2

CHEMICAL
RESEARCH,
DEVELOPMENT &
ENGINEERING
CENTER

CRDEC-TR-372

SYNTHESIS OF BIS-(TRIFLUOROMETHYL) TRISULFIDE AND BIS-(TRIFLUOROMETHYLTHIO) SELENIDE

Shekar Munavalli

GEO-CENTERS, INC.
Fort Washington, MD 20744

David I. Rossman
Dennis K. Rohrbaugh
C. Parker Ferguson

RESEARCH DIRECTORATE

June 1992

Approved for public release; distribution is unlimited.

U.S. ARMY
ARMAMENT
MUNITIONS
CHEMICAL COMMAND

Aberdeen Proving Ground, Maryland 21010-5423

Disclaimer

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
1992 June

3. REPORT TYPE AND DATES COVERED
Final, 89 Mar - 90 Dec

4. TITLE AND SUBTITLE
Synthesis of Bis-(Trifluoromethyl) Trisulfide
and Bis-(Trifluoromethylthio) Selenide

5. FUNDING NUMBERS
PR-1L162622A553

6. AUTHOR(S)
Munavalli, Shekar (GEO-CENTERS, Inc.);
Rossman, David I; Rohrbaugh, Dennis K.;
and Ferguson, C. Parker (CRDEC)

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
GEO-CENTERS, Inc., Fort Washington, MD 20744
CDR, CRDEC, ATTN: SMCCR-RSC-O, APG, MD 21010-5423

8. PERFORMING ORGANIZATION REPORT NUMBER
CRDEC-TR-372

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The reaction of trifluoromethylsulfenyl chloride with hydrogen sulfide at -78 °C and in the presence of a catalyst, namely 4-dimethylaminopyridine, furnished excellent yields of the desired bis-(trifluoromethyl) trisulfide in under 24 hrs. The previous preparation of this product required 30 days at room temperature. Bis-(trifluoromethyl) di- and pentasulfides were characterized as by-products by their gas chromatographic/mass spectrometric data. Replacement of the above catalyst with pyridine or N,N-dimethylaniline or triethylamine considerably reduced the yields of the expected product. Under similar experimental conditions, using hydrogen selenide bis-(trifluoromethylthio) selenide has been prepared for the first time. The structures assigned to these compounds have been confirmed by their mass spectral data.

14. SUBJECT TERMS
Bis-(trifluoromethyl) trisulfide
Bis-(trifluoromethylthio) selenide
Mass spectral data

(continued on page 2)

15. NUMBER OF PAGES
21

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

19. SECURITY CLASSIFICATION OF ABSTRACT
UNCLASSIFIED

20. LIMITATION OF ABSTRACT
UL

14. SUBJECT TERMS (Continued)

Bis-(trifluoromethy) di- and pentasulfides
Dichlorofluoromethyl trifluoromethyl disulfide

PREFACE

The work described in this report was authorized under Project No. 1L162622A553, CB Defense/General Investigation. This work was started in March 1989 and completed in December 1990. The experimental data are recorded in laboratory notebook 88-0161.

The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

Reproduction of this document in whole or in part is prohibited except with permission of the Commander, U.S. Army Chemical Research, Development and Engineering Center, ATTN: SMCCR-SPS-T, Aberdeen Proving Ground, MD 21010-5423. However, the Defense Technical Information Center and the National Technical Information Service are authorized to reproduce the document for U.S. Government purposes.

This report has been approved for release to the public.

Acknowledgments

The authors acknowledge the technical contributions of Linda L. Szafraniec and William Beaudry for the ^{13}C and ^{19}F NMR Spectra.

Blank

CONTENTS

LIST OF FIGURES

LIST OF TABLES

SYNTHESIS OF BIS-(TRIFLUOROMETHYL) TRISULFIDE AND BIS-(TRIFLUOROMETHYLTHIO) SELENIDE

1. INTRODUCTION:

In view of the wide occurrence of the di- and trisulfides in nature and the novel biological reactions associated with them, the chemistry of the polysulfides, in particular that of the S-S bond, has attracted considerable interest. These compound have found application in energy transfer processes [1,2] and in the vulcanization of rubber [3]. Perfluoroalkyl groups, in particular, trifluoromethyl and trifluoromethylthio functionalities, exhibit unusual biological properties [4]. In fact, the incorporation of the latter group has been reported to considerably enhance the anti-psychotic properties of the parent compound [4b].

In connection with an on-going project [5a-b], bis-(trifluoromethyl) trisulfide (**1**) was required. An earlier preparation of **1** required thirty days at room temperature [6]. When a mixture of carbon disulfide and iodopentafluoride was heated at 200 °C, **1** was formed and characterized as one of the minor products of the reaction [6]. A 7 to 12% yield of **1** was obtained when a mixture of trifluoromethyl iodide and sulfur was heated at 310 °C for 36 hrs [6-8]. However, trifluoromethylsulfenyl chloride (**2**) reacted slowly with hydrogen sulfide (**3**) at room temperature to furnish acceptable yields of **1** [6]. The reaction of trifluoromethychloro disulfide, obtained by the photolysis of a mixture of bis-(trifluoromethyl) disulfide (**4**) and sulfur dichloride (**5**), with trifluoromethylthiol (**6**) has been described to yield **1** [9]. Trifluoromethyl radicals, generated from a glow-discharge of hexafluoroethane, reacted with sulfur vapor exposed to radio frequency to give polysulfides containing **1** and carbon disulfide [8].

We now wish to report that the use of 4-dimethylaminopyridine (**7**) as a catalyst in the reaction of **2** with **3** at -78 °C furnishes **1** in satisfactory yields (75-80%), accompanied by trace amounts of the corresponding di-, tetra- and pentasulfides. Recently, we have developed and described an efficient method for the synthesis trifluoromethylthiocopper (**8**) in a crystalline form [10]. The reaction of **5** with **8** at room temperature for 45 minutes also gives **1** in a slightly reduced yield, accompanied by di- and polysulfides. Replacement of **7** with either pyridine, or N, N-dimethyl-aniline or triethylamine as a catalyst resulted in a considerably lower yield of **1**. In fact, the reaction of **2** with **3** using triethylamine as a catalyst gave a complex mixture containing twelve components. Substitution of 3 with hydrogen selenide (9) in the above preparation gave the selenium analog of 1, namely bis-(trifluoromethylthio) selenide (**10**). Dichloro-fluoromethyl trifluoromethyl disulfide (**11**) and 4 were identified as impurities accompanying 9. Table 1 describes the by-products of the reaction of 2 with 3 and 9 and of 5 with **8**.

2. EXPERIMENTAL PART:

2.1 General Procedure: Warning!! Because of the high toxicity associated with 1 via inhalation, extreme care should be exercised in working with it and all reactions should be carried out in efficient hoods. NMR spectra (^{13}C and ^{19}F) were recorded in $CDCl_3$ on a Varian VXR-400S spectrometer at 100 MHz and 376 MHz respectively. The external reference for the ^{19}F data was CCl_3F. Mass spectra were obtained on a Finnigan Model 5100 GC/MS equipped with a silica 25 m x 0.31 mm. i.d. SE-54 capillary column (J and W Scientific, Rancho Cordova, CA). Routine GC analyses were accomplished with a Hewlett-Packard 5890A gas chromatograph equipped with a 30 m x 0.53 mm i.d. DB-5 column (J and W Scientific, Folsom, CA). The solvents were dried and freshly distilled before use. The reactions were carried out in a flame dried, argon purged 10 or 25 ml three-necked round bottom flask equipped with a magnetic stirrer, a gas inlet, a pressure equalizing dropping funnel and a reflux condenser carrying a dry ice-acetone trap. The temperature of the coolant passing through the reflux condenser was maintained at -20 °C. After the reaction was over, the mixture was cooled to room temperature, flash distilled under reduced pressure, the distillate collected into a receiver cooled to -78 °C, and finally fractionally distilled through a silvered, vacuum jacketed metal helix packed column.

2.2 Bis-(trifluoromethyl) trisulfide (1): Hydrogen sulfide (3) (0.68 gm., 0.02 mole) was sparged into a solution of **2** (5.4 gm., 0.027 mole) in freshly distilled, dry methylene chloride (5 mL) cooled to -78 °C. A solution of 7 (1.2 gm., 0.01 mole) in dry methylene chloride was added dropwise. The reaction mixture was stirred at -78 °C for two hrs and then at ambient temper-ature for one half hour. GC/MS analysis of the crude distillate obtained by flash distillation indicated the presence of bis-(trifluoro-methyl) di-, tetra- and pentasulfides in addition to the expected product. The crude distilled material was processed as described above to give a colorless liquid, b.p. 85-87 °C (lit. [6] 86.2 °C) in 75% yield and a purity of 96% by glc (retention time=1.5 min). NMR: ^{13}C: $\delta = 128.7$

quartet); J = 314 ± 1 Hz (Fig. 1). ^{19}F δ = 44.5 (singlet) (Fig. 2). MS: [M^+] = 234; 215(M-F); 165(M-CF_3); 133(M-SCF_3); 96(SSS); 82(CSF_2); 69(CF_3); and 64(SS) (Fig. 3).

2.3 Bis-(trifluoromethyl) trisulfide Using Trifluoromethylthio-copper: A solution of sulfur dichloride (5) (3.1 gm., 80%, 0.024 mole) in 5 mL of dry xylene was added dropwise to a slurry of trifluoromethylthio-copper (**8**) (3.1 gm., 0.19 mole) in 5 mL of dry xylene at ambient temterature. The reaction was exothermic. After the addition was complete, the reaction was stirred for an additional thirty to fortyfive minutes and flashed distilled into a dry ice/acetone cooled receiver. GC/MS examination of the crude distillate indicated the presence of the di-, tetra- and pentasulfide as minor impurities. Further purification furnished the desired product (61%).

2.4 Bis-(trifluoromethylthio) selenide (10): To a solution containing **2** (5.4 gm., 0.27 mole) and hydrogen selenide (0.8 gm., 0.01 mole) in 5 mL of dry methylene chloride cooled to -78 °C, was added with stirring, a solution of **7** (1.2 gm.,0.01 mole) in 5 mL of dry methylene chloride. After the addition was complete, the reaction mixture was allowed to warm to ambient temperature. The reaction mixture, after *flash distillation under reduced pressure*, was further fractionally distilled to yield the title compound in 86% yield, b.p. 100-102 °C with a purity of 94% by glc (retention time=8.4 min). NMR: ^{13}C: δ = 128.6 (quartet); J = 312.5 ± 1 Hz (Fig. 4). ^{19}F δ = 41.5 (singlet) (Fig. 5). MS: [M^+] = 282; 263 (M-F); 213(M-CF_3); 101(SCF_3); 82(CSF_2); 69(CF_3); 63(CSF); 50(CF_2); and 32(S) (Fig. 6).

3. RESULTS AND DISCUSSION:

Table 1 lists, in addition to the expected products (**1** and **10**), the various by-products that have been identified from their mass spectral fragmentation patterns. The examination of the origin, formation and distribution of the by-products listed in Table 1 clearly suggests the involvement of free radicials in these reactions. It has been reported that the reaction between carbon disulfide and iodopentafluoride follows a free radical process [5]. A similar suggestion has been made about the reaction between trifluoromethyl iodide and sulfur [7]. Scheme 1 attempts to rationalize the origin and formation of the polysulfides and **11** identified by the GC/MS examination of the flash-distllate of the reaction mixture.

In a sense, Scheme 1 is an extention of an earlier suggestion [6] made to account for the formation of tri- and tetrasulfides. The disulfide, **4**, is a ubiquitous product of the reaction of trifluoromethylthiocopper (**8**) with various substrates [11]. It is often accompanied by polysulfides. All of the compounds listed in Steps 1-6 have been characterized by their mass spectral fragmentation patterns. Steps 7-9 describe the formation of **11**, initiated by the attack of the trifluoromethylthiyl radical on **2**. The structure of **11** has been confirmed by its mass spectral fragmentation data. Tetrafluoromethane, hexafluoroethane and bis-(trifluoromethyl) sulfide (**4**) (Steps 10-12), though in principle should have been formed, were not detected. Even though they were formed, they could have been blown away by argon gas passing through the reaction mixture. Or else, the origin of **11** may be **2** itself (Scheme 2), instead of Steps 8-9 of Scheme 1. The initially formed difluoromethylenesulfenyl chloride radical (Step 1 of Scheme 2) may undergo a rearrangement to give the thiyl radical. There are precedents for this type of rarrangement [12]. The rest of the free radical process (Steps 3-6) follows the accepted course.

The ^{13}C and ^{19}F chemical shifts of **1** and **10** are consistant with the structure assigned to these compounds. The introduction of Se in **10**, shifted the ^{19}F signal upfield by about 3 ppm, whereas the ^{13}C chemical shift is unaffected. The ^{19}F chemical shift of bis-(trifluoromethyl) disulfide itself appears as a singlet at 46.0 ppm [13]. Thus, the insertion of Se into the sulfur-sulfur bond of the disulfide to form **10**, elicits a more pronounced effect on the ^{19}F chemical shift than does the insertion of S to yield **1**.

The polysulfides give the parent ion peak $[M^+]$ and the ion corresponding to m/e = 69 $[CF_3]^+$. Other peaks which are conspicuously present are: $[CF_3SSS]^+$ (m/e = 165); $[CF_3SS]^+$ (m/e = 133); $[CF_3S]^+$ (m/e = 101) and $[CSF_2]^+$ (m/e = 82). Their mass spectra have already been reported by others [8, 14]. The prominent peaks in the mass spectrum of **11** are: $[M^+]$ = 234; 199 (M-Cl); 133 (M-SCF_3); 101 (SCF_3); 69 (CF_3); 63 (CSF); and 44 (CS).

Scheme 1: Genesis of Bis-(trifluoromethyl) di- and polysulfides.

$H_2S + CF_3SCl \longrightarrow CF_3SSSCF_3$ 1

$CF_3SSSCF_3 \longrightarrow CF_3S^{\bullet} + CF_3SS^{\bullet}$ 2

$2\ CF_3S^{\bullet} \longrightarrow CF_3SSCF_3$ 3

$2\ CF_3SS^{\bullet} \longrightarrow CF_3SSSSCF_3$ 4

$CF_3SSSSCF_3 \longrightarrow CF_3SSSS^{\bullet} + {}^{\bullet}CF_3$ 5

$CF_3SSSS^{\bullet} + {}^{\bullet}SCF_3 \longrightarrow CF_3SSSSSCF_3$ 6

$CF_3SCl + {}^{\bullet}SCF_3 \longrightarrow CF_3SSCF_3 + Cl^{\bullet}$ 7

$CF_3SSCF_3 + Cl^{\bullet} \longrightarrow CF_3SSCF_2Cl + F^{\bullet}$ 8

$CF_3SSCF_2Cl + Cl^{\bullet} \longrightarrow CF_3SSCCl_2F + F^{\bullet}$ 9

${}^{\bullet}CF_3 + F^{\bullet} \longrightarrow CF_4^{*}$ 10

${}^{\bullet}CF_3 + {}^{\bullet}CF_3 \longrightarrow C_2F_6^{*}$ 11

$CF_3S^{\bullet} + {}^{\bullet}CF_3 \longrightarrow CF_3SCF_3^{*}$ 12

* Were not detected.

Scheme 2: Postulated Route to Dichlorofluoromethyltrifluoromethyl disulfide.

$CF_3SCl \longrightarrow F_2C^{\bullet}SCl + F^{\bullet}$ 1

$F_2C^{\bullet}SCl \longrightarrow F_2(Cl)CS^{\bullet *}$ 2

$F_2(Cl)CS^{\bullet} \longrightarrow F(Cl)C(S) + F^{\bullet}$ 3

$CF_3SCl \longrightarrow F_3CS^{\bullet} + Cl^{\bullet}$ 4

$F(Cl)C(S) + Cl^{\bullet} \longrightarrow FCl_2CS^{\bullet}$ 5

$FCl_2CS^{\bullet} + {}^{\bullet}SCF_3 \longrightarrow FCl_2CSSCF_3$ 6

*Undergoes a rearrangement.

4. CONCLUSIONS:

In the presence of the catalyst, 4-dimethylaminopyridine, the reaction of trifluoromethylsulfenyl chloride with hydrogen sulfide at -78 °C gives excellent yields of bis-(trifluoromethyl) trisulfide in 24 hrs. Bis-(trifluoromethyl) di-, tetra- and pentasulfides accompany the trisulfide as minor products. An earlier preparation of the trisulfide required 30 days. Using this procedure, bis-(trifluoromethylthio) selenide has been prepared for the first time. The influence of other catalysts on the course of the reaction, the formation of unusual by-products, and the mass spectral fragmentation data are presented in this communication. A new procedure has been developed for the synthesis of the title compounds and the participation of free radicals has been invoked to rationalize the formation of the by-products of the reaction.

LITERATURE CITED

[1] Y. A. Vladimirov, D. I. Roshchupkin andd E. E. Fesenko, "Photochemical Reactions in aminoacid residues and inactivation of enzymes during uv-irradiation", Photochem. Photobiol. **11**, 1970, 227.

[2] S. Arian, M. Benjamini, J. Feitelson and G. Stein, "Interaction between tyrosine and divalent sulfur in fluoresence quenching and in the photochemistry of ribonuclease", Photochem. Photobiol. **12**, 1970, 481.

[3] M. Morton, "Rubber Technology", Van Nostrand-Reinhold, 3rd ed. New York, (1987).

[4] (a) Filler, R. , Kobayashi, Y. (Eds), "Biomedical Aspects of Fluorine Chemistry", Kodasha/Elsevier, New York, (1982). (b) W. C. Randall, P.S. Anderson, E. L. Cresson, C. A. Hunt, T. F. Lyon, K. E. Rittle. D. C. Reny, J. P. Springer, J. M. Hirsfield, K. Hoogsteen, W. Williams, E. A. Risley and J. A. Totaro, "Synthesis, Assignment of Absolute Configuration and Receptor Biding Studies Relevant to the Neuroleptic Activities os a Series of Chiral 3-Substituted Cyproheptadine Atropisomers". J. Med. Chem., **22**, 1979, 1222 (references cited therein).

[5] (a) S. Munavalli, D. I. Rossman, D. K. Rohrbaugh, C. P. Ferguson and L. J. Szafraniec, "Simultaneous Scission of C-S and S-S Bonds of Bis-(trifluoromethyl) trisulfide by Grignard Reagents" J. Fluorine Chem., (in press).. (b) S. Munavalli, D. I. Rossman, D. K. Rohrbaugh, C. P. Ferguson and H. D. Banks. "Single Electron Transfer Catalyzed Simultaneous Cleavage of C-S and S-S Bonds", J. Fluorine Chem., (in press).

[6] R. N. Haszeldine and J. M. Kidd, "Reactions of Fluorocarbon Radicals. Part XI. Synthesis and Some Reactions of Trifluoromethanethiol and Trifluoromethanesulfentyl chloride", J. Chem. Soc., 1953, 3219.

[7] G. R. A. Brandt, H. J. Emeleus and R. N. Haszeldine, "Organometallic and Organometalloidal Fluorine Compounds. Part III. Trifluoromethyl Derivatives of Sulfur", J. Chem. Soc., 1952, 2198.

[8] T. Yasumura and R. J. Lagow, "A Plasma Synthesis for the Perfluoroalkyl Di-, Tri- and Tetrasulfides: Reaction of Trifluoromethyl Radicals with Sulfur Vapor", Inorg. Chem., **17**, 1978, 3108.

[9] N. R. Zack and J. M. Shreeve, "Synthesis of Chloro(trifluoromethyl) disulfane", Inorg. Nucl. Chem. Lett., **10**, 1974, 619.

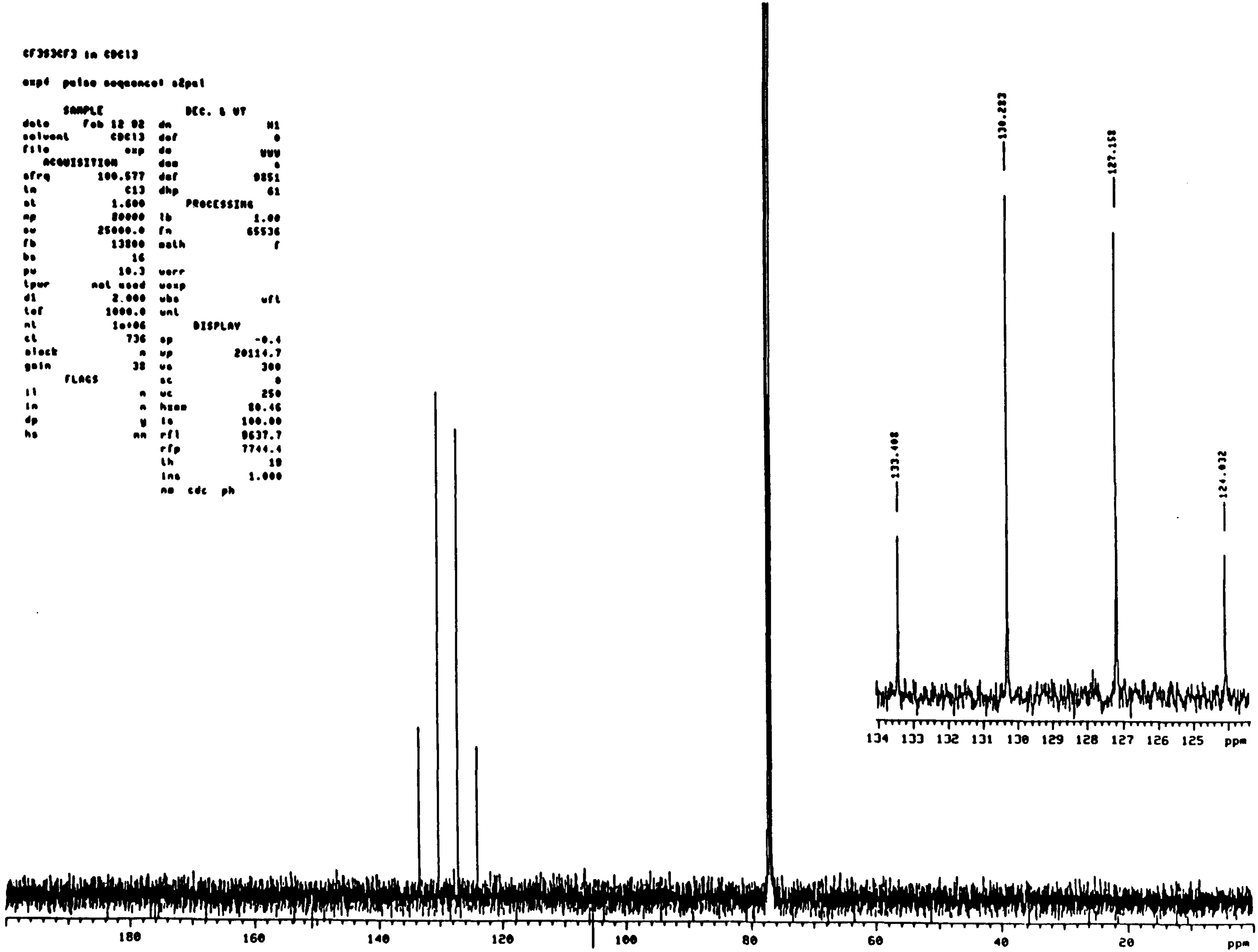
[10] (a) S. Munavalli, D. I. Rossman, D. K. Rohrbaugh, C. P. Ferguson and F-L. Hsu, "Preparation and Reactions of Trifluoromethylthiocopper", Heteroatom Chemistry (in press). (b) S. Munavalli and D. I. Rossman (patent pending).

[11] S. Munavalli and D. I. Rossman (unpublished results).

[12] A. Hass and D. Winkler, "Darstellung und Eigenschaften von Perfluoromethylmercaptophosphoryldichloriden und -chlorophosphanen", Z. Anorg. Allg. Chem., **468**, 1980, 48.

[13] A. Haas and W. Klug, "Darstellung perhalogenierter Dimethyldisulfane durch photochemische Reaction von CSF_2 and CsFCl mit Sulfenylbromiden bzw-chloriden", Ber, **101**, 2617, 1968.

[14] N. R. Zack and J. M. Shreeve, "A Mass Spectral Study of Some Symmetric and Unsymmetric Sulfides, Disulfides and Trisulfides", J. Fluorine Chem., **5**, 1975, 153.

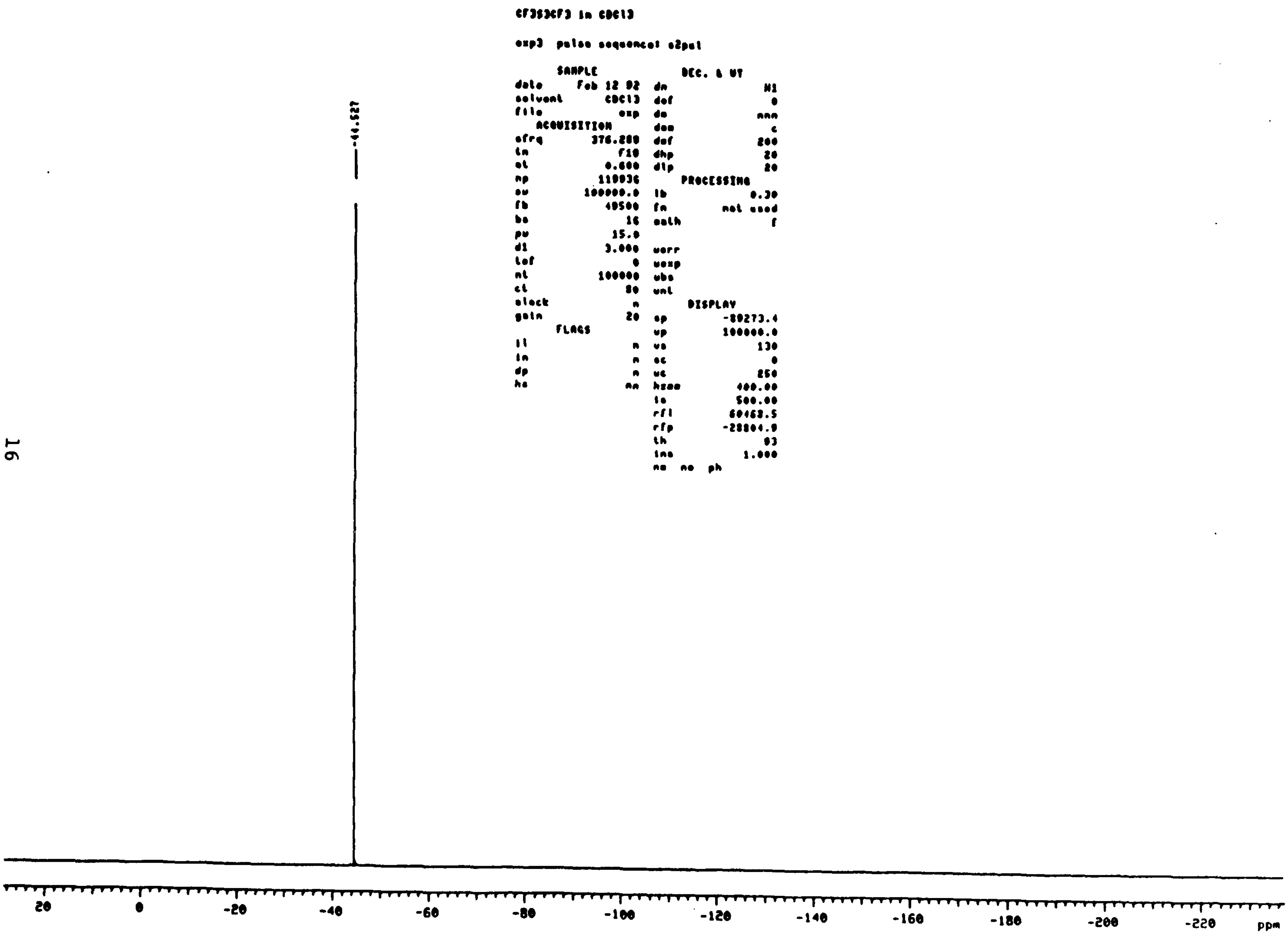


```
CF3S3CF3 in CDCl3

exp4  pulse sequence: s2pul

        SAMPLE              DEC. & VT
date       Feb 12 02   dn              H1
solvent        CDCl3   dof              0
file             exp   dm             yyy
    ACQUISITION        dmm              w
sfrq         100.577   dmf           9851
tn               C13   dhp             61
at             1.600        PROCESSING
np             80000   lb            1.00
sw           25000.0   fn           65536
fb             13800   math             f
bs                16
pw              10.3   werr
tpwr        not used   wexp
d1             2.000   wbs            wft
tof           1000.0   wnt
nt             1e+06        DISPLAY
ct               736   sp            -0.4
alock              n   wp         20114.7
gain              38   vs             300
       FLAGS           sc               0
il                 n   wc             250
in                 n   hzmm         80.46
dp                 y   is          100.00
hs                nn   rfl         8637.7
                       rfp         7744.4
                       th              10
                       ins          1.000
                       nm  cdc  ph
```

Figure 1: ^{13}C-NMR of Bis-(trifluoromethyl) trisulfide



```
CF3S3CF3 in CDCl3

exp3  pulse sequence: s2pul

       SAMPLE              DEC. & VT
date      Feb 12 92  dn            H1
solvent       CDCl3  dof            0
file            exp  dm           nnn
   ACQUISITION       dmm            c
sfrq        376.280  dmf          200
tn              F19  dhp           20
at            0.600  dlp           20
np           110036      PROCESSING
sw         100000.0  lb          0.30
fb            49500  fn      not used
bs               16  math           f
pw             15.0
d1            3.000  werr
tof               0  wexp
nt           100000  wbs
ct               80  wnt
alock             n        DISPLAY
gain             20  sp      -80273.4
        FLAGS        wp      100000.0
il                n  vs           130
in                n  sc             0
dp                n  wc           250
hs               nn  hzmm      400.00
                     is        500.00
                     rfl      60463.5
                     rfp     -28804.9
                     th            83
                     ins        1.000
                     nm  no  ph
```

Figure 2: ^{19}F-NMR of Bis-(trifluoromethyl) trisulfide

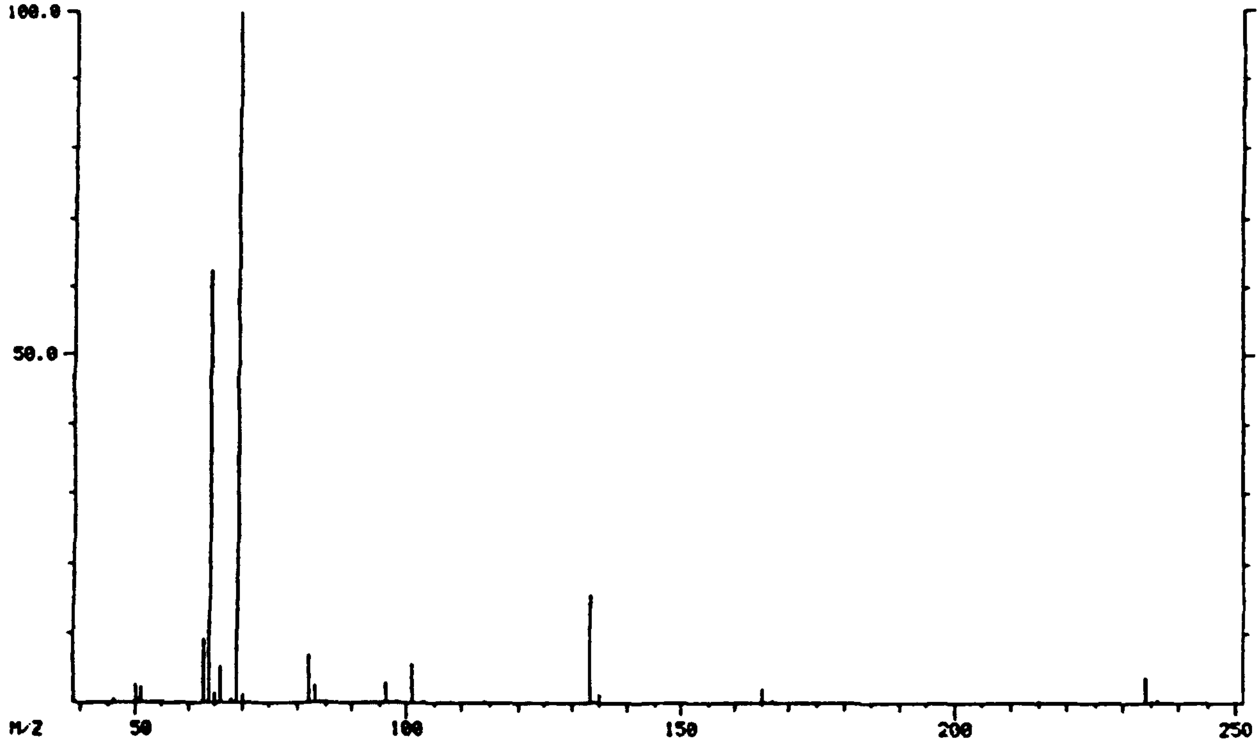
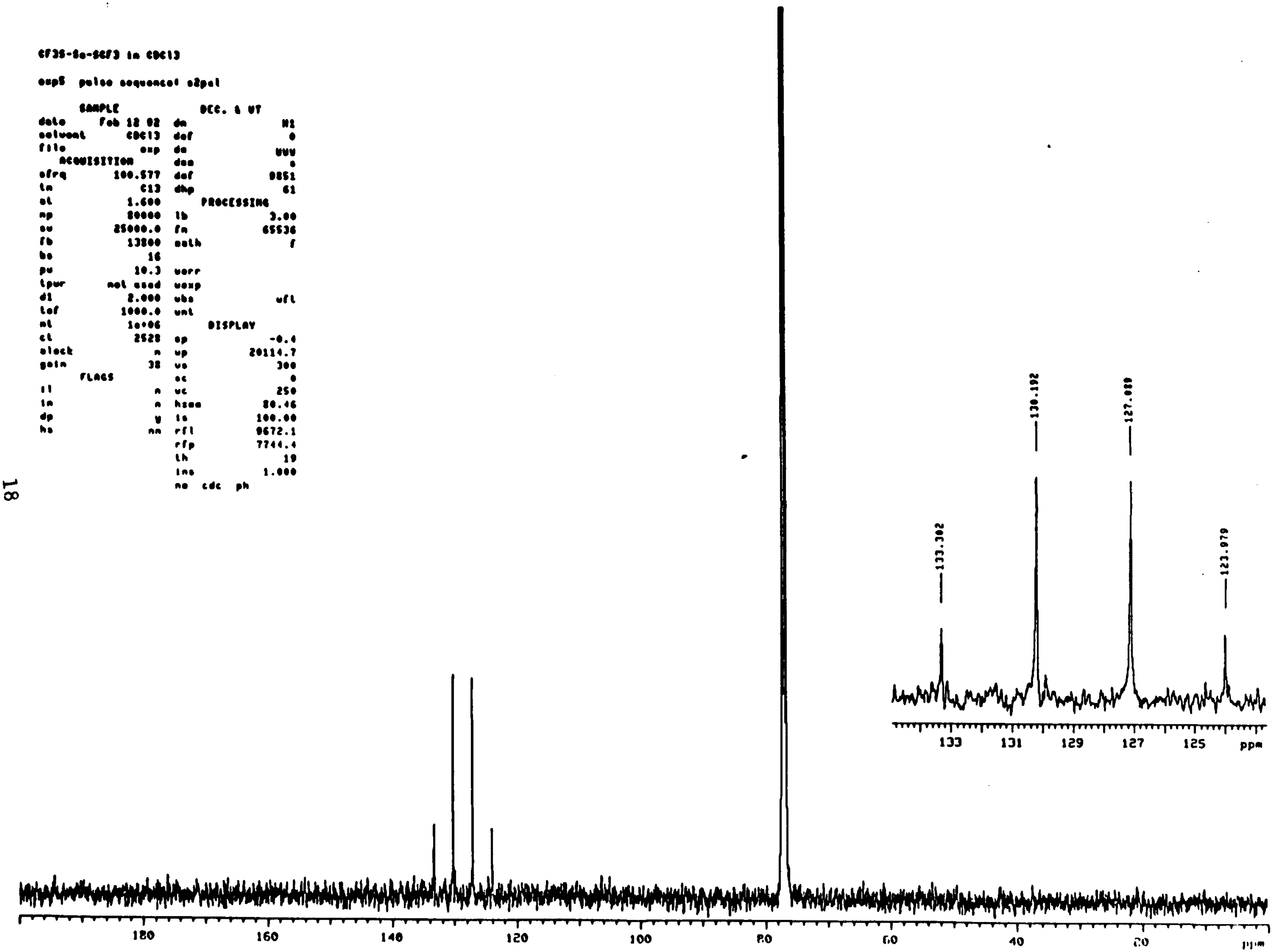


Figure 3: Mass Spectrum of Bis-(trifluoromethyl) trisulfide

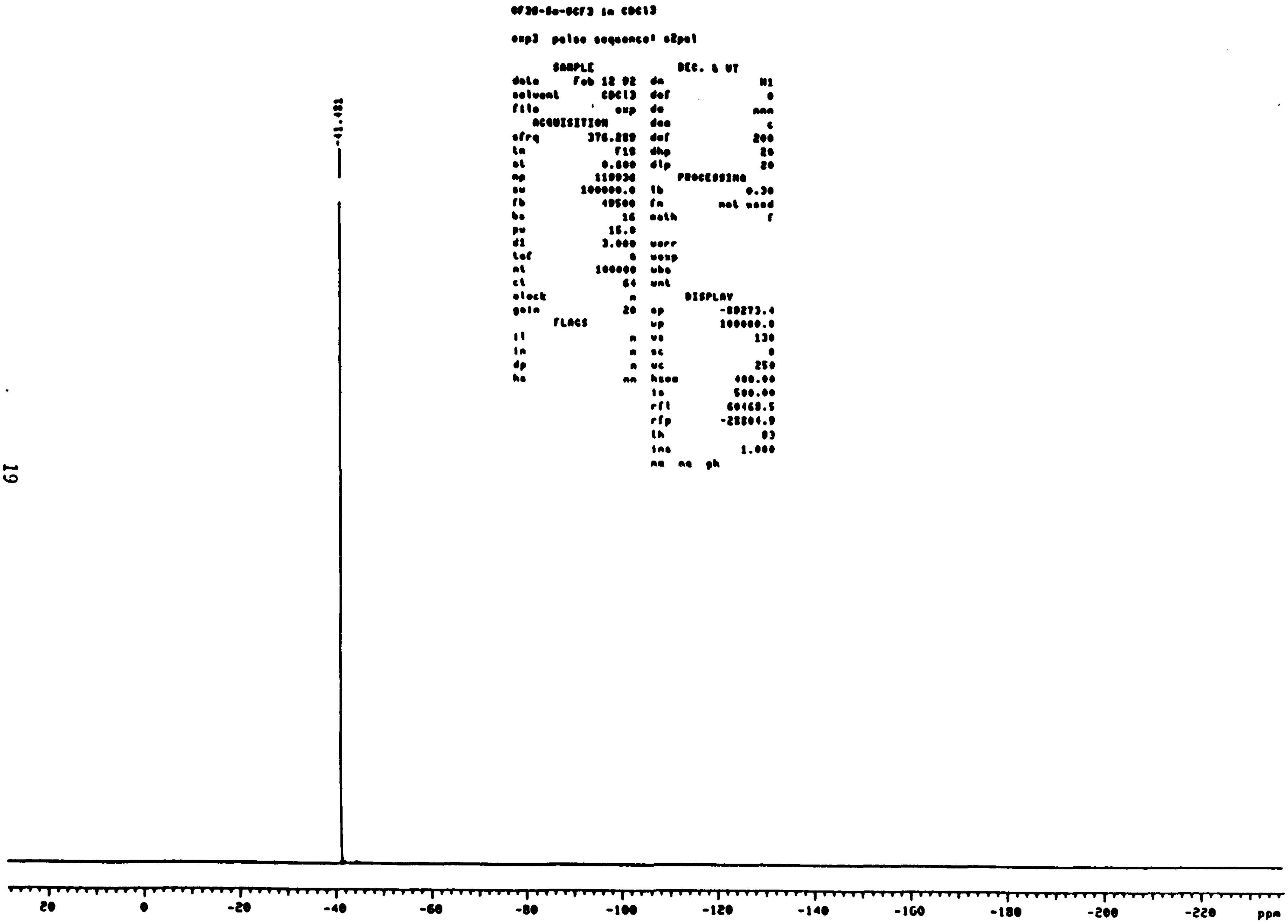


```
CF3S-Se-SCF3 in CDCl3

exp5  pulse sequence: s2pul

      SAMPLE            DEC. & VT
date      Feb 12 92  dn          H1
solvent       CDCl3  dof          0
file            exp  dm         yyy
   ACQUISITION       dmm          w
sfrq        100.577  dmf       9851
tn              C13  dhp         61
at            1.600       PROCESSING
np            80000  lb        3.00
sw          25000.0  fn       65536
fb            13800  math         f
bs               16
pw             10.3  werr
tpwr       not used  wexp
d1            2.000  wbs        wft
tof          1000.0  wnt
nt            1e+06        DISPLAY
ct             2528  sp        -0.4
alock             n  wp     20114.7
gain             38  vs         300
      FLAGS          sc           0
il                n  wc         250
in                n  hzmm     80.46
dp                y  is      100.00
hs               nn  rfl     9672.1
                     rfp     7744.4
                     th          19
                     ins      1.000
                     nm  cdc  ph
```

Figure 4: ^{13}C-NMR of Bis-(trifluoromethyl) trisulfide



```
CF3S-Se-SCF3 in CDCl3

exp3  pulse sequence: s2pul

      SAMPLE              DEC. & VT
date     Feb 12 92  dn              H1
solvent      CDCl3  dof              0
file           exp  dm             nnn
   ACQUISITION      dmm              c
sfrq       376.289  dof            200
tn             F19  dhp             20
at           0.600  dlp             20
np          110036       PROCESSING
sw        100000.0  lb            0.30
fb           49500  fn        not used
bs              16  math             f
pw            15.0
d1           3.000  werr
tof              0  wexp
nt          100000  wbs
ct              64  wnt
alock            n          DISPLAY
gain            20  sp        -80273.4
      FLAGS         wp        100000.0
il               n  vs             130
in               n  sc               0
dp               n  wc             250
hs              nn  hzmm        400.00
                    is          500.00
                    rfl        60468.5
                    rfp       -28804.9
                    th              83
                    ins          1.000
                    nm  no  ph
```

Figure 5: ^{19}F-NMR of Bis-(trifluoromethylthio) selenide

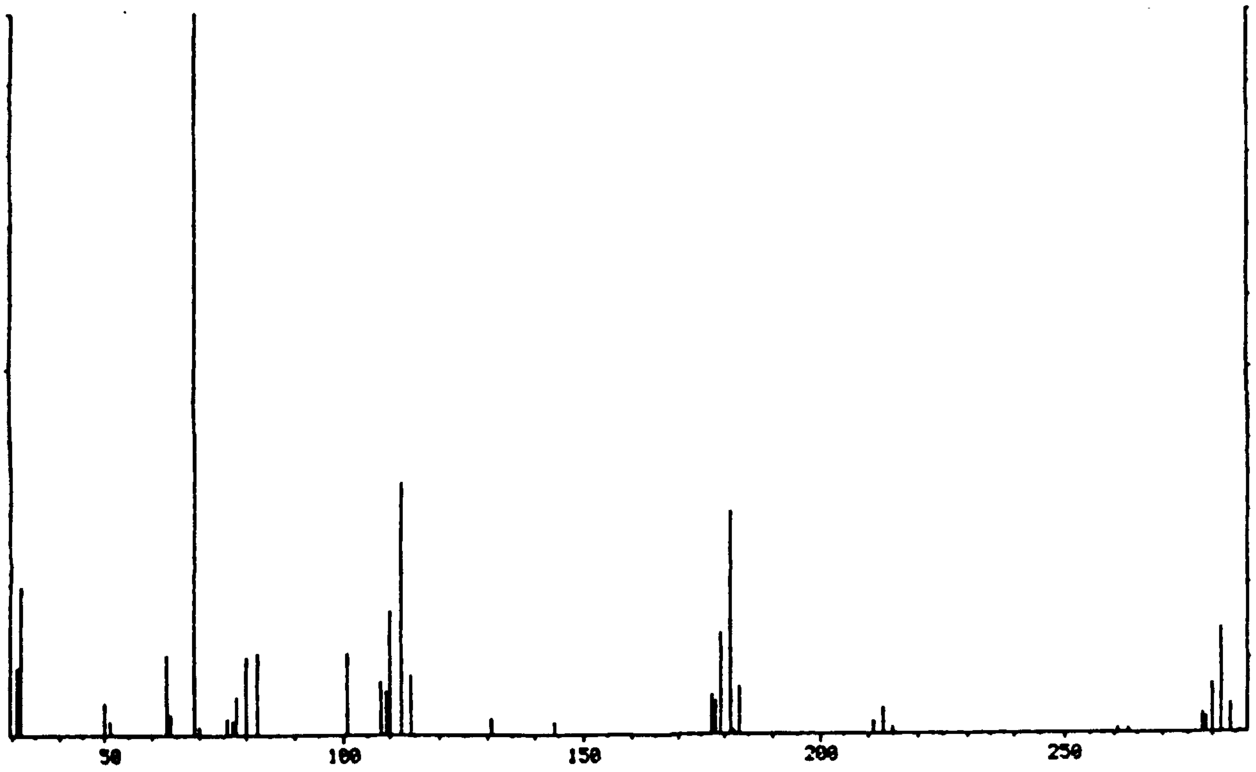


Figure 6: Mass Spectrum of Bis-(trifluoromethylthio) selenide

Table 1: By-products of the Reaction of Trifluoromethanesulfenyl chloride.

Substrates	By-products
H_2S	$CF_3SSCFCl_2$* + $(CF_3S)_2$* + $(CF_3SS)_2S$*
H_2Se	$CF_3SSCFCl_2$ + $(CF_3S)_2$
CF_3SCu	$(CF_3S)_2$ +$(CF_3SS)_2$ + $(CF_3SS)_2S$

* Were not detected in an earlier report [6].

Table 2: Mass Spectral Fragmentation of the Products Listed in Table 1.

$(CF_3S)_2$ [R. T.*=1.18 min]	M$^+$=202; 183(M-F); 133(CF_3SS); 114(CF_3SS); 101(CF_3S); 95(CFSS); 69(CF_3, **100%**); 64(SS); and 50(CF_2).
$(CF_3SS)_2$ [R. T.=3.1 mim]	M$^+$=266; 197(M-F); 165(CF_3SSS); 133(CF_3SS); 96(SSS); 82(CSF_2; 69(CF_3,**100%**); 64(SS) and 50(CF_2).
$(CF_3SS)_2S$ [R. T =5.29 min.]	M$^+$=298; 234(M-SS); 165(CF_3SSS); 133(CF_3SS); 69(CF_3, **100%**) and 64(SS, **100%**).
$(CF_3SSCFCl_2)$ [R. T.=8.9 min]	M$^+$=234; 199(M-Cl); 133(M-SCF_3); 101(SCF_3); 69(CF3,**100%**); 63(CSF) and 44(CS).

*=Retention Time.