SUPPORTING INFORMATION

EDA Mediated S-N Bond Coupling of Nitroarenes and Sodium Sulfinate salts

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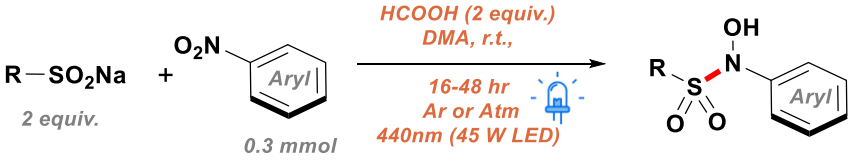
1. General experimental procedures:

Solvents and reagents were purchased from Sigma-Aldrich and Fisher scientific chemical companies and were used without further purification unless otherwise specified. 1H and 13C NMR were recorded on Bruker 500 MHz spectrometers, which uses the deuterium lock signal to reference the spectra. The solvent residual peaks, e.g., of chloroform (CDCl3: δ 7.26 ppm and δ 77.23 ppm), were used as references. Data are reported as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, dd = doublet of doublet, etc), coupling constant (J/Hz) and integration. All NMR spectra were recorded at room temperature. High-resolution mass spectrometry was conducted by using atmospheric pressure chemical ionization (APCI) or electro-spraying ionization (ESI) performed by McGill University on a Thermo-Scientific Exactive Orbitrap. Protonated/deprotonated molecular ions (M±H)+ or sodium adducts (M+Na)+ were used for empirical formula confirmation. All reactions are stirred magnetically unless otherwise specified. Short packed column chromatography was performed with E. Merck silica gel 60 (230–400 mesh) or SORBENT silica gel 30-60 μm. Flash column chromatography was performed with IsoleraTM Prime advanced automatic flash purification system. Analytical thin layer chromatography (TLC) was performed using Merck silica gel 60 F254 pre-coated plates (0.25 mm). The reactions were conducted in 10x75 fischer culture-tubes and were irradiated utilizing Kessil PR160L 390(54W), 427nm, 440nm (45W) LED lamps. The reactions were conducted in sealed tubes. All the reactions were conducted under inert atmosphere unless otherwise noted.

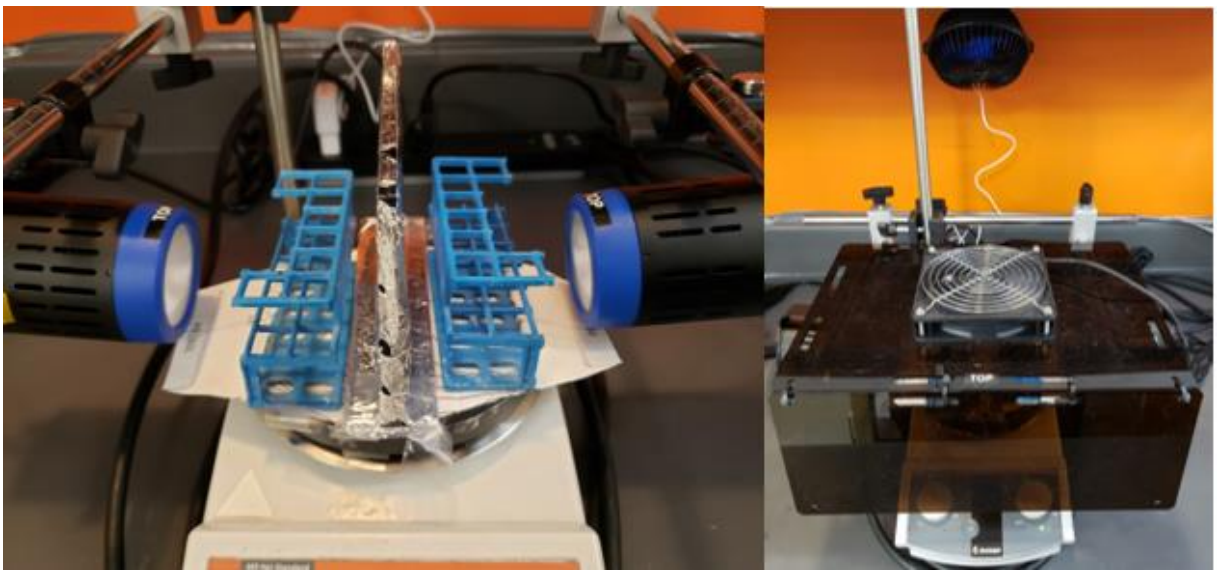
2. General procedure for the synthesis of *N*-hydroxylsulfonamides



The aromatic substrate (0.3 mmol), the corresponding sulfinate sodium salt (0.6 mmol), and formic acid (0.6 mmol) were added into 1.5 mL of DMA in a glass culture tube capped with a rubber septum. Three freeze-pump-thaw cycles were carefully performed before setting the reaction under light irradiation at 20°C-25°C using a 40 W LED Kessil lamp (440 nm) equipped with a fan. After the reaction was finished (16-48 h), usually evidenced by the loss of yellow coloration in the solution over time, DMA was removed by mildly heating the mixture (30°C-40°C) under a constant stream of air. The remaining mixture of solids was then dissolved in acetone and sonicated, before proceeding to filter the remaining sulfinate salts through a small celite plug. This solution was then evaporated under reduced pressure and the product purified through column chromatography or preparative TLC.

While most aromatic substrates were commercially available, the triflate derivative featured in 3q was obtained from the corresponding phenol according to Jiang et al.[1] Starting

materials for 3w and 3x were obtained from the corresponding carboxylic acids according to et al. Lastly, starting materials for 3y and 3z were obtained from the corresponding acyl chlorides according to Najer, et al.[2] and Wang, et al.[3], correspondingly



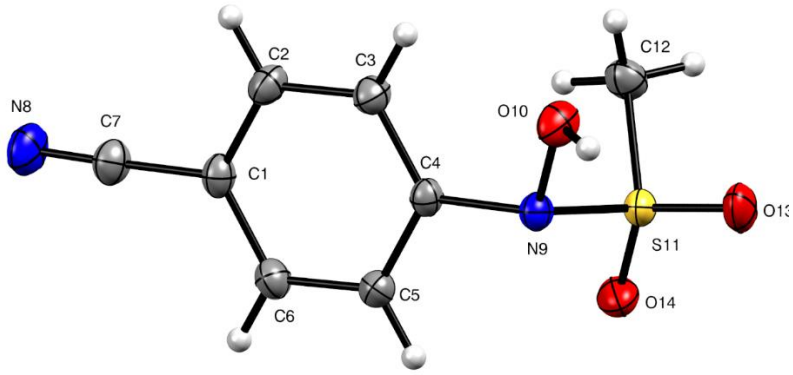
Left: close-up of the Kessil lamp setup, allowing for multiple reactions at the same time, all absorbing around 200000 mW/cm^2. Right: Covered setup and the two auxiliary fans to keep the temperature below 25°C.

3. Single-crystal X-Ray Diffraction of 3f

Product was recrystallized from methanol over the course of 3 days at 4°C to yield colorless needles. A Bruker D8 Advance powder X-ray diffractometer was used for the structure refinement and collection of the following crystal data:

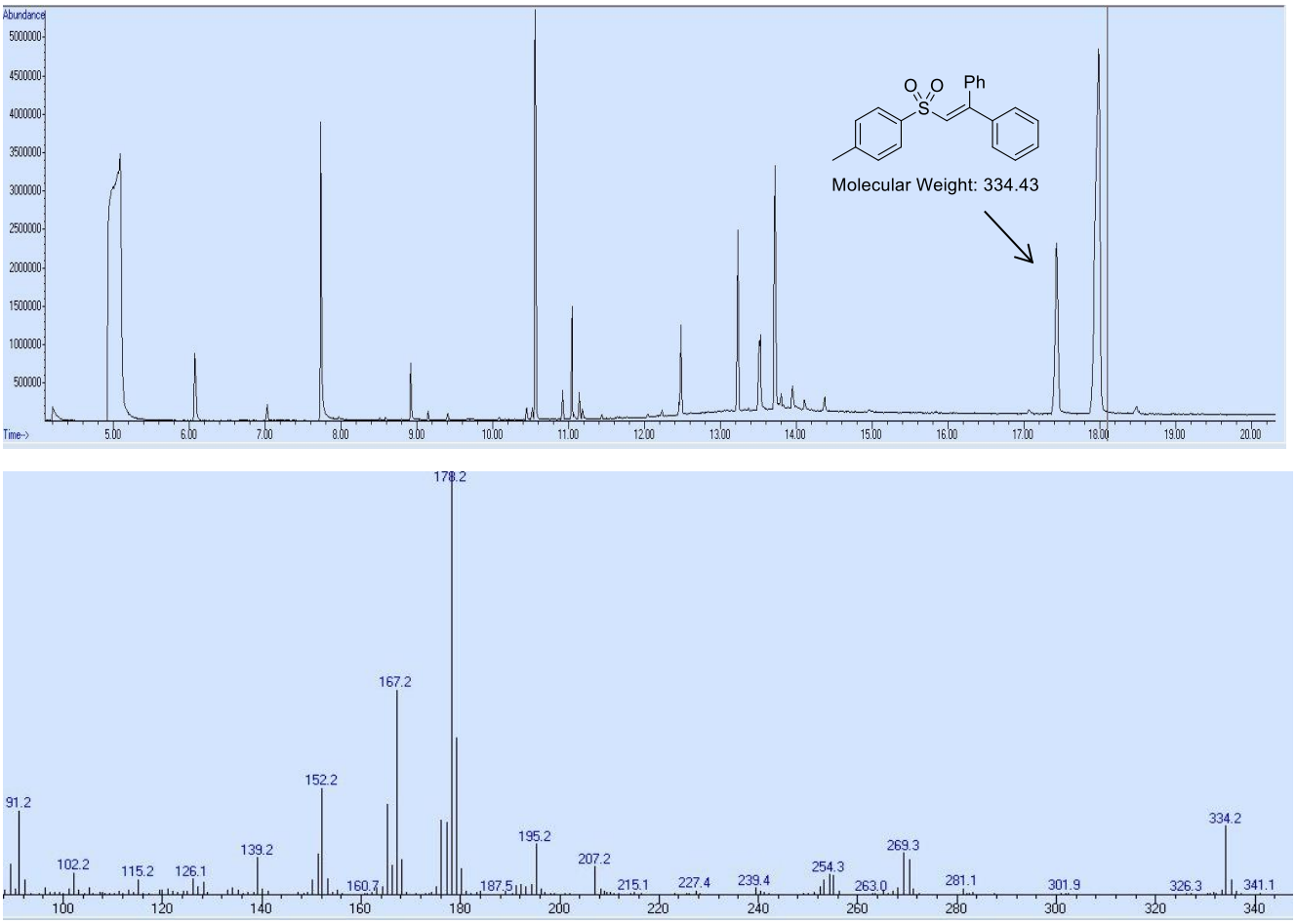
Empirical formula: $C_8H_8N_2O_3S$	Crystal size/mm3 0.353 × 0.272 × 0.203
Formula weight: 212.22	Radiation CuKα (λ = 1.54178)
Temperature/K: 298(2)	2Θ range for data collection/° 11.764 to 144.608
Crystal system: monoclinic	Index ranges -10 ≤ h ≤ 10, -4 ≤ k ≤ 6, -25 ≤ l ≤ 13264
Space group: $P2_1/n$	Reflections collected: 13264
a/Å: 8.2861(15)	Independent reflections: 1809 [R_{int} = 0.0341, R_{sigma} = 0.0228]
b/Å: 5.4731(10)	Data/restraints/parameters: 1809/0/130
c/Å: 20.821(4)	
α/°: 90, β/°: 93.606(5), γ/°: 90	

Volume/Å^3: 942.4(3) Z: 4 ρcalcg/cm^3: 1.496 μ/mm^{-1}: 2.951 F(000): 440.0	Goodness-of-fit on F2: 1.088 Final R indexes [I>=2σ (I)] R_1 = 0.0338, wR_2 = 0.0920 Final R indexes [all data] R_1 = 0.0342, wR_2 = 0.0925 Largest diff. peak/hole / e Å-3 0.20/-0.26

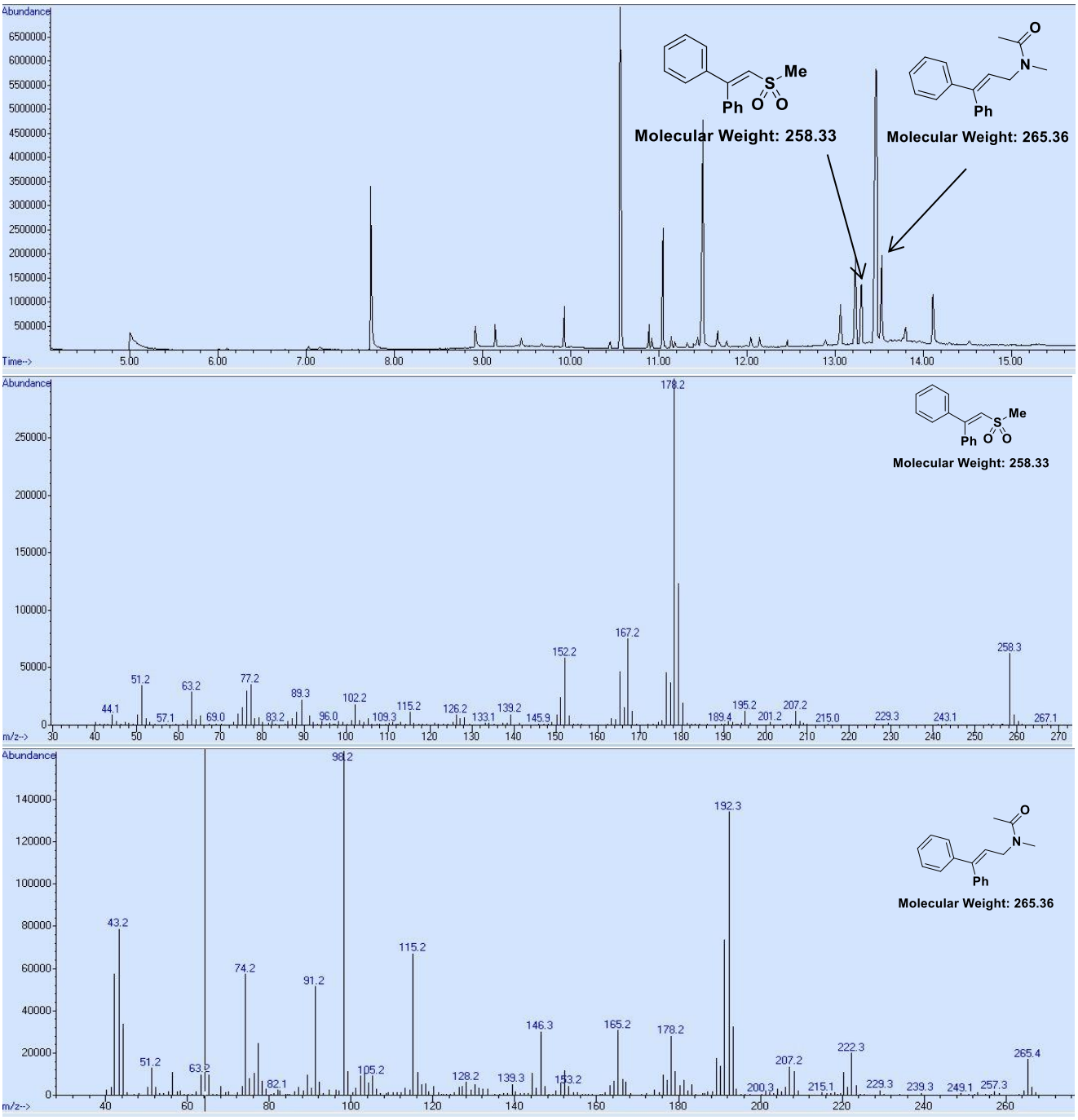


4. Mechanistic evidence

GC/MS Data:



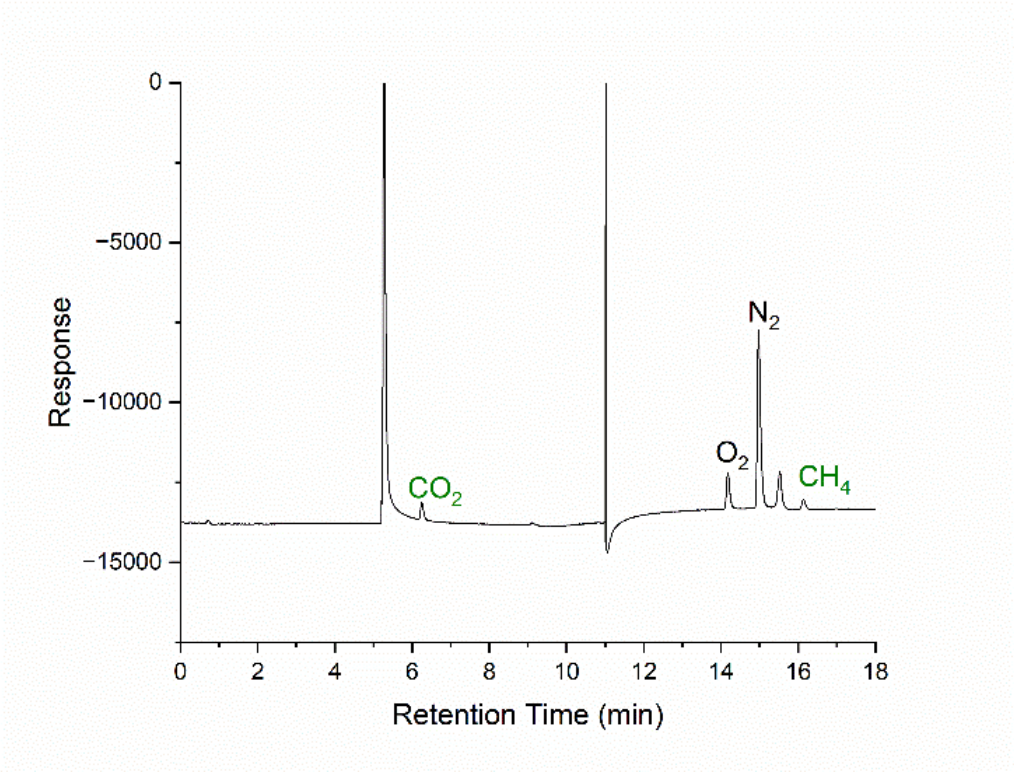
Top: Reaction chromatogram for Sodium Toluene sulfinate. Bottom: Mass Spectrum of radical addition product.



Top: Reaction chromatogram for Sodium Methane sulfinate. Middle: Mass Spectrum of radical addition product. Bottom: Radical adduct of solvent

GC/TCD Data

The headspace gas of a standard 0.1 mmol sulfonamidation reaction of para-chloronitrobenzene left to react for 16 hours was syringed out and directly inserted into GC/TCD. Raw data was imported and plotted in OriginPro 2022. Analysis and identification of response peaks was conducted by cross referencing standard values generously provided by the McGill Electrocatalysis Laboratory.



Left: plot of the GC/TCD trace obtained from headspace of standard optimized conditions.

5. Computational details:

All calculations were carried out with the Gaussian 16 suite of programs, at the ωB97XD/cc-pVTZ level of theory. Natural Population Analysis was carried out with the NBO3.1 program[4] as provided with the previously mentioned suite. In every calculation the Polarizable Continuum Model (PCM) solvation model was used (solvent = N,N-dimethylacetamide, DMA). Atomic populations were added within each molecular fragment in the ground and the excited state, the difference was then ascribed to the electron transfer from donor to acceptor in the complex.

Calculated excited states, orbital compositions, and oscillator strengths for each excited state

Conformation a (Excited State 8 was selected for population analysis on the basis of their oscillator strength value

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.1085 eV 398.86 nm f=0.0043 <S**2>=0.000
56 -> 59 -0.11230
58 -> 59 0.69339

This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1187.56377917
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.0827 eV 303.68 nm f=0.0016 <S**2>=0.000
52 -> 59 0.46689
52 -> 64 -0.20488
53 -> 59 0.19693
54 -> 59 0.40414
54 -> 64 -0.16261

Excited State 3: Singlet-A 4.3941 eV 282.16 nm f=0.0003 <S**2>=0.000
58 -> 60 0.69206

Excited State 4: Singlet-A 4.4991 eV 275.58 nm f=0.0003 <S**2>=0.000
50 -> 59 -0.20303
55 -> 59 0.16711
57 -> 59 0.64190

Excited State 5: Singlet-A 4.5336 eV 273.48 nm f=0.0003 <S**2>=0.000
50 -> 59 0.60829
50 -> 64 -0.24155
57 -> 59 0.21998

Excited State 6: Singlet-A 4.6880 eV 264.47 nm f=0.0105 <S**2>=0.000
58 -> 61 0.60595
58 -> 63 -0.15637
58 -> 65 0.26306

Excited State 7: Singlet-A 5.0906 eV 243.55 nm f=0.0075 <S**2>=0.000
55 -> 59 -0.20055
56 -> 59 0.63336
58 -> 59 0.12014
58 -> 64 0.13052

Excited State 8: Singlet-A 5.2345 eV 236.86 nm f=0.0163 <S**2>=0.000
52 -> 60 0.17162
53 -> 59 0.47226
53 -> 60 -0.11771
54 -> 59 -0.27658
54 -> 60 -0.22006
55 -> 59 0.20496
56 -> 59 0.15029

Excited State 9: Singlet-A 5.4323 eV 228.23 nm f=0.0066 <S**2>=0.000
56 -> 59 -0.15438

58 -> 62 -0.39454
58 -> 64 0.52624
58 -> 67 -0.10463

Excited State 10: Singlet-A 5.4967 eV 225.56 nm f=0.0233 <S**2>=0.000
55 -> 59 -0.13197
58 -> 62 0.50918
58 -> 64 0.37038
58 -> 67 0.16466

Conformation b (Excited State 8 was selected for population analysis on the basis of their oscillator strength value
Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.6303 eV 471.36 nm f=0.0003 <S**2>=0.000
56 -> 59 0.11266
58 -> 59 0.69248
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1187.59043662
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.9568 eV 313.35 nm f=0.0079 <S**2>=0.000
52 -> 59 0.22245
53 -> 59 -0.11992
55 -> 59 0.18379
57 -> 59 0.61522

Excited State 3: Singlet-A 4.1007 eV 302.35 nm f=0.0098 <S**2>=0.000
52 -> 59 0.53961
52 -> 64 -0.14248
53 -> 59 -0.29958
57 -> 59 -0.27927

Excited State 4: Singlet-A 4.5770 eV 270.88 nm f=0.0135 <S**2>=0.000
54 -> 59 0.13142
55 -> 59 0.14761
56 -> 59 0.64786
58 -> 59 -0.11047

Excited State 5: Singlet-A 4.6818 eV 264.82 nm f=0.0137 <S**2>=0.000
50 -> 59 -0.27231
51 -> 59 -0.11995
53 -> 61 -0.14825
54 -> 59 0.58217
56 -> 59 -0.13787

Excited State 6: Singlet-A 4.8445 eV 255.93 nm f=0.0095 <S**2>=0.000
49 -> 59 0.13655
50 -> 59 0.50653
50 -> 64 -0.11925
51 -> 59 0.22032
53 -> 59 -0.14978
54 -> 59 0.30365
55 -> 59 -0.11110

Excited State 7: Singlet-A 4.8683 eV 254.68 nm f=0.0056 <S**2>=0.000
58 -> 60 0.60254
58 -> 65 0.29493
58 -> 69 -0.10844

Excited State 8: Singlet-A 5.0567 eV 245.19 nm f=0.0908 <S**2>=0.000
52 -> 59 -0.23208
53 -> 59 -0.34996
55 -> 59 0.48903
56 -> 59 -0.12687
57 -> 59 -0.11227
58 -> 61 0.15774

Excited State 9: Singlet-A 5.1004 eV 243.09 nm f=0.0097 <S**2>=0.000
53 -> 59 0.13908
58 -> 61 0.66662

Excited State 10: Singlet-A 5.1662 eV 239.99 nm f=0.0758 <S**2>=0.000
50 -> 59 0.18929
52 -> 59 0.19564
53 -> 59 0.45269
55 -> 59 0.41367

Conformation c (Excited State 10 was selected for population analysis on the basis of their oscillator strength value)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.6306 eV 471.31 nm f=0.0003 <S**2>=0.000
56 -> 59 0.11267
58 -> 59 0.69248
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1187.59042541
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.9569 eV 313.34 nm f=0.0079 <S**2>=0.000
52 -> 59 0.22294

53 -> 59 -0.12020
55 -> 59 0.18381
57 -> 59 0.61496

Excited State 3: Singlet-A 4.1006 eV 302.35 nm f=0.0098 <S**2>=0.000
52 -> 59 0.53937
52 -> 64 -0.14242
53 -> 59 -0.29951
57 -> 59 -0.27985

Excited State 4: Singlet-A 4.5772 eV 270.87 nm f=0.0135 <S**2>=0.000
54 -> 59 0.13168
55 -> 59 0.14759
56 -> 59 0.64779
58 -> 59 -0.11046

Excited State 5: Singlet-A 4.6819 eV 264.82 nm f=0.0137 <S**2>=0.000
50 -> 59 -0.27248
51 -> 59 -0.12009
53 -> 61 -0.14818
54 -> 59 0.58199
56 -> 59 -0.13813

Excited State 6: Singlet-A 4.8445 eV 255.93 nm f=0.0095 <S**2>=0.000
49 -> 59 0.13639
50 -> 59 0.50648
50 -> 64 -0.11924
51 -> 59 0.22038
53 -> 59 -0.14986
54 -> 59 0.30381
55 -> 59 -0.11079

Excited State 7: Singlet-A 4.8684 eV 254.67 nm f=0.0056 <S**2>=0.000
58 -> 60 0.60256
58 -> 65 0.29490
58 -> 69 -0.10843

Excited State 8: Singlet-A 5.0568 eV 245.18 nm f=0.0908 <S**2>=0.000
52 -> 59 -0.23216
53 -> 59 -0.34998
55 -> 59 0.48876
56 -> 59 -0.12673
57 -> 59 -0.11221
58 -> 61 0.15843

Excited State 9: Singlet-A 5.1004 eV 243.09 nm f=0.0097 <S**2>=0.000

53 -> 59 0.13938
58 -> 61 0.66647

Excited State 10: Singlet-A 5.1664 eV 239.98 nm f=0.0757 <S**2>=0.000
50 -> 59 0.18921
52 -> 59 0.19554
53 -> 59 0.45253
55 -> 59 0.41397
SavETr: write IOETrn= 770 NScale= 10 NData= 16 NLR=1 NState= 10 LETran= 190.

Trimolecular Conformation Methylsulfinate-Nitrophenyl-DMA (Excited State 10 was selected for population analysis on the basis of their oscillator strength value)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.4488 eV 359.50 nm f=0.0013 <S**2>=0.000
82 -> 83 0.69961
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1475.43672610
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.1123 eV 301.50 nm f=0.0035 <S**2>=0.000
74 -> 83 0.65670
74 -> 87 -0.10461
74 -> 88 0.15239
75 -> 83 -0.14598

Excited State 3: Singlet-A 4.3106 eV 287.62 nm f=0.0148 <S**2>=0.000
78 -> 83 0.57587
79 -> 83 0.18634
80 -> 83 -0.32541

Excited State 4: Singlet-A 4.6445 eV 266.95 nm f=0.0047 <S**2>=0.000
72 -> 83 -0.28721
76 -> 83 0.14707
78 -> 83 0.31867
80 -> 83 0.49076
81 -> 83 -0.16853

Excited State 5: Singlet-A 4.7633 eV 260.29 nm f=0.0134 <S**2>=0.000
72 -> 83 -0.25375
75 -> 84 0.17177
76 -> 83 0.55699
78 -> 83 -0.14055
80 -> 83 -0.20048

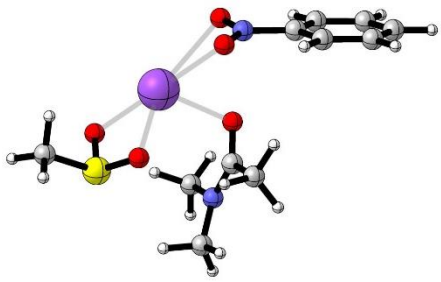
Excited State 6: Singlet-A 4.8108 eV 257.72 nm f=0.0039 <S**2>=0.000
72 -> 83 0.39816
76 -> 83 0.23546
80 -> 83 0.23939
81 -> 83 0.41680

Excited State 7: Singlet-A 4.8202 eV 257.22 nm f=0.0049 <S**2>=0.000
72 -> 83 -0.36359
76 -> 83 -0.24481
81 -> 83 0.51435

Excited State 8: Singlet-A 5.1059 eV 242.82 nm f=0.2322 <S**2>=0.000
74 -> 83 0.13477
75 -> 83 0.65576
76 -> 84 -0.10974
80 -> 83 -0.10129

Excited State 9: Singlet-A 5.3744 eV 230.70 nm f=0.0021 <S**2>=0.000
78 -> 83 -0.13040
79 -> 83 0.66304
80 -> 83 0.13546

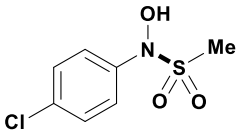
Excited State 10: Singlet-A 5.4653 eV 226.86 nm f=0.0418 <S**2>=0.000
82 -> 85 0.46068
82 -> 87 -0.19820
82 -> 89 -0.43936
82 -> 92 0.11025
SavETr: write IOETrn= 770 NScale= 10 NData= 16 NLR=1 NState= 10 LETran= 190.



Optimized structure of EDA with an explicit solvent (DMA) molecule as part of the ensemble.

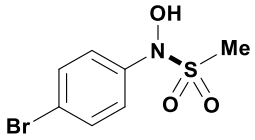
6. Characterization data of reported compounds:

3a



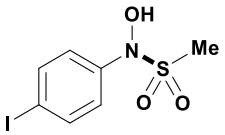
***N*-(4-chlorophenyl)-*N*-hydroxymethanesulfonamide (3a):** Off-white solid. Yield: 71 % (Gradient 20 % to 40 % EtOAc in hexanes). Spectra in agreement with the literature.[5] 1H NMR (500 MHz, acetone) δ 10.25 (s, 1H), 7.53 (d, J = 8.9 Hz, 2H), 7.44 (d, J = 8.9 Hz, 2H), 2.89 (s, 3H). 13C NMR (126 MHz, Acetone) δ 141.88, 131.81, 128.55, 123.85, 30.74.

3b



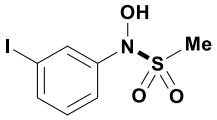
***N*-(4-bromophenyl)-*N*-hydroxymethanesulfonamide (3b):** Yellow solid. Yield: 75 % (Gradient 20 % to 40 % EtOAc in hexanes). 1H NMR (500 MHz, acetone) δ 10.26 (s, 1H), 7.61 – 7.58 (d, J = 8.86 Hz, 2H), 7.50 – 7.47 (d, J = 8.85 Hz, 2H), 2.91 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 142.36, 131.58, 124.15, 119.75, 30.81.

3c

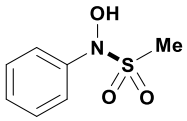


***N*-(4-iodophenyl)-*N*-hydroxymethanesulfonamide (3c):** Yellow solid. Yield: 47 % (Gradient 20 % to 40 % EtOAc in hexanes). ^{1}H NMR (500 MHz, acetone) δ 10.26 (s, 1H), 7.81 – 7.76 (d, J = 8.83 Hz, 2H), 7.37 – 7.33 (d, J = 8.86 Hz, 2H), 2.90 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 137.63, 124.27, 90.97, 30.81.

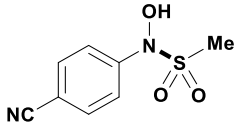
3d



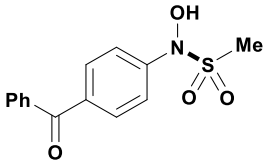
***N*-(3-iodophenyl)-*N*-hydroxymethanesulfonamide (3d):** Yellow solid. Yield: 68 % (Gradient 20 % to 40 % EtOAc in hexanes). ^{1}H NMR (500 MHz, acetone) δ 10.29 (s, 1H), 7.91 (t, *J* = 1.9 Hz, 1H), 7.68 (m, *J* = 7.9, 1.7, 1.0 Hz, 1H), 7.57 (m, *J* = 8.2, 2.1, 1.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 2.93 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 144.27, 135.72, 130.66, 130.39, 121.70, 92.98, 31.07.

3e 

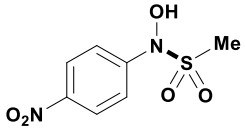
***N*-hydroxy-*N*-phenylmethanesulfonamide (3e):** White solid. Yield: 61% (Gradient 20 % to 40 % EtOAc in hexanes). Spectra in agreement with literature report.[5] ^{1}H NMR (500 MHz, acetone) δ 10.12 (s, 1H), 7.54 (d, *J* =8.4 Hz, 2H), 7.42 (t, *J* = 7.49 Hz, 2H), 7.33 – 7.28 (t, J=7.77 Hz, 1H), 2.87 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 143.01, 128.51, 126.87, 122.43, 30.60.

3f 

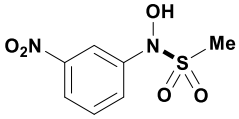
***N*-(4-cyanophenyl)-*N*-hydroxymethanesulfonamide (3f):** Yellow solid. Yield: 64 % (Gradient 20 % to 40 % EtOAc in hexanes). Spectra in agreement with literature report.[5] ^{1}H NMR (500 MHz, acetone) δ 10.46 (s, 1H), 7.86 – 7.80 (d, J=8.77 Hz, H), 7.78 – 7.70 (d, J=8.85 Hz, 2H), 2.96 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 146.84, 122.05, 118.15, 109.78, 31.55, 28.55.

3g 

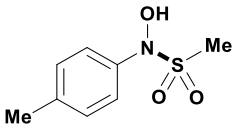
N-(4-benzoylphenyl)-N-hydroxymethanesulfonamide (3g): Off-white solid. Yield: 89 %. 1H NMR (500 MHz, acetone) δ 10.43 (s, 1H), 7.85(d, J=8.40, 2H), 7.8 (d, J=7.87 Hz, 2H), 7.71 (d, J=8.41 2H), 7.66 (t, J=7.56 Hz 1H), 7.56 (t, J = 7.47 Hz, 2H), 2.96 (s, 3H). 13C NMR (126 MHz, acetone) δ 194.80, 146.50, 137.61, 135.47, 132.45, 130.40, 129.68, 128.45, 121.37, 31.34.

3h 

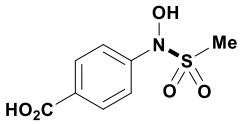
***N*-hydroxy-*N*-(4-nitrophenyl)methanesulfonamide (3h):** Brown solid. Yield: 53 % (Gradient 20 % to 40 % EtOAc in hexanes). 1H NMR (500 MHz, Acetone) δ 8.50 (d, J = 8.8 Hz, 2H), 8.26 (d, J = 8.9 Hz, 2H), 3.27 (s, 3H). 13C NMR (126 MHz, Acetone) δ151.77, 147.50 129.05, 124.49, 43.06.

3i 

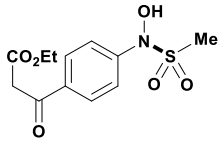
***N*-hydroxy-*N*-(3-nitrophenyl)methanesulfonamide (3i):** Brown solid. Yield: 57 % (Gradient 20 % to 40 % EtOAc in hexanes). ^{1}H NMR (500 MHz, acetone) δ 10.56 (s, 1H), 8.39 (t, *J* = 2.2 Hz, 1H), 8.18 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.74 (t, *J* = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, Acetone) δ 148.46, 144.22, 129.88, 128.09, 121.22, 116.16, 31.31.

3j 

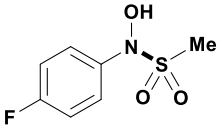
***N*-hydroxy-*N*-(p-tolyl)methanesulfonamide (3j):** Off-white solid. Yield: 50 % (Gradient 20 % to 40 % EtOAc in hexanes). ^{1}H NMR (500 MHz, acetone) δ 10.05 (s, 1H), 7.41 (d, J= 8.48 Hz, 2H), 7.22 (d, J=8.48 2H), 2.86 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 140.54, 136.71, 129.01, 122.53, 30.42, 20.04.

3k 

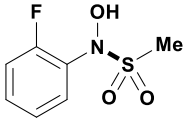
***N*-(4-chlorophenyl)-*N*-hydroxymethanesulfonamide (3k):** Off-white solid Yield: 32 % (Preparative TLC 5% MeOH in DCM). ^{1}H NMR (500 MHz, acetone) δ 8.75 (d, J=8.55 Hz, 2H), 7.66 (d, J= 8.57 Hz, 2H), 2.93 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 166.23, 146.95, 130.11, 128.53, 121.42, 31.19.

3l 

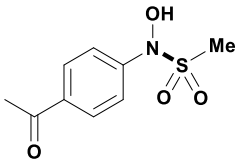
***N*-(4-chlorophenyl)-*N*-hydroxymethanesulfonamide (3l):** Yellow solid. Yield: 30 % (Gradient 20 % to 40 % diethyl ether in hexanes). Compound enolizes when dissolved. ^{1}H NMR (500 MHz, acetone) δ 10.39 (s, 1H), 8.06 (d, J= 8.74 Hz, 2H), 7.69 (m, J=8.75 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.93 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Acetone) δ 129.11, 121.42, 60.67, 45.44, 31.40, 13.54.

3m 

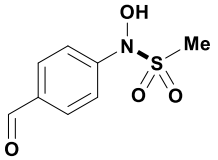
***N*-(4-chlorophenyl)-*N*-hydroxymethanesulfonamide (3m):** Off-white solid Yield: 55 % (Gradient 20 % to 40 % EtOAc in hexanes). ^{1}H NMR (500 MHz, acetone) δ 10.22 (s, 1H), 7.59 – 7.54 (m, 2H), 7.22 – 7.17 (m, 2H), 2.90 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 162.04 (d, J = 244.1 Hz), 139.87 (d, J = 3.0 Hz), 125.32 (d, J = 8.6 Hz), 115.90 (d, J = 23.1 Hz).

3n 

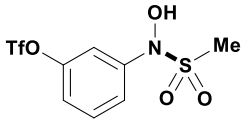
***N*-(4-chlorophenyl)-*N*-hydroxymethanesulfonamide (3n):** Off-white solid. Yield: 40 % (Gradient 20 % to 40 % EtOAc in hexanes). ^{1}H NMR (500 MHz, acetone) δ 10.31 (s, 1H), 7.71 (td, *J* = 7.8, 1.7 Hz, 1H), 7.42 (m, 1H), 7.29 (t, *J* = 8.1, 1H), 7.24 (t, *J* = 8.2, 1H), 3.06 (s, 3H) 13C NMR (126 MHz, Acetone) δ 158.37 (d, J = 251.8 Hz), 131.49 (d, J = 10.8 Hz), 130.67 (d, J = 8.1 Hz), 126.74, 125.34 (d, J = 4.0 Hz), 117.28 (d, J = 20.4 Hz).

3o 

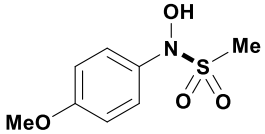
***N*-(4-acetylphenyl)-*N*-hydroxymethanesulfonamide (3o):** Off-white solid. Yield: 85 % (Gradient 20 % to 40 % EtOAc in hexanes). ^{1}H NMR (500 MHz, acetone) δ 10.34 (s, 1H), 8.03 (d, J=8.75 Hz, 2H), 7.66 (d, J= 8.76 Hz, 2H), 2.93 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 196.28, 146.80, 135.28, 128.80, 121.46, 31.28, 25.85.

3p 

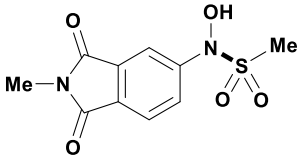
***N*-(4-formylphenyl)-*N*-hydroxymethanesulfonamide (3p):** Yellow solid. Yield: 61 % (Gradient 20 % to 40 % EtOAc in hexanes). ^{1}H NMR (500 MHz, acetone) δ 10.41 (s, 1H), 10.05 (s, 1H), 7.98 (d, J=8.54 Hz, 2H), 7.76 (d, J=8.54 Hz, 2H), 2.95 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 191.14, 134.74, 129.93, 121.81, 31.45.

3q 

3-(*N*-hydroxymethylsulfonamido)phenyl trifluoromethanesulfonate (3q): Off-white solid. Yield: 67 % (Gradient 20 % to 40 % EtOAc in hexanes). ^{1}H NMR (500 MHz, acetone) δ 10.87 (s, 1H), 7.69 – 7.61 (m, 3H), 7.40 (m, 1H), 2.95 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 150.42, 146.03, 123.62, 120.48, 119.81 (q, J = 320.0 Hz), 115.80, 32.18.

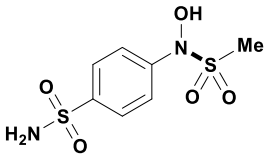
3r 

***N*-hydroxy-*N*-(4-methoxyphenyl)methanesulfonamide (3r):** Off-white solid. Yield: 43 % (Gradient 20 % to 40 % EtOAc in hexanes). ^{1}H NMR (500 MHz, acetone) δ 10.03 (s, 1H), 7.47 – 7.44 (d, J=8.79 Hz, 2H), 6.96 (d, J=8.79 Hz, 2H), 3.82 (s, 3H), 2.87 (s, 3H). ^{13}C NMR (126 MHz, cdcl3) δ 159.72, 136.56, 125.31, 125.26, 125.19, 114.52, 55.77, 31.27.

3s 

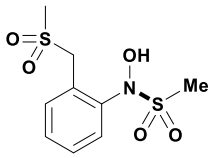
***N*-hydroxy-*N*-(2-methyl-1,3-dioxoisoindolin-5-yl)methanesulfonamide (3s):** Yellow solid. Yield: 34 % (Gradient 20 % to 40 % EtOAc in hexanes). ^{1}H NMR (500 MHz, acetone) δ 10.55 (s, 1H), 7.96 – 7.91 (m, 2H), 7.90 – 7.86 (d, J=8.45 Hz, 1H), 3.11 (s, 3H), 3.00 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 167.31, 167.29, 148.15, 133.33, 129.90, 126.56, 123.31, 115.66, 31.60, 23.20.

3t



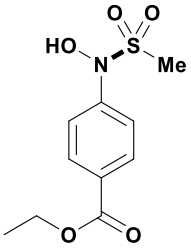
4-(*N*-hydroxymethylsulfonamido)benzenesulfonamide (3t): Off-white solid. Yield: 77 % (100 % EtOAc). ^{1}H NMR (500 MHz, CD_3CN) δ 9.13 (s, 1H), 7.91 (d, J=8.90 Hz, 2H), 7.67 (d, J=8.89, 2H), 5.80 (s, 2H), 2.90 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 127.44, 122.47, 121.92, 117.39, 31.90.

3u



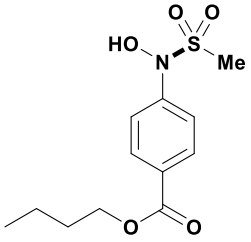
***N*-hydroxy-*N*-(2-((methylsulfonyl)methyl)phenyl)methanesulfonamide (3u):** Off-white solid. Yield: 46 % (Gradient 0% to 20 % acetone in hexanes). ^{1}H NMR (500 MHz, acetone) δ 10.20 (s, 1H), 7.81 (d, *J* = 8.2, 1H), 7.66 (d, *J* = 7.8, 1H), 7.58 – 7.49 (t, J=7.6 Hz, 1H), 7.45 (t, *J* = 7.6, 1H), 4.63 (s, 2H), 3.13 (s, 3H), 2.84 (d, 3H). ^{13}C NMR (126 MHz, Acetone) δ 141.81, 131.94, 129.58, 128.61, 127.96, 124.75, 55.72, 39.39, 32.18.

3v

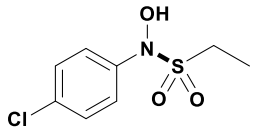


Ethyl 4-(*N*-hydroxymethylsulfonamido)benzoate (3v): Off-white solid. Yield: 88 % (Gradient 20 % to 40 % EtOAc in hexanes). ^{1}H NMR (500 MHz, acetone/$CHCl_3$) δ 10.34 (s, 1H), 8.05 (d, J=8.56 Hz, 2H), 7.66 (d, J=8.50 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Acetone) δ 165.27, 146.93, 129.79, 128.51, 121.41, 60.69, 31.19, 13.74.

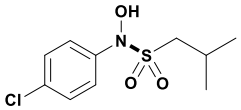
3w



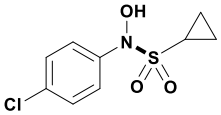
Butyl 4-(*N*-hydroxymethylsulfonamido)benzoate (3w): Off-white solid. Yield: 91 % (Gradient 20 % to 40 % EtOAc in hexanes). ^{1}H NMR (500 MHz, acetone/$CHCl_3$) δ 8.09 – 8.04 (m, 2H), 7.69 – 7.63 (m, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 2.92 (s, 3H), 1.76 (dq, *J* = 7.9, 6.6 Hz, 2H), 1.49 (h, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, Acetone) δ 165.33, 146.96, 129.80, 128.48, 121.44, 64.48, 31.22, 30.65, 19.04, 13.18.

4a 

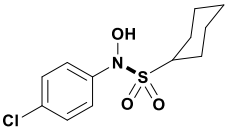
***N*-(4-chlorophenyl)-*N*-hydroxyethanesulfonamide (4a):** Off-white solid. Yield: 51 % (Gradient 20 % to 40 % EtOAc in hexanes). Spectra in agreement with literature report.[5] ^{1}H NMR (500 MHz, acetone) δ 10.16 (s, 1H), 7.59 – 7.52 (d, J=8.73 Hz, 2H), 7.47 – 7.40 (d, J=8.76 Hz, 2H), 3.19 (q, *J* = 7.5 Hz, 2H), 1.28 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, Acetone) δ 141.75, 131.55, 128.51, 123.68, 39.98, 6.72.

4b 

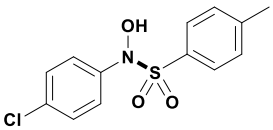
***N*-(4-chlorophenyl)-*N*-hydroxy-2-methylpropane-1-sulfonamide (4b):** Off-white solid. Yield: 44 % (Gradient 20 % to 40 % EtOAc in hexanes). ^{1}H NMR (500 MHz, acetone) δ 10.17 (s, 1H), 7.54 (d, J=8.71, 2H), 7.44 (d, J= 8.70 Hz, 2H), 3.00 (d, *J* = 6.7 Hz, 2H), 2.22 (sept, *J* = 13.4, 6.7 Hz, 1H), 1.06 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, Acetone) δ 141.77, 131.57, 128.52, 123.65, 51.71, 24.15, 21.76.

4c 

***N*-(4-chlorophenyl)-*N*-hydroxycyclopropanesulfonamide (4c):** Off-white solid. Yield: 82 % (Gradient 20 % to 40 % EtOAc in hexanes). ^{1}H NMR (500 MHz, acetone) δ 10.08 (s, 1H), 7.61 – 7.54 (d, J=8.83 Hz, 2H), 7.46 – 7.40 (d, J=8.83 Hz, 2H), 2.66 (m, 1H), 1.06 – 0.96 (m, 2H), 0.99 – 0.85 (m, 2H). ^{13}C NMR (126 MHz, Acetone) δ 142.17, 131.66, 128.35, 124.19, 23.39, 3.96.

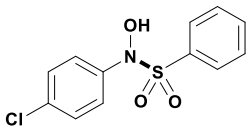
4d 

***N*-(4-chlorophenyl)-*N*-hydroxycyclohexanesulfonamide (4d):** Off-white solid Yield: 76 % (Gradient 20 % to 40 % EtOAc in hexanes). ^{1}H NMR (500 MHz, Acetone) δ 9.99 (s, 1H), 7.56 (d, J=8.78 Hz, 2H), 7.42(m, J=8.78 Hz, 2H), 3.49 (tt, *J* = 11.9, 3.6 Hz, 1H), 2.07 – 2.01 (m, 1H), 1.86 – 1.76 (m, 2H), 1.64 (dddt, *J* = 12.9, 4.9, 3.2, 1.5 Hz, 1H), 1.52 (qd, *J* = 12.4, 3.3 Hz, 2H), 1.32 (qt, *J* = 12.8, 3.4 Hz, 2H), 1.21 (qt, *J* = 12.8, 3.4 Hz, 1H). ^{13}C NMR (126 MHz, Acetone) δ 141.91, 131.07, 128.47, 123.25, 57.47, 26.67, 24.93, 24.78.

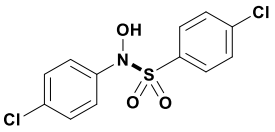
4e 

***N*-(4-chlorophenyl)-*N*-hydroxy-4-methylbenzenesulfonamide (4e):** Off-white solid. Yield: 74 % (Gradient 20 % to 40 % EtOAc in hexanes). Spectra in agreement with literature.[6] ^{1}H NMR (500 MHz, acetone) δ 10.23 (s, 1H), 7.43 (d, J=8.38 Hz, 2H), 7.38 – 7.29 (m, 4H), 7.19 (d,

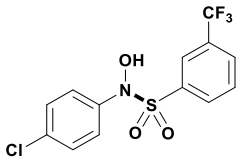
J=8.83 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 145.04, 141.93, 131.84, 129.95, 129.57, 129.14, 128.19, 124.15, 20.70.

4f 

***N*-(4-chlorophenyl)-*N*-hydroxybenzenesulfonamide (4f):** Off-white solid. Yield: 49 % (Gradient 20 % to 40 % EtOAc in hexanes). Spectra in agreement with literature.[6] ^{1}H NMR (500 MHz, acetone) δ 10.30 (s, 1H), 7.73 (m, Hz, 1H), 7.60 – 7.52 (m, 4H), 7.36 – 7.30 (d, J=8.80 Hz, 2H), 7.22 – 7.16 (d, J=8.80 Hz, 2H). ^{13}C NMR (126 MHz, Acetone) δ 141.76, 134.04, 132.78, 131.99, 129.52, 128.62, 128.25, 124.19.

4g 

4-chloro-*N*-(4-chlorophenyl)-*N*-hydroxybenzenesulfonamide (4g): Off-white solid. Yield: 54 % (Gradient 20 % to 40 % EtOAc in hexanes). Spectra in agreement with literature.5 1H NMR (500 MHz, acetone) δ 10.26 (s, 1H), 7.54 – 7.47 (m, 4H), 7.29 – 7.24 (d, 2H), 7.16 – 7.12 (d, 2H).13C NMR (126 MHz, Acetone) δ 141.73, 140.60, 132.78, 131.64, 131.56, 129.20, 129.18, 128.73, 124.53.

4h 

***N*-(4-chlorophenyl)-*N*-hydroxy-3-(trifluoromethyl)benzenesulfonamide (4h):** Off-white solid. Yield: 38 % (Gradient 20 % to 40 % EtOAc in hexanes). ^{1}H NMR (500 MHz, Acetone) δ 10.57 (s, 3H), 8.12 (d, J=7.56 Hz 1H), 7.85 (m, 2H), 7.75 (bs,1H), 7.37 (d, J= 8.86 Hz, 2H), 7.22 – 7.16 (d, J=8.83 Hz, 2H). ^{13}C NMR (126 MHz, Acetone) δ 141.29, 133.70, 133.21, 132.49, 130.70, 130.67, 130.18, 128.45, 126.07, 126.04, 124.22.

7. References

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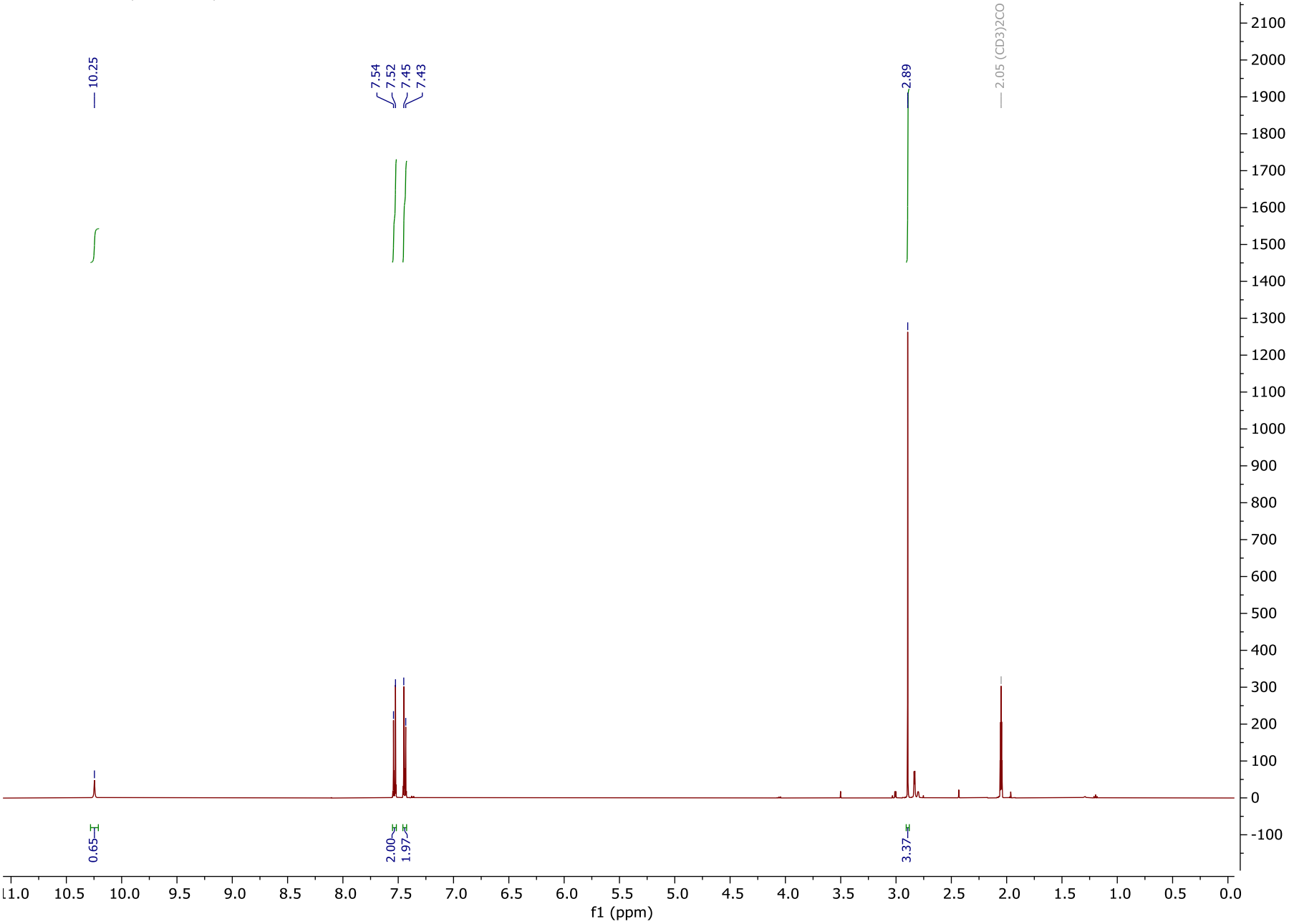
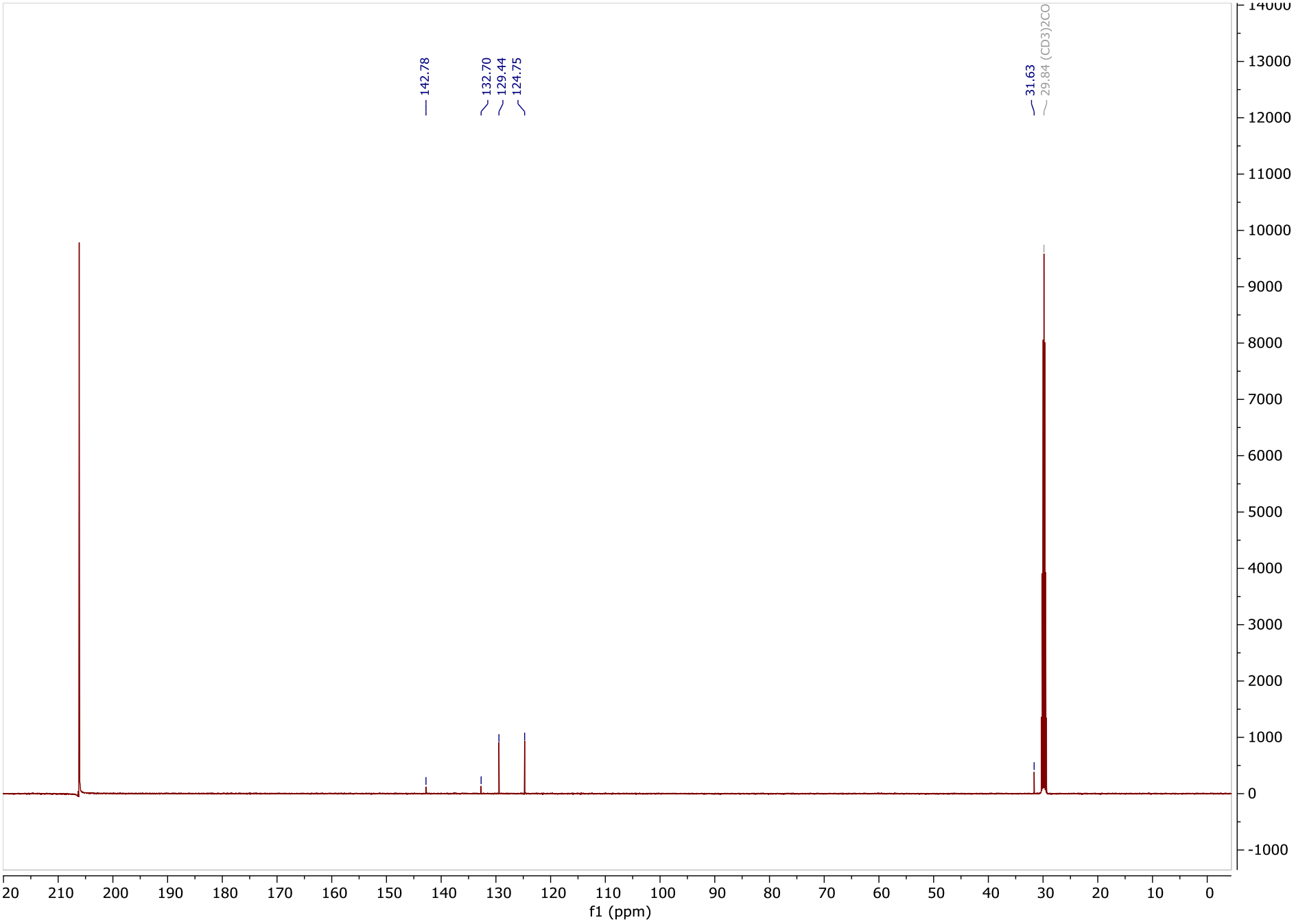
8. Spectra collection

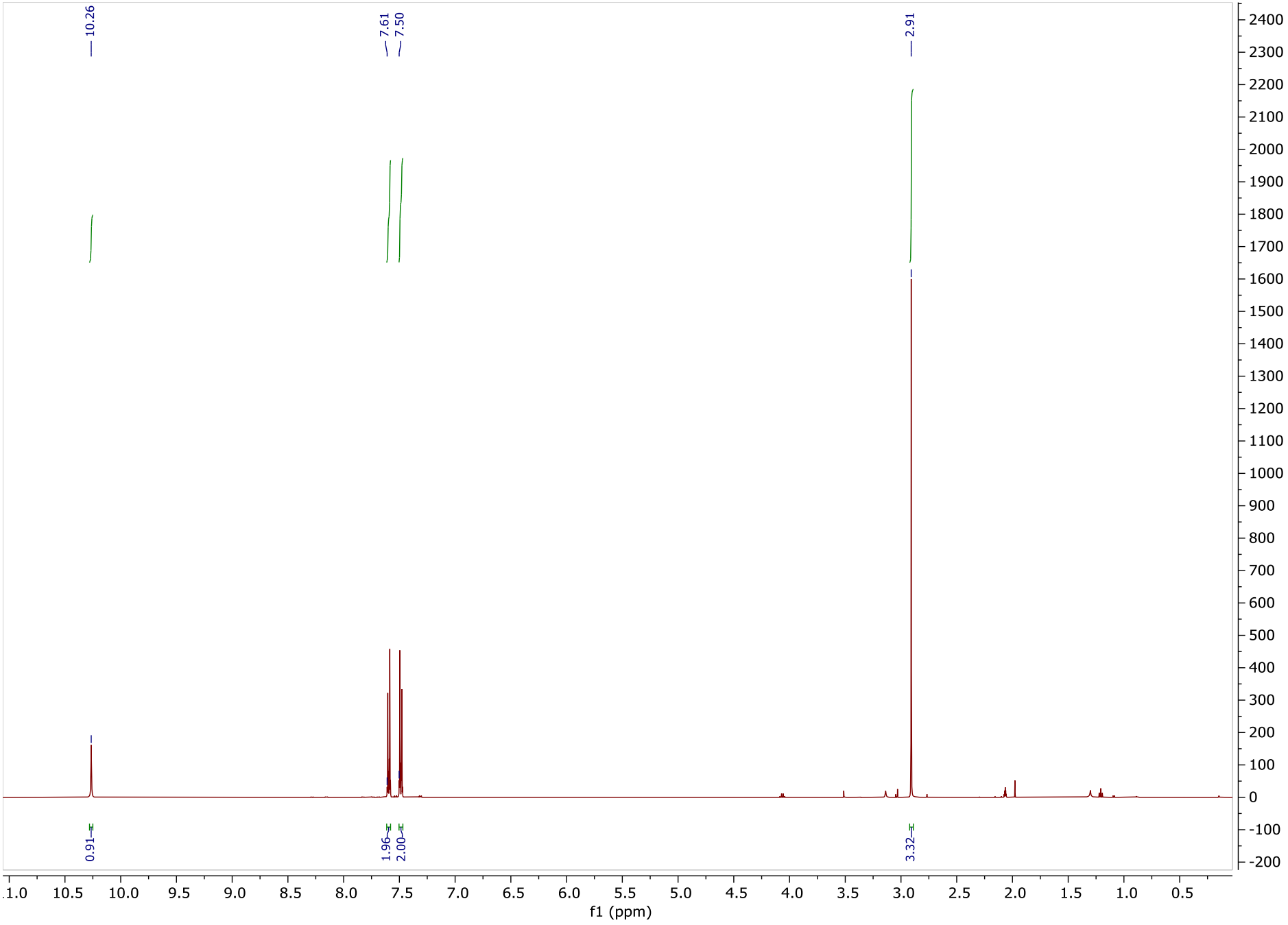
^{1}HNMR of 3a, acetone, 500 MHz



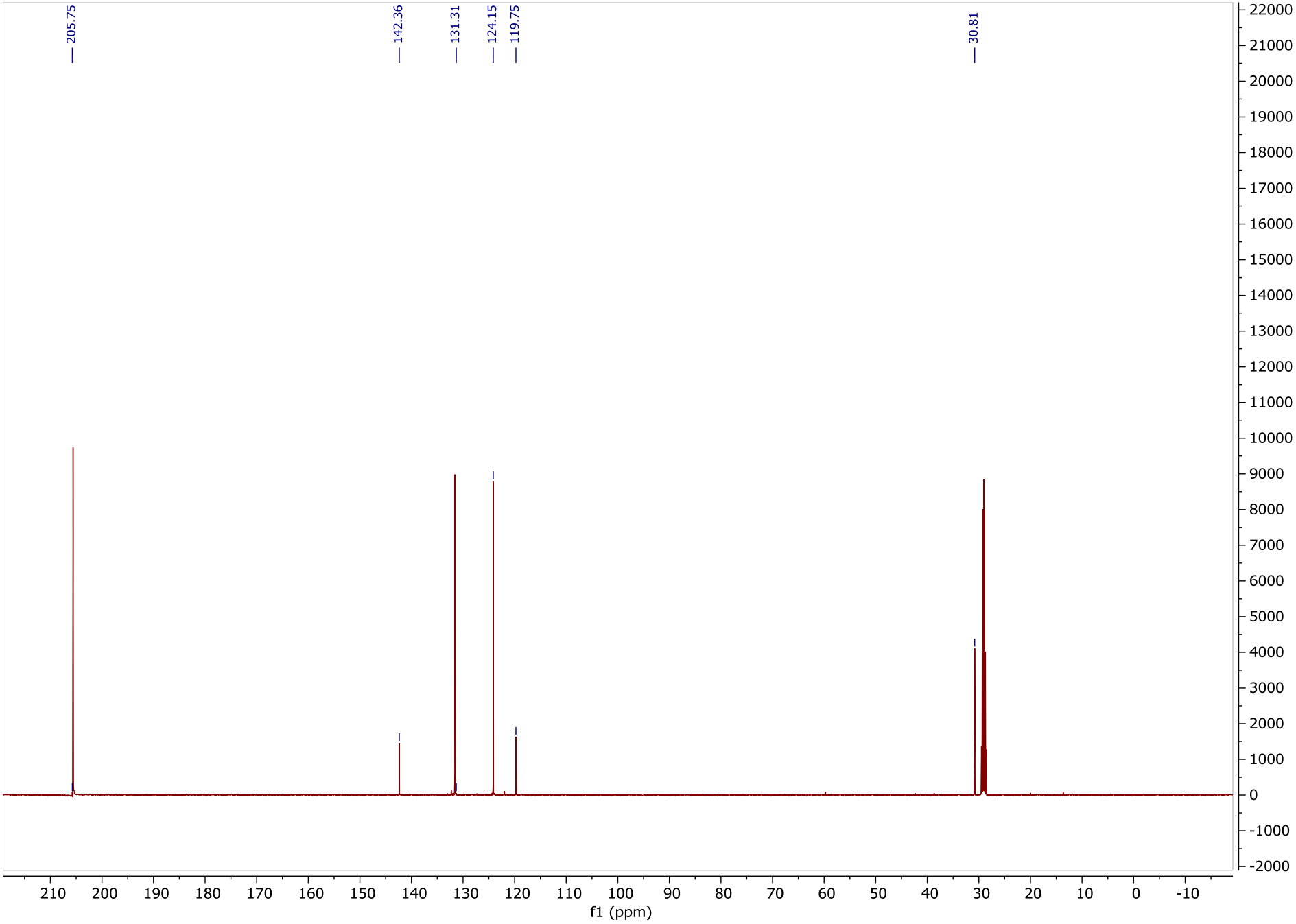
^{13}C NMR of 3a, acetone, 126 MHz



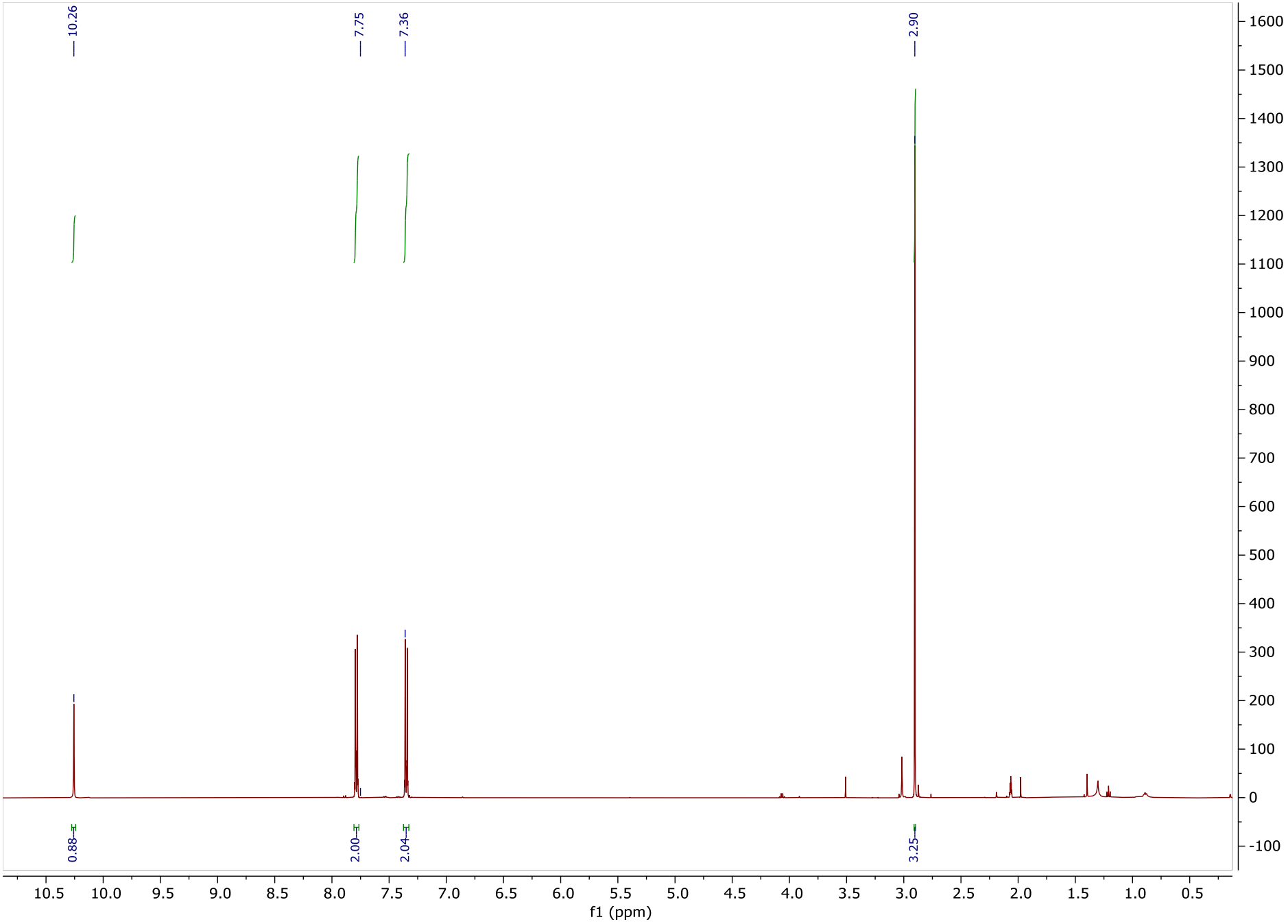
^{1}H NMR of 3b, acetone, 500 MHz



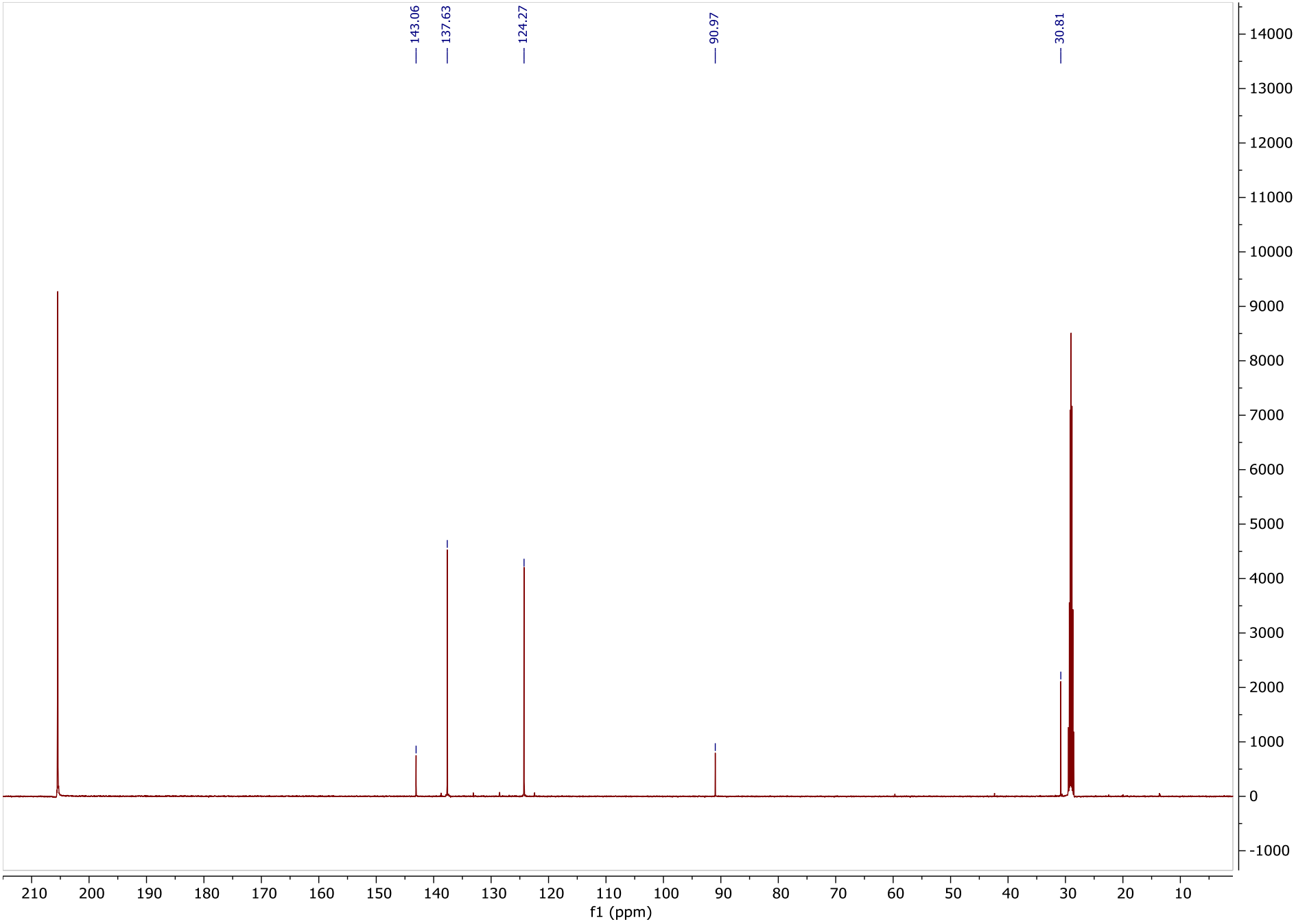
^{13}C NMR of 3b, acetone, 126 MHz



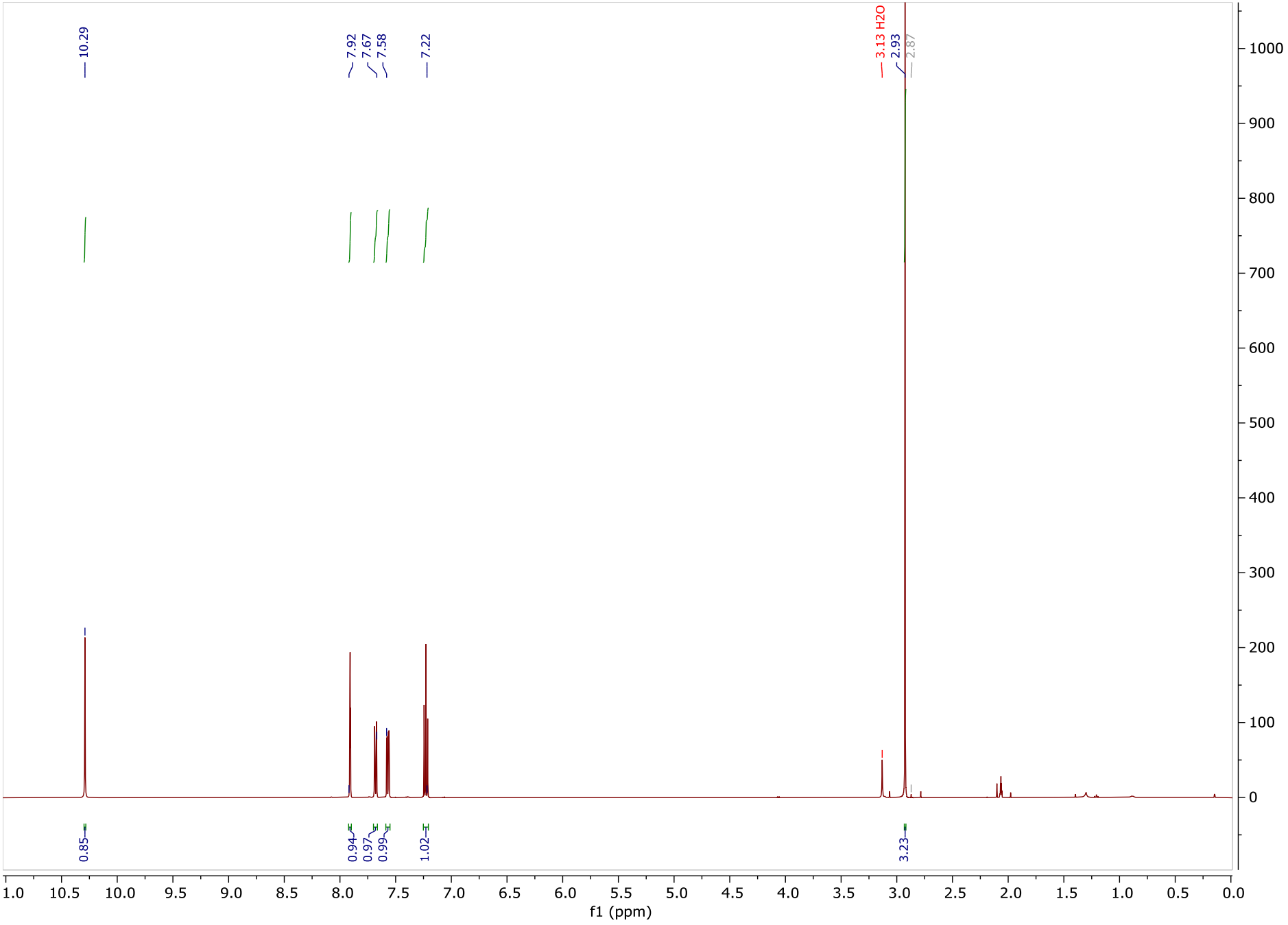
^{1}H NMR of 3c, acetone, 500 MHz



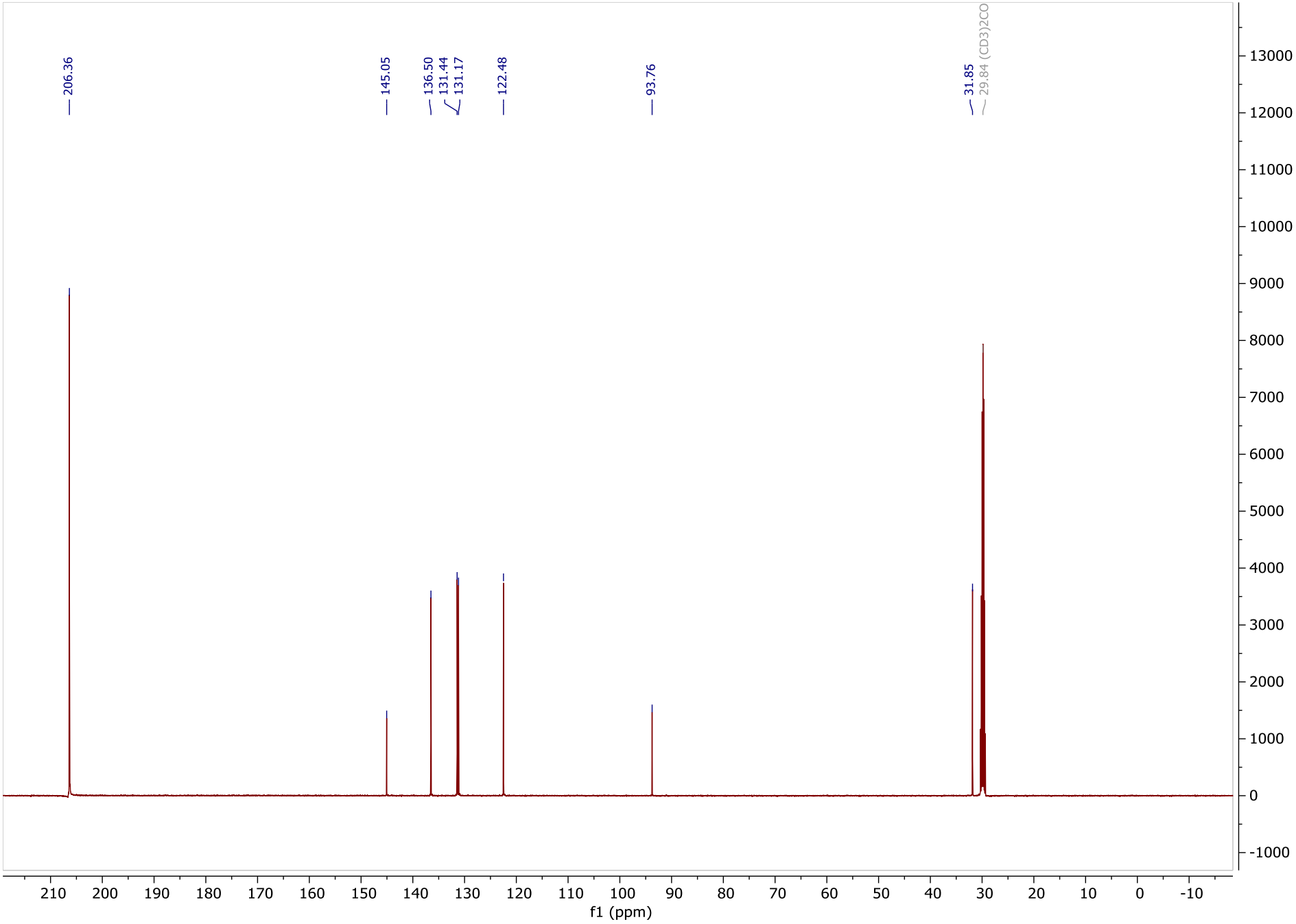
^{13}C NMR of 3c, acetone, 126 MHz



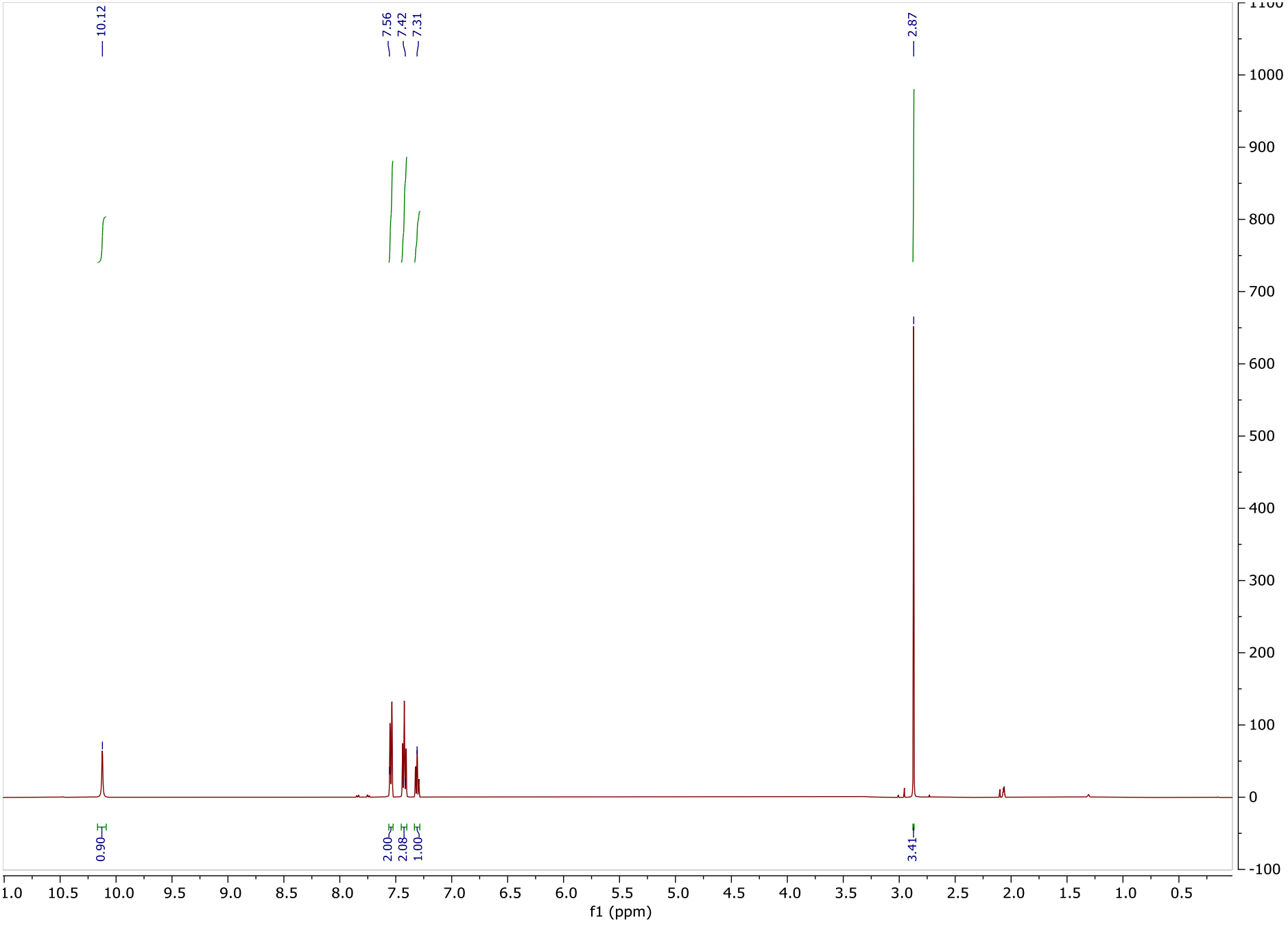
^{1}H NMR of 3d, acetone, 500 MHz



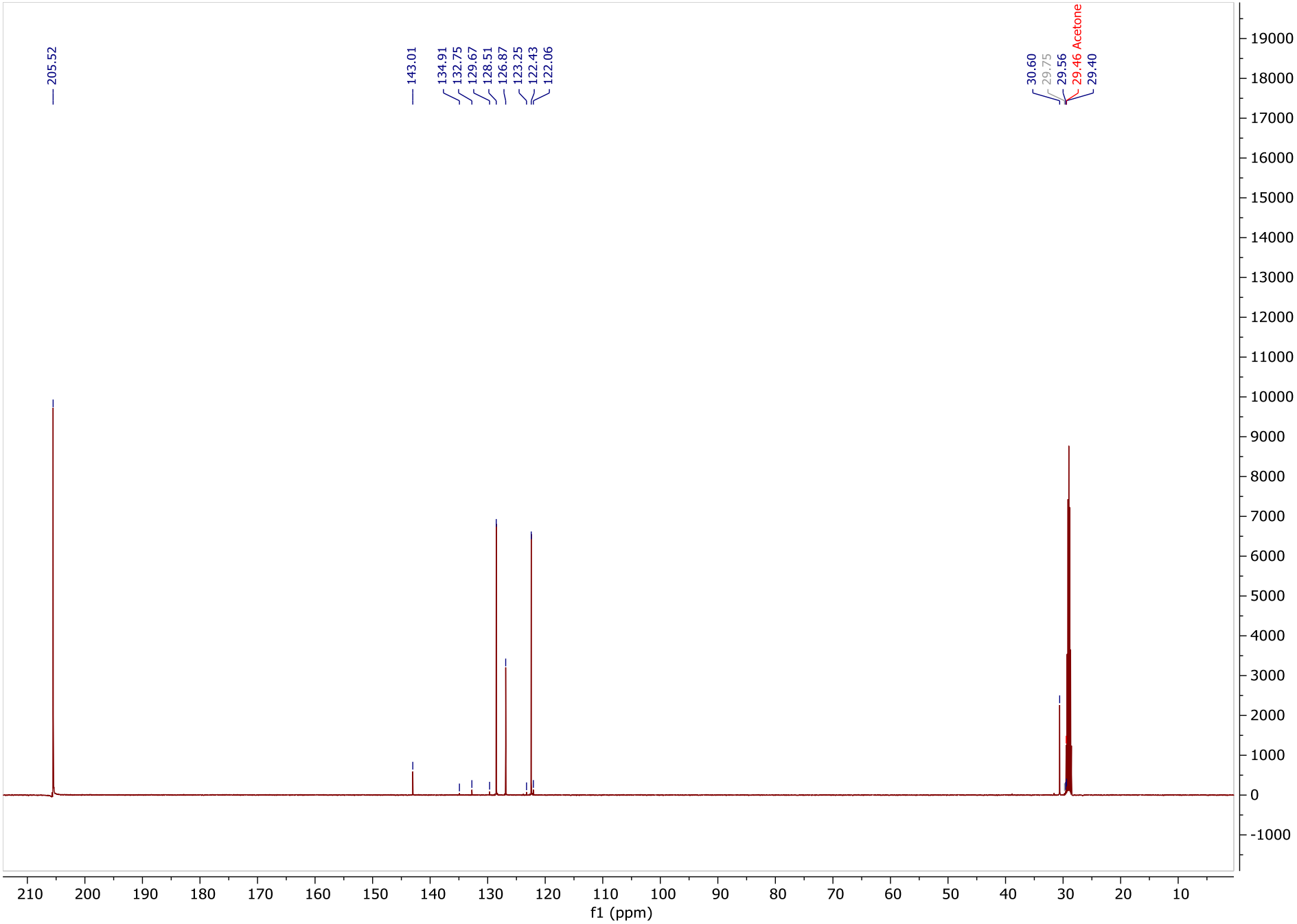
^{13}C NMR of 3d, acetone, 126 MHz



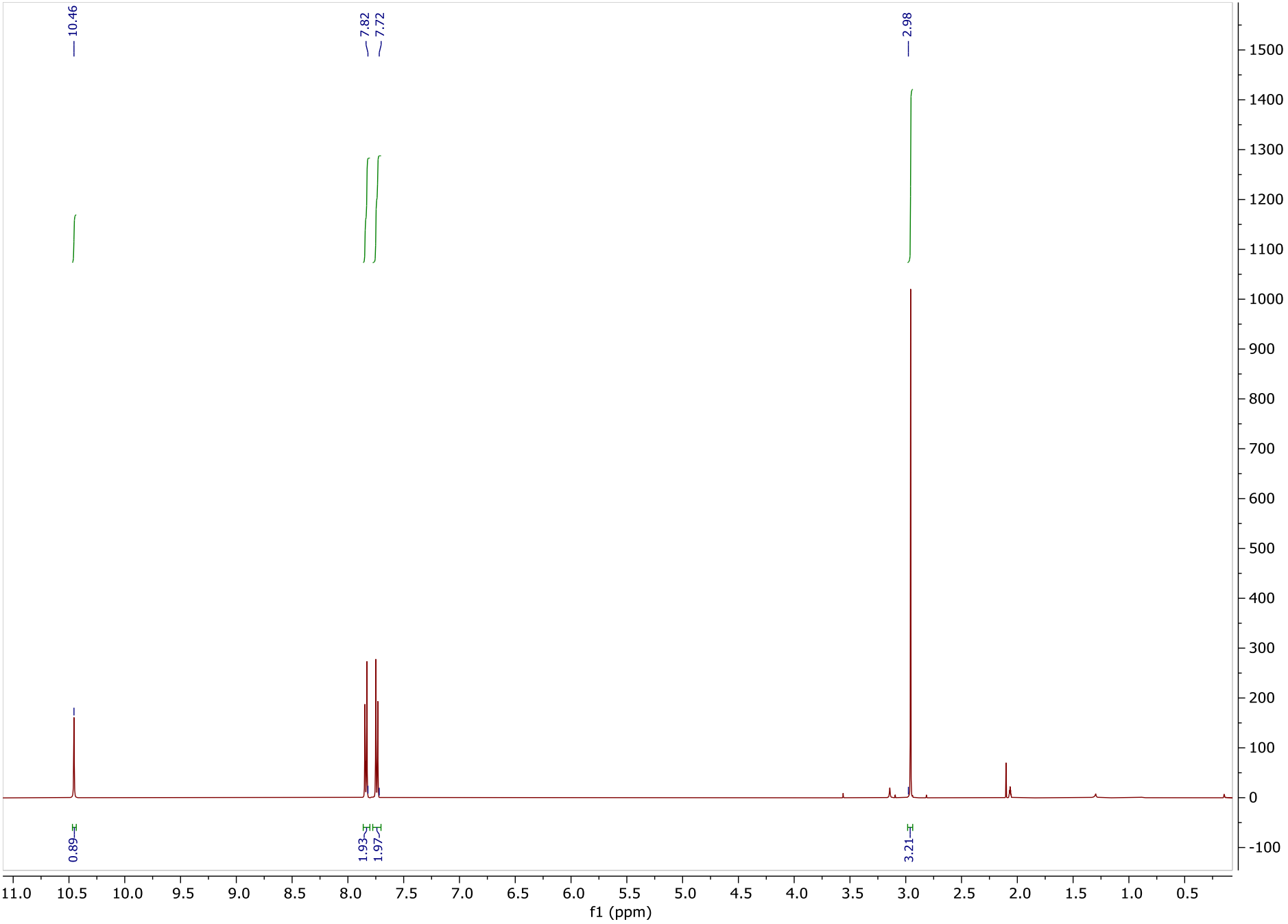
^{1}H NMR of 3e, acetone, 500 MHz



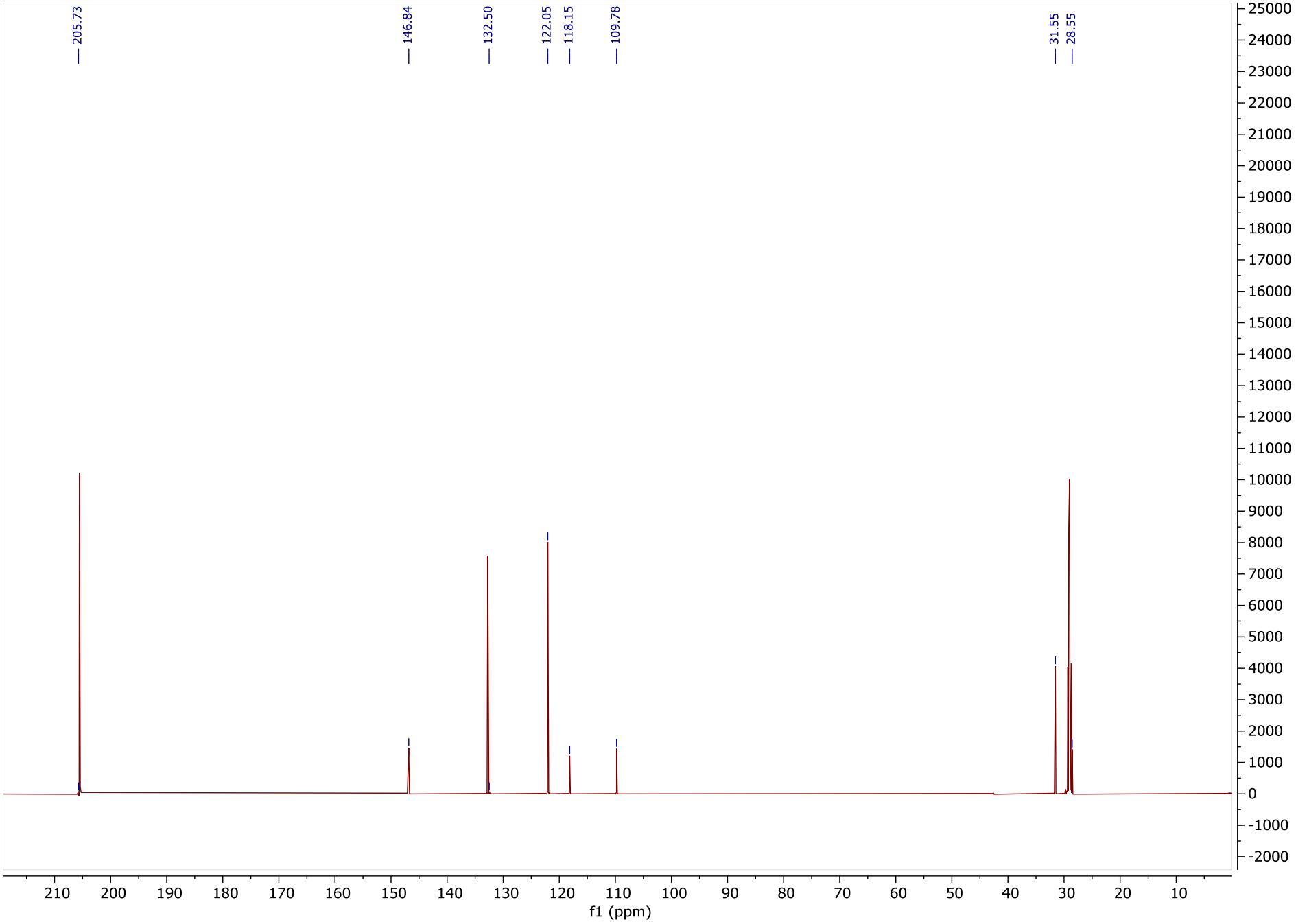
^{13}C NMR of 3e, acetone, 126 MHz



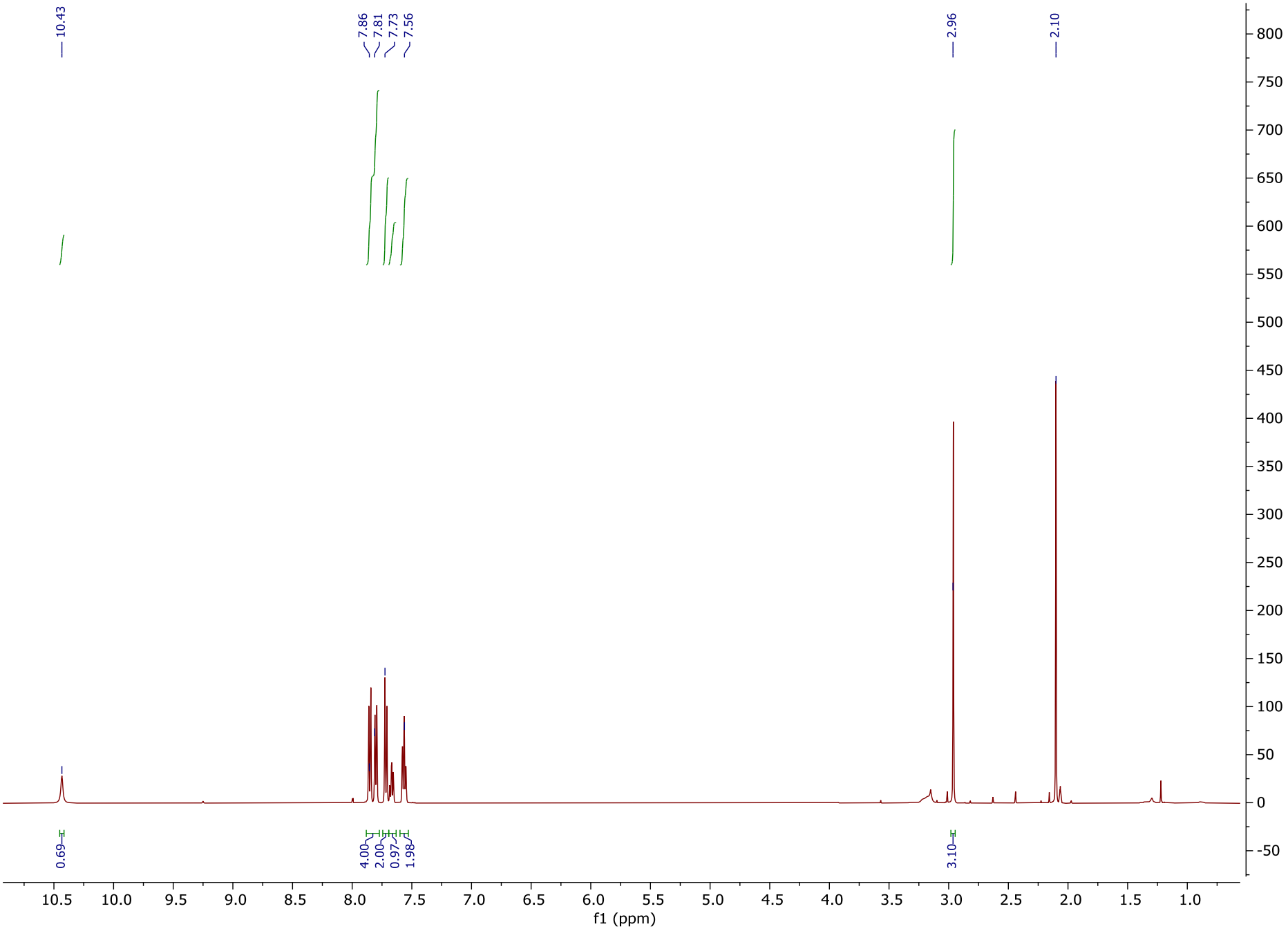
^{1}H NMR of 3f, acetone, 500 MHz



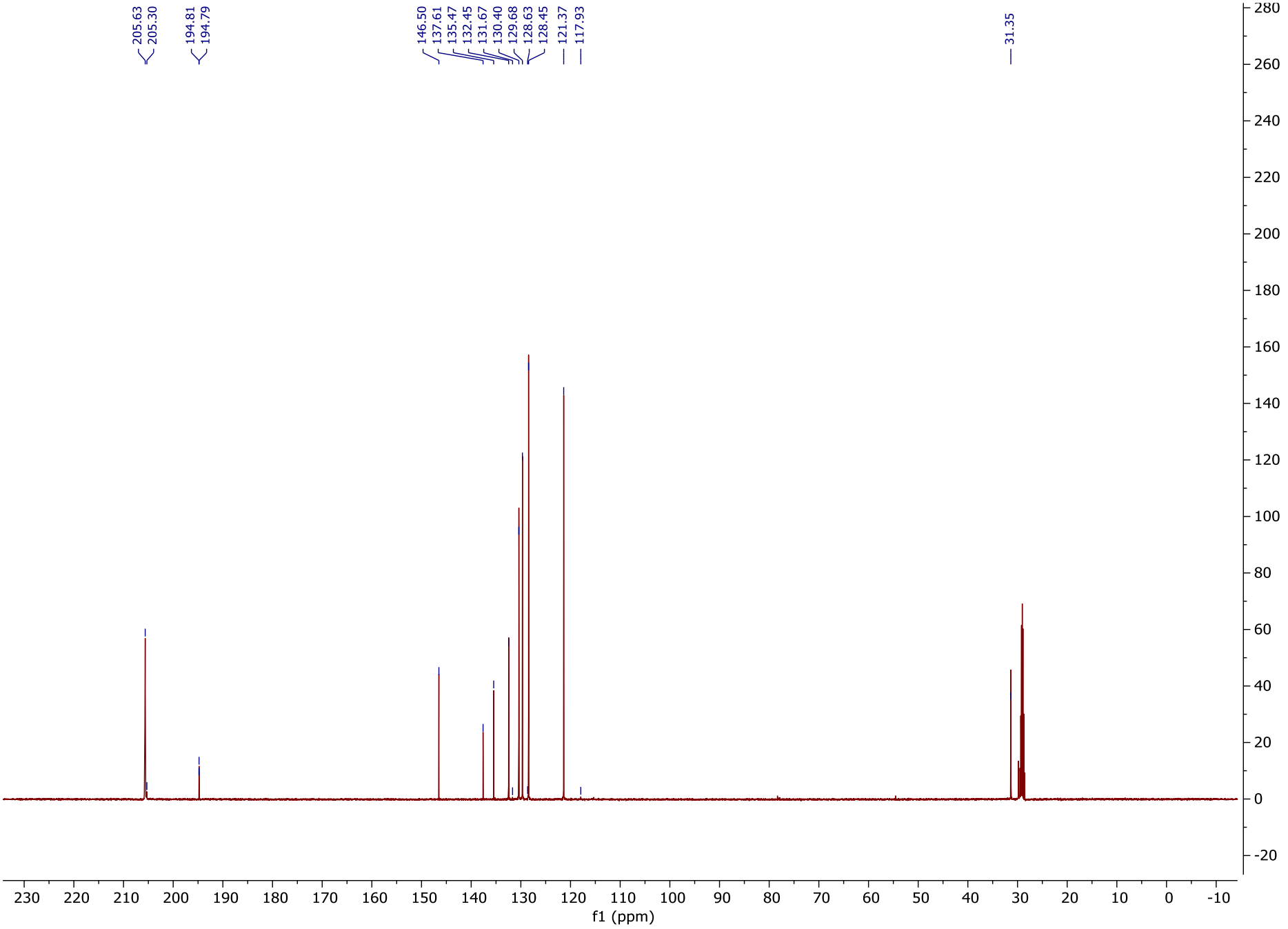
^{13}C NMR of 3f, acetone, 126 MHz



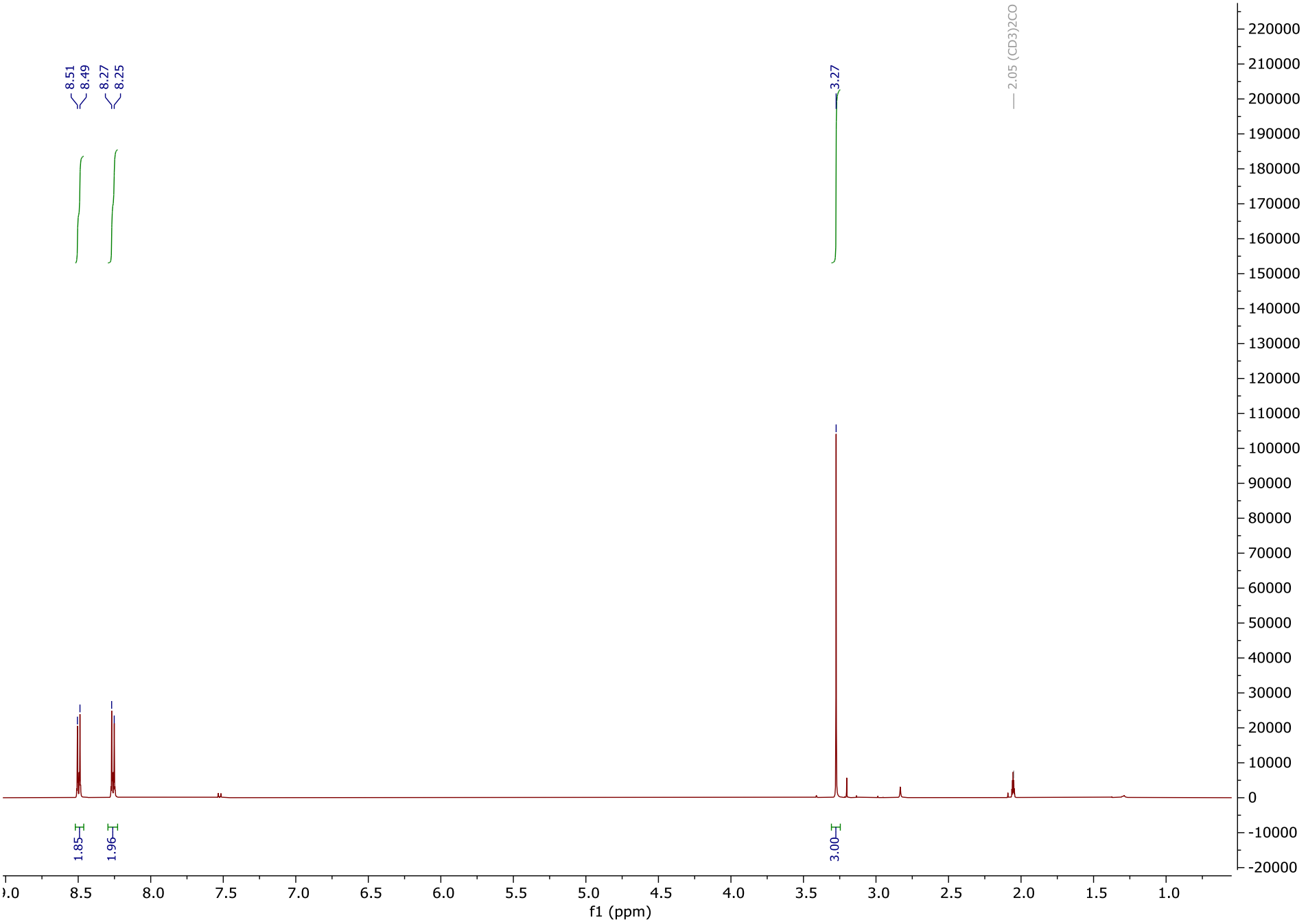
^{1}H NMR of 3g, acetone, 500 MHz



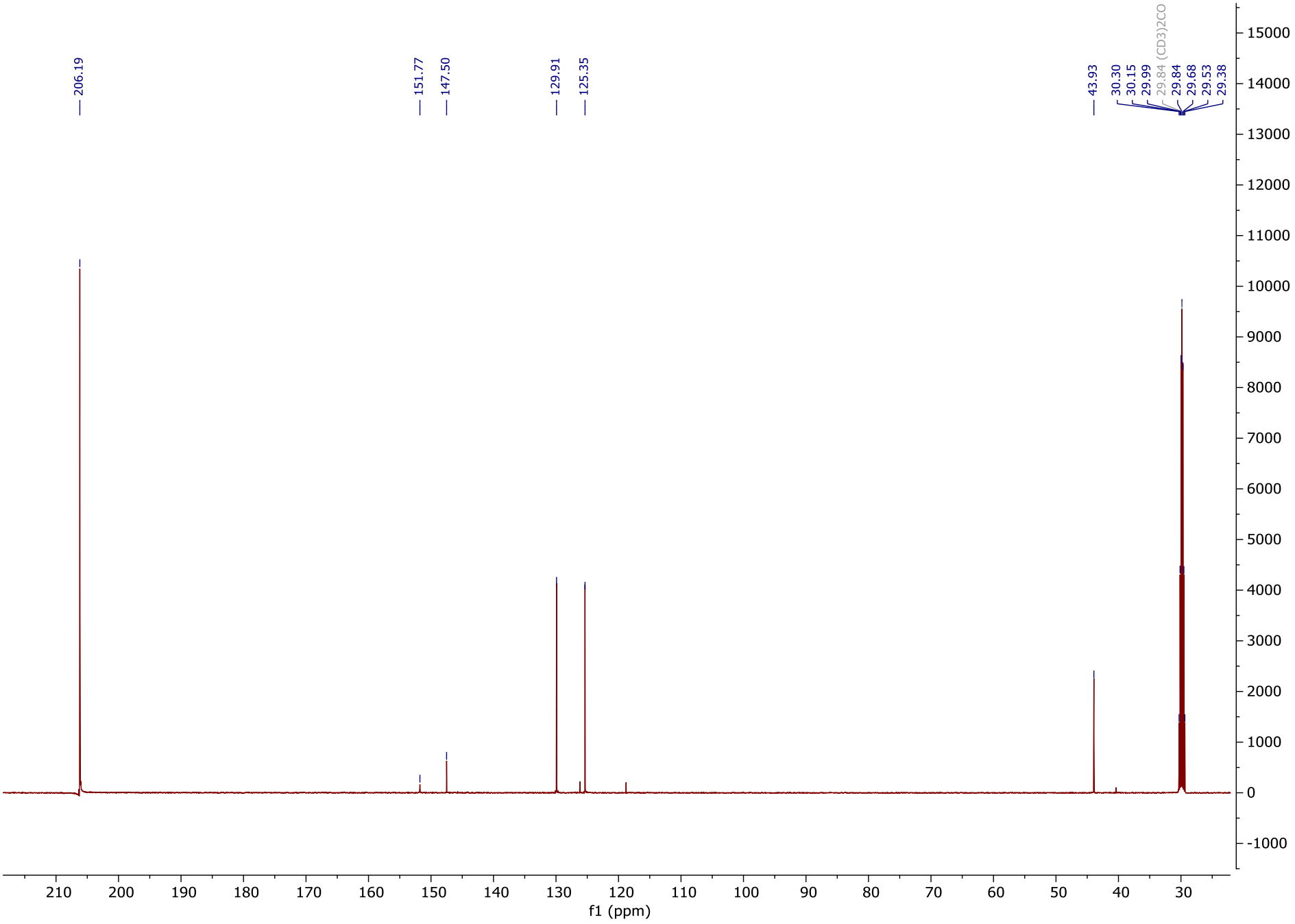
^{13}C NMR of 3g, acetone, 126 MHz



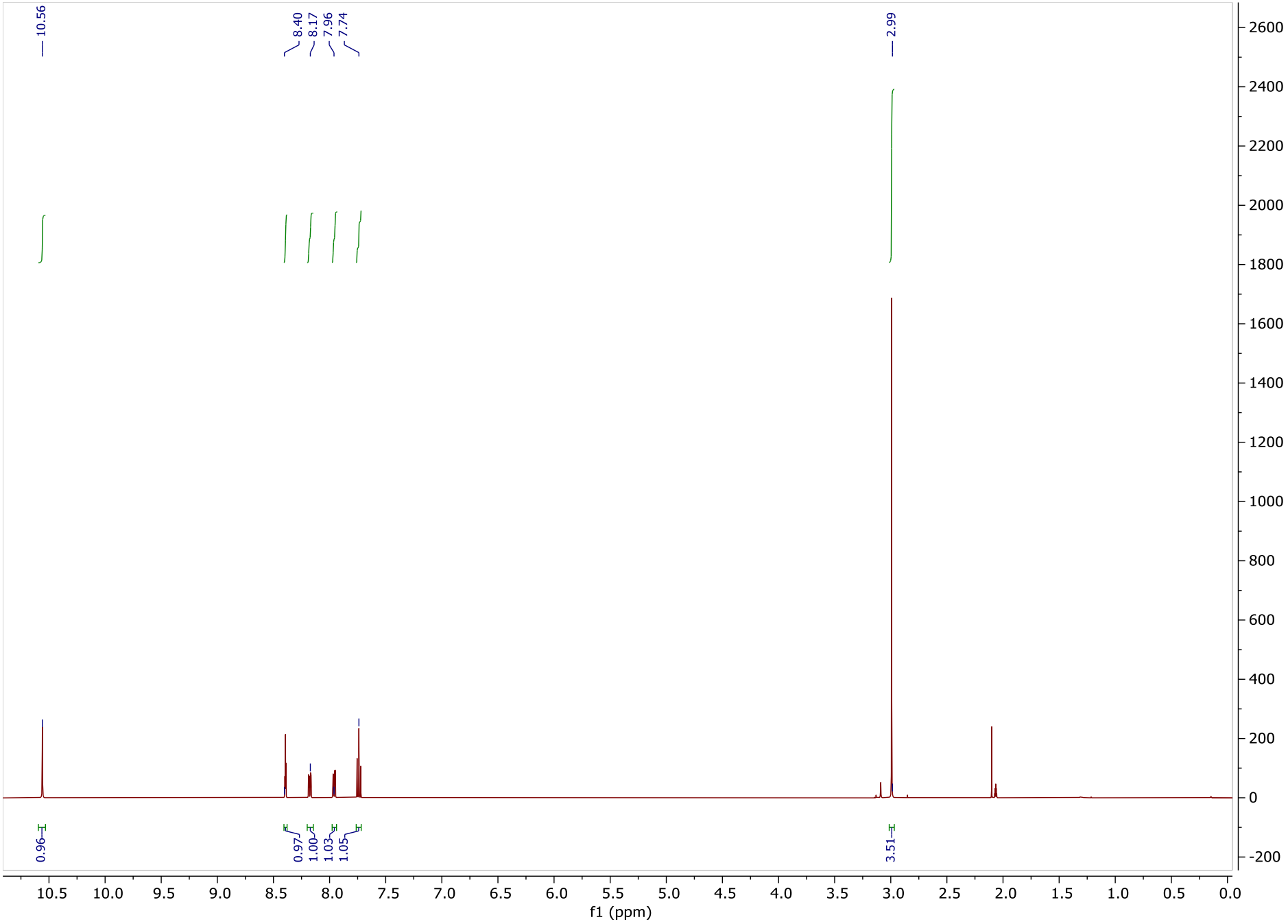
^{1}H NMR of 3h, acetone, 500 MHz



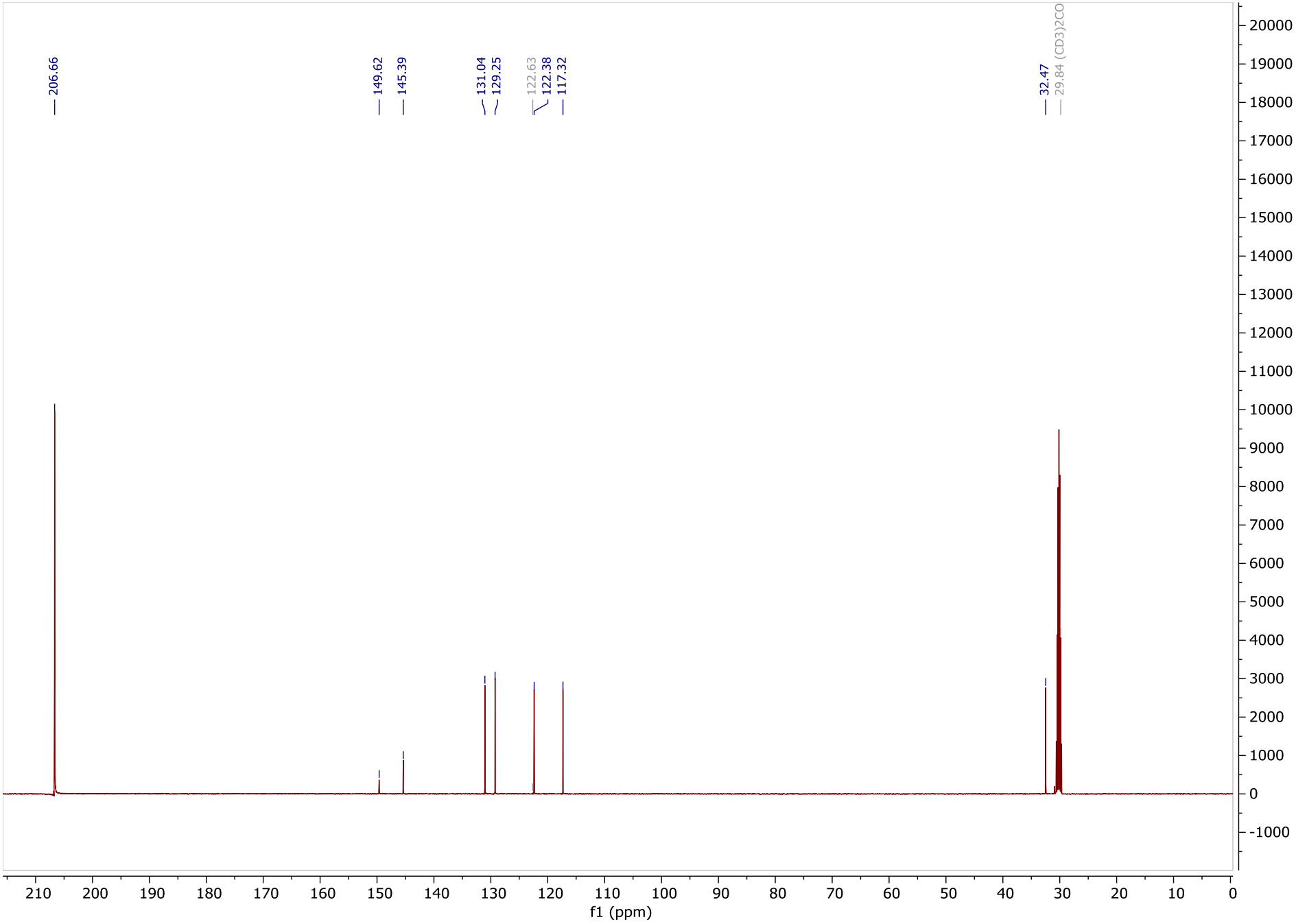
^{13}C NMR of 3h, acetone, 126 MHz



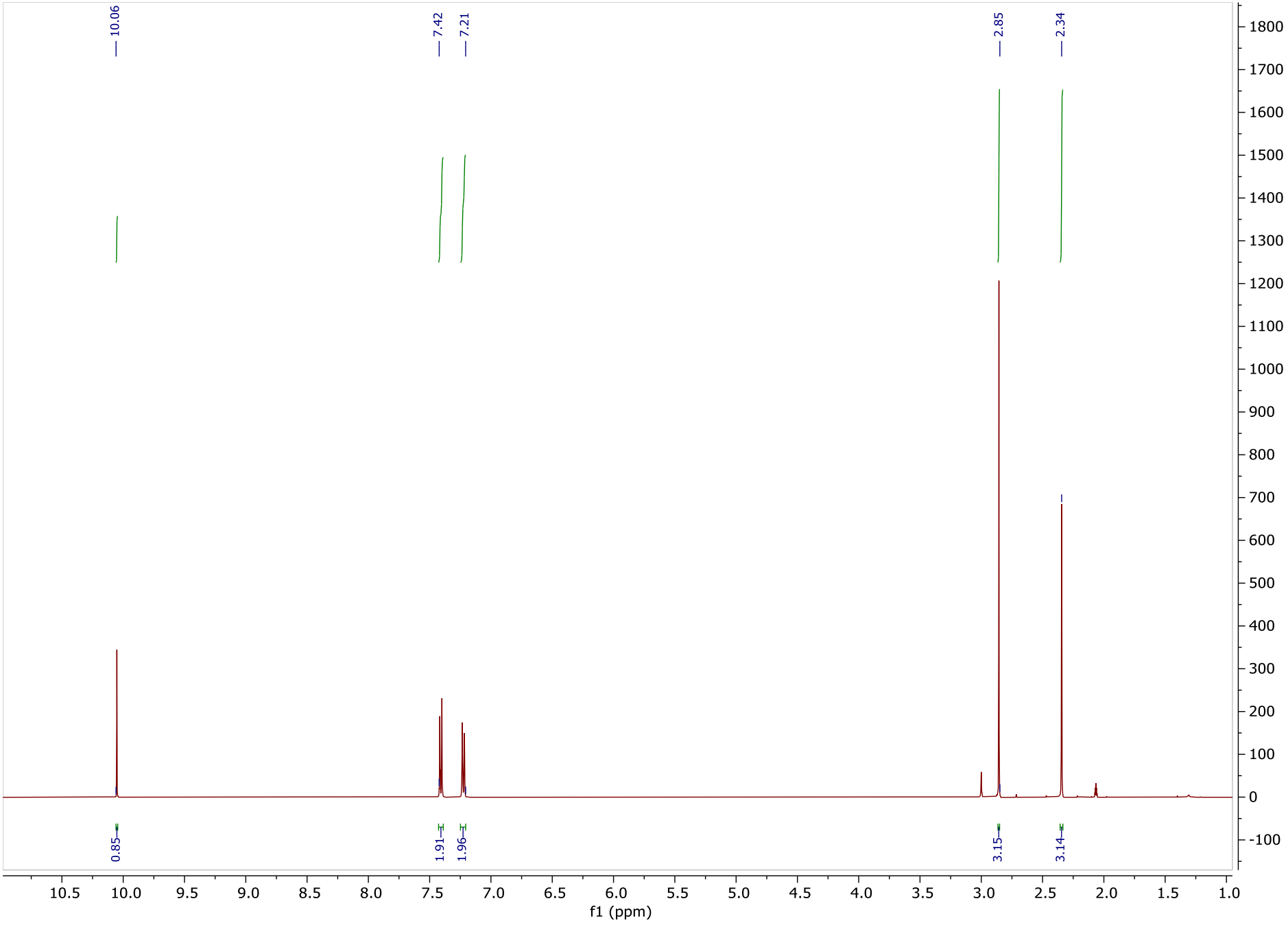
^{1}H NMR of 3i, acetone, 500 MHz



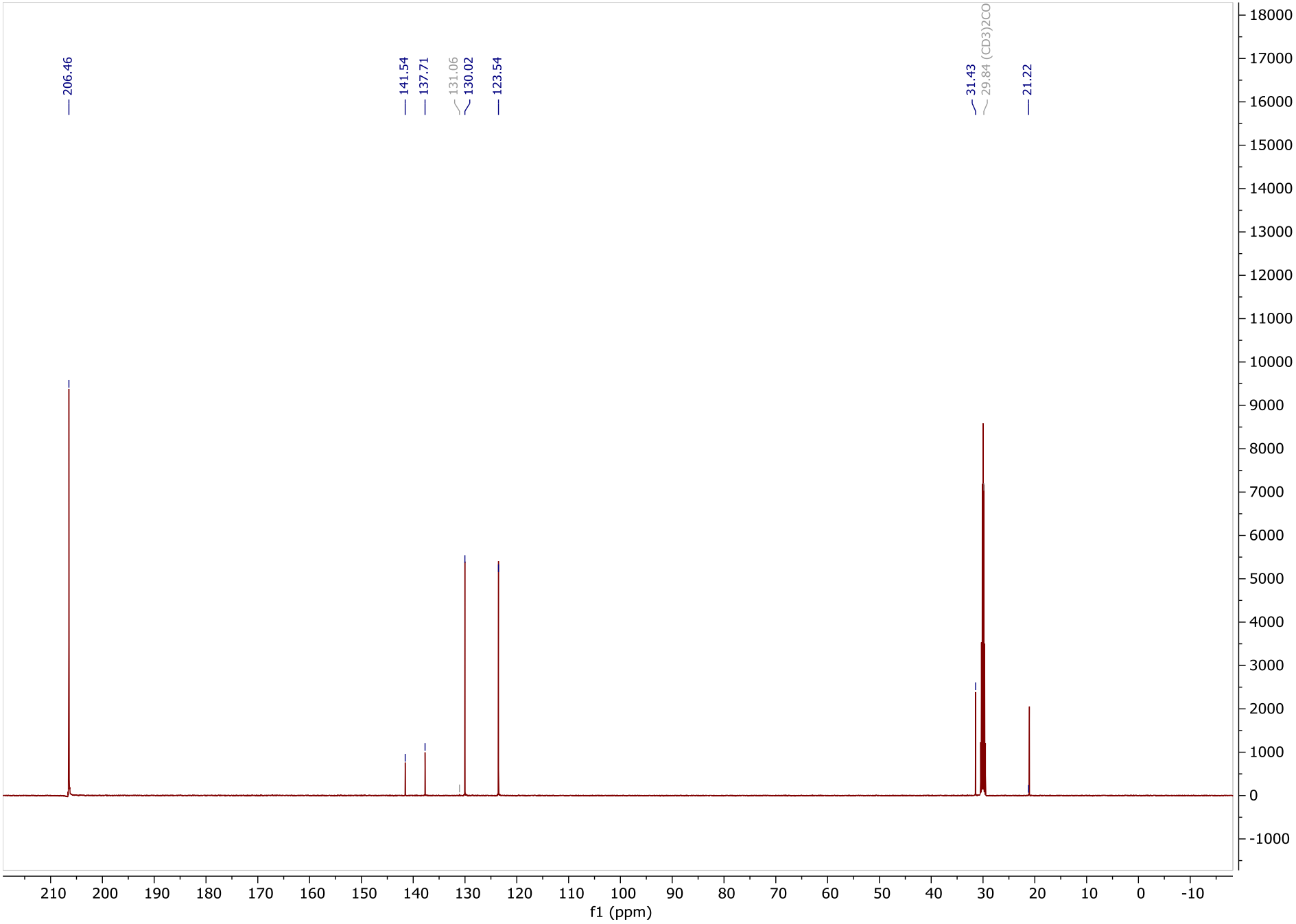
^{13}C NMR of 3i, acetone, 126 MHz



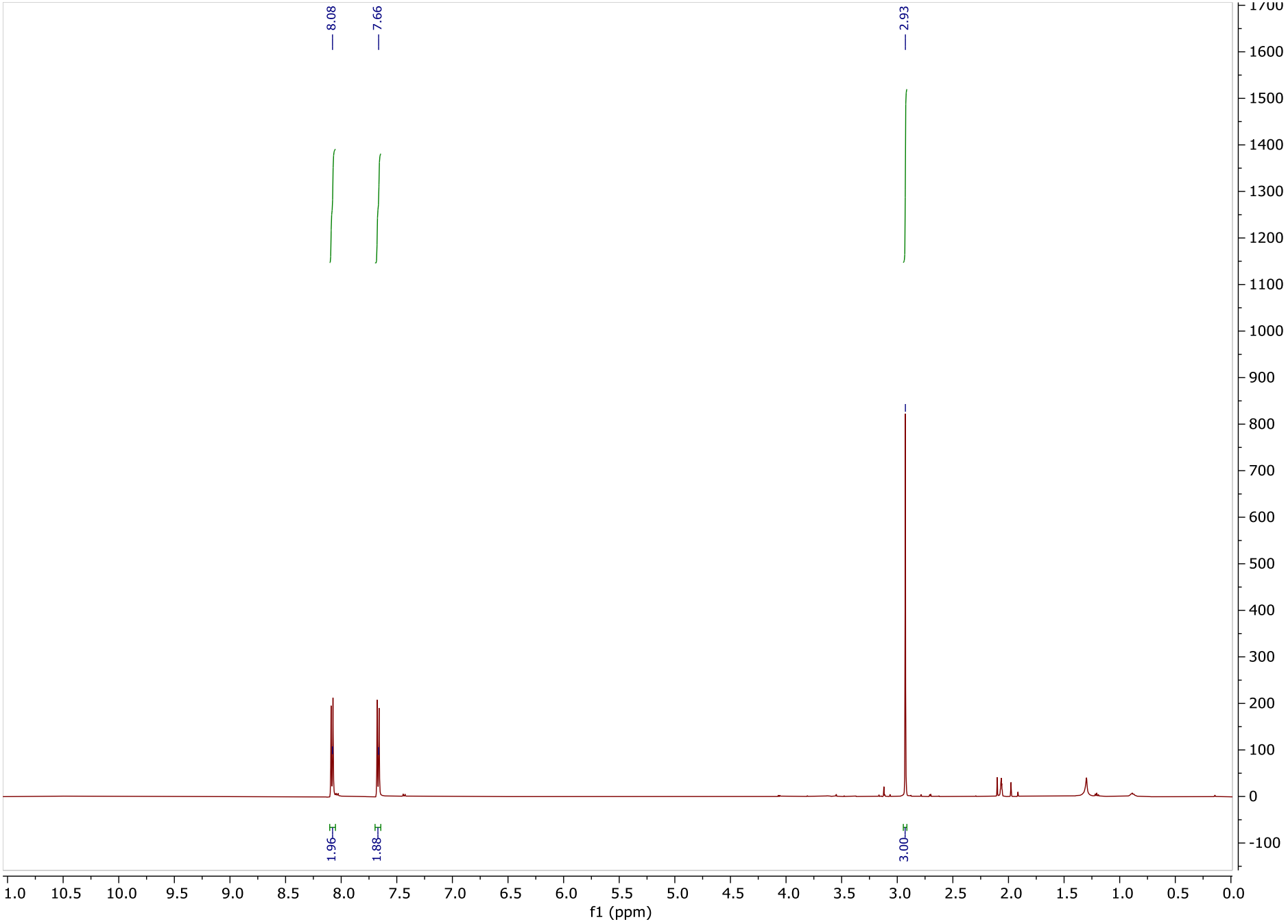
^{1}H NMR of 3j, acetone, 500 MHz



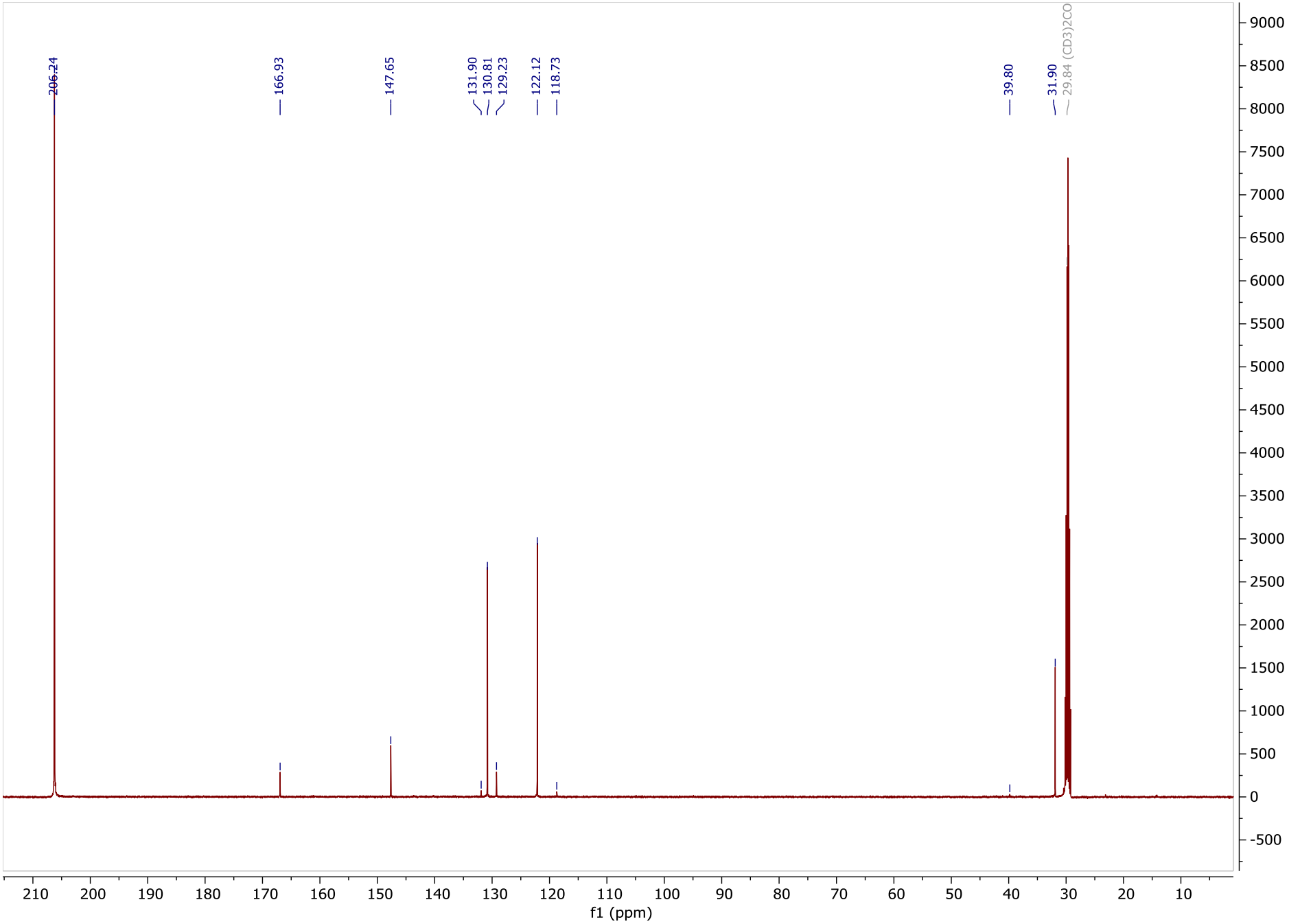
^{13}C NMR of 3j, acetone, 126 MHz



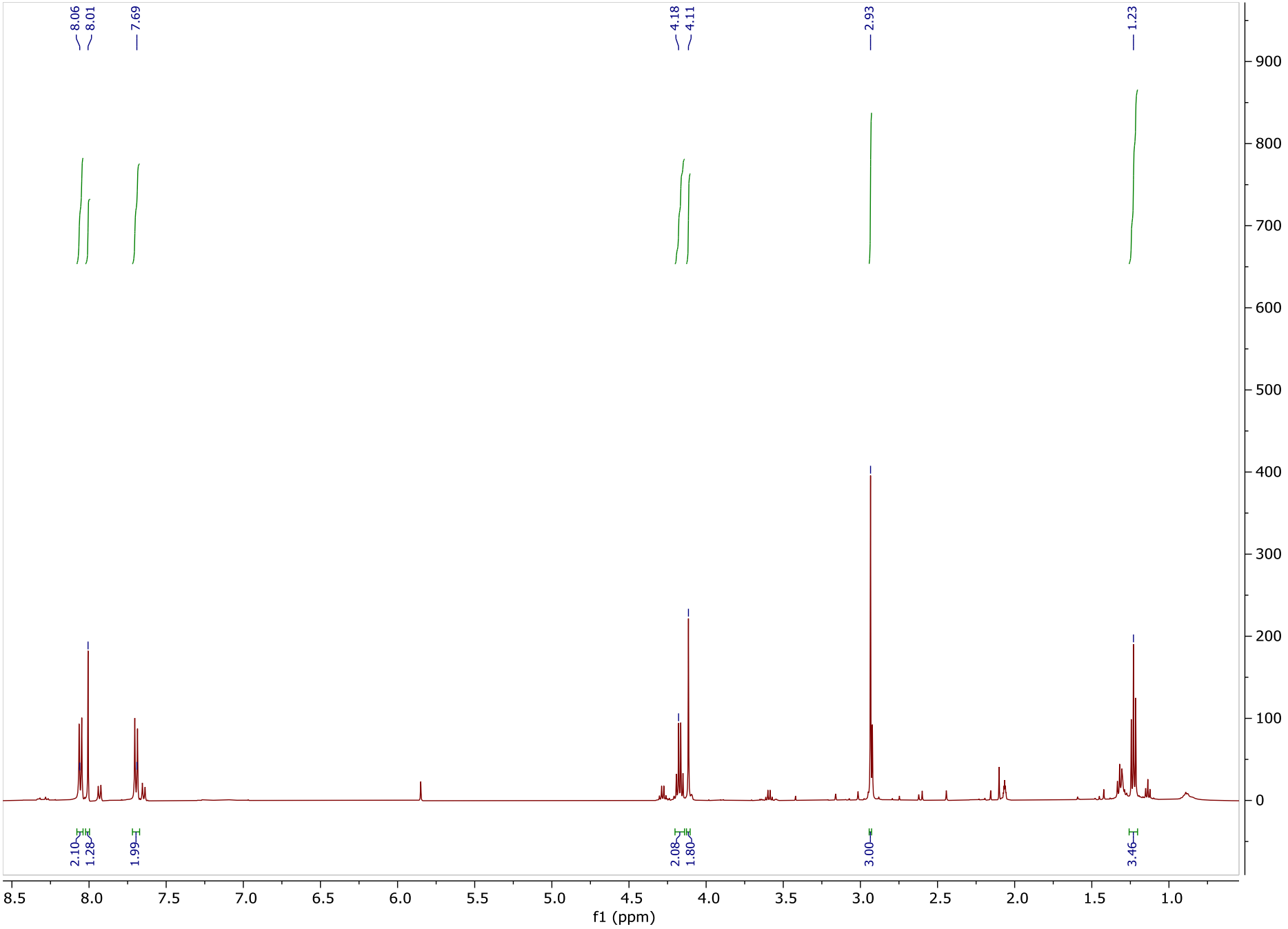
^{1}H NMR of 3k, acetone, 500 MHz



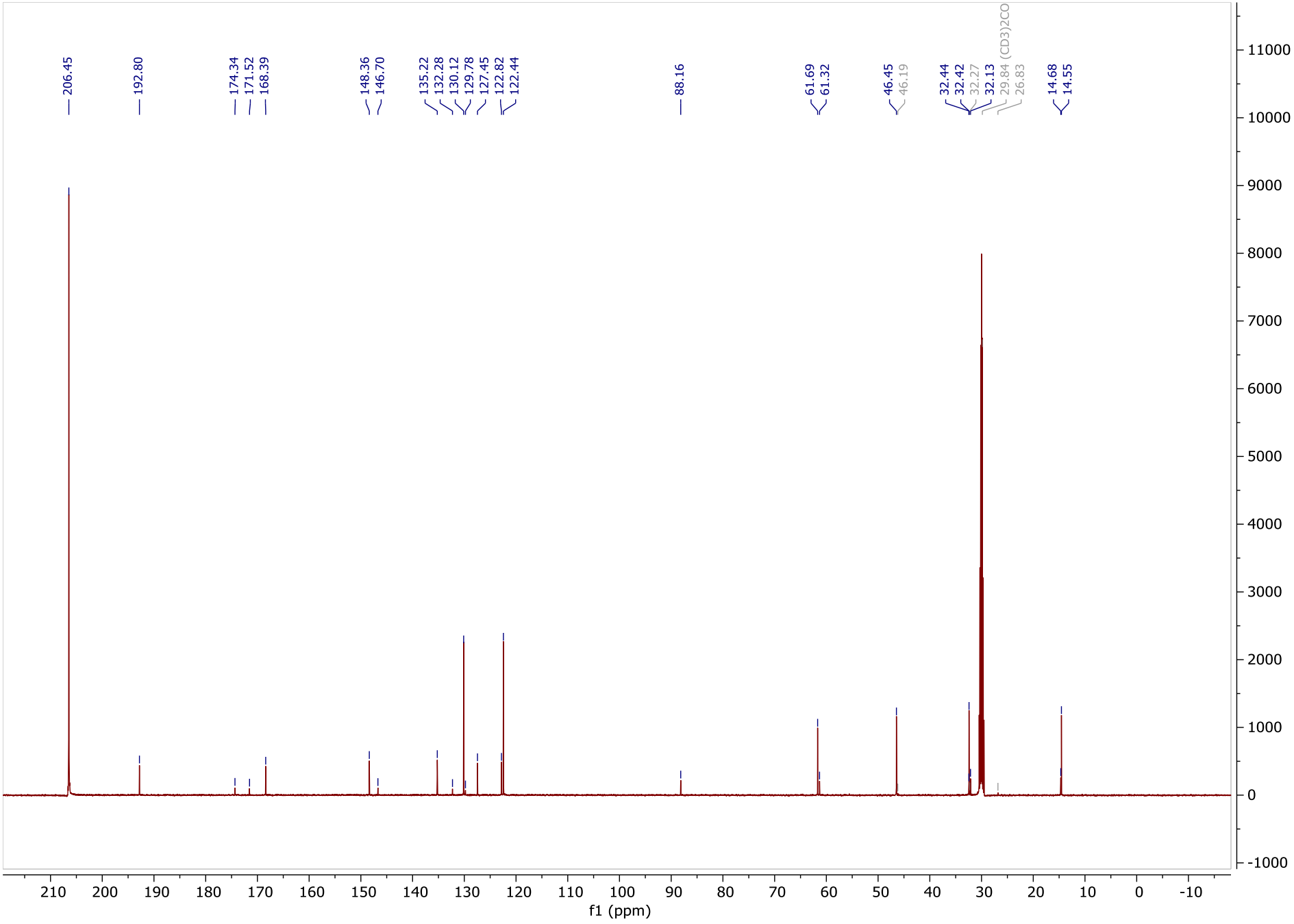
^{13}C NMR of 3k, acetone, 126 MHz



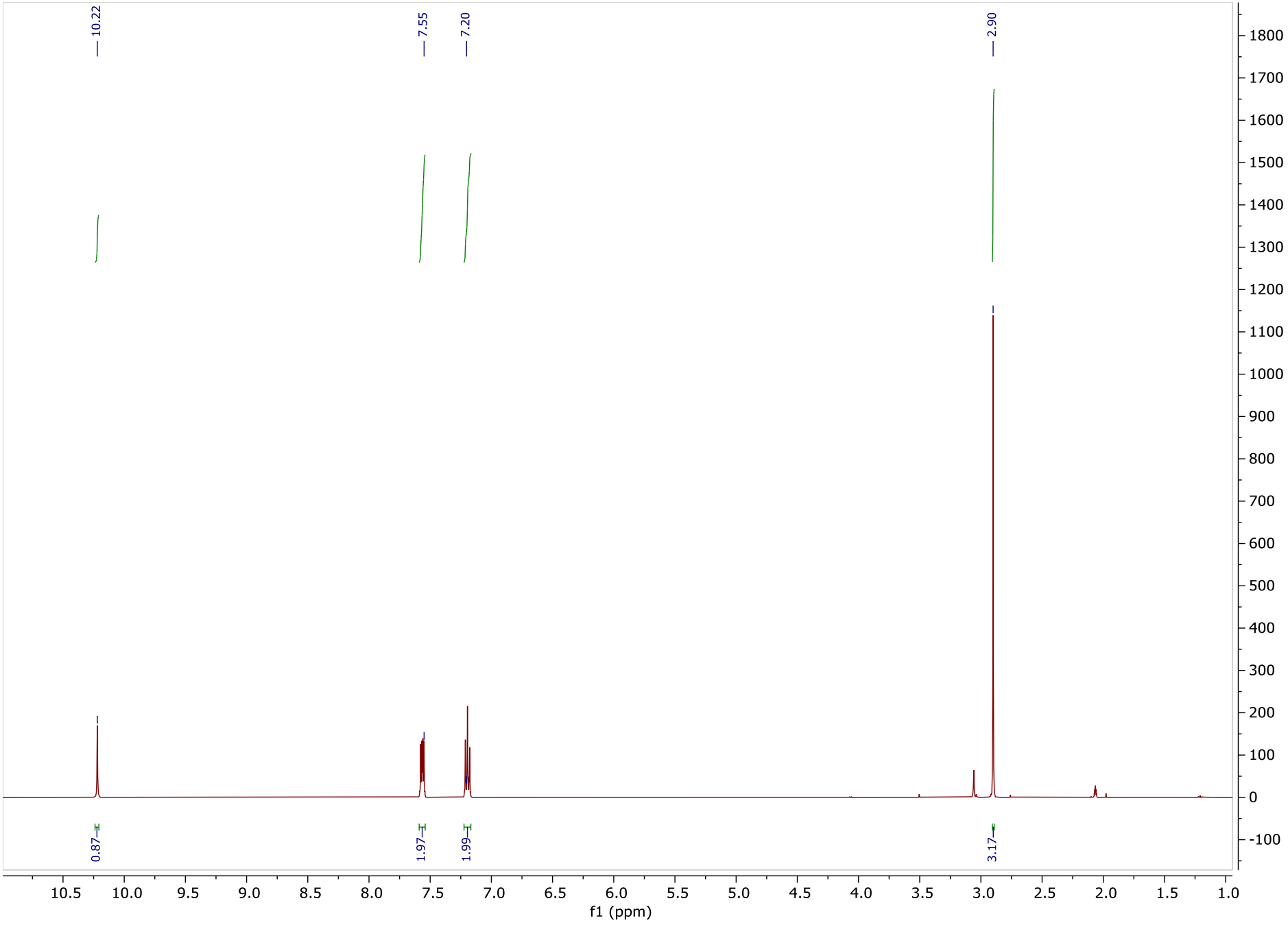
^{1}H NMR of 3l, acetone, 500 MHz



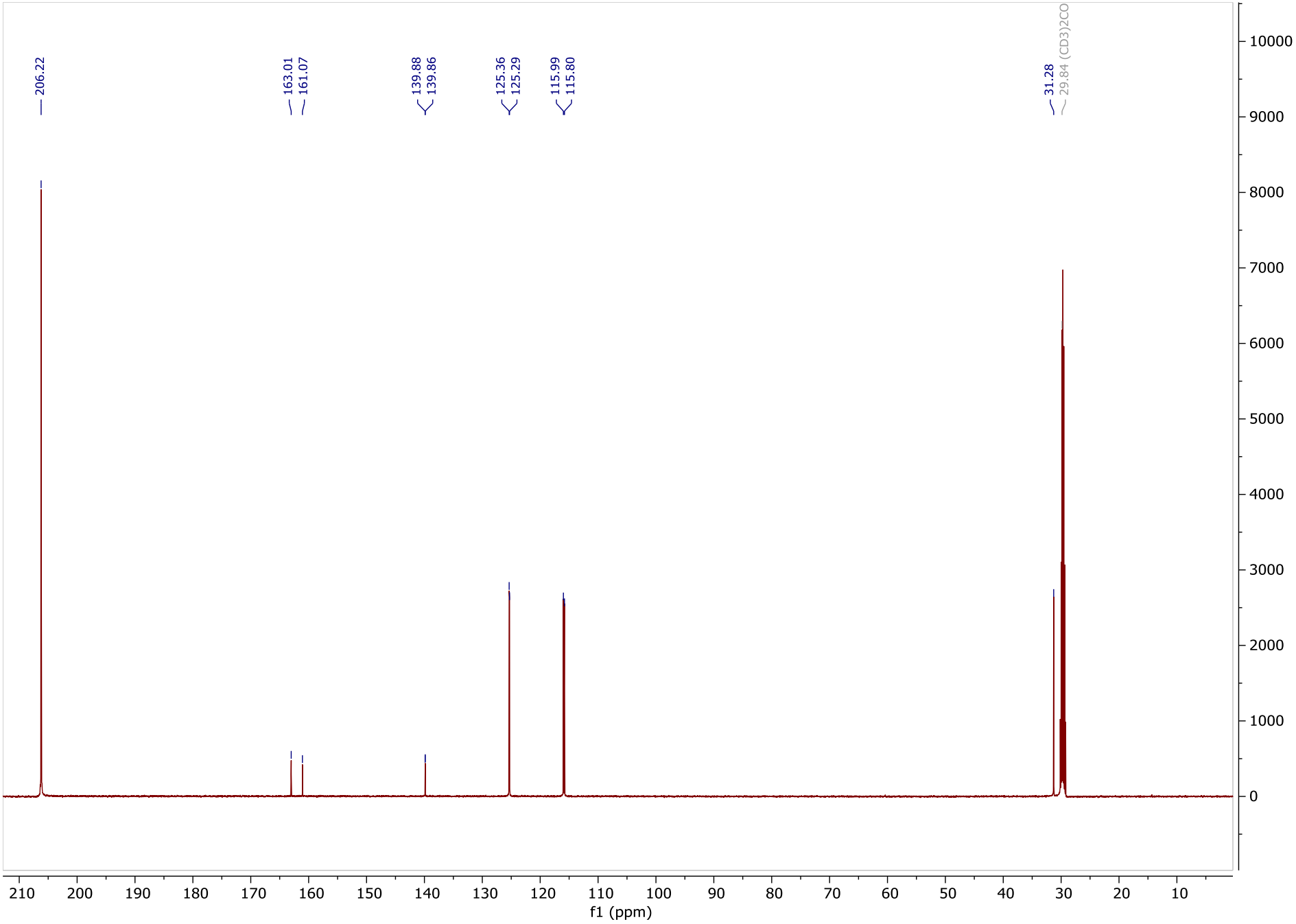
^{13}C NMR of 3l, acetone, 126 MHz



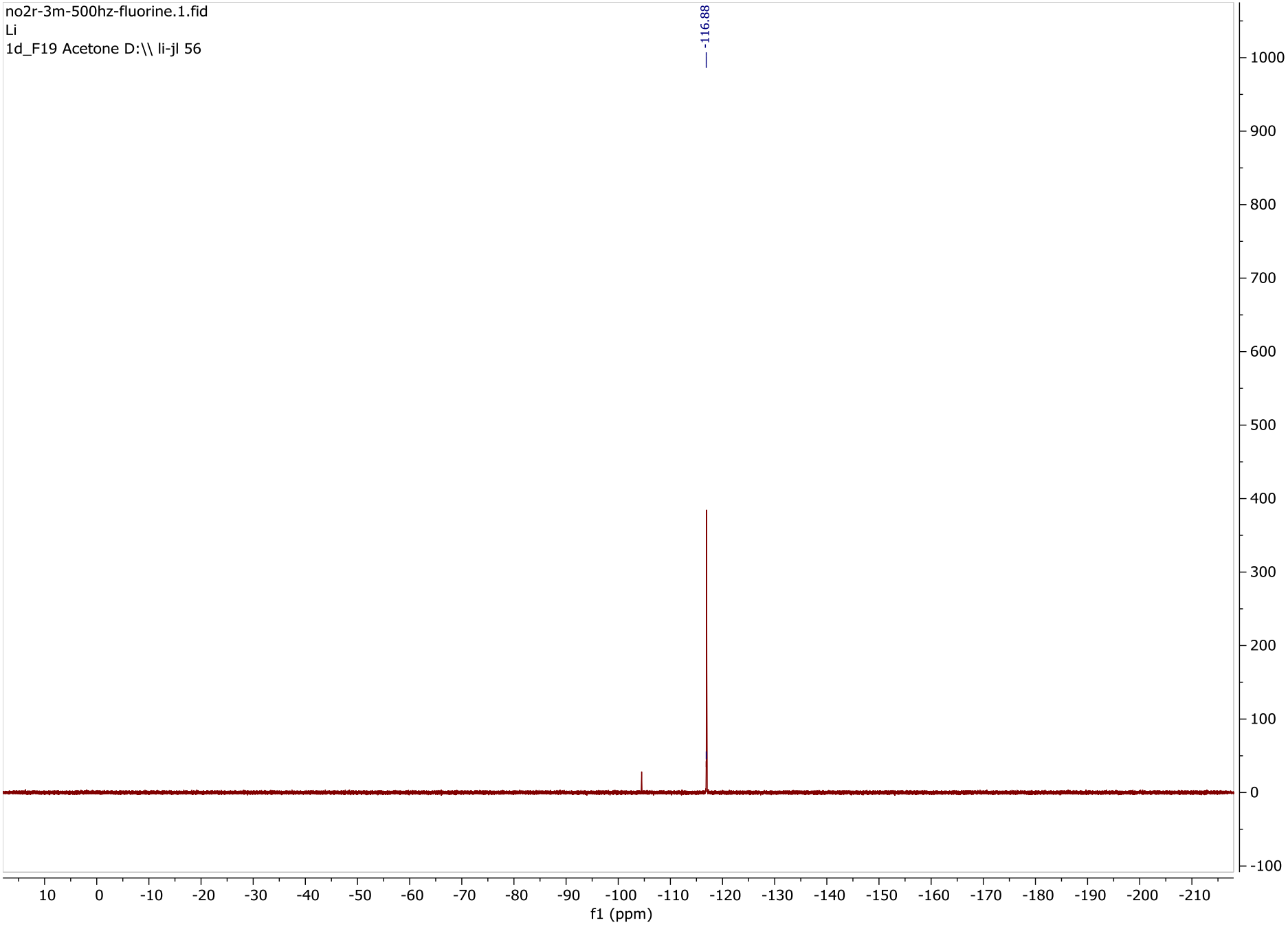
^{1}H NMR of 3m, acetone, 500 MHz



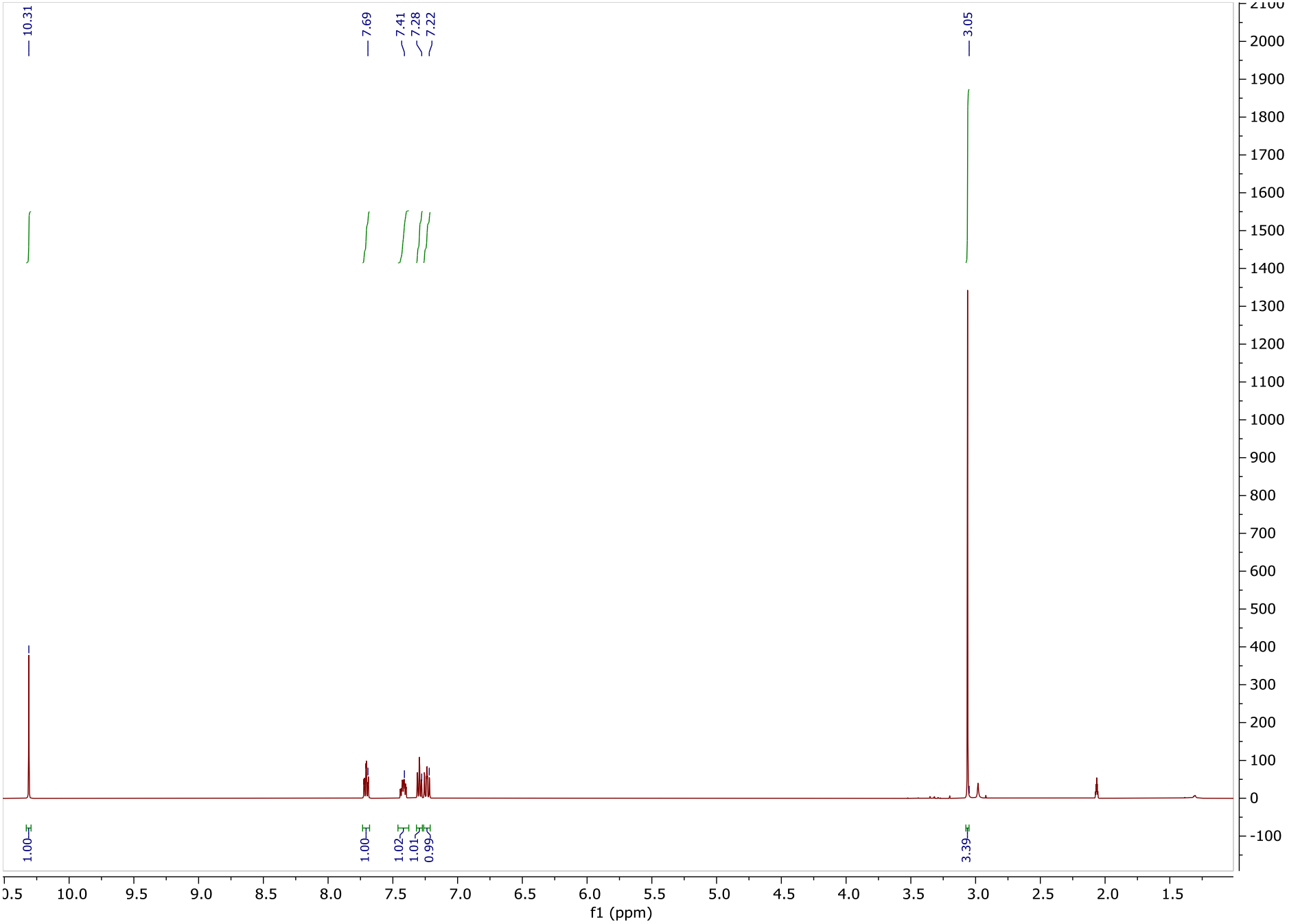
^{13}C NMR of 3m, acetone, 126 MHz



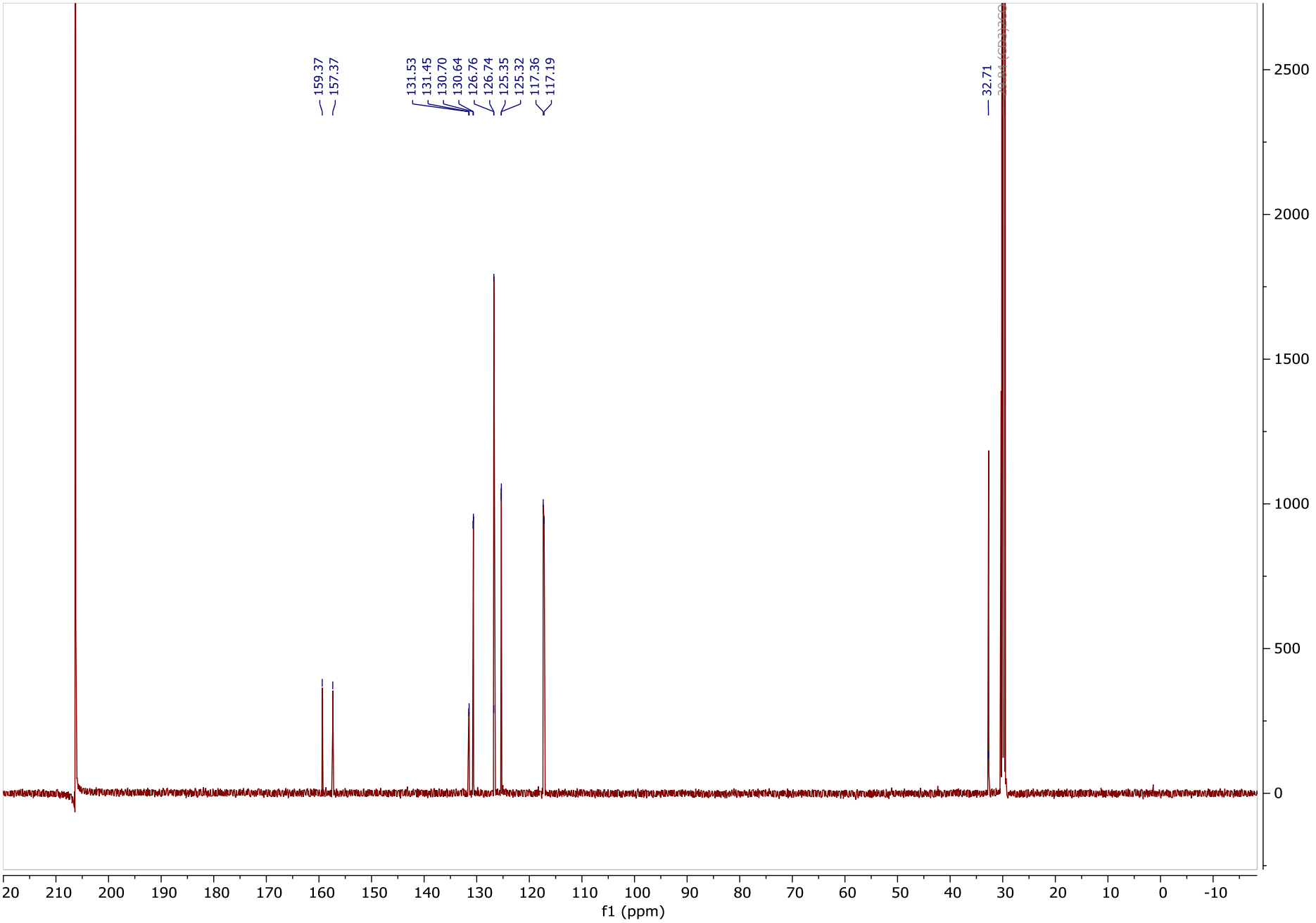
^{19}F NMR of 3m, acetone, 471 MHz



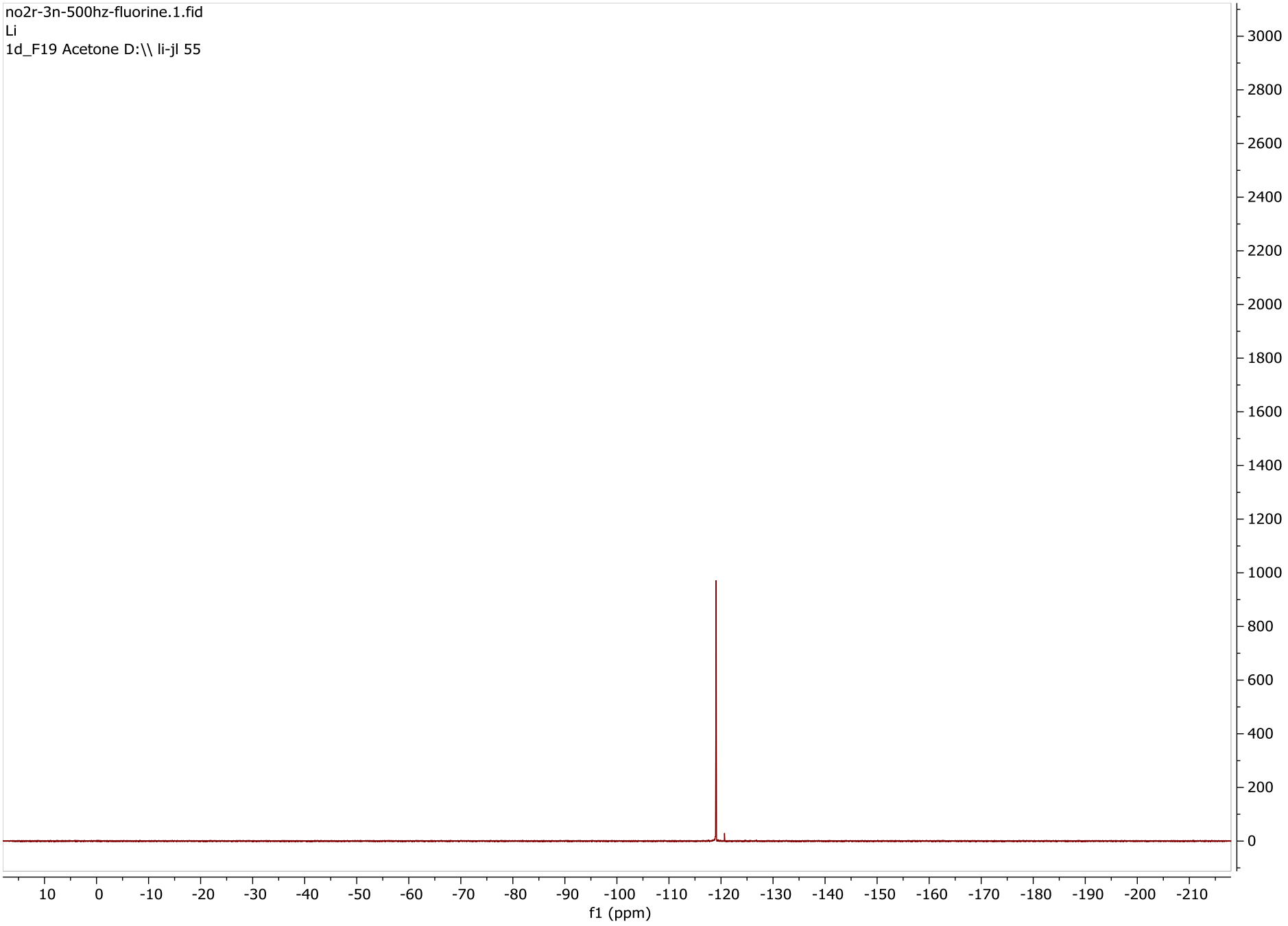
^{1}H NMR of 3n, acetone, 500 MHz



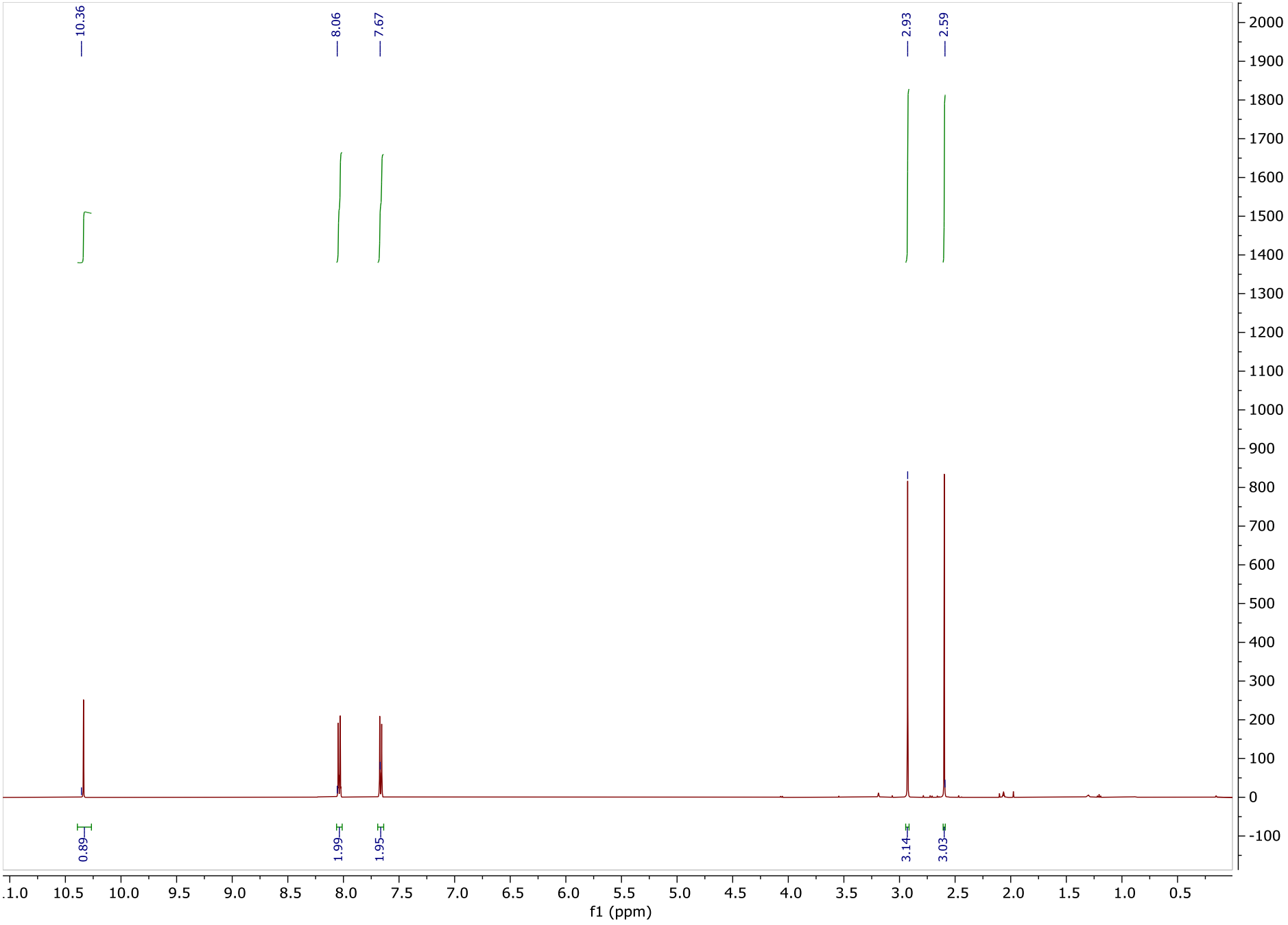
^{13}C NMR of 3n, acetone, 126 MHz



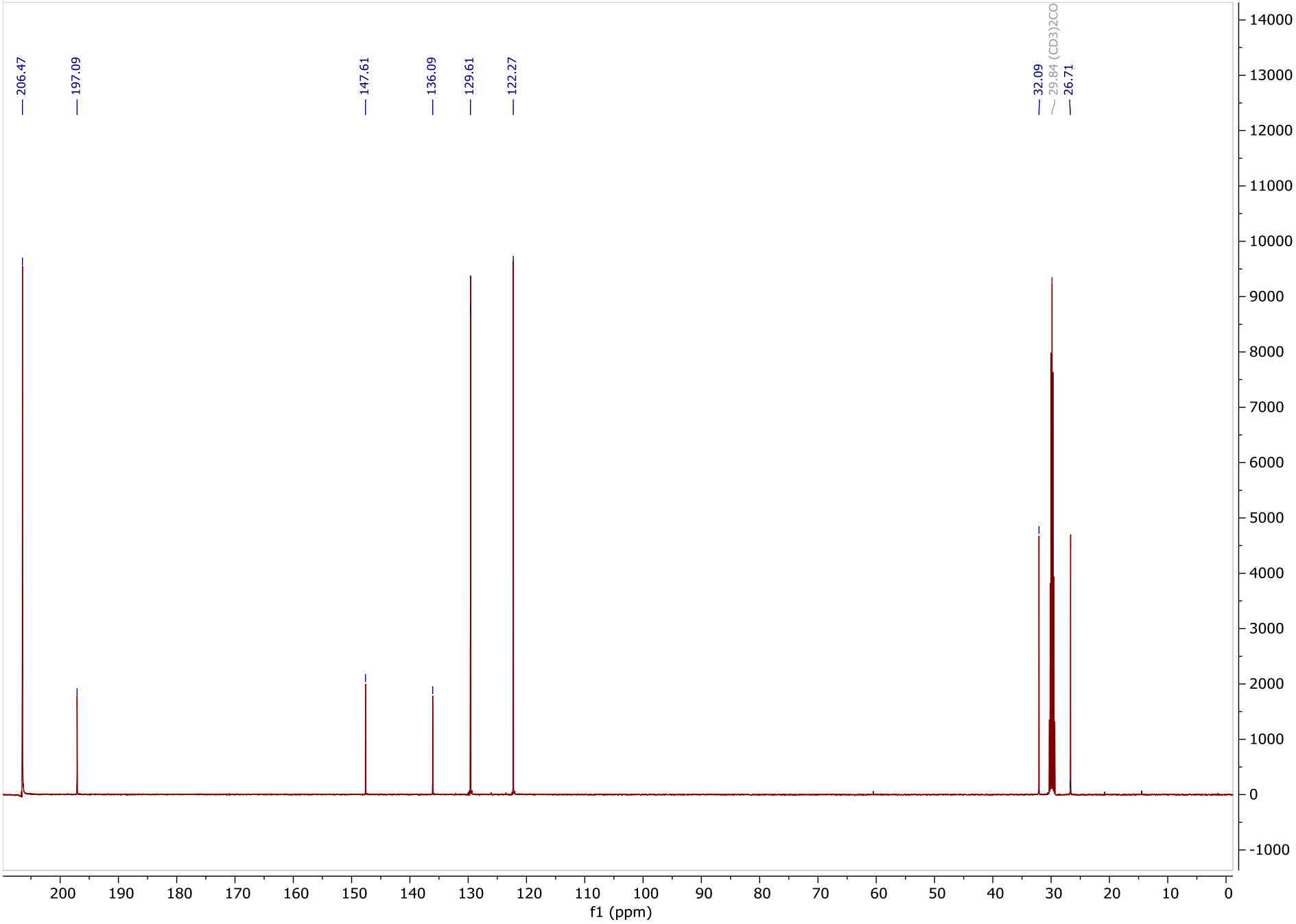
^{19}F NMR of 3n, acetone, 471 MHz



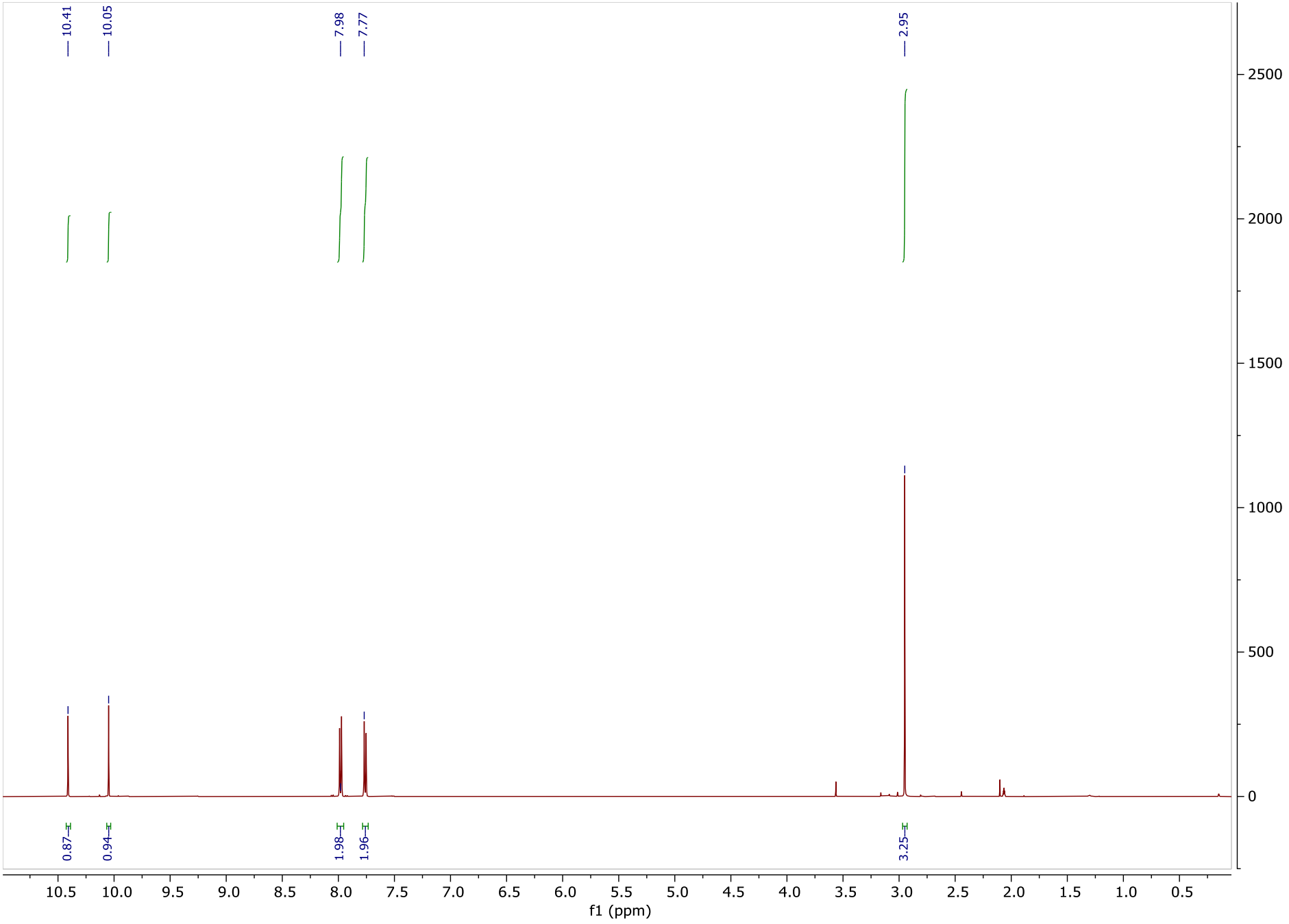
^{1}H NMR of 3o, acetone, 500 MHz



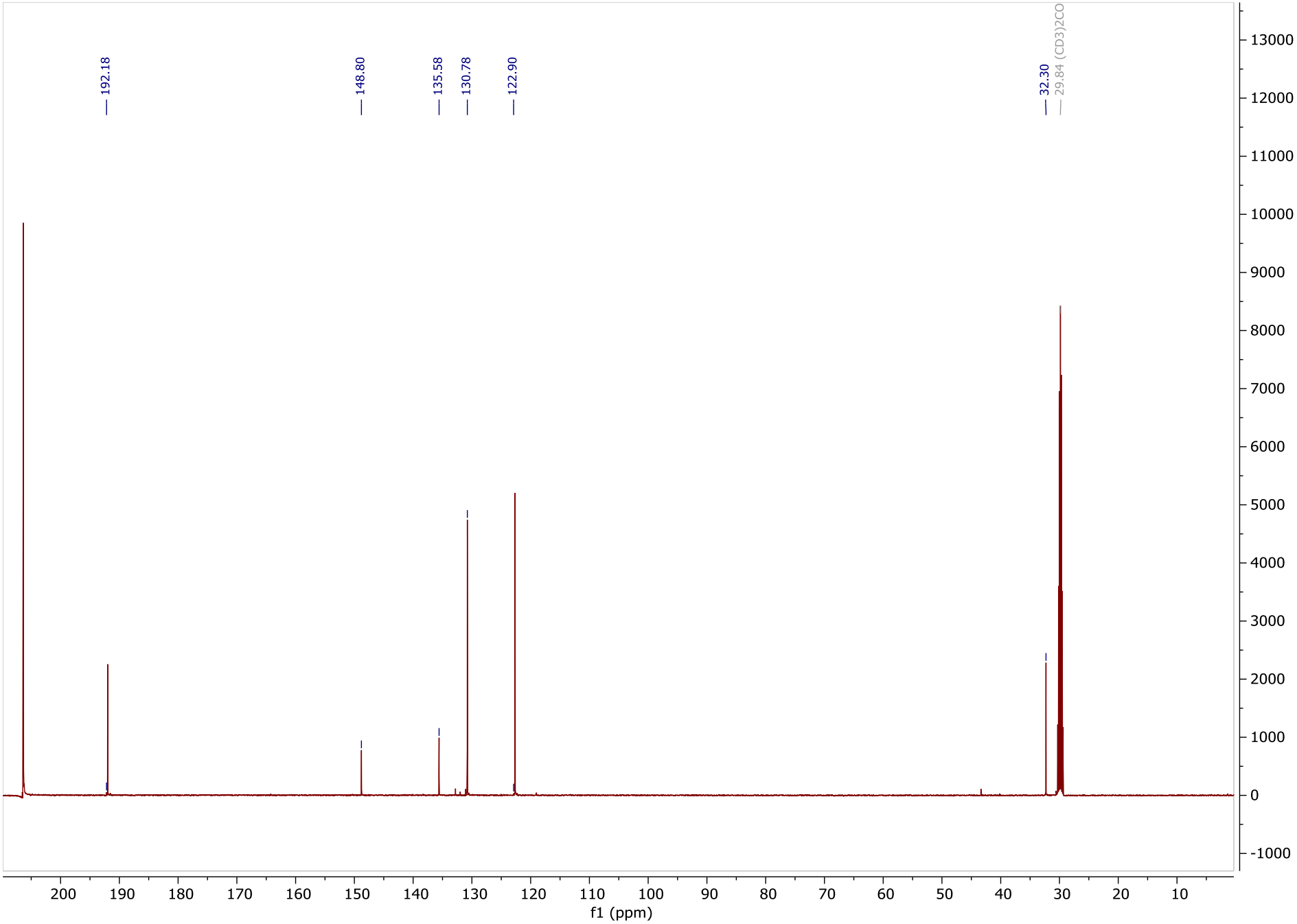
^{13}C NMR of 3o, acetone, 126 MHz



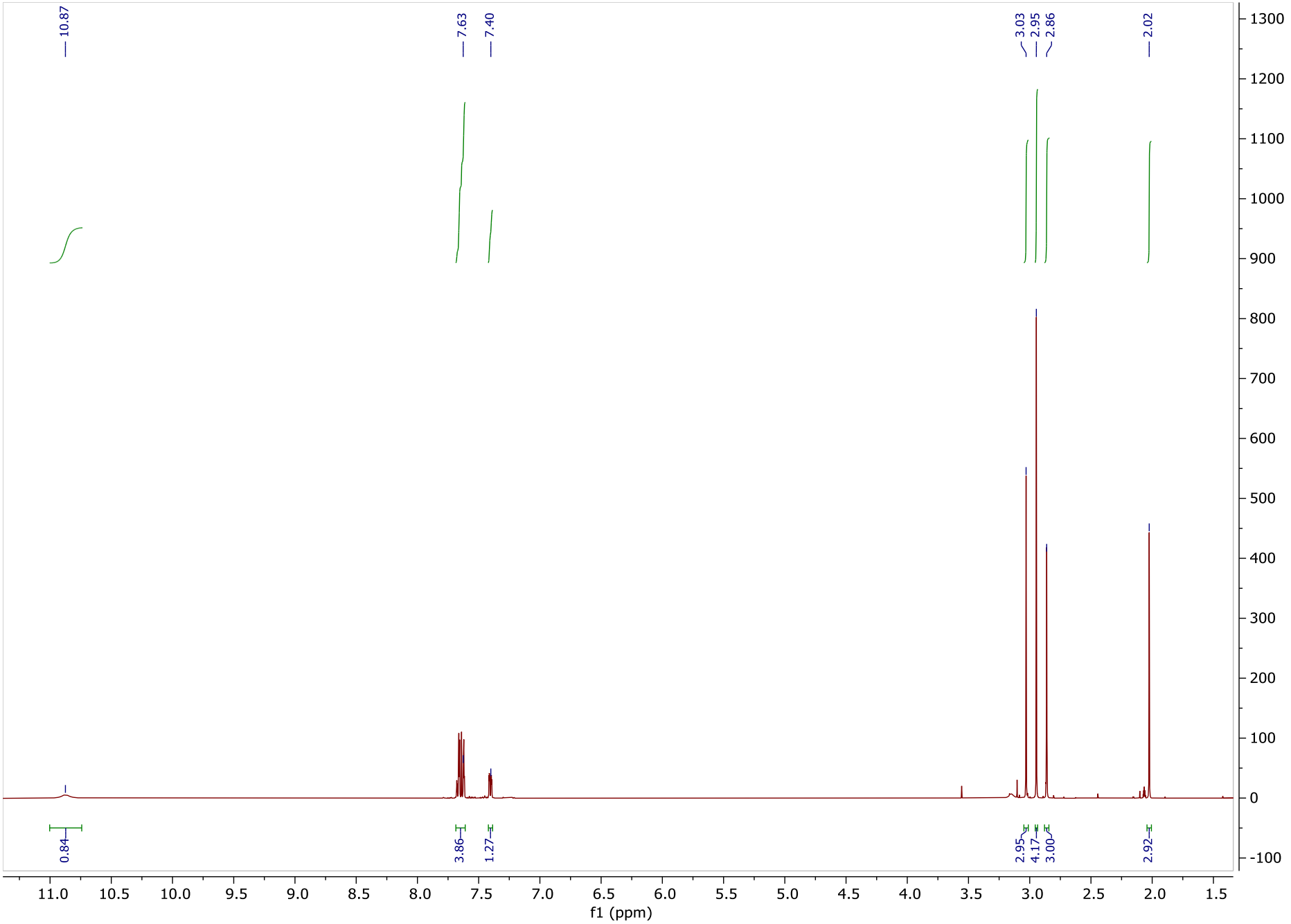
^{1}H NMR of 3p, acetone, 500 MHz



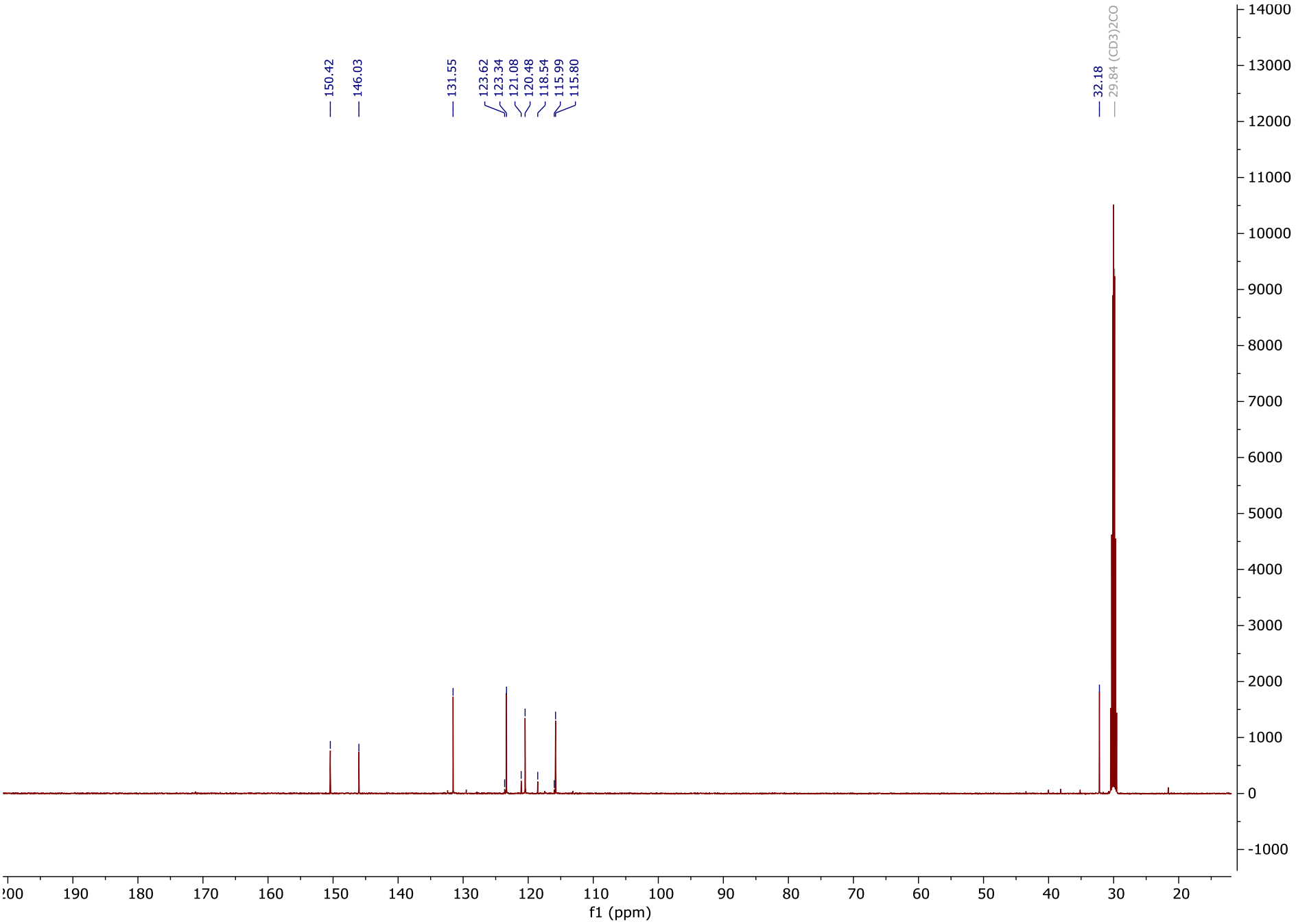
^{13}C NMR of 3p, acetone, 126 MHz



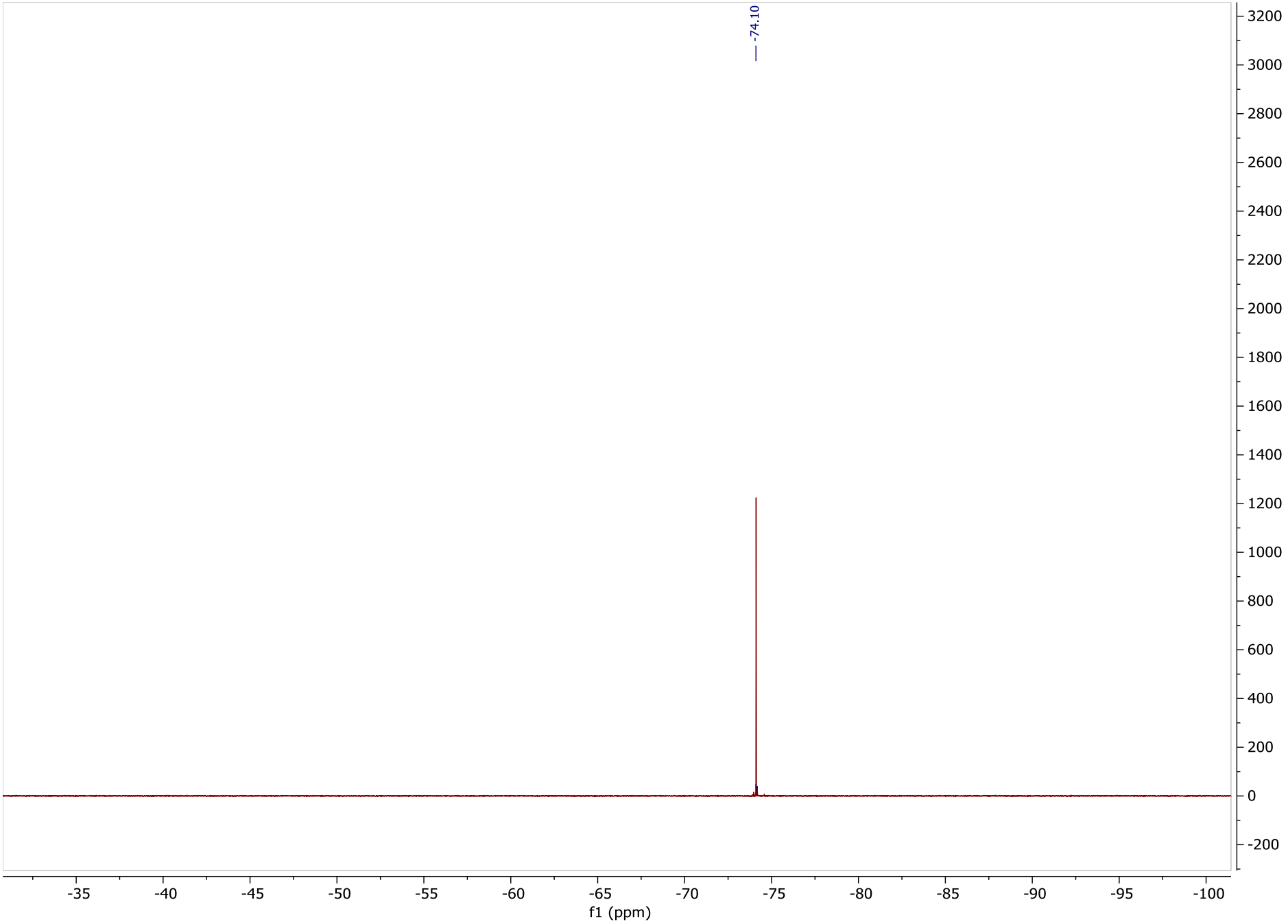
^{1}H NMR of 3q, acetone, 500 MHz



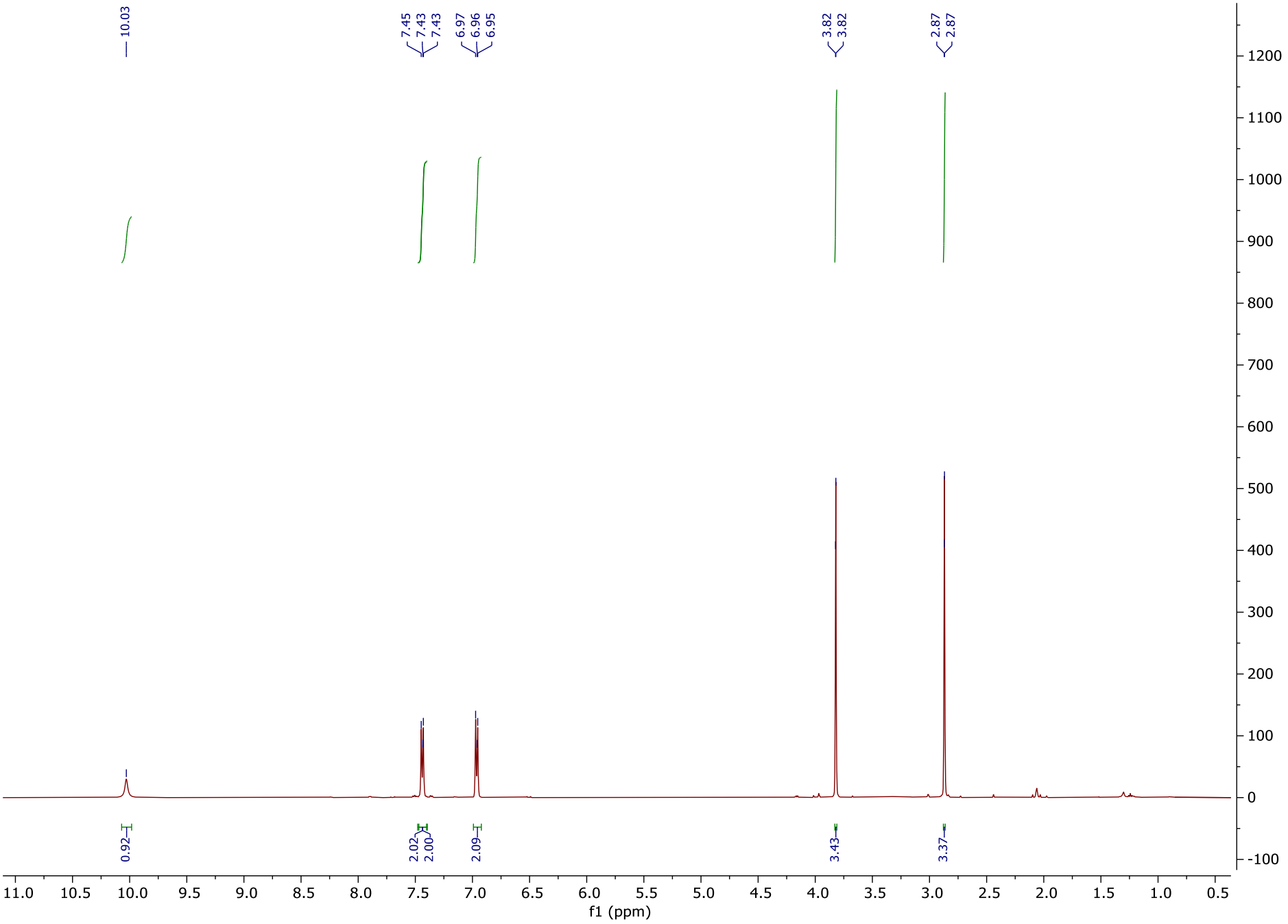
^{13}C NMR of 3q, acetone, 126 MHz



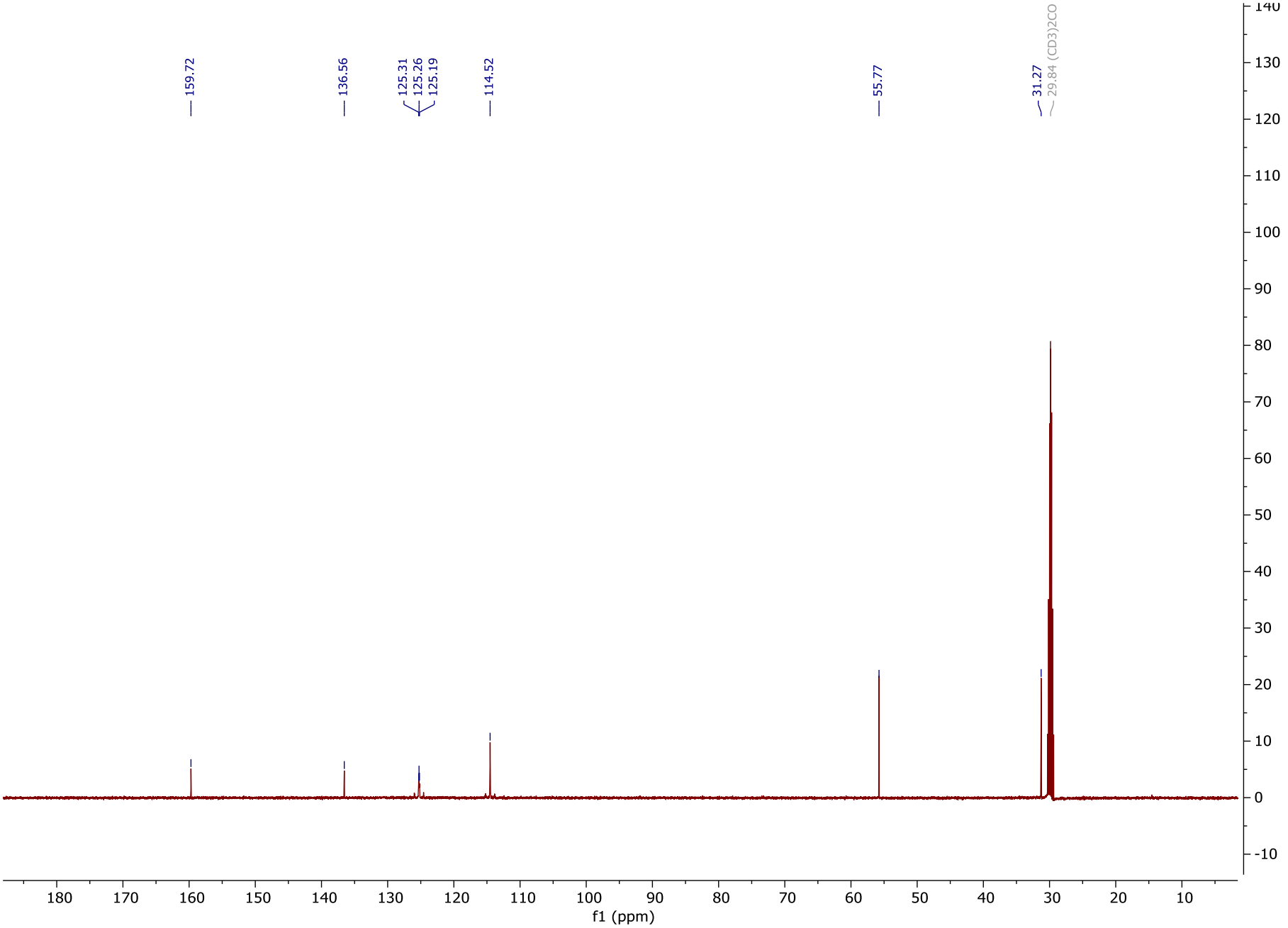
^{19}F NMR of 3q, acetone, 471 MHz



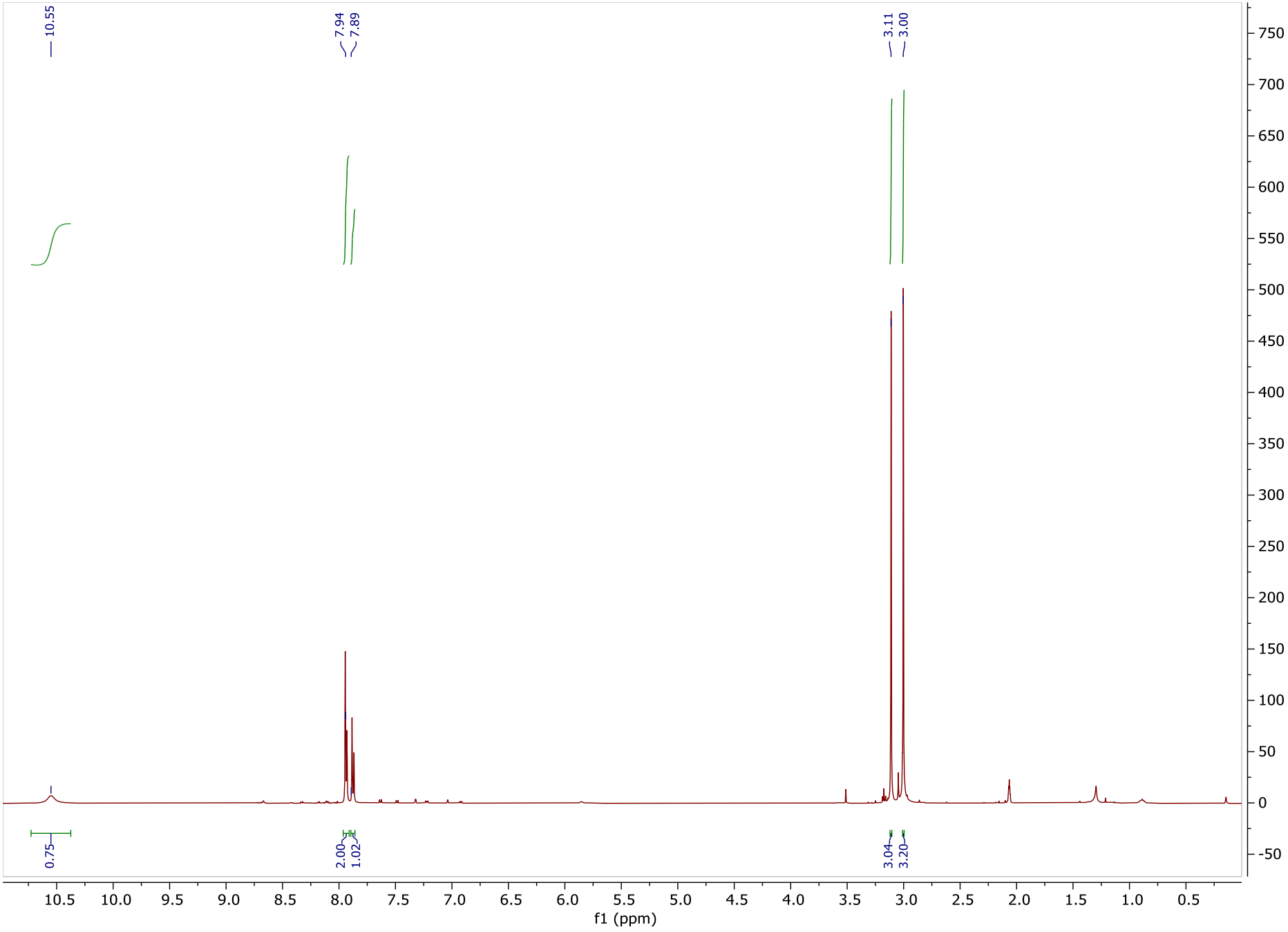
^{1}H NMR of 3r, acetone, 500 MHz



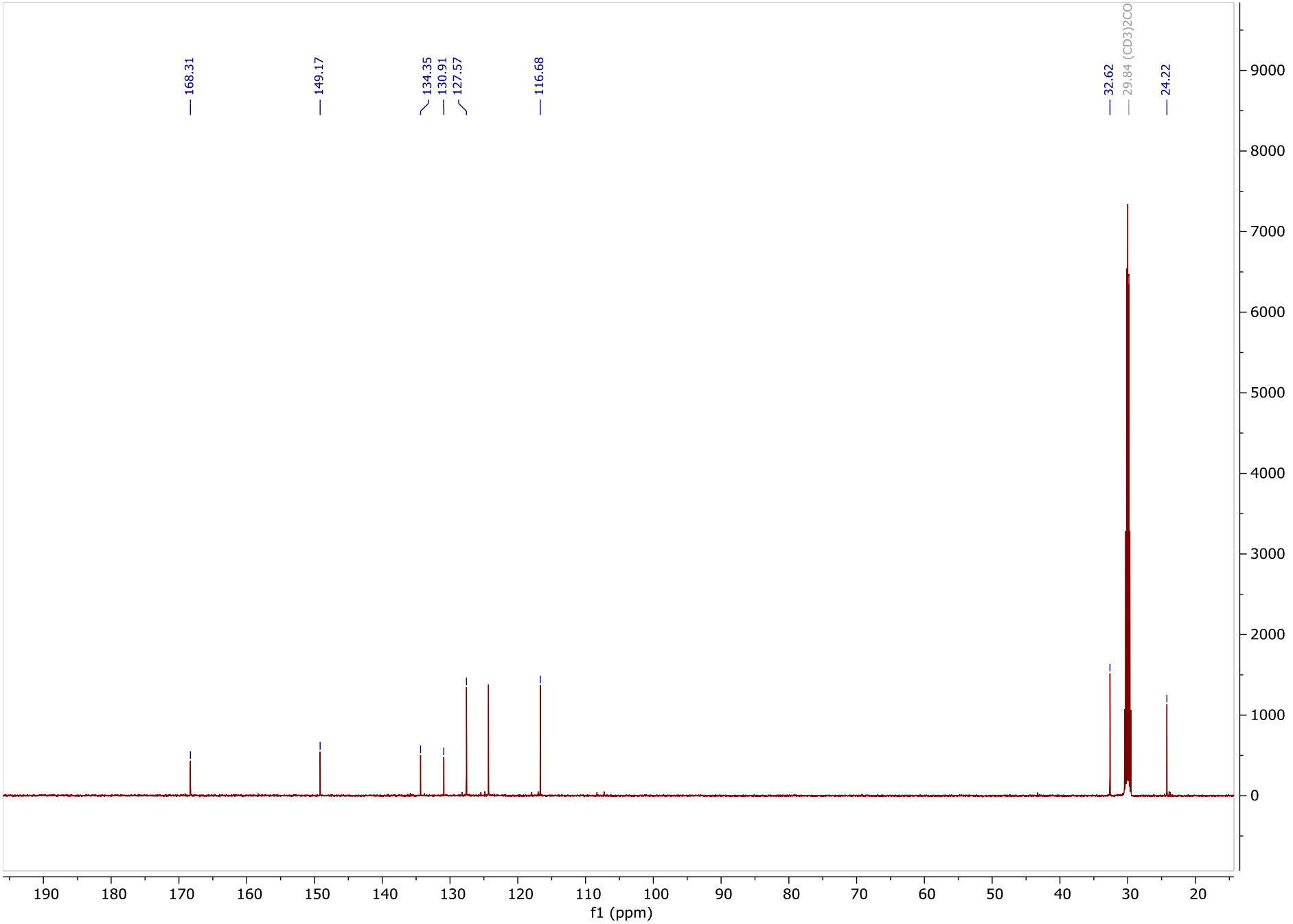
^{13}C NMR of 3r, acetone, 126 MHz



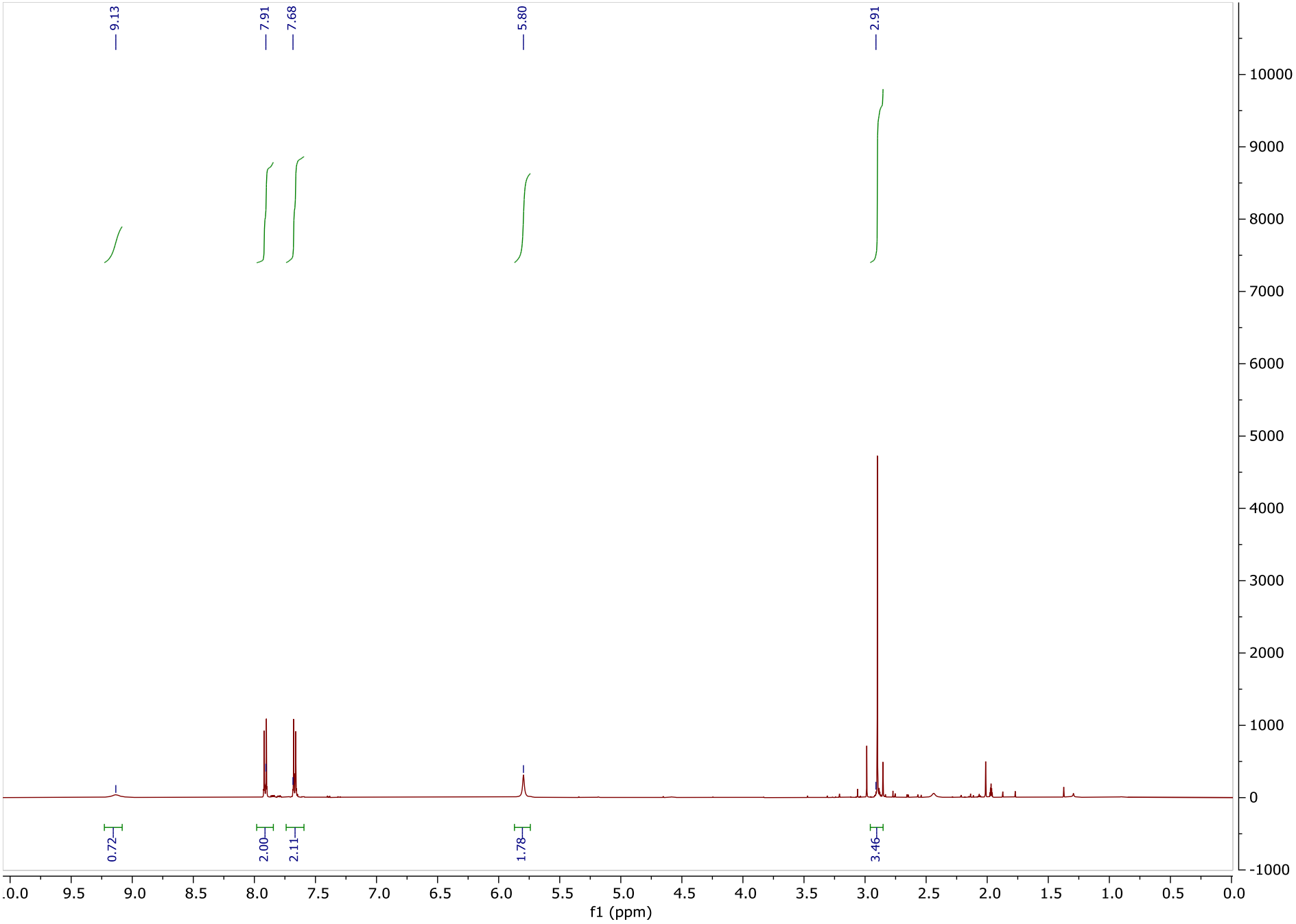
^{1}H NMR of 3s, acetone, 500 MHz



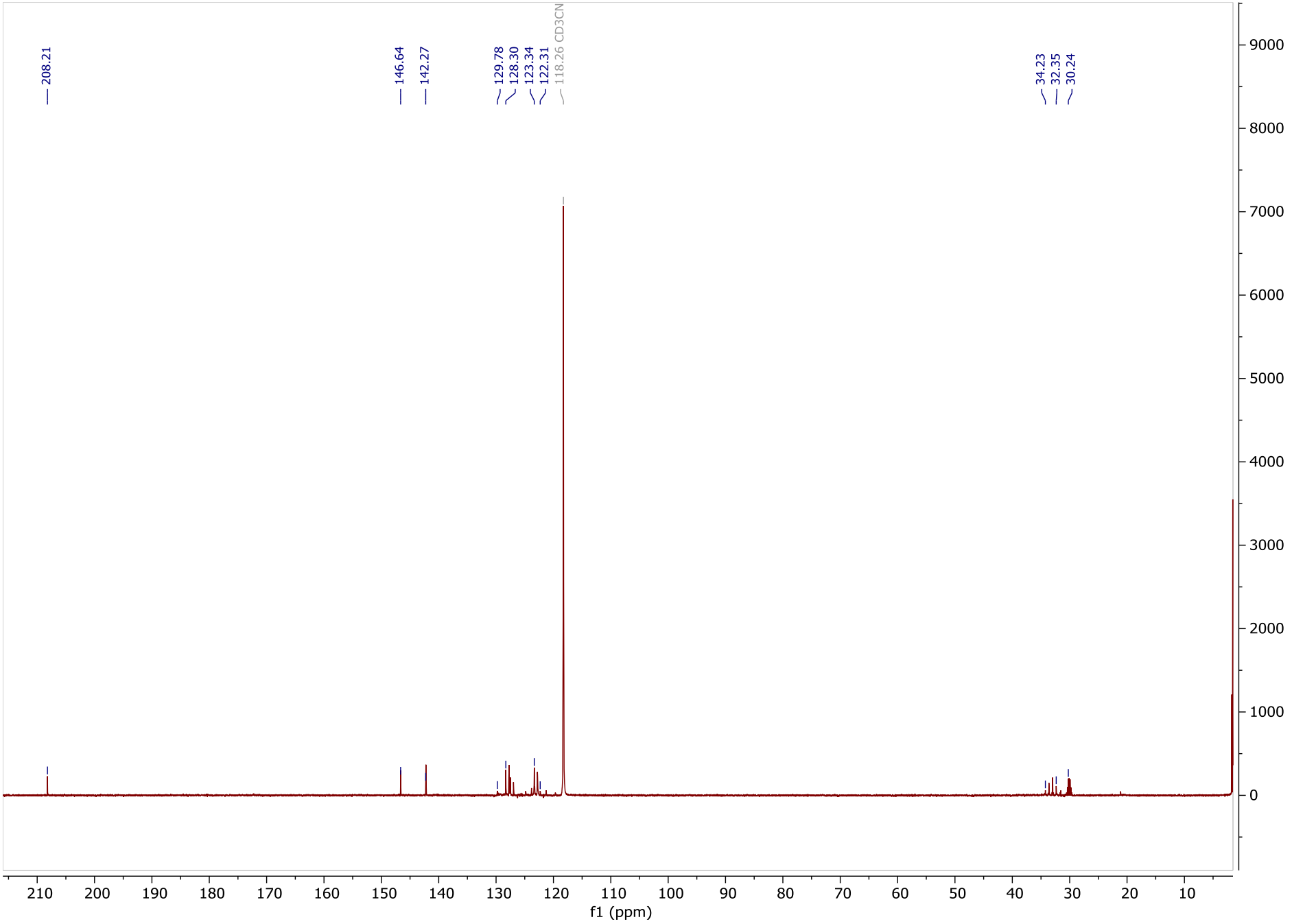
^{13}C NMR of 3s, acetone, 126 MHz



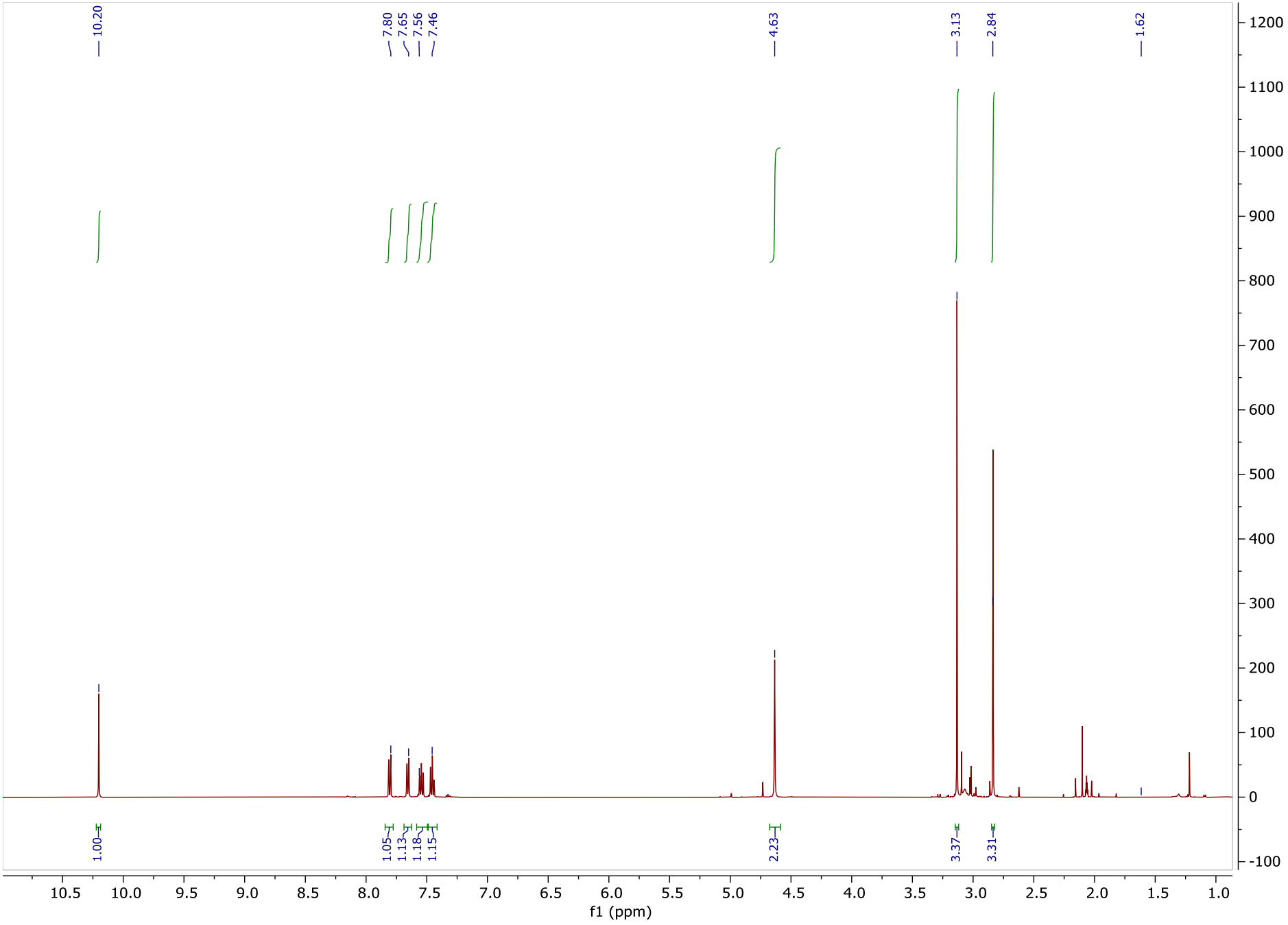
^{1}H NMR of 3t, MeCN/acetone, 500 MHz



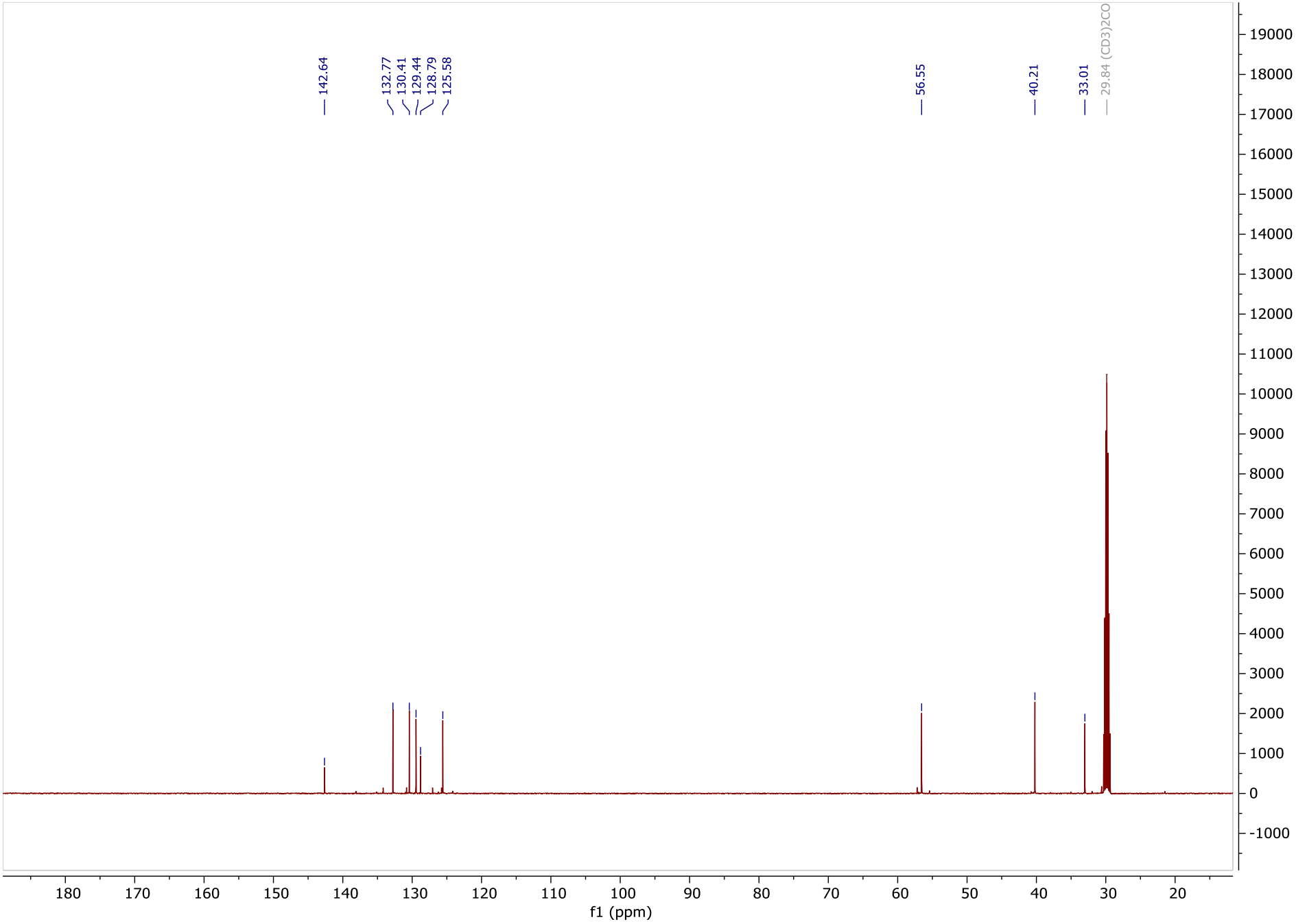
^{13}C NMR of 3t, MeCN/acetone, 126 MHz



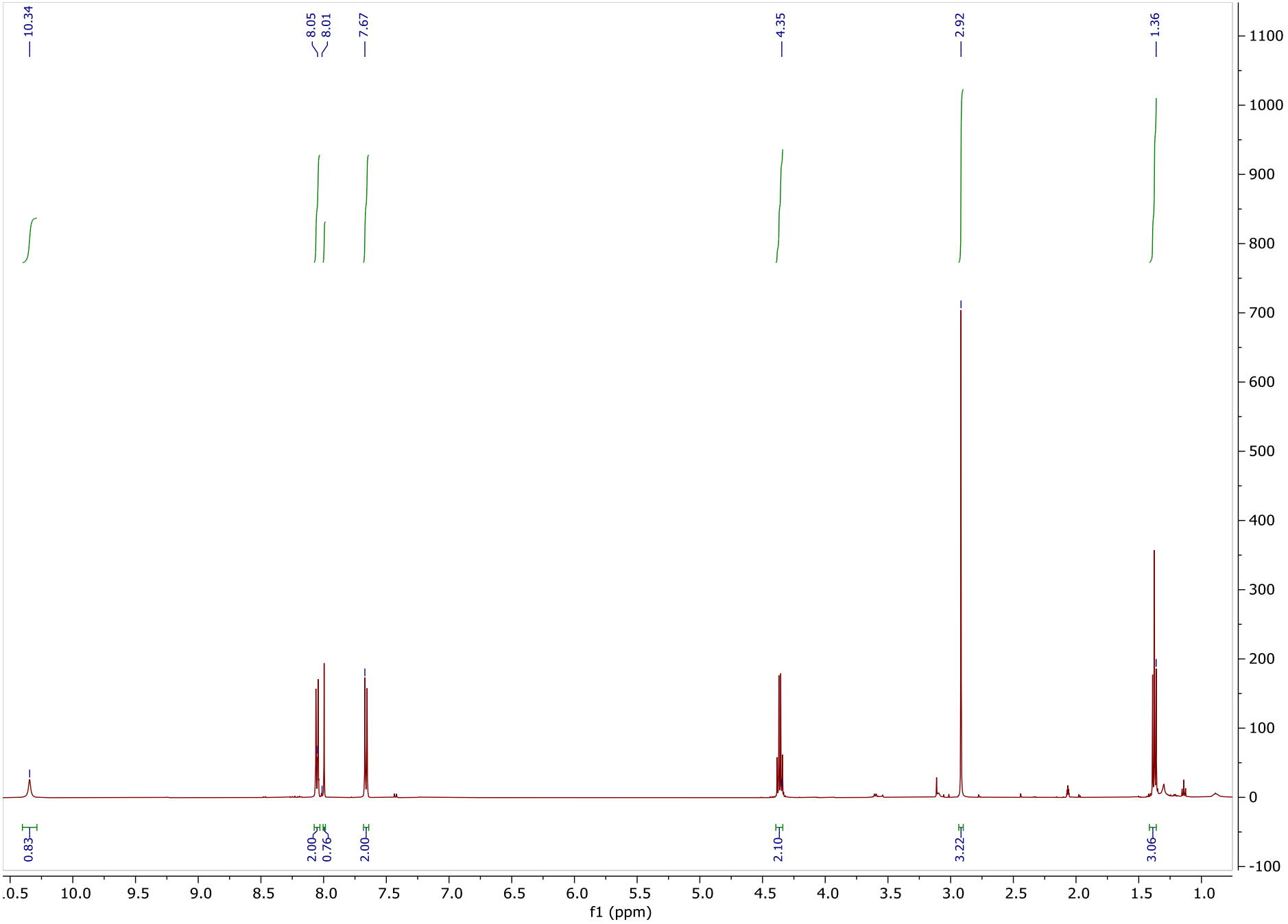
^{1}H NMR of 3u, acetone, 500 MHz



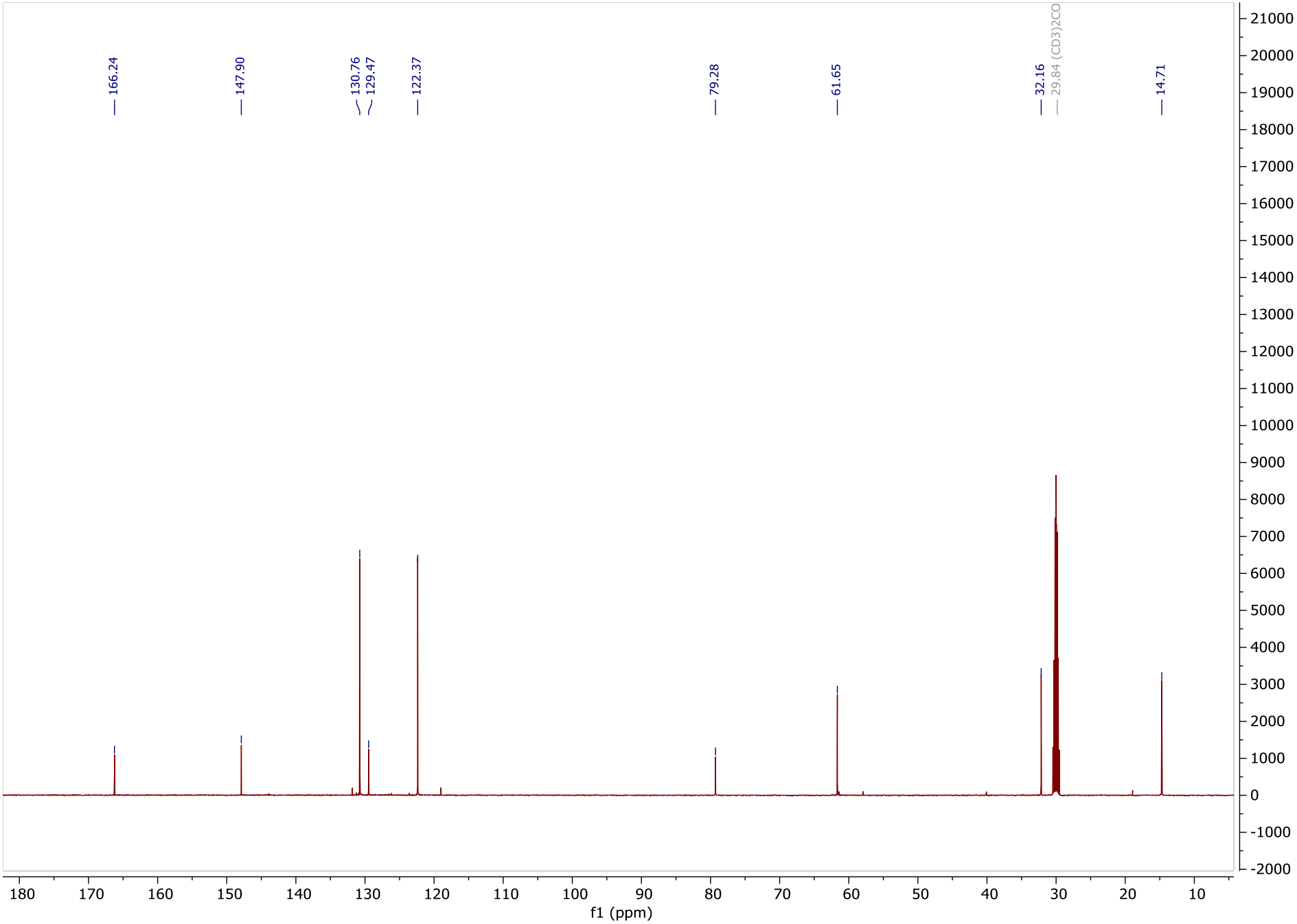
^{13}C NMR of 3u, acetone, 126 MHz



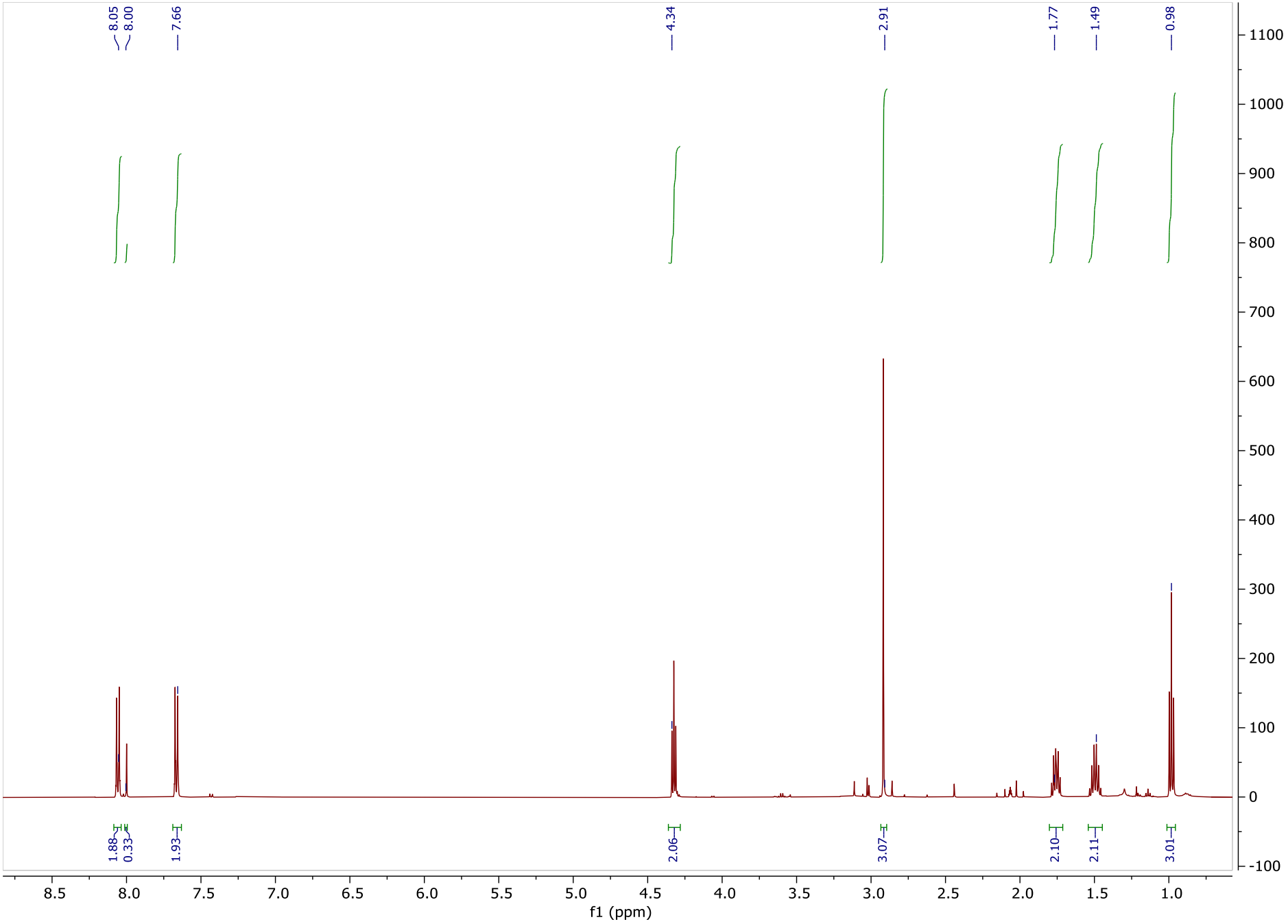
^{1}H NMR of 3v, acetone, 500 MHz



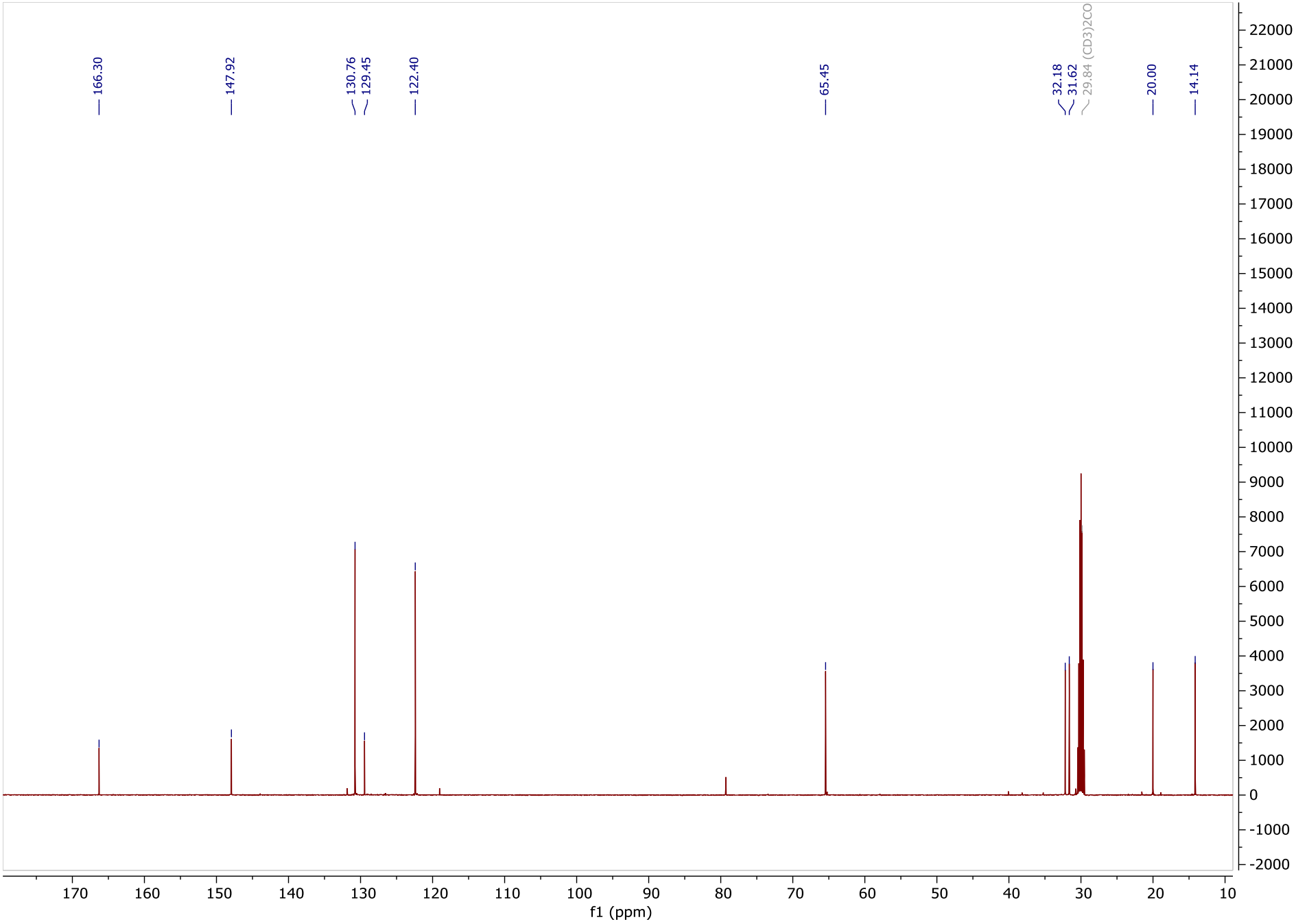
^{13}C NMR of 3v, acetone, 126 MHz



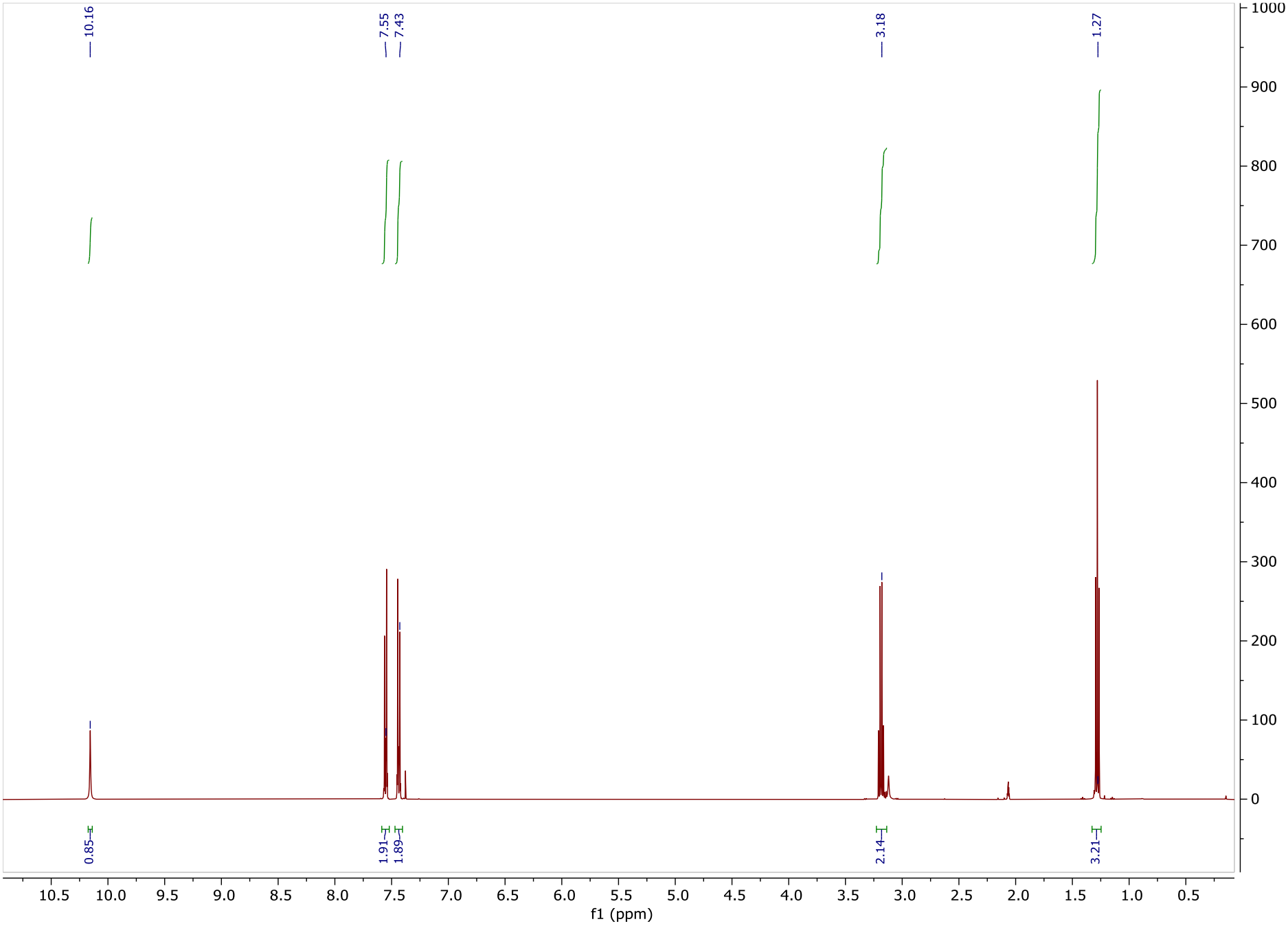
^{1}H NMR of 3w, acetone, 500 MHz



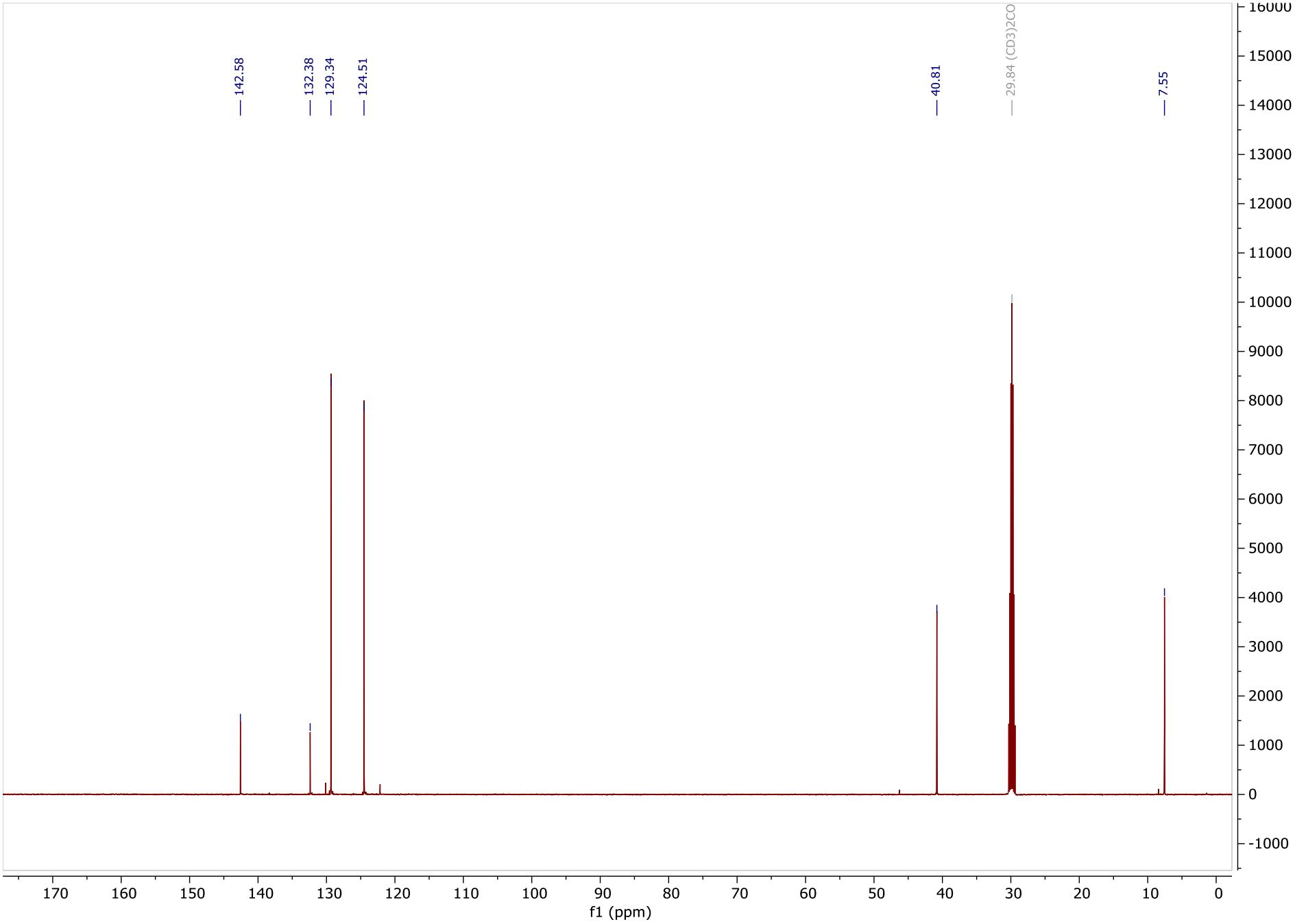
^{13}C NMR of 3w, acetone, 126 MHz



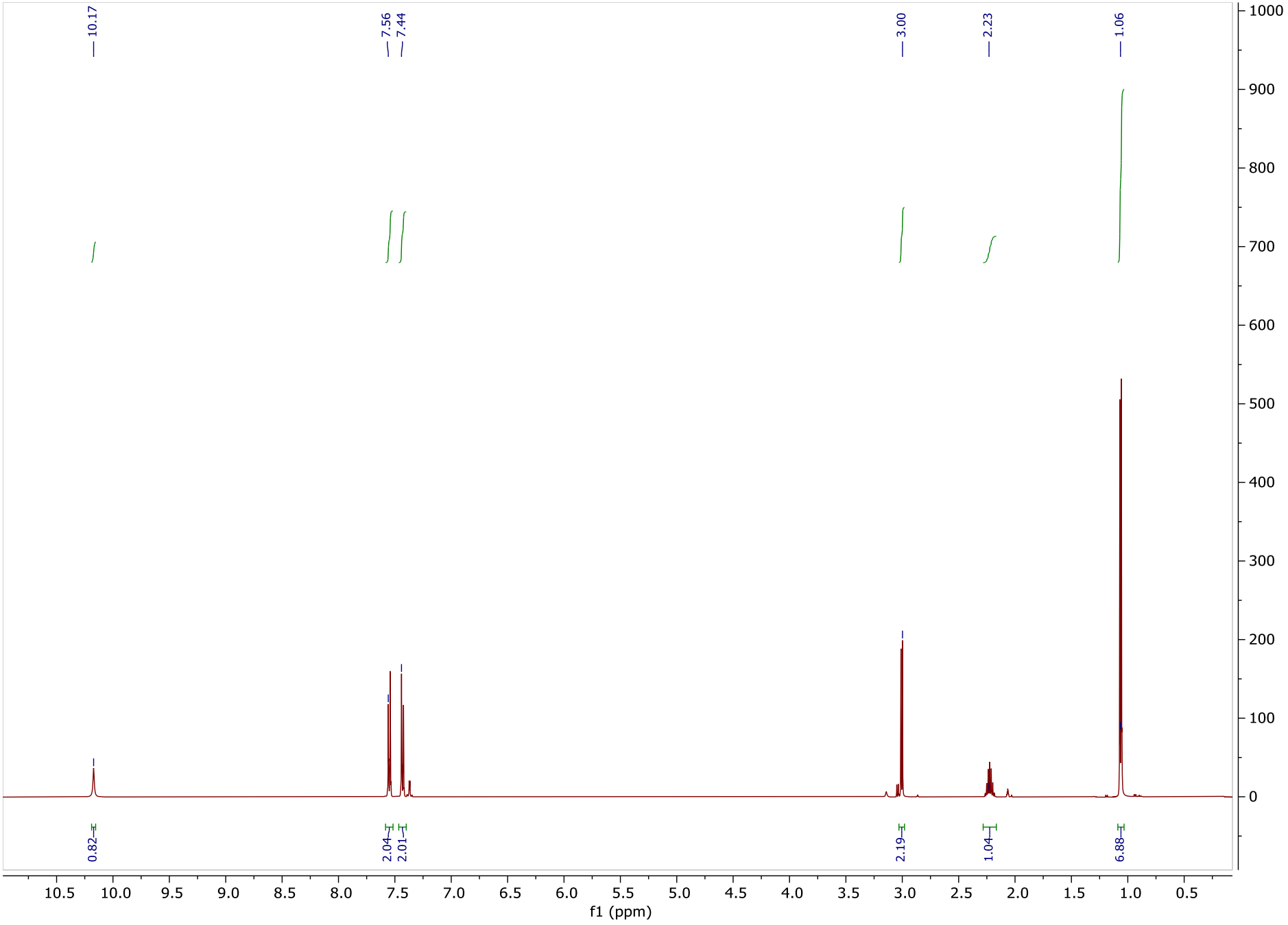
^{1}H NMR of 4a, acetone, 500 MHz



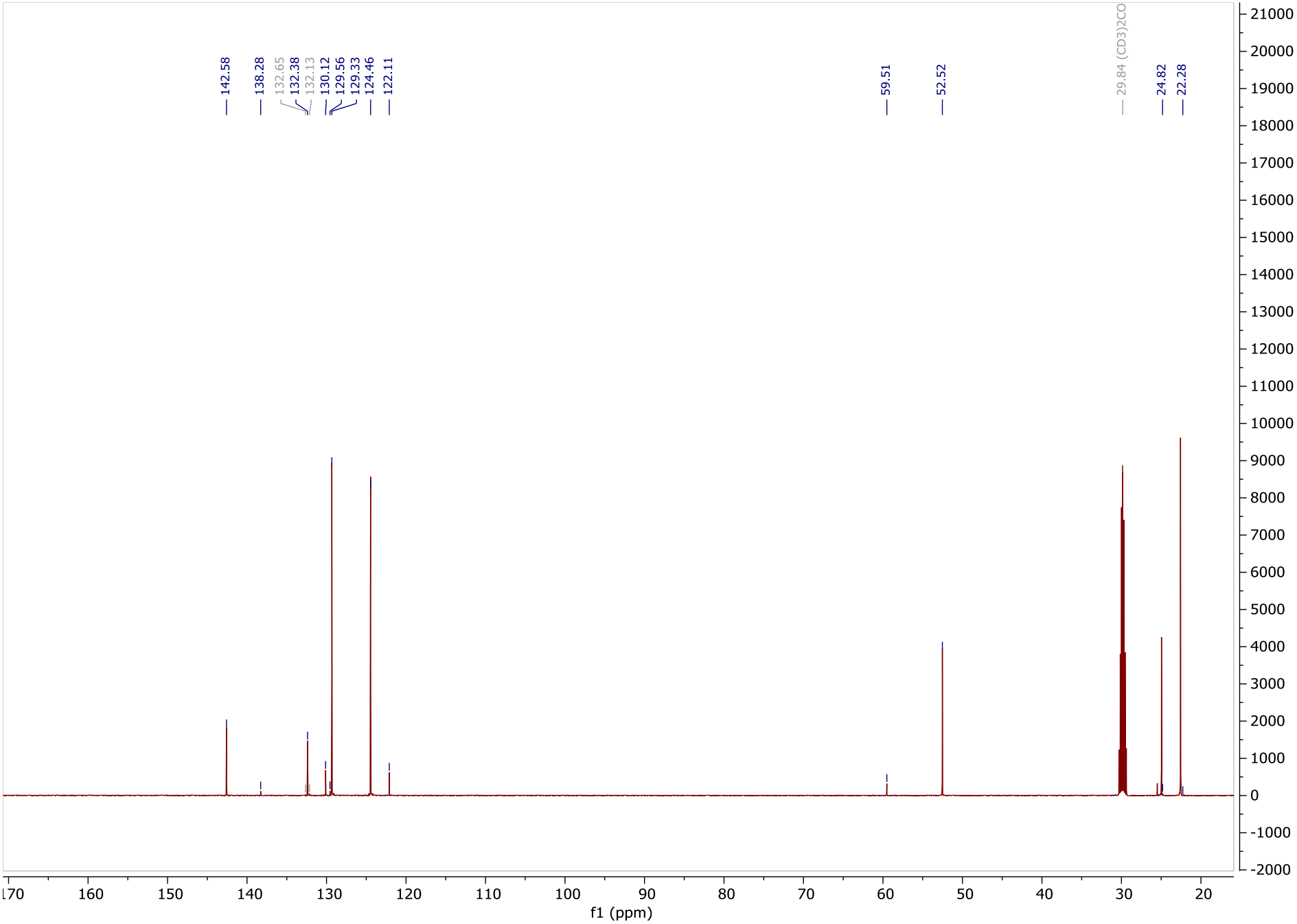
^{13}C NMR of 4a, acetone, 126 MHz



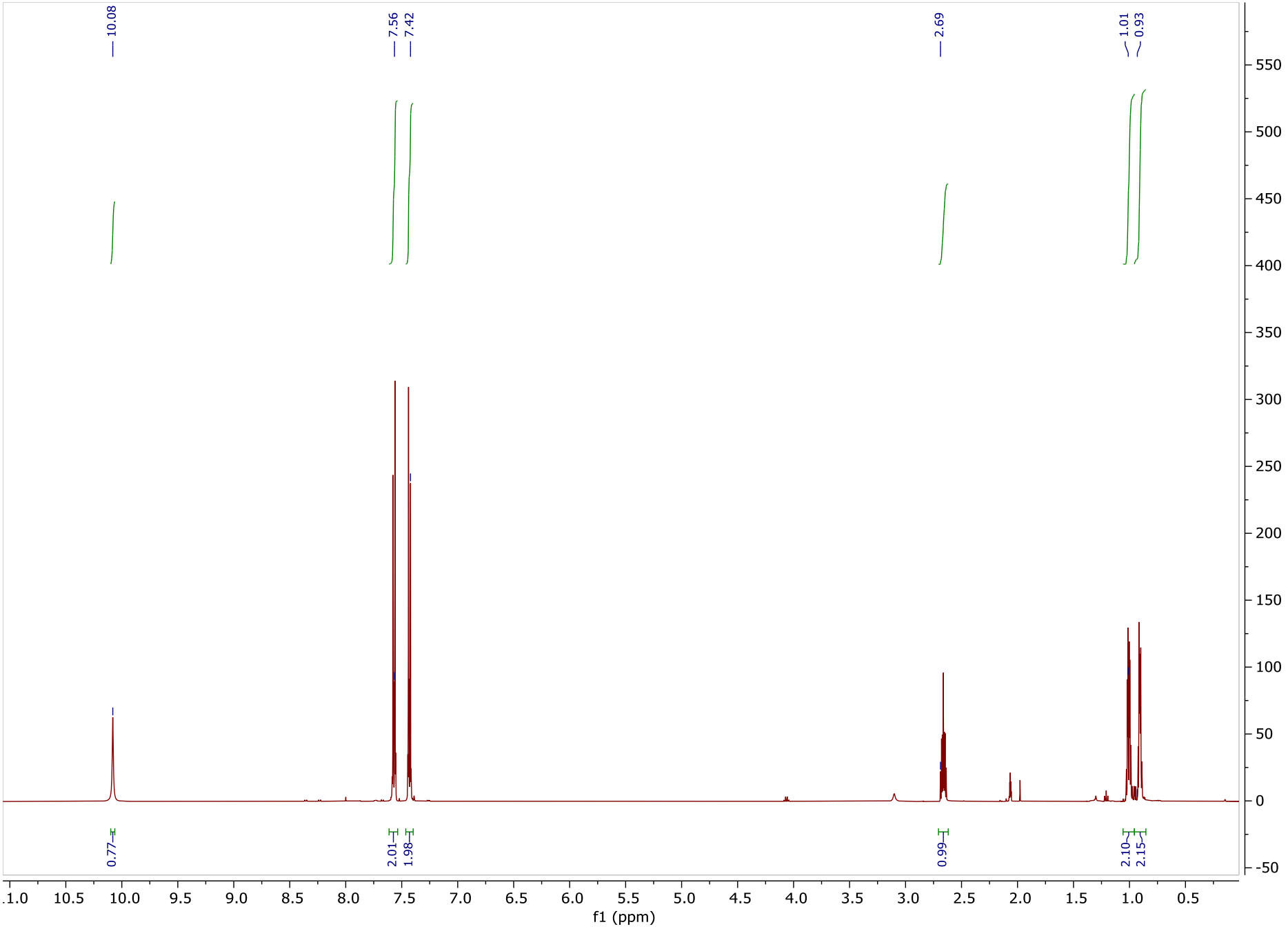
^{1}H NMR of 4b, acetone, 500 MHz



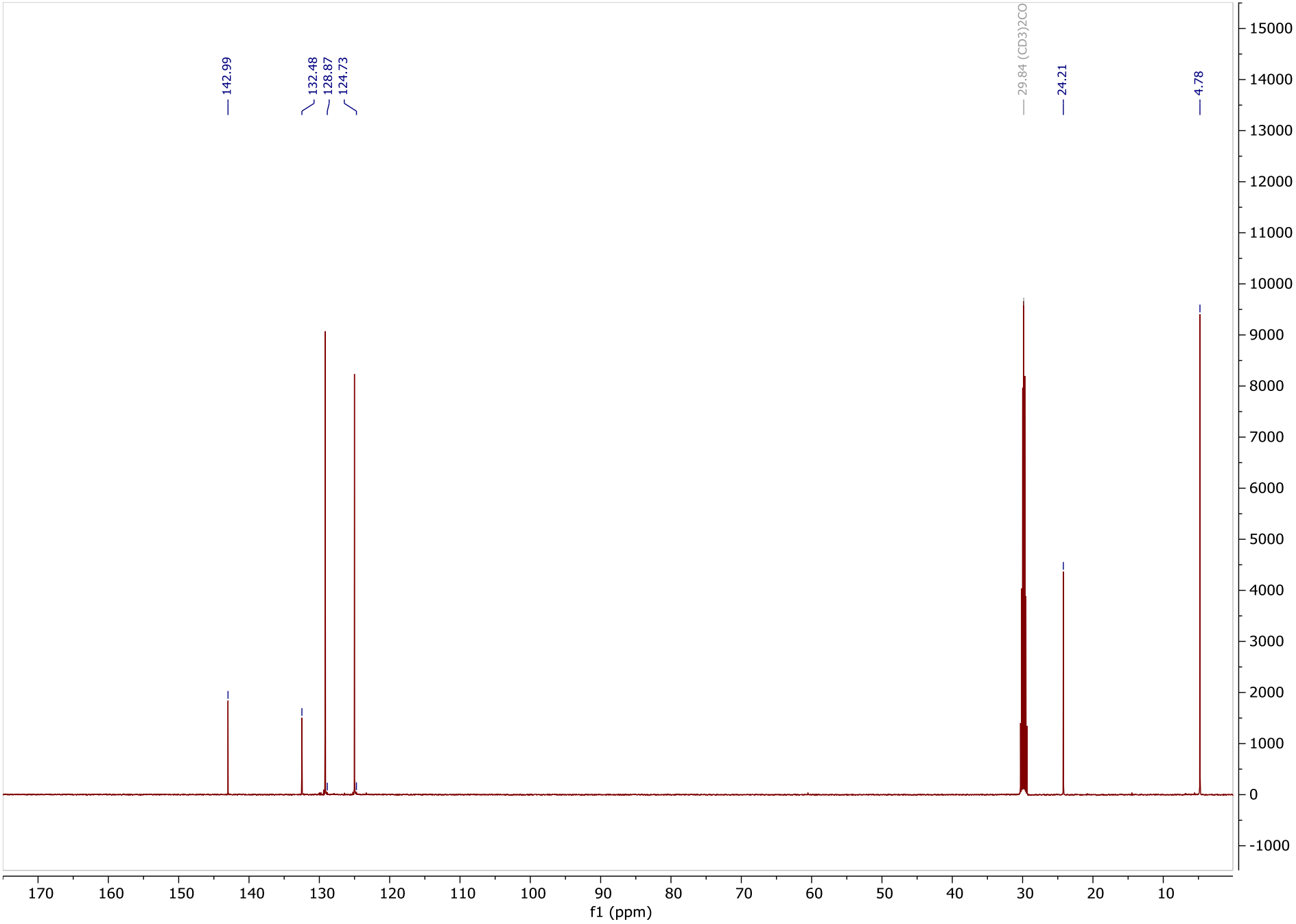
^{13}C NMR of 4b, acetone, 126 MHz



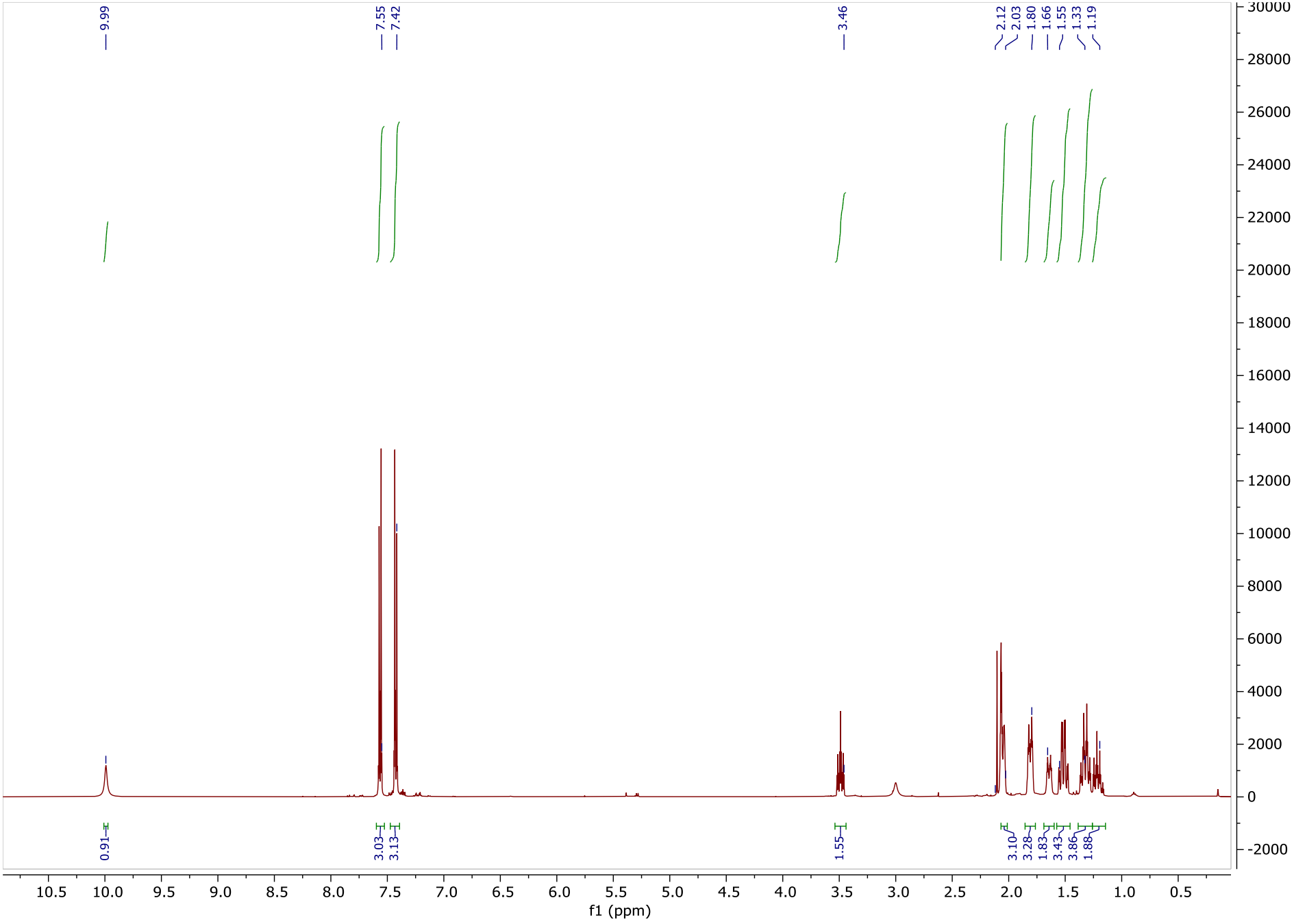
^{1}H NMR of 4c, acetone, 500 MHz



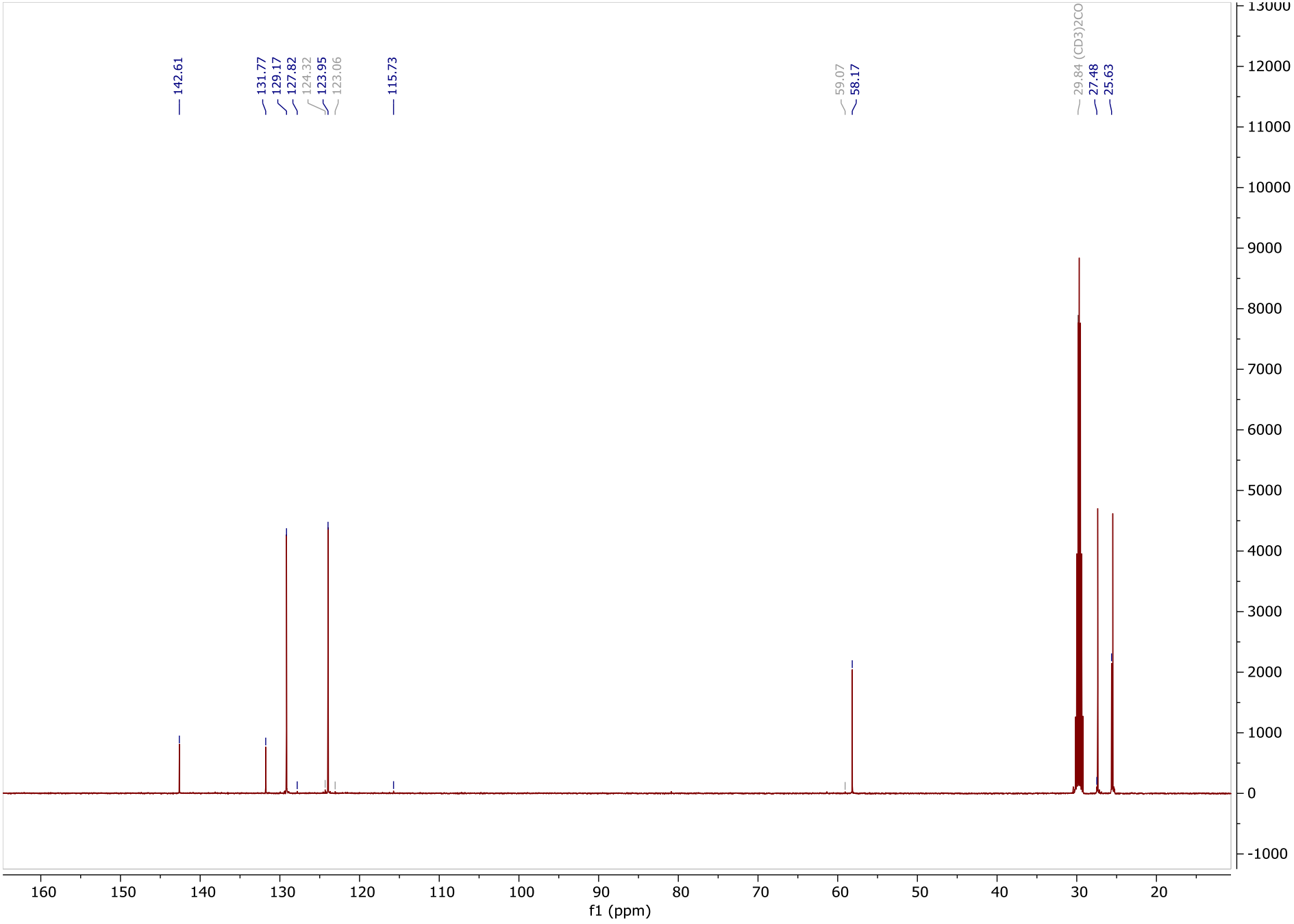
^{13}C NMR of 4c, acetone, 126 MHz



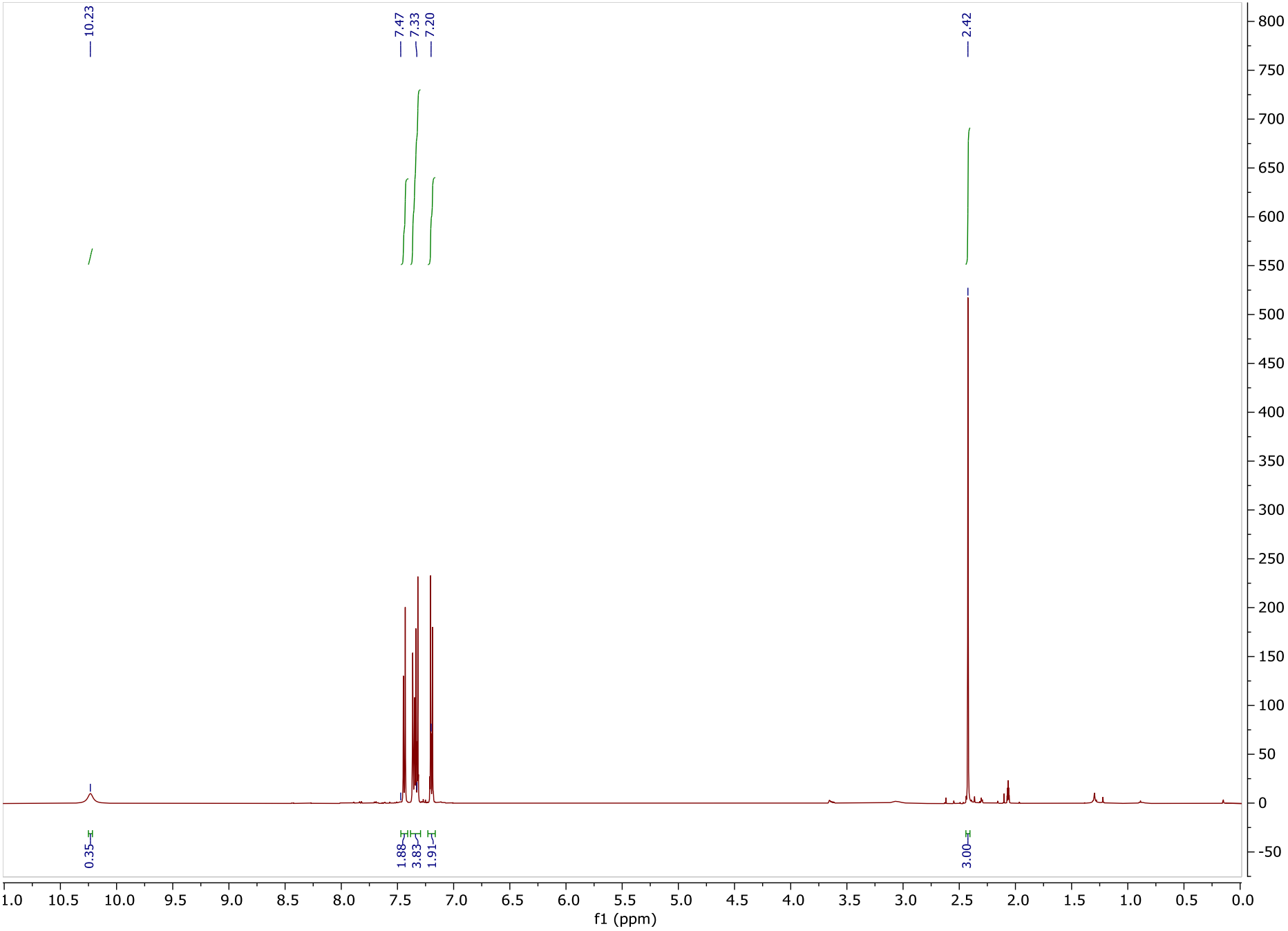
^{1}H NMR of 4d, acetone, 500 MHz



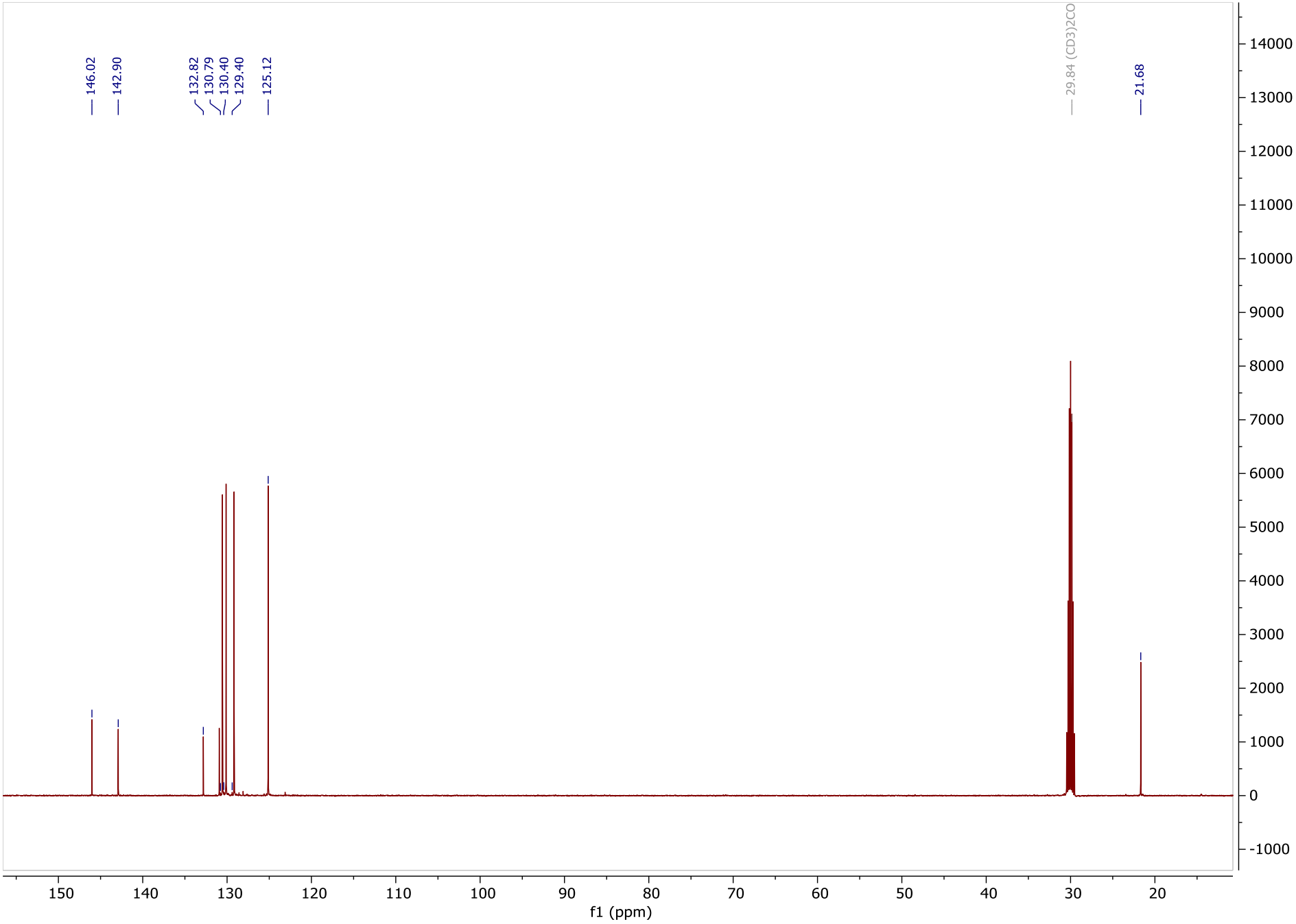
^{13}C NMR of 4d, acetone, 126 MHz



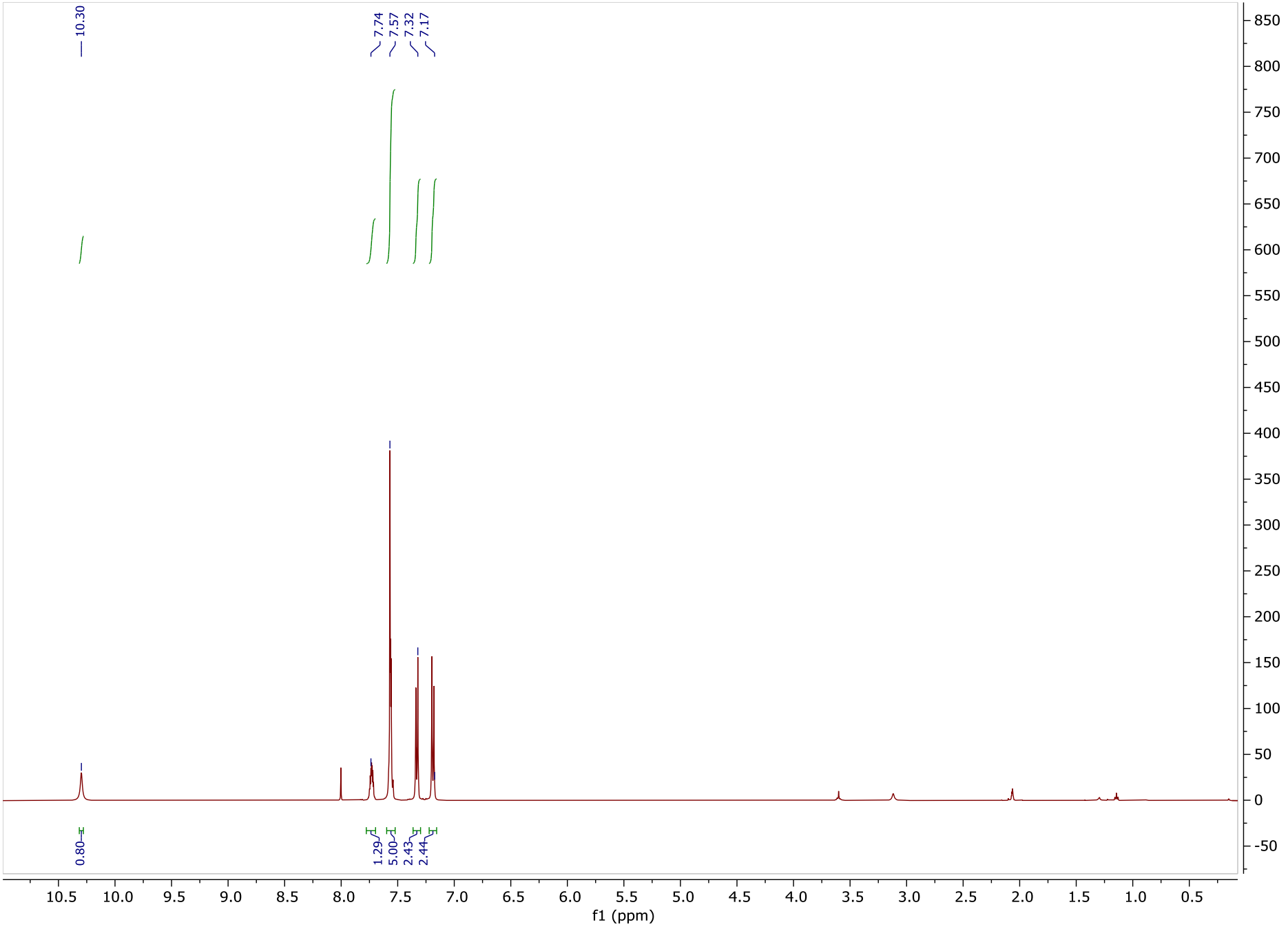
^{1}H NMR of 4e, acetone, 500 MHz



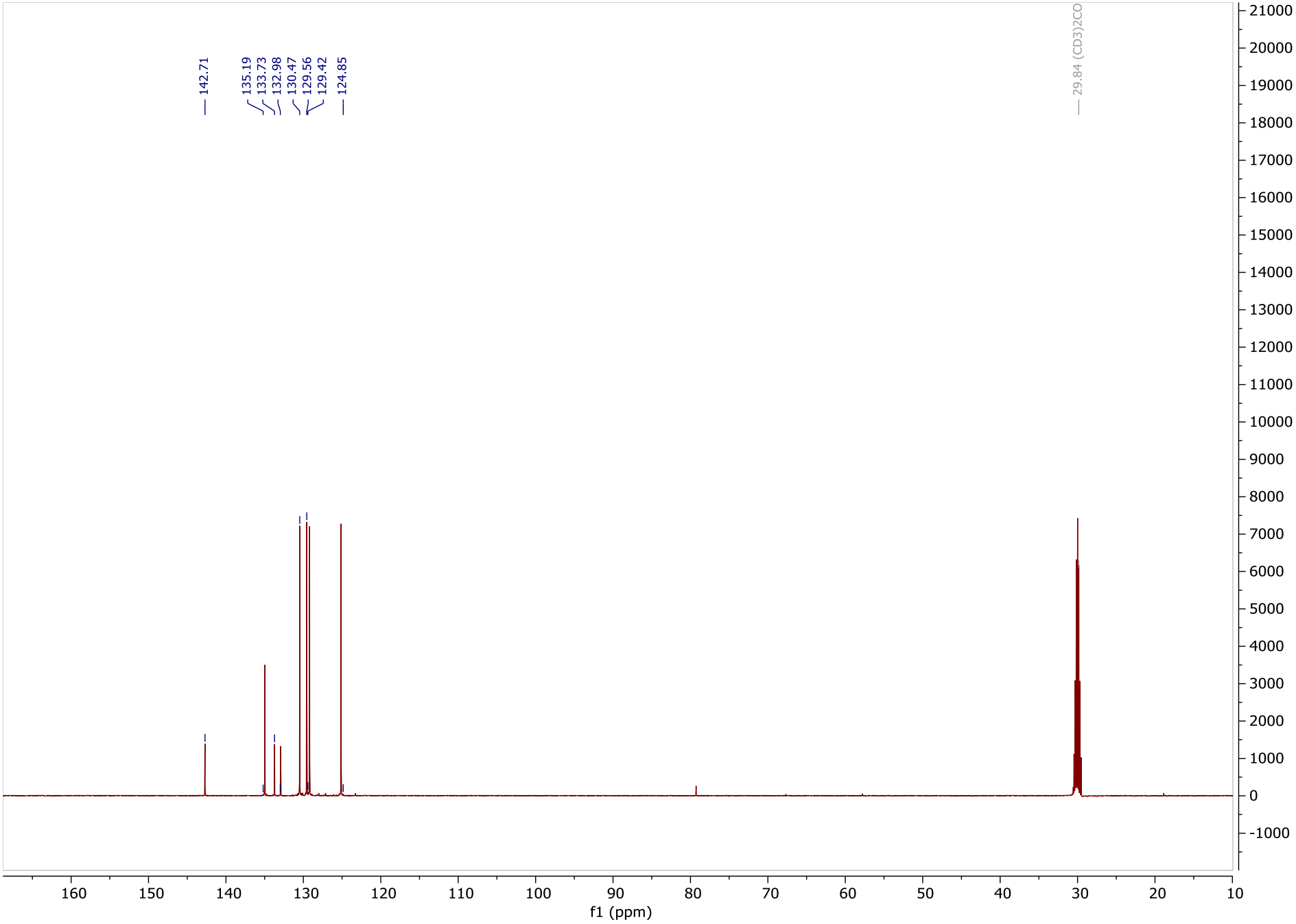
^{13}C NMR of 4e, acetone, 126 MHz



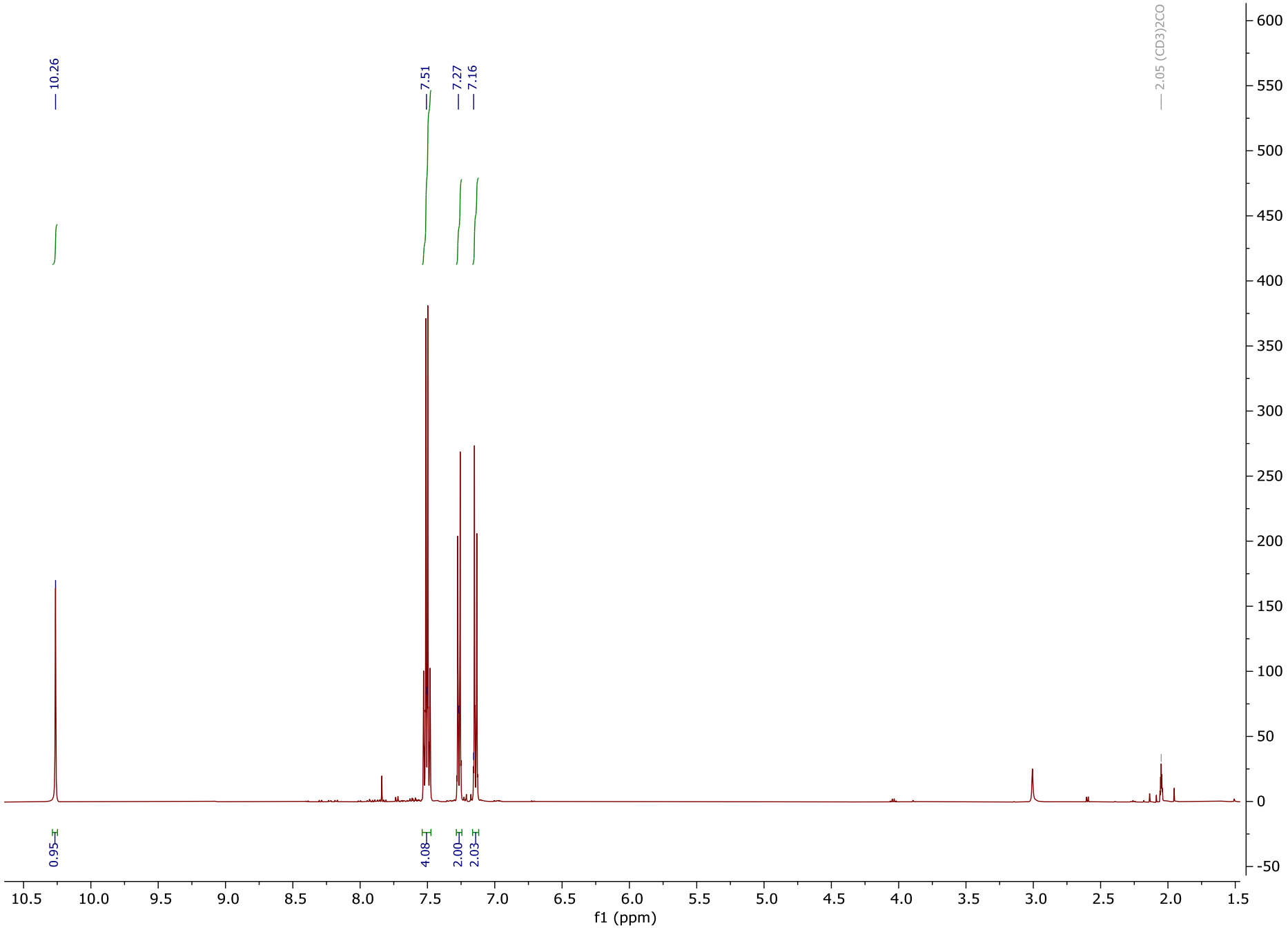
^{1}H NMR of 4f, acetone, 500 MHz



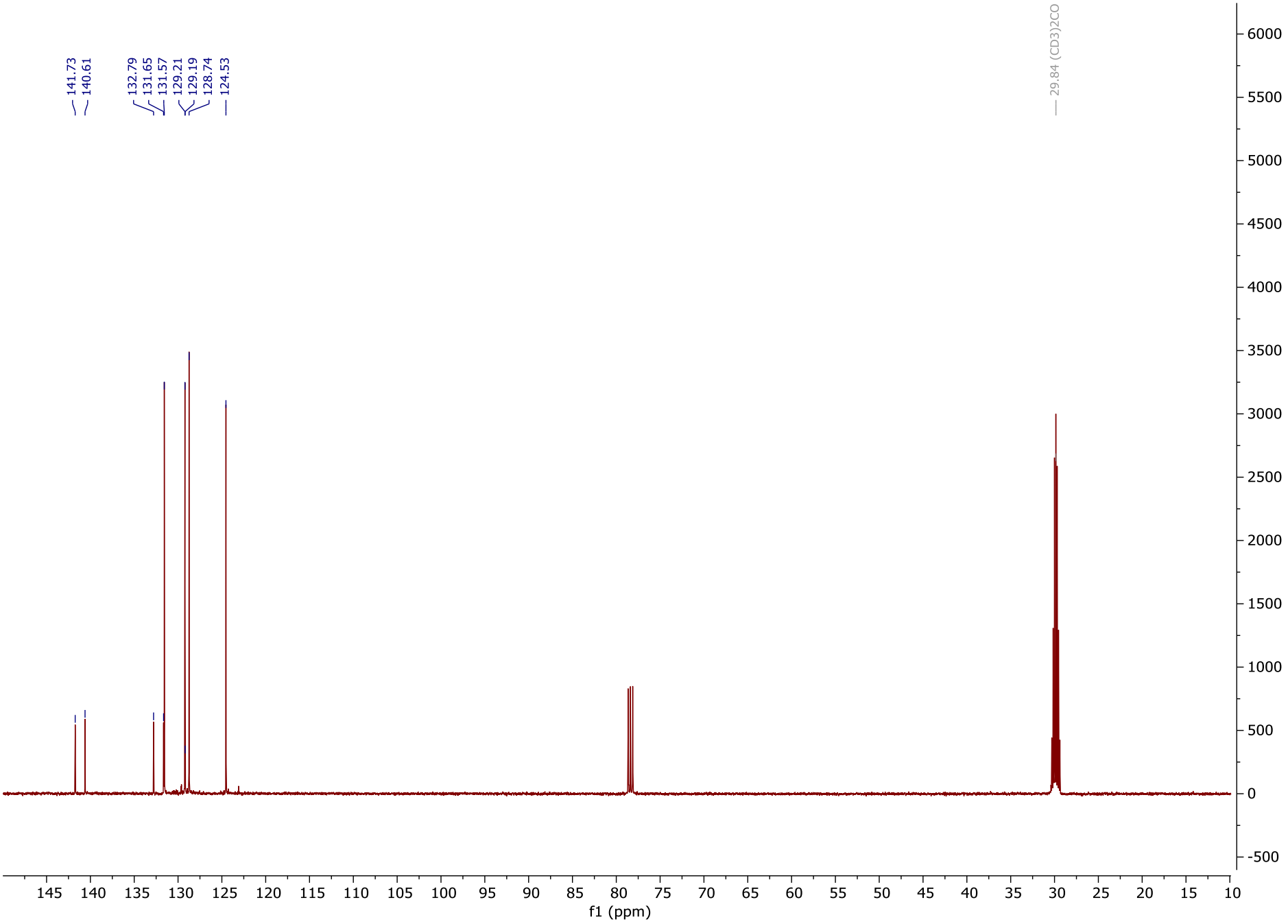
^{13}C NMR of 4f, acetone, 126 MHz



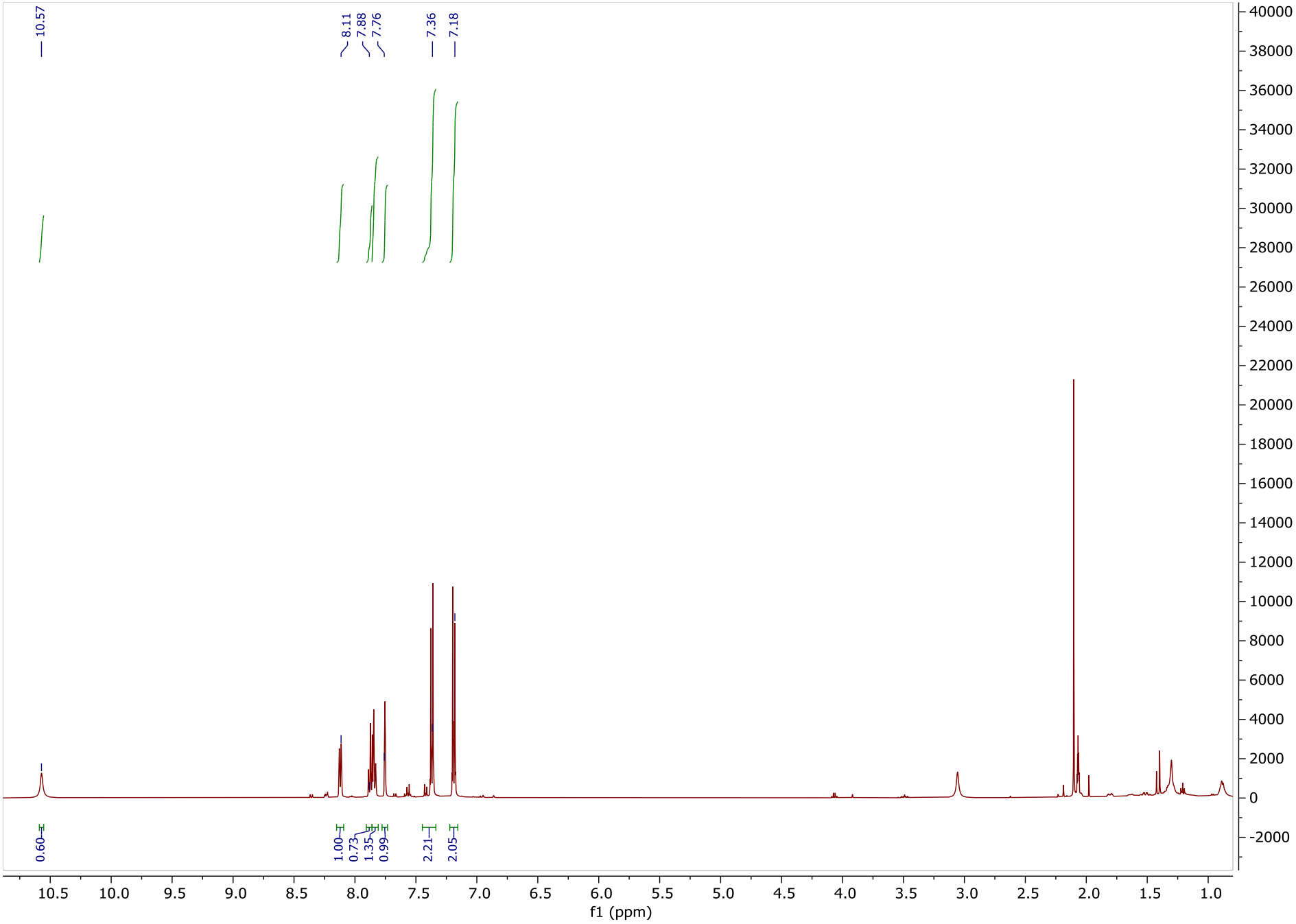
^{1}H NMR of 4g, acetone, 500 MHz



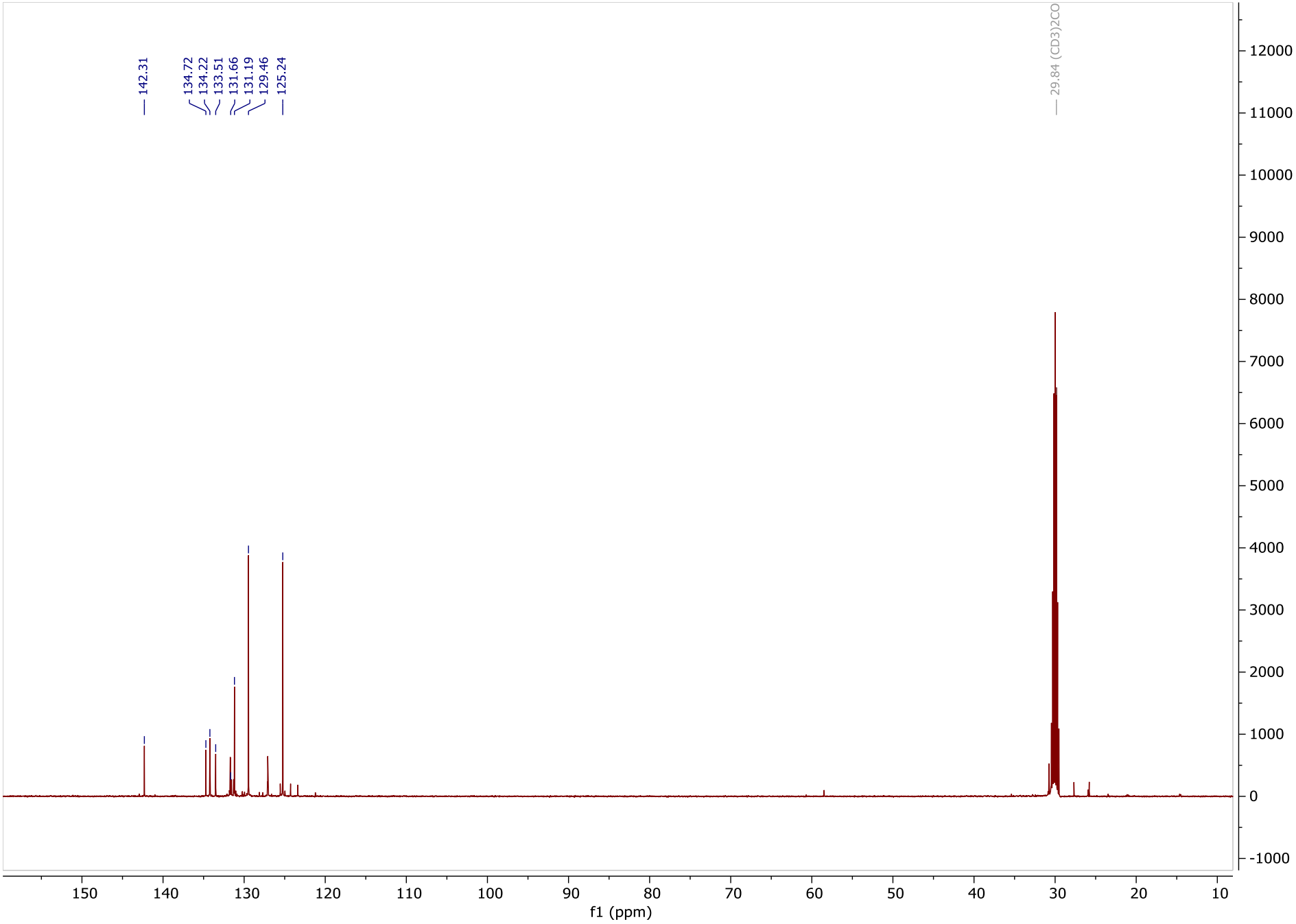
^{13}C NMR of 4g, acetone/$CDCl_3$, 126 MHz



^{1}H NMR of 4h, acetone, 500 MHz



^{13}C NMR of 4h, acetone, 126 MHz



^{19}F NMR of 4h, acetone, 471 MHz