SYNTHESIS OF PERFLUORINATED ETHERS BY SOLUTION PHASE DIRECT FLUORINATION: AN ADAPTATION OF THE LA-MAR TECHNIQUE

This thesis is dedicated to my wife, Teresa.

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by

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THESIS

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ABSTRACT

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The synthesis of several perfluorinated ethers of pentaerythritol, dipentaerythritol, and tripentaerythritol by direct fluorination in solution is described. These ethers were perfluorinated using elemental fluorine in a two step process. In the first step, up to 95 percent of the hydrogens were replaced by fluorine while the ether was dissolved in a chlorofluorocarbon solvent. The remaining hydrogens were replaced by exposing the partially fluorinated product to pure fluorine at elevated temperature.

The hydrocarbon ethers used as starting material were prepared by applying the use of phase transfer catalysis

to the Williamson ether synthesis. Six of the perfluorinated ethers prepared have been previously synthesized by other methods: perfluoro-5,5-bis(ethoxymethyl)-3,7-dioxanonane, perfluoro-6,6-bis(propyloxymethyl)-4,8-dioxaundecane, perfluoro-7,7-bis(butyloxymethyl)-5,9-dioxatridecane, perfluoro-8,8-bis(pentyloxymethyl)-6,10-dioxapentadecane, perfluoro-7,7-bis(2-methoxyethoxymethyl)-2,5,9,12-tetraoxatridecane, and perfluoro-4,4,8,8-tetrakis(methoxymethyl)-2,6,10-trioxaundecane.

In addition, the following compounds were isolated and characterized: perfluoro-2,12-dimethyl-7,7-bis(2-methylbutyloxymethyl)-5,9-dioxatridecane, perfluoro-9,9-bis(hexyloxymethyl)-7,11-dioxaheptadecane, perfluoro-10,10-bis(heptyloxymethyl)-8,12-dioxanonadecane, perfluoro-11,11-bis(octyloxymethyl)-9,13- dioxaheneicosane, perfluoro-5,5,9,9-tetrakis(ethoxymethyl)-3,7,11- trioxatridecane, perfluoro-6,6,10,10-tetrakis(propyloxymethyl)-4,8,12-trioxapentadecane, perfluoro-7,7,11,11-tetrakis(butyloxymethyl)-5,9,13-trioxaheptadecane, perfluoro-7,7,11,11-tetrakis(2-methoxyethoxymethyl) -2,5,9,13,16-pentaoxaheptadecane, perfluoro-4,4,8,8,12,12-hexakis(methoxymethyl) -2,6,10,14- tetraoxapentadecane,

and perfluoro-5,5,9,9,13,13-hexakis(ethoxymethyl)-3,7,11,15-tetraoxaheptadecane.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter 1

Introduction

The extremely energetic process which occurs when elemental fluorine is substituted for hydrogen in an organic molecule has been recognized for many years. The relatively low dissociation energy (37 kcal mole^{-1}) has been generally accepted as the reason for the rapid reactivity and one of the reasons for the high heat of reaction [1]. Comparisons of fluorine reactions with organic molecules to combustion processes were common in texts on fluorine chemistry less than 35 years ago [2]. However, it was also noted that the "combustion" process observed when elemental fluorine was brought into contact with organic material was essentially the same as the effect observed when the temperature of an organic chlorination reaction (using Cl_2) was allowed to

get too high [1]. Bigelow and coworkers realized that reactions with elemental fluorine could be moderated and suggested several means for accomplishing that task [3]. Their suggestions included dilution of fluorine by an inert gas to help slow down the reaction rate and conducting the reaction in an inert solvent to better dissipate the heat generated by the exothermic reaction. Several examples of successful direct fluorination using a variety of methods (with and without solvent) to synthesize partially fluorinated or perfluorinated products were reported in the literature in the 1930's and 1940's. The results were generally in low yield with significant fragmentation occurring even in simple organic substrates [4,5,6,7,8]. Still, these successful experiments showed that direct fluorination was a viable synthetic technique.

In the last two decades, direct fluorination has become a very successful tool for the synthesis of a wide range of perfluorinated compounds, some of which have not been obtainable by other methods. This has been due to a large extent to the discovery of the La-Mar gradient low temperature direct fluorination process [9]. This solventless technique overcame the problems

associated with the use of elemental fluorine by using very low initial temperatures (-80 to -100°C), very low initial fluorine concentrations (diluted with helium), and by distributing the substrate on a surface designed to rapidly dissipate heat (for example, by condensation onto the walls of a zoned reactor or dispersion in sodium fluoride over copper turnings). Another similar method, aerosol direct fluorination, has since been developed which likewise uses temperature and fluorine concentration gradients, but the substrate is deposited on a thermally generated aerosol of sodium fluoride to dissipate the heat [10]. Other significant differences between this method and the La-Mar technique are the need for a photochemical finishing step if a perfluorinated product is desired and the requirement of the starting material to be fairly volatile [11]. The low temperature direct fluorination method developed by Lagow and Margrave has been used extensively by this research group and previously at the Massachusetts Institute of Technology in the perfluorination of branched and cyclic alkanes [12,13], crown ethers [14,15], cryptands [16], amines [17], orthocarbonates [18], orthoformates [19], and a wide variety of simple

and branched ethers and polyethers [16,17,20,21,22,23,24]. Although the advent of this method has seemingly made the synthesis of new perfluorinated compounds limited only by the availability of the organic analog as the starting material, there are a few limitations to its success that have not yet been overcome. To date no perfluorinated unsaturated or aromatic compounds have been successfully synthesized by this or any other method of direct fluorination. In addition, close attention must be paid to the conditions of temperature and fluorine concentration, especially in the initial stages of a reaction, to prevent extensive fragmentation, degradation, and polymerization of the starting material.

The reasons for liquid phase direct fluorination (also known as solution fluorination) not receiving more attention in the synthesis of perfluorinated compounds, after a relatively large amount of early work, are not clear. Bockemuller is generally acknowledged as being the first experimenter to successfully fluorinate an organic molecule in solution using elemental fluorine [7]. Among other experiments, he successfully obtained

fluorohexadecane and difluorohexadecane by the reaction of fluorine diluted with carbon dioxide with hexadecane in carbon tetrachloride solvent and fluorocyclohexane from F_2/CO_2 with cyclohexane in dichlorodifluoromethane solvent (now commonly known as Freon 12). Bigelow and Pearson reacted pure fluorine with hexachlorobenzene in carbon tetrachloride and obtained small quantities of tetrafluorohexachlorocyclohexene and hexafluorohexachlorocyclohexane [5]. Miller fluorinated a variety of aliphatic chlorinated hydrocarbons using pure fluorine in either neat liquid starting material or $Cl_2FCCClF_2$ (Freon 113) solvent and found a variety of products in which fluorine substituted for both hydrogen and chlorine and where, in some cases, chlorine was found to have substituted for hydrogen [6]. Miller and coworkers later used elemental fluorine diluted with nitrogen in Freon 113 or Freon 11 ($CFCl_3$) solvents to fluorinate perfluoro- and chloroperfluoro-olefins [8]. In this manner they were able to obtain small yields of saturated chlorofluorocarbons where the observed products included compounds resulting from fluorine addition across the double bond, fluorine substitution for chlorine, chlorine addition to the double bond, and

polymerization of the starting material. Although not all of the above examples used pure hydrocarbons as starting material and no perfluorinated products resulted, the experiments did show that early solution phase direct fluorination was at least partially successful. They also demonstrated some of the problems encountered in early solution phase work and why most work after that was in systems that avoided the use of solvent. Bigelow and coworkers noted several drawbacks to the use of solvents in direct fluorination [3]. They realized that nearly all organic solvents reacted with fluorine and that perfluorocarbons were not particularly good solvents for the organic compounds they wished to fluorinate. Carbon tetrachloride was also found to be far from an "inert" solvent. Earlier work by Bigelow and others in the attempted direct fluorination of toluene in CCl_4 resulted in the only isolable product being a small amount of hexachlorobenzene [25]. This was presumeably the result of fluorine attack on the solvent releasing chlorine in a form suitable to attack toluene and leave its aromaticity intact. It was probably with these considerations in mind that Tedder in a 1961 review commented that liquid phase direct fluorination

was unlikely to be useful in the synthesis of perfluorinated compounds [1].

However, most of the experiments discussed above in carbon tetrachloride were carried out at temperatures at or above 0°C. Only Bockemuller's experiments [7] in Freon 12 (at -80°C) and some of Miller's experiments [8] in Freon 113 (at -55°C) were conducted in the range where the La-Mar technique begins fluorination. The results obtained by Miller and coworkers in Freon solvents also showed much less apparent solvent induced chlorination at -55°C (versus 0°C) although it is difficult to say whether the solvent caused any chlorination since the substrates themselves were highly chlorinated olefins. Because solvated reactions in general are far better at dissipating heat than reactions in the gas phase, it is somewhat surprising that low temperature direct fluorination in solution has not received more attention since the advent of the La-Mar synthetic technique. Only very recently have examples appeared in the literature where organic compounds have been successfully perfluorinated using a technique invloving solution fluorination. Modena and coworkers prepared the perfluoroethers of diglyme and

tetraglyme using nitrogen diluted fluorine in the perfluoropolyether liquid Fomblin Y (a product manufactured by Montefluos SpA.) at 100°C [26]. Feher and coworkers have applied for a patent on a solvent reactor used in a process similar to the one presented later in this paper to obtain the perfluoroether of heptaglyme [27]. Feher's experiment used a fluorine concentration gradient (diluted with nitrogen) in a Freon 113 solution from 15 to 25°C to achieve a 90 to 95% fluorinated product. Two additional steps using much more concentrated fluorine mixtures (up to 100%) and higher temperatures (up to 253°C) in the absence of solvent were necessary to completely fluorinate the substrate. The success of these experiments and the results provided in this paper provide excellent support for the premise that more complex hydrocarbons can be perfluorinated in solution.

The highly branched ethers of pentaerythritol, dipentaerythritol, and tripentaerythritol were chosen as candidates for the study of solution phase direct fluorination for several reasons. First, the starting material was relatively easy to synthesize. Many of the hydrocarbon ethers have been known for over 50 years

[28]. Nouguier and coworkers have studied the phase transfer catalysis etherification technique developed by Freedman and Dubois [29] specifically in higher molecular weight pentaerythritol ethers [30,31,32] making more of these ethers available as starting materials. Although not studied by Nouguier, the same technique was found to be useful in the synthesis of the dipentaerythritol and tripentaerythritol ethers. Second, few examples of the perfluorinated ethers of pentaerythritol and its dimer and trimer have been synthesized. Some of these perfluorinated ethers (compounds 1-4, 9 and 10 presented in Chapter 2) have been prepared without the use of solvent in this laboratory using a sodium fluoride dispersion over copper turnings in a disc reactor [16,33]. In addition, two of the same perfluorinated ethers (compounds 1 and 2) were prepared by the electrochemical fluorination process from partially fluorinated starting material [34]. Third, as with perfluoroalkanes and simple perfluoroethers, Clark's experimental results indicated that increasing the size of the alkyl groups of the pentaerythritol ethers caused their boiling points to increase in an almost predictable fashion [16]. Given

the known thermal stability of perfluorinated ethers [2] it was believed by further increasing the molecular weight of these perfluorinated ethers and by synthesizing the perfluorinated ethers of di- and tripentaerythritol , compounds with industrially (as well as chemically) interesting properties could be obtained. Besides possible uses as synthetic lubricants or hydraulic fluids (common uses for many of the perfluoropolyether fluids [24,35,36,37,38]), stable high boiling point liquids would also be candidates as vapor phase soldering fluids. Another possible application area considered was in the field of artificial blood. Several perfluoroethers previously synthesized in this laboratory have been named as candidates for this application [17,23]. Finally, and very important for this work, the hydrocarbon ether starting materials for this study were all found to be soluble in a variety of halogenated solvents, including Freon 11 and 113 and carbon tetrachloride.

Chapter 2

Experimental

2.1 General

Infrared absorption spectra were obtained on a Bio-Rad Digilab FTS-40 Fourier transform spectrometer. All routine spectra were taken using 64 scans at 2 wavenumber resolution. Electron impact ionization mass spectrometry was performed on a Bell and Howell 21-491 mass spectrometer. Chemical ionization and fast atom bombardment (FAB) mass spectrometry were performed using a Finnigan MAT TSQ-70 with methane as the ionizing gas (for CI). For all fluorocarbons, an ion corresponding to the parent molecule minus fluorine was observed in the positive ion mode. As noted in previous work with perfluorinated pentaerythritol ethers, electron impact

ionization caused fragmentation of the parent molecule to the extent that parent and parent minus fluorine ions were never observed [16]. Nuclear magnetic resonance spectra were performed on a Varian EM390 spectrometer. Fluorine magnetic resonance was performed with the probe tuned to 84.6 MHz using $CFCl_3$ as an internal reference. All fluorine chemical shifts were reported relative to $CFCl_3$ with negative values assigned to shifts upfield. Elemental analysis was done by Schwartzkopf Microanalytical Laboratory of Woodside, New York. Boiling points were determined at atmospheric pressure by heating a few drops of the product in a small vial in a perfluorinated polyether oil bath until a steady stream of bubbles issued from the open end of an inverted melting point capillary tube submerged in the liquid. This method is one of several suggested by Pasto and Johnson [39].

Fluorine gas was used as delivered from Air Products and Chemicals. Helium was supplied by the University of Texas Physics Department. The reagents used to synthesize all of the hydrocarbon ether starting materials were purchased from Aldrich Chemical Company, J. T. Baker, Mallinckrodt, or EM Industries either

directly or from the U. T. Chemistry Department stockroom. Solvents used in the fluorination process and to work up hydrocarbon and fluorocarbon products came from the same sources.

2.2 Hydrocarbon Synthesis

All hydrocarbon ethers used as starting material for fluorination reactions were synthesized using a slightly modified version of the method of phase transfer catalysis described by Freedman and Dubois [29]. Phase transfer catalysis has been applied specifically to pentaerythritol by several experimenters [16,30,32,40]. Pentaerythritol, dipentaerythritol, and tripentaerythritol were alkylated using iodomethane, bromoethane, 1-bromopropane, 1-bromobutane, 1-bromopentane, 1-bromo-3-methylbutane, 1-bromohexane, 1-bromoheptane, 1-bromooctane, and 2-chloroethyl methyl ether to produce the corresponding ethers. Although Clark used Adogen 464 as the phase transfer catalyst for many of the same compounds listed above with excellent results [16], a different catalyst was used in the synthesis of the hydrocarbon ethers in this study.

$$C(CH_2OH)_4 + 4RX + 4NaOH \xrightarrow{PTC} C(CH_2OR)_4 + 4NaX + 4H_2O$$

$R = C_2H_5$, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, i-C_5H_{11}, n-C_6H_{13}, n-C_7H_{15}, n-C_8H_{17}, $CH_2CH_2OCH_3$

$$([HOCH_2]_3CCH_2)_2O + 6RX + 6NaOH \xrightarrow{PTC}$$
$$([ROCH_2]_3CCH_2)_2O + 6NaX + 6H_2O$$

$R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9, $CH_2CH_2OCH_3$

$$([HOCH_2]_3CCH_2OCH_2)_2C(CH_2OH)_2 + 8RX + 8NaOH \xrightarrow{PTC}$$
$$([ROCH_2]_3CCH_2OCH_2)_2C(CH_2OR)_2 + 8NaX + 8H_2O$$

$R = CH_3$, C_2H_5

Figure 2-1: Synthesis of hydrocarbon ethers.

Freedman and Dubois [29] obtained the best results in their study using tetrabutyl ammonium bisulfate (TBAB) and obtained satisfactory results using tetrabutyl ammonium iodide (TBAI). Nouguier and coworkers found tetrabutyl ammonium bromide to be a quite satisfactory catalyst for the etherification of pentaerythritol [30,40]. Because purification of some of the hydrocarbons by vacuum distillation was next to impossible due to the extremely high boiling points of the products, a water soluble catalyst was desireable since it could be easily removed from the organic phase of the reaction. Adogen 464, also a quartenary ammonium salt, did not meet the water solubility requirement and was used only in the synthesis of some early batches of lower molecular weight hydrocarbons that could be easily distilled before being abandoned in favor of other catalysts. Most of the ethers of pentaerythritol (and all of the ethers of dipentaerythritol and tripentaerythritol) were synthesized using either TBAB or TBAI as the phase transfer catalyst.

In a typical reaction, 25 grams of the alcohol and a 5 percent molar equivalent (based on hydroxyl group equivalents, not on the moles of the polyalcohol) of

catalyst were first dissolved in water in a 500 ml roundbottom flask. The amount of water was determined so that when a 5 fold excess of NaOH was added (again based on hydroxyl group equivalents) a 50 percent NaOH solution resulted. Once all of the NaOH dissolved and the alcohol and catalyst formed a homogeneous mixture, a dropwise addition of the alkylating agent commenced and continued over several hours. During this time the solution was vigorously stirred and heated to 70°C. The reaction flask was fitted with a reflux condenser to ensure that no solvent or reagent was lost. When addition of the alkylating agent was complete, the solution was kept at 70°C for two days before further workup. A fifty to one hundred percent excess of alkylating agent was included in the addition to provide additional solvent for the organic phase. After two days, the solution was allowed to cool to room temperature and transferred to a separatory funnel. Additional water and diethyl ether were usually added to dissolve any salt byproduct and facilitate separation. After separation, the aqueous phase was extracted with two 100 ml portions of diethyl ether then discarded. The ether extracts were combined with the organic layer and

the entire organic solution washed with at least four 100 ml portions of water. In some cases, additional washes were needed to completely remove some sediment evident in the organic solution. The remaining organic solution was dried over $MgSO_4$ for several hours (usually overnight) after which the $MgSO_4$ was removed by suction filtration and the solvent stripped by rotary evaporation. The desired product was then obtained by fractional distillation (under vacuum) of the remaning organic solution. In cases where the product was not volatile enough to be vacuum distilled without a significant amount of decomposition, the organic solution was cleaned up by heating to 200-250°C at approximately 1 mm Hg pressure to remove any volatile byproducts and leftover alkylating agent. While the product in these cases was not pure enough for definitive characterization by proton N.M.R., it proved to be sufficient as a starting material for direct fluorination. All hydrocarbon ethers synthesized were verified by infrared and mass spectral analyses prior to being subjected to fluorination.

2.3 Hydrocarbon Ethers

5,5-Bis(ethoxymethyl)-3,7-dioxanonane. Synthesized by alkylation of pentaerythritol with bromoethane in the presence of TBAB catalyst in 64% yield. Final product obtained by fractional distillation at 96-98°C and 5 mm Hg. IR (thin film, KBr): 2975(s), 2931, 2867(s), 2800, 1488, 1377, 1297, 1200, 1108(vs), 1071, 1036, 885, cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 249$(P+H)^+$, 233$(P-CH_3)^+$, 221, 203$(P-C_2H_5O)^+$, 175, 157, 143, 129, 113, 103, 99, 85, 83, 71(base).

6,6-Bis(propyloxymethyl)-4,8-dioxaundecane. Synthesized by alkylation of pentaerythritol with 1-bromopropane in the presence of TBAB catalyst in 57% yield. Final product obtained by fractional distillation at 97-99°C and 1 mm Hg. IR (thin film, KBr): 2961, 2934, 2865, 1462, 1376, 1175, 1107(vs), 1052, 960 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 305$(P+H)^+$, 275, 263, 245, 231, 203, 185, 171, 157, 143, 131, 127, 113, 99, 89, 85, 83, 73, 71, 65(base).

7,7-Bis(butyloxymethyl)-5,9-dioxatridecane. Synthesized

by alkylation of pentaerythritol with 1-bromobutane in the presence of TBAB catalyst in 61% yield. Final product obtained by fractional distillation at 139-144°C and 1 mm Hg. IR (thin film, KBr): 2958(s), 2933, 2866(s), 1465, 1374, 1303, 1109(vs), 1054 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 361$(P+H)^+$, 317$(P-C_3H_7)^+$, 305, 287$(P-C_4H_9O)^+$, 231, 199, 159, 141, 127, 103, 85, 71, 57, 43, 41(base). [m/e=41 could have been from the ionization gas, next largest fragment was m/e=287]

8,8-Bis(pentyloxymethyl)-6,10-dioxapentadecane. Synthesized by alkylation of pentaerythritol with 1-bromopentane in the presence of TBAB catalyst in 53% yield. Final product obtained by fractional distillation at 165-170°C and 1 mm Hg. IR (thin film, KBr): 2955(vs), 2929(vs), 2859(vs), 2796, 2735, 1463, 1375, 1302, 1172, 1108(vs), 1070, 891, 780, 730 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 417$(base,P+H)^+$, 401, 359, 347, 329, 289, 259, 247, 240, 227, 205, 187, 169, 155, 141. ; (electron impact ionization): m/e 240, 187, 169, 154, 141, 117, 99, 87, 85, 84, 83, 72, 71(base), 70, 69, 57, 55, 43, 41.

2,12-Dimethyl-7,7-bis(2-methylbutyloxymethyl)-5,9-dioxatridecane. Synthesized by alkylation of pentaerythritol with 1-bromo-3-methylbutane in the presence of TBAB catalyst in 14% yield. Final product obtained by fractional distillation at 133-138°C and 1 mm Hg. IR (thin film, KBr): 2958(vs), 2927(s), 2870(vs), 1468, 1367, 1171, 1108(vs), 1051 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 445$(P+29)^+$, 417(base, $P+H)^+$, 401$(P-CH_3)^+$, 359$(P-C_4H_9)^+$, 347, 329$(P-C_5H_{11}O)^+$, 259, 240, 227, 187, 141.

9,9-Bis(hexyloxymethyl)-7,11-dioxaheptadecane. Synthesized by alkylation of pentaerythritol with 1-bromohexane in the presence of TBAB catalyst in approximately 66% yield. Final product obtained by heating organic solution to 196°C at 1 mm Hg and saving remaining organic liquid. IR (thin film, KBr): 2955(s), 2929(vs), 2858(s), 1464, 1376, 1108(vs), 1053, 924(w), 726(w) cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 502$(P+29+H)^+$, 474(base,$P+2H)^+$, 472, 457$(P-CH_3)^+$, 444$(P-C_2H_5+H)^+$, 401$(P-C_5H_{11})^+$, 389, 371$(P-C_6H_{13}O)^+$, 287, 268, 255, 215, 155.

10,10-Bis(heptyloxymethyl)-8,12-dioxanonadecane. Synthesized by alkylation of pentaerythritol with 1-bromoheptane in the presence of TBAB catalyst in approximately 20% yield. Final product obtained by saving organic liquid leftover after heating solution for several hours at 1 mm Hg. IR (thin film, KBr): 2955, 2927(vs), 2856(vs), 2796, 2733, 1465(s), 1376, 1315, 1109(vs), 1052, 724 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 529(base,P+H)$^+$, 513(P-CH_3)$^+$, 459, 431, 429(P-C_7H_{15})$^+$, 413(P-$C_7H_{15}O$)$^+$, 345, 315, 296, 283, 243, 215, 198, 169; (electron impact ionization): m/e 296, 269, 243, 199, 168, 145, 129, 99, 87, 83, 70, 57(base), 43.

11,11-Bis(octyloxymethyl)-9,13-dioxaheneicosane. Synthesized by alkylation of pentaerythritol with 1-bromooctane in the presence of TBAB catalyst in approximately 52% yield. Final product obtained by saving organic liquid leftover after heating solution to 210°C at 1 mm Hg for several hours. IR (thin film, KBr): 2955, 2928(vs), 2856(s), 1465, 1377, 1108(vs), 1052, 723(w) cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 585(base,P+H)$^+$, 584, 570,

555(P-C_2H_5)$^+$, 513, 485, 473, 471(P-C_8H_{17})$^+$, 455(P-$C_8H_{17}O$)$^+$, 373, 343, 324, 311, 271, 212, 183, 113(C_8H_{17})$^+$.

7,7-Bis(2-methoxyethoxymethyl)-2,5,9,12-tetraoxatridecane. Synthesized by alkylation of pentaerythritol with 2-chloroethyl methyl ether in the presence of TBAB catalyst in 19% yield. Final product obtained by fractional distillation at 152-155°C and 1 mm Hg. IR (thin film, KBr): 2977, 2875(s), 2817, 1453, 1359, 1302, 1198(s), 1134(s), 1109(vs), 1032, 851 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 369(base, P+H)$^+$, 337(P-CH_3O)$^+$, 293(P-$C_3H_7O_2$)$^+$, 217, 203, 173, 163, 143, 129; (electron impact ionization): m/e 216, 203, 163, 89($C_4H_9O_2$), 59(base, C_3H_7O), 45(C_2H_5O).

4,4,8,8-Tetrakis(methoxymethyl)-2,6,10-trioxaundecane. Synthesized by alkylation of dipentaerythritol with iodomethane in the presence of TBAI catalyst in 40% yield. Final product obtained by fractional distillation at 130-131°C and 1 mm Hg. IR (thin film, KBr): 2978, 2920, 2891, 2809, 1482, 1457, 1200, 1179, 1109(vs), 970

cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 339(base, P+H)$^+$, 325, 307(P-CH_3O)$^+$, 274, 242, 221, 191, 161, 129, 115.

5,5,9,9-Tetrakis(ethoxymethyl)-3,7,11-trioxatridecane. Synthesized by alkylation of dipentaerythritol with bromoethane in the presence of TBAB catalyst in 52% yield. Final product obtained by fractional distillation at 142-145°C and 1 mm Hg. IR (thin film, KBr): 2974(s), 2931, 2893, 2866(s), 2800, 1377(s), 1357, 1297, 1175(s), 1109(vs), 1072, 1027, 887 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 423(P+H)$^+$, 395, 377(P-C_2H_5O)$^+$, 367, 349, 330, 317, 303, 277, 233, 221, 203(base, $C_{11}H_{23}O_3$)$^+$, 189, 175, 157, 143, 129, 113, 103, 99, 85, 75, 71; (electron impact ionization): m/e 277, 221, 203, 181, 175, 156, 143, 127, 113, 103, 99, 85, 75, 71, 59, 55, 43, 36(base).

6,6,10,10-Tetrakis(propyloxymethyl)-4,8,12-trioxapentadecane. Synthesized by alkylation of dipentaerythritol with 1-bromopropane in the presence of TBAB catalyst in approximately 67% yield. Final product obtained by saving organic liquid leftover after heating solution

under vacuum (1 mm Hg) and filtering through a glass frit (to remove $MgSO_4$ not removed in earlier filtration). IR (thin film, KBr): 2961, 2932, 2865(s), 1484, 1462, 1107(vs), 1052, 960 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e $535(P+29)^+$, $507(P+H)^+$, $465(base,P-C_3H_7+2H)^+$, 423, 405, 333, 263, $245(C_{14}H_{29}O_3)^+$, $231(C_{13}H_{27}O_3)^+$, 184, 131; (electron impact ionization): m/e 263, $245(C_{14}H_{29}O_3)$, 231, 203, 184, 171, 143, 142, 141, 131(base), 126, 113, 99, 89, 87, 85, 83, 73, 71, 57, 55, 43, 41.

7,7,11,11-Tetrakis(butyloxymethyl)-5,9,13-trioxaheptadecane. Synthesized by alkylation of dipentaerythritol with 1-bromobutane in the presence of TBAB catalyst in approximately 72% yield. Final product obtained by saving organic liquid leftover after heating solution to 275°C at 1 mm Hg. IR (thin film, KBr): 2963(vs), 2935(s), 2873, 1465, 1374, 1108(vs), 1054 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e $619(P+29)^+$, $591(P+H)^+$, 535, 479, 442, 389, 305, $287(C_{17}H_{35}O_3)^+$, 259(base), 212, 159, 140, 103; (electron impact ionization): m/e 305, 287, 259, 212, 159, 140, 127, 103, $87(C_5H_{11}O)$, 71, $57(base,C_4H_9)$, 41.

7,7,11,11-Tetrakis(2-methoxyethoxymethyl)-2,5,9,13,16-pentaoxaheptadecane. Synthesized by alkylation of dipentaerythritol with 2-chloroethyl methyl ether in the presence of TBAI catalyst in approximately 14% yield. Final product obtained by saving organic liquid leftover after gently heating solution for 45 minutes at 1 mm Hg. IR (thin film, KBr): 2959, 2875, 1452, 1256, 1198, 1104(vs), 1052 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 603(base, $P+H)^+$, 545, $527(P-C_3H_7O_2)^+$, 450, 397, $323(C_{15}H_{31}O_7)^+$, $293(C_{14}H_{29}O_6)^+$, 263, 203, 163, 89.

4,4,8,8,12,12-Hexakis(methoxymethyl)-2,6,10,14-tetraoxapentadecane. Synthesized by alkylation of tripentaerythritol with iodomethane in the presence of TBAI catalyst in approximately 52% yield. Final product obtained by saving the organic liquid remaining after the solution was heated to 220°C at 1 mm Hg. IR (thin film, KBr): 2978, 2920, 2891(s), 2809, 1482, 1458, 1200, 1109(vs), 1051, 971 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 485(base, $P+H)^+$, 483, 471, $453(P-CH_3O)^+$, $439(P-C_2H_5O)^+$, 420, 340, 339, 337, 325, 307, 293, 274, 261, 221, 191, 161, 129, 115.

5,5,9,9,13,13-Hexakis(ethoxymethyl)-3,7,11,15-tetraoxaheptadecane. Synthesized by alkylation of tripentaerythritol with bromoethane in the presence of TBAB catalyst in approximately 25% yield. Final product obtained by saving the organic liquid remaining after the solution was heated to 200°C at 1 mm Hg for 30 minutes. IR (thin film, KBr): 2974, 2931, 2866(s), 1488, 1377, 1176, 1109(vs), 1028, 887(w) cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 598$(P+2H)^+$, 570, 542, 504, 451, 431, 395, 377, 349, 330, 277, 221, 203$(base, C_{11}H_{23}O_3)^+$, 175, 156, 127, 112, 103; (electron impact ionization): m/e 504, 431, 395, 377, 349, 277, 233, 221, 203(base), 189, 175, 156, 143, 127, 113, 103, 99, 85, 71, 59.

2.4 Fluorocarbon Synthesis

All fluorocarbon ethers in this study were synthesized by direct fluorination of their respective hydrocarbon analogs (figure 2-2). A two phase process was used. In the first phase, where most of the fluorination was accomplished, a fluorine/helium gas mixture was bubbled through a rapidly stirred

$$C(CH_2OR)_4 \xrightarrow[\substack{CFCl_3 \\ Cl_2FCCClF_2}]{F_2/He} \xrightarrow[50-75^\circ C]{F_2} C(CF_2OR_f)_4$$

$$([ROCH_2]_3CCH_2)_2O \xrightarrow[\substack{CFCl_3 \\ Cl_2FCCClF_2}]{F_2/He} \xrightarrow[50-75^\circ C]{F_2} ([R_fOCF_2]_3CCF_2)_2O$$

$$([ROCH_2]_3CCH_2OCH_2)_2C(CH_2OR)_2 \xrightarrow[\substack{CFCl_3 \\ Cl_2FCCClF_2}]{F_2/He} \xrightarrow[50-75^\circ C]{F_2}$$

$$([R_fOCF_2]_3CCF_2OCF_2)_2C(CF_2OR_f)_2$$

Figure 2-2: Synthesis of branched perfluorinated ethers.

chlorofluorocarbon solution of the hydrocarbon and NaF. In the second phase, the partially fluorinated product from the first phase was combined with fresh NaF in a Teflon boat, placed in a tube reactor, and heated in pure fluorine (and an absence of solvent). The technique used was basically the same as that of the La-Mar low temperature gradient fluorination process [9,16] except that in all cases the majority of fluorination occurred in solution rather than in the "solid" phase. The fluorine/helium delivery system and the tube reactor were the same as those used in the La-Mar method and have been previously described [9]. The solution reactor, however, was different from the types of reactor (disk, multi-zone, or tube type) previously used. Although similar in some respects to solution reactors that have been used recently in the direct fluorination of diglyme and tetraglyme [26] and the synthesis of perfluorinated polyethers [27], the reactor used in the experiments reported here differed substantially enough that a more detailed description was warranted.

The solution reactor design (figure 2-3) was modified slightly from a reactor obtained by this research group

from Exfluor Research Corporation. Modifications included a decrease in the size of the reaction chamber in order to scale down the quantities of reagent and solvent needed for a reaction, a change in the spring seal to better protect the stirring shaft bearings from fluorine, and a change in the location of gas inlet and outlet to accomodate the smaller reaction chamber. The reactor itself was fabricated by the U. T. Chemistry Department Machine Shop. The upper assembly was machined from aluminum stock and used standard size sealed ball bearings (a) obtained from Capitol Bearing Company in Austin, Texas, and a standard size spring seal (b) obtained from Fluorocarbon Mechanical Seal Division of Los Alamitos, California. The spring seal originally intended for use was made of butyl rubber and was discovered to be insufficiently tolerant to fluorine for the amount of time needed to run these reactions. As a result, the spring seals mentioned above were obtained. The seals were made of carbon/graphite filled Teflon (referred to as Fluoroloy SL by the manufacturer). The remainder of the upper assembly consisted of a stainless steel stirring shaft (c) fitted to receive a zinc plated steel, double paddled paint stirrer (d) obtained from

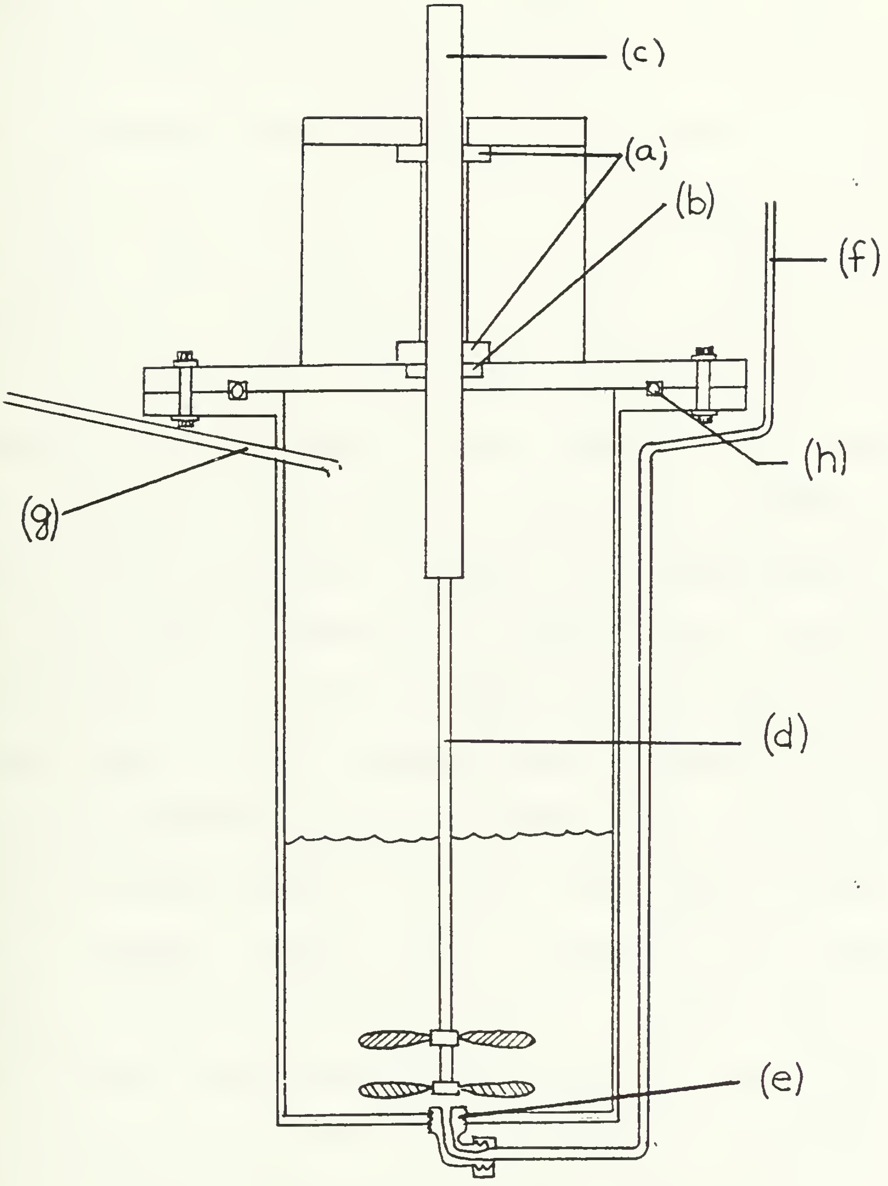


Figure 2-3: Solution Reactor - normal liquid level for beginning of reaction shown.

Stiffler Handy Products through Aldrich Chemical Company. The cylindrically shaped lower assembly or reaction chamber was made entirely of stainless steel with a threaded hole drilled in the bottom to accept a 90° brass elbow fitting (e) to connect the one quarter inch copper tubing F_2/He inlet line (f). The gas inlet was physically located directly below the stirring shaft when the reactor was completely assembled. The outlet connection (g) was made of one quarter inch stainless steel tubing and was welded to the lower assembly after penetrating through the vessel wall approximately one half inch. This penetration (rather than a flush weld) was necessary to prevent solvent overflow when stirring at high speed. Once charged with a reaction solution, the two halves were bolted together with a butyl rubber O-ring (h) preventing F_2 escape from the reactor. The entire reactor assembly was placed in an insulated chamber up to the bolted flange so that the entire reaction zone was below the insulated top (see figure 2-4). A simple plywood box with fiberglass insulation was used in these experiments. The temperature of the reaction was regulated by a thermocouple (a) and temperature controller (b) that operated a solenoid

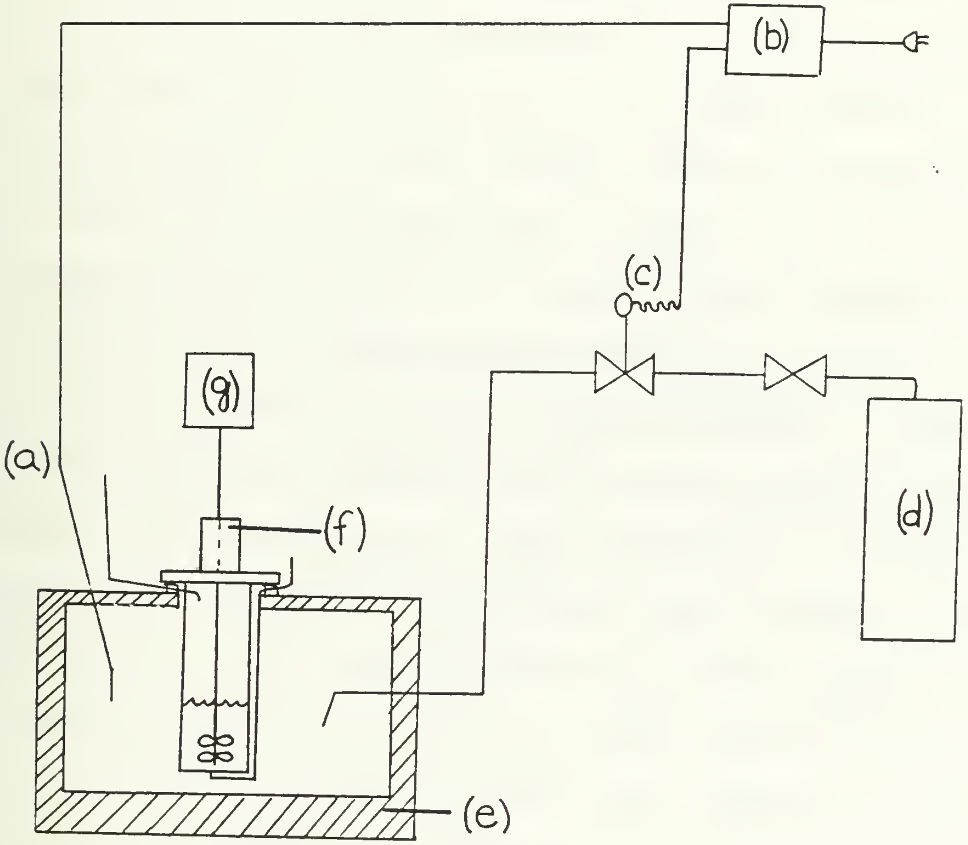


Figure 2-4: Temperature control system.

valve (c) to control the amount of liquid nitrogen (d) vented into the box (e). The stirring shaft of the reactor (f) was coupled to a stirring motor (g) mounted vertically above the box and aligned with the stirring shaft. Two different alternating current electric motors were used. For most experiments a one third horsepower motor operating at 1725 rpm was used. Later, as it became evident that this higher speed was overly harsh on the shaft bearings and caused the solvent to evaporate more quickly, a similar motor fitted with a clutched 400 rpm reduction gear was substituted.

In a typical reaction, approximately 5 grams of hydrocarbon was dissolved in a slurry of NaF (used to absorb HF generated by the fluorination process and insoluble in chlorofluorocarbons) and 350 ml of $CFCl_3$ (Freon 11). The amount of NaF used was roughly a 10% excess of the theoretical HF yield. This solution was placed into a solvent reactor and purged with helium while the reactor was cooled to -60 to -80°C. Once at the starting temperature, the stirring motor was started and the helium purge allowed to continue for an additional two to four hours. Fluorine concentration was started at 2-5% and increased in stepped increments over

several days to a maximum of 25%. The actual fluorine flow rate never exceeded 5 cc/min. In coordination with the F_2 concentration increase, the temperature was gradually stepped up to a maximum of 0 to +10°C during the same period. The temperature increases were controlled so that after three days the reaction temperature had reached -15°C. An additional 150-200 ml of Cl_2FCClF_2 (Freon 113) was then added to the reaction to make up for the anticipated loss of Freon 11 as the reaction temperature was increased. This addition was accomplished by temporarily securing F_2 for 15 minutes to purge the inlet line and then injecting the additional solvent by syringe through a septum on a T-connection in the inlet line. Once the addition was made, F_2 was restored to its original flow rate. An additional 200 ml of Freon 113 was similarly added during the next two days. After seven days of fluorination in solution, the fluorine and stirring motor were secured and the reactor was purged with helium while warming to room temperature. When a two hour purge was completed, the reactor was disconnected from the system. The contents of the solution reactor were transfered to a flask and the reactor and stir

blades were rinsed with an additional 150 ml of Freon 113. Typically 250-400 ml of solvent were intact after this phase of fluorination. The combined reaction solution and rinse were filtered and the solvent stripped by rotary evaporation. The remaining partially fluorinated product, a clear, usually odorless liquid, was then combined with 10-12 grams of fresh NaF and spread into a Teflon boat (approximately 0.5"x12" and 0.5" deep) and placed in a one inch diameter nickle tube reactor. After being purged with helium for 2-3 hours, fluorination was completed by exposing the partially fluorinated material to a stream of pure fluorine at ambient and elevated temperatures. The maximum temperature used was 75°C. After two or three days the fluorine and heating were stopped and the reactor was allowed to cool for several hours to room temperature under a helium purge. The boat contents were emptied into a beaker and combined with 100 ml of Freon 113 used to rinse the boat. The rinse was combined with the reactor contents in order to dissolve the crude product. The slurry was suction filtered to remove the $NaF/NaHF_2$ and the filtrate washed with an additional 50 ml of Freon 113. The crude product was obtained by again

stripping the solvent on a rotary evaporator. The final product was purified by vacuum distillation and characterized by infrared, mass, and ^{19}F N.M.R. spectrometry and by elemental analysis.

2.5 Fluorocarbon Ethers

Perfluoro-5,5-bis(ethoxymethyl)-3,7-dioxanonane, (1). 5.023 grams of hydrocarbon starting material were dissolved in a slurry of 26.81 grams of NaF and 350 ml Freon 11 in a solution reactor. The solution was cooled to -80°C under a helium purge and fluorinated as described above using the conditions listed in table 2-1. Fractional distillation of the crude product was performed at 40 mm Hg. 3.688 grams of product were collected at 75-80°C for a 24% yield. The perfluorinated ether was a clear liquid with a boiling point of 176°C. IR (thin film, KBr): 1267(s), 1231(vs), 1195(s), 1110(vs), 979, 698 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 733$(P-F)^+$, 617$(P-C_2F_5O)^+$, 595$(C_{11}F_{21}O_4)^+$, 479$(C_9F_{17}O_3)^+$, 414$(C_7F_{14}O_4)^+$, 341$(C_7F_{11}O_3)^+$, 185$(C_3F_7O)^+$, 135$(C_2F_5O)^+$, 119(base, $C_2F_5)^+$; (chemical ionization, negative ion):

Flow rates (cc/min)		Temperature (°C)	Solvent*	Time (hrs)
He	F_2			
47	3	-80	A	20.5
45	5	-60	A	24
28	5	-40	A	24
28	5	-15	A/B	24
20	5	0	A/B	72
20	5	amb.	none	14
0	5	amb.	none	72

Table 2-1: Fluorination conditions for compound 1.

* A=$CFCl_3$; B=$Cl_2FCCClF_2$; none=second phase of fluorination (tube reactor)

m/e 567$(C_{10}F_{21}O_3)^-$, 467$(C_8F_{17}O_3)^-$, 151, 135(base). ^{19}F N.M.R. analysis: $\delta(CFCl_3)$ -66.3, -87.7, -89.0 ppm. Elemental analysis: calculated C 20.76%, F 70.73%; found C 20.29%, F 70.27%.

Perfluoro-6,6-bis(propyloxymethyl)-4,8-dioxaundecane, (2). 5.072 grams of hydrocarbon starting material were dissolved in a slurry of 27.06 grams of NaF and 350 ml Freon 11 in a solution reactor. The solution was cooled to -80°C under a helium purge and fluorinated as described above using the conditions listed in table 2-2. Fractional distillation of the crude product was performed at 10 mm Hg. 7.601 grams of product were collected at 83-103°C for a 48% yield. The perfluorinated ether was a clear liquid with a boiling point of 216°C. IR (thin film, KBr): 1346, 1270(s), 1235(vs), 1205, 1144(s), 1110, 1020, 1005, 703 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 933$(P-F)^+$, 899, 855, 811, 783$(P-C_3F_7)^+$, 767(base, $P-C_3F_7O)^+$, 745$(C_{14}F_{27}O_4)^+$, 579$(C_{11}F_{21}O_3)^+$. ^{19}F N.M.R. analysis: $\delta(CFCl_3)$ -65.5, -81.7, -84.0, -129.5 ppm. Elemental analysis: calculated C 21.45%, F 71.83%; found C 21.25%, F 71.73%.

Flow rates (cc/min)		Temperature (°C)	Solvent*	Time (hrs)
He	F_2			
35	5	-80	A	15
28	5	-60	A	24
20	5	-40	A	29
20	5	-15	A/B	20
20	5	-5	A/B	72
0	5	amb.	none	15
0	5	+50	none	54

Table 2-2: Fluorination conditions for compound 2.

* A=$CFCl_3$; B=Cl_2FCClF_2; none=second phase of fluorination (tube reactor)

Perfluoro-7,7-bis(butyloxymethyl)-5,9-dioxatridecane, (3). 6.311 grams of hydrocarbon starting material were dissolved in a slurry of 35.42 grams of NaF and 350 ml Freon 11 in a solution reactor. The solution was cooled to -80°C under a helium purge and fluorinated as described above using the conditions listed in table 2-3. Fractional distillation of the crude product was performed at 9 mm Hg. 4.219 grams of product were collected at 95-110°C for a 21% yield. The perfluorinated ether was a clear liquid with a boiling point of 238°C. Over 3 grams of clear, viscous liquid was left undistilled and was later tentatively identified as a polymerization product of the perfluorinated ether. IR (thin film, KBr): 1316, 1266(s), 1241(vs), 1145(vs), 984, 892 cm^{-1}. Mass spectral analysis (fast atom bombardment [FAB], positive ion): m/e 1133$(P-F)^+$, 917$(P-C_4F_9O)^+$, 895$(C_{17}F_{33}O_4)^+$, 679$(C_{13}F_{25}O_3)^+$, 397$(C_8F_{15}O)^+$, 219, 181, 131(base, $C_3F_5)^+$, 119, 100. ^{19}F N.M.R. analysis: $\delta(CFCl_3)$ -65.3 -81.8, -82.9, -126.2, -126.7 ppm. Elemental analysis: calculated C 21.89%, F 72.55%; found C 21.65%, F 72.76%.

Perfluoro-8,8-bis(pentyloxymethyl)-6,10-dioxapentadecane

Flow rates (cc/min) He	F_2	Temperature (°C)	Solvent*	Time (hrs)
45	5	-80	A	13
35	5	-60	A	24
28	5	-40	A	24
20	5	-15	A/B	24
20	5	0	A/B	72
0	5	amb.	none	16.5
0	5	+50	none	24
0	5	+75	none	24

Table 2-3: Fluorination conditions for compound 3.

* A=$CFCl_3$; B=$Cl_2FCCClF_2$; none=second phase of fluorination (tube reactor)

(4). 5.241 grams of hydrocarbon were dissolved in a slurry of 28.31 grams of NaF and 350 ml Freon 11 in a solution reactor. The solution was cooled to -70°C under a helium purge and fluorinated as described above using the conditions listed in table 2-4. Fractional distillation of the crude product was performed at 10 mm Hg. 7.061 grams of product were collected at 100-125°C for a 41% yield. The perfluorinated ether was a clear liquid with a boiling point of 253°C. IR (thin film, KBr): 1336, 1242(vs), 1214(vs), 1146(s), 1127, 979, 876 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 1333(base, P-F)$^+$, 1233$(P-C_2F_5)^+$, 1183$(P-C_3F_7)^+$, 1133$(P-C_4F_9)^+$, 1067$(P-C_5F_{11}O)^+$, 1045$(C_{20}F_{39}O_4)^+$, 1017$(P-C_6F_{13}O)^+$, 917$(C_{17}F_{35}O_3)^+$, 779$(C_{15}F_{29}O_3)^+$, 491$(C_{10}F_{17}O_3)^+$, 269$(C_5F_{11})^+$. ^{19}F N.M.R. analysis: $\delta(CFCl_3)$ -65.5, -81.4, -83.0, -123.0 -125.3, -126.3 ppm. Elemental analysis: calculated C 22.21%, F 73.06%; found C 21.86%, F 73.35%.

Perfluoro-2,12-dimethyl-7,7-bis(2-methylbutyloxymethyl)-5,9-dioxatridecane, (5). 5.065 grams of hydrocarbon were dissolved in a slurry of 30.00 grams of NaF and 350 ml Freon 11 in a solution reactor. The solution was cooled

Flow rates (cc/min) He	F_2	Temperature (°C)	Solvent*	Time (hrs)
35	5	-70	A	19
28	5	-50	A	26.5
20	5	-30	A	18
20	5	-15	A/B	24
20	5	-5	A/B	72
0	5	amb.	none	16
0	5	+50	none	48

Table 2-4: Fluorination conditions for compound 4.

* A=$CFCl_3$; B=Cl_2FCClF_2; none=second phase of fluorination (tube reactor)

to -75°C under a helium purge and fluorinated as described above using the conditions listed in table 2-5. Fractional distillation of the crude product was performed at 8 mm Hg. 3.098 grams of product were collected at 140-145°C for a yield of 19%. A significant amount (almost 4 grams) of a byproduct impurity was collected at 110-120°C and was identified by N.M.R. to be mainly the fluorinated product of the hydrocarbon triether with some other impurity mixed in. In addition a small amount of polymerized byproduct was collected at 160-190°C. The desired perfluorinated product was a clear liquid with a boiling point of 270°C. IR (thin film, KBr): 1250(vs), 1202, 1156, 1111, 985(s), 889, 729, 701, 541 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 1333$(P-F)^+$, 1195$(C_{23}F_{45}O_4)^+$, 1083$(P-C_5F_{11})^+$, 1045(base, $C_{20}F_{39}O_4)^+$, 895$(C_{17}F_{33}O_4)^+$, 779$(C_{15}F_{29}O_3)^+$, 295, 285, 269, 247, 181. ^{19}F N.M.R. analysis: $\delta(CFCl_3)$ -65.7, -72.7, -82.7, -118.0, -186.1 ppm. Elemental analysis: calculated C 22.21%, F 73.06%; found C 21.78%, F 73.04%.

Perfluoro-9,9-bis(hexyloxymethyl)-7,11-dioxaheptadecane, (6). 5.060 grams of hydrocarbon were dissolved in a

Flow rates (cc/min)		Temperature (°C)	Solvent*	Time (hrs)
He	F_2			
45	5	-75	A	15.5
20	5	-55	A	48
20	5	-35	A	8
20	5	-15	A/B	16
20	5	-5	A/B	72
0	5	amb.	none	15
0	5	+50	none	52

Table 2-5: Fluorination conditions for compound 5.

* A=$CFCl_3$; B=$Cl_2FCCClF_2$; none=second phase of fluorination (tube reactor)

slurry of 30.61 grams of NaF and 350 ml Freon 11 in a solution reactor. The solution was cooled to -75°C under a helium purge and fluorinated as described above using the conditions listed in table 2-6. Fractional distillation of the crude product was performed at 1 mm Hg. 4.848 grams of product were collected at 100-135°C for a 29% yield. The perfluorinated ether was a clear liquid with a boiling point of 292°C. IR (thin film, KBr): 1337, 1244(vs), 1208(vs), 1149(s), 1109(s), 984, 862, 712 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 1533$(P-F)^+$, 1495$(C_{29}F_{57}O_4)^+$, 1333$(P-C_4F_9)^+$, 1234$(P-C_6F_{13}+H)^+$, 1195, 1045$(C_{20}F_{39}O_4)^+$, 995, 945, 895, 879(base, $C_{17}F_{33}O_3)^+$, 829, 813, 779, 729, 679, 629, 579, 563, 541, 513, 497. ^{19}F N.M.R. analysis: $\delta(CFCl_3)$ -65.3, -81.5, -83.0, -122.3, -122.8, -125.0, -126.3 ppm. Elemental analysis: calculated C 22.44%, F 73.44%; found C 22.00%, F 73.48%.

Perfluoro-10,10-bis(heptyloxymethyl)-8,12-dioxanonadecane, (7). 7.729 grams of hydrocarbon were dissolved in a slurry of 36.28 grams of NaF and 350 ml Freon 11 in a solution reactor. The solution was cooled to -60°C under a helium purge and fluorinated as described above

Flow rates (cc/min) He	F_2	Temperature (°C)	Solvent*	Time (hrs)
45	5	-75	A	16
35	5	-55	A	24
28	5	-35	A	24
20	5	-15	A/B	24
20	5	0	A/B	72
0	5	amb.	none	19
0	5	+50	none	48

Table 2-6: Fluorination conditions for compound 6.

* A=$CFCl_3$; B=$Cl_2FCCClF_2$; none=second phase of fluorination (tube reactor)

using the conditions listed in table 2-7. Fractional distillation of the crude product was performed at 1 mm Hg. 1.908 grams of product were collected at 160-175°C for a 7% yield. Several byproducts were collected as well. A significant amount (1.989 grams) of perfluorinated diheptyl ether (identified by N.M.R.) was collected at 54°C. A large amount (4.905 grams) of byprodoct related to the hydrocarbon triether (as in compound 5) was collected at 128-146°C. The desired perfluorinated ether was a clear liquid with a boiling point of 353°C. IR (thin film, KBr): 1340(s), 1239(vs), 1210(vs), 1149(vs), 1118(s), 1054, 704, 661 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 1733$(P-F)^+$, 1383$(P-C_7F_{15})^+$, 1368$(P-C_7F_{15}O+H)^+$, 1345$(C_{26}F_{51}O_4)^+$, 1329$(C_{26}F_{51}O_3)^+$, 979(base, $C_{19}F_{37}O_3)^+$, 395, 369, 281. ^{19}F N.M.R. analysis: $\delta(CFCl_3)$ -65.7, -81.4, -83.0, -122.3, -125.2, -126.3 ppm. Elemental analysis: calculated C 22.62%, F 73.73%; found C 22.23%, F 73.42%.

Perfluoro-11,11-bis(octyloxymethyl)-9,13-dioxaheneicosane, (8). 5.074 grams of hydrocarbon were dissolved in a slurry of 28.29 grams of NaF and 350 ml Freon 11 in

Flow rates (cc/min)		Temperature (°C)	Solvent*	Time (hrs)
He	F_2			
45	5	-60	A	20
45	5	-40	A	20
20	5	-15	A/B	28
20	5	0	A/B	14
20	5	+10	A/B	96
0	5	amb.	none	24
0	5	+50	none	48

Table 2-7: Fluorination conditions for compound 7.

* A=$CFCl_3$; B=Cl_2FCClF_2; none=second phase of fluorination (tube reactor)

a solution reactor. The solution was cooled to -80°C under a helium purge and fluorinated as described above using the conditions listed in table 2-8. Fractional distillation of the crude product was performed at 1 mm Hg. 3.213 grams of product were collected at 150-160°C for a 19% yield. The perfluorinated ether was a clear liquid which decomposed at 336°C when boiling point determination was attempted. IR (thin film, KBr): 1345, 1211(vs), 1151(vs), 1006, 979, 880, 705, 659 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 1933$(P-F)^+$, 1533$(P-C_8F_{17})^+$, 1517$(P-C_8F_{17}O)^+$, 1495$(C_{29}F_{57}O_4)^+$, 1095, 1079$(C_{21}F_{41}O_3)^+$, 1013$(C_{20}F_{39}O_2)^+$, 597, 547, 463, 445, 435(base, $C_8F_{17}O)^+$, 419, 397, 369, 181. ^{19}F N.M.R. analysis: $\delta(CFCl_3)$ -65.5, -81.7, -83.2, -122.1, -122.8, -125.3, -126.3 ppm. Elemental analysis: calculated C 22.76%, F 73.96%; found C 22.58%, F 74.07%.

Perfluoro-7,7-bis(2-methoxyethoxymethyl)-2,5,9,12-tetraoxatridecane, (9). 5.409 grams of hydrocarbon were dissolved in a slurry of 25.60 grams of NaF and 350 ml Freon 11 in a solution reactor. The solution was cooled to -80°C under a helium purge and fluorinated as described above using the conditions listed in table

Flow rates (cc/min) He	F_2	Temperature (°C)	Solvent*	Time (hrs)
45	5	-80	A	15
35	5	-60	A	24
28	5	-40	A	24
20	5	-15	A/B	24
20	5	0	A/B	72
0	3	amb.	none	24
0	3	+50	none	24

Table 2-8: Fluorination conditions for compound 8.

* A=$CFCl_3$; B=$Cl_2FCCClF_2$; none=second phase of fluorination (tube reactor)

2-9. Vacuum distillation of the crude product was performed at 10 mm Hg. 3.573 grams of product were collected at 90-97°C for a 24% yield. The perfluorinated ether was a clear liquid with a boiling point of 215°C. IR (thin film, KBr): 1400, 1252(vs), 1192(s), 1147(vs), 1114(s), 980, 902, 681 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 997(base,P-F)$^+$, 881$(P-C_2F_5O)^+$, 815$(P-C_3F_7O_2)^+$, 793, 727, 611$(C_{11}F_{21}O_5)^+$, 341, 201$(C_3F_7O_2)^+$, 185, 119. ^{19}F N.M.R. analysis: $\delta(CFCl_3)$ -56.3, -66.3, -89.0, -91.2 ppm. Elemental analysis: calculated C 20.09%, F 67.31%; found C 19.92%, F 67.42%.

Perfluoro-4,4,8,8-tetrakis(methoxymethyl)-2,6,10-trioxaundecane, (10). 5.050 grams of hydrocarbon were dissolved in a slurry of 28.47 grams of NaF and 350 ml Freon 11 in a solution reactor. The solution was cooled to -55°C under a helium purge and fluorinated as described above using the conditions listed in table 2-10. Fractional distillation of the crude product was performed at 9 mm Hg. 5.676 grams of product were collected at 87-90°C for a 40% yield. The perfluorinated ether was a clear liquid with a boiling point of 203°C.

Flow rates (cc/min)		Temperature (°C)	Solvent*	Time (hrs)
He	F_2			
45	5	-80	A	14
35	5	-60	A	26
28	5	-40	A	26
20	5	-15	A/B	21
20	5	-5	A/B	68
0	3	amb.	none	16
0	3	+50	none	72

Table 2-9: Fluorination conditions for compound 9.

* A=$CFCl_3$; B=$Cl_2FCCClF_2$; none=second phase of fluorination (tube reactor)

Flow rates (cc/min)		Temperature	Solvent*	Time
He	F_2	(°C)		(hrs)
45	5	-55	A	20
45	5	-35	A	24
35	5	-15	A/B	24
28	5	0	A/B	96
0	5	amb.	none	16
0	5	+50	none	52

Table 2-10: Fluorination conditions for compound 10.

* A=$CFCl_3$; B=$Cl_2FCCClF_2$; none=second phase of fluorination (tube reactor)

IR (thin film, KBr): 1309, 1260(vs), 1226(vs), 1184(s), 1110(vs), 1079, 994, 821, 724, 668 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 931(base,P-F)$^+$, 865(P-CF$_3$O)$^+$, 843($C_{15}F_{29}O_7$)$^+$, 815(P-C$_2$F$_5$O)$^+$, 483($C_8F_{17}O_4$)$^+$, 467($C_8F_{17}O_3$)$^+$, 379($C_7F_{13}O_3$)$^+$, 313, 247, 151. ^{19}F N.M.R. analysis: δ(CFCl$_3$) -55.7, -65.7, -68.8 ppm. Elemental analysis: calculated C 20.23%, F 67.99%; found C 20.19%, F 68.07%.

Perfluoro-5,5,9,9-tetrakis(ethoxymethyl)-3,7,11-trioxatridecane, (11). 7.527 grams of hydrocarbon were dissolved in a slurry of 30.33 grams of NaF and 350 ml Freon 11 in a solution reactor. The solution was cooled to -55°C under a helium purge and fluorinated as described above using the conditions listed in table 2-11. Fractional distillation of the crude product was performed at 1 mm Hg. 12.86 grams of product were collected at 86-97°C for a 58% yield. A small amount of apparently polymerized byproduct was collect at 160-165°C. The perfluorinated ether was a clear liquid with a boiling point of 243°C. IR (thin film, KBr): 1405, 1232(vs), 1195(s), 1113(vs), 982, 698, 528 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion):

Flow rates (cc/min) He	F_2	Temperature (°C)	Solvent*	Time (hrs)
45	5	-55	A	22
45	5	-35	A	24
28	5	-15	A/B	24
28	5	0	A/B	24
20	5	0	A/B	24
20	5	+10	A/B	48
0	5	amb.	none	16
0	5	+50	none	24

Table 2-11: Fluorination conditions for compound 11.

* A=$CFCl_3$; B=$Cl_2FCCClF_2$; none=second phase of fluorination (tube reactor)

m/e 1231(base,P-F)$^+$, 1093($C_{20}F_{39}O_7$)$^+$, 1065(P-C_3F_7O)$^+$, 617($C_{11}F_{23}O_3$)$^+$, 479($C_9F_{17}O_3$)$^+$. ^{19}F N.M.R. analysis: δ($CFCl_3$) -65.3, -66.3, -87.5 -88.9 ppm. Elemental analysis: calculated C 21.14%, F 69.90%; found C 20.90%, F 70.02%.

Perfluoro-6,6,10,10-tetrakis(propyloxymethyl)-4,8,12-trioxapentadecane, (12). 5.285 grams of hydrocarbon were dissolved in a slurry of 28.39 grams of NaF and 350 ml Freon 11 in a solution reactor. The solution was cooled to -80°C under a helium purge and fluorinated as described above using the conditions listed in table 2-12. Vacuum distillation of the crude product was performed at 1 mm Hg. 4.869 grams of product were collected at 95-120°C for a yield of 30%. The perfluorinated ether was a clear, slightly viscous liquid with a boiling point of 271°C. IR (thin film, KBr): 1348, 1238(vs), 1207, 1144(s), 1112, 1006, 702, 535(w) cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 1531(P-F)$^+$, 1344($C_{25}F_{49}O_7$+H)$^+$, 1315(P-C_4F_9O)$^+$, 1127($C_{21}F_{41}O_6$)$^+$, 783($C_{14}F_{29}O_4$)$^+$, 767(base,$C_{14}F_{29}O_3$)$^+$, 667($C_{12}F_{25}O_3$)$^+$, 579($C_{11}F_{21}O_3$)$^+$, 551($C_{10}F_{21}O_2$)$^+$, 413($C_8F_{15}O_2$)$^+$,

Flow rates (cc/min) He	F_2	Temperature (°C)	Solvent*	Time (hrs)
45	5	-80	A	16
35	5	-60	A	24
28	5	-40	A	24
20	5	-15	A/B	24
20	5	0	A/B	72
0	2	amb.	none	8
0	2	+50	none	64

Table 2-12: Fluorination conditions for compound 12.

* A=$CFCl_3$; B=$Cl_2FCCClF_2$; none=second phase of fluorination (tube reactor)

363$(C_7F_{13}O_2)^+$, 235, 219. ^{19}F N.M.R. analysis: $\delta(CFCl_3)$ -65.3, -81.8, -84.0, -129.7 ppm. Elemental analysis: calculated C 21.69%, F 71.08%; found C 21.38%, F 70.81%.

Perfluoro-7,7,11,11-tetrakis(butyloxymethyl)-5,9,13-trioxaheptadecane, (13). 4.527 grams of hydrocarbon were dissolved in a slurry of 24.37 grams of NaF and 350 ml Freon 11 in a solution reactor. The solution was cooled to -80°C under a helium purge and fluorinated as described above using the conditions listed in table 2-13. Vacuum distillation of the crude product was performed at 1 mm Hg. 2.802 grams of product were collected at 130-140°C for a yield of 20%. The perfluorinated ether was a clear, viscous liquid with a boiling point of 308°C. IR (thin film, KBr): 1313, 1241(vs), 1145(vs), 987, 893, 702, 535(w) cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 1831$(P-F)^+$, 1681$(P-C_3F_7)^+$, 1593$(C_{30}F_{59}O_7)^+$, 1377$(C_{26}F_{51}O_6)^+$, 1139$(C_{22}F_{41}O_6)^+$, 933$(C_{17}F_{35}O_4)^+$, 917(base,$C_{17}F_{35}O_3)^+$, 695$(C_{13}F_{25}O_4)^+$, 679$(C_{13}F_{25}O_3)^+$, 441, 397, 285, 235, 219, 169. ^{19}F N.M.R. analysis: $\delta(CFCl_3)$ -65.8, -81.8, -83.2, -126.2, -126.8 ppm. Elemental analysis: calculated C 22.07%, F 71.88%; found

Flow rates (cc/min) He	F_2	Temperature (°C)	Solvent*	Time (hrs)
45	5	-80	A	12
35	5	-60	A	24
28	5	-40	A	24
20	5	-15	A/B	24
20	5	-5	A/B	72
0	5	amb.	none	16
0	5	+50	none	48

Table 2-13: Fluorination conditions for compound 13.

* A=$CFCl_3$; B=$Cl_2FCCClF_2$; none=second phase of fluorination (tube reactor)

C 21.66%, F 71.60%.

Perfluoro-7,7,11,11-tetrakis(2-methoxyethoxymethyl)-2,5,9,13,16-pentaoxaheptadecane, (14). 5.042 grams of hydrocarbon were dissolved in a slurry of 25.45 grams of NaF and 350 ml Freon 11 in a solution reactor. The solution was cooled to -60°C under a helium purge and fluorinated as described above using the conditions listed in table 2-14. Fractional distillation of the crude product was performed at 1 mm Hg. 3.011 grams of product were collected at 112-120°C for a yield of 22%. A small amount of polymerized byproduct was collected at 150-190°C. The perfluorinated ether was a clear, colorless liquid with a boiling point of 277°C. IR (thin film, KBr): 1400, 1248(vs), 1192(s), 1151(vs), 1113(vs), 984, 901, 681 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 1627$(P-F)^+$, 1561$(P-CF_3O)^+$, 1511$(P-C_2F_5O)^+$, 1445$(P-C_3F_7O_2)^+$, 1395$(P-C_4F_9O_2)^+$, 1241$(C_{22}F_{43}O_{10})^+$, 831$(C_{14}F_{29}O_7)^+$, 815(base,$C_{14}F_{29}O_6)^+$, 749$(C_{13}F_{27}O_5)^+$, 699, 611$(C_{11}F_{21}O_5)^+$, 545$(C_{10}F_{19}O_4)^+$, 429$(C_8F_{15}O_3)^+$, 363$(C_7F_{13}O_2)^+$, 211, 185. ^{19}F N.M.R. analysis: $\delta(CFCl_3)$ -56.2, -65.3, -66.3, -88.7, -91.0 ppm. Elemental

Flow rates (cc/min)		Temperature (°C)	Solvent*	Time (hrs)
He	F_2			
45	5	-60	A	20
45	5	-40	A	24
28	5	-15	A/B	24
28	5	0	A/B	48
20	5	0	A/B	48
0	5	amb.	none	24
0	5	+50	none	24

Table 2-14: Fluorination conditions for compound 14.

* A=$CFCl_3$; B=$Cl_2FCCClF_2$; none=second phase of fluorination (tube reactor)

analysis: calculated C 20.43%, F 66.94%; found C 20.29%, F 67.02%.

Perfluoro-4,4,8,8,12,12-hexakis(methoxymethyl)-2,6,10,14-tetraoxapentadecane, (15). 6.019 grams of hydrocarbon were dissolved in a slurry of 27.74 grams of NaF and 350 ml Freon 11 in a solution reactor. The solution was cooled to -80°C under a helium purge and fluorinated as described above using the conditions listed in table 2-15. Vacuum distillation of the crude product was performed at 1 mm Hg. 4.251 grams of product were collected at 92-97°C for a yield of 25%. The perfluorinated ether was a clear, viscous liquid with a boiling point of 254°C. IR (thin film, KBr): 1311(s), 1230(vs), 1185(s), 1112(vs), 1080, 995 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 1329$(P-F)^+$, 1242$(C_{22}F_{43}O_{10}+H)^+$, 947$(C_{16}F_{33}O_8)^+$, 931$(C_{16}F_{33}O_7)^+$, 881, 843$(C_{15}F_{29}O_7)^+$, 493, 467(base,$C_8F_{17}O_3)^+$, 379$(C_7F_{13}O_3)^+$, 313, 247, 135, 113. ^{19}F N.M.R. analysis: $\delta(CFCl_3)$ -55.3, -65.0, -68.2 ppm. Elemental analysis: calculated C 20.49%, F 67.64%; found C 20.37%, F 67.68%.

Flow rates (cc/min) He	F_2	Temperature (°C)	Solvent*	Time (hrs)
45	5	-80	A	15
35	5	-60	A	24
28	5	-40	A	24
20	5	-15	A/B	24
20	5	0	A/B	72
0	5	amb.	none	16
0	5	+50	none	8
0	5	+75	none	21

Table 2-15: Fluorination conditions for compound 15.

* A=$CFCl_3$; B=$Cl_2FCCClF_2$; none=second phase of fluorination (tube reactor)

Perfluoro-5,5,9,9,13,13-hexakis(ethoxymethyl)-3,7,11,15-tetraoxaheptadecane, (16). 4.812 grams of hydrocarbon were dissolved in a slurry of 22.53 grams of NaF and 350 ml Freon 11 in a solution reactor. The solution was cooled to -80°C under a helium purge and fluorinated as described above using the conditions listed in table 2-16. Vacuum distillation of the crude product was performed at 1 mm Hg. 2.621 grams of product were collected at 110-125°C for a yield of 19%. The perfluorinated ether was a clear, viscous liquid with a boiling point of 278°C. IR (thin film, KBr): 1405, 1233(s), 1117(vs), 983, 698, 528 cm^{-1}. Mass spectral analysis (chemical ionization, positive ion): m/e 1729$(P-F)^+$, 1591$(C_{29}F_{57}O_{10})^+$, 1425$(C_{26}F_{51}O_9)^+$, 1093$(C_{20}F_{39}O_7)^+$, 949$(C_{17}F_{35}O_5)^+$, 633$(C_{11}F_{23}O_4)^+$, 617(base,$C_{11}F_{23}O_3)^+$, 567$(C_{10}F_{23}O_3)^+$, 479$(C_9F_{17}O_3)^+$, 451$(C_8F_{17}O_2)^+$, 413$(C_8F_{15}O_2)^+$, 297, 219. ^{19}F N.M.R. analysis: $\delta(CFCl_3)$ -65.3, -66.3 -87.7, -89.0 ppm. Elemental analysis: calculated C 21.30%, F 69.55%; found C 21.05%, F 69.31%.

Flow rates (cc/min)		Temperature (°C)	Solvent*	Time (hrs)
He	F_2			
45	5	-80	A	14
35	5	-60	A	24
28	5	-40	A	24
20	5	-15	A/B	24
20	5	-5	A/B	72
0	3	amb.	none	16
0	3	+50	none	30

Table 2-16: Fluorination conditions for compound 16.

* A=$CFCl_3$; B=Cl_2FCClF_2; none=second phase of fluorination (tube reactor)

Compound	^{19}F NMR Assignment	Relative Intensity	
	ppm, $\delta(CFCl_3)$	Theor.	Obs.
$C(\underset{a}{CF_2}O\underset{b}{CF_2}\underset{c}{CF_3})_4$ (1)	(a)-66.3	2	27
	(b)-89.0	2	28
	(c)-87.7	3	44
$C(\underset{a}{CF_2}O\underset{b}{CF_2}\underset{c}{CF_2}\underset{d}{CF_3})_4$ (2)	(a)-65.5	2	27
	(b)-84.0	2	26
	(c)-129.5	2	25
	(d)-81.7	3	41
$C(\underset{a}{CF_2}O\underset{b}{CF_2}\underset{c}{CF_2}\underset{d}{CF_2}\underset{e}{CF_3})_4$ (3)	(a)-65.3	2	44
	(b)-82.9	2	46
	(c)-126.2	2	44
	(d)-126.7	2	44
	(e)-81.8	3	70
$C(\underset{a}{CF_2}O\underset{b}{CF_2}\underset{c}{CF_2}\underset{d}{CF_2}\underset{e}{CF_2}\underset{f}{CF_3})_4$ (4)	(a)-65.5	2	22
	(b)-83.0	2	30
	(c)-123.0	2	31
	(d)-125.3	2	28
	(e)-126.3	2	30
	(f)-81.4	3	52
$C(\underset{a}{CF_2}O\underset{b}{CF_2}\underset{c}{CF_2}\underset{d}{CF}[\underset{e}{CF_3}]_2)_4$ (5)	(a)-65.7	2	20
	(b)-82.7	2	23
	(c)-118.0	2	24
	(d)-186.1	1	12
	(e)-72.7	6	74
$C(\underset{a}{CF_2}O\underset{b}{CF_2}\underset{c}{CF_2}\underset{d}{CF_2}\underset{e}{CF_2}\underset{f}{CF_2}\underset{g}{CF_3})_4$ (6)	(a)-65.3	2	17
	(b)-83.0	2	20
	(c)-122.3	2	22.5
	(d)-122.8	2	22.5
	(e)-125.0	2	21
	(f)-126.3	2	23
	(g)-81.5	3	35

Table 2-17: ^{19}F N.M.R. assignments.

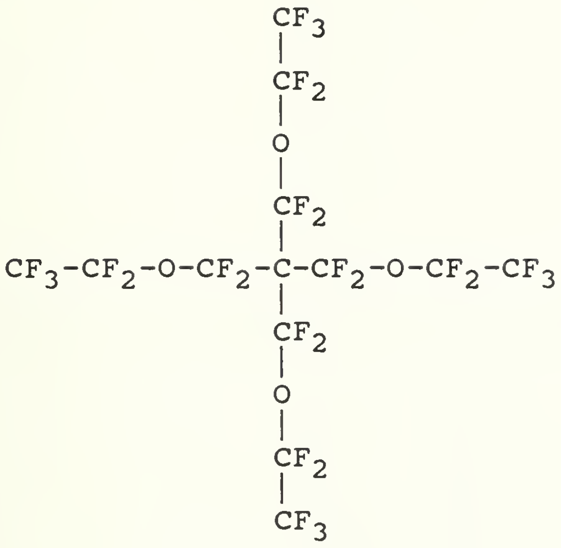
Compound	^{19}F NMR Assignment	Relative	Intensity
	ppm, $\delta(CFCl_3)$	Theor.	Obs.
$C(\underset{a}{CF_2}O\underset{b}{CF_2}\underset{c}{CF_2}\underset{d}{CF_2}\underset{e}{CF_2}\underset{f}{CF_2}\underset{g}{CF_2}\underset{h}{CF_3})_4$ (7)			
	(a) -65.7	2	9
	(b) -83.0	2	11
	(c) -122.3	2	11
	(d) -122.3	2	11
	(e) -122.3	2	11
	(f) -125.2	2	11
	(g) -126.3	2	12
	(h) -81.4	3	16
$C(\underset{a}{CF_2}O\underset{b}{CF_2}\underset{c}{CF_2}\underset{d}{CF_2}\underset{e}{CF_2}\underset{f}{CF_2}\underset{g}{CF_2}\underset{h}{CF_2}\underset{i}{CF_3})_4$ (8)			
	(a) -65.5	2	15
	(b) -83.2	2	15
	(c) -122.1	2	16
	(d) -122.1	2	16
	(e) -122.1	2	16
	(f) -122.8	2	16
	(g) -125.3	2	14
	(h) -126.3	2	18
	(i) -81.7	3	26
$C(\underset{a}{CF_2}O\underset{b}{CF_2}\underset{c}{CF_2}O\underset{d}{CF_3})_4$ (9)	(a) -66.3	2	26
	(b) -89.0	2	26
	(c) -91.2	2	26
	(d) -56.3	3	41
$([\underset{a}{CF_3}O\underset{b}{CF_2}]_3C\underset{c}{CF_2})_2O$ (10)			
	(a) -55.7	9	20
	(b) -68.8	6	13
	(c) -65.7	2	4
$([\underset{a}{CF_3}\underset{b}{CF_2}O\underset{c}{CF_2}]_3C\underset{d}{CF_2})_2O$ (11)			
	(a) -87.5	9	24
	(b) -88.9	6	17
	(c) -66.3	6	16
	(d) -65.3	2	5

Table 2-17: ^{19}F N.M.R. assignments, continued.

Compound	^{19}F NMR Assignment ppm, $\delta(CFCl_3)$	Relative Intensity Theor.	Obs.
$([\underset{a}{CF_3}\underset{b}{CF_2}\underset{c}{CF_2}O\underset{d}{CF_2}]_3C\underset{e}{CF_2})_2O$ (12)			
	(a) -81.8	9	34
	(b) -129.7	6	21
	(c) -84.0	6	21
	(d) -65.3	6	19
	(e) -65.3	2	6
$([\underset{a}{CF_3}\underset{b}{CF_2}\underset{c}{CF_2}\underset{d}{CF_2}O\underset{e}{CF_2}]_3C\underset{f}{CF_2})_2O$ (13)			
	(a) -81.8	9	37
	(b) -126.8	6	23.5
	(c) -126.2	6	23.5
	(d) -83.2	6	23
	(e) -65.8	6	25
	(f) -65.8	2	8
$([\underset{a}{CF_3}O\underset{b}{CF_2}\underset{c}{CF_2}O\underset{d}{CF_2}]_3C\underset{e}{CF_2})_2O$ (14)			
	(a) -56.2	9	37
	(b) -91.0	6	25
	(c) -88.7	6	25
	(d) -66.3	6	24
	(e) -65.3	2	6
$([\underset{a}{CF_3}O\underset{b}{CF_2}]_3C\underset{c}{CF_2}O\underset{c}{CF_2})_2C(\underset{b}{CF_2}O\underset{a}{CF_3})_2$ (15)			
	(a) -55.3	3	71
	(b) -68.2	2	44
	(c) -65.0	1	24
$([\underset{a}{CF_3}\underset{b}{CF_2}O\underset{c}{CF_2}]_3C\underset{d}{CF_2}O\underset{d}{CF_2})_2C(\underset{c}{CF_2}O\underset{b}{CF_2}\underset{a}{CF_3})_2$ (16)			
	(a) -87.7	3	36
	(b) -89.0	2	24
	(c) -66.3	2	24
	(d) -65.3	1	11

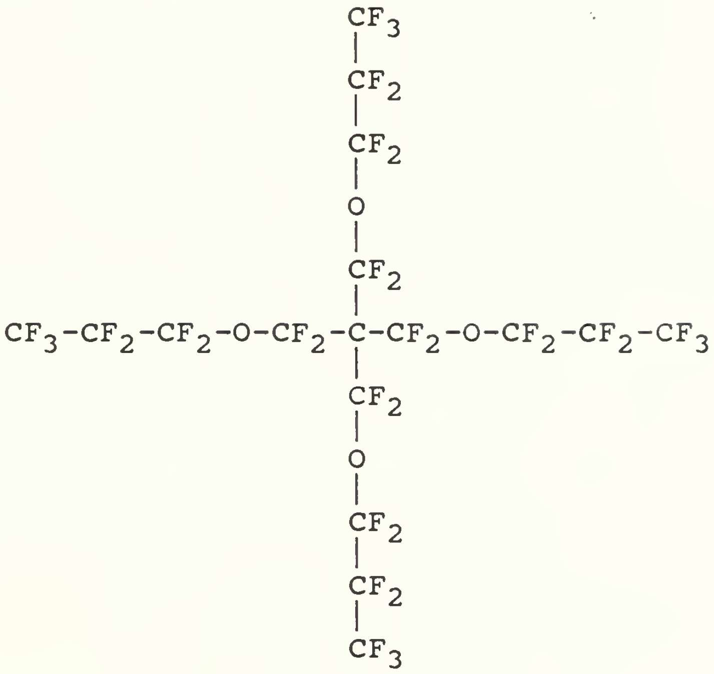
Table 2-17: ^{19}F N.M.R. assignments, continued.

Compound 1:



$$\begin{array}{c} CF_3 \\ | \\ CF_2 \\ | \\ O \\ | \\ CF_2 \\ | \\ CF_3-CF_2-O-CF_2-C-CF_2-O-CF_2-CF_3 \\ | \\ CF_2 \\ | \\ O \\ | \\ CF_2 \\ | \\ CF_3 \end{array}$$

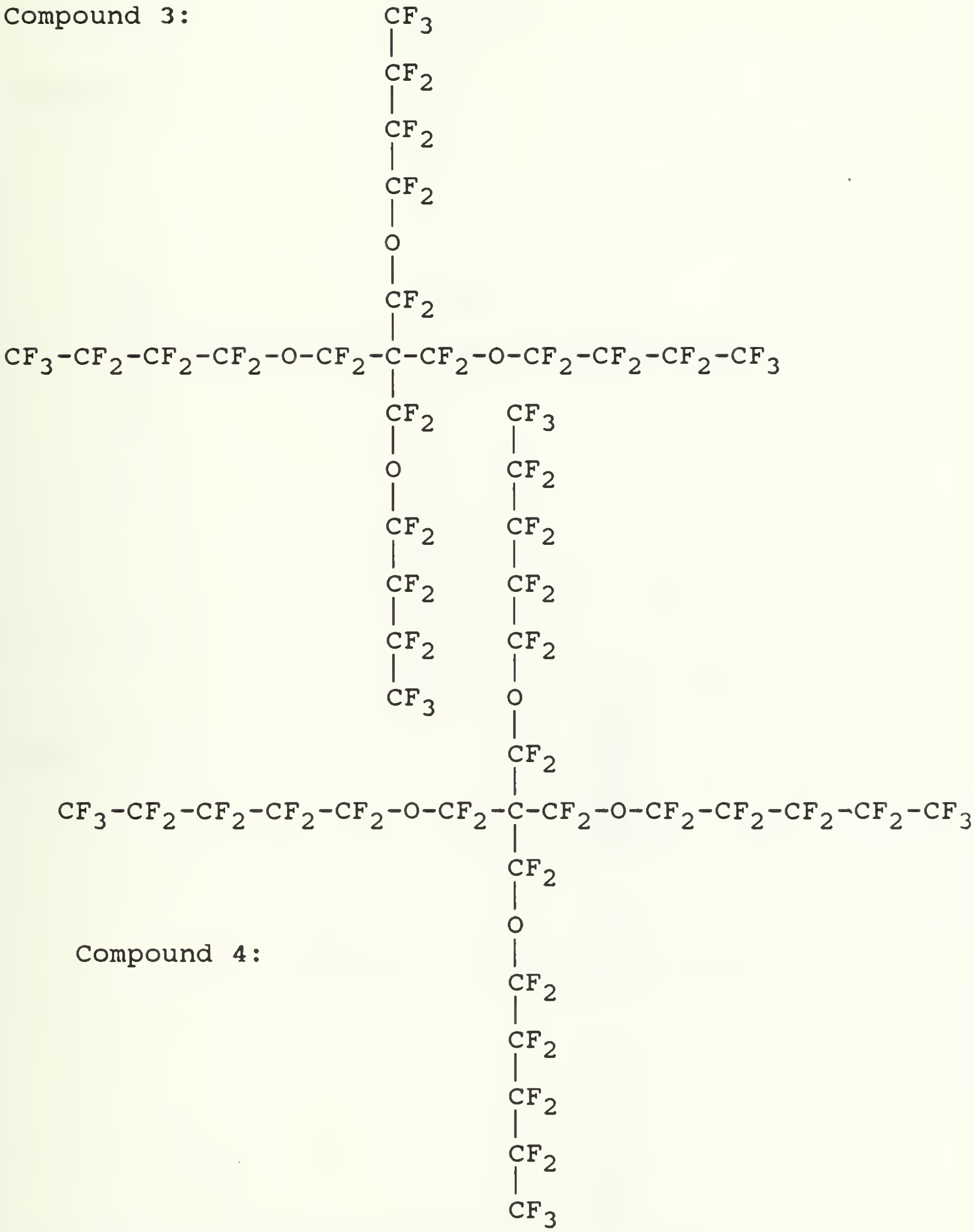
Compound 2:



$$\begin{array}{c} CF_3 \\ | \\ CF_2 \\ | \\ CF_2 \\ | \\ O \\ | \\ CF_2 \\ | \\ CF_3-CF_2-CF_2-O-CF_2-C-CF_2-O-CF_2-CF_2-CF_3 \\ | \\ CF_2 \\ | \\ O \\ | \\ CF_2 \\ | \\ CF_2 \\ | \\ CF_3 \end{array}$$

Figure 2-5: Branched perfluorinated ethers.

Compound 3:



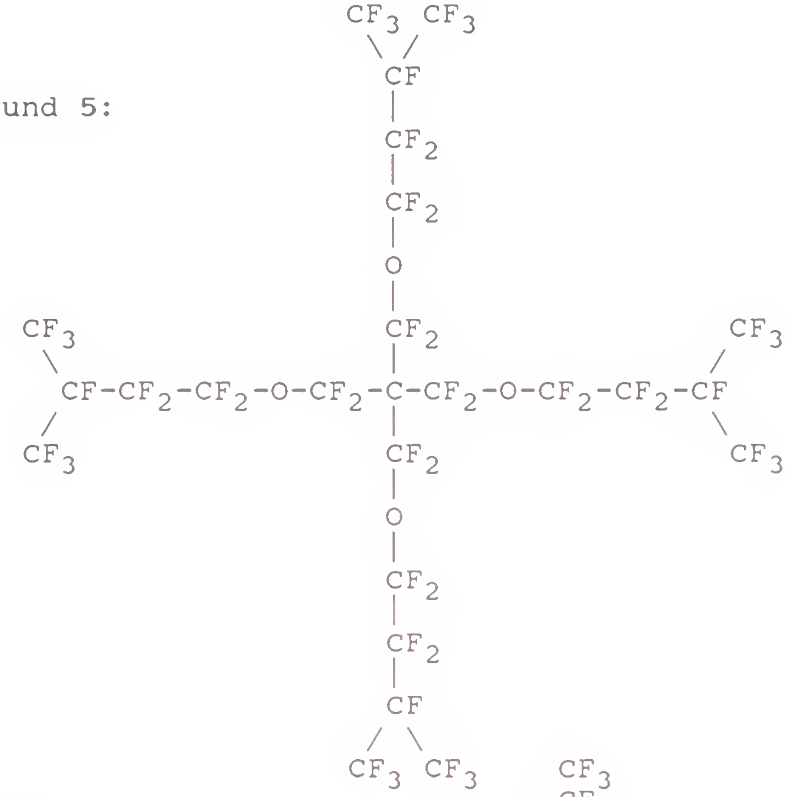
$$CF_3-CF_2-CF_2-CF_2-O-CF_2-\underset{\substack{|\\CF_2\\|\\O\\|\\CF_2\\|\\CF_2\\|\\CF_2\\|\\CF_3}}{\overset{\substack{CF_3\\|\\CF_2\\|\\CF_2\\|\\CF_2\\|\\O\\|\\CF_2\\|}}{C}}-CF_2-O-CF_2-CF_2-CF_2-CF_3$$

Compound 4:

$$CF_3-CF_2-CF_2-CF_2-CF_2-O-CF_2-\underset{\substack{|\\CF_2\\|\\O\\|\\CF_2\\|\\CF_2\\|\\CF_2\\|\\CF_2\\|\\CF_3}}{\overset{\substack{CF_3\\|\\CF_2\\|\\CF_2\\|\\CF_2\\|\\CF_2\\|\\O\\|\\CF_2\\|}}{C}}-CF_2-O-CF_2-CF_2-CF_2-CF_2-CF_3$$

Figure 2-5: Branched perfluorinated ethers, continued.

Compound 5:



Compound 6:

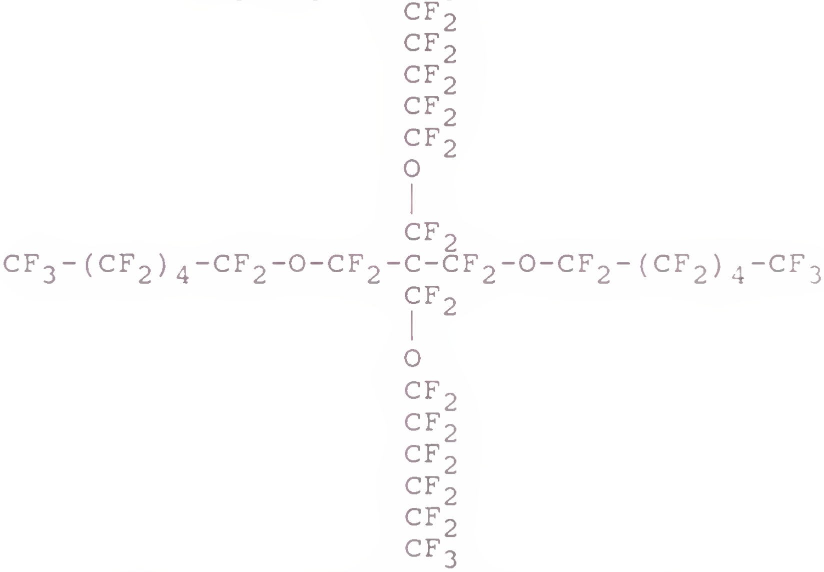
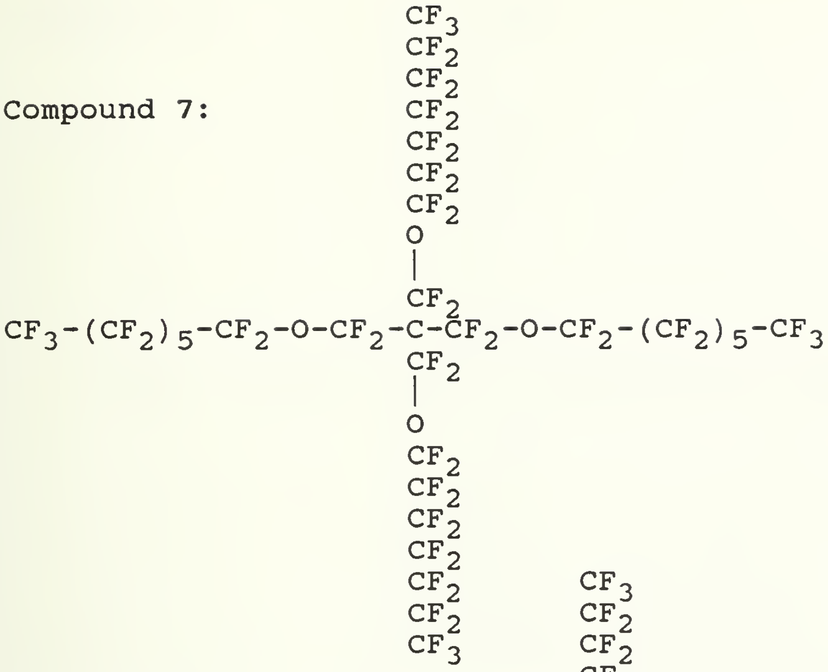


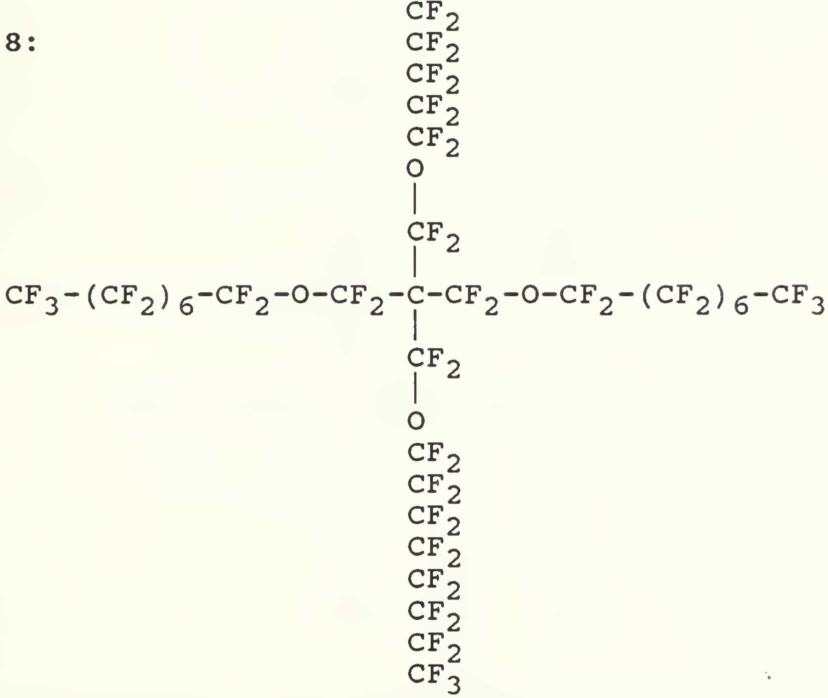
Figure 2-5: Branched perfluorinated ethers, continued.

Compound 7:



$$\begin{array}{rcl} & CF_3 & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & O & \\ & | & \\ & CF_2 & \\ CF_3-(CF_2)_5-CF_2-O-CF_2- & C & -CF_2-O-CF_2-(CF_2)_5-CF_3 \\ & CF_2 & \\ & | & \\ & O & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & CF_3 & \end{array}$$

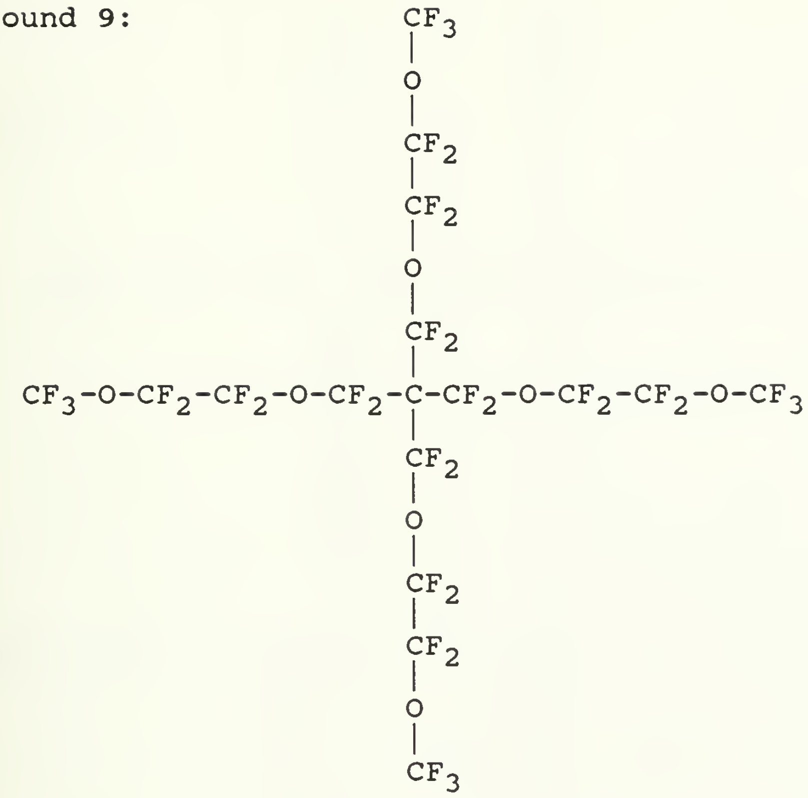
Compound 8:



$$\begin{array}{rcl} & CF_3 & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & O & \\ & | & \\ & CF_2 & \\ & | & \\ CF_3-(CF_2)_6-CF_2-O-CF_2- & C & -CF_2-O-CF_2-(CF_2)_6-CF_3 \\ & | & \\ & CF_2 & \\ & | & \\ & O & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & CF_2 & \\ & CF_3 & \end{array}$$

Figure 2-5: Branched perfluorinated ethers, continued.

Compound 9:



Compound 10:

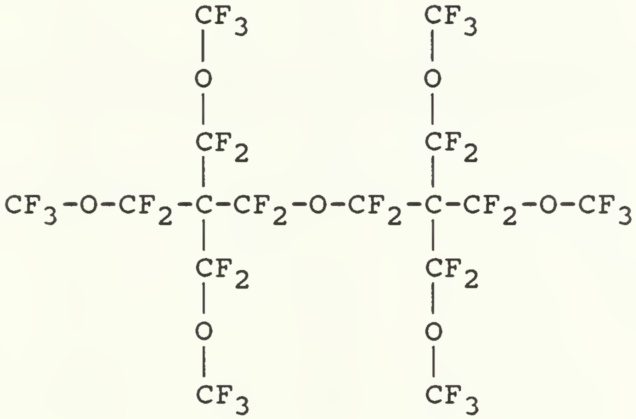
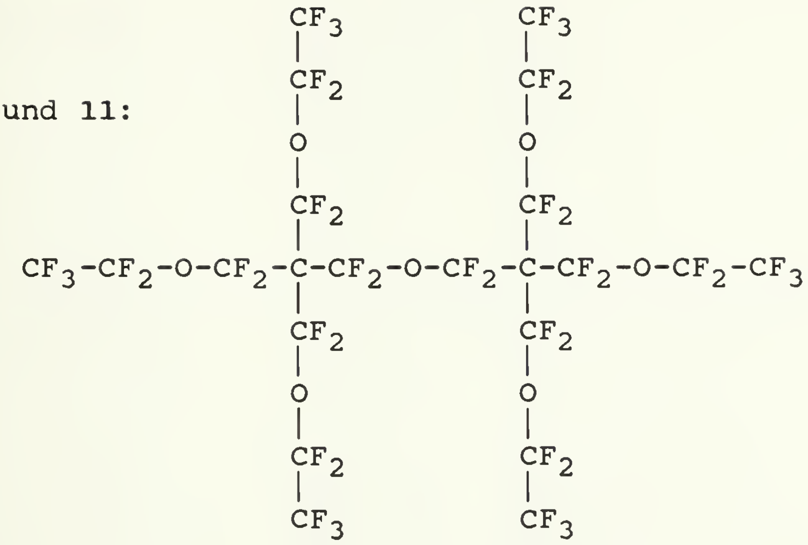


Figure 2-5: Branched perfluorinated ethers, continued.

Compound 11:



Compound 12:

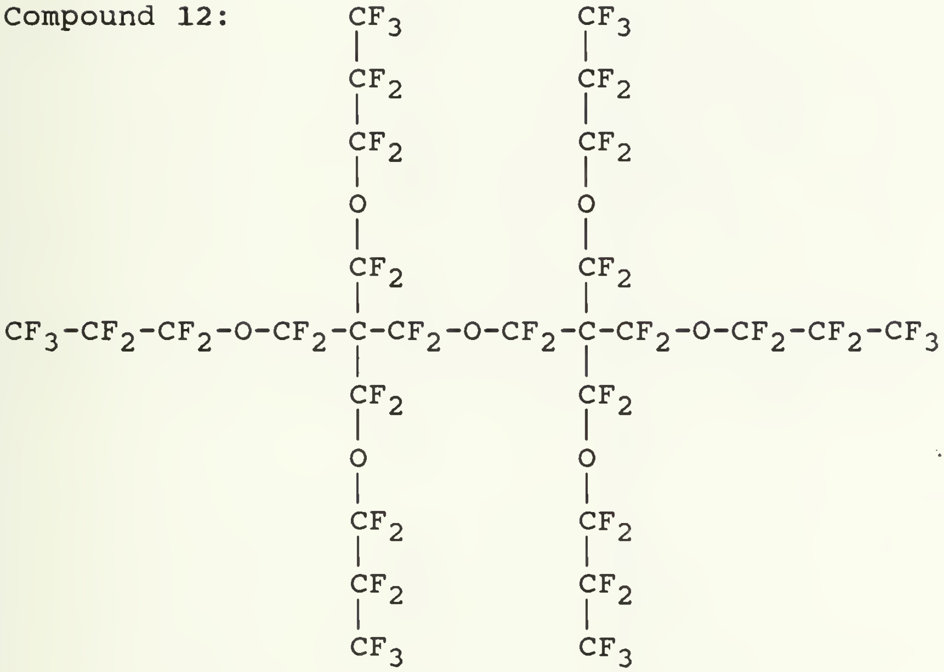
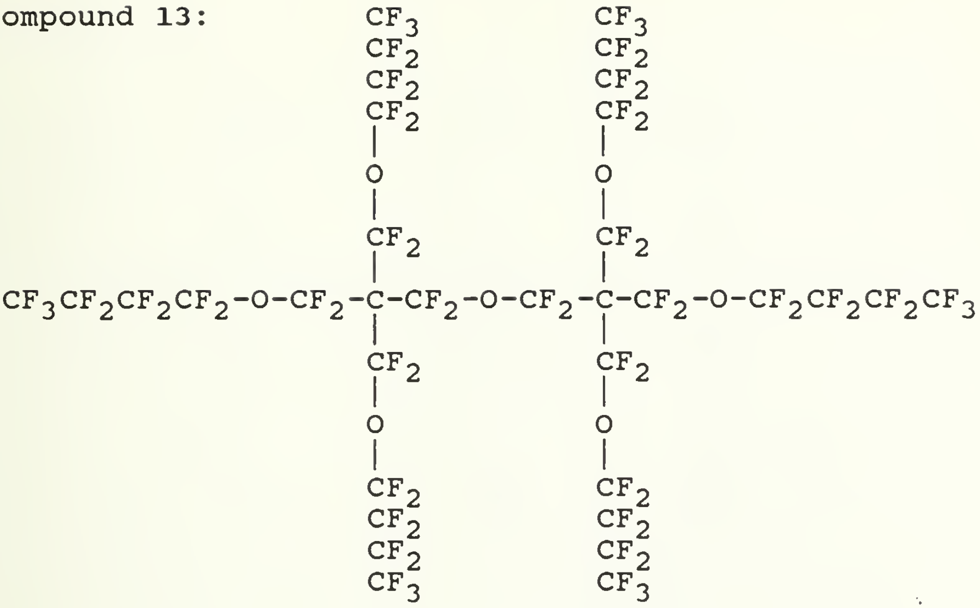


Figure 2-5: Branched perfluorinated ethers, continued.

Compound 13:



Compound 14:

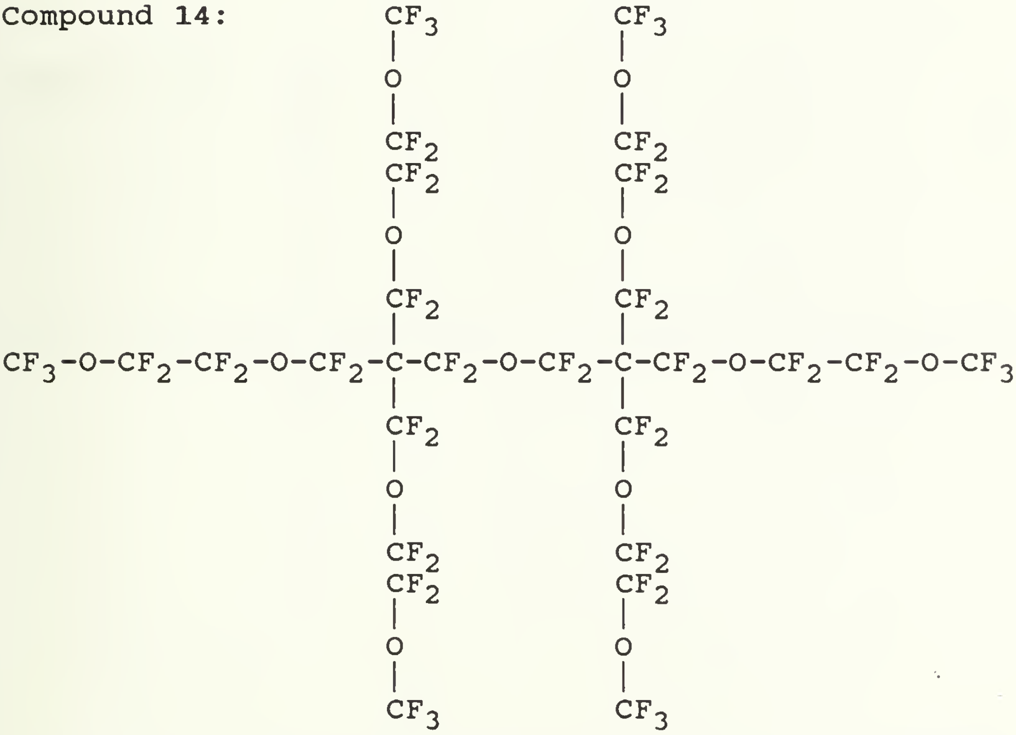
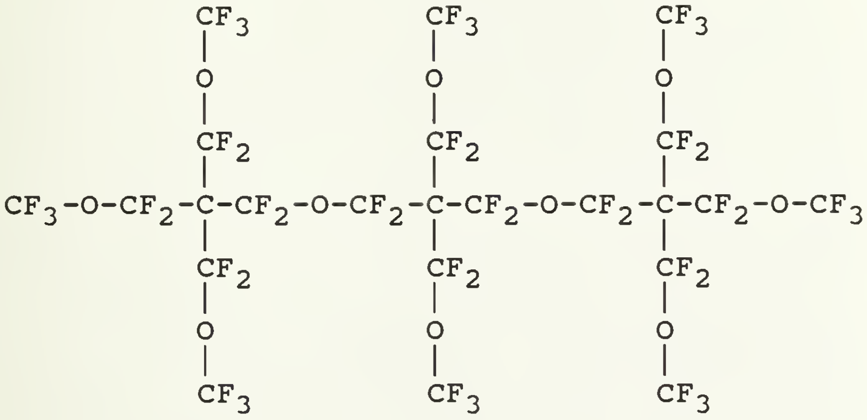


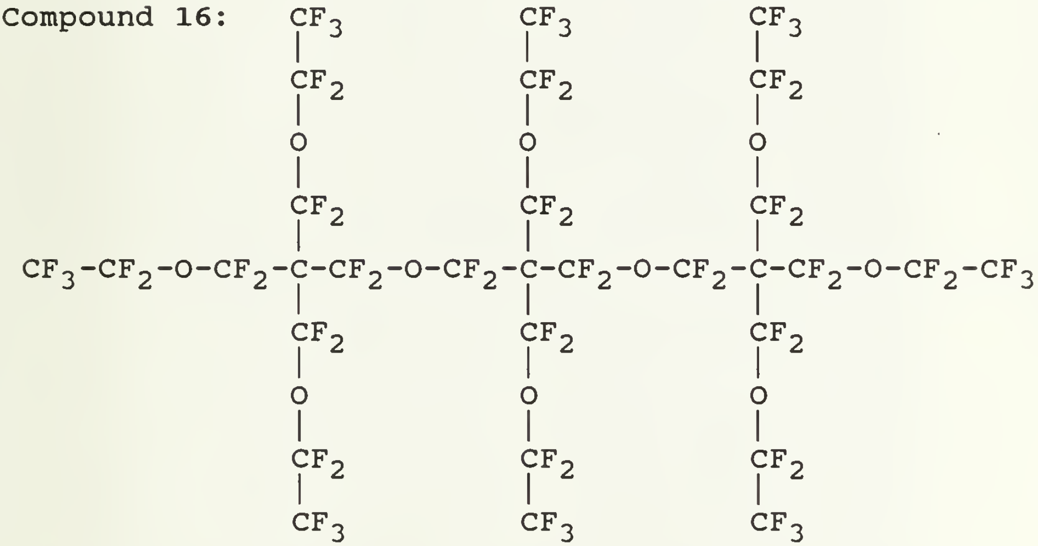
Figure 2-5: Branched perfluorinated ethers, continued.

Compound 15:



$CF_3-O-CF_2-C(CF_2-O-CF_3)_2-CF_2-O-CF_2-C(CF_2-O-CF_3)_2-CF_2-O-CF_2-C(CF_2-O-CF_3)_2-CF_2-O-CF_3$

Compound 16:



$CF_3-CF_2-O-CF_2-C(CF_2-O-CF_2-CF_3)_2-CF_2-O-CF_2-C(CF_2-O-CF_2-CF_3)_2-CF_2-O-CF_2-C(CF_2-O-CF_2-CF_3)_2-CF_2-O-CF_2-CF_3$

Figure 2-5: Branched perfluorinated ethers, continued.

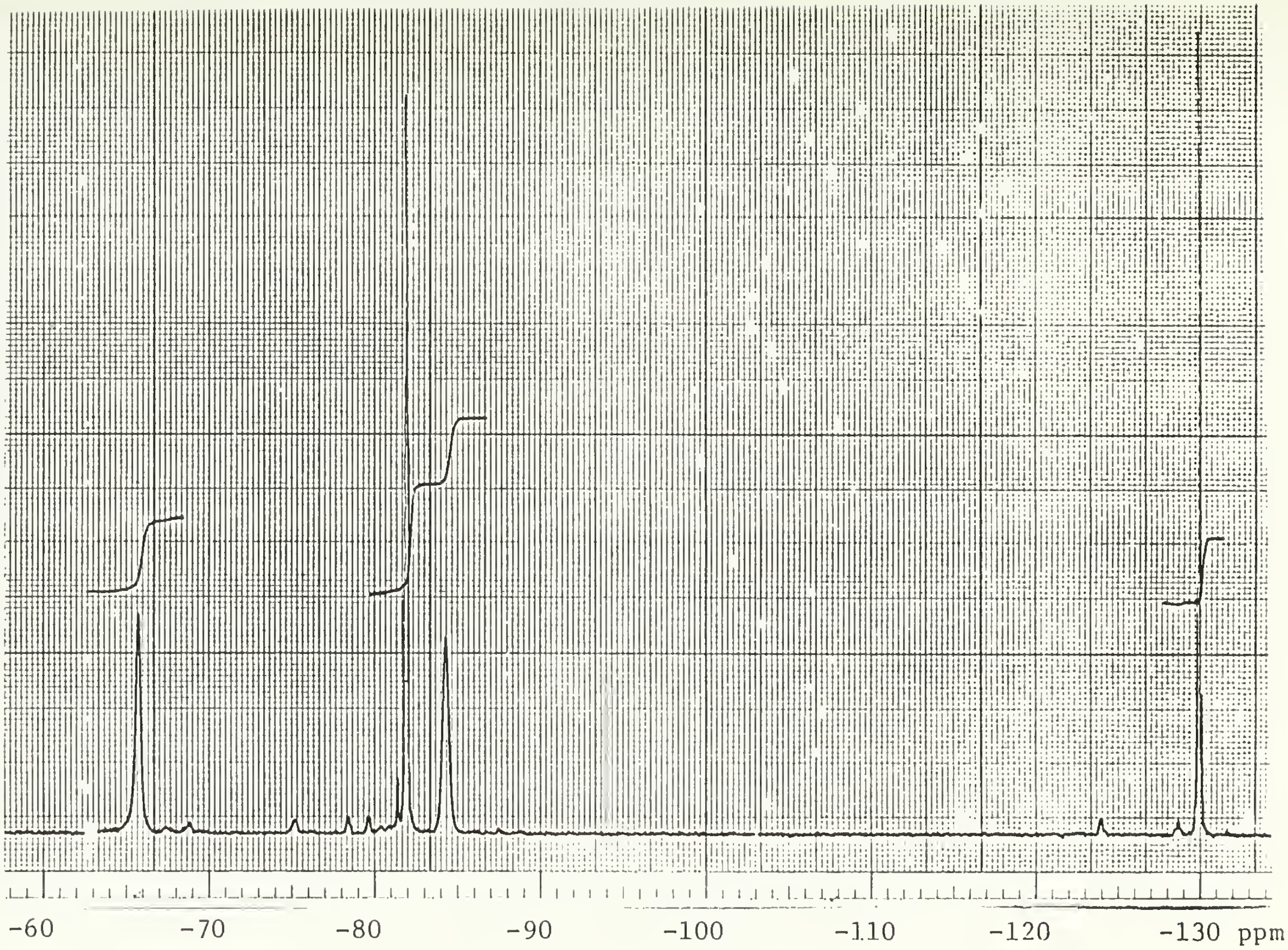


Figure 2-6: ^{19}F N.M.R. spectrum of compound 2.

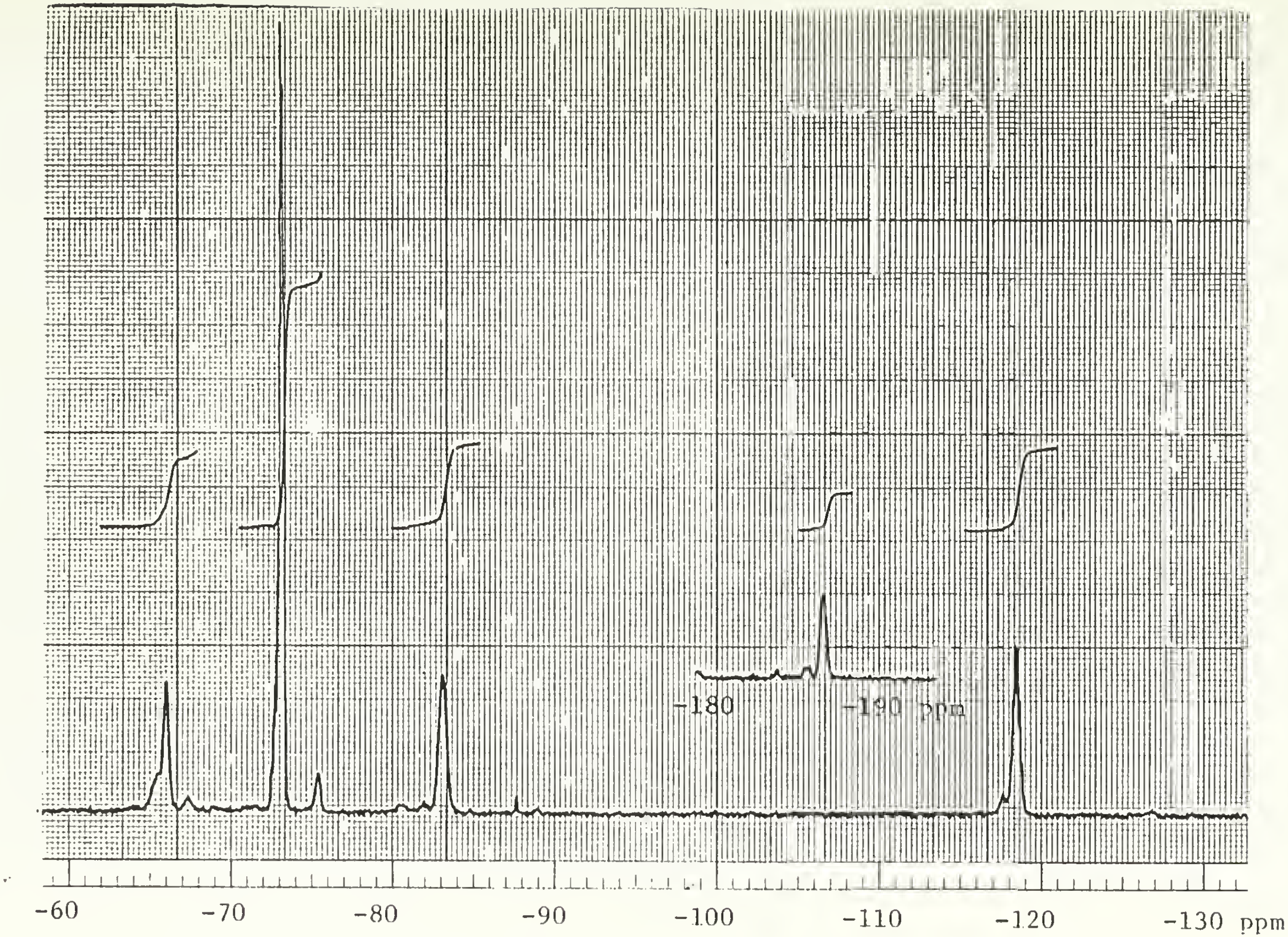


Figure 2-7: ^{19}F N.M.R. spectrum of compound 5.

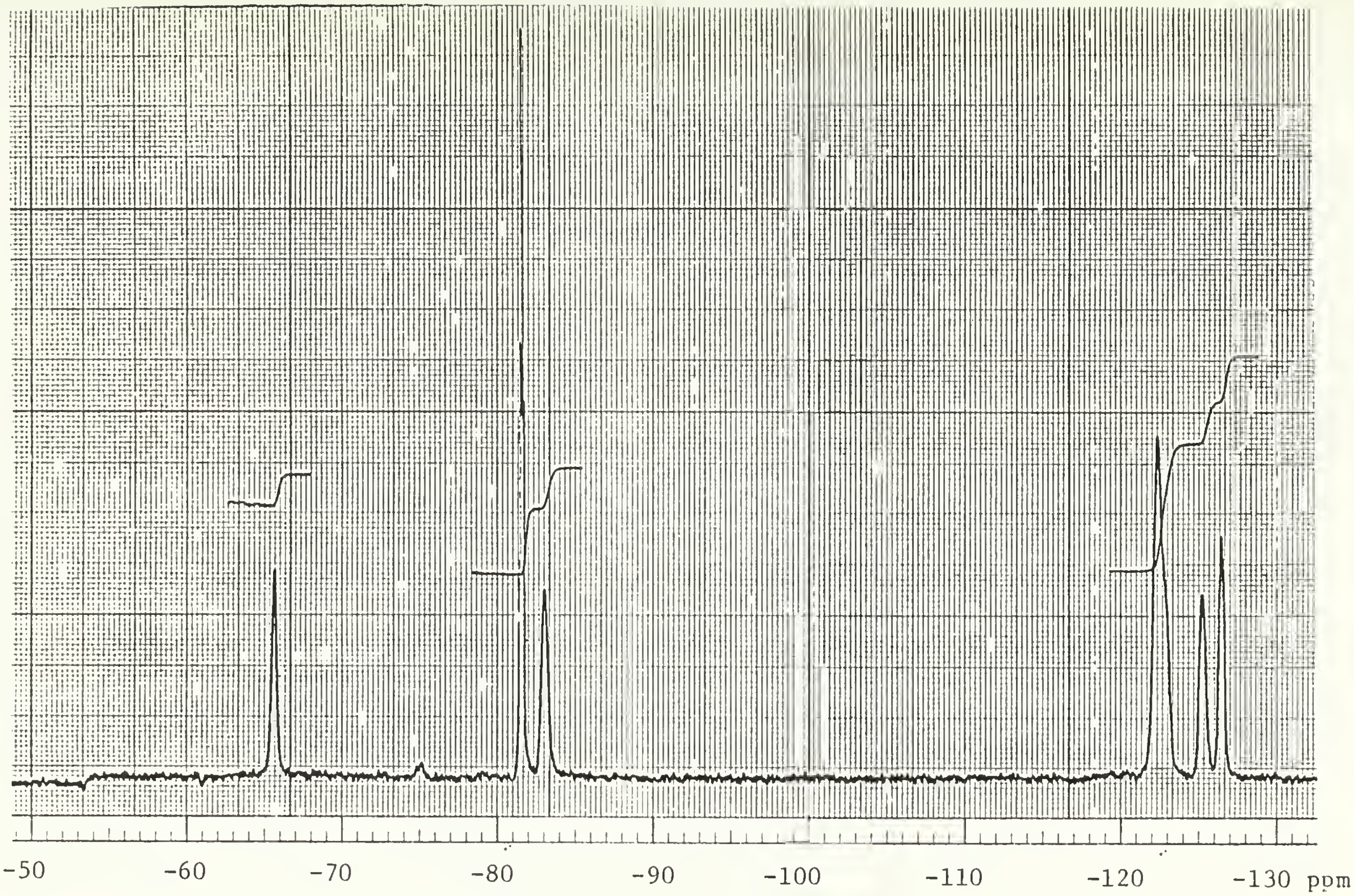


Figure 2-8: ^{19}F N.M.R. spectrum of compound 7.

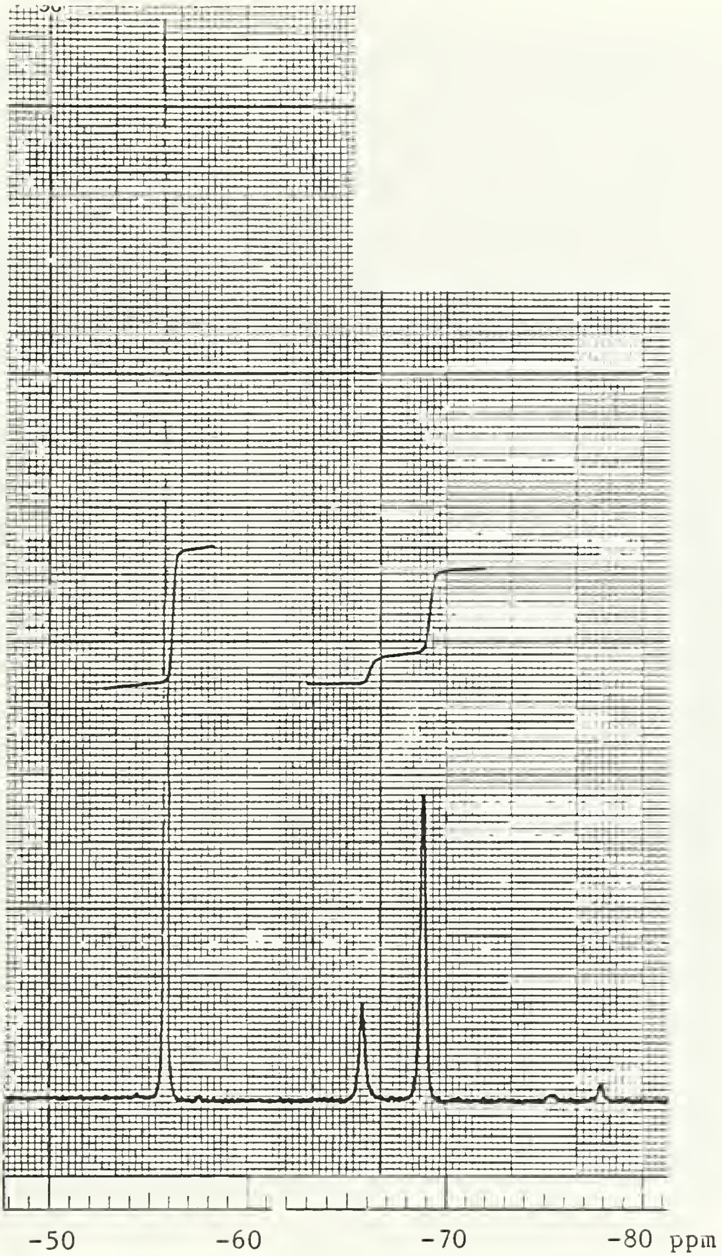


Figure 2-9: ^{19}F N.M.R. spectrum of compound 10.

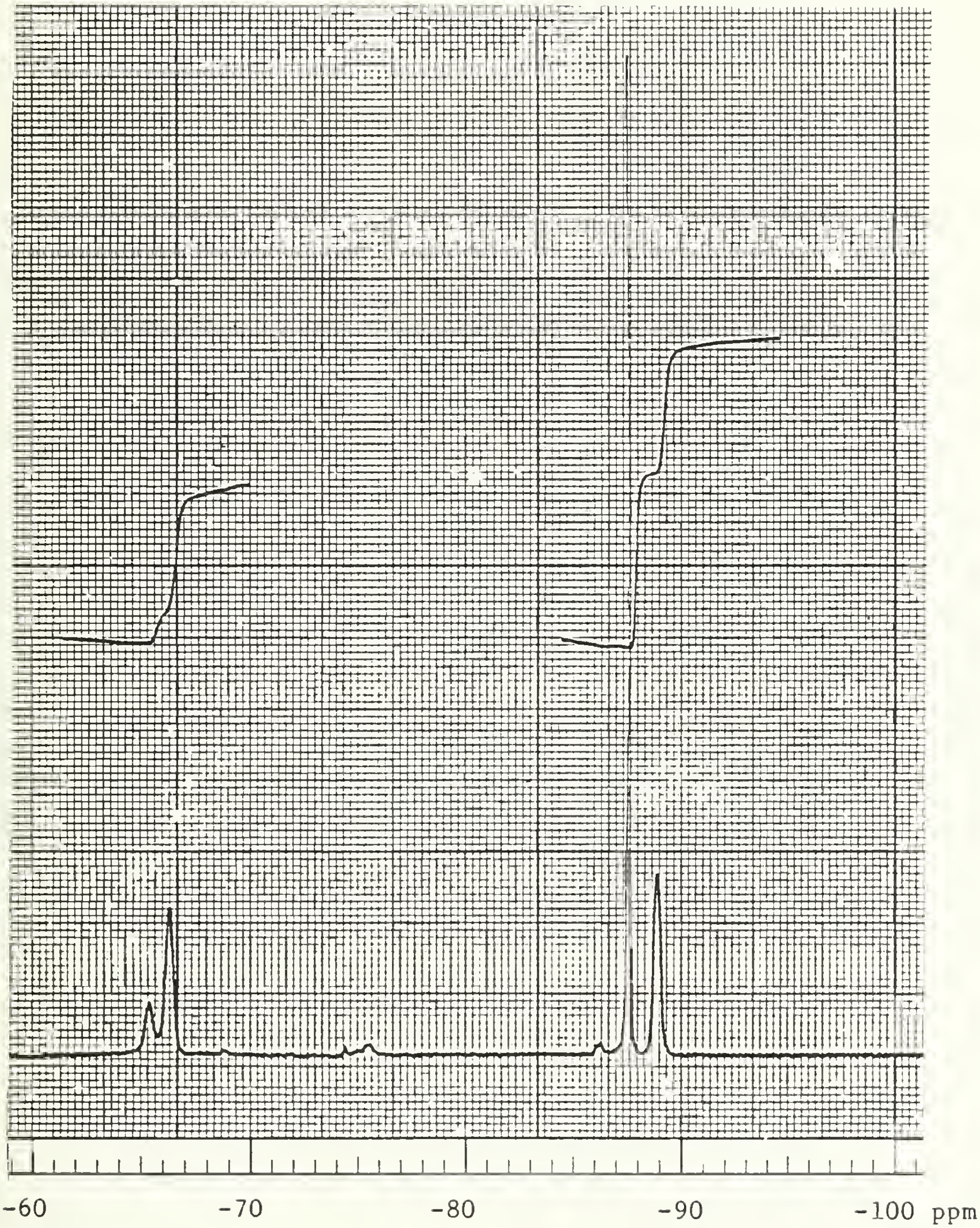


Figure 2-10: ^{19}F N.M.R. spectrum of compound 11.

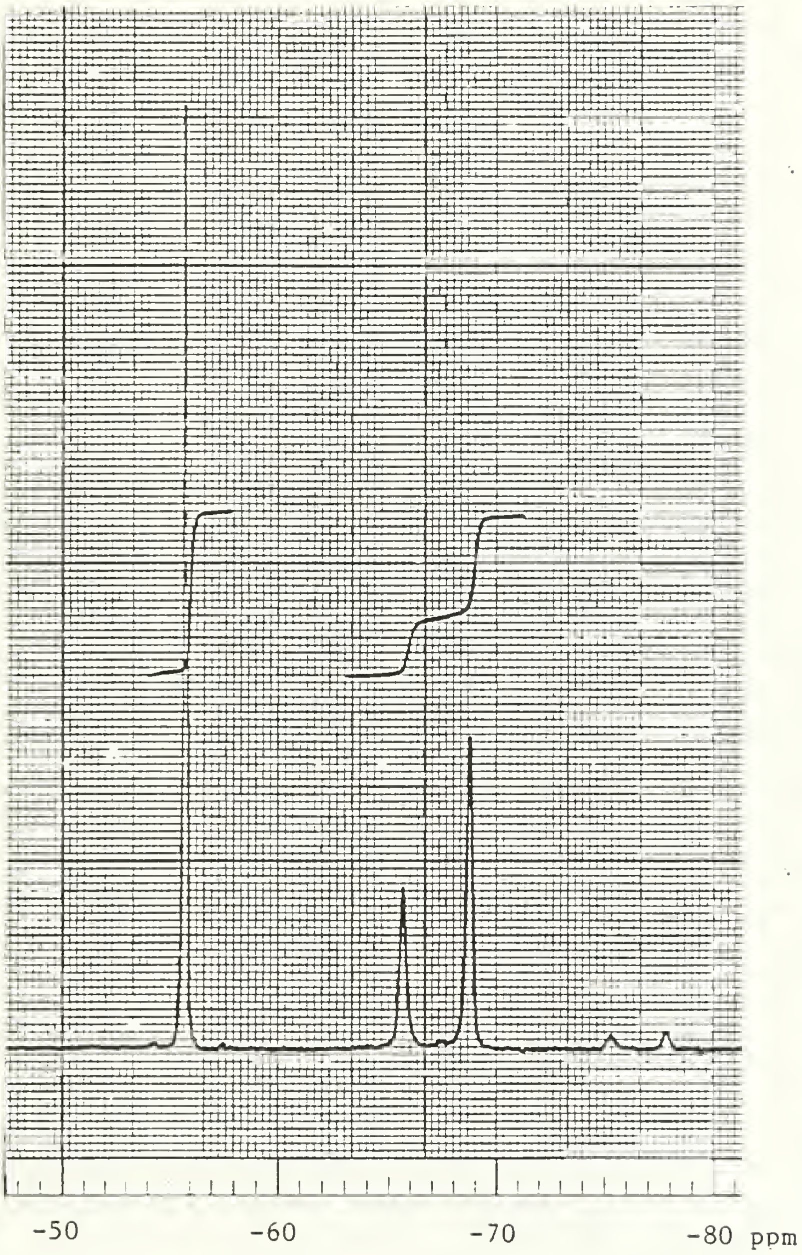


Figure 2-11: ^{19}F N.M.R. spectrum of compound 15.

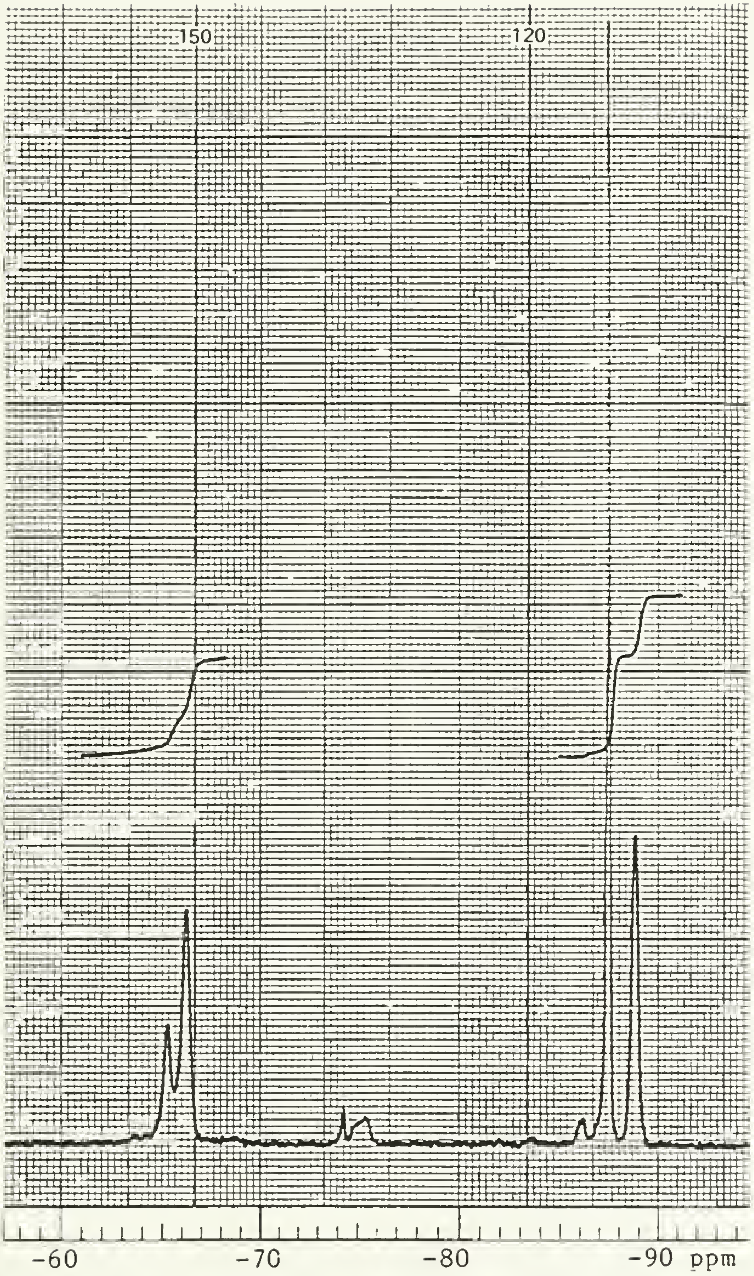


Figure 2-12: ^{19}F N.M.R. spectrum of compound 16.

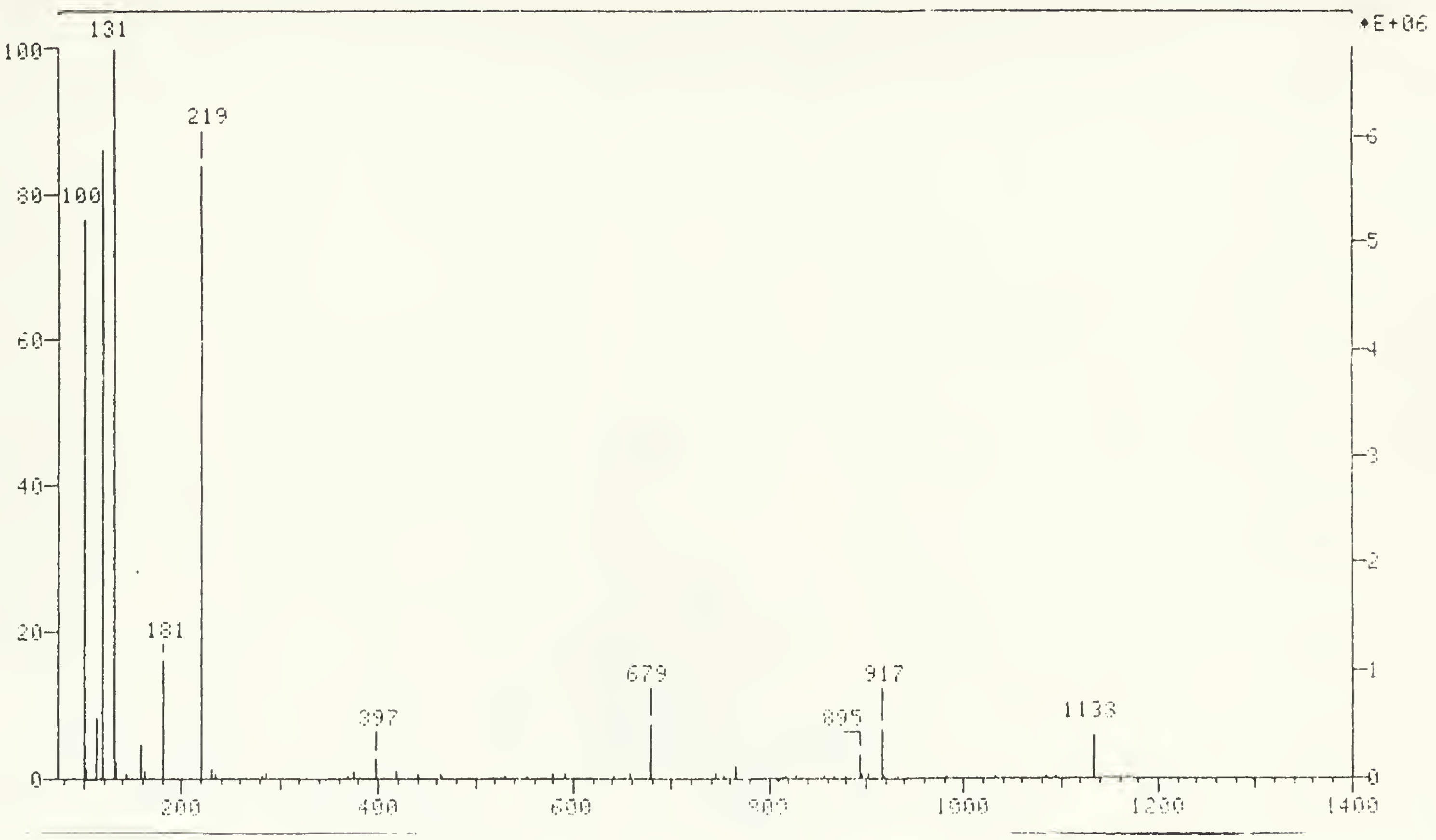


Figure 2-13: Mass spectrum of compound 3.

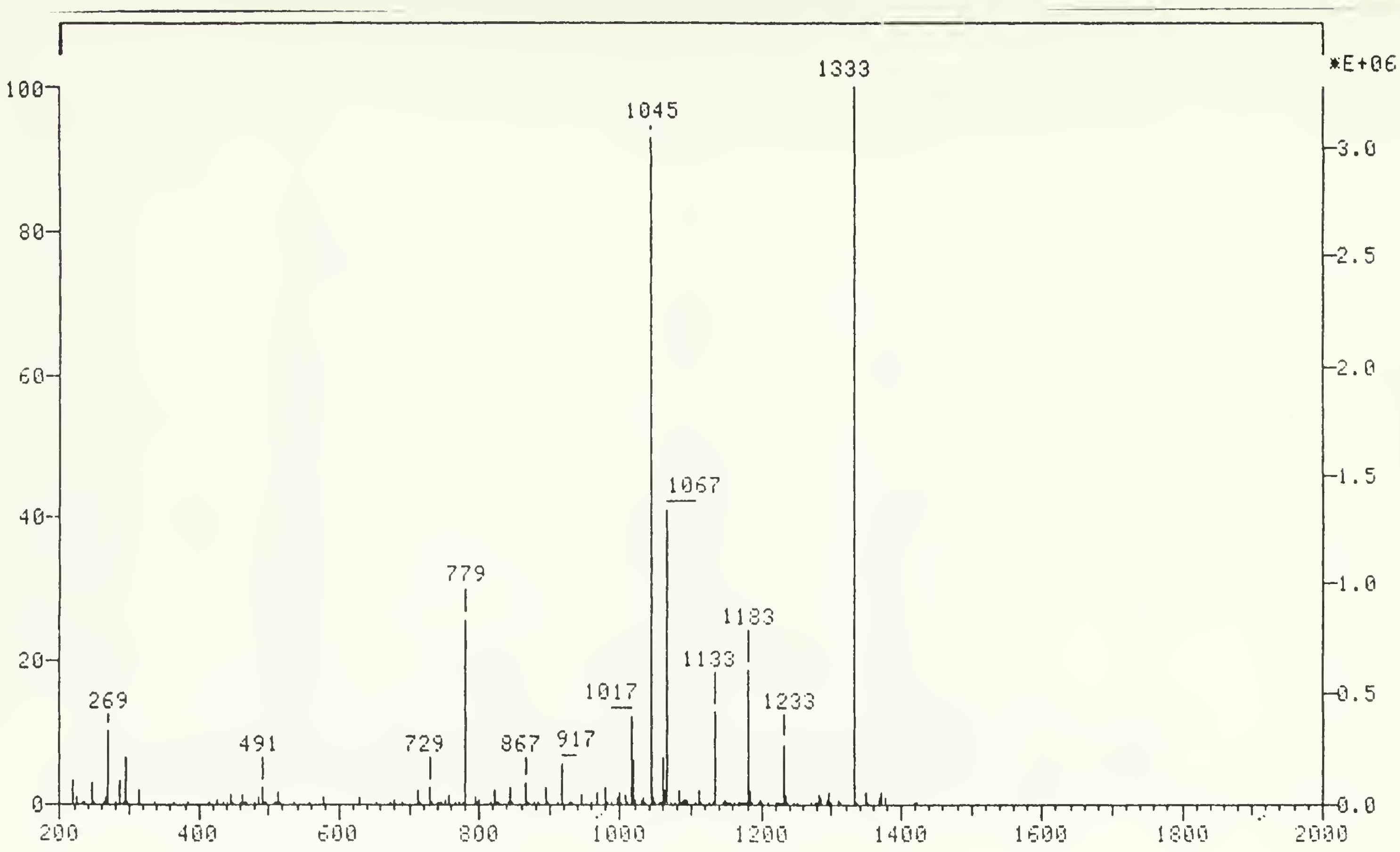


Figure 2-14: Mass spectrum of compound 4.

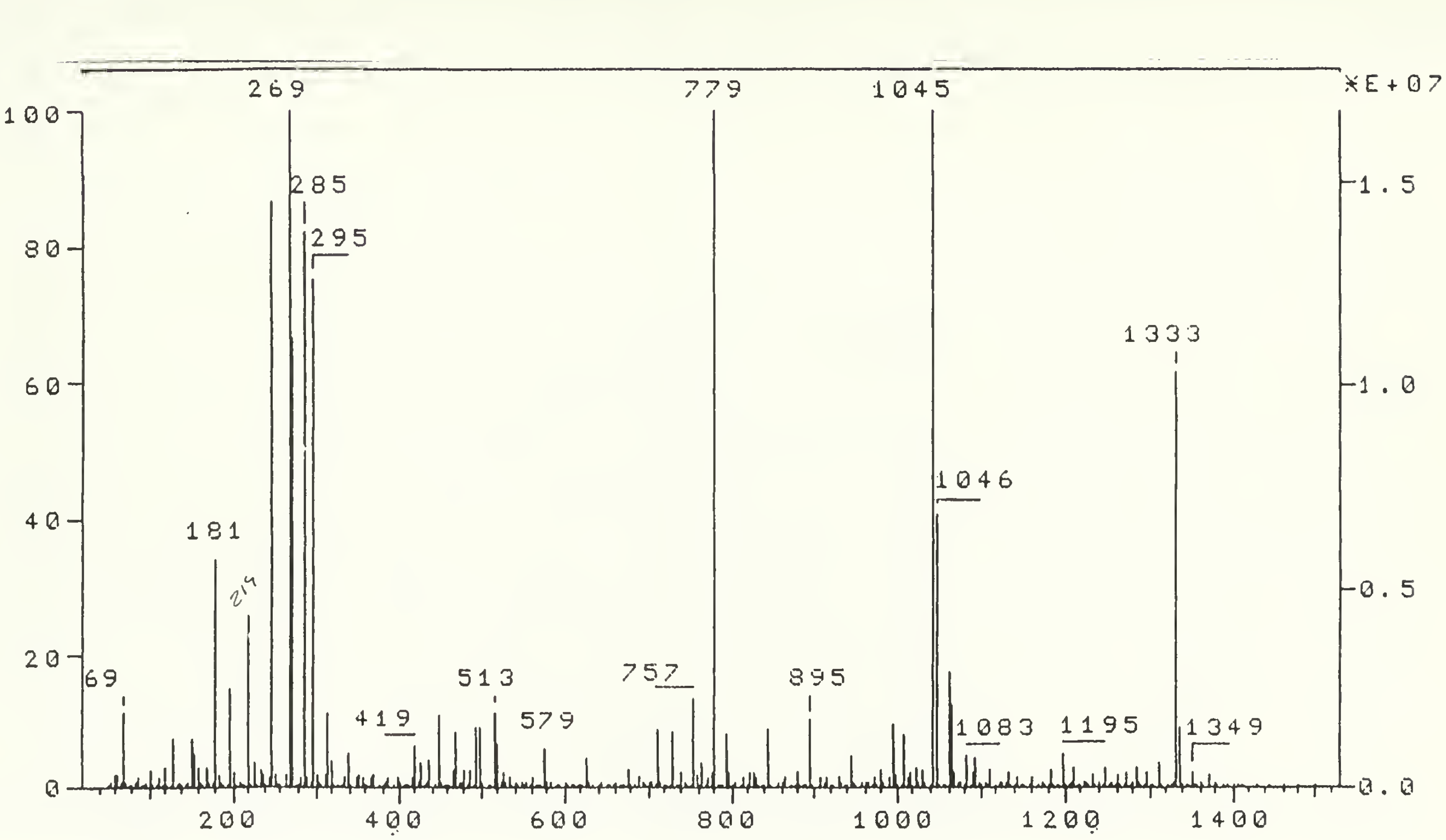


Figure 2-15: Mass spectrum of compound 5.

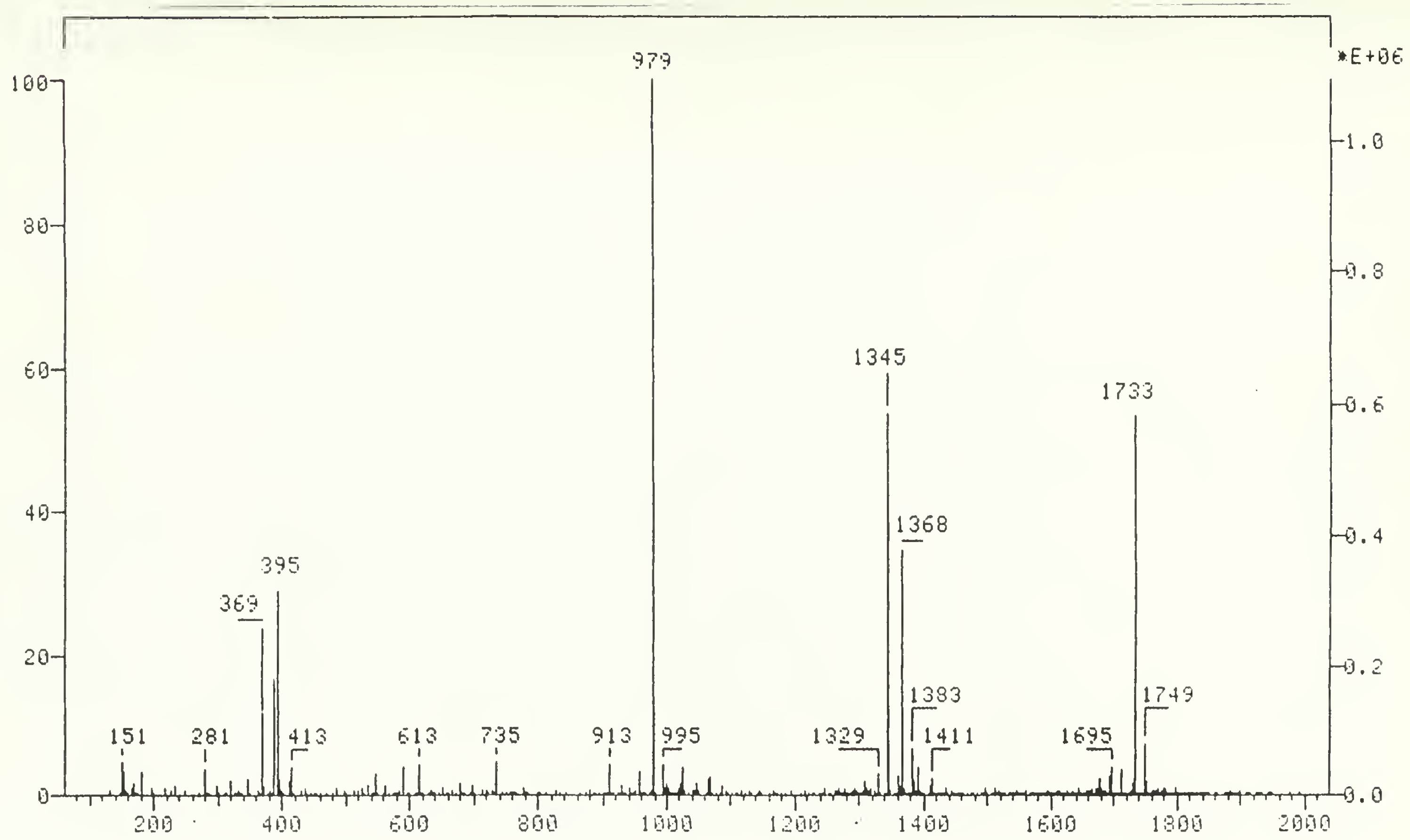


Figure 2-16: Mass spectrum of compound 7.

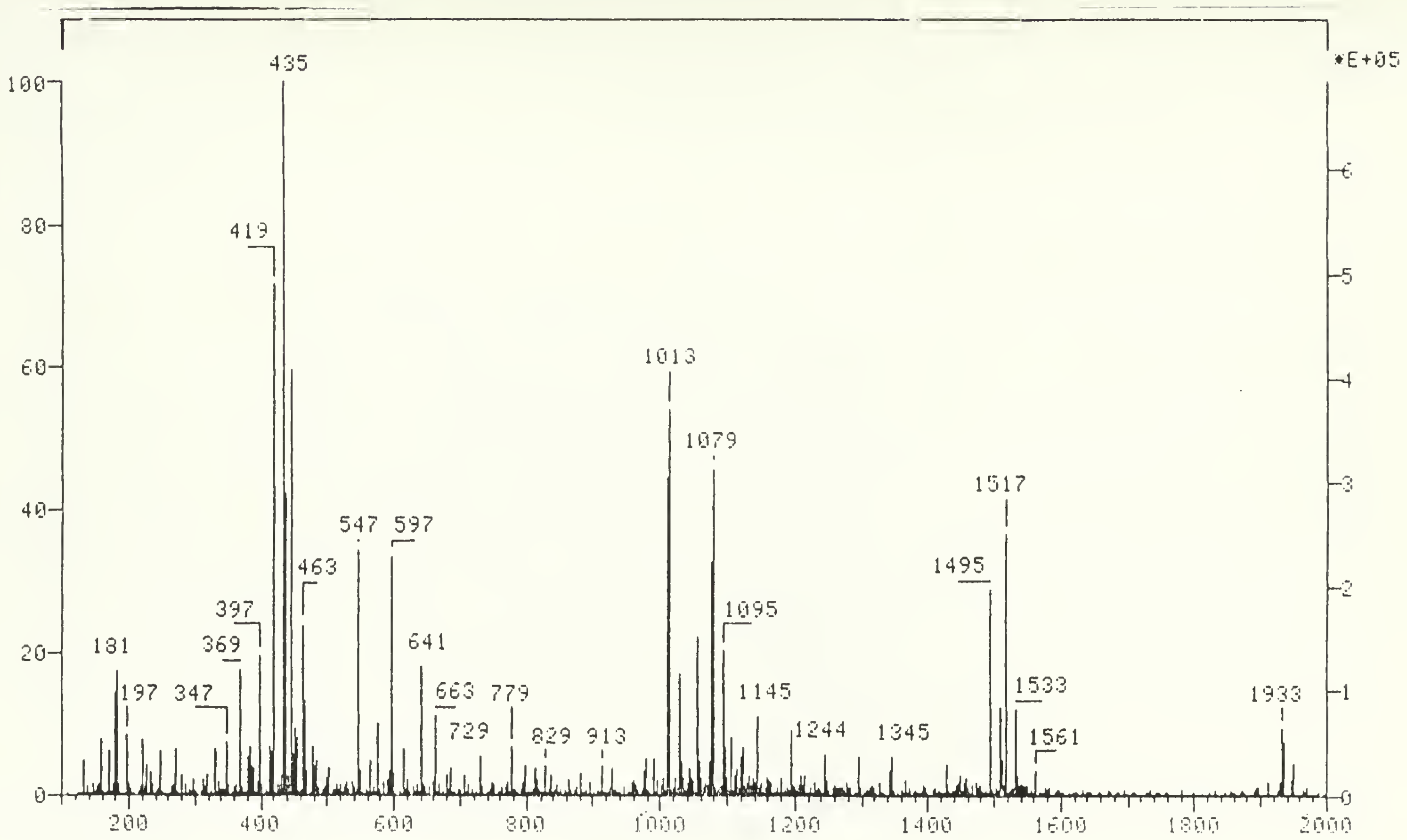


Figure 2-17: Mass spectrum of compound 8.

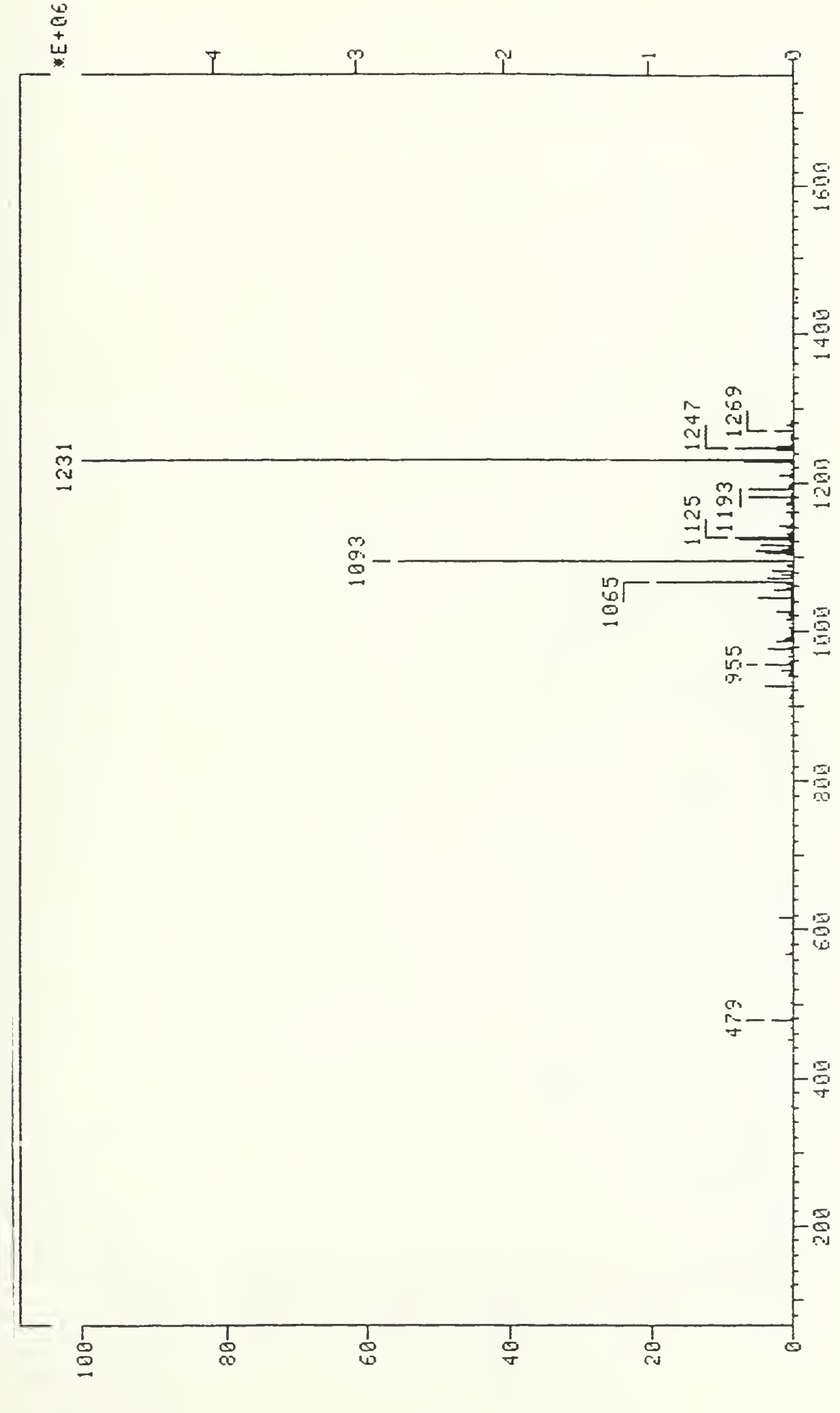


Figure 2-18: Mass spectrum of compound 11.

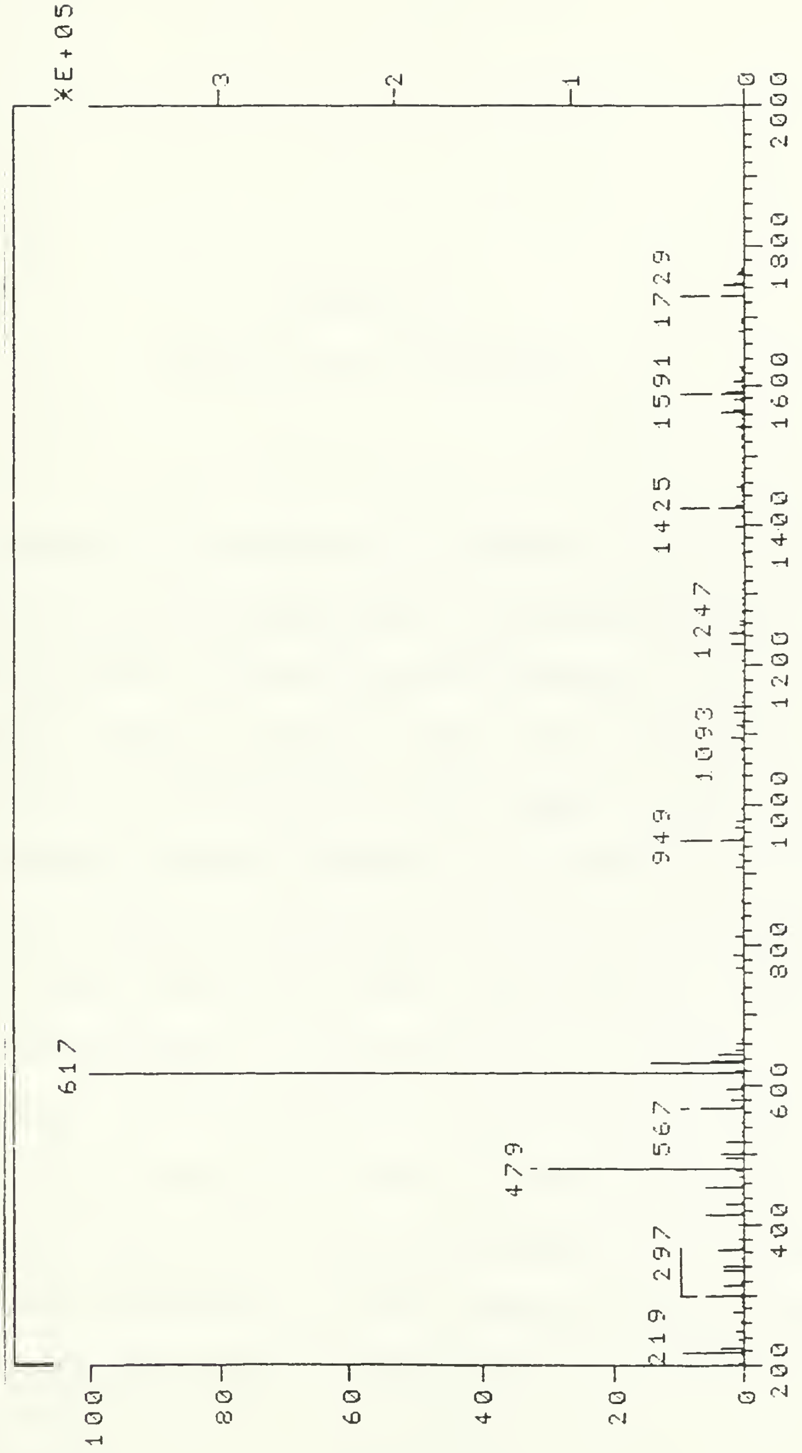


Figure 2-19: Mass spectrum of compound 16.

Chapter 3

Results and Discussion

The purpose of studying the direct fluorination of the ethers of pentaerythritol, dipentaerythritol, and tripentaerythritol in solution was twofold. First, these experiments were carried out to determine the feasability of synthesizing this type of compound (a highly branched perfluoroether) by direct fluorination in solution. Second, since some of these perfluorinated compounds had been previously synthesized either by direct fluorination in the absence of solvent [16,32] (compounds 1-4, 9, and 10) or by electrochemically fluorinating a partially fluorinated precursor [34] (compounds 1 and 2), it was desireable to synthesize several new compounds of the same general type to further explore their properties. In most of the

experiments undertaken, no attempt was made to maximize the yield of any particular compound. However, improvements in the reaction conditions discovered synthesizing a particular compound were applied in later attempted syntheses of not only the same compound, but several others as well. The syntheses of compounds 1-4, 9, and 10 were carried out primarily to define the reaction conditions and solvents needed to successfully carry out solution phase direct fluorination. Since the physical characterization of these compounds had been published, the simultaneous problems of attempting to synthesize new compounds and working out the particulars of a new synthetic technique (at least to this laboratory) were avoided. The first problem tackled in this study was that of finding a suitable solvent system and set of reaction conditions that would successfully perfluorinate an organic substrate. Coupled with this problem were the design and equipment changes that had to be made to the solution reactor to get it to withstand the fluorination conditions applied for the duration of an experiment. As it happened, many of the problems associated with finding the right reaction conditions were tied to eqipment problems so that in

many cases, fixing one problem solved another as well.

The combination of solvents used in these experiments was the result of several unsuccessful fluorination attempts. Early experiments attempted using Freon 113 as the solvent and starting at -30°C with a 1-3% fluorine concentration resulted in a product that rapidly decomposed upon removal of solvent to a black tarry substance. Although in retrospect (given Feher and coworkers' results with heptaglyme [27]) this was probably more the result of the low fluorine concentration and flow rate used, at the time it was assumed that the problem was the high initial temperature. Since previous syntheses using the La-Mar technique were started at much lower temperatures (-80 to -100°C) [16], and because Freon 113 freezes at about -36°C, a switch was made to Freon 11 (f.p. -111°C). In addition, higher fluorine concentrations were used and longer reaction times were attempted. The use of Freon 11 (b.p. 23.7°C) dictated a lower finishing temperature. The resulting product IR and mass spectra showed that the fluorination was still far from complete. Many of these partially fluorinated products, however, were more stable than the first compounds, turning only yellow

over a period of days or weeks instead of the black tar mentioned above. These results did indicate, though, that higher temperatures were going to be needed to continue the reaction. The two solvent system was thus initiated to allow higher temperatures to be used in the later stages of solution fluorination. Despite the problems with carbon tetrachloride discussed in Chapter 1, its use was attempted in some experiments in this study. This was in an attempt to allow solution phase fluorination to continue up to ambient temperature and possibly higher as in Clark's "solventless" work [16]. The use of carbon tetrachloride in this manner was not successful. Chlorination of the organic starting material was not observed, but the loss of carbon tetrachloride as reaction solvent as it became fluorinated (and as a result more volatile) was a significant problem. Also a minor annoyance was that the FCl generated as a byproduct of the fluorination of CCl_4 tended to blow through the alumina trap intended to prevent unreacted F_2 from being released into the hood. The main result of this was the decomposition of the mineral oil in the flow bubblers used in the gas delivery system.

Freon 113 was found to be more inert toward fluorine and at lower temperatures (0°C and below) did not boil off any faster than CCl_4. It thus ended up being used as the second solvent. But, because Freon 113 had a significantly lower boiling point (47.7°C versus 76.5°C for CCl_4), lower final solution temperatures (maximum of +10°C) had to be used to prevent excessive solvent loss. Regardless of which second solvent was used, the product coming out of the solvent reactor was never quite perfluorinated. This made the final fluorination of the product in the absence of solvent at elevated temperature necessary.

As mentioned above, sometimes more than one problem was solved by a single change in the reaction system. The initial amount of solvent used in a reaction was figured by determining the maximum amount that could be put in the reactor and not be blown out the gas outlet when the stirring motor was turned on. Likewise, the amount and frequency of solvent additions during the course of a reaction was driven to some extent by how much solvent could be added without coming out of the outlet port. This had not been a problem with the earlier reaction design where the gas outlet came

straight out of the top of the reactor (see figure 2-3), but when the size of the lower half of the reactor was reduced to scale down the size of the reaction, the bearing housing in the top half prevented a similar arrangement from being used. The problem was apparently due to the stirring paddles driving the solvent up the sides of the reactor and was partially solved by extending the outlet tube into the reactor and turning it slightly down. A better solution was discovered later when a slower stirring motor (400 versus 1725 rpm) was introduced. The slower stirring rate drove the solvent up the reactor sides less, decreasing the liklihood of overflow. It also solved other problems with the reactor. The slower stirring speed apparently caused less solvent loss since less surface area for evaporation was created. Also, the slower speed resulted in fewer stirring shaft bearing failures and less vibration. Vibration was suspected as the primary cause of outlet tube weld failure in two early fluorination attempts.

The slower stirring speed also apparently had no detrimental effects on gas mixing and the resultant product yields. Although yields were not maximized, the

six compounds that were synthesized at the slower stirring rate (4, 5, 7, 10, 11, and 14) all had yields comparable to those seen for the other compounds which were synthesized at the higher stirring rate. In the case of compound 11, the product yield was much better than previous successful attempts to perfluorinate the same compound. Although other changes made in the temperature and fluorine concentration gradients may also have contributed, the slower stirring speed and resulting larger amount of solvent was probably a factor. In general, the yields by solution fluorination were comparable to those reported for direct fluorination without solvent. Clark's reported yields [16] for compounds 1-4, 9, and 10 ranged from 25 to 37% while yields for the same compounds prepared here ranged from 21 to 41%, although Clark did not attempt to maximize yields either. One trend noted in the relationship between yields and solvent in these experiments was that yields were generally higher when a greater amount of solvent was left after the solution fluorination phase of a particular run was complete. This was true whether more solvent was left because of the slower stirring motor or because more solvent

additions were made during the experiment. In many unsuccessful experiments where the solvent had almost completely boiled off, a large amount of sticky, apparently polymerized material was evident coating the inside of the reactor. This seemed to indicate that by losing solvent, the action of fluorine helped to polymerize substrate molecules in close proximity to one another instead of just fluorinating them.

As a synthetic technique, the direct fluorination process presented here fell just short of accomplishing the goal of perfluorinating an organic substrate in solution. However, this process did achieve at least 90 to 95% fluorination in solution which is similar to the degree of fluorination in the process reported by Feher and coworkers [27] used to fluorinate a simpler, unbranched ether at only a slightly higher temperature (25°C). The successful perfluorination in solution by Modena and coworkers [26] at 100°C provided additional evidence that higher temperatures were needed to completely fluorinate most hydrocarbon ethers. Modena's report referred to the Fomblin Y solvent used as an ideal solvent for solution fluorination. It undoubtedly is, as probably are many of the compounds synthesized in

this study (given sufficient quantities). However, for economic reasons, the chlorofluorocarbon solvents will probably remain the solvent of choice for conducting research in solution fluorination for laboratories without an inexpensive source of a perfluoropolyether solvent. Also, more potential organic starting materials are soluble in chlorofluorocarbons.

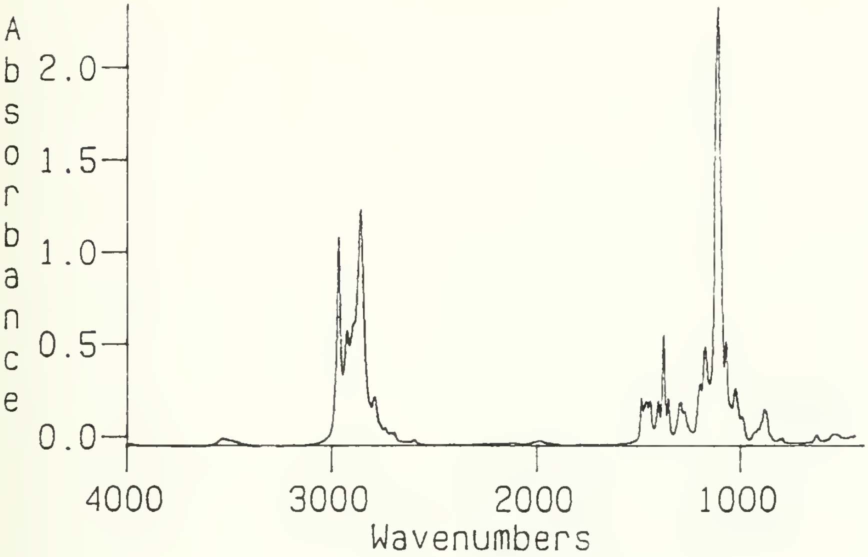
In conducting the finishing phase in pure fluorine, some of the previously noted problems experienced in solution fluorination noted by Bigelow and others [25] may have been avoided. Although extensive chlorination was not noted in the infrared or mass spectra of the partially fluorinated intermediate products coming out of the solvent reactor, the conditions used to complete the fluorination process in the tube reactor would likely have eliminated any chlorinated sites on the starting material. Somewhat surprising was that the temperature required to complete fluorination in the tube reactor (50 to 75°C) did not vary with the substrate, regardless of its molecular weight or structural complexity. However, the degree of partial fluorination seen in the shorter chained ethers (see discussion below) seemed to indicate that a lower

temperature would probably have been just as effective in completing the fluorination of those molecules.

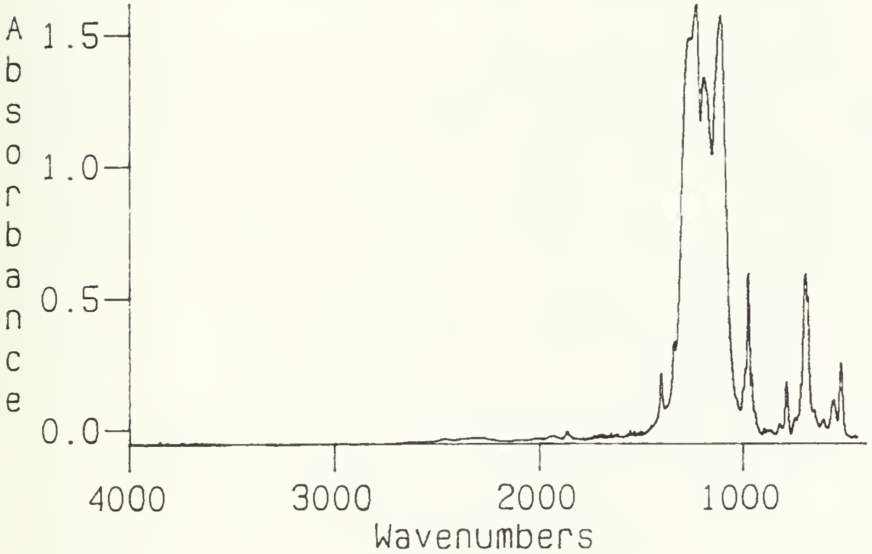
All of the compounds synthesized in this study were verified "proton free" by infrared and mass spectral analysis when they came out of the tube reactor as crude product before undergoing further workup. Any evidence of CH stretch (2900-3000 cm^{-1}) in the infrared spectrum or a mixture of partially fluorinated mass fragments (groups of peaks in the mass spectrum separated by increments of 18 mass units) resulted in further fluorination in the tube reactor and prevented the unecessary workup of an incompletely fluorinated product. Once the crude product passed this simple test, it was distilled and full characterization of the distillate (reported in Chapter 2) ensued. Although not reported as part of the characterization, proton N.M.R. of the distilled product was performed to ensure no protons (to the maximum sensitivity of the instrument) were present. Following the progress of a reaction in this manner was also helpful in identifying a set of conditions that was successful in attaining a perfluorinated product. Infrared and mass spectra were also obtained for the partially fluorinated product that

came out of the solution reactor. These spectra were particularly useful in gaining a qualitative feel for the degree of fluorination achieved in the solution reactor.

Figures 3-1 and 3-2 show the differences between the infrared spectra of two of the compounds reported in this paper, the perfluorinated tetraethyl ether of pentaerythritol (compound 1, figure 3-1) and the perfluorinated tetrahexyl ether of pentaerythritol (compound 6, figure 3-2). Of particular interest is the CH stretch absorbance around 2900 to 3000 wavenumbers. In the hydrocarbon starting material, figures 3-1(a) and 3-2(a), strong absorbance was evident in this region. The partially fluorinated crude intermediate product removed from the solution reactor, figures 3-1(b) and 3-2(b), had lost almost all of its original CH absorbance. Figures 3-1(e) and 3-2(e) were enlarged and centered in the CH absorbance region to demonstrate that some hydrogen was still present. The perfluorinated crude product, figures 3-1(c) and 3-2(c), had lost all detectable hydrogens and distillation to the final product, figures 3-1(d and f) and 3-2(d and f), was completed. What was also observed in comparing the

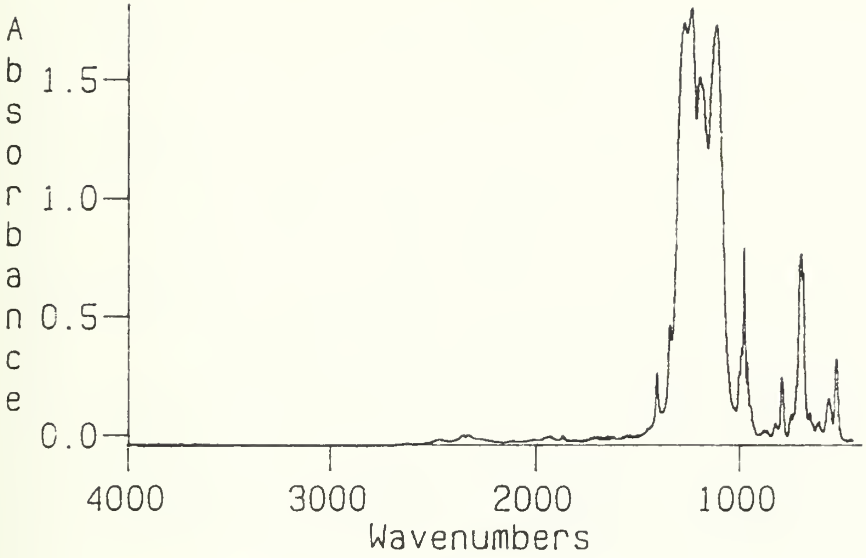


(a) starting material

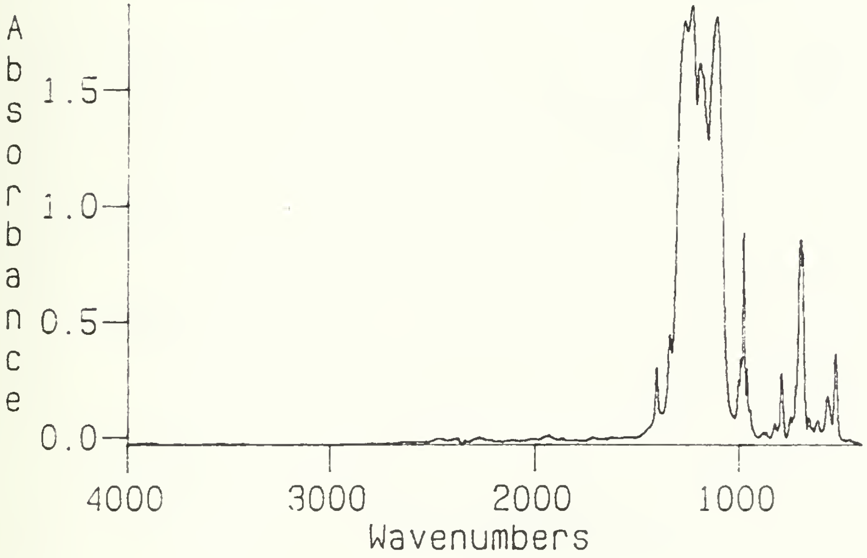


(b) partially fluorinated intermediate product

Figure 3-1: IR spectra for compound 1.

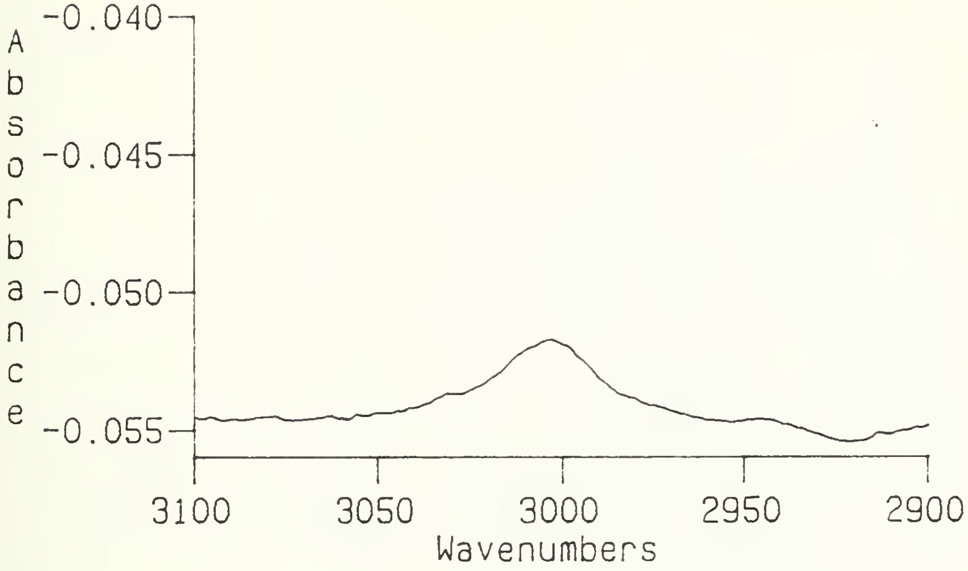


(c) perfluorinated crude product

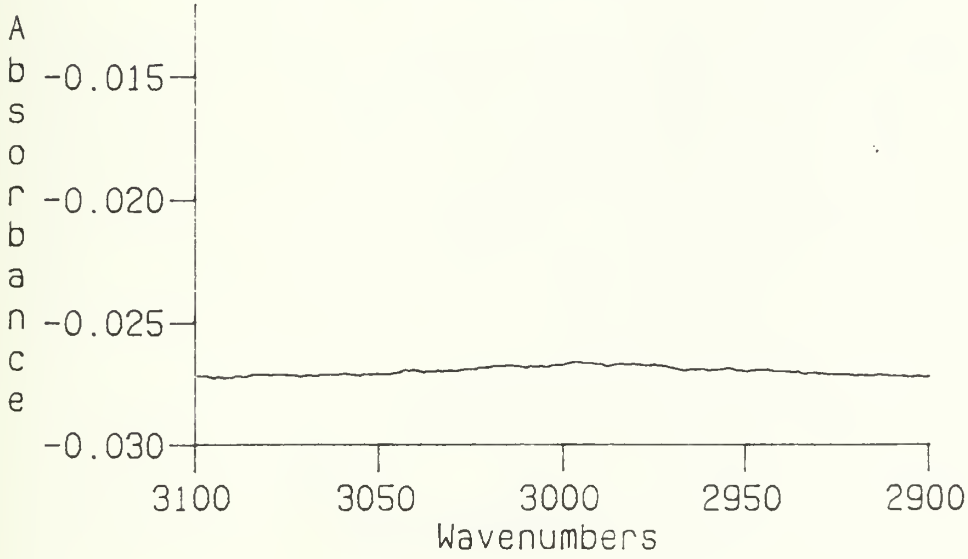


(d) distilled perfluorinated product

Figure 3-1: IR spectra for compound 1, continued.

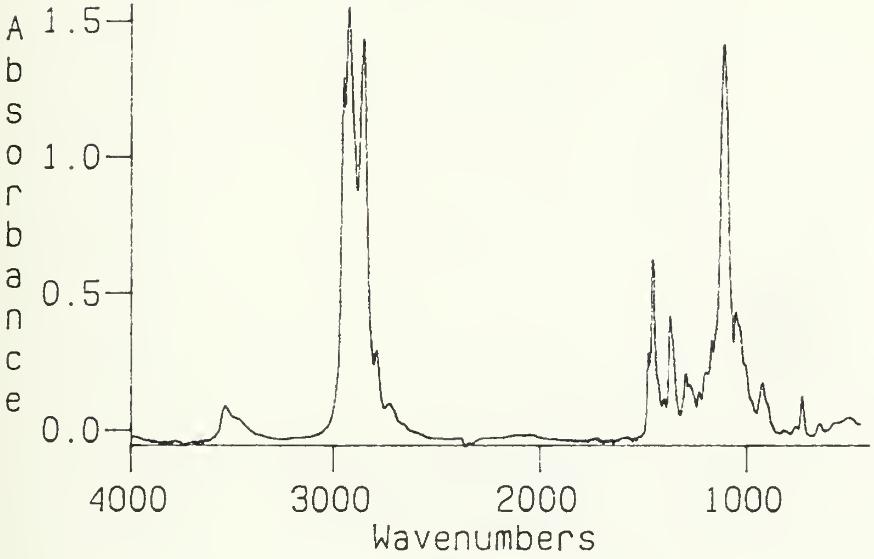


(e) CH stretch of intermediate, enlarged 100 times

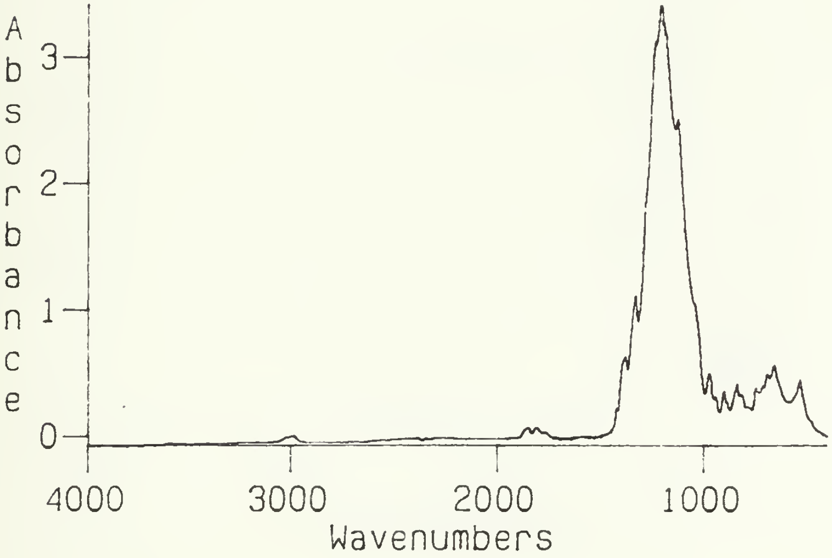


(f) CH stretch of distilled product, enlarged 100 times

Figure 3-1: IR spectra for compound 1, continued.

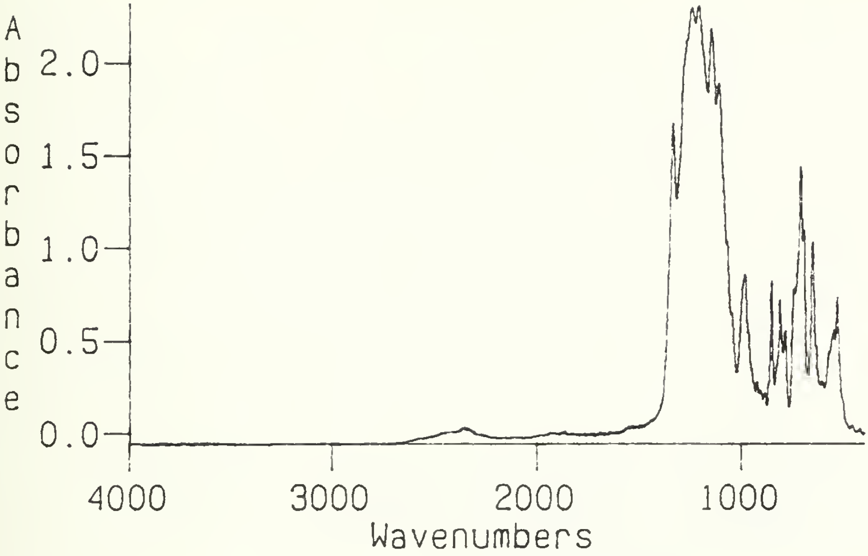


(a) starting material

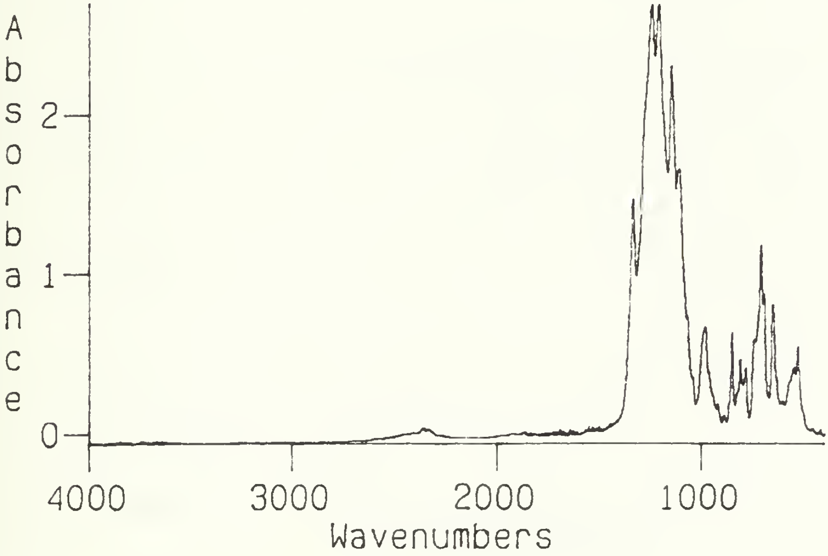


(b) partially fluorinated intermediate product

Figure 3-2: IR spectra for compound 6.

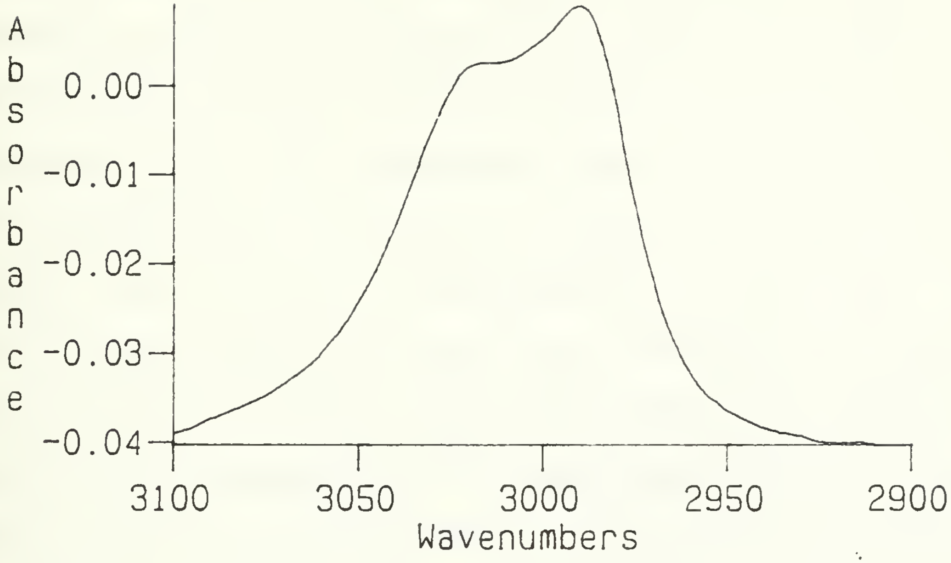


(c) perfluorinated crude product

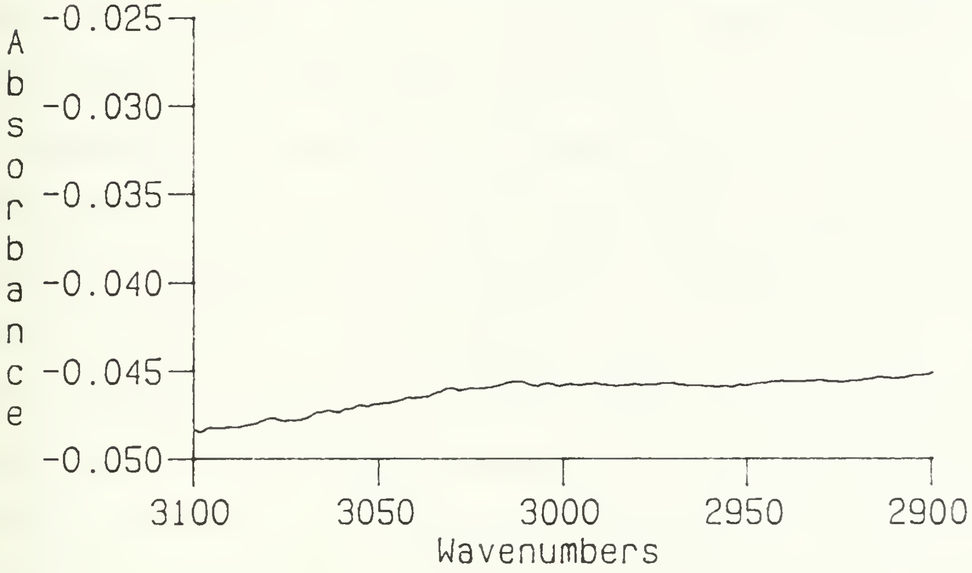


(d) distilled perfluorinated product

Figure 3-2: IR spectra for compound 6, continued.



(e) CH stretch of intermediate, enlarged 50 times



(f) CH stretch of distilled product, enlarged 100 times

Figure 3-2: IR spectra for compound 6, continued.

infrared spectra of the intermediate products (and can be seen in comparing figures 3-1(e) and 3-2(e)) was that the shorter chained ethers (methyl and ethyl) had comparatively less hydrogen left after solution fluorination than did their longer chained (hexyl, heptyl, and octyl) counterparts. This was not particularly surprising since the chains were probably fluorinated first before the inner methylenic hydrogens originally belonging to the pentaerythritol. Longer perfluoroalkyl groups would be expected to sterically hinder attack by fluorine on the inner hydrogens more and thus result in a slightly lower degree of fluorination for the same conditions.

Chemical ionization in the positive ion mode was the most effective means of obtaining useful mass spectra for these compounds. As mentioned in Chapter 2, a parent minus fluorine ion was observed for all compounds. This was somewhat surprising for the higher molecular weight compounds (7 and 8 for example) and the more highly branched compounds (15 and 16 for example). Although the relative intensities of fragments varied from compound to compound, all compounds of a given class had many of the same type of fragments. This similar fragmentation

pattern was helpful in identifying successful experiments. Table 3-1 lists the most common fragments observed (not including parent(P) minus fluorine). Although some of these fragments seemed to indicate the presence of acid fluoride byproducts, the C=O stretch of the acid fluoride (@ 1875 cm^{-1}) was not present in the product infrared spectra. The mass spectra of the intermediate products were often useful in getting a rough idea of the amount of fluorination that was accomplished in solution. Even though the intermediate "product" was actually a mixture of partially fluorinated species, all of the compounds present fragmented in the same manner as described in table 3-1. This usually created several groups of fragments in the spectrum that were not only separated by increments of 18 (the mass difference between atomic fluorine and hydrogen), but were also a multiple of 18 lower than a common perfluorinated fragment. In this way the mixed intermediate product fragments could be assigned empirical formulas of the type $C_nF_{2n-1-x}H_xO_3$ and a rough idea of the degree of fluorination accomplished could be obtained.

As noted previously for perfluorinated alkanes and

Pentaerythritol Ethers, $C(CF_2OR_f)_4$

$P-R_fO$

$(R_fOCF_2)_3C-C-O$

$(R_fOCF_2)_2C(CF_2)(CFO)$

R_fO

R_f

$R_f = C_2F_5, C_3F_7, C_4F_9, C_5F_{11}, C_6F_{13}, C_7F_{15}, C_8F_{17},$
$C_2F_4OCF_3$

Dipentaerythritol Ethers, $([R_fOCF_2]_3CCF_2)_2O$

$P-R_fO$

$(R_fOCF_2)_3CCF_2OCF_2C(CF_2OR_f)_2(-C-O)$

$P-R_fOCF_2$

$(R_fOCF_2)_3CCF_2O$

$(R_fOCF_2)_3CCF_2$

$(R_fOCF_2)_2C(CF_2)(CFO)$

$R_f = CF_3, C_2F_5, C_3F_7, C_4F_9, C_2F_4OCF_3$

Table 3-1: Common fragments in mass spectra.

Tripentaerythritol Ethers,

$([R_fOCF_2]_3CCF_2OCF_2)_2C(CF_2OR_f)_2$

$(R_fOCF_2)_3CCF_2OCF_2C(CF_2OR_f)_2CF_2OCF_2C(CF_2OR_f)_2(-C-O)$

$(R_fOCF_2)_3CCF_2OCF_2C(CF_2OR_f)_2(-C-O)$

$(R_fOCF_2)_3CCF_2$

$(R_fOCF_2)_2C(CF_2)(CFO)$

$R_f = CF_3, C_2F_5$

Table 3-1: Common fragments in mass spectra, continued.

simple ethers [2,23] and by Clark in his work with perfluorinated ethers of pentaerythritol [16], the boiling points of the series of perfluorinated ethers within a given class (tables 3-2 through 3-4 and figures 3-3 through 3-5) increased as the molecular weight increased. Compound 8 was somewhat anomalous in that it decomposed when boiling occurred. This may have been due to the length of the alkyl group and its possible instability at higher temperatures. The increased branching in compound 5 was probably responsible for its boiling point being higher than compound 4. Also as noted previously in perfluorinated ethers [2], the perfluorinated product had a much lower boiling point than its hydrocarbon analog. This property was essential in the isolation of compounds 6 through 8 and 12 through 16.

The ^{19}F N.M.R. assignments listed in table 2-17 for compounds 1-4, 9, and 10 are slightly different from the assignments made by Clark for the same compounds, although the chemical shifts are the same. Clark assigned the chemical shift observed at about -65 ppm (relative to Freon 11) to the terminal CF_3 group and the shifts in the -80 ppm range to the methylene groups

R_f	b.p. (°C) @ 760 mm Hg
CF_3	130 (a)
C_2F_5	176
n-C_3F_7	216
n-C_4F_9	238
n-C_5F_{11}	253
i-C_5F_{11}	270
n-C_6F_{13}	292
n-C_7F_{15}	353
n-C_8F_{17}	336 (b)
$C_2F_4OCF_3$	215

Table 3-2: Boiling points of the perfluorinated ethers of pentaerythritol, $C(CF_2OR_f)_4$.

(a) reference [16]

(b) decomposed

R_f	b.p. (°C) @ 760 mm Hg
CF_3	203
C_2F_5	243
n-C_3F_7	271
n-C_4F_9	308
$C_2F_4OCF_3$	277

Table 3-3: Boiling points of the perfluorinated ethers of dipentaerythritol, $([R_fOCF_2]_3CCF_2)_2O$

R_f	b.p. (°C) @ 760 mm Hg
CF_3	254
C_2F_5	278

Table 3-4: Boiling points of the perfluorinated ethers of tripentaerythritol, $([R_fOCF_2]_3CCF_2OCF_2)_2C(CF_2OR_f)_2$

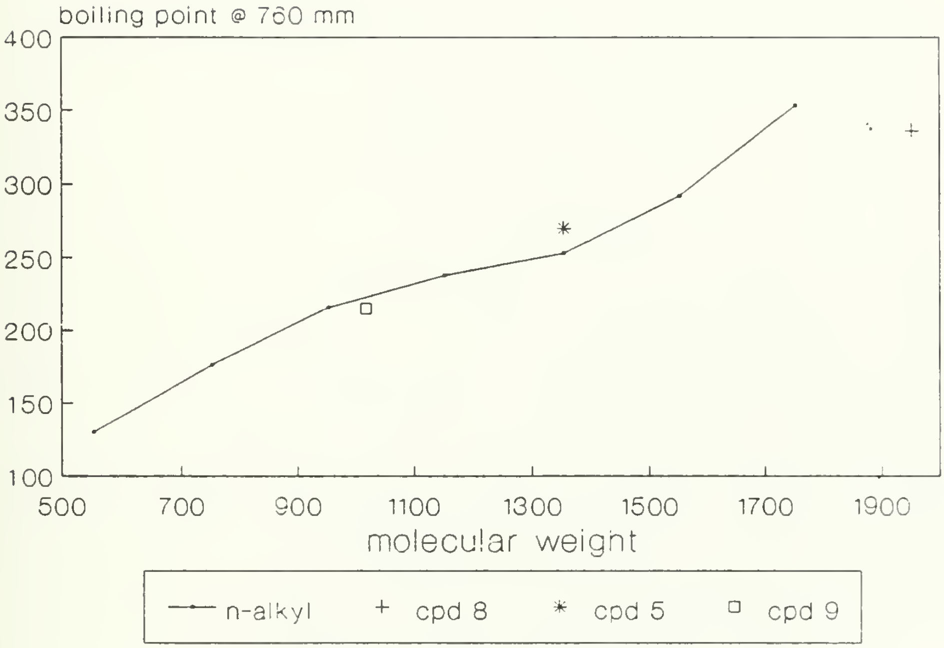


Figure 3-3: Boiling point trend, perfluorinated pentaerythritol ethers.

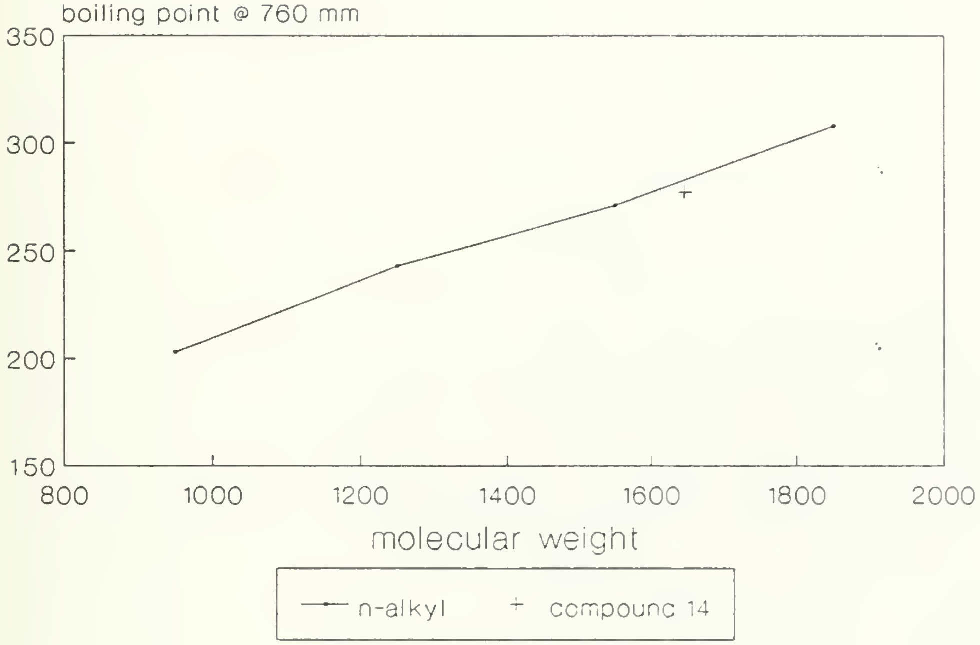


Figure 3-4: Boiling point trend, perfluorinated dipentaerythritol ethers.

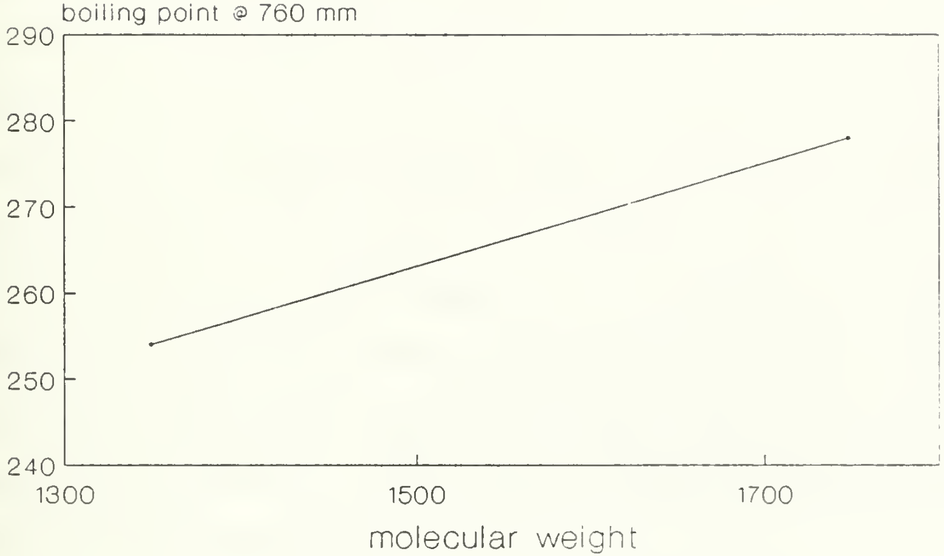


Figure 3-5: Boiling point trend, perfluorinated tripentaerythritol ethers.

($-CF_2-$) on either side of the ether functionality. These assignments did not correlate with the observed intensities or with shifts observed in the perfluorinated orthocarbonates [18] and ethers [17,22,23] previously reported. Clark's assignments also did not correlate with the relative intensities observed in the perfluorinated orthoformates recently prepared in this laboratory [19]. One of the reasons the preparation of compound 5 was undertaken was to attempt to resolve this discrepancy. The assignments an table 2-17 reflect the trends observed in the above published data as well as those observed in the perfluorinated ethers of di- and tripentaerythritol.

Although the lower boiling points indigenous to perfluorinated compounds proved to be instrumental in the isolation of the perfluorinated ethers (compounds 6-8 and 12-16) whose hydrocarbon analogs were not volatile enough for distillation, a decrease in observed yield was evident due to impurities in the starting materials. The principle impurities observed in the hydrocarbon starting materials were the diethers of the alkylating agents and the incompletely etherified poly alcohols (triethers of pentaerythritol, etc.). The dialkyl ethers

were easily removed by heating under vacuum. Nouguier and Mchich studied this problem extensively in the tetraheptyl ether of pentaerythritol [30,31,40] and though they came up with some methods of improving the amount of tetraether present in the mixture of products [32], some triether impurity was unavoidable. The perfluorinated tetraether was easily separated by vacuum distillation, but the presence of impurities impacted experimental yield since not all of the starting material was the tetraether. In addition, the perfluorinated triether and its alcohol group (possibly converted to an acid fluoride) may have accounted for some of the polymeric byproduct observed in these reactions. An analogous situation apparently affected the observed yields of the perfluorinated ethers of dipentaerythritol and tripentaerythritol whose starting materials were similarly affected. The best example of this problem was in the synthesis of compound 7. After recovering such a low yield (7%) compared to many of the other products, the starting material preparation was reexamined. Here it was discovered that the organic starting material was not heated sufficiently under vacuum, causing a large amount of diheptyl ether to

remain in the product as impurity. This explained the large amount of perfluorinated diheptyl ether recovered from the reaction. Experimental yield of this compound could doubtless be improved by improving the purity of the starting material using the suggestions of Nouguier and Mchich.

Chapter 4

Conclusion

Solution phase direct fluorination using fluorine concentration and temperature gradients similar to those used in the La-Mar method is a viable synthetic tool for the development of new fluorocarbon materials and may be useful in obtaining fluorocarbons not producible by other methods. The higher heat dissipating ability of the solvent allows harsher conditions to be used without sacrificing yield. This includes the use of higher initial reaction temperature, higher initial fluorine concentration, and steeper temperature and concentration gradients than previously applied in many of the direct fluorinations cited throughout this paper that were performed in the absence of solvent. The most applicable example of this is Clark's work with some of the same

compounds [16]. With only minor attempts to improve yields over previous experiments, yields as high as 58% (compound 11) were achieved. However, some drawbacks with solution fluorination still exist. The most important of these is the requirement for the starting material to be soluble in whatever solvent (chlorofluorocarbon, fluorocarbon, perfluoropolyether, etc.) is used. Additionally, the starting material must be non-reactive with the solvent.

The compounds synthesized in this study are themselves very interesting. Almost all (compound 8 being the possible exception) are thermally stable in air at least to their respective boiling point. In many cases this temperature exceeds 275°C. Although at least one study [24] showed the temperature-viscosity relationship of the perfluorinated tetramethyl ether of pentaerythritol to be less favorable than commercially available perfluoropolyether fluids (like the Fomblin fluids of Monticatini Edison of Italy or the Krytox fluids of Du Pont), more study of these branched perfluoroethers should be done before their utility as nonflammable lubricants or hydraulic fluids is dismissed. Other possible uses include vapor phase

soldering applications in the electronics industry and biomedical applications like artificial blood [17,23]. Finally, many of these compounds, in sufficient quantity, would probably make excellent solvents for use in solution phase direct fluorination.

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