The chemistry of trifluoroethene

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UNIVERSITY OF DURHAM

A THESIS

entitled

THE CHEMISTRY OF TRIFLUOROETHENE

submitted by

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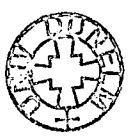

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Memorandum

The work described in this thesis was carried out at the University of Durham between October 1994 and September 1997. This thesis is the work of the author, except where acknowledged by reference, and has not been submitted for any other degree.

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Abbreviations

The following are used throughout this thesis:

DTBP	Di-tert butyl peroxide
GLCMS	Gas-liquid chromatography-mass spectrometry
HF	Hydrogen fluoride
HFP	Hexafluoropropene
IR	Infrared
NMR	nuclear magnetic resonance
TFE	Tetrafluoroethene
VDF	1,1-difluoroethene
s	singlet
d	doublet
t	triplet
q	quartet
quint	quintet
sex	sextet
m	multiplet

Abstract

The Chemistry of Trifluoroethene
by A. H. S. Gilani

The research described within this thesis may be divided into three main subject areas:

1) Free radical additions and telomerisations with trifluoroethene using alcohols, ethers, amines and aldehydes as chain transfer agents to produce a range of functionalised, fluorinated species. The effect of various reactions of the adducts of trifluoroethene have been studied.

2) Free radical polymerisation of trifluoroethene both with and without solvents and also on the surface of titanium dioxide. Fluorination and pyrolysis of the polymers prepared has been studied

3) Cohalogenation of trifluoroethene with a variety of alcohols and bromine or iodine to produce a range of halofluoroethers. The cohalogenation has been extended to other fluorinated alkenes.

Contents

Chapter 1

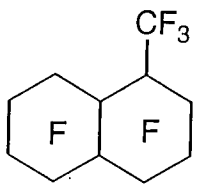
Chemistry of Trifluoroethene

1.1 Fluorine in Organic Chemistry

There are very few naturally occurring compounds containing fluorine. Therefore, replacement of hydrogen with fluorine in an organic molecule (either singly, multiply or completely) opens up a new field of chemistry that is almost entirely synthetic. Methods for the introduction of fluorine into organic compounds have been reviewed elsewhere.[1, 2]

Organofluorine compounds have found wide ranging and commercially very important applications.[3] Perfluorinated compounds have found widespread application such as inert lubricants, coatings and polymers due to their possessing desirable properties such as high chemical and thermal stability and non-stick properties. The ability of perfluoromethyldecalin (**1**) to absorb large quantities of oxygen and carbon dioxide has prompted study into its use as a blood substitute.

In addition, partially fluorinated organic compounds have demonstrated valuable biological activity, for example the anti-depressant Prozac (**2**) and the plant protection agent Trifluralin (**3**).



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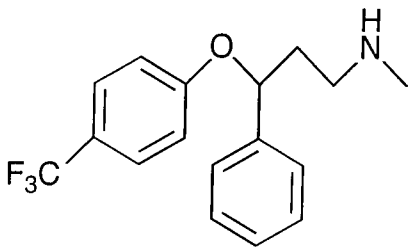

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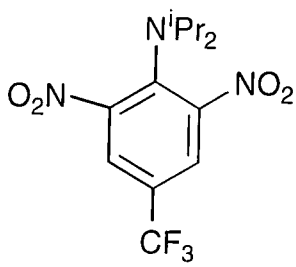


(3)

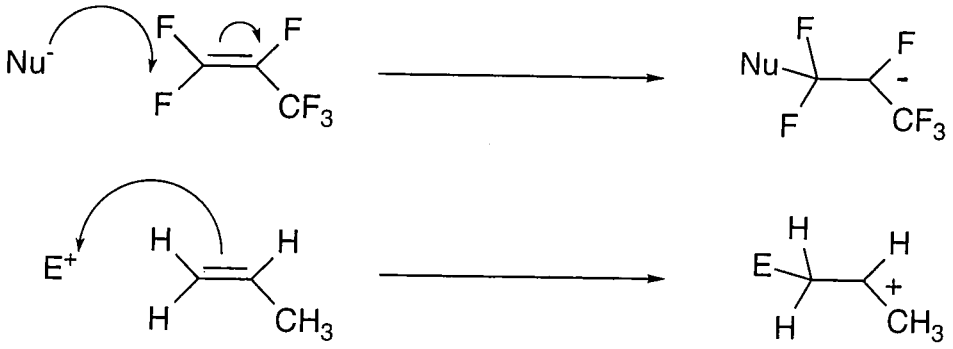
In addition to these applications, organofluorine compounds open up a new field of chemistry. Replacing hydrogen with fluorine (atomic radii 1.2 Å and 1.35 Å respectively) in a given molecule does not have a major steric effect, particularly in comparison with other halogens. On the other hand, fluorine drastically alters the electronic environment of the molecule due to the high electronegativity of fluorine. Hence fluorocarbon and hydrofluorocarbon compounds display properties that complement the chemistry of the corresponding hydrocarbon compounds.[1]

These effects are illustrated by the influence of fluorine substituents on the properties of alkenes.

The relatively small steric effect of fluorine is illustrated by the fact that most highly substituted alkenes, e.g. tetrachloroethene, are not polymerisable except under very forcing conditions due to steric demand. However, highly substituted fluoro-alkenes, e.g. tetrafluoroethene and trifluoroethene, constitute a special case as these alkenes are polymerisable.

In contrast, the electronic effect of fluorine completely transforms the chemistry of alkenes. Hydrocarbon alkenes are electron rich and therefore susceptible to

electrophilic attack to give carbocation intermediates whereas fluorocarbon alkenes are electron deficient relative to their hydrocarbon analogues, hence their ionic chemistry is dominated by nucleophilic attack to give carbanion intermediates.

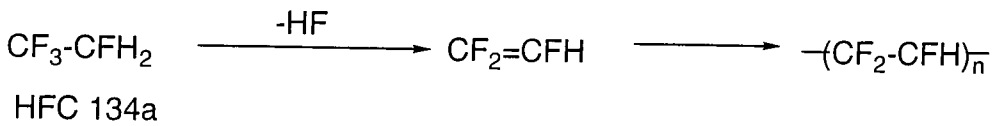


Scheme 1.1.1

1.2 Aims of the Project

The aims of this project are to study the chemistry of trifluoroethene and its derivatives. At present, trifluoroethene is not readily available and this has resulted in its chemistry (e.g. polymerisation) being neglected, particularly in comparison with that of the more readily available fluoro-olefins such as 1,1-difluoroethene, tetrafluoroethene, hexafluoropropene and chlorotrifluoroethene.

The preparation of trifluoroethene by the dehydrofluorination of 1,1,1,2-tetrafluoroethane (HFC 134a) has recently been reported[4] (scheme 1.2.2). HFC 134a is now being produced on a large scale as a CFC replacement that is not detrimental to the ozone layer, hence this is a potential route to trifluoroethene as a commodity chemical.



Scheme 1.2.2

Some older syntheses of trifluoroethene are given in table 1.2.1. These generally involve dehydrohalogenation or dehalogenation of a halofluoroalkane.

Table 1.2.1 Syntheses of trifluoroethene

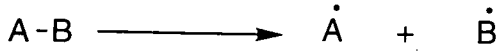
Precursor	Reagent	Reference
ClF_2C-CClFH	Zn / EtOH	5
F_2C=CFCl	i) HBr, 100°C ii) Zn	6
HF_2C-CFHBr	Zn / dioxane	7
BrClFC-CF_2Br	Na / Hg, aq. H_2SO_4	8
F_2C=CFCl	H_2 / Pd	9
F_2C=CFBr	Mg / tetrahydrofuran	10

This introduction is intended to be a general overview of the chemistry of trifluoroethene. This has been subdivided into five categories: synthesis, free radical addition and telomerisation, nucleophilic chemistry, electrophilic chemistry and organometallic chemistry. Wherever possible, the chemistry of trifluoroethene is contrasted with that of other fluoro-alkenes

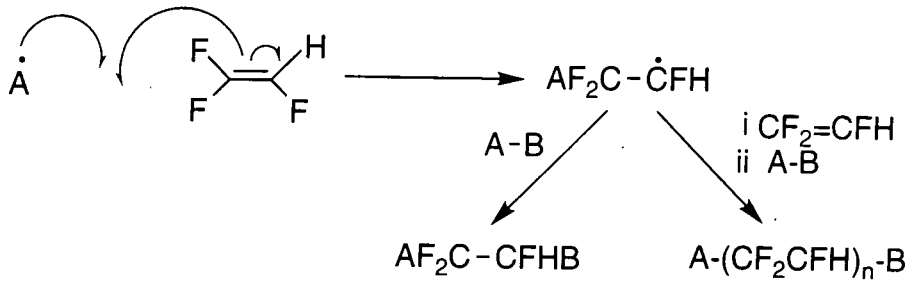
1.3 Free Radical Addition and Telomerisation

Free radical additions to alkenes are a synthetically valuable method in the formation of carbon-carbon bonds and in the case of fluoro-alkenes it is a useful method for the introduction of polyfluoralkyl groups to give functionalised, fluorinated compounds. These reactions follow a well established chain reaction mechanism (scheme 1.3.1).

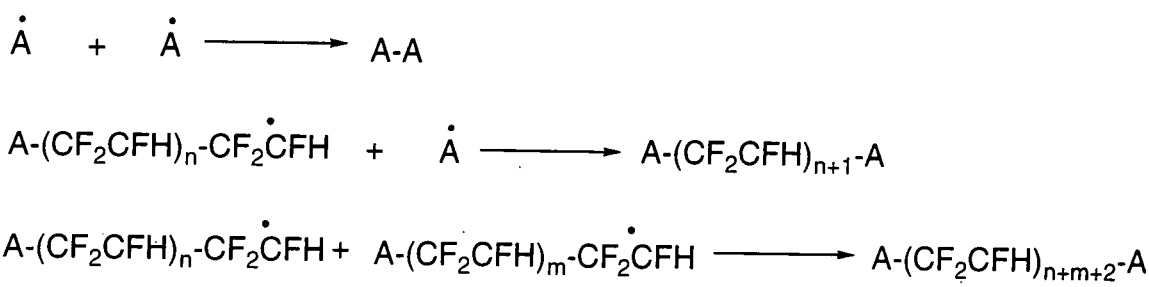
Initiation



Propagation

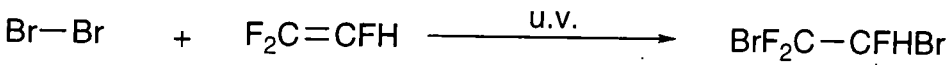


Termination



Scheme 1.3.1

For example, the addition of bromine to trifluoroethene reported by Park in 1951[6] (scheme 1.3.2). This was the first reported free radical addition to trifluoroethene.



Scheme 1.3.2

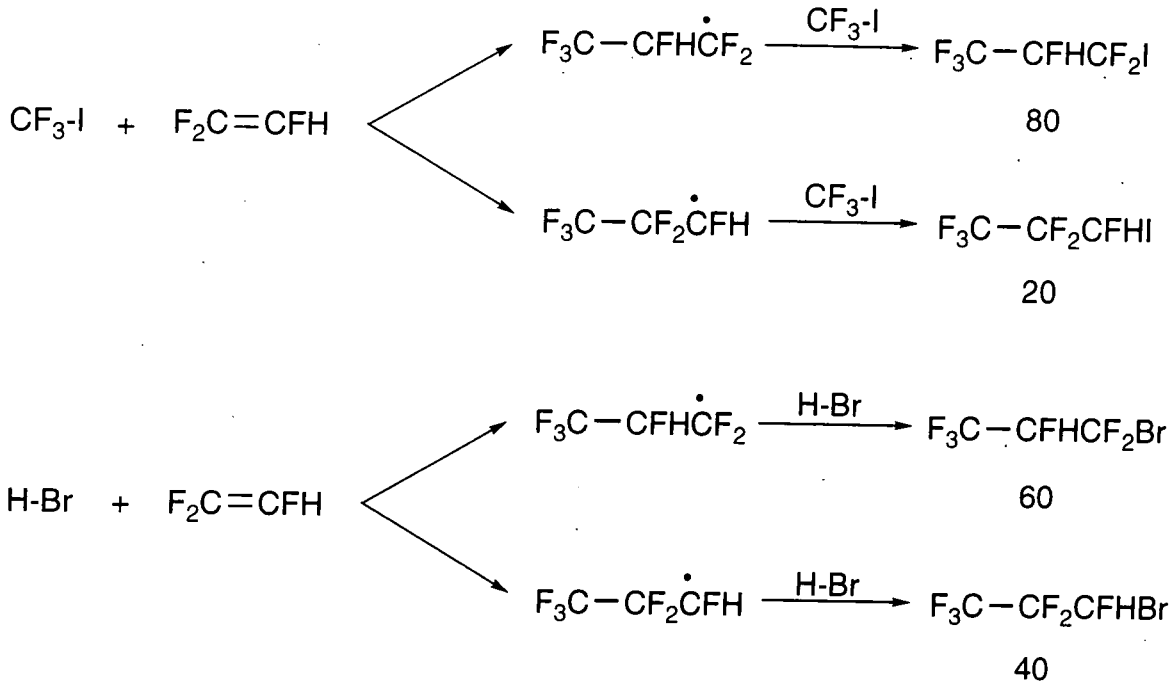
In the case of trifluoroethene, this mechanism raises three issues to be addressed:

i) orientation of addition of the chain transfer agent to trifluoroethene
ii) subsequent orientation of addition of trifluoroethene to the radical during chain propagation
iii) degree of propagation, i.e. the extent of telomerisation

The bulk of investigations into free-radical additions and the factors affecting orientation of addition, etc. have made use of carbon radicals, in particular the use of fluoalkyl iodides which are a convenient source of poly- and perfluoralkyl radicals.

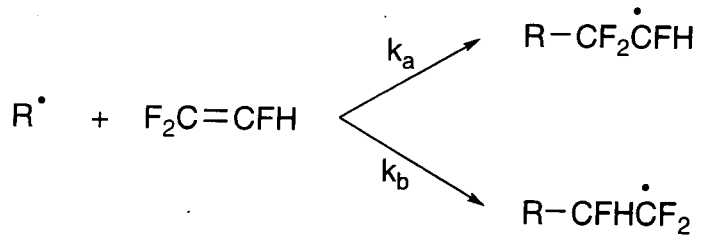
1.3.1 Orientation of Addition

The additions of hydrogen bromide and trifluoromethyl iodide to trifluoroethene reported by Haszeldine in 1957[11] (scheme 1.3.3) constituted the first instances of free radical addition at both ends of an unsymmetrical alkene.



Scheme 1.3.3

The ratio of adducts in an addition reaction to an unsymmetrical olefin is equal to the ratio of rate constants for the formation of the intermediate radicals (k_a / k_b)(scheme 1.3.4). Haszeldine initially suggested that the orientation of addition was governed by the thermodynamic stability of the intermediate radical,[11] however subsequent extensive studies by Tedder and Walton[12-14] demonstrated that other factors have an influence.



Scheme 1.3.4

Their work led to the conclusion that the rate and orientation of addition is determined by a 'complex interplay of polar, steric and bond strength terms' [13] and that

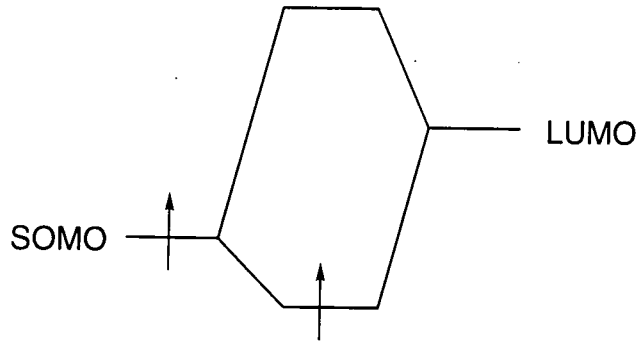
no simple rule could be formulated to determine the orientation of addition. However, it was found that steric demand is commonly the overriding factor when there is a considerable difference in the bulkiness of the substituents on the vinylic carbons. Fluoro - alkenes present a special case in that substituting hydrogen for fluorine (atomic radii 1.2 Å and 1.35 Å respectively) does not have a major impact on steric demand as illustrated by the fact that tetrafluoroethene is homopolymerisable. Hence in the case of trifluoroethene steric requirements at either end of the double bond (i.e. CF_2 vs. CFH) do not have a major impact. In consequence, other factors have a more pronounced effect.

In the absence of any great steric effect, polarity becomes the predominant factor in determining the orientation of addition to trifluoroethene. The importance of the polarity of the attacking radical in determining the overall rate of addition to symmetrical fluoro-olefins is illustrated by the addition of a series of increasingly electrophilic radicals to ethene and tetrafluoroethene.[14]

Table 1.3.1 Relative rates of radical additions to ethene and tetrafluoroethene

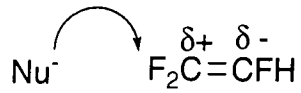
Radical	$^kC_2F_4$ / $^kC_2H_4$
CH_3•	9.5
CH_2F•	3.4
CF_2H•	1.1
CF_3•	0.1

The heightened reactivity of fluoro-olefins with nucleophilic radicals has been explained in molecular orbital terms[15] whereby reaction is between the the SOMO of the radical and the LUMO of the alkene (scheme 1.3.5). Electron withdrawing groups on the alkene lower the LUMO energy and thus increase the reaction rate with electron rich radicals by decreasing the SOMO - LUMO gap.



Scheme 1.3.5

In the case of trifluoroethene, attack at the α (CHF) end increases with increasing electrophilicity of the radical which is consistent with the fact that ionic nucleophilic attack occurs exclusively at the CF_2 site.

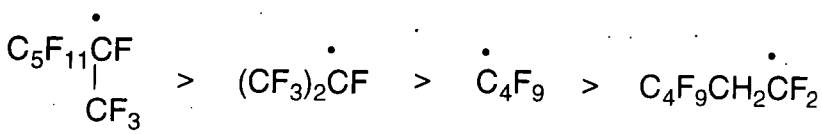


This is illustrated by the addition of a series of radicals from methyl to trifluoromethyl.[14]

Radical	$^kC_2HF_3$ / $^kC_2H_4$	α : β CHF=CF2
CH_3•	5.8	1 : 2.1
CH_2F•	-	1 : 2.0
CF_2H•	0.3	1 : 0.9
CF_3•	0.05	1 : 0.5

Table 1.3.2

The addition of perfluoroalkyl radicals has been reported by Haszeldine[11] in a study of orientation of radical addition. More recently, Ameduri *et al* [16] have reported the telomerisation of trifluoroethene with a series perfluoroalkyl iodides. Here, the orientation of addition was again found to be increasingly selective for the CHF site with increasing electrophilicity of the attacking radical with the order of selectivity as shown in scheme 1.3.6.



Scheme 1.3.6

As stated above, the steric effect of fluorine in trifluoroethene is relatively small, however a steric effect has been observed with trifluoroethene by reaction with a series of increasingly bulky bromofluoromethyl radicals (table 1.3.3). On a purely polar basis, it would be anticipated that the proportion of attack at the β site of trifluoroethene would be higher for the less electronegative radicals, however the opposite is observed which, on the basis of the principles described above, can only be attributed to steric demand.[14]

Table 1.3.3 Addition of bromofluoroalkyl radicals to trifluoroethene

Radical	α : β $CHF=CF_2$
CF_3•	1 : 0.5
CF_2Br•	1 : 0.47
$CFBr_2$•	1 : 0.36
CBr_3•	1 : 0.25

The regioselectivity studies discussed above have all been performed in the gas phase. Kotora and Hajek[17] have reported the influence of copper (I) complexes on the orientation of addition of carbon tetrachloride in the liquid phase. The use of secondary amines as ligands has the greatest effect on the orientation of addition, as illustrated in table 1.3.4. The amine ligand on the copper (I) complex is believed to influence regioselectivity by interacting with the trichloromethyl radical, however the nature of this interaction has not been elucidated.

Table 1.3.4 Orientation of addition of CCl_4 to trifluoroethene in the liquid phase

Ligand L in CuL_2Cl	α : β $CHF=CF_2$
Ethylamine	63 : 37
Diethylamine	46 : 54
Triethylamine	71 : 29

Further instances of addition and telomerisation with trifluoroethene are given in table 1.3.5. The table illustrates a general trend in regioselectivity, though it should be noted that the reactions listed were mostly performed under different conditions.

Table 1.3.5 Free radical additions and telomerisations of trifluoroethene

Molecule	Initiator	Products (% of adduct isomer)	Telomers	Ref.
Br_2	photo	$BrCFH\text{-}CF_2Br$	none	11
HBr	photo	$BrCFHCF_2H$ (58) $Br\text{-}CF_2\text{-}CFH_2$ (42)	none	11
ICl	photo	$IF_2C\text{-}CFHCl$ (74) $ClF_2C\text{-}CFHI$ (26)	none	18
CH_2ClI	thermal	$CH_2ClCFH\text{-}CF_2I$ (49) $CH_2ClCF_2\text{-}CFHI$ (51)	telomer formed	19
CH_2I_2	thermal	$CH_2ICFH\text{-}CF_2I$ (52) $CH_2ICF_2\text{-}CFHI$ (48)	none	19
$CFCl_2I$	thermal / peroxide	$Cl_2CF\text{-}CFHCF_2I$	none	7
CH_2FI	photo	$CH_2FCFH\text{-}CF_2I$ $CH_2FCF_2\text{-}CFHI$	none	20
CHF_2I	photo	$CHF_2CFH\text{-}CF_2I$ (54) $CHF_2CF_2\text{-}CFHI$ (46)	none	21
CF_3I	thermal	$CF_3CFH\text{-}CF_2I$ (68) $CF_3CF_2\text{-}CFHI$ (32)	30 %	22
CF_2Br_2	thermal / peroxide	$CF_2Br\text{-}CFHCF_2Br$ (9%)	18 %	23
CBr_3H	thermal	$CHBr_2CFH\text{-}CF_2Br$ $CHBr_2CF_2\text{-}CFHBr$ $CBr_3CFH\text{-}CF_2Br$ $CBr_3CF_2\text{-}CFHBr$	none	24

CBr_4	thermal	$BrCF_2$-CFHBr $CHBr_2CFH$-CF_2Br $CHBr_2CF_2$-CFHBr CBr_3CFH-CF_2Br CBr_3CF_2-CFHBr	3.5 %	24
CCl_4	thermal	CCl_3CFH-CF_2Cl (83) CCl_3CF_2-CFHCl (17)	telomer formed	25
CF_2Br-CFClBr	thermal	$CF_2BrCFCl$-$CFHCF_2Br$	n = 1-2	26
CF_2Cl-CFICl	thermal	$CF_2ClCFCl$-$CFHCF_2I$	none	26
isobutane	thermal	$(CH_3)_3CCF_2$-CFH_2 (55) $(CH_3)_3CCFH$-CF_2H (45)	telomer formed	27
$(CF_3)_2CFI$	thermal (190°C)	$(CF_3)_2CF$-$CFHCF_2I$ (85) $(CF_3)_2CF$-CF_2CFHI (15)	none	28
$(CF_3)_2CFI$	photo	$(CF_3)_2CF$-$CFHCF_2I$ (96) $(CF_3)_2CF$-CF_2CFHI (4)	none	28
$(CF_3)_2CFI$	thermal	$(CF_3)_2CF$-$CFHCF_2I$ (89) $(CF_3)_2CF$-CF_2CFHI (11)	n = 2 (19%) n > 2 (3%)	16
C_4F_9I	thermal	C_4F_9-$CFHCF_2I$ (75) C_4F_9-CF_2CFHI (25)	n = 2 (20%) n > 2 (5%)	16
$C_4F_9CH_2CF_2I$	thermal	$C_4F_9CH_2CF_2$-$CFHCF_2I$ (60) $C_4F_9CH_2CF_2$-CF_2CFHI (40)	n = 2 (20%) n > 2 (15%)	16

$C_5F_{11}CFICF_3$	thermal	$C_4F_9CF_2CFCF_3$- $CFHCF_2I$ (93) $C_4F_9CF_2CFCF_3$- CF_2CFHI (7)	n = 2 (22%) n > 2 (7%)	16
$F_2C=CFI$	photo	$CF_2=CFCFHCF_2I$	none	29
$F_2C=CFCl$	photo	$CF_2=CClCFHCF_2I$	none	30

Sulfur centred radicals readily participate in chain transfer reactions as shown in table 1.3.6. These reactions are so rapid that 1:1 addition products dominate, even at high olefin : telogen ratios. Less active agents are disulfides, which undergo chain transfer by scission of S-S bonds as illustrated by reaction of bis(trifluoromethyl)disulfide which does give telomers.[31] Harris and Stacey have reported the additions of methanethiol and trifluoromethanethiol. Here again, the effect of electrophilicity of the attacking radical is illustrated.

Trifluoromethanesulfenyl chloride displays an unusually high selectivity for attack at the CF_2 site of trifluoroethene. It has been suggested that this is due to initial attack on the alkene by the chlorine atom as opposed to $CF_3S\bullet$.

Table 1.3.6 Addition and telomerisation of trifluoroethene with sulfur centred radicals.

H_2S	X - ray	HS-$CFHCF_2H$ (85) HS-CF2CFH_2 (15)	none	32
CH_3SH	X - ray	CH_3S-$CFHCF_2H$ (75) CH_3S-CF_2CFH_2 (25)	none	33
CF_3SH	X - ray	CF_3S-$CFHCF_2H$	none	33
CF_3SH	u. v.	CF_3S-$CFHCF_2H$ (98) CF_3S-CF_2CFH_2 (2)	none	33
CF_3SCl	u. v.	CF_3SCF_2CFHCl (82) $CF_3SCFHCF_2Cl$ (18)	none	34
CF_3SSCF_3	photo	CF_3SCFH-CF_2SCF_3	n = 1-7	31
CF_3COSH	photo	$CF_3COSCFH$-CF_2H	none	35

SF_5Cl	photo	$SF_5CFH\text{-}CF_2Cl$ (70) $SF_5CF_2\text{-}CFHCl$ (30)	none	36
SF_5Cl	thermal	$SF_5CFH\text{-}CF_2Cl$ (95) $SF_5CF_2\text{-}CFHCl$ (5)	none	37
SF_5Br	room temp.	$SF_5\text{-}CFHCF_2Br$	none	38
F_3CSF_4Cl	photo	$F_4(CF_3)S\text{-}CFHCF_2Cl$	none	39

Several additions of radicals of group 5 elements to trifluoroethene have been reported as outlined in table 1.3.7. As for sulfur compounds, these readily undergo chain transfer, hence little telomerisation is observed. Haszeldine *et al* [40]have reported the addition of dimethylphosphine and bis(trifluoromethyl)phosphine, once again illustrating the effect of radical polarity on orientation of addition.

Table 1.3.7 Addition of trifluoroethene to radicals centred on Group 5 elements

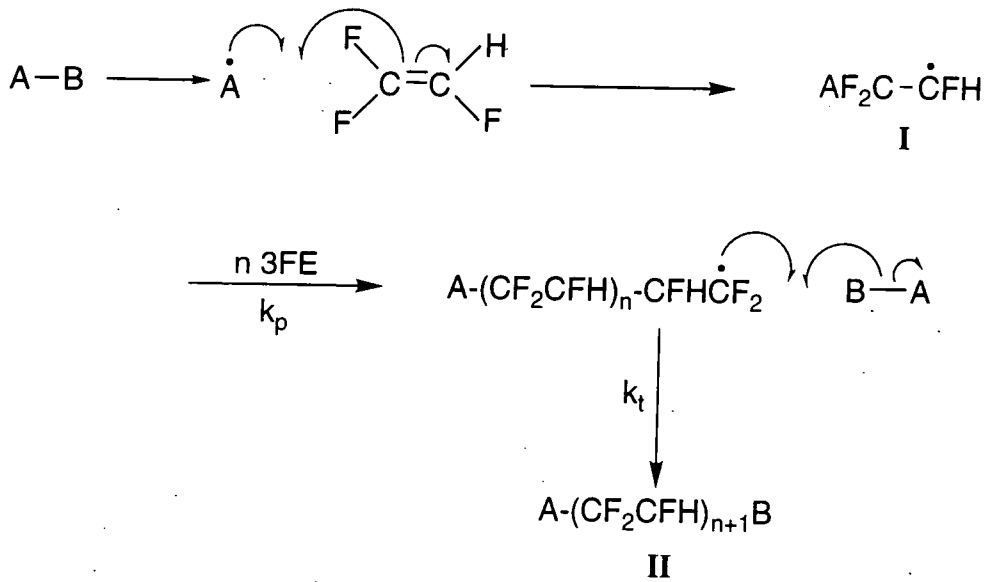
PH_3	photo	$PH_2CFH\text{-}CF_2H$ (85) $PH_2CF2\text{-}CFH_2$ (15)	none	41
$(CH_3)_2PH$	photo	$(CH_3)_2PCF_2\text{-}CFH_2$ (52) $(CH_3)_2PCFH\text{-}CF_2H$ (48)	none	40
$(CF_3)_2PH$	photo	$(CF_3)_2PCFH\text{-}CF_2H$ (98) $(CF_3)_2PCF_2\text{-}CFH_2$ (2)	none	40
$(CH_3)_2P\text{-}P(CH_3)_2$	photo	$(CH_3)_2P\text{-}CF2CFHP(CH_3)_2$	none	40
$(CH_3)_2As\text{-}As(CH_3)_2$	photo	$(CH_3)_2As\text{-}CF2CFHAs(CH_3)_2$	none	42

$(CF_3)_2N$-Cl	photo	$(CF_3)_2N$-$CFHCF_2Cl$ (86) $(CF_3)_2N$-CF_2CFHCl (14)	none	43
$(CF_3)_2N$-Br	photo	$(CF_3)_2N$-$CFHCF_2Cl$ (78) $(CF_3)_2N$-CF_2CFHCl (22)	none	44
$(CF_3)_2N$-Br	photo	$(CF_3)_2N$-$CFHCF_2Cl$ (74) $(CF_3)_2N$-CF_2CFHCl (26)	none	43
F_2N-NF_2	thermal	F_2N-CF_2CFH-NF_2	none	45

1.3.2 Telomerisation of Trifluoroethene

Telomerisation describes a kinetic situation in which chain propagation (k_p) can compete effectively with chain transfer (k_t).

As discussed above, trifluoroethene is homopolymerisable and so the intermediate radical **I** formed by reaction of trifluoroethene with the radical A may then telomerise to furnish telomeric mixture **II** (scheme 1.3.7).



Scheme 1.3.7

The effect of the telogen and the telogen : alkene ratio on telomer distribution has been studied in this laboratory for VDF with some perfluoroalkyl iodides[46] (table 1.3.8). Similarly, Ameduri *et al* have recently studied the telomerisation of trifluoroethene with some perfluoroalkyl iodides[16] (table 1.3.5).

Telogen (Telogen: VDF ratio)	Temp. (°C)	Time (hr)	Conversion of Iodide(%)	Composition of $R(CH_2CF_2)_nI$ (%)					
				n=1	n=2	n=3	n=4	n=5	n=6
CF_3I (1:1)	200	17	35	33	14.5	5.5	1		
C_2F_5I (1:1)	190	45	55	92	6	2			
n-C_3F_7I (1:1)	200	36	88	70	25	5			
$(CF_3)_2CFI$ (1:1)	185	36	88	90	10	trace			
$(CF_3)_2CFI$ (1:2)	220	36	90	87	13	trace			
$(CF_3)_2CFI$ (1:3)	220	36	100	14	34	38	11	3	
$(CF_3)_2CFI$ (1:4)	220	36	100	2	21	29	26	18	4

Table 1.3.8

Factors affecting the length of the telomer chain:

- A-B bond strength - If the A-B bond is strong then chain transfer is not a favourable process and chains will be long. Conversely, a weak A-B bond will favour formation of adducts with little or no telomer being formed. Thus, heptafluoro-2-iodopropane is a better chain transfer agent than heptafluoro-1-iodopropane as the secondary iodide has a weaker C-I bond.

- Relative concentrations of olefin and chain transfer agent (telogen) - if a large excess of telogen is used, telomerisation may be kept to a minimum since the propagating radical is more likely to encounter the telogen than trifluoroethene. Conversely, use of a small amount of telogen will result in longer chains. Thus, using less heptafluoro-2-iodopropane results in longer chains.

- Temperature. Higher temperatures result in less selectivity of the radical towards chain transfer or chain propagation and hence relative quantities of telogen and

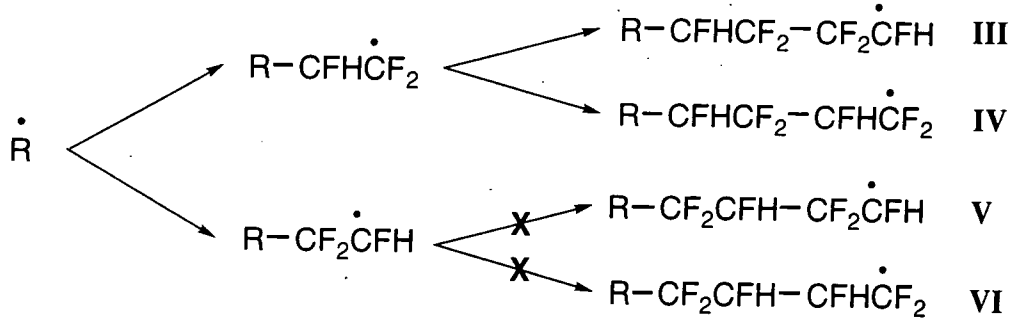
alkene become more significant at higher temperatures in terms of determining chain length.

Sharp[31] has reported the telomerisation of trifluoroethene and other alkenes with bis(trifluoromethyl) disulfide (table 1.3.9).

Table 1.3.9 Telomerisation of trifluoroethene and other alkenes with bis(trifluoromethyl) disulfide at 200°C

Alkene A (disulfide : alkene ratio)	Time (hr)	Conversion of alkene (%)	Composition of $CF_3S(A)_nSCF_3$ (%)						
			n=1	n=2	n=3	n=4	n=5	n=6	n=7
$CH_2=CH_2$ (1:1)	44	48.8	100						
$CH_2=CHCH_3$ (1:1)	20	59.9	100						
$CF_2=CH_2$ (1:1)	26	100	67.8	19.5	7.0		5.5		
$CF_2=CFH$ (0.9:1)	28	100	36.8	25.6	16.8	12.5	8.3		
$CF_2=CFCl$ (0.9:1)	24	100	26	24.8	22.2	19.9	7		
$CF_2=CF_2$ (1:1)	16	100	3	97					
$CF_2=CFCF_3$ (0.8:1)	184	48.5	9.5	90.5					

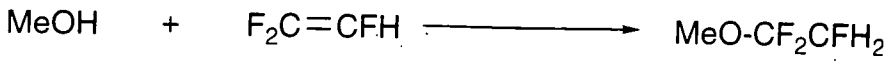
In the case of trifluoroethene, four regio-isomers may conceivably be formed by reaction of each of the two adduct radicals with a further equivalent of trifluoroethene. However, it has been reported that **V** and **VI** are not observed for telomerisation with 2-propanol[47], 1,2-dichloro-4-iodoperfluorobutane[48] and bis(trifluoromethyldisulfide);[31] only **III** and **IV** are formed in approximately equal amounts. The absence of **V** and **VI** has not been accounted for.



Scheme 1.3.8

1.4 Reactions with Nucleophiles

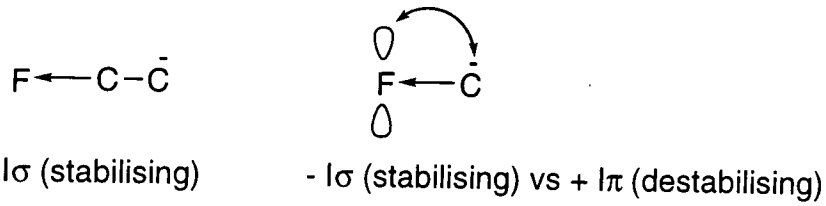
The first instance of nucleophilic addition to trifluoroethene was the addition of methanol to trifluoroethene reported by Swarts[49] (scheme 1.4.1).



Scheme 1.4.1

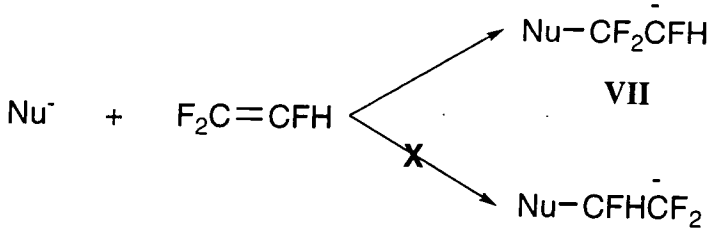
Likewise, reaction of ethanol and trifluoroethene has been reported by Park *et al.* [6]

Unlike radical additions, nucleophilic ionic additions are completely regioselective. The regioselectivity may be explained with reference to the influence of fluorine atoms on the carbanion intermediate.[50]



Scheme 1.4.2

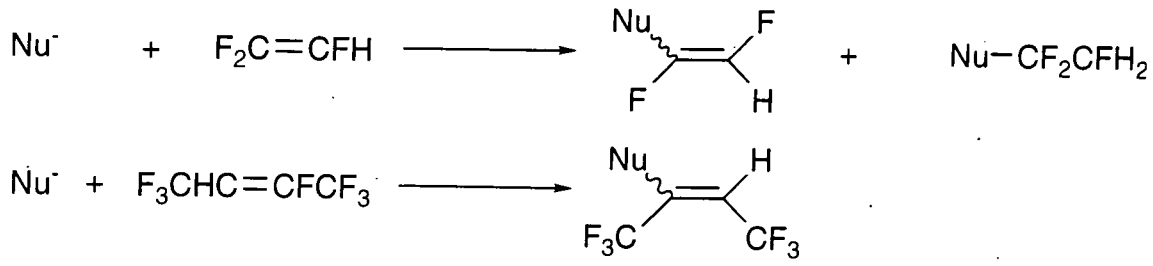
Fluorine contributes two opposing effects; a stabilising effect ($-I_\sigma$) and a destabilising ($+I_\pi$) effect. The extent of the destabilising effect is dependant on the degree of orbital overlap which is in turn dependant on the geometry of the system; the destabilising effect is greater for an sp^2 over an sp^3 hybridised carbon. In the case of trifluoroethene the net effect is that trifluoroethene undergoes nucleophilic attack at the CF_2 site to generate a carbanion on the CFH site.



Scheme 1.4.3

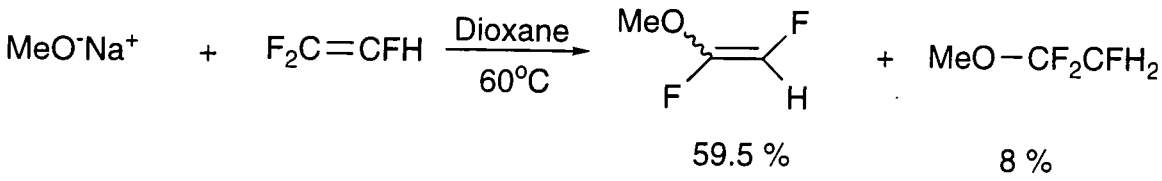
It has since been established that nucleophilic attack may follow one of two pathways via the common carbanion intermediate **VII**. The intermediate may either protonate or eliminate fluoride ion. The tendency for fluoride ion elimination increases for more stable carbanion intermediates. For example, nucleophilic reactions with 2H-

heptafluorobutene invariably entail fluoride ion displacement[51] whereas reaction with trifluoroethene under similar conditions commonly results in formation of a mixture of both addition and substitution products (scheme 1.4.4).



Scheme 1.4.4

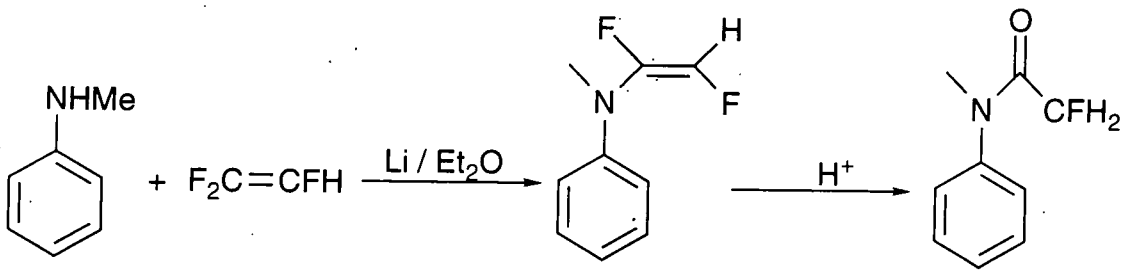
The degree of vinylic nucleophilic substitution over nucleophilic addition may be increased by use of metal salts (scheme 1.4.5). For instance, reaction of alkoxides with trifluoroethene furnishes the fluoralkenylated ether as the predominant product.[52]

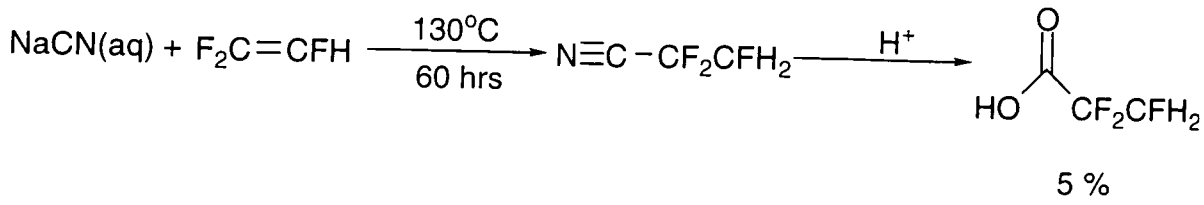


Scheme 1.4.5

Formation of alkenyl ethers is favoured in reaction with electron rich alcohols. Conversely, use of electron deficient alcohols results in the formation of more of the saturated ether.

Further examples are the reactions with N-methyl aniline[53] and sodium cyanide. In each case, further derivatives have been reported by acid hydrolysis.

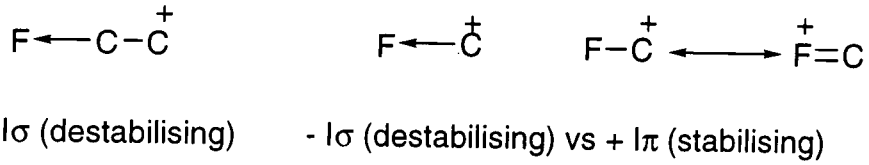




Scheme 1.4.6

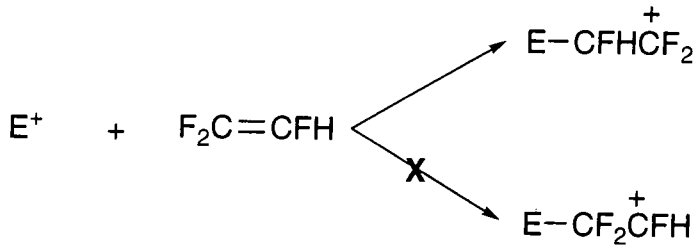
1.5 Electrophilic Chemistry

Although fluoro-olefins are generally regarded as electrophilic species as a consequence of the inductive electron withdrawing effect ($-I_\sigma$) of a fluorine substituent on a double bond, the nonbonding pair of electrons in the 2p orbital of fluorine can also give rise to an electron donating ($+I_\pi$) effect (scheme 1.5.1). This pair of electrons stabilises a carbocation relative to hydrogen.[54] As a consequence, fluoro-olefins may exhibit susceptibility to electrophilic attack. These reactions have been the subject of extensive study and have been reviewed.[55]



Scheme 1.5.1

The effect of fluorine substituents on the stability of the intermediate ion may be used to rationalise the observed orientation of addition of electrophiles to fluoro-olefins. The orientation of addition of electrophiles is the reverse of that observed for nucleophilic addition (scheme 1.5.2). In the case of trifluoroethene, the net effect is that electrophilic attack occurs at the CHF end. Unlike nucleophilic additions, however, this orientation is not universal as discussed below.

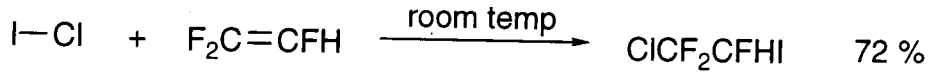


Scheme 1.5.2

1.5.1 Addition of Halogens

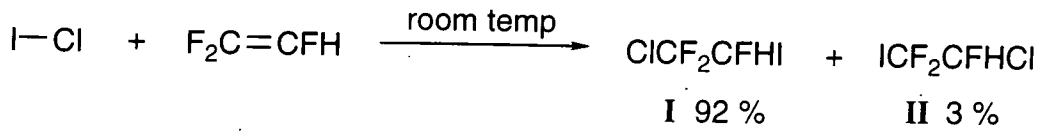
The addition of halogens to fluoro-olefins is usually via a radical mechanism under either thermal or photochemical conditions as discussed above. Additions under ionic conditions are more scarce. In the case of trifluoroethene, the first reported reaction was the addition of chlorine in the presence of $FeCl_3$ at 100°C.[6] Such vigorous conditions are not necessary; the addition of bromine has been reported at room temperature in the dark at 20°C.[56]

Low temperature and the use of Lewis acid catalysts are indicative of an electrophilic mechanism, however there is a degree of uncertainty as to the radical or ionic nature of these reactions. Additions of the mixed halogen compounds IF, BrF, ICl and IBr are unambiguously ionic in nature; indeed, additions are most facile for the more polarised of these compounds. The first addition of ICl to trifluoroethene was by Park *et al* in 1956[29] (scheme 1.5.3) who reported the formation of a single product.



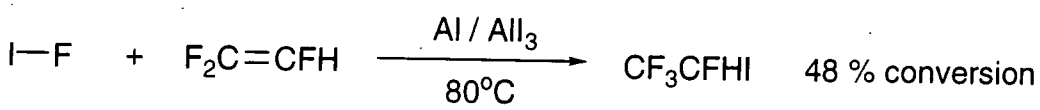
Scheme 1.5.3

Later work revealed that a small quantity of isomer **II** also forms.[18] The corresponding reaction under radical conditions gives **II** as the major isomer with **I** forming in a 26-36% yield.



Scheme 1.5.4

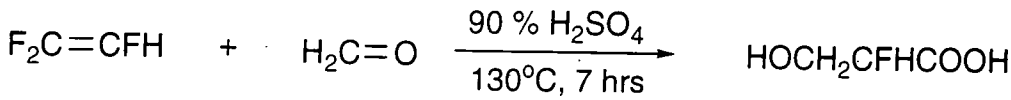
Addition of IF, produced from a stochiometric mixture of iodine and iodine pentafluoride,[57] has been reported to give a single product under Lewis acid catalysed conditions. A recent addition of IF using ICl / HF is discussed in the section on conjugate additions.



Scheme 1.5.5

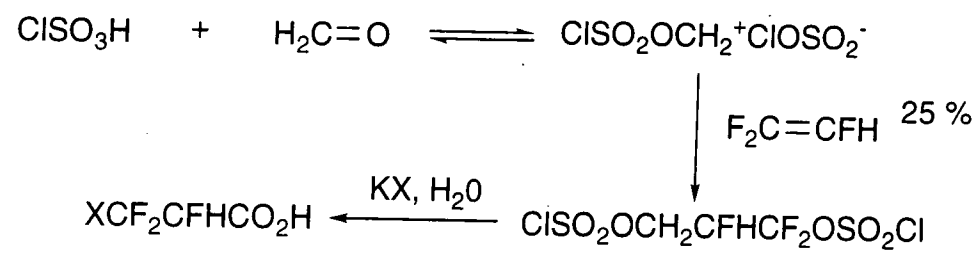
1.5.2 Addition of Other Electrophiles

In 1949, the reaction of tetrafluoroethene with paraformaldehyde was reported to proceed in the presence of 80 % sulfuric acid to give α,α-difluorohydracrylic acid.[58] Only trifluoroethene among other fluoro-olefins undergoes this reaction.[59]



Scheme 1.5.6

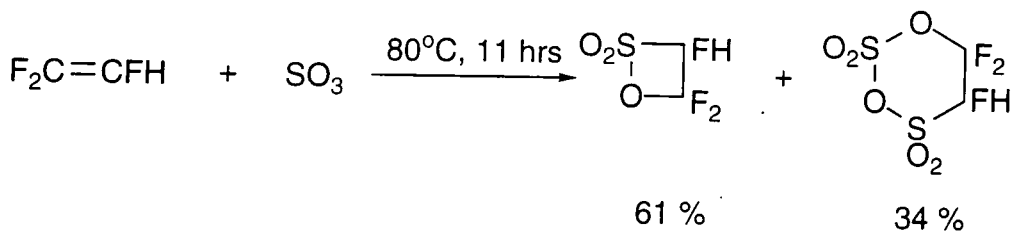
In the presence of chlorosulfonic acid with subsequent KCl or KBr treatment, trifluoroethene undergoes condensation with formaldehyde to give β-halotrifluoropropanoic acid.[59]



X = Cl : 40°C, 7 hrs, 26 % yield
X = Br : 40°C, 4 hrs, 29 % yield

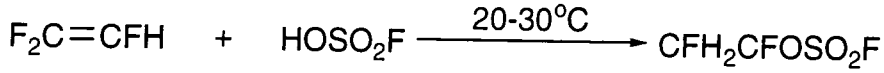
Scheme 1.5.7

Sulfur trioxide is a particularly strong electrophile as a consequence of the positively charged atom of sulfur which readily attacks the double bond of fluoro-olefins. In the case of trifluoroethene the main product is a sultone, however a significant amount of the 1:2 adduct is also observed[60] (scheme 1.5.8). Increasing the hydrogen content of the fluoro-olefin decreases the yield of sultone and so 1,1-difluoroethene gives only the 1:2 adduct while tetrafluoroethene gives only the sultone. Once again, chlorotrifluoroethene undergoes electrophilic attack at both ends of the double bond to give two isomers.

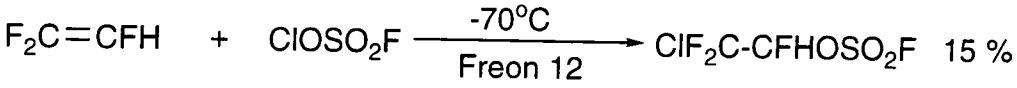


Scheme 1.5.8

Fluorosulfonic acid adds to trifluoroethene under ambient conditions via attack of H^+ on trifluoroethene (scheme 1.5.9). This is reversed for chlorine fluorosulfate for which the initial step is attack of FO_2SO^+[61] (scheme 1.5.10).



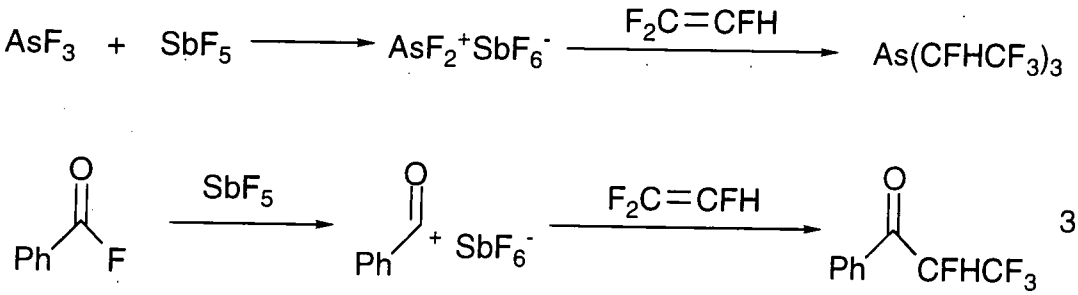
Scheme 1.5.9



Scheme 1.5.10

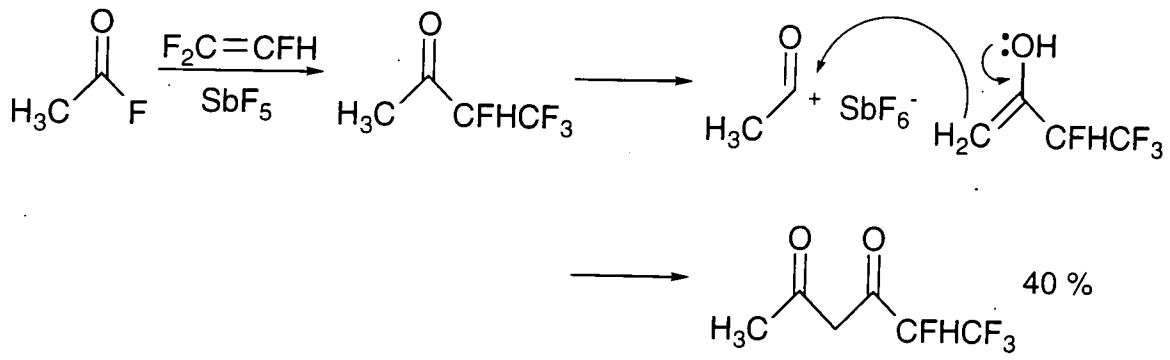
1.5.3 Additions Induced by Antimony Pentafluoride

Arsenic trifluoride has been reported to add to fluoro-olefins in the presence of SbF_5 to give the corresponding fluorinated arsines as illustrated for trifluoroethene. This methodology was applied to acyl fluorides which readily form acyl cations with SbF_5 to give the corresponding fluorinated ketones as illustrated with benzoyl fluoride.[62]



Scheme 1.5.11

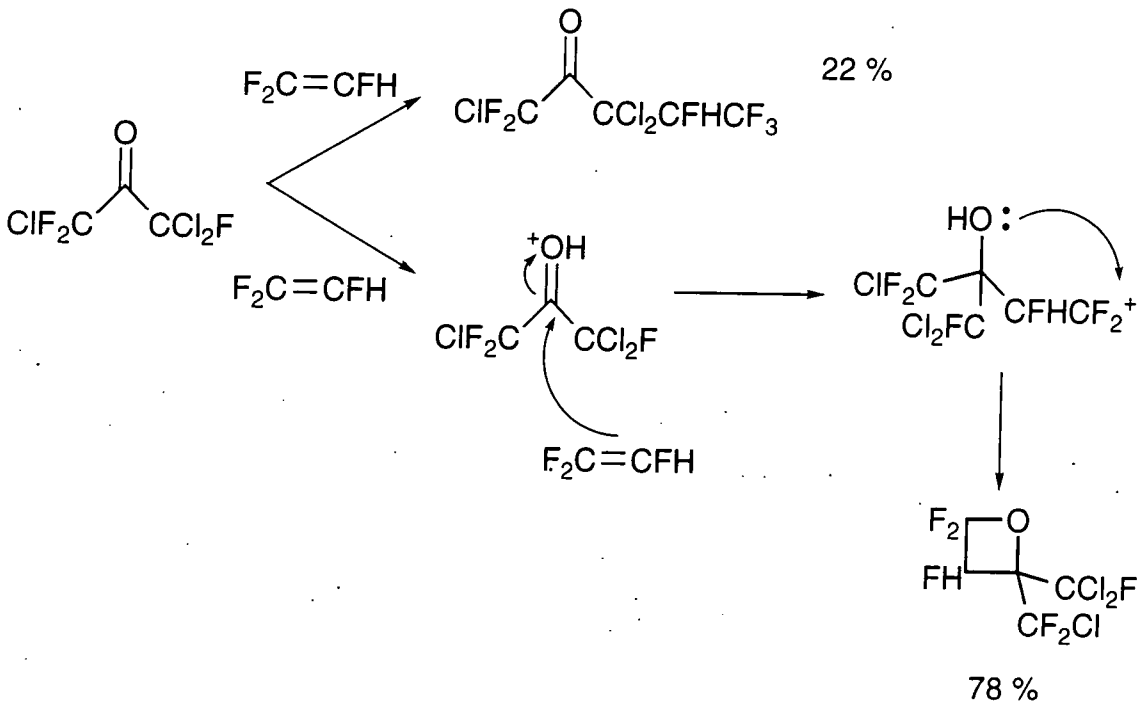
In the case of acyl fluoride, however, the ketone was observed to undergo condensation with acyl fluoride via it's enol tautomer to furnish a dione.



Conditions: 20°C, 5 hrs

Scheme 1.5.12

An analogous reaction was performed with 1,2,2-dichloro-1,1,2-difluoroacetone, however in this instance the main product is the oxetane.[63]

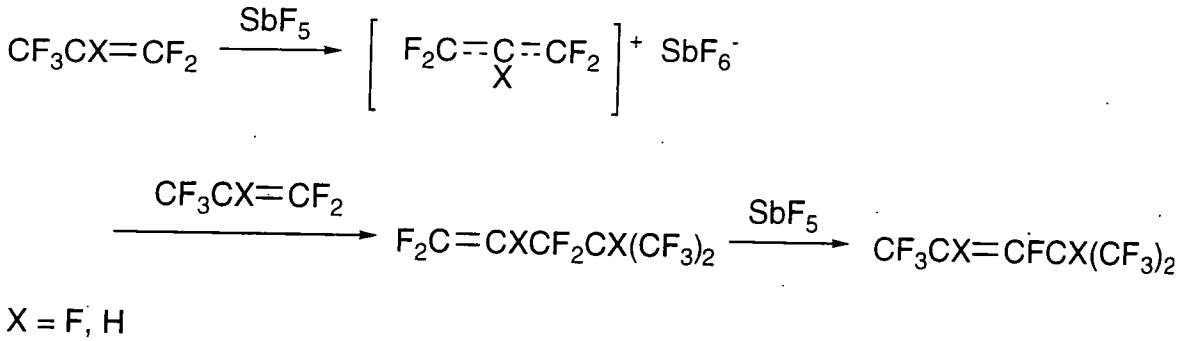


Conditions: SbF5, -20°C, 5 hrs

Scheme 1.5.13

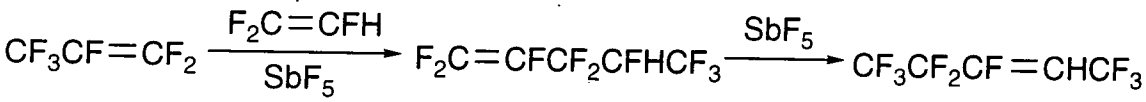
Belen'kii *et al*[64] and Chambers *et al*[65] have reported the dimerisation of pentafluoropropene and hexafluoropropene in the presence of SbF_5 via an allyl cation

which attacks the multiple bond of the propene. The terminal alkene produced thus then undergoes an SbF_5 catalysed rearrangement to generate a more stable isomer.



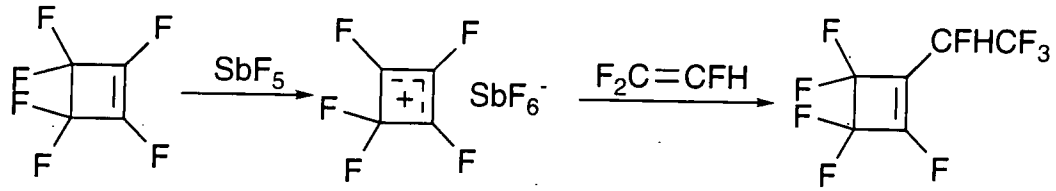
Scheme 1.5.14

Analogous reactions were subsequently reported using tetrafluoroethene and trifluoroethene.[64] Again, the intermediate terminal alkene undergoes rearrangement to a more stable isomer.



Scheme 1.5.15

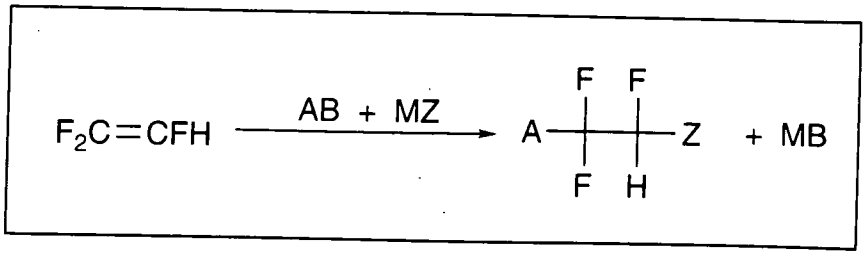
An analogous reaction has been reported with perfluorocyclobutene[66]

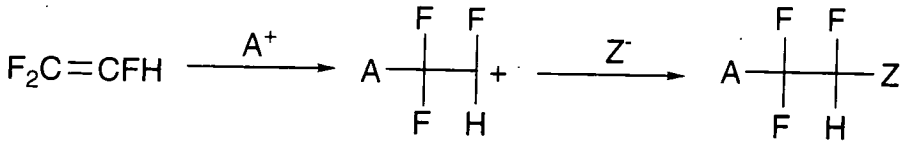


Scheme 1.5.16

1.5.4 Conjugate Addition

Conjugate addition is a process whereby two fragments, not joined to each other in the starting material, are added across a double bond. Conjugate electrophilic additions to fluoro-alkenes have been the subject of extensive studies[67]. A general reaction scheme for conjugate additions to trifluoroethene is given below (scheme 1.5.17).



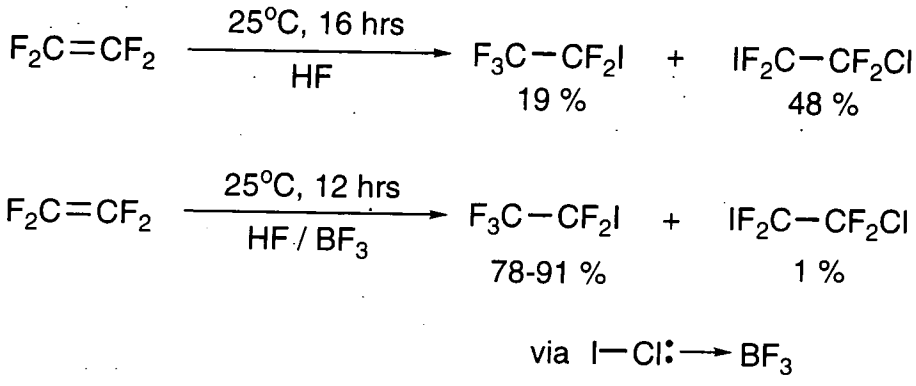


Scheme 1.5.17

A-B is commonly a polar organic substrate with a sufficiently electrophilic centre and M-Z is a halide ion source, e.g. HF or a halogen.

Hydrogen fluoride has been employed as a reaction medium for a wide range of conjugate electrophilic additions. HF performs a dual role in these reactions in that it acts as both a fluoride ion source for the quenching of the intermediate carbocation and as an acid catalyst for the reaction by activating the electrophile by protonation.

The acidity of the reaction medium can have a pronounced effect on the distribution of products, for example the reaction of ICl with tetrafluoroethene in HF furnishes the the thermal addition product of ICl with tetrafluoroethene as the major product and the product of conjugate iodofluorination as the minor product. Increasing the acidity of the system by use of BF_3 drastically increases the relative ratio in favour of the iodofluorination product.[67]



Scheme 1.5.18

These conditions have been employed recently for an efficient iodofluorination of trifluoroethene[68] (scheme 1.5.19). The fact that only one product is formed with trifluoroethene is noteworthy since the corresponding reaction with

chlorotrifluoroethene again furnishes the two regioisomers produced from attack of "I+" at both ends of the alkene.

$$F_2C{=}CFH \xrightarrow[HF\,/\,BF_3]{25^\circ C,\ 16\ hrs} F_3C{-}CFHI \quad 73\ \%$$

Scheme 1.5.19

A high yielding conjugate nitrofluorination of trifluoroethene has been reported[69] (scheme 1.5.20). These fluoronitroalkanes are synthetically useful starting materials for a range of transformations[70-72]. The electron withdrawing influence of fluorine attached directly to a double bond is observed in this reaction; at -60°C, the rate of reaction of trifluoroethene is 1/6 of the rate for the corresponding reaction with 1,1-difluoroethene and no reaction is observed for tetrafluoroethene. At higher temperature, reaction with tetrafluoroethene was reported, however no reaction was observed for hexafluoropropene.

$$F_2C{=}CFH + HNO_3 \xrightarrow[-60^\circ C]{HF} CF_3CFHNO_2 \quad 86\%$$

Scheme 1.5.20

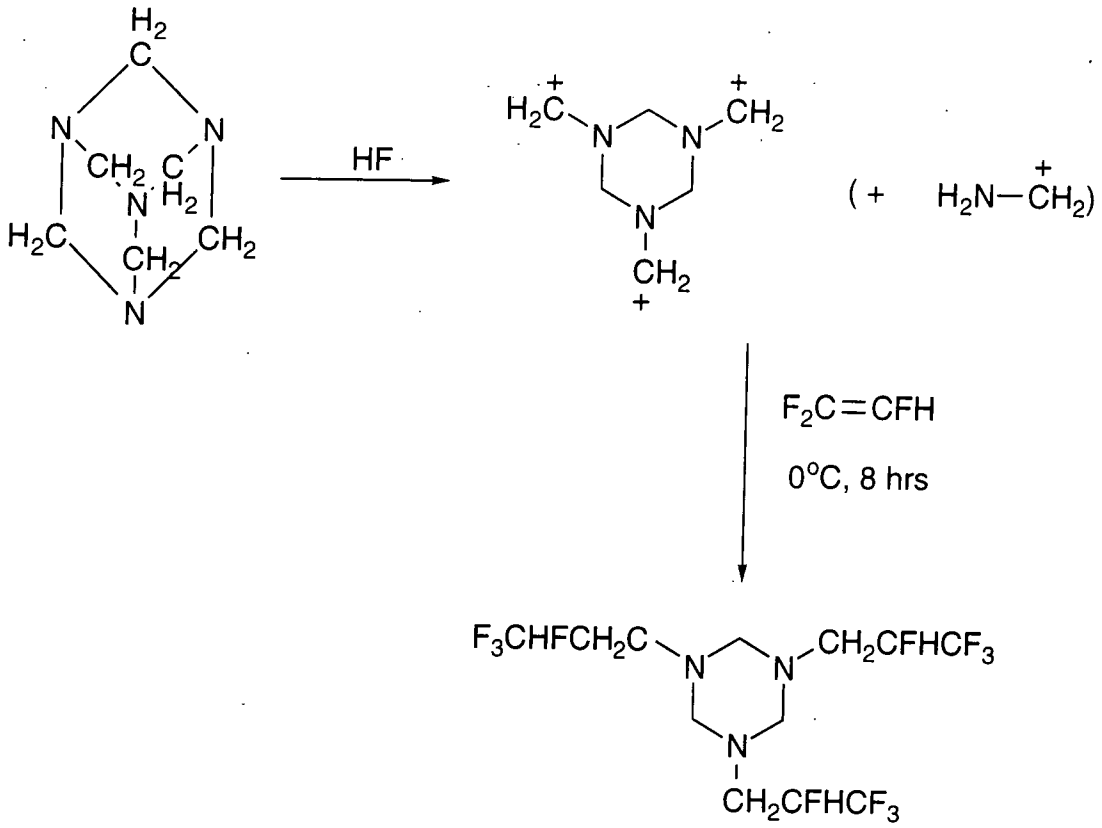
The electrophilic α-hydroxylation of olefins (Prins reaction) is often used for the synthesis of 1,3-dioxolanes, 1,3-glycols, etc. The Prins reaction in HF with fluoro-alkenes affords a route to fluorinated oxygen containing compounds. The reaction of HF with paraformaldehyde gives fluoromethanol[73] which may then dissociate in HF to give the hydroxymethyl cation which can then react with fluoro-alkenes to give fluoro-alcohols. These alcohols may react further to furnish symmetrical fluorinated ethers, as in the case of trifluoroethene.[74]

$$FCH_2OH \rightleftharpoons HOCH_2^+ \xrightarrow{F_2C{=}CFH} HOCH_2CFHCF_3$$

$$\xrightarrow[CH_2O,\ H^+]{-H_2O} O\begin{matrix}\diagup CH_2CFHCF_3 \\ \diagdown CH_2^+\end{matrix} \xrightarrow{F_2C{=}CFH} O\begin{matrix}\diagup CH_2CFHCF_3 \\ \diagdown CH_2CFHCF_3\end{matrix}$$

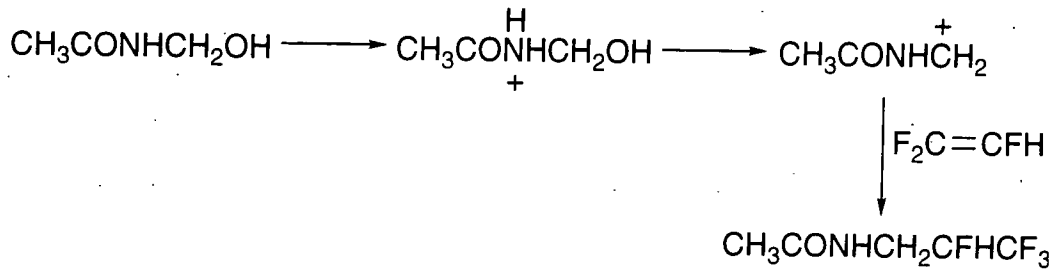
Scheme 1.5.20

In a variation of these reactions, the susceptibility of hexamethylenetetramine towards deamination under acidic conditions has been utilised in a conjugate fluoroaminomethylation reaction.[75]



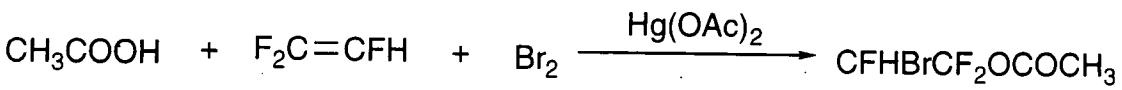
Scheme 1.5.21

This same methodology has been applied with (N-hydroxymethyl)acetamide in a conjugate fluoroacylaminomethylation reaction.[75]



Scheme 1.5.22

Another example of a conjugate addition involves addition of bromine and acetate in acetic acid.[76]



Scheme 1.5.23

1.6 Organometallic Chemistry

The reaction of trifluorovinyllithium with a variety of electrophiles to furnish a range of fluoralkenylated species has been the subject of a number of studies. Trifluorovinyllithium was originally prepared by halogen exchange of bromotrifluoroethene with alkyllithium reagents,[77] however it may also be prepared by proton exchange with trifluoroethene (scheme 1.6.1). This reaction was first reported by Tarrant *et al* in 1968.[78] Recently, preparation of trifluorovinyllithium in one step from HFC 134a via trifluoroethene has been reported (scheme 1.6.2).[79]

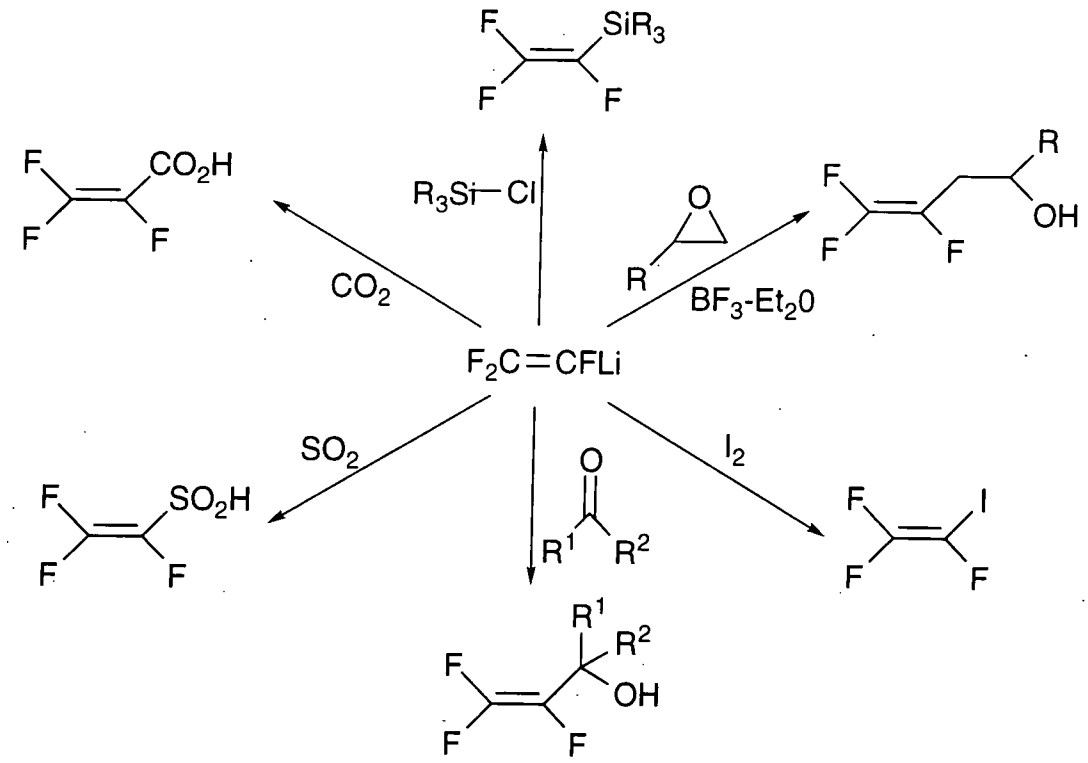
$$F_2C{=}CFH \;+\; BuLi \xrightarrow[\text{Ether / pentane}]{-\,100^{\circ}C} F_2C{=}CFLi$$

Scheme 1.6.1

$$F_3C{-}CFH_2 \;+\; 2\,BuLi \xrightarrow[\text{Ether}]{-\,78^{\circ}C} F_2C{=}CFLi$$

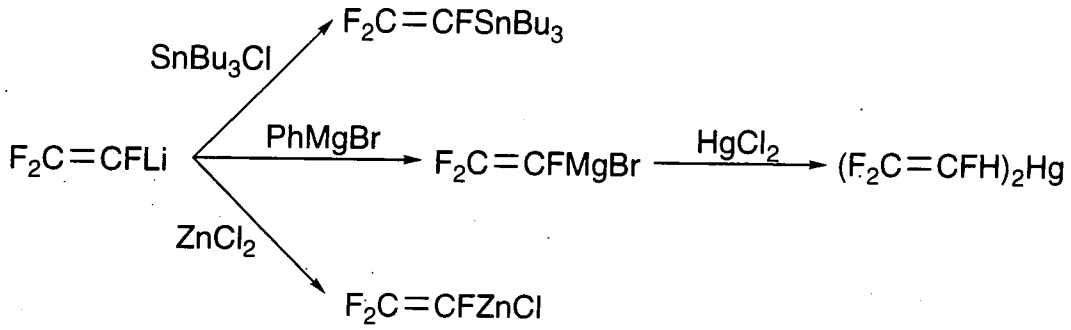
Scheme 1.6.2

Examples of derivatives from trifluorovinyllithium prepared by reaction with appropriate electrophiles include trifluorovinylsilylanes[80], α,β unsaturated alcohols by reaction with carbonyls[81], β,γ unsaturated alcohols by reaction with oxiranes and γ,δ unsaturated alcohols by reaction with oxetanes[82], iodotrifluoroethene from iodine[83], trifluoroacrylic acid from carbon dioxide and vinyl sulfinates by reaction with sulfur dioxide (scheme 1.6.3).[81]



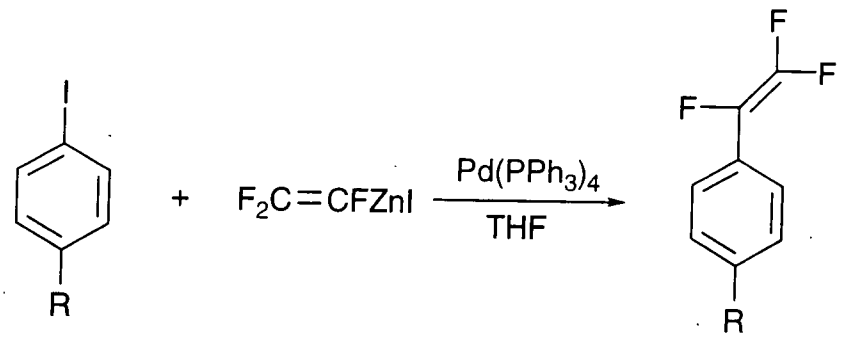
Scheme 1.6.3

In addition, trifluorovinyllithium has been used to prepare the trifluorovinyl derivatives of other metals (Sn, Mg[80], Hg[77], Zn[84] ,scheme 1.6.4) which have exhibited greater stability than trifluorovinyllithium and hence have more synthetic utility.



Scheme 1.6.4

The zinc derivative has been used in a variety of palladium catalysed cross-coupling reactions,[85,86] e.g. reaction with iodobenzenes



Scheme 1.6.5

Chapter 2

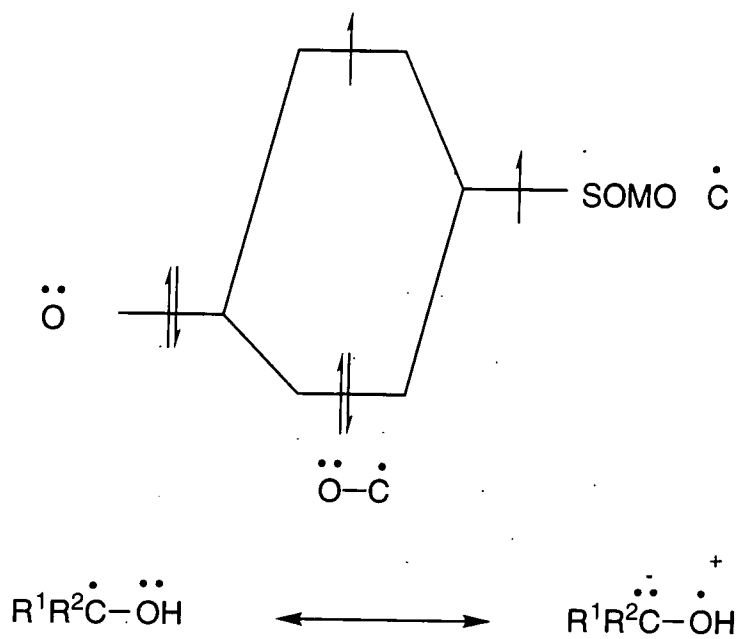
Free Radical Addition and Telomerisation of Trifluoroethene

2.1 Introduction

The introduction of fluoroalkyl groups into organic molecules by the insertion of a fluoro-alkene into a carbon-hydrogen bond has been studied extensively for alkanes, alcohols, amines and aldehydes. A brief review of this work is given here. In contrast to more readily available fluoro-alkenes, such as tetrafluoroethene and hexafluoropropene, examples of free radical additions of these chain transfer agents with trifluoroethene are very limited. In the present work, this methodology has been applied to trifluoroethene and the chemistry of the adducts produced has been studied.

2.1.1 Effect of Substituents on the Radical

The intermediate radical generated by hydrogen abstraction in alcohols, ethers amines and aldehydes occurs at the carbon atom neighbouring the heteroatom since the lone pair on the heteroatom (oxygen or nitrogen) is capable of stabilising the radical, thus increasing the chain transfer efficiency of these telogens. This stabilisation is expressed below for oxygen in valence bond and molecular orbital terms[15] (scheme 2.1.1).



Scheme 2.1.1:

In addition to its stabilising effect, this resonance increases the nucleophilicity of the radical, thus facilitating reaction with fluoro-alkenes which behave as electrophiles in these additions.

The effect of substituents on chain transfer efficiency has been studied by comparison of chain transfer coefficients C, defined below:

$$C = \frac{\text{Rate Constant for Chain Transfer}}{\text{Rate Constant for Chain Growth}}$$

Although no C values have been determined for any fluoro-alkenes, Mortimer[87-89] has reported C values for a variety of telogens with ethene.

Table 2.1.1 Chain transfer co-efficients for telogens with ethene at 130°C and 1360 atm.

Telogen	C
Methane	0.0000015
Ethane	0.00060
Propane	0.0030
Methanol	0.0021
Ethanol	0.0075
2-propanol	0.0144
Tetrahydrofuran	0.0288
Trimethylamine	0.033
Tri-n-butylamine	0.082
Formaldehyde	0.056
Propanal	0.33

2.1.2 Methods of Initiation

Reported methods of free-radical initiation include irradiaton (UV or γ-ray), thermal and peroxide initiation. In the present work, either peroxides or γ-rays have been used.

Initiation using peroxides involves thermolysis of the weak O-O bond of the peroxide. The radical thus generated then reacts with the substrate[90] (scheme 2.1.2).

$$RO{-}OR \overset{\Delta}{\rightleftharpoons} 2\,RO\bullet$$

$$RO\bullet + A{-}H \longrightarrow A\bullet + ROH$$

R = *t*-butyl : Δ = 140°C

R = benzoyl: Δ = 80°C

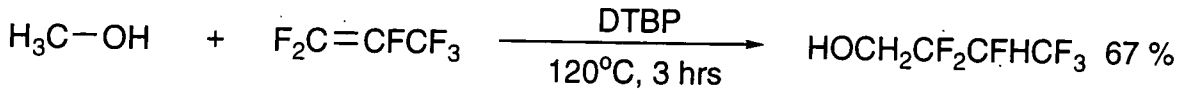
Scheme 2.1.2

Initiation using γ-rays is convenient in that reaction time and temperature may be varied. In addition, the presence of chemical initiators in the system is not required.

Free Radical Additions to Fluoro-alkenes

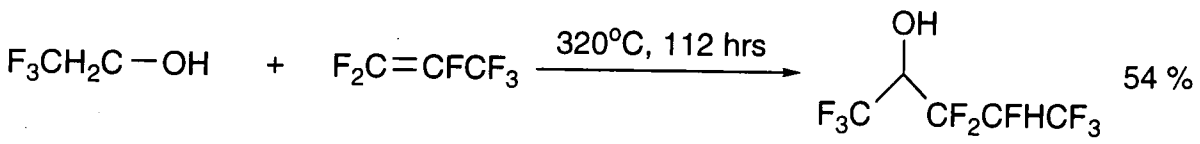
2.1.3 Telomerisation of Alcohols

An early example of addition to an oxygen containing compound is the addition of methanol to hexafluoropropene performed by Lazerte[91] (scheme 2.1.3). The addition of alcohols to HFP has been studied in greater depth by Muramatsu[92] and Haszeldine.[93]



Scheme 2.1.3

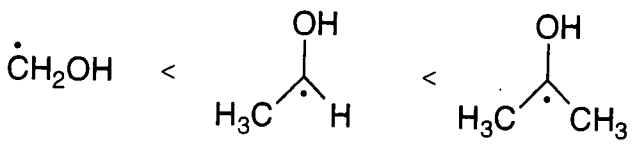
The importance of radical polarity is illustrated by reaction of trifluoroethanol with hexafluoropropene[93]; addition of methanol and ethanol to hexafluoropropene occurs readily as outlined above whereas the more electrophilic radical derived from trifluoroethanol only undergoes addition under substantially more forcing conditions.



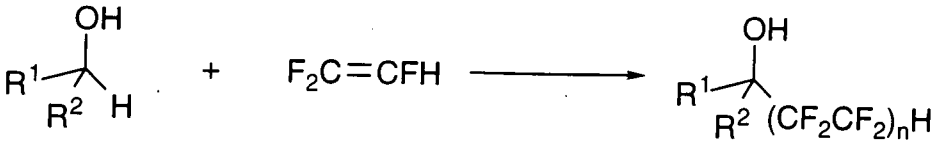
Scheme 2.1.4

As discussed in chapter 1, hexafluoropropene is not homopolymerisable hence telomers are not observed in free radical additions to hexafluoropropene. On the other hand, telomers do form with tetrafluoroethene which is homopolymerisable.

The effect of radical stabilising groups is reflected in the C values for methanol, ethanol and 2-propanol (table 2.1.1). The ease of formation of the radicals derived from these species increases in the order:



The increase in chain transfer efficiency in this series is manifested in the telomerisation of these three alcohols with tetrafluoroethene reported by Paleta *et al* [94] (scheme 2.1.5).



Conditions: UV, DBP, -30°C, 6-8 hrs

R^1, R^2 = Me or H

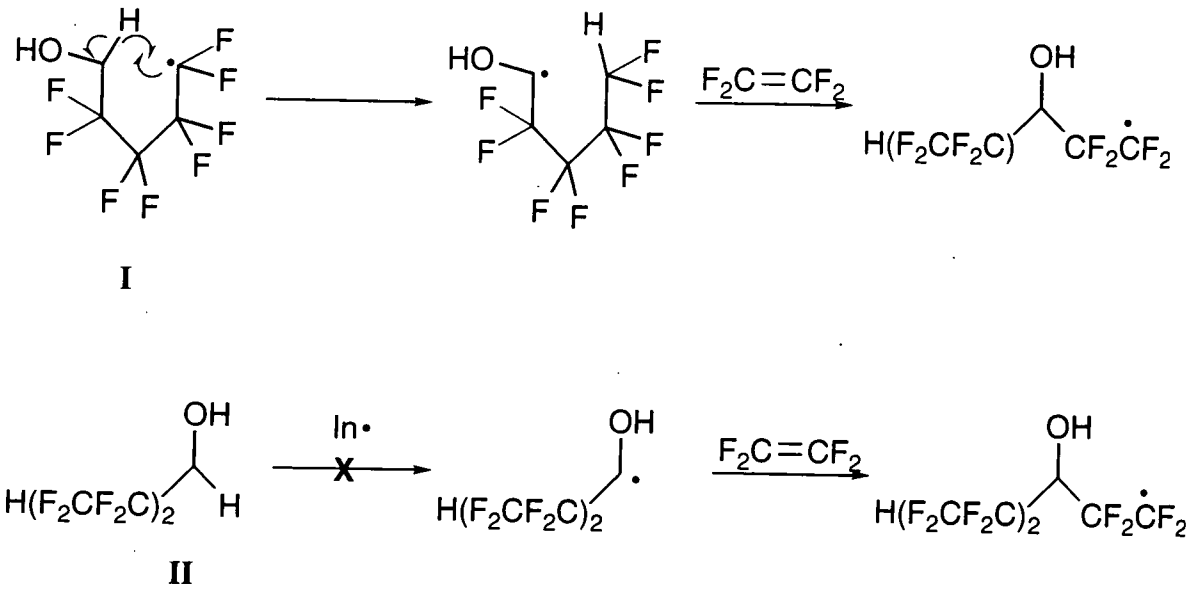
Scheme 2.1.5

The quantity of telomer formed decreases from methanol to 2-propanol as a consequence of the increasing chain transfer efficiency in this series (table 2.1.2). This effect even overrides the decreasing quantity of telogen used in this series which favours formation of telomer.

Table 2.1.2 Telomerisation of alcohols with tetrafluoroethene

Telogen (moles used)	% 1:2 telomer relative to 1:1 adduct
Methanol (6.18)	46
Ethanol (4.28)	22
2-propanol (3.26)	11

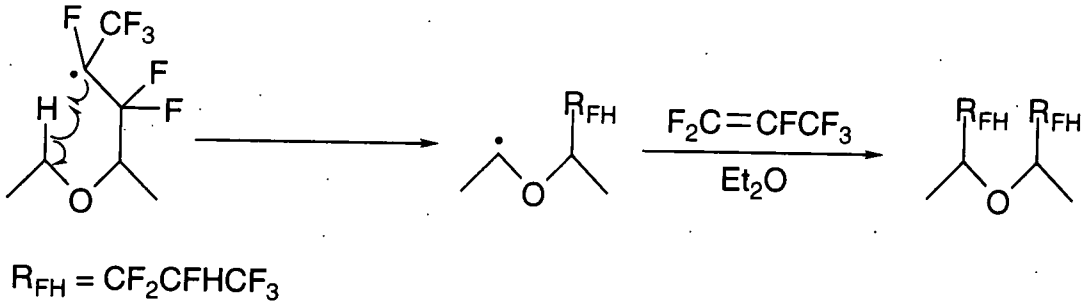
Formation of branched telomers has been reported for the TFE / methanol system.[95] This is assumed to occur via hydrogen abstraction from the the six-membered 1 : 2 adduct intermediate radical **I** (scheme 2.1.6), as opposed to hydrogen abstraction from the 1:2 adduct **II**. Evidence supporting the 'backbiting' mechanism is the poor chain transfer ability of trifluoroethanol discussed above as well as evidence from additions to HFP with ethers.



Scheme 2.1.6 1:2

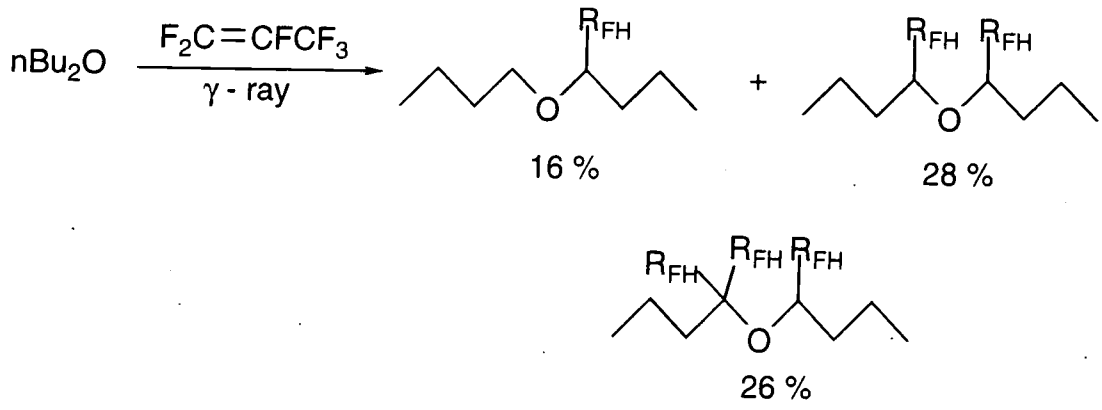
2.1.4 Addition of Ethers

The additions of ethers to HFP were first reported Muramatsu[92] and Abroskina.[96] These were subsequently studied in greater depth by Chambers *et al.*[97,98] Muramatsu[92] observed the formation of a diadduct with diethyl ether. The HFP / diethyl ether monoadduct displays markedly less reactivity towards HFP than diethyl ether which again indicates that diadduct formation is via hydrogen abstraction in a six-membered transition state of the 1 : 1 adduct radical (scheme 2.1.7).



Scheme 2.1.7

Similarly, Chambers *et al* [97, 98] observed the formation of di- and tri-adducts in the addition of di-n-butyl ether to HFP (scheme 2.1.8). As for telomerisation, the extent of multiple alkene additions is dependent on the alkene : chain transfer agent ratio. Thus multiple additions of the alkene is favoured when more than one equivalent of alkene is used.



$R_{FH} = CF_2CFHCF_3$

Scheme 2.1.8

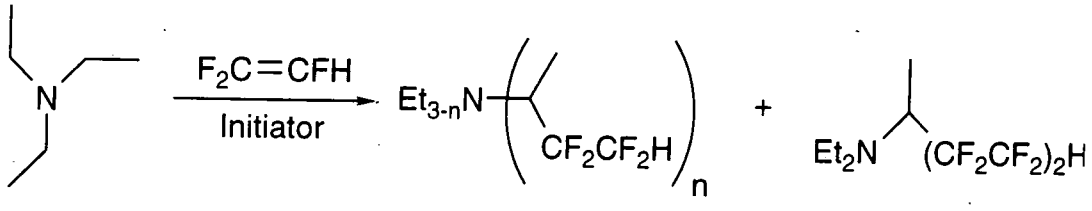
2.1.5 Addition of Amines

The UV and γ-^{60}Co radiation initiated additions of triethylamine and N-methylpiperidene to tetrafluoroethene have been reported by Liska *et al*[99] (scheme 2.1.9). These reactions furnish 1:1 and 1:2 adducts as the major products with 1:2 telomers forming as minor products. Small quantities of the 1:3 adducts are also observed.

Under γ-ray initiation, the di-adduct is a major component of the product mixture even when a large excess of amine is used. This indicates that intramolecular hydrogen abstraction occurs efficiently in this system. Use of the more energetic UV initiator means that intermolecular hydrogen abstraction can compete more effectively with intramolecular hydrogen abstraction resulting in formation of the mono-adduct as the predominant product.

The small quantity of tri-adduct observed may be attributed to the high electrophilicity of the amine radical bearing two fluoralkyl groups. This radical would not compete favourably with the more nucleophilic radical derived from triethylamine for addition to tetrafluoroethene.

These results are summarised in table 2.1.3.



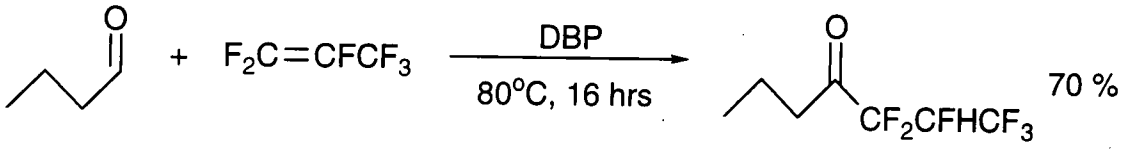
Scheme 2.1.9

Table 2.1.3 Telomerisation of triethylamine with tetrafluoroethene

Initiator	Amine / olefin ratio	n = 1	n = 2	n = 3	Telomer	Other
^{60}Co	7.6	43	41	2.5	8	5
UV	2.7	81	8.5	-	-	10

2.1.6 Addition of Aldehydes

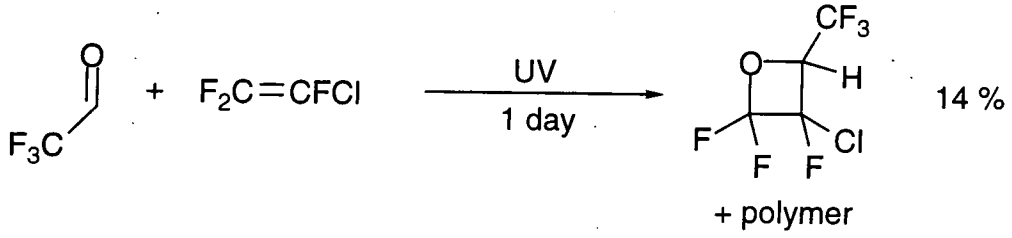
Addition of butanal to HFP reported by Lazerte[91] (scheme 2.1.10) constituted the first example of radical addition of an aldehyde to a fluoro-alkene. This work was subsequently extended by Murumatsu[100] to include addition to dichlorodifluoroethenes.



Scheme 2.1.10

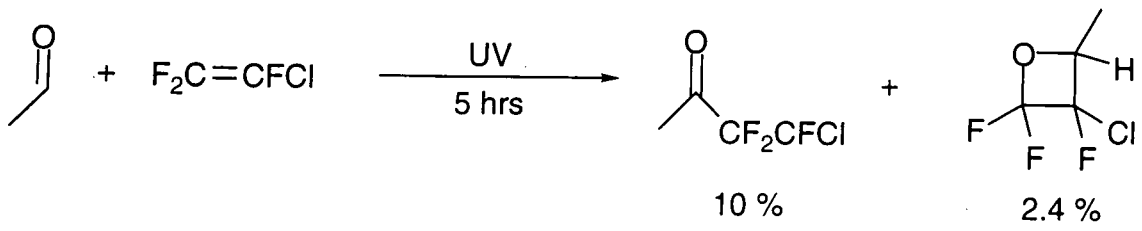
These reactions were reported using non-fluorinated aldehydes under peroxide initiated conditions.

Harris[101] reported the synthesis of polyfluoro-oxetanes by photoinitiated addition of fluoro-alkenes to fluorocarbonyl compounds (i.e. aldehydes, ketones and acyl fluorides), as illustrated for chlorotrifluoroethene and trifluoroacetaldehyde (scheme 2.1.11).



Scheme 2.1.11

Bissel[102] subsequently established that non-fluorinated aldehydes will react under UV initiation to furnish a mixture of ketone and oxetane, as illustrated by reaction of acetaldehyde and chlorotrifluoroethene (scheme 2.1.12).



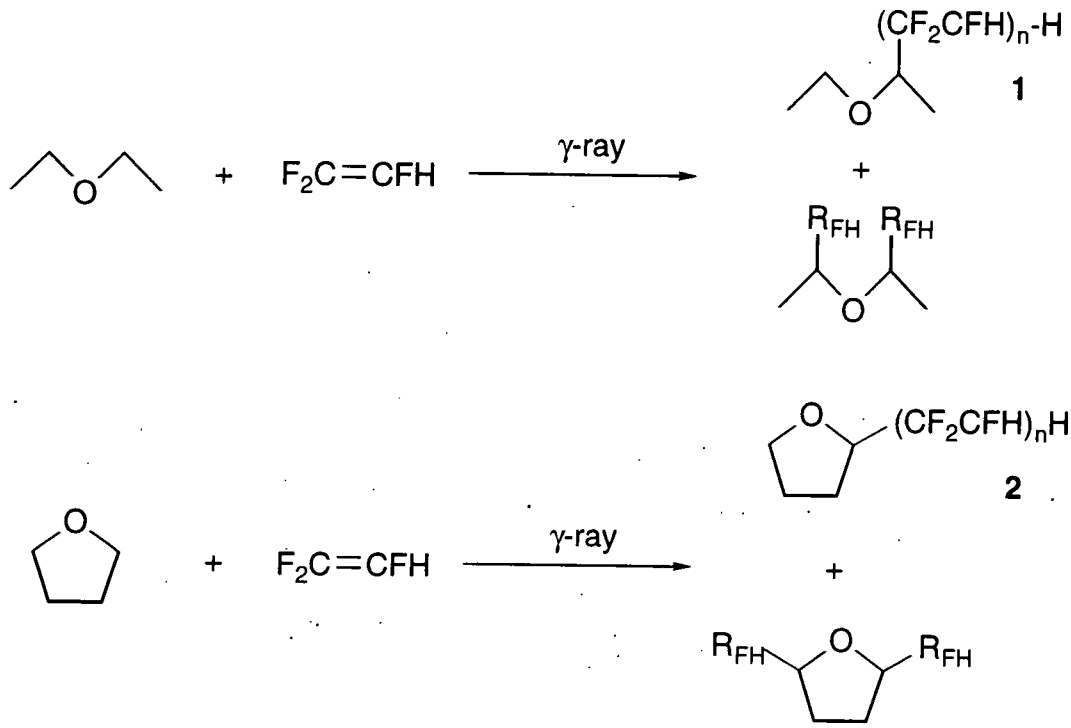
Scheme 2.1.12

Results and Discussion

2.2 Telomerisation of Trifluoroethene

2.2.1 Telomerisation of Trifluoroethene with Ethers

Trifluoroethene was telomerised with diethyl ether and tetrahydrofuran by γ-ray initiation. Both chain transfer agents gave quantitative conversion of trifluoroethene.



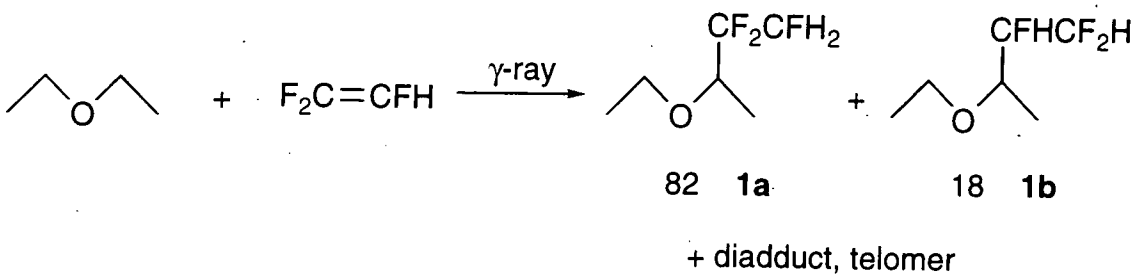
R_{FH} = CF_2CFH_2 or $CFHCF_2H$

Scheme 2.2.1

Five equivalents of telogen were employed in these reactions. In consequence, the predominant product in the telomeric mixture was the 1:1 adduct in both cases. In addition to telomer formation, 1:2 adduct formation was also observed, however di-adducts were not isolated due to the complexity of the mixture of 1:2 telomer isomers

and 1:2 adduct isomers produced. The addition of diethyl ether to tetrafluoroethene and isolation of 1:1 and 1:2 adducts has been reported by Knunyants.[103]

Trifluoroethene undergoes bidirectional attack by both diethyl ether and tetrahydrofuran, with predominant radical attack at the CF_2 site (scheme 2.2.2).



Scheme 2.2.2

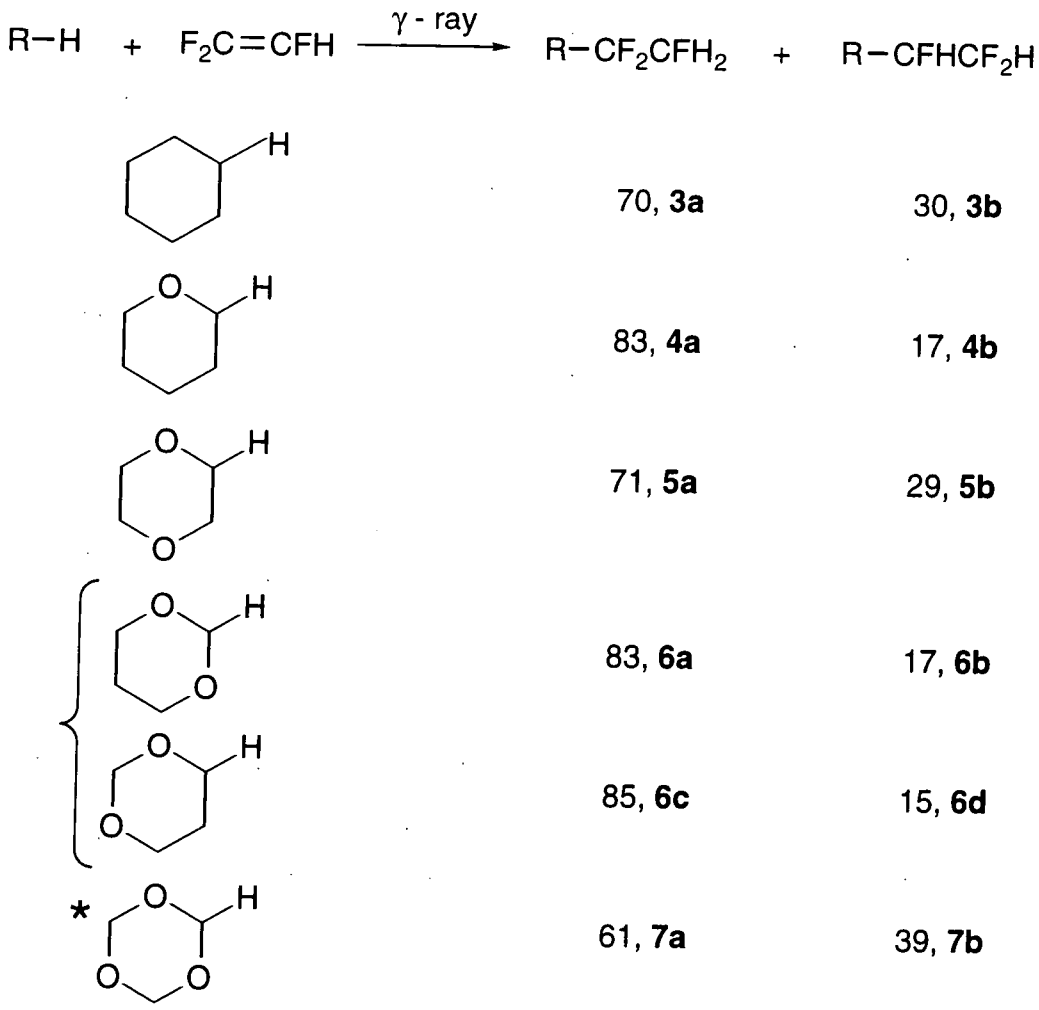
Identification of products. - Mixtures of adducts (**1a** and **1b**, tetrahydrofuran adducts **2a** and **2b**)were isolated by distillation. Throughout the course of the present work, all adducts have been characterised as a mixture of regio-isomers **a** and **b** unless stated otherwise. Compound **1a** was separated from **1b** by preparative scale GLC.

The ratio of isomers **a** and **b** was determined by GLC peak integration and corroborated by ^{19}F NMR integration. Discrimination between the $-CF_2CFH_2$ and $-CFHCF_2H$ isomers was made on the basis of their ^{19}F NMR spectra; the $-CF_2-$ group of **1a** appears as an AB quartet (-121.5 ppm) as a consequence of these two fluorine atoms being inequivalent due to the asymmetic site in this molecule, and the $-CFH_2$ site appears at as a triplet ($^2J_{F-H}$ 46.2) of triplets ($^3J_{F-F}$ 13.9). The $-CF_2H$ groups of the diastereomers of **1b** appear as overlapping signals at -133 ppm which have not been resolved for each diastereomer. The -CFH- groups of the diastereomers appear as two discrete signals at -213 ppm and -216 ppm.

The fact that free radical attack occurs at the α-carbon of the ether was demonstrated by ^{13}C NMR. Thus, the α-carbon of **1a** appears as a doublet of doublets at 74.1 ppm.

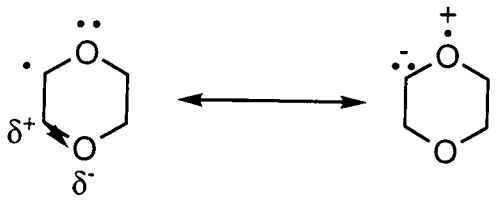
Similar characterisation has been applied throughout the course of the present work in identifying free radical adducts.

The unusually high degree of attack at the CF_2 site of trifluoroethene may be attributed to the nucleophilicity of the radical (section 2.1.1). The effect of nucleophilicity was studied by the telomerisation of trifluoroethene with a series of increasingly electrophilic cyclic ethers (scheme 2.2.3). A large excess of chain transfer agent was used in these reactions, hence the major component of the product mixture was the 1:1 adduct.



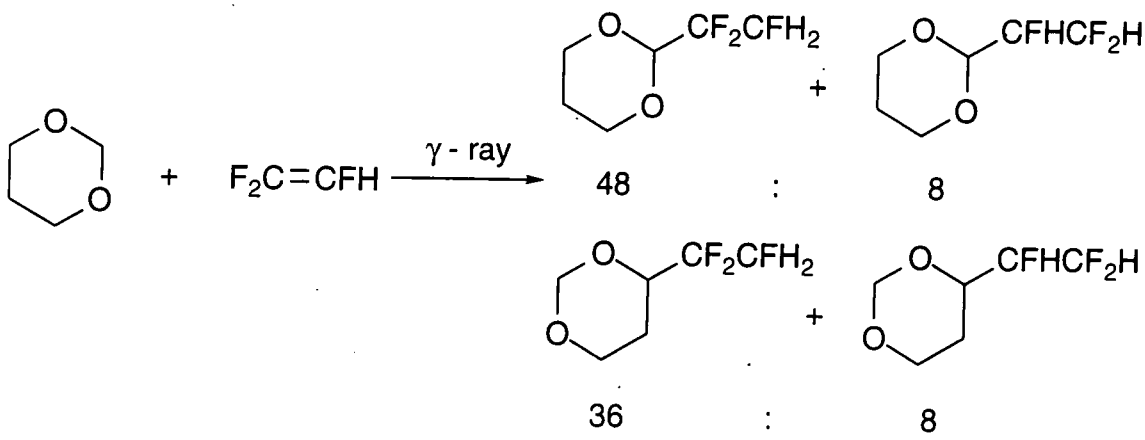
Scheme 2.2.3

On the basis of radical polarity, the degree of radical attack at the more electrophilic CF_2 site would be expected to decrease with decreasing nucleophilicity of the attacking radical. This is the general trend observed in moving from cyclohexane to 1,3,5-trioxane. Thus, for example, 1,4-dioxane shows less regioselectivity than tetrahydropyran. Whereas the one oxygen in tetrahydropyran can contribute towards the nucleophilicity of a radical by radical - lone pair interaction (see section 2.1.1), the second oxygen in 1,4-dioxane contributes a solely electron withdrawing effect, thus increasing the electrophilicity of the radical:



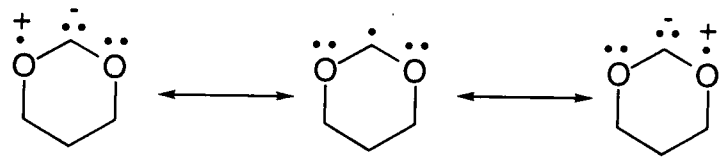
The relatively low regioselectivity of cyclohexane may be due to the fact that the cyclohexyl radical, unlike the other systems studied, is not stabilised by an adjacent oxygen. Hence the cyclohexyl radical is a higher energy species and therefore less selective.

In the case of 1,3-dioxane, addition may occur at the 2 or 4 position. Here, two surprising results were obtained. Firstly, addition at the 2 position is greater than that at the 6 position. Secondly, addition at the 2 position shows a surprisingly high degree of radical attack at the CF_2 site (scheme 2.2.4).



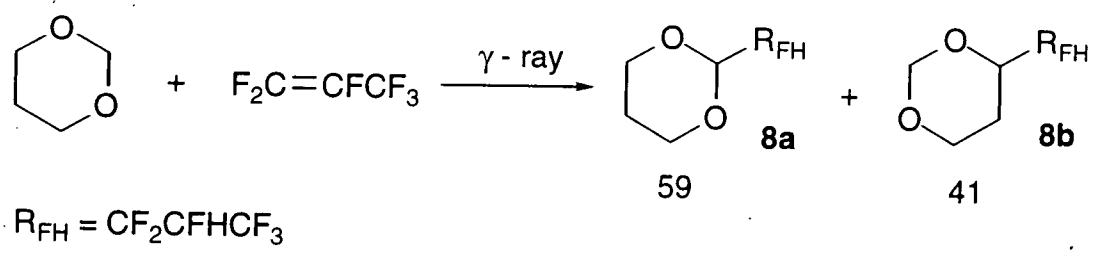
Scheme 2.2.4

These observations may be explained in terms of an interaction of the radical centred on the 2-position with lone pairs of electrons on *both* the 1- and 3- oxygen atoms increasing the nucleophilicity of the radical.



Scheme 2.2.5

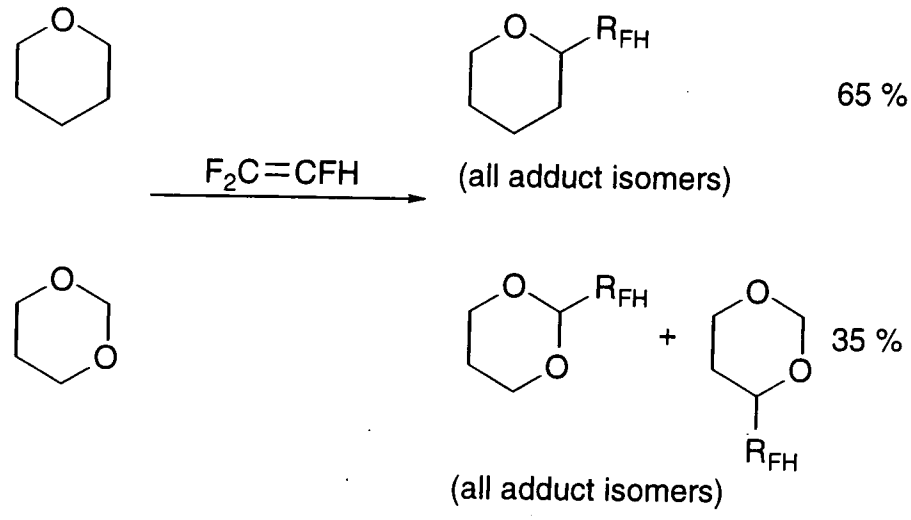
The product distribution obtained in the addition of 1,3 - dioxane to hexafluoropropene supports this explanation; once again, a marginal preference for addition at the 2- position is observed.



$R_{FH} = CF_2CFHCF_3$

Scheme 2.2.6

The nucleophilicity of the radicals derived from 1,3-dioxane was studied in a competition reaction between tetrahydropyran and 1,3-dioxane. The results from this competition reaction suggest that tetrahydropyran is the more nucleophilic species which contradicts the findings from the study of regiochemistry of addition (above).



$R_{FH} = -CF_2CFH_2$ or $-CFHCF_2H$

Scheme 2.2.7

1,3,5-trioxane is the most electrophilic species in the series of ethers studied. Its addition to trifluoroethene by γ-ray initiation is of interest because the corresponding reaction with hexafluoropropene has been attempted unsuccessfully in this laboratory; addition of 1,3,5-trioxane to hexafluoropropene was only achieved by use of UV initiation. This illustrates the greater nucleophilicity of trifluoroethene in comparison to hexafluoropropene.

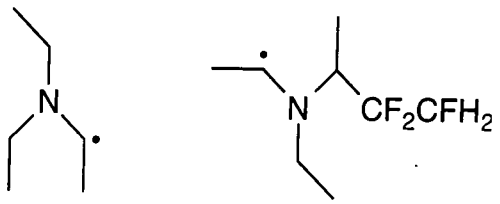
Identification of products. - Adducts **3**, **4** and **5** were isolated by distillation and characterised as a mixture of isomers **a** and **b**. Compounds **6a** and **6b** were separated as a mixture by preparative scale GLC. Compound **7a** was not isolated.

Discrimination between the $-CF_2CFH_2$ and $-CFHCF_2H$ isomers was made as described for compounds **1** and **2**, however it should be noted that in the cases of compounds **3a, 6a** and **7a** there is no asymmetric site and hence the fluorine atoms in the $-CF_2-$ group are equivalent and therefore do not appear as an AB quartet. Likewise, **3b** and **6b** contain only one asymmetric site, hence the $-CF_2H$ group for these compounds appears as an AB quartet as opposed to the more complex signal observed for compounds consisting of a mixture of diastereomers such as **4b** and **5b**..

2.2.2 Telomerisation of Trifluoroethene with Triethylamine

Trifluoroethene has been telomerised with triethylamine for the purpose of comparison with diethyl ether. Amines are excellent chain transfer agents, as illustrated in table 2.1.1, and hence this reaction furnished a mixture of mono-, di- and tri-adducts as the predominant components of the reaction product mixture with very little telomer forming, even at a low (1:1) triethylamine:trifluoroethene ratio. Diethyl ether is a substantially poorer chain transfer agent by comparison, giving more telomer even at higher telogen: alkene ratios.

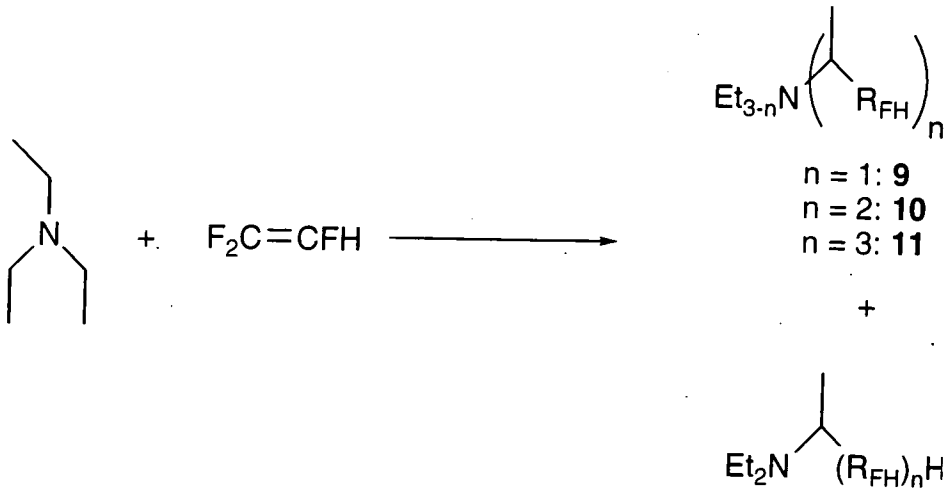
Triethylamine also displays greater regioselectivity than diethyl ether, indicating a more nucleophilic radical. Regioselectivity is lower for the di-adduct than for the mono-adduct. This is expected due to the electrophilicity of the 1:1 adduct radical **II**, from which the di-adduct is produced being greater than the radical derived from triethylamine **I**, from which the 1:1 adduct is produced:



I **II**

Regioselectivity in the tri-adduct was not established due to the complexity of the mixture of isomers observed by GC.

Unlike telomerisation with ethers, conversion of trifluoroethene is not quantitative. This may be attributed to the small quantity of triethylamine employed in this reaction (1 equivalent) as opposed to the 5 equivalents used for diethyl ether.



R_{FH} = $-CF_2CFH_2$ or $-CFHCF_2H$

Conditions: γ-ray, 7 days, room temp.

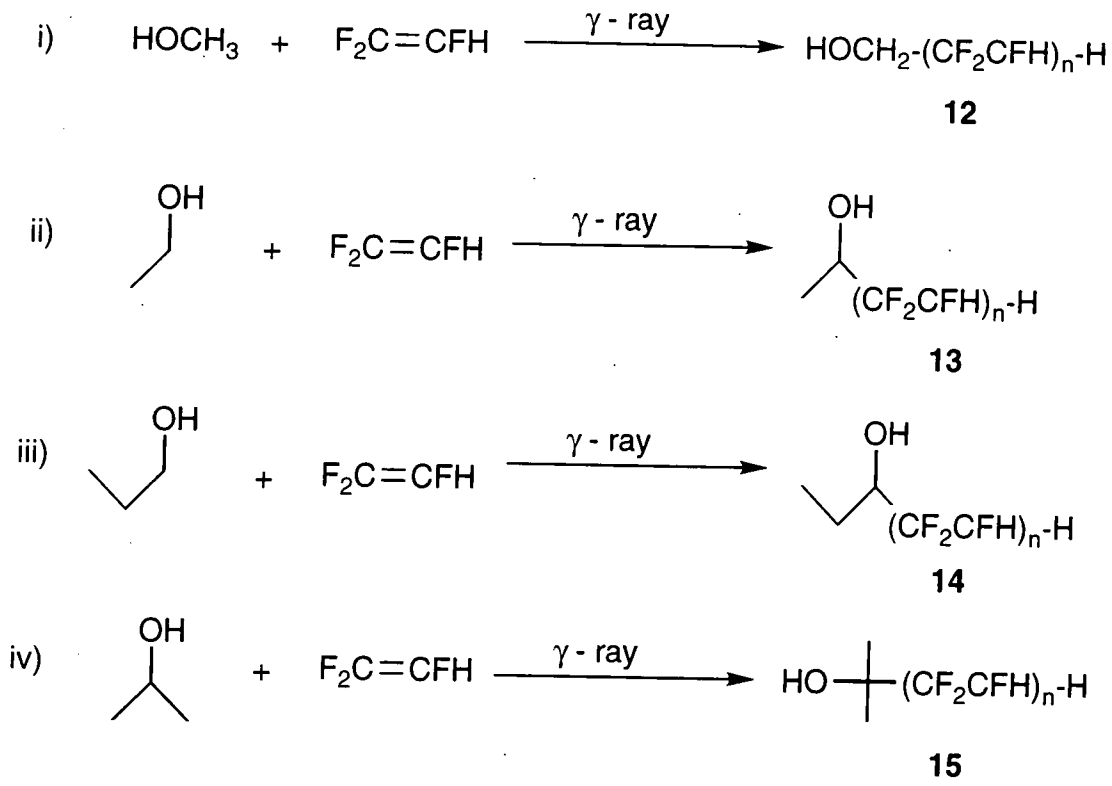
Scheme 2.2.8

Table 2.2.1 Telomerisation with triethylamine

	1:1 adduct	1:2 adduct	1:3 adduct
Composition (%)	49	43	8
$-CFH_2$: $-CF_2H$	95 : 5	76 : 24	-

2.2.3 Telomerisation of Trifluoroethene with Alcohols

Trifluoroethene was telomerised with methanol, ethanol, propanol and 2-propanol using γ-ray initiation with the telogens i) methanol, ii) ethanol, iii) isopropyl alcohol to furnish primary, secondary and tertiary telomer alcohols respectively (scheme 2.2.9). Conversion of trifluoroethene was quantitative in all cases. Average chain lengths and regioselectivities in the telomer mixtures were determined by ^1H and ^{19}F NMR spectra (table 2.2.2).



Conversion of alkene = 100% in all cases

Scheme 2.2.9

Adducts of **13**, **14** and **15** were isolated by distillation and characterised as a mixture of isomers. **12a** (below) was separated by preparative scale GLC.

$HOCH_2CF_2CFH_2$

12a

Table 2.2.2: Telomerisation using alcohols

Chain transfer agent	R_o*	Chain length	$-CFH_2$ end group (%)
Methanol	5	3.5	36
Methanol	10	2.2	51
Ethanol	5	1.5	67
Ethanol	10	1.2	80
1-propanol	10	1.2	82
2-propanol	10	1.1	87

$$*R_o = \frac{\text{Moles of telogen used}}{\text{Moles of trifluoroethylene used}}$$

Chain lengths were calculated by ^{1}H and ^{19}F NMR using trifluoromethylbenzene as an internal integration reference. Thus, the ratio of protons tc fluorine atoms (r) could be found for any given sample since the ratio of protons to fluorine atoms in the reference is known to be 5 : 3. From this, the average chain length n may be established, for example for the methanol / trifluoroethene telomer $HOCH_2(CF_2CFH)_nH$:

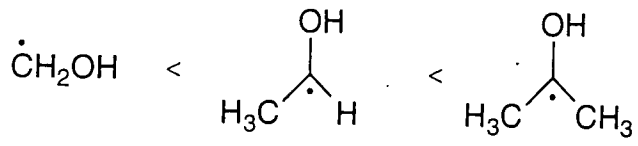
$$r = \frac{\text{number of fluorine atoms}}{\text{number of hydrogen atoms}} = \frac{3n}{n+4}$$

Therefore, $$n = \frac{4r}{3-r}$$

The efficiency of chain transfer, as reflected in the average chain length, increased in the order:

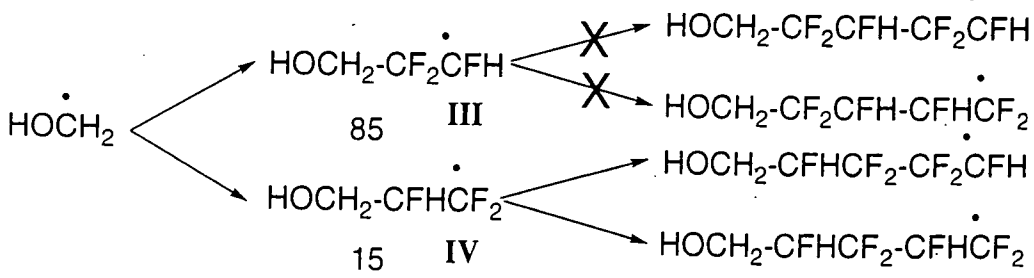
Methanol < Ethanol < Isopropyl alcohol

for which the respective radicals are:



Shorter chains are produced, as expected, from telogens for which the corresponding radical is more stable.

The 1:2 telomer of trifluoroethene prepared using methanol as the telogen consists of only two regio-isomers (as seen by GLC-MS) instead of the four conceivable regio-isomers (scheme 2.2.10). This is due to the fact that only one of the 1:1 adduct radicals undergoes telomerisation. The predominant radical **III** does not add to trifluoroethene. The same observation has been made by Liska[47] in the telomerisation of 2-propanol with trifluoroethene.



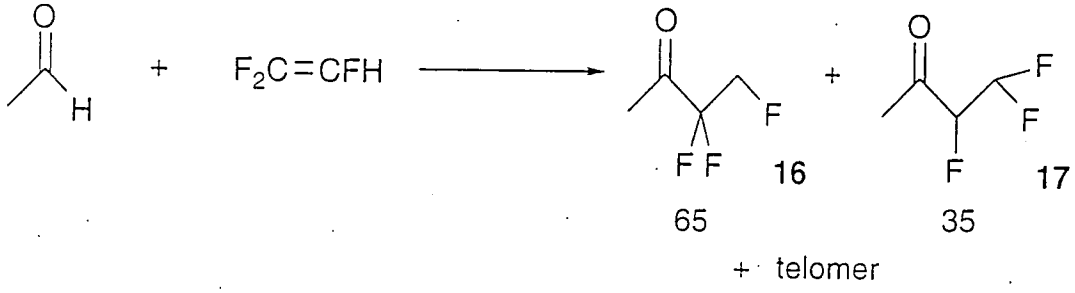
Scheme 2.2.10

A possible explanation may be the relatively high nucleophilicity of trifluoroethene which was illustrated in its addition to the electrophilic species 1,3,5-trioxane (scheme 2.2.3).

The regioselectivity drops for shorter chains (table 2.2.2); this may be attributed to radical polarity. The radical derived from methanol is nucleophilic as discussed in section 2.1.1 and hence preferentially attacks the more elecrophilic CF_2 site of trifluoroethene. The radical **IV** thus produced is far more electrophilic and hence reaction with trifluoroethene is far less regioselective.

2.2.4 Telomerisation of Trifluoroethene with Aldehydes

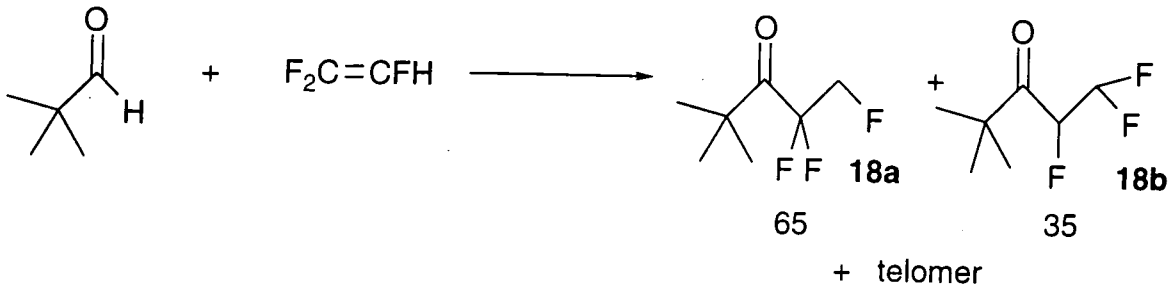
Aldehydes are excellent chain transfer agents, as shown in table 2.1.1. Acetaldehyde readily adds to trifluoroethene under peroxide initiation to give a mixture of the two mono-adducts **16** and **17** (scheme 2.2.11). Very little telomer was formed under the conditions employed. Reaction by γ-ray initiation is complicated by the formation of the acetaldehyde trimer, paraldehyde, at this lower temperature. Unlike other systems described above, the adducts **16** and **17** may be separated by distillation which allows their chemistry to be studied independently of each other.



Conditions: DTBP, 140°C, 24 hrs

Scheme 2.2.11

Similarly, trimethylacetaldehyde was added to trifluoroethene. Trimethylacetaldehyde does not trimerise due to the steric demand of the *t* -butyl group, hence addition was performed by γ-ray initiation.



Conditions: γ-ray, 7 days

Scheme 2.2.12

2.2.5 Large Scale Reactions

Most of the telomerisations described above have been performed under γ-ray initiated conditions. The advantages of γ-ray initiation have been described above (section 2.1.2) however a drawback of this method is that, for reasons of safety, reactions may only be performed in this department on a fairly small (ca. 10g) scale. Telomerisations were performed on a large scale (ca. 40g) for methanol, ethanol, diethyl ether and acetaldehyde in an autoclave using di-*tert*-butyl peroxide as the initiator. Difficulty was encountered with peroxide decomposition on the metal surface of the autoclave, leading to low conversion of trifluoroethene. High conversions of alkene were achieved only when a PTFE lined autoclave fitted with a glass liner was used with a large quantity of peroxide. Under these conditions, conversion of trifluoroethene was high or quantitative, however a drawback of using large quantities of peroxide is that large quantities of *t*-butanol is present in the product mixture. In some cases, e.g. in telomerisation with methanol, difficulty was encountered in separating the telomer product from *t*-butanol.

2.3 Reactions of Trifluoroethene Adducts

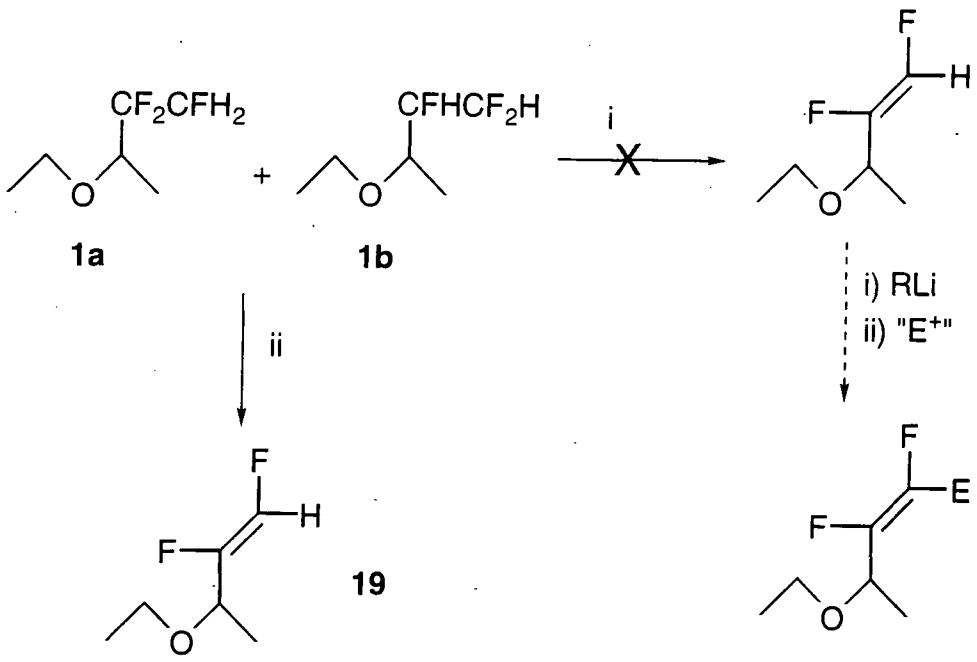
1:1 adducts of the systems described above were isolated from their telomeric mixtures by distillation and the chemistry of these adducts was studied.

2.3.1 Reactions of the Diethyl Ether Adduct

Dehydrofluorination

The preparation of trifluorovinyllithium in one step from HFC 134a and the use of trifluorovinyllithium in synthesising trifluorovinyl compounds has been discussed (section 1.6). An analogous process was attempted with the mixture of adducts **1a** and

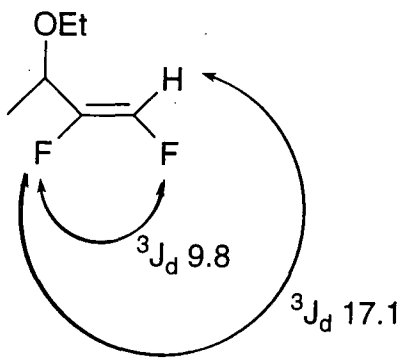
1b in an attempt to prepare a range of difluorovinyl compounds via the lithiation of **19** (scheme 2.3.1). Surprisingly, no dehydrofluorination was observed with a range of alkyllithium reagents. Dehydrofluorination of **1** to give **19** was accomplished using potassium hydroxide.



i) RLi (R = Me, ^{n}Bu, ^{t}Bu, Ph, (i-C_3H_7)$_2$N), Et_2O, -78°C⟶ room temp.
ii) KOH powder, Carius tube, 60°C, 24 hrs

Scheme 2.3.1

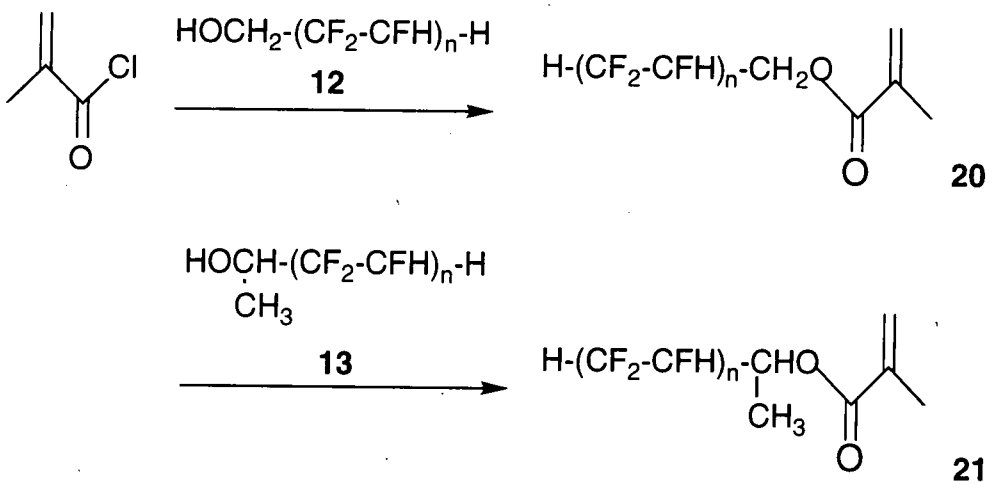
The geometry around the double bond was determined by the magnitude of $^{3}J_{H\text{-}F}$ and $^{3}J_{F\text{-}F}$ couplings across the double bond.



2.3.2 Reactions of Alcohol / Trifluoroethene Adducts

Esterification

Methacrylate esters of the telomer alcohols **12** and **13** were prepared using methacryloyl chloride according to the method described for trifluoroethanol.[104] The polymerisation of **20** and **21** constitutes a separate project in this department.[105]



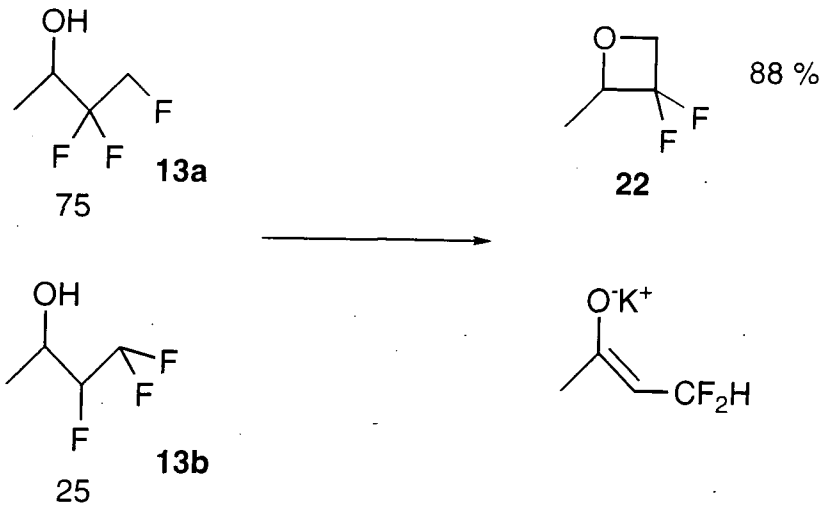
Scheme 2.3.2

Methacrylates of the 1:1 alcohol / trifluoroethene adducts for **20** and **21** were isolated from their respective telomeric mixtures by preparative scale GLC.

Dehydrofluorination

i) Dehydrofluorination to give Oxetanes

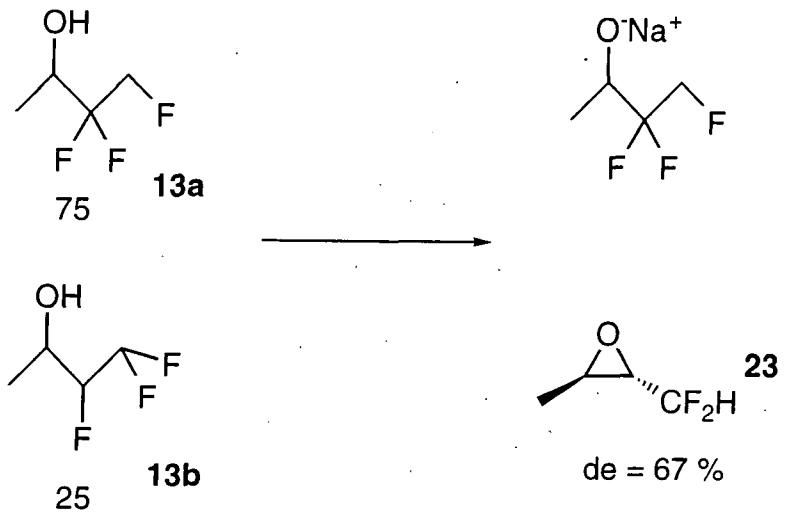
The mixture of adducts **13a** and **13b** were treated with potassium hydroxide in an attempt to produce a difluoroallylic alcohol. Surprisingly, the reaction instead furnished oxetane **22** derived from **13a** with **13b** apparently undergoing dehydrofluorination to produce the potassium salt of an enolate which was not isolated (scheme 2.3.3). Compound **22** was readily isolated by vacuum transfer from the reaction mixture. The nucleophilic displacement of fluoride ion from a saturated and highly fluorinated system, as observed here, is an unusual process.



Conditions: KOH powder, 60°C, 16 hrs

Scheme 2.3.3

Conversely, reaction of **13a** and **13b** with sodium hydroxide furnished **23** only by vacuum transfer (scheme 2.3.4). The reaction of racemic mixture **13b** with sodium hydroxide displayed a degree of stereoselectivity; the anti isomer reacted most readily to furnish **23** in 67 % de. ^{19}F NMR of the residue showed that **13a** was unchanged.



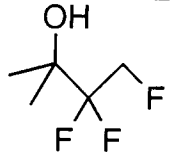
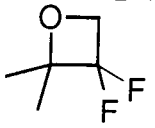
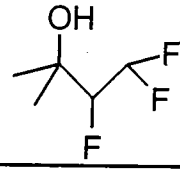
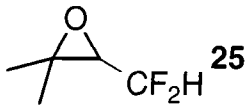
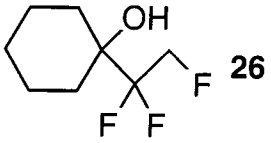
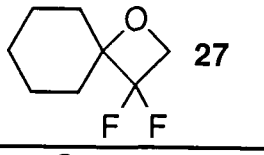
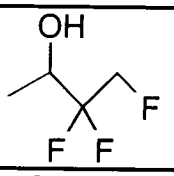
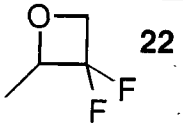
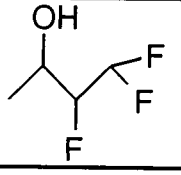
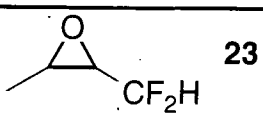
Conditions: NaOH powder, 60°C, 16 hrs

Scheme 2.3.4

In addition, cyclisation has been performed with the 2-propanol / trifluoroethene adducts **15a** and **15b** to furnish a mixture of oxetane **24** and epoxide **25**, and with the cyclohexanol / trifluoroethene adduct **26** to furnish oxetane **27** (table 2.3.1). During the course of this work, the cyclisation of **15** to give **24** and **25** using aqueous potassium

hydroxide was reported by Liska,[47] however no ^{13}C NMR data was given for **15**, **24** or **25** in this work. In the present work, ^{13}C NMR data has been obtained for these three compounds.

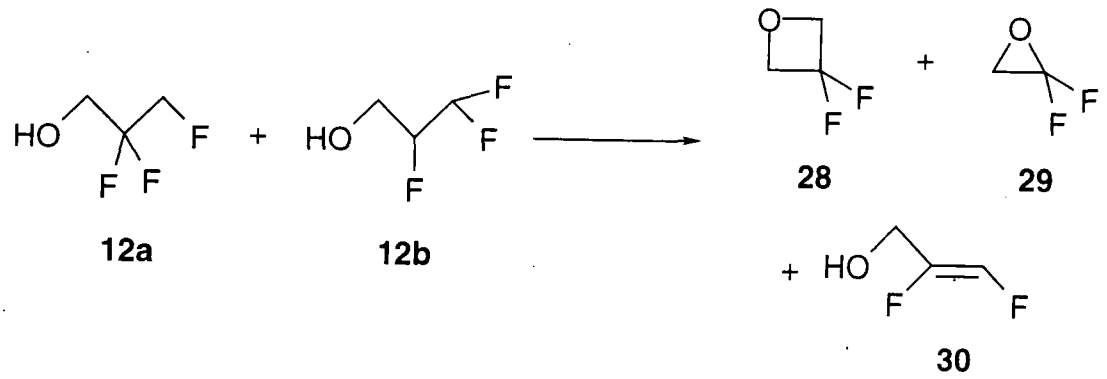
Table 2.3.1 Cyclisation of alcohol adducts

Alcohol	Product	Base	Yield
 **15a**	 **24**	KOH	90
 **15b**	 **25**		
 **26**	 **27**	KOH	79
 **13a**	 **22**	KOH	88
 **13b**	 **23**	NaOH	53

Identification of products. - The ^{19}F NMR spectra of the oxetanes and oxiranes show the disappearance of peaks in the $-CFH_2$ and -CFH- region, leaving only signals for the $-CF_2-$ group and $-CF_2H$ groups respectively. Thus, the $-CF_2-$ group in **22** appears as an AB quartet at -109 ppm. The two fluorine atoms in the $-CF_2-$ groups of are equivalent **24** and **27** hence these appear as triplets ($^3J_{FH}$ = 13.2 Hz) at 500MHz.

Attempts to cyclise **12a** and **12b** were less successful; **28** and **29** have been observed, however they have not been isolated. In addition, difluoroallylic alcohol **30** was observed (scheme 2.3.5). No such allylic alcohol formation was observed for the other systems studied.

Similar findings were made by Liska *et al*[106] in the cyclisation of alcohol / chlorotrifluoroethene adducts whereby cyclisation did not occur for the methanol adduct but did occur for the adducts of higher alcohols (scheme 2.3.6). The explanation offered for this was that the presence of an alkyl R moiety is necessary to force the alcohol into a configuration that favours cyclisation.



Conditions: KOH, 60°C, 16 hrs

Scheme 2.3.5

R^1=H, R^2=alkyl: reaction
R^1=alkyl, R^2=alkyl: reaction
R^1=R^2=H: no reaction

Conditions: aq. NaOH, reflux

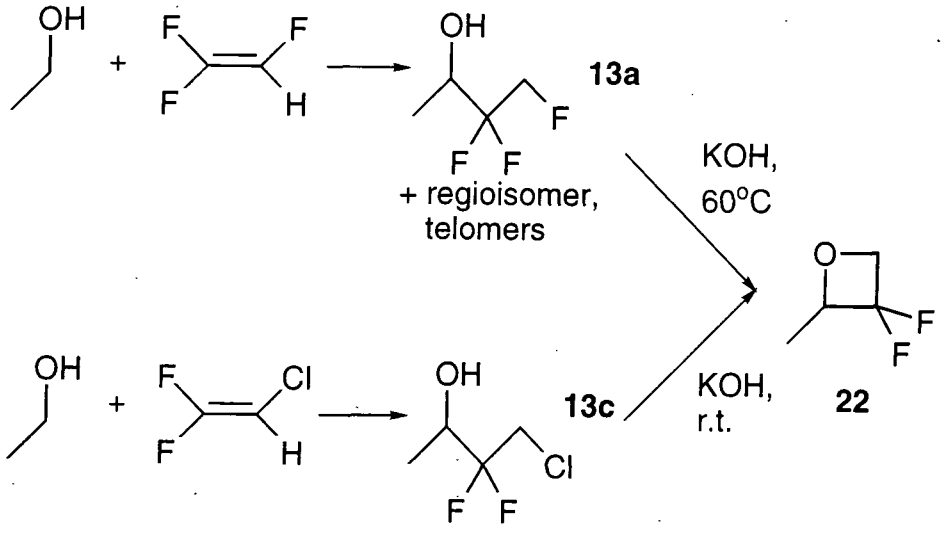
Scheme 2.3.6

Compounds **28** and **29** were identified as described above. Compound **30** was identified as described for alkene **19**.

Use of 1-Chloro-2,2-difluoroethene as a More Efficient Route to Oxetanes

Synthesis of **22** is a two step process; i) telomerisation of ethanol with trifluoroethene to give **13a** and ii) cyclisation over potassium hydroxide to give **22**. Although the second step is an efficient process, the first step is poor in the context of the synthesis of **13a** since substantial quantities of the isomer **13b** and a significant amount of telomer also form in this reaction. Hence, method of improving the overall yield of oxetane **22** over two steps was sought by improving the first step. This was accomplished by adding ethanol to 1-chloro-2,2-difluoroethene to give **44** which underwent cyclisation to give **22** (scheme 2.3.7).

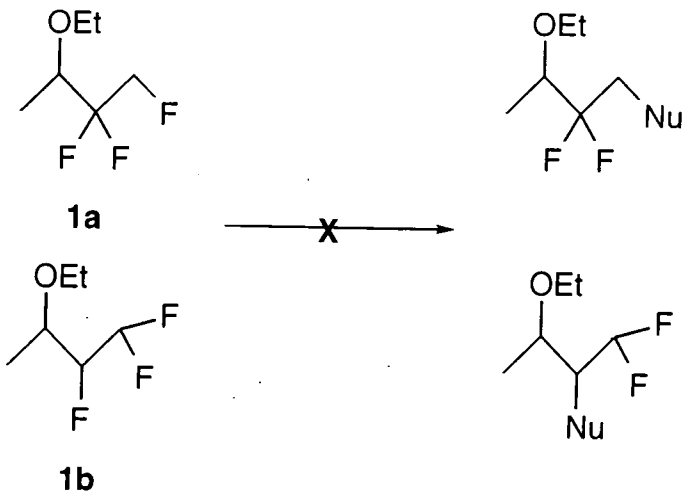
The advantages of 1-chloro-2,2-difluoroethene over trifluoroethene in the synthesis of **22** are twofold; firstly, the addition of ethanol to 1-chloro-2,2-difluoroethene is completely regioselective and no telomer formation is observed. Secondly, cyclisation of **44** occurs at ambient temperature whereas **13a** requires a temperature of 60°C which is due to the relative ease of displacement of chloride ion in comparison to fluoride ion.



Scheme 2.3.7

Attempted nucleophilic displacement

A corresponding intermolecular fluoride ion displacement was attempted with the diethyl ether / trifluoroethene adduct **1**, however this was unsuccessful. The failure of this reaction may be attributed to the entropy for this intermolecular process being less favourable.

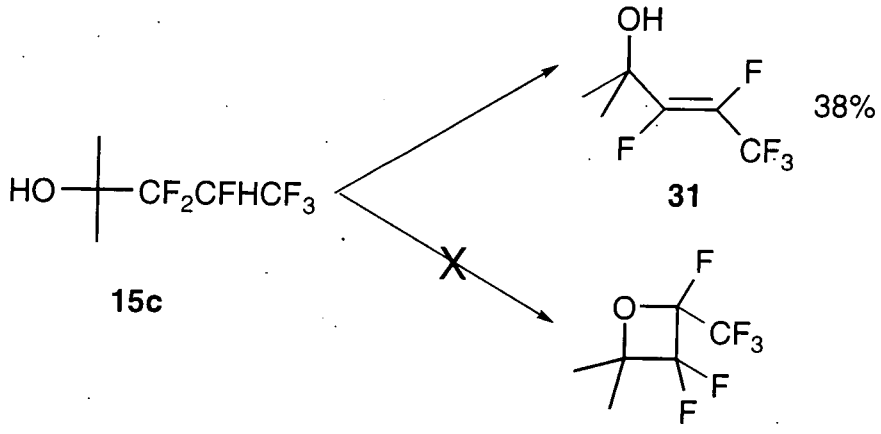


i) KOH, EtOH, reflux, 24 hrs
ii) EtO^-Na^+, MeCN, reflux, 24 hrs

Scheme 2.3.8

Attempted Cyclisation of a Hexafluoropropene / Alcohol Adduct

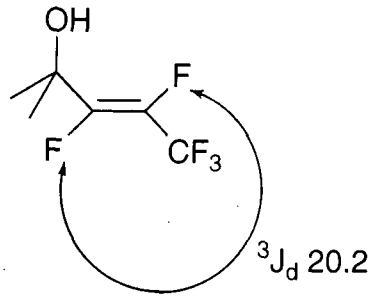
An attempt was made to extend this methodology to hexafluoropropene adducts. Thus cyclisation of the 2-propanol / HFP adduct **15c** was attempted (scheme 2.3.9). This reaction was unsuccessful; **15c** underwent dehydrofluorination to furnish allylic alcohol **31**. The different modes of reactivity of trifluoroethene and hexafluoropropene adducts is due to the acidity of the hydrogen in the fluoroalkyl group being greater for HFP adducts than for trifluoroethene adducts.



Conditions: KOH powder, 60°C, 24 hrs

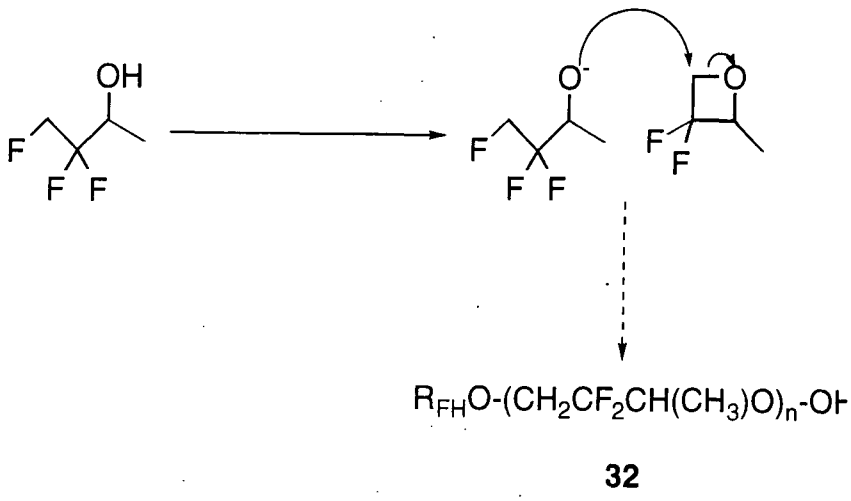
Scheme 2.3.9

The geometry around the double bond was determined by the magnitude of $^3J_{F-F}$ coupling across the double bond.



Oligomerisation of Oxetanes

In addition to the oxetanes and epoxides isolated from reaction of trifluoroethene / alcohol adducts with base, oligomer **32** formed by ring opening of the oxetane was isolated from the solid residue of the reaction mixture.

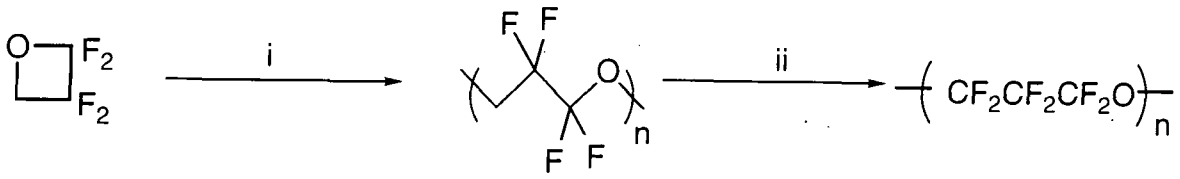


32

Conditions: KOH powder, mechanical stirrer, 1 atm, 80°C

Scheme 2.3.10

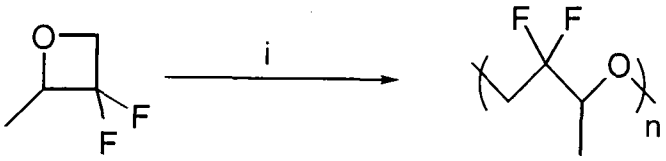
A process for the preparation of such a polymer by caesium fluoride induced oligomerisation of tetrafluoro-oxetane and subsequent fluorination of the oligomer has been patented (scheme 2.3.11).[107]



i) CsF, diglyme, 60°C, 24 hrs

2.3.11

Oligomerisation of the isolated oxetane **22** has also been perfomed. This is more desirable than the one step process as oligomerisation of the isolated oxetane gives a greater degree of control in terms of the chain length of the oligomer. Thus oligomerisation of **22** was attempted with caesium fluoride, however this reaction gave only a trace of oligomer. A higher yield of oligomer was obtained by treatment of **22** with triflic acid.



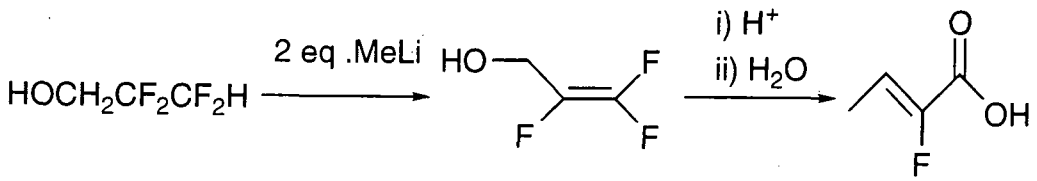
22

i) CsF, diglyme, 80°C, 24 hr: trace of oligomer
ii) CF_3SO_3H, 80°C, 24 hrs: 78%

Scheme 2.3.12

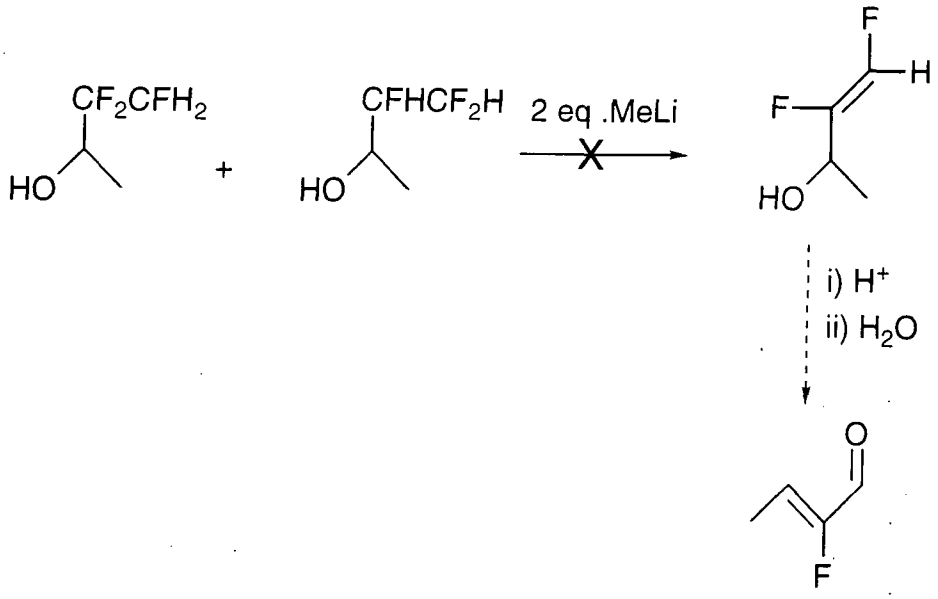
ii) Attempted Dehydrofluorination to give Allylic Alcohols

Attempts to prepare an allylic alcohol by dehydrofluorination of **13** were unsuccessful; as for the diethyl ether adduct discussed above, **13** displayed surprisingly high resistance to dehydrofluorination. The dehydrofluorination of the methanol / tetrafluoroethene adduct, and subsequent reaction of the allylic alcohol thus produced, has been reported by Wakselman[108] (scheme 2.3.13). An attempt to perform the analogous reaction with **13** was unsuccessful (scheme 2.3.14).



Conditions: Et_2O, -78°C ⟶ room temp.

Scheme 2.3.13

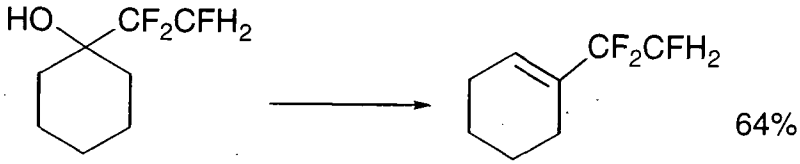


Conditions: Et_2O, -78°C ⟶ room temp.

Scheme 2.3.14

Dehydration

The dehydration of cyclic alcohol / HFP adducts has been carried out in this laboratory.[109] This reaction was applied to the cyclohexanol / trifluoroethene adduct **26** to furnish alkene **33**.



26 **33**

Conditions; $SOCl_2$, pyridine, room temp., 24 hrs

Scheme 2.3.15

The attempted dehydration of **15** under similar conditions was unsuccessful due to the low acidity of hydrogens on the methyl group. However, the conversion was accomplished at a higher temperature and, surprisingly, in the absence of base using a method developed in this laboratory.[110]

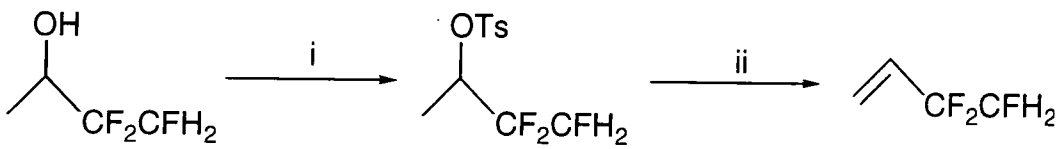
15 **34**

Conditions: $SOCl_2$, reflux, 24 hrs

Scheme 2.3.16

Identification of products - The formation of the alkene moiety was observed in the ^{13}C NMR spectrum for **33** in which carbon 1 appears as a triplet ($^2J_{CF}$ = 9 Hz) at 130 ppm and carbon 2 appears as a singlet at 132 Hz. In compound **34** the $=CH_2$ group appears as a doublet ($^3J_{HH}$ = 26 Hz) at 5.4 ppm.

Dehydration of **14** via its tosylate ester **35** was also successful, giving quantitative conversion of **35** to alkene **36**, however attempts to isolate **36** from the reaction mixture were unsuccessful.



35 78% **36**

Conditions: i) TsCl, pyridine, room temp.
ii) K^+OtBu^-, DMSO, 0°C

Scheme 2.3.17

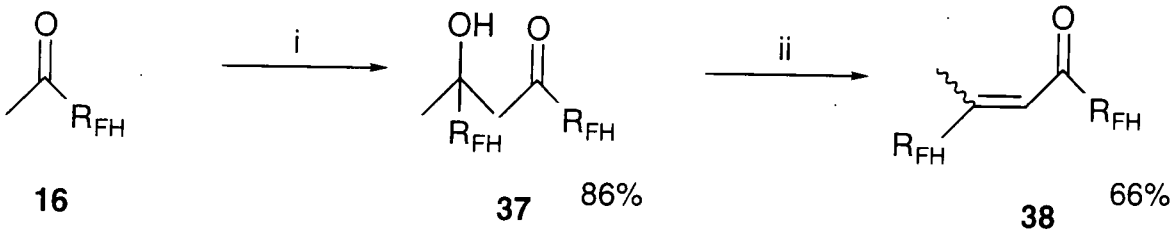
2.3.3 Reactions of the Aldehyde / Trifluoroethene Adducts

Reactions with Base

The reactions of the acetaldehyde adducts in the presence of base were studied. A competition arises here since these compounds may conceivably undergo dehydrofluorination or enolate chemistry in the presence of base.

The rate of enolisation has been established as being of the order of 1000 times faster for trifluoroacetone than for acetone,[111] thus enolate chemistry of fluoro-ketones is facile. McBee *et al* [112] have described the aldol condensation of trifluoroacetone with sodium methoxide. Treatment of **16a** under these conditions gave the corresponding

compound **37** with no accompanying dehydrofluorination (scheme 2.3.18). Treatment of **37** with concentrated sulfuric acid furnished enone **38**. The aldol condensation reaction and subsequent dehydration was also performed for the acetaldehyde hexafluoropropene adduct **16b**.



16 **37** 86% **38** 66%

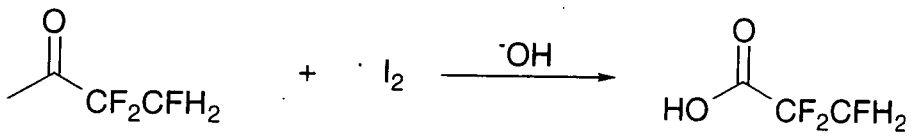
R_{FH} = CF_2CFH_2 **(a)**, CF_2CFHCF_3 **(b)**

Conditions: i) NaOEt, Et_2O, 0°C, 5 hrs
ii) conc. H_2SO_4

Scheme 2.3.18

The ^{19}F NMR spectrum of compound **37a** shows pairs of signals in the $-CF_2-$ and $-CFH_2$ regions. The formation of a carbon-carbon bond is shown in the ^1H NMR spectrum in which the protons in the $-CH_2-$ group appear at 3.20 ppm as an AB quartet as a consequence of these two protons being inequivalent. Enones **38a** and **38b** underwent decomposition over a period of days, hence these species were not fully characterised. However, the ^1H NMR spectra of these species do show a vinylic methyl group (2.2 ppm) and a vinylic proton (6.9 ppm).

Similarly, the iodoform reaction was performed to give the acid **39** and again no dehydrofluorination was observed.

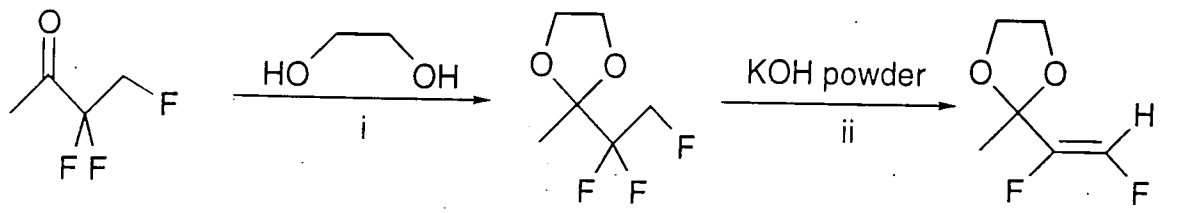


39

Conditions: aq. Na_2CO_3, KI, room temp.

Scheme 2.3.19

Dehydrofluorination of **16a** was accomplished by protection with ethylene glycol and treatment of dioxolane **40** with potassium hydroxide. Attempts to produce a fluorinated enone by deprotection of **41** were unsuccessful.



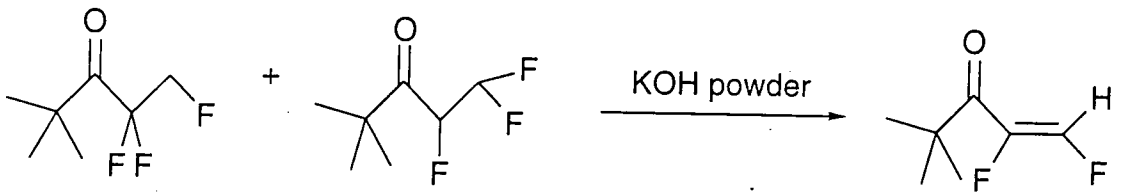
40 58%

41 60%

Conditions: i) $AlCl_3$, 100°C, 24 hrs
ii) 60°C, 24 hrs

Scheme 2.3.20

A fluorinated enone has been prepared by reaction of the pivaldehyde / trifluoroethene adduct **18**, which cannot undergo enolisation, with potassium hydroxide.



18a **18b** **42** 63%

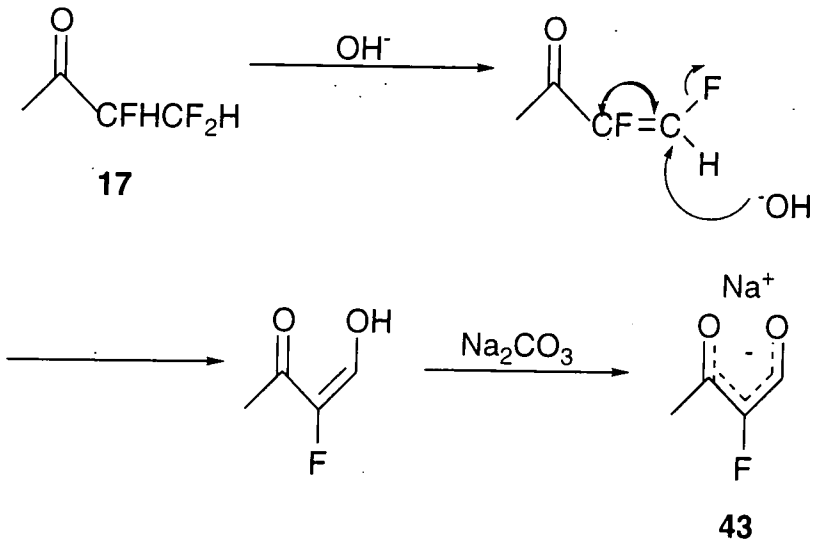
Conditions: 60°C, 24 hrs

Scheme 2.3.21

The geometry around the double bond was determined by the magnitude of $^3J_{F-H}$ and $^3J_{F-F}$ couplings, as described for **19**.

These results show that **16** has a preference for enolisation over dehydrofluorination. The opposite was observed for it's regio-isomer **17** which was treated with base in an attempt to produce the aldol condensation product. However, this reaction gave a product which was identified tentatively as **43** (scheme 2.3.22). Compound **43** underwent decomposition over a period of days hence identification was by ^1H and ^{19}F NMR spectra only.

A possible mechanism for this transformation entails dehydrofluorination as the first step. The propensity of **17** for dehydrofluorination in comparison to **16** may be attributed to the high acidity of the α proton in **17**.



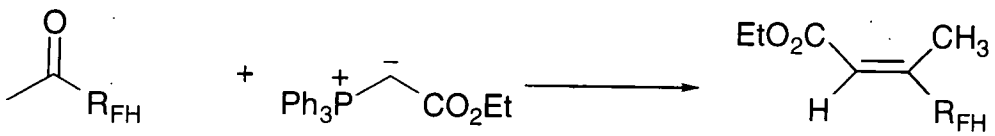
17 **43**

Conditions: aq. Na_2CO_3, room temp.

Scheme 2.3.22

Wittig Reactions

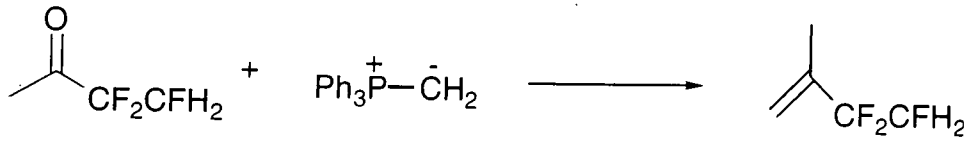
The electron withdrawing effect of a fluoralkyl group renders fluoro-ketones highly susceptible to nucleophilic attack, for example hexafluoroacetone will form it's hydrate on standing in air. This nucleophilicity was exploited by reacting **16** with both a stabilised and a non-stabilised ylide to furnish a fluorinated α, β unsaturated ester **44** and a fluorinated pentene **34** (scheme 2.3.23), which has also been prepared by dehydration of **15** (scheme 2.3.15).



16 **44**

R_{FH} = CF_2CFH_2 **(a)** 40%, CF_2CFHCF_3 **(b)** 87%

Conditions: diethyl ether, room temperature, 16 hours



16 **34**

Conditions: THF, room temperature, 16 hours

Scheme 2.3.23

Chapter 3

Preparation and Reactions of Polymers of Trifluoroethene

3.1 Introduction

Poly(trifluoroethene) has been prepared both with and without solvents and on the surface of titanium dioxide pigments. The fluorination and pyrolysis of the polymers have been studied.

The polymerisation of fluoro-ethenes, including trifluoroethene, by β and γ-ray initiation has been studied by Fokin et al.[113]

Results and Discussion

3.2 Preparation of Polymers

3.2.1 Bulk Polymerisation

Bulk poly(trifluoroethene) **45** was prepared by irradiation of the monomer using a ^{60}Co γ-ray source (scheme 3.2.1). Polymerisation was performed at theoretical pressures of 6 atm. and 12 atm. Significantly, the polymer prepared at the lower pressure is soluble in acetone whereas that prepared at the higher pressure is only sparingly soluble, indicating a higher degree of cross linking and greater molecular weight in the polymer prepared at the higher pressure.

45

Conversion = 100%
Conditions: γ - ray, 7 days, room. temp.

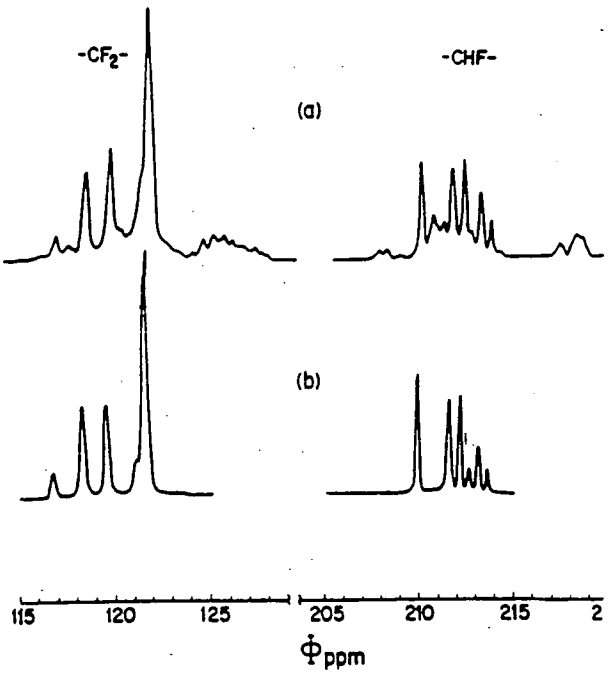
Scheme 3.2.1

The regioregularity of poly(trifluoroethene) has been studied by Tonelli[114] who compared the ^{19}F NMR spectrum of a completely regioregular sample of poly(trifluoroethene), prepared by reductive dechlorination of poly(chlorotrifluoroethene) (Kel-F), with that of a sample containing defects, prepared at 0°C using trichloroacetyl peroxide as the initiator. Tonelli established that the sample prepared at 0°C contained 11.6% defect from complete regioregularity.

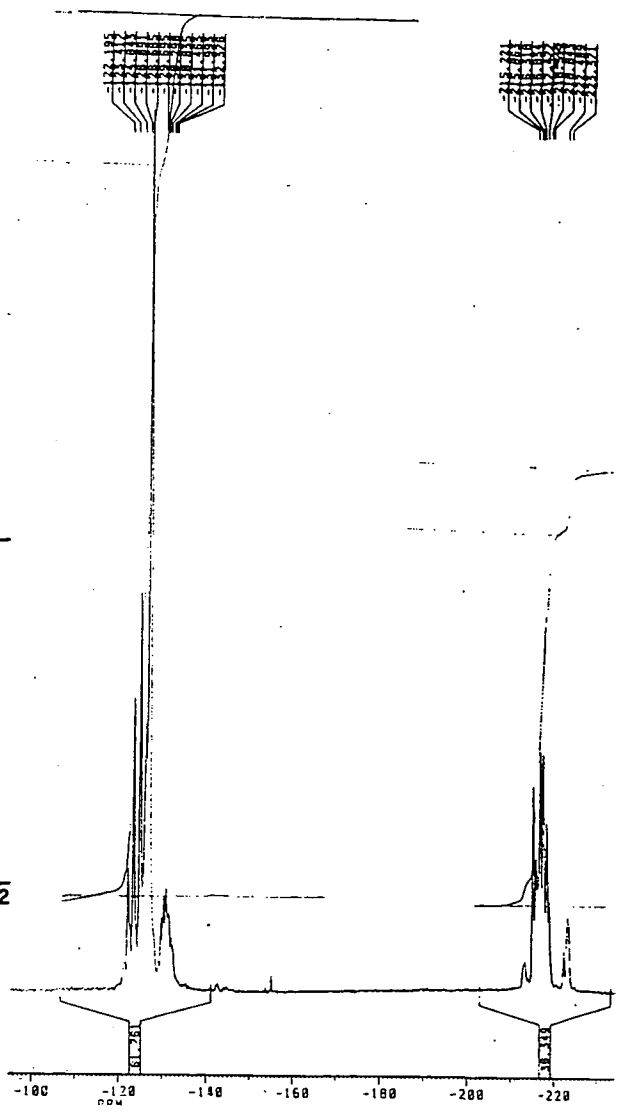
The ^{19}F NMR spectra of poly(trifluoroethene) studied by Tonelli is shown below for both the -CF_2- and -CFH- regions in which (a) is a sample containing defects and (b) is regioregular poly(trifluoroethene) . The signals arising from defects are distinct from those of the regioregular material, hence the degree of the defect may be established by integration.

Using this method, **45** was established to have 15% head-head or tail-tail defect from the completely regioregular head-tail polymer.

^{19}F NMR of Polytrifluoroethene reported by Tonelli.[114]



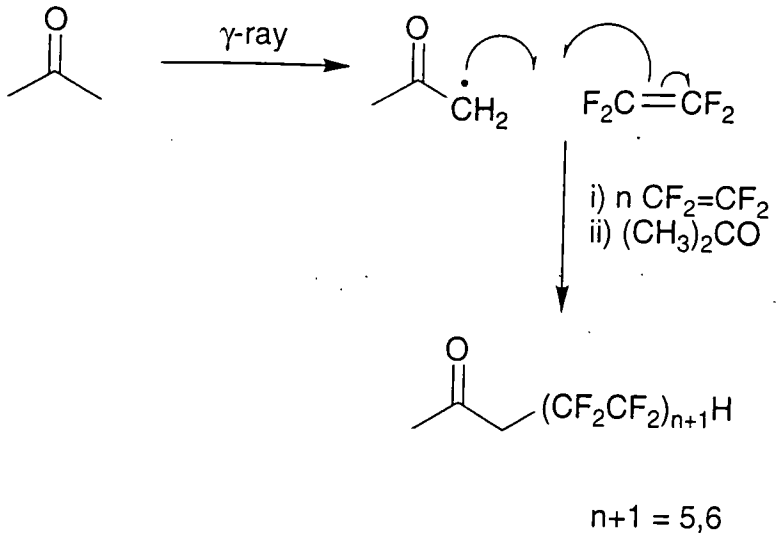
^{19}F NMR spectrum of **45**



3.2.2 Polymerisation using Solvents

Chain Shortening with Acetone

Kiryukhin *et al*[115] have reported the telomerisation of tetrafluoroethene in acetone to produce soluble, transparent telomers (scheme 3.2.2). Acetone is a poor chain transfer agent in comparison to the telogens discussed in chapter 2, hence the average chain length of the telomers is greater.



Scheme 3.2.2

In the present work, the analogous reaction has been performed with trifluoroethene to give chain shortened polymers **46** (scheme 3.2.3). The chain length of the polymer may be controlled by variation of the acetone / trifluoroethene ratio to give a range of average chain lengths. Once again, these polymers are soluble in acetone.

46

Conversion = 100%
Conditions: γ - ray, 7 days, room. temp.

Scheme 3.2.3

The average chain lengths of the polymers prepared at different acetone / trifluoroethene ratios are given in table 3.2.1.

Table 3.2.1 Average chain lengths of **46**

R_0*	Average Chain Length
1	45
2	38
5	15
15	11

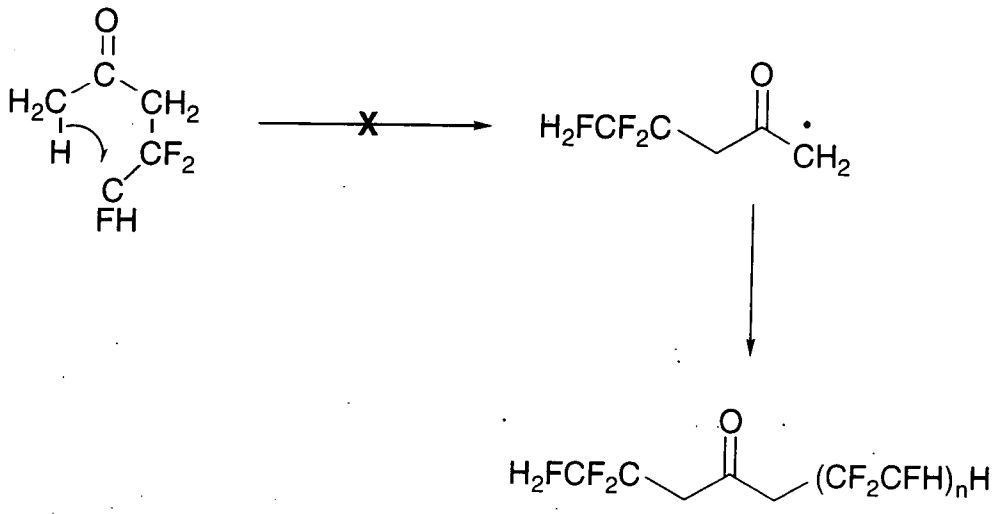
$$*R_o = \frac{\text{Moles of telogen used}}{\text{Moles of trifluoroethylene used}}$$

n values were calculated by two different methods for each sample:

i) the methyl of the end group of compound **64** is visible in the ^1H NMR spectrum at ca. 2.5 ppm which allows average chain lengths to be calculated by comparison of the integrals in the ^1H NMR spectrum of the methyl group (3 hydrogens) and the -CFH- group (n hydrogens)

ii) comparison of the sum of integrals of the ^1H NMR spectrum and the ^{19}F NMR spectrum, using trifluoromethylbenzene as an internal integration reference.

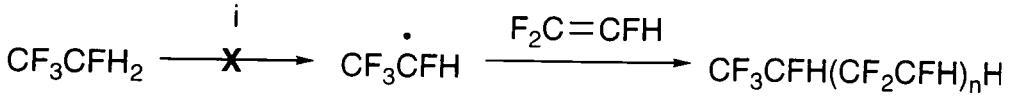
The chain lengths calculated by these methods were in good agreement for all samples which indicates that there is no significant amount of backbiting (as illustrated in scheme 3.2.4). The absence of any observable backbiting is further demonstrated by the fact that the ^1H NMR integrals of the methyl and the $-CH_2-$ moieties in the acetone end group of the polymer gives a ratio of 3:2.



Scheme 3.2.4

Polymerisation in HFC 134a

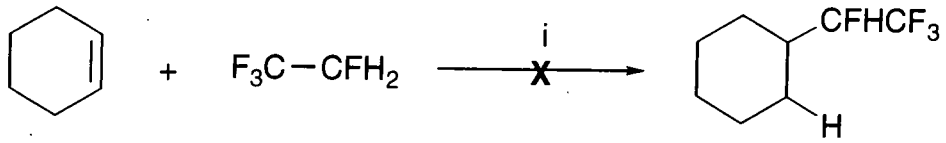
Polymerisation was attempted using HFC 134a as a solvent, however this gave very little polymer, suggesting that HFC 134a was acting as an efficient chain transfer agent. However, no telomeric material was detected in the reaction mixture (scheme 3.2.5).



i γ - ray, room temperature, 7 days

Scheme 3.2.5

It would be expected that reaction would be more favourable with a nucleophilic alkene as the radical produced from HFC 134a is electrophilic. Therefore, addition of 134a to cyclohexene was attempted, however this gave no conversion of trifluoroethene by γ-ray, UV or peroxide initiation (scheme 3.2.6).



i γ-ray, room temp., 7 days, or
DTBP, 140°C, 24 hrs or
UV, 48 hrs

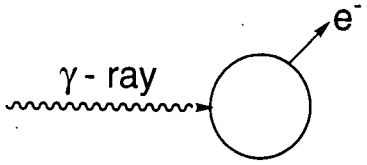
Scheme 3.2.6

The inhibition of radical chemistry by HFC 134a observed here has not been explained, however an explanation may be the possibility of a radical inhibitor present as an impurity in the HFC 134a used.

3.2.3 Titanium Dioxide Encapsulation

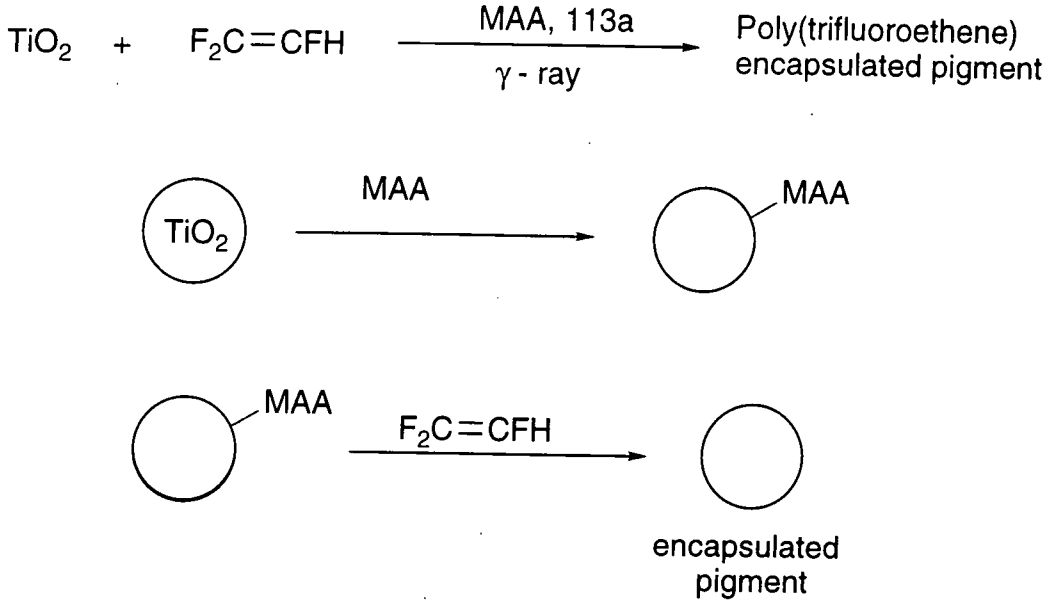
Titanium dioxide may be encapsulated by polymers by irradiation of TiO_2 in the presence of monomer. This has been performed in this laboratory for a number of fluorinated and non fluorinated monomers.[116, 117]

Irradiation of TiO_2 results in the production of secondary electrons which initiate polymerisation at the TiO_2 surface (scheme 3.2.7). TiO_2 has a large γ-ray capture cross section, hence polymerisation occurs predominantly at the surface of TiO_2 rather than in solution.



Scheme 3.2.7

Use of methacrylic acid promotes polymerisation at the surface, apparently by adsorbtion and subsequent initiation. In the present work, this methodology has been applied using trifluoroethene (scheme 3.2.8).



MAA = methacrylic acid

Conversion = 100%
Conditions: γ-ray, 7 days

Scheme 3.2.8

Complete conversion of trifluoroethene was achieved for the two TiO_2 pigments studied (table 3.2.2). Electron microscopy studies showed that polymerisation has occurred mainly at the TiO_2 surface, however some free polymer is also formed. Encapsulation was shown to be uniform and complete.

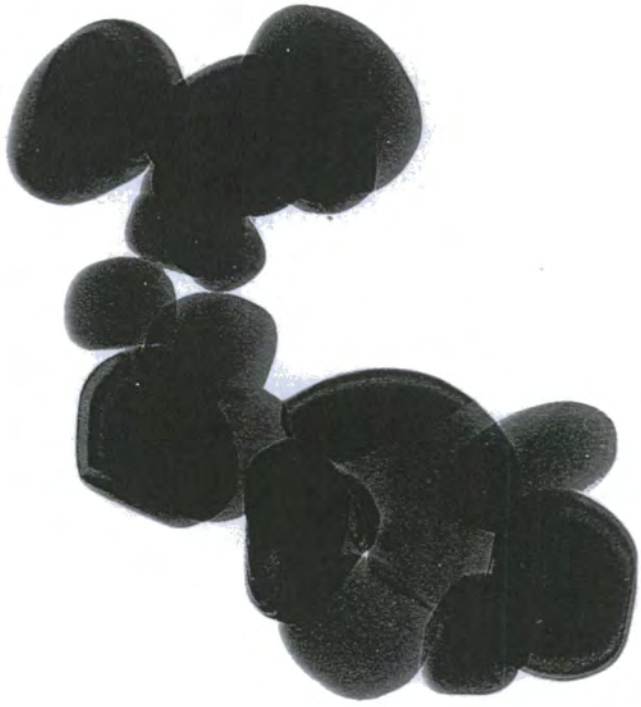
Table 3.2.2. Conversions for TiO_2 encapsulation reactions.

TiO_2 pigment	Conversion of trifluoroethene (%)
TC90	100
TR92	100

Electron Micrographs of Encapsulated Samples

i) TR90

ii) TC90



3.3 Reactions of Polymers

3.3.1 Fluorination of Polymers

i) Bulk polytrifluoroethene

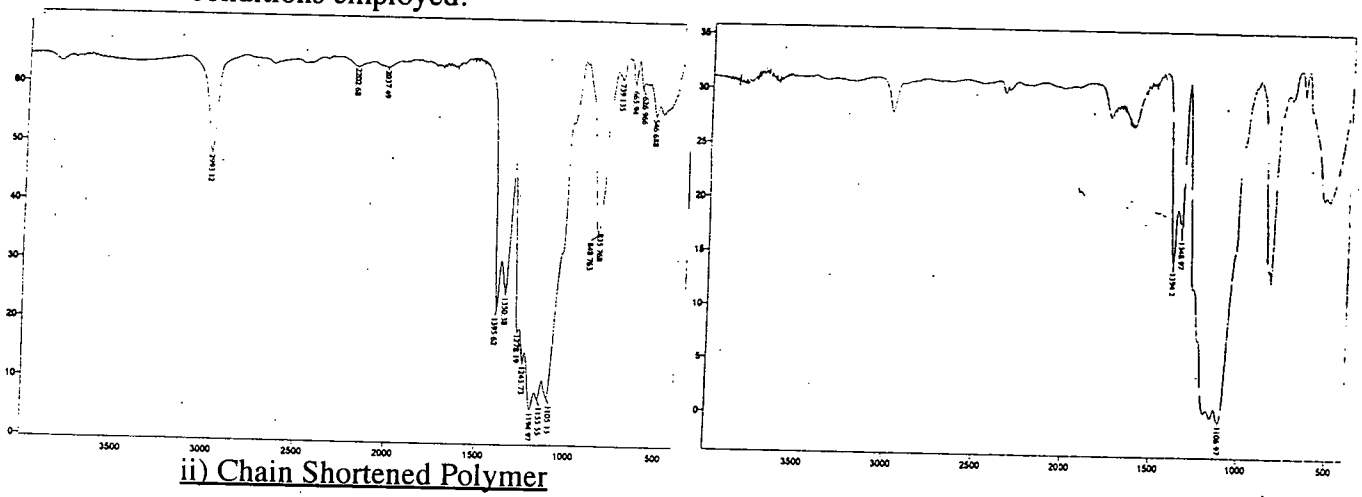
As stated above, polytrifluoroethene prepared at low monomer pressure is soluble in acetone, hence films of polytrifluoroethene may be cast. This is significant since polytetrafluoroethene (PTFE) is not soluble. In the present work, a polytrifluoroethene film was fluorinated to produce a PTFE film **47**. This was accomplished by coating a glass rod with a thin film of **45** and exposing it to elemental fluorine (scheme 3.3.1).

45 **47**

Conditions: 5 bar of 50:50 F_2/N_2, 50°C, autoclave 24 hrs

Scheme 3.3.1

Identification of the product. - Elemental analysis of **47** showed a decrease in hydrogen content and the IR spectrum of the product gave a much smaller absorbtion in the C-H region and showed changes in the C-F region (below). Attempts to establish the degree of fluorination by X-ray photoelectron spectroscopy were unsuccessful since the polymer films used became inhomogeneous upon exposure to fluorine under the conditions employed.



ii) Chain Shortened Polymer

The polymer chain shortened with acetone (**46**) was fluorinated under the same conditions employed for the bulk polymer (scheme 3.3.2). **46** appears to fluorinate more readily than the bulk polymer as illustrated by the IR spectrum of the product

which shows no residual C-H absorptions and no carbonyl absorption. This may be due to the fact that polymers **46** have substantially shorter chain lengths than **45** which may result in the whole of the surface of **46** being more exposed, and therefore more readily attacked by fluorine, than **45**.

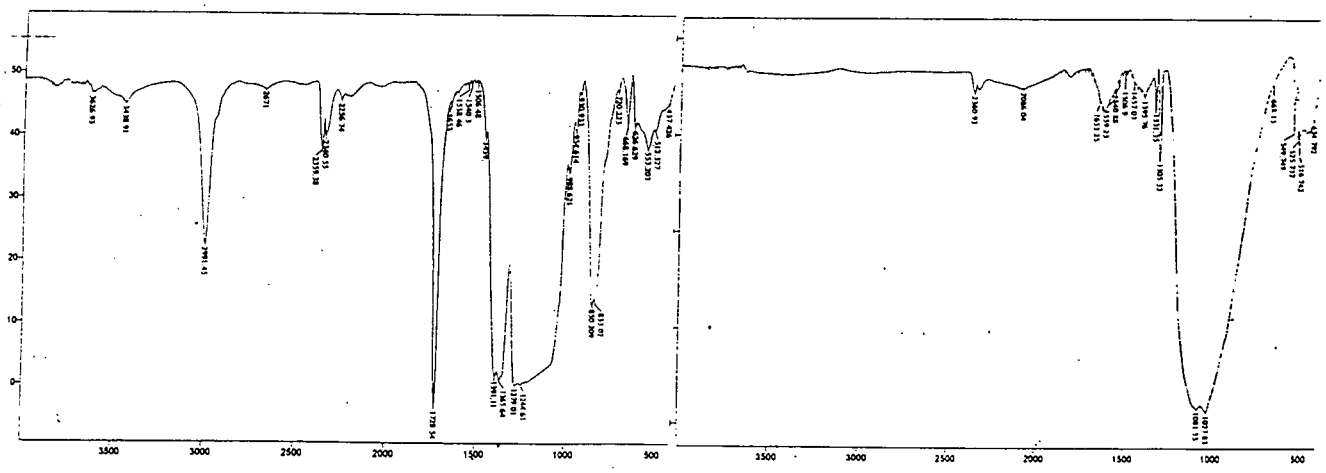
An alternative explanation is that fluorination of the acetone end group occurs very readily and this may help initiate free radical fluorination of the polymer chain. This possibility was investigated by fluorinating **45** in the presence of a small quantity of acetone, however no significant improvement in the degree of fluorination was observed.

46 **48**

Conditions: 5 bar of 50:50 F_2/N_2, 50°C, autoclave, 24 hrs

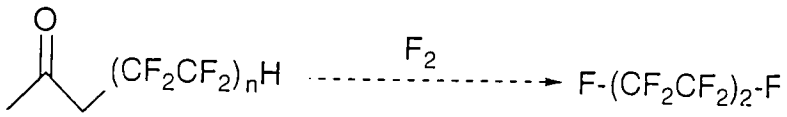
Scheme 3.3.2

Identification of the product. - Elemental analysis of **48** showed a decrease in hydrogen content and the IR spectrum of the product gave no absorbtion in the C-H or C=O regions and showed changes in the C-F region (below).



Kiryukhin has proposed the use of the acetone / tetrafluoroethene telomer discussed above (section 3.2.2) as a water repellent and chemically stable coating. The fluorinated telomer **48** would be more desirable as a coating as it would perform these functions more effectively.

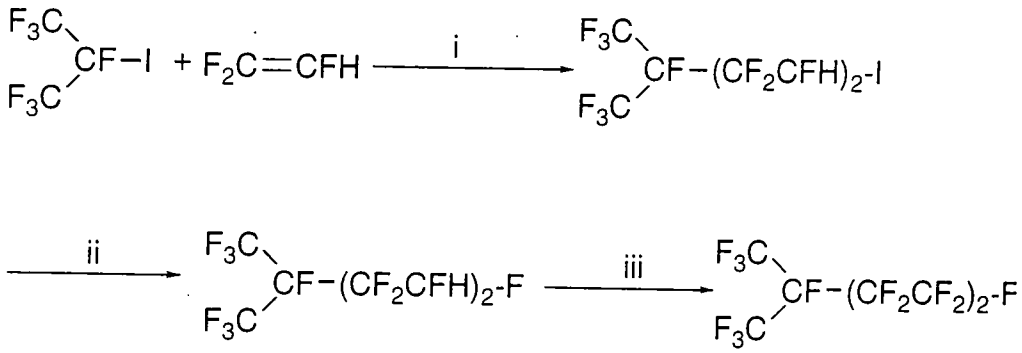
Fluorination of the acetone / tetrafluoroethene telomer (scheme 3.3.3) would be a more facile process than that described above for **46** as it does not involve the fluorination of a highly fluorinated chain, however this has not been performed in this project.



Scheme 3.3.3

iii) Model compound

In addition to evidence obtained by IR spectroscopy and elemental analysis, further evidence for the fluorination of trifluoroethene chains was obtained by the fluorination of the model compound **49** prepared by telomerisation of perfluoroisopropyl iodide with trifluoroethene as reported by Ameduri *et al*[16] and fluorodeiodination of the telomer with antimony pentafluoride, as performed in this laboratory for the corresponding VDF telomer.[118] **49** was fluorinated under the conditions employed for polymer fluorination to give **50** (scheme 3.3.4).



49 **50**

i) sealed metal tube, 200°C, 24 hrs, fractional distillation
ii) SbF_5, 0°C
iii) 5 bar of 50:50 F_2/N_2, autoclave, 24 hrs

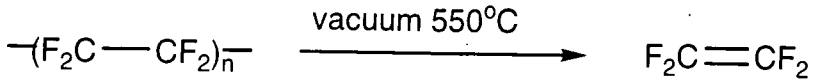
Scheme 3.3.4

Identification of the product. - **50** was observed by GLC-MS in addition to some starting material and minor unidentified products. The ^{19}F NMR spectrum of **49** is complex, consisting of a number of regio- and diastereoisomers. The ^{19}F NMR spectrum of **50** was simpler and gave no resonances in the -CFH- or -CFH_2 regions.

3.3.2 Pyrolysis

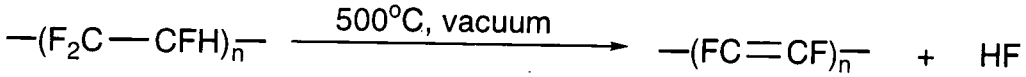
i) Bulk Polymer

PTFE 'unzips' back to it's monomer upon pyrolysis under vacuum (scheme 3.3.5).



Scheme 3.3.5

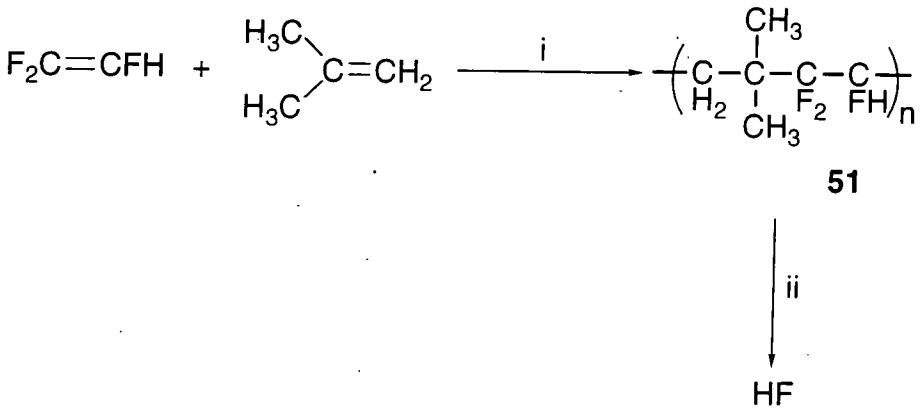
An attempt to perform a similar reaction with polytrifluoroethene resulted in elimination of HF and formation of a black, insoluble solid which would appear to be a fluorinated polyacetylene (scheme 3.3.6), however no characterisation has been obtained for this material. The pyrolysis of polytrifluoroethene has also been reported by Madorsky[119] to give only HF and no monomer.



Scheme 3.3.6

ii) Isobutene / trifluoroethene Copolymer

The isobutene / trifluoroethene copolymer **51** was prepared and pyrolysed (scheme 3.3.7) in an attempt to break C-C bonds at the sterically crowded quaternary sites, thus producing novel fluorinated alkenes, however the only reaction observed was again elimination of HF.



i DTBP, 140°C, 24 hrs
ii 500°C, vacuum

Scheme 3.3.7

Chapter 4

Cohalogenation using Trifluoroethene

4.1 Introduction

The preparation of fluoroethers and halofluoroethers via nucleophilic attack of alkoxides on fluoro-alkenes is well known; this work is reviewed briefly below. In the present work, similar compounds have been prepared via an *electrophilic* cohalogenation methodology, using trifluoroethene and other fluoro-alkenes. The cohalogenation reaction has found widespread application in organic synthesis[120], however it has not previously been applied to fluoro-alkenes as a route to fluorinated ethers. The electrophilic chemistry of fluoro-alkenes often requires forcing conditions, however it has been performed in the present work under fairly mild conditions. The electrophilic chemistry of trifluoroethene has been reviewed in section 1.5.

4.1.1 Reported Halofluoroether Syntheses via a Nucleophilic Methodology

The first syntheses of halofluoroethers were performed by Swarts[49, 121] by nucleophilic substitution reactions with halofluoroalkanes as illustrated in scheme 4.1.1. The nucleophilic additions of alcohols to CF_2=CFCl reported by Park *et al* in 1948[122] is an early example of the synthesis of halofluoroethers via a nucleophilic methodology (scheme 4.1.2).

$$BrF_2C-CFBrH + CH_3CH_2OH \xrightarrow{KOH} CH_3CH_2OCF_2CFBrH$$

Scheme 4.1.1

$$ROH + F_2C=CFCl \xrightarrow[\text{room temp.}]{KOH} ROCF_2CFClH$$

70 - 85 %

Scheme 4.1.2

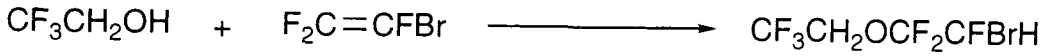
This reaction was subsequently extended to a variety of other fluoro-alkenes[123-125] (CF_2=CF_2, CF_2=CHBr, CF_2=CFI, CF_2=CFBr, CF_2=CH_2 and CF_2=CHI) as illustrated by reaction of sodium butoxide with tetrafluoroethene (scheme 4.1.3).

$$^nBuO^-Na^+ + F_2C=CFCl \longrightarrow BuOCF_2CF_2H$$

Conditions: autoclave, room temp., 5 hrs,
10% solution of butoxide in butanol

Scheme 4.1.3

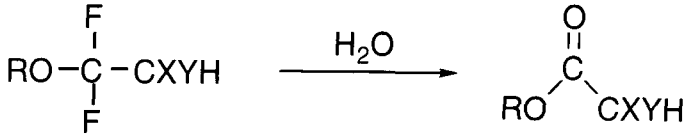
Similarly additions of fluorinated alcohols with a range of fluorinated alkenes have been reported,[126] as illustrated by the addition of trifluoroethanol to bromotrifluoroethene (scheme 4.1.4).



Scheme 4.1.4

4.1.2 Hydrolysis of Halofluoroethers

The $-CF_2-$ moiety in the fluoroethers produced thus displays varying degrees of susceptibility towards hydrolysis to form esters (scheme 4.1.5); some ethers undergo hydrolysis on standing in air. A general trend of hydrolytic stability for ethers of the type $ROCF_2CXYH$ (X = F, H; Y = F, halogen) has been established[125] whereby stability increases for more electron withdrawing -CXYH groups. This is the anticipated trend; loss of fluoride ion is less favourable in the more electron deficient species.



Scheme 4.1.5

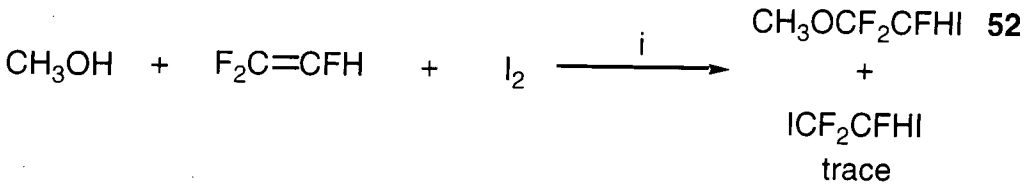
Tarrant[127] has reported a method for the acid hydrolysis of ethers derived from chlorotrifluoroethene (scheme 4.1.6). This method was subsequently employed by Park[123] with a wider range of ethers.

Conditions: H_2SO_4, 0°C, 3 hrs

Scheme 4.1.6

4.2.1 Methanol

Trifluoroethene underwent cohalogenation in the presence of methanol and iodine to furnish iodofluoroether **52** and a small quantity of diiodotrifluoroethane (scheme 4.2.1). The preparation of **52** has been reported by Park *et al.*[123]

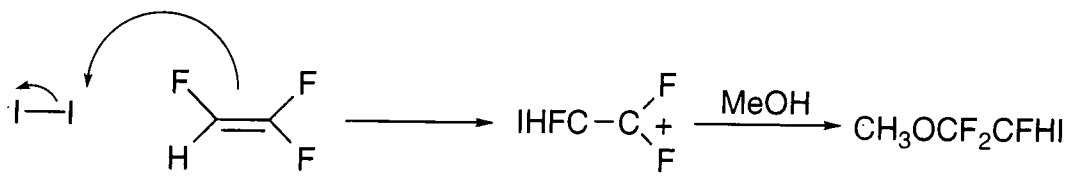


Conversion of trifluoroethene = 85 %; yield = 68%

i) Carius tube, 60°C, 40 hrs

Scheme 4.2.1

The mechanism of this reaction is given in scheme 4.2.2. The reaction is completely regioselective; the carbocation intermediate is centred on the CF_2 site, as observed for other electrophilic reactions of trifluoroethene (section 1.5).



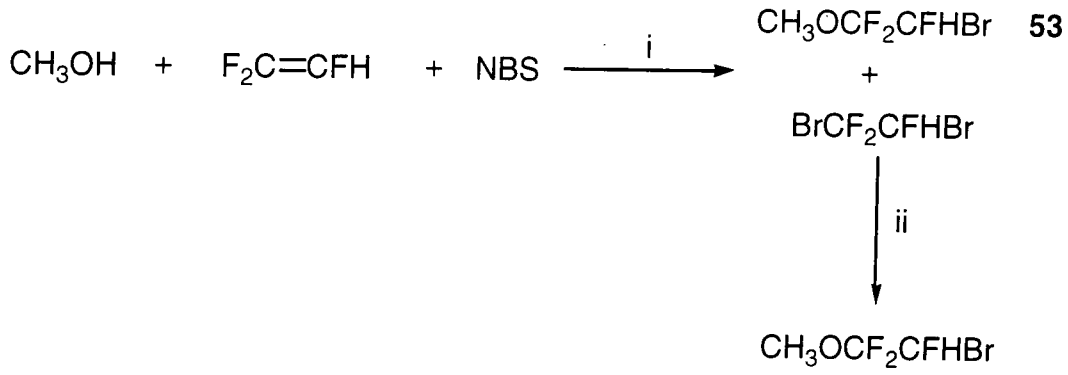
Scheme 4.2.2

The analogous reaction with bromine gave quantitative conversion of trifluoroethene to give dibromotrifluoroethene and compound **53** in a 3:1 ratio. The disparity in quantities of halogen addition products formed with bromine and iodine may be attributed to the substantially greater steric demand of the diiodo compound which makes its formation less favourable. Use of N-bromosuccinimide (NBS) in place of bromine gave **53** as the main product with the dibromo compound as the minor product (scheme 4.2.3), thus throughout the course of these cohalogenation reactions, NBS and iodine have been employed as sources of bromonium and iodonium ions respectively. In general, reactions with iodine gave only small or trace amounts of diiodotrifluoroethane whereas reactions with NBS gave more significant quantities of

dibromotrifluoroethane. A large excess of alcohol was used for all reactions in order to minimise dihalotrifluoroethane formation.

Dibromotrifluoroethane was removed from the product mixture by treatment with zinc powder.

The preparation of **53** by reaction of methanol with bromotrifluoroethene under basic conditions has been reported by Demiel.[125]



Conversion of trifluoroethene = 75 %; yield = 46%

i) Carius tube, 60°C, 40 hrs

ii) Zn powder, room temp.

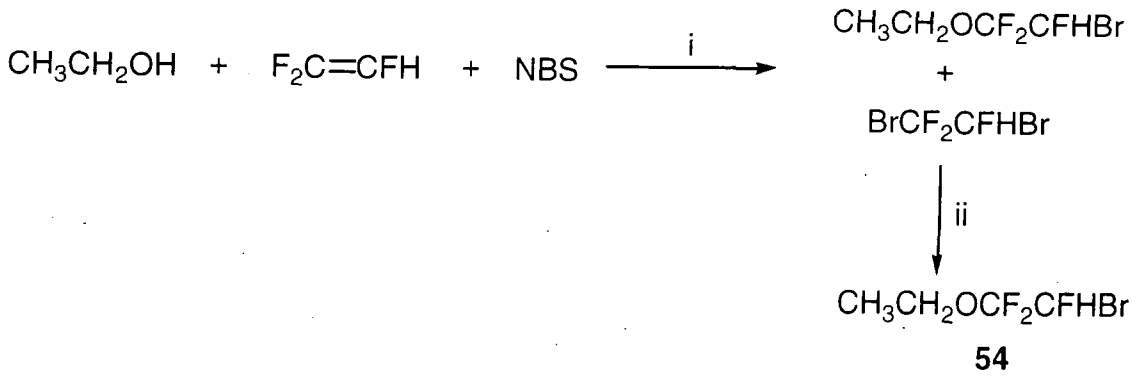
Scheme 4.2.3

Identification of Products. - The two fluorines in the $-CF_2-$ group of **52** are inequivalent due to the neighbouring asymmetric -CFHI group, hence the $-CF_2-$ group appears in the ^{19}F NMR spectrum as an AB quartet (-86.9 ppm). The -CFHI group appears as a doublet of triplets (-166.6 ppm). The $-CF_2-$ group appears in the ^{13}C NMR spectrum as a triplet of doublets (120.9 ppm) and the -CFHI group appears as a doublet of triplets (65.6 ppm). The more electron deficient -CFHBr group of **53** appears at higher frequency (87.9 ppm). The $-CF_2CFHX$ (X = Br or I) has been observed thus throughout the course of cohalogenations with alcohols other than methanol.

4.2.2 Ethanol

Likewise, reaction of ethanol and NBS gave **54** (scheme 4.2.4). In this instance, treatment of the reaction mixture with zinc powder to remove dibromotrifluoroethane also resulted in decomposition of **54**. Dehalogenation of dibromotrifluoroethane without affecting **54** was successfully performed with potassium hydroxide powder.

The preparation of **54** by reaction of ethanol with bromotrifluoroethene under basic conditions has been reported by Park *et al.*[123]

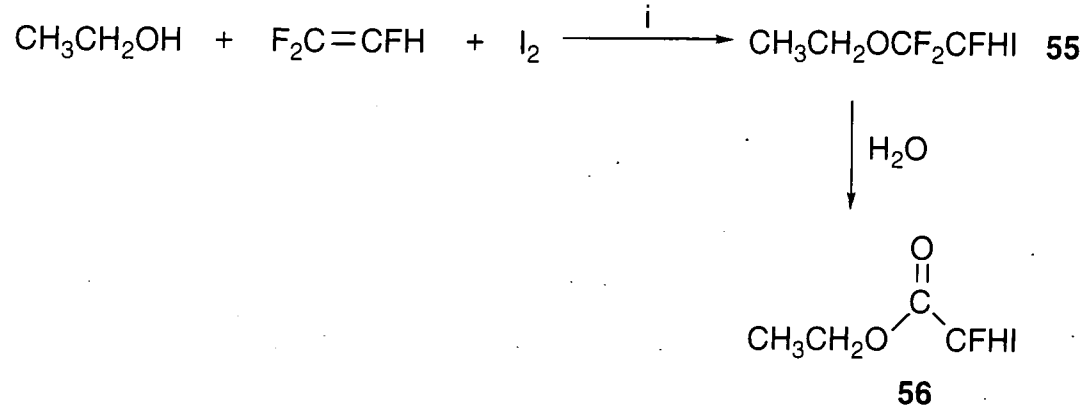


Conversion of trifluoroethene = 63 %; yield = 35%

i) Carius tube, 60°C, 40 hrs
ii) KOH, 0°C

Scheme 4.2.4

Reaction of ethanol and iodine gave **55** as expected, however this underwent partial hydrolysis during the course of work up, unlike the analogous methanol / iodine compound **52**, to give **56** (scheme 4.2.5).

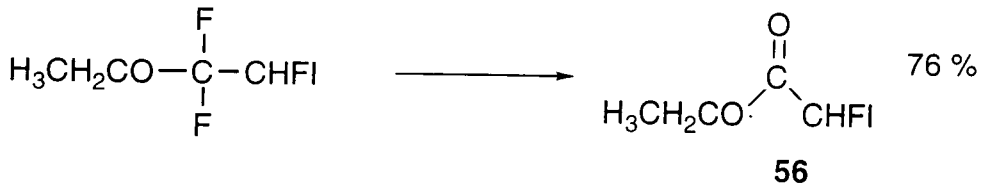


Conversion of trifluoroethene = 74 %

i) Carius tube, 60°C, 40 hrs

Scheme 4.2.5

Complete hydrolysis in the presence of water over a prolonged period did not occur; complete hydrolysis was accomplished using the method of Tarrant[127] (scheme 4.2.6).



56

Conditions: H_2SO_4, 0°C, 3 hrs

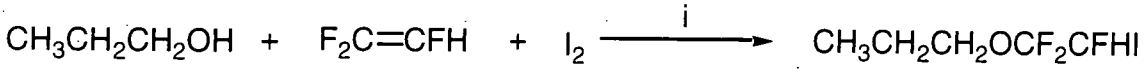
Scheme 4.2.6

Identification of the product. - The fluorine in the CFHI group in **56** couples to the hydrogen to appear in the ^{19}F NMR spectrum as a doublet (-161.6 ppm) and it couples in the ^{13}C NMR spectrum to appear as a doublet (167.4 ppm).

4.2.3 1-Propanol

Reaction of 1-propanol with trifluoroethene and iodine gave **57** and a trace of diiodotrifluoroethane (scheme 4.2.7). The analogous reaction with NBS was performed (scheme 4.2.8) to give **58**, however all attempts to remove diiodotrifluoroethane without affecting **58** were all unsuccessful. Dehalogenationwas attempted with potassium hydroxide powder and with a variety of metals (Zn, Cu, Mg, Al, Hg, Fe) and solvents (THF, DMF, HMPA). In all cases either no dehalogenation was observed or dehalogenation was accompanied by transformation of **58** to unidentified compounds, hence **58** was not isolated.

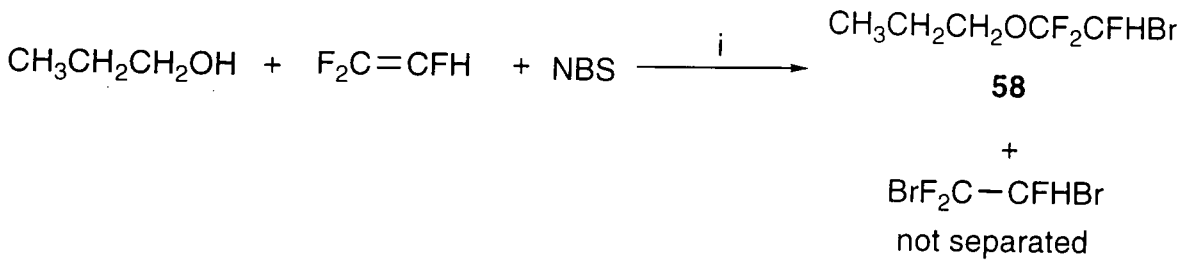
The preparation of **58** by reaction of propanol with bromotrifluoroethene under basic conditions has been reported by Demiel.[125]



57

Conversion of trifluoroethene = 85 %; yield = 60%
i) Carius tube, 60°C, 40 hrs

Scheme 4.2.7

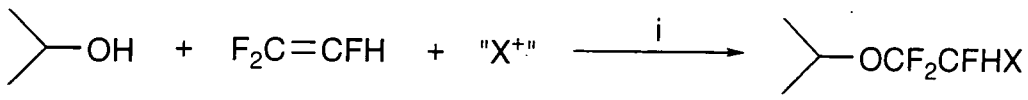


i) Carius tube, 60°C, 40 hrs

Scheme 4.2.8

4.2.4 2-Propanol

Cohalogenation was attempted with a secondary alcohol, 2-propanol (scheme 4.2.9), with both NBS and iodine. In both cases, conversion of trifluoroethene was low which demonstrates the steric demand in going from a primary to a secondary alcohol. No products were isolated from these reactions.



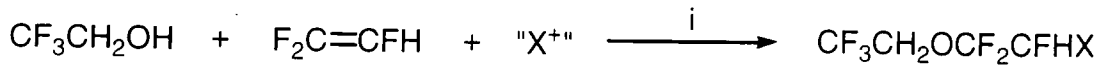
i) Carius tube, 60°C, 40 hrs
X = Br: conversion = 21 %
X = I: conversion = 18 %

Scheme 4.2.9

4.2.5 Trifluoroethanol

Whereas steric effects significantly inhibit the cohalogenation reaction, the effect of alcohol polarity was shown to have no such effect. Indeed, more electron deficient alcohols gave more facile reactions, with higher conversions of trifluoroethene and little or no dihalo formation. Thus, reaction of trifluoroethanol and NBS with trifluoroethene gave **59** (scheme 4.2.10). The analogous reaction with iodine gave no conversion of trifluoroethene due to the sparing solubility of iodine in trifluoroethanol. Hence in this instance N-iodosuccinimide (NIS) was employed in place of iodine to give **60**.

The preparation of **59** by reaction of trifluoroethanol with bromotrifluoroethene under basic conditions has been reported.[126]



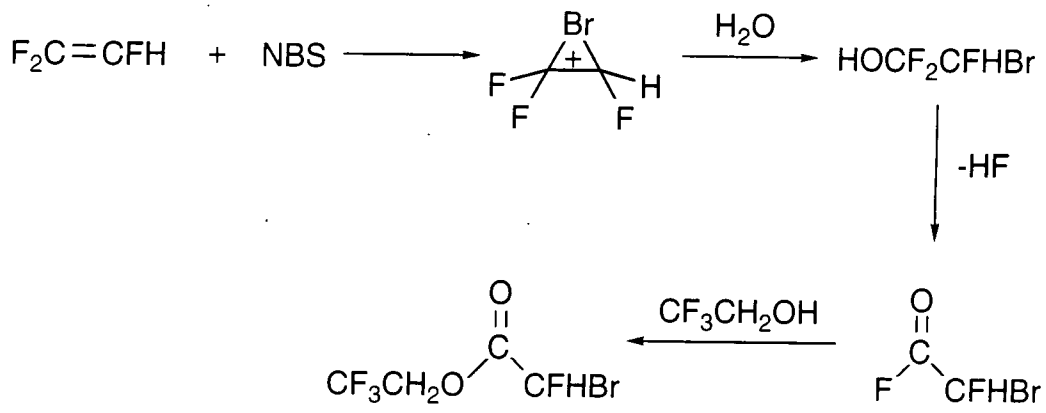
i) Carius tube, 60°C, 40 hrs

X = Br: conversion of trifluoroethene = 100%, compound **59** (56%)

X = I: conversion of trifluoroethene = 100%, compound **60** (54%)

Scheme 4.2.10

Cohalogenations with trifluoroethanol require the alcohol to be rigorously dried; the initial reaction was performed with wet trifluoroethanol which resulted in formation of **61** via quenching of the halonium intermediate with water.



61

Conversion of trifluoroethene = 100 %

Conditions: Carius tube, 60°C, 40 hrs

Scheme 4.2.11

4.2.6 2-Chloroethanol

Reactions of 2-chloroethanol and trifluoroethene with NBS and iodine gave **62** and **63** respectively. Once again, use of a more electron deficient alcohol gave a facile reaction.

i) Carius tube, 60°C, 40 hrs

X =Br: conversion of trifluoroethene = 100%, compound **62** (70%)

X = I: conversion of trifluoroethene = 100%, compound **63** (66%)

Scheme 4.2.12

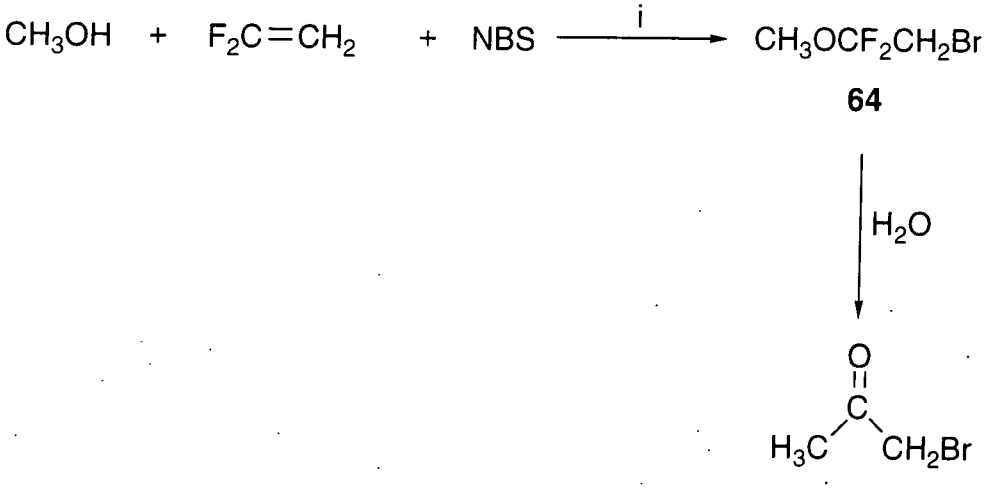
4.3. Cohalogenation with Other Fluoro-alkenes

The cohalogenation methodology was extended to fluoro-alkenes other than trifluoroethene. Thus cohalogenation was performed using VDF, TFE and HFP with methanol and NBS or iodine.

4.3.1 Cohalogenation with 1,1-Difluoroethene

Cohalogenation of VDF with methanol and NBS gave **64** with quantitative conversion of alkene (scheme 4.3.1). No dibromo formation was observed in this reaction. Park has reported that the attempted nucleophilic addition of methanol to VDF was unsuccessful, even under autogenous pressure. Here, a similar product to that sought by Park has been prepared by using an electrophilic, as opposed to a nucleophilic, methodology. Compound **64** underwent hydrolysis to give methyl bromoacetate on standing.

The preparation of **64** by reaction of methanol with 1-bromo-2,2-difluoroethene under basic conditions has been reported by Demiel.[125]



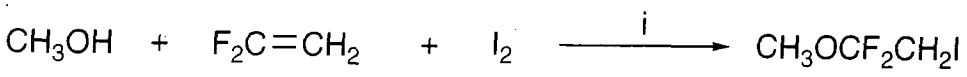
Conversion of trifluoroethene = 76 %

i) Carius tube, 60°C, 40 hrs

Scheme 4.3.1

Identification of the product. - The $-CF_2CH_2Br$ group of compound **64** was identified by its ^1H, ^{19}F NMR spectra in which the fluorine and hydrogen atoms couple to appear as triplets ($^3J_{CF}$ = 8 Hz). The $-CF_2-$ group appears as a triplet ($^1J_{C-F}$ = 259 Hz) in the ^{13}C NMR spectrum at 123 ppm.

The analogous reaction with iodine gave quantitative conversion of alkene (scheme 4.3.2), however the product was not isolated. The same product has been prepared by Park[123] by reaction of methanol with 1,1,-difluoroiodoethene in the presence of base. Park also reported that the product could not be isolated.



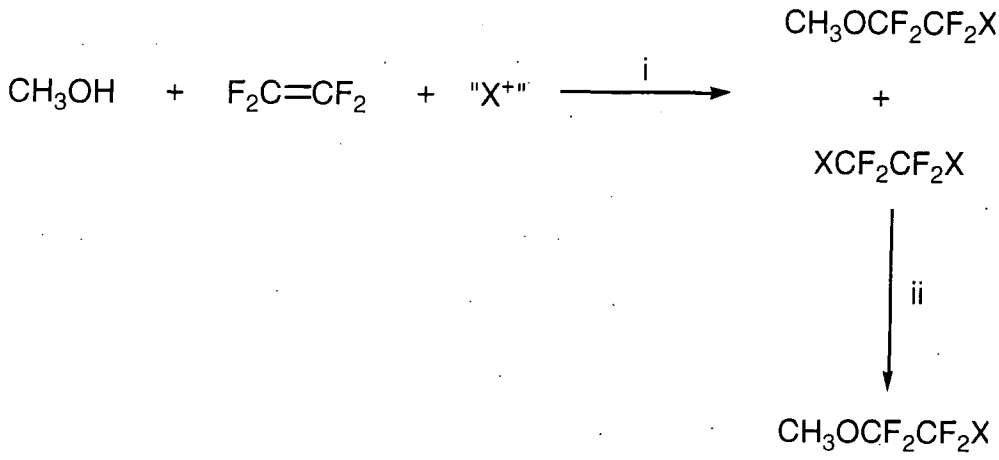
Conversion of trifluoroethene = 100 %

i) Carius tube, 60°C, 40 hrs

Scheme 4.3.2

4.3.2 Cohalogenation with Tetrafluoroethene

Tetrafluoroethene and methanol underwent cohalogenation in the presence of NBS and iodine to give **65** and **66** respectively (scheme 4.3.3). In both cases, substantial quantities of halogen addition products were formed. These were separated from the cohalogenation products by treatment with copper powder at 60°C.



i) Carius tube, 60°C, 40 hrs
X = Br: conversion of trifluoroethene = 75%, compound **65** (15%)
X = I: conversion of trifluoroethene = 82%, compound **66** (40%)

ii) Cu powder, Carius tube, 60°C, 16 hrs

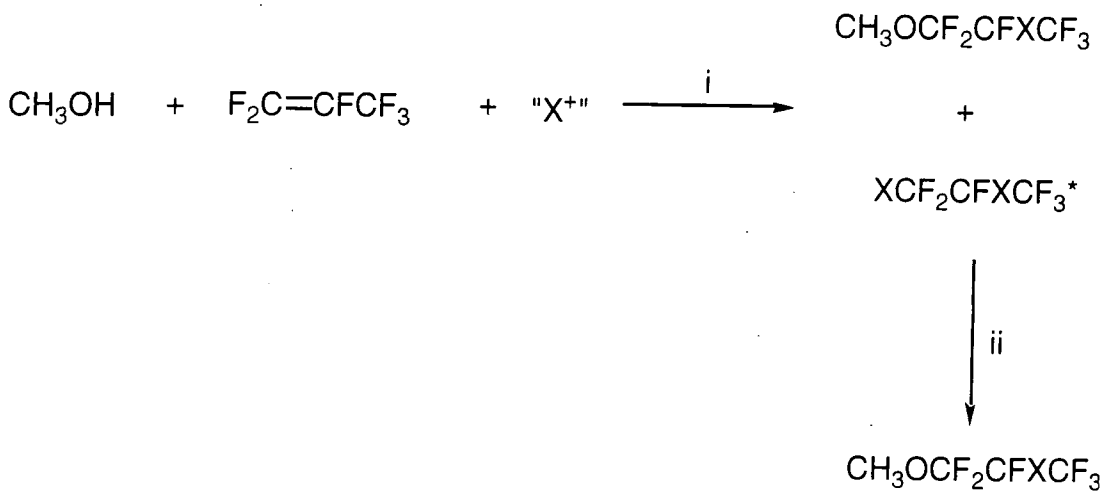
Scheme 4.3.3. Reaction with tetrafluoroethene and NBS or iodine.

Identification of the product. - The two $-CF_2-$ groups in the $-CF_2CF_2X$ (X = Br or I) group couple to each other to appear in the ^{19}F NMR spectrum as triplets ($^3J_{F-F}$

= 9 Hz). The $-CF_2-$ groups both appear in the ^{13}C NMR spectrum as triplets (^1J) of triplets (^2J).

4.3.3. Cohalogenation with Hexafluoropropene

Hexafluoropropene underwent cohalogenation with methanol and NBS or iodine to give **67** and **68**. Reaction with NBS gave a substantial quantity of dibromohexafluoropropane, however reaction with iodine gave no diiohexafluoropropane. This may be attributed to the steric demand of the trifluoromethyl group, making formation of the diiodo compound unfavourable.



* X = Br

i) Carius tube, 60°C, 40 hrs
X =Br: conversion of trifluoroethene = 66%, compound **67** (27%)
X = I: conversion of trifluoroethene = 55%, compound **68** (47%)

ii) Zn powder, room temp, 16 hrs (for X = NBS)

Scheme 4.3.4

Identification of the product. - The -CFX- group in the $-CF_2CFXCF_3$ (X = Br or I) moiety appears in the ^{19}F NMR spectrum as a pseudo sextet by coupling to both the adjacent $-CF_2-$ and $-CF_3$ groups. The two fluorines in the $-CF_2-$ group are inequivalent hence these appear as an AB quartet.

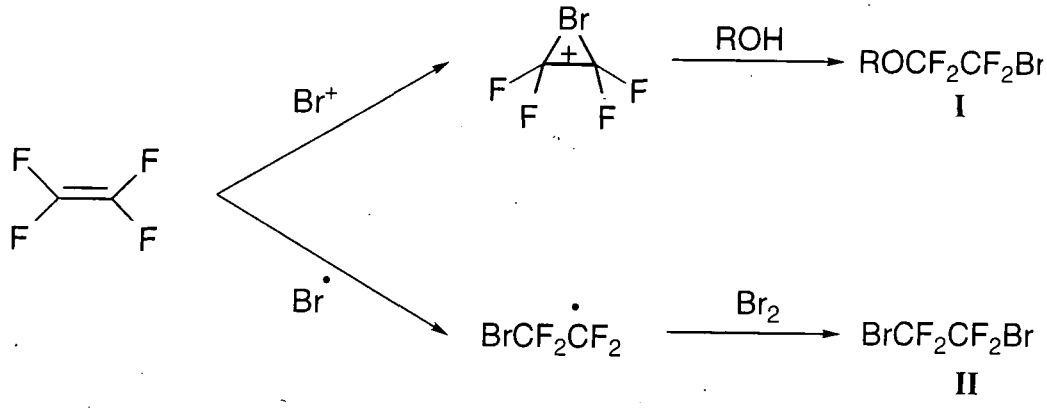
4.4 Relative Reactivity of Fluoro-alkenes

The reactions described here vary a great deal in the degree of dihaloalkane formation. For example, reaction of methanol and NBS with VDF gives no dibromodifluoroethane whereas the corresponding reaction with tetrafluoroethane gives dibromotetrafluoroethane as the predominant product.

Table 4.4.1. Halofluoroether : dibromofluoroalkane ratios in reaction of fluoro-alkenes with methanol and NBS.

Alkene	$CF_2=CH_2$	$CF_2=CFH$	$CF_2=CF_2$	$CF_2=CFCF_3$
Ether : Dibromo	100:0	64:36	28:72	65:35

The formation of halofluoroether **I**, which is an electrophilic process, and dihaloethane **II**, which is a radical process, are in competition as illustrated for tetrafluoroethane (scheme 4.4.1).



Scheme 4.4.1

With respect to radical attack, the effect of increasing the number of fluorine atoms on the double bond is to increase the stability of the intermediate radical, thus increasing the favourability of formation of **II**.

With respect to electrophilic attack, the effect of increasing the number of fluorine atoms on the double bond is ambiguous due to the opposing effects of inductive electron withdrawal and the influence of the pairs of non-bonding electrons. However, the studies of Polishchuk *et al*[128] indicates that a fluorine atom attached to an sp^2 hybridised carbon atom decreases the activity of the double bond towards electrophilic reagents, although this decrease may only be marginal. On the basis of this principle, increasing the number of fluorine atoms on the double bond would decrease the favourability of formation of **I**.

Hence, the net effect of increasing fluorine substitution is to increase the degree of formation of **II**.

Instrumentation

Gas Liquid Chromatographic Analysis

Analyses were performed on a Fisons Trio 1000 spectrometer linked to a Hewlett Packard 5890 Series II gas liquid chromatograph equipped with a 20m cross-linked methyl silicone capillary column. All GLC mass spectra were generated by electron ionization.

Preparative scale GC was performed on a Varian Aerograph Model 920 (catharometer detector) gas chromatograph, fitted with a 3m 10% SE30 packed column.

Elemental Analysis

Carbon, hydrogen and nitrogen elemental analyses were obtained using a Perkin-Elmer 240 Elemental Analyser or a Carlo Erba Strumentazione 1106 Elemental Analyser.

NMR Spectra

^{1}H NMR spectra were recorded on a Varian VXR400S spectrometer operating at 400 MHz or a Brücker AC250 spectrometer operating at 250 MHz. ^{19}F NMR spectra were recorded on the Varian VXR400S spectrometer operating at 376 MHz or on the Brücker AC250 spectrometer operating at 235 MHz. ^{13}C NMR spectra were recorded on the Varian VXR400S spectrometer operating at 100 MHz. All spectra were recorded in d_6 acetone with tetramethylsilane and fluorotrichloromethane as internal references for ^{1}H NMR and ^{19}F NMR spectra respectively, unless otherwise stated. *J* Values are given in Hz.

FT-IR Spectra

Infrared spectra were recorded using a Perkin-Elmer 1600 FT-IR spectrometer using KBr discs.

Mass Spectra

Mass spectra of solid samples were recorded on a VG7070E spectrometer.

Distillation

Fractional distillation of product mixtures was carried out using a Vigreux column. Boiling points were recorded during the distillation.

Reagents and Solvents

Unless otherwise stated, chemicals were used as received from suppliers (Aldrich, Fluorochem, Fluka, BDH).

Chapter 5

Experimental to Chapter 2

Due to the potential hazard of polymerisation of trifluoroethene, this material was stored over the radical inhibitor dipentene. In order to ensure that no dipentene was present in the trifluoroethene used in the reactions described, trifluoroethene was placed in a glass tube by vacuum transfer before being transferred again into the reaction vessel. This process of two vacuum transfers ensured that dipentene was not transferred into the reaction vessel due to its involatility.

γ-Ray initiated telomerization.

General procedure - Telogen was introduced into a 360 cm^3 glass tube fitted with a Rotaflo tap and degassed in three freeze-thaw cycles. Pre-weighed trifluoroethene was introduced into the tube by vacuum transfer and the tube was sealed and irradiated using a ^{60}Co source for 7 days to a dosage of 10 Mrads. Any remaining trifluoroethene was recovered by vacuum transfer; conversion of trifluoroethene is quantitative unless stated otherwise. Excess telogen was removed by distillation, a sample of the telomeric mixture was taken and the remainder was further distilled to furnish the trifluoroethene / telogen mono-adduct.

Peroxide initiated telomerization.

General procedure using di-tert-butyl peroxide - Reactions were carried out using either a 140 cm^3 or a 500 cm^3 autoclave fitted with a bursting disc (maximum pressure 200 bar), lined with PTFE and fitted with a glass liner. The autoclave was charged with di-*tert*-butyl peroxide and sealed using a copper gasket annealed in methanol. Telogen and trifluoroethene were degassed separately in three freeze-thaw cycles. Telogen and trifluoroethene were then placed in the autoclave by vacuum transfer. The autoclave valve was then closed and the autoclave was transferred to a purpose-built high pressure cell where it was heated to 140°C for 24 hours. Any remaining trifluoroethene was recovered by vacuum transfer; conversion of trifluoroethene is quantitative unless stated otherwise. Excess telogen was removed by distillation through a vigreux column, a sample of the telomeric mixture was taken and the remainder was further distilled to furnish the trifluoroethene / telogen mono-adduct.

General procedure using dibenzoyl peroxide - As above, using dibenzoyl peoxide at a temperature of 80°C.

It should be noted that the ratios of regio-isomers of trifluoroethene / telogen mono-adducts isolated thus are different to the ratios given in chapter 2. This is due to the two regio-isomers for any given trifluoroethene / telogen mono-adduct having different boiling points. The ratios quoted below apply only to the boiling range specified.

Free Radical Telomerisation of Trifluoroethene using Ethers

Diethyl ether

γ-ray initiation - - Diethyl ether (133g, 0.85 mols) and trifluoroethene (7.0g, 85 mmols) gave a colourless, telomeric liquid mixture (11.8g). Fractional distillation of the liquid gave 1,2,2-trifluoro-3-ethoxybutane **1a** and 1,1,2-trifluoro-3-ethoxybutane **1b** (b.p. 62-66°C, 9.6g, 72%) in an 80:20 ratio. The product was contaminated with a significant quantity of diethyl ether. Preparative scale GLC afforded **1,2,2-trifluoro-3-ethoxybutane 1a** (Found: C, 46.2; H, 7.1. $C_6H_{11}F_3O$ requires C, 46.2; H, 7.1); NMR no. 1; mass spectrum no. 1; IR no. 1.

DTBP initiation - A 500 cm^3 autoclave was charged with diethyl ether (158g, 2.1 mols), trifluoroethene (35.0g, 0.43 mols) and DTBP (6.0g). After reaction, the autoclave was opened and remaining trifluoroethene (30%) was recovered. Fractional distillation of the reaction mixture gave a mixture of **1,2,2-trifluoro-3-ethoxybutane 1a** and 1,1,2-trifluoro-3-ethoxybutane **1b** (b.p. 62-66°C, 32.6g, 49% crude) with a significant quantity of diethyl ether.

Tetrahydrofuran

γ-ray initiation - Tetrahydrofuran (64.1g, 0.89 mols) and trifluoroethene (7.3g, 89 mmols) gave a colourless, telomeric liquid mixture (12.3g). Fractional distillation of the liquid gave a mixture of **2-(1',1',2'-trifluoro-1'-ethyl)-tetrahydrofuran 2a** and 2-(1',2',2'-trifluoro-1'-ethyl)-tetrahydrofuran **2b** in a 94:6 ratio (68%, 9.3g), b.p. 82-84°C (Found: C, 46.8; H, 5.8. $C_6H_9F_3O$ requires C, 46.7; H, 5.9); NMR no. 2; mass spectra nos. 3 and 4.

Cyclohexane

γ-ray initiation - Cyclohexane (74.0g, 0.88 mols) and trifluoroethene (7.2g, 88 mmols) gave a colourless, telomeric liquid mixture (11.9g). Fractional distillation of the liquid gave a mixture of **1-(1',1',2'-trifluoro-1'-ethyl)-cyclohexane 3a** and 1-(1',2',2'-trifluoro-1'-ethyl)-cyclohexane **3b** in a 60:40 ratio (10.3g, 71%), b.p. 140-142°C (Found: C, 57.6; H, 7.8. $C_8H_{13}F_3$ requires C, 57.8; H, 7.9); NMR nos. 3 and 4; mass spectra nos. 5 and 6; IR no. 4.

Tetrahydropyran

γ-ray initiation - Tetrahydropyran (64.1g, .88 mols) and trifluoroethene (7.2g, 0.88 mmols) gave a colourless, telomeric liquid mixture (12.6g). Fractional distillation of the liquid gave a mixture of **1-(1',1',2'-trifluoro-1'-ethyl)-tetrahydropyran 4a** and

1-(1',2',2'-trifluoro-1'-ethyl)-tetrahydropyran **4b** in a 82:18 ratio (10.8g, 73%), b.p. 130-132°C (Found: C, 50.0; H, 6.6. $C_7H_{11}F_3O$ requires C, 50.0; H, 6.6); NMR no. 5; mass spectra nos. 7 and 8; IR no. 3.

1,4-dioxane

γ-ray initiation - 1,4-dioxane (78.0g, 0.89 mols) and trifluoroethene (7.3g, 89 mmols) gave a colourless, telomeric liquid mixture (12.3g). Fractional distillation of the liquid gave a mixture of **2-(1',1',2'-trifluoro-1'-ethyl)-1,4-dioxane 5a** and 2-(1',2',2'-trifluoro-1'-ethyl)-1,4-dioxane **5b** in a 68:32 ratio (10.0 g, 66%), b.p. 138-140°C (Found: C, 42.3; H, 5.4. $C_6H_9F_3O_2$ requires C, 42.3; H, 5.3); NMR no. 6; mass spectra nos. 9 and 10; IR no. 7.

1,3-dioxane

γ-ray initiation - A 60 cm^3 Carius tube was charged with degassed 1,3-dioxane (5.0g, 56.8 mmols) and trifluoroethene (0.95g, 11.6 mmols). The tube was sealed and irradiated using a ^{60}Co source for 7 days to a dosage of 10 Mrads. Excess 1,3-dioxane was removed by distillation to give a telomeric mixture (1.7g). The main component of the mixture was isolated by preparative scale GLC to give a mixture of **2-(1',1',2'-trifluoro-1'-ethyl)-1,3-dioxane 6a** and 2-(1',2',2'-trifluoro-1'-ethyl)-1,3-dioxane **6b** (Found: C, 42.3; H, 5.3. $C_6H_9F_3O_2$ requires C, 42.3; H, 5.3); NMR no. 7; mass spectra nos. 11, 12, 13 and 14; IR no. 8.

1,3,5-trioxane

γ-ray initiation- A 360 cm^3 glass tube fitted with a Rotaflo tap was charged with 1,3,5-trioxane (75.80g, 0.90 mols) in trifluoroethanol (120 cm^3). The solution was degassed in three freeze thaw cycles and degassed trifluoroethene (7.40g, 0.09 mols) was added to the tube by vacuum transfer. The tube was sealed and irradiated for 10 days using a ^{60}Co g-source. The resultant solution was distilled in an attempt to remove trifluoroethanol and excess 1,3,5-trioxane, however isolation from these impurities was not successful and 2-(1',1',2'-trifluoro-1'-ethyl)-1,3,5-trioxane **7a** and 2-(1',2',2'-trifluoro-1'-ethyl)-1,3,5-trioxane **7b** were observed by GLC-MS only; mass spectra nos. 15 and 16.

Free Radical Telomerisation of Trifluoroethene using Triethylamine

γ-ray initiation - Triethylamine (8.9 g, 88 mmols) and trifluoroethene (7.2g, 88 mmols) gave a 74% conversion of trifluoroethene to a telomeric mixture (10.7g) from which was isolated a mixture of **1,2,2-trifluoro-3-(diethylamino)butane 9a** and 1,1,2-trifluoro-3-(diethylamino)butane **9b** by distillation in a 95:5 ratio (4.5g, 28%), b.p. 114-118°C (found: C, 52.6; H, 8.8; N, 7.6. $C_8H_{16}F_3N$ requires C, 52.5; H, 8.8, N; 7.6). NMR no. 9; mass spectra no. 19; IR no. 9.

Further distillation gave a mixture of **di(1,2,2-trifluorobut-3-yl) ethylamine 10a** and isomers in a 92:8 ratio (4.2g, 36%), b.p. 69-71°C / 74mm Hg (Found: C, 45.4; H, 6.5; N, 5.2. $C_{10}H_{17}F_6N$ requires C, 45.3; H, 6.4; N, 5.3); NMR no. 10; mass spectrum no. 20; IR no. 10.

Free Radical Telomerisation of Trifluoroethene using Alcohols

Methanol

γ-ray initiation - Methanol (29.0g, 0.91 mols) and trifluoroethene (7.5 g, 91 mmols) gave a colourless, telomeric liquid mixture (8.9g). Fractional distillation of the liquid gave a mixture of **2,2,3-trifluoro-1-propanol 12a** and 2,3,3-trifluoro-1-propanol **12b** in a 78:22 ratio (5.7g, 55%), b.p. 95-97°C. Preparative scale GLC afforded 2,2,3-trifluoro-1-propanol **12a** (Found: C, 31.4; H, 4.0. $C_3H_5F_3O$ requires C, 31.6; H, 4.4); NMR no. 11; mass spectrum no. 22; IR no. 11.

DTBP initiation - A 500 cm^3 autoclave was charged with methanol (130 g, 4.0 mols), trifluoroethene (33.2 g, 0.40 mols) and DTBP (6.5 g). After reaction, the autoclave was opened and remaining trifluoroethene was recovered. Excess methanol was removed by distillation to give a telomeric mixture (30.8 g).

Ethanol

γ-ray initiation - Ethanol (42.0g, 0.90 mols) and trifluoroethene (7.4 g, 90 mmols) gave a colourless, telomeric liquid mixture (10.1g). Fractional distillation of the liquid gave a mixture of **3,3,4-trifluoro-2-butanol 13a** and 3,4,4-trifluoro-2-butanol **13b** in a 75:25 ratio (7.8g, 68%), b.p. 119-122°C (Found: C, 37.7; H, 5.6. $C_4H_7F_3O$ requires C, 37.5; H, 5.5); NMR no. 12; mass spectra nos. 23 and 24; IR no. 12.

DTBP initiation - A 500 cm^3 autoclave was charged with ethanol (174 g, 3.8 mols), trifluoroethene (31.0 g, 0.38 mols) and DTBP (6.5 g). After reaction, the autoclave was opened and any remaining trifluoroethene was recovered. Fractional distillation of the residual liquid gave a mixture of 3,3,4-trifluoro-2-butanol **13a** and 3,4,4-trifluoro-2-butanol **13b** by distillation in a 75:25 ratio (31.5 g, 65%).

1-propanol

γ-ray initiation - 1-propanol (56g, 0.93 mols) and trifluoroethene (7.6g, 93 mmols) gave a colourless, telomeric liquid mixture (10.5g). Fractional distillation of the liquid gave a mixture of **4,4,5-trifluoro-2-propanol 14a** and 4,5,5-trifluoro-2-propanol **14b** in a 75:25 ratio (9.8g, 74%), b.p. 124-127°C (Found: C, 42.0; H, 6.5. $C_5H_9F_3O$ requires C, 42.2; H, 6.4); NMR no. 14; mass spectra nos. 26 and 27; IR no. 14.

2-propanol

γ-ray initiation - 2-propanol (54g, 0.90 mols) and trifluoroethene (7.4g, 90 mmols) gave a colourless, telomeric liquid mixture (10.8g). Fractional distillation of the liquid gave a mixture of 3,3,4-trifluoro-2-methyl-2-butanol **15a** and 3,4,4-trifluoro-2-methyl-2-butanol **15b** in an 80:20 ratio (9.6g, 75%), b.p. 120-123°C (Found: C, 42.2; H, 6.5. $C_5H_9F_3O$ requires C, 42.2; H, 6.4); NMR nos. 15 and 16; mass spectrum no. 28; IR no. 15. Data obtained was in agreement with literature values.[47]

Cyclohexanol

γ-ray initiation - Cyclohexanol (88.0g, 0.88 mols) and trifluoroethene (7.2g, 88 mmols) gave a colourless, telomeric liquid mixture (6.2g). Fractional distillation of the liquid gave a mixture of **1-(1',1',2'-trifluoro-1'-ethyl)-cyclohexanol 26a** and 1-(1',2',2'-trifluoro-1'-ethyl)-cyclohexanol **26b**, contaminated with a significant quantity of cyclohexanol, in an 90:10 ratio (3.2g, crude 20%), b.p. 76-78°C / 70 mmHg; NMR nos. 18 and 19; mass spectra nos. 29 and 30.

Free Radical Telomerisation of Trifluoroethene using Aldehydes

Acetaldehyde

DTBP initiation - A 500 cm^3 autoclave was charged with acetaldehyde (86.4g, 2.0 mols), trifluoroethene (32.2g, 0.39 mols) and DTBP (3.0 g). Remaining trifluoroethene was recovered by vacuum transfer. Fractional distillation of the residual liquid gave **3,3,4-trifluoro-2-butanone 16** (18.6g, 58 %), b.p. 46-47°C (Found: C, 38.3; H, 4.0. $C_4H_5F_3O$ requires C, 38.1; H, 4.0); NMR no. 20; mass spectrum no. 31; IR no. 16, and 3,4,4-trifluoro-2-butanone **17** (7.8g, 45 %), b.p. 62-66°C (Found: C, 38.3; H, 4.1. $C_4H_5F_3O$ requires C, 38.1; H, 4.0); NMR no. 21; mass spectrum no. 32; IR no. 17.

Pivaldehyde

γ-ray initiation - A 140 cm^3 autoclave was charged with pivacetaldehyde (20.0g) and trifluoroethene (9.5g, 0.11 mols) and irradiated for 20 days. After this time the autoclave was cooled to -78C and vented in a fume cupboard to release carbon monoxide and *t*-butane. Remaining trifluoroethene was then recovered by vacuum transfer. Repeated fractional distillation of the residual liquid gave a mixture of **4,4,5-trifluoro-2,2-dimethyl-3-pentanone 18a** and 4,5,5-trifluoro-2,2-dimethyl-3-pentanone **18b** in a 74: 26 ratio (2.1 g, 11%), b.p. 85-88°C (Found: C, 50.0; H, 6.6. $C_7H_{11}F_3O$ requires C, 50.0; H, 6.6); NMR no. 22; mass spectrum no. 32; IR no. 18.

Free Radical Additions using Other Fluoro-alkenes

γ-ray initiated telomerization.

General procedure. The chain transfer agent was introduced into a 60 cm^3 Carius tube and degassed in three freeze-thaw cycles. Pre-weighed alkene was introduced into the tube by vacuum transfer and the tube was sealed and irradiated using a ^{60}Co source for 7 days to a dosage of 10 Mrads. Any remaining alkene was recovered by vacuum transfer. Residual chain transfer agent was removed by distillation to furnish the mono-adduct.

Peroxide initiated telomerization.

General procedure using di-tert-butyl peroxide - Reactions were carried out in a 140 cm^3 autoclave fitted with a bursting disc (maximum pressure 200 bar). The autoclave was lined with PTFE and fitted with a glass liner. The autoclave was charged with di-*tert*-butyl peroxide and sealed using a copper gasket annealed in methanol. The telogen and alkene were degassed separately in three freeze-thaw cycles. Telogen and alkene were then placed in the autoclave by vacuum transfer. The autoclave valve was then closed and the autoclave was transferred to a purpose-built high pressure cell where it was heated to 140°C for 24 hours. Any remaining alkene was recovered by vacuum transfer. Residual chain transfer agent was removed by distillation to furnish the mono-adduct.

Addition of 1,3-Dioxane to Hexafluoropropene

γ-ray initiation - 1,3-dioxane (5.0 g, 56.8 mmols) and hexafluoropropene (7.1 g, 47.3 mmols) gave 76% conversion of hexafluoropropene to give a mixture of mono-adduct isomers from which preparative scale GLC afforded **2-(1',1',2',3',3',3'-hexafluoropropyl)-1,3-dioxane 8a** (found: C, 35.3; H, 3.4. $C_6H_9F_3O_2$ requires C, 35.3; H, 3.3); NMR no. 8; mass spectra nos. 17 and 18; IR no. 8, and 4-(1,1,1,2,3,3-hexafluoropropyl)-1,3-dioxane **8b**.

Addition of Acetaldehyde to Hexafluoropropene

DTBP initiation - Addition was performed in a 140 cm^3 autoclave charged with acetaldehyde (22.0 g, 0.5 mols), hexafluoropropene (15.0 g, 0.1 mols) and dibenzoyl peroxide (3.0 g). Upon completion of the reaction, remaining hexafluoropropene was recovered by vacuum transfer; conversion of hexafluoropropene = 90%. Fractional distillation of the residual liquid gave 3,3,4,5,5,5-hexafluoropropylpentanone **16b** contaminated with a small quantity of benzene produced by initiator decompsition, b.p. 82-85°C, (13.2g, 68%). Spectral data obtained was in agreement with literature values.[129]

Addition of Ethanol to 1-Chloro-2,2-Difluoroethene

γ-ray initiation - Ethanol (9.9 g, 0.21 mols) and 1-chloro-2,2-difluoroethene (7.1g, 72.1 mmols) gave 65% conversion of alkene to a colourless liquid. Residual ethanol was removed by distillation to give 4-chloro-3,3-difluoro-2-butanol **44** (3.72 g, 36%) (Found M^+, 162.0497. $C_4H_7ClF_2O$ requires M^+ 162.1341); NMR no. 13; mass spectrum no. 25; IR no. 13.

Reactions of Adducts

Reactions of a mixture of 1,2,2-trifluoro-3-ethoxybutane **1a** and 1,1,2-trifluoro-3-ethoxybutane **1b**

Attempted Dehydrofluorination using Alkyllithiums - Compound **1** (1.50 g, 9.6 mmols) was dissolved in dry diethyl ether (3 cm^3) in a 50 cm^3 round bottomed flask and cooled to -78°C. Methyllithium (2.0 M in ether, 7.2 cm^3, 14.4 mmols) was added dropwise to the stirred solution under an atmosphere of dry nitrogen. Upon completion of addition the flask was allowed to warm to room temperature and stirring was continued for a further 5 hours. ^{19}F NMR of the reaction mixture showed no reaction.

Similarly, unsuccessful reactions were attempted using n-BuLi, t-BuLi, PhLi and LDA.

Dehydrofluorination over Potassium Hydroxide - A 60 cm^3 Carius tube was charged with **1** (1.2 g, 7.7 mmols) contaminated with a small quantity of diethyl ether and heated at 60°C for 40 hours. Upon completion of the reaction, the tube was cooled in liquid air, opened and volatile materials were separated to give **(Z)-1,2-difluoro-3-ethoxy-1-butene 19** (0.45 g, 43%) contaminated with a small quantity of diethyl ether. NMR no. 24; mass spectrum no. 34; IR no. 19.

Attempted Fluoride Ion Displacement

i) Alcoholic Potassium Hydroxide - A 50 cm^3 round bottomed flask fitted with a reflux condenser was charged with **1** (1.5 g, 9.6 mmols), and ethanolic potassium hydroxide (10%, 20 cm^3). The flask was heated at reflux for 24 hours after which the ^{19}F NMR spectrum showed no reaction.

ii) Sodium ethoxide in Acetonitrile - A 50 cm^3 round bottomed flask fitted with a reflux condenser was charged with **1** (1.5 g, 9.6 mmols), acetonitrile (10 cm^3) and sodium ethoxide (1.96g, 28.8 mmols). The flask was heated at reflux for 24 hours after which the ^{19}F NMR spectrum showed no reaction.

Esterification

i. Methanol / Trifluoroethene Telomer **12** - Methacryloyl chloride (10.0 g) was purified by vacuum transfer and heated to 60°C in a 100ml three necked round bottomed flask fitted with a condenser, a pressure equalizing dropping funnel, a thermometer and a stirrer under an atmosphere of nitrogen. Methanol / trifluoroethene telomer **12** (5.0 g) was added from the dropping funnel as quickly as possible with stirring. The reaction mixture was heated to 75°C overnight. The reaction mixture was washed with water and the lower ester layer was further washed thoroughly with water to give a telomeric mixture of esters (11.2 g). The ester was decolourized by vacuum transfer and a small quantity of **2,2,3-trifluoropropyl methacrylate 20a** was isolated by preparative scale GLC (found: C, 46.1; H, 5.0. $C_7H_9F_3O_2$ requires C, 46.2; H, 5.0); NMR nos. 25 and 26; mass spectra nos. 35 and 36; IR no. 20.

ii. Ethanol / Trifluoroethene Telomer **13** - As for the methanol telomer, using methacryloyl chloride (10.0 g) and ethanol / trifluoroethene telomer **13** (5.0g) to give a telomeric mixture of esters (11.4 g) to give a small quantity of **3,3,4-trifluoro-2-butyl methacrylate 21a** (found: C, 49.3; H, 5.8. $C_8H_{11}F_3O_2$ requires C, 49.0; H, 5.7); NMR no. 27; mass spectra nos. 37 and 38; IR no. 21.

Cyclisation of alcohols

General Procedure - A 60 cm^3 Carius tube was charged with potassium hydroxide powder (7.0 g) or sodium hydroxide powder (7.0 g) and a mixture of alcohol isomers. The tube was sealed and heated at 60°C for 16 hours. Oxetane and/or oxirane was isolated from the reaction mixture by vacuum transfer. Yields given are with respect to the reacting isomer.

3,3,-difluoro-4-methyl oxetane

i. From the ethanol / trifluoroethene adduct **13** - Potassium hydroxide and **13** (1.90 g, 14.8 mmols) gave **3,3,-difluoro-4-methyl oxetane 22** (1.06g, 88%), b.p. 39-41°C.(Found C, 44.7; H, 5.6. $C_4H_6F_2O$ requires C, 44.5; H, 5.6); NMR no. 28; mass spectrum no. 39; IR no. 22.

ii. From the ethanol / 1-chloro-2,2-difluoroethene adduct **44** - A 50 cm^3 round bottomed flask was charged with **44** (1.50 g, 10.4 mmols) and cooled to 0°C. Potassium hydroxide powder was added slowly to the well stirred alcohol. Upon completion of addition the flask was allowed to stand at room temperature for 2 hours. Volatile materials were separated from the flask by vacuum transfer to give **3,3,-difluoro-4-methyl oxetane 22** (0.92 g, 82%)

1-difluoromethyl-2-methyl oxirane - Sodium hydroxide and **13** (2.03 g, 15.9 mmols) gave **1-difluoromethyl-2-methyl oxirane 23** (0.23 g, 53%). (Found C, 44.7; H, 5.6. $C_4H_6F_2O$ requires C, 44.5; H, 5.6); NMR no. ;29; mass spectrum no. 40; IR no. 23.

3,3-difluoro-4,4-dimethyl oxetane and 3-(difluoromethyl)-2,2-dimethyl oxirane - Potassium hydroxide and **15** (2.10 g, 14.8 mmols) gave 3,3-difluoro-4,4-dimethyl oxetane **24** and 3-(difluoromethyl)-2,2-dimethyl oxirane **25** in an 80:20 ratio (1.62 g, 90%), b.p. 60-62°C. (Found C, 49.2; H, 6.8. $C_5H_8F_2O$ requires C, 49.2; H, 6.6); NMR nos. 30 and 31; mass spectra nos. 41 and 42; IR no. 24. Data obtained was in agreement with literature values.[47]

3-(difluoromethyl)-2,2-dimethyl oxirane - Sodium hydroxide and **15** (2.10 g, 14.8 mmols) gave 3-(difluoromethyl)-2,2-dimethyl oxirane **25** (0.35 g, 78%).

3,3-difluoro-2-spirocyclohexyloxetane - Potassium hydroxide and **26** (1.13g, 6.2 mmols) gave **3,3-difluoro-2-spirocyclohexyloxetane 27** (0.79 g, 79%). (Found: C, 59.5; H, 7.7. $C_8H_{12}F_2O$ requires C, 59.2; H, 7.5); NMR no. 32; mass spectrum no. 43; IR no. 25.

3,3-difluoro-oxetane and 2-(difluoromethyl) oxirane - A 60 cm^3 Carius tube was charged with **12** (1.2 g, 10.5 mmols). Potassium hydroxide powder (5.0g) was added slowly to the tube which was then sealed and heated at 60°C for 16 hours. After this time the tube was cooled in liquid air, opened and volatile materials were isolated from the flask to give a small quantity of crude 3,3-difluoro-oxetane **28** and 2-(difluoromethyl) oxirane **29**. These products were not isolated from the unidentified impurities and were identified by their ^1H and ^{19}F NMR spectra only; NMR nos. 33 and 34.

2,3-difluoro-allyl alcohol - A 50 cm^3 round bottomed flask fitted with a reflux condenser was charged with **12** (1.5 g, 13.2 mmols). Potassium hydroxide powder (5.0g) was added slowly to the well stirred flask. Upon completion of addition, the flask was heated at 60°C for 16 hours. Upon completion of the reaction, volatile materials were isolated from the flask to give a small quantity of crude 2,3-difluoro-allyl alcohol **30**. This product was not isolated from the unidentified impurities and was identified by its ^1H and ^{19}F NMR spectra only; NMR no. 35.

3,4,5,5,5-pentafluoro-2-methyl-4-buten-2-ol - A 50 cm^3 round bottomed flask fitted with a reflux condenser was charged with **15c** (2.00 g, 9.5 mmols). Potassium hydroxide powder (5.0g) was added slowly to the well stirred flask. Upon completion

of addition, the flask was heated at 60°C for 16 hours. Upon completion of the reaction, volatile materials were isolated from the flask to give **3,4,5,5,5-pentafluoro-2-methyl-4-propen-2-ol 31** (0.69 g, 38 %). NMR no. 36; mass spectrum no. 44; IR no. 26.

Oligomerisation of Oxetane **22**

i. Using caesium fluoride - A 5cm^3 glass tube fitted with a Rotaflo tap was charged with dry diglyme (2.5 cm^3), caesium fluoride (1.0g) and oxetane **22** (0.8g). The tube was sealed and heated at 80C with stirring for 24 hrs. The reaction mixture was then poured into water to give a trace of a white precipitate.

ii. Using triflic acid - Oxetane **22** (0.4g) was added dropwise to triflic acid (10 cm^3). The reaction mixture was allowed to stand for 8 hours before being quenched by careful addition of ice to give a precipitate which was separated by filtration (0.3g). Mass spectrum no. 27.

Attempted Dehydrofluorination of the Ethanol / Trifluoroethene Adduct with MeLi - A 50 cm^3 round bottomed flask was charged with **13** (2.00 g, 15.6 mmols) and dry diethyl ether (5 cm^3) and cooled to -78°C. Methyllithium (2.0 M in ether, 17.2 cm^3, 34.4 mmols) was added dropwise to the stirred solution under an atmosphere of dry nitrogen. Upon completion of addition the flask was allowed to warm to room temperature and stirring was continued for a further 5 hours. ^{19}F NMR of the reaction mixture showed no reaction.

Dehydration

3,3,4-trifluoro-2-methyl-1-butene - A 50 cm^3 round bottomed flask was charged with **15** (3.00g, 21.1 mmols) and thionyl chloride (11.4g, 63.3 mmols) and heated to reflux for 16 hours. The flask was then allowed to cool and the reaction mixture was quenched with ice. The lower layer was separated to give 3,3,4-trifluoro-2-methyl-1-butene (1.78 g, 68%). NMR no. 38; mass spectrum no. 46; IR no. 28.

1-(1,1,2-trifluoroethyl)-1-cyclohexene - A 500 cm^3 two-necked round bottomed flask was charged with thionyl chloride (26.2g, 0.22 mols) and **26** (4.0g, 22 mmols) and cooled in an ice bath. Pyridine (20.5g, 0.26 mols) was added dropwise to the stirred solution. Upon completion of addition, stirring was continued overnight. The reaction was quenched by careful addition of water (150 cm^3) to the cooled reaction mixture which was then extracted into dichloromethane (3 x 50 cm^3). The combined organic extracts were washed with dilute hydrochloric acid (2 x 50 cm^3) and water (50 cm^3), dried over magnesium sulfate and distilled to give crude **1-(1',1',2'-trifluoroethyl)-1-cyclohexene 33**, b.pt 138-142°C (2.3g, 64%) which was subsequently purified by

preparative scale GLC. (Found: C, 58.6; H, 6.8. $C_8H_{11}F_3$ requires C, 58.3; H, 6.5); NMR no. 37; mass spectrum no. 47; IR no. 29.

Two Step Preparation of 3,3,4-trifluoro-1-butene

i. 3,3,4-trifluoro-2-butyl tosylate **35** - Compound **13** (7.00 g, 51 mmols) and p-toluenesulfonyl chloride (14.68g, 77 mmols) were placed in a 100ml two necked round bottomed flask equipped with a 100 ml dropping funnel, a condenser and a stirrer. Pyridine (11.67, 148 mmols) was added dropwise to the stirred flask at 0°C. The reaction mixture was allowed to warm to room temperature and stirred for 6 hours. The reaction was quenched with ice - water (100 cm^3) and shaken for five minutes to hydrolyse any remaining tosyl chloride. The mixture was extracted with diethyl ether (3 x 50 cm^3) and the combined extracts were washed with 5% sulfuric acid (100 cm^3), water (100 cm^3), 5% sodium hydroxide (100 cm^3) and water (100 cm^3). The ether extract was dried over magnesium sulfate and filtered and the ether was removed under reduced pressure to produce the tosylate **3,3,4-trifluoro-2-butyl tosylate 35** (11.60g, 78%). (Found: C, 46.5; H, 4.9. $C_{11}H_{13}F_3O_3S$ requires C, 46.8; H, 4.6); NMR no. 40; mass spectra nos. 49 and 50; IR no. 30.

ii. Tosyl Ester Cleavage - Potassium t-butoxide (6.36g, 56 mmols)was dissolved in dimethyl sulfoxide in a 100 ml 2 necked round bottomed flask under an atmosphere of nitrogen fitted with a pressure equalizing dropping funnel, a condenser and a stirrer. The tosylate (4.00g, 28 mmols) was added dropwise to the stirred flask at 0°C. The reaction mixture immediately turned black. Upon completion of addition, the reaction mixture was stirred for a further 60 minutes. ^{19}F NMR showed complete conversion to 3,3,4-trifluoro-1-butene **36,** however attempts to separate **36** from DMSO were unsuccessful, hence **36** was identified by its ^{19}F NMR and mass spectra. NMR no. 41; mass spectrum no. 51.

Reactions of Aldehyde adducts

i) Reaction with Base

1,2,2,6,6,7-hexafluoro-5-methyl-4-hydroxy-heptan-3-one - A 50ml 2-necked round bottomed flask fitted with a condenser and a dropping funnel was charged with sodium ethoxide (3.51 g, 52 mmols) and diethyl ether (35 cm^3) and cooled in an ice / salt bath. To the well stirred ether was added **16** (5.0 g, 40mmol) such that the temperature was maintained below 0°C. After the solution had been stirred for two hours it was poured onto a mixture of concentrated sulfuric acid (20 cm^3) and ice (200 cm^3). The aqueous layer was extracted with diethyl ether (3 x 40 cm^3), dried over magnesium sulfate, filtered and distilled to remove diethyl ether to give **1,2,2,6,6,7-hexafluoro-5-methyl-**

4-hydroxy-heptan-3-one **37a** (4.30g, 86%), b.pt. 150-155°C. (Found: C, 38.1; H, 4.0. $C_8H_{10}F_6O_2$ requires C, 38.1; H, 4.0); NMR no. 42; mass spectrum no. 52; IR no. 31.

1,2,2,6,6,7-hexafluoro-5-methyl-4-hepten-3-one - Condensation product **37a** (1.0 g, 4mmol) was added to concentrated sulfuric acid (30 cm^3) and allowed to stand for two hours. The reaction mixture was diluted with water (200 cm^3) and extracted with diethyl ether (3 x 30 cm^3). The ether extracts were dried over magnesium sulfate, filtered and the ether removed by distillation to give 1,2,2,6,6,7-hexafluoro-5-methyl-4-hepten-3-one **38a** (0.61g, 66%) which underwent decomposition over a period of days on standing, hence no ^{13}C NMR spectrum was recorded. NMR no. 42; mass spectrum no. 53; IR no. 33.

1,1,1,2,3,3,7,7,8,9,9,9-dodecafluoro-6-methyl-6-hydroxy-heptan-4-one - As for **37a** using sodium ethoxide (2.08 g, 31 mmols, 1.2 eq.) in diethyl ether (35 cm^3) and **16b** (5.0 g, 26 mmols) to give 1,1,1,2,3,3,7,7,8,9,9,9-dodecafluoro-6-methyl-6-hydroxy-heptan-4-one **37b** which was not isolated.

1,1,1,2,3,3,7,7,8,9,9,9-dodecaafluoro-6-methyl-5-hepten-4-one - As for **37b** to give **a** small quantity of 1,1,1,2,3,3,7,7,8,9,9,9-dodecaafluoro-6-methyl-5-hepten-4-one **38b** which underwent decomposition over a period of days on standing, hence no ^{13}C NMR spectrum was recorded. NMR no. 44; mass spectrum no. 54.

2,2,3-trifluoropropanoic acid - A potassium iodide-iodine solution was prepared by dissolving 35g of potassium iodide and 35 g of iodine in water (150 cm^3). **16** (5.0g, 39.7 mmols) was dissolved in 10% aqueous sodium hydroxide (150 cm^3) and the potassium iodide-iodine solution was added over a 5 minute period with stirring. Upon completion of the addition, stirring was continued for a further 90 minutes. Iodoform was separated from the solution by filtration and excess iodine was removed by treatment with aqueous sodium metabisulfite. The volume of the solution was reduced 50 cm^3 under reduced pressure and acidified with concentrated hydrochloric acid. The acidified solution was extracted into ether (3 x 40 cm^3) and the ether was removed by distillation to give a small quantity of **2,2,3-trifluoropropanoic acid** **39** (Found: C, 28.4; H, 2.9. $C_3H_3F_3O_2$ requires C, 28.1; H, 2.3); NMR no. 45; mass spectrum no. 55; IR no. 34.

2-methyl-2-(1',1',2'-trifluoro-1'-ethyl)-1,3-dioxolane - A 100 cm^3 round bottomed flask fitted with a reflux condenser was charged with **16** (5.00g, 39.7 mmols), ethylene glycol (25 cm^3) and aluminium (III) chloride (1.0 g). The flask was heated at reflux for 16 hours and allowed to cool to room temperature. The product mixture was poured into water (150 cm^3) and extracted into diethyl ether (3 x 50 cm^3). The combined

ethereal extracts were washed with dilute hydrochloric acid (50 cm^3) and water (50 cm^3) and dried over magnesium sulfate and distilled to give **2-methyl-2-(1',1',2'-trifluoro-1-ethyl)-1,3-dioxolane 40** (3.9 g, 58%), b.p 132-135°C (Found: C, 42.2; H, 5.3. $C_6H_9F_3O_2$ requires C, 42.3; H, 5.3);; NMR no. 46; mass spectrum no. 56.

(E)-2-(1,2-difluoroethenyl)-2-methyl-1,3-dioxolane - A 60 cm^3 Carius tube was charged with potassium hydroxide powder (6.0g) and 2-methyl-2-(1,1,2-trifluoroethyl)-1,3-dioxolane **40** (1.5 g, 8.8 mmols) and heated to 60°C for 40 hours. The tube was opened and volatile materials were separated by vaccum transfer to give (E)-2-(1,2-difluoroethenyl)-2-methyl-1,3-dioxolane **41** (0.79g, 5.3 mmols, 60%). NMR no. 48; mass spectrum no. 58; IR no. 35.

(Z)-2,2-dimethyl-4,5-difluoro-5-penten-3-one - A 60 cm^3 Carius tube was charged with potassium hydroxide powder (6.0g) and **18** (1.2 g, 7.1 mmols) and heated to 60°C for 40 hours. The tube was opened and volatile materials were separated by vaccum transfer to give **(Z)-2,2-dimethyl-4,5-difluoro-5-penten-3-one 42** (0.66 g, 4.5 mmols, 63%). NMR no. 49; mass spectrum no. 59; IR no. 36.

Reaction of 17 with Base - A small quantity of **17** was added to a 5% solution of sodium carbonate and a colourless precipitate was immediately formed. The precipitate was collected by filtration to give the sodium salt of 3-fluoro-2,4-butadione **43**. This material underwent decomposition over a period of days, hence full characterisation was not obtained; NMR no. 50.

4,4,5-trifluoro-3-methyl-2-pentenoic acid, ethyl ester - Ketone **16** (3.00 g, 32 mmols) was added dropwise to a stirred suspension of (carboxymethyl)triphenyl phosphorane (10.04g, 29 mmols) in diethyl ether (25 cm^3). The reaction mixture was stirred for 16 hours. The resulting suspension was vacuum transferred and diethyl ether removed by distillation to furnish **1,2,2-trifluoro-3-methyl-3-pentenoic acid, ethyl ester 44a** (2.3g, 40%) (found: C, 49.1; H, 5.8. $C_8H_{11}F_3O_2$ requires C, 49.0; H, 5.7);; NMR no. 51; mass spectrum no. 60; IR no. 37.

4,4,5,6,6,6-hexafluoro-3-methyl-2-hexenoic acid, ethyl ester - As for **44a** using **16b** (5.00 g, 25.8 mmols) and (carboxymethyl)triphenyl phosphorane (8.90 g, 25 mmols) to give **4,4,5,6,6,6-hexafluoro-3-methyl-2-hexenoic acid, ethyl ester 44b** (5.85g, 87%) (Found C, 40.9; H, 3.8. $C_9H_{10}F_6O_2$ requires C, 40.9; H, 3.8); NMR no. 52; mass spectrum no. 61; IR no. 38.

3,3,4-trifluoro-2-methyl-1-butene - Methyltriphenyl phosphonium bromide (21.42 g, 60 mmols) and sodium hydride (2.16 g, 90 mmols) were refluxed in tetrahydrofuran (200

cm^3) under an atmosphere of nitrogen for 16 hours. The resultant suspension was filtered under vacuum to furnish a solution of methylenetriphenyl phosphorane.

16 (5g, 40 mmols) was cooled to 0°C under an atmosphere of nitrogen in a 250 cm^3 two necked round bottomed flask fitted with a pressure equalising dropping funnel and a condenser. The dropping funnel was charged with the solution of methylenetriphenyl phosphorane which was added over a 30 minute period to the well stirred ketone. Upon competion of addition, the reaction mixture was stirred overnight. The reaction mixture was poured into water and the lower layer decanted to furnish crude 3,3,4-trifluoro-2-methyl-1-butene **34**

Chapter 6

Experimental to Chapter 3

Due to the potential hazard of polymerisation of trifluoroethene, this material was stored over the radical inhibitor dipentene. In order to ensure that no dipentene was present in the trifluoroethene used in the reactions described, trifluoroethene was placed in a glass tube by vacuum transfer before being transferred again into the reaction vessel. This process of two vacuum transfers ensured that dipentene was not transferred into the reaction vessel due to its involatility.

Bulk polymerisation of Trifluoroethene

i. Theoretical pressure = 12 atm. - Trifluoroethene (2.30 g, 28.0 mmols) was degassed in three freeze-thaw cycles and introduced into a 60 cm^3 Carius tube by vacuum transfer. The tube was sealed and irradiated to a dose of 10 Mrads over a period of 7 days using a ^{60}Co γ-ray source to give quantitative conversion of trifluoroethene to an insoluble polymer.

ii. Theoretical pressure = 6 atm. - Trifluoroethene (7.12 g, 86.8 mmols) was degassed in three freeze-thaw cycles and introduced into a 360 cm^3 tube fitted with a Rotaflo tap by vacuum transfer. The tube was sealed and irradiated to a dose of 10 Mrads over a period of 7 days using a ^{60}Co γ-ray source to give to give quantitative conversion of trifluoroethene to an acetone soluble polymer. IR no. 39.

Polymerisation in Acetone - General Procedure - Acetone (see table 3.2.1 for quantities) was degassed in three freeze thaw cycles in a 60 cm^3 Carius tube. Preweighed trifluoroethene (2.0 - 2.2 g) was introduced into the tube by vacuum transfer. The tube was then sealed and irradiated to a dose of 10 Mrads over a period of 7 days using a ^{60}Co γ-ray source to give quantitative conversion of trifluoroethene in all cases to an acetone soluble polymer. IR no. 40.

Attempted Polymerisation in HFC 134a

i. γ-ray initiation - Trifluoroethene (1.30 g, 16 mmols) and HFC 134a (8.08g, 80 mmols) were degassed separately in three freeze-thaw cycles and introduced into a 360 cm^3 tube fitted with a Rotaflo tap by vacuum transfer. The tube was sealed and irradiated to a dose of 10 Mrads over a period of 7 days using a ^{60}Co γ-ray source. The tube was then opened and volatile materials collected by vacuum transfer. A very small quantity of acetone soluble polymer was obtained.

ii. DTBP initiation - Tert-butyl peroxide (0.2 g) was placed in a 60 cm^3 Carius tube. Degassed trifluoroethene (0.80 g, 9.8 mmols) and degassed 1,1,1,2-tetrafluoroethane (0.9 g, 8.8 mmols) were added to the tube by vacuum transfer. The tube was sealed and heated to 140°C overnight. No change was observed by ^{19}F NMR.

Attempted Addition of HFC 134a to Cyclohexene

i. γ-ray initiation - Cyclohexene (2.0 g, 24 mmols) was placed in a 60 cm^3 Carius tube and degassed in three freeze-thaw cycles. Degassed HFC 134a (3.0 g, 29 mmols) was added by vacuum transfer. The Carius tube was sealed and exposed to a ^{60}Co source for 14 days. Remaining 134a was recovered by vacuum transfer. Conversion of HFC 134a = 0%.

ii. DTBP initiation - Cyclohexene (1.04g, 13 mmols) and tert-butyl peroxide (0.2g) were placed in a 60 cm^3 Carius tube and degassed in three freeze-thaw cycles. Degassed 1,1,1,2-tetrafluoroethane (1.30g, 13 mmols) was added to the tube by vacuum transfer. The tube was sealed and heated to 140°C overnight. ^{19}F NMR -79.3 ppm (s)

iii UV initiation - Cyclohexene (0.08g, 0.01 mmols) and acetone (0.02g) were placed in a quartz NMR tube and degassed in three freeze-thaw cycles. Degassed 1,1,1,2-tetrafluoroethane (0.10g, 0.01 mmols) was added to the tube by vacuum transfer. The tube was sealed and irradiated for 24 hours using a UV mercury lamp. No change was seen by ^{19}F NMR.

Titanium Dioxide Encapsulation

i. TiO_2 pigment TR 92 - A 60 cm^3 Carius tube was charged with powdered pigment TR 92 (5.0 g), 1,1,2-trichlorotrifluoroethane (20 cm^3) and methacrylic acid (0.2 g) and degassed in three freeze-thaw cycles. Preweighed, degassed trifluoroethene (1.0 g) was introduced to the Carius tube by vacuum transfer. The tube was sealed and irradiated to a dose of 10 Mrads over a period of 7 days using a ^{60}Co γ-ray source whilst being agitated by end over end rotation. The tube was then opened and volatile materials collected by vacuum transfer; conversion of trifluoroethene = 100%. The pigment was separated by filtration and dried under vacuum.

ii. TiO_2 pigment TC 90 - As for pigment TR 92 to give quantitative conversion of trifluoroethene.

Polymer Fluorination

i. Bulk Polytrifluoroethene - Bulk polytrifluoroethene was dissolved in acetone and coated as a thin film on a glass rod which was placed in a 140 cm^3 metal tube passivated by exposure to elemental fluorine. All solvent was evaporated from the film at room temperature under vacuum. was sealed, charged with elemental fluorine (5 bar, 50:50 F_2:N_2) and heated at 50°C for 24 hours. The tube was then purged with nitrogen and opened to give an insoluble film. IR no. 41.

ii. Polymer Chain Shortened with Acetone - As for the bulk polymer to give an insoluble film. IR no. 42.

iii. Model Compound

Preparation of the Model Compound - A 140 cm^3 metal tube was charged with degassed perfluoroisopropyl iodide (60g, 0.24 mols) and degassed trifluoroethene (20.1g, 0.25 mols) by vacuum transfer. The tube was sealed and heated to 200°C for 24 hours. Remaining trifluoroethene (14%) was recovered by vacuum transfer and any residual perfluoroisopropyl iodide was removed by distillation. Further fractional distillation gave the 1:2 telomer which was identified by comparison with literature data.[16]

Fluoro-deiodination of the perfluoroisopropyl 1:2 telomer - A 100 cm^3 2-necked round bottomed flask fitted with a reflux condenser and a 50 cm^3 pressure equalising dropping funnel was charged with 1,1,2-trichloro-1,2,2-trifluoroethane (113) and the perfluoroisopropyl / trifluoroethene 1:2 telomer. A solution of antimony pentafluoride in 113 was added dropwise to the stirred flask under an atmosphere of nitrogen at 0°C. Upon completion of addition, stirring was continued for a further 1 hour. The reaction was quenched by dropwise addition of water (50 cm^3) to the well-stirred flask. The lower, fluorous layer was separated, dried over anhydrous magnesium sulfate and 113 was removed by distillation to give **49**. No attempt was made to characterise the complex NMR spectra of this material; IR no. 43.

Fluorination of **49** - A passivated 140 cm^3 autoclave fitted with a glass liner was charged with **49** (0.8g). The tube was purged with nitrogen and charged with 5 bar of a 50:50 F_2: N_2 mixture. The tube was sealed and allowed to stand for 24 hours before being purged and recharged with the same F_2:N_2 mixture and allowed to stand for a further 24 hours. The tube was then purged with nitrogen and opened. Vacuum transfer from the tube gave a mixture of **49** and **50** and unidentified product. Mass spectrum no. 62; IR no. 44.

Polymer Pyrolysis

Bulk Polytrifluoroethene - Polytrifluoroethene **45** (5.0 g) was placed in a quartz pyrolysis tube in a furnace. The outlet of the tube was attached to a liquid air trap. The temperature of the furnace was increased from 200°C to 500°C over a three hour period at which point collection of material was observed in the liquid air trap. Heating was continued at 500°C for a further hour after which time the tube was allowed to cool and a sample of the contents of the liquid air trap was transferred into a sealable quartz NMR tube by vacuum transfer. The material collected was identified as HF by ^{19}F NMR.

Pyrolysis of the Isobutene / Trifluoroethene Copolymer **51**

Preparation of **51** - A 140 cm^3 autoclave was charged with di-*tert*-butyl peroxide (2.5 g) and sealed using a copper gasket annealed in methanol. Isobutene (3.9 g, 0.07 mols) and trifluoroethene (12.4 g, 0.15 mols) were degassed separately in three freeze-thaw cycles. Telogen and trifluoroethene were then placed in the autoclave by vacuum transfer. The autoclave valve was then closed and the autoclave was transferred to a high pressure cell where it was heated to 140°C for 24 hours. Volatile materials (4.6 g) were recovered by vacuum transfer. The autoclave was opened and polymer in the autoclave was dissolved in acetone. The acetone solution was transferred to a round bottomed flask and the solvent was removed under reduced pressure to give **51** (9.2 g). IR no. 45.

Pyrolysis of **51** - As for bulk polytrifluoroethene to give HF.

Chapter 7

Experimental to Chapter 4

Cohalogenation - General Procedure

A 60 cm^3 Carius tube was charged with alcohol and one of NBS, NIS or iodine. Pre-weighed alkene was introduced into the tube by vacuum transfer. The tube was then sealed and heated to 60°C for 40 hours. Any remaining alkene was recovered by vacuum transfer and the residual liquid was poured into water (unless otherwise stated). The lower layer was separated. For reactions with iodine, excess iodine was removed by treatment with aqueous sodium metabisulfite. The product was separated from any dihaloethane present in the product mixture by treatment with an appropriate dehalogenation agent followed by vacuum transfer.

Reactions with Trifluoroethene

Methanol and iodine - A 60 cm^3 Carius tube was charged with methanol (10 cm^3), iodine (6.26 g, 24.6 mmols) and trifluoroethene (2.02 g, 24.6 mmols) and heated to 60°C for 40 hours to give 85% conversion of trifluoroethene to **(1,2,2-trifluoro-1-iodoethyl) methyl ether 52** (4.02g, 68%). (Found: C, 14.7; H, 1.8. $C_3H_4F_3IO$ requires C, 15.0; H, 1.7); NMR no. 54; mass spectrum no. 63; IR no. 46.

Methanol and NBS - A 60 cm^3 Carius tube was charged with methanol (10 cm^3), NBS (1.95 g, 23.8 mmols) and trifluoroethene (1.95 g, 23.8 mmols) and heated to 60°C for 40 hours to give 75% conversion of trifluoroethene. Dibromotrifluoroethane was separated from the product by treatment with zinc powder to give (1,2,2-trifluoro-1-bromoethyl) methyl ether **53** (2.11 g, 46%). (Found: C, 18.6; H, 1.9. $C_3H_4F_3IO$ requires C, 18.7; H, 2.1); NMR no. 53; IR no. 47. Data obtained was in agreement with literature values.[125]

Ethanol and NBS - A 60 cm^3 Carius tube was charged with ethanol (10 cm^3), NBS (4.67 g, 26.2 mmols) and trifluoroethene (2.15 g, 26.2 mmols) and heated to 60°C for 40 hours to give 63% conversion of trifluoroethene. Dibromotrifluoroethane was separated from the product by treatment with potassium hydroxide powder at 0°C to give (1,2,2-trifluoro-1-bromoethyl) ethyl ether **54** (1.90 g, 35%); NMR no. 55; mass spectrum no. 64; IR no. 48. Data obtained was in agreement with literature values.[123]

Ethanol and iodine - A 60 cm^3 Carius tube was charged with ethanol (10 cm^3), iodine (6.38 g, 25.1 mmols) and trifluoroethene (2.06 g, 25.1 mmols) and heated to 60°C for 40 hours to give 74% conversion of trifluoroethene to **(1,2,2-trifluoro-1-iodoethyl) ethyl ether 55** and a trace of di-iodotrifluoroethane. NMR no. 56; mass spectrum no. 65.

1-propanol and iodine - A 60 cm^3 Carius tube was charged with 1-propanol (10 cm^3), iodine (6.69 g, 26.3 mmols) and trifluoroethene (2.16 g, 26.3 mmols) and heated to 60°C for 40 hours to give 70% conversion of trifluoroethene to (1,2,2-trifluoro-1-iodoethyl) propyl ether **57** (4.20 g, 60%) and a trace of di-iodotrifluoroethane (Found M^+, 267.9572. $C_5H_8F_3IO$ requires M^+, 268.0128); NMR no. 59; mass spectrum no. 67; IR no. 50.

Trifluoroethanol and iodine - A 60 cm^3 Carius tube was charged with trifluoroethanol (10 cm^3), iodine (6.29 g, 24.8 mmols) and trifluoroethene (2.03 g, 24.8 mmols) and heated to 60°C for 40 hours. No reaction was observed.

Trifluoroethanol and NIS - A 60 cm^3 Carius tube was charged with trifluoroethanol (10 cm^3), NIS (5.65 g, 25.1 mmols) and trifluoroethene (2.06g, 25.1 mmols) and heated to 60°C for 40 hours to give quantitative conversion of trifluoroethene. The residual liquid was distilled to remove excess trifluoroethanol to give **(1,2,2-trifluoro-1-iodoethyl) trifluoroethyl ether 60** (4.18g, 54%) (Found M^+, 307.9133. $C_4H_3F_6IO$ requires M^+, 307.9575); NMR no. 61; mass spectrum no. 69; IR no. 52.

Trifluoroethanol and NBS - A 60 cm^3 Carius tube was charged with dry trifluoroethanol (10 cm^3), NBS (2.15 g, 26.2 mmols) and trifluoroethene (4.67 g, 26.2 mmols) and heated to 60°C for 40 hours to give quantitative conversion of trifluoroethene. The residual liquid was distilled to remove excess trifluoroethene to give **(1,2,2-trifluoro-1-bromoethyl) trifluoroethyl ether 59** (3.83g, 56 %) (found: C, 18.4; H, 1.2. $C_4H_3F_6BrO$ requires C, 18.4; H, 1.2); NMR no. 60; IR no. 51. Data obtained was in agreement with literature values.[126]

Wet Trifluoroethanol and NBS - A 60 cm^3 Carius tube was charged with undried trifluoroethanol (10 cm^3), NBS (4.56 g, 25.6 mmols) and trifluoroethene (2.10 g, 25.6 mmols) and heated to 60°C for 40 hours to give quantitative conversion of trifluoroethene. The residual liquid was distilled to remove excess trifluoroethene to give **trifluoroethyl bromofluoroacetate 61** (2.88g, 48%) NMR no. 62; mass spectrum no. 70; IR no. 47.

2-chloroethanol and NBS - A 60 cm^3 Carius tube was charged with 2-chloroethanol (10 cm^3), NBS (4.41 g, 24.8 mmols) and trifluoroethene (2.03 g, 24.8 mmols) and heated to 60°C for 40 hours to give quantitative conversion of trifluoroethene to **(1,2,2-trifluoro-1-bromoethyl) 2-chloroethyl ether 62**. (4.18g, 70%); NMR no. 63; mass spectrum no. 71; IR no. 54.

2-chloroethanol and iodine - A 60 cm^3 Carius tube was charged with 2-chloroethanol (10 cm^3), iodine (6.66 g, 26.2 mmols) and trifluoroethene (2.15 g, 26.2 mmols) and heated to 60°C for 40 hours to give quantitative conversion of trifluoroethene to **(1,2,2-trifluoro-1-iodoethyl) 2-chloroethyl ether 63** (4.99g, 66%); (found M^+, 237.9253. $C_4H_5ClF_3IO$ requires 237.9781); NMR no. 64; mass spectrum no. 72; IR no. 55.

Reactions with Other Fluoro-alkenes and Methanol

VDF and NBS - A 60 cm^3 Carius tube was charged with methanol (10 cm^3), NBS (5.14 g, 28.9 mmols) and VDF (1.85g, 28.9 mmols) and heated to 60°C for 40 hours to give 76% conversion of VDF to (2,2-difluoro-1-bromopropyl) methyl ether **64**.(1.56g, 75%); NMR no. 65; mass spectrum no. 73; IR no. 56. Data obtained was in agreement with literature values.[125]

Tetrafluoroethene and NBS - A 60 cm^3 Carius tube was charged with methanol (10 cm^3), NBS (4.30 g, 24.0 mmols), tetrafluoroethene (2.40 g, 24.0 mmols) and two drops of dipentene and heated to 60°C for 40 hours to give 75% conversion of tetrafluoroethene. Dibromotetrafluoroethane was separated from the product by treatment with copper powder at 60°C for 16 hours in a sealed and evacuated Carius tube to give **(1,1,2,2-tetrafluoro-1-bromoethyl) methyl ether 65** (0.76g, 15%) NMR no. 66; mass spectrum no. 74; IR no. 57.

Tetrafluoroethene and iodine - A 60 cm^3 Carius tube was charged with methanol (10 cm^3), iodine (5.59 g, 22.0 mmols), tetrafluoroethene (2.20 g, 22.0 mmols) and two drops of dipentene and heated to 60°C for 40 hours to give 82% conversion of tetrafluoroethene. Di-iodotetrafluoroethane was separated from the product by treatment with copper powder at 60°C for 16 hours in a sealed and evacuated Carius tube to give **(1,1,2,2-tetrafluoro-1-iodoethyl) methyl ether 66** (2.24g, 40%) NMR no. 67; mass spectrum no. 75.

Hexafluoropropene and iodine - A 60 cm^3 Carius tube was charged with methanol (10 cm^3), iodine (6.76 g, 26.6 mmols) and hexafluoropropene (3.99 g, 26.6 mmols) and heated to 60°C for 40 hours to give 55% conversion of hexafluoropropene to **(1,1,1,2,3,3-hexafluoro-2-iodopropyl) methyl ether 68** (3.83g, 47%) (Found: C, 15.6; H, 1.0. $C_4H_3F_6IO$ requires C, 15.6; H, 0.9); NMR no. 68; mass spectrum no. 76; IR no. 58.

Hexafluoropropene and NBS - A 60 cm^3 Carius tube was charged with methanol (10 cm^3), NBS (5.22 g, 29.3 mmols) and hexafluoropropene (4.40 g, 29.3 mmols) and heated to 60°C for 40 hours to give 66% conversion of hexafluoropropene.

Dibromohexafluoropropane was separated from the product by treatment with zinc powder to give **(1,1,1,2,3,3-hexafluoro-2-bromopropyl) methyl ether 67** (2.10g, 27%) (Found: C, 18.7; H, 1.1. $C_3H_3F_6BrO$ requires C, 18.4; H, 1.2); NMR no. 69; mass spectrum no. 77; IR no. 59.

Hydrolysis

(1,2,2-trifluoro-1-iodoethyl) ethyl ether **55** - Ether **55** (1.80g, 7.1 mmols) was added dropwise to stirred sulfuric acid (10 cm^3) at 0°C in a 50cm^3 round bottomed flask. The flask was allowed to warm to room temperature and stirring was continued for a further 2 hours. The reaction was quenched with ice and the lower layer was separated to give **fluoroiodoethyl acetate 56** (1.25g, 76 %) (Found M^+, 231.9397. $C_4H_6FIO_2$ requires M^+ 231.9886); NMR no. 57; mass spectrum no. 66; IR no. 49.

Appendices and References

Appendix 1

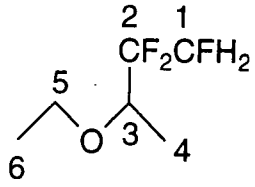
NMR Spectra

All ^{1}H NMR spectra were recorded at 400 MHz, ^{19}F NMR at 376 MHz and ^{13}C NMR at 100 MHz unless stated otherwise

1. 1,2,2-trifluoro-3-ethoxybutane **1a**
2. 2-(1',1',2'-trifluoro-1'-ethyl)-tetrahydrofuran **2a**
3. 1-(1',1',2'-trifluoro-1'-ethyl)-cyclohexane **3a**
4. 1-(1',2',2'-trifluoro-1'-ethyl)-cyclohexane **3b**
5. 1-(1',1',2'-trifluoro-1'-ethyl)-tetrahydropyran **4a**
6. 1-(1',1',2'-trifluoro-1'-ethyl)-1,4-dioxane **5a**
7. 2-(1',1',2'-trifluoro-1'-ethyl)-1,3-dioxane **6a**
8. 2-(1',1',2',3',3',3'-hexafluoropropyl)-1,3-dioxane **8a**
9. 1,2,2-trifluoro-3-(diethylamino)butane **9a**
10. di(2-(1',2',2'-trifluoroethyl)ethyl) ethyl amine **10a**
11. 2,2,3-trifluoro-1-propanol **12a**
12. 3,3,4-trifluoro-2-butanol **13a**
13. 4-chloro-3,3-difluoro-2-butanol **13c**
14. 4,4,5-trifluoro-2-propanol **14a**
15. 3,3,4-trifluoro-2-methyl-2-butanol **15a**
16. 3,4,4-trifluoro-2-methyl-2-butanol **15b**
17. 3,3,4,5,5,5-hexafluoro-2-methyl-2-pentanol **15c**
18. 1-(1',1',2'-trifluoro-1'-ethyl)-cyclohexanol **26a**
19. 1-(1',2',2'-trifluoro-1'-ethyl)-cyclohexanol **26b**
20. 3,3,4-trifluoro-2-butanone **16**
21. 3,4,4-trifluoro-2-butanone **17**
22. 4,4,5-trifluoro-2,2-dimethyl-3-pentanone **18a**
23. 4,5,5-trifluoro-2,2-dimethyl-3-pentanone **18b**
24. (Z)-1,2-difluoro-3-ethoxy-1-butene **19**
25. 2,2,3-trifluoropropyl methacrylate **20a**
26. 2,3,3-trifluoropropyl methacrylate **20b**
27. 3,3,4-trifluoro-2-butyl methacrylate **21a**
28. 3,3-difluoro-4-methyl oxetane **22**
29. 1-difluoromethyl-2-methyl oxirane **23**
30. 3,3-difluoro-4,4-dimethyl oxetane **24**
31. 3-(difluoromethyl)-2,2-dimethyl oxirane **25**
32. 3,3-difluoro-2-spirocyclohexyloxetane **27**
33. 3,3-difluoro-oxetane **28**

34. 2-(difluoromethyl) oxirane
35. 2,3-difluoro-2-propen-1-ol
36. 3,4,5,5,5-pentafluoro-2-methyl-4-propen-2-ol **31**
37. 1-(1',1',2'-trifluoro-1'-ethyl)-1-cyclohexene **33**
38. 3,3,4-trifluoro-2-methyl-1-butene **34**
39. 3,4,4-trifluoro-2-methyl-1-butene **34**
40. 3,3,4-trifluoro-2-butyl tosylate **35**
41. 3,3,4-trifluoro-1-butene **36**
42. 1,2,2,6,6,7-hexafluoro-5-methyl-4-hydroxy-heptan-3-one **37a**
43. 1,2,2,6,6,7-hexafluoro-5-methyl-4-hepten-3-one **38a**
44. 1,1,1,2,3,3,7,7,8,9,9,9-dodecafluoro-6-methyl-6-hydroxy-heptan-4-one **37b**
45. 2,2,3-trifluoropropanoic acid **39**
46. 2-methyl-2-(1',1',2'-trifluoro-1'-ethyl)-dioxolane **40a**
47. 2-methyl-2-(1',2',2'-trifluoro-1'-ethyl)-1,3-dioxolane **40b**
48. 2-((E)-1',2'-difluoroethenyl)-2-methyl-1,3-dioxolane **41**
49. 2,2-dimethyl-4-penten-3-one **42**
50. 2-fluoro-3-keto-butanal, sodium salt
51. 4,4,5-trifluoro-3-methyl-2-pentenoic acid, ethyl ester **44a**
52. 4,4,5,6,6,6-hexafluoro-3-methyl-2-hexenoic acid, ethyl ester **44b**
53. (1,2,2-trifluoro-1-bromoethyl) methyl ether **53**
54. (1,2,2-trifluoro-1-iodoethyl) methyl ether **52**
55. (1,2,2-trifluoro-1-bromoethyl) ethyl ether **54**
56. (1,2,2-trifluoro-1-iodoethyl) ethyl ether **55**
57. Ethyl fluoroiodoacetate **56**
58. (1,2,2-trifluoro-1-bromoethyl) propyl ether **58**
59. (1,2,2-trifluoro-1-iodoethyl) propyl ether **57**
60. (1,1,1-trifluoroethyl) (1,2,2-trifluoro-1-bromoethyl) ether **59**
61. (1,1,1-trifluoroethyl) (1,2,2-trifluoro-1-iodoethyl) ether **60**
62. Trifluoroethyl bromofluoroacetate **61**
63. (1,2,2-trifluoro-1-bromoethyl) 2-chloroethyl ether **62**
64. (1,2,2-trifluoro-1-iodoethyl) 2-chloroethyl ether **63**
65. (2,2-difluoro-1-bromopropyl) methyl ether **64**
66. (1,1,2,2-tetrafluoro-1-bromoethyl) methyl ether **65**
67. (1,1,2,2-tetrafluoro-1-iodoethyl) methyl ether **66**
68. (1,1,1,2,3,3-hexafluoro-2-bromopropyl) methyl ether **67**
69. (1,1,1,2,3,3-hexafluoro-2-iodopropyl) methyl ether **68**

1. 1,2,2-trifluoro-3-ethoxybutane **1a**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.16	t, $^{3}J_{HH}$ 7.2	3H	6
1.24	d, $^{3}J_{HH}$ 6.7	3H	4
3.61	dq, $^{2}J_{HF}$ 52.8, $^{3}J_{HH}$ 7.2	2H	5
3.81	ddq, $^{3}J_{HF}$ 18.6, 14.2, $^{3}J_{HH}$ 6.7	1H	3
4.70	m	2H	1

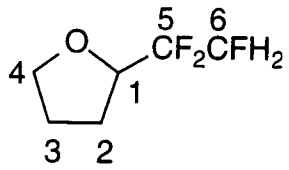
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-121.5	ABq; A = -117.1, B = - 126.0, J_{AB} = 263	2F	$-CF_2-$
-240.2	tt, $^{2}J_t$ = 46.2, $^{3}J_t$ = 13.9	1F	$-CFH_2$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
12.8	s	6
15.6	s	4
66.1	s	5
74.1	dd, $^{2}J_{CF}$ 29.4, 24.7	3
80.6	ddd, $^{1}J_{CF}$ 176, $^{2}J_{CF}$ 35.1, 28.1	1
120.8	ddd, $^{1}J_{CF}$ 245, 248, $^{2}J_{CF}$ 19.4	2

2. 2-(1',1',2'-trifluoro-1'-ethyl)-tetrahydrofuran **2a**



^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.93	m	2H	3
2.07	m	2H	4
3.83	m	2H	2
4.19	m	1H	1
4.66	m	2H	6

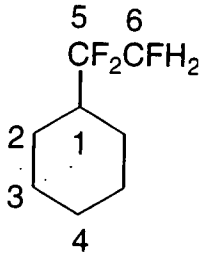
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-121.2	ABq; A = -116.9, B = - 125.1, J_{AB} = 268	2F	$-CF_2-$
-239.8	tt, $^2J_{HF}$ 45.2, $^3J_{FF}$ 14.1	1F	$-CFH_2$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
25.3	s	3
26.4	s	2
70.0	s	4
76.6	dd, $^2J_{CF}$ 32.1, 24.3	1
80.9	ddd, $^1J_{CF}$ 175, $^2J_{CF}$ 36.7, 27.2	6
120.7	td, $^1J_{CF}$ 245, $^2J_{CF}$ 19.8	5

3. 1-(1',1',2'-trifluoro-1'-ethyl)-cyclohexane **3a**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.2-1.3	m	5H	3,4
1.7-1.9	m	6H	1,2
4.63	dt, $^{2}J_{HF}$ 46.4, $^{3}J_{HF}$ 12.8	2H	-CFH_2

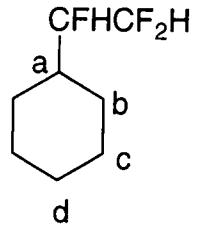
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-115.9	pseudo quint, ^{3}J 13.2	2F	-CF_2-
-238.6	tt, $^{2}J_{FH}$ 46.4, $^{3}J_{FF}$ 13.9	1F	-CFH_2

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
25.8	s	4
26.1	s	3
26.5	s	2
41.9	t, $^{2}J_{CF}$ 22.1	1
81.4	dt, $^{1}J_{CF}$ 176 Hz, $^{2}J_{CF}$ 34.3	6
122.8	td, $^{1}J_{CF}$ 244, $^{2}J_{CF}$ 20.2	5

4. 1-(1',2',2'-trifluoro-1'-ethyl)-cyclohexane **3b**



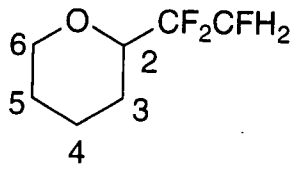
^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.2-1.3	m	5H	a,b
1.7-1.9	m	6H	c,d
4.42	dm	1H	-CFH-
6.14	dddd $^{2}J_{HF}$ 54.4, $^{3}J_{HF}$ 9.6, $^{3}J_{HH}$ 3.6	1H	$-CF_2H$

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-131.5	dABq, $^{2}J_{FH}$ 54.4; A = -130.4, B = -132.6	2F	$-CF_2H$
-238.6	dm, $^{2}J_{FH}$ 46.9	1F	-CFH-

5. 2-(1',1',2'-trifluoro-1'-ethyl)-tetrahydropyran **4a**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.54	m	4H	4 (a*, e*), 3a, 5a
1.73	m	1H	5e
1.92	m	1H	3e
3.47	m	1H	6a
3.68	m	1H	6e
3.98	dm	2H	2
4.62	dm	2H	$-CFH_2$

* a = axial proton, e = equitorial proton

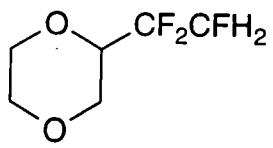
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-123.2	ABq, A = -126.6, B = -119.8, J_{AB} = 263	2F	$-CF_2-$
-242.6	tt, $^{2}J_{HF}$ 46.3, $^{3}J_{HF}$ 13.5	1F	$-CFH_2$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
22.9	s	C4
24.0	s	C5
26.3	s	C3
69.3	s	C6
76.1	dd, $^{2}J_{CF}$ 31.4, 24.9	C2
80.5	ddd, $^{1}J_{CF}$ 179.2, $^{2}J_{CF}$ 35.8, 27.2	$-CFH_2$
119.8	td, $^{1}J_{CF}$ 242, $^{2}J_{CF}$ 19.4	$-CF_2-$

6. 2-(1',1',2'-trifluoro-1'-ethyl)-1,4-dioxane **5a**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
3.2 - 4.0	m	7H	Ring protons
4.7	m	2H	$-CFH_2$

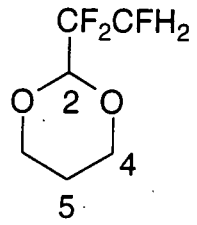
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
M = -117.1	ABq, A = -120.0, B = -114.2, J_{AB}= 269 Hz	2F	$-CF_2-$
-236.7	tt, $^{2}J_{FH}$ 45.9, $^{3}J_{FH}$ 13.9	1F	$-CFH_2$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
66.8	s	C5 and C6
67.7	s	C3
73.8	dd, $^{2}J_{CF}$ 31.7, 24.3	C2
80.1	ddd, $^{1}J_{CF}$ 176, $^{2}J_{CF}$ 35.2, 28.1	$-CFH_2$
119.5	td, $^{1}J_{CF}$ 244, $^{2}J_{CF}$ 20.6	$-CF_2-$

7. 2-(1',1',2'-trifluoro-1'-ethyl)-1,3-dioxane **6a**



d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.45	m	1H	5 ax.
1.5	m	1H	5 eq.
3.90	t, $^3J_{HH}$ 11.8	4H	4
4.58	dt, $^2J_{HF}$ 46.2, $^3J_{HF}$ 13.4	2H	$-CFH_2$
5.01	t, $^3J_{HF}$ 13.1	1H	2

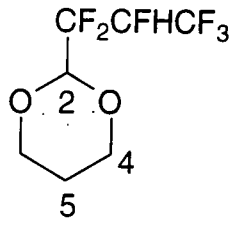
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-120.6	pseudo quint, ^3J 13.2	2F	$-CF_2-$
-240.5	tt, $^2J_{FH}$ 46.2, $^3J_{FF}$ 13.4	1F	$-CFH_2$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
25.8	s	5
67.6	s	4
93.9	t, $^2J_{CF}$ 28.4	2
81.4	dt, $^1J_{CF}$ 176 Hz, $^2J_{CF}$ 34.3	$-CF_2-$
122.8	td, $^1J_{CF}$ 247, $^2J_{CF}$ 20.4	$-CFH_2$

8. 2-(1',1',2',3',3',3'-hexafluoro-1'-propyl)-1,3-dioxane **8a**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.48	m	1H	5 ax.
1.51	m	1H	5 eq.
3.97	t, $^{3}J_{HH}$ 12.0	4H	4
5.04	m	1H	2
5.56	ddq, $^{2}J_{HF}$ 43.9, $^{3}J_{HF}$ 18.1, 6.7	1H	-CFH-

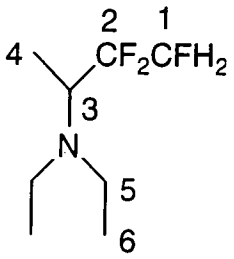
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-74.9	s	3F	$-CF_3$
-128.7	AB q, A = - 127.7, B = -129.7, J_{AB} 259	2F	$-CF_2-$
-216.9	dm, $^{2}J_{FH}$ 43.9	1F	-CFH-

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
26.1	s	5
67.5	s	4
96.9	t, $^{2}J_{CF}$ 28.2	2
80.2	dt, $^{1}J_{CF}$ 179, $^{2}J_{CF}$ 28.3	-CFH-
118.0	ddd, $^{1}J_{CF}$ 247, 241, $^{2}J_{CF}$ 20.9	$-CF_2-$
119.7	qd, $^{1}J_{CF}$ 276, $^{2}J_{CF}$ 24.7	$-CF_3$

9. 1,2,2-trifluoro-3-(diethylamino)butane **9a**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.00	t, $^{3}J_{HH}$ 7.2	6H	6
1.10	d, $^{3}J_{HH}$ 6.8	3H	4
2.46	q, $^{3}J_{HH}$ 7.2	4H	5
3.20	m	1H	3
4.75	ddd, $^{2}J_{HF}$ 46.4, $^{3}J_{HF}$ 16.8, 13.2	2H	1

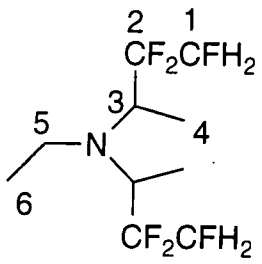
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-117.4	ABq; A = -111.2, B = - 123.6, J_{AB} 259	2F	$-CFH_2$
-239.1	tt, $^{2}J_{FH}$ 46.4, $^{3}J_{FH}$ 14.7	1F	$-CFH_2$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
14.4	s	6
26.4	s	4
47.1	s	5
56.1	dd, $^{2}J_{CF}$ 29.0, 21.4	3
81.6	ddd, $^{1}J_{CF}$ 176, $^{2}J_{CF}$ 37.7, 25.5	1
120.7	td, $^{1}J_{CF}$ 246, $^{2}J_{CF}$ 18.7	2

10. di(2-(1,2,2-trifluorobut-3-yl) ethylamine **10a**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.04	t, $^{3}J_{HH}$ 7.2	3H	6
1.26	d, $^{3}J_{HH}$ 6.9	6H	4
2.77	q, $^{3}J_{HH}$ 7.2	2H	5
3.4	m	2H	3
4.75	m	4H	1

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-117.2	ABq; A = -114.3, B = - 120.1, J_{AB} 59	2F	$-CF_2-$
-117.7	ABq; A = -111.9, B = - 123.5, J_{AB} 260	2F	$-CF_2-$
-238.3	tt, $^{2}J_{FH}$ 47.0, $^{3}J_{FF}$ 14.4	1F	$-CFH_2$
-239.5	tt, $^{2}J_{FH}$ 45.9, $^{3}J_{FF}$14.5	1F	$-CFH_2$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
9.8	s	6
14.8	s	4
42.8	s	5
55.5	m	3
81.5	dm, $^{1}J_{CF}$ 176	1
122.8	td, $^{1}J_{CF}$ 247, $^{2}J_{CF}$ 19.1	2

11. 2,2,3-trifluoro-1-propanol **12a**

$$\underset{1}{HO}\underset{2}{CH_2}\underset{3}{CF_2}CFH_2$$

^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
3.82	t, $^3J_{HF}$ 12.5	1H	1
4.67	dt, $^2J_{HF}$ 46.3, $^3J_{HF}$ 12.5	1H	3

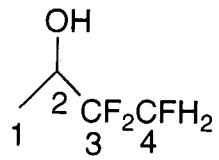
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-118.9	pseudo sex, ^3J_s = 12.5	2F	2
-239.9	tt, $^2J_{FH}$ 46.3, $^3J_{FF}$ 12.6	1F	3

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
65.2	t, $^2J_{CF}$ 32.4	1
84.4	dt, $^1J_{CF}$ 175, $^2J_{CF}$ 32.7	3
125.5	td, $^1J_{CF}$ 244, $^2J_{CF}$ 21.0	2

12. 3,3,4-trifluoro-2-butanol **13a**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.27	d, $^{3}J_{HH}$ 6.8	3H	1
4.08	m	1H	2
4.78	m	2H	4

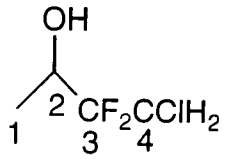
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-123.1	ABq; A = -118.3, B = - 127.8, J_{AB} 259	2F	$-CF_2-$
-241.6	tt, $^{2}J_{FH}$ 46.4, $^{3}J_{FF}$ 13.7	1F	$-CFH_2$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
15.6	s	1
66.5	t, $^{2}J_{CF}$ 29.7	2
80.5	dt, $^{1}J_{CF}$ 176, $^{2}J_{CF}$ 32.1	4
121.1	td, $^{1}J_{CF}$ 248, $^{2}J_{CF}$ 18.7	3

13. 4-chloro-3,3-difluoro-2-butanol **13c**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.26	d, $^{3}J_{HH}$ 6.4	3H	1
3.9	m	2H	4
4.1	m	1H	2

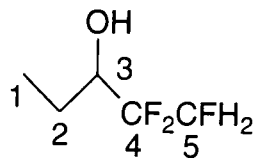
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-126.2	ABq; A = -122.8, B = - 129.6, J_{AB} 225	2F	$-CF_2-$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
14.9	s	1
42.2	t, $^{2}J_{CF}$ 27.2	2
66.2	t, $^{2}J_{CF}$ 28.5	4
120.6	t, $^{1}J_{CF}$ 247	3

14. 4,4,5-trifluoro-2-propanol **14a**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.11	t, $^{3}J_{HH}$ 6.8	3H	1
1.50	pseudo p, ^{3}J 6.8	2H	2
3.75	m	1H	3
4.70	m	2H	5

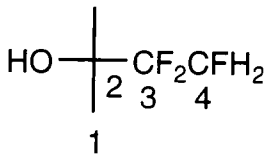
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-122.0	ABq; A = -117.9, B = - 126.1, J_{AB}259	2F	$-CF_2-$
-240.5	tt, $^{2}J_{FH}$ 46.4, $^{3}J_{FF}$ 13.9	1F	$-CFH_2$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
10.6	s	1
15.6	s	2
72.0	t, $^{2}J_{CF}$ 25.5	3
80.6	ddd, $^{1}J_{CF}$ 175, $^{2}J_{CF}$ 34.5, 29.1	5
121.3	td, $^{1}J_{CF}$ 246, $^{2}J_{CF}$ 19.1	4

15. 3,3,4-trifluoro-2-methyl-2-butanol **15a**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.28	s	3H	1
4.78	dt, $^{2}J_{HF}$ 46.8, $^{3}J_{HF}$ 13.6	1H	4

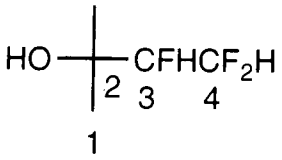
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-121.1	pseudo q, ^{3}J 13.5	2F	3
-241.0	tt, $^{2}J_{FH}$ 46.8, $^{3}J_{FF}$ 12.8	1F	4

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
23.8	s	1
72.0	t, $^{2}J_{CF}$ 25.1	2
80.5	dt, $^{1}J_{CF}$ 177, $^{2}J_{CF}$ 29.0	4
121.9	td, $^{1}J_{CF}$ 249, $^{2}J_{CF}$ 16.1	3

16. 3,4,4-trifluoro-2-methyl-2-butanol **15b**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.12	d, $^{4}J_{HH}$ 6.4	6H	1
4.26	ddd, $^{2}J_{HF}$ 46.2, ^{3}J 9.5	1H	3
6.15	td, $^{2}J_{HF}$ 53.3, ^{3}J 9.6	1H	4

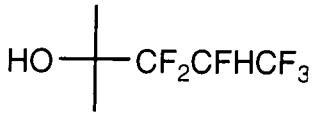
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-124.1	dABq, A = -121.3, B = -126.9, J_{AB} = 297, J_d 53.1	2F	4
-209.7	d, $^{2}J_{FH}$ 53.3	1F	3

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
23.8	s	1
69.9	d, $^{2}J_{CF}$ 26.3	2
94.9	ddd, $^{1}J_{CF}$ 185, $^{2}J_{CF}$ 24.4, 18.3	3
114.1	$^{1}J_{CF}$ 239, $^{2}J_{CF}$ 23.6,	4

17. 3,3,4,5,5,5-hexafluoro-2-methyl-2-pentanol **15c**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.42	s	6H	-CH_3
5.24	ddqd, $^{2}J_{HF}$ 43.4, $^{3}J_{HF}$ 18.0, 6.4, 1.2	1H	-CFH-

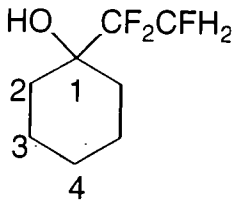
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-74.0	s	3F	-CF_3
-125.1	AB q, A = - 123.7, B = -126.5, J_{AB} 263	2F	-CF_2-
-207.2	dm, $^{2}J_{FH}$ 43.4	1F	-CFH-

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
22.9	s	-CH_3
72.8	t, $^{2}J_{CF}$ 25.9	$(CH_3)_2C$-
80.5	dt, $^{1}J_{CF}$ 177, $^{2}J_{CF}$ 29.0	-CFH-
118.0	ddd, $^{1}J_{CF}$ 250, 241, $^{2}J_{CF}$ 21.7	-CF_2-
119.7	qd, $^{1}J_{CF}$ 283, $^{2}J_{CF}$ 25.9	-CF_3

18. 1-(1',1',2'-trifluoro-1'-ethyl)-cyclohexanol **26a**



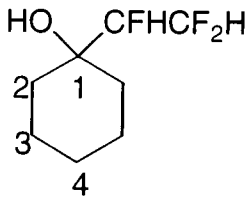
^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.2	m	2H	4
1.6	m	8H	2, 3
4.78	dt, $^2J_{HF}$ 46.8, $^3J_{HF}$ 14.4	2H	$-CFH_2$

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-121.4	pseudo q, $^3J_{F-FH}$ 13.5	2F	$-CF_2-$
-240.8	tt, $^2J_{FH}$ 46.8, $^3J_{FF}$ 13.1	1F	$-CFH_2$

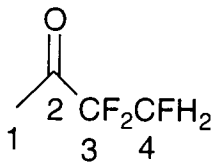
19. 1-(1',2',2'-trifluoro-1'-ethyl)-cyclohexanol **26b**



^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-124.6	dABq, A = -122.1, B = -127.1, J_{AB} 298, J_d 53.4	2F	$-CF_2H$
-209.5	dq, $^2J_{FH}$ 45.9, $^3J_{F-FH}$ 9.8	1F	-CFH-

20. 3,3,4-trifluoro-2-butanone **16**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
2.41	t, $^{4}J_{HF}$ 1.6	3H	1
4.84	dt, $^{2}J_{HF}$ 46.0, $^{3}J_{HF}$ 13.2	2H	4

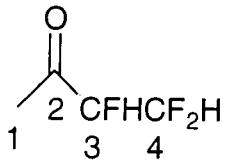
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-117.9	pseudo q, ^{3}J 13.5	2H	3
-242.3	tt, $^{2}J_{FH}$ 46.0, $^{3}J_{FF}$ 13.4	1F	2

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
24.7	s	1
81.0	dt, $^{1}J_{CF}$ 176, $^{2}J_{CF}$ 30.2	4
114.2	td, $^{1}J_{CF}$ 254, $^{2}J_{CF}$ 22.5	3
197.8	t, $^{2}J_{CF}$ 29.4	2

21. 3,4,4-trifluoro-2-butanone **17**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
2.32	d, $^{4}J_{HF}$ 4.8	3H	1
5.26	ddd, $^{2}J_{HF}$ 46.8, ^{3}J 10.4, 8.8	1H	3
6.33	td, $^{2}J_{HF}$ 52.6, ^{3}J 12.8	1H	4

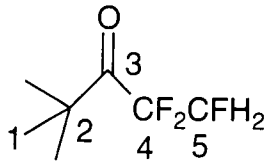
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-124.5	dABq, A = -121.3, B = -126.9, J_{AB} = 297, J_{FH} 52.6	2F	4
-211.7	dm, $^{2}J_{FH}$ 46.8	1F	3

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
26.9	d, $^{3}J_{CF}$ 1.5	1
92.3	dt, $^{1}J_{CF}$ 195, $^{2}J_{CF}$ 22.1	4
113.7	ddd $^{1}J_{CF}$ 243, $^{2}J_{CF}$ 21.7	3
202.2	d, $^{2}J_{CF}$ 27.5	2

22. 4,4,5-trifluoro-2,2-dimethyl-3-pentanone **18a**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.08	s	9H	1
4.72	dt, $^{2}J_{HF}$ 46.3, $^{3}J_{HF}$ 13.6	2H	5

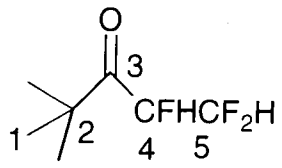
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-119.4	pseudo q, ^{3}J 13.4	2F	4
-238.7	tt, $^{2}J_{FH}$ 46.3, $^{3}J_{FF}$ 13.2	1F	5

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
24.0	s	1
25.4	s	2
81.0	dt, $^{1}J_{CF}$ 178, $^{2}J_{CF}$ 32.1	5
123.9	td, $^{1}J_{CF}$ 247, $^{2}J_{CF}$ 16.8	
197.5	t, $^{2}J_{CF}$ 29.2	3

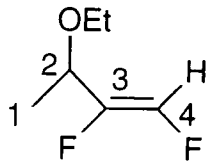
23. 4,5,5-trifluoro-2,2-dimethyl-3-pentanone **18b**



^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-122.3	dABq, A = -119.0, B = -125.6, J_{AB} = 295, J_{FH} 51.9	2F	4
-211.5	dm, $^2J_{FH}$ 45.8	1F	3

24. -1,2-difluoro-3-ethoxy-1-butene **19**



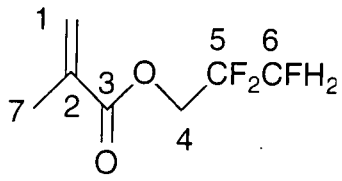
^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.18	t, $^{3}J_{H-H}$ 7.2	3H	CH_3CH_2-
1.25	d, $^{3}J_{H-H}$ 6.8	3H	1
3.48	q, $^{3}J_{H-H}$ 7.2	2H	CH_3CH_2-
4.0	m	1H	2
6.80	dd, $^{2}J_{H-F}$ 73.4, $^{3}J_{H-F}$ 17.6	1H	4

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-152.1	dd, $^{3}J_{F-H}$ 17.6, $^{3}J_{F-F}$ 10.1	1F	3
-165.0	dd, $^{2}J_{F-H}$ 73.4, $^{3}J_{F-F}$ 10.1	1F	4

25. 2,2,3-trifluoropropyl methacrylate **20a**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.95	s	3H	7
4.55	t, $^{3}J_{HF}$ 13.2	2H	4
4.79	dt, $^{2}J_{HF}$ 46.0, $^{3}J_{HF}$ 13.9	2H	6
5.75	m	1H	1
6.17	m	1H	1

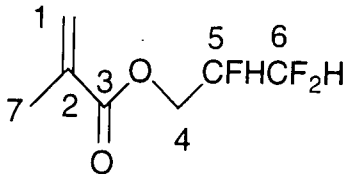
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-118.9	pseudo sex, ^{3}J 13.6	2F	$-CF_2-$
-240.2	tt, $^{2}J_{FH}$ 46.0, $^{3}J_{FF}$ 13.9	1F	$-CFH_2$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
18.2	s	7
61.8	t, $^{2}J_{CF}$ 31.0	4
80.6	dt, $^{1}J_{CF}$ 176, $^{2}J_{CF}$ 32.1	6
119.1	td, $^{1}J_{CF}$ 244, $^{2}J_{CF}$ 21.3	5
136.3	s	1
166.3	s	2

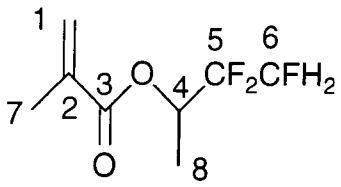
26. 2,3,3-trifluoropropyl methacrylate **20b**



^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-124.2	dABq, A = -121.4, B = -127.0, J_{AB} = 292, J_d 52.3	2F	$-CF_2H$
-209.7	dm, $^2J_{FH}$ 52.8	1F	-CFH-

27. 3,3,4-trifluoro-2-butyl methacrylate **21a**



^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.39	d, $^3J_{HH}$ 6.4	3H	8
1.94	s	3H	7
4.77	ddd, $^2J_{HF}$ 45.8, $^3J_{HF}$ 14.4, 11.2	2H	6
5.30	m	1H	4
5.73	m	1H	1
6.15	m	1H	1

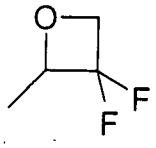
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-121.5	ABq; A = -119.1, B = - 123.9, J_{AB} 264	2F	$-CF_2-$
-241.4	tt, $^2J_{FH}$ 45.8, $^3J_{FF}$ 14.3	1F	$-CFH_2$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
15.6	s	8
66.1	s	7
68.5	dd, $^2J_{CF}$ 21.3, 26.0	4
81.1	ddd, $^1J_{CF}$ 177, $^2J_{CF}$ 34.0, 30.5	6
119.8	td, $^1J_{CF}$ 246, $^2J_{CF}$ 20.9	5
136.6	s	1
146.7	s	2

28. 3,3-difluoro-4-methyl oxetane **22**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.35	d, $^{3}J_{HH}$ 6.4	3H	Me
4.62-4.77	m	2H	$-CH_2-$
5.00	m	1H	-CH(Me)-

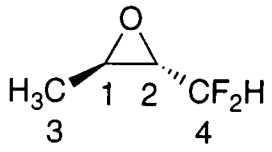
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-108.8	ABq, A = -101.2, B = -116.4, J_{AB} 195 Hz	-	$-CF_2-$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
15.3	dd, $^{3}J_{CF}$ 3.5	Me
78.2	t, $^{2}J_{CF}$ 24.8	$-CH_2-$
87.4	t, $^{2}J_{CF}$ 24.3	-CH(Me)-
119.4	dd, $^{1}J_{CF}$ 277.3	$-CF_2-$

29. 1-difluoromethyl-2-methyl oxirane **23**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.33	d, $^{3}J_{HH}$ 5.2	3H	3
3.10	m	1H	1
4.70	m	1H	2
5.76	td, $^{2}J_{HF}$ 54.9, $^{3}J_{HH}$ 4.8	1H	4

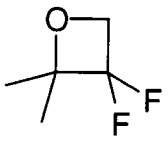
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-124.3	ddd, $^{2}J_{d}$ 54.9, 35.4; $^{3}J_{d}$ 7.5	-	$-CF_2-$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
16.8	s	3
51.6	t, $^{3}J_{CF}$ 4.4	1
56.4	t, $^{2}J_{CF}$ 31.5	2
116.0	t, $^{1}J_{CF}$ 238	4

30. 3,3-difluoro-4,4-dimethyl oxetane **24**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.39	s	6H	Me
4.62	t, $^{3}J_{HF}$ 14.4	2H	$-CH_2-$

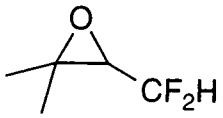
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-113.0	t, $^{3}J_{FH}$ 14.4	-	$-CF_2-$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
22.1	t, $^{3}J_{CF}$ 4.2	Me
76.0	t, $^{2}J_{CF}$ 25.3	$-CH_2-$
92.6	t, $^{2}J_{CF}$ 22.9	$-C(Me)_2-$
120.3	t, $^{1}J_{CF}$ 281.1	$-CF_2-$

31. 3-(difluoromethyl)-2,2-dimethyl oxirane **25**



^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.35	s	6H	Me
4.72	m	1H	-C*H*(CF_2H)
5.78	td, $^2J_{HF}$ 54.3, $^3J_{HH}$ 6.8	1H	-CF_2H

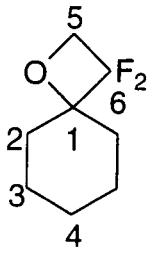
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-122.0	dm, $^2J_{FH}$ 54.3	-	-CF_2-

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
19.0	s	Me
60.7	dd, $^2J_{CF}$ 33.5	C3
57.1	s	-$C(Me)_2$-
116.4	t, $^1J_{CF}$ 237	-CF_2H

32. 3,3-difluoro-2-spirocyclohexyloxetane **27**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.50	m	4H	3a, 4a, 4e
1.69	m	4H	3e, 2a
1.85	m	2H	2e
4.60	t, $^{3}J_{HF}$ 14.4	2H	6

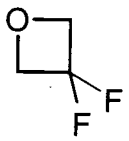
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-113.5	t, $^{3}J_{FH}$ 14.4	-	$-CF_2-$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
22.8	s	4
25.3	s	3
32.0	s	2
75.7	t, $^{2}J_{CF}$ 24.7	6
93.7	t, $^{2}J_{CF}$ 21.3	1
120.9	t, $^{1}J_{CF}$ 281	5

33. 3,3-difluoro-oxetane **28**



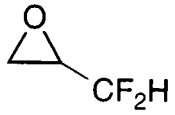
^{1}H NMR (d_6 acetone, 250 MHz)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
4.84	t, $^{3}J_{H-F}$ 14.7	-	$-CH_2-$

^{19}F NMR (d_6 acetone, 235 MHz)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-102.2	s	-	$-CF_2-$

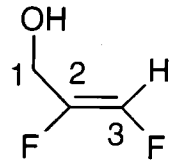
34. 2-(difluoromethyl) oxirane



^{19}F NMR (d_6 acetone, 235 MHz)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-121.0	dABq, A = -118.5, B = -123.5, J_{AB} 294 Hz, $^2J_{FH}$ 48.9	-	$-CF_2-$

35. (Z)-2,3-difluoro-2-propen-1-ol



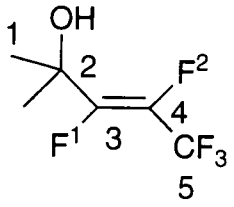
^{1}H NMR (d_6 acetone, 235 MHz)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
4.04	d, $^{3}J_{H-F}$ 9.2	2H	1
6.91	dd, $^{2}J_{H-F}$ 73.6, $^{3}J_{H-F}$ 16.4	1H	3

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-147.7	s	1F	2
-167.3	d, $^{2}J_{H-F}$ 73.6	1F	3

36. (E)-3,4,5,5,5-pentafluoro-2-methyl-4-propen-2-ol **31**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.50	s	-	$-CH_3$

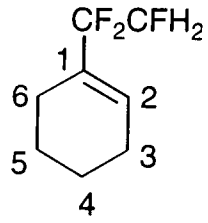
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-67.2	dd, $^{3}J_{FF}$ 23.0, $^{4}J_{FF}$ 9.8	3F	$-CF_3$
-145.5	dq, $^{3}J_{FF}$ 132, $^{4}J_{FF}$ 9.8	1F	F^1
-170.5	dm, $^{3}J_{FF}$ 132	1F	F^2

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
27.1	s	C1
70.8	d, $^{2}J_{CF}$ 26.4	C2
122.6	qd, $^{1}J_{CF}$ 282, $^{3}J_{CF}$ 26.3	C5
137.7	ddq, $^{1}J_{CF}$ 244, $^{2}J_{CF}$ 49.6, $^{2}J_{CF}$ 39.2	C4
159.9	qd, $^{1}J_{CF}$ 282, $^{3}J_{CF}$ 26.3	C3

37. 1-(1',1',2'-trifluoro-1'-ethyl)-1-cyclohexene **33**



^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.50	m	4H	3a, 5a, 4a, 4e
1.69	m	4H	3e, 5e, 6a, 6e
4.64	dt, $^2J_{HF}$ 46.3, $^3J_{HF}$ 12.5	2H	$-CFH_2$
6.17	s	1H	2

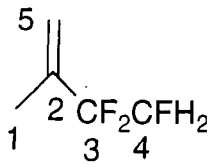
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-113.3	pseudo q, ^3J 15.8	2F	$-CF_2-$
-235.6	tt, $^2J_{FH}$ 46.3, $^3J_{FF}$ 17.2	1F	$-CFH_2$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
22.2	s	4
22.6	s	5
23.2	t, $^3J_{CF}$ 3.0	6
25.2	s	3
81.9	dt, $^1J_{CF}$ 180, $^2J_{CF}$ 35.2	$-CFH_2$
119.9	td, $^1J_{CF}$ 241, $^2J_{CF}$ 20.2	$-CF_2-$
130.3	t, $^3J_{CF}$ 8.8	1
131.6	s	2

38. 3,3,4-trifluoro-2-methyl-1-butene **34**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.88	s	3H	1
4.70	dt, $^{2}J_{HF}$ 46.0, $^{3}J_{HF}$ 12.8	2H	4
5.39	d, $^{2}J_{HH}$ 25.6	2H	5

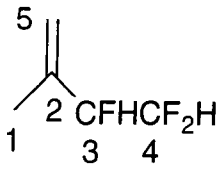
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-110.6	pseudo q, ^{3}J 13.7	2F	$-CF_2-$
-235.2	tt, $^{2}J_{FH}$ 46.0, $^{3}J_{FF}$ 16.9	1F	$-CFH_2$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
17.1	s	1
81.8	dt, $^{1}J_{CF}$ 179, $^{2}J_{CF}$ 34.7	4
118.2	t, $^{3}J_{CF}$ 8.3	5
119.5	td, $^{1}J_{CF}$ 241, $^{2}J_{CF}$ 20.6	3
138.3	t, $^{2}J_{CF}$ 23.3	2

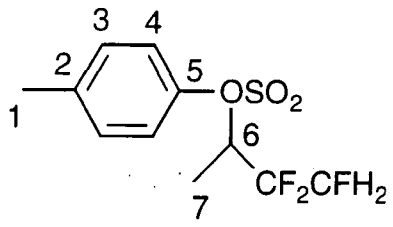
39. 3,4,4-trifluoro-2-methyl-1-butene **34**



^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-130.0	dABq, A = -127.2, B = -132.8, J_{AB} = 296, J_d 53.0	2F	$-CF_2H$
-199.7	dm, $^2J_{FH}$ 53.2	1F	-CFH

40. 3,3,4-trifluoro-2-butyl tosylate **35**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.42	d, $^{3}J_{HH}$ 6.4	3H	7
2.46	s	3H	1
4.47	dm, $^{2}J_{HF}$ 46.1	2H	-CFH_2
4.86	pseudo sex, ^{3}J 7.2	2H	6
7.59	ABq, A = 7.37, B = 7.81, J_{AB} 8.4	4H	3, 4

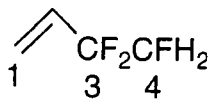
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-123.3	ABq; A = -118.5, B = - 128.1, J_{AB} 263	2F	-CF_2-
-241.6	tt, $^{2}J_{FH}$ 46.1, $^{3}J_{FF}$ 14.0	1F	-CFH_2

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
15.2	s	7
21.6	s	1
73.9	dd, $^{2}J_{CF}$ 34.0, 27.2	6
78.8	ddd, $^{1}J_{CF}$ 179, $^{2}J_{CF}$ 37.0, 30.8	-CFH_2
117.1	td, $^{1}J_{CF}$ 250, $^{2}J_{CF}$ 21.4	-CF_2-
127.8	s	3
130.0	s	4
131.1	s	2
145.5	s	5

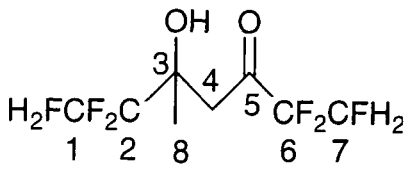
41. 3,3,4-trifluoro-1-butene **36**



^{19}F NMR (d_6 acetone, 250 MHz)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-111.5	s	2F	$-CF_2-$
-238.8	t, $^2J_{FH}$ 46.0	1F	$-CFH_2$

42. 1,2,2,6,6,7-hexafluoro-5-methyl-4-hydroxy-heptan-3-one **37a**



^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.54	s	3H	8
3.20	ABq; A = 3.05, B = 3.35, J_{AB} 16.8	2H	4
4.89	dt, $^2J_{HF}$ 46.1, $^3J_{HF}$ 13.6	2H	1
4.90	dt, $^2J_{HF}$ 45.8, $^3J_{HF}$ 13.2	2H	7

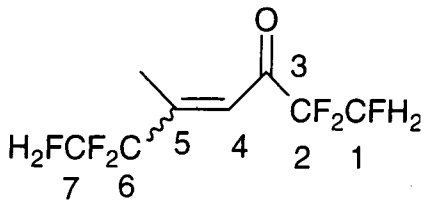
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-117.9	pseudo q, ^3J 13.1	2F	6
-241.1	tt, $^2J_{FH}$ 45.8, $^3J_{FF}$ 13.5	1F	7
-121.6	pseudo q, ^3J 13.2	2F	2
-242.7	tt, $^2J_{FH}$ 46.1, $^3J_{FF}$ 13.4	1F	1

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
20.7	s	8
41.3	s	4
73.7	t, $^2J_{CF}$ 25.1	3
80.1	dt, $^1J_{CF}$ 177, $^2J_{CF}$ 29.7	1
80.3	dt, $^1J_{CF}$ 177, $^2J_{CF}$ 29.8	7
114.0	td, $^1J_{CF}$ 255, $^2J_{CF}$ 21.7	2
121.2	td, $^1J_{CF}$ 251, $^2J_{CF}$ 16.8	6
197.2	t, $^2J_{CF}$ 29.0	5

43. 1,2,2,6,6,7-hexafluoro-5-methyl-4-hepten-3-one **38a**



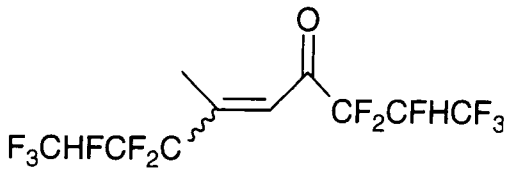
^{1}H NMR (d_6 acetone, 250 MHz)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
2.25	s	3H	$-CH_3$
4.86	dt, $^{2}J_{FH}$ 45.8, $^{3}J_{FH}$ 12.5	2H	$-CFH_2$ (7)
4.95	dt, $^{2}J_{FH}$ 45.5, $^{3}J_{FH}$ 13.2	2H	$-CFH_2$ (1)
6.95	s	1H	=CH

^{19}F NMR (d_6 acetone, 250 MHz)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-117.9	s	2F	$-CF_2-$ (2)
-121.5	s	2F	$-CF_2-$ (6)
-241.1	t, $^{2}J_{FH}$ 45.5	1F	$-CFH_2$ (1)
-242.6	t, $^{2}J_{FH}$ 45.8	1F	$-CFH_2$ (7)

44. 1,1,1,2,3,3,7,7,8,9,9,9-dodecafluoro-6-methyl-6-hydroxy-heptan-4-one **37b**



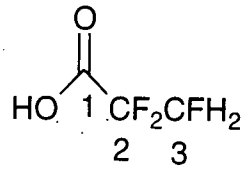
^{1}H NMR (d_6 acetone, 250 MHz)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
2.35	s	3H	$-CH_3$
6.0	m	2H	-CFH-
7.07	s	1H	=CH

^{19}F NMR (d_6 acetone, 250 MHz)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-73.6	s	6F	$-CF_3$
ABq; M = -113.4, A = -111.3, B = -115.5	ABq, J_{AB} 264	2F	$-CF_2-$ (C7)
ABq; M = -119.4, A = -116.5, B = -122.3	ABq, J_{AB} 290	2F	$-CF_2-$ (C3)
-212.0	s	1F	-CFH- (C8)
-215.7	s	1F	-CFH- (C2)

45. 2,2,3-trifluoropropanoic acid **39**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
4.88	dt, $^{2}J_{HF}$ 45.7, $^{3}J_{HF}$ 12.8	-	3

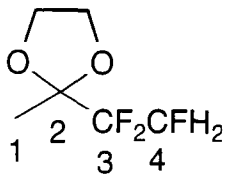
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-117.7	pseudo q, ^{3}J 12.4	2F	3
-240.6	tt, $^{2}J_{FH}$ 45.7, $^{3}J_{FF}$ 13.7	1F	2

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
81.2	dt, $^{1}J_{CF}$ 177, $^{2}J_{CF}$ 30.5	3
113.0	td, $^{1}J_{CF}$ 251, $^{2}J_{CF}$ 23.2	2
163.2	t, $^{2}J_{CF}$ 30.1	1

46. 2-methyl-2-(1',1',2'-trifluoro-1'-ethyl)-dioxolane **40a**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.39	s	3H	1
4.05	m	4H	$-CH_2-$
4.71	dt, $^{2}J_{HF}$ 46.7, $^{3}J_{HF}$ 14.0	2H	4

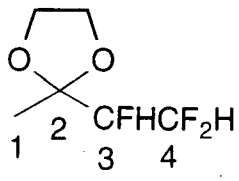
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-122.5	pseudo q, $^{3}J_{q}$ 13.6	2F	$-CF_2-$
-243.5	tt, $^{2}J_{FH}$ 46.7, $^{3}J_{FF}$ 12.4	1F	$-CFH_2$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
19.8	s	1
66.9	s	5, 6
80.5	dt, $^{1}J_{CF}$ 178, $^{2}J_{CF}$ 28.2	4
107.1	t, $^{2}J_{CF}$ 25.5	2
119.6	td, $^{1}J_{CF}$ 252, $^{2}J_{CF}$ 16.7	3

47. 2-methyl-2-(1',2',2'-trifluoro-1'-ethyl)-1,3-dioxolane **40b**



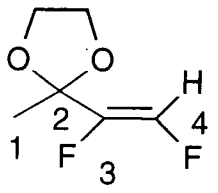
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
ABq; M = -118.6, A = -116.2, B = -121.0	dABq; J_{AB} 296, $^2J_{FH}$ 46.1	2F	$-CF_2H$
-201.6	dm, $^2J_{FH}$ 45.9	1F	-CFH-

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
17.5	s	1
66.0	s	$-CH_2-$
91.3	ddd, $^1J_{CF}$ 189 Hz, $^2J_{CF}$ 19.1	3
103.5	d, $^2J_{CF}$ 25.5	2
113.7	ddd, $^1J_{CF}$ 240 Hz, $^2J_{CF}$ 22.9	4

48. 2-((E)-1,2-difluoroethenyl)-2-methyl-1,3-dioxolane **41**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.50	s	3H	$-CH_3$
3.96	m	4H	$-CH_2-$
6.91	dd, $^{2}J_{H-F}$ 73.7, $^{3}J_{H-F}$ 16.4	1H	=CFH

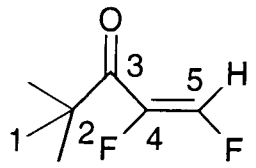
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-147.9	dd, $^{3}J_{F-H}$ 16.4, $^{3}J_{F-F}$ 8.3	1F	3
-167.4	dd, $^{2}J_{F-H}$ 73.7, $^{3}J_{F-F}$ 8.3	1F	4

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
22.9	s	$-CH_3$
65.2	s	$-CH_2-$
104.6	d, $^{2}J_{C-F}$ 29.8	2
135.6	dd, $^{1}J_{C-F}$ 255, $^{2}J_{C-F}$ 10.7	4
157.8	dd, $^{1}J_{C-F}$ 2561 $^{2}J_{C-F}$ 5.7	3

49. (E)-2,2-dimethyl-4-penten-3-one **42**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.12	s	9H	1
6.58	dd, $^{2}J_{H-F}$ 74.9, $^{3}J_{H-F}$ 19.2	1H	5

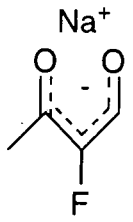
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-142.9	dd, $^{3}J_{F-H}$ 19.2, $^{3}J_{F-F}$ 10.2	1F	4
-173.0	dd, $^{2}J_{F-H}$ 74.9, $^{3}J_{F-F}$ 10.2	1F	5

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
26.7	s	1
25.6	s	2
133.3	dd, $^{1}J_{C-F}$ 247, $^{2}J_{C-F}$ 14.5	5
157.8	dd, $^{1}J_{C-F}$ 254, $^{2}J_{C-F}$ 6.1	4
205.9	s	3

50. 2-fluoro-3-keto-butanal, sodium salt



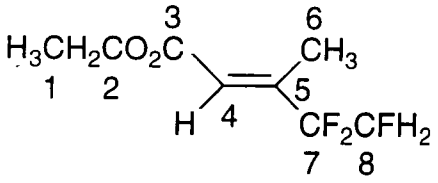
^{1}H NMR (d_6 acetone, 250 MHz)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
2.30	s	3H	$-CH_3$
6.58	d, $^{3}J_{H-F}$ 18.5	1H	-CHO

^{19}F NMR (d_6 acetone, 235 MHz)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-148.3	s	-	-CF

51. 4,4,5-trifluoro-3-methyl-2-pentenoic acid, ethyl ester **44a**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.27	$^{3}J_{HH}$ 7.2	3H	1
2.22	s	3H	6
4.19	$^{3}J_{HH}$ 7.2	2H	2
4.80	dt, $^{2}J_{HF}$ 46.1, $^{3}J_{HF}$ 12.7	2H	8
6.19	s	1H	4

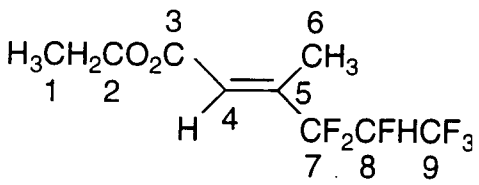
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-112.5	pseudo q, ^{3}J 12.8	2F	-CF_2-
-235.1	tt, $^{2}J_{FH}$ 46.1, $^{3}J_{FF}$ 12.7	1F	-CFH_2

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
14.4	s	1
61.4	s	2
81.6	dt, $^{1}J_{CF}$ 179, $^{2}J_{CF}$ 34.4	8
119.4	td, $^{1}J_{CF}$ 244, $^{2}J_{CF}$ 20.9	7
122.0	t, $^{3}J_{CF}$ 8.8	4
146.6	t, $^{2}J_{CF}$ 22.5	5
165.6	s	3

52. 4,4,5,6,6,6-hexafluoro-3-methyl-2-hexenoic acid, ethyl ester **44b**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.28	t, $^{3}J_{HH}$ 7.2	3H	1
3.41	q, $^{3}J_{HH}$ 7.2	2H	2
2.27	s	3H	6
5.89	dm	1H	8
6.29	s	1H	4

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-78.8	s	3F	$-CF_3$
ABq; M = -117.9, A = -115.9, B = -119.9	ABq, J_{AB} 253	2F	$-CF_2-$
-217.1	dq, $^{2}J_{FH}$ 27.5, $^{3}J_{FF}$ 11.3	1F	-CFH-

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
14.4	s	1
61.4	s	2
66.1	s	2
80.5	dt, $^{1}J_{CF}$ 177, $^{2}J_{CF}$ 29.0	-CFH-
118.0	ddd, $^{1}J_{CF}$ 250, 241, $^{2}J_{CF}$ 21.7	$-CF_2-$
119.7	qd, $^{1}J_{CF}$ 283, $^{2}J_{CF}$ 25.9	$-CF_3$
123.4	t, $^{3}J_{CF}$ 8.9	4
144.8	t, $^{2}J_{CF}$ 22.2	5
165.3	s	3

53. (1,2,2-trifluoro-1-bromoethyl) methyl ether **53**

CH_3OCF_2CFHBr

^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
3.71	s	3H	$-CH_3$
6.92	ddd, $^2J_{H-F}$ 47.1, $^3J_{H-F}$ 5.6 and 4.4	1H	-CFHBr

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-89.1	ddABq, A = -88.9, B = -89.3, J_{AB} 142, $^3J_{F-F}$ 14.3, $^3J_{F-H}$ 4.1	2F	$-CF_2-$
-157.4	dt, $^2J_{F-H}$ 47.1, $^3J_{F-F}$ 14.3	1F	-CFHBr

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
51.9	t, $^3J_{C-F}$ 6.5	CH_3-
87.9	dt, $^1J_{C-F}$ 257, $^2J_{C-F}$ 42.6	-CFHBr
120.5	td, $^1J_{C-F}$ 265, $^2J_{C-F}$ 24.8	$-CF_2-$

54. (1,2,2-trifluoro-1-iodoethyl) methyl ether **52**

CH_3OCF_2CFHI

^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
3.69	s	3H	$-CH_3$
7.23	ddd, $^2J_{H-F}$ 46.8, $^3J_{H-F}$ 5.2 and 4.4	1H	-CFHI

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-86.9	ddABq, A = -88.0, B = -85.8, J_{AB} 140, $^3J_{F-F}$ 18.4, $^3J_{F-H}$ 5.1	2F	$-CF_2-$
-166.6	dt, $^2J_{F-H}$ 46.8, $^3J_{F-F}$ 18.1	1F	-CFHI

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
51.8	t, $^3J_{C-F}$ 6.9	CH_3-
65.6	dt, $^1J_{C-F}$ 254, $^2J_{C-F}$ 41.1	-CFHI
120.9	td, $^1J_{C-F}$ 264, $^2J_{C-F}$ 24.0	$-CF_2-$

55. (1,2,2-trifluoro-1-bromoethyl) ethyl ether **54**

$CH_3CH_2OCF_2CFHBr$

^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.31	t, $^3J_{H-H}$ 7.2	3H	$-CH_3$
4.09	q, $^3J_{H-H}$ 7.2	2H	$-CH_2-$
6.86	ddd, $^2J_{H-F}$ 46.9, $^3J_{H-F}$ 5.4 and 4.5	1H	-CFHBr

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-88.6	dABq, A = -88.4, B = -88.8, J_{AB} 143, $^3J_{F-F}$ 14.3	2F	$-CF_2-$
-156.8	dt, $^2J_{F-H}$ 46.9, $^3J_{F-F}$ 13.6	1F	-CFHBr

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
15.0	s	$-CH_3$
61.8	t, $^3J_{C-F}$ 6.1	$-CH_2-$
87.6	dt, $^1J_{C-F}$ 257, $^2J_{C-F}$ 42.7	-CFHBr
120.3	td, $^1J_{C-F}$ 264, $^2J_{C-F}$ 24.8	$-CF_2-$

56. (1,2,2-trifluoro-1-iodoethyl) ethyl ether **55**

$CH_3CH_2OCF_2CFHI$

^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.30	t, $^3J_{H-H}$ 7.2	3H	$-CH_3$
4.05	q, $^3J_{H-H}$ 7.2	2H	$-CH_2-$
7.21	ddd, $^2J_{H-F}$ 46.7, $^3J_{H-F}$ 5.3 and 4.5	1H	-CFHI

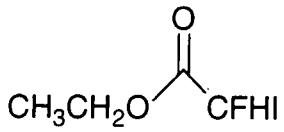
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-87.5	dABq, A = -87.2, B = -90.0, J_{AB} 141, $^3J_{F-F}$ 14.1	2F	$-CF_2-$
-166.4	dt, $^2J_{F-H}$ 46.7, $^3J_{F-F}$ 14.5	1F	-CFHI

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
15.0	s	$-CH_3$
61.9	t, $^3J_{C-F}$ 6.1	$-CH_2-$
66.1	dt, $^1J_{C-F}$ 255, $^2J_{C-F}$ 42.5	-CFHI
120.0	td, $^1J_{C-F}$ 264, $^2J_{C-F}$ 24.6	$-CF_2-$

57. Ethyl fluoroiodioacetate **56**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
1.28	t, $^{3}J_{H-H}$ 7.2	3H	$-CH_3$
4.30	q, $^{3}J_{H-H}$ 7.2	2H	$-CH_2-$
7.46	d, $^{2}J_{H-F}$ 50.4	1H	-CFHI

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-161.6	d, $^{2}J_{F-H}$ 50.4	1F	-CFHI

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
13.9	s	$-CH_3$
57.6	d, $^{1}J_{C-F}$ 258	-CFHI
63.0	s	$-CH_2-$
206.2	s	C=O

58. (1,2,2-trifluoro-1-bromoethyl) propyl ether **58**

$CH_3CH_2CH_2OCF_2CFHBr$

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-88.8	dABq, A = -88.6, B = -89.0, J_{AB} 147, $^3J_{F-F}$ 14.2	2F	$-CF_2-$
-156.5	dt, $^2J_{F-H}$ 46.8, $^3J_{F-F}$ 13.8	1F	-CFHBr

59. (1,2,2-trifluoro-1-iodoethyl) propyl ether **57**

$CH_3CH_2CH_2OCF_2CFHI$

^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
0.98	t, $^3J_{H-H}$ 7.2	3H	$-CH_3$
1.69	sex, $^3J_{H-H}$ 7.2	2H	CH_3CH_2-
3.97	t, $^3J_{H-H}$ 7.2	2H	$-CH_2O-$
7.24	dt, $^2J_{H-F}$ 47.1, $^3J_{H-F}$ 6.0	1H	-CFHI

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-84.2	dd, $^2J_{F-H}$ 17.7	2F	$-CF_2-$
-166.3	dt, $^2J_{F-H}$ 47.1, $^3J_{F-F}$ 17.3	1F	-CFHI

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
9.4	s	$-CH_3$
22.1	s	CH_3CH_2-
65.1	dt, $^1J_{C-F}$ 254, $^2J_{C-F}$ 41.6	-CFHI
66.1	t, $^3J_{C-F}$ 5.3	$-CH_2O-$
119.7	td, $^1J_{C-F}$ 264, $^2J_{C-F}$ 24.0	$-CF_2-$

60. (1,1,1-trifluoroethyl) (1,2,2-trifluoro-1-bromoethyl) ether **59**

$CF_3CH_2OCF_2CFHBr$

^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
4.65	q, $^3J_{H-F}$ 8.0	2H	$-CH_2-$
7.28	ddd, $^2J_{H-F}$ 46.5, $^3J_{H-F}$ 5.4	1H	-CFHBr

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-75.1	s	3F	$-CF_3$
-88.3	ABq, A = -88.1, B = -88.5, J_{AB} 142	2F	$-CF_2-$
-159.0	dt, $^2J_{F-H}$ 46.5, $^3J_{F-F}$ 17.3	1F	-CFHBr

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
61.9	q, $^2J_{C-F}$ 37.4	$-CH_2-$
88.2	dt, $^1J_{C-F}$ 254, $^2J_{C-F}$ 41.2	-CFHBr
120.3	td, $^1J_{C-F}$ 264, $^2J_{C-F}$ 24.8	$-CF_2-$
126.2	q, $^1J_{C-F}$ 281	$-CF_3$

61. (1,1,1-trifluoroethyl) (1,2,2-trifluoro-1-iodoethyl) ether **60**

$CF_3CH_2OCF_2CFHI$

^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
4.63	q, $^3J_{H-F}$ 8.0	2H	$-CH_2-$
7.35	ddd, $^2J_{H-F}$ 46.8, $^3J_{H-F}$ 5.2	1H	-CFHI

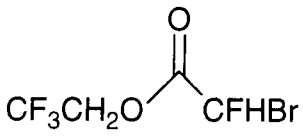
^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-75.1	s	3F	$-CF_3$
-85.3	ABq, A = -85.1, B = -85.6, J_{AB} 139	2F	$-CF_2-$
-168.9	dt, $^2J_{F-H}$ 46.8, $^3J_{F-F}$ 17.3	1F	-CFHI

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
61.9	q, $^2J_{C-F}$ 37.4	$-CH_2-$
64.1	dt, $^1J_{C-F}$ 254, $^2J_{C-F}$ 39.3	-CFHI
120.3	td, $^1J_{C-F}$ 268, $^2J_{C-F}$ 24.4	$-CF_2-$
126.0	q, $^1J_{C-F}$ 278	$-CF_3$

62. Trifluoroethyl bromofluoroacetate **61**



^{1}H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
3.97	q, $^{3}J_{HF}$ 9.2	2H	$-CH_2-$
7.00	d, $^{2}J_{H-F}$ 49.8	1H	-CFHBr

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-77.6	t, $^{3}J_{F-H}$ 9.2	3F	$-CF_3$
-150.0	d, $^{2}J_{F-H}$ 49.8	1F	-CFHBr

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
60.8	q, $^{2}J_{C-F}$ 34.4	$-CH_2-$
82.3	d, $^{1}J_{C-F}$ 260	-CFHBr
126.1	q, $^{1}J_{C-F}$ 279	$-CF_3$
206.5	s	C=O

63. (1,2,2-trifluoro-1-bromoethyl) 2-chloroethyl ether **62**

$ClCH_2CH_2OCF_2CFHBr$

^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
3.84	t, $^3J_{H-H}$ 5.2	2H	$ClCH_2$-
4.31	t, $^3J_{H-H}$ 5.2	2H	-CH_2O-
6.96	dt, $^2J_{H-F}$ 46.7, $^3J_{H-F}$ 14.1	1H	-CFHBr

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-85.3	ABq, A = -85.1, B = -85.5, J_{AB} 141,	2F	-CF_2-
-157.0	dt, $^2J_{F-H}$ 46.7, $^3J_{F-F}$ 13.9	1F	-CFHBr

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
42.7	s	$ClCH_2$-
66.0	s	-CH_2O-
87.7	dt, $^1J_{C-F}$ 257, $^2J_{C-F}$ 42.0	-CFHBr
120.1	td, $^1J_{C-F}$ 266, $^2J_{C-F}$ 24.7	-CF_2-

64. (1,2,2-trifluoro-1-iodoethyl) 2-chloroethyl ether **63**

$ClCH_2CH_2OCF_2CFHI$

^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
3.82	t, $^3J_{H-H}$ 6.0	2H	$ClCH_2$-
4.29	t, $^3J_{H-H}$ 6.0	2H	-CH_2O-
7.23	ddd, $^2J_{H-F}$ 47.1, $^3J_{H-F}$ 5.6	1H	-CFHI

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-85.8	ABq, A = -85.6, B = -86.0, J_{AB} 140	2F	-CF_2-
-168.4	dt, $^2J_{F-H}$ 47.1, $^3J_{F-F}$ 17.3	1F	-CFHI

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
42.5	s	$ClCH_2$-
65.7	s	-CH_2O-
65.2	dt, $^1J_{C-F}$ 255, $^2J_{C-F}$ 40.4	-CFHI
120.4	td, $^1J_{C-F}$ 266, $^2J_{C-F}$ 24.0	-CF_2-

65. (2,2-difluoro-1-bromopropyl) methyl ether **64**

$CH_3OCF_2CH_2Br$

^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
3.60	s	3H	$-CH_3$
3.77	t, $^3J_{H-F}$ 8.0	2H	$-CH_2-$

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-78.7	t $^3J_{F-H}$ 8.0	-	$-CF_2-$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
29.6	t, $^2J_{C-F}$ 39.3	$-CH_2-$
51.2	t, $^3J_{C-F}$ 6.8	$-CH_3$
123.1	t, $^1J_{C-F}$ 259	$-CF_2-$

66. (1,1,2,2-tetrafluoro-1-bromoethyl) methyl ether **65**

$CH_3OCF_2CF_2Br$

^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
3.81	s	-	$-CH_3$

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-68.4	t $^3J_{F-F}$ 9.2	2F	$-CF_2-$
-91.5	t $^3J_{F-F}$ 9.2	2F	$-CF_2Br$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
52.9	s	CH_3-
109.8	tt, $^1J_{C-F}$ 251, $^2J_{C-F}$ 35.8	$-CF_2Br$
118.1	tt, $^1J_{C-F}$ 270, $^2J_{C-F}$ 31.3	$-CF_2-$

67. (1,1,2,2-tetrafluoro-1-iodoethyl) methyl ether **66**

$CH_3OCF_2CF_2I$

^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
3.78	s	-	$-CH_3$

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-66.2	t $^3J_{F-F}$ 9.3	2F	$-CF_2-$
-92.7	t $^3J_{F-F}$ 9.3	2F	$-CF_2I$

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
52.7	s	CH_3-
105.2	tt, $^1J_{C-F}$ 252, $^2J_{C-F}$ 35.3	$-CF_2Br$
117.8	tt, $^1J_{C-F}$ 268, $^2J_{C-F}$ 31.0	$-CF_2-$

68. (1,1,1,2,3,3-hexafluoro-2-bromopropyl) methyl ether **67**

$CH_3OCF_2CFBrCF_3$

^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
3.81	s	3H	$-CH_3$

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-76.2	s	3F	$-CF_3$
-83.9	ABq, A = -86.2, B = -81.7, J_{AB} 139	2F	$-CF_2-$
-141.8	pseudo sex, $^3J_{F-F}$ 9.0	1F	-CFBr-

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
52.7	s	CH_3-
76.0	dsex, $^1J_{C-F}$ 262, $^2J_{C-F}$ 35.5	-CFBr-
120.7	td, $^1J_{C-F}$ 270, $^2J_{C-F}$ 25.1	$-CF_2-$
121.6	qd, $^1J_{C-F}$ 283, $^2J_{C-F}$ 28.3	$-CF_3$

69. (1,1,1,2,3,3-hexafluoro-2-iodopropyl) methyl ether **68**

$CH_3OCF_2CFICF_3$

^1H NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
3.77	s	3H	$-CH_3$

^{19}F NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Integral	Assignment
-73.9	s	3F	$-CF_3$
-82.8	ABq, A = -80.1, B = -85.5, J_{AB} 139	2F	$-CF_2-$
-148.8	pseudo sex, $^3J_{F-F}$ 13.2	1F	-CFI-

^{13}C NMR (d_6 acetone)

d (ppm)	Multiplicity, J (Hz)	Assignment
52.6	t, $^3J_{C-F}$ 6.4	CH_3-
76.0	dsex, $^1J_{C-F}$ 262, $^2J_{C-F}$ 35.8	-CFI-
120.7	td, $^1J_{C-F}$ 270, $^2J_{C-F}$ 25.1	$-CF_2-$
121.6	qd, $^1J_{C-F}$ 283, $^2J_{C-F}$ 28.3	$-CF_3$

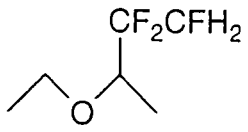
Appendix 2

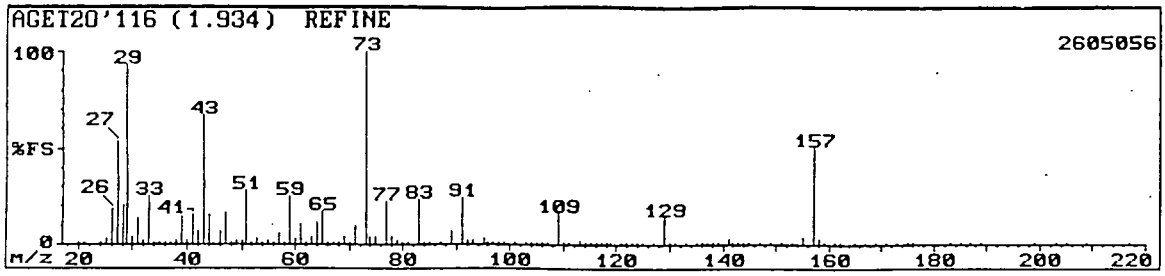
Mass Spectra

1. 1,2,2-trifluoro-3-ethoxybutane **1a**
2. 1,1,2-trifluoro-3-ethoxybutane **1b**
3. 2-(1',1',2'-trifluoro-1'-ethyl)-tetrahydrofuran **2a**
4. 2-(1',2',2'-trifluoro-1'-ethyl)-tetrahydrofuran **2b**
5. 1-(1',1',2'-trifluoro-1'-ethyl)-cyclohexane **3a**
6. 1-(1',2',2'-trifluoro-1'-ethyl)-cyclohexane **3b**
7. 2-(1',1',2'-trifluoro-1'-ethyl)-tetrahydropyran **4a**
8. 2-(1',2',2'-trifluoro-1'-ethyl)-tetrahydropyran **4b**
9. 2-(1',1',2'-trifluoro-1'-ethyl)-1,4-dioxane **5a**
10. 2-(1',2',2'-trifluoro-1'-ethyl)-1,4-dioxane **5b**
11. 2-(1',1',2'-trifluoro-1'-ethyl)-1,3-dioxane **6a**
12. 2-(1',2',2'-trifluoro-1'-ethyl)-1,3-dioxane **6b**
13. 4-(1',1',2'-trifluoro-1'-ethyl)-1,3-dioxane **6c**
14. 4-(1',2',2'-trifluoro-1'-ethyl)-1,3-dioxane **6d**
15. 2-(1',1',2'-trifluoro-1'-ethyl)-1,3,5-trioxane **7a**
16. 2-(1',2',2'-trifluoro-1'-ethyl)-1,3,5-trioxane **7b**
17. 2-(1',1',2',3',3',3'-hexafluoro-1'-propyl)-1,3-dioxane **8a**
18. 4-(1',1',2',3',3',3'-hexafluoro-1'-propyl)-1,3-dioxane **8b**
19. 1,2,2-trifluoro-3-(diethylamino)butane **9a**
20. di(1,2,2-trifluorobut-3-yl) ethylamine **10a**
21. tri(1,2,2-trifluorobut-3-yl) amine **11a**
22. 2,2,3-trifluoro-1-propanol **12a**
23. 3,3,4-trifluoro-2-butanol **13a**
24. 3,4,4-trifluoro-2-butanol **13b**
25. 4-chloro-3,3-difluoro-2-butanol **13c**
26. 4,4,5-trifluoro-2-propanol **14a**
27. 4,5,5-trifluoro-2-propanol **14b**
28. 3,3,4-trifluoro-2-methyl-2-butanol **15a**
29. 1-(1',1',2'-trifluoro-1'-ethyl)-cyclohexanol **26a**
30. 1-(1',2',2'-trifluoro-1'-ethyl)-cyclohexanol **26b**
31. 3,3,4-trifluoro-2-butanone **16**
32. 3,4,4-trifluoro-2-butanone **17**
33. 4,4,5-trifluoro-2,2-dimethyl-3-pentanone **18a**
34. (Z)-1,2-difluoro-3-ethoxy-1-butene **19**
35. 2,2,3-trifluoropropyl methacrylate **20a**
36. 2,3,3-trifluoropropyl methacrylate **20b**
37. 3,3,4-trifluoro-2-butyl methacrylate **21a**

38. 3,4,4-trifluoro-2-butyl methacrylate **21b**
39. 3,3,-difluoro-4-methyl oxetane **22**
40. 1-difluoromethyl-2-methyl oxirane **23**
41. 3,3-difluoro-4,4-dimethyl oxetane **24**
42. 3-(difluoromethyl)-2,2-dimethyl oxirane **25**
43. 3,3-difluoro-2-spirocyclohexyloxetane **27**
44. (E)-3,4,5,5,5-pentafluoro-2-methyl-4-propen-2-ol **31**
45. Oligomer **32**
46. 1-(1',1',2'-trifluoro-1'-ethyl)-1-cyclohexene **33**
47. 3,3,4-trifluoro-2-methyl-1-butene **34a**
48. 3,4,4-trifluoro-2-methyl-1-butene **34b**
49. 3,3,4-trifluoro-2-butyl tosylate **35a**
50. 3,4,4-trifluoro-2-butyl tosylate **35b**
51. 3,3,4-trifluoro-1-butene **36**
52. 1,2,2,6,6,7-hexafluoro-5-methyl-4-hydroxy-heptan-3-one **37a**
53. 1,2,2,6,6,7-hexafluoro-5-methyl-4-hepten-3-one **38a**
54. 1,1,1,2,3,3,7,7,8,9,9,9-dodecaafluoro-6-methyl-5-hepten-4-one **38b**
55. 2,2,3-trifluoropropanoic acid **39**
56. 2-methyl-2-(1',1',2'-trifluoro-1'-ethyl)-1,3-dioxolane **40a**
57. 2-methyl-2-(1',2',2'-trifluoro-1'-ethyl)-1,3-dioxolane **40b**
58. 2-((E)-1,2-difluoroethenyl)-1,3-dioxolane **41**
59. 2,2-dimethyl-4,5-difluoro-3-pentan-4-one **42**
60. 4,4,5-trifluoro-3-methyl-2-pentenoic acid, ethyl ester **44a**
61. 4,4,5,6,6,6-hexafluoro-3-methyl-2-hexenoic acid, ethyl ester **44b**
62. perfluoro(2-methylhexane) **50**
63. (1,2,2-trifluoro-1-iodoethyl) methyl ether **52**
64. (1,2,2-trifluoro-1-bromoethyl) ethyl ether **54**
65. (1,2,2-trifluoro-1-iodoethyl) ethyl ether **55**
66. Ethyl fluoroiodioacetate **56**
67. (1,2,2-trifluoro-1-iodoethyl) propyl ether **57**
68. (1,2,2-trifluoro-1-bromoethyl) propyl ether **58**
69. (1,1,1-trifluoroethyl) (1,2,2-trifluoro-1-iodoethyl) ether **60**
70. Trifluoroethyl bromofluoroacetate **61**
71. (1,2,2-trifluoro-1-bromoethyl) 2-chloroethyl ether **62**
72. (1,2,2-trifluoro-1-iodoethyl) 2-chloroethyl ether **63**
73. (2,2-difluoro-1-bromopropyl) methyl ether **64**
74. (1,1,2,2-tetrafluoro-1-bromoethyl) methyl ether **65**
75. (1,1,2,2-tetrafluoro-1-iodoethyl) methyl ether **66**
76. (1,1,1,2,3,3-hexafluoro-2-bromopropyl) methyl ether **67**
77. (1,1,1,2,3,3-hexafluoro-2-iodopropyl) methyl ether **68**

1. 1,2,2-trifluoro-*sec*-butyl ethyl ether **1a**

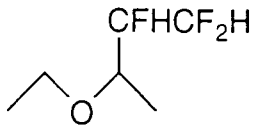


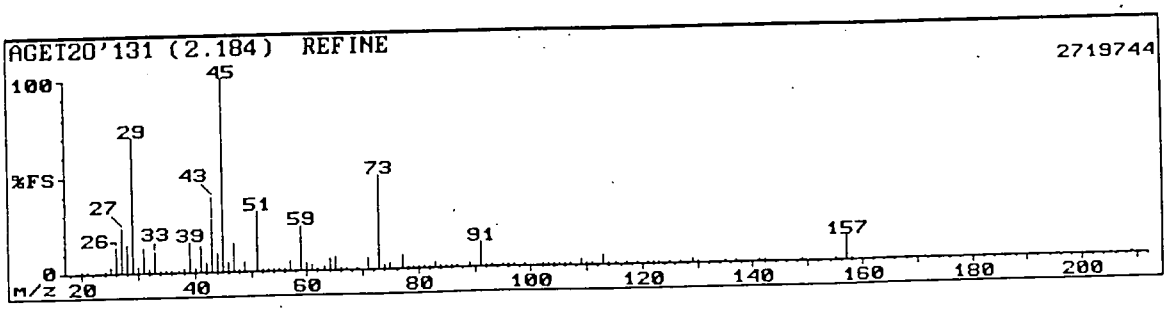


AGET20'116 (1.934) REFINE 2605056

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.93	56	0.74	96	0.12	138	0.03
21	0.09	57	6.21	97	0.27	139	0.07
24	1.10	58	1.26	98	0.03	141	2.87
25	3.03	59	25.63	99	0.11	142	0.13
26	18.08	60	2.71	101	0.50	143	0.40
27	53.46	61	11.16	103	0.73	144	0.02
28	20.13	62	0.65	104	0.08	145	0.03
29	93.08	63	3.62	105	0.13	147	0.02
30	4.05	64	11.79	106	0.10	149	0.03
31	13.99	65	17.30	107	0.43	151	0.02
32	2.22	66	0.46	109	16.82	153	0.02
33	25.63	67	0.91	110	0.72	155	4.32
34	0.38	68	0.25	111	0.24	157	50.31
35	0.07	69	3.50	113	2.21	158	3.03
36	0.12	70	0.74	114	0.11	159	0.21
37	1.02	71	9.59	115	0.52	161	0.99
38	1.81	73	100.00	116	0.06	162	0.06
39	14.62	74	4.32	117	0.20	165	0.04
40	1.62	75	3.97	118	0.02	167	0.11
41	15.88	77	22.17	119	0.10	169	0.06
42	7.00	78	3.42	121	0.89	171	0.03
43	66.67	79	1.56	122	0.10	173	0.03
44	15.57	80	0.55	123	0.70	175	0.67
46	7.08	81	0.83	124	0.04	176	0.03
47	16.19	83	23.43	125	0.04	183	0.01
48	0.57	84	0.52	127	1.41	185	0.17
49	2.42	85	0.23	129	14.15	187	0.05
50	2.37	87	0.43	130	0.58	189	0.12
51	28.14	89	6.49	131	0.05	199	0.03
52	1.22	91	24.06	133	0.11	203	0.03
53	3.22	92	1.74	135	0.37	205	0.08
54	0.35	93	1.86	136	0.09	209	0.36
55	2.40	95	3.34	137	0.71	217	0.02

2. 1,1,2-trifluoro-*sec*-butyl ethyl ether **1b**





AGET20'131 (2.184) REFINE 2719744

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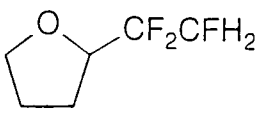
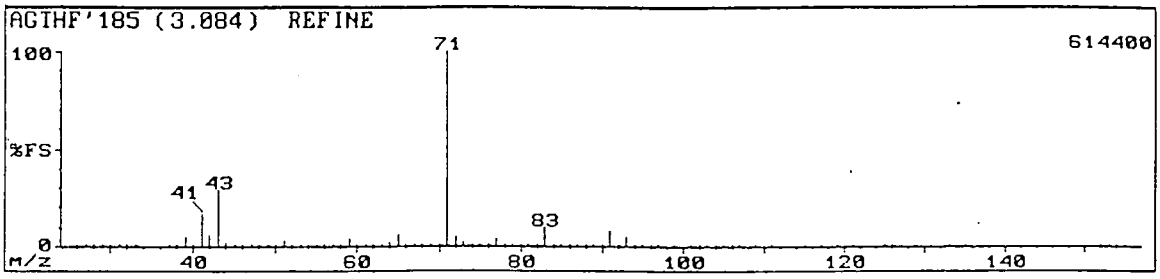
21	0.06	48	0.49	79	0.24	111	0.23
24	1.03	49	4.48	80	0.03	113	5.23
25	2.45	51	31.17	81	0.22	114	0.14
26	13.86	52	0.85	82	0.74	115	0.02
27	23.34	53	1.16	83	3.35	117	0.07
28	14.61	54	0.12	84	0.07	119	0.02
29	69.88	55	1.30	85	0.34	121	0.61
30	3.24	56	0.56	86	0.06	122	0.04
31	12.20	57	5.08	87	0.18	123	0.01
32	2.22	59	22.89	89	1.98	125	0.03
33	10.39	60	4.29	91	12.65	127	0.73
34	0.17	61	2.48	92	0.83	129	1.61
35	0.07	62	1.11	93	0.86	130	0.06
36	0.12	63	1.75	95	1.16	135	0.02
37	1.18	64	5.80	96	0.06	137	0.05
38	1.94	65	6.81	97	0.04	141	0.42
39	15.36	66	0.20	99	0.04	142	0.02
40	1.79	67	0.21	102	0.02	149	0.02
41	13.55	69	1.32	103	0.05	155	0.57
42	5.05	71	5.53	104	0.02	157	12.35
43	39.16	73	48.80	105	0.04	158	0.62
44	10.09	74	2.16	106	0.07	209	0.03
45	100.00	75	2.71	107	0.15		
46	4.52	77	6.63	109	2.82		

3. 2-(1',1',2'-trifluoro-1'-ethyl)-tetrahydrofuran **2a**

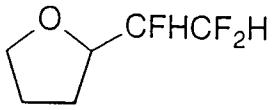


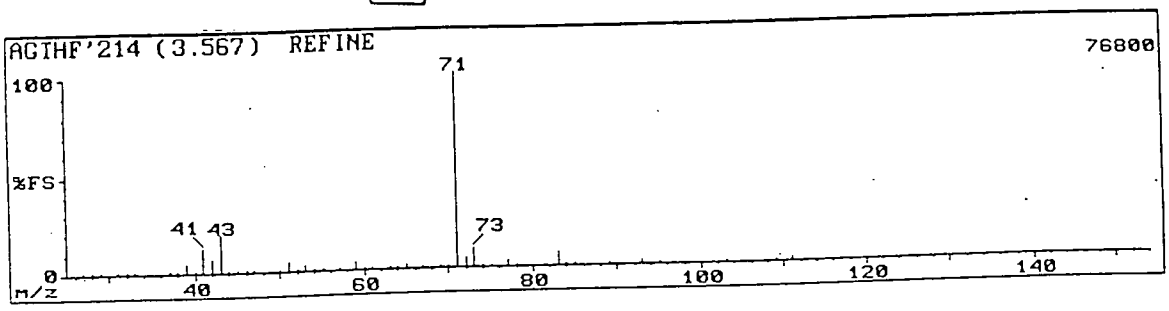


AGTHF'185 (3.084) REFINE 614400

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.10	52	0.17	75	0.69	99	0.09
27	0.90	53	0.90	76	0.18	101	0.53
28	0.21	54	0.11	77	3.88	102	0.07
29	0.95	55	1.01	78	0.49	103	0.50
30	0.10	56	0.18	79	0.21	104	0.17
31	0.25	57	0.90	80	0.08	105	0.34
32	0.06	58	0.14	81	0.22	106	0.04
33	1.40	59	4.33	82	0.51	107	0.08
37	0.15	60	0.30	83	9.38	109	0.10
38	0.52	61	0.50	84	0.41	111	0.06
39	4.96	62	0.11	85	0.75	115	0.10
40	1.26	63	0.74	86	0.08	117	0.07
41	16.17	64	2.38	87	0.52	119	0.04
42	5.63	65	5.63	88	0.17	121	0.06
43	29.17	66	0.21	89	0.56	125	0.05
44	1.49	67	0.65	90	0.79	126	0.04
45	0.85	68	0.24	91	7.46	133	0.04
46	0.36	69	1.36	92	0.50	135	0.07
47	1.23	70	0.42	93	4.50	152	0.08
48	0.04	71	100.00	94	0.19	153	0.57
49	0.12	72	5.29	95	0.76	154	0.42
50	0.30	73	1.48	96	0.14	155	0.17
51	3.29	74	0.33	97	0.10		

4. 2-(1',2',2'-trifluoro-1'-ethyl)-tetrahydrofuran **2b**

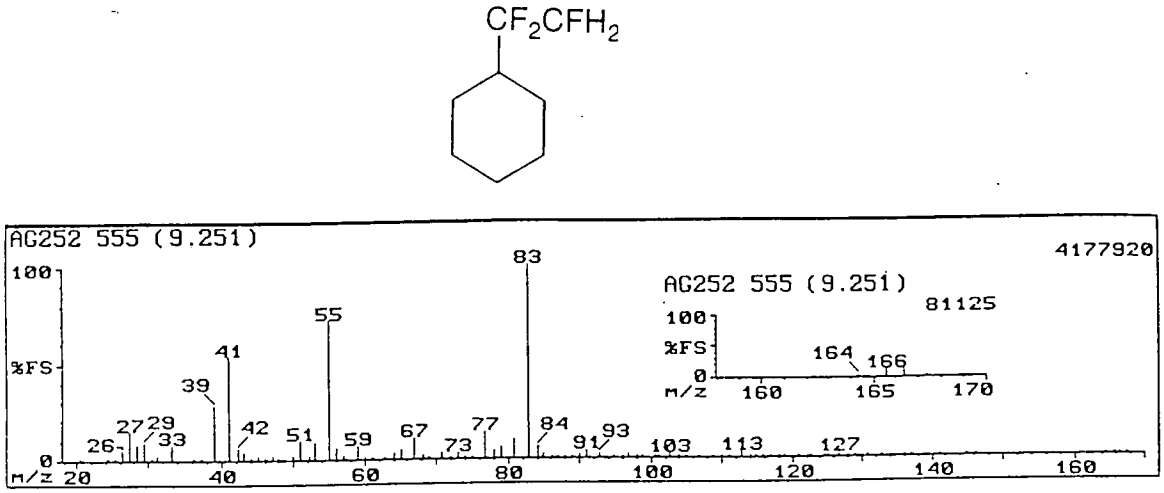




AGTHF'214 (3.567) REFINE 76800

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
27	1.38	44	1.06	61	0.83	78	0.27
28	0.36	45	0.89	63	0.49	83	6.50
29	1.35	46	0.68	64	1.38	84	0.48
31	0.39	47	1.23	65	2.06	85	1.00
32	0.10	50	0.44	67	0.30	89	1.01
33	1.03	51	5.33	69	1.18	93	1.77
37	0.24	52	0.32	70	0.53	95	0.73
38	0.55	53	2.92	71	100.00	103	0.78
39	4.44	54	0.33	72	5.17	109	0.34
40	1.38	55	1.11	73	9.75	111	2.33
41	12.42	57	1.05	74	0.59	152	0.29
42	6.58	59	3.96	75	0.82		
43	19.50	60	0.49	77	2.63		

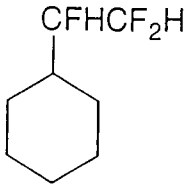
5. 1-(1',1',2'-trifluoro-1'-ethyl)-cyclohexane **3a**

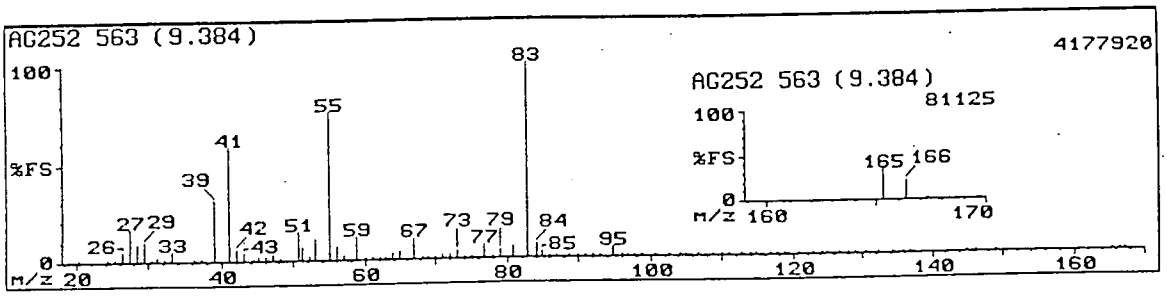


AG252 555 (9.251) 4177920

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.38	53	8.82	85	2.43	115	0.25
24	0.29	55	71.76	86	0.16	116	0.03
25	0.82	56	5.88	87	0.67	117	0.10
26	4.41	57	1.74	88	0.28	118	0.07
27	14.22	59	7.25	89	0.77	119	0.02
28	8.04	60	0.42	90	1.46	121	0.04
29	8.63	61	0.79	91	4.31	123	0.29
30	0.27	63	1.43	93	2.13	125	0.28
31	1.55	64	2.89	95	1.38	125	0.11
33	8.14	65	4.51	96	0.56	127	2.01
36	0.18	67	10.49	97	1.48	128	0.11
37	1.07	68	1.46	98	0.12	129	0.05
39	28.24	69	1.13	99	0.37	131	0.03
41	53.73	71	3.19	100	0.40	133	0.31
42	5.49	72	1.07	101	0.13	136	0.04
43	3.41	73	3.24	103	2.06	137	0.02
44	1.38	74	0.36	104	1.27	141	0.01
45	1.64	75	0.94	105	1.05	145	0.55
46	0.84	77	13.53	107	0.99	146	0.32
47	2.01	78	3.48	109	1.02	164	0.06
48	0.08	79	6.10	110	0.19	166	0.23
50	2.28	81	9.41	111	0.32	166	0.21
51	9.80	83	100.00	113	2.89	167	0.02
52	1.86	84	6.27	114	0.26		

6. 1-(1',2',2'-trifluoro-1'-ethyl)-cyclohexane **3b**

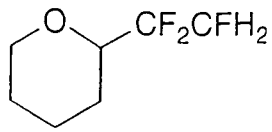


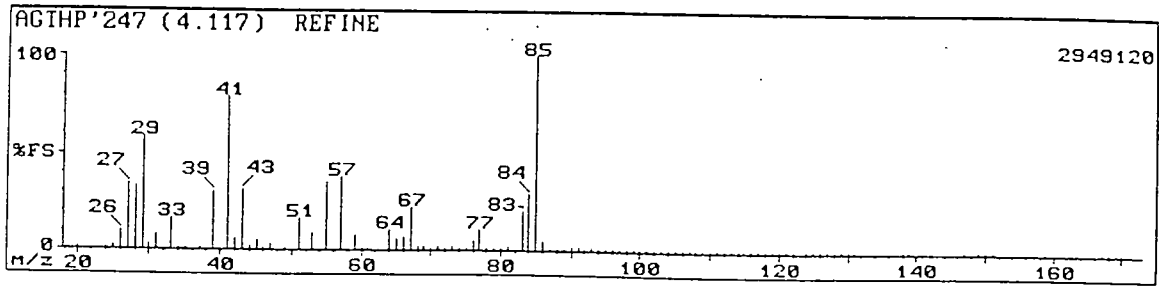


AG252 563 (9.384) 4177920

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.42	52	2.06	81	5.66	113	0.16
24	0.31	53	10.78	83	100.00	114	0.09
25	0.93	55	75.29	84	6.57	115	0.12
26	4.73	56	6.67	85	2.72	117	0.10
27	16.18	57	2.30	86	0.46	118	0.04
28	8.33	59	12.06	87	1.10	119	0.02
29	9.90	60	0.62	89	0.97	121	0.08
30	0.26	61	0.67	90	0.59	123	0.24
31	1.84	62	0.34	91	1.45	124	0.05
32	1.12	63	1.40	92	0.23	125	0.18
33	4.44	64	2.79	93	0.68	127	0.41
36	0.19	65	4.24	95	4.63	128	0.04
37	1.13	67	10.69	96	0.68	129	0.02
39	30.59	68	1.02	97	1.16	131	0.04
41	58.43	69	1.38	98	0.13	132	0.00
42	5.76	70	0.61	99	0.27	134	0.00
43	3.85	71	1.62	101	0.34	136	0.04
44	0.74	72	2.35	103	1.18	137	0.02
45	2.11	73	4.34	104	0.25	145	0.33
46	1.69	74	0.42	105	0.44	146	0.03
47	2.57	75	0.47	107	0.43	149	0.02
48	0.14	77	7.16	109	0.85	165	0.66
51	14.12	78	1.03	110	0.16	166	0.40
51	7.25	79	3.87	111	0.13	167	0.04

7. 2-(1',1',2'-trifluoro-1'-ethyl)-tetrahydropyran **4a**

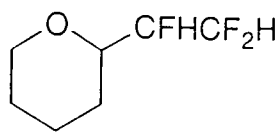


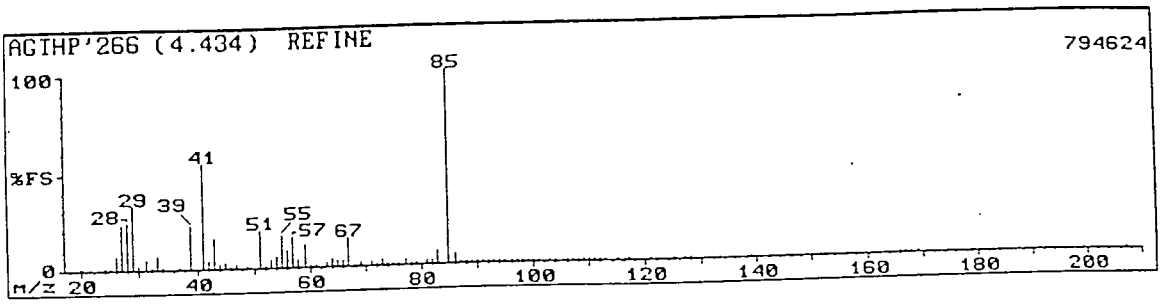


AGTHP'247 (4.117) REFINE 2949120

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.27	60	0.67	90	1.57	117	0.13
24	0.49	61	0.95	91	2.20	118	0.03
25	1.49	64	10.97	92	0.78	119	0.09
26	9.31	65	6.01	93	1.91	120	0.04
27	34.03	66	6.67	94	0.33	121	0.09
28	33.06	67	22.36	95	0.81	122	0.02
29	58.33	68	1.90	96	0.41	124	0.02
30	2.57	69	1.77	97	0.68	125	0.08
31	7.99	70	1.07	98	0.24	126	0.08
33	16.81	71	2.08	99	0.59	127	0.40
34	0.14	72	1.28	100	0.15	128	0.06
35	0.03	73	2.29	101	0.38	129	0.13
37	0.82	74	0.70	102	0.28	130	0.05
39	30.14	75	1.10	103	0.92	131	0.08
41	78.33	76	4.41	104	0.28	138	0.01
42	5.42	77	10.97	105	0.31	139	0.07
43	31.11	78	1.00	106	0.08	147	0.03
44	2.33	79	1.38	107	0.11	149	0.30
45	4.65	80	0.85	108	0.13	150	0.02
46	1.41	81	1.54	109	0.40	151	0.15
47	2.53	83	20.28	110	0.11	167	0.37
49	0.89	84	29.31	111	0.27	168	0.45
51	16.53	85	100.00	112	0.04	169	0.41
53	8.75	86	4.79	113	0.09	170	0.02
55	35.00	87	0.69	114	0.08		
57	38.33	88	0.36	115	0.09		
59	8.19	89	0.76	116	0.05		

8. 2-(1',2',2'-trifluoro-1'-ethyl)-tetrahydropyran **4b**

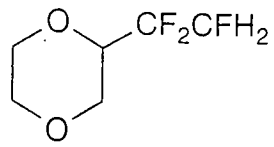


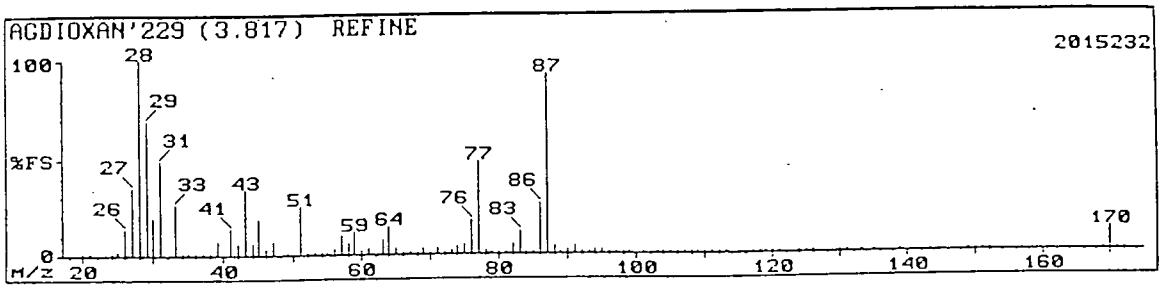


AGTHP'266 (4.434) REFINE 794624

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.17	52	1.30	78	0.39	104	0.06
24	0.21	53	4.22	79	0.56	106	0.06
25	0.97	54	5.41	81	1.58	107	0.39
26	6.80	55	16.75	82	1.48	108	0.14
27	23.07	56	8.76	83	7.22	109	0.35
28	24.48	57	15.08	85	100.00	110	0.27
29	32.60	58	3.93	86	4.41	111	1.17
30	1.82	59	11.98	87	0.65	112	0.07
31	5.25	60	0.97	88	0.19	113	0.06
32	1.10	61	0.83	89	0.43	115	0.05
33	6.80	63	2.32	90	0.89	117	0.05
34	0.06	64	4.32	91	0.90	121	0.04
37	0.75	65	2.77	92	0.23	125	0.08
39	22.04	66	3.25	93	1.04	127	0.63
41	54.12	67	14.69	94	0.14	128	0.03
42	3.70	69	1.71	95	0.66	139	0.04
43	15.21	71	1.64	96	0.21	166	0.07
44	1.55	72	1.39	97	0.32	167	0.18
45	2.90	73	2.55	98	0.13	168	0.12
46	1.06	74	0.34	99	0.54	169	0.07
47	1.47	75	0.89	100	0.06	207	0.03
49	0.33	76	0.71	101	0.21		
51	19.33	77	2.90	103	0.37		

9. 2-(1',1',2'-trifluoro-1'-ethyl)-1,4-dioxane **5a**

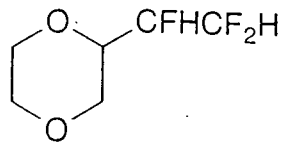


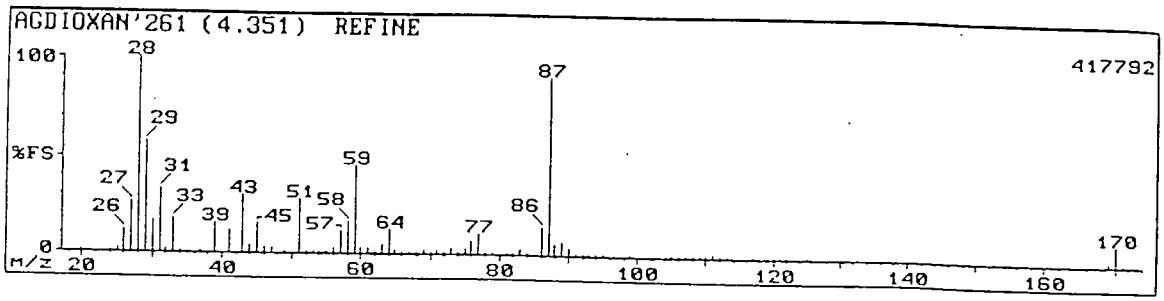


AGDIOXAN'229 (3.817) REFINE 2015232

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.31	53	0.98	81	0.73	110	0.07
21	0.02	54	0.38	82	4.47	111	0.04
24	0.57	55	0.79	83	11.43	112	0.10
25	1.61	56	3.25	84	0.33	113	0.41
26	13.41	57	9.35	85	0.52	117	0.02
27	34.76	58	6.20	86	26.22	118	0.03
28	100.00	59	11.23	87	92.68	119	0.16
29	69.11	60	1.61	88	4.17	120	0.11
30	19.11	61	2.90	89	1.22	121	0.51
31	48.37	63	7.47	90	2.03	124	0.03
33	25.81	64	15.04	91	3.71	125	0.16
34	0.27	65	2.92	92	0.89	126	0.03
35	0.07	66	0.10	93	1.14	130	0.02
36	0.08	67	0.28	94	1.59	131	0.03
37	0.59	68	1.08	95	1.89	133	0.10
38	1.13	69	2.72	96	0.10	135	0.05
39	7.27	70	1.27	97	0.04	139	0.05
41	14.02	71	2.46	98	0.03	149	0.03
42	5.74	72	1.13	99	0.08	150	0.06
43	33.94	73	2.38	101	0.04	151	0.49
44	5.44	74	3.46	103	0.05	152	0.03
45	18.50	75	4.67	104	0.07	169	1.31
46	3.24	76	17.48	105	0.28	170	11.89
47	7.11	77	47.97	106	0.44	171	0.85
49	1.36	78	1.87	107	1.13	172	0.07
51	25.41	79	0.80	108	0.21		
52	0.56	80	0.59	109	0.07		

10. 2-(1',2',2'-trifluoro-1'-ethyl)-1,4-dioxane **5b**

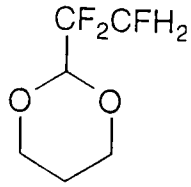


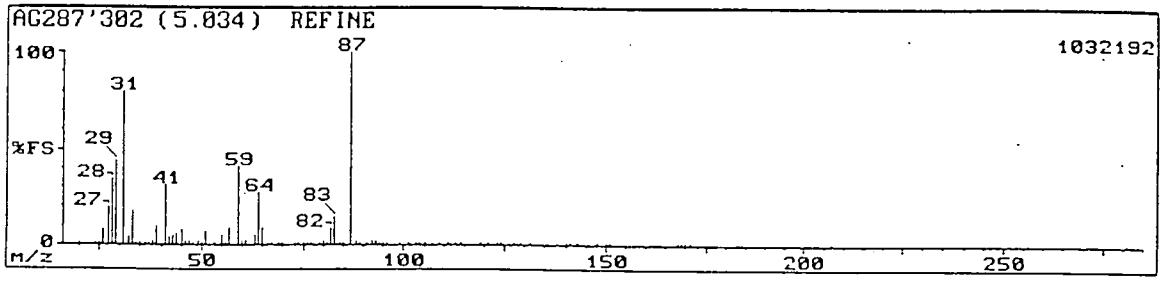


AGDIOXAN'261 (4.351) REFINE 417792

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.23	51	28.19	72	1.27	95	0.55
24	0.24	52	0.62	73	3.13	99	0.11
25	1.49	53	0.48	74	1.07	105	0.15
26	11.58	54	0.22	75	3.22	106	0.15
27	26.47	55	0.65	76	6.50	107	0.67
28	100.00	56	3.26	77	10.72	108	0.19
29	56.86	57	11.58	78	0.58	109	0.48
30	16.67	58	16.91	79	0.28	110	0.98
31	32.84	59	45.34	81	0.42	111	1.69
32	2.39	60	3.20	82	1.33	112	0.27
33	17.65	61	3.19	83	3.02	113	0.88
34	0.19	62	1.42	84	0.20	117	0.12
37	0.74	63	4.90	86	14.40	120	0.03
39	15.26	64	12.99	87	91.18	121	0.13
41	11.46	65	2.07	88	5.51	122	0.14
43	29.90	66	0.12	89	6.50	125	0.13
44	3.92	67	0.06	90	4.35	169	1.49
45	15.93	68	0.61	91	1.36	170	10.36
46	3.05	69	1.90	92	0.86	171	0.74
47	2.99	70	0.84	93	1.30		
49	1.10	71	1.50	94	0.61		

11. 2-(1',1',2'-trifluoro-1'-ethyl)-1,3-dioxane **6a**

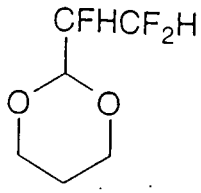


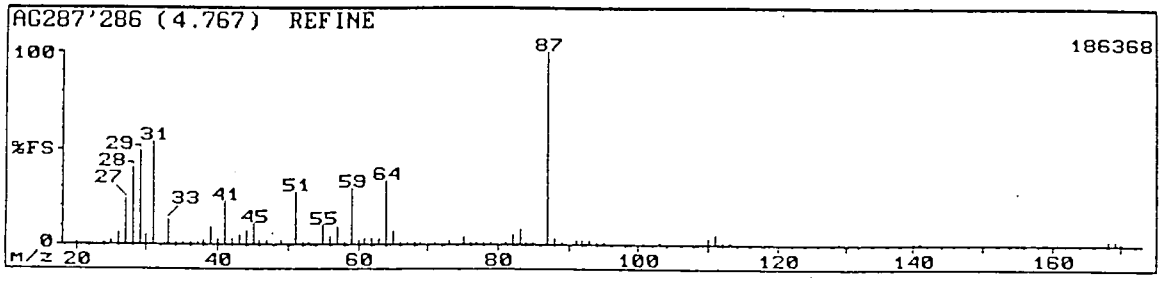


AG287'302 (5.034) REFINE 1032192

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.10	48	0.04	79	0.35	113	0.86
24	0.27	49	1.86	80	1.51	114	0.02
25	0.84	50	1.07	81	0.14	119	0.01
26	7.94	51	6.35	82	9.03	121	0.03
27	19.54	53	0.70	83	14.98	123	0.34
28	33.73	55	4.39	84	0.57	124	0.02
29	44.05	56	1.37	85	0.57	127	0.06
31	79.76	57	8.43	87	100.00	129	0.01
32	3.60	59	40.87	88	2:26	131	0.08
33	17.86	60	1.66	89	0.30	140	0.09
34	0.19	61	2.36	91	0.98	141	0.06
35	0.03	63	5.03	92	2.23	143	0.03
36	0.17	64	26.98	93	2.28	148	0.02
37	0.87	65	8.43	94	0.61	150	0.03
38	1.56	66	0.40	95	0.72	151	0.03
39	9.33	67	0.48	96	0.07	168	0.69
41	31.35	69	0.62	99	0.05	169	0.90
42	3.89	70	0.07	101	0.05	170	0.18
43	4.46	73	1.22	103	0.10	171	0.18
44	5.36	74	0.81	104	0.02	207	0.03
45	7.64	75	0.76	105	0.02	281	0.04
46	1.59	76	0.13	109	0.07		
47	1.59	77	0.61	111	0.15		

12. 2-(1',2',2'-trifluoro-1'-ethyl)-1,3-dioxane **6b**

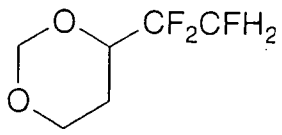


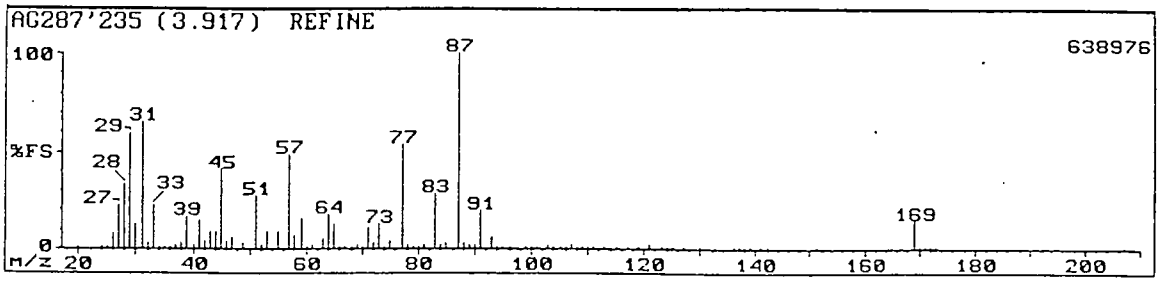


AG287'286 (4.767) REFINE 186368

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.14	43	4.98	65	6.97	89	0.47
24	0.41	44	6.90	66	0.20	91	2.40
25	1.79	45	10.99	67	0.59	92	1.93
26	6.04	46	2.04	68	0.29	93	1.49
27	23.08	47	1.80	69	0.46	94	0.30
28	40.11	49	2.23	71	0.98	95	0.37
29	48.90	51	26.92	73	2.06	103	0.42
30	4.95	52	1.13	75	3.47	110	2.78
31	53.30	53	0.88	76	0.13	111	4.84
33	12.23	55	9.48	77	1.02	112	0.87
34	0.18	56	3.54	78	0.16	113	0.88
35	0.13	57	8.93	79	0.20	129	0.15
36	0.47	58	1.39	81	0.12	140	0.27
37	1.24	59	28.98	82	5.29	141	0.32
38	2.15	60	2.15	83	7.49	168	1.47
39	9.07	61	2.54	84	0.66	169	1.85
40	2.64	62	2.51	85	0.43	170	0.18
41	21.98	63	2.78	87	100.00		
42	3.06	64	32.97	88	2.82		

13. 4-(1',1',2'-trifluoro-1'-ethyl)-1,3-dioxane **6c**

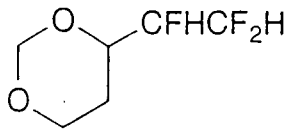


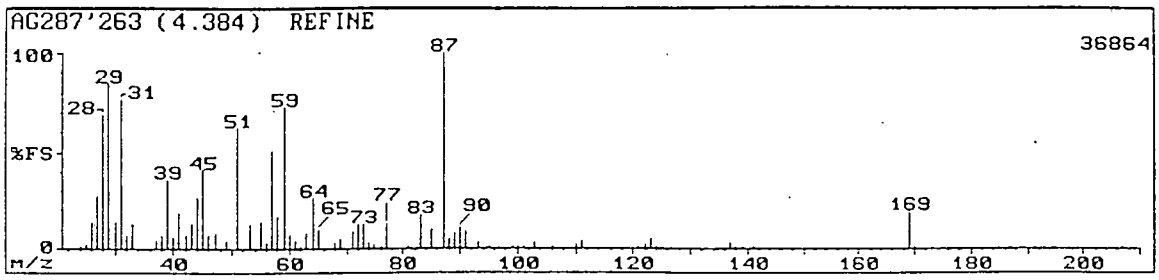


AG287'235 (3.917) REFINE 638976

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.14	49	2.56	79	0.78	110	0.12
24	0.33	51	27.40	80	0.53	111	0.10
25	0.85	52	1.62	81	1.69	113	0.49
26	8.21	53	8.65	83	28.37	115	0.06
27	22.28	55	8.73	84	1.99	117	0.12
28	33.17	57	48.08	85	2.56	119	0.13
29	59.62	58	7.21	87	100.00	121	1.73
30	12.98	59	15.87	88	2.84	123	0.60
31	65.38	60	1.07	89	1.98	124	0.09
32	3.37	61	2.01	90	2.24	125	0.03
33	22.12	63	4.97	91	19.23	127	0.71
34	0.33	64	17.79	93	6.01	130	0.04
35	0.09	65	12.66	94	0.58	136	0.16
36	0.29	66	0.34	95	0.67	137	0.47
37	1.52	67	0.58	96	0.09	138	0.33
38	2.96	68	0.76	99	0.41	139	0.25
39	16.03	69	1.98	100	0.14	141	0.22
40	2.35	70	1.31	101	1.21	142	0.04
41	14.58	71	10.26	103	2.15	151	0.06
42	3.49	72	2.96	104	0.49	169	14.26
43	9.01	73	12.98	105	0.36	170	0.73
44	9.01	74	0.84	106	0.40	171	0.32
45	40.38	75	3.57	107	1.46	172	0.02
46	3.97	77	53.85	108	0.24	173	0.03
47	5.89	78	1.72	109	0.29	207	0.06

14. 4-(1',2',2'-trifluoro-1'-ethyl)-1,3-dioxane **6d**

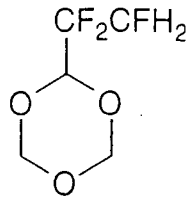


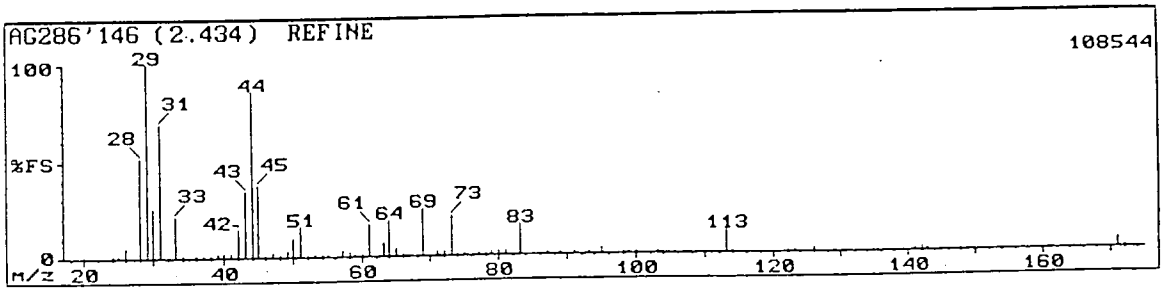


AG287'263 (4.384) REFINE 36864

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
24	0.52	45	40.63	69	4.73	99	1.13
25	2.03	46	7.25	71	9.03	100	0.55
26	13.72	47	7.86	72	12.50	101	0.53
27	27.60	49	4.17	73	12.85	103	2.70
28	68.75	51	62.50	74	2.59	106	0.27
29	84.72	53	12.33	75	1.69	110	2.16
30	14.06	55	13.72	76	0.31	111	3.43
31	76.39	56	2.86	77	12.15	121	0.67
32	6.68	57	50.69	81	1.19	122	1.64
33	12.85	58	16.32	83	17.71	123	4.69
37	3.86	59	72.92	85	9.42	124	0.51
38	6.55	60	7.07	87	100.00	137	2.86
39	35.76	61	3.69	88	4.47	138	1.03
40	5.99	62	1.24	89	7.29	139	0.77
41	18.23	63	7.38	90	10.63	141	0.66
42	7.03	64	25.87	91	8.42	169	19.79
43	13.02	65	9.59	93	2.44	170	0.84
44	26.39	68	2.53	95	0.87	207	0.27

15. 2-(1',1',2'-trifluoro-1'-ethyl)-1,3,5-trioxane **7a**

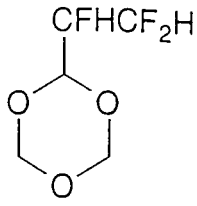


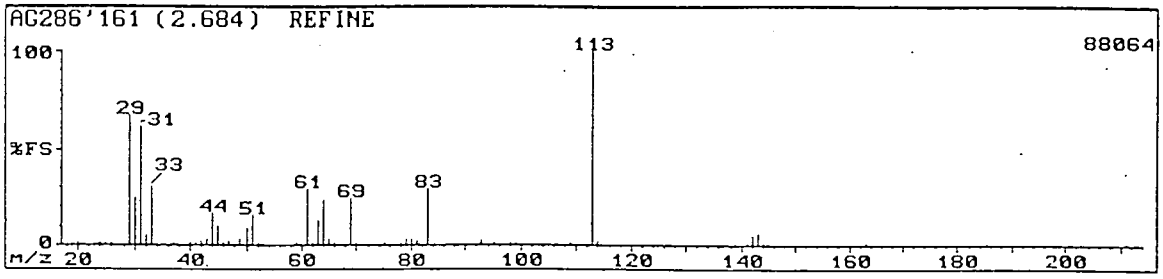


AG286'146 (2.434) REFINE 108544

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.18	44	85.85	64	18.63	93	0.52
24	0.53	45	36.79	65	3.60	95	2.98
25	1.40	46	1.44	66	0.34	98	0.41
26	4.66	47	2.05	69	24.53	99	0.31
28	51.42	48	0.29	71	2.06	100	0.15
29	100.00	49	2.99	72	2.05	103	0.34
30	25.24	50	9.91	73	20.75	113	12.03
31	68.87	51	15.33	74	0.31	114	0.69
33	21.70	52	0.55	75	0.51	122	0.46
34	0.39	53	0.24	77	1.03	123	0.86
36	0.38	54	0.20	78	1.19	126	1.93
37	0.48	55	0.41	79	1.77	141	0.41
38	0.68	57	3.32	80	2.42	142	1.52
39	1.70	58	1.92	81	1.55	143	1.02
40	2.17	59	1.42	83	15.57	171	4.60
41	2.27	60	1.44	87	0.42	172	0.29
42	14.98	61	16.51	89	0.31		
43	33.73	63	6.90	91	0.16		

16. 2-(1',2',2'-trifluoro-1'-ethyl)-1,3,5-trioxane **7b**

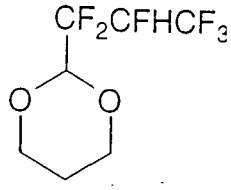


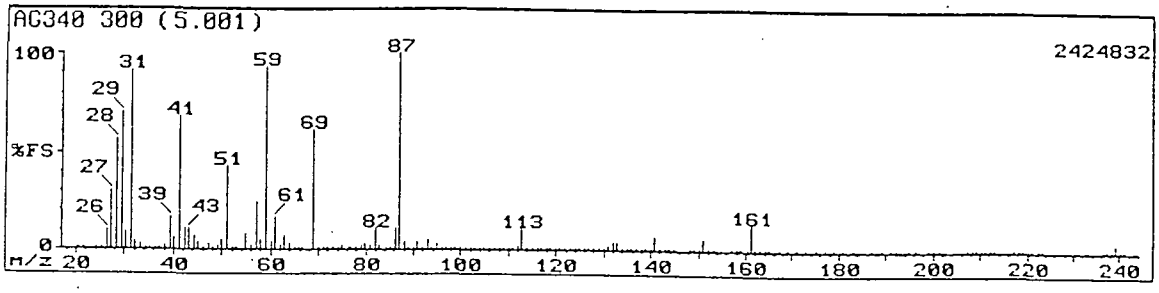


AG286'161 (2.684) REFINE 88064

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.17	43	2.93	64	22.97	98	0.28
24	0.39	44	16.35	65	2.63	99	0.41
25	1.04	45	10.03	66	0.40	109	0.55
26	1.16	46	0.79	69	23.84	113	100.00
29	67.15	47	2.23	70	0.24	114	2.09
30	24.13	49	2.87	75	0.18	141	1.25
31	61.34	50	8.87	78	1.22	142	5.09
32	4.72	51	15.77	79	2.96	143	5.81
33	29.94	52	0.45	80	3.18	144	0.27
37	0.29	59	1.11	81	2.00	163	0.35
40	1.36	61	29.36	83	29.07	211	0.60
41	0.64	62	0.72	93	1.85		
42	2.00	63	12.72	95	0.24		

17. 2-(1',1',2',3',3',3'-hexafluoro-1'-propyl)-1,3-dioxane **8a**

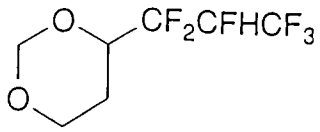


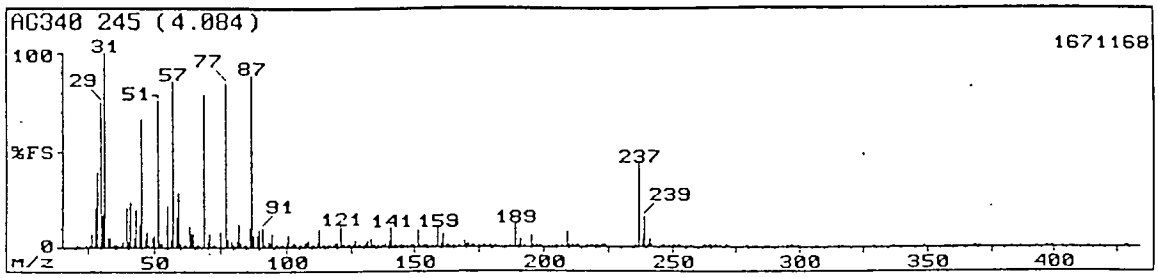


AG340 300 (5.001) 2424832

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.32	67	0.33	112	1.97	161	13.85
21	0.01	69	60.81	113	10.81	162	0.50
24	0.38	70	0.65	114	0.40	163	0.70
25	1.06	71	1.30	115	0.19	164	0.04
26	9.59	72	0.26	116	0.01	165	0.03
27	30.07	73	0.88	117	0.04	167	0.03
28	56.08	74	0.90	118	0.07	169	0.03
29	70.27	75	2.07	119	0.15	171	0.37
30	8.49	76	0.15	120	0.04	173	0.10
31	91.22	77	1.09	121	0.22	175	0.03
32	3.63	78	0.97	122	0.11	177	0.03
33	3.29	79	1.97	123	0.32	179	0.14
34	0.09	80	2.43	124	0.15	181	0.83
35	0.13	81	2.42	125	0.98	183	0.24
36	0.18	82	10.98	126	0.08	187	0.05
37	0.84	83	1.55	127	0.13	189	0.04
38	1.59	84	0.06	128	0.09	191	1.03
39	16.72	85	0.27	129	0.51	192	0.03
40	6.00	86	10.43	130	0.27	195	0.60
41	68.24	87	100.00	131	2.29	196	0.02
42	10.22	88	4.31	132	4.05	199	0.31
43	10.81	89	0.69	133	3.55	200	0.02
44	6.80	90	0.59	134	0.10	201	0.06
45	4.05	91	3.67	135	0.04	207	0.03
46	0.62	92	1.16	136	0.26	208	0.03
47	3.21	93	5.19	137	0.07	209	0.15
48	0.24	94	1.02	138	0.02	210	0.14
49	1.86	95	2.51	139	0.15	211	0.34
50	4.43	96	0.14	140	0.79	212	0.02
51	42.57	97	0.14	141	6.55	213	0.03
52	0.61	98	0.16	142	0.21	217	0.03
53	1.13	99	1.07	143	0.36	218	0.06
55	7.60	100	1.01	144	0.04	219	0.39
56	1.94	101	1.33	145	0.07	220	0.03
57	24.66	102	0.04	148	0.05	221	0.09
58	5.07	103	0.22	149	0.55	222	0.02
59	93.24	104	0.05	150	0.98	223	0.05
60	3.84	105	0.08	151	5.53	236	0.17
61	16.39	106	0.04	152	0.14	237	1.38
62	1.86	107	0.09	153	0.07	238	0.41
63	7.26	108	0.09	157	0.03	239	3.55
64	2.83	109	0.34	158	0.07	240	0.22

18. 4-(1',1',2',3',3',3'-hexafluoro-1'-propyl)-1,3-dioxane **8b**

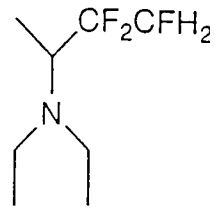


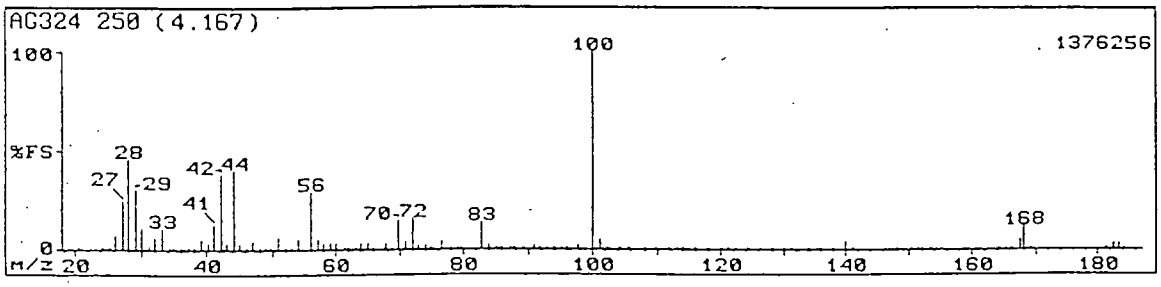


AG340 245 (4.084) 1671168

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.23	81	2.97	135	0.05	212	0.04
24	0.34	82	11.34	136	0.05	213	0.27
25	0.83	83	2.30	137	0.31	217	0.27
26	6.37	84	0.33	138	0.43	218	0.05
27	20.34	85	1.26	139	2.42	219	0.19
28	38.73	86	9.56	140	2.51	220	0.13
29	74.51	87	88.24	141	9.50	221	0.92
30	16.91	88	5.58	142	0.56	222	0.11
31	100.00	89	5.70	143	0.18	223	0.44
32	4.47	90	8.58	144	0.18	224	0.03
33	4.84	91	9.93	145	1.44	235	0.02
34	0.13	92	0.95	146	0.07	237	43.14
35	0.17	93	3.09	147	0.03	238	4.29
36	0.22	94	1.55	148	0.15	239	15.93
37	1.16	95	6.68	149	1.36	240	1.46
38	2.53	96	0.34	150	1.36	241	4.04
39	20.59	97	0.30	151	8.33	242	0.28
40	3.00	98	0.16	152	0.31	246	0.03
41	23.77	99	0.94	153	0.16	247	0.09
42	4.90	100	1.50	154	0.04	249	0.03
43	19.36	101	5.70	155	0.18	250	0.09
44	11.58	102	0.76	157	0.53	251	0.21
45	65.69	103	1.53	158	1.42	252	0.02
46	3.86	104	0.43	159	9.56	253	0.04
47	8.15	105	0.27	160	2.31	257	0.03
48	0.54	106	0.85	161	7.05	262	0.02
49	4.41	107	1.75	162	0.30	263	0.20
50	5.94	108	2.16	163	0.17	264	0.03
51	75.49	109	2.83	165	0.03	265	0.11
52	1.69	110	0.26	167	0.33	266	0.03
53	2.31	111	0.47	169	3.19	267	0.16
55	21.32	112	1.69	170	0.35	268	0.03
56	4.17	113	8.76	171	2.21	270	0.02
57	85.29	114	0.48	172	0.28	271	0.14
58	15.69	115	0.59	173	0.22	279	0.03
59	27.94	116	0.08	175	0.10	295	0.04
60	2.11	117	0.33	176	0.06	296	0.02
61	0.97	118	0.24	177	0.06	297	0.11
62	1.35	119	1.49	179	0.19	299	0.17
63	10.91	120	1.70	181			

19. 1,2,2-trifluoro-3-(diethylamino)butane **9a**

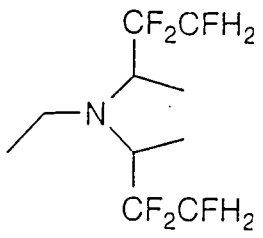


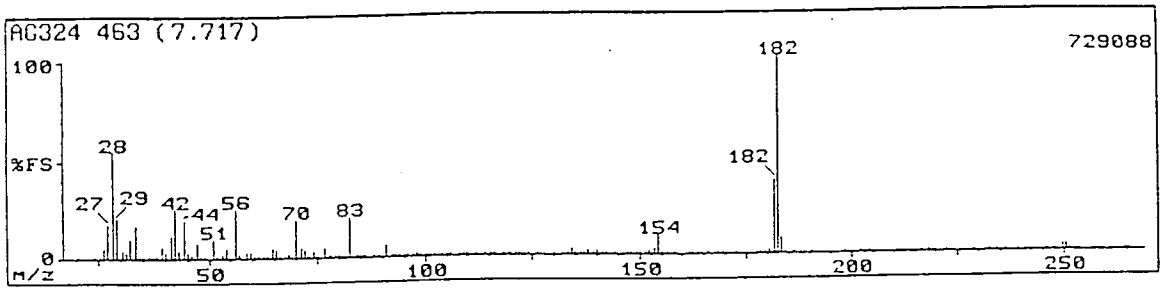


AG324 250 (4.167) 1376256

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
21	0.10	51	5.65	85	1.02	126	0.14
24	0.28	52	1.00	86	1.40	128	0.04
25	0.96	53	1.41	87	0.15	130	0.07
26	6.47	54	4.58	88	0.60	131	0.03
27	23.81	56	28.87	89	0.09	134	0.47
28	45.54	57	5.06	91	1.99	135	0.19
29	29.76	58	3.07	92	1.01	136	0.43
30	10.42	59	2.83	93	0.15	138	0.30
31	2.05	60	3.14	94	0.18	140	3.74
32	5.73	61	0.18	95	0.09	141	0.25
33	10.79	62	0.89	96	0.09	148	0.12
34	0.16	63	0.98	98	1.69	150	0.10
35	0.12	64	2.64	100	100.00	151	0.20
36	0.40	65	2.55	101	4.99	152	0.56
37	0.45	66	0.64	102	0.26	154	0.31
38	0.86	68	2.51	104	0.20	154	0.66
39	4.99	70	14.36	106	0.65	155	0.05
40	3.16	71	4.33	108	0.21	164	0.86
41	12.50	72	16.00	110	0.31	165	0.16
42	38.10	73	1.90	112	0.82	166	0.22
43	2.53	74	2.05	113	0.04	168	4.56
44	39.88	75	0.56	114	0.07	168	11.46
45	2.98	77	3.50	116	0.11	169	0.79
46	1.04	78	0.72	118	0.07	181	0.94
47	3.66	79	0.10	120	1.36	182	2.81
48	0.89	80	0.42	121	0.09	183	3.11
49	0.19	83	13.62	122	0.08	184	0.69
50	0.54	84	2.10	124	0.10		

20. di(1,2,2-trifluorobut-3-yl) ethylamine **10a**

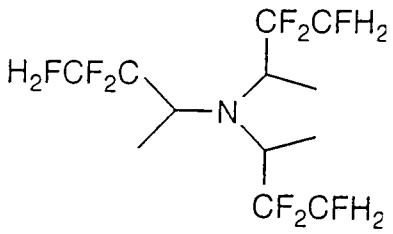


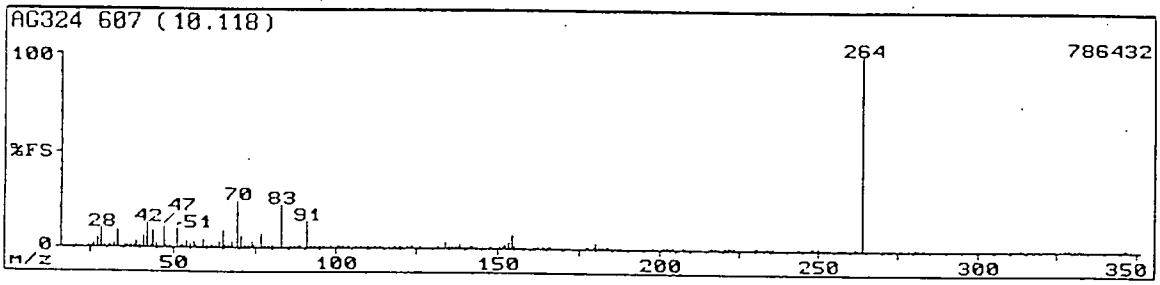


AG324 463 (7.717) 729088

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
21	0.16	63	1.38	109	0.28	162	0.44
24	0.26	64	4.78	110	0.52	163	0.05
25	0.84	65	3.48	112	0.62	164	0.05
26	4.78	66	0.68	114	0.30	166	0.49
27	16.99	67	1.34	115	0.08	166	1.29
28	53.93	68	1.99	116	0.05	167	0.30
29	20.37	70	19.66	118	0.30	168	0.43
30	3.62	71	4.78	119	0.23	169	0.04
31	2.95	72	3.76	120	0.56	172	0.05
32	10.11	73	1.40	121	0.07	178	0.07
33	16.57	74	3.23	122	0.10	180	0.48
34	0.24	75	0.51	124	0.29	180	1.74
35	0.20	77	4.92	126	0.31	182	38.20
36	0.44	78	0.66	130	0.12	182	100.00
37	0.33	79	0.30	132	0.09	183	7.72
38	1.34	80	0.31	133	0.69	184	0.38
39	5.90	83	20.37	134	2.67	186	0.05
40	2.84	84	1.01	135	0.22	190	0.03
41	11.38	85	0.25	136	0.23	198	0.19
42	25.28	86	0.78	137	0.48	202	0.21
43	3.48	88	1.15	138	1.65	204	0.16
44	19.24	89	0.30	139	0.65	216	0.14
45	3.09	91	5.76	140	1.78	218	0.54
46	1.55	92	0.84	141	0.18	220	0.06
47	8.08	93	0.14	142	0.27	222	0.91
48	0.92	94	0.36	144	0.08	232	0.19
49	0.21	95	0.24	147	0.13	232	0.16
51	9.97	96	0.16	148	0.43	234	0.12
52	1.02	97	0.84	149	0.07	236	0.13
53	1.85	98	2.25	150	0.09	246	1.22
54	4.74	99	0.83	151	0.86	247	0.06
56	25.56	100	0.57	152	2.35	250	2.88
57	2.35	101	0.20	153	3.16	250	2.53
59	2.70	102	0.15	154	9.69	251	0.22
59	3.13	104	0.34	155	0.63	264	0.56
60	1.30	105	0.31	156	0.10	265	0.35
61	0.29	106	0.62	158	0.05		
62	0.51	108	0.41	162	0.14		

21. tri(1,2,2-trifluorobut-3-yl) amine **11a**



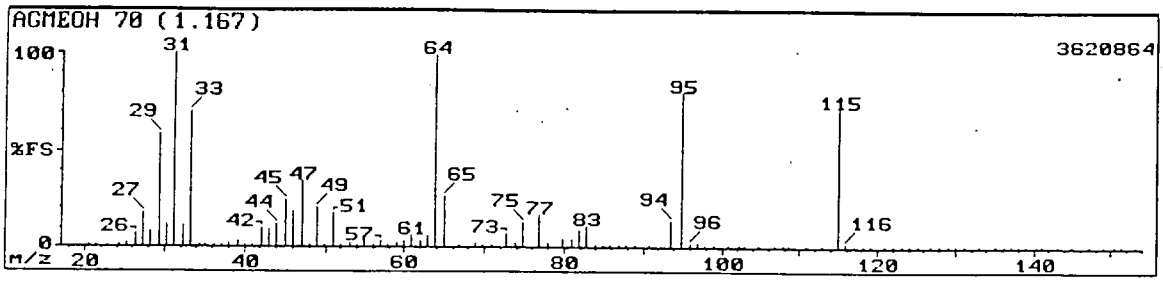


AG324 607 (10.118) 786432

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
21	0.14	61	0.55	108	0.55	182	0.28
24	0.11	62	0.42	110	0.27	183	0.07
25	0.31	63	1.20	112	0.46	184	0.11
26	1.51	64	3.16	114	0.32	198	0.14
27	4.39	65	8.59	118	0.39	202	0.16
28	10.16	66	0.63	120	0.27	202	0.20
29	1.25	67	0.49	122	0.03	204	0.15
30	0.55	68	2.60	123	0.12	207	0.07
31	1.41	70	24.35	124	0.21	216	0.36
32	2.08	71	5.66	126	0.30	216	0.32
33	8.72	72	0.94	132	0.18	218	0.62
35	0.08	73	1.14	134	2.67	220	0.27
36	0.27	74	2.86	135	0.18	222	0.58
37	0.29	75	0.77	136	0.05	222	0.69
38	0.64	77	6.45	137	0.94	223	0.05
39	3.06	78	1.09	138	1.49	230	0.10
40	1.06	79	0.53	141	0.08	230	0.10
41	5.96	80	0.20	142	0.12	234	0.12
42	12.37	83	22.40	148	0.07	236	0.45
43	1.44	86	1.31	150	0.06	244	0.30
44	8.72	87	0.17	152	1.28	248	0.19
45	1.98	88	1.44	152	2.38	248	0.16
47	10.55	89	0.51	154	3.16	250	0.06
48	0.72	91	13.28	154	6.80	262	0.29
49	0.12	92	0.81	155	0.47	264	100.00
51	9.51	93	0.13	162	0.21	281	0.05
52	0.70	95	0.33	164	0.06	314	0.30
53	1.26	96	0.40	166	0.11	328	0.76
54	3.09	98	0.42	166	0.23	328	0.61
55	1.57	100	0.50	178	0.04	332	1.00
56	2.99	101	0.27	178	0.07	346	0.16
57	1.29	102	0.20	180	1.12	347	0.29
59	4.13	104	0.80	180	2.44		
60	0.85	106	1.17	182	0.34		

22. 2,2,3-trifluoro-1-propanol **12a**

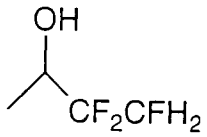
$HOCH_2CF_2CFH_2$

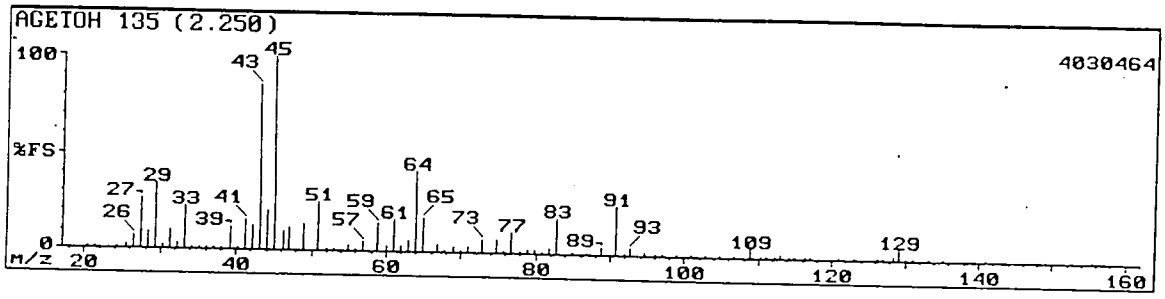


AGMEOH 70 (1.167) 3620864

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.98	50	1.45	83	10.41	121	0.08
21	0.19	51	17.19	84	0.53	122	0.02
24	0.64	52	0.38	85	0.12	123	0.04
25	1.63	53	1.53	86	0.03	124	0.01
26	6.62	54	0.40	87	0.07	125	0.02
27	17.76	55	2.60	88	0.08	127	0.89
28	8.14	56	0.67	89	0.17	128	0.07
29	57.92	57	3.25	91	1.28	129	0.03
30	11.43	58	0.52	94	13.35	130	0.01
31	100.00	59	1.92	95	79.64	131	0.02
32	10.41	60	3.11	96	2.26	133	0.08
33	69.68	61	6.08	97	1.50	135	0.07
34	0.81	62	2.77	98	0.03	136	0.02
35	0.28	63	5.35	99	0.14	137	0.03
36	0.32	64	99.10	101	0.11	138	0.02
37	1.42	65	26.24	102	0.01	139	0.04
38	1.80	67	0.84	103	0.07	140	0.01
39	3.34	69	1.46	105	0.08	141	0.06
40	0.40	70	0.05	107	0.15	143	0.07
41	0.98	71	0.59	108	0.06	145	0.22
42	10.18	73	6.99	109	0.05	147	0.04
43	8.71	74	1.66	111	0.13	149	0.59
44	11.76	75	12.22	113	0.81	150	0.04
45	24.66	77	16.18	115	71.49	151	0.02
46	18.89	78	1.49	116	2.32	153	0.01
47	33.94	80	4.04	117	0.23		
48	0.93	81	3.62	118	0.04		
49	20.70	82	9.16	119	0.02		

23. 3,3,4-trifluoro-2-butanol **13a**



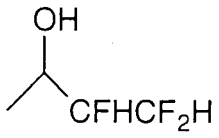


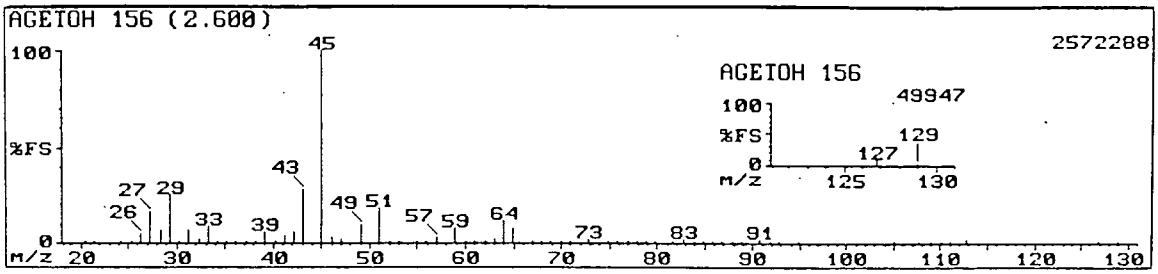
AGETOH 135 (2.250)

4030464

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.32	45	100.00	75	6.61	109	5.21
21	0.08	46	9.35	76	1.05	110	0.20
24	0.71	47	11.59	77	10.67	111	0.26
25	1.63	49	13.62	78	1.19	112	0.55
26	7.11	51	25.10	79	1.57	113	1.46
27	25.91	52	0.77	80	1.75	114	0.07
28	8.64	53	0.98	81	1.29	115	0.02
29	33.74	55	3.20	82	2.74	116	0.00
30	1.80	56	0.73	83	18.90	117	0.01
31	9.35	57	4.83	85	0.16	121	0.02
32	3.10	59	14.74	87	0.36	123	0.02
33	22.66	60	2.74	89	3.96	126	0.30
34	0.36	61	16.16	91	25.30	127	0.81
35	0.11	62	2.64	92	1.16	128	2.06
36	0.16	63	5.44	93	3.40	129	5.79
37	0.89	64	41.87	95	1.58	130	0.27
38	1.45	65	17.17	96	0.06	131	0.03
39	11.69	67	4.19	97	0.05	133	0.01
40	1.40	68	0.26	99	0.05	135	0.01
41	15.65	69	2.57	101	0.03	141	0.03
42	12.91	70	0.43	103	0.04	155	0.01
43	84.96	71	3.28	105	0.05		
44	20.02	73	6.71	107	0.40		

24. 3,4,4-trifluoro-2-butanol **13b**

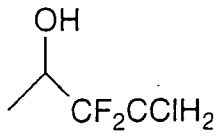


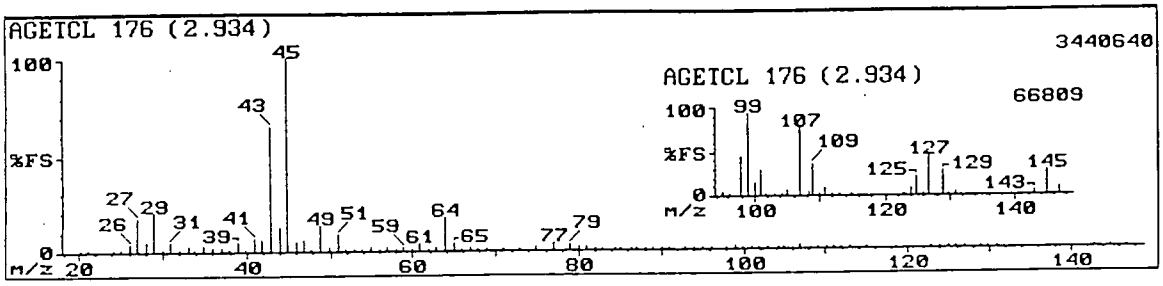


AGETOH 156 (2.600) 2572288

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.13	40	0.74	63	2.22	85	0.09
21	0.04	41	4.30	64	11.78	86	0.01
24	0.33	42	5.61	65	7.40	87	0.05
25	0.99	43	27.71	67	0.41	88	0.12
26	4.46	45	100.00	68	0.14	89	0.35
27	16.56	46	3.26	69	0.43	91	2.28
28	7.21	47	2.36	70	0.18	92	0.30
29	25.32	49	10.19	71	0.75	93	0.78
30	1.03	51	18.15	73	2.11	95	0.26
31	6.41	52	0.28	75	1.04	105	0.01
32	2.21	53	0.36	76	0.42	108	0.28
33	8.92	55	1.09	77	0.89	109	0.09
34	0.16	56	0.30	78	0.08	110	0.04
35	0.06	57	2.55	79	0.10	111	0.07
36	0.13	59	7.76	80	0.06	113	1.58
37	0.60	60	1.22	82	0.81	127	0.15
38	1.06	61	1.15	83	2.27	129	0.06
39	6.01	62	1.38	84	0.07		

25. 4-chloro-3,3-difluoro-2-butanol **13c**

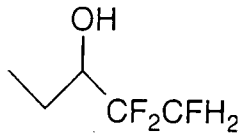


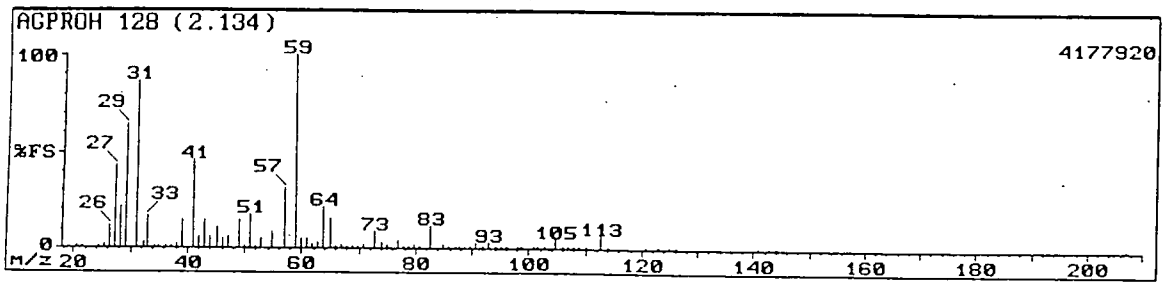


AGETCL 176 (2.934) 3440640

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.13	46	4.88	71	0.92	101	0.58
21	0.03	47	5.39	73	1.41	102	0.01
24	0.48	48	0.78	75	1.63	103	0.01
25	1.06	49	13.57	77	3.63	104	0.01
26	4.23	50	1.76	79	3.33	105	0.12
27	17.14	51	9.05	80	1.76	107	1.50
28	4.43	52	0.38	81	1.75	108	0.08
29	20.60	53	1.35	82	0.41	109	0.72
30	1.09	54	0.19	83	0.38	110	0.05
31	5.18	55	1.54	84	0.02	111	0.17
32	0.84	56	0.25	85	0.12	112	0.01
33	3.04	57	1.48	86	0.02	113	0.03
34	0.02	58	0.23	87	0.15	115	0.00
35	3.15	59	2.26	88	0.10	123	0.03
36	1.70	60	0.83	89	0.43	124	0.16
37	1.62	61	4.23	90	0.11	125	0.40
38	1.24	62	0.46	91	0.64	126	0.04
39	5.06	63	2.05	93	0.36	127	0.85
40	0.88	64	17.62	94	0.12	129	0.53
41	6.82	65	3.72	95	0.06	130	0.01
42	6.22	66	0.07	96	0.02	131	0.09
43	65.24	67	1.99	98	0.87	143	0.10
44	12.86	68	0.07	99	1.83	145	0.53
45	100.00	69	0.75	100	0.30	147	0.16

26. 4,4,5-trifluoro-2-propanol **14a**

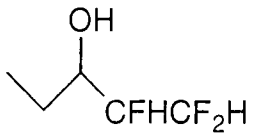


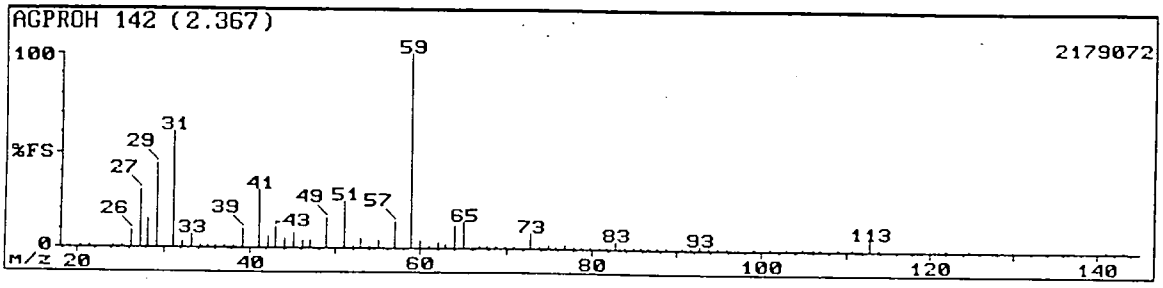


AGPROH 128 (2.134) 4177920

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.10	46	4.71	73	8.53	99	0.05
21	0.03	47	6.03	74	2.70	101	0.14
24	0.55	49	14.12	75	2.38	102	0.02
25	1.64	50	1.11	77	3.77	103	0.64
26	11.57	51	17.94	78	0.30	105	5.05
27	42.35	52	0.50	79	0.30	106	0.19
28	20.88	53	5.10	80	1.99	107	0.04
29	64.31	55	8.73	81	1.32	108	0.02
31	86.27	57	31.37	83	11.57	109	0.04
32	3.31	59	100.00	85	1.76	110	0.06
33	16.67	60	5.12	86	0.14	113	6.47
34	0.22	61	4.53	87	0.10	114	0.13
35	0.26	62	2.28	88	0.14	121	0.03
36	0.48	63	3.31	89	0.53	123	0.07
37	1.01	64	21.76	90	0.10	125	0.51
38	1.62	65	15.88	91	3.21	126	0.03
39	14.41	66	0.32	92	0.34	141	0.20
41	45.49	67	2.21	93	3.28	143	0.36
42	6.25	68	0.21	94	0.58	144	0.01
43	14.90	69	0.97	95	0.25	207	0.01
44	6.10	70	0.24	96	0.04		
45	10.20	71	1.84	98	0.01		

27. 4,5,5-trifluoro-2-propanol **14b**

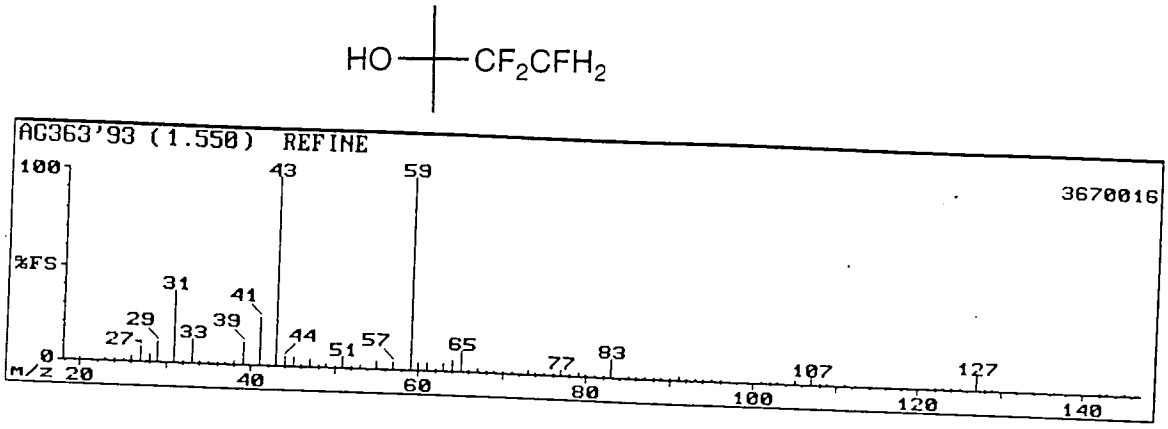




AGPROH 142 (2.367) 2179072

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.82	44	4.46	69	0.56	91	0.52
21	0.03	45	7.66	70	0.23	92	0.42
24	0.39	46	3.48	71	0.75	93	2.13
25	1.22	47	3.48	73	7.85	94	0.12
26	8.60	49	15.60	74	1.09	95	0.27
27	30.08	51	24.62	75	1.63	96	0.04
28	14.85	52	0.71	76	0.11	99	0.02
29	43.23	53	4.70	77	1.75	101	0.04
31	60.15	54	0.43	78	0.09	103	0.15
32	2.78	55	4.28	79	0.20	105	1.05
33	7.24	57	13.53	80	0.09	106	0.06
34	0.18	59	100.00	81	0.24	107	0.01
35	0.22	60	3.67	82	0.54	109	0.02
36	0.43	61	1.28	83	3.48	111	0.16
37	0.68	62	3.01	84	0.08	113	5.45
38	1.36	63	2.23	85	0.68	114	0.14
39	9.40	64	11.42	86	0.04	122	0.03
41	29.89	65	13.53	87	0.04	125	0.31
42	5.87	67	0.51	88	0.06	141	0.13
43	10.29	68	0.12	89	0.28	143	0.02

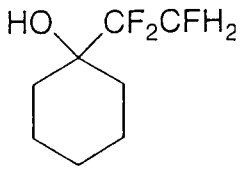
28. 3,3,4-trifluoro-2-methyl-2-butanol **15a**

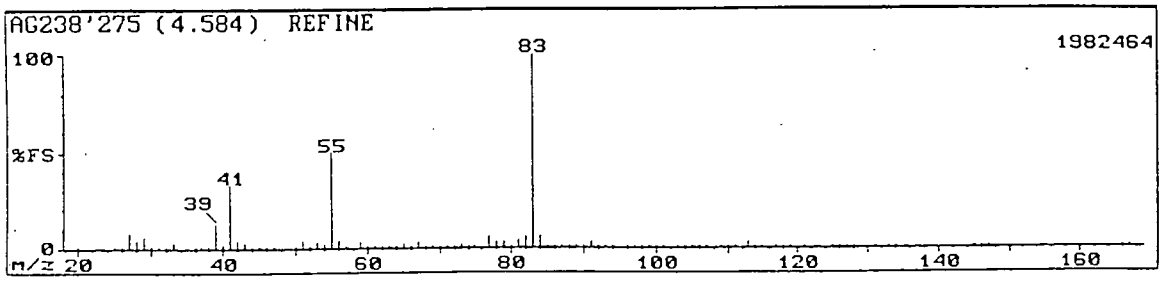


AG363'93 (1.550) REFINE 3670016

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.40	47	4.07	73	1.95	96	0.02
23	0.01	48	0.14	74	0.37	101	0.05
24	0.17	49	1.95	75	1.23	102	0.01
25	0.61	50	1.12	76	0.31	103	0.09
26	2.73	51	6.19	77	2.62	105	1.49
27	7.37	52	0.24	78	0.20	107	3.77
28	3.77	53	1.93	79	1.81	108	0.32
29	10.49	55	3.99	80	0.10	109	0.28
31	37.95	57	4.19	81	0.25	111	0.06
32	1.30	59	100.00	82	0.87	122	0.06
33	12.83	60	3.52	83	9.60	123	0.15
34	0.13	61	4.35	85	0.35	124	0.13
35	0.04	62	0.35	86	0.11	125	0.16
36	0.09	63	3.82	87	0.32	127	7.48
37	0.75	64	5.72	88	0.20	128	0.22
38	1.56	65	10.60	89	0.71	129	0.02
39	11.94	66	0.25	90	1.16	142	0.02
41	25.22	67	1.90	91	1.63	143	0.02
43	98.21	68	0.20	92	0.28	145	0.01
44	5.30	69	0.55	93	0.71		
45	4.52	70	0.24	94	0.77		
46	1.22	71	0.91	95	0.04		

29. 1-(1',1',2'-trifluoro-1'-ethyl)-cyclohexanol **26a**

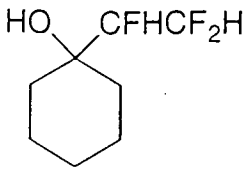


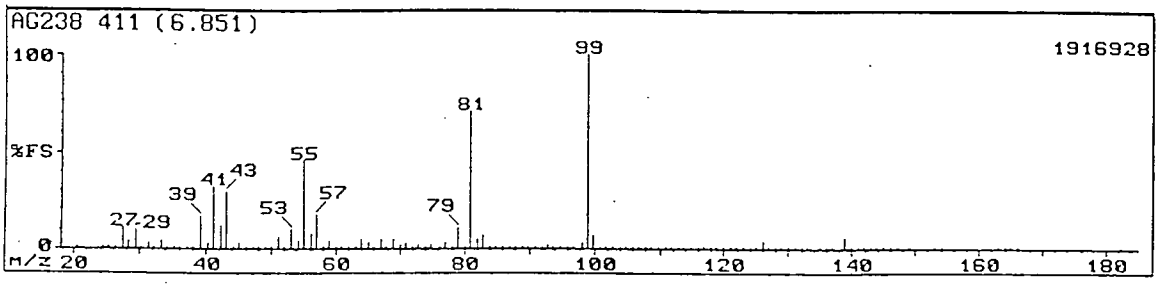


AG238'275 (4.584) REFINE 198246

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.02	53	3.20	80	0.38	107	0.54
25	0.02	54	1.83	81	4.34	109	0.43
26	0.65	55	49.17	82	5.99	110	0.06
27	7.80	56	4.18	83	100.00	111	0.16
28	3.51	57	0.78	84	6.04	113	2.80
29	5.94	59	2.96	85	1.41	114	0.23
30	0.14	60	0.15	86	0.16	115	0.12
31	0.29	61	0.44	87	0.46	117	0.05
32	0.25	62	0.06	88	0.11	118	0.05
33	3.28	63	0.33	89	0.30	119	0.02
36	0.02	64	0.71	90	0.51	121	0.02
37	0.14	65	1.56	91	2.49	123	0.15
38	0.60	66	0.43	92	0.14	125	0.18
39	12.96	67	3.03	93	1.12	126	0.31
40	1.96	68	0.83	94	0.09	127	0.89
41	33.47	69	0.56	96	0.23	128	0.06
42	3.41	70	0.14	97	0.77	131	0.03
43	2.71	71	1.03	98	0.10	133	0.37
44	0.17	72	0.26	99	0.27	134	0.03
45	0.38	73	2.00	100	0.06	145	0.25
46	0.30	74	0.12	101	0.26	146	0.55
47	1.20	75	0.37	103	0.92	147	0.04
50	0.56	77	5.58	104	1.14	166	0.92
51	3.82	78	2.51	105	0.84	167	0.05
52	0.60	79	3.31	106	0.05		

30. 1-(1',2',2'-trifluoro-1'-ethyl)-cyclohexanol **26b**

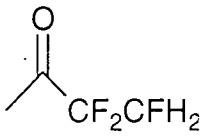


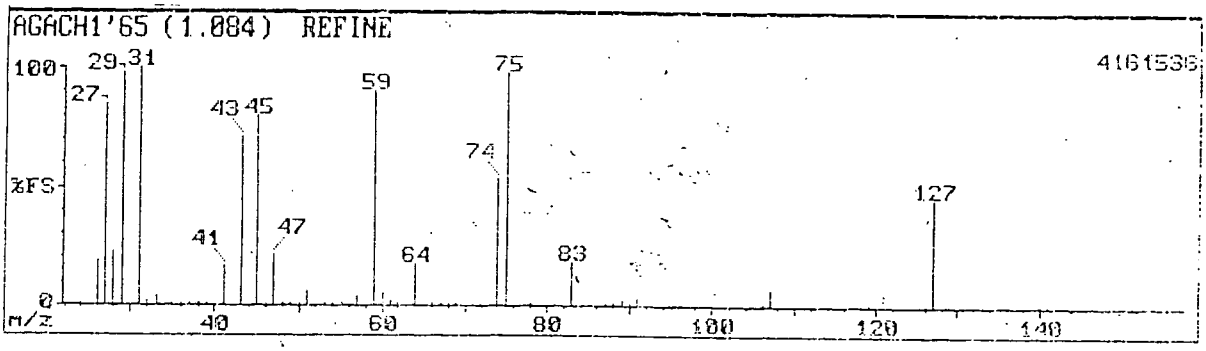


AG238 411 (6.851) 1916928

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	56	8.07	89	0.43	122	0.04
24	0.01	57	17.09	90	0.18	123	0.46
25	0.04	58	1.00	91	1.18	124	0.05
26	0.93	59	3.47	92	0.31	125	0.39
27	10.68	60	0.60	93	1.55	126	3.47
28	4.27	61	0.78	94	0.08	127	0.74
29	9.94	62	0.29	95	0.92	128	0.07
30	0.26	63	1.27	96	0.21	129	0.08
31	3.14	64	4.70	97	0.97	130	0.03
32	0.31	65	3.18	98	3.26	131	0.16
33	4.33	66	0.91	99	100.00	132	0.01
34	0.24	67	4.38	100	6.41	133	0.02
35	0.09	68	0.50	101	0.68	135	0.01
36	0.06	69	5.29	102	0.09	136	0.03
37	0.19	70	2.10	103	0.66	137	0.01
38	0.85	71	2.44	104	0.12	139	5.66
39	16.03	72	0.40	105	0.42	140	0.43
40	2.94	73	1.82	106	0.42	141	0.07
41	31.84	74	0.15	107	0.23	142	0.02
42	11.75	75	1.80	108	0.06	143	0.07
43	29.06	76	0.32	109	0.56	144	0.01
44	1.40	77	3.04	110	0.13	145	0.26
45	2.47	78	0.88	111	0.61	146	0.03
46	0.38	79	10.68	112	0.07	147	0.02
47	1.44	80	0.99	113	0.48	149	0.05
48	0.58	81	70.94	114	0.13	153	0.23
49	1.32	82	5.13	115	0.27	154	0.05
50	1.01	83	6.73	116	0.04	163	0.52
51	6.04	84	0.30	117	0.11	164	0.75
52	1.10	85	0.56	118	0.02	165	0.18
53	10.04	86	0.10	119	0.42	166	0.02
54	3.42	87	0.19	120	0.10	182	0.02
55	45.73	88	0.25	121	0.08		

31. 3,3,4-trifluoro-2-butanone **16**

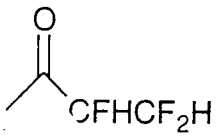


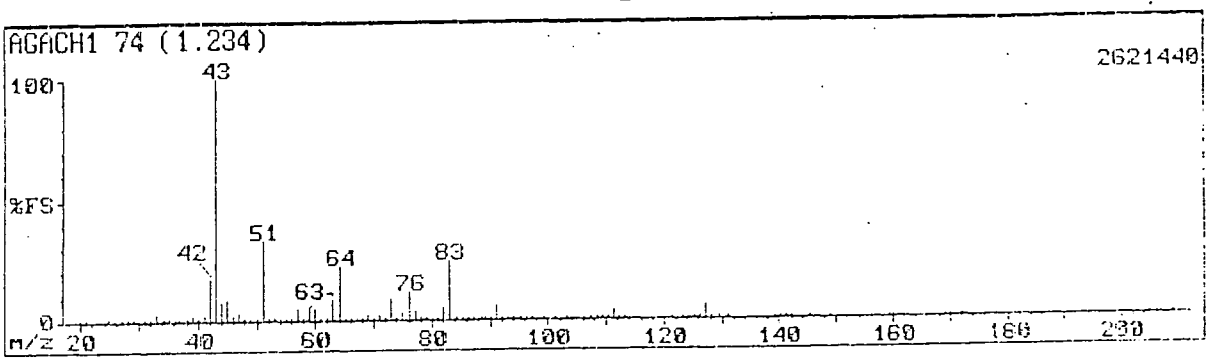


AGACH1'65 (1.084) REFINE 4161536

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
24	0.27	32	1.47	39	0.94	48	0.65	55	1.35	64	17.72	74	53.54	89	1.46	126	0.16
26	18.21	33	4.04	41	16.44	49	0.39	57	4.26	66	0.09	75	98.43	90	0.21	127	45.67
27	84.25	35	0.15	43	70.87	50	1.43	59	90.55	67	0.43	78	1.06	91	2.63	140	0.31
28	22.15	36	0.18	45	79.13	51	6.85	60	5.04	68	0.17	83	18.21	106	0.21	141	0.33
29	98.43	37	0.18	46	1.31	53	0.91	61	2.31	69	0.73	87	0.35	107	6.48	142	0.39
31	100.00	38	0.23	47	21.56	54	0.12	62	0.41	70	0.20	88	0.18	119	0.47	156	0.83

32. 3,4,4-trifluoro-2-butanone **17**

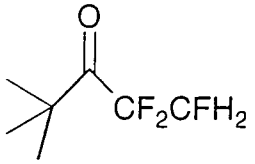


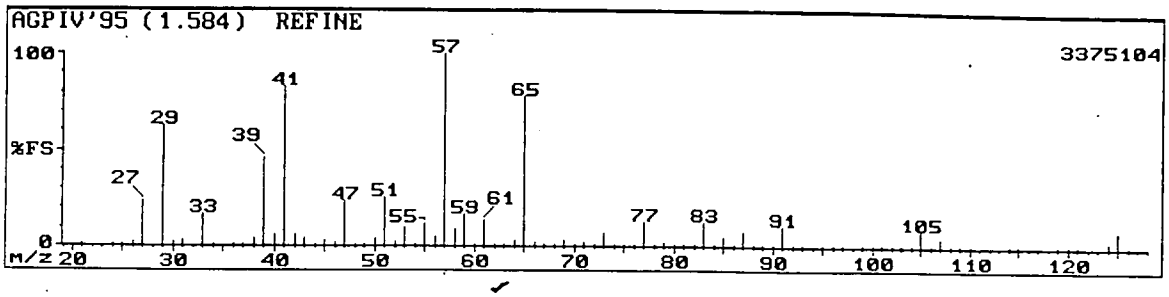


AGACH1 74 (1.234) 2621440

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	36	0.06	48	0.16	60	4.41	72	0.63	84	0.39	96	0.03	113	0.13	142	0.11
21	0.01	37	0.36	49	1.08	61	1.43	73	8.40	85	0.05	97	0.03	121	0.02	145	0.01
25	0.35	38	0.52	50	1.29	62	0.43	74	0.35	86	0.01	99	0.01	123	0.02	149	0.02
26	1.28	39	1.77	51	33.13	63	9.18	75	3.01	87	0.11	101	0.03	125	0.01	159	0.02
27	1.02	40	0.28	52	0.55	64	22.81	76	11.25	88	0.36	103	0.02	126	0.22	160	0.00
28	0.41	41	1.66	53	1.40	65	1.41	77	3.67	89	0.46	106	0.43	127	5.47	169	0.11
29	0.57	42	17.50	54	0.15	66	0.08	78	0.17	90	0.44	107	0.63	128	0.24	170	0.01
31	1.35	43	100.00	55	1.34	67	0.11	79	0.61	91	6.13	108	0.04	129	0.02	172	0.02
32	0.96	44	7.66	56	1.01	68	0.32	80	0.03	92	0.63	109	0.25	131	0.01	209	0.03
33	2.93	45	8.52	57	4.73	69	1.55	81	0.69	93	0.07	110	0.07	139	0.02		
34	0.04	46	1.95	58	1.18	70	0.28	82	4.53	94	0.03	111	3.48	140	0.01		
35	0.02	47	2.70	59	5.74	71	1.91	83	24.53	95	0.41	112	0.11	141	0.07		

33. 4,4,5-trifluoro-2,2-dimethyl-3-pentanone **18a**

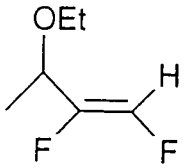


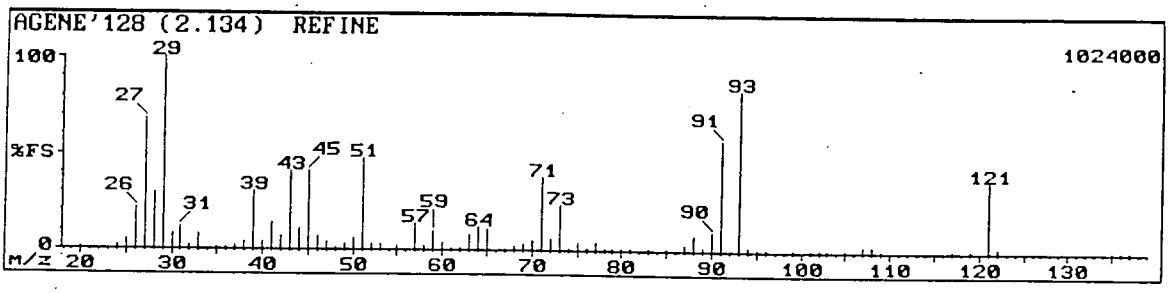


AGPIV'95 (1.584) REFINE

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Re
21	0.01	37	1.31	48	0.61	59	16.02	70	
24	0.02	38	4.25	49	0.41	60	0.91	71	
25	0.10	39	45.63	50	3.46	61	13.35	72	
26	1.90	40	5.37	51	25.24	62	0.64	73	
27	22.82	41	82.52	52	1.61	63	1.11	74	
29	62.14	42	5.46	53	10.07	64	2.91	75	
30	1.59	43	3.91	54	1.03	65	77.67	76	
31	2.67	44	0.90	55	11.65	66	1.90	77	
33	16.14	45	2.94	56	4.37	67	0.90	78	
34	0.21	46	1.93	57	100.00	68	0.28	79	
36	0.06	47	23.42	58	8.37	69	2.67	80	

34. 1,2-difluoro-3-ethoxy-1-(Z)-butene **19**

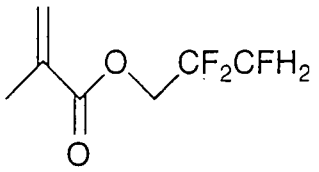


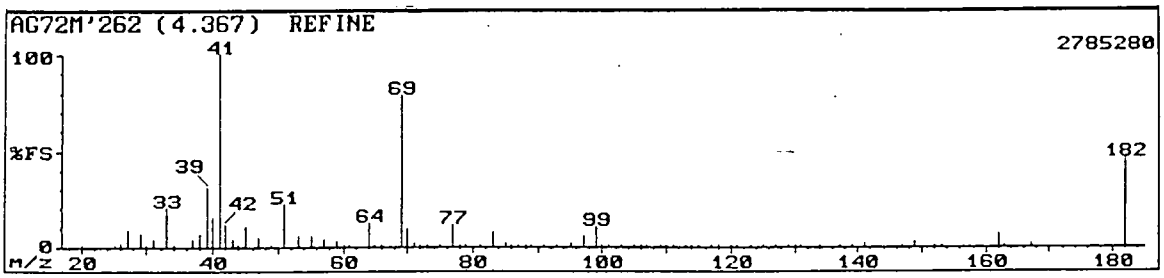


AGENE'111 (1.850) REFINE 1507328

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.32	43	17.93	63	0.94	89	0.33
24	0.67	45	100.00	64	3.92	91	6.18
25	2.00	46	2.82	65	4.26	92	0.44
26	10.73	47	4.82	67	0.16	93	0.56
27	27.99	48	0.07	68	0.11	94	0.09
28	12.91	49	1.02	69	0.48	95	0.59
29	45.65	50	0.99	70	0.17	96	0.03
30	2.02	51	6.66	71	2.31	107	0.09
31	6.25	52	0.44	73	23.91	109	0.65
32	0.84	53	0.39	74	1.09	111	0.04
33	10.39	54	0.10	75	0.95	113	1.48
35	0.06	55	0.49	77	3.99	121	0.04
36	0.05	56	0.22	78	0.94	127	0.15
37	0.19	57	1.21	79	0.12	129	0.15
38	0.24	58	0.41	80	0.16	141	0.35
39	3.38	59	3.38	81	0.25	154	0.06
40	0.56	60	0.45	83	6.25	155	0.08
41	4.16	61	2.21	87	0.06	157	0.06
42	1.43	62	0.17	88	0.14		

35. 2,2,3-trifluoropropyl methacrylate **20a**

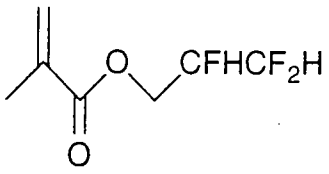


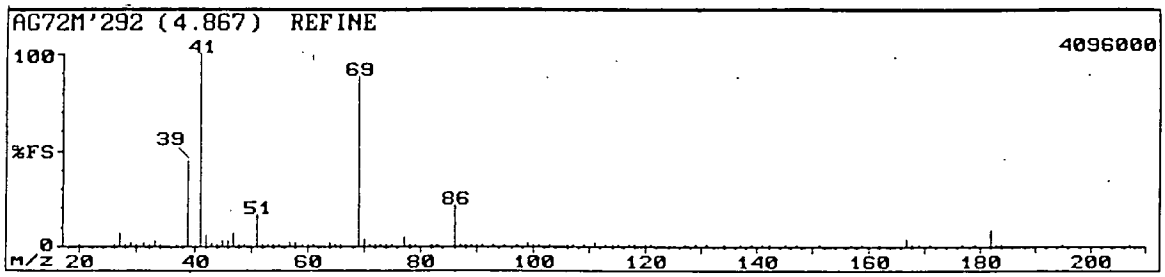


AG72M'262 (4.367) REFINE 2785280

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.04	55	6.03	88	0.12	121	0.07
25	0.19	57	3.64	89	0.11	123	0.35
26	1.82	59	2.68	91	0.53	125	0.10
27	8.90	60	0.57	93	0.28	127	0.06
29	6.36	61	0.26	95	1.54	129	1.34
30	1.02	64	12.79	97	6.07	130	0.09
31	3.42	65	0.93	99	10.29	131	0.02
33	20.15	66	0.65	100	0.62	134	0.05
34	0.23	69	78.24	101	0.54	137	0.34
37	3.42	70	10.00	103	0.62	139	0.27
38	6.62	71	1.88	105	0.75	141	2.43
39	30.59	72	0.10	106	0.19	147	0.05
40	15.44	73	0.85	107	0.07	149	2.65
41	100.00	75	1.13	109	0.58	152	0.82
42	11.62	77	12.06	110	0.03	153	0.05
43	4.08	78	1.03	111	0.07	162	6.62
44	0.68	79	0.24	113	0.23	163	0.58
45	10.59	81	0.82	114	1.23	167	1.83
47	4.45	83	8.09	115	0.26	182	45.29
49	0.41	85	1.76	117	0.58		
51	22.35	86	0.63	118	0.58		
53	5.66	87	0.45	120	0.26		

36. 2,3,3-trifluoropropyl methacrylate **20b**

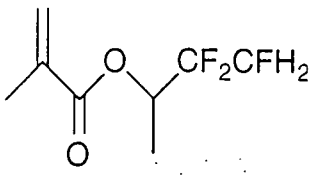


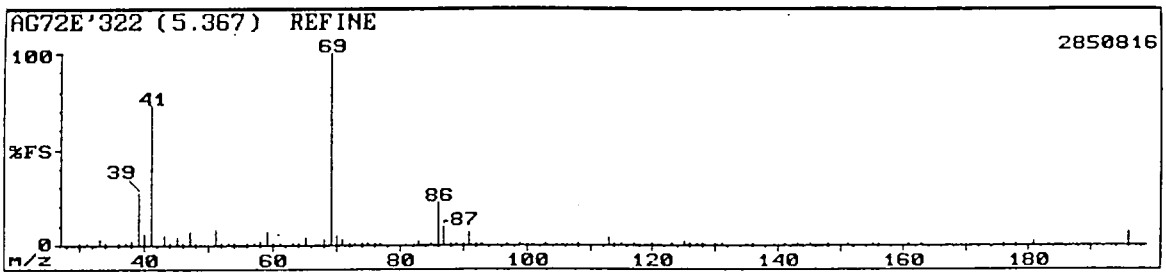


AG72M'292 (4.867) REFINE 4096000

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	54	0.15	88	0.13	131	0.67
26	1.04	55	1.29	89	0.09	134	0.41
27	6.90	57	1.75	90	0.03	137	0.28
28	1.00	58	1.68	91	0.10	139	0.05
29	1.85	59	0.41	93	0.03	141	0.06
30	0.35	60	0.16	95	1.16	142	0.03
31	1.50	61	0.03	97	1.15	145	0.11
32	0.20	64	1.73	99	1.59	147	0.10
33	3.08	65	0.74	100	0.06	151	0.09
34	0.05	66	0.11	101	0.03	157	0.02
37	1.41	69	88.00	103	0.21	159	0.09
39	44.40	70	3.95	106	0.15	162	0.09
41	100.00	71	0.76	107	0.01	167	3.95
42	5.45	72	0.10	109	0.13	168	0.16
43	2.13	73	0.24	111	2.10	169	0.02
44	1.00	74	0.06	113	1.21	171	0.02
45	2.55	75	0.33	114	0.27	177	0.03
46	2.97	77	4.68	115	0.08	179	0.02
47	6.40	78	0.32	117	0.49	182	8.90
48	0.15	79	0.04	118	0.09	183	0.68
49	0.09	82	0.29	120	0.15	184	0.05
51	16.50	83	0.46	121	0.01	195	0.02
52	0.14	86	21.40	127	0.11	207	0.02
53	1.21	87	0.99	129	0.07		

37. 3,3,4-trifluoro-2-butyl methacrylate **21a**

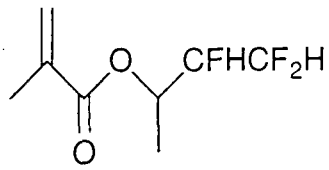


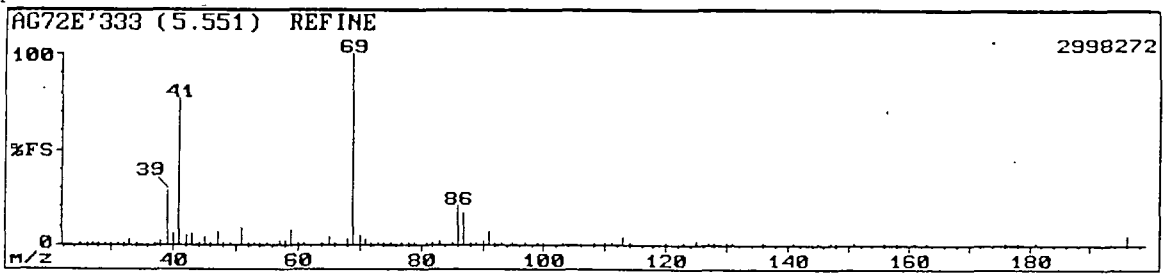


AG72E'322 (5.367) REFINE 2850816

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
30	0.08	56	0.09	85	0.97	126	0.07
31	0.44	57	1.45	86	22.56	127	0.84
33	2.48	58	1.87	87	9.77	128	0.13
34	0.03	59	6.68	88	0.66	130	0.16
36	0.04	60	1.28	89	0.16	131	0.41
37	0.60	61	0.20	90	1.20	136	0.06
38	1.77	63	0.20	91	6.68	141	0.06
39	27.16	64	1.04	92	0.44	143	0.03
40	5.85	65	3.45	93	0.06	145	0.04
41	72.99	68	2.91	97	0.29	148	0.19
43	5.03	69	100.00	99	0.18	151	0.15
44	0.74	70	4.67	103	0.06	155	0.02
45	3.81	71	3.20	108	0.22	156	0.08
46	0.27	72	0.23	113	4.35	161	0.12
47	6.54	73	0.29	114	0.19	163	0.03
48	0.12	74	0.67	115	0.04	176	0.06
51	8.12	75	0.14	117	0.04	178	0.04
52	0.14	76	0.04	120	0.07	181	1.79
53	0.66	77	0.82	123	0.03	196	6.50
54	0.11	83	1.51	125	1.81		

38. 3,4,4-trifluoro-2-butyl methacrylate **21b**

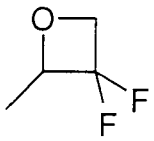


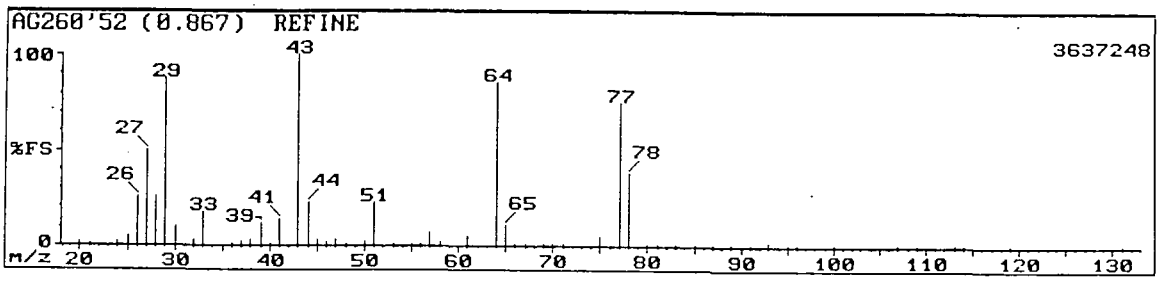


AG72E'333 (5.551) REFINE 2998272

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
25	0.02	51	8.61	79	0.12	120	0.06
26	0.34	52	0.13	81	0.08	123	0.03
27	1.34	53	0.76	82	0.19	125	1.60
28	0.56	54	0.14	83	1.56	127	0.79
29	1.17	55	0.77	85	0.98	128	0.16
30	0.07	57	1.60	86	19.95	130	0.23
31	0.43	58	2.05	87	16.94	131	0.47
32	0.18	59	7.68	88	0.90	136	0.05
33	2.49	60	1.37	89	0.16	141	0.09
34	0.02	61	0.19	90	2.29	145	0.05
37	0.61	64	1.16	91	6.69	147	0.02
38	1.85	65	3.76	92	0.40	148	0.14
39	27.87	66	0.08	93	0.05	151	0.13
40	5.70	68	2.94	95	0.51	156	0.07
41	77.05	69	100.00	97	0.27	158	0.01
42	4.64	70	4.47	99	0.18	161	0.11
43	6.05	71	3.24	100	0.06	163	0.02
44	0.77	72	0.21	103	0.07	176	0.06
45	4.34	73	0.34	108	0.20	178	0.04
46	0.29	74	0.59	110	0.88	181	1.45
47	7.14	75	0.15	111	0.82	196	4.95
48	0.12	77	0.91	113	4.20		
49	0.15	78	0.03	114	0.19		

39. 3,3,-difluoro-4-methyl oxetane **22**

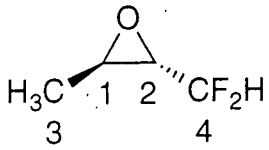


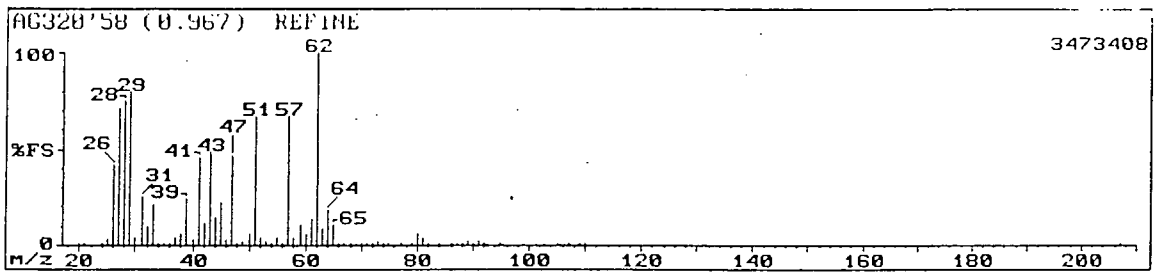


AG260'52 (0.867) REFINE 3637248

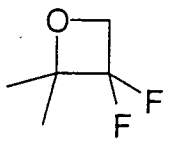
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.47	40	0.80	61	4.56	87	0.28
21	0.04	41	13.51	64	85.59	89	0.36
24	1.46	43	100.00	65	11.15	91	0.40
25	4.53	44	22.52	66	0.25	93	1.70
26	24.89	45	2.76	67	0.14	95	0.05
27	50.00	46	1.97	69	1.24	96	0.03
28	24.89	47	3.13	70	0.13	100	0.07
29	86.94	48	0.10	71	0.38	107	0.26
30	9.46	50	1.89	75	5.21	109	0.23
32	2.53	51	21.85	77	74.32	113	0.01
33	17.00	53	0.68	78	37.39	114	0.04
36	0.49	55	0.65	80	0.27	119	0.03
37	2.36	56	1.27	81	0.22	131	0.02
38	3.18	57	7.01	83	0.04		
39	11.60	58	1.60	85	0.07		

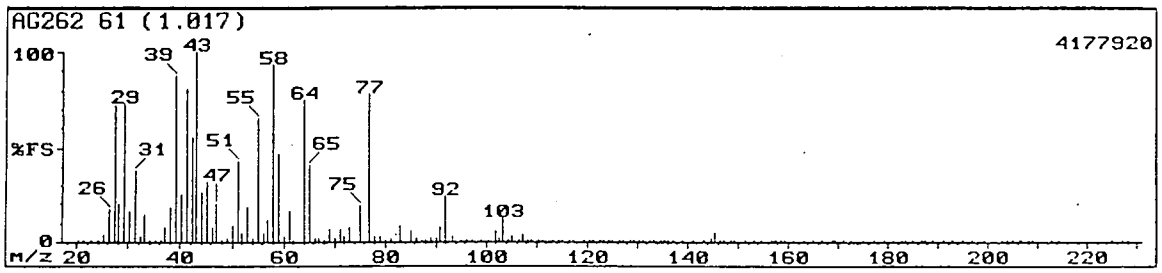
40. 1-difluoromethyl-2-methyl oxirane **23**





41. 3,3-difluoro-4,4-dimethyl oxetane **24**

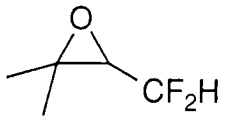


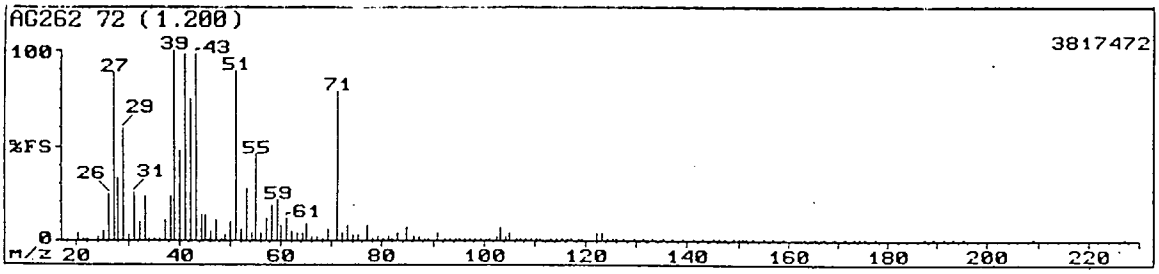


AG262 61 (1.017) 4177920

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.44	61	16.57	108	0.24	157	0.04
21	0.12	62	1.43	109	0.38	157	0.08
23	0.01	64	74.90	110	0.11	159	0.04
24	1.32	65	40.78	111	0.26	159	0.05
25	3.73	66	1.86	113	0.19	161	0.08
26	17.94	67	1.76	115	0.04	163	0.04
27	72.16	68	0.63	115	0.17	165	0.09
28	20.49	69	6.86	117	0.03	167	0.04
29	72.94	70	2.35	117	0.11	169	0.02
30	16.27	71	6.47	119	0.11	169	0.03
31	37.65	72	2.87	121	0.09	171	0.12
32	2.72	73	7.84	121	0.47	173	0.03
33	14.61	75	19.12	123	0.18	175	0.03
34	0.16	77	77.65	123	0.77	177	0.08
35	0.17	78	2.57	124	0.13	179	0.07
36	0.63	79	2.45	125	0.31	181	0.08
37	7.75	80	0.58	126	0.07	183	0.02
38	18.24	81	1.64	127	0.15	183	0.02
39	87.45	83	8.33	129	0.02	185	0.31
40	25.49	85	5.96	129	0.08	187	0.06
41	80.39	86	1.86	131	0.04	187	0.03
42	54.90	87	1.40	131	0.17	189	0.01
43	100.00	88	0.88	133	0.03	191	0.03
44	26.27	89	1.67	133	0.09	193	0.01
45	32.16	90	1.69	135	0.03	195	0.07
46	7.94	91	8.04	135	0.13	197	0.01
47	20.49	92	24.12	136	0.05	199	0.05
48	0.72	93	2.75	137	0.07	203	0.01
49	1.59	95	0.56	139	0.12	204	0.01
50	8.63	96	0.21	141	0.08	205	0.04
51	42.35	97	0.32	143	0.13	206	0.01
52	4.73	99	0.80	145	1.49	207	0.05
53	18.04	100	0.34	145	4.49	208	0.01
54	1.99	102	5.42	146	0.37	209	0.01
55	64.71	103	2.43	147	0.07	213	0.02
56	5.00	103	12.35	149	0.05	214	0.08
57	11.27	104	1.45	149	0.07	225	0.02
58	93.33	105	3.31	151	0.03	227	0.05
59	47.06	106	0.83	153	0.03	228	0.01
60	2.77	107	3.48	155	0.01		

42. 3-(difluoromethyl)-2,2-dimethyl oxirane **25**

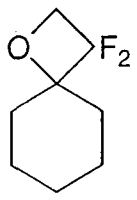


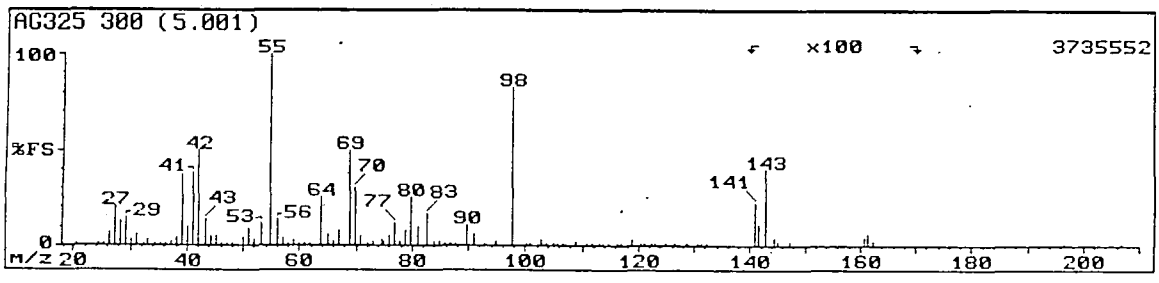


AG262 72 (1.200) 3817472

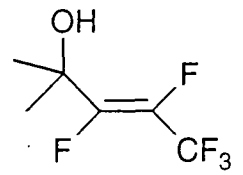
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	3.54	55	45.49	93	1.17	133	0.03
21	0.13	56	4.05	94	0.28	135	0.04
22	0.01	57	12.12	95	0.46	137	0.03
24	2.41	58	18.13	96	0.19	139	0.06
25	4.53	59	21.24	97	0.27	141	0.04
26	24.03	60	7.94	98	0.19	143	0.02
27	88.41	61	11.48	99	0.38	145	1.13
28	33.05	62	4.80	100	0.17	146	0.07
29	59.23	63	3.49	101	0.47	147	0.05
30	2.47	64	4.18	102	2.01	149	0.04
31	25.32	65	9.12	103	6.63	150	0.01
32	9.76	66	1.60	104	1.53	151	0.01
33	23.18	67	2.23	105	4.10	152	0.01
34	0.48	68	1.04	107	0.31	153	0.02
35	0.34	69	5.87	107	0.76	155	0.01
36	0.87	71	78.54	108	0.16	157	0.05
37	10.73	72	4.16	109	0.28	159	0.06
38	23.18	73	7.83	110	0.12	163	0.02
39	100.00	74	3.11	111	0.18	165	0.04
40	47.64	75	2.71	113	0.15	167	0.01
41	97.85	77	7.40	114	0.04	169	0.01
42	75.11	78	0.70	115	0.08	171	0.02
43	97.85	79	1.54	117	0.02	173	0.31
44	13.20	80	1.27	117	0.08	174	0.03
45	13.84	81	1.82	119	0.02	175	0.01
46	4.40	82	1.15	119	0.08	177	0.01
47	10.94	83	3.65	122	3.49	187	0.01
48	0.85	85	6.84	123	4.16	189	0.02
49	2.84	86	2.17	124	0.30	191	0.01
50	9.55	87	1.53	125	0.33	193	0.14
51	88.84	88	0.48	126	0.03	195	0.02
52	5.87	89	0.74	127	0.06	209	0.03
53	26.82	91	3.89	129	0.04	227	0.01
54	4.08	92	0.52	131	0.04		

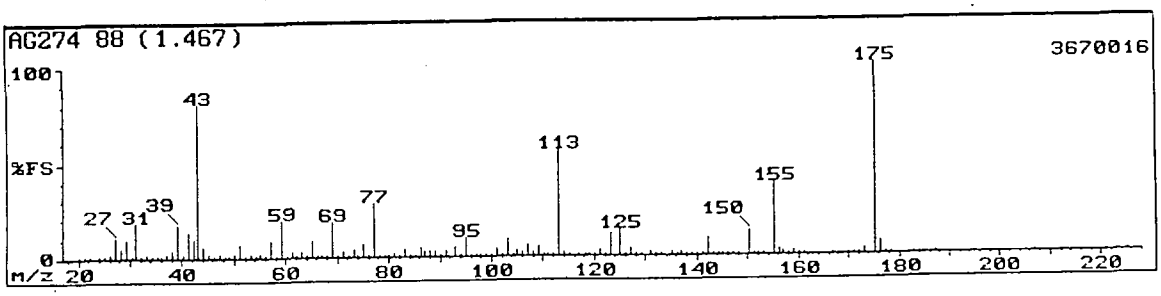
43. 3,3-difluoro-2-spirocyclohexyloxetane **27**





44. 3,4,5,5,5-pentafluoro-2-methyl-4-propen-2-ol **31**

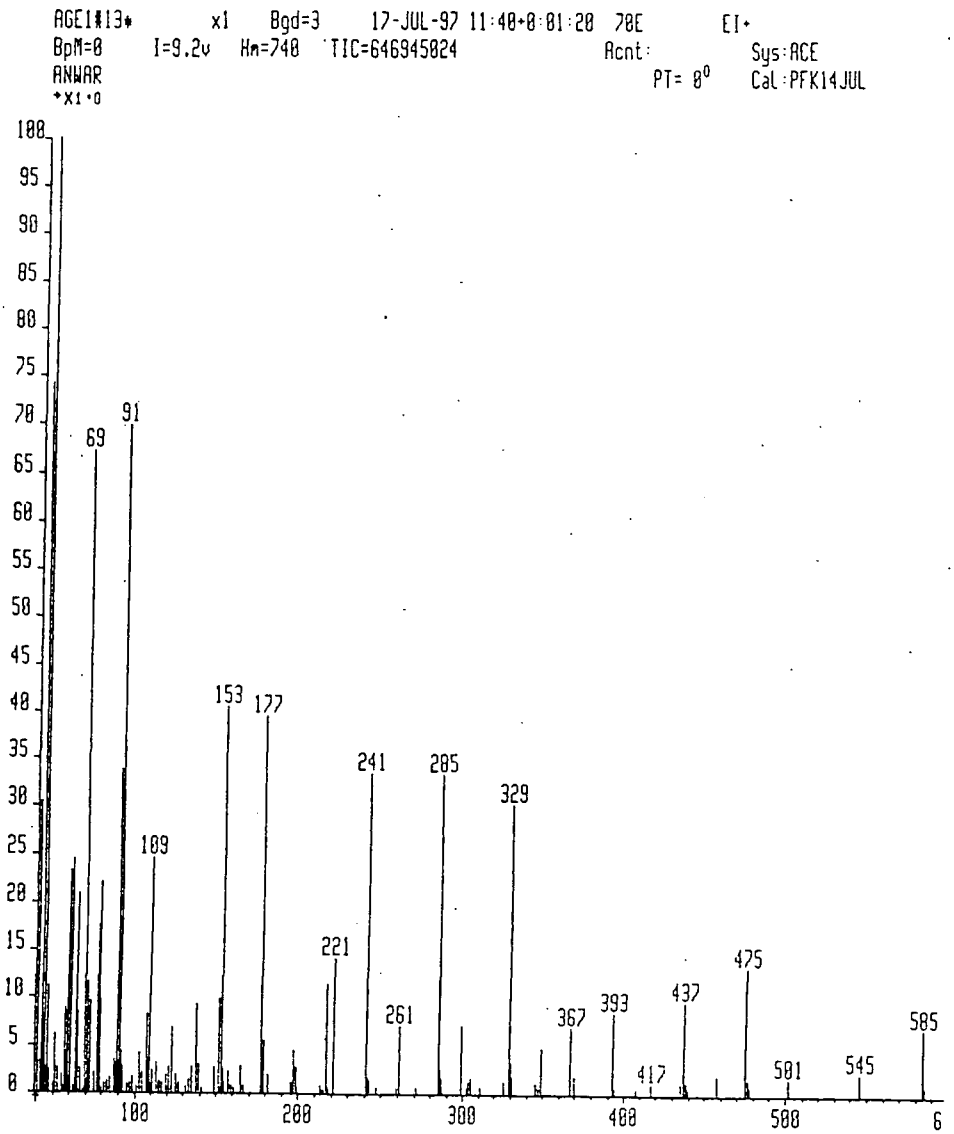




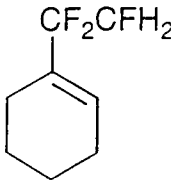
AG274 88 (1.467) 3670016

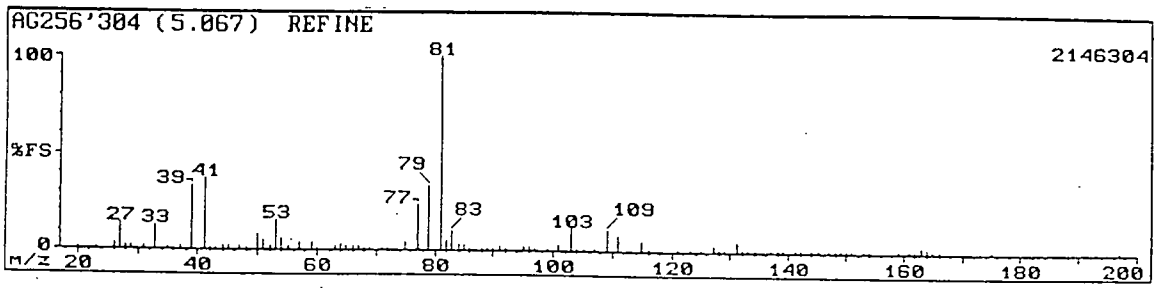
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.10	58	1.22	96	0.36	137	1.87
21	0.01	59	19.20	97	0.53	138	0.13
22	0.01	60	1.03	98	0.10	139	0.57
24	0.03	61	2.48	99	1.07	140	0.28
25	0.18	62	1.06	100	1.04	141	0.34
26	1.98	63	2.79	101	4.05	142	8.26
27	11.05	64	0.66	102	0.86	143	0.46
28	4.46	65	9.04	103	8.59	144	0.03
29	9.38	66	0.32	104	0.90	145	1.11
30	0.39	67	1.00	105	2.90	146	0.07
31	18.75	68	0.84	106	2.20	147	0.02
32	1.07	69	18.86	107	6.22	148	0.02
33	1.67	70	1.36	108	2.09	150	12.17
34	0.04	71	2.93	109	5.08	151	1.44
35	0.02	72	0.42	110	0.19	152	0.12
36	0.12	73	3.66	111	0.97	153	0.21
37	1.68	74	0.89	112	1.31	155	37.95
38	3.63	75	6.47	113	55.80	156	2.99
39	17.19	76	0.91	114	1.77	157	1.46
40	2.15	77	27.68	115	0.32	158	0.12
41	13.39	78	1.19	117	0.35	159	1.72
42	9.60	79	0.34	118	0.03	160	0.08
43	80.36	80	0.35	119	1.34	161	0.11
44	5.44	81	1.67	120	0.20	167	0.02
45	2.18	82	0.98	121	3.26	170	1.09
46	0.66	83	3.46	122	1.02	171	0.07
47	2.26	84	0.60	123	11.72	172	0.61
48	0.13	85	0.54	125	13.95	173	3.26
49	1.08	86	4.52	126	1.28	175	100.00
50	2.18	87	2.54	127	3.88	176	7.14
51	6.56	88	2.57	128	0.49	177	0.46
52	0.43	89	2.76	129	0.31	178	0.03
53	2.18	90	0.52	131	2.20	187	0.01
54	0.24	91	3.10	132	0.24	207	0.02
55	1.84	93	5.19	133	1.15	225	0.01
56	1.39	94	0.55	135	1.79		
57	8.48	95	9.38	136	0.19		

45. Oligomer **32**



46. 1-(1',1',2'-trifluoro-1'-ethyl)-1-cyclohexene **33**

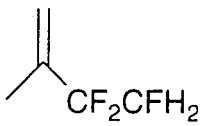


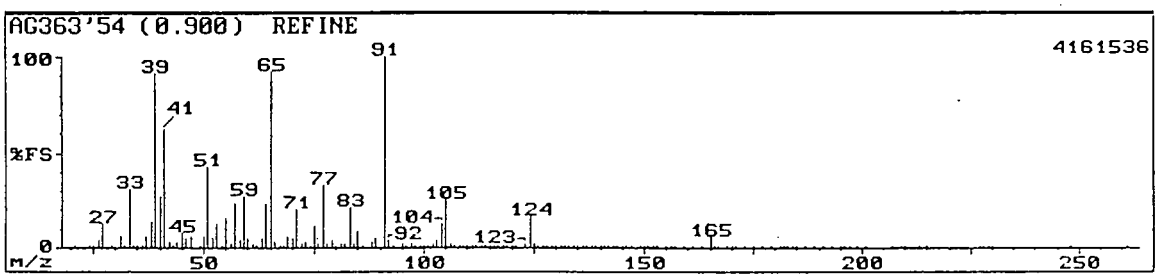


AG256'304 (5.067) REFINE 2146304

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.31	57	3.72	91	1.65	134	0.04
23	0.01	59	3.86	92	0.58	137	0.05
26	2.83	60	0.27	95	1.94	138	0.03
27	13.93	63	1.97	96	2.36	139	0.05
28	2.33	64	2.55	97	1.06	141	0.07
29	2.27	65	1.75	99	0.94	142	0.09
31	2.03	66	1.47	101	2.89	144	0.64
33	12.21	67	1.56	103	11.69	145	0.79
35	0.04	68	0.55	104	1.41	147	0.03
37	1.68	69	0.18	105	0.41	148	0.08
39	33.21	71	1.16	107	0.18	149	0.11
41	37.21	72	1.46	109	10.83	150	0.02
42	1.24	75	4.25	111	7.92	151	0.01
43	0.22	77	23.28	115	4.91	153	0.01
44	1.63	79	32.82	116	0.51	154	0.01
45	1.91	81	100.00	121	0.54	159	0.02
47	2.19	82	5.20	123	1.38	161	0.07
48	0.09	83	10.07	125	0.54	162	0.39
50	7.44	84	2.52	127	2.59	163	3.15
51	4.82	85	2.56	128	0.21	164	2.36
52	1.90	86	0.32	129	0.45	165	0.33
53	15.27	88	1.36	131	4.63	166	0.01
54	5.92	89	1.29	132	0.17	175	0.01
55	1.91	90	1.36	133	0.07	197	0.00

47. 3,3,4-trifluoro-2-methyl-1-butene **34a**

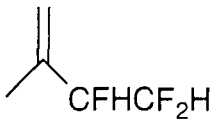


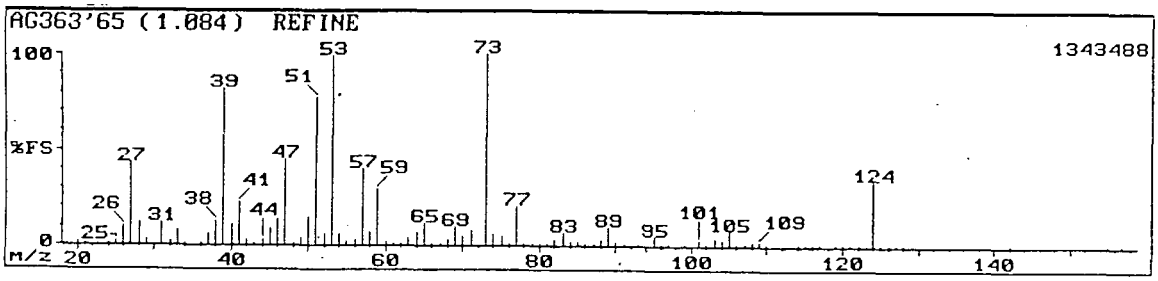


AG363'54 (0.900) REFINE 4161536

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
21	0.03	67	0.91	111	0.44	155	0.36
24	0.45	68	1.11	112	0.06	156	0.03
25	0.90	69	5.98	113	0.12	157	0.03
26	3.54	70	4.85	114	0.31	159	0.21
27	12.80	71	20.67	115	0.55	161	0.18
29	1.18	72	2.26	116	0.26	163	0.25
31	5.98	73	3.40	117	0.34	165	6.18
32	1.45	74	0.24	118	0.08	166	0.46
33	31.50	75	11.52	119	0.08	167	0.13
34	0.36	76	1.75	120	0.14	169	0.19
35	0.16	77	33.07	121	0.24	170	0.03
36	0.34	78	1.48	123	2.02	171	0.02
37	5.71	79	3.57	124	16.34	173	0.05
38	13.88	80	0.66	125	1.62	175	0.07
39	90.94	81	2.04	126	0.26	177	0.06
40	26.77	82	1.77	127	0.31	179	0.13
41	62.20	83	21.56	128	0.19	181	0.17
42	2.56	84	1.57	129	0.23	182	0.01
43	0.62	85	9.15	130	0.22	183	0.06
44	2.88	86	1.08	131	0.34	184	0.02
45	7.97	88	3.22	132	0.09	185	0.01
46	5.12	89	5.02	133	0.09	187	0.03
47	5.59	91	100.00	134	0.10	189	0.04
49	1.34	92	4.23	135	0.25	191	0.02
50	5.78	93	0.36	136	0.16	193	0.01
51	42.52	95	1.46	137	0.18	195	0.22
52	4.38	96	0.19	138	0.06	196	0.02
53	12.40	97	1.87	139	0.06	197	0.02
54	1.16	98	0.19	140	0.18	199	0.02
55	15.35	99	0.55	141	0.39	201	0.04
56	1.50	100	0.66	142	0.14	207	0.03
57	23.13	101	1.06	143	0.20	209	0.10
58	4.06	102	1.57	144	0.10	210	0.01
59	27.17	103	3.42	145	0.27	213	0.01
60	5.09	104	12.80	146	0.08	215	0.47
61	1.82	105	25.20	147	0.08	227	0.05
62	1.22	106	1.49	149	0.46	228	0.06
63	5.12	107	0.25	150	0.05	229	0.12
64	22.93	108	0.66	151	0.05	230	0.01
65	92.13	109	1.01	152	0.01	248	0.07
66	3.05	110	0.28	153	0.05	261	0.00

48. 3,4,4-trifluoro-2-methyl-1-butene **34b**

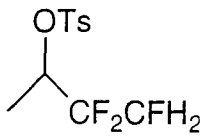


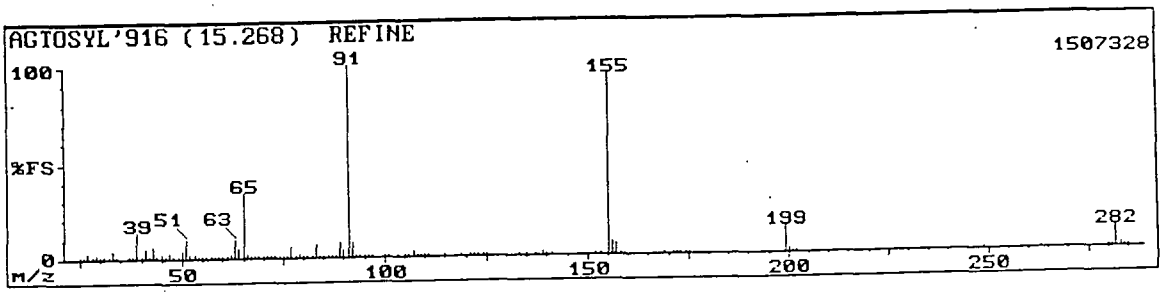


AG363'65 (1.084) REFINE 1343488

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.47	49	3.47	75	5.11	104	2.97
21	0.04	50	14.56	76	1.01	105	7.47
24	0.93	51	76.52	77	20.43	106	0.61
25	2.25	52	5.49	78	1.01	107	0.49
26	9.91	53	98.78	79	0.21	108	1.51
27	42.38	54	5.41	80	0.28	109	2.36
28	11.59	55	1.94	81	1.20	110	0.12
29	2.72	56	3.35	82	2.61	114	0.03
31	12.04	57	39.63	83	7.09	115	0.03
32	2.19	58	6.86	84	2.25	116	0.02
33	8.08	59	29.57	85	2.29	117	0.02
34	0.09	60	1.98	86	0.25	119	0.15
36	0.65	61	1.39	87	0.15	120	0.17
37	5.72	62	1.35	88	2.95	121	0.30
38	12.58	63	4.31	89	10.06	122	0.08
39	81.71	64	7.01	90	2.12	124	33.64
40	10.98	65	12.12	91	0.45	125	1.22
41	21.95	66	0.94	93	0.13	126	0.04
42	3.01	67	0.12	95	5.03	127	0.05
43	0.86	68	2.55	96	0.36	128	0.02
44	3.35	69	9.45	97	0.10	142	0.02
45	9.07	70	4.95	99	0.23	155	0.15
46	13.34	71	7.93	101	2.48	157	0.01
47	44.21	73	100.00	102	0.80		
48	1.39	74	5.56	103	3.53		

49. 3,3,4-trifluoro-2-butyl tosylate 35a

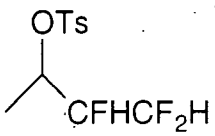


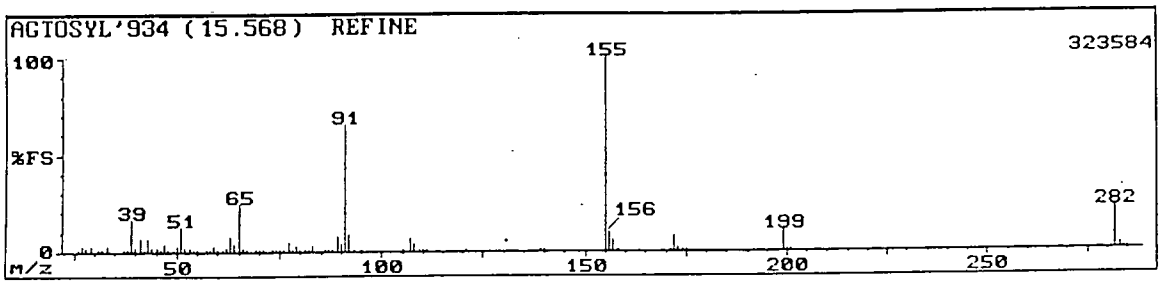


AGTOSYL'916 (15.268) REFINE 1507328

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
25	0.04	57	0.34	87	0.35	137	0.01
26	0.43	58	0.11	88	0.15	139	1.49
27	2.77	59	0.83	89	7.81	140	0.18
28	0.66	60	0.12	90	4.01	141	0.12
29	1.75	61	0.48	91	100.00	152	0.04
30	0.03	62	2.24	92	8.22	153	0.06
31	0.29	63	9.44	93	0.51	155	94.57
32	0.18	64	4.62	94	0.08	156	7.27
33	3.92	65	33.70	95	0.28	157	5.37
34	0.05	66	2.04	96	0.06	158	0.57
37	0.19	67	0.43	97	0.07	159	0.10
38	1.00	68	0.06	100	0.08	169	0.03
39	14.06	69	0.40	101	0.05	171	0.27
40	1.17	70	0.13	103	0.05	172	0.88
41	5.23	71	0.80	105	0.21	173	0.58
42	0.62	72	0.07	106	0.07	174	0.30
43	6.18	73	0.08	107	3.40	175	0.11
44	1.27	74	0.49	108	0.58	199	13.65
45	2.04	75	0.65	109	0.21	200	1.77
46	0.30	76	0.48	110	0.06	201	0.93
47	2.87	77	6.18	111	0.15	202	0.07
48	0.43	78	1.14	115	0.05	249	0.06
49	0.14	79	1.77	119	0.03	263	0.09
50	3.45	80	0.33	121	0.27	280	0.05
51	9.31	81	0.09	122	0.11	281	0.07
52	2.07	82	0.30	123	0.16	282	10.87
53	1.49	83	6.45	124	0.04	283	1.60
54	0.04	84	0.18	125	0.04	284	0.62
55	0.20	85	0.12	133	0.03	285	0.07
56	0.04	86	0.29	135	0.04		

50. 3,4,4-trifluoro-2-butyl tosylate 35b

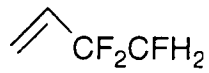


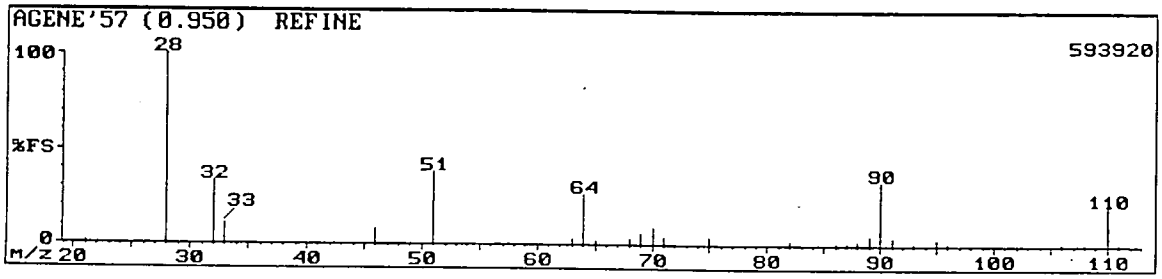


AGTOSYL'934 (15.568) REFINE 323584

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.54	52	2.08	77	4.83	121	0.23
27	3.05	53	1.66	78	1.11	139	0.94
28	1.76	54	0.12	79	2.67	140	0.14
29	2.61	55	0.24	80	0.89	155	100.00
31	0.46	57	0.76	81	0.14	156	9.41
32	0.54	58	0.19	82	0.21	157	6.17
33	3.32	59	3.38	83	2.49	158	0.37
37	0.28	60	0.96	86	0.31	171	0.51
38	1.31	61	0.44	87	0.37	172	7.44
39	16.46	62	1.90	88	0.17	173	1.62
40	1.50	63	7.44	89	7.75	174	0.52
41	7.12	64	4.05	90	4.07	175	0.28
42	0.79	65	24.68	91	65.19	199	10.44
43	6.88	66	1.46	92	8.78	200	1.14
44	1.70	67	0.31	93	0.59	201	0.55
45	1.76	69	0.36	95	0.32	282	21.20
46	0.36	70	0.10	105	0.19	283	2.77
47	3.50	71	0.94	107	6.41	284	1.22
48	0.65	73	0.15	108	3.92	285	0.15
49	0.21	74	0.50	109	0.64		
50	3.13	75	0.66	110	0.13		
51	12.74	76	0.49	111	0.21		

51. 3,3,4-trifluoro-1-butene **36**

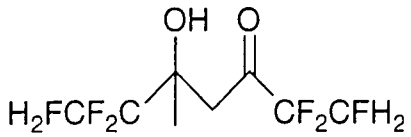


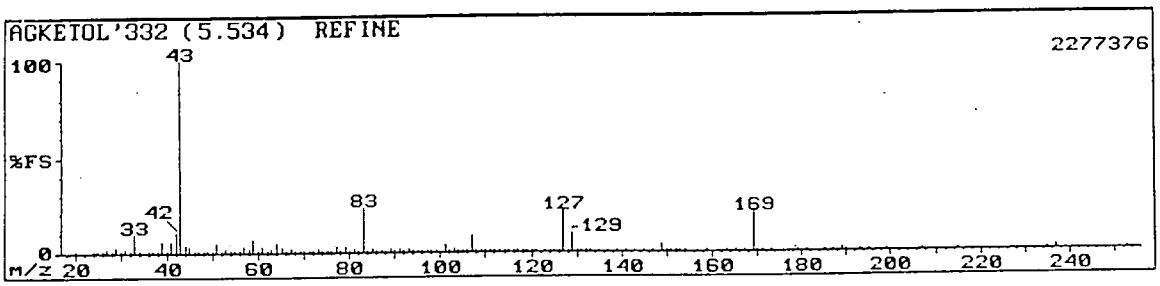


AGENE'57 (0.950) REFINE 593920

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
21	0.05	64	26.03	82	1.88	93	0.09
28	100.00	65	1.77	86	0.09	95	2.80
32	33.28	68	2.80	87	0.40	96	0.12
33	10.82	69	5.95	88	2.31	106	0.09
46	7.84	70	8.41	89	5.26	108	0.22
51	37.59	71	3.53	90	32.76	110	20.34
63	2.89	75	3.49	91	3.58	111	0.63

52. 1,2,2,6,6,7-hexafluoro-5-methyl-4-hydroxy-heptan-3-one **37a**

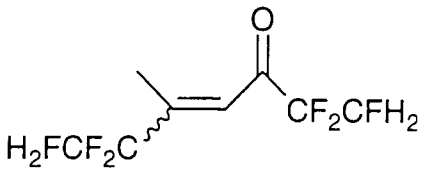


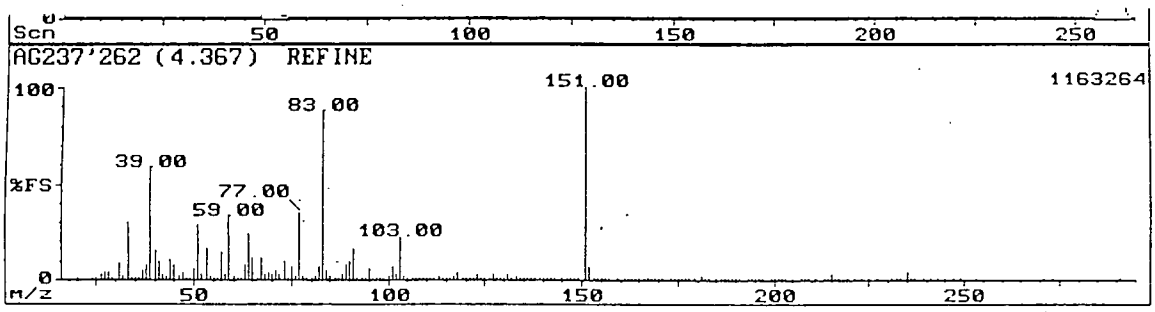


AGKETOL'332 (5.534) REFINE 2277376

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.05	60	0.27	96	0.03	135	0.05
24	0.02	61	2.43	97	0.35	137	0.03
25	0.04	62	0.17	98	0.03	139	0.04
26	0.47	63	2.06	99	0.08	141	0.13
27	2.37	64	4.95	101	3.42	143	0.02
28	0.71	65	2.79	102	0.21	145	0.12
29	3.28	66	0.11	103	1.47	147	0.09
30	0.17	67	1.90	104	0.16	149	4.27
31	2.17	68	0.12	105	1.27	150	0.26
32	0.29	69	1.09	106	0.57	151	0.91
33	9.40	70	0.17	107	8.95	152	0.05
34	0.14	71	0.57	108	0.46	153	0.55
36	0.02	72	0.08	109	0.73	154	0.03
37	0.23	73	1.89	110	0.03	159	0.04
38	0.67	74	0.11	111	0.39	163	0.04
39	5.53	75	0.57	112	0.02	165	0.32
40	0.98	76	0.22	113	0.18	167	0.24
41	5.49	77	3.19	114	0.03	169	20.68
42	10.34	78	0.46	115	0.15	170	1.12
43	100.00	79	3.06	116	0.02	171	0.17
44	4.14	80	0.08	117	0.18	173	0.04
45	2.71	81	2.28	118	0.04	179	0.26
46	0.53	82	0.51	119	0.08	181	0.02
47	1.24	83	23.56	120	0.03	185	0.06
48	0.03	84	0.66	121	0.22	187	0.05
49	1.38	85	1.82	123	0.69	189	1.50
50	0.56	86	0.12	124	0.04	190	0.07
51	4.54	87	1.18	125	0.05	193	0.07
52	0.19	88	0.35	126	1.39	195	0.03
53	1.47	89	1.72	127	21.76	199	0.03
54	0.16	90	0.13	128	0.92	207	0.02
55	1.36	91	2.00	129	9.76	215	0.15
56	0.45	92	0.14	130	0.72	235	0.03
57	2.79	93	2.25	131	0.27	237	2.15
58	1.70	94	0.43	132	0.03	253	0.05
59	7.01	95	0.23	133	0.14		

53. 1,2,2,6,6,7-hexafluoro-5-methyl-4-hepten-3-one **38a**

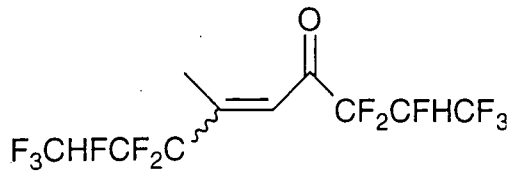


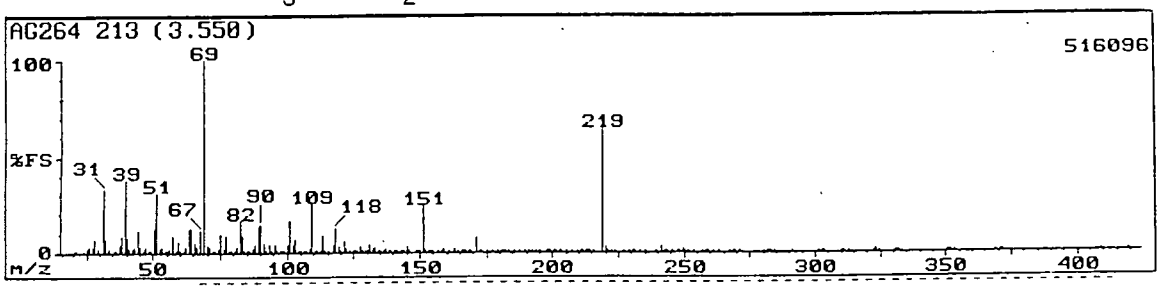


AG237'262 (4.367) REFINE 1163264

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20.00	0.21	75.00	6.43	126.00	0.22	183.00	0.06
24.00	0.46	76.00	2.38	127.00	3.15	185.00	0.12
25.00	1.08	77.00	35.21	128.00	0.21	186.00	0.04
26.00	3.32	78.00	1.80	129.00	0.11	187.00	1.43
27.00	3.63	79.00	0.36	130.00	0.43	188.00	0.13
28.00	4.03	80.00	0.26	131.00	2.64	189.00	0.11
29.00	0.97	81.00	1.89	132.00	0.92	190.00	0.31
31.00	8.63	82.00	6.87	133.00	2.29	191.00	0.18
32.00	1.98	83.00	86.97	134.00	0.11	193.00	0.09
33.00	30.28	84.00	4.86	135.00	0.35	194.00	0.24
34.00	0.42	85.00	1.87	136.00	0.04	195.00	0.73
35.00	0.09	86.00	0.43	137.00	0.17	196.00	0.13
36.00	0.31	87.00	1.16	138.00	0.16	197.00	0.07
37.00	4.58	88.00	2.60	139.00	0.19	199.00	0.73
38.00	7.31	89.00	7.57	140.00	0.25	200.00	0.06
39.00	58.45	90.00	9.24	141.00	0.48	201.00	0.59
40.00	15.23	91.00	16.73	142.00	0.09	202.00	0.06
41.00	9.51	92.00	1.41	143.00	0.16	203.00	0.05
42.00	2.60	93.00	0.50	145.00	0.97	205.00	0.08
43.00	1.83	94.00	0.42	146.00	0.16	207.00	0.06
44.00	10.21	95.00	5.63	147.00	0.70	208.00	0.05
45.00	7.83	96.00	0.53	148.00	0.21	209.00	0.06
46.00	2.07	97.00	0.56	149.00	0.34	211.00	0.03
47.00	3.63	98.00	0.14	151.00	100.00	213.00	0.22
48.00	0.45	99.00	0.74	152.00	6.34	214.00	0.13
49.00	1.19	100.00	2.24	153.00	0.80	215.00	3.01
50.00	6.07	101.00	6.43	154.00	0.10	216.00	0.25
51.00	29.58	102.00	2.46	155.00	0.19	217.00	0.07
52.00	2.88	103.00	22.18	156.00	0.06	219.00	0.02
53.00	16.37	104.00	1.76	157.00	0.09	221.00	0.04
54.00	2.00	105.00	0.27	159.00	0.19	223.00	0.03
55.00	0.95	106.00	0.13	161.00	0.61	225.00	0.06
56.00	1.29	107.00	0.52	162.00	0.13	227.00	0.06
57.00	14.96	108.00	0.48	163.00	0.39	231.00	0.05
58.00	2.68	109.00	1.39	164.00	0.06	232.00	0.05
59.00	33.45	110.00	0.08	165.00	0.20	233.00	0.12
60.00	1.47	111.00	0.56	166.00	0.18	235.00	4.09
61.00	0.85	112.00	0.37	167.00	0.99	236.00	0.34
62.00	1.10	113.00	1.47	168.00	0.14	237.00	0.05
63.00	7.48	114.00	0.72	169.00	0.08	239.00	0.03
64.00	24.65	115.00	0.96	170.00	0.04	241.00	0.04
65.00	11.88	116.00	0.16	171.00	0.07	243.00	0.01
66.00	1.33	117.00	1.69	173.00	0.84	245.00	0.12
67.00	11.97	118.00	4.05	174.00	0.14	247.00	0.02
68.00	2.88	119.00	0.74	175.00	0.20	249.00	0.02
69.00	3.74	120.00	0.19	176.00	0.05	253.00	0.07
70.00	2.55	121.00	1.01	177.00	0.16	271.00	0.02
71.00	5.04	122.00	0.75	178.00	0.02	273.00	0.10
72.00	2.66	123.00	3.26	179.00	0.20	291.00	0.05
73.00	9.60	124.00	0.19	181.00	1.47		

54. 1,1,1,2,3,3,7,7,8,9,9,9-dodecaafluoro-6-methyl-5-hepten-4-one **38b**

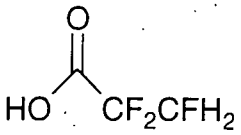


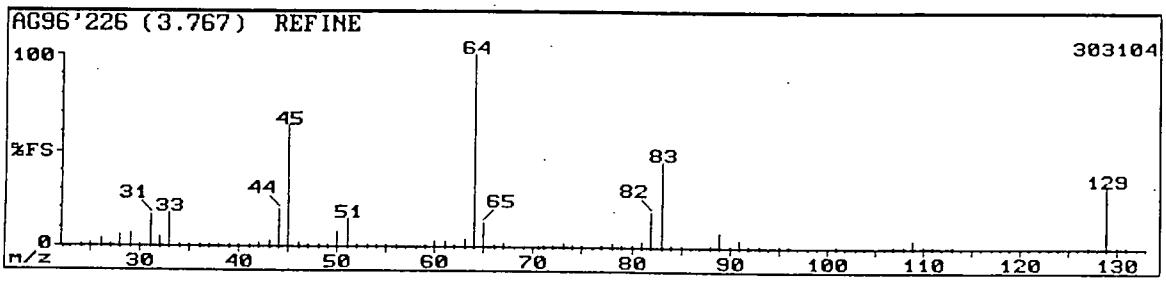


AG264 213 (3.550) 516096

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.79	79	0.29	134	0.24	203	0.25
21	0.08	80	0.56	135	0.17	205	0.11
24	0.95	81	3.37	136	0.16	207	0.08
25	2.12	82	16.07	137	1.53	209	0.18
26	2.59	83	8.68	138	0.79	210	0.04
27	2.90	84	0.91	139	1.17	211	0.06
28	6.75	85	0.61	140	0.99	212	0.13
29	2.24	86	0.25	141	0.57	213	0.49
31	32.54	87	1.51	143	0.26	214	0.11
32	7.04	88	3.92	144	0.07	215	0.11
33	2.33	89	13.69	145	3.32	219	64.29
35	0.06	90	14.68	146	0.17	220	3.37
36	0.49	91	5.06	148	0.47	221	0.87
37	4.02	92	0.58	149	1.15	222	0.12
38	8.38	93	3.72	150	0.45	223	0.12
39	37.70	94	1.09	151	24.01	227	0.07
40	8.13	95	4.07	152	1.44	229	0.23
41	1.81	96	0.29	153	1.14	230	0.08
42	1.71	97	0.21	154	0.12	231	0.18
43	2.85	98	0.24	155	0.04	233	0.45
44	11.41	99	1.35	157	0.44	235	0.04
45	2.69	100	3.57	158	0.05	239	0.24
46	0.77	101	16.07	159	1.88	241	2.48
47	2.68	102	4.22	161	0.68	242	0.12
48	0.32	103	6.70	163	1.77	243	0.11
49	0.98	104	0.51	164	0.17	245	0.09
50	12.40	105	0.21	165	0.07	247	0.05
51	30.75	106	0.43	166	0.21	248	0.17
52	1.65	107	1.05	167	0.73	249	1.48
53	2.78	108	2.23	168	0.45	250	0.19
54	0.26	109	24.80	169	1.03	251	0.09
55	1.02	110	1.14	171	7.99	253	0.13
56	2.02	111	0.31	172	0.35	257	0.11
57	8.38	112	1.40	173	0.04	258	0.07
58	1.35	113	8.38	175	0.21	259	0.10
59	5.75	114	0.94	177	0.55	261	0.07
60	0.45	115	0.51	179	1.29	263	0.33
61	0.78	117	3.77	180	0.24	267	0.50
62	2.55	118	12.35	181	1.00	268	0.19
63	12.55	119	2.47	182	0.25	269	1.26
64	13.10	120	1.38	183	0.40	270	0.13
65	4.51	121	5.65	185	0.16	271	0.26
66	2.47	122	1.49	187	0.11	280	0.06
67	11.86	123	0.22	189	0.25	281	0.20
69	100.00	124	0.07	191	1.33	282	0.09
70	3.67	125	0.53	193	0.07	283	0.57
71	2.80	126	0.40	193	0.14	284	0.05
72	1.24	127	2.46	195	0.70	291	0.19
73	0.53	128	0.19	197	0.06	301	0.08
74	2.37	129	0.33	198	0.14	302	0.08
75	9.33	130	1.19	199	0.82	303	0.60
76	1.97	131	3.92	200	0.57	310	0.09
77	9.03	132	1.77	201	0.78	311	0.45
78	0.57	133	3.32	202	0.15	313	0.02
322	0.19	331	1.04	352	0.09	371	0.66
323	1.75	332	0.11	353	0.07	409	0.05
324	0.16	351	0.14	369	0.03	419	0.06
330	0.20	351	0.94	371	0.14		

55. 2,2,3-trifluoropropanoic acid **39**

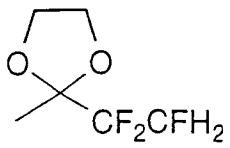


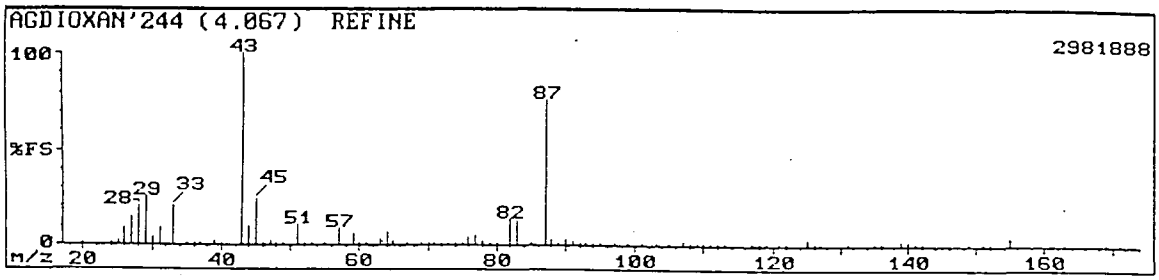


AG96'226 (3.767) REFINE 303104

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
24	0.18	43	2.91	64	100.00	89	7.52
25	1.88	44	19.85	65	12.50	90	0.78
26	3.63	45	62.84	66	0.44	91	3.55
27	0.90	46	2.41	67	2.34	92	0.69
28	6.08	47	1.06	71	0.79	93	0.24
29	6.67	48	0.54	72	0.29	95	0.87
30	0.73	49	0.84	73	1.65	96	0.23
31	16.13	50	7.52	74	0.12	101	0.34
32	4.84	51	14.53	75	0.23	107	0.21
33	17.74	52	0.32	77	0.58	108	0.37
34	0.77	53	1.13	78	1.86	109	4.08
35	1.15	54	0.17	79	0.42	110	0.21
36	0.79	55	0.29	80	0.69	111	0.54
37	0.50	56	0.15	81	3.29	113	0.38
38	0.42	59	0.33	82	17.99	127	0.10
39	0.51	60	2.49	83	44.93	129	32.09
40	0.32	61	3.10	84	1.30	130	1.16
41	0.56	62	1.37	85	0.33	131	0.14
42	1.96	63	4.18	88	0.70		

56. 2-methyl-2-(1',1',2'-trifluoro-1'-ethyl)-1,3-dioxolane **40a**

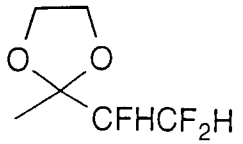


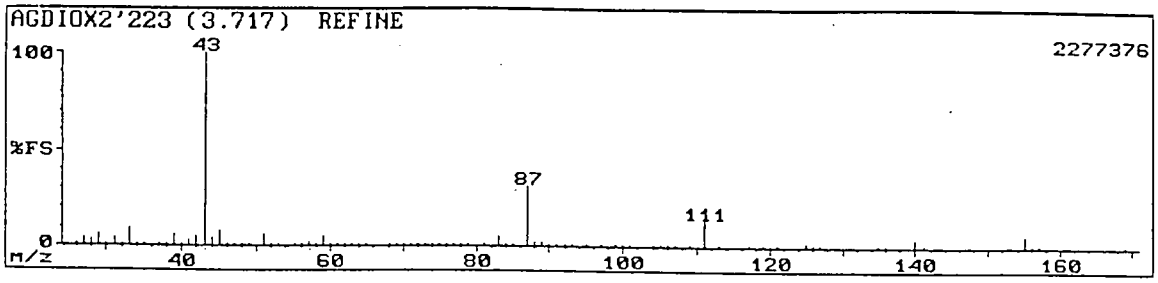


AGDIOXAN'244 (4.067) REFINE 2981888

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.57	52	0.30	82	13.74	113	0.05
24	0.67	53	0.44	83	12.77	117	0.11
25	1.95	55	0.58	85	0.89	118	0.02
26	8.79	57	9.07	87	75.27	119	0.01
27	14.42	59	6.01	88	3.13	121	0.36
28	19.92	60	0.41	89	1.31	122	0.16
29	25.14	61	1.37	90	2.82	125	2.85
30	3.67	63	2.71	91	2.20	126	0.14
31	9.07	64	7.04	92	0.42	127	0.18
33	20.19	65	2.11	93	0.12	131	0.03
35	0.23	67	0.31	94	0.53	135	0.20
36	0.25	69	1.30	95	0.60	136	0.05
37	0.47	70	0.58	97	0.08	139	1.58
39	2.12	71	1.18	99	0.04	140	1.67
40	0.79	72	1.44	101	0.13	141	0.11
43	100.00	73	1.42	103	0.03	142	0.04
44	10.16	74	0.95	105	0.13	149	0.07
45	24.04	75	1.35	107	1.91	151	0.27
46	1.34	76	4.26	108	0.75	152	0.02
47	1.61	77	5.08	109	0.93	155	3.40
48	0.25	78	1.49	110	0.22	169	0.19
49	0.40	79	1.16	111	0.06	171	0.46
51	10.85	80	0.46	112	0.04		

57. 2-methyl-2-(1',2',2'-trifluoro-1'-ethyl)-1,3-dioxolane **40b**

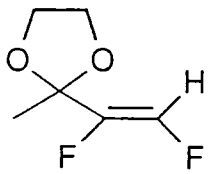


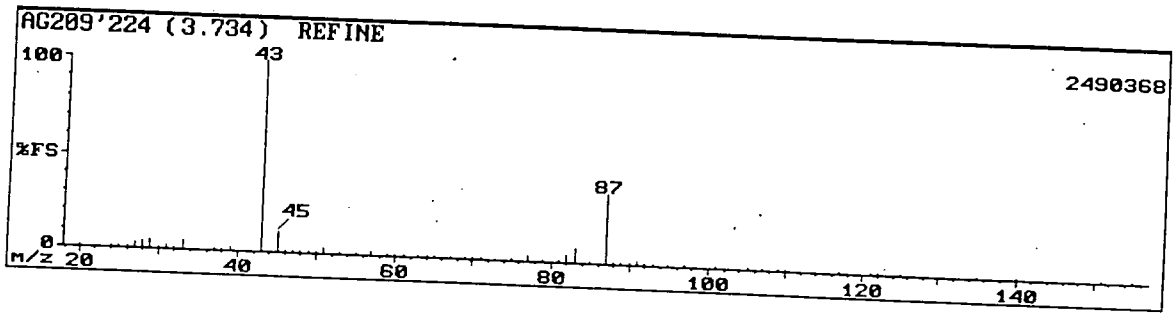


AGDIOX2'223 (3.717) REFINE 2277376

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.89	49	0.21	75	0.23	105	0.04
27	3.42	51	6.21	76	0.07	106	0.09
28	2.48	52	0.11	77	1.14	107	0.19
29	5.76	53	0.12	78	0.04	109	1.08
30	0.60	55	0.46	79	0.14	111	13.67
31	3.91	56	0.14	81	0.06	113	0.06
32	0.69	57	1.91	83	5.17	117	0.08
33	8.27	58	0.42	84	0.12	119	0.03
34	0.11	59	4.77	85	0.10	121	0.30
35	0.05	60	0.80	87	31.12	125	2.08
37	0.25	61	0.34	88	1.50	126	0.12
38	0.61	62	0.03	89	2.41	127	0.19
39	6.16	63	0.54	90	1.06	135	0.11
40	0.49	64	1.16	91	1.37	136	0.01
41	2.77	65	0.18	92	0.11	140	3.87
42	5.17	68	0.04	93	0.03	141	0.14
43	100.00	69	0.17	95	0.45	155	6.21
44	4.27	70	0.11	97	0.06	156	0.31
45	8.05	71	0.22	99	0.03	157	0.03
46	0.67	72	0.08	100	0.03	169	0.02
47	1.36	73	0.66	101	0.03		
48	0.04	74	0.04	104	0.11		

58. 2-((E)-1,2-difluoroethenyl)-1,3-dioxolane **41**



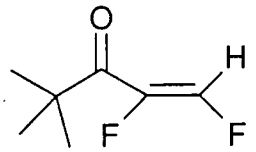


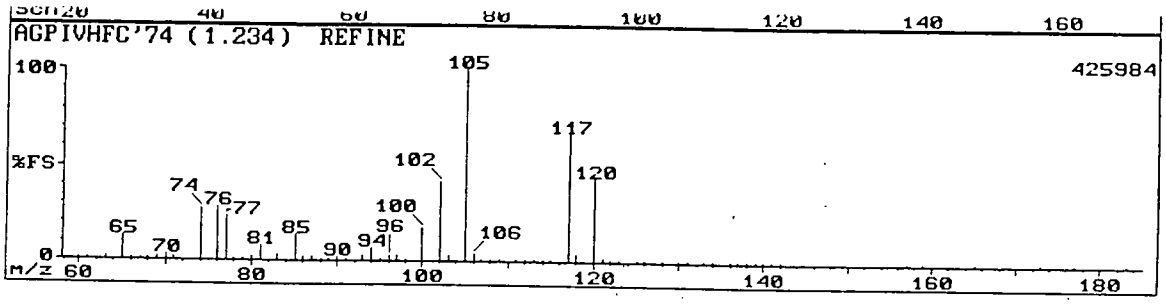
AG209'224 (3.734) REFINE

2490368

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.04	46	0.62	69	0.26	93	0.07
24	0.09	47	0.54	70	0.13	95	0.49
25	0.22	48	0.04	71	0.26	97	0.04
26	1.34	49	0.10	75	0.48	101	0.04
27	2.54	50	0.36	77	2.71	105	0.06
28	3.54	51	3.00	79	0.65	107	0.51
29	4.48	53	0.09	81	0.20	109	0.43
30	0.65	55	0.07	82	3.54	110	0.08
31	1.85	57	1.75	83	8.02	117	0.05
32	0.28	59	1.02	85	0.23	121	0.07
33	4.65	60	0.12	87	37.17	122	0.02
37	0.13	61	0.24	88	1.35	125	0.96
38	0.17	63	0.54	89	0.61	135	0.12
39	2.20	64	1.15	90	1.24	140	0.73
43	100.00	65	0.49	91	2.12	151	0.03
45	10.20	67	0.06	92	0.16	155	0.86

59. 2,2-dimethyl-4,5-difluoro-3-pentan-4-one **42**



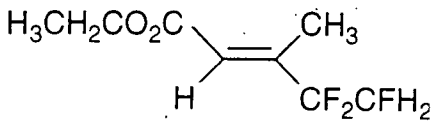


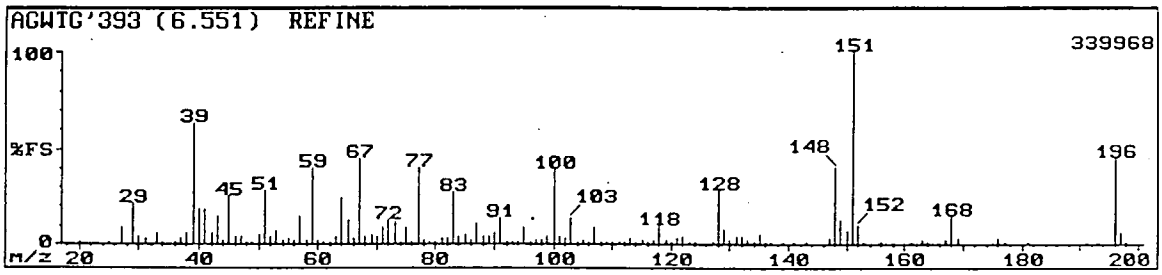
AGPIVHFC'74 (1.234) REFINE

425984

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
60	0.92	85	13.82	107	0.58	131	0.06
61	0.43	86	1.46	108	0.13	133	0.17
63	1.86	87	1.67	109	0.09	134	0.07
65	12.14	88	0.96	111	0.48	136	0.10
66	0.78	89	1.38	112	0.18	137	0.13
67	0.96	90	2.30	113	0.14	138	0.30
68	0.81	91	0.93	114	0.15	139	0.37
69	1.97	93	2.94	115	0.03	140	0.06
70	3.29	94	7.21	117	67.31	141	0.15
71	2.40	95	0.48	118	3.53	142	0.03
74	26.92	96	2.54	120	43.51	157	0.35
76	28.13	97	3.29	121	1.76	159	0.35
77	23.08	98	1.23	122	0.15	165	0.06
78	1.20	100	17.31	123	0.09	173	0.03
79	1.31	102	41.83	125	0.08	177	0.62
80	2.36	103	3.23	126	0.04	183	0.03
81	8.05	105	100.00	128	0.17		
83	2.73	106	3.85	130	1.31		

60. 4,4,5-trifluoro-3-methyl-2-pentenoic acid, ethyl ester **44a**

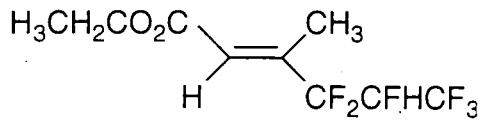


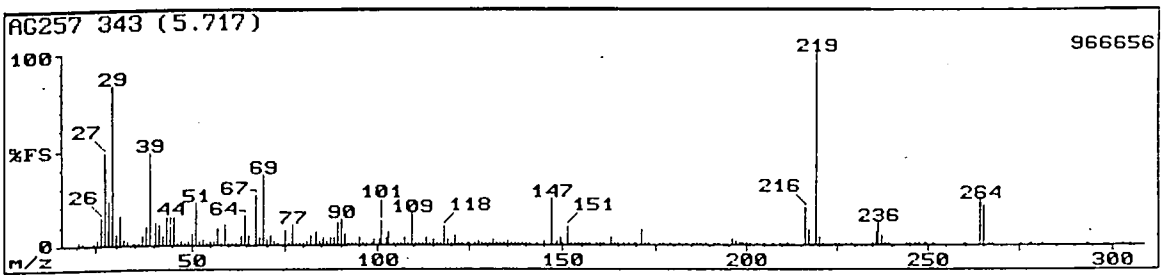


AGWTG'393 (6.551) REFINE 339968

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	61	1.45	94	0.12	129	7.76
25	0.15	62	0.42	95	8.81	130	1.79
27	8.96	63	3.97	96	0.60	131	3.63
29	21.39	64	23.80	97	1.96	132	3.95
30	3.43	65	12.20	98	1.69	133	1.47
31	3.24	66	2.73	99	4.14	134	0.19
33	6.17	67	44.58	100	38.55	135	5.05
34	0.40	68	3.84	101	3.61	136	0.19
36	0.14	69	4.56	102	2.80	137	0.14
37	2.90	70	3.84	103	13.48	139	0.13
38	5.35	71	8.58	104	1.43	141	0.79
39	62.95	72	12.58	105	1.77	143	0.38
40	18.45	73	11.82	106	0.31	147	2.52
41	18.22	74	0.80	107	8.43	148	39.76
42	5.42	75	8.89	108	0.60	149	12.95
43	14.46	76	1.41	109	0.83	150	6.48
44	2.28	77	39.76	110	0.40	151	100.00
45	25.00	78	1.56	111	0.98	152	9.71
46	3.56	79	0.71	112	0.91	153	0.85
47	3.65	80	1.20	113	3.01	156	0.22
48	0.13	81	2.75	114	0.18	161	1.10
49	0.92	82	3.20	115	2.13	163	1.71
50	4.76	83	26.81	116	0.42	164	0.24
51	28.61	84	4.16	117	2.16	167	1.90
52	3.67	85	5.20	118	9.34	168	14.31
53	7.15	86	1.84	119	1.54	169	2.90
54	2.20	87	10.62	120	0.29	176	2.60
55	2.79	88	3.45	121	3.11	177	0.26
56	1.81	89	3.48	122	4.12	181	0.72
57	14.98	90	5.65	123	0.78	196	44.88
58	1.86	91	13.55	124	0.14	197	6.17
59	39.46	92	0.88	127	0.32	198	0.27
60	2.03	93	0.40	128	28.61		

61. 4,4,5,6,6,6-hexafluoro-3-methyl-2-hexenoic acid, ethyl ester **44b**



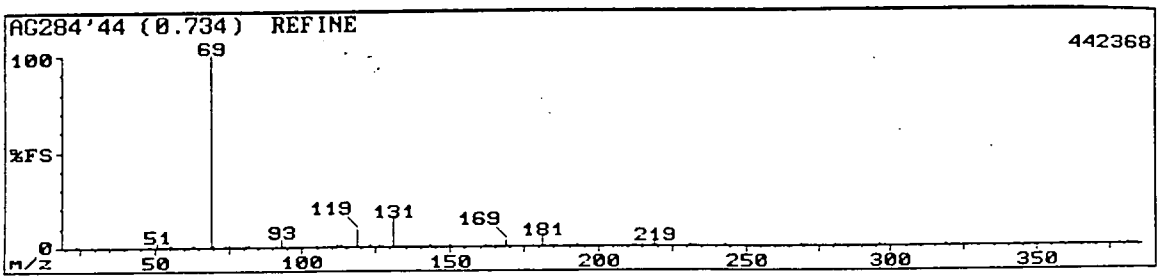


AG257 343 (5.717) 966656

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.69	75	8.16	126	0.27	191	0.38
21	0.08	76	0.76	127	1.56	192	0.06
24	1.06	77	10.70	128	0.46	196	2.73
25	2.75	78	0.51	129	0.67	197	2.36
26	14.19	79	0.40	130	0.74	198	0.11
27	48.31	80	0.23	131	3.15	199	1.03
28	23.52	81	1.64	132	1.01	199	1.23
29	83.47	82	5.30	133	1.24	200	0.94
30	5.85	83	6.99	134	0.31	201	0.15
31	15.25	84	1.80	135	1.52	203	0.07
32	2.91	85	3.81	136	0.22	205	0.14
33	2.20	86	2.01	137	0.99	207	0.05
35	0.07	87	4.26	138	0.10	209	0.08
35	0.06	88	3.81	139	1.31	211	0.03
36	0.46	89	11.97	140	0.35	216	19.07
37	5.01	90	13.77	141	0.41	217	7.94
38	9.32	91	5.91	143	0.11	219	100.00
39	48.31	92	0.39	145	1.75	220	4.21
40	12.08	93	1.19	147	23.94	221	0.29
41	10.49	94	0.55	148	2.25	224	0.09
42	4.77	95	3.58	149	3.87	225	0.03
43	14.41	96	0.34	150	0.45	227	0.06
44	9.43	97	0.40	151	9.32	229	0.37
45	14.94	98	0.22	152	0.71	235	0.34
46	1.34	99	2.62	153	0.64	236	7.20
47	1.80	100	2.54	154	0.09	236	11.76
48	0.37	101	12.82	155	0.18	237	4.37
49	1.49	102	3.60	156	0.05	238	0.32
50	6.12	103	6.38	157	0.46	239	0.06
51	22.14	104	0.56	159	0.28	244	0.84
52	1.85	105	0.74	160	0.05	245	0.77
53	3.34	106	0.89	161	0.07	246	0.07
54	0.54	107	4.24	163	4.29	247	0.04
55	1.96	108	1.36	164	0.16	249	0.07
56	1.99	109	16.10	165	0.14	249	0.12
57	8.90	110	0.83	167	0.12	251	0.07
58	1.36	111	0.42	168	0.77	260	0.07
59	11.02	112	0.49	169	1.17	260	0.09
60	0.87	113	3.42	170	0.21	264	22.99
61	0.48	114	0.76	171	7.84	265	20.76
62	1.20	115	2.54	172	0.64	266	1.28
63	5.19	116	0.29	173	0.72	267	0.13
64	15.25	117	1.37	176	0.91	275	0.10
65	5.14	118	9.85	177	0.79	278	0.03
67	26.69	119	2.89	179	1.07	278	0.03
68	3.65	120	1.24	181	0.16	281	0.06
69	36.86	121	4.98	183	0.09	293	0.15
70	3.05	122	1.30	185	0.06	303	0.17
71	4.61	123	0.19	186	0.05	305	0.08
72	1.93	124	0.07	187	0.09		
73	0.66	125	0.29	189	1.38		

62. perfluoro(2-methylhexane) **50**

$$(CF_3)_2CF(CF_2CF_2)_2F$$

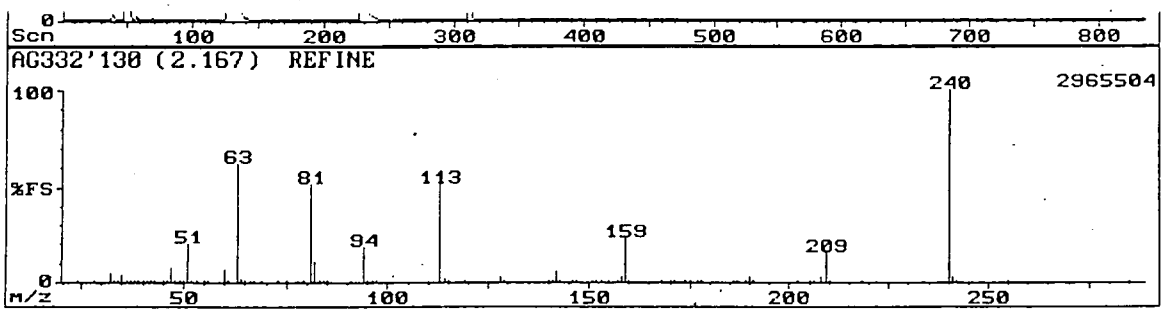


AG284'44 (0.734) REFINE 442368

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
24	0.13	75	0.06	126	0.22	219	2.20
51	2.31	81	1.26	131	14.70	231	0.75
55	0.30	82	0.19	143	0.31	243	0.15
56	0.07	93	3.94	150	0.79	269	0.91
63	0.16	112	0.97	162	0.21	281	0.02
69	100.00	113	0.18	169	2.56	296	0.05
70	1.22	119	8.33	181	5.21	319	0.16
74	0.91	123	0.12	193	0.18	381	0.29

63. (1,2,2-trifluoro-1-iodoethyl) methyl ether **52**

CH_3OCF_2CFHI

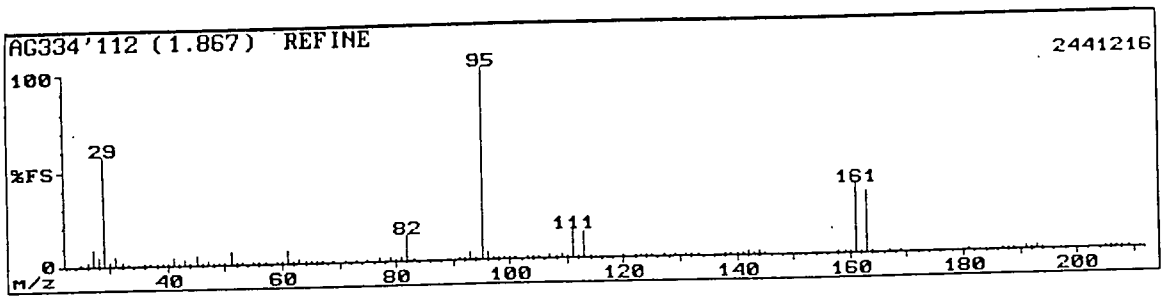


AG332'130 (2.167) REFINE 2965504

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
24	0.02	55	0.03	97	0.04	171	0.12
28	0.24	56	0.02	113	51.38	174	0.14
32	4.56	60	7.04	114	1.79	175	0.03
33	1.27	61	0.49	115	0.16	177	0.63
34	0.05	63	61.88	119	0.06	178	0.04
35	3.63	64	2.03	128	3.25	186	0.05
36	0.05	65	0.55	129	0.35	187	0.44
37	0.01	66	0.12	140	0.60	189	0.46
38	0.01	67	0.09	141	0.54	190	2.80
39	0.01	69	0.24	142	5.77	191	0.30
40	0.02	73	0.05	143	0.28	202	0.10
41	0.59	75	0.03	146	0.22	205	0.27
42	0.19	78	0.26	147	0.06	206	0.49
43	0.63	79	0.78	151	0.06	208	2.76
45	0.88	81	51.38	152	0.09	209	15.33
46	0.27	82	11.05	153	0.03	210	0.13
47	7.29	83	1.23	155	0.13	218	0.02
48	0.15	84	0.04	157	0.35	240	100.00
49	0.11	85	0.13	158	3.35	241	3.04
50	0.41	91	0.03	159	23.48	242	0.25
51	20.58	94	18.37	160	0.20	255	0.07
52	0.50	95	0.22	168	0.11	285	0.03
53	0.03	96	0.10	170	0.06		

64. (1,2,2-trifluoro-1-bromoethyl) ethyl ether **54**

$$CH_3CH_2OCF_2CFHBr$$

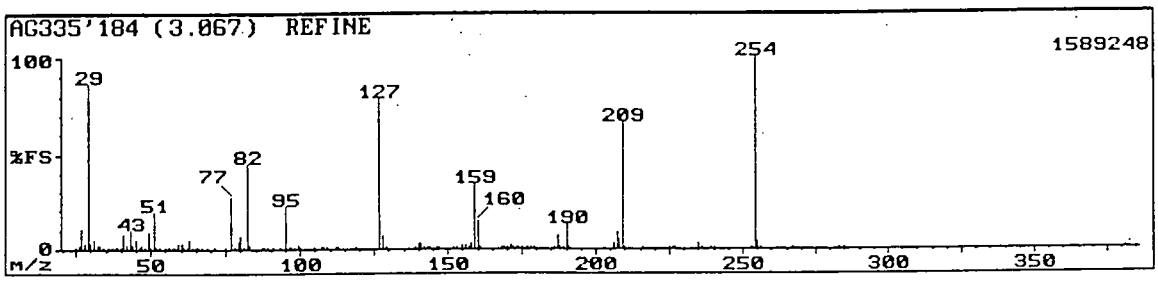


AG334'112 (1.867) REFINE 2441216

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
25	0.10	56	0.03	98	0.04	141	1.22
26	1.48	57	0.14	99	0.19	142	2.12
27	8.31	59	0.94	100	0.03	143	0.37
28	4.74	60	1.32	101	0.01	144	1.92
29	57.05	61	7.26	103	0.01	145	0.21
30	2.28	62	0.41	104	0.03	158	0.06
31	5.03	63	1.86	105	0.06	159	0.76
32	2.36	64	0.25	107	2.18	160	1.18
33	0.77	65	0.11	108	0.07	161	35.74
36	0.02	66	0.15	109	2.16	162	1.28
37	0.02	67	0.82	110	0.47	163	32.38
38	0.03	69	0.15	111	14.09	164	0.74
39	0.18	71	0.02	112	0.73	167	0.02
40	0.06	73	0.02	113	13.59	169	0.02
41	3.98	75	0.16	114	0.29	181	0.02
42	0.90	77	1.67	120	0.14	187	0.93
43	3.06	79	1.92	122	0.20	188	0.04
44	0.81	80	1.39	123	0.12	189	0.91
45	4.74	81	1.75	124	0.08	191	2.03
46	0.17	82	13.93	125	0.14	192	0.03
47	1.84	83	0.54	127	0.08	193	1.98
48	0.06	91	0.53	129	0.32	194	0.06
49	1.07	92	0.99	131	0.30	205	1.25
50	0.70	93	4.36	132	0.01	206	0.21
51	6.71	94	0.99	133	0.02	207	1.33
52	0.11	95	100.00	138	0.03	208	0.21
53	0.02	96	3.57	139	1.07	209	0.15
55	0.04	97	0.31	140	0.23		

65. (1,2,2-trifluoro-1-iodoethyl) ethyl ether **55**

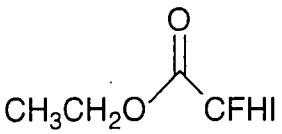
$CH_3CH_2OCF_2CFHI$

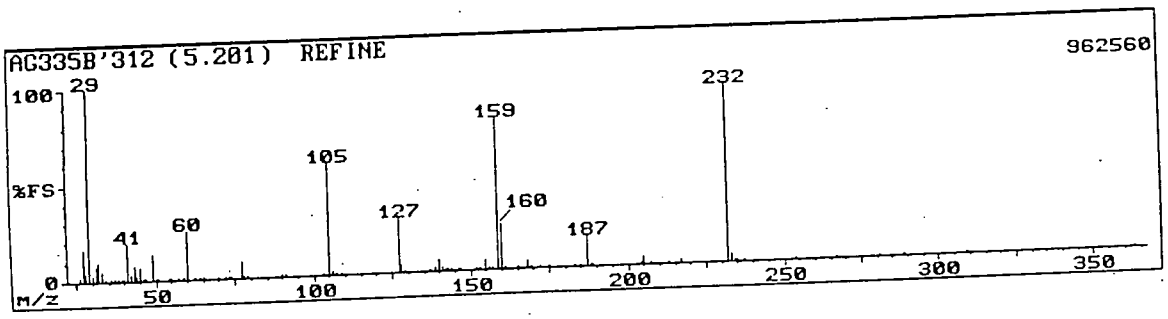


AG335'184 (3.067) REFINE 1589248

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
25	0.10	59	2.75	108	1.24	175	0.14
26	1.61	60	2.96	109	0.13	177	1.01
27	10.82	61	0.50	112	0.21	178	0.05
28	2.71	62	0.65	113	0.03	179	0.04
29	86.60	63	4.64	119	0.46	186	0.17
30	2.92	64	0.81	127	78.35	187	6.51
31	4.45	65	0.11	128	7.02	188	0.46
32	2.24	66	0.15	129	0.56	189	0.60
33	1.80	67	0.99	139	1.40	190	12.37
34	0.04	69	0.29	140	3.35	191	0.64
36	0.02	71	0.08	141	2.74	206	2.72
37	0.03	75	0.11	142	0.89	207	8.31
38	0.05	77	27.58	143	0.19	208	4.83
39	0.41	78	1.05	144	0.20	209	65.98
40	0.10	79	4.12	146	0.69	210	1.34
41	7.60	80	6.51	147	0.25	216	0.02
42	2.22	81	0.70	152	0.09	225	0.03
43	9.41	82	44.85	153	0.08	226	0.03
44	1.59	83	1.64	155	1.95	227	0.09
45	4.70	87	0.06	156	2.05	235	2.67
46	0.21	88	0.03	157	0.37	236	0.12
47	2.40	89	0.05	158	2.63	239	1.35
48	0.12	91	0.02	159	34.28	240	0.05
49	9.02	93	0.05	160	14.88	253	0.63
50	0.91	95	21.91	161	0.20	254	100.00
51	19.07	96	0.76	168	0.75	255	4.19
52	0.27	97	0.11	169	0.03	256	0.27
53	0.03	98	0.08	170	0.51	267	0.02
55	0.07	99	1.51	171	1.82	283	0.06
56	0.04	100	0.05	172	0.06	285	0.04
57	1.11	105	0.03	173	0.06	381	0.17
58	0.06	107	0.08	174	0.03		

66. Ethyl fluoroiodioacetate **56**



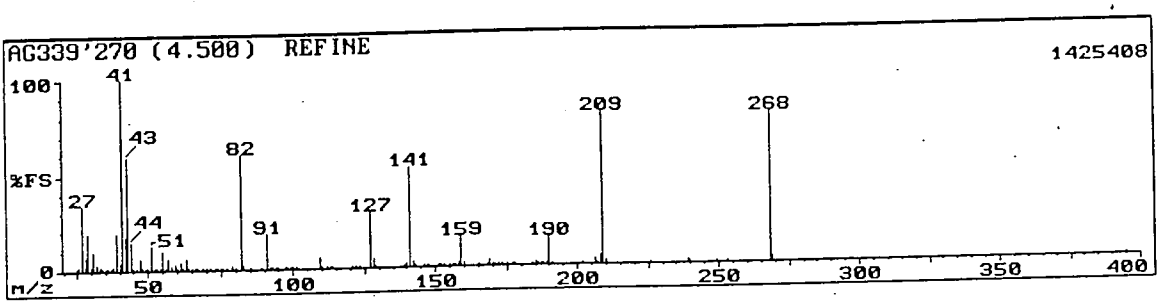


AG335B'312 (5.201) REFINE 962560

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	1.70	51	0.05	127	28.51	172	0.06
27	16.06	54	0.04	128	3.72	175	0.12
28	4.34	55	0.07	129	0.43	183	0.09
29	100.00	57	0.54	137	0.28	185	0.62
30	3.30	59	0.82	139	1.64	187	15.21
31	7.87	60	25.32	140	5.53	188	0.40
32	9.68	62	0.22	141	2.15	189	0.12
33	5.13	64	0.13	142	0.23	204	0.65
34	0.16	65	0.02	143	0.41	205	3.40
36	0.06	70	0.04	144	0.15	207	0.08
37	0.05	72	0.09	146	0.11	213	0.06
38	0.09	73	0.26	147	0.07	217	1.56
39	0.90	74	0.02	152	0.08	232	92.34
40	0.24	77	8.62	153	0.10	233	4.02
41	19.47	78	0.53	155	4.71	234	0.50
42	2.95	79	0.07	156	0.42	235	0.27
43	8.19	90	0.17	157	1.18	237	0.07
44	1.52	91	0.09	159	78.72	254	0.25
45	6.41	103	0.14	160	23.30	267	0.06
46	0.29	105	58.72	161	0.31	281	0.35
47	0.62	106	2.31	165	0.17	289	0.10
49	13.51	107	0.31	168	4.34	309	0.22
50	0.28	109	0.07	169	0.32	363	0.13

67. (1,2,2-trifluoro-1-iodoethyl) propyl ether **57**

$CH_3CH_2CH_2OCF_2CFHI$

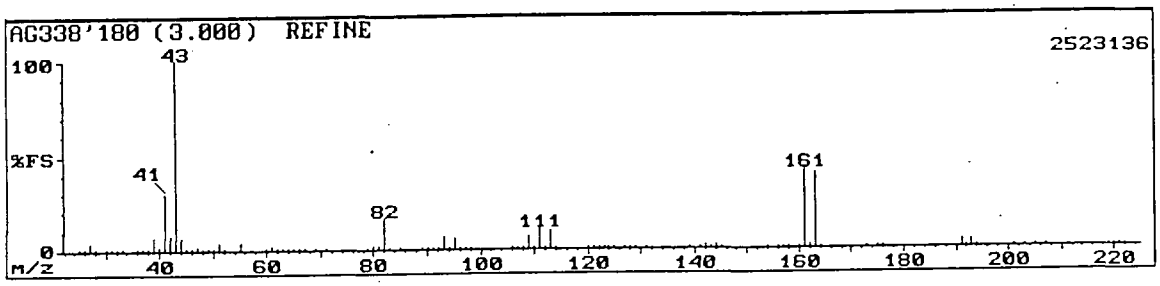


AG339'270 (4.500) REFINE 1425408

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
25	0.08	57	5.75	99	0.68	169	2.55
26	1.99	58	1.63	100	0.03	170	0.72
27	34.20	59	2.95	101	0.06	171	0.88
28	6.47	60	1.44	109	5.68	172	0.04
29	19.25	61	3.75	110	0.29	173	0.08
30	2.32	62	0.14	112	0.45	175	0.09
31	9.63	63	5.82	113	0.51	177	0.77
32	2.73	64	1.22	114	0.03	178	0.05
33	1.67	65	0.58	121	0.43	184	0.13
34	0.05	66	0.24	122	0.68	185	1.89
35	0.07	67	0.50	123	0.05	186	0.11
36	0.05	69	0.29	127	29.31	187	0.67
37	0.76	70	0.03	128	4.96	188	0.22
38	2.08	71	0.07	129	0.68	189	0.62
39	19.83	73	0.21	139	1.15	190	14.94
40	4.20	74	0.05	140	2.10	191	1.14
41	100.00	75	0.14	141	52.30	202	0.04
42	17.74	76	0.02	142	2.89	206	2.95
43	59.48	77	0.08	143	0.32	207	0.12
44	14.22	79	1.80	146	0.62	208	5.17
45	1.40	80	0.51	147	0.17	209	79.31
46	0.25	82	60.06	151	0.03	210	1.74
47	6.03	83	2.08	152	0.08	226	0.27
48	0.27	85	0.06	153	0.07	239	2.32
49	0.80	89	0.06	155	0.53	240	0.09
50	0.61	91	18.68	156	0.58	249	0.32
51	12.14	92	0.81	157	0.52	253	0.04
52	0.24	93	0.21	158	1.85	268	78.16
53	0.43	94	0.10	159	15.59	269	3.38
54	0.10	95	0.06	160	1.58	395	0.15
55	9.55	97	0.06	165	0.04		
56	0.71	98	0.06	168	0.51		

68. (1,2,2-trifluoro-1-bromoethyl) propyl ether **58**

$$CH_3CH_2CH_2OCF_2CFHBr$$

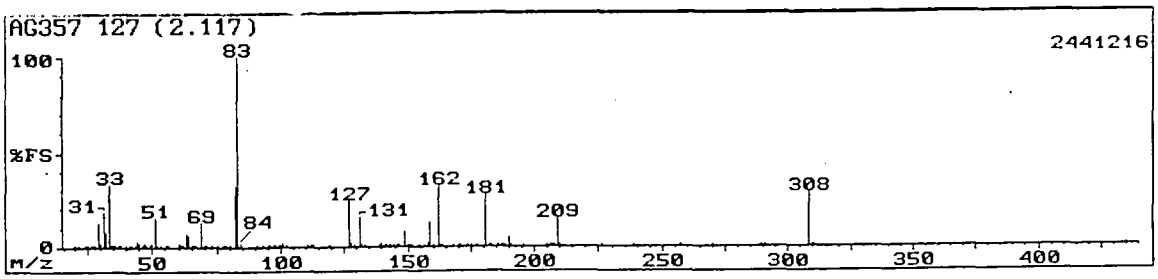


AG338'180 (3.000) REFINE 2523136

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
25	0.02	60	0.39	106	0.02	156	0.05
26	0.54	61	2.37	107	0.15	157	0.02
27	4.02	62	0.18	108	0.06	158	0.06
28	0.83	63	1.38	109	6.90	160	1.19
30	0.22	64	0.25	110	0.77	161	42.21
31	1.36	65	0.22	111	10.39	162	1.80
32	0.54	66	0.13	112	0.57	163	39.77
33	0.20	67	0.22	113	10.15	164	0.72
36	0.02	69	0.11	114	0.15	173	0.20
37	0.24	71	0.03	120	0.06	175	0.30
38	0.76	79	0.97	121	0.02	176	0.01
39	7.02	80	1.54	122	0.11	191	4.34
40	1.60	81	2.32	123	0.12	192	0.12
41	30.19	82	16.07	124	0.06	193	4.34
42	7.87	83	0.56	125	0.13	194	0.13
43	100.00	85	0.03	127	0.05	201	0.04
44	6.86	89	0.08	128	0.02	203	0.03
45	1.18	90	0.02	129	0.22	205	0.02
46	0.11	91	0.32	131	0.20	207	0.02
47	1.52	92	0.56	139	0.95	219	0.19
48	0.06	93	6.33	141	1.16	220	0.04
49	0.15	94	0.63	142	2.39	221	0.19
50	0.34	95	5.76	143	0.53	222	0.03
51	3.77	96	0.08	144	2.37		
52	0.09	97	0.03	145	0.32		
55	3.45	98	0.02	154	0.07		

69. (1,1,1-trifluoroethyl) (1,2,2-trifluoro-1-iodoethyl) ether **60**

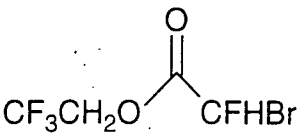
$CF_3CH_2OCF_2CFHI$

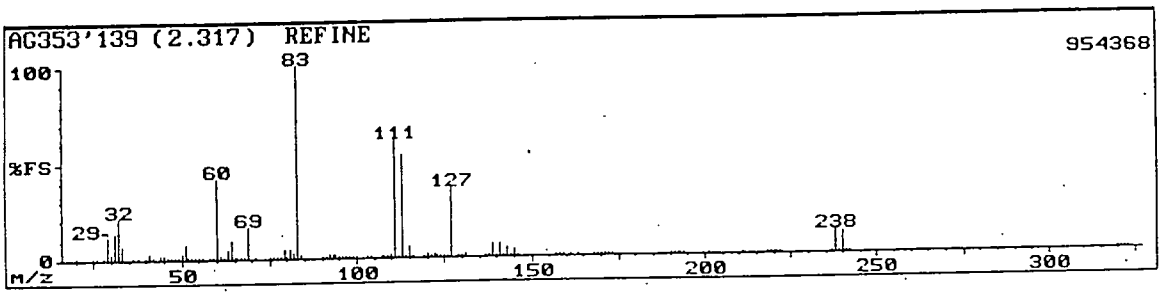


AG357 127 (2.117) 2441216

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.07	56	0.01	112	0.03	174	0.02
21	0.01	60	2.11	113	0.09	175	0.03
24	0.10	61	0.86	119	0.01	177	0.98
25	0.29	62	0.31	127	24.66	181	26.85
26	0.50	63	6.96	128	2.11	182	1.02
27	0.24	64	6.17	129	0.19	183	0.04
28	1.15	65	0.26	131	15.10	186	0.03
29	12.75	66	0.06	132	0.45	187	0.62
30	2.15	67	0.13	133	0.05	188	0.06
31	18.12	69	12.58	139	0.89	189	0.16
32	8.14	70	0.16	140	1.46	190	4.99
33	33.22	71	0.02	141	0.53	191	0.78
34	0.44	73	0.03	142	0.04	196	0.01
35	0.03	75	0.05	143	0.10	205	0.09
36	0.04	77	0.02	145	0.01	206	0.58
37	0.02	78	0.12	146	0.48	207	0.11
38	0.02	79	0.89	147	0.05	208	1.20
40	0.09	80	1.45	149	7.55	209	14.77
41	0.47	82	31.71	150	0.23	210	0.34
42	0.14	83	100.00	151	0.04	226	0.16
43	0.48	84	2.35	152	0.04	239	0.35
44	2.85	91	0.06	155	0.18	257	0.02
45	1.90	93	0.29	157	0.53	270	0.06
46	0.10	95	0.19	158	1.55	289	0.62
47	2.12	96	0.01	159	12.42	290	0.02
48	0.05	97	0.09	160	0.16	308	27.68
49	0.39	98	0.03	162	32.21	309	0.93
50	2.13	99	0.26	163	1.25	310	0.08
51	15.60	100	0.03	164	0.10	435	0.03
52	0.21	101	1.80	168	0.13		
53	0.03	102	0.04	170	0.21		
55	0.02	111	0.06	171	0.08		

70. Trifluoroethyl bromofluoroacetate **61**



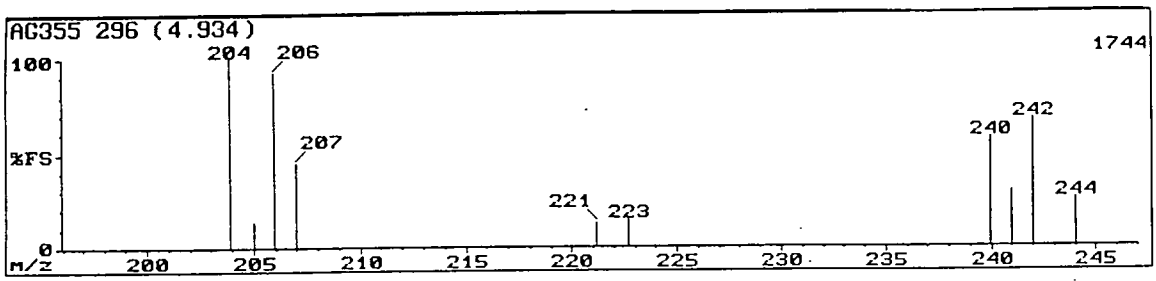


AG353'139 (2.317) REFINE 954368

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	63	5.31	108	0.02	158	0.03
25	0.29	64	9.44	109	0.31	159	1.34
26	0.30	65	0.33	110	2.20	161	0.11
28	0.35	66	0.01	111	61.37	163	0.08
29	11.80	67	0.02	112	1.29	168	0.02
30	3.17	68	0.79	113	53.65	169	0.60
31	13.84	69	16.95	114	0.53	170	0.03
32	21.78	71	0.04	115	5.39	171	0.93
33	6.41	75	0.06	116	0.14	172	0.04
36	0.03	76	0.04	119	0.04	173	0.13
38	0.02	77	0.04	120	1.50	190	0.03
40	0.20	78	0.36	121	0.07	191	0.82
41	2.95	79	5.31	122	1.48	192	0.03
42	0.39	80	1.17	123	0.56	193	0.78
44	2.39	81	4.83	124	0.02	194	0.03
45	2.23	82	2.82	125	0.41	201	0.02
46	0.11	83	100.00	126	0.95	211	0.02
47	0.86	84	2.07	127	36.05	218	0.02
48	0.25	90	0.17	129	0.72	219	0.37
49	0.81	91	0.95	130	0.06	220	0.02
50	2.66	92	2.20	131	2.04	221	0.37
51	7.40	93	1.90	137	0.02	222	0.03
52	0.18	94	2.25	138	0.52	237	0.33
53	0.03	95	1.19	139	6.49	238	11.37
54	0.02	96	0.03	140	1.41	239	1.06
55	0.02	97	0.08	141	6.55	240	10.41
56	0.72	98	0.06	142	0.13	241	0.74
58	0.14	99	0.11	143	4.77	242	0.07
59	0.84	100	0.03	144	0.25	320	0.02
60	41.63	103	0.03	145	4.29	321	0.29
61	2.15	104	0.04	146	0.09	322	0.02
62	0.42	107	0.20	157	0.02	323	0.30

71. (1,2,2-trifluoro-1-bromoethyl) 2-chloroethyl ether **62**

$ClCH_2CH_2OCF_2CFHBr$



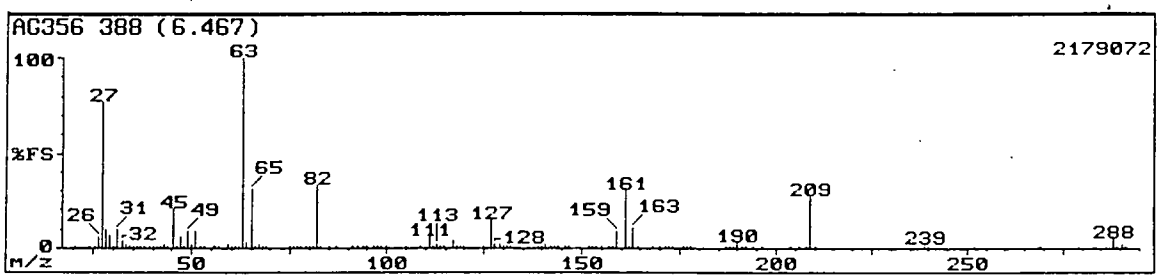
2670592

AG355 296 (4.934)

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	53	0.03	96	0.13	139	0.65
21	0.01	55	0.01	97	0.55	140	0.02
24	0.08	56	0.02	98	0.07	141	0.77
25	0.65	57	0.06	99	0.14	142	1.74
26	7.90	59	4.79	100	0.03	143	0.33
27	68.71	60	0.75	101	0.03	144	1.65
28	12.27	61	1.76	104	0.04	145	0.20
29	8.63	62	2.84	105	0.05	147	0.02
30	1.78	63	100.00	107	0.52	158	0.03
31	13.34	64	3.22	108	0.02	161	31.90
32	4.98	65	31.29	109	0.57	162	0.77
33	1.11	66	0.53	110	0.36	163	30.06
34	0.02	67	0.56	111	16.41	164	0.39
35	0.67	69	0.23	112	0.51	174	0.01
36	0.57	73	0.02	113	16.10	176	0.02
37	0.32	75	0.47	114	0.19	179	0.02
38	0.24	76	0.10	116	0.03	191	9.97
39	0.09	77	0.13	117	0.35	192	0.08
40	0.09	78	0.07	118	0.01	193	9.59
41	0.44	79	1.59	119	0.12	194	0.24
42	1.44	80	0.73	120	0.07	204	0.07
43	1.42	81	1.66	122	0.16	205	0.01
44	1.08	82	12.88	123	0.12	206	0.06
45	1.44	83	0.46	124	0.07	207	0.03
46	0.08	85	0.03	125	0.15	221	0.01
47	2.24	87	0.02	127	0.11	223	0.01
48	1.04	91	0.45	129	28.22	240	0.04
49	8.55	92	0.64	130	0.73	241	0.02
50	1.75	93	4.95	131	9.16	242	0.04
51	8.24	94	0.79	132	0.26	244	0.02
52	0.35	95	5.44	133	0.02		

72. (1,2,2-trifluoro-1-iodoethyl) 2-chloroethyl ether **63**

$ClCH_2CH_2OCF_2CFHI$

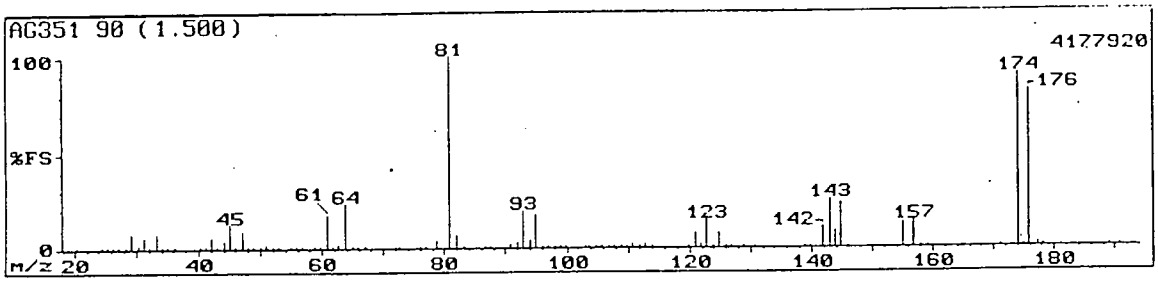


AG356 388 (6.467) 2179072

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.07	57	0.07	111	5.78	163	10.29
24	0.06	59	2.02	112	0.26	164	0.35
25	0.41	60	0.87	113	2.04	168	0.15
26	5.69	61	1.39	114	0.07	170	0.32
27	76.69	62	0.81	115	0.09	171	0.12
28	9.35	63	100.00	117	3.62	172	0.01
29	7.00	64	3.29	118	0.09	173	0.03
30	1.28	65	30.64	119	1.20	176	0.49
31	9.63	66	0.85	120	0.02	177	0.24
32	3.76	67	1.74	125	0.04	178	0.14
33	1.46	68	0.02	127	14.47	187	0.20
34	0.04	69	0.62	128	2.23	188	0.02
35	0.43	75	0.06	129	1.70	189	0.11
36	0.59	76	0.09	130	0.04	190	3.38
37	0.21	77	0.32	131	0.48	191	0.25
38	0.22	78	0.05	132	0.01	192	0.02
39	0.11	79	0.79	139	0.55	194	0.31
40	0.07	80	0.46	140	1.08	196	0.06
41	0.38	81	0.33	141	1.59	204	0.02
42	1.23	82	33.27	142	0.58	206	0.32
43	1.94	83	1.27	143	0.09	208	1.22
44	0.75	85	0.02	144	0.16	209	27.44
45	19.92	87	0.03	146	0.26	210	0.31
46	0.59	91	0.02	147	0.06	239	2.20
47	5.64	93	0.06	152	0.04	240	0.03
48	0.88	94	0.02	153	0.06	252	0.02
49	8.83	95	0.05	154	0.02	269	0.03
50	1.57	97	0.02	155	0.30	288	4.79
51	8.46	98	0.07	157	0.20	289	0.16
52	0.39	99	0.08	158	0.80	290	1.60
53	0.02	100	0.02	159	8.65	291	0.06
55	0.02	105	0.02	161	30.45		
56	0.03	109	0.01	162	1.21		

73. (2,2-difluoro-1-bromopropyl) methyl ether **64**

$CH_3OCF_2CH_2Br$

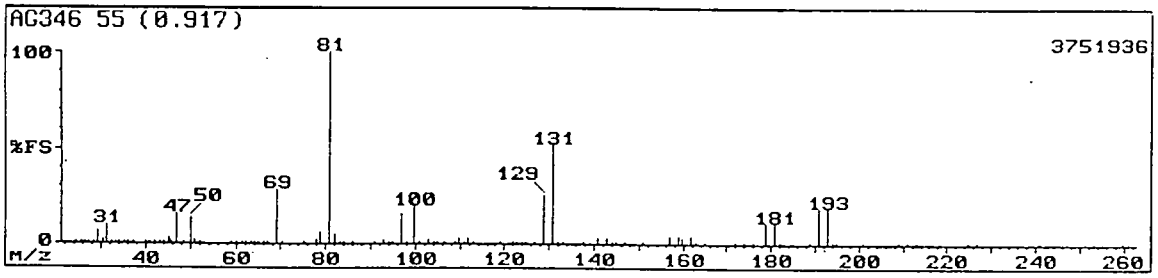


AG351 90 (1.500) 4177920

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	52	0.06	92	3.04	125	7.45
24	0.02	53	0.02	93	19.02	126	0.28
25	0.15	55	0.10	94	3.43	127	0.38
26	0.51	56	0.02	95	17.75	129	0.26
27	0.94	57	0.02	96	0.37	131	0.15
28	0.62	59	0.01	97	0.10	139	0.19
29	7.84	60	0.25	98	0.02	140	0.50
30	1.46	61	17.84	99	0.01	142	10.20
31	5.61	62	0.28	100	0.03	143	25.49
32	0.66	63	1.96	103	0.03	144	8.92
33	7.75	64	23.04	104	0.11	145	23.63
34	0.13	65	1.29	105	0.11	146	0.55
35	0.03	66	0.06	106	0.13	155	12.65
36	0.01	67	0.26	107	0.28	157	13.14
40	0.03	72	0.03	108	0.78	158	0.37
41	0.66	73	0.01	109	0.26	159	0.03
42	6.15	75	0.77	110	1.10	171	0.02
43	0.75	76	1.13	111	1.89	174	90.20
44	3.95	77	0.05	112	0.30	175	1.18
45	12.45	79	3.68	113	1.89	176	81.18
46	1.16	81	100.00	114	0.02	177	1.62
47	8.63	82	7.25	120	1.26	178	0.22
48	0.13	83	0.77	121	7.75	189	0.44
49	0.03	87	0.05	122	1.62	191	0.45
50	0.60	88	0.03	123	14.71		
51	1.64	91	1.64	124	0.89		

74. (1,1,2,2-tetrafluoro-1-bromoethyl) methyl ether **65**

$CH_3OCF_2CF_2Br$

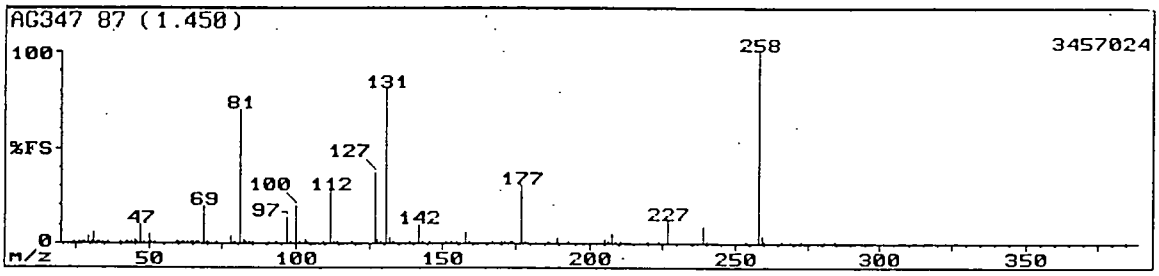


AG346 55 (0.917) 3751936

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
24	0.01	59	0.03	101	0.55	151	0.03
25	0.01	60	0.03	103	2.05	157	3.74
26	0.06	62	0.25	104	0.07	159	4.09
27	0.04	62	0.38	105	0.07	160	3.03
28	0.39	63	0.25	107	0.42	162	3.41
29	7.10	64	0.50	109	0.63	163	0.21
30	1.56	65	0.72	110	2.65	165	0.08
31	10.15	66	0.27	111	0.32	172	0.02
32	0.42	67	0.21	112	2.97	174	0.02
33	0.78	69	28.38	113	0.17	176	0.01
34	0.03	70	0.26	119	0.04	179	10.48
35	0.02	75	0.03	122	0.12	181	10.70
36	0.01	78	1.91	123	0.04	182	0.19
37	0.01	79	5.46	124	0.13	189	0.12
40	0.07	81	100.00	125	0.04	191	18.01
41	0.02	82	4.53	127	0.01	193	18.23
42	0.27	83	0.50	129	24.78	194	0.47
43	1.22	84	0.04	131	51.53	195	0.05
44	0.24	86	0.03	132	1.17	201	0.02
45	2.51	91	1.05	133	0.08	209	0.49
46	0.05	93	2.16	138	0.06	211	0.53
47	15.17	94	0.83	141	2.65	213	0.09
48	0.16	95	1.04	143	2.65	225	0.20
50	13.76	97	15.83	144	0.08	227	0.20
51	1.49	98	0.38	145	0.08	241	0.02
52	0.03	100	19.10	147	0.09	260	0.02

75. (1,1,2,2-tetrafluoro-1-iodoethyl) methyl ether **66**

$CH_3OCF_2CF_2I$

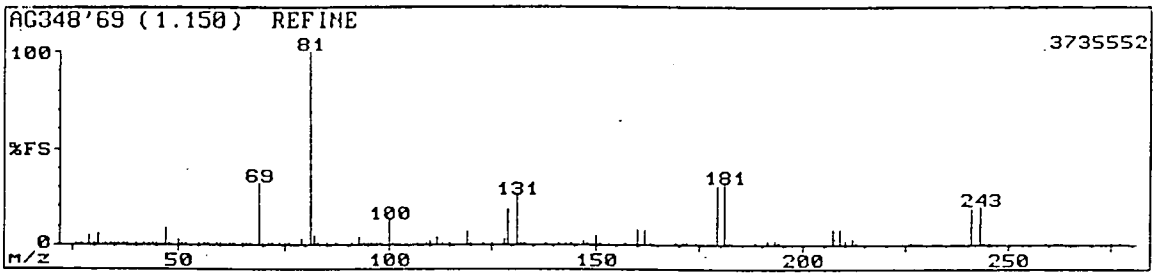


AG347 87 (1.450) 3457024

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
24	0.01	62	0.30	112	26.78	178	0.25
26	0.04	63	0.29	113	0.90	186	0.06
27	0.05	64	0.44	114	0.08	189	2.46
28	0.31	65	0.72	119	0.02	193	0.03
29	3.82	66	0.18	127	36.49	205	1.73
30	0.79	67	0.17	128	1.90	206	0.03
31	6.28	69	19.67	129	0.28	208	4.74
32	0.26	70	0.18	131	81.04	209	0.16
33	0.49	73	0.02	132	2.81	211	0.05
34	0.02	78	3.91	133	0.22	220	0.05
36	0.01	79	0.10	139	1.28	224	0.20
40	0.04	81	69.67	142	10.19	227	11.85
42	0.26	82	1.87	143	0.27	239	8.29
43	0.89	83	0.29	146	0.50	240	0.22
44	0.08	84	0.01	151	0.06	254	0.03
45	1.93	85	0.02	153	0.01	258	100.00
46	0.05	91	0.03	155	0.72	259	3.47
47	9.95	93	0.01	158	6.10	260	0.27
48	0.07	97	13.27	159	0.12	266	0.03
50	5.18	98	0.30	167	0.02	269	0.02
51	1.01	100	19.67	170	0.29	273	0.17
52	0.02	101	0.64	171	0.02	281	0.02
59	0.02	103	2.01	173	0.04	285	0.15
60	0.05	104	0.06	174	0.07	385	0.15
61	0.16	109	0.02	177	30.33		

76. (1,1,1,2,3,3-hexafluoro-2-bromopropyl) methyl ether **67**

$CH_3OCF_2CFBrCF_3$

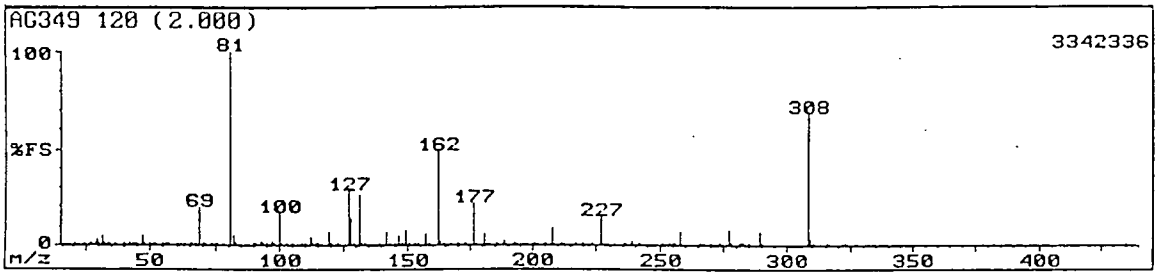


AG348'69 (1.150) REFINE 3735552

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.04	63	0.19	109	0.90	171	0.10
27	0.07	65	0.61	110	2.25	172	0.15
29	5.26	66	0.13	112	4.28	174	0.15
30	1.33	67	0.12	113	0.30	179	29.82
31	6.28	69	32.02	115	0.01	181	31.14
33	0.41	70	0.31	119	6.91	182	0.58
34	0.03	71	0.31	120	0.17	188	0.39
35	0.03	72	0.01	123	0.06	191	2.41
36	0.01	74	0.55	125	0.06	193	2.00
37	0.02	75	0.15	128	2.88	194	0.03
38	0.01	76	0.01	129	18.31	207	7.46
40	0.04	79	3.10	131	25.66	209	7.89
42	0.18	81	100.00	132	0.51	210	2.33
43	0.51	82	5.02	133	0.03	212	2.47
44	0.19	83	0.78	138	0.13	213	0.13
45	0.58	85	0.21	141	1.28	226	0.02
47	8.55	87	0.04	143	1.24	241	18.86
48	0.13	91	1.03	144	0.05	243	19.08
50	2.47	93	3.76	147	1.86	244	0.68
51	0.66	94	0.42	148	0.06	245	0.05
52	0.04	95	0.54	150	4.88	259	0.30
55	0.10	96	0.29	151	0.15	261	0.31
56	0.02	97	1.26	157	0.48	262	0.02
57	0.02	98	0.05	160	7.35	263	0.02
59	0.02	100	12.83	162	7.79	275	0.11
60	0.02	101	0.32	163	0.20	277	0.10
62	0.94	107	0.24	169	0.09		

77. (1,1,1,2,3,3-hexafluoro-2-iodopropyl) methyl ether **68**

$CH_3OCF_2CFICF_3$



AG349 120 (2.000) 3342336

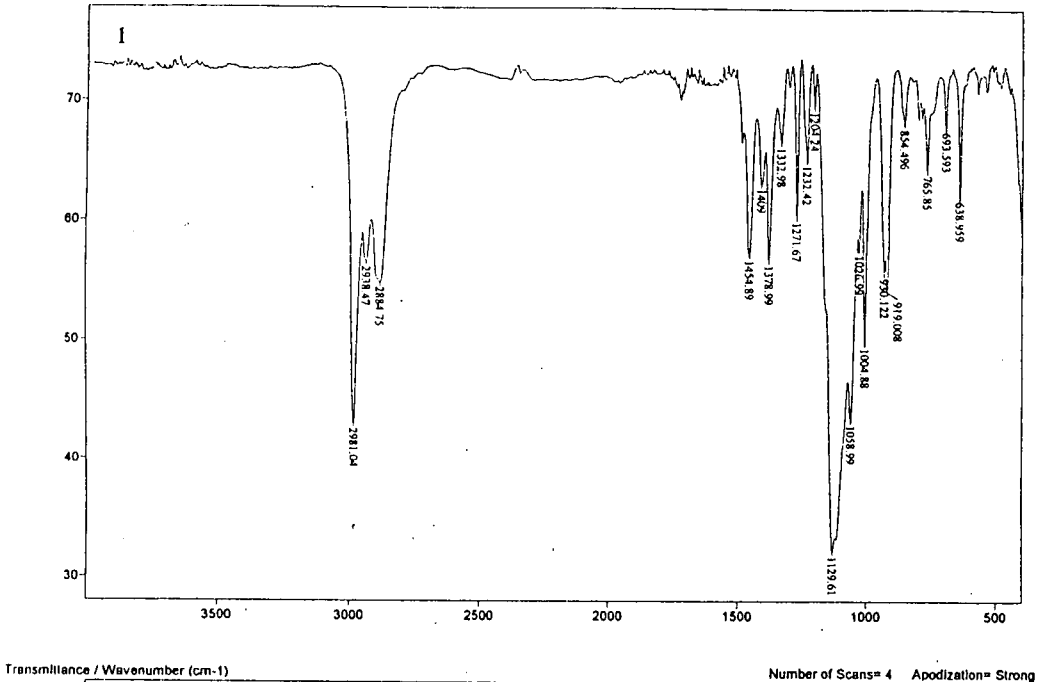
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	69	19.85	128	13.60	211	0.02
24	0.01	70	0.20	129	0.90	217	0.13
26	0.03	71	0.29	131	25.98	220	0.04
27	0.06	74	0.43	132	0.86	223	0.02
28	0.23	75	0.15	133	0.09	227	14.34
29	3.31	76	0.02	139	0.97	236	0.64
30	0.87	78	0.77	142	7.23	239	2.39
31	4.90	81	100.00	143	0.19	242	0.02
32	0.16	82	4.53	146	0.49	251	0.02
33	0.36	83	0.42	147	4.72	254	0.20
34	0.02	90	0.22	148	0.13	255	0.93
36	0.01	91	0.07	150	7.84	256	0.03
40	0.03	93	2.33	151	0.51	258	6.95
42	0.11	94	0.28	153	0.04	266	0.02
43	0.41	95	0.14	155	0.25	267	0.01
44	0.08	97	2.30	158	5.76	270	0.20
45	0.45	98	0.06	159	0.11	274	0.36
47	5.24	100	16.54	162	49.02	277	7.35
48	0.03	101	0.55	163	1.96	278	0.19
50	1.42	103	0.11	164	0.11	281	0.06
51	0.77	105	0.02	167	0.02	282	0.01
52	0.03	109	0.99	170	0.61	283	0.01
55	0.10	110	0.08	173	0.04	285	0.06
56	0.02	112	4.01	177	21.08	289	6.92
57	0.01	113	0.48	181	6.13	290	0.27
60	0.03	114	0.03	186	0.07	308	68.14
62	0.78	115	0.02	189	1.95	309	2.60
63	0.15	119	7.11	193	0.01	310	0.18
65	0.40	120	0.15	201	0.04	316	0.02
66	0.09	123	0.01	205	0.40	323	0.14
67	0.09	127	28.43	208	8.33	435	0.11

Appendix 3

IR Spectra

1. 1,2,2-trifluoro-3-ethoxybutane **1a** and 1,1,2-trifluoro-3-ethoxybutane **1b**
2. 2-(1',1',2'-trifluoro-1'-ethyl)-tetrahydrofuran **2a** and 2-(1',2',2'-trifluoro-1'-ethyl)-tetrahydrofuran **2b**
3. 1-(1',1',2'-trifluoro-1'-ethyl)-cyclohexane **3a** and 1-(1',2',2'-trifluoro-1'-ethyl)-cyclohexane **3b**
4. 2-(1',1',2'-trifluoro-1'-ethyl)-tetrahydropyran **4a** and 2-(1',2',2'-trifluoro-1'-ethyl)-tetrahydropyran **4b**
5. 2-(1',1',2'-trifluoro-1'-ethyl)-1,4-dioxane **5a** and 2-(1',2',2'-trifluoro-1'-ethyl)-1,4-dioxane **5b**
6. 2-(1',1',2',3',3',3'-hexafluoropropyl)-1,3-dioxane **8a**
7. 1,2,2-trifluoro-3-(diethylamino)butane **9a**
8. di(1,2,2-trifluorobut-3-yl) ethylamine **10a** and isomers
9. 2,2,3-trifluoro-1-propanol **12a** and 2,3,3-trifluoro-1-propanol **12b**
10. 3,3,4-trifluoro-2-butanol **13a** and 24. 3,4,4-trifluoro-2-butanol **13b**
11. 4-chloro-3,3-difluoro-2-butanol **13c**
12. 4,4,5-trifluoro-2-propanol **14a** and 4,5,5-trifluoro-2-propanol **14b**
13. 3,3,4-trifluoro-2-methyl-2-butanol **15a** and 3,4,4-trifluoro-2-methyl-2-butanol **15b**
14. 3,3,4-trifluoro-2-butanone **16**
15. 3,4,4-trifluoro-2-butanone **17**
16. 4,4,5-trifluoro-2,2-dimethyl-3-pentanone **18a** and 4,5,5-trifluoro-2,2-dimethyl-3-pentanone **18a**
17. (Z)-1,2-difluoro-3-ethoxy-1-butene **19**
18. 2,2,3-trifluoropropyl methacrylate **20a** and 2,3,3-trifluoropropyl methacrylate **20b**
19. 3,3,4-trifluoro-2-butyl methacrylate **21a** and 3,4,4-trifluoro-2-butyl methacrylate **21b**
20. 3,3,-difluoro-4-methyl oxetane **22**
21. 1,-difluoromethyl-2-methyl oxirane **23**
22. 3,3-difluoro-4,4-dimethyl oxetane **24**
23. 3,3-difluoro-2-spirocyclohexyloxetane **27**
24. (E)-3,4,5,5,5-pentafluoro-2-methyl-4-propen-2-ol **31**
25. Oligomer **32**
26. 1-(1',1',2'-trifluoro-1'-ethyl)-1-cyclohexene **33**
27. 3,3,4-trifluoro-2-methyl-1-butene **34a** and 3,4,4-trifluoro-2-methyl-1-butene **34b**

28. 49. 3,3,4-trifluoro-2-butyl tosylate **35a** and 3,4,4-trifluoro-2-butyl tosylate **35b**
29. 1,2,2,6,6,7-hexafluoro-5-methyl-4-hydroxy-heptan-3-one **37a**
30. 1,2,2,6,6,7-hexafluoro-5-methyl-4-hepten-3-one **38a**
31. 1,1,1,2,3,3,7,7,8,9,9,9-dodecaafluoro-6-methyl-5-hepten-4-one **38b**
32. 2,2,3-trifluoropropanoic acid **39**
33. 2-((E)-1,2-difluoroethenyl)-1,3-dioxolane **41**
34. 2,2-dimethyl-4,5-difluoro-3-penten-4-one **42**
35. 4,4,5-trifluoro-3-methyl-2-pentenoic acid, ethyl ester **44a**
36. 4,4,5,6,6,6-hexafluoro-3-methyl-2-hexenoic acid, ethyl ester **44b**
37. Bulk poly(trifluoroethene) **45**
38. Acetone / trifluoroethene polymer **46**
39. Fluorination of bulk poly(trifluoroethene) **47**
40. Fluorination of acetone / trifluoroethene polymer **48**
41. Perfluoroisopropyl iodide / trifluoroethene 1:2 telomer **49**
42. Perfluoro(2-methylhexane) **50**
43. Isobutene / trifluoroethene copolymer **51**
44. (1,2,2-trifluoro-1-iodoethyl) methyl ether **52**
45. (1,2,2-trifluoro-1-bromoethyl) ethyl ether **54**
46. (1,2,2-trifluoro-1-iodoethyl) ethyl ether **55**
47. Ethyl fluoroiodioacetate **56**
48. (1,2,2-trifluoro-1-iodoethyl) propyl ether **57**
49. (1,1,1-trifluoroethyl) (1,2,2-trifluoro-1-bromoethyl) ether **59**
50. (1,1,1-trifluoroethyl) (1,2,2-trifluoro-1-iodoethyl) ether **60**
51. Trifluoroethyl bromofluoroacetate **61**
52. (1,2,2-trifluoro-1-bromoethyl) 2-chloroethyl ether **62**
53. (1,2,2-trifluoro-1-iodoethyl) 2-chloroethyl ether **63**
54. (2,2-difluoro-1-bromopropyl) methyl ether **64**
55. (1,1,2,2-tetrafluoro-1-bromoethyl) methyl ether **65**
56. (1,1,1,2,3,3-hexafluoro-2-bromopropyl) methyl ether **67**
57. (1,1,1,2,3,3-hexafluoro-2-iodopropyl) methyl ether **68**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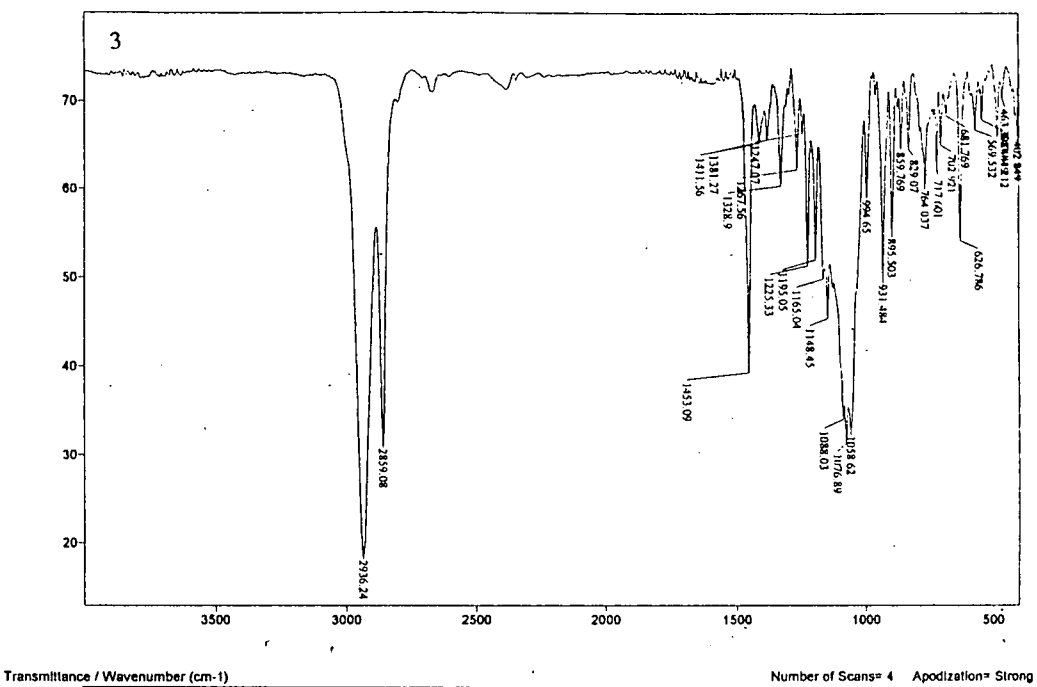
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong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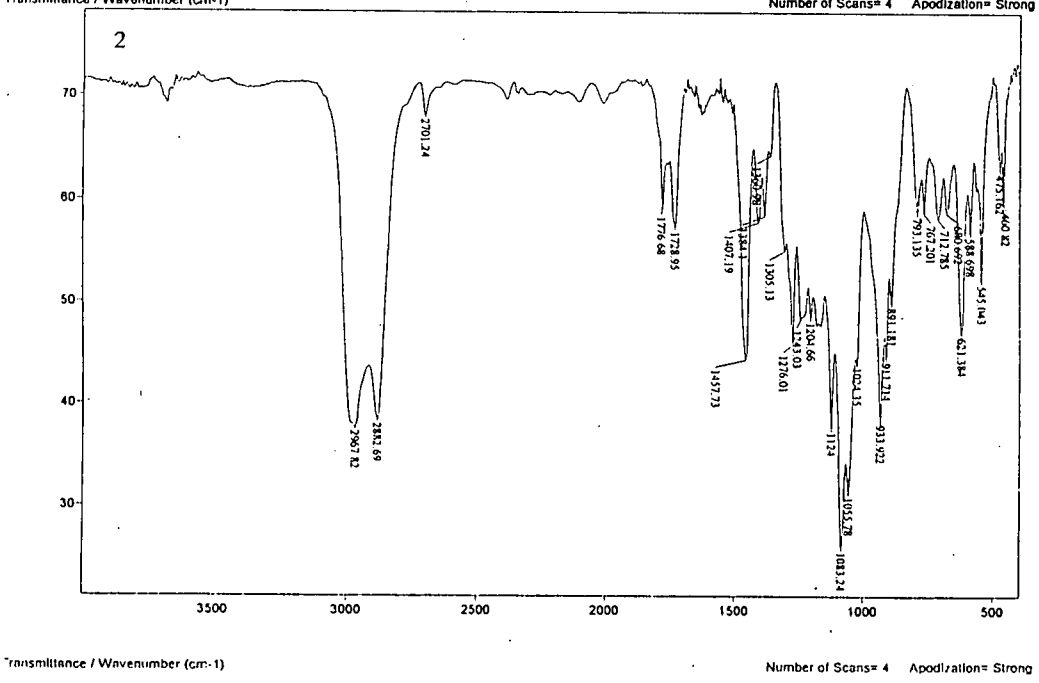
Number of Scans= 4 Apodization= Strong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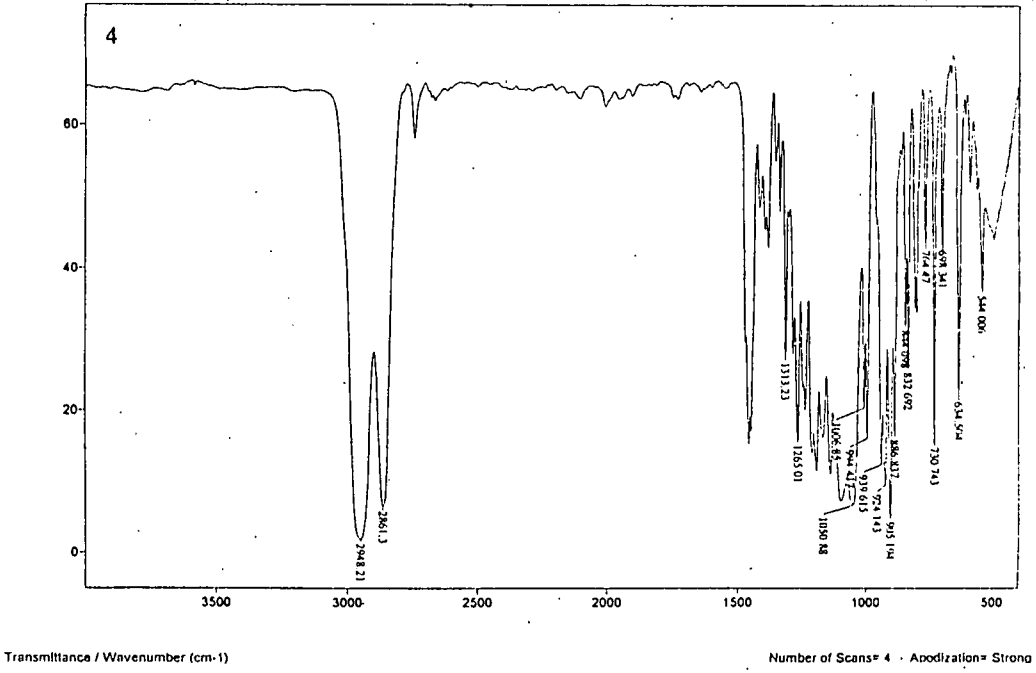
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong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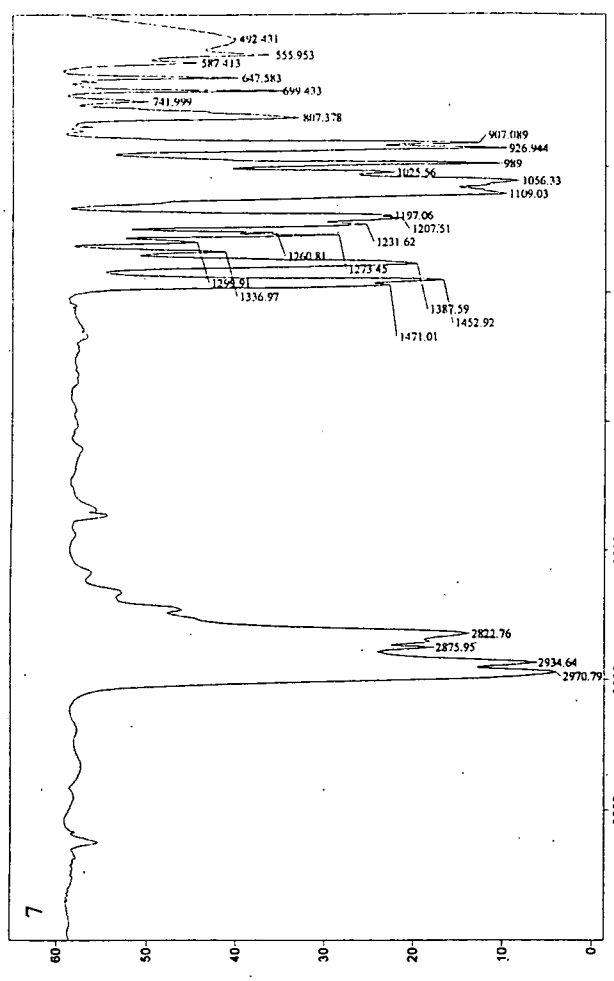
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong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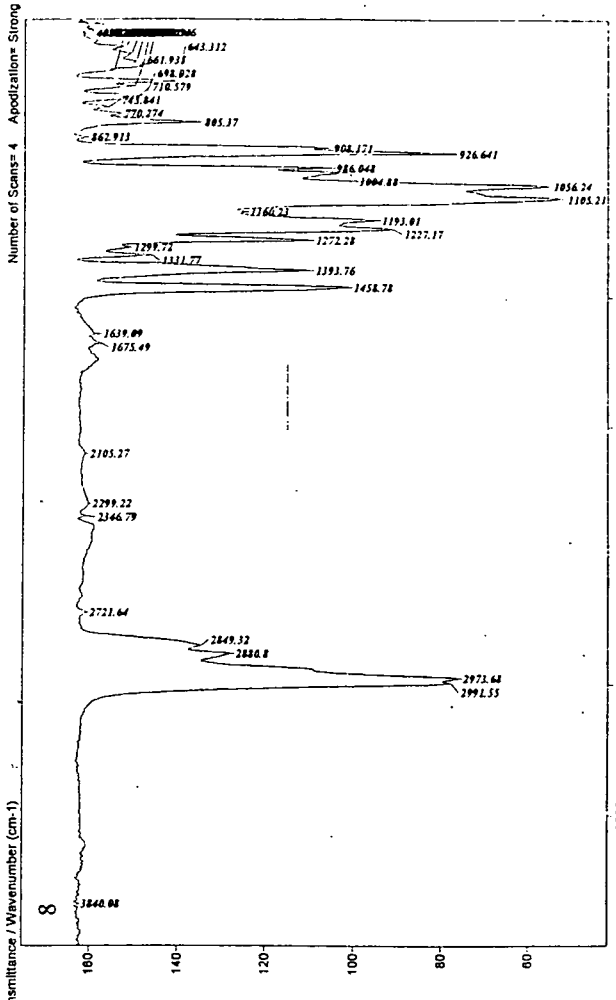
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong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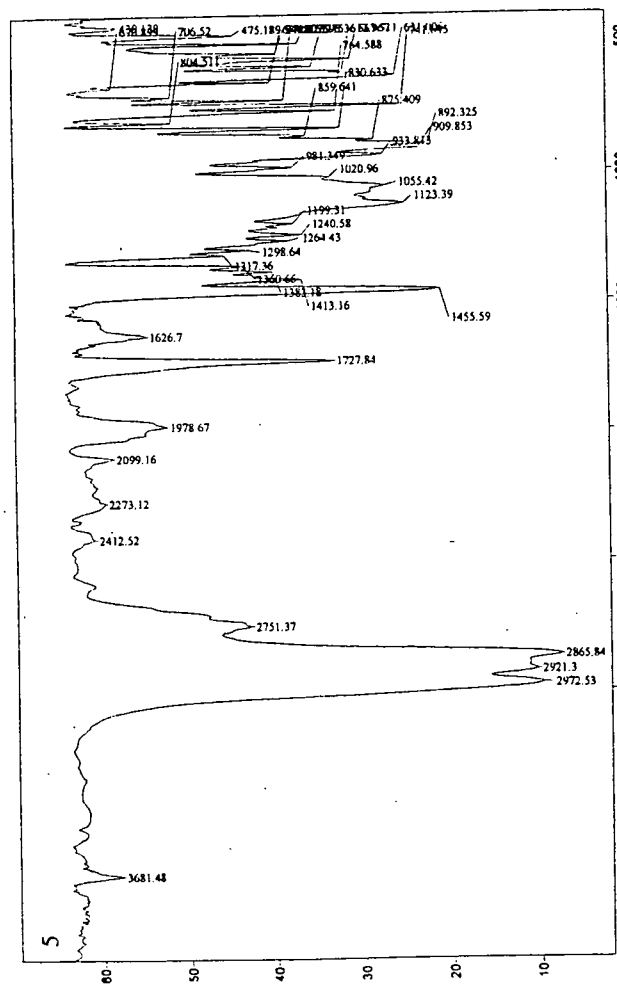
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong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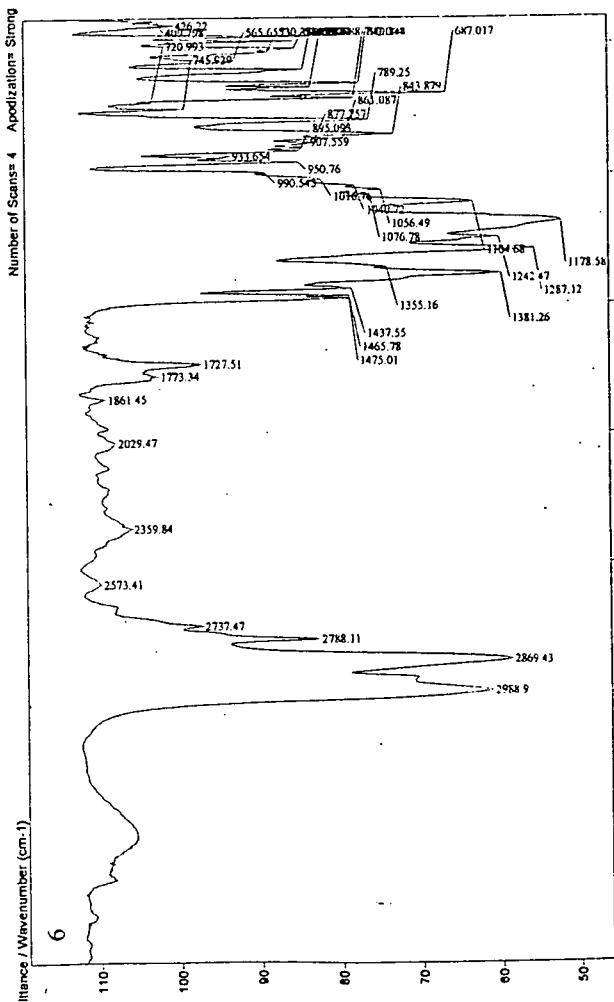
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong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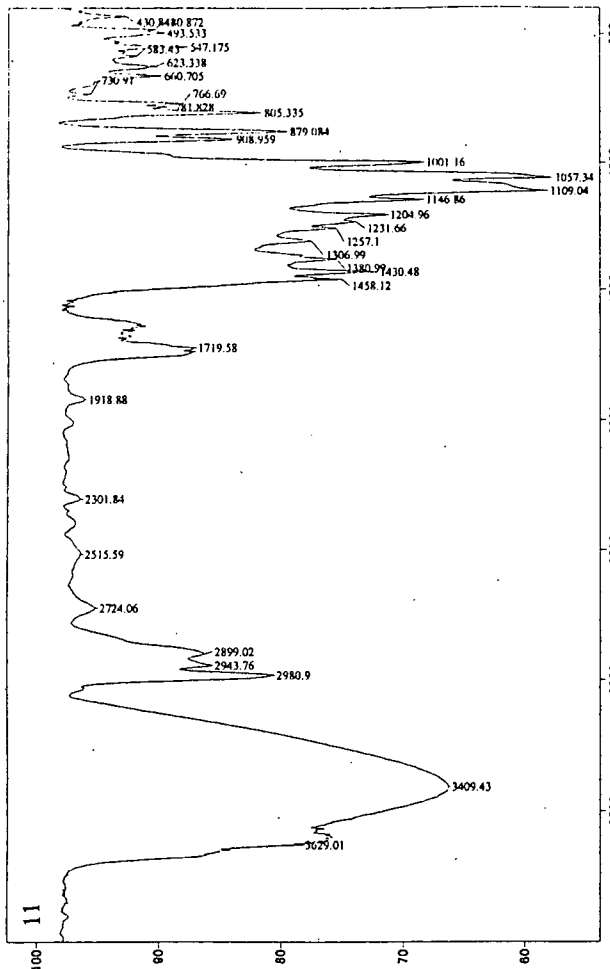
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong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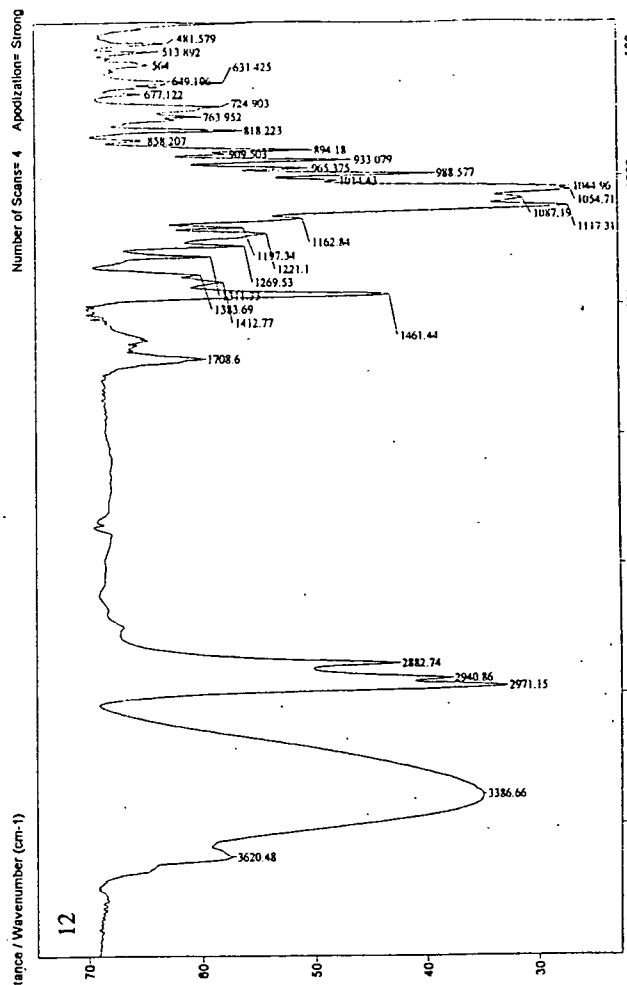
Transmittance / Wavenumber (cm-1)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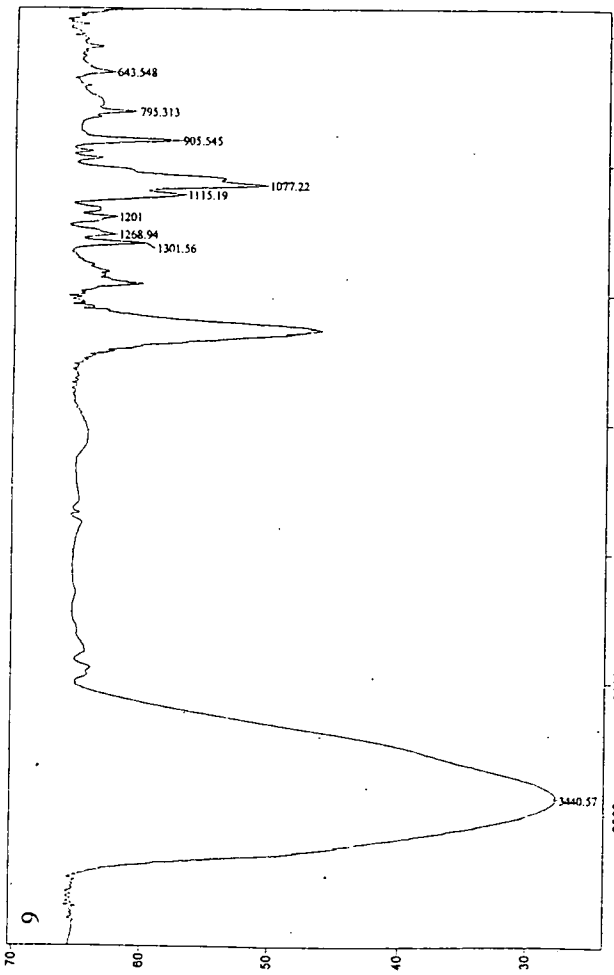
Transmittance / Wavenumber (cm-1)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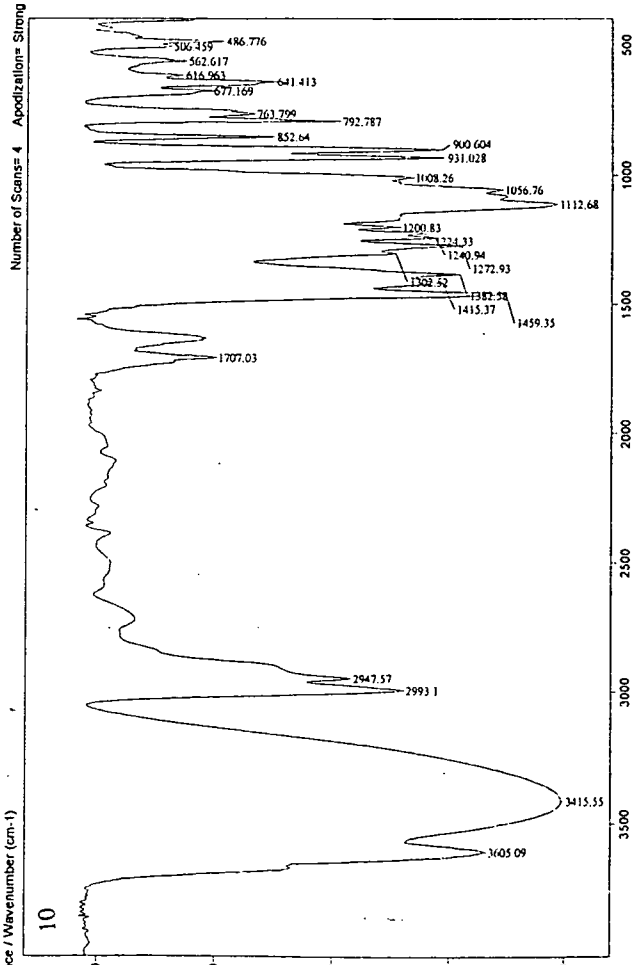
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1415.37
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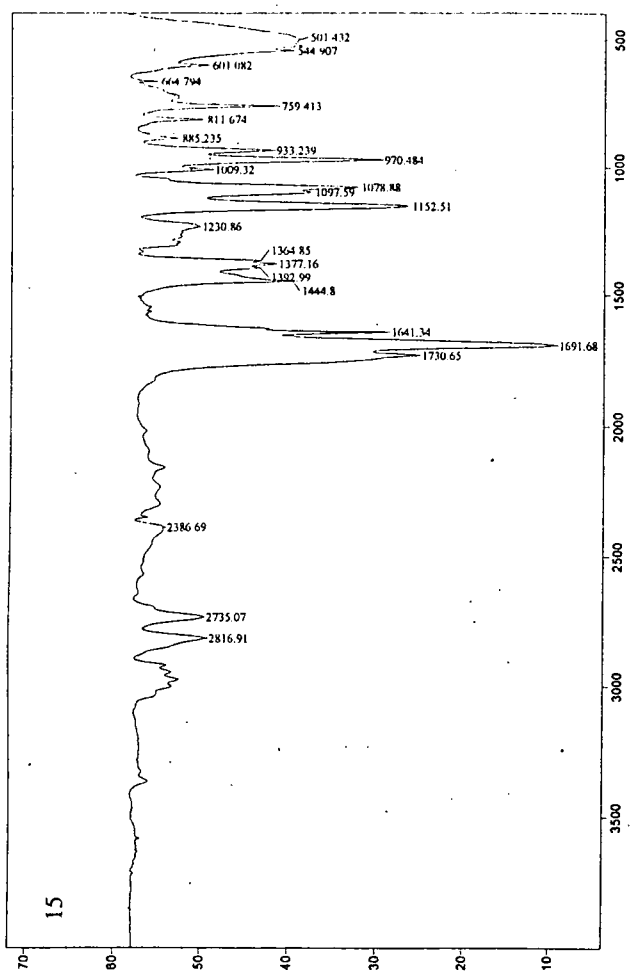
Transmittance / Wavenumber (cm-1)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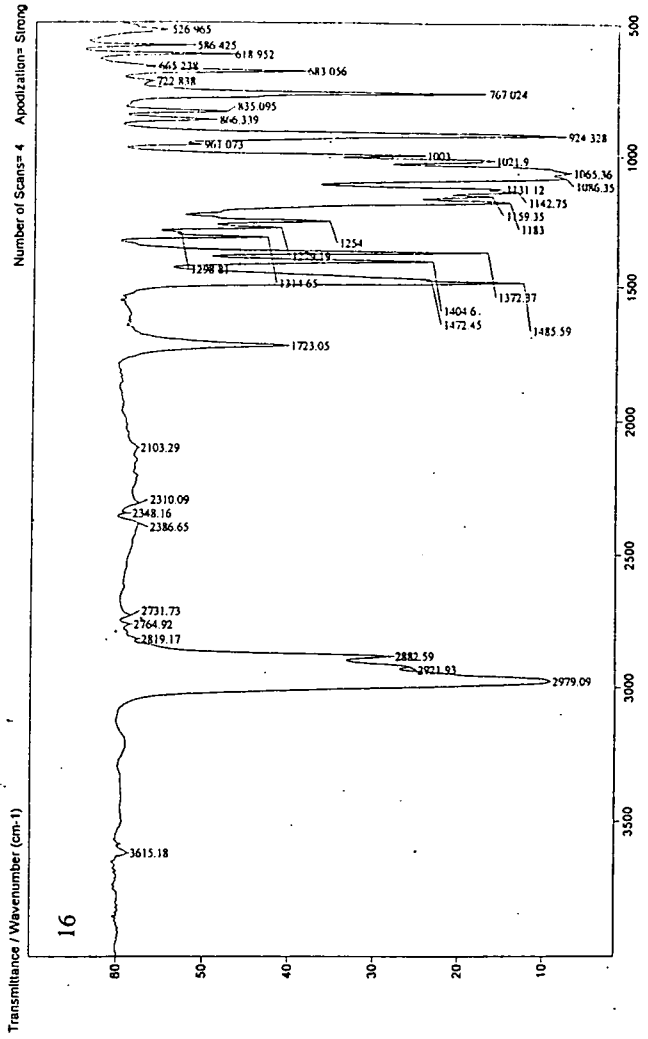
Transmittance / Wavenumber (cm-1)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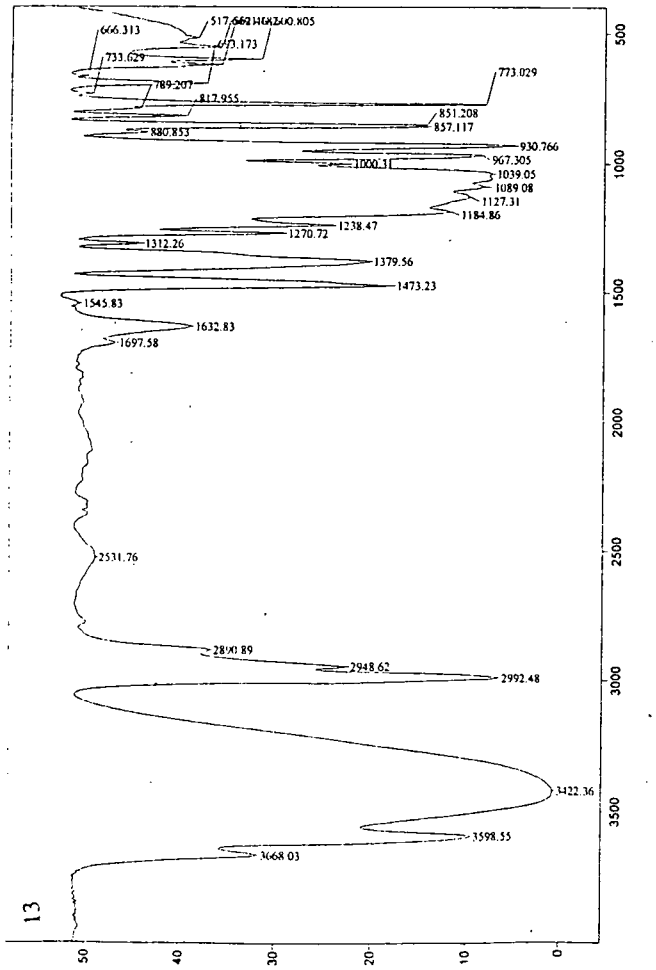
Transmittance / Wavenumber (cm-1)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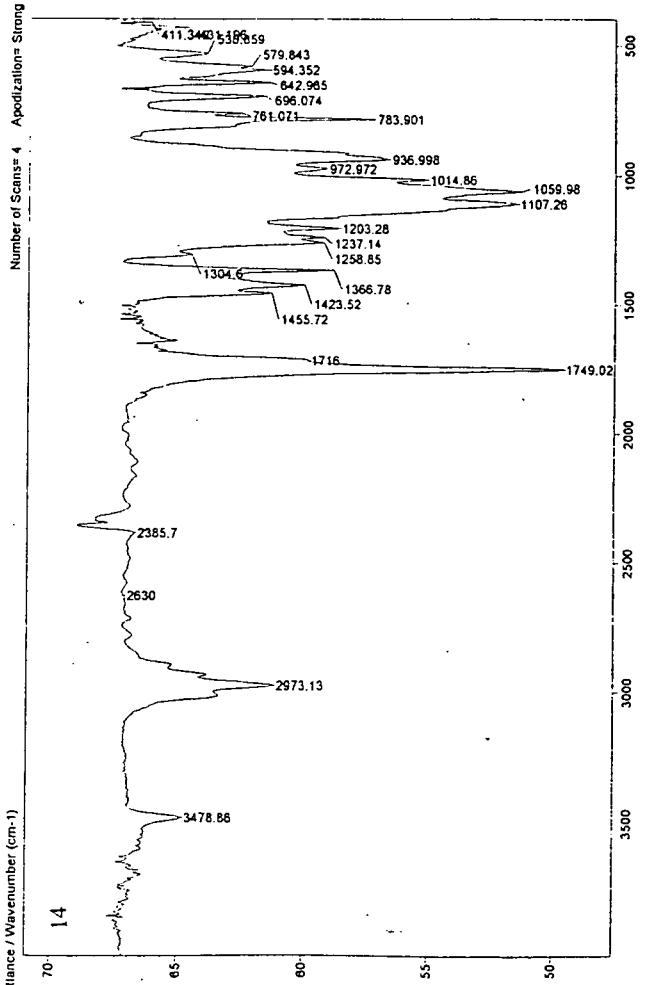
Transmittance / Wavenumber (cm-1)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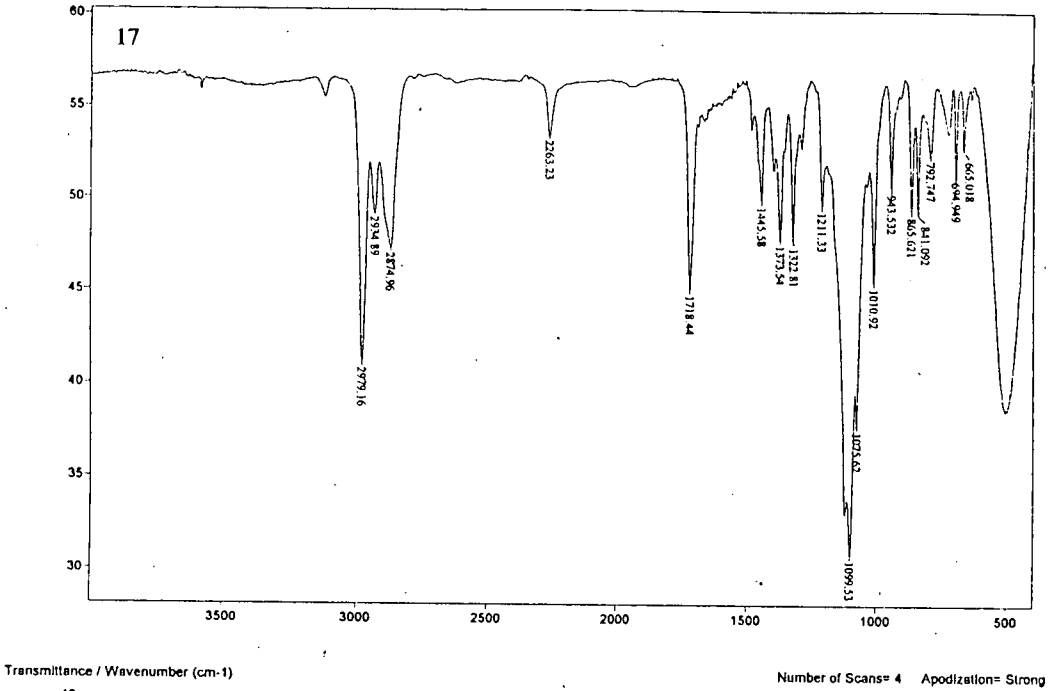
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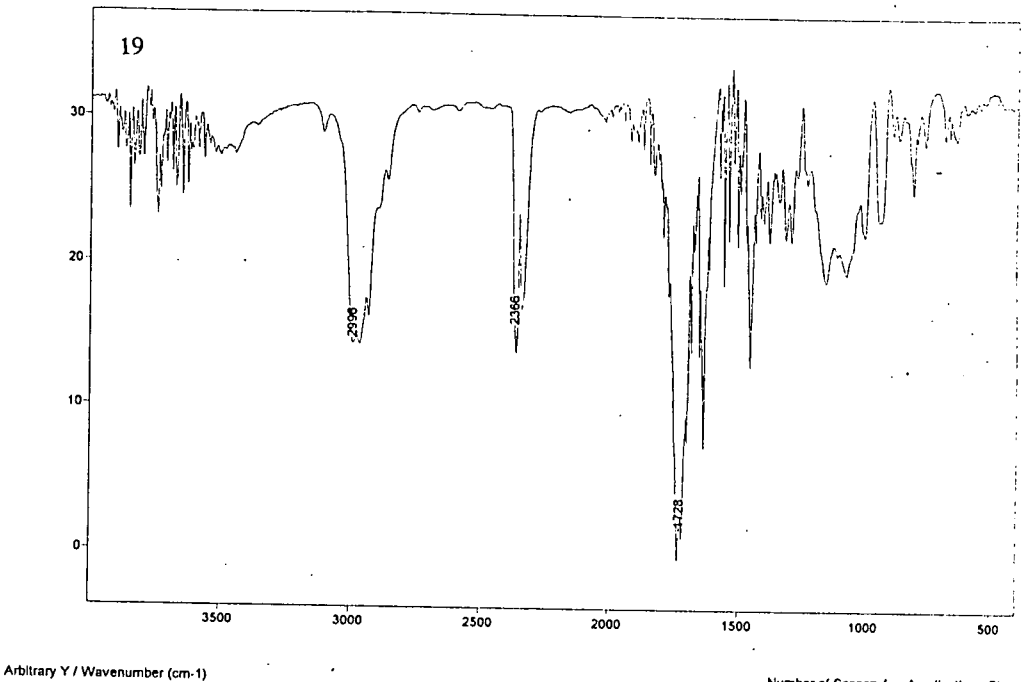
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong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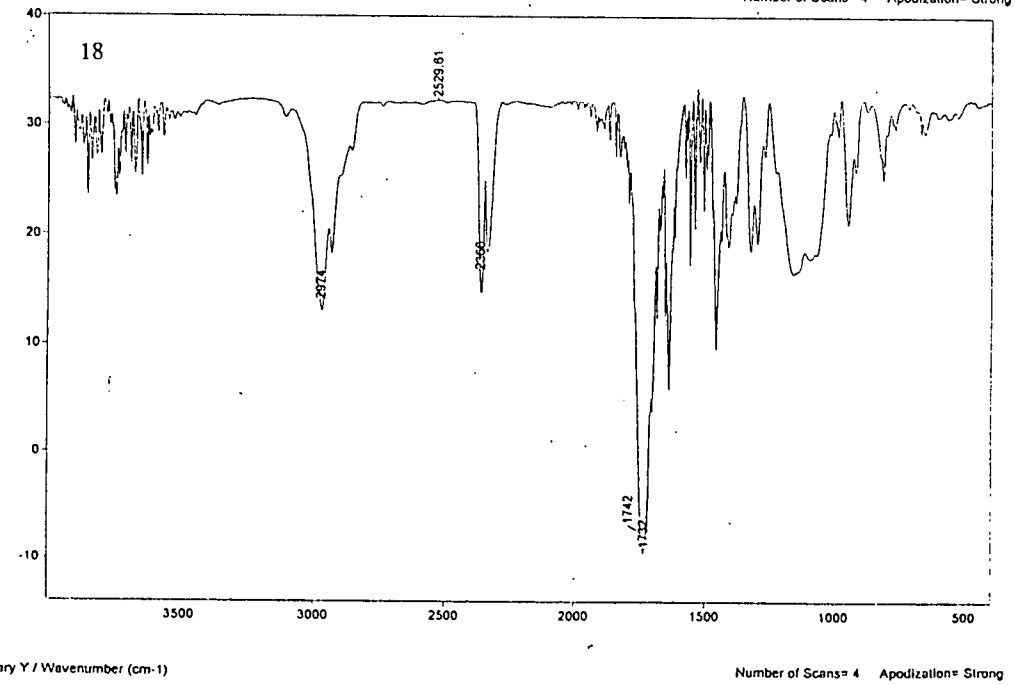
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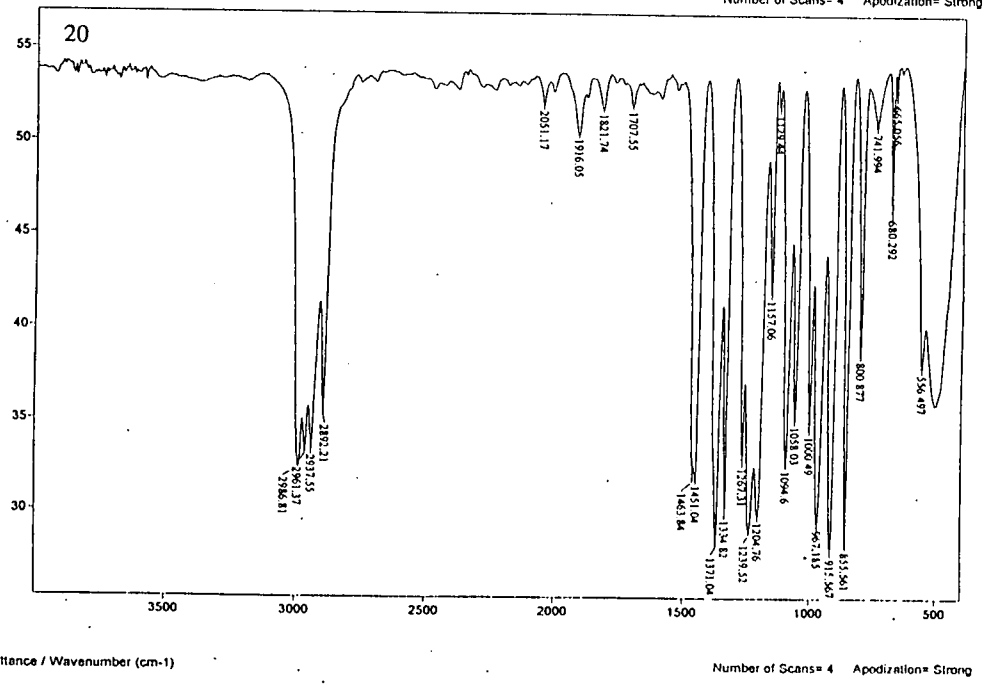
Number of Scans= 4 Apodization= Strong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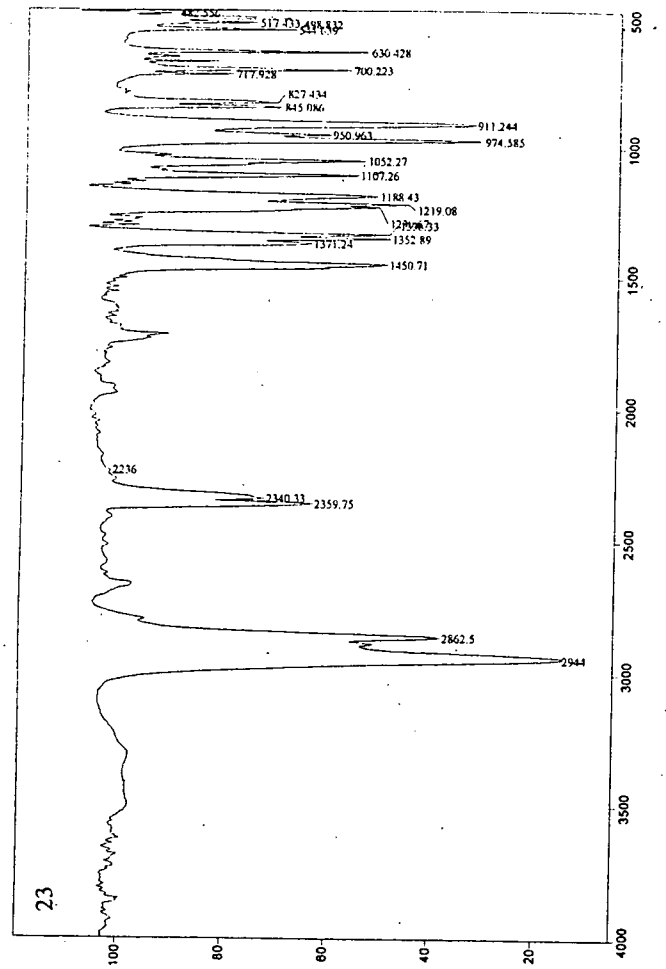
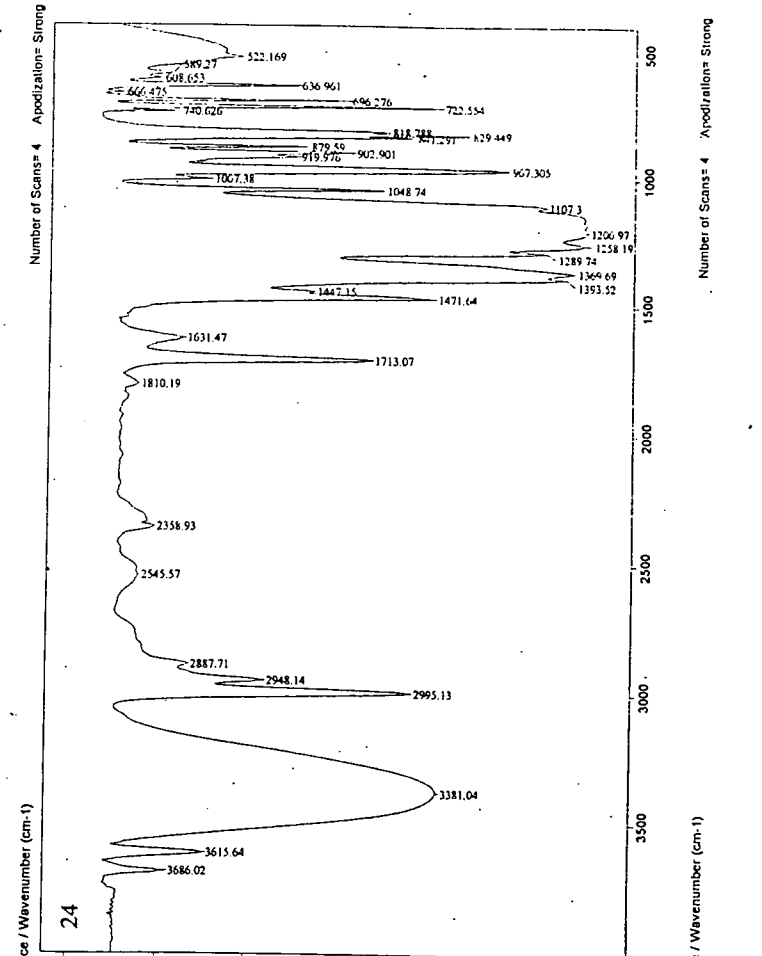
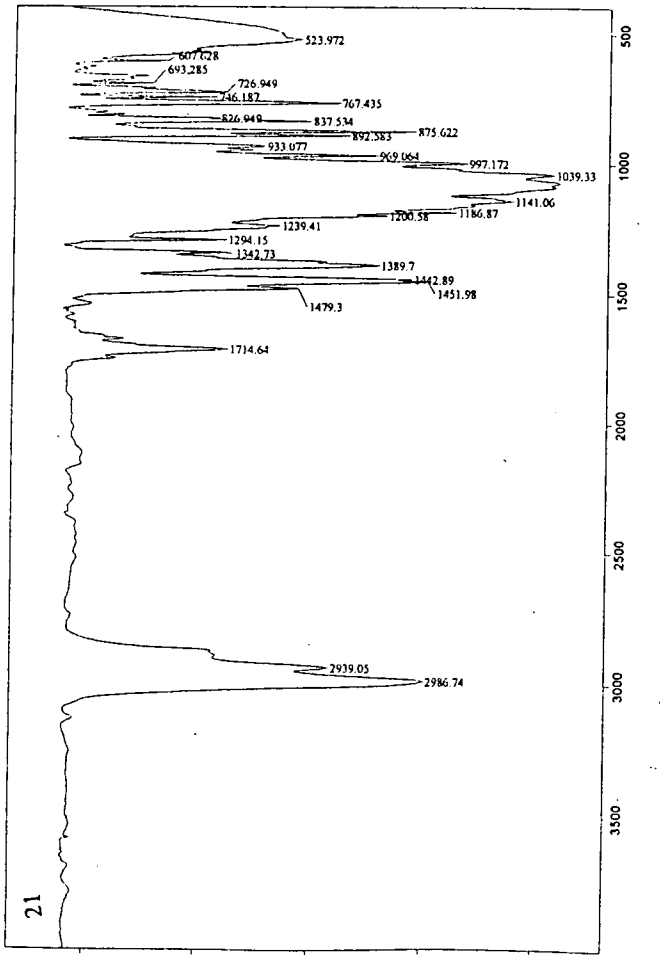
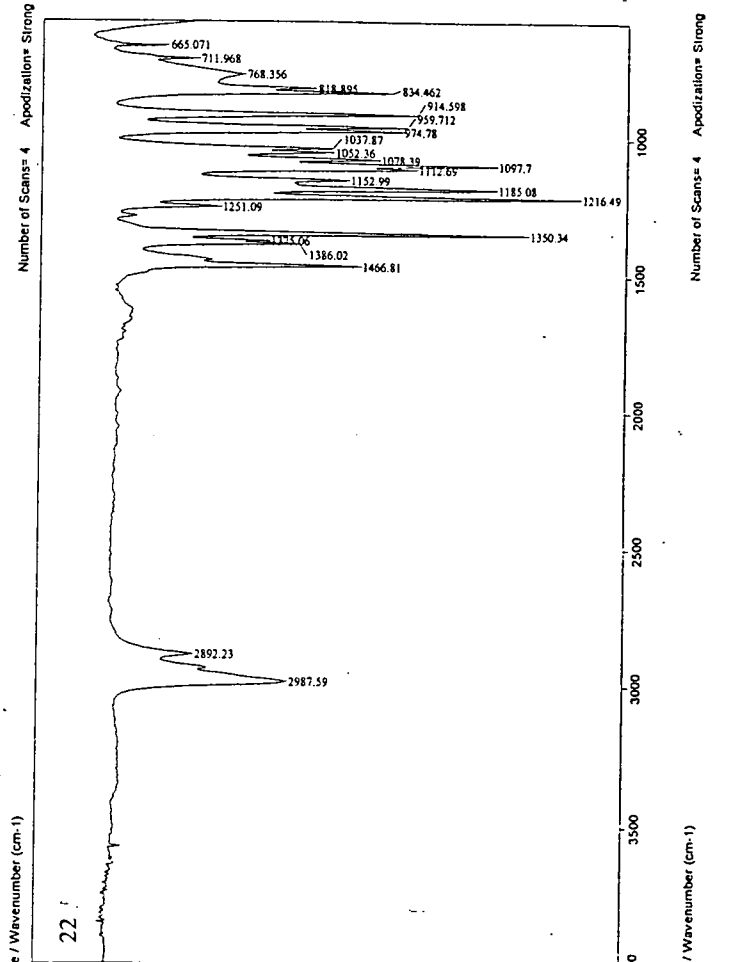
596.497
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong

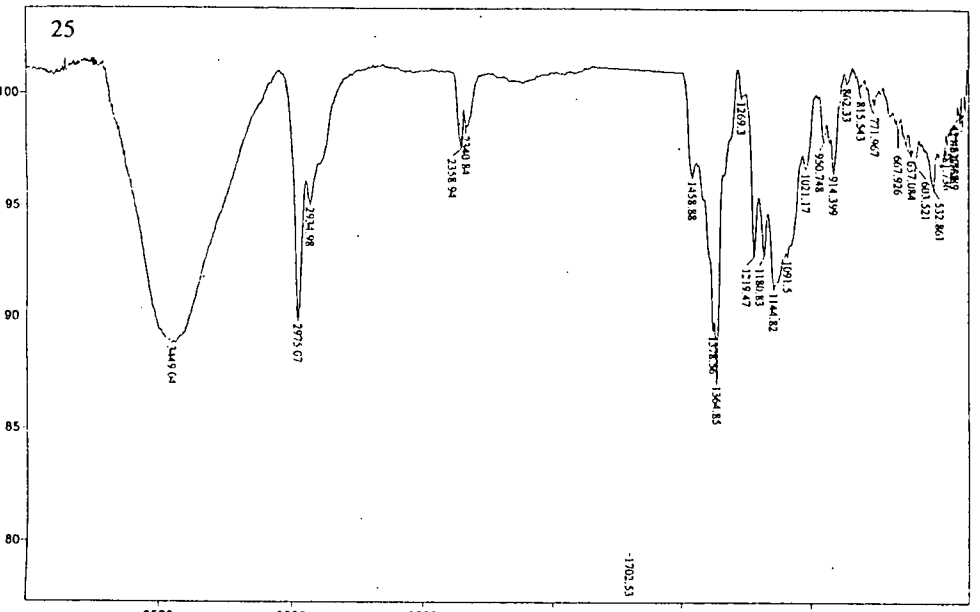

517.433
630.428
700.223
777.928
827.434
911.244
950.963
974.585
1052.27
1107.26
1188.43
1219.08
1352.89
1371.24
1450.71
2236
2340.33
2359.75
2862.5
2944
23


Number of Scans= 4 Apodization= Strong
522.169
608.653
636.961
696.276
722.554
879.59
902.901
967.305
1048.74
1107.3
1200.97
1258.19
1289.74
1369.69
1393.52
1471.64
1631.47
1713.07
1810.19
2358.93
2545.57
2887.71
2948.14
2995.13
3381.04
3615.64
3686.02
24
Transmittance / Wavenumber (cm-1)


523.972
607.628
693.285
726.949
767.435
826.949
837.534
875.622
933.077
997.172
1039.33
1141.06
1186.87
1239.41
1294.15
1342.73
1389.7
1442.89
1451.98
1479.3
1714.64
2939.05
2986.74
21


Number of Scans= 4 Apodization= Strong
665.071
711.968
768.356
818.895
834.462
914.598
959.712
974.78
1037.87
1052.36
1078.39
1112.69
1097.7
1152.99
1185.08
1216.49
1251.09
1350.34
1386.02
1466.81
2892.23
2987.59
22
Transmittance / Wavenumber (cm-1)

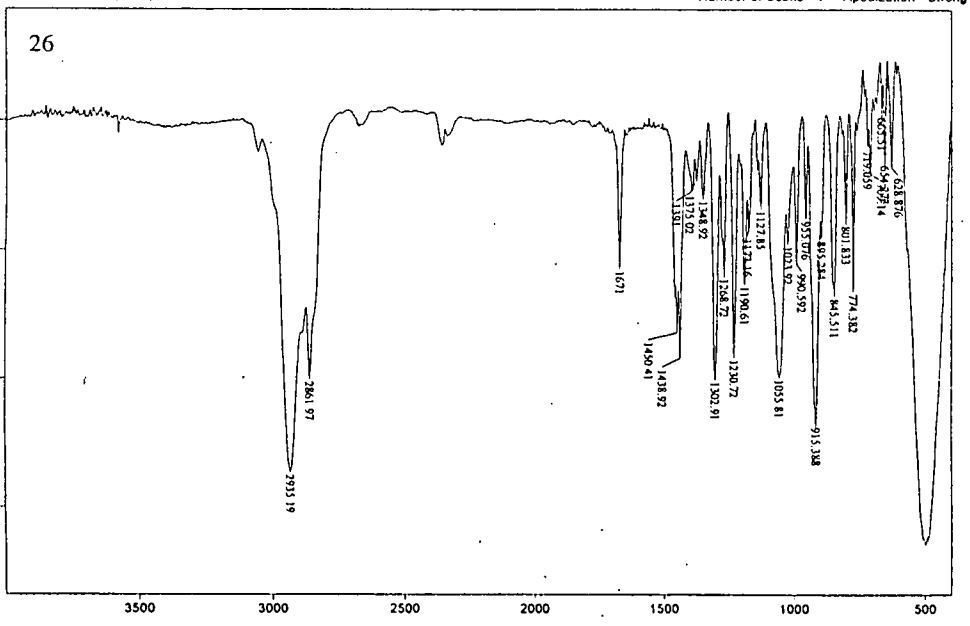
25



Transmittance / Wavenumber (cm-1)

Number of Scans= 4 Apodization= Strong

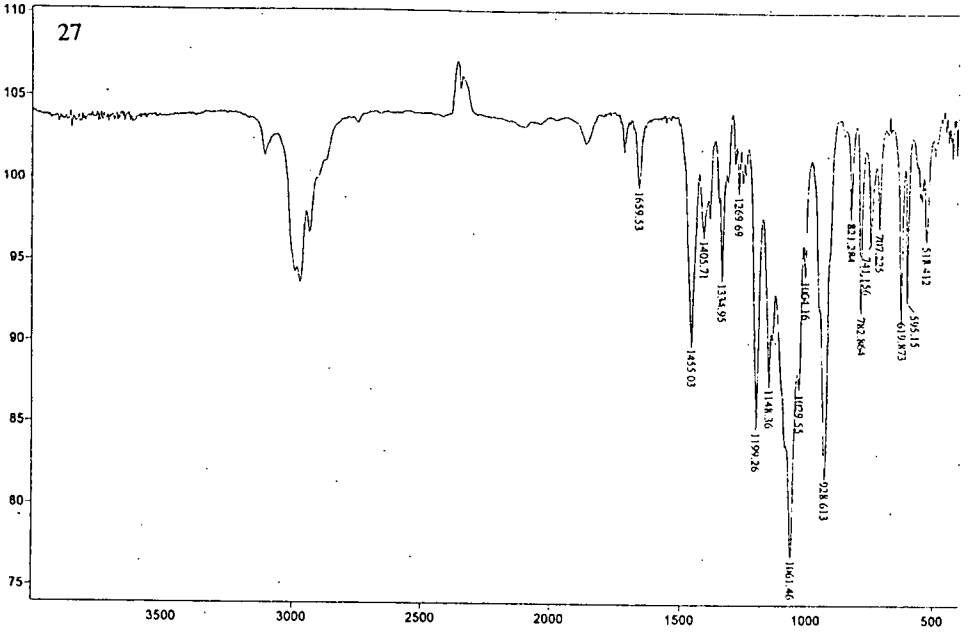
26



Transmittance / Wavenumber (cm-1)

Number of Scans= 4 Apodization= Strong

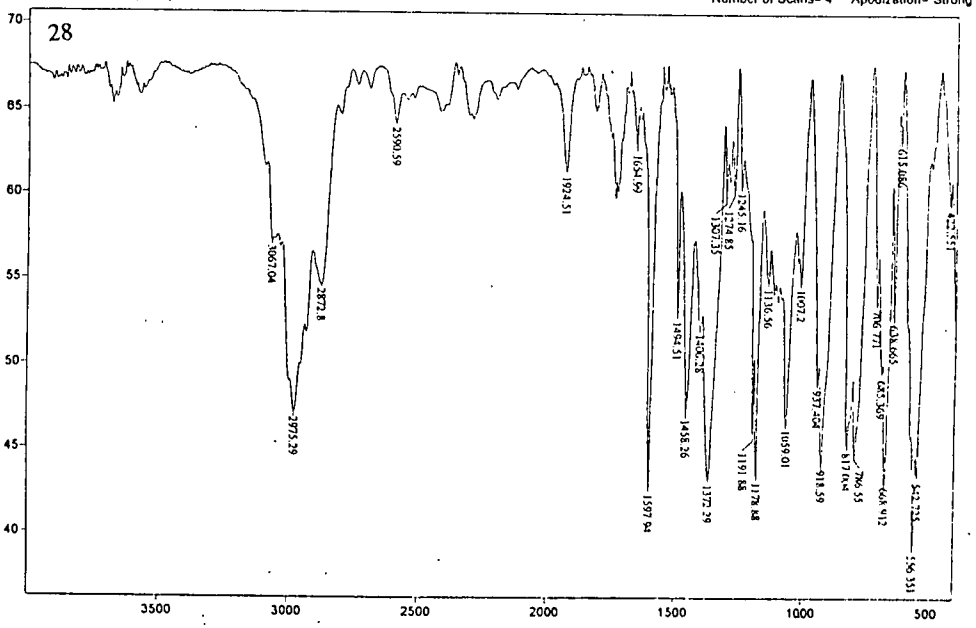
27



Transmittance / Wavenumber (cm-1)

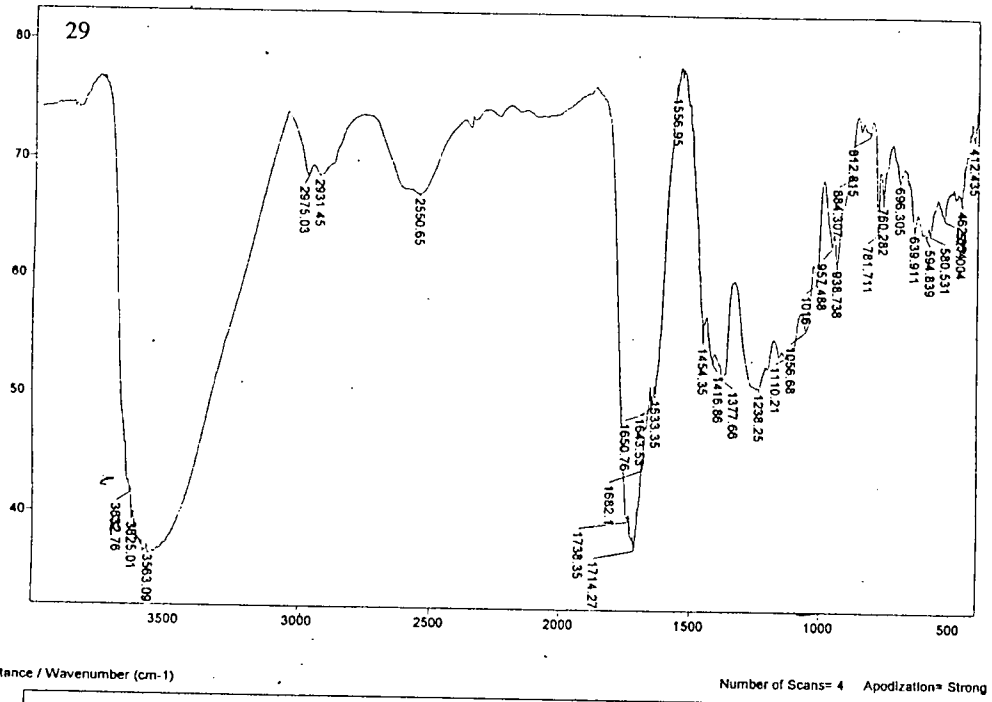
Number of Scans= 4 Apodization= Strong

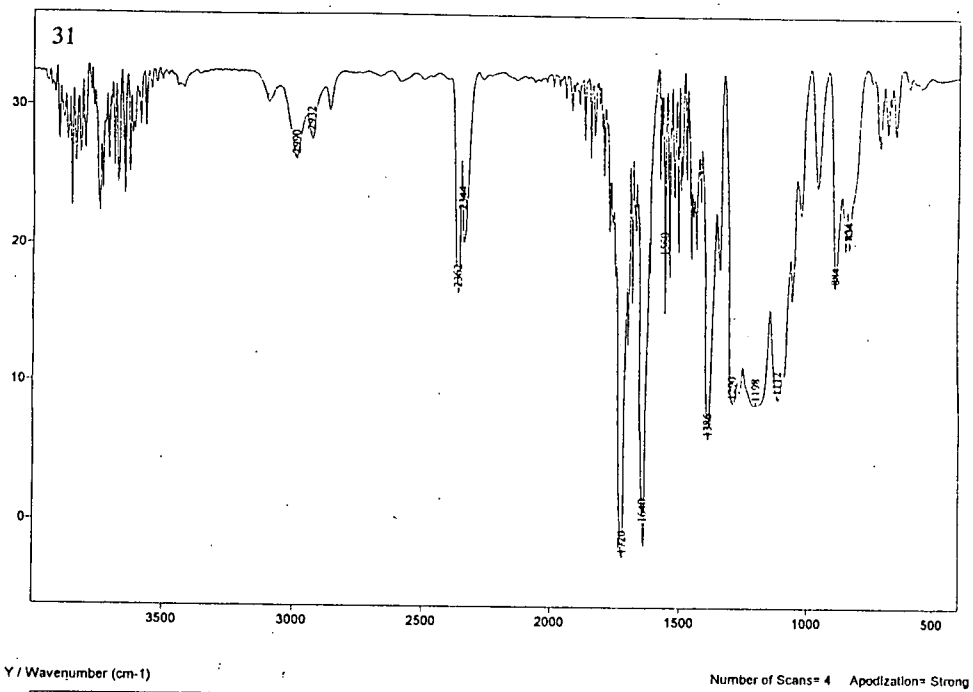
28

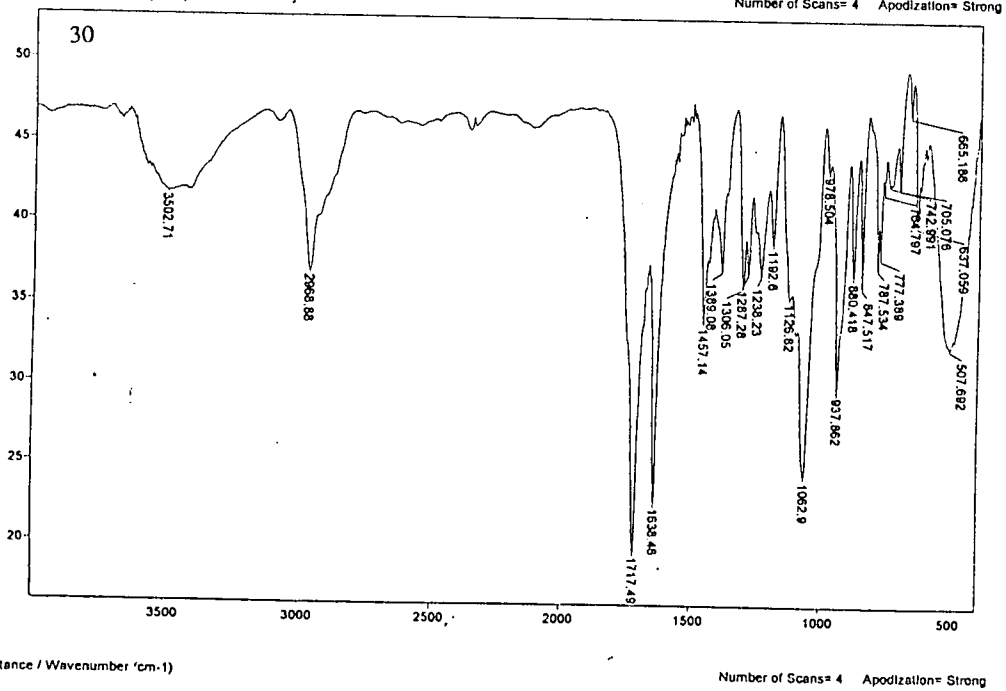


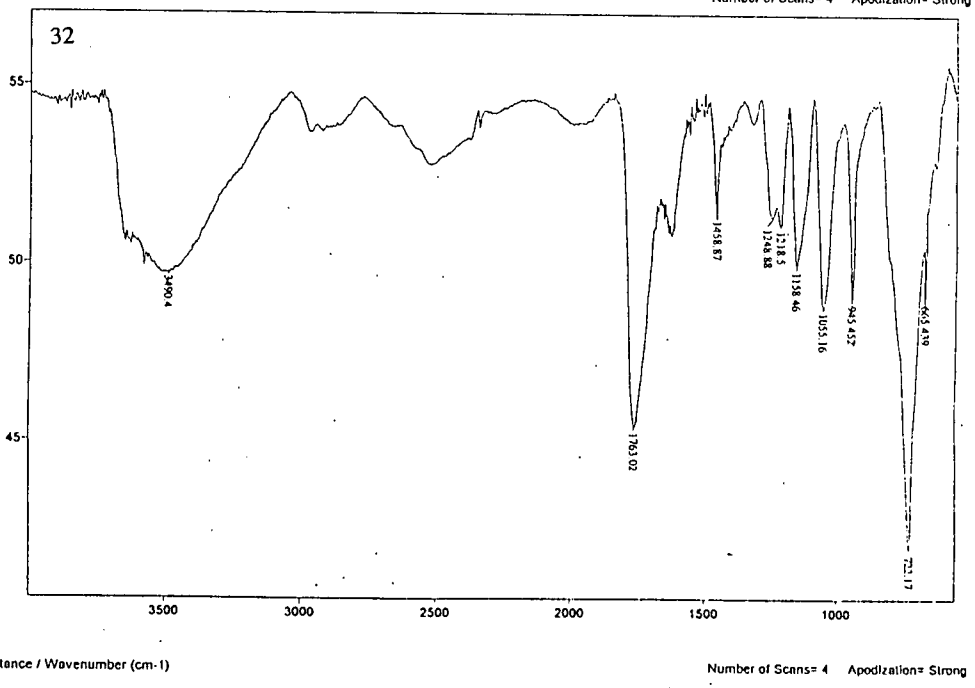
Transmittance / Wavenumber (cm-1)

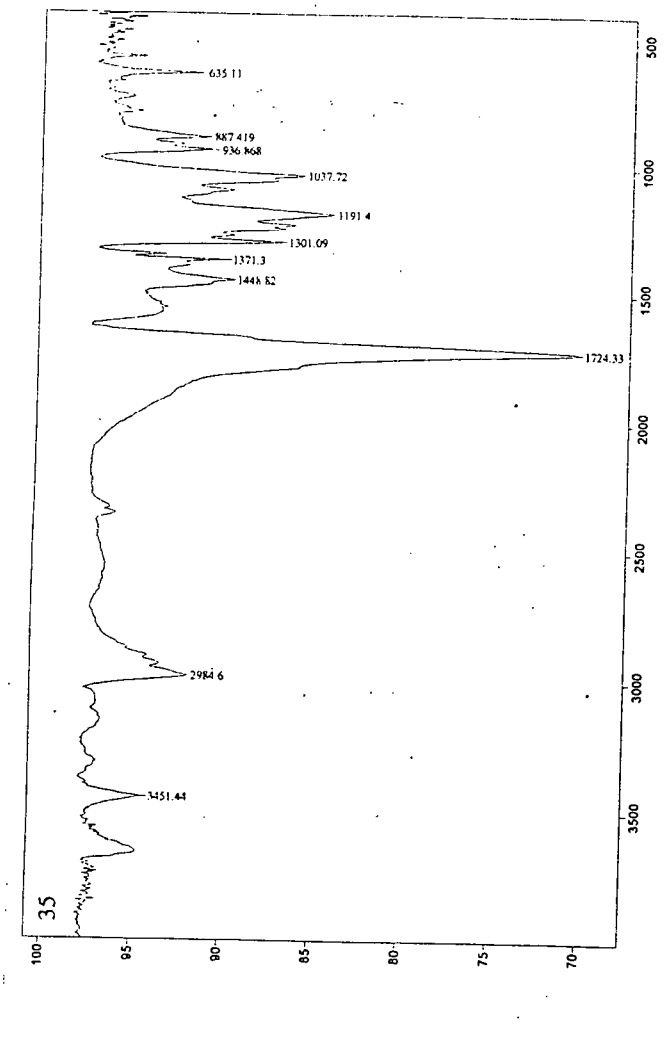
Number of Scans= 4 Apodization= Strong

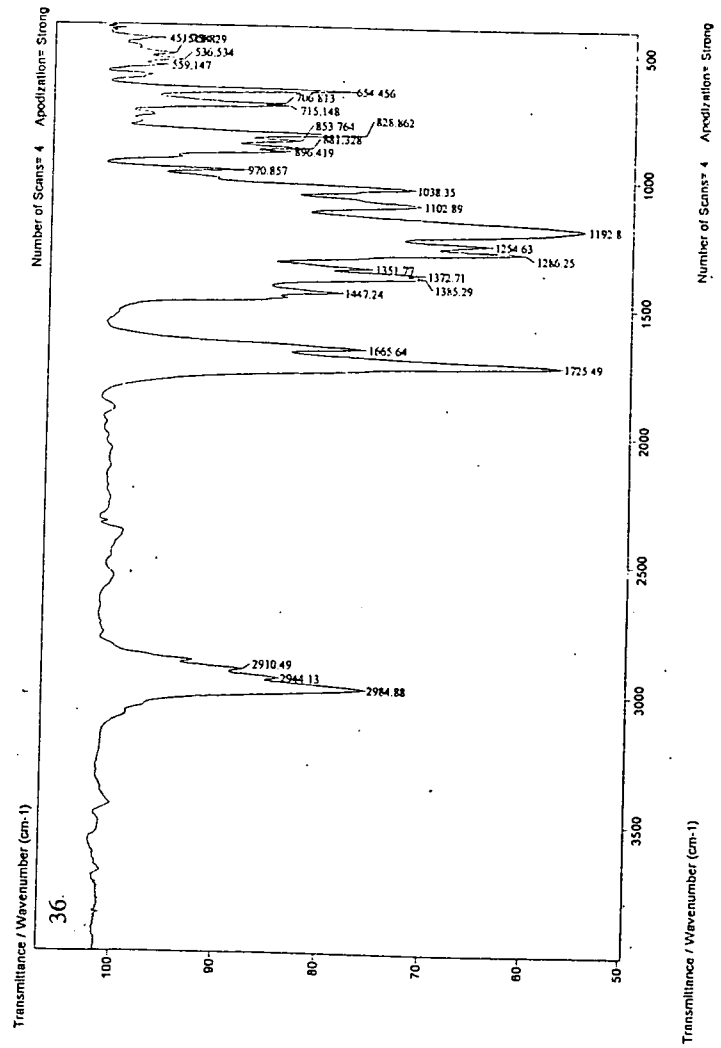

29
3632.76
3525.01
3463.09
2975.03
2931.45
2550.65
1738.35
1714.27
1682.1
1650.76
1647.53
1633.35
1556.95
1454.35
1416.86
1377.66
1238.25
1110.21
1056.68
1016.
957.488
938.738
884.307
812.815
781.711
760.282
696.305
639.911
594.839
580.531
412.435
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong

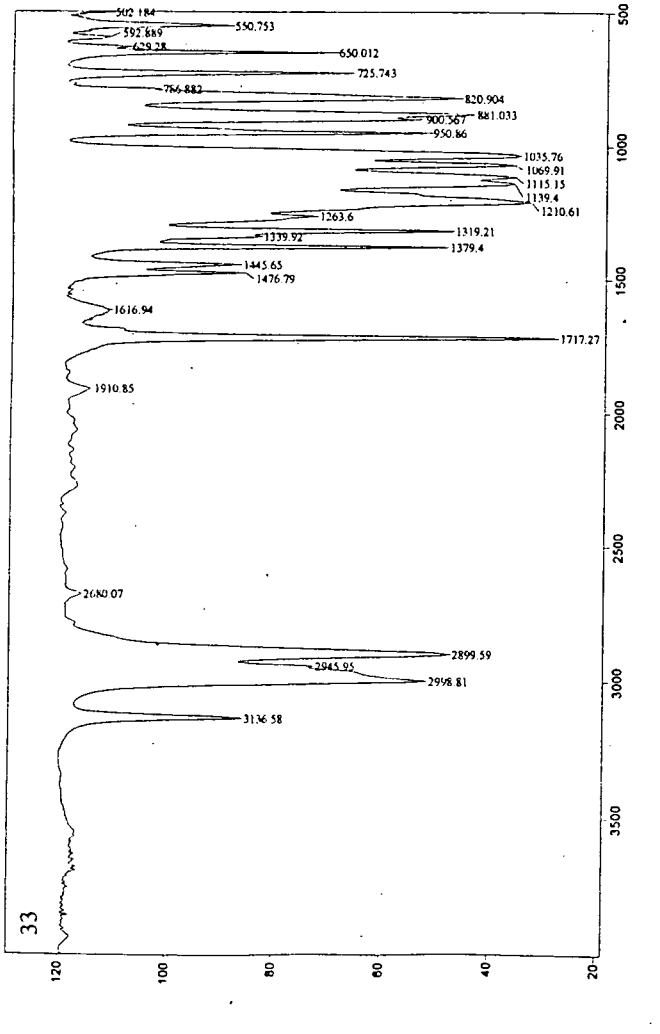

31
Arbitrary Y / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong

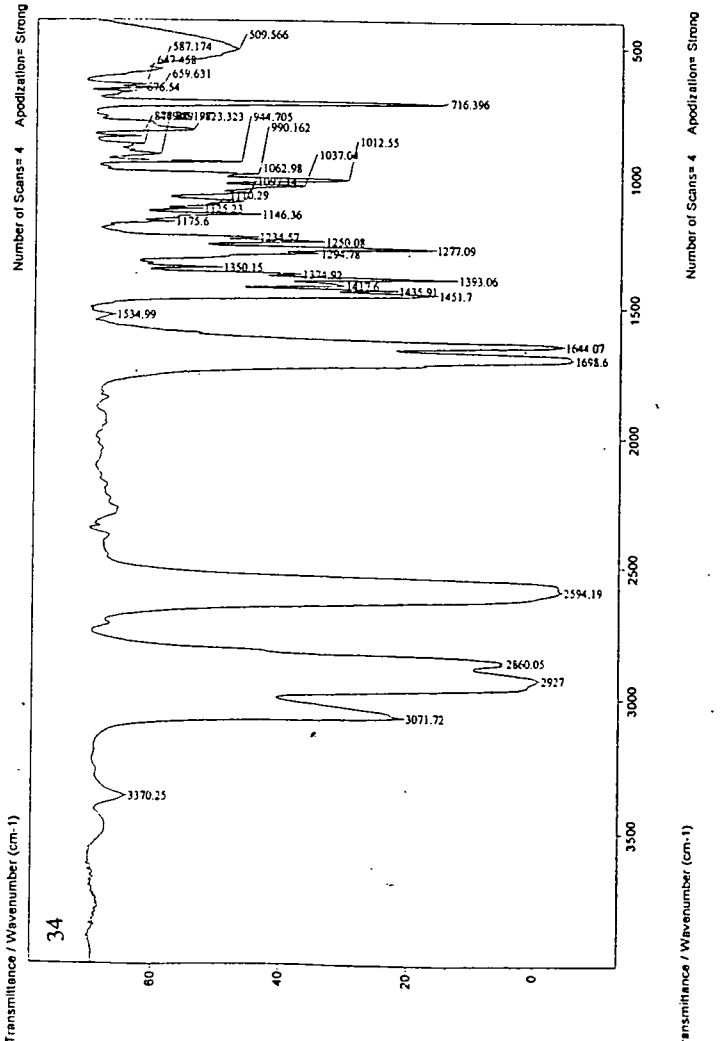

30
3502.71
2968.88
1717.49
1632.46
1457.14
1389.08
1306.05
1287.28
1238.23
1192.6
1126.82
1062.9
978.504
937.862
880.418
847.517
787.534
777.398
764.797
742.991
705.076
665.186
637.059
507.692
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong

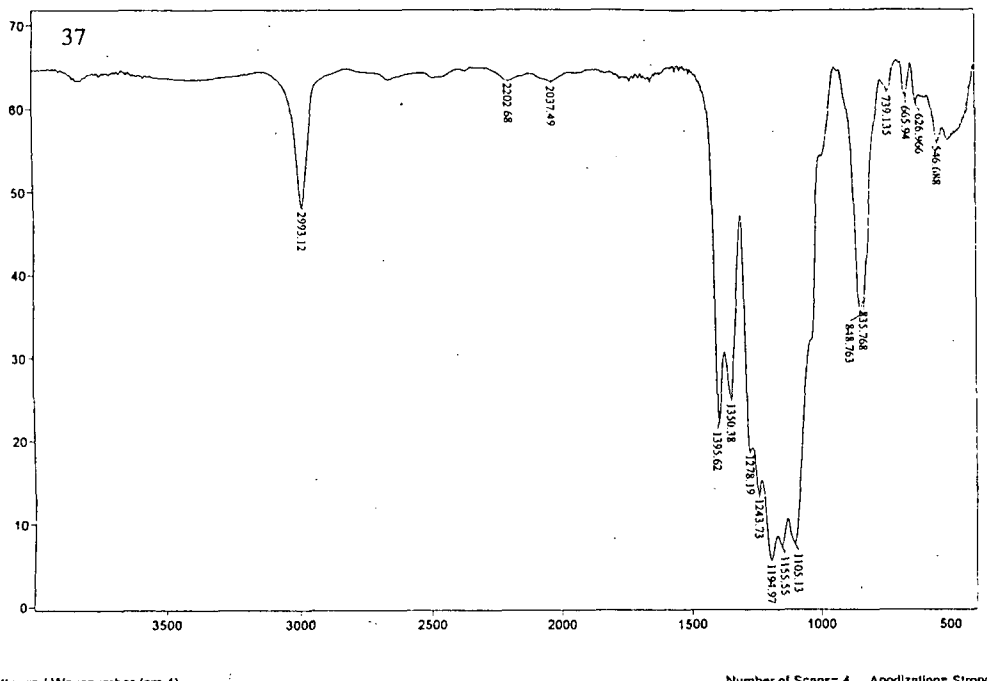

32
3490.4
1763.02
1458.87
1248.88
1218.5
1158.46
1055.16
945.457
722.17
665.439
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong

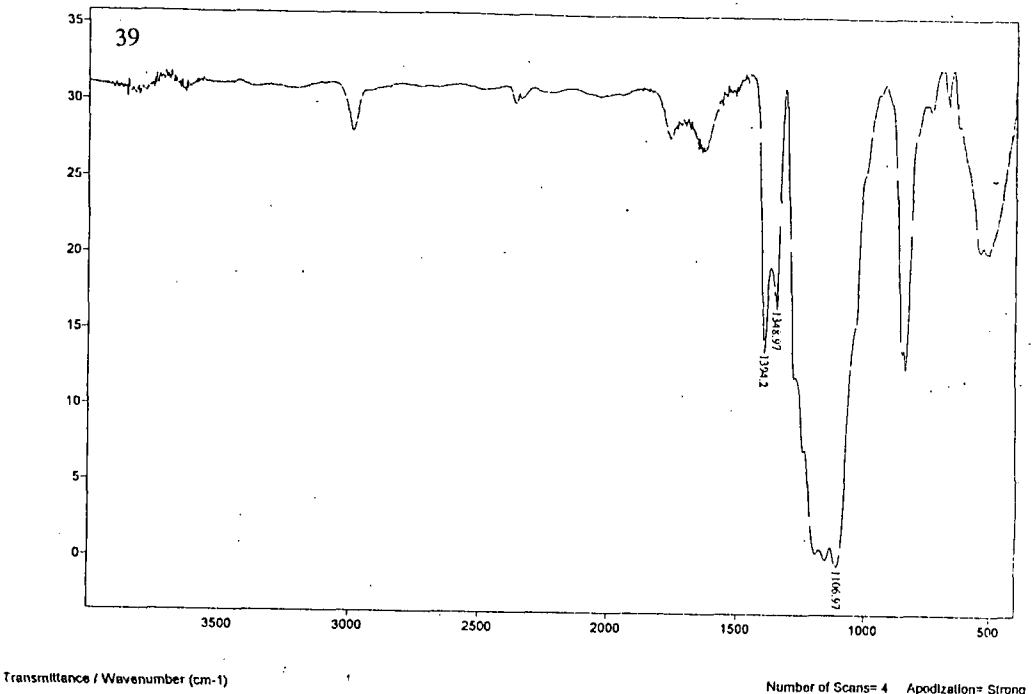

635.11
887.419
936.868
1037.72
1191.4
1301.09
1371.3
1448.82
1724.33
2984.6
3451.44
35

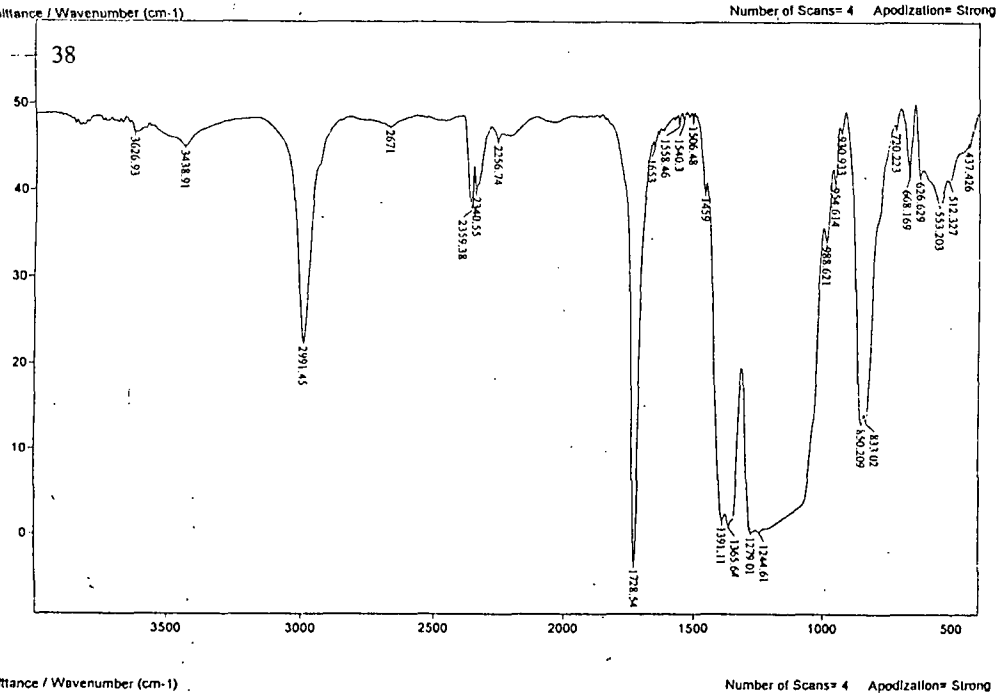

Number of Scans= 4 Apodization= Strong
536.534
559.147
654.456
715.148
828.862
970.857
1038.35
1102.89
1192.8
1254.63
1286.25
1351.77
1372.71
1385.29
1447.24
1665.64
1725.49
2910.49
2944.13
2984.88
Transmittance / Wavenumber (cm-1)
36

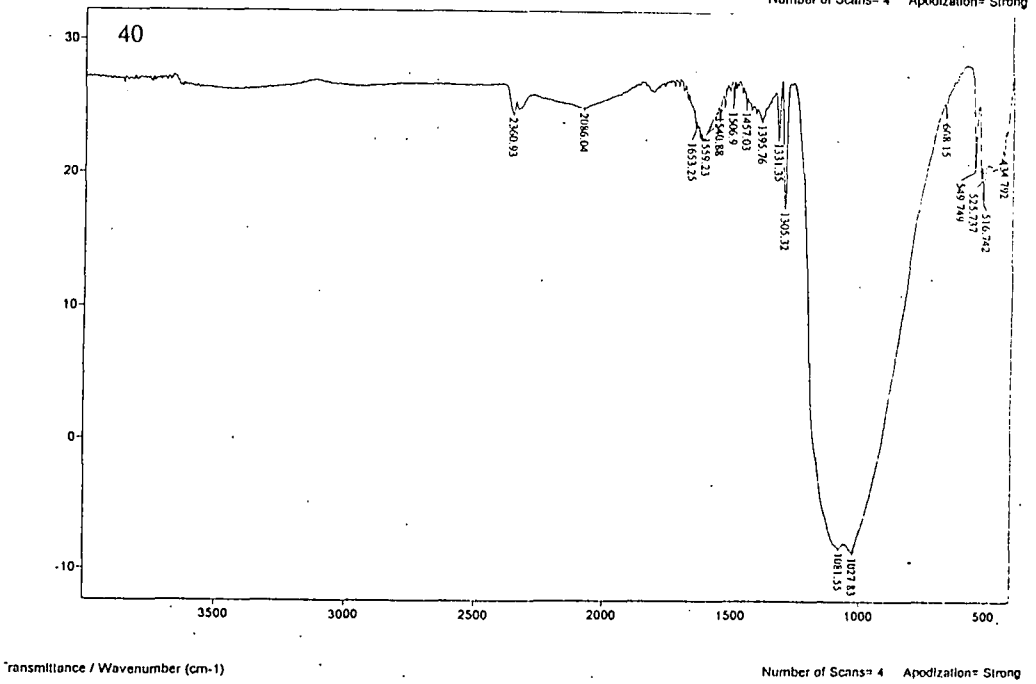

502.184
550.753
592.689
650.012
725.743
786.882
820.904
881.033
900.567
950.86
1035.76
1069.91
1115.15
1139.4
1210.61
1263.6
1319.21
1339.92
1379.4
1445.65
1476.79
1616.94
1717.27
1910.85
2680.07
2899.59
2945.95
2998.81
3136.58
Transmittance / Wavenumber (cm-1)
33

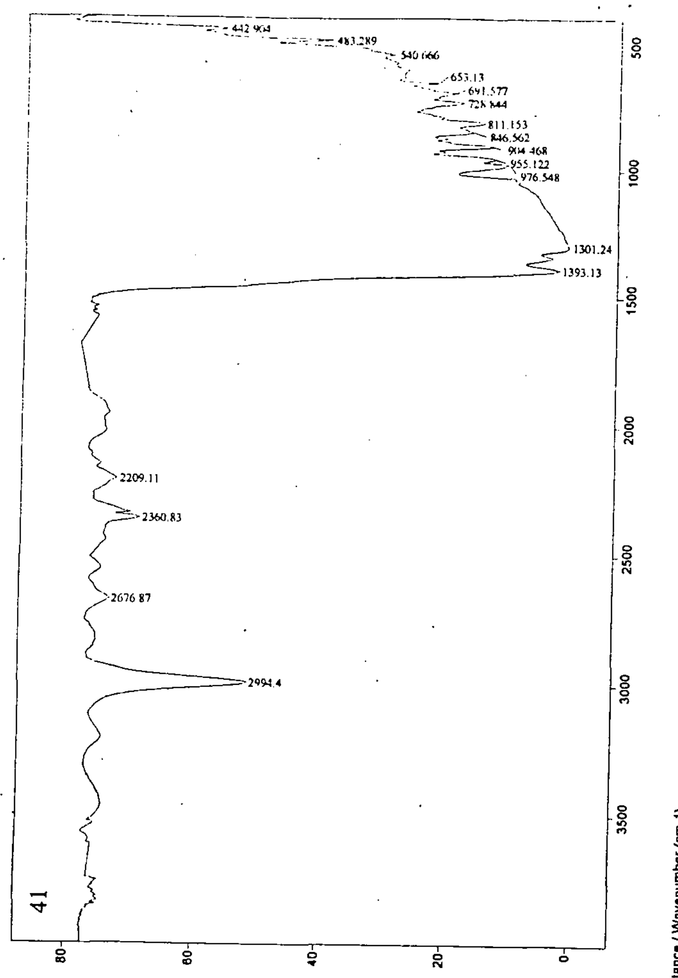

Number of Scans= 4 Apodization= Strong
509.566
587.174
659.631
716.396
990.162
1012.55
1037.64
1062.98
1146.36
1234.57
1250.08
1277.09
1350.15
1393.06
1435.91
1451.7
1534.99
1644.07
1698.6
2594.19
2860.05
2927
3071.72
3370.25
Transmittance / Wavenumber (cm-1)
34

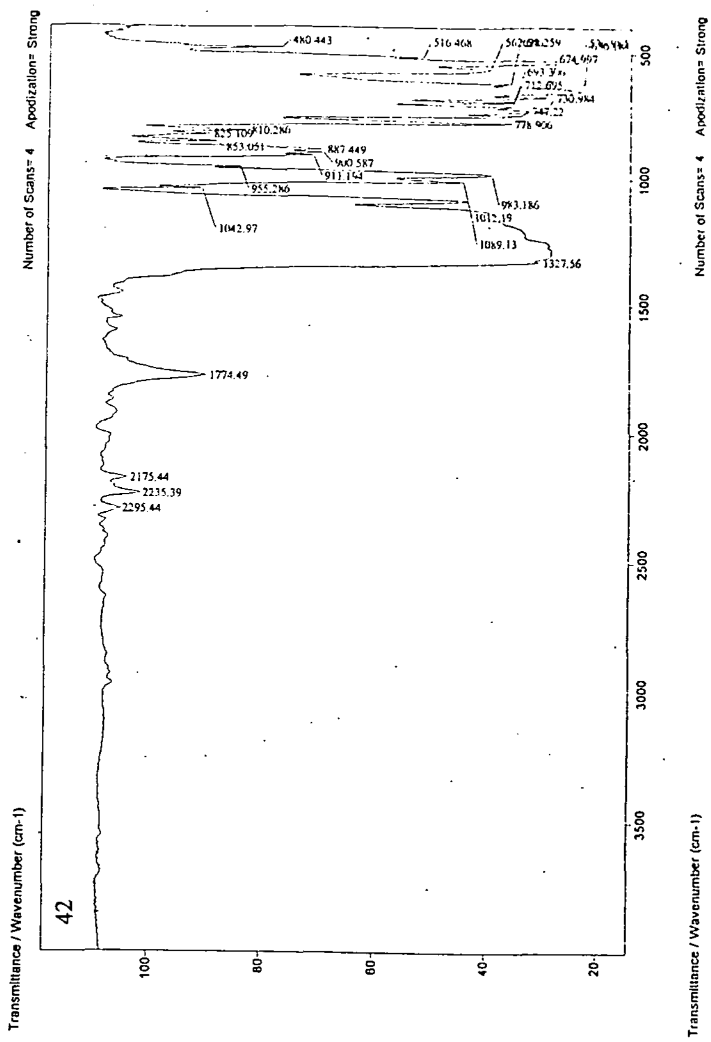

37
2993.12
2320.68
2037.49
1395.62
1350.38
1278.19
1243.73
1194.97
1155.55
1105.13
848.763
835.768
739.133
665.94
626.966
546.048
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong

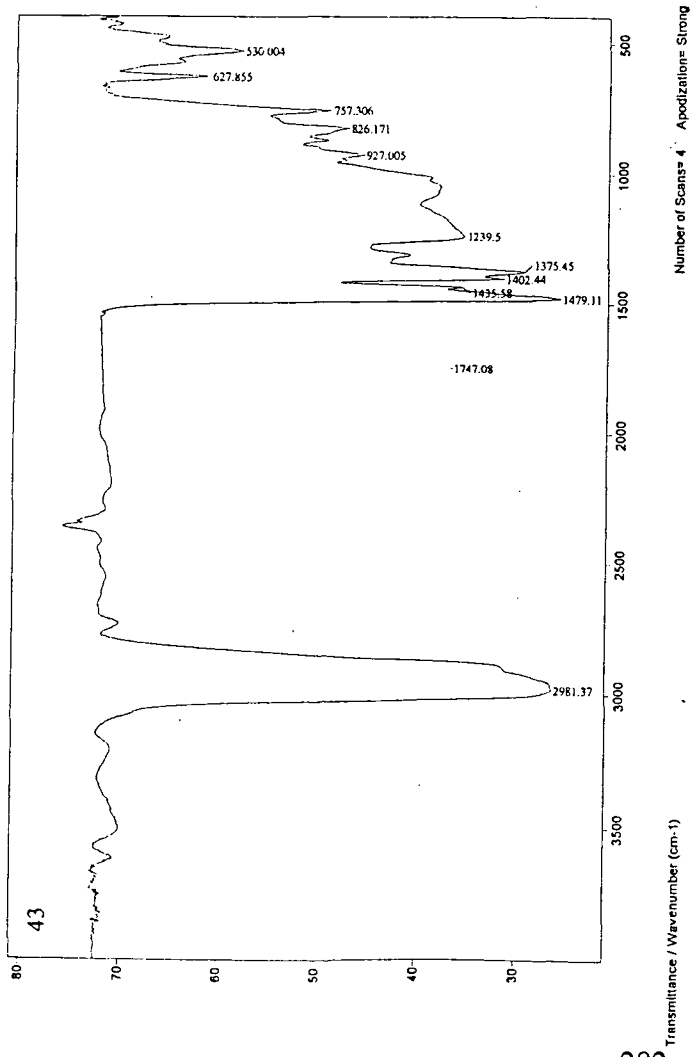

39
1394.2
1348.97
1106.97
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong

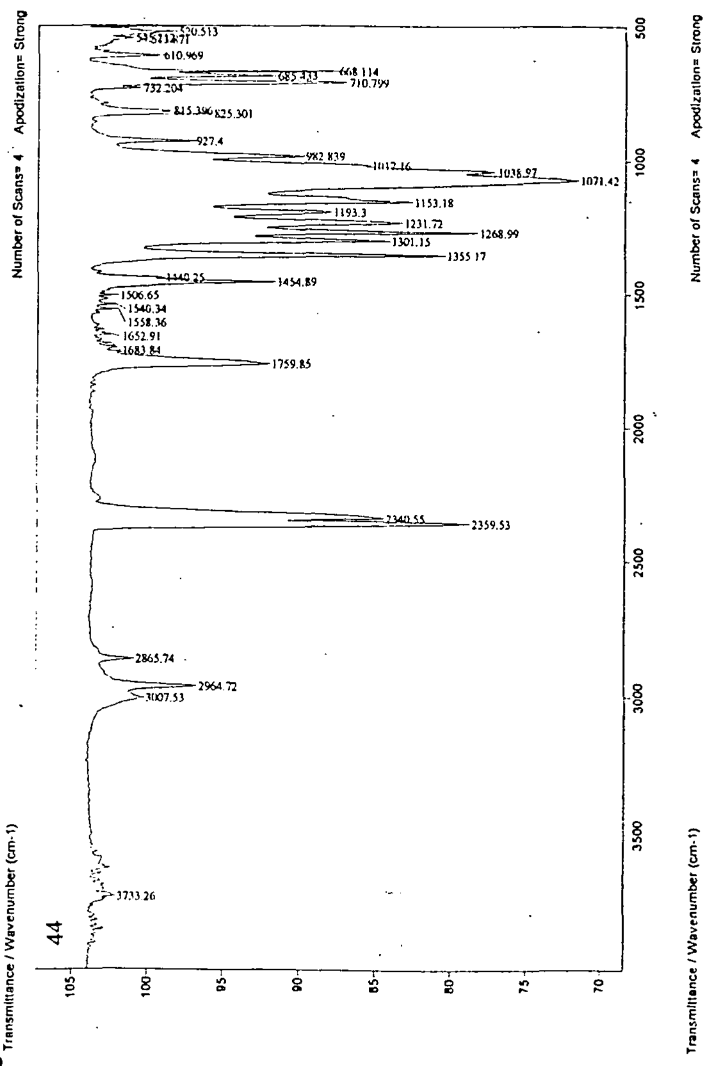

38
3626.93
3438.91
2991.45
2671
2359.38
2340.55
2256.74
1728.54
1653
1558.46
1540.3
1506.48
1459
1391.11
1365.64
1279.01
1244.61
888.621
854.034
830.231
730.223
650.209
648.169
626.629
553.203
512.327
437.426
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong

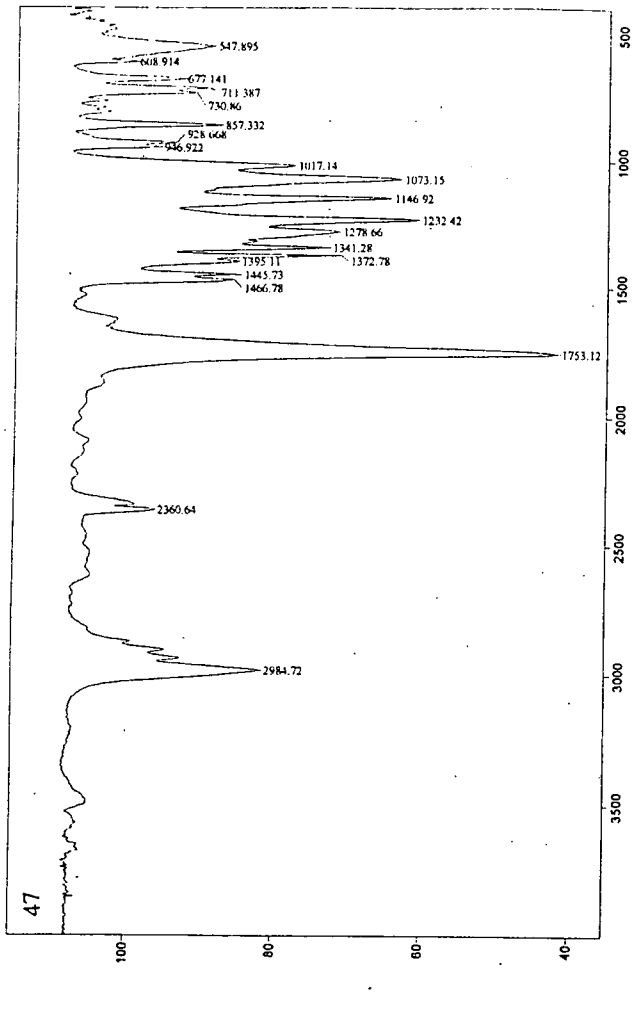

40
2360.93
2066.04
1653.23
1559.23
1540.88
1506.9
1457.03
1395.76
1331.35
1305.32
1081.35
1027.83
668.15
549.749
535.257
516.742
434.792
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong

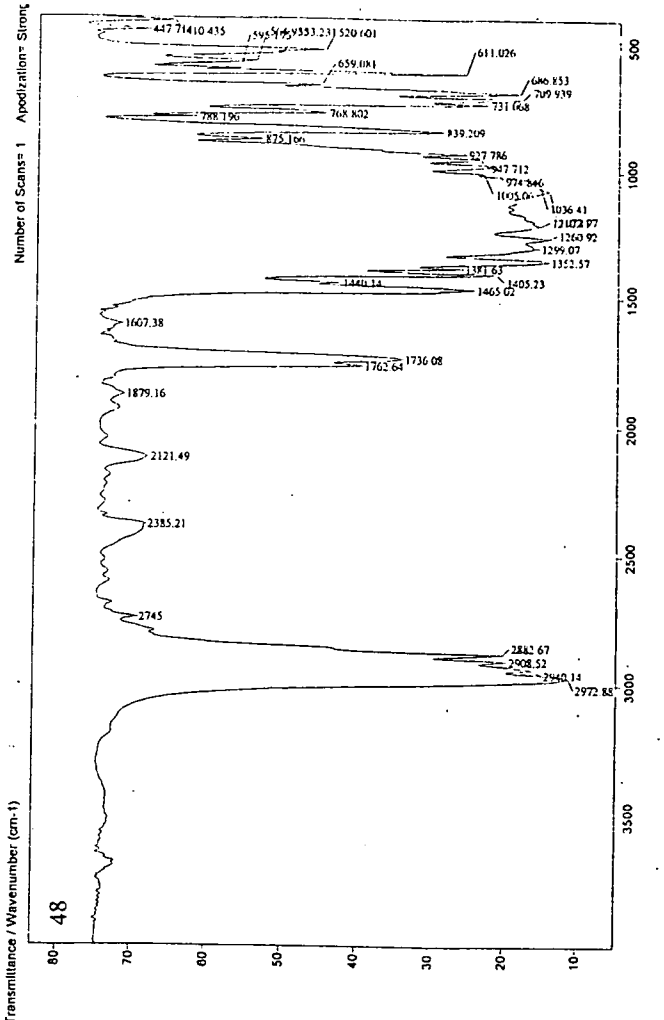

41
442.904
483.289
540.666
653.13
691.577
728.644
811.153
846.562
904.468
955.122
976.548
1301.24
1393.13
2209.11
2360.83
2676.87
2994.4

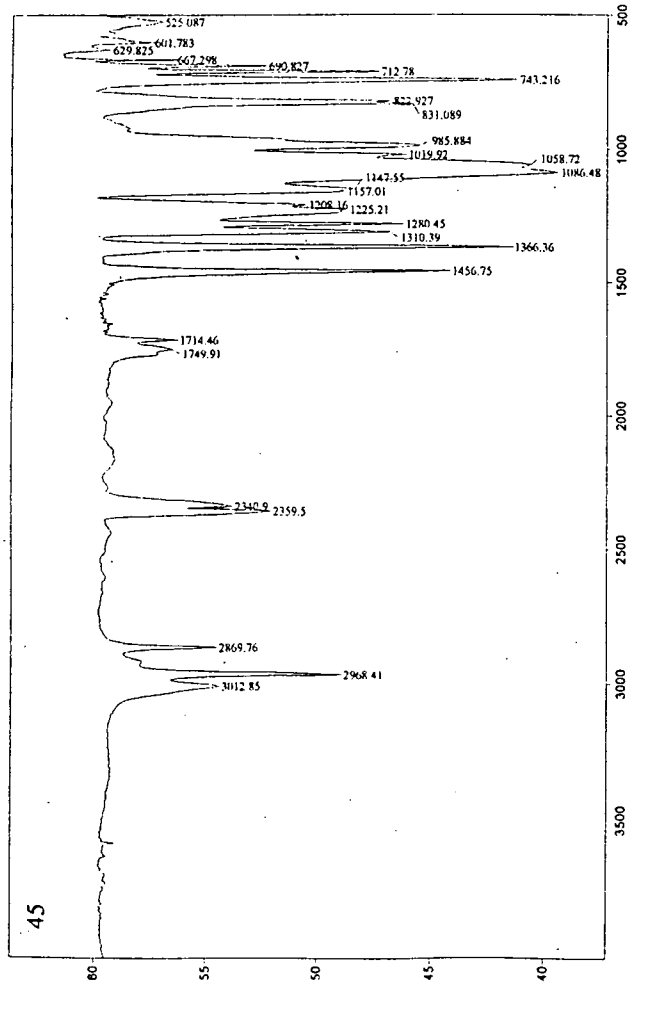

42
Number of Scans= 4
Apodization= Strong
Transmittance / Wavenumber (cm-1)
480.443
516.468
674.997
730.984
747.22
778.906
825.109
853.051
887.449
900.587
911.164
955.286
983.186
1012.19
1042.97
1089.13
1327.56
1774.49
2175.44
2235.39
2295.44

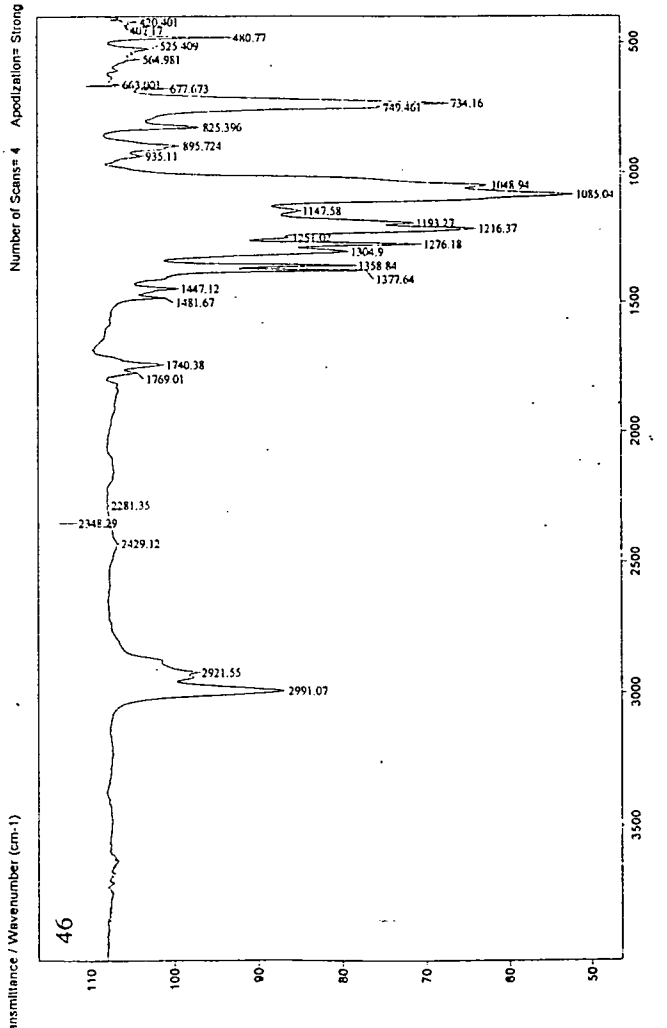

43
Number of Scans= 4
Apodization= Strong
Transmittance / Wavenumber (cm-1)
530.004
627.855
757.306
826.171
927.005
1239.5
1375.45
1402.44
1435.58
1479.11
1747.08
2981.37

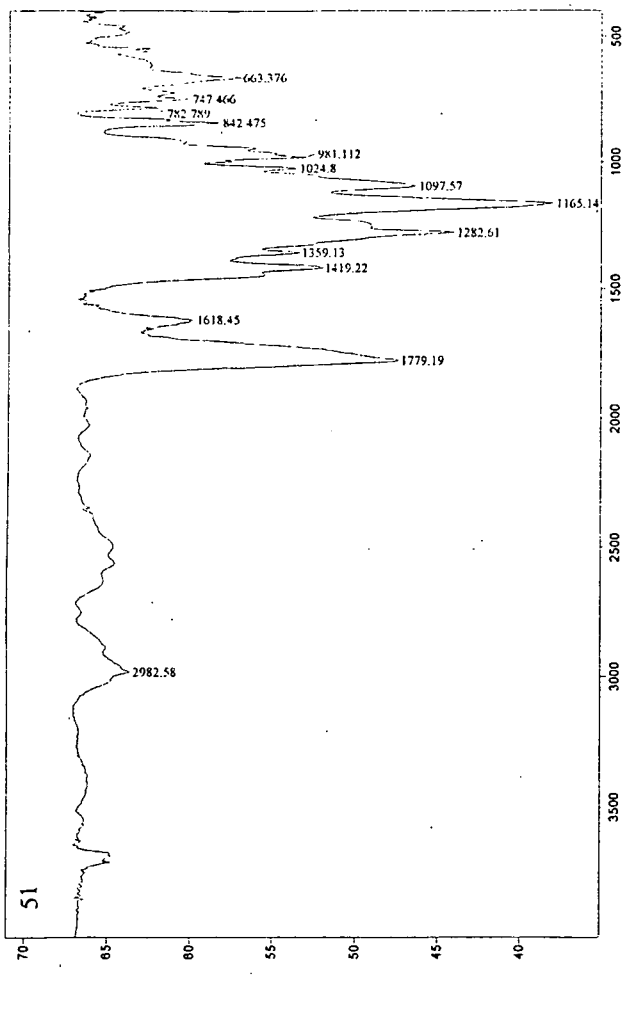

44
Number of Scans= 4
Apodization= Strong
Transmittance / Wavenumber (cm-1)
520.513
610.969
668.114
685.433
710.799
732.204
815.396
825.301
927.4
982.839
1012.16
1038.97
1071.42
1153.18
1193.3
1231.72
1268.99
1301.15
1355.17
1440.25
1454.89
1506.65
1540.34
1558.36
1652.91
1683.84
1759.85
2340.55
2359.53
2865.74
2964.72
3007.53
3733.26

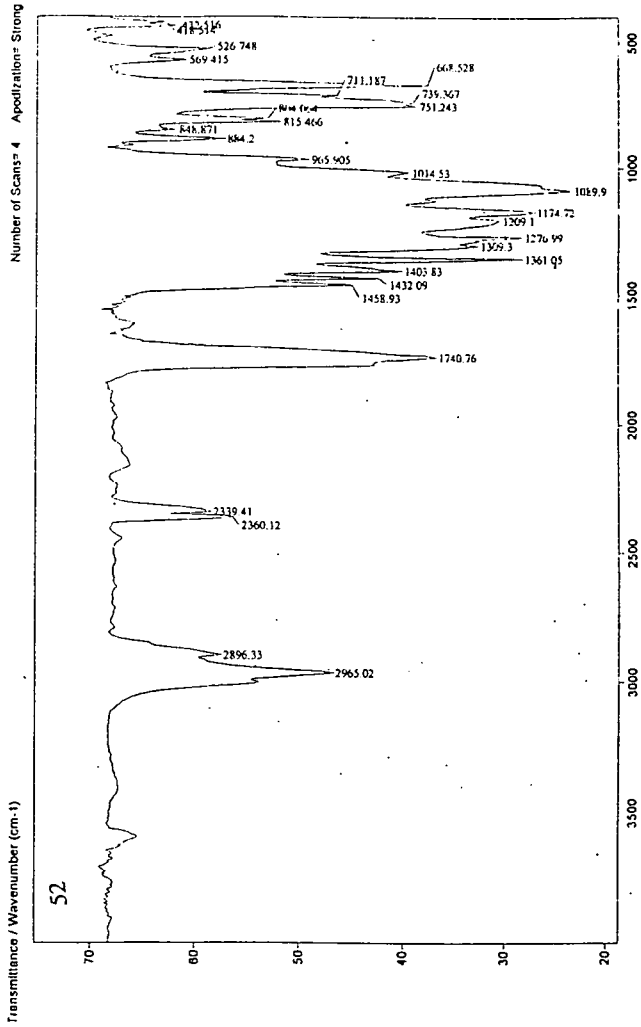

547.895
608.914
677.141
711.387
730.86
857.332
928.668
936.922
1017.14
1073.15
1146.92
1232.42
1278.66
1341.28
1372.78
1395.11
1445.73
1466.78
1753.12
2360.64
2984.72
47
100
80
60
40
500
1000
1500
2000
2500
3000
3500


Number of Scans= 1
Apodization= Strong
447.71
410.435
520.601
611.026
659.081
686.853
709.939
731.608
768.802
788.796
839.209
875.166
927.786
947.712
974.846
1036.41
1263.92
1299.07
1352.57
1391.63
1405.23
1441.14
1465.02
1607.38
1736.08
1762.64
1879.16
2121.49
2385.21
2745
2882.67
2908.52
2940.14
2972.85
48
Transmittance / Wavenumber (cm-1)
80
70
60
50
40
30
20
10
500
1000
1500
2000
2500
3000
3500


525.087
601.783
629.825
667.298
690.827
712.78
743.216
822.927
831.089
985.884
1019.92
1058.72
1086.48
1147.55
1157.01
1208.16
1225.21
1280.45
1310.39
1366.36
1456.75
1714.46
1749.91
2340.9
2359.5
2869.76
2968.41
3012.85
45
Transmittance / Wavenumber (cm-1)
80
55
50
45
40
500
1000
1500
2000
2500
3000
3500


Number of Scans= 4
Apodization= Strong
630.401
525.409
504.981
663.901
677.673
749.461
734.16
825.396
895.724
935.11
1048.94
1085.04
1147.58
1193.22
1216.37
1251.07
1276.18
1304.9
1358.84
1377.64
1447.12
1481.67
1740.38
1769.01
2281.35
2348.29
2429.12
2921.55
2991.07
46
Transmittance / Wavenumber (cm-1)
110
100
90
80
70
60
50
500
1000
1500
2000
2500
3000
3500


663.376
747.466
792.789
842.475
981.112
1024.8
1097.57
1165.14
1282.61
1359.13
1419.22
1618.45
1779.19
2982.58
51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1276.99
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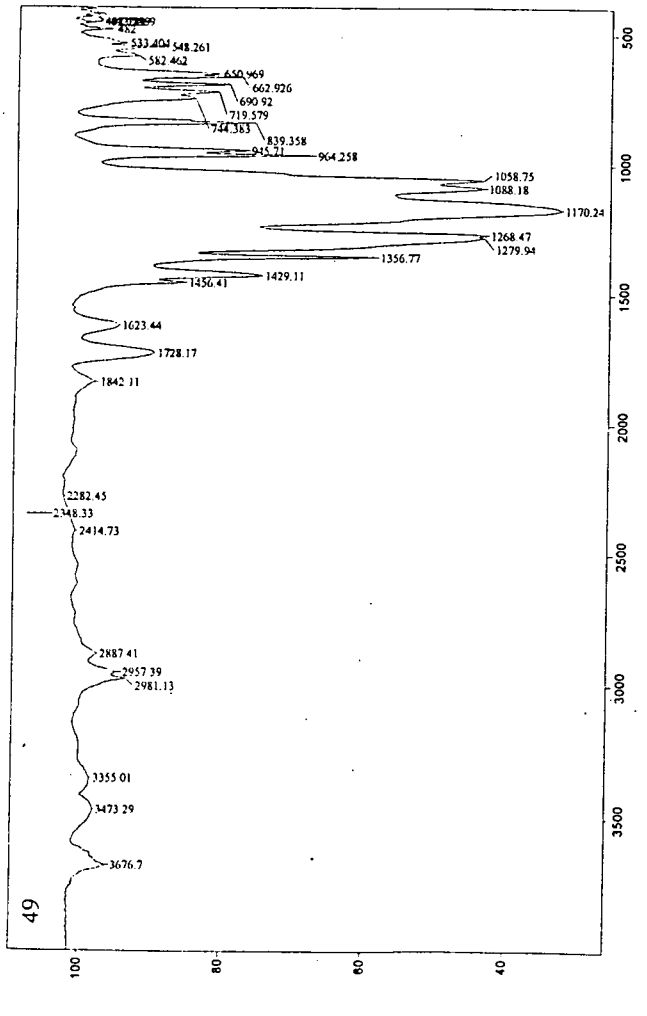
52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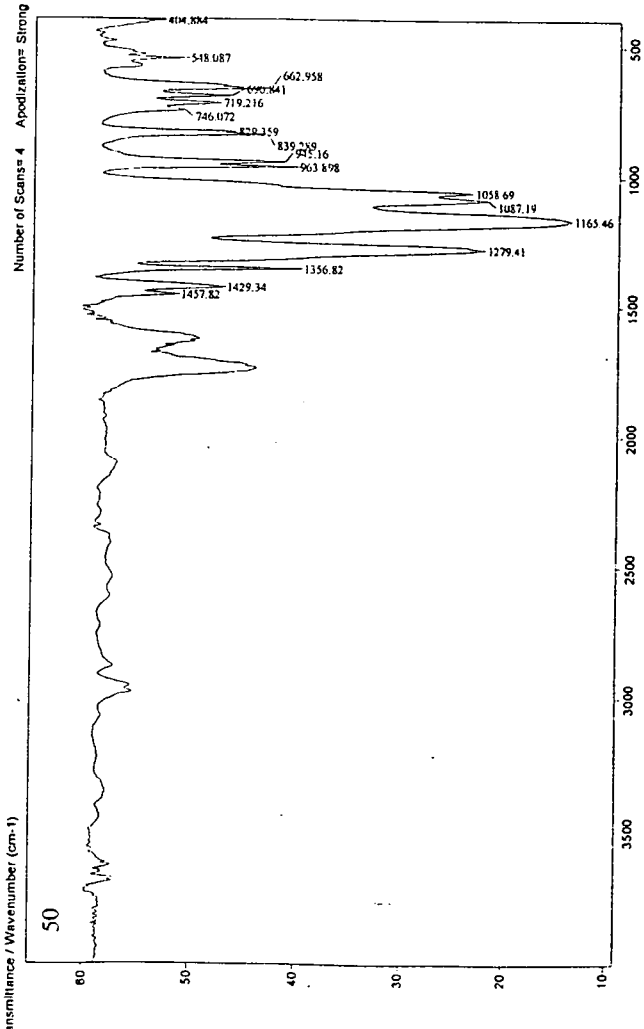
49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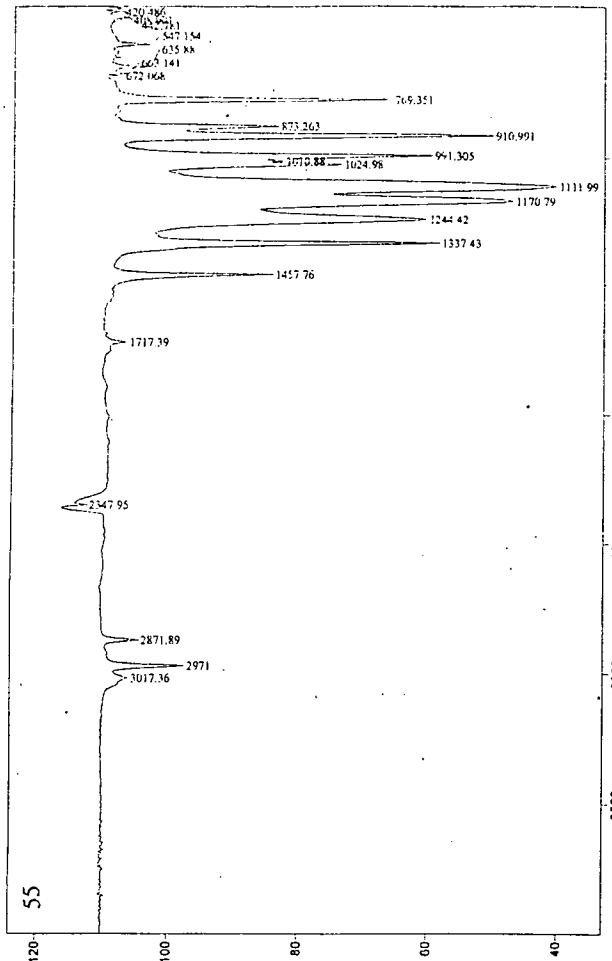
50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Transmittance / Wavenumber (cm-1)
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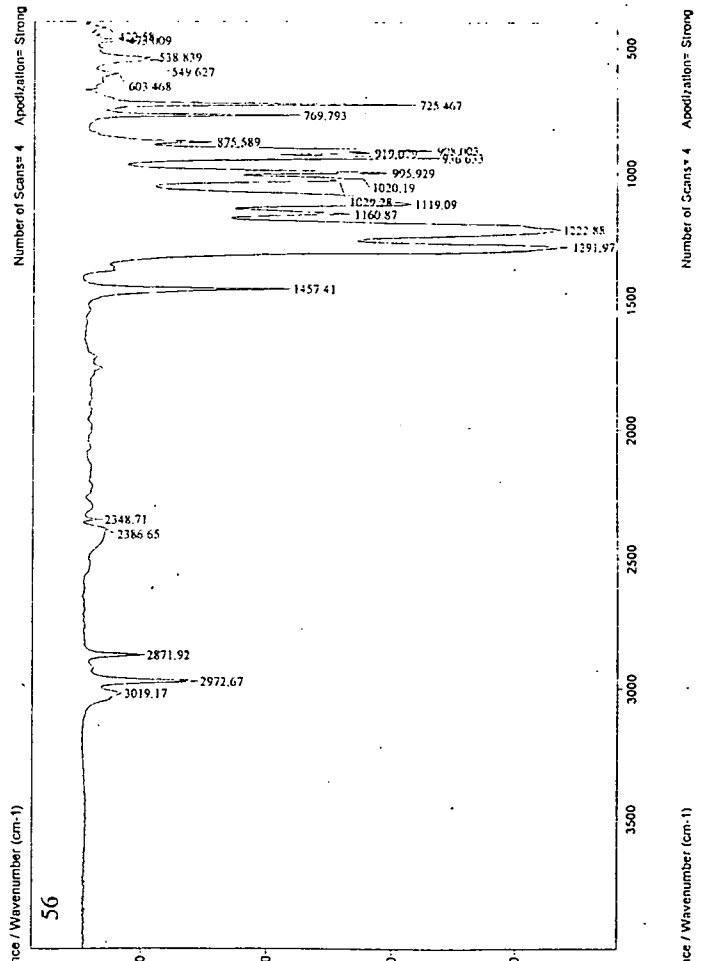
2971
3017.36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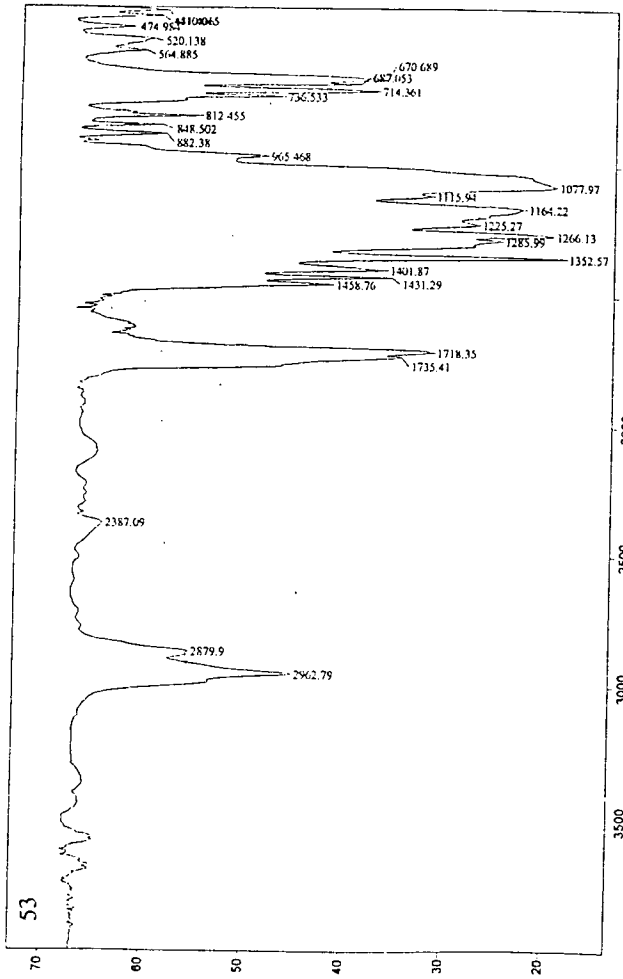
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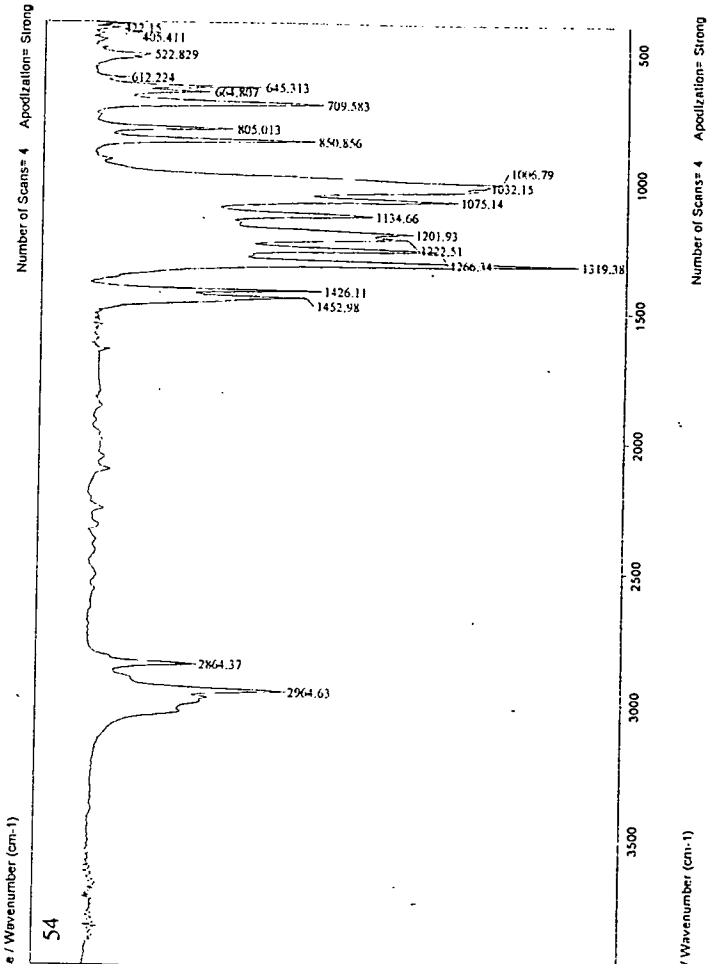
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Transmittance / Wavenumber (cm-1)
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1006.79
1032.15
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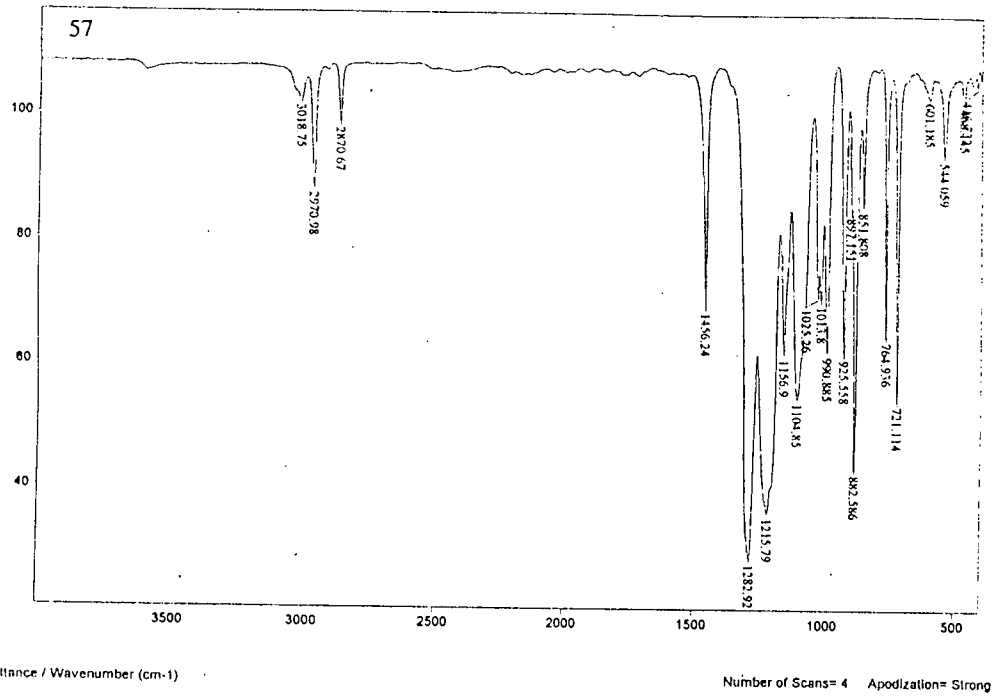
2964.63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990.885
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892.566
764.936
721.114
601.185
544.059
3500
3000
2500
2000
1500
1000
500
Transmittance / Wavenumber (cm-1)
Number of Scans= 4
Apodization= Strong

Appendix 4.

Requirements of the Board of Studies

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing:-

(**A**) all research colloquia, seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student;

(**B**) lectures organised by Durham University Chemical Society;

(**C**) details of postgraduate induction courses;

(**D**) all research conferences attended and papers presented by the author during the period when research for the thesis was carried out.

Colloquia, Lectures and Seminars From Invited Speakers 1994-1997

1994

October 5 Prof. N. L. Owen, Brigham Young University, Utah, USA*
Determining Molecular Structure - the INADEQUATE NMR way

October 19 Prof. N. Bartlett, University of California*
Some Aspects of Ag(II) and Ag(III) Chemistry

November 2 Dr P. G. Edwards, University of Wales, Cardiff
The Manipulation of Electronic and Structural Diversity in Metal Complexes - New Ligands

November 3 Prof. B. F. G. Johnson, Edinburgh University*
Arene-metal Clusters

November 9 Dr G. Hogarth, University College, London
New Vistas in Metal-imido Chemistry

November 10 Dr M. Block, Zeneca Pharmaceuticals, Macclesfield*
Large-scale Manufacture of ZD 1542, a Thromboxane Antagonist Synthase Inhibitor

November 16 Prof. M. Page, University of Huddersfield*
Four-membered Rings and b-Lactamase

November 23 Dr J. M. J. Williams, University of Loughborough*
New Approaches to Asymmetric Catalysis

December 7 Prof. D. Briggs, ICI and University of Durham*
Surface Mass Spectrometry

1995

January 11 Prof. P. Parsons, University of Reading*
Applications of Tandem Reactions in Organic Synthesis

January 18 Dr G. Rumbles, Imperial College, London
Real or Imaginary Third Order Non-linear Optical Materials

January 25 Dr D. A. Roberts, Zeneca Pharmaceuticals*
The Design and Synthesis of Inhibitors of the Renin-angiotensin System

February 1 Dr T. Cosgrove, Bristol University*
Polymers do it at Interfaces

February 8 Dr D. O'Hare, Oxford University
Synthesis and Solid-state Properties of Poly-, Oligo- and Multidecker Metallocenes

February 22 Prof. E. Schaumann, University of Clausthal*
Silicon- and Sulphur-mediated Ring-opening Reactions of Epoxide

March 1 Dr M. Rosseinsky, Oxford University
Fullerene Intercalation Chemistry

March 22 Dr M. Taylor, University of Auckland, New Zealand
Structural Methods in Main-group Chemistry

April 26 Dr M. Schroder, University of Edinburgh
Redox-active Macrocyclic Complexes : Rings, Stacks and Liquid Crystals

May 4 Prof. A. J. Kresge, University of Toronto
The Ingold Lecture Reactive Intermediates : Carboxylic-acid Enols and Other Unstable Species

October 11 Prof. P. Lugar, Frei Univ Berlin, FRG
Low Temperature Crystallography

October 13 Prof. R. Schmutzler, Univ Braunschweig, FRG.
Calixarene-Phosphorus Chemistry: A New Dimension in Phosphorus Chemistry

October 18 Prof. A. Alexakis, Univ. Pierre et Marie Curie, Paris*
Synthetic and Analytical Uses of Chiral Diamines

October 25 Dr.D.Martin Davies, University of Northumbria
Chemical reactions in organised systems.

November 1 Prof. W. Motherwell, UCL London*
New Reactions for Organic Synthesis

November 3 Dr B. Langlois, University Claude Bernard-Lyon*
Radical Anionic and Psuedo Cationic Trifluoromethylation

November 8 Dr. D. Craig, Imperial College, London*
New Stategies for the Assembly of Heterocyclic Systems

November 15 Dr Andrea Sella, UCL, London
Chemistry of Lanthanides with Polypyrazoylborate Ligands

November 17 Prof. David Bergbreiter, Texas A&M, USA*
Design of Smart Catalysts, Substrates and Surfaces from Simple Polymers

November 22 Prof. I Soutar, Lancaster University
A Water of Glass? Luminescence Studies of Water-Soluble Polymers.

November 29 Prof. Dennis Tuck, University of Windsor, Ontario, Canada
New Indium Coordination Chemistry

December 8 Professor M.T. Reetz, Max Planck Institut, Mulheim
Perkin Regional Meeting

1996

January 10 Dr Bill Henderson, Waikato University, NZ
Electrospray Mass Spectrometry - a new sporting technique

January 17 Prof. J. W. Emsley , Southampton University*
Liquid Crystals: More than Meets the Eye

January 24 Dr Alan Armstrong, Nottingham Univesity*
Alkene Oxidation and Natural Product Synthesis

January 31 Dr J. Penfold, Rutherford Appleton Laboratory,
Soft Soap and Surfaces

February 7 Dr R.B. Moody, Exeter University

Nitrosations, Nitrations and Oxidations with Nitrous Acid

February 12 Dr Paul Pringle, University of Bristol
Catalytic Self-Replication of Phosphines on Platinum(O)

February 14 Dr J. Rohr, Univ Gottingen, FRG
Goals and Aspects of Biosynthetic Studies on Low Molecular Weight Natural Products

February 21 Dr C R Pulham , Univ. Edinburgh
Heavy Metal Hydrides - an exploration of the chemistry of stannanes and plumbanes

February 28 Prof. E. W. Randall, Queen Mary & Westfield College
New Perspectives in NMR Imaging

March 6 Dr Richard Whitby, Univ of Southampton*
New approaches to chiral catalysts: Induction of planar and metal centred asymmetry

March 7 Dr D.S. Wright, University of Cambridge
Synthetic Applications of Me_2N-p-Block Metal Reagents

March 12 RSC Endowed Lecture - Prof. V. Balzani, Univ of Bologna
Supramolecular Photochemistry

March 13 Prof. Dave Garner, Manchester University*
Mushrooming in Chemistry

April 30 Dr L.D.Pettit, Chairman, IUPAC Commission of Equilibrium Data
pH-metric studies using very small quantities of uncertain purity

October 9 Professor G. Bowmaker, University Aukland, NZ
Coordination and Materials Chemistry of the Group 11 and Group 12 Metals : Some Recent Vibrational and Solid State NMR Studies

October 14 Professor A. R. Katritzky, University of Gainesville,University of Florida, USA*
Recent Advances in Benzotriazole Mediated Synthetic Methodology

October 16 Professor Ojima, Guggenheim Fellow, State University of New York at Stony Brook
Silylformylation and Silylcarbocyclisations in Organic Synthesis

October 22 Professor Lutz Gade, Univ. Wurzburg, Germany*
Organic transformations with Early-Late Heterobimetallics: Synergism and Selectivity

October 22 Professor B. J. Tighe, Department of Molecular Sciences and Chemistry, University of Aston
Making Polymers for Biomedical Application - can we meet Nature's Challenge?
Joint lecture with the Institute of Materials

October 23 Professor H. Ringsdorf (Perkin Centenary Lecture), Johannes Gutenberg-Universitat, Mainz, Germany
Function Based on Organisation

October 29 Professor D. M. Knight, Department of Philosophy, University of Durham.
The Purpose of Experiment - A Look at Davy and Faraday

October 30 Dr Phillip Mountford, Nottingham University
Recent Developments in Group IV Imido Chemistry

November 6 Dr Melinda Duer, Chemistry Department, Cambridge
Solid-state NMR Studies of Organic Solid to Liquid-crystalline Phase Transitions

November 12 Professor R. J. Young, Manchester Materials Centre, UMIST*
New Materials - Fact or Fantasy?
Joint Lecture with Zeneca & RSC

November 13 Dr G. Resnati, Milan*
Perfluorinated Oxaziridines: Mild Yet Powerful Oxidising Agents

November 18 Professor G. A. Olah, University of Southern California, USA*
Crossing Conventional Lines in my Chemistry of the Elements

November 19 Professor R. E. Grigg, University of Leeds*

Assembly of Complex Molecules by Palladium-Catalysed Queueing Processes

November 20 Professor J. Earnshaw, Deptartment of Physics, Belfast
Surface Light Scattering: Ripples and Relaxation

November 27 Dr Richard Templer, Imperial College, London
Molecular Tubes and Sponges

December 3 Professor D. Phillips, Imperial College, London*
"A Little Light Relief"

December 4 Professor K. Muller-Dethlefs, York University
Chemical Applications of Very High Resolution ZEKE Photoelectron Spectroscopy

December 11 Dr Chris Richards, Cardiff University*
Stereochemical Games with Metallocenes

1997

January 15 Dr V. K. Aggarwal, University of Sheffield*
Sulfur Mediated Asymmetric Synthesis

January 16 Dr Sally Brooker, University of Otago, NZ
Macrocycles: Exciting yet Controlled Thiolate Coordination Chemistry

January 21 Mr D. Rudge, Zeneca Pharmaceuticals*
High Speed Automation of Chemical Reactions

January 22 Dr Neil Cooley, BP Chemicals, Sunbury
Synthesis and Properties of Alternating Polyketones

January 29 Dr Julian Clarke, UMIST
What can we learn about polymers and biopolymers from computer-generated nanosecond movie-clips?

February 4 Dr A. J. Banister, University of Durham
From Runways to Non-metallic Metals - A New Chemistry Based on Sulphur

February 5 Dr A. Haynes, University of Sheffield
Mechanism in Homogeneous Catalytic Carbonylation

February 12 Dr Geert-Jan Boons, University of Birmingham*
New Developments in Carbohydrate Chemistry

February 18 Professor Sir James Black, Foundation/King's College London
My Dialogues with Medicinal Chemists

February 19 Professor Brian Hayden, University of Southampton
The Dynamics of Dissociation at Surfaces and Fuel Cell Catalysts

February 25 Professor A. G. Sykes, University of Newcastle
The Synthesis, Structures and Properties of Blue Copper Proteins

February 26 Dr Tony Ryan, UMIST*
Making Hairpins from Rings and Chains

March 4 Professor C. W. Rees, Imperial College
Some Very Heterocyclic Chemistry

March 5 Dr J. Staunton FRS, Cambridge University*
Tinkering with biosynthesis: towards a new generation of antibiotics

March 11 Dr A. D. Taylor, ISIS Facility, Rutherford Appleton Laboratory
Expanding the Frontiers of Neutron Scattering

March 19 Dr Katharine Reid, University of Nottingham
Probing Dynamical Processes with Photoelectrons

* lectures attended

First Year Induction Courses

This course consists of a series of one hour lectures on the services available in the department.

Departmental Organisations -	Dr. E. J. F. Ross
Safety Matters -	Dr. G. M. Brook
Electrical Appliances -	Mr. B. T. Barker
Chromatography and Microanalysis -	Mr. T. F. Holmes
Atomic Absorptiometry and Inorganic Analysis -	Mr. R. Coult
Library Facilities -	Mrs. M. Hird
Mass Spectroscopy -	Dr. M. Jones
NMR Spectroscopy -	Dr. A. Kenwright
Glass-blowing Techniques -	Mr. R. Hart
	Mr. G. Haswell

Research Conferences Attended

April 1995	North Eastern Graduate Symposium, University of Durham.
August 1997	15th International Symposium on Fluorine Chemistry, University of British Columbia, Vancouver, CANADA.

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