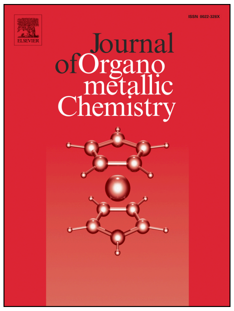

Facile synthesis and complete characterization of homoleptic and heteroleptic cyclometalated Iridium(III) complexes for photocatalysis

Anuradha Singh , Kip Teegardin , Megan Kelly , Kariate S. Prasad , Sadagopan Krishnan , Jimmie D. Weaver

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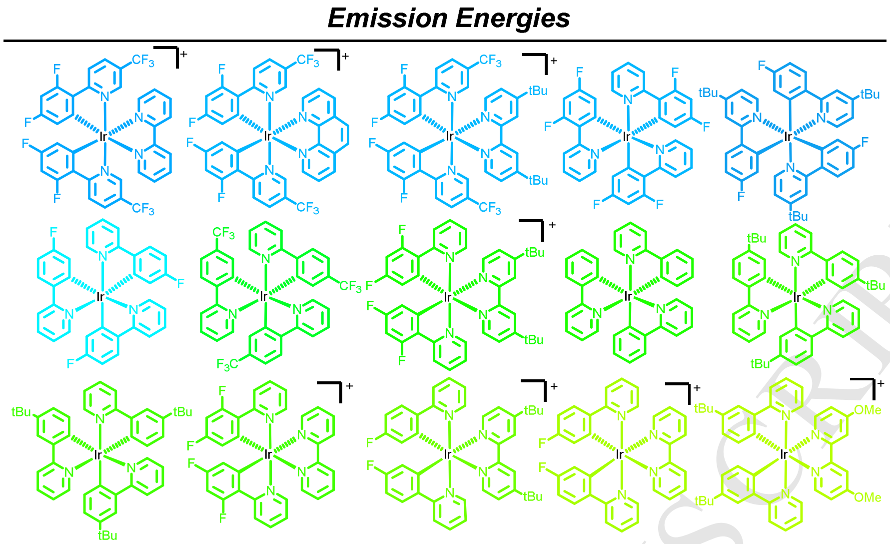
The emission energies of the cyclometalated iridium-complexes span the range of 473-560 nm and are shown pictographically by their corresponding color. This range corresponds to a 9 kcal/mol energy difference in available triplet state energy.


Emission Energies
+
CF3
F
N
Ir
tBu
OMe
F3C

Facile Synthesis and Complete Characterization of Homoleptic and Heteroleptic Cyclometalated Iridium(III) Complexes for Photocatalysis

Anuradha Singh, Kip Teegardin, Megan Kelly, Kariate S. Prasad, Sadagopan Krishnan, Jimmie D. Weaver*

Department of Chemistry, Oklahoma State University, 107 Physical Science, Stillwater, OK 74078

Corresponding author JDW:

Email: jimmie.weaver@okstate.edu

Phone: +14057443966

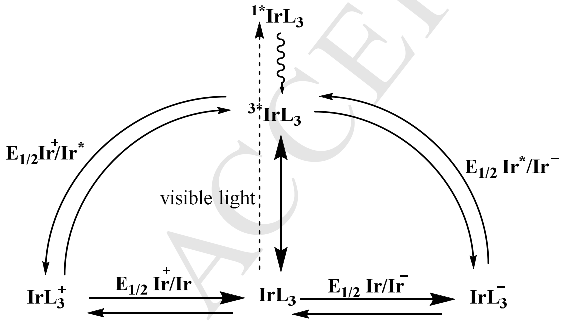
Postal Mail: Oklahoma State University, 107 Physical Science, Stillwater, OK 74078

Introduction

Cyclometalated iridium(III) complexes constitute an exceptional class of organometallic complexes that possess remarkable photophysical and photochemical properties.[1, 2] Consequently, these complexes have been utilized in a number of applications in diverse fields. They have been especially important in the fields of organic light emitting diodes (OLEDs),[3-8] dye sensitized solar cells,[9, 10] sensing[11-14] and biology.[15-17] More recently, these complexes have been utilized as photocatalysts in the area of synthetic organic chemistry to perform unique chemical transformations that take place by catalytic removal (or addition) of an electron as well as by serving as photosensitizers.[18-23] Exploration of these complexes as photocatalysts is still in its infancy and will likely continue to expand and give rise to powerful chemical methodologies. Consequently, substantial quantities of complexes with a range of properties will be needed.

Despite a rich history of exploration in the properties of these complexes, syntheses for many the facial homoleptic variants[1] are scattered, and often lack complete chemical, photophysical, and electrochemical characterization. Within our own research, we have also utilized this type of an iridium photocatalyst. Recently, we have disclosed several photocatalytic reactions which utilize commercially available *fac*-tris-(2-phenylpyridine) iridium (Ir(ppy)$_3$) in which the substrates are activated directly (or indirectly) via electron transfer or energy transfer from Ir(ppy)$_3$.[24-27] However, we often found our research was restricted by the photophysical and electrochemical properties of the limited number of commercially available photocatalysts. Herein, we report a simple synthetic method to access these complexes readily in sufficient quantities for use within the laboratory. Furthermore, we also report and discuss the photophysical and electrochemical properties of the synthesized complexes within the context of photoredoxcatalysis.

Scheme1. Energy and electron transfer processes in triscyclometalated iridium complexes



^{1}*IrL$_3$ represents the higher energy spin allowed excited state and ^{3}*IrL$_3$ represents the lowest spin forbidden excited state

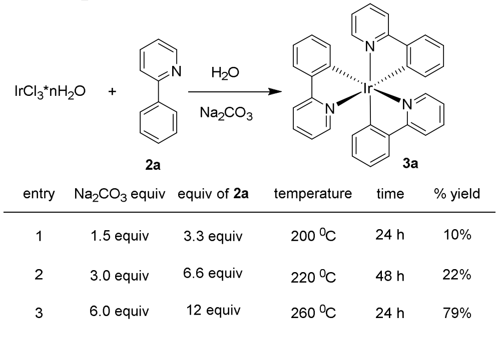
The iridium complexes are tris-cyclometalated d-6, 18-electron complexes that are remarkably stable in the ground state. However, upon absorption of photons of the appropriate energy-in the blue region of the visible spectrum, the complexes undergo excitation (Scheme 1). Initially, an excited singlet state is produced but it rapidly relaxes to its long-lived, triplet state.[28, 29] The triplet state has undergone a metal-to-ligand charge transfer and by virtue of charge transfer, it can serve as both a potent oxidant and reductant. By knowing the excited state redox potentials of $E_{1/2}(Ir^+/Ir^*)$ and $E_{1/2}(Ir^*/Ir^-)$ complexes, one can begin to rationally design novel chemical transformations provided the relevant potentials of substrates are known. With this goal in mind, we desired to develop a simple and robust method that would allow us to modulate the redox potentials and triplet state energies of the iridium photocatalysts, allowing us to more fully explore possible synthetic transformations.

A survey of the literature revealed that there are a number of reported synthetic methods that use more expensive Ir(acac)$_{3}$[30-33] or alternatively require two steps- forming the chloro-bridged dimer and then subsequently adding the third ligand. This is done even in the case of the tris-homoleptic-cyclometalated complexes, which is less than ideal since it requires additional chemical steps. Furthermore, a stoichiometric chloride scavenger like AgOTf is often employed.[34, 35] Konno reported microwave synthesis of tris-cyclometalated iridium complexes, but this required a large excess of ligand (50-100 equiv.) which limits the scope of the reaction to readily available ligands such as 2-phenylpyridine.[36] Therefore, we set about to develop a general and simple synthesis that would allow us to acquire the facial homoleptic iridium complexes in high chemical yield via a simple and selective one step process.

Results and Discussion

In our initial attempt, a glass pressure vial was charged with IrCl$_3$•nH$_2$O, 2-phenylpyridine, Na$_2$CO$_3$ and water and heated at 200 °C for 48 h.[37] Unfortunately, this reaction resulted in extremely low yield (<8%) of the desired complex, Ir(ppy)$_3$. However, it was observed that the reaction was heterogeneous until temperatures reached nearly 200 °C. Concerned that even higher temperatures may be needed to ensure homogeneity, reproducibility, and faster reaction rates the remaining reactions were performed in Parr reactor for safety purposes, allowing us to safely heat H$_2$O to 260 °C. Routine optimization (Table1) of this reaction provided improvement in yields on increasing the equivalents of base from 1.5 to 6, 2-phenylpyridine from 3.3 to 12, and the temperature from 200 to 260 °C. Using optimized conditions (entry 3), the reaction yielded 79% of Ir(ppy)$_3$, **3a**, in just 24 h.

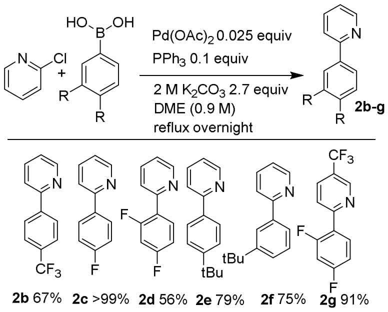
Table 1. Optimization of Reaction Conditions



entry	Na$_2$CO$_3$ equiv	equiv of **2a**	temperature	time	% yield
1	1.5 equiv	3.3 equiv	200 ^{0}C	24 h	10%
2	3.0 equiv	6.6 equiv	220 ^{0}C	48 h	22%
3	6.0 equiv	12 equiv	260 ^{0}C	24 h	79%

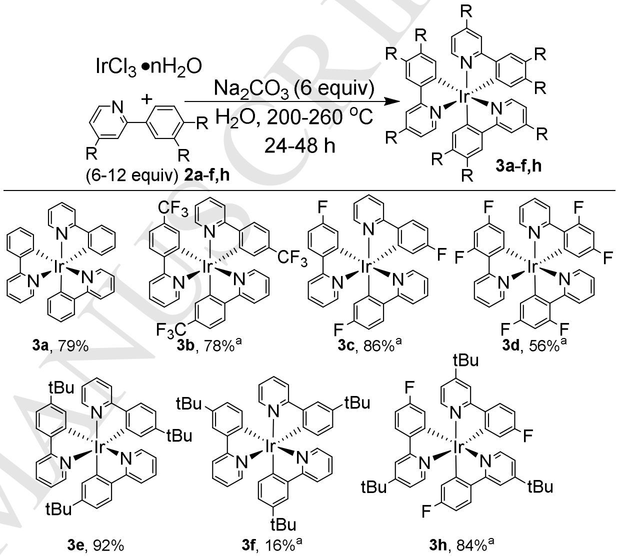
Pleased with this result, we next attempted to investigate the scope of the method which required the syntheses of the requisite 2-phenylpyridine ligands **2b-g** (Scheme 2) which we hoped would lead to catalyst with a range of properties. The ligands were synthesized quite easily via Suzuki coupling of 2-chloropyridine (1 equiv.) and the requisite boronic acid (1.2 equiv.) with only minor modifications to the literature procedure.[38] Conveniently, the procedure could be performed outside the glovebox. In all cases, the Suzuki coupling reaction led to good yields of the desired phenylpyridine products and in one case (**2c**) approached quantitative yields. Ligand **2h** (4-(tert-butyl)-2-(4-fluorophenyl)pyridine) was synthesized via Baran's procedure.[39]

Scheme 2. Ligand Synthesis



With ligands (**2a-h**) in hand, we returned to the cyclometalation reaction (Scheme 3). However, under the standard reaction conditions, several of the substrates presented problems. Upon modification of our initial conditions, yields were improved and substantial quantities were obtained. For instance, when 2-(3-*tert*-butyl) phenylpyridine) (**2e**) was subjected to the reaction conditions the expected **3e** was not formed. Rather, **3a** Ir(ppy)$_3$ along with 2-phenylpyridine, **2a**, were the primary products recovered which apparently resulted from the detertbutylation of either (or both) ligand or Ir-complex at 260 $^{\circ}$C. However, by lowering the temperature to 200 $^{\circ}$C we were able to suppress detertbutylation and obtain **3e** in high yield. Moreover, our initial attempts to synthesize **3c** resulted in a mixture of iridium complexes in which partial hydrolysis of fluorine had occurred. Additionally, we observed a migration of fluorine on the ring of the ligand recovered from the reaction mixture.[40] To avoid this problem, reaction with 2-(4-fluorophenyl) pyridine, **2c**, ligand was performed in the absence of sodium carbonate and at lower temperatures (200 °C for 48 h). Surprisingly, using these conditions the reaction proceeded smoothly to achieve **3c** in excellent yield. This experiment suggested that no base is required to synthesize triscyclometalated iridium complexes and, to the best of our knowledge, this is the first report that suggests that the base is not necessary for the formation of these complexes. Thus, for the remainder of the fluorinated substrates, the reactions were carried out with no base which allowed us to acquire **3b-e**, and **3h** complexes in moderate to high yields. **3h** was synthesized in 84% yield and was very recently used as a catalyst for the deacarboxylative arylation of α-amino acids and α-etheral acids though its synthesis and properties have never been reported.[41] A more modest yield was observed for **3d** but is likely a result of the effectively lower concentration of **2d**, since only 6 equiv. were used due to smaller quantities on hand. Using standard conditions, new complex, **3f**, was obtained only in trace amounts and addition of base did not prove helpful. In these cases, the major product was the choro-bridged dimer. However, **3f** was finally successfully obtained by subjecting the chloro-bridging dimer to excess ligand in the presence of AgOAc.

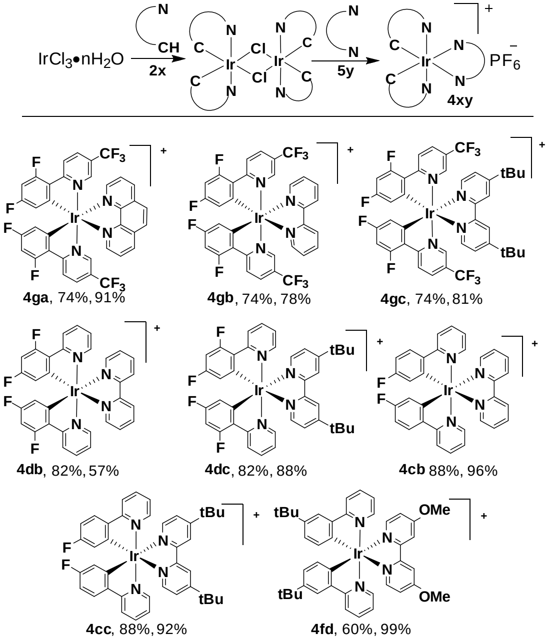
Scheme 3. Synthesis of Facial Homoleptic Tris-Cyclometalated Iridium Complexes



^{a}**No Na$_2$CO$_3$ used.**

While our initial focus was in the syntheses of the homoleptic iridium complexes, cationic heteroleptic iridium complexes[2] have also proven to be effective photocatalysts and we sought to synthesize the cationic complexes as well. In the cationic complexes, the third 2-phenylpyridine ligand is replaced with 2,2'-bipyridine type ligand. Thus, in order to be able to modify the third ligand, the dichloro-bridged iridium dimer was selectively synthesized according to Nonoyama's procedure[42] which was then subsequently treated with the third, bipyridyl ligand to afford cationic heteroleptic iridium complexes (scheme 4).[43]

Scheme 4. Synthesis of Cationic Iridium Complexes



Cationic heteroleptic Ir(III) Complexes 4a-h with PF_6^- counteranion. First step yield followed by second step.

The cyclometalated iridium(III) chloro-bridged dimer $[Ir(ligand)_2Cl]_2$ was prepared by following Nonoyama's procedure[42] in which hydrated iridium(III) chloride was heated with substituted phenylpyridine ligand in a 2:1 methoxyethanol/H_2O mixture at only 120 °C. Upon cooling, the chloro-bridging dimer precipitated and was carried onto the second step. The catalysts were diversified by use of several bipyridine ligands. Finally, anion metathesis was achieved by the addition of aqueous NH_4PF_6. In this manner, complexes **4xy** (Scheme 4) were synthesized. In some cases, complexes were further purified by recrystallization. This is the first report for complexes **3f**, **4ab**, **4cb** and **4fd**. All synthesized facial homoleptic and cationic heteroleptic complexes were characterized by ^{1}H, ^{13}C, ^{19}F, ^{31}P NMR, LCMS, and new complexes by elemental analysis.

With iridium complexes in hand, we next turned to the investigation of the photophysical properties of the facial homoleptic **3a-f** and the heteroleptic **4xy** complexes. Absorbance of the facial homoleptic (Figure 1) and the heteroleptic (Figure 2) were measured in acetonitrile (10 µM). As depicted in Figure 1 and 2 all the complexes show intense UV absorption band below 325 nm-characteristic of spin allowed transition of ligand (π-π□)[44] and weaker, broad and unresolved absorption band into visible region from 320-480 nm generally assigned as both allowed and spin-forbidden metal to ligand charge transfer (MLCT) transitions.[44]

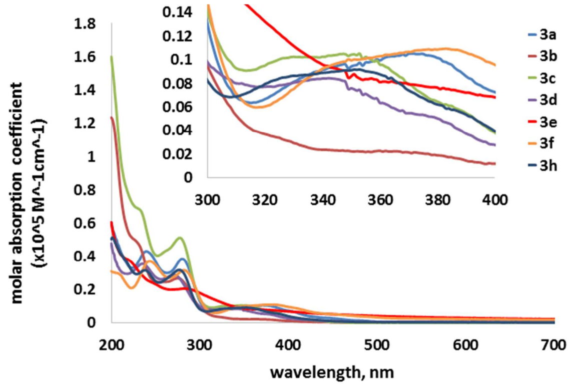


Figure 1. Absorbance Spectra of Facial Homoleptic Iridium Complexes (**3a-f**,**h**) 10 µM in MeCN.

From a catalysis standpoint, the emission frequency corresponds to the energy available for energy transfer to substrates, (i.e., the triplet state energy, TSE). The complexes were excited in the region of 370-390 nm which corresponds to the metal-to-ligand charge transfer excitation.[45] In general, electron-withdrawing substituents on the phenyl ring such as fluorine lowers the energy of HOMO resulting in larger HOMO-LUMO gaps and greater emission energies (more blue shifted). Whereas electron-donating substituents such as alkyl groups raise the HOMO energy, resulting in smaller HOMO-LUMO gaps and lower emission energies (more red shifted).[46, 47] As expected, in complexes that have electron-withdrawing groups (**3b-d** and **3h** Figure 3), a 10-40 nm hypsochromic shift is observed whereas bathochromic shift of 5-10 nm is observed in alkyl substituted complexes (on the phenyl ring), **3e** and **3f**, when compared to that of $Ir(ppy)_3$ (**3a**). Furthermore, as the degree of fluorine substitution increases, more blue shifting was observed (**3d** vs. **3c**). Similar trends were observed in the case of heteroleptic cationic iridium complexes (Figure 4).

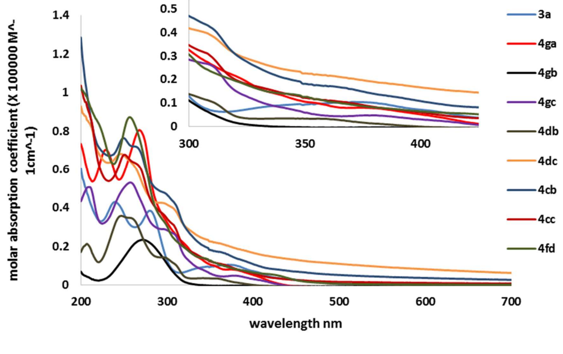


Figure 2. Absorbance spectra of **3a** and cationic heteroleptic iridium complexes (**4xy**) 10 µM in MeCN.

Electron withdrawing groups (**4ga, gb, gc**) resulted in a 42-45 nm blue shift with respect to $Ir(ppy)_3$ (**3a**). Complex **4db** shows 55 nm bathochromic shift relative to more fluorinated complexes **4ga, gb, gc**. Addition of electron donating *tert*-butyl groups on bipyridyl (**4de**) resulted in a 12 nm hypsochromic shift compared to complex **4db**. In the mono-fluoro series, a similar trend was observed (**4cb** and **4cc**). Complexes **4db**, **4fcb**, **4cc** and **4fd** depict a 10-42 nm red shift and **4ga**, **4gb**, **4gc**, **4dc** a 2-45 nm blue shift from Ir(ppy)$_3$ (**3a**). Furthermore, among these complexes, complex **4fd** was found to be the most red shifted (vs. **3a**) with poor emission which could be due to the methoxy substituents.[48] In most complexes, broad emission spectra were observed which could be due to significant degree of charge transfer (CT) whereas structured spectra in **4ga** and **4gc** suggest a small CT contribution.[49]

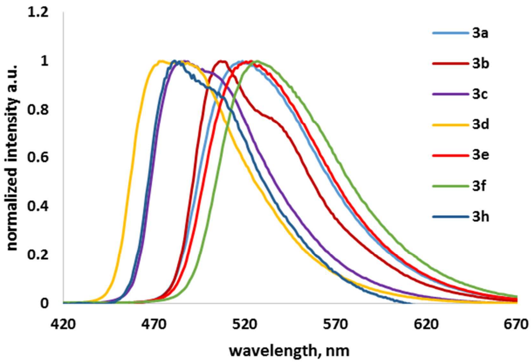


Figure 3 Emission spectra of facial homoleptic iridium complexes (**3a-f**,**h** excited at 385 nm, 372 nm, 380 nm, 378 nm, 390 nm, 383 nm, 385 nm respectively) 5 µM in MeCN except **3a** 10 µM in MeCN.

In all complexes emission is from the lowest energy triplet state which is likely formed by mixing of the ^{3}MLCT, ^{3}LC and ^{3}LLCT states.[17, 50, 51] The emission maximum (λ_{max}) is the triplet state energy which can be used in photocatalysis for energy transfer processes (Scheme 1).[25-27]

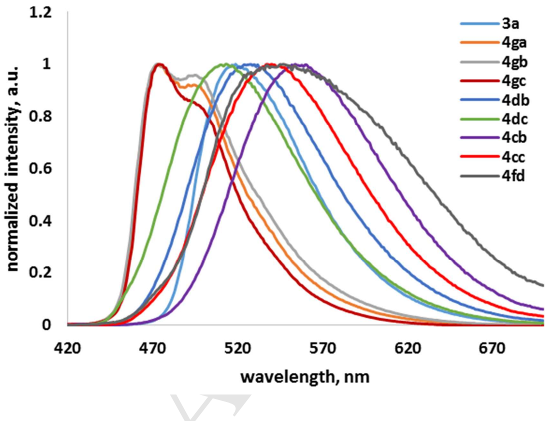


Figure 4 Emission spectra of **3a** and heteroleptic iridium complexes (**4xy**, excitation wavelength, concentration in MeCN) (**4ga** 376 nm 2.5 µM, **4gb** 370 nm 10 µM, **4gc** 375 nm 5 µM, **4db** 368 nm 10 µM, **4dc** 365 nm 10 µM, **4cb** 380 nm 10 µM, **4cc** 370 nm 10 µM, **4fd** 390 nm **4h** 50 µM).

Having investigated the photophysical properties, we next turned to the electrochemical properties of the iridium complexes via cyclic voltammetry (CV) which is reported relative to ferrocenium/ferrocene redox couple as shown in Table 4. The cyclic voltammograms of complexes were collected at a scan rate of 50 mV/s. As anticipated, complexes having electron withdrawing fluorine groups (**3b-d**. vs **3a**) show higher ground state $E_{ox}^{1/2}$ (Ir$^+$/Ir) due to lowering of HOMO energy level. All cationic complexes show higher ground state $E_{ox}^{1/2}$ (Ir$^+$/Ir) when compare to that of **3a**, and among all complexes **4ga** and **4gc** exhibit the highest ground state $E_{ox}^{1/2}$. Whereas, lower $E_{ox}^{1/2}$ potentials were observed when an electron donating tBu-substituent was located on the ligand (**3e**, **3f** vs. **3a**) as this group is expected to raise the HOMO energy level making it more easily oxidized.[52]

Complexes that have electron withdrawing fluorines on the ligand make them less reducing (smaller negative ground state) $E_{red}^{1/2}$ (Ir/Ir$^-$) as observed in **3b-d** and **3h** relative to **3a**. Complexes that have an electron donating alkyl group (**3e** vs **3a**) possess a more negative $E_{red}^{1/2}$ (Ir/Ir$^-$) potential-though **3f** is slightly less reducing than **3a**. Among cationic complexes **4fd** found to be the most reducing as it contains electron rich *t*Bu- and methoxy substituent on ligands. Furthermore, *t*Bu-bipyridine complexes are more reducing (**4da** vs **4dc**, **4cb** vs **4cc**)

Knowing the excited state redox values is a key element in designing photocatalytic reactions, but the excited state redox potentials cannot be directly evaluated. However, they can be calculated from the electrochemically determined ground state $E_{ox}^{1/2}$ and $E_{red}^{1/2}$ potentials and the energy gap (E_{gap}). E_{gap} values were determined from the CV.

$$E^{1/2}\ (\mathrm{Ir}^+/\mathrm{Ir}^*) = E_{ox}^{1/2} - E_{gap}\ \mathrm{eV} \qquad \text{(eq 1)}$$

$$E^{1/2}\ (\mathrm{Ir}^*/\mathrm{Ir}^-) = E_{gap}\ \mathrm{eV} + E_{red}^{1/2} \qquad \text{(eq 2)}$$

We calculated the redox values of the excited state complexes, $E^{1/2}$ (Ir*/Ir$^+$) and $E^{1/2}$ (Ir*/Ir$^-$) using equations 1 and 2 and the potentials are shown in Table 4. The table is arranged in descending emission energy values.

Table 4. Photophysical and electrochemical data for iridium complexes

complex	λmax	TSE kcal/mol	$E_{1/2}$ ox V	$E_{1/2}$ red V	E gap eV	$E_{1/2}$ (Ir$^+$/Ir□)	$E_{1/2}$ (Ir□/Ir$^-$)
4gb	473	60.4	1.23	-1.23	2.2	-0.97	0.97
4ga	475	60.2	1.81	-1.25	2.64	-0.83	1.39
4gc	476	60.1	1.77	-1.35	2.77	-1	1.42
3d	476	60.1	0.98	-1.82	2.21	-1.23	0.39
3h	481	59.4	0.926	-1.58	2.2	-1.274	0.62
3c	488	58.6	1	-2.13	2.86	-1.86	0.73
3b	507	56.4	1.11	-2.13	2.76	-1.65	0.63
4dc	516	55.4	1.63	-1.42	2.56	-0.93	1.14
3a	518	55.2	0.78	-2.2	2.75	-1.97	0.55
3e	525	54.5	0.69	-2.27	2.59	-1.9	0.32
3f	528	54.2	0.7	-2.03	2.28	-1.59	0.25
4db	528	54.2	1.66	-1.32	2.46	-0.8	1.14
4cc	540	53	1.49	-1.45	2.52	-1.04	1.07
4cb	556	51.4	1.51	-1.37	2.4	-0.89	1.03
4fd	560	51.2	1.17	-1.5	2.35	-1.12	0.85

Conclusions

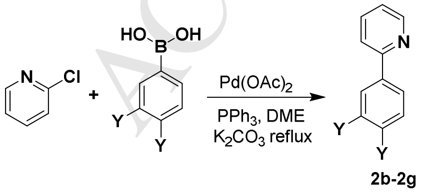
In conclusion, we have reported simple synthetic procedures that allow rapid access to an important class of iridium photoredox catalysts. We have successfully developed a simple and general synthesis that provides efficient access to facial tris-cyclometalated iridium complexes directly from less expensive $IrCl_3{\bullet}nH_2O$. In addition, we applied Nonoyama's method in order to synthesize a number of cationic heteroleptic iridium complexes. Importantly, we have provided the chemical, photophysical and electrochemical characterization necessary to facilitate catalysis. This should significantly aid in the design of novel chemical transformations via photocatalysis by facilitating access to the catalysts and by providing the relevant photophysical and electrochemical properties necessary to rationally design new synthetic methods.

General Experimental

All reagents were obtained from commercial suppliers (Sigma-Aldrich, Oakwood chemicals, Alfa Aesar, Strem, and VWR) and used without further purification unless otherwise noted. NMR spectra were obtained on 400 MHz Bruker Avance III spectrometer and 400 MHz Unity Inova spectrometer. ^1H, and ^{13}C, NMR chemical shifts are reported in ppm relative to the residual solvent peak while ^{19}F and ^{31}P NMR are set relative to an external standard. Purifications were carried out using Teledyne Isco Combiflash Rf 200i flash chromatograph with Redisep Rf normal phase silica (24 g, 40 g, or 80 g) column with product detection at 254 and 280 nm and by ELSD (evaporative light scattering detector). Substrate synthesis reactions were monitored by thin layer chromatography (TLC) obtained from Sorbent Technology; Silica XHL TLC Plates, w/UV254, glass backed, 250 µm, and were visualized with ultraviolet light. Photophysical properties were studied on Varian Cary Eclipse spectrophotometer and LCMS was taken on Shimadzu liquid chromatograph mass spectrometer (LCMS-2010 E). Electrochemical measurements were performed with CH instruments using a glassy-carbon electrode as a working electrode with a Ag/AgCl reference electrode and a platinum wire as counter electrode. All sample solutions were prepared in acetonitrile and degassed with nitrogen bubbling for 20 min. prior to voltammetric studies. Tetra-(n-butyl)-ammonium hexafluorophosphate (NBu_4PF_6, 0.1 M in acetonitrile) was used as supporting electrolyte. The HOMO and LUMO energy is calculated from equation eq 3.

$$E_{\text{HOMO/LUMO}} = -(E_{\text{onset oxi/red}} \text{ vs Fc} + 4.8)\ \text{eV} \qquad \text{(eq 3)}$$

General procedure A for the synthesis of ligands (**2b-2g**)



To a two necked, 100 mL round bottom flask equipped with a magnetic stir bar were added 2-chloropyridine (1 equiv), phenylboronic acid (1.2 equiv), triphenylphosphine (0.1 equiv), 2 M potassium carbonate (2.7 equiv) and ethylene glycol dimethyl ether (0.9 M). The mixture was degased with Ar for 15 min. Then $Pd(OAc)_2$ (2.5 mol%) was added to the reaction mixture and degassing continued for 15 more minutes and then the outlet was removed. The reaction mixture was heated to reflux. The progress of reaction was monitored by TLC (hexane:EtOAc 90:10). Upon completion (typically 18-24 h), reaction mixture was cooled to room temperature and then extracted with DCM (3 x 20 mL). The combined organic portion was washed with water (3 x 20 mL) and brine (1 x 20 mL), dried over anhydrous sodium sulfate and then concentrated *in vacuo*. The crude material was purified by flash chromatography to obtain pure ligand.

2b, the general procedure A was followed using 2-chloropyridine (2.0 g, 17.62 mmol), (4-(trifluoromethyl)phenyl)boronic acid (4.08 g, 21.15 mmol), 2 M K_2CO_3 (6.55 g, 47.52 mmol), PPh_3 (461 mg, 1.760 mmol), $Pd(OAc)_2$ (99 mg, 0.4420 mmol) and ethylene glycol dimethyl ether (20 mL). The crude material was purified by flash chromatography using hexane: ethyl acetate (0-5 % EtOAc for 40 cv and ramped to 100 % EtOAc for 40-70 cv and then held at 100% EtOAc 70-80 cv on 24 g silica column) to afford **2b** in 67% yield (2.60 g, 11.65 mmol) as a white solid. ^1H NMR matches literature values.[53]

2c, the general procedure A was followed using 2-chloropyridine (2.0 g, 17.62 mmol), (4-fluorophenyl) boronic acid (2.96 g, 21.15 mmol), 2 M K_2CO_3 (6.55 g, 47.52 mmol), PPh_3 (461 mg, 1.760 mmol), $Pd(OAc)_2$ (99 mg, 0.4420 mmol) and ethylene glycol dimethyl ether (20 mL). The crude material was purified by flash chromatography using hexane:ethyl acetate (0-5 % EtOAc for 40 cv and ramped to 100 % EtOAc for 40-70 cv and then held at 100% EtOAc 70-80 cv on 24 g silica column) to afford **2c** in quantitative yield (3.0 g, 17.32 mmol) as a white solid. ^1H NMR matches literature values.[54]

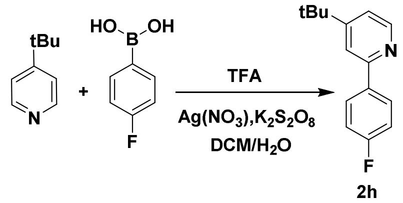
2d, the general procedure A was followed using 2-chloropyridine (1.0 g, 8.80 mmol), (2,4-difluorophenyl) boronic acid (1.67 g, 10.56 mmol), 2 M K_2CO_3 (3.28 g, 23.76 mmol), PPh_3 (231 mg, 0.8817 mmol), $Pd(OAc)_2$ (49 mg, 0.2188 mmol) and ethylene glycol dimethyl ether (10 mL). The crude material was purified by flash chromatography using hexane:ethyl acetate (0-5 % EtOAc for 40 cv and ramped to 100 % EtOAc for 40-70 cv and then held at 100% EtOAc 70-80 cv on 24 g silica column) to afford **2d** in 56% yield (0.94 g, 4.92 mmol) as colorless oily liquid. ^1H NMR matches literature values.[55]

2e, the general procedure A was followed using 2-chloropyridine (2.0 g, 17.62 mmol), (4-(tert-butyl) phenylboronic acid (3.76 g, 21.15 mmol), 2 M K_2CO_3 (6.55 g, 47.52 mmol), PPh_3 (461 mg, 1.760 mmol), $Pd(OAc)_2$ (99 mg, 0.4442 mmol) and ethylene glycol dimethyl ether (20 mL). The crude material was purified by flash chromatography using hexane:ethyl acetate (0-5 % EtOAc for 40 cv and ramped to 100 % EtOAc for 40-70 cv and then held at 100% EtOAc 70-80 cv on 24 g silica column) to afford **2e** in 79% yield (2.93 g, 13.90 mmol) as colorless oily liquid. ^1H NMR matches literature values.[56]

2f, the general procedure A was followed using 2-chloropyridine (2.0 g, 17.62 mmol), (3-(tert-butyl)phenyl) boronic acid (3.76 g, 21.15 mmol), 2 M K_2CO_3 (6.55 g, 47.52 mmol), PPh_3 (461 mg, 1.760 mmol), $Pd(OAc)_2$ (99 mg, 0.4420 mmol) and ethylene glycol dimethyl ether (20 mL). The crude material was purified by flash chromatography using hexane:ethyl acetate (0-5 % EtOAc for 40 cv and ramped to 100 % EtOAc for 40-70 cv and then held at 100% EtOAc 70-80 cv on 24 g silica column) to afford **2f** in 79% yield (2.76 g, 13.09 mmol) as colorless oily liquid. ^{1}H NMR (Chloroform-*d*, 400 MHz): δ = 8.75 – 8.71 (m, 1H), 8.07 (t, 1H, *J*=1.8 Hz), 7.83 – 7.71 (m, 3H), 7.53 – 7.41 (m, 2H), 7.25 (ddd, 1H, *J*=6.7, 4.8, 2.1 Hz), 1.42 (s, 9H) ppm.

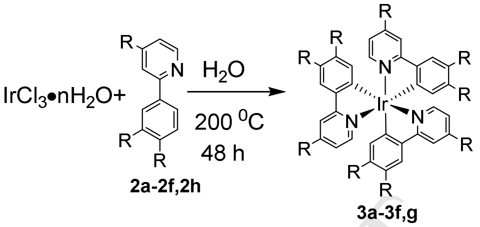
2g, the general procedure A was followed using 2-chloro-5-(trifluoromethyl) pyridine (2.0 g, 11.02 mmol), (2,4-difluorophenyl) boronic acid (2.09 g, 13.22 mmol), 2 M K_2CO_3 (4.11g, 29.75 mmol), PPh_3 (288 mg, 1.099 mmol), $Pd(OAc)_2$ (62 mg, 0.2881 mmol) and ethylene glycol dimethyl ether (20 mL). The crude material was purified by flash chromatography using hexane:ethyl acetate (0-5 % EtOAc for 40 cv and ramped to 100 % EtOAc for 40-70 cv and then held at 100% EtOAc 7080 cv on 24 g silica column) to afford **2g** in 79% yield (2.58 g, 9.961 mmol) as white solid. ^{1}H NMR matches literature values.[43]

Procedure for the synthesis of **2h**



A two necked 250 mL round bottom flask was equipped with a magnetic stir bar, 4-*tert*-butyl pyridine (1.00 g, 7.41 mmol, 1 equiv) and 40 mL dichloromethane. Then trifluoroacetic acid (567 uL, 7.41 mmol 1 equiv), 40 mL of an aqueous silver nitrate solution (0.03 M), 4-flourophenylbronic acid (1.54 mg, 11.1 mmol, 1.5 equiv), and potassium persulfate (3.09 g, 22.2 mmol, 3 equiv) were added. The reaction was stirred vigorously at room temperature for 6 hours and a second addition of silver nitrate (252 mg, 1.48 mmol, 0.2 equiv) and potassium persulfate (3.09 g, 22.2 mmol, 3 equiv) were added. After 18 h, another addition of 4-fluorobenzene boronic acid (515 mg, 3.71 mmol, 0.5 mmol) and potassium persulfate (1.03 g, 7.41 mmol, 1 equiv) were added. The progress of reaction was monitored by TLC (hexane:EtOAc 90:10). Upon completion, the reaction mixture was diluted with a 5% sodium bicarbonate solution and extracted with DCM (3 x 20 mL). The combined organic layer was dried over anhydrous magnesium sulfate and then concentrated *in vacuo*. The crude material was purified by flash chromatography using hexane:ethyl acetate (0-5 % EtOAc for 40 cv and ramped to 100 % EtOAc for 40-70 cv and then held at 100% EtOAc 70-80 cv on 24 g silica column) to afford **2h** in 29% (492 mg, 2.15 mmol) as a clear oil. ^{1}H NMR matches literature values.[39]

General procedure B for the synthesis of homoleptic *fac*-Ir $(C^\wedge N)_3$ complexes (**3a-3f,h**)



A Parr reactor (1 L model 4533, figure S1) was charged with iridium (III) chloride (1 equiv), ligand (12 equiv), sodium carbonate (6 equiv) and DI water (.03 M). The reaction mixture was pressurized (30 PSI) and depressurized with Ar (3x) and finally charged again with Ar before sealing. The reaction mixture was heated at 200 °C for 24-48 h. After cooling to room temperature, reaction mixture was extracted with DCM (3 x 20 mL). The combined organic portion was filtered through celite pad which was then concentrated to obtain crude product. The pure compound 3a-3f was obtained by performing flash chromatography. For most complexes, (3a-3d) crude samples were dry loaded on silica prior to running the column due to low solubility of the complex. After elution of the ligand with hexane/ethylacetate the eluting solvent was switched to dichloromethane, which faciliated the elution of the iridium complexes (3a-3f).

3a, the general procedure B was followed at 260 °C using iridium (III) chloride (192 mg, 0.64 mmol), 2-phenylpyridine (1.19 g, 7.7 mmol), Na_2CO_3 (407 mg, 3.8 mmol), and DI water (850 mL). The crude material was purified by flash chromatography (dry loaded) using hexane:ethyl acetate (0-10 % EtOAc for 40 cv to isolate ligand and then switched to DCM as well as ramped to 100 % DCM for 40-70 cv and then held at 100% DCM 70-80 cv) on 24 g silica column to afford **3a** in 79% yield (311 mg, 0.47 mmol) as a yellow solid which matched with the literature.[57] LC/MS (m/z) calculated for $C_{33}H_{24}IrN_3$ 655.16 found, 654.50.

3b, the general procedure B was followed except that **no sodium carbonate** was used, using iridium (III) chloride (100 mg, 0.33 mmol), 2-(4-(trifluoromethyl) phenyl) pyridine **2b** (896 mg, 4.0 mmol) and DI water (100 mL). The crude material was purified by flash chromatography (dry loaded) using hexane:DCM (0 % DCM for 16 cv and ramped to DCM 100 % for 16-20 cv and then held at 100% DCM for 20-23 cv) on 80 g silica column) to afford **3b** in 78 % yield (221 mg, 0.26 mmol) as a yellow solid. ^{1}H NMR(Chloroform-*d*, 400 MHz): δ = 7.99 (d, 3H, *J*=8.3 Hz), 7.77 – 7.69 (m, 6H), 7.55 (dd, 6H, *J*=6.0, 1.3 Hz), 7.20 – 7.15 (m, 3H), 7.02 (ddd, 3H, *J*=7.1, 5.2, 1.1 Hz), 6.96 (b, 3H) ppm. ^{13}C NMR (Methylene Chloride-d_2, 101 MHz): δ = 165.0, 159.2, 147.5 – 147.4 (m), 147.3, 137.0,132.4 (m), 130.6, 123.9, 123.4, 120.0, 117.3 – 117.2 (m), 100.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.76 (s). LC/MS (m/z) calculated for $C_{36}H_{21}F_9IrN_3$ 859.12 found M, 858.70

3c, the general procedure B was followed except that **no sodium carbonate** was used, using iridium (III) chloride (100 mg, 0.33 mmol), 2-(4-fluorophenyl)pyridine **2c** (678 mg, 3.9 mmol) and DI water (100 mL). The crude material was purified by flash chromatography (dry loaded) using hexane: DCM (0-50 % DCM for 25 cv, held at 50% for 25-35 cv and ramped to 100 % DCM for 35-36 cv and then held at 100% DCM 36-41 cv) on 40 g silica column to afford **3c** in 78 % yield (202 mg, 0.29 mmol) as a yellow-green solid. ^{1}H NMR(Methylene Chloride-d_2, 400 MHz): δ = 7.88 (d, 3H, *J*=8.2 Hz), 7.72 – 7.64 (m, 6H), 7.52 (ddd, 3H, *J*=5.5, 1.6, 0.8 Hz), 6.94 (ddd, 3H, *J*=7.1, 5.6, 1.3 Hz), 6.63 (td, 3H, *J*=8.7, 2.7 Hz), 6.39 (dd, 3H, *J*=10.3, 2.7 Hz) ppm. ^{13}C NMR(Methylene Chloride-d_2, 101 MHz): δ = 165.3 (d, *J*=5.4 Hz), 163.4 (d, *J*=5.7 Hz), 162.8, 147.2, 140.2, 136.6, 125.8 (d, *J*=9.2 Hz), 122.0, 121.8 (d, *J*=16.4 Hz), 118.9, 107.4 (d, *J*=23.6 Hz) ppm. ^{19}F NMR (376 MHz, Methylene Chloride-d_2) δ -112.33 (ddd, *J* = 10.3, 9.1, 5.7 Hz).). LC/MS (m/z) calculated for $C_{33}H_{21}F_3IrN_3$ 709.13 found, 708.60.

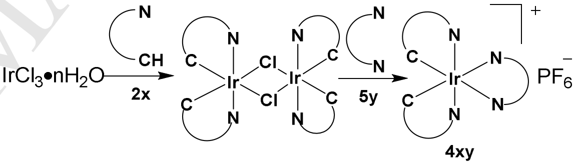
3d, the general procedure B was followed except that **no sodium carbonate** was used, using iridium (III) chloride (50 mg, 0.16 mmol), 2-(2,4-difluorophenyl)pyridine **2d** (184 mg, 0.96 mmol) and DI water (100 mL). The crude material was purified by flash chromatography (dry loaded) using hexane:ethyl acetate (0-40% EtOAc for 30 cv, changed EtOAc to DCM and ramped to 100 % DCM for 30-31 cv and then held at 100% DCM 31-39 cv) on 40 g silica column to afford **3d** in 56 % yield (68 mg, 0.09 mmol) as a pale yellow solid. The NMR specta matched with the literature.[31] ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27 (d, 3H, *J* = 8.6 Hz), 7.95 (t, 3H, *J* = 7.5 Hz), 7.54 (d, 3H *J* = 5.1 Hz), 7.26 (t, 3H, *J* = 6.4 Hz), 6.70 (td, 3H, *J* = 10.1, 9.2, 5.0 Hz), 6.06 (dd, 3H, *J* = 8.7, 2.2 Hz). ^{13}C NMR(Methylene Chloride-d_2, 101 MHz): δ = 162.9 (d, *J*=7.5 Hz), 162.5 (d, *J*=11.5 Hz), 161.3, 147.2, 137.4, 123.3 (d, *J*=20.9 Hz), 122.4, 117.8 (dd, *J*=16.1, 2.8 Hz), 96.6 (t, *J*=27.2 Hz) ppm. ^{19}F NMR (376 MHz, Methylene Chloride-d_2) δ -109.68 (q, 3F, *J* = 9.3 Hz), -110.86 (ddd, 3F, *J* = 12.6, 9.9, 2.3 Hz). LC/MS (m/z) calculated for $C_{33}H_{18}F_6IrN_3$ 763.10 found 763.00.

3e, the general procedure B was followed using iridium (III) chloride (100 mg, 0.33 mmol), 2-(4-(tert-butyl)phenyl)pyridine **2e** (844 mg, 4.0 mmol), sodium carbonate (210 mg, 2.0 mmol) and DI water (200 mL). The crude material was purified by flash chromatography using hexane:ethyl acetate (0-20 % EtOAc for 40 cv, switched EtOAc to DCM and ramped to 100 % DCM for 40-60 cv and then held at 100% DCM 60-65 cv) on 24 g silica column to afford **3e** in 92 % yield (249 mg, 0.30 mmol) as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, 3H, *J* = 8.2 Hz), 7.60 – 7.48 (m, 9H), 6.93 – 6.86 (m, 6H), 6.83 (ddd, 3H, *J* = 7.0, 5.6, 1.1 Hz), 1.10 (s, 27H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 161.5, 152.4, 147.5, 141.6, 136.0, 134.9, 123.5, 121.8, 118.8, 117.2, 34.8, 31.8. LC/MS (m/z) calculated for $C_{45}H_{48}IrN_3$ 823.35 found 822.65

3f, the general procedure B was followed using iridium (III) chloride (25 mg, 0.083 mmol), 2-(3-(tert-butyl) phenyl)pyridine **2f** (200 mg, 0.95 mmol), and DI water (50 mL). The crude material was purified by flash chromatography using hexane:EtOAc (0-10 % EtOAc for 32 cv, switched EtOAc to DCM and ramped to 100 % DCM for 32-42 cv and then held at 100% DCM 42-44 cv) on 24 g silica column to afford **3f** in 16 % yield (11 mg, 0.013 mmol) as a yellow solid. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.99 (dd, 3H, *J* = 8.3, 5.6 Hz), 7.82 – 7.56 (m, 9H), 6.95 (ddd, 6H, *J* = 10.2, 6.0, 1.8 Hz), 6.67 (dd, 3H, *J* = 7.8, 5.7 Hz), 1.35 (s, 27H). ^{13}C NMR (101 MHz, Methylene Chloride-d_2) δ 167.1, 157.3, 147.4, 143.3, 142.4, 136.4, 136.1, 127.6, 122.0, 120.7, 118.9, 34.2, 31.4. Anal. Calcd for $C_{45}H_{48}IrN_3$: C, 65.66; H, 5.88; N, 5.11. Found: C, 64.82; H, 4.98; N, 5.57. LC/MS (m/z) calculated for $C_{45}H_{48}IrN_3$ 823.35 found 822.90.

3h, the general procedure B was followed except that **no sodium carbonate** was used, using iridium (III) chloride (25 mg, 0.083 mmol), 4-(*tert*-butyl)-2-(4-fluorophenyl)pyridine **2h** (230 mg, 1 mmol) and DI water (100 mL). The crude material was purified by flash chromatography (**dry loaded**) using hexane: DCM (0-50 % DCM for 25 cv, held at 50% for 25-35 cv and ramped to 100 % DCM for 35-36 cv and then held at 100% DCM 36-41 cv) on 40 g silica column to afford **3h** in 84 % yield (61 mg, 0.070 mmol) as a yellowish green solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.69 (m, 3H), 7.56 (dd, 3H, *J* = 8.6, 5.7 Hz), 7.28 (d, 3H, *J* = 5.9 Hz), 6.83 (dd, 3H, *J* = 5.9, 1.8 Hz), 6.53 (td, 3H, *J* = 8.7, 2.6 Hz), 6.44 – 6.38 (m, 3H), 1.26 (s, 27H). 13C NMR (101 MHz, Chloroform-d) δ 164.0 , 163.0 (d, *J* = 251.5 Hz), 163.0 (d, *J* = 5.6 Hz), 159.1, 145.4, 139.2, 124.2 (d, *J* = 9.1 Hz), 121.3 (d, *J* = 16.1 Hz), 118.3, 114.37, 106.1 (d, *J* = 23.7 Hz), 33.9, 29.5. 19F NMR (376 MHz, Chloroform-d) δ -112.01 (s, 1F). LC/MS (m/z) calculated for $C_{45}H_{45}F_3IrN_3$ 877.32 found 877.20.

General Procedure C for the synthesis of cationic heteroleptic [Ir (C^N)$_2$(bpy)]$^+$ $PF_6$$^-$ complexes (**4xy**)



Heteroleptic iridium **4xy** were synthesized in a two-step procedure.[42, 43] In the first step, chloro-bridged dimer was synthesized by charging a two-necked reaction flask with magnetic stir bar, iridium(III) chloride (1 equiv), ligand (2.26 equiv), and a 2:1 v:v mixture of 2-methoxyethanol/water. The mixture was degased with Ar (via Ar bubbling) and heated under reflux at 120 °C with constant stirring overnight. The reaction mixture cooled to room temperature and filtered. The precipitate was washed with water (3 x 10 mL), dried in air and taken onto the second step without further purification unless noted. In the second step, the chloro-bridging dimer (1equiv), bipyridyl ligand (2.2 equiv) and ethyleneglycol were placed in a two-necked flask and then flushed with Ar. The mixture was heated at 150 °C for 15 h and then cooled. The cooled reaction mixture was washed hexane (3 x 10 mL) and mixture was heated to 85 °C for 5 min. to remove residual hexane. Aqueous ammonium hexafluorophosphate (sat. solution) was added to the reaction mixture causing the iridium-PF_6 salt to precipitate, which was filtered, dried and recrystallized (acetone/ether).

4ga, the general procedure C was followed using iridium(III) chloride (178 mg, 0.60 mmol), 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine pyridine **2g** (352 mg, 1.4 mmol) and a 2:1 mixture of 2-methoxyethanol/water (12 mL) to obtain the dimer in 74%

yield (326 mg, 0.22 mmol) as yellow solid. **4ga** was synthesized using the dimer (50 mg, 0.034 mmol), phenanthroline (**5a**, 14 mg, 0.075 mmol) and ethylene glycol (2 mL). **4ga** was obtained in 91% yield (64 mg, 0.062 mmol) as yellow crystals after recrystallization with acetone and hexane. ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.01 (dd, 2H, J = 8.3, 1.4 Hz), 8.68 (dd, 2H, J = 5.1, 1.4 Hz), 8.62 (dd, 2H J = 8.8, 2.6 Hz), 8.46 (s, 2H), 8.35 (dd, 2H, J = 8.8, 1.8 Hz), 8.15 (dd, 2H, J = 8.3, 5.1 Hz), 7.92 – 7.83 (m, 2H), 6.92 (ddd, 2H, J = 12.7, 9.3, 2.3 Hz), 6.08 (dd, 2H, J = 8.5, 2.3 Hz). ^{13}C NMR (101 MHz, Acetone-d_6) δ 167.7 (d, J = 6.8 Hz), 164.8 (dd, J = 209.3, 13.1 Hz), 162.2 (dd, J = 212.7, 12.9 Hz), 154.7 (d, J = 7.3 Hz), 152.3, 146.8, 146.4 (q, J = 4.7 Hz), 139.7, 137.2, 131.9, 128.6, 127.4, 127.1 (dd, J = 4.5, 2.6 Hz), 125.2 (d, J = 34.9 Hz), 123.8 (d, J = 20.9 Hz), 114.7 (dd, J = 18.0, 3.0 Hz), 99.4 (apparent t, J = 27.1 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -63.68 (s, 6F), -72.66 (d, 6F, J = 707.3 Hz), -104.86 (q, 2F J = 10.3, 9.3 Hz), -108.12 (td, 2F, J = 12.4, 2.7 Hz). ^{31}P NMR (162 MHz, Acetone-d_6) δ -130.00 – -157.36 (hept, J = 701.46 Hz). Anal. Calcd for $C_{36}H_{18}F_{16}IrN_4P$: C, 41.83; H, 1.76; N, 5.42. Found: C, 41.96; H, 1.89; N, 5.23. LC/MS (m/z) calculated for $C_{36}H_{18}F_{10}IrN_4$ 889.10 found M+, 888.60.

4gb, the general procedure C was followed using iridium(III) chloride (178 mg, 0.60 mmol), 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine **2g** (352 mg, 1.4 mmol) and a 2:1 mixture of 2-methoxyethanol/water (12 mL) to the obtain dimer in 74% yield (326 mg, 0.22 mmol) as yellow solid. **4gb** was synthesized using the dimer (100 mg, 0.067 mmol), 2,2' bipyridyl (**5b**, 23 mg, 0.15 mmol) and ethylene glycol (4 mL). 4b was obtained in 78 % yield (105 mg, 0.10 mmol) as yellow-green solid. ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.01 (d, 2H, J = 7.6 Hz), 8.64 (dd, 2H, J = 8.8, 2.5 Hz), 8.47 – 8.38 (m, 4H), 8.31 (d, 2H, J = 5.3 Hz), 8.00 (s, 2H), 7.81 (t, 2H, J = 8 Hz), 6.87 (ddd, 2H, J = 12.7, 9.3, 2.3 Hz), 5.98 (dd, 2H, J = 8.5, 2.3 Hz). ^{13}C NMR (101 MHz, Acetone-d_6) δ 167.7 (d, J = 6.9 Hz), 164.8 (dd, J = 210.8, 12.9 Hz), 162.2 (dd, J = 214.1, 12.9 Hz), 156.1, 155.2 (d, J = 7.0 Hz), 151.4, 146.2 (q, J = 4.7 Hz), 140.7, 137.5 – 137.1 (m), 129.1, 126.9 (dd, J = 4.3, 2.6 Hz), 125.7, 125.3, 123.9 (d, J = 21.0 Hz), 122.1 (d, J = 271.6 Hz), 114.5 (dd, J = 18.0, 3.0 Hz), 99.4 (apparent t, J = 27.1 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -63.56 (s, 6F), -72.65 (d, 6F, J = 707.3 Hz), -104.62 – -104.81 (m, 2F), -107.74 – -108.15 (m, 2F). ^{31}P NMR (162 MHz, Acetone-d_6) δ -131.24 – -157.38 (hept, J = 707.94 Hz). LC/MS (m/z) calculated for $C_{34}H_{18}F_{10}IrN_4$ 865.10 found M+, 864.50.

4gc, the general procedure C was followed using iridium(III) chloride (178 mg, 0.60 mmol), 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine **2g** (352 mg, 1.4 mmol) and a 2:1 mixture of 2-methoxyethanol/water (12 mL) to obtain the dimer in 74% yield (326 mg, 0.22 mmol) as yellow solid. **4gc** was synthesized using the dimer (100 mg, 0.067 mmol), 4,4'-di-tbutyl-2,2'-bipyridyl (**5c**, 39 mg, 0.147 mmol) and ethylene glycol (4 mL). 4c was obtained in 81% yield (121 mg, 0.11 mmol) as yellow solid. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.95 (d, 2H, J = 1.8 Hz), 8.63 (dd, 2H, J = 8.8, 2.6 Hz), 8.42 (dd, 2H, J = 8.8, 1.9 Hz), 8.20 (d, 2H, J = 5.9 Hz), 7.85 – 7.81 (m, 4H), 6.88 (ddd, 2H, J = 12.7, 9.3, 2.3 Hz), 5.98 (dd, 2H, J = 8.4, 2.3 Hz), 1.45 (s, 18H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 167.9 (d, J = 7.5 Hz), 165.4, 164.6 (dd, J = 258.5, 12.7 Hz), 162.5 (dd, J = 261.8, 13.1 Hz), 156.0, 155.8 (d, J = 7.0 Hz), 151.1, 145.7 (q, J = 4.8 Hz), 137.2 (d, J = 3.0 Hz), 126.8 (dd, J = 4.4, 2.5 Hz), 126.0, 125.3 (d, J = 35.3 Hz), 123.9 (d, J = 21.0 Hz), 122.6, 122.2 (d, J = 271.7 Hz), 114.5 (dd, J = 17.8, 3.0 Hz), 99.3 (apparent t, J = 27.1 Hz), 35.7, 29.5. ^{19}F NMR (376 MHz, Acetone-d_6) δ -63.69 (s, 6F), -72.68 (d, 6F, J = 707.3 Hz), -104.76 (dt, 2F, J = 11.9, 9.0 Hz), -108.09 (td, 2F, J = 12.4, 2.4 Hz). ^{31}P NMR (162 MHz, Acetone-d_6) δ -131.17 – -157.37 (hept, J = 706.32 Hz). LC/MS (m/z) calculated for $C_{42}H_{34}F_{10}IrN_4$ 977.23 found M+, 977.20.

4db, the general procedure C was followed using iridium(III) chloride (89 mg, 0.30 mmol), 2-(2,4-difluorophenyl)pyridine **2d** (130 mg, 0.68 mmol) and a 2:1 mixture of 2-methoxyethanol/water (6 mL) to obtain the dimer in 82% yield (150 mg, 0.12 mmol) as yellow solid. **4db** was synthesized using the dimer (**5b**, 150 mg, 0.12 mmol), 2,2'-bipyridyl (34 mg, 0.22 mmol) and ethylene glycol (6 mL). 4d was obtained in 57% yield (100 mg, 0.11 mmol) as yellow solid. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.89 (d, 2H, J = 8.1 Hz), 8.46 – 8.33 (m, 4H), 8.24 (ddd, 2H, J = 5.4, 1.5, 0.6 Hz), 8.11 – 8.05 (m, 2H), 7.94 (ddd, 2H, J = 5.8, 1.5, 0.7 Hz), 7.77 (ddd, 2H, J = 7.6, 5.5, 1.2 Hz), 7.27 (ddd, 2H, J = 7.4, 5.9, 1.4 Hz), 6.78 (ddd, 2H, J = 12.7, 9.3, 2.4 Hz), 5.82 (dd, 2H, J = 8.5, 2.4 Hz). ^{13}C NMR (101 MHz, Acetone-d_6) δ 164.8 (d, J = 7.1 Hz), 163.5 (dd, J = 39.4, 12.7 Hz), 163.5 (dd, J = 476.4, 12.7 Hz), 156.8, 155.6 (d, J = 6.6 Hz), 152.0, 150.8, 141.2, 140.8, 130.0, 128.9 (dd, J = 4.5, 2.8 Hz), 126.1, 125.2, 124.6 (d, J = 20.2 Hz), 114.7 (dd, J = 17.7, 3.0 Hz), 99.7 (apparent t, J = 27.1 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -72.67 (d, 6F, J = 707.2 Hz), -107.74 – -107.86 (m, 2F), -110.00 – -110.13 (m, 2F). ^{31}P NMR (162 MHz, Acetone-d_6) δ -131.16-157.38 (hept, J = 707.94 Hz). LC/MS (m/z) calculated for $C_{32}H_{20}F_4IrN_4$ 729.13 found M+, 728.55.

4dc, the general procedure C was followed using iridium(III) chloride (89 mg, 0.29 mmol), 2-(2,4-difluorophenyl)pyridine **2d** (130 mg, 0.68 mmol) and a 2:1 mixture of 2-methoxyethanol/water (6 mL)to obtain the dimer in 82% yield (150 mg, 0.12 mmol) as yellow solid. **4dc** was synthesized using the dimer (126 mg, 0.10 mmol), 4,4'-di-tbutyl-2,2'-bipyridyl (**5c**, 59 mg, 0.22 mmol) and ethylene glycol (6 mL). 4e was obtained in 88% yield (174 mg, 0.18 mmol) as yellow solid. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.79 (d, 2H, J = 1.8 Hz), 8.27 (d, 2H, J = 8.4 Hz), 7.98 – 7.90 (m, 4H), 7.76 – 7.72 (m, 2H), 7.62 (dd, 2H, J = 5.9, 2.0 Hz), 7.09 (ddd, 2H, J = 7.4, 5.9, 1.3 Hz), 6.64 (ddd, 2H, J = 12.6, 9.4, 2.4 Hz), 5.65 (dd, 2H, J = 8.6, 2.4 Hz), 1.28 (s, 18H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 164.6, 165.4 – 163.8 (m), 162.5 (dd, J = 37.2, 12.6 Hz), 160.1 (d, J = 12.8 Hz), 155.7, 155.2 (d, J = 6.2 Hz), 150.5, 149.6, 139.7, 125.8, 124.1, 123.6 (d, J = 20.5 Hz), 122.4, 113.6 (dd, J = 17.6, 2.9 Hz), 98.6 (apparent t, J = 27.2 Hz), 35.6, 29.5. ^{19}F NMR (376 MHz, Acetone-d_6) δ -72.61 (dd, 6F, J = 707.2, 8.6 Hz), -107.90 (q, 2F, J = 9.7 Hz), -110.17 (t, 2F, J = 11.7 Hz). ^{31}P NMR (162 MHz, Acetone-d_6) δ -130.58 – -157.12 (hept, J = 707.94 Hz). LC/MS (m/z) calculated for $C_{40}H_{36}F_4IrN_4$ 841.25 found M+, 840.60.

4cb, the general procedure C was followed using iridium(III) chloride (89 mg, 0.30 mmol), 2-(4-fluorophenyl)pyridine **2c**, and a 2:1 mixture of 2-methoxyethanol/water (6 mL) to obtain the dimer in 82% yield (150 mg, 0.12 mmol) as yellow solid. 4f was synthesized using the dimer (35 mg, 0.031 mmol), 2,2'-bipyridyl (**5b**, 10.5 mg, 0.067 mmol) and ethylene glycol (5 mL). **4cb** was obtained in 94% yield (48 mg, 0.070 mmol) as yellow solid. ^{1}H NMR(Acetone-d_6, 400 MHz): δ = 8.87 (d, 2H, *J*=8.2 Hz), 8.33 (td, 2H, *J*=8.0, 1.6 Hz), 8.24 (d, 2H, *J*=8.1 Hz), 8.17 (ddd, 2H, *J*=5.4, 1.5, 0.7 Hz), 8.05 – 7.95 (m, 4H), 7.83 (ddd, 2H, *J*=5.8, 1.4, 0.7 Hz), 7.75 (ddd, 2H, *J*=7.6, 5.5, 1.2 Hz), 7.23 – 7.14 (m, 2H), 6.84 (td, 2H, *J*=8.9, 2.6 Hz), 5.95 (dd, 2H, *J*=9.5, 2.6 Hz) ppm ^{13}C NMR(Acetone-d_6, 101 MHz): δ = 167.6, 166.0, 157.0, 154.5 (d, *J*=5.9 Hz), 151.9, 150.3, 141.5 (d, *J*=2.1 Hz), 140.9, 140.1, 129.8, 128.3 (d, *J*=9.4 Hz), 126.0, 124.7, 121.2, 118.4 (d, *J*=17.9 Hz), 110.7 (d, *J*=23.3 Hz) ppm ^{19}F NMR(Acetone-d_6, 376 MHz): δ = -72.63 (d, 6F, *J*=707.4 Hz), -110.75 (s, 2F) ppm ^{31}P NMR(Chloroform-*d*, 162 MHz): δ = -129.39 – -148.65 (m) ppm. Anal. calcd for $C_{32}H_{22}F_8IrN_4P$: C, 45.88; H, 2.65; N, 6.69. Found: C, 45.75; H, 7.48; N, 7.08. LC/MS (m/z) calculated for $C_{32}H_{22}F_2IrN_4$ 693.14 found M+, 692.60.

4cc, the general procedure C was followed using iridium(III) chloride (89 mg, 0.31 mmol), 2-(4-fluorophenyl)pyridine **2c**, and a 2:1 mixture of 2-methoxyethanol/water (6 mL)to obtain the dimer in 82% yield (150 mg, 0.12 mmol) as yellow solid. **4cc** was synthesized using the dimer (106 mg, 0.10 mmol), 4,4'-di-tbutyl-2,2'-bipyridyl (**5c**, 54 mg, 0.20 mmol) and ethylene glycol (5 mL). 4g was obtained in 83% yield (158 mg, 0.19 mmol) as yellow solid.. ^{1}H NMR(Acetone-d_6, 400 MHz): δ = 8.90 (d, 2H, *J*=1.7 Hz), 8.24 (d, 2H, *J*=8.1 Hz), 8.05 – 7.95 (m, 6H), 7.80 – 7.77 (m, 2H), 7.74 (dd, 2H, *J*=5.9, 2.0 Hz), 7.16 (ddd, 2H, *J*=7.3, 5.9, 1.4 Hz), 6.83 (td, 2H, *J*=8.9, 2.6 Hz), 5.94 (dd, 2H, *J*=9.5, 2.6 Hz), 1.41 (s, 18H) ppm ^{13}C NMR (101 MHz, Acetone-d_6) δ 167.7, 165.3, 164.7 (d, *J* = 252.8 Hz), 156.8, 155.09 (d, *J* = 5.8 Hz), 151.4, 150.0, 141.5 (d, *J* = 2.0 Hz), 140.0, 128.2 (d, *J* = 9.4 Hz), 126.7, 124.5, 123.1, 121.1, 118.3 (d, *J* = 17.8 Hz), 110.5 (d, *J* = 23.2 Hz), 36.5 . ^{19}F NMR (376 MHz, Acetone-d_6) δ -72.61 (d, 6F, *J* = 707.4 Hz), -110.86 (s, 2F).^{31}P NMR(Chloroform-*d*, 162 MHz): δ = -139.08 (p, *J*=707.6 Hz) ppm. LC/MS (m/z) calculated for $C_{40}H_{38}F_2IrN_4$ 805.27 found M+, 804.70.

4fd, the general procedure C was followed using iridium(III) chloride (178 mg, 0.60 mmol), 2-(3-(tert-butyl)phenyl)pyridine **2f** (287 mg, 1.4 mmol), and a 2:1 mixture of 2-methoxyethanol/water (12 mL) to obtain the dimer in 60% yield (232 mg, 0.18 mmol) as yellow solid. **4fd** was synthesized using the dimer (28 mg, 0.022 mmol), 4,4'-di-methoxy-2,2'-bipyridyl (**5d**, 11 mg, 0.048 mmol) and ethylene glycol (2 mL). 4h was obtained in > 99% yield (43 mg, 0.044 mmol) as orange solid. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.35 (d, 2H, *J* = 2.6 Hz), 8.32 (d, 2H, *J* = 8.1 Hz,), 7.99 – 7.92 (m, 4H), 7.91 – 7.87 (m, 2H), 7.83 (d, 2H, *J* = 6.4 Hz), 7.24 (dd, 2H, *J* = 6.4, 2.6 Hz), 7.17 (ddd, 2H, *J* = 7.3, 5.8, 1.4 Hz), 7.02 (dd, 2H, *J* = 8.0, 2.1 Hz), 6.32 (d, 2H, *J* = 8.0 Hz), 4.09 (s, 6H), 1.32 (s, 18H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.5, 168.1, 157.7, 151.5, 149.3, 147.3, 144.9, 143.9, 138.4, 131.6, 128.0, 123.4, 121.9, 119.9, 114.1, 111.6, 56.6, 34.2, 31.0. ^{31}P NMR (162 MHz, Acetone-d_6) δ -130.19 – -157.39 (hept, *J* = 707.94 Hz). Anal. calcd for $C_{42}H_{44}F_6IrN_4O_2P$: C, 51.79; H, 4.55; N, 5.75. Found: C, 51.61; H, 4.38; N, 5.94. LC/MS (m/z) calculated for $C_{42}H_{44}IrN_4O_2$ 829.31 found M+, 828.70.

ASSOCIATED CONTENT

Supporting Information

Spectra, figures and tables of properties for the compounds. This material is available free of charge via the Internet at

AUTHOR INFORMATION

Corresponding Author

* E-mail for JDW: jimmie.weaver@okstate.edu

Notes

The authors declare no competing financial interests.

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Complex	λmax	TSE kca/mol	$E_{1/2Ox}$ V	$E_{1/2Red}$ V	E_{gap} eV	$E_{1/2(Ir+/Ir*)}$	$E_{1/2(Ir*/Ir-)}$
4gb	473	60.4	1.23	-1.23	2.20	-0.97	0.97
4ga	475	60.2	1.81	-1.25	2.64	-0.83	1.39
4gc	476	60.1	1.77	-1.35	2.77	-1.00	1.42
3d	476	60.1	0.98	-1.82	2.21	-1.23	0.39
3h	481	59.4	0.93	-1.58	2.20	-1.27	0.62
3c	488	58.6	1.00	-2.13	2.86	-1.86	0.73
3b	507	56.4	1.11	-2.13	2.76	-1.65	0.63
4dc	516	55.4	1.63	-1.42	2.56	-0.93	1.14
3a	518	55.2	0.78	-2.20	2.75	-1.97	0.55
3e	525	54.5	0.69	-2.27	2.59	-1.90	0.32
3f	528	54.2	0.70	-2.03	2.28	-1.59	0.25
4db	528	54.2	1.66	-1.32	2.46	-0.80	1.14
4cc	540	53.0	1.49	-1.45	2.52	-1.04	1.07
4cb	556	51.4	1.51	-1.37	2.40	-0.89	1.03
4fd	560	51.1	1.17	-1.50	2.35	-1.18	0.85

- Synthesis of iridium photocatalysts directly from $IrCl_3$ in 1 step and high yields
- Determination of redox properties
- Determination of triplet state energies
- Spectral characterization

Facile Synthesis and Complete Characterization of Homoleptic and Heteroleptic Cyclometalated Iridium(III) Complexes for Photocatalysis

Anuradha Singh, Kip A. Teegardin, Kariate S. Prasad, Megan Kelly, Sadagopan Krishnan, Jimmie D. Weaver*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

jimmie.weaver@okstate.edu

Supporting Information

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Figure S1 Parr temperature controller model 4838

Electrochemical Measurements: Ground state redox potential of all complexes were determined (table S1) by CV. Measured $E_{ox}^{1/2}$, $E_{red}^{1/2}$ and E_{gap} (value determined by CV) was utilized to calculate excited state potentials using equation 2 and 3.

$$E_{1/2}\ Ir^+/Ir^* = E_{1/2\ ox} – E\ gap = \text{(eq 2)}$$

$$E_{1/2}\ Ir^*/Ir^- = E\ gap + E_{1/2\ red}\ \text{(eq 3)}$$

Table S1 Data from electrochemical measurements

complex	λmax	TSE Kcal/mol	$E_{1/2}$ ox V	$E_{1/2}$ red V	E gap eV	$E_{1/2}$ (Ir^+/Ir^*)	$E_{1/2}$ (Ir^*/Ir^-)
4gb	473	60.4	1.23	-1.23	2.20	-0.97	0.97
4ga	475	60.2	1.81	-1.25	2.64	-0.83	1.39
4gc	476	60.1	1.77	-1.35	2.77	-1.00	1.42
3d	476	60.1	0.98	-1.82	2.21	-1.23	0.39
3h	481	59.4	0.93	-1.58	2.20	-1.27	0.62
3c	488	58.6	1.00	-2.13	2.86	-1.86	0.73
3b	507	56.4	1.11	-2.13	2.76	-1.65	0.63
4dc	516	55.4	1.63	-1.42	2.56	-0.93	1.14
3a	518	55.2	0.78	-2.20	2.75	-1.97	0.55
3e	525	54.5	0.69	-2.27	2.59	-1.90	0.32
3f	528	54.2	0.70	-2.03	2.28	-1.59	0.25

4db	528	54.2	1.66	-1.32	2.46	-0.80	1.14
4cc	540	53.0	1.49	-1.45	2.52	-1.04	1.07
4cb	556	51.4	1.51	-1.37	2.40	-0.89	1.03
4fd	560	51.2	1.17	-1.50	2.35	-1.12	0.85

Note: TSE=triplet state energy determined from emission spectra

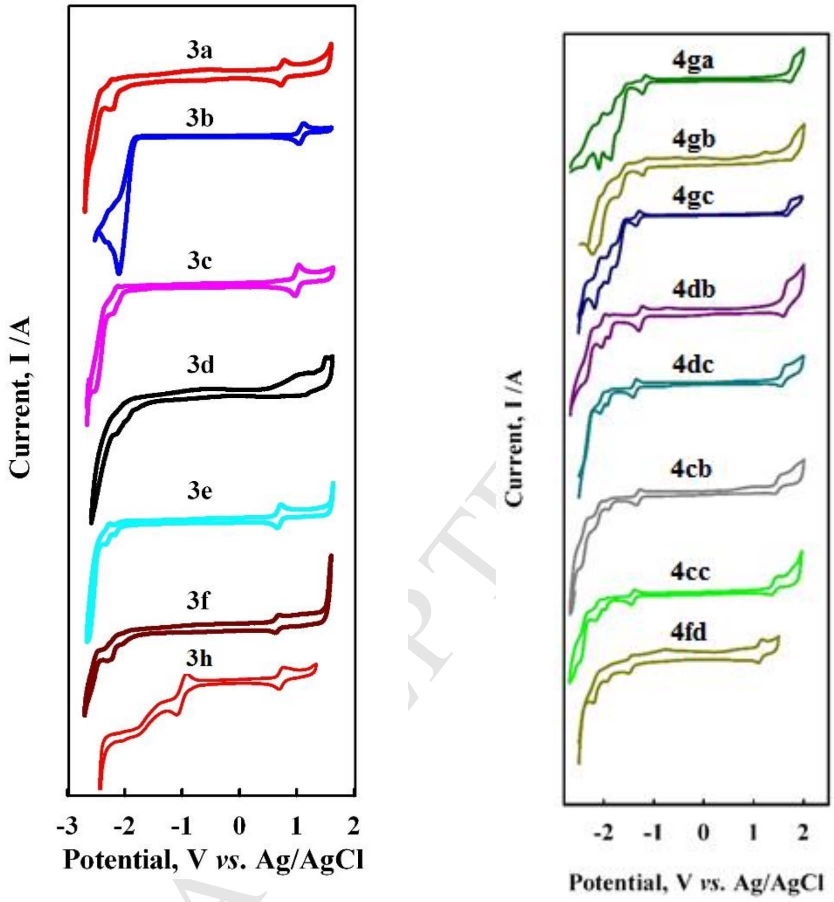
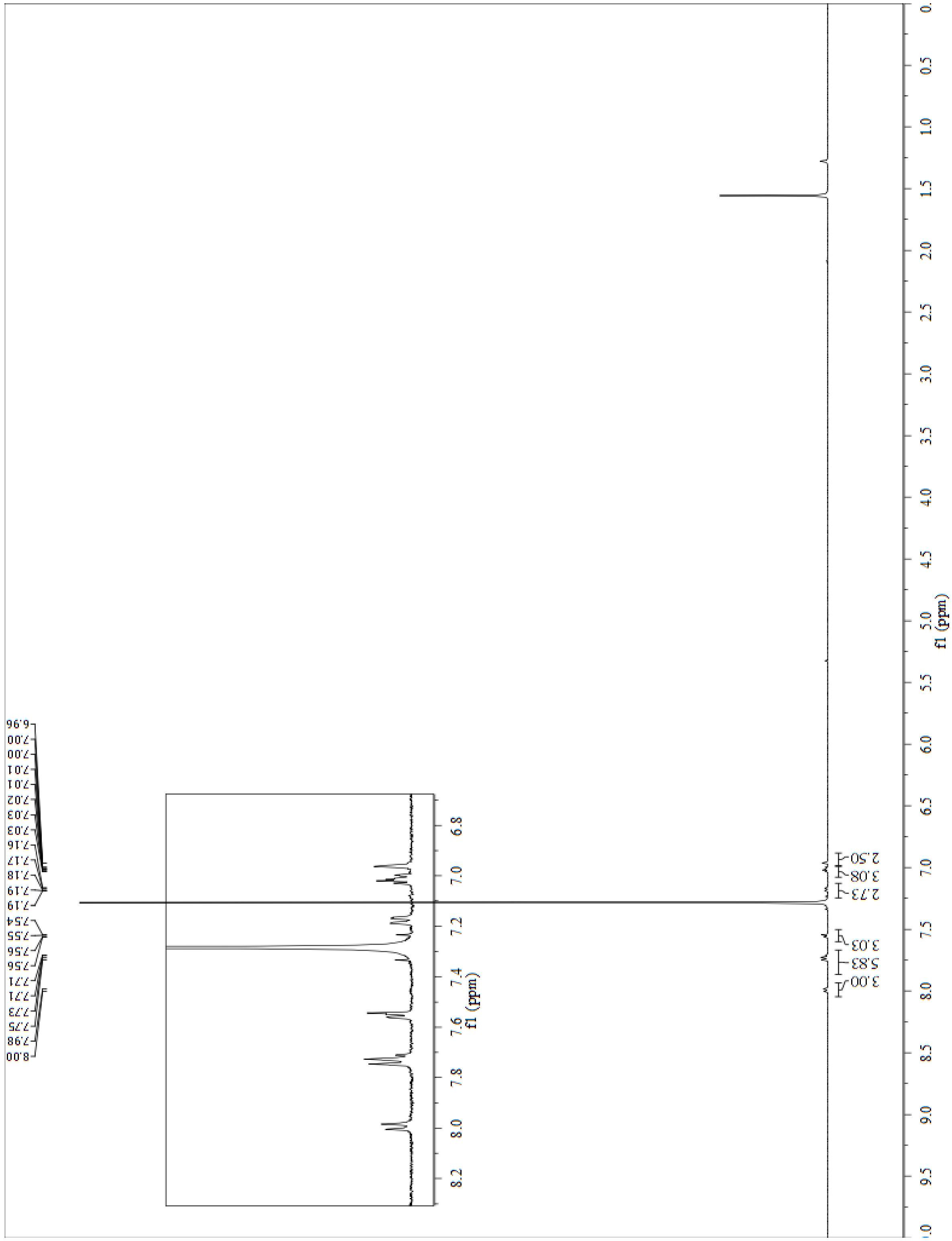
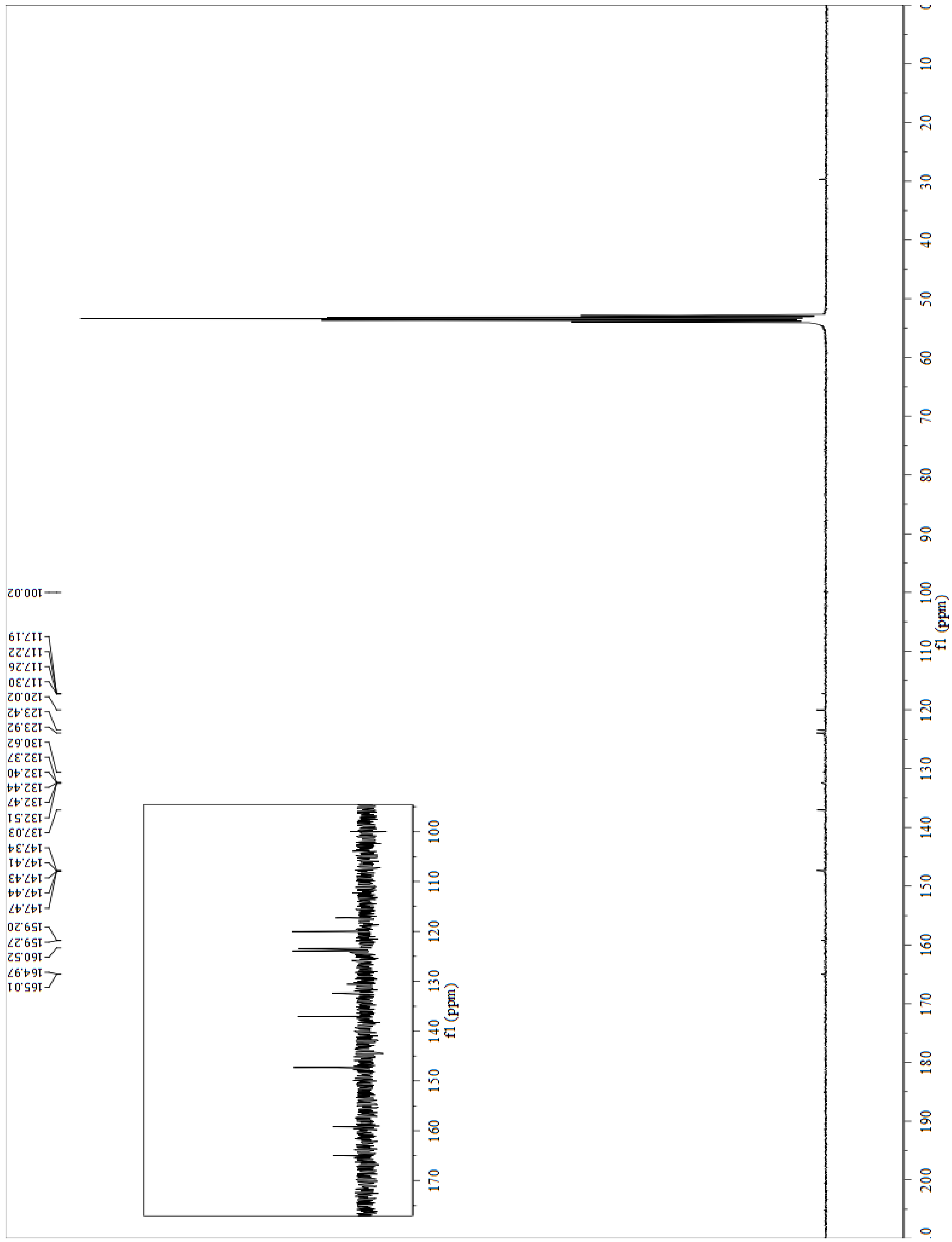


Figure S2 Cyclic Voltammogram of 3a-3f, 3h (left) and 4ga-4fd (right)

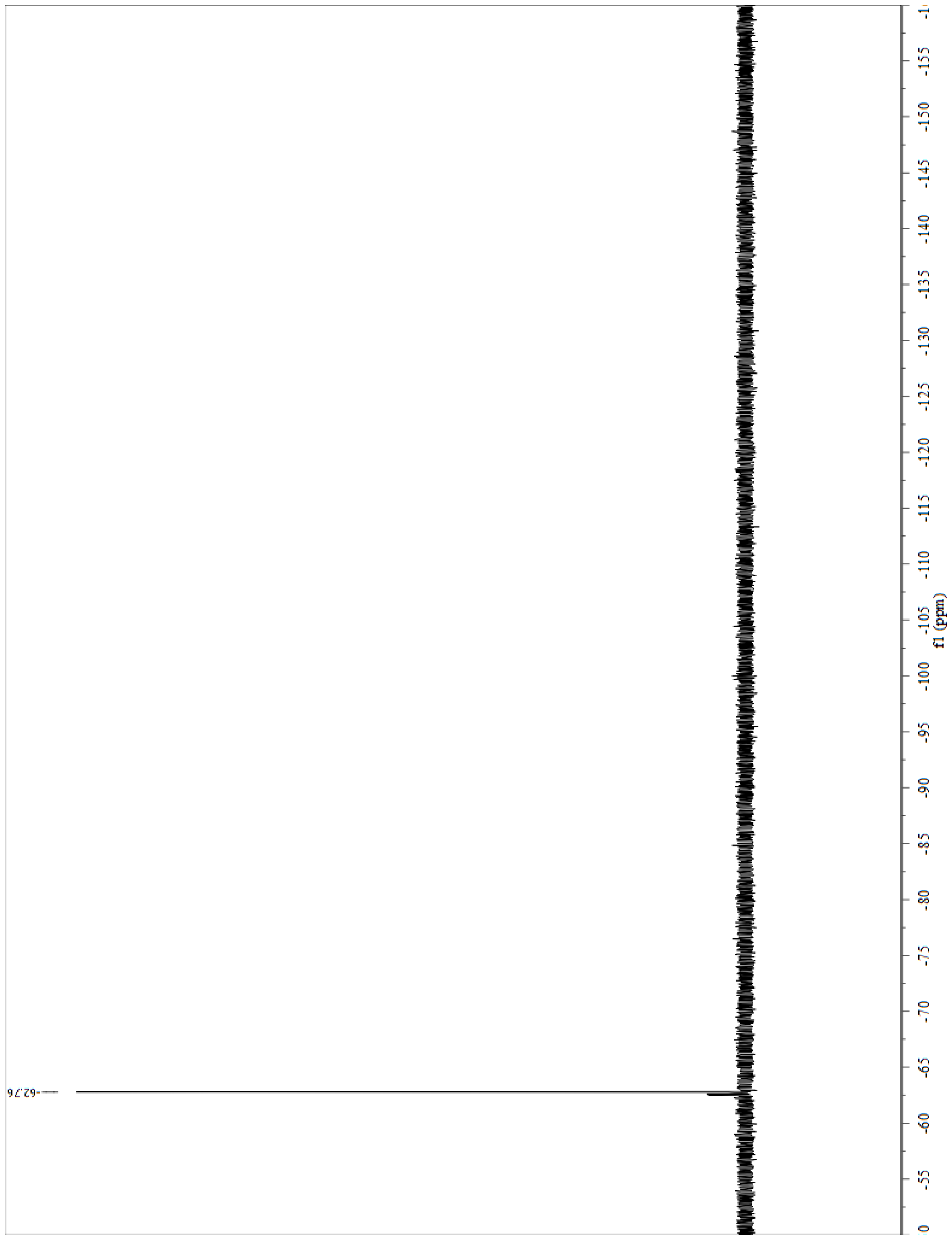
^{1}H NMR spectrum of **3b**



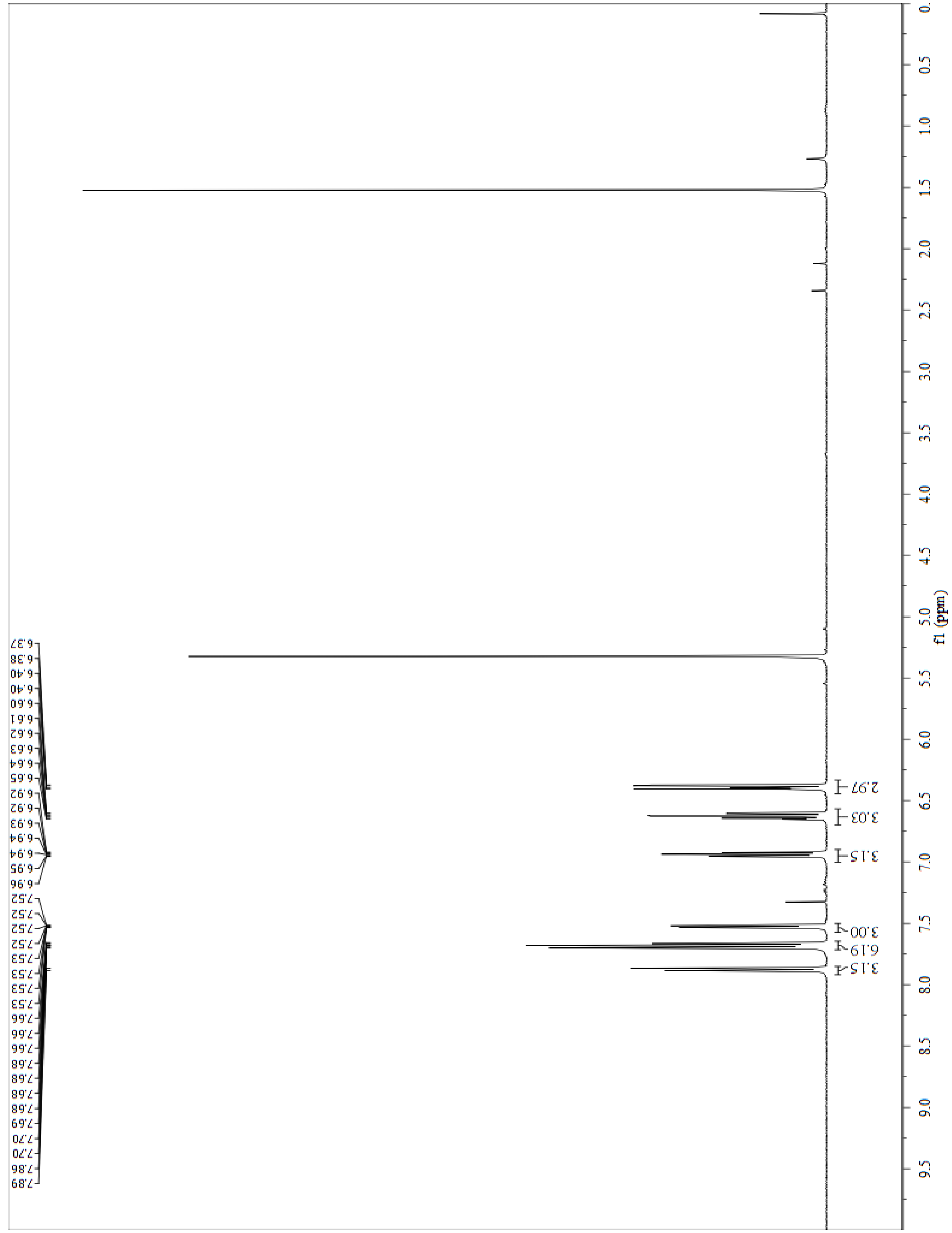
^{13}CNMR spectrum of **3b**



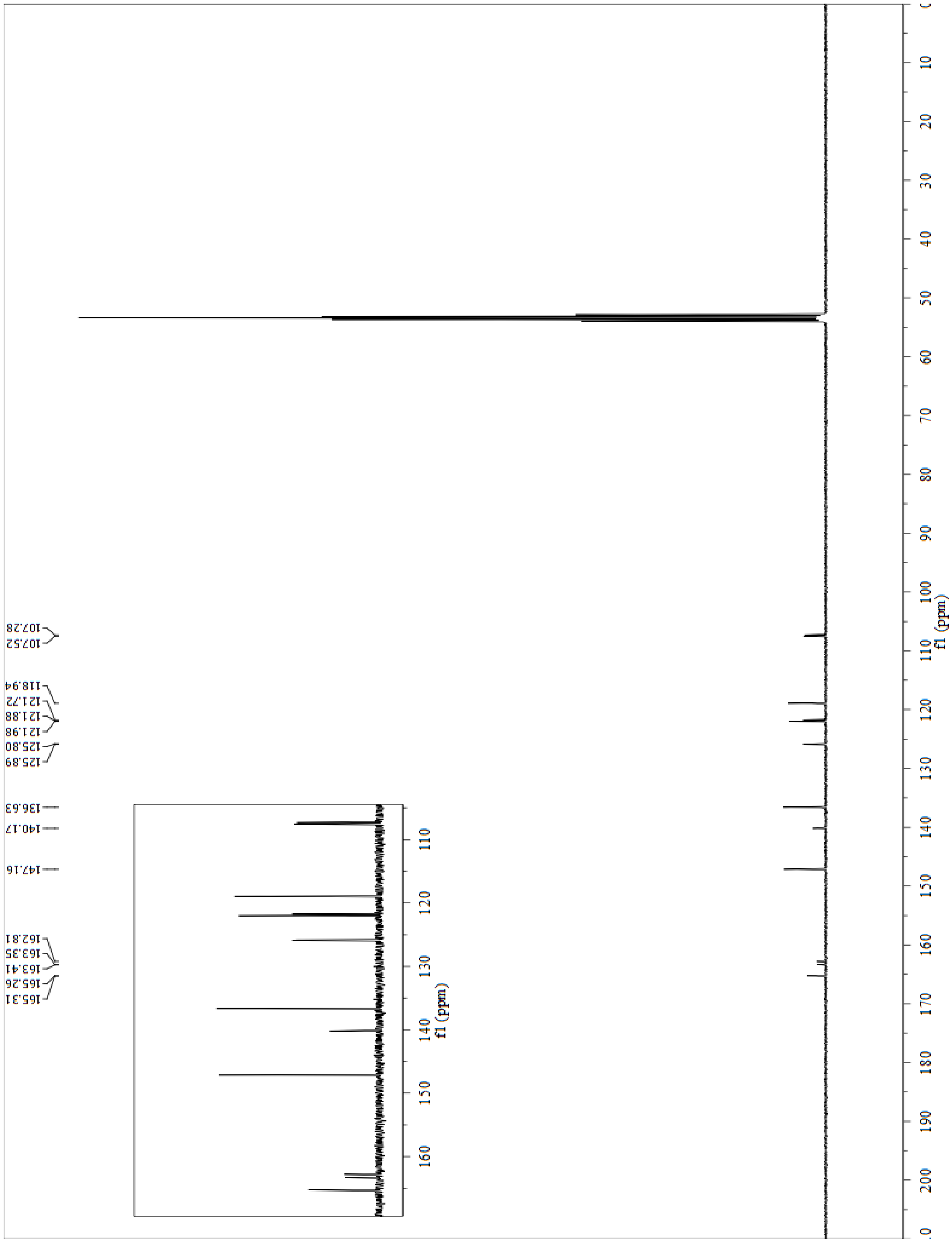
^{19}FNMR spectrum of **3b**



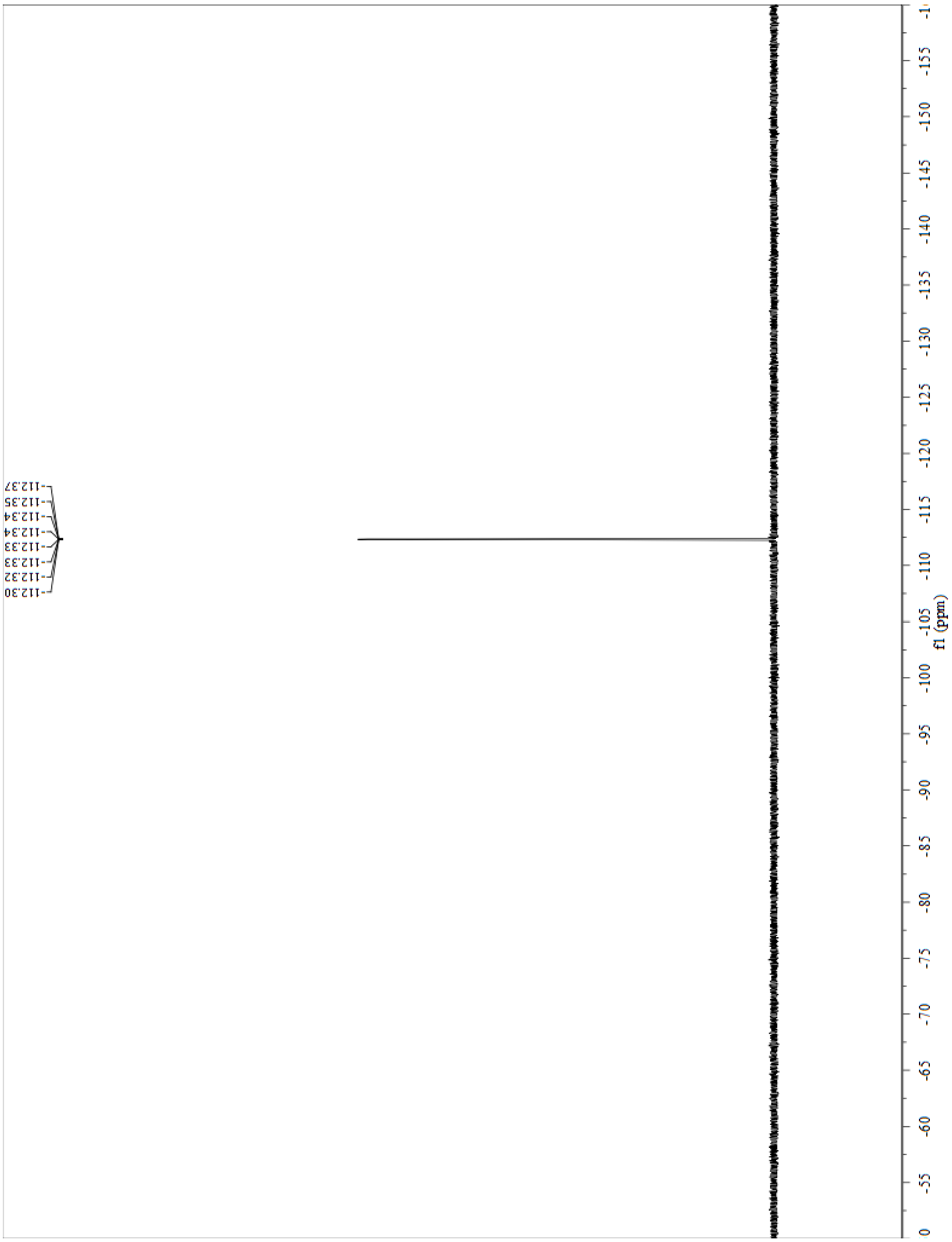
^{1}H NMR spectrum of **3c**



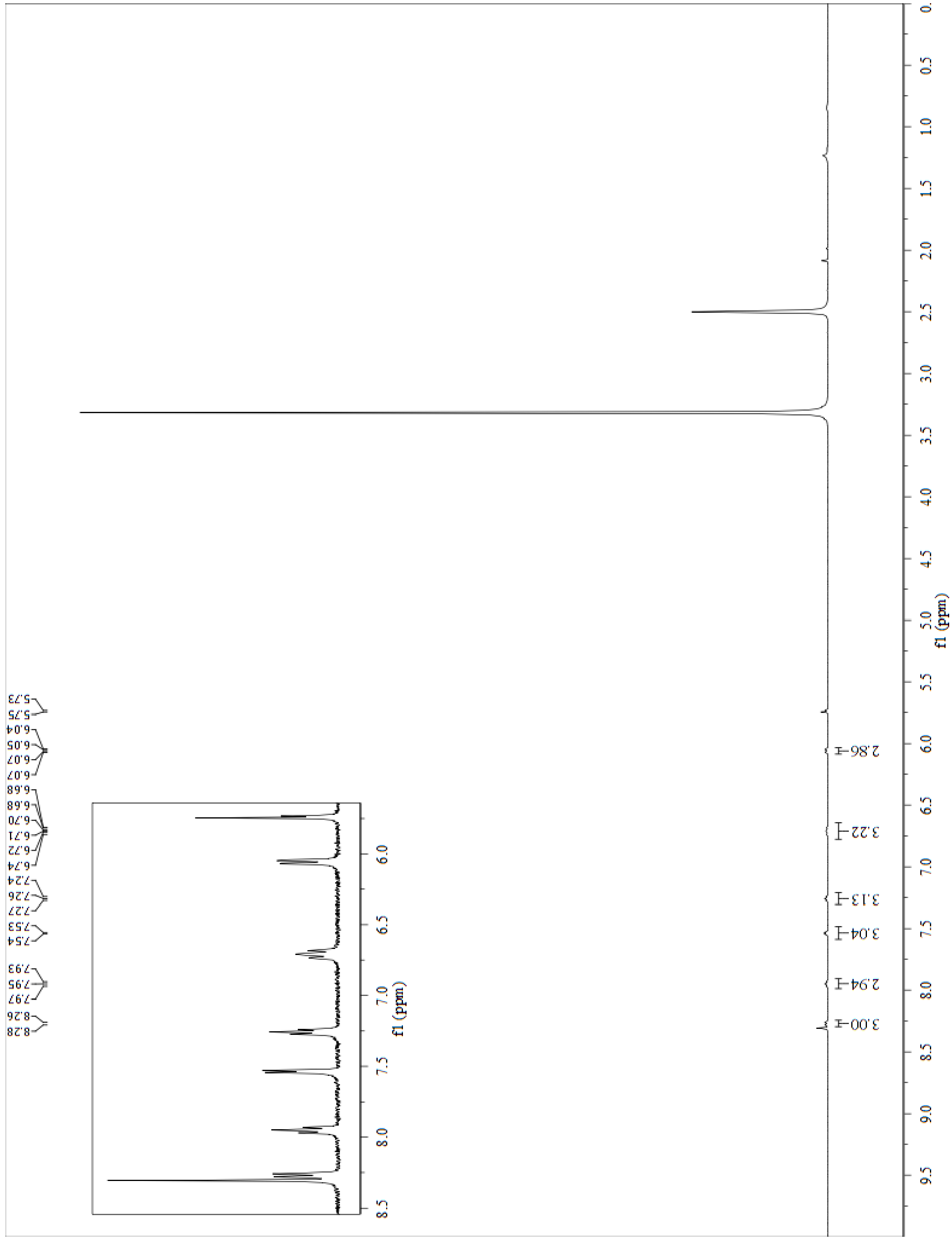
^{13}CNMR spectrum of **3c**



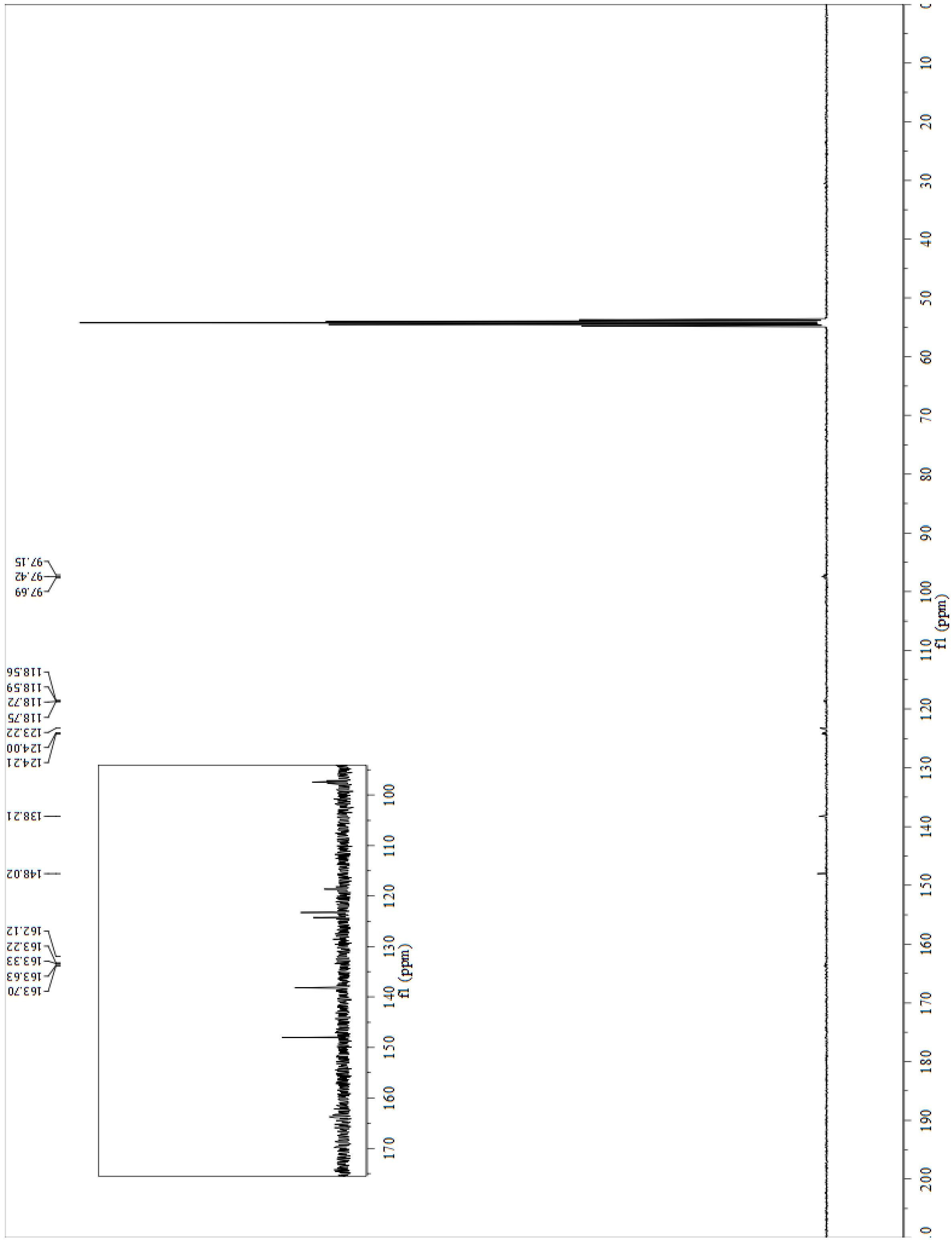
^{19}FNMR spectrum of **3c**



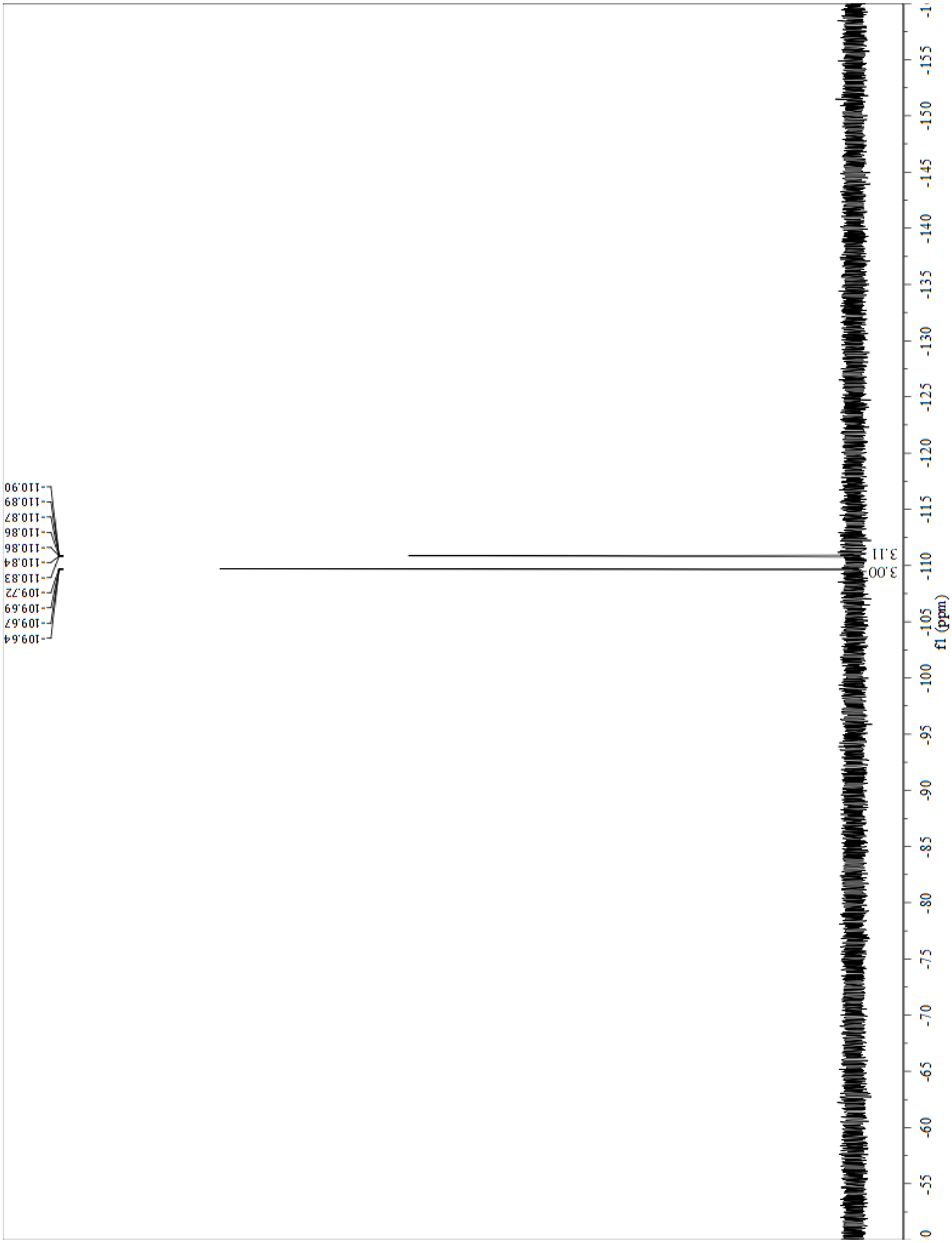
^{1} H NMR spectrum of **3d**



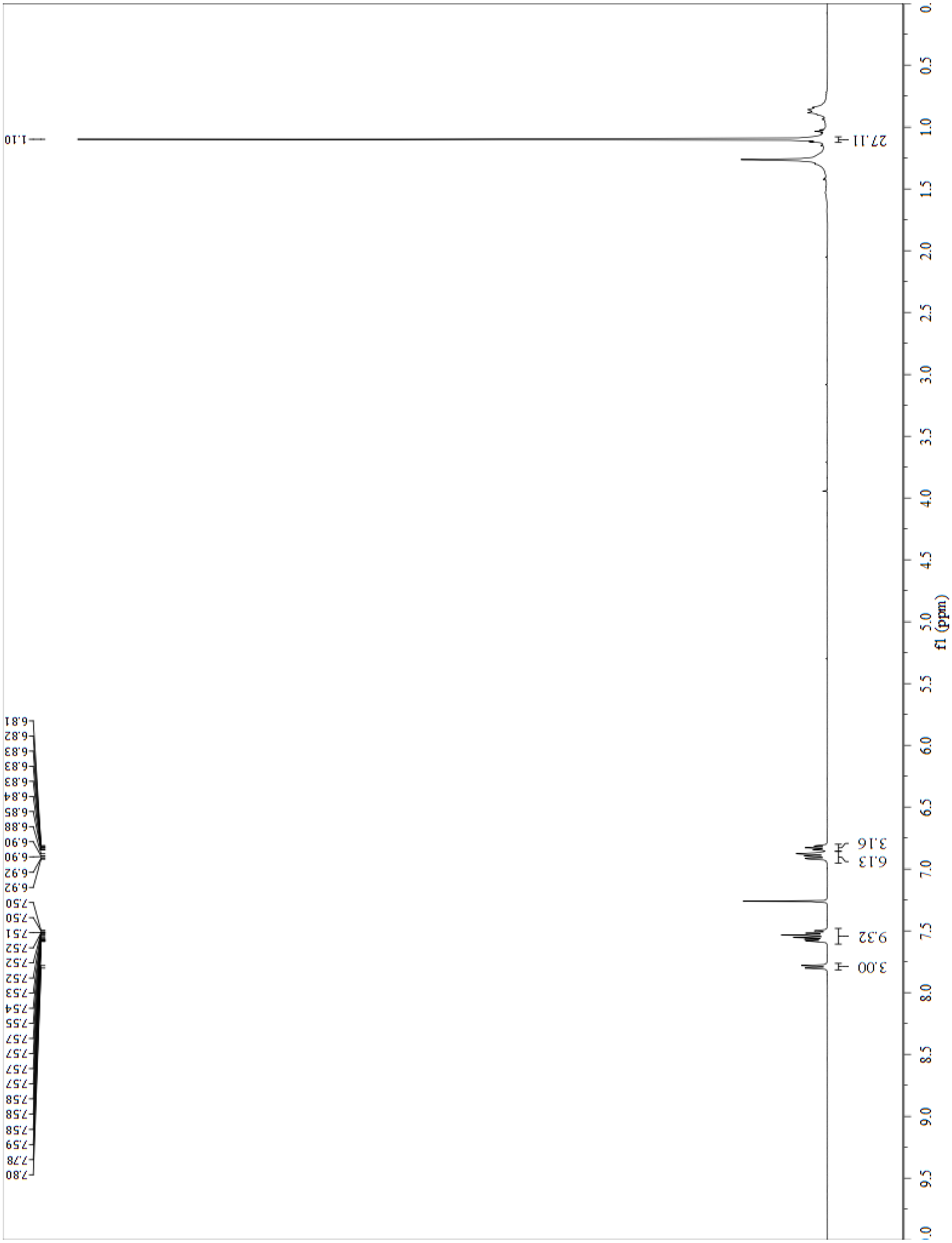
^{13}CNMR spectrum of **3d**



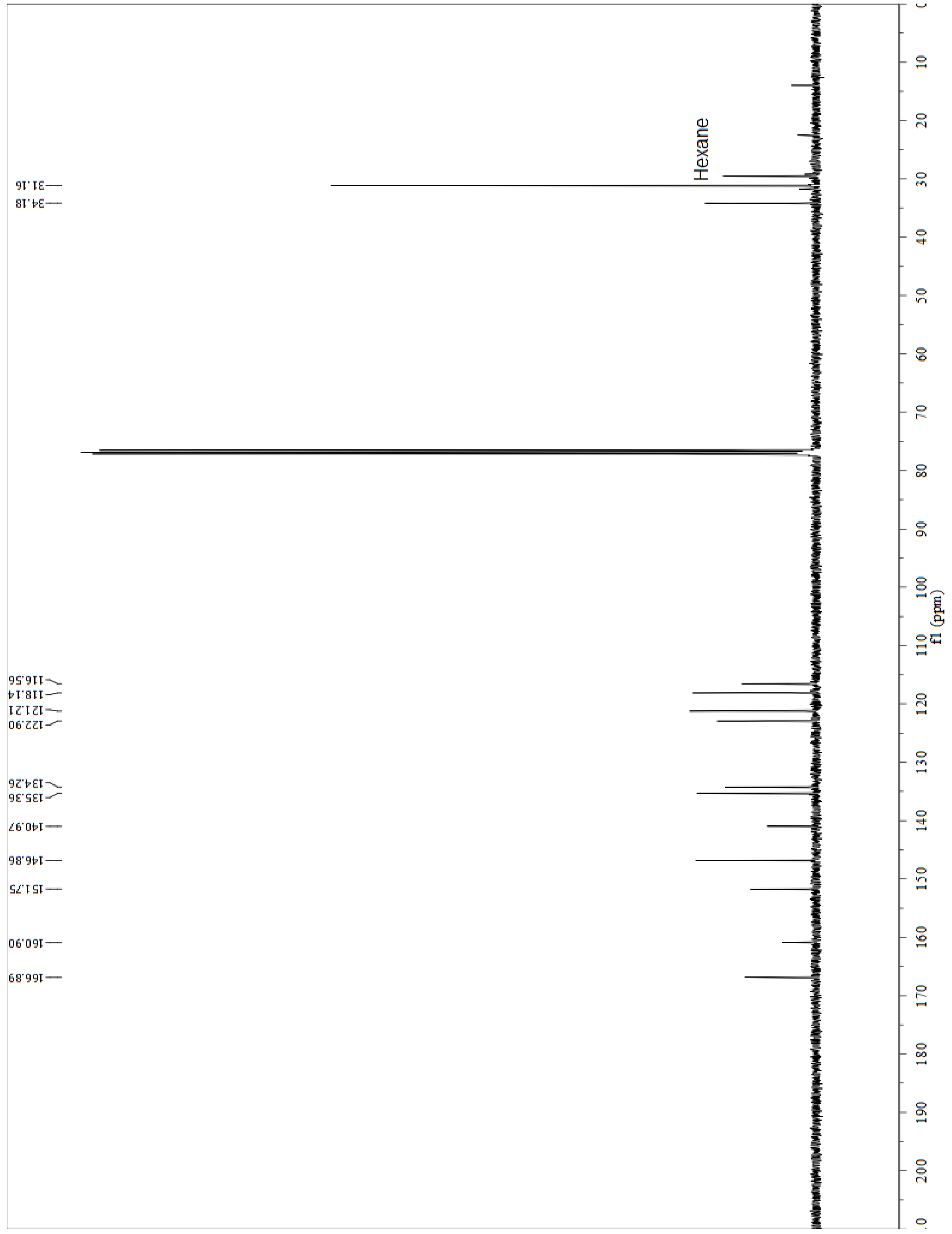
^{19}FNMR spectrum of **3d**



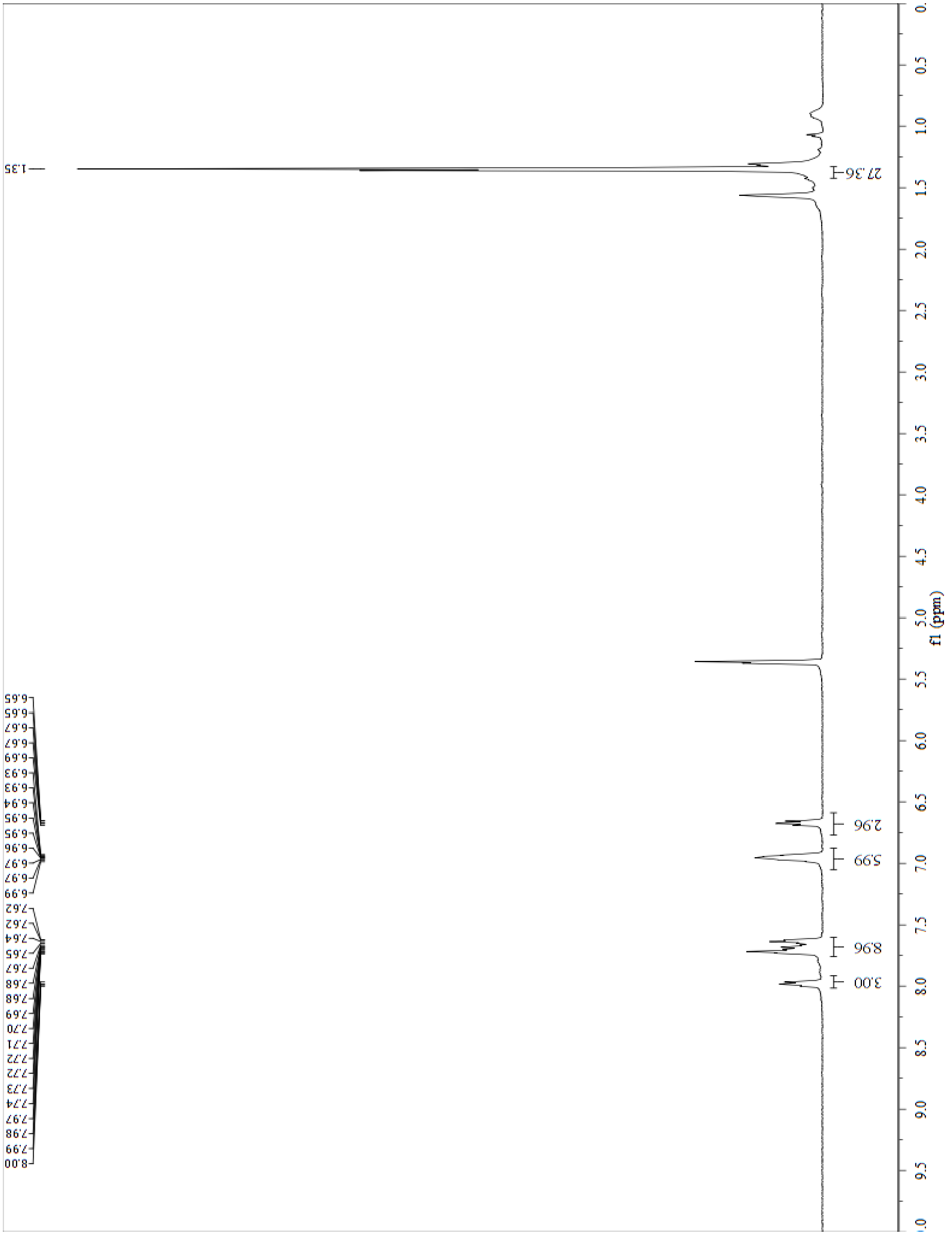
^{1} H NMR spectrum of **3e**



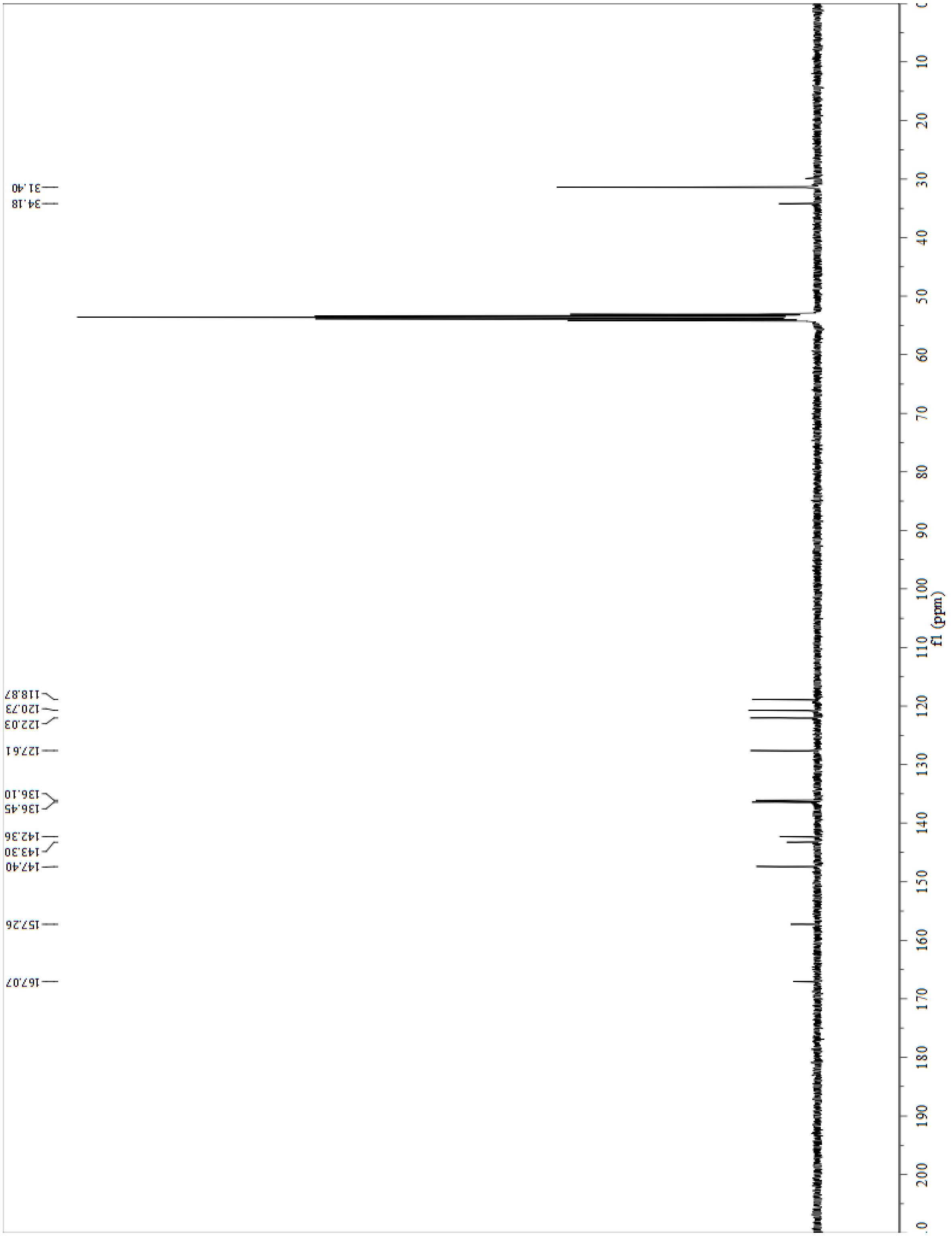
^{13}CNMR spectrum of **3e**



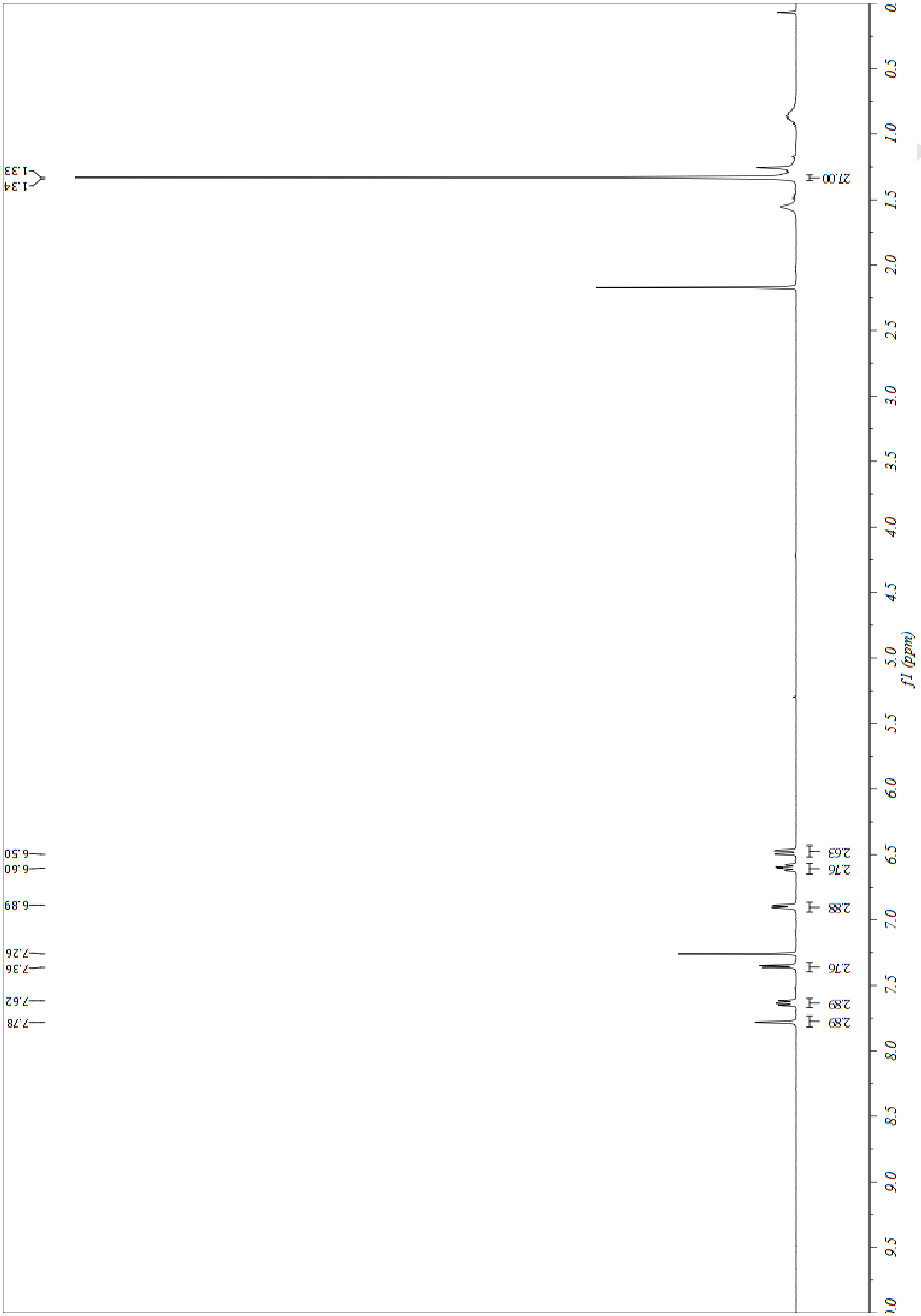
^{1} H NMR spectrum of **3f**



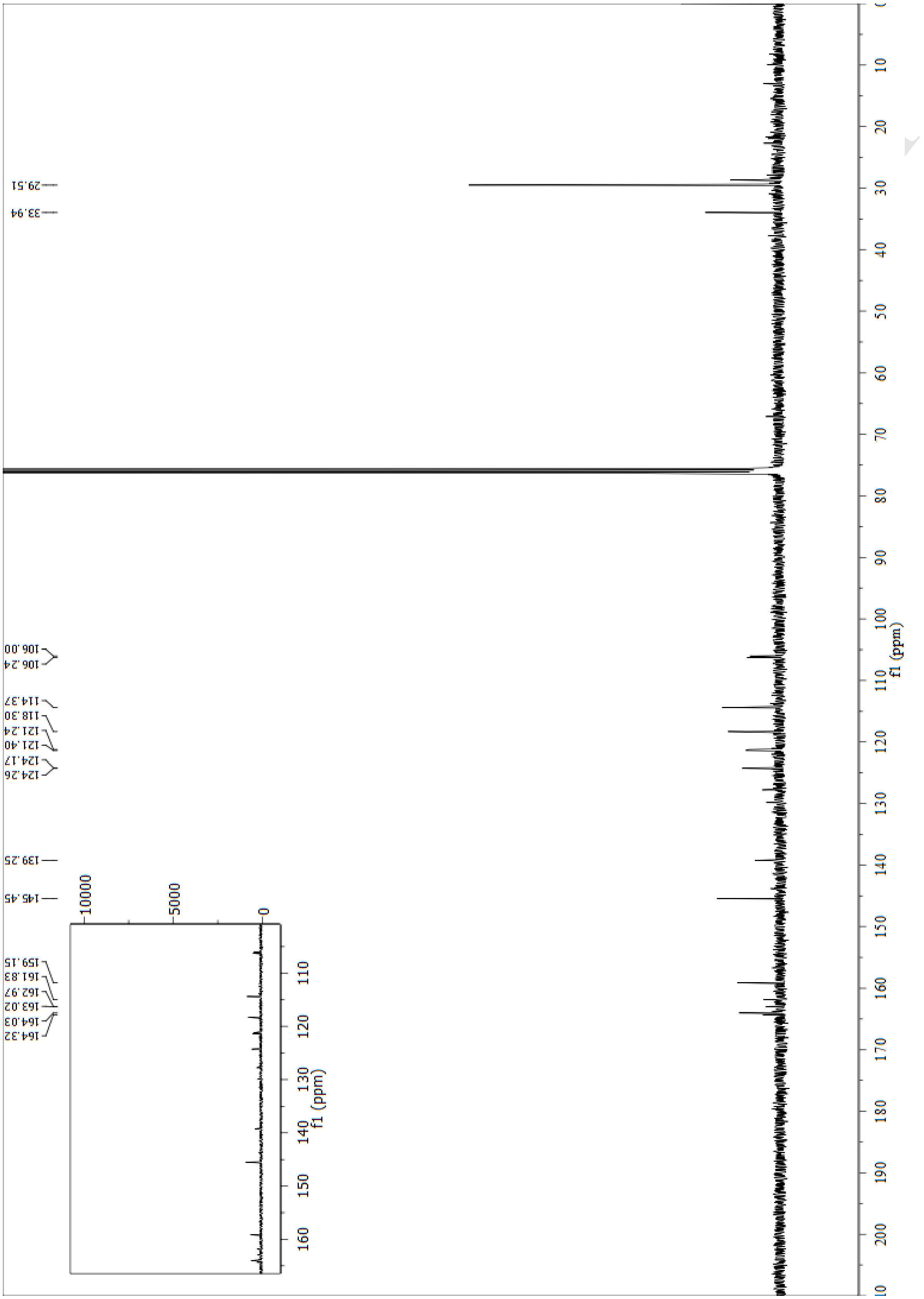
^{13}CNMR spectrum of **3f**



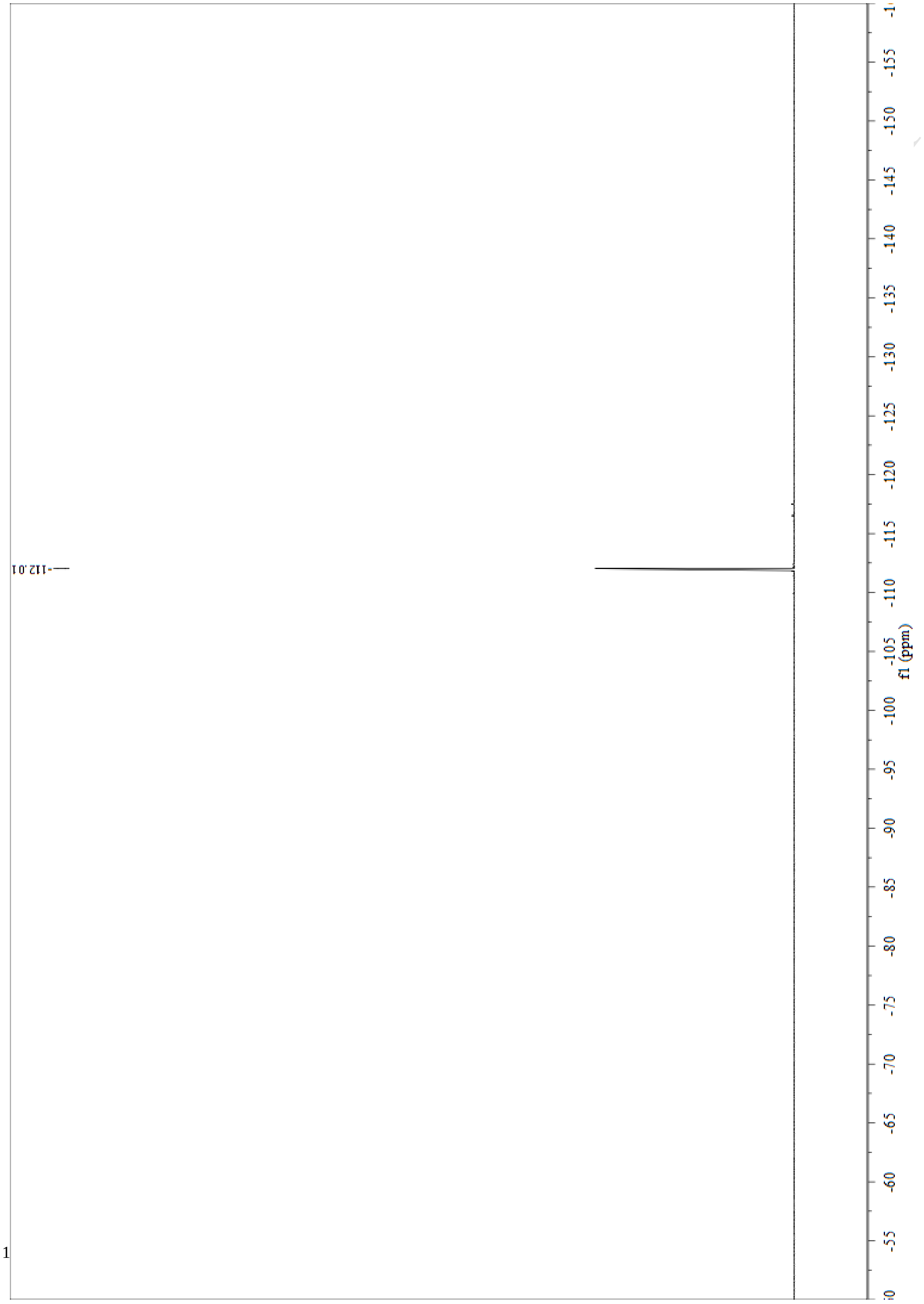
^{1} H NMR spectrum of **3h**

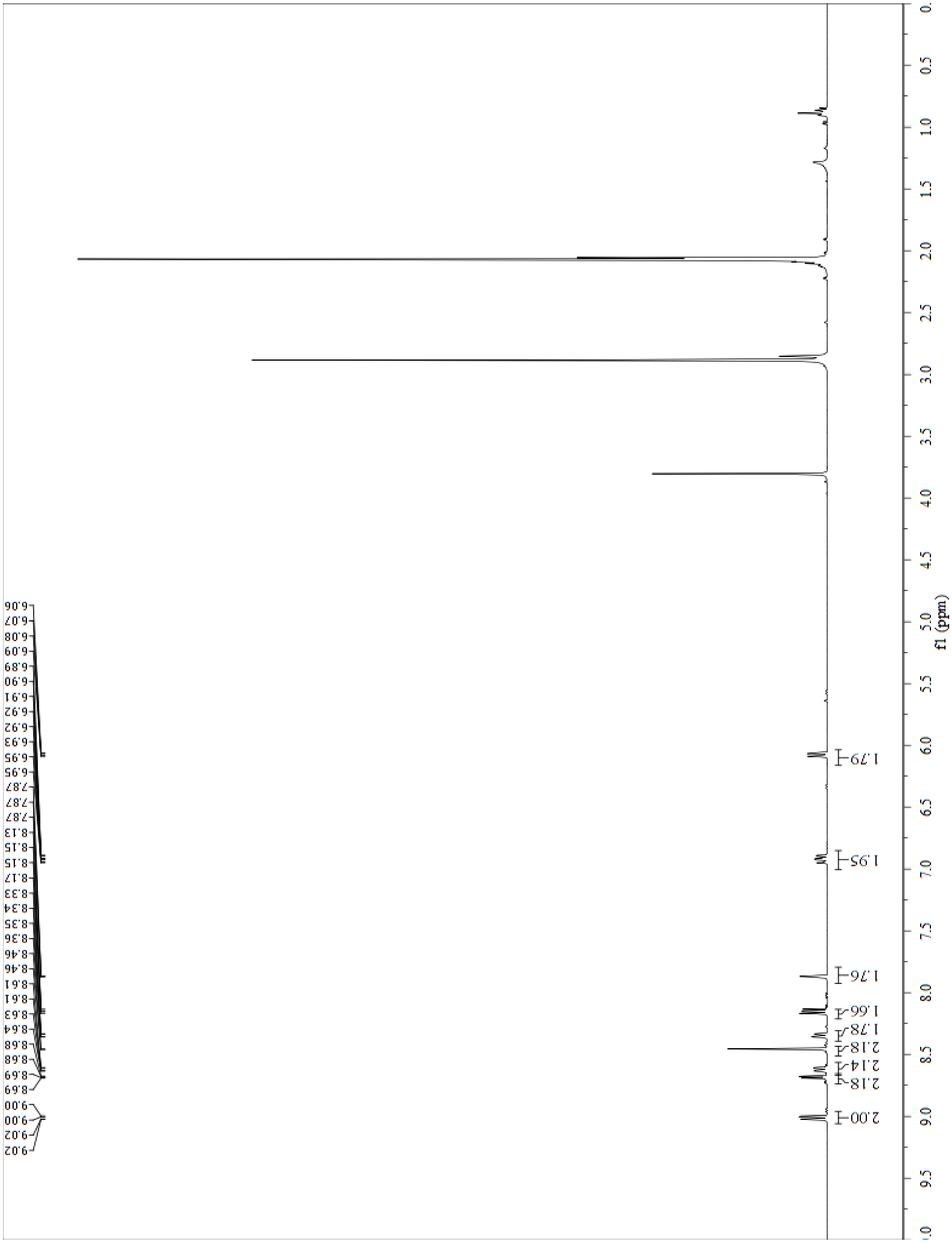


^{13}CNMR spectrum of **3h**



^{19}FNMR spectrum of **3h**




9.02
9.02
9.00
9.00
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8.68
8.68
8.64
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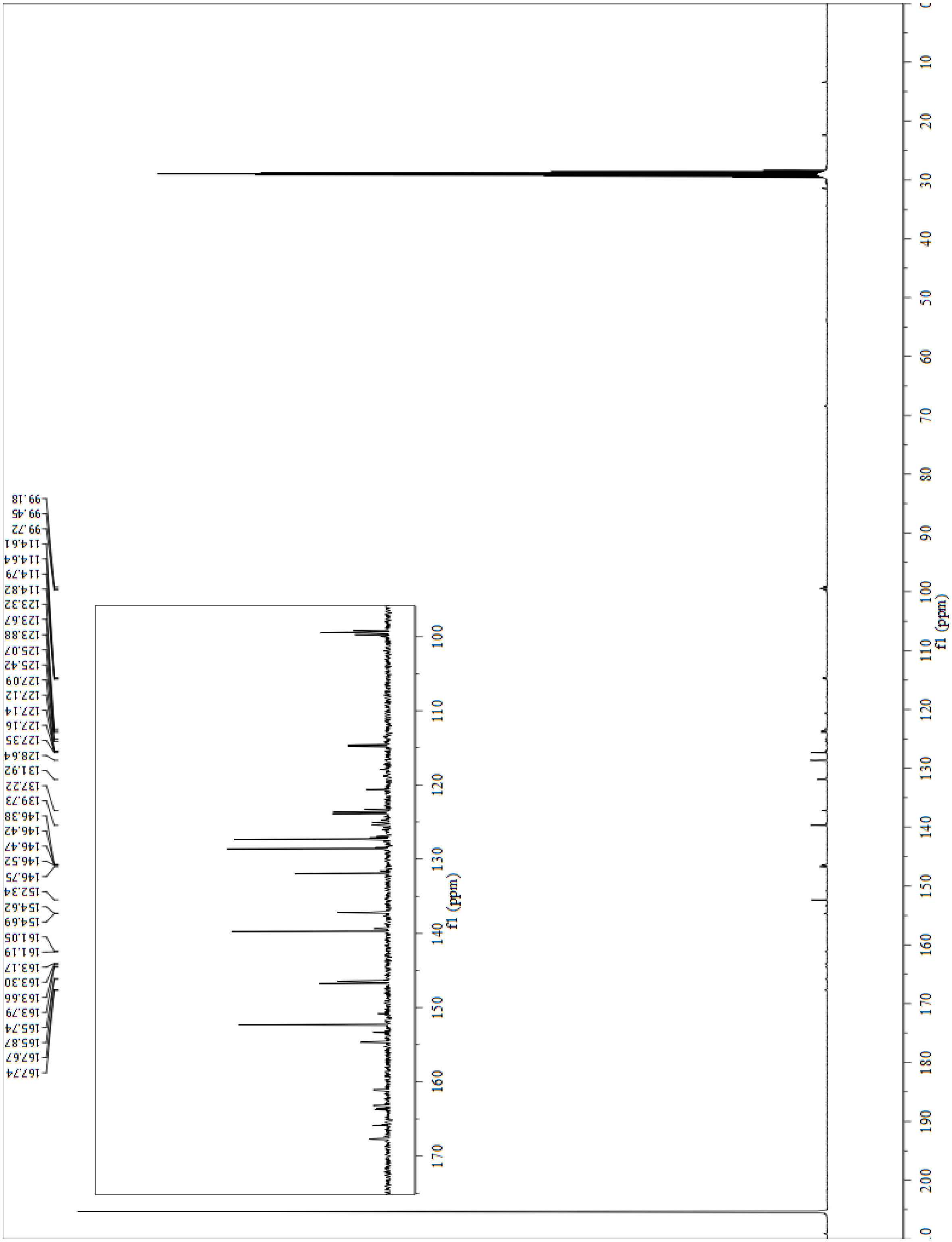
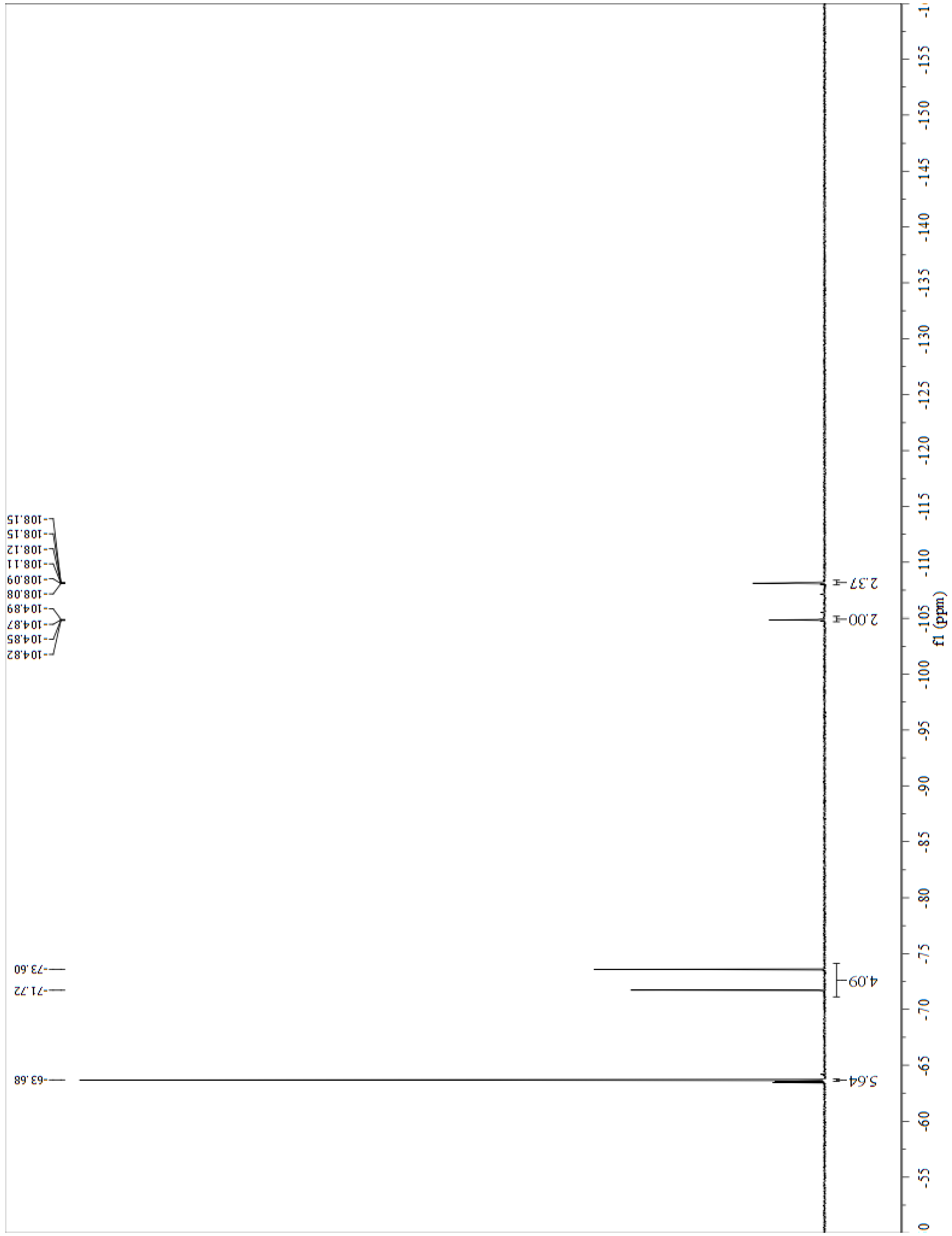
8.61
8.46
8.46
8.36
8.35
8.34
8.33
8.17
8.15
8.15
8.13
7.87
7.87
7.87
6.95
6.95
6.93
6.92
6.92
6.91
6.90
6.89
6.09
6.08
6.07
6.06
2.00
2.18
2.14
2.18
1.78
1.66
1.76
1.95
1.79
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

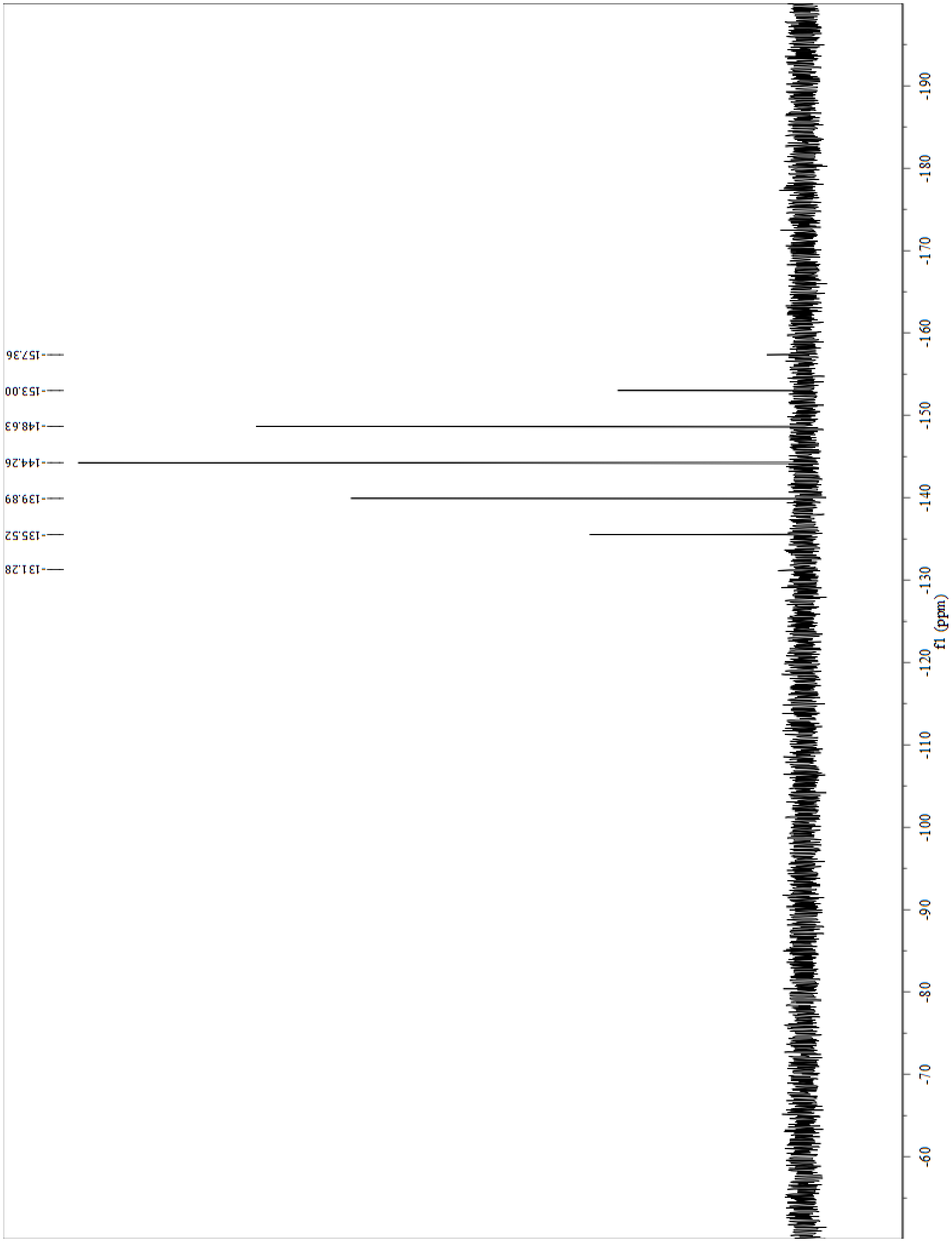
^{13}CNMR spectrum of **4ga**



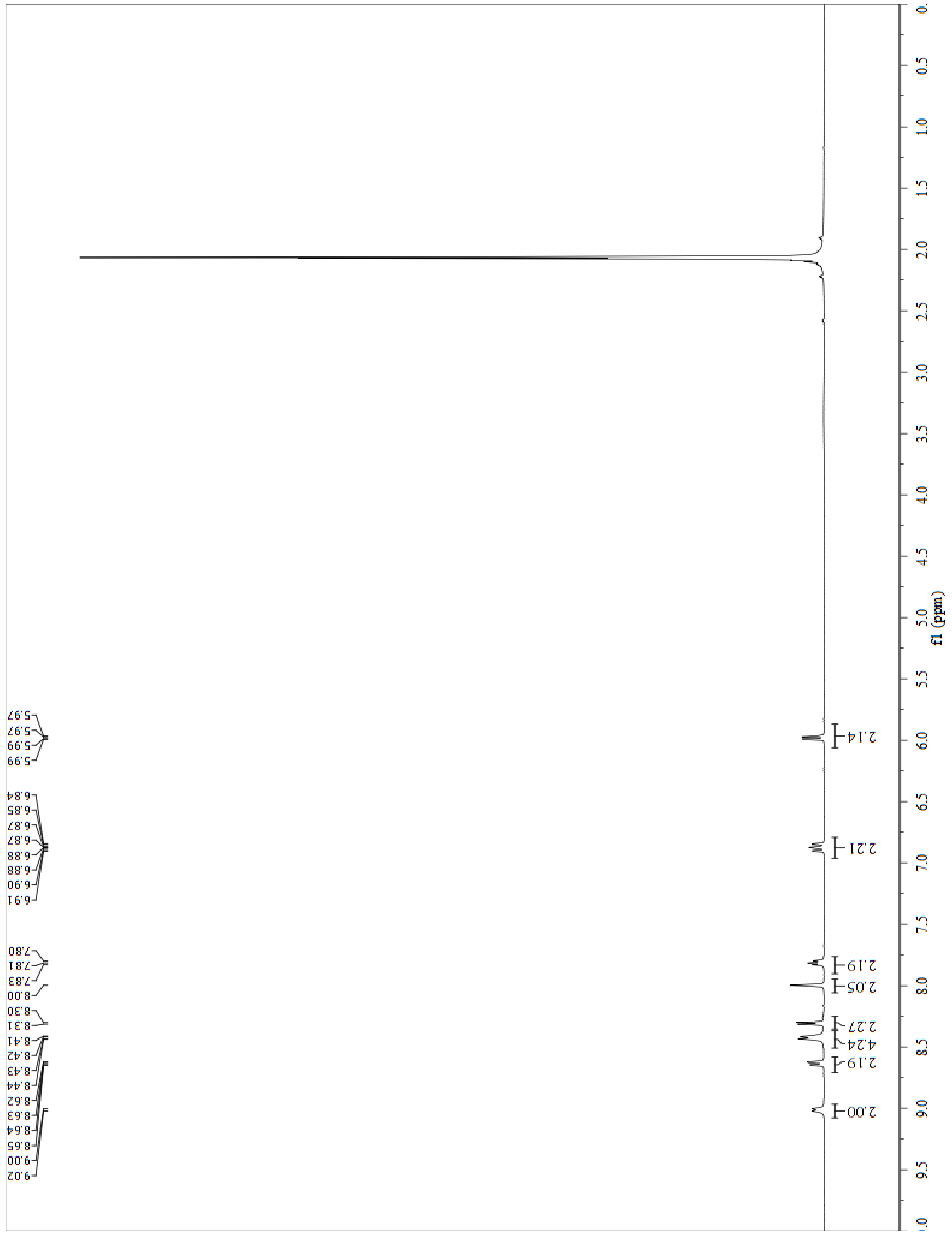
^{19}FNMR spectrum of **4ga**



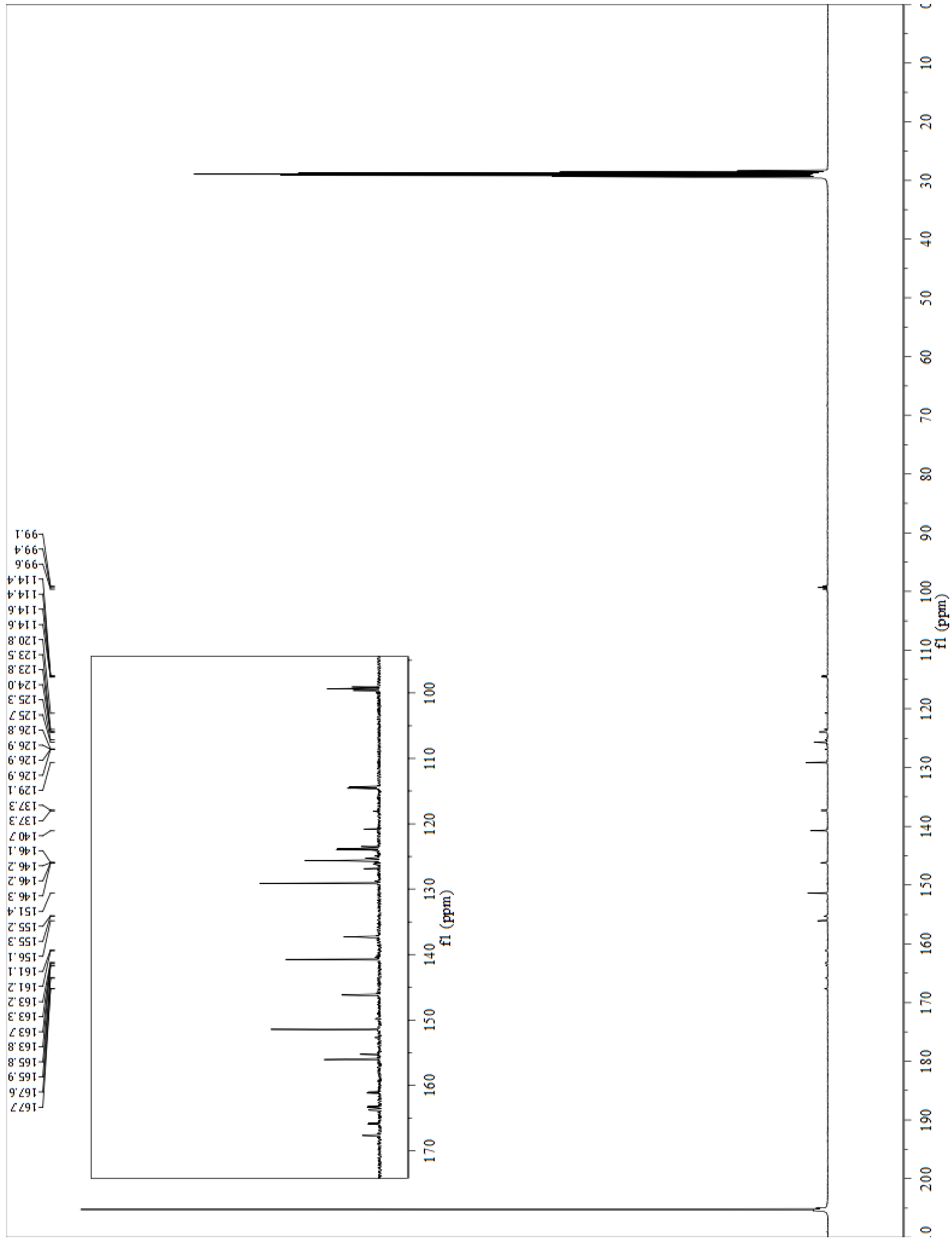
^{31}PNMR spectrum of **4ga**



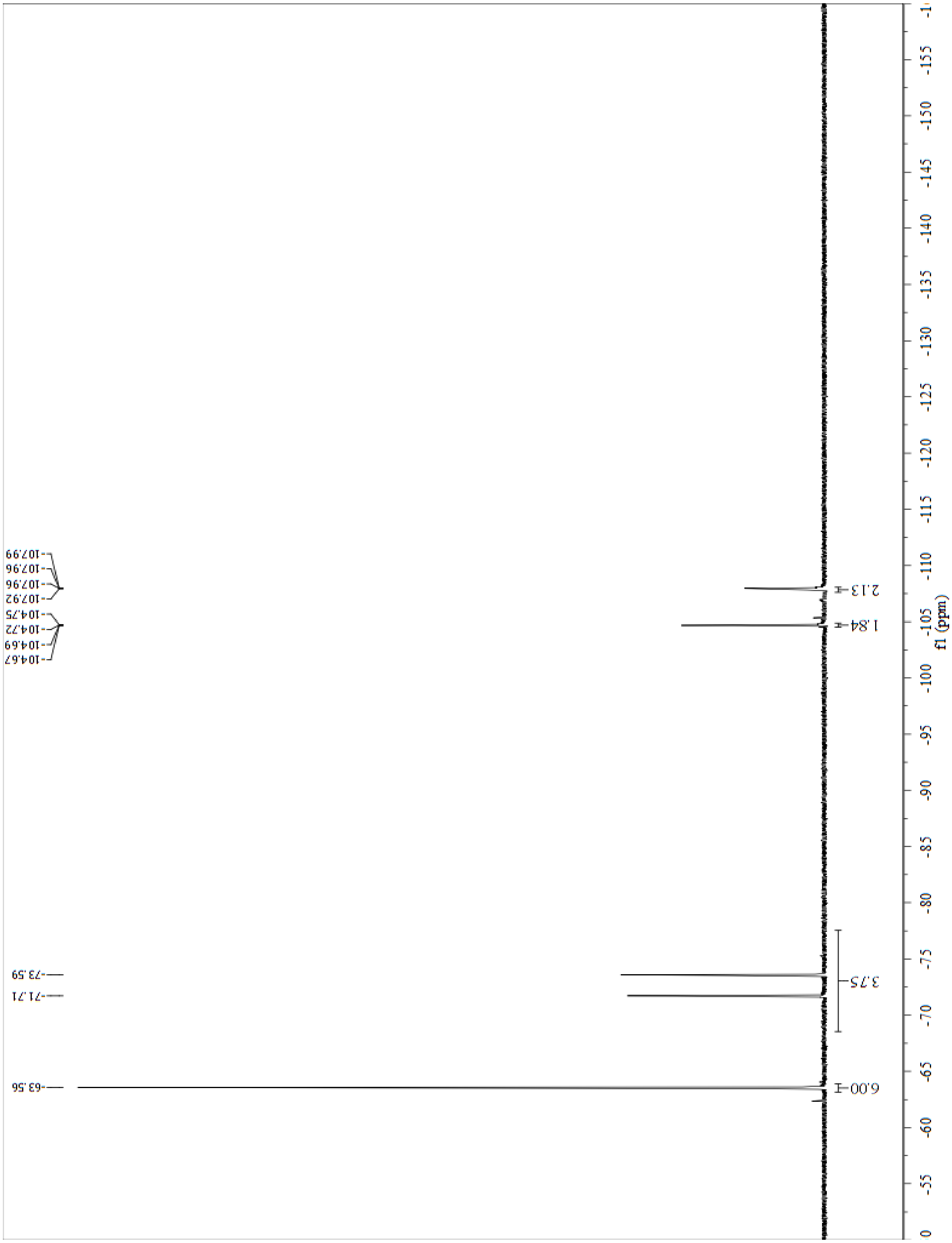
^{1} H NMR spectrum of **4gb**



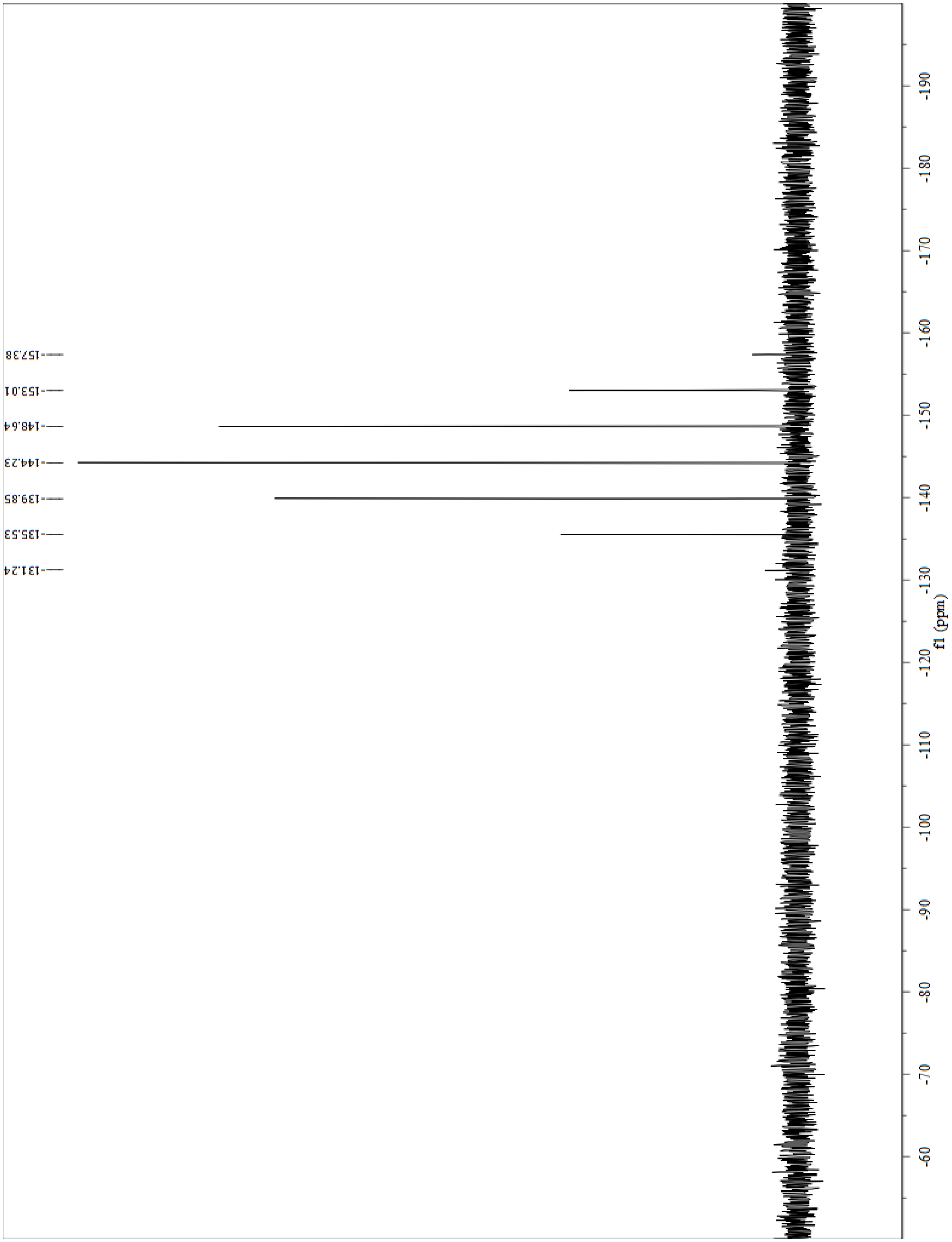
^{13}CNMR spectrum of **4gb**



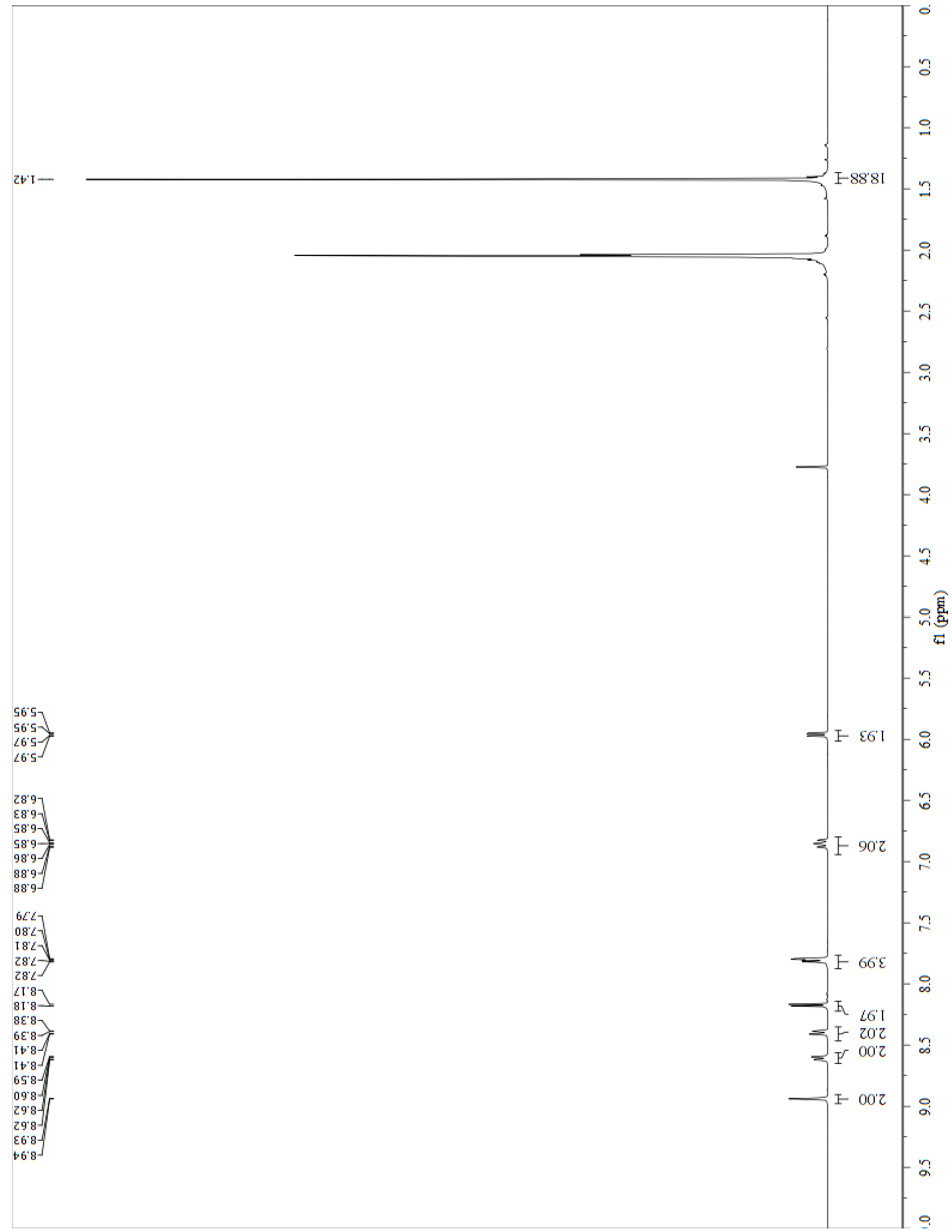
^{19}FNMR spectrum of **4gb**



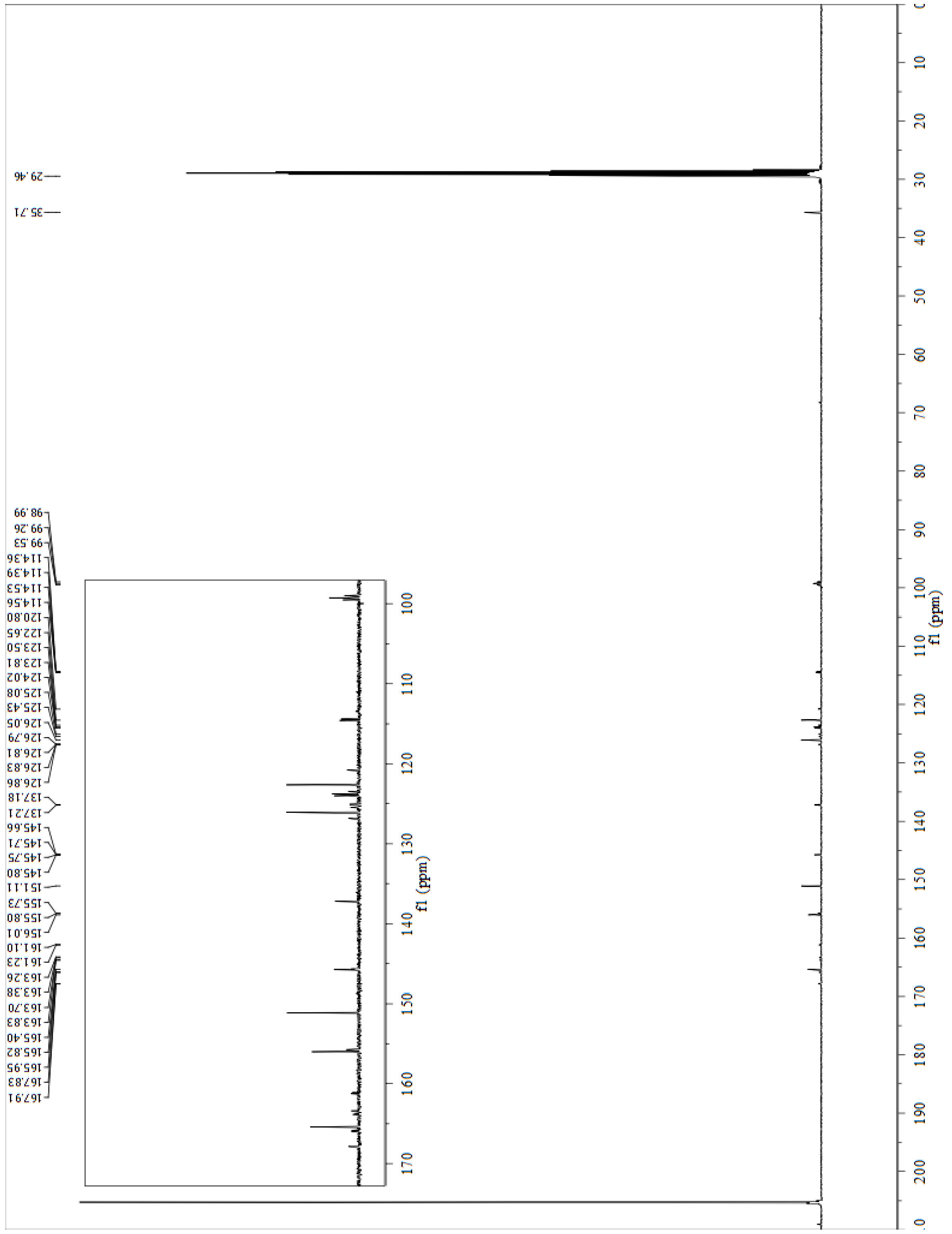
^{31}PNMR spectrum of **4gb**



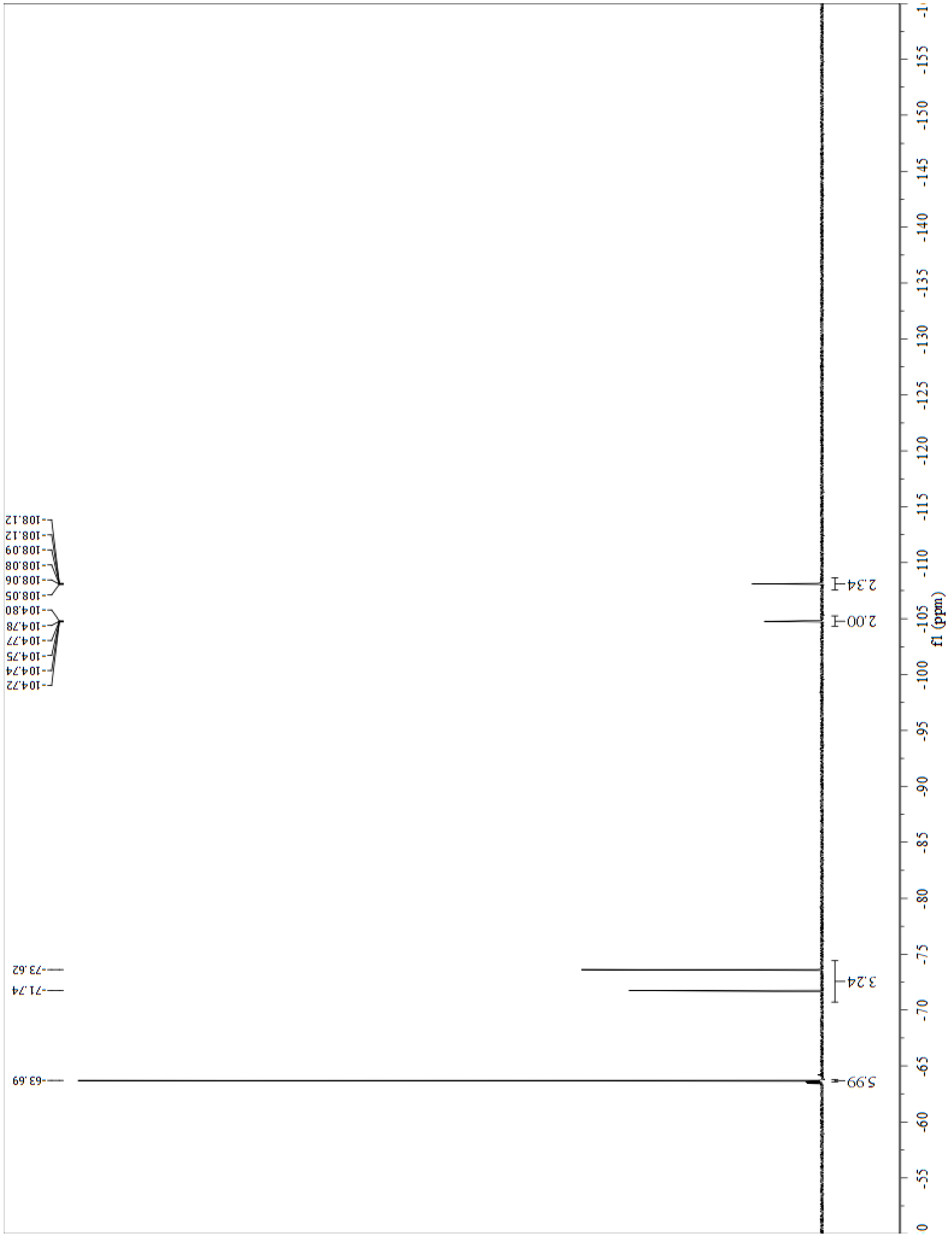
^{1} H NMR spectrum of **4gc**



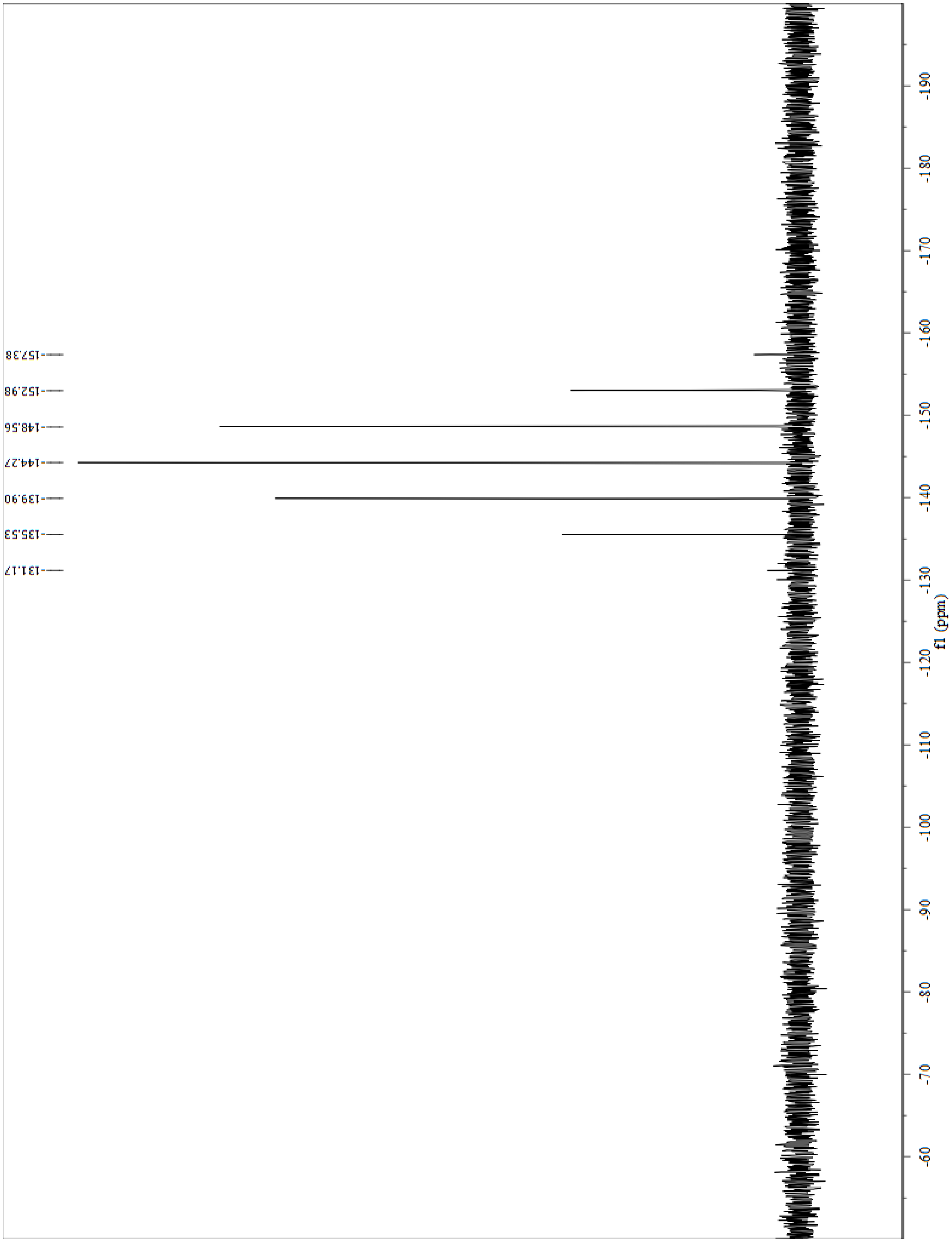
^{13}CNMR spectrum of **4gc**



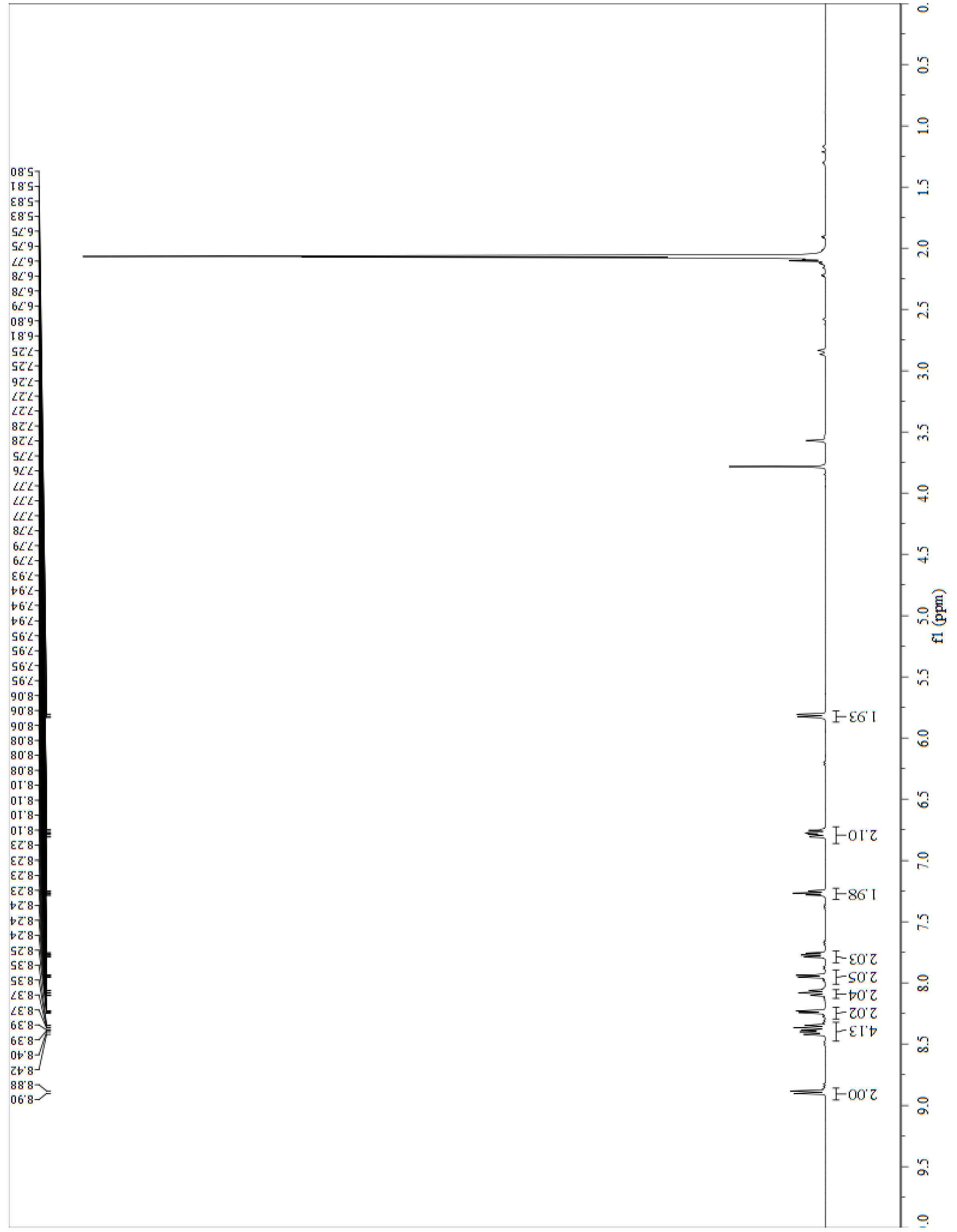
^{19}FNMR spectrum of **4gc**



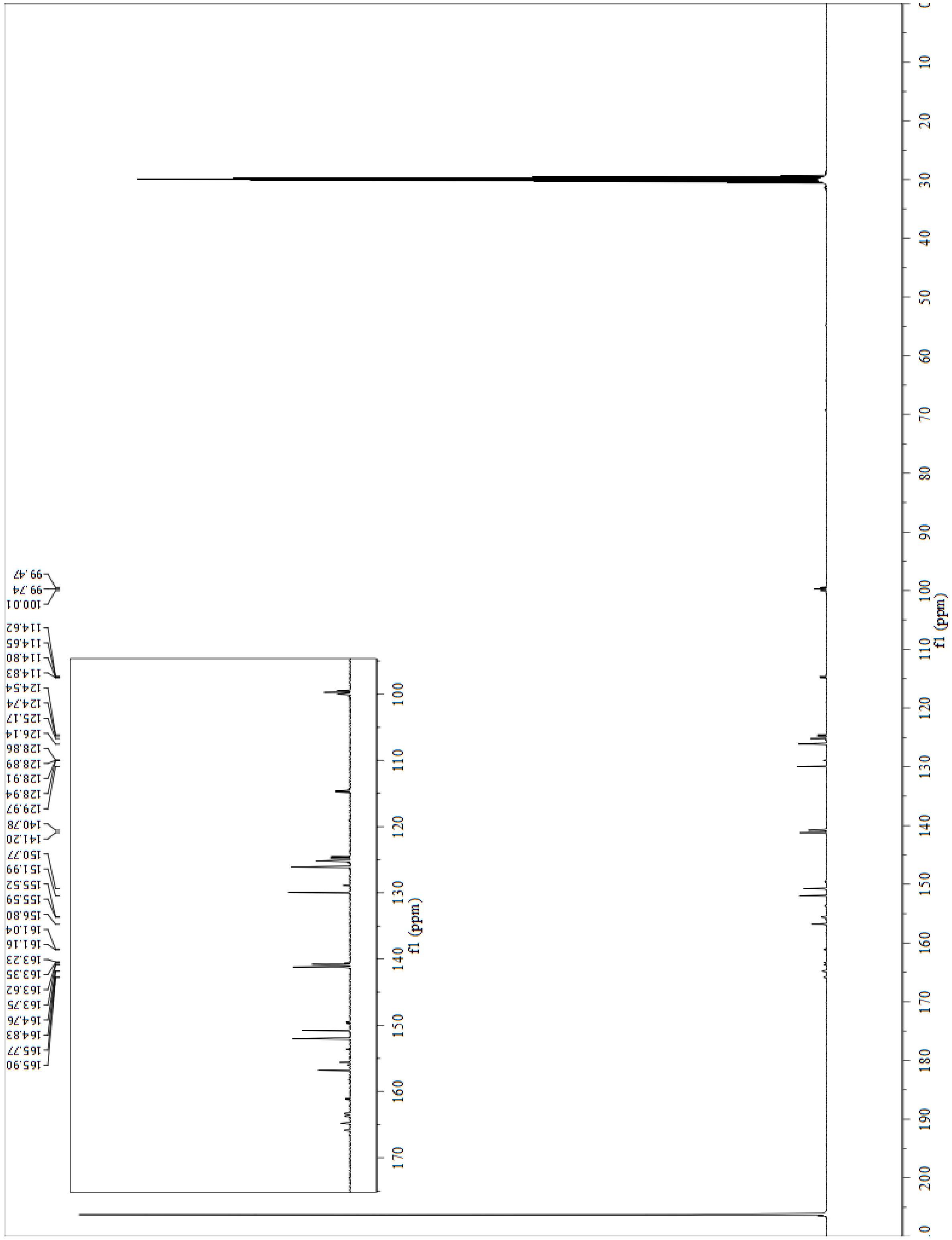
^{31}PNMR spectrum of **4gc**



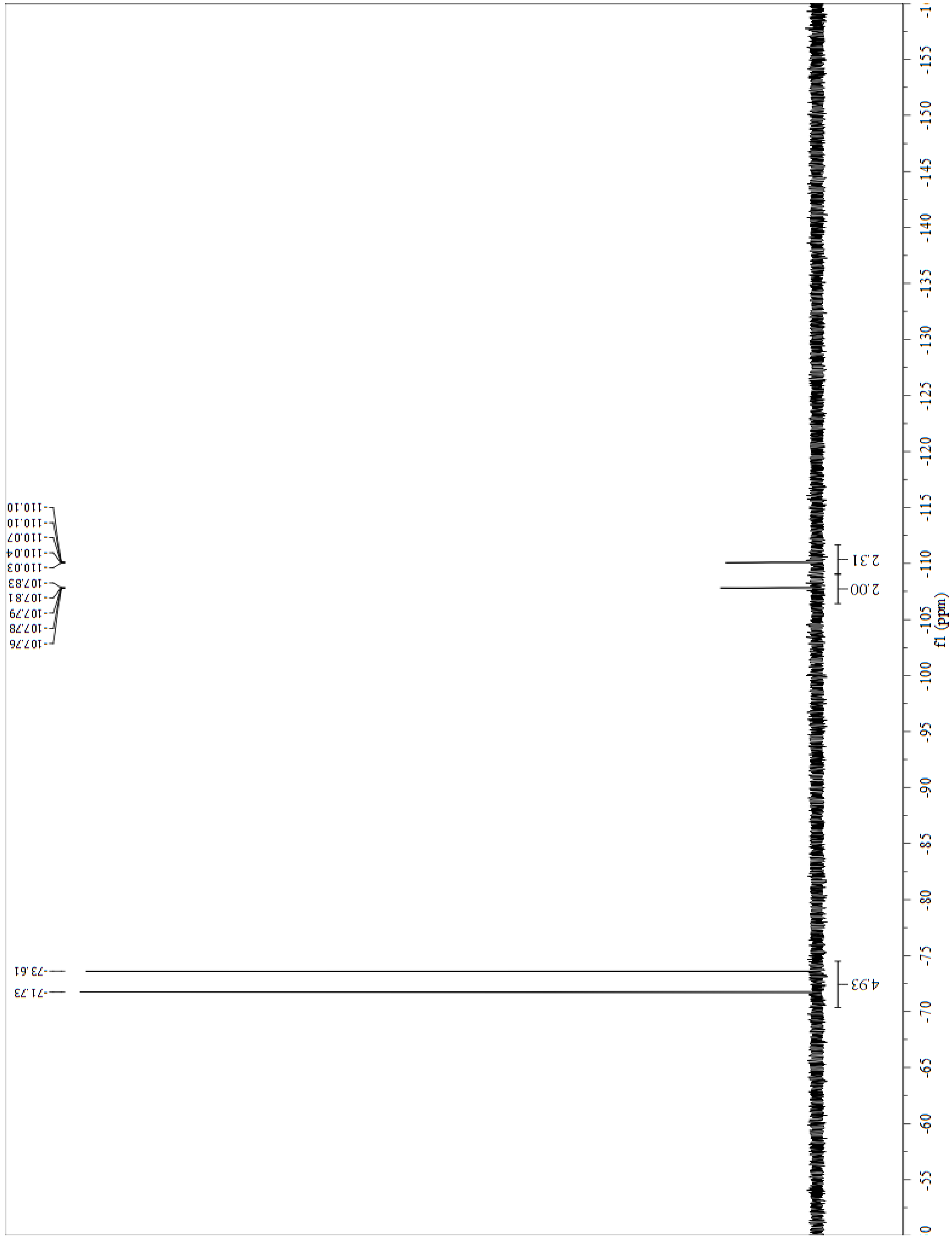
^{1} H NMR spectrum of **4db**



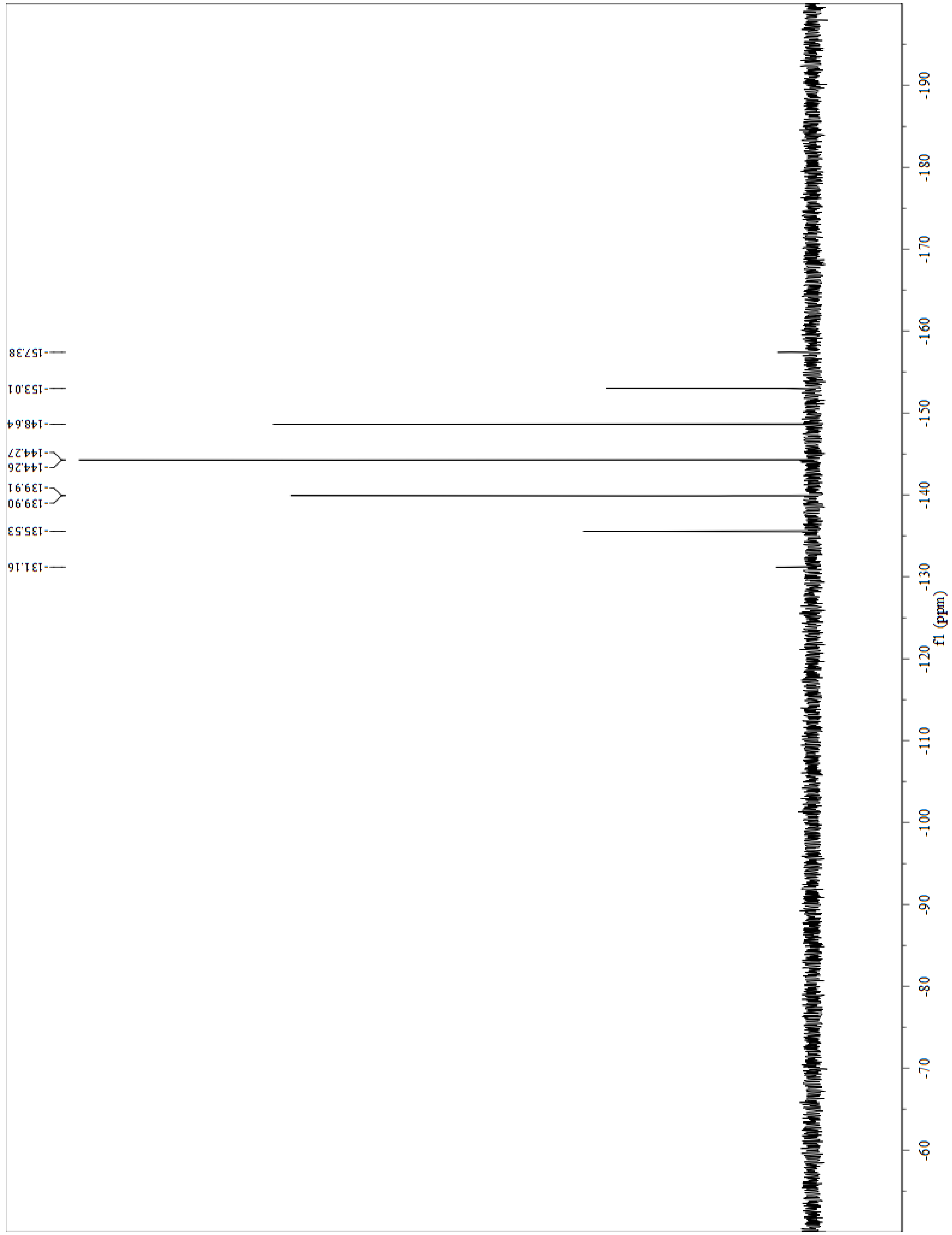
^{13}CNMR spectrum of **4db**



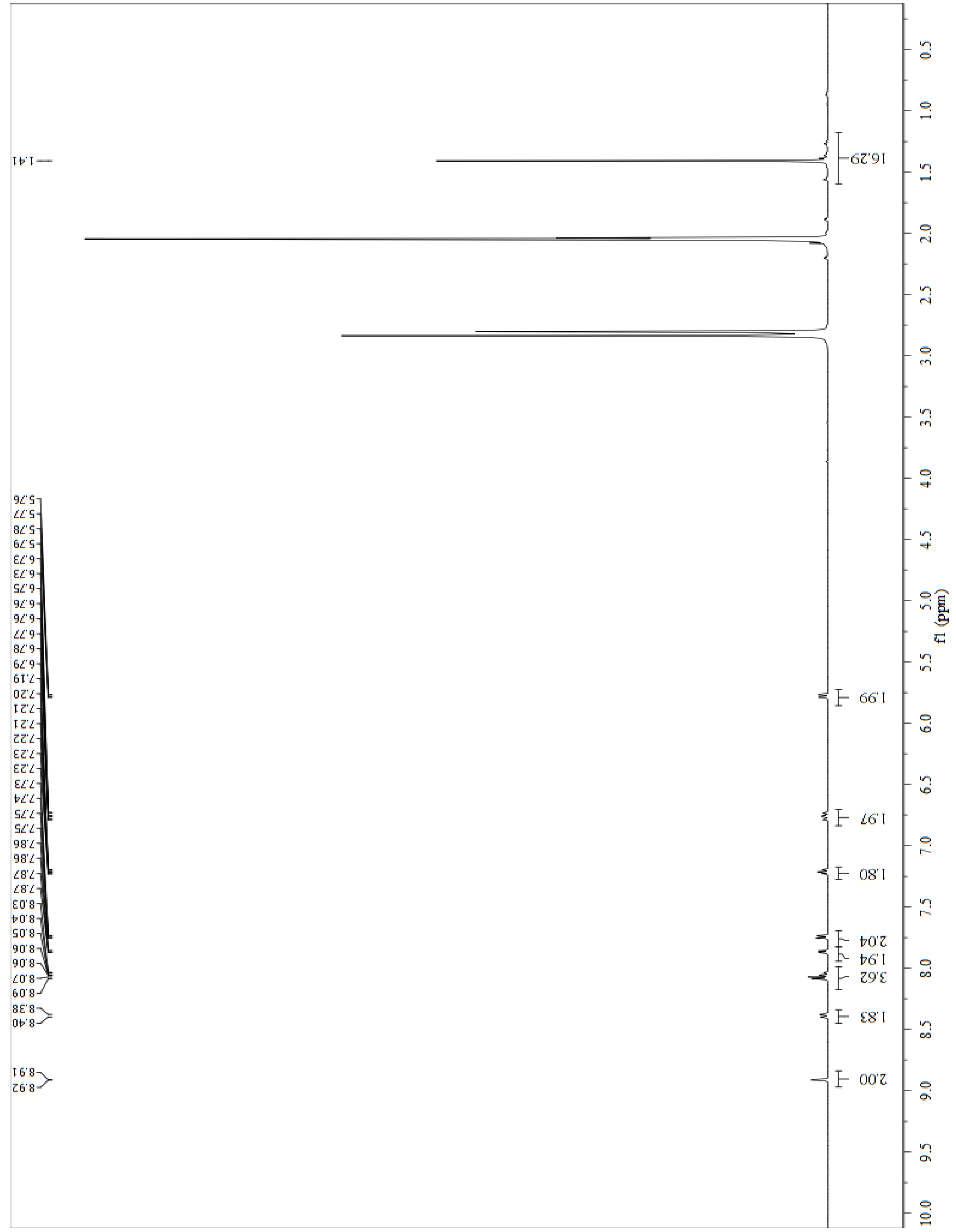
^{19}FNMR spectrum of **4db**



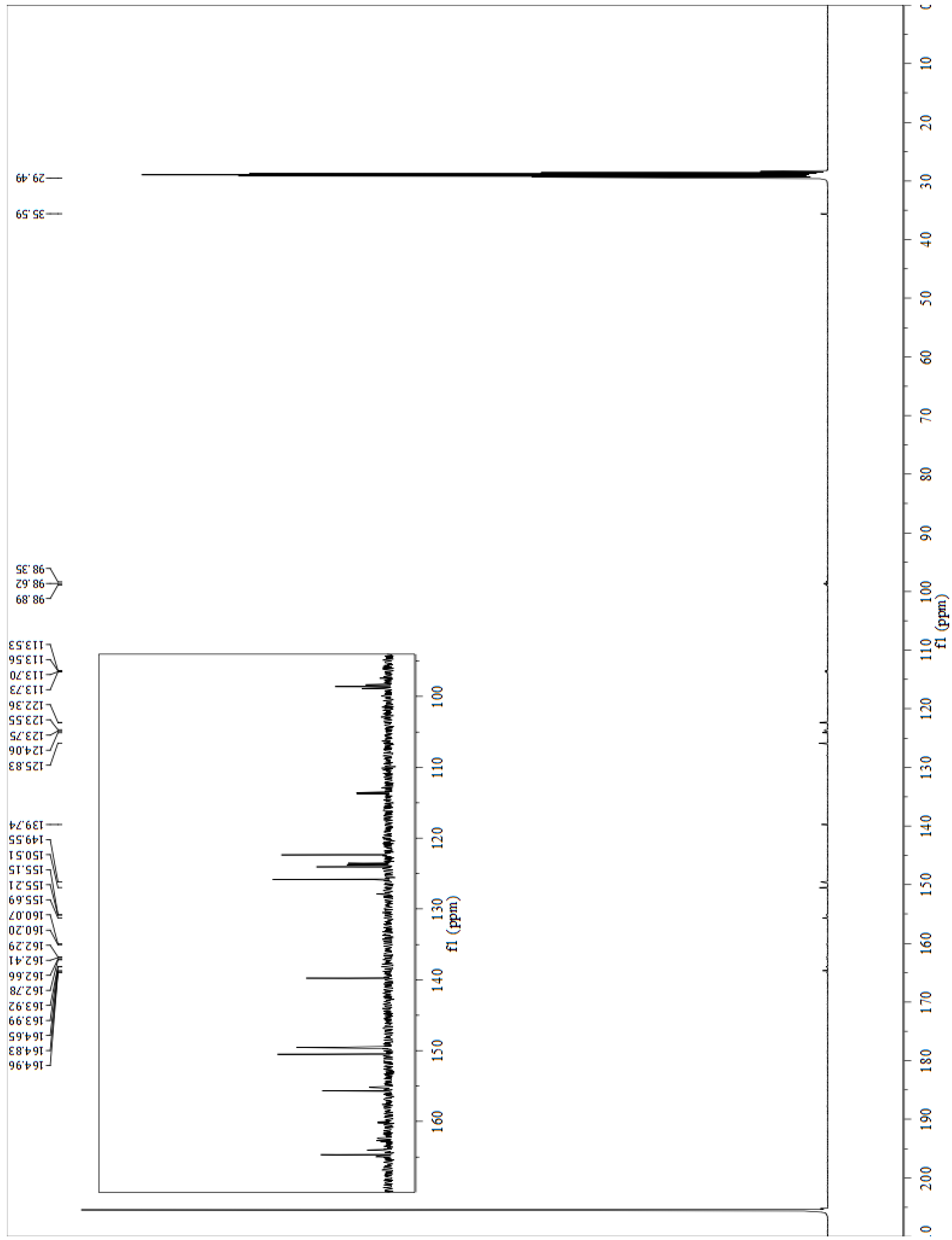
^{31}PNMR spectrum of **4db**



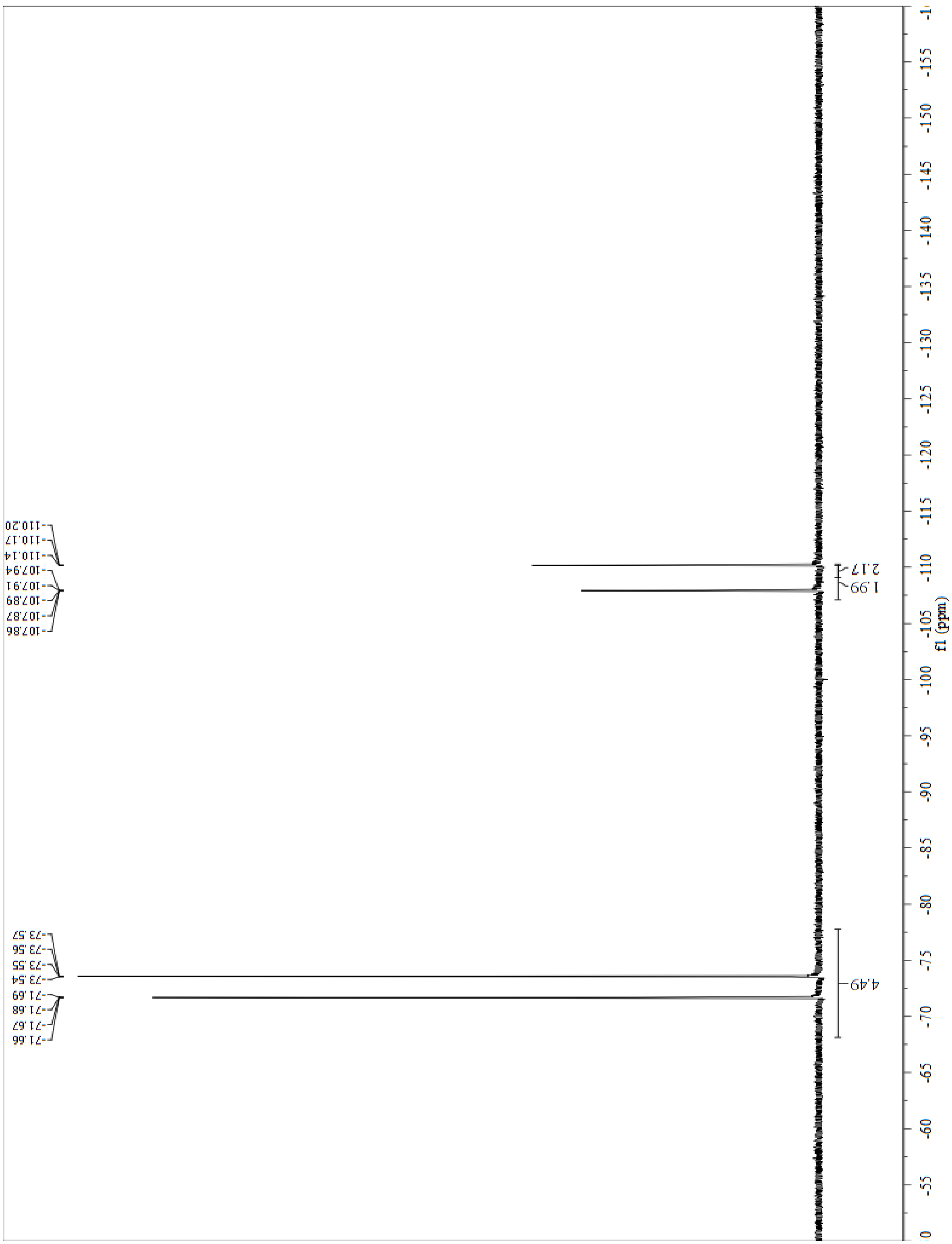
^{1} H NMR spectrum of **4dc**



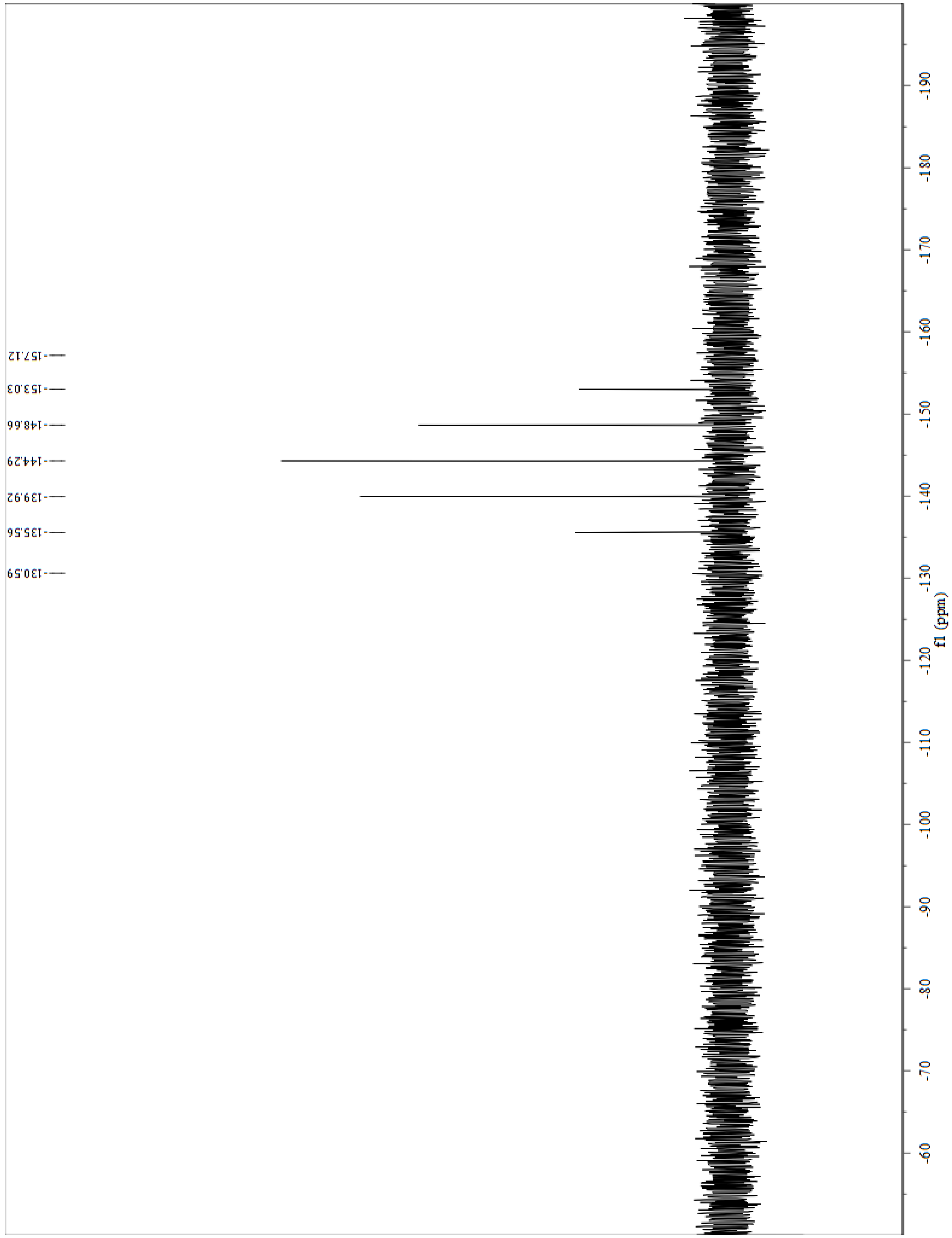
^{13}CNMR spectrum of **4dc**



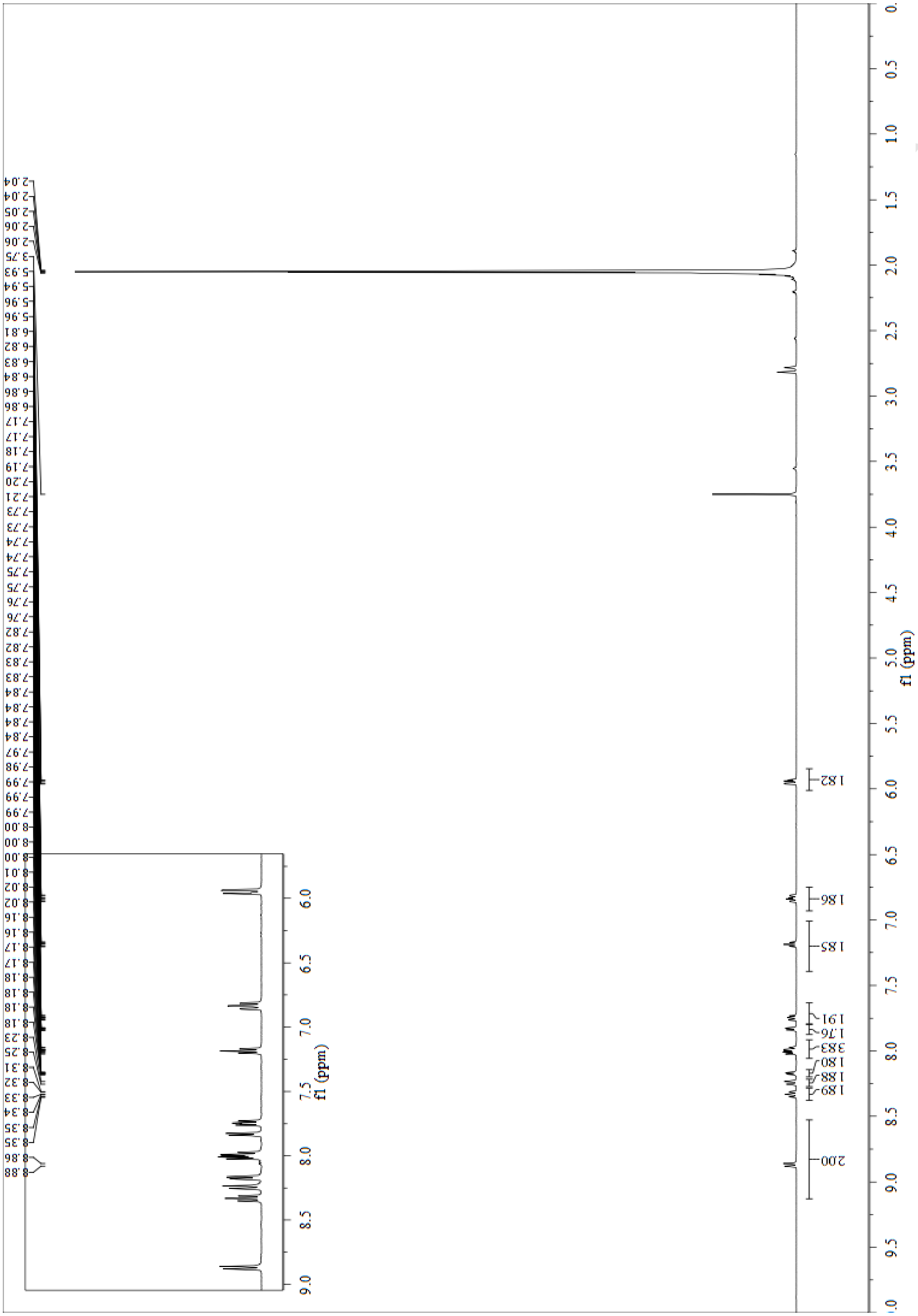
^{19}FNMR spectrum of **4dc**



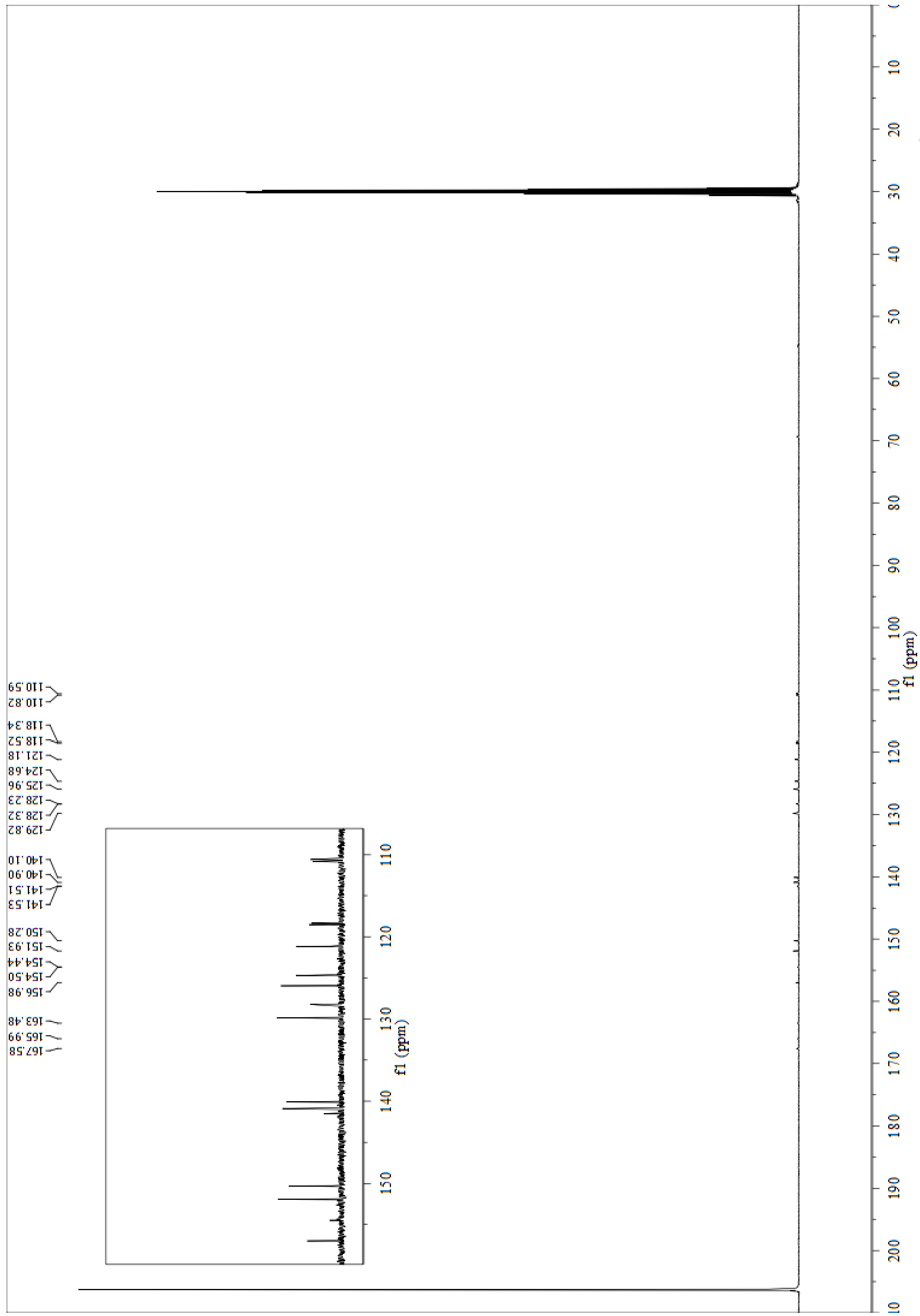
^{31}PNMR spectrum of **4dc**



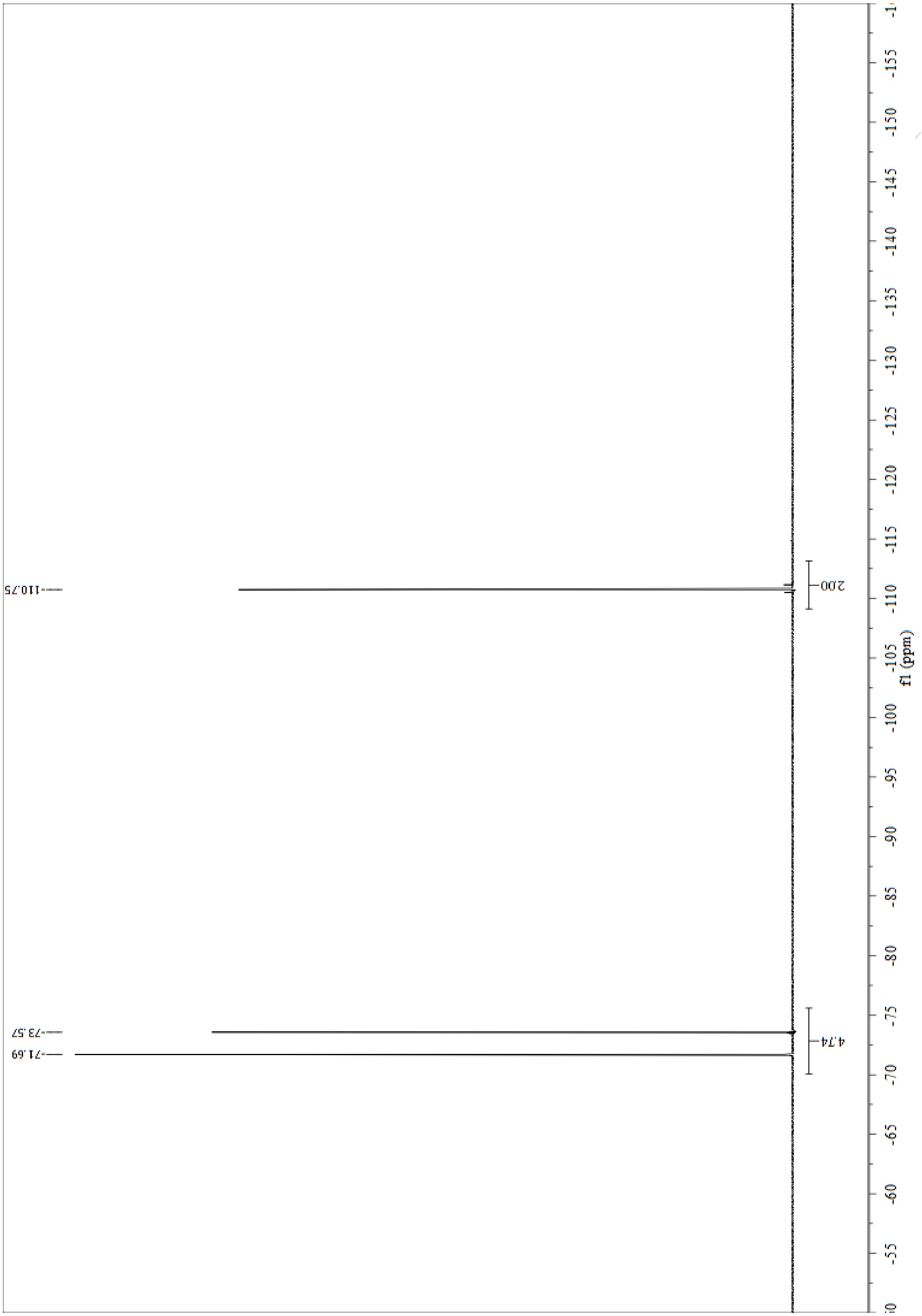
^{1} H NMR spectrum of **4cb**



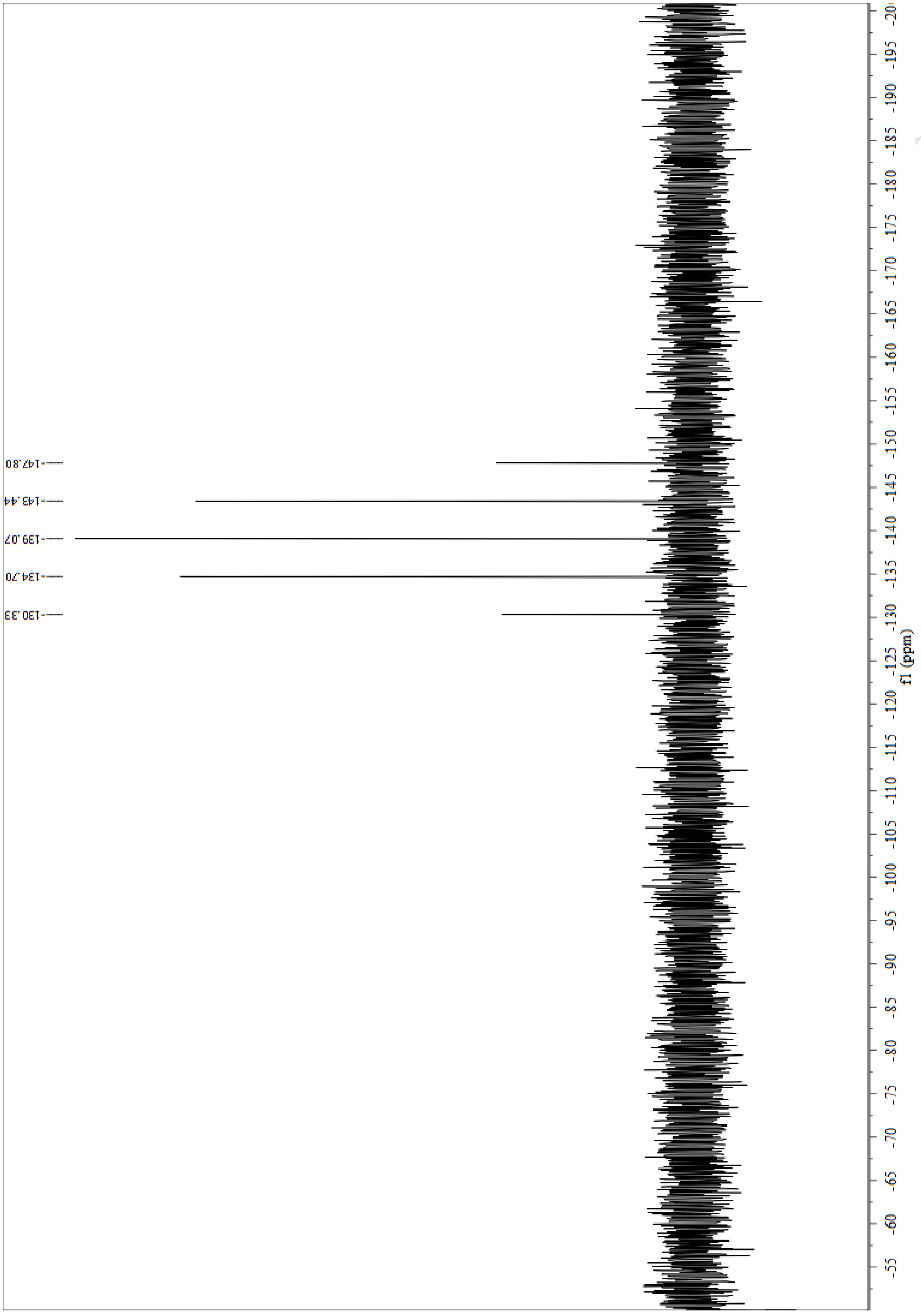
^{13}C NMR spectrum of **4cb**



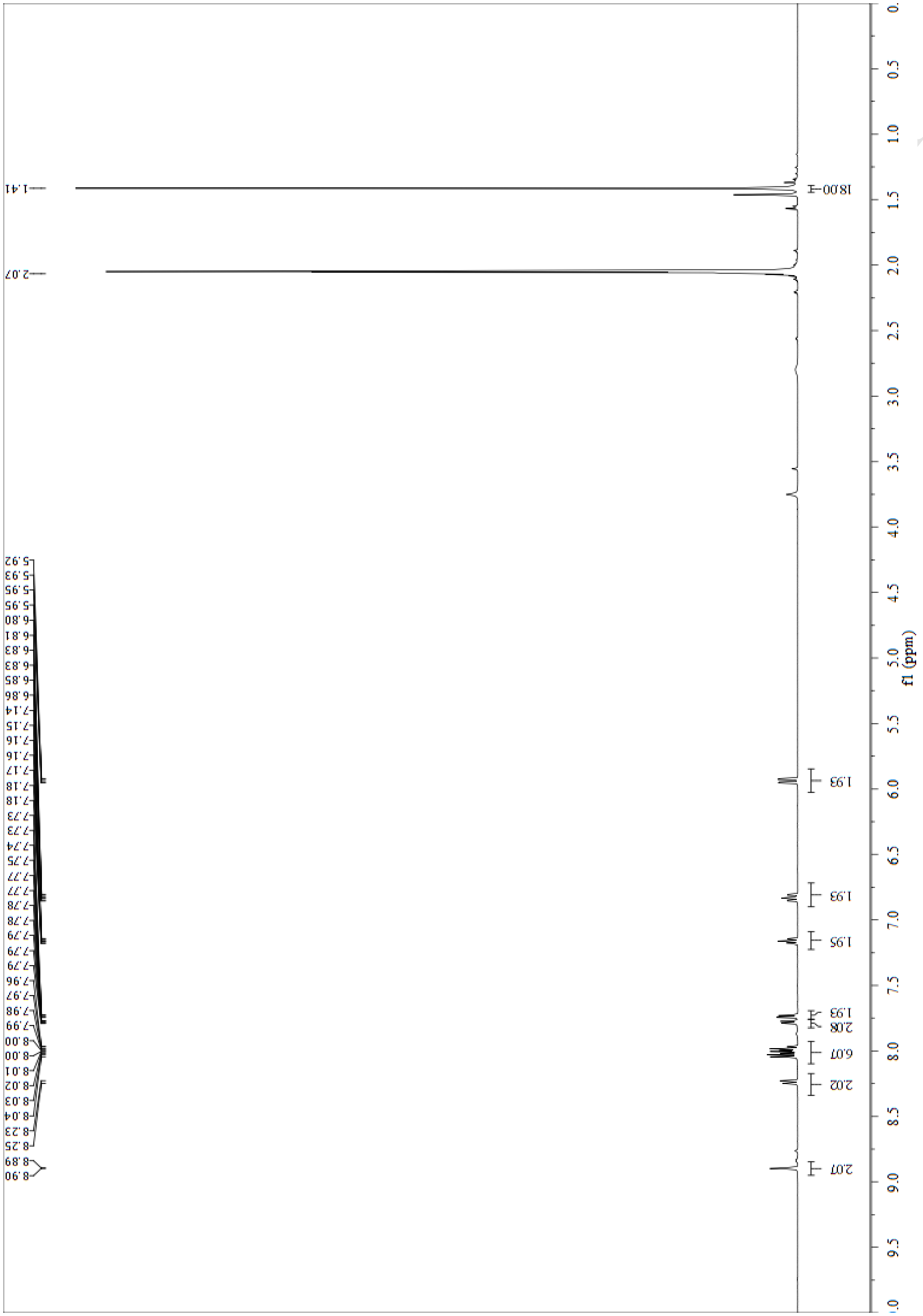
^{19}FNMR spectrum of **4cb**



^{31}PNMR spectrum of **4cb**



^{1} H NMR spectrum of **4cc**



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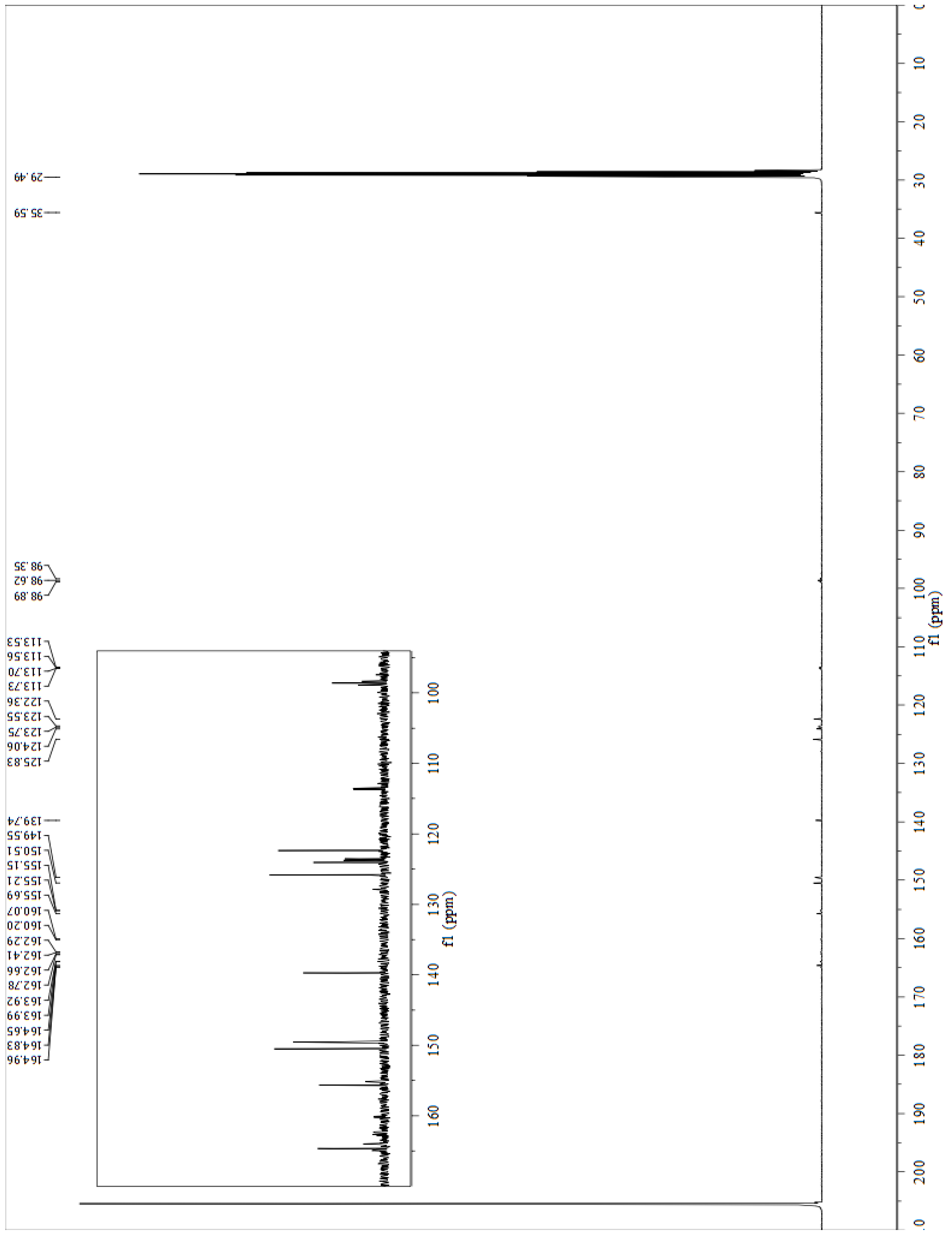

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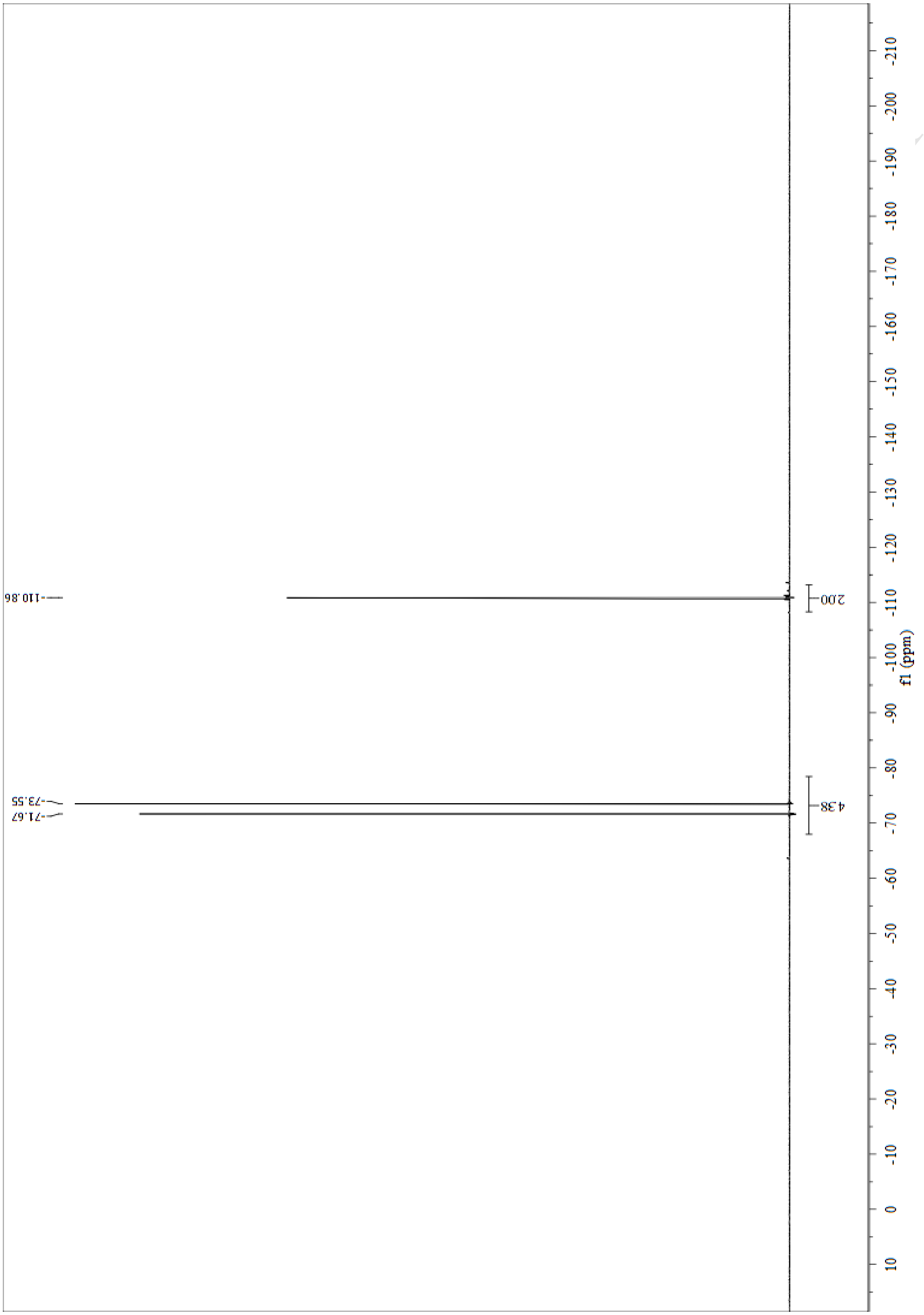

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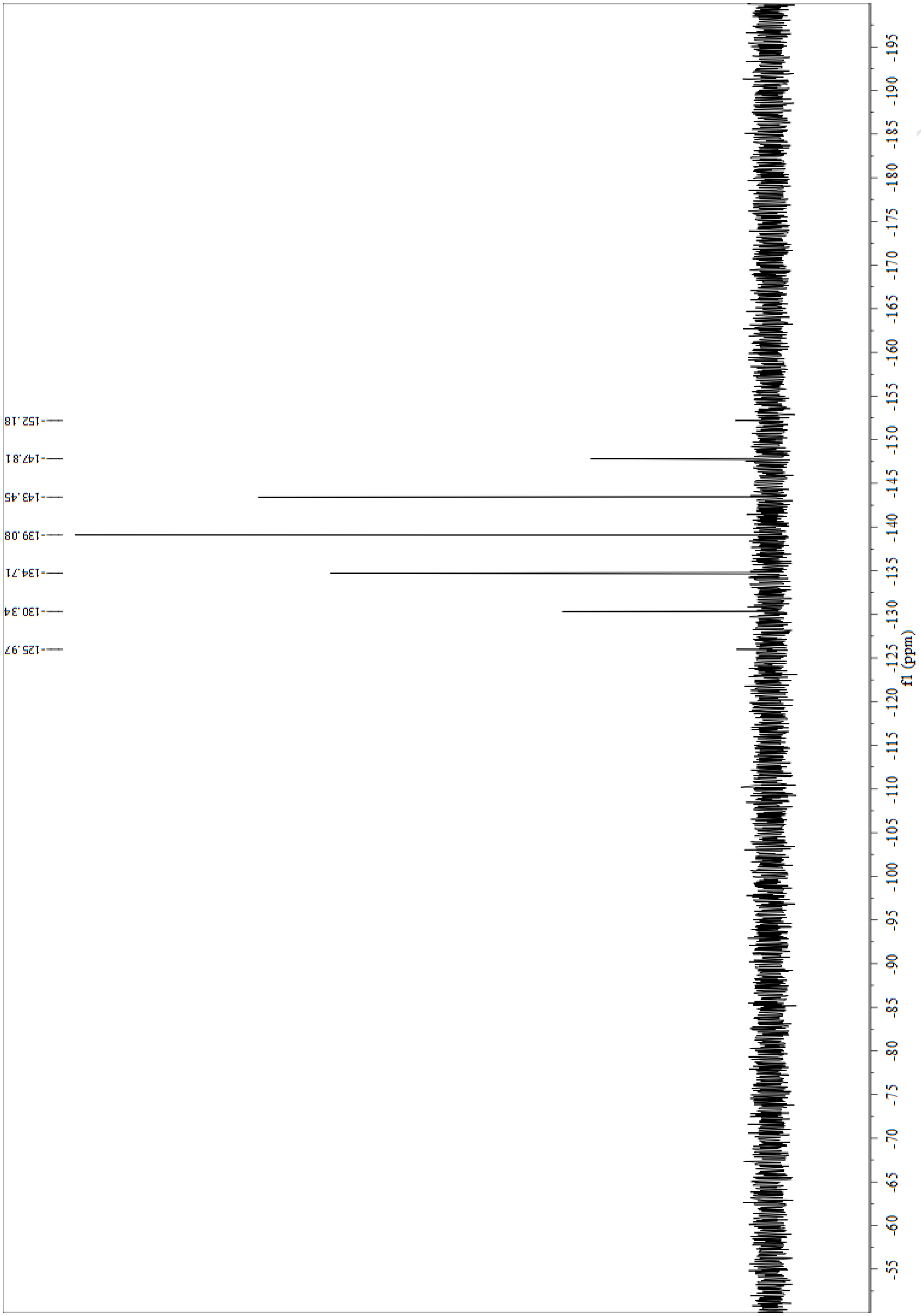
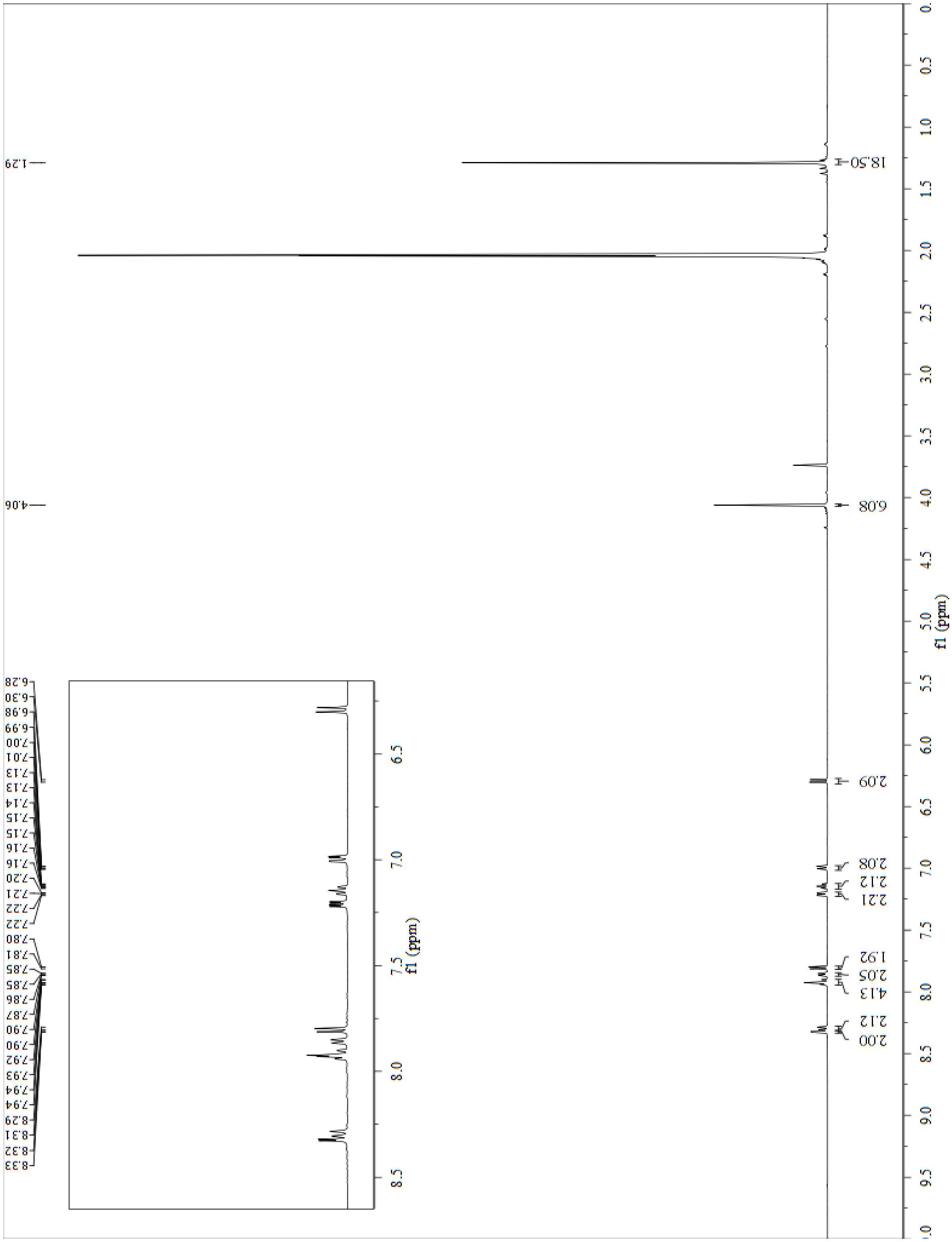
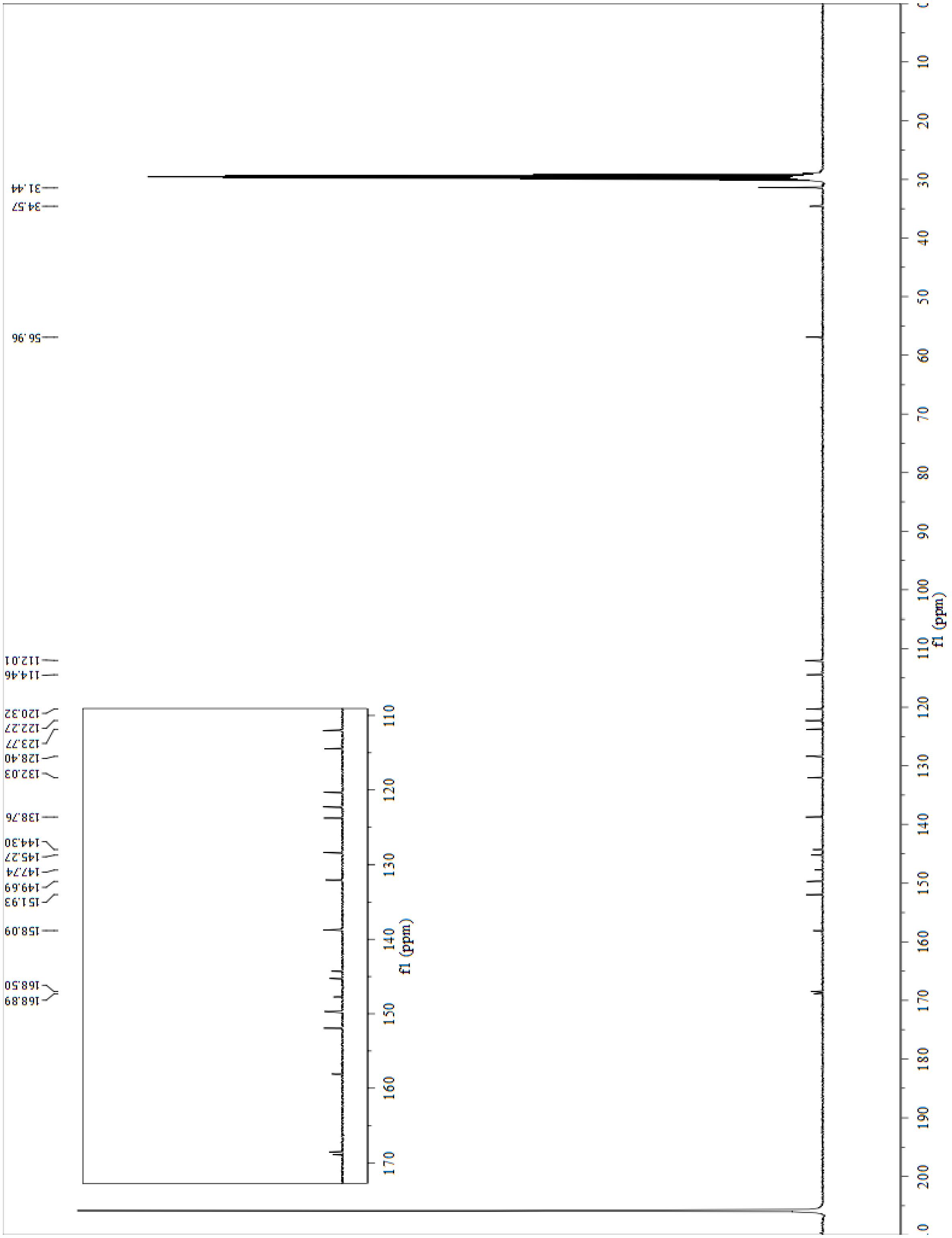


^{1} H NMR spectrum of **4fd**



^{13}C NMR spectrum of **4fd**



^{31}PNMR spectrum of **4fd**