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Fluorinated Esters: Synthesis and Identification

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Reactions of different alcohols with 2-hydroxy - 1-trifluoromethyl -1,2,2-trifluoroethanesulfonic acid sultone $F_3C\overline{CFCF_2OS}O_2$ were studied. Six new esters were prepared: $C_6F_5OC(O)CF(CF_3)SO_2F$, $CH_3CH_2OC(O)CF(CF_3)SO_2F$, $CF_3CH_2OC(O)CF(CF_3)SO_2F$, $(CF_3)_2CHOC(O)CF(CF_3)SO_2F$, $CH_2=CHCH_2OC(O)CF(CF_3)SO_2F$, $(CH_2OC(O)CF(CF_3)SO_2F)_2$ Analytical data, infrared, nmr and mass spectra are presented supporting the proposed structures for these new compounds.

FLUORINATED ESTERS, SYNTHESIS AND IDENTIFICATION

by

JILLA (KHALILOLAHI) SCHAFF

A thesis submitted in partial fulfillment
of the requirements for the degree of

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INTRODUCTION

The interest in monofluorinated esters dates back to 1896 when Swarts(1) prepared the first "published" method for the synthesis of such esters; this involved a fluorine exchange through the use of silver or mercurous fluoride, as shown below:

$$2\ ICH_2CO_2CH_3 + Hg_2F_2 \text{ ------> } 2FCH_2CO_2CH_3 + Hg_2I_2$$

The interest in monofluorocarbon esters began in Belguim and was later picked up in Germany because of their possible use as insecticides. The British government became interested in fluorocarbons in the early 1940's when it was important to look at the toxicity of fluoroesters in case they were used against the Allies in World War II(2). The main work was done by Saunders and some of his work will be discussed later in this portion of the thesis. The interest in fluorinated esters and fluorine compounds in general, in addition to their potential toxic properties, lies in their use as monomers for polymers, oil lubricants and possible blood substitute. It is the purpose of this portion of the thesis to present a summary of several synthetic methods discovered by various investigators. Our research group is interested in fluorinated esters, particularly esters containing the sulfonyl fluoride group (SO_2F). These esters can be converted to fluorinated sulfonic acids which are useful as fuel cell electrolytes, Nafion-like products and strong acids.

While it is possible to present a review of fluoroesters from several different view points it was decided to follow the chronological approach.

In 1911, the following method was introduced(3):

$(o,m,p)\ FC_6H_4CO_2H + CH_3OH \text{ -----> } (o,m,p)\ FC_6H_4CO_2CH_3+H_2O$

As shown in the above equation, an aryl fluorinated ester was obtained through reaction of an aryl carboxylic acid with alcohol. As will be seen later, this method was widely used to synthesize many different esters. At the same time another investigator(4) independently reported the synthesis of the same ester via a different process:

$(o,m,p)FC_6H_4COCl + CH_3OH \text{ ----> } (o,m,p)FC_6H_4CO_2CH_3 + HCl$

This method too was used later for synthesis of several esters.

Swarts(5) used the basic technique of halogen exchange again in 1914 to synthesize the following fluoroesters:

$H_3CCO_2CH_2CH_2Br + AgF \text{ -----> } CH_3CO_2CH_2CH_2F + AgBr$

In 1933, chlorocarbonic acid(6) reacted with thallous fluoride according to the following equations:

$ClCO_2CH_3 + TlF \text{ ----> } FCO_2CH_3 + TlCl$

$ClCO_2CH_2CH_3 + TlF \text{ ----> } FCO_2CH_2CH_3 + TlCl$

Thallous fluoride was also used by Ray(7) for the following equations:

$BrCH_2CO_2CH_3 + TlF \text{ -----> } FCH_2CO_2CH_3 + TlBr$

$BrCH_2CO_2CH_2CH_3$ + TlF -----> $FCH_2CO_2CH_2CH_3$ + TlBr

Hanford(8), working for DuPont patented a technique in 1947 for the preparation of polyfluorocarbonyl compounds. These carbonyl compounds included esters, acids, aldehydes, ketones and acid anhydrides. These compounds were prepared by treating the carbonyl compound with $CF_2=CF_2$ under pressure at 75 - 350°C and in the presence of an initiator such as benzoyl peroxide. Some of the esters which were prepared through this method are:

$H(CF_2CF_2)_nCO_2CH_3$ (where n varies from 1 to 25)

Some of the starting carbonyl compounds were:

$CH_3CH_2CO_2CH_2CH_3$, CH_3CO_2H, $CH_3CH_2CO_2H$, $CH_2(CO_2CH_2CH_3)_2$ $H_3CCO_2CH_2CH_2OCOCH_3$, $CH_2(CH_2)_4CO$, $CH_3CH_2COCH_3$, $(CH_3C(O))_2O$ and $H_3CCO_2CH_2CH_2OCOCH_3$

The chemical equation through which these esters are prepared may be shown as:

6 $CF_2=CF_2$ + HCO_2CH_3 + Bz_2O_2 -----> $H(CF_2CF_2)_6\ CO_2CH_3$

These esters were reported to be nonflammable, noncorrosive and nontoxic. They also have high thermal and chemical stability. They are reported to be useful as lubricants and as solvents and reaction media.

In the same year, Henne reported the synthesis of aceto fluoroesters through Claisen condensation of a fluorinated ester with another ester or a ketone to synthesize ester such as(9):

$CF_3COCH_2CO_2CH_2CH_3$, $CHF_2COCH_2CO_2CH_2CH_3$

All condensations were performed in ether using sodium ethoxide which was freshly prepared by treating one equivalent of absolute ethanol with one equivalent of finely dispersed sodium; one equivalent of dry fluorinated ester was then added. To the product of this reaction, the second ester was added and the mixture was refluxed for about fifty hours. This was then followed by a series of steps taken to isolate a product. Although the author does not specify the specific reagents used for the synthesis of esters shown above, the following equations represents the possible reagents which <u>may</u> have been used:

$$CF_3CO_2CH_2CH_3 \quad \xrightarrow[\text{2. } CH_3CO_2CH_2CH_3]{\text{1. } NaOCH_2CH_3} \quad CF_3COCH_2CO_2CH_2CH_3$$

$$CHF_2CO_2CH_2CH_3 \quad \xrightarrow[\text{2. } CH_3CO_2CH_2CH_3]{\text{1. } NaOCH_2CH_3} \quad CHF_2COCH_2CO_2CH_2CH_3$$

Also in 1947, Henne(10) reported the synthesis of $CH_3CF_2CH_2CO_2C_2H_5$ and $CH_3CH_2CF_2CO_2C_2H_5$. Tetrolic acid $CH_3C{\equiv}CCO_2H$ was esterified to its ethyl ester derivative. To the ester was added hydrogen fluoride (in a steel bomb). Both of the two isomers were obtained:

$$H_3CC{\equiv}CCO_2CH_2CH_3 + 2HF \xrightarrow{-70^{\circ}C} CH_3CF_2CH_2CO_2CH_2CH_3 + CH_3CH_2CF_2CO_2CH_2CH_3$$

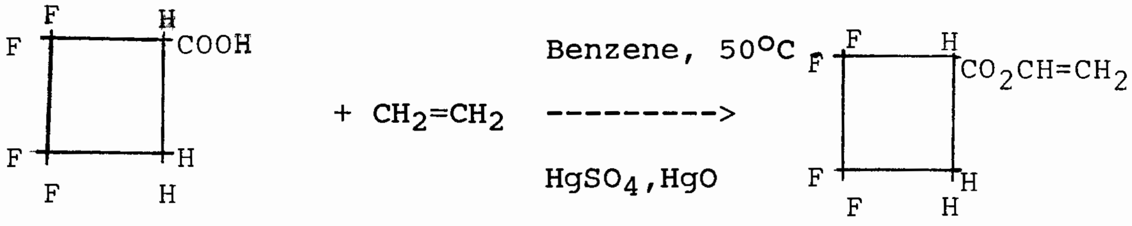
A year later Miller et al.(11) reported on the vapor phase fluorination of acetyl fluorides by reacting equivalent amounts of fluorine and acetyl fluoride, both diluted with nitrogen. This mixture was passed into a steam-jacketed copper reactor which was packed with ethyl alcohol. The esters formed were fractionally distilled, the ratio between the isolated ethyl fluoroacetate and ethyl difluoroacetate was 6:1 and trace amounts of ethyl trifluoroacetate was formed:

$$CH_3COF + F_2 \xrightarrow[NaF]{Cu} [CF_3COF + CH_2FCOF + CHF_2COF] = A$$

$$A + CH_3CH_2OH \longrightarrow CF_3CO_2CH_2CH_3,\ CH_2FCO_2CH_2CH_3,\ CHF_2CO_2CH_2CH_3$$

Ratio: Trace : 6 : 1

The Imperial Chemical Industries Ltd of Britain(12) reported synthesis of a new class of polymerizable fluorine containing vinyl esters. These esters were prepared by treating C_2H_2 with a fluorine containing saturated four carbon cyclic carboxylic acids which have at least 2F atoms attached directly to the ring. Example of such acids are: tetrafluoro, tetrafluoromonochloro, trifluoromonochloro carboxylic acids. An example of such reaction:



The above reaction was done in the presence of hydroquinone, and formation of a dark liquid is reported which was then filtered and distilled at reduced pressure.

Saunders and Stacy(13) published in 1948 the result of a study that they had done on the toxicity of fluorinated esters. They reported synthesis of several fluorinated esters as shown in the following equations:

$CH_2ClCO_2H + CH_3CH_2OH \xrightarrow{\text{NaF}} CH_2FCO_2CH_2CH_3 + NaCl + H_2O$

$CH_2ClCO_2H + CH_3CH_2CH_2OH \xrightarrow{\text{NaF}} CH_2FCO_2CH_2CH_2CH_3 + NaCl + H_2O$

$CH_2ClCO_2H + CH_3CH(OH)CH_3 \xrightarrow{\text{NaF}} CH_2FCO_2CH(CH_3)_2 + NaCl + H_2O$

(All the reactions listed above were carried out in a rotating autoclave). Also

$(CH_3)_2C(Br)CO_2CH_2CH_3 + AgF \dashrightarrow (CH_3)_2CFCO_2CH_2CH_3 + AgBr$

$CH_3CBrHCO_2CH_2CH_3 + AgF \dashrightarrow CH_3CFHCO_2CH_2CH_3 + AgBr$

$C_6H_5OH + CH_2FCOCl \xrightarrow{\text{Pyridine}} CH_2FCO_2C_6H_5$

$ClCO_2CH_2CH_3 + KF \dashrightarrow FCO_2CH_2CH_3 + KCl$

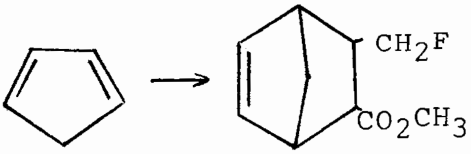
In continuation of their studies, Saunders(14-17) et al. studied the toxicity of other fluorinated esters, which were prepared as shown below.

1. (15) $CH_2FCOCl+CH_2FCH_2OH \dashrightarrow CH_2FCO_2CH_2CH_2F$
2. $CH_2ClCOCl+CH_2FCH_2OH \dashrightarrow ClCH_2CO_2CH_2CH_2F$
3. $CH_2FCOCl+H_2C = CHCH_2OH \dashrightarrow CH_2FCO_2CH_2CH = CH_2$
4. $H_3CIHC(CH_2)_2CO_2CH_2CH_3+AgF \dashrightarrow H_3CFCH(CH_2)_2CO_2CH_2CH_3+AgI$
5. (16) $BrCH_2(CH_2)_4CO_2CH_2CH_3+AgF \dashrightarrow FCH_2(CH_2)_4CO_2CH_2CH_3+AgBr$
6. (16) $BrCH_2(CH_2)_4CO_2CH_2CH_2F+AgF \dashrightarrow FCH_2(CH_2)_4CO_2CH_2CH_2F+AgBr$
7. (16) $ICH_2(CH_2)_6CO_2CH_2CH_3+AgF \dashrightarrow FCH_2(CH_2)_6CO_2CH_2CH_3+AgI$
8. (17) $BrCH_2C(CH_3)_2CH_2CO_2CH_2CH_3+AgF \dashrightarrow$

   $FCH_2(CH_3)_2CH_2CO_2CH_2CH_3+AgBr$
9. (16) $ICH_2(CH_2)_6CO_2CH_2CH_2F+AgF \dashrightarrow FCH_2(CH_2)_6CO_2CH_2CH_2F+AgI$
10. (16) $BrCH_2(CH_2)_8CO_2CH_2CH_3+AgF \dashrightarrow FCH_2(CH_2)_8CO_2CH_2CH_3+AgBr$
11. (16) $BrCH_2(CH_2)_8CO_2CH_2CH_2F+AgF \dashrightarrow FCH_2(CH_2)_8CO_2CH_2CH_2F+AgBr$
12. (16) $BrCH_2(CH_2)_9CO_2CH_2CH_3+AgF \dashrightarrow FCH_2(CH_2)_9CO_2CH_2CH_3+AgBr$
13. (16) $BrCH_2(CH_2)_{10}CO_2CH_2CH_3+AgF \dashrightarrow FCH_2(CH_2)_{10}CO2CH_2CH_3+AgBr$

14. (17)$BrCH_2CH = CHCO_2Me + AgF$ ---------> $FCH_2CH = CHCO_2CH_3$

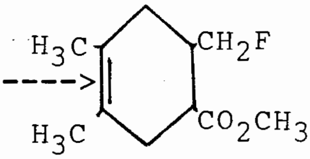
15. (17)$FCH_2CH = CHCO_2CH_3$ +



(B)

B was hydrogenated at room temperature and at atmospheric pressure in the presence of palladium as catalyst which yielded the reduced form of B.

16. (17)$FCH_2CH=CHCO_2CH_3+CH_2=C(CH_3)C(CH_3)=CH_2$ ----->



(C)

Hydrogenation was carried out according to the procedure described previously, to make the reduced form of C.

In December 1951 Haszeldine reported the mechanism involved in the synthesis of esters such as trifluoromethyl trifluoroacetate and heptafluoropropyl heptafluorobutyrate (note that unlike the esters discussed thus far these esters are perfluorinated esters) and according to Haszeldine were the first completely fluorinated esters to be reported(18). According to his studies the esters were believed to arise by a free radical mechanism such as the following:

$CF_3CO_2Ag + I_2$ -----------> $CF_3CO_2I + AgI$

$CF_3CO_2I \xrightarrow{\text{heat}} CF_3COO + I$

$CF_3CO_2I \xrightarrow{\text{heat}} CF_3 + CO_2 + I$

$CF_3COO + CF_3$ ------------> $CF_3CO_2CF_3$

Listed below are other esters along with references which were prepared through similar methods discussed so far:

1.(19)$FCH_2CH_2OH + ClCH_2COCl \xrightarrow{100^oC} FCH_2CH_2OCOCH_2Cl + HCl$

2. $FCH_2CH_2OH + BrCH_2COBr \xrightarrow[3\ hrs]{100°C} FCH_2CH_2OCOCH_2Br + HBr$

3. $FCH_2CH_2OH + ICH_2COCl \longrightarrow CFH_2CH_2OCOCH_2I + HCl$

4. $FCH_2CH_2OH + CH_3COCl \longrightarrow CFH_2CH_2OCOCH_3 + HCl$

5. $ICH_2COCl + FCH_2CH(CH_3)OH \longrightarrow ICH_2CO_2CH(CH_3)CH_2F + HI$

6. $ICH_2CO_2CH(CH_3)CH_2F + HgF_2 \xrightarrow{KF} FCH_2CO_2CH(CH_2F)CH_3 + HgIF$

7. $ICH_2COCl + (FCH_2)_2CHOH \xrightarrow{40-50°C} (FCH_2)_2CHOCOCH_2I + HCl$

8. $2(FCH_2)_2CHOCOCH_2I + HgF_2 \xrightarrow{KF} 2(FCH_2)_2CHOCOCH_2F + HgI_2$

9. (20) $CF_3CO_2H + CH_3CH_2CH_2CH(CH_3)CH_2OH \xrightarrow{CH_3Cl}$

$CF_3CO_2CH_2CH(CH_3)CH_2CH_2CH_3$

10. $C_3F_7CO_2H + EtOH \longrightarrow C_3F_7CO_2CH_2CH_3$

11. (21) $C_3F_7CHO + (CH_2CHCO)_2O \longrightarrow C_3F_7CH(O_2CCHCH_2)_2$

reaction conditions:

1. H_2SO_4
2. Let stand overnight at 10°C
3. Wash with H_2O + 10% $NaHCO_3$
4. Distill in presence of $Cu(OAc)_2$

12. $C_3F_7CH(OH)_2+Ac_2O \xrightarrow{Pyridine} C_3F_7CH(OCOCH_3)_2+C_3F_7CH_2OAc$

13. (22) $P_2O_5 + C_3F_7CO_2H + HgO + C_2H_2 \xrightarrow{H_2SO_4} C_3F_7CO_2CHCH_2$

0°C, 12 hr.

14. $C_4F_9CO_2H + HgO + P_2O_5 + C_2H_2 \longrightarrow C_4F_9CO_2CHCH_2$

Other esters prepared through the same procedures are:

$C_5F_{11}CO_2CHCH_2$, $C_9F_{19}CO_2CHCH_2$, $C_6F_{11}CO_2CHCH_2$

15. (23) $C_3F_7CH_2OH+C_3F_7COCl \xrightarrow[2\ days]{reflux\ for} C_3F_7CO_2CH_2C_3F_7+HCl$

The mixture was washed with 10% K_2CO_3 and dried with $MgSO_4$, and the product was obtained through fractionation.

16. $C_7F_{15}COCl + C_3F_7CH_2OH \longrightarrow C_7F_{15}CO_2CH_2C_3F_7 + HCl$

17. $CF_3CH_2OH + C_3F_7COCl \xrightarrow{\text{reflux}} C_3F_7CO_2CH_2CF_3 + HCl$

18. $2C_3F_7COCl+CF_2(CF_2CH_2OH)_2 \xrightarrow{150^{\circ}C\quad 10\%K_2CO_3}$

$(C_3F_7CO_2CH_2CF_2)_2CF_2$

19. $(CF_2CF_2CH_2OH)_2 + 2C_3F_7COCl \longrightarrow (C_3F_7CO_2CH_2CF_2CF_2)_2$

20. $OC(CF_2)_3COO+C_3F_7CH_2OH \xrightarrow[\text{2 days}]{180^{\circ}C} (C_3F_7CH_2O_2CCF_2)_2CF_2$

21. $C_3F_7CH_2O_2C(CF_2)_3CO_2H+PCl_5\ (10\%) \longrightarrow$

$C_3F_7CH_2OOC(CF_2)_3C(O)Cl$

22. $C_3F_7CH_2O_2C(CF_2)_3COCl \xrightarrow{C_3F_7CH_2OH}$

$C_3F_7CH_2OOC(CF_2)_3CO_2CH_2C_3F_7$

23(24) $2C_3F_7CO_2Ag+I(CH_2)_6I \xrightarrow[\text{reflux, 2 hrs}]{CCl_2FCClF_2} [C_3F_7CO_2(CH_2)_3]_2$

$(C_3F_7CO_2CH_2)_2CH_2$ and $[C_3F_7CO_2(CH_2)_5]_2$ were prepared by the same method.

24. $2C_3F_7CO_2H+HO(CH_2)_5OH \xrightarrow{PhCH_3+NaHSO_4}$

$[C_3F_7CO_2(CH_2)_2]_2CH_2$

$[C_3F_7CO_2(CH_2)_2]_2$ and $[CF_3CO_2(CH_2)_2]_2CH_2$ were prepared through the same technique.

25. $C_7F_{15}COCl+HO(CH_2)_5OH \xrightarrow{\text{reflux 6 hrs}} [C_7F_{15}CO_2(CH_2)_2]_2CH_2$

$[C_5F_{11}CO_2(CH_2)_2]_2CH_2$ and $[C_9F_{19}CO_2(CH_2)_2]_2CH_2$ were prepared through the same way.

26. $[(CF_2)_2CO_2H]_2 + t\text{-}BuOH \xrightarrow[NaHSO_4]{C_6H_6} [t\text{-}BuO_2C(CF_2)_2]_2$

This method was used to prepare the following esters:

$[RO_2C(CF_2)_2]_2$ where R is:

C_4H_9, sec-C_4H_9, C_6H_{13}, $(C_4H_9)(C_2H_5)CHCH_2$

27.(25) $C_3F_7CO_2H + CH_3OH \xrightarrow{H_2SO_4} C_3F_7CO_2CH_3$

$2C_3F_7CH_2OH + (CH_2CH_2COCl)_2 \xrightarrow[\text{for 2 days}]{\text{reflux at } 18^{\circ}} (CH_2CH_2CO_2CH_2C_3F_7)_2$

The following esters were prepared through the same method:

$(CH_2CH_2CO_2CH_2CF_3)_2$, $CH_2(CH_2CH_2CO_2CH_2CH_2C_3F_7)_2$, $[(CH_2)_3CO_2CH_2C_3F_7]_2$, $CH_2[(CH_2)_3CO_2CH_2C_3F_7]_2$, $[(CH_2)_4CO_2CH_2C_3F_7]_2$, $[(CH_2)_2CO_2CH(C_2H_5)C_3F_7]_2$,$C_3F_7CO_2CH_2CF_3$

28.(26) $C_2F_5CO_2H + CH_3OH \xrightarrow{H_2SO_4} C_2F_5CO_2CH_3$

29. $C_2F_5CO_2H + CH_3CH_2OH \xrightarrow{H_2SO_4} C_2F_5CO_2CH_2CH_3$

30. $C_2F_5CO_2H + \text{iso-PrOH} \xrightarrow{H_2SO_4} C_2F_5CO_2CH(CH_3)_2$

31.(27) $CH_3(CH_2)_3CF_2(CH_2)_4COOH + CH_3CH_2OH \xrightarrow{\text{Bezene}} CH_3(CH_2)_3CF_2(CH_2)_4COOCH_2CH_3$

32.(28) $CH_3(CH_2)_3CH_2OH + CH_2FCO_2CH_2CH_2CH_3 \xrightarrow{H_2SO_4} CH_2FCO_2CH_2(CH_2)_3CH_3 + CH_3(CH_2)_2OH$

33.$CH_3(CH_2)_4CH_2OH + CH_2FCO_2CH_2CH_3 \xrightarrow{H_2SO_4} CH_2FCO_2CH_2(CH_2)_4CH_3$

34.$CH_3(CH_2)_6CH_2OH + CH_2FCO_2CH_2CH_3 \xrightarrow{H_2SO_4} CH_2FCO_2CH_2(CH_2)_6CH_3$

35.$CH_3(CH_2)_2CH_2OH + CH_2FCO_2CH_2CH_3 \xrightarrow{H_2SO_4} CH_2FCO_2CH_2(CH_2)_2CH_3$

36.$(CH_3)_3CHOH + CH_2FCO_2CH_2CH_3 \xrightarrow{H_2SO_4} CH_2FCO_2CH(CH_3)_2$

A series of fluoroformate esters were prepared by Jensen(29)et al. These esters were then heated to eliminate carbon dioxide and form the corresponding fluorinated alkyl compounds. The fluoroformate esters were:

FCO_2R, where R is one of the following:

CH_3CH_2, $(CH_3)_2CH$, $CH_3CH_2CH(CH_3)$, C_6H_{11}, C_5H_9

The general equation for preparation of these esters was:

$$ClCO_2C_2H_5 + TlF \longrightarrow FCO_2C_2H_5 + TlCl$$

A series of vinyl esters were reported by Bauery(30) et al. These esters are listed below, also below is an example of the equation which shows how they were prepared. The carboxylic acids were first mixed with red mercuric oxide. The reaction mixture was then heated to 30°C after addition of the corresponding anhydride and acetylene:

$$CF_3CF_2CF_2CO_2H \longrightarrow CF_3CF_2CF_2CO_2CH{=}CH_2$$

Reaction conditions:

1. HgO
2. $[CF_3(CF_2)_2CO]_2O$
3. acetylene
4. 30°C

The product was finally obtained through distillation. Unsaturated esters which were prepared through this method are listed in Table I, along with the corresponding carboxylic acid.

TABLE I

SYNTHESIS OF UNSATURATED ESTERS-PART I

ester	carboxylic acid
$CF_3CO_2CH = CH_2$	CF_3CO_2H
$CF_3CF_2CO_2CH = CH_2$	$CF_3CF_2CO_2H$
$CF_3(CF_2)_2CO_2CH = CH_2$	$CF_3(CF_2)_2CO_2H$
$CF_3(CF_2)_3CO_2CH = CH_2$	$CF_3(CF_2)_3CO_2H$

$CF_3(CF_2)_4CO_2CH = CH_2$	$CH_3(CF_2)_4CO_2H$
$CF_3(CF_2)_8CO_2CH = CH_2$	$CF_3(CF_2)_8CO_2H$
$C_6F_{11}CO_2CH = CH_2$	$C_6F_{11}CO_2H$

Esters of dicarboxylic acids were prepared by Shahask(31) in 1959; diethyl difluoromalonate was synthesized as shown below:

$$CH_3CH_2OOCCBr_2COOCH_2CH_3 \xrightarrow[2NaF]{acetamide} CH_3CH_2OOCCF_2COOCH_2CH_3$$

Synthesis of pentafluorophenyl benzoate was done by Haszeldine et al.(32) as shown below:

$$C_6F_5OH + C_6H_6COCl \xrightarrow{Pyridine} C_6H_6CO_2C_6F_5$$

Cohen(33), et al. reported in 1961, the synthesis of the following esters:

$$CFH_2CO_2CH_2CH_3 + CH_3COCH_2CH_3 \xrightarrow[0°C, H_2SO_4]{Ether}$$

$$CH_3CH_2C(OH)(CH_3)CFH_2C(O)OCH_2CH_3 + CFH_2C(O)CH_2C(O)CH_2CH_3$$

Analogously, ethyl-2-methyl-2-hydroxyl-3-fluorobutyrate was prepared through reaction of ethyl fluoroacetate with acetone.

In 1964, McLaughlin et al.(34) were able to synthesize fluoro-β-keto esters through the Claisen condensation of two different esters. Ethyl-1,1,1-trifluoroacetoacetate was obtained in a condenser charged with sodium wire. A mixture of ethyl trifluoroacetate and ethyl acetate was rapidly added to the sodium wire and produced an exothermic reaction; after cooling the reaction mixture ether was added and refluxed for 16 hours. Evaporation under vacuum left behind a dark brown tar which was then washed in ether and 15% sulfuric acid; the final product ethyl 1,1,1-trifluoro-3-methyl acetoacetate was obtained through distillation. Other esters obtained through this method are: ethyl 1,1,1-trifluoro-3-methylacetoacetate which was obtained through the reaction of ethyl trifluoroacetate with ethyl propionate through the same procedure listed above. Ethyl 4,4,5,5,6,6,6-heptafluorobutyrylacetate was obtained through reaction of ethyl heptafluorobutyrate and ethyl acetate.

In 1965, Inukai(35) reported the synthesis of a series of esters of trifluoroacetate, which were prepared by mixing trifluoroacetic anhydride with phenol derivatives in the presence of benzene. The product was obtained after drying the solution. The following list contains the esters and the phenyl compounds from which the corresponding esters were prepared:

Ester	Phenol Compound
P-nitrophenyl trifluoroacetate	*p*-nitrophenol
Phenyl trifluoroacetate	phenol
P-chlorophenyl trifluoroacetate	*p*-chlorophenol
2,4,5-trichlorophenyl trifluoroacetate	2,4,5-trichlorophenol
Pentachlorophenyl trifluoroacetate	Pentachlorophenol
P-methoxyphenyl trifluoroacetate	*p*-methoxyphenol

In the same year, Ellingboe et al.(36) reported a process for producing fluorine containing organic compounds in which carbonyl fluoride COF_2 is allowed to react with carbonyl compounds such as ketones, aldehydes, esters etc. The result was an organic compound containing CF_2 groups. However, esters of fluoroformic acid were produced as intermediate products of reactions of aldehydes and ketones with carbonyl fluoride and have the general formula $R'(R'')CFO-C(O)F$ where R' and R" preferably contain up to 17 carbons and may be hydrogen, alkyl, aryl, haloalkyl, haloaryl etc. Example of such reaction is:

$$\underbrace{CH_2(CH_2)_4CO} + COF_2 \xrightarrow{\text{dimethylformamide}} C_6H_{10}FO_2CF$$

The following list shows additional esters along with the carbonyl compounds from which these esters were formed:

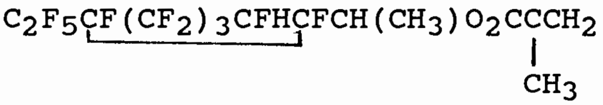
Ester	Carbonyl Compound
α-fluorocyclohexyl fluoroformate	$C_6H_{10}O$
α-fluoroethyl fluoroformate	CH_3COH
2-fluoro-2-propyl fluoroformate	CH_3COCH_3
α-fluorocyclopentyl fluoroformate	C_5H_8O
α-fluorododecyl fluoroformate	$C_{10}H_{18}O$
α-fluorobenzyl fluoroformate	C_6H_5COH
α-fluoro- -phenylethyl fluoroformate	$C_6H_5C(O)CH_3$
α-fluorooctadecyl fluoroformate	$C_{18}H_{35}OH$
α-diphenyl fluoromethylfluoroformate	$(C_6H_5)_2CO$
2-fluoro-2-butyl fluoroformate	$CH_3COCH_2CH_3$

In 1966, Dow Corning Corporation(38) reported the synthesis of esters which were obtained through the reaction of alcohols listed below with different carboxylic acids.

The esters shown below were obtained from reaction of an alcohol with methacrylic acid in the presence of trifluoroacetic anhydride:

Alcohol Product

$C_2F_5\underline{CF(CF_2)_3CFHC}FCH(CH_3)OH$,



$C_2F_5\underline{CF(CF_2)_3CFHC}FCH(CH_3)O_2C\underset{CH_3}{C}CH_2$

$\underline{CF_2(CF_2)_3CFHC}FCH(C_2H_5)OH$, $\underline{CF_2(CF_2)_3CFHC}FCH(C_2H_5)O_2CC(CH_3)CH_2$

$CF_3\underline{CF(CFH)_3CFHC}FCH_2OH$, $CF_3\underline{CF(CFH)_3CFHC}FCH_2O_2CC(CH_3)CH_2$

The esters shown below were the results of esterification of the following alcohols with acrylic acid:

Alcohol Product

$\underline{CF_2CF_2CHFC}FC(CH_3)_2OH$, $\underline{CF_2CF_2CHFC}FC(CH_3)_2O_2CCH{=}CH_2$

$C_9F_{19}\underline{CFCF_2CHFC}FCH(C_6H_{13})OH$, $C_9F_{19}\underline{CFCF_2CHFC}FCH(C_6H_{13})O_2CCH{=}CH_2$

$CF_3\underline{CH(CF_2)_2CFHC}FCH(CH(CH_3)CH_2CH_3)OH$,

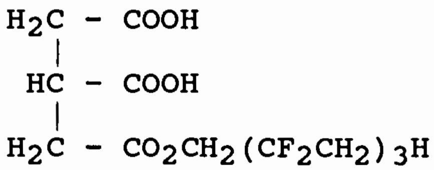
$CF_3\underline{CH(CF_2)_2CFHC}FCH(CH(CH_3)CH_2CH_3)O_2CCH{=}CH_2$

The esters reported above were important because of their ability to polymerize. Their polymers are plastic or elastomer materials possessing "unusually good chemical and thermal stability".

Metro(37) patented a procedure for synthesis of esters of fluoroalcohols and aliphatic carboxylic acids. These esters are important as they can be used as lubricating oil. They include mono and di-esters of C_6 to C_8 alkanetrioic acid and mono-, di and tri-esters of C_6 to C_8 alkanetetraoic acids. The preferred acids are 1,2,3-tricarboxy propane; 1,2,4-tricarboxy butane and 1,2,3,4-tetracarboxy butane. Fluorinated alcohols used have 3 to 20, preferably 5 to 13, carbon atoms and with the formula $X(CF_2)_nCH_2OH$ where X is either a hydrogen or fluorine and n is an integer from 2-19, examples of such alcohols are:

tetrafluoro 1-propanol ($CHF_2CF_2CH_2OH$), and pentafluoro 1-propanol $CF_3CF_2CH_2OH$.

The following is an example of one of the esters prepared:



$$\begin{array}{l} H_2C - COOH \\ \quad | \\ \ HC - COOH \\ \quad | \\ H_2C - CO_2CH_2(CF_2CH_2)_3H \end{array}$$

(D)

which was prepared by:

$$H(CF_2)_6CH_2OH + (CH_2)_3(COOH)_3 \xrightarrow{\text{Heptane}} \quad (D)$$

A triester may be obtained for example by esterifying one mole of 1,2,3,4-tetracarboxy butane with three moles of alcohol ($CF_3CF_2CH_2OH$) through the procedure shown above.

In 1970(39), Toren et al. reported synthesis of $(CF_3)_3CCO_2CH_3$ and $(CF_3)_3CCO_2CCF_3$ through the following reaction:

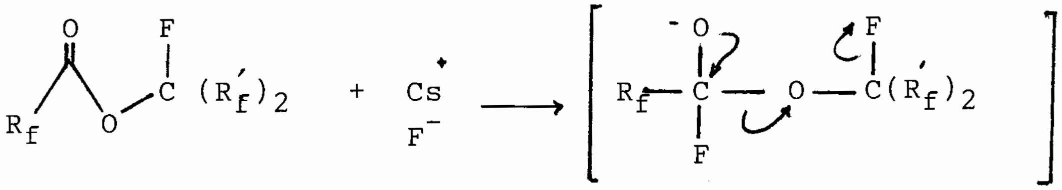
1. $(CF_3)_3COH + (CH_3CO)_2O \xrightarrow{\text{2-methyl Pyridine}} CH_3CO_2C(CF_3)_3$
2. $(CF_3)_3COH + (CF_3CO)_2O \xrightarrow{\text{2-methyl Pyridine}} CF_3CO_2C(CF_3)_3$

The reaction was allowed to proceed at room temperature for 48 hours, with the product being obtained through distillation.

In 1972, Shreeve et al.(40) reported isolation of $CF_3CO_2C(NF_2)_2CF_3$ during a study of reaction of HNF_2 - KF adduct with perfluoroacyl fluorides at -78°C. And when the reaction temperature was lowered to -105°C, $CF_3CO_2C_2F_5$ (the dimer of CF_3COF) was obtained. These esters once isolated were reported to be stable but in the presence of alkali metal fluorides would undergo decomposition at temperatures of -78°C or above.

In continuation of their studies, Shreeve et al.(41) reported synthesis of fluorinated esters of the type $R_fCO_2CF(CF_3)_2$ which contain fluorine on the alkoxy-carbon. These were reported to be unstable in the presence of fluoride ion at -78°C or above. However esters which contain substituents other than fluorine at this position are very stable in the presence of fluoride ion even at higher temperatures. This was explained as follows:

R_f is an electronegative group and as a result enhances the electrophilicity of the carbonyl carbon atom which promotes the addition to the carbonyl double bond. The following mechanism shows how this happens:



(A)

Complex A ------→ $R_f\overset{O}{\overset{\|}{C}}F + (R_f)_2CO + CsF$

According to the diagram above, the nucleophilicity of fluoride ion allows it to attack at the carbon of the carbonyl group, which gives rise to complex A. Complex A then undergoes further rearrangement to form acyl fluoride, ketone and CsF.

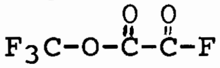
Since F has a very strong inductive effect, its departure as a F^-, will be favored. The inductive effects of CF_3 and particularly of H and CH_3 are very much less than that of fluorine, therefore they are not very good leaving groups. The esters which were prepared in this study were:

$CF_3CO_2R_f$ where R_f is

$(CF_3)_3C$, $C_2F_5(CF_3)_2C$, $(CF_3)_2(CH_3)C$ and $(CF_3)_2CH$

These esters were prepared from reaction of the corresponding alcohols (e.g. CF_3CH_2OH) with trifluoroacetyl fluoride in the presence of CsF.

In 1975, another group(42), reported a method for the synthesis of aliphatic fluorinated esters some of which were reported by Shreeve(41). In their studies, esters were prepared with reaction of $KOC(CF_3)_3$ with acyl fluorides. This provides a "convenient method" for the synthesis of these esters which are listed as follows:

Reactant	Product
COF_2	$FCO_2C(CF_3)_3$
CF_3COF	$F_3CCO_2C(CF_3)_3$
CH_3COF	$H_3CCO_2C(CF_3)_3$
 $F_3C-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-F$	$CF_3COOCO_2C(CF_3)_3$

In 1978, another(43) method was introduced which involved reaction of a fluorinated acyl hypochlorite with a fluorine containing alkene as shown below:

$$R_fCO_2Cl + CF_2 = CFCF_3 \xrightarrow{-78^{o}C} R_fCO_2CF_2CFClCF_3$$

$$R_f = CF_3,\ ClCF_2$$

This procedure was used a year later by DesMarteau(44) to synthesize the esters shown in Table II.

TABLE II

SYNTHESIS OF FLUOROESTERS-PART II

	R_f	Olefin	Ester
1.	CF_3	$CF_2 = CF_2$	$CF_3CO_2(CF_2)_2Cl$
2.	CF_3	$CF_2 = CH_2$	$CF_3CO_2CF_2CH_2Cl$
3.	CF_3	$CF_2 = CFCl$	$CF_3CO_2CFClCF_2Cl$
4.	CF_3	$CF_2 = CCl_2$	$CF_3CO_2CCl_2CF_2Cl$
5.	CF_3	$CH_2 = CH_2$	$CF_3CO_2CH_2CH_2Cl$
6.	CF_3	<u>cis</u> CFH = CFH	erythro$CF_3CO_2CFHCFHCl$
7.	CF_3	<u>trans</u> CFH = CFH	threo$CF_3CO_2CFHCFHCl$
8.	C_2F_5	$CF_2 = CF_2$	$C_2F_5CO_2CF_2CF_2Cl$
9.	C_2F_5	$CF_2 = CH_2$	$C_2F_5CO_2CF_2CH_2Cl$
10.	n-C_3F_7	$CF_2 = CF_2$	n-$C_3F_7CO_2CF_2CF_2Cl$
11.	n-C_3F_7	$CF_2 = CH_2$	n-$C_3F_7CO_2CF_2CH_2Cl$
12.	$ClCF_2$	$CF_2 = CF_2$	$ClCF_2CO_2CF_2CF_2Cl$
13.	$ClCF_2$	$CF_2 = CH_2$	$ClCF_2CO_2CF_2CH_2Cl$
14.	HCF_2	$CF_2 = CF_2$	$HCF_2CO_2CF_2CF_2Cl$
15.	HCF_2	$CF_2 = CH_2$	$HCF_2CO_2CF_2CH_2Cl$

In 1981 Brace(45) reported synthesis of esters shown below:

1. $CH_3CO_2CH_2CHICH_2C_6F_{13}$

2. $CH_3CO_2CH_2CHICH_2C_7F_{15}$

3. $CH_3CO_2CH_2CHICH_2C_4F_9$

these esters were prepared through reactions shown below:

$C_6F_{13}I + CH_3CO_2CH_2CHCH_2 \xrightarrow{\text{Benzoyl Peroxide}}$ (1)

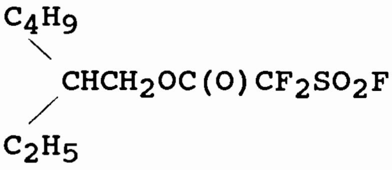
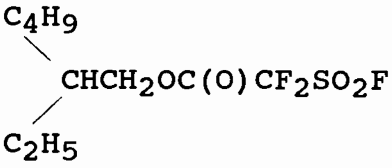
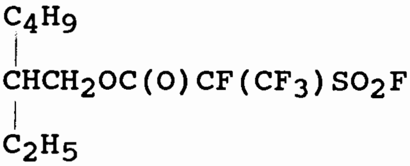
$C_7F_{15}I + CH_3CO_2CH_2CHCH_2 \xrightarrow{\text{Benzoyl Peroxide}}$ (2)

$C_4F_9I + CH_3CO_2CH_2CHCH_2$ azo-bis isobutyronitrile (3)

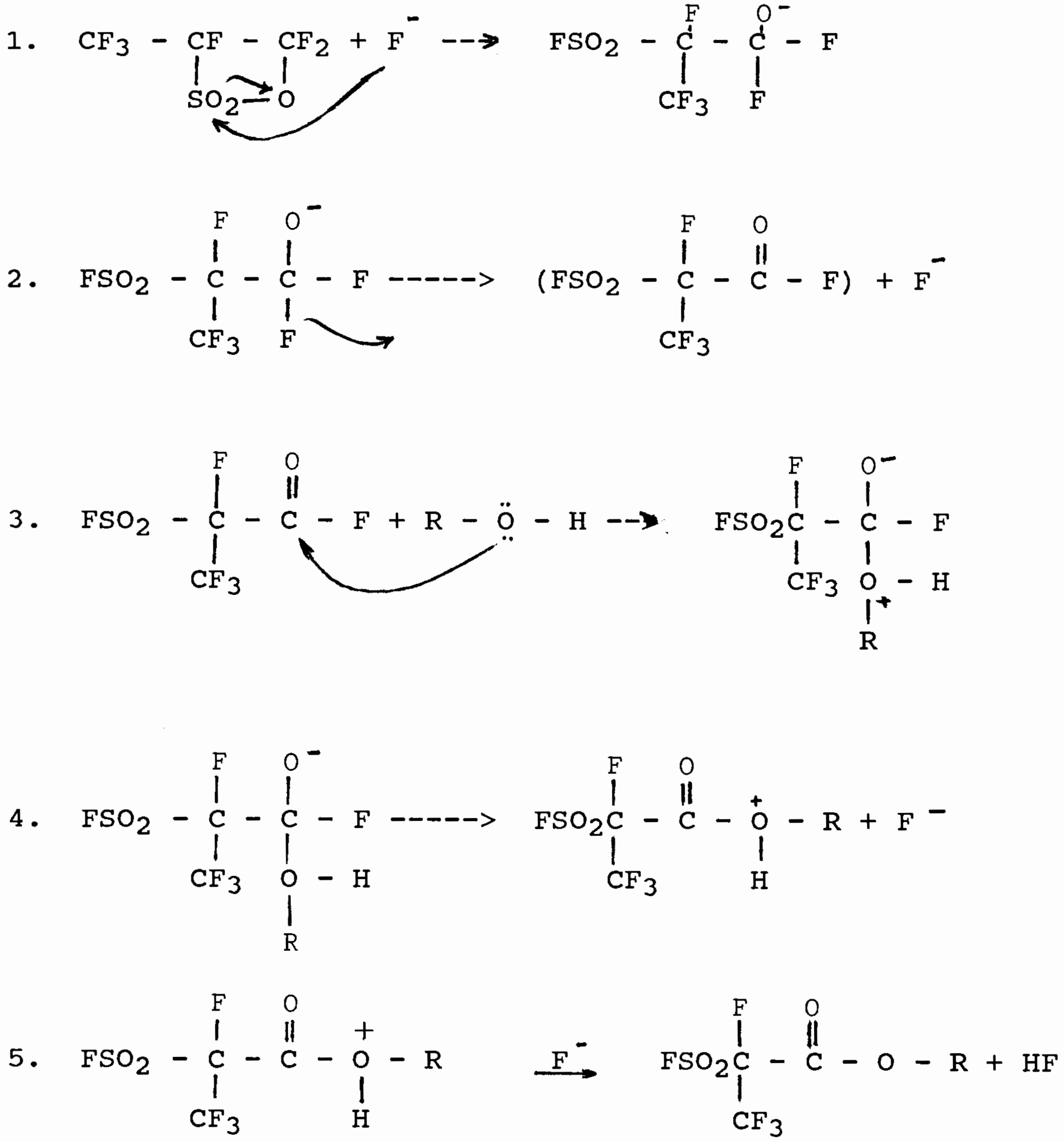
As part of our program to prepare fluorosulfonic acids we became interested in finding ways to prepare precursors for these acids. England et al.(48) found that the B-fluorosultone $\underline{CF_2CF_2OS}O_2$ reacted with alcohols to yield esters containing the SO_2F group (any compound containing this group is a precursor to sulfonic acids). These esters and the reactants from which they were prepared are listed in Table V. We have extended the scope of this reaction to include the sultone, $CF_3\underline{CFCF_2OS}O_2$. Using this sultone, new fluoroesters containing the SO_2F group were prepared and characterized by NMR, IR and Mass Spectral techniques.

TABLE III

SYNTHESIS OF ESTERS-PART III

Reactant	Sultone	Product
Sodium Methoxide	$CF_2CF_2OSO_2$	$CH_3OC(O)CF_2SO_2F$
Isopropyl alcohol	$CF_2CF_2OSO_2$	$C_3H_7OC(O)CF_2SO_2F$
Octanol-1	$CF_2CF_2OSO_2$	$C_8H_{17}OC(O)CF_2SO_2F$
2-Ethylhexanol	$CF_2CF_2OSO_2$	 $\begin{array}{l} C_4H_9 \\ \quad\diagdown \\ \qquad CHCH_2OC(O)CF_2SO_2F \\ \quad\diagup \\ C_2H_5 \end{array}$
2-Ethylhexanol	$ClCFCF_2OSO_2$	 $\begin{array}{l} C_4H_9 \\ \quad\diagdown \\ \qquad CHCH_2OC(O)CF_2SO_2F \\ \quad\diagup \\ C_2H_5 \end{array}$
2-Ethylhexanol	$CF_2CF(CF_3)OSO_2$	 $\begin{array}{l} C_4H_9 \\ \vert \\ CHCH_2OC(O)CF(CF_3)SO_2F \\ \vert \\ C_2H_5 \end{array}$
Octafluoroamyl alcohol	$CF_2CF_2OSO_2$	$H(CF_2)_4CH_2OC(O)CF_2SO_2F$
Ethylene glycol	$CF_2CF_2OSO_2$	$(CH_2OC(O)CF_2SO_2F)_2$
Phenol	$CF_2CF_2OSO_2$	$C_6H_5OC(O)CF_2SO_2F$

The proposed mechanism for the reactions is as follows:



1. $CF_3 - \underset{\displaystyle SO_2 - O}{\underset{|\qquad\;\;|}{CF - CF_2}} + F^- \longrightarrow FSO_2 - \overset{F}{\underset{CF_3}{C}} - \overset{O^-}{\underset{F}{C}} - F$

2. $FSO_2 - \overset{F}{\underset{CF_3}{C}} - \overset{O^-}{\underset{F}{C}} - F \longrightarrow (FSO_2 - \overset{F}{\underset{CF_3}{C}} - \overset{O}{\overset{\|}{C}} - F) + F^-$

3. $FSO_2 - \overset{F}{\underset{CF_3}{C}} - \overset{O}{\overset{\|}{C}} - F + R - \ddot{\underset{..}{O}} - H \longrightarrow FSO_2\overset{F}{\underset{CF_3}{C}} - \overset{O^-}{\underset{\underset{R}{\overset{+}{O}} - H}{C}} - F$

4. $FSO_2 - \overset{F}{\underset{CF_3}{C}} - \overset{O^-}{\underset{\underset{R}{O} - H}{C}} - F \longrightarrow FSO_2\overset{F}{\underset{CF_3}{C}} - \overset{O}{\overset{\|}{C}} - \underset{H}{\overset{+}{O}} - R + F^-$

5. $FSO_2 - \overset{F}{\underset{CF_3}{C}} - \overset{O}{\overset{\|}{C}} - \underset{H}{\overset{+}{O}} - R \xrightarrow{F^-} FSO_2\overset{F}{\underset{CF_3}{C}} - \overset{O}{\overset{\|}{C}} - O - R + HF$

CHAPTER II

EXPERIMENTAL METHODS

Vacuum System

The vacuum system used in this work was an all "Pyrex" glass system which consisted of a manifold connected to a "Welch Duo-Seal" rotary pump. The manifold consisted of 8 mm and 22 mm I.D. "Pyrex"-glass tubing which was connected to a two leg mercury manometer and also had four taps for attaching vessels. The taps were Eck and Krebs 2 mm high vacuum stopcocks to which "Pyrex" 10/30 outer glass joints were attached. A "Televac" gauge was used to monitor the system and it usually attained a vacuum at 10^{-2} - 10^{-3} torr. All joints were greased with "Apiezon-M" grease or "Kel-F" grease. The system is illustrated in Figure-1.

Reaction Vessels

For all the reactions studied, "Pyrex" glass vessels were used. The vessels were equipped with a stirrer, for mixing the reactants and had 2 mm high-vacuum "Teflon" stopcocks for an outlet. The connecting portion consisted of 10/30 inner joints for attaching to the vacuum line.

Physical Methods

<u>Vacuum Distillation</u>. Products were purified by

distilling in a "Bantam-ware" (Kontes) distillation apparatus. A heater and an oil bath were used to provide heat, and the unit was connected to the vacuum line through a trap cooled to -198°C.

The distillations which were done under atmospheric pressure had the same set-up with the exception that the unit was connected to the atmosphere via a trap was cooled to -78°C.

Infrared Spectra

Infrared spectra were obtained using a 20DX Nicolet-FTIR spectrometer. Liquid samples were placed on KBr windows. Gas samples were contained in a "Monel" cell fitted with KBr windows. The cell was equipped with a Pyrex glass 10/30 outer joint. The IR range was 4000-400 cm^{-1}.

Nuclear Magnetic Resonance

Nuclear magnetic resonance spectra were taken on a Varian Model EM-390 spectrometer operating at 90MHZ for proton and 84.7 MHZ for F^{19}. This work was done by Dr. Roger Sheets.

Mass Spectra

Mass spectra were taken on a CEC 21-110B double focus Mass Spectrometer with a 6KV ion accelator set at 70 volts. The internal standard used was perfluorokerosine (PKF). This work was done at the University of Idaho.

Chemical Analysis

Chemical analyses were performed by Beller

Microanalytical Laboratory in Gottingen, West Germany.

Reagents:

Ethanol. CH_3CH_2OH was obtained from U.S. Industrial Chemical Company and was used without further purification.

Allyl Alcohol. $CH_2 = CHCH_2OH$ was obtained from Matheson Coleman and Bell, and was used without further purification.

Trifluoroethanol. CF_3CH_2OH was obtained from Peninsular Chemical Research Inc. (PCR/SCM) and was used without further purification.

Hexfluoroisopropanol. $(CF_3)_2CHOH$ was obtained from PCR/SCM Specialty Chemical and was used without further purification.

Pentafluorophenol. C_6F_5OH was obtained from PCR/SCM Research Chemicals Inc. and distilled at atmospheric pressure before it was used.

Ethylene Glycol. CH_2OHCH_2OH was obtained from Mallinckrodt and was used without further purification.

Sodium Fluoride. NaF powder was obtained from Baker Analyzed Reagent and was dried by heat under vacuum in the reaction vessel.

2-hydroxy-1-trifluoromethyl-1,2,2-trifluoroethanesulfonic Acid Sultone. $CF_3CFCF_2OSO_2$ was prepared and distilled by Javid Mohtasham. (Chem. Dept. Portland State University)

Potassium Persulfate. $K_2S_2O_4$ was obtained from Mallinckrodt and was used with further purification.

Sodium Lauryl Sulfate. $(C_{12}H_{25}O)SO_3Na$ was obtained from Aldrich Chemical Company Inc. and was used without further purification.

Benzoyl Peroxide. $(C_6H_5CO_2)_2$ was obtained from Aldrich Chemical Company Inc. and was used without further purification.

Perfluoro-2-butyl-tetrahydrofuran

$C_4F_7OCF_2CF_2CF_2CF_3$ was obtained from PCR/SCM Specialty Chemicals and was used without further purification.

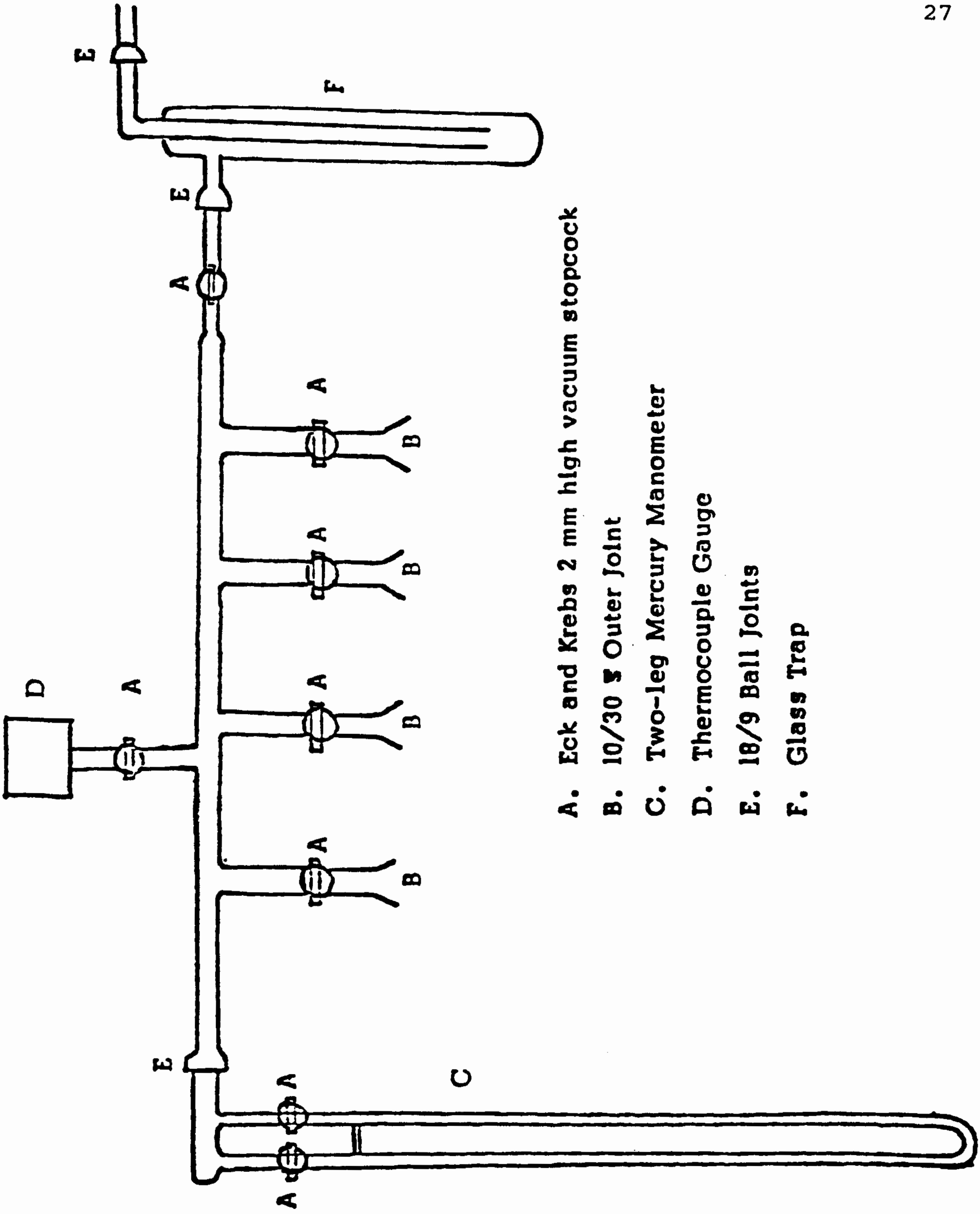


Figure 1. Glass Vacuum Manifold

CHAPTER III

SYNTHESIS OF FLUORINATED ESTERS

To prepare the new esters 2-hydroxy-1-trifluoromethyl-1,2,2-trifluoroethanesulfonic acid sultone ($(CF_3\overline{CFCF_2OSO_2})$) was allowed to react with the following alcohols,

CF_3CH_2OH, CH_3CH_2OH, $CH_2{=}CHCH_2OH$, CH_2OHCH_2OH, C_6F_5OH, and $(CF_3)_2CHOH$ according to the following equations:

1. $CF_3\underline{CFCF_2OSO_2}+CF_3CH_2OH \xrightarrow[40^{o}C,\ 3\ days]{NaF} CF_3(SO_2F)CFCO_2CH_2CF_3+NaHF_2$

2. $CF_3\underline{CFCF_2OSO_2}+CH_2{=}CHCH_2OH \xrightarrow[r.t,\ 10\ days]{NaF} CF_3CF(SO_2F)CO_2CH_2CH{=}CH_2 + NaHF_2$

3. $2CF_3\underline{CFCF_2OSO_2}+OHCH_2CH_2OH \xrightarrow[r.t,\ 10\ days]{NaF} (CF_3CF(SO_2F)CO_2CH_2)_2 + 2NaHF_2$

4. $CF_3\underline{CFCF_2OSO_2}+CH_3CH_2OH \xrightarrow[r\cdot t,\ 23\ days]{NaF} CF_3CF(SO_2F)CO_2CH_2CH_3 + NaHF_2$

5. $CF_3\underline{CFCF_2OSO_2}+C_6F_5OH \xrightarrow[60^{o}C,\ 13\ days]{NaF} CF_3(SO_2F)CFCO_2C_6F_5OH + NaHF_2$

6. $CF_3\underline{CFCF_2OSO_2}+(CF_3)_2CHOH \xrightarrow[r.t,\ 13\ days]{NaF} CF_3CF(SO_2F)CO_2CH(CF_3)_2 + NaHF_2$

All of the new products were clear, colorless liquids, and some were distillable at atmospheric pressure. All products have been identified by their mass spectra, nmr spectra and infrared spectra.

(1) Reaction of CF_3CH_2OH with the $CF_3\text{-}\overline{CF\text{-}CF_2OS}O_2$

Sodium fluoride (0.2534 moles) was dried in a 105-mL "Pyrex" glass reaction vessel under vacuum. Trifluoroethanol (0.0586 moles) was transferred to the reaction vessel under vacuum followed by the vacuum transfer of the $CF_3\overline{CFCF_2OS}O_2$ (0.0580 moles). The reaction was then allowed to proceed for three days at 40°C. The reaction mixture was transferred to a 25-mL "Pyrex" glass round bottom flask, through a by-pass line, under vacuum. The product was distilled and a fraction was collected at 123-124°C (0.0418 moles) at atmospheric pressure, yield was 72%.

The infrared spectrum of the distilled product showed the following absorptions (cm^{-1}):

2994(VW), 1806(VS), 1461(VS), 1412(M), 1315(VS), 1281(VS), 1246(VS), 1187(VS), 1165(VS), 1128(M), 1059(S), 1034(M), 978(S), 903(VW), 875(VW), 825(S), 793(M), 746(MW), 690(VW), 659(MW), 603(S), 559(VW), 546(VW), 515(VW).

(2) Reaction of CH_3CH_2OH with $CF_3\overline{CFCF_2OS}O_2$

Sodium fluoride (0.2216 moles) was transferred into a 70.1 mL "Pyrex" glass reaction vessel via a glove bag, then dried under vacuum. Ethanol (0.0488 moles) was transferred into the reaction vessel under vacuum followed by the vacuum transfer of the sultone (0.0437 moles). The reaction was allowed to proceed at room temperature for fourteen days. The reaction mixture was then transferred into a 25 mL Pyrex glass round bottom flask and distilled under reduced presssure, boiling point 107.5 ± 2.5°C/522 mm. The product was isolated in 66.4% yield (0.0290 moles).

The infrared spectrum of the distilled product showed the following absorptions (cm^{-1}):

2994(M), 1793(VS), 1459(VS), 1393(M), 1375(S),
1306(VS), 1246(VS), 1162(VS), 1100(M), 1034(VS),
1018(VS), 987(M), 853(S), 831(VS)M 806(VS),
746(S), 690(M), 606(VS), 546(W), 518(VW).

(3) Reaction of $CH_2=CHCH_2OH$ with $CF_3\overline{CFCF_2OS}O_2$

Sodium fluoride (0.1783 moles) was transferred into a 70.1 mL "Pyrex" glass reaction vessel via a glove bag and dried under vacuum. Allyl alcohol (0.0326 moles) was vacuum transferred into the reaction vessel followed by the vacuum transfer of the sultone (0.0323 moles). The reaction was allowed to proceed at room temperature for ten days. The solution was transferred to a 25 mL "Pyrex" glass round bottom flask. The product was distilled and a fraction was collected at 142°-143°C. The yield was 64.1% (0.021 moles).

The infrared spectrum of the distilled product gave the following absorptions (cm^{-1}):

2966(VW), 1792(VS), 1775(S), 1653(VW), 1456(VS),
1365(W), 1303(S), 1243(VS), 1159(S), 1084(VW),
1025(M), 990(M), 940(M), 893(W), 821(M), 790(M),
746(W), 690(VW), 603(S), 546(VW)

(4) Reaction of $HOCH_2CH_2OH$ with $CF_3\overline{CFCF_2OS}O_2$

Sodium fluoride (0.0680 moles) was transferred into a 105 mL Pyrex glass reaction vessel via a glove bag and then dried under vacuum. Ethylene glycol (0.0097 moles) was placed inside the vessel via a Pasteur pipet in the glove bag. The sultone (0.0193 moles) was vacuum transferred into the reaction vessel. The reaction was allowed to proceed at room temperature for 23 days. The reaction mixture was placed inside a 25 mL "Pyrex" glass round bottom flask. Vacuum distillation was performed under pressure of 10^{-3} mm and the product (0.0069 moles) was collected over the range 78-98°C, yield was 36.5%.

The infrared spectrum of the distilled product showed the following absorptions (cm^{-1}):

2980(VW), 1793(VS), 1459(VS), 1409(W), 1378(M),
1300(VS), 1250(VS), 1231(VS), 1162(VS), 1056(S),
1021(S), 984(M), 825(VS), 803(VS), 746(S),
687(M), 603(VS), 546(M)

(5) Reaction of C_6F_5OH with $CF_3\overline{CFCF_2OS}O_2$

Sodium fluoride (0.4032 moles) was added to a 105 mL "Pyrex" glass reaction vessel via a glove bag and dried under vacuum. Freshly distilled pentafluorophenol (0.0311 moles) was transferred into the reaction vessel under vacuum followed by vacuum transfer of the sultone (0.0296 moles). The reaction was allowed to proceed at 60°C for thirteen days. The reaction mixture was then transferred into a 25 mL Pyrex glass round bottom flask. The product was distilled under reduced pressure (5 mm) and a fraction was collected at 87-89°C and the yield was 42.8% (0.0126 moles).

The infrared spectrum of the distilled product showed the following absorptions (cm^{-1}):

2685(VW), 2474(VW), 1820(VS), 1653(W), 1521(VS), 1462(VS), 521(VS), 1462(VS), 1365(W), 1321(W), 1284(S), 1240(VS), 1165(VS), 1131(S), 1015(VS), 1003(VS), 943(W), 846(M), 812(S), 750(M), 715(W), 678(VW), 637(W), 625(W), 600(VS), 568(W), 546(W)

(6) Reaction of $(CF_3)_2CHOH$ with $CF_3\overline{CFCF_2OS}O_2$

Sodium fluoride (0.1288 moles) was transferred into a 106 mL "Pyrex" glass reaction vessel via a glove bag, then dried under vacuum. Hexafluoroisopropanol (0.0371 moles) was transferred into the reaction vessel under vacuum, followed by vacuum transfer of the sultone (0.0326 moles). The reaction was allowed to proceed at room temperature for thirteen days. The solution was then transferred into a 25 mL "Pyrex" glass round bottom flask. The product was distilled at atmospheric pressure and a fraction was collected at 109-110°C and the yield was 53.6% (0.0173 moles).

The infrared spectrum of the distilled product showed the following absorptions (cm^{-1}):

2987(VW), 1820(VS), 1468(VS), 1384(VS), 1368(S), 1284(VS), 1246(VS), 1212(VS), 1165(VS), 1118(VS), 1078(S), 1059(M), 1009(VW), 987(W), 912(M), 900(M), 828(S), 793(S), 750(W), 725(M), 693(M), 675(W), 600(VS), 550(VW).

(7) Attempted Polymerization of $CH_2=CHCH_2OCCF(SO_2F)CF_3$

Two attempts were made to polymerize this ester. The reactions were carried out in a 6 mL "Pyrex" glass ampule.

First Trial:

Benzoyl peroxide (0.0001238 moles) was placed inside the ampule. Perfluoro-2-butylteterahydrofuran (0.0086 moles) was added followed by the addition of the ester (0.0069 moles). The ampule was sealed under vacuum, then heated at 60°C for seventeen hours (with occasionally shaking), the temperature was then increased to 85°C for twenty hours, followed by fifteen days of heating at 93°C. No change in the viscosity of the solution was observed, unlike what was expected(30).

The infrared spectrum of the solution in the ampule showed the following absorptions (cm^{-1}):

3100(VW), 2966(VW), 1792(S), 1653(W), 1456(VS),
1365(M), 1303(VS), 1243(VS), 1159(VS), 1084(S),
1025(S), 990(M), 690(W), 603(S), 546(W)

Second Trial:

Sodium lauryl sulfate (0.06g) was placed in a 6 mL "Pyrex" glass ampule. Sodium persulfate (0.02g) was added followed by addition of distilled water (3.59g). The ester $CH_2=CHCH_2O_2CCF(SO_2F)CF_3$ (1.02g) was then added to the mixture. The ampule was then sealed under vacuum and heated at 45°C for three hours. The temperature was then increased to 75°C for 24 hours. The ampule was occasionally shaken during this time. After heating the ampule at 70°C for four days, it was opened, the aqueous layer was removed from the organic layer. The infrared spectrum of the organic layer showed the following absorptions (cm^{-1}):

3437(VS), 2931(S), 2860(S), 1771(S), 1714(W),
1651(M), 1454(S), 1363(M), 1243(VS), 1159(S),
1025(M), 990(M), 941(M), 821(VS), 793(VS),
793(VS), 744(S), 603(VS), 546(M)

(8) Attempted Decarboxylation of $CF_3CH_2O_2CCF(CF_3)SO_2F$

$CF_3CH_2O_2CCF(CF_3)SO_2F$ (0.00126 moles) was vacuum transferred to a 70.6 mL "Pyrex" glass reaction vessel. The reaction vessel was heated in a furnace at 300°C for an hour. A black precipitate was formed, and some of the starting liquid had remained in the vessel.

The infrared spectrum of the liquid showed the following absorptions (cm^{-1}):

2987(VW), 1820(W), 1468(M), 1418(W), 1371(VS),
1359(VS), 1350(VS), 1290(S), 1240(S), 1190(VS),
1153(VS), 1059(M), 1028(S), 975(W), 909(VW),
821(W), 796(VW), 668(W), 606(W), 534(M)

(9) Attempted Decarbonoxylation of $(CF_3)_2CHO_2CCF(CF_3)SO_2F$

The ester $(CF_3)_2CHO_2CCF(CF_3)SO_2F$ (0.0007 moles) was added to a 105 mL "Pyrex" glass reaction vessel under vacuum. The reaction vessel was placed in a furnace and heated at 300°C for one hour. The presence of black precipitate was observed and some of the starting liquid was also present. The infrared spectrum of the liquid showed the following absorptions (cm^{-1}):

2987(VW), 1828(W), 1809(M), 1471(VW), 1375(S),
1340(VS), 1275(VS), 1250(VS), 1218(VS), 1153(S),
1128(M), 1028(VS), 971(VS), 918(W), 840(VW), 778(VW),
718(M), 668(W), 531(W)

CHAPTER IV

ANALYTICAL RESULTS

Infrared Spectra

The infrared spectra absorption peaks for the new compounds are listed in Figures 2-10 followed by the spectrum of each ester in Tables VIII-XIII. The absorption bands in the region 2966 cm^{-1} to 2994 cm^{-1} are assigned to the C-H stretching frequency. This band is very weak in some cases, and many times this absorption in fluorinated compounds may easily be missed.

The band which is most indicative of the presence of an ester is the carbonyl stretching vibration and is the most reliable region for diagnostic purposes.

Brown and Morgan have assigned the 1850-1600 cm^{-1} region to the carbonyl stretching vibration. The fluorinated esters discussed here, show a strong to very strong absorption within the range of 1790-1820 cm^{-1} which is due to C=O.

This is in close agreement with those values reported by Shreeve et al.(40). They assigned for fluorinated esters the region 1840-1850 cm^{-1} to the carbonyl stretching frequency of their esters. As expected, the absorption frequencies of carbonyl groups is affected by the surrounding groups; as the electron withdrawing character of the group on the single bonded oxygen increases the carbonyl stretching frequency increases(50). See Table VI.

The very strong band in the region 1454-1468 cm^{-1} is assigned to S=O antisymmetric (asymmetric) stretching frequency(49). Robinson(51), assigned the 1401-1463 cm^{-1} region to S=O antisymmetric stretching vibration. However, the presence of fluorine in the sulfonyl fluoride group and fluorines on the attached carbon atom cause this band to shift to higher frequencies. As Robinson explains, groups having a greater effective electronegativity, shift the S=O absorption to a higher frequency. Robinson(51) assigns S=O symmetric stretching frequencies to the 1203-1210 cm^{-1} region; the exact assignment of this frequency for these esters is very difficult because of complex pattern in this region caused by the fluorinated portion of the molecules. If one is allowed to make an assignment, the absorption bands at 1250 cm^{-1} to 1240 cm^{-1} may be assigned to S-O symmetrical stretching frequency.

C-O single bond stretching vibration is reported(64) to occur between 1300 cm^{-1} and 1000 cm^{-1} and is of little diagnostic value, especially in these esters because it overlaps with the C-F and CF_3 complex absorption pattern in this region(41). Christe(43) assigns the region 1093-1120 cm^{-1} to this frequency and all the esters discussed here show absorption in this region.

The band at 1653 cm^{-1} in the spectrum of

CH_2=$CHCH_2OCCF(CF_3)SO_2F$ is assigned to C=C stretching frequency(64).

The series of strong bands between 1212 cm^{-1} and 1375 cm^{-1} are assigned to C-F stretching vibration, which is in good agreement with those reported by Temple(53) (Part III) and those reported by other investigators(43,54,55).

The very strong bands observed between 1153-1165 cm^{-1} is assigned to CF_3 symmetrical stretching frequency, which is in close agreement with what is reported by Temple(56); and the antisymmetric stretching is reported to be at 1230 cm^{-1} frequency(56). The same investigator reports that the presence of bands at 968 cm^{-1} and 540 cm^{-1} to be due to CF_3 rocking deformation and CF_3 symm. deformation frequencies, while the skeleton deformation is assigned to 606 cm^{-1} which is in agreement with the 693-781 cm^{-1} range reported by Christe(43). Therefore, for esters reported in this thesis the bands between 600-693 may be assigned to the CF_3 deformation mode in addition to the bands at 546 cm^{-1}; these assignments are in good agreement with the values reported by Christe(43) and Temple(56).

Christe(43) assigned the 844 cm^{-1} band to C-C stretching vibration, and Temple(56) assigned the 828 cm^{-1} absorbance frequency to this bond. For the esters reported here, the C-C frequency is assigned to the bands found between 793 cm^{-1} - 903 cm^{-1} which is in good agreement with those reported by other investigators(43,56).

The S-F stretching frequency is reported to appear between 815-755 cm^{-1} as a strong intensity infrared band. For these esters this band is assigned to the region between 746 cm^{-1} -831 cm^{-1}.

The region, 705 cm^{-1}-570 cm^{-1} is assigned to C-S stretching frequency(58-59), which for the esters reported here applies to the bands between 546 cm^{-1}-693 cm^{-1}. In the case of $C_6F_5OC(O)CF(CF_3)SO_2F$ the strong bands between 1651 cm^{-1}-1525 cm^{-1} are assigned to the C_6F_5 ring-skeletal stretching frequencies.

Due to the presence of many groups with overlapping absorption frequencies, the carbonyl frequency remains the best group for diagnostic purposes. Table X summarizes the frequencies at which C=O stretching occurs for different esters. From this table one may derive the following conclusion:

As the electron withdrawing character of the group attached to C-O single bond increases, the C=O stretching vibration frequency increases. This is due to the increase in the multiple bond character of C=O, and the absorption is shifted to higher frequencies(50). The same reasoning may be used to explain the increase in the absorption frequency of S=O.

TABLE IV

SUMMARY OF IR SPECTRA OF NEW ESTERS

Ester	C=O stretching	S=O stretching
$CH_2=CHCH_2OC(O)CF(CF_3)SO_2F$	1792 cm^{-1}	1456 cm^{-1}
$(CH_2OC(O)CF(CF_3)SO_2F)_2$	1793 cm^{-1}	1459 cm^{-1}
$CH_3CH_2OC(O)CF(CF_3)SO_2F$	1793 cm^{-1}	1461 cm^{-1}
$CF_3CH_2OC(O)CF(CF_3)SO_2F$	1806 cm^{-1}	1461 cm^{-1}
$(CF_3)_2CHOC(O)CF(CF_3)SO_2F$	1820 cm^{-1}	1462 cm^{-1}
$C_6F_5OC(O)CF(CF_3)SO_2F$	1820 cm^{-1}	1468 cm^{-1}

TABLE V

INFRARED SPECTRUM OF $CF_3CH_2OC(O)CF(CF_3)SO_2F$

Band (cm^{-1})		Intensity
1.	2994	VW
2.	1806	VS
3.	1461	VS
4.	1412	M
5.	1315	VS
6.	1281	VS
7.	1246	VS
8.	1187	VS
9.	1165	VS
10.	1128	M
11.	1059	S
12.	1034	M
13.	978	S
14.	903	VW
15.	875	VW
16.	825	S
17.	793	M
18.	746	MW
19.	690	VW
20.	659	MW
21.	603	S
22.	559	VW
23.	546	VW

TABLE VI

INFRARED SPECTRA OF $CH_3CH_2OC(O)CF(CF_3)SO_2F$

Band (cm^{-1})		Intensity
1.	2994	M
2.	1793	VS
3.	1459	VS
4.	1393	M
5.	1375	S
6.	1306	VS
7.	1246	VS
8.	1162	VS
9.	1100	M
10.	1034	VS
11.	1018	VS
12.	987	M
13.	853	S
14.	831	VS
15.	806	VS
16.	746	S
17.	690	M
18.	606	VS
19.	546	W
20.	518	VW

TABLE VII

INFRARED SPECTRUM OF $CH_2=CHCH_2OC(O)CF(CF_3)SO_2F$

Band (cm^{-1})		Intensity
1.	2966	VW
2.	1792	VS
3.	1775	S
4.	1653	VW
5.	1456	VS
6.	1365	W
7.	1303	S
8.	1243	VS
9.	1159	S
10.	1084	VW
11.	1025	M
12.	990	M
13.	940	M
14.	893	W
15.	821	M
16.	790	M
17.	746	W
18.	690	VW
19.	603	S
20.	546	VW

TABLE VIII

INFRARED SPECTRA OF $(CH_2OC(O)CF(CF_3)SO_2F)_2$

Band (cm^{-1})		Intensity
1.	2980	VW
2.	1793	VS
3.	1459	VS
4.	1409	W
5.	1378	M
6.	1300	VS
7.	1250	VS
8.	1231	VS
9.	1162	VS
10.	1056	S
11.	1021	S
12.	984	M
13.	825	VS
14.	803	VS
15.	746	S
16.	687	M
17.	603	VS
18.	546	M

TABLE IX

INFRARED SPECTRUM OF $C_6F_5OC(O)CF(CF_3)SO_2F$

Band (cm^{-1})		Intensity
1.	2685	VW
2.	2474	VW
3.	1820	VS
4.	1653	W
5.	1521	VS
6.	1462	VS
7.	1365	W
8.	1321	W
9.	1284	S
10.	1240	VS
11.	1160	VS
12.	1131	S
13.	1015	VS
14.	1003	VS
15.	943	W
16.	846	M
17.	812	S
18.	750	M
19.	715	W
20.	678	VW
21.	637	W
22.	625	W
23.	600	VS
24.	568	W
25.	546	W

TABLE X

INFRARED SPECTRUM OF $(CF_3)_2CHOC(O)CF(CF_3)SO_2F$

Band (cm^{-1})		Intensity
1.	2987	VW
2.	1820	VS
3.	1468	VS
4.	1384	VS
5.	1368	S
6.	1284	VS
7.	1246	VS
8.	1212	VS
9.	1165	VS
10.	1118	VS
11.	1078	S
12.	1059	M
13.	1009	VW
14.	987	W
15.	912	M
16.	900	M
17.	828	S
18.	793	S
19.	750	W
20.	725	M
21.	693	M
22.	675	W
23.	600	VS
24.	550	VW

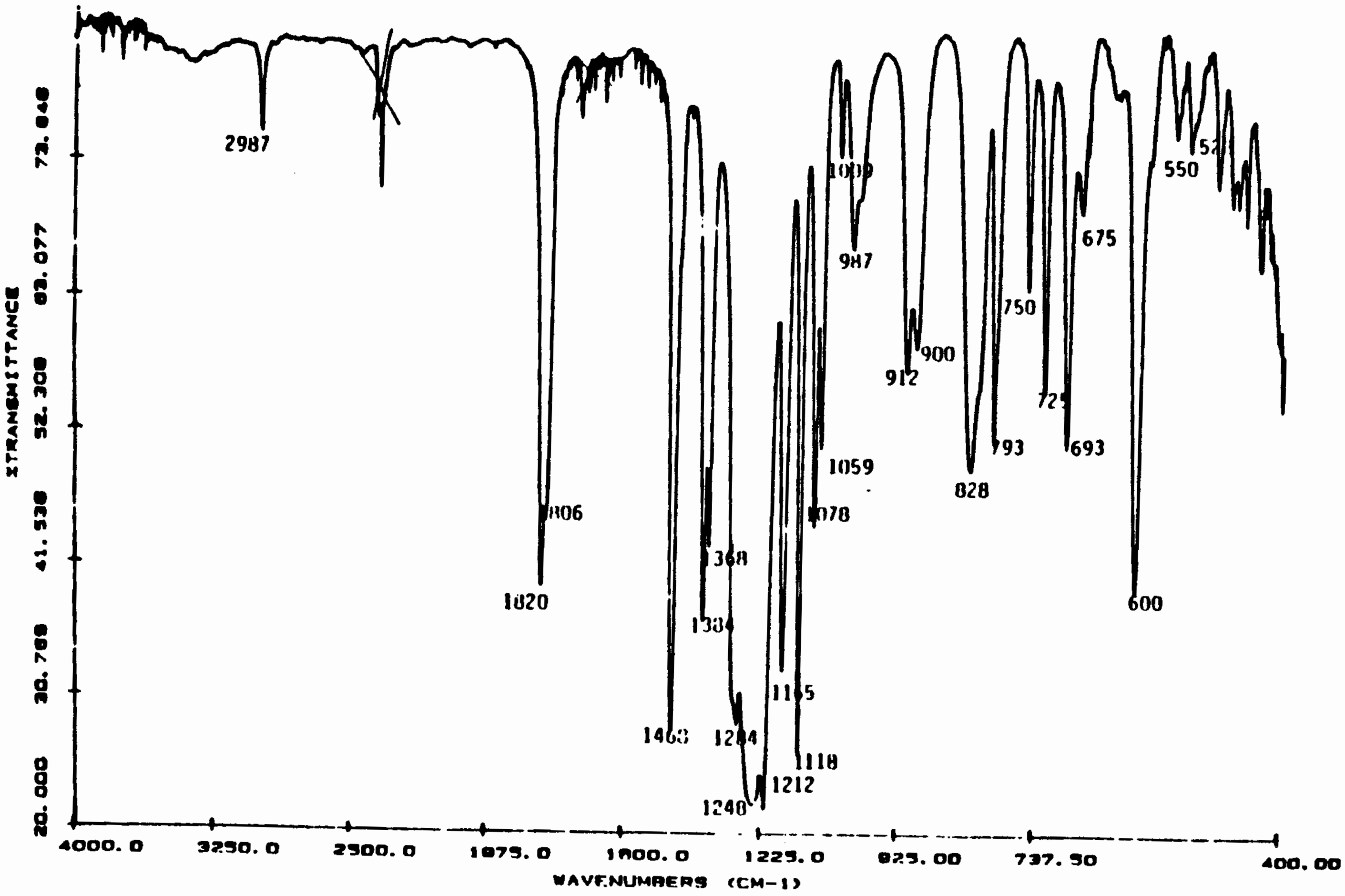


Figure 2. Infrared spectrum of $(CF_3)_2CHOC(O)CF(CF_3)SO_2F$.

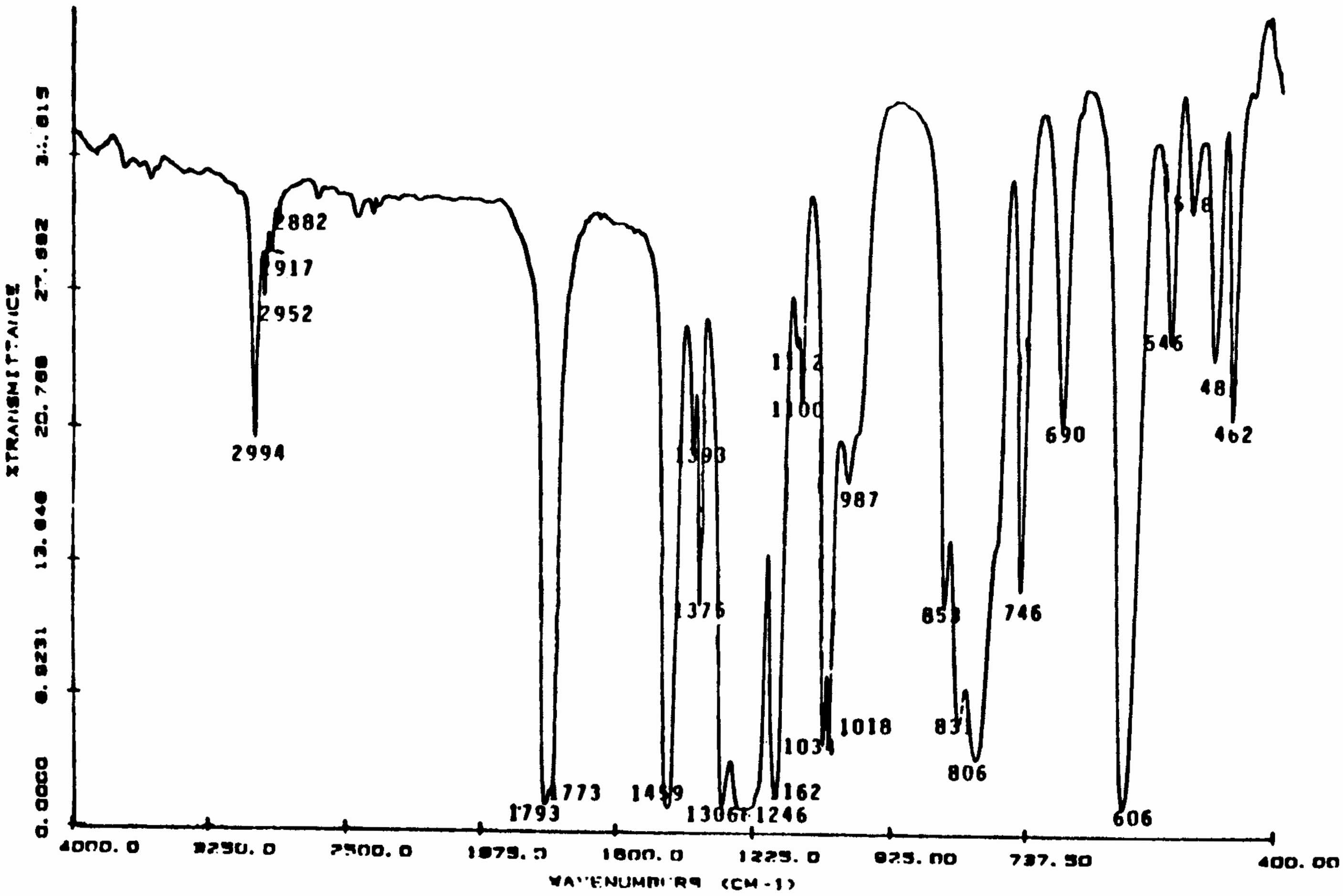


Figure 3. Infrared spectrum of $CH_3CH_2OC(O)CF(CF_3)SO_2F$.

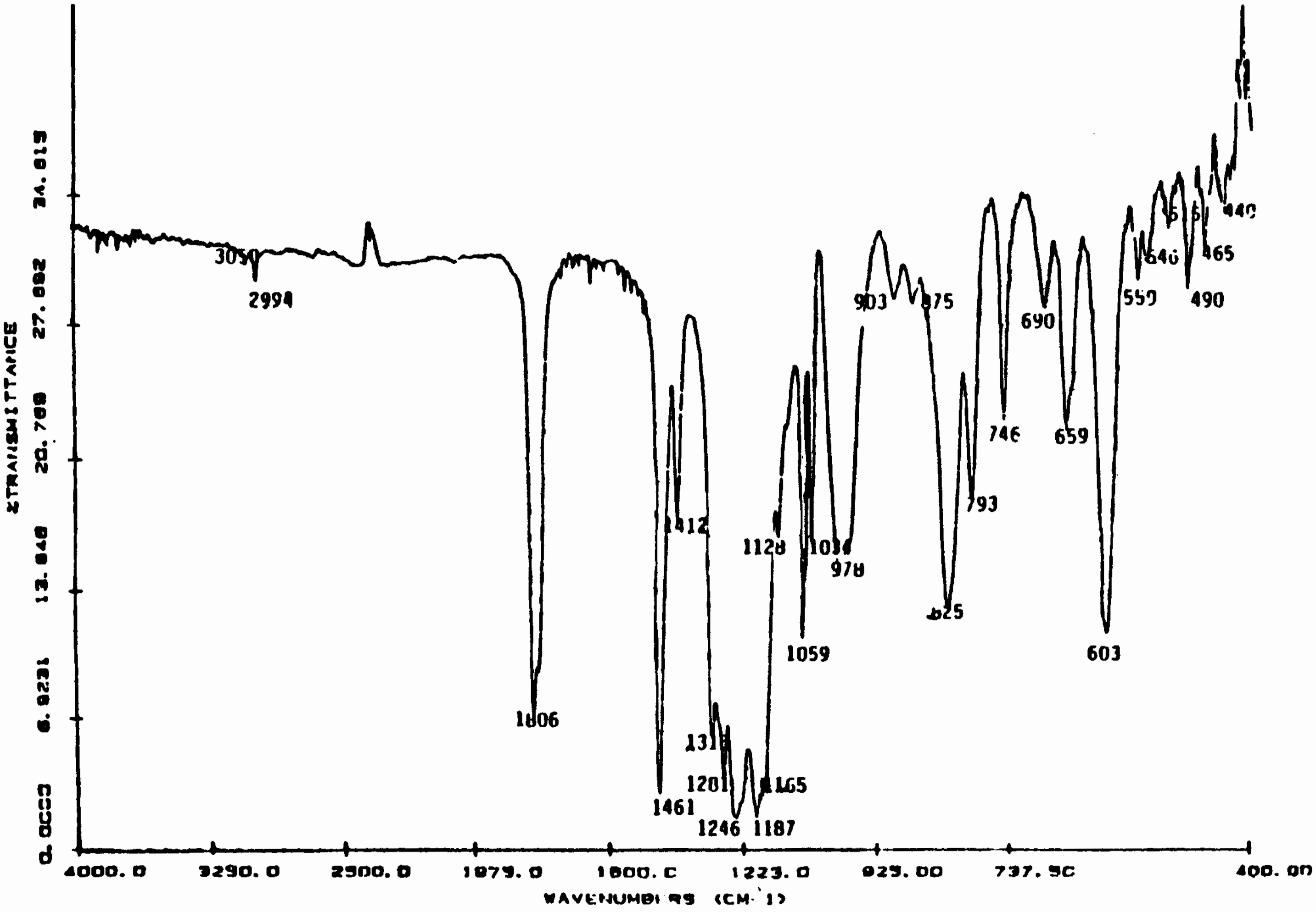


Figure 4. Infrared spectrum of $CF_3CH_2OC(O)CF(CF_3)SO_2F$.

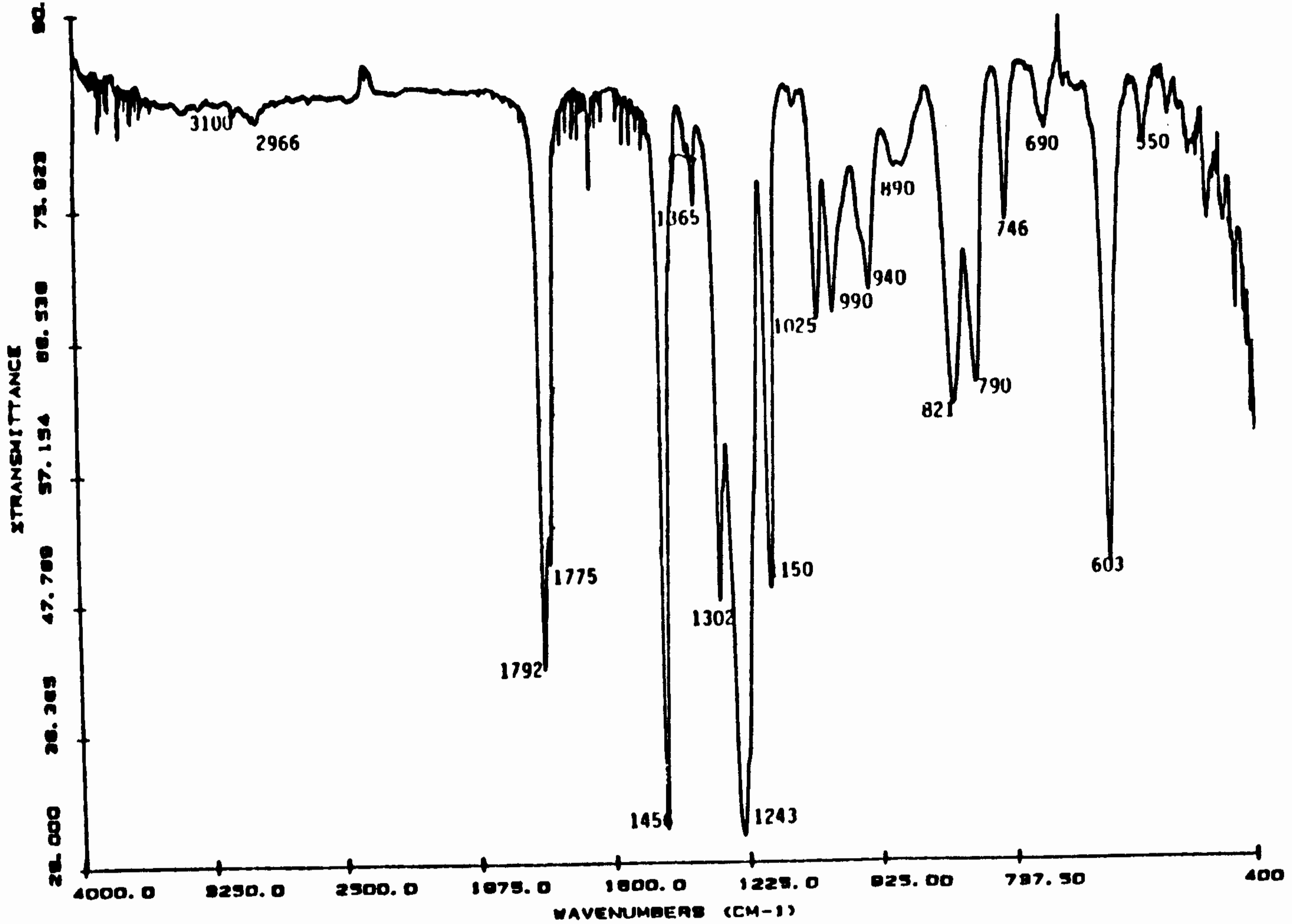


Figure 5. Infrared spectrum of $CH_2=CHCH_2OC(O)CF(CF_3)SO_2F$.

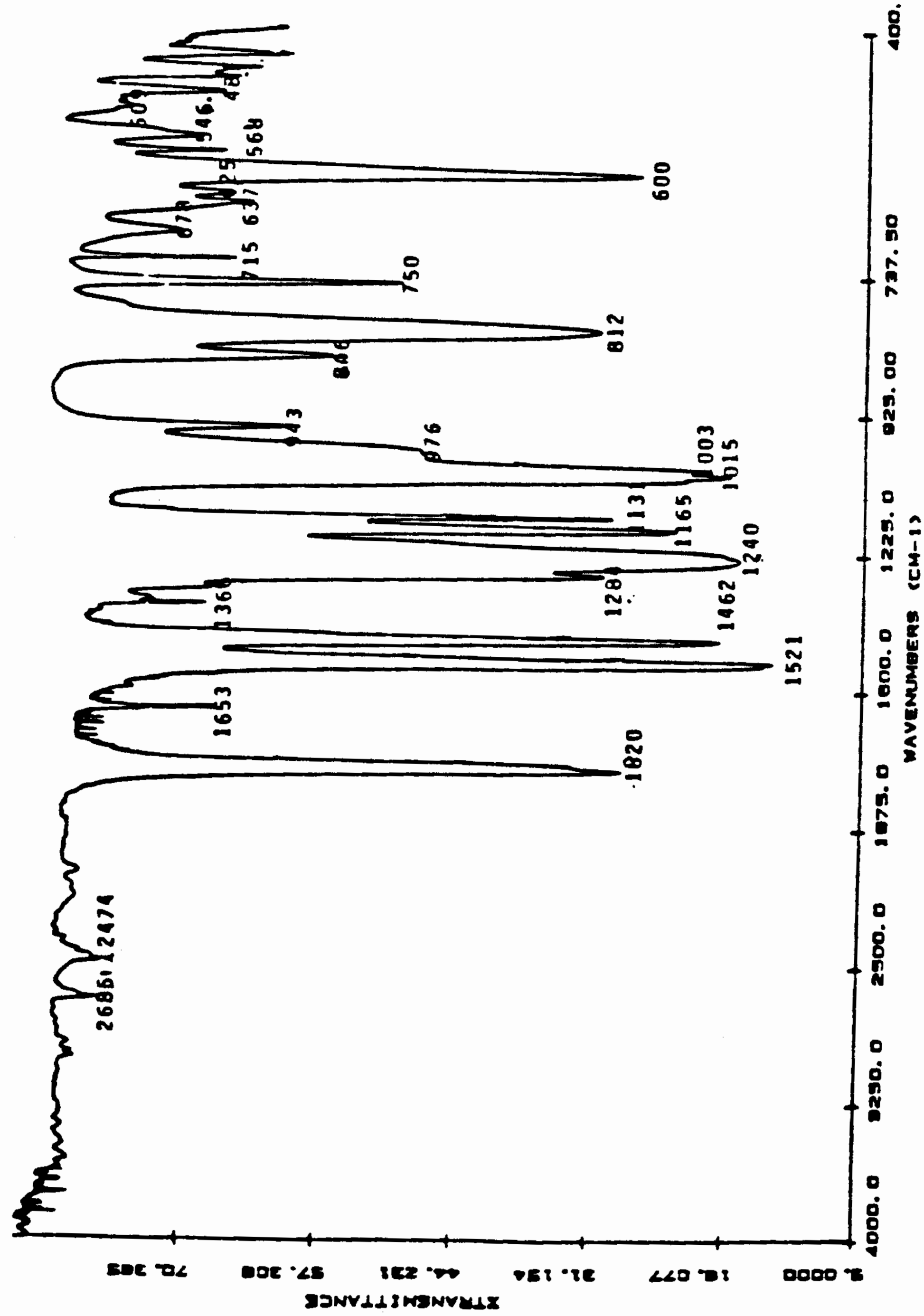


Figure 6. Infrared spectrum of $C_6F_5OC(O)CF(CF_3)SO_2F$.

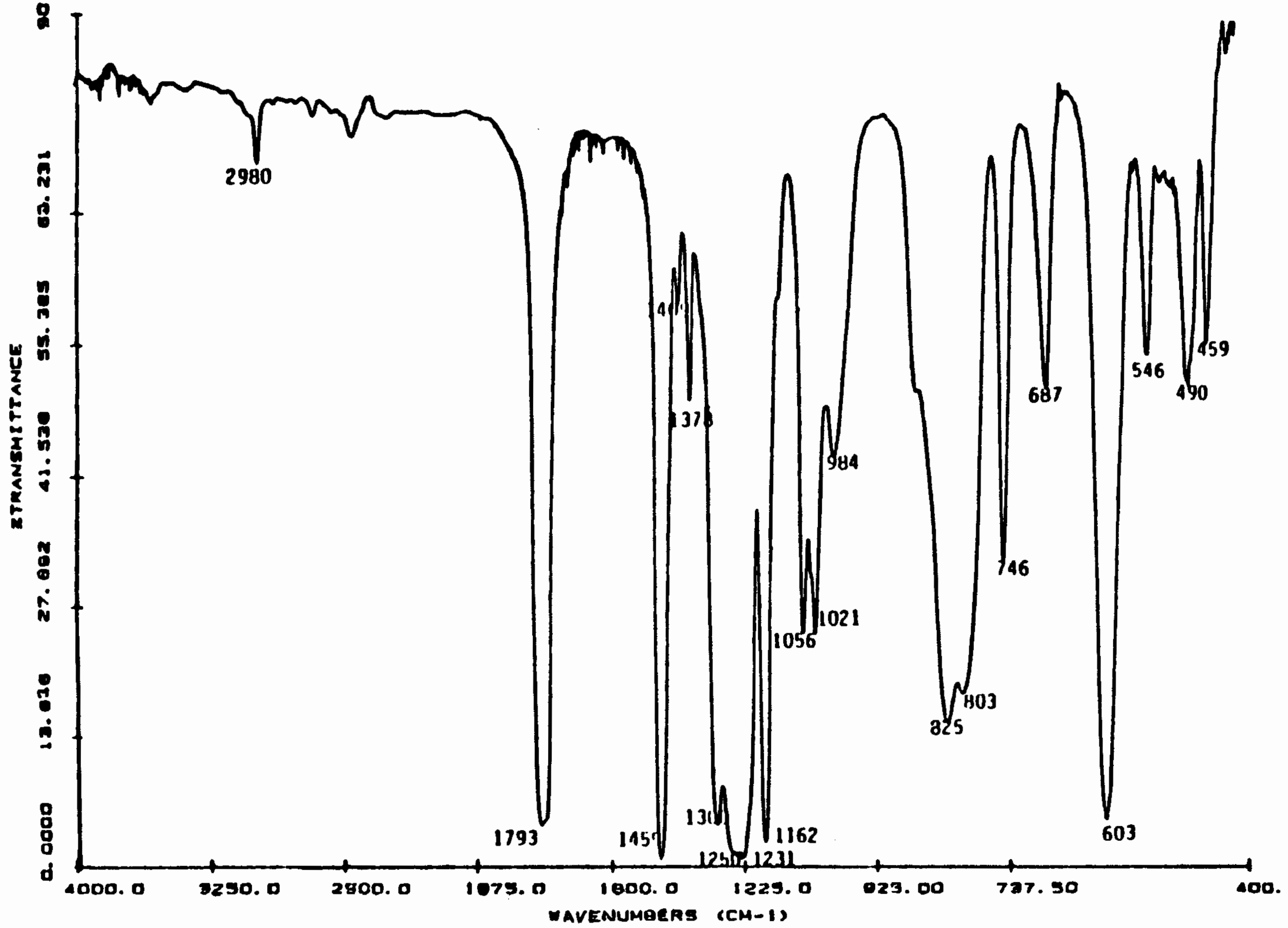


Figure 7. Infrared spectrum of $(CH_2OC(O)CF(CF_3)SO_2F)_2$.

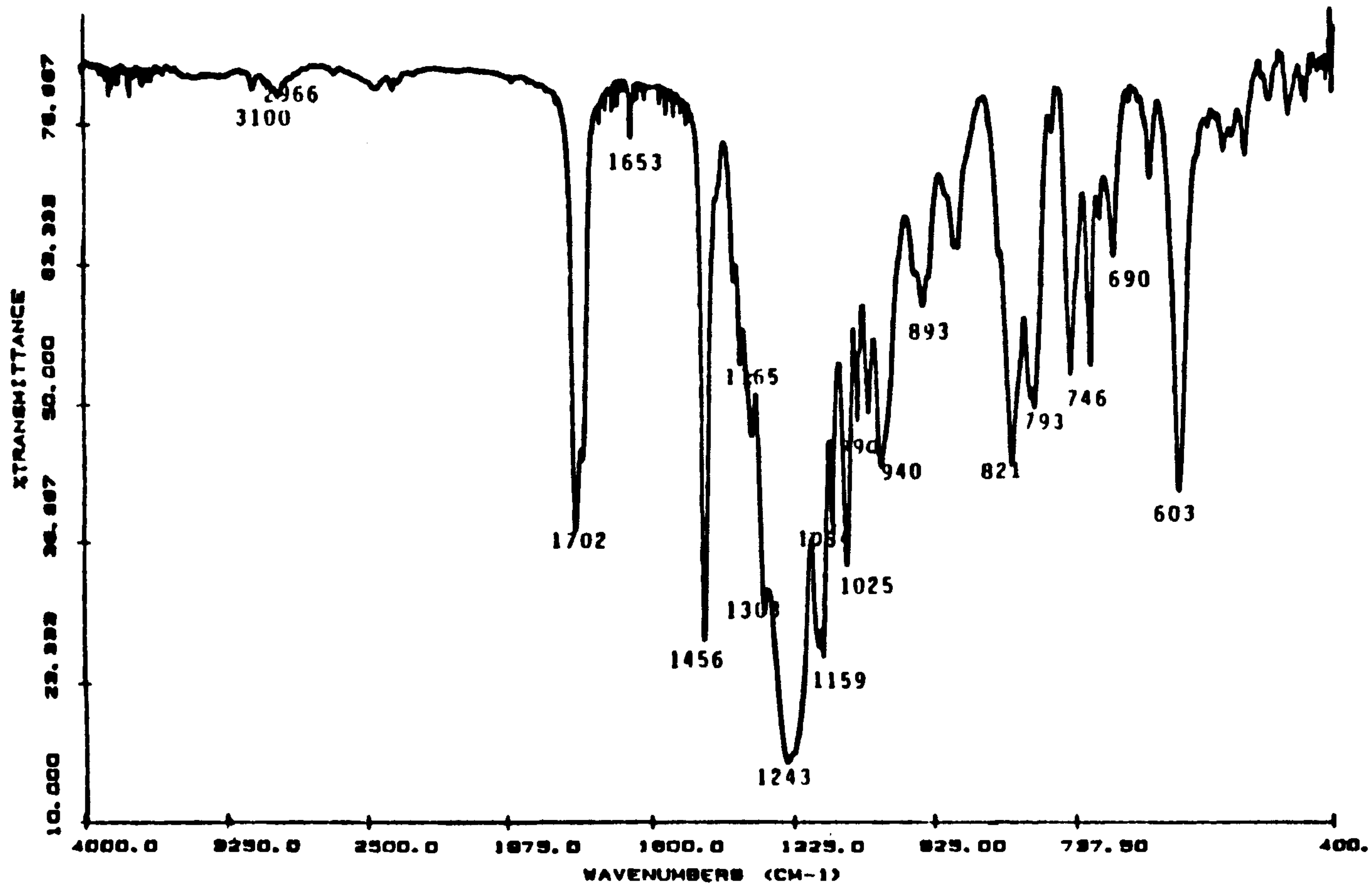


Figure 8. Infrared spectrum of the first polymerization trial of $CH_2=CHCH_2OC(O)CF(CF_3)SO_2F$.

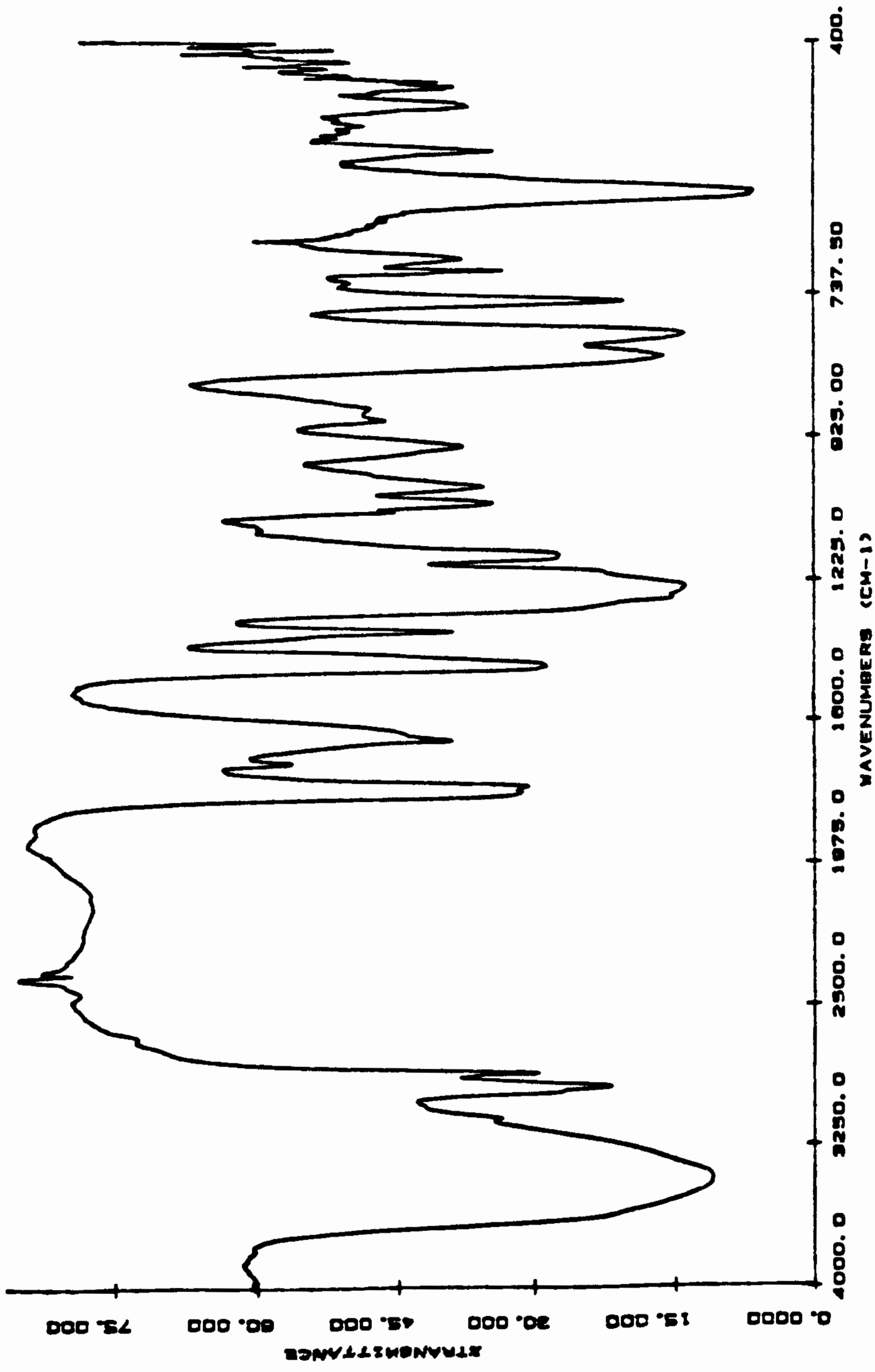


Figure 9. Infrared spectrum of the second polymerization trial of $CH_2=CHCH_2OC(O)CF(CF_3)SO_2F$.

Mass Spectra

The major peaks in the mass spectra for the new fluorinated esters are listed in Tables XI-XV. The peaks for these esters are listed, although not all fragments are identified, there is strong evidence for the presence of these esters for the following reasons:

1. Two of the esters ($CH_2{=}CHCH_2OC(O)CF(SO_2F)CF_3$ and $C_6F_5OC(O)CF(SO_2F)CF_3$) show parent peaks at 268 (5.1%) and 394 (29.0%) respectively. The rest of the esters which do not have a parent peak show peaks such as $(M-H)^+$ for $CH_3CH_2OC(O)CF(SO_2F)CF_3$ at 255 (3.5%) $(M-F)^+$ for $(CF_3)_2CHOC(O)CF(SO_2F)CF_3$ at 359 (1.1%) and $(M-F)^+$ for $CF_3CH_2OC(O)CF(SO_2F)CF_3$ at 291 (0.5%).

2. For three of these esters the most intense peak is due to $(SOF)^+$ at 67 with 100% base for esters: $CH_3CH_2OC(O)CF(SO_2F)CF_3$, $CH_2{=}CHCH_2OC(O)CF(SO_2F)CF_3$ and $C_6F_5OC(O)CF(SO_2F)CF_3$. However for the other esters which do not show 100% base for SOF, they still show high percentage at this peak namely:

for $(CF_3CH_2OC(O)CF(SO_2F)CF_3)^+$ 67 (20.1%)

and $((CF_3)_2CHOC(O)CF(SO_2F)CF_3)^+$ 67 (33.7%)

3. All esters show relatively intense peaks due to the CF_3 group. For example $(CF_3)^+$ peak (69) shows 100% base for $(CF_3)_2CHOC(O)CF(SO_2F)CF_3$ and lower percent base for the rest of the esters.

4. For all the esters one observes a peak due to (SO_2F), ranging from 100% base for $CF_3CH_2OC(O)CF(SO_2F)CF_3$ to a 0.4% base for $C_6F_5OC(O)CF(SO_2F)CF_3$.

5. All the esters also show a peak due to the $(OCCF(SO_2F)CF_3)^+$ portion of the esters (211 peak). They all show the presence of peaks due to the $(M\text{-}CF(CF_3)SO_2F)^+$ portion of the esters which are:

for $(CH_3CH_2OC(O)CF(SO_2F)CF_3)^+$	73 at 0.4% base
$(CH_2{=}CHCH_2OC(O)CF(SO_2F)CF_3)^+$	85 at 3.9% base
$(C_6F_5OC(O)CF(SO_2F)CF_3)^+$	211 at 37.6% base
$(CF_3CH_2OC(O)CF(SO_2F)CF_3)^+$	127 at 17.6% base
$((CF_3)_2CHOC(O)CF(SO_2F)CF_3)^+$	195 at 19.6% base

6. Two other peaks common with these esters are (CO_2), (M/e=44) and $(CFCF_3)^+$, (M/e=100)

In brief, all these esters show fragments corresponding to:

R_fOC, $M\text{-}R_f$, CO_2, $CF(CF_3)$, SO_2F, SOF, etc.

All of which are indicative of the presence of the ester as the initial compound.

TABLE XI

MASS SPECTRUM FOR $CH_2=CHCH_2OC(O)CF(SO_2F)CF_3$

	M/e	%Rel. Int.	Fragment	Assignment
1.	268	5.1	$C_6H_5O_4F_5S$	M+
2.	211	9.8	$C_6H_5O_4FS$	$(CCCF(CF_3)SO_2F)^+$
3.	186	2.4	$C_6H_5O_2F_4$	$(M-SO_2F)^+$
4.	185	45.6	$C_6H_4O_2F_4$	$(M-HSO_2F)^+$
5.	184	13.0	$C_6H_3O_2F_4$	$(M-H_2SO_2F)^+$
6.	165	1.3	C_6HOF_4	$(CCCHOCCFCF_3)^+$
7.	164	5.4	C_6OF_4	$(CCCOCCFCF_3)^+CF_2CFSO_2F$
8.	156	8.0	C_6HO_2FS	$(CCCHOC(O)CFCS)^+$
9.	147	5.1	C_5HOF_2S	$(CCHOCC(CF_2)_3)^+$
10.	145	1.5	C_6OF_3	$(CCCO-CCCF_3)^+$
11.	137	2.2	C_6HO_2S	$(HCCCOC(O)C(C)S)^+$
12.	129	1.5	C_5H_2OFS	$(CCH_2OCCF(C)S)^+$
13.	128	34.1	C_5HOFS	$(CCHOCCF(C)S)^+$
14.	121	18.7	C_6HOS	$(CCCHOCC(C)S)^+$
15.	119	37.1	C_3O_2FS	$(OC(O)CF(C)S)^+$
16.	117	1.9	C_4H_2OFS	$(CH_2OCCF(C)S)^+$
17.	109	9.9	C_5HOS	$(CHC-O-C-C(C)S)^+$
18.	108	3.2	C_5OS	$(CCOCC(C)S)^+$
19.	102	1.5	$C_4H_3O_2F$	$(CHCH_2OC(O)CF)^+$
20.	101	31.3	$C_4H_2O_2F$	$(CCH_2OC(O)CF)^+$
21.	100	19.0	C_4HO_2F	$(CCHOC(O)CF)^+$
22.	97	2.0	C_5H_2OF	$(CCCH_2OC(O)CF)^+$
23.	95	5.0	C_5OF	$(CCCOC(O)CF)^+$
24.	91	1.6	C_6H_3O	$(CCHCH_2OCCC)^+$
25.	90	1.0	C_6H_2O	$(CCCH_2OCCC)^+$
26.	89	2.8	$C_6HO, C_3H_2O_2F$	$(CH_2OC(O)CF)^+$
27.	87	19.4	C_3O_2F	$(COC(O)CF)^+$
28.	85	3.9	$C_4H_5O_2$	$(CH_2CHCH_2OC(O))^+$
29.	83	1.6	SO_2F	--------
30.	81	5.4	C_4HO_2	$(CCCHO-C)^+$
31.	77	3.7	C_5HO	$(CCCHO-C-C)^+$
32.	70	1.9	$C_3H_2O_2$	$(CCH_2OCO)^+$
33.	69	25.4	CF_3	------
34.	68	1.7	C_4H_4O	$(HCCHCH_2OC)^+$
35.	67	100.0	SOF	------
36.	65	2.2	C_4HO	$(CCCHOC)^+$
37.	64	5.1	C_4O	$(CCCOC)^+$
38.	63	1.2	CSF	$(C-SF)^+$
39.	59	7.9	C2FO	$(C(O)CF)^+$

TABLE XI

MASS SPECTRUM FOR $CH_2=CHCH_2OC(O)CF(SO_2F)CF_3$ (Continued)

	M/e	%Rel. Int.	Fragment	Assignment
40.	58	1.9	$C_2H_2O_2$	$(CH_2OC(O))^+$
41.	57	19.5	C_2HO_2	$(CHOC(O))^+$
42.	56	8.7	C_2O_2	$(COC(O))^+$
43.	55	17.0	C_3H_3O	$(CCHCH_2O)^+$
44.	51	4.3	SF	-------
45.	50	2.7	CF_2	-------
46.	48	5.8	SO	-------
47.	47	1.9	COF	COF^+
48.	45	6.5	?	
49.	44	12.3	CO_2	$(CO_2)^+$
50.	43	6.8	C_2F	$(CCF)^+$
51.	42	13.5	C_2H_2O	$(CCH_2O)^+$

TABLE XII

MASS SPECTRUM FOR $CH_3CH_2OCCF(SO_2F)CF_3$

	M/e	% Rel. Int.	Fragment	Assignment
1.	255	3.5	$C_5H_4O_4F_5S$	$(M - H)^+$
2.	241	6.8	$C_4H_2O_4F_5S$	$(M - CH_3)+$
3.	229	1.2	?	
4.	213	3.3	$C_5O_4F_3S$	$(CCOC(O)C(CF_3)SO_2)^+$
5.	212	2.8	?	
6.	211	70.8	$C_3O_4F_5S$	$(OCCF(CF_3)SO_2F)^+$
7.	173	2.3	$C_5H_5O_2F_4$	$(M - SO_2F)^+$
8.	165	1.5	$C_4H_2O_4F_3$	$(CCH_2OC(O)CFSO_2)^+$
9.	164	3.9	C_4HO_4FS	$(CCHOC(O)CFSO_2)^+(CF_2CFSO_2F)^+$
10.	147	8.3	H_4O_2FS	$(CH_2CH_2OC(O)CF(C)S)^+$
11.	145	1.0	$C_5H_2O_2FS$	$(CCH_2OC(O)CF(C)S)^+$
12.	144	2.6	C_5HO_2FS	$(CCHOC(O)CF(C)S)^+$
13.	128	22.9	C_5H_4OFS	$(CCHOCCF(C)S)^+$
14.	127	2.2	$C_5H_3O_2S$	$(CCOCCF(C)S)^+$
15.	119	33.3	C_3O_2FS	$(CCF(C)SO_2)^+$
16.	109	8.3	C_5HOS	$(CCHOCCCS)^+$
17.	106	1.0	$C_3O_2F_2$	$(O_2CC(CF_2))^+$
18.	105	2.9	C_3H_2OFS	$(CH_2OCCFS)^+$
19.	101	1.0	$C_4H_2O_2F$	$(CCH_2O_2CCF)^+$
20.	100	22.7	C_4HO_2F, C_2F_4	$(CFCF_3)^+$
21.	97	4.8	$C_5H_5O_2$	$(CH_3CH_2OC(O)CC)^+$
22.	90	1.1	C_3OF_2	$(OCCCF_2)^+$
23.	89	3.2	$C_3H_2O_2F$	$(H_2CO_2CCF)^+$
24.	83	2.2	SO_2F	------
25.	81	7.5	C_4HO_2	$(CCHOC(O)C)^+$
26.	73	0.4	C_3H_5	$(CH_3CH_2OCO)^+$
27.	71	1.5	$C_3H_3O_2$	$(CHCH_2O_2C)^+$
28.	69	35.2	CF_3	------
29.	68	1.3	C_3O_2	$(CCO_2C)^+$
30.	67	100	SOF	-----
31.	65	1.8	C_4HO	$(CCHOCC)^+$
32.	63	1.7	CFS	-----
33.	59	1.6	C_2OF	$(C(O)CF)^+$
34.	51	6.5	SF	------
35.	50	3.6	CF_2	------
36.	48	7.3	SO	------
37.	47	2.6	COF^+	COF^+
38.	45	16.9	C_2H_5O	$(CH_3CH_2O)+$
39.	44	7.7	CO_2	$(CO_2)^+$

TABLE XII

MASS SPECTRUM FOR $CH_3CH_2OCCF(SO_2F)CF_3$
(Continued)

	M/e	% Rel. Int.	Fragment	Assignment
40.	43	23.7	C_2F	$(CCF)^+$
41.	42	3.8	C_2H_2O	$(CCH_2O)^+$

TABLE XIII

MASS SPECTRUM FOR $(CF_3)_2CHOCCF(SO_2F)CF_3$

	M/e	% Rel. Int.	Fragment	Assignment
1.	359	1.1	$C_6HO_4F_{11}S$	M^+
2.	339	2.5	$C_6O_4F_9S$	$(M-HF_2)^+$
3.	276	5.0	$C_5O_2F_8S$	$((CF_3)COC(O)CFSF)^+$
4.	275	4.7	$C_6O_2F_9$	$(CF_2)_2COC(O)C(CF_3))^+$
5.	256	1.1	$C_6O_2F_8$	$(CF_3)_2COC(O)CF(CF))^+$
6.	211	13.4	$C_3O_3F_5S$	$(OCCF(CF_3)SO_2F)^+$
7.	195	19.6	$C_3O_2F_5S, C_4HO_2F_6$	$((CF_3)_2CHOC)^+$
8.	152	1.4	C_5OF_4	$(CCOCCF(CF_3))^+$
9.	151	45.2	C_3HF_6	$((CF_3)_2CH)^+$
10.	147	4.5	C_4O_3FS	$(CC-O-C-C-SO_2F)^+$
11.	128	8.8	C_4O_3S	$(CCO-C-C-SO_2)^+$
12.	119	14.6	C_3O_2FS	$(C-C-(C)SO_2F)^+$
13.	113	1.3	C_2F_3S	$(C(CF_3)S)^+$
14.	109	2.7	C_5HOS	$(CCHO-C-C-(C)S)^+$
15.	101	1.3	?	?
16.	100	6.9	C_4HO_2F	$(CHOC(O)CF(C))^+$
17.	97	1.2	C_4HOS	$(CHOC(O)C(C)S)^+$
18.	82	1.3	C_2HF_3	$(CF_3)CH)^+$
19.	81	1.8	C_2F_3	$((CF3)C)^+$
20.	70	1.1	?	?
21.	69	100	$(CF_3)^+$	-------
22.	67	33.7	$(SOF)^+$	-------
23.	64	1.0	$(SO_2)^+$	-------
24.	51	8.4	$(SF)^+$	------
25.	50	1.5	$(CF_2)^+$	------
26.	48	1.7	$(SO)^+$	------
27.	44	1.4	$(CO_2)^+$	------

TABLE XIV

MASS SPECTRUM FOR $CF_3CH_2OCCF(SO_2F)CF_3$

	M/e	% Rel. Int.	Fragment	Assignment
1.	291	0.5	$C_5H_2O_4F_7S$	$(M-F)^+$
2.	241	2.7	$C_4H_2O_4F_5S$	$(MCF_3)^+$
3.	211	7.8	$C_3O_3F_5S$	$(OCCF(SO_2F)CF_3)^+$
4.	208	45	$C_3O_4F_4S$	$(O_2CCF(SO_2F)CF_3)^+$
5.	149	1.3	$C_4H_2O_3FS$	$(CH_2OCCF(SO_2)C)^+$
6.	147	2.1	C_4O_3FS	$(COCCF(SO_2)C)^+$
7.	128	5.2	C_4O_3S	$(COCC(SO_2)C)^+$
8.	127	17.6	$C_3H_2O_2F_3$	$(CF_3CH_2OCO)^+$
9.	119	7.3	$C_4HO_2F_2$	$(CF_2CHOCOC)$
10.	109	1.8	C_3OF_3	$(CF_3COC)^+$
11.	100	5.1	C_2F_4	$(CFCF_3)^+$
12.	84	2.1	C_4HOF	$(CCHOCCF)^+$
13.	83	100.0	SO_2F	$(SO_2F)^+$
14.	81	1.4	C_2F_3	(CF_3C)
15.	69	10.9	CF_3	$(CF_3)^+$
16.	67	20.1	SOF	$(SOF)^+$
17.	64	1.3	SO_2	$(SO_2)^+$
18.	63	2.4	C_2HF_2	$(CF_2CH)^+$
19.	51	2.2	SF	$(SF)^+$
20.	50	1.0	CF_2	$(CF)^+$
21.	48	1.3	SO	$(SO)^+$
22.	44	1.5	CO_2	$(CO_2)^+$

TABLE XV

MASS SPECTRUM FOR $C_6F_5OC(O)CF(SO_2F)CF_3$

	M/e	% Rel. Int.	Fragment	Assignment
1.	396	1.5	?	M^+ (S=34)
2.	395	3.1	?	?
3.	394	29.0	$C_9O_4F_{10}S$	$(M)^+$
4.	292	1.6	$C_9O_2F_8$	$(C_6F_5OCOCCF_3)^+$
5.	233	1.5	$C_8O_3F_3S$	$(C_6F_3OC-C(SO_2))^+$
6.	213	1.8	?	?
7.	212	1.5	$C_6O_2F_4S$	$(C_3F_3-OC-CF-S)^+$
8.	211	37.6	$C_3O_3F_5S(C_6F_5OC)^+$	$(OCCF(SO_2F)CF_3)^+$
9.	184	3.6	C_5OF_4S	$(C_3F_3-OC-CF-S)^+$
10.	183	32.1	$C_2O_2F_5S$	$(CF(CF_3)SO_2F)^+C_6F_5O$
11.	156	1.9	$C_4O_2F_4$	$(C-OC-CF(CF_3))^+$
12.	155	35.2	C_6O_2FS	$(C_4-OCCF(S))^+$
13.	147	9.0	C_4O_3FS	$(C_2O-CCF-SO_2)^+$
14.	136	2.7	C_6O_2S	$(C_4O-C-C-S)^+$
15.	128	14.3	C_4O_3S	$(C_2-OC-C-SO_2)^+$
16.	124	1.6	C_4F_4	$(C_4F_4)^+$
17.	119	37.0	C_3O_2FS	$(C-C-(SO_2F)C)^+$
18.	117	12.9	C_5F_4	$(C_5F_4)^+$
19.	109	8.3	C_3F_3O	$(C_3F_3-O)^+$
20.	105	6.6	C_4F_3	(C_4F_3)
21.	100	11.0	C_2F_4	$(CFCF_3)^+$
22.	98	1.9	C_5F_2	$(C_5F_2)^+$
23.	97	1.5	CF_2COF	CF_2COF
24.	93	6.5	C_3F_2	$(C_3F_3)^+$
25.	86	3.0	C_4F_2	$(C_4F_2)^+$
26.	83	0.4	SO_2F	$(SO_2F)^+$
27.	81	3.3	C_2F_3	$(CCF_3)^+$
28.	74	1.9	C_3F_2	$(CCCF_2)$
29.	69	27	CF_3	$(CF_3)^+$
30.	67	100	SOF	$(SOF)^+$
31.	64	2.2	SO_2	$(SO_2)^+$
32.	57	?	?	?
33.	55	1.3	C_3F	$(CCCF)^+$
34.	50	1.3	CF_2	$(CF_2)^+$
35.	48	1.9	SO	$(SO)^+$
36.	47	1.0	COF	COF
37.	44	4.2	CO_2	$(CO_2)^+$
38.	43	1.2	C_2F	$(CCF)^+$

Nuclear Magnetic Resonance Spectra

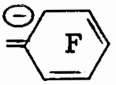
The proton and F^{19} NMR spectra were recorded for $CH_3CH_2OC(O)CF(CF_3)SO_2F$, $(CH_2OC(O)CF(CF_3)SO_2F)_2$, $CF_3CH_2OC(O)CF(CF_3)SO_2F$, $CH_2{=}CHCH_2OC(O)CF(CF_3)SO_2F$, $C_6F_5OC(O)CF(CF_3)SO_2F$, and $(CF_3)_2CHOC(O)CF(CF_3)SO_2F$. Tables XX-XXV show the data obtained from these spectra.

The spectra of $CH_2{=}CHCH_2OC(O)CF(CF_3)SO_2F$ shows a doublet of a doublet for CF_3 which may be explained by the fact that it is coupled to the CF and SF groups; the two fluorine atoms have different coupling constants to the CF_3 group. The spectrum for the SF group appears as a quartet of doublets which is what one would expect considering the presence of the CF_3 group which forms the quartet; each part of the quartet is split into a doublet due to the presence of the neighboring CF group. The same splitting pattern is observed for CF which again may be explained by a similar interpretation as given above. The proton NMR of the allyl ester gives rise to a complex splitting pattern with very low resolution. However the assignment of the chemical shifts to each proton is justified as follows: CH_2^4 protons appear at the higher field chemical shift compared to CH^5 and CH^6 or CH^7 (see Table XVIII protons) because protons of CH^5, CH^6 and CH^7 are being deshielded due to the circulation of the electrons around the axis of the bond. The CH^5 proton appears at the lowest shift because in addition to the deshielding explained above, it is experiencing an additional electron withdrawing effect caused by the oxygen atom. The integration of these protons is in good agreement with with was expected CH_2^4:CH^5:CH^6:CH^7 = 2.2:1.0:1.0:1.0 compared to the theoretical ratio 2:1:1:1.

The integration of CF:SF and CF_3 results in the ratio of 1:0:1.0:2.7 compared to the theoretical ratio or 1:1:3. For $(CH_2OC(O)CF(CF_3)SO_2F)_2$ one observes the same patterns for CH_3, SF and CF as that discussed for the allyl ester. The integration of CF:SF and CF_3 peak areas results in the ratio of 1.0:1.0:3.1 which is in close agreement with the calculated ratio of 1:1:3. A singlet is observed for CH_2 as was expected.

For $(CF_3)_2CHOC(O)CF(CF_3)SO_2F$ one observes the same doublet of a doublet pattern for CF_3, however, the CF_3 groups in the alkoxide portion of the ester give rise to an unresolved (broad singlet) peak at a chemical shift slightly higher than that of acyl CF_3. The integration of the peaks proves this assignment to be a correct one as it gives a ratio of 2.7:5.9 between CF_3 and CF_3 which is in good agreement with 1:2 theoretical ratio. The splitting pattern for CF and SF is as explained for previous esters and the integration of the peaks for CF:SF:CF_3:CF_3 shows a ratio of 1.0:1.0:2.7:5.9. The CH group shows a septet splitting pattern due to the effect of six fluorine atoms on the adjacent CF_3 groups.

The assignment of chemical shifts and coupling constants to the phenyl portion of $C_6F_5OC(O)CF(CF_3)SO_2F$ is made very difficult as a result of the complex splitting pattern between ortho, meta and para fluorine atoms. The chemical shifts, however, are assigned as explained below.

As a result of conjugation between oxygen atom and the ring structures such as O  and O  more deshielding of the ortho and para atoms will occur. Therefore, ortho fluorine atoms are expected to have the lowest field chemical shift and meta fluorines are in turn going to have the highest field chemical shift; and indeed this is what is seen; the para fluorine has a chemical shift between these two values. The coupling constant values calculated for the fluorines on the benzene ring agree well with those reported for similar compounds(63). From the resolution of the bands, calculations of $J_{1,4}$ and $J_{1,5}$ were not possible. However, these values are reported to be 4.4 Hz and 2.8 Hz, respectively for pentafluorophenol. However, for another compound such as pentafluoroanisol, the values are 4.6 Hz for $J_{1,4}$ and 0.8 Hz for $J_{1,5}$. Therefore, various substitutes seem to have some effect on these values.

The rest of the molecule shows the same pattern as the previous esters. The integration results show ratios of 2.1:1.1:2.1 for ortho, para and meta respectively; the theoretical values are 2:1:2. The integration for CF_3:SF and CF groups results in the ratio 2.9:1.1:1.0; the theoretical values are 3:1:1.

The NMR spectrum of $CH_3CH_2OC(O)CF(CF_3)SO_2F$ gives rise to a pattern which is in complete agreement with what was expected. The same splitting pattern is observed for CF, SF and CF_3 groups as discussed earlier. The CH_3 group shows a triplet due to the neighboring CH_2 group, while a quartet is observed for the CH_2 group as one would expect. The integration ratio for CF_3, SF and CF group is 3.1:1.0:1.0 compared to the theoretical ratio of 3:1:1.

The ^1H and ^{19}F spectra of $CF_3CH_2OC(O)CF(CF_3)SO_2F$ gave the expected patterns. The alkyl CF_3 group is split into a triplet due to the presence of the adjacent CH_2 group; the CH_2 group is in turn split into a quartet by the CF_3 group. The integration ratio of CF_3:CF:SF:CF_3 is 3.3:1.1:1.0:3.1; the theoretical values are 3:1:1:3.

TABLE XVI

SUMMARY OF CHEMICAL SHIFTS FOR VARIOUS MOLECULAR GROUPS

Ester	S-F	C-F	CF_3	other CF_3	CH	CH_2
allyl ester	50.2	-161.8	-74.4	-	6.1	5.1
ethylene glycol ester	50.9	-163.5	-75.2	-	-	4.98
hexafluoro propanol ester	50.6	-167.6	-74.4	-75.1	4.9	-
pentafluoro-phenol	50.1	-162.7	-74.9	-	-	-
	meta	-164.1				
	para	-157.1				
	ortho	-155.1				
ethanol-ester	50.5	-162.6	-75.0	-	-	4.55
CF_3CH_2 ester	49.6	-162.9	-74.4	-76.0	-	-

Among the CH_2 chemical shifts listed in Table XVI, $CH_3CH_2OC(O)CF(CF_3)SO_2F$ shows the lowest chemical shift; it is at a slightly lower field than that reported by Shreeve(41) et al. for $CF_3CO_2CH_2CH_3$. This may be due to the deshielding effect created through an SO_2F electron withdrawing effect. As the electron withdrawing character of the neighboring groups increases, the chemical shift is shifted to a lower field as seen for $(CH_2OC(O)CF(CF_3)SO_2F)_2$.

The CH group chemical shifts move to lower field as the CH group is deshielded by the adjacent groups. In the case of $(CF_3)_2CHOC(O)CF(CF_3)SO_2F$, the chemical shift is in very good agreement with that reported by Shreeve(41) et al. for $CF_3CO_2CH(CF_3)_2$; a slight shift to a lower field may be due to the presence of the electron withdrawing groups on the carbonyl side of the molecule. The CH group in $CH_2{=}CHCH_2OC(O)CF(CF_3)SO_2F$ appears at a yet lower field.

The CF_3 groups on the alkoxyl portions of $CF_3CH_2OC(O)CF(CF_3)SO_2F$ and $(CF_3)_2CHOC(O)CF(CF_3)SO_2F$ appear at -76.0 ppm and -75.1 ppm. The relative position of these chemical shifts is as expected(41). The chemical shifts of CF_3 groups on the carbonyl portions of these esters seem to appear at a very narrow range of $\phi = -74.4$ to $\phi = -75.2$.

The presence of other electron withdrawing groups on the alkoxy portion of these esters may be responsible for changes in their chemical shifts; for example, the presence of two CF_3 groups in $(CF_3)_2CHOC(O)CF(CF_3)SO_2F$ creates shielding for the CF group. Shreeve(42) et al. reported through space interactions which may be responsible for this shift to higher field.

The S-F chemical shift in $(CH_2OC(O)CF(CF_3)SO_2F)_2$ appears at the lowest field compared to all other esters reported here.

TABLE XVII

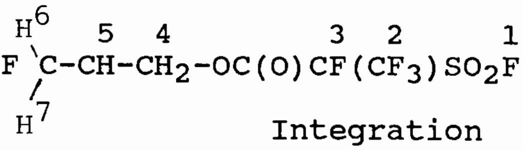
SUMMARY OF NMR SPECTRUM OF $(\overset{4}{C}H_2OC(O)\overset{3}{C}F(\overset{2}{C}F_3)SO_2\overset{1}{F})_2$

Chemical Shift	Coupling Constant	Integration
$0_1 = 50.9$	$J_{1,2} = 9.9$	1.0
$0_2 = -75.2$	$J_{2,3} = 7.8$	3.1
$0_3 = -163.2$	$J_{3,1} = 3.5$	1.0
$0_4 = 4.98$	*	

* Broadened singlet.

TABLE XVIII

SUMMARY OF NMR SPECTRUM OF



$(H^6)(H^7)C{-}\overset{5}{C}H{-}\overset{4}{C}H_2{-}OC(O)\overset{3}{C}F(\overset{2}{C}F_3)SO_2\overset{1}{F}$

Chemical Shift	Coupling Constant	Integration
$0_1 = 50.2$	$J_{1,2} = 9.9$	1.0
$0_2 = -73.4$	$J_{2,3} = 7.8$	2.7
$0_3 = -161.8$	$J_{3,1} = 3.5$	1.0
$0_4 = 5.1$	$J_{4,5} = 7.0$	2.2
$0_5 = 6.1$	$J_{5,6} = 10.1$	1.0
$0_6 = 5.5$	$J_{6,7} = 2.1$	1.0
$0_7 = 5.8$	$J_{7,5} = 17.0$	1.0

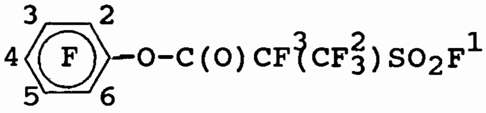
TABLE XIX

SUMMARY OF NMR SPECTRUM OF $(\overset{5}{CF_3})_2\overset{4}{C}HOC(O)\overset{3}{C}F(\overset{2}{CF_3})SO_2\overset{1}{F}$

Chemical Shift	Coupling Constant	Integration
$\phi_1 = 50.6$	$J_{1,2} = 9.9$	1.0
$\phi_2 = -74.4$	$J_{2,3} = 7.8$	2.7
$\phi_3 = -166.6$	$J_{3,1} = 3.5$	1.0
$\phi_4 = 5.9$	$J_{4,5} = 5.4$	1.0
$\phi_5 = -75.1$		5.9

TABLE XX

SUMMARY OF NMR SPECTRUM OF



Chemical Shift	Coupling Constant	Integration
$\phi_1 = 50.1$	$J_{1,2} = 9.9$	1.1
$\phi_2 = -74.0$	$J_{2,3} = 7.8$	2.9
$\phi_3 = -162.7$	$J_{3,1} = 3.5$	1.0
$\phi_{ortho} = -155.1$		2.1
$\phi_{para} = -157.1$		1.1
$\phi_{meta} = -164.1$		2.1

TABLE XXI

SUMMARY OF NMR SPECTRUM OF $C\overset{5}{H_3}C\overset{4}{H_2}OC(O)C\overset{3}{F}(C\overset{2}{F_3})SO_2\overset{1}{F}$

Chemical Shift	Coupling Constant	Integration
$\phi_1 = 50.5$	$J_{1,2} = 9.9$	1.0
$\phi_2 = -75.0$	$J_{2,3} = 7.8$	3.1
$\phi_3 = -162.6$	$J_{3,1} = 3.5$	1.0
$\phi_4 = 4.55$	$J_{4,5} = 7.5$	---
$\phi_5 = 1.5$		---

TABLE XXII

SUMMARY OF NMR SPECTRUM OF $C\overset{5}{F_3}C\overset{4}{H_2}OC(O)C\overset{3}{F}(C\overset{2}{F_3})SO_2\overset{1}{F}$

Chemical Shift	Coupling Constant	Integration
$\phi_1 = 49.6$	$J_{1,2} = 9.9$	1.0
$\phi_2 = -74.4$	$J_{2,3} = 7.8$	3.1
$\phi_3 = -162.9$	$J_{3,1} = 3.5$	1.1
$\phi_4 = 4.82$	$J_{4,5} = 7.5$	---
$\phi_5 = -76.0$		

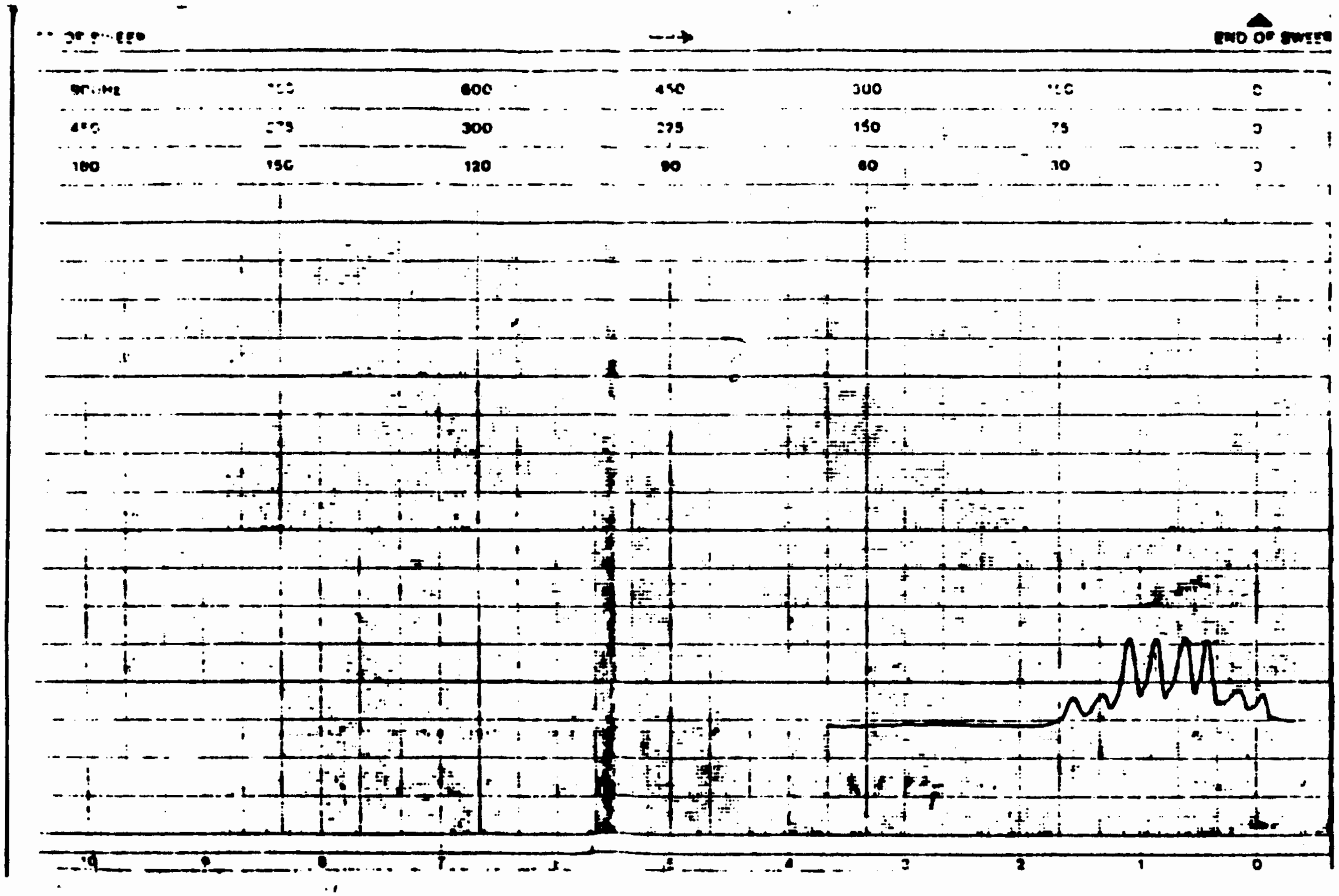


Figure 10. Fluorine nmr spectrum of $(CF_3)_2CHOC(O)CF(CF_3)SO_2F$, CF region.

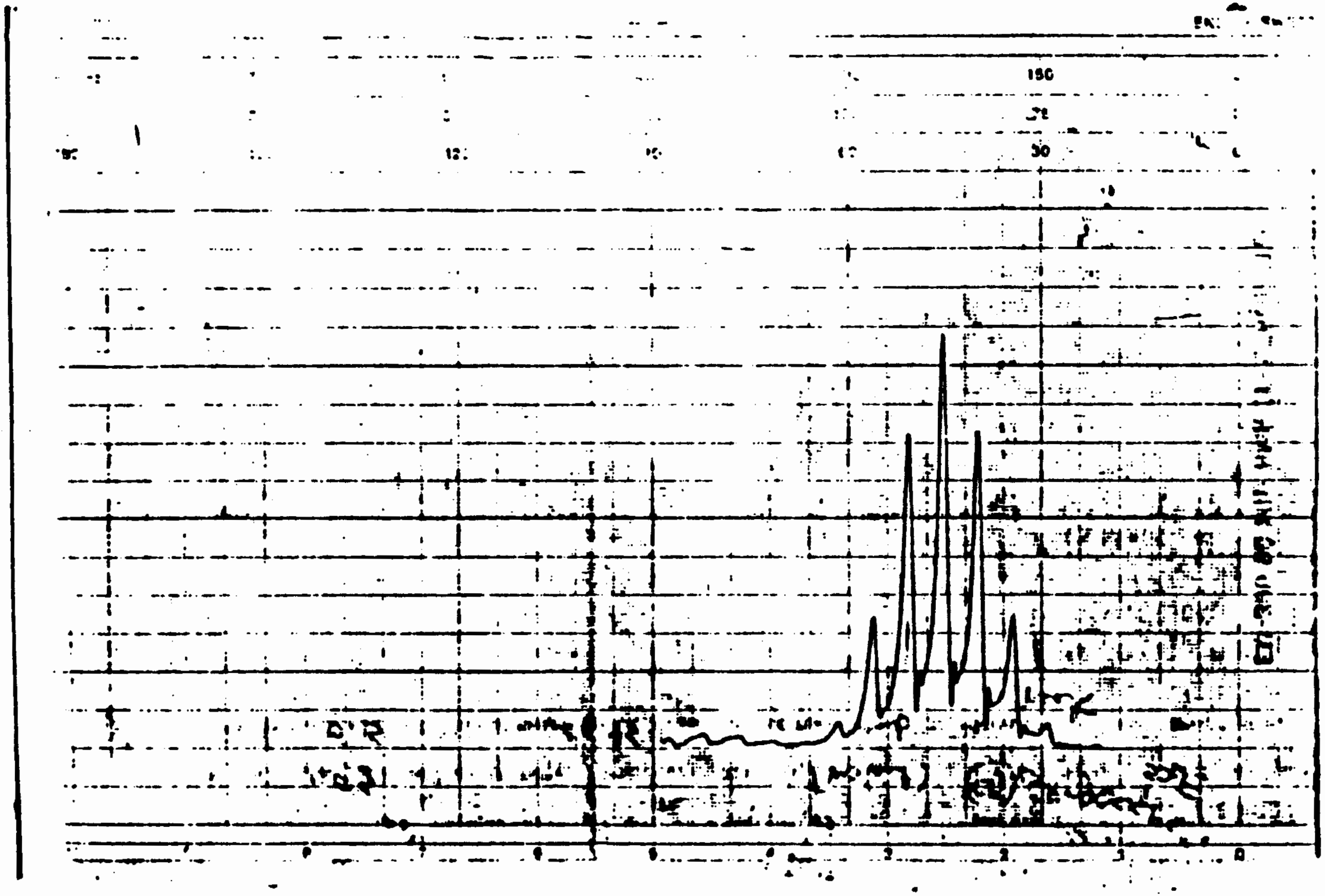


Figure 11. Proton nmr spectrum of $(CF_3)_2CHOC(O)CF(CF_3)SO_2F$.

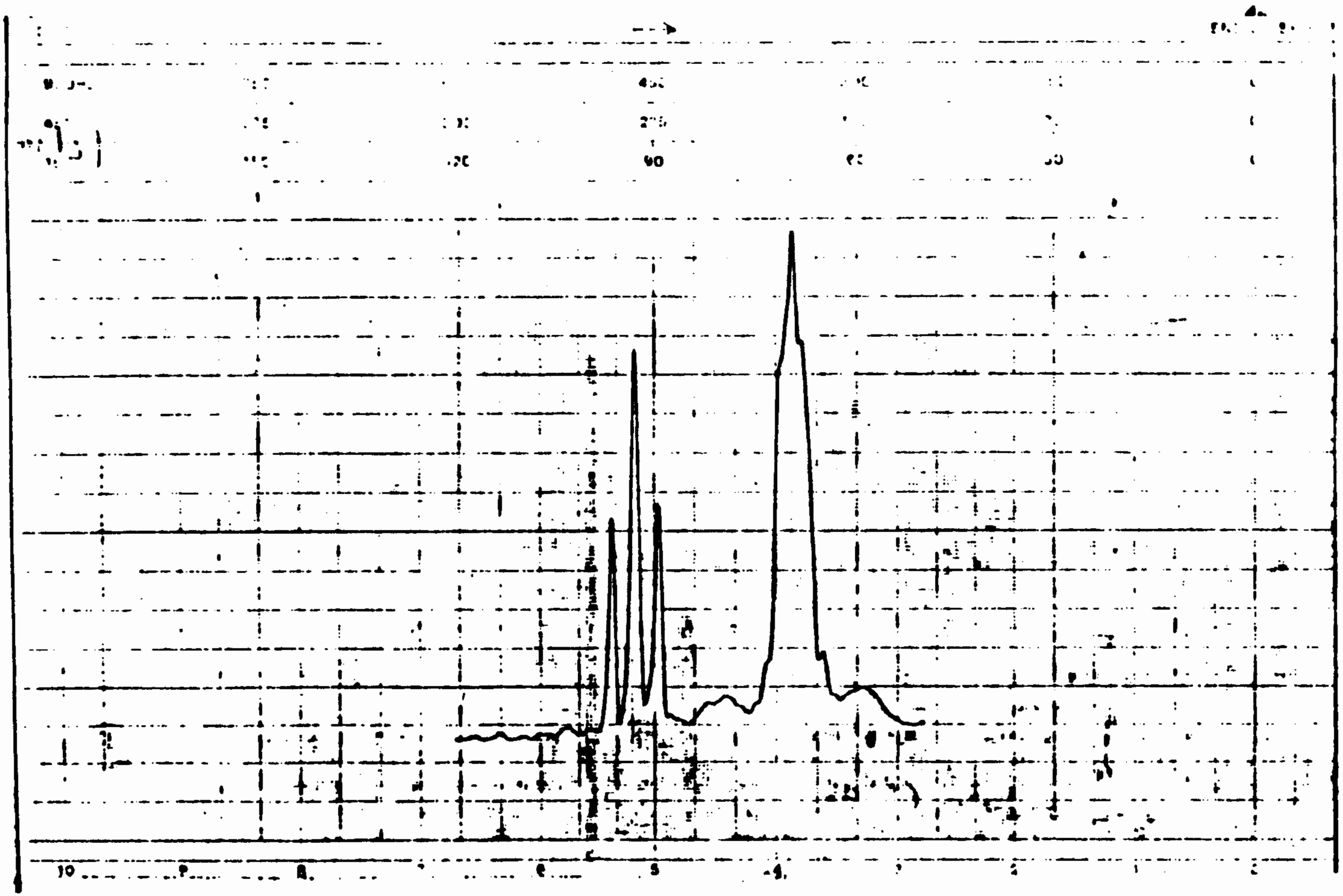


Figure 12. Fluorine nmr spectrum of $(CF_3)_2CHOC(O)CF(CF_3)SO_2F$, CF_3 region.

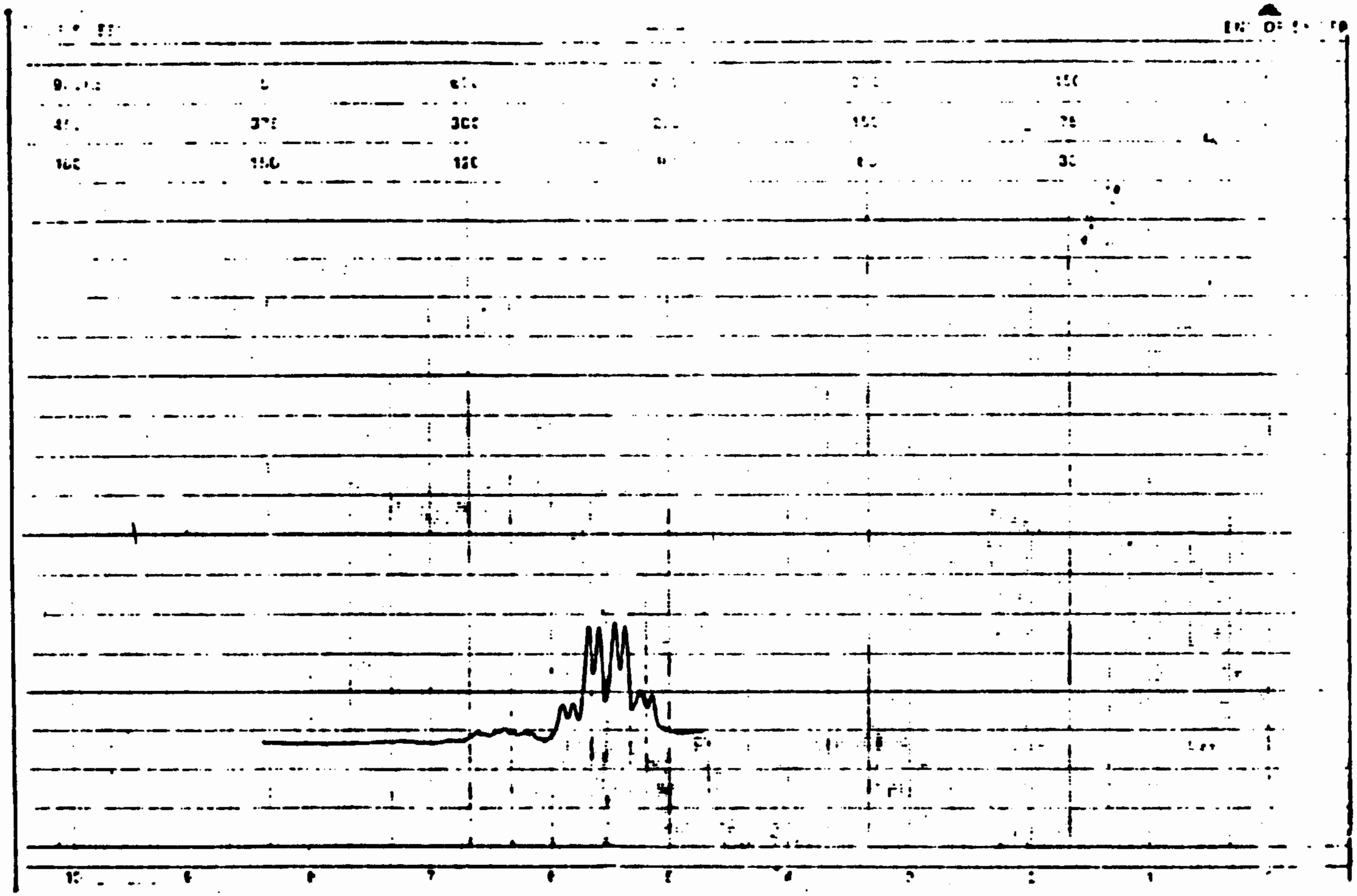


Figure 13. Fluorine nmr spectrum of $(CF_3)_2CHOC(O)CF(CF_3)SO_2F$, SF region.

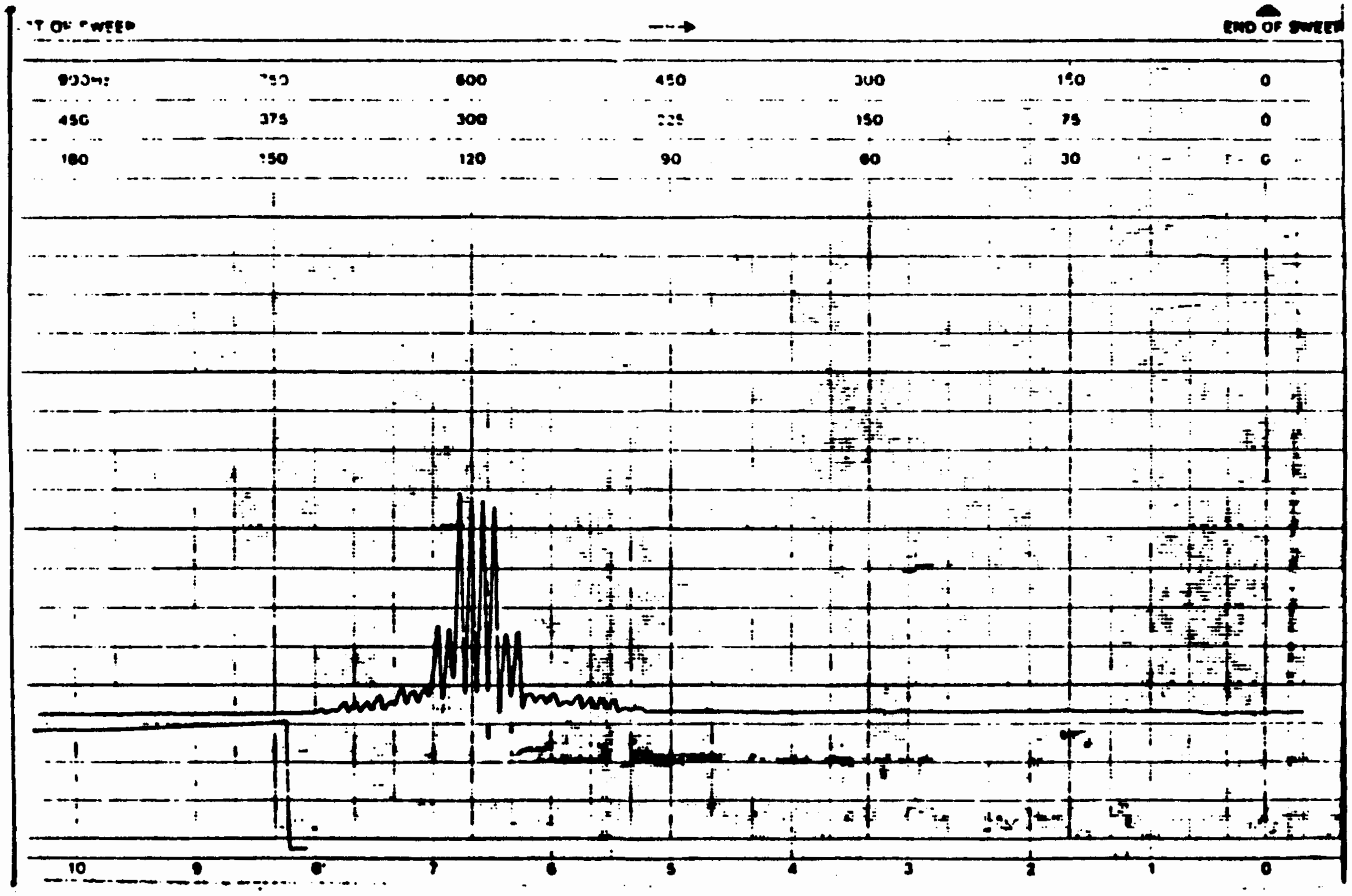


Figure 14. Fluorine nmr spectrum of CH_2=$CHCH_2OC(O)CF(CF_3)SO_2F$, CF region.

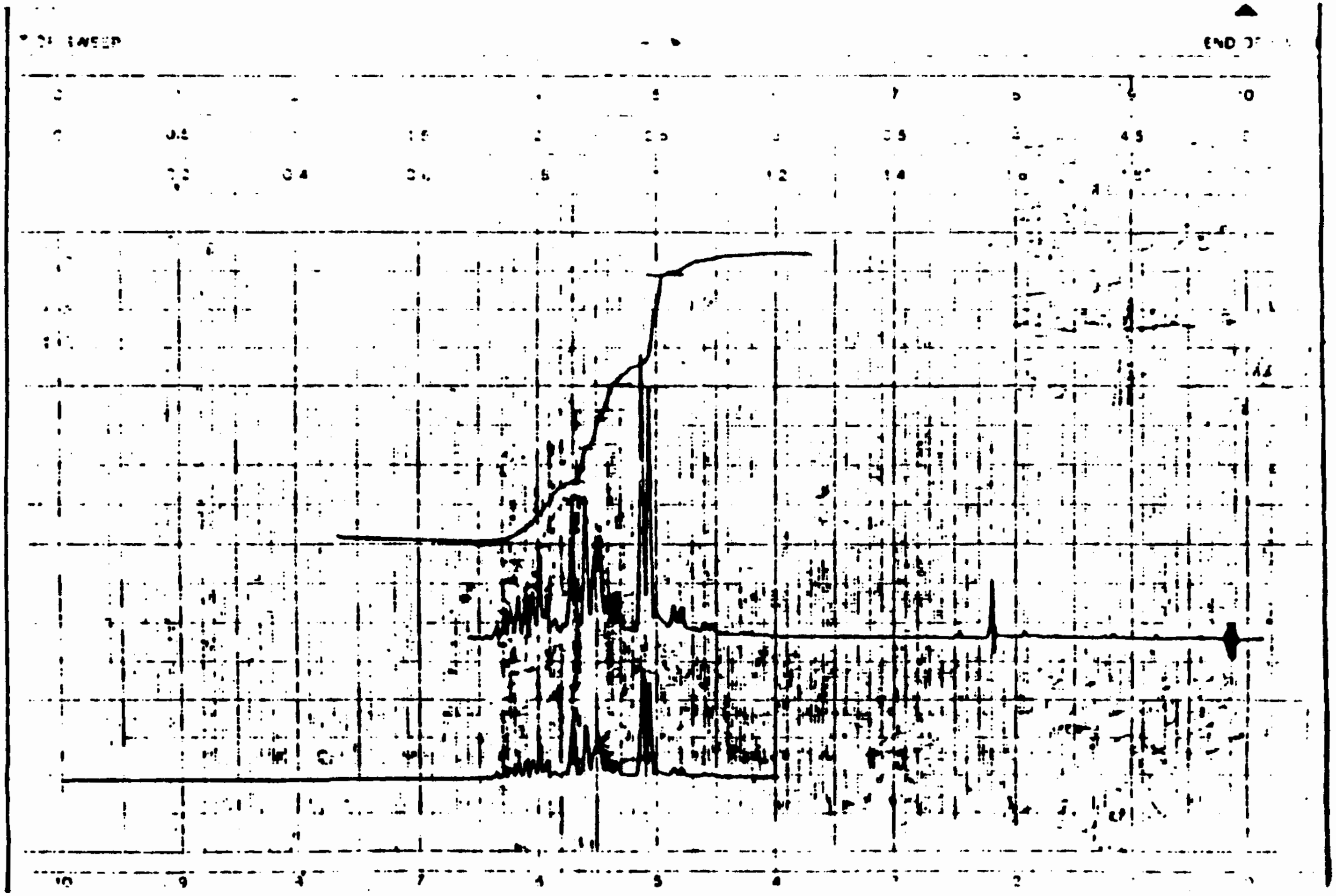


Figure 15. Proton nmr spectrum of $CH_2=CHCH_2OC(O)CF(CF_3)SO_2F$.

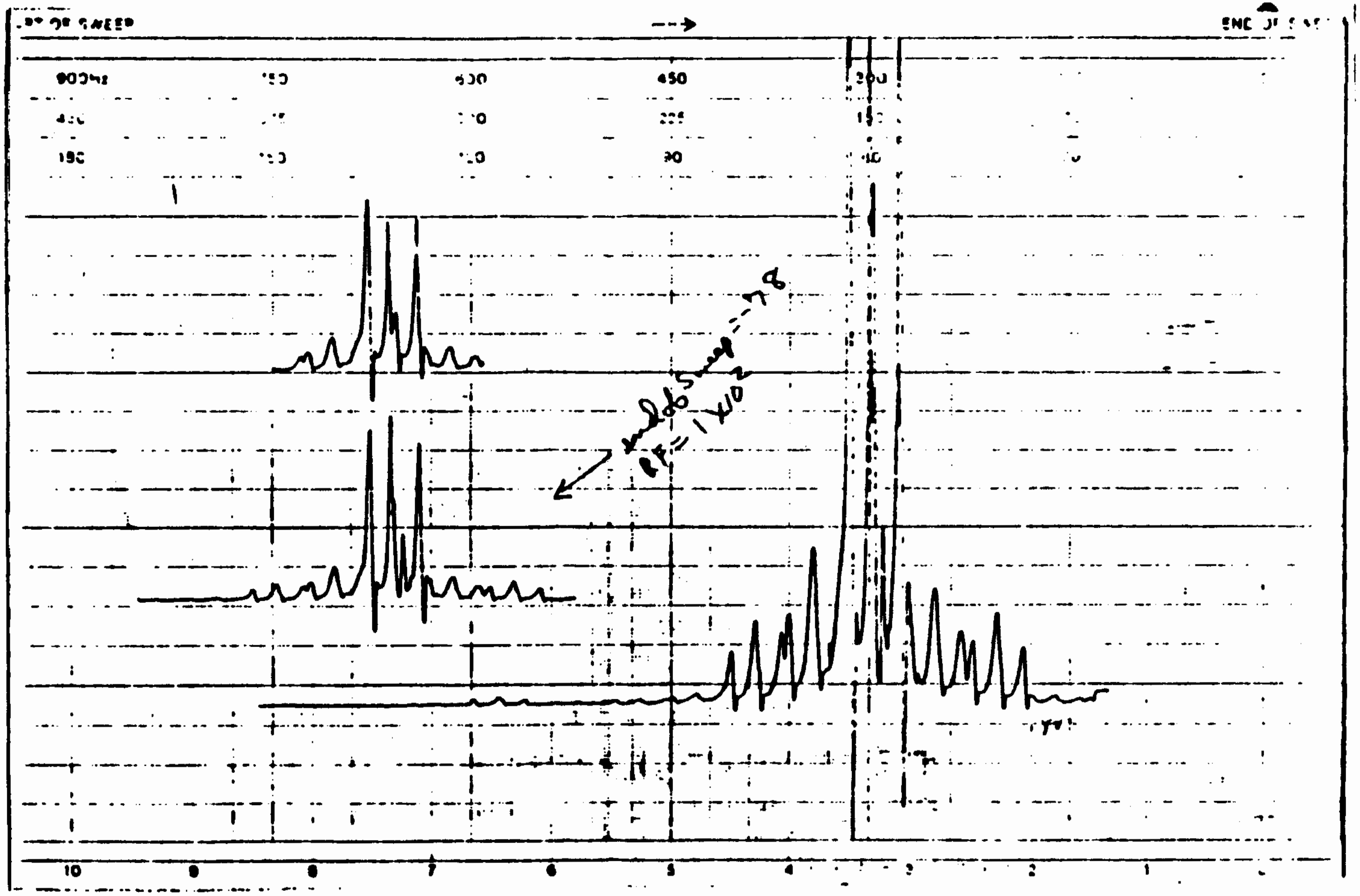


Figure 16. Fluorine nmr spectrum of $CH_2=CHCH_2OC(O)CF(CF_3)SO_2F$, CF_3 region.

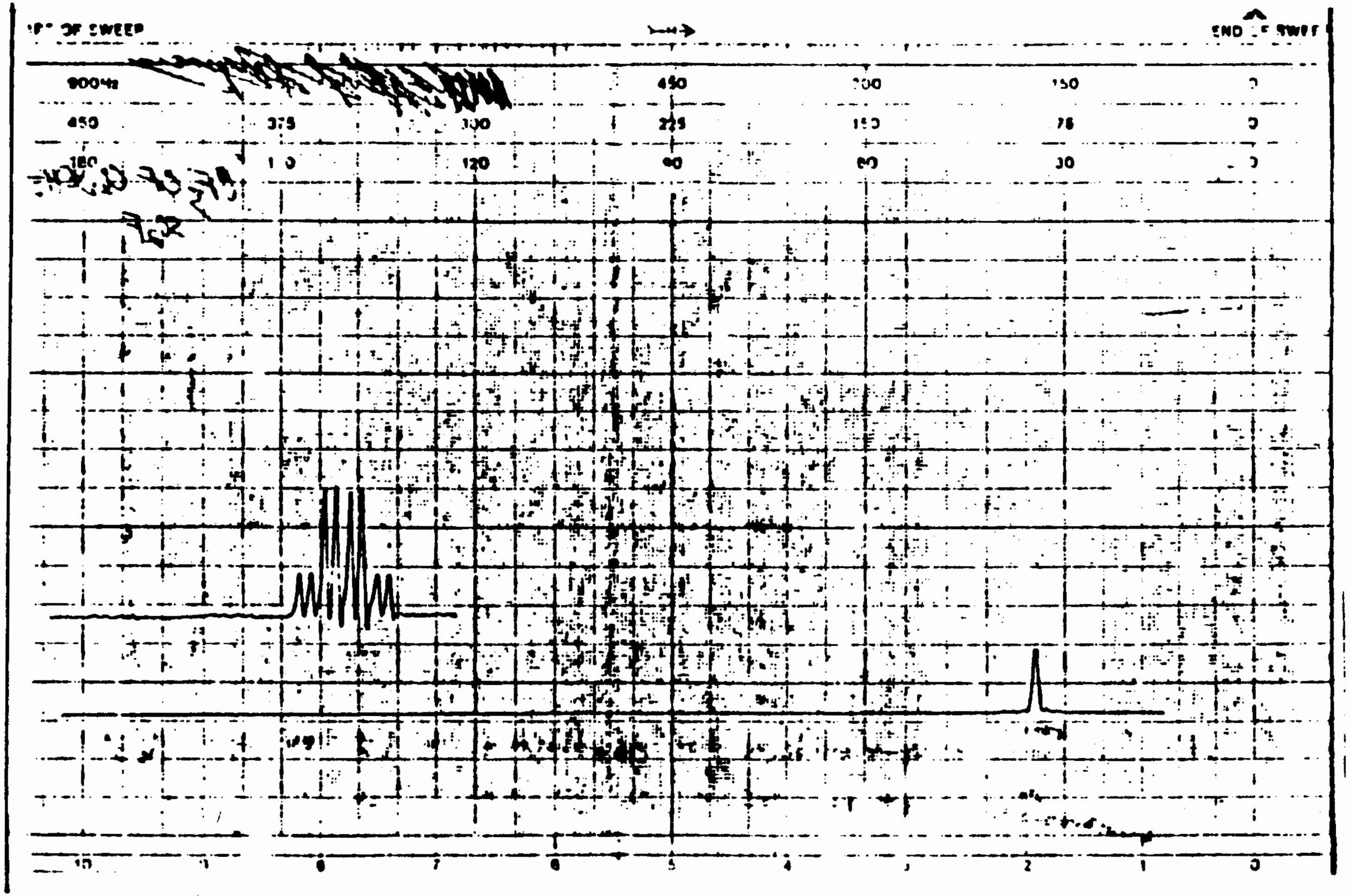


Figure 17. Fluorine nmr spectrum of $CH_2=CHCH_2OC(O)CF(CF_3)SO_2F$, SF region.

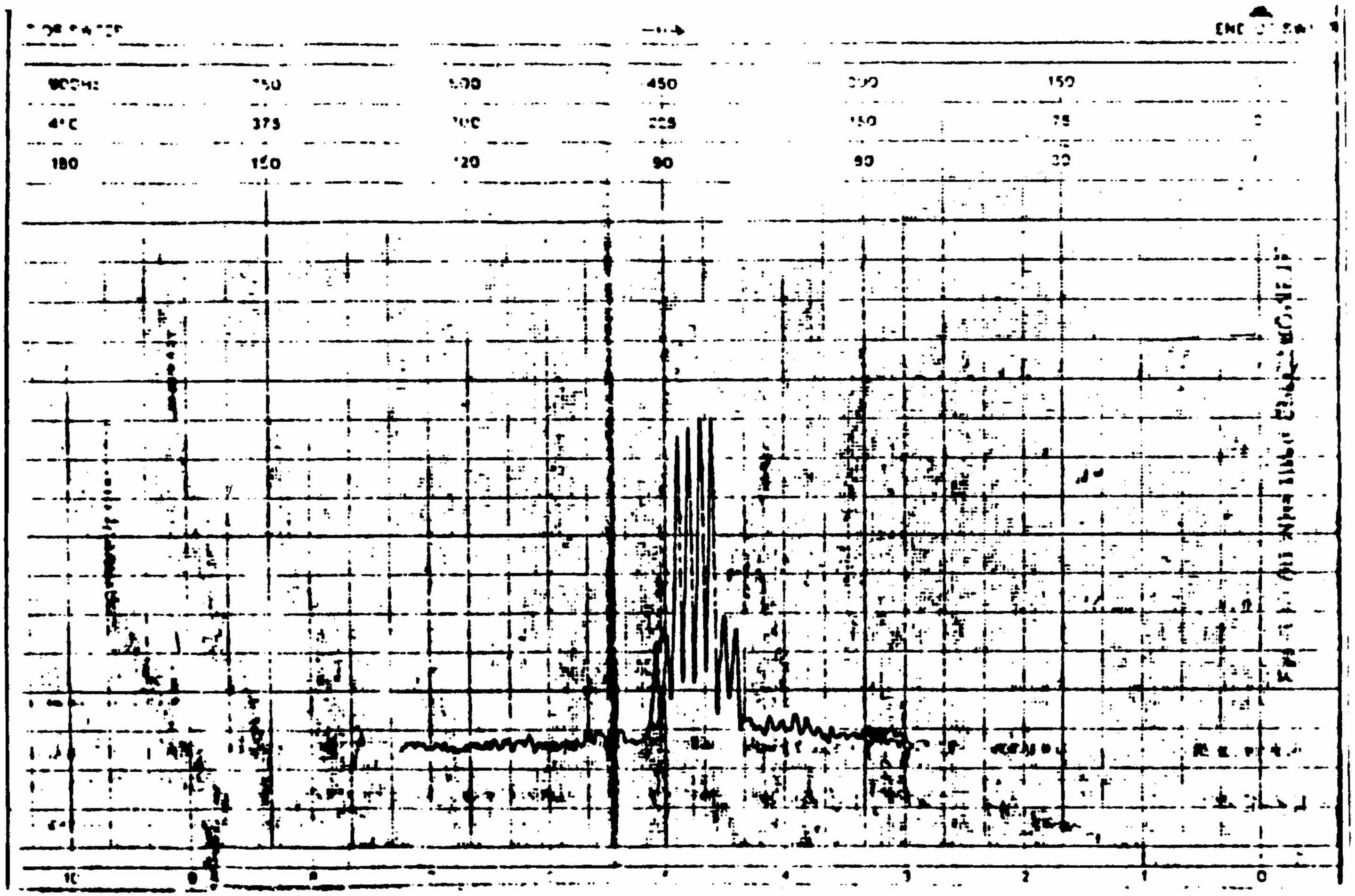


Figure 18. Fluorine nmr spectrum of $CH_3CH_2OC(O)CF(CF_3)SO_2F$, CF region.

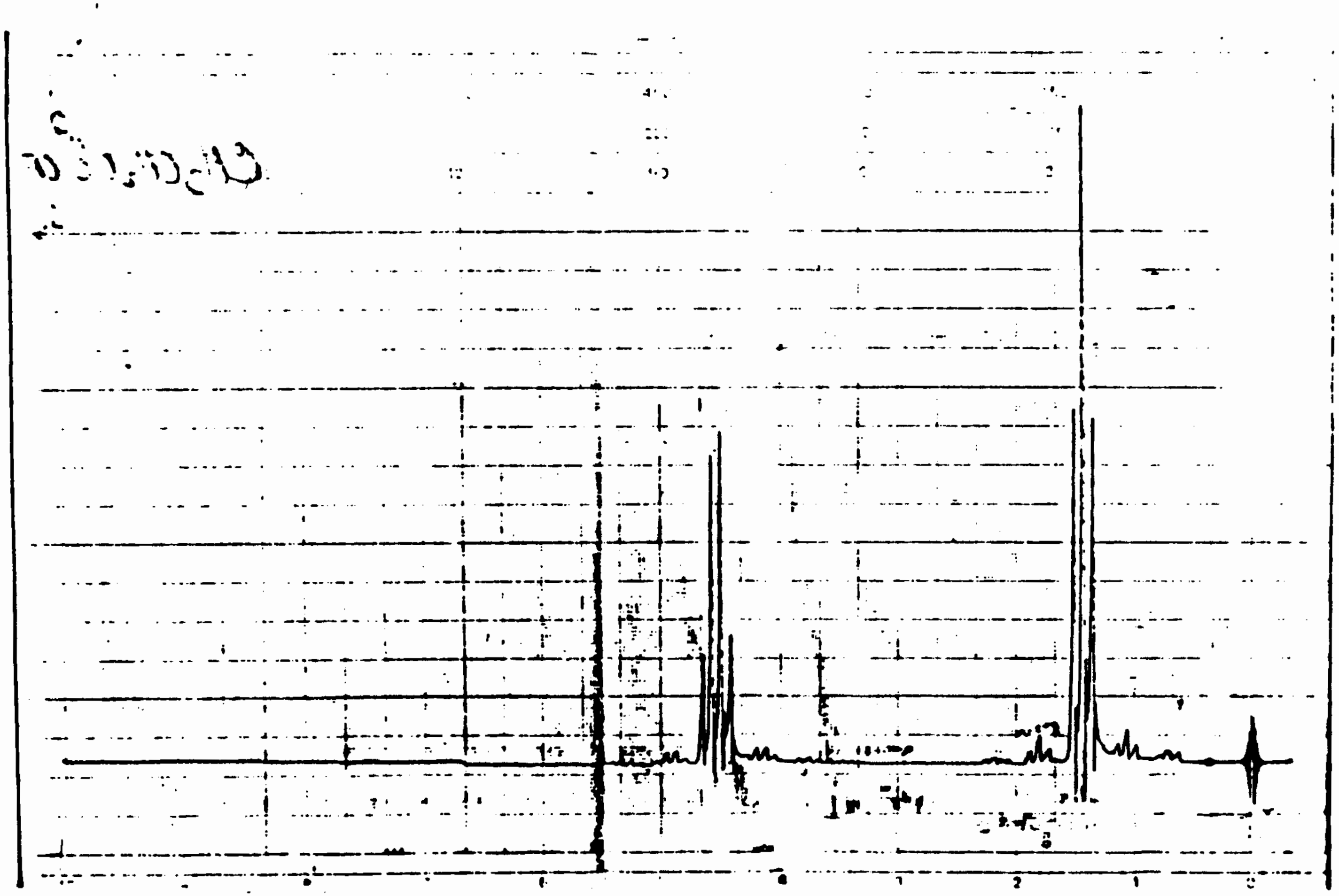
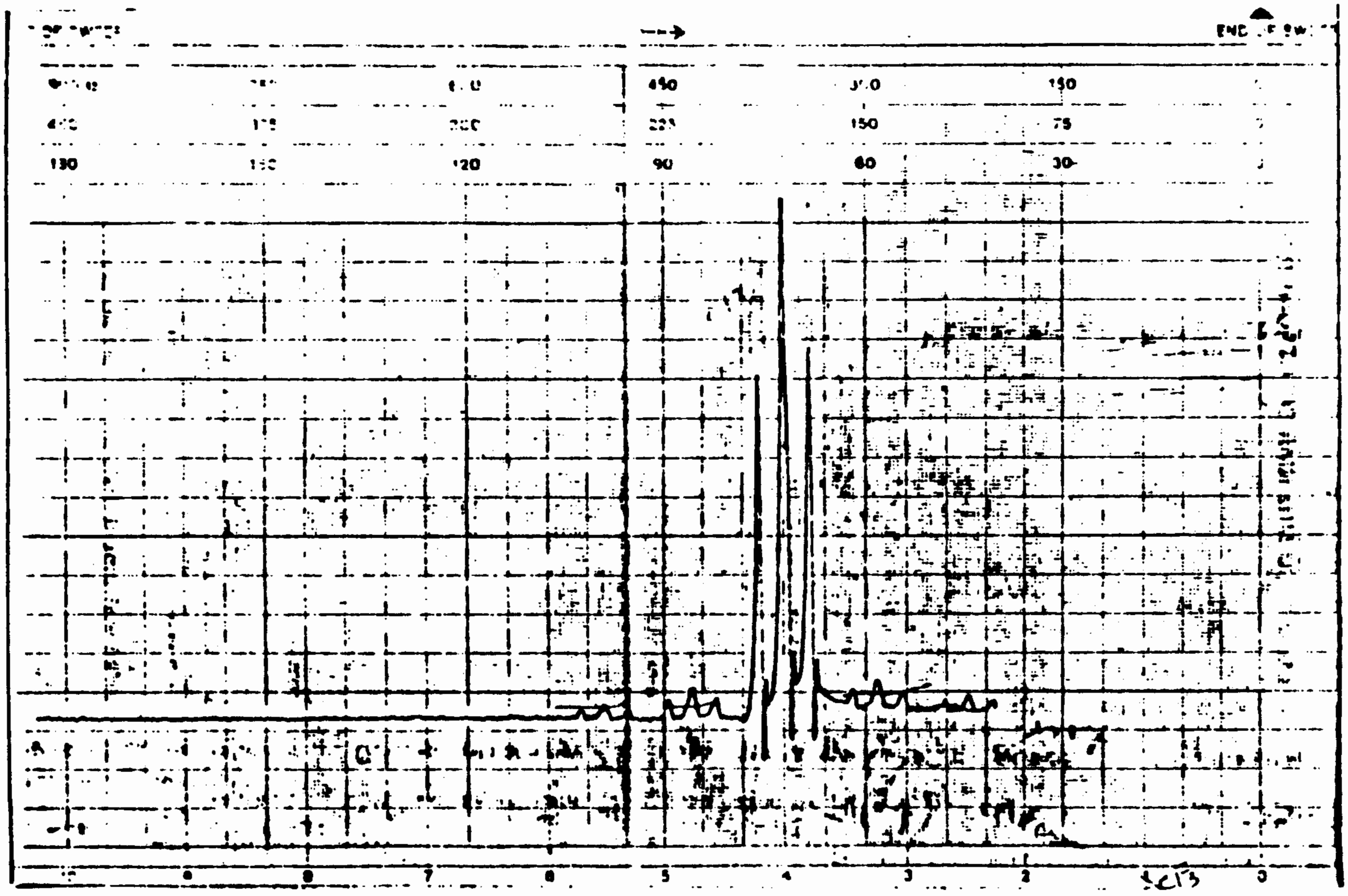


Figure 19. Proton nmr spectrum of $CH_3CH_2OC(O)CF(CF_3)SO_2F$.



<u>Figure 20</u>. Fluorine nmr spectrum of $CH_3CH_2OC(O)CF(CF_3)SO_2F$, CF_3 region.

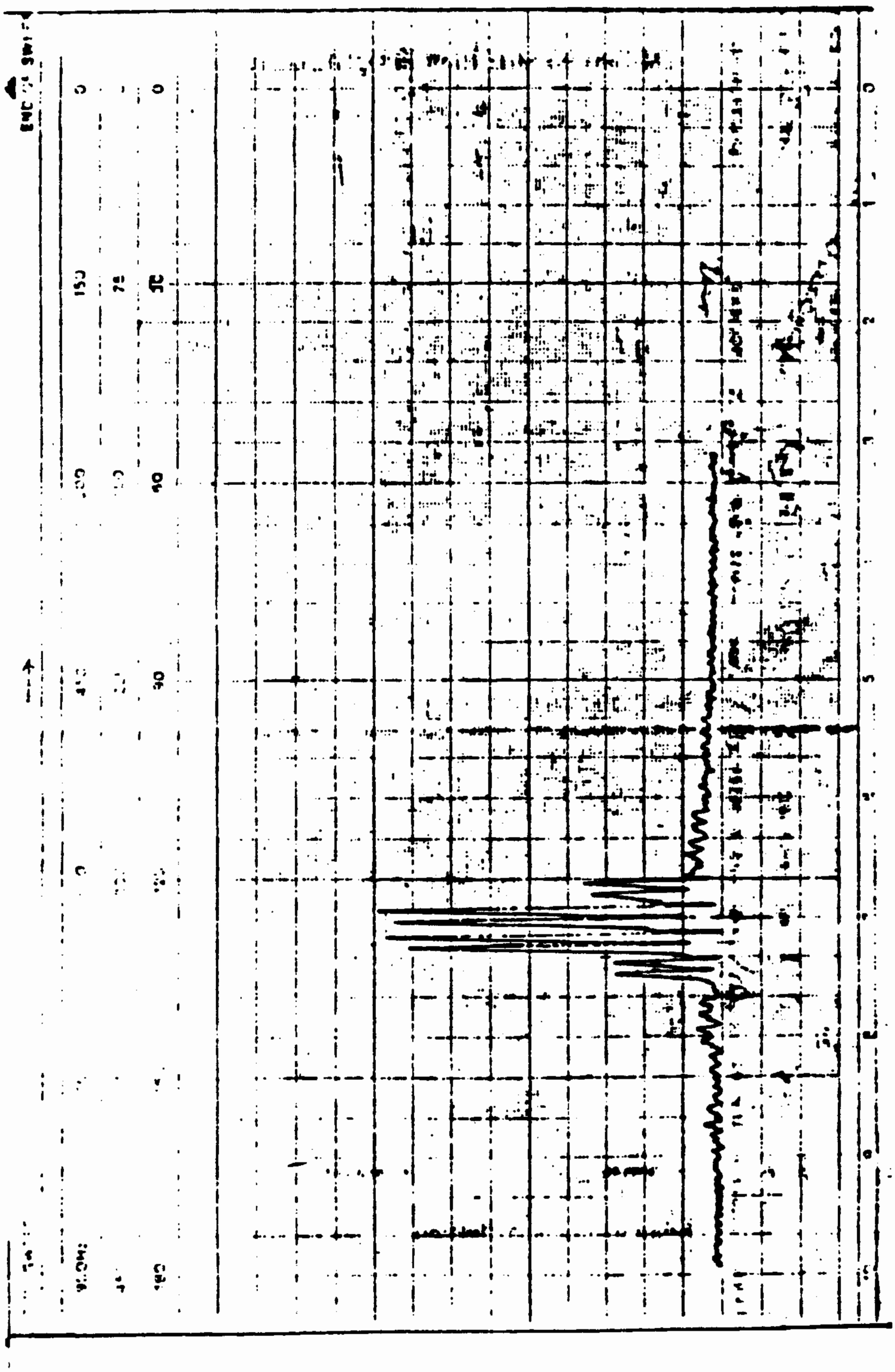


Figure 21. Fluorine nmr spectrum of $CH_3CH_2OC(O)CF(CF_3)SO_2F$, SF region.

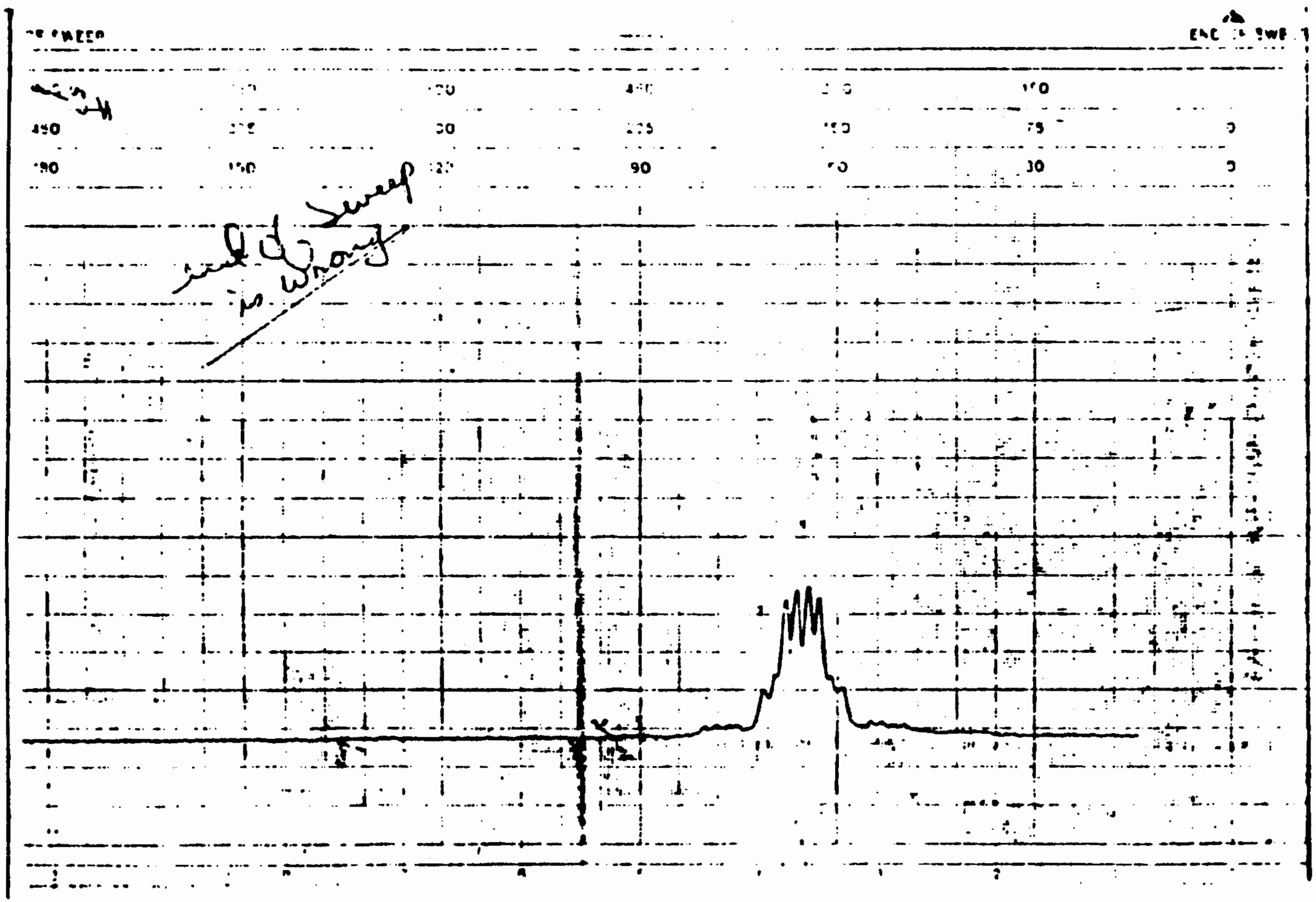


Figure 22. Fluorine nmr spectrum of $(CH_2OC(O)CF(CF_3)SO_2F)_2$, CF region.

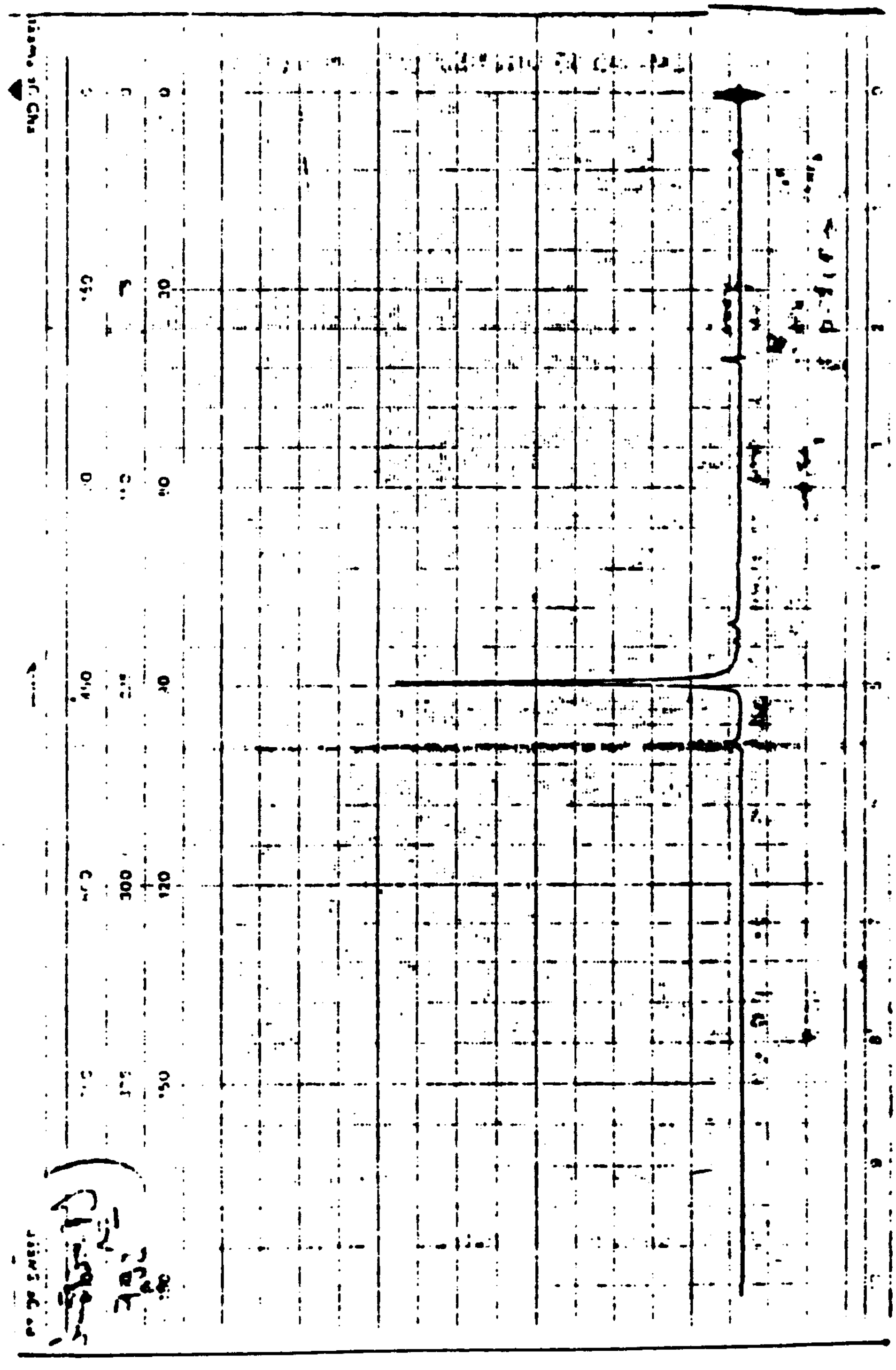


Figure 23. Proton nmr spectrum of $(CH_2OC(O)CF(CF_3)SO_2F)_2$.

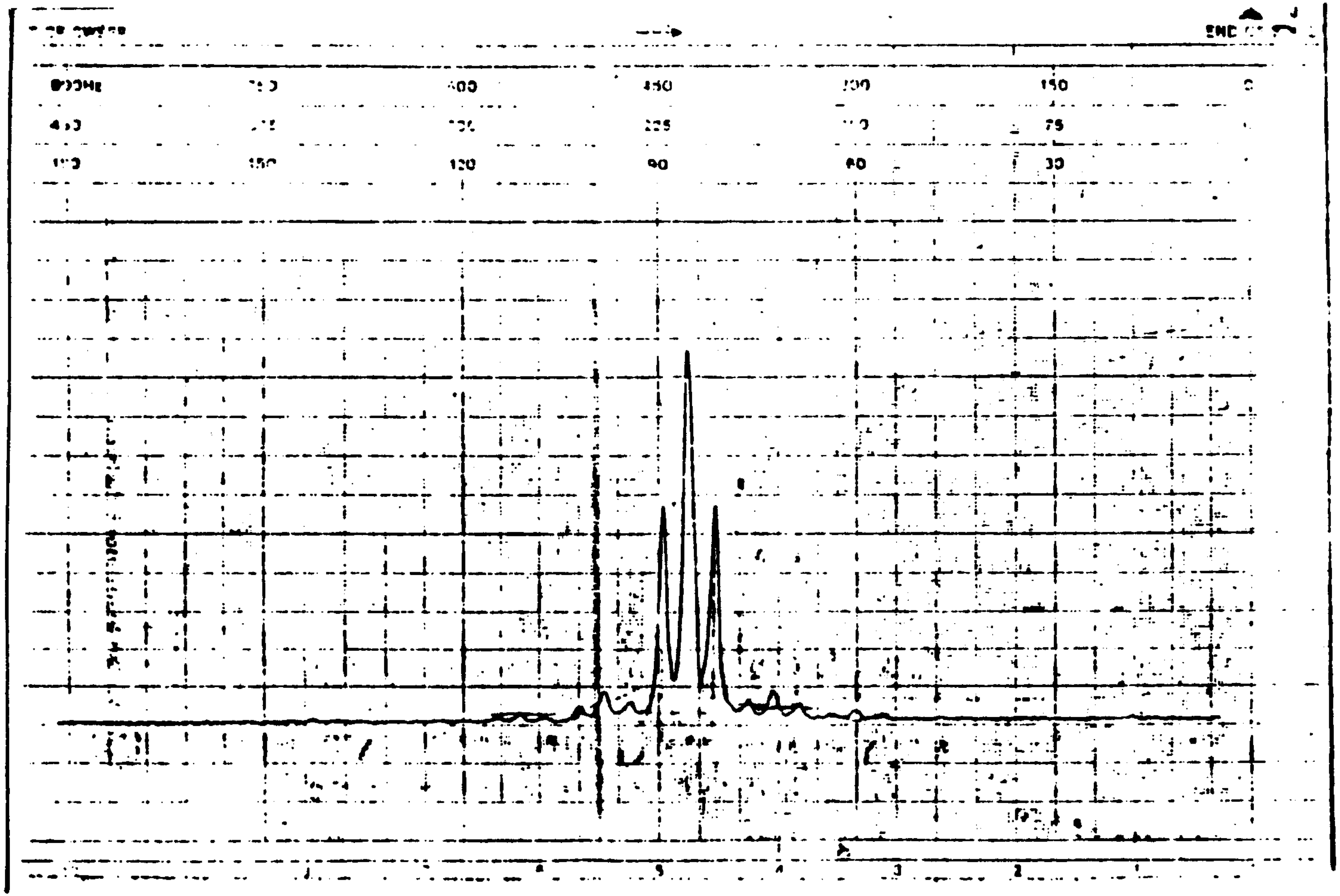


Figure 24. Fluorine nmr spectrum of $(CH_2OC(O)CF(CF_3)SO_2F)_2$, CF_3 region.

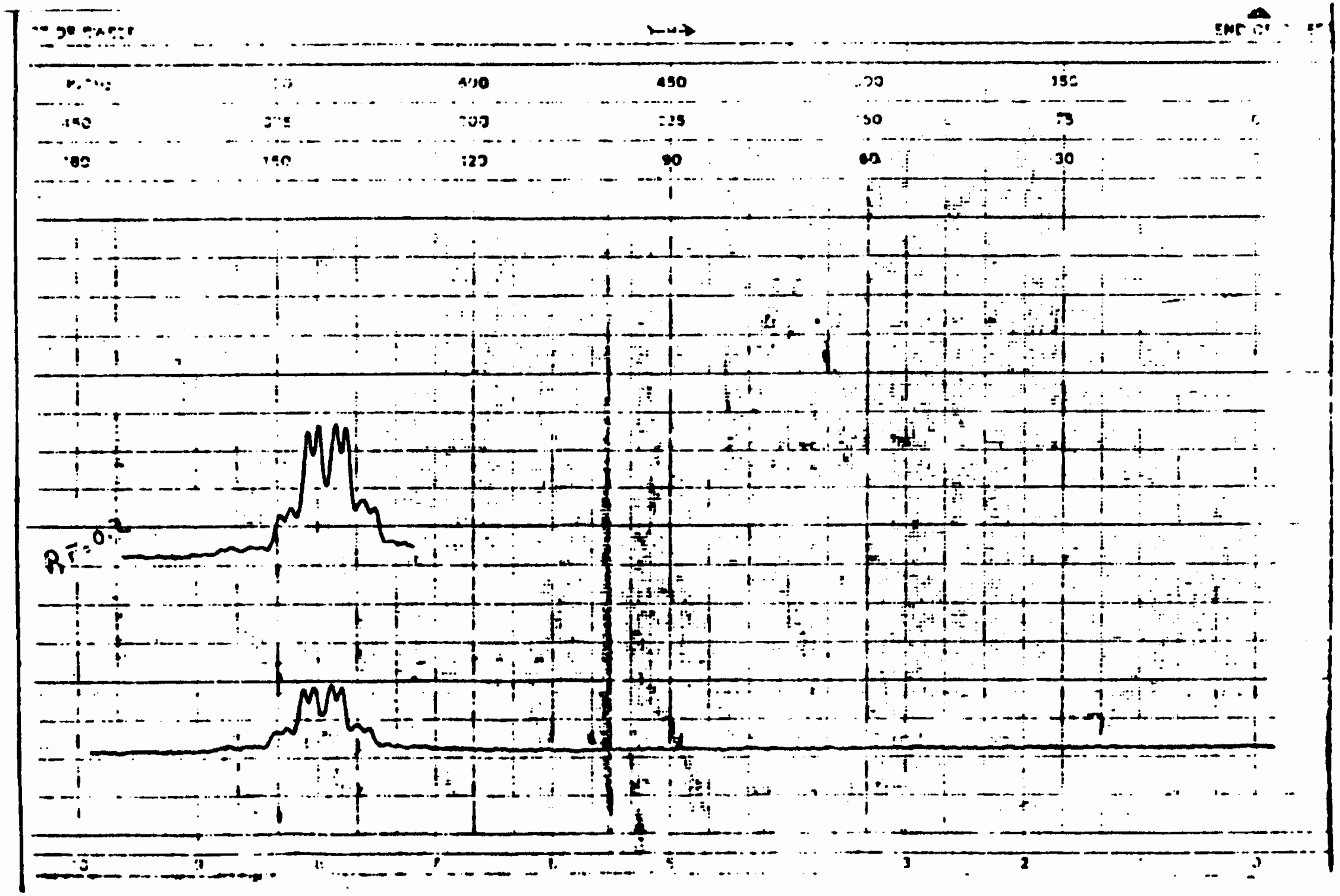


Figure 25. Fluorine nmr spectrum of $(CH_2OC(O)CF(CF_3)SO_2F)_2$, SF region.

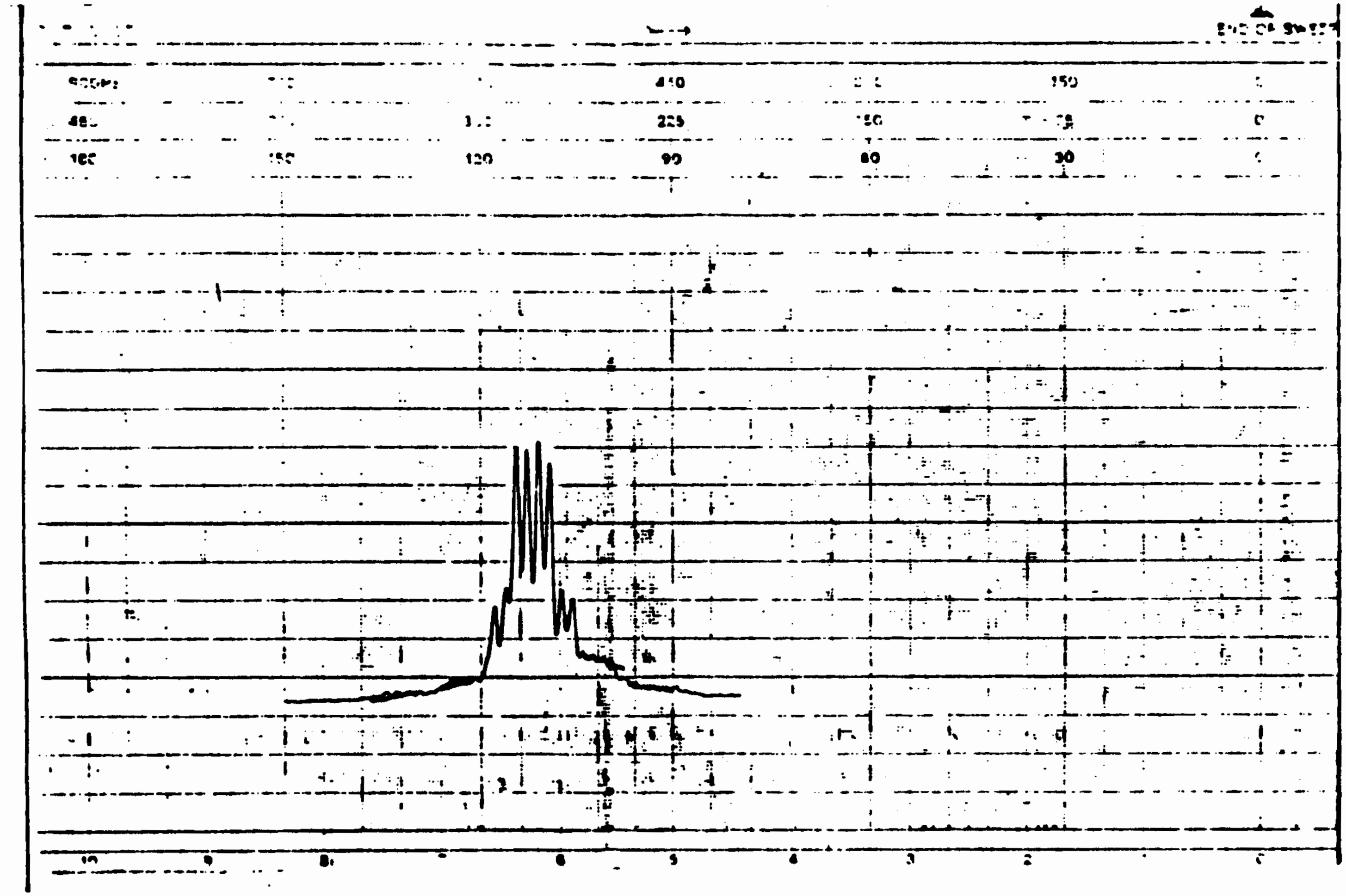


Figure 26. Fluorine nmr spectrum of $CF_3CH_2OC(O)CF(CF_3)SO_2F$, CF region.

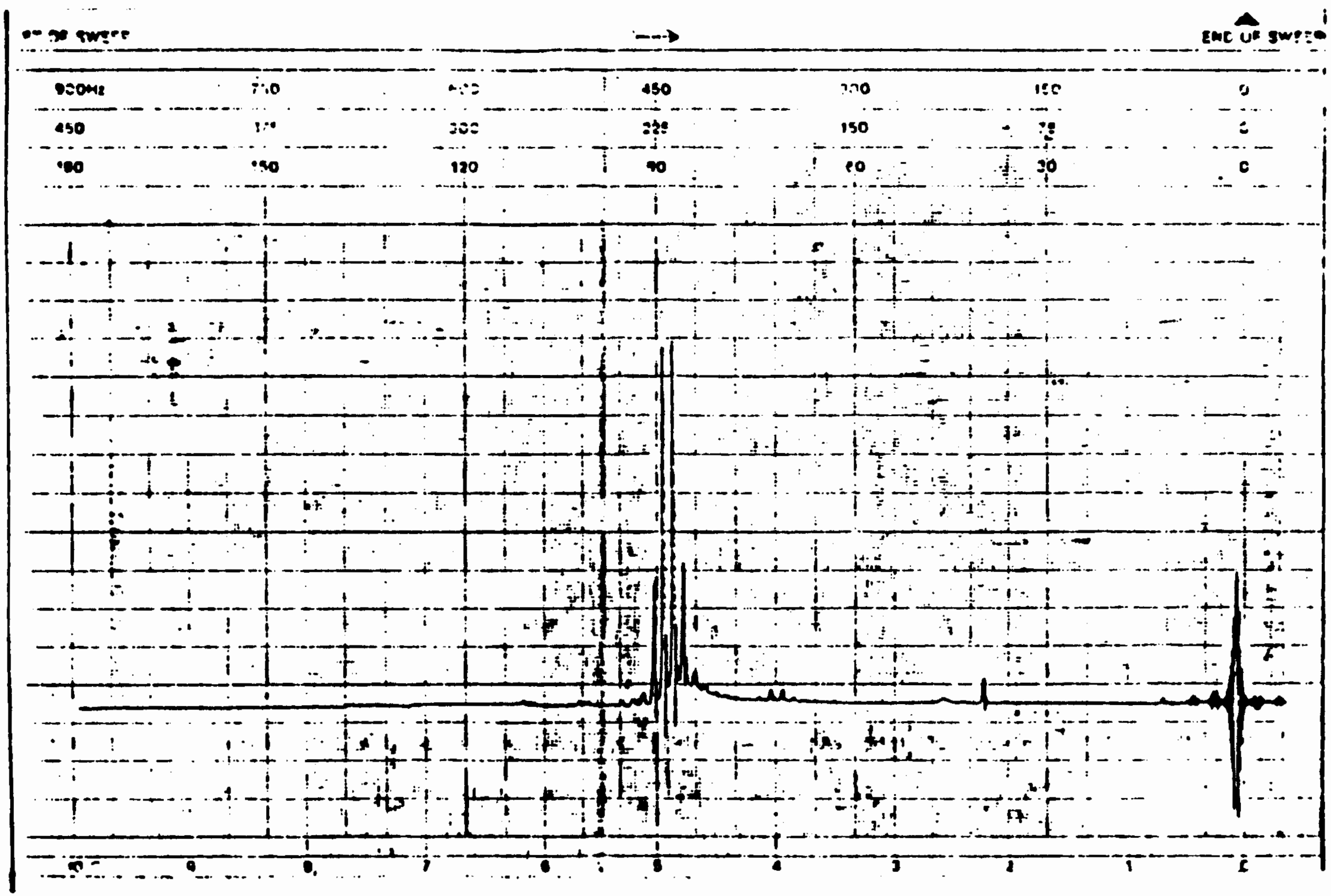


Figure 27. Proton nmr spectrum of $CF_3CH_2OC(O)CF(CF_3)SO_2F$.

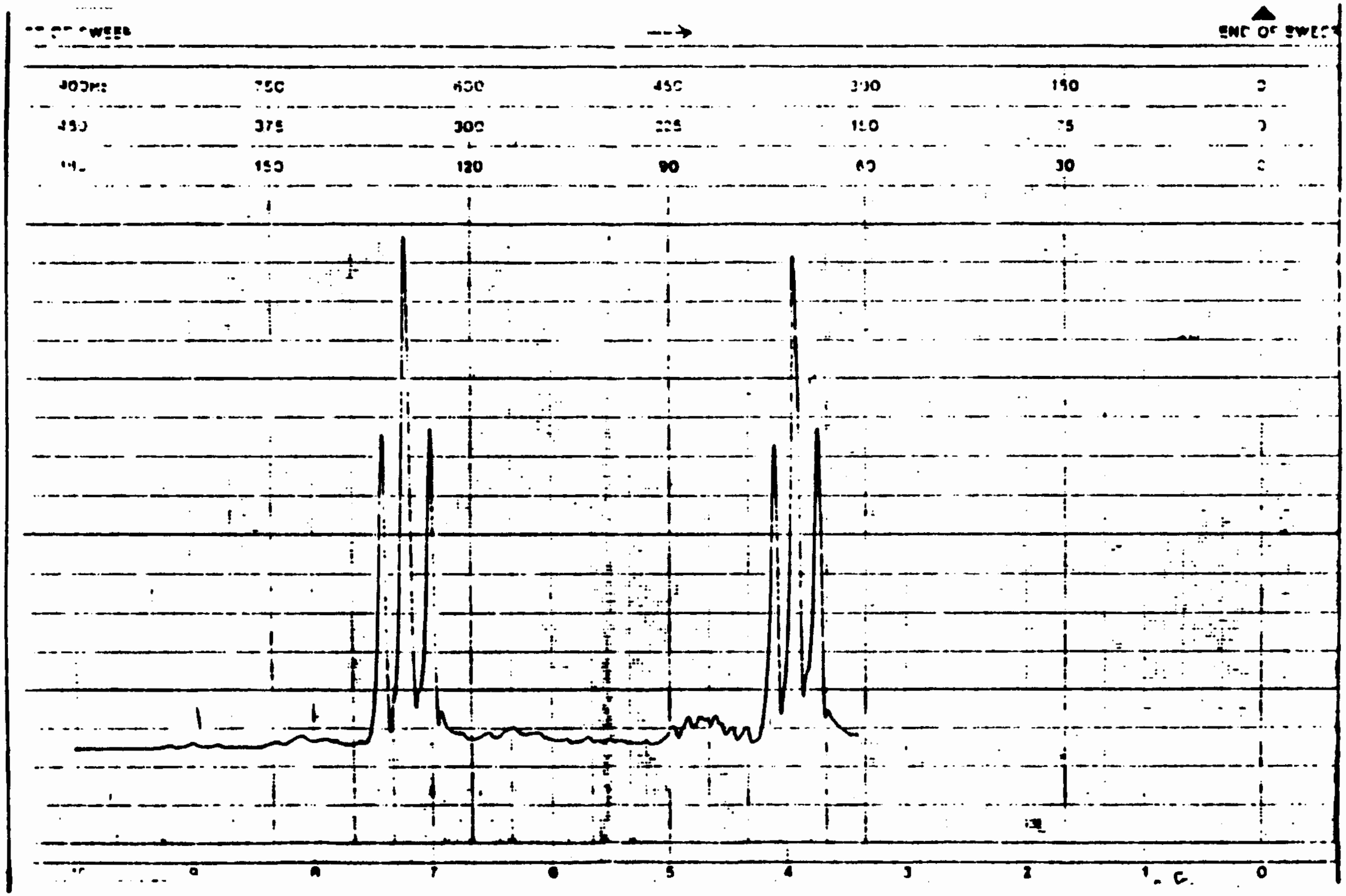


Figure 28. Fluorine nmr spectrum of $CF_3CH_2OC(O)CF(CF_3)SO_2F$, CF_3 region.

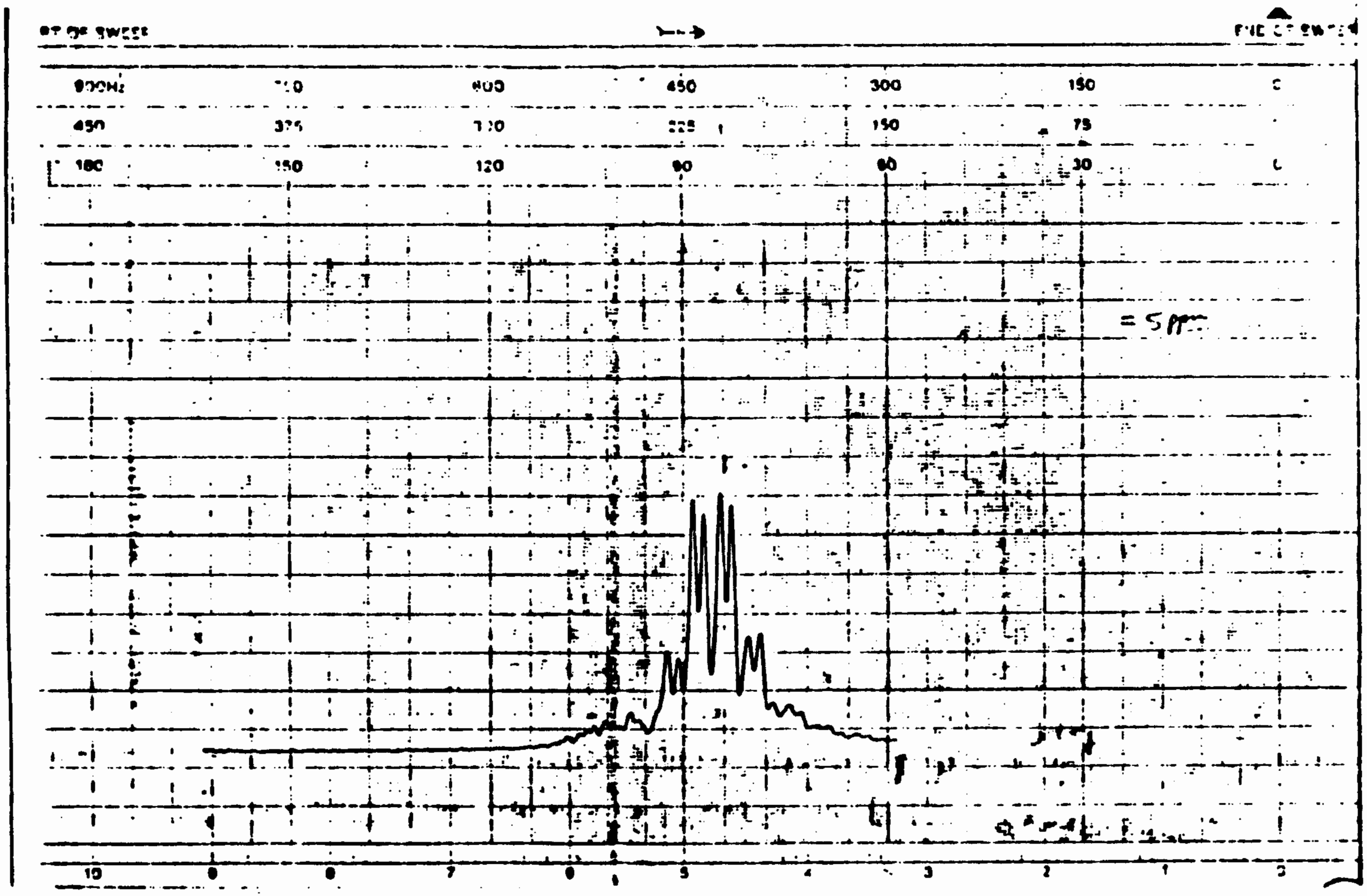


Figure 29. Fluorein nmr spectrum of $CF_3CH_2OC(O)CF(CF_3)SO_2F$, SF region.

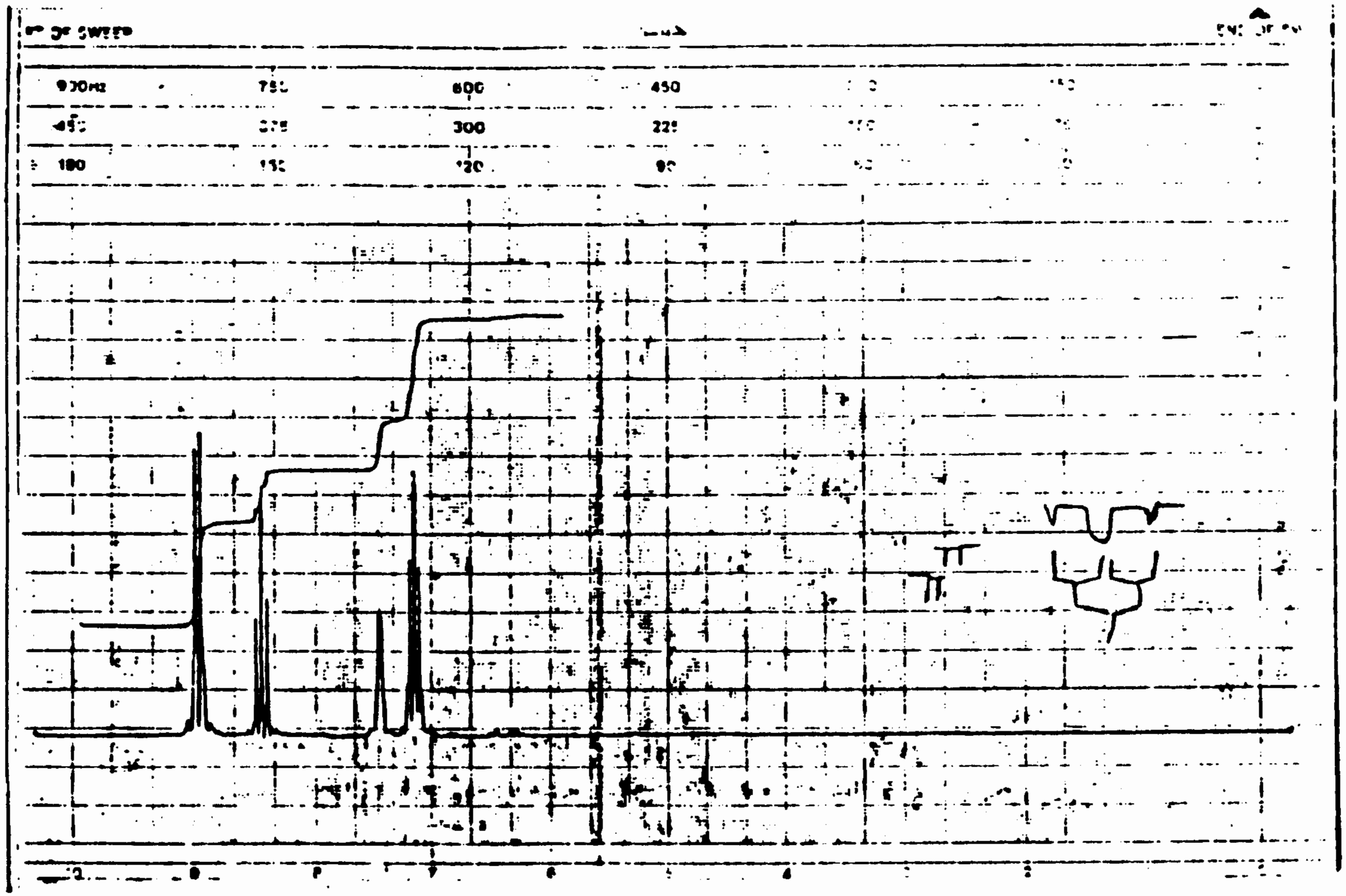


Figure 30. Fluorine nmr spectrum of $C_6F_5OC(O)CF(CF_3)SO_2F$, CF region.

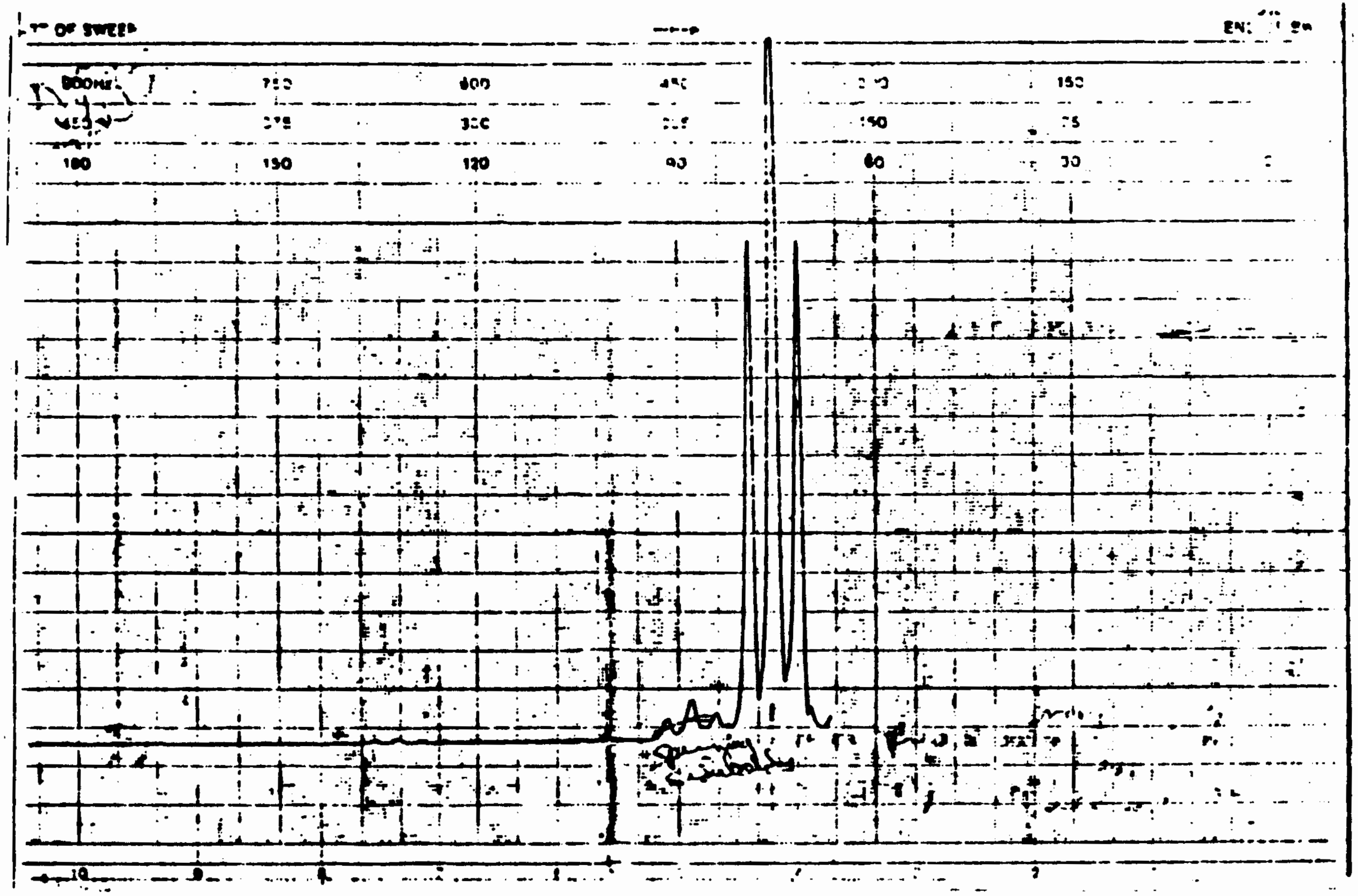


Figure 31. Fluorine nmr spectrum of $C_6F_5OC(O)CF(CF_3)SO_2F$, CF_3 region.

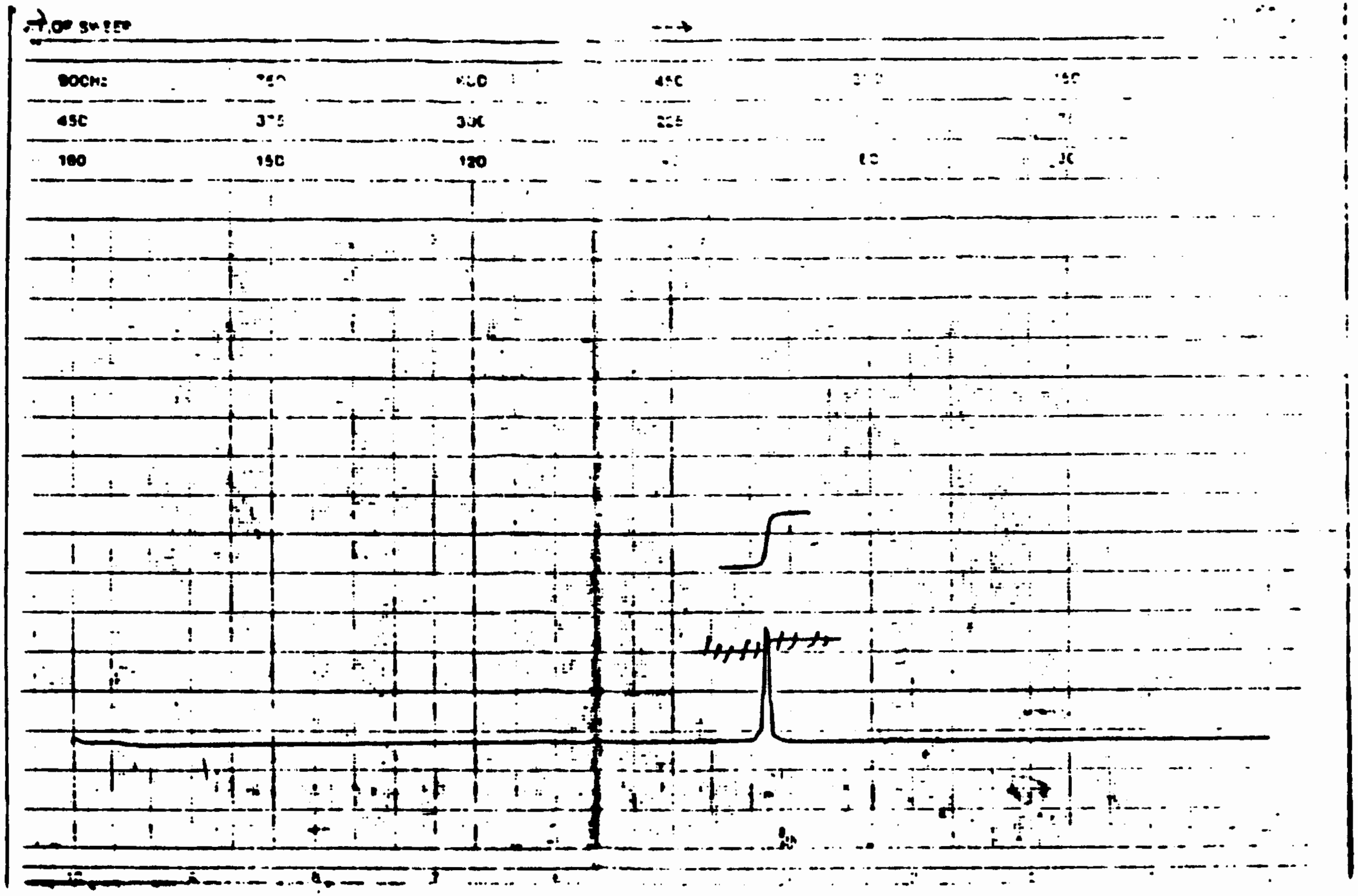


Figure 32. Fluorine nmr spectrum of $C_6F_5OC(O)CF(CF_3)SO_2F$, SF region.

Elemental Analysis

The esters were analyzed by Beller Microanalytical Laboratory for C, H, S and F. There was good agreement between the calculated and experimental values as shown in the Table XXV.

TABLE XXV

ELEMENTAL ANALYSIS OF FLUORINATED ESTERS: (THEORETICAL/EXPERIMENTAL)

		C	H	S	F
1.	$CF_3CH_2OC(O)CF(CF_3)SO_2F$	19.36	0.65	10.34	49.0
		19.49	0.67	10.37	49.2
2.	$(CF_3)_2CHOC(O)CF(CF_3)SO_2F$	19.06	0.27	8.48	55.3
		19.19	0.38	8.68	55.6
3.	$CH_3CH_2OC(O)CF(CF_3)SO_2F$	23.44	1.97	12.52	37.1
		23.54	1.99	12.61	37.4
4.	$CH_2{=}CHCH_2OC(O)CF(CF_3)SO_2F$	26.87	1.88	11.96	48.2
		26.71	1.96	12.17	47.9
5.	$C_6F_5OC(O)CF(CF_3)SO_2F$	27.42	----	8.13	48.2
		27.53		7.89	47.9
6.	$CH_2CH_2[O{-}C(O)CF(CF_3)SO_2F]_2$	19.93	0.84	13.30	39.40
		20.17	0.91	13.34	38.9

CHAPTER V

CONCLUSION

The methods discussed in the introduction part of this report, were a compilation of different methods of preparation of fluorinated esters. As was mentioned earlier, these esters have a wide range of applicability. The esters reported here have proven to be important in the synthesis of fluorinated esters. The conversion of these esters to ethers was studied by DePasquale(60). The reaction involves:

$$R_fC(O)\text{-}OR_f + SF_4 \xrightarrow{HF} R_fC\text{-}O\text{-}R_f$$

The esters which were used in preparing the corresponding ethers were:

$C_7F_{15}CO_2CH_2C_2F_5$

$C_7F_{15}CO_2CH(CF_3)_2$

$C_7F_{15}CO_2C(CF_3)_3$

$(CF_3)_2CHOC(O)(CF_2)_4CO_2CH(CF_3)_2$

$C_2F_5O(CF_2CF_2O)_2CF_2CO_2CH_2C_2F_5$

The toxicity properties of some fluorinated esters was studied in detail by Saunders et al(13,14,15,16,17). They studied the toxicity of esters such as methyl fluoroacetate both as inhalant and direct injection into the blood stream of animals such as mice, rats, rabbits etc.

The investigators were actually so curious about the toxicity of these esters that they decided to test it themselves:

> When four of us were exposed to a concentration of 1:1,000,000 in a 10 M^3 chamber, we were unable to detect the compound. Even at 1:100,000 (30 seconds for reasons of safety) the compound was found to possess only a faint fruit like odor indistinguishable from that of many harmless esters not containing fluorine(17).

The thermal stability of three fluorinated esters was studied by Shraydih et al.(32), which resulted in the followings:

1. Ethyl Trifluoroacetate decomposes between 311-413°C at pressures from 25 to 100 Torr.
2. Isopropyl trifluoroacetate decomposes between 278-352°C at pressures from 20 to 100 Torr.
3. <u>t</u>-butyl trifluoroacetate decomposes at 111-181°C, the mechanism of this decomposition is proposed to be:

$$CF_3CO_2CH_2CH_3 \text{ -------> } CF_3CO_2H+C_2H_4$$

$$CF_3CO_2H \text{ ------------> } HF+CF_2CO_2$$

$$CF_2CO_2 \text{ -------------> } CF_2+CO_2$$

$$4HF+SiO_2 \text{ -----------> } SiF_4+2H_2O$$

Other reactions which may take place:

$$CF_3CO_2 \text{ -------------> } CF_3H+CO_2$$

$$CF_2CO_2 \text{ -------------> } CF_2O+CO$$

Due to the characteristics of these esters they are of interest in different fields; fluorinated hydrocarbons with a sulfonyl fluoride group are being studied as potential blood substitutes(47). Therefore the esters which have been prepared through this research have been shown to be important in their ability to be converted by SF_4 to form ethers(60). These esters are also potential intermediates from which sulfonic acids could be prepared.

In brief, the main goal of this research, synthesis and identification of fluorinated esters containing the unique SO_2F group, was achieved. As a result of which some questions were answered and some new questions are raised which may be the subject of future studies.

The subject of some future studies may be conversion of these esters to a hydrocarbon chain without affecting the sulfonyl fluoride group.

Since the completion of this project the following papers have been published on the synthesis of new fluorinated esters(65):

$$CF_2CF_2OSO_2 + R_fOH + NaF \text{ ---> } FSO_2CF_2C(O)OR_f + NaHF_2$$

$R_f = CF_3CH_2, (CF_3)_3C, C_6F_5$

(66)

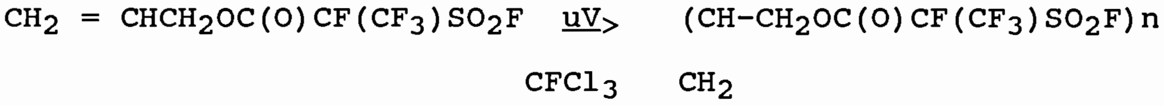
$FSO_2CF_2C(O)OAg + RBr \text{ ----> } FSO_2CF_2C(O)OR + AgBr$

$R = BrCH_2CH_2,\ CH_3CH_2OC(O)CH_2,\ CH_2 = CHCH_2$

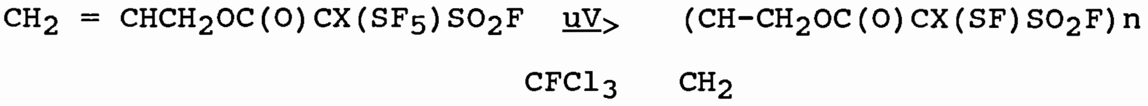
$FSO_2CF_2(O)OAg + RI \text{ ---> } FSO_2CF_2C(O)OR + AgI$

$R = CH_3,\ CH_3CH_2CH_2, (CH_3)_3Si$

Also Robin J. Terjeson et al.(67) reported successful polymerization of $CH_2 = CHCH_2OC(O)CF(CF_3)SO_2F$ and $CH_2=CHCH_2OC(O)CX(SF_5)SO_2F$ as shown below:



$$CH_2 = CHCH_2OC(O)CF(CF_3)SO_2F \xrightarrow[CFCl_3]{uV} (\underset{CH_2}{CH}-CH_2OC(O)CF(CF_3)SO_2F)n$$



$$CH_2 = CHCH_2OC(O)CX(SF_5)SO_2F \xrightarrow[CFCl_3]{uV} (\underset{CH_2}{CH}-CH_2OC(O)CX(SF)SO_2F)n$$

where x = F, H.

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