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Office of Naval Research, Attn: Richard Miller Code 1132P
800 North Quincy Street
Arlington, Virginia 22217-5000

For
Naval Surface Warfare Center, Attn: H. G. Adolph
Silver Springs, MD 20903-5000

FLUOROCHEM, INC.

680 South Ayon Avenue
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Fluorodinitroethanol (FDNE) has been produced without the use of elemental fluorine. Nitration of 1,2-dichlorodifluoroethylene gave chlorofluoronitroacetic acid, which was converted to chlorofluoronitronitrosomethane with red fuming nitric acid and water. Oxidization of the nitroso compound gave chlorofluorodinitromethane, which was reduced to FDNE with iodide in the presence of formaldehyde.

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INTRODUCTION

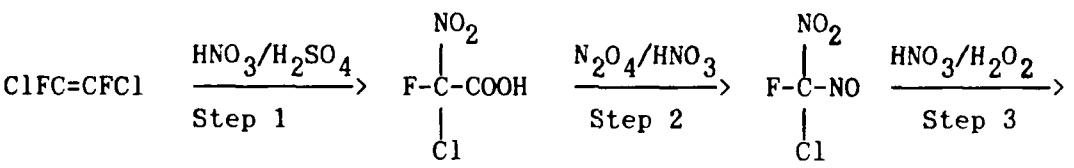
Fluorodinitroethanol (FDNE) is a basic building block for energetic plasticizers and binders. Without compromising thermal stability, FDNE provides greater energy content than dinitropropanol, which has been used in large quantities for manufacture of plasticizers. However, the current production cost limits use of FDNE to special applications, and there is a need for a new, low cost production method. Readily available, inexpensive FDNE and derivative compounds could be used to improve the performance of rocket propellants and explosives.

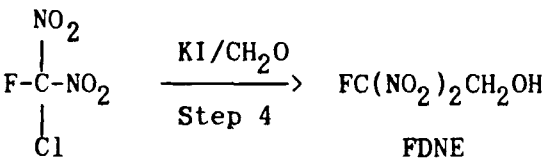
Two methods[1] have been used previously for manufacturing fluorodinitroethanol and both have significant difficulties. One was based on the fluorination of nitroform and the other on the fluorination of 2,2-dinitropropanediol (A-diol). Nitroform was available at low cost from Sweden until the supply was curtailed by a plant explosion in the 1970's. Environmental and safety problems still inhibit resumption of the large-scale production of nitroform. In the alternate process, A-diol was deformylated with base and the salt fluorinated. This aqueous fluorination process was complicated by the formation of large amounts of insoluble sodium fluoride, the expense of the A-diol and difficulty in purifying the product. Both of these processes require elemental fluorine, with attendant high plant capital costs.

Prior to this study no practical synthesis of fluorodinitromethyl compounds was known which did not require elemental fluorine or other electrophilic fluorinating reagents. The objective of this Phase I program was to evaluate new approaches to the industrial synthesis of FDNE based on the nitration of inexpensive fluorocarbons.

RESULTS AND DISCUSSION

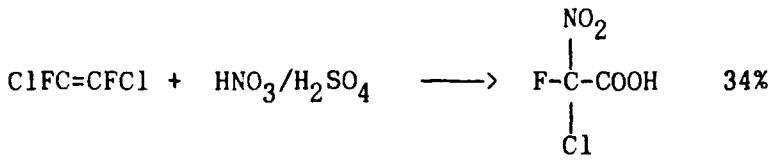
It has been reported in the Russian literature that nitration of 1,2-dichlorodifluoroethylene gives chlorofluoronitroacetic acid, and reaction of the latter with red fuming nitric acid gives chlorofluoronitronitrosomethane. This work was reinvestigated as the basis of an FDNE process. It was expected that oxidation of chlorofluoronitronitrosomethane could give chlorofluorodinitromethane (CFDNM), and that CFDNM could be reduced to give fluorodinitromethane. Fluorodinitromethane is known to react with formaldehyde to give FDNE. These reactions are summarized below.





Step 1. Nitration of 1,2-Dichlorodifluoroethylene.

We have repeated the reaction of 1,2-dichlorodifluoroethylene with 99% nitric acid and 95% sulfuric acid at room temperature by the procedure of Martynov[2] and have obtained a 34% yield of chlorofluoronitroacetic acid which is comparable to the 36% yield that was reported. The product was isolated from the insoluble organic layer, and assay of the acid layer by ^{19}F NMR showed the presence of additional product.



Chlorofluoronitroacetic acid is stable and is readily purified by vacuum distillation at 80°C (10 mm). However, in the presence of water, the acid decarboxylates instantaneously to give chlorofluoronitromethane which was found to be inert to further nitration.

Table I. CHLOROFLUORONITROACETIC ACID

Solvent	Yield	Notes
1. 95% H_2SO_4 100% HNO_3	34%	Some Product in Acid Layer
2. 30% Oleum 100% HNO_3	44%	
3. 30% Oleum, CF_3COOH 100% HNO_3	77%	63% Chlorofluoronitroacetic acid 14% 1,2-Addition Product
4. 95% H_2SO_4, CF_3COOH 100% HNO_3, CH_2Cl_2	50%	
5. $(CF_3CO)_2O$, CH_2Cl_2 100% HNO_3	60%	
6 30% Oleum, CF_3SO_3OH 100% HNO_3		22% 1,2-Addition Product

Preliminary attempts were made to improve the yield of the nitration reaction. The moisture sensitivity of chlorofluoronitroacetic acid suggested the use of anhydrous reaction conditions, and replacing sulfuric acid with oleum was found to improve the yield to 44%. However, the reaction mixture contained several unidentified fluorinated material with ^{19}F NMR signals in the δ -50 to -70 range. In reactions without nitric acid, the olefin has been reported to react with oleum to give high yields of the corresponding cyclic sulfone.[3]

Chlorofluoronitroacetic acid was obtained in 63% yield when a mixture of oleum, nitric acid and trifluoracetic acid was reacted with 1,2-dichlorodifluoroethylene. The 1,2-addition product, 1,2-dichloro-1,2-difluoro-2-nitroethyl trifluoroacetate, was isolated in 14% yield, bringing the effective yield of nitration to 77%. Apparently the 1,2-addition product was formed first and then was hydrolyzed *in situ*, to give the acetic acid derivative. The lower boiling point and diminished water sensitivity of the 1,2-addition product makes it a potentially attractive alternative to chlorofluoronitroacetic acid in subsequent nitration reactions.

$$ClFC{=}CFCl \xrightarrow{HNO_3/H_2SO_4/CF_3COOH} NO_2\text{-}CFCl\text{-}CFCl\text{-}OC(O)CF_3 \;(14\%) + F\text{-}\overset{\displaystyle NO_2}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}}\text{-}COOH \;(63\%)$$

This nitration in a mixture of sulfuric, nitric and trifluoroacetic acids in methylene chloride gave a 50% yield of chlorofluoronitroacetic acid on the basis of ^{19}F NMR assay. Similar nitration with N_2O_5 prepared from trifluoroacetic anhydride and nitric acid in methylene chloride gave a 60% yield of chlorofluoronitroacetic acid. When a mixture of nitric acid, oleum and triflic acid was used as the nitration medium, the 1,2-addition product 1,2-dichloro-1,2-difluoro-2-nitroethyl triflate was isolated 22% yield, but only trace amounts of chlorofluoronitroacetic acid were formed.

Variables such as reaction temperature, order of addition, concentration and methods of isolation on the yields of the nitration reactions were not investigated extensively. Since nitrations of other fluoroolefins such as tetrafluoroethylene[4] give yields as high as 92% of the corresponding nitro-

acetic acids, it is probable that under optimum conditions, 1,2-dichlorodifluoroethylene can be converted to chlorofluoronitroacetic acid in yields exceeding 77%.

The 1,2-dichlorodifluoroethylene used in this study was either purchased from PCR or prepared in 80% yield from commercially available 1,2-difluorotetrachloroethane by zinc mediated reduction.[5] The olefin from both sources was identical and was found to be an equal mixture of *cis* and *trans* isomers of 1,2-difluorotetrachloroethane, contaminated by 10% of 1,1-difluorodichloroethylene. Yields in this report were corrected for the presence of the latter isomer. The source of the unsymmetrical isomer was found to be a 10% impurity of 1,1-difluorotetrachloroethane in the 1,2-difluorotetrachloroethane used as the starting material.

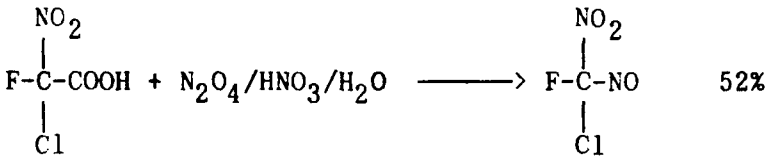
The presence of the 1,1-difluoro isomer in the starting material presented the potential problem that nitration might lead to formation of a highly toxic byproduct, difluoronitroacetic acid. This acid, however, was not detected in the product mixtures. The problem can be avoided by using another synthesis of 1,2-dichlorodifluoroethylene; the pyrolysis of fluorodichloromethane[6] has been reported to give pure 1,2-dichlorodifluoroethylene in a process similar to that used in the manufacture of tetrafluoroethylene.

$$HCFCl_2 \xrightarrow{650^\circ C} [CFCl] \longrightarrow CFCl{=}CFCl$$

Step 2. Chlorofluoronitronitrosomethane.

Chlorofluoronitroacetic acid is decarboxylated rapidly in the presence of water to give chlorofluoronitromethane. However, it has been reported that

the decarboxylation reaction in the presence of fuming nitric acid gave a nitroso compound.[7] During this program, we repeated this reaction and isolated a 51% yield of chlorofluoronitronitrosomethane; the reported yield was 52%. The reaction was conducted at 80°C in 90% nitric acid containing 20% N_2O_4 and chlorofluornitronitrosomethane was distilled from the reaction mixture as an intensely blue liquid contaminated with N_2O_4. The yield was confirmed by ^{19}F NMR using trifluorotoluene an internal reference. This intermediate was stable for several days at ambient temperature, but was generally used directly in the next step without further isolation or purification.



A possible route for this reaction consists of decarboxylation of chlorofluoronitroacetic acid to give chlorofluoro-*aci*-nitromethane, followed by nitrosation by oxides of nitrogen to give chlorofluoronitronitrosomethane. Reaction of other *aci*-nitro compounds with N_2O_4 to give pseudonitroles under similar conditions has been reported.[8] The reaction of 1,2-dichlorodifluoroethylene with fuming nitric acid did not give chlorofluoronitronitrosomethane, but when the mixture was diluted with water, the nitronitroso compound was formed in 24% yield. This result suggests that nitration conditions may be found to combine step 1 and step 2 into a one-pot reaction.

Step 3. Chlorofluorodinitromethane

Oxidation of chlorofluoronitronitrosomethane with 30% hydrogen peroxide

in nitric acid at ambient temperature gave chlorofluorodinitromethane in 62% isolated yield. The reaction was 90% complete after 15 minutes (See Table II).

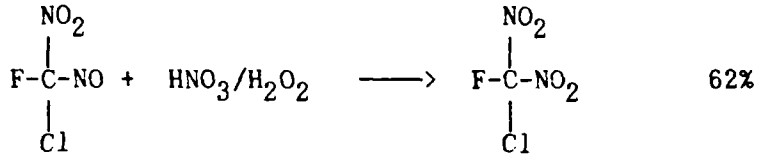
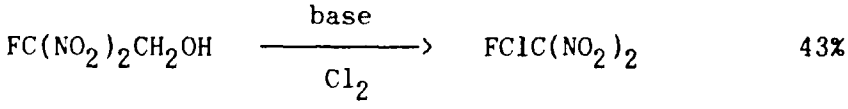


Table II. OXIDATION OF CHLOROFLUORONITRONITROSOMETHANE TO CFDNM

Time, min	$ClFC(NO_2)NO$ %	$ClFC(NO_2)_2$ %
0	100	0
15	10.8	56.7
30	8.2	61.7
45	5.1	60

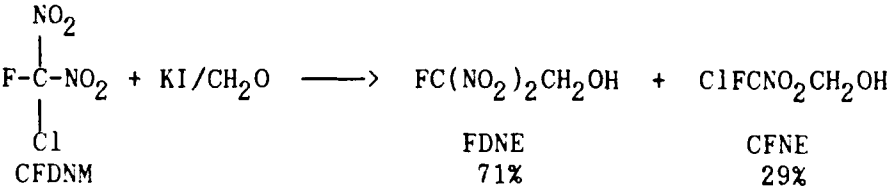
Chlorofluorodinitromethane was first prepared by the direct aqueous fluorination of potassium chlorodinitromethane[9] and more recently by the unusual reaction of chlorofluoronitroacetic acid with xenon difluoride.[10] To obtain a reference sample for this program, authentic chlorofluorodinitromethane was synthesized by the reaction of FDNE with aqueous bleach in 43% yield.



Step 4. Reduction of CFDNM to FDNE.

FDNE has been prepared by reduction of fluorotrinitromethane with sodium hydroxide and hydrogen peroxide in the presence of formaldehyde.[1] Attempted reduction of CFDNM under these conditions resulted in substantial hydrolysis to fluoride ion and the formation of small amounts of chlorofluoro-

nitroethanol.[11] Only trace amounts of FDNE were produced either in aqueous solution or when alcohols were used as cosolvents.



However, yields of FDNE as high as 71% were realized when KI was use as the reducing agent. Results using a 30% aqueous ethanolic solution of CFDNM (1 eq), KI (2.3 eq) and 30% formaldehyde solution (1.3 eq) at 70°C are summarized in the Table III. Formation of both FDNE and chlorofluoronitroethanol (CFNE) was observed with the maximum amount of FDNE observed at 1 h reaction time.

Table III. REACTION OF CHLOROFLUORODINITROMETHANE (CFDNM) WITH KI/CH_2O

Time at 70°C min	CFDNM %	FDNE %	CFNE %	F^- %
0	100	-	-	-
30	9.0	56.5	18.8	1.8
60	4.7	66.6	23.8	2.8
90	3.6	63.1	24.8	4.9
120	3.0	60.2	25.7	4.9

Other reaction variations are summarized in Table IV. The reaction with KI was found to be slow at room temperature, with less than 10% of the CFDNM reduced after 3 hours. Reactions conducted at 40 to 75°C for short periods and then continued for several days as room temperature gave the best results. When the reaction temperature exceeded 75°C, no FDNE was formed and complete hydrolysis to fluoride ion occurred.

Table IV. REDUCTIVE DEHALOGENATIONS OF CFDNM IN THE PRESENCE OF FORMALDEHYDE

Protocols	Products (Yields from ^{19}F NMR integration) CFDNM	FDNE	CFNE	F^-
H_2O_2/NaOH/CH_2O in water 0°C, 1 h	trace	trace	5%	95%
H_2O_2/NaOH/CH_2O in aq. MeOH 0°C for 1 h then RT for 1 h	5%	none	2%	95%
H_2O_2/NaOH/CH_2O in aq. EtOH 0°C for 1 h then RT for 1 h	40%	trace	trace	60%
KI/CH_2O in aq. EtOH 3 h at RT	90%	5%	5%	none
then 2 days at RT	8%	50%	34%	5%
KI/CH_2O in aq. EtOH 2 h at 40°C	33%	44%	23%	none
then 2 days at RT	none	71%	29%	trace
KI/CH_2O in aq. EtOH 1/2 h at 75°C	15%	58%	24%	3%
then 2 days at RT	none	67%	30%	3%
KI in aq. EtOH 1/2 h at 75°C	none	none	trace	99%

Small amounts of chlorofluoronitroethanol (CFNE) were observed as a byproduct in most KI reductions. The boiling point of CFNE (40°C/0.4 mm) is close to that of FDNE (41°C/0.1 mm) and these materials could not be separated readily by distillation. Pure chlorofluoronitroethanol was prepared for use as a reference standard by chlorination of 2-fluoro-2-nitro-1,3-propanediol in 45% yield. CFNE was also prepared in small yield by decarboxylation of chlorofluoronitroacetic acid in aqueous formaldehyde.

$$HOCH_2CF(NO_2)CH_2OH \xrightarrow{\text{bleach}} ClFC(NO_2)CH_2OH \quad (CFNE) \qquad 45\%$$

$$ClFC(NO_2)COOH \xrightarrow[RT \text{ or } 70^\circ C]{\text{Aq. } CH_2O} ClFC(NO_2)H$$

$$ClFC(NO_2)H \xrightarrow{CH_2O/NaOH} ClFC(NO_2)CH_2OH \quad (CFNE)$$

In an effort to eliminate CFNE formation, several other reduction conditions were investigated. Fluorotrinitromethane reacts with aqueous formaldehyde solution to give FDNE in 36% yield in the absence of other reducing agents.[12] However, under similar conditions, CFDNM failed to give FDNE. Other reactions of CFDNM with various "soft" nucleophiles and reducing agents are summarized in Table V below. The best results were obtained with sodium sulfide and sodium thiosulfate. However, sodium sulfide also reacted with formaldehyde to give insoluble trithiane. At room temperature, even after 16 h, these reactions were not complete. The reaction mixture containing sodium thiosulfate gave two phases after it was heated at 70°C for 10 h. The aqueous phase showed only FDNE and the organic phase showed several unidentified products in addition to FDNE.

Table V. REDUCTION OF CFDNM

	Temp	FDNE	CFNE	F^-	Comments
KBr	RT	-	-		no rxn
	70°C	-	-		no rxn
CH_3COOK	RT	-	-		no rxn
	70°C	-	-		no rxn
$NaNO_2$	RT	-	-		no rxn
	70°C	-	-		no rxn
Na_2SO_3	RT	-	-		no rxn
	70°C	-	-		no rxn
$K_3Fe(CN)_6$	RT	-	-		no rxn
	70°C	-	-		no rxn
KOCN	RT	-	-		no rxn
	70°C	2%	5%	16%	unreacted CFDNM
KCN	RT	22%	18%	17%	unreacted CFDNM
	70°C	7%	50%	40%	
$Na_2S_2O_3$	RT	60%	trace	trace	unreacted CFDNM
KSCN	RT	-	-		no rxn
	70°C	35%	trace		unreacted CFDNM solid in rxn mixt
Na_2S	RT	30%	trace	40%	unreacted CFDNM
	70°C	50%	7%	40%	water insoluble solid in mixt

CONCLUSIONS

The feasibility of a new synthetic route to FDNE based on the nitration of 1,2-dichlorodifluoroethylene has been demonstrated during this Phase I program. This work shows that direct fluorination is not necessary for the synthesis of the fluorodinitromethyl group.

Nitration of 1,2-dichlorodifluoroethylene gave chlorofluoronitroacetic acid,

which was converted to chlorofluoronitronitrosomethane with red fuming nitric acid and water. Oxidization of the nitroso compound gave CFDNM, which was reduced to FDNE with iodide. This new sequence has the potential to provide low-cost FDNE on an industrial scale in an environmentally acceptable process. Since the first three steps involve variations of reactions in nitric acid, it is possible that a one-pot reaction can be developed. Optimum reaction conditions have not been established, but the best results during this program are summarized in Table VI.

Table VI. YIELDS OF REACTIONS LEADING TO FDNE.

STEP	STARTING MATERIAL	PRODUCT	YIELD
1.	$ClFC{=}CFCl$	$ClFCNO_2COOH$	77%
2.	$ClFCNO_2COOH$	$ClFCNO_2NO$	52%
3.	$ClFCNO_2NO$	$ClFC(NO_2)_2$ (CFDNM)	62%
4.	$ClFC(NO_2)_2$	$FC(NO_2)CH_2OH$ (FDNE)	71%

EXPERIMENTAL

IR spectra were recorded in CH_2Cl_2 on a Perkin-Elmer 700 spectrometer. ^1H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Brucker AC200 spectrometer and are reported in ppm relative to TMS and $FCCl_3$. Warning: Fluorodinitroethanol is a powerful skin irritant.

1,2-Dichlorodifluoroethylene: A suspension of zinc powder (144 g, 2.2 mol) and zinc chloride (0.1 mg) in ethanol (200 mL) was stirred mechanically in a 2-L three neck flask equipped with a 12" vigreux column, fraction splitter, and a condenser cooled to -20°C. Approximately 20 mL of a solution of 1,1- and 1,2-difluorotetrachloroethanes (240 g, 1.17 mol, 1:9 mixture) in ethanol (40 mL) was added and the mixture was heated to 45-55°C. The remainder of the solution was added dropwise over 4 h, while the product was distilled at 18-20°C through the column operated at a 1:1 reflux ratio and collected in a receiver cooled to -78°C. The resulting distillate contained 125 g (80%) of a mixture of *cis*- and *trans*-1,2-dichlorodifluoroethylene and 1,1-difluorotetrachloroethane (45:45:10 ratio by ^{19}F NMR): No signals in ^1H NMR; ^{19}F NMR ($CDCl_3$) δ -119.6 (s, *trans*-isomer), -105.1 (s, *cis*-isomer), and -88.5 (1,1-dichlorodifluoroethylene).[13] This material was identical to that obtained commercially.

Chlorofluoronitroacetic Acid, Sulfuric Acid Procedure. A solution of 100% HNO_3 (30 mL) in conc. H_2SO_4 (35 mL) was added over 30 min to neat 1,2-dichlorodifluoroethylene (48 g, 0.35 mol) at 10-15°C; an exothermic reaction was observed. The mixture was stirred for 10 min at 10°C. The organic layer was separated, and distilled to give 14 g (34%) of chlorofluoronitroacetic acid, bp 45-65°C (0.5 mm) (Lit[2] bp 90°C / 8 mm): ^{19}F NMR ($CDCl_3$) δ -89.71; ^{13}C NMR δ 113.69 (d, J = 303 Hz), 161.21 (d, J = 29 Hz).

Chlorofluoronitroacetic Acid, Oleum Procedure. A solution of 100% nitric acid (9 mL) in 30% oleum (11 mL) was added over 25 min to 1,2-dichlorodifluoroethylene (13.3 g, 0.1 mol) at 14-17°C. The mixture was stirred for 30 min at 10-14°C. The organic layer was separated, and distilled to give 6.84 g (44%) of chlorofluoronitroacetic acid, bp 80-85°C (8 mm), identical to the material prepared above.

Chlorofluoronitroacetic Acid, Oleum-Trifluoroacetic Acid Procedure. A solution of 100% nitric acid (5 mL) and trifluoroacetic acid (4.2 mL, 54 mmol) in 30% oleum (6 mL) was added over 25 min to 1,2-dichlorodifluoroethylene (7.5 g, 56 mmol) at 10-15°C. The mixture was stirred for 60 min at 10-14°C. The organic layer was separated, and fractionally distilled to give 2.1 g (14.5%) of 1,2-dichloro-1,2-difluoro-1-nitroethyl trifluoroacetate, as a 50:50 mixture of diasterimers, bp 48-50°C (0.5 mm): ^{19}F NMR ($CDCl_3$) δ -76.27 (s, 6 F), -77.50 (s, 1 F), -78.49 (s, 1F), -94.37 (s, 1 F), -95.30 (s, 1 F). The second fraction contained 4.0 g of chlorofluoronitroacetic acid, bp 55-65°C (0.5 mm), identical to the authentic material prepared above. The oleum layer was heated to 80°C under vacuum (0.5 mm) to give an additional 1.61 g (63% combined yield) of chlorofluoronitroacetic acid.

Chlorofluoronitroacetic Acid, Oleum-Triflic Acid Procedure. A solution of 100% nitric acid (5.5 mL) and trifluoromethanesulfonic acid (5.6 mL, 63 mmol) in 30% oleum (6.5 mL) was added over 30 min to 1,2-dichlorodifluoroethylene (8.4 g, 63 mmol) at 10-15°C. The mixture was stirred for 60 min at 10-14°C. The organic layer was separated, and distilled to give 4.9 g (24%) of 1,2-dichloro-1,2-difluoro-1-nitroethyl trifluoromethanesulfonate, bp 60-65°C (0.5 mm), as a 50:50 mixture of diasterimers: ^{19}F NMR ($CDCl_3$) δ -68.47 (s, 1 F), -69.60 (s, 1 F), -73.32 (s, 6 F, OSO_2CF_3), -92.84 (s, 1 F), -93.52 (s, 1 F).

Chlorofluoronitronitrosomethane. Red fuming HNO_3 (7 mL) was added to a mixture of chlorofluoronitroacetic acid (2.4 g, 15.3 mmol) and water (2 mL). The mixture was heated to 100°C and the distillate boiling at 45-92°C was collected until the reaction mixture ceased to be blue in color. The blue distillate contained a mixture of N_2O_4 and 1.1 g (51%) of chlorofluoronitronitrosomethane (assayed by ^{19}F NMR using trifluorotoluene as the internal standard.) ^{19}F NMR ($CDCl_3$) -85.8 (t, J = 10 Hz) (Lit[7] -85.6).

Chlorofluorodinitromethane from Fluorodinitroethanol. A solution of KOH (24.7 g, 0.44 mol) in bleach (12.5% NaClO solution, 400 mL) was added to a solution of fluorodinitroethanol (67.8 g, 0.44 mol) in water (100 mL) at 0-5°C. The mixture was stirred at 0°C for 15 min and the layers were separated. The aqueous layer was extracted with methylene chloride (3 X 50 mL) and the combined organic layers were washed with 100 mL of brine and dried ($MgSO_4$). The solvent was evaporated and the residue was distilled to give 29.4 g (43% yield) of chlorofluorodinitromethane, bp 70-80°C (Lit bp 83-84°C / 747 mm): ^{19}F NMR ($CDCl_3$, Freon 113) δ -67.75 (q, J = 11.1 Hz) (Lit[14] -67.68); ^{13}C NMR ($CDCl_3$) δ 122.5 (2 x 5, J_{CF} = 333.4 Hz, J_{CN} = 11.9 Hz).

Chlorofluorodinitromethane from Chlorofluoronitronitrosomethane. A solution of chlorofluoronitronitrosomethane (3.8 mg, 0.027 mmol) in 0.5 mL of $CDCl_3$ in an NMR tube was cooled to 5°C and 0.2 mL of 100% HNO_3 and 0.1 mL of 30% H_2O_2 solution were added. The temperature was kept at 5°C until the exothermic reaction subsided. The solution was then shaken at room temperature for 0.5 h until the blue color disappeared. The residue contained 2.5 mg (62% yield) of chlorofluorodinitromethane by ^{19}F NMR analysis (trifluorotoluene internal standard). This material was identical to authentic chlorofluorodinitromethane prepared above.

Fluorodinitroethanol from Chlorofluorodinitromethane. A solution of chlorofluorodinitromethane (0.95 g, 6.0 mmol), KI (2.5 g, 15 mmol), and 37% aqueous formaldehyde (0.6 mL, 7 mmol) in 30% aqueous ethanol (10 mL) was heated at 70°C for 1 h. The solution was cooled and was found to contain 0.62 g (67%) of fluorodinitroethanol and 0.19 g (23%) of chlorofluoronitroethanol by ^{19}F NMR assay (trifluoroethanol internal standard).

Chlorofluoronitroethanol. A solution of 2-fluoro-2-nitro-1,3-propanediol (3.0 g, 21.6 mmol) in of 12.5% bleach (NaClO, 100 mL) was stirred at ambient temperature for 3 h and then extracted with methylene chloride (2 X 100 mL). The combined organic solutions were dried ($MgSO_4$) and filtered through a pad of silica gel, and evaporated to give a yellow oil. The residual oil was distilled to give 1.3 g (42%) of chlorofluoronitroethanol, bp 39-40°C (0.4 mm): ^1H NMR ($CDCl_3$) δ 3.58 (b, 1H), 4.16-4.49 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 62.29 (d, J = 23.7 Hz), 119.97 (d, J = 293.2 Hz); ^{19}F NMR ($CDCl_3$) δ -98.19 (dd, J = 6.8, 22 Hz). Anal. Calcd for $C_2H_3ClFNO_3$: C, 16.74; H, 2.11; N, 9.76. Found: C, 16.72; H, 2.37; N, 9.68.

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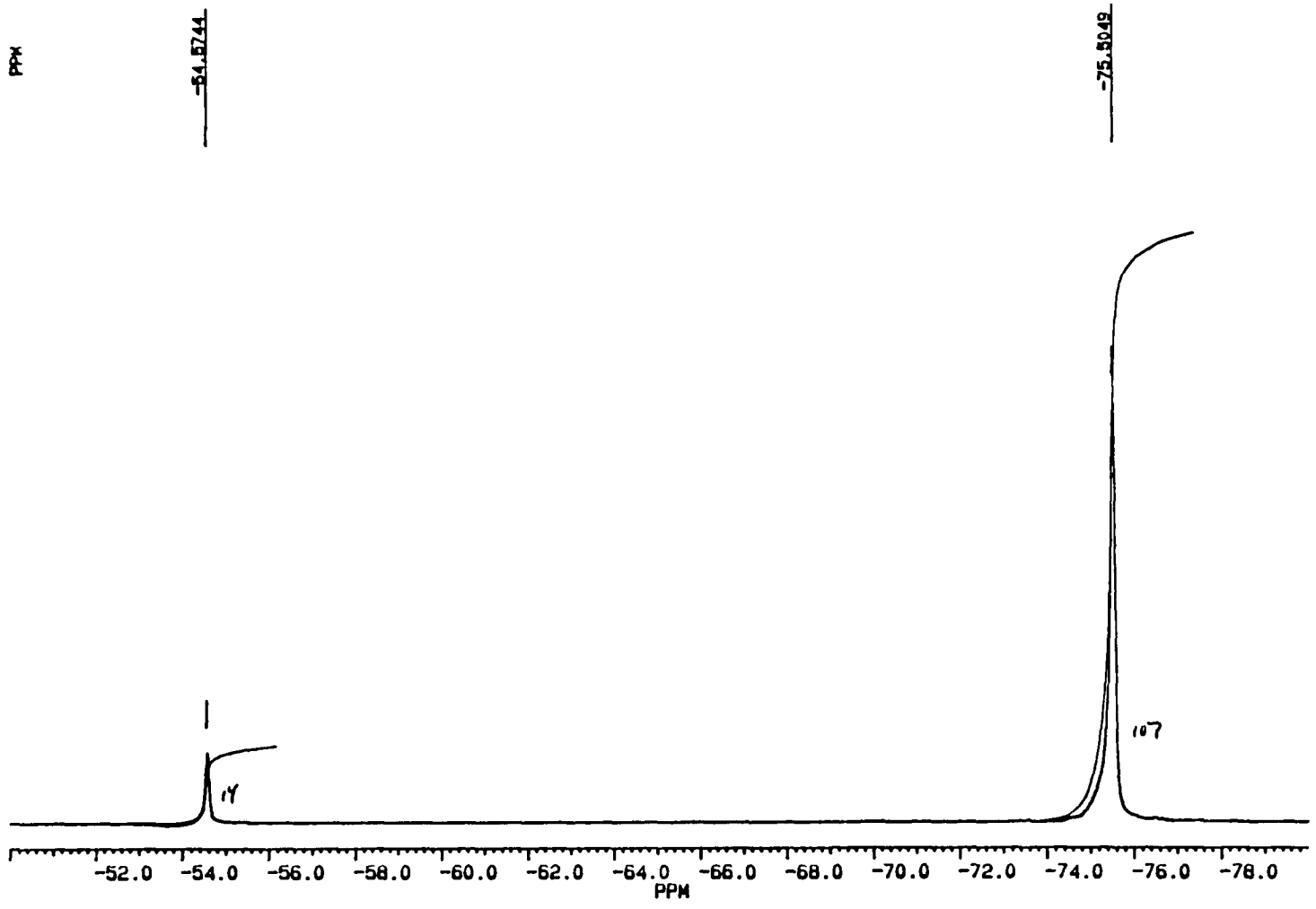


FIGURE 1. ^{19}F NMR SPECTRUM OF 1,2-DIFLUOROTETRACHLOROETHANE (PCR)

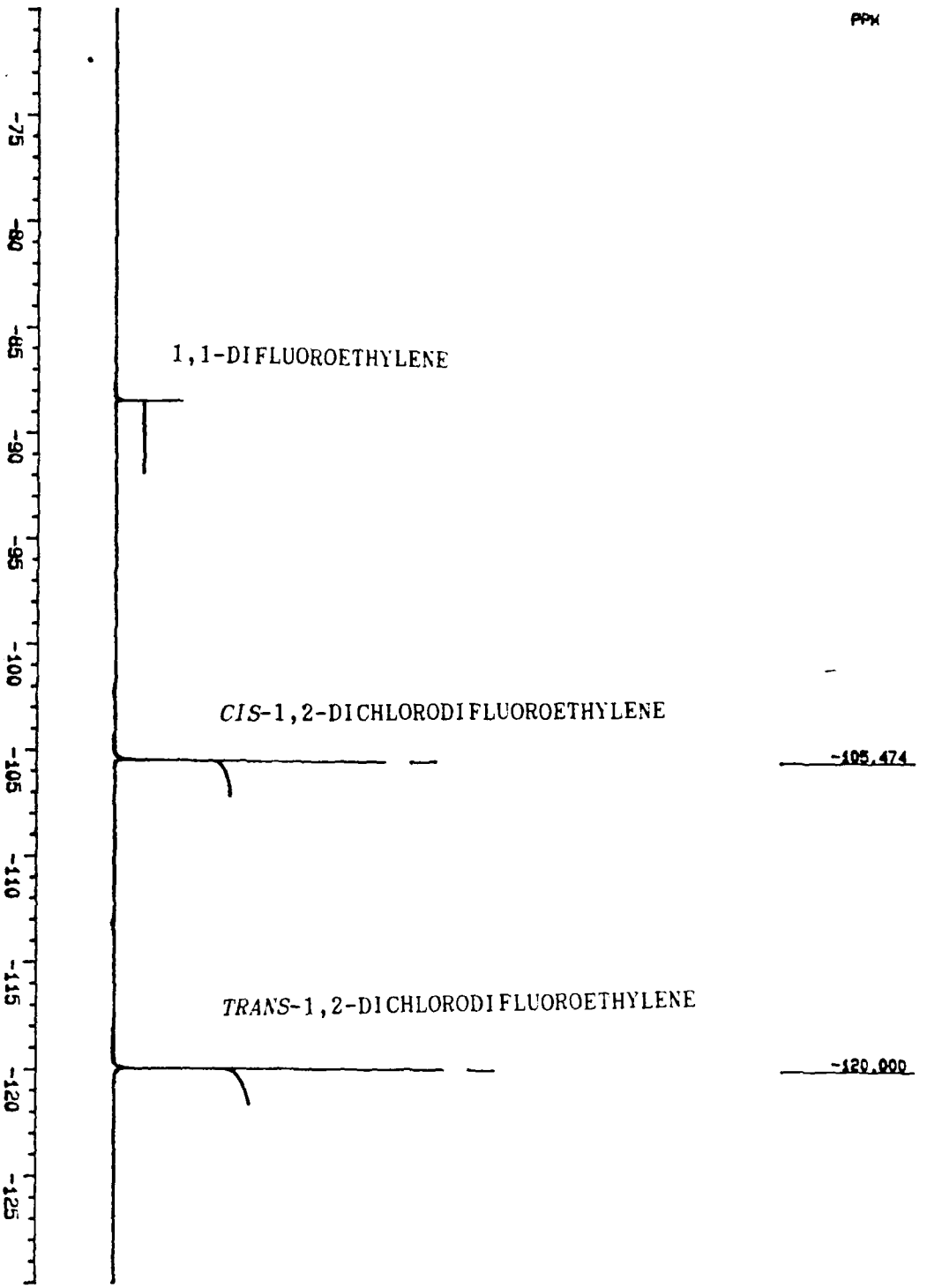


FIGURE 2. ^{19}F NMR SPECTRUM OF 1,2-DICHLORODIFLUOROETHYLENE

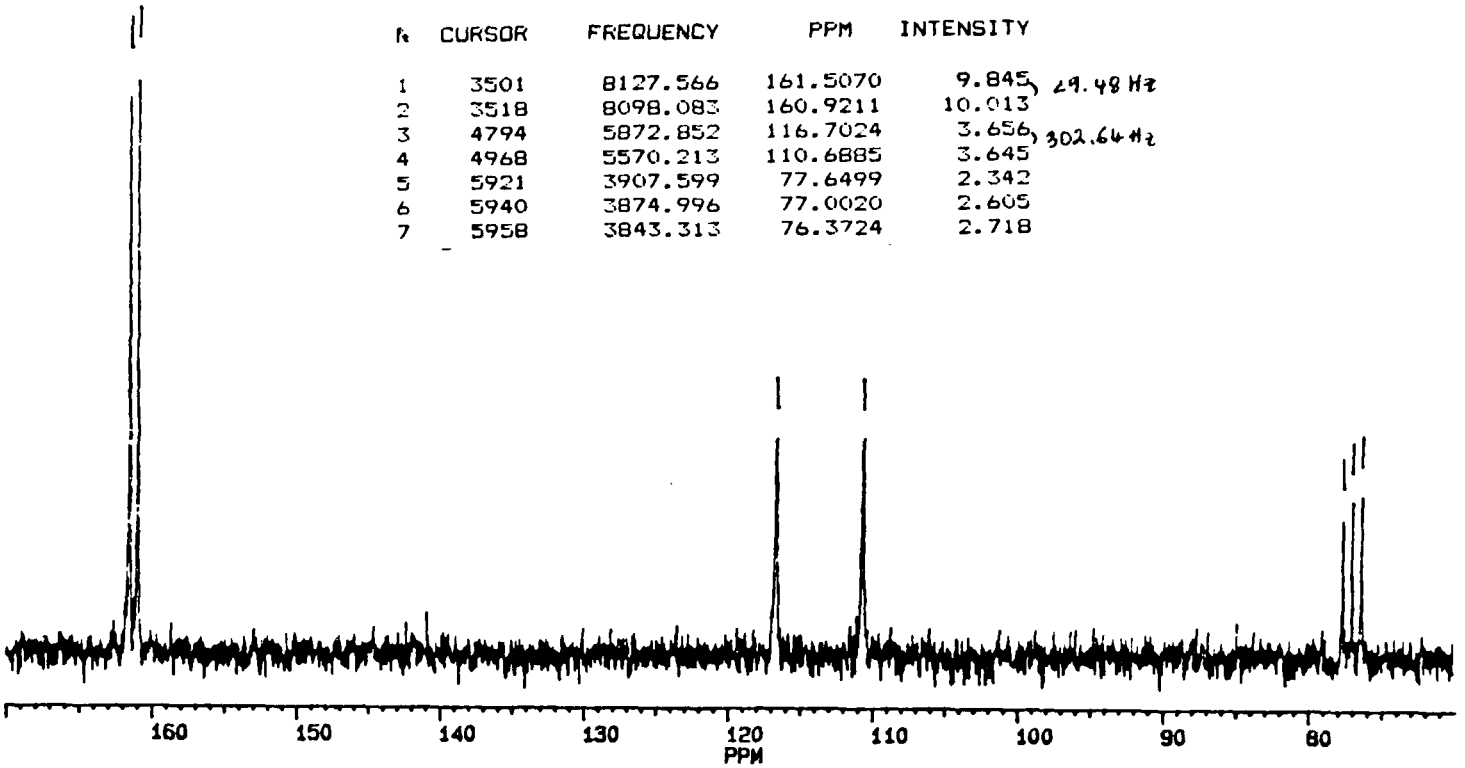


FIGURE 3. ^{13}C NMR SPECTRUM OF CHLOROFLUORONITROACETIC ACID

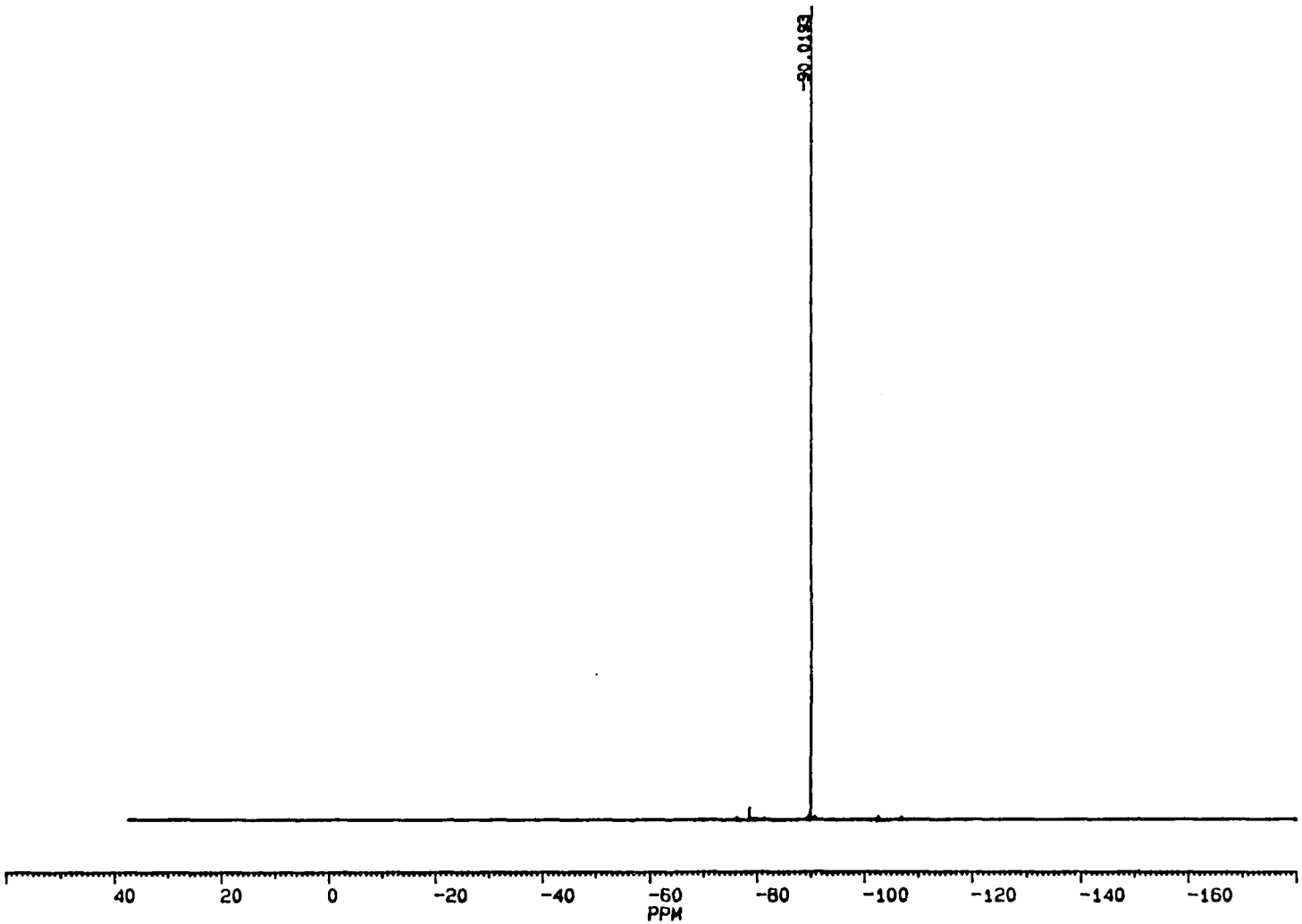


FIGURE 4. ^{19}F NMR SPECTRUM OF CHLOROFLUORONITROACETIC ACID

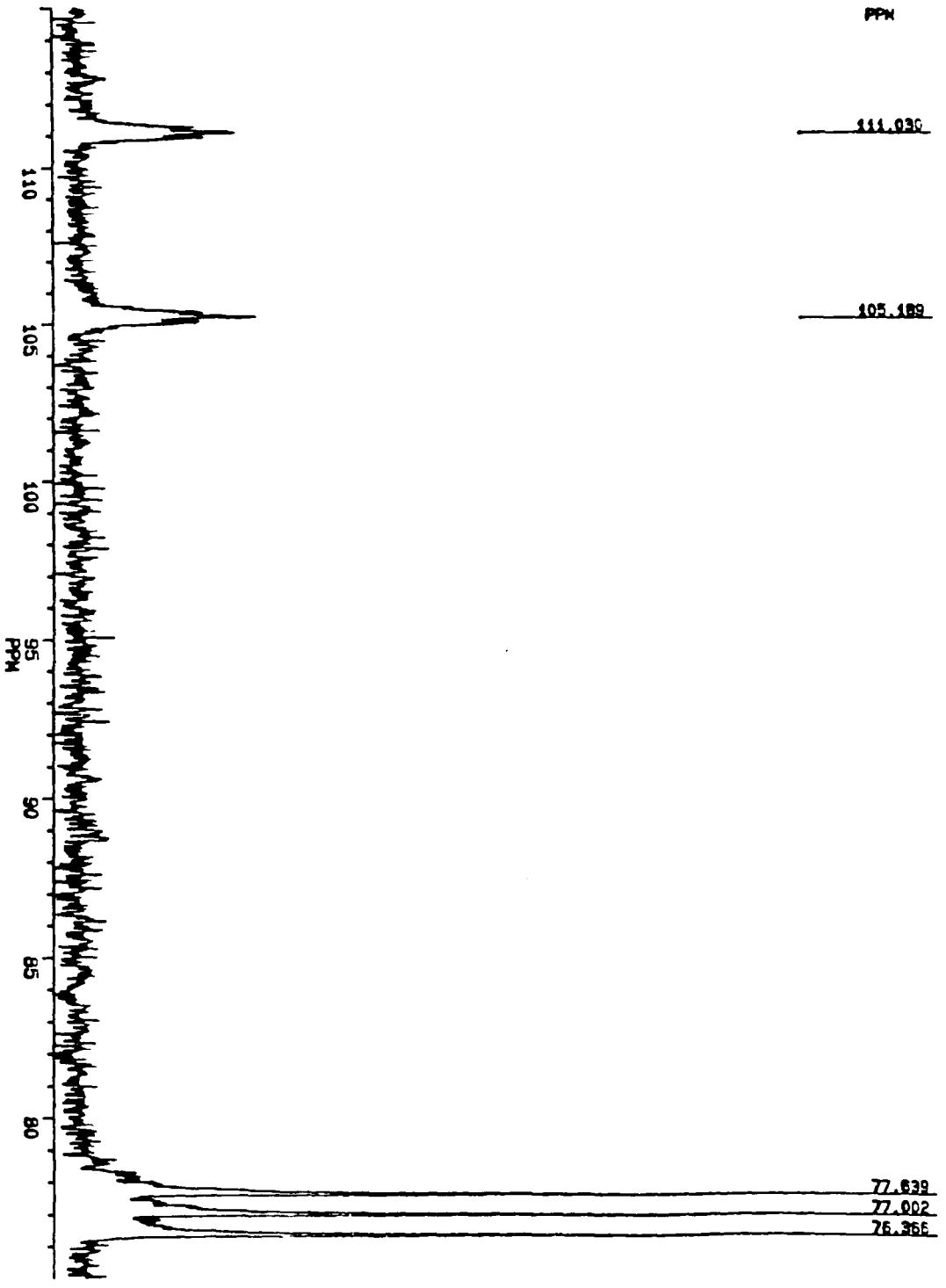


FIGURE 5. ^{13}C NMR SPECTRUM OF CHLOROFLUORONITROMETHANE

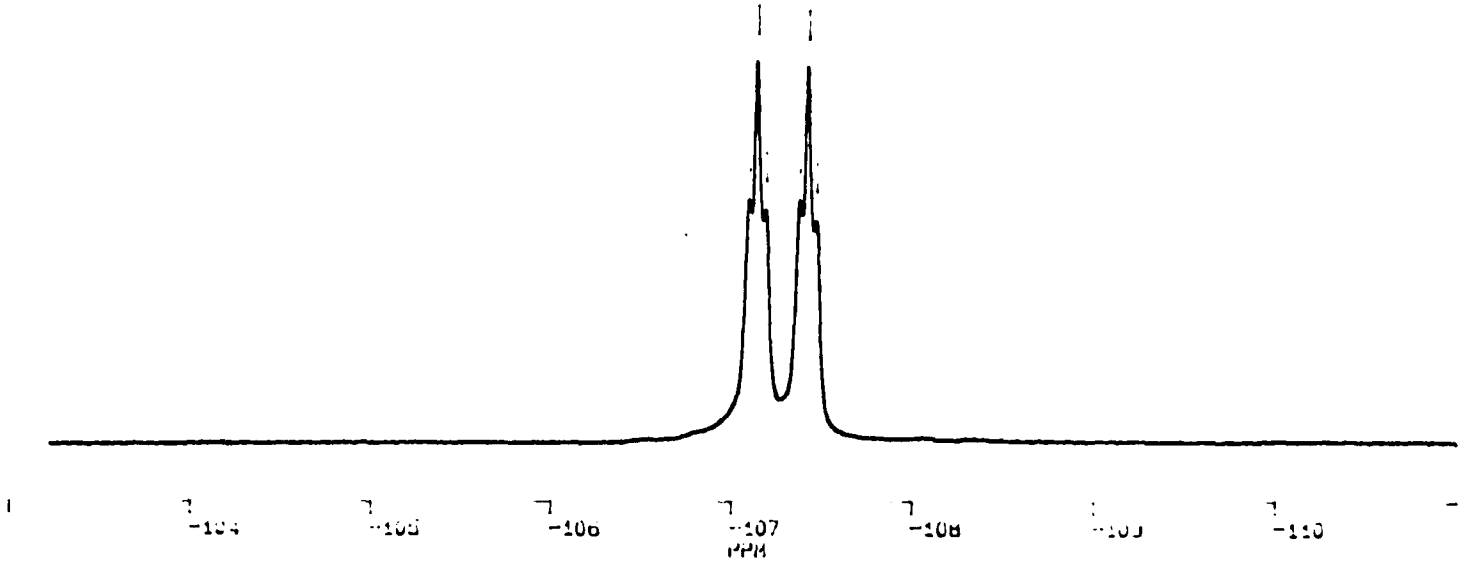


FIGURE 6. ^{19}F NMR SPECTRUM OF CHLOROFLUORONITROMETHANE

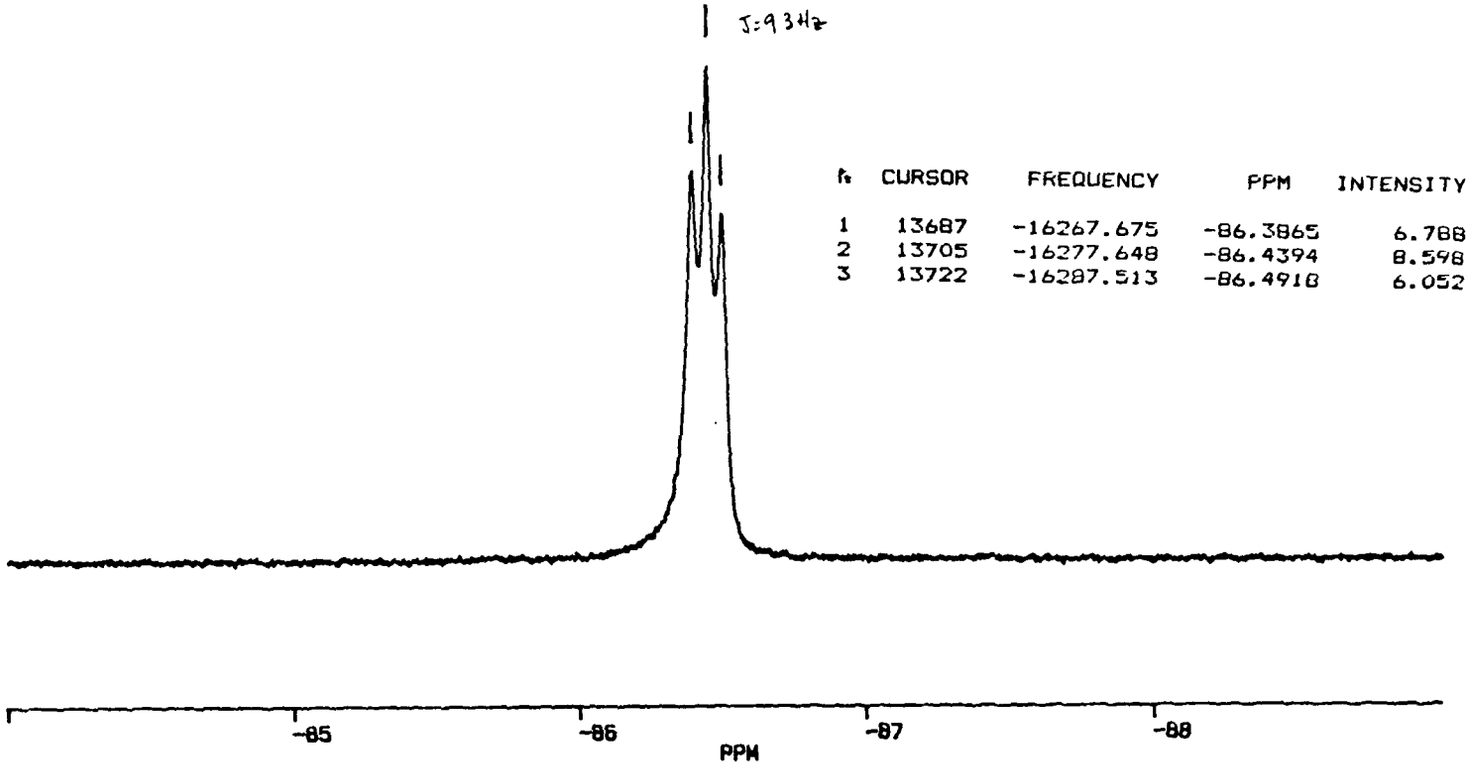


FIGURE 7. ^{19}F NMR SPECTRUM OF CHLOROFLUORONITRONITROSOMETHANE

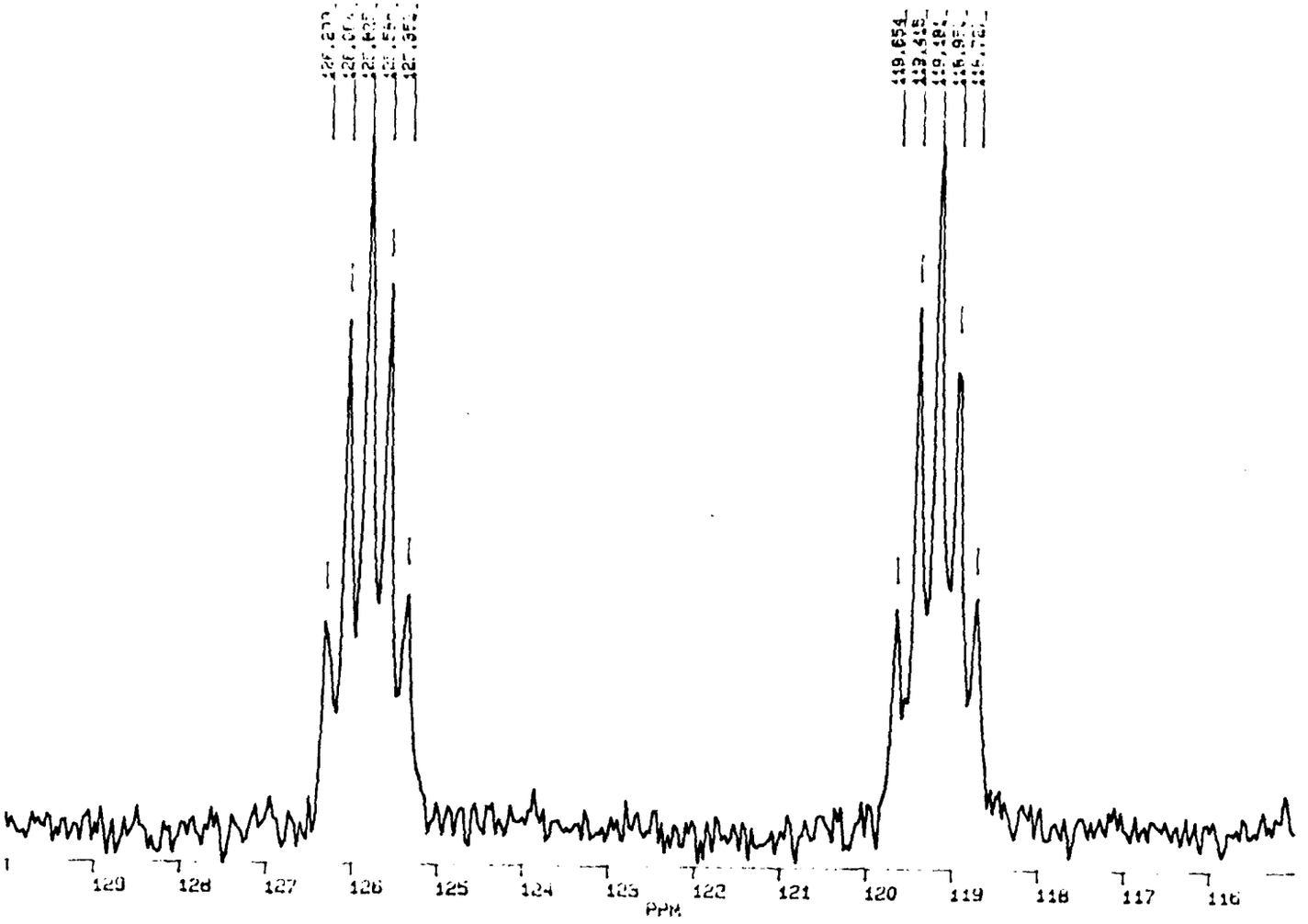
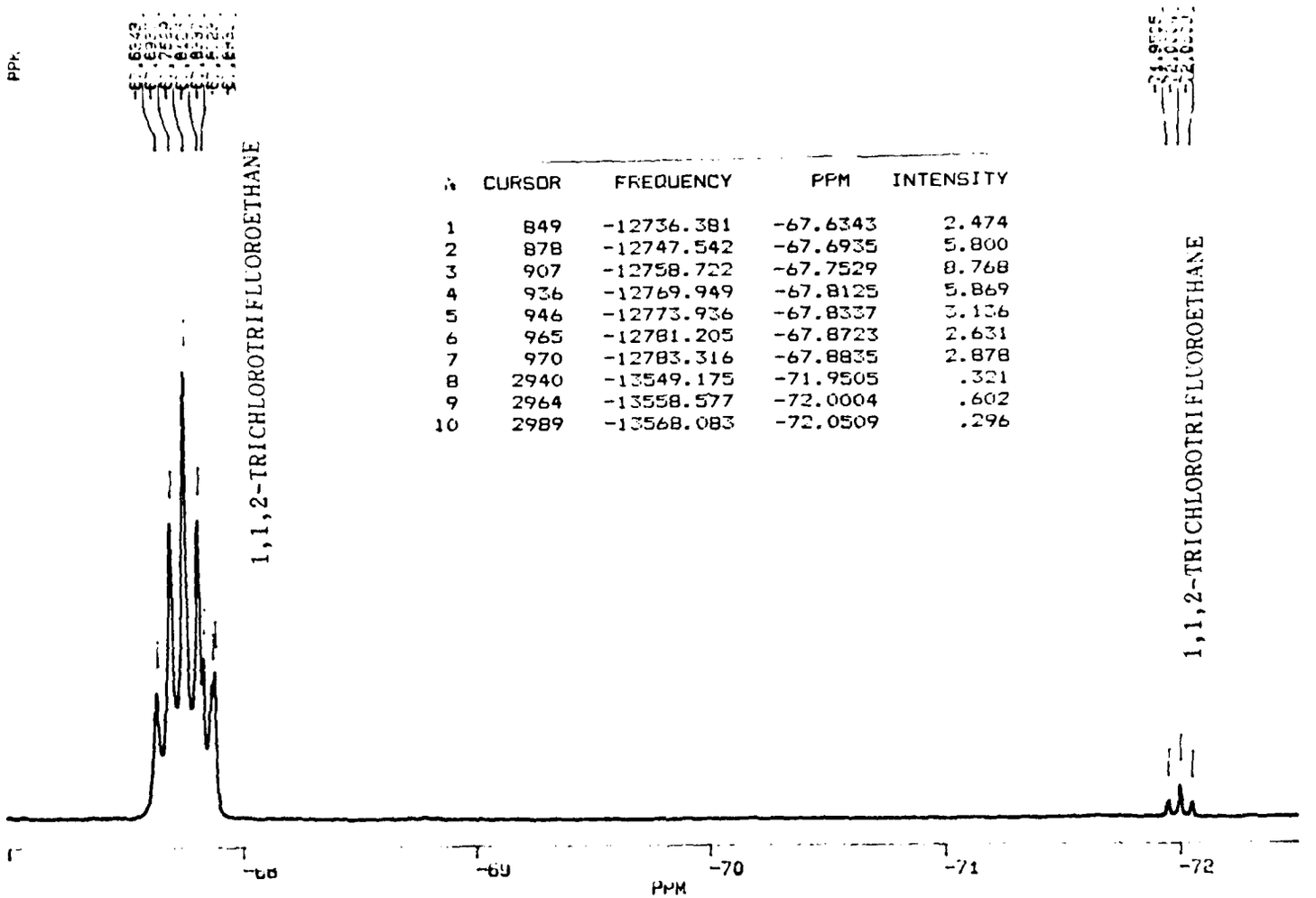


FIGURE 8. ^{13}C NMR SPECTRUM OF CHLOROFLUORODINITROMETHANE



#	CURSOR	FREQUENCY	PPM	INTENSITY
1	849	-12736.381	-67.6343	2.474
2	878	-12747.542	-67.6935	5.800
3	907	-12758.722	-67.7529	8.768
4	936	-12769.949	-67.8125	5.869
5	946	-12773.936	-67.8337	3.136
6	965	-12781.205	-67.8723	2.631
7	970	-12783.316	-67.8835	2.878
8	2940	-13549.175	-71.9505	.321
9	2964	-13558.577	-72.0004	.602
10	2989	-13568.083	-72.0509	.296

FIGURE 9. ^{19}F NMR SPECTRUM OF CHLOROFLUORODINITROMETHANE

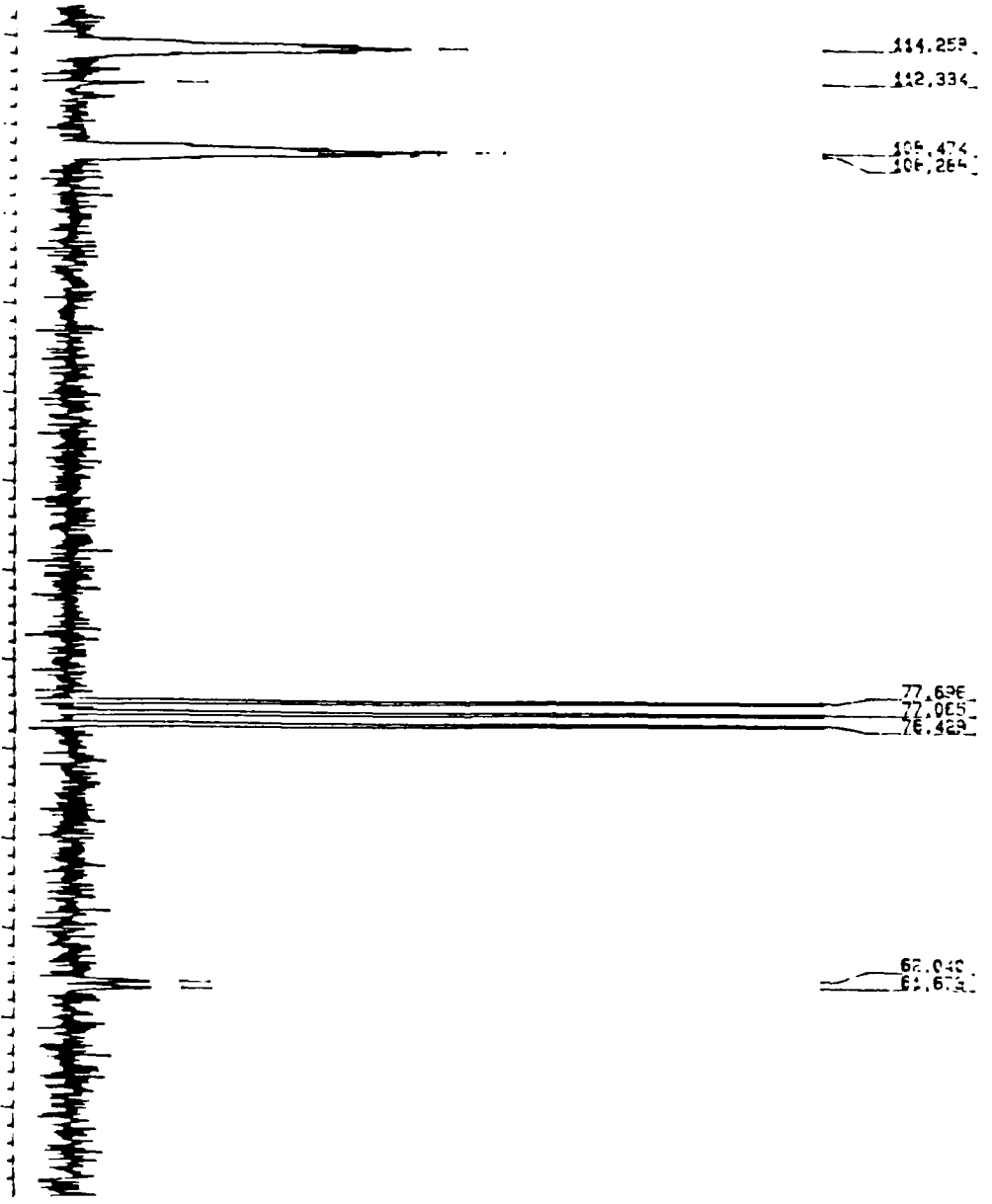


FIGURE 10. ^{13}C NMR SPECTRUM OF FLUORODINITROMETHANE

FIGURE 11. ^{19}F NMR SPECTRUM OF FLUORODINITROMETHANE

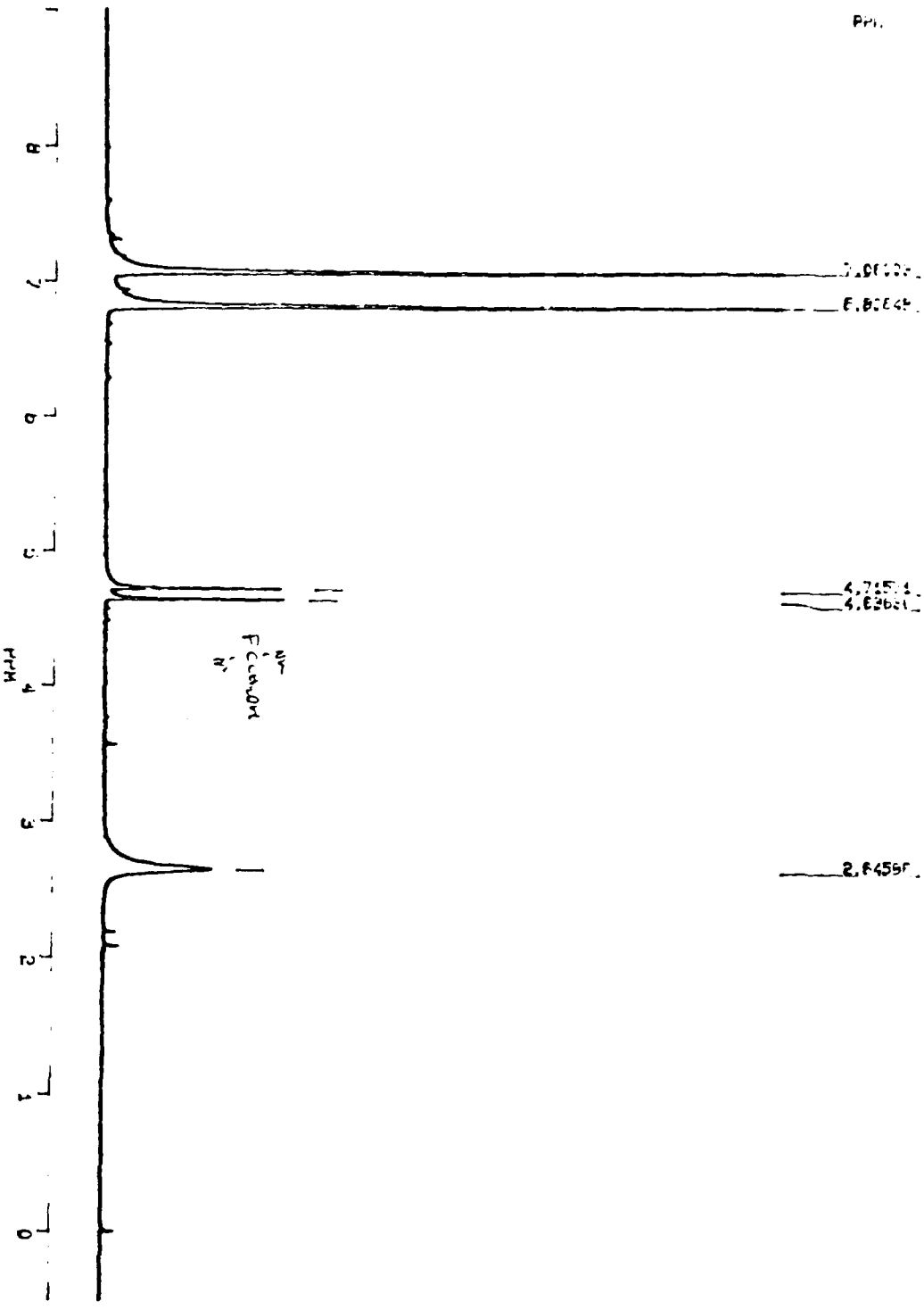


FIGURE 12. ^{1}H NMR OF FLUORODINITROMETHANE AND FLUORODINITROETHANOL

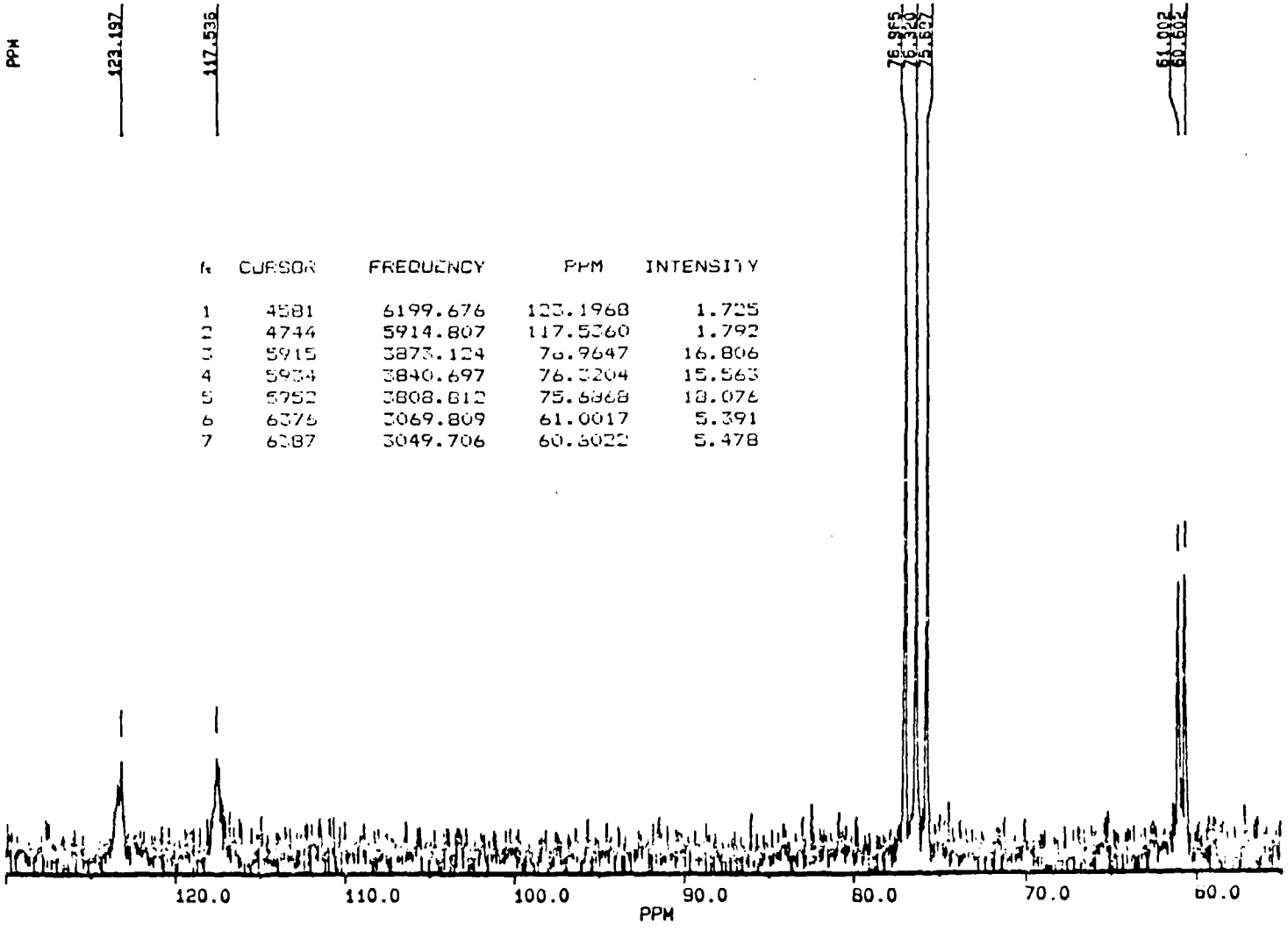


FIGURE 13. ^{13}C NMR SPECTRUM OF FLUORODINITROETHANOL

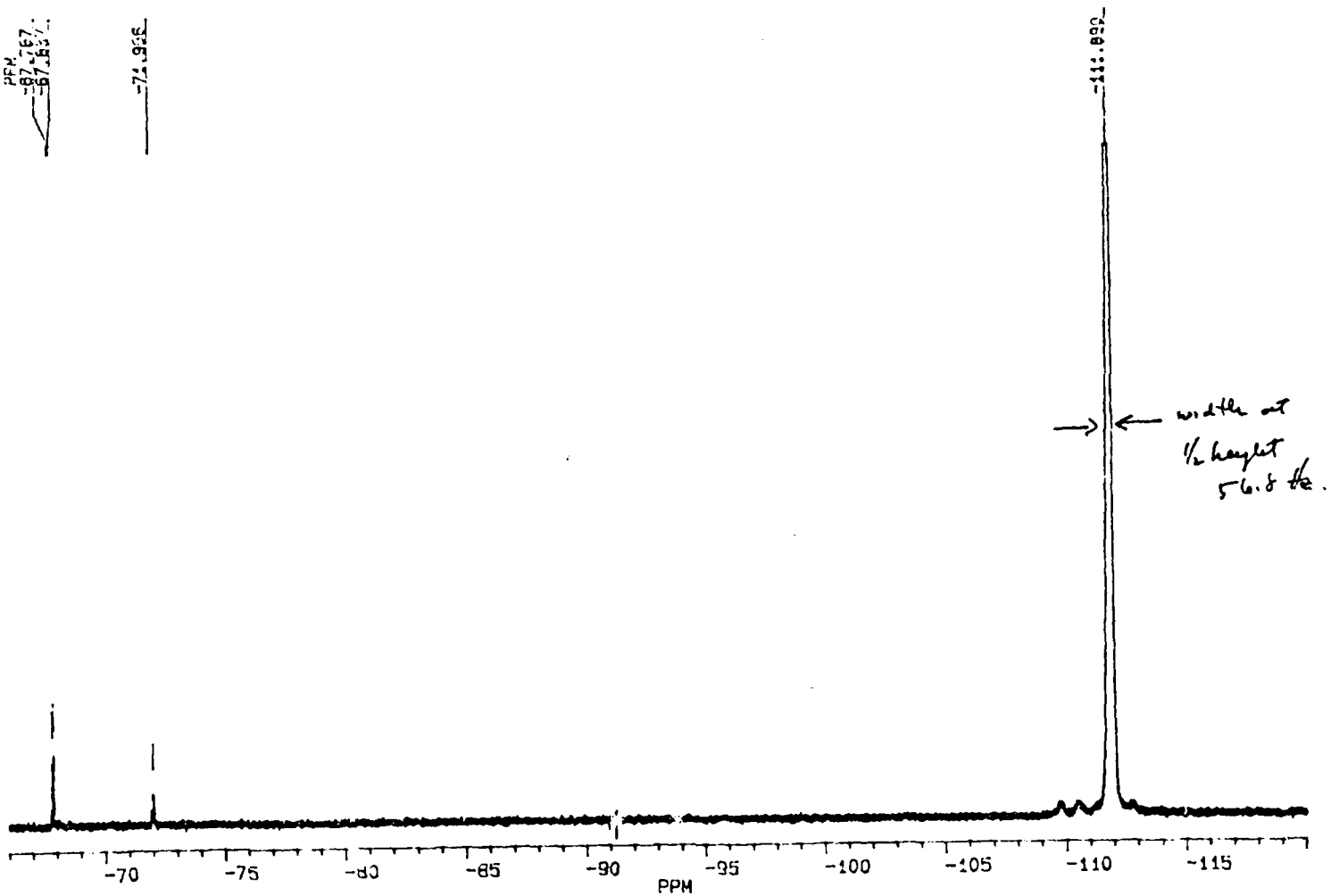


FIGURE 14. ^{19}F NMR SPECTRUM OF FLUORODINITROETHANOL

I	CURSOR	FREQUENCY	PPM	INTENSITY
1	2129	900.186	4.4980	4.128
2	2150	886.622	4.4302	7.023
3	2164	877.608	4.3851	3.426
4	2185	864.079	4.3175	7.560
5	2200	854.396	4.2692	6.974
6	2212	846.332	4.2289	7.583
7	2220	840.923	4.2018	4.194
8	2233	832.782	4.1612	3.048
9	2410	717.634	3.5858	1.785
10	2413	715.807	3.5767	1.880

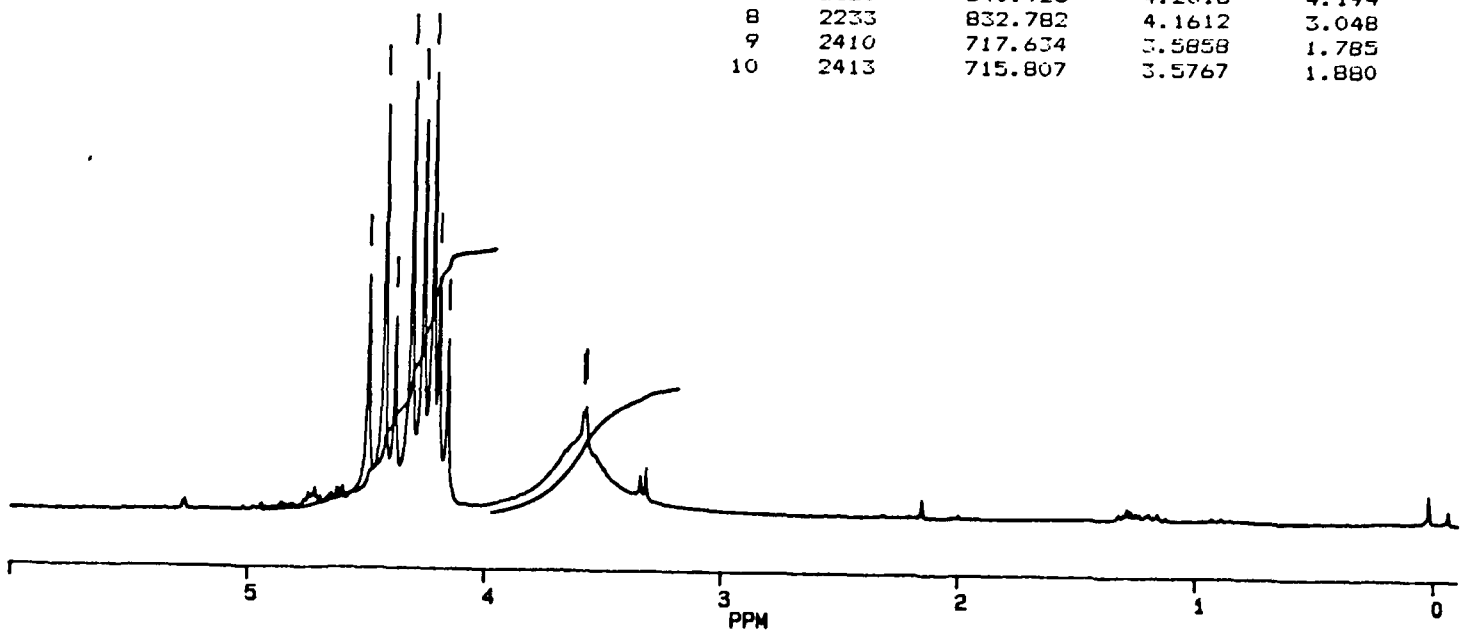


FIGURE 15. ^{1}H NMR SPECTRUM OF CHLOROFLUORONITROETHANOL

#	CURSOR	FREQUENCY	PPM	INTENSITY
1	4611	6183.957	122.8845	1.034
2	5917	3906.185	77.6218	4.770
3	5935	3874.179	76.9858	4.093
4	5954	3841.918	76.3447	5.414
5	6237	3347.966	66.5291	16.573
6	6251	3324.329	66.0594	15.517

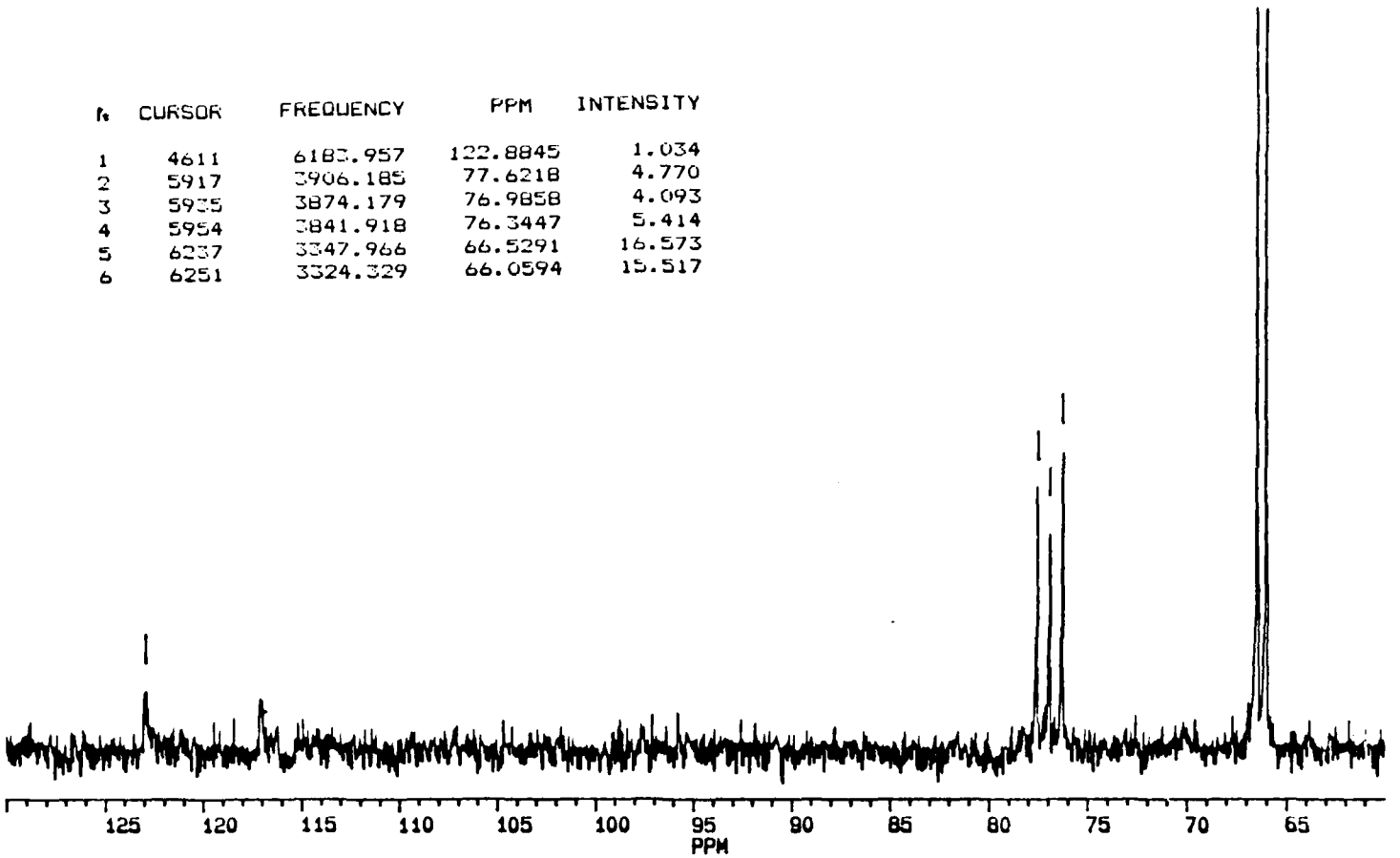


FIGURE 16. ^{13}C NMR SPECTRUM OF CHLOROFLUORONITROETHANOL

#	CURSOR	FREQUENCY	PPM	INTENSITY
1	1824	-18476.538	-98.1163	7.922
2	1828	-18483.393	-98.1527	8.166
3	1837	-18498.672	-98.2339	7.989
4	1841	-18505.530	-98.2703	7.448

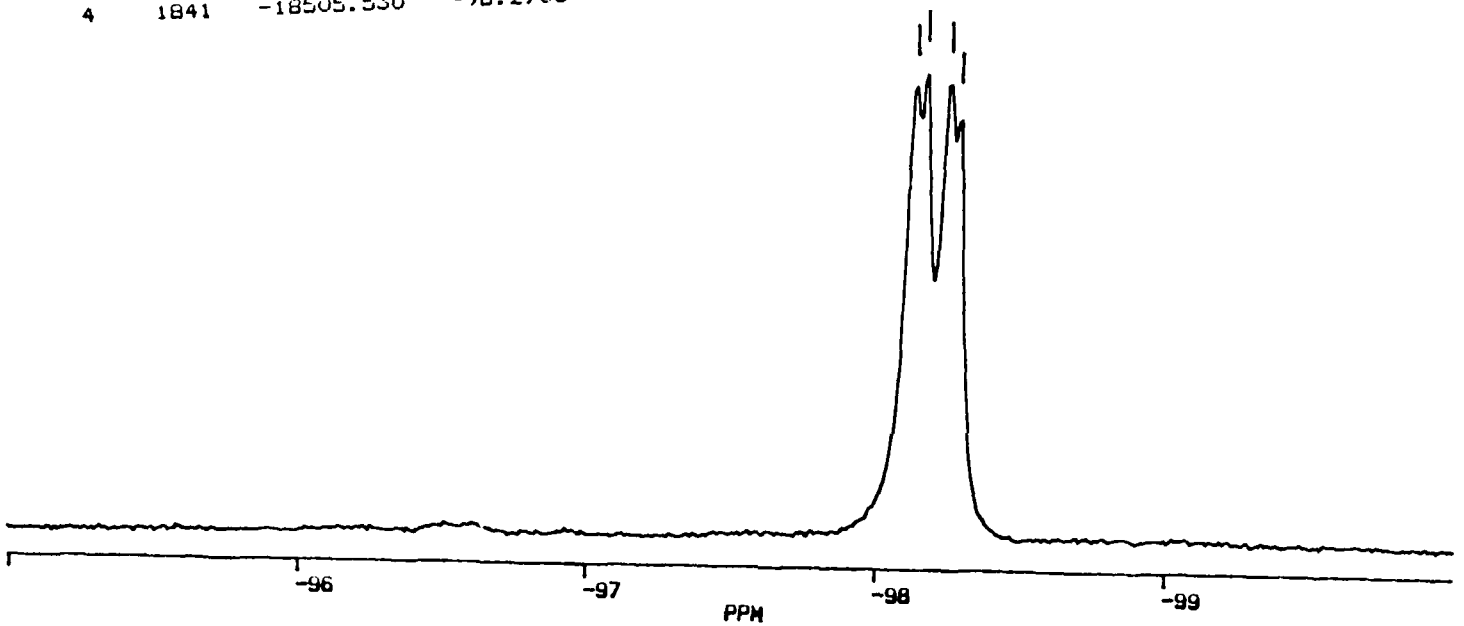


FIGURE 17. ^{19}F NMR SPECTRUM OF CHLOROFLUORONITROETHANOL

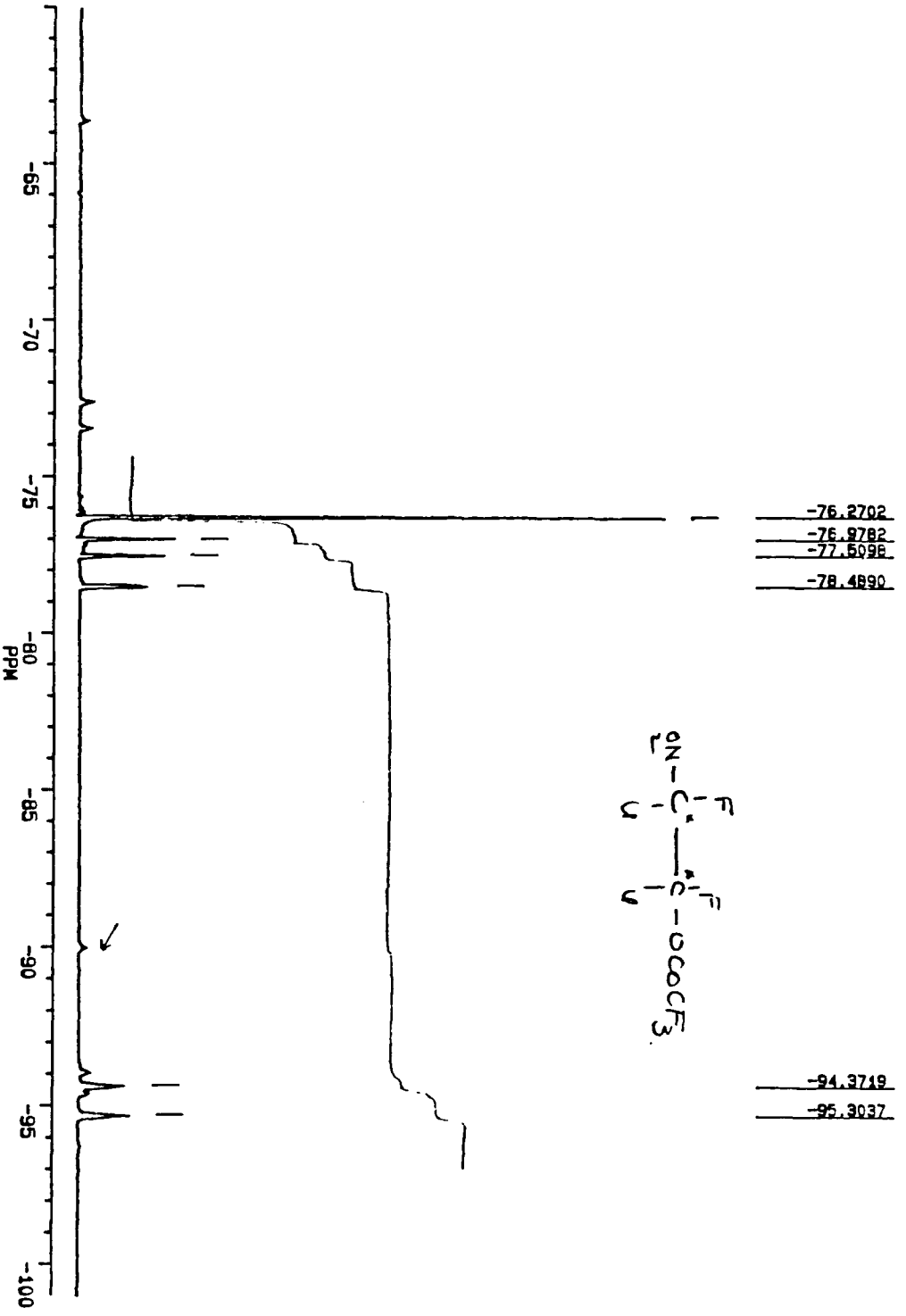


FIGURE 18. ^{19}F NMR SPECTRUM OF 1,2-DICHLORO-1,2-DIFLUORO-2-NITRO-1-ETHANOL TRIFLUOROACETATE

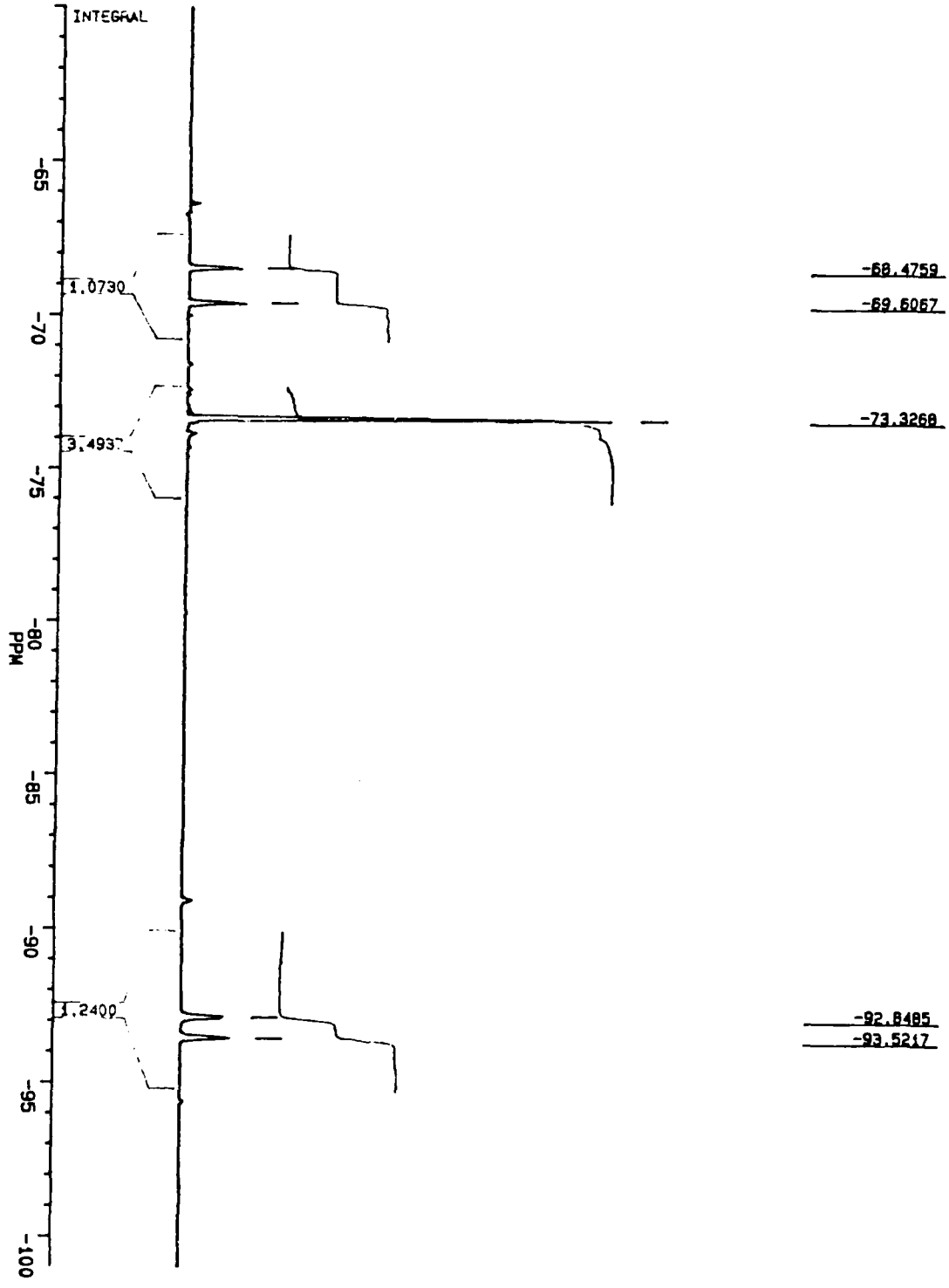


FIGURE 19. ^{19}F NMR SPECTRUM OF 1,2-DICHLORO-1,2-DIFLUORO-2-NITRO-1-ETHANOL TRIFLUOROMETHANESULFONATE