Free radical routes to functional fluorine-containing organic compounds

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A Thesis Entitled

FREE RADICAL ROUTES TO FUNCTIONAL FLUORINE-CONTAINING ORGANIC COMPOUNDS

Submitted by

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This is for my parents, who have given me considerable support throughout, and for Mrs. J. Little, a friend I will miss a lot.

Teacher, starve your child, P.C. approved

As long as the right words are used

Systemised atrocity ignored

- *PCP*, Manic Street Preachers

MEMORANDUM

NOMENCLATURE

Throughout this thesis an 'F' in the centre of a ring is used to denote that all unmarked bonds are to fluorine.

ACKNOWLEDGEMENTS

The assistance of university technical staff, and others outwith, is acknowledged.

Most importantly, I am grateful to my parents for their considerable support throughout.

ABSTRACT

Free radical additions of functional hydrocarbons such as alcohols, aldehydes and ethers to the highly fluorinated alkenes *2H*-pentafluoropropene and hexafluoropropene have been studied. In particular, reactions involving *2H*-pentafluoropropene have given rise to a series of new fluorinated alcohols and ketones. For the purpose of synthesising the 1:1 adducts, γ-ray initiation was shown to provide a superior method to ultra violet radiation or peroxides.

Competition reactions were carried out between homologous alcohols and between different species, *viz* alcohol, aldehyde, amine, ether. These reactions enabled reactivity series to be established.

Chemistry of the derived polyfluorinated alcohols was investigated, and it has been shown that these compounds may be reacted with a broad spectrum of electrophiles to give new esters, carbonates, sulphonates and ethers, including the first reported such reactions with perfluorinated aromatic and heteroaromatic compounds as electrophiles.

Interestingly, it was observed that tosylated polyfluoroalcohols would not undergo nucleophilic displacement, in contrast to the situation which exists with non-fluorinated analogues.

2-(1,1,2,3,3,3-Hexafluoropropyl)oxolane was chlorinated selectively at the 5-position, and subsequently reacted with a range of different types of nucleophile. This study gave a number of novel compounds, and reasons were proposed for the variation in reactivity of nucleophiles under study.

Direct chlorination of this ketone gave rise to the chloromethyl and dichloromethyl ketones, as did direct chlorination of 3,3,4,5,5,5-hexafluoropentan-2-ol. A pathway for the latter reaction is proposed, involving 1,1,1,2,3,3-hexafluoropentan-2-one as an intermediate.

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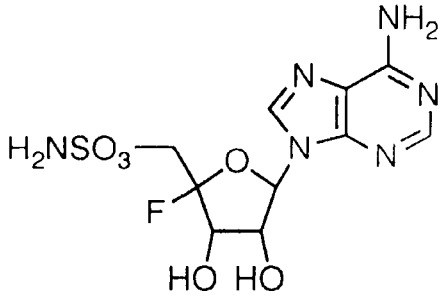
CHAPTER ONE

GENERAL INTRODUCTION

A. NATURAL OCCURRENCE OF FLUORINE

Fluorine is the thirteenth most abundant terrestrial element, representing *ca.* 0.065% of the earth's crust.[1] However it is present almost exclusively as inorganic salts, chiefly fluorspar (calcium fluoride), cryolite (sodium hexafluoroaluminate) and fluoroapatite (calcium hydroxyphosphate in which fluoride replaces some hydroxide),[1] due to its high electronegativity.

Naturally occurring organic compounds containing fluorine are few in number, examples known thus far include fluoroacetate (the toxic constituent of gifblaar or *Dichapetalum cymosum*),[2] ω-fluorooleic acid (found in ratsbane or *Dichapetalum toxicarium* seeds)[2] and the fluorinated nucleoside, nucleocidin (**1**).[3]



(1)

B. HISTORICAL PERSPECTIVE

Though hydrogen fluoride was discovered in 1771 by Scheele, it was not until 1886 that Moissan prepared elementary fluorine.[4,5]

Even well into the twentieth century, little consideration was given to the field of organofluorine chemistry until the potential was realised for the industrial and military application of such materials. In the 1930s the unreactive nature of chlorofluorocarbons was harnessed for use as refrigerants,[7] and the Manhattan Project provided further impetus for organofluorine research in the quest for materials which exhibited high thermal stability and remained chemically intact when exposed to such

strong oxidising agents as uranium hexafluoride at elevated temperatures.[8]

C. PROPERTIES OF FLUORINATED ORGANIC COMPOUNDS

The C-F bond has unique properties. As can be seen from Table 1.1[9] this bond is the strongest single bond to carbon, and is in fact stronger than the C-C bond itself.

TABLE 1.1: C-X BOND STRENGTHS[9]

Bond	Bond Strength (kcal mol^{-1})
C-F	106-121
C-Cl	81
C-Br	68
C-I	57
C-O	85.5
C-N	72.8
C-S	65
C-H	98.7
C-C	82[11]

This property, and the shielding effect of fluorine as a substituent, gives rise to the remarkable thermal stability of organofluorine compounds which, even on thermal degradation, tend to decompose by means of skeletal fragmentation to lower molecular weight analogues (Equation 1.1).

$$(CF_2CF_2)_n \xrightarrow{\Delta} CF_2{=}CFCF_3 + CF_2{=}CFC_2F_5 + CF_2{=}C(CF_3)_2 \quad [1.1]^{10}$$

The existence of fully fluorinated alkanes contrasts with analogues of other halogens, whose steric requirements induce instability and prevent formation of higher perchloro-, perbromo- or periodocarbons.

The length of the C-F bond is comparable with that of the C-H bond (C-F 1.317Å, *c.f.* C-H 1.091Å, *c.f.* C-Cl 1.766Å), enabling

exchange of fluorine for hydrogen in a molecule without dramatic alteration of the geometry or steric requirements of the molecule. The significantly different electronic properties of fluorine affect the physical properties of such materials.[12,13] As the number of fluorine substituents increases, the remaining hydrogens assume more acidic natures, and hydrogen bonding increases, resulting in increased boiling points of partially fluorinated hydrocarbons (Figure 1.1).

FIGURE 1.1: BOILING POINTS OF THE SERIES CF_nH_{4-n}

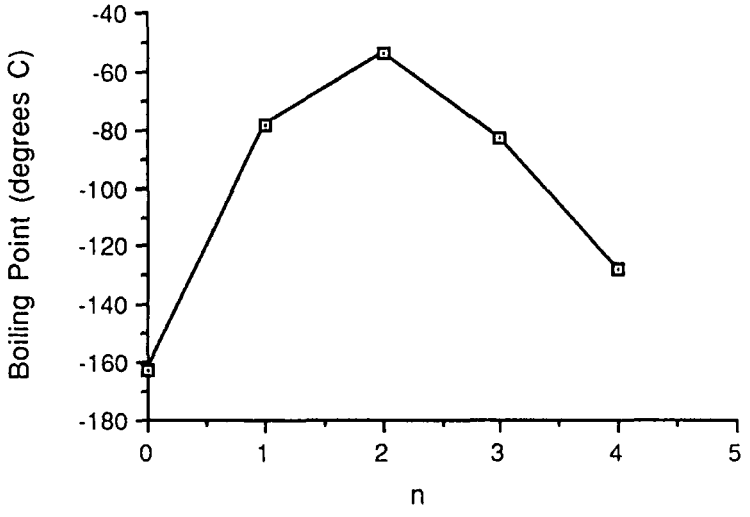
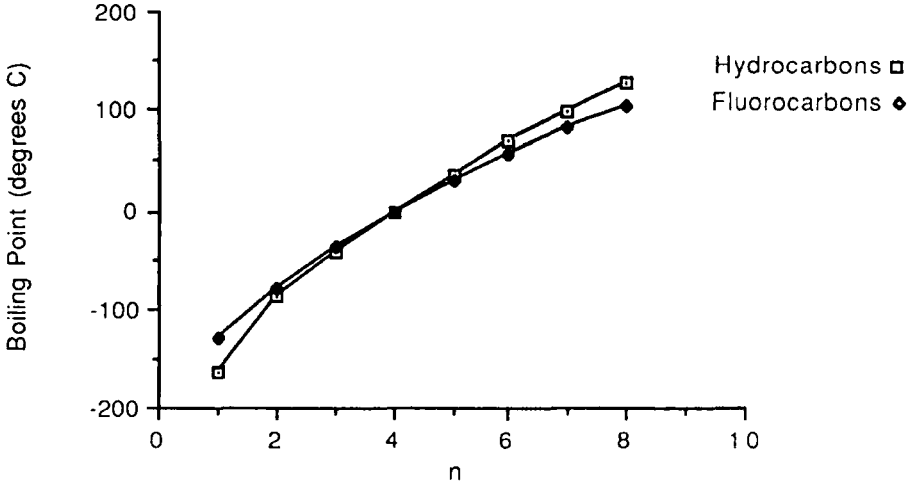


FIGURE 1.2: BOILING POINTS OF THE SERIES n-C_nX_{2n+2} (X=H,F)



However the fully fluorinated compounds, in which no hydrogen bonding effects can increase intermolecular attractions,

do not show boiling points significantly different from those of the corresponding hydrocarbons despite the increase in molecular weight (Figure 1.2).

This is attributable to the competition between electronic repulsion, which serves to decrease intermolecular forces and boiling points, and increasing molecular weight.

D. APPLICATIONS OF FLUORINATED ORGANIC COMPOUNDS

D.1 BIOLOGICALLY USEFUL COMPOUNDS

D.1.a. BIOLOGICAL ACTIVITY

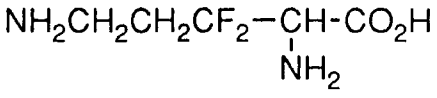
Fluorinated organic compounds can show biological activity[14-16] because of the fulfilment of certain necessary conditions. An important condition governs the acceptability of fluorinated compounds in biological systems, and is fulfilled by the similarity in bond lengths (C-F = 1.317Å, C-H = 1.091Å, C-O = 1.43Å), steric similarities (van der Waal's radii: F = 1.35Å; H = 1.1Å), and the isoelectronic and isosteric properties of CF_2 with respect to O, in some systems.[17]

Geometrically and sterically, enzymes and other active sites accept fluorinated organic compounds, but cannot metabolise them correctly, as a result of the second condition for biological activity, *i.e.* altered electronic effects, which may involve *in vivo* hydrogen bonding, prevention of enzyme substrate complexation and prevention of metabolism of the compound due to the high C-F bond strength relative to C-H or C-O.

D.1.b. EXAMPLES OF BIOLOGICALLY ACTIVE FLUORINATED ORGANIC COMPOUNDS

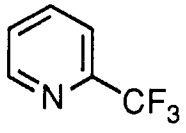
A wide range of biologically active fluorinated organic compounds is now known, spanning a vast scope of modes of activity.[16] Only a small selection of examples is given here.

Fungicides: *e.g.* α-Difluoromethylornithine (**2**) inhibits cell proliferation.[18,19]



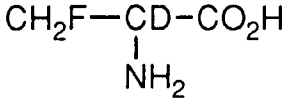
(**2**)

Herbicides: *e.g.* 2-Trifluoromethylpyridine (**3**).[20]



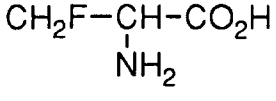
(**3**)

Antimicrobial: *e.g.* 3-Fluoro-2-[^{2}H]-D-alanine (**4**).[21]

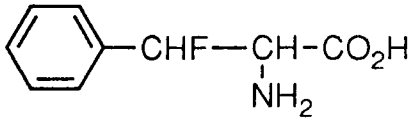


(**4**)

Antibacterial: *e.g.* 3-Fluoro-D-alanine (**5**),[22]
3-fluorophenylalanine (**6**).[23]

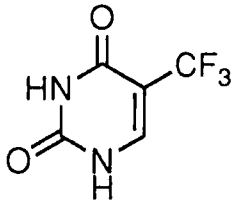


(**5**)

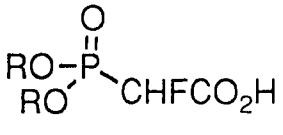


(**6**)

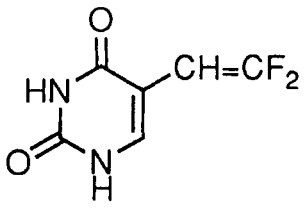
Antiviral: In this area, anti-herpes active compounds are of considerable interest and commercial value, *e.g.* 5-trifluoromethyluracil (**7**),[24] α-fluorophosphonacetic acid (**8**),[25] 5-(2,2-difluorovinyl)uracil (**9**).[26] Other examples of compounds exhibiting antiviral activity include 2-fluorohistidine (**10**),[27,28] which inhibits the synthesis of cellular protein and also shows antimetabolite activity.



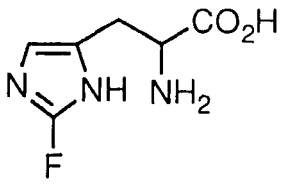
(**7**)



(**8**)

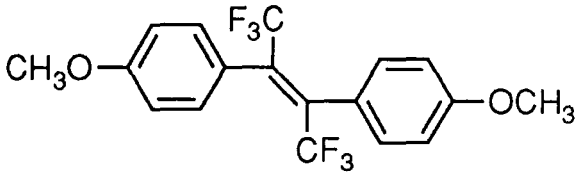


(**9**)



(**10**)

Antimetabolites: *e.g.* *(Z)*-2,3-Bis-(4-methoxyphenyl)hexafluoro-but-2-ene (**11**) retards growth of breast tumours.[29]



(**11**)

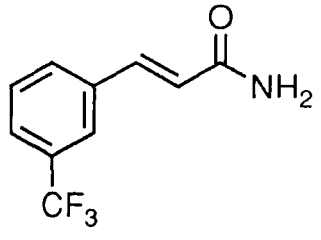
In this area, fluorinated steroids and fluoro- and trifluoromethyl-substituted amino acids, such as α-fluoro-β-alanine (**12**),[30,31] are particularly effective.[32-34]

$NH_2CH_2CHFCO_2H$

(**12**)

Enzyme Inhibitors: Fluorinated ketones have been shown to inhibit hydrolytic enzymes by formation of stable hemiketals with the active site.[35]

Muscle Relaxants: Trifluoromethyl substituted aromatic compounds have been shown to promote muscle relaxation, have anti-convulsant action and to induce sleep, *e.g.* 2-(3-trifluoromethylphenyl)propenamide (**13**).[36]



(**13**)

D.1.c. ANAESTHETICS

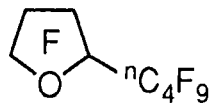
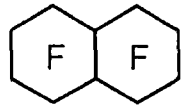
Fluorinated organic compounds have found application in the field of anaesthesia[37] due to their volatility and their low to moderate toxicity, under conditions of use. The most commonly used surgical inhalation anaesthetics are:[37]

Halothane	-	$CF_3CHBrCl$
Methoxyflurane	-	$CH_3OCF_2CHCl_2$
Fluroxene	-	$CF_3CH_2OCH{=}CH_2$
Enflurane	-	CHF_2OCF_2CHClF

D.1.d. ARTIFICIAL BLOOD SUBSTITUTES

Perfluorinated organic compounds are virtually inert, and so can be safe for use in the body. Since these compounds are entirely synthetic in nature they are unrecognised by the body and are not rejected by the immune system. However, the main purpose of blood is to transport oxygen round the body and remove carbon dioxide, and perfluorocarbons are ideal for this purpose due to their high gas solubility (Table 1.2).

TABLE 1.2 : OXYGEN SOLUBILITIES

Liquid*	Oxygen Solubility**	Carbon Dioxide Solubility**
$(n\text{-}C_4F_9)_3N$	40.3	142
$(n\text{-}C_3F_7)_3N$	45.3	166
 **(14)**	45.0	126
 **(15)**	48.5	160
Water	2.5	65
Plasma	2.3	54
Blood	20.6	-

* Perfluorocarbons in emulsion form

** % volume at 1atm and 37°C

In 1967, (**14**) was the first successfully used artificial blood substitute.[38,39] The problem of transportation of essential minerals which are insoluble in perfluorocarbons was overcome by using the perfluorocarbons in emulsion form. To date, (**14**) and *cis*- and *trans*- (**15**) have achieved most success as artificial blood substitutes.

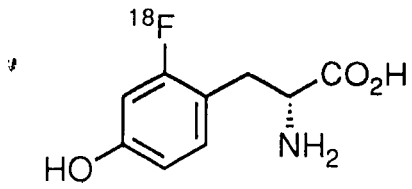
D.1.e. POSITRON EMISSION TOPOGRAPHY

The half life of the isotope ^{18}F, 110 minutes, makes it useful for positron emission topography (PET) studies,[40] where positron emitting isotopes of other elements have half lives too short to permit synthesis and administration of active species, *e.g.* ^{11}C ($t_{1/2}$=20 minutes), ^{13}N ($t_{1/2}$=10 minutes), ^{15}O ($t_{1/2}$=2 minutes).

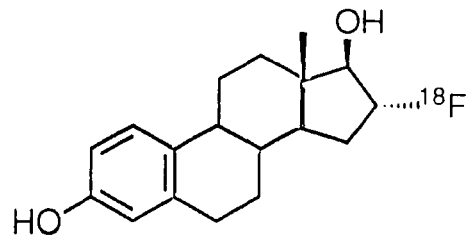
This isotope decays by positron emission as shown:

$$^{18}_{9}F \longrightarrow {}^{18}_{8}O + {}^{0}_{1}\beta^{+} \qquad [1.2]$$

The technique of PET allows safe study of living tissue in such areas as brain imaging, *e.g.* in instances of Parkinson's disease, for which 6α-[^{18}F]-fluoro-L-dopa is used, and for breast cancer examination, employing the fluorinated steroid 16α-[^{18}F]-fluoroestradiol-17β.



6α-[^{18}F]-Fluoro-L-dopa



16α-[^{18}F]-Fluoroestradiol-17β

D.2. SURFACTANTS

Compounds such as perfluoroalkyl substituted carboxylic and sulphonic acids, or the salts of such compounds, have been used as surface-active materials[41] due to their extremely low surface energies, which reduces surface tension in aqueous media, even at low concentrations.

e.g. *n*-$C_7F_{15}CO_2NH_4$ (3M's FC®-26)

D.3. INERT FLUIDS

Various applications exist for fluorinated organic compounds as inert fluids (Table 1.3).

TABLE 1.3: INERT FLUID APPLICATIONS OF FLUORINATED ORGANIC COMPOUNDS

Application	Fluorinated Organic Compound
Fire Retardant	Brominated Fluorocarbons, *e.g.* CF_3Br
Coolant	*e.g.* CF_2Cl_2
Refrigerant	*e.g.* CF_2Cl_2, $CFCl_3$
Lubricant	Perfluoropolyethers *e.g.* Fomblin®, Krytox®

E. SYNTHETIC ROUTES TO FLUORINATED ORGANIC COMPOUNDS

Several articles on fluorination methods exist,[42-44] and only a brief discussion is presented here.

E.1. FLUORINATING AGENTS

E.1.a. ELEMENTARY FLUORINE

A great deal of work has gone into the 'harnessing' of highly reactive elementary fluorine to the task of fluorination of organic compounds. Early work was extremely hazardous, with frequent explosions due to the exotherm associated with formation of the carbon fluorine bond (ΔH_f(C-F) = 447-485kJ mol^{-1}, ΔH_f(C-H) = *ca.* 413kJ mol^{-1}),[9] and consequently little progress was made. In time, however, a number of successful techniques have been developed for this application, such as cryogenic direct fluorination,[45-47] aerosol direct fluorination[48-58] and liquid phase fluorination,[59] carried out using a substrate solution in perhalogenated solvent, *e.g.* 1,1,2-trichlorotrifluoroethane.

A number of reviews on the direct fluorination of organic compounds are now available.[45,60-62]

E.1.a.(i). THE LAMAR PROCESS

Cryogenic direct fluorination, the so-called 'LaMar Process', has as its essential features to control reaction, use of low reaction temperatures, and use of elementary fluorine at extremely high dilutions, in an inert carrier gas.

The process involves charging of the gaseous organic compound into the reaction vessel, which consists of several sections at different temperatures, typically from -78°C to ambient temperature. As reaction proceeds the concentration of fluorine is increased and temperature may be adjusted to ensure perfluorination.

Examples of compounds fluorinated by this method are shown in Equations 1.3-1.5.

40% [1.3]

$(CH_3)_3COH \longrightarrow (CF_3)_3CF$ 44% [1.4]

$CH_3OCH_2CH_2OCH_3 \longrightarrow CF_3OCF_2CF_2OCF_3$ 16% [1.5]

E.1.a.(ii). AEROSOL DIRECT FLUORINATION

This method utilises adsorption of the organic species onto a sodium fluoride aerosol (generated by heating sodium fluoride to *ca.* 1000°C in a stream of helium). The aerosol thus generated is passed through a reactor column and elementary fluorine diffused through the walls of the reactor.

Similarly to the LaMar process, the aerosol direct fluorination reactor employs zones of different temperature

(typically -78°C to -40°C) to effect reaction to completion. In the final stage, photofluorination is employed to ensure perfluorination of the substrate.

Examples of materials fluorinated by this method are given in Equations 1.6-1.8.

$$C(OCH_3)_4 \longrightarrow C(OCF_3)_4 \quad 8\% \qquad [1.6]$$

$$(CH_3)_3CCl \longrightarrow (CF_3)_3CCl \quad 74\% \qquad [1.7]$$

$$CH_3OCH_2CH_2OCH_3 \longrightarrow CF_3OCF_2CF_2OCF_3 \quad 86\% \qquad [1.8]$$

E.1.a.(iii) LIQUID PHASE FLUORINATION

This method provides a simple route by which solutions of organic materials in a fully halogenated solvent are reacted with elementary fluorine in an inert carrier gas, at a reaction temperature of between -10°C and 50°C.[59,63] A free radical initiator has been used to promote dissociation of fluorine in the later stages of reaction, as an alternative method to photofluorination, to effect perfluorination.

$$CH_3CO(CH_2)_5CH_3 \longrightarrow CF_3CO(CF_2)_5CF_3 \quad 87\% \qquad [1.9]$$

$$CH_3O(CH_2CH_2O)_2OCH_3 \longrightarrow CF_3O(CF_2CF_2O)_2OCF_3 \quad 56\% \qquad [1.10]$$

52% [1.11]

E.1.b. HIGH VALENCY METAL FLUORIDES

High valency metal fluorides such as CoF_3,[64-66] $KCoF_4$,[67] AgF_2,[68] MnF_4,[68,69] CeF_4,[68,69] enable fluorination of organic materials in a more controllable manner since the heats of reaction associated with this method are considerably lower than those

associated with the use of elementary fluorine (Equations 1.12, 1.13). Indeed, while reactions with elementary fluorine are generally performed at ambient temperature or below, reactions involving high valency metal fluorides are often performed at temperatures as high as 440°C.

$$2\ CoF_3 + C\text{-}H \longrightarrow C\text{-}F + HF + 2\ CoF_2 \qquad \Delta H\ \text{kcal mol}^{-1}\ ca.\text{-}50 \qquad [1.12]$$

$$F_2 + C\text{-}H \longrightarrow C\text{-}F + HF \qquad ca.\text{-}102 \qquad [1.13]$$

Cobalt trifluoride fluorination may be viewed as use of elementary fluorine with a metal fluoride catalyst, since, when fluorination proceeds and the metal is reduced to its lower valent fluoride, elementary fluorine is used to regenerate the original high valency species (Scheme 1.1).

SCHEME 1.1: OVERALL REACTION SCHEME OF COBALT TRIFLUORIDE FLUORINATION

$$F_2 + 2CoF_2 \longrightarrow 2CoF_3$$

$$2CoF_3 + R\text{-}H \longrightarrow 2CoF_2 + R\text{-}F + H\text{-}F$$

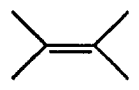
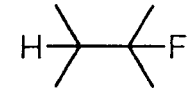
$$F_2 + R\text{-}H \longrightarrow R\text{-}F + H\text{-}F$$

E.1.c. HYDROGEN FLUORIDE

Hydrogen fluoride is a highly corrosive, volatile (boiling point 19°C) liquid, which must be handled with great care. An easier method of handling this reagent is in the form of a solution, up to 70% w/w HF, in pyridine, a technique developed by Olah and co-workers.[70]

E.1.c.(i). ADDITION ACROSS MULTIPLE BONDS

In these classical reactions, hydrogen fluoride adds across a double or triple bond in the conventional manner of a hydrogen halide (Equations 1.14, 1.15).

e.g. HF +   [1.14]

e.g. HF + $RC{\equiv}CR \longrightarrow RCH_2CF_2R$ [1.15]

This may be achieved with[71-76] or without[77] catalysis.

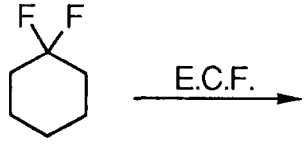
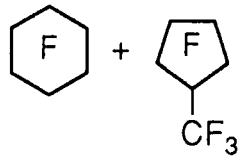
E.1.c.(ii). SUBSTITUTION

Hydrogen fluoride is a mild fluorinating agent with respect to the displacement of leaving groups, *i.e.* a moderate nucleophile. Typically, assistance is required, either by activation of the leaving group[78] or by catalysis with antimony pentafluoride[79] or mixed tri- and pentafluorides of antimony.[80]

E.1.d. ELECTROCHEMICAL FLUORINATION

Developed in the course of the Manhattan Project by Simons,[81-86] this procedure involves the setting up of a low voltage across a dilute solution of reactant in anhydrous hydrogen fluoride. Conditions of voltage, current density and temperature are such as to prevent evolution of fluorine, but allow perfluorinated materials to form at the nickel anode, hydrogen gas being liberated at the nickel or steel cathode.

Electrochemical fluorination has the advantage of being a controlled reaction, allowing replacement of hydrogen by fluorine, saturation of carbon carbon multiple bonds, but retaining many functional groups. Skeletal rearrangement can occur (Equation 1.16), limiting product yields and this factor, combined with electricity costs, limit the application of electrochemical fluorination.

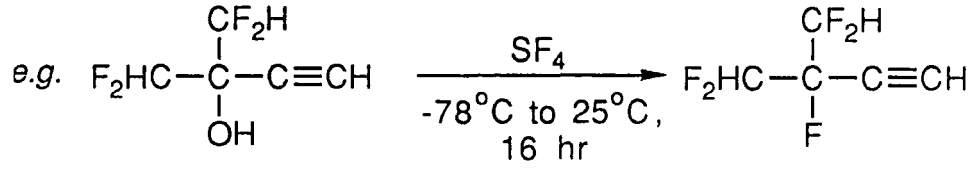
e.g.  E.C.F.  + $n\text{-}C_6F_{14}$ + $i\text{-}C_6F_{14}$ [1.16]

<3%

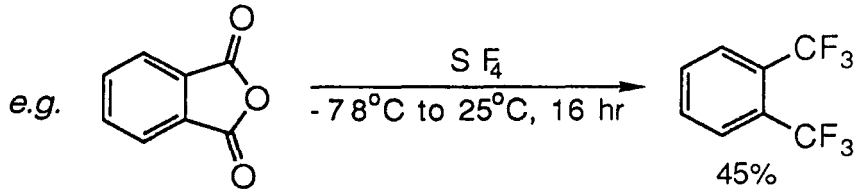
29% 40%

E.1.e. SULPHUR TETRAFLUORIDE

Sulphur tetrafluoride is a gaseous reagent (boiling point -40°C), which is generally used for the conversion of carbonyl and thiocarbonyl functionalities to difluoromethyl, and of hydroxyl to fluoro, selectively:



[1.17]



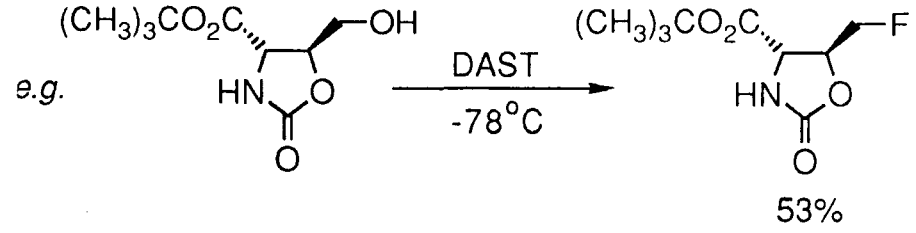
[1.18]

Other functionalities can also be manipulated, *e.g.* fluoroformates to trifluoromethyl ethers, fluoroformyl anilines to *N*-trifluoromethyl anilines.

Disadvantages of sulphur tetrafluoride lie in its volatility, toxicity (comparable to phosgene), ease of hydrolysis, which produces hydrogen fluoride, and the elevated temperatures necessary for some transformations, which can result in decomposition.

E.1.f. DIETHYLAMINO SULPHUR TRIFLUORIDE

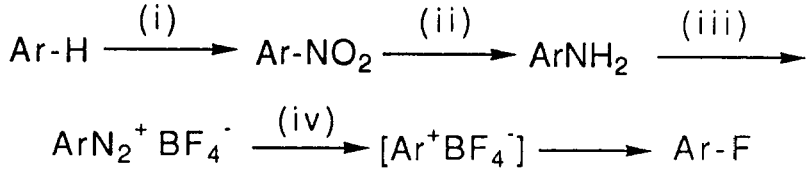
Diethylamino sulphur trifluoride (DAST) brings about similar transformations to sulphur tetrafluoride,[87] but is less volatile and hence easier to handle, and requires less forcing conditions.[88] The mild conditions used enable high selectivity to be achieved, and hence subtle structural modifications may be carried out with the knowledge that other functionalities remain unchanged (Equation 1.19).[89]



[1.19]

E.1.g. BORON TRIFLUORIDE/TETRAFLUOROBORIC ACID - (THE BALZ-SCHIEMANN REACTION)

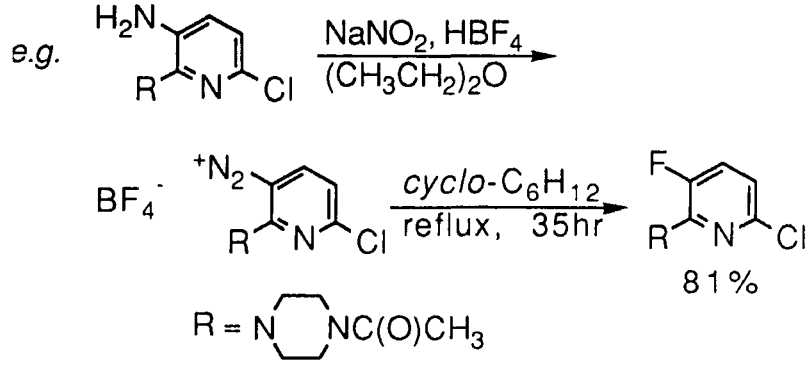
This classical reaction (Equation 1.20) remains in many cases the best method for selective incorporation of fluorine into an aromatic ring.[90,91]



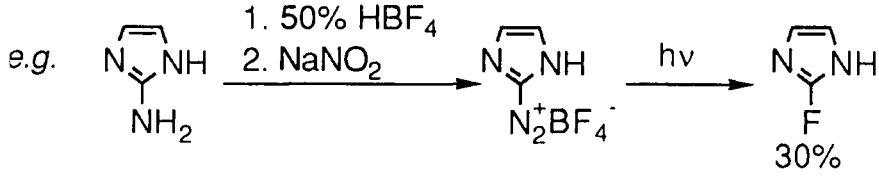
[1.20]

(i) = HNO_3, (ii) = H_2/Pt,
(iii) = 50% $HBF_4/NaNO_2$, (iv) = Δ or hv

No more than four fluorine substituents may be incorporated into a benzene ring *via* this step-wise process, since further attempted nitration results in expulsion of *para*-fluorines, giving 2,5-difluorobenzoquinone.[92]



[1.21]



[1.22]

Despite this limitation, the Balz-Schiemann reaction is a useful synthetic method for the introduction of fluorine into both

aromatic (Equation 1.21)[93] and heteroaromatic (Equation 1.22)[94,95] systems.

E.1.h. INTERHALOGEN COMPOUNDS

Species of the form XF_n (n=1,3,5,7), where X is another halogen, can be used to add XF across a multiple bond (Equations 1.26-1.28).[96] Generally, for halogen monofluorides (n=1), the gaseous reagents are prepared *in situ* (Equations 1.23-1.25),[96-99] while liquid halogen polyfluorides (n= 3, 5 or 7) are more stable and can be stored for use as required.

$$\textit{e.g.}\ AgF + Cl_2 \xrightarrow[55^\circ C,\ 24.5hr]{} [ClF] \qquad [1.23]$$

$$\textit{e.g.}\ HF + CH_3C(O)NHBr \xrightarrow[-78^\circ C]{(CH_3CH_2)_2O} [BrF] \qquad [1.24]$$

$$\textit{e.g.}\ IF_5 + 2I_2 \xrightarrow[150^\circ C,\ 24\ hr]{} [IF] \qquad [1.25]$$

Non-specificity of these reagents imposes a limit on their application (Equations 1.26-1.28).

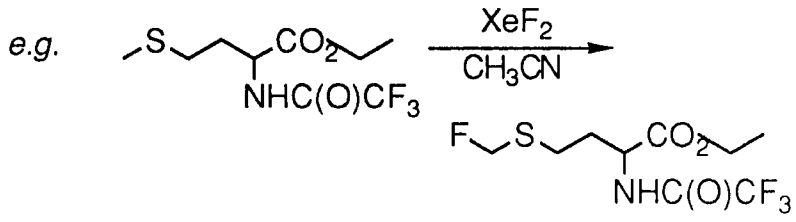
$$\textit{e.g.}\ CHCl{=}CHCl \xrightarrow[55^\circ C,\ 24.5hr]{ClF_3} \underset{25\%}{CHClF\text{-}CHCl_2} + \underset{42\%}{CHClF\text{-}CHClF} \qquad [1.26]$$

$$\textit{e.g.}\ CFCl{=}CF_2 \xrightarrow[20^\circ C,\ 2hr]{BrF_3/Br_2} \underset{13\%}{CFClBr\text{-}CF_3} + \underset{73\%}{CF_2Cl\text{-}CF_2Br} \qquad [1.27]$$

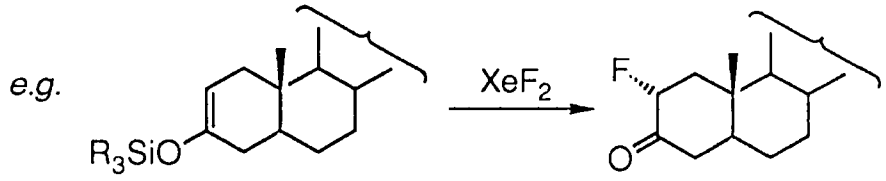
$$\textit{e.g.}\ CFCl{=}CF_2 \xrightarrow[20^\circ C,\ 2hr]{IF_5/2I_2} \underset{37\%}{CFClI\text{-}CF_3} + \underset{45\%}{CF_2Cl\text{-}CF_2I} \qquad [1.28]$$

E.1.i. XENON DIFLUORIDE

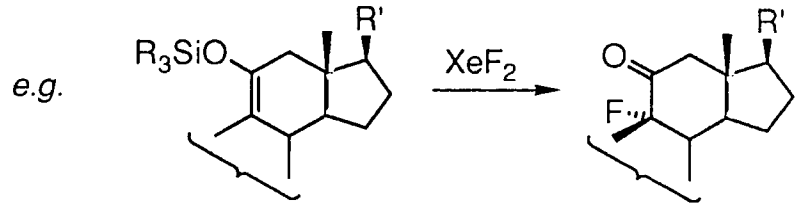
First prepared in 1962,[100] xenon difluoride of high purity (99%) may be produced by passing an electrical discharge through a mixture of the component gases at room temperature, or exposure of the mixture to ultra violet radiation. As a thermodynamically stable solid, xenon difluoride is a commercially available, easy to handle, mild and selective fluorinating agent.[44,101,102]



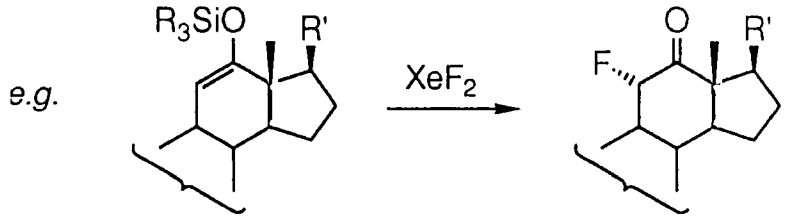
[1.29]



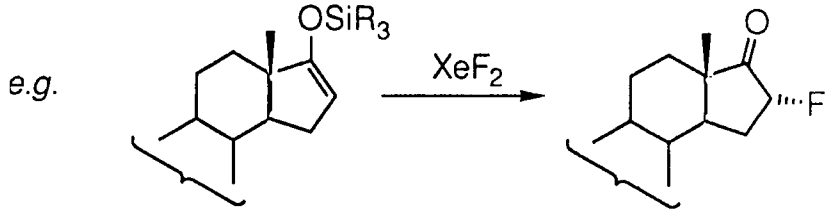
[1.30]



[1.31]



[1.32]



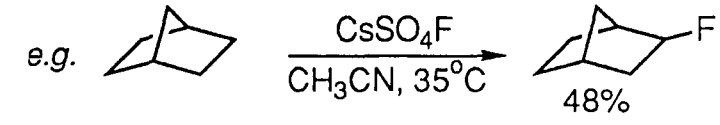
[1.33]

Fluorination proceeds *via* a radical cationic pathway,[103-108] and the reagent can be used in a variety of applications, such as addition of fluorine across double bonds[109,110] and replacement of

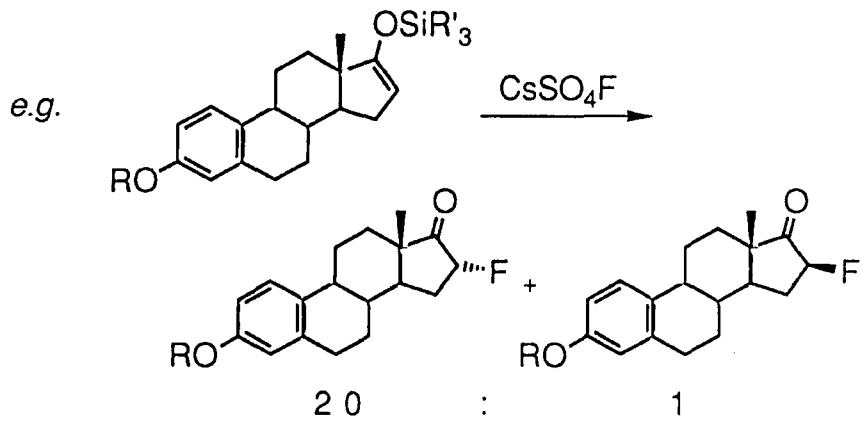
hydrogen by fluorine in aromatic systems[111,112] and in saturated hydrocarbons.[102,113]

E.1.j. CAESIUM FLUOROXYSULPHATE

Caesium fluoroxysulphate is prepared by passage of elementary fluorine through aqueous caesium sulphate solution.[114,115] The reagent operates under mild conditions as a selective fluorinating agent and can be both regio- (Equation 1.34)[116,117] and stereospecific (Equation 1.35).[3]



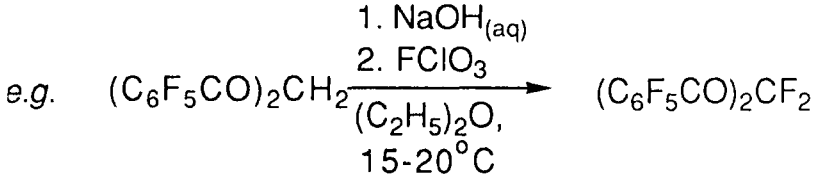
[1.34]



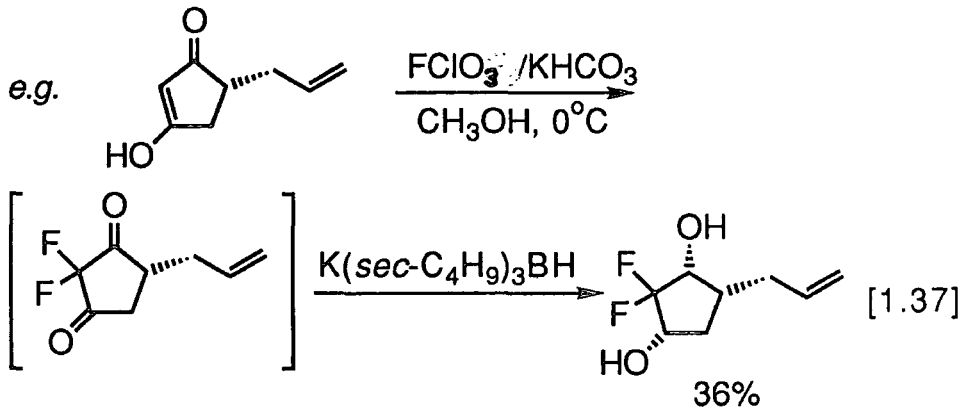
[1.35]

E.1.k. PERCHLORYL FLUORIDE

Perchloryl fluoride is an electrophilic fluorinating agent,[118,119] used under mild conditions, but with little selectivity.[120] Care must be taken in the use of perchloryl fluoride, for an explosive danger exists if the neat liquid contacts organic material.



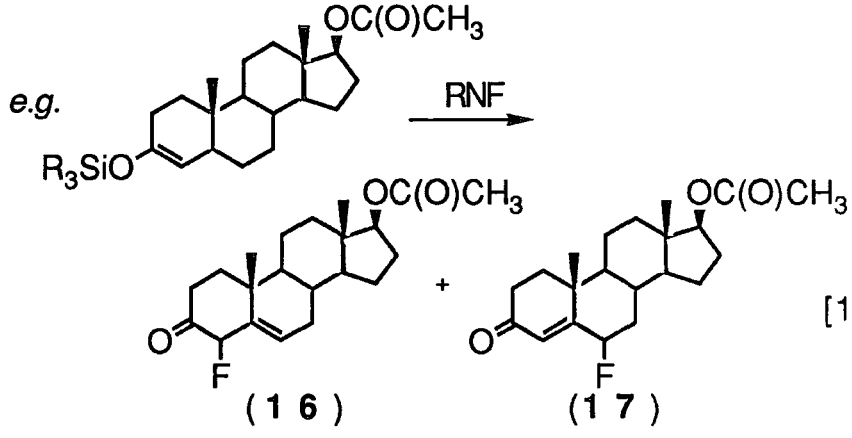
[1.36]



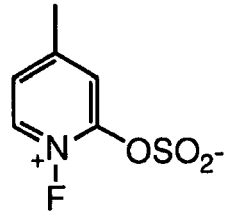
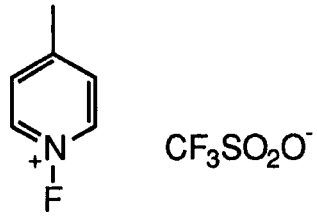
[1.37]

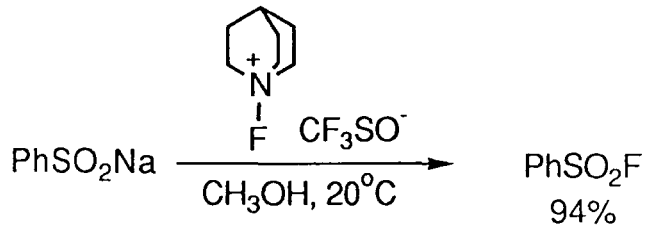
E.1.1. *N*-FLUORO COMPOUNDS

These relatively inexpensive, easily handled selective fluorinating agents have a highly specific electrophilic mode of action.[121-125]



[1.38]

RNF	Yield of (16)	Yield of (17)
	4%	68%
	15%	36%



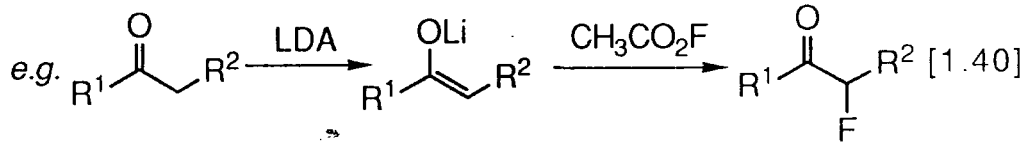
[1.39]

Many *N*-fluoro alicyclic and aromatic amines have been employed to effect fluorination of organic compounds,[44] and the use of *N*-fluoroamines and *N*-fluoroamides is a rapidly expanding field.

E.1.m. HYPOFLUORITES

E.1.m.(i). ACETYL HYPOFLUORITE

Acetyl hypofluorite is produced by direct fluorination of sodium acetate,[126] and reacts cleanly with metal enolates to form the corresponding α-fluoro ketones (Equation 1.40),[126] and with activated aromatic compounds.[127]

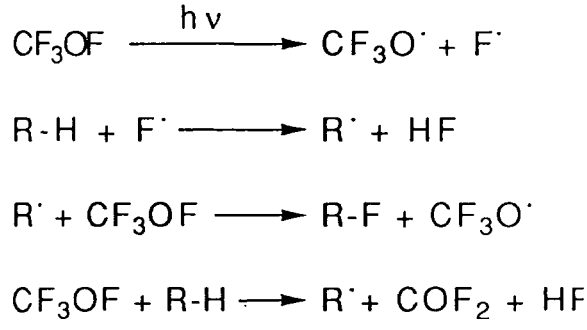


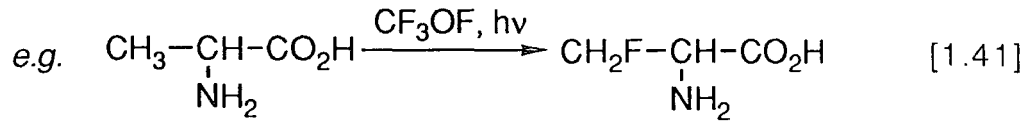
[1.40]

E.1.m.(ii). TRIFLUOROMETHYL HYPOFLUORITE

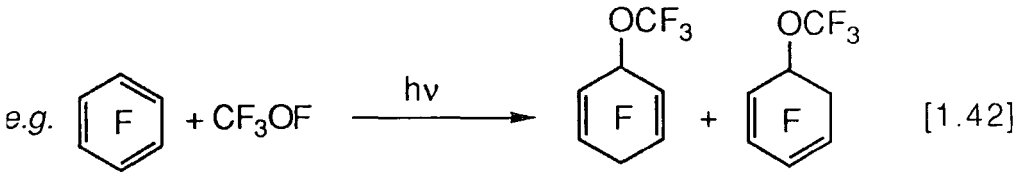
Trifluoromethyl hypofluorite, most efficiently (90% yield) prepared from carbon monoxide and elementary fluorine at 350°C,[128] provides a one-step method of introducing fluorine *via* a free radical (Scheme 1.2),[21] (Equations 1.41, 1.42)[21,22] or electrophilic process (Scheme1.3),[129,130] (Equation 1.43).[130]

SCHEME 1.2: FREE RADICAL MECHANISM OF FLUORINATION BY CF_3OF



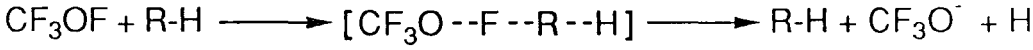


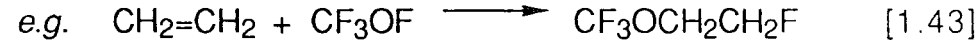
[1.41]



[1.42]

SCHEME 1.2: ELECTROPHILIC MECHANISM OF FLUORINATION BY CF_3OF





[1.43]

Low regiospecificity limits the application of trifluoromethyl hypofluorite for synthetic purposes.

E.2. FREE RADICAL POLYFLUOROALKYLATION

Free radical polyfluoroalkylation represents a quite different approach to the incorporation of fluorine into an organic compound since it differs from the examples of fluorination methods mentioned in previous sections by incorporation of a polyfluoroalkyl group rather than the substitution of hydrogen, or other leaving group, by fluorine, or addition of fluorine or hydrogen fluoride across a multiple bond.

Since the earliest days of modern fluorine chemistry in the 1940s, many reactions of this type have been carried out. From these pioneering experiments of low product selectivity,[131-134] increasing expertise in this area, mainly carried out by workers in the U.K.,[135-140] Japan[141-146] and the U.S.S.R.[147] has resulted in development of methodology for synthesis of a wide range of fluorinated organic compounds *via* these free radical processes. Chapter Two provides a fuller discussion of polyfluoroalkylation *via* free radical addition reactions.

CHAPTER TWO

FREE RADICAL ADDITION TO FLUOROALKENES

A. REVIEW OF FREE RADICAL ADDITION TO ALKENES

A.1. GENERAL INTRODUCTION

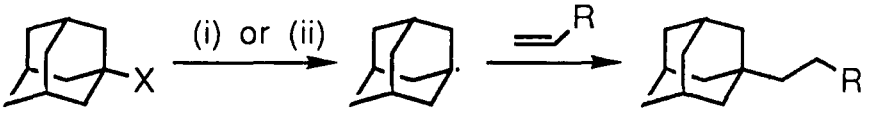
Much work has been carried out on the free radical addition to unsaturated hydrocarbons[148-151] and to highly fluorinated alkenes.[135-138,141-147,152-154] The clearest difference between these systems is the reversal of electron density, *i.e.* hydrocarbon alkenes are electron rich and so react with electrophiles, while the effect of electron withdrawing fluorine substituents is to render the double bond electron deficient, hence highly fluorinated alkenes are reactive towards nucleophilic species, in the case of this study towards nucleophilic radicals.

Recent general reviews of free radical reactions of fluorinated alkenes are available,[155-162] and this discussion will instead focus more specifically on recent developments in the area of free radical addition reactions of alkenes.

A.2. REVIEW OF RECENT WORK ON FREE RADICAL ADDITION TO ALKENES

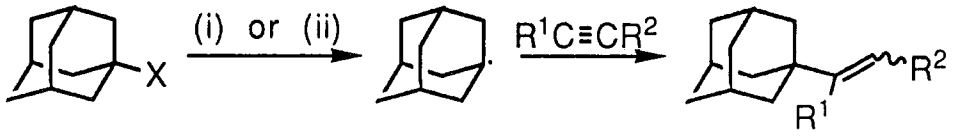
A.2.a. FREE RADICAL ADDITION OF ACYL RADICALS TO ELECTRON DEFICIENT ALKENES

Non-halogenated alkenes rendered electron deficient by the presence of electron withdrawing substituent groups are also subject to attack by nucleophilic radicals. Recent work in this area has involved the addition of the 1-adamantyl radical to alkenes and alkynes (Equations 2.1, 2.2)[163] and intermolecular addition of the acyl radical (Equation 2.15) to electron deficient alkenes (Equations 2.3, 2.4)[164] and cyclisation reactions (Equation 2.5).[165]



[2.1]

X = Cl, Br, I (i) = $(n\text{-}C_4H_9)_3SnH$, AIBN, Δ (ii) = Zn-CuI, sonication R = CN, $C(O)CH_3$, CO_2R', $S(O)C_6H_5$



[2.2]

X = Cl, Br, I

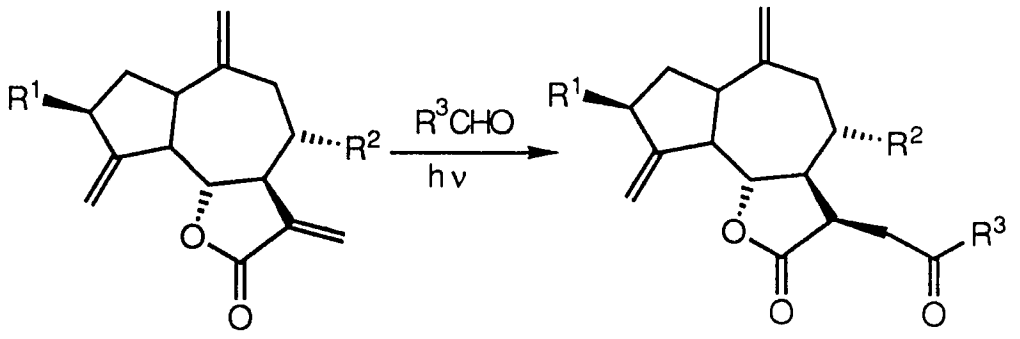
(i) = $(n\text{-}C_4H_9)_3SnH$, AIBN, Δ

(ii) = Zn-CuI, sonication

R^1 = H, R^2 = CN, CO_2CH_3, C_6H_5

R^1 = Cl, R^2 = CN

$R^1 = R^2 = CO_2CH_3$



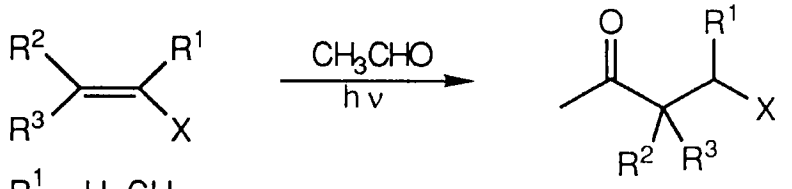
[2.3]

R^1 = H, OH, $OSi(CH_3)_2(t\text{-}C_4H_9)_2$

R^2 = H, OH, $OC(O)C(=CH_2)CH_2OH$

R^3 = CH_3, C_6H_5

up to 63%



[2.4]

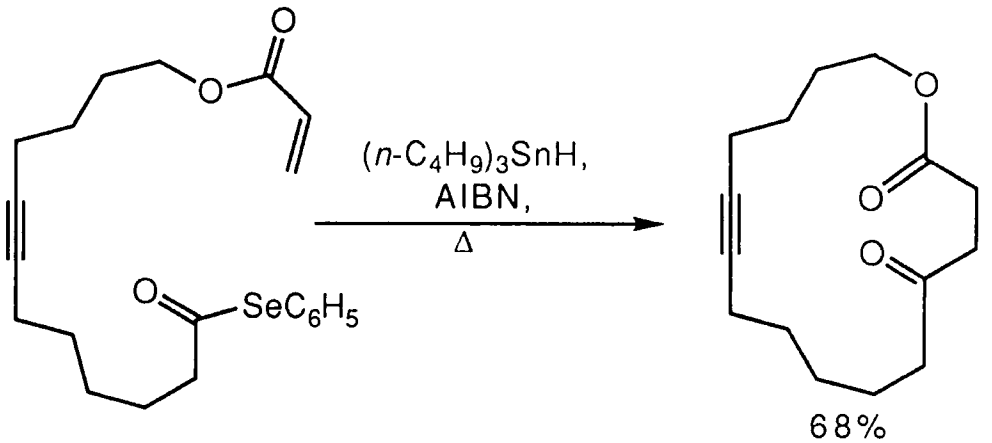
R^1 = H, CH_3

R^2 = H, CH_3, C_6H_5

R^3 = H, CH_3

X = C(O)R (R = alkyl, alkoxy, NH_2), CN

up to 99%



[2.5]

68%

A.2.b. FREE RADICAL ADDITION TO FLUOROALKENES AND FLUOROALKYNES

A number of research groups have recently reported their results on free radical reactions of unsaturated fluorinated compounds, and a summary of this work is given here.

The only reaction recently reported in which a perfluoroalkyne was made to undergo free radical addition to organic compounds was the radiation induced addition of alcohols to hexafluorobut-2-yne (Equation 2.6).[166]

$$CF_3C{\equiv}CCF_3 + R^1R^2CHOH \xrightarrow{\gamma\text{-rays}} \underset{E}{\overset{F_3C}{\underset{H}{\overset{CR^1R^2OH}{\underset{CF_3}{=}}}}} + \underset{Z}{\overset{F_3C}{\underset{H}{\overset{CF_3}{\underset{CR^1R^2OH}{=}}}}} \qquad [2.6]$$

$R^1 = R^2 = H$, 29%(E/Z = 100/0)
$R^1 = H$, $R^2 = CH_3$, 67% (E/Z = 55/45)
$R^1 = H$, $R^2 = C_2H_5$, 26% (E/Z = 47/53)
$R^1 = R^2 = CH_3$, 88%(E/Z = 9/91)

Product stereochemistry was observed to be dependant on steric interactions between trifluoromethyl groups on the alkyne and alkyl substituent groups on the alcohol.

Chen[167] has carried out a series of reactions in which thermal addition of carbon tetrachloride to the terminal alkene perfluorohept-1-ene was effected (Equation 2.7).

$$n\text{-}C_5F_{11}CF{=}CF_2 + CCl_4 \xrightarrow[\Delta]{\text{(i) or (ii) or (iii) or (iv)}} n\text{-}C_5F_{11}CFClCF_2CCl_3 \quad \text{up to 60\%} \qquad [2.7]$$

(i) = $Ni(P(C_6H_5)_3)_4$,
(ii) = $Ni(P(C_6H_5)_3)_2(CO)_2$,
(iii) = benzoyl peroxide,
(iv) = AIBN

These reactions proceeded in an entirely unidirectional manner most probably as a result of steric considerations.

Much work has been carried out regarding the free radical reactions of tetrafluoroethene and chlorotrifluoroethene, generally the telomerisation reactions thereof. One study, however, is an interesting exception.[168] This publication reports the ease with which the selectivity of the reaction between these fluoroalkenes and perfluoroalkyl dichloroamines of the form R_FNCl_2 (R_F = CF_3, C_2F_5) may be controlled (Equations 2.8, 2.9) by means of reaction temperature.

$$R_FNCl_2 + CF_2{=}CFX \xrightarrow[12\text{-}14\ hr]{65\text{-}70^\circ C} R_FN(CF_2CFXCl)Cl \qquad [2.8]$$

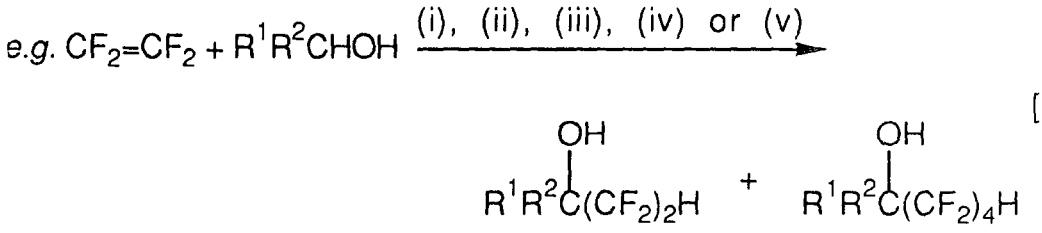
60-80%

$$R_FNCl_2 + CF_2{=}CFX \xrightarrow[12\text{-}14\ hr]{95\text{-}100^\circ C} R_FN(CF_2CFXCl)_2 \qquad [2.9]$$

R_F = CF_3, C_2F_5
X = F, Cl

60-65%

Czech workers[169-172] have reported the peroxide or photochemically initiated reactions between perfluoroalkenes and aliphatic alcohols. In reactions involving addition of alcohols to tetrafluoroethene (Equation 2.10), use of longer wavelength ultra violet radiation was claimed to give high yields (73-82%) of 1:1 adduct and 2:1 telomer, with high selectivity between these species being possible under certain conditions. No higher telomers were reported.

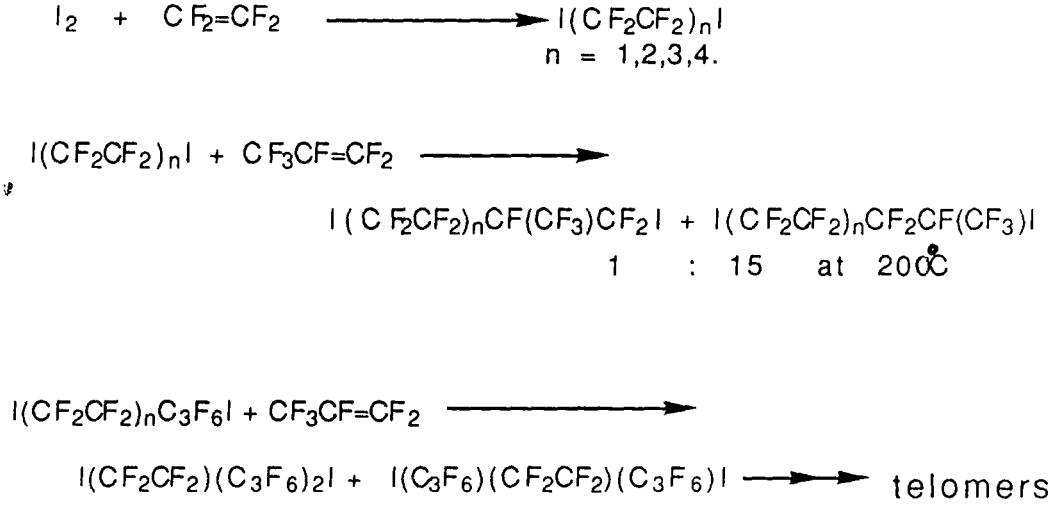


[2.10]

(i) = AIBN, hv (ii) = benzoin methyl ester, hv
(iii) = benzophenone, hv (iv) = acetone, hv
(v) = benzoyl peroxide

Two papers examining the telomerisation of tetrafluoroethene,[173] hexafluoropropene[173] and chlorotrifluoroethene[174] have been published. These publications are primarily concerned with the telogens used to effect telomerisation. Both papers cite the use of diiodoperhaloalkanes as effective telogens (Scheme 2.1).

SCHEME 2.1: TELOMERISATION OF TETRAFLUOROETHENE AND HEXAFLUOROPROPENE



Formation of telomers of tetrafluoroethene may be controlled by altering reaction parameters, *e.g.* temperature, reactant ratios. However, no discrete telomers of hexafluoropropene have been isolated, instead only 'bands' of approximate composition may be produced.

SCHEME 2.2: TELOMERISATION OF CHLOROTRIFLUOROETHENE

$$I_2 + CF_2{=}CFCl \xrightarrow{\gamma\text{-rays}} ICF_2CFClI \quad \text{quantitative}$$

$$I_2 + CF_2{=}CFCl \xrightarrow{h\nu} I(CF_2CFCl)_nI$$

$$I(CF_2CFCl)_nI + CH_2{=}CH_2 \xrightarrow{Pt/C} ICH_2CH_2(CF_2CFCl)_nCH_2CH_2I \quad 32\%$$

Chlorotrifluoroethene may be telomerised as shown (Scheme 2.2), and the telomers thus formed reacted with ethene, using a catalyst, to produce telechelic cooligomers.

A.3. REVIEW OF CHEMISTRY OF *2H*-PENTAFLUOROPROPENE

It is unfortunate that the only review of chemistry carried out using the unusual polyfluorinated alkene *2H*-pentafluoropropene was written in Russian,[234] thereby limiting its potential readership. The following section is intended to provide a brief account of recent work in this area.

A.3.a. PREPARATION

2H-Pentafluoropropene is readily prepared in good yield by decarboxylative decomposition of the sodium salt, or mixed sodium and potassium salts, of hexafluoro-*i*-propanoic acid (Equation 2.11)[235,236]

$$(CF_3)_2CHCO_2M \xrightarrow[-CO_2]{} CF_3CH{=}CF_2 + MF \qquad [2.11]$$

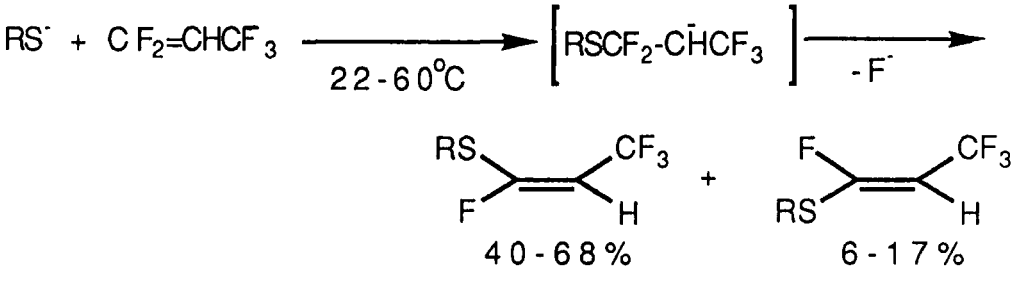
M = Na, K/Na

M = Na, 83%
M = Na/K, 88%

A.3.b. REACTIONS OF *2H*-PENTAFLUOROPROPENE

A.3.b.(i). CARBANION CHEMISTRY

Haszeldine and co-workers[181] have made a thorough examination of nucleophilic attack on *2H*-pentafluoropropene by sulphide ions (Equation 2.12).

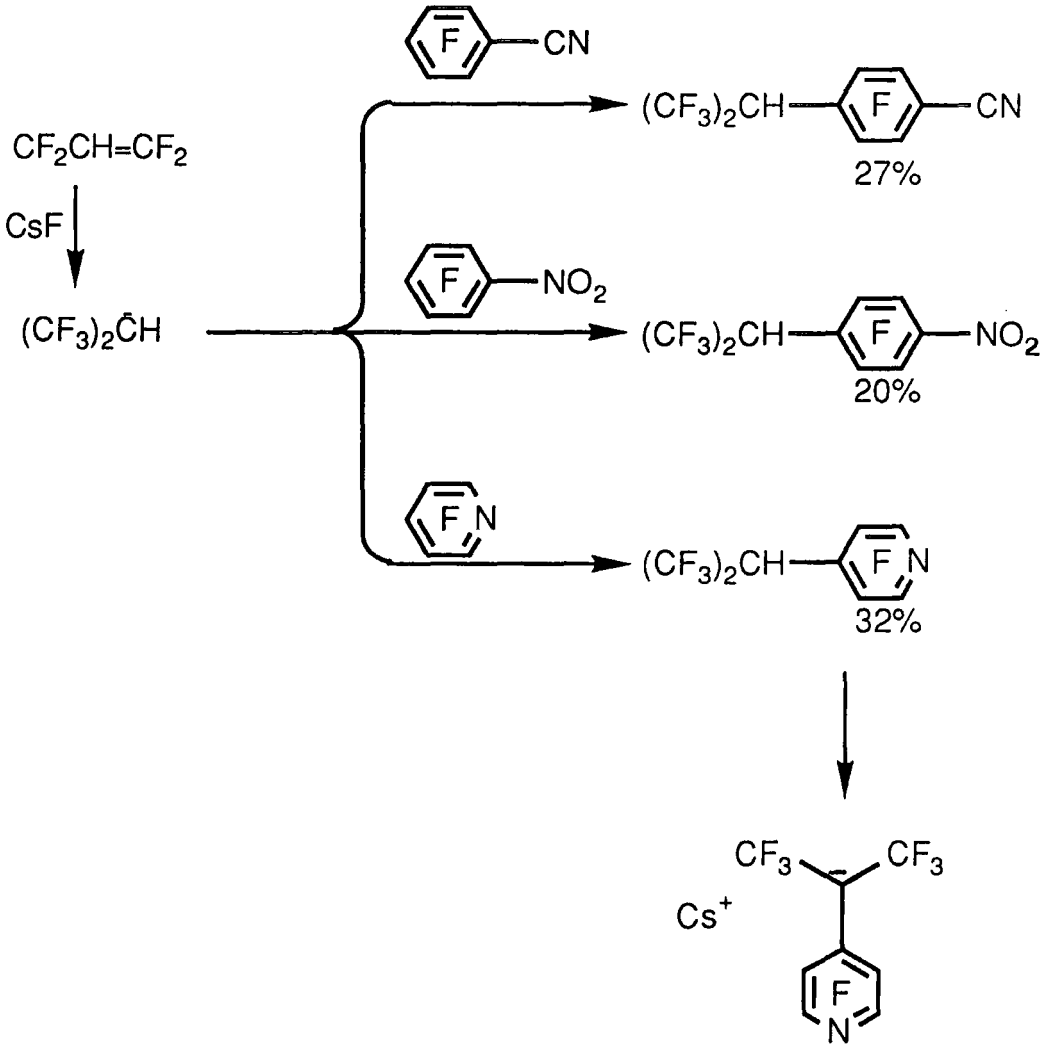


[2.12]

It can be seen that the carbanion thus generated does not preferentially proton abstract to give the saturated analogue (though low levels of saturated species were detected in two experiments), but instead loses fluoride ion to give the substitution products, predominantly the product of *anti* addition.

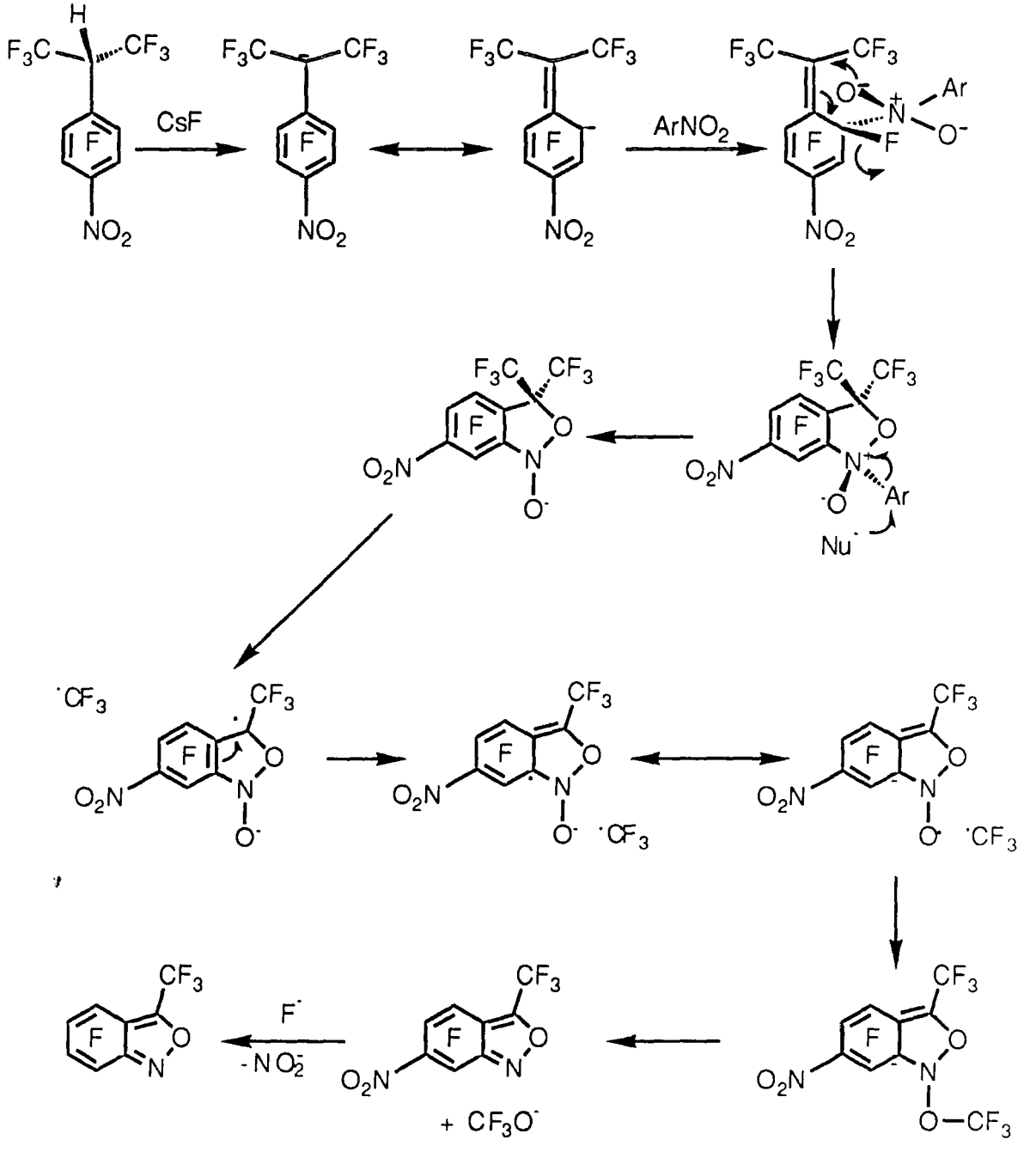
Further reactions of carbanions derived from *2H*-pentafluoropropene have been reported.[177-179] Chambers and coworkers[179] have used caesium fluoride as the nucleophilic species to generate the hexafluoro-*i*-propyl carbanion, which was subsequently trapped using activated fluorobenzenes (Scheme 2.3).

SCHEME 2.3: TRAPPING OF *2H*-PENTAFLUOROPROPENE DERIVED CARBANIONS



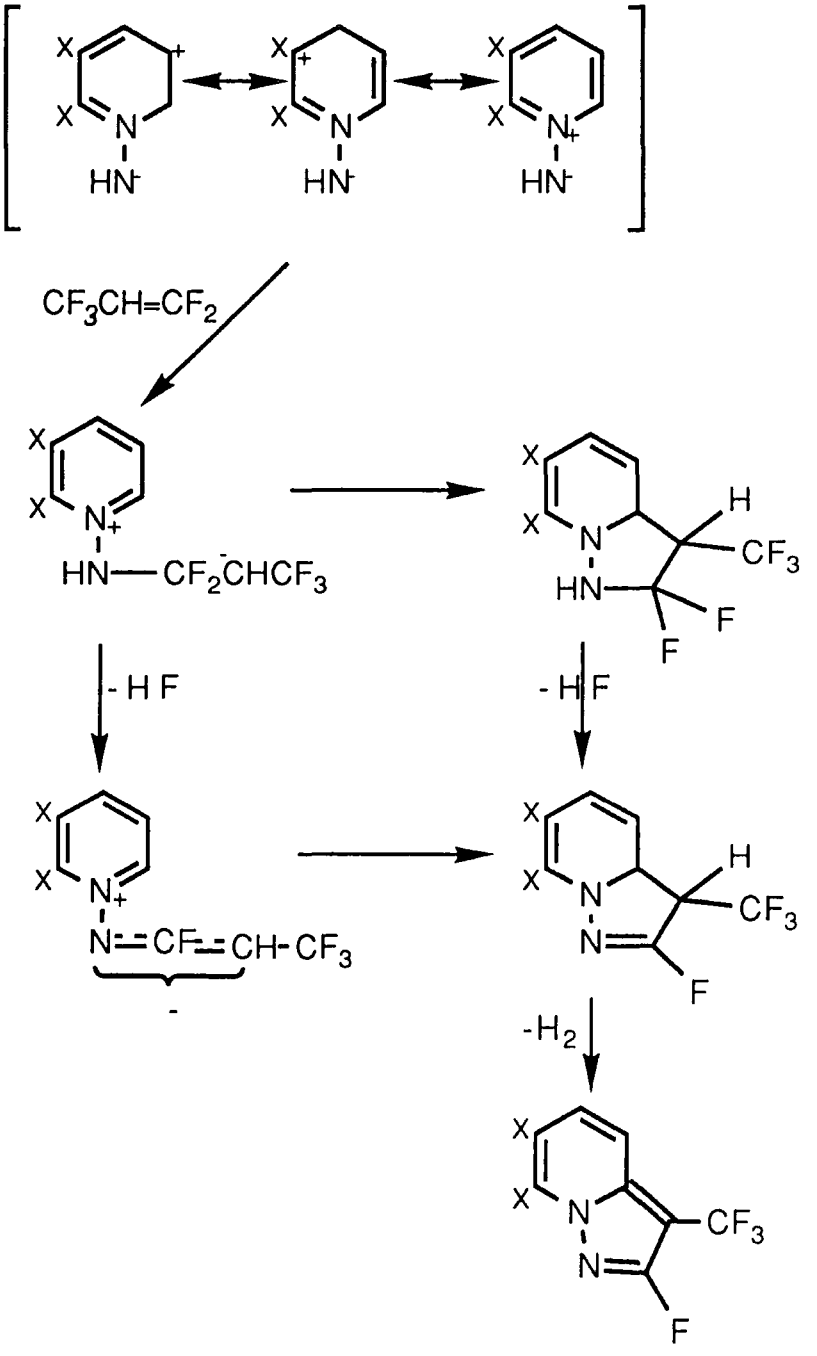
The product of the reaction with perfluoronitrobenzene can undergo further reaction to give an isoxazole, and a mechanism has been proposed by which this transformation may occur (Scheme 2.4).

SCHEME 2.4: ISOXAZOLE FORMATION



Banks and co-workers[177,178] have reacted *2H*-pentafluoropropene with *N*-iminopyridinium ylides, producing the addend carbanion, which subsequently cyclises to pyrazolo-[1,5-a]-pyridine (Scheme 2.5). The mechanism which has been suggested, though as yet unconfirmed, is a stepwise one.

SCHEME 2.5: PYRAZOLO-[1,5-a]-PYRIDINE FORMATION



A.3.b.(ii). ADDITION OF INORGANIC COMPOUNDS TO THE DOUBLE BOND

Addition of inorganic species to the double bond of *2H*-pentafluoropropene has been reported, and a summary of these reactions is given here.

Photochemical addition of RS-Cl ($R=(CF_3)_2N$) has been reported by Tipping[182] to proceed bidirectionally (Equation 2.13), while the thermal addition of S_2Cl_2 gave rise to a mixture of products (Equation 2.14).[237]

$$(CF_3)_2NS\text{-}Cl + CF_2{=}CHCF_3 \xrightarrow[30\ hr]{h\nu} \begin{matrix} (CF_3)_2NSCH(CF_3)CF_2Cl\ 35\% \\ + \\ (CF_3)_2NSCF_2CHClCF_3\ 22\% \end{matrix} \quad [2.13]$$

$$S_2Cl_2 + CF_2{=}CHCF_3 \xrightarrow{150\text{-}160^{\circ}C} \begin{matrix} CF_3CHClCF_2S_nCl \\ + \\ (CF_3CHClCF_2)_2S_n \\ n = 2,3 \end{matrix} \quad [2.14]$$

Soviet workers[238,239] have succeeded in adding fluorosulphates to *2H*-pentafluoropropene (Equations 2.15, 2.16).

$$ISO_3F + CF_2{=}CHCF_3 \longrightarrow FSO_3CF_2CHICF_3 \quad [2.15]$$

$$O_2NSO_3F + CF_2{=}CHCF_3 \longrightarrow FSO_3CF_2CH(CF_3)NO_2 \quad [2.16]$$

Photochemical reaction of SF_5Cl with *2H*-pentafluoropropene gives the simple addition product (Equation 2.17),[180] which may be further manipulated by dehydrochlorination and indirect addition of the elements of HF as shown in Equation 2.18.[180]

$$CF_2{=}CHCF_3 + SF_5Cl \longrightarrow SF_5CH(CF_3)CF_2Cl \quad [2.17]$$

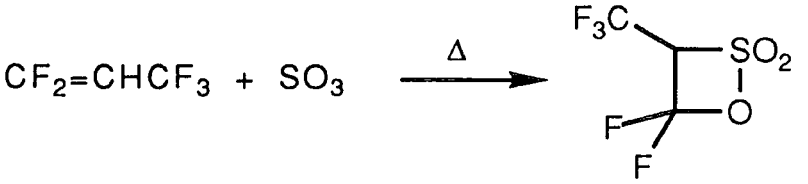
$$SF_5CH(CF_3)CF_2Cl \xrightarrow{KOH} \begin{matrix} F_3C \\ F_5S \end{matrix}\!\!>\!\!=CF_2$$

$$\xrightarrow{KF/HC(O)NH_2} SF_5CH(CF_3)CF_3 \quad [2.18]$$

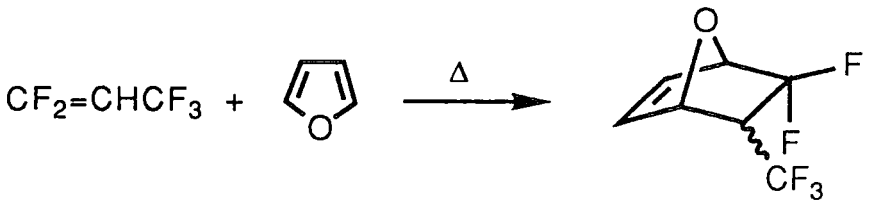
A.3.b.(iii). CYCLOADDITION

Few cycloaddition reactions involving *2H*-pentafluoropropene have been carried out, and only two papers[175,176] have been published in recent years.

Knunyants and co-workers[175] have synthesised a β–sultone in 1975 from the thermal [2+2] cycloaddition of sulphur trioxide and *2H*-pentafluoropropene (Equation 2.19) and in 1988 another paper by Knunyants' team[176] reported the [4+2] thermal cycloaddition of furan and *2H*-pentafluoropropene (Equation 2.20).



[2.19]

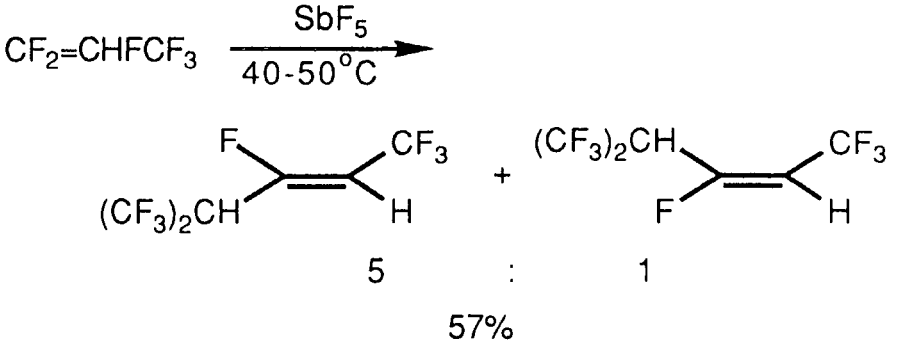


[2.20]

A.3.b.(iv). MISCELLANEOUS REACTIONS OF *2H*-PENTAFLUOROPROPENE

Other miscellaneous reactions of *2H*-pentafluoropropene reported in recent years have originated in Soviet laboratories.[183,248]

One group found that dimerisation of *2H*-pentafluoropropene under pressure and in the presence of antimony pentafluoride gave predominantly *cis* product (Equation 2.21),[248] while the free radical copolymerisation of *2H*-pentafluoropropene and 1,2-difluoroethene (vinylidene fluoride) was reported by a group at Tashkent University.[183]



[2.21]

A.3.c. CONCLUSIONS

It is clear that relatively little work has been carried out with *2H*-pentafluoropropene, though some areas, principally carbanion chemistry, addition of inorganic species across double bonds and cycloadditions have been shown to give good results.

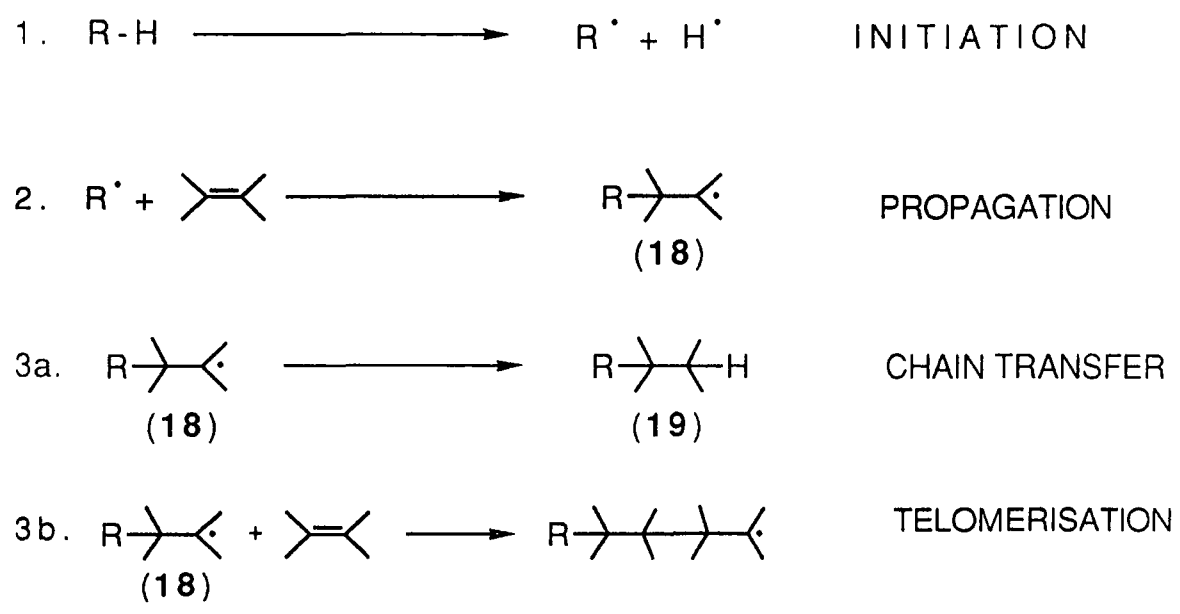
It is surprising that little free radical chemistry of *2H*-pentafluoropropene has been investigated since the free radical chemistry of so many other fluoroalkenes is well documented. Consequently, study of the free radical chemistry of *2H*-pentafluoropropene was made in parallel to its fully fluorinated analogue.

A.4. MECHANISM OF FREE RADICAL ADDITION

In the generally applicable case in which R-H is added across a double bond, the mechanism of addition follows the steps shown in Scheme 2.6.

Initially, homolytic cleavage of the R-H bond occurs to produce the organic radical R•, which reacts with an alkene molecule to give the radical mono-adduct (**18**), which may then proceed to Step 3a, giving rise to molecular mono-adduct (**19**), or to Step 3b, if thermodynamically favourable, to give rise to telomeric species. If the latter pathway is followed, Step 3b may occur several more times before chain transfer *via* hydrogen atom abstraction, similar to Step 3a, terminates the chain growth.

SCHEME 2.6: MECHANISM OF FREE RADICAL ADDITION TO ALKENES



A.4.a. INITIATION METHODS

Three main methods of initiation are used: chemical initiation, radiation initiation, and redox initiation. The first two forms were employed in this study and will now be discussed. Discussion of initiation methods using single electron reduction or oxidation processes may be found elsewhere.[184]

A.4.a.(i). CHEMICALLY INDUCED INITIATION

Chemically induced initiation involves homolytic thermolysis of weak bonds in organic species such as peroxides to give the corresponding radicals (Equation 2.22), which initiate reaction by hydrogen atom abstraction (Equation 2.23).

$$RO\text{-}OR \xrightarrow{\Delta} 2RO^{\cdot} \qquad [2.22]$$

$$2RO^{\cdot} + R'\text{-}H \longrightarrow ROH + R'^{\cdot} \qquad [2.23]$$

Peroxide initiation can give rise to a high yield of products but is useful only within a narrow temperature range over which the half life of the peroxide of choice is suitably short. Such reaction temperatures can lead to thermal degradation of reactants or products. Contamination of products with chemical initiators or peroxide degradation products necessitates an additional step of purification following reaction.

A.4.a.(ii). RADIATION INDUCED INITIATION

Radiation induced initiation is a 'cleaner' method of initiation, since no chemical additives need be present in the reactant mixture, and reactions of this type are generally temperature independant, relying on the energy of the incident initiating radiation or electrons. Hence, photons or electrons must have an energy equal to, or greater than, that of the bond to be cleaved.

Ultraviolet radiation has been used effectively in some circumstances,[139,147,171,172] but can be less selective a technique than initiation by γ-radiation. This is due to the high energy species (R*) produced by this method, resulting from initial excitation of a ultraviolet active chromophore, *e.g.* C=O, promoting an electron from a π to a π^* orbital (Equation 2.24), which subsequently loses energy through collisions which in turn may, in some cases, cause bond cleavage, *i.e.* initiation.

$$\underset{\text{ground state}}{R\ (\pi)} \xrightarrow{h\nu} \underset{\text{excited state}}{[R^{\cdot}]\ (\pi^{*})} \qquad [2.24]$$

In contrast, it is believed that secondary electrons produced from interaction between γ-rays and the metal γ-source housing are of a lower energy and hence the corresponding initiating species are less energetically excited, thus more selectively inducing C-H bond cleavage.

Additional factors which could have a bearing on these reactions are the increased temperature at which ultraviolet reactions which will subsequently be discussed took place (measured to be *ca.* 60°C), because of the heating effect of the ultraviolet lamp, and the possibly greater radical flux produced by ultraviolet radiation, since a higher proportion of this radiation may interact with matter while the majority of γ-photons pass through unaffected.

The processes by which radiation may interact with matter are summarised in Figure 2.1. At energies below *ca.* 1MeV ($\lambda=1.2\times10^{-12}$m) the Photoelectric Effect is predominant. This process involves interaction of the γ-photon with an inner shell electron, whereby the energy of the photon is used to overcome electrostatic attractive forces binding the electron within the atom. Any residual energy of the photon is observed as kinetic energy of the freed electron.

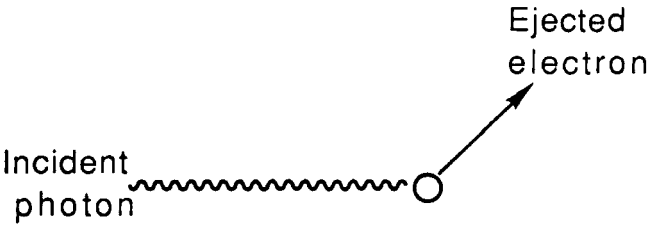
The Compton Effect is observed for photon energies around 1MeV, and is the method by which ^{60}Co γ-radiation interacts with matter and initiates free radical reactions, as this nucleus decays to ^{60}Ni (Equation 2.25), emitting β-particles which are absorbed by the source housing, and γ-rays with energies of1.332MeV and 1.173MeV. The Compton Effect involves interaction between incident radiation and an outer shell electron such that the photon is deflected from its original pathway with a reduced energy and the electron is accelerated as shown. Decrease in photon energy is dependent on angle of deflection, θ, and energy imparted to the electron.

$$^{60}_{27}\mathrm{Co} \longrightarrow {}^{60}_{28}\mathrm{Ni} + {}^{0}_{-1}\beta^{-} + \gamma \qquad [2.25]$$

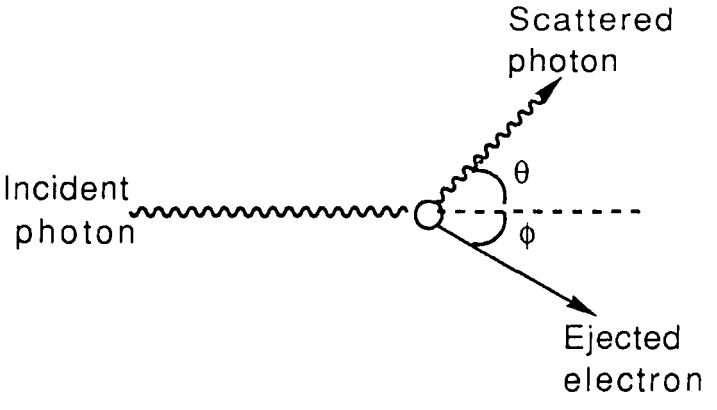
The third method by which high energy radiation may interact with matter is *via* pair production. In this scenario photon energy is used to produce an electron and a positron near to the nucleus. For this to occur the photon must possess an energy of 1.02MeV or greater, since this is the rest mass of the electron-positron pair produced. Residual photon energy is observed following pair production as kinetic energy of the pair.

FIGURE 2.1: METHODS OF INTERACTION BETWEEN RADIATION AND MATTER

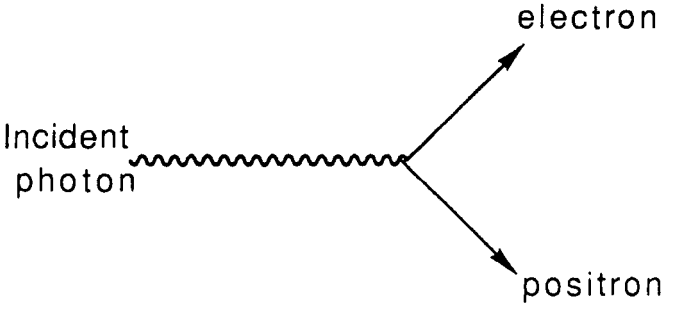
The Photoelectric Effect



The Compton Effect



Pair Production

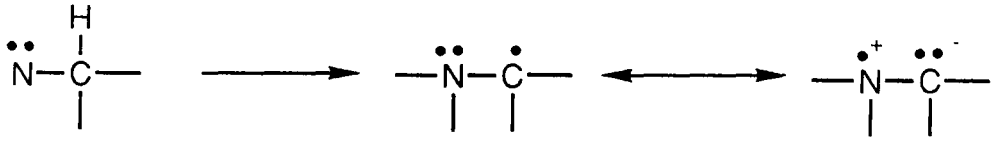


The result of any of these processes is production of high energy secondary electrons, which lose energy by collisions with matter, causing consequent excitation of the molecules within. Such excited

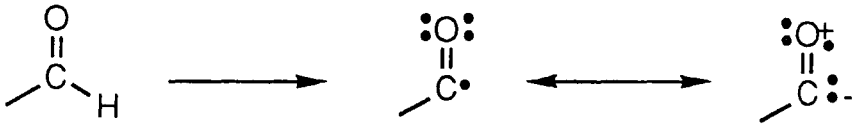
molecules can lose energy in a variety of ways,[185] one common way being cleavage to give free radicals.

A.4.b. RADICAL STABILITY

If a heteroatom with a lone pair of electrons, *e.g.* O, N, S, or a functionality with π-electrons, is present in a molecule in a position α to C-H, radical formation at that site will be favoured[186] due to donor substituent group stabilisation of the radical (Equation 2.26, 2.27).



[2.26]



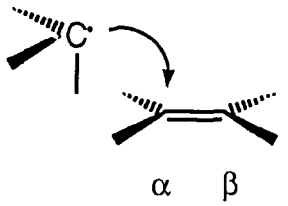
[2.27]

A.4.c. FACTORS AFFECTING ORIENTATION OF ADDITION

A.4.c.(i). THEORETICAL CONSIDERATIONS

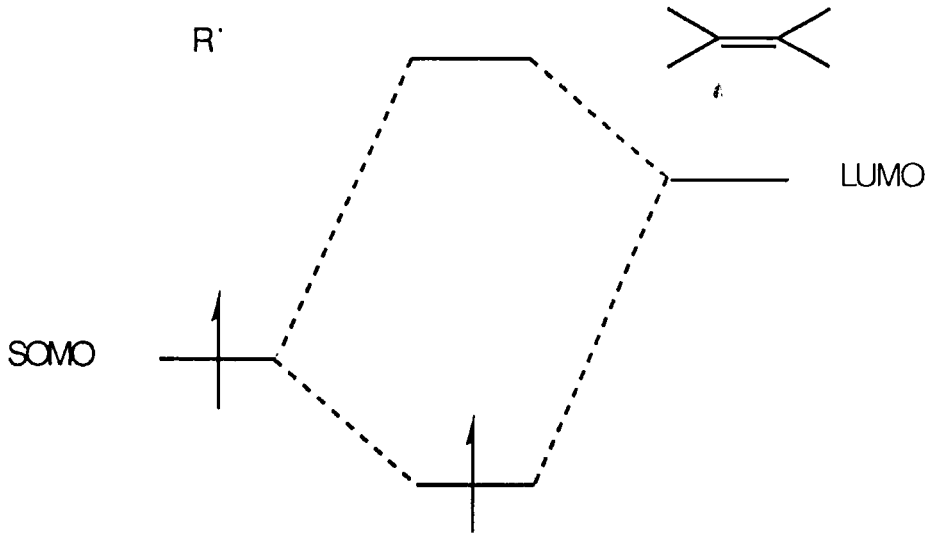
The addition of an alkyl or acyl radical to an alkene is an exothermic process and the Hammond postulate[187] indicates that an early transition state will exist, with the geometry of this transition state most closely resembling that of reactants. Hence it can be seen (Figure 2.2) that the transition state is unsymmetrical and interactions between α-substituents and the approaching radical will dominate over those between β-substituents and the radical.

FIGURE 2.2: ATTACK OF RADICAL ON ALKENE



This early transition state geometry and the ability to neglect β-effects enables a Frontier Orbital (FO) theory approach to be considered.[150] In the case of the reaction between a highly fluorinated alkene and a nucleophilic radical, the relevant frontier orbitals of interest are the alkene Lowest Unoccupied Molecular Orbital (LUMO) and the radical Singly Occupied Molecular Orbital (SOMO) (Figure 2.3).

FIGURE 2.3: FRONTIER ORBITAL INTERACTIONS



Since substitution of the alkene by electronegative species, such as fluorine, reduces LUMO energy, and nucleophilic radicals have high SOMO energies, the difference in energy between these MOs is small, and reaction is thus promoted.

A.4.c.(ii) EXPERIMENTAL FINDINGS ON STERIC AND ELECTRONIC INFLUENCES ON ORIENTATION OF ATTACK

For an unsymmetrical alkene, it is found that the less sterically hindered end of the double bond will be preferentially attacked.[188,189] It is also found that the polarity of the attacking radical, and that of the alkene, will have a bearing on the orientation of attack. In the examples given in Equation 2.28, these factors are working in unison to promote attack at the most electrophilic carbon. However, in the case of the free radical addition of RSH to $CF_2=CFCF_3$, polar effects

were shown to be of considerable importance, where steric influences did not work in concert.[188]

As electrophilicity of the attacking radical species increases a greater proportion of attack is observed to occur at the less electrophilic end of the double bond, despite steric factors which promote attack at the opposite end.

e.g. $RSH + CF_2{=}CFCF_3 \longrightarrow$

$$RSCF_2CHFCF_3 + RSCF(CF_3)CHF_2 \quad [2.28]$$

	(**20**)	(**21**)
$R = CH_3$,	92%	8%
$R = CH_2CF_3$,	70%	30%
$R = CF_3$,	45%	55%

The conclusion which can be drawn is that both steric and electronic effects play a significant part in the process of free radical addition to alkenes, though it is generally accepted[150,186,190,191] that steric influences play the major role.

A.4.d. TELOMERISATION

Telomerisation can be seen (Scheme 2.6) to compete with chain transfer. Many factors affect whether or not telomerisation will occur:[192] reaction conditions, such as temperature of reaction and reactant ratios; thermodynamics of each reaction step; steric considerations; electronic considerations, *i.e.* polarity of species, lone pair repulsive interactions. While, for a given monomer species, some of these factors are fixed, changing reaction conditions or telogen used can lead to changes in product (Equations 2.29, 2.30).

$$CH_2{=}CF_2 + C_2F_5I \xrightarrow[190^\circ C,\ 45hr]{} C_2F_5(CH_2CF_2)_nI \quad [2.29]$$

n=1, 92%
n=2, 6%
n=3, 2%

$$CH_2{=}CF_2 + i\text{-}C_3F_7I \xrightarrow[220^{\circ}C,\ 36hr]{} i\text{-}C_3F_7(CH_2CF_2)_nI \quad [2.30]$$

n=1, 2%
n=2, 21%
n=3, 29%
n=4, 26%
n=5, 18%
n=6, 4%

B. PRESENT WORK - FREE RADICAL ADDITION REACTIONS OF FLUORINATED ALKENES

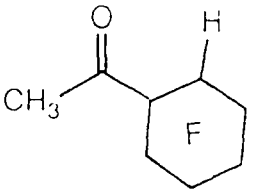
B.1 OBJECTIVES OF THE PROJECT

The aim of this section was to synthesise, *via* free radical routes, functionalised organic compounds containing polyfluorinated substituent groups. Since the free radical chemistry of *2H*-pentafluoropropene is largely unknown, it was of interest to examine its reactions in parallel with those of hexafluoropropene, and to compare and contrast results.

In addition, the relative reactivity of different species in these types of reaction was explored.

B.2. ADDITION OF ALDEHYDES TO FLUOROALKENES

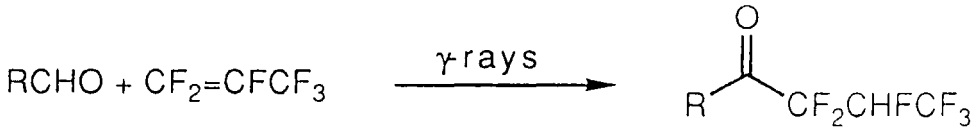
Previous workers have reported the addition of saturated aldehydes to perfluoroalkenes[137,139,143] and perhaloalkenes, in high yield.

e.g. CH_3CHO +  $\xrightarrow[85^{\circ}C]{\text{benzoyl peroxide}}$  [2.31]

89%

B.2.a. REACTIONS WITH ALIPHATIC ALDEHYDES

Results of free radical addition reactions between hexafluoropropene and saturated aldehydes are given in Table 2.1. Previously studied reactions are indicated by reference.



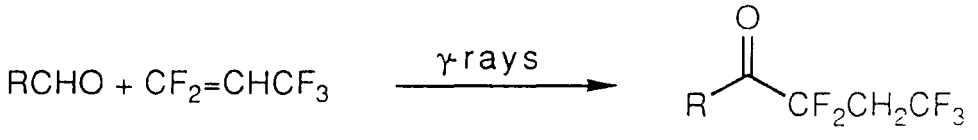
[2.32]

TABLE 2.1: REACTIONS BETWEEN HEXAFLUOROPROPENE AND ALDEHYDES

R	conversion	References
CH_3	100%	137
C_2H_5	100%	-
n-C_3H_7	100%	193
n-C_4H_9	87% (**66**)	-
$(CH_3)_3C$	54% (**68**)	194
$OHC(CH_2)_{10}$*	100% (**70**) (diadduct)	194

* Dodecanedial supplied by Shell U.K.

Syntheses of novel pentafluoro substituted ketones, from reactions of *2H*-pentafluoropropene, are given in Table 2.2.



[2.33]

TABLE 2.2: REACTIONS BETWEEN *2H*-PENTAFLUOROPROPENE AND ALDEHYDES

R	conversion
CH_3 (**61**)	73%
C_2H_5 (**63**)	83%
n-C_3H_7 (**65**)	87%
n-C_4H_9 (**67**)	80%
$(CH_3)_3C$ (**69**)	27%

B.2.b. CONCLUSIONS

From Table 2.1, it can be seen that the difunctional compound dodecanedial, which may be prepared by sequential ring opening of

cyclo-dodecene,[195,196] electrochemical oxidation of 1,12-dodecanediol,[197,198] chemical reduction of 1,12-dodecanedioic acid[199] or rhodium catalysed hydroformylation of 1,9-decadiene,[200] reacted quantitatively with hexafluoropropene. This is a particularly interesting area since it touches on the effect of one functionality on the reactivity of another within the same molecule. In the case of dodecanedial it is clear that no detrimental effect occurs, however in this case the two functionalities are well separated structurally. Few compounds containing two closer functionalities relevant to this study are commercially available, but Section B.7 gives an example of an internal competition reaction with one such compound, 1-pyrrolidinecarboxaldehyde, and a more detailed study of the effect of two functionalities on reactivity is available elsewhere.[160]

While only two hexafluoro substituted ketones are previously unreported, all five pentafluoropropyl ketones are new compounds.

From the NMR spectra of pentafluoropropyl ketones which were synthesised (Table 2.2), it is clear that free radical addition to *2H*-pentafluoropropene was unidirectional.

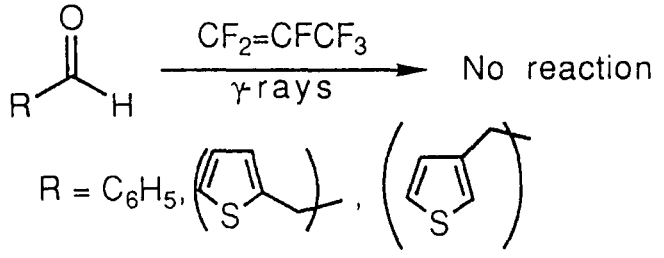
The ^{19}F NMR spectra of these compounds are characteristic of the geminal dihydropentafluoropropyl group, i.e. a triplet of triplets in the region of -61 ppm (due to CF_3) and a multiplet - resolved as a triplet of quartets at 400 MHz - at around -106 ppm (due to CF_2). Integration of these peaks shows the ratio to be 3:2. No other signals were observed to indicate some degree of bidirectionality of addition occurring, e.g. a high field doublet, perhaps with finer coupling, due to the difluoromethylene group.

Similarly, the ^1H NMR revealed only two types of hydrogen environment, neither at a sufficiently low field to suggest the presence of geminal fluorine substituents.

Had bidirectionality of addition occurred, it is likely that gas chromatography/mass spectrometry would have indicated the presence of a second compound of identical molecular weight to the addition products identified, but with a slightly different retention time on the GC column, and a different fragmentation pattern under mass spectrometry. No such compounds were detected.

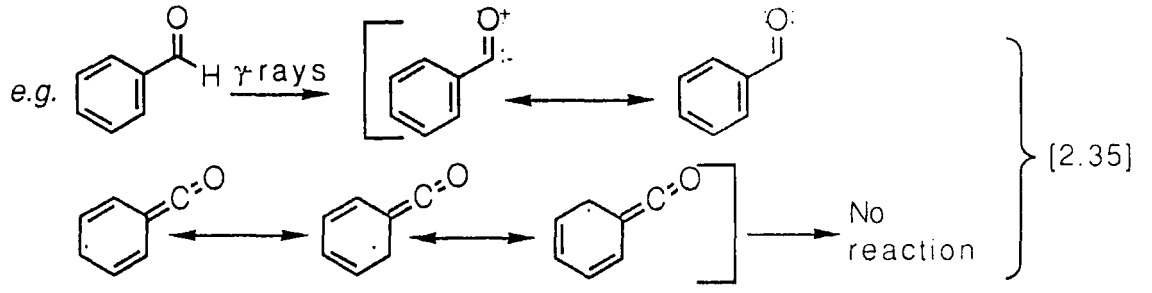
B.2.c. REACTIONS WITH AROMATIC ALDEHYDES

Some experiments between fluoroalkenes and aromatic and heteroaromatic aldehydes were performed (Equation 2.34). In these cases no fluorinated products were obtained.



[2.34]

This is thought to be due to the reluctance of the resonance stabilised α-aryl radical formed to react further (Equation 2.35).



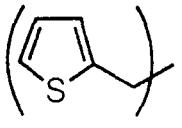
[2.35]

B.3. ADDITION OF ALCOHOLS TO FLUOROALKENES

The field of free radical addition reactions between aliphatic alcohols and fluoroalkenes has seen a great deal of research activity.[137,139,140,142-145,169,171,172] Reactions between hexafluoropropene and alcohols have been studied previously, as noted by references.

$$R\text{-}CH_2\text{-}OH + CF_2{=}CFCF_3 \xrightarrow{\gamma\text{-rays}} R\text{-}\underset{\displaystyle CF_2CHFCF_3}{\underset{|}{C}}H\text{-}OH \qquad [2.36]$$

TABLE 2.3: REACTIONS BETWEEN ALCOHOLS AND HEXAFLUOROPROPENE

R	conversion	References
H	99%	137,139,144, 193,201
CH_3	100%	139,144,201
C_2H_5	100% (**73**)	144
n-C_3H_7	100% (**74**)	139,201
n-C_4H_9	86% (**75**)	139,201
n-C_5H_{11}	100%(**76**)	139,201
	0% (**77**)	-

Novel fluorinated alcohols were synthesised by the reaction between *2H*-pentafluoropropene and alcohols, as shown in Equation 2.37.

$$R\text{-}CH_2\text{-}OH + CF_2{=}CHCF_3 \xrightarrow{\gamma\text{-rays}} R\text{-}\underset{\displaystyle CF_2CH_2CF_3}{\underset{|}{C}}H\text{-}OH \qquad [2.37]$$

R = H, 90% (**71**)

R = CH_3, 100% (**72**)

It is seen that conversions in reactions involving either aldehydes or alcohols and *2H*-pentafluoropropene are lower than those with hexafluoropropene. This can be interpreted by consideration of electronic factors, *i.e.* due to the lesser number of electron withdrawing fluorine substituents, *2H*-pentafluoropropene is less electrophilic than its fully fluorinated analogue.

As in the case of the polyfluorinated ketones synthesised through free radical addition of aldehydes to *2H*-pentafluoropropene, spectroscopic analyses of the products of reaction between alcohols and *2H*-pentafluoropropene show no evidence to suggest bidirectionality of addition.

All products from reactions carried out between alcohols and *2H*-pentafluoropropene showed only two ^{19}F NMR resonances, once again indicative of difluoromethylene and trifluoromethyl groups, i.e. around -110 ppm (2F) and around -61 ppm (3F). In the case of the addition of *2H*-pentafluoropropene to ethanol, the difluoromethylene fluorine signal shows these fluorines to be diastereotopic and hence magnetically inequivalent, giving rise to a characteristic AB type system. This signal is quite different to that which would be expected had the product of addition at the opposite end of the double bond been formed; in such a case, diastereoisomers would have been formed, and would have been clearly identifiable from NMR and gas chromatography/mass spectrometry analyses.

The ^1H NMR spectrum reveals a characteristic pattern arising from methylene protons shifted to low field as a result of being sandwiched between fluorine-bearing carbons. Coupling interactions between the protons and the adjacent difluoromethylene fluorines show that these fluorine atoms are magnetically inequivalent. Had the alternative orientation of addition occurred, two different peaks (of equal area) would have been observed in the ^1H NMR spectrum, corresponding to a trisubstituted CH and a difluoromethyl group.

Gas chromatography/mass spectrometry shows no evidence for the presence of products arising from addition at the opposite end of the double bond of the polyfluoroalkene, e.g. by observation of the presence of a second compound of identical molecular weight to the addition products identified, but with a slightly different retention time on the GC column, and a different fragmentation pattern under mass spectrometry.

B.3.a. SOLVENT EFFECTS

For higher alcohols, *i.e. n*-propanol and above, an inert solvent such as acetone was used to reduce viscosity of the liquid phase and increase miscibility of reactants, since it was found that low conversions were achieved in the absence of a solvent (Table 2.4).

TABLE 2.4: EFFECT OF SOLVENT ON CONVERSION

	conversion to monoadduct	
Alcohol	no solvent	acetone solvent
CH_3OH	99%	100%
C_2H_5OH	100%	100%
n-C_3H_7OH	54%	100%
n-C_4H_9OH	14%	100%
n-$C_5H_{11}OH$	17%	100%

The choice of solvent for free radical reactions is important since one must be selected which will not interfere with the reaction process. Solvents of this type include 2,2,2-trifluoroethanol, acetone and *t*-butanol, which are found to be unreactive under conditions used.

When peroxide initiated reactions were carried out, no improvement on conversions or yields was noted. Ultra violet initiated reactions were found to show low selectivity, *i.e.* over three equivalents of hexafluoropropene were incorporated in one ultra violet initiated reaction. Possible reasons for this finding are discussed in Section A.3.a.(ii).

Consequently, the most effective initiation method for our purposes was γ-irradiation, and this method was employed thereafter.

B.4. ADDITION OF DIOLS TO FLUOROALKENES

Though the free radical reactions of aliphatic alcohols with hexafluoropropene and other fluorinated alkenes have been documented, no literature reports exist regarding the study of aliphatic diols in analogous reactions. Therefore it was of interest to undertake a study of these reactions, in order to determine whether the presence of the second heteroatom had an effect on the reactivity of the compounds.

Aliphatic diols studied were viscous liquids, or solid in the case of 1,6-hexanediol, and so it was essential to use a solvent in all of these reactions.

Peroxide initiated reactions, or standard γ-irradiation periods of *ca.* five days failed to produce the required incorporation of fluoroalkene, despite use of a large excess of the fluoroalkene and repeated reaction of partially reacted materials. It was found that substantially increased (*ca.* fivefold) irradiation times led to synthesis of the mono- (**22**) and α,ω-di-adducts (**23**) of 1,4-butanediol and the α,ω-di-adduct (**24**) of 1,5-pentanediol, though extensive decomposition limited yields. A combination of mass spectrometric breakdown patterns and NMR spectra ensured unambiguous identification of (**22**), (**23**) and (**24**).

$$HOCH_2CH_2CH_2CH_2CH_2OH \xrightarrow[\gamma\,rays]{\text{deficiency of } CF_2{=}CFCF_3} HOCH_2CH_2CH_2CH(OH)CF_2CHFCF_3 \quad [2.38]$$

2%

(**22**)

$$HOCH_2CH_2CH_2CH_2CH_2OH \xrightarrow[\gamma\,rays]{\text{excess } CF_2{=}CFCF_3} CF_3CHFCF_2CH(OH)CH_2CH_2CH(OH)CF_2CHFCF_3 \quad [2.39]$$

29%

(**23**)

$$HOCH_2CH_2CH_2CH_2CH_2CH_2OH \xrightarrow[\gamma\,rays]{\text{excess } CF_2{=}CFCF_3} CF_3CHFCF_2CH(OH)CH_2CH_2CH_2CH(OH)CF_2CHFCF_3 \quad [2.40]$$

64%

(**24**)

1,6-Hexanediol performed less well. The reason for this finding is unclear since low solubility was ruled out by performing a peroxide initiated reaction with no improvement on incorporation of hexafluoropropene, and purification of reagents (recrystallisation and distillation) was carried out to eliminate impurities which may act as radical scavengers and hence halt the reaction.

TABLE 2.5: REACTIONS BETWEEN DIOLS AND HEXAFLUOROPROPENE

Diol (acetone solvent)	Fluoroalkene incorporation (max.)
1,2-Ethanediol	0.75 eq.
1,3-Propanediol	0.60 eq.
1,4-Butanediol	2.00 eq.
1,5-Pentanediol	2.21 eq.
1,6-Hexanediol	0.12 eq.

In summary, lower reactivity was observed for diols than for alcohols, and since the possibility of inhibitor inpurities was excluded and solvents used to increase mobility of, and contact between, reactants, it must be concluded that the reason for this

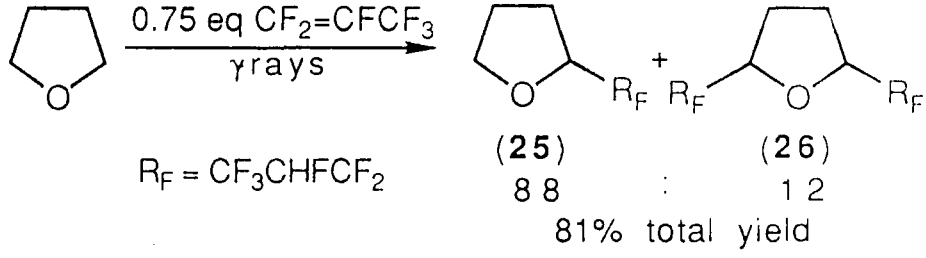
decrease in reactivity was the deactivating effect of the second electronegative heteroatom.

B.5. ADDITION OF ETHERS TO FLUOROALKENES

Dialkyl ethers of the form $R^1R^2CHOCHR^1R^2$ may not only form 1:1 adducts, but also symmetrical diadducts[135,136] or higher species if R^1=H and/or R^2=H.

In some cases polyaddition can be beneficial, *e.g.* in the synthesis of perfluorinated polyether precursors,[159] but it can be disadvantageous for synthetic applications where discrete products are desired. While it is possible to modify product distribution, *e.g.* by using a vast excess of ether for the synthesis of monoadduct, it is difficult to selectively synthesise one product only.

The addition of oxolane to hexafluoropropene has been described,[135,144,147] and this reaction was repeated, with product distribution shown (Equation 2.41), to produce materials for subsequent derivatisation (see Chapter Four).



[2.41]

B.6. ADDITION OF SILANES TO FLUOROALKENES

Methoxytrimethylsilane contains only one site which is subject to radical stabilisation, and so, following preliminary study in this area,[156] we were able to cleanly synthesise the monoadduct in high yield:

$$(CH_3)_3SiOCH_3 + CF_2{=}CFCF_3 \xrightarrow{\gamma\text{rays}} (CH_3)_3SiOCH_2CF_2CHFCF_3 \quad [2.42]$$

73%

(80)

B.7. COMPETITION REACTIONS

Though the free radical addition reactions of highly fluorinated alkenes to organic compounds have been well studied, little work has been carried out by way of characterisation of the reactivities of different species. This section represents an attempt to systematically analyse the relative reactivities within a homologous series of alcohols and also across a range of different functional compounds.

In order to examine the relative reactivities of different species in free radical additions to fluorinated alkenes, a series of competition reactions was carried out. In these reactions a stoichiometric amount, rather than simply equimolar to take into account the polyfunctionality of ethers and amines, of the two species under study was reacted with a deficiency of fluoroalkene, and the relative ratios before and after reaction compared.

B.7.a. ALCOHOLS

The reactivities of the series methanol to *n*-pentanol was found to be:

$$\underset{1.3x}{C_2H_5OH} > CH_3OH \approx \underset{1.3x}{C_3H_7OH} > C_4H_9OH \approx C_5H_{11}OH$$

Although individually these alcohols can be made to react quantitatively with hexafluoropropene, there was found to be a small difference in their reactivities. That is, a reactivity difference of the order of 1.3 was found to exist between ethanol and the next most reactive members of the series, methanol and *n*-propanol, and a similar difference in reactivity between those compounds and the higher alcohols *n*-butanol and *n*-pentanol was observed.

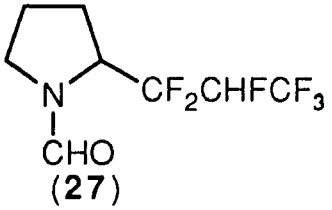
B.7.b. BETWEEN SPECIES

Competition reaction between different functionalities were carried out, using the ethyl derivatives of each species. The following reactivity series was discovered:

Alcohol ≥ Amine > Ether > Aldehyde
1.1x 3.2x 1.25x

A very small difference in reactivities was observed between the most reactive species, alcohols and amines, and a greater difference noted between the other species, *i.e.* alcohols were found to be 3.5 times more reactive than the analogous ether, and 4.0 times more reactive than the analogous aldehyde.

One intramolecular competition reaction was carried out, using 1-pyrrolidinecarboxaldehyde. In this reaction, quantitative conversion to the new fluorinated compound (**27**) was achieved.



(**27**)

These data give only an empirical guide to the reactivity of species and it is not possible to postulate further the reason for such differences. It may be the case that, for example, adjacent π electrons stabilise a radical less effectively than a heteroatom bearing an electron lone pair, though it could equally well be that the radical species themselves are more reactive.

Study has been made elsewhere[202] of the stabilising effect of substituent groups on radicals, and the order of reactivity above is in general agreement with the findings of those workers.

CHAPTER THREE

DERIVATISATION OF POLYFLUORINATED ALCOHOLS

A. INTRODUCTION

Fluorinated alcohols produced *via* free radical reactions have been known for some years, and it is perhaps surprising that little investigation of the chemistry of these compounds has been carried out.

Since the principle effect of incorporation of fluorine substituents into an alcohol is to increase the acidity of the compound, it was interesting to attempt nucleophilic reactions of alcohols discussed in Chapter Two. What must be considered in addition to increased acidity, however, is the stabilising effect of fluorine substituents on an anion, an effect which lowers the nucleophilicity of such compounds. Therefore, the question posed is this: will polyfluorinated alcohols react well, if at all, as nucleophiles?

B. NUCLEOPHILIC REACTIONS OF POLYFLUORINATED ALCOHOLS

B.1. ESTERIFICATIONS

The simple acetate esters were the first synthesised in our study (Equation 3.1).

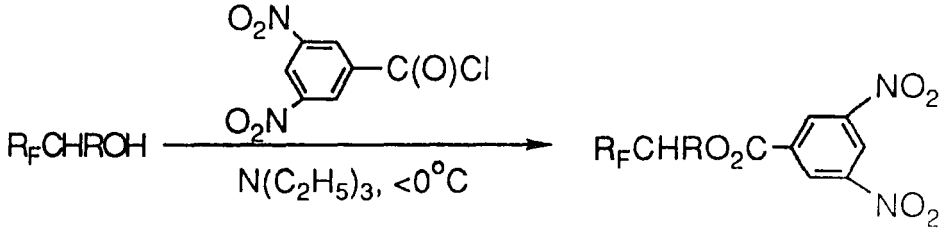
$$R_FCHROH \xrightarrow[(Base)]{CH_3C(O)Cl} R_FCHRO\text{-}\overset{\overset{O}{\|}}{C}CH_3 \qquad [3.1]$$

$R_F = CF_3CHFCF_2$

R	Base	Yield
H	-	52% (**81**)
CH_3	-	59% (**82**)
CH_3	$N(C_2H_5)_3$	25% (**82**)

Addition of base resulted in a lower yield, probably due to the added purification necessary.

New crystalline derivatives were produced by reaction of fluorinated alcohols with 3,5-dinitrobenzoyl chloride (Equation 3.2). In these reactions, a reduced yield was achieved with the alkoxide of 3,3,4,5,5,5-hexafluoropentan-2-ol (**28**), and this may be attributed to steric congestion between the bulky electrophile and the attacking alkoxide. Reaction temperatures above *ca.* 0°C resulted in decomposition, giving no identifiable products.

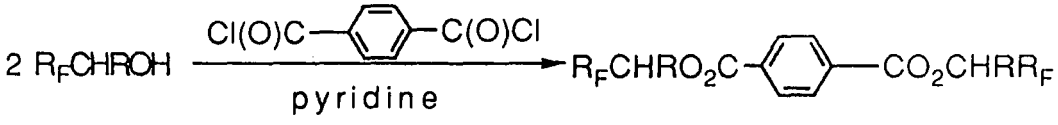


[3.2]

$R_F = CF_3CHFCF_2$ R = H, 99% (**83**)

R = CH_3, 22% (**84**)

Reaction of the alcohol with a difunctional acid chloride as a model study towards polymer synthesis gave low yield of a novel diester. This may be due to low solubility of the diacid chloride in solvents appropriate to the reaction.



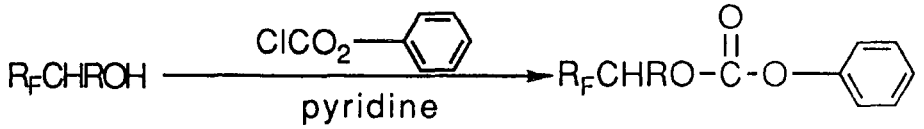
[3.3]

$R_F = CF_3CHFCF_2$ 12%

R = CH_3 (**85**)

B.2. CARBONATE SYNTHESIS

Analogous to the reaction with acid chlorides to produce esters, alcohols will react with chloroformates to give carbonates. The new phenyl carbonates of hexafluoropropyl substituted alcohols were synthesised as shown (Equation 3.4).



[3.4]

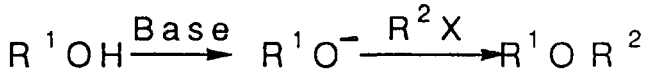
$R_F = CF_3CHFCF_2$

R = H, 58% (**86**)

$R = CH_3$, 54% (**87**)

B.3. ETHER SYNTHESIS

Following the Williamson method for synthesis of ethers from alcohols (Equation 3.5), a range of novel polyfluorinated ethers was synthesised from corresponding alcohols.

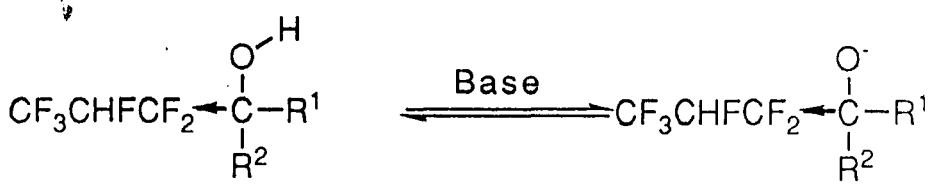


[3.5]

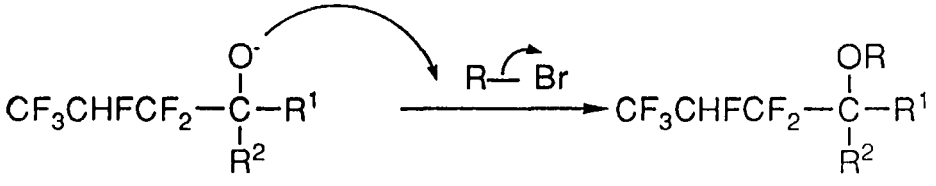
X = leaving group

This procedure normally requires a strong base such as sodium hydride to deprotonate the alcohol,[203] and it is indicative of the increased acidity of fluorinated alcohols that the following reactions proceed with hydroxide ion, a much weaker base.

Although the alkoxide anion may be readily formed (Equation 3.6), its further reaction to form an ether (Equation 3.7) is not encouraged by the fluorine substituents since their effect serves to reduce the nucleophilicity of the alkoxide by withdrawing electron density.



[3.6]



[3.7]

B.3.a. ALKYL HALIDES

Alkyl halides were employed as R^2X in Equation 3.5, and the results of these reactions are given in Table 3.1.

TABLE 3.1 REACTIONS BETWEEN FLUORINATED ALCOHOLS AND ALKYL HALIDES

R^1	R^2X	Base	Temperature	Conversion
$R_FCH(CH_3)$	CH_3I	NaOH	ambient	14% **(88)**
$R_FCH(CH_3)$	*n*-C_3H_7Br	NaOH	ambient	25% **(89)**
$R_FCH(CH_3)$	*n*-C_3H_7Br	NaOH	56°C	55%
$R_FCH(CH_3)$	*i*-C_3H_7Br	NaOH	ambient	0%*
$R_FCH(CH_3)$	CF_3CH_2I	NaOH	ambient	0%

R_F= CF_3CHFCF_2, *HBr evolved

Though reasonable results were obtained for reactions with 1-bromopropane, it was found that, in general, conversions were disappointing. This is indicative of the lowering of nucleophilicity experienced on incorporation of a number of fluorine substituents. It was proposed to investigate reactions with more reactive organic halides as a possible way of increasing yields of ethers.

B.3.b. ACTIVATED HALIDES

Allylic and benzylic halides are more reactive than alkyl halides towards nucleophilic attack (Table 3.2).

The reason for the greater reactivity of allylic species is principally a steric one. As the reaction intermediate in S_N2 reactions with alkyl halides has trigonal bipyramidal geometry, the steric requirements of a bromine substituent will adversely affect rate of reaction, while S_N2' attack on an allylic system results in a tetrahedral intermediate where hindrance by bromine at the β-position is negligable.

TABLE 3.2: RELATIVE REACTIVITY RATES OF SELECTED ALKYL SUBSTITUENTS[204]

Alkyl substituent	Relative reactivity
Methyl	30
Ethyl	1
n-Propyl	0.4
i-Propyl	0.025
neo-Pentyl	10^{-5}
Allyl	40
Benzyl	120

In the case of the benzylic species, electronic factors play the major part. The electron withdrawing effect of the phenyl ring serves to weaken the C-Br σ-bond, consequently its cleavage requires a lesser energy input. In addition, allylic and benzylic species are activated towards reaction by their transition states' unhybridised p orbitals' ability to interact with both the incoming nucleophile and the leaving group.

Therefore reactions were carried out between examples of these activated alkyl halides and fluorinated alcohols.

TABLE 3.3: REACTIONS BETWEEN FLUORINATED ALCOHOLS AND ACTIVATED ALKYL HALIDES

R^1	R^2X	Base	Temperature	Yield	
R_FCH_2	$CH_2{=}CHCH_2Br$	NaOH	50°C	trace	**(90)**
$R_FCH(CH_3)$	$CH_2{=}CHCH_2Br$	NaOH	ambient	58%	**(91)**
R_FCH_2	$C_6H_5CH_2Br$	NaOH	56°C	67%	**(92)**
$R_FCH(CH_3)$	$C_6H_5CH_2Br$	NaOH	ambient	78%	**(93)**

$R_F = CF_3CHFCF_2$

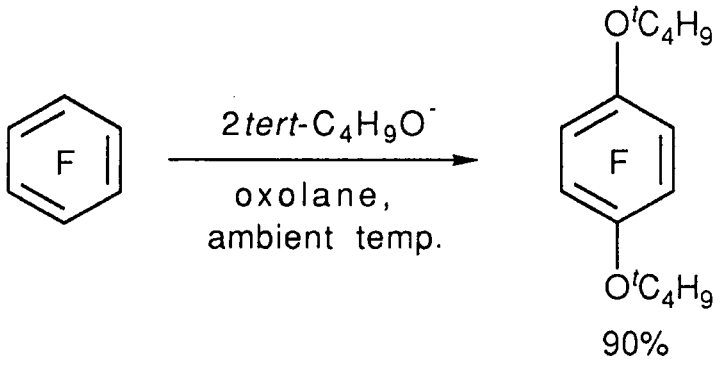
These activated electrophiles gave generally higher yields of novel ether products than alkyl halides. Yields for the derivatives of 2,2,3,4,4,4-hexafluorobutanol (**29**) were generally lower than those for derivatives of (**28**). This was attributed to the dominance

of electronic factors over steric factors in these reactions, *i.e.* the alkoxide generated from (**28**) is a stronger nucleophile since the effect of the methyl substituent is electron donating, resulting in increased nucleophilicity of the alkoxide.

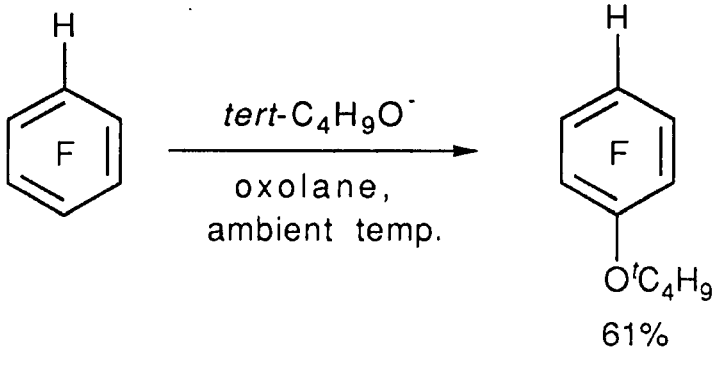
B.3.c. FLUOROAROMATIC COMPOUNDS

It has been shown that fluoroaromatic compounds react with nucleophiles (Equations 3.8, 3.9).[205]

The experiments carried out involved highly fluorinated or perfluorinated aromatic compounds, and consequently it was of interest to investigate whether fluorobenzenes activated towards nucleophilic attack by electron withdrawing substituent groups were sufficiently activated to react with fluorinated alcohols.



90% [3.8]



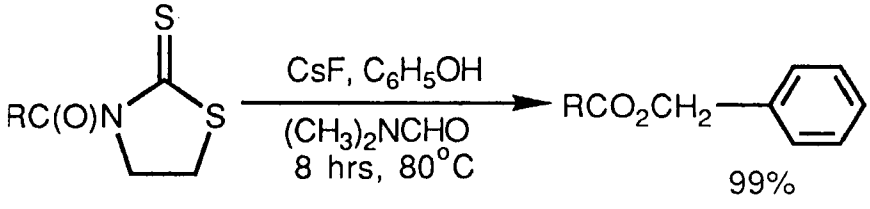
61% [3.9]

B.3.c.(i). CAESIUM FLUORIDE AS A BASE

Use of a metal fluoride as base increases the nucleophilicity of alcohols by means of hydrogen bonding,[206] and reduces the

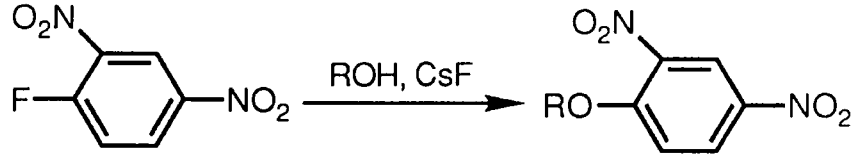
possibility of side reactions, *e.g.* nucleophilic displacement by the base itself. The reason for choosing caesium fluoride in preference to potassium fluoride, a less expensive reagent, lies in its higher activity and greater solubility, though it is accepted that even caesium fluoride is only moderately soluble in most protic solvents, and that surface reaction is commonplace. Precautions must be taken to ensure the anhydrous nature of the reagent, since complexation with water masks the fluoride ion, lowering its availability for reaction.

Examples in which caesium fluoride has been used as base in syntheses of ethers from alcohols are given in Equations 3.10-12.[207-209]



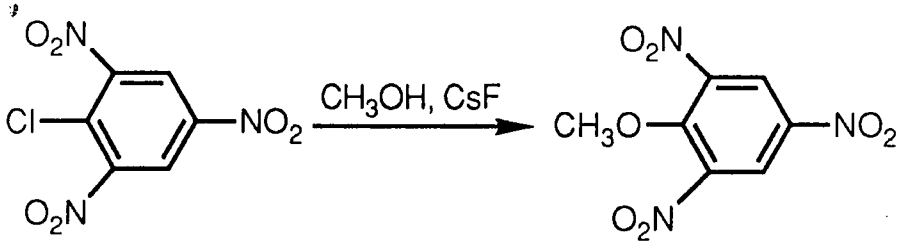
[3.10]

R = $C_6H_5CH_2CH_2$



[3.11]

R = *t*-Alk



[3.12]

B.3.c.(ii). REACTIONS INVOLVING FLUOROAROMATIC COMPOUNDS

An investigation was carried out into the reactivity of a number of fluorobenzenes activated towards nucleophilic displacement by the presence of electron withdrawing substituent

groups at the 4-position. It was found that those less reactive compounds did not undergo reaction (Equation 3.13, Table 3.4), but more highly activated compounds could be made to react in the manner hoped for (Equations 3.14, 3.15), producing four new polyfluorinated substituted benzenes.

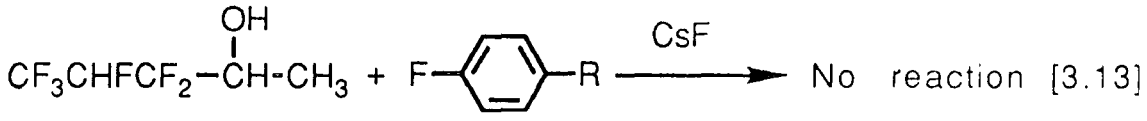
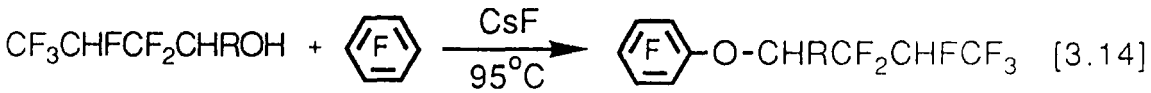
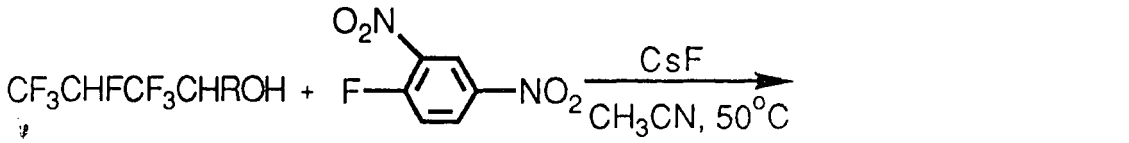


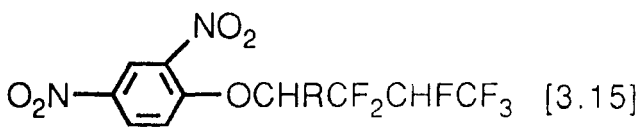
TABLE 3.4: UNSUCCESSFUL REACTIONS BETWEEN ACTIVATED FLUOROBENZENES AND FLUORINATED ALCOHOLS

R	Temperature	Solvent
CN	82°C	CH_3CN
CN	100°C	-
CH_3CO	100°C	-
C_6H_5CO	100°C	-
CF_3	100°C	-



R = H, 4% (**98**)
R = CH_3, 15% (**99**)

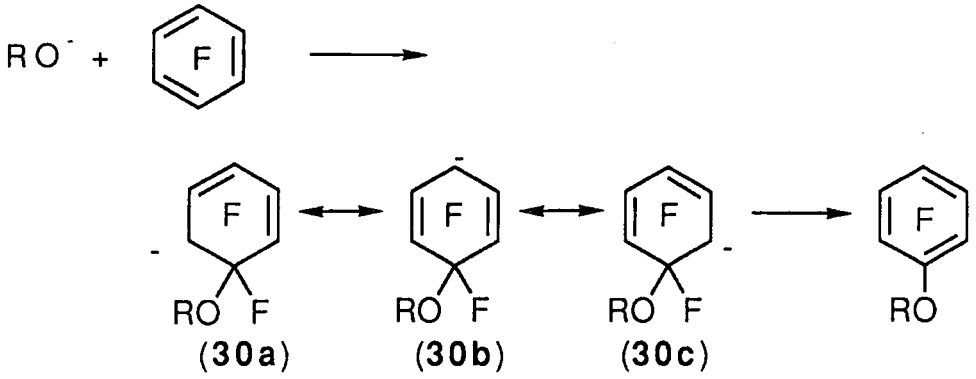




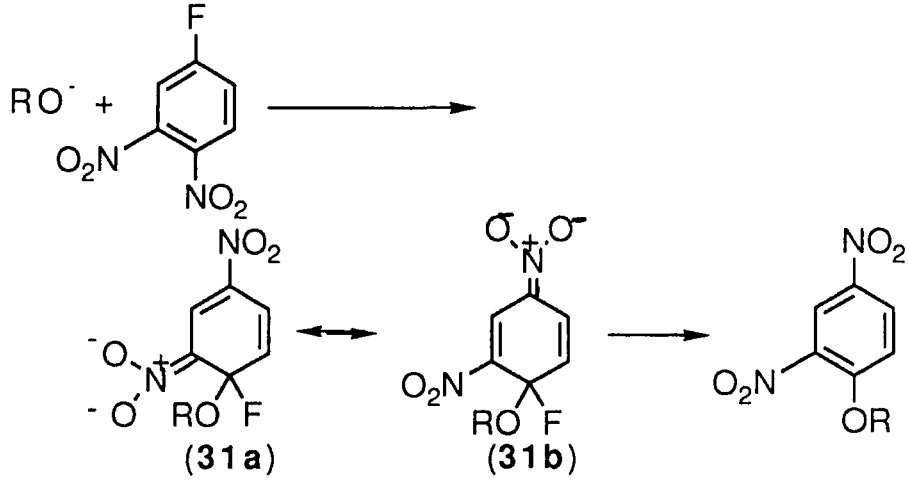
R = H, 100% (**100**)
R = CH_3, 92% (**101**)

The reason for some 4-substituted fluorobenzenes reacting in this way, and not others, may be understood by consideration of the reaction intermediates (**30**) and (**31**), in which the negative charge is stabilised, by perfluorination in the case of reaction with hexafluorobenzene (Equation 3.16) and by the presence of two nitro

groups in the case of reaction with fluoro-2,4-dinitrobenzene (Equation 3.17). No such stabilisation is possible with the other substituted fluorobenzenes tested.



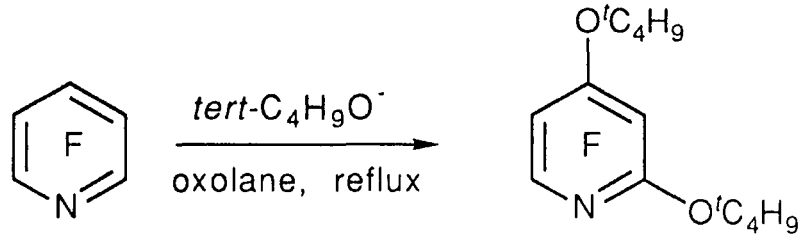
[3.16]



[3.17]

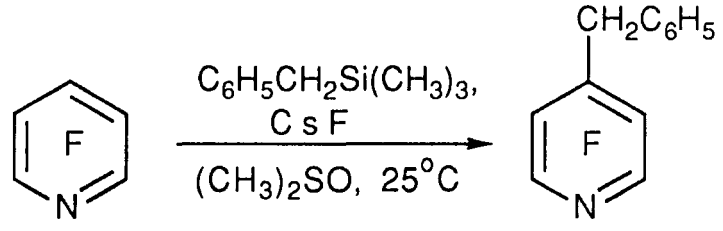
B.3.d. PERFLUOROAROMATIC COMPOUNDS

Nucleophilic displacement reactions involving fluorinated aromatic compounds have been reported, from nucleophilic substitution reactions involving penta- and hexa-fluorobenzene[210] to anion trapping experiments with pentafluoropyridine to give 4-substituted tetrafluoropyridines[179,211-213] (Equations 3.18, 3.19)[205] and substitution of polyhetero species[211,214-216] (Equations 3.20, 3.21).[217]



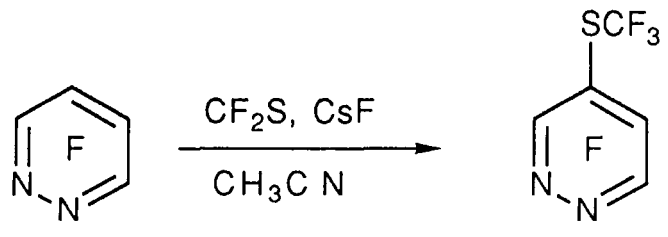
34%

[3.18]



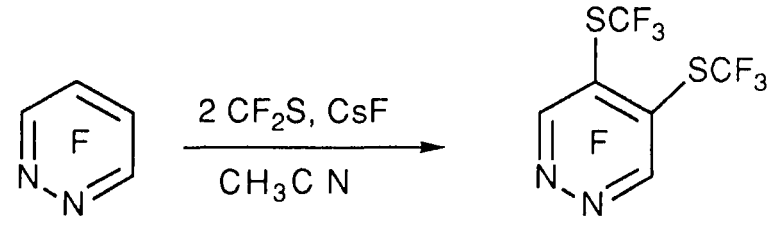
45%

[3.19]



89%

[3.20]

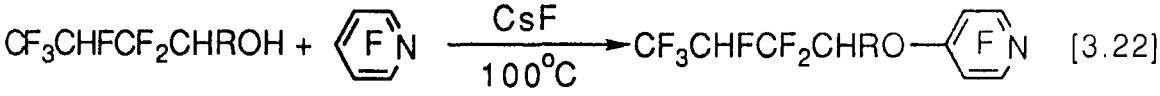


82%

[3.21]

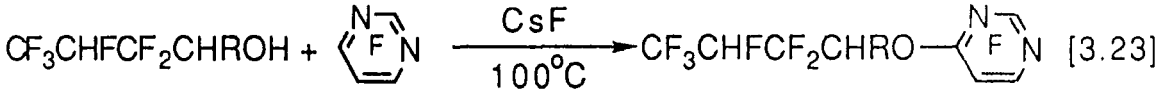
Since little work has been carried out in the area of reacting **fluorinated** nucleophiles with fluoroheteroaromatics, a number of reactions of this type were performed and it was discovered that the nucleophiles which were employed, fluorinated alkoxides derived from the fluorinated alcohols produced in Chapter Two, behaved in the hoped for manner, *viz* nucleophilic displacement of fluorine at the most reactive sites in the heterocycle. Results of reactions with perfluorinated pyridine and three diazabenzenes, in

which moderate to quantitative yields of eight readily isolated new highly fluorinated substituted aromatic compounds were obtained, are given in Equations 3.22-3.25.



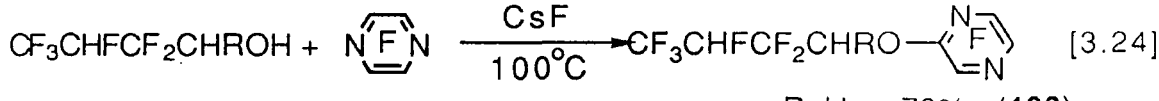
[3.22]

R=H, 81% (**102**)
R=CH_3, 65% (**103**)



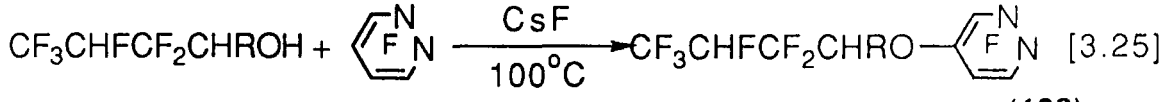
[3.23]

R=H, 57% (**104**)
R=CH_3, 39% (**105**)



[3.24]

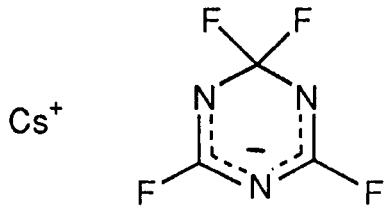
R=H, 73% (**106**)
R=CH_3, 25% (**107**)



[3.25]

R=H, 69% (**108**)
R=CH_3, 100% (**109**)

Analogous reactions carried out with trifluoro-*s*-triazine and perfluoro-*iso*-propyl-*s*-triazine failed to produce identifiable products. As it is known that the salt (**32**) is readily formed from the reaction of caesium fluoride with perfluoro-*iso*-propyl-*s*-triazine, it seems likely that preferential formation of (**32**) occurred, and that this compound was subsequently hydrolysed in the course of the work-up procedure.



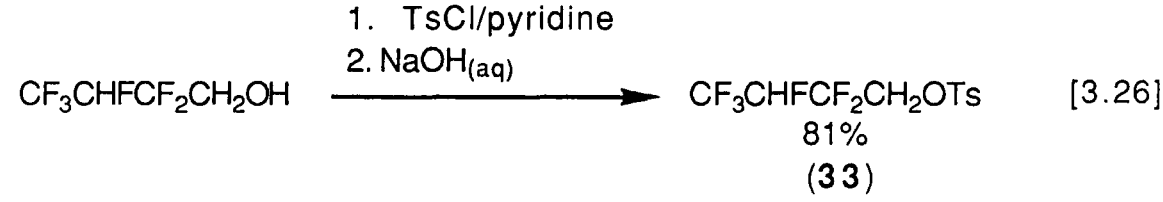
(**32**)

B.4. SULPHONATION

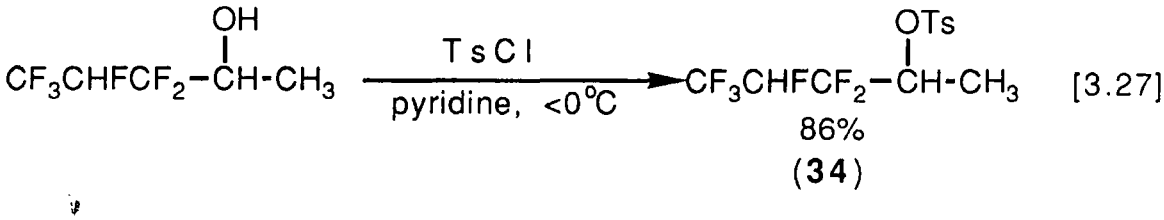
B.4.a. SYNTHESIS OF SULPHONATES

Further nucleophilic chemistry of partially fluorinated alcohols was carried out when the 4-methylbenzenesulphonate derivatives (tosylates) of the compounds were synthesised, in a confirmation of previous workers results.[140]

Two methods for synthesis of tosylated alcohols were examined: Haszeldine's heterogeneous method (Equation 3.26)[140] and homogeneous low temperature conditions, employing pyridine as both solvent and base (Equation 3.27). Both methods were seen to give good yields of tosylated product, though long reaction times (*ca.* 2 days) were necessary for high yield, and temperature increase resulted in decomposition.

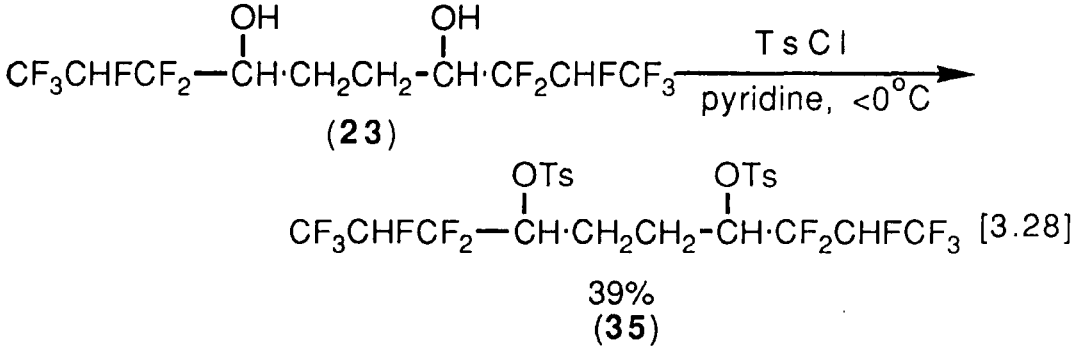


[3.26]



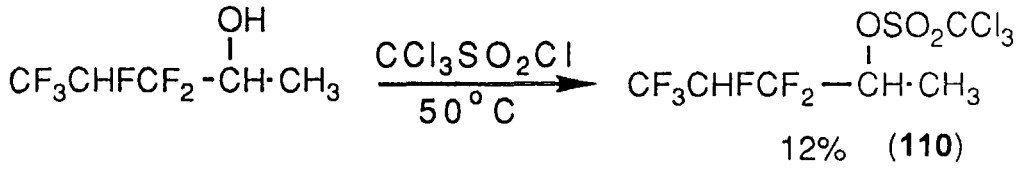
[3.27]

The new ditosylate (**35**) was also synthesised from (**23**) in 39% yield (Equation 3.28).

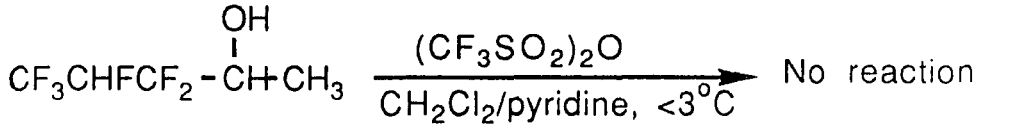


[3.28]

Attempts to synthesise halogenated sulphonates gave poor results (Equations 3.29, 3.30).



[3.29]

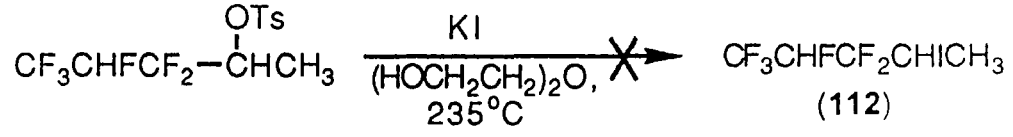


[3.30]

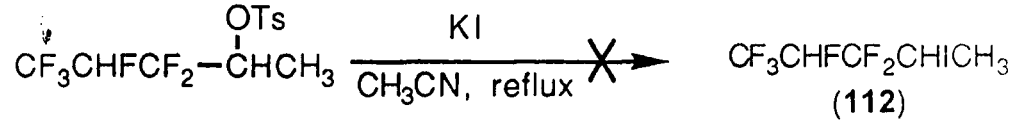
B.4.b. REACTIONS OF SULPHONATES

B.4.b.(i). HALOGEN NUCLEOPHILES

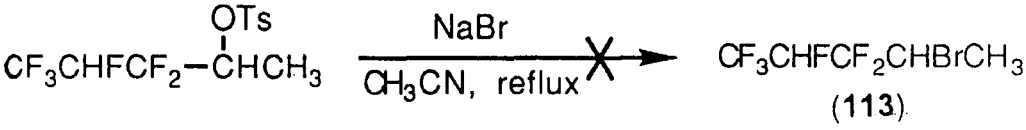
One report detailing the iodination of (**28**) and (**29**) *via* tosylation and subsequent displacement of the leaving group by iodide ion exists.[140] An attempt was made to repeat the iodination step under identical conditions (Equation 3.31), but no product was observed. Reactions carried out under different conditions (Equation 3.32), and reactions with bromide ion (Equation 3.33), failed to produce the corresponding halogenated compounds.



[3.31]



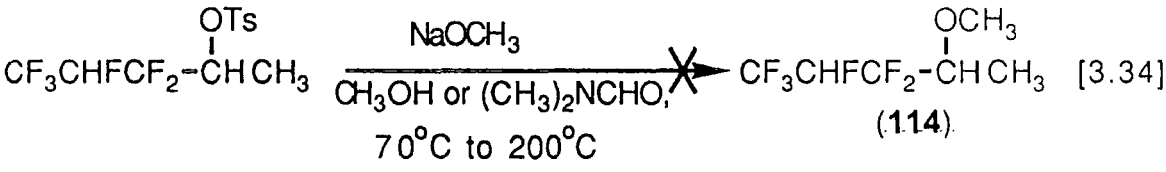
[3.32]



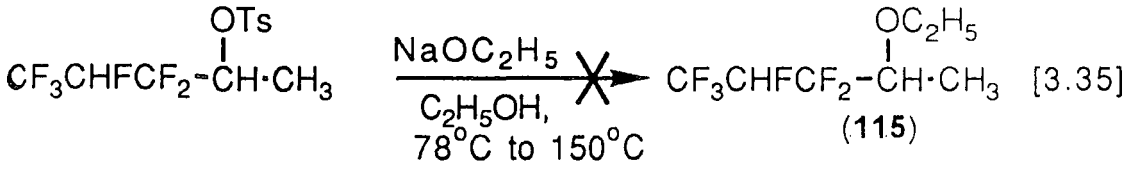
[3.33]

B.4.b.(ii). OXYGEN NUCLEOPHILES

The alkoxides methoxide and ethoxide were ineffective in displacing the tosyl group, under various reaction conditions (Equations 3.34, 3.35).



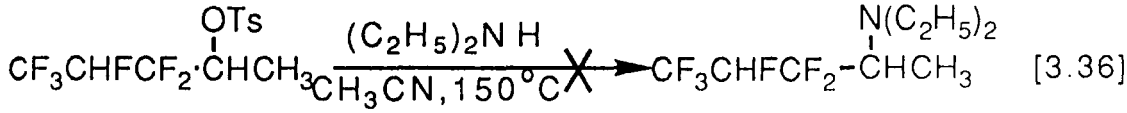
(114) [3.34]



(115) [3.35]

B.4.b.(iii). NITROGEN NUCLEOPHILES

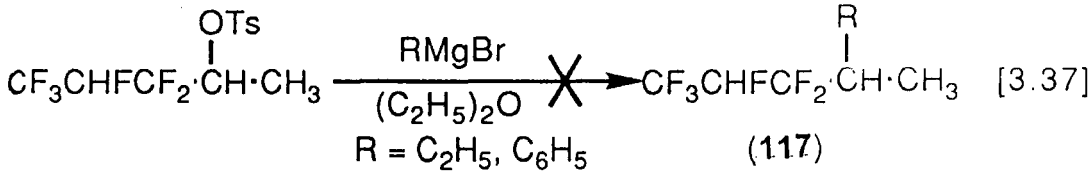
Diethylamine (Equation 3.36) was found to be ineffective in displacing the tosyl group.



(116) [3.36]

B.4.b.(iv). CARBON NUCLEOPHILES

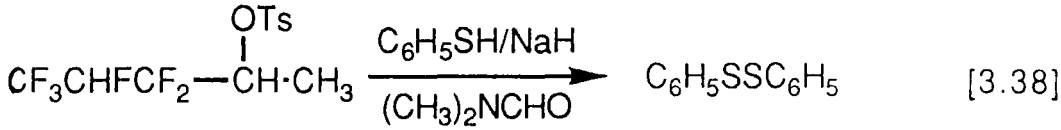
Grignard reagents, both aliphatic and aromatic, were used in these reactions. No displacement of the tosyl group occured.



(117) [3.37]

B.4.b.(v). SULPHUR NUCLEOPHILES

Attempted displacement of the tosyl group by thiophenate ion gave diphenyl disulphide as the only isolable product.



(118) [3.38]

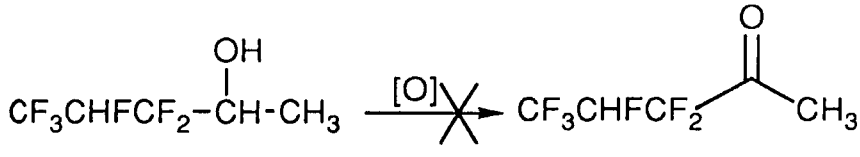
B.4.c. CONCLUSION

The tosylate group is commonly used as a leaving group in organic chemistry. However from the reactions carried out, it is clear that the tosylate group does not function effectively in this capacity with the polyfluorinated alcohols (**28**) and (**29**). It has not been proven whether the combination of steric effects of the six fluorine substituents hindering approach, and the electronic repulsion between the fluorine lone pairs and an incoming nucleophile is the reason for this lack of reactivity, but it is not unreasonable to conclude that this factor must be a significant one.

C. MISCELLANEOUS REACTIONS OF POLYFLUORINATED ALCOHOLS

C.1. OXIDATION

It has been reported[143] that partial oxidation of fluorinated alcohols had been achieved under mild conditions, though no attempt was made to isolate ketones thus produced. Neither repetition of these experiments nor use of alternative oxidising agents and reaction conditions resulted in oxidation of (**28**) to the corresponding ketone (**36**). It is suggested that a possible reason for this lies in the electronic repulsion or steric hindrance effects between the polyfluorinated alkyl group and the bulky incoming complexed metal, which prevents formation of the metal ester oxidation intermediate. Methods investigated are found in Table 3.5.



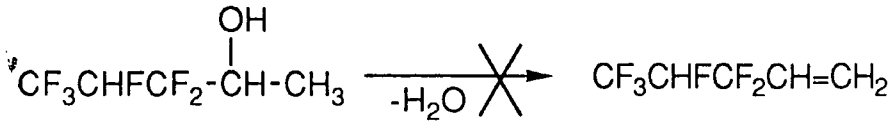
(**28**) (**36**) [3.39]

TABLE 3.5: ATTEMPTED OXIDATION OF (28)

Oxidising agent	Solvent	Reaction time	Temperature
Jones' reagent [218]	Acetone	3 hr	0°C
Chromic acid[219]	Diethyl ether	3 hr	ambient
Chromic acid[219]	Diethyl ether	18 hr	ambient
Chromic acid	CH_2Cl_2	5 hr	ambient
Chromic acid	Water	18 hr	ambient
Chromic acid	Water	18 hr	100°C
Chromic acid	Water	70 hr	100°C
Chromic acid	Water	18 hr	160°C
$KMnO_4/H^+$	Water	18 hr	ambient
$KMnO_4/H^+$	Water	18 hr	100°C

C.2. DEHYDRATION

As with oxidation, some reference has been made to dehydration of (**28**) to the alkene (**37**), using phosphorus pentoxide.[145] However, when this experiment was repeated, no dehydration product was observed. Table 3.6 gives details of the various dehydrating agents and reaction conditions employed during attempts to effect dehydration. None of the experiments were successful in producing (**37**).



(**28**) (**37**) [3.40]

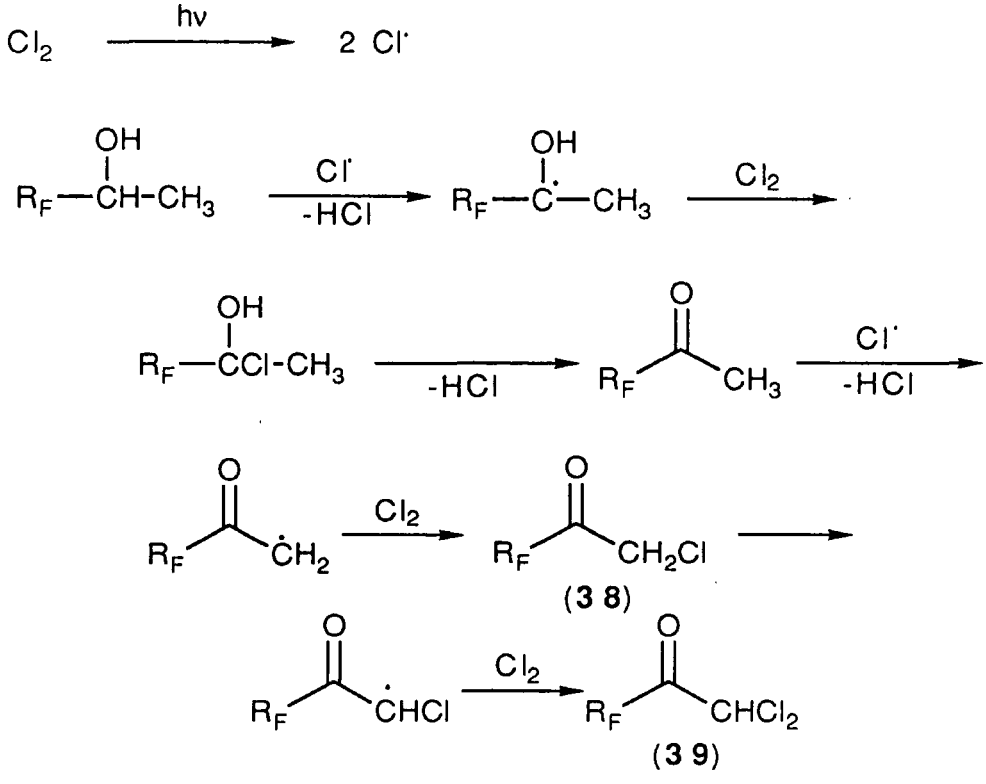
TABLE 3.6: ATTEMPTED DEHYDRATION OF (28)

Dehydrating agent	Temperature
P_2O_5	50°C to100°C
P_2O_5	120°C
P_2O_5/H_2SO_4	90°C
t-$C_4H_9O^-$	45°C

C.3. DIRECT CHLORINATION

Reaction of elementary chlorine with alcohol (**28**) gave rise to a complex mixture of compounds, in which the new ketones 1-chloro-3,3,4,5,5,5-hexafluoropentan-2-one (**38**) (75% by g.l.c.) and 1,1-dichloro-3,3,4,5,5,5-hexafluoropentan-2-one (**39**) (18% by g.l.c.) were identified (by mass spectrometry).

SCHEME 3.1: CHLORINATION OF (28)



D. CONCLUSION

In the introduction to this chapter, the question was posed: will the polyfluorinated alcohols under study react as nucleophiles, due to their increased acidity, or not, due to the stabilising effect of fluorine substitution? It has been shown in this chapter that reactions which were carried out with electrophilic species

such as acid chlorides, chloroformates, alkyl and activated halides, and sulphonyl chlorides indicate that (**28**) and (**29**) can indeed be made to react nucleophilically, though experimental evidence has been advanced for the lowered nucleophilicity, *viz* lower yields or lack of reaction altogether in some cases involving less reactive electrophilic species.

The lack of reactivity of tosylated alcohol (**34**) towards displacement by a range of nucleophiles may be due to one of two reasons. It may be that the bulk of the hexafluoropropyl group hinders approach (*cf.* low reactivity of *neo*-pentyl tosylate) or it may be that electronic repulsion between the fluorine lone pairs and the incoming nucleophile is the cause of the low reactivity of this compound, but whichever factor dominates, it is seen from the systematic study of a range of nucleophiles which has been carried out that no further reaction will take place.

Direct chlorination provides a one-pot synthesis of the chlorinated ketones (**38**) and (**39**) from (**29**), presumably *via* an oxidative chlorination/dehydrochlorination route.

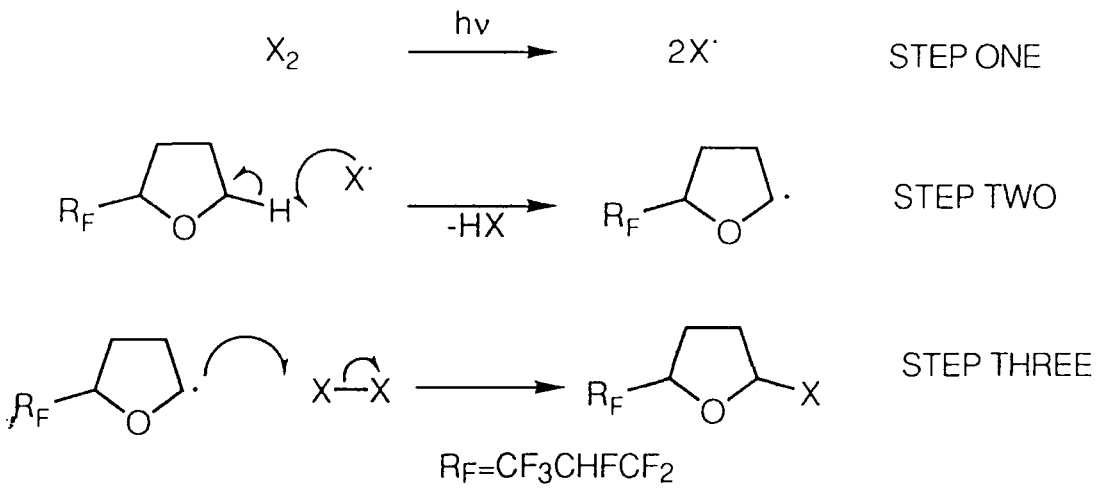
CHAPTER FOUR

DERIVATISATION OF POLYFLUORINATED ETHERS

A.1.b. MECHANISM OF DIRECT HALOGENATION

Direct halogenation is a free radical process (Scheme 4.1), the first step being dissociation of the diatomic halogen, commonly achieved by irradiation with visible or ultraviolet radiation. Step Two involves the abstraction of a hydrogen atom by the radical halogen atom. Factors affecting which hydrogen atom is abstracted include the ease of cleavage of the C-H bond (*i.e.* bond strength), stability of the intermediate organic radical thus formed, polar interactions between the incoming radical species and the sité of attack and steric hindrance to approach of the halogen atom.

SCHEME 4.1: MECHANISM OF DIRECT HALOGENATION OF (25)

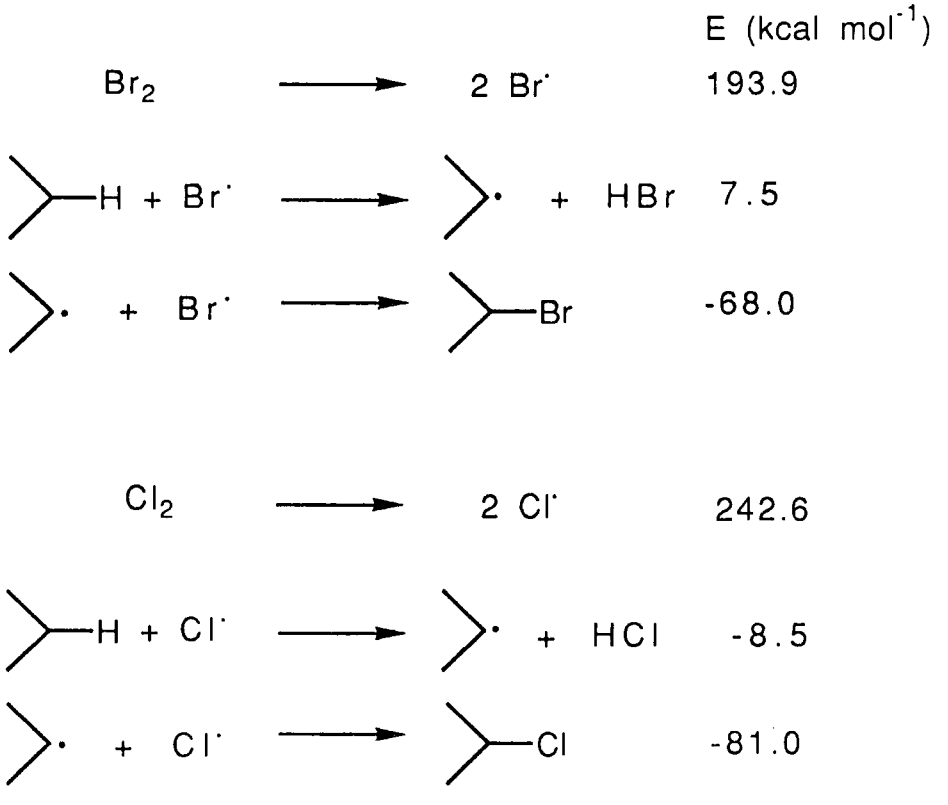


In the case illustrated in Scheme 4.1, the influences of steric constraints, *i.e.* the bulky hexafluoropropyl substituent group prevents approach of the large incoming halogen radical at the 2-position, and polar factors, *i.e.* electrophilic halogen radicals are discouraged from attack at that electron deficient position, combine to prevent reaction at the 2-position, and so halogenation proceeds exclusively at the 5-position.

The reason for the observed difference in reactivities towards halogenation of (**25**) may be found on examination of the thermodynamics of halogenation reactions.

Whilst increasing temperature or using higher energy irradiation will increase radical flux, it is not lack of dissociation of halogen molecules (Step One) which prevents reaction. Examination of Steps Two (hydrogen atom abstraction) and Three (C-X bond formation) shows that chlorination is much more readily achieved than bromination, due to more favourable thermodynamic factors. The result is a good yield of chlorinated oxolane derivative (**41**), while bromination by this method is a less thermodynamically feasible proposition. Since thermally assisted reaction between bromine and (**25**) failed to increase conversion to (**40**) above trace amounts, it is presumed that the energy barriers to be overcome are significant ones. Though no data are available for the specific reactions under study, an example of comparison of thermodynamic data for halogenation of an alkane is given in Figure 4.1.

FIGURE 4.1: THERMODYNAMIC PARAMETERS FOR HALOGENATION OF PROPANE



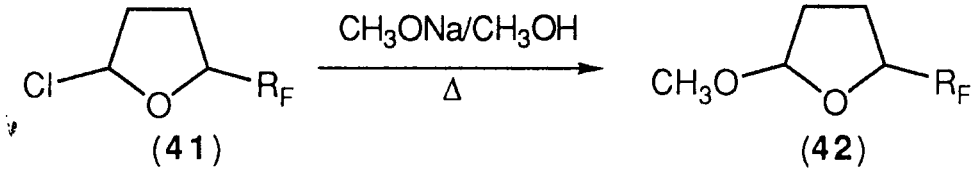
Attempts to halogenate (**26**) yielded no products. This can be explained by the fact that radical approach at the position α to oxygen is prevented by the bulk of the polyfluoroalkyl substituent groups, and that polar effects discourage reaction at that site, *i.e.* both attacking radical and α-carbon are electrophilic species.

B. NUCLEOPHILIC SUBSTITUTION REACTIONS OF (41)

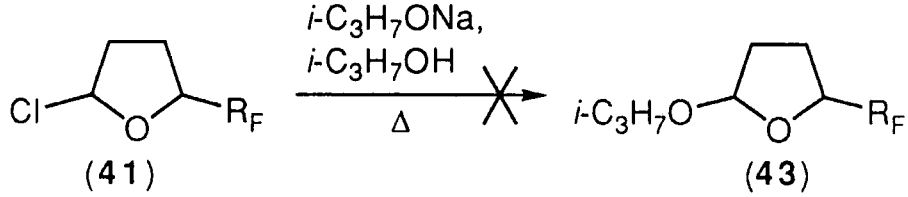
The easily synthesised chloro derivative (**41**) was thought to provide an accessible route to further derivatives of (**25**) *via* nucleophilic substitution. Hence a series of reactions of this type were attempted.

B.1. OXYGEN NUCLEOPHILES

Oxygen nucleophiles are among the most efficient nucleophiles for nucleophilic substitution reactions. Sodium methoxide (Equation 4.3) and sodium *i*-propoxide (Equation 4.4) were reacted with (**41**), but only a trace amount of new acetal (**42**) was observed, by gas chromatography, and no (**43**) was produced.



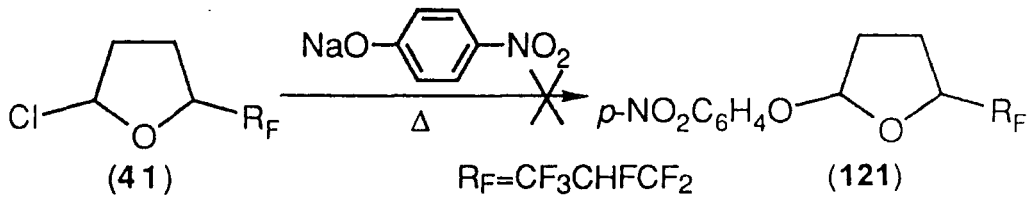
(**41**) (**42**) trace [4.3]



(**41**) (**43**) [4.4]

R_F=CF_3CHFCF_2

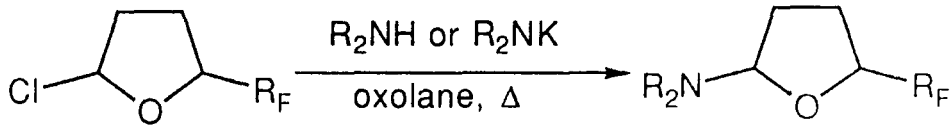
In an attempt to produce a crystalline derivative, sodium 4-nitrophenoxide was reacted with (**41**). No reaction occurred.



(41) $R_F=CF_3CHFCF_2$ (121) [4.5]

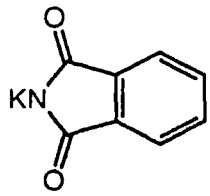
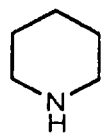
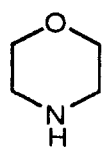
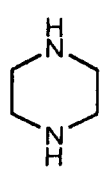
B.2. NITROGEN NUCLEOPHILES

A series of aliphatic amino compounds was reacted with (**41**). These reactions, summarised in Table 4.1, gave rise to a series of novel substituted amines.



(41) $R_F=CF_3CHFCF_2$ (44) [4.6]

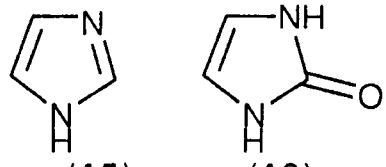
TABLE 4.1: REACTIONS OF AMINES WITH (41)

R_2NH or R_2NK	Conversion
$(C_2H_5)_2NH$	0%
	21%
	50%
	trace
	0%

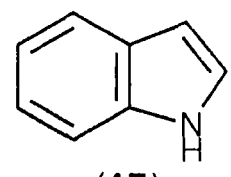
Piperidine gave the highest conversion to (**44**) of the cyclic amines. This can be rationalised by consideration of the inductive effect experienced by the nitrogen atom in each of these compounds. Piperazine and morpholine contain a second electronegative heteroatom which withdraws charge from the nitrogen, thereby reducing its effectiveness as a nucleophile by decreasing the availability of the lone pair. This is also true for phthalimide, where charge is withdrawn by both the phenyl ring and the carbonyl groups, but this deactivation is overcome to some extent by the existance of a formal negative charge on the nitrogen.

It is less easy to understand the lack of reactivity of diethylamine, which has none of these factors working against reaction, and no explanation can be given at this stage for this finding.

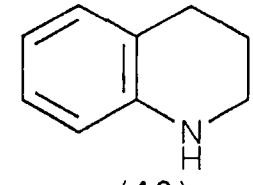
Aromatic nitrogen nucleophiles (**45-48**) were reacted with (**41**), without success, presumably once more due to withdrawal of electron density from the nitrogens, thereby reducing their nucleophilicity.



(**45**) (**46**)



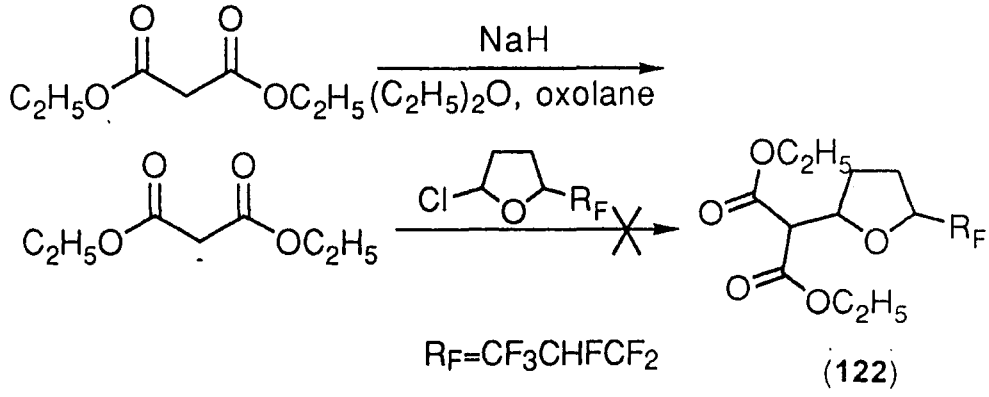
(**47**)



(**48**)

B.3. CARBON NUCLEOPHILES

Diethyl malonate was reacted with (**41**). No trace of product was observed.



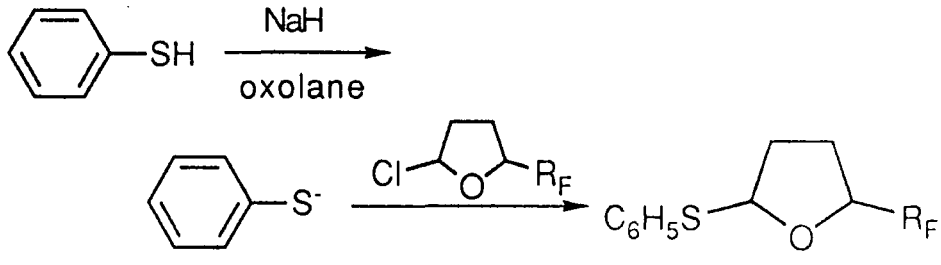
[4.9]

$R_F=CF_3CHFCF_2$

(**122**)

B.4. SULPHUR NUCLEOPHILES

Thiophenate anion, generated *in situ* by the reaction of thiophenol and sodium hydride, reacted with (**41**) to give rise to the new sulphide (**49**).

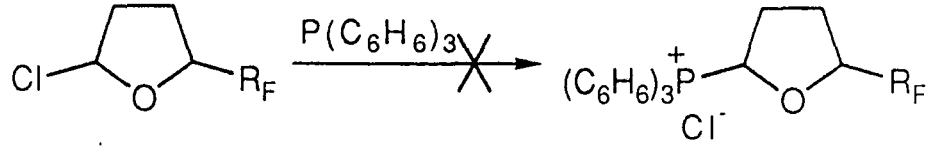


[4.10]

R_F=CF_3CHFCF_2 (**49**) 28%

B.5. PHOSPHORUS NUCLEOPHILES

Triphenyl phosphine did not react with (**41**). This finding was not unexpected as it is known[203] that reaction of triphenyl phosphine with most primary alkyl halides proceeds readily, but rarely does reaction occur with secondary alkyl halides.



[4.11]

(**41**) R_F=CF_3CHFCF_2 (**123**)

B.6. CONCLUSIONS

Not all nucleophiles will react thus with (**41**). Those which did react, sulphur and electronically favoured nitrogen nucleophiles, fulfil three conditions, *viz* they are soft nucleophiles, are not hindered by steric constraints, and have no electronic factors disfavouring reaction. In accordance with this postulate, those nucleophiles which do not react do not fulfil these conditions, *e.g.* alkoxides are hard nucleophiles and hence do not react with the soft electrophile (**41**), phosphorus and carbon nucleophiles examined do not react because of steric congestion and those nitrogen nucleophiles which do not react

do so as a result of electronic factors such as withdrawal of charge lowering nucleophilicity (see Section B.2).

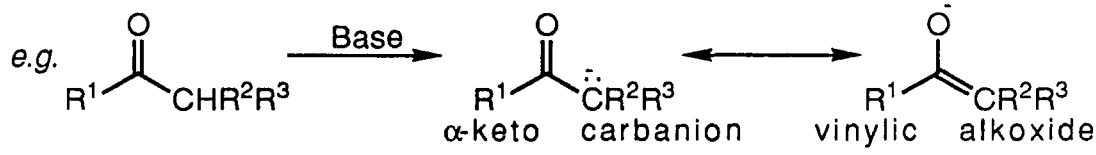
CHAPTER FIVE

DERIVATISATION OF POLYFLUORINATED KETONES

A. ENOLATE CHEMISTRY

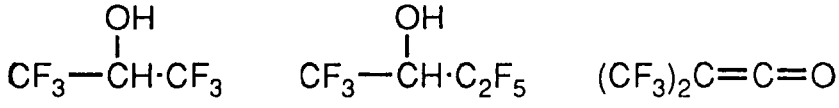
A.1. ENOLATES IN ORGANIC CHEMISTRY

The role of enolates in organic chemistry is a central one, enabling various synthetically useful transformations to be carried out through reactivity at one of two nucleophilic sites: carbon or oxygen (Equation 5.1).



[5.1]

It would therefore be reasonable to believe that fluorinated enolates could assume a correspondingly important role in organofluorine chemistry, providing a method by which organofluorine compounds could be accessed. The major difficulty associated with this strategy is that fluorinated enolates themselves are not easily produced due to the lack of suitable precursor species. Compounds which have been employed as precursors have included perfluorinated alcohols (**50**)[220,221] and (**51**)[220] and ketene (**52**).[222]

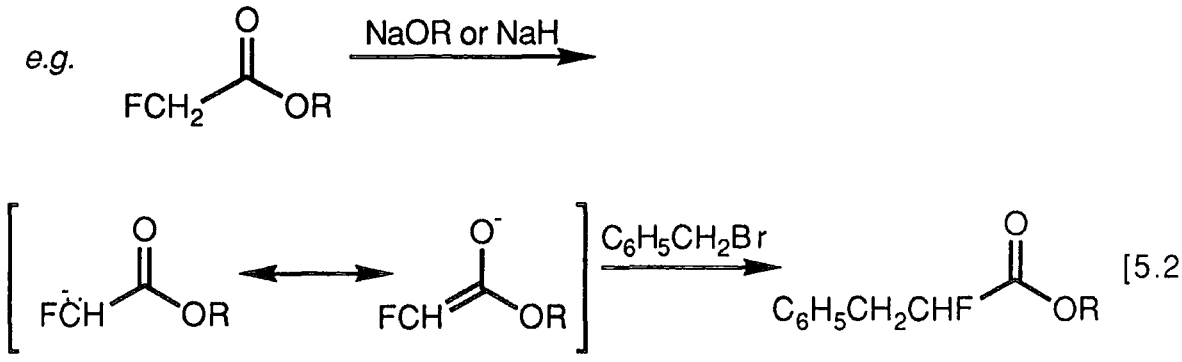


(**50**) (**51**) (**52**)

A.2. FLUOROENOLATES

A.2.a. EARLY FLUOROENOLATE CHEMISTRY

The first reported work on fluoroenolates was carried out by Bergmann and co-workers,[31,223-227] (Equation 5.2) who studied the standard enolate chemistry undergone by α-fluoroacetates and structurally related compounds.

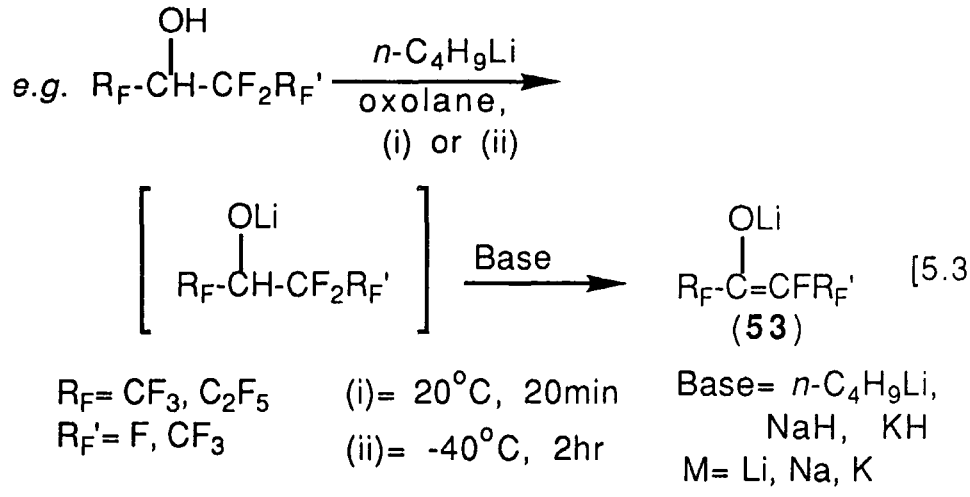


[5.2]

In more recent years Japanese and American teams have made a more thorough investigation of the properties and reactivity of poly- and perfluorinated enolates.

A.2.b. PERFLUOROENOLATES

Perfluoroenolates are formed quantitatively by the action of two molar equivalents of strong base on highly fluorinated alcohols such as *2H*-hexafluoropropan-2-ol (Equation 5.3).



[5.3]

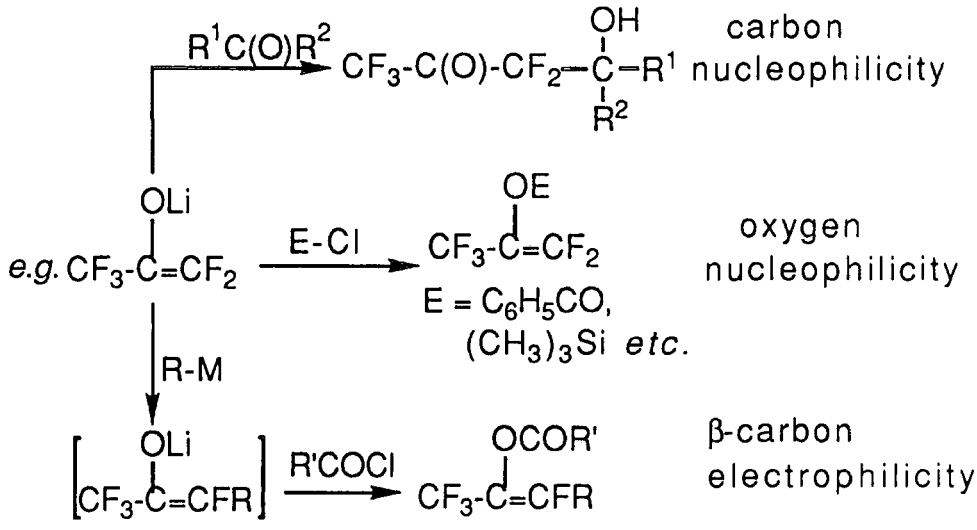
R_F= CF_3, C_2F_5
R_F'= F, CF_3

(i)= 20°C, 20min
(ii)= -40°C, 2hr

Base= *n*-C_4H_9Li, NaH, KH
M= Li, Na, K

Enolates such as (**53**), which is stable even at room temperature, participate in reactions typical of metal enolates, *i.e.* carbon and oxygen nucleophilicity, and also react electrophilically (Scheme 5.1) at the β position as a result of loss of electron density due to the inductive effect of the fluorine substituents. Such reactions are typical of highly fluorinated alkenes.

SCHEME 5.1: REACTIVITY OF (53)

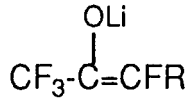


R-M = *n*-C_4H_9Li, C_6H_5Li, C_6H_5MgBr *etc.*

Aldol reactions may be carried out with β,β-difluoro substituted enolates, but not with β–perfluoroalkyl-β-fluoro substituted enolates since the effect of β–perfluoroalkyl substitution serves to decrease the nucleophilicity of the α carbon. In contrast, β carbon electrophilicity, and hence rate of nucleophilic substitution of β fluorine, is increased. These effects are due to the greater electron withdrawing effect of the trifluoromethyl group over a single fluorine substituent, since back donation exhibited by fluorine does not occur with the trifluoromethyl group.

A.2.c. POLYFLUOROENOLATES

Polyfluoroenolates such as (**54**) show reactivity typical of metal enolates, *i.e.* carbon and oxygen nucleophilicity, but do not react with nucleophiles *via* fluoride ion displacement at the β position. This is due to the electron donating effect of alkyl substituents which impart electron density to the β carbon.

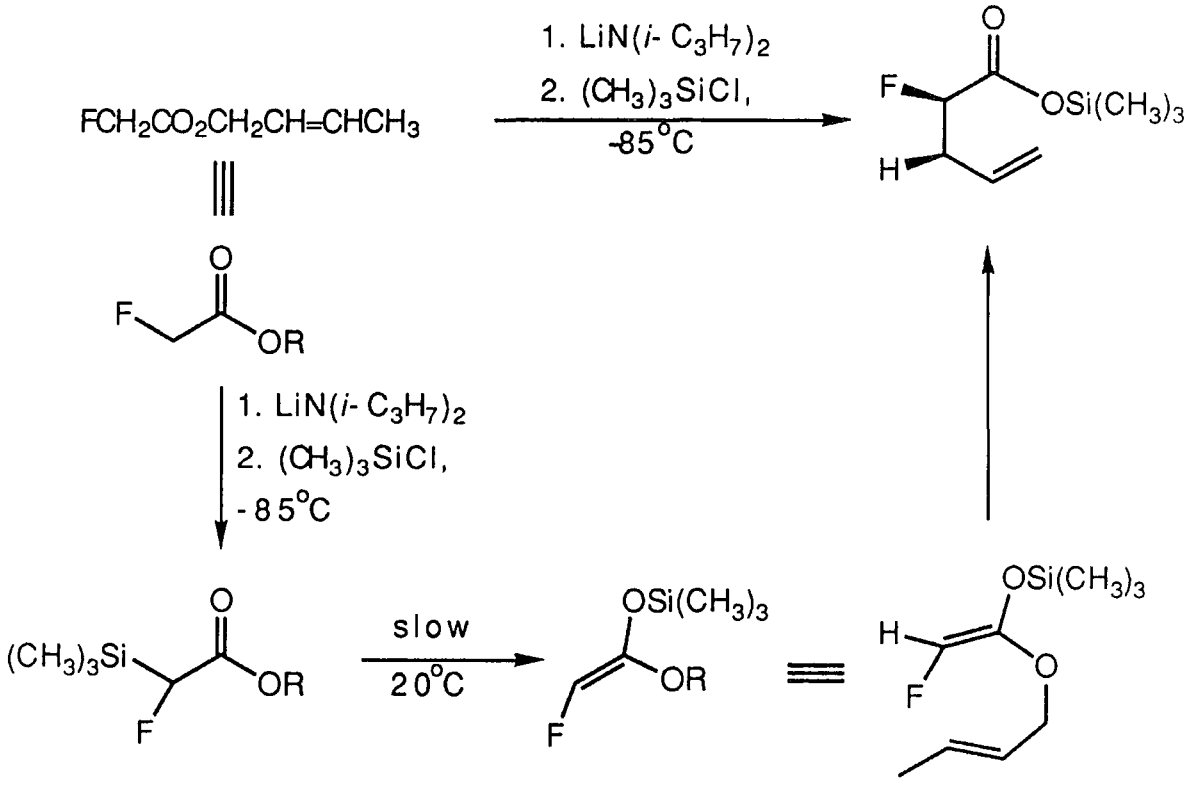


(**54**)

R= H, *n*-C_4H_9

An interesting rearrangement undergone by β,γ unsaturated polyfluoroenolate esters is the Ester Enolate Claisen Rearrangement (Scheme 5.2).[228-230]

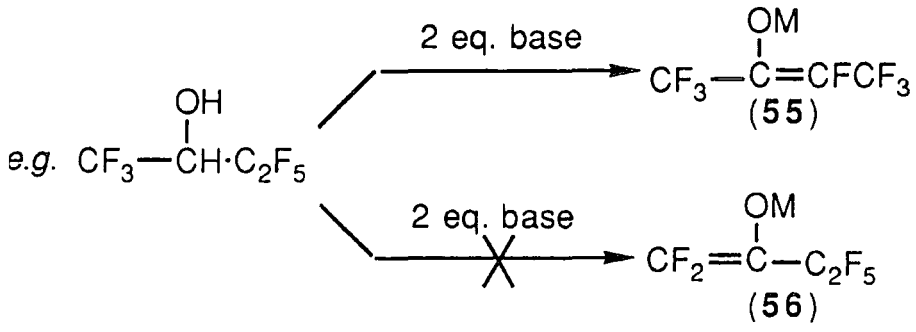
SCHEME 5.2: ESTER ENOLATE CLAISEN REARRANGEMENT



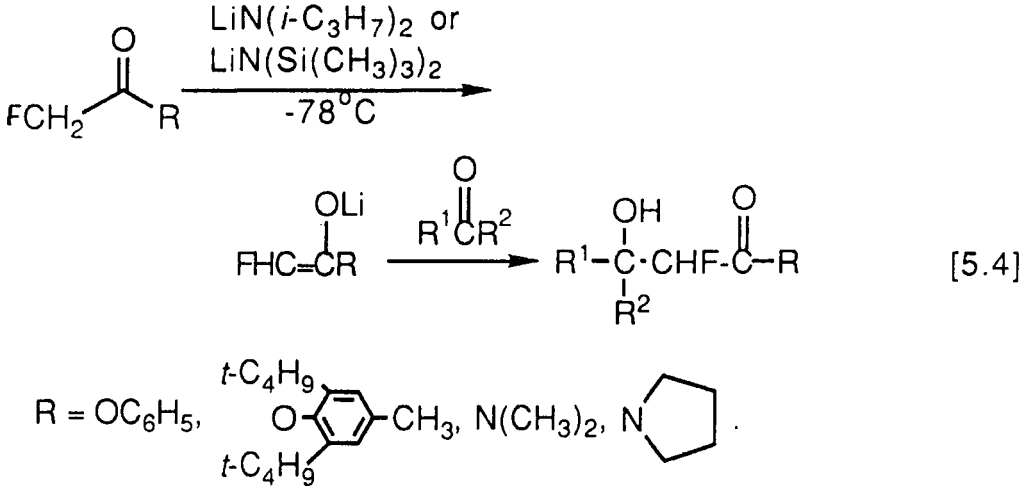
A.2.d. 'INTERNAL' *VERSUS* 'EXTERNAL' ENOLATE FORMATION

In cases where asymmetry allows for the potential for synthesis of two distinct enolates (Scheme 5.3), it is observed that the 'internal' enolate (**55**) is formed in preference to the 'external' enolate (**56**). Both thermodynamic and kinetic factors favour production of (**55**).

SCHEME 5.3: 'INTERNAL' *VERSUS* 'EXTERNAL' ENOLATE FORMATION



Formation of 'external' enolates may be forced by use of α-fluoro esters (Equation 5.4) in which no 'internal' enolate formation is possible.

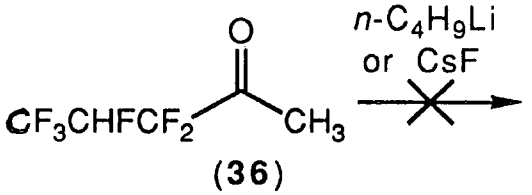


A.3. REACTIONS OF (36)

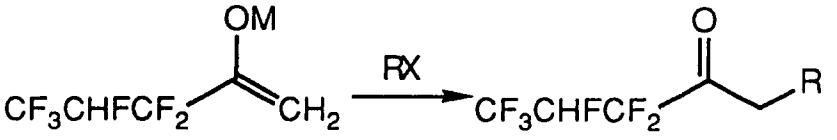
It was decided to investigate whether (**36**), synthesised *via* a free radical process (see Chapter Two), could be made to undergo enolate type chemistry, by utilisation of the increased acidity of the methyl ketone protons as a result of polyfluoro substitution.

Anion trapping experiments involving attempted abstraction of these protons using fluoride ion or butyl lithium as base, and subsequent generation of the corresponding enolate anion

(Scheme 5.5), failed to produce evidence for the reaction proceeding in this manner, since no anion was trapped.



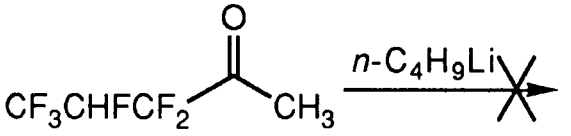
(36)

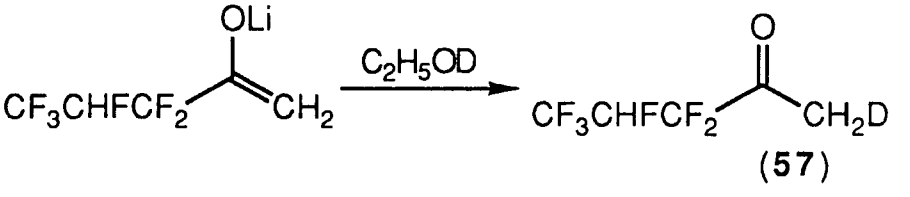


[5.5]

RX = *n*-$C_3H_7C(O)Cl$, 

The attempted enolisation reaction was repeated, then the reaction quenched using ethanol-*d*. No deuterated ketone (**57**) was observed (Scheme 5.6).





(**57**)

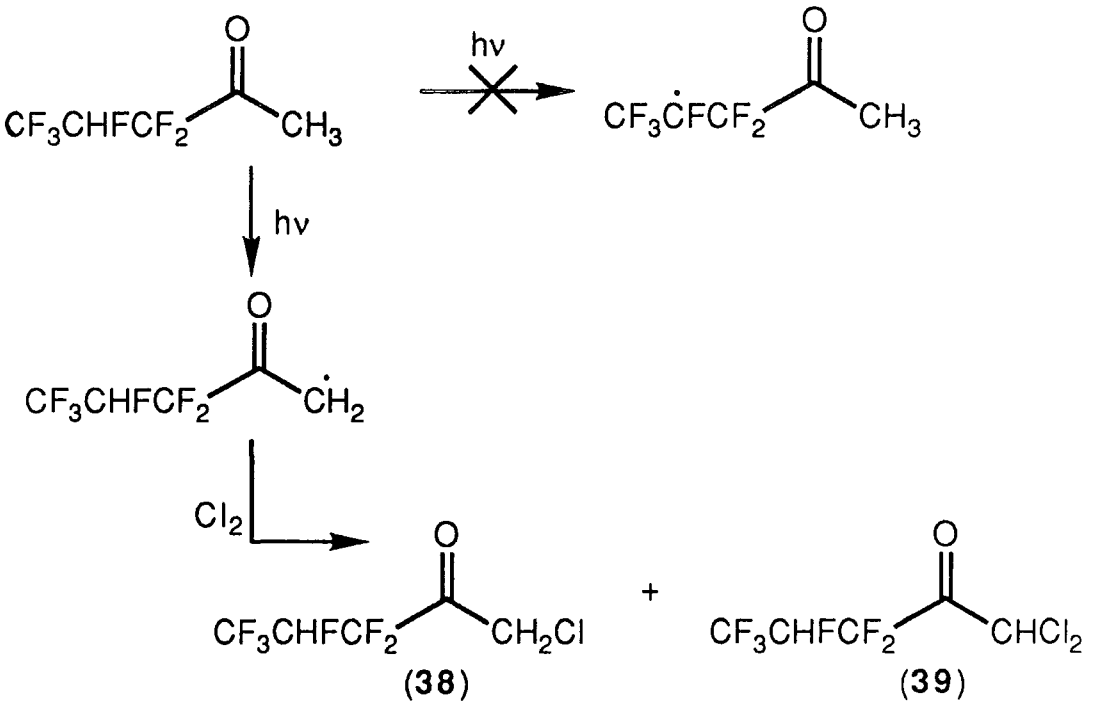
[5.6]

The attempted reactions produced a great many compounds, with highly complex n.m.r. spectra and gas chromatographs which precluded interpretation.

B. OTHER ATTEMPTED REACTIONS OF (36)

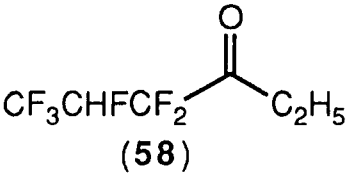
Elementary chlorine was reacted with ketone (**36**) to give a complex mixture containing the new chloromethyl ketone (**38**) (17%) and the new dichloromethyl ketone (**39**) (4%).

SCHEME 5.4: DIRECT CHLORINATION OF (36)

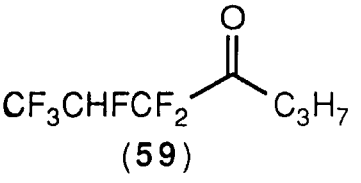


Chloromethyl ketones are formed since the initial hydrogen abstraction step occurs to form the more stable radical, *i.e.* abstraction of a methyl hydrogen to give a radical stabilised by adjacent π electrons rather than abstraction of a fluoromethylene hydrogen to give a radical destabilised by the presence of α perfluoroalkyl substituents.[202,231]

Some attempts were made to effect perfluorination of (**36**) and two higher homologues (**58**) and (**59**) by means of cobalt trifluoride fluorination, without success. However, doubt was cast on the effectiveness of the apparatus used when earlier work, involving fluorination of (**25**) and (**26**),[64] could not be repeated.



(**58**)



(**59**)

C. CONCLUSION

Using a variety of methods, we have been unable to react ketone (**36**) through its enolate form. It seems likely that this compound will not prove feasible as a fluoroenolate precursor.

Direct chlorination of the compound produced the new chloromethyl (**38**) and dichloromethyl (**39**) ketones, in low yield. Since a substantially greater yield was obtained from alcohol (**28**), it seems possible that radical inhibitors may have been present as impurities.

CHAPTER SIX

EXPERIMENTAL TO CHAPTER TWO

INSTRUMENTATION

GAS LIQUID CHROMATOGRAPHY

Gas liquid Chromatography (g.l.c.) was carried out on a Hewlett Packard 5890A gas chromatograph fitted with a 25m. cross-linked methyl silicone capillary column (time programmed, temperature controlled). Preparative scale g.l.c. was performed on a Varian Aerograph Model 920 (catharometer detector) gas chromatograph.

DISTILLATION

Fractional distillation of product mixtures was carried out using a Fischer Spahltrohr MMS 255 small concentric tube apparatus. Boiling points were recorded during distillation.

BOILING POINTS

Boiling points were carried out at atmospheric pressure and are uncorrected.

ELEMENTAL ANALYSES

Carbon, hydrogen and nitrogen elemental analyses were obtained using a Perkin-Elmer 240 Elemental Analyser or a Carlo Erba 1106 Elemental Analyser. Analyses for halogens were performed as described in the literature.[232]

INFRA RED SPECTRA

Infra Red spectra were recorded on either a Perkin-Elmer 457 or 577 Grating Spectrophotometer using conventional techniques.

NMR SPECTRA

Proton NMR spectra were recorded on a Bruker AC250 (250MHz), Varian Gemini (200MHz) or Varian VXR400S (400MHz) NMR

spectrometer.

Fluorine NMR spectra were recorded on a Bruker AC250 (235MHz) or a Varian VXR400S (365MHz) NMR spectrometer.

Carbon NMR were recorded on a Bruker AC250 (63MHz) or Varian VXR400S (100MHz) NMR spectrometer.

MASS SPECTRA

Mass spectra of solid samples were recorded on a VG 7070E spectrometer. G.C. mass spectra were recorded on the VG 7070E spectrometer linked to a Hewlett Packard 5790A gas chromatograph fitted with a 25m cross-linked methyl silicone capillary column.

REAGENTS AND SOLVENTS

In general chemicals were used as received from suppliers (Aldrich, Fluka. Fluorochem, Janssen, Lancaster) and solvents were dried by standard procedures.

A. GENERAL PROCEDURES

A.0 IRRADIATION FACILITY

A purpose-built irradiation facility is available to the university, and was used for all gamma ray initiated free radical reactions reported. The facility consists of an irradiation chamber connected to an outer room by a labyrinthine corridor. Interlocked multiple gates linked to the source withdrawal mechanism ensure that entry to the irradiation chamber is impossible when the ^{60}Co source is in the irradiation position.

Reaction mixtures, suitably contained within an autoclave or a Carius tube shielded within a metal sleeve to prevent injury or damage in the event of violent release of the pressurised contents, are placed in one of a number of positions in a circular array centred on the source. Knowledge of the geometry permits accurate calculation of doses received by the reaction mixtures.

A.1. γ-RAY INITIATED REACTIONS

Reactions were carried out *in vacuo* in a sealed Carius tube (capacity *ca.* 30ml or 60 ml) into which reactants and solvent, if used, were charged. Solid reagents were dissolved in a suitable, *i.e.* inert, solvent before being placed in the Carius tube. Gaseous reagents were introduced by means of standard vacuum line techniques. After the Carius tube was twice degassed, it was frozen down (liquid air) and sealed under vacuum, placed in a metal sheath and allowed to warm to ambient temperature in a fume cupboard, before being transferred to the irradiation facility. The Carius tube was irradiated at a controlled temperature of 18°C for a standard period of *ca.* 5 days (*ca.* 12 MRads) unless otherwise stated. After this time, the tube was removed from the irradiation source, frozen down (liquid air), opened, and gaseous species transferred under vacuum.

A.2. ULTRAVIOLET INITIATED REACTIONS

Carius tube procedures were as described in the preceding section. The charged Carius tube was irradiated for 3-5 days with ultraviolet light (1000W, medium pressure, mercury lamp, at a distance of *ca.* 0.1m) whilst being cooled by an electric fan to prevent overheating.

A.3. PEROXIDE INITIATED REACTIONS

Peroxide initiated reactions were carried out in stainless steel autoclaves (capacity 100ml or 250ml) fitted with a bursting disc. Autoclaves were charged by the same methods as were Carius tubes. The charged autoclaves were transferred, frozen to liquid air temperature, to the high pressure facility and fitted into a rocking furnace, connected to a catchpot in the event of rupture of the bursting disc, before being heated to the appropriate temperature for the appropriate time (programmed). On completion of the programme, the autoclave was permitted to cool to ambient temperature before

being discharged identically to a Carius tube.

B. SYNTHESIS

B.1 SYNTHESIS OF POLYFLUORINATED KETONES

B.1.a. γ-RAY INITIATED FREE RADICAL ADDITION OF ETHANAL TO HEXAFLUOROPROPENE

A Carius tube was charged with ethanal (6.3 g, 143 mmol) and hexafluoropropene (23.1 g, 154 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (16.0 g, 28 mmol) was removed and the remaining liquid distilled to give 3,3,4,5,5,5-hexafluoropentan-2-one (**36**) (10.1 g, 52 mmol, 36%); b.p. 78°C; (Found: C, 31.24; H, 2.29; F, 57.4%; $C_5H_4F_6O$ requires C, 30.93; H 2.06; F, 58.7%); IR spectrum 1; NMR spectrum 1; mass spectrum 1.

B.1.b. γ-RAY INITIATED FREE RADICAL ADDITION OF ETHANAL TO *2H*-PENTAFLUOROPROPENE

A Carius tube was charged with ethanal (2.4 g, 54 mmol) and *2H*-pentafluoropropene (14.1 g, 107 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (8.9 g, 67 mmol) was removed and the remaining liquid distilled to give 3,3,5,5,5-pentafluoropentan-2-one (5.3 g, 30 mmol, 76%); b.p. 25°C (74 mmHg); (Found: C, 34.30; H, 2.40; F, 53.5%. Calc. for $C_5H_5F_5O$ C, 34.09; H, 2.87; F, 54.0%); IR spectrum 2; NMR spectrum 2; mass spectrum 2. Compound No. (**61**)

B.1.c. γ-RAY INITIATED FREE RADICAL ADDITION OF PROPANAL TO HEXAFLUOROPROPENE

A Carius tube was charged with propanal (12.1 g, 208 mmol) and hexafluoropropene (49.0 g, 327 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (19.9 g, 133 mmol) was removed and the remaining liquid distilled to give 4,4,5,6,6,6-hexafluorohexan-3-one (**58**) (39.3 g, 189 mmol, 98%); (Found: C, 34.86; H, 3.66; F, 54.1%. Calc. for $C_6H_6F_6O$ C, 34.62; H, 3.40; F, 54.8%); IR spectrum 3; NMR

spectrum 3; mass spectrum 3.

B.1.d. γ-RAY INITIATED FREE RADICAL ADDITION OF PROPANAL TO *2H*-PENTAFLUOROPROPENE

A Carius tube was charged with propanal (2.2 g, 39 mmol) and *2H*-pentafluoropropene (10.0 g, 76 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (5.7 g, 43.6 mmol) was removed and the remaining liquid distilled to give 4,4,6,6,6-pentafluorohexan-3-one (4.9 g, 26 mmol, 80%); b.p. 39°C (70 mmHg); (Found: C, 37.81; H, 3.98; F, 50.3%. Calc. for $C_6H_7F_5O$ C, 37.90; H, 3.72; F, 50.0%); IR spectrum 4; NMR spectrum 4; mass spectrum 4. Compound No. (**63**)

B.1.e. γ-RAY INITIATED FREE RADICAL ADDITION OF BUTANAL TO HEXAFLUOROPROPENE

A Carius tube was charged with butanal (24.5 g, 340 mmol) and hexafluoropropene (61.6 g, 411 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (13.3 g, 89 mmol) was removed and the remaining liquid distilled to give 1,1,1,2,3,3-hexafluoroheptan-4-one (**59**) (48.32 g, 322 mmol, 95%); (Found: C, 37.49; H, 3.56; F, 51.8%. $C_7H_8F_6O$ requires C, 37.84; H, 3.60; F, 51.2%); IR spectrum 5; NMR spectrum 5; mass spectrum 5.

B.1.f. γ-RAY INITIATED FREE RADICAL ADDITION OF BUTANAL TO *2H*-PENTAFLUOROPROPENE

A Carius tube was charged with butanal (2.6 g, 36 mmol) and *2H*-pentafluoropropene (9.4 g, 71 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (5.34 g, 40 mmol) was removed and the remaining liquid distilled to give 1,1,1,3,3-pentafluoroheptan-4-one (4.48 g, 22 mmol, 71%); b.p. 39°C (31 mmHg); (Found: C, 40.86; H, 4.80; F, 46.1%. Calc. for $C_7H_9F_5O$ C, 41.18; H, 4.46; F, 46.6%); IR spectrum 6; NMR spectrum 6; mass spectrum 6. Compound No. (**65**)

B.1.g. γ-RAY INITIATED FREE RADICAL ADDITION OF PENTANAL TO HEXAFLUOROPROPENE

A Carius tube was charged with pentanal (4.0 g, 47 mmol) and hexafluoropropene (16.5 g, 110 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (8.1 g, 54 mmol) was removed and the remaining liquid distilled to give 1,1,1,2,3,3-hexafluorooctan-4-one (4.4 g, 18 mmol, 38%); b.p. 86°C (16 mmHg); (Found: C, 40.24; H, 4.60; F, 42.7%. $C_8H_{10}F_6O$ requires C, 40.67; H, 4.28; F, 48.3%); IR spectrum 7; NMR spectrum 7; mass spectrum 7. Compound No. (**66**)

B.1.h. γ-RAY INITIATED FREE RADICAL ADDITION OF PENTANAL TO *2H*-PENTAFLUOROPROPENE

A Carius tube was charged with pentanal (4.0 g, 47 mmol) and *2H*-pentafluoropropene (14.1 g, 107 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (9.1 g, 69 mmol) was removed and the remaining liquid distilled to give 1,1,1,3,3-pentafluorooctan-4-one (7.0 g, 32 mmol, 84%); b.p. 92°C (18.5 mmHg); (Found: C, 44.22; H, 5.30; F, 42.9%. Calc. for $C_8H_{11}F_5O$ C, 44.04; H, 5.10; F, 43.6%); IR spectrum 8; NMR spectrum 8; mass spectrum 8. Compound No. (**67**)

B.1.i. γ-RAY INITIATED FREE RADICAL ADDITION OF DIMETHYLPROPANAL TO HEXAFLUOROPROPENE

A Carius tube was charged with dimethylpropanal (5.0 g, 58 mmol) and hexafluoropropene (16.4 g, 109 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (7.9 g, 53 mmol) was removed and the remaining liquid distilled to give 4,4,5,6,6,6-hexafluoro-2,2-dimethylhexan-3-one (7.11 g, 30 mmol, 54%); b.p. 29°C (47 mmHg); (Found: C, 40.27; H, 4.30; F, 47.8%. $C_8H_{10}F_6O$ requires C, 40.68; H, 4.28; F, 48.3%); IR spectrum 9; NMR spectrum 9; mass spectrum 9. Compound No. (**68**)

B.1.j. γ-RAY INITIATED FREE RADICAL ADDITION OF DIMETHYLPROPANAL TO *2H*-PENTAFLUOROPROPENE

A Carius tube was charged with dimethylpropanal (5.0 g, 58 mmol) and *2H*-pentafluoropropene (13.2 g, 100 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (9.4 g, 71 mmol) was removed and the remaining liquid distilled to give 4,4,6,6,6-pentafluoro-2,2-dimethylhexan-3-one (1.5 g, 7 mmol, 27%); b.p. 45°C (68 mmHg); (Found: C, 43.95; H, 5.03; F, 44.0%. Calc. for $C_8H_{11}F_5O$ C, 44.04; H, 5.10; F, 43.6%); IR spectrum 10; NMR spectrum 10; mass spectrum 10. Compound No. (**69**)

B.1.k. γ-RAY INITIATED FREE RADICAL ADDITION OF DODECANEDIAL TO HEXAFLUOROPROPENE

A Carius tube was charged with dodecanedial (0.9 g, 5 mmol), acetone (20 ml) and hexafluoropropene (5.1 g, 34 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (3.6 g, 24 mmol) was removed and the remaining solid recrystallised (acetone) to give 1,1,1,2,3,3,16,16,17,18,18,18-dodecafluorooctadecan-4,15-dione (1.2 g, 2 mmol, 40%); (Found: C, 73.04; H, 11.06; F, 46.0%. Calc. for $C_{18}H_{22}F_{12}O_2$ C, 72.72; H, 11.11; F, 45.8%); IR spectrum 11; NMR spectrum 11; mass spectrum 11. Compound No. (**70**)

B.1.l. ATTEMPTED γ-RAY INITIATED FREE RADICAL ADDITION OF AROMATIC ALDEHYDES TO HEXAFLUOROPROPENE

Experiments were carried out as shown in the following example:

A Carius tube was charged with the aldehyde (*ca.* 50 mmol), acetone (*ca.* 10 ml) in the case of viscous aldehydes, and hexafluoropropene (*ca.* 100 mmol) and irradiated with γ-rays. On opening the tube, no hexafluoropropene was found to have reacted.

B.2. SYNTHESIS OF POLYFLUORINATED ALCOHOLS

B.2.a. γ-RAY INITIATED FREE RADICAL ADDITION OF METHANOL TO HEXAFLUOROPROPENE

A Carius tube was charged with methanol (4.4 g, 138 mmol) and hexafluoropropene (32.1 g, 214 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (14.1 g, 94 mmol) was removed and the remaining liquid distilled to give 2,2,3,4,4,4-hexafluorobutan-1-ol (**29**) (18.2 g, 100 mmol, 83%); (Found: C, 26.40; H, 2.60; F, 63.0%. $C_4H_4F_6O$ requires C, 26.37; H, 2.22; F, 62.6%); IR spectrum 12; NMR spectrum 12; mass spectrum 12.

B.2.b. γ-RAY INITIATED FREE RADICAL ADDITION OF METHANOL TO *2H*-PENTAFLUOROPROPENE

A Carius tube was charged with methanol (2.0 g, 62 mmol) and hexafluoropropene (15.6 g, 118 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (11.3 g, 86 mmol) was removed and the remaining liquid distilled to give 2,2,4,4,4-pentafluorobutan-1-ol (4.7 g, 29 mmol, 90%); b.p. 48°C (30 mmHg); (Found: C, 30.22; H, 3.29; F, 58.0%. Calc. for $C_4H_5F_5O$ C, 29.27; H, 3.08; F, 57.9%); IR spectrum 13; NMR spectrum 13; mass spectrum 13. Compound No. (**71**)

B.2.c. γ-RAY INITIATED FREE RADICAL ADDITION OF ETHANOL TO HEXAFLUOROPROPENE

A Carius tube was charged with ethanol (9.3 g, 203 mmol) and hexafluoropropene (59.7 g, 398 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (28.8 g, 192 mmol) was removed and the remaining liquid distilled to give 3,3,4,5,5,5-hexafluoropentan-2-ol (**28**) (39.0 g, 199 mmol, 98%); b.p. 118°C; (Found: C, 31.04; H, 3.17; F, 57.8%. $C_5H_6F_6O$ requires C, 30.61; H, 3.09; F, 58.2%); IR spectrum 14; NMR spectrum 14; mass spectrum 14.

B.2.d. γ-RAY INITIATED FREE RADICAL ADDITION OF ETHANOL TO *2H*-PENTAFLUOROPROPENE

A Carius tube was charged with ethanol (2.5 g, 53 mmol) and *2H*-pentafluoropropene (18.7 g, 142 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (12.7 g, 102 mmol) was removed and the remaining liquid distilled to give 3,3,5,5,5-pentafluoropentan-2-ol (7.1 g, 40 mmol, 100%); b.p. 54°C (45 mmHg); (Found: C, 34.05; H, 4.30; F, 53.0%. Calc. for $C_5H_7F_5O$ C, 33.71; H, 3.97; F, 53.4%); IR spectrum 15; NMR spectrum 15; mass spectrum 15. Compound No. (**72**)

B.2.e. γ-RAY INITIATED FREE RADICAL ADDITION OF PROPAN-1-OL TO HEXAFLUOROPROPENE

A Carius tube was charged with propan-1-ol (4.0 g, 67 mmol) and hexafluoropropene (20.7 g, 138 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (8.1 g, 54 mmol) was removed and the remaining liquid distilled to give 4,4,5,6,6,6-hexafluorohexan-3-ol (11.1 g, 53 mmol, 79%); b.p. 67°C (7 mmHg); (Found: C, 33.93; H, 4.02; F, 53.9%. $C_6H_8F_6O$ requires C, 34.29; H, 3.85; F, 54.3%); IR spectrum 16; NMR spectrum 16; mass spectrum 16. Compound No. (**73**)

B.2.f. γ-RAY INITIATED FREE RADICAL ADDITION OF BUTAN-1-OL TO HEXAFLUOROPROPENE

A Carius tube was charged with butan-1-ol (4.1 g, 55 mmol), acetone (10 ml) and hexafluoropropene (21.7 g, 145 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (13.5 g, 90 mmol) was removed and the remaining liquid distilled to give 1,1,1,2,3,3-hexafluoroheptan-4-ol (5.4 g, 18 mmol, 33%); b.p. 40°C (4 mmHg); (Found: C, 33.96; H, 4.04; F, 54.0%. $C_5H_7F_5O$ C, 34.29; H, 3.85; F, 54.3%); IR spectrum 17; NMR spectrum 17; mass spectrum 17. Compound No. (**74**)

B.2.g. γ-RAY INITIATED FREE RADICAL ADDITION OF PENTAN-1-OL TO HEXAFLUOROPROPENE

A Carius tube was charged with pentan-1-ol (4.1 g, 46 mmol),

acetone (10 ml) and hexafluoropropene (17.7 g, 118 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (11.7 g, 78 mmol) was removed and the remaining liquid distilled to give 1,1,1,2,3,3-hexafluorooctan-4-ol (2.5 g, 11 mmol, 25%); b.p. 56°C (14 mmHg); (Found: C, 40.38; H, 5.19; F, 48.4%. $C_8H_{12}F_5O$ requires C, 40.34; H, 5.09; F, 47.9%); IR spectrum 18; NMR spectrum 18; mass spectrum 18. Compound No. (**75**)

B.2.h. γ-RAY INITIATED FREE RADICAL ADDITION OF HEXAN-1-OL TO HEXAFLUOROPROPENE

A Carius tube was charged with hexan-1-ol (4.1 g, 40 mmol), acetone (10 ml) and hexafluoropropene (19.7 g, 131 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (11.2 g, 75 mmol) was removed and the remaining liquid distilled to give 1,1,1,2,3,3-hexafluorononan-4-ol (2.7 g, 12 mmol, 30%); b.p. 56°C (4 mmHg); (Found: C, 43.23; H, 6.02; F, 45.2%. $C_9H_{14}F_6O$ requires C, 42.86; H, 5.61; F, 45.2%); IR spectrum 19; NMR spectrum 19; mass spectrum 19. Compound No. (**76**)

B.2.i. γ-RAY INITIATED FREE RADICAL ADDITION OF 2-THIOPHENEMETHANOL TO HEXAFLUOROPROPENE

A Carius tube was charged with 2-thiophenemethanol (5.0 g, 44 mmol) and hexafluoropropene (15.3 g, 102 mmol), and irradiated with γ-rays for 20 days. On opening the tube, no reaction was observed to have occured and all hexafluoropropene was recovered.

B.3. SYNTHESIS OF POLYFLUORINATED DIOLS

B.3.a. γ-RAY INITIATED FREE RADICAL ADDITION OF 1,2-ETHANEDIOL TO HEXAFLUOROPROPENE

A Carius tube was charged with 1,2-ethanediol (2.3 g, 37 mmol), acetone (10 ml) and hexafluoropropene (18.1 g, 121 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (13.9 g, 93 mmol) was removed. Having established the degree (by recovered

fluoroalkene) and nature (by ^{19}F NMR) of incorporation, no further analysis was carried out. Compound No. (**78**)

B.3.b. γ-RAY INITIATED FREE RADICAL ADDITION OF 1,3-PROPANEDIOL TO HEXAFLUOROPROPENE

A Carius tube was charged with 1,3-propanediol (3.1 g, 41 mmol), acetone (10 ml) and hexafluoropropene (14.1 g, 94 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (10.4 g, 69 mmol) was removed. Having established the degree (by recovered fluoroalkene) and nature (by ^{19}F NMR) of incorporation, no further analysis was carried out. Compound No. (**79**)

B.3.c. γ-RAY INITIATED FREE RADICAL ADDITION OF 1,4-BUTANEDIOL TO HEXAFLUOROPROPENE

B.3.c.(i). SYNTHESIS OF 5,5,6,7,7,7-HEXAFLUOROHEPTANE-1,4-DIOL

An autoclave (125ml capacity) was charged with 1,4-butanediol (16.0 g, 177 mmol), acetone (20 ml) and hexafluoropropene (108.1 g, 721 mmol), and irradiated with γ-rays for *ca.* 29 days. On opening the tube, it was discovered that gaseous reagents had escaped over an unknown period of time. However, it was possible to isolate from the materials remaining in the autoclave 5,5,6,7,7,7-hexafluoroheptane-1,4-diol (**22**) (0.9 g, 4mmol, 2%); (Found: C, 35.21; H, 4.05; F, 47.2%. Calc. for $C_7H_{10}F_6O_2$ C, 35.03; H, 4.21; F, 47.5%; IR spectrum 20; NMR spectrum 20; mass spectrum 20.

B.3.c.(ii). SYNTHESIS OF 1,1,1,2,3,3,8,8,9,10,10,10-DODECAFLUORODECANE-4,7-DIOL

A Carius tube was charged with 1,4-butanediol (4.0 g, 44 mmol), acetone (10 ml) and hexafluoropropene (31.8 g, 212 mmol), and irradiated with γ-rays for *ca.* 27 days. On opening the tube, excess alkene (18.6 g, 124 mmol) was removed, and the remaining solid purified by sublimation to give 1,1,1,2,3,3,8,8,9,10,10,10-dodecafluorodecane-4,7-diol (**23**) (5.1 g, 13 mmol, 29%); (Found: C,

30.75; H, 2.55; F, 58.1%. Calc. for $C_{10}H_{10}F_{12}O_2$ C, 30.77; H, 2.56; F, 58.4%); IR spectrum 21; NMR spectrum 21; mass spectrum 21.

B.3.d. γ-RAY INITIATED FREE RADICAL ADDITION OF 1,5-PENTANEDIOL TO HEXAFLUOROPROPENE

A Carius tube was charged with 1,5-pentanediol (4.1 g, 39 mmol), acetone (10 ml) and hexafluoropropene (23.5 g, 157 mmol), and irradiated with γ-rays for *ca.* 29 days.

On opening the tube, excess alkene (10.6 g, 71 mmol) was removed, and the crude product purified by distillation (Kugelrohr apparatus) to give 1,1,1,2,3,3,9,9,10,11,11,11-dodecafluoroundecane-4,8-diol (**24**) (10.1 g, 25 mmol, 64%); b.p. 170°C (0.2 mmHg); (Found: C, 33.04; H, 3.13; F, 55.8%. Calc. for $C_{11}H_{12}F_{12}O_2$ C, 32.67; H, 2.97; F, 56.4%); IR spectrum 22; NMR spectrum 22; mass spectrum 22.

B.3.e. γ-RAY INITIATED FREE RADICAL ADDITION OF 1,6-HEXANEDIOL TO HEXAFLUOROPROPENE

A Carius tube was charged with 1,6-hexanediol (5.1 g, 43 mmol), acetone (*ca.* 10 ml) and hexafluoropropene (12.9 g, 86 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (10.6 g, 71 mmol) was removed. Having established the degree (by recovered fluoroalkene) and nature (by ^{19}F NMR) of incorporation, no further analysis was carried out.

B.4. SYNTHESIS OF POLYFLUORINATED ETHERS

B.4.a. γ-RAY INITIATED FREE RADICAL ADDITION OF OXOLANE TO HEXAFLUOROPROPENE

A Carius tube was charged with oxolane (14.1 g, 195 mmol) and hexafluoropropene (21.6 g, 144 mmol), and irradiated with γ-rays. On opening the tube, all alkene was found to have reacted. The remaining liquid was distilled to give 2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (**25**) (22.7g, 102 mmol, 71%); b.p. 39°C (14 mmHg); (Found: C, 37.29; H, 3.96; F, 51.5%. $C_7H_8F_6O$ requires C, 37.84; H, 3.64; F, 51.4%); IR

spectrum 23; NMR spectrum 23; mass spectrum 23, and 2,5-bis(1,1,2,3,3,3-hexafluoropropyl)oxolane (**26**) (10.1 g, 27 mmol, 9%); b.p. 66°C (8 mmHg); (Found: C, 32.38; H, 2.25; F, 60.9%. $C_{10}H_8F_{12}O$ requires C, 32.26; H, 2.17; F, 61.3%); IR spectrum 24; NMR spectrum 24; mass spectrum 24.

B.5. SYNTHESIS OF POLYFLUORINATED SILANES

B.5.a. γ-RAY INITIATED FREE RADICAL ADDITION OF METHOXYTRIMETHYLSILANE TO HEXAFLUOROPROPENE

A Carius tube was charged with methoxytrimethylsilane (7.4 g, 71 mmol) and hexafluoropropene (26.4 g, 176 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (14.2 g, 101 mmol) was removed. The remaining liquid was distilled to give 2,2,3,4,4,4-hexafluorobutoxytrimethylsilane (13.2 g, 52 mmol, 73%); b.p. 44°C (48 mmHg); (Found: C, 29.41; H, 4.10; F, 40.3%. $C_7H_{12}F_6OSi$ requires C, 29.37; H, 4.24; F, 39.9%); IR spectrum 25; NMR spectrum 25; mass spectrum 25. Compound No. (**80**)

C. COMPETITION REACTIONS

C.1. GENERAL PROCEDURES

Competitive reactions between different alcohols were carried out as illustrated below:

A Carius tube was charged with an equimolar mixture of alcohols A and B, and a deficiency (*ca.* one third of the molar quantity) of hexafluoropropene, and irradiated with γ-rays. When the Carius tube was opened, all alkene had reacted. Comparison was made, by gas chromatographic means, of the relative proportions of A and B prior to and following reaction, and hence their relative reactivities towards free radical addition to hexafluoropropene was determined.

Competitive reactions between different species, *e.g.* alcohols and amines, were carried out as above, but with the modification that,

should either species under study be di- (*e.g.* diethyl ether) or trifunctional (*e.g.* triethylamine) the appropriate correction was made to the molar proportion of each reactant to ensure an equal number of reactive sites of each kind., *e.g.* competition between alcohols and aldehydes employed a 1:1 molar mixture while competition between triethylamine and ethanol employed a 1:3 molar mixture.

C.2. SYNTHESIS OF 2-(1,1,2,3,3,3-HEXAFLUOROPROPYL)PYRROLIDINE-1-CARBOXALDEHYDE

A Carius tube was charged with pyrrolidine-1-carboxaldehyde (8.8 g, 89 mmol) and hexafluoropropene (13.8 g, 92 mmol), and irradiated with γ-rays. On opening the tube, excess alkene (0.6 g, 4 mmol) was removed. The remaining liquid was purified by vacuum transfer to give 2-(1,1,2,3,3,3-hexafluoropropyl)pyrrolidine-1-carboxaldehyde (**27**) (17.7 g, 71 mmol, 79.8%); (Found: C, 39.04; H, 4.00; N, 5.22; F, 45.4%. Calc. for $C_8H_9F_6NO$ requires C, 38.55; H, 3.65; N, 5.62; F, 45.8%); IR spectrum 26; NMR spectrum 26; mass spectrum 26.

CHAPTER SEVEN

EXPERIMENTAL TO CHAPTER THREE

A. ESTERIFICATIONS

A.1. ACETYLATION

A.1.a. ACETYLATION OF (29)

(**29**) (3.0 g, 16 mmol) was stirred under an atmosphere of nitrogen, and acetyl chloride (1.6 g, 21 mmol) added dropwise. Evolution of HCl was observed. The reaction was stirred for 27 hrs, a small volume of water added, and product extracted into diethyl ether. Combined organic fractions were washed with aqueous $CaCO_3$ until neutral, dried ($MgSO_4$), and ether removed under reduced pressure to give 2,2,3,4,4,4-hexafluorobutyl ethanoate (1.9 g, 8 mmol, 52%); (Found: C, 32.06; H, 2.71; F, 50.4%. $C_6H_6F_6O_2$ requires C, 32.14; H, 2.67; F, 50.9%); IR spectrum 27; NMR spectrum 27; mass spectrum 27.
Compound No. (**81**)

A.1.b. ACETYLATION OF (28)

Method 1: (**28**) (3.3 g, 17 mmol) was stirred under an atmosphere of nitrogen, and acetyl chloride (1.7 g, 22 mmol) added dropwise. Evolution of HCl was observed. The reaction was stirred for 1.5 hrs, a small volume of water added, and product extracted into diethyl ether. Combined organic fractions were washed with aqueous $CaCO_3$ until neutral, dried ($MgSO_4$), and ether removed under reduced pressure to give 3,3,4,5,5,5-hexafluoropent-2-yl ethanoate (2.3 g, 10 mmol, 59%); (Found: C, 35.20; H, 3.48; F, 48.4%. $C_7H_8F_6O_2$ requires C, 35.29; H, 3.39; F, 47.9%); i.r spectrum 28; NMR spectrum 28; mass spectrum 28.
Compound No. (**82**)

Method 2: A mixture of (**28**) (4.6 g, 24 mmol) and triethylamine (3.6 g, 36 mmol) was stirred under an atmosphere of nitrogen, and acetyl chloride (2.3 g, 29 mmol) added dropwise, maintaining temperature below 20°C. The reaction was stirred for 1 hr, a small volume of water added, and product extracted into diethyl ether. Combined organic fractions were washed with aqueous $CaCO_3$ until neutral, dried ($MgSO_4$), and ether removed under reduced pressure to give 3,3,4,5,5,5-hexafluoropent-2-yl ethanoate (1.3 g, 5 mmol, 25%); (Found: C, 35.30; H, 3.45; F, 47.0%. $C_7H_8F_6O_2$ requires C, 35.29; H,

3.39; F, 47.9%); i.r spectrum 28; NMR spectrum 28; mass spectrum 28.

A.2. 3,5-DINITROBENZOYLATION

A.2.a. 3,5-DINITROBENZOYLATION OF (29)

A mixture of (**29**) (1.0 g, 5 mmol) and triethylamine (0.6 g, 6 mmol) was stirred at -5°C under an atmosphere of nitrogen, and 3,5-dinitrobenzoyl chloride (1.1 g, 5 mmol) in anhydrous diethyl ether (25 ml) added dropwise. The reaction was stirred for 3 hrs, a small volume of water added, and product extracted into diethyl ether. Combined organic fractions were washed with aqueous $CaCO_3$ until neutral, dried ($MgSO_4$), and ether removed under reduced pressure to give 2,2,3,4,4,4-hexafluorobutyl 3,5-dinitrobenzoate (0.4 g, 1 mmol, 22%); (Found: C, 34.93; H, 1.79; N, 7.18; F, 30.8%. Calc. for $C_{11}H_6F_6N_2O_6$: C, 35.10; H, 1.61; N, 7.45; F, 30.3%); i.r spectrum 29; NMR spectrum 29; mass spectrum 29. Compound No. (**83**)

A.2.b. 3,5-DINITROBENZOYLATION OF (28)

A mixture of (**28**) (5.9 g, 26 mmol) and triethylamine (2.6 g, 26 mmol) was stirred at -5°C under an atmosphere of nitrogen, and 3,5-dinitrobenzoyl chloride (3.1 g, 16 mmol) added dropwise. The reaction was stirred for 30 mins, a small volume of water added, and product extracted into diethyl ether. Combined organic fractions were washed with aqueous $CaCO_3$ until neutral, dried ($MgSO_4$), and ether removed under reduced pressure to give 3,3,4,5,5,5-hexafluoropent-2-yl 3,5-dinitrobenzoate (6.1 g, 16 mmol, 99%); (Found: C, 36.65; H, 2.26; N, 7.33; F, 29.4%. Calc. for $C_{12}H_8F_6N_2O_6$: C, 36.92; H, 2.07; N, 7.18; F, 29.2%); i.r spectrum 30; NMR spectrum 30; mass spectrum 30. Compound No. (**84**)

A.3. 1,4-DIBENZOYLATION (TEREPHTHALOYLATION)

A.3.a. 1,4-DIBENZOYLATION OF (28)

A suspension of 1,4-dibenzoyl chloride (1.0 g, 5 mmol) in pyridine (31 ml) was stirred under an atmosphere of nitrogen, and

(**28**) (2.4 g, 12 mmol) added dropwise. The reaction was stirred for 24 hrs, a small volume of water added, and product extracted into diethyl ether. Combined organic fractions were washed with aqueous $CaCO_3$ until neutral, dried ($MgSO_4$), and ether removed under reduced pressure to give bis(3,3,4,5,5,5-hexafluoropent-2-yl) 1,4-dibenzoate (0.3 g, 0.6 mmol, 12%); (Found: C, 40.89; H, 3.30; F, 49.1%. Calc. for $C_{16}H_{14}F_{12}O_2$ requires C, 41.19; H, 3.03; F, 48.9%); i.r spectrum 31; NMR spectrum 31; mass spectrum 31. Compound No. (**85**)

B. SYNTHESIS OF CARBONATES

B.1. SYNTHESIS OF PHENYL CARBONATE OF (29)

To a stirred solution of (**29**) (3.0 g, 16 mmol) in pyridine (1.3 g), phenyl chloroformate (3.4 g, 22 mmol) was added dropwise. The reaction was stirred for 27 hrs, a small volume of water added, and product extracted into diethyl ether. Combined organic fractions were washed with aqueous $CaCO_3$ until neutral, dried ($MgSO_4$), and ether removed under reduced pressure. Molecular distillation gave 2,2,3,4,4,4-hexafluorobutyl phenyl carbonate (2.9 g, 10 mmol, 58%); (Found: C, 43.66; H, 2.79; F, 38.2%. Calc. for $C_{11}H_8F_6O_3$: C, 43.71; H, 2.68; F, 37.7%); i.r spectrum 32; NMR spectrum 32; mass spectrum 32. Compound No. (**86**)

B.2. SYNTHESIS OF PHENYL CARBONATE OF (28)

To a stirred solution of (**28**) (1.8 g, 9 mmol) in pyridine (1.2 g), phenyl chloroformate (1.6 g, 10 mmol) was added dropwise. The reaction was stirred for 17 hrs, a small volume of water added, and product extracted into diethyl ether. Combined organic fractions were washed with aqueous $CaCO_3$ until neutral, dried ($MgSO_4$), and ether removed under reduced pressure. Molecular distillation gave 3,3,4,5,5,5-hexafluoropent-2-yl phenyl carbonate (1.6 g, 5 mmol, 54%); (Found: C, 45.70; H, 3.51; F, 35.9%. Calc. for $C_{12}H_{10}F_6O_3$: C, 45.57; H, 3.20; F, 36.1%); i.r spectrum 33; NMR spectrum 33; mass spectrum 33. Compound No. (**87**)

C. SYNTHESIS OF ETHERS

C.1. REACTION WITH ALKYL HALIDES

C.1.a. REACTION OF (28) WITH IODOMETHANE

To a stirred solution of NaOH (0.9 g, 22 mmol) in acetone (10 ml) under an atmosphere of nitrogen, (**28**) (2.0 g, 10 mmol) was added dropwise. Stirring was continued for a further 4 hrs, before addition of iodomethane (1.7 g, 12 mmol). The reaction was stirred for 18 hrs, a small volume of water added, and product extracted into diethyl ether. Combined organic fractions were washed with aqueous $CaCO_3$ until neutral, dried ($MgSO_4$), and ether removed under reduced pressure. Molecular distillation gave a mixture which was shown to contain 14% (by g.l.c.) of 3,3,4,5,5,5-hexafluoro-2-methoxypentane; IR spectrum 34; NMR spectrum 34. Compound No. (**88**)

C.1.b. REACTION OF (28) WITH 1-BROMOPROPANE

Method 1: To a stirred solution of NaOH (0.6 g, 14 mmol) in acetone (10 ml) under nitrogen, (**28**) (1.3 g, 7 mmol) was added dropwise. Stirring was continued for a further 2 hrs, before addition of 1-bromopropane (1.2 g, 10 mmol). The reaction was stirred for 18 hrs, a small volume of water added, and product extracted into diethyl ether. Combined organic fractions were washed with aqueous $CaCO_3$ until neutral, dried ($MgSO_4$), and ether removed under reduced pressure. Molecular distillation gave a mixture which was shown to contain 25% (by NMR) of 3,3,4,5,5,5-hexafluoro-2-propoxypentane; IR spectrum 35; NMR spectrum 35; mass spectrum 34. Compound No. (**89**)

Method 2: To a stirred, refluxing solution of NaOH (0.5 g, 12 mmol) in acetone (6 ml) under nitrogen, (**28**) (1.5 g, 7 mmol) was added dropwise, before addition of 1-bromopropane (1.0 g, 8 mmol). The reaction was stirred for 18 hrs, a small volume of water added, and product extracted into diethyl ether. Combined organic fractions were washed with aqueous $CaCO_3$ until neutral, dried ($MgSO_4$), and ether removed under reduced pressure. Molecular distillation gave a mixture

which was shown to contain 55% (by NMR) of 3,3,4,5,5,5-hexafluoro-2-propoxypentane; IR spectrum 35; NMR spectrum 35; mass spectrum 34.

C.1.c. REACTION OF (28) WITH 2-BROMOPROPANE

To a stirred solution of NaOH (0.8 g, 20 mmol) in acetone (10 ml) under nitrogen, (**28**) (3.1 g, 16 mmol) was added dropwise. Stirring was continued for a further 1.5 hrs, before addition of 2-bromopropane (1.8 g, 15 mmol). The reaction was stirred for 18 hrs, a small volume of water added, and product extracted into diethyl ether. Combined organic fractions were washed with aqueous $CaCO_3$ until neutral, dried ($MgSO_4$), and ether removed under reduced pressure. G.l.c. showed that no 3,3,4,5,5,5-hexafluoro-2-(1-methylethoxy)pentane had been formed.

C.1.d. REACTION OF (28) WITH 1,1,1-TRIFLUORO-2-IODOETHANE

To a stirred solution of NaOH (0.8 g, 21 mmol) in acetone (10 ml) under nitrogen, (**28**) (1.1 g, 6 mmol) was added dropwise. Stirring was continued for a further 2 hrs, before addition of 1,1,1-trifluoro-2-iodoethane (1.6 g, 11 mmol). The reaction was stirred for 18 hrs, a small volume of water added, and product extracted into diethyl ether. Combined organic fractions were washed with aqueous $CaCO_3$ until neutral, dried ($MgSO_4$), and ether removed under reduced pressure. G.l.c. showed that no 3,3,4,5,5,5-hexafluoro-2-(1,1,1-trifluoro-2-iodoethoxy)pentane had been formed.

C.2. REACTION WITH ACTIVATED HALIDES

C.2.a. REACTION OF (29) WITH ALLYL BROMIDE

To a stirred solution of NaOH (0.8 g, 21 mmol) in acetone (20 ml), heated to 50°C, under an atmosphere of nitrogen, (29) (2.0 g, 11 mmol) was added dropwise. Stirring was continued for a further 2 hrs, before addition of allyl bromide (1.4 g, 11 mmol). The reaction was allowed to cool to room temperature and stirred for 18 hrs. A

small volume of water was then added and product extracted into diethyl ether. Combined organic fractions were washed with aqueous $CaCO_3$ until neutral, dried ($MgSO_4$), and ether removed under reduced pressure. Molecular distillation gave a mixture which was shown by g.l.c/mass spectrometry to contain a trace amount of 2,2,3,4,4,4-hexafluoro(prop-2-enoxy)-butane; mass spectrum 35. Compound No. (**90**)

C.2.b. REACTION OF (**28**) WITH ALLYL BROMIDE

To a stirred solution of NaOH (0.5 g, 12 mmol) in acetone (5 ml) under an atmosphere of nitrogen, (**28**) (2.1 g, 11 mmol) was added dropwise. Stirring was continued for a further 2 hrs, before addition of allyl bromide (1.2 g, 10 mmol). The reaction was stirred for 3 hrs, a small volume of water added, and product extracted into diethyl ether. Combined organic fractions were washed with aqueous $CaCO_3$ until neutral, dried ($MgSO_4$), and ether removed under reduced pressure. Molecular distillation gave 3,3,4,5,5,5-hexafluoro-2-(prop-2-enoxy)pentane (1.3 g, 6 mmol, 58%); (Found: C, 40.28; H, 4.40; F, 48.2%. Calc. for $C_8H_{10}F_6O$: C, 40.68; H, 4.28; F, 48.3%); i.r spectrum 36; NMR spectrum 36; mass spectrum 36. Compound No. (**91**)

C.2.c. REACTION OF (**29**) WITH BENZYL BROMIDE

To a stirred solution of NaOH (0.8 g, 20 mmol) in acetone (20 ml) under an atmosphere of nitrogen, (**29**) (2.0 g, 11 mmol) was added dropwise. Stirring was continued for a further 2 hrs, before addition of benzyl bromide (1.9 g, 11 mmol). The reaction was stirred under reflux for 18 hrs, allowed to cool to ambient temperature, and worked up as before. Molecular distillation gave a mixture which was shown to contain 67% (by g.l.c.) 2,2,3,4,4,4-hexafluoro-1-(phenylmethoxy)-butane; NMR spectrum 37; mass spectrum 37. Compound No. (**92**)

C.2.d. REACTION OF (**28**) WITH BENZYL BROMIDE

To a stirred solution of NaOH (0.6 g, 16 mmol) in acetone (5 ml) under an atmosphere of nitrogen, (**36**) (1.8 g, 9 mmol) was added dropwise. Stirring was continued for a further 2 hrs, before addition

of benzyl bromide (1.4 g, 8 mmol). The reaction was stirred for 18 hrs and worked up as before. Molecular distillation gave 3,3,4,5,5,5-hexafluoro-2-(phenylmethoxy)pentane (1.9 g, 7 mmol, 78%); (Found: C, 50.16; H, 4.28; F, 38.9%. Calc. for $C_{12}H_{12}F_6O$: C, 50.35; H, 4.23; F, 39.9%); i.r spectrum 37; NMR spectrum 38; mass spectrum 38. Compound No. (**93**)

C.3. REACTION WITH FLUOROBENZENES

C.3.a. REACTION OF (28) WITH 4-FLUOROBENZONITRILE

Method 1: A mixture of (**28**) (2.1 g, 11 mmol), 4-fluorobenzonitrile (2.4 g, 20 mmol) and caesium fluoride (3.6 g, 24 mmol) in acetonitrile (20 ml) was heated under reflux for 6 hrs. No 4-(3,3,4,5,5,5-hexafluoro-pent-2-oxy)benzonitrile was produced (by NMR). Compound No. (**94**)

Method 2: A Carius tube was charged with (**28**) (4.0 g, 20 mmol), 4-fluorobenzonitrile (2.5 g, 20 mmol) and caesium fluoride (3.7 g, 24 mmol), sealed under vacuum and heated to 100°C for 17.5 hrs. The tube was frozen down (liquid air), opened, and the contents discharged and organic materials extracted into diethyl ether. Combined organic fractions were dried ($MgSO_4$), and solvent removed under reduced pressure. No 4-(3,3,4,5,5,5-hexafluoropent-2-oxy)benzonitrile was produced (by NMR).

C.3.b. REACTION OF (28) WITH 4-FLUOROACETOPHENONE

A Carius tube was charged with (**28**) (5.0 g, 25 mmol), 4-fluoroacetophenone (3.4 g, 25 mmol) and caesium fluoride (6.0 g, 40 mmol), sealed under vacuum and heated to 100°C for 17.5 hrs. The tube was frozen down (liquid air), opened, and the contents discharged and organic materials extracted into diethyl ether. Combined organic fractions were dried ($MgSO_4$), and solvent removed under reduced pressure. No 4-(3,3,4,5,5,5-hexafluoropent-2-oxy)acetophenone was produced (by NMR). Compound No. (**95**)

C.3.c. REACTION OF (28) WITH 4-FLUOROBENZOPHENONE

A Carius tube was charged with (**28**) (4.0 g, 21 mmol), 4-fluoroacetophenone (3.8 g, 19 mmol) and caesium fluoride (5.2 g, 35 mmol), sealed under vacuum and heated to 100°C for 17.5 hrs. The tube was frozen down (liquid air), opened, and the contents discharged and organic materials extracted into diethyl ether. Combined organic fractions were dried ($MgSO_4$), and solvent removed under reduced pressure. No 4-(3,3,4,5,5,5-hexafluoropent-2-oxy)benzophenone was produced (by NMR). Compound No. (**96**)

C.3.d. REACTION OF (28) WITH 4-(TRIFLUOROMETHYL)FLUOROBENZENE

A Carius tube was charged with (**28**) (2.9 g, 15 mmol), 4-(trifluoromethyl)fluorobenzene (2.4 g, 15 mmol) and caesium fluoride (4.8 g, 32 mmol), sealed under vacuum and heated to 100°C for 17.5 hrs. The tube was frozen down (liquid air), opened, and the contents discharged and organic materials extracted into diethyl ether. Combined organic fractions were dried ($MgSO_4$), and solvent removed under reduced pressure. No 4-(3,3,4,5,5,5-hexafluoropent-2-oxy)(trifluoromethyl)benzene was produced (by NMR). Compound No. (**97**)

C.3.e. REACTION OF (29) WITH HEXAFLUOROBENZENE

A Carius tube was charged with (**29**) (2.1 g, 12 mmol), hexafluorobenzene (2.9 g, 15 mmol) and caesium fluoride (3.3 g, 22 mmol), sealed under vacuum and heated to 100°C for 16.5 hrs. The tube was frozen down (liquid air), opened, and the contents discharged and organic materials extracted into diethyl ether. Combined organic fractions were dried ($MgSO_4$), and solvent removed under reduced pressure. Molecular distillation gave (2,2,3,4,4,4-hexafluorobutoxy)pentafluorobenzene (0.2 g, 0.5 mmol, 4%); (Found: C, 34.40; H, 0.99; F, 60.9%. Calc. for $C_{10}H_3F_{11}O$: C, 34.48; H, 0.87; F, 60.1%); i.r spectrum 38; NMR spectrum 39; mass spectrum 39. Compound No. (**98**)

C.3.f. REACTION OF (28) WITH HEXAFLUOROBENZENE

A Carius tube was charged with (28) (3.0 g, 18 mmol), hexafluorobenzene (3.9 g, 21 mmol) and caesium fluoride (5.8 g, 38 mmol), sealed under vacuum and heated to 100°C for 17.5 hrs. The tube was frozen down (liquid air), opened, and the contents discharged and organic materials extracted into diethyl ether. Combined organic fractions were dried ($MgSO_4$), and solvent removed under reduced pressure. Molecular distillation gave (3,3,4,5,5,5-hexafluoropent-2-oxy)pentafluorobenzene (0.1 g, 0.3 mmol, 15%); i.r spectrum 39; NMR spectrum 40; mass spectrum 40. Compound No. (**99**)

C.3.g. REACTION OF (29) WITH 2,4-DINITROFLUOROBENZENE

A Carius tube was charged with (**29**) (2.9 g, 16 mmol), 2,4-dinitrofluorobenzene (2.5 g, 13 mmol) and caesium fluoride (2.8 g, 19 mmol), sealed under vacuum and heated to 100°C for 16.5 hrs. The tube was frozen down (liquid air), opened, and the contents discharged and organic materials extracted into diethyl ether. Combined organic fractions were dried ($MgSO_4$), and solvent removed under reduced pressure. Molecular distillation gave (2,2,3,4,4,4-hexafluorobutoxy)-2,4-dinitrobenzene (4.5 g, 13 mmol, 100%); (Found: C, 34.07; H, 1.77; N, 8.25; F, 33.4%. Calc. for $C_{10}H_6F_6N_2O_5$: C, 34.48; H, 1.74; N, 8.05; F, 32.8%); i.r spectrum 40; NMR spectrum 41. Compound No. (**100**)

C.3.h. REACTION OF (28) WITH 2,4-DINITROFLUOROBENZENE

A mixture of (**28**) (3.1 g, 16 mmol), 2,4-dinitrofluorobenzene (2.7 g, 14 mmol) and caesium fluoride (2.8 g, 19 mmol) in acetonitrile (25 ml) was heated to 50°C for 2.5 hrs. The reaction mixture was allowed to cool to ambient temperature and products extracted into diethyl ether. Combined organic fractions were dried ($MgSO_4$), and solvent removed under reduced pressure. Molecular distillation gave (3,3,4,5,5,5-hexafluoropent-2-oxy)-2,4-dinitrobenzene (4.7 g, 13 mmol, 92%); (Found: C, 36.79; H, 7.99; N, 2.63; F, 30.8%. Calc. for $C_{11}H_8F_6N_2O_5$: C, 36.46; H, 7.73; N, 2.23; F, 31.5%); i.r spectrum 41; NMR

spectrum 42; mass spectrum 41. Compound No. (**101**)

C.4. REACTION WITH PERFLUOROHETEROAROMATIC COMPOUNDS

C.4.a. REACTION OF (29) WITH PENTAFLUOROPYRIDINE

A mixture of (**29**) (4.2 g, 23 mmol), pentafluoropyridine (3.6 g, 21 mmol) and caesium fluoride (4.0 g, 26 mmol) was heated to 100°C for 16 hrs. The reaction mixture was allowed to return to ambient temperature and products extracted into diethyl ether. Combined organic fractions were dried ($MgSO_4$), and solvent removed under reduced pressure. Molecular distillation gave 4-(2,2,3,4,4,4-hexafluorobutoxy)tetrafluoropyridine (5.0 g, 15 mmol, 81%); (Found: C, 32.77; H, 1.16; N, 3.97; F, 57.0%. Calc. for $C_9H_3F_{10}NO$: C, 32.63; H, 0.92; N, 4.23; F, 57.4%); i.r spectrum 42; NMR spectrum 43; mass spectrum 42. Compound No. (**102**)

C.4.b. REACTION OF (28) WITH PENTAFLUOROPYRIDINE

A mixture of (**28**) (3.5 g, 18 mmol), pentafluoropyridine (2.7 g, 23 mmol) and caesium fluoride (4.3 g, 29 mmol) was heated to 100°C for 18 hrs. The reaction mixture was allowed to return to ambient temperature and products extracted into diethyl ether. Combined organic fractions were dried ($MgSO_4$), and solvent removed under reduced pressure. Molecular distillation gave 4-(3,3,4,5,5,5-hexafluoropent-2-oxy)tetrafluoropyridine (4.0 g, 12 mmol, 65%); (Found: C, 34.26; H, 1.66; N, 3.82; F, 54.7%. Calc. for $C_{10}H_5F_{10}NO$: C, 34.78; H, 1.46; N, 4.06; F, 55.1%); i.r spectrum 43; NMR spectrum 44; mass spectrum 43. Compound No. (**103**)

C.4.c. REACTION OF (29) WITH TETRAFLUOROPYRIMIDINE

A Carius tube was charged with (**29**) (4.7 g, 26 mmol), tetrafluoropyrimidine (3.9 g, 26 mmol) and caesium fluoride (4.3 g, 29 mmol) and heated to 100°C for 16 hrs. The Carius tube was frozen down (liquid air), opened, and products extracted into diethyl ether. Combined organic fractions were dried ($MgSO_4$), and solvent removed

under reduced pressure. Molecular distillation gave 4-(2,2,3,4,4,4-hexafluorobutoxy)trifluoropyrimidine (3.7 g, 12 mmol, 57%); (Found: C, 30.62; H, 1.19; N, 8.68; F, 53.8%. Calc. for $C_8H_3F_9N_2O$: C, 30.57; H, 0.96; N, 8.92; F, 54.5%); i.r spectrum 44; NMR spectrum 45; mass spectrum 44. Compound No. (**104**)

C.4.d. REACTION OF (**28**) WITH TETRAFLUOROPYRIMIDINE

A Carius tube was charged with (**28**) (5.1 g, 26 mmol), tetrafluoropyrimidine (3.9 g, 26 mmol) and caesium fluoride (4.1 g, 27 mmol) and heated to 100°C for 16 hrs. The Carius tube was frozen down (liquid air), opened, and products extracted into diethyl ether. Combined organic fractions were dried ($MgSO_4$), and solvent removed under reduced pressure. Molecular distillation gave 4-(3,3,4,5,5,5-hexafluoropent-2-oxy)trifluoropyrimidine (3.2 g, 10 mmol, 39%); (Found: C, 33.30; H, 1.20; N, 8.22; F, 52.7%. Calc. for $C_9H_5F_9N_2O$: C, 32.93; H, 1.54; N, 8.54; F, 52.1%); i.r spectrum 45; NMR spectrum 46; mass spectrum 45. Compound No. (**105**)

C.4.e. REACTION OF (**29**) WITH TETRAFLUOROPYRAZINE

A Carius tube was charged with (**29**) (2.0 g, 11 mmol), tetrafluoropyrazine (2.9 g, 19 mmol) and caesium fluoride (3.3 g, 22 mmol) and heated to 100°C for 17 hrs. The Carius tube was frozen down (liquid air), opened, and products extracted into diethyl ether. Combined organic fractions were dried ($MgSO_4$), and solvent removed under reduced pressure. Molecular distillation gave 5-(2,2,3,4,4,4-hexafluorobutoxy)trifluoropyrazine (2.4 g, 8 mmol, 73%); (Found: C, 32.74; H, 1.80; N, 8.29; F, 52.7%. Calc. for $C_9H_5F_9N_2O$: C, 32.93; H, 1.54; N, 8.54; F, 52.1%); i.r spectrum 46; NMR spectrum 47; mass spectrum 46. Compound No. (**106**)

C.4.f. REACTION OF (**28**) WITH TETRAFLUOROPYRAZINE

A Carius tube was charged with (**28**) (3.2 g, 16 mmol), tetrafluoropyrazine (9.3 g, 61 mmol) and caesium fluoride (5.9 g, 39 mmol) and heated to 100°C for 17.5 hrs. The Carius tube was frozen

down (liquid air), opened, and products extracted into diethyl ether. Combined organic fractions were dried ($MgSO_4$), and solvent removed under reduced pressure. Molecular distillation gave 5-(3,3,4,5,5,5-hexafluoropent-2-oxy)trifluoropyrazine (1.4 g, 4 mmol, 25%); (Found: C, 32.72; H, 1.38; F, 51.9%. Calc. for $C_9H_5F_9N_2O$: C, 32.93; H, 1.54; N, 8.54; F, 52.1%); i.r spectrum 47; NMR spectrum 48; mass spectrum 47. Compound No. (**107**)

C.4.g. REACTION OF (29) WITH TETRAFLUOROPYRIDAZINE

A Carius tube was charged with (**29**) (2.1 g, 11 mmol), tetrafluoropyridazine (1.5 g, 10 mmol) and caesium fluoride (2.6 g, 17 mmol) and heated to 100°C for 17.5 hrs. The Carius tube was frozen down (liquid air), opened, and products extracted into diethyl ether. Combined organic fractions were dried ($MgSO_4$), and solvent removed under reduced pressure. Molecular distillation gave 4-(2,2,3,4,4,4-hexafluorobutoxy)trifluoropyridazine (2.1 g, 7 mmol, 69%); (Found: C, 33.18; H, 1.35; N, 8.88; F, 51.9%. Calc. for $C_9H_5F_9N_2O$: C, 32.93; H, 1.54; N, 8.54; F, 52.1%); i.r spectrum 48; NMR spectrum 49; mass spectrum 48. Compound No. (**108**)

C.4.h. REACTION OF (28) WITH TETRAFLUOROPYRIDAZINE

A Carius tube was charged with (**28**) (3.6 g, 18 mmol), tetrafluoropyridazine (4.1 g, 27 mmol) and caesium fluoride (6.0 g, 40 mmol) and heated to 100°C for 17.5 hrs. The Carius tube was frozen down (liquid air), opened, and products extracted into diethyl ether. Combined organic fractions were dried ($MgSO_4$), and solvent removed under reduced pressure. Molecular distillation gave 4-(3,3,4,5,5,5-hexafluoropent-2-oxy)trifluoropyridazine (6.0 g, 18 mmol, 100%); (Found: C, 33.38; H, 1.26; N, 8.29; F, 52.0%. Calc. for $C_9H_5F_9N_2O$: C, 32.93; H, 1.54; N, 8.54; F, 52.1%); i.r spectrum 49; NMR spectrum 50; mass spectrum 49. Compound No. (**109**)

D. SYNTHESIS OF SULPHONATES

D.1. SYNTHESIS OF 4-METHYLBENZENESULPHONATES (TOSYLATION)

D.1.a. TOSYLATION OF (29)

Method 1:[140] To a stirred solution of (**29**) (4.8 g, 26 mmol), 4-methylbenzenesulphonyl chloride (6.3 g, 33 mmol) in water (15 ml), aqueous NaOH (1.4 g, 35 mmol) was added dropwise. Stirring was continued for 4 days, and product extracted into petroleum ether. Combined organic fractions were washed with aqueous $CaCO_3$ until neutral, dried ($MgSO_4$), and solvent removed under reduced pressure. Molecular distillation gave 2,2,3,4,4,4-hexafluorobutyl 4-methylbenzenesulphonate (**33**) (7.5 g, 21 mmol, 81%); (Found: C, 39.32; H, 3.36; F, 33.2%. Calc. for $C_{11}H_{10}F_6O_3S$ requires C, 39.29; H, 3.01; F, 33.9%); i.r spectrum 50; NMR spectrum 51; mass spectrum 50.

D.1.b. TOSYLATION OF (28)

Method 2: To a stirred solution of (**28**) (5.4 g, 28 mmol) in pyridine (5 ml) at -5°C, 4-methylbenzenesulphonyl chloride (16.2 g, 85 mmol) in pyridine (30 ml) was added dropwise over a period of 2 hrs, maintaining a temperature of <0°C. Stirring was continued for 3 days, and reaction mixture quenched by pouring onto ice/water (*ca.* 750 ml), whereupon crude tosylate precipitated out. Recrystallisation (ethanol) gave 3,3,4,5,5,5-hexafluoropentyl 2-(4-methylbenzenesulphonate) (**34**) (9.8 g, 28 mmol, 100%); (Found: C, 40.65; H, 3.22; F, 32.4%. $C_{12}H_{12}F_6O_3S$ requires C, 41.14; H, 3.43; F, 32.6%); i.r spectrum 51; NMR spectrum 52; mass spectrum 51.

D.1.c. TOSYLATION OF (23)

Method 2: To a stirred solution of (**23**) (5.0 g, 13 mmol) in pyridine (9 ml) at -5°C, 4-methylbenzenesulphonyl chloride (13.1 g, 69 mmol) in pyridine (40 ml) was added dropwise over a period of 2 hrs, maintaining a temperature of <0°C. Stirring was continued for 6 days, and reaction mixture quenched by pouring onto ice/water (*ca.* 500 ml),

whereupon crude tosylate precipitated out. Recrystallisation (ethanol) gave 1,1,1,2,3,3,4,8,8,9,10,10,10-dodecafluorodecyl 4,7-di-(4-methylbenzenesulphonate) (**35**) (3.5 g, 5 mmol, 39%); (Found: C, 41.00; H, 326; F, 33.0%. Calc. for $C_{24}H_{22}F_{12}O_6S_2$ requires C, 41.26; H, 3.18; F, 32.7%); i.r spectrum 52; NMR spectrum 53; mass spectrum 52.

D.2. SYNTHESIS OF TRICHLOROMETHANESULPHONATES (TRICLATION)

D.2.a. TRICLATION OF (28)

Following the method of Steinman *et al*,[233] to a stirred solution of (**28**) (4.4 g, 22 mmol), trichloromethanesulphonyl chloride (5.1 g, 23 mmol) in water (20 ml) at a temperature of 50°C, NaOH (1.0 g, 25 mmol) in water (5 ml) was added dropwise. Stirring was continued for 2 hrs, and the reaction mixture allowed to cool overnight. Product was then extracted into petroleum ether. Combined organic fractions were washed successively with aqueous NH_3 and water until neutral, dried ($MgSO_4$), and solvent removed under reduced pressure to give an opalescent white solid, which was purified by sublimation to give 3,3,4,5,5,5-hexafluoropentyl 2-(trichloromethanesulphonate) (1.0 g, 3 mmol, 12%); (Found: C, 19.27; H, 1.60%. Calc. for $C_6H_5Cl_3F_6O_3S$: C, 19.07; H, 1.33%); i.r spectrum 53; NMR spectrum 54; mass spectrum 53. Compound No. (**110**)

D.3. SYNTHESIS OF TRIFLUOROMETHANESULPHONATES (TRIFLATION)

D.3.a. TRIFLATION OF (28)

To a stirred solution of (**28**) (3.5 g, 18 mmol) and pyridine (6.1 g, 8 mmol) in dichloromethane (45 ml) at a temperature of 0°C, trifluoromethanesulphonic anhydride (5.1 g, 23 mmol) was added dropwise, maintaining temperature <3°C. Stirring was continued for 1.5 hrs, and the reaction mixture extracted into diethyl ether, washed with aqueous HCl and water, dried ($MgSO_4$), and solvent removed under reduced pressure. No 3,3,4,5,5,5-hexafluoropentyl 2-trifluoromethanesulphonate was present. Compound No. (**111**)

E. ATTEMPTED REACTION OF SULPHONATES

E.1. HALOGEN NUCLEOPHILES

E.1.a. REACTION WITH IODIDE

Method 1: A solution of (**34**) (1.3 g, 4 mmol) and potassium iodide (0.7 g, 4 mmol) in acetonitrile (15 ml) was heated under reflux for 3 days. No 1,1,1,2,3,3-hexafluoro-4-iodopentane was formed (by NMR); (**34**) (0.7 g, 2 mmol, 54%) was recovered. Compound No. (**112**)

Method 2: [140] A Carius tube was charged with (**34**) (2.1 g, 6 mmol), potassium iodide (1.0 g, 6 mmol) and 2-(2-hydroxyethoxy)ethanol (15 g) was heated to 235°C for 4.5 hrs. No 1,1,1,2,3,3-hexafluoro-4-iodopentane was formed (by NMR).

E.1.b. REACTION WITH BROMIDE

A solution of (**34**) (0.7 g, 2 mmol) and sodium bromide (0.5 g, 5 mmol) in acetonitrile (10 ml) was heated under reflux for 18 hrs. No 1,1,1,2,3,3-hexafluoro-4-bromopentane was formed (by NMR). Compound No. (**113**)

E.2. OXYGEN NUCLEOPHILES

E.2.a. REACTION WITH METHOXIDE

Various reaction conditions, *i.e.* temperatures and solvents, were tried. A typical experiment is outlined below:

An autoclave (capacity 150 ml) was charged with a solution of sodium methoxide (0.25 g, 5 mmol) in anhydrous methanol (10.2 g) and (**34**) (1.5 g, 4 mmol) and heated to 200°C for 2.75 hrs. No 1,1,1,2,3,3-hexafluoro-4-methoxypentane was formed (by NMR and g.c./mass spec.). Compound No. (**114**)

E.2.b. REACTION WITH ETHOXIDE

Various reaction conditions, *i.e.* temperatures and solvents, were tried. A typical experiment is outlined below:

An autoclave (capacity 150 ml) was charged with sodium (0.29 g, 13 mmol) in anhydrous ethanol (10.6 g) and (**34**) (2.4 g, 7 mmol) and heated to 150°C for 3 hrs. No 1,1,1,2,3,3-hexafluoro-4-ethoxy-pentane was formed (by NMR and g.c./mass spec.). Compound No. (**115**)

E.3. NITROGEN NUCLEOPHILES

E.3.a. REACTION WITH DIETHYLAMINE

An autoclave (capacity 150 ml) was charged with a solution of (**34**) (1.6 g, 4 mmol) and diethylamine (0.8 g, 11 mmol) in acetonitrile (16 g) and heated to 150°C for 5.5 hrs. Reaction was worked up by extraction with diethyl ether, washing with aqueous Na_2CO_3 until neutral. Combined organic fractions were dried ($MgSO_4$), and solvent removed under reduced pressure. No 3,3,4,5,5,5-hexafluoropent-2-yl diethylamine was formed (by NMR and g.c./mass spec.) Compound No. (**116**)

E.4. CARBON NUCLEOPHILES

E.4.a. REACTION WITH GRIGNARD REAGENTS

Grignard reagents ethyl magnesium bromide and phenyl magnesium bromide were prepared by standard methods.[203]. To ethereal solutions thus prepared (typically 8-10 mmol), (**34**) (8-10 mmol) in diethyl ether (*ca.* 10-25 ml) was added, and the solution stirred from 3.5 to 64 hrs. Workup by extraction into diethyl ether showed that no 4-alkyl-1,1,1,2,3,3-hexafluoropentane was formed (by NMR). Compound No. (**117**)

E.5. SULPHUR NUCLEOPHILES

E.5.a. REACTION WITH THIOPHENATE

Thiophenate ion was generated by adding thiophenol (2.1g, 19 mmol) dropwise to a stirred solution, under a nitrogen atmosphere, of sodium hydride (0.5 g, 21 mmol) in *N,N*-dimethylformamide (18 ml). (**34**) (1.0 g, 3 mmol) in *N,N*-dimethylformamide (5 ml) was added dropwise and the solution stirred for 5 days. Workup by extraction into diethyl ether, washing with base and subsequent concentration gave only diphenyl disulphide. Compound No. (**118**)

F. OXIDATION

F.1. CHROMIC ACID OXIDATIONS

Typically reactions by this method involved stirring a solution of (**28**) (*ca.* 10 mmol) and aqueous chromic acid (twofold or greater excess), prepared by standard methods,[218,219] in the appropriate solvent for a set period at a given temperature, before workup by extraction (diethyl ether) and concentration. Sealed tube experiments were also carried out to enable temperatures above the normal boiling points of solvents used to be attained. Oxidation by this method was unsuccessful.

F.2. PERMANGANATE OXIDATIONS

Typically reactions by this method involved stirring an acidic (*ca.* 1M H_2SO_4) solution of (**28**) (*ca.* 10 mmol) and aqueous potassium permanganate (twofold or greater excess), at a given temperature, before workup by extraction (diethyl ether) and concentration. Oxidation by this method was unsuccessful.

G. DEHYDRATION

G.1. PHOSPHORUS PENTOXIDE DEHYDRATION

Apparatus consisted of a two-necked 50 ml or 100 ml round bottom flask with a dropping funnel and stillhead with condenser, receiver adapter and collecting vessel cooled by an ice/salt bath attached. Reactions were carried out by dropping (**28**) (*ca.* 20 mmol) onto phosphorus pentoxide (*ca.* 30 mmol) supported on glass wool. The reaction flask was heated to *ca.* 100°C to achieve flash distillation of dehydration product. No dehydration by this method was accomplished, the general result being extensive decomposition to black tarry residues.

G.2. PHOSPHORUS PENTOXIDE/SULPHURIC ACID DEHYDRATION

Apparatus was constructed as described in Section G.1. Oleum was produced *in situ* by dehydration of sulphuric acid (*ca.* 10 ml) by phosphorus pentoxide (*ca.* 3 g). To this solution at 145°C, (**28**) (3.7 g, 19.1 mmol) was added dropwise. No material was distilled across and hence no dehydration by this method was accomplished.

H. DIRECT CHLORINATION

A Pyrex® tube fitted with a Rotaflo® tap was charged with (**28**) (4.2 g, 23 mmol) and elementary chlorine (1.9 g, 27 mmol), by standard vacuum line techniques. The tube was exposed to visible radiation from a 60W Tungsten lamp for 21 hrs, by which time decolourisation was complete. A mixture of compounds was produced, and 1-chloro-3,3,4,5,5,5-hexafluoropentan-2-one (**38**) (75% by g.l.c.); mass spectrum 54, and 1,1-dichloro-3,3,4,5,5,5-hexafluoropentan-2-one (**39**) (18% by g.l.c.); mass spectrum 55 were identified as being present.

CHAPTER EIGHT

EXPERIMENTAL TO CHAPTER FOUR

A. HALOGENATION

A.1. DIRECT HALOGENATION OF (25)

A.1.a. DIRECT CHLORINATION OF (25)

A Pyrex® tube fitted with a Rotaflo® tap was charged with (**25**) (5.0 g, 23 mmol) and elementary chlorine (1.6 g, 23 mmol), by standard vacuum line techniques. The tube was exposed to visible radiation from a 60W Tungsten lamp for 3 hrs, by which time decolourisation was complete. Evolved HCl was vented in a fume cupboard leaving 2-chloro-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane (**41**) (5.8 g , 23 mmol, 100%); (Found: C, 32.19; H, 3.06; F, 44.8%. Calc. for $C_7H_7ClF_6O$: C, 32.75; H, 2.76; F, 44.4%); i.r spectrum 54; NMR spectrum 55; mass spectrum 56.

A.1.b. DIRECT BROMINATION OF (25)

A Carius tube was charged with (**25**) (5.2 g, 23 mmol) and elementary bromine (9.4 g, 59 mmol), frozen down (liquid air) and sealed under vacuum. The tube was exposed to ultra violet radiation (1000W, medium pressure, mercury lamp, at a distance of *ca.* 0.1m) for 3 days as.detailed for earlier experiments. A trace amount of 2-bromo-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane (**40**) was identified by gas chromatography; mass spectrum 57.

A.2. DIRECT HALOGENATION OF (26)

A.2.a. DIRECT CHLORINATION OF (26)

A Pyrex® tube fitted with a Rotaflo® tap was charged with (**26**) (4.0 g, 11 mmol) and elementary chlorine (1.8 g, 26 mmol), by standard vacuum line techniques. The tube was exposed to visible radiation from a 60W Tungsten lamp for 4 days, by which time little decolourisation was evident. No 2-chloro-2,5-bis(1,1,2,3,3,3-hexafluoropropyl)oxolane was produced (by g.c./mass spec. and NMR). Compound No. (**119**)

A.2.b. DIRECT BROMINATION OF (26)

A Carius tube was charged with (26) (13.7 g, 37 mmol) and elementary bromine (5.9 g, 37 mmol), frozen down (liquid air) and sealed under vacuum. The tube was exposed to ultraviolet radiation (1000W, medium pressure, mercury lamp, at a distance of *ca.* 0.1m) as detailed for earlier experiments. No 2-bromo-2,5-bis(1,1,2,3,3,3-hexafluoropropyl)oxolane was produced (by NMR). Compound No. (**120**)

A.3. NUCLEOPHILIC DISPLACEMENT REACTIONS OF (41)

A.3.a. OXYGEN NUCLEOPHILES

A.3.a.(i). METHOXIDE

(**41**) (10.7 g, 42 mmol) was added dropwise to a stirred solution of sodium methoxide (2.6 g, 49 mmol) in anhydrous methanol (30 ml). The solution was heated under reflux for 50 hrs and allowed to cool to ambient temperature. Following ether extraction, a trace amount of 2-methoxy-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane (42) was observed, by gas chromatography; mass spectrum 58.

A.3.a.(ii). 2-PROPOXIDE

Sodium (1.1 g, 48 mmol) was dissolved in *i*-propanol (20 ml) under an atmosphere of nitrogen. When all of the sodium had reacted, (**41**) (10.7 g, 42 mmol) was added dropwise to the stirred solution. The solution was heated to 50°C for *ca.* 18 hrs, then allowed to cool to ambient temperature. No 2-(1-methylethoxy)-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane was produced (by NMR).

A.3.a.(iii). 4-NITROPHENOXIDE

A Carius tube was charged with sodium 4-nitrophenoxide (6.9 g, 43 mmol) and (**41**) (11.7 g, 46 mmol), sealed under vacuum and heated to 150°C for *ca.* 18 hrs, then allowed to cool to ambient temperature, frozen down (liquid air) and opened. Work-up by ether extraction

showed that no 2-(4-nitrophenoxy)-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane was produced (by NMR). Compound No. (**121**)

A.3.b. NITROGEN NUCLEOPHILES

A.3.b.(i). DIETHYLAMINE

(**41**) (11.3 g, 44 mmol), diethylamine (3.2 g, 44 mmol), sodium carbonate (10.5 g, 99 mmol) in anhydrous oxolane (45 ml) was stirred for 7 hrs. Following ether extraction, no 2-diethylamino-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane was produced (by NMR).

A.3.b.(ii). POTASSIUM PHTHALIMIDE

A solution of (**41**) (11.3 g, 44 mmol) and potassium phthalimide (7.5 g, 40 mmol) in anhydrous *N,N*-dimethylformamide (35 ml) was stirred for *ca.* 18 hrs, solvent removed by distillation, and residue extracted into diethyl ether to give crude product, which was recrystallised (CH_2Cl_2) to give 2-phthalimido-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane (3.0 g , 8 mmol, 21%); (Found: C, 48.85; H, 2.80; N, 3.73; F, 31.2%. Calc. for $C_{15}H_{11}F_6NO_3$: C, 49.05; H, 3.03; N, 3.81; F, 31.1%); i.r spectrum 55; NMR spectrum 56; mass spectrum 59.

A.3.b.(iii). PIPERIDINE

(**41**) (11.0 g, 43 mmol), piperidine (3.8 g, 45 mmol) and sodium carbonate (5.4 g, 51 mmol) in anhydrous oxolane (20 ml) was stirred for *ca.* 18 hrs, and worked up by extraction (diethyl ether) to give an inseparable mixture containing 2-piperidino-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane (50% by g.l.c.); i.r spectrum 56; NMR spectrum 57; mass spectrum 60.

A.3.b.(iv). MORPHOLINE

(**41**) (11.3 g, 44 mmol), morpholine (4.0 g, 46 mmol) and triethylamine (6.5 ml, 47 mmol) in anhydrous oxolane (10 ml) was stirred for 3 days. Following extraction (diethyl ether), a trace

amount of 2-morpholino-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane; i.r spectrum 57; NMR spectrum 58; mass spectrum 61.

A.3.b.(v). PIPERAZINE

(**41**) (11.3 g, 44 mmol), piperazine (3.8 g, 44 mmol) and sodium carbonate (7.2 g, 68 mmol) in anhydrous oxolane (30 ml) was stirred for 25 days. Following extraction (diethyl ether), no displacement products were observed (by NMR).

A.3.b.(vi). AROMATIC AMINES

Reactions involving the aromatic amines imidazole, 2-imidazolidinone, indole and 1,2,3,4-tetrahydroquinoline were carried out in identical ways to those already described. In these reactions no products were obtained (by NMR).

A.3.c. CARBON NUCLEOPHILES

A.3.c.(i). DIETHYLMALONATE

The diethyl malonate anion was produced by adding diethyl malonate (7.4 g, 46 mmol) to a stirred solution, under a nitrogen atmosphere, of sodium hydride (1.1 g, 46 mmol) in anhydrous diethyl ether (30 ml) and oxolane (15 ml). To this solution, (**41**) (12.7 g, 48 mmol) was added and the reaction mixture stirred for *ca.* 18 hrs, before extraction (diethyl ether). No displacement product was obtained (by NMR). Compound No. (**122**)

A.3.d. SULPHUR NUCLEOPHILES

A.3.d.(i). THIOPHENATE

To a solution of thiophenol (5.1 g, 47 mmol) and sodium carbonate (4.7 g, 44 mmol) in anhydrous oxolane (15 ml), (**41**) (11.3 g, 44 mmol) was added and the reaction mixture heated under reflux for 22 hrs, before extraction (diethyl ether), and molecular distillation to

give 2-(1,1,2,3,3,3-hexafluoropropyl)-5-thiophenyloxolane (**49**) (4.0 g, 12 mmol, 28%); (Found: C, 47.70; H, 3.39; F, 35.1%. $C_{13}H_{12}F_6OS$ requires C, 47.27; H, 3.67; F, 34.5%); NMR spectrum 59; mass spectrum 62.

A.3.e. PHOSPHORUS NUCLEOPHILES

A.3.e.(i). TRIPHENYL PHOSPHINE

A solution of triphenyl phosphine (8.1 g, 31 mmol) and (**41**) (10.7 g, 42 mmol) in anhydrous oxolane (15 ml) was stirred for 2 days. No reaction was observed (by NMR). Compound No. (**123**)

CHAPTER NINE

EXPERIMENTAL TO CHAPTER FIVE

A. ENOLATE CHEMISTRY

A.1. DERIVATISATION OF (36) BY ENOLATE TRAPPING

A.1.a. BUTYL LITHIUM METHOD

A solution of (**36**) (1.0 g, 5 mmol) in anhydrous oxolane (10 ml) was stirred at -78°C, and *n*-butyl lithium (5.1 mmol) in hexanes added by syringe. After 3.5 hrs stirring at -78°C under an atmosphere of nitrogen, the solution was allowed to return to ambient temperature and propanoyl chloride (0.5 g, 5.4 mmol) added. After stirring for *ca.* 18 hrs, work-up by extraction (diethyl ether) failed to show any enolate derived product (by NMR).

A.1.b. CAESIUM FLUORIDE METHOD

A solution of (**36**) (3.3 g, 10 mmol) and caesium fluoride (3.0 g, 20 mmol) in pentafluoropyridine (7.7 g, 46 mmol) was stirred under a nitrogen atmosphere for 4 days, before work-up by extraction (diethyl ether). No enolate derived product was detected (by NMR).

A.2 ENOLATE QUENCHING WITH ETHANOL-*d*

A solution of (**36**) (1.0 g, 5 mmol) in anhydrous oxolane (10 ml) was stirred at -78°C under an atmosphere of nitrogen, and *n*-butyl lithium (5.5 mmol) in hexanes added slowly. The reaction was stirred for 2.5 hrs, allowed to warm to 5°C and ethanol-*d* (0.3 g, 6 mmol) added. Work-up by extraction (diethyl ether) showed no α-deuterated ketone was present (by NMR).

B. DIRECT CHLORINATION

A Pyrex® tube fitted with a Rotaflo® tap was charged with (**36**) (4.4 g, 23 mmol) and elementary chlorine (1.4 g, 20 mmol), by standard vacuum line techniques. The tube was exposed to visible radiation from a 60W Tungsten lamp for 10 days. Evolved HCl was vented in a fume cupboard and the remaining liquid found (by g.l.c. and NMR) to

contain 1-chloro-3,3,4,5,5,5-hexafluoropentan-2-one (**38**) (17% by g.l.c.); mass spectrum 54, and 1,1-dichloro-3,3,4,5,5,5-hexafluoropentan-2-one (**39**) (4% by g.l.c.); mass spectrum 55.

APPENDIX ONE

NMR SPECTRA

Unless otherwise stated, spectra of samples were recorded as solutions in deuterochloroform ($CDCl_3$).

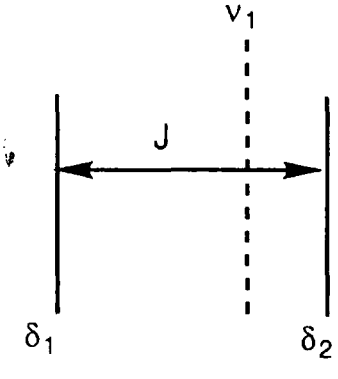
For proton and carbon spectra, shifts are quoted in ppm, relative to internal tetramethylsilane, with downfield shifts positive. For fluorine spectra, shifts are quoted in ppm relative to external trichlorofluoromethane, with upfield shifts negative.

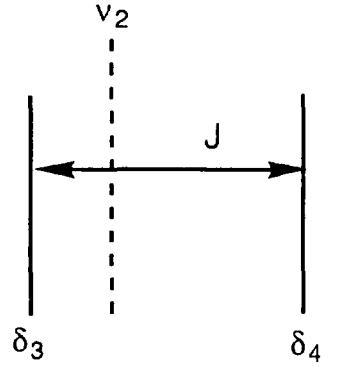
For the splitting patterns on NMR resonances, the following abbreviations are used:

s = singlet
d = doublet
t = triplet
q = quartet
br = broad

For an AB system, shifts are quoted as the 'centre of gravity', or $\pm(\nu/2)$ from the midpoint of the pattern, calculated from:

$$(\delta_1-\delta_3) = (\delta_2-\delta_4) = \sqrt{[(\delta_\nu)^2 + J^2]}.$$

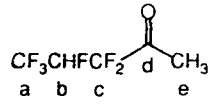




CONTENTS

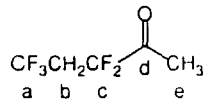
37. 2,2,3,4,4,4-Hexafluoro-1-(phenylmethoxy)butane
38. 3,3,4,5,5,5-Hexafluoro-2-(phenylmethoxy)pentane
39. (2,2,3,4,4,4-Hexafluorobutoxy)pentafluorobenzene
40. (3,3,4,5,5,5-Hexafluoropent-2-oxy)pentafluorobenzene
41. (2,2,3,4,4,4-Hexafluorobutoxy)-2,4-dinitrobenzene
42. (3,3,4,5,5,5-Hexafluoropent-2-oxy)-2,4-dinitrobenzene
43. 4-(2,2,3,4,4,4-Hexafluorobutoxy)tetrafluoropyridine
44. 4-(3,3,4,5,5,5-Hexafluoropent-2-oxy)tetrafluoropyridine
45. 4-(2,2,3,4,4,4-Hexafluorobutoxy)trifluoropyrimidine
46. 4-(3,3,4,5,5,5-Hexafluoropent-2-oxy)-trifluoropyrimidine
47. 5-(2,2,3,4,4,4-Hexafluorobutoxy)trifluoropyrazine
48. 5-(3,3,4,5,5,5-Hexafluoropent-2-oxy)-trifluoropyrazine
49. 4-(2,2,3,4,4,4-Hexafluorobutoxy)trifluoropyridazine
50. 4-(3,3,4,5,5,5-Hexafluoropent-2-oxy)-trifluoropyridazine
51. 2,2,3,4,4,4-Hexafluorobutyl 4-methylbenzenesulphonate
52. 3,3,4,5,5,5-Hexafluoropentyl 2-(4-methylbenzenesulphonate)
53. 1,1,1,2,3,3,8,8,9,10,10,10-Dodecafluorodecyl 4,7-bis(4-methylbenzenesulphonate)
54. 3,3,4,5,5,5-Hexafluoropentyl 2-(trichloromethanesulphonate)
55. 2-Chloro-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane
56. 2-Phthalimido-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane
57. 2-Piperidino-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane
58. 2-Morpholino-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane
59. 2-(1,1,2,3,3,3-Hexafluoropropyl)-5-thiophenyloxolane

1. 3,3,4,5,5,5-Hexafluoropentan-2-one



Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
2.44	ddd	$^{4}J_{HF}$=2.4Hz $^{4}J_{HF'}$=$^{5}J_{HF}$= 0.4Hz	3	e
5.25	dddq	$^{2}J_{HF}$=43.2Hz $^{3}J_{HFc}$=14.2Hz $^{3}J_{HFc'}$=6.8Hz $^{3}J_{HFa}$=6.0Hz	1	b
^{19}F:				
-74.40	dddd	$^{3}J_{FF}$=19.2Hz $^{4}J_{FF}$=10.9Hz $^{4}J_{FF'}$=8.3Hz $^{3}J_{HFa}$=5.6Hz	3	a
-116.54	ddqd	J_{AB}=297.3Hz $^{3}J_{FF}$=$^{4}J_{FF}$= 10.2Hz $^{3}J_{HF}$=6.4Hz	1	c
-121.91	ddqd	J_{AB}=298.0Hz $^{3}J_{FF}$=$^{4}J_{FF}$= 3.0Hz $^{3}J_{HF}$=1.9Hz	1	c
-216.07	dddq	$^{2}J_{HF}$=43.3Hz $^{3}J_{FFc}$=$^{3}J_{FFc'}$= $^{3}J_{FFa}$=11.9Hz	1	b
^{13}C:				
24.17	s			e
83.61	dqdd	$^{1}J_{CF}$=196.5Hz $^{2}J_{CFa}$=35.4Hz $^{2}J_{CFc}$=30.9Hz $^{2}J_{CFc'}$=24.7Hz		b
110.74	ddd	$^{1}J_{CF}$=267.0Hz $^{1}J_{CF}$=260.5Hz $^{2}J_{CF}$=25.5Hz		c
120.42	qdd	$^{1}J_{CF}$=282.2Hz $^{2}J_{CF}$=25.5Hz $^{3}J_{CF}$=1.9Hz		a
195.33	dd	$^{2}J_{CF}$=30.9Hz $^{2}J_{CF'}$=27.1Hz		d

2. 3,3,5,5,5-Pentafluoropentan-2-one

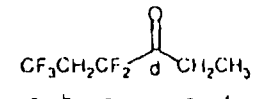


Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
2.40	t	$^4J_{HF}$=1.6Hz	3	e
2.98	tq	$^3J_{HFc}$=13.9Hz $^3J_{HFa}$=9.9Hz	2	b
^{19}F:				
-61.05	tt	$^3J_{FH}$=9.8Hz $^4J_{FF}$=8.3Hz	3	a
-105.67	tqq	$^3J_{FH}$=15.0Hz $^4J_{FF}$=8.3Hz $^4J_{FH}$=1.5Hz	2	c
^{13}C:				
23.19	s			e
36.70	qt	$^2J_{CFa}$=30.7Hz $^2J_{CFc}$=24.6Hz		b
113.70	td	$^1J_{CF}$=255.5Hz $^3J_{CF}$=2.6Hz		c
123.32	qt	$^1J_{CF}$=276.7Hz $^3J_{CF}$=5.0Hz		a
196.48	t	$^2J_{CF}$=31.7Hz		d

3. 3,3,4,5,5,5-Hexafluorohexan-3-one

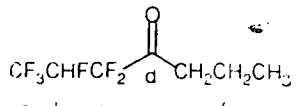
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
1.17	dd	$^3J_{HH}$=$^3J_{HH'}$=7.2Hz	3	f
2.79	q	$^3J_{HH}$=7.2Hz	1	e
2.80	q	$^3J_{HH}$=7.2Hz	1	e
5.27	ddqd	$^2J_{HF}$=43.2Hz $^3J_{HFc}$=13.4Hz $^3J_{HFa}$=6.8Hz $^3J_{HFc'}$=5.6Hz	1	b
^{19}F:				
-73.55	s		3	a
-115.69	dd	J_{AB}=295.0Hz $^3J_{FF}$=10.2Hz	1	c
-123.05	dd	J_{AB}=295.2Hz $^3J_{FF}$=5.0Hz	1	c
-215.33	dm	$^2J_{FH}$=43.3Hz	1	b
^{13}C:				
6.44	s			f
30.68	s			e
84.05	dqdd	$^1J_{CF}$=196.3Hz $^2J_{CFa}$=35.3Hz $^2J_{CFc}$=31.3Hz $^2J_{CFc'}$=24.8Hz		b
111.34	ddd	$^1J_{CF}$=266.3Hz $^1J_{CF'}$=259.8Hz $^2J_{CF}$=25.9Hz		c
120.74	qd	$^1J_{CF}$=282.1Hz $^2J_{CF}$=24.6Hz		a
198.73	dd	$^2J_{CF}$=29.8Hz $^2J_{CF'}$=25.9Hz		d

4. 3,3,5,5,5-Pentafluorohexan-3-one



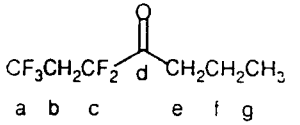
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H :				
1.15	t	$^{3}J_{HH}$ = 7.2Hz	3	f
2.77	qt	$^{3}J_{HH}$ = 7.2Hz	2	e
		$^{4}J_{HF}$ = 1.2Hz		
2.99	tq	$^{3}J_{HFc}$ = 14.8Hz	2	b
		$^{3}J_{HFa}$ = 10.0Hz		
^{19}F :				
-61.05	tt	$^{3}J_{HF}$ = 9.8Hz	3	a
		$^{4}J_{FF}$ = 8.5Hz		
-105.93	tq	$^{3}J_{FH}$ = 14.7Hz	2	c
		$^{4}J_{FF}$ = 8.5Hz		
^{13}C :				
6.61	s			f
29.25	s			e
37.02	qt	$^{2}J_{CFa}$ = 30.5Hz		b
		$^{2}J_{CFc}$ = 24.8Hz		
113.99	tq	$^{1}J_{CF}$ = 255.6Hz		c
		$^{3}J_{CF}$ = 2.8Hz		
123.37	qt	$^{1}J_{CF}$ = 277.1Hz		a
		$^{3}J_{CF}$ = 5.1Hz		
199.60	t	$^{2}J_{CF}$ = 30.1Hz		d

5 3,3,4,5,5,5-Hexafluoroheptan-4-one



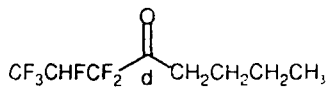
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H :-				
0.97	t	$^3J_{HH}$=7.2Hz	3	g
1.70	tq	$^3J_{HHe}$= $^3J_{HHg}$=7.2Hz	2	f
2.74	t	$^3J_{HH}$=7.2Hz	2	e
5.27	dqdd	$^2J_{HF}$=42.8Hz $^3J_{HFa}$=6.4Hz $^3J_{HFc}$= $^3J_{HFc'}$=5.8Hz	1	b
^{19}F :-				
-73.62	s		3	a
-115.92	d	J_{AB}=295.8Hz	1	b
-123.09	d	J_{AB}=295.8Hz	1	b
-215.55	d	$^2J_{FH}$=40.7Hz	1	b
^{13}C :-				
13.49	s			g
16.48	s			f
39.21	s			e
84.43	dqdd	$^1J_{CF}$=195.9Hz $^2J_{CFa}$=35.3Hz $^2J_{CFc}$=31.7Hz $^2J_{CFc'}$=24.8Hz		b
111.67	ddd	$^1J_{CF}$=266.7Hz $^1J_{CF'}$=259.8Hz $^2J_{CF}$=25.5Hz		a
121.19	dq	$^1J_{CF}$=282.0Hz $^2J_{CF}$=25.5Hz		a
198.4	dd	$^2J_{CF}$=30.6Hz		d

6 3,3,5,5,5-Pentafluoroheptan-4-one



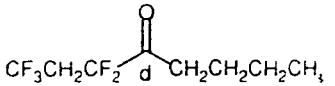
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H :-				
0.96	t	$^3J_{HH}$=7.6Hz	3	g
1.68	t t	$^3J_{HHe}$= $^3J_{HHg}$=7.2Hz	2	f
2.71	t t	$^3J_{HH}$=7.2Hz $^4J_{HF}$=1.2Hz	2	e
2.99	tq	$^3J_{HFc}$=14.8Hz $^3J_{HFa}$=9.9Hz	2	b
^{19}F :-				
-61.02	t t	$^3J_{FH}$=9.9Hz $^4J_{FF}$=8.3Hz	3	a
-106.07	tq	$^3J_{FH}$=15.1Hz $^4J_{FF}$=8.3Hz	2	c
^{13}C :-				
13.35	s			f or g
16.07	s			f or g
36.93	m			b
37.49	s			e
113.91	t	$^1J_{CF}$=256.4Hz		c
123.38	q	$^1J_{CF}$=275.4Hz		a
198.92	t	$^2J_{CF}$=30.1Hz		d

7. 3,3,4,5,5,5-Hexafluorooctan-4-one



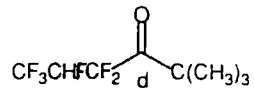
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
0.94	t	$^3J_{HH}$=7.3Hz	3	i
1.37	tq	$^3J_{HHg}$=$^3J_{HHi}$= 7.2Hz	2	h
1.65	tt	$^3J_{HHf}$=$^3J_{HHh}$= 7.4Hz	2	g
2.76	t	$^3J_{HH}$=7.2Hz	2	f
5.27	ddq	$^2J_{HF}$=42.8Hz $^3J_{HFc}$=20.4Hz $^3J_{HFa}$=6.0Hz	1	b
^{19}F:-				
-74.82	s		3	a
-117.01	d	J_{AB}=294.4Hz	1	c
-124.31	d	J_{AB}=294.9Hz	1	c
-216.67	d	$^2J_{HF}$=35.3Hz	1	b
^{13}C:-				
13.46	s			i
21.89	s			h
24.34	s			g
36.51	s			f
83.73	dqdd	$^1J_{CF}$=196.0Hz $^2J_{CFa}$=35.1Hz $^2J_{CFc}$=31.3Hz $^2J_{CFc'}$=24.3Hz		b
111.02	ddd	$^1J_{CF}$=265.8Hz $^1J_{CF'}$=259.8Hz $^2J_{CF}$=25.9Hz		c
120.69	qdd	$^1J_{CF}$=282.3Hz $^2J_{CF}$=25.5Hz $^3J_{CF}$=1.9Hz		a
198.00	dd	$^2J_{CF}$=30.2Hz $^2J_{CF'}$=25.6Hz		d

8 3,3,5,5,5-Pentafluorooctan-4-one



Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
0.93	t	$^3J_{HH}$=7.2Hz	3	i
1.37	tq	$^3J_{HHg}$=$^3J_{HHi}$= 7.2Hz	2	h
1.64	tt	$^3J_{HHf}$=$^3J_{HHh}$= 7.2Hz	2	g
2.73	t	$^3J_{HH}$=7.2Hz	2	f
2.99	tq	$^3J_{HFc}$=14.8Hz $^3J_{HFa}$=10.0Hz	2	b
^{19}F:-				
-61.90	s		3	a
-106.88	s		2	c
^{13}C:-				
13.42	s			i
21.87	s			h
24.46	s			g
35.17	s			f
36.68	qt	$^2J_{CFa}$=30.5Hz $^2J_{CFc}$=24.7Hz		b
113.93	tq	$^1J_{CF}$=255.6Hz $^3J_{CF}$=3.0Hz		c
123.39	qt	$^1J_{CF}$=276.6Hz $^3J_{CF}$=5.1Hz		a
198.88	t	$^2J_{CF}$=30.3Hz		e

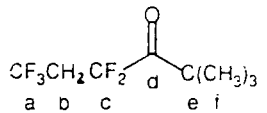
9 4,4,5,6,6,6-Hexafluoro-2,2-dimethylhexan-3-one



Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
1.14	s		9	f
4.92	ddqd	$^2J_{HFc}$=43.6Hz $^3J_{HF}$=19.6Hz $^3J_{HFa}$=6.0Hz $^3J_{HFc'}$=1.1Hz	1	b
^{19}F:-				
-73.94	dddd	$^3J_{FF}$=24.5Hz $^4J_{FF}$=10.2Hz $^3J_{HF}$=6.0Hz $^4J_{FF'}$=4.1Hz	3	a
-117.45	ddq	J_{AB}=270.2Hz $^3J_{FF}$=13.0Hz $^4J_{FF}$=3.8Hz	1	c
-125.50	dq	J_{AB}=271.3Hz $^4J_{FF}$=10.2Hz	1	c
-206.28	dm	$^2J_{HF}$=42.5Hz	1	b
^{13}C:-				
23.64	ddd	$^4J_{CF}$=7.7Hz $^4J_{CF'}$=4.2Hz $^5J_{CF}$=3.4Hz		f
28.45	dd	$^3J_{CF}$=22.1Hz $^3J_{CF'}$=21.3Hz		e
84.38	ddqd	$^1J_{CF}$=197.2Hz $^3J_{CFc}$=41.9Hz $^3J_{CFa}$=33.8Hz $^3J_{CFc'}$=26.2Hz		b

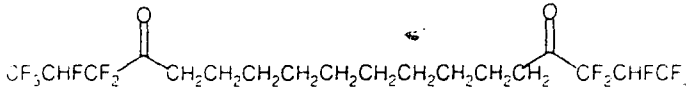
120.52	ddd	$^1J_{CF}$=261.2Hz $^1J_{CF}$=246.9Hz $^2J_{CF}$=12.6Hz	c
121.14	qd	$^1J_{CF}$=283.4Hz $^2J_{CF}$=26.1Hz	a
165.64	s		d

10 4,4,6,6,6-Pentafluoro-2,2-dimethylhexan-3-one



Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
1.06	s (br)		9	f
2.69	tq	$^3J_{HFc}$=17.6Hz $^3J_{HFa}$=10.0Hz	2	b
^{19}F:				
-61.68	s		3	a
-112.37	s		2	c
^{13}C:				
23.38	t	$^4J_{CF}$=4.2Hz		f
36.04	tq	$^2J_{CFc}$=25.7Hz $^2J_{CFa}$=29.4Hz		b
38.43	t	$^3J_{CF}$=22.6Hz		e
123.44	tq	$^1J_{CF}$=248.7Hz $^3J_{CF}$=1.8Hz		c
124.55	q	$^1J_{CF}$=277.4Hz		a
206.20	s			d

11 1,1,1,2,3,3,16,16,17,18,18,18-dodecafluorooctadecane-4,15-dione



a b c d e f g h i

Spectra run in acetone-d_6

Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
1.30	s (br)		6	g, h, i
1.65	t t	$^3J_{HHe}$=7.2Hz $^3J_{HHg}$=6.8Hz	2	f
2.75	t	$^3J_{HH}$=7.2Hz	2	e
5.26	dddq	$^2J_{HF}$=43.2Hz $^3J_{HFc}$=14.4Hz $^3J_{HFc'}$= $^3J_{HFa}$=6.0Hz	1	b
^{19}F:				
-73.25	dm	$^3J_{FF}$=11.3Hz	3	a
-115.50	d	J_{AB}=295.4Hz	1	c
-122.74	d	J_{AB}=295.4Hz	1	c
-215.12	dqdd	$^2J_{FH}$=43.6Hz $^3J_{FFa}$=$^3J_{FFc}$= $^3J_{FFc'}$=11.5Hz	1	b
^{13}C:				
22.36	s			i
28.78	s			f or g or h
29.22	s			f or g or h
29.30	s			f or g or h
36.90	s			e
83.79	dqdd	$^1J_{CF}$=196.2Hz $^2J_{CFa}$=35.1Hz $^2J_{CFc}$=6.9Hz $^2J_{CFc'}$=3.8Hz		b
111.05	ddd	$^1J_{CF}$=266.4Hz $^1J_{CF'}$=259.9Hz $^2J_{CF}$=26.0Hz		c
120.55	qd	$^1J_{CF}$=282.3Hz $^2J_{CF}$=25.1Hz		a
198.05	dd	$^2J_{CF}$=30.2Hz $^2J_{CF}$=25.9Hz		d

12 2,2,3,4,4,4-Hexafluorobutanol

$CF_3CHFCF_2CH_2OH$

a b c d e

Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^1H:				
3.94	m		2	d
4.22	s		1	e
5.04	dm	$^2J_{HF}$= 43.2Hz	1	b
^{19}F:				
-75.31	ddd	$^3J_{FF}$= 16.6Hz	3	a
		$^2J_{FF}$= 10.9Hz		
		$^3J_{HF}$= 6.4Hz		
-119.63	d	J_{AB}= 274.7Hz	1	c
-123.59	d	J_{AB}= 274.7Hz	1	c
-214.88	dm	$^2J_{HF}$= 42.9Hz	1	b
^{13}C:				
61.51	dd	$^2J_{CF}$= 32.4Hz		d
		$^2J_{CF'}$= 26.4Hz		
84.53	ddqd	$^1J_{CF}$= 193.8Hz		b
		$^2J_{CFc}$= 70.2Hz		
		$^2J_{CFa}$= 35.1Hz		
		$^2J_{CF'}$= 27.1Hz		
118.13	ddd	$^1J_{CF}$= 251.7Hz		c
		$^1J_{CF'}$= 247.5Hz		
		$^2J_{CF}$= 24.8Hz		
121.63	qd	$^1J_{CF}$= 281.5Hz		a
		$^2J_{CF}$= 25.5 Hz		

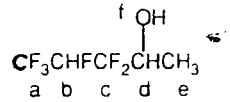
13 2,2,4,4,4-Pentafluorobutanol

$CF_3CH_2CF_2CH_2OH$

a b c d e

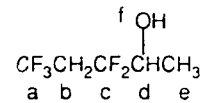
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^1H:				
2.88	tq	$^3J_{HFc}$=14.6Hz	2	b
		$^3J_{HFa}$=10.4Hz		
3.49	s		1	e
3.84	t	$^3J_{HF}$=12.6Hz	2	d
^{19}F:				
-61.80	tt	$^3J_{FH}$=10.8Hz	3	a
		$^4J_{FF}$=9.4Hz		
105.92	ttq	$^3J_{FHb}$=15.2Hz	2	c
		$^3J_{FHd}$=13.2Hz		
		$^4J_{FF}$=9.4Hz		
^{13}C:				
37.29	qt	$^2J_{CFa}$=30.5Hz		b
		$^2J_{CFc}$=26.6Hz		
63.34	tq	$^2J_{CF}$=31.0Hz		d
		$^4J_{CF}$=1.4Hz		
119.19	tq	$^1J_{CF}$=244.5Hz		c
		$^3J_{CF}$=2.9Hz		
123.68	qt	$^1J_{CF}$=276.6Hz		a
		$^3J_{CF}$=5.7Hz		

14. 3,3,4,5,5,5-Hexafluoropentan-2-ol



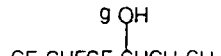
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
1.39	d	$^3J_{HH}$=5.9Hz	3	f
2.50	s (br)		1	e
4.15	m		1	d
5.13	dm	$^2J_{HF}$=43.7Hz	1	b
^{19}F:				
-74.41	m		3	a
-74.80	m			
-124.05	d	J_{AB}=270.4Hz	1	c
-129.35	d	J_{AB}=270.4Hz	1	c
-213.60	d	$^2J_{HF}$=41.0Hz	1	b
-215.90	d	$^2J_{HF}$=42.4Hz		

15. 3,3,5,5,5-Pentafluoropentan-2-ol



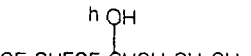
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
1.32	dt	$^3J_{HH}$=6.8Hz $^4J_{HF}$=3.0Hz	3	e
2.14	s (br)		1	f
2.86	ddq	$^3J_{HFc}$=21.4Hz $^3J_{HFc'}$=11.7Hz $^3J_{HFa}$=9.6Hz	2	d
3.98	ddq	$^3J_{HF}$=13.9Hz $^3J_{HF}$=$^3J_{HH}$= 6.4Hz	1	e
^{19}F:				
-61.26	t t	$^3J_{FH}$=$^4J_{FF}$= 10.2Hz	3	a
-109.20	d	J_{AB}=258.9Hz	1	c
-114.33	d	J_{AB}=258.5Hz	1	c
^{13}C:				
15.54	t	$^3J_{CFa}$=3.6Hz		e
36.53	qdd	$^2J_{CFa}$=30.2Hz $^2J_{CFc}$=27.1Hz $^2J_{CFc'}$=24.4Hz		b
68.91	t	$^2J_{CF}$=28.7Hz		d
120.10	ddq	$^1J_{CF}$=$^1J_{CF'}$= 246.3Hz $^3J_{CF}$=2.7Hz		c
124.06	qdd	$^1J_{CF}$=277.0Hz $^3J_{CF}$=5.7Hz $^3J_{CF'}$=1.1Hz		a

16. 4,4,5,6,6,6-Hexafluorohexan-3-ol



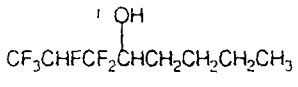
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
1.06	t	$^3J_{HH}$=7.2Hz	3	f
1.58	dq	$^3J_{HHd}$=$^3J_{HHl}$=7.2Hz	1	e
1.80	dq	$^3J_{HHd}$=$^3J_{HHl}$=7.1Hz	1	e
2.85	s (br)		1	g
3.81	m		1	d
5.11	dm	$^2J_{HF}$=40.0Hz	1	b
^{19}F:				
-74.71	s		]3	a
-74.80	s		]	
-120.72	d	J_{AB}=272.5Hz	]1	c
-125.58	d	J_{AB}=273.0Hz	]	
-126.19	d	J_{AB}=271.6Hz	]1	c
-130.73	d	J_{AB}=271.6Hz	]	
-213.78	d	$^2J_{HF}$=38.1Hz	]1	b
-216.05	d	$^2J_{HF}$=40.2Hz	]	

17. 1,1,1,2,3,3-Hexafluoroheptan-4-ol



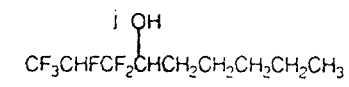
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
0.95	t	$^3J_{HH}$=7.2Hz	3	g
1.37	q	$^3J_{HH}$=7.1Hz	2	f
1.56	m (br)		2	e
3.61	m		1	d
3.83	s		1	h
5.14	dm	$^2J_{HF}$=43.4Hz	1	b
^{19}F:				
-74.43	s		]3	a
-74.83	s		]	
-120.25	d	J_{AB}=271.6Hz	]1	c
-125.21	d	J_{AB}=270.4Hz	]	
-125.89	d	J_{AB}=270.6Hz	]1	c
-130.58	d	J_{AB}=270.6Hz	]	
-213.55	d	$^2J_{HF}$=36.0Hz	]1	b
-216.73	d	$^2J_{HF}$=44.7Hz	]	

18 1,1,1,2,3,3-Hexafluorooctan-4-ol



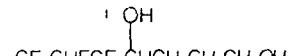
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
0.91	t	$^3J_{HH}$=6.8Hz	3	h
1.33	m		4	f,g
1.56	t	$^3J_{HH}$=6.2Hz	2	e
3.45	s (br)		1	i
3.60	t m	$^3J_{HH}$=6.3Hz	1	d
5.21	dm	$^2J_{HF}$=37.1Hz	1	b
^{19}F:-				
-74.45	s		3	a
-74.83	s			
-120.24	d	J_{AB}=270.2Hz	1	c
-125.42	d	J_{AB}=274.4Hz		
-125.99	d	J_{AB}=269.5Hz	1	c
-130.84	d	J_{AB}=270.4Hz		
-213.78	d	$^2J_{HF}$=39.1Hz	1	b
-216.05	d	$^2J_{HF}$=38.1Hz		

19 1,1,1,2,3,3-Hexafluorononan-4-ol



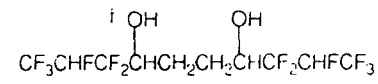
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
0.91	m		3	i
1.32	m		6	f,g,h
1.55	m		2	e
3.12	s (br)		1	j
3.63	t m	$^3J_{HH}$=6.6Hz	1	d
5.24	m		1	b
^{19}F:-				
-74.43	s		3	a
-74.81	s			
-120.25	d	J_{AB}=294.2Hz	1	c
-125.43	d	J_{AB}=294.2Hz		
-126.00	d	J_{AB}=286.7Hz	1	c
-130.85	d	J_{AB}=286.7Hz		
-213.60	d	$^2J_{HF}$=37.9Hz	1	b
-215.91	d	$^2J_{HF}$=37.9Hz		

20 5,5,6,7,7,7-Hexafluoroheptane-1,4-diol



Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
1.70	t t	$^3J_{HHg}$=5.1Hz $^3J_{HHe}$=2.6Hz	2	f
1.83	m		2	e
2.00	s (br)		1	h
3.11	s		1	i
3.69	t	$^3J_{HH}$=5.1Hz	1	g
5.19	dm	$^2J_{HF}$=39.4Hz	1	b
^{19}F:				
-74.43	s		3	a
-74.69	s			
-122.50	d	J_{AB}=275.2Hz	1	c
-127.80	d	J_{AB}=272.9Hz	1	c
-213.40	m		1	b
-215.02	m			

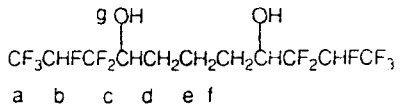
21 1,1,1,2,3,3,8,8,9,10,10,10-Dodecafluorodecane-4,7-diol



Spectra run in acetone-d_6

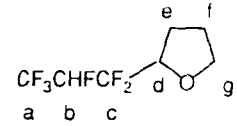
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
1.94	m		2	e
2.75	s (br)		1	f
4.04	m		1	d
5.16	dm	$^2J_{HF}$=38.9Hz	1	b
^{19}F:				
-73.96	m		3	a
-74.70	m			
-122.45	d	J_{AB}=279.5Hz	1	c
-127.50	d	J_{AB}=277.0Hz	1	c
-213.92	d	$^2J_{HF}$=38.1Hz	1	b
-215.90	d	$^2J_{HF}$=41.2Hz		

22 1,1,1,2,3,3,9,9,10,11,11,11-Dodecafluoroundecane-4,8-diol



Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
1.77	m		3	e,f
3.10	s		1	g
5.24	m		1	d
5.68	dm	$^2J_{HF}$=40.3Hz	1	b
^{19}F:-				
-73.48	s		3	a
-73.85	s			
-119.53	d	J_{AB}=267.6Hz	2	c
-124.23	d	J_{AB}=270.2Hz		
-124.67	d	J_{AB}=270.9Hz		
-129.34	d	J_{AB}=268.3Hz		
-213.46	m		1	b
-215.49	m			

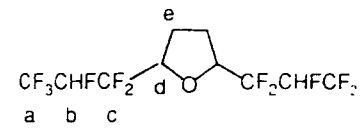
23 2-(1,1,2,3,3,3-Hexafluoropropyl)oxolane



Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
1.98	m		2	f
2.11	m	J=6.0Hz	1	e
2.19	m	J=6.4Hz	1	e
3.90	m		2	g
4.29	ddtm	$^3J_{HF}$=$^3J_{HF'}$= 25.6Hz, $^3J_{HH}$= 3.6Hz	1	d
5.09	ddq	$^2J_{HF}$=43.2Hz, $^3J_{HFc}$=20.8Hz, $^3J_{HFa}$=6.0Hz	1	b
^{19}F:-				
-73.82	dddd	$^3J_{FF}$=27.5Hz, $^4J_{FF}$=21.8Hz, $^4J_{FF'}$=16.9Hz, $^3J_{HF}$=11.3Hz	3	a
-74.34	dddd	$^3J_{FF}$=30.1Hz, $^4J_{FF}$=21.8Hz, $^4J_{FF'}$=18.1Hz, $^3J_{HF}$=11.3Hz		
-119.88	dm	J_{AB}=269.4Hz	1	c
-124.12	dm	J_{AB}=269.4Hz		

-124.66	ddq	J_{AB}=269.4Hz $^3J_{FF}$=$^4J_{FF}$= 10.9Hz	1	c
-130.19	ddqd	J_{AB}=270.6Hz $^3J_{FF}$=$^4J_{FF}$= 12.4Hz $^3J_{HF}$=3.8Hz		
-212.91	dm	$^2J_{HF}$=42.9Hz	1	b
-218.23	dm	$^2J_{HF}$=39.9Hz		
^{13}C :				
24.28	d	$^4J_{CF}$=4.2Hz		f
25.82	dd	$^3J_{CF}$=16.8Hz $^3J_{CF'}$=0.7Hz		e
69.94	s			g
70.09	s			g
75.40	dd	$^2J_{CF}$=34.0Hz $^2J_{CF'}$=22.9Hz		d
83.36	ddqd	$^1J_{CF}$=143.0Hz $^2J_{CFc}$=39.7Hz $^2J_{CFa}$=34.3Hz $^2J_{CFc'}$=24.0Hz		b
85.29	ddqd	$^1J_{CF}$=144.5Hz $^2J_{CFc}$=54.9Hz $^2J_{CFa}$=34.7Hz $^2J_{CFc'}$=27.5Hz		b
117.59	ddd	$^1J_{CF}$=254.1Hz $^1J_{CF'}$=251.3Hz $^2J_{CF}$=18.7Hz		c
117.89	ddd	$^1J_{CF}$=277.7Hz $^1J_{CF'}$=252.1Hz $^2J_{CF}$=25.5Hz		c
120.79	qdd	$^1J_{CF}$=281.9Hz $^2J_{CF}$=25.9Hz $^3J_{CF}$=7.6Hz		a
121.20	qdd	$^1J_{CF}$=272.3Hz $^2J_{CF}$=25.9Hz $^3J_{CF}$=1.5Hz		a

24 2,5-Bis(1,1,2,3,3,3-hexafluoropropyl)oxolane



Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H :				
2.30	d	$^3J_{HH}$=3.6Hz	2	e
4.51	m		1	d
5.02	dm	$^2J_{HF}$=44.0Hz	1	b
^{19}F :				
-73.80	dddd	$^3J_{FF}$=35.0Hz $^4J_{FF}$=22.2Hz $^3J_{HF}$=10.5Hz $^4J_{FF'}$=5.6Hz	3	a
-74.33	m			
-119.25	dm	J_{AB}=272.8Hz	1	c
-124.33	dm	J_{AB}=273.9Hz		
-124.80	dm	J_{AB}=282.6Hz	1	c
-130.44	dm	J_{AB}=283.7Hz		
-212.50	m			b
-217.65	ddq	$^2J_{HF}$=44.4Hz $^3J_{FFc}$=11.7Hz $^3J_{FFc}$=10.5Hz	1	b
^{13}C :				
24.02	dd	$^3J_{CF}$=29.1Hz $^3J_{CF'}$=25.9Hz		e
25.03	d	$^3J_{CF}$=21.3Hz		e
77.47	d	$^2J_{CF}$=59.2Hz $^2J_{CF'}$=23.2Hz		d
78.84	dd	$^2J_{CF}$=31.6Hz $^2J_{CF'}$=24.8Hz		d

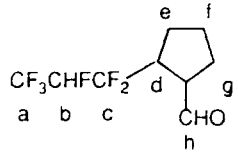
83.44	ddqd	$^1J_{CF}$=170.7Hz $^2J_{CFc}$=38.9Hz $^2J_{CFa}$=35.1Hz $^2J_{CFc'}$=23.9Hz	b
85.04	dm	$^1J_{CF}$=167.1Hz	b
116.78	ddd	$^1J_{CF}$=272.8Hz $^1J_{CF'}$=253.7Hz $^2J_{CF}$=20.2Hz	c
117.29	ddd	$^1J_{CF}$=280.8Hz $^1J_{CF'}$=255.2Hz $^2J_{CF}$=25.9Hz	c
120.63	qdd	$^1J_{CF}$=276.6Hz $^2J_{CF}$=18.7Hz $^3J_{CF}$=6.8Hz	a
120.99	qd	$^1J_{CF}$=282.6Hz $^2J_{CF}$=24.7Hz	a

25 2,2,3,4,4,4-Hexafluorobutoxytrimethylsilane

$CF_3CHFCF_2OSiC(CH_3)_3$
a b c d e

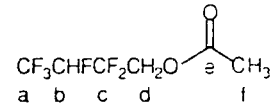
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
0.17	s		9	e
3.96	dddd	$^3J_{HF}$=24.0Hz $^2J_{HH}$=11.6Hz $^3J_{HF'}$=$^4J_{HF}$=4.4Hz	2	d
5.05	dddq	$^2J_{HF}$=43.2Hz $^3J_{HFc}$=$^3J_{HFc}$=10.8Hz $^3J_{HFa}$=5.6Hz	1	b
^{19}F:				
-74.27	m		3	a
-119.39	d	J_{AB}=271.3Hz	1	c
-123.83	d	J_{AB}=271.6Hz	1	c
-214.92	dm	$^2J_{HF}$=41.8Hz	1	b
^{13}C:				
1.15	s			e
61.38	dd	$^2J_{CF}$=36.2Hz $^2J_{CF}$=26.7Hz		d
83.08	ddqd	$^1J_{CF}$=193.4Hz $^2J_{CFa}$=$^2J_{CFc}$=35.1Hz $^2J_{CFc'}$=25.0Hz		b
117.65	ddd	$^1J_{CF}$=$^1J_{CF'}$=250.5Hz ^{2}JCF=24.5Hz		c
121.18	qd	$^1J_{CF}$=281.8Hz $^2J_{CF}$=25.7Hz		a

26. 2-(1,1,2,3,3,3-Hexafluoropropyl)pyrrolidine-1-carboxaldehyde



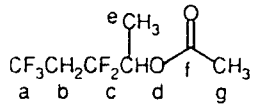
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
2.01	m (br)		4	e,f
3.38	m		1	g
3.63	m		1	g
4.24	dm	$^3J_{HF}$=18.1Hz	1	d
4.53	dm	$^3J_{HF}$=23.4Hz		
5.07	m (br)		1	b
8.14	s		1	h
8.17	s			
^{19}F:-				
-74.69	s		3	a
-75.02	s			
-120.07	d	J_{AB}=275.4Hz	1	c
-123.38	d	J_{AB}=280.0Hz		
-122.86	d	J_{AB}=287.4Hz	1	c
-127.90	d	J_{AB}=274.0Hz		
-211.57	d	$^2J_{HF}$=36.2Hz	1	b
-212.26	d	$^2J_{HF}$=41.7Hz		

27. 2,2,3,4,4,4-Hexafluorobutyl ethanoate



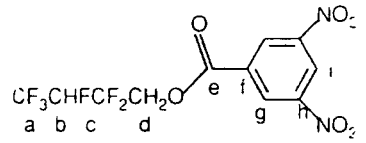
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
2.16	s		3	f
4.46	m		2	d
5.00	dm	$^2J_{HF}$=43.6Hz	1	b
^{19}F:-				
-74.15	m		3	a
-115.44	dm	J_{AB}=279.2Hz	1	c
-120.17	dm	J_{AB}=278.8Hz	1	c
-212.86	dm	$^2J_{HF}$=43.5Hz	1	b
^{13}C:-				
19.99	s			f
60.75	dd	$^2J_{CF}$=35.0Hz $^2J_{CF'}$=26.9Hz		d
83.97	ddqd	$^1J_{CF}$=195.7Hz $^2J_{CFa}$=$^2J_{CFc}$=35.1Hz $^2J_{CFc'}$=27.0Hz		b
115.83	ddd	$^1J_{CF}$=$^1J_{CF'}$=250.9Hz $^2J_{CF}$=24.8Hz		c
120.44	qd	$^1J_{CF}$=282.0Hz $^2J_{CF}$=25.3Hz		a
169.30	s			e

28. 3,3,4,5,5,5-Hexafluoropent-2-yl ethanoate



Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
1.41	d	$^{3}J_{HH}$=6.4Hz	3	e
2.14	s		3	g
4.92	dm	J unresolved	1	b
5.29	m		1	d
^{19}F:-				
-73.73	dddd	$^{3}J_{FF}$=$^{4}J_{FF}$= $^{4}J_{FF'}$=10.8Hz $^{3}J_{HF}$=5.5Hz	1	a
-74.13	m			
-123.11	d	J_{AB}=276.6Hz	1	c
-124.50	d	J_{AB}=276.9Hz	1	c
-212.47	d	$^{2}J_{HF}$=43.6Hz	1	b
-213.51	dq	$^{2}J_{HF}$=43.1Hz $^{3}J_{FF}$=10.2Hz		
^{13}C:-				
11.74	d	$^{3}J_{CF}$=3.0Hz		e
13.16	d	$^{3}J_{CF}$=3.1Hz		e
20.65	s			g
20.72	s			g
67.28	dd	$^{2}J_{CF}$=35.1Hz $^{2}J_{CF'}$=24.7Hz		d
68.35	dd	$^{2}J_{CF}$=28.7Hz $^{2}J_{CF'}$=27.8Hz		d
83.50	dm	$^{1}J_{CF}$=195.2Hz		b
116.57	ddd	$^{1}J_{CF}$=252.5Hz $^{1}J_{CF'}$=234.6Hz $^{2}J_{CF}$=25.2Hz		c
121.69	qd	$^{1}J_{CF}$=282.3Hz $^{2}J_{CF}$=25.5Hz		a
168.78	s			f
169.03	s			f

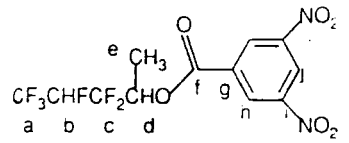
29 2,2,3,4,4,4-Hexafluorobutyl 3,5-dinitrobenzoate



Spectra run in acetone-d_6

Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H :				
5.04	ddd	$^3J_{HF}$=14.9Hz $^3J_{HF'}$=10.3Hz $^4J_{HF}$=2.2Hz	2	d
5.98	ddqd	$^2J_{HF}$=42.2Hz $^3J_{FFc}$=10.7Hz $^3J_{FFa}$=$^3J_{FFc'}$=5.5Hz	1	b
9.05	d	$^4J_{HH}$=2.0Hz	1	i
9.15	d	$^4J_{HH}$=1.8Hz	1	g
^{19}F :				
-74.78	s		3	a
-116.83	d	J_{AB}=276.1Hz	1	c
-120.98	d	J_{AB}=275.8Hz	1	c
-215.86	d	$^3J_{HF}$=39.5Hz	1	b

30 3,3,4,5,5,5-Hexafluoropent-2-yl 3,5-dinitrobenzoate

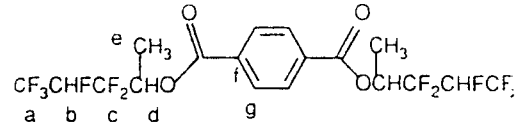


Spectra run in acetone-d_6

Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H :				
1.63	dd	$^3J_{HH}$=6.4Hz $^4J_{HF}$=0.8Hz	1	e
1.67	dd	$^3J_{HH}$=6.8Hz $^4J_{HF}$=1.2Hz		
5.80	m		1	d
9.13	d	$^4J_{HH}$=2.0Hz	2	h
9.14	d	$^4J_{HH}$=2.4Hz		
^{19}F :				
-78.86	m		3	a
-79.14	m			
-124.72	dd	J_{AB}=274.1Hz $^3J_{FF}$=5.3Hz	1	c
-128.19	dd	J_{AB}=275.2Hz	1	c
-218.38	dm	$^2J_{HF}$=39.5Hz	1	b
-219.31	dm	$^2J_{HF}$=39.9Hz		
^{13}C :				
12.26	m			e
13.36	ddd	$^3J_{CF}$=$^3J_{CF'}$=4.6Hz $^4J_{CF}$=3.4Hz		e
69.81	dd	$^2J_{CF}$=34.9Hz $^2J_{CF'}$=24.2Hz		d
71.04	dd	$^2J_{CF}$=29.1Hz $^2J_{CF'}$=26.5Hz		d
133.14	s			g

133.25	s	g
149.66	s	i
149.75	s	i
162.14	s	f
162.24	s	f

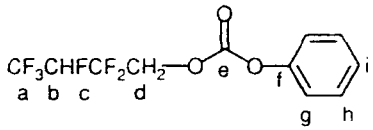
31 3,3,4,5,5,5-Hexafluoropent-2-yl 1,4-phenylenedibenzoate



Spectra run in acetone-d_6

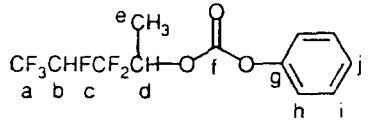
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
2.06	m		3	e
5.66	m		1	d
5.96	m		1	b
8.20	m		2	h
^{19}F:-				
-73.26	m		3	a
-118.92	d	J_{AB}=272.8Hz	2	c
-122.17	d	J_{AB}=273.6Hz		
-122.67	d	J_{AB}=274.7Hz		
-124.01	d	J_{AB}=274.7Hz		
-212.99	dm	$^2J_{HF}$=42.1Hz	1	b
-213.92	dm	$^2J_{HF}$=41.8Hz		

32 2,2,3,4,4,4-Hexafluorobutyl phenyl carbonate



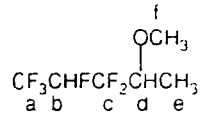
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
4.66	ddd	$^3J_{HF}=^3J_{HF'}=$ 8.4Hz $^4J_{HF}=3.2$Hz	2	d
5.08	ddqd	$^2J_{HF}=43.3$Hz $^3J_{HFc}=15.4$Hz $^3J_{HFa}=5.6$Hz $^3J_{HFc'}=0.8$Hz	1	b
7.22	dd	$^3J_{HH}=7.6$Hz $^4J_{HHi}=1.2$Hz	2	g
7.30	t t	$^3J_{HH}=7.6$Hz $^4J_{HH}=1.0$Hz	1	j
7.43	dd	$^3J_{HHg}=^3J_{HHi}=$ 7.6Hz	2	h
^{19}F:-				
-74.21	dddd	$^3J_{FF}=^4J_{FF}=$ 7.6Hz $^3J_{HF}=^4J_{HFF'}=$ 6.4Hz	3	a
-115.87	dm	$J_{AB}=294.2$Hz	1	c
-120.95	dm	$J_{AB}=295.2$Hz	1	c
-212.88	dm	$J_{HF}=46.4$Hz	1	b
^{13}C:-				
64.20	dd	$^2J_{CF}=36.2$Hz $^2J_{CF'}=27.1$Hz		d
83.85	ddqd	$^1J_{CF}=196.0$Hz $^2J_{CFa}=^2J_{CFc}=$ 35.1Hz		b
115.46	ddd	$^1J_{CF}=251.7$Hz $^1J_{CF'}=251.0$Hz $^2J_{CF}=25.1$Hz		c
120.42	qd	$^1J_{CF}=282.2$Hz $^2J_{CF}=25.6$Hz		a
120.63	s			h
126.56	s			j
129.63	s			i

33. 3,3,4,5,5,5-Hexafluoropent-2-yl phenyl carbonate



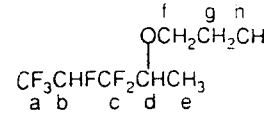
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
1.56	d	$^{3}J_{HH}$=6.4Hz	3	e
5.08	dm	$^{2}J_{HF}$=44.2Hz	1	b
5.20	m		1	d
7.19	ddd	$^{4}J_{HHi}$=7.2Hz $^{3}J_{HH}$=6.0Hz $^{4}J_{HHj}$=0.8Hz	1	h
7.28	t t	$^{3}J_{HH}$=7.2Hz $^{4}J_{HH}$=0.8Hz	1	j
7.41	dd	$^{3}J_{HHj}$=7.3Hz $^{3}J_{HHh}$=6.4Hz	1	i
^{19}F:-				
-73.73	dddd	$^{3}J_{FF}$=$^{4}J_{FF}$=10.9Hz $^{3}J_{HF}$=$^{4}J_{HFF'}$=6.0Hz	3	a
-74.16	m			
-117.99	d	J_{AB}=278.1Hz	2	c
-123.09	d	J_{AB}=276.9Hz		
-123.60	d	J_{AB}=276.9Hz		
-124.81	d	J_{AB}=275.1Hz		
-212.49	dm	$^{2}J_{HF}$=43.6Hz	1	b
-213.71	dm	$^{2}J_{HF}$=43.3Hz		
^{13}C:-				
11.61	d	$^{3}J_{CF}$=5.4Hz		e
11.17	d	$^{3}J_{CF}$=6.6Hz		e
71.49	dd	$^{2}J_{CF}$=36.2Hz $^{2}J_{CF'}$=24.7Hz		d
83.85	m			b
116.43	m			c
121.03	m			a
120.73	s			h
121.10	s			h
126.00	s			j
126.55	s			j
129.49	s			i
129.68	s			i

34 3,3,4,5,5,5-Hexafluoro-2-methoxypentane



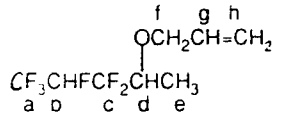
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
1.39	t	$^3J_{HH}$=6.3Hz	3	e
2.12	s		3	f
4.98	dm	$^2J_{HF}$=43.3Hz	1	b
5.27	m		1	d
^{19}F:-				
-74.50	s		3	a
-74.91	s			
series of lines between 118.11 & 133.39			2	c
-212.49	d	$^2J_{HF}$=39.8Hz	1	b
-213.71	d	$^2J_{HF}$=42.1Hz		

35 3,3,4,5,5,5-Hexafluoro-2-propoxypentane



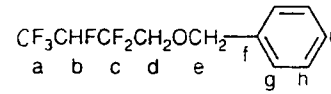
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
0.92	t	$^3J_{HH}$=7.4Hz	3	h
0.93	t	$^3J_{HH}$=7.4Hz		
1.60	m		2	g
2.16	d	$^3J_{HH}$=10.6Hz	3	e
3.36	tq	$^3J_{HH}$=9.2Hz $^4J_{HH}$=6.8Hz	1	i
3.59	tq	$^3J_{HH}$=8.8Hz $^4J_{HH}$=6.8Hz	1	f
3.79	m		1	d
5.14	ddm	$^2J_{HF}$=42.4Hz $^3J_{HFc}$=6.4Hz	1	b
^{19}F:-				
-73.71	dddd	$^3J_{FF}$=$^3J_{HF}$= $^4J_{FF}$=11.1Hz $^4J_{FF'}$=5.6Hz	3	a
-74.30	dddd	$^3J_{FF}$=$^3J_{HF}$= $^4J_{FF}$=11.3Hz $^4J_{FF'}$=6.8Hz		
-118.65	d	J_{AB}=271.7Hz	2	c
-123.26	d	J_{AB}=271.7Hz		
-124.14	d	J_{AB}=272.8Hz		
-129.05	d	J_{AB}=272.6Hz		
-213.13	dm	$^2J_{HF}$=42.5Hz	1	b
-216.19	dqdd	$^2J_{HF}$=42.5Hz $^3J_{FFa}$=$^3J_{FFc}$= $^3J_{FFc'}$=10.7Hz		

36. 3,3,4,5,5,5-Hexafluoro-2-(prop-2-enoxy)pentane



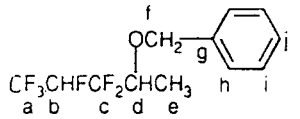
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
2.11	d	$^3J_{HH}$= 2.6Hz	3	e
3.79	m		2	f
3.81	m		1	d
5.22	dm	$^2J_{HF}$= 40.0Hz	1	b
6.07	m		2	h
6.28	m		1	g
^{19}F:-				
-74.75	s		3	a
-117.78	d	J_{AB}=275.1Hz	1	c
-124.14	d	J_{AB}=275.1Hz	1	c
-215.04	d	$^2J_{HF}$=39.3Hz	1	b

37. 2,2,3,4,4,4-Hexafluoro-2-(phenylmethoxy)butane



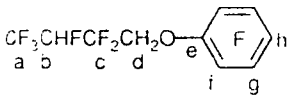
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
4.06	m		2	d or e
4.61	m	J_{AB}=11.5Hz	2	d or e
5.21	dm	$^2J_{HF}$=43.0Hz	1	b
7.36	m		5	h, i, j
7.38	m			
^{19}F:-				
-74.18	m		3	a
-119.90	d	J_{AB}=270.8Hz	2	c
-124.22	d	J_{AB}=272.0Hz		
-218.06	dm	$^2J_{HF}$=42.1Hz	1	b

38 3,3,4,5,5,5-Hexafluoro-2-(phenylmethoxy)pentane



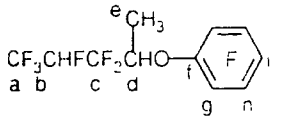
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
1.33	d	$^3J_{HH}$=6.1Hz	3	e
3.94	m		1	d
4.54	d	J_{AB}=11.5Hz	2	f
4.65	d	J_{AB}=11.5Hz		
4.48	d	J_{AB}=11.4Hz		
4.68	d	J_{AB}=11.4Hz		
5.14	ddqd	$^2J_{HF}$=42.8Hz $^3J_{HFc}$=20.8Hz $^3J_{HFa}$=6.3Hz $^3J_{HFc'}$=1.6Hz	1	b
7.33	m		5	h, i, j
7.34	m			
^{19}F:-				
-73.75	dddd	$^3J_{FF}$=$^3J_{HF}$= $^4J_{FF}$=11.3Hz $^4J_{FF}$=6.8Hz	3	a
-118.14	dm	J_{AB}=272.8Hz	2	c
-122.98	ddddq	J_{AB}=272.8Hz $^3J_{FF}$=$^3J_{HF}$= $^3J_{H'F}$=$^4J_{FF}$= 9.4Hz		
-123.99	ddddq	J_{AB}=273.6Hz $^3J_{FF}$=$^3J_{HF}$= $^3J_{H'F}$=$^4J_{FF}$= 11.0Hz		
-128.54	ddddq	J_{AB}=273.6Hz $^3J_{FF}$=$^4J_{FF}$= 12.0Hz $^3J_{HF}$=11.3Hz $^3J_{H'F}$=3.5Hz		
-213.11	dm	$^2J_{HF}$=42.8Hz	1	b
-215.29	dddq	$^2J_{HF}$=43.4Hz $^3J_{FFc}$=$^3J_{FFc'}$= $^3J_{FFa}$=10.7Hz		
^{13}C:-				
10.79	d	$^4J_{CF}$=4.9Hz		e
13.04	d	$^4J_{CF}$=3.0Hz		e
53.84	s			f
72.18	dd	$^2J_{CF}$=32.4Hz $^2J_{CF}$=22.8Hz		a
74.62	dd	$^2J_{CF}$=27.2Hz $^2J_{CF}$=26.7Hz		a
83.26	dqdd	$^1J_{CF}$=193.0Hz $^2J_{CFa}$=34.5Hz $^2J_{CFc}$=24.4Hz $^2J_{CFc'}$=2.8Hz		b
83.27	dqdd	$^1J_{CF}$=191.9Hz $^2J_{CFa}$=34.2Hz $^2J_{CFc}$=24.1Hz $^2J_{CFc'}$=2.2Hz		b
117.64	ddd	$^1J_{CF}$=249.8Hz $^1J_{CF'}$=249.5Hz $^2J_{CF}$=21.0Hz		c
117.78	ddd	$^1J_{CF}$=$^1J_{CF'}$= 253.7Hz $^2J_{CF}$=25.9Hz		c
121.25	qd	$^1J_{CF}$=282.4Hz $^2J_{CF}$=25.5Hz		a
128.00	s			h
128.10	s			h
128.27	s			j
128.36	s			j
128.67	s			i
128.70	s			i
136.87	s			g
137.06	s			g

39 (2,2,3,4,4,4-Hexafluorobutoxy)pentafluorobenzene



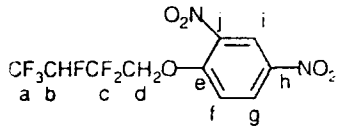
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H :				
4.62	m		2	d
5.21	m		1	b
^{19}F :				
-75.16	s		3	a
series of lines between -118.85 & -129.06			2	c
-156.95	s		1	h
-157.54	s		2	i
-158.86	s		2	g
-214.39	d	$^2J_{HF}$=36.7Hz	1	b
-215.44	d	$^2J_{HF}$=30.1Hz	1	

40 (3,3,4,5,5,5-Hexafluoropent-2-oxy)pentafluorobenzene



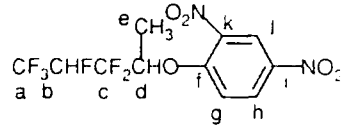
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H :				
1.05	m		3	e
1.29	d	$^3J_{HH}$=4.3Hz		
4.22	m		1	d
4.71	m			
4.82	m		1	b
^{19}F :				
-75.65	s		3	a
-76.00	s			
-119.89	d	J_{AB}=280.0Hz	1	
-124.64	d	J_{AB}=279.8Hz	2	c
-125.26	d	J_{AB}=277.5Hz		
-130.66	d	J_{AB}=277.5Hz		
-157.12	s		2	g
-162.20	s		1	i
-164.52	s		2	h
-214.29	s		1	b

41 (2,2,3,4,4,4-Hexafluorobutoxy)-2,4-dinitrobenzene



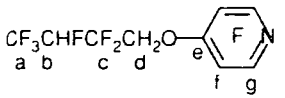
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^1H:				
4.72	m		2	d
5.32	dm	$^2J_{HF}$=40.5Hz	1	b
7.36	d	$^3J_{HH}$=17.7Hz	1	f
8.49	dd	$^3J_{HH}$=21.3Hz	1	g
		$^4J_{HH}$=2.7Hz		
8.75	d	$^4J_{HH}$=2.7Hz	1	i
^{19}F:				
-74.95	s		3	a
-116.90	d	J_{AB}=279.4Hz	2	c
-122.24	d	J_{AB}=280.1Hz		
-214.48	d	$^2J_{HF}$=36.2Hz	1	b

42 (3,3,4,5,5,5-Hexafluoropent-2-oxy)-2,4-dinitrobenzene



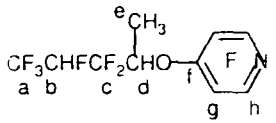
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^1H:				
1.64	d	$^3J_{HH}$=6.5Hz	3	e
1.67	d	$^3J_{HH}$=6.5Hz		
5.03	m		1	d
5.35	m		1	b
7.25	d	$^3J_{HH}$=10.3Hz	1	g
8.50	dd	$^3J_{HH}$=9.5Hz	1	h
		$^4J_{HH}$=2.8Hz		
8.81	d	$^4J_{HH}$=2.9Hz	1	j
^{19}F:				
-74.31	s		3	a
-74.81	s			
-117.90	d	J_{AB}=277.2Hz	1	c
-122.72	d	J_{AB}=275.8Hz		
-124.21	d	J_{AB}=276.1Hz	1	c
-126.56	d	J_{AB}=275.8Hz		
-213.57	d	$^2J_{HF}$=38.4Hz	1	b
-215.54	d	$^2J_{HF}$=40.0Hz		

43 4-(2,2,3,4,4,4-Hexafluorobutoxy)tetrafluoropyridine



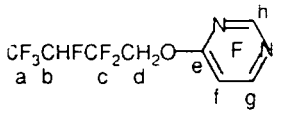
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H :				
4.79	m		2	d
5.18	ddqd	$^2J_{HF}$=43.2Hz $^3J_{HFc}$=16.0Hz $^3J_{HFa}$=5.6Hz $^3J_{HFc'}$=4.8Hz	1	b
^{19}F :				
-74.51	m		3	a
-88.98	ddd	$^3J_{FF}$=14.7Hz	2	g
-116.80	dm	J_{AB}=282.2Hz	1	c
-121.85	dm	J_{AB}=279.2Hz	1	c
-158.34	ddd	$^3J_{FF}$=14.7Hz	2	f
-213.45	dm	$^2J_{HF}$=42.9Hz	1	b
^{13}C :				
70.24	dd	$^3J_{CF}$=37.4Hz $^3J_{CF'}$=27.1Hz		d
83.53	ddqd	^{1}JCF=196.1Hz $^2J_{CFc}$=$^2J_{CFa}$=35.5Hz $^2J_{CFc'}$=26.4Hz		b
115.66	ddd	$^1J_{CF}$=$^1J_{CF'}$=253.0Hz $^2J_{CF}$=25.5Hz		c
120.44	qd	$^1J_{CF}$=282.3Hz $^2J_{CF}$=25.3Hz		a
135.09	ddm	$^1J_{CF}$=259.2Hz $^2J_{CF}$=39.0Hz		g
144.11	dddd	$^1J_{CF}$=243.8Hz $^2J_{CF}$=15.6Hz $^3J_{CF}$=14.1Hz $^4J_{CF}$=3.0Hz		f
145.46	m			e

#4 4-(3,3,4,5,5,5-Hexafluoropent-2-oxy)tetrafluoropyridine



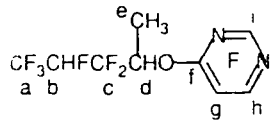
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
1.61	d	$^3J_{HH}$=6.4Hz	3	e
5.14	m		1	o
^{19}F:-				
-73.79	ddd	$^3J_{FF}$=21.8Hz $^4J_{FF}$=10.9Hz $^3J_{HF}$=6.0Hz	3	a
-74.10	ddd	$^3J_{FF}$=19.3Hz $^4J_{FF}$=8.7Hz $^3J_{HF}$=6.0Hz		
-88.34	m		2	h
-117.98	dm	J_{AB}=279.2Hz	2	c
-122.64	dm	J_{AB}=280.0Hz		
-123.19	dm	J_{AB}=276.9Hz		
-127.23	dm	J_{AB}=277.3Hz		
-157.17	m		2	g
-212.44	dm	$^2J_{HF}$=43.3Hz	1	b
-213.42	ddq	$^2J_{HF}$=43.6Hz $^3J_{HFc}$=12.8Hz $^3J_{HFa}$=9.8Hz		
^{13}C:-				
12.05	d	$^3J_{CF}$=4.6Hz		e
79.48	dd	$^2J_{CF}$=$^2J_{CF}$=27.7Hz		d
83.44	dm	$^1J_{CF}$=197.4Hz		b
116.19	ddd	$^1J_{CF}$=$^1J_{CF}$=254.9Hz $^2J_{CF}$=26.8Hz		c
120.52	qm	$^1J_{CF}$=282.7Hz		a
135.51	dd	$^1J_{CF}$=259.4Hz $^2J_{CF}$=39.3Hz		g
144.13	dm	$^1J_{CF}$=244.5Hz		h
144.33	m			f

45 4-(2,2,3,4,4,4-Hexafluorobutoxy)trifluoropyrimidine



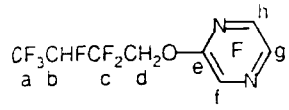
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
4.87	m		1	d
5.12	ddqd	$^{3}J_{HF}$=43.6Hz $^{3}J_{HFc}$=15.2Hz $^{3}J_{HFa}$=5.6Hz $^{3}J_{HFc'}$=5.1Hz	1	b
^{19}F:-				
-74.67	m		3	a
-78.01	d	$^{4}J_{HF}$=17.7Hz	1	h
-115.47	dm	J_{AB}=272.4Hz	1	c
-120.93	dm	J_{AB}=272.4Hz	1	c
-174.76	dd	$^{3}J_{FF}$=26.2Hz J_{FF}=17.5Hz	1	f or g
-176.74	dd	$^{3}J_{FF}$=26.2Hz J_{FF}=17.7Hz	1	f or g
-213.19	d	$^{2}J_{HF}$=44.0Hz	1	b
^{13}C:-				
64.86	dd	$^{2}J_{CF}$=36.8Hz $^{2}J_{CF'}$=27.3Hz		d
84.02	ddqd	$^{1}J_{CF}$=196.1Hz $^{2}J_{CFc}$=70.5Hz $^{2}J_{CFa}$=35.5Hz $^{2}J_{CFc'}$=29.0Hz		b
115.57	ddd	$^{1}J_{CF}$=$^{1}J_{CF'}$= 252.1Hz $^{2}J_{CF}$=25.5Hz		c
120.46	qd	$^{1}J_{CF}$=282.0Hz $^{2}J_{CF}$=25.5Hz		a
129.84	ddd	$^{1}J_{CF}$=262.8Hz $^{3}J_{CF}$=23.4Hz $^{4}J_{CF}$=29.0Hz		h
153.26	ddd	$^{1}J_{CF}$=225.5Hz $^{2}J_{CF}$=20.9Hz $^{4}J_{CF}$=10.2Hz		f
158.99	ddd	$^{1}J_{CF}$=253.9Hz $^{2}J_{CF}$=17.2Hz $^{3}J_{CF}$=12.0Hz		g
160.62	ddd	$^{2}J_{CF}$=15.6Hz $^{3}J_{CF}$=9.9Hz $^{3}J_{CF'}$=7.2Hz		e

46 4-(3,3,4,5,5,5-Hexafluoropent-2-oxy)-trifluoropyrimidine



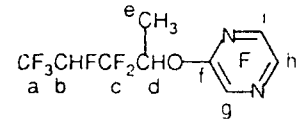
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
1.62	d	$^3J_{HH}$=6.4Hz	3	e
5.12	m		1	b
5.66	m		1	d
^{19}F:-				
-74.31	dddd	$^3J_{FF}$=21.4Hz $^4J_{FF}$=17.3Hz $^3J_{HF}$=10.9Hz $^4J_{FF'}$=5.6Hz	1	
-74.63	dddd	$^3J_{FF}$=20.3Hz $^4J_{FF}$=17.3Hz $^3J_{HF}$=10.9Hz $^4J_{FF'}$=6.4Hz	3	a
-78.20	m		1	i
-117.96	ddm	J_{AB}=278.8Hz J_{AB}=9.8Hz	1	
-122.83	dm	J_{AB}=278.8Hz	2	c
-125.89	dm	J_{AB}=271.3Hz		
-132.59	dm	J_{AB}=271.7Hz		
-174.43	m		1	g or h
-176.23	dd	$^3J_{FF}$=25.6Hz $^4J_{FF}$=17.3Hz	1	g or h
-212.89	dm	$^2J_{HF}$=44.0Hz	1	b
-213.42	dm	$^2J_{HF}$=43.8Hz		
^{13}C:-				
11.22	d	$^3J_{CF}$=5.5Hz		e
14.29	d	$^3J_{CF}$=4.8Hz		e
72.29	dd	$^2J_{CF}$=36.4Hz $^2J_{CF'}$=25.4Hz		d
73.43	dd	$^2J_{CF}$=$^2J_{CF'}$=29.0Hz		d
83.67	m			b
116.29	ddd	$^1J_{CF}$=$^1J_{CF'}$=254.1Hz $^2J_{CF}$=26.3Hz		c
120.58	qd	$^1J_{CF}$=282.3Hz $^2J_{CF}$=25.5Hz		a
129.85	dm	$^1J_{CF}$=262.1Hz		i
153.36	ddd	$^1J_{CF}$=225.7Hz $^2J_{CF}$=20.8Hz $^4J_{CF}$=4.9Hz		g
158.94	ddd	$^1J_{CF}$=254.1Hz $^2J_{CF}$=17.2Hz $^3J_{CF}$=12.2Hz		h
160.36	m			f

47 5-(2,2,3,4,4,4-Hexafluorobutoxy)trifluoropyrazine



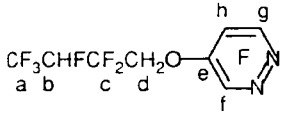
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H :				
4.71	dd	$^3J_{HF}$=14.7Hz $^3J_{HF}$=7.7Hz	2	a
5.09	d	$^2J_{HF}$=43.6Hz	1	b
^{19}F :				
-75.28	s		3	d
-93.41	d	$^3J_{FF}$=44.6Hz	1	f or g
-94.37	d	$^3J_{FF}$=46.1Hz		
-99.08	d	$^3J_{FF}$=45.9Hz	1	f or g
-100.58	d	$^3J_{FF}$=46.4Hz		
-103.49	s		1	h
-108.02	s			
-116.37	d	J_{AB}=281.0Hz	1	c
-121.75	d	J_{AB}=280.8Hz	1	c
-214.06	d	$^2J_{HF}$=41.2Hz	1	b

48 5-(3,3,4,5,5,5-Hexafluoropent-2-oxy)-trifluoropyrazine



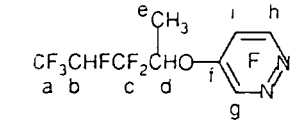
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H :				
1.58	d	$^3J_{HH}$=5.9Hz	3	e
5.11	m		1	d
5.48	m		1	b
^{19}F :				
-75.14	m		3	a
-75.53	m			
-93.63	s		1	g
-98.87	d	$^3J_{FF}$=27.1Hz	1	i
-103.76	s		1	h
-119.02	d	J_{AB}=277.5Hz	2	c
-123.76	d	J_{AB}=281.5Hz		
-124.06	d	J_{AB}=284.1Hz		
-126.31	d	J_{AB}=272.5Hz		
-213.83	m		1	b
-215.36	m			

49 4-(2,2,3,4,4,4-Hexafluorobutoxy)trifluoropyridazine



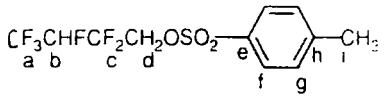
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
4.80	ddd	$^3J_{HF}$=17.1Hz $^3J_{HF}$=7.7Hz $^4J_{HF}$=2.7Hz	2	d
5.13	dm	$^2J_{HF}$=43.5Hz	1	b
^{19}F:				
-75.10	s		3	a
-93.61	m		1	g
-99.61	m			f
-116.17	d	J_{AB}=281.3Hz	1	c
-121.58	d	J_{AB}=280.8Hz	1	c
-163.06	m		1	h
-213.87	d	$^2J_{HF}$=39.8Hz	1	b

50 4-(3,3,4,5,5,5-Hexafluoropent-2-oxy)-trifluoropyridazine



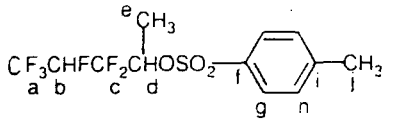
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
1.54	d	$^3J_{HH}$=6.3Hz	3	e
1.65	d	$^3J_{HH}$=6.2Hz		
5.06	m		1	d
5.23	m			b
^{19}F:				
-74.81	s		3	a
-75.05	s			
-88.25	s		1	g
-94.50	m		1	h
-119.46	d	J_{AB}=278.9Hz	2	c
-123.47	d	J_{AB}=272.1Hz		
-123.95	d	J_{AB}=277.9Hz		
-127.45	d	J_{AB}=274.2Hz		
-144.46	m		1	i
-213.24	m		1	b

51 2,2,3,4,4,4-Hexafluorobutyl 4-methylbenzenesulphonate



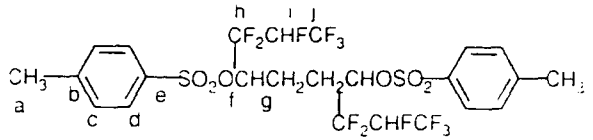
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
2.48	d	$^4J_{HH}$=6.0Hz	3	i
4.32	m		2	d
4.96	m		1	b
7.40	d	$^3J_{HH}$=8.0Hz	2	g
7.81	d	$^3J_{HH}$=7.6Hz	2	f
^{19}F:-				
-73.79	dddd	$^3J_{FF}$=$^4J_{FF}$= 10.9Hz $^3J_{HF}$=$^4J_{FF'}$= 6.4Hz	3	a
-115.46	dm	J_{AB}=280.3Hz	1	c
-120.95	dm	J_{AB}=280.3Hz	1	c
-212.68	dm	$^3J_{HF}$=43.6Hz	1	b
^{13}C:-				
21.66	s			i
64.97	dd	$^2J_{CF}$=38.5Hz $^2J_{CF'}$=27.5Hz		d
83.26	dqm	$^1J_{CF}$=195.3Hz $^2J_{CFa}$=25.9Hz		b
115.12	ddd	$^1J_{CF}$=253.4Hz $^1J_{CF'}$=252.5Hz $^2J_{CF}$=25.5Hz		c
120.32	qd	$^1J_{CF}$=282.3Hz $^2J_{CF}$=25.5Hz		d
127.02	s			h
128.10	s			g
130.25	s			f
131.42	s			e

52 3,3,4,5,5,5-Hexafluoropentyl 2-(4-methylbenzenesulphonate)



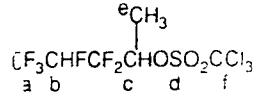
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
1.12	ddd	$^3J_{HH}$=7.2Hz $^4J_{HF}$=3.6Hz $^4J_{HF'}$=6.8Hz	3	e
2.48	s		3	l
5.15	m		1	d
5.53	dm	$^2J_{HF}$=42.8Hz	1	b
7.54	d	$^3J_{HH}$=8.4Hz	2	h
7.90	d	$^3J_{HH}$=8.4Hz	2	g
^{19}F:-				
-73.95	s		3	a
-74.12	s			
-120.38	d	J_{AB}=272.5Hz	1	c
-123.04	d	J_{AB}=272.8Hz		
-123.86	d	J_{AB}=276.1Hz	1	c
-125.80	d	J_{AB}=276.8Hz		
-213.12	s		1	b
-213.48	d	$^2J_{HF}$=44.5Hz		

53 1,1,1,2,3,3,8,8,9,10,10,10-Dodecafluorodecyl 4,7-bis(4-methylbenzenesulphonate)



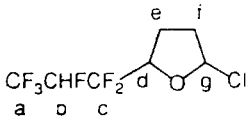
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
1.85	m		2	g
2.48	s		3	a
5.14	m		1	f
5.53	dm	$^2J_{HF}$=42.8Hz	1	b
7.54	m	$^3J_{HH}$=8.4Hz	1	c
7.89	m	$^3J_{HH}$=8.4Hz	1	d
^{19}F:				
-73.31	s		3	a
-117.86	d	J_{AB}=277.3Hz	1	c
-120.25	d	J_{AB}=277.3Hz	1	c
-221.47	d	$^2J_{HF}$=32.2Hz	1	b

54 3,3,4,5,5,5-Hexafluoropentyl 2-(trichloromethanesulphonate)



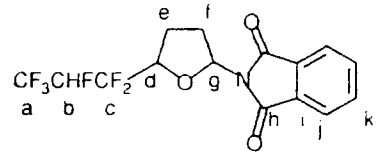
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
1.75	d	$^3J_{HH}$=5.6Hz	3	e
5.05	ddqd	$^2J_{HH}$=43.6Hz $^3J_{HFc}$=19.6Hz $^3J_{HFa}$=6.0Hz $^4J_{HFc'}$=2.0Hz	1	b
5.31	m		1	d
^{19}F:				
-73.41	dddd	$^3J_{FF}$=$^4J_{FF}$=11.3Hz $^3J_{HF}$=$^4J_{FF'}$=5.3Hz		
-73.72	dddd	$^3J_{FF}$=$^4J_{FF}$=10.5Hz $^3J_{HF}$=$^4J_{FF'}$=5.3Hz	3	a
-117.70	d	J_{AB}=273.9Hz		
-120.73	d	J_{AB}=273.6Hz	2	c
-122.85	d	J_{AB}=281.5Hz		
-124.98	d	J_{AB}=275.4Hz		
-210.99	d	$^2J_{HF}$=43.3Hz	1	b

55. 2-Chloro-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane



Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
2.33	m		2	e or f
2.50	m		2	e or f
4.40	m		1	d
5.33	m		1	b
5.51	m		1	g
^{19}F:-				
-73.65	m		3	a
-74.02	m			
-117.29	dm	J_{AB}=279.4Hz	1	c
-120.24	d	J_{AB}=280.3Hz		
-120.98	d	J_{AB}=276.4Hz	1	c
-122.54	d	J_{AB}=277.1Hz		
-212.08	m		1	b
-215.40	m			

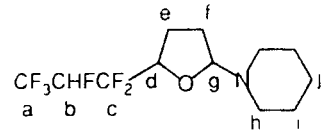
56. 2-Phthalimido-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane



Spectra run in acetone-d_6

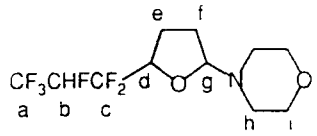
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
2.29	m		2	e or f
2.66	m		2	e or f
4.42	m		1	a
4.75	m			
5.42	m		1	b
6.00	m		1	g
6.15	m			
^{19}F:-				
-79.22	dddd	$^3J_{FF}$=27.1Hz $^4J_{FF}$=16.9Hz $^3J_{HF}$=10.9Hz $^4J_{FF'}$=6.0Hz	3	a
-79.61	m			
-124.45	dm	J_{AB}=272.0Hz	2	c
-126.08	dm	J_{AB}=270.2Hz		
-128.29	dm	J_{AB}=272.1Hz		
-129.46	dm	J_{AB}=270.2Hz		
-130.04	dm	J_{AB}=258.9Hz		
-130.71	dm	J_{AB}=268.4Hz		
-132.82	dm	J_{AB}=263.8Hz		
-134.31	dm	J_{AB}=270.9Hz		

57 2-Piperidino-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane



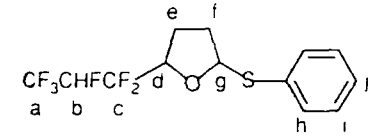
Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
1.49	m		2	j
1.57	m		4	i
series of lines between 1.98 & 2.13			4	e,f
2.74	m		4	h
4.22	m		1	d
5.08	dm	$^2J_{HF}$=49.8Hz	1	b
6.16	m		1	g
6.20	m			
^{19}F:				
-74.05	ddm	J=6.4Hz J=4.1Hz	3	a
-74.62	dm	J=6.4Hz		
-121.41	dm	J_{AB}=263.8Hz	2	c
-125.10	dm	J_{AB}=256.3Hz		
-126.98	dm	J_{AB}=268.7Hz		
-131.31	dm	J_{AB}=269.1Hz		
-213.10	dm	$^2J_{HF}$=42.5Hz	1	b
-218.70	dm	$^2J_{HF}$=44.2Hz		
^{13}C:				
24.66	s			j
24.78	s			j
26.17	s			i
26.30	s			i
26.79	s			f
26.83	s			f
27.68	s			e
-218.53	m			
-219.00	m			
-220.73	ddq	$^2J_{HF}$=43.3Hz $^3J_{FFa}$=$^3J_{FFc}$= $^3J_{FFc}$=9.8Hz	1	b
-221.99	ddq	$^2J_{HF}$=42.1Hz $^3J_{FFa}$=$^3J_{FFc}$= $^3J_{FFc}$=7.9Hz		
^{13}C:				
28.03	s			i
28.08	s			f
29.89	s			e
30.55	s			e
77.39	dd	$^2J_{CF}$=36.3Hz $^2J_{CF}$=23.2Hz		d
82.62	s			g
82.99	s			g
84.95	m			b
121.00	m			a,c
123.99	s			k
124.31	s			k
132.75	s			i
132.80	s			i
135.27	s			j
135.71	s			j

58. 2-Morpholino-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane



Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:-				
series of lines between 1.62 & 1.78			4	e,f
2.24	m		2	h
2.45	m		2	h
3.31	m		4	i
4.43	dm	$^2J_{HF}$=20.7Hz	1	d
4.88	dm	$^2J_{HF}$=36.8Hz	1	b
5.90	m		]1	g
5.97	m		]	
^{19}F:-				
-75.39	m		3	a
series of lines between -121.27 & -132.85			2	c
-214.49	m		]1	b
-219.47	m		]	
27.88	s			e
48.58	s			h
48.88	s			h
73.93	dd	$^2J_{CF}$=35.1Hz $^2J_{CF}$=22.9Hz		d
75.58	m			g
84.16	m			b
117.65	m			c
121.32	qd	$^1J_{CF}$=282.3Hz $^2J_{CF}$=24.0Hz		a

59. 2-(1,1,2,3,3,3-hexafluoropropyl)-5-thiophenylcyclopentane



Shift (ppm)	Multiplicity	Coupling	Relative Intensity	Assignment
^{1}H:				
2.02	m		2	e
2.45	m		2	f
3.87	m		1	d
4.33	m		1	g
5.08	dm	$^2J_{HF}$=43.6Hz	1	b
7.21	m		2	j
7.30	m		2	i
7.47	m		1	k
^{19}F:				
-74.36	s		3	a
-74.83	d	$^3J_{HF}$=34.6Hz		
-119.85	d	J_{AB}=274.6Hz	2	c
-120.37	d	J_{AB}=268.8Hz		
-124.67	d	J_{AB}=268.1Hz		
-125.24	d	J_{AB}=259.3Hz		
-125.84	d	J_{AB} unresolved		
-130.44	d	J_{AB}=274.6Hz		
-130.77	d	J_{AB}=274.68Hz		
-213.34	m		1	b
-213.39	m			
-215.53	m			
-218.71	m			

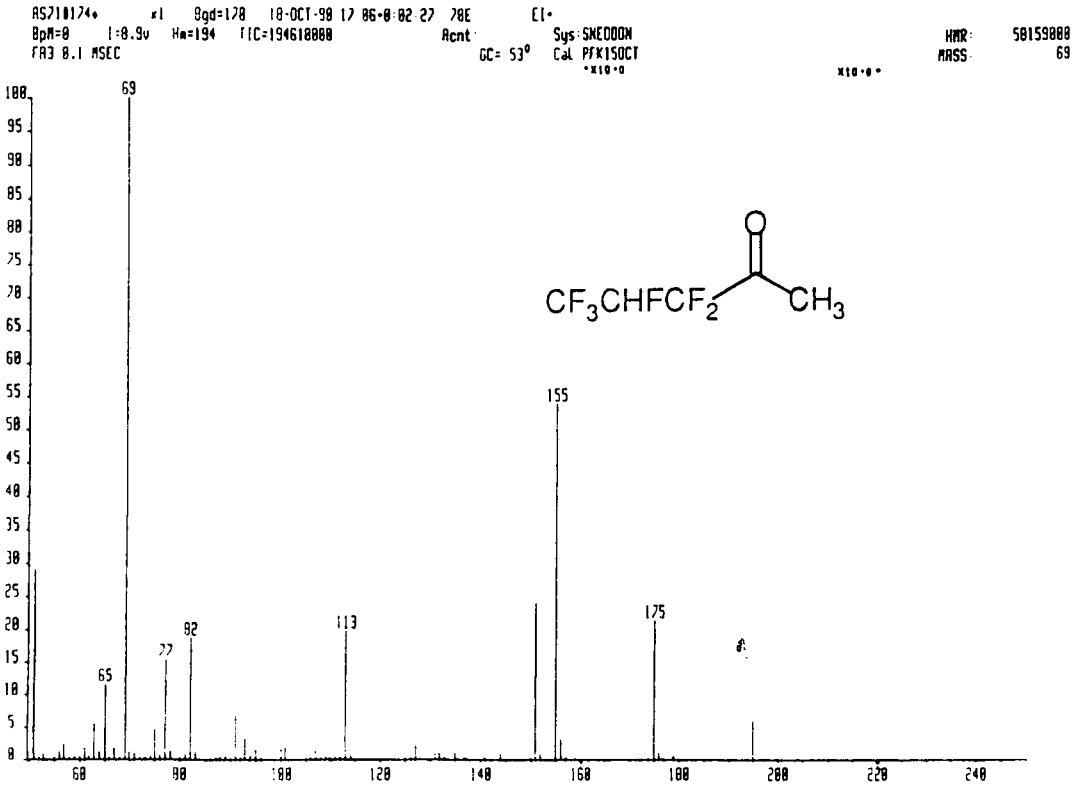
APPENDIX TWO

MASS SPECTRA

CONTENTS

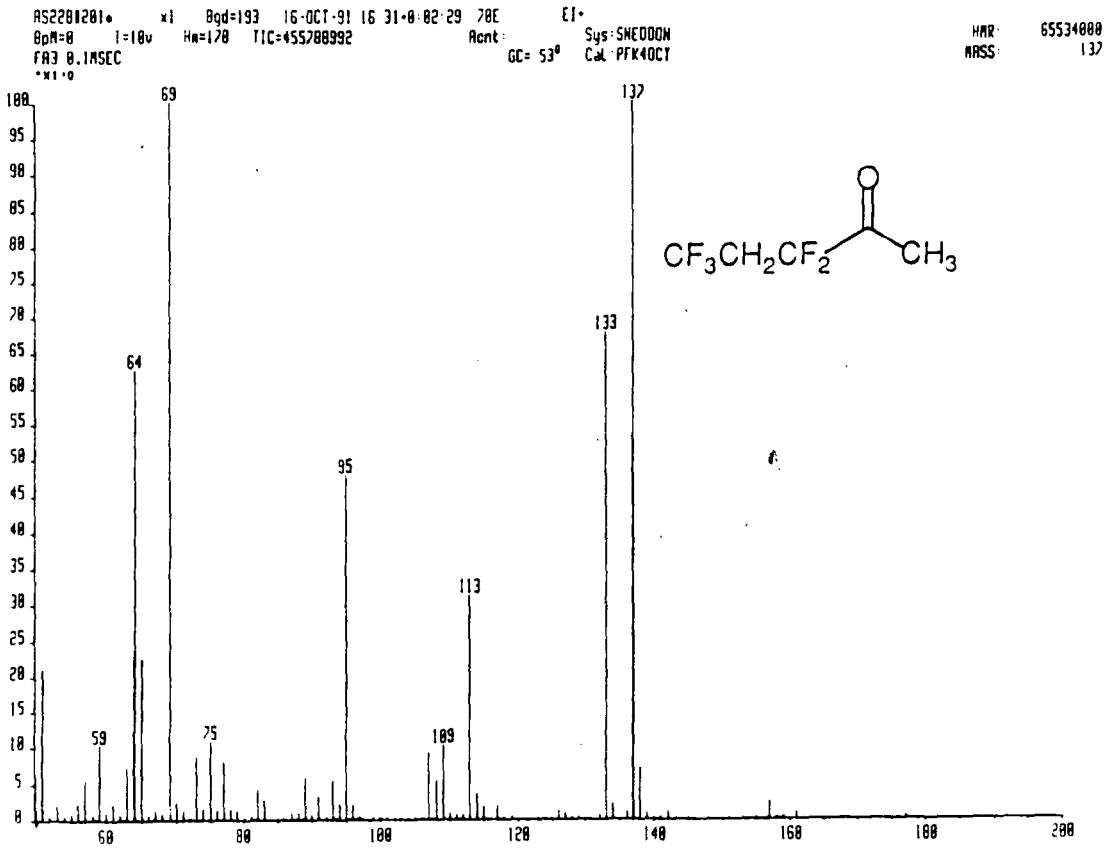
35. 2,2,3,4,4,4-Hexafluoro-1-(prop-2-enoxy)butane
36. 3,3,4,5,5,5-Hexafluoro-2-(prop-2-enoxy)pentane
37. 2,2,3,4,4,4-Hexafluoro(phenylmethoxy)butane
38. 3,3,4,5,5,5-Hexafluoro-2-(phenylmethoxy)pentane
39. (2,2,3,4,4,4-Hexafluorobutoxy)pentafluorobenzene
40. (3,3,4,5,5,5-Hexafluoropent-2-oxy)pentafluorobenzene
41. (3,3,4,5,5,5-Hexafluoropent-2-oxy)-2,4-dinitrobenzene
42. 4-(2,2,3,4,4,4-Hexafluorobutoxy)tetrafluoropyridine
43. 4-(3,3,4,5,5,5-Hexafluoropent-2-oxy)tetrafluoropyridine
44. 4-(2,2,3,4,4,4-Hexafluorobutoxy)trifluoropyrimidine
45. 4-(3,3,4,5,5,5-Hexafluoropent-2-oxy)-trifluoropyrimidine
46. 5-(2,2,3,4,4,4-Hexafluorobutoxy)trifluoropyrazine
47. 5-(3,3,4,5,5,5-Hexafluoropent-2-oxy)-trifluoropyrazine
48. 4-(2,2,3,4,4,4-Hexafluorobutoxy)trifluoropyridazine
49. 4-(3,3,4,5,5,5-Hexafluoropent-2-oxy)-trifluoropyridazine
50. 2,2,3,4,4,4-Hexafluorobutyl 4-methylbenzenesulphonate
51. 3,3,4,5,5,5-Hexafluoropentyl 2-(4-methylbenzenesulphonate)
52. 1,1,1,2,3,3,8,8,9,10,10,10-Dodecafluorodecyl 4,7-bis(4-methylbenzenesulphonate)
53. 3,3,4,5,5,5-Hexafluoropentyl 2-(trichloromethanesulphonate)
54. 1-Chloro-3,3,4,5,5,5-hexafluoropentan-2-one
55. 1,1-Dichloro-3,3,4,5,5,5-hexafluoropentan-2-one
56. 2-Chloro-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane
57. 2-Bromo-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane
58. 2-Methoxy-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane
59. 2-Phthalimido-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane
60. 2-Piperidino-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane
61. 2-Morpholino-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane
62. 2-(1,1,2,3,3,3-Hexafluoropropyl)-5-thiophenyloxolane

1. 3,3,4,5,5,5-Hexafluoropentan-2-one



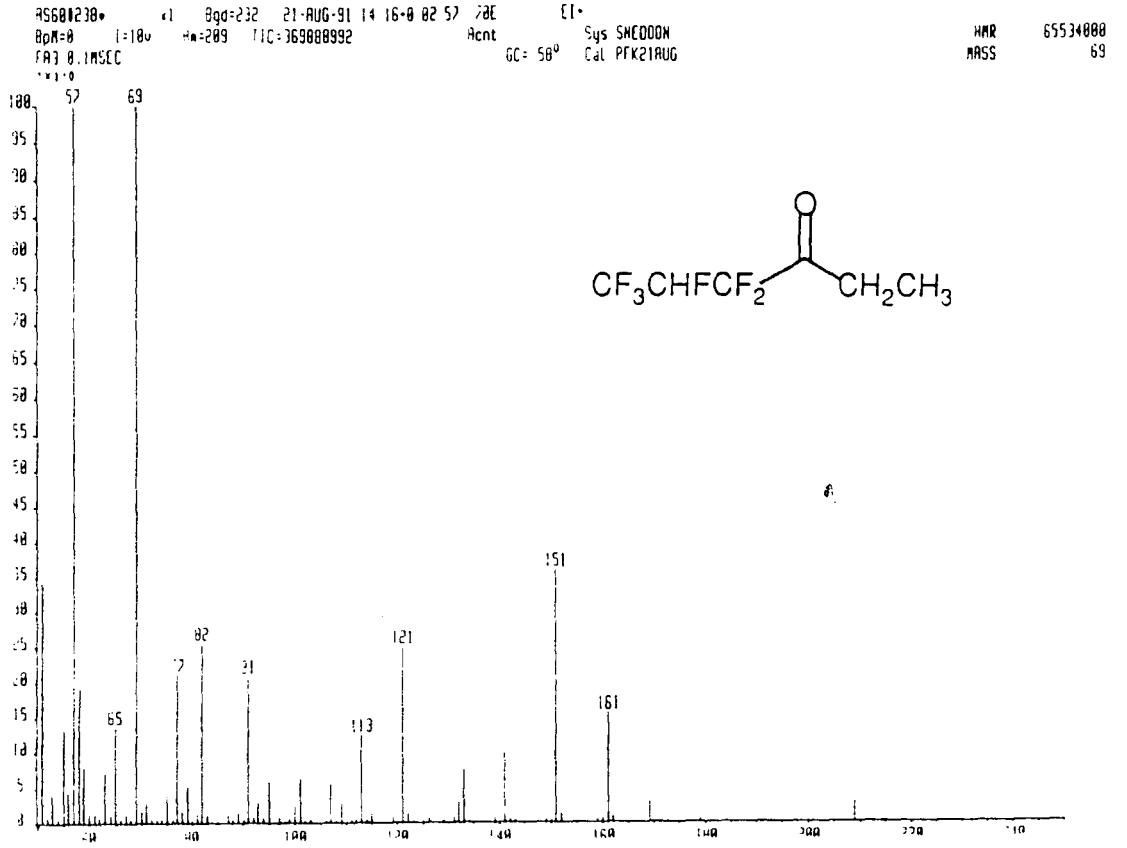
Mass	% Base				
52.03	0.42	91.08	8.87	128.12	0.20
53.03	1.05	92.09	0.27	131.09	1.35
55.03	0.68	93.09	4.49	132.09	0.90
56.04	1.42	94.10	0.62	133.11	0.26
57.05	3.60	95.10	3.07	135.11	0.87
58.05	0.37	96.10	0.13	137.38	2.78
59.07	0.75	97.13	2.71	141.13	0.13
60.04	0.51	99.10	0.11	144.14	1.03
61.05	2.43	100.09	2.12	145.15	0.13
62.05	3.10	101.10	2.20	147.15	2.78
63.05	7.74	104.12	0.20	150.11	0.17
64.06	2.71	105.12	0.10	151.12	18.69
65.07	15.54	106.11	0.28	152.13	0.60
66.08	0.36	107.11	2.90	154.13	0.12
67.06	1.56	108.12	0.40	155.13	71.49
68.06	0.28	109.12	1.76	156.14	3.87
69.05	100.00	110.11	0.24	157.14	0.35
70.06	1.37	111.10	0.11	159.16	0.24
71.05	0.97	112.09	2.73	175.15	9.89
72.07	0.16	113.10	25.40	176.16	0.52
73.07	0.58	114.11	2.80	177.15	2.87
74.06	1.01	119.11	2.71	195.16	5.31
75.07	6.63	121.11	0.16	196.19	0.30
76.08	0.88	125.11	1.00	209.19	0.23
77.09	22.45	126.10	0.45		
78.07	1.67	127.11	5.32		
79.12	0.13				
81.09	3.71				
82.08	28.79				
83.09	1.43				
87.09	0.12				
88.09	0.31				
89.10	0.94				
90.11	0.17				

2. 3,3,5,5,5-Pentafluoropentan-2-one



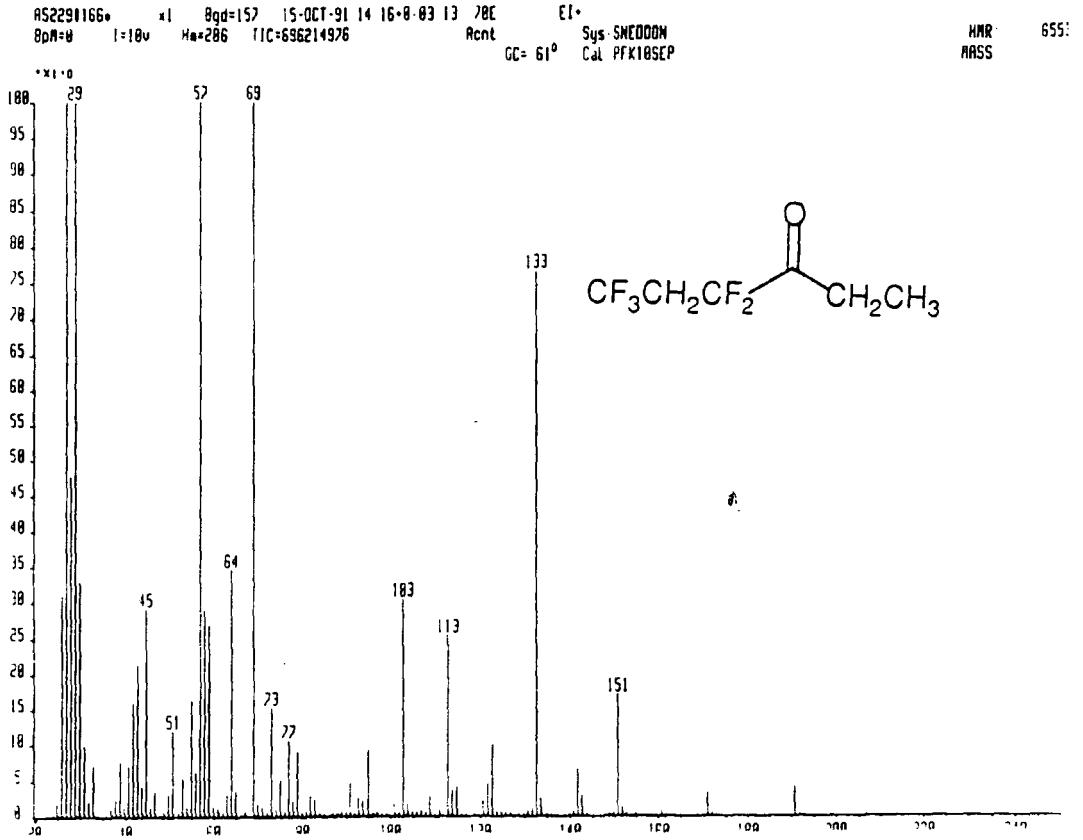
Mass	% Base		Mass	% Base		Mass	% Base	
49 01	0 99		81 01	0 49		137 05	100 00	FO
50 00	6 25		82 00	4 14		138 03	6 98	F
51 01	21 09		83 01	2 58		139 03	0 78	
52 02	0 49		87 04	0 88		141 00	0 30	
53 01	1 83		88 01	0 88		142 01	1 07	
54 01	0 43		89 02	5 76		157 02	2 34	
55 01	0 83		90 02	0 56		161 00	0 87	
56 01	2 34		91 00	3 13		177 02	0 43	
57 01	5 57		93 00	5 31				
58 02	0 55		94 00	2 01				
59 03	10 19		95 03	47 81	F			
60 02	0 89		96 01	1 85				
61 01	2 12		107 02	9 27				
62 00	0 52		108 02	5 32				
63 01	7 11	F	109 02	10 26				
63 97	23 67	F	110 02	0 78				
64 03	62 58	F	111 00	0 51				
65 02	22 48		112 05	0 55	F			
66 04	0 63		113 00	31 30	F			
67 00	1 17		114 00	3 54				
68 02	0 78	F	115 02	1 59				
69 03	100 00	FO	117 01	1 79				
70 00	2 36		126 03	1 10				
71 00	1 18		127 03	0 79				
73 03	8 60		132 03	0 64	F			
74 00	1 41		133 04	67 78	F			
75 00	10 85		134 00	2 08	F			
76 01	1 17		136 04	1 07	F			
77 02	7 86		136 90	53 35	F			
78 00	1 38							
79 03	1 19							

3. 3,3,4,5,5,5-Hexafluorohexan-3-one



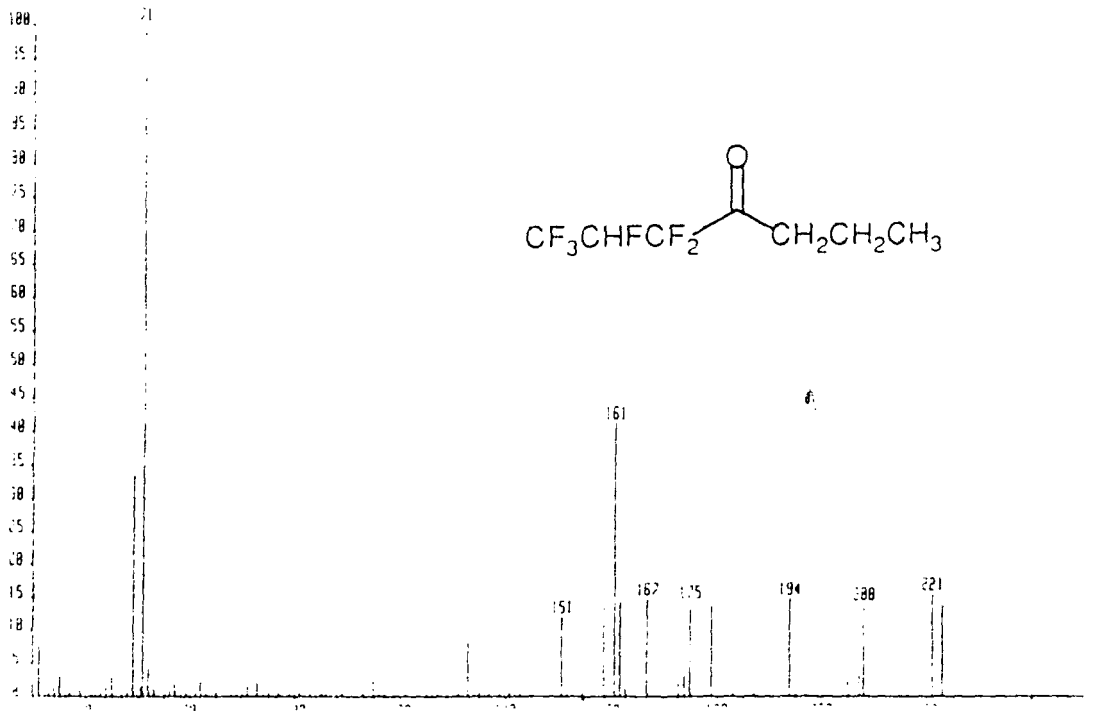
Mass	% Base					
48 92	0 83	82.02	25.56	131 02	2 34
49 82	3 91	83.03	1.23	132.03	2 82
50 93	34 38	87 04	1.17	133 04	7 42
51 84	0 78	88.04	0.39	139.06	0 78
52 95	3.91	89 04	1 56	141.05	9 77
53 86	0 78	90.05	0.39	142.06	0.39
54 87	13 28	91.03	20.94	149 05	0 39
55.89	4 55	92.04	0.78	151 02	35 97
56.94	100 00 C	93.02	2.73	152.03	1.17
57 91	19.14	94 02	0.78	159.05	0.39
58 92	7 81	95.03	5.86	160.03	1.17
59 92	1.17	97 05	0.78	161 04	15.63
60 91	1 17	99.03	0.39	162.04	0 78
61 91	0 78	100 02	2.34	169.07	2.73
62.93	7 03	101 04	6.25	179.04	0 39
63 94	1 22	103 06	0 39	209 08	2.78
64 95	10 78	107 05	5 55		
65 96	0 39	109 04	2.73		
66 95	1 17	111 02	0 39		
67 97	0 39	112.02	0.39		
68 96	100 00 0	113.02	12.50		
69 98	1 56	114 03	0.39		
71 00	2.73	115.04	1 21		
72.00	0 39	119.05	0 78		
73 01	0.39	121 06	25.00		
73.99	0 39	122.06	1.17		
75.00	3 91	126 06	0 78		
76 01	0 39	129 03	0 39		
77 02	21 09				
78 01	1 66				
79 04	5 47				
81 02	1 17				

4. 3,3,5,5,5-Pentafluorohexan-3-one



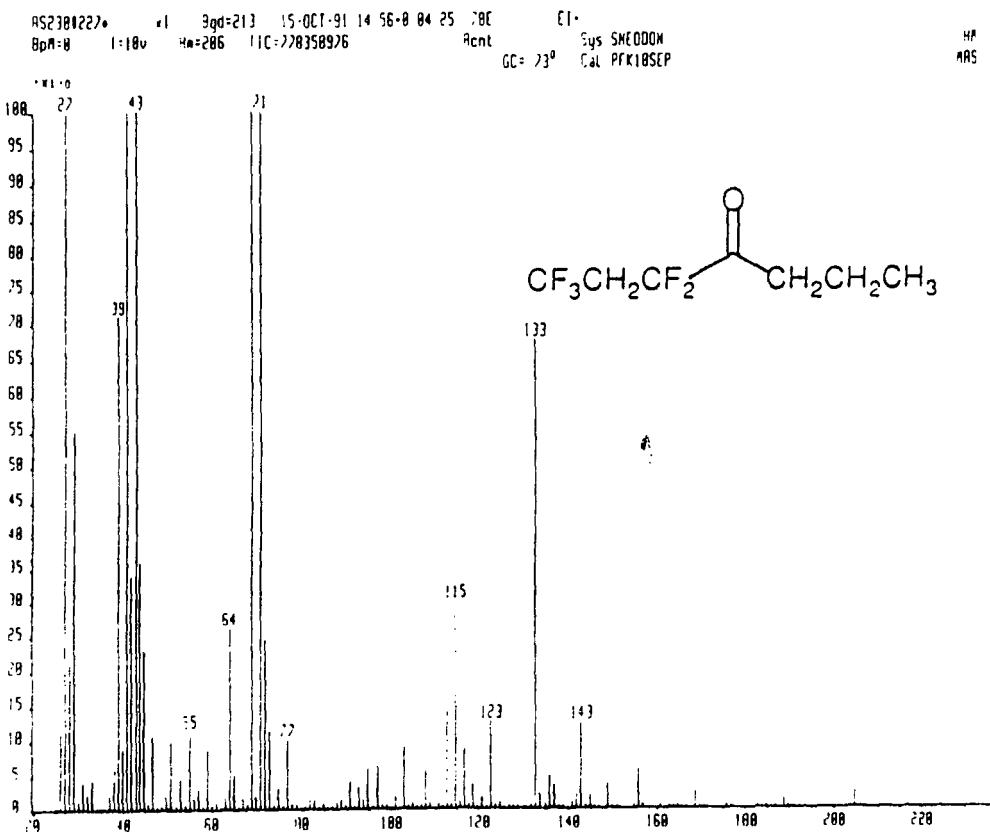
Mass	% Base					
40.92	7.04	74.84	5.03	112.77	25.26	
41.90	16.02	75.84	0.60	113.78	3.44	
42.90	21.26	76.85	10.55	114.79	3.91	
43.89	4.09	77.84	2.21	120.80	2.11	
44.89	29.04	78.86	8.98	121.78	4.48	
45.90	1.18	79.85	0.40	122.79	9.93	
46.90	3.31	80.83	0.52	123.79	0.54	
48.89	0.59	81.82	2.73	124.78	0.49	
49.88	3.13	82.84	2.15	125.78	0.32	
50.88	12.01	86.83	0.44	130.76	0.78 F	
51.89	0.40	87.82	0.44	131.69	1.07 F	
52.88	5.24	88.83	0.78	132.74	76.38 F	
53.88	1.31	89.83	0.39	133.75	2.37 F	
54.88	16.41 F	90.82	4.55	140.75	0.61	
55.88	6.09 F	92.80	2.42	141.74	6.49	
56.94	100.00 FO	93.80	2.06	142.74	2.56	
57.90	28.89 F	94.81	9.21	149.71	0.58 F	
58.89	26.93	95.81	0.39	150.75	16.97 F	
59.89	1.19	96.79	0.39	151.76	1.14	
60.87	1.01	100.82	1.56	160.71	0.61	
61.87	0.42	101.82	0.78 F	170.73	3.13	
62.86	3.13	102.82	30.31 F	190.71	3.92	
63.86	34.40	103.82	1.60			
64.87	3.43	104.80	0.39			
66.84	0.54	105.77	0.44			
68.86	100.00 O	106.80	0.88			
69.83	1.66 F	107.80	0.50			
70.85	1.21 F	108.80	2.77			
71.87	0.44	110.78	0.83			
72.85	15.12					
73.84	0.97					

5. 3,3,4,5,5,5-Hexafluoroheptan-4-one



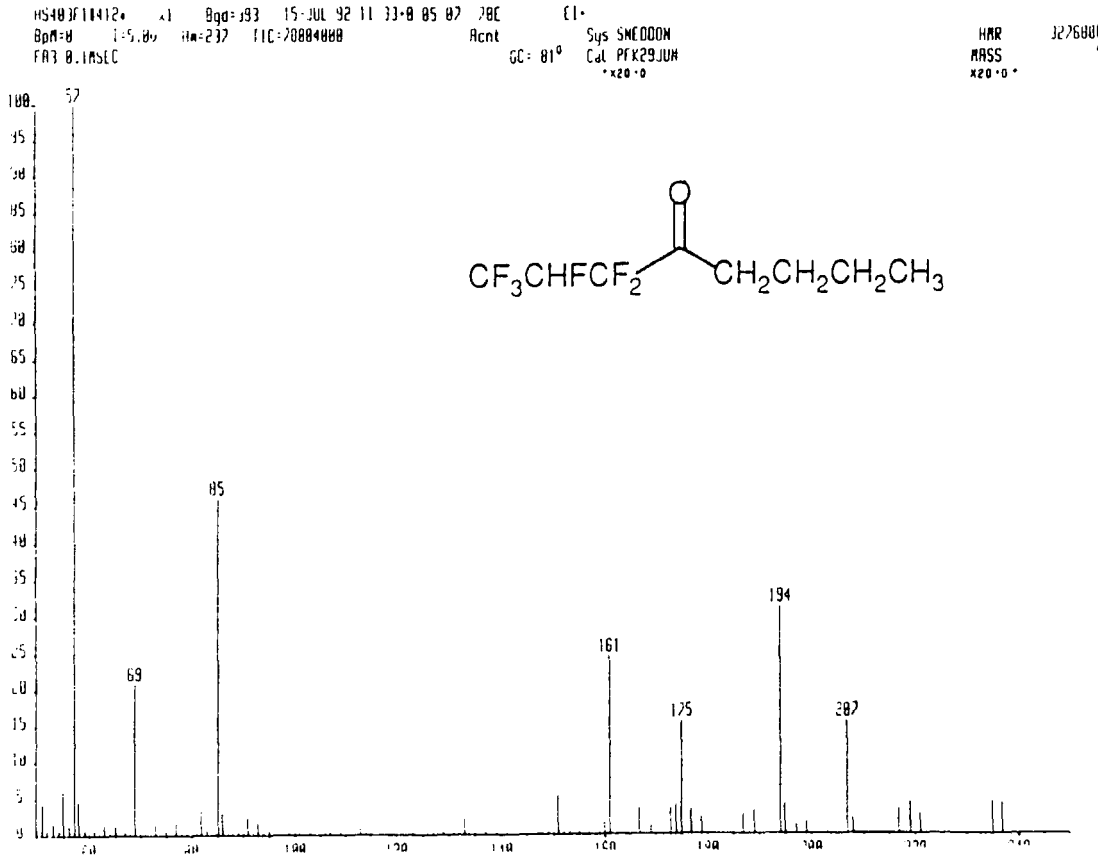
Mass	% Base								
50	99	1	58	97	00	1	37	206	98	0	77
51	01	1	59	98	99	1	38	207	99	1	40
54	01	1	37	99	98	0	35	221	00	1	55
55	01	3	23	100	98	0	55	223	00	1	38
56	01	0	33	103	02	0	79				
57	01	0	59	104	99	1	37				
59	02	2	75	109	00	1	17				
62	99	1	38	112	97	2	26				
64	00	1	53	115	01	2	80				
65	01	2	92	121	01	0	35				
66	99	0	60	124	99	1	42				
68	00	1	42	126	99	0	52				
68	98	33	73	130	96	1	42				
70	00	0	37	132	98	8	11				
70	61	1	39	F 135	01	1	19				
71	03	100	00	FD 137	00	0	38				
72	04	4	53	139	00	0	32				
73	03	1	45	140	97	1	75				
74	99	0	68	143	02	1	44				
75	99	1	41	150	97	11	91				
77	00	2	89	151	98	0	34				
79	02	0	53	155	00	0	69				
81	00	1	38	158	98	1	40				
81	99	4	16	160	97	4	12				
85	03	1	53	162	00	1	43				
89	01	1	50	166	97	1	47				
90	00	1	38	173	97	0	41				
90	99	2	08	174	99	1	42				
92	99	3	55	178	98	1	38				
94	99	1	41	193	97	1	47				

6. 3,3,5,5,5-Pentafluoroheptan-4-one

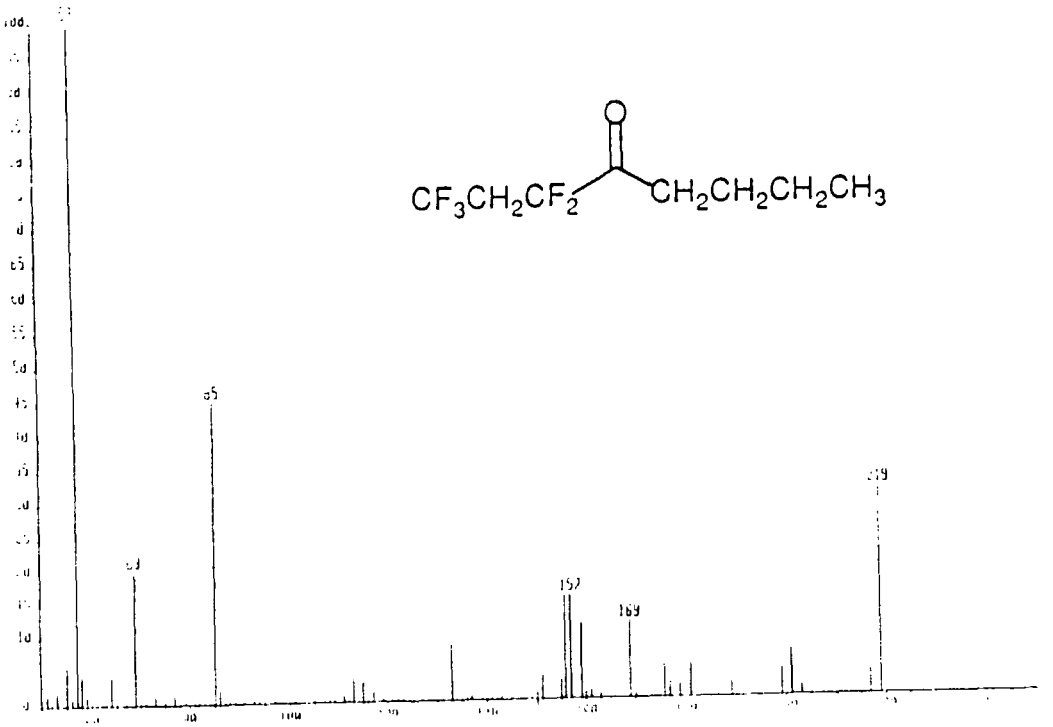


Mass	% Base		Mass	% Base		Mass	% Base
40 95	100 00	FO	154 76	0 87		202 70	1 32
41 91	33 99	F	155 15	0 02		203 71	0 14
42 97	100 00	FO	155 73	6 25		204 71	2 45
43 94	36 01	F	156 74	0 52		205 72	0 20
44 90	23 09		157 74	0 03		206 72	0 05
46 91	10 73		158 71	0 03			
50 88	9 97		160 70	0 62			
54 89	11 51		161 70	0 05			
58 89	8 72		162 74	0 23			
63 86	26 29		163 74	0 08			
64 87	5 14		164 75	0 50			
68 84	100 00	FO	165 49	0 03			
70 93	100 00	FO	165 76	0 07			
71 88	24 61	F	166 73	0 14			
72 86	11 50		167 68	0 03			
76 84	10 16		168 72	2 47			
94 81	6 10		169 72	0 20			
96 83	6 47		170 68	0 03			
102 82	9 02		170 79	0 03			
107 79	5 82		175 71	1 17			
112 77	14 84		176 71	0 09			
114 78	30 07	F	182 72	0 19			
116 81	8 81		183 74	0 07			
122 77	12 75		184 74	0 31			
132 75	67 61	F	185 70	0 03			
142 74	12 61		186 74	0 16			
150 79	0 07		188 70	1 26			
151 03	0 03		189 72	0 08			
151 12	0 03		190 68	0 03			
151 17	0 03						
151 27	0 02						

7. 3,3,4,5,5,5-Hexafluorooctan-4-one



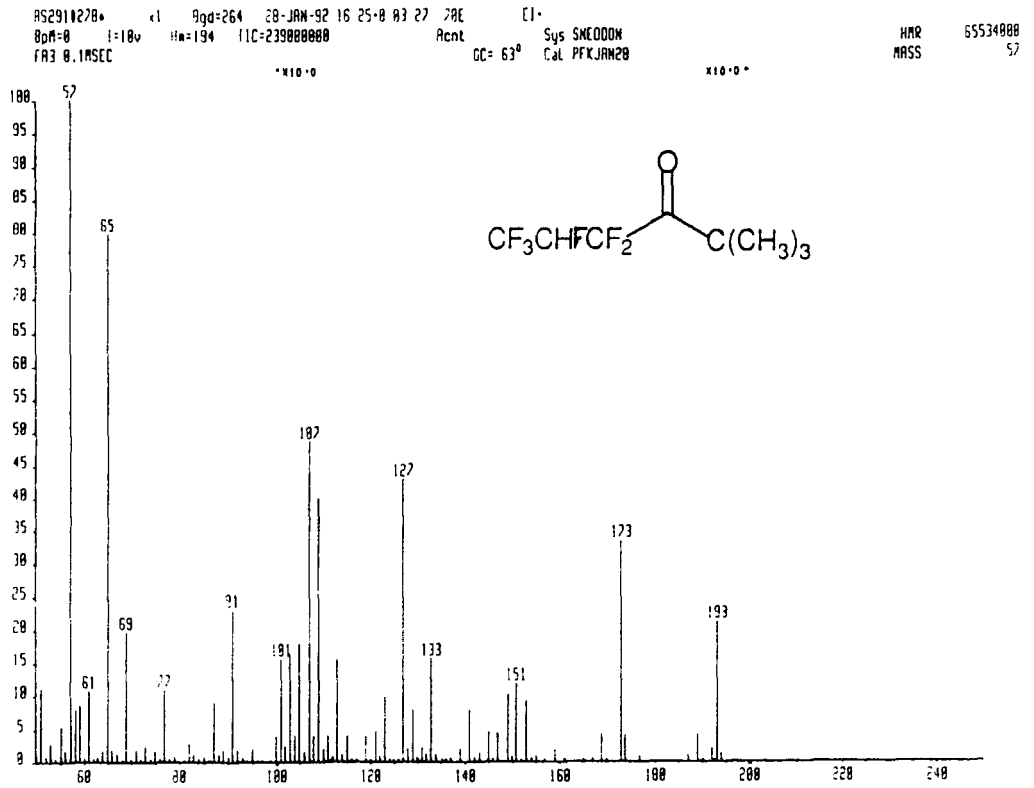
8. 3,3,5,5,5-Pentafluorooctan-4-one



Mass	Base
39 05	1 33
41 07	1 59
42 07	3 10
43 02	3 85
44 02	3 29
45 03	3 38
46 03	3 04
47 06	1 54
48 04	1 84
49 04	1 24
50 04	1 29
51 05	3 37
52 06	1 14
53 08	0 11
54 10	3 35
55 03	8 46
56 03	3 22
57 06	2 13
58 03	3 22
59 04	3 27
60 04	3 27
61 04	3 27
62 05	3 27
63 01	3 27
64 02	3 27
65 03	3 27
67 05	3 27
68 03	3 27
69 00	20 00
70 02	3 25
71 04	3 16
72 05	3 05
73 03	1 65
74 01	3 37
75 01	3 27
76 02	3 07
77 03	1 54
78 03	3 08
79 06	0 11
81 06	3 09
82 01	3 23
83 04	3 58
84 05	3 11
84 58	3 05
84 66	3 05
84 77	3 04
85 07	45 00
86 07	2 35
87 07	0 58
88 04	3 21
89 04	3 21
90 05	3 05
91 05	3 79
93 03	0 27
94 02	3 28
95 03	3 27
97 06	3 27
98 07	3 06
99 01	3 05
99 04	3 06
101 03	3 27
102 05	3 06
103 05	1 15
105 06	3 10
107 03	3 27

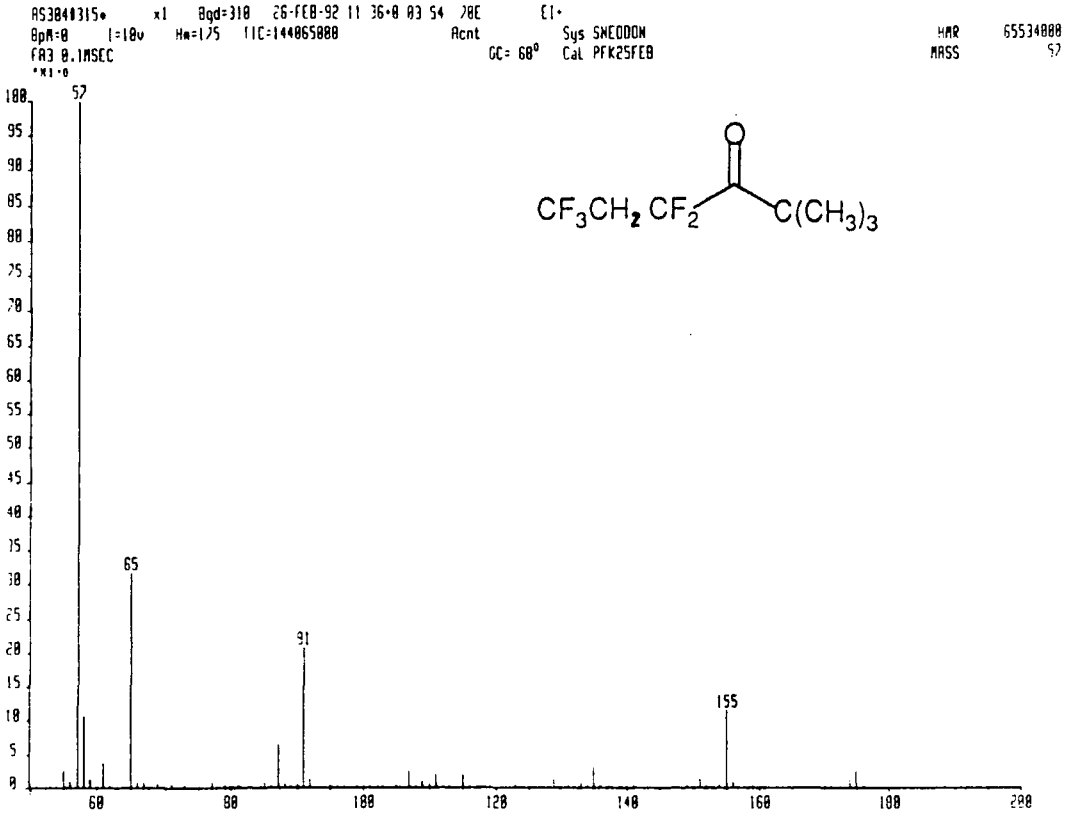
Mass	Base
109 05	1 33
111 07	1 59
112 07	3 10
113 02	3 85
114 02	3 29
115 03	3 38
116 03	3 04
117 06	1 54
119 04	1 84
121 04	1 24
122 04	1 29
123 04	3 37
127 05	3 27
129 06	1 14
131 08	0 11
132 10	3 35
133 07	8 46
134 03	3 22
135 06	2 13
136 03	3 22
137 04	3 27
139 06	3 21
140 05	3 05
141 04	1 77
142 03	3 27
143 03	3 27
149 04	3 27
150 05	3 08
151 09	3 18
155 05	3 17
156 03	3 27
157 04	3 27
159 07	3 56
160 08	3 06
161 06	3 07
163 05	3 04
169 07	3 56
170 08	3 07
176 06	3 26
177 07	3 13
179 11	3 10
181 10	3 25
189 06	3 13
199 09	3 23
201 09	3 36
203 06	3 07
217 08	3 19
219 12	1 54
220 14	3 08

9. 4,4,5,6,6,6-Hexafluoro-2,2-dimethylhexan-3-one



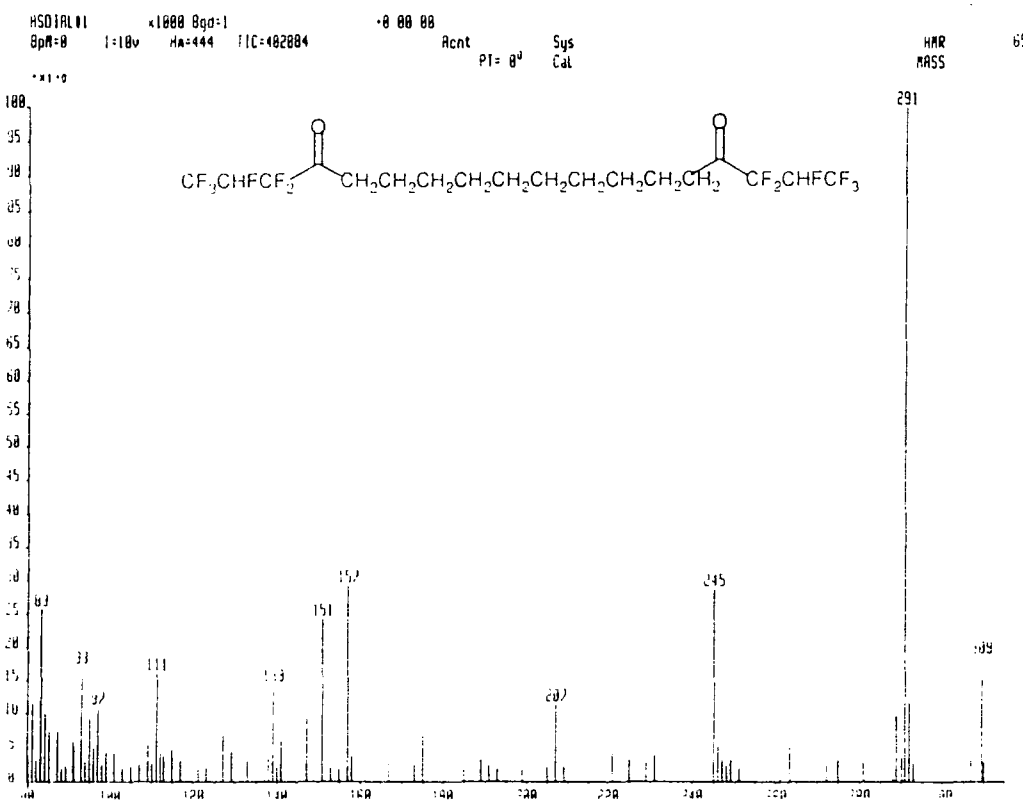
Mass	% Base						
48 06	1 22	84 08	0 39	145 09	0 45		
50 04	1 17	85 09	0 91	147 11	0 42		
51 04	11 08	87 11	8 98	149 15	1 02		
52 06	0 78	88 10	1 17	151 08	1 18		
53 07	2 73	89 07	1 95	153 12	0 93		
54 08	0 39	90 08	0 78	169 15	0 42		
55 09	5 24	91 09	23 06	173 14	3 32		
56 09	1 56 F	92 10	1 76	174 14	0 39		
57 14	100 00 FO	93 06	0 39	189 18	0 41		
58 11	7 82	95 07	1 95	193 16	2 11		
59 07	8 60	100 05	0 39				
60 08	0 48	101 07	1 56				
61 09	10 86	103 10	1 61				
62 08	0 41	104 10	0 39				
63 05	0 78	105 11	1 81				
64 05	1 56 F	107 13	4 86				
65 06	79 76 F	108 12	0 39				
66 07	1 69	109 09	4 01				
67 10	1 17	111 11	0 39				
69 04	19 78	113 07	1 56				
70 06	0 51	115 10	0 39				
71 06	1 76	119 09	0 39				
72 08	0 39	121 11	0 47				
73 09	2 34	123 13	0 99				
74 09	0 39	127 10	4 30				
75 05	1 56	129 12	0 78				
76 06	0 39	133 11	1 56				
77 07	10 94	141 12	0 78				
78 07	0 47						
79 08	0 78						
82 05	2 74						
83 07	1 17						

10. 4,4,6,6,6-Pentafluoro-2,2-dimethylhexan-3-one



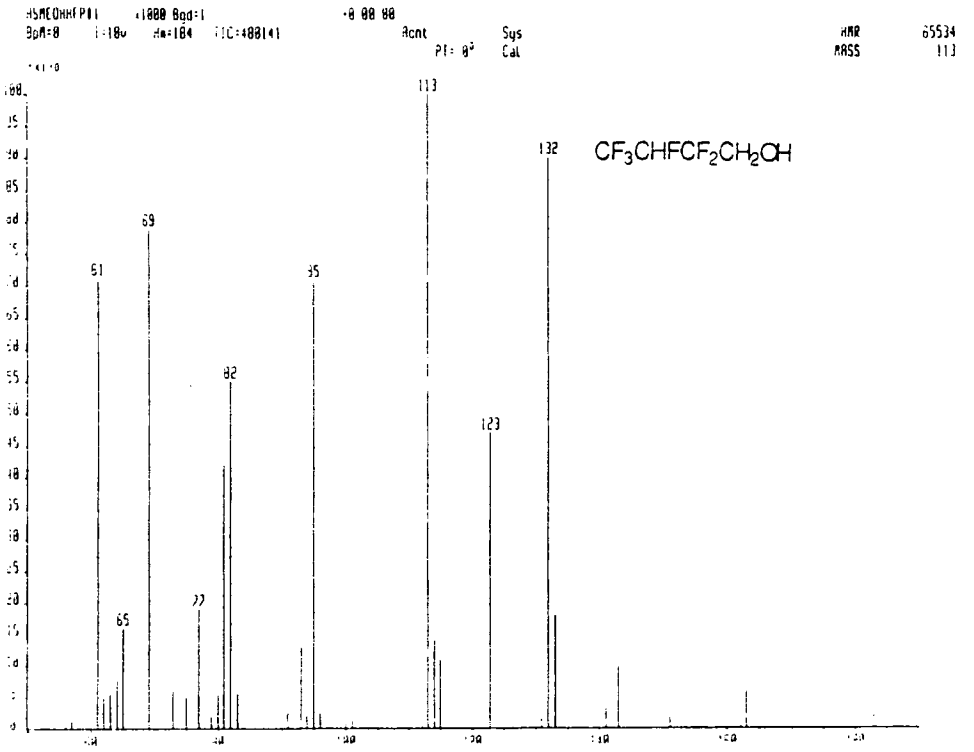
Mass	% Base		Mass	% Base
48.00	0.39		105.00	0.39
55.02	2.44		107.01	2.34
56.02	0.90	F	108.97	0.81
57.06	100.00	FO	109.97	0.46
58.04	10.55		110.98	1.95
59.00	1.17		114.97	1.95
61.01	3.62		122.98	0.40
64.98	31.64		128.97	1.17
65.98	0.78		131.00	0.39
67.01	0.78		132.94	0.78
68.96	0.42		134.97	3.13
70.99	0.40		151.00	1.17
76.97	0.78		153.95	0.39
84.99	0.78		154.95	11.33
87.00	6.25		155.96	0.80
88.01	0.39		171.00	0.39
89.97	0.39		173.97	1.17
90.97	20.71		174.97	2.34
91.98	1.17			
94.96	0.39			

11. 1,1,1,2,3,3,16,16,17,18,18,18-dodecafluorooctadecane-4,15- dione



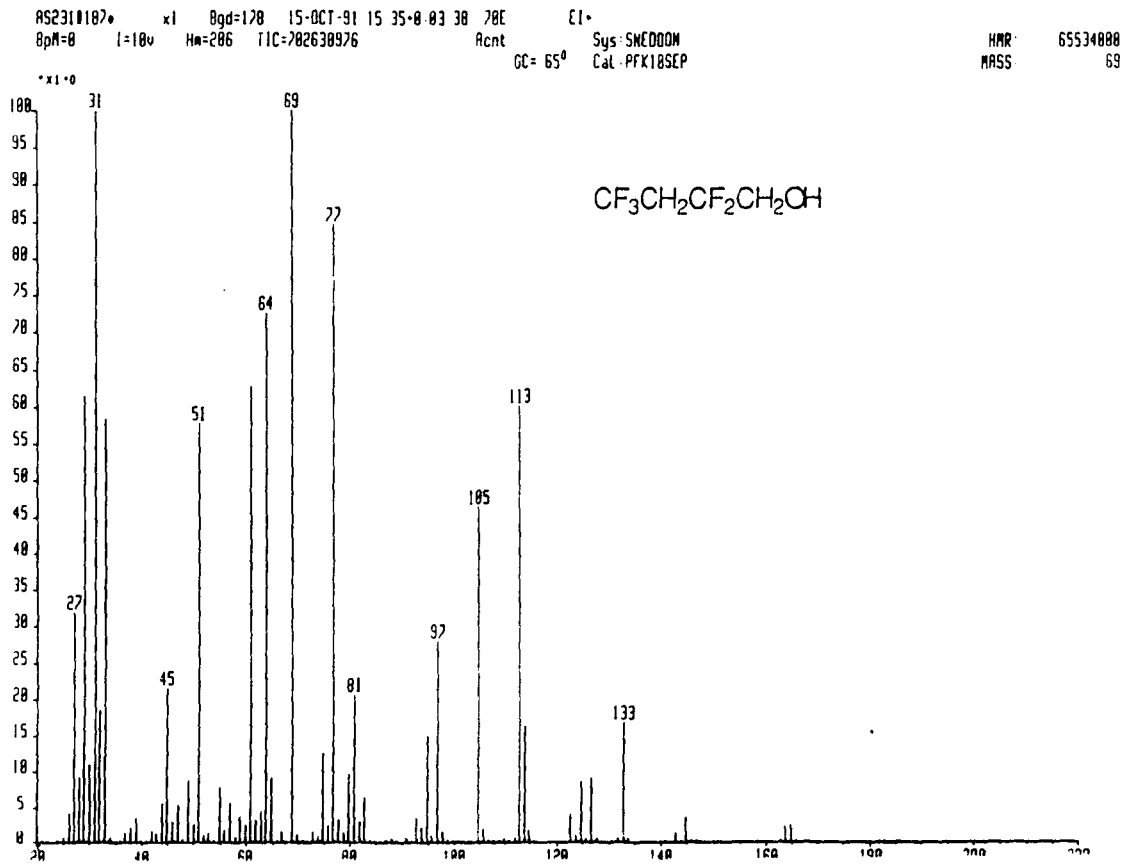
mass	Base						
80 [illegible]	3 50	117 04	3 19	225 02	2 92		
81 [illegible]	7 95	121 08	2 56	225 06	3 45		
81 06	11 78	123 07	2 67	229 02	2 96		
82 05	3 72	127 04	7 01	231 00	4 39		
83 06	25 66	129 07	4 72	245 03	28 76		
84 04	10 01	133 03	3 15	246 02	5 21		
84 09	2 25	137 05	3 93	247 01	3 38		
85 04	7 30	138 07	3 80	248 01	2 39		
87 04	7 40	139 06	14 40	249 02	3 41		
88 03	2 10	140 07	1 78	251 01	2 07		
89 02	2 40	141 08	6 15	261 03	3 55		
90 99	5 93	147 06	3 65	263 33	5 58		
91 05	4 97	150 99	24 20	272 04	2 42		
93 05	17 13	153 06	2 10	274 97	3 16		
94 05	3 23	155 00	2 10	281 01	2 96		
95 05	9 46	157 07	29 40	288 04	2 42		
96 05	5 18	158 08	3 95	289 01	10 94		
97 06	10 99	167 02	2 82	290 03	3 48		
98 06	2 60	173 02	2 69	291 01	100 00		
99 05	4 16	175 07	1 09	292 03	12 31		
101 04	4 16	185 04	2 29	293 01	2 59		
103 03	2 01	189 01	3 46	307 00	5 43		
105 05	2 30	191 01	2 53	309 32	18 52		
107 06	3 28	193 01	2 05	310 04	3 05		
109 06	5 63	199 02	2 07	443 04	2 02		
110 06	2 94	205 01	2 52				
111 07	16 07	207 01	11 46				
112 07	4 61	209 01	2 29				
113 01	3 92	221 00	5 99				
113 06	3 13						
115 06	2 [illegible]						

12. 2.2.3.4.4.4-Hexafluorobutanol



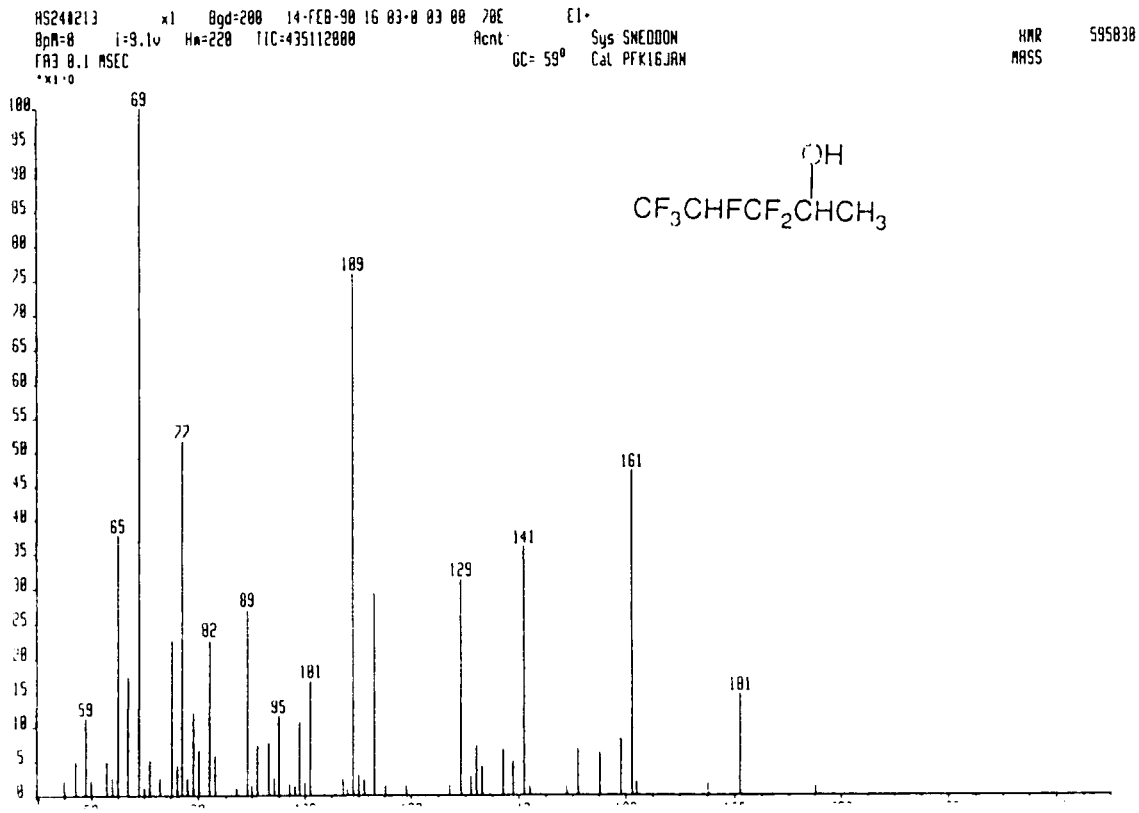
Mass	% Base		
52.00	0.84	96.07	2.54
53.01	0.58	97.05	0.84
56.01	1.03	100.05	1.28
57.02	1.68	101.05	2.66
60.01	0.96	111.06	0.82
61.02	71.26	112.04	1.07
62.03	4.95	113.05	100.00
63.02	5.77	114.06	14.03
64.03	8.36	115.07	10.86
65.04	16.39	116.07	0.44
67.02	0.47	123.04	47.07
69.02	79.34	124.05	0.77
73.04	5.77	131.04	1.63
74.04	0.72	132.04	89.70
75.04	5.04	133.05	17.86
77.05	18.61	134.04	0.77
79.04	2.15	141.05	3.36
80.04	5.65	143.06	10.11
81.05	41.61	145.05	0.44
82.04	54.91	151.06	1.66
83.04	5.46	162.09	1.45
88.06	0.58	163.08	6.05
91.04	3.06	183.09	3.60
93.05	13.17		
94.06	1.66		
95.06	71.21		

13. 2,2,4,4,4-Pentafluorobutanol



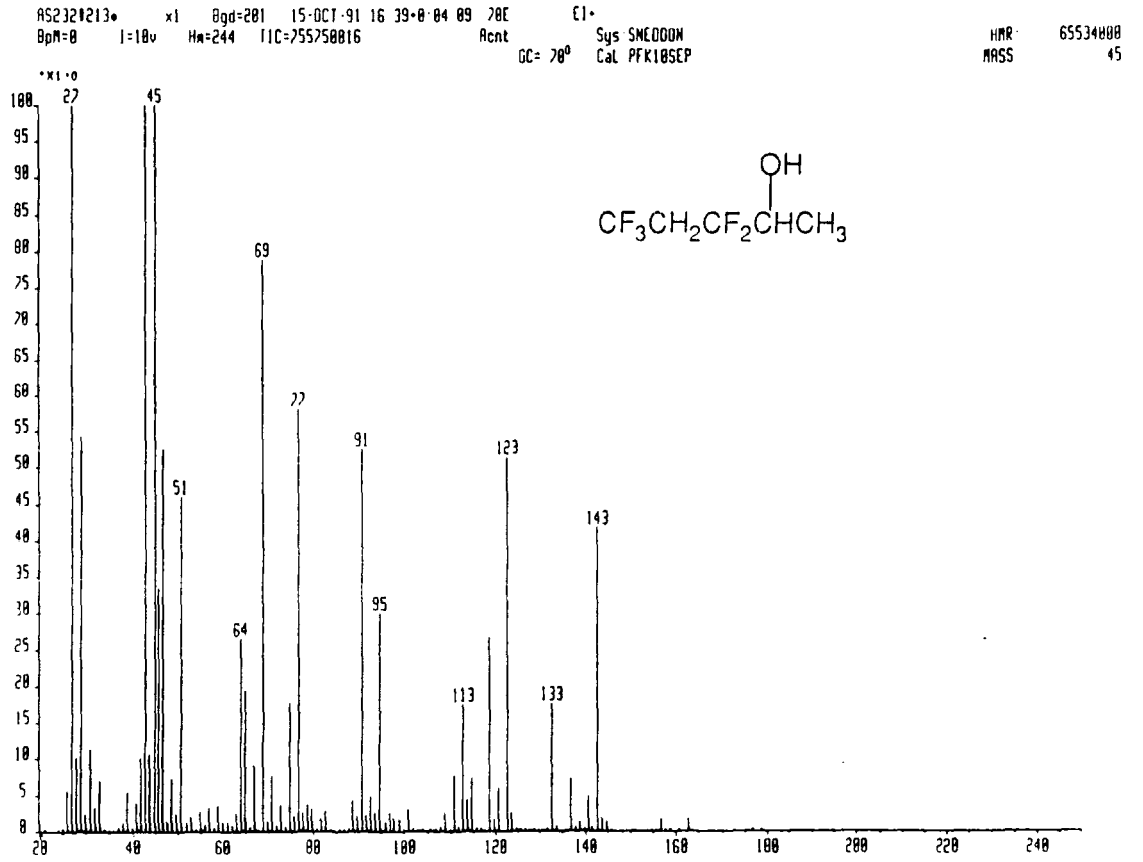
Mass	% Base
24.94	0 53
25 94	4 06
26 95	32.02
27 94	9 20
28.92	61 42
29 93	10 94 F
30 96	100 00 FO
31.93	18 65
32.93	58 40
33.93	0 61
36 91	1.25
37.92	2.05
38.92	3 55
41 91	1 44
42.91	1 17
43 90	5 58
44 90	21.61
45 91	2 78
46.91	5 31
48.89	8 75
49 88	2 42
50.88	57 82
51.89	0 87
52.89	1 17
54.89	7 72
55.88	1 60 F
56.88	5 48 F
57 89	0 57
58.90	3 52
59 87	2 40 F
60 87	62 77 F
61 86	3 13
62.86	4 36
63 87	72 66
64 88	8 99
66 85	1 47
68 85	100 00 0
69.85	1 03
72 85	1 27
73 84	0.78
74 85	12 53 F
75 85	2.34 F
76 85	84 61 F
77 85	3.03
78.83	1 29
79 83	9.58
80 84	20 75
81.83	2.79
82.84	6.32
87 95	0 39
90 81	0 59
92.81	3 42
93 81	1 99
94 82	15.03
95 83	0 80 F
96.82	28.08 F
97 82	1 46
104 80	46 39
105 81	1 96
106 80	0 33
109 78	0 48
111.80	0 78 F
112.77	60.16 F
113.79	16 41 F
114 79	1 56
122.77	3.91
123.78	0.87
124 79	8 68
125.79	0 48
126.78	9.17
127.78	0 48
131.74	0 56
132.76	16.98
133.76	0.51
142.75	1.31
144 76	3 53
163.74	2.23
164 74	2.37

14. 3,3,4,5,5,5-Hexafluoropentan-2-ol



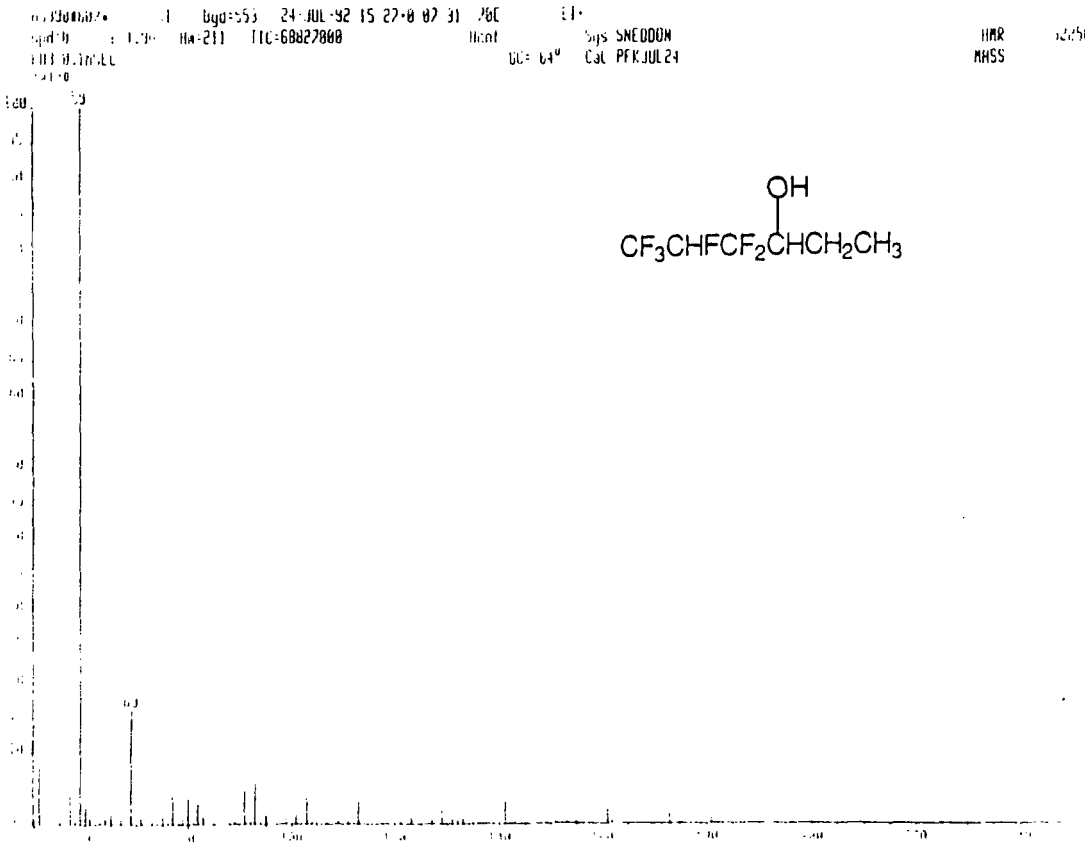
Mass	% Base						
55.09	3.01	100.17	1.88	129.18	22.88		
56.09	1.73	101.17	13.38	130.19	0.51		
57.10	6.13	102.18	0.50	131.19	2.46		
59.12	10.76	104.19	0.13	132.19	4.96		
60.10	2.55	105.20	0.17	133.20	2.01		
63.11	7.38	106.18	0.31	137.23	4.39		
64.12	3.66	107.21	1.94	137.68	0.05		
65.13	30.14	108.20	1.08	138.23	0.11		
67.11	15.38	108.73	0.08	139.22	2.76		
69.11	100.00	109.21	64.24	140.24	0.15		
70.13	1.29	110.21	2.26	141.21	22.26		
71.14	3.98	111.20	1.58	142.22	1.17		
73.14	2.35	112.19	0.46	143.24	0.21		
75.15	19.15	113.19	25.39	143.42	0.05		
76.16	3.54	114.19	0.83	143.56	0.16		
77.15	42.78	115.20	1.17	143.70	0.04		
78.16	2.10	116.21	0.04	145.26	0.09		
79.14	7.99	117.19	0.48	149.23	1.15		
80.15	7.17	119.18	1.17	150.22	0.21		
81.14	1.07	122.96	0.07	151.23	5.27		
82.14	20.98	123.53	0.07	152.23	0.15		
83.15	3.93	123.64	0.08	155.24	3.58		
89.17	21.27	123.83	0.04	156.26	0.22		
90.18	1.56	123.99	0.06	157.26	0.82		
91.17	2.24	124.18	0.10	158.25	0.06		
93.17	3.61	124.42	0.05	159.26	2.36		
94.18	3.07	125.20	0.20	160.26	0.11		
95.18	9.49	126.20	0.11	161.24	24.57		
97.19	1.17	127.21	0.91	162.25	0.85		
99.17	6.03	128.16	0.05	163.25	0.46		
				175.26	1.05		
				177.32	0.08		
				178.32	0.04		
				181.26	8.77		
				182.27	0.47		
				195.30	0.88		

15. 3,3,5,5,5-Pentafluoropentan-2-ol



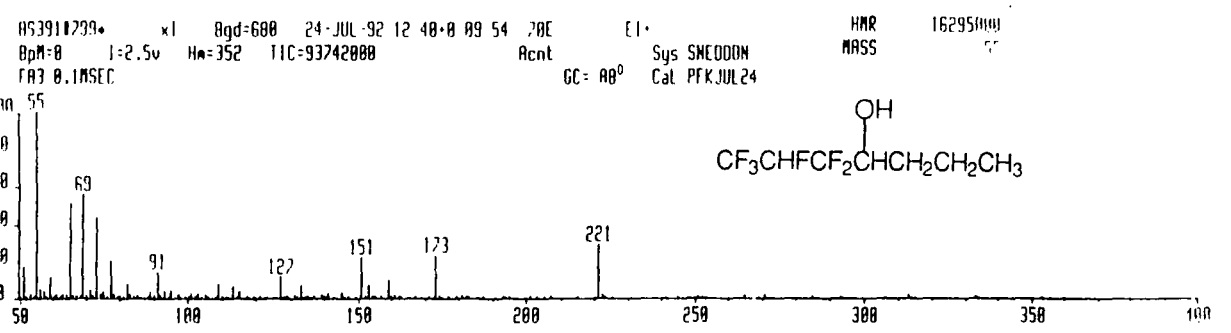
Mass	% Base								
40 92	3 74		73 84	0 51	F	118 77	26 61		
41 89	3 99	F	74 84	17 72	F	119 78	1 56		
42 89	100 00	FO	75 83	2 03	F	120 77	9 99	F	
43 89	10 56	F	76 83	57 93	F	122 74	51 27	F	
44 94	100 00	FO	77 84	2 45		123 76	2 46		
45 91	33 40	F	78 82	3 67		131 70	0 31		
46 90	52 57		79 82	3 01		132 73	17 50		
47 90	1 29		81 81	1 56		133 73	0 62		
48 88	7 23		82 82	2 77		136 75	7 04		
49 88	2 37		87 81	0 43		137 75	0 47		
50 87	46 00		88 82	4 20		138 75	1 17		
51 88	0 96		89 81	2 05	F	140 75	4 69	F	
52 89	1 98		90 82	52 39	F	141 67	0 47	F	
54 88	2 61		91 83	2 17		142 72	41 56	F	
55 87	0 84		92 80	4 62		143 72	1 81		
56 87	3 19		93 80	2 48	F	144 72	1 17		
57 88	0 45		94 79	29 94	F	156 72	1 56		
58 88	3 53		95 80	1 23		158 73	0 36		
59 86	1 17		96 81	2 50		162 71	1 56		
60 88	1 20		97 78	1 68					
61 86	0 79		98 79	1 64					
62 85	2 54		100 80	3 13					
63 85	26 48		107 78	0 55					
64 86	19 23		108 79	2 42					
65 86	0 42		110 77	7 57					
66 84	3 98		111 77	0 53	F				
68 82	78 81	F	112 76	17 39	F				
69 84	1 36	F	113 76	4 30					
70 86	7 42		114 77	7 08					
71 86	0 78								
72 85	3 45	F							

16. 4,4,5,6,6,6-Hexafluorohexan-3-ol

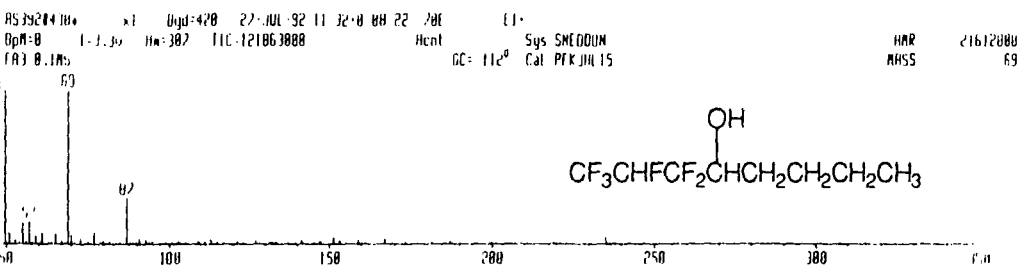


Mass	% Base				
49 00	4 00	95 02	1 35		
50 00	1 43	99 02	2 85		
51 00	3 48	101 02	1 81		
53 03	2 82	103 05	3 96		
55 02	1 59	109 04	2 66		
56 02	2 36	113 01	3 50		
57 03	5 61	121 04	2 52		
58 04	2 89	123 05	1 07		
59 05	100 00	127 02	2 75		
60 04	3 17	129 00	1 19		
61 04	2 28	131 01	2 83		
62 02	2 38	132 11	1 [illegible]		
63 01	2 96	133 03	2 89		
64 02	2 80	141 00	3 81		
65 02	1 83	151 12	1 15		
67 00	1 10	153 05	2 34		
69 00	18 26	161 01	1 [illegible]		
71 03	1 35	162 03	1 [illegible]		
73 03	2 89	173 05	1 [illegible]		
75 01	1 19	181 02	2 19		
77 02	1 11				
79 01	1 88				
80 01	2 74				
82 11	3 26				
83 03	2 99				
89 03	1 34				
91 03	1 36				
92 03	1 04				

17. 1,1,1,2,3,3-Hexafluoroheptan-4-ol

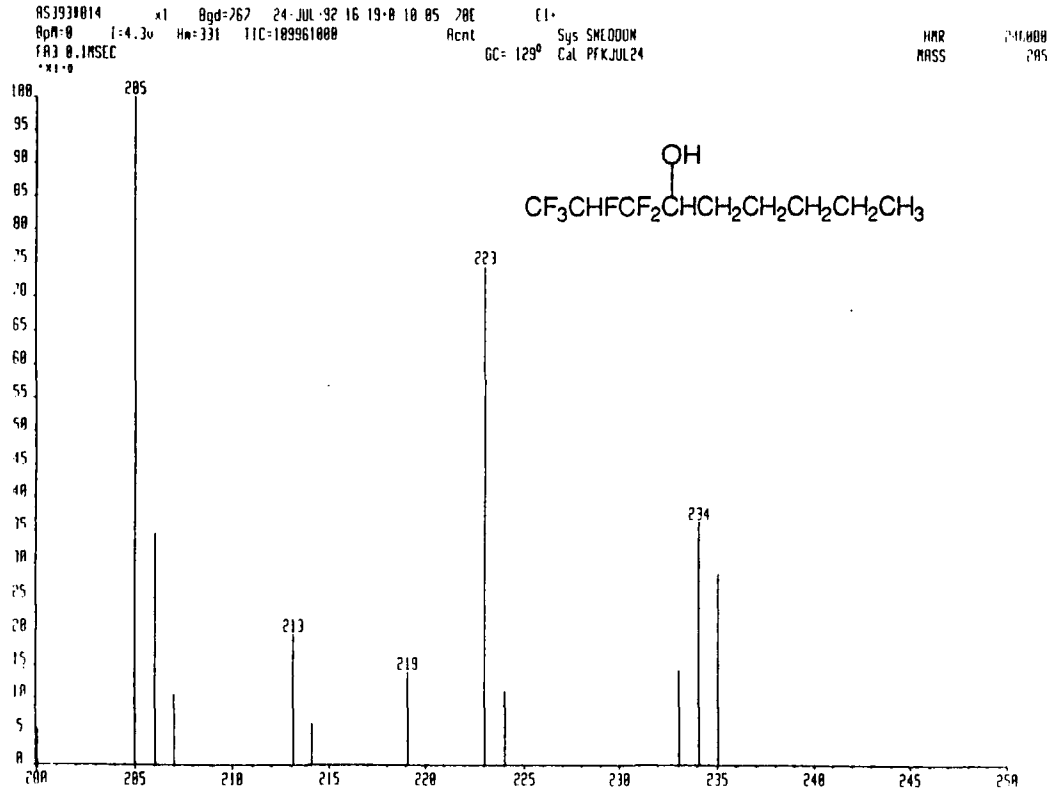


18. 1,1,1,2,3,3-Hexafluorooctan-4-ol



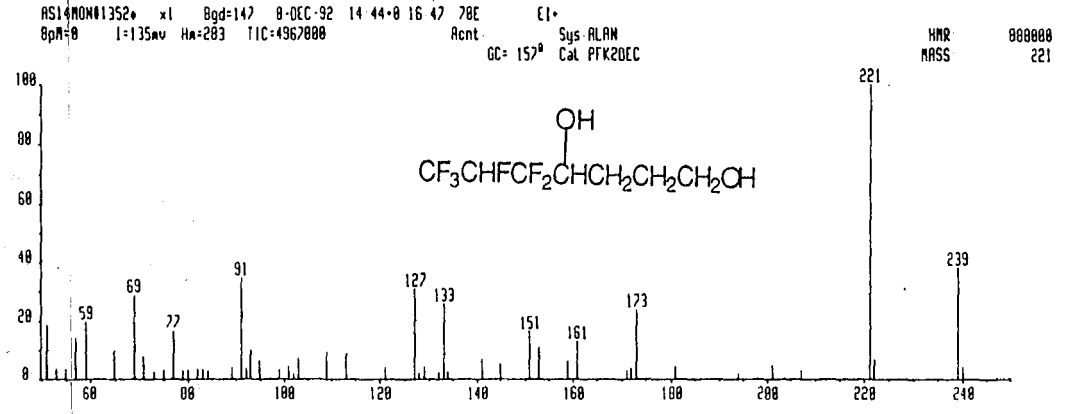
Mass	% Base	Mass	% Base
41 01	77 77	133 18	0 77
42 02	34 52	137 18	4 34
43 02	25 51	139 18	3 55
44 01	3 23	141 17	3 17
45 02	10 91	145 18	0 61
46 02	0 38	147 21	1 05
47 02	3 65	151 17	3 56
49 01	1 36	153 20	1 62
50 02	0 49	155 20	0 31
51 02	7 51	157 19	0 32
52 04	0 44	159 20	2 85
53 06	2 67	161 19	0 96
54 07	0 53	167 23	2 95
55 05	13 31	173 24	1 29
56 08	1 38	181 26	0 64
57 09	14 64	187 27	2 03
58 09	1 19	219 31	0 45
59 07	4 84	221 31	0 41
60 07	0 47	235 33	4 60
61 09	7 20	236 34	0 44
63 06	0 67	287 44	0 37
64 07	0 81		
65 08	6 35		
67 11	1 64		
69 13	100 00		
70 14	5 64		
71 12	0 81		
73 12	3 59		
75 12	1 10		
77 11	7 94		
78 12	0 32		
79 12	0 88		
80 11	1 16		
82 11	2 39		
83 12	0 95		
85 15	0 44		
87 19	30 01		
88 19	1 71		
89 12	0 78		
90 14	0 57		
91 14	3 17		
92 15	0 31		
93 13	2 81		
94 13	0 37		
95 13	1 79		
97 16	0 69		
99 16	0 85		
101 13	1 12		
103 16	1 60		
105 17	0 50		
109 15	1 24		
111 16	0 72		
113 14	2 71		
115 16	0 94		
119 17	0 31		
121 17	1 20		
123 16	0 57		
127 17	1 70		
131 17	0 51		
22 15	41		

19. 1,1,1,2,3,3-Hexafluorononan-4-ol



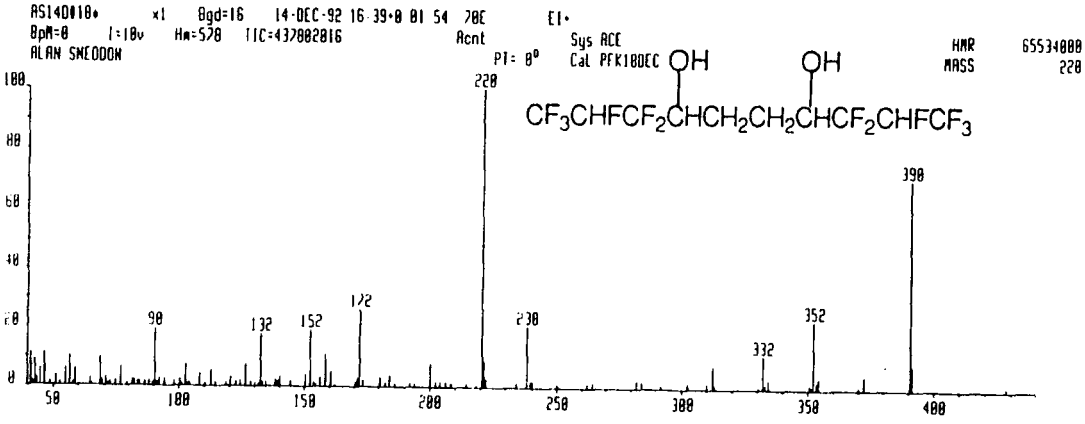
49 00	1 11	94 09	5 18	157 02	0 27
50 01	1 47	95 05	3 45	159 02	1 15
51 00	3 41	97 26	1 86	161 01	1 46
52 02	1 34	99 03	1 52	165 04	0 33
53 03	3 05	90 03	3 34	172 04	0 71
54 04	1 04	91 02	1 81	173 04	0 95
55 05	100 00	93 02	2 24	185 04	3 64
56 06	91 01	95 02	1 11	195 08	0 64
57 35	12 71	99 03	2 57	205 04	0 87
58 05	0 86	101 10	72 99	206 04	0 30
59 03	5 90	102 10	1 58	223 06	0 65
60 02	3 41	103 05	3 99	234 06	0 32
61 04	1 47	105 05	0 82		
63 01	3 37	109 03	3 81		
64 01	1 46	111 03	3 43		
65 02	2 49	113 01	1 82		
67 04	1 72	115 04	0 57		
68 26	3 45	117 05	3 37		
69 39	1 21	121 03	1 69		
69 07	1 30	123 05	54		
70 05	3 40	127 03	89		
71 07	3 09	132 02	1 47		
72 06	0 32	133 03	71		
73 04	3 47	135 05	29		
75 02	3 77	139 02	3 44		
77 02	4 64	141 00	2 27		
79 02	3 79	145 02	1 54		
80 01	1 55	151 01	1 52		
81 07	3 75	155 04	1 38		
82 01	1 59				
83 08	30 12				

20. 5,5,6,7,7,7-Hexafluoroheptane-1,4-diol



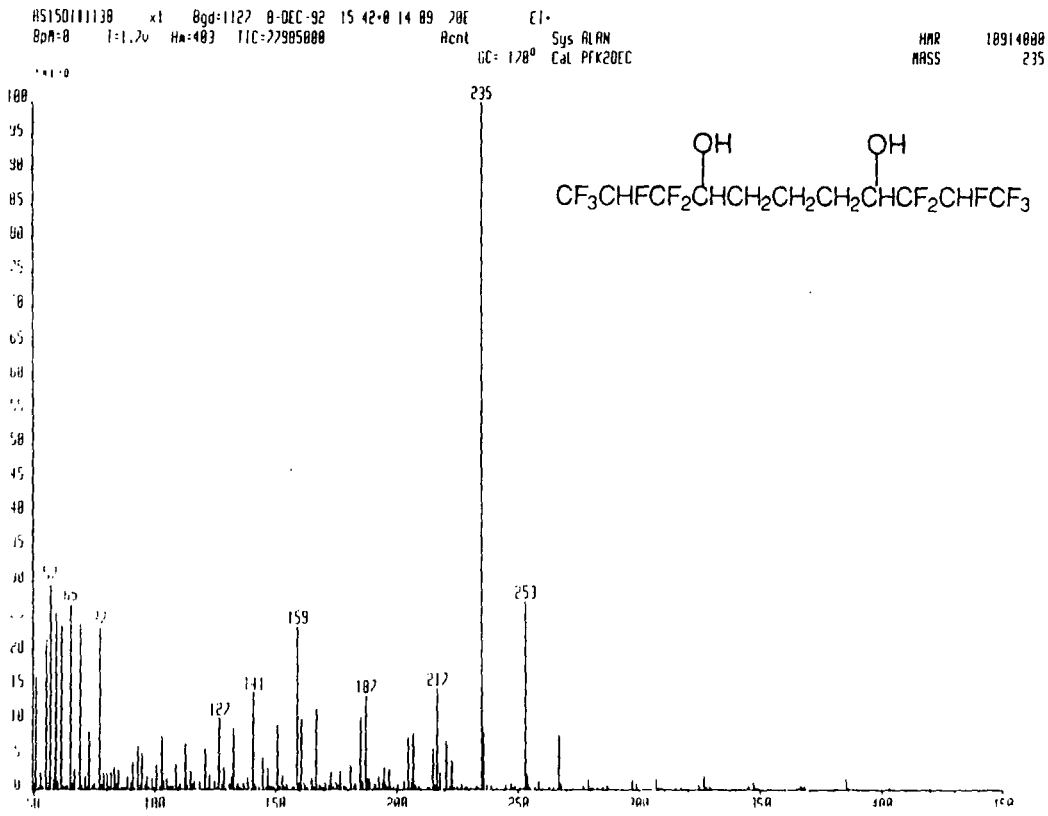
Mass	% Base
48 98	4 28
50 98	18 47
53 01	2 93
54 99	3 49
57 01	13 96
59.00	19 37
64 99	9 57
68.96	28 83
71 01	7 66
73 01	2 48
74 98	2 93
76 99	16.44
78.97	3 15
79 01	2 03
79 98	2 93
81 98	3 38
83 00	3 15
84 00	2 25
88 99	3 83
90 99	34 46
92 01	3 49
92 98	9 57
94 98	6 19
98 97	3 04
100 97	4 17
101 99	1 80
103 00	6 76
108 98	9 35
112 97	9 45
120 99	3 60
126 98	30 86
127 98	1 91
128.97	3 60
131.98	2 03
132.98	25 56
133.99	2 25
140 96	6 64
144 97	4 84
150 96	15 99
152.99	10 59
158 98	5 86
160 96	12.73
170 97	2 82
172.00	3 60
172 99	23 54
180 95	3 94
193 96	1 69
201 00	4 39
206 99	2 70
221 00	100 00
222 02	6 42
239 02	37 95
240 03	3 72

2i 1,1,1,2.3,3,8,8,9,10,10,10-Dodecafluorodecane-4,7-diol

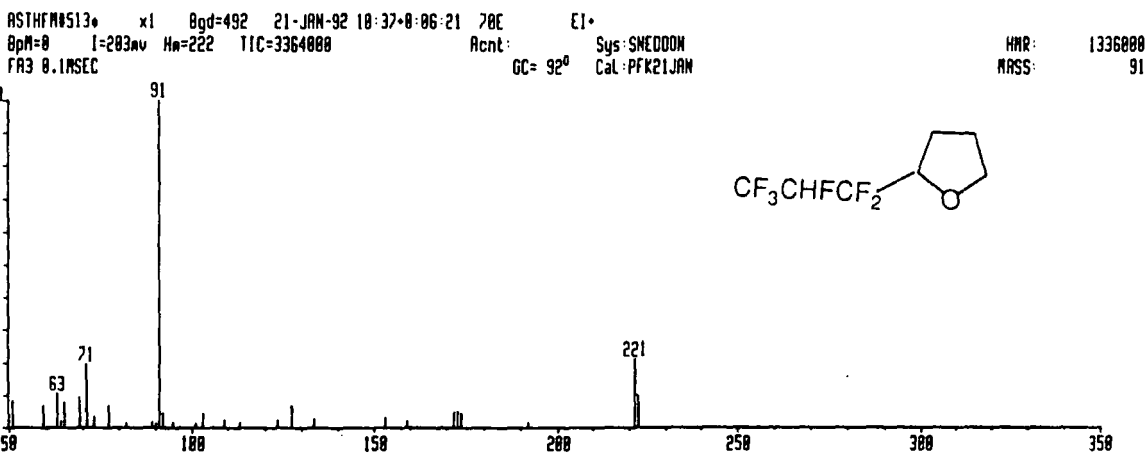


Mass	% Base		Mass	% Base	
40 69	11 05		152 27	18 71	
41 67	9 90		153 27	1 44	
42 66	8 40		154 26	0 83	
43 66	2 32		156 25	3 10	
44 66	5 42		158 25	10 67	
46 65	10 96		160 23	5 10	
48 61	1 10		162 24	0 79	
50 60	3 44		170 25	2 09	
52 62	0 99		171 24	2 65	
54 59	6 05		172 25	26 15	
56 59	9 77		173 24	2 03	
57 60	1 06		180 22	3 23	
58 58	5 46		182 22	1 04	
64 55	2 34		184 23	3 99	
68 46	9 64	F	186 21	1 17	
68 54	9 76	F	192 23	0 92	
69 54	1 56		194 21	0 99	
70 53	2 78		200 21	7 89	
71 53	0 79		202 21	1 61	
72 51	1 44		203 96	1 66	
74 50	2 01		206 20	1 75	
76 49	6 60		208 19	1 42	
79 46	0 99		214 19	1 05	
81 45	2 19		218 19	0 79	
82 47	1 66		220 19	100 00	0
83 48	1 32		221 20	8 59	
84 48	1 22		222 21	2 64	
86 46	1 44		234 19	1 55	
88 45	2 19		238 19	20 57	
89 45	1 18		239 20	1 63	
90 45	19 30		240 21	2 13	
91 45	0 86		250 18	0 94	
92 42	2 64		262 18	1 46	
94 41	2 48		264 17	1 88	
98 41	1 62		282 15	2 84	
100 40	2 36		284 15	1 90	
101 41	0 80		292 16	1 07	
102 41	7 15		302 17	1 57	
103 41	0 80		310 18	1 59	
104 39	0 98		312 16	7 67	F
108 38	4 15		313 21	1 00	F
110 36	1 06		330 19	0 91	
112 34	5 48		332 15	10 97	F
114 37	1 32		333 20	1 37	F
118 35	0 92		334 19	3 25	F
120 35	3 00		350 20	1 27	
122 35	1 20		351 18	0 90	F
124 33	1 57		352 18	22 89	F
126 32	7 11		353 20	2 49	F
128 30	1 22		354 18	3 75	F
130 31	1 07		370 24	1 00	
131 29	1 19		372 25	4 55	
132 31	17 56		390 25	70 99	F
133 32	1 21		391 28	7 93	F
134 52	1 31		428 35	0 90	
138 29	2 34				
139 30	1 62				
140 27	3 29				
144 27	1 62				
150 26	4 16				

22. 1,1,1,2,3,3,9,9,10,11,11,11-Dodecafluoroundecane-4,8-diol

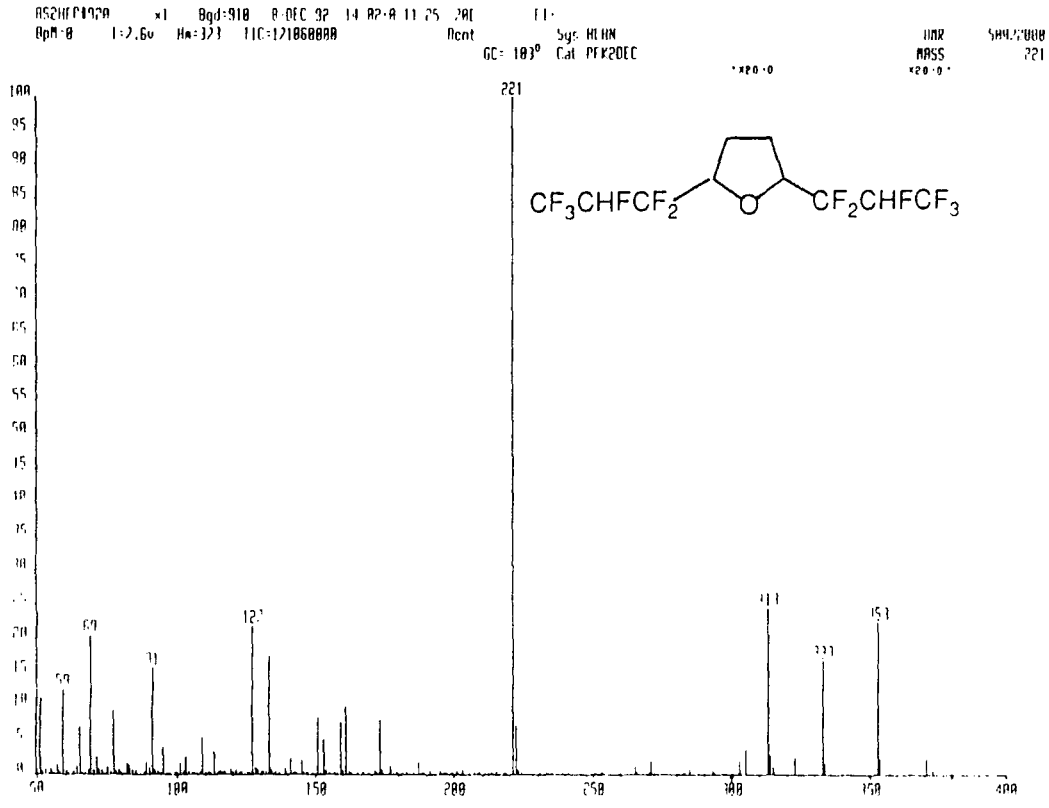


23. 2-(1,1,2,3,3,3-Hexafluoropropyl)oxolane



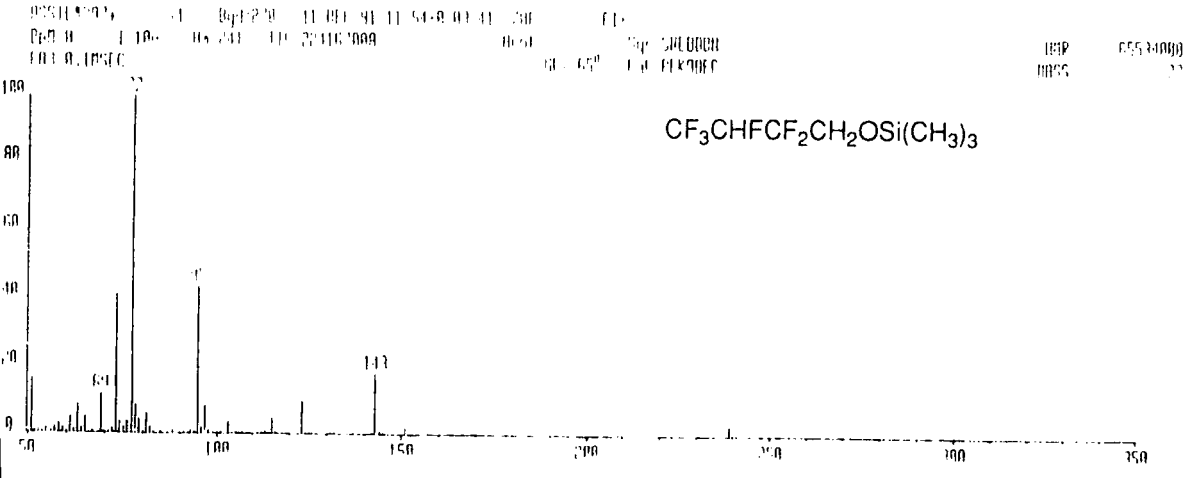
Mass	% Base
51.01	7.78
59.04	6.59
63.03	10.18
64.01	1.80
65.02	7.56
69.01	8.91
71.04	19.16
73.05	2.99
77.03	6.44
82.00	1.20
89.02	1.50
90.02	1.20
91.04	100.00
92.04	4.19
94.98	1.35
95.01	1.12
101.03	1.20
103.05	4.27
109.04	1.95
113.03	1.27
123.04	2.17
127.03	6.59
133.03	2.47
153.05	2.84
159.04	1.72
172.04	4.42
173.06	4.94
174.07	4.27
192.05	1.27
221.07	20.96
222.08	9.51

24. 2,5-Bis(1,1,2,3,3,3-hexafluoropropyl)oxolane

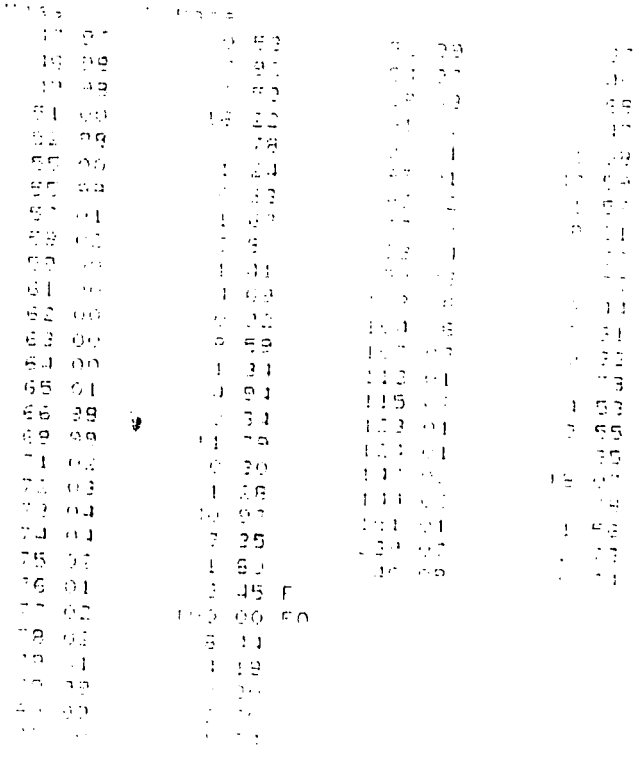


Mass	Base						
48 02	1 12	101 00	1 62	162 00	0 42		
48 99	0 39	102 01	0 36	171 01	0 47		
50 99	11 15	103 02	0 42	173 02	8 10		
53 03	0 68	104 03	0 39	174 02	0 58		
55 01	0 84	109 01	5 33	176 99	1 23		
57 00	1 24	110 99	0 30	179 00	0 36		
59 02	12 41	112 99	3 42	186 99	1 79		
60 02	0 48	115 01	0 49	191 02	0 41		
63 00	0 46	117 00	0 39	195 01	0 39		
64 00	1 11	119 01	0 77	201 02	0 45		
65 01	6 83	121 01	0 61	203 03	0 52		
68 01	0 51	123 02	0 32	209 01	0 32		
68 99	20 49	127 00	21 94	221 02	100 00	F	
70 01	0 63	128 00	0 86	222 03	7 06	F	
71 01	2 42	128 99	0 60	223 04	0 55		
72 02	0 69	130 99	0 48	245 02	0 33		
73 02	0 53	131 99	0 34	265 03	1 10		
74 99	1 03	133 00	17 33	271 03	1 83		
77 00	8 30	134 01	0 63	285 03	0 74		
78 99	0 61	135 36	0 35	293 03	0 59		
81 99	1 68	139 00	0 84	313 03	1 22		
83 01	1 22	140 99	0 39	333 04	0 83		
84 02	0 60	144 99	0 11	353 04	1 12		
85 03	0 47	150 99	8 44				
89 00	1 71	151 99	0 33				
90 01	0 90	153 01	5 14				
91 02	15 59	154 02	0 37				
92 02	0 65	159 00	0 97				
92 99	0 46	160 00	0 39				
94 99	0 89	160 99	9 93				

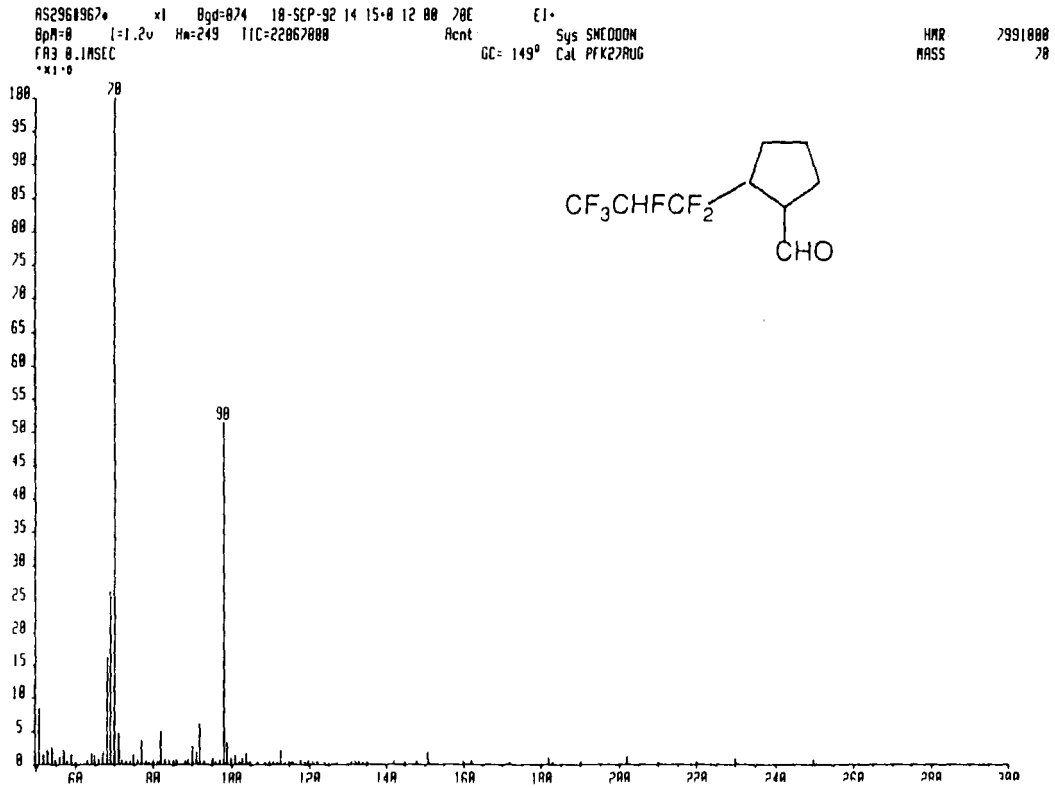
25. 2,2,3,4,4,4-Hexafluorobutoxytrimethylsilane



$CF_3CHFCF_2CH_2OSi(CH_3)_3$

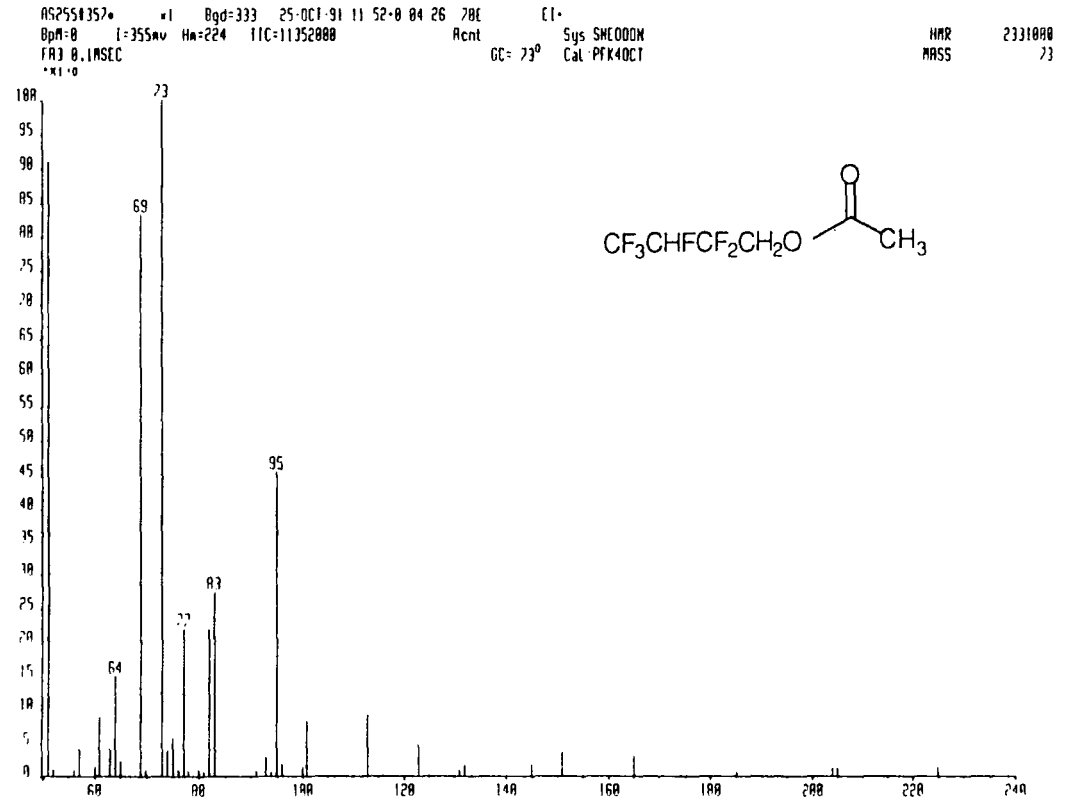


26. 2-(1,1,2,3,3,3-Hexafluoropropyl)pyrrolidine-1-carboxaldehyde



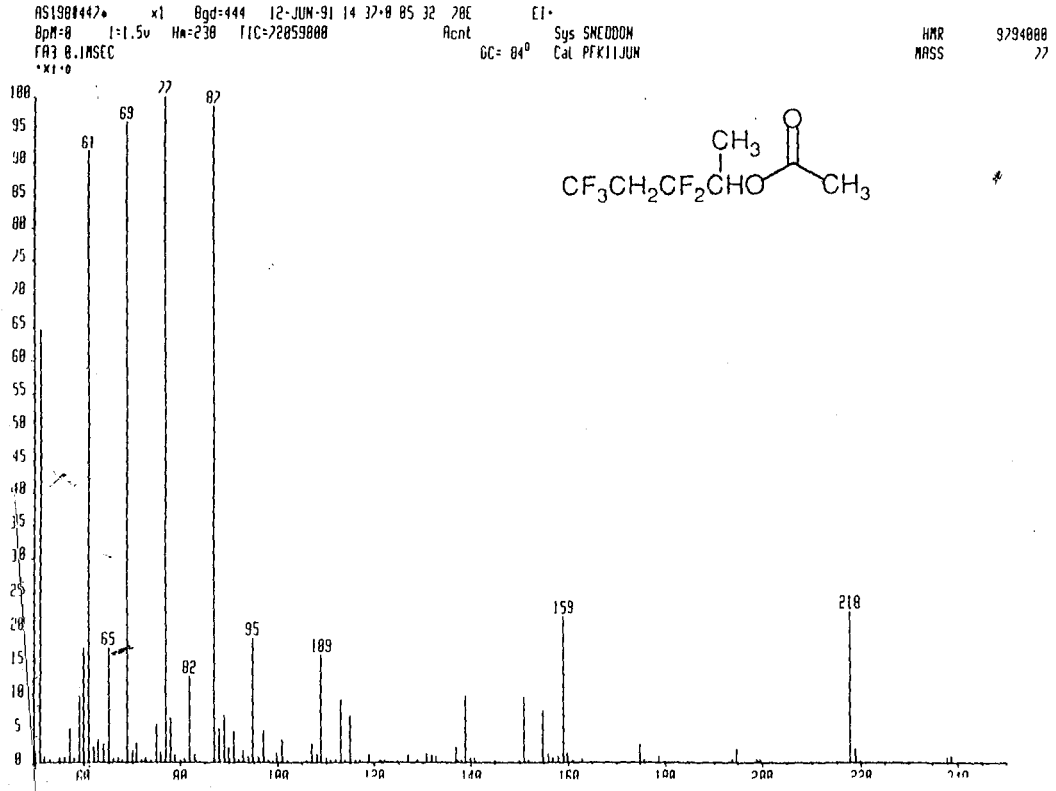
Mass	% Base					
49.93	0.79	82.92	0.76	133.90	0.30	
50.93	8.27	83.93	0.60	141.89	0.50	
51.94	1.44	84.94	0.53	147.92	0.40	
52.96	2.08	85.94	0.76	150.84	1.86	
53.96	2.44	87.92	0.43	159.87	0.56	
54.97	0.73	88.92	0.68	161.90	0.39	
55.94	1.03	89.92	2.60	171.86	0.31	
56.93	2.10	90.93	1.81	181.91	1.01	
57.94	0.39	91.93	6.02	189.88	0.38	
58.95	1.51	92.91	0.49	201.89	1.13	
62.92	0.59	94.91	0.91	209.88	0.36	
63.93	1.60	95.93	0.31	229.86	0.75	
64.94	1.26	96.95	0.65	249.87	0.76	
65.94	0.69	97.95	51.45			
66.95	1.89	98.95	3.24			
67.96	16.17	99.90	0.90			
68.90	26.12 F	100.91	1.33			
68.97	3.43 F	102.91	0.86			
69.97	100.00	103.91	1.56			
70.96	4.53	109.91	0.45			
71.93	0.61	110.93	0.33			
72.95	0.46	111.94	0.33			
73.91	0.44	112.87	2.25			
74.91	1.51	114.90	0.50			
75.91	0.65	115.91	0.34			
76.92	3.53	117.92	0.63			
77.92	0.38	118.92	0.36			
79.95	0.59	119.92	0.55			
81.90	4.88	123.89	0.30			
		131.91	0.49			
		132.89	0.39			

27. 2,2,3,4,4,4-Hexafluorobutyl ethanoate



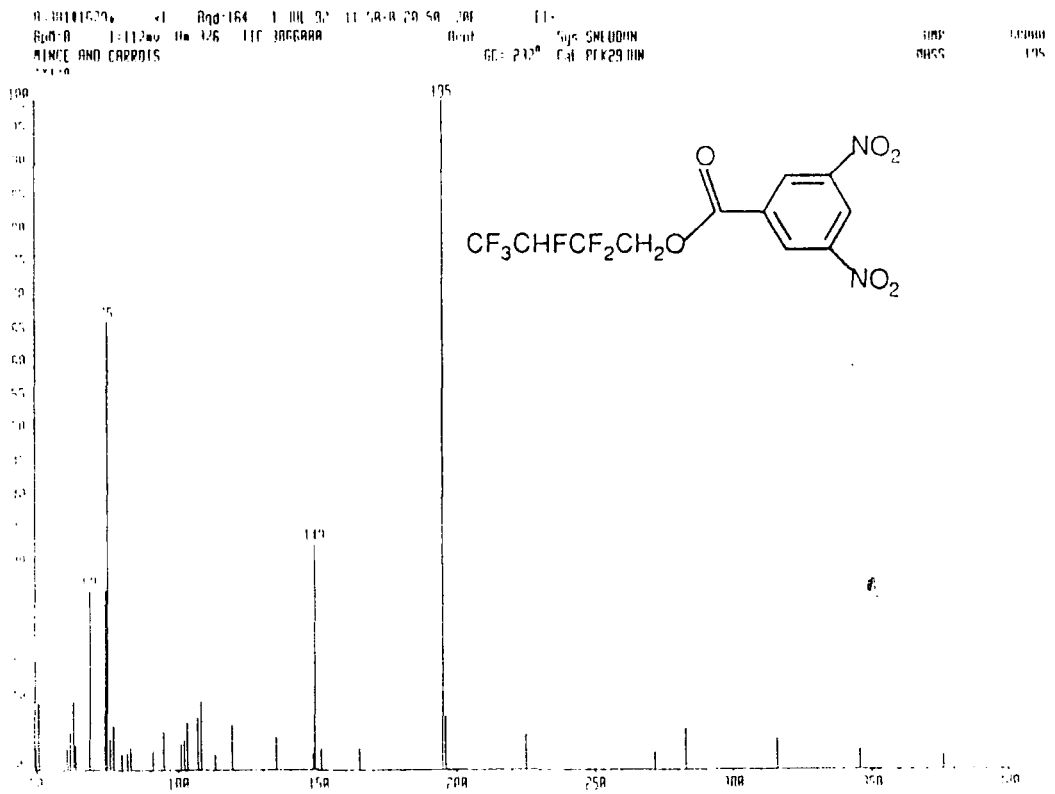
Mass	% Base				
49 95	1 72	81 94	21 96
50 95	90 95	82 94	27 28
51 97	0 94	90 93	0 77
55 97	0 86	92 94	2 75
56 97	4 03	93 96	0 51
59 97	1 24	94 93	45 35
60 96	8 79	95 94	1 76
62 95	4 03	99 92	1 12
63 96	14 93	100 92	8 15
64 97	2 15	112 92	9 18
68 93	83 14	122 93	4 63
69 91	0 60	130 91	0 90
69 95	0 86	131 91	1 54
72 96	100 00	144 92	1 76
73 96	3 86	150 92	3 56
74 95	5 71	164 90	2 87
75 96	0 90	184 98	0 64
76 95	21 96	203 88	1 12
77 96	0 69	204 93	1 12
79 96	0 94	224 90	1 20
80 95	0 51		

28. 3,3,4,5,5,5-Hexafluoropent-2-yl ethanoate



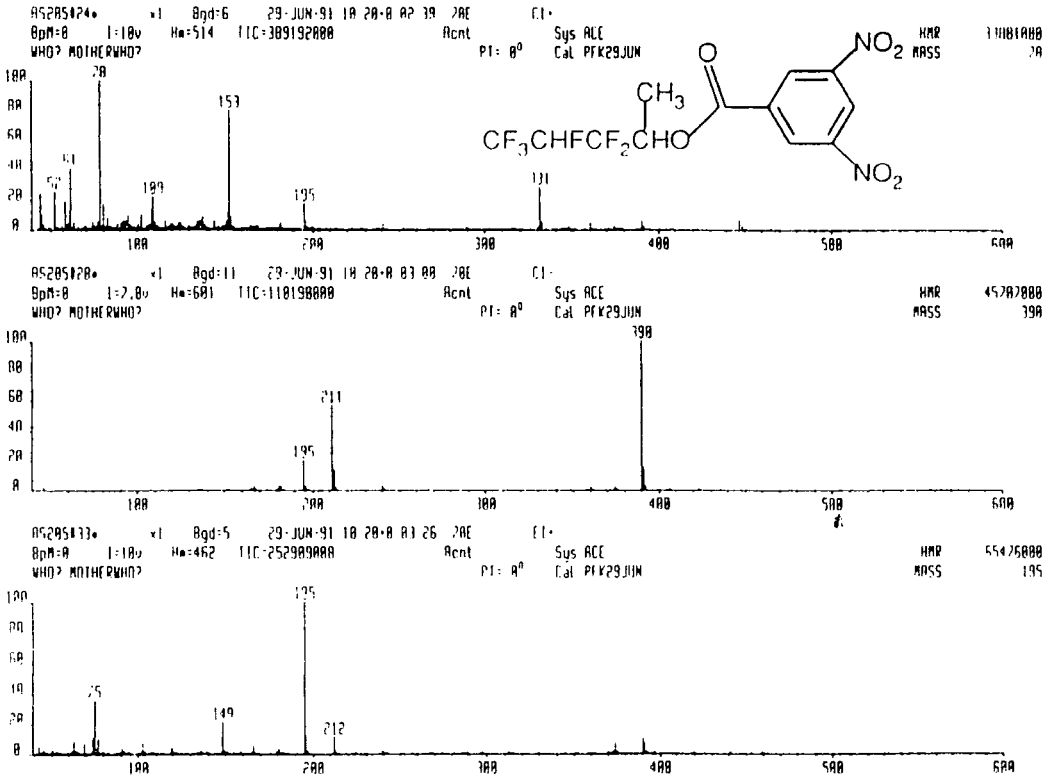
Mass	% Base					
49.04	0.54	87.98	4.89	140.90	0.57
50.03	1.64	88.95	6.84	150.88	9.66
51.03	64.67	89.96	2.03	151.88	0.33
52.04	0.88	90.96	4.49	154.89	7.55
55.04	0.64	91.96	0.36	155.90	1.10
56.02	0.74	92.93	1.74	156.90	0.58
57.02	4.89	93.94	0.83	157.89	0.86
58.03	0.64	94.94	18.33	158.89	21.57
59.03	9.71	95.95	0.68	159.90	1.31
60.02	16.96	96.96	4.57	162.86	0.40
61.02	91.86	99.92	1.35	174.88	2.70
62.02	2.26	100.93	3.18	175.88	0.49
63.00	3.21	106.95	2.58	178.88	0.88
64.00	2.70	107.94	1.10	194.85	1.85
65.00	16.88	108.95	15.85	217.85	22.32
66.00	0.42	109.95	0.64	218.85	1.90
66.97	0.55	112.92	9.22	237.86	0.69
67.98	0.34	113.92	0.35	238.84	0.86
68.96	96.17	114.93	6.81		
69.97	1.71	118.92	1.16		
70.99	2.77	126.92	1.02		
72.98	0.62	128.92	0.31		
73.97	0.36	130.90	1.17		
74.96	5.54	131.90	1.04		
75.96	1.50	132.91	0.77		
76.96	100.00	136.94	2.22		
77.97	6.58	138.91	9.90		
78.95	1.04	139.91	0.61		
80.95	0.50				
81.94	12.75				
82.95	1.22				
86.98	98.58				

29. 2,2,3,4,4,4-Hexafluorobutyl 3,5-dinitrobenzoate



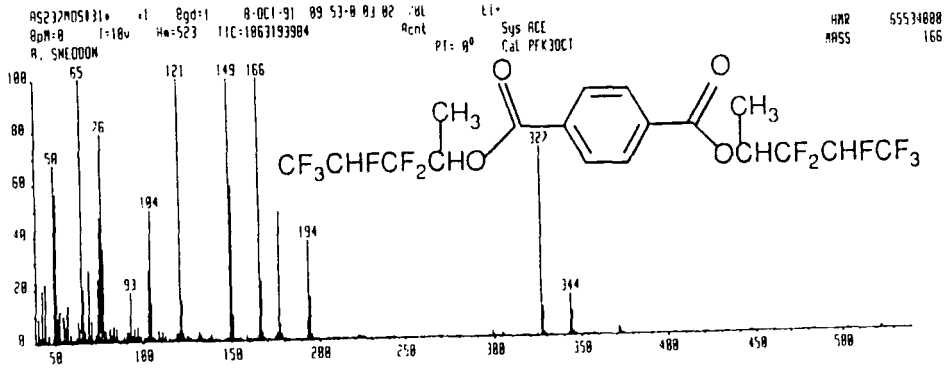
Mass	% Base	Mass	% Base
50.02	3.13	107.09	7.55
51.03	9.77	108.11	9.90
61.04	2.99	113.04	2.21
62.05	5.34	119.07	6.64
63.05	9.90	135.09	4.82
64.06	3.52	148.05	2.21
69.03	26.30	149.08	33.33
74.05	26.56	151.09	2.99
75.06	66.67	165.11	2.99
76.06	4.56	195.08	100.00
77.06	6.39	196.08	7.81
90.09	2.21	225.07	5.09
92.04	2.34	272.14	2.47
93.05	3.26	293.10	5.99
91.09	2.60	316.17	4.43
95.06	5.60	346.13	2.73
101.05	3.65	376.17	1.08
102.06	4.30		
103.07	5.99		

30. 3,3,4,5,5,5-Hexafluoropent-2-yl 3,5-dinitrobenzoate



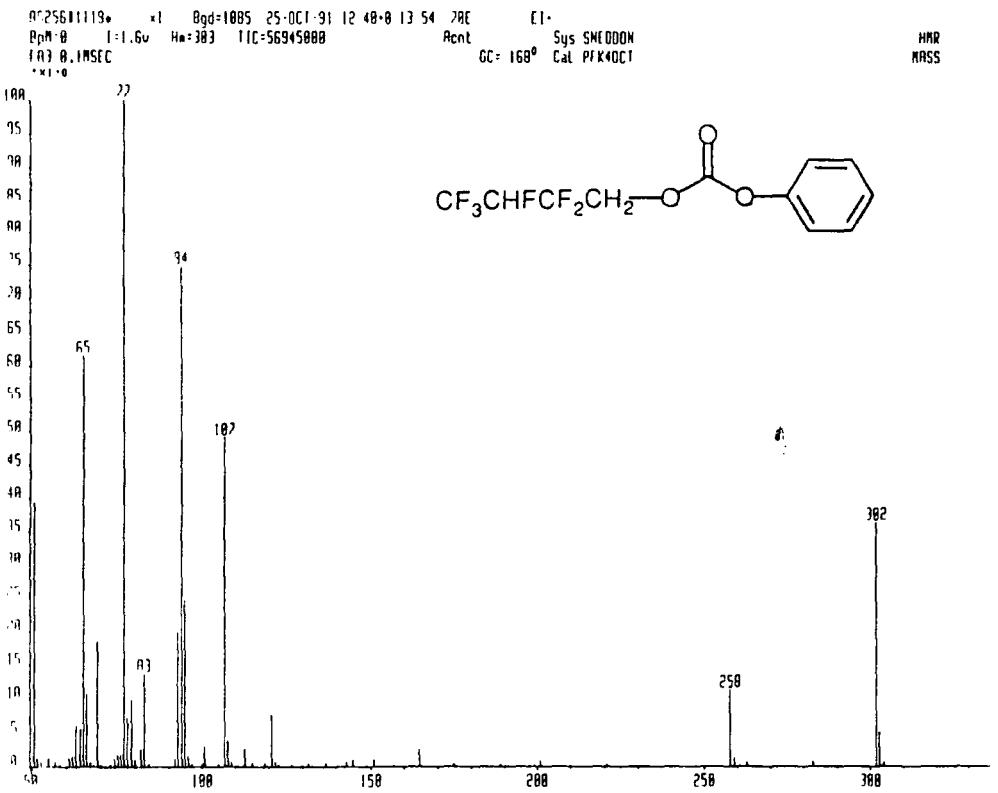
Mass	% Base	CI-
45 92	1 05	
151 93	0 32	
164 95	1 21	
165 95	0 58	
166 94	2 28	
167 95	0 33	
173 94	0 34	
179 92	0 57	
180 93	2 36	
181 93	2 26	
194 90	19 79	
195 90	2 56	
196 91	0 58	
210 88	57 11	F
211 92	13 44	F
212 92	1 69	
213 93	0 58	
239 97	3 34	
240 97	0 38	
357 95	0 33	
359 94	2 17	
360 93	0 53	
373 93	1 89	
374 94	0 65	
389 91	100 00	F
390 96	14 45	F
392 10	2 35	F
405 98	0 46	
422 91	0 42	

31. 3,3,4,5,5,5-Hexafluoropent-2-yl 1,4-dibenzoate



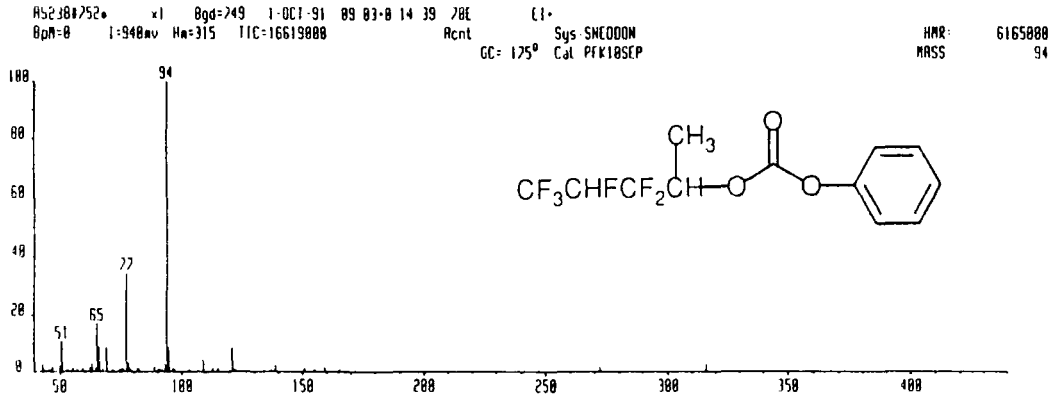
mass	% Base																			
40 99	8 86	94 91	3 96 F	155 99	0 18	229 92	0 12	346 99	0 17											
41 98	2 11	95 00	4 81 F	156 94	0 13	230 99	0 14	352 92	0 14											
42 99	19 46	96 01	1 64	157 92	0 12	233 07	0 14	353 93	0 14											
43 97	1 93	97 02	5 54	158 92	1 98	234 98	0 22	354 93	0 10											
44 97	21 80	98 02	1 75 F	159 93	0 25	236 09	0 12	356 92	0 40											
45 42	0 10	99 04	1 79 F	160 95	0 35	237 07	0 12	371 79	2 81											
45 98	0 84	100 93	1 21	161 95	0 20	238 11	0 11	372 95	2 10											
46 98	2 69	101 93	1 31	162 98	0 44	239 06	0 19	373 97	0 38											
47 96	0 13	102 94	26 52	164 01	0 23	239 95	0 13	390 93	0 14											
48 96	1 95	103 94	49 85	164 93	1 73 F	240 93	0 34	408 95	0 11											
49 97	67 46	104 95	13 67	165 90	100 00 F	241 94	0 16	418 94	0 10											
50 97	56 33	105 96	1 21	166 92	22 33 F	242 92	1 17	420 93	0 24											
51 46	0 29	106 98	1 02	167 93	3 10	243 92	0 18	432 85	0 34											
51 97	8 73	107 97	0 49	169 00	0 55	247 09	0 10	446 02	0 43											
52 47	0 49	108 97	3 77	169 99	0 14	249 10	0 13	447 00	0 26											
52 96	11 50	110 00	1 07	170 96	0 25	251 01	0 13	474 96	0 11											
53 98	1 03	111 03	3 35	172 94	0 16	253 06	0 16	482 92	0 50											
55 00	9 99	112 02	0 82	174 93	1 26	258 95	0 31	483 94	0 11											
55 55	0 14	112 95	2 19	175 93	2 60	259 98	0 12	502 93	0 24											
56 01	5 85	114 91	1 01	176 93	49 02	261 07	0 12	521 94	0 88											
57 01	13 85	115 97	0 21	177 95	5 69	263 11	0 13	522 96	0 79											
58 01	0 73	116 98	0 57	178 95	2 12	264 12	0 11	523 96	0 14											
58 98	2 93	117 96	0 18	179 99	0 34	265 12	0 10													
59 97	0 61	118 93	2 69	180 96	0 78	267 14	0 14													
60 96	0 78	119 92	2 90 F	182 03	0 24	268 92	0 28													
61 96	2 22	120 93	99 65 F	183 04	0 33	270 94	0 21													
62 97	7 44	121 94	15 14 F	184 97	0 13	275 03	0 11													
63 97	5 18	122 97	2 90	186 96	0 20	277 13	0 11													
65 00	100 00 O	124 01	0 78	187 92	0 17	278 11	0 11													
65 45	0 15	125 07	1 89 F	188 99	0 18	278 97	0 18													
65 97	19 41	126 01	0 62 F	190 99	0 32	279 96	0 26													
66 45	0 94	127 02	0 90	192 00	0 20	280 98	0 22													
66 99	3 76	127 98	0 24	192 92	6 65 F	286 96	0 16													
67 99	1 32	128 97	0 39	193 93	38 08 F	289 09	0 11													
68 95	27 13	129 95	0 25	194 95	16 02 F	291 15	0 11													
70 00	2 45	130 94	1 56	195 96	2 01	295 16	0 10													
71 01	7 72 F	131 92	3 34	197 00	0 49	296 91	0 32													
72 00	0 56 F	132 94	1 94 F	197 94	0 42	297 90	0 26													
72 95	2 76	133 74	0 70 F	198 94	0 24	298 90	2 03													
73 95	23 31	134 93	0 82 F	203 00	0 15	299 91	0 57													
74 96	47 23	135 98	0 35	204 98	0 64	300 97	0 14													
75 96	78 74	136 99	1 08	206 00	0 17	303 02	0 11													
76 96	34 96	137 95	1 75	207 01	0 30	303 99	0 10													
77 97	4 27	138 95	2 43	207 98	0 20	304 91	1 22													
78 98	3 91	140 00	0 45	208 99	0 30	305 96	0 23													
79 97	1 06 F	141 01	0 78	210 08	0 18	306 97	0 14													
80 98	4 95 F	141 99	0 24	211 04	0 25	309 04	0 11													
81 96	2.56	142 96	0 39	212 95	0 19	319 18	0 10													
83 01	5 45	143 97	0 10	213 94	0 14	323 09	0 11													
84 02	1 45	144 94	0 22	214 94	0 22	324 67	0 78 F													
85 03	4 83	145 95	0 16	216 99	0 14	326 86	72 18 F													
86 00	0 40	146 89	0 78 F	217 98	0 10	327 88	10 65 F													
86 96	0 39	147 89	2 59 F	219 05	0 20	328 90	1 23 F													
87 95	0 61	148 91	100 00 FO	221 00	0 35	329 95	0 18													
88 95	1 91	149 92	58 79 F	221 97	1 00	332 97	0 29													
89 95	0 96	150 92	9 12 F	222 98	1 02	336 93	0 15													
90 96	3 73	151 96	0 79	224 02	0 24	342 76	0 66 F													
91 95	3 29	153 01	0 74	224 98	0 57	343 88	15 58 F													
92 96	18 47	154 02	0 40	225 97	0 13	344 90	8 97 F													
93 97	2 05	154 99	1 04	226 94	0 11	345 92	1 29 F													

32. 2,2,3,4,4,4-Hexafluorobutyl phenyl carbonate



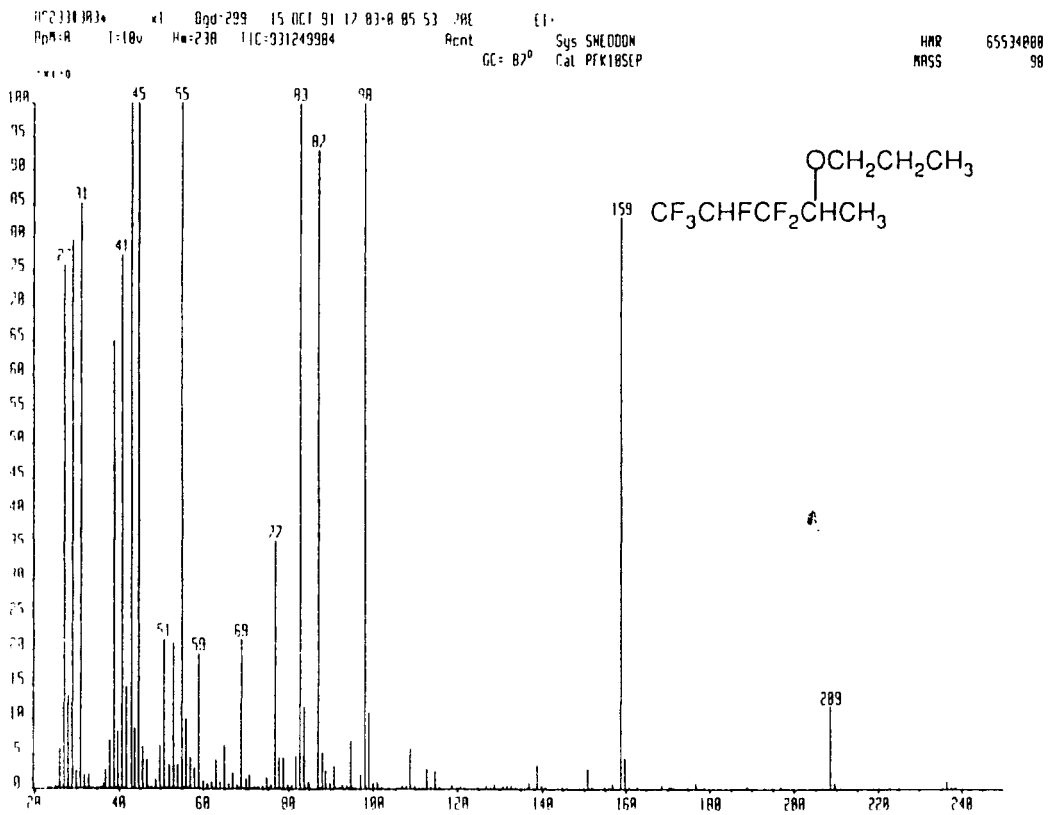
Mass	% Base		
49.96	5 27	100 91	2 87
50 96	39 29	104 94	0 33
51 97	1 15	106 95	49 12
52.96	0 61	107 95	3.85
54 96	1.22	108 95	0.63
56.96	0.56	112.91	2 46
60.95	1 14	114 93	0.45
61 96	1 52	120 92	7 56
62 96	6 00	121 93	0 58
63.97	5 56	136.94	0 47
64 98	61 40	142.92	0.54
65 98	10.64	144 91	0 81
66 99	0.53	150 92	1 00
68 93	18 39	164 89	2 48
73 95	0 99	200 88	0.75
74 95	1 67	257 88	11 02
75 96	1 67	258 88	1 24
76 96	100 00	262 88	0 48
77 97	7 20	282 89	0 56
78.98	9.83	301 83	36 20 F
79 97	0 84	302 85	4 91 F
81.94	2 46	303.91	0.46
82.93	13.54		
83.94	0 33		
91 94	1 02		
92 95	19 65		
93 96	74 72		
94 93	24 56		
95 95	1 11		

33. 3,3,4,5,5,5-Hexafluoropent-2-yl phenyl carbonate



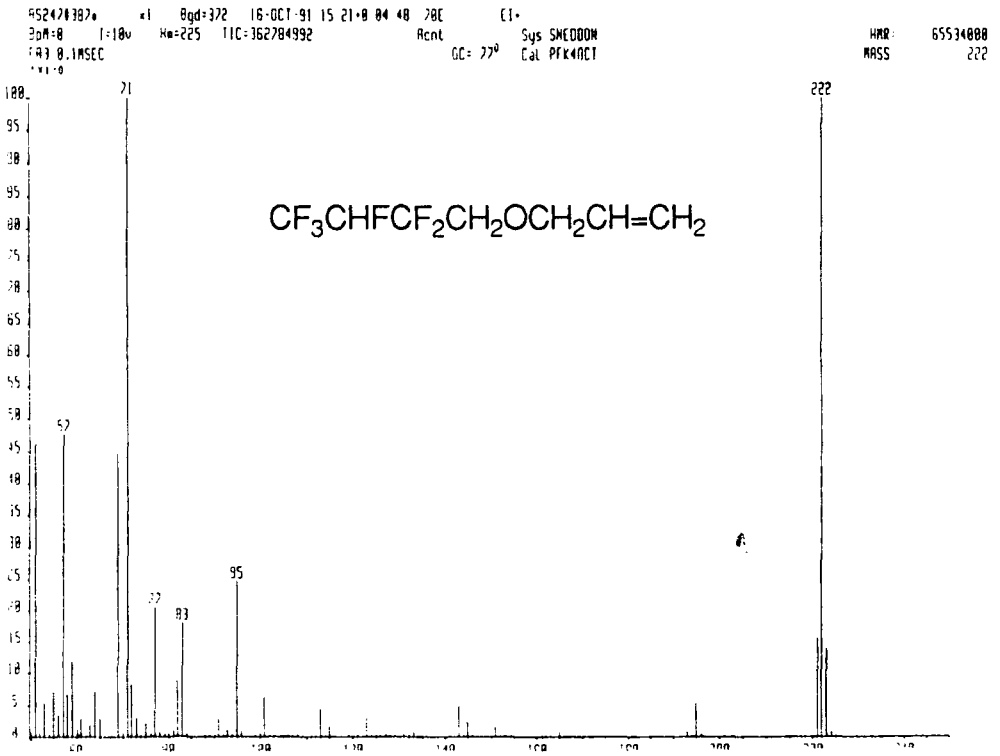
Mass	% Base		
42.95	2.51	88.93	1.59
43.93	0.49	89.94	0.32
44.97	0.45	90.95	0.84
46.96	1.69	91.93	0.42
49.95	2.22	92.95	2.71
50.94	10.56	93.95	100.00
52.93	0.31	94.94	8.30
54.95	0.88	95.95	0.70
56.94	0.47	96.94	0.83
58.96	0.79	102.97	0.32
61.94	0.96	106.97	0.45
62.95	2.42	108.93	4.15
63.95	1.10	112.90	1.05
64.96	16.61	114.91	1.01
65.97	8.61	120.95	8.30
66.97	0.55	121.96	0.39
68.91	8.32	136.94	0.42
70.94	0.47	138.92	2.00
73.94	0.37	150.88	1.09
74.92	0.63	158.92	1.49
75.94	0.70	271.95	1.49
76.95	34.24	315.95	2.51
77.95	2.63		
78.95	0.37		
81.91	0.86		
82.45	0.32		

34. 3,3,4,5,5,5-Hexafluoro-2-propoxypentane



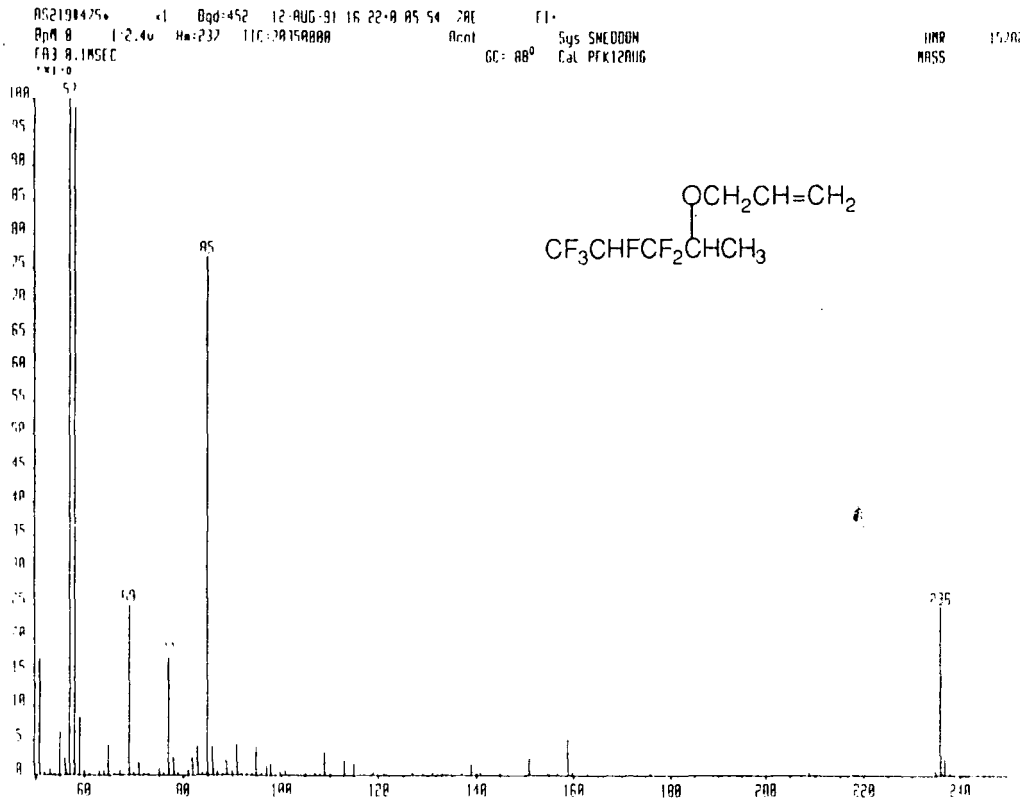
Mass	% Base		Mass	% Base	
40.92	77.41		86.88	93.13	
41.92	14.53	F	87.88	5.07	
42.96	100.00	FO	94.80	6.88	
43.93	8.60	F	97.86	100.00	FO
44.94	100.00	FO	98.86	10.96	
45.92	5.93		108.79	5.70	
49.89	6.11		158.71	83.14	F
50.88	21.49		206.66	0.06	
52.90	21.09		208.66	11.85	
54.94	100.00	FO	209.67	0.78	
55.92	9.97		210.68	0.05	
58.90	19.42		222.68	0.06	
64.87	6.27		235.72	0.03	
68.83	21.50		236.69	1.07	
76.84	35.79	F	237.69	0.10	
82.89	100.00	FO	238.70	0.17	
83.96	11.72	F			

35. 2,2,3,4,4,4-Hexafluoro-1-(prop-2-enoxy)butane



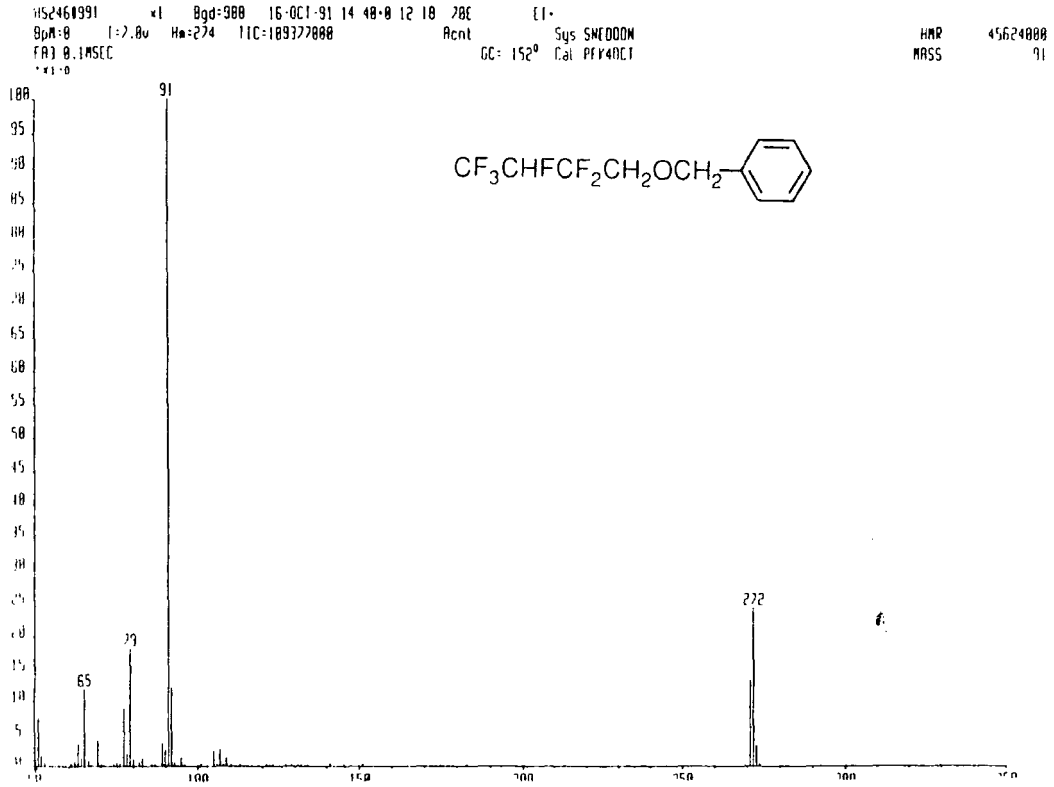
Mass	% Base		Mass	% Base	
50.00	0.78		91.04	2.61	
51.00	46.15		93.01	1.00	
52.01	0.48		95.01	24.50	
53.04	5.31		96.02	0.78	
54.03	0.42		100.00	0.57	
55.03	7.03		101.00	6.12	
56.04	3.33		113.01	4.30	
57.03	47.66		115.02	1.58	
58.05	6.64		119.00	0.43	
59.04	11.88		123.01	2.89	
60.04	1.10		132.00	0.78	
61.02	2.73		133.02	0.78	
63.02	1.71		143.02	4.69	
64.02	7.03		145.02	2.21	
65.03	2.74		146.03	0.33	
68.99	44.56		151.02	1.47	
70.00	0.53	F	165.02	0.78	
71.08	100.00	FO	193.01	0.78	
72.05	8.24		195.02	5.06	
73.05	2.91		220.99	15.53	F
75.01	2.04		222.02	100.00	FO
76.02	0.46		223.03	13.67	F
77.02	20.40		224.03	0.80	F
78.03	0.78				
81.05	1.69				
82.01	8.71				
83.01	17.98				
84.02	0.40				

36. 3,3,4,5,5,5-Hexafluoro-2-(prop-2-enoxy)pentane



Mass	% Base		
46.98	3.24	85.99	4.06
49.96	0.39	86.98	0.44
50.96	16.92	88.94	2.03
52.98	0.68	89.95	0.63
54.99	6.32	90.95	4.35
56.01	2.40	94.93	4.14
56.98	100.00	96.94	1.34
57.99	98.68	97.99	1.65
58.99	8.36	100.92	0.80
59.99	0.63	108.93	3.24
62.96	0.65	112.91	1.98
63.96	0.61	114.92	1.57
64.96	4.43	118.91	0.34
66.99	0.53	126.91	0.30
68.94	24.81	138.90	1.50
69.95	0.34	140.88	0.31
70.97	1.74	150.88	2.35
74.94	1.06	158.89	5.15
76.95	17.10	159.90	0.34
77.96	2.48	234.87	0.43
78.96	0.36	235.88	24.58
80.99	0.74	236.88	2.13
81.93	2.46		
82.97	4.03		
84.99	76.67		

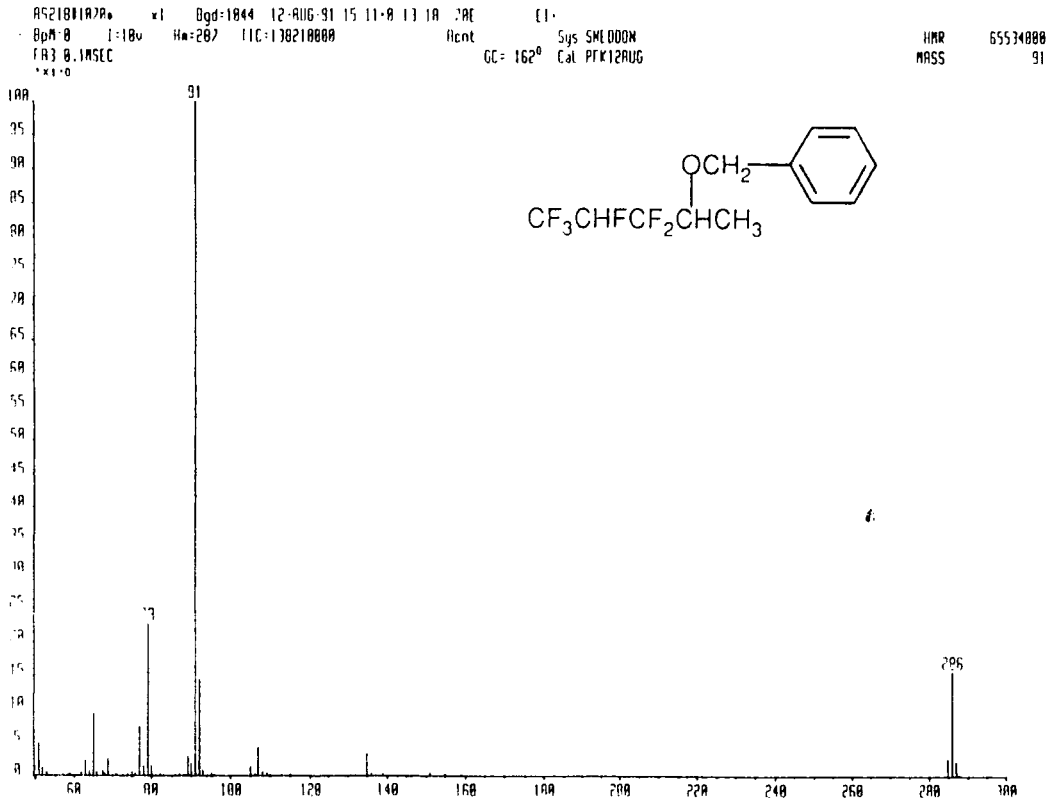
37. 2,2,3,4,4,4-Hexafluoro(phenylmethoxy)butane



$CF_3CHFCF_2CH_2OCH_2$-C$_6$H$_5$

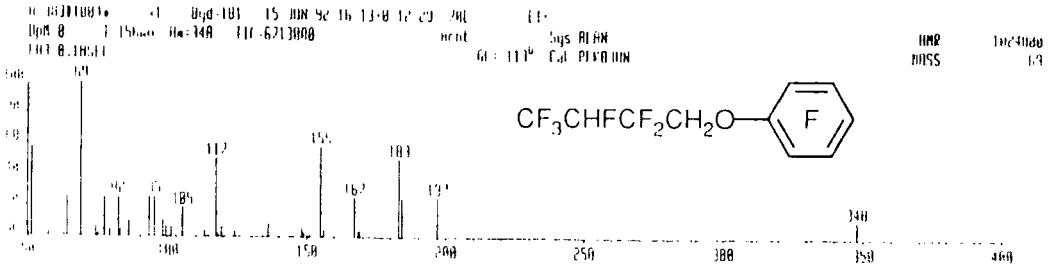
Mass	% Base		
50 02	2 75	91 06	100 00
51 02	11 68	92 07	23 40
52 04	2 28	93 07	1 35
53 04	0 70	95 02	4 69
57 03	0 32	105 04	4 61
60 55	0 65	106 05	1 65
62 02	0 99	107 05	4 25
63 03	4 25	108 07	0 50
64 03	1 45	109 05	0 53
65 05	13 43	113 00	0 51
66 05	0 70	128 91	0 40
69 00	4 25	131 94	0 55
74 02	0 61	133 92	0 36
75 04	0 74	145 03	0 71
76 04	0 69	153 06	0 37
77 04	14 89	183 04	0 51
78 05	2 91	222 04	1 10
79 06	32 05	252 04	2 02
80 07	2 13	271 04	17 99
82 01	0 55	272 05	26 15
89 04	4 28	273 05	3 01
90 05	1 69		

38. 3,3,4,5,5,5-Hexafluoro-2-(phenylmethoxy)pentane



Mass	% Base	
65.01	9 19	
77 00	7 28	
79 01	22 75	
91 02	100 00	0
92.01	13 74	
283 72	0 02	
284 04	0 04	
284.93	2 34	F
285 94	15 18	F
286.95	1 98	F
287 95	0 15	

39. (2,2,3,4,4,4-Hexafluorobutoxy)pentafluorobenzene



[illegible]	[illegible]	[illegible]	[illegible]	113	05	3	13
51	[illegible]	[illegible]	[illegible]	117	03	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	119	03	[illegible]	15
[illegible]	[illegible]	[illegible]	[illegible]	119	04	[illegible]	86
[illegible]	[illegible]	[illegible]	[illegible]	131	03	[illegible]	03
[illegible]	[illegible]	[illegible]	[illegible]	136	04	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	140	04	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	143	04	[illegible]	02
[illegible]	[illegible]	[illegible]	[illegible]	150	03	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	151	04	[illegible]	16
[illegible]	[illegible]	[illegible]	[illegible]	155	04	[illegible]	[illegible]
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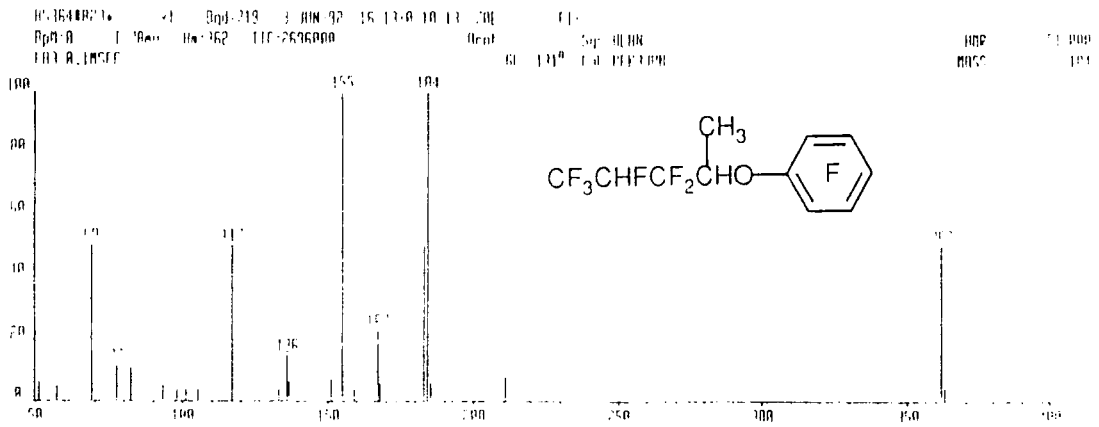
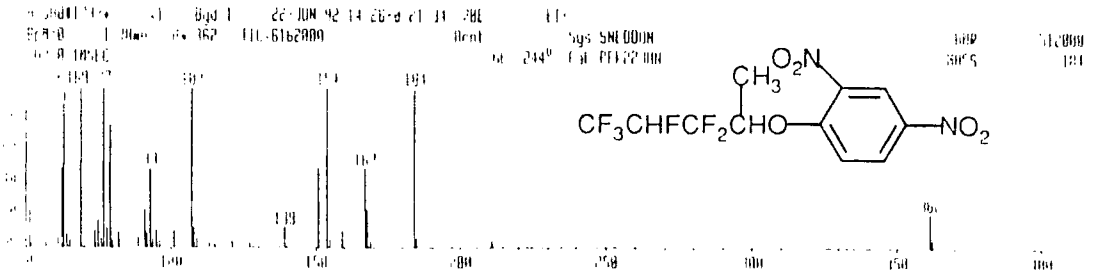
[illegible]	[illegible]	[illegible]	[illegible]	169	07	[illegible]	19
[illegible]	[illegible]	[illegible]	[illegible]	183	04	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	184	05	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	197	06	[illegible]	02
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
101	04	[illegible]	66				
[illegible]	[illegible]	[illegible]	[illegible]				

40. (3,3,4,5,5,5-Hexafluoropent-2-oxy)pentafluorobenzene



31	5 95
57	4 15
69	10 00
77	11 33
82	10 74
92	4 88
98	3 32
100	3 52
105	3 52
116	50 00
123	3 52
135	14 84
137	5 66
151	6 84
154	100 00
159	3 52
166	12 46
167	5 27
182	50 00
183	100 00
191	5 47
211	7 62
361	50 00
362	3 71

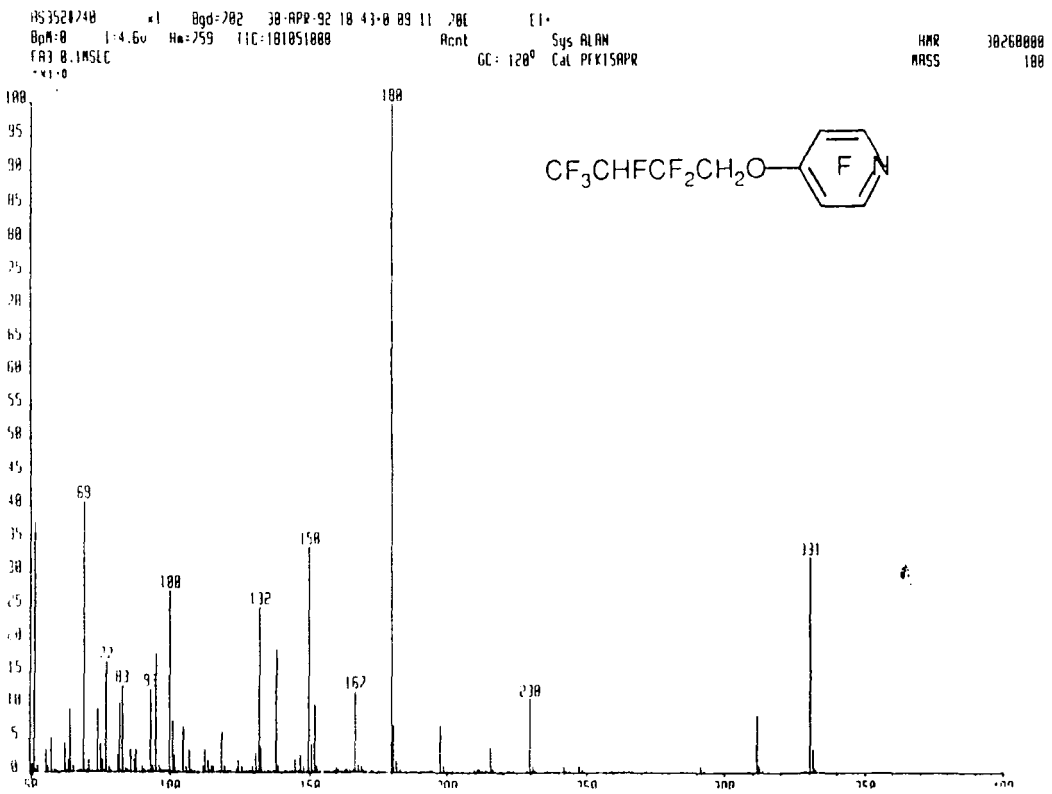
41. (3,3,4,5,5,5-Hexafluoropent-2-oxy)-2,4-dinitrobenzene



[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
50	98	[illegible]	[illegible]	93	97
51	99	[illegible]	[illegible]	94	95
52	97	6	05	95	94
56	99	3	91	100	94
60	97	6	64	106	91
61	98	50	00	107	94
62	98	100	00	108	95
63	98	9	77	112	94
64	98	[illegible]	[illegible]	114	96
68	95	[illegible]	[illegible]	120	93
73	96	9	96	126	92
74	97	16	99	138	93
75	97	9	01	150	97
76	97	[illegible]	[illegible]	153	94
77	98	11	91	154	94
78	96	[illegible]	[illegible]	158	93
79	96	3	71	166	91
81	95	9	77	167	91
98	96	3	64	169	92
99	97	3	93	183	94
91	[illegible]	[illegible]	[illegible]	194	97
[illegible]	[illegible]	[illegible]	[illegible]	195	91
[illegible]	[illegible]	[illegible]	[illegible]	361	97
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

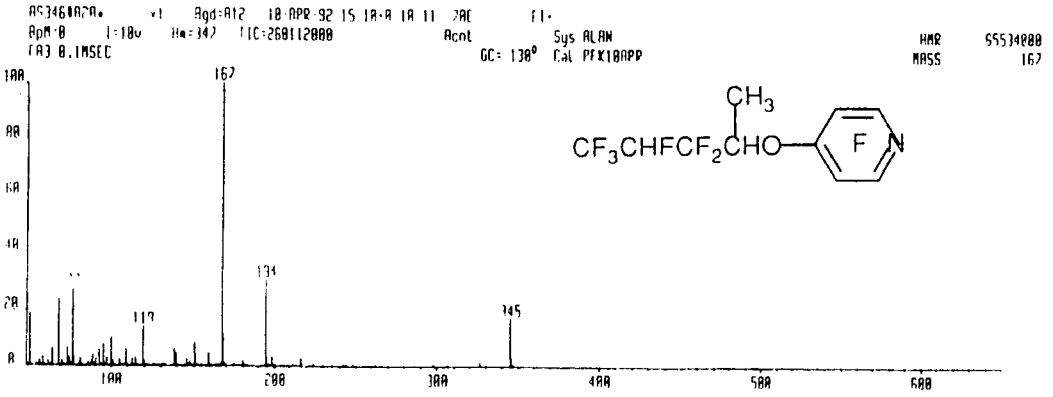
[illegible]	[illegible]
00	00
1	89
11	33
2	91
11	13
100	00
12	30
7	42
3	32
3	13
3	71
3	13
12	39
50	00
100	00
5	27
10	74
50	00
13	83
2	91
100	00
6	64
1	19
71	88
5	27

42. 4-(2,2,3,4,4,4-Hexafluorobutoxy)tetrafluoropyridine



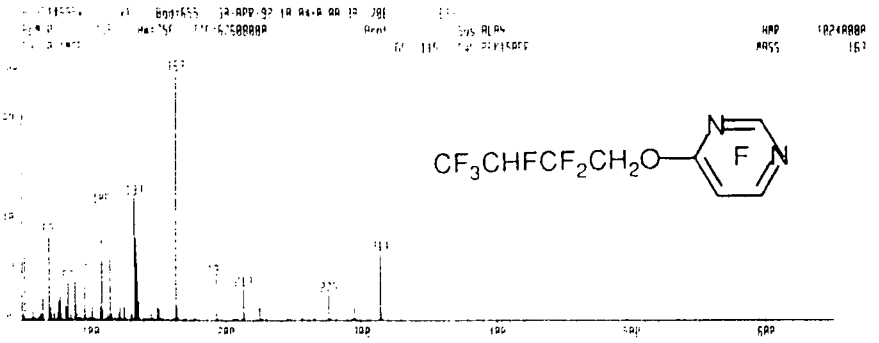
Mass	% Base										
50	29	0	73	107	01	2	41	179	98	100	00
51	23	25	82	111	99	0	50	180	99	7	22
55	23	1	57	112	99	2	46	181	99	1	20
56	22	0	55	114	01	1	20	197	95	6	02
57	21	2	68	115	01	0	45	198	96	1	20
62	12	2	95	115	99	0	40	215	97	2	92
63	11	1	20	118	99	3	99	216	97	0	33
64	09	6	02	120	00	0	41	221	98	0	37
65	09	0	33	125	00	1	30	229	98	9	04
68	98	27	94	126	00	0	39	230	98	0	62
69	99	0	43	130	00	2	33	241	99	0	44
70	97	0	72	130	99	2	41	247	96	0	69
73	96	5	03	131	99	18	05	291	97	0	52
74	96	2	94	133	00	3	61	311	96	6	14
75	96	1	20	137	98	9	63	312	97	0	59
76	97	10	36	139	00	3	78	330	95	37	30
77	97	0	33	144	99	1	37	331	96	4	24
80	92	1	80	146	98	1	66	332	97	0	48
81	93	6	54	147	98	0	43				
82	94	9	63	149	98	27	89				
85	95	2	60	150	99	3	61				
86	97	0	94	152	00	6	52				
87	97	1	57	159	99	0	71				
89	97	0	61	165	98	0	46				
92	99	1	46	166	98	9	88				
94	00	0	51	167	98	1	20				
95	01	13	78	168	98	1	34				
96	01	0	59								
100	00	18	11								
101	01	4	81								
102	02	1	62								
105	00	4	15								
106	00	0	55								

43. 4-(3,3,4,5,5,5-Hexafluoropent-2-oxy)tetrafluoropyridine



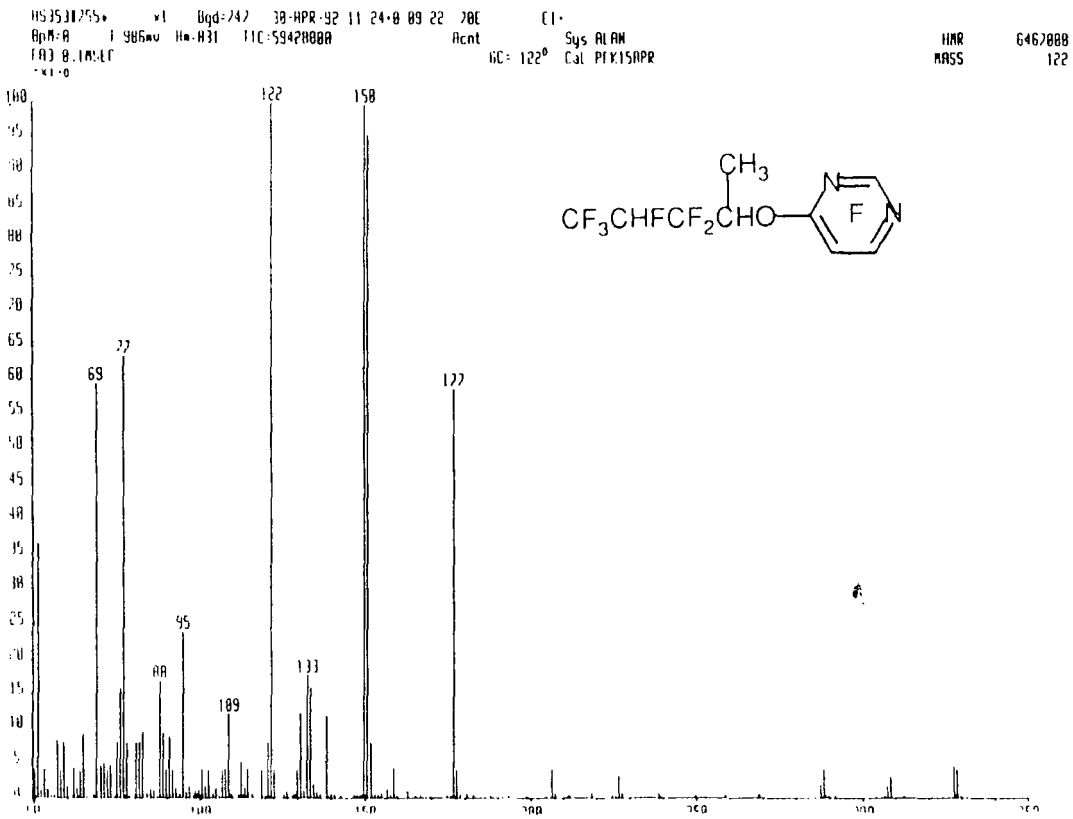
Mass		Base					
50	01	0	39	146	04	2	48
51	02	18	50	147	03	0	81
52	02	0	39	148	02	1	57
55	01	0	79	149	03	0	39
56	02	0	39	150	02	8	20
57	03	1	56	151	02	3	91
59	04	3	18	152	03	0	51
60	05	0	39	154	03	0	39
62	01	1	62	159	04	4	30
63	02	0	41	160	05	0	39
64	02	0	78	164	05	0	39
65	03	6	26	166	04	0	78 F
69	00	23	45	167	02	100	00 FO
70	02	0	48	168	03	10	00
71	02	1	56	169	04	0	78
74	00	6	30	174	05	0	78
75	01	2	88	180	04	1	56
76	01	0	94	181	04	0	39
77	02	26	63	194	04	30	20
78	03	2	82	195	05	2	73
81	01	0	78	198	02	3	18
82	01	2	34	199	03	0	31
83	02	0	39	212	04	0	39
86	01	1	17	216	03	2	34
87	02	0	39	217	04	0	39
88	01	1	56	242	06	0	39
89	03	3	92	244	07	0	49
90	03	0	78	248	04	0	47
91	05	2	34	262	06	0	39
93	01	5	55	298	06	0	40
94	02	0	78	306	08	0	39
95	02	7	81	326	09	1	21
96	03	0	78	345	08	16	80
97	04	2	86	346	09	2	47
100	02	9	77				
101	03	1	78				
105	01	1	95				
106	02	0	39				
107	02	0	39				
108	03	0	39				
109	03	5	90				
110	05	0	39				
112	01	0	39				
113	02	2	34				
114	02	0	39				
115	03	2	77				
116	03	0	44				
119	01	13	54				
120	02	1	75				
121	03	0	39				
122	02	0	39				
126	03	0	78				
127	04	0	39				
131	02	0	81				
132	02	0	78				
133	04	0	39				
138	02	5	97				
139	03	1	30				
140	04	0	39				

44 4-(2,2,3,4,4,4-Hexafluorobutoxy)trifluoropyrimidine

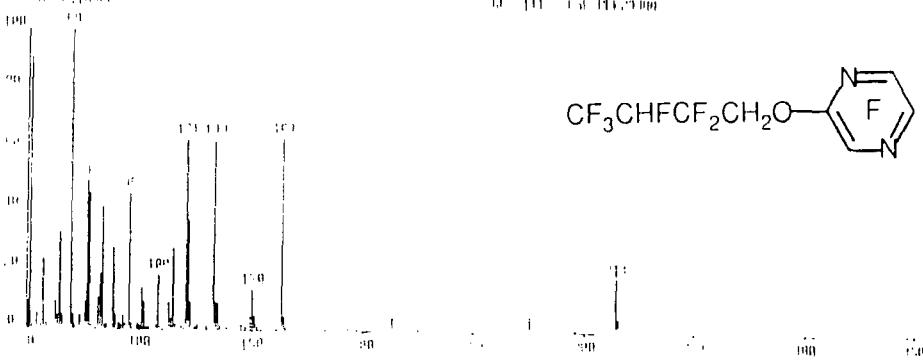


Mass	Base	Mass	Base
50 10	2 50	122 00	5 25
51 29	27 66	123 01	3 80
52 29	0 41	125 00	6 00
53 27	0 63	126 00	1 88
54 24	0 66	129 98	1 25
56 23	2 82	131 00	2 50
57 21	5 25	132 99	50 30
58 20	3 93	134 00	33 32
59 19	65	135 01	22 63
60 16	45	135 99	1 50
61 15	1 11	142 98	0 39
62 12	52	145 00	2 50
63 11	2 50	146 00	3 34
64 10	0 52	149 99	6 00
65 09	1 34	151 00	4 05
68 99	14 23	152 00	0 43
72 00	6 00	157 00	2 31
72 99	1 35	162 99	100 00
73 98	3 61	164 00	6 30
74 97	2 84	165 00	1 05
75 97	3 33	169 99	3 32
76 97	3 01	192 98	37 51
78 96	1 80	193 99	2 50
79 97	10 20	206 01	0 35
80 96	2 50	207 00	3 33
81 95	3 37	208 00	2 45
82 92	6 96	212 98	12 78
91 93	6 00	214 00	2 50
92 94	6 30	224 99	6 30
93 96	3 41	226 00	0 15
94 95	2 50	226 99	0 40
95 81	2 33	244 98	0 66
95 96	1 30	254 97	1 03
97 97	15 79	256 02	0 37
99 98	6 82	263 99	0 65
100 00	2 50	274 97	10 25
101 00	3 85	275 99	0 50
101 99	3 92	293 98	0 15
103 01	1 53	294 97	6 30
105 01	17 50	295 99	3 47
106 02	1 87	313 96	27 50
107 16	1 32	314 97	2 95
108 17	1 35		
109 01	1 23		
121 01	6 00		
122 01	3 96		
103 02	0 31		
105 02	0 41		
107 00	5 00		
108 00	46 70		
109 00	3 39		
111 81	3 40		
111 98	0 30		
113 00	2 57		
114 00	1 05		
115 00	29 00		
116 01	2 50		
119 01	3 61		
119 99	1 42		

45. 4-(3,3,4,5,5,5-Hexafluoropent-2-oxy)-trifluoropyrimidine



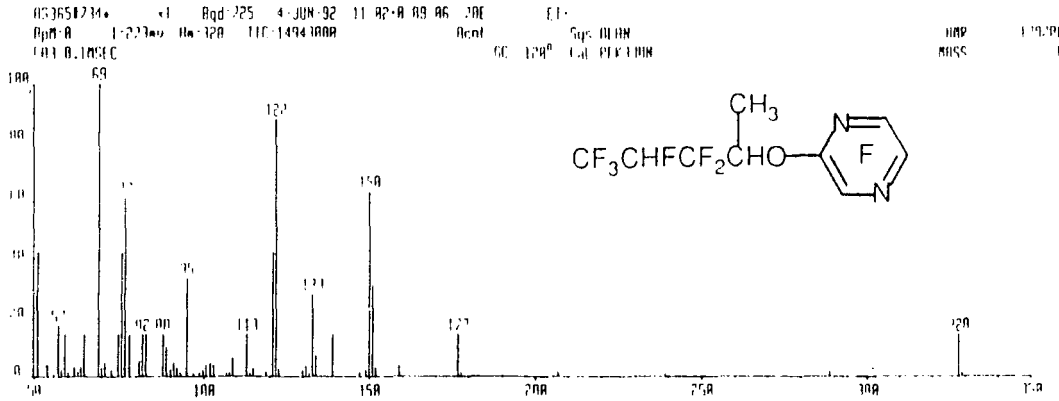
46. 5-(2,2,3,4,4,4-Hexafluorobutoxy)trifluoropyrazine



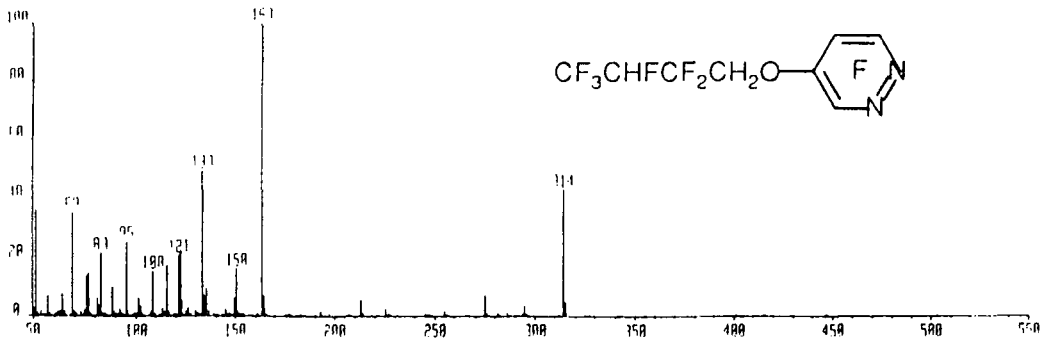
Mass	Mass
50 1	9 35
51 02	90 54
52 01	99
53 03	3 30
54 02	5 08
55 03	3 46
56 03	1 40
57 03	23 45
58 04	1 87
61 04	3 65
62 02	9 05
63 03	4 53
64 04	92 61
65 05	4 53
68 04	62
69 02	100 00
70 04	4 53
71 04	1 08
73 03	4 53
74 04	3 67
75 04	9 05
76 03	49 80
77 05	45 27
78 05	1 08
81 03	10 38
82 04	88 11
83 04	40 74
84 05	1 11
85 04	1 40
88 04	27 16
89 05	4 53
90 06	1 82
91 05	1 22
92 04	4 53
93 05	1 57
94 05	2 55
95 05	45 27
96 06	1 73
98 13	1 49
99 04	1 82
100 04	3 88
101 04	13 59
102 05	3 05
103 06	2 46
104 03	1 37
107 05	1 47
108 05	18 11
109 06	2 60
111 00	2 46
113 05	3 05
114 05	3 34
115 06	27 16
116 08	1 26
119 04	3 92
120 05	3 34
121 05	63 38
122 05	76 22
123 05	3 05
124 [illegible]	[illegible]
125 [illegible]	[illegible]

Mass	Mass
126 06	1 37
130 06	1 26
131 07	2 74
132 05	2 35
133 05	63 38
134 06	3 05
135 07	3 07
136 08	1 26
139 07	2 71
143 03	2 27
145 07	1 59
147 07	2 95
149 06	4 58
150 06	13 58
151 07	4 53
152 07	3 90
161 07	2 37
163 07	63 86
164 08	4 53
165 08	1 54
177 14	2 28
181 11	2 37
183 06	2 37
193 07	1 78
197 09	2 48
202 11	2 35
213 07	4 53
225 11	1 08
227 12	2 73
232 16	2 34
247 16	2 35
255 10	2 76
275 08	5 13
276 10	2 73
295 11	1 56
296 11	2 88
314 09	13 11
315 08	4 53
316 15	28

47. 5-(3,3,4,5,5,5-Hexafluoropent-2-oxy)-trifluoropyrazine

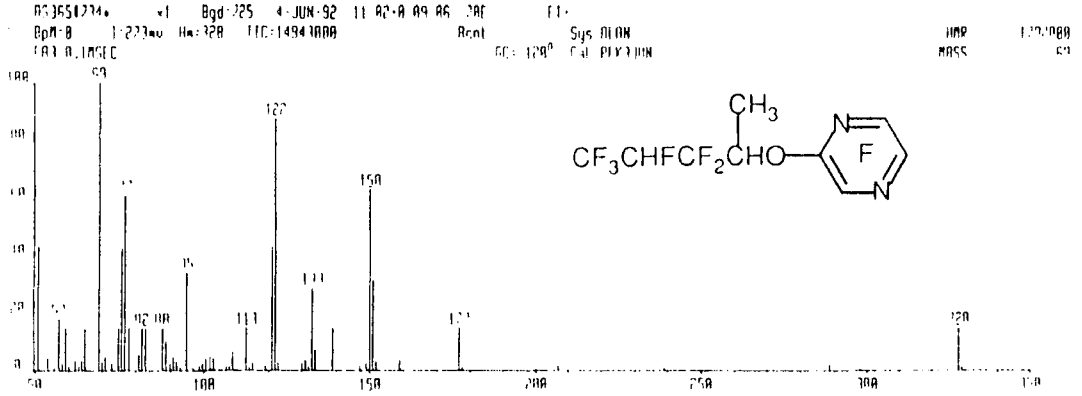


48. 4-(2,2,3,4,4,4-Hexafluorobutoxy)trifluoropyridazine

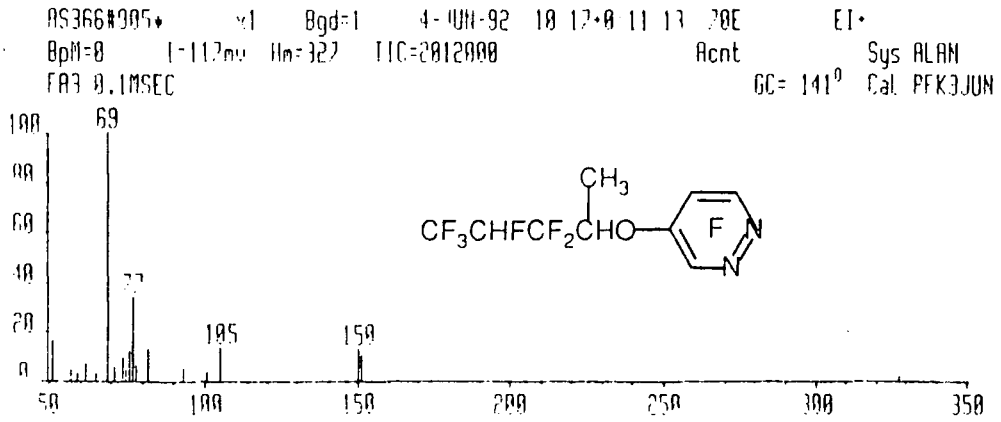


Mass	Base		Mass	Base	
50 03	2 54		149 08	5 71	
51 04	35 52		150 08	15 86	
52 04	0 63		151 08	1 46	
54 03	1 36		152 09	0 63	
57 04	6 34		161 09	0 63	
58 05	0 63		163 11	100 00	
61 05	0 63		164 10	6 34	
62 04	1 49		165 10	1 90	
63 05	1 27		177 10	0 44	
64 05	1 21		193 10	1 27	
65 06	1 27		213 10	5 21	
69 04	34 93		214 11	0 63	
70 05	1 27		225 09	1 90	
71 05	0 63		227 10	0 71	
73 04	1 27 F		247 13	0 44	
73 10	1 27 F		255 12	1 27	
75 05	2 02		275 09	6 98	
76 05	13 32		276 10	0 63	
77 07	14 27		281 14	0 63	
79 07	0 63		286 12	0 63	
81 05	5 71		294 13	0 63	
82 05	3 58		295 13	0 17	
83 06	21 38		314 12	42 82	
84 07	2 66		315 13	4 53	
85 06	0 71		316 14	0 63	
88 05	9 51				
99 06	1 27				
90 07	0 78				
91 07	0 63				
92 05	1 90				
93 06	0 63				
95 07	24 96				
96 07	1 27				
99 06	0 67				
100 06	0 63				
101 06	5 72				
102 07	3 18				
103 08	0 63				
107 07	1 27				
108 08	15 22				
109 09	0 63				
113 08	2 54				
114 08	1 27				
115 08	17 13				
116 09	1 27				
119 07	0 63				
121 07	20 72				
122 08	22 20				
123 08	4 86				
125 08	1 27				
126 08	2 54				
130 08	1 39				
131 08	0 63				
133 08	18 98				
134 08	5 35				
135 08	3 88				
36					
39	46				
145	35				
17	29				

47. 5-(3,3,4,5,5,5-Hexafluoropent-2-oxy)-trifluoropyrazine

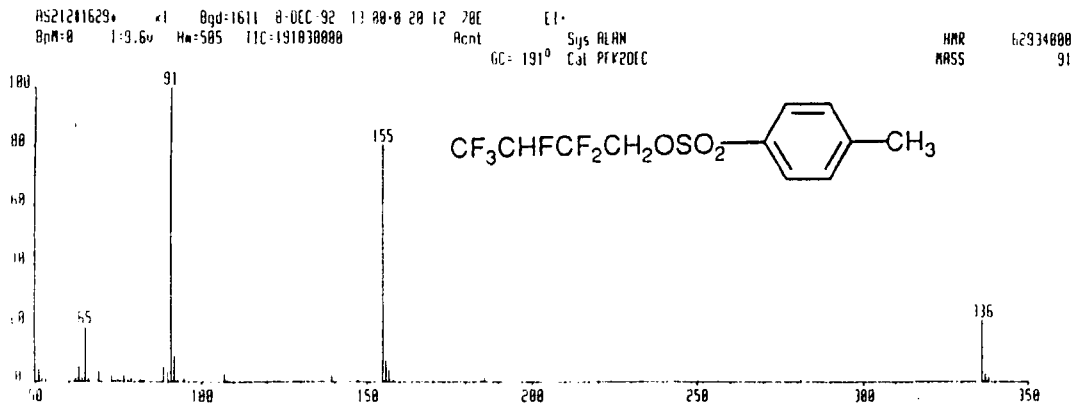


49. 4-(3,3,4,5,5,5-Hexafluoropent-2-oxy)-trifluoropyridazine



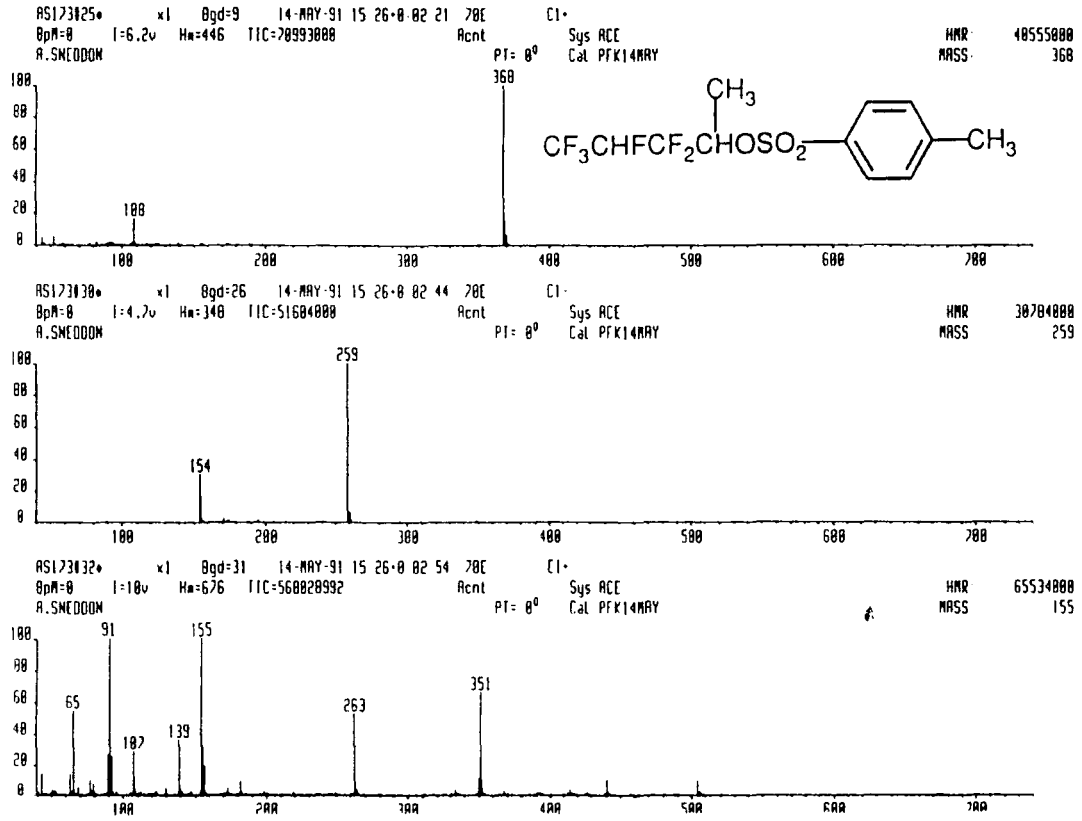
Mass	% Base
49 96	4 95
50 97	15 10
56 97	3 91
59 00	2 33
61 96	2 25
64 97	1 69
64 99	2 60
68 95	100 00
70 96	4 82
73 96	9 11
74 97	3 91
75 96	11 59
76 98	33 33
77 99	5 60
81 96	12 24
92 96	4 56
100 95	3 39
104 95	13 02
149 95	12 34
150 93	9 37
228 00	1 95

50. 2,2,3,4,4,4-Hexafluorobutyl 4-methylbenzenesulphonate



Mass		% Base	
49	98	1 70	
50	98	3 95	
52	00	1 02	
53	00	0 60	
61	98	1 23	
62	99	5 05	
63	98	1 78	
65	00	18 61	
66	01	1 18	
68	96	3 69	
73	00	1 64	
73	99	0 40	
74	99	0 58	
75	99	0 42	
76	99	2 33	
78	00	0 71	
79	00	1 13	
81	96	0 56	
82	97	0 68	
88	99	4 96	
89	99	3 33	F
91	01	100 00	F
92	01	8 85	
93	01	0 38	
94	96	1 01	
107	00	2 76	
108	00	0 32	
138	96	2 11	
147	01	0 75	
150	94	0 38	
154	95	80 79	
155	95	7 19	
156	95	4 23	
157	96	0 31	
184	95	0 45	
185	95	1 46	
280	99	0 53	
335	94	21 38	
336	96	2 73	
337	96	1 22	
355	00	0 40	

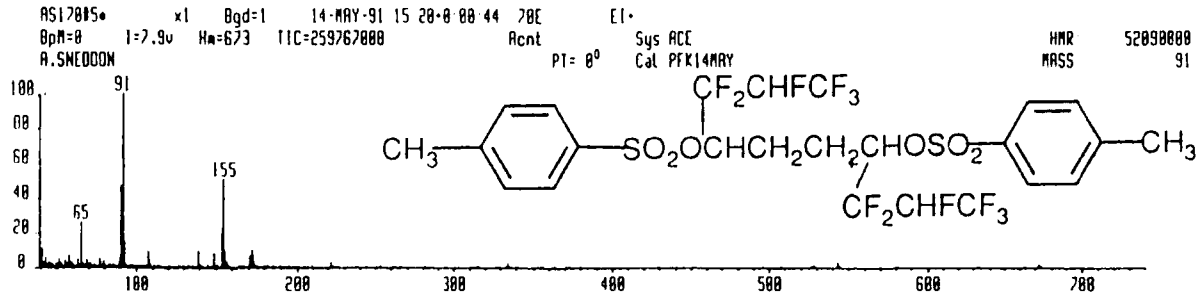
51. 3,3,4,5,5,5-Hexafluoropentyl 2-(4-methylbenzenesulphonate)

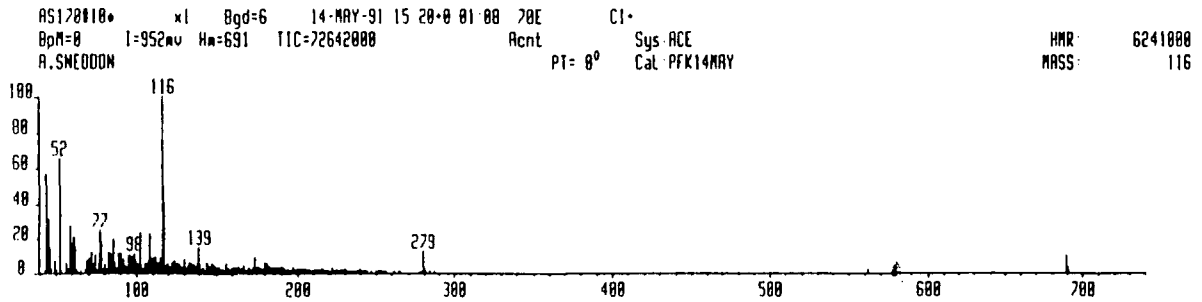


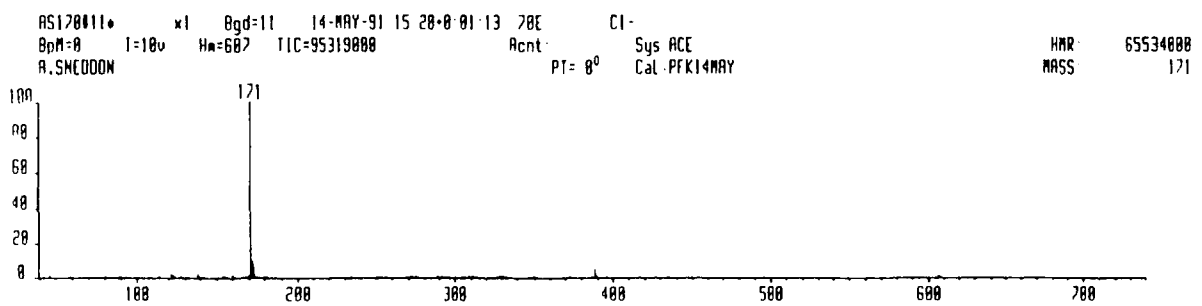
C1+

Mass	% Base		
44.00	3.66	107.99	16.14
45.00	0.53	108.99	1.44
52.04	5.08	117.04	0.56
58.01	0.52	123.97	0.75
64.98	0.48	125.00	0.47
77.00	0.53	138.91	1.32
77.99	0.59	154.90	0.68
79.98	0.32	155.92	0.50
81.99	2.05	173.93	0.92
88.96	0.57	188.93	0.74
89.97	0.36	349.86	0.31
90.97	1.58	367.83	100.00 F
92.97	1.56	368.84	14.39 F
93.98	0.48	369.83	5.96 F
105.97	0.72	370.83	0.75 F
106.97	1.34		

52. 1,1,1,2,3,3,8,8,9,10,10,10-Dodecafluorodecyl
4,7-bis(4-methylbenzenesulphonate)







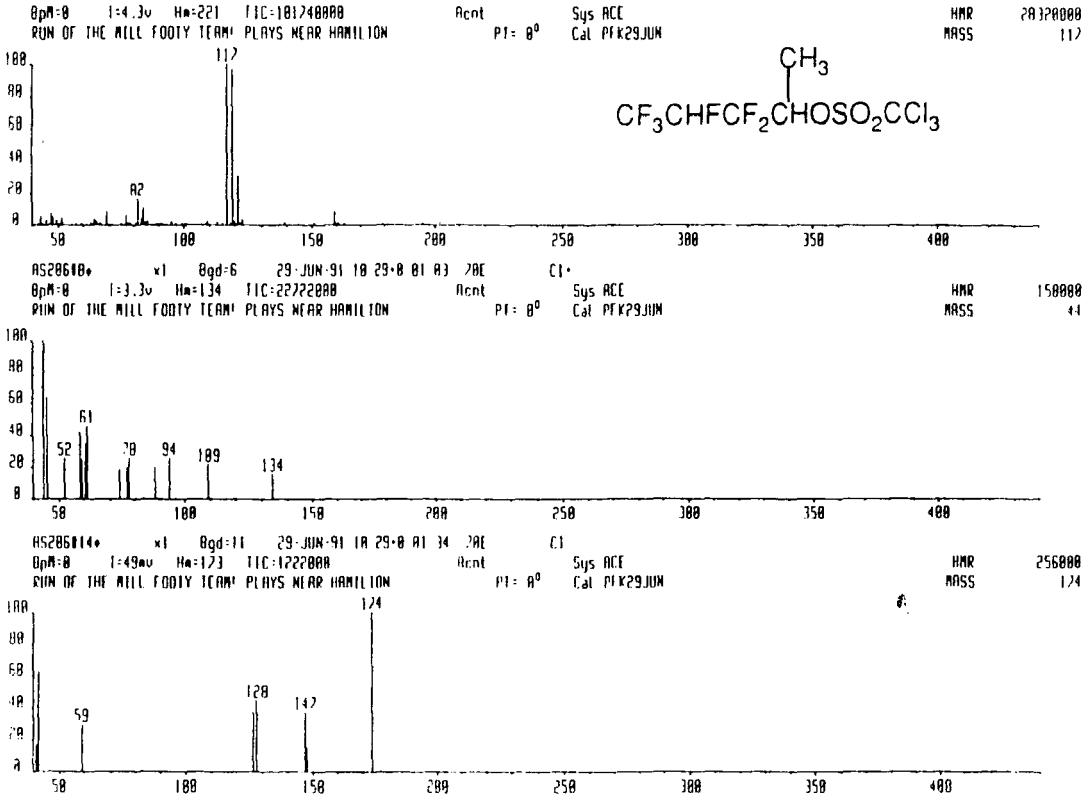
Mass	Rate
43.00	0.80
44.01	56.21
45.01	30.80
46.03	13.97
47.03	1.67
49.03	6.43
50.04	1.23
52.05	65.23
53.04	0.93
56.01	5.29
57.01	1.62
58.03	27.19
59.02	16.42
60.02	20.59
61.01	14.50
62.02	1.60
63.00	0.82
64.99	0.75
68.01	1.78
69.00	6.92
70.02	8.08
71.02	3.96
72.03	11.78
73.03	4.97
74.02	10.30
75.02	1.60
75.99	5.10
77.02	24.50
78.02	17.50
78.99	1.63
79.99	4.61
80.99	1.99
82.01	11.79
83.01	9.20
84.01	10.88
85.01	19.08
86.02	5.85
87.01	2.66
88.02	10.75
89.01	2.74
90.00	10.93
91.02	7.48
92.00	1.04
92.99	3.99
94.00	9.79
94.99	9.90
96.00	9.12
97.00	9.72
98.00	11.02
99.01	6.25
100.02	4.98
101.01	4.47
102.01	23.03
103.04	4.07
104.01	2.02
105.03	5.29
106.00	4.98
107.00	6.75
108.01	22.45
109.01	5.09

Mass	Rate
110.01	8.40
111.01	6.28
112.00	9.12
113.01	5.90
114.01	5.48
115.02	8.36
116.03	100.00
117.06	19.82
118.04	3.75
119.03	5.03
120.00	3.85
121.00	3.43
122.01	5.50
123.00	4.98
124.01	6.95
125.01	4.97
126.01	4.85
127.00	3.70
128.02	3.28
129.00	2.58
130.02	3.84
131.02	2.87
132.00	3.72
133.02	5.74
134.00	5.11
134.99	4.61
136.00	4.71
136.99	3.20
138.01	5.32
138.96	4.45
139.99	4.71
140.99	2.15
142.01	2.47
143.00	1.33
144.02	5.77
145.00	2.56
146.00	3.81
147.00	5.35
148.00	4.26
148.98	3.83
149.99	3.48
151.00	2.32
152.01	3.08
153.01	1.84
154.01	1.91
154.99	1.60
155.98	5.06
156.97	1.73
158.02	2.74
159.01	2.24
160.00	2.55
161.02	3.11
162.00	3.22
163.01	3.28
164.00	2.96
165.02	2.16
165.98	2.18
167.00	4.09
167.99	1.60
168.99	1.22

Mass	Rate
170.04	2.26
171.02	1.33
172.02	1.86
173.00	3.01
173.97	9.57
175.00	2.68
176.00	3.35
177.00	2.44
178.01	1.95
179.01	1.51
180.04	9.90
181.00	4.90
182.01	1.83
182.98	3.48
184.00	2.29
185.00	1.57
186.00	2.34
187.00	2.40
187.99	2.13
188.99	2.76
189.99	3.43
190.99	2.66
192.00	1.62
193.00	0.98
194.01	1.22
194.99	1.19
196.00	1.28
196.99	3.25
198.00	1.87
199.00	1.57
200.00	2.24
200.98	1.78
202.00	1.95
202.99	1.47
204.00	1.71
204.99	2.18
205.99	1.03
206.99	1.06
208.00	1.07
208.99	0.90
210.01	1.28
210.99	1.15
212.01	1.71
212.99	1.01
214.01	1.38
214.98	2.21
215.98	1.68
217.01	0.99
218.00	1.20
218.99	1.11
219.99	0.87
221.03	0.61
222.00	2.42
222.98	1.72
224.01	1.19
224.99	1.15
225.97	1.01
226.98	1.11
228.03	1.14
229.01	1.15

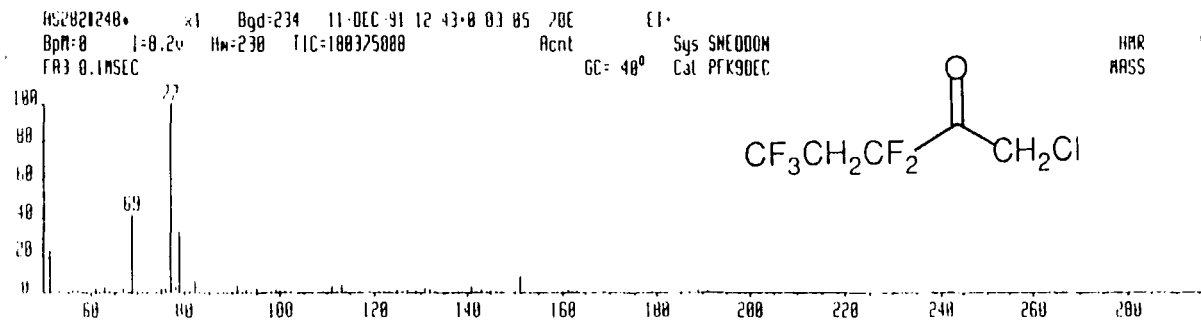
Mass	Rate
229.99	1.68
230.99	1.03
231.97	0.67
232.96	0.58
234.99	0.90
235.99	0.73
236.99	0.67
238.00	0.91
238.98	1.92
240.02	1.01
241.00	0.66
242.02	1.12
244.04	0.74
247.00	0.61
250.01	0.69
251.01	0.54
252.04	1.06
252.98	0.83
254.00	0.67
255.00	0.67
256.05	0.82
261.00	0.77
263.94	0.59
264.99	0.71
278.00	0.51
279.00	12.08
280.01	2.42
280.99	0.79
284.10	0.51
287.03	0.53
561.80	2.21
689.34	9.87
690.31	3.00
691.26	1.79

53. 3,3,4,5,5,5-Hexafluoropentyl 2-(trichloromethanesulphonate)



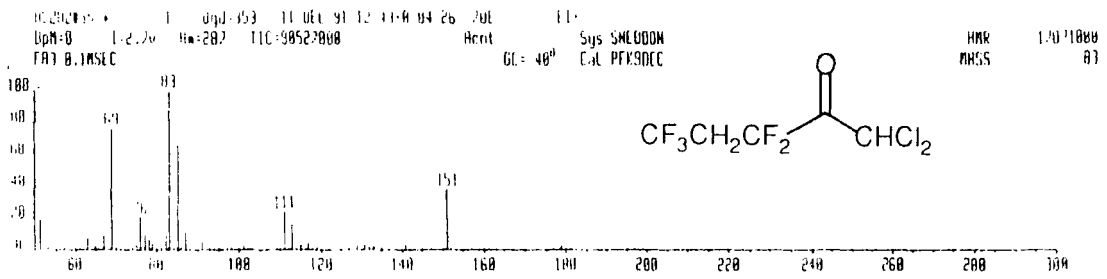
Mass	% Base	Mass	% Base
40 98	0 30	89 03	0 71
41 97	0 45	91 04	0 60
42 98	5 38	95 02	2 04
43 96	0 78	97 04	0 44
45 00	2 57	98 94	0 55
46 96	6 90	100 99	0 38
47 95	4 27	109 04	1 94
48 96	2 40	113 01	1 30
51 01	3 89	115 03	0 70
57 03	0 33	116 92	100 00
59 04	0 72	117 93	1 09
62 98	1 42	118 92	96 97
63 96	3 81	119 92	1 03
64 95	1 73	120 92	30 90
65 02	1 98	121 92	0 32
66 95	0 46	122 92	3 30
68 99	8 47	139 04	1 07
71 04	0 31	151 02	1 41
75 01	0 47	159 06	8 28
77 03	5 87	160 06	0 47
78 03	0 68	160 98	1 00
78 96	0 89	162 98	0 91
80 95	0 34	179 06	0 89
81 95	15 79	195 05	0 39
82 95	3 25		
83 94	10 21		
84 95	1 44		
85 94	1 66		

54. 1-Chloro-3,3,4,5,5,5-hexafluoropentan-2-one



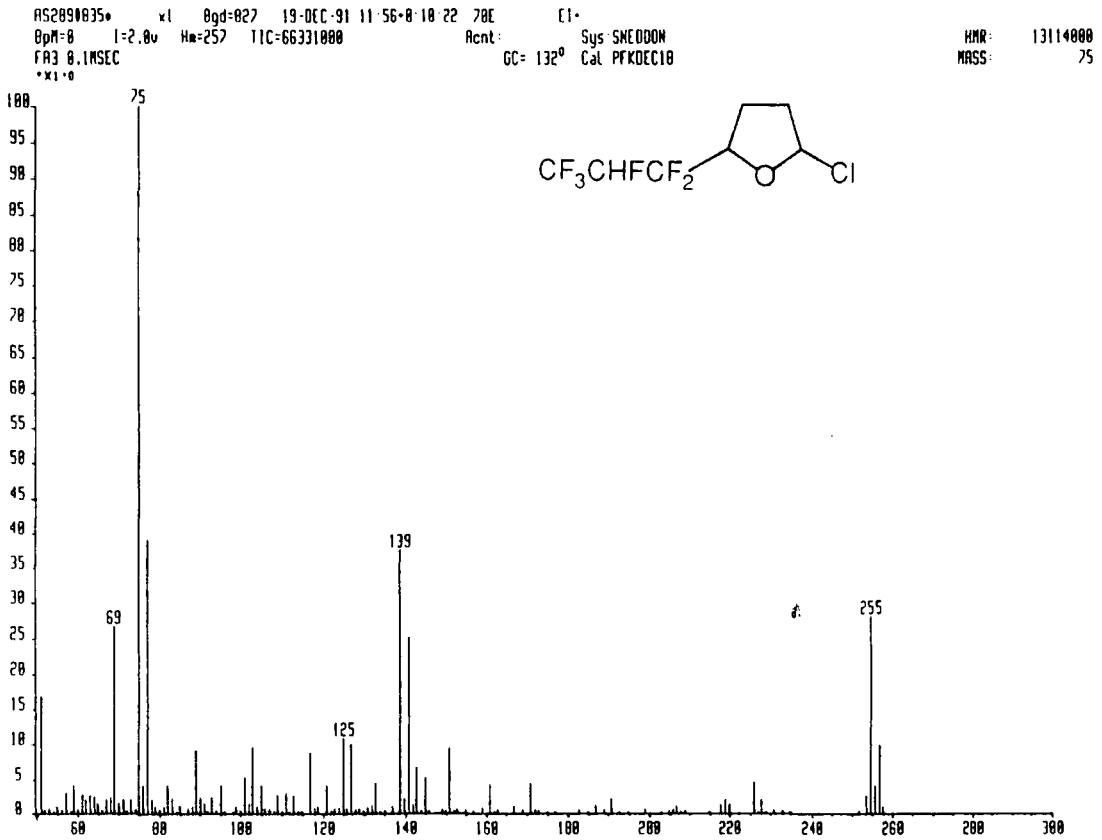
Mass		Mass	
47	9?		1 87
48	98		61 04
49	96		1 10
50	99		11 07
51	99		3 31
56	01		1 42
57	02		6 95
61	00		1 44
63	00		1 26
64	01		1 40
66	98		1 99
68	99		41 80
70	00		40
74	00		1 36
75	01		1 74
75	98		1 96
76	98	100	00
77	99		3 33
78	98	30	36
79	98		1 72
80	99		0 38
82	01		6 12
83	02		1 78
84	98		1 95
91	01		3 32
93	01		1 04
95	03		1 90
99	00		1 51
100	01		2 59
101	01		1 13
111	00		3 59
113	01		3 79
125	02		0 36
127	00		1 22
128	99		2 64
131	01		1 90
132	02		1 21
141	00		3 49
142	99		1 04
145	03		1 32
161	02		8 54
161	00		1 41
163	0?		1 ??
189	01		1 13
191	01		? 36

55. 1,1-Dichloro-3,3,4,5,5,5-hexafluoropentan-2-one

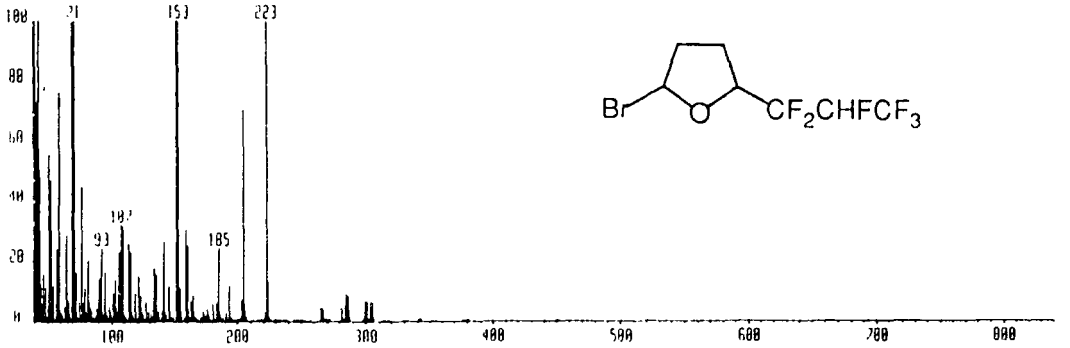


Mass	Base			
47 97	17	63	179 00	2 86
48 98	6	87	194 98	0 74
49 98	5	95	196 98	0 51
51 96	18	66		
52 01	1	37		
53 01	0	51		
56 01	0	80		
57 02	0	82		
60 00	1	74		
60 99	0	34		
62 98	6	13		
64 96	1	90		
66 98	2	83		
68 99	75	88		
70 00	0	82		
71 00	0	68		
73 99	0	51		
75 00	0	89		
75 97	19	68		
76 98	10	51		
77 97	6	51		
78 98	3	47		
80 99	1	35		
81 0	0	01		
82 96	1	00		
83 96	1	22		
84 96	88	14		
85 96	1	20		
86 96	10	59		
91 01	4	30		
93 00	1	16		
94 01	0	37		
94 99	1	43		
96 96	0	64		
97 99	0	61		
100 01	0	80		
101 01	2	86		
108 99	0	36		
110 96	23	89		
111 96	0	93		
112 96	15	16		
113 98	0	50		
114 95	2	43		
116 98	3	20		
118 99	1	15		
125 00	0	35		
126 99	0	48		
128 99	3	17		
131 00	2	94		
132 02	1	50		
132 97	1	13		
134 97	1	14		
141 01	2	86		
144 97	1	39		
146 97	1	91		
151 02	100	00		
151 97	1	43		
161 98	1	52		
161 99		50		
		11		

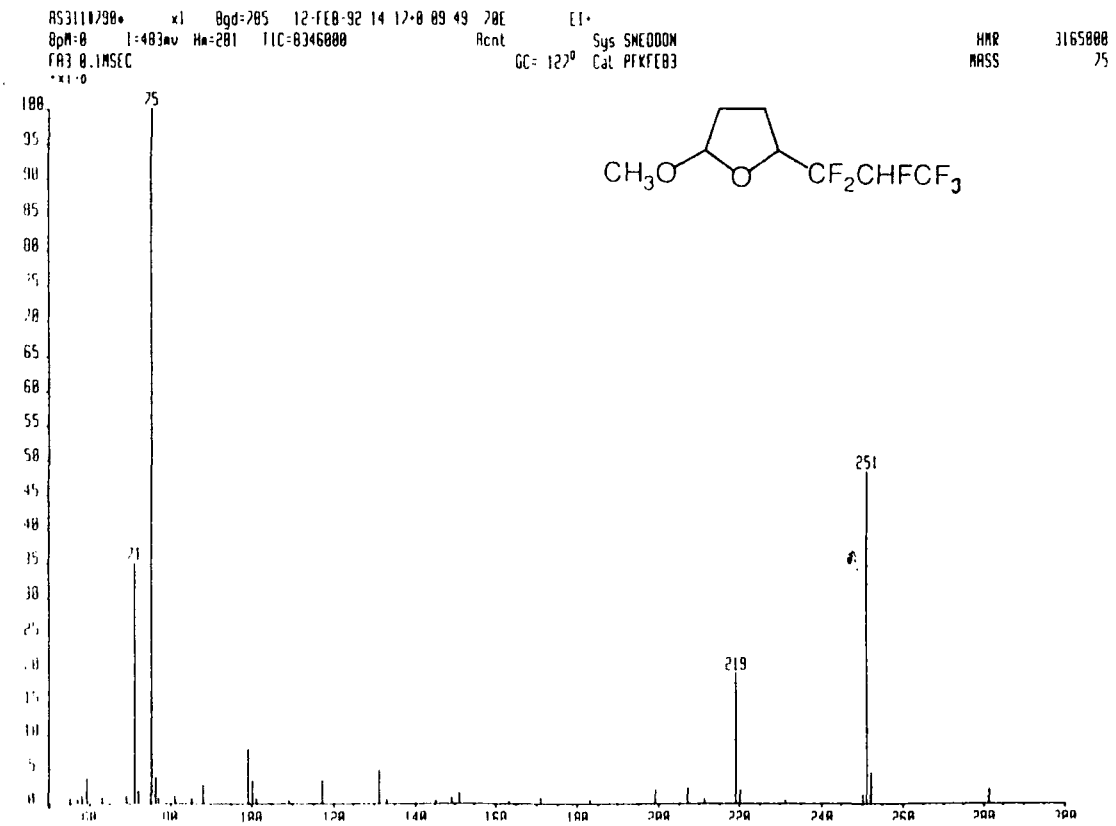
56. 2-Chloro-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane



57. 2-Bromo-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane

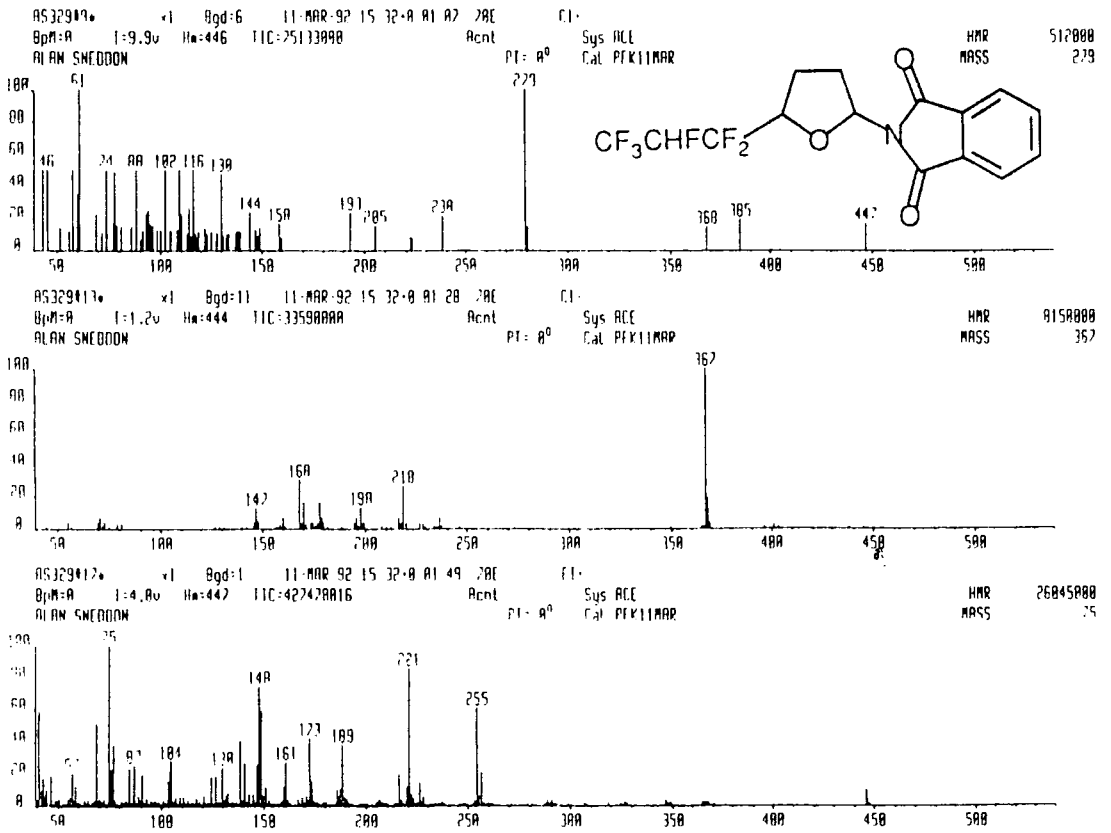


58. 2-Methoxy-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane



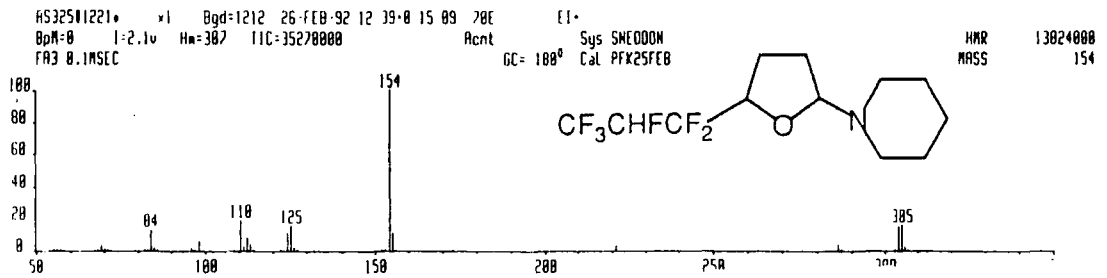
Mass	% Base		
55.06	0.73	131.19	4.77
57.07	0.57	133.15	0.63
58.10	1.17	145.14	0.44
59.09	3.67	149.15	0.88
63.08	0.85	151.13	1.64
69.10	1.17	163.24	0.35
71.11	35.01	171.17	0.85
72.12	1.83	183.12	0.63
75.11	100.00	199.20	2.09
76.12	3.76	207.23	2.12
77.10	0.85	211.24	0.73
81.09	1.04	219.22	19.24
85.10	0.79	220.24	1.83
88.13	2.84	231.19	0.51
99.14	8.09	231.28	0.44
100.15	3.41	250.25	1.33
101.14	0.70	251.27	48.53
109.15	0.47	252.27	4.45
117.12	3.29		

59. 2-Phthalimido-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane



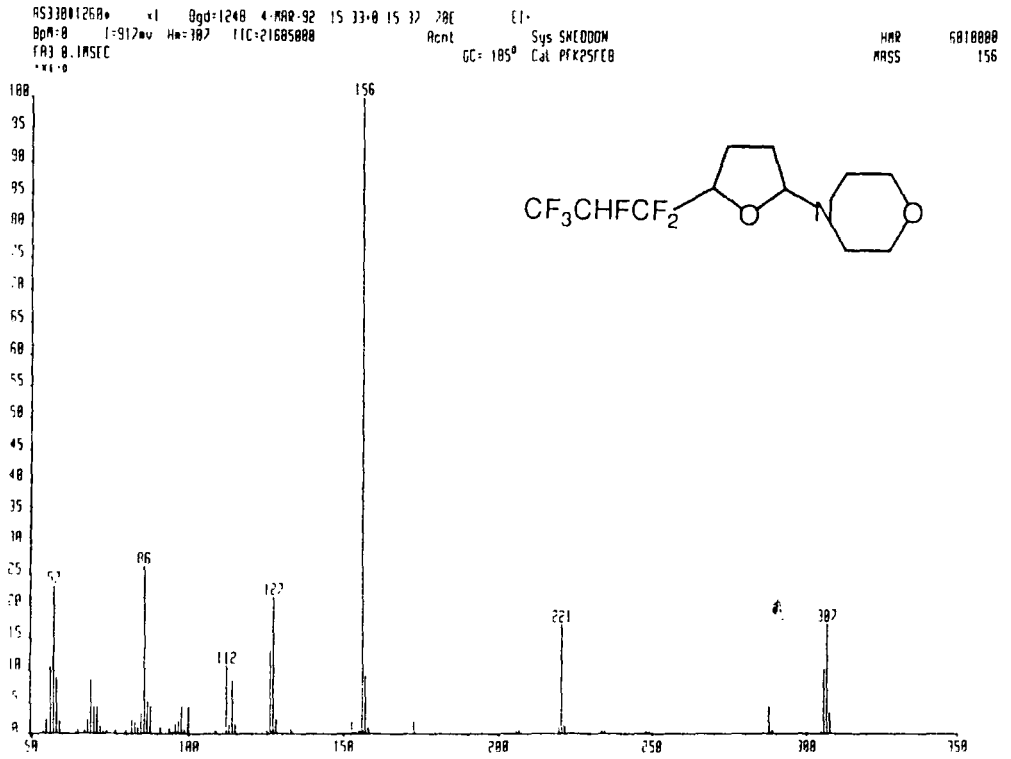
Mass	% Base						
44 94	3 58	177 91	16 07	349 83	0 45
54 92	3 14	178 91	6 28	364 87	0 99
56 92	0 74	179 91	3 14	365 83	1 25
69 87	3 14	181 93	0 64	366 87	100 00
70 88	6 50	188 90	0 95	367 88	18 85
71 86	1 44	194 89	3 07	368 89	3 14
72 87	3 88	195 90	6 49	395 84	0 59
74 87	0 52	196 90	1 04	400 81	2 00
78 86	2 74	197 91	13 12	402 79	0 63
80 86	2 87	198 92	3 14	437 86	0 72
126 83	0 98	199 91	3 14	444 90	0 82
128 93	0 58	207 89	1 15		
130 91	0 79	209 83	0 49		
139 91	0 92	211 88	0 75		
141 93	0 48	215 87	6 28		
145 93	3 14	216 91	3 14		
146 94	11 88	217 91	26 37		
147 93	3 80	218 91	3 14		
155 86	0 40	225 88	3 14		
156 88	0 66	227 90	2 58		
157 90	1 66	228 91	0 96		
158 88	0 64	232 86	0 52		
159 88	6 32	233 86	0 82		
160 93	0 77	234 87	0 77		
167 92	29 98	235 90	6 28		
168 93	3 14	236 90	1 36		
169 91	15 72	245 91	0 85		
170 91	1 68	272 97	3 92		
173 92	3 14				
174 90	3 14				
175 89	1 35				
176 91	3 14				

60. 2-Piperidino-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane



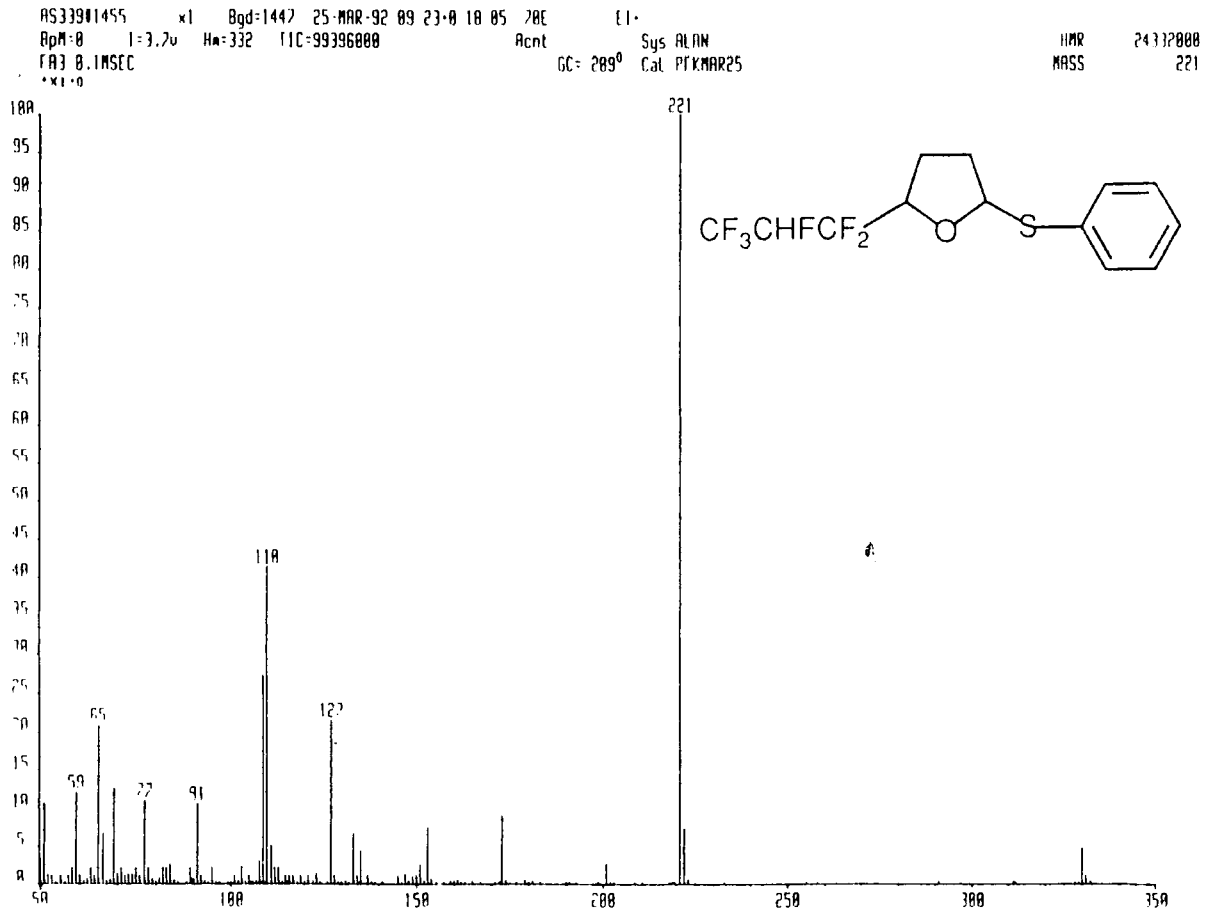
Mass	% Base			
55.04	0.52	123.10	0.31	
56.05	0.83	124.10	11.11	
57.06	0.75	125.11	15.47	
68.05	0.51	126.11	2.05	
69.05	3.70	127.02	0.62	
70.06	1.01	131.99	0.33	
71.04	0.93	152.09	0.81	
82.05	0.46	153.06	0 72	
83.06	0.91	154.09	100.00	
84.06	12.96	155.09	11.11	
85.06	1.85	156.10	0.73	
86.07	0.86	173.03	0.53	
96.07	1.87	221.03	3.07	
97.08	0.49	286.10	3.95	
98.07	5.56	287.10	0.54	
110.08	18.53	303.10	0.45	
111.09	2.34	304.07	14.81	F
112.06	7.90	305.09	15.13	F
113.06	3.70	306.09	2.16	
114.07	0.62			
122.08	0.44			

61. 2-Morpholino-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane



Mass	% Base		
54.01	0.35	100.02	4.26
55.01	2.16	108.97	0.47
56.02	10.48	112.01	10.72
57.03	22.88	113.01	1.50
58.03	8.80	113.99	8.52
59.01	1.83	115.00	1.43
64.99	0.65	125.01	0.47
67.01	0.42	126.03	12.95
68.01	2.10	127.01	21.30
69.00	8.52	128.02	2.20
70.01	4.26	132.95	0.73
71.01	4.26	152.95	1.90
72.01	1.13	154.96	0.37
76.98	0.37	155.57	0.32
79.99	0.37	156.00	100.00
82.01	2.03	157.01	9.20
83.01	1.76	158.01	0.87
84.02	1.03	172.95	1.96
85.00	3.24	206.90	0.48
86.00	26.16	219.93	0.93
87.01	4.99	220.93	17.04
88.02	4.26	221.93	1.23
90.98	0.85	233.92	0.50
93.98	0.93	234.92	0.42
96.03	1.45	287.95	4.26
97.03	1.93	288.94	0.43
98.02	4.26	305.91	10.25
99.02	0.60	306.93	17.25
		307.93	3.21

62. 2-(1,1,2,3,3,3-hexafluoropropyl)-5-thiophenyloxolane



Mass	Base		Mass	Base	
48 03	1 99		134 01	0 99	
49 01	5 35		135 04	3 98	
50 01	2 45		137 03	0 99	
51 01	10 94		145 01	0 99	
52 03	0 99		147 03	1 23	
53 04	0 99		149 05	0 99	
55 02	0 99		150 05	0 76	
57 01	0 99		151 00	2 71	
57 99	1 99		153 03	6 96	
59 03	10 12		154 04	0 56	
60 03	0 38		160 03	0 35	
62 02	0 45		161 01	0 48	
63 02	1 99		173 03	8 74	
64 01	0 99		174 04	0 99	
65 04	18 15		179 05	0 42	
66 05	5 96		181 03	0 44	
68 03	0 99		201 03	2 98	
69 05	10 84		221 02	100 00	F
70 01	1 65		222 02	7 23	F
71 02	1 99		223 01	0 42	
72 03	0 99		311 04	0 32	
73 02	1 10		333 05	4 43	
74 01	0 99		333 04	0 99	
75 02	1 09				
76 02	0 99				
77 01	8 94				
78 04	1 99				
79 04	0 44				
80 98	0 99				
81 98	1 99				
83 01	1 25				
84 03	1 99				
85 01	0 32				
89 03	1 99				
89 53	0 48				
90 03	0 99				
91 04	9 94				
92 05	0 99				
95 02	1 99				
99 03	0 33				
101 32	0 99				
102 04	0 31				
103 04	1 99				
104 06	0 42				
105 05	0 99				
108 01	2 24				
109 01	26 84				
110 01	37 76				
111 01	4 28				
112 01	1 99				
113 00	1 99				
115 05	0 99				
116 07	0 49				
117 05	1 08				
119 03	0 99				
121 02	1 99				
123 02	1 63				
127 01	19 88				
128 02	0 99				
131 01	2 29				

APPENDIX THREE

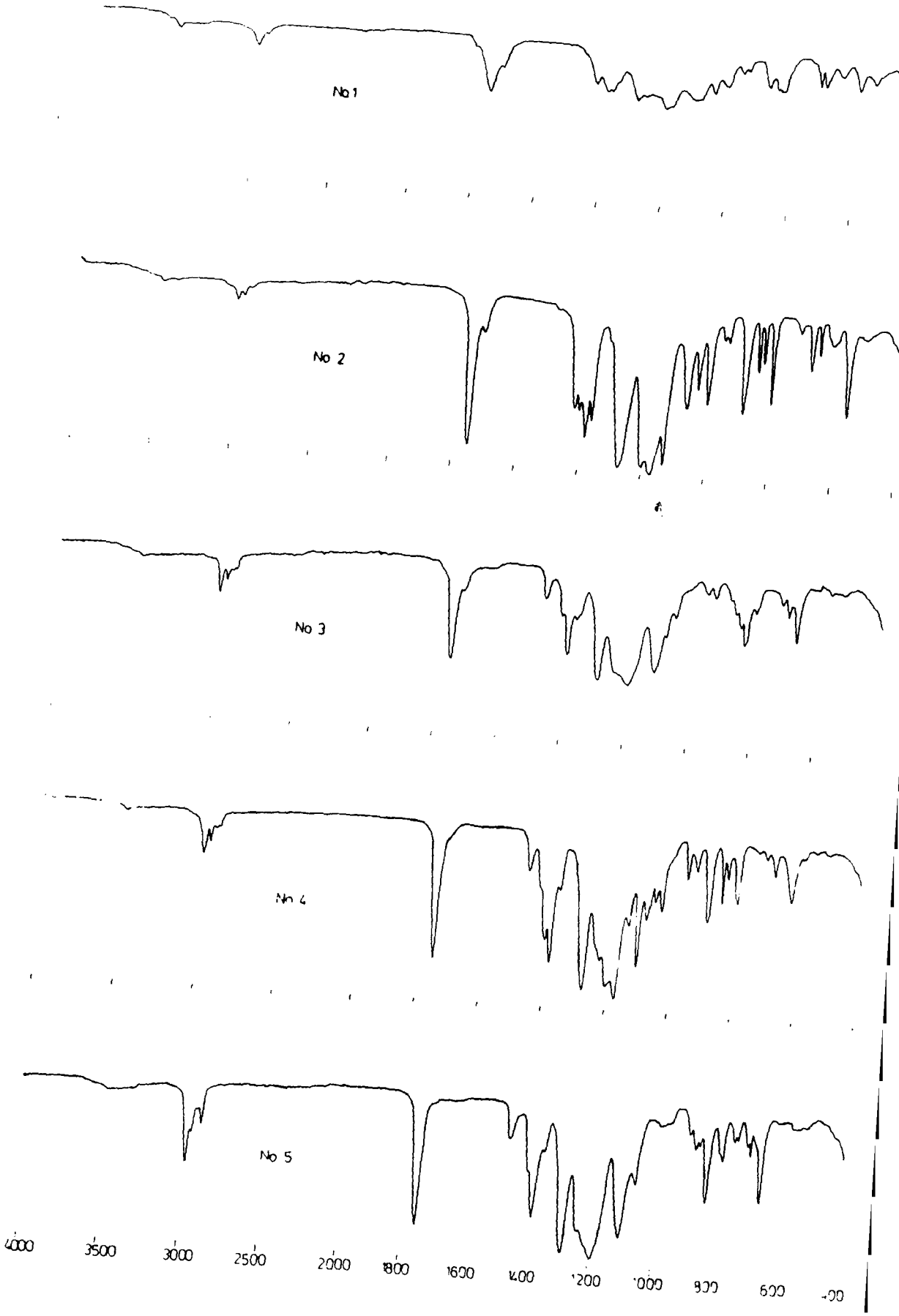
INFRA RED SPECTRA

All infra red spectra were run as thin films for liquid samples, or KBr discs for solids.

Scale in wavenumbers (cm^{-1}) is shown at the foot of each page.

CONTENTS

36. 3,3,4,5,5,5-Hexafluoro-2-(prop-2-enoxy)pentane
37. 3,3,4,5,5,5-Hexafluoro-2-(phenylmethoxy)pentane
38. (2,2,3,4,4,4-Hexafluorobutoxy)pentafluorobenzene
39. (3,3,4,5,5,5-Hexafluoropent-2-oxy)pentafluorobenzene
40. (2,2,3,4,4,4-Hexafluorobutoxy)-2,4-dinitrobenzene
41. (3,3,4,5,5,5-Hexafluoropent-2-oxy)-2,4-dinitrobenzene
42 4-(2,2,3,4,4,4-Hexafluorobutoxy)tetrafluoropyridine
43. 4-(3,3,4,5,5,5-Hexafluoropent-2-oxy)tetrafluoropyridine
44. 4-(2,2,3,4,4,4-Hexafluorobutoxy)trifluoropyrimidine
45. 4-(3,3,4,5,5,5-Hexafluoropent-2-oxy)-trifluoropyrimidine
46. 5-(2,2,3,4,4,4-Hexafluorobutoxy)trifluoropyrazine
47. 5-(3,3,4,5,5,5-Hexafluoropent-2-oxy)-trifluoropyrazine
48. 4-(2,2,3,4,4,4-Hexafluorobutoxy)trifluoropyridazine
49. 4-(3,3,4,5,5,5-Hexafluoropent-2-oxy)-trifluoropyridazine
50. 2,2,3,4,4,4-Hexafluorobutyl 4-methylbenzenesulphonate
51. 3,3,4,5,5,5-Hexafluoropentyl 2-(4-methylbenzenesulphonate)
52. 1,1,1,2,3,3,8,8,9,10,10,10-Dodecafluorodecyl
    4,7-bis(4-methylbenzenesulphonate)
53. 3,3,4,5,5,5-Hexafluoropentyl 2-(trichloromethanesulphonate)
54. 2-Chloro-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane
55. 2-Phthalimido-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane
56. 2-Piperidino-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane
57. 2-Morpholino-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane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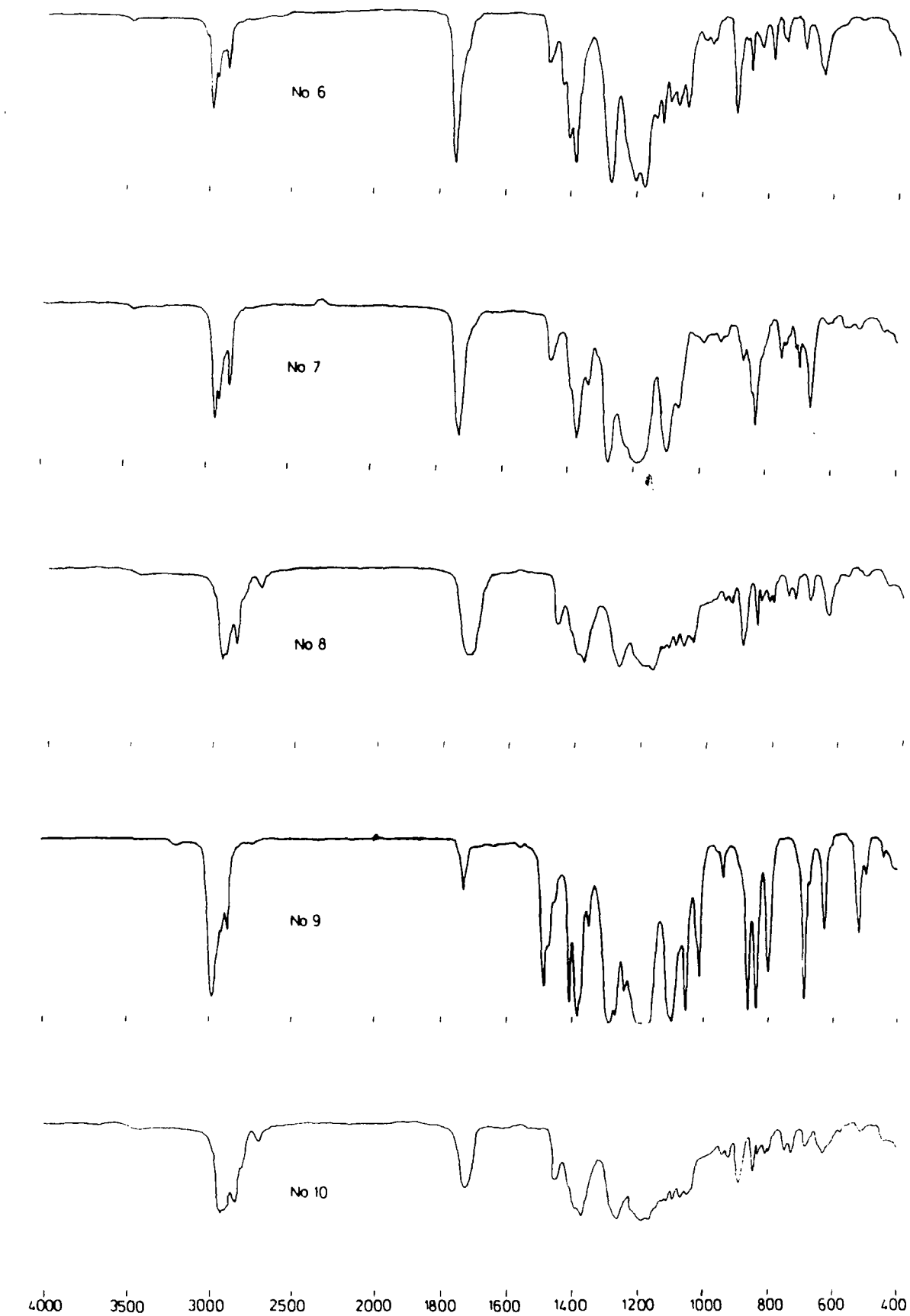
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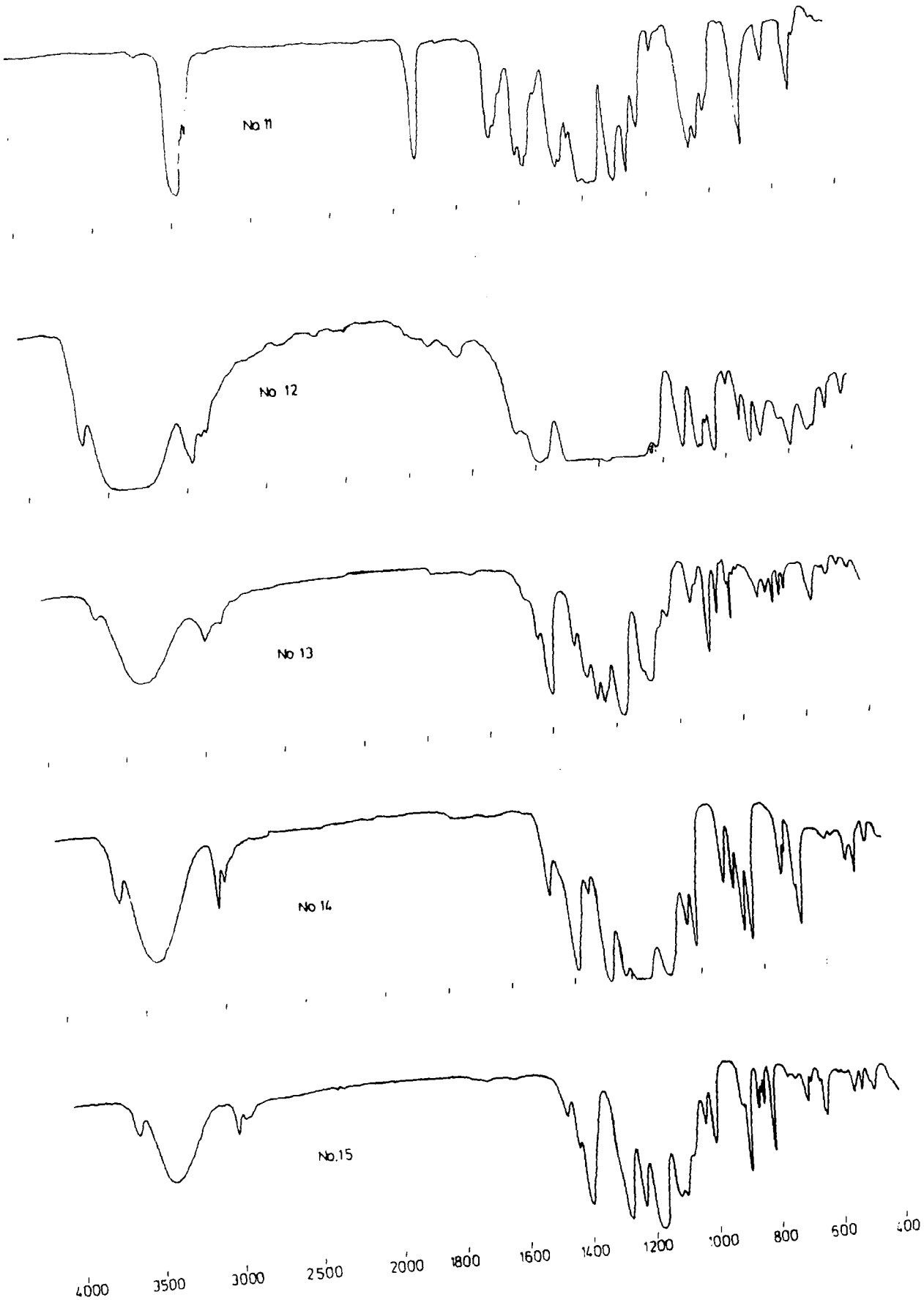
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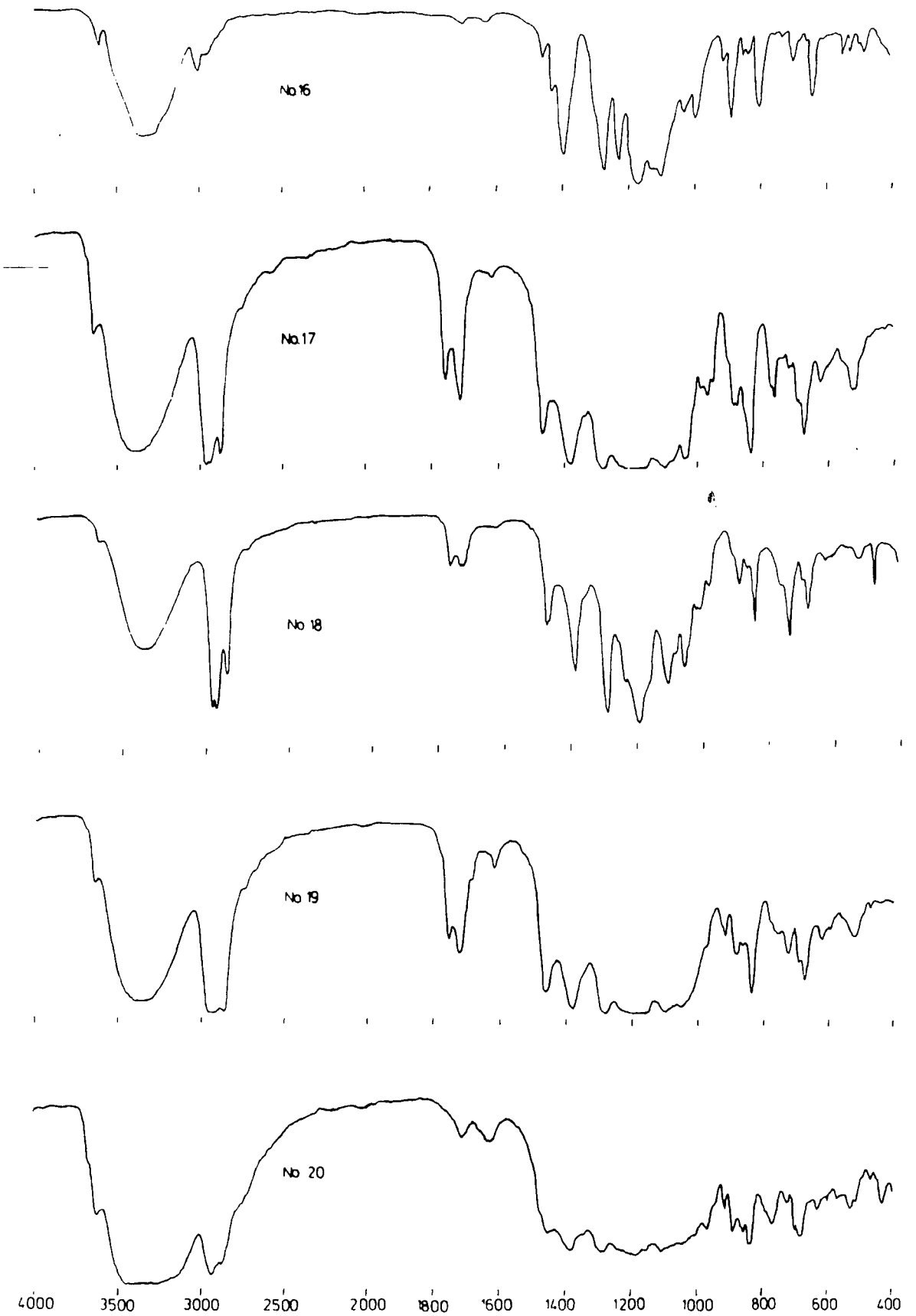
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1200
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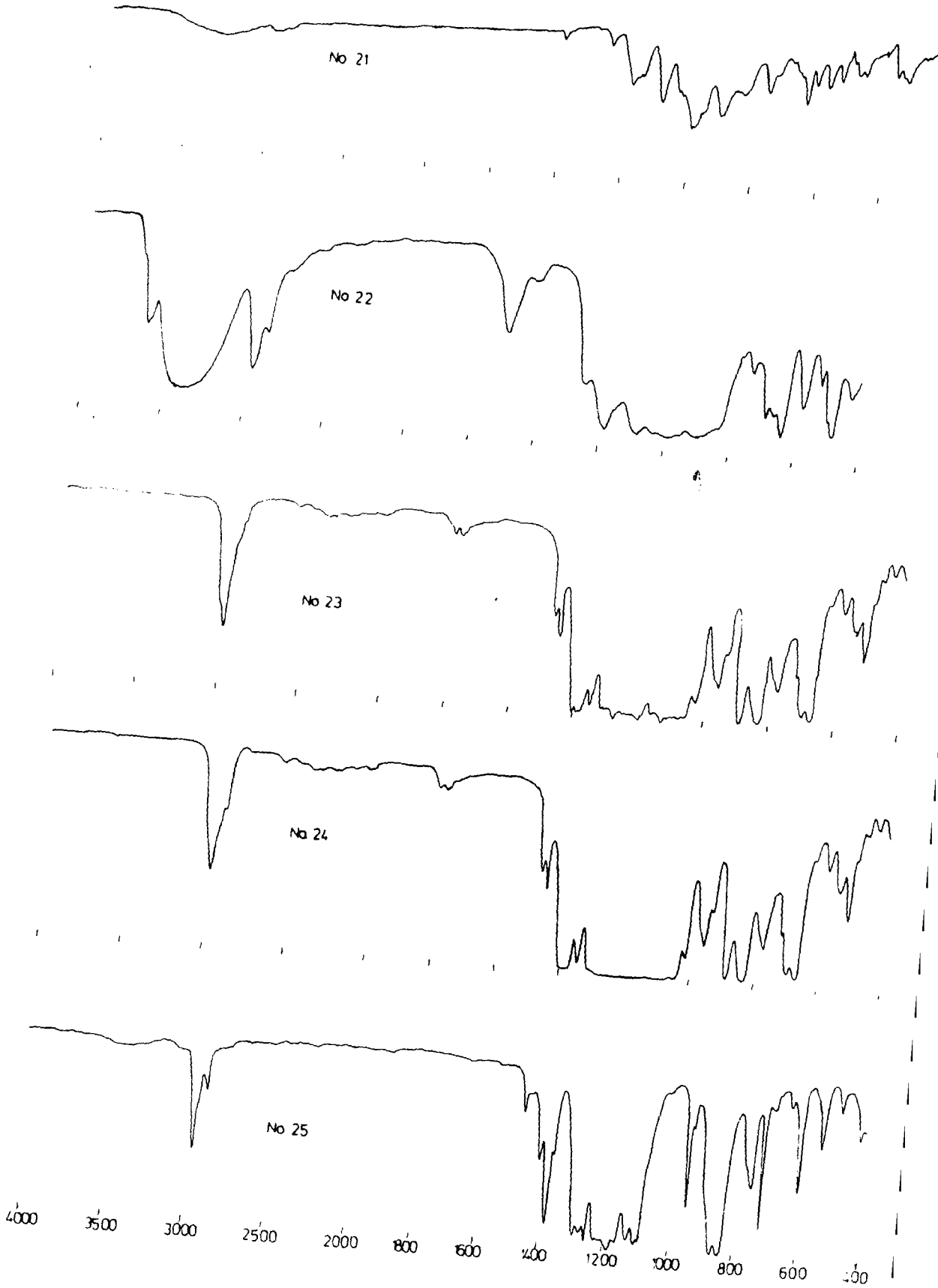
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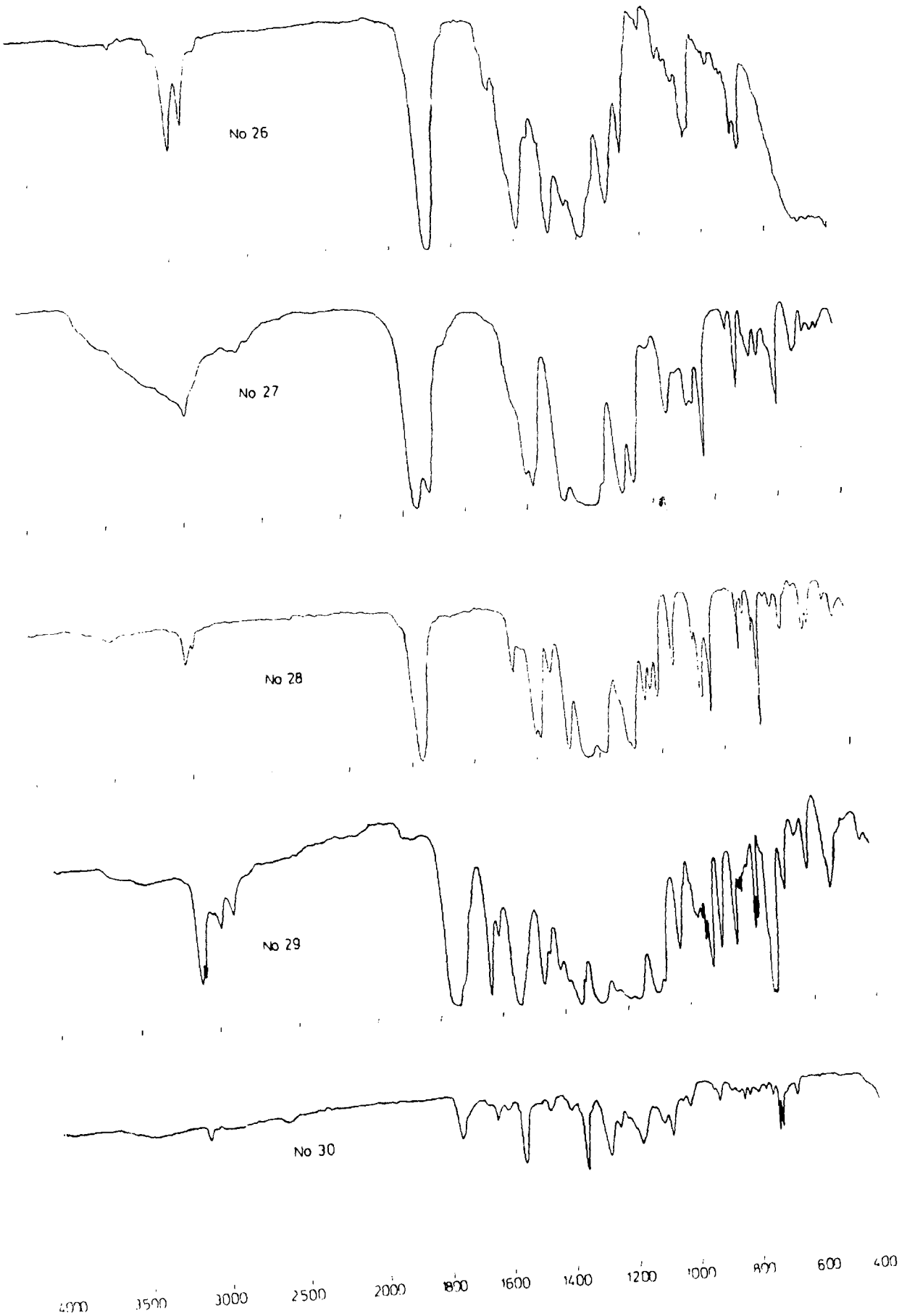
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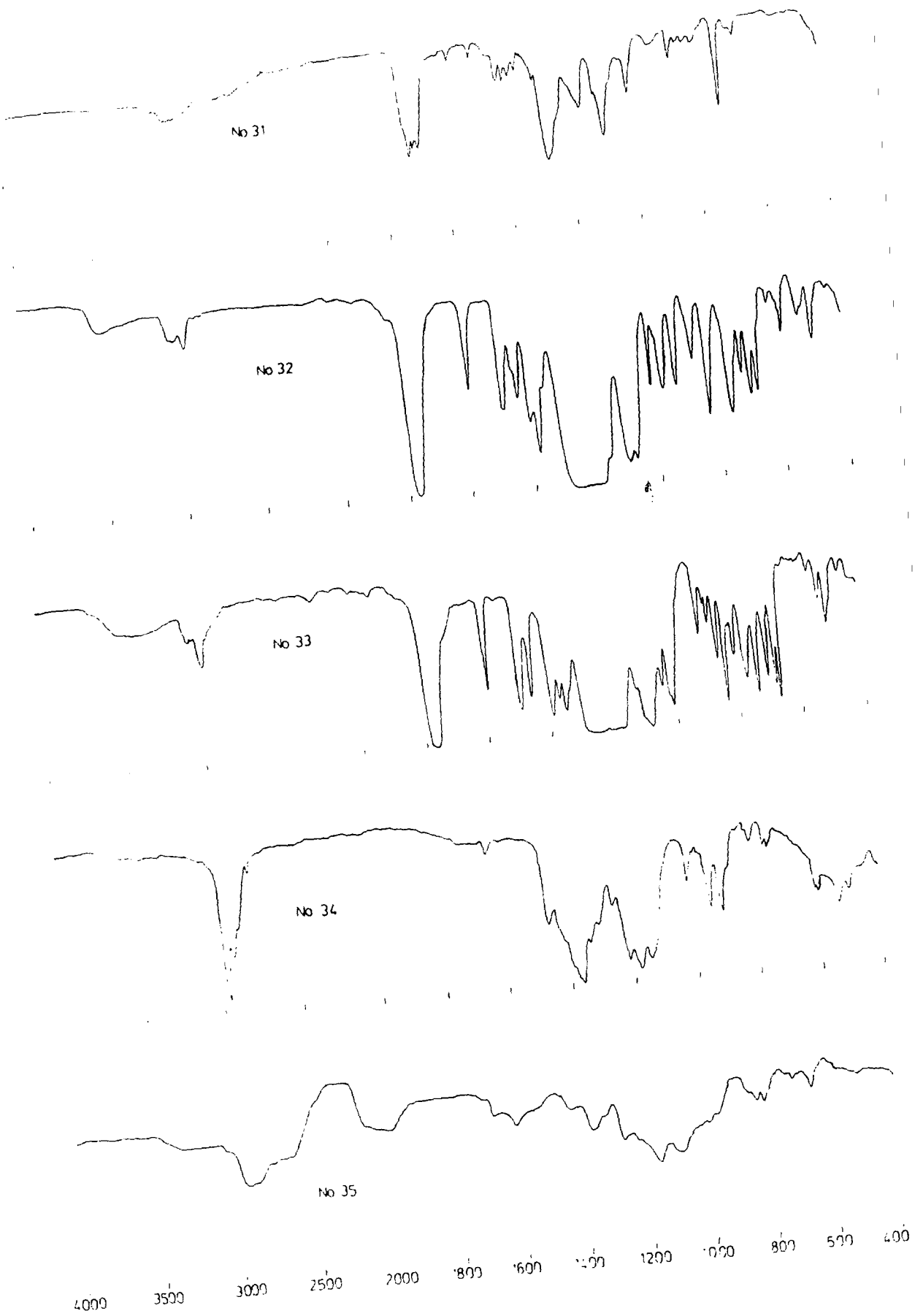
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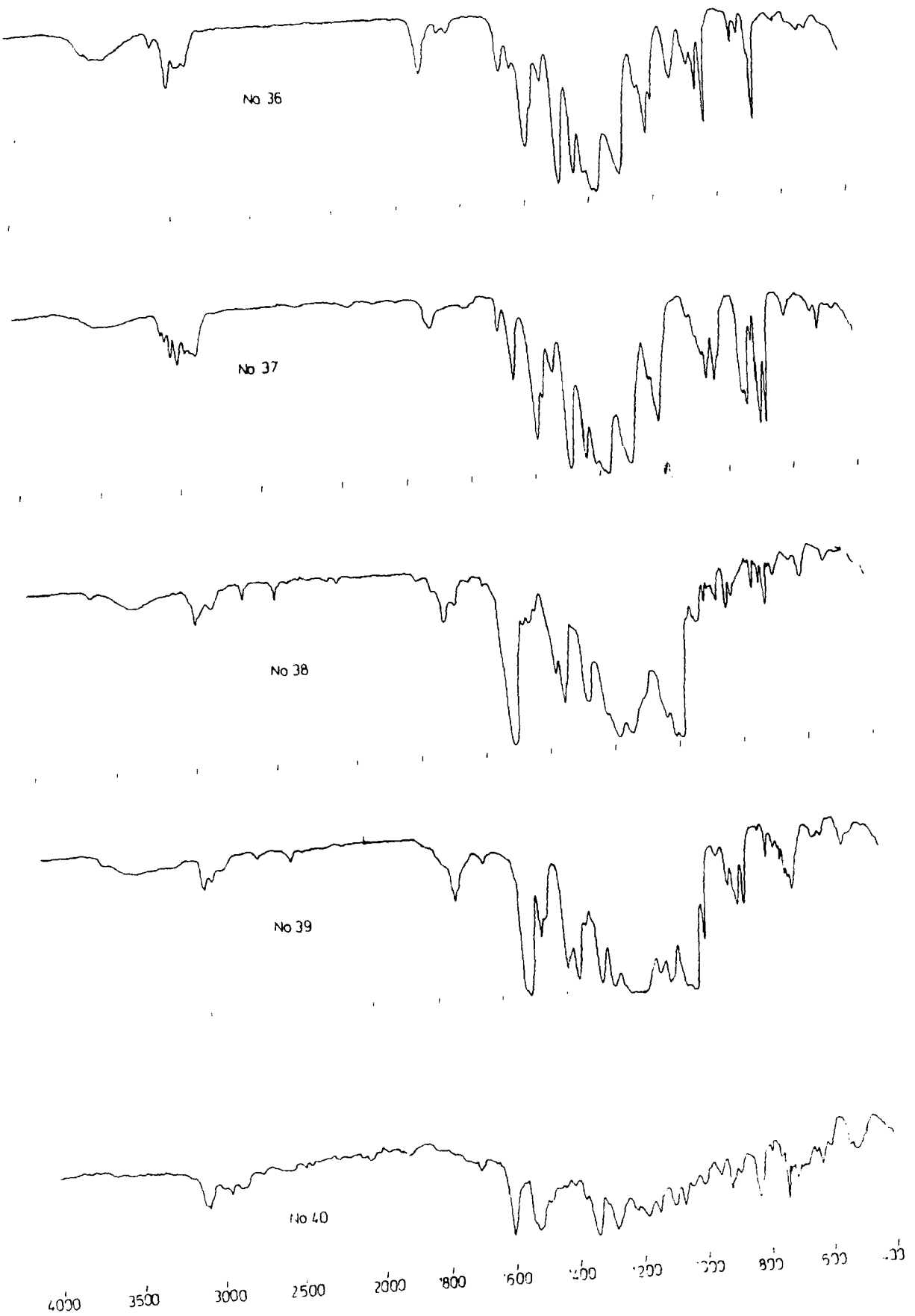
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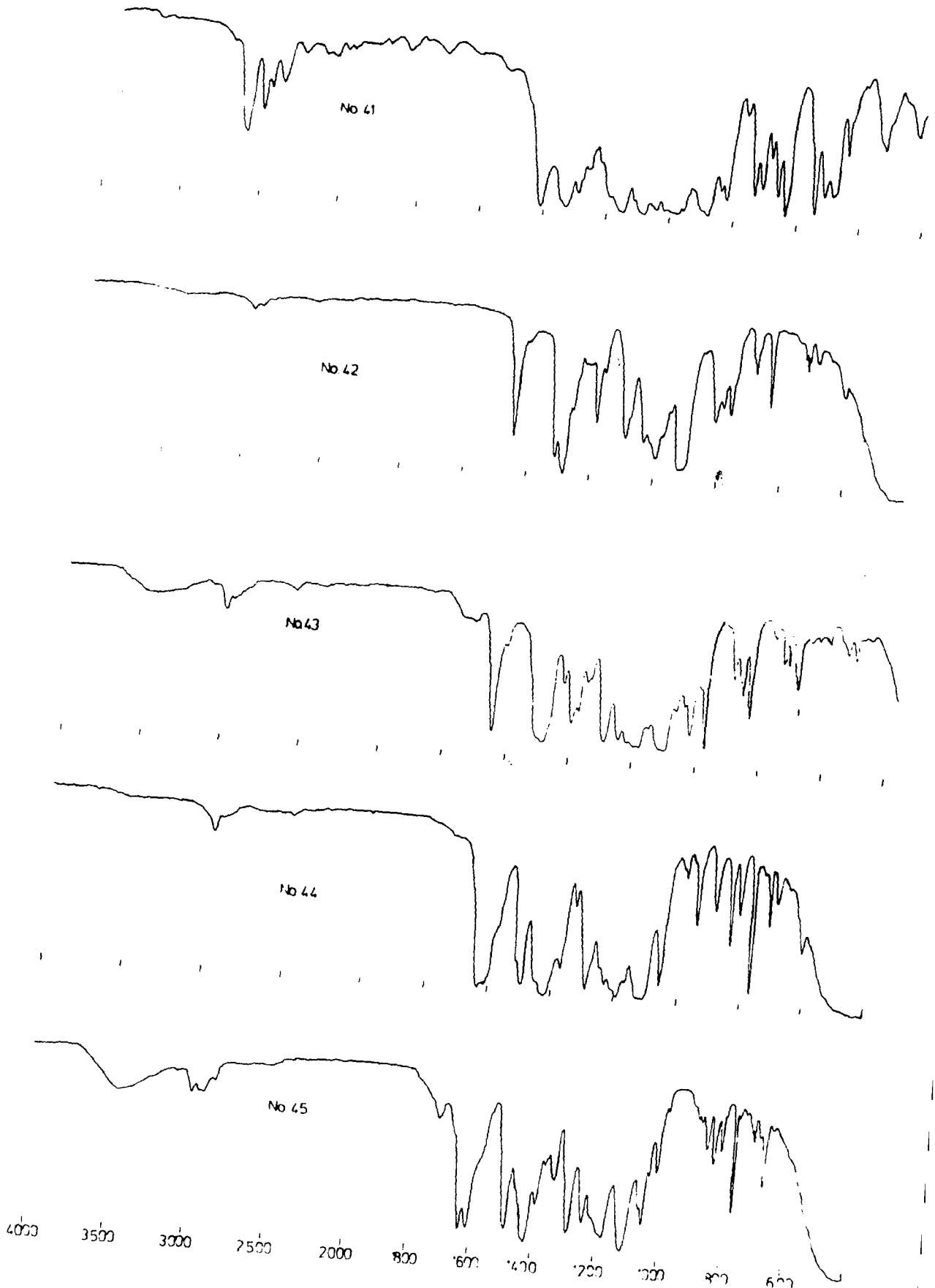
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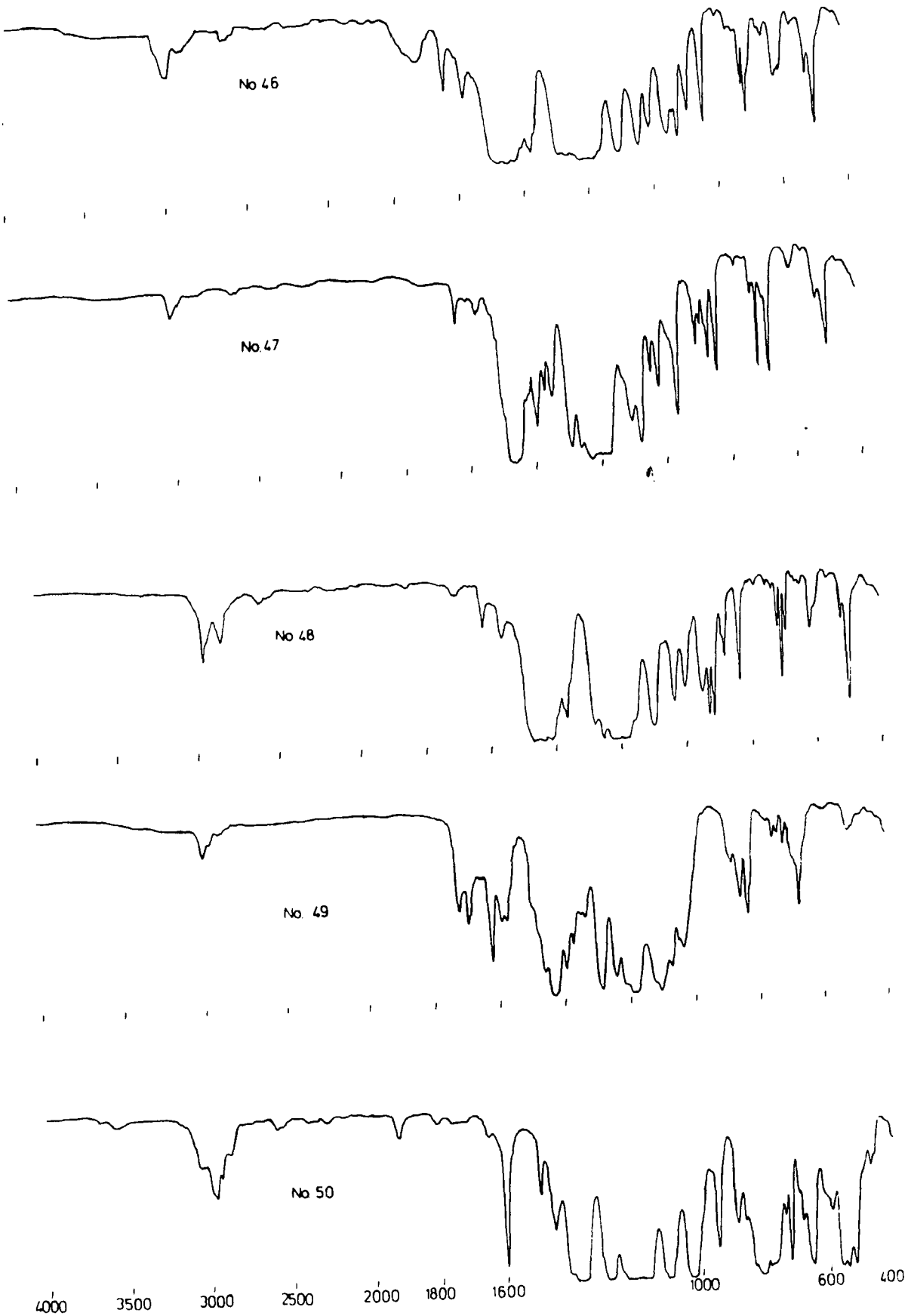
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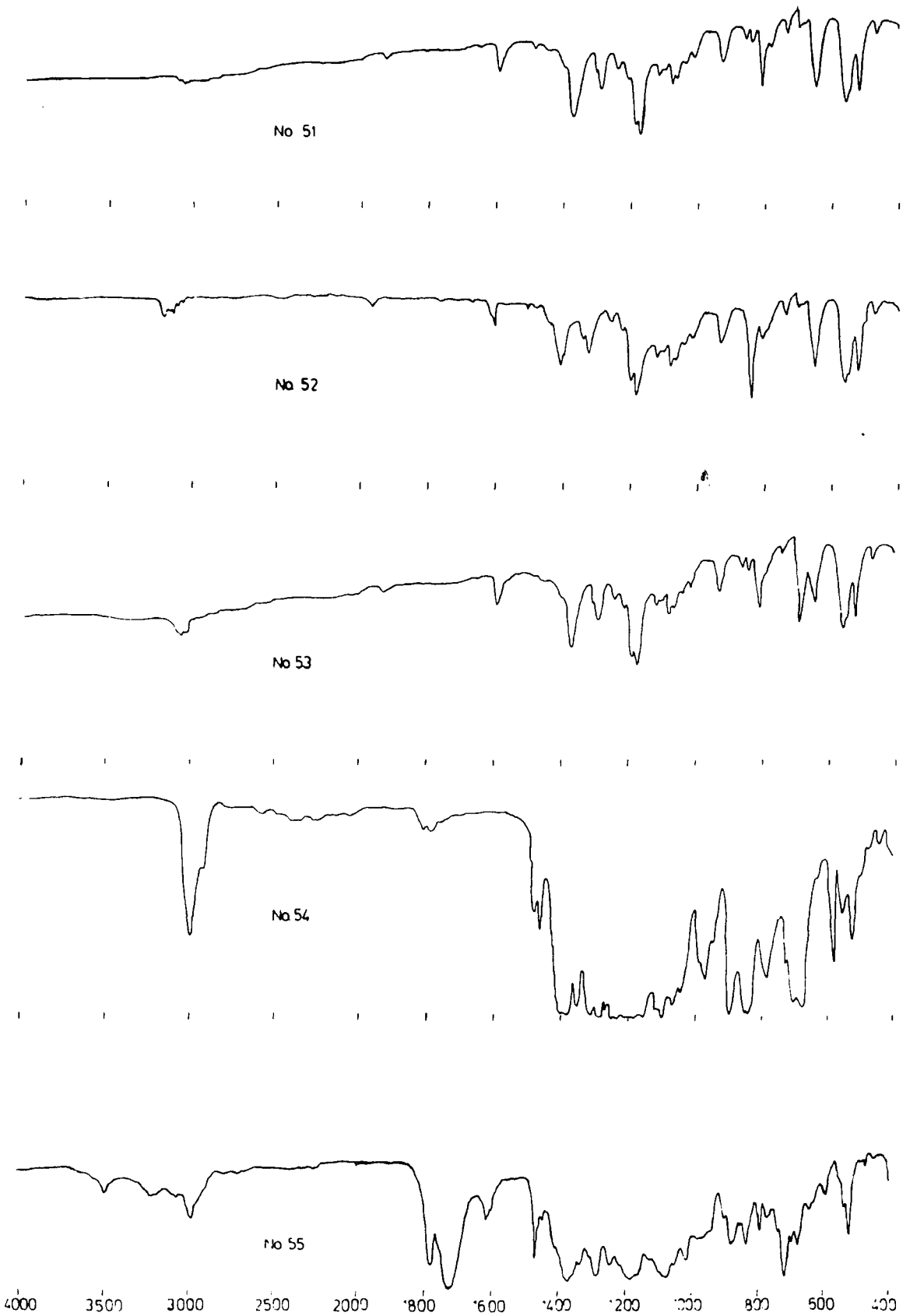
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APPENDIX FOUR

RESEARCH COLLOQUIA, SEMINARS, LECTURES AND CONFERENCES

FIRST YEAR INDUCTION COURSES: OCTOBER 1989

The course consists of a series of one hour lectures on the services listed below:

1. Departmental Organisation
2. Safety Matters
3. Electrical Appliances and Infrared Spectroscopy
4. Chromatography and Microanalysis
5. Atomic Absorption and Inorganic Analysis
6. Library Facilities
7. Mass Spectroscopy
8. Nuclear Magnetic Resonance
9. Glass Blowing Techniques

EXAMINED LECTURE COURSE (OCTOBER - NOVEMBER 1989)

The course consisted of six one-hour lectures followed by a written examination:

"Modern N.M.R. Techniques"- Prof. R.K. Harris.

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS
(* indicates attendance by the author)

BADYAL, Dr J.P.S. (Durham University) 1st November 1989
Breakthroughs in Heterogeneous Catalysis

*BECHER, Dr.J. (Odense University) 13th November 1989
Synthesis of New Macrocyclic Systems using Heterocyclic Building Blocks.

BERCAW, Prof. J.E. (Calif. Inst. of Tech.) 10th November 1989
Synthetic and Mechanistic Approaches to Zieger-Natta Polymerisation of Olefins

BLEASDALE, Dr. C. (Newcastle University) 21st February 1990
The Mode of Action of some Anti-Tumour Agents

BOWMAN, Prof. J.M. (Emory University) 23rd March 1990
Fitting Experiment with Theory in Ar-OH

*BUTLER, Dr. A. (St. Andrews University) 7th December 1989
The Discovery of Penicillin: Facts and Fancies

CHEETHAM, Dr.A.K. (Oxford University) 8th March 1990
Chemistry of Zeolite Cages

*CLARK, Prof. D.T. (ICI Wilton) 22nd February 1990
Spatially Resolved Chemistry (using Nature's Paradigm in the Advanced Materials Arena).

COLE-HAMILTON, Prof. D.J. (St. Andrews Uni.) 29th November 1989
New Polymers from Homogeneous Catalysis

CROMBIE, Prof. L. (Nottingham University) 15th February 1990
The Chemistry of Cannabis and Khat

DYER, Dr. U. (Glaxo) 31st January 1990
Synthesis and Conformation of C-Glycosides

FLORIANI, Prof. C. (Lausanne Uni., Switz'land) 25th October 1989
Molecular Aggregates- A Bridge Between Homogeneous and Heterogeneous Systems

*GERMAN, Prof. L.S. (USSR Academy of Sciences) 9th July 1990
New Syntheses in Fluoroaliphatic Chemistry:
Recent Advances in the Chemistry of Fluorinated Oxiranes.

GRAHAM, Dr.D. (B.P. Research Centre) 4th December 1989
How Proteins Absorb to Interfaces

GREENWOOD, Prof. N.N. (University of Leeds) 9th November 1989
Novel Cluster Geometries in Metalloborane Chemistry

*HOLLOWAY, Prof. J.H. (University of Leicester) 1st February 1990
Noble Gas Chemistry

*HUGHES, Dr.M.N. (King's College, London) 30th November 1989
A Bug's Eye View of the Periodic Table

*HUISGEN, Prof. R. (Universität München) 15th December 1989
Recent Mechanistic Studies of [2+2] Additions

KLINOWSKI, Dr.J. (Cambridge University) 13th December 1989
Solid State NMR Studies of Zeolite Catalysts

*LANCASTER, Rev. R. (Kimbolton Fireworks) 8th February 1990
Fireworks - Principles and Practice.

LUNAZZI, Prof. L. (University of Bologna) 12th February 1990
Application of Dynamic NMR to the Study of Conformational Enantiomerism

PALMER, Dr. F. (Nottingham University) 17th October 1989
Thunder and Lightning

*PARKER, Dr. D. (Durham University) 16th November 1989
Macrocycles, Drugs and Rock'N'Roll

PERUTZ, Dr. R.N. (York University) 24th January 1990
Plotting the Course of C-H Activations with Organometallics.

*PLATONOV, Prof. V.E. (USSR Academy of Sciences)9th July 1990
Polyfluoroindanes: Synthesis and Transformation

*POWELL, Dr.R.L. (ICI) 6th December 1989
The Development of CFC Replacements

POWIS, Dr. I. (Nottingham University) 21st March 1990
Spinning off in a Huff: Photodissociation of Methyl Iodide

*ROZHKOV, Prof. I.N. (USSR Academy of Sciences) 9th July 1990
Reactivity of Perfluoroalkyl Bromides

STODDART, Dr.J.F. (Sheffield University) 1st March 1990
Molecular Lego

SUTTON, Prof. D. (Simon Fraser University., Vancouver B.C.)
14th February 1990
Synthesis and Applications of Dinitrogen and Diazo Compounds of Rhenium and Iridium.

THOMAS, Dr.R.K. (Oxford University) 28th February 1990
Neutron Reflectometry from Surfaces

THOMPSON, Dr. D.P. (Newcastle University) 7th February 1990
The Role of Nitrogen in Extending Silicate Crystal Chemistry.

ALDER, Dr. B.J. (Lawrence Livermore Labs., California)
15th January 1991
Hydrogen in all its glory

BELL, Prof. T. (SUNY, Stoney Brook, U.S.A.) 14th November 1990
Functional Molecular Architecture and Molecular Recognition

BOCHMANN, Dr. M. (University of East Anglia) 24th October 1990
Synthesis, Reactions and Catalytic Activity of Cationic Ti Alkyls

*BRIMBLE, Dr. M.A. (Massey University, N. Z.) 29th July 1991
Synthetic Studies Towards the Antibiotic Griseusin-A

BROOKHART, Prof. M.S. (Uni. of N. Carolina) 20th June 1991
Olefin Polymerisations, Oligomerisations and Dimerisations Using Electrophilic Late Transition Metal Catalysts

BROWN, Dr. J. (Oxford University) 28th February 1991
Can Chemistry Provide Catalysts Superior to Enzymes?

BUSHBY, Dr. R. (Leeds University) 6th February 1991
Biradicals and Organic Magnets

COWLEY, Prof A.H. (University of Texas) 13th December 1990
New Organometallic Routes to Electronic Materials

*CROUT, Prof. D. (Warwick University) 29th November 1990
Enzymes in Organic Synthesis

DOBSON, Dr. C.M. (Oxford University) 6th March 1991
NMR Studies of Dynamics in Molecular Crystals

GERRARD, Dr. D. (British Petroleum) 7th November 1990
Raman Spectroscopy for Industrial Analysis

*HUDLICKY, Prof. T. (Virginia Polytech. Inst.) 25th April 1991
Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products

*JACKSON, Dr. R. (Newcastle University) 31st October 1990
New Synthetic Methods: a-Amino Acids and Small Rings

KOCOVSKY, Dr. P. (Uppsala University) 6th November 1990
Stereo-Controlled Reactions Mediated by Transition and Non-Transition Metals

LACEY, Dr. D. (Hull University) 31st January 1991
Liquid Crystals

LOGAN, Dr. N. (Nottingham University) 1st November 1990
Rocket Propellants

*MACDONALD, Dr. W.A. (ICI Wilton) 11th October 1990
Materials for the Space Age

MARKAM, Dr.J. (ICI Pharmaceuticals) 7th March 1991
DNA Fingerprinting

PETTY, Dr. M. (Durham University) 14th February 1991
Molecular Electronics

PRINGLE, Dr. P.G. (Bristol University) 5th December 1990
Metal Complexes with Functionalised Phosphines

PRITCHARD, Prof. J. (Queen Mary & Westfield College, London Univ.)
21st November 1990
Copper Surfaces and Catalysts

SADLER, Dr. P.J. (Birbeck College, London) 24th January 1991
Design of Inorganic Drugs: Precious Metals, Hypertension + HIV

*SARRE, Dr. P. (Nottingham University) 17th January 1991
Comet Chemistry

SCHROCK, R.R. (Massachusetts Institute of Technology)
24th April 1991
Metal-ligand Multiple Bonds and Metathesis Initiators

*SCOTT, Dr. S.K. (Leeds University) 8th November 1990
Clocks, Oscillations and Chaos

SHAW, Prof. B.L. (Leeds University) 20th February 1991
Syntheses with Coordinated, Unsaturated Phosphine
Ligands

SINN, Prof. E. (Hull University) 30th January 1991
Coupling of Little Electrons in Big Molecules. Implications for the
Active Sites of (Metalloproteins and other) Macromolecules

SOULEN, Prof. R. (South Western University, Texas)
26th October 1990
Preparation and Reactions of Bicycloalkenes

WHITAKER, Dr. B.J. (Leeds University) 28th November 1990
Two-Dimensional Velocity Imaging of State-Selected Reaction Products

ANDERSON, Dr. M. (Shell Research) 30th January 1992
Recent Advances in the Safe and Selective Chemical Control of Insect Pests

BILLINGHAM, Dr. N.C. (University of Sussex) 5th March 1992
Degradable Plastics - Myth or Magic?

BUTLER, Dr. A.R. (St. Andrews University) 7th November 1991
Traditional Chinese herbal drugs: a different way of treating disease

COOPER, Dr. W.D. (Shell Research) 11th December 1991
Colloid science: theory and practice

FENTON, Prof. D.E. (Sheffield University) 12th February 1992
Polynuclear complexes of molecular clefts as models for copper biosites

GANI, Prof. R. (St. Andrews University) 13th November 1991
The chemistry of PLP-dependent enzymes

GEHRET, Dr. J-C (Ciba-Geigy, Basel) 13th May 1992
Some aspects of industrial agrochemical research

GRIGG, Prof. R. (Leeds University) 4th December 1991
Palladium-catalysed cyclisation and ion-capture processes

HANN, Dr. R.A. (ICI Imagedata) 12th March 1992
Electronic Photography - An Image of the Future

HARRIS, Dr. K.D.M. (St. Andrews University) 22nd January 1992
Understanding the properties of solid-inclusion compounds

HITCHMAN, Prof. M.L. (Stratchlyde Univ.) 26th February 1992
Chemical vapour deposition

*HOLMES, Dr. A. (Cambridge University) 29th January 1992
Cycloaddition reactions in the service of the synthesis of piperidine and indolizidine natural products

JOHNSON, Prof. B.F.G. (Edinburgh University) 6th November 1991
Cluster-surface analogies

KEELEY, Dr. R. 31st October 1991
Modern forensic science

KNIGHT, Prof. D.M. (University of Durham) 7th April 1992
Interpreting experiments: the begining of electrochemistry

MASKILL, Dr. H. (Newcastle University) 18th March 1992
Concerted or stepwise fragmentation in a deamination-type reaction

*MORE O'FERRALL, Dr. R. (Univ. Coll., Dublin) 20th November 1991
Some acid-catalysed rearrangements in organic chemistry

NIXON, Prof J.F. (University of Sussex) 25th February 1992
The Tilden Lecture Phosphaalkynes: new building blocks in inorganic and organometallic chemistry

*SALTHOUSE, Dr. J.A. (University of Manchester) 17th October 1991
Son et Lumiere - a demonstration lecture

SAUNDERS, Dr. J. (Glaxo Group Research Limited) 13th February 1992
Molecular Modelling in Drug Discovery

SMITH, Prof. A.L. (ex Unilever) 5th December 1991
Soap, detergents and black puddings

THOMAS, Prof. E.J. (Manchester University) 19th February 1992
Applications of organostannanes to organic synthesis

THOMAS, Dr. S.E. (Imperial College) 11th March 1992
Recent advances in organoiron chemistry

*VOGEL, Prof. E. (University of Cologne) 20th February 1992
The Musgrave Lecture Porphyrins: Molecules of Interdisciplinary Interest

*WARD, Prof. I.M. (IRC in Polymer Science and Tech., Uni. of Leeds) 28th November 1991
The SCI Lecture The Science and Technology of Orientated Polymers

RESEARCH CONFERENCES ATTENDED

SCI Fine Chemicals Group,
Graduate Symposium,
University of York.
March 1990.

North East Graduate Symposium,
University of Durham.
April 1991.

13th International Symposium on Fluorine Chemistry,
Bochum,
Germany.
2-6th September 1992.

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REFERENCES

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72. USP 3 178 484.
73. USP 1178 483.
74. Fr P 1 383 927.
75. Fr P 1 396 709.
76. BP 612 914.
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