To the Graduate Council:

I am submitting herewith a dissertation written by Kenneth M. Smith entitled "The Synthesis and Reactions of Substituted Perfluoroadamantanes, Fluorofullerenes and Norbornane Carbocations." I have examined the final paper copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Jamie L. Adcock, Major Professor

We have read this dissertation
and recommend its acceptance:

Accepted for the Council:

Vice Provost and Dean of
Graduate Studies

The Synthesis and Reactions of Substituted Perfluoroadamantanes, Fluorofullerenes and Norbornane Carbocations

A Dissertation

Presented for the

Doctor of Philosophy

Degree

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Kenneth Smith

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Dedication

To Mom and Dad

Without your support and encouragement this would not have been possible

Acknowledgments

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Abstract

Fluoro and trifluoromethyl groups are becoming increasingly popular in pharmaceuticals, as their inductive effects can be used to tailor a drug's specific interactions. Fluorous syntheses are also now becoming commonplace due to the efficient partitioning possible between fluorous and organic phases. Several new F-adamantyl derivatives were synthesized from F-Adamantyl lithium as targets for future incorporation into pharmaceuticals or for use as fluorous tags. They are: Ethyl-F-Adamantane from ethyl iodide, methyl F-adamantyl ketone and enolate from acetyl chloride, and TIPS protected F-Adamantyl ethanol from TIPS protected 2-bromoethanol. The synthesis of F-adamantyl sulfonyl halides was attempted, however, the F-adamantyl anion attacks the chlorine of sulfonyl chloride fluoride rather than the sulfur in an S_NX reaction. Also, F-adamantyl sulfonyl bromide formed by the reaction of F-Adamantyl Lithium with sulfur dioxide and bromine desulfonylated to form F-adamantyl bromide.

No fluorofullerene other than $C_{60}F_{48}$ has been produced as a pure compound. Also, no derivatized fluorofullerenes have been produced. Our goal here was to either produce a new fluorofullerene as a pure compound, or produce significant amounts of a functionalized fluorofullerene. Fullerene was reacted with fluorine at various temperatures (150°, 100°, and 50°C) and the product distribution was observed using negative ion chemical ionization mass spectrometry. These distributions ranged from $C_{60}F_{48}$ to $C_{60}F_{36}$ with lower temperatures favoring lower distributions. No products with less than 36 fluorines were observed, although unreacted fullerene was recovered at 50°C. The cyanofullerenes $C_{60}HCN$ and $C_{60}(CN)_2$ were also fluorinated at various temperatures. (250°, 150°, 100°, and 50°C) Although substituted

cyanofullerenes such as $C_{60}F_{47}CN$ were observed, it was only in very small quantities. The majority of the products were similar to fluorinating fullerene at the same temperatures. A unique exception to this was the presence of the series $C_{60}F_{18}$ to $C_{60}F_{24}$ as well, in these two systems.

The reactions producing 1-chloronorbornane are widely used, but the mechanistic aspects have not been thoroughly explored. We have observed an ion, which is an intermediate in these reactions and have characterized it by high resolution 2D NMR. Although the 2-norbornyl carbocation has been widely studied in the past, we have reexplored this ion using high resolution 2D NMR techniques which were not possible when this work was first completed. COSY and HMQC agreed with previous assignments. An EXSY kinetics study of the system yielded rate constants for the proton exchange in this system at 193K, 208K, and 223K. The 2-chloro-2-norbornyl carbocation was observed by NMR for the first time. This new cation was characterized using NOESY, COSY, HMQC, as well as 1D spectra.

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Chapter 1 - Introduction

Since the isolation of elemental fluorine by Moisson in the 1890's, the goal of using the most reactive of the elements had gradually grown into a substantial field, with arms into nearly every area of chemistry. Fluorine chemistry, however, had a rather slow start - as it was not until the Manhattan project that the element was first widely explored. Due to the necessity of using fluorine to separate uranium isotopes, large amounts of valuable information were gathered about the element, and more importantly all aspects of handling the dangerous element were tackled.

Today, fluorinated compounds are widely used due to their inertness to chemical attack, and often non-toxicity. Of course, Dupont's Teflon is the most widely used fluorochemical, but both 1st generation and today's 'ozone safe' refrigerants are fluorocarbons, and the list goes on.

It is not well appreciated, however, how often fluorine appears in some of today's most prescribed pharmaceuticals. The fluoro and trifluoromethyl groups have unique properties based on their high electronegativity and electron withdrawing effects on neighboring groups. Today, when derivatives of a new drug are being explored, fluoro and trifluoromethyl groups are often included. This is because their unique electronegativities can tailor the required interactions, as well as the problem that the use of chloro groups is now frowned upon in pharmaceuticals. Finally, fluorinated groups aid in transport of a pharmaceutical through the blood/brain barrier if this is required. Trifluoromethyl groups are found in diuretics (hydroflumethiazide), anti-psychotics (penfluridal and fluphenazine), neuroleptics (oxaflumazine), and even experimental analgesics (antraferic). Fluoro groups

are more widely used, being popular in inhaled anesthetics, beta-lactamase resistant penicillins, and most importantly in several widely prescribed steroids, which have many uses from dermatosis treatments (clobetasone), to bronchial anti-inflamatory agents for asthma (betamethasone), which alleviate the symptoms of millions of asthma sufferers. See Figure 1 for structures of several of these compounds.

Another rather new development in organo-fluorine chemistry exploits the often immiscibility of fluorocarbons in other common organic solvents. This leads to what are now called fluorous separations. Large perfluorinated groups are tethered to synthons, to allow

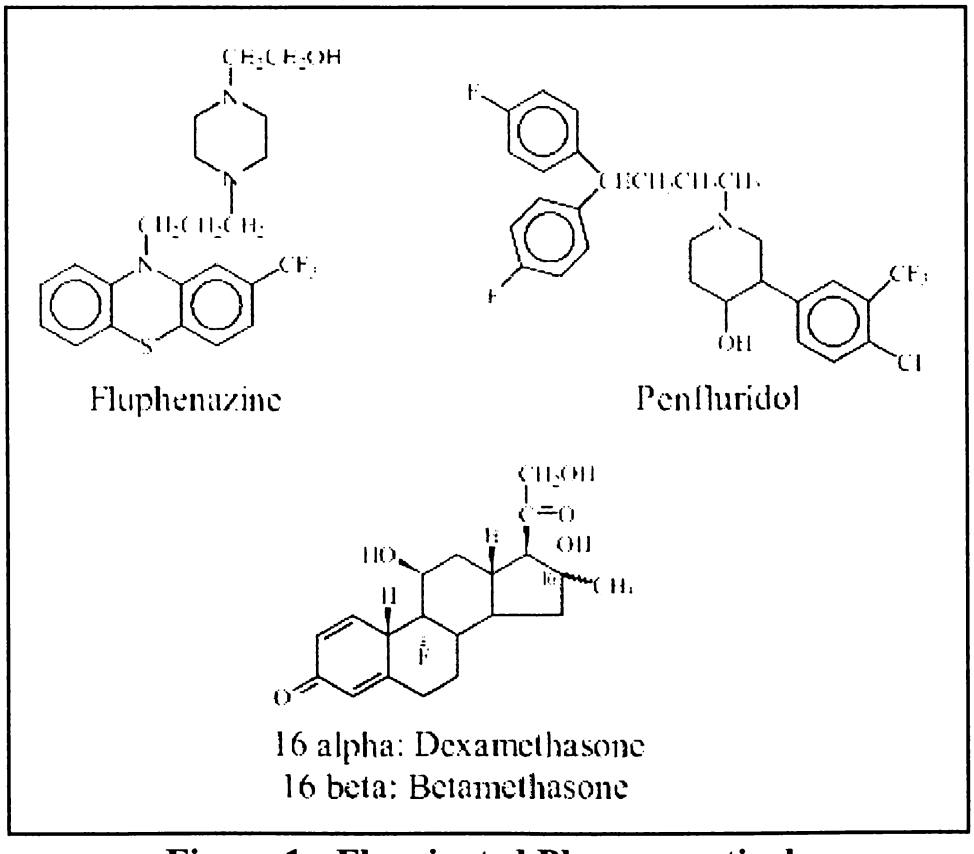


Figure 1 - Fluorinated Pharmaceuticals

the product to be partitioned in the fluorous phase, while unreacted material remains in the organic phase. The opposite is also possible, where a reactant and an unwanted byproduct carry the fluorous group, removing them from the desired product in the organic layer. These methods often remove the need for chromatography between reactions, and could feasibly be used in combinatorial synthesis. Fluorous phase syntheses in this manner, could revolutionize the synthesis of derivatives in pharmaceutical chemistry. See Figure 2.[1]

These perfluorinated groups may be attached to the target reagent/precursor in several ways. Most recently, a perfluorinated group has been attached to a silicon, which is then used to protect an alcohol. Alcohols may also be protected by forming fluorine containing ethers[2],

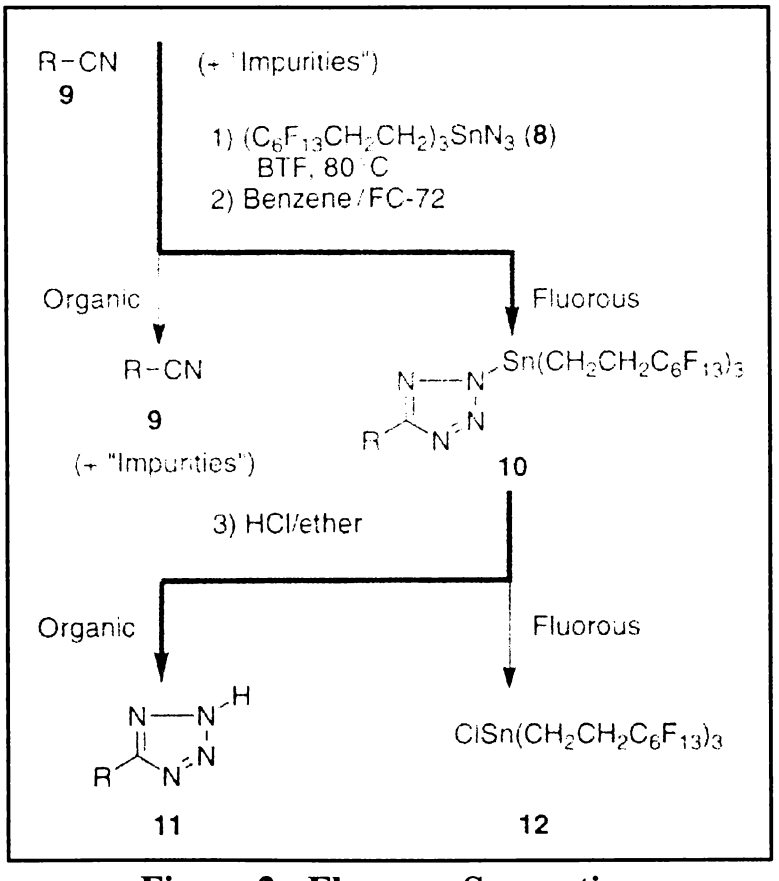


Figure 2 - Fluorous Separation

or a reagent such as tributyl tin hydride may be substituted with fluorinated groups, allowing easy removal of the unreacted hydride, as well as the reacted tin containing byproduct.[3]

Over the years, our lab has perfected the technique of aerosol direct fluorination (AF).[4,5] There are two problems with directly reacting fluorine and an organic molecule. The first is the high exothermicity of the attachment of the first fluorines. This heat often causes, among other things, fragmentation of carbon skeletons. Efficient removal of this heat, however - as with low temperature fluorination techniques, often causes much of the organic substrate to fail to be perfluorinated. This is due to the second factor, that with increasing fluorination, the last few hydrogens are very difficult to replace. On the other hand, not removing the excess heat would cause run-away exothermic reactions.

The aerosol direct fluorination technique stabilizes both of these effects. AF is a flow technique, meaning that the organic is introduced in the reactor in a stream of inert gas. Sodium fluoride is heated to a temperature high enough for it to melt and then vaporize into a flow of an inert gas. This flow is rapidly cooled to liquid nitrogen temperature which creates an aerosol of sodium fluoride. This aerosol is then combined with the fluorine and organic in a reactor tube, in which the amounts of fluorine can be controlled in four separate phases, as can the temperatures. Fluorination occurs on the surface of the aerosol particles, which act as a heat sink to dissipate the heat, most of which is lost to the inert gas. Cooling the outside of the reactor tube to zero to -10°C also helps ensure that all heat produced in the system is efficiently removed..

These four phases are carefully controlled. The first phase has low temperature and low fluorine concentration. This minimized the amount of fragmentation and crosslinking as

only the most reactive hydrogens are replaced with fluorines. The second and third stages have higher temperatures and fluorine concentrations helping to increase the efficiency of collisions with fluorine radicals. In the fourth stage, UV irradiation is applied. This increases the concentration and energy of the fluorine radicals to insure that the last, most unreactive hydrogens in the now mostly fluorinated molecule are efficiently replaced with fluorine.

This method, then, controls the reaction exothermicity, fragmentation, and crosslinking. It results in high yields of nearly 100% of perfluorinated product, and makes efficient use of the rather expensive fluorine.

This lab has used the aerosol fluorination method to perfluorinate a wide variety of organic functionalities. These include alkanes, which are effectivly perfluorinated as long as no ring strain exists[6], ethers[7, 8], esters[8], ketones[9, 10], and alkyl halides. Alkyl chlorides give good yields of perfluorinated products[11, 12], occasionally with rearrangement. Alkyl bromides can be fluorinated, but lose the bromine as it is attacked during the reaction and is likely lost as BrF_3. This results in perfluorinated product without functionality.

The aerosol fluorinator has shown itself to be especially useful in fluorinating diamondoid alkanes[13, 14]. Although adamantane and its deriviatives are often solids, they have high volatility, and no ring strain, which allows us to fluorinate them in high yield and purity. More importantly, their derivatives may also be fluorinated. Good results have been shown with 1-chloroadamantane[15], 2-chloroadamantane, 1,3-dichloroadamantane, 1,3,5-trichloroadamantane, 1,3,5,7-tetrachloroadamantane[16], 2-adamantanone[17], and 1-adamantane carboxylic acid methyl ester[18].

This lab has also shown that F-chloroadamantanes can be reduced to the

corresponding hydryl adamantanes by a variety of methods[15]. F-2-adamantanone can be reduced to 2-hydryl-F-adamantan-1-ol[17], and although the perfluorinated 1-adamantane carboxylic acid methyl ester is unstable to hydrolysis, the trifluoromethyl group may easily be replaced by a methyl in a transesterification reaction, resulting in that part of the ester not being fluorinated which greatly increases its resistance to hydrolysis[18]. These esters can also be reduced to hydryl compounds with lithium aluminum hydride..

These hydryl F-adamantanes are the primary focus of this work. They very readily react with methyl lithium to form methane and a very stable, highly ionic F-lithioadamantane[19]. The lithio compound leads to a wide variety of reactions, which may be useful in introducing the F-adamantyl group into organic molecules, potentially yielding pharmaceuticals with unique properties, or by using this group as a tag for fluorous phase separations. The ways we have explored doing this include using the F-lithioadamantane to react with alkyl halides, alkyl halides containing a protected functionality, and acyl halides.

Our lab is also the first in the world to produce significant amounts of fluorofullerene compounds. Fullerene is fluorinated in a sodium fluoride matrix at high temperature, which produces high purity $C_{60}F_{48}$[20]. Another focus of this work is to explore the possibility of derivitizing $C_{60}F_{48}$ to give it greater synthetic usability, as well as reduce it using a variety of reagents to possibly form other pure fluorofullerenes. No functionalized fluorofullerenes have yet been produced. These compounds could show interesting oxidizing and fluorinating properties on their own. There is also the possibility of further modifying a functionalized fluorofullene, again with the goal of attaching these to other molecules.

The final focus will be to revisit the low temperature formation of the norbornyl

carbocation in superacid media. The goal of this work is to use new high resolution NMR techniques to probe the structure and kinetics of this unique cation, as well as explore the reactivity of chlorinated norbornanes in super-acid media. Also, I will report the first NMR characterization of a new ion formed from 2,2-dichloronorbornane and antimony pentafluoride. This ion is the 2-chloro-2-norbornyl carbocation. It is extremely stable at -80°C, and was characterized at -100°C. Upon warming this ion isomerizes to a different ion, which we believe is the 1-chloro-2-norbornyl carbocation. This work is of great interest to us because it potentially gives new mechanistic information on the well known reaction which converts 2,2-dichloronorbornane to 1-chloronorbornane in the presence of a strong Lewis acid.

Chapter 2 - Experimental Procedure

A. The Aerosol Fluorinator

The principle of the aerosol direct fluorinator was discussed earlier and it has been described in detail elsewhere[5]. To summarize, nucleating aerosol particles of sodium fluoride are generated in a furnace which is heated to above 1050° C. These particles are then carried in a flow of helium through a trap at -196°C and then into the main reactor section. The hydrocarbon (in a solvent which is co-fluorinated) is introduced into the reactor by liquid solution injection. Both the hydrocarbon and the solvent are evaporated and carried by a flow of helium into the reactor as well. Finally fluorine, also diluted with helium in introduced into the reactor through four modules establishing a fluorine gradient along the reactor tube, which is comprised of a porous monel tube. The aerosol, hydrocarbon, and fluorine are carried through the reactor modules, the last of which is irradiated by an ultraviolet lamp and finally into a stainless steel product trap which is cooled by liquid nitrogen. The trap also contains sodium fluoride pellets to absorb much of the HF which is produced. After the fluorination is complete, the product trap is disconnected and connected to a vacuum line for further separation. See Figure 3 for a schematic of the fluorinator.

The ratio of hydrocarbon to co-fluorinating solvent is typically 1:3.5(g:g). The solution is injected via a syringe pump at the rate of 1.5 ml/hr. Trap to trap fractionation follows, typically including traps at -22°, -76°, and -196°C. The fluorinated adamantanes collect in the -22° trap, fluorinated solvent in the -76° trap, and other byproducts in the -196° trap.

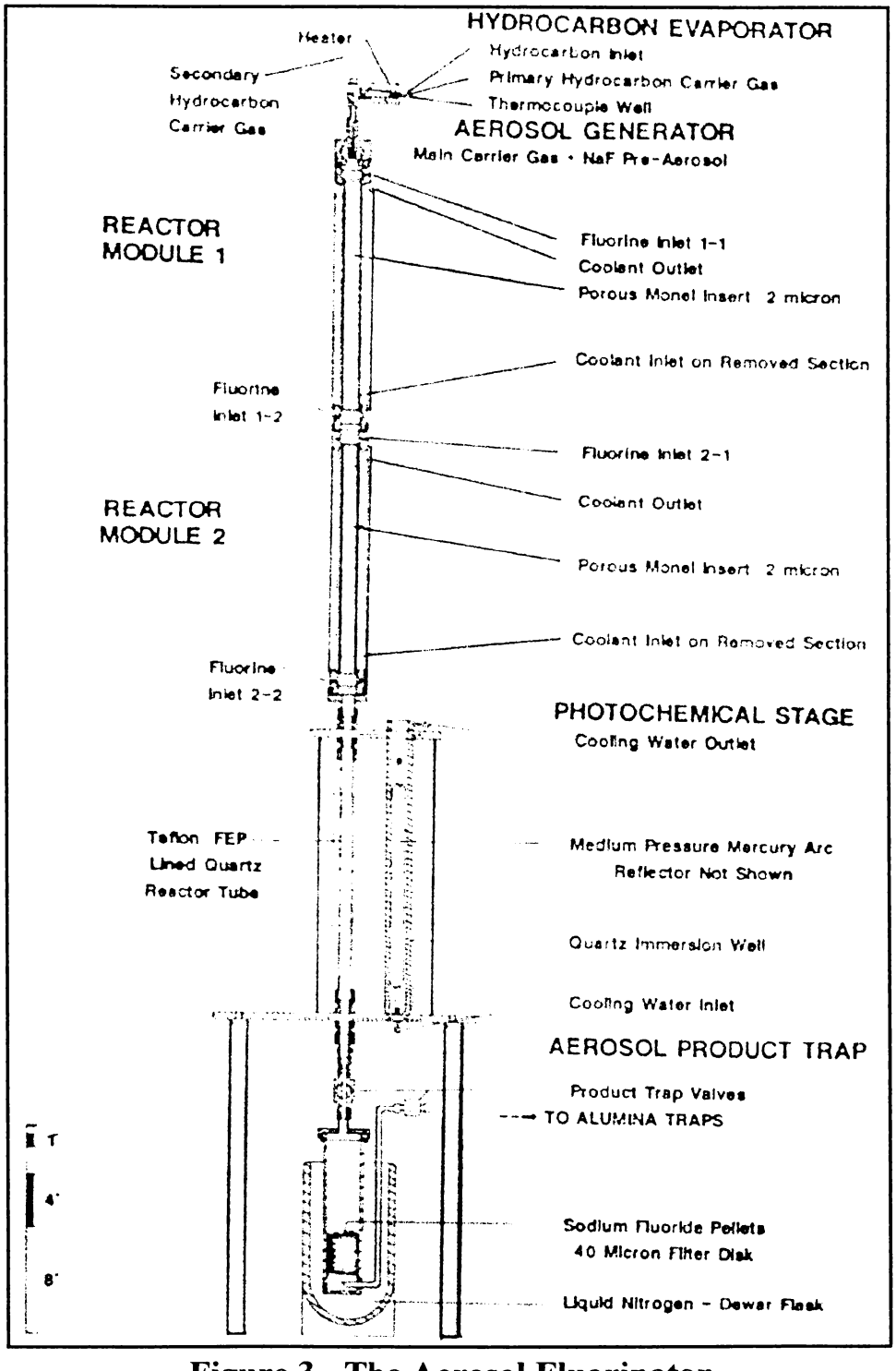


Figure 3 - The Aerosol Fluorinator

B. Vacuum line

An all pyrex vacuum line was used for transfer and fractionation of perfluorinated compounds. All stopcocks were Kontes Hi Vacuum Teflon and a Welch Duo-seal (1402B) pump supplied the vacuum.

C. Instrumentation

1. Gas Chromatography

The fluorinated products were separated and purified by gas chromatography using a Bendix 2300 prep scale instrument. The column used was a 7 meter by 3/8 inch column filled with 13% fluorosilicone QF-1 stationary phase on 60-80 mesh, acid washed chromosorb P conditioned at 225°C for 12 hours. The carrier gas was helium.

2. Nuclear Magnetic Resonance

All ^{19}F, ^{1}H and ^{13}C spectra are obtained on a Varian Mercury 300MHz 4 nucleus spectrometer. Typically deuterochloroform containing 1% tetramethylsilane was used as the solvent and roughly 100 ul of $CFCl_3$ was added as the standard for ^{19}F. Low temperature and 2D spectra were obtained on a Varian INOVA 600MHz or on a Bruker AVANCE 400MHz spectrometer.

3. Mass spectra

Mass spectra were recorded on a VG ZAB-EQ mass spectrometer operating in negative chemical ionization mode.

D. Commercially Available Materials

All materials used were reagent grade and were used as received unless noted otherwise.

Acetyl Chloride: Aldrich Chemical (98%)

1-Adamantane Carboxylic Acid: Eastman

Aluminum Chloride, anhydrous: Aldrich Chemical (99%)

Antimony Pentafluoride: Cationics Inc. (technical)

Bromine: Acros

2-Bromoethanol: Acros (97%)

1-Chloroadamantane: Aldrich Chemical (98%) or Acros (98%)

Chloroform-d: Aldrich Chemical (99.8%D, 1% v/v TMS)

exo-2-Chloronorbornane: Aldrich Chemical (98%)

Cyclohexane: Acros (99+%)

1,2-Dichlorobenzene: Acros (99%)

N,N-Dimethylformamide: Acros (99%)

Ethanol Absolute: Aaper

Ethyl Acetate: Fisher

Ethyl Ether (anhydrous): Fisher

Ethyl Iodide: Fisher

Fluorine: Air Products, 97% technical grade

Fullerene: Southern Chemical group (99.5%)

Hydrochloric Acid (37%): Fisher

Iron pentacarbonyl: Aldrich

Lithium Aluminum Hydride (powder): Aldrich Chemical (95+%)

Methanol: Fisher

Methyl Lithium: Aldrich Chemical (1.4M in ether) or Acros (1.6M in ether)

Methyl Trifluoromethansulfonate: Aldrich (99+%)

Norbornane-2-carboxylic Acid: Alfa (98%) (bicyclo[2.2.1]heptane-2-carboxylic acid)

Norcamphor

Pentane

Phosphorus trichloride: Aldrich (98%)

Phosphorus pentachloride: Aldrich (95%)

Silicagel: Acros (0.060-0.200mm) 6nm pore diameter

Sodium Bifluoride (pellets): Harshaw Catalysts

Sodium Cyanide: Acros

Sodium Fluoride: Aldrich Chemical (99.8%)

Sodium Hydroxide: Mallinckrodt Chemical

Sodium Sulfate (anhydrous): Fisher

Sulfuric Acid: Fisher

Sulfuryl Chloride Fluoride: Lancaster (99%)

Sulfuryl Fluoride: Lancaster (99%)

Toluene: Fisher

p-Toluenesulfonyl cyanide: Aldrich (95% tech)

Tri-n-butyl tin hydride: Aldrich (97%)

1,1,2-Trichloroethane: Fluka (>98%)

Trichlorofluoromethane (R-11): Pennwalt Corporation

Trifluoroacetic Acid: Fisher

Triisopropylsilyl chloride: Aldrich (98%)

E. Preparation of Starting Materials

1. Synthesis of 1-Adamantane carboxylic acid methyl ester

1-Adamantane carboxylic acid methyl ester was made by a simple acid catalyzed esterification reaction due to its high stability to acid hydrolysis. 1-adamantane carboxylic acid (6.0 g, .033 mol) was dissolved in 50 ml methanol. 18M H_2SO_4 was then added slowly and the mixture was refluxed for 4 hours. After cooling, the methanol solution was poured into water and the water was extracted with ether. The ether layers were dried and the ether was evaporated to yield an oil which solidified when placed in the freezer. It showed the expected five peaks in the carbon spectrum: 184.62, 40.44, 38.49, 36.362, and 27.77.

2. Synthesis of TIPS protected 2-Bromoethanol

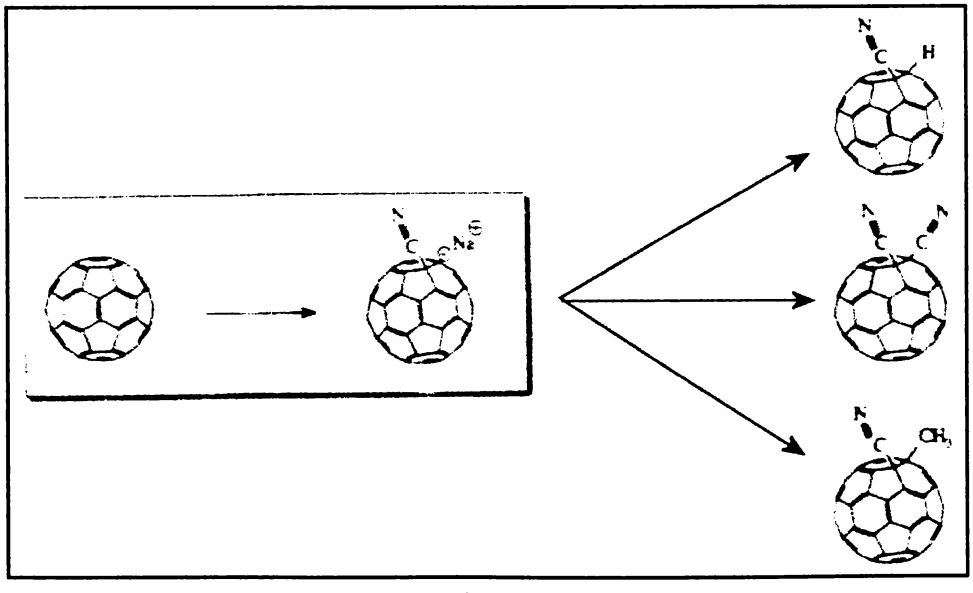
2-Bromoethanol was protected with a triisopropylsilyl group (TIPS) using a generalized literature procedure[21] for TIPS protecting alcohols. 2-bromoethanol (10 g, 0.080 mol) was added to 20 ml of DMF in which imidazole (13.6 g, 0.200 mol) had been dissolved. TIPS chloride (18.5 g 0.96 mol) was then slowly added. The mixture was stirred overnight at room temperature. It was then poured into water and extracted with methylene chloride

which is then evaporated to yield a clear liquid (7.36 g, 65.4%) ^{1}H peaks at 1.04(s), 1.05(s), 3.37(t), 3.94(t). ^{13}C peaks at 12.0, 17.7, 33.0, 63.8.

3. Synthesis of $C_{60}HCN$, $C_{60}(CN)_2$, and $C_{60}(CH_3)CN$ (see Scheme 1)

Synthesis of these fullerene derivatives followed the literature procedures[22]. To a solution of C_{60} in o-dichlorobenzene (250 mg in 20 ml) was added a solution of NaCN (3.5 ml of 0.1M solution in DMF) dropwise over a 5 minute period. The color immediately changed from purple to blue and gradually to very deep green. After stirring for 15 min, various electrophiles are added to the $C_{60}(CN)^-$ anion which has been formed.

To prepare $C_{60}HCN$, 0.25 ml of trifluoroacetic acid were added to the above solution. After 30 minutes, the mixture was loaded onto a silica column. Unreacted C_{60} eluted with cyclohexane/toluene 8:2, and then the product with cyclohexane/toluene 1:1. The solvents were removed under reduced pressure and the product was washed with cyclohexane,



Scheme 1 - Formation of cyanofullerenes

methanol and then with ether.

To prepare $C_{60}(CH_3)CN$, the mixture was treated with methyl trifluoromethanesulfonate (0.2 ml). After stirring overnight, the brown mixture was precipitated with ether and the solid was isolated by decantation. It was then dissolved in CS_2 and loaded on a silica column. Unreacted C_{60} was eluted with cyclohexane/CS_2 9:1, and the product with cyclohexane/toluene 7:3. Solvents were removed under reduced pressure and the residue was first washed with methanol and then with ether.

To prepare $C_{60}(CN)_2$, the mixture was treated with 130 mg of p-Toluenesulfonyl cyanide in o-dichlorobenzene (5 ml). After 2 hours the brown mixture was loaded onto a silica column. The unreacted C_{60} was eluted with cyclohexane/toluene 8:2, and the desired product with cyclohexane/toluene 2:8. The solvents were removed under pressure and the residue was first washed with methanol and then with ether.

4. Synthesis of 2,2-dichloronorbornane

2,2-Dichloronorbornane was prepared by literature procedures[23]. Phosphorus trichloride (10 ml) was charged into a 250-ml three-neck flask equipped with a $CaCl_2$ drying tube. The flask was cooled to -5°C in an ice-salt bath and norcamphor (15 g) was added in portions. After the norcamphor had dissolved, phosphorus pentachloride (31.7 g) was added over 20 minutes with efficient stirring and cooling. The mixture was allowed to warm to room temperature and stand over night with stirring. It was then poured onto 200 g of ice in a 500-ml flask and the hydrolysis was allowed to proceed while the flask was kept in an ice-salt bath. After 30 minutes, the mixture was allowed to warm to room temperature and was

extracted with pentane (4x80 ml). The combined pentane extracts were washed with water (2x100 ml) and dried over anyhydrous Na_2SO_4. The pentane was evaporated to give 19 g of a yellowish oil. Distillation of this yellowish oil under vacuum gave 14.5 g of a colorless liquid which solidified to a low-melting solid. The ^{13}C spectrum of the 2,2-dichloronorbornane showed the expected seven peaks at 94.10, 55.97, 55.37, 37.69, 27.58, and 25.38.

F. F-Adamantanes

1. Aerosol Direct Fluorination

a. Aerosol Fluorination of 1-Chloroadamantane

Details of the aerosol fluorination parameters for 1-chloroadamantane are listed in Table 1. 1-Chloroadamantane (2.50 g) was fluorinated as a solution in 1,1,2-trichloroethane (5.50 g) over a period of 4.5 hours. (Total volume of solution ~7 ml, injected at 1.5 ml/hour.) The products were transferred to the vacuum line and fractionated. The F-1-chloroadamantane was trapped at -22°C. After warming to room temperature, the product is dissolved in a 4/1 $CFCl_3$/chloroform mixture (the chloroform raised the boiling point of the solution to make injecting the solution easier) and purified by prep scale GC, as described above. The ^{19}F NMR spectrum showed three peaks at -114, -120, and -219ppm integrating to 6:6:3.

b. Aerosol Fluorination of 1-Adamantane Carboxylic Acid Methyl Ester

Details of the aerosol fluorination parameters for 1-Adamantane Carboxylic Acid Methyl Ester are listed in Table 2. 1-Adamantane Carboxylic Acid Methyl Ester (2.50 g) was fluorinated as a solution in 1,1,2-trichloroethane (5.50 g) over a period of 4.5 hours. (Total volume of solution ~7 ml, injected at 1.5 ml/hour.) The products were transferred to the vacuum line and fractionated. The F-1-Adamantane Carboxylic Acid Methyl Ester was trapped at -22°C. The product was then immediately hydrolyzed (see below).

Table 1

Aerosol Fluorination of 1-Chloroadamantane

Parameters	
FLUORINE FLOWS (ml/min)	
Module 1-1	8
Module 1-2	70
Module 1-3	63
Module 1-4	6
REACTION TEMPERATURES (°C)	
Module 1	-10
Module 2	0
Evaporator	110
Injector	115
AMOUNT OF STARTING MATERIAL	2.6g
AMOUNT OF SOLVENT	7.3g
STARTING MATERIAL/SOLVENT RATIO	1/2.8
PRODUCT YIELD (grams)	3.70g
PRODUCT YIELD (GC pure, grams)	1.70g
FINAL PRODUCT YIELD (GC pure, %)	25.3

Table 2

Aerosol Fluorination of 1-Adamantane Carboxylic Acid Methyl Ester

Parameters	
FLUORINE FLOWS (ml/min)	
Module 1-1	8
Module 1-2	70
Module 1-3	63
Module 1-4	6
REACTION TEMPERATURES (°C)	
Module 1	-10
Module 2	0
Evaporator	120
Injector	115
AMOUNT OF STARTING MATERIAL	2.2g
AMOUNT OF SOLVENT	6.0g
STARTING MATERIAL/SOLVENT RATIO	1/2.7

2. Formation of 1-Hydryl-F-adamantane

a. Reaction of F-1-Chloroadamantane with $LiAlH_4$

1.33 g of lithium aluminum hydride were transferred to a flask in a dry box and 50 ml of ethyl ether were added. This solution was cooled in an ice bath and stirred for 10 minutes. 2.5 g of F-Adamantyl Chloride were dissolved in 10 ml of ethyl ether. This solution was added dropwise to the LAH solution with stirring. The solution was then allowed to warm to room temperature over a period of 2-3 hours and then was stirred at room temperature overnight. The solution is again cooled to near zero degrees. 16 ml of cold absolute ethanol are slowly added, ensuring that the ether solution never boiled. Finally 120 g of 50% sulfuric

acid was added, slowly at first. Enough ether was then added and the ether layer separated. The aqueous layer was extracted with ether a total of three times, the ether was then washed once with water and dried over sodium sulfate. The ether was then evaporated to yield 0.570 g F-adamantyl hydride. (25.0% yield) ^{19}F peaks at -108.7(s), -120.9(m), -219.3(m). ^{1}H peak at 3.90. An alternate workup was to pump on the mixture after adding the ethanol. This eliminates the need for the acid hydrolysis and liquid work-ups. The vessel is pumped on at RT and all volatiles are collected at -196°C. The volatile products are then fractionated with pure F-adamantyl hydride remaining in the -22°C trap. (Does not improve yield)

b. Hydrolysis of F-1-Adamantane Carboxylic Acid Methyl Ester

After being fractionated from the reactor trap, the F-ester was held at -22°C. A solution of 3 g of NaOH in 10 ml of water was then added, and the solution was allowed to warm to room temperature for an hour. To ensure complete decarboxylation, the solution was then acidified with 3M sulfuric acid, and again allowed to stand for an hour. Finally the solution was extracted with ethyl ether 3 times, washed with water, dried with sodium sulfate, and evaporated to yield 510 mg of F-adamantyl hydride. (Yield from unfluorinated starting material - 11.0%)

c. Methanolysis of F-1-Adamantane Carboxylic Acid Methyl Ester and subsequent reduction

As above, after being fractionated from the reactor trap, the F-ester was held at -22°C. A large excess of methanol in ethyl ether was added (10 ml of each) and the solution

was warmed to room temperature. The organic was washed twice with water, and dried with sodium sulfate. The ether was then carefully evaporated to yield 630 mg of a colorless liquid, shown to be NMR pure, methyl F-1-adamantanoate. (Yield from unfluorinated starting material - 12.0%) ^{19}F peaks at -108.2, -120,1, and -219.3

The ester was then reduced with lithium aluminum hyride as above. 600 mg of ester were reacted with 400 mg of LAH in a total of 20 ml of ethyl ether. After hydrolysis, extraction, and evaporating the solvent, 200 mg of F-adamantyl hydride were produced (38% yield).

3. Synthesis of F-adamantane derivatives

a. Reaction of F-lithioadamantane and TIPS protected 2-Bromoethanol

1-Hydryl-F-adamantane (0.090 g) dissolved in ethyl ether (1.0 ml) was placed in an ampule (~5 ml) capped with a septum. A diethyl ether solution of methyl lithium (1.6M, 0.2 ml) was injected dropwise through the septum at -80°C. The mixture was allowed to sit for 2 hours. After 2 hours, an excess of TIPS protected 2-bromoethanol (0.080 ml) in 0.100 ml of ethyl ether was added to the above mixture, still at -80°. The solution was then allowed to warm to room temperature for 2 hours. The contents of the tube are pumped off any solid formed (LiBr) to a trap held at -196°C. The trap is then warmed to -22°C, allowed the ether and unreacted protected alcohol to be pumped off. 110 mg of a colorless solid results, shown by NMR to be TIPS protected F-adamantyl ethanol (82.1% yield). ^{19}F peaks at -113.2(s), -121.5(s), -219.3(s). ^{1}H peaks at 1.05(s), 1.07(s), 2.51(t), 4.03(t). ^{13}C peaks at 12.0, 17.8, 23.6, 54.3(m), 57.8, 86.3(m), 90.1(m), 106.7(m), 109.7(m), 111.3(m), 114.1(m), 115.8(m),

116.5(m). The full carbon spectrum with assignments can be found in Appendix A.

b. Reaction of F-lithioadamantane and acetyl chloride

1-Hydryl-F-adamantane (0.450 g) dissolved in ethyl ether (2.5 ml) was placed in an ampule (~10 ml) capped with a septum. A diethyl ether solution of methyl lithium (1.6M, 0.9 ml) was injected dropwise through the septum at -80°C. The mixture was allowed to sit for 2 hours. 0.200 ml of acetyl chloride in 1 ml of ethyl ether was then added. An immediate reaction is observed with LiCl being formed. The solution was allowed to warm to room temperature for an hour. The contents of the tube are pumped off any solid formed (LiCl) to a trap held at -196°C. The trap is then warmed to -22°C, allowed the ether, unreacted acetyl chloride, and any acetone by product to be pumped off. The resulting solid was analyzed by NMR to be a mixture of methyl F-adamantyl ketone and its enol. The mixture can then be converted completely to the keto form by adding a methanol/HCl mixture and extracting with ether. ^{19}F peaks at: ketone- -110.8(s), -121.1(s), -218.9(s), enolate- -111.5(s), -121.2(s), -219.3(s). ^{1}H peaks at: ketone- 2.2(s), enolate- 5.6(d), 5.9(d). ^{13}C peaks at: ketone- 20.7, enol- 118.5, 119.6.

c. Reaction of F-lithioadamantane and sulfuryl chloride fluoride

1-Hydryl-F-adamantane (0.260 g) dissolved in ethyl ether (2.0 ml) was placed in an ampule (~5ml) capped with a septum. A diethyl ether solution of methyl lithium (1.6M, 0.6 ml) was injected dropwise through the septum at -80°C. The mixture was allowed to sit for 2 hours. After 2 hours, the solution was frozen with liquid nitrogen and a large excess of

sulfuryl chloride fluoride (0.900 g) was condensed onto the above mixture. The mixture was allowed to warm first to -80°C, and then over a period of 2 hours to room temperature. A small amount of white precipitate was formed. The ampule was then reattached to the vacuum line and while holding the tube at -22°C, the volatiles were pumped out. The tube was then returned to atmospheric pressure with dry nitrogen and warmed to room temperature. The product was extracted with $CFCl_3$, analyzed by ^{19}F NMR. The sample was found to be F-adamantyl chloride.

d. Reaction of F-lithioadamantane and sulfur dioxide

1-Hydryl-F-adamantane (0.260 g) dissolved in ethyl ether (2.0 ml) was placed in an ampule (~5ml) capped with a septum. A diethyl ether solution of methyl lithium (1.6M, 0.6 ml) was injected dropwise through the septum at -80°C. The mixture was allowed to sit for 2 hours. After 2 hours, the solution was frozen with liquid nitrogen and a large excess of sulfur dioxide was condensed onto the above mixture (760 mg). The solution was warmed to -30°C, at which time a precipitate formed and settled to the bottom. After an hour the solution, while still held at -30°C, was pumped on, removing the ether solvent and any remaining sulfur dioxide. 1 ml of $CFCl_3$ was added, followed by 200 mg of bromine dissolved in 1 ml of $CFCl_3$. This mixture was allowed to sit at room temperature for 30 minutes, after which time the solvent and excess bromine were evaporated, the solids were again dissolved in $CFCl_3$ and the solution was filtered and the solvent evaporated again. Finally the remaining solid was dissolved in deuterochloroform and its fluorine NMR spectrum was obtained. The NMR showed the product to be a mixture of F-adamantyl bromide and F-adamantyl hydride.

e. Reaction of F-lithioadamantane and ethyl bromide

1-Hydryl-F-adamantane (0.090 g) dissolved in ethyl ether (1.0 ml) was placed in an ampule (~5 ml) capped with a septum. A diethyl ether solution of methyl lithium (1.6M, 0.2 ml) was injected dropwise through the septum at -80°C. The mixture was allowed to sit for 2 hours. After 2 hours, an excess of ethyl bromide (0.2 ml) was added to the above mixture, still at -80°C. After 3 min the solution is allowed to warm to RT over 30 minutes after which the ampule is attached to the vacuum line. Following trap to trap fractionation, 0.045 mg of Ethyl-F-adamantane was isolated (47% yield). ^{19}F peaks at -113.7(s), -121.2(s), -219.2(s). ^{1}H peaks at 1.34(t), 2.39(q).

G. Fluorofullerenes

1. Synthesis of $C_{60}F_{48}$

100 mg of fullerene was ground in an agate mortar until very fine. 2.75 g of NaF was slowly added to the ground mixture with further grinding until the NaF was a uniform brown/grey color. The reactor consisted of a 3/8" monel tube 8 inches long, affixed with Monel swagelock fittings. The tube was then packed with the NaF/C_{60} mixture. This was done by inserting a roughly 3/8" solid glass rod which has teflon tape wrapped around one end 1/4 of the way into the monel tube. The NaF/C_{60} mixture is then added using a funnel and is very slightly tamped down. The plug needs to stay in its spot in the tube without cascading down or moving when gas pressure is applied, on the other hand, if the tube is packed too tightly the F_2 /N_2 mixture is not able to pass through the tube. The tube is then carefully connected to the fluorine system, which consisted of two fluorine-proof gas transducers, one

of which was connected to 100% F_2, the other to N_2. Using a valve system, any percentage of F_2 /N_2 mixture or either alone is possible. The other end of the monel tube is attached to a teflon tube which was buried in a flask of alumina to trap excess fluorine. The first half of the monel tube was wrapped with heating tape, and the very end of the monel tube was wrapped with a heat sink made from aluminum foil. (See figure 4 for an illustration of the apparatus.) The front of the tube is heated to 250°C under a flow of nitrogen to ensure everything is dry for 30 minutes, and then the fluorine percentage is gradually increased to pure fluorine. The reaction is allowed to proceed for 20 hours. The tube is cooled to RT and then purged with nitrogen for 30 minutes.

The tube is then washed through with $CFCl_3$ (washing out the plug), the solid is extracted a few times with $CFCl_3$ and the solvent is then dried and evaporated. An off-white/tan solid results. This solid is again triturated with 3.3 g of sodium fluoride, and a new

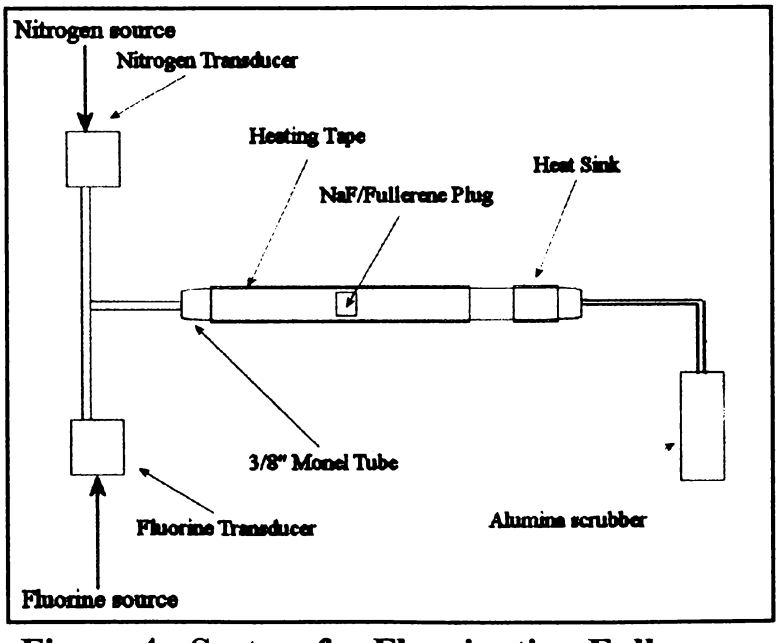


Figure 4 - System for Fluorinating Fullerenes

plug is formed in the monel tube. This plug is fluorinated at 275°C for 16-18 hours. The extraction process is repeated. The solid resulting from the extraction now should be snow white, indicative of very pure $C_{60}F_{48}$. Purity was verified using ^{19}F NMR and/or neg CI MS. Typical amount produced was 160 mg, 70% yield.

In later runs, the middle extraction step was omitted, simply allowing the fluorine to flow through the plug for roughly 40 hours at 250°C. This method worked nearly as well with only a slight reduction in yield.

2. Reaction of fullerene with fluorine at various temperatures

The apparatus and methods used were the same as in the synthesis of $C_{60}F_{48}$, however lower tempuratures were used for 20 hours, the cream to brownish solids resulting from the extractions were then analyzed using neg CI MS. The product consisted of fluorofullerenes from $C_{60}F_{48}$ to $C_{60}F_{36}$. (m/z 1632 to 1404 with the predominant peaks following the formula 1632- (n x 38)).

3. Reaction of $C_{60}HCN$, $C_{60}(CH_3)CN$, and $C_{60}(CN)_2$ with fluorine at various temperatures

The apparatus and methods used were the same as in the synthesis of $C_{60}F_{48}$, however lower tempuratures were used for 20 hours, the cream to brownish solids resulting from the extractions were then analyzed using neg CI MS. The product consisted of fluorofullerenes from $C_{60}F_{48}$ to $C_{60}F_{18}$, as well as small amounts of substituted fluorofullerenes.

4. Reaction of $C_{60}F_{48}$ with reducing agents

a. Heat

A small sample (50 mg) of $C_{60}F_{48}$ was placed in a 1/4" diameter quartz tube, roughly 4 inches long. The tube was attached to a nitrogen source using swagelock with teflon ferrules. A slow stream of nitrogen was passed over the fluorofullerene for 90 minutes while heating the sample to 150°C. After this time period, the tube was allowed to cool, the sample was removed and analyzed using negative CI/MS. The product consisted of fluorofullerenes from $C_{60}F_{48}$ to $C_{60}F_{36}$.

b. Thiophenol, Borane/Dimethyl thioether, Mg/Fe/Zn metals, $Fe(CO)_5$

In all cases, a small sample (50 mg) of $C_{60}F_{48}$ was placed in a 2 dram vial. The solid was then dissolved in 1 ml of $CFCl_3$. The reducing agents were then added in large excess, 100 µl of the liquids/solutions or 100 mg of the metals. The vials were then tightly capped and placed in a cool dark spot for 16 hours. After this time the solution was decanted from any solids, solids were washed with $CFCl_3$, and the solvent was then evaporated and the resulting yellow/tan material was analyzed using negative CI/MS. The product consisted of fluorofullerenes from $C_{60}F_{48}$ to $C_{60}F_{36}$.

c. Hydrogen

A small sample (50 mg) of $C_{60}F_{48}$ was placed in a 1/4" diameter quartz tube, roughly 4 inches long. The tube was attached to hydrogen and nitrogen sources using swagelock with teflon ferrules. A slow stream of hydrogen was passed over the fluorofullerene for 90

minutes while heating the sample to 150°C. After this time period, the tube was allowed to cool, the sample was removed and analyzed using negative CI/MS. The product consisted of fluorofullerenes from $C_{60}F_{48}$ to $C_{60}F_{36}$.

H. Norbornyl cation

1. Formation of cation

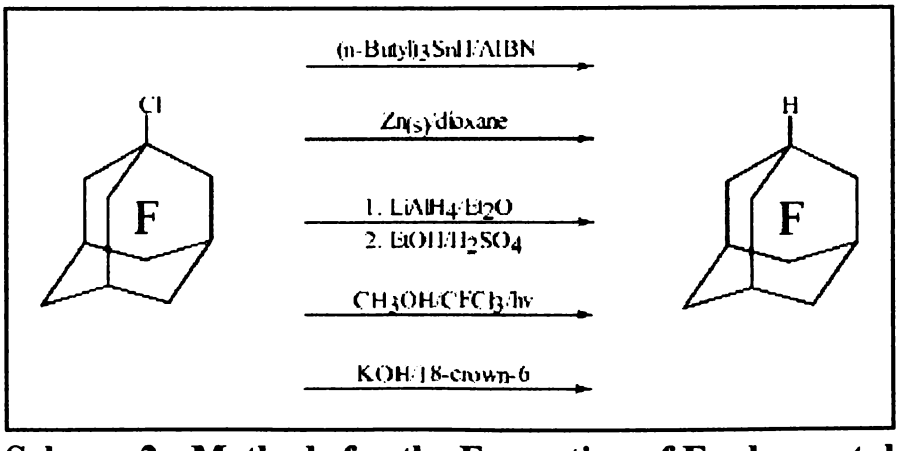
In a typical experiment 0.25 g of 2-chloronorbornane or 2,2-dichloronorbornane was placed into a valved ampule and attached to the vacuum line. 0.500 g of SO_2ClF was then condensed onto the chloride and the solution was brought back to atmospheric pressure with nitrogen and allowed to warm to room temperature. In similar fashion, 1.25 g of SbF_5 and 2.0 g of SO_2ClF were mixed, also forming a solution at room temperature. In a glove bag equal amounts of the two solutions were mixed, with care being exercised to keep both solutions below -50° Celsius. After being mixed together, the solution containing the carbocation is added to an NMR tube fitted with a J Young valve and after being sealed it is kept at -80°C until the NMR is ready to receive the sample.

Chapter 3 - Results and Discussion

A. Methods for the formation of 1-hydryl-F-adamantane

Our lab has now successfully produced 1-hydryl-F-adamantane by a variety of methods. In short these consist of either reducing 1-chloro-F-adamantane or reducing or hydrolyzing an F-adamantane ester. See Scheme 2.

The first method for the reduction of F-adamantyl chloride is using tributyltin hydride[15]. Tributyltin hydride is ideal for converting a Cl to an H, and using AIBN as an initiator proceeds via a free radical mechanism. This reaction has a relatively short reaction time (5 hrs), and has an easy workup, simply pumping on the mixture held at -22°C pulls everything off of the hydryl. The yield for the reaction, however, is still typically less than 50%. While this isn't currently understood, it is a running theme in these reduction reactions. Also, with possible intent to scale up these reaction mixtures, tributyltin hydride is expensive and not trivial to handle. This reaction would also be useful in systems with other



Scheme 2 - Methods for the Formation of F-adamantyl Hydride

functionalities, as long as they are not sensitive to free radical hydride donors.

F-adamantyl chloride can also be reduced using zinc metal in dioxane. This method requires a long reflux and standing time (24 hrs)[24]. Luo also reports that some starting material precipitates. This is due to the poor solubility of F-adamantyl chloride in ethers. As above, the reported yield was only 42%. This reaction would be poorly suited to scale up due to the limited amount of active zinc surface at any particular time.

The most promising reaction with respect to yield is the photochemical reduction of F-adamantyl chloride[24]. In this reaction, chloride is dissolved in a methanol/$CFCl_3$ mixture and irradiated using a 550W medium-pressure mercury lamp. Again the reaction most likely proceeds with a free radical mechanism. Luo reports yields as high as 86%, but this was on a small scale, still using long irradiation times. To achieve those yields on a larger scale irradiation times as long as 70 hours were necessary. This reaction is ideal on a small scale for high yields, or for systems where several chlorides are being replaced. In these systems, the hydride donor is in large excess and the chloride solution is rather dilute which lessens the amount of side reactions. This is probably why this reaction is highly efficient with respect to yield. This reaction may not be as useful with more volatile halides because it is difficult to control the temperature near the mercury lamp.

Zhang reported[17], in an attempt to make F-adamantyl alcohol from F-adamantyl chloride and sodium hydroxide, that hydryl was formed instead. The reaction conditions are quite harsh, 120°C for 48 hours in the presence of 18-crown-6 using benzene/water as the solvent in a sealed stainless steel canister. The 18-crown-6 could be omitted if tetraethylene glycol dimethyl ether was used as the solvent. In similar reactions, poly F-adamantyl

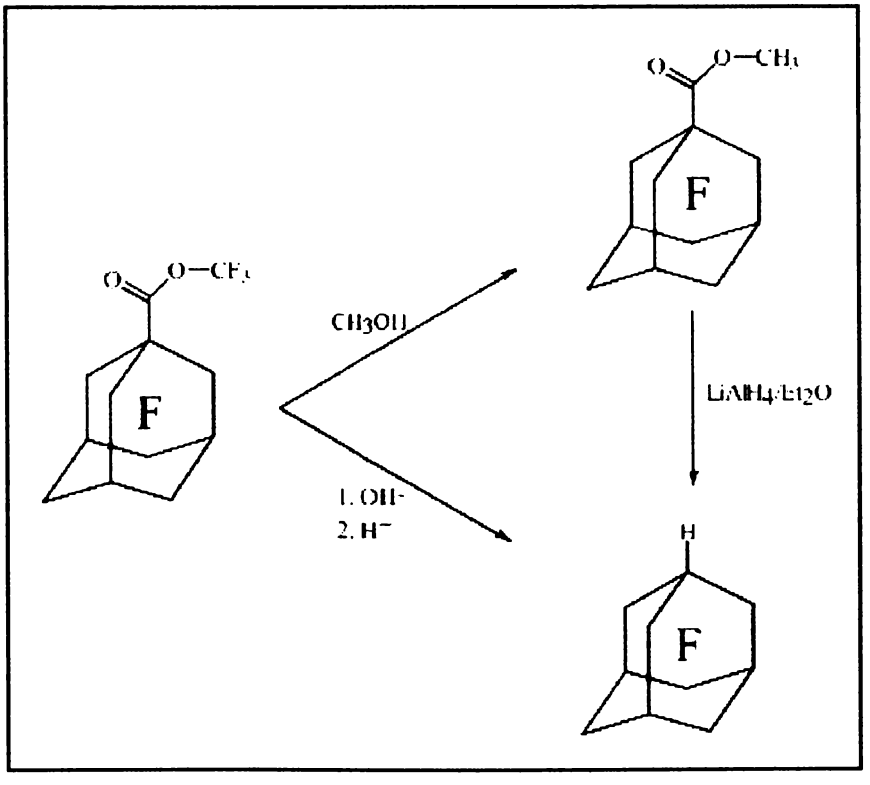
chlorides could be reduced to the corresponding hydrides. The yield for this reaction is quite good, reported as 73%.

Zhang also has reported using lithium aluminum hydride[17] to reduce F-adamantyl chloride. Although the yield again is always less than 50%, it is the method prefered by the author, and it has been scaled up to reduce several grams of F-adamantyl chloride at a time. Although LAH is difficult to handle, after unreacted LAH is hydrolyzed, the work-up is simple. It is possible to proceed with a conventional work-up (solvent extraction), or can attach the vessel to the vacuum line and pump it. Using the conventional work-up, some product is lost due to heating of the ether solution during hydrolysis which is very difficult to control. Using the vacuum work-up, all product is collected, although some may remain either physically or chemically bound to the aluminum byproducts because they are never fully solubilized. Either way, yields are similar and high quality F-adamantyl hydride is formed and is the only compound (including starting material) which is isolated by either work-up. This seems to indicate that byproducts are either being formed which are volatile (broken cages), involatile (polymer), or ionic compounds which are only slowly hydrolyzed by acid. This reaction has little utility with other functionalities because of the high reactivity of LAH, but for this particular compound, this reaction is ideal.

The last two methods involve F-1-Adamantane Carboxylic Acid Methyl Ester[18]. This ester is rather sensitive to hydrolysis which makes it ideal for modification. In the first method, this ester can be transesterified to a non-perfluorinated methyl ester. This ester is much more stable to water and can be isolated and purified easily. It has been shown before that perfluorinated esters are reduced to hydryl compounds, which is also true in this case.

Again the yields, however, are less than 50%.

An even simpler way to produce the hydryl compound from this perfluoroester is to hydrolyze it essentially in situ with aqueous base. Perfluorocarboxylic acids readily decarboxylate, therefore by saponifying the ester, you immediately form a pathway to the hydryl compound. The F-carboxylate is somewhat more stable than the ester however, so I have also then included an acid step in the work-up to ensure that everything is protonated and hence, decarboxylates. Although this synthesis is simple, just adding a work-up step to isolating the product from the reactor, it was very difficult to obtain clean product. Due to these impurities, even if the actual yields were good, the need for GC purification will decrease the overall yield by over 50%. See Scheme 3.



Scheme 3 - Reactions of F-Adamantyl Esters

B. Synthesis of new F-adamantane derivatives

The facile formation of F-lithioadamantane[19] allows a huge variety of synthetic derivatives containing the F-adamantyl group. F-lithioadamantane undergoes reactions characteristic of an alkyl lithium and is even more effective than non-perfluorinated alkyl lithiums at some reactions, such as a simple S_N2 on a primary alkyl halide. At low temperatures, methyl lithium is ineffective in this transformation due to the large covalent character of the Li-C bond. F-lithioadamantane, however, is highly ionic, and quickly undergoes the S_N2 reaction with ethyl iodide to form ethyl-F-adamantane.

With a potential future application of this group being included in drug design, or as fluorous tags, I have adapted the ethyl iodide reaction to include a protected functionality for future modification. F-lithioadamantane also reacts with TIPS protected bromoethanol to form TIPS protected F-adamantylethanol. Due to the high solubility of this compound in deuterochloroform, we were able to see, for the first time, the ^{13}C peaks from the F-adamantyl moiety itself. See Figure 5.

Another reaction of organolithium reagents that we have shown to also take place with F-adamantyl lithium, is nucleophilic attack of carbonyl groups. F-adamantyl lithium attacks acetyl chloride very quickly, even at -80°C. This reaction forms an interesting system. Due to the basic conditions of the reaction and stabilization due to the electron withdrawing F-adamantyl group, the major product is the lithium enolate. Upon addition of acid, the enolate tautamerizes to the ketone, in this case F-adamantyl methyl ketone. Again, should the goal be adding functionality, the acyl halide would contain whatever linker or synthon was desired.

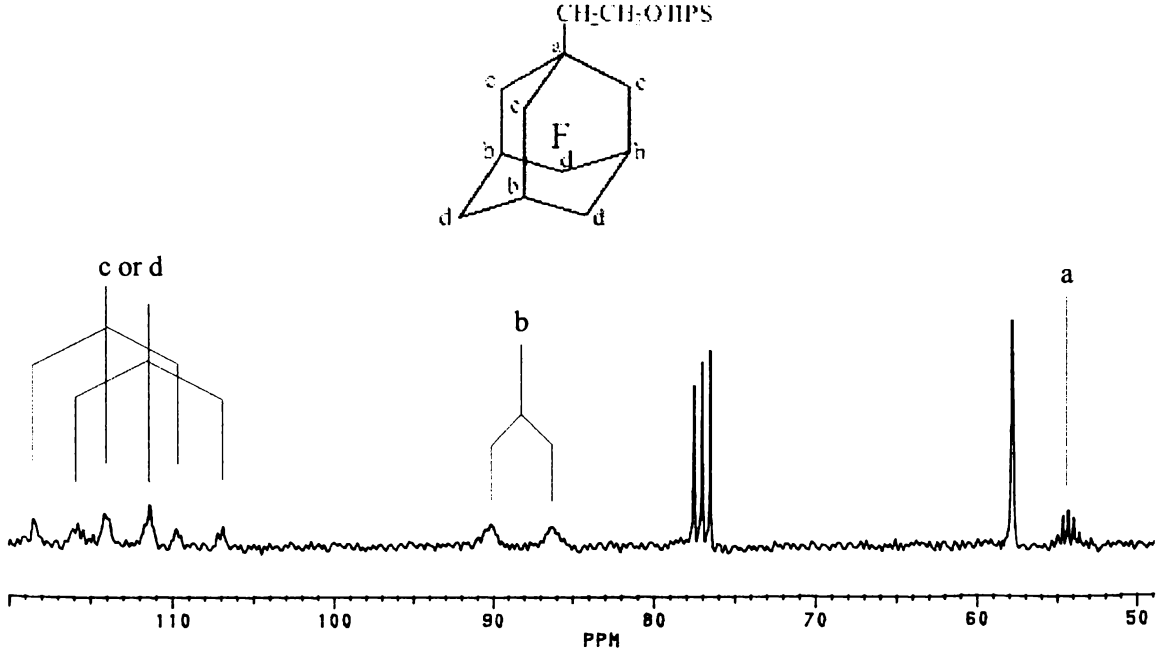


Figure 5 - Carbon spectrum of the F-adamantyl group

Another interesting possibility is the formation of F-adamantyl sulfonic acid. This acid is potentially a rather strong acid which may be soluble both in aqueous and fluorous media. If we could prepare this acid, it would then be trivial to form di and tri acids in this system and perhaps even F-1,3,5,7-adamantyl tetrasulfonic acid, a very interesting aqueous species.

In our first attempt to form the F-adamantyl sulfonic acid, we reacted F-adamantyl lithium with sulfuryl chloride fluoride, expecting it to attack the sulfonyl group just as it attacked the carbonyl group, losing chloride and forming F-adamantyl sulfuryl fluoride. This unfortunately was not the case. Instead of the anion attacking the sulfonyl, it underwent an S_NX reaction, preferentially attacking the chloride of the sulfuryl chloride fluoride. This formed F-adamantyl chloride and a lithium salt which probably lost SO_2, leaving LiF. See

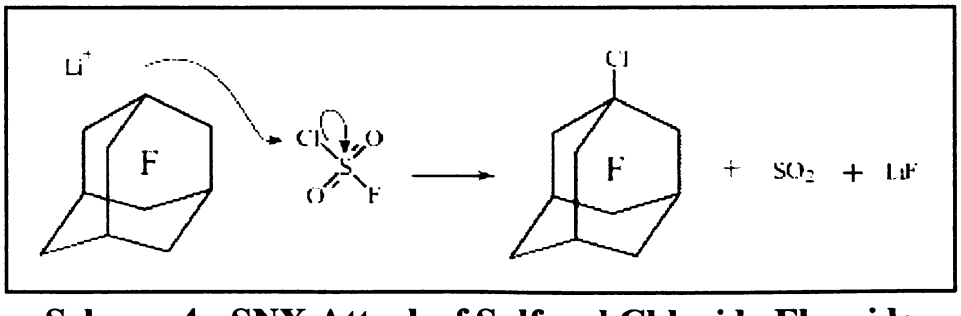
scheme 4.

To circumvent this problem, we decided to use SO_2 to react with the anion instead. It is well known that Grignard reagents react with both CO_2 and SO_2.[25] The lithium salt thus formed would then be oxidized with bromine, hopefully forming the F-adamantyl sulfonyl bromide which could then be easily hydrolyzed to the sulfonic acid. Unfortunately again, this wasn't the case. The product formed instead was F-adamantyl bromide. It appeared as though the reaction with sulfur dioxide had occurred with the formation of the lithium salt which precipitated. Upon oxidation with bromine, however, the compound apparently desulfonylated which left F-adamantyl bromide.

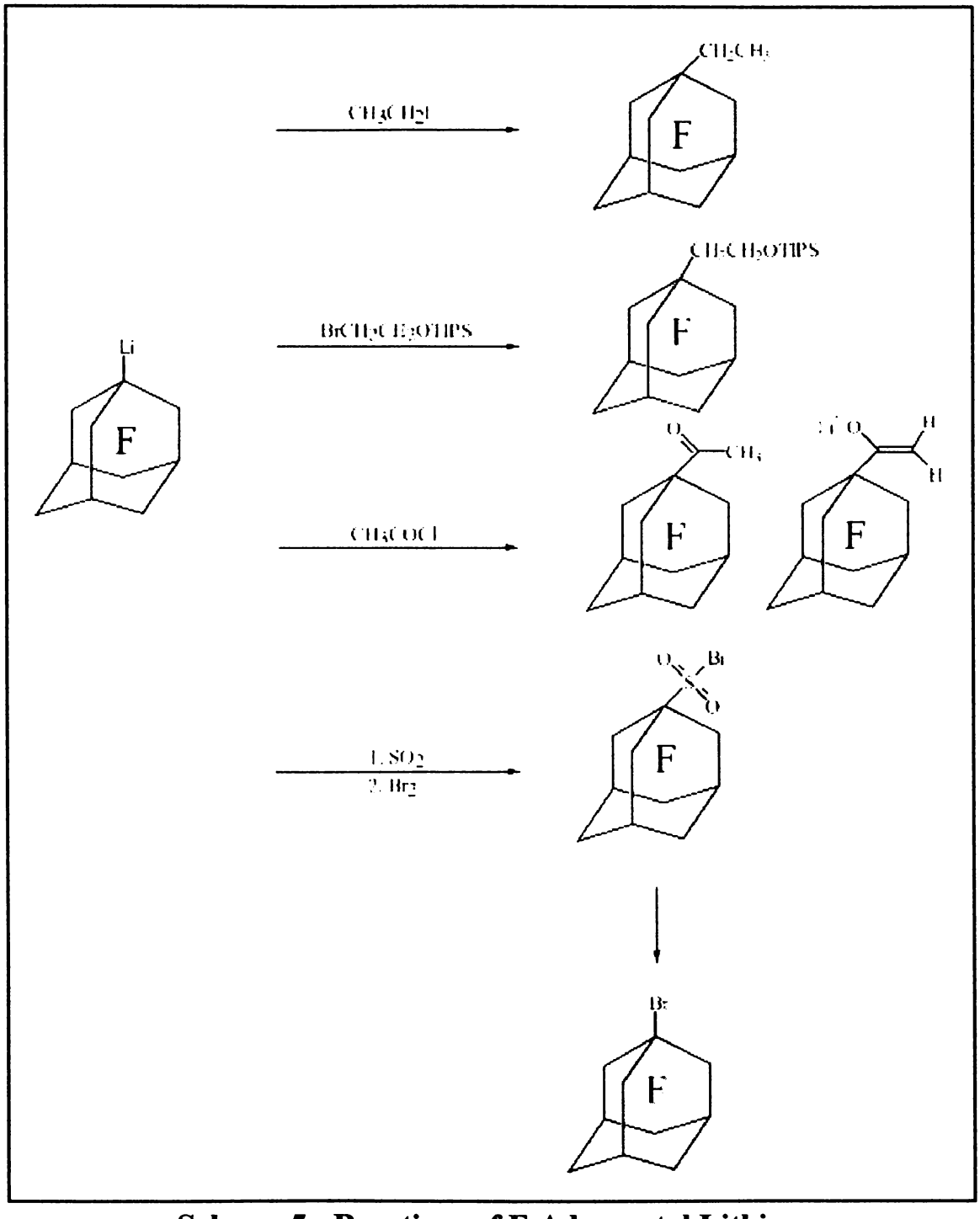
See Scheme 5 for a summary of these new compounds.

C. The electronegativity of the F-adamantyl group by NMR

The electronegativity of a new group can easily be determined by NMR[25]. The chemical shift of protons neighboring a group is roughly proportional to the electronegativity of the group. We graphed the chemical shift of ethyl halides, both the methylene and methyl protons versus the electronegativity of the halide. This method only works, of course, if there



Scheme 4 - SNX Attack of Sulfuryl Chloride Fluoride



Scheme 5 - Reactions of F-Adamantyl Lithium

is zero or constant magnetic anisotropy in the groups. Although there are fluorines in close proximity to the ethyl group, the F- adamantyl group is highly symmetric and should not show anisotropy. Table 3 presents the data and Figure 6 shows the two plots used to determine the results discussed below. Note that the chemical shift for the methyl protons in the ethyl group are inversely related to electronegativity.

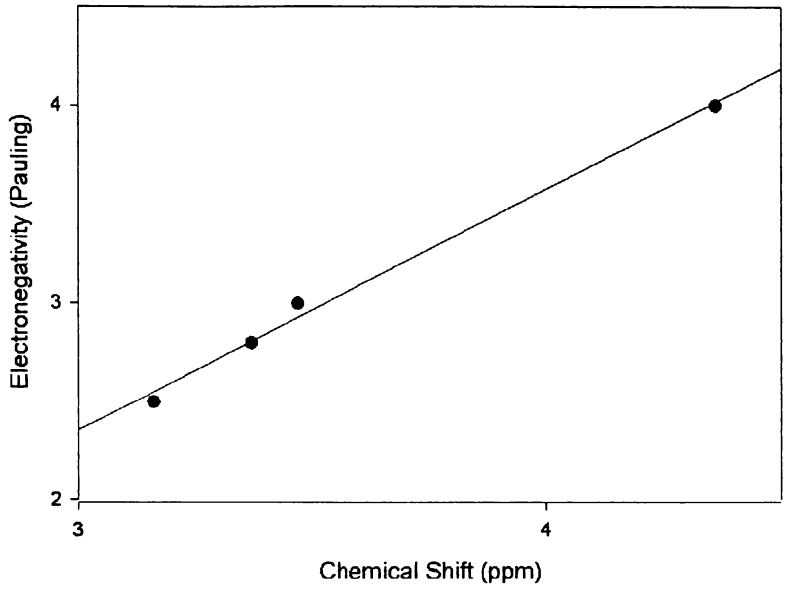
The proton chemical shifts for ethyl-F-adamantane are 2.39 ppm for the methylene and 1.34 ppm for the methyl. Using the data in Table 3, the methylene protons give an abnormally low chemical shift, this is most likely due to excess shielding from the six fluorines which are very close in proximity to the methylene protons. The methyl protons give a more reliable chemical shift resulting in an electronegativity near that of chlorine (3.0).

The electronegativity of the trifluoromethyl group has been calculated by a variety of methods.[26] Table 4 shows a summary of these results. All of the various methods in this paper agree that the electronegativity of the trifluoromethyl group is somewhat greater than that of chlorine. Our result, then, for the F-adamantyl group having an electronegativity very

Table 3 - Chemical Shifts of Ethyl Halides

	Electronegativity (Pauling)	Methylene Chemical Shift (ppm)	Methyl Chemical Shift (ppm)
EtF	4.0	4.36	1.24
EtCl	3.0	3.47	1.33
EtBr	2.8	3.37	1.66
EtI	2.5	3.16	1.88

Chemical Shift vs. Electronegativity of the Methylene Protons of Ethyl Halides



Chemical Shift vs. Electronegativity for the Methyl Protons of Ethyl Halides

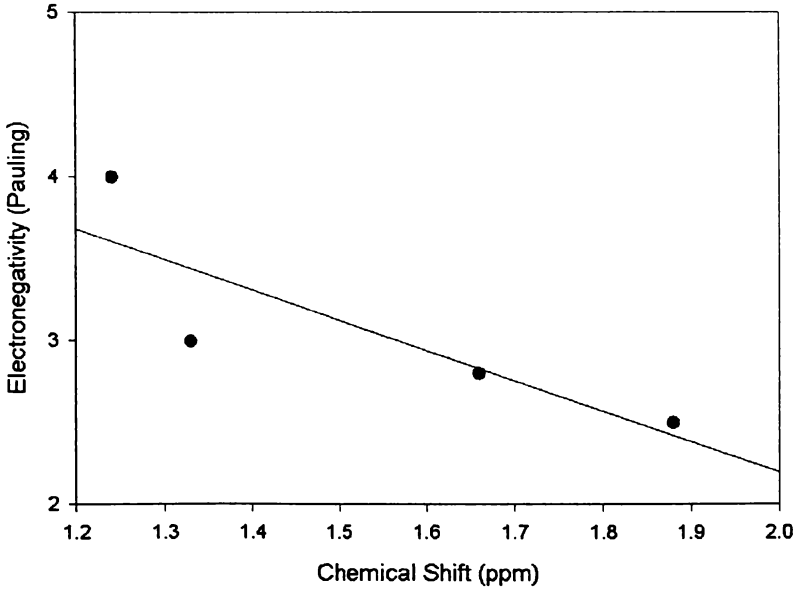


Figure 6 - Graphs of Chemical Shift vs. Electronegativity

Table 4 - The Electronegativity of the Trifluoromethyl Group

	Wells	Huheey	Sanderson	Bratch	Mullay
CF_3	3.35	3.46	3.45	3.49	3.10

close to that of chlorine seems to make sense.

D. The large scale synthesis of $C_{60}F_{48}$ and fluorination of fullerene at lower temperatures

In this lab, Gakh et al, were the first to prepare $C_{60}F_{48}$, and properly report its composition[20]. It is a unique molecule. Space filling models show that the 48 fluorines essentially fill up the space surrounding the sphere. Fitting any more fluorines on the molecule would require breaking open the sphere. This is why we can use rather intense (250°C for 2 days) conditions to ensure that all of the fullerene is fluorinated, and also, is fluorinated faster than it is decomposed at the same temperature. Also aiding us in this process, is that the higher fluorofullerenes are more volatile than fullerene itself, so they tend to leave the plug and migrate to the cooler areas of the reaction tube. Gakh did this reaction on a several milligram scale using a small diameter quartz tube. Since the price of fullerene had dropped considerably over the years, I attempted to scale up his procedure to make large quantities of fluorofullerene at once. The apparatus and procedure were described above.

This technique is also useful because the temperature can be carefully controlled, so I have also run the experiment at other temperatures and shorter times to see what the distribution of products would look like, hoping to possibly hit on a 'magic' temperature, where enough of another fluorofullerene compound would predominate that it could be purified in some manner and studied just as we have with $C_{60}F_{48}$.

Before discussing the results, it is important to consider the processes occurring in the mass spectrometer. Chemical ionization is a technique which minimizes the amount of fragmentation occurring. This is achieved by using a reagent gas to thermalize the electrons. The electrons are first absorbed by this gas (usually ammonia or methane). When observing negative ions, we are interested in the following processes: the ionized gas then participates in electron transfer from itself to the parent, or abstracts a proton from the parent. In our case, the fluorofullerenes form stable negative ions, so these are the ions which we observe. The fragmentation which occurs is from loss of fluoride from the parent. Thus, the pattern seen is in multiples of 19, with the major peaks at multiples of 38. Using the spectrum of pure $C_{60}F_{48}$ as a benchmark for the amount of fragmentation occurring, we can hypothesize that peaks in higher abundance are actually due to compounds in the sample. The only exception to this would be compounds with widely different electron affinities, but due to the extraction work-up, all products injected are fluorofullerenes, and therefore have similar electron affinities to each other.

The results are as expected and are summarized in Table 5. In all cases except as noted above at 250°C, a distribution of products was formed (see Appendix B for spectra). At 150°C, a sizeable amount of $C_{60}F_{44}$ was formed, as well as $C_{60}F_{36}$, with all those in between also being present. At 100°C, $C_{60}F_{42}$ and $C_{60}F_{44}$ were formed and at 50°C, $C_{60}F_{36}$ was the major product with very little density of peaks with less than 36 fluorines. This seems to indicate that similar to 48 fluorines, 36 fluorines may be a sort of 'magic' number due to its high symmetry. This also suggests that 18 fluorines would also be a more stable compound, although at 50°C, $C_{60}F_{36}$ predominates and the spectrum is then rather clean at lower masses,

Table 5 - Fluorination of C_{60} at various temperatures

Temperature (for 20 hours)	Major Product	Other Products
250°C (40 hours)	$C_{60}F_{48}$ (m/z=1632)	
150°C	$C_{60}F_{44}$ (m/z=1556)	$C_{60}F_{36}$ (m/z=1404)
100°C	$C_{60}F_{42}$ (m/z=1518)	$C_{60}F_{44}$ (m/z=1556)
50°C	$C_{60}F_{36}$ (m/z=1404)	$C_{60}F_{38}$, unreacted C_{60}

but unreacted C_{60} could be recovered from the reaction mixture. The hypothesis is then that $C_{60}F_{18}$ is not as thermodynamically stable, but perhaps could be formed with kinetic controls.

E. The fluorination of cyanofullerenes

Furthur expanding on this project, I attempted to directly fluorinate the cyanofullerenes, $C_{60}HCN$, $C_{60}(CN)_2$, and $C_{60}CN(CH_3)$. The goal here was either to make substituted fluorofullerenes, hopefully as a large percentage of the reaction mixture if the CN group is retained. Conversely if theCN group falls off easily, the group may activate some or all of the sphere to attack by fluorine at lower temperatures, forming perhaps F18 or F36 cleanly.

Unfortunately, neither was the case. The results are very similar to those when fluorinating fullerene itself, with only a few anomalies. At 250°C, $C_{60}F_{48}$ and $C_{60}F_{46}$ are by far the major products. Careful inspection of the spectum however, shows two peaks which do not follow the 48F-xF pattern. These are at m/z=1639 and m/z=1601. These peaks correspond to $C_{60}F_{47}CN$, and probably from loss of fluorine in the mass spectrometer

$C_{60}F_{45}CN$. These compounds are present in very tiny amounts. It is well known that perfluorinated nitriles are highly stable, especially to oxidizers, including fluorine. Also, knowing that the starting material is stable at this temperature to loss of HCN, we can speculate that in the presence of fluorine, the formation and loss of HF is favored at this temperature. This loss of HF is then subsequently catalyzing the loss of FCN, or furthur fluorinated products such as CF_4 and NF_3 as the fullerene then regains the pi bond. In summary, it appears as though the HCN substitution may be activating itself, or the surrounding area to attack by fluorine, with the functionality being lost very early in the fluorination. As we explore the fluorination of other similar compounds, we'll see if this holds true.

At 150°C, the results are nearly identical to the fluorination of C_{60} at that temperature. The only difference is again the added presence of $C_{60}F_{47}CN$, still in very small amounts. At 100°C, however, we see an interesting change. The distribution of products is slightly lower than that of fullerene itself. Looking at 50°C, we now see a significant change. Instead of F36 being the dominant species, we are now seeing $C_{60}F_{18}$ and $C_{60}F_{18}O$ as the major species, as well as unreacted starting material. The oxide is due to the fact that water plays a role in this fluorination because of the temperature of the reaction being only 50°C. This seems to verify that attack on the cyanofullerene is easier. Similar to fluorinating fullerene itself at lower temperatures where products with 38-40 fluorines are ending up as thermodynamically more stable $C_{60}F_{36}$; products with 20-24 fluorines are ending up as $C_{60}F_{18}$. See Table 6.

The fluorination of $C_{60}(CN)_2$, shows similar trends. At 250°C, the distribution is similar, although now we have caught a new product, also in very small amounts - this

Table 6 - Fluorination of $C_{60}HCN$ at various temperatures

Temperature (for 20 hours)	Major Product	Other Products
250°C	$C_{60}F_{48}$ (m/z=1632)	$C_{60}F_{47}CN$ (m/z=1639)
150°C	$C_{60}F_{44}$ (m/z=1556)	$C_{60}F_{47}CN$ (m/z=1639)
100°C	$C_{60}F_{40}$ (m/z=1480)	$C_{60}F_{42}$ (m/z=1518)
50°C	$C_{60}F_{18}O$ (m/z=1078)	$C_{60}F_{18}$ (m/z=1062)

appears to be $C_{60}F_{47}(CF{=}NF)$. This would be due to partial fluorination of the CN group. At 150°C, $C_{60}F_{47}CN$ is also observed in this system. Again at 100°C, the distribution is lower than with fullerene and at 50°C, F18 again is prominant, although F36 is also present. A new feature in this spectrum is the presence of the entire series from F18 to F36. Again, in the case of fullerene itself, no species below F36 are observed. Looking back to the case of $C_{60}HCN$, since this compounds shows similar results, it may not be the loss of HF which is catalyzing the loss of these groups. It is more likely that for some reason, perhaps loss of symmetry, that cyano substituted fluorofullerenes are simply thermodynamically unstable. See Table 7 for a summary of these results.

Finally, one experiment was done on $C_{60}CN(CH_3)$ at 250°C. In a very surprising result, no methyl or trifluoromethyl groups were seen on the fullerene skeleton, although again $C_{60}F_{47}CN$ is observed. It is obvious that this fluorination process, or the fluorofullerenes themselves, are not friendly to substituents, but it is difficult to hypothesize why or at what stage these groups are being lost.

We can make some guesses about the $C_{60}F_{36}/C_{60}F_{18}$ abundances. With fullerene itself, it appears that at 50°C, products higher than $C_{60}F_{36}$ are formed, but then lose fluorine to form

Table 7 - Fluorination of $C_{60}(CN)_2$ at various temperatures

Temperature (for 20 hours)	Major Product	Other Products
250°C	$C_{60}F_{48}$ (m/z=1632)	$C_{60}F_{47}(CFNF)$ (m/z=1677)
150°C	$C_{60}F_{42}$ (m/z=1518)	$C_{60}F_{47}CN$ (m/z=1639)
100°C	$C_{60}F_{40}$ (m/z=1480)	$C_{60}F_{42}$ (m/z=1518)
50°C	$C_{60}F_{18}$ (m/z=1062)	$C_{60}F_{18}O$, $C_{60}F_{36}$

the more thermodynamically stable $C_{60}F_{36}$. In the cyanofullerenes, however, the attack of fluorine on the sphere occurs at an overall lower energy. Thus the amount of overall fluorination is lower, and some molecules remain at $C_{60}F_{18}$ which is perhaps marginally stable at these lower temperatures. In the case of fullerene itself at 50°C, attack is more difficult, so those molecules with enough energy to initially react also have enough energy to take them above F36.

F. The reduction of $C_{60}F_{48}$

Gakh *et.al.* also showed that $C_{60}F_{48}$ was a strong oxidizer[27], reacting with iodide (4.3 moles of iodine released per mole of $C_{60}F_{48}$), bromide (only 0.2 moles of bromine per mole of $C_{60}F_{48}$) and also reacting with 2-propanol at elevated temperatures to form acetone. Seeing that these fluorofullerenes barely react with bromide tells us that their oxidizing power is somewhere near that of bromine. More importantly when analyzing the fluorofullerene left over after the reaction with iodine, it contained $C_{60}F_{36}$ - $C_{60}F_{40}$. Is it possible then, that there would be a reducing agent that would give a good yield of one fluorofullerene isomer,

perhaps $C_{60}F_{36}$?

We know that the formation of $C_{60}F_{48}$ as the sole product is difficult, requiring long fluorination times at high temperatures. At 250°C, an equilibrium is established between the formation of $C_{60}F_{48}$ and its decomposition. In an atmosphere of fluorine, and allowing the more volatile $C_{60}F_{48}$ to sublime out of the hottest portions of the tube, we can optimize the formation of $C_{60}F_{48}$. We wanted to see what product would be formed by heating $C_{60}F_{48}$ in an inert atmosphere, in this case nitrogen. Heating it for 2 hours at 150°C, gave a distribution of products, with the largest being $C_{60}F_{44}$, followed by $C_{60}F_{46}$ and $C_{60}F_{42}$. Heating with hydrogen instead of nitrogen did not change this distribution, and essentially the hydrogen had no effect on the reduction.

We also tried using metals as reducing agents, allowing $C_{60}F_{48}$ to react with the metal powder for at least 12 hours in $CFCl_3$. These reactions were very poor, magnesium, iron, and zinc - all giving similar results. A wide range of products including starting material to $C_{60}F_{36}$.

Also, two organic reducing agents gave similar results, thiophenol and borane/dimethylthioether. Both of these reagents gave distributions of products, with the largest being $C_{60}F_{44}$, followed by $C_{60}F_{46}$ and $C_{60}F_{42}$. The only reducer which gave a notable result was $Fe(CO)_5$. It gave a primary product of $C_{60}F_{40}$, followed by $C_{60}F_{42}$, and then $C_{60}F_{38}$ and $C_{60}F_{36}$. This reagent gave a much stronger reaction resulting in a lower distribution of products. This may be due to the fact that the higher fluorofullerenes were acting both as oxidizers and fluorinators, as it is well known that xenon difluoride fluorinates and oxidizes zero valent metal carbonyl complexes[28].

G. Low temperature NMR studies of norbornyl carbocations (see Appendix C for spectra)

1. Low temperature COSY and HMQC of the non-classical norbornyl carbocation

Olah *et.al.* were the first to observe the interesting character of the norbornyl carbocation by treating 2-chloronorbornane with SbF_5 in SO_2ClF at -80°C[29]. This ion is considered a "non-classical" carbocation, with the positive charge delocalized on the face of the norbornane (C1, 2 and 6). The proton and carbon spectra of the ion at this temperature consist only of three peaks. This is due to rapid exchange of 2 and 6 protons (6, 2 hydride shift) on the NMR timescale, see Figure 7.

These original results were obtained using low-field instruments, and although the assignments seemed sound, we decided to revisit this extremely interesting ion with modern 2D techniques. Both the COSY and HMQC of this ion do agree with Olah's original

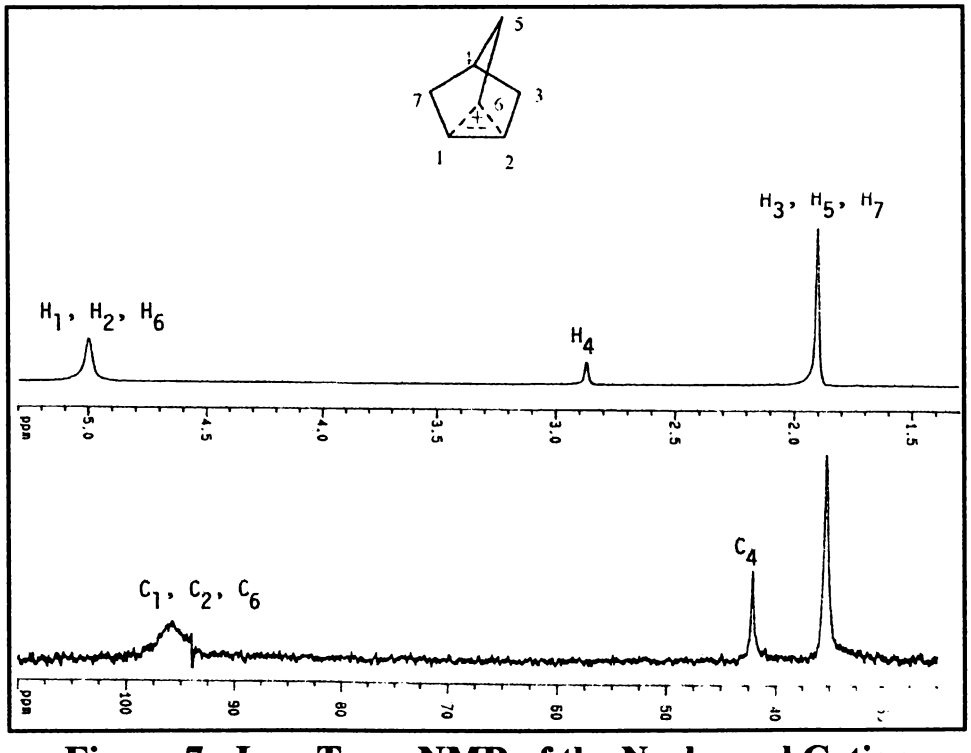


Figure 7 - Low Temp NMR of the Norbornyl Cation

assignments. As expected on the COSY spectrum, there is no crosspeak between the peak corresponding to H_4 and the peak for H_1, H_2, and H_6, but H_3, H_5 and H_7 show crosspeaks to both other peaks. This is because H_4 and H_1, H_2, and H_6 show no scalar coupling. The HMQC shows that the most deshielded peaks in both the carbon and proton spectra correspond to H and C 1, 2, and 6, the smaller middle peak to H and C 4, and the most shielded peak to H and C 3, 5, and 7.

2. Low temperature kinetic study of the norbornyl carbocation using EXSY

The kinetics of this ion are also of interest. Although Olah has estimated the rate constants using line shape analysis,[26] this method relies strongly on theoretical models. We have determined the kinetic data for this ion directly, using EXSY.

2D NOESY-EXSY is a technique which can be used to probe exchange at low temperatures. Qualitatively, a phase-sensitive proton 2D EXSY spectrum shows only NOESY crosspeaks at a temperature where the exchange is frozen out, but new, low intensity crosspeaks begin to appear at higher temperatures where exchange is occurring. The 2D EXSY data can also be treated qualitatively using methods summarized by Perrin and Dwyer.[30]

In order to quantitate this experiment, the exchange rate constants must be estimated, then the relaxation times of the exchanging protons are determined using the standard inversion-recovery technique to find T_1. Olah had already reported these rate constants using line shape analysis,[29] these values, as well as the T_1 are then plugged into Equation 1. These

$$\text{optimal mixing time} \sim 1/(T_1^{-1} + k_{AB} + k_{BA}) \qquad (1)$$

values are summarized on top of Figure 8. The 2D EXSY spectra were then obtained and the data was processed using equations 2 and 3, where t_m is the mixing time, X is the mole fraction, k' is the sum of the forward and reverse exchange rate constants, I_{AA} and I_{BB} are the diagonal crosspeak intensities and I_{AB} and I_{BA} are the crosspeak intensities. Considering that

$$k' = (1/t_m) \times \ln[(r+1)/(r-1)] \qquad (2)$$

$$r = \{4X_AX_B(I_{AA} + I_{BB})/(I_{AB} + I_{BA})\} - (X_A/X_B)^2 \qquad (3)$$

the forward and reverse rates are equal, the rate constant for the conversion of A to B is given by equation 4. These rate constants are also listed in Figure 8.

$$k^{AB} = k'/(1 + X_A/X_B) \qquad (4)$$

Activation parameters for the exchange process were then obtained by an Eyring analysis of the k values. They agree well with the values obtained by the line shape analysis by Olah.

3. Characterization of a new ion, the 2-chloro-2-norbornyl carbocation

The reactions for the formation of 1-chloronorbornane from norcamphor are very interesting from a couple of standpoints. One of these is the now well-studied rearrangement that occurs in the second reaction. We believe we have caught this Wagner-Meerwein 1, 2 alkyl shift[31] by NMR. First I will describe the steps in the reaction, see Scheme 6. In the first chlorination step, norcamphor is treated with PCl_5 in PCl_3, forming

Summary of EXSY and T1 experiments of 2-norbornyl cation

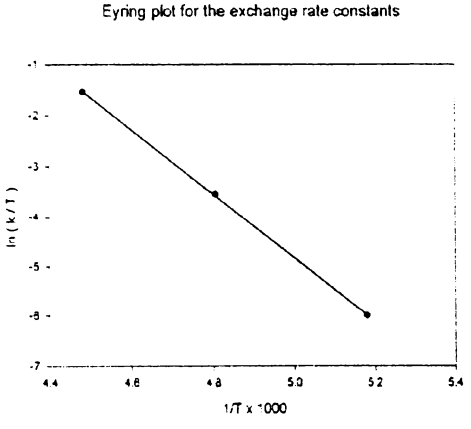
Peaks	193K		208K		223K	
(ppm)	T1(s)	Mixing time (s)	T1 (s)	Mixing time (s)	T1 (s)	Mixing time (s)
4.93	0.95	0.3	1.47	0.06	2.11	0.01
2.82	1.06		1.52		2.10	
1.85	1.60		1.73		2.06	

Exchange rate constant from EXSY experiment

Exchange sites	Rate Constant k (s^{-1}) at 193k	Rate constant k (s^{-1}) at 208K	Rate constant k (s^{-1}) at 223K
1 - 4	0.52	5.42	45.99
2, 6 – 3, 5	0.45	6.47	50.38
Average k	0.485	5.945	48.185

Eyring plot of exchange rate constant

	193K	208K	223K
ln(k/T)	-5.986	-3.555	-1.532
1/T	$5.181 * 10^{-3}$	$4.808 * 10^{-3}$	$4.484 * 10^{-3}$



Linear fitting result: Slop = -6393.428, Constant = 27.153

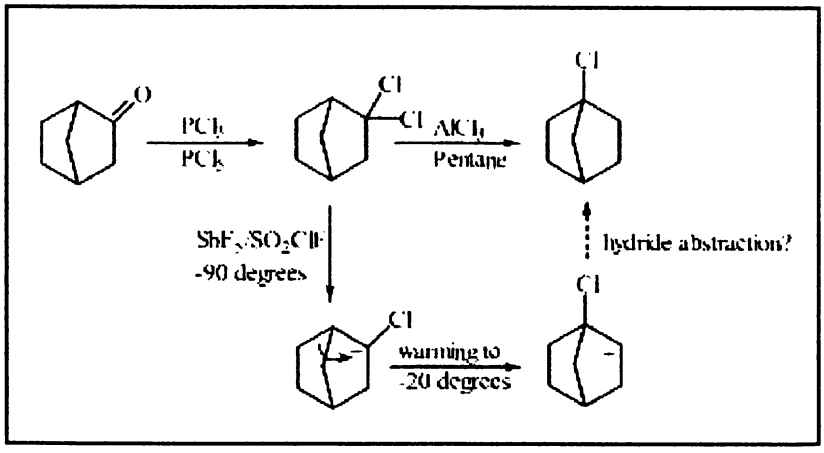
From the equation: $\ln(k/T) = -\Delta H/(RT) + (\Delta S/R) + \ln(k_B/h)$

$R = 8.314$ J / (mol*k), $k_B = 1.38 * 10^{-23}$ J/k, $h = 6.626 * 10^{-34}$ J / Hz

$\Delta H = 6393.428 * R = 6393.428 * 8.314 = 53.15 * 10^3$ J /mol.

$\Delta S = R*\{27.153 - \ln(k_B/h)\} = 8.314 * \{27.153 - 23.760\}$
$= 8.314 * 3.393) = 28.2$J / (mol * k) = 6.74 eu

Figure 8 - EXSY Kinetics Data



Scheme 6 - Reactions of Chloronorbornanes

2,2-dichloronorbornane. The second step is also Lewis acid mediated, this time using $AlCl_3$. A carbocation/tetrachloroaluminate complex is formed which then undergoes the Wagner-Meerwein rearrangement. Finally a hydride is abstracted forming 1-chloronorbornane. Our goal was to reproduce the Lewis acid conditions by treating 2,2-dichloronorbornane with SbF_5 in SO_2ClF. The superacid media allowed us to study the carbocation formed at low temperature. We believe this new ion to be the 2-chloro-2-norbornyl carbocation, formed by the loss of chloride. We obtained proton and carbon spectra of this ion, as well as COSY, HMQC, DEPT, and NOESY spectra. See appendix C for all spectra.

The first thing we found interesting about this cation was that unlike the norbornyl cation formed from either 1 or 2-chloronorbornane, this cation was classical. It showed seven clear resonances in the ^{13}C spectrum, only one of which showed an extreme amount of deshielding. Were the carbocation non-classical, this deshielding due to the positive charge would have been spread over 3 carbons. The most deshielded peak was the carbocation at 284.5 ppm. The DEPT spectrum showed that this peak indeed did not have a proton attached to it. The DEPT also showed the presence of two C-H carbons and four H-C-H carbons.

Already knowing that 1-chloronorbornane does not form a bridgehead cation, and that these are highly unstable, we were not surprised by the presence of the two bridgehead C-H's. Essentially this was enough information to deduce the structure shown below (Figure 9). At first glance, a halogen directly attached to a carbocation would be thought to be unstable, however, these are well known[32,33]. The chlorine (and fluorine as well) tends to stabilize the carbocation by back donation from the filled halogen p orbital into the empty carbocation p orbital.

We assigned the proton and carbon spectra using the HMQC, as well as previous assignments made by Olah for the 2-methyl-2-norbornyl cation. Table 8 is a summary of those results. Finally, we checked our results by verifying crosspeaks on the COSY and NOESY spectra. Those results are summarized in Table 9.

There are a few very interesting properties to this ion. The proton spectrum of this

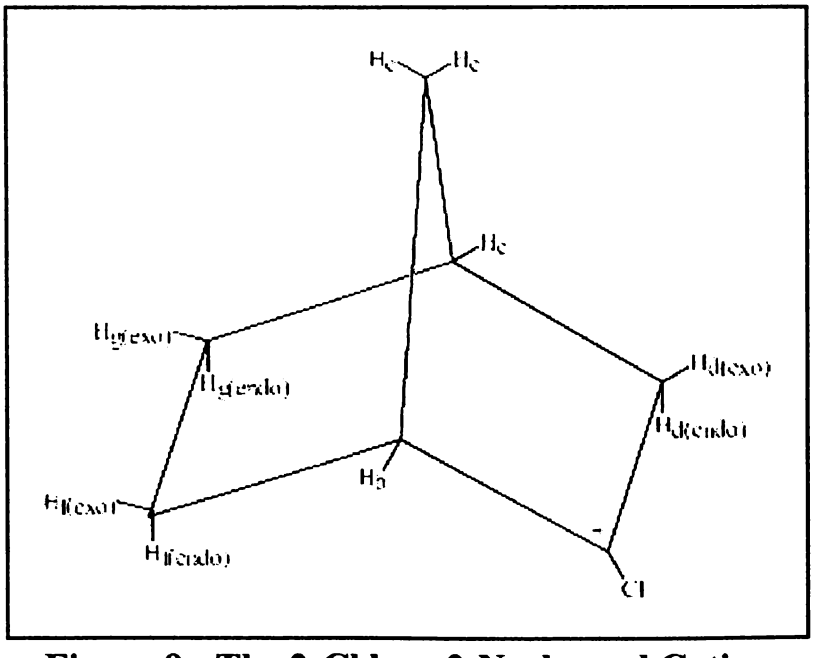


Figure 9 - The 2-Chloro-2-Norbornyl Cation

Table 8 - Summary of HMQC Results

^{13}C peak	Correlated Proton Peaks	Assignment
284.5		a
76.9	4.93	b
61.0	~3.6*(exo), 3.52/3.48(endo)	d
42.5	3.40	c
40.5	~3.6*(exo), 2.32(endo)	f
36.0	2.47	e
22.2	2.07(exo), 1.66(endo)	g

Table 9 - Summary of COSY and NOESY results

Proton peak(s)	COSY Crosspeaks	NOESY Crosspeaks
b	f(weak)	e(weak), f(weak), g(weak)
c	d(weak)	d(weak)
d	d(strong), c(weak)	d(strong), c(weak)
e	d or f(weak)*	b(weak), f(weak), g(weak)
f	g(strong), b(weak)	g(strong), b(weak), e(weak)
g	g(strong), f(strong)	f(strong), g(strong), b(weak), e(weak)

*NOTE - the chemical shift of one F and D proton lie on top of each other

ion matches closely with the spectrum of the 2-phenyl-2-norbornyl cation, much more so than with the 2-methyl and 2-ethyl cations. Again this implies that the chlorine bond does indeed have some double bond character, just as the phenyl cation would due to resonance with the aromatic system. In our system, as well as the other three, the f protons have widely different chemical shifts, over 1.2 ppm in our system. Olah attributes this, as well as the very deshielded b methine proton (4.9 ppm in our system) to the fact that there is indeed some nonclassical nature to these carbocations, with significant amounts of deshielding being experience by H_b and H_f(exo). Also, we were able to resolve the d pair, and g pair. The e pair, however, in our system is not diastereotopic.

We also predicted that if we warmed the sample to -20°C we may see the ion beginning the Wagner-Meerwein rearrangement. Unfortunately the ions are highly unstable and quickly polymerize at that temperature, but we were able to catch a quick carbon and proton spectrum. Both are very interesting, the carbon spectrum coalesced to only 5 peaks, as well as two very broad peaks. These peaks indicate exchange, most likely a hydride shift between the two secondary centers. The carbocation peak moved very little (294.4), but the key in this spectrum is a new peak at 91.1 which is possibly the carbon attached to the now bridgehead chlorine. In the proton spectrum, the peak for H_c has moved from 3.4 ppm to 3.6 ppm (now closer to the carbocation), but more interestingly the peak for H_b moved from 4.9 ppm to 5.6 ppm, possible indicative of this old bridgehead proton now becoming the proton on the carbocation. So we can confidently hypothesize that the 2-chloro-2-carbocation is indeed becoming the 1-chloro-2 or 3-carbocation at this higher temperature.

Chapter 4 - Conclusions

This project has explored many new aspects of the chemistry of the F-adamantyl group. The F-adamantyl anion is remarkable, showing incredible stability as a lithium salt, being an excellent nucleophile, both in classical S_N2 reactions, as well as attack on carbonyl and sulfonyl groups. Unfortunately, these properties also make it ideal for undergoing decarboxylation and as we have now shown, and more surprising - desulfonylation as well. Also, because of its bulk, it undergoes an S_NX reaction with sulfuryl chloride fluoride, rather than attack the sulfonyl itself. Even though, in the case of the sulfonic acids, we couldn't form the target molecule, the ability of this ion to undergo these new types of reactions reveals that there is much very interesting chemistry still hidden here.

More importantly, we have shown that it is possible to use this group as a substituent or building block for larger molecules, or as a fluorous tag. It is well known that the trifluoromethyl group has an electronegativity (hence inductive effect) between that of fluorine and chlorine, and thus can be used to fine tune the specific activity of a pharmaceutical. The F-adamantyl group is very close to chlorine in electronegativity, but would have unique properties due to its large size and fluorophilicity. We have also shown the ability to substitute the F-adamantyl group so it can be used as a fluorous tag. We suspect that this group would have unique solubility properties which would need to be explored. For example F-adamantyl chloride is soluble in $CFCl_3$, but only slightly in chloroform. F-adamantyl hydride is soluble in $CFCl_3$, more soluble in chloroform than the chloride and rather soluble in ether, probably with hydrogen bonding. Ethyl-F-adamantane is not particularly soluble in either $CFCl_3$ or ethanol, but is very soluble in a 50/50 mixture. Finally, the TIPSO

protected F-adamantylethanol is highly soluble in chloroform and ether. Obviously, the F-adamantyl group would show novel partitioning useful in many new areas. Not only could this group be used as a fluorous tag, but simply by adding a substituent, the partitioning of the compound could be fine tuned to whatever solvent or polarity was needed. This could even extend as far as making these compounds soluble in water, fluorous phases, and organic phases, and altering this tuning in the middle of a separation.

Although making controlled substitutions and otherwise functionalizing fullerene is now a field of its own, no one had investigated fluorinating these new compounds, or derivitizing $C_{60}F_{48}$ itself. Even though we were not successful in producing either a substituted fluorofullerene, or a single fluorofullerene apart from other compounds as is possible with $C_{60}F_{48}$. We did learn a great deal about these fascinating compounds. The various cyanofullerenes fluorinated very similarly to fullerene itself and did not retain the cyano, or other functionality that may be present in any useful amount. We did see though, that through these compounds, we could access compounds between $C_{60}F_{18}$ and $C_{60}F_{36,}$ which were not seen by simply fluorinating fullerene itself.

Gakh *et.al.* showed that $C_{60}F_{48}$ is an oxidizer, but is it possible to use this property to form a single fluorofullerene isomer? Most reducing agents showed the same trend of removing 2 to 6 fluorines, similar to letting $C_{60}F_{48}$ decompose at a slightly elevated temperature with no reducing agent. Only $Fe(CO)_5$ produced a different result, showing more reduction. This is most likely due to the fact that $Fe(CO)_5$ could be fluorinated as well as oxidized, proving that similar to other highly fluorinated compounds, $C_{60}F_{48}$ is an oxidative fluorinator.

Although the rearrangements of norbornanes have been known now for over a century, and the formation of 1-chloronorbornane from norcamphor via 2,2-dichloronorbornane is a well known reaction. We believe we are the first to catch this rearrangement by NMR. We have also characterized a new ion using these same techniques. The 2-chloro-2-norbornyl ion is very interesting in itself, being rather stable and having chemical shifts similar to the 2-phenyl-2-norbornyl ion, showing the impressive degree of double bonding in the carbocation-chlorine bond. As the wider picture, in catching this ion and watching it rearrange, we believe we can now explore the next step in the reaction. This step is the hydride abstraction which forms the final 1-chloronorbornane product. It is believed that the hydride is abstracted from another chloronorbornane resulting in a polymer which lowers the yield of the reaction below 50%. We can now show that it may be possible to form the 2-chloro-2-norbornyl carbocation at low temperature, warm it to allow it to rearrange and again freeze out the cations at low temperature, and then finally quench with a weak hydride donor before warming the solution. Carefully done, this could give a nearly quantitative yield of product.

Although the three focuses of this thesis are not apparently related, the goals were still the same. That is to explore these three very unique chemical systems to learn more about how they undergo chemistry, but more importantly to then apply them to areas where they may be useful, now or in the future.

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Appendices

Appendix A
Substituted F-Adamantane Spectra

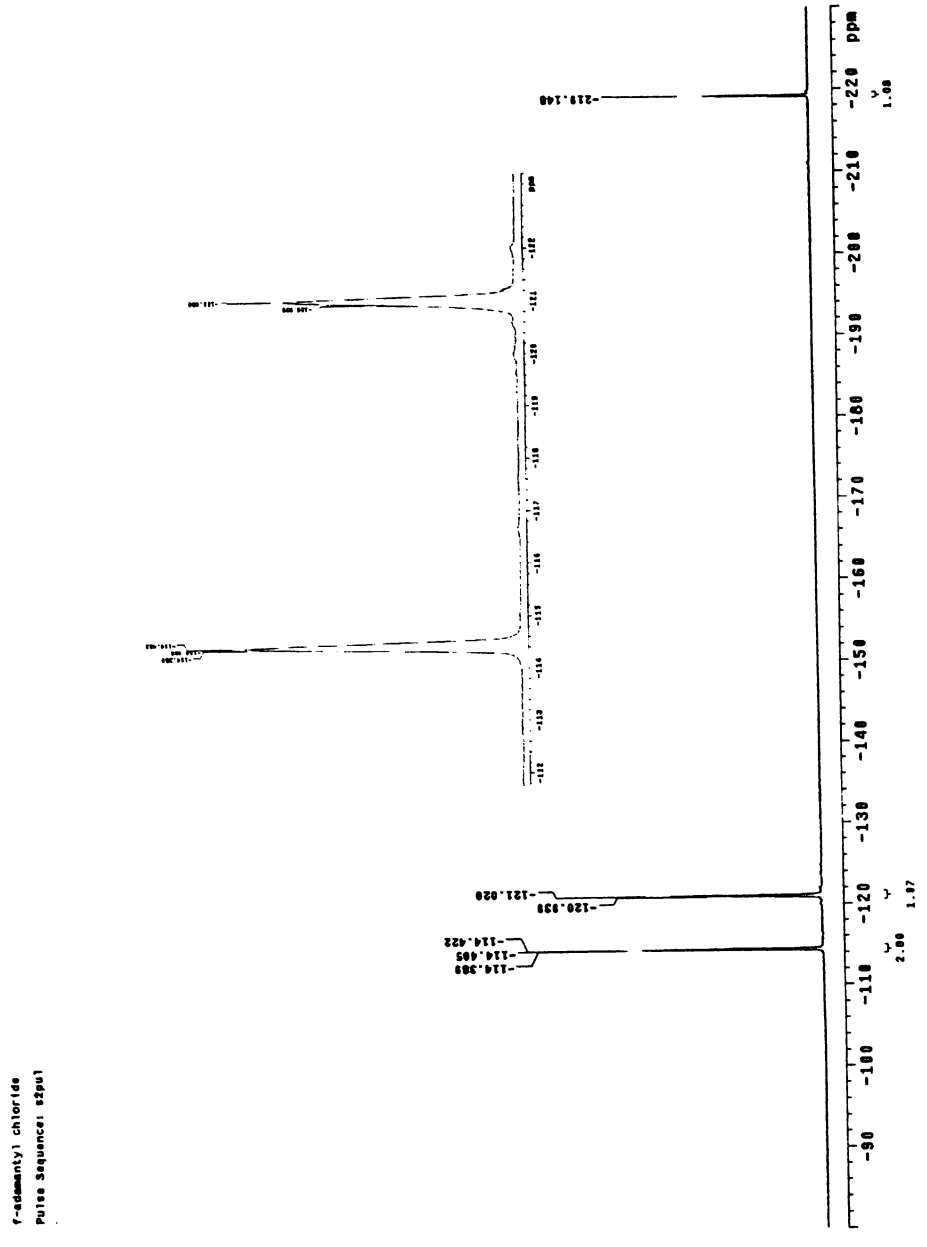


Figure A-1 1-Chloro-F-Adamantane (^{19}F)

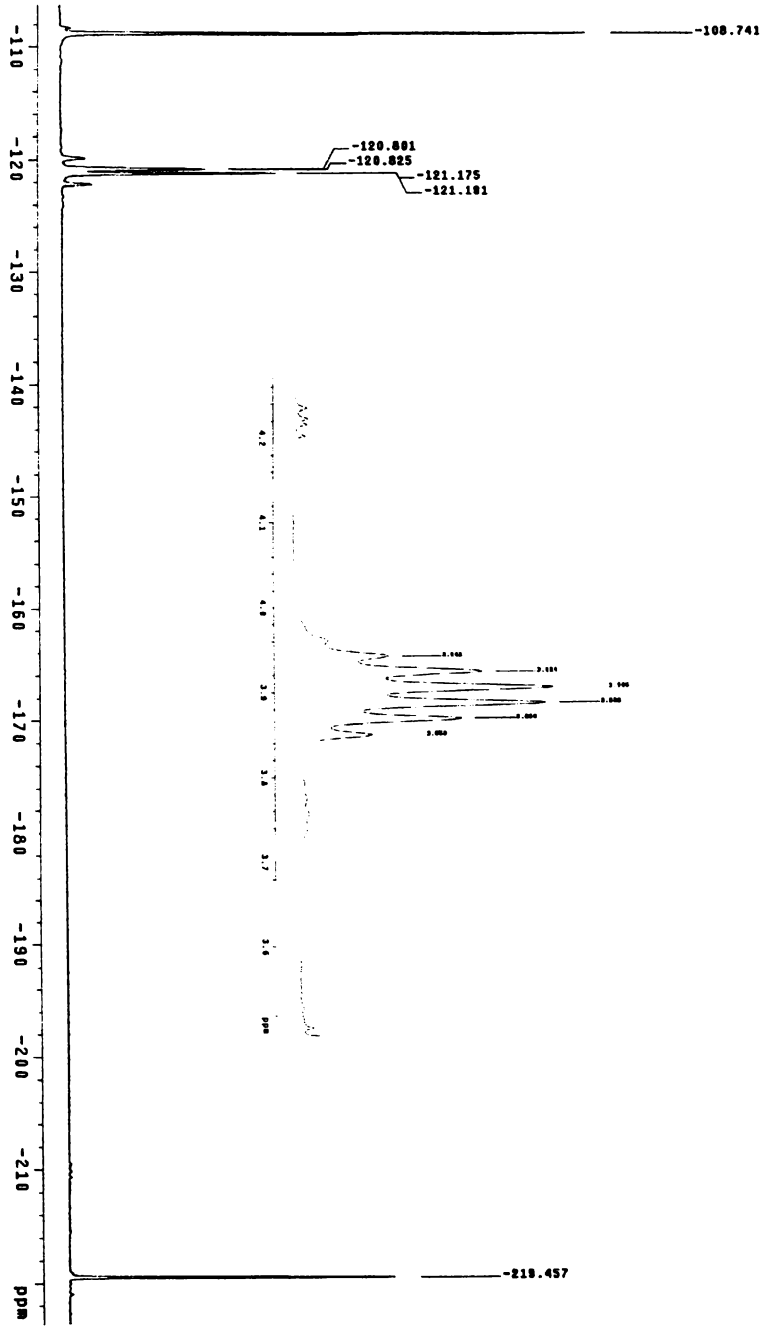


Figure A-2 1-Hydryl-F-Adamantane (^{19}F and ^{1}H)

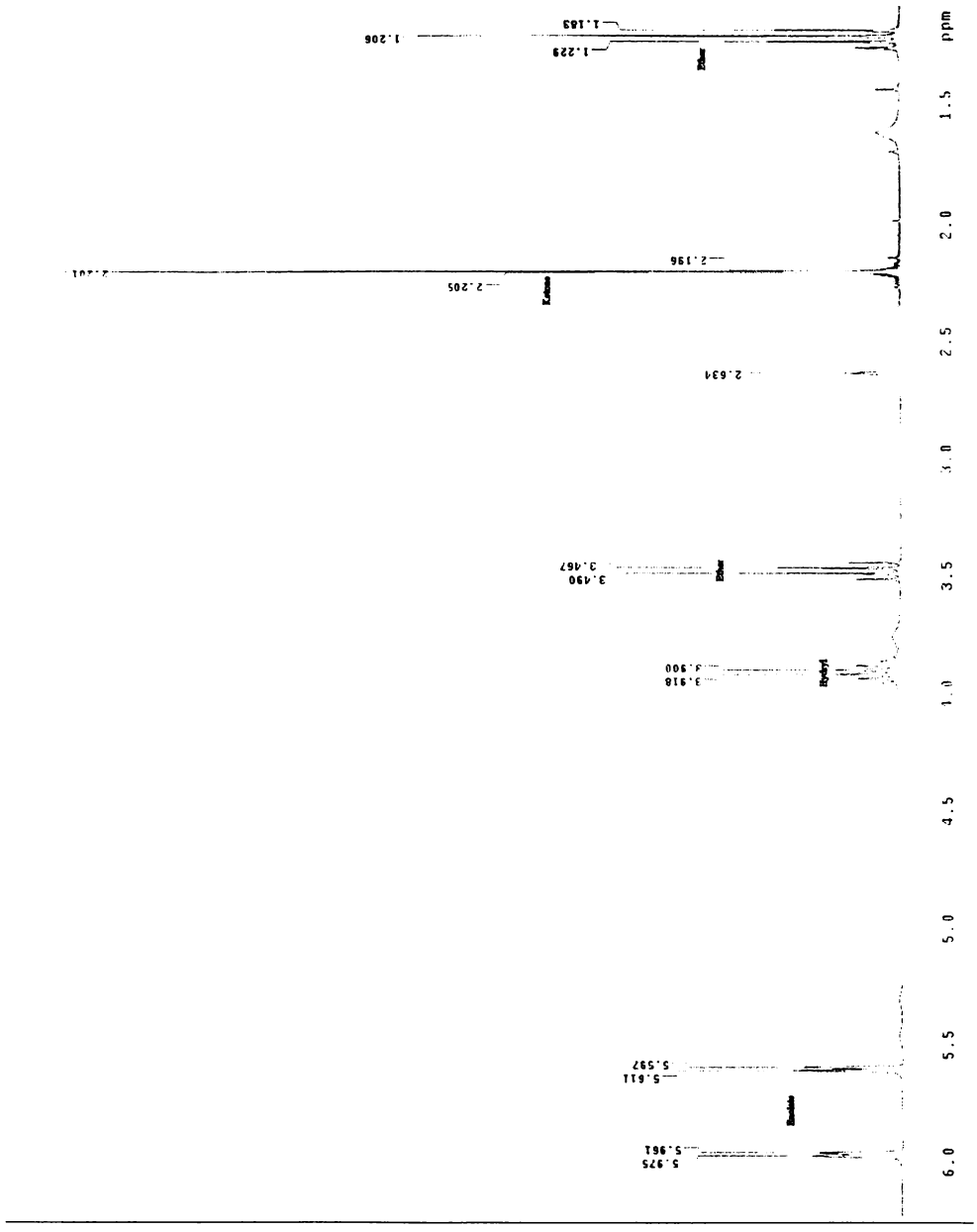


Figure A-3 F-Adamantyl Methyl Ketone and Enolate (^{1}H)

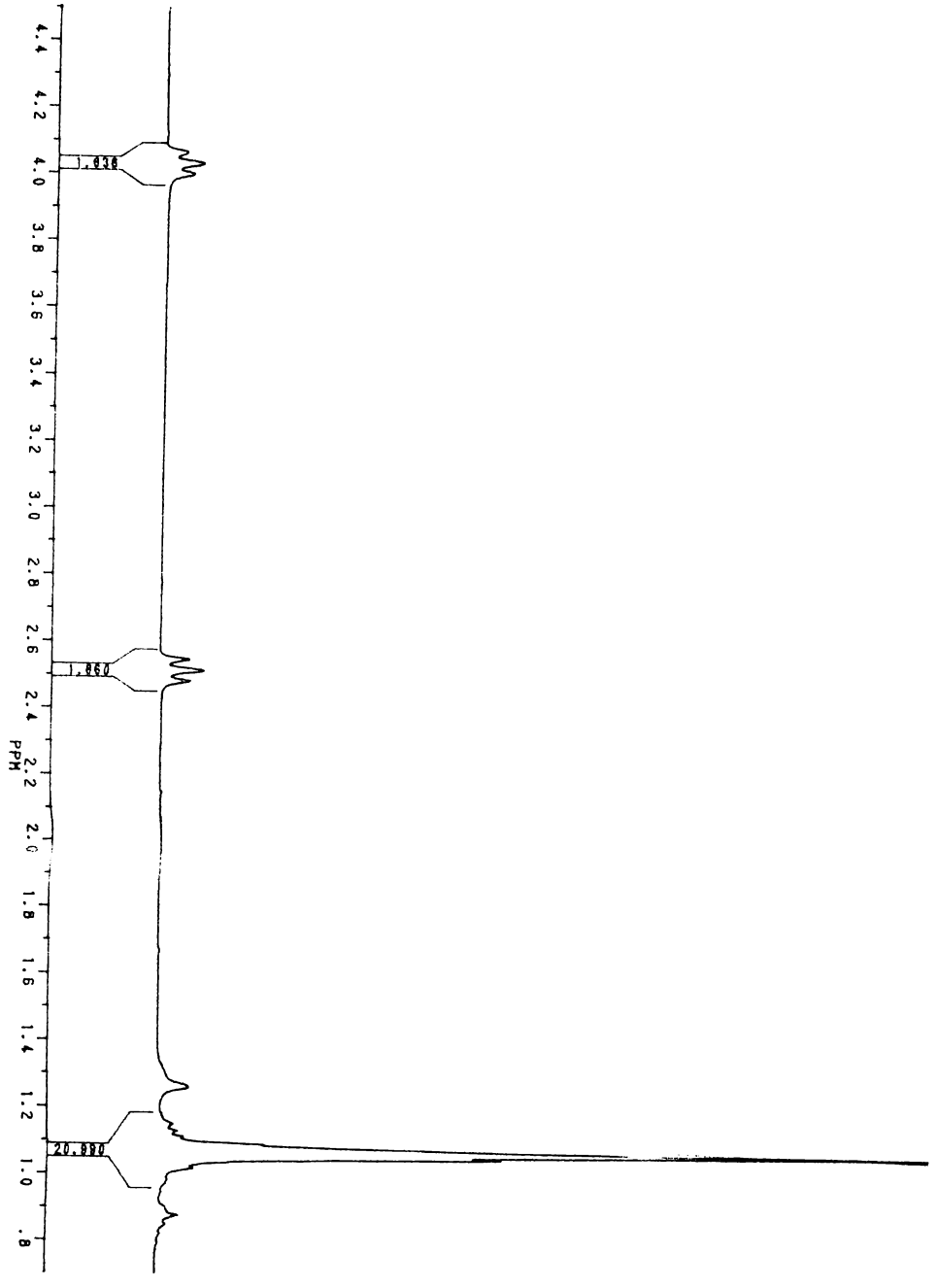


Figure A-4 TIPSO protected F-Adamantylethanol (^{1}H)

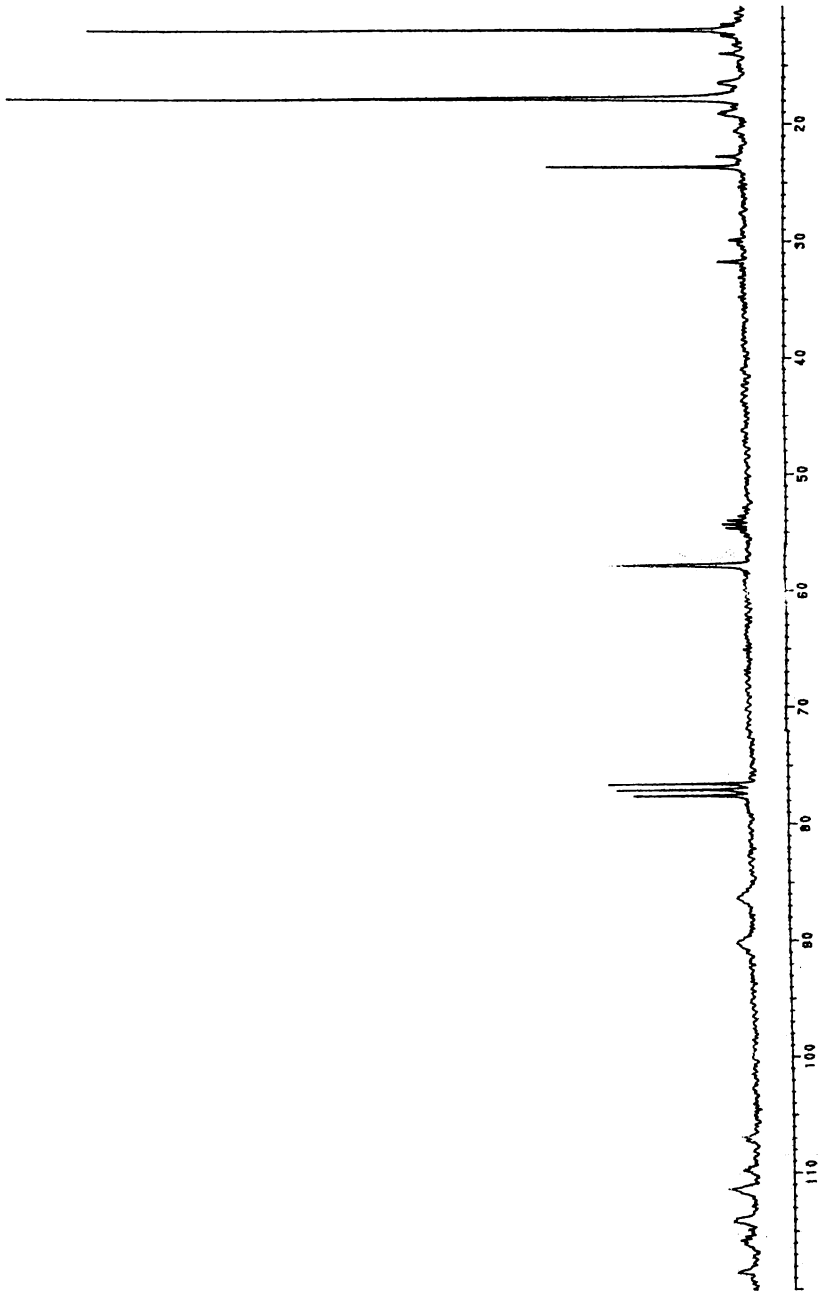


Figure A-5 TIPSO protected F-Adamantylethanol (^{13}C)

Appendix B
Fluorofullerene Mass Spectra

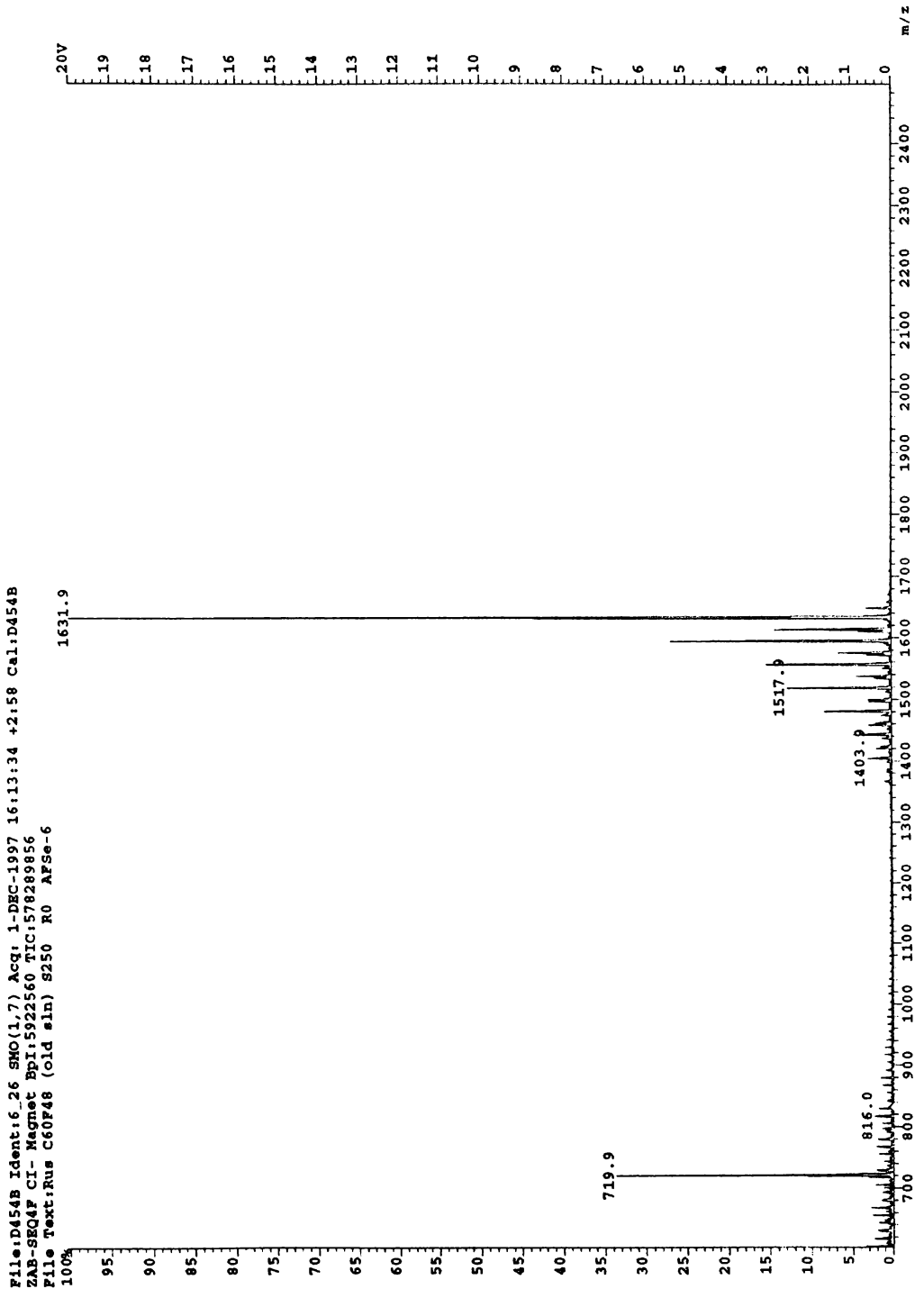


Figure B-1 Pure $C_{60}F_{48}$

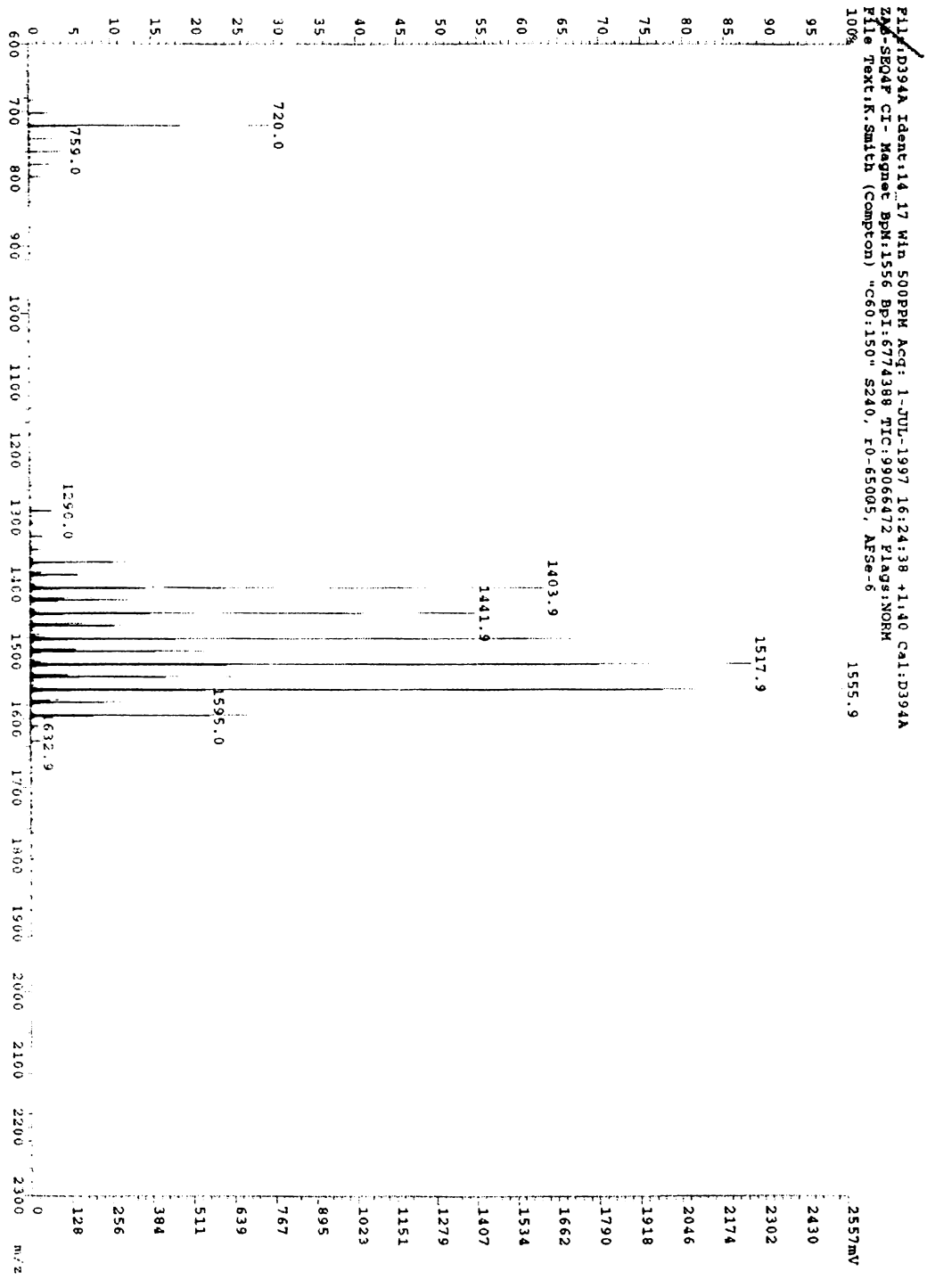


Figure B-2 $C_{60} + F_2$ at 150°C

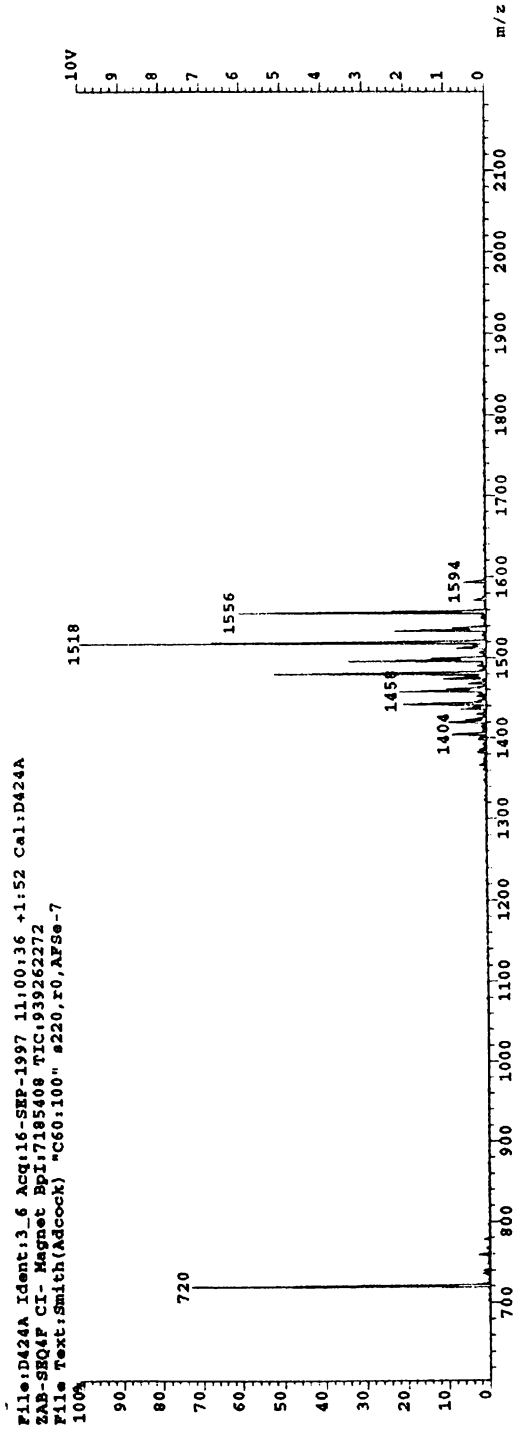


Figure B-3 $C_{60} + F_2$ at 100°C

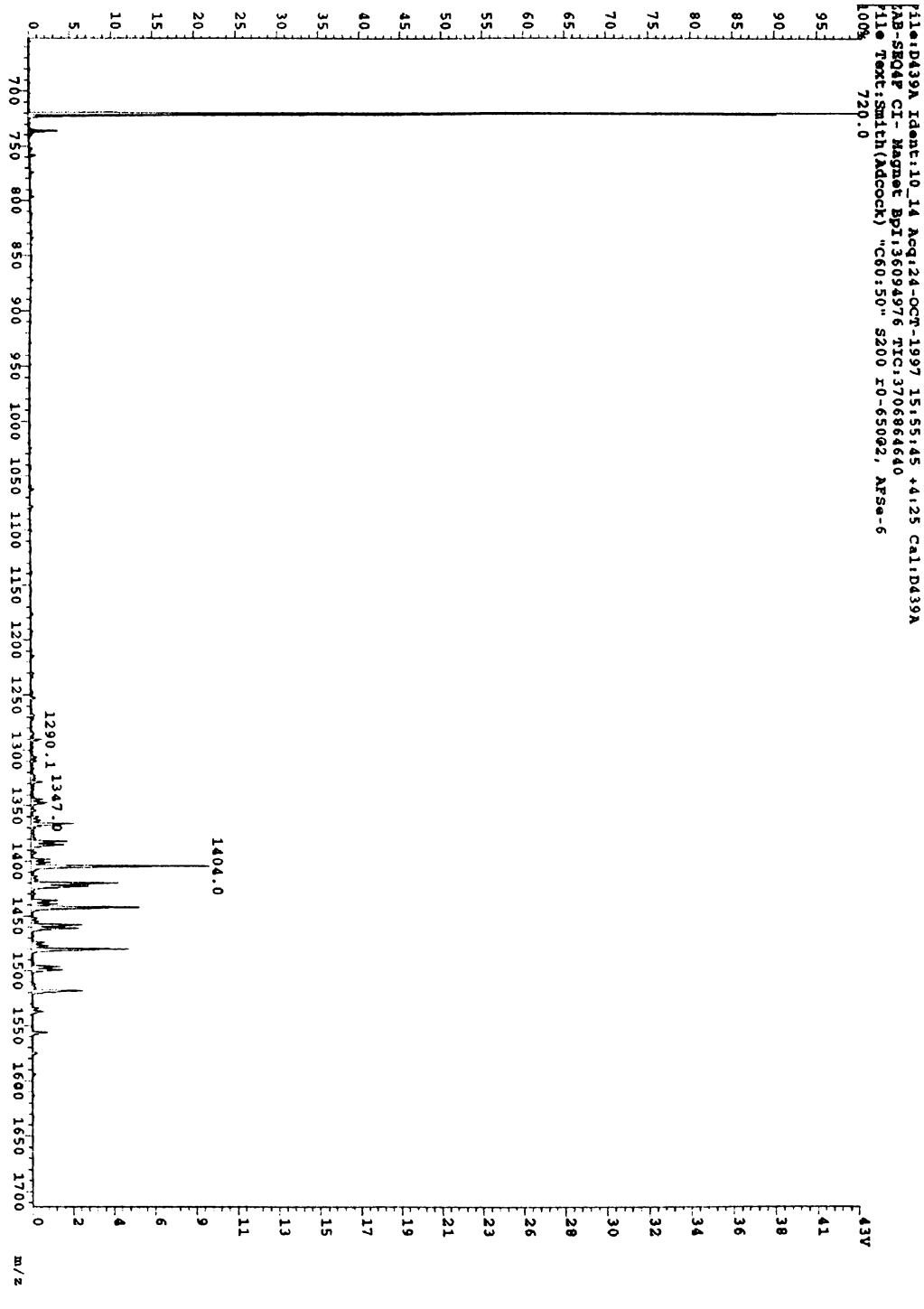


Figure B-4 $C_{60} + F_2$ at 50°C

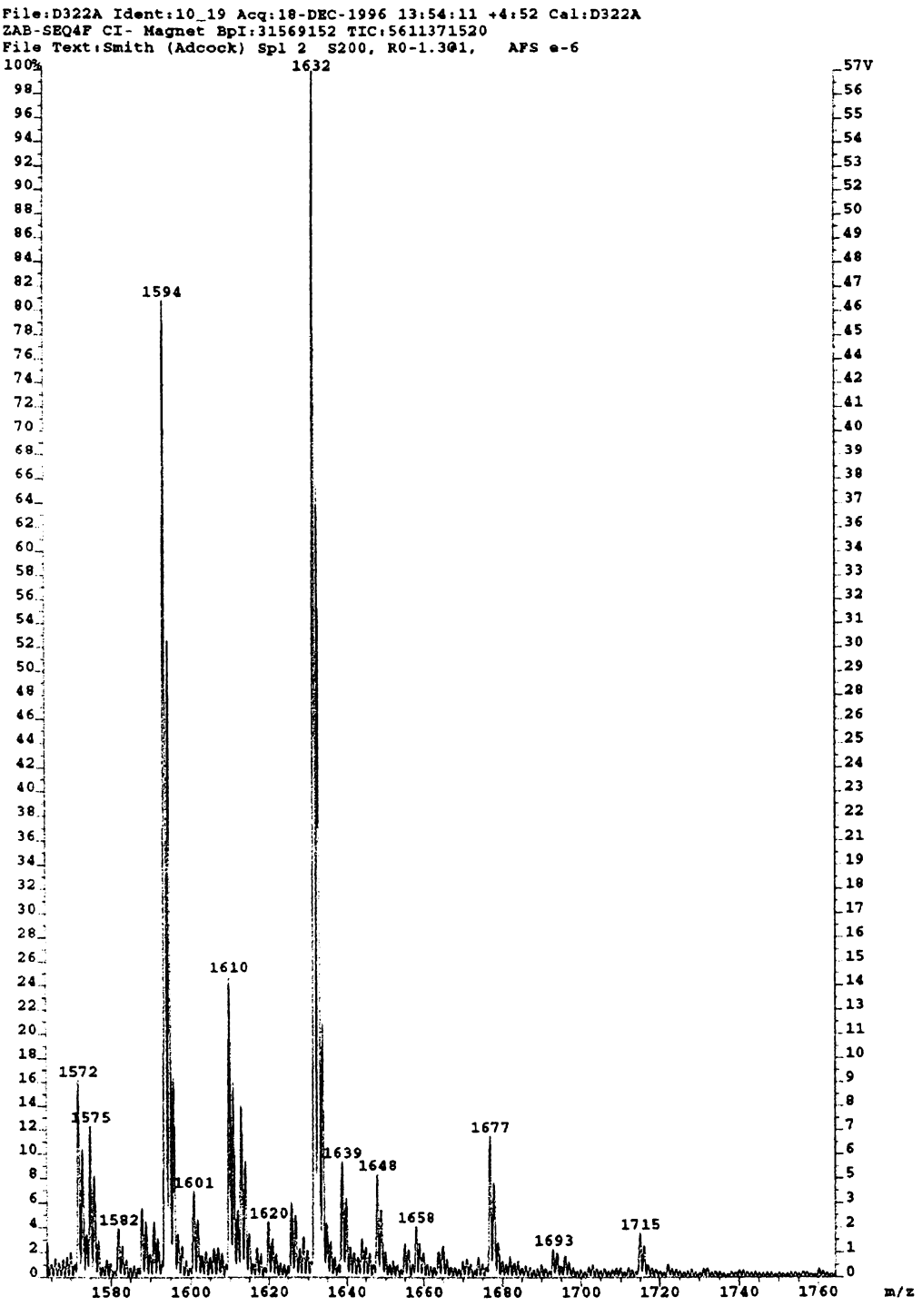


Figure B-5 $C_{60}HCN + F_2$ at 250°C

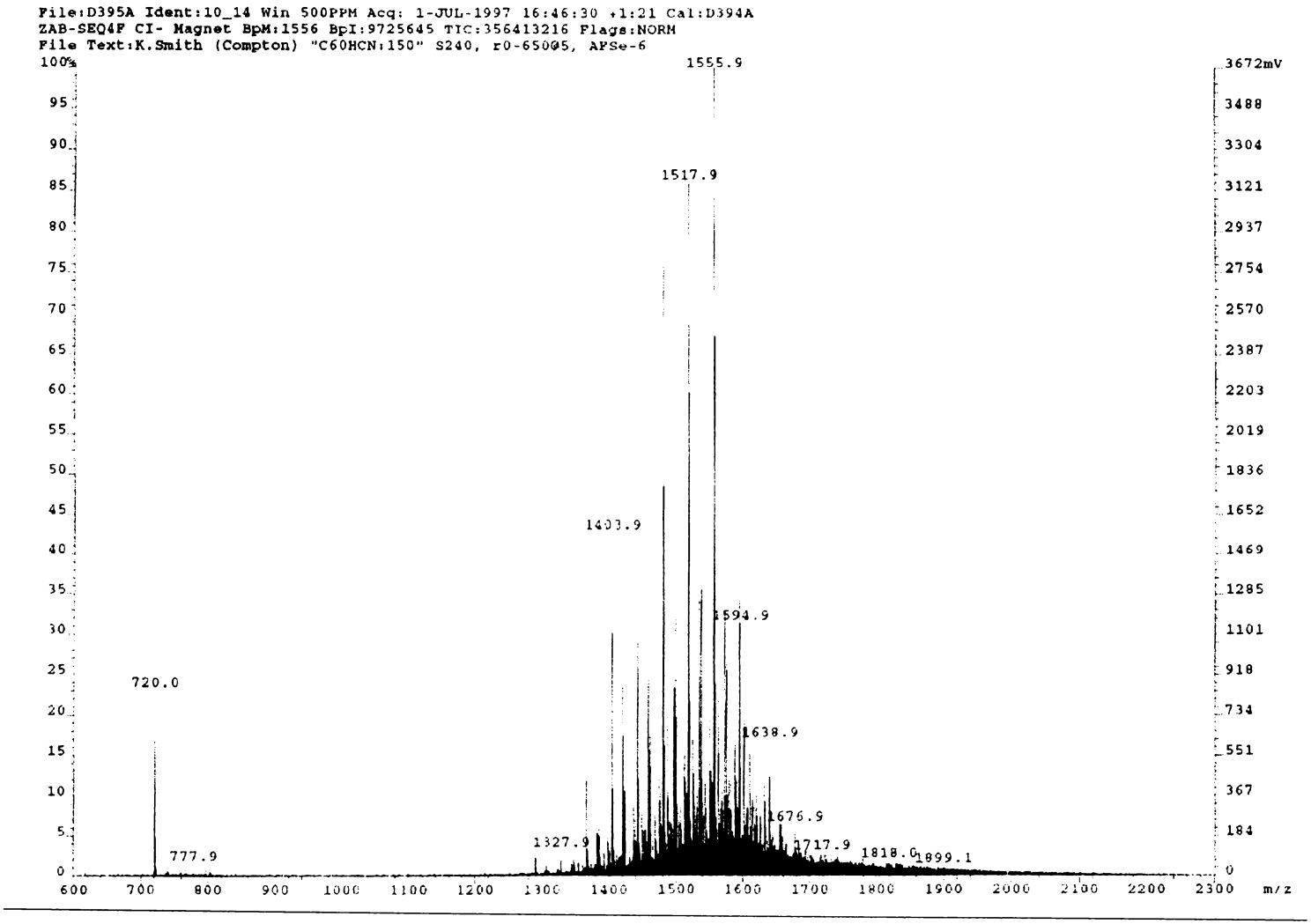


Figure B-6 $C_{60}HCN + F_2$ at 150°C

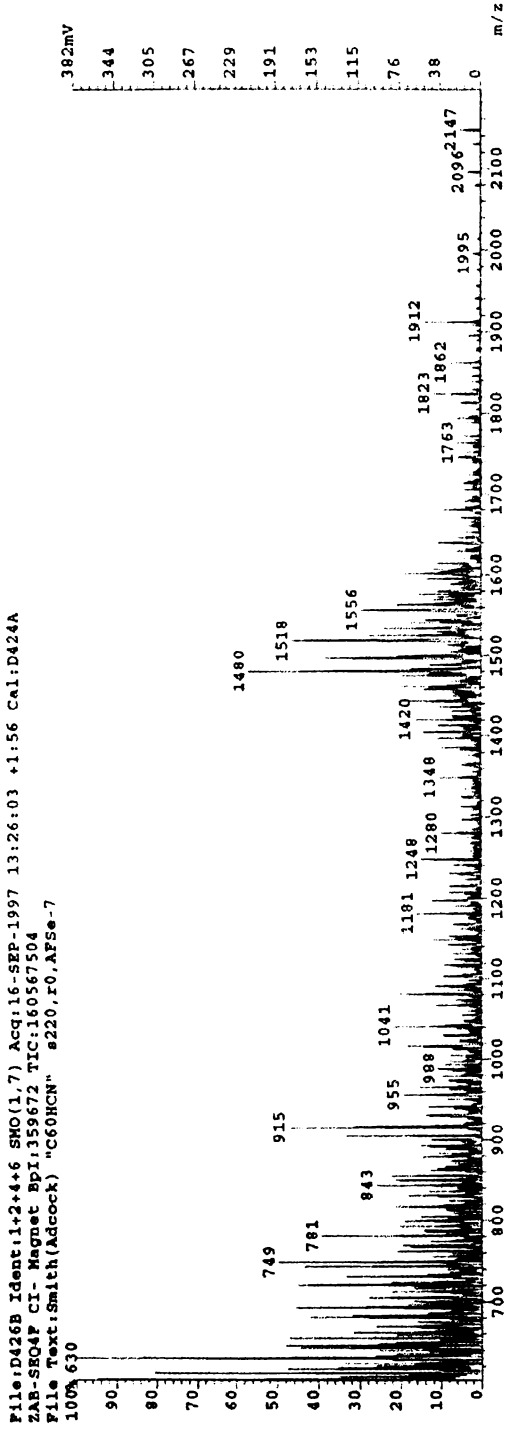


Figure B-7 $C_{60}HCN + F_2$ at 100°C

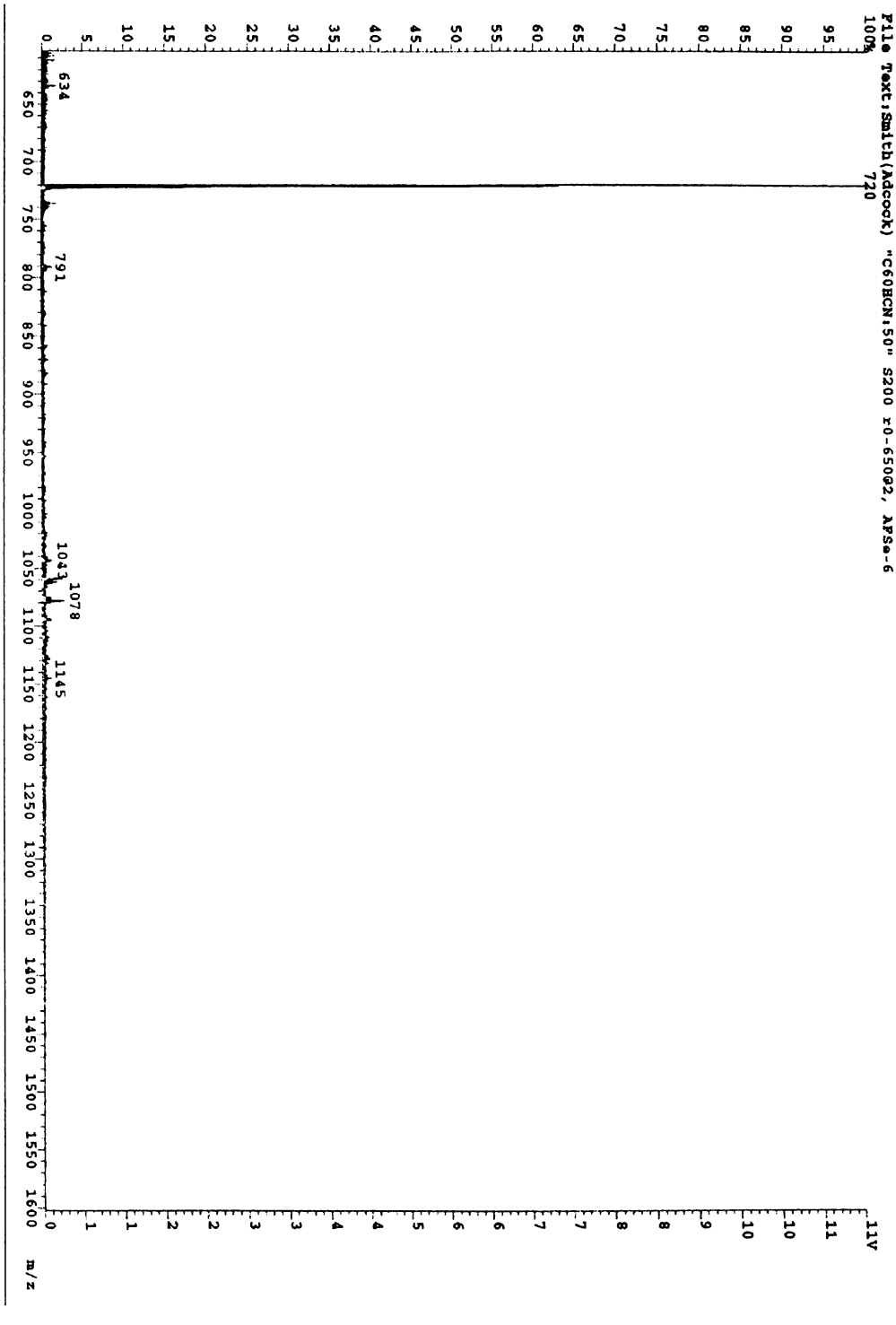


Figure B-8 $C_{60}HCN + F_2$ at 50°C

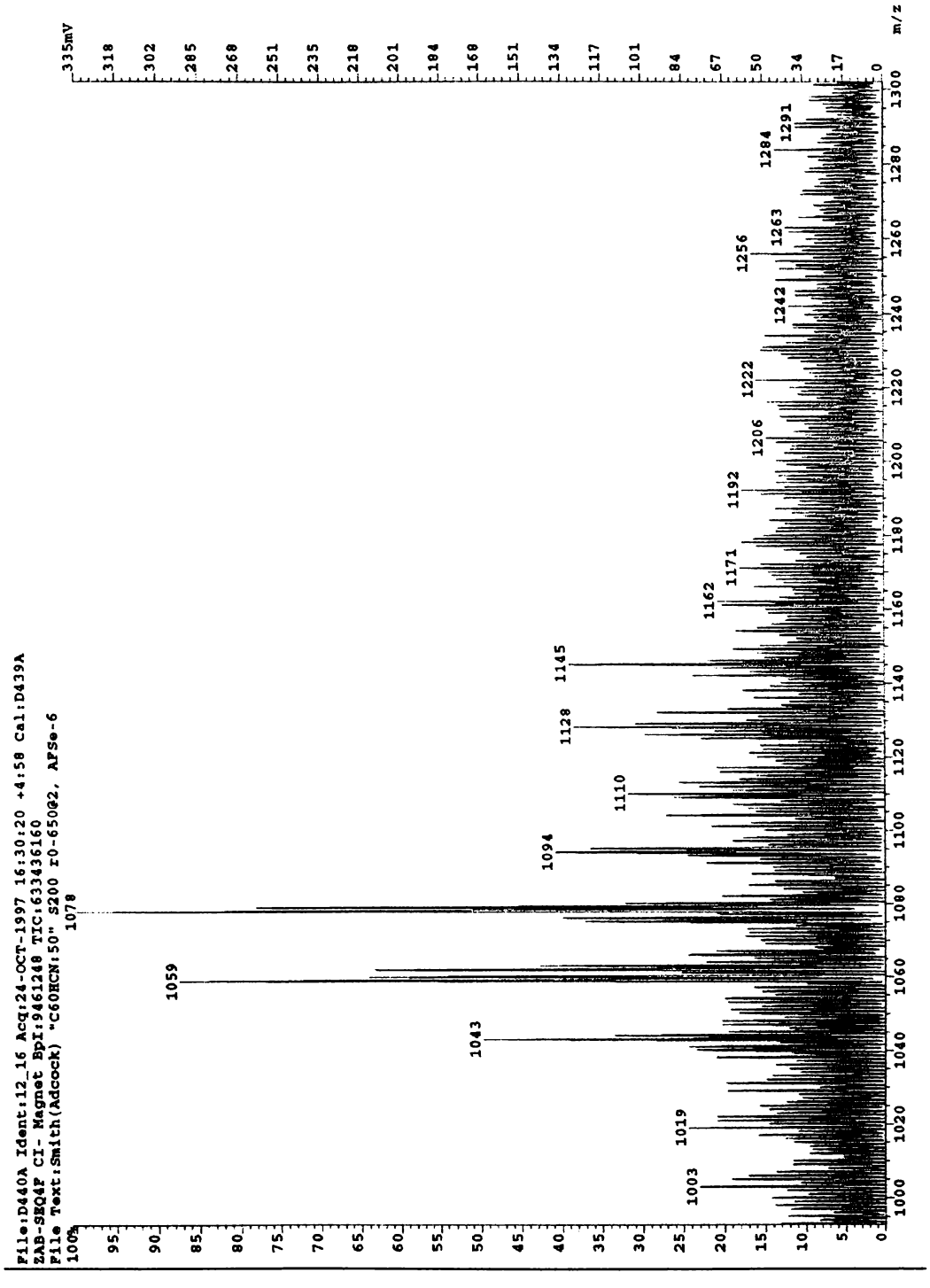


Figure B-9 $C_{60}HCN + F_2$ at 50°C - Blowup

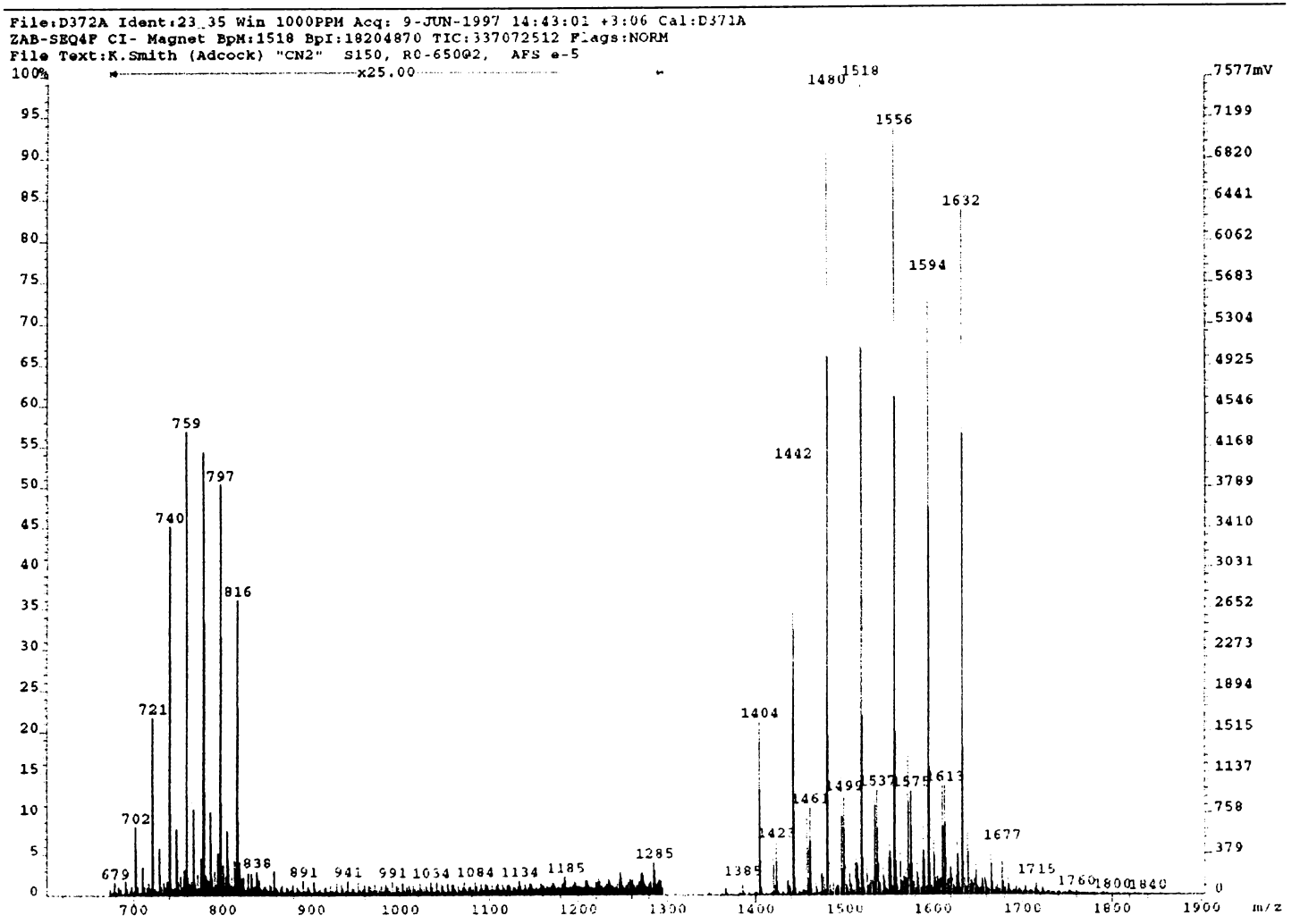


Figure B-10 $C_{60}(CN)_2 + F_2$ at 250°C

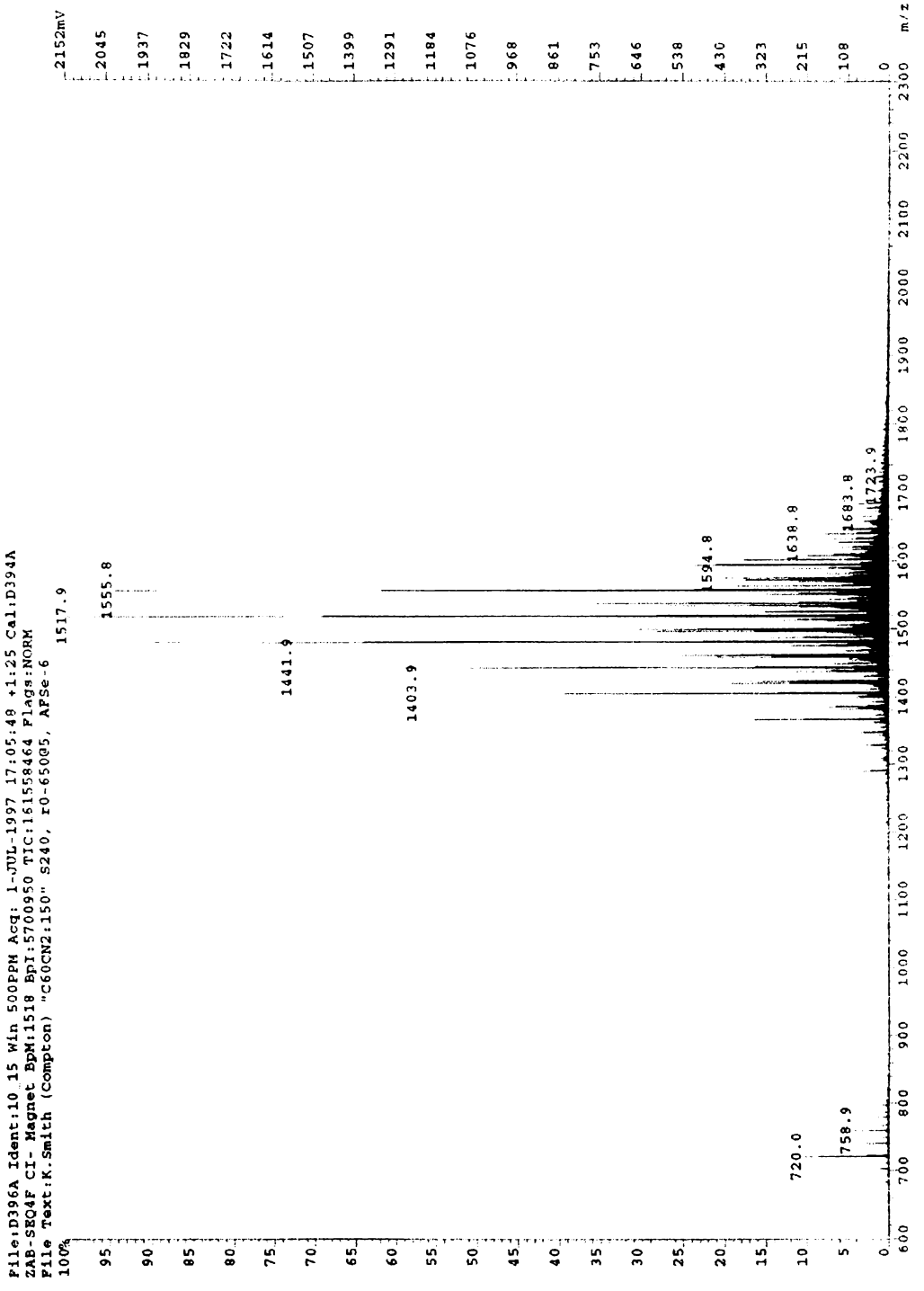


Figure B-11 $C_{60}(CN)_2 + F_2$ at 150°C

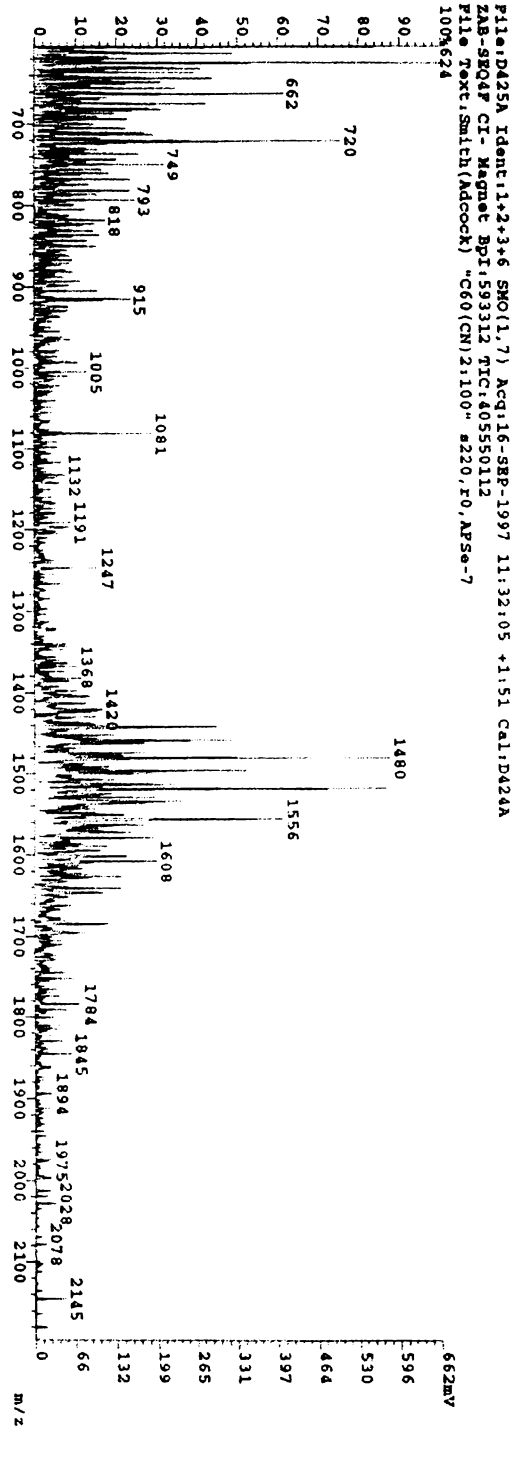


Figure B-12 $C_{60}(CN)_2 + F_2$ at 100°C

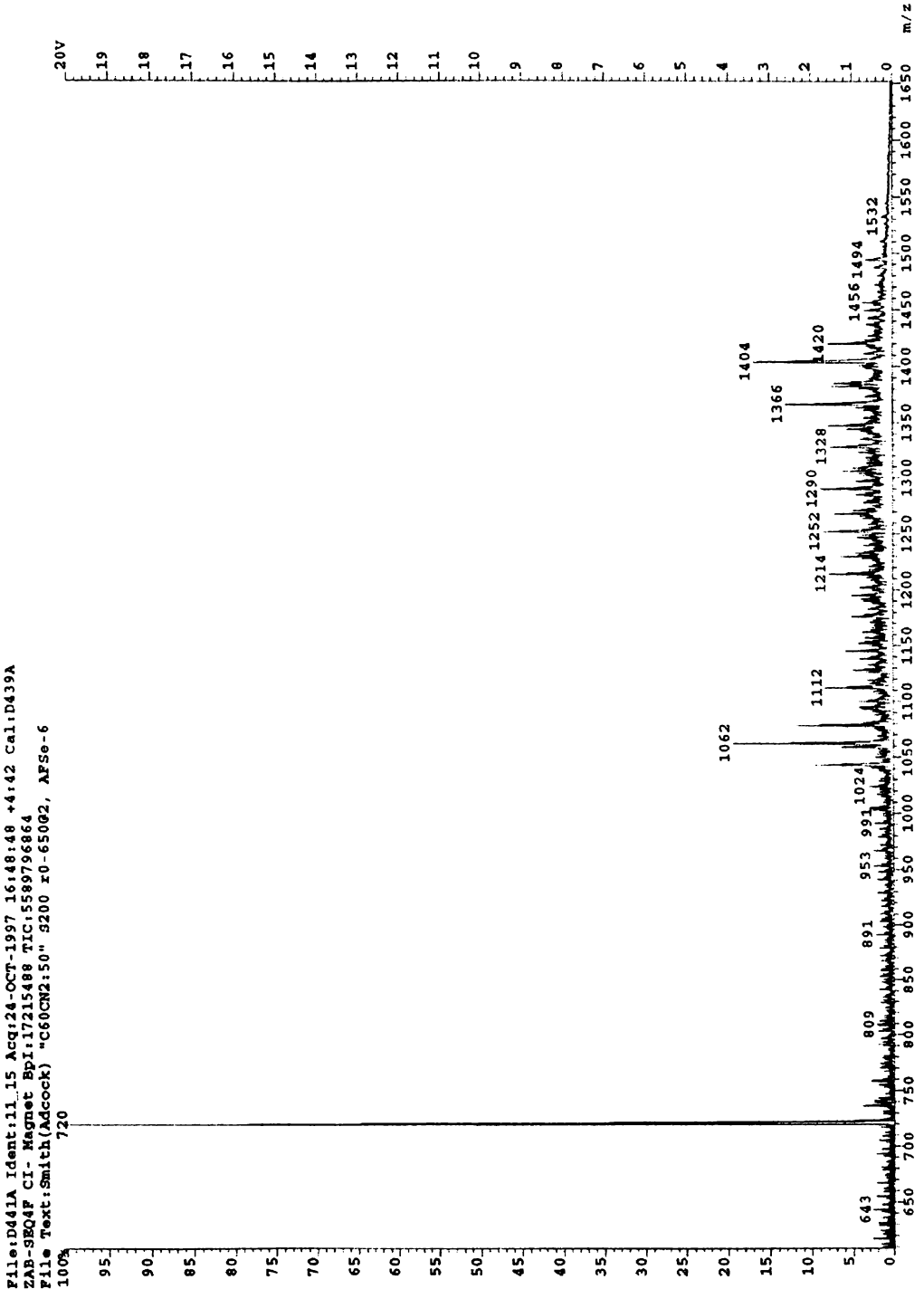


Figure B-13 $C_{60}(CN)_2 + F_2$ at 50°C

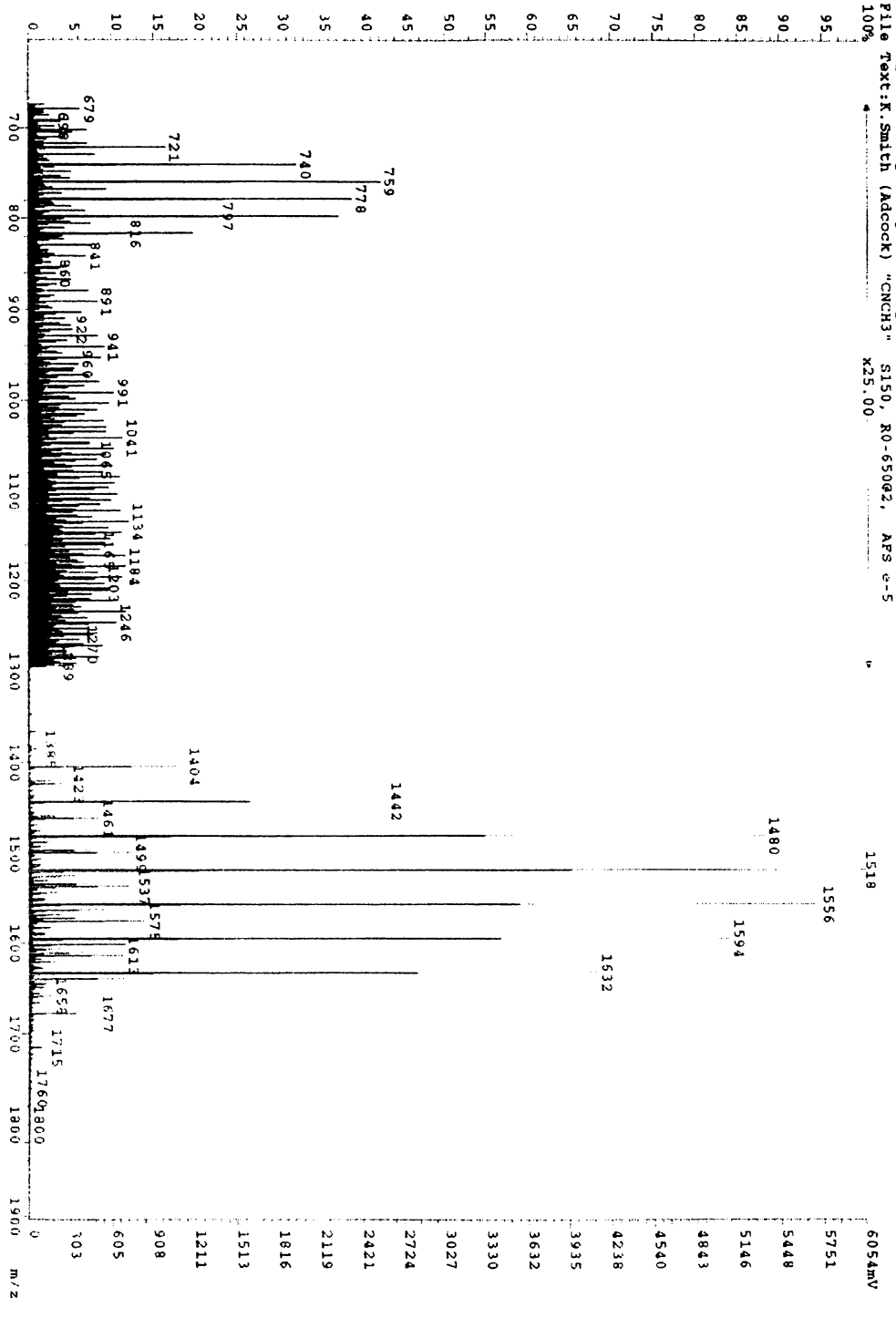


Figure B-14 $C_{60}CN(CH_3) + F_2$ at 250°C

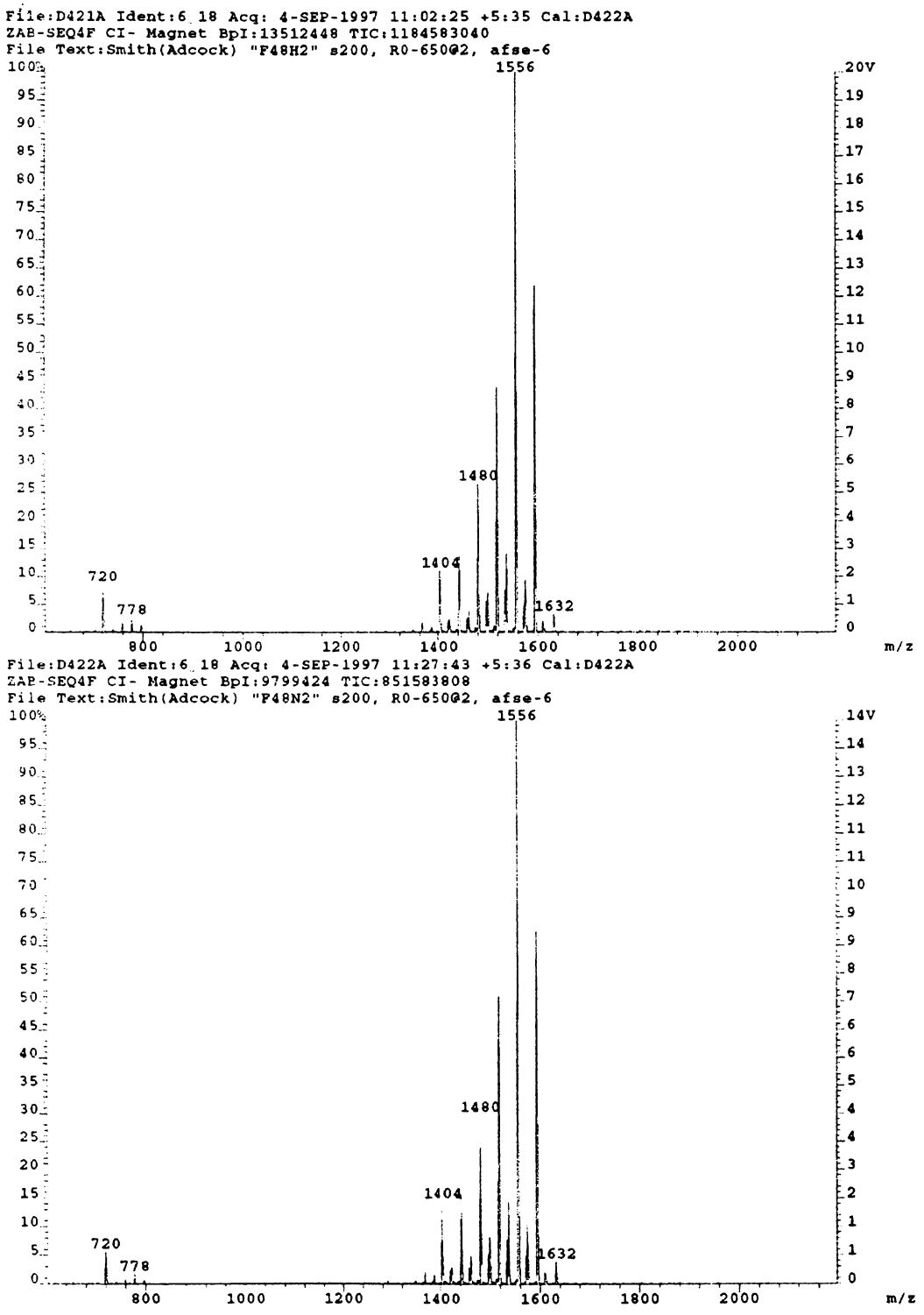


Figure B-15 $C_{60}F_{48}$ with N_2 and H_2 at 150°C

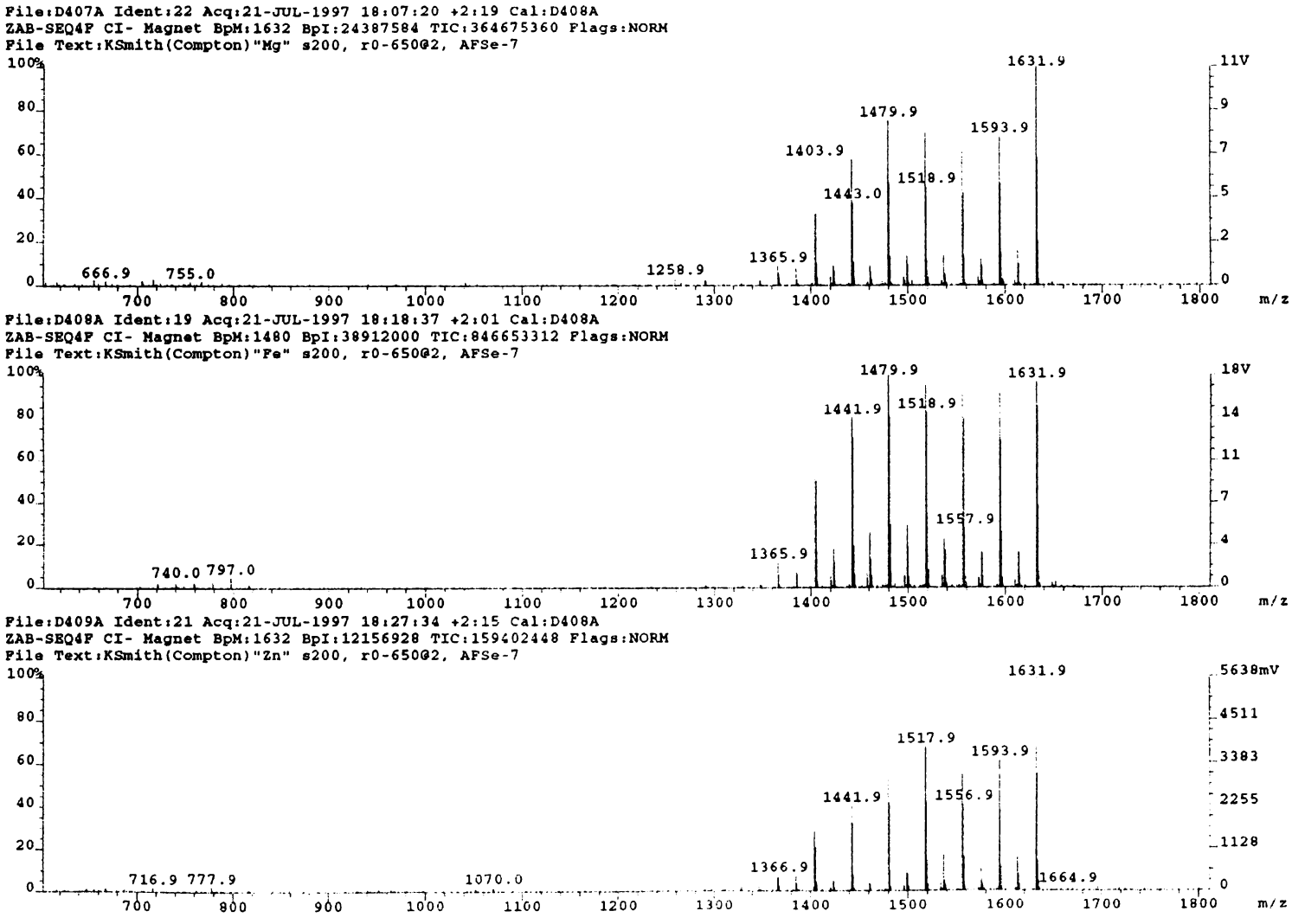


Figure B-16 $C_{60}F_{48}$ with Mg, Fe, and Zn metals

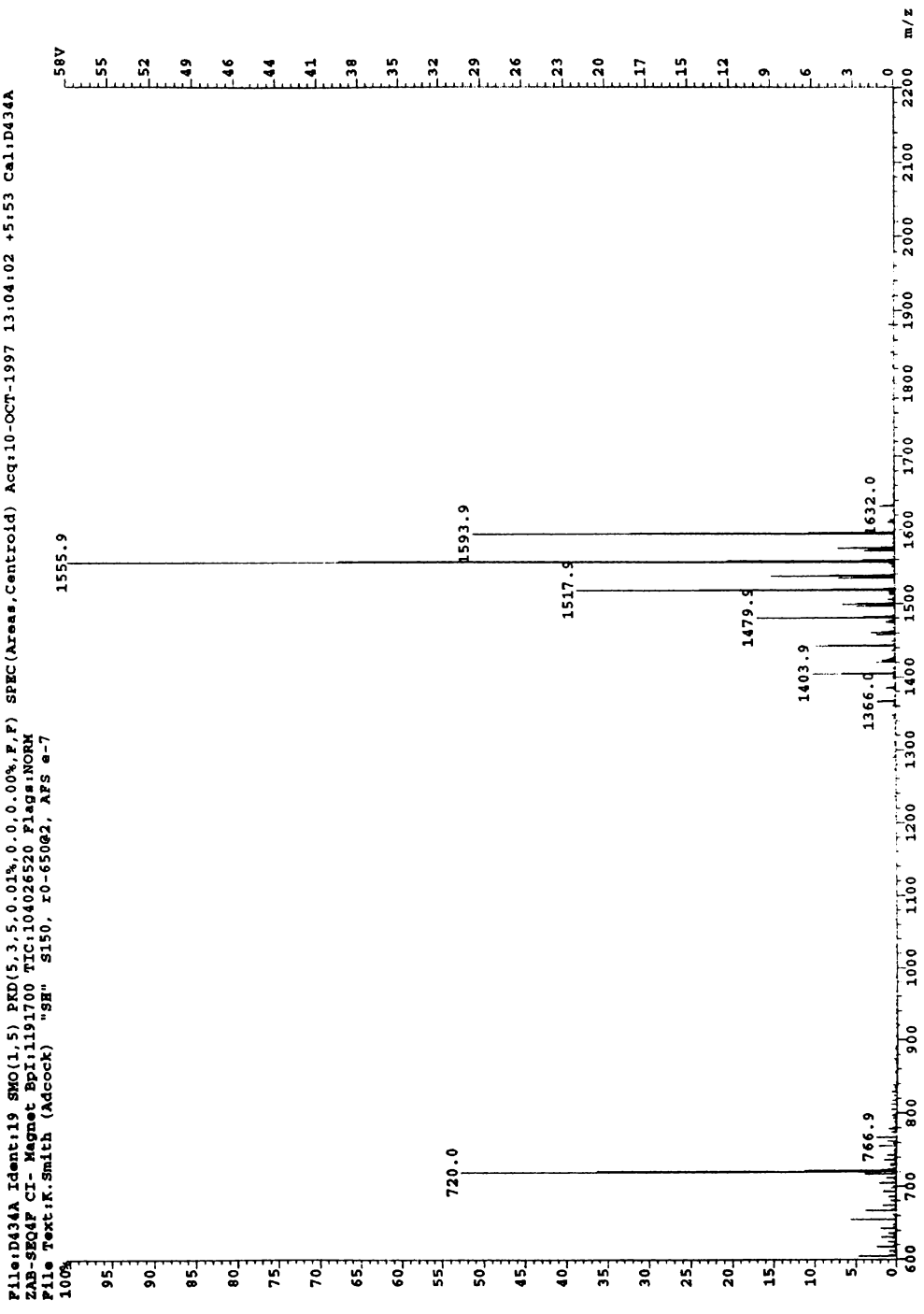


Figure B-17 $C_{60}F_{48}$ + Thiophenol

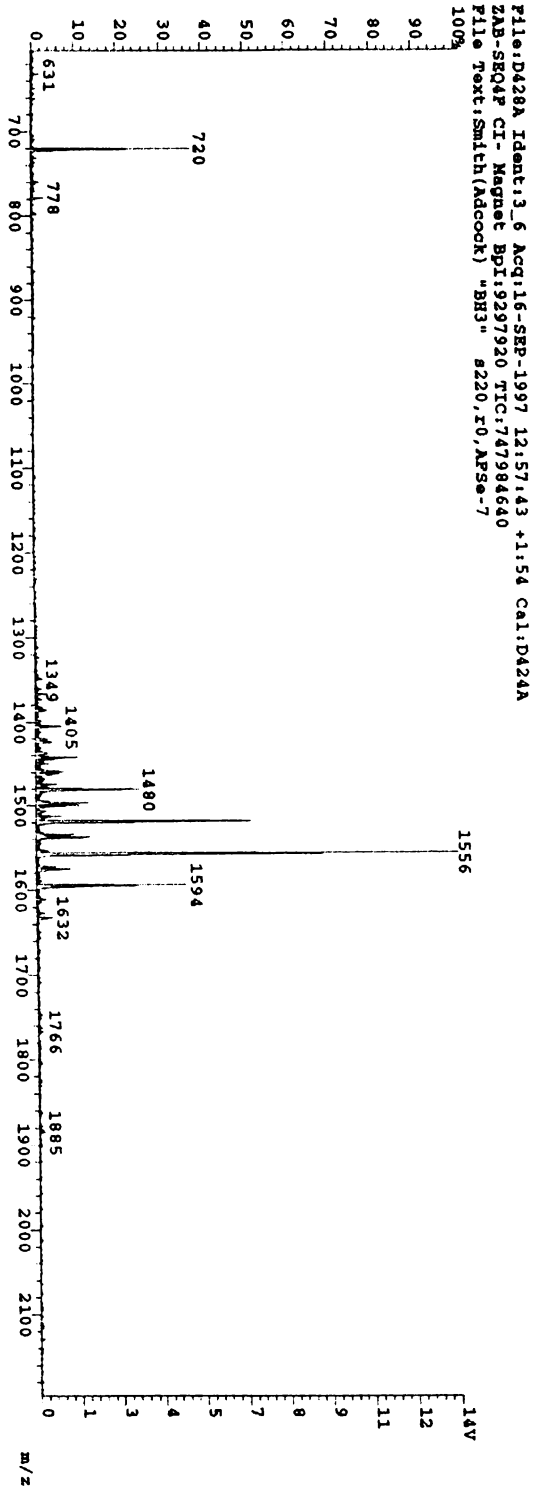


Figure B-18 $C_{60}F_{48}$ + Borane

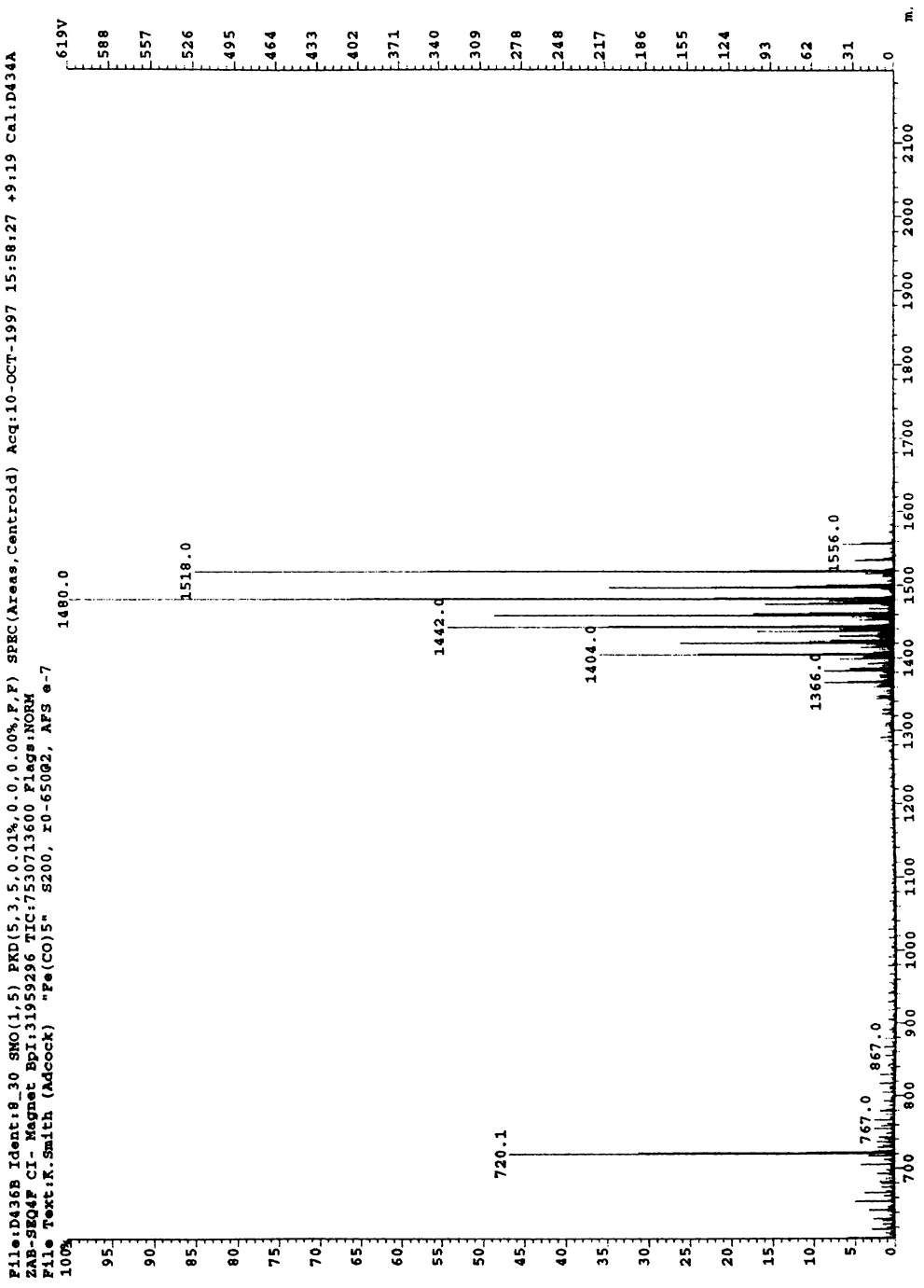


Figure B-19 $C_{60}F_{48} + Fe(CO)_5$

Appendix C
Norbornyl Cation Spectra

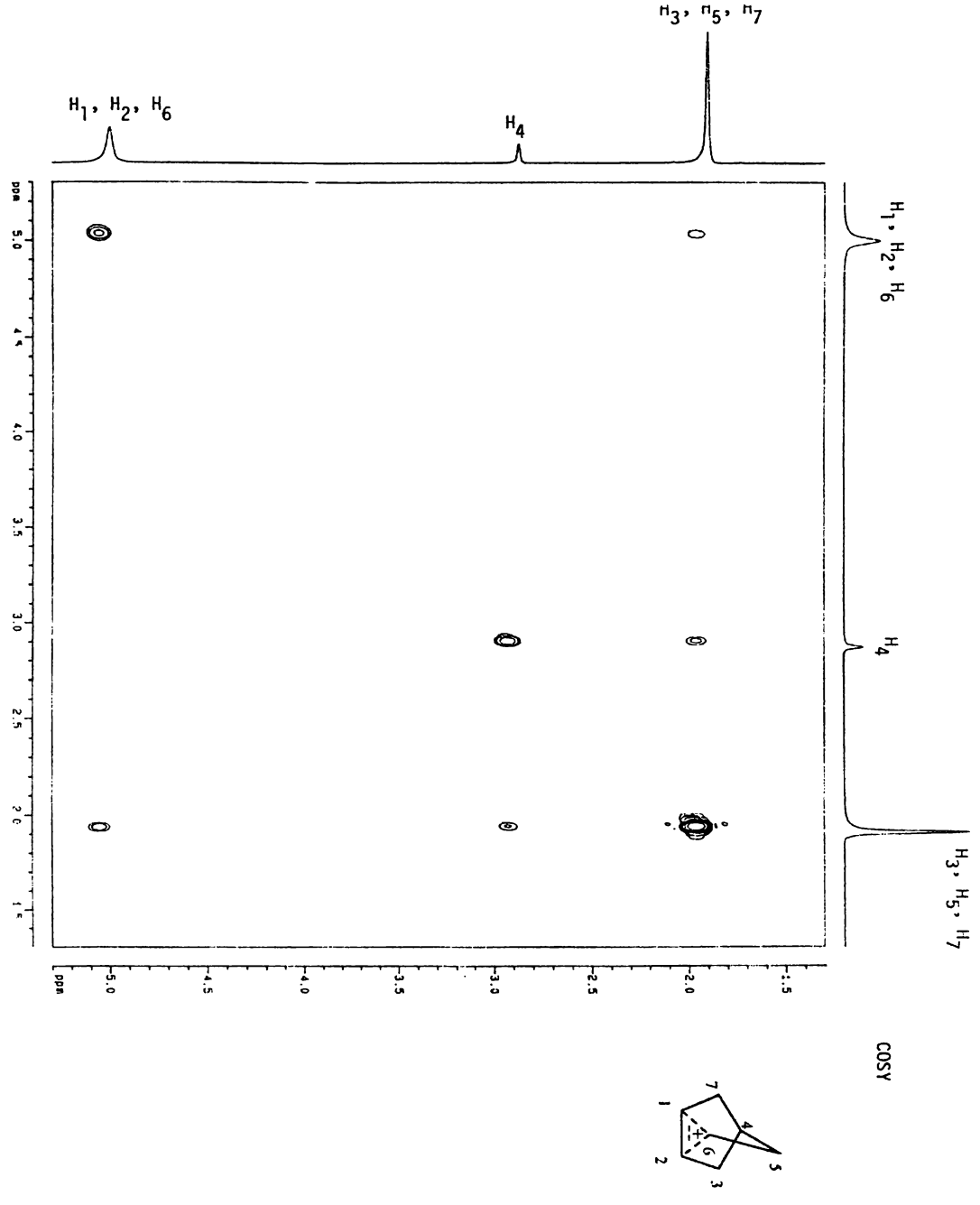


Figure C-1 COSY of the 2-Norbornyl Cation at -80°C

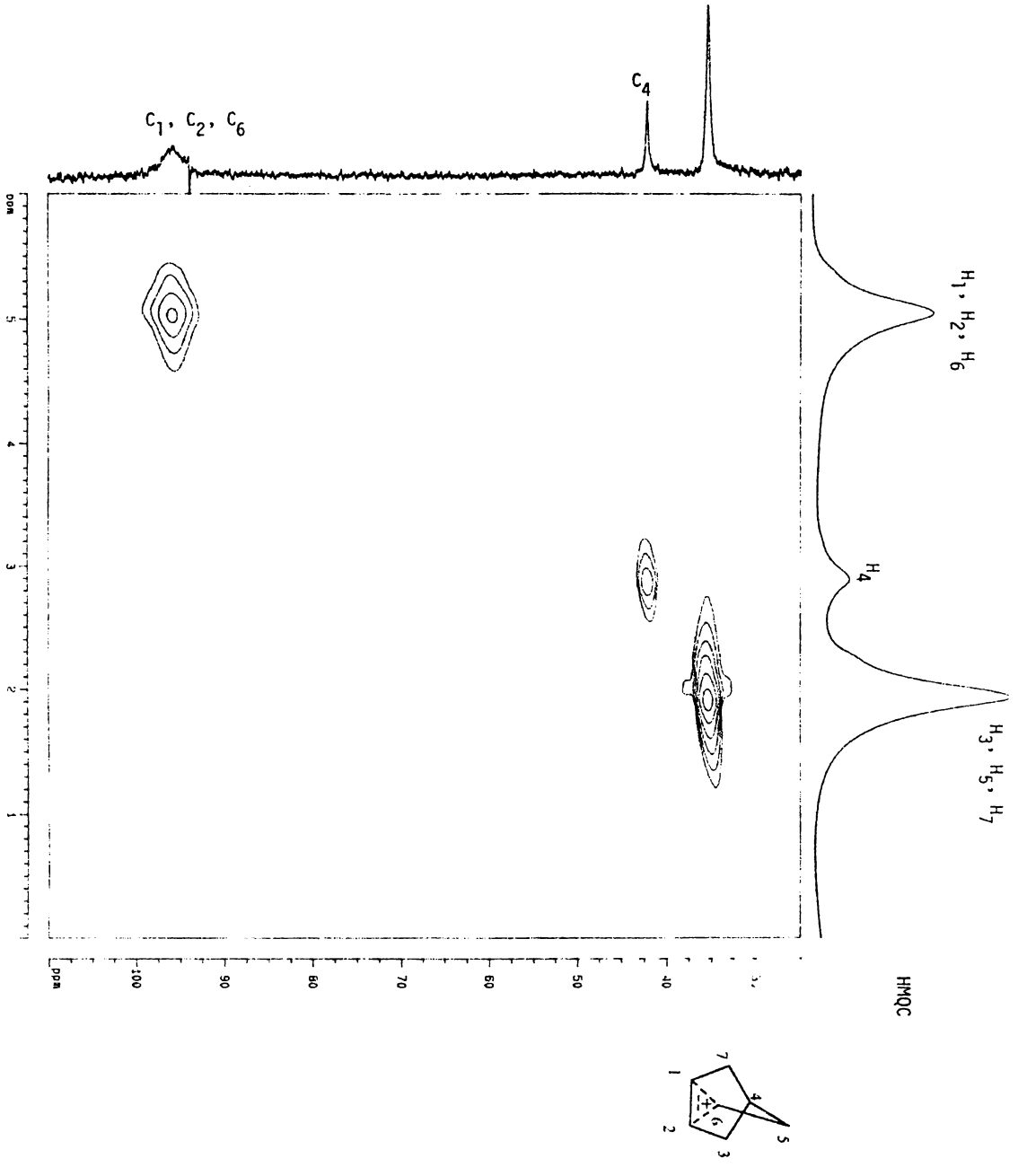


Figure C-2 HMQC of the 2-Norbornyl Cation at -80°C

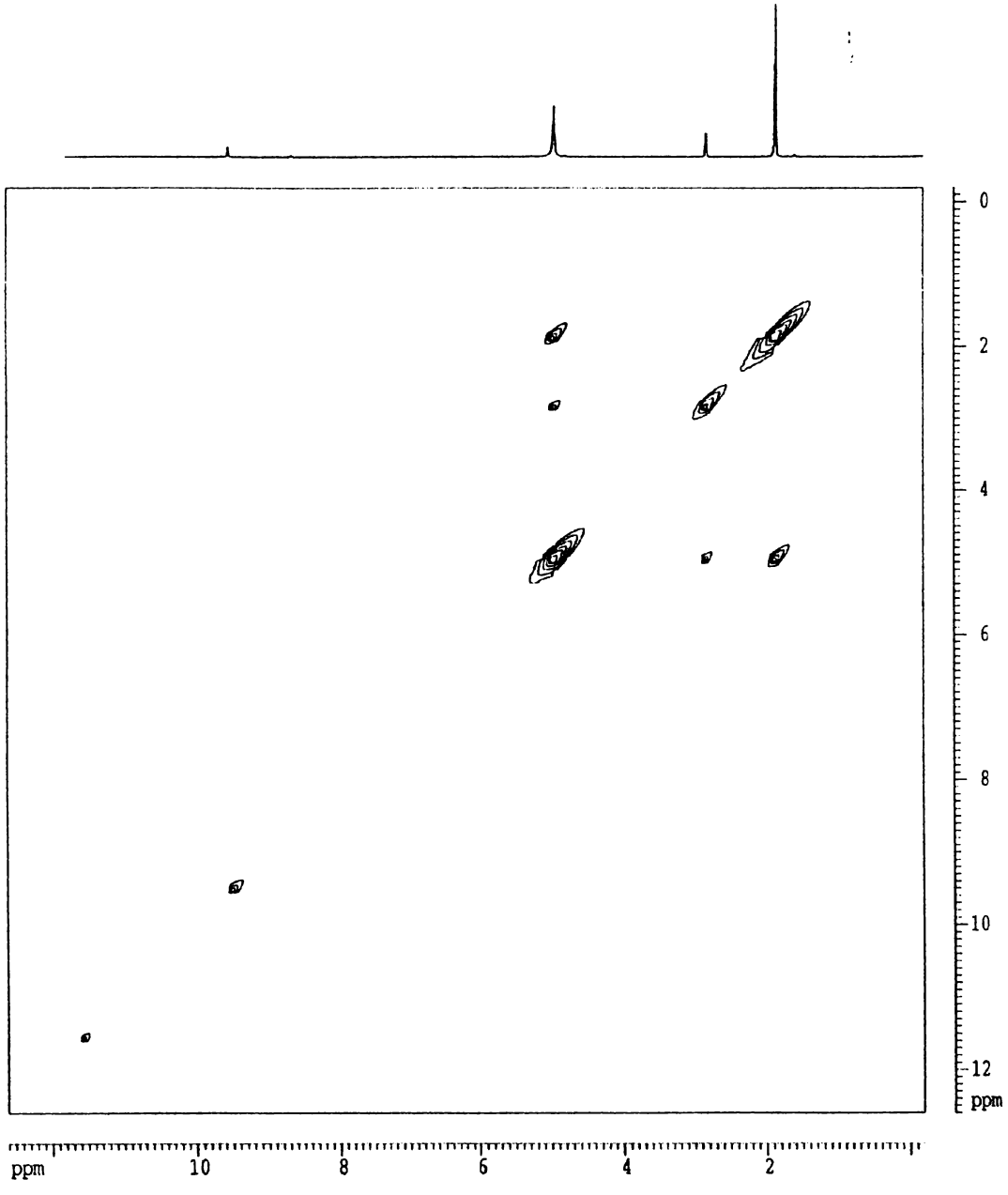


Figure C-3 2D EXSY of the 2-Norbornyl Cation at 193K

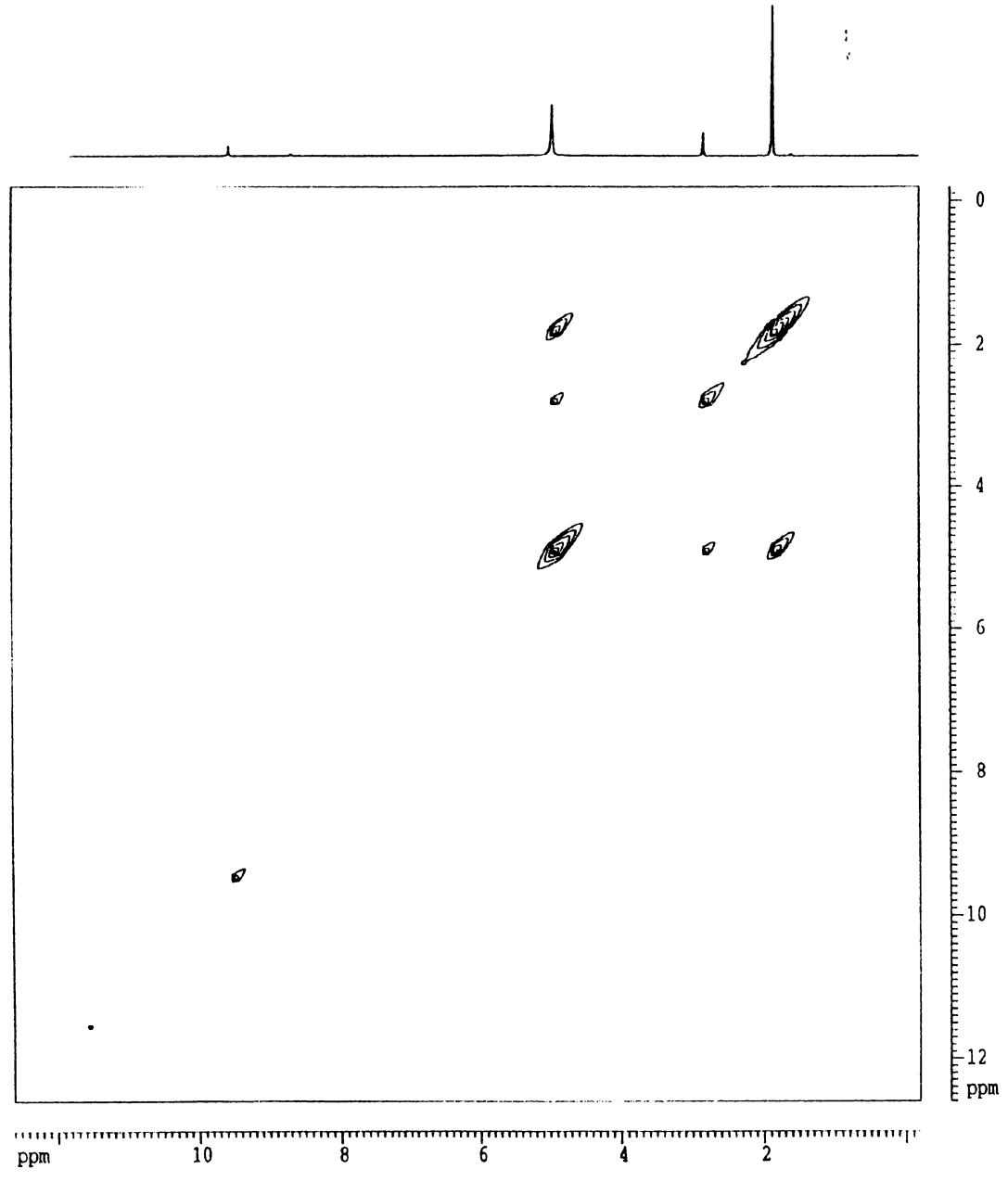


Figure C-4 2D EXSY of the 2-Norbornyl Cation at 208K

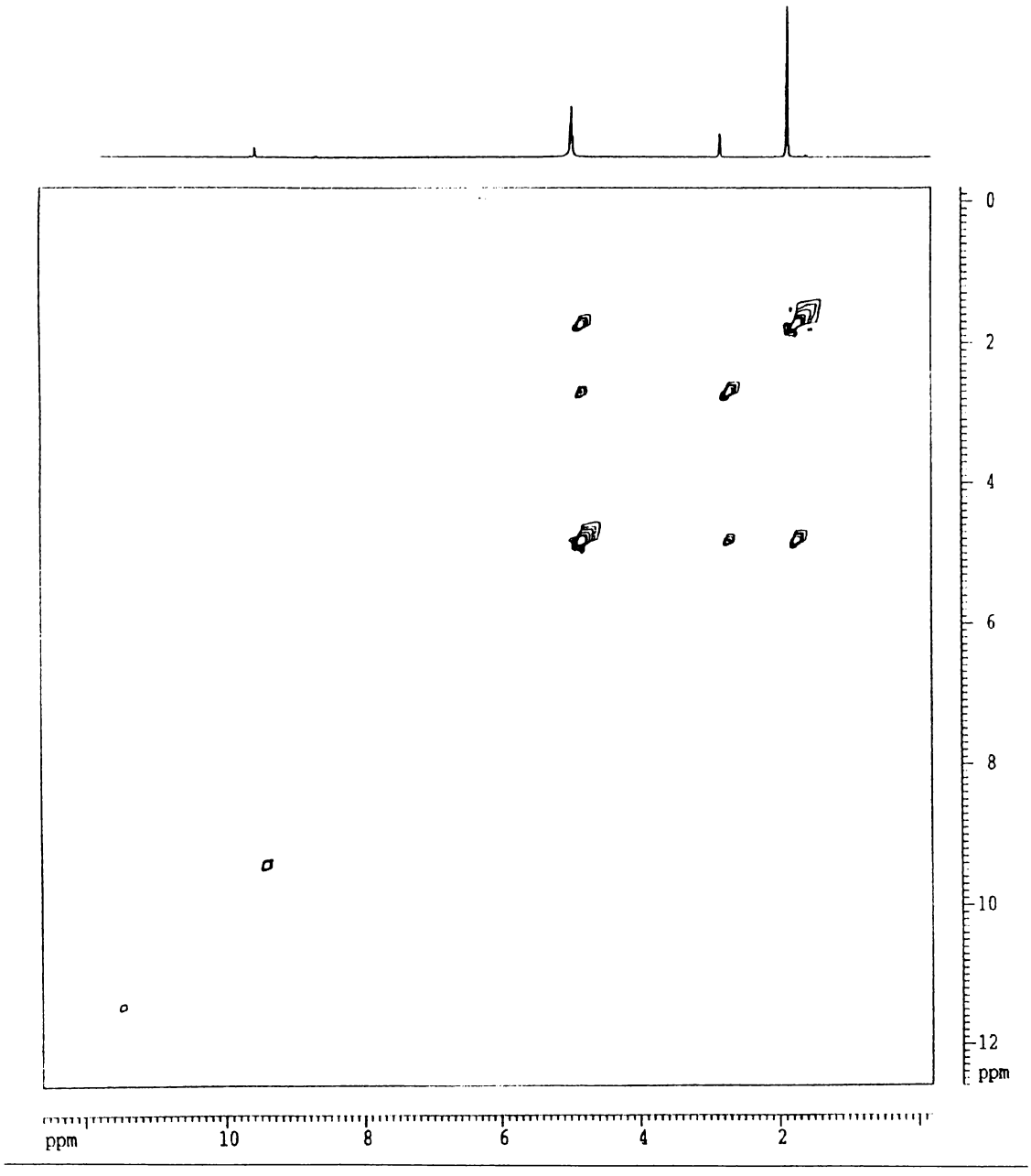


Figure C-5 2D EXSY of the 2-Norbornyl Cation at 223K

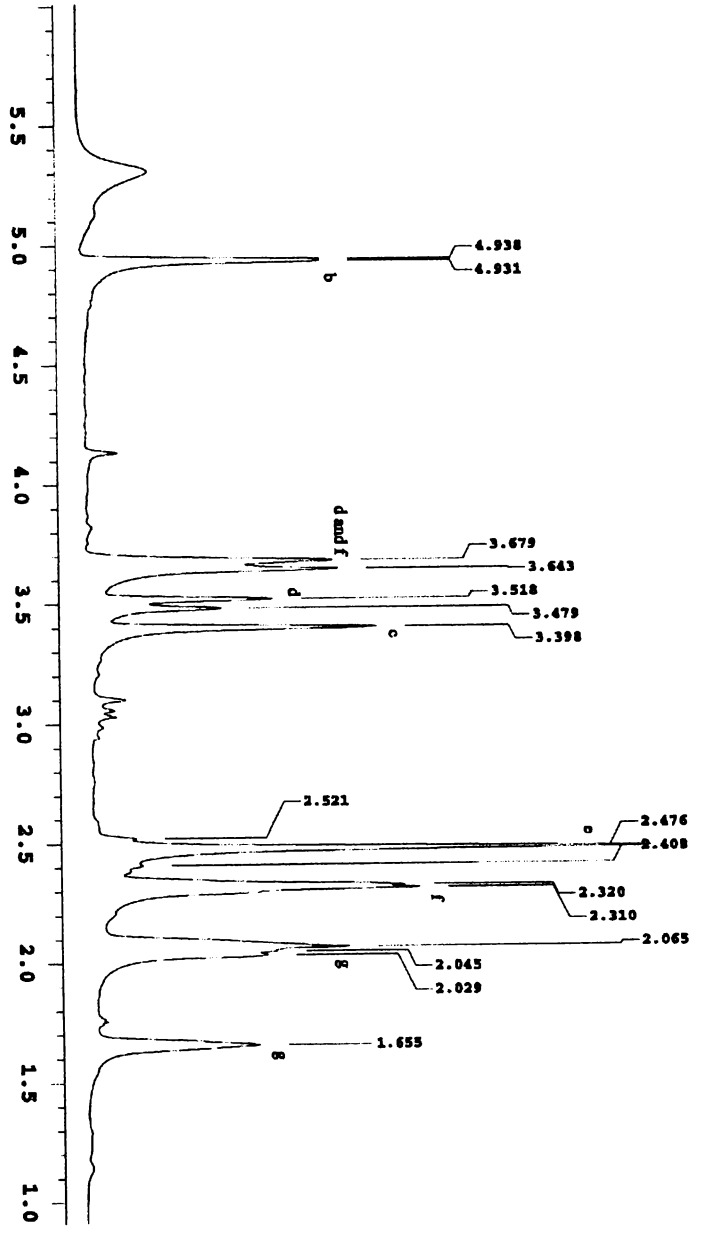


Figure C-6 ^{1}H of the 2-Chloro-2-Cation at -90°C

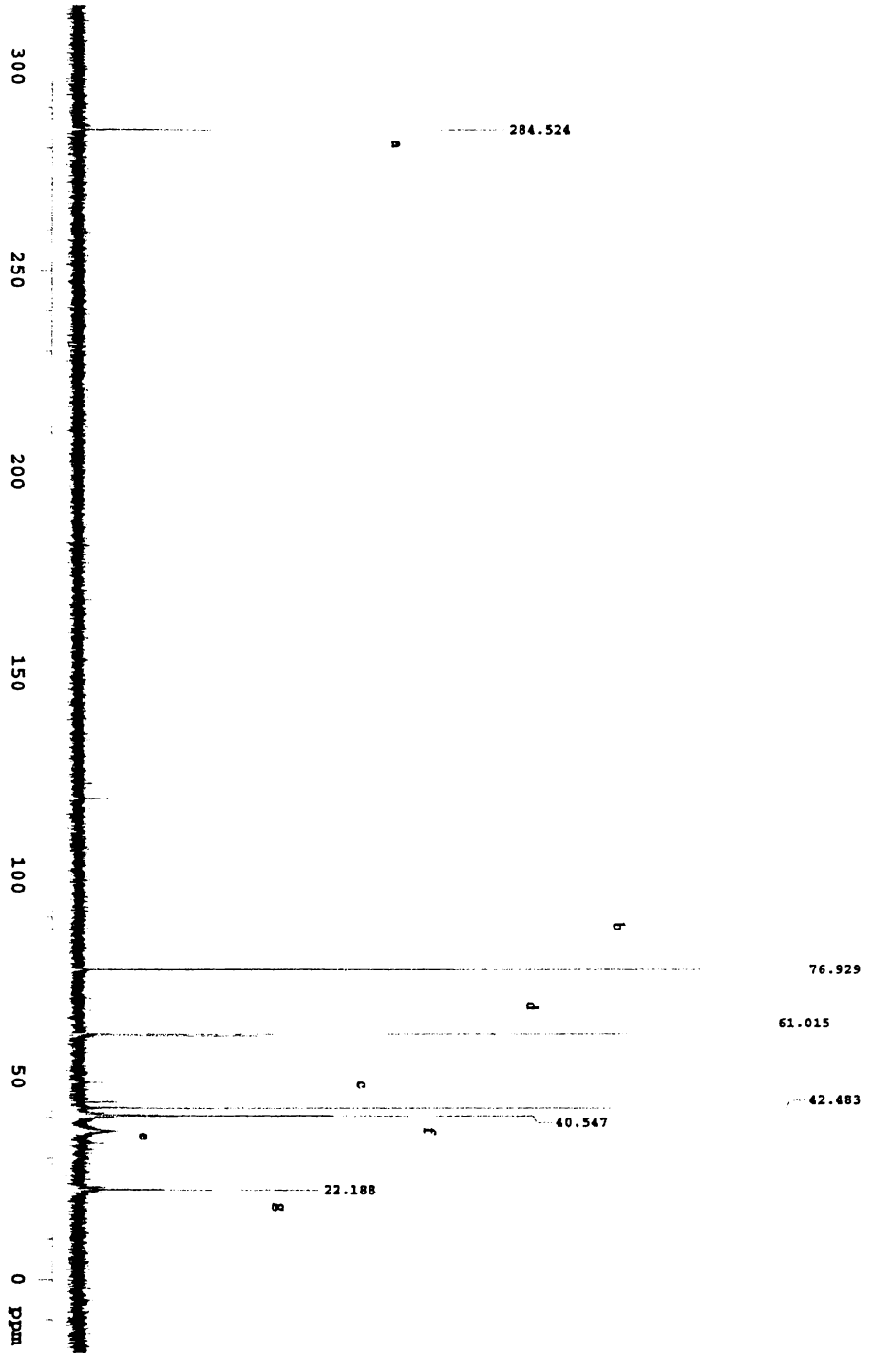


Figure C-7 ^{13}C of the 2-Chloro-2-Cation at -90°C

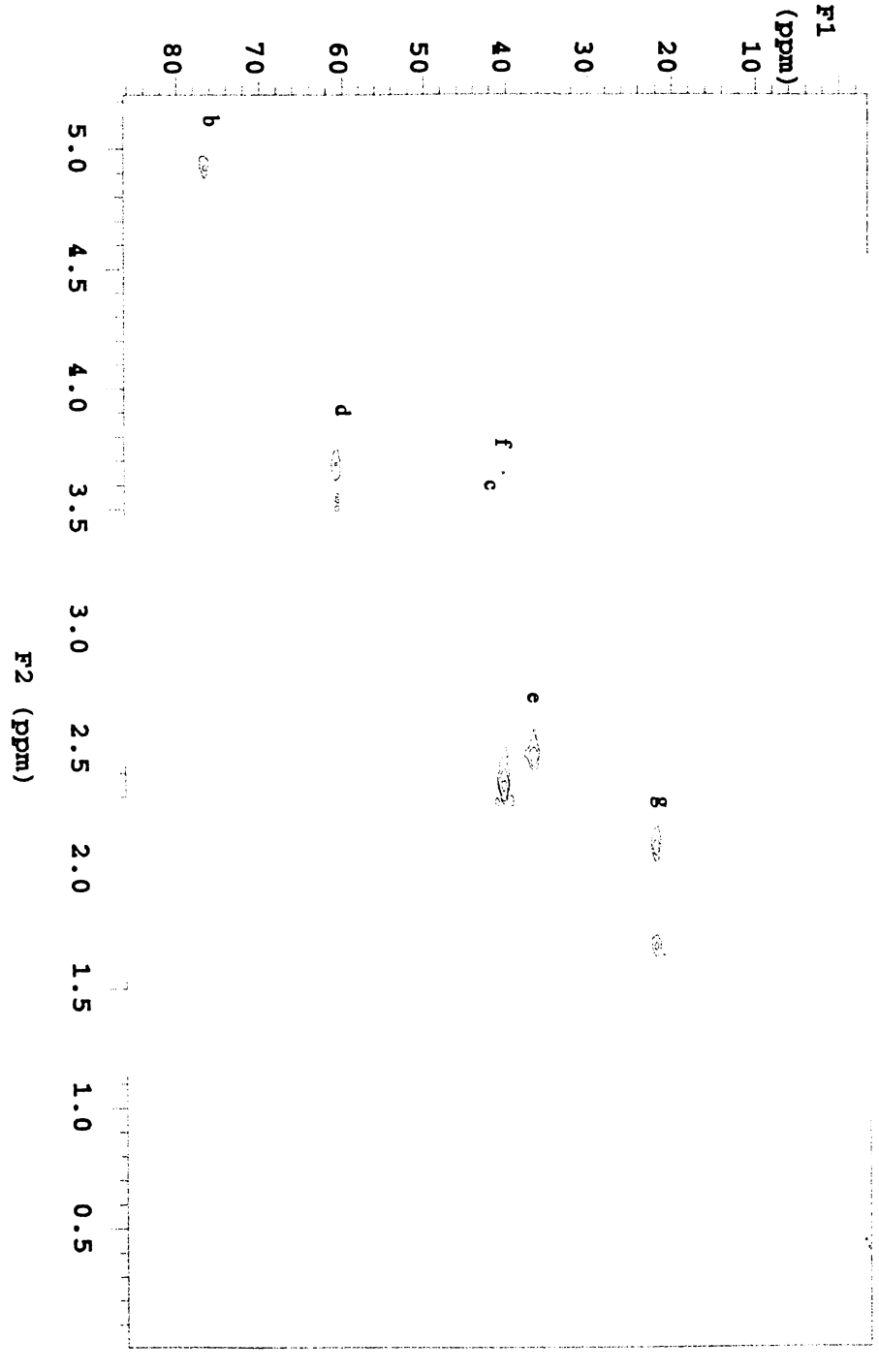


Figure C-8 HMQC of the 2-Chloro-2-Cation at -90°C

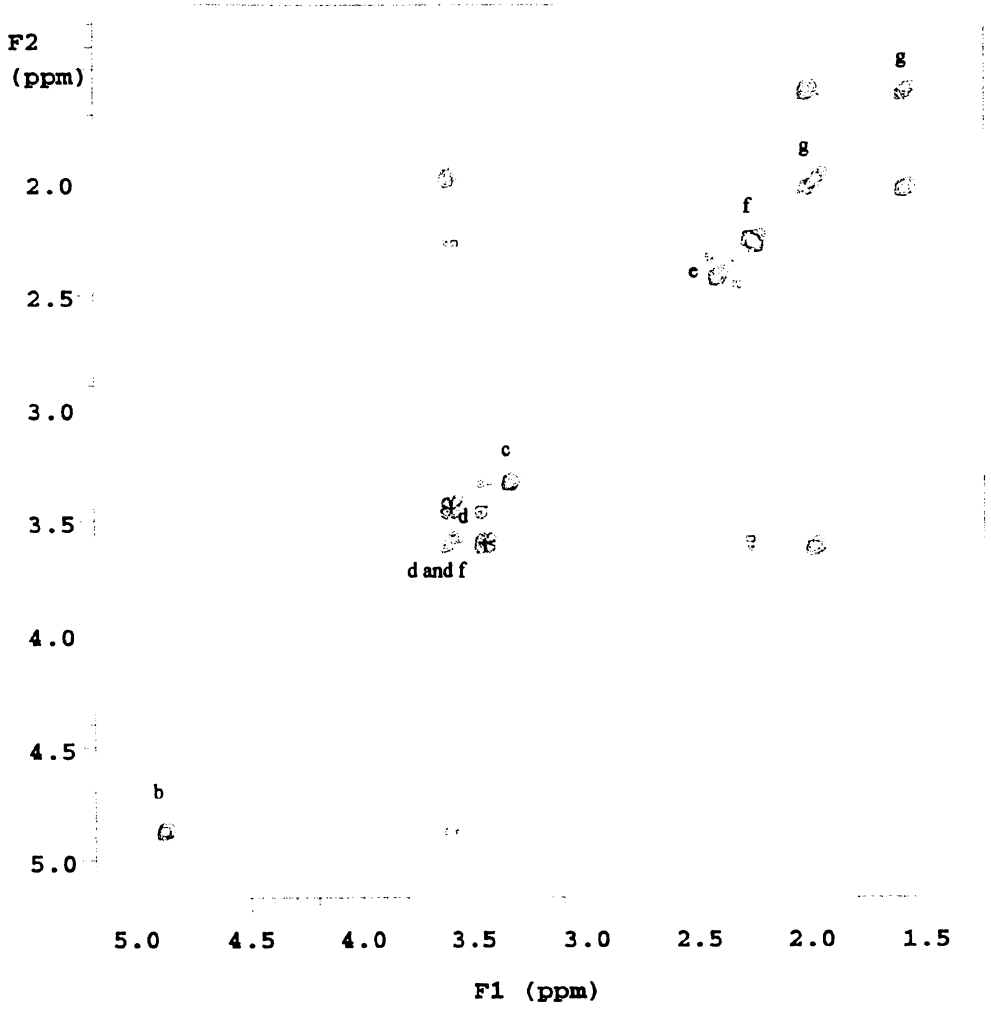


Figure C-9 COSY of the 2-Chloro-2-Cation at -90°C

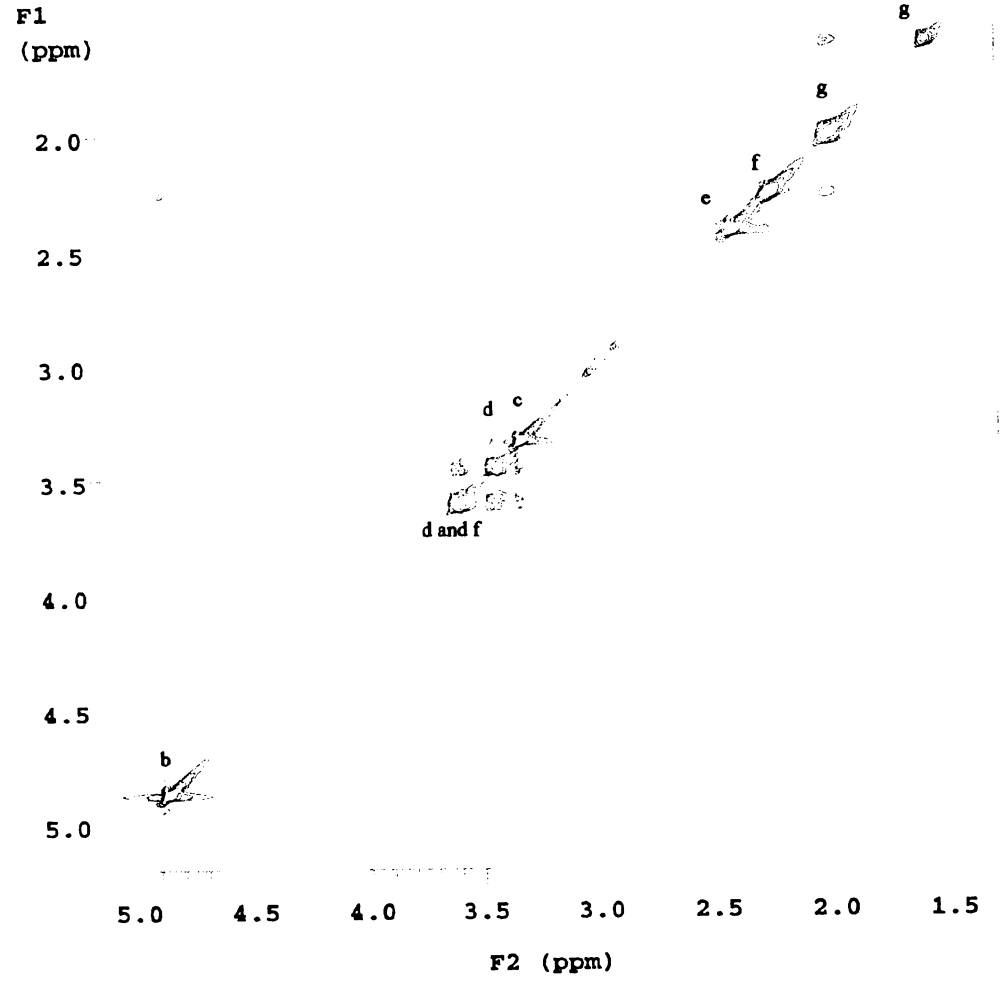


Figure C-10 NOESY of the 2-Chloro-2-Cation at -90°C

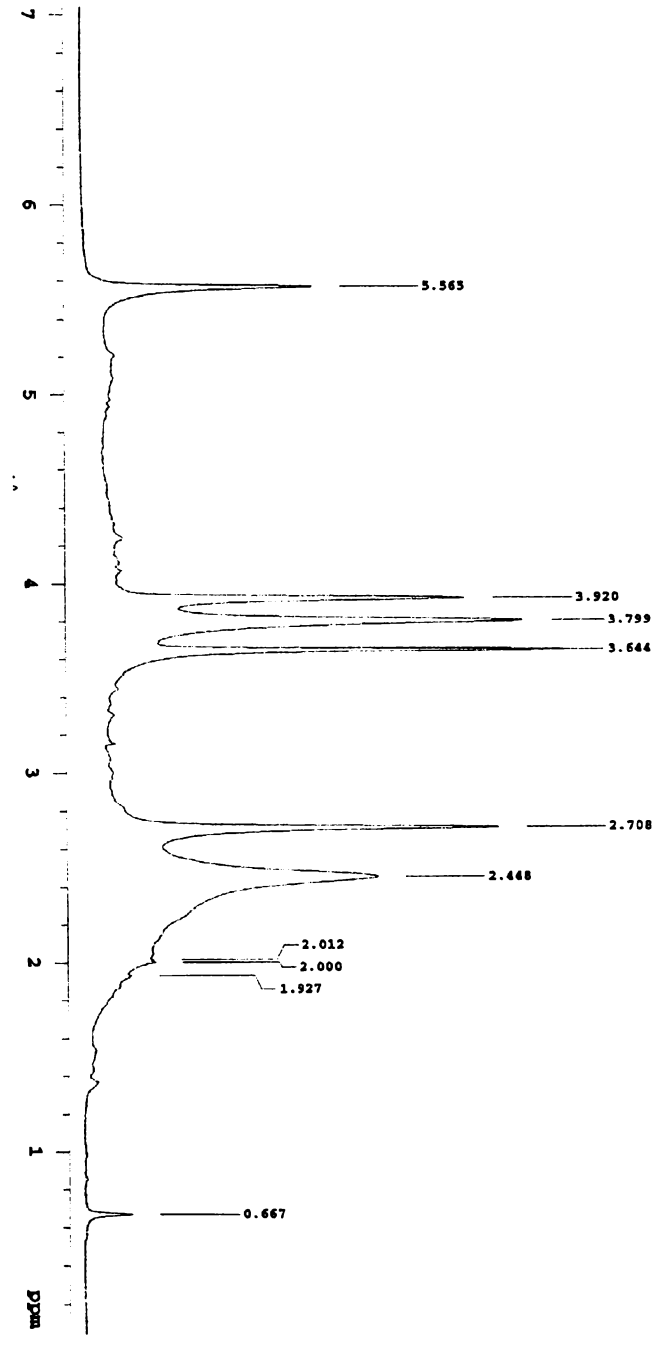


Figure C-11 ^{1}H of the 2-Chloro-2-Cation warmed to -20°C

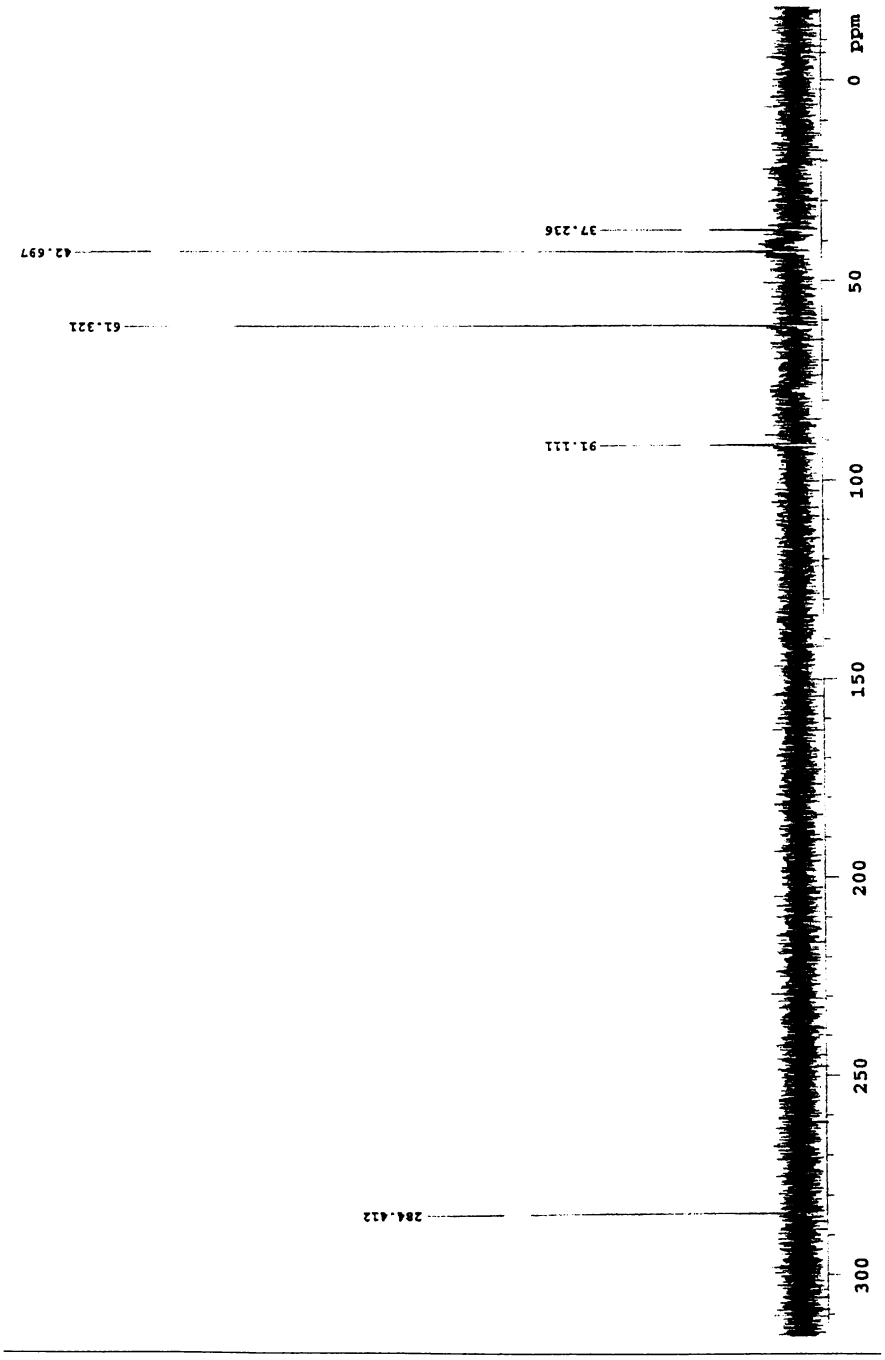


Figure C-11 ^{13}C of the 2-Chloro-2-Cation warmed to -20°C

VITA

Kenneth Smith was born in Hanover, Pennsylvania on October 4th, 1972. He graduated from Delone Catholic High School in 1990. He received a B.S. in chemistry from Shippensburg University in 1994. He entered the graduate school at the University of Tennessee in 1994.

His interests in the field of chemistry include noble gas compounds, the chemistry of strong oxidizers, and stable carbocations, as well as pharmaceutical chemistry and biochemistry, specifically the production and uses of plant secondary products.

His interests outside of chemistry are widely varied including astronomy, computers, tropical fish. His hobbies include computer gaming, as well as drawing and writing.

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