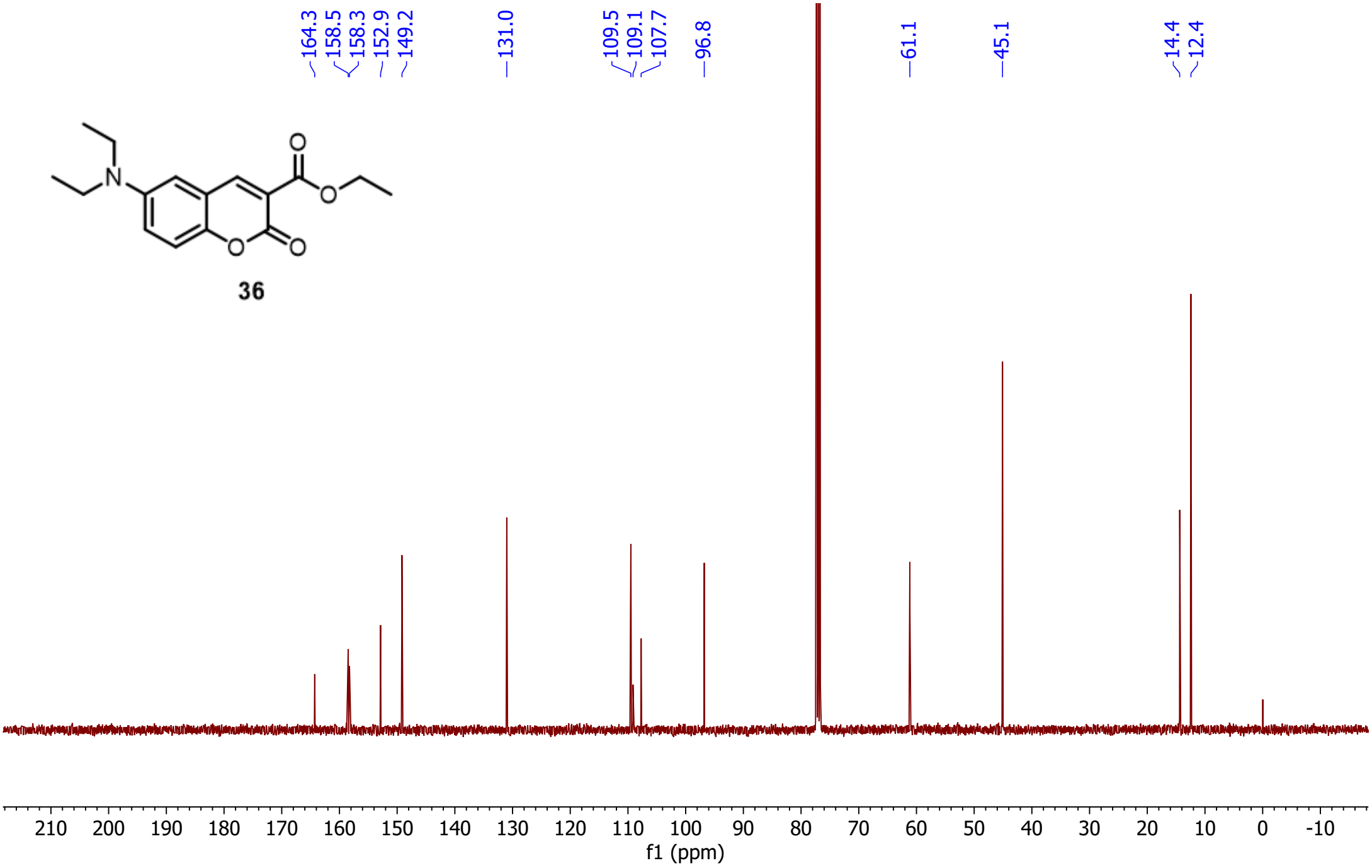
1H (CDCl3, 400 MHz)



36

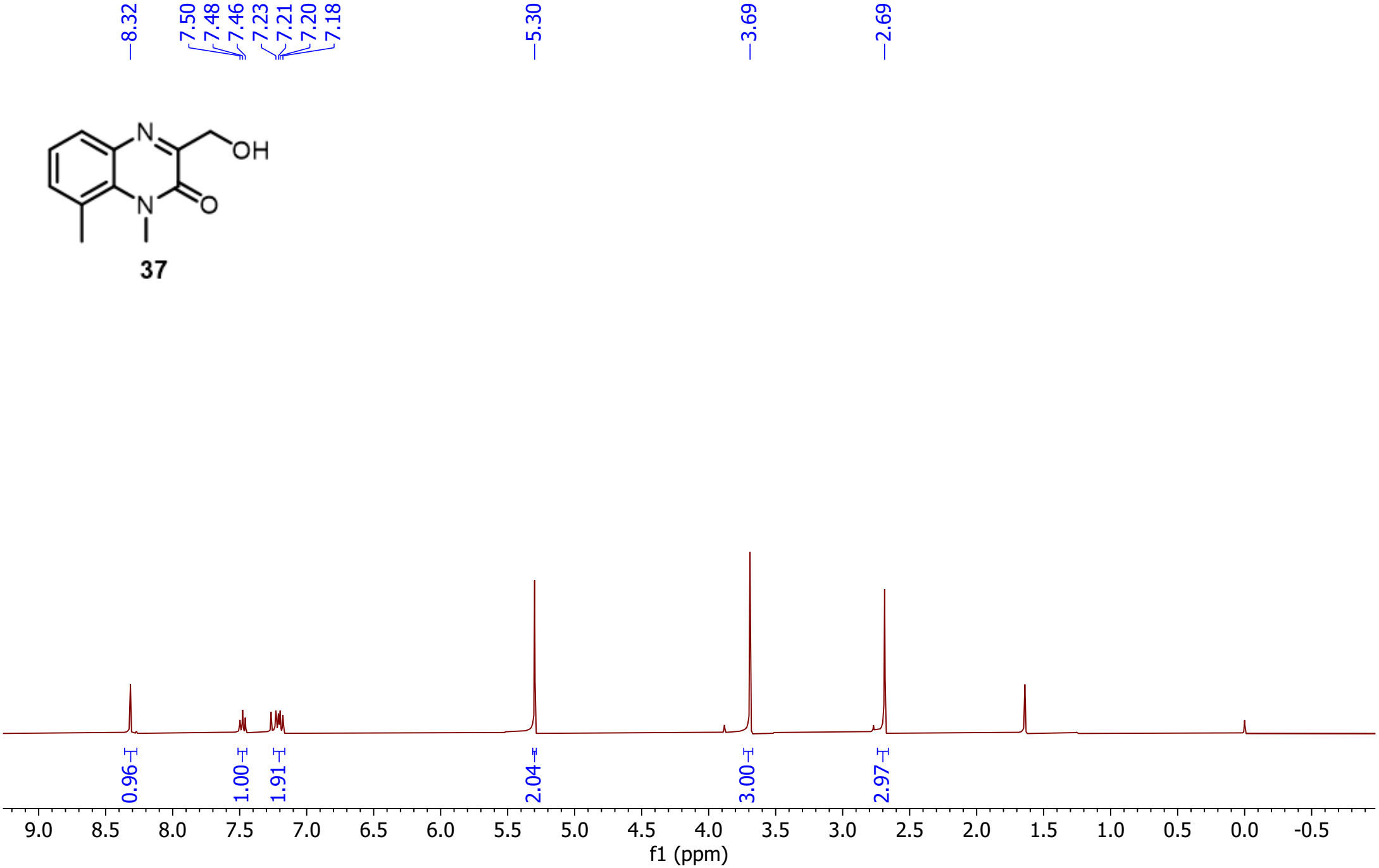
^{1}H NMR Spectrum of **36**

13C (CDCl3, 101 MHz)



^{13}C NMR Spectrum of **36**

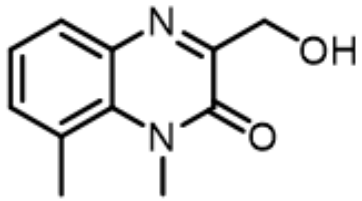
1H (CDCl3, 400 MHz)



37

^{1}H NMR Spectrum of **37**

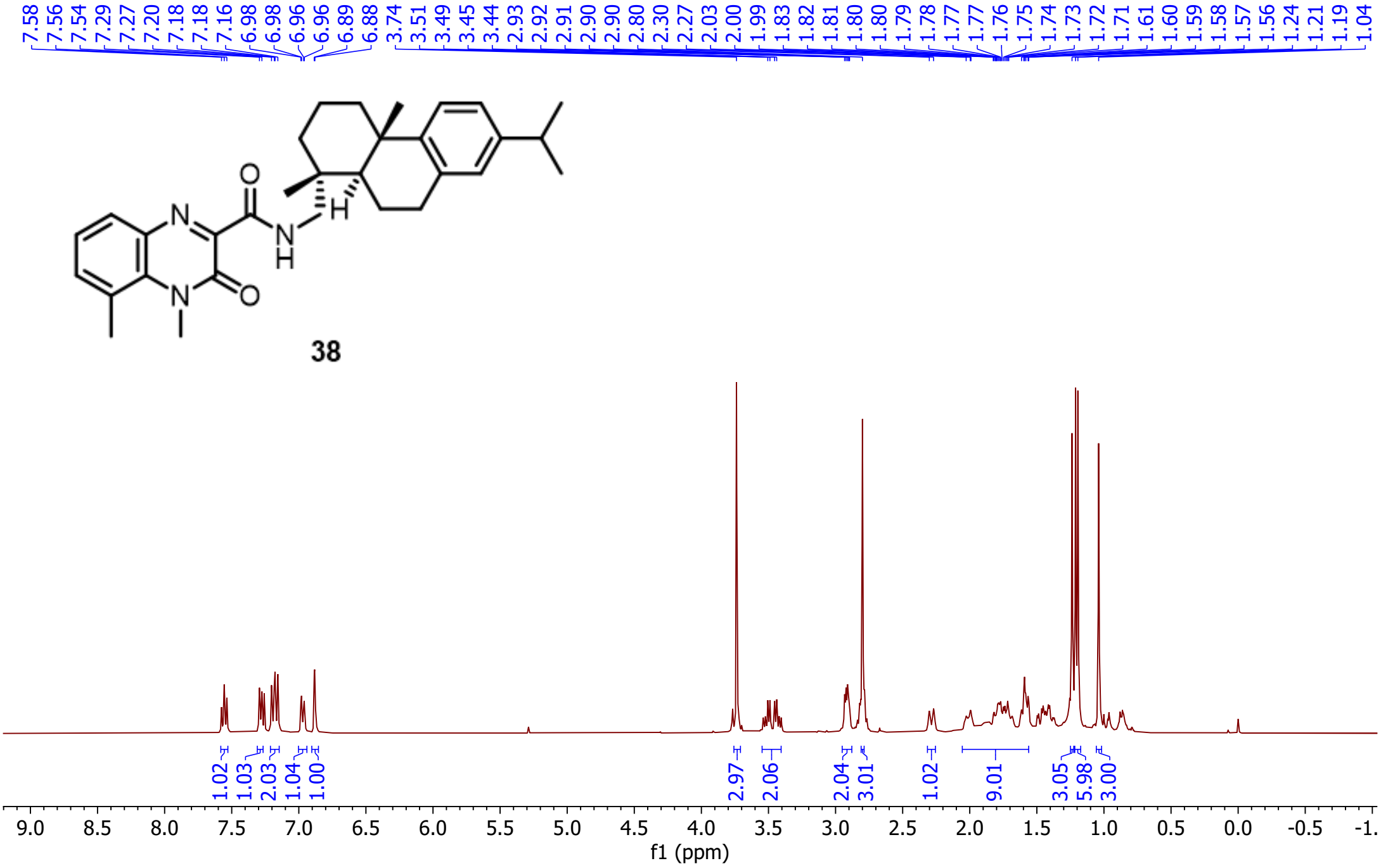
13C (CDCl3, 101 MHz)



37

^{13}C NMR Spectrum of **37**

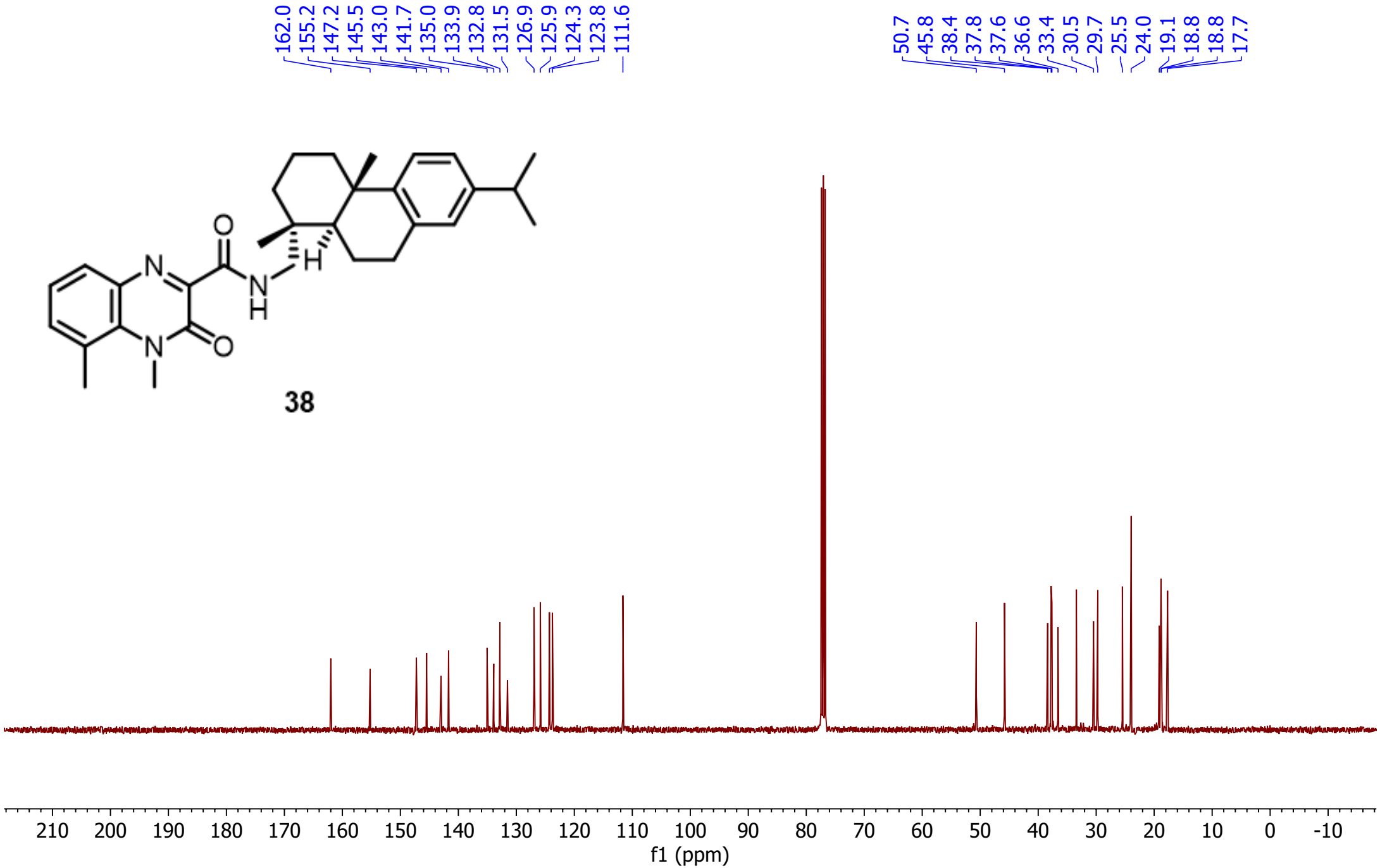
1H (CDCl3, 400 MHz)



38

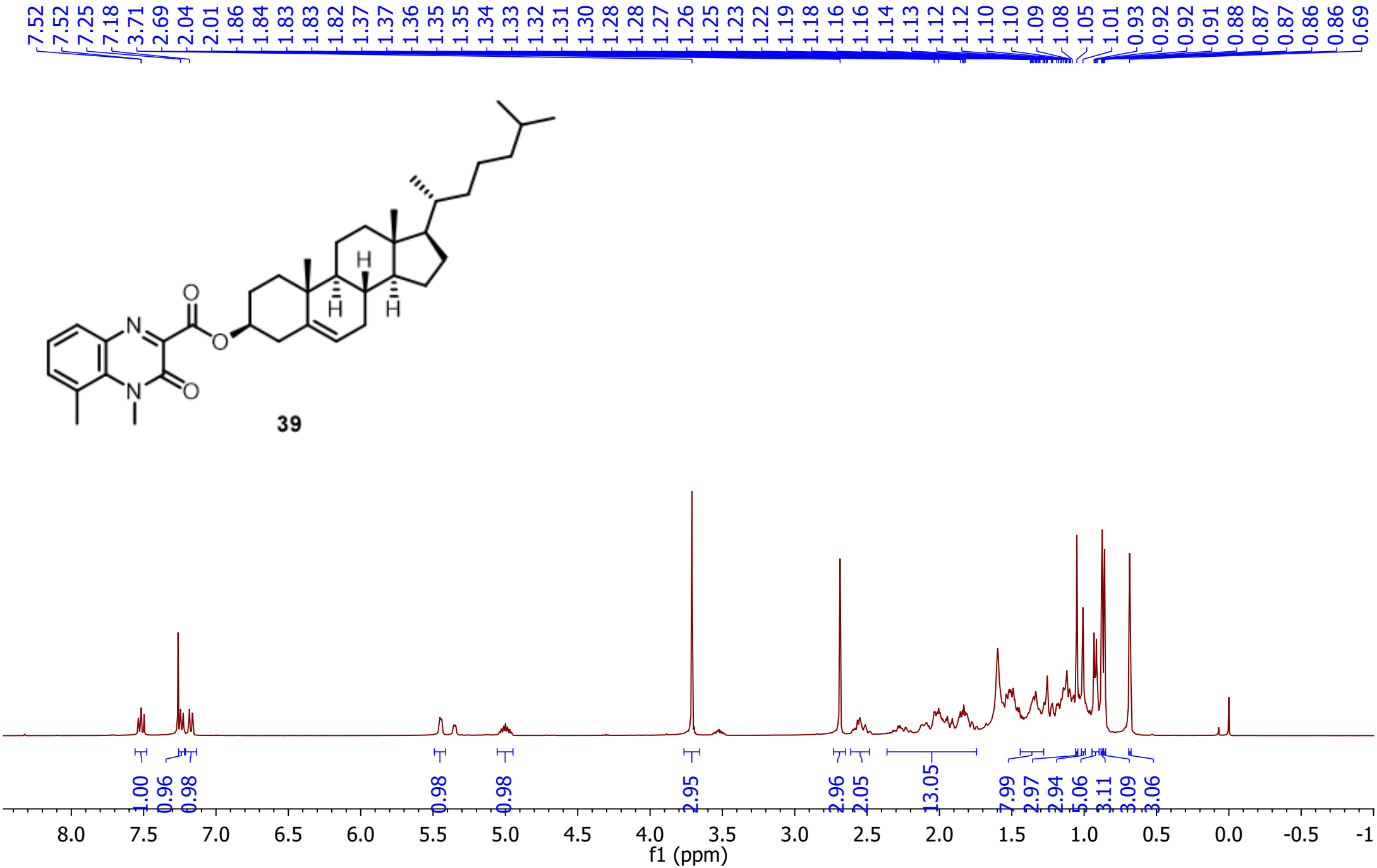
^{1}H NMR Spectrum of **38**

13C (CDCl3, 101 MHz)



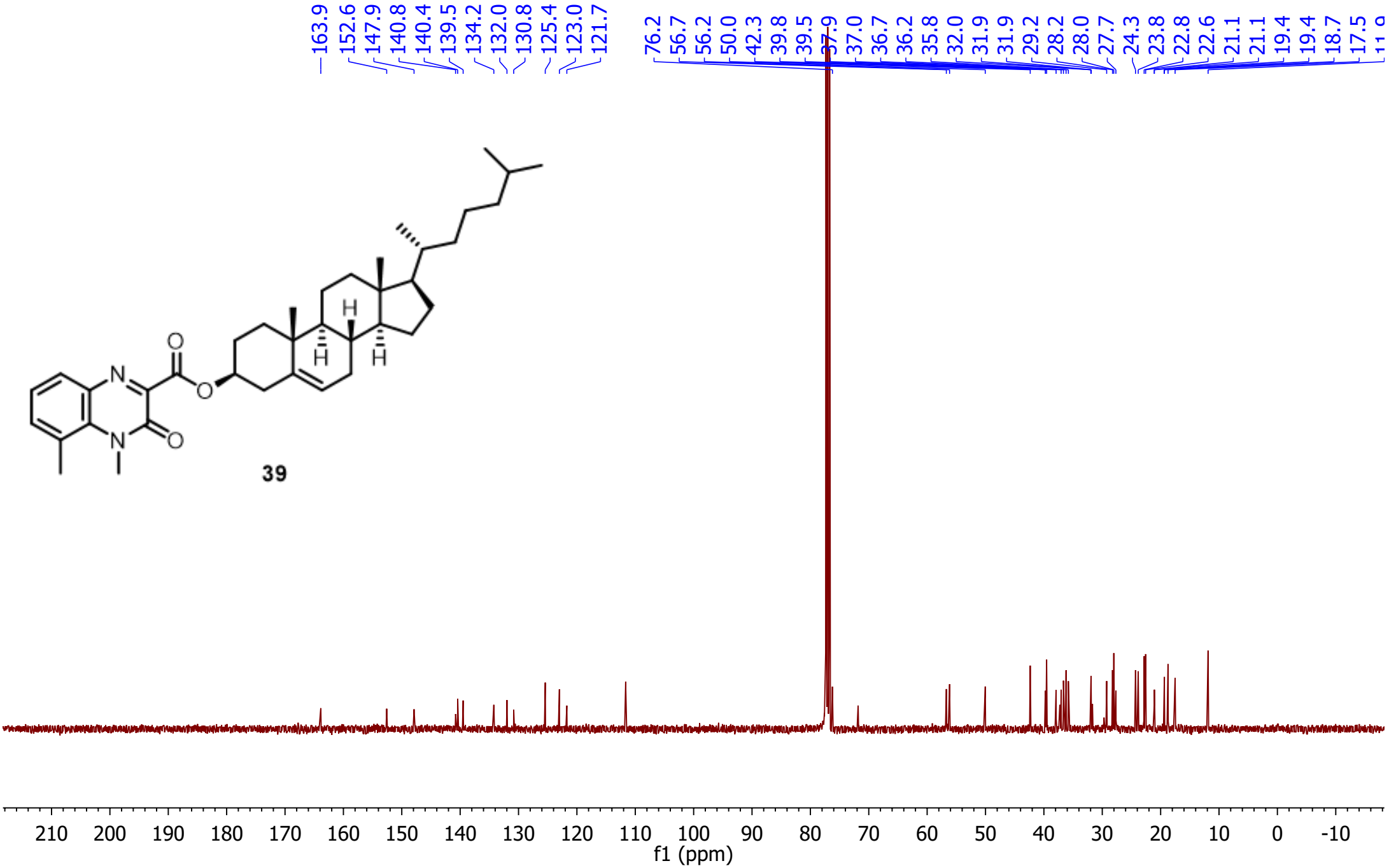
^{13}C NMR Spectrum of **38**

1H (CDCl3, 400 MHz)



^{1}H NMR Spectrum of **39**

13C (CDCl3, 101 MHz)



^{13}C NMR Spectrum of **39**