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UNIVERSITY OF DURHAM

A THESIS
entitled

FUNCTIONALISATION OF HYDROCARBONS USING FLUORINATED ALKENES

submitted by

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(Hatfield College)

A candidate for the degree of Doctor of Philosophy
1996

In Memory of Daniel John Spink

(13th December 1994-14th December 1995)

For God so loved the world, he gave his only son.

John 3 : 16

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Memorandum

The work described in this thesis was carried out at the University of Durham between October 1992 and September 1995. This thesis is the work of the author, except where acknowledged by reference, and has not been submitted for any other degree.

The work has been presented, in part, by the author at:

9th. European Symposium on Fluorine Chemistry, Bled, Slovenia

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Nomenclature

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

The following abbreviations are also used:

DTBP	Di-tert-butyl peroxide
DBPO	Di-benzoyl peroxide
FEP	Fluorinated ethylene-propylene (HFP/TFE copolymer)
GLC	Gas chromatography
HF	Hydrogen fluoride
HFP	Hexafluoropropene
IR	Infra red
MS	Mass spectrometry
NMR	Nuclear magnetic resonanec
PY	Pyridine
TFE	Tetrafluoroethylene
UV	Ultra violet

Abstract

Functionalisation of Hydrocarbons using Fluorinated Alkenes

Functionalisation of hydrocarbons is a field of continuing activity and a variety of approaches to this field, have been taken. This thesis is concerned with the functionalisation of the carbon-hydrogen bond,in hydrocarbons, using fluorinated alkenes via a free radical chain mechanism.

$$\text{R-H} \xrightarrow[\text{CF}_2\text{=CFCF}_3]{\text{Radical initiator}} \text{R-CF}_2\text{CFHCF}_3$$

Addition of the nucleophilic alkyl radical to the electrophilic fluorinated alkene, specifically hexafluoropropene, occurs readily to give incorporation of the polyfluoroalkyl group into a number of hydrocarbons, including aliphatic, mono-, bi- and polycyclic systems.

Further chemistry of these polyfluoroalkylated systems has been investigated, including dehydrofluorination of the polyfluoralkyl group to give a series of novel mono- di- and poly-enes with polyfluoroalkenyl groups.

$$\text{R-CF}_2\text{CFHCF}_3 \xrightarrow{\text{- HF}} \text{R-CF=CFCF}_3$$

Perfluorination of the polyfluoroalkylated systems, using high valency metal fluorides, produced a range of new perfluorocarbons of interest and the monocyclic polyfluoroalkylated systems were further functionalised, by radical chemistry, to give isomeric products.

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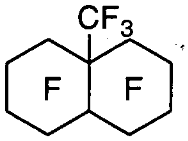
Chapter One

Introduction of Highly Fluorinated Groups Into Organic Compounds

1.1 Fluorine in Organic Chemistry

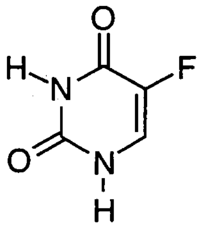
There are very few naturally occurring organic compounds containing fluorine. Therefore organofluorine chemistry is an almost entirely synthetic field which is continually expanding. Three general approaches have been used for the synthesis of fluorinated organic compounds, which can be categorised as perfluorination, selective fluorination and the incorporation of an already fluorinated group.

A variety of methods are available for selective and perfluorination which have been reviewed elsewhere[1,2]. Perfluorinated compounds have found a wide range of uses, such as inert fluids and coatings, because of their high chemical and thermal stability and 'non-stick' properties. Their ability to absorb oxygen and carbon dioxide created interest in compounds such as perfluoromethyldecalin (**1**) as 'blood substitutes'.

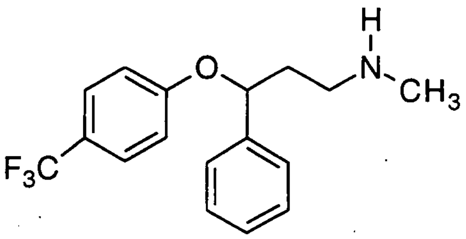


(1)

Selective fluorination of certain organic compounds can lead to increased biological activity, as replacing a hydrogen with fluorine has a significant effect of the electronic properties of the molecule with minimal steric disruption. For example 5-fluoro-uracil (**2**) has shown anti-cancer properties.

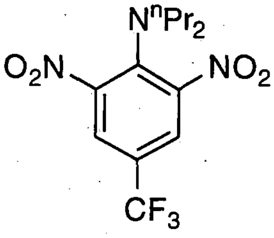


(2)



(3)

The introduction of a fluorinated group, such as a trifluoromethyl group, into an organic compound can also lead to high biological activity, for example the anti-depressant Prozac™ (**3**). The fluoroalkyl group can also increase the lipophilicity of a molecule, for example the plant protection agent Trifluralin™ (4) has a high activity due to its high lipophilicity.



(4)

This thesis is concerned with methodology for the introduction of polyfluoroalkyl groups via free radical additions to fluorinated alkenes. Therefore this introduction will include a general discussion of methods available to introduce perfluoro- and polyfluoroalkyl groups, some basic principles of free radical chemistry and a more comprehensive review of free-radical additions to hexafluoropropene (HFP), which is employed extensively in the original work done here.

1.2 Methods of Introducing Fluoroalkyl Groups

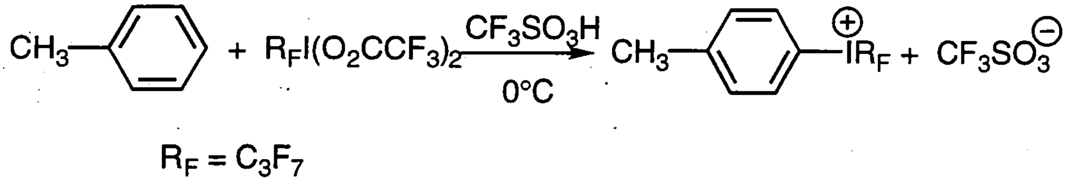
A wide range of methods, including electrophilic, nucleophilic and free-radical processes, have been devised to introduce fluoroalkyl groups into organic compounds and the following sections give brief introductions to these methods.

1.21 Electrophilic Fluoroalkylating Agents

A series of perfluoroalkyl and polyfluoroalkyl arylidonium salts have been prepared[3]. These act as sources of electrophilic fluoroalkyl equivalents (R_F^+) and react with nucleophiles, such as carbanions, phenyl derivatives, alkenes and alkynes.

Generally, the best method of preparation of the fluoroalkyl arylidonium salts is the reaction of an arene, e.g. toluene, with [bis(trifluoroacetoxy)iodo]perfluoroalkane (scheme 1.1), which is usually produced *in situ* via oxidation of iodoperfluoroalkanes with trifluoroperacetic acid[4].

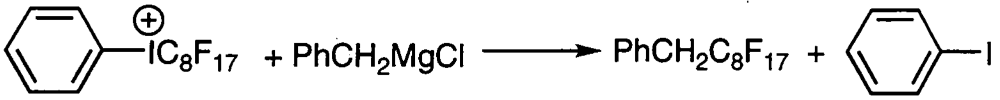
Scheme 1.1



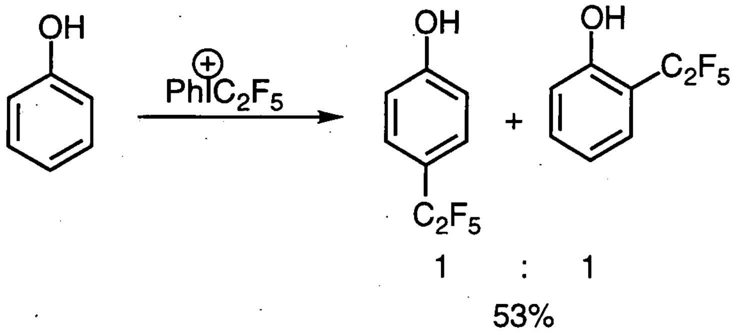
The preferred counterion is the triflate anion, because of its electron withdrawing trifluoromethyl group which reduces its nucleophilicty and consequently it does not participate in the reactions of the salt.

Grignard reagents (scheme 1.2) and perfluoroalkynyllithium reagents reacted with the iodonium salts to give the expected products, perfluoroalkyllithium reagents also reacted, but gave lower yields[5,6]. Enolate ions of β-diketones and β-ketoesters reacted to give alkylation at both the carbon and oxygen[6].

Scheme 1.2

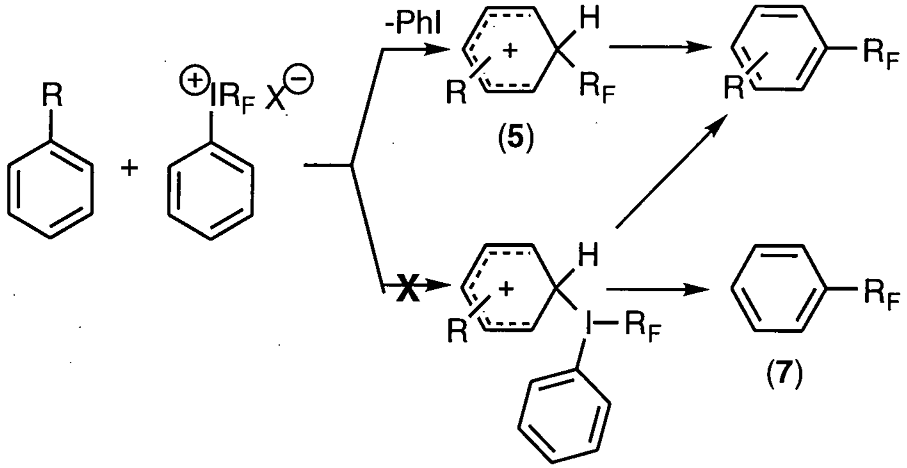


Aryl systems reacted with the iodonium salts to give electrophilic aromatic substitution products[7,8].



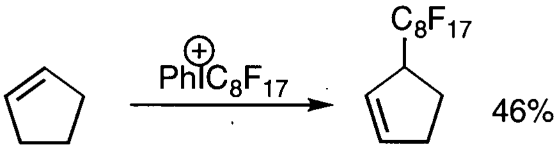
The reaction mechanism (scheme 1.3) is thought to proceed via intermediate (**5**), rather than (**6**), as compound (**7**) is not produced and, in general, a high proportion of ortho products are observed, which would also favour the less sterically hindered intermediate (**5**).

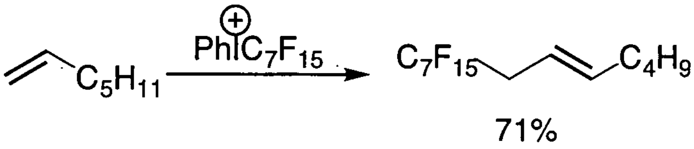
Scheme 1.3 Addition of electrophilic fluoroalkyl group to phenyl systems



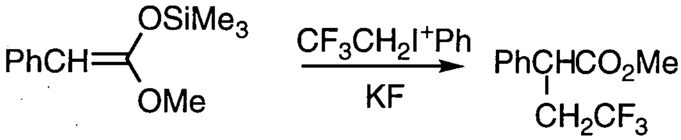
(**6**)

In general, addition of iodonium salts to alkenes, with allylic hydrogens, is followed by rearrangement of the double bond[9].





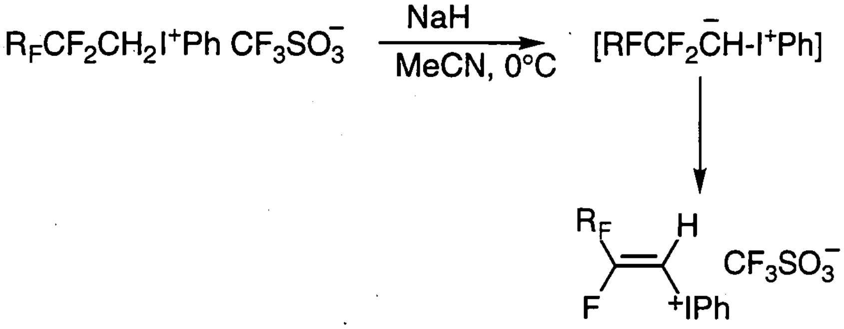
Alkynes are less reactive than alkenes and give a mixture of substitution and addition products, depending on the solvent[10]. Trimethyl silyl enol ethers react to produce carbonyl compounds in good yield[11-13].



$$\mathrm{PhCH{=}C(OSiMe_3)(OMe)} \xrightarrow[\mathrm{KF}]{\mathrm{CF_3CH_2I^+Ph}} \mathrm{PhCH(CH_2CF_3)CO_2Me}$$

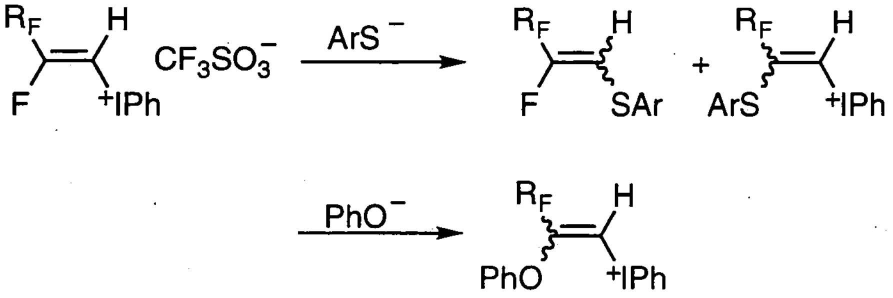
$$\mathrm{CH_2{=}CHCH{=}CHOSiMe_3} \xrightarrow[\mathrm{Py}]{\mathrm{C_8F_{17}I^+Ph}} \mathrm{C_8F_{17}CH_2CH{=}CHCHO}$$

Sodium hydride eliminated hydrogen fluoride from some polyfluoroalkyl aryliodonium salts[12] to produce the alkenyl salts (**8**).



(8)

The alkenyl salt reacts at both vinylic carbons, with loss of fluoride ion or iodobenzene, but this can be controlled to an extent by the hardness of the nucleophile. For example, the soft *t*-butylthiophenoxide ion reacts at both sites whereas with the hard phenoxide ion only fluorine substitution occurs[7].



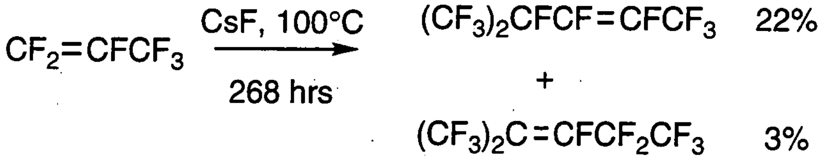
1.22 Nucleophilic Perfluoroalkylating Agents

Nucleophilic perfluoroalkyl groups can be produced by addition of fluoride ion to perfluoroalkenes, for example, the reaction between HFP and caesium fluoride in aprotic solvent.

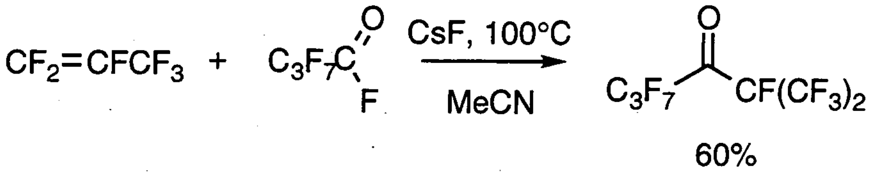
$$CF_2{=}CFCF_3 \xrightarrow[\text{Aprotic solvent}]{F^{\ominus}} \left[(CF_3)_2\overset{\ominus}{C}F\right]$$

(9)

The resulting carbanion (**9**) reacts with perfluoroacyl fluorides[14,15], perfluoroalkenes[16], and electrophilic fluoroaromatics[17], *in situ.*



$$CF_2{=}CFCF_3 \xrightarrow[\text{268 hrs}]{\text{CsF, 100°C}} \begin{array}{ll} (CF_3)_2CFCF{=}CFCF_3 & 22\% \\ + & \\ (CF_3)_2C{=}CFCF_2CF_3 & 3\% \end{array}$$



1.23 Perfluoroalkylorganometallics

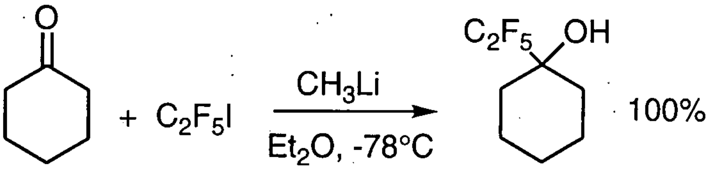
There are many examples of perfluoroorganometallic reagents in the literature and several excellent reviews[18-21]. and this is just a brief introduction to some of the most commonly used perfluoroalkyl organometallic reagents. Examples of reactions between organometallic reagents and organofluorine compounds are known, but are beyond the scope of this review and are reviewed elsewhere[22,23].

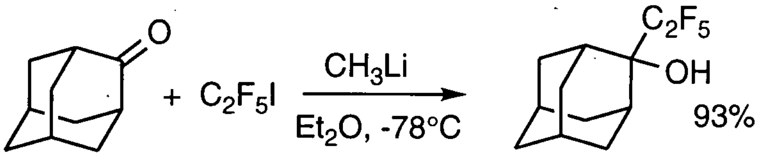
Perfluoroalkyllithium reagents

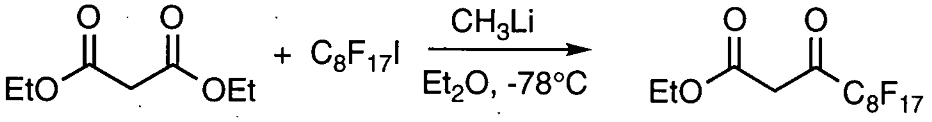
Initial attempts to produce perfluoroalkyllithium reagents failed because of their instability and only fluoro-alkenes were produced. It was assumed that the perfluoroalkyllithium reagent decompose, with β-elimination of lithium fluoride. The most general method of producing a perfluoroalkyllithium reagent is by halogen-lithium exchange at low temperature[24].

$$C_3F_7I \xrightarrow[\text{Et}_2\text{O, -74°C}]{CH_3Li} C_3F_7Li$$

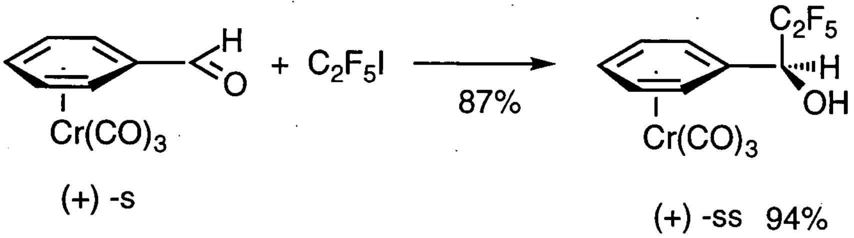
Perfluoroalkyllithium reagents react with a wide variety of electrophiles, including carbonyl compounds[25-27]. Lithium-halogen exchange, *in situ* is preferred because of the instability of the perfluoroalkyl lithium reagent.





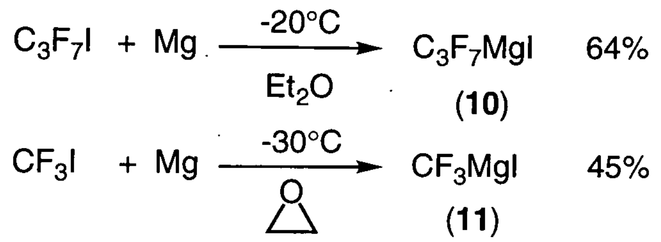


Perfluoroalkyllithium reagents react with chromiun tricarbonyl complexes of benzaldehydes, attacking at the least sterically hindered face of the molecule to give high asymmetric induction[28,29].



Perfluoroalkyl magnesium reagents

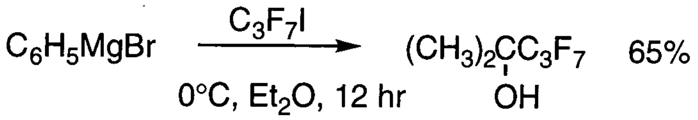
Perfluoroalkyl magnesium reagents are more stable than perfluoroalkyl lithium reagents, but still must be prepared at low temperature with pure magnesium. The favoured method is insertion of magnesium in to a carbon-halogen bond[30,31]. Trifluoromethyl magnesium halides are more difficult to produce than the longer chain perfluoroalkyl magnesium reagents. The maximum yield of trifluoromethyl magnesium iodide **(11)** was only 45% and it was much less reactive perfluoropropyl magnesium iodide[32] **(10)**.



(10)

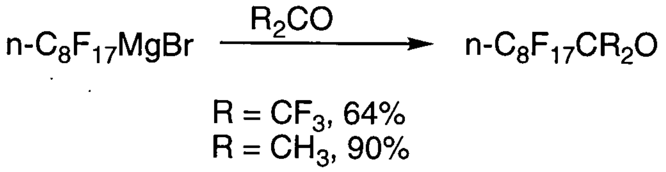
(11)

An alternative method to perfluoro Grignard reagents was developed by reacting an unfluorinated Grignard reagent with a perfluoroalkyl iodide at low temperature. These reagents reacted *in situ* with acetone to give the corresponding alcohol[33,34].



$$C_6H_5MgBr \xrightarrow[0°C,\ Et_2O,\ 12\ hr]{C_3F_7I} (CH_3)_2\underset{\displaystyle OH}{C}C_3F_7 \quad 65\%$$

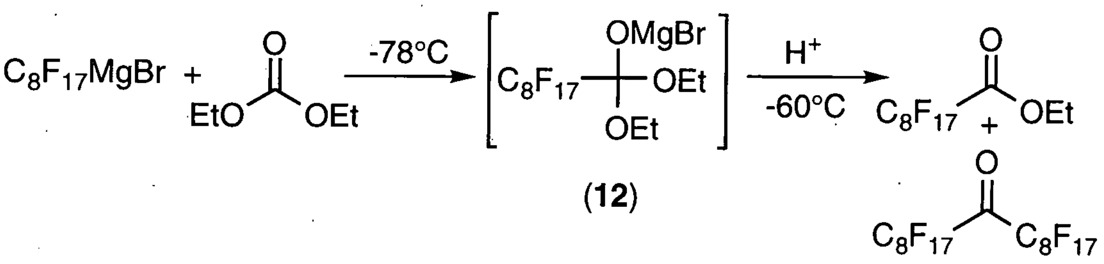
Perfluoroalkyl Grignard reagents react with a variety of electrophiles, including carbonyl compounds[35].



$$n\text{-}C_8F_{17}MgBr \xrightarrow{R_2CO} n\text{-}C_8F_{17}CR_2O$$

$R = CF_3$, 64%
$R = CH_3$, 90%

At low temperature, perfluoroalkyl esters can be produced from dialkyl carbonates, with perfluoroalkyl ketones only produced as byproducts, because of the stability of the hemiketal salt intermediate[36] (**12**).



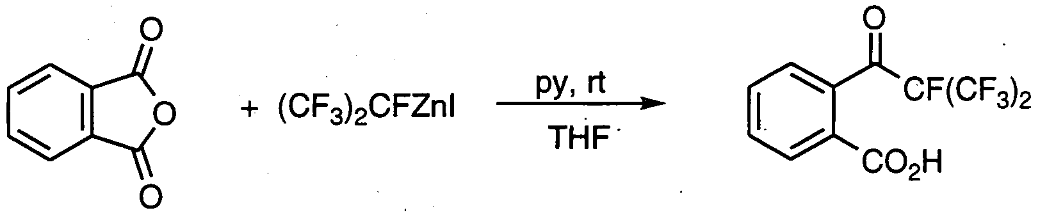
(12)

Perfluoroalkyl zinc reagents

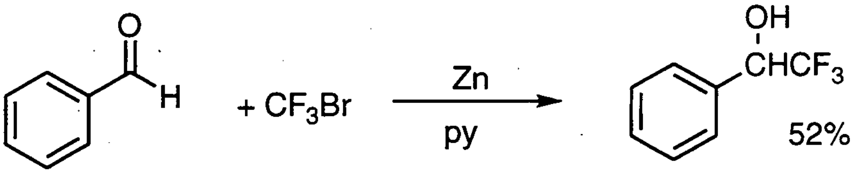
Solvated perfluoroalkyl zinc reagents are produced by reaction of zinc with perfluoroalkyl iodides in ethereal solutions[37].

$$C_3F_7I + Zn \xrightarrow[\text{Dioxane}]{0°C} C_3F_7ZnI \qquad 50\text{-}60\%$$

They can also be prepared by ligand exchange with other perfluoroalkylated metals. Solvated perfluoroalkyl zinc are too stable to react with carbonyl compounds, unless they are activated by pyridine[38].



Perfluoroalkyl halides react with electrophiles in the presence of zinc, presumably via a perfluoroalkyl zinc halide intermediate[39].

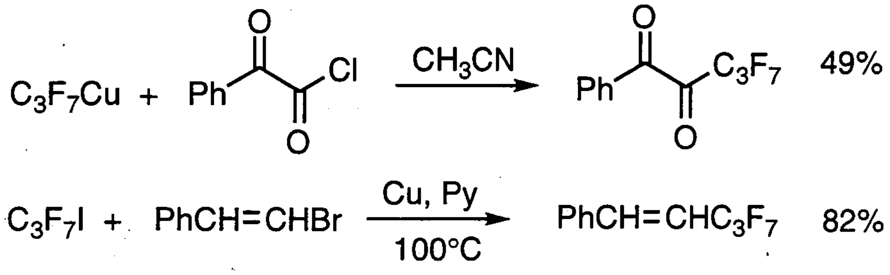


Perfluoroalkyl copper reagents

Perfluoroalkyl copper reagents were first prepared by addition of copper metal to perfluoroalkyl iodides in a co-ordinating solvent[40]. They can also be produced by decarboxylation of perfluorocarboxylates in the presence of copper (I) halide and metathesis of other perfluoroalkylorganometallic reagents with copper metal or copper (I) salts.

$$R_FI + 2Cu \xrightarrow[110\text{-}120°C]{DMSO} R_FCu + CuI$$

Reactions with organic halides can be carried out using pregenerated perfluoroalkyl copper[41] or *in situ* [42].



Perfluoroalkyl copper reagents react with alkenes, presumably via the perfluoroalkyl radical generated from decomposition of the perfluoroalkyl reagent[43].

$$\begin{array}{c} C_7F_{15}Cu \\ + \\ CH_2{=}CHC_5H_{11} \end{array} \xrightarrow[\text{DMSO}]{110°\text{C}} \begin{array}{ccc} C_7F_{15}CH_2CH_2C_5H_{11} & + & C_7F_{15}CH_2CH{=}CHC_4H_9 \\ 1 & : & 2 \end{array}$$

A lot of interest has been generated by the addition of perfluoroalkyl copper reagents to aryl halides and there are many excellent reviews on this in the literature[19,20].

1.24 Fluoroalkylation Via Radicals

The most common source of perfluoroalkyl radicals is homolytic bond cleavage of the carbon-halogen bond in perfluoroalkyl halides. This can be initiated by thermolysis, ultraviolet light, gamma rays, electrolysis or chemical initiators, such as peroxides. The trifluoromethyl radical has been produced by these methods and its reactions with aromatics, heteroaromatics, alkenes and alkanes have been reviewed by Chambers[21] and McClinton[44] .

1.25 Functionalisation of the Carbon-Iodine Bond

Perfluoroalkyl iodides are also used as telogens in free-radical telomerisations with perfluoroalkenes[45-46], and polyfluoroalkenes[47], for example trifluoromethyl iodide and tetrafluoroethylene[48].

$$CF_3I \xrightarrow{h\nu \text{ or } \Delta} \dot{C}F_3 + {}^{\bullet}I$$

$$CF_3I \xrightarrow{CF_2{=}CF_2} CF_3CF_2\dot{C}F_2$$

$$CF_3CF_2\dot{C}F_2 \xrightarrow{n(CF_2{=}CF_2)} CF_3(CF_2CF_2)_nCF_2\dot{C}F$$

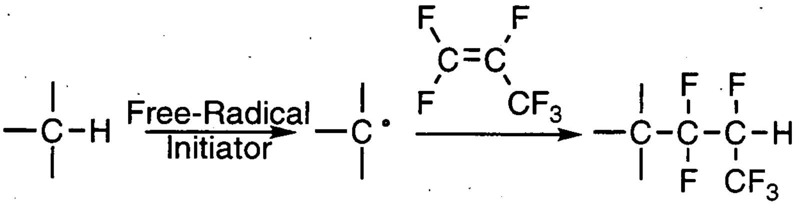
$$CF_3(CF_2CF_2)_nCF_2\dot{C}F_2 \xrightarrow{CF_3I} CF_3(CF_2CF_2)_{n+1}CF_3$$

Telomerisations proceed via a free-radical chain mechanism, which is discussed more fully in the next section. The chain length of such telomers can be controlled by the ratio of the reactants. Increasing the proportion of perfluoroalkyl iodide reduces the telomer chain length, whereas increasing the proportion of perfluoroalkene increases the telomer chain length.

1.3 Functionalisation of the Carbon-Hydrogen Bond

1.31 Free Radical Additions to Fluorinated Alkenes

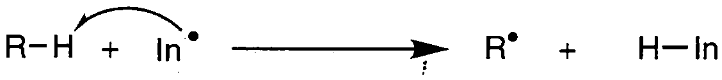
A further method of introducing a fluoroalkyl group into an organic compound is insertion of a fluorinated alkene into a carbon-hydrogen bond, via a free-radical chain mechanism, which is an on going project in this laboratory[49].



Free-radicals are uncharged species and therefore are not as easily stabilised by solvents as ions[50], although solvent effects can be important[51]. A free-radical chain reaction (scheme 1.4) can consist of thousands of steps which can be categorised into three important stages: initiation, propagation and termination.

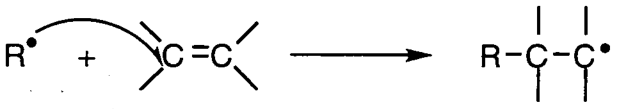
Scheme 1.4 Free-Radical Addition Chain Mechanism

Initiation

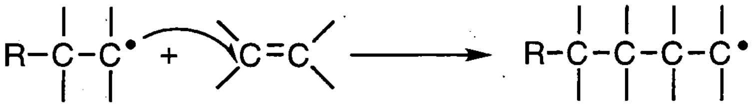


Propagation

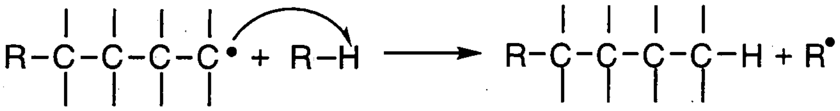
Addition



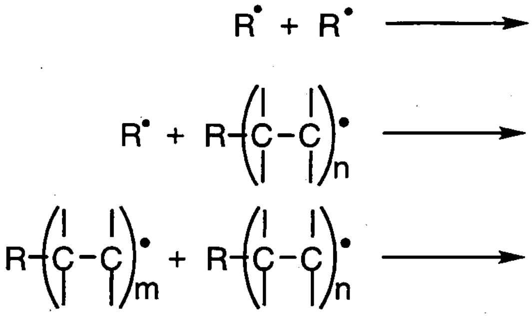
Telomerisation



Chain transfer



Termination



In free-radical addition reactions the propagation stage consists of three separate processes: addition, telomerisation and chain transfer.

Hexafluoropropene (HFP) is a particularly useful fluorinated alkene for free-radical addition reactions, as is it an industrially available fluorinated alkene that only forms a homopolymer under extreme conditions[52], because of steric inhibition by its trifluoromethyl group. Consequently in free-radical additions to HFP, chain transfer competes successfully with telomerisation and only addition products are observed.

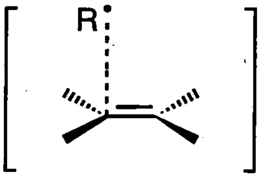
1.32 Reaction Rate and Regiochemistry

The propagation stages dominates the radical chain and are therefore the major processes in determining the regiochemistry and rate of the reaction. In additions to HFP, the propagation stage consists of two processes, addition of the radical to the double bond and abstraction of a hydrogen by the fluoroalkyl radical.

Many reviews [53-58]have been published on the factors affecting radical additions to double bonds and hydrogen-abstraction reactions and they concluded that both processes depend on the complex interplay of polar effects, steric effects and radical stabilisation.

Free-radical addition

Radical addition to a double bond is an exothermic process[59], as a π-bond is broken and a σ-bond is formed, and therefore an early 'reactant-like' transition state (**13**) is expected.



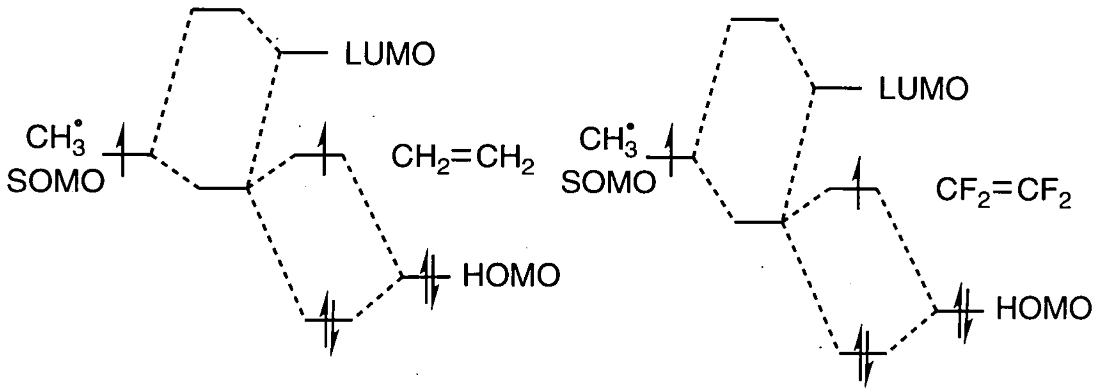
(13)

In an early transition state the stability of the radical formed is not of major importance, and polar and steric effects are the dominating factors affecting the rate and regiochemistry of addition. Tedder[55] concluded from experimental data that polar effects had a major affect on the overall rate of addition to fluorinated alkenes. This was demonstrated by comparing the reactivities of methyl and trifluoromethyl radicals towards ethene and tetrafluoroethylene (Table 1.1). It was reported that the electrophilic trifluoromethyl radical reacted with ethene at a faster rate than the methyl radical, whereas the methyl radical reacted faster with the electrophilic alkene tetrafluoroethylene.

Table 1.1 Ratio of radical addition rates to Tetrafluoroethene/ ethene[55].

	$k_{C_2F_4}/k_{C_2H_4}$ (164°C)
$CH_3\bullet$	9.5
$CF_3\bullet$	0.1

Giese[58] explained the effect of polarity on rate of addition by Molecular Orbital theory. In the addition of a methyl radical to ethene the methyl radical's SOMO is situated approximately between the HOMO and LUMO of ethene and interacts about equally with both resulting in stabilisation of the HOMO. For an electrophilic alkene, such as tetrafluoroethylene, the electron-withdrawing substituents on the double bond lower the energy of the alkene LUMO increasing its interaction with the methyl radical's SOMO which results in stabilisation of the SOMO and HOMO and an increased reaction rate.



The regiochemistry of addition to unsymmetrical alkenes was more complex. A study by Tedder[55] of mono-fluorine substituted alkenes ($CH_2=CHF$) found that both nucleophilic and electrophilic radicals favoured addition at the CH_2 of the alkene (table 1.2).

Table 1.2 Orientation Ratios (α : β) for addition at 150°C

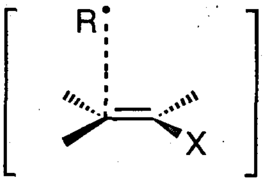
	α β $CH_2=CHF$
$CH_3\bullet$	1 : 0.09
$CH_2F\bullet$	1 : 0.3
$CHF_2\bullet$	1 : 0.2
$CF_3\bullet$	1 : 0.2

As the size of the attacking radical was increased, from a trifluoromethyl radical to a perfluoro-*tert*-butyl radical, the proportion of addition at the less substituted vinylic carbon also increased (table 1.3).

Table 1.3 Orientation Ratio (α : β) for addition at 150°C

	α β $CH_2=CHF$
$CF_3\bullet$	1 : 0.1
$(CF_3)_2CF\bullet$	1 : 0.02
$(CF_3)_3C\bullet$	1 : 0.005

These results suggested that steric effects dominated in this system. Giese explained the preference of an attacking radical for the least substituted end of the alkene by an unsymmetrical transition state (**14**) in which steric interactions between the radical and alkene substituents are minimised.



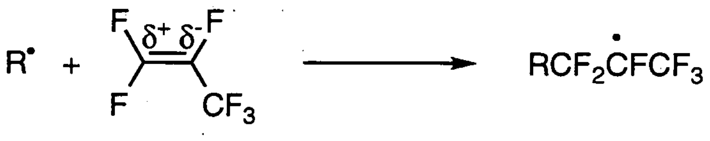
(14)

Nevertheless a small polar effect was observed, as increasing the nucleophilicity of the radical did increase the proportion of addition at the fluorine-substituted vinylic carbon. Increasing the number of fluorine substituents on the alkene complicated the system. For trifluoroethylene (table 1.4), it was found that addition of the nucleophilic methyl radical favoured addition at the more substituted vinylic carbon, suggesting that polar effects were dominant in this system.

Table 1.4 Orientation Ratio (α : β) for addition at 150°C

	α β $CHF=CF_2$
$CH_3\bullet$	1 : 2.1
$CH_2F\bullet$	1 : 2.0
$CHF_2\bullet$	1 : 0.9
$CF_3\bullet$	1 : 0.5

In additions to HFP, nucleophilic carbon radicals preferentially attack the difluoromethylene group. In this case there is no conflict between polar and steric effects as the CF_2 group is the more electrophilic (c.f. nucleophilic additions to HFP[60]) and the less sterically hindered site.



Hydrogen Abstraction

Generally, hydrogen-abstraction has a larger activation energy than radical addition and therefore the transition state usually occurs later and so the stability of the radical formed must be considered, along with polar and steric effects.

Studies by Tedder[56] on hydrogen abstraction by trifluoromethyl and methyl radicals on alkanes (table 1.5) produced evidence of an Evans-Polyani relationship ($E_A = \alpha[D(R\text{-}H)] + \beta$), i.e. there was a direct relationship between the strength of the bond broken in the alkane and the activation energy of hydrogen-abstraction, confirming the importance of the stability of the radical formed in hydrogen abstraction. This relationship was only valid when polar effects were constant, indicating the importance of polarity in hydrogen abstraction.

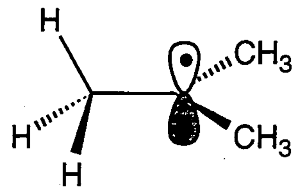
Table 1.5 Evans-Polyani Relationship

$$R\text{-}H + X\bullet \longrightarrow R\bullet + HX$$

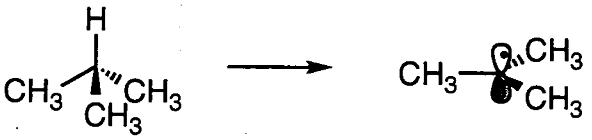
$$E_A = \alpha[D(R\text{-}H)] + \beta$$

X	α	β (kcalmol^{-1})
$CH_3\bullet$	0.49	74
$CF_3\bullet$	0.53	84

In alkanes, radical stability increases as the number of alkyl substituents are increased, as the radical formed is stabilised by its neighbouring alkyl substituents via hyperconjugation. This was confirmed in ESR studies on the *tert*-butyl radical[61].



Steric factors also affect the rate and site of addition. Steric hindrance can block hydrogen-abstraction at certain sites in a molecule, whereas the release of steric compression on formation of radical, which increases with the number of substituents, also has a beneficial effect on stability of the radical.



Again polarity has a major influence on the rate and selectivity of hydrogen-abstraction. Tedder[57] showed that electrophilic radicals, such as the trifluoromethyl radical, abstract hydrogens at a faster rate than nucleophilic radicals, such as the methyl radical, from carbons with electron-repelling substituents, whereas nucleophilic radicals abstract hydrogens at a faster rate than electrophilic radicals from carbons with electron-withdrawing substituents (table 1.6).

Table 1.6 Relative rates of H-abstraction by CH_3• and CF_3• (ethane as standard)

	D(R-H) Kcalmol^{-1}	[164] k_{rel} (CH_3•)	[164] k_{rel} (CF_3•)
$(CH_3)_3C$-D	91	14	60
CH_3COCH_2-H	92	2.1	0.5

The fluoroalkyl radical (**15**) produced from addition to HFP, is a large electrophilic radical and therefore will preferentially abstract hydrogens from nucleophilic carbons, for example the carbon with an α-oxygen, although steric hindrance may occur in some systems.

$$\underset{\textbf{(15)}}{RCF_2\dot{C}FCF_3} + CH_3OCH_3 \longrightarrow RCF_2CFHCF_3 + \dot{C}H_2OCH_3$$

1.33 Methods of Initiation

Although various methods of free radical initiaton, such as thermal and UV initiation, have been used in the additions to HFP this project is primarily concerned with chemical (peroxide) and gamma ray initiation.

Chemical initiation of radical reactions is affected by thermal decomposition of compounds with unusually weak bonds, such as the O-O bond in peroxides. It involves homocleavage of the initiator first, which then reacts with the substrate[62].

Peroxide Initiation

$$\text{R-O-O-R} \xrightarrow{\Delta} 2\ \text{R-O}\bullet$$

$$\text{R-O}\bullet + \text{R-H} \longrightarrow \text{R}\bullet + \text{R-OH}$$

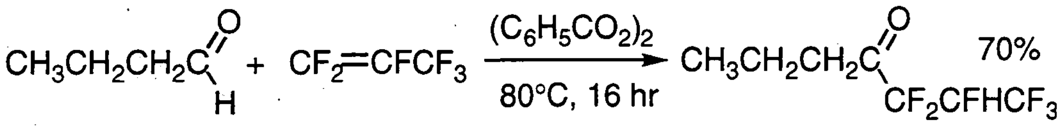
Dibenzoyl peroxide (DBPO) and *tert*-butyl peroxide (DTBP) are typical examples, and their reactions are generally conducted at 80°C and 140°C respectively[63], at which temperature their half lives are *ca.* four hours.

Gamma irradiation provides a flexible method of initiation as not only can the duration of the reaction be varied, but also, unlike peroxides, it is temperature independent and therefore reactions can also be performed at a variety of temperatures[64]. However, a radiation source, such as the Co^{60} source available to our laboratory, is needed. Gamma rays do not homolytically cleave the substrate directly. The Co^{60} source is encased in a steel sheath, which absorbs the radiation and produces secondary electrons. The secondary electrons ejected from the metal then interact with the organic substrate to produce excited molecules which disassociate into radicals which start the chain reaction.

1.4 Free-Radical Additions to Hexafluoropropene (HFP)

1.41 Addition of Oxygen Containing Compounds

The first free-radical additions to HFP were performed by Lazerte[65], on butanal and methanol.



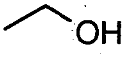
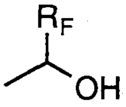
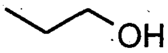
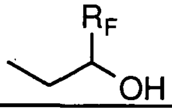
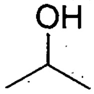
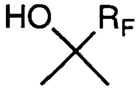
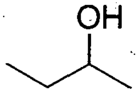
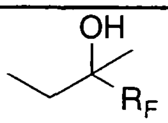
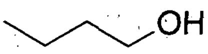
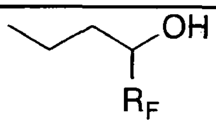
$$CH_3CH_2CH_2CHO + CF_2{=}CFCF_3 \xrightarrow[80°C,\ 16\ hr]{(C_6H_5CO_2)_2} CH_3CH_2CH_2C(O)CF_2CFHCF_3 \quad 70\%$$

$$\underset{5.5}{CH_3OH} \; + \; \underset{1}{CF_2{=}CFCF_3} \;\; \xrightarrow[120°C,\ 3\ hr]{(C_6H_5CO_2)_2} \;\; \underset{67\%}{HOCH_2CF_2CFHCF_3}$$

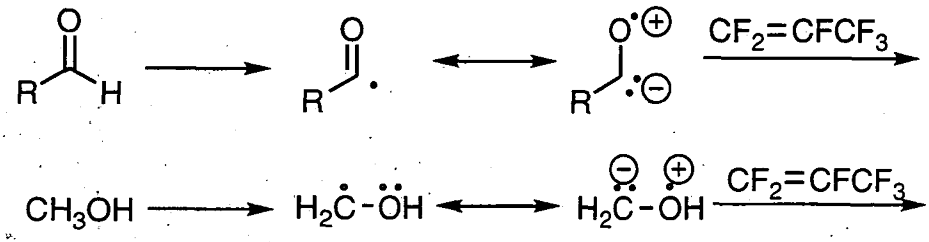
$$5.5 \quad : \quad 1$$

Muramatsu[66] and Haszeldine[67] have investigated additions to HFP of alcohols using γ-ray, uv, thermal and peroxide initiation (Table 1.7).

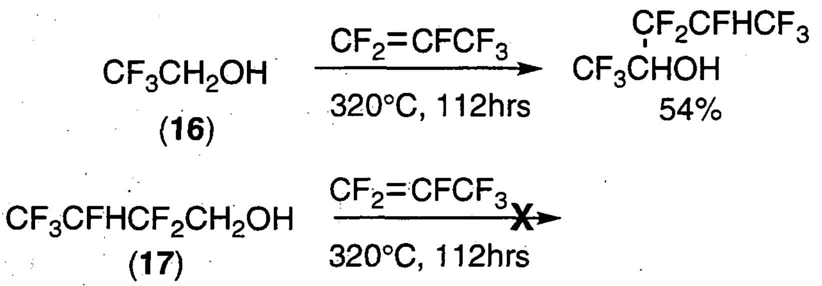
Table 1.7 Free-radical additions of alcohols to HFP ($R_F = CF_2CFHCF_3$)

Alcohol	Alcohol / HFP	Initiator	Products and yields (%)		Ref
CH_3OH	1 : 2.7	γ–rays	$HOCH_2R_F$	76	[66]
	3 : 1	Δ, 280°C		83	[67]
	3 : 1	uv, 40°C		86	[67]
	3 : 1	DTBP,150°C		93	[67]
	1 : 2.3	γ–rays		99	[66]
	3 : 1	Δ, 280°C		43	[67]
	3 : 1	uv, 40°C		51	[67]
	3 : 1	DTBP,150°C		60	[67]
	1 : 2.3	γ–rays		96	[66]
	1 : 2.0	γ–rays		100	[66]
	3 : 1	Δ, 280°C		57	[67]
	3 : 1	uv, 40°C		93	[67]
	3 : 1	DTBP,150°C		87	[67]
	3 : 1	Δ, 280°C		35	[67]
	3 : 1	uv, 40°C		95	[67]
	3 : 1	DTBP,150°C			[67]
	3 : 1	uv, 40°C		44	[67]

Hydrogen abstraction, in alcohols and aldehydes, occurred at the carbons atom neighbouring the oxygen, as the oxygen lone pairs stabilise the intermediate radical via resonance. This interaction also increases the nucleophilicity of the alkoxy radical in the addition step.

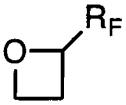
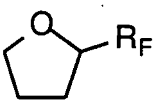
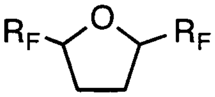
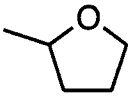
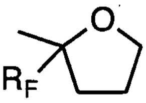
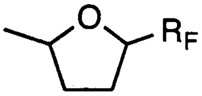
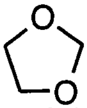
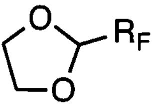
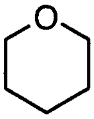
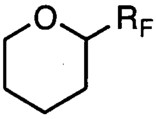
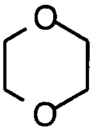
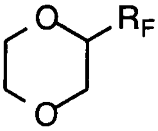
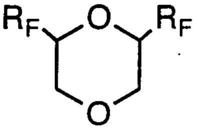
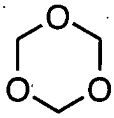
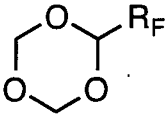
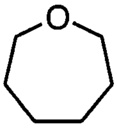
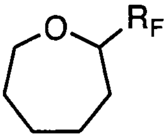
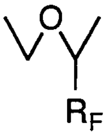
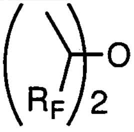
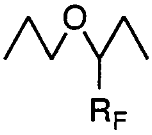
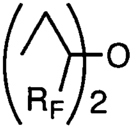


The importance of steric hindrance in radical attack was emphasised by Haszeldine, who successfully added 1,1,1-trifluoroethanol (**16**) to HFP, but observed no addition of 2,2,3,4,4,4-hexafluorobutan-1-ol[67] (**17**) to HFP.

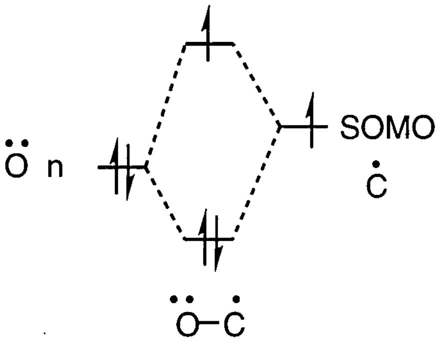


Muramatsu[66] and Abroskina[68] performed some preliminary investigations into additions of ethers to HFP, using gamma rays. This was followed by a more systematic investigation by Chambers et al[69-71]. Other workers have successfully used other types of initiation[72-74] and additions of ethers are summarised in table 1.8. More recently successful additions of polyethers to HFP have also been achieved[75,76].

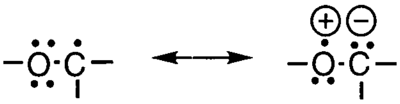
Table 1.8 Free-radical additions of ethers to HFP

Ether	Ether / HFP	Initiator	Products and yields (%)				Ref
	1.9 : 1	γ-rays		65			[81]
	2.3 : 1	γ-rays		91			[66]
	3.9 : 1	γ-rays		95			[72]
	1 : 1.1	UV		73			[75]
	2 : 1	DBPO		80			[68]
		γ-rays		59-5		34-95	[68]
	1.6 : 1	γ-rays		64		31	[71]
		DBPO		90			[72]
	1.6 : 1	γ-rays		70			[71]
	3 : 1	300°C		10			[74]
	3 : 1	UV		82			[73]
	1.4 : 1	γ-rays		81		7	[66]
	3.2 : 1	γ-rays		79			[71]
	3 : 1	UV		95			[73]
	1 :1.3	UV		51			[75]
	1 : 2	UV		31			[75]
	2.9 : 1	γ-rays		70			[81]
	2.3 : 1	γ-rays		68			[69]
	3 : 1	280°C		61			[74]
	3 : 1	UV		65			[73]
	2.8 : 1	γ-rays		38		43	[69]
	2.9 : 1	γ-rays		44		57	[66]
	1 : 1.6	UV				39	[75]
	2.3 : 1	γ-rays		12		28	[69]

Hydrogen abstraction in ethers occurs at the carbon neighbouring the oxygen, again as the resulting radical is resonance stabilised by the neighbouring oxygen. This stabilisation can be explained by M.O. theory.

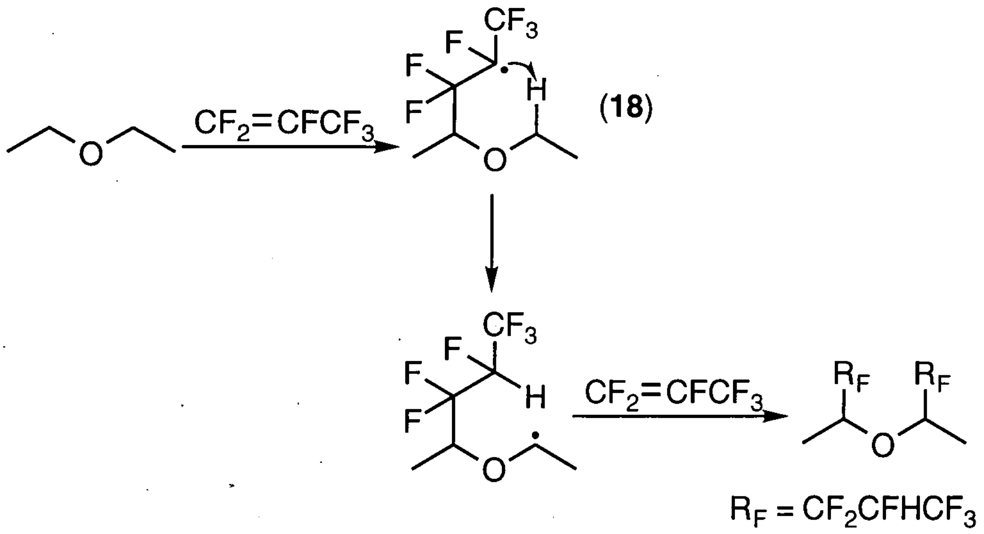


The interaction of the heteroatom lone pair with the adjacent carbon radical producing a nucleophilic radical which attacks the electrophilic alkene[75]. This is shown in valence bond form below.



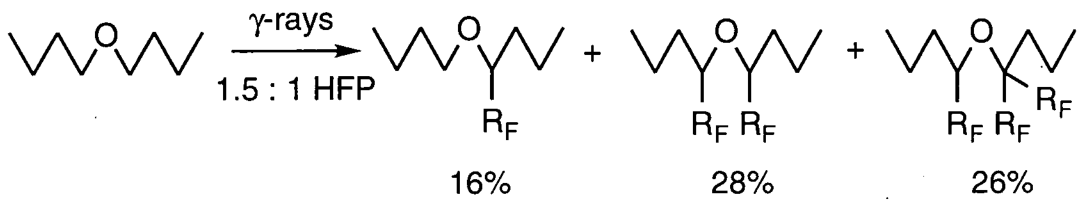
Chambers[71] established a reactivity order for cyclic ethers of oxolane > oxepane > oxane, by competition reactions. The increased reactivity of the five and seven membered rings over the six-membered ring was attributed to the increased energy barrier to an eclipsing interaction between the orbital containing the radical and a lone pair on the neighbouring oxygen, in the six-membered ring.

Muramatsu[77] observed that addition of the mono-adduct of diethyl ether to HFP only yielded a small amount of di-adduct, which was in contrast to diethyl ether itself. Therefore he suggested that the di-adducts of acyclic ethers were formed by intramolecular hydrogen abstraction, via a six membered transition state **(18)**.

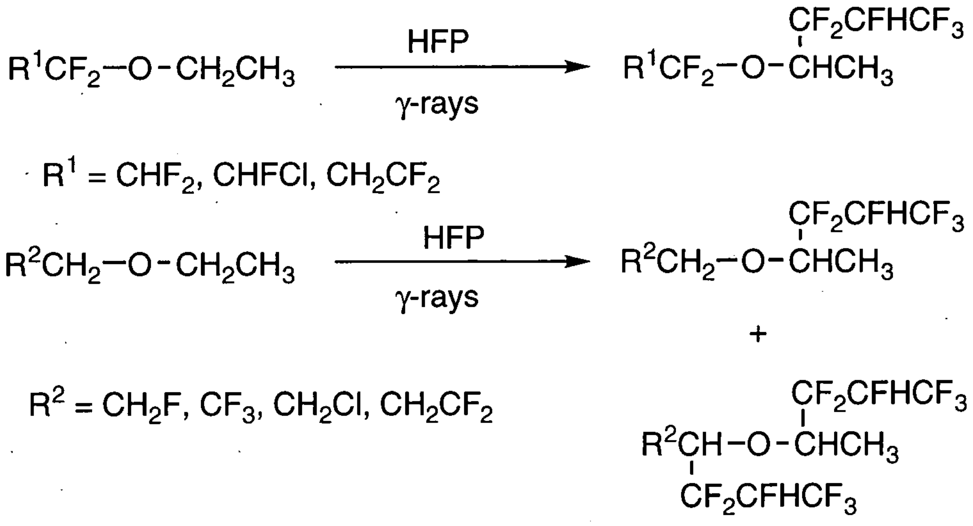


(18)

Chambers[69] observed tri-adduct formation with n-dibutyl ether and postulated that it was also formed by intramolecular hydrogen abstraction, in a similar mechanism as proposed by Muramatsu.



Addition to HFP of a series of ethers, with electron withdrawing substituents[77], highlighted the effect of polarity on radical additions.



$$R^1CF_2{-}O{-}CH_2CH_3 \xrightarrow[\gamma\text{-rays}]{HFP} R^1CF_2{-}O{-}\overset{CF_2CFHCF_3}{CH}CH_3$$

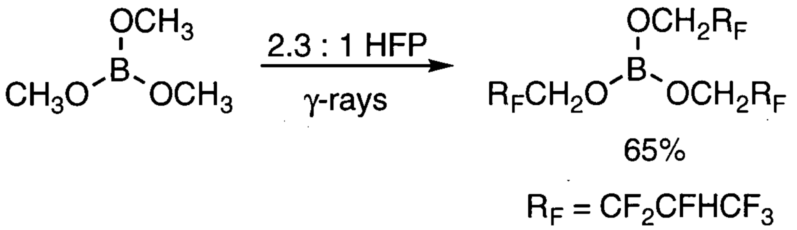
$R^1 = CHF_2, CHFCl, CH_2CF_2$

$$R^2CH_2{-}O{-}CH_2CH_3 \xrightarrow[\gamma\text{-rays}]{HFP} R^2CH_2{-}O{-}\overset{CF_2CFHCF_3}{CH}CH_3 + R^2\underset{CF_2CFHCF_3}{CH}{-}O{-}\overset{CF_2CFHCF_3}{CH}CH_3$$

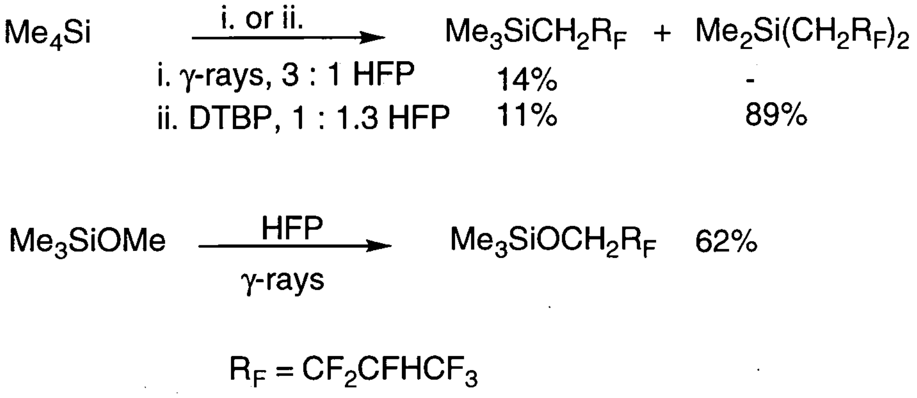
$R^2 = CH_2F, CF_3, CH_2Cl, CH_2CF_2$

The ethers with α–fluorine atoms were less reactive than those without, suggesting that the fluorine atoms were reducing the nucleophilicity of the ether radical attacking the HFP. The electron-withdrawing substituents of both sets of ethers directed hydrogen abstraction by the fluoroalkyl radical to the opposite side of the molecule in formation of the mono-adducts

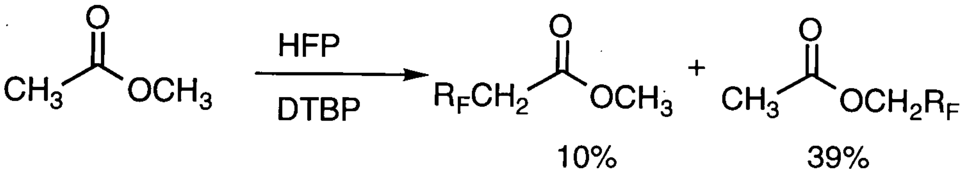
Surprisingly, borate ethers readily undergo HFP addition[69]. It was suggested that the intermediate carbon radical was stabilised by extensive 'allylic-type' conjugation with neighbouring oxygen and boron (B=O-C•).



Although tetramethylsilane reacts with HFP to give the mono-addition product, reaction occurs at the methoxy group in methoxytrimethylsilane, as the oxygen provides greater stabilisation of the carbon radical. Jones[78] was able to add HFP to several siloxanes, including silicon oil.



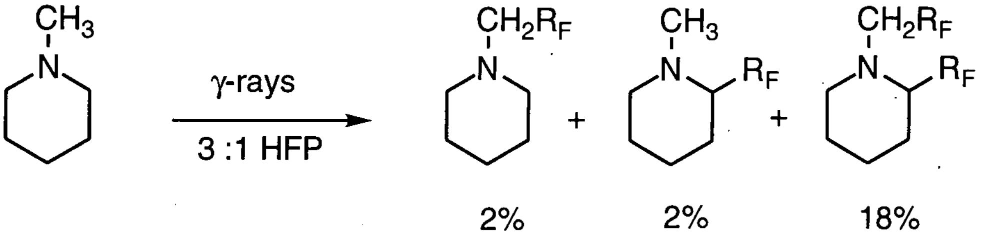
Several isomers of the mono-adducts were afforded from addition to HFP of esters[69,79], but the preferred site of addition was at the carbon neighbouring the ether oxygen.



$R_F = CF_2CFHCF_3$

1.42 Additions of Nitrogen Containing Compounds

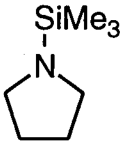
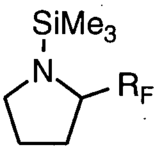
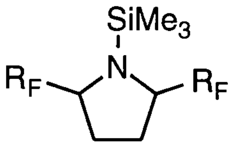
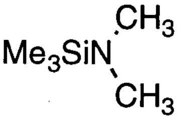
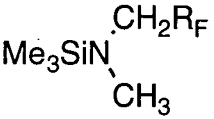
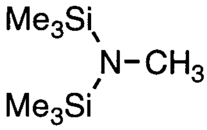
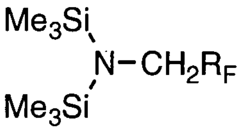
Addition of nitrogen containing substrates have been investigated in this laboratory[78,80,81]. Free-radical additions of amines to HFP were complicated by competition with nucleophilic attack on HFP by the nitrogen of the amine[81]. Tertiary amines did undergo radical addition to HFP, as nucleophilic attack by the nitrogen is sterically hindered by its substiuents.



$R_F = CF_2CFHCF_3$

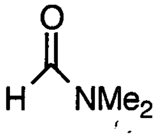
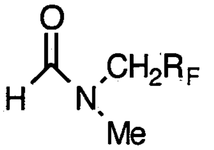
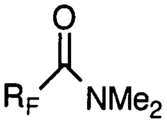
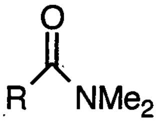
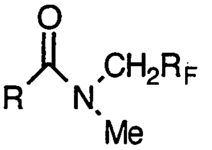
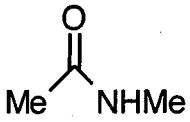
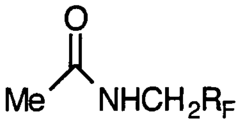
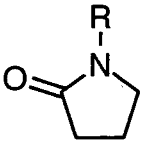
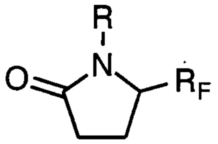
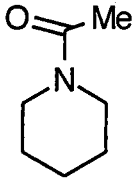
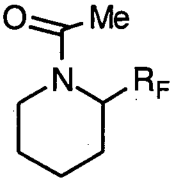
A route to HFP adducts of primary and secondary amines was found by protecting the amine with trimethylsilyl groups before adding HFP (table 1.9) and then hydrolysing the product[80].

Table 1.9 Free-radical addition of silyl amines[80] to HFP ($R_F = CF_2CFHCF_3$)

Silyl amine	Initiator	Products and yields (%)				Ref
	γ–rays		21		40	[80]
 $Me_3SiN(CH_3)_2$	γ–rays	 $Me_3SiN(CH_2R_F)CH_3$	87			[80]
 $(Me_3Si)_2N{-}CH_3$	γ–rays	 $(Me_3Si)_2N{-}CH_2R_F$	86			[80]

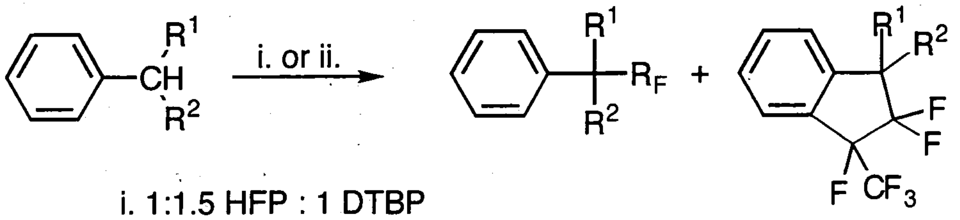
Addition of amides[78,80-82] (table 1.10) was more successful than to amines. The carbonyl group of the amide reduces the electron donating ability of the nitrogen and therefore reduced its nucleophilicity, although it also reduces the nucleophilicity of the nitrogen-stabilised radical. The amide adducts could then be hydrolysed or reduced to amines[80].

Table 1.10 Free radical addition of amides to HFP ($R_F = CF_2CFHCF_3$)

Amide	Initiator	Products and yields (%)				Ref
	γ-rays		50		23	[81]
	γ-rays DTBP γ-rays			R= Me, 82 R= Ph, 30 R= NMe_2, 55		[81]
	γ-rays					[78]
	γ-rays DTBP			R = Me, 98 R = H		[78] [82]
	γ-rays		40			[82]

1.43 Additions of Alkenes and Aryl Derivatives

Muramatsu et al[83] used equimolar amounts of the alkyl benzene and DTBP to get addition to HFP in low yields. Indanes (**20**) were formed as well as the expected mono-adduct (**19**). Haszeldine[84,85] produced similar results using thermal initiation.



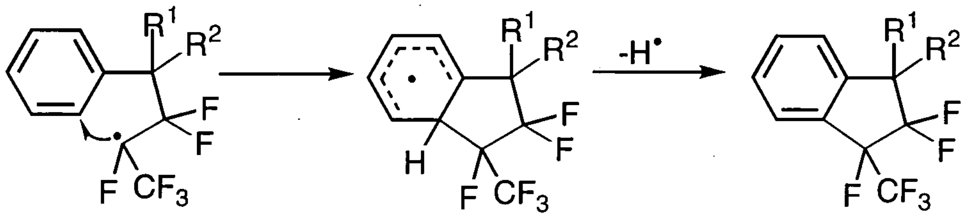
[83-85]

i. 1:1.5 HFP : 1 DTBP
ii.3 : 1 HFP, 250-300°C

(19)
3-28%

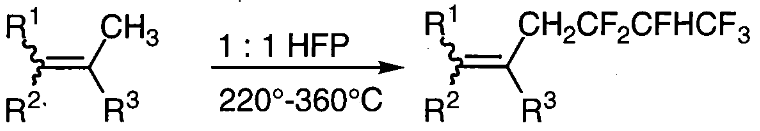
(20)
6-14%

Indane formation was believed to occur by cyclisation of the fluoroalkyl radical. A similar mechanism was proposed for indane formation in benzylic derivatives of alcohols[79], ethers[86] and carbonyl compounds[79].



[83]

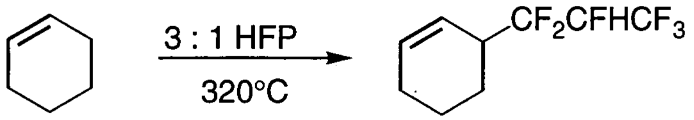
Thermal additions of alkenes[87,88] were complicated by cyclic products and only low yields of mono-adducts were produced by allylic insertion.



[87]

2-16%

The patent literature claimed cyclohexene gave a significantly greater yield of the mono-adduct (**21**), using thermal initiation[89], but only trace amounts could be produced by DTBP initiation, in this laboratory[90].



[89]

(**21**) 60%

Chapter Two

Free Radical Additions of Hydrocarbons to Hexafluoropropene

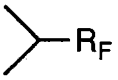
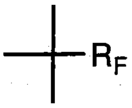
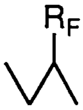
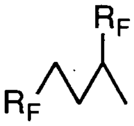
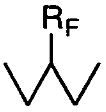
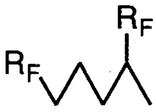
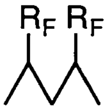
2.1 Introduction

The functionalisation of hydrocarbons is a field of continuing activity and a variety of approaches in this field have been taken[91-93]. In the present work the reactions of several alkanes and cycloalkanes with hexafluoropropene have been investigated, as a remarkably simple method of functionalisation.

2.11 Additions of Alkanes to Hexafluoropropene (HFP)

Addition to HFP, of several short, straight or branched chained hydrocarbons (C_2-C_4) were claimed in the patent literature, using thermal[89] and UV irradiation[94] (table 2.1). Haszeldine *at al* also added HFP to n-butane and n-pentane[95]. All the reactions were performed using a three fold excess of the hydrocarbon.

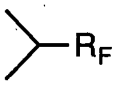
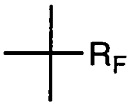
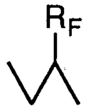
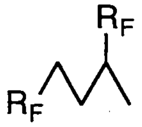
Table 2.1 Addition of alkanes to HFP (thermal & UV initiation)

	Initiator	Products ($R_F = CF_2CFHCF_3$) & yields (%, calculated, based on HFP)								Ref.
C_2H_6	300°C		40							[89]
C_3H_8	295°C UV, ~50°C		54 9							[89] [94]
i-C_4H_{10}	UV, ~50°C		15							[94]
n-C_4H_{10}	325°C, UV, ~50°C		29 24		6 4		19 17			[89] [94]
n-C_5H_{12}	300°C		23		12		12		6	[89]

Both types of initiation gave low to moderate yields of HFP adducts. For the straight chain alkanes, with four or more carbon atoms, there is little selectivity at the site of hydrogen abstraction which led to mixtures of isomeric HFP adducts. Di-adducts were only produced by systems with four or more carbons. This may be due to the electronic or steric effect of the fluoroalkyl group in the mono-adducts deactivating the systems to further attack.

Preliminary work, in this laboratory[90], has also been performed on aliphatic hydrocarbons, using γ-rays and peroxide initiation (table 2.2).

Table 2.2 Addition of alkanes to HFP (γ-rays and Peroxide)

Alkane	alkane / HFP	Initiator	Products ($R_F = CF_2CFHCF_3$) & yields (%, calculated, based on HFP)						Ref
CH_4	1:2	DTBP[a]	No Reaction						[90]
C_3H_8	1:2	γ-rays[b]		21		2			[90]
i-C_4H_{10}	1:2	γ-rays[b]		42					[90]
n-C_4H_{10}	1:2	γ-rays[b]		6		11			[90]
n-C_6H_{14}	1:2	DTBP[a]	$C_6H_{13}R_F$	1	$C_6H_{13}(R_F)_2$	8	$C_6H_{13}(R_F)_3$	5	[90]

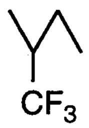
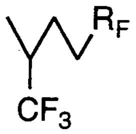
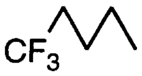
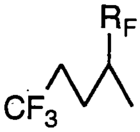
[a]140°C, 24 hrs. [b]10 Mrads, 18°C, 4 days

Again, only low to moderate yields were achieved. The low reactivity of n-hexane may have been due to impurities in the hydrocarbon (8% cyclohexene), as competition reactions with cyclohexane, showed that they have comparable reactivities. Several isomeric adducts, which were inseparable, were produced in the n-hexane reaction, demonstrating the lack of selectivity of hydrogen abstraction from the secondary carbons.

2.12 Addition of Partially Fluorinated Alkanes to Hexafluoropropene

Additions to 2-trifluoromethylbutane and 1,1,1-trifluoropentane, using thermal initiation, were attempted[96] (table 2.3). They are especially of interest as the trifluoromethyl group has a similar electron withdrawing effect as the C_3F_6H group, but has lower steric requirements. Therefore it should be possible to determine which effect has the greater influence on di-adduct production.

Table 2.3 Addition of partially fluorinated alkanes to HFP (thermal initiation)

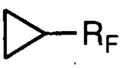
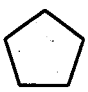
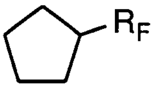
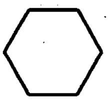
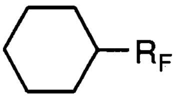
	Conditions	Products ($R_F = CF_2CFHCF_3$) & yields (%, calculated, based on HFP)		Ref
	292°C, 4 days		7	[96]
	280°C, 4 days		25	
	260°C, 4 days		10	
	295°C, 4 days		23	[96]
	277°C, 4 days		20	
	260°C, 4 days		10	

Generally, as the temperature increased so did the reaction conversion, but the yields of the desired products decreased. In neither case were mono-adducts formed from insertion into carbon-hydrogen bond β- to the trifluoromethyl group. This strongly suggests that it is the inductive effect of the fluoroalkyl group, and not its steric bulk, that dictates the site of addition of a second HFP group.

2.13 Addition of Cycloalkanes to Hexafluoropropene

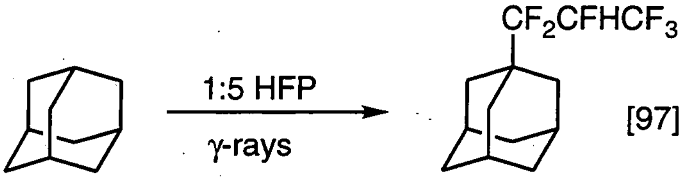
Additions to HFP, of cyclic hydrocarbons have been claimed in the patent literature using thermal initiation[89] and UV irradiation[94] (table 2.4).

Table 2.4 Addition to HFP of Cycloalkanes (thermal and UV initiation)

	Alkane / HFP.	Initiator	Products & yields(%, calculated, based on HFP) ($R_F = CF_2CFHCF_3$)		Ref
	3:1	310°C		5	[89]
	3:1	290°C			[89]
	3:1	UV, ~50°C		43	[94]
	3:1	280°C		54	[89]
	3:1	UV, ~50°C		38	[94]

The reactions were generally done on a very small scale and only the mono-adducts were claimed, characterised by elemental analysis only, and no additional products were indicated. These should not be discounted especially in the thermal reactions where the hydrocarbon is susceptible to fragmentation from which many addition products may result. All the systems gave moderate to poor yields using these initiators.

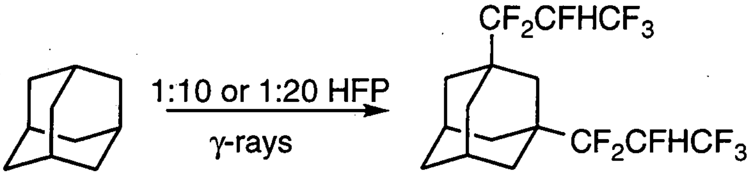
Use of γ-rays to initiate addition to HFP of a cyclic hydrocarbon system was reported by Russian workers in 1976. Their initial studies were on the adamantane system[97]. They conducted a series of reactions using gamma rays, varying the temperatures (20-100°C) and reaction time. In general they used a five fold excess of HFP to produce 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane (**22**).



[97]

(22)

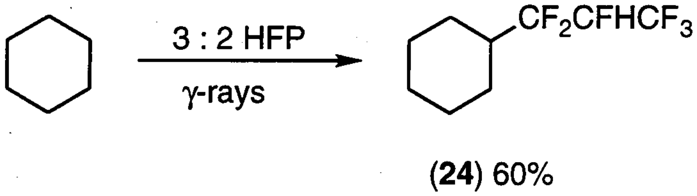
Using up to a twenty-fold excess of HFP, they also produced 1,3-bis(1,1,2,3,3,3-hexafluoropropyl)adamantane[98] (**23**).



[98]

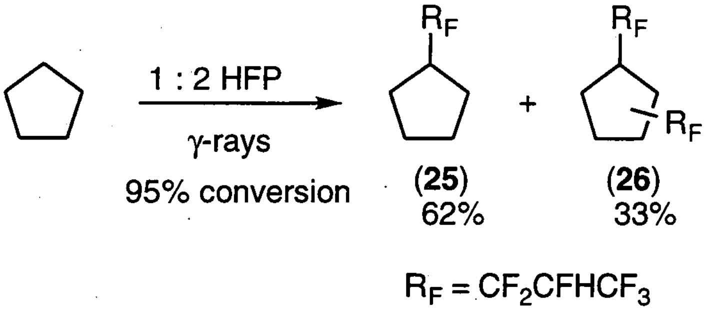
(23)

Podkhalyuzin and Nazarova also investigated the addition to cyclohexane[99]. The yield of (1,1,2,3,3,3-hexafluoropropyl)cyclohexane (**24**) was optimised using a 1.5 excess of cyclohexane over HFP. Several reactions were performed for kinetic studies with the temperature being varied from 20°C , 25°C and 81°C. The reaction was very clean giving only the mono-adduct. It was found that the reaction was almost completely inhibited by benzene or iodine, which confirmed the radical nature of the reaction.



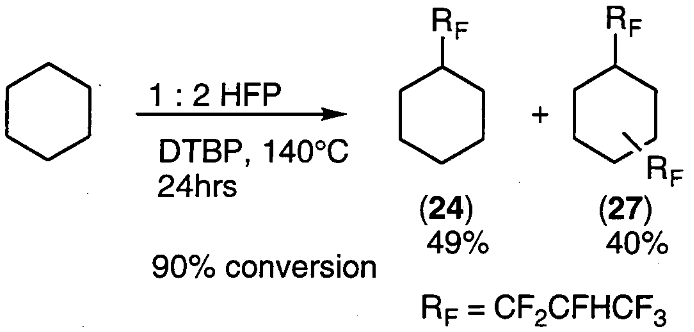
[99]

More recently other systems have been studied, in preliminary work done in this laboratory[90], with varying success. No reaction occurred with cyclopropane and only a small amount of addition to decalin occurred, whereas addition to cyclopentane gave a mixture of mono- (**25**) and di-adducts (**26**).



[90]

Peroxide initiation (DTBP) was also used in the addition to cyclohexane. An increased proportion of di-adducts to mono-adducts was observed, which is presumably due to the increase in temperature of the system.

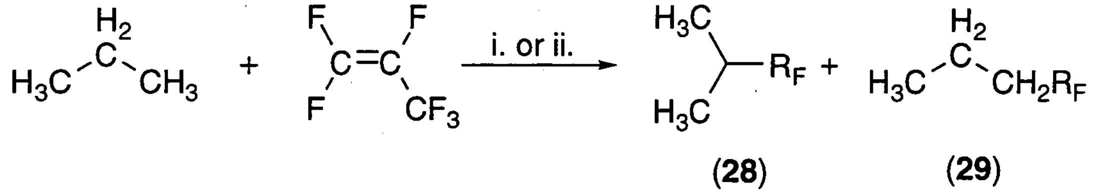


[90]

2.2. Addition of Alkanes

2.21. Propane

In the present work a more complete investigation into the addition of propane to HFP was undertaken, using both γ-ray and DTBP initiation.



$R_F = CF_2CFHCF_3$

i, γ-rays, r. t.
ii, DTBP, 140°C, 24hrs

Initiator	Ratio	Yields (%)	
	C_3H_8 : HFP	**(28)**	**(29)**
γ-rays, 4 days, 6 Mrads	1 : 1	8	trace
γ-rays, 8 days, 12 Mrads	1 :1.2	19	1
DTBP	1 : 1.5	75	3

Reactions initiated by γ-rays gave low to moderate conversions to the mono-adducts (**28**) and (**29**), whereas using DTBP initiation gave a greatly enhanced reaction conversion, which can be simply attributed to the increased temperature of the reaction.

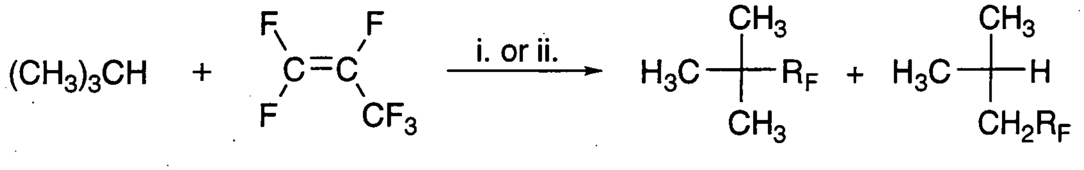
A GLC/MS analysis of the product mixture from the DTBP initiated reaction identified two isomers of the mono-adduct, which could not be separated. The ^{19}F and ^1H NMR spectra of the product mixture confirmed that the major isomer was 1,1,1,2,3,3-hexafluoro-4-methylpentane (**28**) and the minor isomer was 1,1,1,2,3,3-hexafluorohexane (**29**), agreeing with previous data[90] from this laboratory.

Three major signals in the ^{19}F NMR spectrum corresponding to a CF_3 (-74.5, broad singlet), CF_2 (-117.7 & 121.8, AB system), and a CFH group (-212.0, doublet) were assigned to the 2H-hexafluoropropyl group of compound (**28**). The CF_2 group is observed as an AB system since the fluorines are not equivalent due to the adjacent chiral CFH group. The ^1H NMR spectrum exhibited three major resonances at 1.12, 2.34, and 4.82 ppm in a 6 : 1 : 1 ratio which corresponded to the two equivalent CH_3, CH, and CFH groups respectively.

Addition to propane occurred at the secondary carbon in preference to the primary carbon despite it having a 1 : 3 statistical ratio of methylene to methyl hydrogens. This is rationalised by the increased stability of the hydrocarbon's secondary radical over its primary radical, primarily due to increased hyperconjugation in the secondary carbon radical.

2.22. 2-Methylpropane

Addition of 2-methylpropane to HFP was affected using both γ-ray and DTBP initiation.



(30) **(31)**

$R_F = CF_2CFHCF_3$

i, γ-rays, r.t.
ii, DTBP, 140°C, 24hrs

Initiator	Ratio C_4H_{10} : HFP	Yields (%) (30)	 (31)
γ-rays, 5 days, 7.5 Mrads	1 : 1	17	trace
DTBP	1 : 1.3	80	3

The γ-ray initiated reaction gave a low conversion to essentially one product, which was confirmed as 1,1,1,2,3,3-hexafluoro-4,4-dimethylpentane (**30**) by comparison of its EI^+ mass spectrum, ^{19}F NMR and ^{1}H NMR spectra with the data from previous work in this laboratory[90].

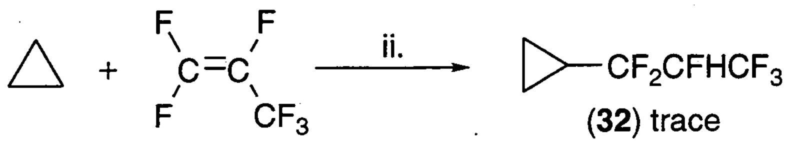
At elevated temperature, using DTBP initiator, the reaction conversion was greatly increased. There was also a slight decrease in the selectivity of the reaction. Again the major product was compound (**30**), but a minor component (>5%) was also detected. The EI^+ spectrum confirmed the minor product as a mono-adduct with a (M^+-H) peak at 207 and a base peak at 43 which concurs with loss of a $^+CH_2CF_2CFHCF_3$ fragment, suggesting addition occurred at a methyl carbon. Minor signals in the ^{19}F NMR of the product mixture confirmed the presence of a second 2H-hexafluoropropyl group and the ^1H NMR spectrum of the product mixture observed small additional resonances at 0.88 (doublet), 1.39 (broad singlet) and 1.61 (broad singlet), which correspond to two equivalent CH_3's, a CH and a CH_2CF_2 group of 1,1,1,2,3,3-hexafluoro-4,4-dimethylhexane (**31**).

Addition occurred primarily at the methyne group rather than the methyl groups despite the 1 : 9 statistical relationship between them. Again this is rationalised by the increased hyperconjugation in the tertiary carbon radical.

2.3. Addition of Monocyclic Hydrocarbons

2.31. Cyclopropane

Cyclopropane failed to react in a γ-ray initiated reaction performed over an extended period of time (15 Mrads). Cyclopropane's low reactivity may be due to its high C-H bond strength[100] and greater electronegativity compared with the larger cycloalkanes. A reaction at elevated temperature, using DTBP initiation, was attempted to try to increase the reactivity of the cyclopropyl radical.



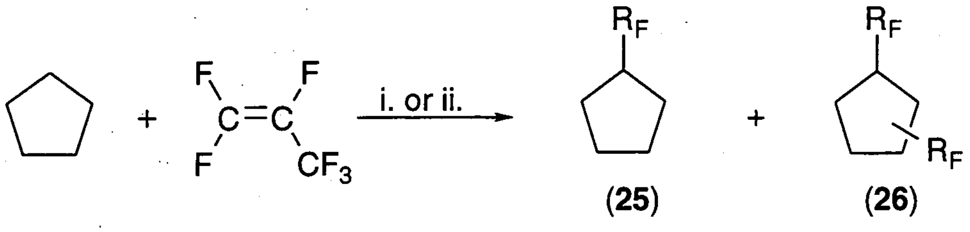
(**32**) trace

ii, *t*-butyl peroxide, 140°C, 24hrs

Although a small amount of the mono-adduct (**32**) was identified by GC.-ms (M^+ peak at 192) the product mixture was very complex and the adduct could not be isolated. The complexity of the products was most likely due to ring opening of the cyclopropane, from a large release of ring strain after H-abstraction, followed by polymerisation.

2.32. Cyclopentane

The cyclopentane obtained for these reactions had only a guaranteed purity of 95+%. Addition to HFP was attempted initially using γ-rays and subsequent reactions were performed using DTBP initiation.



i, γ-rays, r.t.
ii, DTBP, 140°C, 24hrs

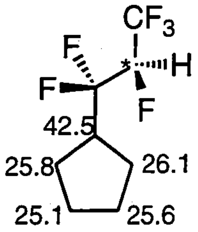
$R_F = CF_2CFHCF_3$

Initiator	Ratio C_5H_{12} : HFP	Conversion w.r.t. C_5H_{12}	Yields (%) (25)	(26)
γ-rays, 5 days, 7.5 Mrads	1 : 1.6	54	86	9
DTBP	1 : 1.6	96	49	38
DTBP	1 : 2	100	57	23

Using γ-ray initiation moderate conversion was achieved. A pure sample of the major product (**25**), was obtained by fractional distillation. A ^{19}F NMR spectrum, ^{1}H NMR spectrum and EI^{+} spectrum of the pure sample concurred with the previous data[90] for 1,1,1,2,3,3-hexafluoropropylcyclopentane (**25**).

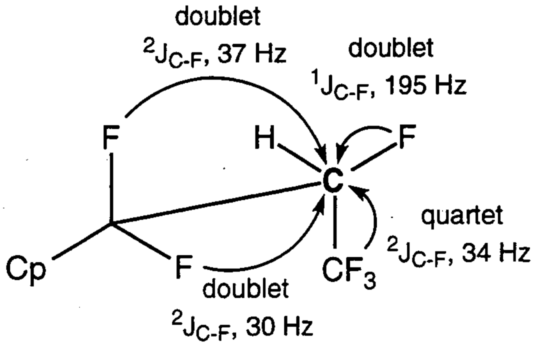
A broad band proton decoupled ^{13}C NMR experiment was run on compound (**25**) to use as a model for other hydrocarbon adducts of HFP. Four resonances were observed in the 0-30 ppm region and were assigned to CH_2 ring carbons (figure 2.1). The chiral CFH group in the fluoroalkyl side chain destroys the symmetry of the cyclopentane ring and consequently separate signals are observed for each ring carbon. A fifth resonance at 42.5 ppm appears as a triplet ($^{2}J_{C\text{-}F}$ 22 Hz) and can be assigned to the tertiary ring carbon, which couples with the neighbouring β-fluorines of the CF_2 group.

Figure 2.1 ^{13}C NMR chemical shifts (ppm) for the cyclopentane ring of compound (25)



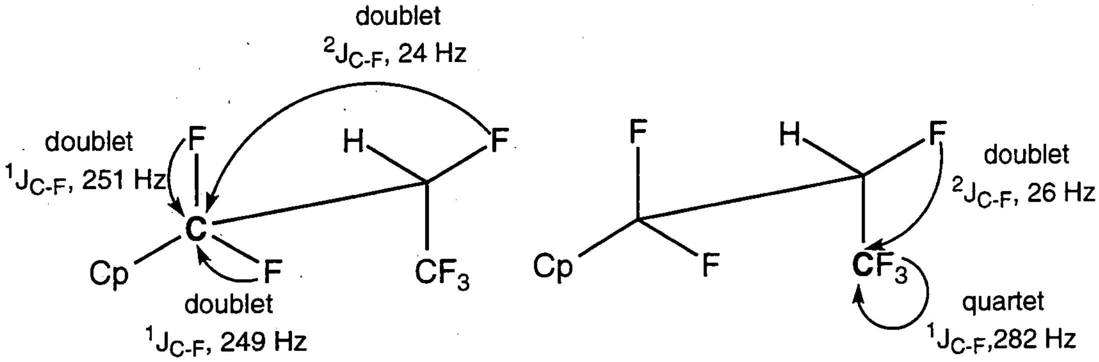
Three further resonances appear at very high field and can be attributed to the carbon atoms in the hexafluoropropyl side chain. The first, at 86.0 ppm, was observed as a doublet ($^{1}J_{C-F}$ 195 Hz) of doublets ($^{2}J_{C-F}$ 37 Hz) of quartets ($^{2}J_{C-F}$ 34 Hz) doublets ($^{2}J_{C-F}$ 30 Hz). This coupling was characteristic of the CFH carbon (figure 2.2).

Figure 2.2 Carbon-Fluorine coupling to the CFH carbon in compound (25)



The second, a doublet ($^{1}J_{C-F}$ 251 Hz) of doublets ($^{1}J_{C-F}$ 249 Hz) of doublets ($^{2}J_{C-F}$ 24 Hz) at 118.9 ppm was assigned to the CF_2 carbon (figure 2). The final resonance at 120.2 ppm was split into a quartet ($^{1}J_{C-F}$ 282 Hz) of doublets ($^{2}J_{C-F}$ 26 Hz) and was assigned to the CF_3 group (figure 2.3).

Figure 2.3 Carbon-Fluorine coupling to the CF_2 & CF_3 carbons in compound (25)

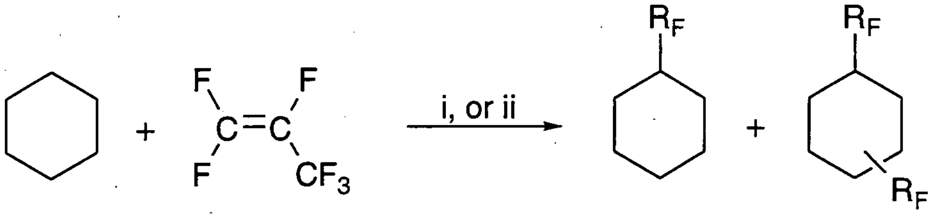


Initiation using DTBP, gave an almost quantitative reaction conversion. Fractional distillation of the products gave compound (**25**) and a higher boiling fraction consisting of six components, in the GC. ratio 1.7 : 1.1 : 2.3 : 2.4 : 1.5 : 1. The EI^+ mass spectra, ^{19}F NMR and ^1H NMR of the second fraction agreed with the literature data for isomers 1,x-bis(1,1,1,2,3,3-hexafluoropropyl)cyclopentane (x=2,3) (**26**) which could not be distinguished from each other.

The introduction of more than one hexafluoropropyl group into a cycloalkane, not only produces the possibility of regioisomers e.g. 1,2- or 1,3-substitution, but also diastereomers of the regioisomers because of the introduction of chiral centres in the fluoroalkyl side chain and at the site of addition in the cycloalkane. Therefore if these chiral centres were removed then characterisation should be easier (see later).

2.33. Cyclohexane

Addition to cyclohexane was initiated using both γ-rays and DTBP. The peroxide reaction was also successfully performed on a larger scale, using a one litre autoclave.



(24) **(27)**

i, γ-rays, r.t.
ii, DTBP, 140°C, 24hrs

$R_F = CF_2CFHCF_3$

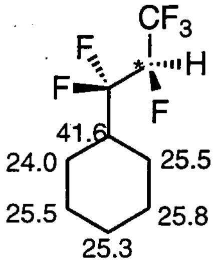
Initiator	Ratio C_6H_{12} : HFP	Conversion w.r.t. C_6H_{12}	Yields (%) (24)	(27)
γ-rays, 5 days, 7.5 Mrads	1 : 1.5	79	90	4
DTBP	1 : 2	99	39	53
DTBP, 1 litre autoclave	1 : 2	50	85	6

A high reaction conversion was achieved using γ-rays and fractional distillation of the product mixture separated, the major product, 1,1,2,3,3,3-

hexafluoropropylcyclohexane (**24**) from isomers of the di-adduct, 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x=2,3,4) (**27**). The ^{19}F NMR and ^{1}H NMR spectra and the EI^{+} mass spectra of compounds (**24**) and (**27**) agreed with previously reported data[90,99].

A broad band proton decoupled ^{13}C NMR experiment was performed on compound (**24**), to use as a model for characterisation of the di-adducts. The three hexafluoropropyl carbons were assigned as in the previous experiment. Six resonances were observed for the cyclohexane ring. A triplet at 41.6 ppm ($^{2}J_{C\text{-}F}$ 21 Hz) was attributed to the methyne carbon of the ring. A multiplet at 25.5 ppm and a triplet at 24.0 ppm ($^{3}J_{C\text{-}F}$ 4 Hz) were assigned to the two carbons neighbouring the methyne group because of their third order coupling to the difluoromethylene fluorines. Three singlets, observed at 25.8, 25.5 and 25.3 ppm, were assigned to the other three methylene carbons, with the methylene group furthest from the electron-withdrawing fluoroalkyl group being assigned the signal at highest field.

Figure 2.4 ^{13}C NMR chemical shifts (ppm) for the cyclohexane ring of compound (24)



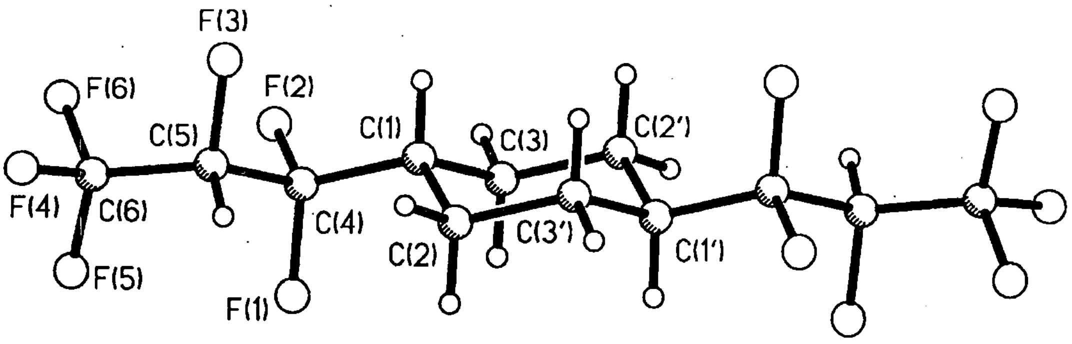
Unfortunately, a ^{1}H NMR and a broad band proton decoupled ^{13}C NMR of the liquid mixture of di-adducts (**27**) could not distinguish the structures of the separate isomers.

Peroxide initiation (DTBP) resulted in complete conversion of the hydrocarbon starting material. The product distribution differed from the γ-ray reaction, in that a greater proportion of di-adducts (**27**) were formed. Fractional distillation separated the mono-adduct (**7**) from the mixture of di-adducts (**27**). On standing, a solid (**27a**) crystallised out from the di-adduct mixture. A methanol solution of the di-adduct mixture was then cooled to -15°C, to remove any further solid di-adduct (**27a**) which was characterised separately (see later). A GC analysis of the liquid di-adducts identified six major components, in a ratio of 1 : 3.5 : 15 : 6 : 11 : 3, which could not be separated individually.

The solid di-adduct (**27a**) had previously[90] been described as 1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane although no conclusive proof of the structure was given. The ^{19}F and ^{1}H NMR solution spectra and EI^{+} mass spectrum of the solid di-adduct (**27a**) agreed with the literature[90], but also a broad band proton decoupled ^{13}C NMR spectrum of a CDCl$_3$ solution of the solid di-adduct (**27a**) was run to determine its structure. Six resonances were observed, three of these signals at 85.0, 119.3 and 120.9 ppm, were assigned to the three carbons of the hexafluoropropyl groups as in compound (**5**). Only three signals were observed for the cyclohexane ring which eliminated the possibility that the solid was the 1,3-bis-adduct. At high field, two triplets were observed at 22.7 and 21.1 ppm ($^{3}J_{C\text{-}F}$ 3-4 Hz), arising from the methylene ring carbons, and another triplet at 40.6 ppm ($^{2}J_{C\text{-}F}$ 22 Hz) due to the methyne ring carbons. The similarity in chemical shifts of the methyne carbons in (**24**) and (**27a**) strongly suggests that (**27a**) is the 1,4-bis-adduct and not the 1,2-bis-adduct and this is supported by the evidence of C-F coupling in both the methylene ring carbons of (**27a**).

A single crystal was grown, and submitted for X-ray crystallographic analysis, which conclusively identified it as a diastereomer of *trans*-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (**27a**) (figure 2.5).

Figure 2.5 *trans*-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (**27a**)

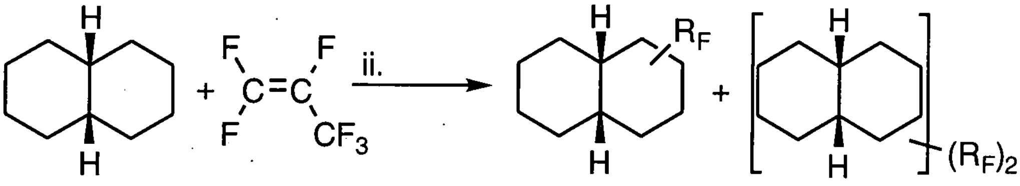


The crystal's symmetry is dominated by a centre of inversion, *i*. The packing of the molecule in the crystal revealed no intermolecular H-bonding interactions with CFH proton.

2.4. Addition of Bicyclic Hydrocarbons

2.41. *Cis*-Decalin

A γ-ray initiated reaction produced only a low conversion (<5%) of *cis*-decalin and so the reaction was repeated using peroxide initiation.



1 : 2 (33) (34)

ii. DTBP, 140°C, 24hrs

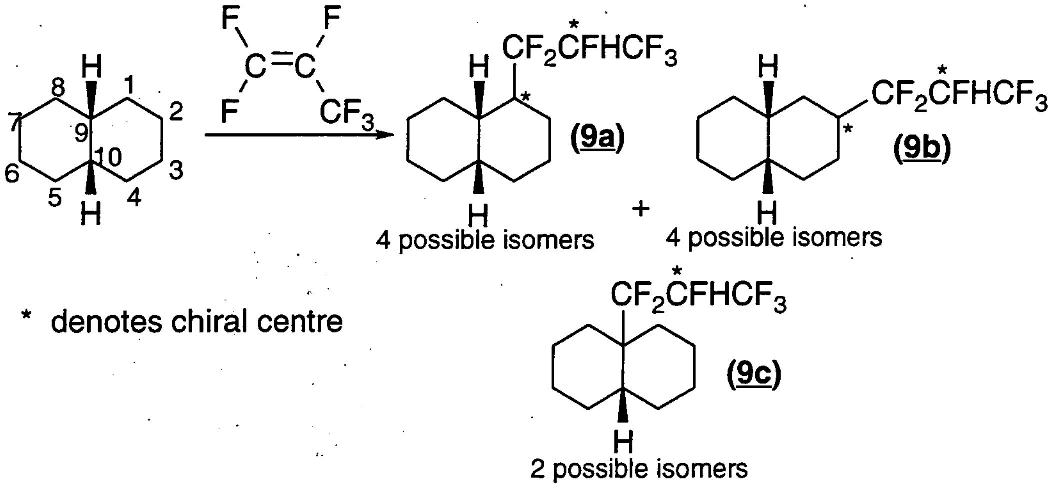
$R_F = CF_2CFHCF_3$

Initiator	Ratio $C_{10}H_{18}$: HFP	Conversion w.r.t. $C_{10}H_{18}$	Yields (%) (33)	(34)
DTBP, 140°C	1 : 2	39%	56	33
DTBP, 140°C, acetone	1 : 2	44%	49	45

The initial reaction using DTBP initiation, produced a disappointing reaction conversion (39%) which may have been due to the immiscibility of the starting materials. Fractional distillation of the reaction mixture gave two fractions, other than starting material. The first fraction contained a group of 7 compounds, which were identified as isomers of x-(1,1,1,2,3,3-hexafluoropropyl)*cis*-decalin (x=1,2,9) (**33**) by their NMR and mass spectra. The ^{19}F NMR of the first fraction identified the presence of several non equivalent hexafluoropropyl groups, but the ^{1}H NMR contained many overlapping multiplets and although the CFH protons were evident, the ring proton assignments were very difficult. The EI^+ mass spectra of compounds (**33**) identified an

M^+ peak at 288, a (M^+-CF_2CFHCF_3) peak at 137 and a base peak at 95, confirming them as isomers of the mono-adduct.

Radical addition to HFP of *cis*-decalin at the one- or two-position, not only generates a chiral centre in the fluoroalkyl side chain, but also at the site of addition. Consequently, four diastereoisomers are possible for addition at each site. Addition at the tertiary carbon (nine-position) does not create a chiral centre at that site, but the tertiary radical produced could invert and therefore produce both *cis*- and *trans*-isomers of 9-(1,1,1,2,3,3-hexafluoropropyl)decalin (**33c**). This explains the large number of isomers of the mono-adduct (**33**) produced.

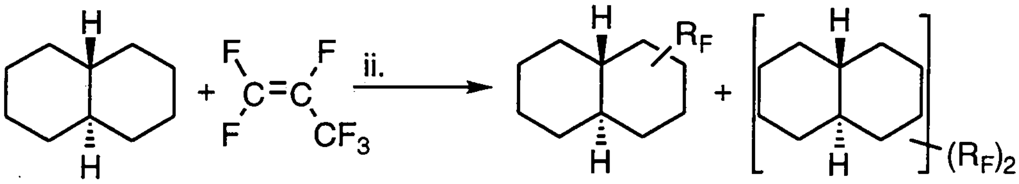


Obviously further addition to HFP to form di-adducts (**34**) leads to an even greater number of possible isomers as other regio-isomers are possible as well as a further increase in chiral centres present. The second distillation fraction contained a group of sixteen compounds identified as isomers of x,y-bis(1,1,1,2,3,3-hexafluoropropyl)*cis*-decalin (x=1, y=2-10; x=2, y=3-10) (**34**) from their NMR and mass spectra. The EI^+ mass spectra identified M^+ peaks at 438, (M^+-CF_2CFHCF_3) peaks at 287 and base peaks at 245. Again, the ^{19}F NMR confirmed the existence of several hexafluoropropyl groups and the ^1H NMR was very complex.

In an effort to increase the reaction conversion dry acetone was added as a co-solvent to improve the miscibility of the reactants, in the subsequent reaction. This did raise the conversion slightly, but still only a moderate reaction conversion was achieved.

2.42 *Trans*-decalin

Addition to *trans*-decalin was attempted using γ-rays at room temperature, but only a low conversion (<5%) of starting materials occurred and so the reaction was repeated using DTBP initiation at 140°C.



1 : 2 (35) 51% (36) 34%

79% conversion

ii. DTBP, 140°C, 24hrs

$R_F = CF_2CFHCF_3$

Again increasing the temperature had a beneficial effect on the system. Fractional distillation, under reduced pressure, of the product mixture gave two separate fractions. The first fraction contained four components, in a GC. ratio of 1 : 4.4 : 10 : 4.9, which were identified as isomers of the mono-adduct (**35**) by their NMR and mass spectra data. Their EI^+ mass spectra identified M^+ peaks at 288 and $(M-CF_2CFHCF_3)^+$ peaks at 137. The ^{19}F NMR of the first fraction identified several 2H-hexafluoropropyl groups and the ^{1}H NMR identified the CFH and ring protons.

The second distillation fraction contained ten major isomers of the di-adduct (**36**). Their EI^+ mass spectra included M^+ peaks at 438 and $(M^+-CF_2CFHCF_3)$ peaks at 287 and the ^{19}F and ^{1}H NMR spectra confirmed the addition of 2H-hexafluoropropyl groups.

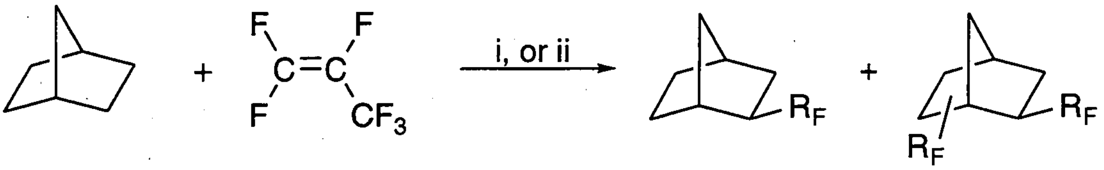
Again the sites of addition could not be conclusively determined because of the large number of isomers produced.

In comparison with addition to *cis*-decalin, the reaction conversion of 79% was surprisingly high and the reaction was more selective. It must be remembered though that a free-radical reaction is a chain process which can easily be several thousand steps long and any inhibitor can have a drastic effect on the overall reaction conversion.

Therefore to get a true comparison of reactivities, a competition reaction must be performed (see later).

2.43. Norbornane

Addition to HFP of norbornane was successful using both γ-ray and DTBP initiation.



(37) (38)

i, γ-rays, r.t.
ii, DTBP, 140°C, 24hrs

$R_F = CF_2CFHCF_3$

Initiator	Ratio	Conversion	Yields (%)	
	C_7H_{12} : HFP	w.r.t. C_7H_{12}	(37)	(38)
γ-rays, 4 days, 6 Mrads	1 : 1.3	65	80	12
DTBP	1 : 1.5	100	44	45

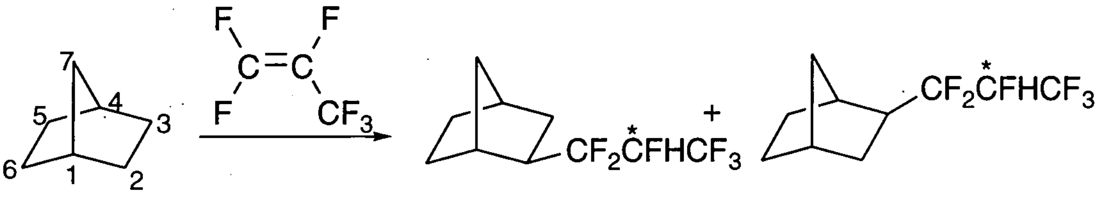
Fractional distillation of the product mixture from the γ-ray initiated reaction gave two fractions. Analysis of the lower boiling fraction, by NMR and GC.-ms., identified two isomers of the mono-adduct (**37**), with very similar GC. retention times (7.95 & 8.00 mins.), in a ratio of 1 : 1.06, which could not be separated. Their EI^+ mass spectra included M^+ peaks at 246 and base peaks at 95 (M^+-CF_2CFHCF_3). A ^{19}F NMR of the mixture identified two sets of signal attributable to two separate 2H-hexafluoropropyl groups and ^{13}C and ^1H NMR spectra were used to further determine the structures of (**37**) (see later).

The higher boiling fraction consisted of a group of four compounds identified as isomers of the di-adduct (**38**), by their EI^+ mass spectra (M^+-F, 377; M^+-$CFCFHCF_3$, 245). This was confirmed by a ^{19}F NMR of the mixture which identified peaks at -74.7 (broad singlet), -114.1 (overlapping multiplets) and -210.8 ppm (broad singlet) corresponding to CF_3, CF_2 and CFH groups of several 2H-hexafluoropropyl side chains.

Complete conversion of norbornane occurred in the DTBP initiated reaction, gave almost equal amounts of the mono-adducts (**37**) and di-adducts (**38**).

2.44. Structure determination of the mono-adducts (37)

A broad band proton decoupled ^{13}C NMR experiment was run on the two component mixture (37) to identify their structures.

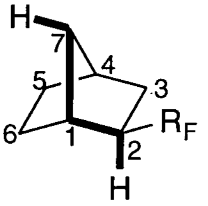


(37)

* denotes chiral centre

At low field two separate 2H-hexafluoropropyl groups were identified. Two overlapping doublets of quartets of doublets were observed a 85.6 and 86.2 ppm and were assigned to the two different CFH groups (c.f. compound (**25**)). The 115-126 ppm region was complex with two overlapping doublet of doublets at 120.1 ppm, assigned to the two difluoromethylene groups, and these signals also overlapped with two overlapping quartets of doublets at 121.2 ppm, attributed to the two trifluoromethyl groups. The high field region, 0-50 ppm, contained 13 distinguishable resonances. To identify which of these signals were from methylene or methyne carbons a ^{13}C DEPT spectrum was also run on the two component mixture (**37**). It identified six methyne carbons, including two overlapping triplets at 44.9 ppm ($^2J_{C\text{-}F}$ 22 Hz) corresponding to the two tertiary carbons attached to the fluoroalkyl group. The other four methyne resonances had no coupling to any fluorines and therefore were assigned as bridgehead carbons. As four bridgehead carbons were observed and no quaternary carbons were detected, addition to HFP must have occurred via a methylene group of norbornane and not at a bridgehead site. Comparison with ^{13}C NMR data of other substituted norbornanes[101], the two lowest field methylene resonances, at 36.9 and 36.6 ppm, were both assigned to carbons at the seven-position and therefore eliminated the likelihood that H-abstraction occurs at the seven-position either.

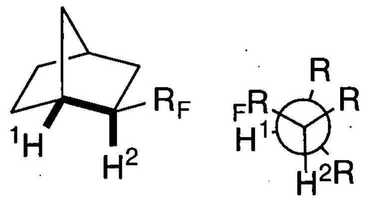
These results indicated that addition occurred at the two-position, but it was still unclear whether the hexafluoropropyl group was in the *exo-* or *endo-* position. To clarify this a $^{13}C/^{1}H$ HETCOR NMR experiment was run to identify the protons associated with the two- and seven-positions and then a $^{1}H/^{1}H$ COSY NMR experiment was run to, locate any coupling between them, in the hope that if the *exo*-isomer was present the $^{4}J_{H\text{-}H}$ 'W' coupling, between the two- and seven-protons would be observed[102].



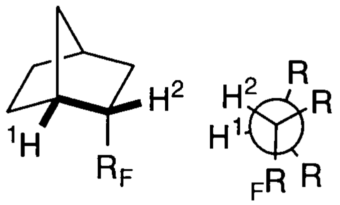
(37)

Unfortunately the protons associated with the seven-position had overlapping signals with the five- and six-position protons and although coupling with the two-position proton, to this region was observed in the $^{1}H/^{1}H$ COSY NMR spectrum it could not be reliably attributed to $^{4}J_{H\text{-}H}$ 'W'.

Alternatively, the protons at the one- and two-positions in the *exo*-isomer (**37**) would have a dihedral angle of almost 90° which, according to the simplified version of the Karplus equation[102] ($J = 10\cos\phi$, where ϕ is the dihedral angle), would result in very little coupling, whereas the same protons in the endo-isomer (**37a**) would have a dihedral angle of approximately 30°, giving rise to coupling of 6-8 Hz.



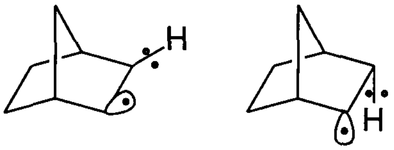
(37)



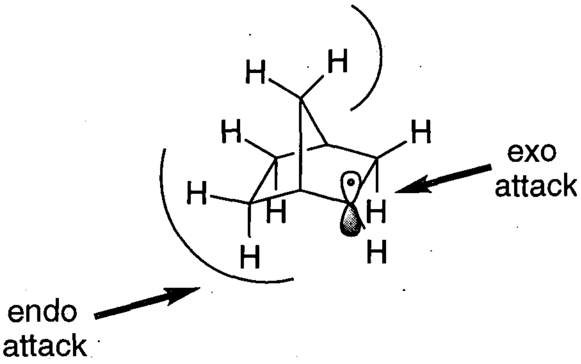
(37a)

The $^{13}C/^{1}H$ HETCOR NMR spectrum identified the one-position protons, as broad singlets, at 2.45 and 2.68 ppm and the two-position protons, as overlapping multiplets at 2.14 ppm. Examination of the $^{1}H/^{1}H$ COSY NMR spectrum showed no coupling between these peaks and therefore the two mono-adducts were characterised as diastereomers of 2-*exo*-(1,1,2,3,3,3-hexafluoropropyl)norbornane (**37**).

The bridgehead position in norbornane is very strained and also unable to invert, for these reasons formation of a bridgehead radical is unlikely [103]. A radical formed at the two-position is probably more stable than the corresponding radical at the seven-position because of the ability to undergo hyperconjugation with the corresponding protons at the three-position .



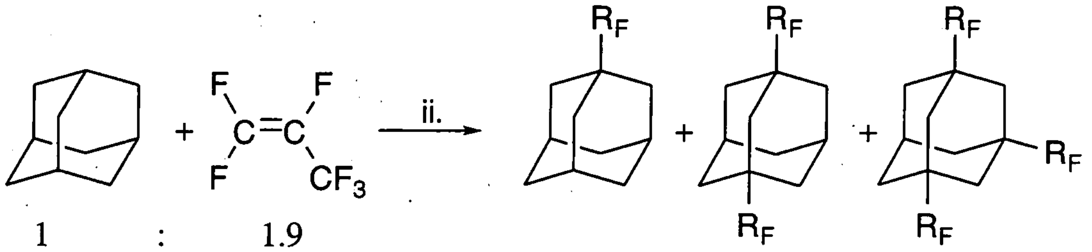
Preference for *exo*-attack, by HFP, is probably due to greater steric hindrance on approach to the endo site .



2.5 Addition of Polycyclic Hydrocarbons

2.51 Adamantane

Previously, Russian workers have successfully added HFP to adamantane using γ-rays initiation[97,98,104,105]. They used various solvents at temperatures between 20°-100°C, and up to a twenty-fold excess of HFP, to produce mono-, di- and tri-adducts. Nevertheless, a reaction was attempted using DTBP, without a solvent and a three-fold excess of HFP.



1 : 1.9

95% conversion

(22) 15% **(23)** 63% **(39)** 13%

$R_F = CF_2CFHCF_3$

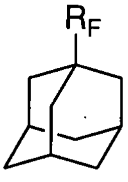
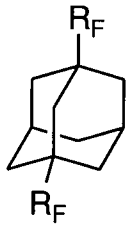
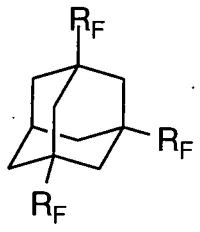
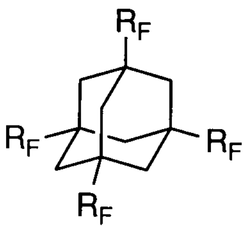
ii, DTBP , 140°C, 24hrs

Almost complete conversion of the adamantane was achieved and fractional distillation, under reduced pressure, of the product mixture gave three fractions. The ^{19}F, ^{1}H, ^{13}C NMR and EI^+mass spectra of each fraction confirmed them as 1-(1,1,1,2,3,3-hexafluoropropyl)adamantane (**22**), 1,3-bis(1,1,1,2,3,3-hexafluoropropyl)adamantane (**23**) and 1,3,5-tris(1,1,1,2,3,3-hexafluoropropyl)adamantane (**39**) respectively, in agreement with the literature.

Hydrogen abstraction occurs at the bridgehead carbons in adamantane in preference to its methylene carbons, which is in contrast to the norbornane. Although the bridgehead radical of adamantane is pyramidal and cannot invert, unlike the reactive *t*-butyl radical, the lack of strain in the radical conformation (sp^3) and the lack of steric hindrance to abstraction of its exposed tertiary hydrogens seem to compensate for the proposed instability of a rigid radical[103].

By varying the molar ratios of the reactants, adducts (**22**), (**23**) and (**39**) could be obtained as the major product (table 2.1).

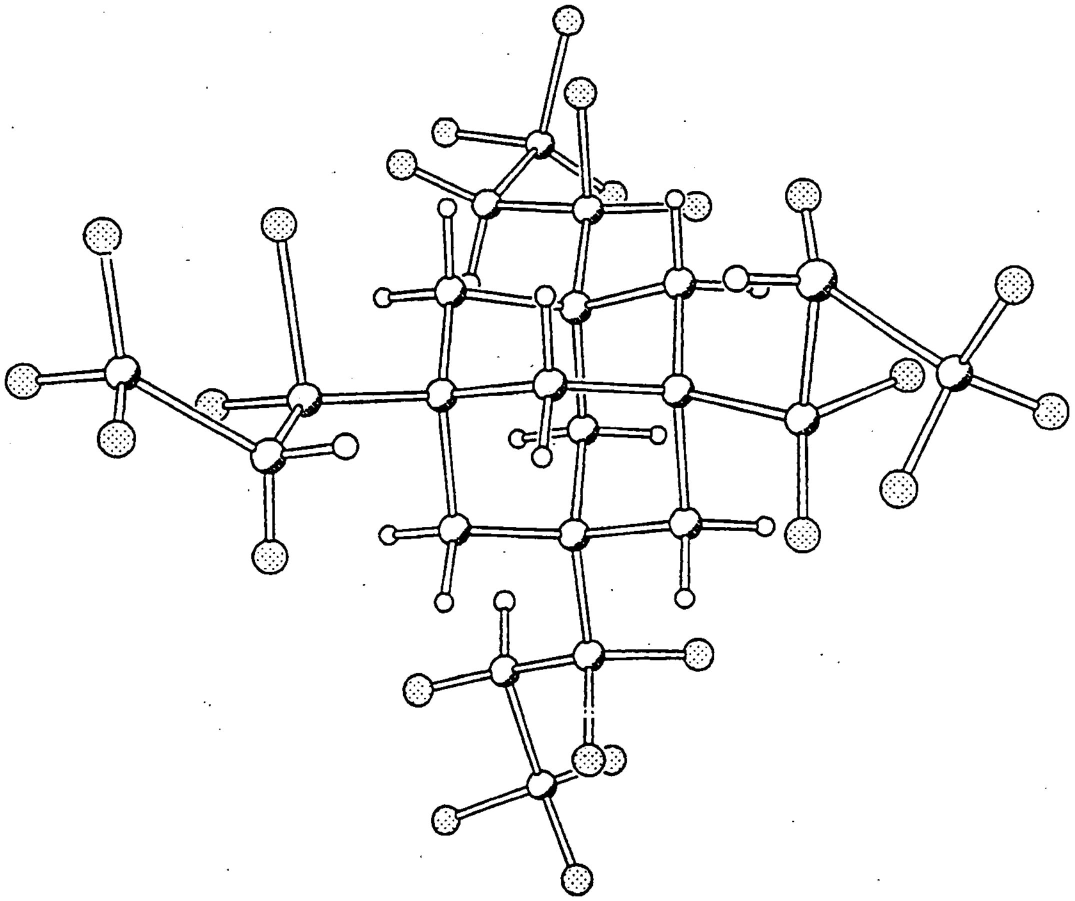
Table 2.1 Additions of adamantane to HFP (DTBP initiator, $R_F = CF_2CFHCF_3$)

	$C_{10}H_{16}$ to HFP molar ratio	Yields(%):  **(22)**	 **(23)**	 **(39)**	 **(40)**
i	1 : 1.2	60	19	-	-
ii	1 : 1.8	25	63	-	-
iii	1 : 3	-	8	82	-
iv	1 : 7	-	-	59	36

In all the reactions the conversion of adamantane was approximately 100%, except for reaction (i), in which the conversion was 92%. The most surprising aspect of these reactions was the ease of production of the higher adducts of adamantane. In other hydrocarbon systems the addition of the fluoroalkyl group significantly reduces its ability to undergo further substitution, unless an intramolecular pathway is available, as in butane[90].

Addition to HFP, using a seven-fold excess, produced a waxy solid which consisted of two components, one of which was identified as compound **(39)**. The two components could not be separated by fractional distillation, under reduced pressure, but when the mixture was dissolved in chloroform, hexane or pentane a white solid **(40)** precipitated from the solution. The EI^+ mass spectrum of the white solid **(40)** suggested that it was the tetra-adduct with a M^+-F peak at 717 and a base peak at 585 (M^+-CF_2CFHCF_3).The ^{19}F solution state NMR spectrum of the solid **(40)** in *d_6*-acetone produced only three sets of signals, at -74.1 (singlet), -121.1 & -127.6 (AB system) and -207.1 ppm (doublet), indicating that all the 2H-hexafluoropropyl groups were equivalent. The high symmetry of the solid **(40)** was confirmed by the ^1H NMR spectrum of the solution which contained only two multiplets at 2.07 ppm (six equivalent CH_2 groups) and 5.99 ppm (four equivalent CFH groups). The broad band proton decoupled ^{13}C NMR spectrum conclusively confirmed that the solid was 1,3,5,7-tetrakis(1,1,1,2,3,3-hexafluoropropyl)adamantane (**40**), as it contained only five resonances at 30.1 (singlet, six methylene carbons), 41.6 (triplet, four quaternary carbons), 83.1 (doublet of doublets of quartets, four fluoromethylene carbons), 119.0 (doublet of doublets of doublets, four difluoromethylene carbons) and 121.4 ppm (quartet of doublets, four trifluoromethyl carbons). A ^{19}F solid state NMR experiment was also run on compound (**40**) and it identified four signals corresponding to the 2H-hexafluoropropyl group. Interestingly, it identified two signals due to the CF_2 group confirming that its fluorines are non equivalent. A single crystal of compound (**40**) was grown and submitted for X-ray crystallographic analysis, which proved the structure beyond any doubt (figure 2.8).

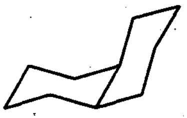
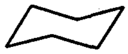
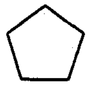
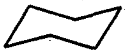
Fig. 2.8 Crystal structure of 1,3,5,7-tetrakis(1,1,1,2,3,3-hexafluoropropyl)adamantane (**40**)



2.6 Competition Reactions

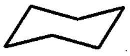
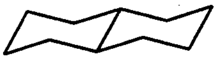
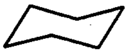
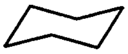
To get a true comparison of relative reactivities of the hydrocarbon systems towards HFP, a series of competition reactions were performed using both γ-ray and DTBP initiation. An equimolar mixture of two hydrocarbons was reacted with a deficiency (0.15 molar ratio) of HFP and the reaction mixture was analysed before and after the reaction by GC.

2.61. DTBP, 140°C

	Hydrocarbon ratio prior to reaction (R_1)	Hydrocarbon ratio after reaction (R_2)	Overall ratio (R_1/R_2)	Ratio per carbon in hydrocarbon
	47.82	43.69	0.90	0.09
	52.18	43.12	1	0.10
	53.41	49.75	0.79	0.08
	46.58	34.46	1	0.17
	45.13	36.94	1	0.20
	54.76	44.54	1.01	0.17

The competition reaction between *cis*- and *trans*-decalin indicates that there is no difference in reactivity between them at elevated temperatures, despite the marked differences in the conversions of their independent reactions. This evidence suggests that the independent *cis*-decalin reactions were inhibited by some undetected impurity. The competition reaction between cyclohexane and *trans*-decalin also shows that there is little difference in reactivities of the two systems, although cyclohexane is slightly more reactive. The greater reactivity of cyclopentane over cyclohexane, although only very slight, maybe due to the lower energy barrier to an eclipsing interaction between the carbon-hydrogen bonds in cyclopentane which stabilise the intermediate radical via hyperconjugation.

2.62 Gamma rays (20°C)

	Hydrocarbon ratio prior to reaction (R_1)	Hydrocarbon ratio after reaction (R_2)	Overall ratio (R_1/R_2)	Ratio per carbon in hydrocarbon
	46.72	41.74*	1	0.17
	52.82	48.46*	0.97	0.10
	42.99	41.14*	1	0.17
	57.01	55.45*	0.98	0.10
	55.58	44.76	0.93	0.17
	44.29	38.83	1	0.20

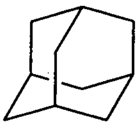
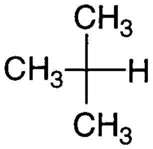
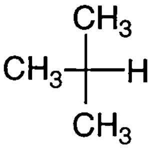
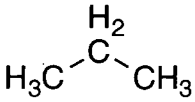
* - HFP recovered from the reaction.

The competition reaction between cyclohexane and *trans*-decalin showed little difference in the reactivities of the two hydrocarbon, even at room temperature. It is interesting to note that not all the HFP (approx. 75% consumption) was consumed in the reaction. This indicates that the reaction was inhibited by undetectable impurities, as other competition reactions involving cyclohexane have completely consumed the HFP. Again there was no significant difference in the reactivities of the cyclohexane and *cis*-decalin. Only 28% of the hexafluoropropene present reacted, even though the reaction was performed over twice the normal time period. This strongly suggests that impurities were present. These inhibitors are likely to have been contained within the *cis*-decalin starting material as the independent reactions involving it also had low conversions. The competition reaction between cyclohexane and cyclopentane did consume all the available HFP, and again there was little difference in their reactivity.

Interestingly, performing the competition reactions at room temperature, rather than 140°C, did not increase the selectivity between the hydrocarbons.

2.63. Crude competition reactions

Crude competition reactions were performed when the ratios of the hydrocarbon starting materials could not be determined by GC, for example if one substrate was either a solid or a gas. These crude competition reactions were performed using DTBP initiation at 140°C and a molar ratio of 1 :1 :1 of hydrocarbon : hydrocarbon : HFP and the ratio of products was measured by NMR or GC.

	GLC. adduct percentages	Ratio of HFP incorporation	Ratio per $3^{ary}/2^{ary}$ Carbon
	32% mono (**22**) 12% di (**23**)	6.2	1.7
 $CH_3-\overset{CH_3}{\underset{CH_3}{\vert}}-H$	9% mono (**30**)	1	1
 $CH_3-\overset{CH_3}{\underset{CH_3}{\vert}}-H$	62% mono (**30**)	2.2	2.2
 $H_3C-\overset{H_2}{C}-CH_3$	28% mono (**28**)	1	1

The competition reaction between adamantane and 2-methylpropane suggests that adamantane is slightly more reactive than 2-methylpropane, when the statistical ratio of tertiary carbons (1 : 4) is taken into account, but this result maybe within the experimental error. The competition reaction between 2-methylpropane and propane suggests that 2-methylpropane is twice as reactive as propane. This can be explained by the increased radical nucleophilicity and stability of the *t*-butyl radical over the isopropyl radical.

2.7 Conclusions

In general, any hydrocarbon system which gave only moderate conversion at room temperature, gave a high reaction conversion at elevated temperature (140°C). The results of the competition reactions, at 140°C and room temperature, indicate that there are only very small differences between the reactivities of all the hydrocarbon systems and that they all produce radicals that react with HFP. The crude competition reactions also showed there are little differences in the reactivity of similar hydrocarbon systems. A notable exception was *cis*-decalin, but results of competition reactions involving *cis*-decalin, at low and high temperatures, suggest that it is as reactive as the other systems. The anomaly must be due to *cis*-decalin containing minute amounts of inhibitors, but sufficient enough to prematurely terminate the radical chain mechanism.

In acyclic systems, the favoured site of attack was in the order tertiary carbon > secondary carbon > primary carbon. This order is in agreement with radical stability in acyclic systems and also reflects the increased nucleophilicity of the radical. The cyclic systems were not so predictable, as in contrast to adamantane, norbornane and decalin systems favoured addition at secondary carbons. This is rationalised by the increased strain at the tertiary site in norbornane and the increased steric crowding in the decalin systems.

The NMR data of the hexafluoropropyl adducts are complex and some simplification is required for di- and poly-substituted products, for example dehydrofluorination of the polyfluoroalkyl group.

$$R{-}CF_2CFHCF_3 \xrightarrow{-\,HF} R{-}CF{=}CFCF_3$$

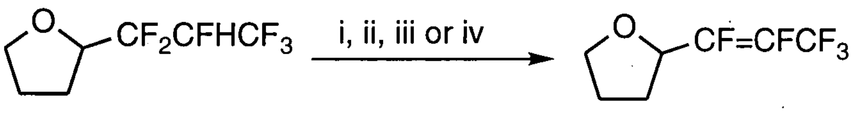
This process eliminates some stereospecific centres and should simplify structure determination.

Chapter Three

Dehydrofluorination of Hexafluoropropene Adducts

3.1 Introduction

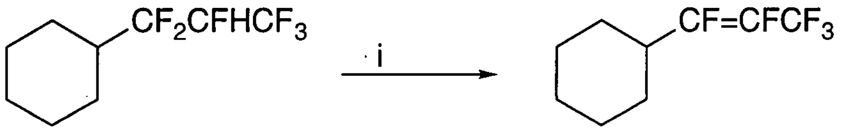
Several methods have been used to remove HF from the ether adducts of hexafluoropropene,[66,78,80,106] such as compound (**41**). In general, alkoxide bases were used with or without solvent and gave moderate to good conversions. In all cases a mixture of the Z- and E-alkenes were produced which could not be separated.



(41) **(42)**

	Conditions	Yield of (**42**) (%)	Ref.
i.	$KOH_{(s)}$, 150°C	47	[66]
ii.	$KOH_{(s)}$, reflux	75	[78]
iii.	KOH, diglyme, 120°C	75	[106]
iv.	KO^tBu, ^tBuOH, 25°C	62	[80]

Alcoholic solutions of sodium hydroxide were used by Russian workers[99,105,107] to dehydrofluorinate the cyclohexane mono-adduct (**24**) and the mono- (**22**) and di-adduct (**23**) of adamantane. The reactions gave good conversions, but again produced a mixture of the Z- and E- isomers of the alkene which were inseparable.



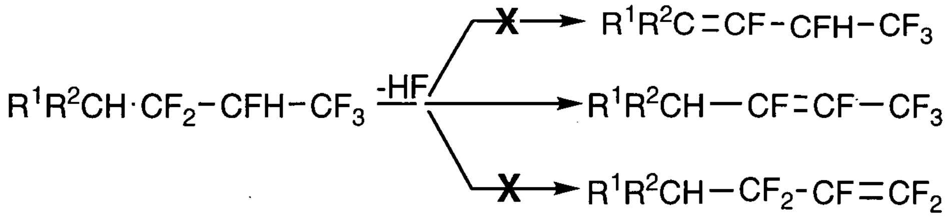
(24) (**43**) 85%

i. NaOH in EtOH, 81°C, 3 hrs

3.2 Regiochemistry of the Double Bond

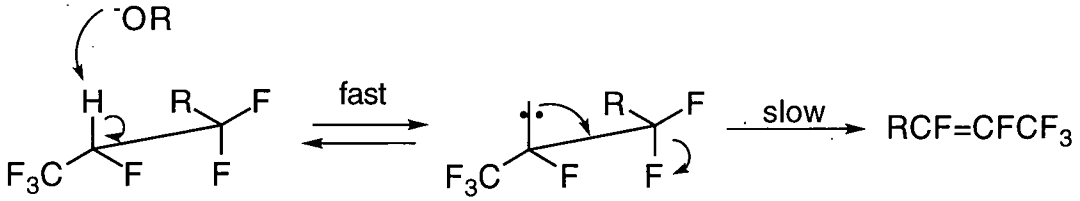
In all the cases illustrated, the double bond is formed at the two-position in fluoroalkyl side chain. This raises an interesting point of regiospecificity, as theoretically, three isomers could be produced (scheme 3.1).

Scheme 3.1

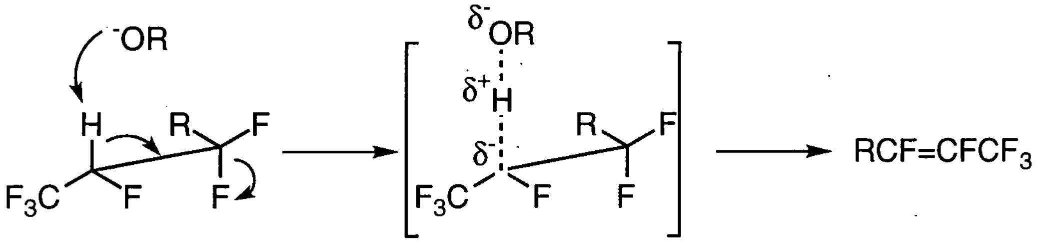


As fluoride ion is a poor leaving group, due to the strength of the C-F bond, and the proton removed is quite acidic the dehydrofluorination mechanism is likely to be E1cB or E2 (concerted) with an 'E1cB-like' *trans*ition state, where C-H bond stretching occurs before C-F bond stretching.

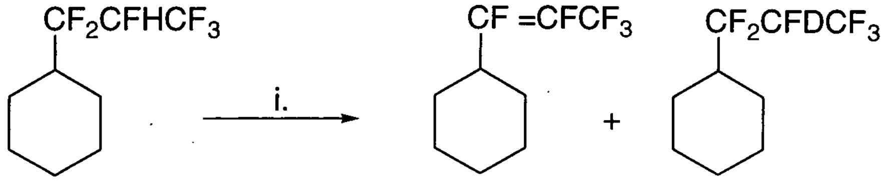
E1cB Mechanism



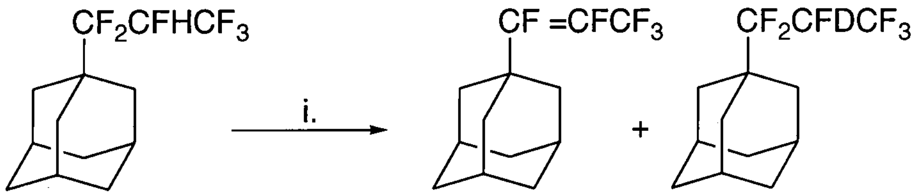
E2 Mechanism (E1cB-like *trans*ition state)



In the present work, deuterium exchange reactions, using a deuterated solvent, were performed on compounds (**24**) and (**22**), in order to determine the mechanism of dehydrofluorination.



(24) **(43)** 90% **(24a)** 4%

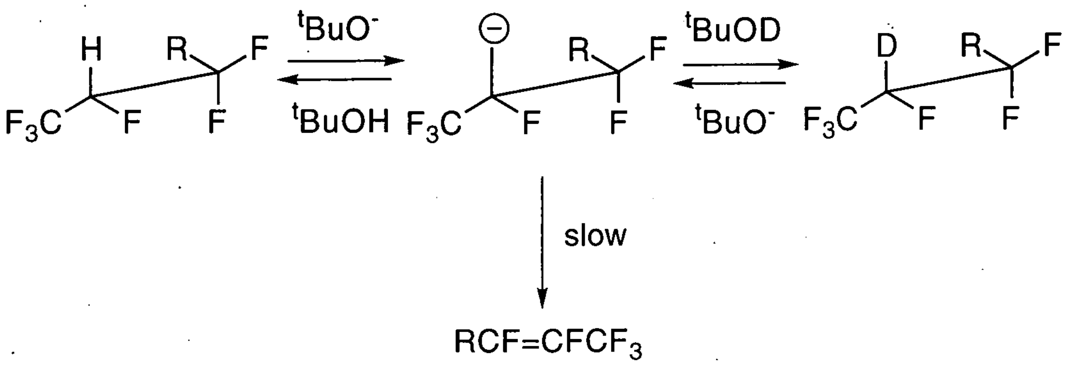


(22) **(45)** 52% **(22a)** 9%

i. 1:0.75 KO^{t}Bu, ^{t}BuOD, 25°C, 15 mins.

In both reactions deuterium was incorporated into the starting material (scheme 3.2) which is consistent with an E1cB mechanism, although the possibility of an independent exchange process cannot be overlooked.

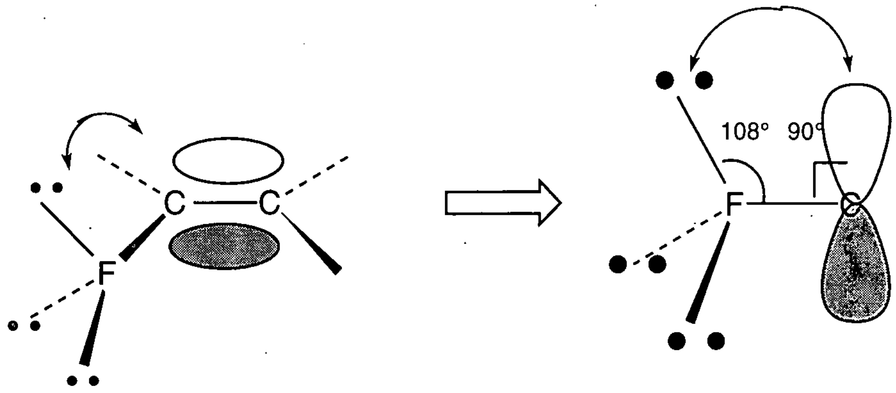
Scheme 3.2 Solvent deuterium exchange in an E1cB process



If dehydrofluorination proceeds via an E1cB mechanism, the regiochemistry of the double bond is governed by the acidity of the proton that is removed and the strength of the C-F bond being broken. The proton at the two-position is the most acidic due to the neighbouring electron-withdrawing CF_2 and CF_3 groups, and therefore deprotonation of it produces the most stable carbanion. The fluoride ion is more easily removed from the

CF_2 group than the CF_3 group, as this leads to a smaller number of vinylic fluorines, whose lone pairs have unfavourable interactions with the electrons of the double bond[1] (Figure 3.1).

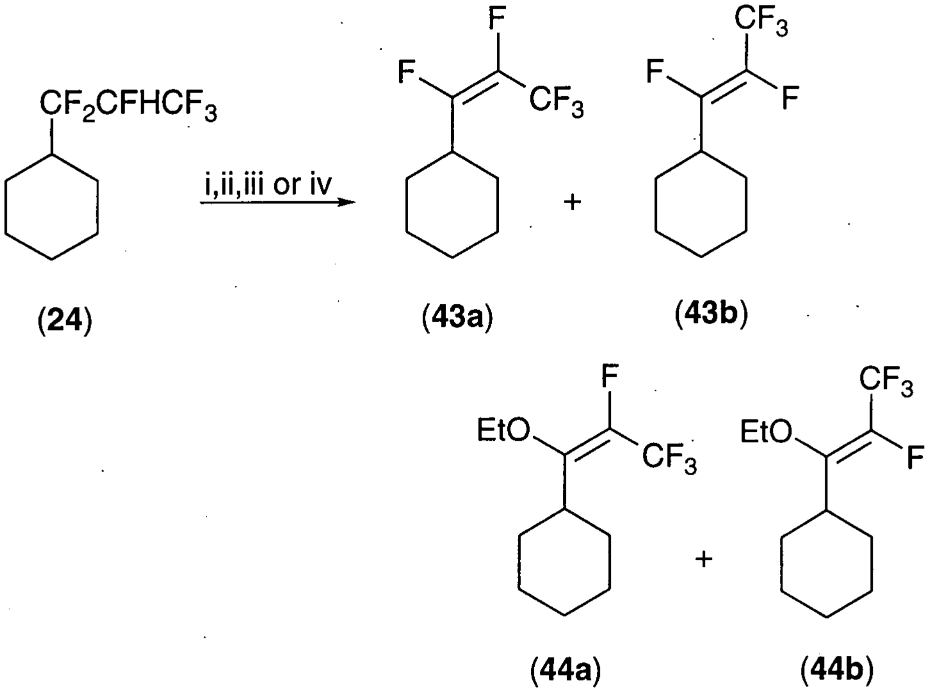
Figure 3.1 Electronic repulsions between vinylic fluorines and π–electrons



3.3 Dehydrofluorinations

3.31. 1,1,2,3,3,3-Hexafluoropropylcyclohexane (**24**)

Dehydrofluorination of the adduct (**24**) was affected by potassium hydroxide or potassium t-butoxide at various temperatures.

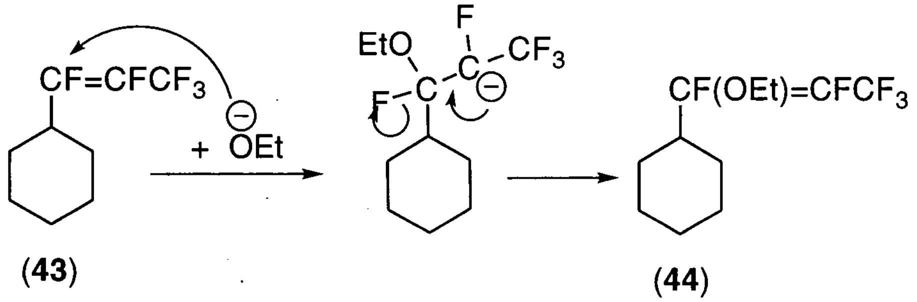


	Conditions	Conversion (%)	Yields (%) (**43a**)	(**43b**)	(**44a**)	(**44b**)
i.	1 : 2 KOH, EtOH, 50°C, 20 hrs	100	71	28	0.7	0.3
ii.	1 : 2 KO^tBu, ^tBuOH, 25°C, 15 min	100	58	2	-	-
iii.	1 : 1.5 KO^tBu, $^iPr_2O$, 0°C, 10 min	100	92	trace	-	-
iv.	1 : 1.5 KO^tBu, C_6H_{14}, 0°C, 15 min	100	85	trace	-	-

A reaction using alcoholic potassium hydroxide, at 50°C, was terminated after two an a half hours. Analysis of the product mixture by GLC/MS and NMR confirmed the major products as E- and Z- isomers of pentafluoroprop-2-enylcyclohexane (**43**) which could not be separated. Two minor products, identified as E- and Z- isomers of 1,1,1,2-tetrafluoro-3-ethoxy-prop-2-enylcyclohexane (**44**) by their EI^+ mass spectra and ^{19}F NMR spectra, were inseparable from compounds (**43**).

Compounds (**44**) were produced as a result of attack by ethoxide ions, from the solvent, on compounds (**43**) (Scheme 3.3), followed by loss of fluoride ion.

Scheme 3.3



In an attempt to eliminate the production of the vinylic ethers (**44**), the steric requirement of the base was increased by using t-butoxide. Three reactions were performed, using various solvents, and were terminated after complete conversion of the starting material. The low yields of products from the reaction in t-butanol solvent were attributed to difficulties in extracting the products. Isopropyl ether and hexane were used instead to make the workup easier, although the solubility of potassium t-butoxide is greatly reduced in these solvents. Changing the solvent also allowed the reaction temperature to be lowered below 25°C, the melting point of t-butanol. Using potassium t-butoxide did eliminate the formation of the vinyl ethers (**44**) and also had the unexpected effect of significantly reducing the proportion of E-alkene (**43b**) formed. The amount of E-isomer (**43b**) was further reduced, to negligible proportions, when the temperature of the reaction was lowered from 25°C to 0°C.

The ability to produce only the Z-isomer (**43a**) was surprising, as on steric grounds it might be expected that the cyclohexyl and trifluoromethyl groups would prefer to be *trans* to one another.

Structure determination of pentafluoroprop-2-enylcyclohexane (43)

The removal of the chiral CFH group not only increases the symmetry of the system over its precursor, but also reduces the number of diastereomers produced in the case of the higher adducts. Therefore the mono-enes are useful model compounds for structure determination of the di-enes.

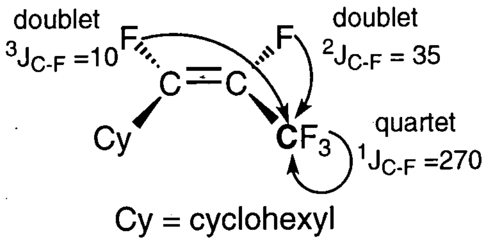
The mixture of E- and Z-isomers of pentafluoroprop-2-enylcyclohexane (**43**) could not be separated, Their EI$^+$ mass spectra both gave M$^+$ peaks at 214 and the two isomers were distinguished by their respective vinylic fluorine resonances in the ^{19}F NMR spectrum of the mixture.

^{19}F NMR - The vinylic fluorines of the E-isomer (**43b**), at -148.3 and -176.5 ppm, were identified by their coupling to one another ($^3J_{trans\text{F-F}}$ = 132 Hz). Such a large coupling is characteristic of *trans*-fluorines[108]. The CF_3, at -68.2 ppm, was assigned by its relative integration to the vinylic *trans*-fluorines. The *cis*-fluorines of the Z-isomer (**43a**) were observed at -131.4 and -161.4 ppm and again the CF_3 group was identified by its relative integration. The vinylic fluorine adjacent to the cyclohexyl group was observed as a doublet ($^3J_{\text{F-H}}$ = 31) due to its antiperiplanar coupling to the CH ring proton. The other vinylic proton was observed as a quartet ($^3J_{\text{F-F}}$ = 11) of doublets ($^4J_{\text{F-H}}$ = 5) due to its coupling to the fluorine atoms of the adjacent CF_3 group and smaller coupling to the CH ring proton. Surprisingly, no vicinal fluorine-fluorine coupling was observed between the two vinylic *cis*-fluorines.

A pure sample of Z-pentafluoroprop-2-enylcyclohexane (**43a**) was characterised separately. Its ^{19}F NMR spectrum, as previously described, established it as the Z-isomer.

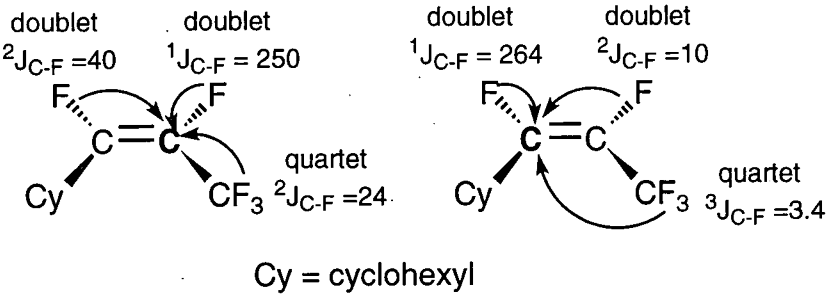
^{13}C NMR - The stereochemistry of the Z-isomer (**43a**) was confirmed by a broad band proton decoupled ^{13}C NMR spectrum which identified three signals at low field corresponding to the three carbons of the pentafluoropropenyl group. The CF_3 group, at 120.4 ppm, was identified as a quartet ($^1J_{C-F}$ = 270 Hz) of doublets ($^2J_{C-F}$ = 35 Hz) of doublets ($^3J_{C-F}$ = 10 Hz) due to its first order coupling to three α-fluorines, followed by second order coupling to the β-fluorine and third order coupling to the γ-fluorine (figure 3.2).

Figure 3.2 Carbon-fluorine coupling (Hz) to the trifluoromethyl carbon of (**43a**)



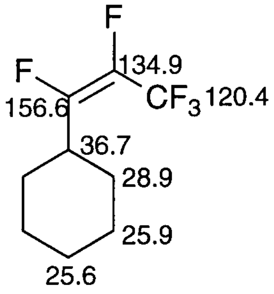
The magnitude of the final coupling to the γ-fluorine (10 Hz) confirmed that this fluorine was *trans* to the CF_3 group and therefore the overall stereochemistry of the double bond was *cis*. A doublet ($^1J_{C-F}$ = 250 Hz) of quartets ($^2J_{C-F}$ = 40 Hz) of doublets ($^2J_{C-F}$ = 24 Hz), at 134.9 ppm, was assigned to the vinylic carbon α to the CF_3 group because of its large coupling to the three equivalent β-fluorines. The vinylic carbon, α to the cyclohexyl group, was observed as a doublet ($^1J_{C-F}$ = 264) of doublets ($^2J_{C-F}$ = 10) of quartets ($^3J_{C-F}$ = 3.4) at 156.6 ppm (figure 3.3).

Figure 3.3 Carbon-fluorine coupling (Hz) to the vinylic carbons of (**43a**)



Four other resonances were identified at 25.6, 25.9, 28.9 (doublet, ${}^3J_{C-F}$ = 2.2) and 36.7 ppm (doublet, ${}^2J_{C-F}$ = 21) were assigned to the CH_2 ring carbons at the four-, three-, two-positions and the CH carbon at the one-position respectively due to the increased deshielding from the perfluoroalkenyl group (figure 3.4).

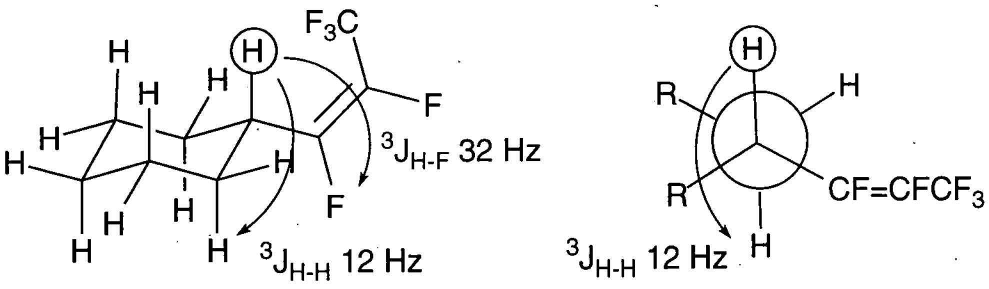
Figure 3.4 ${}^{13}C$ NMR chemical shifts (ppm) of compound (**43a**)



(43a)

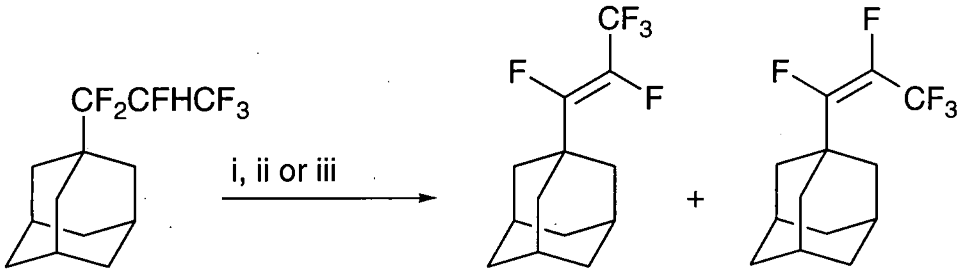
${}^1H$ NMR - A ${}^{13}C$ HETCOR experiment also made it possible to assign the proton spectrum. The methyne ring proton at 2.52 ppm was observed as a doublet (${}^3J_{H-F}$ = 32 Hz), from vicinal coupling to the vinylic fluorine, of triplets (${}^3J_{H-H}$ = 12 Hz), due to coupling to two neighbouring protons. The magnitude of the ${}^3J_{H-H}$ coupling is characteristic of an antiperiplanar relationship between the protons[102] and therefore the fluoroalkenyl group occupies an equatorial site (figure 3.5) on the cyclohexane ring.

Figure 3.5. Antiperiplanar coupling in equatorial conformation of compound (**43a**)



3.33 1-(1,1,2,3,3,3-Hexafluoropropyl)adamantane (22)

Several methods were used to remove HF from 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane (**22**) with surprising results.



(22) **(45a)** **(45b)**

i. 1:2 KOH, EtOH, 80°C
ii. 1:2 KO^{t}Bu, (^{i}Pr)$_2$O, room temp.
iii. 1:2 KO^{t}Bu, (^{i}Pr)$_2$O, -10°C

Conditions	Reaction conversion	Yields: (**45a**)	(**45b**)
KOH, EtOH, 80°C	100%	87	trace
KO^{t}Bu, (^{i}Pr)$_2$O, RT.	100%	92	trace
KO^{t}Bu, (^{i}Pr)$_2$O, 0°C	100%	trace	85

Using potassium hydroxide at elevated temperature the mono-adduct was converted to almost exclusively 1-(E-pentafluoroprop-2-enyl)adamantane (**45a**). Potassium t-butoxide at room temperature gave a similar product distribution as the potassium hydroxide reaction. The reaction was very exothermic and no attempt was made to control the reaction temperature, but when the reaction was repeated and the temperature was held at 0°C then the product distribution changed dramatically. The major component then became 1-(Z-pentafluoroprop-2-enyl)adamantane (**45b**) which was confirmed by a ^{19}F NMR spectrum of the product.

Decreasing the temperature of the reaction completely inverted the product distribution from the E-isomer to the Z-isomer becoming the major product. This suggests that the Z-isomer is kinetically preferred product and at low temperature kinetic control dominates, whereas at higher temperature the reaction is under thermodynamic control (See later).

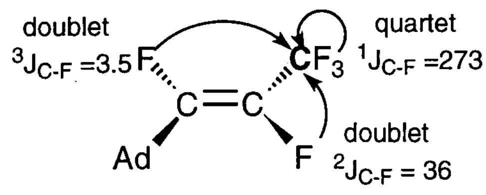
Structure determination of compounds (**45a**) and (**45b**)

The EI^+ mass spectra of both the E-isomer (**45a**) and the Z-isomer (**45b**) identified M^+ peaks at 266 confirming dehydrofluorination had occurred. NMR analysis was performed on separate samples of the two compounds (**45a**) and (**45b**).

^{19}F NMR - The two vinylic fluorines of the E-isomer (**45a**), at -149.3 and -175.6 ppm, were observed as large doublets ($^3J_{F\text{-}F}$ = 131 & 130 Hz) due to their *trans* coupling to each another. The vinylic fluorine *cis* to the CF_3 group, at -149.3 ppm, was further split by the three γ-fluorines into a quartet ($^4J_{F\text{-}F}$ = 23 Hz). The CF_3 group, at -67.6 ppm, was in turn split by the vinylic γ-fluorine into a doublet ($^4J_{F\text{-}F}$ = 21 Hz).

^{13}C NMR - The CF_3 carbon signal, at 119.5 ppm, was split into a quartet ($^1J_{C\text{-}F}$ = 273 Hz), due to its coupling to its three α-fluorines, then into a doublet ($^2J_{C\text{-}F}$ = 36 Hz), from its coupling with the vinylic β-fluorine, and finally another small doublet ($^3J_{C\text{-}F}$ = 3.5 Hz), arising from coupling to the vinylic γ-fluorine. The small magnitude of this coupling confirmed the *cis*- relationship between the CF_3 group and the γ-vinylic fluorine (c.f. Z-pentafluoroprop-2-enylcyclohexane (**43a**) and therefore that the vinylic fluorines were *trans* to each other (figure 3.6).

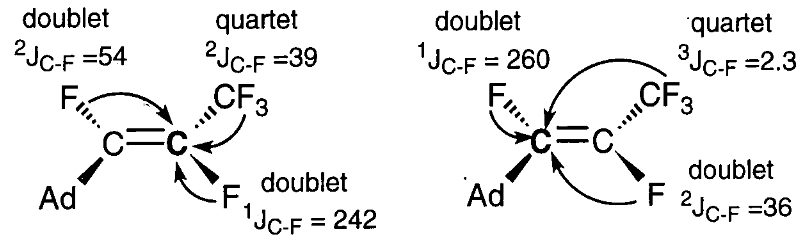
Figure 3.6 Carbon-fluorine coupling (Hz) to the trifluoromethyl carbon of (**45a**)



Ad = adamantyl

The vinylic carbon α to the CF_3 group, was initially split into a doublet ($^1J_{C\text{-}F}$ = 242 Hz) by its α-fluorine, then into a further doublet ($^2J_{C\text{-}F}$ = 54 Hz) by the vinylic β-fluorine and finally into a quartet ($^2J_{C\text{-}F}$ = 39 Hz) by the β-fluorines of the CF_3 group, at 138.2 ppm. The vinylic carbon, α to the adamantyl group, was split into a doublet ($^1J_{C\text{-}F}$ = 260 Hz) by its α-fluorine, then into another doublet ($^2J_{C\text{-}F}$ = 36 Hz) by the other vinylic fluorine and then into a quartet ($^3J_{C\text{-}F}$ = 2.3 Hz) by the fluorines of the CF_3 group, at 160.2 ppm (figure 3.7).

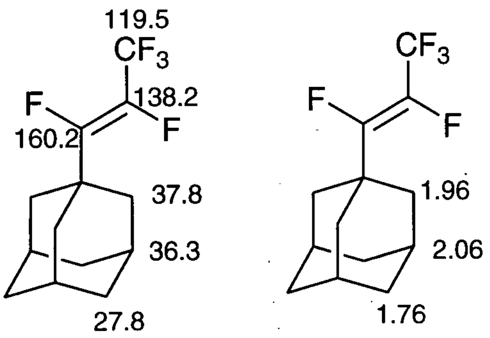
Figure 3.7 Carbon-fluorine coupling (Hz) to the vinylic carbons of (**45b**)



Ad = adamantyl

^{1}H NMR - The high symmetry of the adamantyl group gave only three resonances in the proton spectrum which were assigned as in figure 3.8.

Figure 3.8 ^{13}C and ^{1}H NMR chemical shifts (ppm) of compound (**45a**)



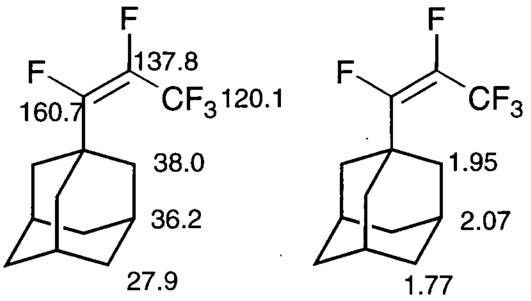
(45a)

A pure sample of 1-(Z-pentafluoroprop-2-enyl)adamantane (**45b**) was characterised separately.

^{19}F NMR - The two vinylic *cis*-fluorines were observed as two broad singlets at -125.2 and -154.7 ppm and the trifluoromethyl group was detected at -60.2 ppm.

The carbon and proton NMR spectra of Z-isomer were similar to those of the E-isomer and are summarised in figure 3.9.

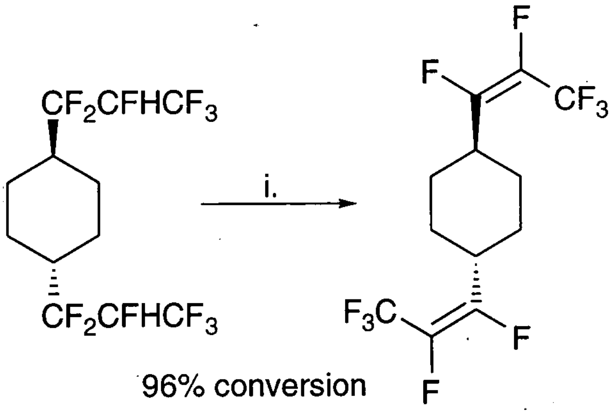
Figure 3.9 ^{13}C and ^{1}H NMR chemical shifts (ppm) of compound (45b)



(45b)

3.34 *trans*-1,4-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (27a)

Compound (**27a**) was used in a separate dehydrofluorination reaction, from the other di-adducts of cyclohexane (**27**).



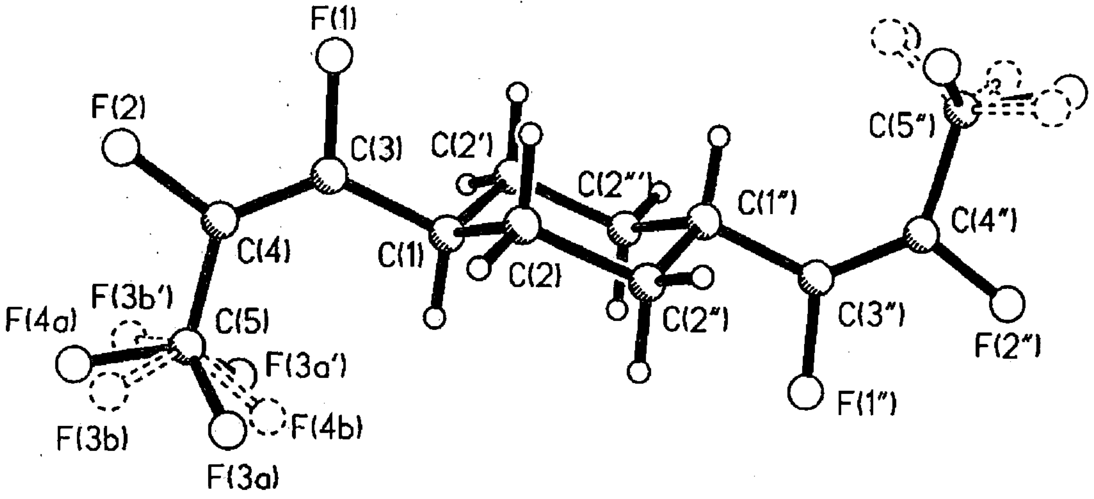
(27a) **(46)** 72%

i. 1:2 KO^{t}Bu, (^{i}Pr)$_2$O, -10°C, 20 mins.

Low temperature crystallisation was used to precipitate the compound (**46**) out of the organic layer. The EI$^+$ spectrum of the white solid (**46**) gave a M$^+$ peak at 344 which confirmed it as a di-ene and the stereochemistry of both, equivalent double bonds was confirmed as *cis* by its ^{19}F NMR spectrum. The high symmetry of the molecule was confirmed by its broad band proton decoupled ^{13}C NMR spectrum which identified five signals, three of which were accounted for by the carbons of the pentafluoropropenyl groups. The two at high field were attributed to the methylene ring carbons (27.8 ppm, singlet) and the methyne ring carbons (35.5 ppm, doublet, $^3J_{C\text{-}F}$

= 21). A crystal was grown for X-ray crystallographic analysis, which confirmed the structure as *trans*-1,4-bis(z-pentafluoroprop-2-enyl)cyclohexane (**46**) (figure 3.10).

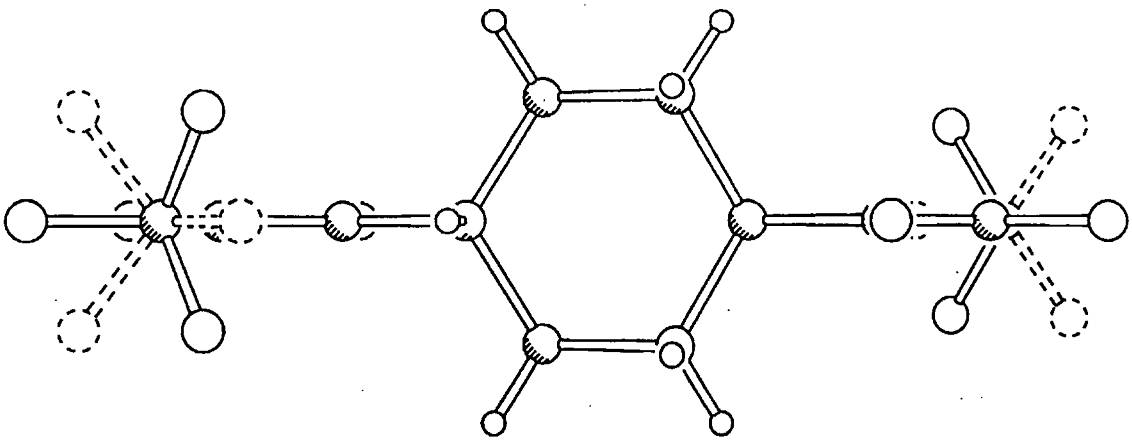
Figure 3.10 *trans*-1,4-bis(z-pentafluoroprop-2-enyl)cyclohexane (**46**)



The C(5)-C(4)-C(3) and C(4)-C(3)-C(1) bond angles are distorted to approximately 130°. This is presumably due to the steric repulsion between the trifluoromethyl and cyclohexyl groups. The distance between F(2) and F(4a) is 2.515 A and between F(4b) and H(1ax) is 2.241 A, so there is no significant repulsive or attractive interactions.

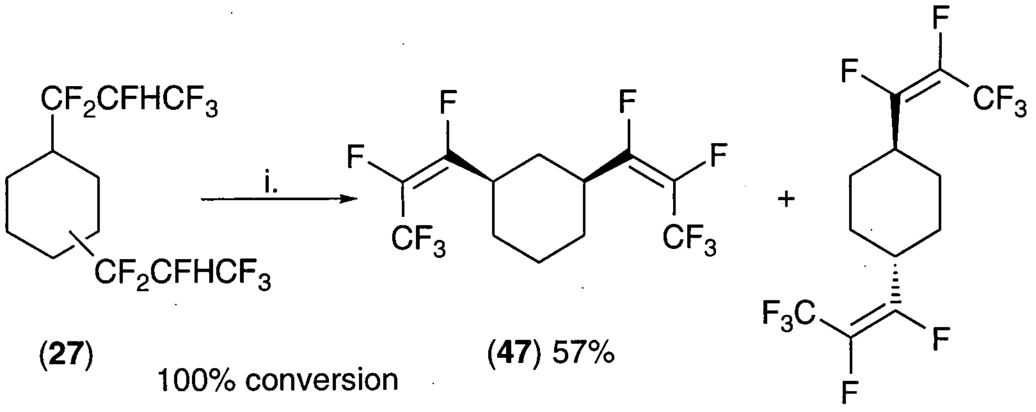
The di-ene (**46**) was observed in two forms (α and β), in a 2 : 1 ratio, which vary in the conformation of their trifluoromethyl groups. However, very high thermal parameters of CF_3 fluorines may indicate further disorder of the trifluoromethyl groups. The α form exists with F(4a) fluorine in the mirror plane and the F(3a) and F(3a') fluorines related via this plane, whereas the β form exists with the F(4b) fluorine in the mirror plane and the F(3b) and F(3b') fluorines related via this plane. The different conformations of the CF_3 group can be seen more clearly in figure 3.11

Figure 3.11 α- and β- forms of Compound (**46**)



3.35 1,x-Bis(1,1,1,2,3,3,3-hexafluoropropyl cyclohexane x=2,3,4

The cyclohexane di-adduct mixture (**27**), including the crystalline isomer (**27a**), was dehydrofluorinated at 0°C



(**27**) 100% conversion

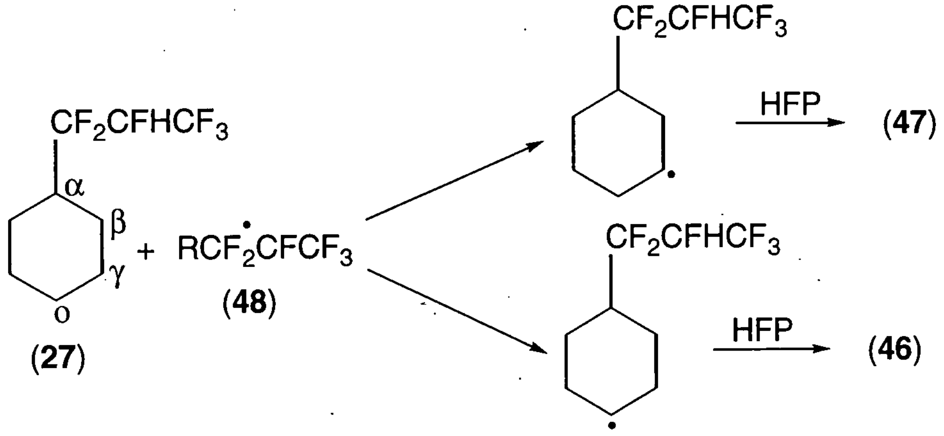
(**47**) 57%

(**46**) 30%

i. 1:4 KO^tBu, $(^iPr)_2O$, 0°C, 20 mins.

A GLC/MS of the product mixture identified four components, two of which existed in trace amounts, all had M^+ peaks at 344 in their EI^+ mass spectra. The two major products, in a 1.92 : 1 ratio, were identified as compounds (**47**) and (**46**) respectively, by their NMR data. Compound (**46**) crystallised out of the product mixture when methanol was added and the system was cooled in an acetone slush bath (-78°C). A separate GLC was run on a solution of the solid and comparison of the retention times identified it as the minor of the two major products.

The major di-adduct formed on addition of HFP to cyclohexane is the *cis*-1,3-isomer (**47**) and not the *trans*-1,4-isomer (**46**). On formation of the di-adducts it would be anticipated that the electron-withdrawing polyfluoroalkyl group in 1,1,2,3,3,3-hexafluoropropylcyclohexane (**27**) would reduce the ease of hydrogen abstraction,by the propagating electrophilic radicals (**48**), from the CH_2 groups β- and γ- to it. No significant production of 1,2-isomer is good evidence for this, however, the effect is clearly rapidly attenuated in this system, as the 1,3-isomer (**47**) is twice as abundant as the 1,4-isomer (**46**).



The 1.9 : 1 excess of the 1,3-adduct (**47**) over the 1,4-adduct (**46**) obviously arises through the statistical effect.

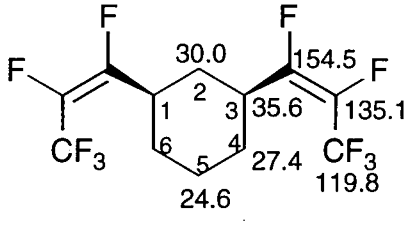
Structure determination of *cis*-1,3-bis(Z-pentafluoroprop-2-enyl)cyclohexane (47)

NMR spectroscopy experiments were run on the remaining mixture, containing essentially only one component, to determine its structure.

^{19}F NMR The ^{19}F NMR spectrum identified three resonances consistent with two equivalent pentafluoroalkenyl groups.

^{13}C NMR - At low field, three resonances at 119.8, 135.1 and 154.5 ppm were assigned to the two equivalent pentafluoropropenyl groups. In the 0-40 ppm region, four resonances were observed, suggesting that the cyclohexyl ring was 1,3-disubstituted rather than 1,2- or 1,4-disubstituted since these isomers would produce omly three and two signals respectively. The doublet at 35.6 ppm ($^2J_{C\text{-}F} = 21$) was assigned to the two equivalent CH groups, at C-1 and C-3, and the singlet at 30.0 ppm was attributed to the methylene carbon, C-2, because of the deshielding due to the two adjacent fluoroalkenyl groups. A further doublet ($^3J_{C-F}$ = 2.3) at 27.4 ppm was identified as the two equivalent methylene groups, at C-4 and C-6, and finally a singlet at 24.6 ppm was assigned to the methylene carbon, C-5, which is deshielded the least (figure 3.12).

Figure 3.12 ^{13}C NMR chemical shifts (ppm) of compound (47)

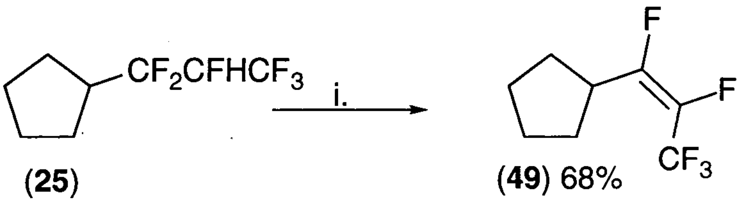


(23)

^{1}H NMR - A doublet ($^2J_{H-F}$ = 31) of triplets ($^3J_{H-H}$ = 12) at 2.64 ppm was identified as the two equivalent CH ring protons. The large antiperiplanar Hydrogen-Hydrogen coupling confirmed that both perfluoroalkenyl groups occupy equatorial sites in the cyclohexane ring.

3.36 1,1,2,3,3,3-Hexafluoropropylcyclopentane (25)

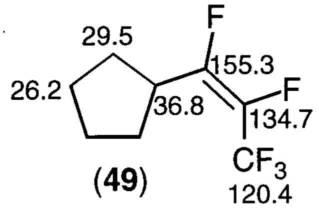
Dehydrofluorination was performed at -78°C, as earlier attempts at higher temperatures had led to tarring of the product.



i. 1:1.5 KO^{t}Bu, $(Et)_2O$, -78°C, 30 mins.

Complete conversion of starting material was achieved to only one product which was identified as Z-pentafluoroprop-2-enylcyclopentane (**49**). The M$^+$ peak was observed at 200 in the EI$^+$ mass spectrum and the compounds ^{19}F NMR data identified the existence of the perfluoroalkenyl group with *cis* stereochemistry only. A broad band proton decoupled ^{13}C NMR spectrum was run on the product to provide a model for the structure determination of the elimination products of the di-adducts of cyclopentane. The ^{13}C NMR detected six resonances (figure 3.14), three of which, at 120.4, 134.7 and 155.3 ppm confirmed the presence of the Z-pentafluoroprop-2-enyl group. The other three signals were assigned to the cyclopentane ring. A doublet ($^2J_{C-F}$ = 22) at 36.8 ppm was attributed to the methyne ring carbon and singlets at 29.5 and 26.2 ppm were assigned to the methylene ring carbons at the two and three positions respectively due to the deshielding effect of the perfluoroalkenyl group (figure 3.13).

Figure 3.13 ^{13}C NMR chemical shifts (ppm) of compound (**49**)

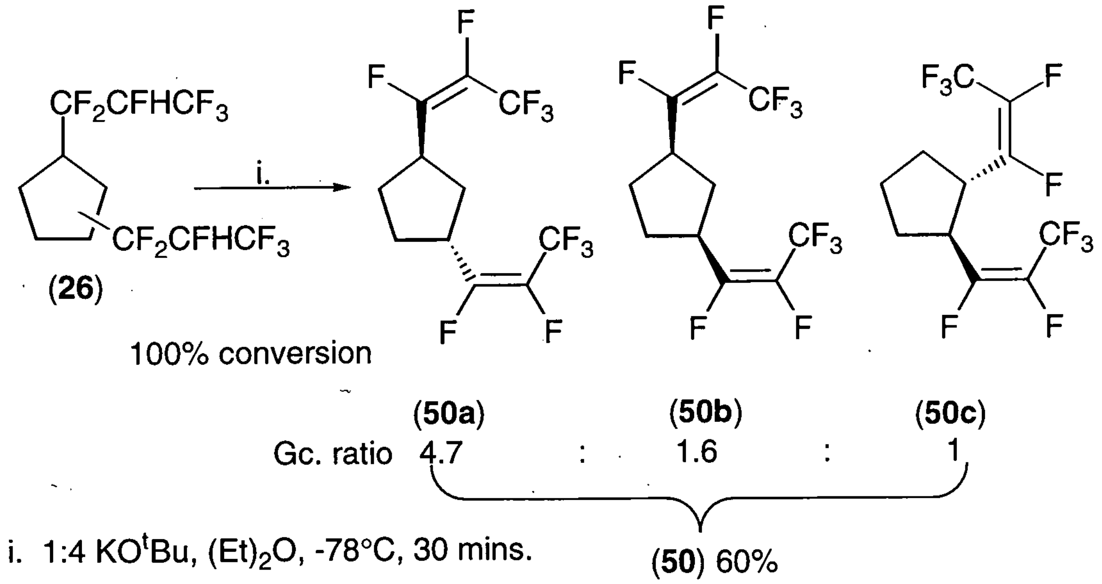


(**49**)

The low temperature at which the reaction was performed seemed to remove any trace of the E-isomer, which suggests that the Z-isomer is kinetically favoured.

3.37 1,x-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclopentane x=2,3 (50)

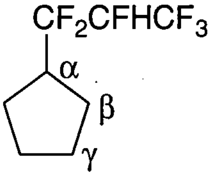
Again the dehydrofluorination was performed at -78°C.



i. 1:4 KO^{t}Bu, (Et)$_2$O, -78°C, 30 mins.

Distillation of the product mixture gave a fraction containing three components, (**50a**), (**50b**) and (**50c**), which could not be separated. A ^{19}F NMR spectrum of the fraction mixture identified three sets of *cis*-fluorine resonances and M^+ peaks at 330 were observed in the mass spectra of all three components, establishing them as isomers of bis(Z-pentafluoroprop-2-enyl)cyclopentane, in a ratio 4.7 : 1.6 : 1. .

Again, a combination of the polar and steric effect of the polyfluoroalkyl group in 1,1,2,3,3,3-hexafluoropropylcyclopentane (**25**) favours further addition of HFP to γ-position, although some addition does occur at the β-position.

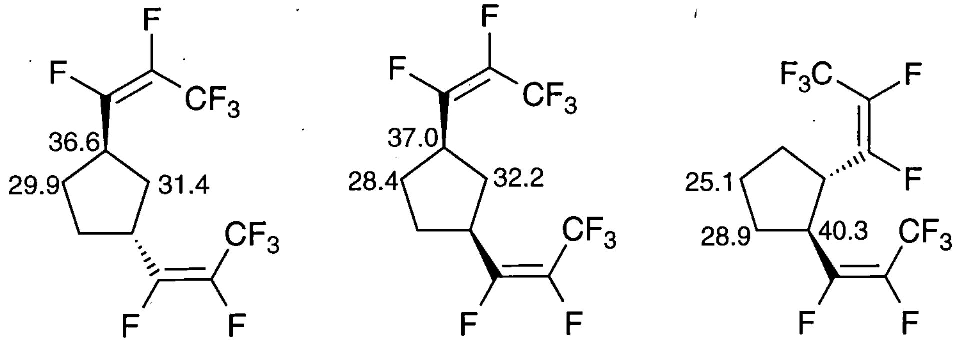


(6)

<u>Structure determination of compounds (**50a**), (**50b**) and (**50c**)</u>

<u>^{13}C NMR</u>- A broad band proton decoupled ^{13}C NMR spectrum was run on the three component mixture. The spectrum was complex at low field, with the perfluoroalkenyl resonances overlapping each other, but between 0-42 ppm the spectrum was much clearer (figure 3.). The major component was identified as *trans*-1,3-bis(Z-pentafluoroprop-2-enyl)cyclopentane (**50a**). A large singlet at 29.9 ppm was assigned to the two equivalent methylene ring carbons, the singlet at 31.4 was attributed to the other methylene ring carbon, because of the shift to higher field from the two adjacent perfluoroalkenyl groups, and a doublet ($^2J_{C\text{-}F}$ = 22 Hz) was assigned to the two equivalent methyne ring carbons attached to the perfluoroalkenyl groups. Similarly, the signals at 28.4, 32.2 and 37.0 ppm (doublet, $^2J_{C\text{-}F}$ = 22 Hz) were assigned to *cis*-1,3-bis(Z-pentafluoroprop-2-enyl)cyclopentane (**50b**). The minor component was identified as *trans*-1,2-bis(Z-pentafluoroprop-2-enyl)cyclopentane (**50c**). The doublet at lowest field (40.3 ppm, $^2J_{C\text{-}F}$ = 23 Hz) was assigned to the methyne ring carbons of the 1,2-isomer due to its increased deshielding. A singlet at 28.9 ppm was assigned to the two methylene ring carbons equivalent to each another and a small singlet (21.5 ppm) at lowest field was assigned to the other methylene ring carbon, because of its increased shielding (figure 3.14).

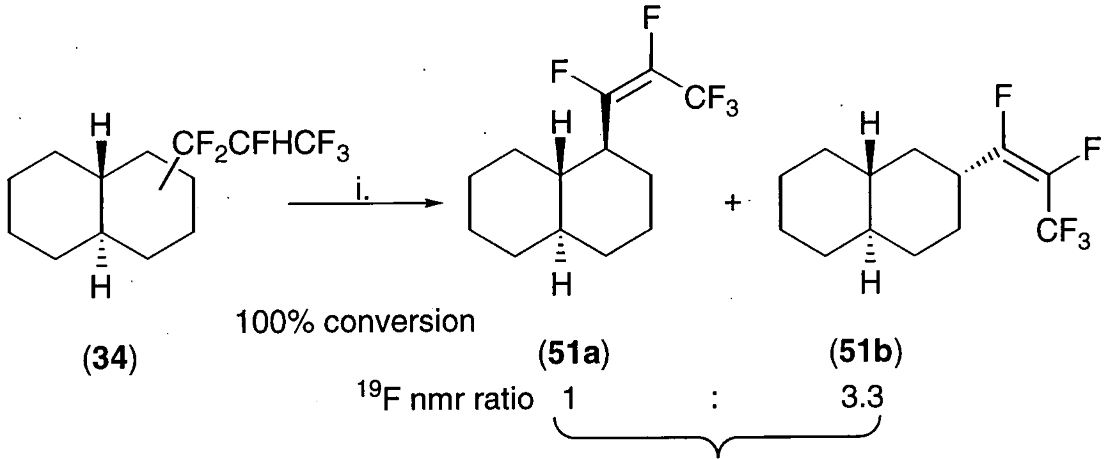
Figure 3.14 ^{13}C NMR chemical shifts (ppm) of the Cyclopentyl rings in compounds (50)



(50a) **(50b)** **(50c)**

3.38 x-(1,1,2,3,3,3-Hexafluoropropyl)*trans*-decalin x=1,2 (34)

Dehydrofluorination of the mono-adducts of *trans*-decalin (**34**) was performed at 0°C.



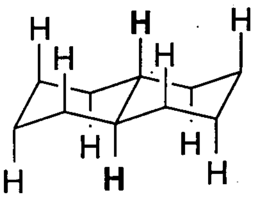
i. 1:1.5 KO^tBu, $(Et)_2O$, 0°C, 15 mins.

(**51**) 82%

A ^{19}F NMR spectrum of the reaction mixture confirmed complete conversion of the starting material, and distillation of the product mixture gave a single fraction of two components, (**51a**) and (**51b**) in a 1 : 3.3 ^{19}F NMR ratio. Further analysis of their NMR and mass spectra identified the components as 1-(Z-pentafluoroprop-2-enyl)*trans*-decalin (**51a**) and 2-(Z-pentafluoroprop-2-enyl)*trans*-decalin (**51b**) respectively .

Therefore it was established that addition of HFP occurred at the secondary carbons and not at the bridgehead position in *trans*-decalin. As in adamantane, the *trans*-decalin bridgehead has an unstrained sp^3 configuration, but in adamantane the bridgehead proton is very exposed whereas in *trans*-decalin each bridgehead proton has four 1,5-hydrogen interactions (figure 3.15).

Figure 3.15 1,5 H-interaction at the bridgeheads in *trans*-decalin



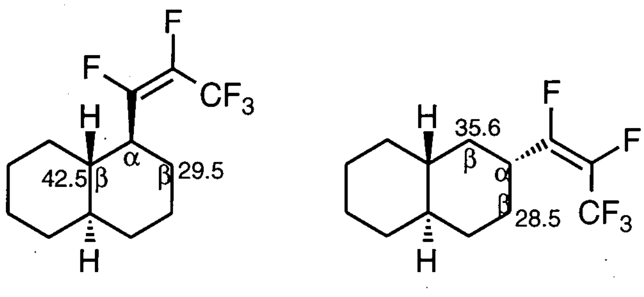
The steric effect of these hydrogens therefore inhibit the addition of HFP at the bridgehead position, whereas there are no steric barriers to addition at the equatorial positions of the methylene ring carbons. Addition preferentially occurred at the two-position rather than the one-position. This can be accounted for by the increased steric demand of the one-position.

Structure determination of compounds **(51a)** and **(51b)**

A broad band proton decoupled ^{13}C NMR experiment and a ^{13}C DEPT NMR experiment were run on the two component mixture.

^{13}C NMR - Three groups of resonances at low field corresponded to the CFH, CF_2 and CF_3 carbons of the two different pentafluoropropenyl groups. Compounds **(51a)** and **(51b)** were distinguished by the signals arising from the carbons (β) neighbouring the carbon attached to the perfluoroalkenyl group. A ^{13}C carbon DEPT spectrum of the mixture identified three doublets, with $^3J_{C\text{-}F}$ coupling constants of *ca.* 3 Hz, as methylene carbons. The two large doublets at 35.6 ppm and 28.5 ppm were assigned to the CH_2 groups β- to the fluoroalkenyl group in compound **(51b)**. The doublet at higher field was assigned to the CH_2 carbon neighbouring the bridgehead, due to the increased deshielding from it. A much smaller doublet at 29.5 ppm was assigned to the CH_2 group β- to the fluoroalkenyl group in compound **(51a)**, and a small, broad CH signal, at 42.5 ppm, was assigned to the bridgehead carbon β- to the fluoroalkenyl group in compound **(51a)** (figure 3.16).

Figure 3.16 ^{13}C NMR chemical shifts (ppm) of the carbons β- to the fluoroalkenyl groups in compounds (**51a**) & (**51b**)



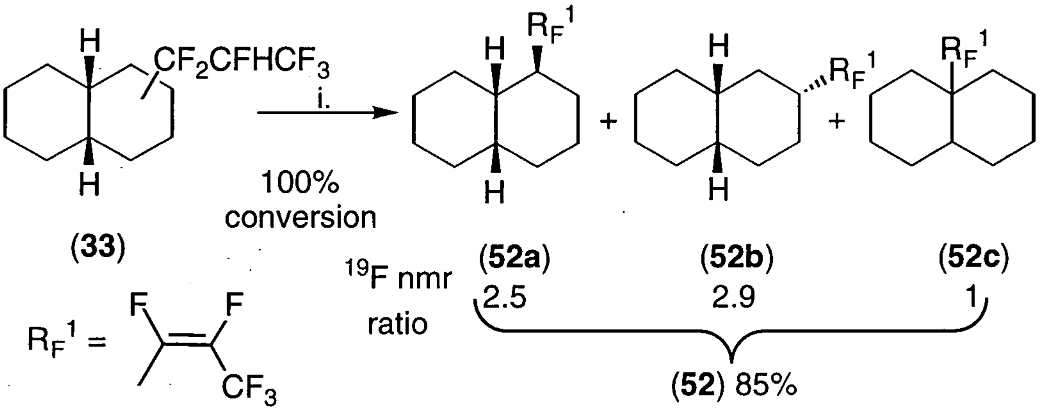
(51a) **(51b)**

The other signals in the ^{13}C NMR spectrum were tentatively assigned, by comparing chemical shifts with data from methyl-substituted *trans*-decalin[109] and Z-pentafluoroprop-2-enylcyclohexane (**43a**).

^{1}H NMR - Two sets of doublets ($^{3}J_{H\text{-}F}$ = 32 Hz) of triplets ($^{3}J_{H\text{-}H}$ = 12 Hz), at 2.24 and 2.58 ppm, in a 1 : 3.3 proton NMR ratio confirmed that the pentafluoropropenyl groups of both (**51a**) and (**51b**) are equatorial. The rest of the proton spectrum was assigned using a ^{13}C/ ^{1}H HETCOR NMR experiment.

3.39 x-(1,1,2,3,3,3-Hexafluoropropyl)*cis*-decalin x=1,2,9 (33)

Dehydrofluorination of the mono-adducts of *cis*-decalin (**33**) gave only the Z-alkenes (**52**), using potassium t-butoxide.

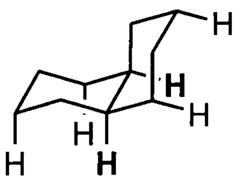


i. 1:2 $KO^{t}Bu$, $(Et)_2O$, -10°C, 15 mins.

Distillation of the product mixture gave a fraction containing three components which could not be separated. Analysis of the fraction, using GLC/MS and NMR, identified the three products as 1-(Z-pentafluoroprop-2-enyl)*cis*-decalin (**52a**), 2-(Z-pentafluoroprop-2-enyl)*cis*-decalin (**52b**) and 9-(Z-pentafluoroprop-2-enyl)decalin (**52c**).

In *cis*-decalin, some addition of the fluoroalkyl group did occur at the bridgehead position, in contrast to *trans*-decalin. This can be rationalised as the bridgehead site in *cis*-decalin has fewer 1,5 Hydrogen interactions (figure 3.17) than the corresponding site in *trans*-decalin.

Figure 3.17. 1,5 Hydrogen interactions at the bridgehead in *Cis*-decalin.



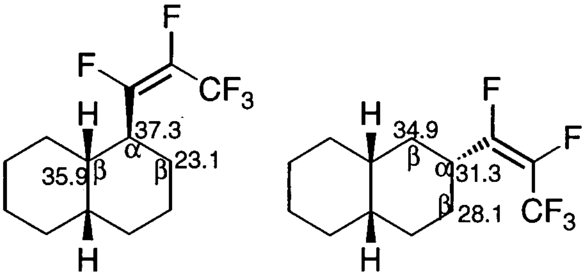
Again the two-position is attacked in preference to the one-position and this can be accounted for by the increased 1,5 hydrogen interactions at the one-position.

Structure determination of compounds (**52a**), (**52b**) and (**52c**)

The ^{19}F NMR spectrum of the three component mixture identified three sets of *cis*-fluorines in the ratio 2.5 : 2.9 : 1. The three products all had M^+ peaks at 268 in their EI^+ mass spectra as alkenes by GLC/MS which identified .

^{13}C NMR - The broad band proton decoupled spectrum was complex and so a ^{13}C DEPT spectrum was also run on the mixture to identify the methyne carbons. Three doublets with $^2J_{C\text{-}F}$ coupling constants *ca.* 20 Hz were assigned as the carbons attached to the perfluoroalkenyl groups. The two larger doublets, at 37.3 and 31.3 ppm, were identified as methyne carbons by the ^{13}C DEPT spectrum and the smaller doublet, at 34.0 ppm, was assigned to the quaternary carbon of 9-(Z-pentafluoroprop-2-enyl)decalin (**52c**). Again the two major components, 1-(Z-pentafluoroprop-2-enyl)*cis*-decalin (**52a**) and 2-(Z-pentafluoroprop-2-enyl)*cis*-decalin (**52b**), were distinguished by their carbons β- to their fluoroalkenyl groups (figure 3.20). Three doublets with $^3J_{C\text{-}F}$ coupling constants *ca.* 3 Hz were observed. The doublets at 28.1 and 34.1 ppm were assigned to the compound (**52b**), with the doublet at lower field assigned to the carbon neighbouring the bridgehead, because of the deshielding effect of the bridgehead. The doublet at 23.1 ppm was assigned to CH_2 group β- to the fluoroalkenyl group in compound (**52a**) (figure 3.18).

Figure 3.18 ^{13}C NMR chemical shifts (ppm) of the carbons α– and β- to the fluoroalkenyl groups in compounds (52a) and (52b)



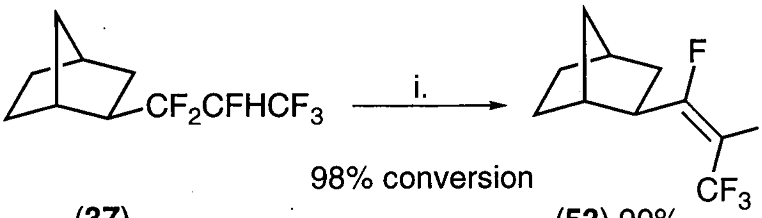
(52a) **(52b)**

Two sets of bridgehead carbons, at 35.9 & 35.7 ppm and 35.3 and 35.2 ppm, were also identified by the ^{13}C DEPT spectrum. The smaller set ,at higher field, was assigned to compound (**52a**) because of the increased deshielding of the perfluoroalkenyl group and the larger set was assigned to compound (**52b**). The rest of the carbon spectrum was assigned tentatively using data on corresponding methyl-substituted *cis*-decalins[109].

^1H NMR - Two doublets of triplets at 2.56 and 2.71 ppm of similar size confirmed that addition of the fluoroalkyl group occurred at the equatorial positions, in the two major components.

3.40 1,1,2,3,3,3-Hexafluoropropylnorbornane (37)

Dehydrofluorination of compound (**37**) was achieved easily using t-butoxide as the base.



98% conversion

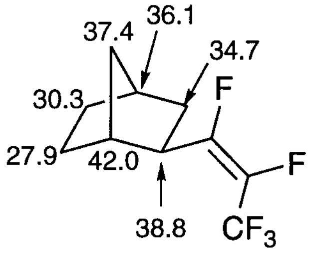
(37) **(53)** 90%

i. 1:2 KO^tBu, $(^iPr)_2O$, 0°C, 20 mins.

A ^{19}F NMR spectrum of the reaction mixture confirmed a 98% conversion of the starting material. Distillation of the reaction mixture gave a pure sample of *exo*-2-(Z-pentafluoroprop-2-enyl)norbornane (**53**) identified by its NMR and mass spectra.

A broad band proton decoupled ^{13}C NMR spectrum was run on compound (**53**) as a model for the higher adducts of norbornane. The removal of the chiral CFH group eliminated the possibility of diastereomers and therefore simplified the ^{13}C NMR spectrum considerably. The Z-pentafluoropropenyl group was identified as three signals at low field. A further seven resonances were observed in the 0-45 ppm region. A ^{13}C DEPT NMR spectrum identified three of these resonances at methyne carbons, a doublet ($^3J_{C\text{-}F}$ = 3.1 Hz), at 42.0 ppm, was assigned as the bridgehead carbon closest to the perfluoroalkenyl group and a singlet, at 36.1 ppm, was assigned to the other bridgehead. The final methyne resonance, a doublet ($^2J_{C\text{-}F}$ = 20 Hz) at 38.8 ppm, was attributed to the carbon attached to the perfluoroalkenyl group. The methylene resonances were assigned by comparison with data from other substituted norbornanes[101] (figure 3.19).

Figure 3.19 ^{13}C NMR chemical shifts (ppm) of the norbornyl group of compound (53)

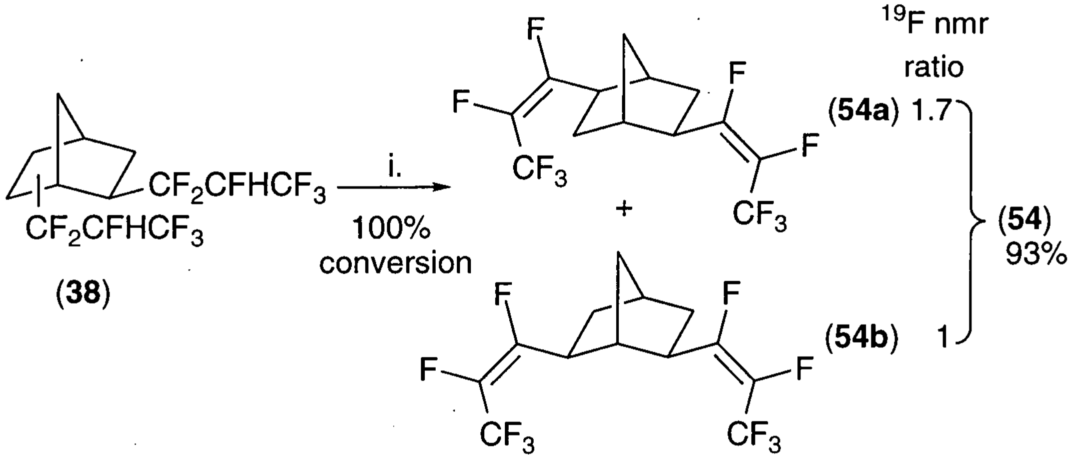


(**53**)

A ^{13}C/^{1}H HETCOR NMR spectrum of compound (**53**) was used to assign its complex proton spectrum and a ^{1}H/^{1}H COSY NMR spectrum was used to identify any proton-proton coupling.

3.41 *exo*-2,x-Bis(1,1,2,3,3,3-hexafluoropropyl)norbornane x=5,6 (**38**)

Dehydrofluorination of the norbornane di-adduct mixture (**38**) also proceeded successfully.



i. 1:3.3 KO^{t}Bu, (^{i}Pr)$_2$O, 0°C, 20 mins.

Distillation of the reaction mixture gave a fraction containing two components, which were inseparable. NMR and mass spectra, of the fraction identified the two components as *exo*-2,5-bis(Z-pentafluoroprop-2-enyl)norbornane (**54a**) and *exo*-2,6-bis(Z-pentafluoroprop-2-enyl)norbornane (**54b**) in a 1.7 to 1 ratio.

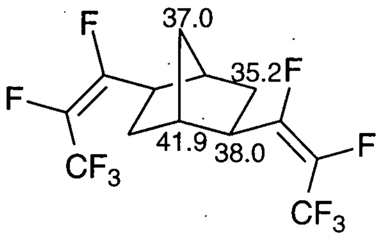
It is unsurprising that the major product was compound (**54a**) as the two fluoroalkenyl groups are in positions, such that steric crowding and electronic effects are minimised in the molecule.

Structure determination of compounds (**54a**) and (**54b**)

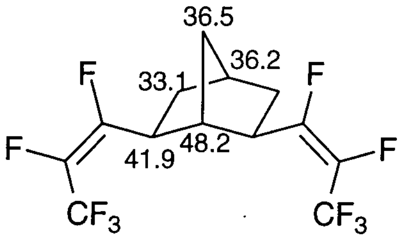
Compounds (**54a**) and (**54b**) were identified as the dehydrofluorinated products by their M$^+$ peaks, at 356, in their EI$^+$ mass spectra.

^{19}F NMR - Two sets of *cis*-fluorine signals, in a ratio of 1.7 : 1, suggested that each diene contained equivalent Z-pentafluoropropenyl groups and therefore addition had only occurred at the *exo*-positions of the methylene groups in norbornane.

^{13}C NMR - Three groups of signals at low field confirmed the presence of two perfluoroalkenyl groups. Nine resonances were observed in the 0-50 ppm region and a ^{13}C DEPT NMR spectrum identified five of them as methyne carbons. Of these, two doublets at 38.0 ($^2J_{C-F}$ = 21 Hz) and 39.9 ppm ($^2J_{C-F}$ = 20 Hz) were assigned as the carbons attached to the perfluoroalkenyl groups and the remaining three as bridgehead carbons. A large doublet ($^2J_{C-F}$ = 2.6 Hz) at 41.9 ppm was assigned as the bridgehead carbon in *exo*-2,5-di-ene (**54a**), because of its similar chemical shift to the analogous bridgehead of the mono-ene (**53**). Singlets at 48.2 and 36.2 ppm were assigned as bridgehead carbons of *exo*-2,6-di-ene (**54b**). The lower field singlet was attributed to the bridgehead carbon between the two perfluoroalkenyl groups, because of the large deshielding from them and the higher field singlet was assigned to the other bridgehead carbon.



(54a)

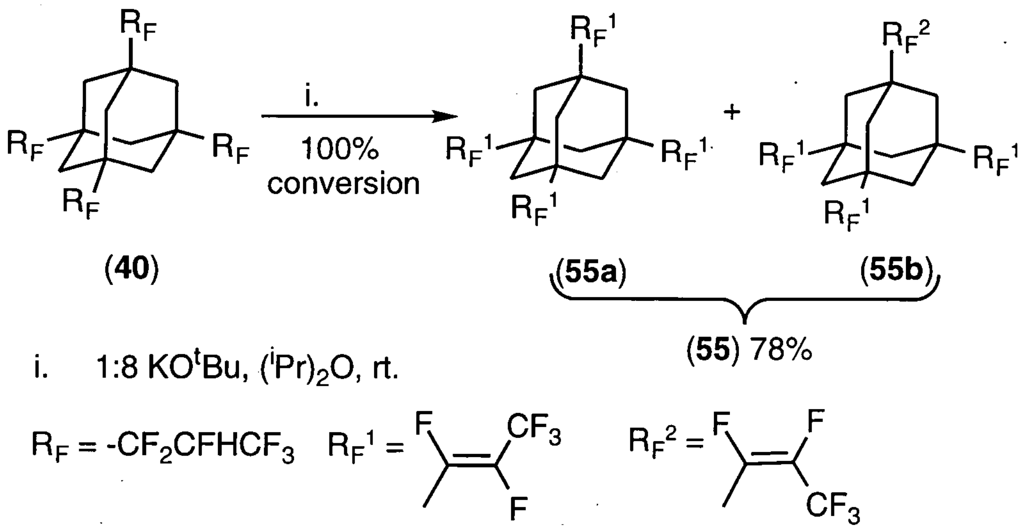


(54b)

The relative sizes of the carbon resonances indicate that the major component of the mixture was *exo*-2,5-bis(Z-pentafluoroprop-2-enyl)norbornane (**54a**).

3.42 1,3,5,7-Tetrakis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**40**)

An eight fold excess of potassium t-butoxide was used to dehydrofluorinate the tetra-adduct (**40**).



Complete conversion of the tetra-adduct was achieved in a very exothermic reaction. Distillation of the product mixture, using a Kugelrohr apparatus under reduced pressure, gave a fraction containing two components, (**55a**) and (**55b**) in a 2 : 1 ratio. The fraction was dissolved in chloroform and cooled (approx. -50°C), at which point, a white solid (**55a**) precipitated out.

The incorporation of an Z-pentafluoropropenyl group into (**55b**) can simply be attributed to statistical probability.

Structure determination of (**55a**) and (**55b**)

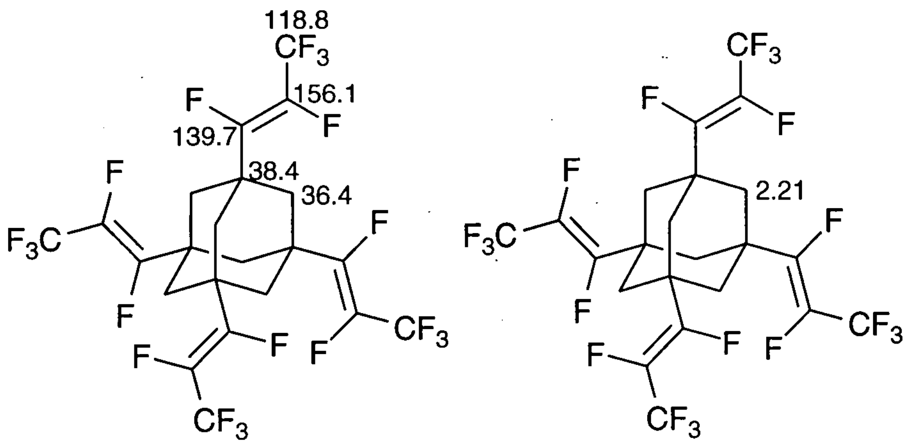
A GLC/MS of the two component mixture identified, M^+ peaks at 656 in both EI^+ mass spectra, indicating that both were isomers of the tetra-ene (**55**).

^{19}F, ^{13}C and ^1H NMR spectra were run on a solution of the white solid, identifying it as 1,3,5,7-tetrakis(E-pentafluoroprop-2-enyl)adamantane (**55a**).

^{19}F NMR - Only three signals were observed in the ^{19}F NMR spectrum indicating the high symmetry of the molecule. The two vinylic fluorines were observed as doublets at -149.7 and -170.3 ppm with coupling constants of 134 & 135 Hz respectively confirming their *trans* -relationship. The trifluoromethyl group was observed as a broad singlet at -67.6 ppm.

^{13}C NMR - Only five signals were observed in the carbon spectrum which is summarised in figure 3.25. Two resonances were observed at high field, a singlet at 36.4 ppm, assigned to the methylene carbons, and a doublet ($^2J_{C\text{-}F}$ = 21 Hz) at 38.4 ppm attributed to the quaternary carbons (figure 3.20).

Figure 3.20 ^{13}C and ^1H NMR chemical shifts (ppm)of compound (**55a**)



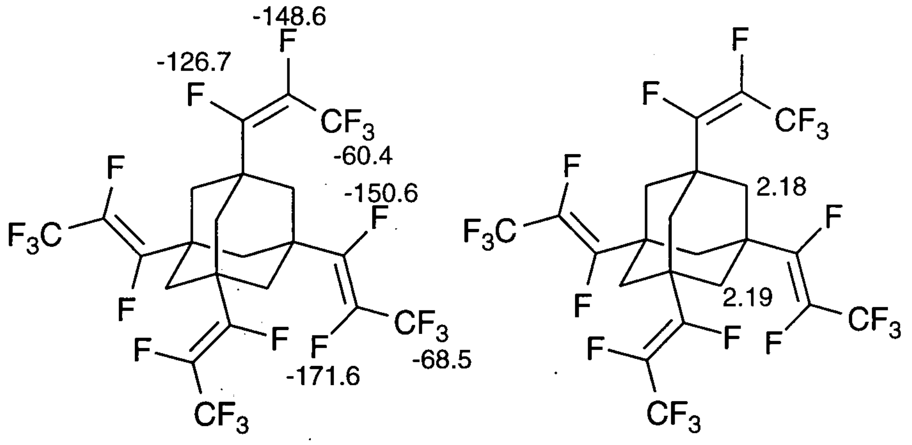
^{1}H NMR - Only one resonance was observed in the proton spectrum, at 2.21 ppm which corresponds to the six equivalent methylene groups.

The minor isomer was identified as 1-(E-pentafluoroprop-2-enyl)-3,5,7-tris(Z-pentafluoroprop-2-enyl)adamantane (**55b**) by its ^{19}F and ^{1}H NMR spectra.

^{19}F NMR - Two CF_3 resonances were observed, at -60.4 and -68.5 in a 1 : 3 ratio, and were assigned to the Z- and E-perfluoroalkenyl groups respectively. Four vinylic resonances were identified. Two broad singlets at -126.7 and -148.6 ppm were assigned to the two *cis*-fluorines and two doublets ($^3J_{F\text{-}F}$ = 135 Hz) at -150.6 and -171.6 were assigned to the six *trans*-fluorines (figure 3.21).

^{1}H NMR - Two singlets were observed in the proton spectrum at 2.19 and 2.18 and were assigned to the two sets of methylene groups.

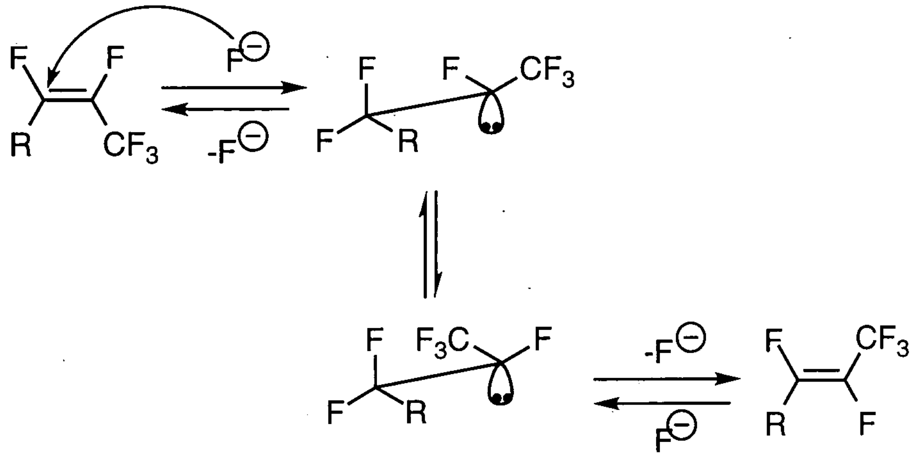
Figure 3.21 ^{19}F and ^{1}H NMR chemical shifts (ppm) of compound (**55b**)



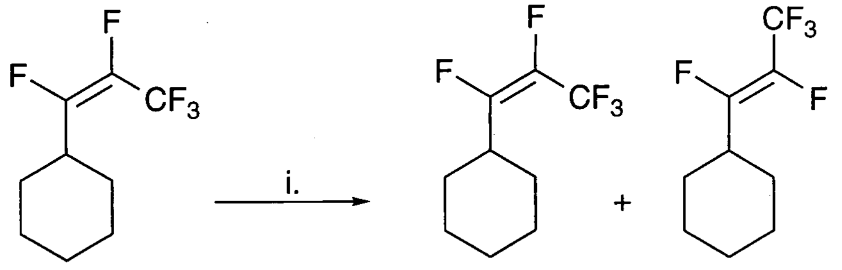
3.5 Kinetic v's Thermodynamic Control

It was thought that, in all the hydrocarbon systems, the E-isomer would have been the more thermodynamically stable alkene, because of the steric interactions between the alkyl and the trifluoromethyl groups. This seemed to be the case in the adamantyl system, but the reactions involving the cyclohexyl system were not so conclusive. Fluoride ion induced double bond isomerisations (scheme 3.4), were performed at high temperature, to give more conclusive evidence of which stereoisomer was the more thermodynamically stable.

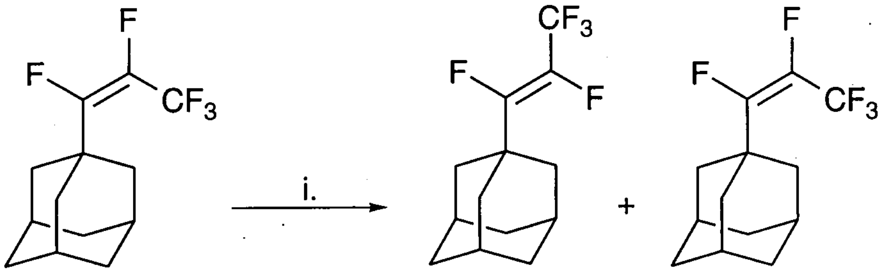
Scheme 3.4 Mechanism of Fluoride ion induced double bond isomerisation



Caesium fluoride isomerisations were performed on compounds (**43a**) and (**45a**).



(**43a**) (**43a**) 49% (**43b**) 37%



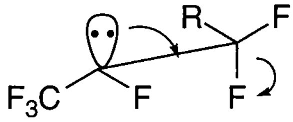
(**45a**) (**45b**) 97% (**45a**) Trace

i. 1: 5 CsF,Tetraglyme, 200°C, 50 hrs.

In the adamantyl system, the Z-alkene (**45a**) was almost completely converted into the E-alkene (**45b**). This established that the E-alkene (**45b**) was thermodynamically more stable. In the cyclohexyl system, the Z-alkene (**43a**) remained the major component in the reaction mixture, even after fifty hours of CsF isomerisation at 200°C. This suggest that the isomerisation process had reached an equilibrium and that the E-alkene (**43b**) and Z-alkene (**43a**) have similar thermodynamic stabilities.

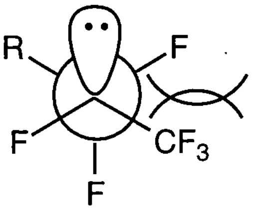
For both systems, the Z-alkenes (**45a**) and (**43a**) were the products favoured by kinetic control. The rate determining step of the E1cB mechanism is loss of fluoride ion from the intermediate anion (Figure 3.22).

Figure 3.22 Rate determining step of E1cB mechanism



The intermediate anion has an sp^3 configuration and is able to take up either the *gauche* or *trans* conformation, consequently the *gauche* conformation of the anion is more stable. This result is surprising given the steric size of the alkyl and trifluoromethyl groups which may have been expected to favour the *trans* conformation. Preference of the *gauche* conformation may be accounted for by the '*gauche* effect' as seen in 1,2-difluoroethane[110,111]. It has been argued that this is due to fluorine-fluorine lone pair attraction[112], whereas others say it is the *trans* conformer which is conjugatively destabilised rather than stabilisation of the *gauche* conformer[113]. Another possibility is that there is a destabilising interaction between the trifluoromethyl fluorines and difluoromethylene fluorines (figure 3.23) which competes successfully with the steric interactions of the alkyl and trifluoromethyl groups.

Figure 3.23 *Gauche* conformer of the intermediate anion



3.6 Conclusions

Dehydrofluorination of the hexafluoropropyl side chain is a convenient route to a novel set of mono-, di- and poly-enes which opens up a new area of chemistry, for example, they could be used as monomers. The tetra-ene (**40**) has possibilities as a monomer in a dendritic polymer because of its tetrahedral shape.

Not only can dehydrofluorination be performed easily, but by reducing the temperature of the t-butoxide system only the Z-isomer of many of the alkenes has been produced. This has not only simplified the product mixtures, which is useful synthetically, but also allowed fuller characterisation of many of the HFP di-adducts.

Better characterisation of the di-adducts allowed a fuller discussion of the factors affecting the incorporation of more than one hexafluoropropyl group. It was concluded that polar and steric effects both contributed to the site of addition in a mono-adduct, although these factors attenuated quickly as the site of addition became more remote from the initial hexafluoropropyl group.

Chapter Four

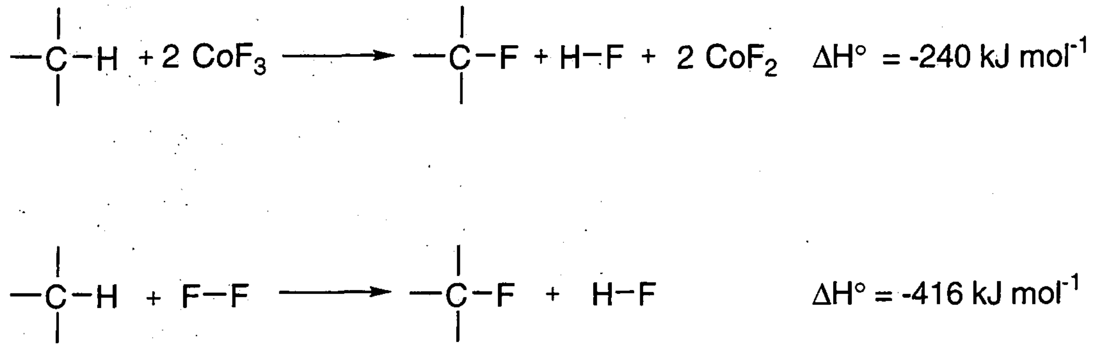
High Valency Metal Fluoride Fluorinations

4.1 Introduction

In the late 19th century it was observed that CeF_4 and PbF_4, evolved fluorine on heating[114]. These observations lead to investigations into using high valency metal fluorides as fluorinating agents in organic chemistry. Various high valency metal fluorides, such as silver difluoride and manganese trifluoride, were investigated, but in general cobalt trifluoride was easy to use, regenerate and provided the best results[115].

Fluorinations using cobalt trifluoride were found to produce less fragmentation than when using direct fluorination, which was attributed to the lower heat of reaction of cobalt trifluoride[116], which is approximately half that of direct fluorination[117] (figure 4.1).

Figure 4.1



$$-\overset{|}{\underset{|}{C}}-H + 2\,CoF_3 \longrightarrow -\overset{|}{\underset{|}{C}}-F + H-F + 2\,CoF_2 \quad \Delta H^\circ = -240\ \mathrm{kJ\,mol^{-1}}$$

$$-\overset{|}{\underset{|}{C}}-H + F-F \longrightarrow -\overset{|}{\underset{|}{C}}-F + H-F \quad \Delta H^\circ = -416\ \mathrm{kJ\,mol^{-1}}$$

In general, a large excess of cobalt trifluoride should be present so that only 25-30% is consumed during the reaction, otherwise the yields of perfluorinated products usually falls[116]. Fluorination of a substrate becomes more difficult as the number of fluorines atoms, in the substrate, increases. The technique is flexible, in that it is possible to control the extent of the reaction by altering the reaction temperature or the input rate of the organic substrate. The level of fluorination can be varied depending on the reaction temperature, but generally the technique is used to attain perfluorination.

Cobalt trifluoride fluorination involves two main stages. Initially cobalt difluoride undergoes oxidative fluorination to cobalt trifluoride, which is achieved by passing fluorine over a cobalt fluoride bed at 250-300°C. When the cobalt trifluoride, in the reactor, has been fully regenerated then the organic substrate is passed over the cobalt trifluoride bed to produce perfluorinated material, cobalt difluoride and hydrogen fluoride (scheme 4.2).

Scheme 4.2

i) Regeneration

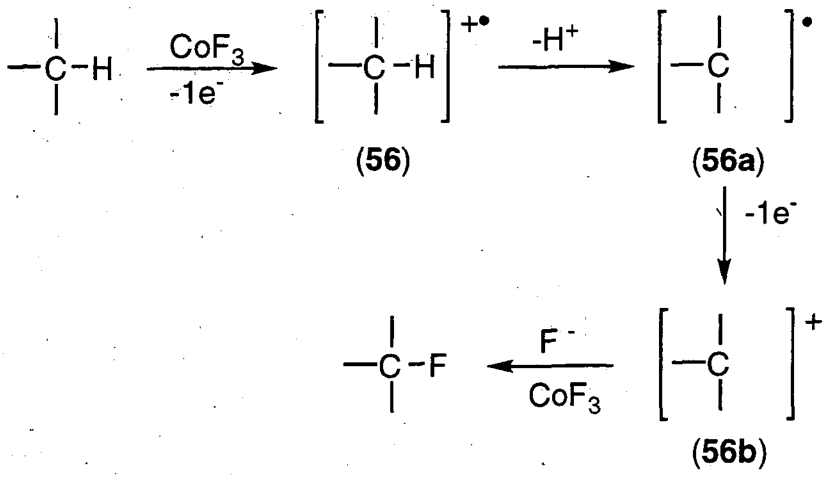
$$2CoF_2 + F_2 \longrightarrow 2CoF_3$$

ii) Fluorination

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

Cobalt trifluoride fluorination is thought to proceed via a radical-cation mechanism[1,118]. Initially the substrate is oxidised to a radical cation (**56**), followed by loss of a proton to form the corresponding radical (**56a**). The radical is then further oxidised to form a cation (**56b**), which then undergoes fluoride ion addition (scheme 4.3).

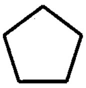
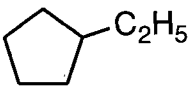
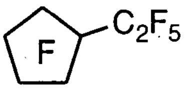
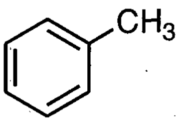
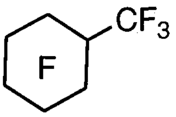
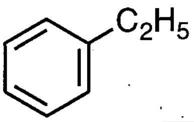
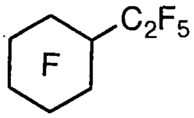
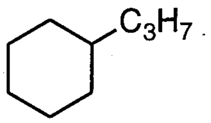
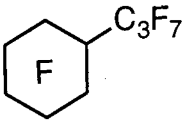
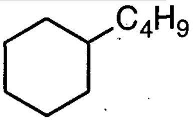
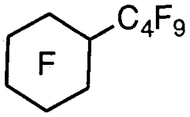
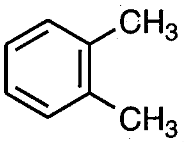
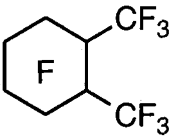
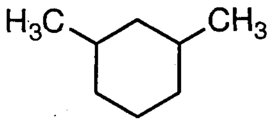
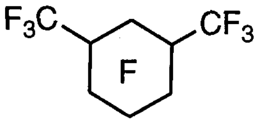
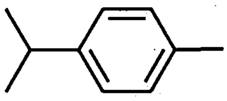
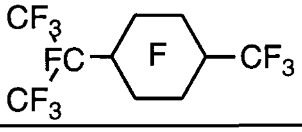
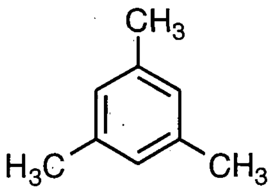
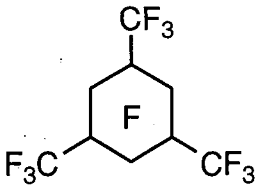
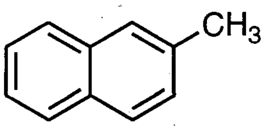
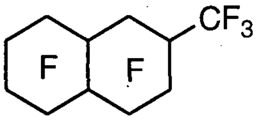
Scheme 4.3



Cobalt trifluoride fluorination of Hydrocarbons

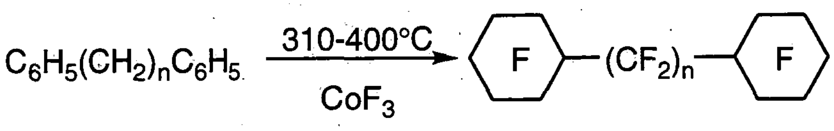
In the late 1940's much interest was generated in perfluorination of hydrocarbons, using cobalt trifluoride, as perfluorocarbons were found to be unaffected by uranium hexafluoride. A series of n-alkanes (C_4-C_{11}) and cyclic hydrocarbons (table 4.1) were successfully perfluorinated[119-124].

Table 4.1 Cobalt Trifluoride Fluorination of Cyclic Hydrocarbons

Hydrocarbon	Reaction Temperature	Major Product	Yield	Ref.
			28%	[119]
			38%	[119]
	300°C		45% (crude)	[121]
	350°C		23%	[121]
	380°C		40% (crude)	[121]
	350°C,		42% (crude)	[121]
	250°C and 350°C		25% (crude)	[121]
	350°C		17%	[121]
	350°C		42% (crude)	[121]
	350°C		21%	[121]
	250-380°C		38% (crude)	[121]

The early reactors were superceded by a horizontal reactor containing cobalt trifluoride in a nickel tube with a central rotating shaft with paddles attached, so as to agitate the cobalt trifluoride and improve the contact with the organic vapour[116] and a series of perfluorodicyclohexyl compounds were produced using this method (scheme 4.4).

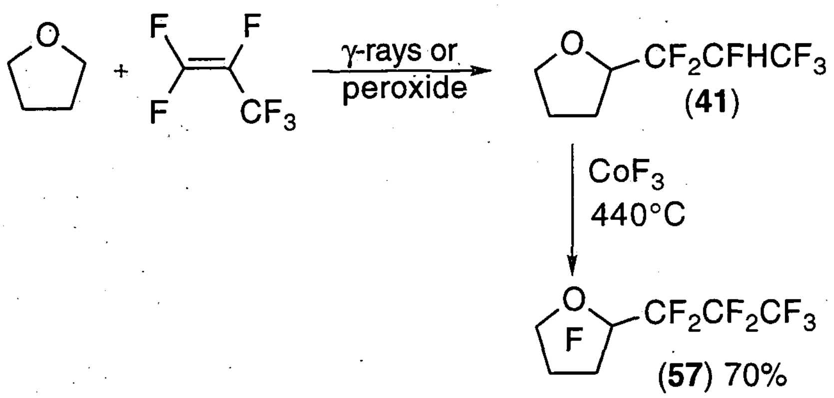
Scheme 4.4



Yield of perfluorocarbon
n = 0, 59%　n = 4, 28%
n = 1, 45%　n = 5, 24%
n = 2, 66%　n = 6, 8%
n = 3, 33%　n = 10, 2%

Polyfluorination[125,126] can also be achieved, usually to give compounds containing one or two remaining hydrogens, but the product mixtures tend to be complex as at high temperatures the fluorination process shows little selectivity. However monofluorination of some hydrofluorocarbons has been accomplished recently[127,128].

Although cobalt trifluoride was generally recognised as the best high valency metal fluoride fluorinating agent, the reactions with hydrocarbons show that the perfluorinated products are produced in moderate yields due to degradation of the substrate. More recently this has been combated, in ethers, by the introduction of a polyfluoroalkyl group into the substrate prior to perfluorination[129].



(**41**)

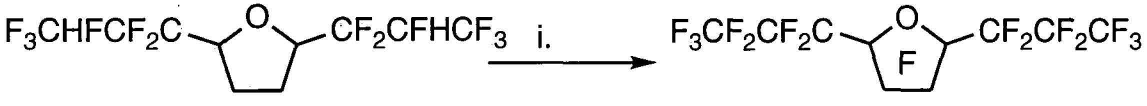
(**57**) 70%

This resulted in much improved yields over perfluorination of the parent ethers[130].

4.2 Cobalt Trifluoride Fluorinations

4.21 2,5-Bis(1,1,1,2,3,3-hexafluoropropyl)tetrahydrofuran (58)

In the present work, a sample of 2,5-bis(1,1,1,2,3,3-hexafluoropropyl)tetrahydrofuran (**58**), which had been previously prepared in this laboratory[75], was passed through the cobalt trifluoride reactor at 400°C, the maximum temperature of the reactor.



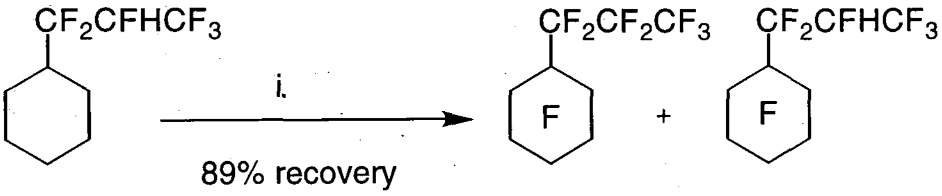
(**58**) (**59**) 80%

i. CoF_3, 400°C, N_2 30 ml min^{-1}
* recovery (%) calculated, based on (**59**)

A GLC/MS, ^{19}F NMR and $^{19}F/^{19}F$ COSY NMR of the product mixture identified the major products as *cis-* and *trans*-perfluoro-2,5-dipropyltetrahydrofuran (**59**), whose data agreed with the literature[75], and also the presence of various polyfluorinated products. The polyfluorinated products were removed from the product mixture by continuous extraction with acetone, but the *cis-* and *trans-* isomers of (**59**) could not be separated. Even at 400°C, there was very little decomposition during the reaction. This can be attributed to the presence of the two polyfluoroalkyl groups in the starting material (**58**) which significantly stabilised the ether to cobalt trifluoride fluorination.

4.22 1,1,2,3,3,3-Hexafluoropropylcyclohexane (24)

The cobalt trifluoride fluorination of 1,1,2,3,3,3-hexafluoropropylcyclohexane (**24**) was conducted at 375°C.



(**24**) (**60**) 63% (**60a**) 17%

i. CoF_3, 375°C, N_2 30 ml min^{-1} + $C_9F_{16}H_2$ 20%
* recovery (%) calculated, based on (**60**)

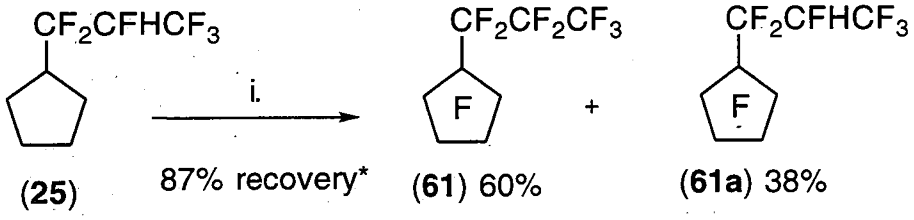
GLC/MS and ^{19}F NMR analysis of the product mixture identified the major product as perfluoropropylcyclohexane (**60**) and the major polyfluorinated product was identified as 2H-perfluoropropylcyclohexane (**60a**). Again the polyfluorinated products were removed by continuous extraction with acetone. A trace amount of perfluorocyclohexane was identified as the only decomposition product and was separated from (**60**) by preparative scale GLC.

Again very little decomposition occurred during the reaction because of the fluoroalkyl group, in fact, the hydrogen in the hexafluoropropyl side chain of (**24**) was the most difficult to fluorinate, presumably because of the electron withdrawing properties of the neighbouring trifluoromethyl and difluoromethylene groups deactivating the site.

The ^{19}F NMR spectrum of the purified perfluoropropylcyclohexane (**60**) agreed with the data published by Lin and Lagow[131] who produced compound (**60**) in moderate yield on a small scale by direct fluorination at -130°C. GLC/MS identified the polyfluorinated products as containing one or two remaining hydrogens (M^+-F peaks at 413 & 395) and 2H-perfluoropropylcyclohexane (**60a**) was identified by its M^+-F peak at 413 and base peak at 151, corresponding to the $^+CF_2CFHCF_3$ fragment..

4.23 1,1,2,3,3,3-Hexafluoropropylcyclopentane (25)

Cobalt trifluoride fluorination of 1,1,2,3,3,3-hexafluoropropylcyclopentane (**25**) was conducted at 375°C.



+ $C_8F_{15}H$, 2%

i. CoF_3 375°C, N_2 30ml/min

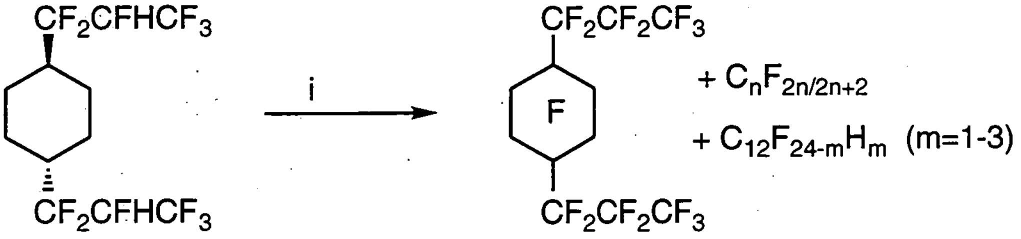
* recovery (%) calculated based on (**61**)

GLC/MS analysis of the product mixture identified the two major products as perfluoropropylcyclopentane (**61**) and 2H-perfluoropropylcyclopentane (**61a**), which were separated by continuous extraction with acetone. The perfluorocarbon mixture contained a small trace of perfluorocyclopentane, but this was removed from (**61**) by preparative scale GLC.

A ^{19}F NMR spectrum of perfluoropropylcyclopentane (**61**) identified three singlets at -81.2, -116.1, and -125.1 ppm, which were assigned to the CF_3 group, the neighbouring CF_2 group and the remaining CF_2 group of the perfluoropropyl side chain respectively. Another smaller singlet was detected at -185.2 ppm and was assigned to the tertiary CF group in the cyclopentane ring. The remaining signals were observed as two AB systems at -123.0 & -128.3 ppm ($^2J_{F\text{-}F}$ =270) and -129.0 & -132.5 ($^2J_{F\text{-}F}$ =259) which were assigned to the two CF_2 groups in the cyclopentane ring. In each AB system, the signals at lower field were assigned to the axial fluorines, as these are expected to be more deshielded than the equatorial fluorines. The EI^+ mass spectrum of (**61**) contained a M^+-F peak at 381 and a base peak at 69, corresponding to the CF_3 fragment. Compound (**61a**) was identified by its EI^+ mass spectrum which contained a M^+-F peak at 363 and a base peak at 151, corresponding to the $^+CF_2CFHCF_3$ fragment.

4.24 *trans*-1,4-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (**27a**)

The cobalt trifluoride fluorination of *trans*-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (**27a**) was conducted at various temperatures to try to identify the optimum temperature of the reaction. The crystalline solid was heated so that it liquefied before entering the reactor.



(**27a**) (**62**)

i. CoF_3, 300-400°C, N_2 30ml/min

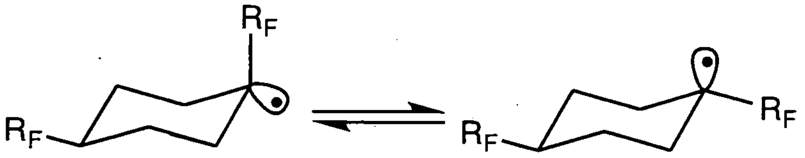
		% Composition of products by GLC/MS			
	Recovery*	$C_nF_{2n/2n+2}$ n<12	$C_{12}F_{24}$ (M^+-19, 581)	$C_{12}F_{23}H$ (M^+-19, 563)	$C_{12}F_{22}H_2$ (M^+-19, 545)
400°C	77%	23.3	64.5	8.8	3.4
350°C	68%	9.8	78.1	10.6	1.5

*calculated, based on (**62**)

The major products in both reactions were identified as the *cis*- and *trans*-isomers of perfluoro-1,4-dipropylcyclohexane (**62**). A GLC/MS analysis of the product mixture from the reaction at 400°C identified a surprisingly large amount of perfluorinated decomposition products, the major component of which was identified as perfluoropropylcyclohexane (**60**) (M^+-19, 431). Lowering the reaction temperature, to 350°C, reduced the proportion of decomposition products, without increasing the proportion of polyfluorinated products. A pure sample of perfluoro-1,4-dipropylcyclohexane (**62**) was obtained by continuous extraction of the product mixture, with acetone, followed by preparative scale GLC. Chlorotrifluoromethane was then added to compound (**62**) and the solution was cooled to -15°C, at which point *trans*-perfluoro-1,4-dipropylcyclohexane (**62a**) crystallised out of the solution.

Both the *cis*- and *trans*-isomers of perfluoro-1,4-dipropylcyclohexane (**62**) were produced from only the *trans*-isomer of the substrate. This is consistent with the proposed oxidative radical mechanism, as the tertiary radical produced can rapidly interconvert (figure 4.3) to give both *cis*- and *trans*-isomers.

Figure 4.3

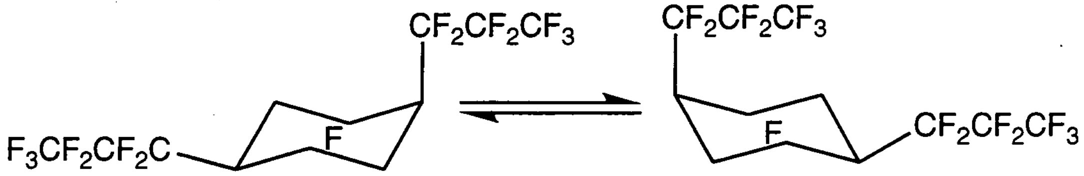


Structure determination of *cis*- and *trans*-perfluoro-1,4-dipropylcyclohexane (39)

The EI^+ mass spectra of the *cis*- and *trans*- isomers of perfluoro-1,4-dipropylcyclohexane (**62**) identified M^+-F peaks at 581. A ^{19}F NMR spectrum of a solution of *trans*-perfluoro-1,4-dipropylcyclohexane (**62a**) identified three singlets at

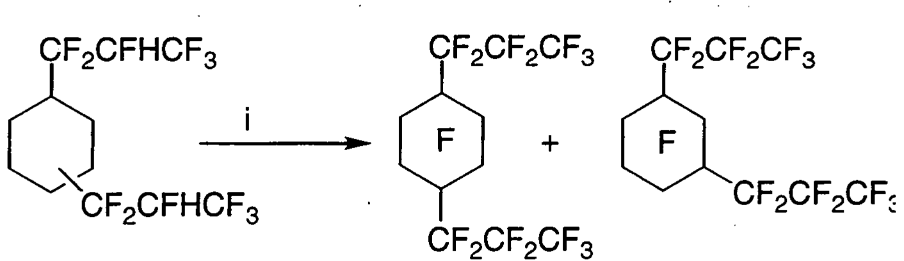
-81.2, -119.4 and -126.1 ppm, in a 3 : 2 : 2 ratio, which were assigned to the perfluoropropyl group. A large AB system at -117.7 & -126.7 ppm was assigned to the four equivalent difluoromethylene groups of the cyclohexane ring and a singlet at -186.7 ppm was assigned as the axial fluorine in the fluoromethyne group due to its similar chemical shift as the corresponding fluorine in perfluoropropylcyclohexane (**60**). *cis*-Perfluoro-1,4-dipropylcyclohexane (**62b**) was identified from the ^{19}F NMR spectrum of mixture of *cis*- and *trans*- isomers of (**62**). The perfluoropropyl fluorines were observed as three singlets at -81.0, -113.4 and -124.8 ppm respectively. The singlet at -119.4 was assigned to all the ring fluorines and the singlet at -183.0 ppm was assigned to the fluoromethyne group. The equivalence of both perfluoropropyl groups and the difluoromethylene groups of the cyclohexane ring were explained by rapid interconversion of the cyclohexane chair conformation (figure 4.2).

Figure 4.2



4.25 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane x=3,4 (27)

Cobalt trifluoride fluorination of compound (**27**) was conducted at both 375°C and 400°C, at both temperatures the major group of products were isomers of perfluorodipropylcylohexane (**62**) and (**63**).



(27) **(62)** **(63)**

i. CoF_3, 300-400°C, N_2 30ml/min

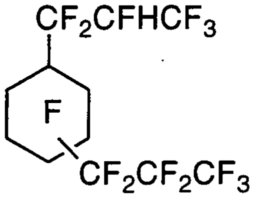
+ $C_nF_{2n/2n+2}$ (n<12)

+ $C_{12}F_{24-m}H_m$ (m=1,2)

Temp	Recovery*	% Composition of products by GLC/MS			
		$C_nF_{2n/2n+2}$ n<12	$C_{12}F_{24}$ (M^+-19, 581)	$C_{12}F_{23}H$ (M^+-19, 563)	$C_{12}F_{22}H_2$ (M^+-19, 545)
400°C	75%	44.5	44.5	10.0	1.0
375°C	83%	10.9	58.1	23.3	7.7

*calculated, based on (**63**)

GLC/MS analyses of both reactions, identified perfluorinated decomposition products and polyfluorinated products, of which 2H-perfluoro-dipropylcyclohexane (**63a**) (M^+-19, 563; base peak, 151) was the major component.



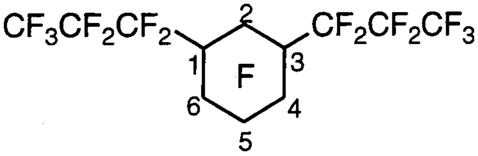
(63a)

Isomers of perfluorodipropylcyclohexane (**62**) and (**63**) were obtained by continuous extraction of the product mixture with acetone, followed by preparative scale GLC, but could not be separated.

Again lowering the temperature, from 400°C to 375°C, reduced the amount of decomposition products greatly and enhanced the proportion of perfluorodipropylcyclohexane (**62**) and (**63**).

Structure determination of perfluoro-1,3-dipropylcyclohexane (**63**)

The ^{19}F NMR spectrum of the pefluorocarbon mixture was complex, especially in the difluoromethylene region and so a $^{19}F/^{19}F$ COSY NMR spectrum was also run on the mixtures.

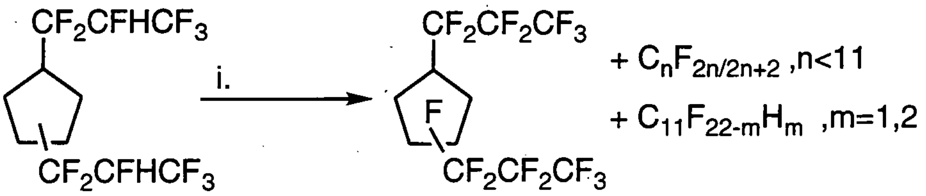


(63)

The CF_3 and CF groups of both isomers of perfluoro-1,3-dipropylcyclohexane (**63**) were readily distinguished at -80.9 ppm and *ca.* -184 ppm. In *trans*-perfluoro-1,3-dipropylcyclohexane (**63a**) the perfluoropropyl groups occupy equatorial positions giving the cyclohexane ring a rigid conformation, and therefore three AB systems at -120.0 & -125.0, -121.3 & -131.3 and -122.8 & -140.8 ppm in a 1 : 2 : 1 ratio were assigned to its CF_2 ring groups at 2, 4/6 and 5 positions respectively. In contrast, the cyclohexane ring of *cis*-perfluoro-1,3-dipropylcyclohexane (**63b**) will be rapidly inverting, as in compound (**63b**), and its three CF_2 ring groups at the 2, 4/6 and 5 positions were tentatively assigned to singlets at -115.6, -115.1 and -126.2 ppm in a 1 : 2 : 1 ratio. Finally two groups of singlets at *ca.* -127 and -114 ppm were assigned to the CF_2 of the perfluoropropyl groups of both isomers.

4.26 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclopentane x=2,3 (26)

The cobalt trifluoride fluorination of compound (**26**) was also conducted at 375°C and 400°C, and isomers of perfluorodipropylcyclopentane (**64**) were identified as the major products in both cases.



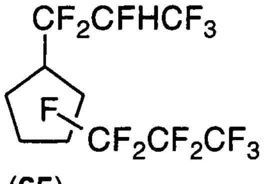
(26) **(64)**

i. CoF_3, 350-400°C, N_2 30ml/min

	Recovery*	% Composition of products by GLC/MS			
		$C_nF_{2n/2n+2}$ n<11	$C_{11}F_{22}$ (M^+-19, 531)	$C_{11}F_{21}H$ (M^+-19, 513)	$C_{11}F_{20}H_2$ (M^+-19, 495)
400°C	48%	20.8	71.3	7.4	0.4
375°C	77%	10.5	71.0	17.1	0.7

*calculated, based on (**64**)

GLC/MS analyses of the product mixtures identified the major perfluorinated decomposition product as perfluorodipropylcyclopentane (**61**) (M^+-19, 381; base peak at 69) and the major polyfluorinated product as 2H-perfluorodipropylcyclopentane (**65**) (M^+-19, 363; base peak at 151).

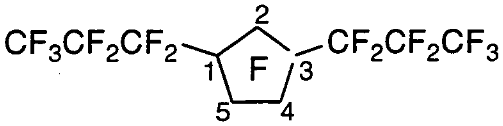


(65)

Lowering the reaction temperature, from 400°C to 375°C, reduced the proportion of perfluorinated decomposition products, but it also had the effect of increasing the percentage of polyfluorinated products and therefore the proportion of perfluorodipropylcyclopentane (**64**) remained unchanged.

Structure determination of perfluoro-1,3-dipropylcyclopentane (**64a**)

The two major isomers of perfluorodipropylcyclopentane (**64**) were identified as a 1 : 1 mixture of *cis*- and *trans*-perfluoro-1,3-dipropylcyclopentane (**64a**) by ^{19}F NMR and $^{19}F/^{19}F$ COSY NMR spectra on the mixture.

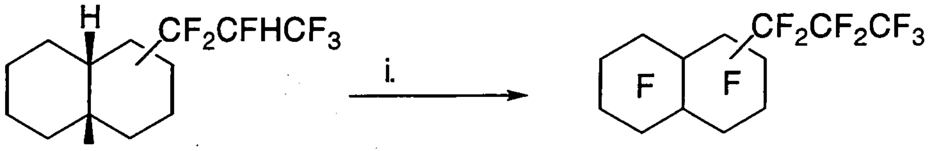


(64a)

As in perfluoro-2,5-dipropyltetrahydrofuran (**59**), five AB systems were observed in the difluoromethylene region. A comparison of the spectra suggested that two singlets, at -114.2 and -122.4 ppm, arose from the CF_2 groups at the two positions, one from each isomer. Two AB systems centred at approx. -126 ppm were assigned to the CF_2 group neighbouring the CF_3 groups because of their characteristic chemical shift, again one from each isomer. Two AB systems at -123.0 & -124.3 ppm and -126.1 & -134.1 ppm, were assigned to the two equivalent CF_2 groups at the four and five positions in the cyclopentane ring, of both isomers. The final AB system and a singlet, both centred at approx. -118 ppm were assigned to the CF_2 groups, neighbouring the tertiary ring CF group, of the perfluoropropyl group in both isomers.

4.27 x-(1,1,2,3,3,3-hexafluoropropyl)*cis*-decalin (x=1,2,9) (33)

The cobalt trifluoride fluorination of compound (**33**) was performed at 375°C.



84% recovery*

(**33**)

(**66**) 68%

+ $C_nF_{2n/2n+2}$ n<10, 19%

+ $C_{13}F_{22-m}H_m$ 13%

i. CoF_3 375°C, N_2 30ml/min

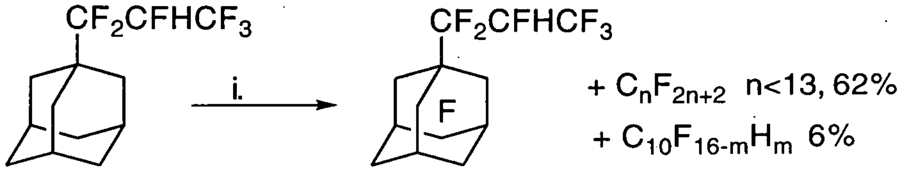
* recovery, calculated based on (**66**)

The major group of products were identified as isomers of perfluoro-x-propyldecalin (x=1,2,9) (**66**), polyfluorinated products contributed 13% to the product mixture, but were removed by continuous extraction with acetone overnight. The major perfluorinated decomposition products were identified by GLC/MS as the two isomers of perfluorodecalin (5%) confirming isomerisation occurred at the bridgehead position during fluorination. The ^{19}F NMR spectrum of the perfluorocarbon mixture was very complex in the difluoromethylene region because of the number of isomers of the product and the number of CF_2 groups within each isomer. A $^{19}F/^{19}F$ COSY NMR was run on the mixture, but still the AB systems could not be resolved.

4.28 1-(1,1,1,2,3,3-hexafluoropropyl)adamantane

Attempts to perfluorinate alkyladamantanes[132] using cobalt trifluoride have led to significant amounts of perfluorinated decomposition products, as occurred with norbornane[133], but by introducing trifluoromethyl groups, in a two step process, and then fluorinating by passing the substrate through a thermally graduated reactor several times, perfluorination was attained.

A simple reaction was performed, where 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane (**22**) was passed through the CoF_3 reactor at 400°C.



(22) **(67)** 32%

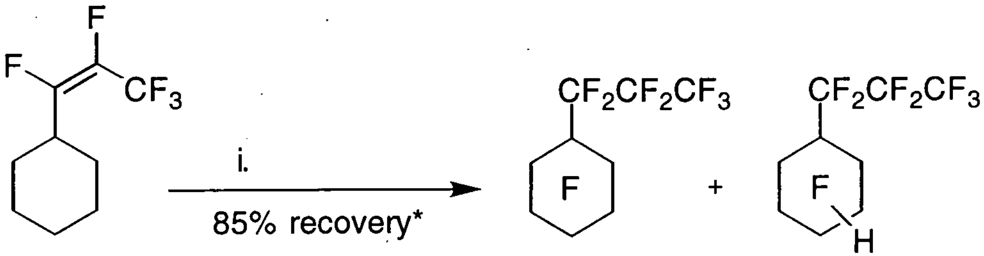
i. CoF_3, 400°C, N_2 30mlmin^{-1}

The product mixture was very complex due to a large amount of perfluorinated decomposition products. A GLC/MS of the mixture indicated that the major product was perfluoro-1-propyl-adamantane (**67**) (M^+-19, 555), but it could not be isolated from the mixture and so no further characterisation was possible. Decomposition presumably occurred as the adamantyl cage structure was unable to withstand the high temperature. In further reactions the temperature was reduced, but this only increased the amount of polyfluorinated products.

Attempts to perfluorinate 1,3-bis(1,1,1,2,3,3-hexafluoropropyl)adamantane (**23**) at 400°C also gave an extremely complex mixture of perfluorinated decomposition products including a small amount of perfluoro-1,3-dipropyl-adamantane (M^+-19, 705) which could not be separated. Therefore it seemed that a further increase in the percentage of fluorine content of the starting material had no beneficial effect on the reaction.

4.29 Z-pentafluoro-2-propenylcyclohexane (43a)

As the CFH proton in the fluoroalkyl group of the hexafluoropropyl adducts proved, consistently, to be the most difficult. to fluorinate, the cyclohexane adduct (**24**) was dehydrofluorinated prior to fluorination.



(43a) **(60)** 90% **(60b)** 10%

i. CoF_3 375°C, N_2 30mlmin^{-1}

* recovery, calculated based on (**60**)

The major product was identified as perfluoropropylcyclohexane (**60**) and only a small amount of polyfluorinated products (**60b**) were identified and no perfluorinated decomposition products were observed.

Removing the CFH group prior to fluorination allowed a lower temperature to be used without resulting in an increased amount of hydrogen containing products. The lower temperature also eliminated any decomposition and this resulted in an increased amount of the desired perfluorocarbon.

4.3 Methanol/TFE. Telomers

Telomers produced from radical addition of methanol to tetrafluoroethylene have long been known[134]. Cobalt trifluoride fluorinations of the heptanol and nonanol derivatives were conducted, at 400°C and 300°C, as a quick convenient route to perfluoroalkanes.

$$H(CF_2CF_2)_4CH_2OH \xrightarrow[N_2\ 30ml/min]{CoF_3,\ 400°C} CF_3(CF_2)_4CF_3$$

(68) 86% recovery[a] **(68a)** 93%

[a] calculated based on **(68a)**

$$H(CF_2CF_2)_3CH_2OH \xrightarrow[\text{i. or ii.}]{CoF_3} CF_3(CF_2)_4CF_3 + HCF_2(CF_2)_4CF_3$$

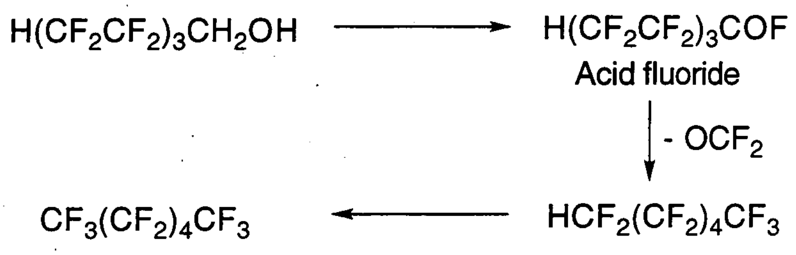
(69)	Recovery[b]	**(69a)**	**(70)**
i. 400°C, N_2 30mlmin^{-1}	65%	90%	2%
ii. 300°C, N_2 30mlmin^{-1}	51%	25%	75%

[b] calculated based on **(69a)**

Fluorination of the nonanol telomer at 400°C, produced perfluorooctane (**68a**) as the major product and similarly perfluorohexane (**69a**) was identified as the major product from the heptanol telomer.

Lowering the temperature of the heptanol derivative, to 300°C, significantly reduced the proportion of perfluorohexane (**69a**) produced and 1H-perfluorohexane (**70**) became the major product. The reaction probably proceeds via an acid fluoride, which then loses OCF_2 (scheme 4.5). When the reaction was repeated at 200°C, a ^{19}F NMR spectrum of the products, identified a signal at +24.3 ppm, characteristic of an acid fluoride.

Scheme 4.5



Both reactions provide quick and simple routes to perfluoroalkanes and also could be used to produce 1H-perfluoroalkanes, if required by simply reducing the reaction temperature.

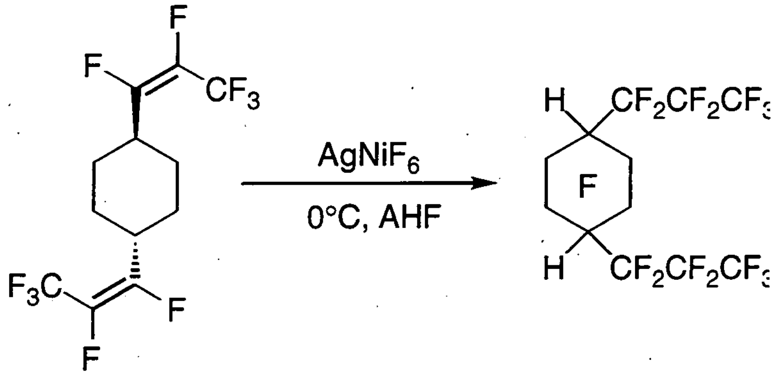
4.4 Fluorinations using high valency nickel fluorides in anhydrous HF

It has long been suspected that electrochemical fluorination (Simons Process) using a nickel anode in anhydrous HF creates higher nickel fluorides than nickel (II) fluoride[135] and therefore such high valence nickel fluorides were possible low temperature, fluorinating agents in their own right.

4.41 Silver (II)Nickel(IV)hexafluoride

trans-1,4-bis(Z-pentafluoroprop-2-enyl)cyclohexane **(46)**

A brown slurry of $AgNiF_6$ in anhydrous HF was slowly added to a slightly soluble mixture of *trans*-1,4-bis(Z-pentafluoroprop-2-enyl)cyclohexane (**46**) in anhydrous HF at approximately 0°C



(46) **(71)**

An exothermic reaction occurred immediately, and the brown $AgNiF_6$ was reduced to an olive green solid, assumed to be $Ag(I)Ni(II)F_3$. When no further reaction was observed the anhydrous HF was allowed to distil into a soda-lime trap and the remaining green solid was washed with Arklone and then analysed using ^{19}F NMR. The ^{19}F NMR spectrum produced a weak set of signals similar to that of the *cis-* and *trans-* isomers of perfluoro-1,4-dipropylcyclohexane, except that no tertiary ring fluorines were evident (normally observed at approx. -185 ppm), suggesting that the tertiary ring protons were not fluorinated and the product was 2H,2'H-perfluoro-1,4-dipropylcyclohexane (**71**).

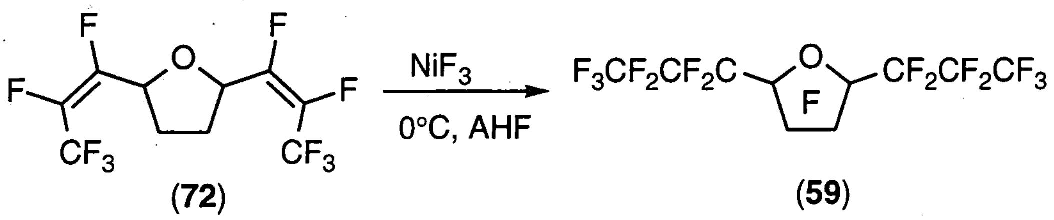
Removing the CFH group from the fluoroalkyl side chains by dehydrofluorination prior to fluorination would make the tertiary ring proton the hardest site to fluorinate, as it is the closest to the electron withdrawing side chain and therefore NiF_6^{2-} was not a strong enough oxidiser to give complete fluorination.

4.42 Nickel (III) trifluoride

2,5-bis(Z-pentafluoro-2-propenyl)tetrahydrofuran (72)

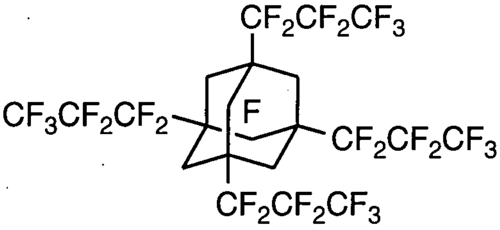
Nickel trifluoride is a stronger oxidiser than NiF_6^{2-} as it does not carry a negative charge. It is formed by adding BF_3 to a solution K_2NiF_6 in anhydrous HF from which it removes fluoride ion to produce nickel (IV) tetrafluoride which is unstable above -40°C and loses fluorine to give nickel (III) trifluoride as a black precipitate.

Compound (**58**) was dehydrofluorinated, using sodium t-butoxide, to form 2,5-bis(Z-pentafluoroprop-2-enyl)tetrahydrofuran (**72**) prior to fluorination. The black slurry of nickel trifluoride in anhydrous HF was added slowly to the slightly soluble 2,5-bis(Z-pentafluoro-2-propenyl)tetrahydrofuran (**72**) in anhydrous HF, at approximately 0°C.



The solid gradually turned a light brown colour as the nickel trifluoride was reduced. The reaction was left overnight to ensure complete conversion and then the anhydrous HF was distilled off and the remaining brown solid was washed with chlorotrifluoromethane. A ^{19}F NMR spectrum of the chlorofluorocarbon solution identified a weak set of signals similar to those of perfluoro-2,5-dipropyltetrahydrofuran (**59**) and there was no evidence of any CFH signals.

Fluorination of the tertiary ring protons may have been aided by the neighbouring activating oxygen, but in more recent work, in collaboration with Bartlett and Roche in this laboratory, perfluoro-1,3,5,7-tetrakispropyladamantane (**73**) was produced via nickel trifluoride fluorination of 1,3,5,7-tetrakis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**55**), confirming that NiF_3 is even able to fluorinate the CFH proton and therefore is a stronger fluorinating agent than $AgNiF_6$.



(73)

4.5 Conclusions

Cobalt trifluoride fluorinations were performed successfully on the mono-adducts of cyclopentane and cyclohexane to produce their perfluorinated derivatives, which could be isolated from their product mixtures, but perfluorination of the di-adducts gave mixtures of perfluorinated *cis-* and *trans-*isomers which were inseparable. Full interpretation of the ^{19}F NMR spectra of these isomers was difficult, but was helped by the use of $^{19}F/^{19}F$ COSY experiments. In all cases the presence of the fluoroalkyl group in the starting material stabilised it to fluorination, lessening the amount of decomposition products, but the proton of the CFH group in the side chain was the most difficult to remove and was the major contributor to the hydrogen before fluorination. In all these reactions any polyfluorinated products were easily removed using continuous extraction with acetone and perfluorinated decomposition products were removed by preparative GLC. Cobalt trifluoride fluorinations of the 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane and 1,3-bis(1,1,2,3,3,3-hexafluoropropyl)adamantane were hampered by decomposition of the adamantyl skeleton, even when the percentage of fluorine was increased in the starting material. Dehydrofluorination of the fluoroalkyl side-chain, as in the cyclohexane adduct, should allow lower temperatures to be used and may reduce the amount of decomposition observed.

Cobalt trifluoride fluorination of the methanol/tetrafluoroethylene telomers provided an convenient method of producing either the perfluoroalkanes or 1H-perfluoroalkanes by simply varying the reaction temperature.

$AgNiF_6$ in anhydrous HF, fluorinated all but the most deactivated hydrogens in the substrate, at 0°C. Whereas NiF_3 in anhydrous HF proved to be strong enough to fluorinate even the hydrogen in the hexafluoropropyl side chain, at 0°C, yet still maintain the adamantyl skeleton in (**73**).

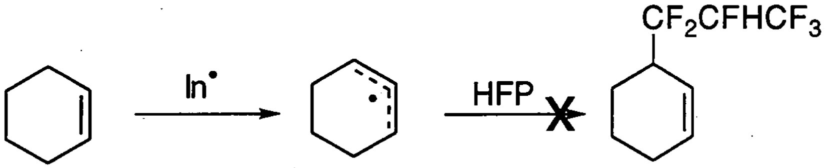
Chapter Five

Functionalisation of Hexafluoropropene Adducts

5.1 Introduction

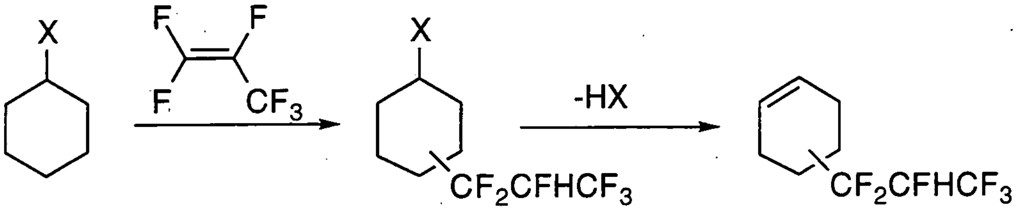
Previous attempts to affect radical addition of HFP to alkenes such as cyclohexene, in this laboratory, led only to trace amounts of the desired products[90], presumably due to formation of allylic radicals which are too stable to react further (scheme 5.1).

Scheme 5.1



Therefore to introduce unsaturation into the hydrocarbon moiety of a hexafluoropropene adduct, another functional group must first be introduced followed by α,β-elimination of it (scheme 5.2).

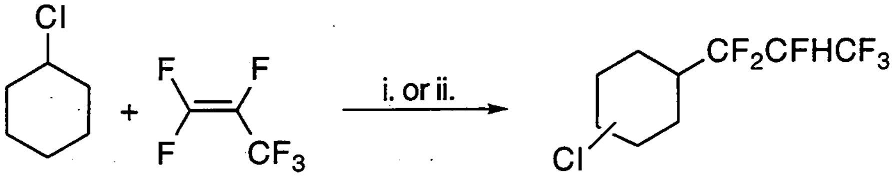
Scheme 5.2



5.2. Attempted additions of Hexafluoropropene (HFP) to Functionalised Hydrocarbons

5.21 Cyclohexyl chloride

In the present work, addition of cyclohexyl chloride to HFP was attempted in repeated experiments, using both γ-rays and peroxide initiation, but only trace amounts of x-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl chloride (**74**) were produced.



1 : 1.5

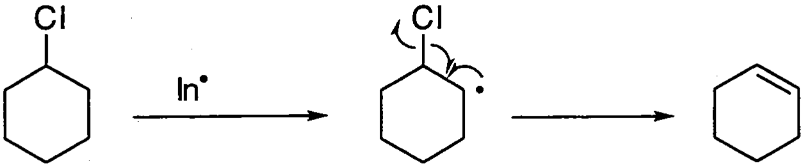
(74) Trace

i. γ-rays, 7Mrads, 4 Days, 18°C
ii. DTBP, 140°C, 24 hours

A GLC/MS of the γ-ray reaction mixture identified a small group of isomers of the mono-chlorinated adduct (**74**) with a $(M-Cl)^+$ peak at 233 and a ^{19}F NMR spectrum of the reaction mixture confirmed HFP incorporation, but no further workup of the reaction was performed. The reaction was repeated using acetone to make the two compounds miscible, but it had no significant effect on the reaction. The low reactivity of the system may be due to the electron withdrawing properties of the chlorine deactivating the system to radical addition.

GLC/MS analysis of the DTBP initiated reaction identified the major product as cyclohexene (6%; M^+, 82). This suggests that a hydrogen β- to the chlorine is abstracted and elimination of a chlorine radical (scheme 5.3) is preferred to addition to HFP.

Scheme 5.3

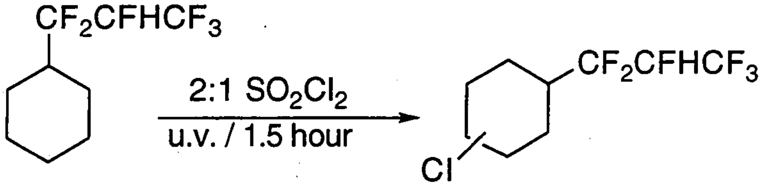


5.3 Chlorination of Hexafluoropropene adducts

5.31 1,1,2,3,3,3-Hexafluoropropylcyclohexane (24)

As an alternative to addition of cyclohexyl chloride to HFP, chlorination of 1,1,2,3,3,3-hexafluoropropylcyclohexane (**24**), using sulphuryl chloride, was performed.

A two-fold excess of compound (**24**) was used in an attempt to produce only the mono-chlorinated adducts (**74**).

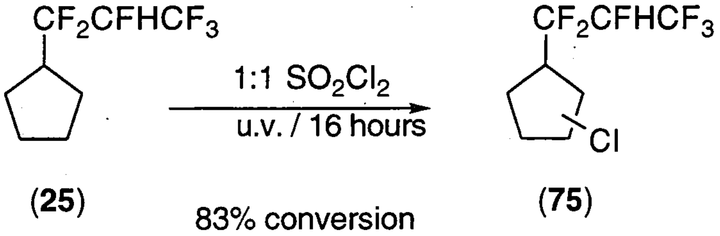


(**74**) 27%

The reaction was terminated when no further gases evolved from the reaction mixture, indicating that no sulphuryl chloride remained. A ^{1}H NMR of the reaction mixture confirmed chlorination of the cyclohexane ring had occurred as several new signals in 3.5-4.5 ppm region were observed. Fractional distillation of the reaction mixture gave two fractions. The major fraction consisted of recovered starting material and the other fraction was identified as isomers of x-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl chloride (**74**).

5.32 Chlorination of 1,1,2,3,3,3-hexafluoropropylcyclopentane (25)

1,1,2,3,3,3-Hexafluoropropyl)cyclopentane (**25**) was chlorinated using sulphuryl chloride (1 : 1 ratio) and uv initiation.



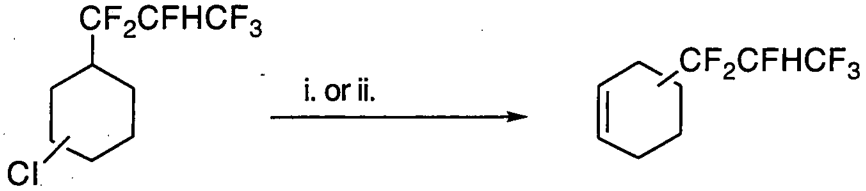
A ^{1}H NMR of the reaction mixture confirmed chlorination had taken place with several new signals in the 4-5 ppm region, corresponding to CHCl protons. GLC/MS analysis identified isomers of x-(1,1,2,3,3,3-hexafluoropropyl)cyclopentyl chloride x =2,3 (**75**) as the major products ((M-Cl)$^+$, 219) but a trace amount of di-chlorinated adducts were also detected (M$^+$, 288).

Six major isomers of compound (**75**) were observed in three groups of two by GLC. Two regioisomers of (**75**) are possible, both containing three chiral centres and therefore sixteen isomers of the mono-chlorinated adduct are possible, making conclusive structure determination virtually impossible.

5.4 Dehydrochlorination of Chlorinated Hexafluoropropene adducts

5.41 x-(1,1,2,3,3,3-Hexafluoropropyl)cyclohexyl chloride x=2,3,4 (74)

Dehydrochlorination of compounds (**74**) using either aqueous sodium hydroxide[136] or triethylamine[137] failed, but a review of the literature[138,139] indicated that the weak base, lithium chloride in dimethyl formamide was an unusual, but successful dehydrochlorinating agent and so dehydrochlorination, using this system, was attempted.

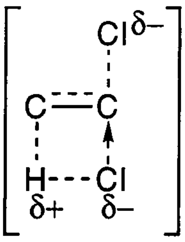


(**74**) (**76**)

i. 1:1.5 LiCl, DMF, 150°C, 20 hrs 89%
ii. DMF, 150°C, 20 hrs 46%

A GLC/MS of the product mixture indicated that nearly all the starting material (89%) had undergone dehydrochlorination to produce isomers of x-(1,1,2,3,3,3-hexafluoropropyl)cyclohex-1-ene x=1,2,3 (**76**) (M^+, 232). Distillation of the reaction mixture gave a pure sample of (**76**), whose IR spectrum confirmed the existence of a double bond (v^{-1}, 1680 cm^{-1}). The ^1H NMR of (**76**) identified vinylic proton resonances in the 5.5-6.5 ppm region, confirmed that the double bond was located in the cyclohexane ring and no vinylic fluorine resonances were observed in the ^{19}F NMR spectrum establishing that dehydrofluorination had not taken place.

A reaction was also carried out using dimethyl formamide alone, to determine whether the lithium chloride participated in the previous reaction. The reaction conversion was significantly lower than in the previous reaction, suggesting that the lithium chloride does have a role in the dehydrochlorination process. The chloride ion may be acting not only as a base, but also as a nucleophile helping to displace chloride ion from the substrate in the transition state (77).

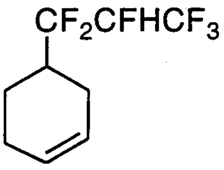


(77)

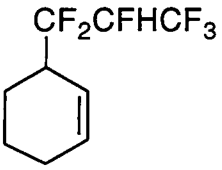
The lithium cation may also co-ordinate to the chlorine leaving group, aiding the loss of chloride ion[140].

Structure determination of x-(1,1,2,3,3,3-hexafluoropropyl)cyclohex-1-ene x=1,2,3 (76)

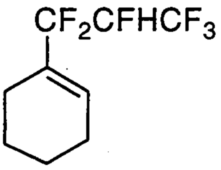
A broad band proton decoupled ^{13}C NMR was run on compounds (**76**) and although it was complex, four major singlets were observed between 124-128 ppm corresponding to vinylic carbons in the cyclohexane ring, suggesting that compounds (**76a**) and (**76b**) were the major isomers.



(76a)



(76b)

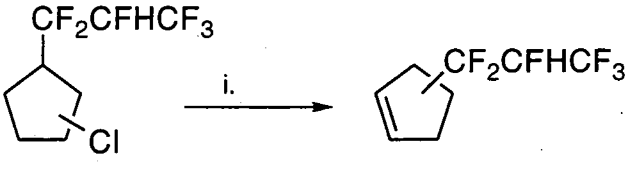


(76c)

Two small triplets, at 129.8 and 131.7 ppm, were also observed indicating that isomer (**76c**) was also produced, but only as a minor product. This was confirmed by a ^{1}H NMR of (**76**) which identified a small multiplet at 6.23 ppm corresponding to the vinylic proton of (**76c**). A large multiplet at 5.71 ppm was also observed and presumably resulted from the vinylic protons of both contained (**76a**) and (**76b**).

5.42 x-(1,1,2,3,3,3-Hexafluoropropyl)cyclopentyl chloride x=2,3 (75)

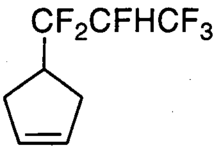
Having successfully dehydrochlorinated the cyclohexyl system, the lithium chloride/DMF procedure was applied to the cyclopentyl derivative (**75**) and again good conversion was achieved to give isomers of x-(1,1,2,3,3,3-hexafluoropropyl)cyclopentene x=2,3 (**78**).



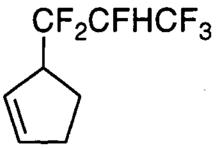
(**75**) (**78**) 72%

i. 1:1.5 LiCl, DMF, 150°C, 20 hrs

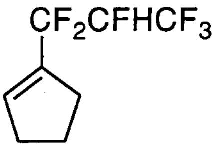
Distillation of the reaction mixture gave a pure sample of compounds (**78**), but the individual isomers were inseparable. A ^{1}H NMR of compounds (**78**) identified three vinylic proton resonances, indicating that compound (**78a**) was the major isomer. The smallest multiplet, at 6.56 ppm, was attributed to the vinylic proton of (**78c**) due to the increased deshielding of neighbouring fluoroalkyl group. Another small multiplet, at 6.13 ppm was assigned to vinylic proton of (**78b**) nearest the fluoroalkyl group, for similar reasons and the final, large multiplet, at 5.60 ppm, was assigned to the remaining vinylic proton of (**78b**) and the two vinylic protons of (**78a**)



(**78a**)



(**78b**)



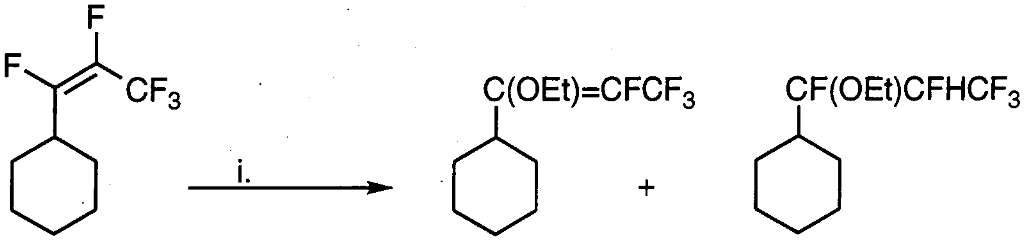
(**78c**)

Although the introduction of unsaturation into the cyclopentyl system was successful, the chlorination reaction showed little selectivity and this was reflected in the mixture of unsaturated products (**78**).

5.5 Ethoxide attack on pentafluoropropenyl derivatives

5.51 Z-Pentafluoroprop-2-enylcylohexane (43)

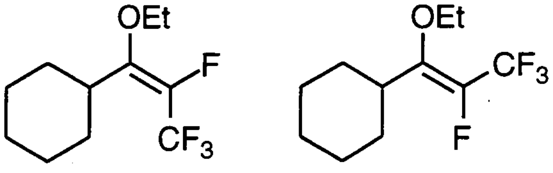
Dmowski showed that the pentafluoropropenyl derivative of tetrahydrofuran readily underwent nucleophilic attack at its double bond, by alkoxide ions[106]. A comparative reaction was performed with z-pentafluoroprop-2-enylcylohexane (**43**).



(**43**) 93% conversion (**44**) 82% (**79**) Trace

i. 1 :2 NaOEt, EtOH, 80°C, 138 hrs

The disappearance of the vinylic fluorine, at -131.4 ppm, in the starting material was monitored by ^{19}F NMR, and after five and a half days the reaction was terminated. A ^{1}H NMR of the product mixture confirmed the incorporation of the vinylic ethoxy-substituents with multiplets at 4.13 & 3.84 ppm corresponding to the CH_2 groups and triplets at 1.29 & 1.26 ppm assigned to the CH_3 groups of both the Z- and E- isomers of the vinylic ether (**44**). The ^{19}F NMR spectrum of the products also identified a small amount of the addition product 1-ethoxy-2,2,3,3,3-pentafluoroprop-2-enylcylohexane (**79**), but this was not isolated. Distillation of the product mixture gave the Z- and E-isomers of 1-ethoxy-2,3,3,3-tetrafluoroprop-2-enylcylohexane (**44**) in a 3.5 : 1 ratio (by ^{19}F NMR), which could not be separated.

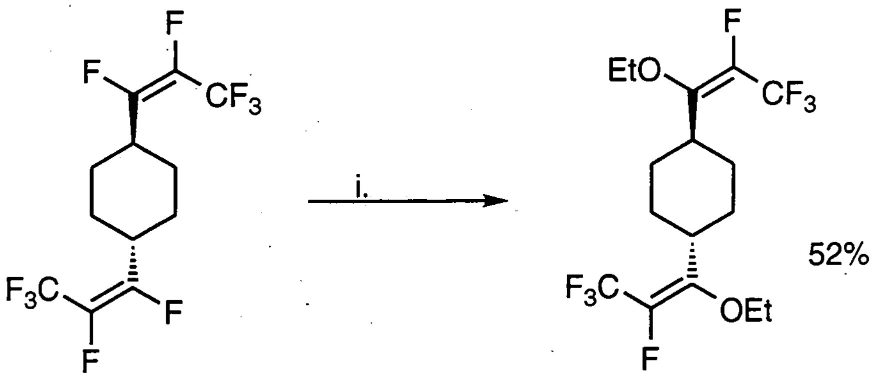


^{19}F nmr ratio 3 : 1

In comparison with pentafluoro-2-propenyltetrahydrofuran (**42**), which achieved almost complete conversion after three hours at 60°C[106], the cyclohexane derivative (**44**) reacted at a much slower rate. This is presumably due to cyclic substituents on the double bond. The oxygen of the tetrahydrofuranyl substituent inductively withdraws electron density from the double bond, increasing its electrophilicity, whereas the cyclohexyl substituent releases electron density to it, making it less electrophilic and therefore less susceptible to nucleophilic attack.

5.52 *trans*-1,4-Bis(Z-pentafluoro-2-propenyl)cyclohexane (**46**)

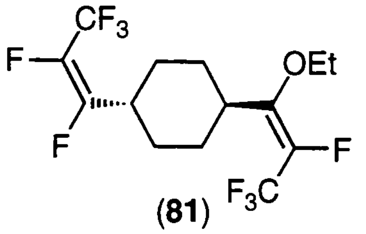
Nucleophilic attack, using ethoxide ion was also attempted on *trans*-1,4(z-pentafluoro-2-propenyl)cyclohexane (**46**).



(46) **(80)**

i. 1:4 NaOEt, EtOH, 80°C, 72 hrs

After three days, a ^{19}F NMR spectrum of the reaction mixture confirmed that all the starting material had reacted and the major product was identified as *trans*-1,4(z-1-ethoxy-2,3,3,3-tetrafluoroprop-2-enyl)cyclohexane (**80**) which was isolated by adding methanol to the liquid product and cooling to -78°C, at which point it crystallised out as a white solid. The ^{19}F NMR spectrum of the reaction mixture indicated that the other major product was *trans*-1-(z-1-ethoxy-2,3,3,3-tetrafluoroprop-2-enyl)-4-(z-pentafluoro-2-propenyl)cyclohexane (**81**) (35%), but this was not isolated.



(81)

The increased reactivity of the cyclohexyl di-ene over the mono-ene is most likely due to the decreased electron withdrawing ability of the cyclohexyl substituent due to the electron withdrawing effect of the extra fluoroalkenyl group.

5.6 Conclusions

Attempts to add cyclohexyl chloride to HFP were unsuccessful, but chlorination of the HFP adducts was possible. The low yields from chlorination may be improved, but the reactions were performed using an excess of the adduct in order to only achieve mono-chlorination. Unfortunately, the low selectivity of the chlorine radical, coupled with the increased number of chiral centres in the chlorinated products, produced a large number of isomers of the chloro-derivative and it was not possible to identify the sites of chlorination unambiguously.

Dehydrochlorination of the chloro-derivatives failed using conventional bases, such as triethylamine, but the weak base lithium chloride in aprotic solvent, selectively dehydrochlorinated the system without any dehydrofluorination occurring. Unfortunately, several inseparable unsaturated products were produced, which reflected the low selectivity of the chlorination reactions.

Z-Pentafluoroprop-2-enylcyclohexane reacted at a slower rate with ethoxide, than the corresponding tetrahydrofuranyl derivative, presumably because of the reduced electrophilicity of its double bond. However the double bonds of the 1,4-di-ene seemed to be more electrophlic as a consequence of the extra fluoroalkenyl group.

Instrumentation

Distillation

Fractional distillation of lower boiling product mixtures (up to 150°C/1 mmHg) was carried out using a Fischer Spahltroh MMS255 small concentric tube apparatus. Higher boiling materials were distilled using a Buchi kugelrohr GKR-51 apparatus. Boiling points were recorded during the distillation or using the Siwoloboff method.

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.

GLC Analysis

Gas liquid Chromatography (GLC) analysis was carried out using a Hewlett Packard 5890A gas liquid chromatograph equipped with a 25m cross-linked methyl silicone capillary column. Preparative GLC was performed on a Varian Aerograph Model 920 (catharometer detector) gas liquid chromatograph with packed columns, which was mainly a 3m 10% SE 30.

IR Spectra

IR spectra were recorded on a Perkin-Elmer 457 or 577 Grating spectrophotometer using conventional techniques.

Mass spectra

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

NMR spectra

^{1}H NMR spectra were recorded on a Bruker AC250 (250.13 MHz), a Varian VXR400S (399.952 MHz) and a Bruker AMX500 (500.14 MHz) NMR spectrometer.

^{13}C NMR spectra were recorded on a Varian VXR400S (100.582 MHz) and a Bruker AMX500 (125.77 MHz) NMR spectrometer.

^{19}F NMR spectra were recorded on a Bruker AC250 (235.34 MHz), a Varian VXR400S (376.29 MHz) and a Bruker AMX500 (470.54 MHz) NMR spectrometer.

Melting Points

Melting points were carried out at atmospheric pressure and are unconnected.

Reagents and Solvent

Unless otherwise stated, reagents were used as supplied. Solvents were dried by standard methods and stored over a molecular sieve (type 4A).

Chapter Six

Experimental to Chapter Two

6.1 General Procedure

6.11 γ–ray initiated reactions

Any liquid or solid reagents and solvent, if used, were introduced into a Pyrex Carius tube (volume ca. 60 ml). The tube was then degassed three times, by freeze-thawing. Any gaseous reagents, including HFP, were also carefully degassed, separately, and then transferred into the cooled (liquid air) Carius tube using standard vacuum line techniques. The tube was sealed *in vacuo*, while frozen (liquid air), placed inside a metal sleeve and then allowed to reach room temperature within a fumehood. The tube was then taken to the ^{60}Co source and irradiated (55 Krad hr^{-1}) 10 cm from the source at room temperature. On termination of the reaction the tube was cooled (liquid air) and opened. Any remaining HFP was recovered as it returned to room temperature and the products were poured out.

6.12 Peroxide initiated reactions

The reactions were carried out in either 150ml, 250ml, or 1 litre nickel autoclaves, fitted with bursting discs (maximum working pressure *ca.* 200 bar). The autoclave was charged with any solid or liquid and solvent and then sealed using a copper gasket. The system was degassed three times by freeze-thawing and then any gasses, degassed separately, were transferred into the liquid air cooled autoclave, using standard vacuum line techniques. The autoclave valve was closed and then transferred, in a Dewar flask of liquid air, to a purpose built high pressure cell where it was allowed to warm and then heated in a thermostatically controlled, rocking furnace for 24 hrs at 140°C. On completion the autoclave was cooled (liquid air), and any remaining HFP was recovered as it returned to room temperature and the products were poured out.

6.2 Free-Radical Additions of Alkanes to Hexafluoropropene

6.21 Propane

i. γ-ray initiation

A Carius tube was charged with propane (2.2g, 50 mmol) and HFP (7.6g, 51 mmol) and then irradiated for 4 days with γ-rays (6 Mrads) at room temperature. The tube was opened and gaseous components (8.7g) were recovered. A colourless liquid was removed and fractional distillation of it (81-82°C) gave 4-methyl-1,1,1,2,3,3-hexafluoropentane (**28**) (0.8g, 8%); (Found: C, 37.4; H, 4.2. $C_6H_8F_6$ calculated: C, 37.1; H, 4.1%); IR, MS and NMR data agreed with work done previously in this laboratory[90]; IR. number 1; Mass spectrum 1; NMR number 1.

ii. γ-ray initiation

A Carius tube was charged with propane (2.3g, 52 mmol) and HFP (9.0g, 60 mmol) and then irradiated for 8 days with γ-rays (12 Mrads) at room temperature. The tube was opened and gaseous components (9.0g) were recovered. A colourless liquid was removed and fractional distillation of it (81-82°C) gave a mixture of mono-adducts (2.0g, 20%) which could not be separated, but were identified as 4-methyl-1,1,1,2,3,3-hexafluoropentane (**28**) (19%) and 1,1,1,2,3,3-hexafluorohexane (**29**) (1%). MS and NMR data agreed with work done previously in this laboratory[90]; Mass spectrum 2; NMR number 2.

iii. DTBP initiation

An autoclave (150ml) was charged with propane (2.4g, 55 mmol), HFP (12.7g, 82 mmol) and DTBP (0.6g, 4 mmol) and then rocked at 140°C for 24 hrs. The autoclave was opened and gaseous products (6.3g) were recovered. A pale yellow liquid was removed and fractional distillation of it (81-82°C) gave a mixture of inseparable mono-adducts (8.3g, 78%), 4-methyl-1,1,1,2,3,3-hexafluoropentane (**28**) (75%) and 1,1,1,2,3,3-hexafluorohexane (**29**) (3%).

6.22 2-Methylpropane

i. γ-ray initiation

A Carius tube was charged with 2-methylpropane (3.5g, 60 mmol) and HFP (8.9g, 60 mmol) and then irradiated with γ-rays for 5 days (7.5 Mrads) at room temperature. The tube was opened and gaseous components (10.2g) were recovered. A colourless liquid was produced and fractional distillation of it (103-104°C) gave 4,4-dimethyl-1,1,1,2,3,3-hexafluoropentane (**30**) (2.1g, 17%); (Found: C, 40.5; H, 4.9. $C_6H_8F_6$ calculated: C, 40.4; H, 4.8%); IR, MS and NMR data agreed with work done previously in this laboratory[90]; IR. number 2; Mass spectrum 3; NMR number 3.

ii. DTBP initiation

An autoclave (150ml) was charged with 2-methylpropane (2.5g, 43 mmol), HFP (8.18g, 55 mmol) and DTBP (0.60g, 4 mmol). The autoclave was opened and gaseous products (3.4g) were recovered. A pale yellow liquid was removed and fractional distillation of it (103-104°C) gave a mixture of inseparable mono-adducts (7.4g, 83%), 4,4-dimethyl-1,1,1,2,3,3-hexafluoropentane (**30**) (80%) and 1,1,1,2,3,3-hexafluoro-5-methylhexane (**31**) (3%); Mass spectrum 4; NMR number 4.

6.3 Free-Radical Additions of Monocyclic hydrocarbons to Hexafluoropropene

6.31 Cyclopropane

i. γ-ray initiation

A Carius tube was charged with cyclopropane (2.5g, 62 mmol) and HFP (9.7g, 62 mmol) and then irradiated for 12 days with γ-rays (18 Mrads) at room temperature. The tube was opened and only gaseous components (11.9g) were recovered, which were identified as starting materials by GLC/MS.

ii. DTBP initiation

An autoclave (150ml) was charged with cyclopropane (2.3g, 54 mmol), HFP (8.8g, 58 mmol) and DTBP (0.7g, 5 mmol) and then rocked at 140°C for 24 hrs. The autoclave was opened and gaseous components (8.5g) were recovered. A pale yellow liquid (2.3g) was removed, but analysis by GLC/MS gave a complex mixture of products including a small component identified as 1,1,2,3,3,3-hexafluoropropylcyclopropane (**32**) (M^+ peak at 192; Mass spectrum 5).

6.32 Cyclopentane

i. γ–ray initiation

A Carius tube was charged with cyclopentane (7.1g, 0.1 mol) and HFP (23.6g, 0.16 mol) and then irradiated with γ–rays for 5 days (7.5 Mrads) at room temperature. The tube was opened and HFP (15.4g) was recovered and a colourless liquid obtained. Cyclopentane (3.2g) was removed by distillation, further fractional distillation gave two fractions, boiling at 134-135°C and 80-81°C/15mm Hg. The first fraction was identified as 1,1,2,3,3,3-hexafluoropropylcyclopentane (**25**) (10.3g, 86%), (Found: C, 43.5; H, 4.6. $C_8H_{10}F_6$ calculated: C, 43.6; H, 4.6%); IR, MS and NMR data agreed with work done previously in this laboratory[90]; IR spectrum 3, Mass spectrum 6, NMR number 5; and the second fraction was identified as a mixture of isomers of 1,x-bis-(1,1,2,3,3,3-hexafluoropropyl)cyclopentane (x=2,3) (**26**) (1.9g, 9%) (Found: C, 36.0; H, 2.9. $C_{11}H_{10}F_{12}$ calculated: C, 35.7; H, 2.7%); IR, MS and NMR data agreed with work done previously in this laboratory[90]; IR. number 4, Mass spectrum 7, NMR number 6.

ii. DTBP initiation

An autoclave (250ml) was charged with cyclopentane (10.5g, 0.15 mol), HFP (36.3g, 0.24 mol) and DTBP (0.75g, 5 mmol) and then rocked at 140°C for 24 hrs. The autoclave was opened and HFP (5.3g) was recovered and a pale brown liquid obtained. Cyclopentane (0.4g) was removed by distillation, further fractional distillation gave two fractions, boiling at 134-135°C and 80-81°C/15mm Hg. The first fraction was identified as 1,1,2,3,3,3-hexafluoropropylcyclopentane (**25**) (15.5g, 49%) and the second fraction was identified as 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclopentane (x=2,3) (**26**) (20.2g, 38%).

iii. DTBP initiation

An autoclave (150ml) was charged with cyclopentane (7.0g, 0.1 mol), HFP (29.5g, 0.2 mol) and DTBP (0.6g, 4 mmol) and then rocked at 140°C for 24 hrs. The autoclave was opened and HFP (15.0g) was recovered and a pale brown liquid obtained. Fractional distillation of the liquid gave two fractions, boiling at 134-135°C and 80-81°C/15mm Hg. The first fraction was identified as 1,1,2,3,3,3-hexafluoropropylcyclopentane (**25**) (12.5g, 57%) and the second fraction was identified as 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclopentane (x=2,3) (**26**) (8.3g, 22%).

6.33 Cyclohexane

i. γ-ray initiation

A Carius tube was charged with cyclohexane (8.4g, 0.1 mol) and HFP (22.9g, 0.15 mol) and then irradiated with γ-rays for 5 days (7.5 Mrads). The tube was opened and HFP (10.9g) was recovered and a colourless liquid obtained. Cyclohexane (1.8g) was removed by distillation, further fractional distillation gave two fractions, boiling at 154-155°C and 105-106°C/15mmHg. The first fraction was identified as 1,1,2,3,3,3-hexafluoropropylcyclohexane (**24**) (16.6g, 90%), (Found: C, 46.4; H, 5.5. $C_8H_{10}F_6$ calculated: C, 46.2; H, 5.2%); IR, MS and NMR data agreed with literature[99], IR. number 5, Mass spectrum 8, NMR number 7; and the second fraction was identified as a mixture of isomers of 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x=2-4) (**27**) (1.2g, 4%) (Found: C, 37.6; H, 3.3. $C_{12}H_{12}F_{12}$ calculated: C, 37.5; H, 3.2%); IR, MS and NMR data agreed with work done previously in this laboratory[90], IR. number 6, Mass spectrum 9, NMR number 8.

ii. DTBP initiation

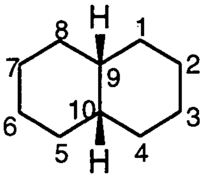
An autoclave (250ml) was charged with cyclohexane (8.3g, 0.1 mol), HFP (30.0g, 0.2 mol) and DTBP (0.6g, 4 mmol) and then rocked at 140°C for 24 hrs. The autoclave was opened and HFP (7.4g) was recovered and a yellow liquid obtained. Cyclohexane (0.7g) was removed by distillation, further fractional distillation of the liquid gave two fractions, boiling at 154-155°C and 105-106°C/15 mmHg. The first fraction was identified as 1,1,2,3,3,3-hexafluoropropylcyclohexane (**24**) (9.0g, 39%), and the second fraction was identified as mixture of isomers of 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x=2-4) (**27**) (20.1g, 53%), from which, <u>2R,2'S-*trans*-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane</u> (**27a**) m.p. 80-81°C, (Found: C, 37.3; H, 3.0. $C_{12}H_{12}F_{12}$ requires: C, 37.5; H, 3.1%); IR. number 7, Mass spectrum 10, NMR number 9; crystallised out on standing.

iii. DTBP initiation, 1 litre autoclave

An autoclave (1 litre) was charged with cyclohexane (454g, 5.4 mol) and DTBP (20.5g, 0.14 mol). The autoclave was degassed three times by compressing with nitrogen which was then removed. The autoclave was heated to 140°C whilst being stirred and HFP (405g, 2.7 mol) added to the mixture, through a one-way valve over a period of 6 hours. The autoclave was allowed to cool to room temperature and then was pressurised with nitrogen, which was then removed and then opened. A yellow oil (856g) was recovered and distillation of it gave cyclohexane (225g), 1,1,2,3,3,3-hexafluoropropylcyclohexane (**24**) (537g, 85%) and 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x=2-4) (**27**) (62.2g, 6%) (mixture of isomers).

<u>6.4 Free-Radical Additions of Bicyclic alkanes to Hexafluoropropene</u>

<u>6.41 *Cis*-decalin</u>



i. γ–ray initiation

A Carius tube was charged with *cis*-decalin (6.9g, 0.05 mol) , HFP (15.3g, 0.1 mol) and dry acetone (8ml) and irradiated with γ–rays at room temperature for 5 days (7.5 Mrads). Nearly all of the HFP (14.5g) was recovered. The colourless liquid product mixture (7.6g) was analysed by GLC/MS and ^{19}F NMR which identified traces of x-(1,1,2,3,3,3-hexafluoropropyl)*cis*-decalin (x=1,2,9) (**33**) (*ca.* 5% by gc.), but no further workup was performed.

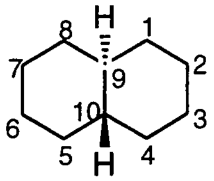
ii. DTBP, 140°C

An autoclave (150ml) was charged with *cis*-decalin (13.8g, 0.1 mol), HFP (29.1g, 0.2 mol) and DTBP (0.6g, 4 mmol) and then rocked at 140°C for 24 hours. The autoclave was opened and HFP (19.8g) was recovered and a yellow liquid (23.3g) obtained. *Cis*-decalin (8.4g) was removed by distillation, further fractional distillation of the liquid gave two fractions, boiling at 120-121°C/20 mmHg and 152-153°C/20 mmHg. The first fraction was identified as a mixture of isomers of x-(1,1,2,3,3,3-hexafluoropropyl)*cis*-decalin (x=1,2,9) (**33**) (6.3g, 56%), (Found: C, 54.2; H, 6.1. $C_{13}H_{18}F_6$ requires: C, 54.2; H, 6.3%); IR spectrum 8, Mass spectrum 11, NMR number 10; and the second fraction was identified as mixture of isomers of x,y-bis(1,1,2,3,3,3-hexafluoropropyl)decalin (x=1,y=2-10; x=2,y=3-10) (**34**) (5.6g, 33%), (Found: C, 43.6; H, 4.0. $C_{16}H_{18}F_{12}$ requires: C, 43.8; H, 4.1%); IR spectrum 9, Mass spectrum 12, NMR number 11.

iii. DTBP, 140°C, acetone

An autoclave (150ml) was charged with *cis*-decalin (7.0g, 0.05 mol), HFP (16.2g, 0.11 mol), DTBP (0.6g, 4 mmol) and dry acetone (8ml) and then rocked at 140°C for 24 hours. The autoclave was opened and HFP (10.7g) was recovered and a yellow liquid (12.3g) obtained. *Cis*-decalin (3.9g) was removed by distillation, further fractional distillation of the liquid gave two fractions, boiling at 120-121°C/20 mmHg and 152-153°C/20 mmHg, the first consisted of x-(1,1,2,3,3,3-hexafluoropropyl)*cis*-decalin (x=1,2,9) (**33**) (3.1g, 49%) and the second consisted of x,y-bis(1,1,2,3,3,3-hexafluoropropyl)*cis*-decalin (x=1,y=2-10; x=2,y=3-10) (**34**) (4.3g, 45%).

6.42 *Trans*-decalin



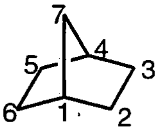
i. γ-ray initiation

A Carius tube was charged with *trans*-decalin (6.9g, 0.05 mol), HFP (15.5g, 0.1 mol) and dry acetone (8 ml) and then irradiated with γ-rays at room temperature for 5 days (7.5 Mrads). Nearly all of the HFP. (14.7g) was recovered. The liquid product mixture (7.5g) was analysed by GLC/MS and ^{19}F NMR which identified traces of x-(1,1,2,3,3,3-hexafluoropropyl)decalin (x=1,2) (**35**) (*ca.* 5% by GLC) and no further workup was performed.

ii. DTBP initiation

An autoclave (250ml) was charged with *trans*-decalin (13.9g, 0.1 mol), HFP (23.1g, 0.15 mol), DTBP (0.8g, 5.5 mmol) and dry acetone (2g) and then rocked at 140°C for 24 hours. The autoclave was opened and HFP (4.1g) was recovered and a yellow liquid (33.3g) obtained. Acetone and *trans*-decalin (2.9g) were removed by distillation, further fractional distillation of the liquid gave two fractions, boiling at 95-97°C/ 6mmHg and 130-135°C/6 mmHg. The first fraction was identified as a mixture of isomers of x-(1,1,2,3,3,3-hexafluoropropyl)decalin (x=1,2) (**35**) (11.5g, 51%), (Found: C, 54.2; H, 6.1. $C_{13}H_{18}F_6$ requires: C, 54.2; H, 6.3%); IR spectrum 10, Mass spectrum 13, NMR number 12; and the second fraction was identified as a mixture of isomers of x, y-bis(1,1,2,3,3,3-hexafluoropropyl)*trans*-decalin (x=1,y=2-10; x=2,y=3-10) (**36**) (9.5g, 27%), (Found: C, 43.6; H, 4.0. $C_{16}H_{18}F_{12}$ requires: C, 43.8; H, 4.1%); IR spectrum 11, NMR number 13, Mass spectrum 14.

6.33 Norbornane



i. γ-ray initiation

A Carius tube was charged with norbornane (7.2g, 75 mmol), HFP (15.7g, 0.1 mol) and dry acetone (8ml) and then irradiated with γ-rays at room temperature for five days (7.5 Mrads). The tube was opened and HFP (5.5g) was recovered and a colourless liquid (17.1g) obtained. Fractional distillation of the liquid gave two fractions, boiling at

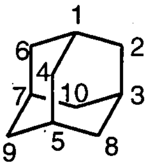
80°C/20 mmHg and 120°C/20 mmHg. The first fraction was identified as two diastereomers of *exo*-2-(1,1,2,3,3,3-hexafluoropropyl)norbornane (**37**) (13.9g, 80%), (Found: C, 48.8; H, 4.8. $C_{10}H_{12}F_6$ requires: C, 48.8; H, 4.9%); IR spectrum 12, Mass spectrum 15, NMR number 14; and the second fraction was identified as a mixture of isomers of 2,x-bis(1,1,2,3,3,3-hexafluoropropyl)norbornane (x=5,6) (**38**) (1.0g, 6%), (Found: C, 39.4; H, 3.0. $C_{13}H_{12}F_{12}$ requires: C, 39.4; H, 3.1%); IR spectrum 13, Mass spectrum 16, NMR number 15.

ii. DTBP initiation

An autoclave (150ml) was charged with norbornane (6.05g, 60 mmol), HFP (14.3g, 90 mmol) and DTBP (0.6g, 4 mmol) and then rocked for 24 hours at 140°C. The autoclave was opened, no HFP was recovered and a pale yellow liquid (19.5g) was obtained. Fractional distillation of the liquid gave two fractions, boiling at 80°C/20 mmHg and 120°C/20 mmHg, the first consisted of *exo*-2-(1,1,2,3,3,3-hexafluoropropyl)norbornane (**37**) (7.1g, 33%) and the second consisted of 2,x-bis(1,1,2,3,3,3-hexafluoropropyl)norbornane (x=5,6) (**38**) (9.5g, 27%).

6.5 Free-Radical Additions of Polycyclic Hydrocarbons to Hexafluoropropene

6.51 Adamantane



i. DTBP initiation

An autoclave (150ml) was charged with adamantane (2.7g, 40 mmol), HFP (4.5g, 60 mmol) and DTBP (0.5g, 4 mmol) and then rocked for 24 hours at 140°C. No HFP was recovered and adamantane (0.14g) crystallised of the liquid product. Fractional distillation gave three fractions, boiling at 99-101°C/ 9 mmHg, 124-126°C/ 9 mmHg and 143-145°C/ 9 mmHg. The first fraction was identified as 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane (**22**) (0.7g, 15%), (Found: C, 54.4; H, 5.5. $C_{13}H_{16}F_6$ calculated: C, 54.5; H, 5.6%); MS and NMR data agreed with literature data[97], IR spectrum 14, Mass spectrum 17, NMR number 16; the second fraction was identified as 1,3-bis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**23**) (4.2g, 63%), (Found: C, 43.7; H, 3.8. $C_{16}H_{16}F_{12}$ calculated: C, 44.0; H, 3.7%); MS and NMR data agreed with literature data [98], IR spectrum 15, Mass spectrum 18, NMR number 17; and the third fraction was identified as 1,3,5-tris(1,1,2,3,3,3-hexafluoropropyl)adamantane (**39**) (1.2g, 13%), (Found: C, 39.1; H, 2.5. $C_{19}H_{16}F_{18}$ calculated: C, 38.9; H, 2.7%); MS and NMR data agreed with literature data[98], IR spectrum 16, Mass spectrum 19, NMR number 18.

ii. DTBP initiation

An autoclave (250ml) was charged with adamantane (13.8g, 0.1 mol), HFP (17.6g, 0.12 mol) and DTBP (0.7g, 5 mmol) and then rocked for 24 hours at 140°C. No HFP was recovered and adamantane (1.1g) crystallised of the liquid product (28.0g). Fractional distillation gave two fractions, boiling at 99-101°C/9 mmHg and 124-126°C/9 mmHg, which consisted of 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane (**22**) (16.3g, 60%) and 1,3-bis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**23**) (7.9g, 19%) respectively.

iii. DTBP initiation

An autoclave (250ml) was charged with adamantane (12.0g, 0.09 mol), HFP (23.1g, 0.15 mol) and DTBP (0.7g, 5 mmol) and then rocked for 24 hours at 140°C. No HFP or adamantane were recovered and distillation of the liquid product (34.2g) gave two fractions, boiling at 99-101°C/ 9 mmHg and 124-126°C/ 9 mmHg, which consisted of 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane (**22**) (6.3g, 25%) and 1,3-bis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**23**) (24.2g, 63%) respectively.

iv. DTBP initiation

An autoclave (250ml) was charged with adamantane (6.8g, 0.05 mol), HFP. (23.5g, 0.15 mol) and DTBP (0.7g, 5 mmol) and then rocked for 24 hours at 140°C. No HFP or adamantane were recovered and distillation of the liquid product (28.3g), and distillation gave two fractions, boiling at 124-126°C/ 9 mmHg and 143-145°C/ 9 mmHg, which consisted of 1,3-bis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**23**) (1.7g, 8%) and 1,3,5-tris(1,1,2,3,3,3-hexafluoropropyl)adamantane (**39**) (24.0g, 82%) respectively.

v. DTBP initiation

An autoclave (250ml) was charged with adamantane (2.7g, 20 mmol), HFP. (20.8g, 140 mmol) and DTBP (0.5g, 4 mmol) and then rocked for 24 hours at 140°C. The autoclave was opened and HFP (8.9g) was recovered and a waxy liquid (12.7g) obtained. Kugelrohr distillation (175°C, 1mmHg) removed any involatile impurities and then the waxy mixture was then dissolved in chloroform at which point a white solid precipitated out. Removal of the solvent from the liquid layer gave 1,3,5-tris(1,1,2,3,3,3-hexafluoropropyl)adamantane (**39**) (6.9g, 59%) and the white solid was identified as 1,3,5,7-tetrakis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**40**) (5.3g, 36%) m.p. 110-112°C, (Found: C, 36.0; H, 2.2. $C_{22}H_{16}F_{24}$ requires: C, 35.9; H, 2.2%); IR spectrum 17, Mass spectrum 20, NMR number 19.

6.6 Competition Reactions

Competition reactions were performed using either DTBP or γ–ray initiation using the usual experimental procedure described previously. A 0.15 molar deficiency of HFP to hydrocarbon was used. The reactions were followed by the disappearance of hydrocarbons from capillary GLC traces (Flame ionisation detector) before and after the reaction, therefore eliminating any differences in detector responses.

6.61 Competition between *cis-* and *trans-*decalin

An autoclave (150ml) was charged with *cis*-decalin (6.9g, 50 mmol), *trans*-decalin (6.9g, 50 mmol), HFP (2.3g, 15 mmol) and DTBP (0.3g, 2 mmol) and then rocked at 140°C for 24 hrs. The autoclave was opened and HFP (0.1g) was recovered. The GLC traces from before and after the reaction showed the peak integration of *cis*-decalin decreased from 52.18% to 43.12% and the peak integration of *trans*-decalin decreased from 47.82% to 43.69%.

6.62 Competition between cyclohexane and cyclopentane

An autoclave (150ml) was charged with cyclohexane (4.2g, 50 mmol), cyclopentane (3.5g, 50 mmol), HFP (2.4g, 16 mmol) and DTBP (0.3g, 2 mmol) and then rocked at 140°C for 24 hrs. No HFP was recovered. The Glc. traces showed the peak integration of cyclohexane decreased from 54.76% to 44.54% and the peak integration of cyclopentane decreased from 45.13% to 36.94%.

6.63 Competition between cyclohexane and *trans*-decalin

An autoclave (150ml) was charged with cyclohexane (4.2g, 50 mmol), *trans*-decalin (6.9g, 50 mmol), HFP (2.4g, 16 mmol) and DTBP (0.3g, 2 mmol) and then rocked at 140°C for 24 hrs. No HFP was recovered and the GLC traces showed the peak integration of cyclohexane decreased from 53.41% to 49.75% and the peak integration of *trans*-decalin decreased from 46.58% to 34.46%.

6.64 Competition between cyclohexane and cyclopentane

A Carius tube was charged with cyclohexane (8.4g, 0.1 mol) and cyclopentane (7.0g, 0.1 mol) and HFP (4.5g, 0.03 mol) and then irradiated with γ–rays at room temperature for four days (6 Mrads). No HFP was recovered and the GLC traces showed the peak integration of cyclohexane decreased from 55.58% to 44.76% and the peak integration of cyclopentane decreased from 44.29% to 38.83%.

6.65 Competition between cyclohexane and *trans*-decalin

A Carius tube was charged with cyclohexane (2.5g, 30 mmol) and *trans*-decalin (4.0g, 30 mmol) and HFP (1.4g, 9 mmol) was irradiated with γ–rays at room temperature for four days (6 Mrads). The tube was opened and HFP (0.35g) was recovered. The GLC traces showed the peak integration of cyclohexane decreased from 46.72% to 41.74% and the peak integration of *trans*-decalin decreased from 52.82% to 48.46%.

6.66 Competition between cyclohexane and *cis*-decalin

A Carius tube was charged with cyclohexane (2.5g, 30 mmol) and *cis*-decalin (4.0g, 30 mmol) and HFP (1.3g, 9 mmol) and then irradiated with γ–rays at room temperature for eight days (12 Mrads). The tube was opened and HFP (0.94g) was recovered. The GLC traces showed the peak integration of cyclohexane decreased from 42.99% to 41.14% and the peak integration of *cis*-decalin decreased from 57.01% to 55.45%.

6.7 Crude competition reactions

Crude competition reactions were performed using DTBP at 140°C and equimolar ratio of each hydrocarbon and HFP, using the same experimental technique as previously outlined. Unfortunately, due to the nature of the reactants, GLC's of the starting materials could not be run and so the GLC ratios of the products included differences in response factors.

6.71 Competition between adamantane and 2-methylpropane

An autoclave (150ml) was charged with adamantane (6.8g, 50 mmol), 2-methylpropane (2.9g, 50 mmol), HFP (7.5g, 50 mmol) and DTBP (0.5g, 3 mmol) and then rocked at 140°C for 24 hrs. Analysis of the product GLC trace showed the peak integration of 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane (**22**) 32%, 1,3-bis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**23**) 12% and 1,1,2,3,3,3-hexafluoro-4,4-dimethylpentane (**30**) 9%.

6.72 Competition between propane and 2-methylpropane

An autoclave (150ml) was charged with propane (4.4g, 0.1 mol), 2-methylpropane (5.8g, 0.1 mol), HFP (15.0g, 0.1 mol) and DTBP (0.6g, 4.1 mmol) and then rocked at 140°C for 24 hrs. Analysis of the product GLC trace showed the peak integration of 1,1,1,2,3,3-hexafluoro-4-methylpentane (**28**) 28% and 1,1,1,2,3,3-hexafluoro-4,4-dimethylpentane (**30**) 62%.

Chapter Seven

Experimental to Chapter Three

7.1 General Procedure

7.11 Potassium hydroxide eliminations

Potassium hydroxide powder was dried under vacuum and then dry ethanol, was added under nitrogen, with stirring. The solution was then heated to the required temperature, with stirring, and the hexafluoropropene adduct added dropwise. The reaction mixture was then heated, with stirring, for the required time span. On termination, the reaction mixture was poured into water and neutralised with 10% hydrochloric acid. The organic layer was extracted with dichloromethane, dried over $MgSO_4$, and then fractionally distilled to give a purified sample of the alkene.

7.12 Sodium *tert*-Butoxide eliminations

Sodium *tert*-Butoxide was dried under vacuum and then dry solvent was added under nitrogen, with stirring. The resulting mixture was cooled to the required temperature and then the hexafluoropropene adduct was added dropwise. The reaction mixture was then stirred, for the required time span at the same temperature. On termination, the reaction mixture was poured into water and neutralised with 10% hydrochloric acid. The organic layer was extracted with dichloromethane, dried over $MgSO_4$, and then fractionally distilled to give a purified sample of the alkene.

7.2 Deuterium exchange reactions

7.21 1,1,2,3,3,3-hexafluoropropylcyclohexane (24)

A sealable NMR tube was charged with Sodium t-butoxide (0.1g, 0.7 mmol), t-butanol(D) (*ca.* 1 ml) and compound (**24**) (0.3g, 1.3 mmol). The tube was sealed under vacuum and then allowed to warm to room temperature and left for a further 15 minutes. A ^{19}F NMR number was then run on the contents, which detected 2D-hexafluoropropylcylohexane (**24a**) (4% by NMR).

7.22 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane (22)

A sealable NMR tube was charged with Sodium t-butoxide (0.1g, 0.6 mmol), t-butanol(D) (*ca.* 1 ml) and compound (**22**) (0.3g, 1 mmol). The tube was allowed to warm to room temperature and left for a further 15 minutes. A ^{19}F NMR number was then run on the contents, which detected which detected 2D-hexafluoropropyladamantane (**22a**) (9% by NMR).

7.3 Dehydrofluorination of Hexafluoropropene Adducts

7.31 1,1,2,3,3,3-hexafluoropropylcyclohexane (24)

i. KOH, 50°C

Dry ethanol (15 ml) was added to potassium hydroxide (1.9g, 33 mmol) and the solution was heated to 50°C. Compound (**24**) (3.5g, 15 mmol) was added, and the mixture was refluxed for two and a half hours. Dichloromethane and ethanol were removed by distillation and further distillation gave a fraction, boiling at 140-143°C, containing two products identified as pentafluoroprop-2-enylcyclohexane (**43**) (2.9g, 90%), MS and NMR data agreed with literature[99]; Mass spectra 21 and 22, NMR number 20 and 21; and 1-ethoxy-2,3,3,3-tetrafluoroprop-2-enylcyclohexane (**44**) (1% by NMR).

ii. Na O^{t}Bu, 25°C

Dry t-butanol (15 ml) was added to sodium t-butoxide (9.0g, 80 mmol) and the suspension was warmed to 25°C. Compound (**24**) (9.4g, 40 mmol) was added, and the mixture was stirred for 15 minutes. Dichloromethane and t-butanol were removed by distillation and further distillation of the organic layer gave the major fraction, boiling at 140-143°C, identified as pentafluoroprop-2-enylcyclohexane (**43**) (5.0g, 60%).

iii. Na O^{t}Bu, 0°C

Dry isopropyl ether (100 ml) was added to sodium t-butoxide (50.5g, 0.45 mol) and the suspension was cooled to 0°C. Compound (**24**) (70.2g, 0.3 mol) was added, and the mixture was stirred for 30 minutes. Dichloromethane, isopropyl ether and t-butanol were removed by distillation and further distillation of the organic layer gave the major fraction, boiling at 142-144°C, identified as Z-pentafluoroprop-2-enylcyclohexane

(**43a**) (59.1g, 92%) (Found: C, 50.6; H, 5.2. $C_9H_{11}F_5$ calculated: C, 50.5; H, 5.2%), NMR number 20, Mass spectrum 21, IR spectrum 18.

iv. Na O^{t}Bu, 0°C

Dry hexane (80 ml) was added to sodium t-butoxide (16.6g, 0.15 mol) and the suspension was cooled to 0°C. Compound (**24**) (23.9g, 0.1 mol) was added, and the mixture was stirred for 10 minutes. Dichloromethane, hexane and t-butanol were removed by distillation and further distillation of the organic layer gave the major fraction, boiling at 143°C, identified as Z-pentafluoroprop-2-enylcyclohexane (**43a**) (18.6g, 85%).

7.32 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane (22)

i. KOH, 81°C

Dry ethanol (12 ml) was added to potassium hydroxide (1.7g, 31 mmol) and the solution was heated to 81°C. Compound (**22**) (4.0g, 14 mmol) was added, and the mixture was refluxed for 15 hrs. Dichloromethane and ethanol were removed by distillation and further distillation gave a fraction, boiling at 220-222°C, identified as E-pentafluoroprop-2-enyladamantane (**45a**) (3.2g, 87%) (Found: C, 58.6; H, 5.9. $C_{13}H_{15}F_5$ requires: C, 58.6; H, 5.7%), NMR number 22, Mass spectrum 23, IR spectrum 19.

ii. Na O^{t}Bu, RT

Dry isopropyl ether (50 ml) was added to sodium t-butoxide (7.9g, 70 mmol) and compound (**22**) (11.4g, 40 mmol) was added to the suspension, at room temperature, and stirred for 30 minutes. Dichloromethane, isopropyl ether and t-butanol were removed by distillation and further distillation gave a fraction, boiling at 219-221°C, which consisted of 1-(E-pentafluoroprop-2-enyl)adamantane (**45a**) (9.6g, 90%).

iii. Na O^tBu, -10°C

Dry isopropyl ether (20 ml) was added to sodium t-butoxide (3.2g, 28 mmol) and cooled to -10°C, using a salt-ice bath. Compound (**22**) (3.75g, 13 mmol) was added dropwise and the mixture was stirred for 30 minutes at -10°C. Dichloromethane, isopropyl ether and t-butanol were removed by distillation and further distillation gave a fraction, boiling at 219-221°C, which consisted 1-(Z-pentafluoroprop-2-enyl)adamantane (**45b**) (3.1g, 85%) (Found: C, 58.7; H, 5.4. $C_{13}H_{15}F_5$ requires: C, 58.6; H, 5.7%), NMR number 23, Mass spectrum 24, IR spectrum 20.

7.33 *trans*-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (27a)

Dry isopropyl ether (25 ml) was added to sodium t-butoxide (2.1g, 18 mmol) and cooled to -10°C, using a salt-ice bath. Compound (**27a**) (3.5g, 9 mmol) was added and the mixture was stirred for 30 minutes at -10°C. Dichloromethane, isopropyl ether and t-butanol were removed by distillation and methanol was added to the organic layer which was then cooled in an acetone slush bath (-78°C). A white solid precipitated out which was identified as *trans*-1,4-bis(Z-pentafluoroprop-2-enyl)cyclohexane (**46**) (2.1g, 72%) mp. 101-102°C, (Found: C, 41.8; H, 2.9. $C_{12}H_{10}F_{10}$ requires: C, 41.9; H, 2.9%), NMR number 24, Mass spectrum 25, IR spectrum 21.

7.34 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x=2-4) (27)

Dry ethyl ether (50 ml) was added to sodium t-butoxide (15.9g, 142 mmol) and cooled to -10°C, using a salt-ice bath. Compounds (**27**) (16.0g, 40 mmol) in ethyl ether (30 ml) was added and the mixture was stirred for 30 minutes at -10°C. Dichloromethane, ethyl ether and t-butanol were removed by distillation and further distillation of the organic layer gave a fraction, boiling at 100-102°C/21mmHg, which was identified as a mixture of *cis*-1,3-bis(Z-pentafluoroprop-2-enyl)cyclohexane (**47**) (8.2g, 57%) (Found: C, 41.7; H, 2.9. $C_{12}H_{10}F_{10}$ requires: C, 41.9; H, 2.9%), NMR number 25, Mass spectrum 26, IR spectrum 22; and *trans*-1,4-bis(Z-pentafluoroprop-2-enyl)cyclohexane (**46**) (4.3g, 30%) which precipitated out on cooling in an acetone slush bath (-78°C).

7.35 1,1,2,3,3,3-hexafluoropropylcyclopentane (**25**)

Dry ethyl ether (40 ml) was added to sodium t-butoxide (5.0g, 40 mmol) and cooled to -78°C, using an acetone slush bath. Compound (**25**) (4.4g, 20 mmol) was added dropwise and the mixture was stirred for 35 minutes at -78°C. On completion the reaction was allowed to slowly warm to room temperature. Dichloromethane, ethyl ether and t-butanol were removed from the organic layer by distillation and further distillation gave a fraction, boiling at 119-121°C, identified Z-pentafluoroprop-2-enylcyclopentane (**49**) (3.0g, 68%), (Found: C, 47.9; H, 4.5. $C_8H_9F_5$ requires: C, 48.0; H, 4.5%), NMR number 26, Mass spectrum 27, IR spectrum 23.

7.36 1,x-(1,1,2,3,3,3-hexafluoropropyl)cyclopentane (x=2,3) (**26**)

Dry ethyl ether (50 ml) was added to sodium t-butoxide (9.0g, 80 mmol) and cooled to -78°C, using an acetone slush bath. Compound (**26**) (7.4g, 20 mol) was added and the mixture was stirred for 35 minutes at -78°C. Dichloromethane, ethyl ether and t-butanol were removed from the organic layer by distillation and further distillation gave a fraction, boiling at 76-77°C/21mm Hg, identified as a mixture of three isomers of 1,x-(Z-pentafluoroprop-2-enyl)cyclopentane (x=2,3) (**50**) (4.0g, 60%) (Found: C, 43.9; H, 2.6. $C_{11}H_8F_{10}$ requires: C, 43.7; H, 2.4%), IR spectrum 24; Mass spectra 28, 29 and 30; NMR number 27, 28 and 29.

7.37 x-(1,1,2,3,3,3-hexafluoropropyl)*trans*-decalin (x=1,2) (**35**)

Dry ethyl ether (20 ml) was added to sodium t-butoxide (4.5g, 40 mmol) and cooled to -10°C, using a salt-ice bath. Compound (**35**) (5.8g, 20 mmol) was added and the mixture was stirred for 30 minutes at -10°C. Dichloromethane, ethyl ether and t-butanol were removed from the organic layer by distillation and further distillation gave a fraction, boiling at 75-77°C/ 6mmHg, identified as a mixture of two isomers of x-(Z-pentafluoroprop-2-enyl)*trans*-decalin (x=1,2) (**51**) (8.8g, 82%) (Found: C, 58.1; H, 6.6. $C_{10}H_{17}F_5$ requires: C, 58.2; H, 6.4%), IR spectrum 25; Mass spectra 31 and 32; NMR number 30 and 31.

7.38 x-(1,1,2,3,3,3-hexafluoropropyl)*cis*-decalin (x=1,2,9) (33)

Dry ethyl ether (40 ml) was added to sodium t-butoxide (4.5g, 40 mmol) and cooled to -10°C, using a salt-ice bath. Compound (**34**) (5.8g, 20 mmol) was added and the mixture was stirred for 30 minutes at -10°C. Dichloromethane, ethyl ether and t-butanol were removed from the organic layer by distillation and further distillation gave a fraction, boiling at 138-140°C/ 20mmHg, identified as a mixture of isomers of x-(Z-pentafluoroprop-2-enyl)cis-decalin (x=1,2,9) (**52**) (4.6g, 85%) (Found: C, 58.1; H, 6.3. $C_{10}H_{17}F_5$ requires: C, 58.2; H, 6.4%), IR spectrum 26; Mass spectra 33 and 34; NMR number 32 and 33.

7.39 *exo*-2-(1,1,2,3,3,3-hexafluoropropyl)norbornane (37)

Dry isopropyl ether (20 ml) was added to sodium t-butoxide (6.8g, 60 mmol) and cooled to -10°C, using a salt-ice bath. Compound (**37**) (7.5g, 30 mmol) was added and the mixture was stirred for 1 hour at -10°C. Dichloromethane, isopropyl ether and t-butanol were removed from the organic layer by distillation and further distillation gave a fraction, boiling at 65-67°C/ 20mmHg, which consisted of *exo*-2-(Z-pentafluoroprop-2-enyl)norbornane (**53**) (6.2g, 90%) (Found: C, 53.1; H, 4.9. $C_9H_{11}F_5$ requires: C, 53.1; H, 4.9%), IR spectrum 27, Mass spectrum 35, NMR number 34.

7.40 *exo*-2,x-(1,1,2,3,3,3-hexafluoropropyl)norbornane (x=5,6) (35)

Dry isopropyl ether (15 ml) was added to sodium t-butoxide (4.5g, 40 mmol) and the suspension was cooled to -10°C, in a salt-ice bath. Compound (**35**) (4.6g, 12 mmol) was added and the mixture was stirred for 30 minutes at -10°C. Dichloromethane, isopropyl ether and t-butanol were removed from the organic layer by distillation and further distillation gave a fraction, boiling at 101103°C/ 20mmHg, identified as a mixture of two isomers of *exo*-2,x-(Z-pentafluoroprop-2-enyl)norbornane (x=5,6) (**54**) (3.8g, 93%) (Found: C, 43.6; H, 2.8. $C_9H_{11}F_5$ requires: C, 43.8; H, 2.8%), IR spectrum 28; Mass spectra 36 and 37; NMR number 35 and 36.

7.41 1,3,5,7-tetrakis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**40**)

Dry ethyl ether (30ml) was added to sodium t-butoxide (4.5g, 40 mmol), and stirred at room temperature. Compound (**40**) (3.7g, 5 mmol) in ethyl ether (20ml) was added and the mixture was stirred for 30 minutes at room temperature. Dichloromethane, ethyl ether and t-butanol were removed from the organic layer by distillation and further Kugelrohr gave a fraction, boiling at *ca.* 175°C/ 1mmHg, identified as a mixture of two isomers of 1,3,5,7-tetrakis(pentafluoroprop-2-enyl)adamantane (**55a**) (2.6g, 78%) (Found: C, 40.2; H, 1.8. $C_{22}H_{12}F_{20}$ requires: C, 40.3; H, 1.8%) Mass spectrum 39, NMR number 38; from which 1,3,5,7-tetrakis(E-pentafluoroprop-2-enyl)adamantane (**55**), IR spectrum 29; Mass spectrum 38, NMR number 37; precipitated out when the mixture was dissolved in chloroform and cooled in an acetone slush bath.

7.5 Caesium Fluoride Isomerisations

7.51 1-(Z-pentafluoroprop-2-enyl)adamantane (**45b**)

A Carius tube was charged with caesium fluoride (7.6g, 50 mmol), dry tetraglyme (10ml) and compound (**45b**) (2.7g, 10 mmol). The tube was cooled (liquid air) and sealed under vacuum. It was allowed to warm to room temperature and then it was heated in a rotating oil bath at 200°C for 50 hrs. On completion the tube was opened and a sample of the product mixture was transferred into an NMR tube and a ^{19}F NMR number was run on it, which showed almost complete conversion to 1-(Z-pentafluoroprop-2-enyl)adamantane (**45a**) (*ca.* 97%).

7.52 Z-pentafluoroprop-2-enylcyclohexane (**43a**)

A Carius tube was charged with caesium fluoride (7.1g, 50 mmol), dry tetraglyme (10ml) and compound (**43a**) (2.1g, 10 mmol). The tube was cooled (liquid air) and sealed under vacuum. It was allowed to warm to room temperature and then it was heated in a rotating oil bath at 200°C for 50 hrs. On completion the tube was opened and a sample of the product mixture was transferred into an NMR tube and a ^{19}F NMR number was run on it, which showed a 37% conversion to E-pentafluoroprop-2-enylcyclohexane (**43b**).

Chapter Eight

Experimental to Chapter Four

8.1 General Procedure

The apparatus for fluorination with cobalt trifluoride consisted of a nickel tube with inlet and outlet pipes and nickel paddles attached to a rod situated along the centre of the tube and rotated by an electric motor. Cobalt trifluoride (440g) was contained in the tube and heated to the required temperature, using an electric heating tape wrapped around the tube, with continual stirring. Dry nitrogen (30ml/min) was passed through the reactor for 10 mins, prior to use. Starting materials were dropped into the reactor at a rate of 1ml/10mins. in a nitrogen flow (30ml/min.). After all the compound for fluorination was added, the reactor was flushed with nitrogen for 30 mins. Products were collected in a trap cooled with liquid air, which was detached from the reactor and left to warm up in an efficient fumehood. A condenser containing anhydrous soda-lime was attached so as to remove any hydrogen fluoride and the product pippetted out. Any polyfluorinated products were removed by continuous extraction with acetone and pure samples of the perfluorinated product were isolated preparative scale GLC.

After fluorination the cobalt fluoride system was regenerated by passing 50% fluorine gas (95ml/min) ,from a cylinder, via FEP tubing through the heated reactor (280°C) until the soda-lime trap, attached to the exit, became detectably warm.

8.2 Cobalt trifluoride fluorinations

8.21 2,5-Bis(1,1,2,3,3,3-hexafluoropropyl)tetrahydrofuran (**58**)

Compound (**58**) (7.4g, 20 mmol) was passed over a fully regenerated cobalt trifluoride bed at 400°C, according to the general procedure outlined above. Continuous extraction, with acetone, of the liquid product (8.9g) removed the polyfluorinated products and preparative scale GLC (Fomblin column, 160°C) of the resulting perfluorocarbon layer, isolated perfluoro-2,5-dipropyltetrahydrofuran (**59**) (7.1g, 80%) NMR and MS in agreement with earlier work in carried out in this laboratory[75,90]. MS spectrum 40 and NMR number 39.

8.22 1,1,2,3,3,3-hexafluoropropylcyclohexane (24)

Compound (**24**) (3.5g, 15 mmol) was passed over the fully regenerated cobalt trifluoride, at 375°C. Continuous extraction, with acetone, followed by preparative scale GLC (Fomblin column, 120°C) of the liquid product (6.0g) gave perfluoropropylcyclohexane (**60**) (63%) b.p. 132-134°C (Siwoloboff); (Accurate mass, M^+-19 found 430.97; $C_9F_{17}^+$; calculated 431.06). NMR and MS in agreement with literature[131], IR spectrum 30, MS spectrum 41 and NMR number 40.

8.23 1,1,2,3,3,3-hexafluoropropylcyclopentane (25)

Compound (**25**) (3.9g, 18 mmol), was passed over the fully regenerated cobalt trifluoride, at 375°C. Continuous extraction followed by preparative scale GLC (Fomblin, 110°C) of the liquid product (6.12g) gave perfluoropropylcyclopentane (**51**) (60%) b.p. 103-105°C (Siwoloboff); (Accurate mass, M^+-19 too weak; $C_9F_{17}^+$; required 381.06). IR spectrum 31, MS spectrum 42 and NMR number 41.

8.24 *trans*-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (27a)

i. 400°C

Compound (**27a**) (2.4g, 6 mmol) was passed over the fully regenerated cobalt trifluoride, at 400°C. Continuous extraction followed by preparative scale GLC (Fomblin, 165°C) of the liquid product (2.9g) gave a mixture of *cis*- and *trans*-isomers of perfluoro-1,4-dipropylcyclohexane (**62**) (60%) (Accurate mass, M^+-19 found 580.96; $C_{12}F_{23}^+$; calculated 581.07); IR spectrum 32, MS spectrum 43 and 44, NMR number 42 and 43. Several recrystallisations from chlorotrifluoromethane cooled to -15°C gave only *trans*-perfluoro-1,4-dipropylcyclohexane (**62a**); m.p. 80-81°C.

ii. 350°C

Compound (**27a**) (3.5g, 9.1 mmol) was passed over the cobalt trifluoride bed at 350°C. Continuous extraction followed by preparative scale GLC (Fomblin, 165°C) of the liquid product (3.7g) gave a mixture of *cis*- and *trans*-isomers of perfluoro-1,4-dipropylcyclohexane (**62**) (70%).

8.25 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x=2-4) (27)

i. 400°C

Compound (**27**) (3.5g, 9 mmol) was passed over cobalt trifluoride, at 400°C. Continuous extraction followed by preparative scale GLC (Fomblin, 165°C) of the liquid product (4.1g) gave a mixture of isomers of perfluoro-1,x-dipropylcyclohexane (x=2-4) (**62**) and (**63**) (44%) b.p. 167-169°C (Siwoloboff); (Accurate mass, M^+-19 found 580.96; $C_{12}F_{23}^+$; calculated 581.07); IR spectrum 33, MS spectrum 45 and 46, NMR number 44 and 45.

ii. 375°C

Compound (**27**) (5.0g, 13 mmol), was passed over cobalt trifluoride, at 375°C. Continuous extraction followed by preparative scale GLC (Fomblin, 165°C) of the liquid product (6.5g) gave a mixture of isomers of perfluoro-1,x-dipropylcyclohexane (x=2-4) (**62**) and (**63**) (58%)

8.26 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclopentane (x=2,3) (25)

i. 400°C

Compound (**25**) (1.9g, 5 mmol) was passed over the CoF_3 bed at 400°C. Continuous extraction of the liquid product (1.3g) with acetone overnight, followed by preparative scale GLC. (Fomblin, 160°C) gave a mixture of isomers of perfluoro-1,x-dipropylcyclopentane (x=2,3) (**64**) (71%), b.p. 159-161°C (Siwoloboff); (Accurate mass, M^+-19 found 530.97); $C_{11}F_{21}^+$ calculated 530.86); IR spectrum 34, MS spectrum 47, NMR number 46.

ii. 375°C

Compound (**25**) (5.0g, 14 mmol), was passed over the CoF_3 bed at 375°C. Continuous extraction of the liquid product (5.7g) with acetone overnight, followed by preparative scale GLC. (Fomblin, 160°C) gave a mixture of isomers of perfluoro-1,x-dipropylcyclopentane (x=2,3) (**64**) (71%)

8.27 x-(1,1,2,3,3,3-hexafluoropropyl)*cis*-decalin (x=1,2,9) (33)

Compound (**33**) (1.8g, 6 mmol) was passed over the CoF_3 bed at 400°C. Continuous extraction of the liquid product (3.0g) gave a perfluorocarbon mixture containing perfluoro-x-propyldecalin (x=1,2,9) (**66**) (68% by GLC)(Accurate mass, M^+-19 found 592.96; $C_{13}F_{23}^+$ calculated 593.08); IR spectrum 35, MS spectrum 48, NMR number 47.

8.28 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane (22)

Compound (**22**) (2.0g, 7 mmol) was passed over the fully regenerated CoF_3 bed at 400°C. The resulting liquid product (2.28g) was very complex, as in table 4.7, and although perfluoro-1-propyladamantane (**67**) (32% by GLC.; M^+, 574; MS spectrum 49) was identified by GLC/MS, it could not be isolated by preparative scale GLC

8.29 Z-pentafluoro-2-propenylcyclohexane (43a)

Compound (**43a**) (4.0g, 19 mmol) was passed over the fully regenerated CoF_3 bed at 375°C. Continuous extraction, with acetone, of the liquid product (7.1g) gave perfluoropropylcyclohexane (**60**) (6.4g, 90%).

8.3 Methanol/TFE Telomers

8.31 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-tetradecafluorononanol (68)

Compound (**68**) (3.9g, 9 mmol) was passed over the CoF_3 bed at 400°C. Continuous extraction, with acetone, of the liquid product (3.4g) gave perfluorooctane (**68a**) (92%); MS spectrum 50, NMR number 48.

8.32 1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoroheptanol (69)

i. 400°C

Compound (**69**) (3.0g, 9 mmol) was passed over the CoF_3 bed at 400°C. Continuous extraction, with acetone, of the liquid product (1.97g) gave perfluorohexane (**69a**) (93%); MS spectrum 51, NMR number 49.

ii. 300°C

Compound (**69**) (2.2g, 7 mmol) was passed over the fully regenerated CoF_3 bed at 300°C. Continuous extraction, with acetone, of the liquid product (1.2g), gave perfluorohexane (**69a**) (24%). Addition of water to the acetone layer gave 1H-perfluorohexane (**70**) (76%); NMR number 50, MS spectrum 52.

8.4 Fluorinations in Anhydrous Hydrogen Fluoride

8.41 General apparatus

A metal vacuum line with Whitey valves, a soda-lime tower and Pyrex glass trap (cooled with liquid N_2) was connected to a Teflon FEP sub-line to which a Teflon FEP T-piece reactor containing the reactants in separate tubes was then attached. The subline was equipped with Teflon valves each having a Kel-F stem with a Teflon tip so as to isolate the sub-line from the metal vacuum line, because anhydrous HF in contact with the metal line is a powerful oxidising system in the presence of fluoroacid.

All the starting materials were weighed and transferred into the dry Teflon FEP T-piece reactor on an aluminium tray inside a dry atmosphere bag, as spillage of the highly oxidising reagents could ignite the polyethylene bag. All the reactions were carried out under vacuum in the Teflon FEP subline

8.42 $AgNiF_6$ Fluorination of *trans*-1,4-bis(z-pentafluoro-2-propenyl)cyclohexane (62)

One leg of the FEP T-piece reactor was charged with compound (**62**) (0.1g, 0.4 mmol) and anhydrous HF (1ml) was distilled on to it. The other leg was charged with $AgNiF_6$ (1.0g, 3.6 mmol) and anhydrous HF (2ml) was distilled onto it to form a slurry. This leg was then poured slowly, at ~ 0°C, onto the substrate. A fast exothermic interaction occurred, but no non-condensable gas (e.g. CF_4) was produced. The supernatant anhydrous HF was decanted back so as to ensure all of the solid oxidiser interacted with the substrate. The $Ag(II)Ni(IV)F_6$ was reduced to an olive green solid ($Ag(I)Ni(II)F_3$).The anhydrous HF and any volatiles were distilled under vacuum in the closed T-apparatus to give a clear distillate. The anhydrous HF was allowed to distil slowly into the soda-lime tower without bumping. When all anhydrous HF had been visibly consumed a very small colourless liquid remained, which was extracted using Arklone, but its ^{19}F NMR number contained only solvent signals. The other reactor limb (which contained the $AgNiF_3$) was washed with Arklone and its ^{19}F NMR number showed a definite set of CF_x signals indicating the product was 1H,4H-perfluorodipropylcyclohexane (**71**).

8.43 NiF_3 Fluorination of 2,5-bis(Z-pentafluoro-2-propenyl)tetrahydrofuran (72)

Tubes A and B of the T-piece reactor were charged with NiF_3 (1.8g, 15 mmol) and compound (**72**) (0.4g, 1.3 mmol) respectively. The reactor was attached to the FEP sub-line and evacuated. Anhydrous HF was distilled onto both the nickel salt (~2 ml), to give a black slurry, and the organic substrate (~2 ml), which was slightly soluble. The black slurry was poured slowly, at ~ 0°C, onto the organic substrate. A fast exothermic interaction occurred with the nickel salt reduced to brown nickel difluoride. The supernatant anhydrous HF was decanted back so as to ensure all of the solid oxidiser interacted with the substrate and when the reaction was complete the anhydrous HF was slowly distilled, without bumping, into the soda-lime trap. The remaining products were extracted with chlorotrifluoromethane and a ^{19}F NMR of the extract identified a set of weak CF_x signals corresponding to perfluoro-2,5-dipropyltetrahydrofuran (**59**).

Chapter Nine

Experimental to Chapter Five

9.1 Attempted additions of cyclohexyl chloride to hexafluoropropene (HFP)

i. γ-ray initiation

A Carius tube was charged with cyclohexyl chloride (8.9g, 75 mmol) and HFP (15.4g, 100 mmol) and then irradiated for 4 days with γ-rays (6 Mrads) at room temperature. The tube was opened and gaseous components (14.7g) were recovered. Analysis of the colourless liquid (9.2g), by GLC/MS and ^{19}F NMR identified traces of x-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl chloride (x=2-4) (**74**), but no further workup was performed.

ii. DTBP initiation

An autoclave (150ml) was charged with cyclohexyl chloride (8.0g, 67 mmol), HFP (15.4g, 100 mmol) and DTBP (0.6g, 4 mmol) and then rocked at 140°C for 24 hrs. The autoclave was opened and gaseous products (14.9g) were recovered. A pale yellow liquid (8.8g) was removed and analysis of the mixture, by GLC/MS and ^{19}F NMR, identified traces of x-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl chloride (x=2-4) (**74**) and cyclohexene (6% by GLC).

9.2 Chlorination of 1,1,2,3,3,3-hexafluoropropylcyclohexane (**24**)

A mixture of compound (**24**) (27.7g, 0.12 mol) and sulphuryl chloride (8.4g, 0.06 mol) was irradiated with UV light (1000W, medium pressure, mercury lamp, at a distance of *ca.* 100mm), whilst being cooled with an electric fan to *ca.* 60°C) until no further gases were evolved from the mixture (1.5 hours). Distillation of the remaining liquid (29.3g) gave a fraction, boiling at 163-165°C, identified as x-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl chloride (x=2-4) (**74**) (8.60g, 27%) (Found: C, 40.2; H, 4.1. $C_9H_{10}ClF_6$ requires: C, 40.2; H, 4.1%), NMR number 51, MS spectrum 53.

9.3 Chlorination of 1,1,2,3,3,3-hexafluoropropylcyclopentane (**25**)

A mixture of compound (**25**) (10.6g, 50 mmol) and sulphuryl chloride (6.5g, 50 mmol) was irradiated was irradiated with UV light, using the procedure outlined above, for 2 hours. Distillation of the remaining liquid gave a fraction, boiling at 153-155°C, identified as x-(1,1,2,3,3,3-hexafluoropropyl)cyclopentyl chloride (x=2-4) (**75**) (9.5g, 83%) (Found: C, 37.5; H, 3.5. $C_8H_9ClF_6$ requires: C, 37.7; H, 3.6%), NMR number 52, MS spectrum 54.

9.5 Dehydrochlorination of x-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl chloride (x=2-4) (74)

i. NaOH (aq)

Compound (**74**) (5.5g, 20 mmol) was added to aqueous 33% Sodium hydroxide (1.4g, 35 mmol) and refluxed at 90°C for 20 hours. The reaction mixture was then cooled and the organic layer was separated and dried with $MgSO_4$. GLC/MS analysis of the reaction mixture identified starting material only.

ii. Et_3N

Compound (**74**) (7.6g, 28 mmol) was added to a mixture of triethylamine (3.6g, 35 mmol) and diethyl ether (10ml) and stirred at room temperature for 20 hours. The reaction mixture was neutralised with 10% HCl and the organic layer was separated and dried with $MgSO_4$. GLC/MS analysis of the reaction mixture identified starting material only.

iii. LiCl, DMF

Lithium chloride (1.3g, 30 mmol) was dried under vacuum and dry dimethyl formamide (20ml) was added. To this mixture was then added compound (**74**) (5.3g, 20 mmol). The resulting miscible mixture was refluxed at 150°C for 20 hours. The reaction mixture was then cooled, neutralised with 10% HCl, washed with water and the organic layer was separated and dried with $MgSO_4$. Distillation of the organic layer gave a fraction, boiling at 146°C, identified as x-(1,1,2,3,3,3-hexafluoropropyl)cyclohex-1-ene (x=2-4) (**76**) (4.1g, 89%) (Found: C, 47.0; H, 4.3. $C_9H_9F_6$ requires: C, 46.7; H, 4.3%), NMR number 53, MS spectrum 55, IR spectrum 36.

iv. DMF

Compound (**74**) (4.3g, 16 mmol) was added to dry dimethyl formamide (15ml) and the mixture was refluxed at 150°C for 20 hours. in a round bottomed flask fitted with a water condenser and a drying tube. The reaction mixture was then cooled, neutralised with 10% HCl, washed with water and the organic layer was separated and dried with $MgSO_4$. Distillation of the organic layer gave a fraction, boiling at 146°C, identified as x-(1,1,2,3,3,3-hexafluoropropyl)cyclohex-1-ene (x=2-4) (**76**) (1.7g, 46%)

9.6 Dehydrochlorination of x-(1,1,2,3,3,3-hexafluoropropyl)cyclopentyl chloride (x=2,3) (**75**)

Lithium chloride (2.7g, 60 mmol) was dried under vacuum and dry dimethyl formamide (20ml) was added and to this mixture compound (**75**) (10.8g, 40 mmol) was then added. The resulting miscible mixture was refluxed at 150°C for 20 hours. The reaction mixture was then cooled, neutralised with 10% HCl, washed with water and the organic layer was separated and dried with $MgSO_4$. Distillation of the organic layer gave a fraction, boiling at 130-132°C, identified as x-(1,1,2,3,3,3-hexafluoropropyl)cyclopent-1-ene (x=2,3) (**78**) (6.6g, 72%) (Found: C, 43.8; H, 3.7. $C_8H_8F_6$ requires: C, 44.0; H, 3.7%), NMR number 54, MS spectrum 56.

9.7 Reactions of the pentafluoropropenyl derivatives of cyclohexane

9.91 Z-pentafluoro-2-propenylcyclohexane (**43a**)

Sodium metal (0.9g, 40 mmol) was added to ethanol (18.4g, 0.4 mol) under nitrogen until it had reacted completely. Compound (**43a**) (4.3g, 20 mmol) was added dropwise to the alkoxide solution and the mixture was warmed to 80°C and refluxed for 138 hours. On termination of the reaction, the product mixture was diluted with water, neutralised with 10% hydrochloric acid and the organic layer was extracted with dichloromethane and dried with magnesium sulphate. Distillation removed any solvents and further distillation of the liquid product gave a fraction, boiling at 178°C, identified as an inseparable mixture of the Z- and E- isomers of 1-ethoxy-2,3,3,3-tetrafluoroprop-2-enylcyclohexane (**44**) (82%, 3.67g) (Found: C, 55.0; H, 6.7. $C_{11}H_{16}F_4O$ requires: C, 55.1; H, 6.7%); NMR number 55 and 56, MS spectra 57 and 58 IR spectrum 37.

9.82 *trans*-1,4-di(z-pentafluoro-2-propenyl)cyclohexane (46)

Compound (**46**) (1.9g, 5 mmol) in ethanol (5ml) was added dropwise to a stirred solution of sodium ethoxide (1.4g, 20 mmol) in ethanol (20ml), and then warmed to 80°C and refluxed for 72 hours, using the same procedure as above. The organic products were dissolved in methanol and cooled to -78°C, in an acetone slush bath, from which a white solid crystallised out and was identified as *trans*-1,4(z-1-ethoxy-2,3,3,3-tetrafluoroprop-2-enyl)cyclohexane (**80**) (1.0g, 52%) m.p. 45-46°C (Found: C, 48.4; H, 5.0. $C_{16}H_{20}F_8O_2$ requires: C, 48.5; H, 5.1%); NMR number 57, MS spectrum 59, IR spectrum 38.

Appendices and References

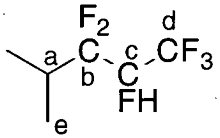
Appendix One

NMR Data

1. 4-Methyl-1,1,1,2,3,3-hexafluoropentane (**28**)
2. 1,1,1,2,3,3-Hexafluorohexane (**29**)
3. 1,1,1,2,3,3-Hexafluoro-4,4-dimethylpentane (**30**)
4. 1,1,1,2,3,3-Hexafluoro-5-methylhexane (**31**)
5. 1,1,2,3,3,3-Hexafluoropropylcyclopentane (**25**)
6. 1,x-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclopentane (x=2,3) (**26**)
7. 1,1,2,3,3,3-Hexafluoropropylcyclohexane (**24**)
8. 1,x-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x=2-4) (**27**)
9. *trans*-1,4-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (**27a**)
10. x-(1,1,2,3,3,3-Hexafluoropropyl)*cis*-decalin (x=1,2,9) (**33**)
11. x,y-Bis(1,1,2,3,3,3-hexafluoropropyl)*cis*-decalin (x=1,y=2-10, x=2,y=3-10) (**34**)
12. x-(1,1,2,3,3,3-Hexafluoropropyl)*trans*-decalin (x=1,2) (**35**)
13. x,y-Bis(1,1,2,3,3,3-hexafluoropropyl)*trans*-decalin (x=1,y=2-10, x=2,y=3-10) (**36**)
14. 2-*exo*-(1,1,2,3,3,3-Hexafluoropropyl)norbornane (**37**)
15. 2,x-Bis(1,1,2,3,3,3-hexafluoropropyl)norbornane (x=5,6) (**38**)
16. 1-(1,1,2,3,3,3-Hexafluoropropyl)adamantane (**22**)
17. 1,3-Bis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**23**)
18. 1,3,5,-Tris(1,1,2,3,3,3-hexafluoropropyl)adamantane (**39**)
19. 1,3,5,7-Tetrakis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**40**)
20. Z-Pentafluoroprop-2-enylcyclohexane (**43a**)
21. E-Pentafluoroprop-2-enylcyclohexane (**43b**)
22. 1-(E-Pentafluoroprop-2-enyl)adamantane (**45a**)
23. 1-(Z-Pentafluoroprop-2-enyl)adamantane (**45b**)
24. *trans*-1,4-Bis(Z-pentafluoroprop-2-enyl)cyclohexane (**46**)
25. *cis*-1,3-Bis(Z-pentafluoroprop-2-enyl)cyclohexane (**47**)
26. Z-Pentafluoroprop-2-enylcyclopentane (**49**)
27. *trans*-1,3-Bis(Z-pentafluoroprop-2-enyl)cyclopentane (**50a**)
28. *cis*-1,3-Bis(Z-pentafluoroprop-2-enyl)cyclopentane (**50b**)
29. *trans*-1,2-Bis(Z-pentafluoroprop-2-enyl)cyclopentane (**50c**)
30. 2-(Z-Pentafluoroprop-2-enyl)*trans*-decalin (**51b**)
31. 1-(Z-Pentafluoroprop-2-enyl)*trans*-decalin (**51a**)
32. 1-(Z-Pentafluoroprop-2-enyl)*cis*-decalin (**52a**)
33. 2-(Z-Pentafluoroprop-2-enyl)*cis*-decalin (**52b**)
34. *exo*-2-(Z-Pentafluoroprop-2-enyl)norbornane (**53**)
35. *exo*-2,5-Bis(Z-pentafluoroprop-2-enyl)norbornane (**54a**)
36. *exo*-2,6-Bis(Z-pentafluoroprop-2-enyl)norbornane (**54b**)
37. 1,3,5,7-Tetrakis(E-pentafluoroprop-2-enyl)adamantane (**55**)

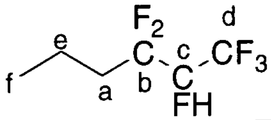
38. 1-(Z-Pentafluoroprop-2-enyl)-3,5,7-tris(E-pentafluoroprop-2-enyl)adamantane (**55a**)
39. Perfluoro-2,5-dipropyltetrahydrofuran (**59**)
40. Perfluoropropylcyclohexane (**60**)
41. Perfluoropropylcyclopentane (**61**)
42. *trans*-Perfluoro-1,4-dipropylcyclohexane (**62a**)
43. *cis*-Perfluoro-1,4-dipropylcyclohexane (**62b**)
44. *trans*-Perfluoro-1,3-dipropylcyclohexane (**63a**)
45. *cis*-Perfluoro-1,3-dipropylcyclohexane (**63b**)
46. Perfluoro-1,x-dipropylcyclopentane (x=2,3) (**64**)
47. Perfluoro-x-propyldecalin (x=1,2,9) (**66**)
48. Perfluorooctane (**68a**)
49. Perfluorohexane (**69a**)
50. 1H-Perfluorohexane (**70**)
51. x-(1,1,2,3,3,3-Hexafluoropropyl)cyclohexyl chloride (x=2-4) (**74**)
52. x-(1,1,2,3,3,3-Hexafluoropropyl)cyclopentyl chloride (x=2,3) (**75**)
53. x-(1,1,2,3,3,3-Hexafluoropropyl)cyclohex-1-ene (x=2-4) (**76**)
54. x-(1,1,2,3,3,3-Hexafluoropropyl)cyclopent-1-ene (x=2,3) (**78**)
55. Z-1-Ethoxy-2,3,3,3-tetrafluoroprop-2-enylcyclohexane (**44a**)
56. E-1-Ethoxy-2,3,3,3-tetrafluoroprop-2-enylcyclohexane (**44b**)
57. *trans*-1,4-Bis(Z-1-ethoxy-2,3,3,3-tetrafluoroprop-2-enyl)cyclohexane (**80**)

1. 4-Methyl-1,1,1,2,3,3-hexafluoropentane (**28**)



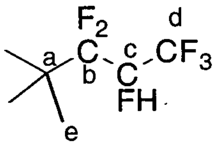
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.12	m		6	e
2.34	m		1	a
4.82	d of m	$^{2}J_{H-F} = 44$	1	c
^{19}F				
-74.5	br s		3	d
-117.7	A of AB	$^{2}J_{F-F} = 265$		
-121.8	B of AB	$^{2}J_{F-F} = 265$	2	b
-212.0	d	$^{2}J_{F-H} = 27$	1	c

2. 1,1,1,2,3,3-Hexafluorohexane (**29**)



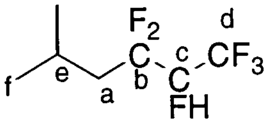
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.00	m		3	e
1.58	m		2	
1.90	m		2	a
4.82	d of m	$^{2}J_{H-F} = 44$	1	c
^{19}F				
-74.5	br s		3	d
-108.0	A of AB	$^{2}J_{F-F} = 269$		
-111.1	B of AB	$^{2}J_{F-F} = 270$	2	b
-211.0.0	br s		1	c

3. 1,1,1,2,3,3-Hexafluoro-4,4-dimethylpentane (**30**)



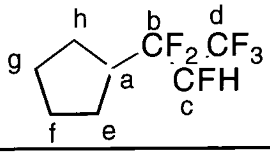
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
1.14	s		9	e
4.91	d	$^2J_{H-F} = 44$	1	c
	d	$^3J_{F-F} = 20$		
	q	$^4J_{F-F} = 5.9$		
^{19}F				
-74.6	s		3	d
-117.6	A of AB	$^2J_{F-F} = 270$		
-126.1	B of AB	$^2J_{F-F} = 270$	2	b
-206.9	d	$^2J_{F-H} = 40$	1	c

4. 1,1,1,2,3,3-Hexafluoro-5-methylhexane (**31**)



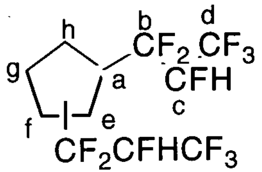
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
0.88	d	$^3J_{H-H} = 4.5$		f
1.39	br s			e
1.61				a
4.91	d of m	$^2J_{H-F} = 44$		c
^{19}F				
-75.5	s		3	d
-105.9	A of AB	$^2J_{F-F} = 265$		
-109.5	B of AB	$^2J_{F-F} = 265$	2	b
-210.3	br s		1	c

5. 1,1,2,3,3,3-Hexafluoropropylcyclopentane (**25**)



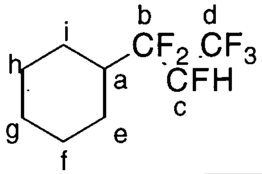
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.63	m		8	e,f
2.52	m		1	a
4.74	d	$^{2}J_{F-H} = 44.3$	1	c
	d	$^{3}J_{F-H} = 20.7$		
	q	$^{3}J_{F-H} = 6.18$		
^{19}F				
-74.8	s		3	d
-114.4	A of AB	$^{2}J_{F-F} = 266$		
-116.6	B of AB	$^{2}J_{F-F} = 266$	2	b
-211.5	d	$^{2}J_{F-H} = 38$	1	c
^{13}C				
25.1	br s			e
25.6	s			f
25.8	s			g
26.1	br s			h
42.5	t	$^{2}J_{C-F} = 22$		a
86.0	d	$^{1}J_{C-F} = 195$		b
	d	$^{2}J_{C-F} = 37$		
	q	$^{2}J_{C-F} = 34$		
	d	$^{2}J_{C-F} = 30$		
120.2	d	$^{1}J_{C-F} = 251$		c
	d	$^{1}J_{C-F} = 249$		
	d	$^{2}J_{C-F} = 24$		
120.2	q	$^{1}J_{C-F} = 282$		d
	d	$^{2}J_{C-F} = 26$		

6. 1,x-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclopentane (x=2,3) (**26**)



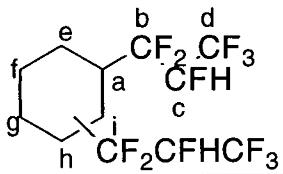
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.97	m		4	e,f,g,h
2.64	m		1	a
4.78	m		1	c
^{19}F				
-74.67	br s		3	d
-74.92	br s			d
-116.64	overlapping m		2	b
-211.10	d	$^2J_{F\text{-}H} = 39.5$	1	c
-211.20	br s			c

7. 1,1,2,3,3,3-Hexafluoropropylcyclohexane (**24**)



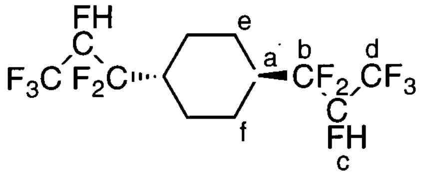
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.24	m		5	$e_{ax},f_{ax},g_{ax},h_{ax},i_{ax}$
1.84	m		6	$a_{ax},e_{eq},f_{eq},g_{eq},h_{eq},i_{eq}$
4.65	d	$^2J_{H\text{-}F} = 41$		
	d	$^3J_{F\text{-}H} = 14$		
	q	$^3J_{F\text{-}H} = 7.0$		
	d	$^3J_{F\text{-}H} = 6.6$	1	c
^{19}F				
-74.8	br s		3	d
-114.4	A of AB	$^2J_{F\text{-}F} = 266$		
-118.8	B of AB	$^2J_{F\text{-}F} = 266$	2	b
-212.3	d	$^2J_{F\text{-}H} = 39$	1	c
^{13}C				
24.0	t	$^3J_{C\text{-}F} = 4.5$		e
25.3	s			f
25.5	s			g
25.5	m			i
25.8	s			h
41.6	t	$^2J_{C\text{-}F} = 21$		a
84.8	d	$^1J_{C\text{-}F} = 195$		c
	d	$^2J_{C\text{-}F} = 37$		
	q	$^2J_{C\text{-}F} = 34$		
	d	$^2J_{C\text{-}F} = 31$		
119.9	d	$^1J_{C\text{-}F} = 252$		b
	d	$^2J_{C\text{-}F} = 248$		
	d	$^2J_{C\text{-}F} = 24$		
121.2	q	$^1J_{C\text{-}F} = 282$		d
	d	$^2J_{C\text{-}F} = 26$		

8. 1,x-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x=2-4) (27)



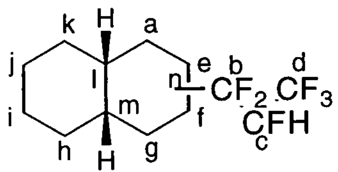
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
1.33	m			a,e,f,g,h,i
1.69	m			a,e,f,g,h,i
2.09	m			a,e,f,g,h,i
4.84	d of m	$^2J_{H-F} = 41$		c
^{19}F				
-76.96	br s		3	d
-120.94	m		2	b
-213.79	br s		1	c
-214.57	br s			

9. *trans*-1,4-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (**27a**)



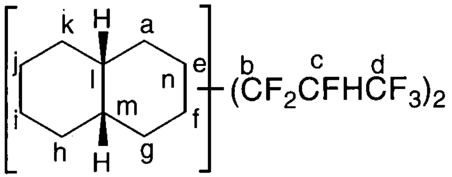
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
1.36	m		2	e_{ax},f_{ax}
2.07	m		3	a,e_{eq},f_{eq}
4.83	d	$^2J_{H\text{-}F}$ = 44	1	c
		$^3J_{F\text{-}H}$ = 21		
		$^3J_{F\text{-}H}$ = 6.0		
^{19}F				
-74.2	s		3	d
-117.1	A of AB	$^2J_{F\text{-}F}$ = 269	2	b
-118.4	B of AB	$^2J_{F\text{-}F}$ = 267		
-211.2	d	$^2J_{F\text{-}H}$ = 44	1	c
^{13}C				
22.8	t	$^3J_{C\text{-}F}$ = 4.4		e
24.1	t	$^3J_{C\text{-}F}$ = 2.9		f
40.6	t	$^2J_{C\text{-}F}$ = 22		a
85.0	d	$^1J_{C\text{-}F}$ = 196		b
	d	$^2J_{C\text{-}F}$ = 38		
	q	$^2J_{C\text{-}F}$ = 34		
	d	$^2J_{C\text{-}F}$ = 31		
119.3	d	$^1J_{C\text{-}F}$ = 253		c
	d	$^1J_{C\text{-}F}$ = 249		
	d	$^2J_{C\text{-}F}$ = 24		
120.9	q	$^1J_{C\text{-}F}$ = 282		d
	d	$^2J_{C\text{-}F}$ = 26		

10. x-(1,1,2,3,3,3-Hexafluoropropyl)*cis*-decalin (x=1,2,9) (**33**)



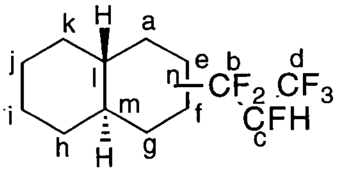
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.31	m			
1.56	m		16	a,e,f,g,h,i,j,k,l,m
1.70	m			
2.08	m		0.5	n
2.20	m		0.5	n
4.80	m		1	c
^{19}F				
-74.6	br s		3	d
-111.4	overlapping			
-118.5	m		2	b
-206.4	m		1	c
-212.1,	m			c

11. x,y-Bis(1,1,2,3,3,3-hexafluoropropyl)*cis*-decalin (x=1,y=2-10, x=2,y=3-10) (**34**)



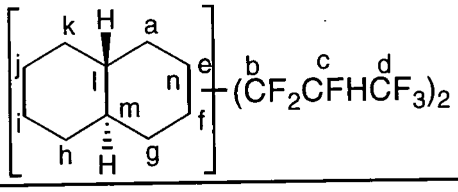
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
1.39 to 2.05	overlapping m		32	a, e, f to m
2.23	m		1	n
2.65	m		1	n
4.80, 4.98	overlapping m		2	c
^{19}F				
-74.2, -74.5	br s		3	d
-111.4	m			
-118.3, to -119.4	overlapping m		2	b
-204.1,	br s		1	c
-206.2	br s			
-211.9	br s			

12. x-(1,1,2,3,3,3-Hexafluoropropyl)*trans*-decalin (x=1,2) (**35**)



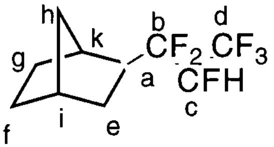
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.00 to 1.75	overlapping m		16	a, e, f to m
2.10	m		1	n
4.83	m		1	c
^{19}F				
-74.4	br s		3	d
-74.8	br s			
-118.9	overlapping m		2	b
-211.9,	br s		1	c
-212.6	d	$^{2}J_{F\text{-}H} = 40$		

13. x,y-Bis(1,1,2,3,3,3-hexafluoropropyl)*trans*-decalin (x=1,y=2-10, x=2,y=3-10) (**36**)



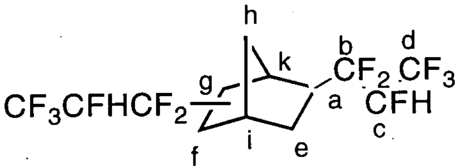
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.19 to 2.20	overlapping m		30	a,e to m,
2.62	m		1	n
4..90	overlapping m		2	c
^{19}F				
-73.5	br s		3	d
-74.1	br s			
-111.5	m			
-118.1 to -119.4	overlapping m		2	b
-204.2 to -211.9	overlapping m		1	c

14. *exo*-2-(1,1,2,3,3,3-Hexafluoropropyl)norbornane (**37**)



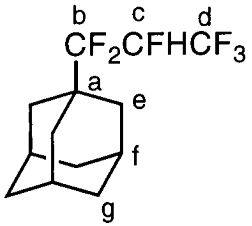
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.26	m		3	h,g_{ax},f_{ax}
1.61	m		4	e_{ax},h,g_{eq},f_{eq}
1.75	m		1	e_{eq}
2.14	m		1	a
2.37	br s		1	i
2.45	br s		1	k
4.81	m		1	c
^{19}F				
-74.7	br s		3	d
113.0	A of AB	$^{2}J_{F\text{-}F}$ =265		
-118.8	B of AB	$^{2}J_{F\text{-}F}$ =265	2	b
-211.2	d	$^{2}J_{F\text{-}H}$ = 44	1	c
^{13}C				
28.0	s			g
30.4	s			f
31.4	s			e
35.8	s			i
36.9	br s			h
37.6	d	$^{4}J_{C\text{-}F}$ = 5		k
44.9	t	$^{2}J_{C\text{-}F}$ = 22		a
86.2	d	$^{1}J_{C\text{-}F}$ = 196		c
	d	$^{2}J_{C\text{-}F}$ = 37		
	q	$^{2}J_{C\text{-}F}$ = 34		
	d	$^{2}J_{C\text{-}F}$ = 31		
120.0	d	$^{1}J_{C\text{-}F}$ = 251		b
	d	$^{1}J_{C\text{-}F}$ = 249		
	d	$^{2}J_{C\text{-}F}$ = 22		
121.3	q	$^{1}J_{C\text{-}F}$ = 282		d
	d	$^{2}J_{C\text{-}F}$ = 29		

15. 2,x-Bis(1,1,2,3,3,3-hexafluoropropyl)norbornane (x=5,6) (**38**)



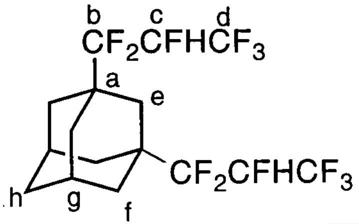
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
1.00	m		3	h,g_{ax},f_{ax}
1.50	m		5	e,h,g_{eq},f_{eq}
2.15	m		1	a
2.32, 2.39	br s		1	i
2.54, 2.80	br s		1	k
4.75	m		1	c
^{19}F				
-74.7	br s		3	d
-114.1	m		2	b
-210.8	m		1	c

16. 1-(1,1,2,3,3,3-Hexafluoropropyl)adamantane (22)



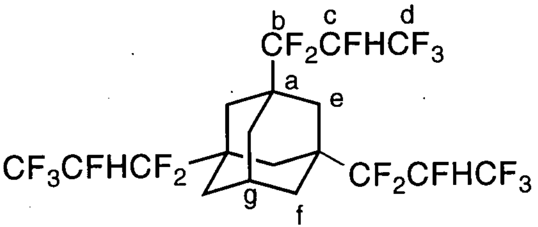
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
1.76	m		12	e,g
2.07	s		3	f
4.93	d	$^2J_{H\text{-}F} = 44$	1	c
	d	$^3J_{H\text{-}F} = 20$		
	q	$^4J_{H\text{-}F} = 6.4$		
^{19}F				
-74.3	s		3	d
-122.6	A of AB	$^2J_{F\text{-}F} = 274$		
-130.0	B of AB	$^2J_{F\text{-}F} = 274$	2	b
-206.9	d	$^2J_{F\text{-}H} = 41$	1	c
^{13}C				
27.5	s			f
34.6	q	$^6J_{C\text{-}F} = 3.4$		e
36.4	s			g
40.0	t	$^2J_{C\text{-}F} = 21$		a
83.6	d	$^1J_{C\text{-}F} = 197$		b
	q	$^2J_{C\text{-}F} = 41$		
	d	$^2J_{C\text{-}F} = 33$		
	d	$^2J_{C\text{-}F} = 26$		
119.5	d	$^1J_{C\text{-}F} = 261$		c
	d	$^1J_{C\text{-}F} = 247$		
	d	$^2J_{C\text{-}F} = 22$		
121.3	q	$^1J_{C\text{-}F} = 283$		d
	d	$^2J_{C\text{-}F} = 26$		

17.1,3-Bis(1,1,2,3,3,3-hexafluoropropyl)adamantane (23)



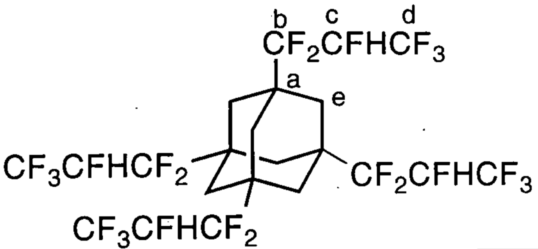
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
1.80	m		6	
2.28	s		1	
4.93	d	$^2J_{H-F} = 44.0$	1	c
	d	$^3J_{H-F} = 20.2$		
	q	$^4J_{H-F} = 6.4$		
^{19}F				
-74.3	s		3	d
-121.7	A of AB	$^2J_{F-F} = 275$		
-129.4	B of AB	$^2J_{F-F} = 275$	2	b
-207.1	d	$^2J_{F-H} = 37$	1	c
^{13}C				
27.0	s			g
31.8	m			e
33.8	s			f
35.3	s			h
40.6	t	$^2J_{C-F} = 21$		a
83.8	d	$^1J_{C-F} = 197$		c
	d	$^2J_{C-F} = 42$		
	q	$^2J_{C-F} = 34$		
	d	$^2J_{C-F} = 26$		
119.1	d	$^1J_{C-F} = 261$		b
	d	$^1J_{C-F} = 247$		
	d	$^2J_{C-F} = 23$		
121.1	q	$^1J_{C-F} = 283$		c
	d	$^2J_{C-F} = 26$		

18. 1,3,5,-Tris(1,1,2,3,3,3-hexafluoropropyl)adamantane (**39**)



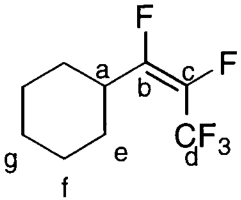
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.83	m		12	e,f
2.15	s		1	g
4.95	d	$^{2}J_{H\text{-}F} = 41$	3	c
	d	$^{3}J_{H\text{-}F} = 19$		
	q	$^{4}J_{H\text{-}F} = 5.3$		
^{19}F				
-74.2	br s		3	d
-120.7	A of AB	$^{2}J_{F\text{-}F} = 273$	2	b
-128.7	B of AB	$^{2}J_{F\text{-}F} = 275$		
-207.3	d	$^{2}J_{F\text{-}H} = 29$	1	c
^{13}C				
26.7	s			g
31.5	s			f
33.2	s			e
41.3	t	$^{2}J_{C\text{-}F} = 22$		a
84.1	d	$^{1}J_{C\text{-}F} = 197$		c
	q	$^{2}J_{C\text{-}F} = 42$		
		$^{2}J_{C\text{-}F} = 34$		
	t	$^{2}J_{C\text{-}F} = 26$		
119.1	d	$^{1}J_{C\text{-}F} = 262$		b
	d	$^{1}J_{C\text{-}F} = 248$		
	d	$^{2}J_{C\text{-}F} = 26$		
121.0	q	$^{1}J_{C\text{-}F} = 283$		c
	d	$^{2}J_{C\text{-}F} = 26$		

19. 1,3,5,7-Tetrakis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**40**)



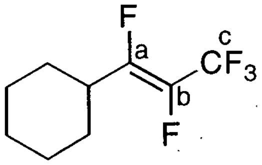
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
2.07	m		3	
5.99	d	$^2J_{H\text{-}F} = 42$	1	c
	d	$^3J_{H\text{-}F} = 20$		
	q	$^4J_{H\text{-}F} = 6.4$		
^{19}F				
-74.1	s		3	d
-121.1	A of AB	$^2J_{F\text{-}F} = 276$		
-127.6	B of AB	$^2J_{F\text{-}F} = 276$	2	b
-207.1	d	$^2J_{F\text{-}H} = 36$	1	c
^{13}C				
30.1	s			e
41.6	t	$^2J_{C\text{-}F} = 22$		a
83.1	d	$^1J_{C\text{-}F} = 194$		c
	d	$^2J_{C\text{-}F} = 39$		
	q	$^2J_{C\text{-}F} = 34$		
119.0	d	$^1J_{C\text{-}F} = 261$		b
	d	$^1J_{C\text{-}F} = 249$		
	d	$^2J_{C\text{-}F} = 22$		
121.4	q	$^1J_{C\text{-}F} = 282$		c
	d	$^2J_{C\text{-}F} = 26$		

20. Z-Pentafluoroprop-2-enylcyclohexane (**43a**)



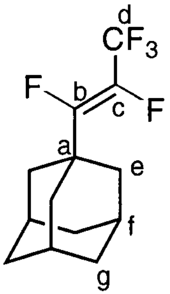
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
1.20	q	$^3J_{H\text{-}F} = 12$	1	g_{ax}
	t	$^3J_{H\text{-}H} = 3.2$		
1.31	q	$^3J_{H\text{-}H} = 12$	2	f_{ax}
1.55	q	$^3J_{H\text{-}H} = 12$	2	e_{ax}
	d	$^3J_{H\text{-}H} = 3.2$		
1.72	d	$^3J_{H\text{-}H} = 12$	3	e_{eq},g_{eq}
1.83	d	$^4J_{H\text{-}F} = 14$	2	f_{eq}
2.52	d	$^3J_{H\text{-}F} = 32$	1	a_{ax}
	t	$^3J_{H\text{-}H} = 12$		
^{19}F				
-66.2	s		3	d
-131.4	d	$^3J_{F\text{-}H} = 31$	1	b
-161.7	q	$^3J_{F\text{-}F} = 11$	1	c
	d	$^4J_{F\text{-}H} = 5$		
^{13}C				
25.6				g
25.9				f
28.9	d	$^3J_{C\text{-}F} = 2.2$		e
36.7	d	$^2J_{C\text{-}F} = 21$		a
120.4	q	$^1J_{C\text{-}F} = 270$		d
	d	$^2J_{C\text{-}F} = 35$		
	d	$^3J_{C\text{-}F} = 9.6$		
134.9	d	$^1J_{C\text{-}F} = 250$		c
	q	$^3J_{C\text{-}F} = 40$		
	d	$^3J_{C\text{-}F} = 24$		
156.6	d	$^1J_{C\text{-}F} = 264$		b
	d	$^3J_{C\text{-}F} = 9.6$		
	q	$^4J_{C\text{-}F} = 3.4$		

21. E-Pentafluoroprop-2-enylcyclohexane **(43b)**



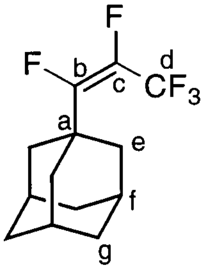
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{19}F				
-68.2	d	$^4J_{F-F} = 19$	3	c
-148.3	d	$^3J_{F-F} = 132$	1	a
	quintet	$^4J_{F-F,H} = 24$		
-176.5	d	$^3J_{F-F} = 132$	1	b

22. 1-(E-Pentafluoroprop-2-enyl)adamantane (**45a**)



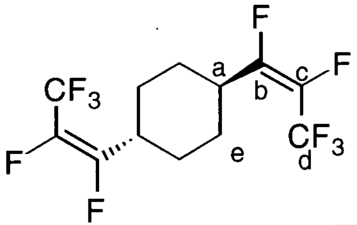
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.76	s		2	e
1.96	s		2	g
2.06	s		1	f
^{19}F				
-67.6	d	$^{3}J_{\text{Fd-Fb}} = 21$	3	d
-149.3	d	$^{3}J_{\text{Fb-Fc}} = 131$	1	b
	q	$^{4}J_{\text{Fb-Fd}} = 22$		
-175.6	d	$^{3}J_{\text{Fc-Fb}} = 130$	1	c
^{13}C				
27.8	s			
36.3	s			
36.8	s			
119.5	q	$^{1}J_{\text{C-F}} = 273$		d
	d	$^{2}J_{\text{C-F}} = 36$		
	d	$^{3}J_{\text{C-F}} = 3.5$		
138.2	d	$^{1}J_{\text{C-F}} = 242$		c
	q	$^{3}J_{\text{C-F}} = 54$		
	d	$^{3}J_{\text{C-F}} = 39$		
160.2	d	$^{1}J_{\text{C-F}} = 260$		b
	d	$^{3}J_{\text{C-F}} = 36$		
	q	$^{4}J_{\text{C-F}} = 2.3$		

23. 1-(Z-Pentafluoroprop-2-enyl)adamantane (**45b**)



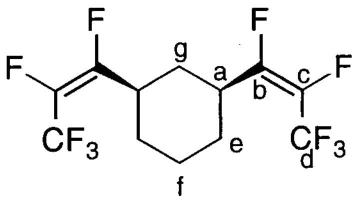
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.77	s		2	e
1.95	s		2	g
2.07	s		1	f
^{19}F				
-59.9	s		3	d
-125.2	br s		1	b
-154.7	q	$^3J_{F\text{-}F} = 11$	1	c
^{13}C				
27.9	s			
36.2	s			
37.1	d	$^2J_{C\text{-}F} = 21$		
38.0	q	$^3J_{C\text{-}F} = 2.3$		
120.1	q	$^1J_{C\text{-}F} = 270$		d
	d	$^2J_{C\text{-}F} = 36$		
	d	$^3J_{C\text{-}F} = 8.4$		
137.8	d	$^1J_{C\text{-}F} = 249$		c
	q	$^3J_{C\text{-}F} = 43$		
	d	$^3J_{C\text{-}F} = 30$		
160.7	d	$^1J_{C\text{-}F} = 264$		b
	d	$^3J_{C\text{-}F} = 13$		

24. *trans*-1,4-Bis(Z-pentafluoroprop-2-enyl)cyclohexane (**46**)



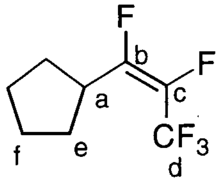
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.69	m		2	e_{ax}
1.89	d	$^{2}J_{H\text{-}H} = 7.2$	2	e_{eq}
2.56	d	$^{3}J_{H\text{-}F} = 32$	1	a
^{19}F				
-65.9	s		3	d
-132.2	d	$^{3}J_{F\text{-}H} = 31$	1	b
-159.2	q	$^{3}J_{F\text{-}F} = 12$	1	c
	d	$^{4}J_{F\text{-}H} = 3.8$		
^{13}C				
27.8	s			e
35.5	d	$^{3}J_{C\text{-}F} = 21$		a
120.2	q	$^{1}J_{C\text{-}F} = 270$		d
	d	$^{2}J_{C\text{-}F} = 35$		
	d	$^{3}J_{C\text{-}F} = 9.6$		
135.3	d	$^{1}J_{C\text{-}F} = 252$		c
		$^{3}J_{C\text{-}F} = 40$		
		$^{3}J_{C\text{-}F} = 24$		
155.3	d	$^{1}J_{C\text{-}F} = 266$		b
	d	$^{3}J_{C\text{-}F} = 10$		

25. *cis*-1,3-Bis(Z-pentafluoroprop-2-enyl)cyclohexane (**47**)



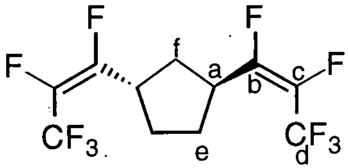
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
1.42	q			f_{ax}
1.57	q	$^3J_{H\text{-}H} = 13$		e_{ax}
	d	$^3J_{H\text{-}H} = 3.6$		
1.77	m			e_{eq}, f_{eq}
1.88	q	$^3J_{H\text{-}H} = 12$		g_{ax}
2.10	d	$^3J_{H\text{-}H} = 13$		g_{eq}
2.64	d	$^4J_{H\text{-}F} = 31$		a_{ax}
	t	$^2J_{H\text{-}H} = 12$		
^{19}F				
-66.3	s		3	d
-132.2	d	$^3J_{F\text{-}H} = 31$	1	b
-159.1	br s		1	c
^{13}C				
24.6	s			f
27.4	d	$^3J_{C\text{-}F} = 2.3$		e
30.0	s			g
35.6	t	$^3J_{C\text{-}F} = 21$		a
119.8	q	$^1J_{C\text{-}F} = 270$		d
	d	$^2J_{C\text{-}F} = 35$		
	d	$^3J_{C\text{-}F} = 9.6$		
135.1	d	$^1J_{C\text{-}F} = 253$		c
	q	$^3J_{C\text{-}F} = 41$		
	d	$^3J_{C\text{-}F} = 24$		
154.5	d	$^1J_{C\text{-}F} = 266$		b
	d	$^3J_{C\text{-}F} = 11$		
	q	$^4J_{C\text{-}F} = 3.5$		

26. Z-Pentafluoroprop-2-enylcyclopentane (49)



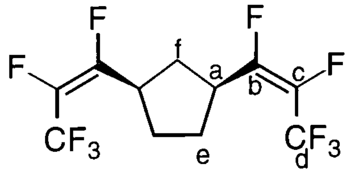
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.63	overlapping m			
2.52	d	$^{3}J_{H\text{-}F} = 32$		
^{19}F				
-65.6	s		3	d
-133.4	d	$^{3}J_{F\text{-}H} = 31$	1	b
-162.2	br s		1	c
^{13}C				
26.2	s			f
29.5	s			e
36.8	d	$^{2}J_{C\text{-}F} = 22$		a
	t	$^{3}J_{C\text{-}F} = 2.3$		
120.4	q	$^{1}J_{C\text{-}F} = 270$		d
	d	$^{2}J_{C\text{-}F} = 35$		
	d	$^{3}J_{C\text{-}F} = 9.6$		
134.7	d	$^{1}J_{C\text{-}F} = 250$		c
	q	$^{3}J_{C\text{-}F} = 40$		
	d	$^{3}J_{C\text{-}F} = 24$		
155.3	d	$^{1}J_{C\text{-}F} = 264$		b
	d	$^{3}J_{C\text{-}F} = 10$		
	q	$^{4}J_{C\text{-}F} = 3.5$		

27. *trans*-1,3-Bis(Z-pentafluoroprop-2-enyl)cyclopentane (**50a**)



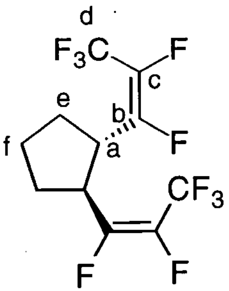
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.65	overlapping m		3	e,f
2.50	overlapping m		1	a
^{19}F				
-66.9	s		3	d
-135.0	d	$^{3}J_{F\text{-}H} = 31$	1	b
-159.3	br s		1	c
^{13}C				
29.9	s			e
31.4	s			f
36.6	d	$^{3}J_{C\text{-}F} = 22$		a
120.0	q	$^{1}J_{C\text{-}F} = 270$		d
	d	$^{2}J_{C\text{-}F} = 35$		
	d	$^{3}J_{C\text{-}F} = 9.6$		
135.2	d	$^{1}J_{C\text{-}F} = 252$		c
	q	$^{3}J_{C\text{-}F} = 40$		
	d	$^{3}J_{C\text{-}F} = 24$		
153.6	d	$^{1}J_{C\text{-}F} = 264$		b
	d	$^{3}J_{C\text{-}F} = 11$		
	q	$^{4}J_{C\text{-}F} = 3.4$		

28. *cis*-1,3-Bis(Z-pentafluoroprop-2-enyl)cyclopentane (**50b**)



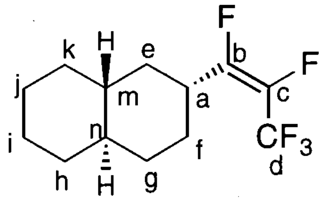
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.65	overlapping m		3	e,f
2.50	overlapping m		1	a
^{19}F				
-66.9	s		3	d
-134.9	d	$^{3}J_{F-H} = 31$	1	b
-159.0	br s		1	c
^{13}C				
28.4	s			e
32.2	s			f
37.0	d	$^{3}J_{C-F} = 22$		a
120.0	q	$^{1}J_{C-F} = 270$		d
135.4	d	$^{1}J_{C-F} = 252$		c
153.4	d	$^{1}J_{C-F} = 266$		b

29. *trans*-1,2-Bis(Z-pentafluoroprop-2-enyl)cyclopentane (**50c**)



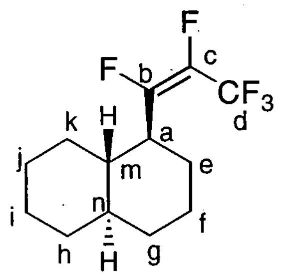
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
1.65	overlapping m		3	e,f
2.50	overlapping m		1	a
^{19}F				
-66.9	s		3	d
-135.9	d	$^3J_{F\text{-}H} = 31$	1	b
-156.5	br s		1	c
^{13}C				
25.1	s			f
28.9	s			e
40.3	d	$^3J_{C\text{-}F} = 23$		a
119.8	q	$^1J_{C\text{-}F} = 270$		d
136.5	d	$^1J_{C\text{-}F} = 250$		c
151.4	d	$^1J_{C\text{-}F} = 268$		b

30. 2-(Z-Pentafluoroprop-2-enyl)*trans*-decalin (**51b**)



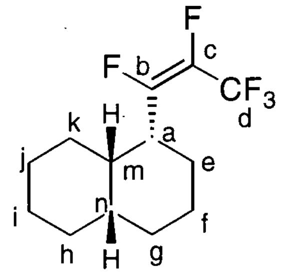
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
1.02,1.25, 1.61,1.72	overlapping m		16	e,f,g,h,i,j,k,l,m, n
2.58	d	$^3J_{H-F} = 32$	1	a
^{19}F				
-66.3	s		3	d
-131.7	d	$^3J_{F-H} = 30$	1	b
-161.5	br s		1	c
^{13}C				
26.4	s			i
26.5	s			j
28.5	d	$^3J_{C-F} = 2.6$		f
32.8	s			g
33.5	s			h
33.6	s			k
35.6	d	$^3J_{C-F} = 2.7$		e
36.4	d	$^2J_{C-F} = 21$		a
42.2	s			n
42.3	s			m
120.1	q	$^1J_{C-F} = 271$		d
	d	$^2J_{C-F} = 35$		
	d	$^3J_{C-F} = 9.6$		
135.5	d	$^1J_{C-F} = 250$		c
	q	$^3J_{C-F} = 40$		
	d	$^3J_{C-F} = 24$		
156.0	d	$^1J_{C-F} = 266$		b
	d	$^3J_{C-F} = 9.4$		
	q	$^4J_{C-F} = 3.4$		

31. 1-(Z-Pentafluoroprop-2-enyl)*trans*-decalin (**51a**)



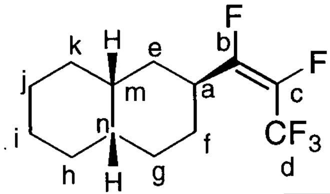
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.02,1.25, 1.61,1.72	overlapping m		16	e,f,g,h,i,j,k,l,m, n
2.24	d	$^{3}J_{H\text{-}F} = 32$	1	a
^{19}F				
-65.7	s		3	d
-133.6	d	$^{3}J_{F\text{-}H} = 30$	1	b
-160.0	br s		1	c
^{13}C				
25.4	s			f
26.3	s			i,j
29.5	d	$^{2}J_{C\text{-}F} = 21$		e
30.1	s			g
33.3	s			h
42.4	s			n
42.5	br s			m

32. 1-(Z-Pentafluoroprop-2-enyl)*cis*-decalin (**52a**)



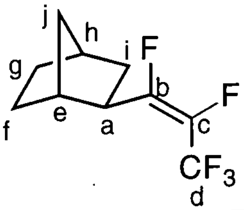
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.29, 1.56 1.75, 1.84	overlapping m			e,f,g,h,i,j,k,l,m, n
2.58	d	$^{3}J_{H\text{-}F} = 32$	1	a
^{19}F				
-66.2	s		3	d
-132.2	d	$^{3}J_{F\text{-}H} = 30$	1	b
-161.5	br s		1	c
^{13}C				
20.9	s			i
23.1	d	$^{3}J_{C\text{-}F} = 2.6$		e
24.9	s			k
26.1	s			g
27.0	d	$^{2}J_{C\text{-}F} = 21$		j,f
32.1	s			h
35.7	s			n
35.9	s			m
37.3	s			a
120.4	q	$^{1}J_{C\text{-}F} = 270$		d
	d	$^{2}J_{C\text{-}F} = 35$		
	d	$^{3}J_{C\text{-}F} = 9.6$		
134.8	d	$^{1}J_{C\text{-}F} = 248$		c
	q	$^{3}J_{C\text{-}F} = 40$		
	d	$^{3}J_{C\text{-}F} = 24$		
156.5	d	$^{1}J_{C\text{-}F} = 265$		b
	d	$^{3}J_{C\text{-}F} = 9.6$		
	q	$^{4}J_{C\text{-}F} = 3.4$		

33. 2-(Z-Pentafluoroprop-2-enyl)*cis*-decalin (**52b**)



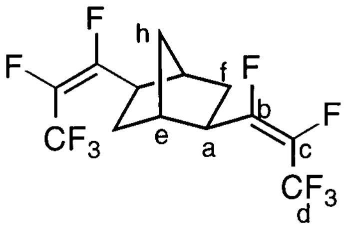
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.29, 1.56 1.75, 1.84	overlapping m			e,f,g,h,i,j,k,l,m, n
2.65	d	$^{3}J_{H\text{-}F} = 32$	1	a
^{19}F				
-66.2	s		3	d
-131.3	d	$^{3}J_{F\text{-}H} = 30$	1	b
-161.3	br s		1	c
^{13}C				
20.8	s			j
25.6	s			h
28.0	d	$^{3}J_{C\text{-}F} = 2.6$		f
28.9	s			g
31.3	d	$^{2}J_{C\text{-}F} = 21$		a
31.6	s			i
32.2	s			k
34.9	d	$^{3}J_{C\text{-}F} = 2.3$		e
35.2	s			n
35.3	s			m
120.4	q	$^{1}J_{C\text{-}F} = 270$		d
	d	$^{2}J_{C\text{-}F} = 35$		
	d	$^{3}J_{C\text{-}F} = 9.6$		
134.9	d	$^{1}J_{C\text{-}F} = 248$		c
	q	$^{3}J_{C\text{-}F} = 40$		
	d	$^{3}J_{C\text{-}F} = 24$		
156.7	d	$^{1}J_{C\text{-}F} = 266$		b
	d	$^{3}J_{C\text{-}F} = 9.6$		
	q	$^{4}J_{C\text{-}F} = 3.4$		

34. *exo*-2-(Z-Pentafluoroprop-2-enyl)norbornane (53)



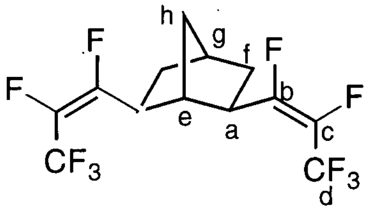
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.25	m		3	f,g,j
1.57	m		4	f,g,i,j
1.71	m		1	i
2.35	s		2	e,h
2.54	d	$^{3}J_{H\text{-}F} = 36$	1	a
^{19}F				
-67.1	s		3	d
-130.7	d	$^{3}J_{F\text{-}H} = 31$	1	b
-162.2	br s		1	c
^{13}C				
20.9	s			i
23.1	d	$^{3}J_{C\text{-}F} = 3.1$		e
26.1	s			g
27.0	s			f
32.1	s			h
35.7	s			n
35.9	s			m
37.3	d	$^{2}J_{C\text{-}F} = 21$		a
120.4	q	$^{1}J_{C\text{-}F} = 270$		d
	d	$^{2}J_{C\text{-}F} = 35$		
	d	$^{3}J_{C\text{-}F} = 9.6$		
134.5	d	$^{1}J_{C\text{-}F} = 250$		c
	q	$^{3}J_{C\text{-}F} = 40$		
	d	$^{3}J_{C\text{-}F} = 25$		
156.5	d	$^{1}J_{C\text{-}F} = 265$		b
	d	$^{3}J_{C\text{-}F} = 9.6$		
	q	$^{4}J_{C\text{-}F} = 3.4$		

35. *exo*-2,5-Bis(Z-pentafluoroprop-2-enyl)norbornane (**54a**)



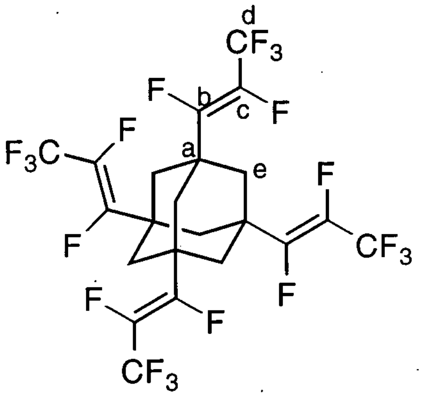
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.65	m			f_{ax},h
1.86	m			f_{eq}
2.46	s			e
2.53	m			g
2.63	m			a
^{19}F				
-66.0	s		3	d
-130.5	d	$^{3}J_{F\text{-}H} = 32$	1	b
-159.3	br s		1	c
^{13}C				
35.2	s			f
37.0	s			h
38.0	d	$^{2}J_{C\text{-}F} = 21$		a
	d	$^{3}J_{C\text{-}F} = 2.3$		
41.9	d	$^{3}J_{C\text{-}F} = 2.6$		e
120.5	q	$^{1}J_{C\text{-}F} = 270$		d
	d	$^{2}J_{C\text{-}F} = 35$		
	d	$^{3}J_{C\text{-}F} = 9.6$		
135.3	d	$^{1}J_{C\text{-}F} = 251$		c
	q	$^{3}J_{C\text{-}F} = 40$		
	d	$^{3}J_{C\text{-}F} = 25$		
155.2	d	$^{1}J_{C\text{-}F} = 266$		b
	d	$^{3}J_{C\text{-}F} = 11$		
	q	$^{4}J_{C\text{-}F} = 3.4$		

36. *exo*-2,6-Bis(Z-pentafluoroprop-2-enyl)norbornane (**54b**)



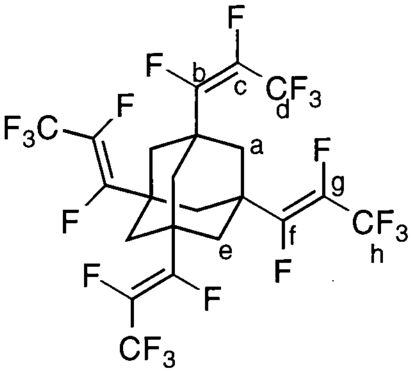
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
1.65	m		4	h,f_{ax}
1.86	m		2	f_{eq}
2.46	m		1	g
2.53	m		1	e
2.63	d	$^3J_{H-F} = 36$	2	a
^{19}F				
66.0	s		3	d
128.7	d	$^3J_{F-H} = 30$	1	b
158.6	br s		1	c
^{13}C				
33.1	s			f
36.2	s			g
36.5	s			h
41.9	d	$^2J_{C-F} = 20$		a
48.2	s			e
120.4	q	$^1J_{C-F} = 269$		d
	d	$^2J_{C-F} = 35$		
	d	$^3J_{C-F} = 9.4$		
135.7	d	$^1J_{C-F} = 252$		c
	q	$^3J_{C-F} = 40$		
	d	$^3J_{C-F} = 25$		
154.7	d	$^1J_{C-F} = 267$		b
	d	$^3J_{C-F} = 11$		
	q	$^4J_{C-F} = 3.4$		

37. 1,3,5,7-Tetrakis(E-pentafluoroprop-2-enyl)adamantane (55)



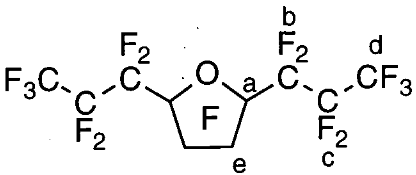
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
2.21	s		2	e
^{19}F				
-67.6	d	$^3J_{Fd\text{-}Fb} = 23$	3	d
149.7	d	$^2J_{Fb\text{-}Fc} = 134$	1	b
	q	$^3J_{Fb\text{-}Fd} = 23$		
170.3	d	$^2J_{Fc\text{-}Fb} = 135$	1	c
	q	$^4J_{Fc\text{-}Fd} = 9.4$		
^{13}C				
36.4	s			e
38.4	d	$^3J_{C\text{-}F} = 21$		a
118.8	q	$^1J_{C\text{-}F} = 273$		d
	d	$^2J_{C\text{-}F} = 36$		
	d	$^3J_{C\text{-}F} = 3.4$		
139.7	d	$^1J_{C\text{-}F} = 248$		c
	q	$^3J_{C\text{-}F} = 52$		
	d	$^3J_{C\text{-}F} = 40$		
156.1	d	$^1J_{C\text{-}F} = 261$		b
	d	$^3J_{C\text{-}F} = 39$		

38. 1-(Z-Pentafluoroprop-2-enyl)-3,5,7-tris(E-pentafluoroprop-2-enyl)adamantane **(55a)**



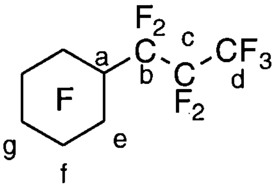
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
2.18	s		1	a
2.19	s		1	e
^{19}F				
-60.4	s		3	d
-68.5	s		9	h
-126.7	s		1	b
-148.6	s		1	c
-150.6	m		3	f
-171.6	d	$^2J_{Fb\text{-}Fc} = 135$	3	g

39. Perfluoro-2,5-dipropyltetrahydrofuran (**59**)



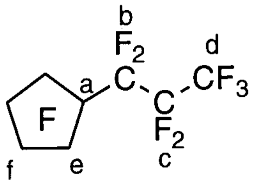
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{19}F				
-81.6	s			d
-120.4	A of AB(1)	$^2J_{F\text{-}F}$=306		b
-121.0	A of AB(2)	$^2J_{F\text{-}F}$=306		b
-121.2	A of AB(3)	$^2J_{F\text{-}F}$=297		e
-121.7	s			a
123.0	s			a
124.3	B of AB(1)	$^2J_{F\text{-}F}$=306		b
124.4	B of AB(2)	$^2J_{F\text{-}F}$=306		b
125.0	A of AB(4)	$^2J_{F\text{-}F}$=261		c
125.5	s			c
-126.7	B of AB(4)	$^2J_{F\text{-}F}$ =261		c
-127.6	A of AB(5)	$^2J_{F\text{-}F}$=258		e
-131.4	B of AB(3)	$^2J_{F\text{-}F}$ =297		e
-132.9	B of AB(5)	$^2J_{F\text{-}F}$=258		e

40. Perfluoropropylcyclohexane (**60**)



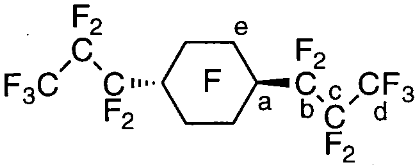
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{19}F				
-80.6	s		3	d
-112.3	s		2	b
-118.2	A of AB(1)	$^2J_{F-F}$ =298	2	e
-121.9	A of AB(2)	$^2J_{F-F}$ =284	2	f
-123.9	A of AB(3)	$^2J_{F-F}$ =288	1	g
-128.4	s		2	c
-128.9	B of AB(1)	$^2J_{F-F}$ =302	2	e
-139.9	B of AB(2)	$^2J_{F-F}$ =287	2	f
-142.2	B of AB(3)	$^2J_{F-F}$ =289	1	g
-185.6	s		1	a

41. Perfluoropropylcyclopentane (**61**)



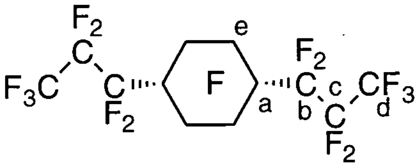
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{19}F				
-81.2	s		3	d
-116.1	s		2	b
-123.0	A of AB(1)	$^2J_{F-F}$=266	2	e
-125.1	s		2	c
-128.3	B of AB(1)	$^2J_{F-F}$ =270	2	e
-129.0	A of AB(2)	$^2J_{F-F}$ =259	2	f
-132.5	B of AB(2)	$^2J_{F-F}$ =259	2	f
-185.2	s		1	a

42. *Trans*-perfluoro-1,4-dipropylcyclohexane (**62a**)



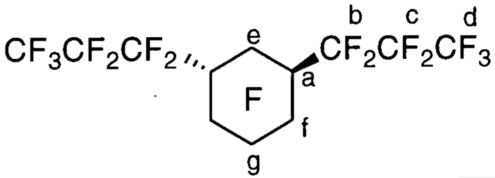
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{19}F				
-81.2	s		3	d
-117.7	A of AB	$^2J_{F\text{-}F}$ =297	4	e
-119.4	s		2	b
-126.1	s		2	c
-126.7	B of AB	$^2J_{F\text{-}F}$ =297	4	e
-186.7	s		1	a

43. *Cis*-perfluoro-1,4-dipropylcyclohexane (**62b**)



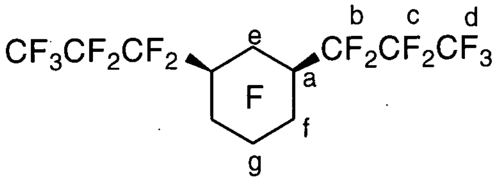
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{19}F				
-81.0	s		3	d
-113.4	s		2	b
-119.4	s		2	c
-124.8	s		4	e
-183.0	s		1	a

44. *trans*-Perfluoro-1,3-dipropylcyclohexane (**63a**)



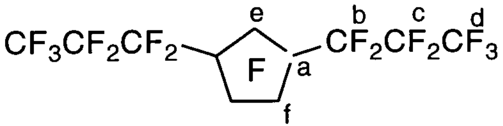
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{19}F				
-80.8	s		6	d
-113.9	s		4	b
-120.0	A of AB(1)	$^2J_{F\text{-}F}$= 288	1	e_{ax}
-121.3	A of AB(2)	$^2J_{F\text{-}F}$= 300	2	f_{ax}
-122.8	A of AB(3)	$^2J_{F\text{-}F}$= 286	1	g_{ax}
-125.0	B of AB(1)	$^2J_{F\text{-}F}$= 289	1	e_{eq}
-127.5	s		4	c
-131.3	B of AB(2)	$^2J_{F\text{-}F}$= 300	2	f_{eq}
-140.8	B of AB(3)	$^2J_{F\text{-}F}$= 287	1	g_{eq}
-184.3	s		2	a

45. *cis*-Perfluoro-1,3-dipropylcyclohexane (**63b**)



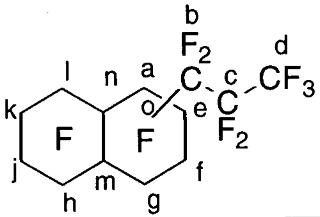
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{19}F				
-80.9	s		6	d
-111.4	s			b
-115.1	s			f
-115.6	s			e
-126.2	s			g
-127.7	s			c
-182.8	s			a

46. Perfluoro-1,x-dipropylcyclopentane x=2,3 **(64)**



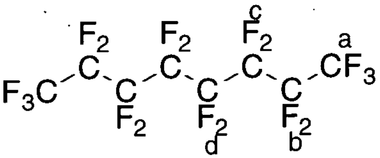
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{19}F				
-83.3	s		6	d
-114.2	m			e
-117.1	A of AB(1)	$^2J_{F\text{-}F}$=295		b
-117.9	m			b
-118.2	B of AB(1)	$^2J_{F\text{-}F}$=295		b
-122.4	m			e
-123.0	A of AB(2)	$^2J_{F\text{-}F}$=267		f
-124.3	B of AB(2)	$^2J_{F\text{-}F}$=267		f
-125.6	A of AB(3)	$^2J_{F\text{-}F}$=295		c
-125.8	A of AB(4)	$^2J_{F\text{-}F}$=295		c
-126.1	A of AB(5)	$^2J_{F\text{-}F}$=278		f
-127.5	B of AB(3)	$^2J_{F\text{-}F}$=295		c
-127.9	B of AB(4)	$^2J_{F\text{-}F}$=296		c
-134.1	B of AB(5)	$^2J_{F\text{-}F}$=277		f
-183.9	s		2	a
-185.9	s			a

47. Perfluoro-x-propyldecalin (x=1,2,9) **(66)**



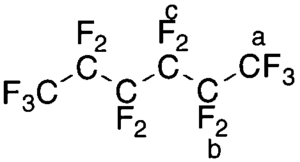
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{19}F				
-80.6	s			d
-108.6 to -140.2	overlapping m			a-c,e-l
-182.2 to -188.2	overlapping m			n,m,o

48. Perfluorooctane (**68a**)



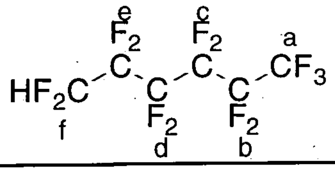
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{19}F				
-81.2	s		3	a
-121.4	s		2	d
-122.2	s		2	c
-126.0	s		2	b

49. Perfluorohexane (**69a**)



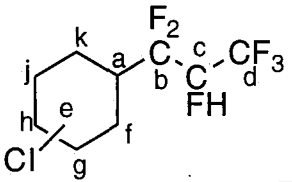
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{19}F				
-80.9	s		3	a
-122.5	s		2	c
-126.1	s		2	b

50. 1H-Perfluorohexane (70)



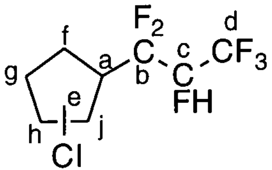
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
8.34	t	$^{2}J_{H\text{-}F} = 52$ $^{4}J_{H\text{-}F} = 5$		f
^{19}F				
-81.4	s		3	a
-122.7	s		2	d
-123.4	s		2	c
-126.2	s		2	b
-129.8	s		2	e
-137.6	d	$^{2}J_{F\text{-}H} = 52$	2	f

51. x-(1,1,2,3,3,3-Hexafluoropropyl)cyclohexyl chloride (x=2-4) (74)



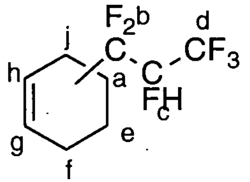
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.35-2.28	overlapping m			a,f,g,h,j,k
2.67	m			a
3.87	m			e
4.48	m			e
4.61	m			e
4.81	d	$J_{H\text{-}F} = 44$		c
^{19}F				
-74.5	s			d
-117.3	m			b
-118.3	m			b
-211.6	br s			c

52. x-(1,1,2,3,3,3-Hexafluoropropyl)cyclopentyl chloride (x=2,3) (**75**)



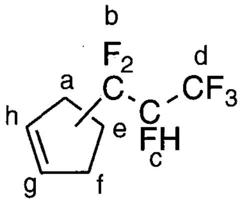
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.70-2.22	overlapping m			f,g,h,j,k
2.45	m			a
2.63	m			a
3.01	m			a
4.30	m			e
4.52	m			e
4.76	d	$J_{H\text{-}F} = 46$		c
^{19}F				
-74.8	s			d
-75.2	s			d
-75.5	s			d
-114.2-118.8	overlapping m			b
-210.1	d	$J_{H\text{-}F} = 38$		c
-211.6	br s			c

53. x-(1,1,2,3,3,3-Hexafluoropropyl)cyclohex-1-ene (x=2-4) (76)



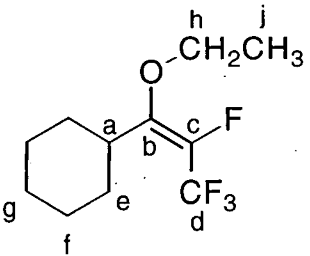
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^{1}H				
1.62, 2.15	m			a,e,f,j
4.84	m			c
5.71	m			h,g
6.00	m			h
6.24	m			g
^{19}F				
-74.7				d
-109.3	A of AB(1)	$J_{F-F} = 260$		b
-103.9	B of AB(1)	$J_{F-F} = 261$		b
-118.0	A of AB(2)	$J_{F-F} = 269$		b
-118.9	m			b
-120.5	B of AB(2)	$J_{F-F} = 267$		b
-212.1	m			c
-211.0	m			c

54. x-(1,1,2,3,3,3-Hexafluoropropyl)cyclopent-1-ene (x=2,3) (**78**)



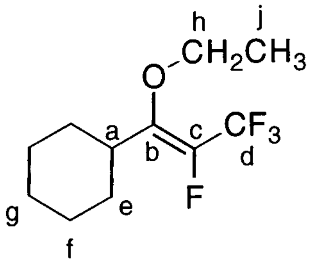
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
1.58,1.97, 2.47	m			a,e,f,j
3.32	m			
4.71	m			c
5.60	m			h,g
5.98	m			h
6.46	m			g
^{19}F				
-74.8				d
-105.7	A of AB(1)	$J_{F\text{-}F} = 260$		b
-109.7	B of AB(1)	$J_{F\text{-}F} = 261$		b
-114.5	A of AB(2)	$J_{F\text{-}F} = 266$		b
-117.0	B of AB(2)	$J_{F\text{-}F} = 266$		b
-210.2	m			c
-211.3	m			c

55. Z-1-Ethoxy-2,3,3,3-tetrafluoroprop-2-enylcyclohexane (**44a**)



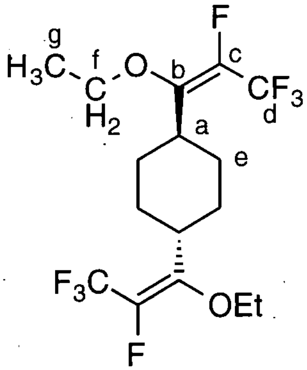
Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
1.29	t	$J_{H\text{-}H} = 7.0$		j
1.56-1.79	m			e,f,g
2.32	m			a
4.13	q	$J_{H\text{-}H} = 6.9$		h
	d	$J_{H\text{-}F} = 3.4$		
^{19}F				
-62.8	br s			d
-161.0	br s			c

56. E-1-Ethoxy-2,3,3,3-tetrafluoroprop-2-enylcyclohexane (**44b**)



Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
1.25	t	$J_{H\text{-}H} = 7.0$		j
1.56-1.79	m			e,f,g
2.48	m			a
3.82	m			h
^{19}F				
-67.0	br s			d
-162.2	br s			c

57. *trans*-1,4-Bis(Z-1-ethoxy-2,3,3,3-tetrafluoroprop-2-enyl)cyclohexane **(80)**



Chemical shift	Multiplicity	Coupling constant Hz	Relative intensity	Assignment
^1H				
1.30	t	$J_{H\text{-}H} = 7.0$		g
1.59,1.67	m			e
2.32	m			a
4.14	q	$J_{H\text{-}H} = 6.8$		f
	d	$J_{H\text{-}F} = 3.4$		
^{19}F				
-63.2	s			d
-161.0	m			c
^{13}C				
15.4	s			g
28.7				e
37.3				a
69.0				f
121.2	q	$J_{F\text{-}F} = 270$		d
	d	$J_{F\text{-}F} = 37$		
133.6	d	$J_{F\text{-}F} = 204$		c
	q	$J_{F\text{-}F} = 39$		
150.0	br s			b

Appendix Two

Selected NMR Spectra

1. *exo*-2-(1,1,2,3,3,3-Hexafluoropropyl)norbornane (**37**)

    2D $^1H^{13}C$ HETCOR NMR spectrum (expansion)

2. *exo*-2-(1,1,2,3,3,3-Hexafluoropropyl)norbornane (**37**)

    2D ^1H COSY NMR spectrum (expansion)

3. Perfluoro-2,5-dipropyltetrahydrofuran (**59**)

    2D ^{19}F COSY NMR spectrum (expansion)

4. Perfluorodipropylcyclohexane (**62**) & (**63**)

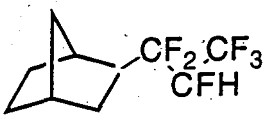
    2D ^{19}F COSY NMR spectrum (expansion)

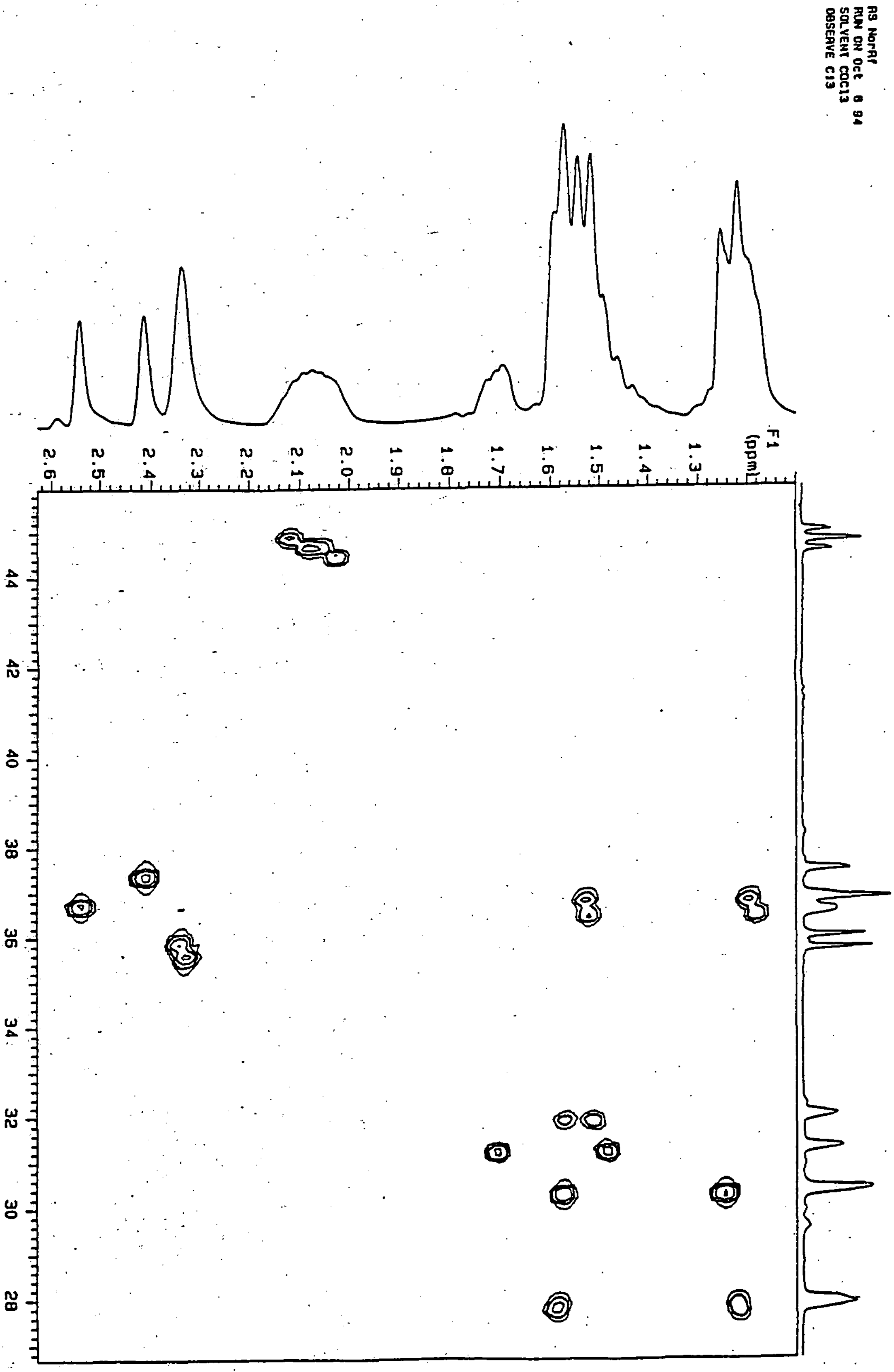
5. Perfluorodipropylcyclopentane (**64**)

    2D ^{19}F COSY NMR spectrum (expansion)

1. *exo*-2-(1,1,2,3,3,3-Hexafluoropropyl)norbornane (37)

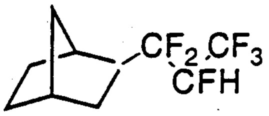
2D $^1H^{13}C$ HETCOR NMR spectrum (expansion)

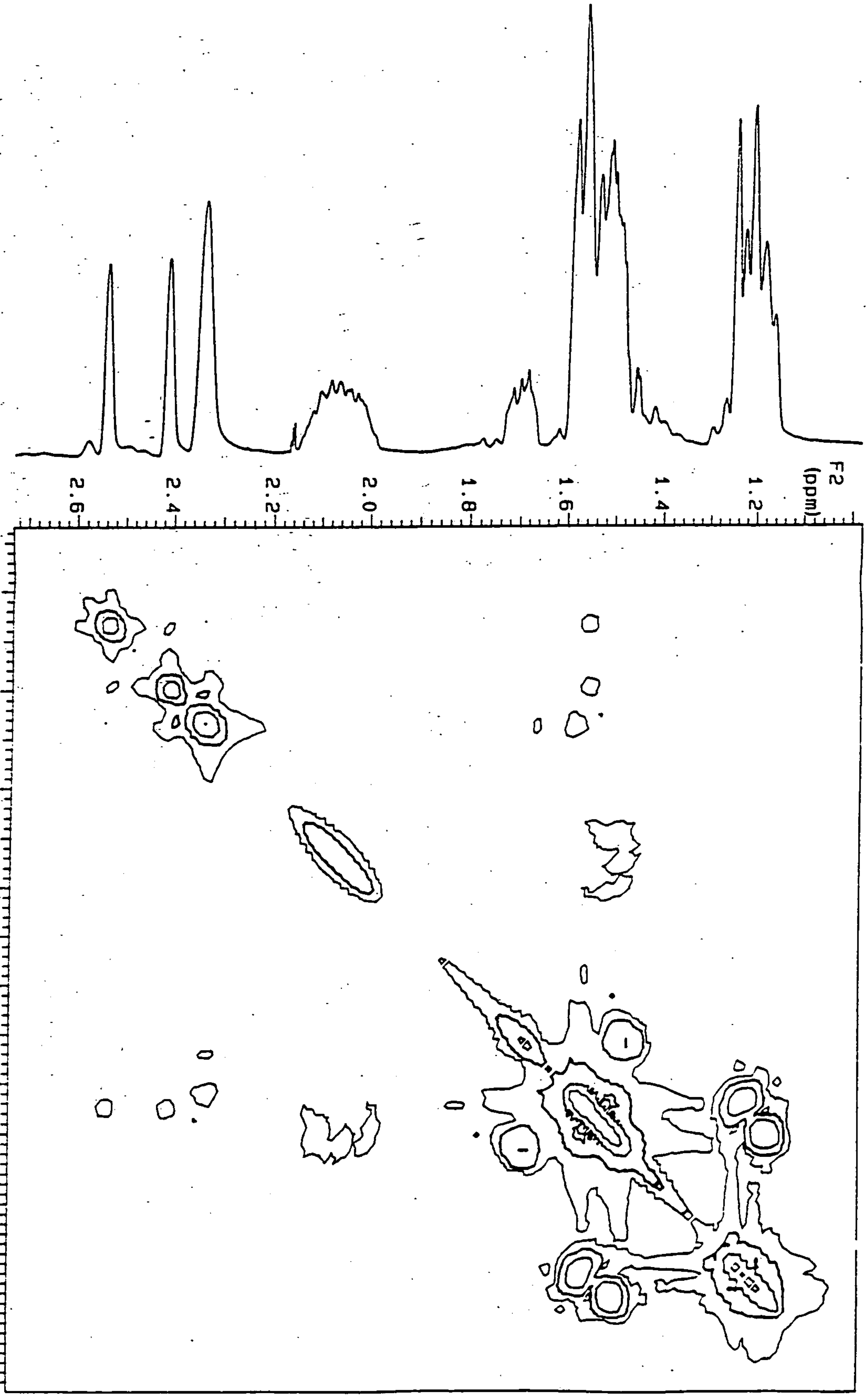




2. *exo*-2-(1,1,2,3,3,3-Hexafluoropropyl)norbornane (37)

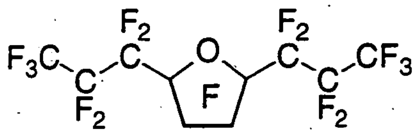
2D ^{1}H COSY NMR spectrum (expansion)

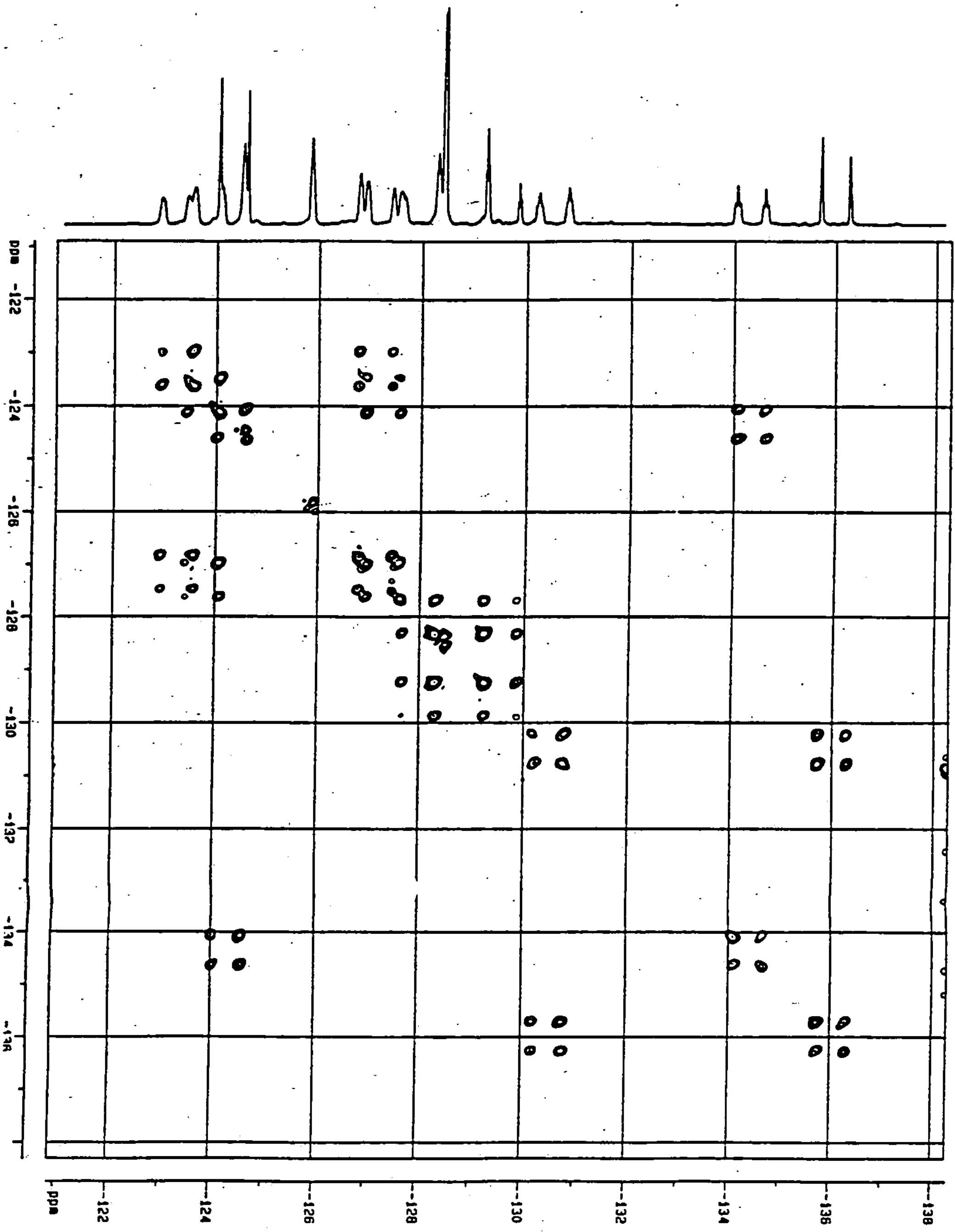




3. Perfluoro-2,5-dipropyltetrahydrofuran (59)

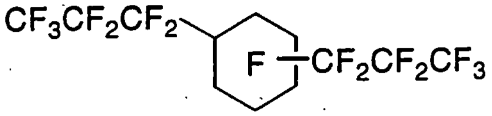
2D ^{19}F COSY NMR spectrum (expansion)

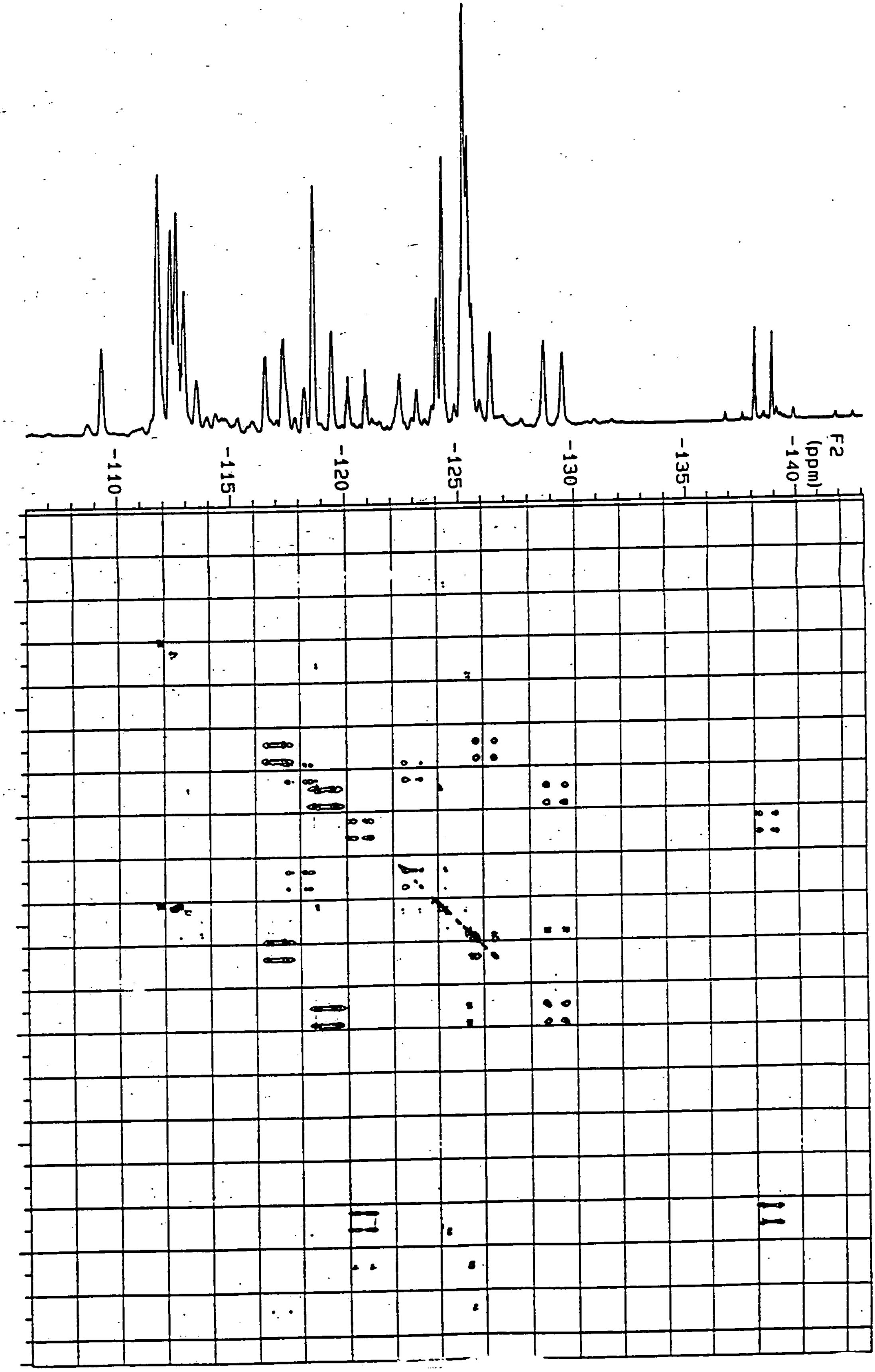




4. Perfluorodipropylcyclohexane (**62**) & (**63**)

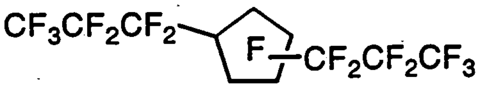
2D ^{19}F COSY NMR spectrum (expansion)

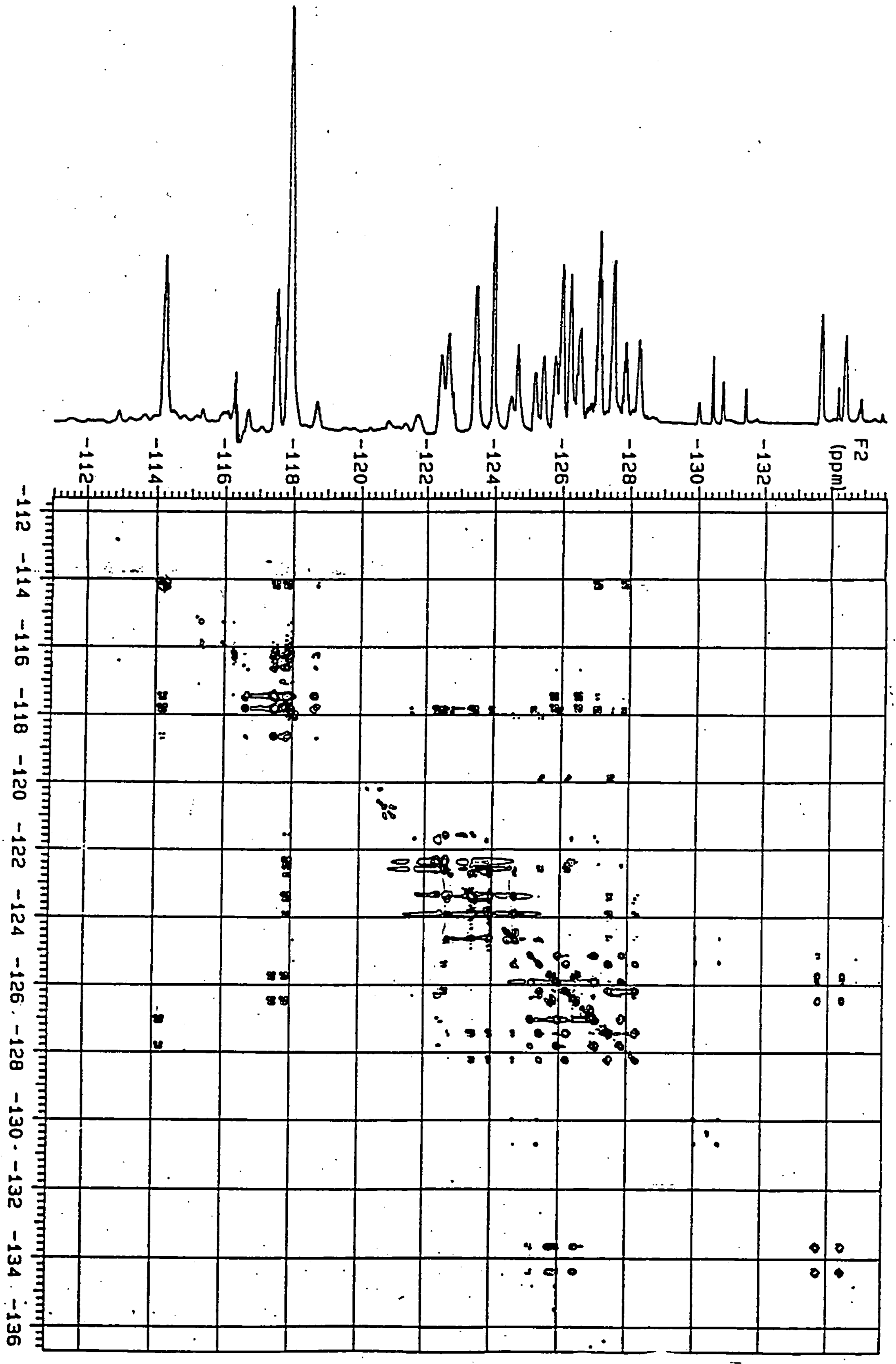




5. Perfluorodipropylcyclopentane (64)

2D ^{19}F COSY NMR spectrum (expansion)

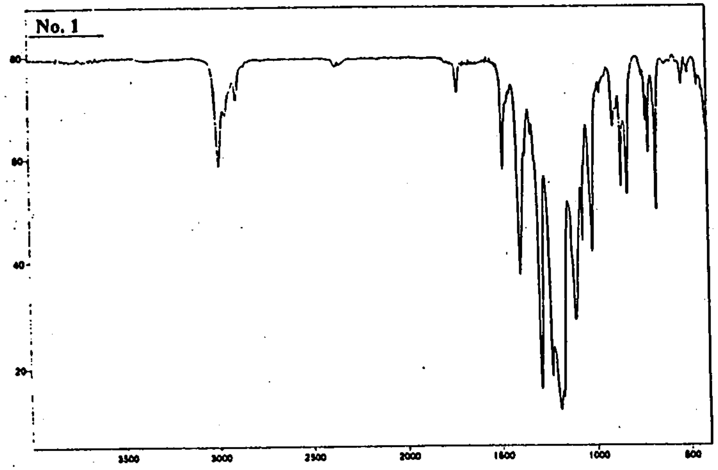




Appendix Three

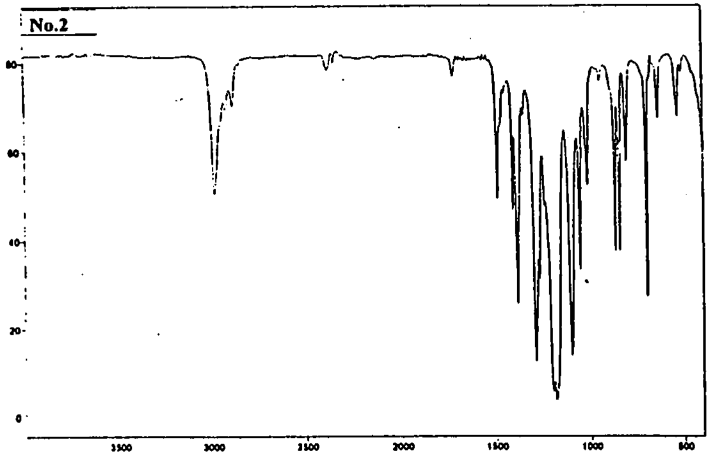
IR Spectra

1. 4-methyl-1,1,1,2,3,3-hexafluoropentane (**28**)
2. 1,1,1,2,3,3-hexafluoro-4,4-dimethylpentane (**30**)
3. 1,1,2,3,3,3-hexafluoropropylcyclopentane (**25**)
4. 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclopentane (x=2,3) (**26**)
5. 1,1,2,3,3,3-hexafluoropropylcyclohexane (**24**)
6. 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x=2-4) (**27**)
7. *2R,2'S-trans*-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (**27a**)
8. x-(1,1,2,3,3,3-hexafluoropropyl)*cis*-decalin (x=1,2,9) (**33**)
9. x,y-bis(1,1,2,3,3,3-hexafluoropropyl)*cis*-decalin (x=1,y=2-10, x=2,y=3-10) (**34**)
10. x-(1,1,2,3,3,3-hexafluoropropyl)*trans*-decalin (x=1,2) (**35**)
11. x,y-bis(1,1,2,3,3,3-hexafluoropropyl)*trans*-decalin (x=1,y=2-10, x=2,y=3-10) (**36**)
12. 2-*exo*-(1,1,2,3,3,3-hexafluoropropyl)norbornane (**37**)
13. 2,x-bis(1,1,2,3,3,3-hexafluoropropyl)norbornane (x=5,6) (**38**)
14. 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane (**22**)
15. 1,3-bis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**23**)
16. 1,3,5,-tris(1,1,2,3,3,3-hexafluoropropyl)adamantane (**39**)
17. 1,3,5,7-tetrakis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**40**)
18. Z-Pentafluoroprop-2-enylcyclohexane (**43a**)
19. 1-(E-pentafluoroprop-2-enyl)adamantane (**45a**)
20. 1-(Z-pentafluoroprop-2-enyl)adamantane (**45b**)
21. *trans*-1,4-bis(Z-pentafluoroprop-2-enyl)cyclohexane (**46**)
22. *cis*-1,3-bis(Z-pentafluoroprop-2-enyl)cyclohexane (**47**)
23. Z-Pentafluoroprop-2-enylcyclopentane (**49**)
24. 1,x-bis(Z-pentafluoroprop-2-enyl)cyclopentane (x=2,3) (**50**)
25. x-(Z-pentafluoroprop-2-enyl)*trans*-decalin (x=1,2) (**51**)
26. x-(Z-Pentafluoroprop-2-enyl)*cis*-decalin (x=1,2,9) (**52**)
27. *exo*-2-(Z-Pentafluoroprop-2-enyl)norbornane (**53**)
28. *exo*-2,x-Bis(Z-pentafluoroprop-2-enyl)norbornane (x=5,6) (**54**)
29. 1,3,5,7-Tetrakis(E-pentafluoroprop-2-enyl)adamantane (**55**)
30. Perfluoropropylcyclohexane (**60**)
31. Perfluoropropylcyclopentane (**61**)
32. Perfluoro-1,4-dipropylcyclohexane (**62**)
33. Perfluoro-1,3-dipropylcyclohexane (**63**)
34. Perfluoro-1,x-dipropylcyclopentane (x=2,3) (**64**)
35. Perfluoro-x-propyldecalin (x=1,2,9) (**66**)
36. x-(1,1,2,3,3,3-Hexafluoropropyl)cyclohex-1-ene (x=2-4) (**76**)
37. 1-Ethoxy-2,3,3,3-tetrafluoroprop-2-enylcyclohexane (**44**)
38. *trans*-1,4-Bis(Z-1-ethoxy-2,3,3,3-tetrafluoroprop-2-enyl)cyclohexane (**80**)



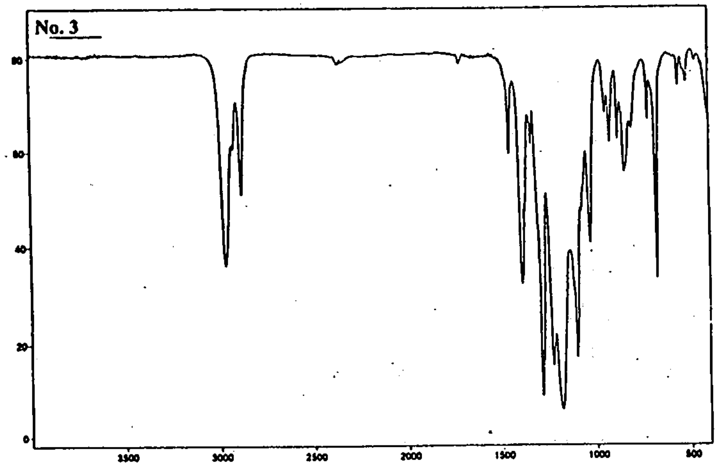
nittance / Wavenumber (cm-1)
1 : PC
exafluoropropyl)propene

Number of Scans= 4 Apodization= Strong
Res=4 cm-1



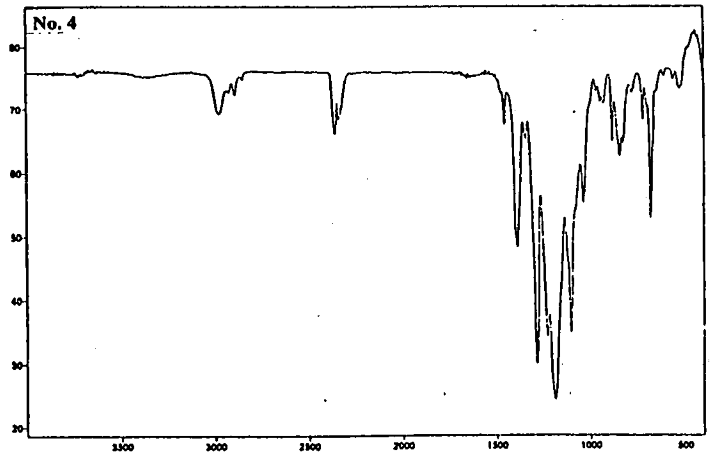
smittance / Wavenumber (cm-1)
1 : PC

Number of Scans= 4 Apodization= Strong
Res=4 cm-1



Transmittance / Wavenumber (cm-1)
File # 1 : PC
2H-hexafluoropropylcyclopentane

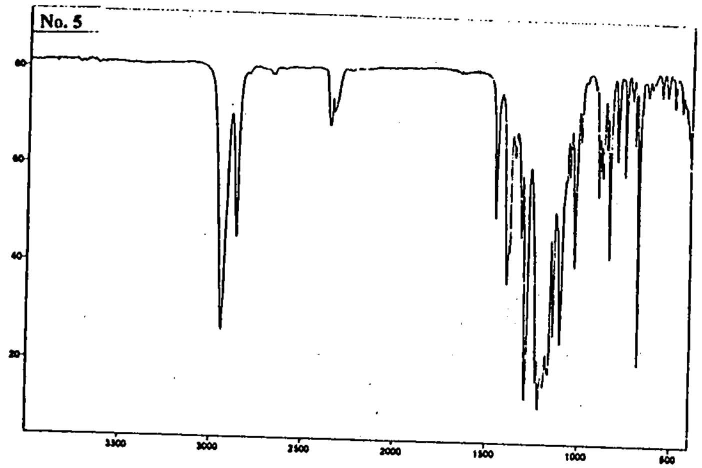
Number of Scans= 4 Apodization= Strong
15:17 Res=4 cm-1



Transmittance / Wavenumber (cm-1)
File # 1 : PC

Number of Scans= 4 Apodization= Strong
Res=4 cm-1

No. 5



mittance / Wavenumber (cm-1)

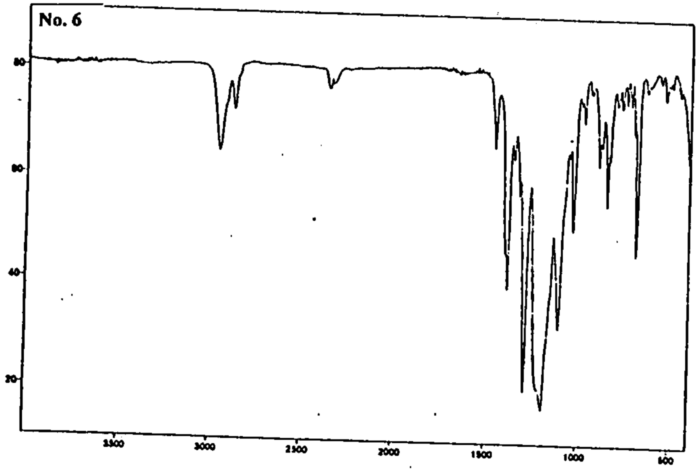
1 : PC

xafluoropropylcyclohexane

Number of Scans= 4 Apodization= Strong

Res=4 cm-1

No. 6



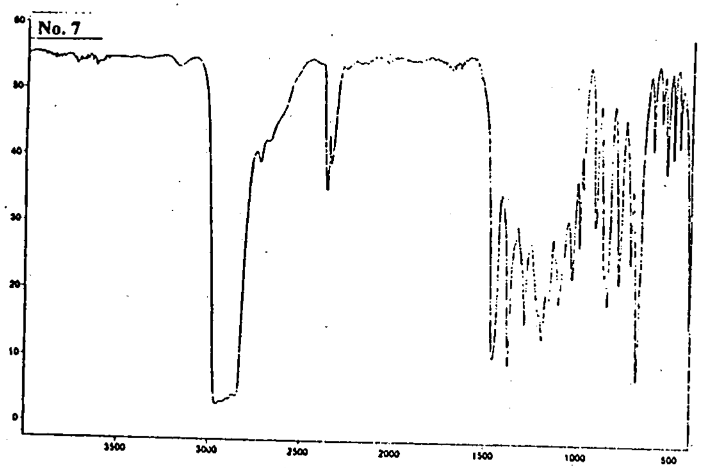
mittance / Wavenumber (cm-1)

1 : PC

Number of Scans= 4 Apodization= Strong

Res=4 cm-1

No. 7



Transmittance / Wavenumber (cm-1)

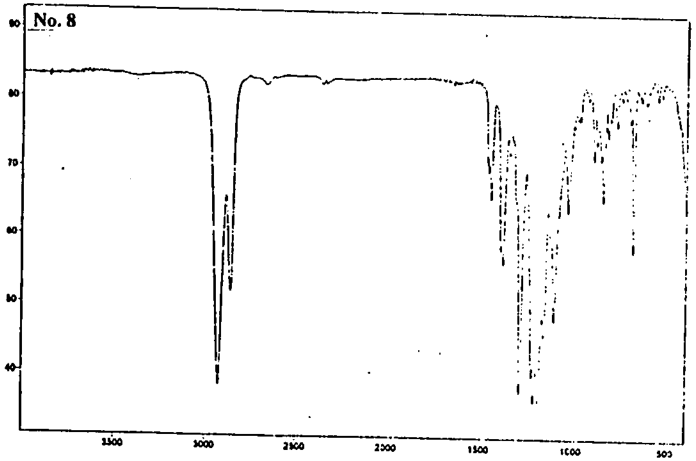
File # 1 : PC

trans-1,4-bis(2H-hexafluoropropyl)cyclohexane/nujol

Number of Scans= 4 Apodization= Strong

Res=4 cm-1

No. 8



Transmittance / Wavenumber (cm-1)

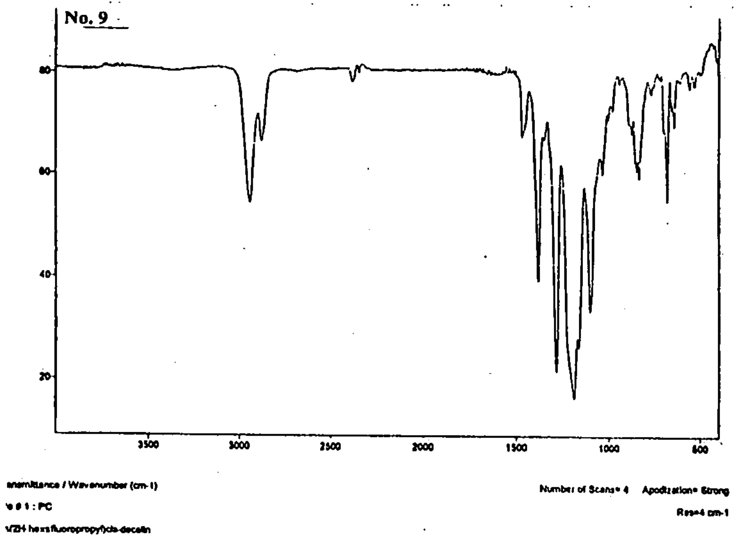
File # 1 : PC

[illegible]

Number of Scans= 4 Apodization= Strong

Res=4 cm-1

No. 9



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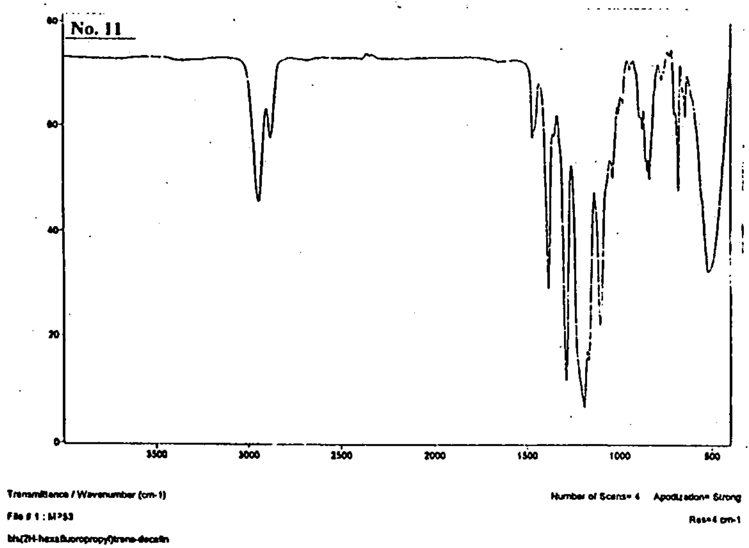

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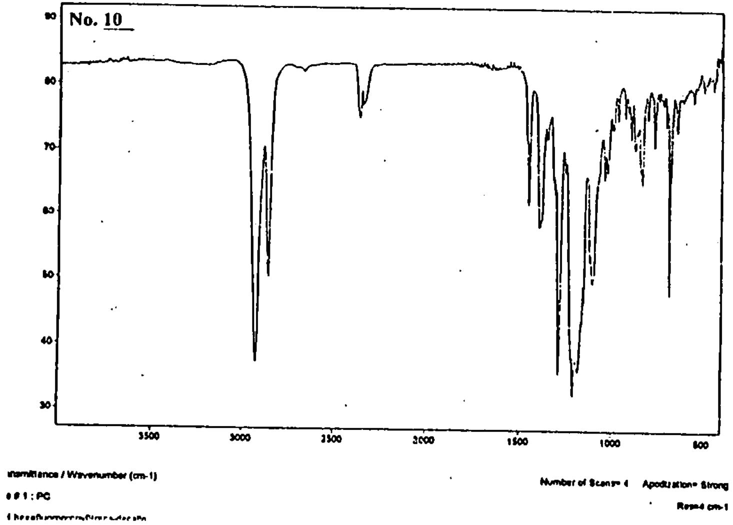

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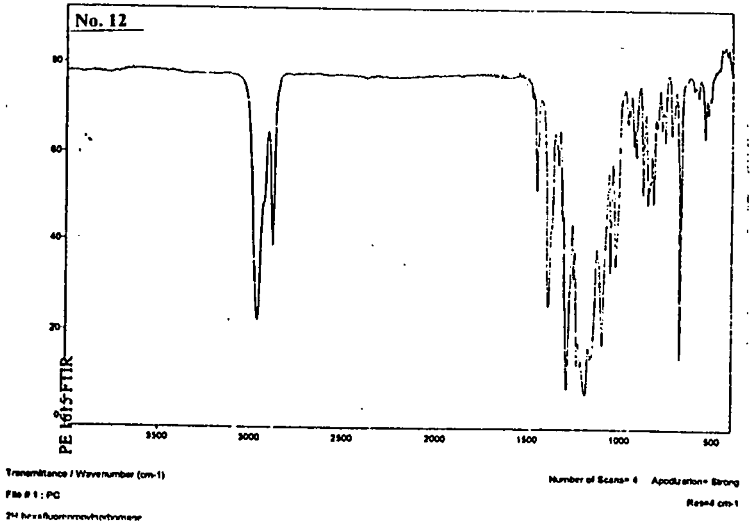
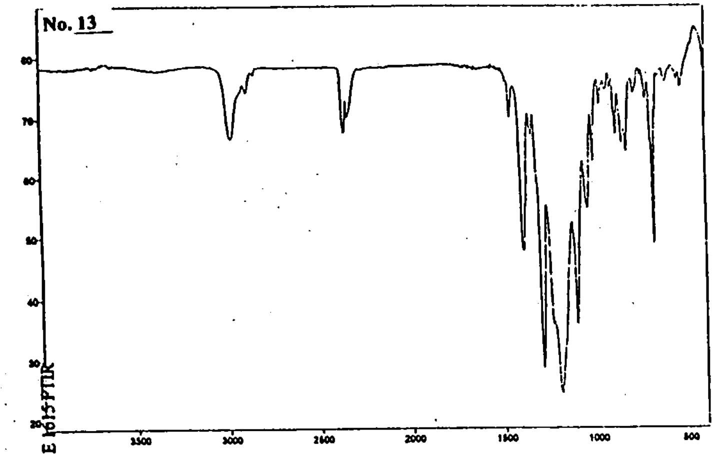
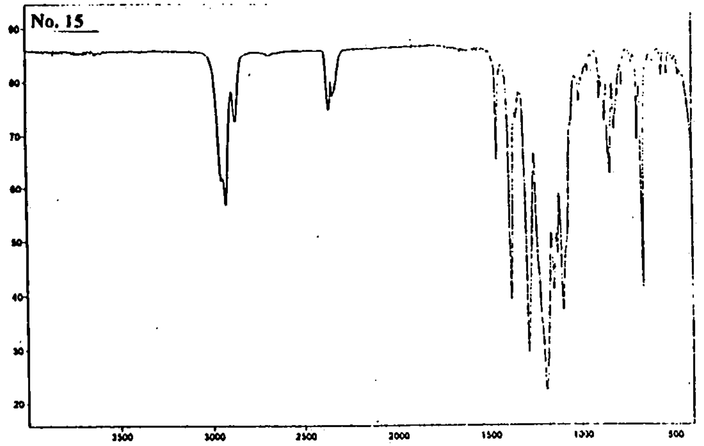
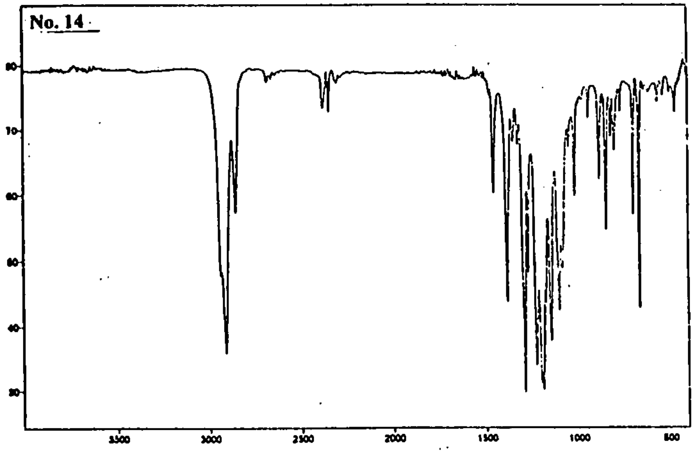




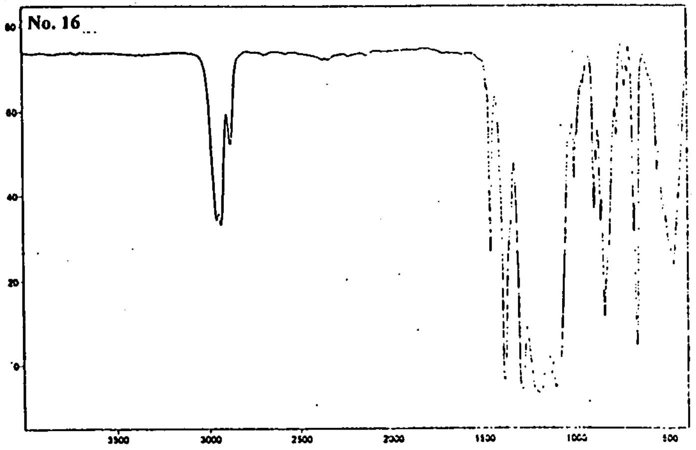
ansmittance / Wavenumber (cm-1) Number of Scans= 4 Apodization= Strong
1 : PC Res=4 cm-1
2H-hexafluoropropyl)norbornane



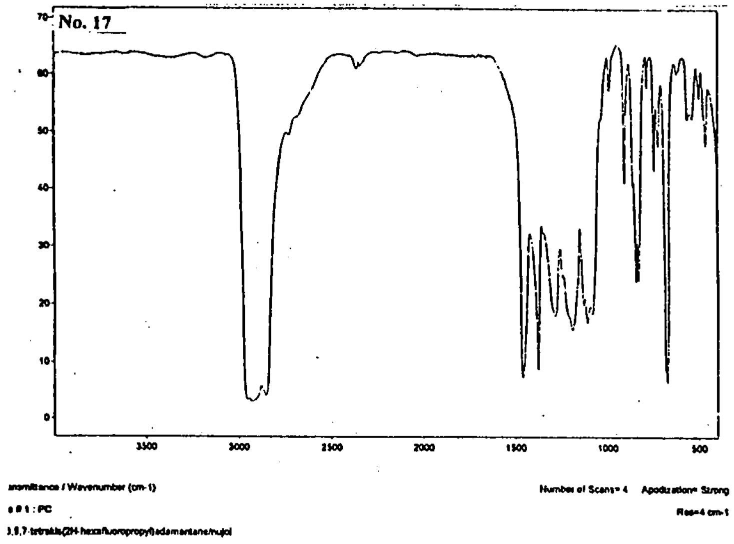
Transmittance / Wavenumber (cm-1) Number of Scans= 4 Apodization= Strong
File # 2 : PC Res=4 cm-1
1,3-bis-(2H-hexafluoropropyl)adamantane



ansmittance / Wavenumber (cm-1) Number of Scans= 4 Apodization= Strong
e # 1 : PC Res=4 cm-1



Transmittance / Wavenumber (cm-1) Number of Scans= 4 Apodization= Strong
File # 1 : MP53 Res=4 cm-1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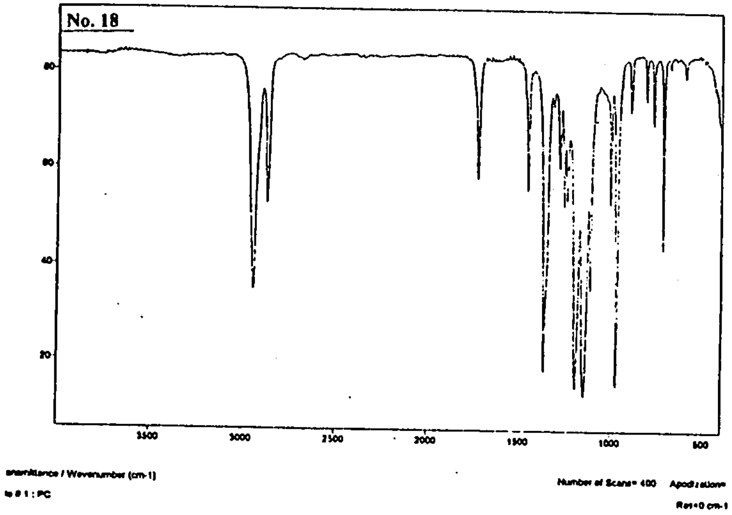
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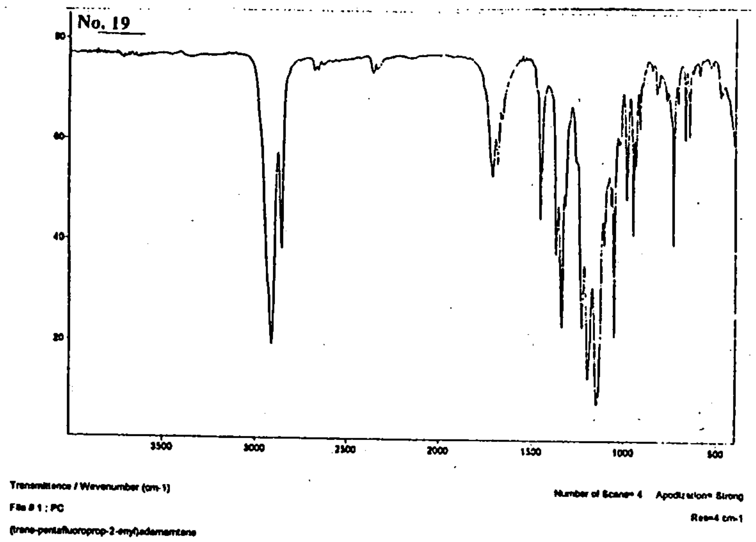
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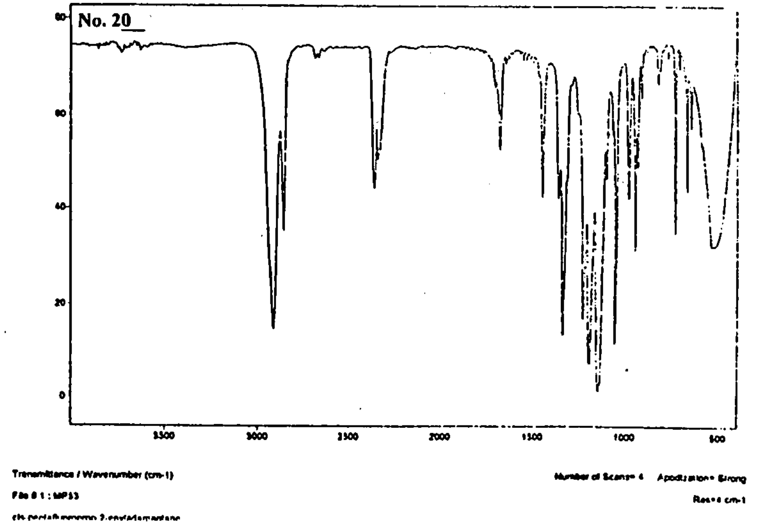
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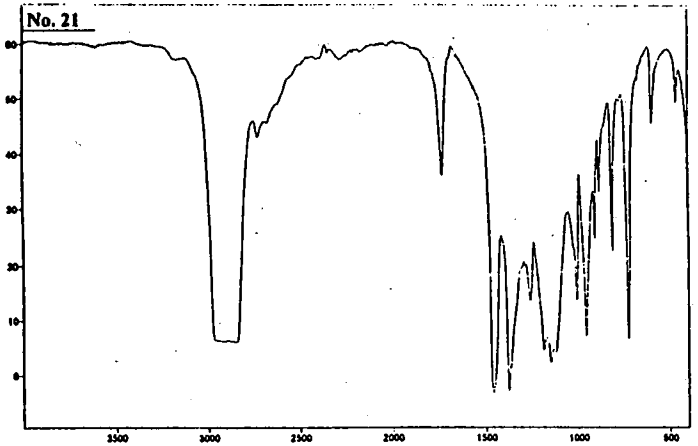
No. 21

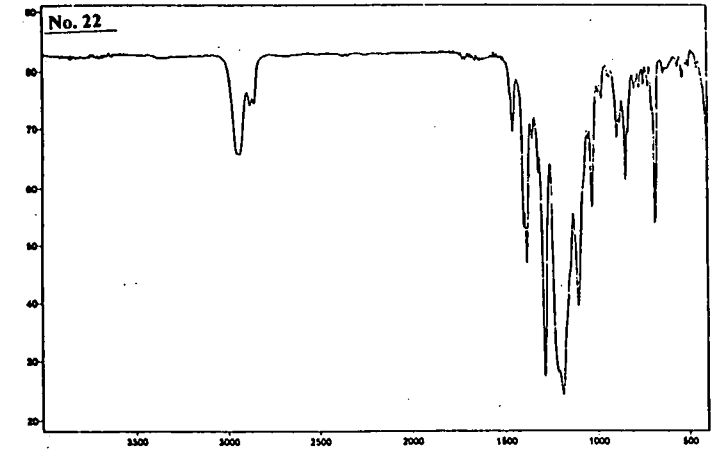


smittance / Wavenumber (cm-1)   Number of Scans= 4   Apodization= Strong

1 : PC   Res=4 cm-1

1,4-bis(cis-pentafluoroprop-2-enyl)cyclohexane/nujol

No. 22

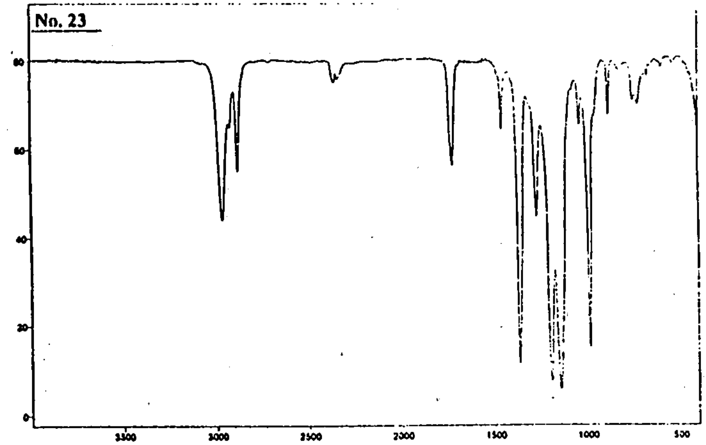


ransmittance / Wavenumber (cm-1)   Number of Scans= 4   Apodization= Strong

1 : PC   Res=4 cm-1

cis-pentafluoroprop-2-enyl)cyclohexane

No. 23

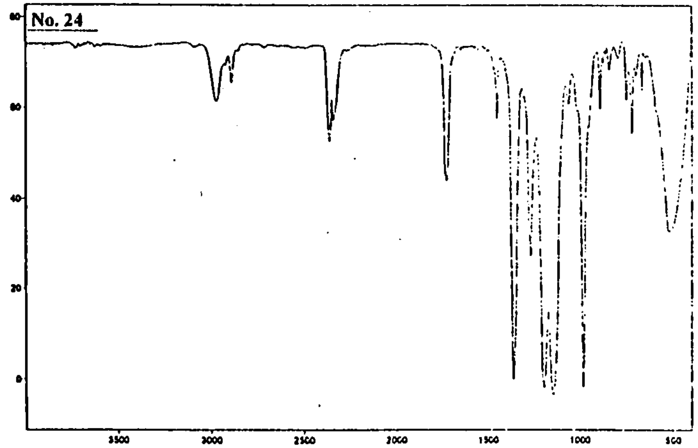


Transmittance / Wavenumber (cm-1)   Number of Scans= 4   Apodization= Strong

File # 1 : PC   Res=4 cm-1

(cis-pentafluoroprop-2-enyl)cyclopentane

No. 24

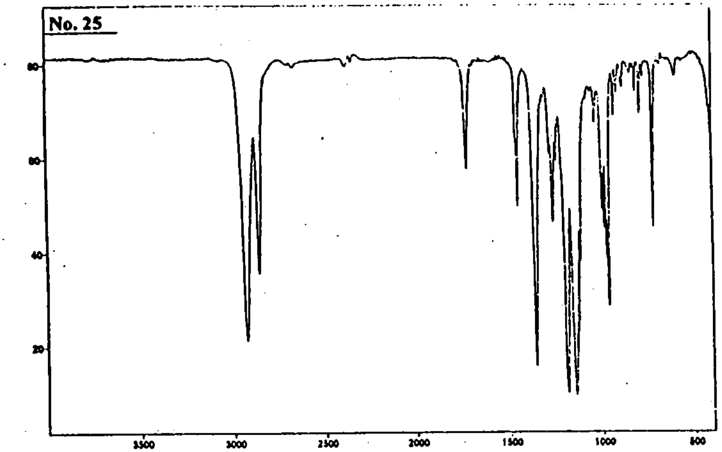


Transmittance / Wavenumber (cm-1)   Number of Scans= 4   Apodization= Strong

File # 1 : MP53   Res=4 cm-1

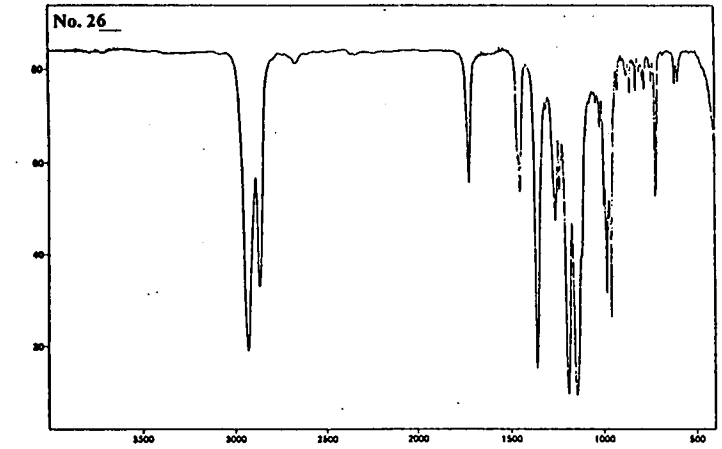
[illegible]

No. 25



-pentafluoroprop-2-enyl)trans-decalin

No. 26



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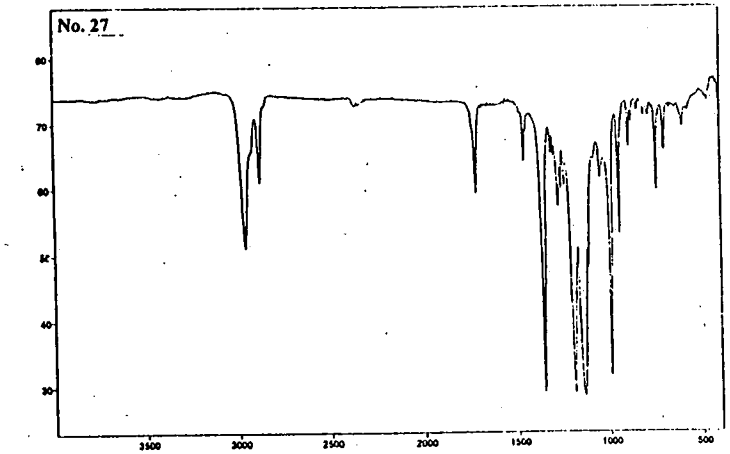
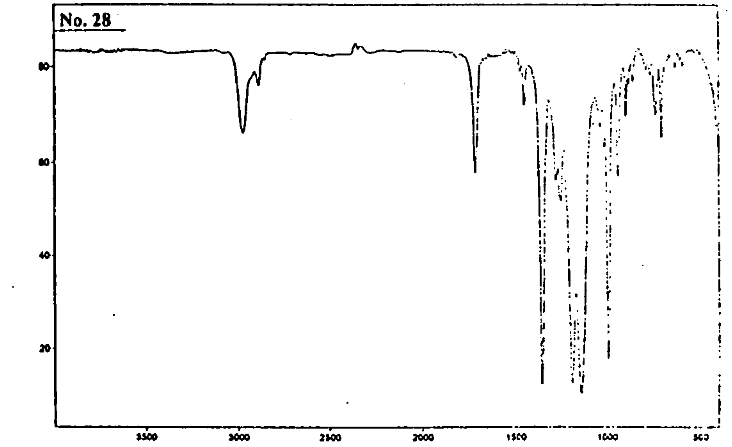
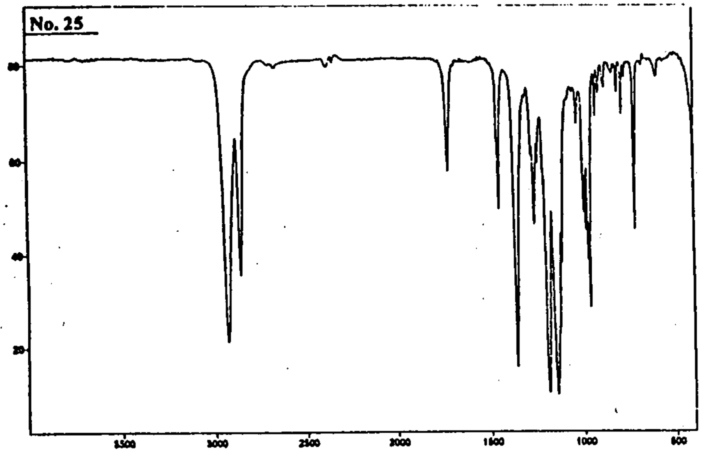


exo-2-(pentafluoroprop-2-enyl)norbornane

No. 28





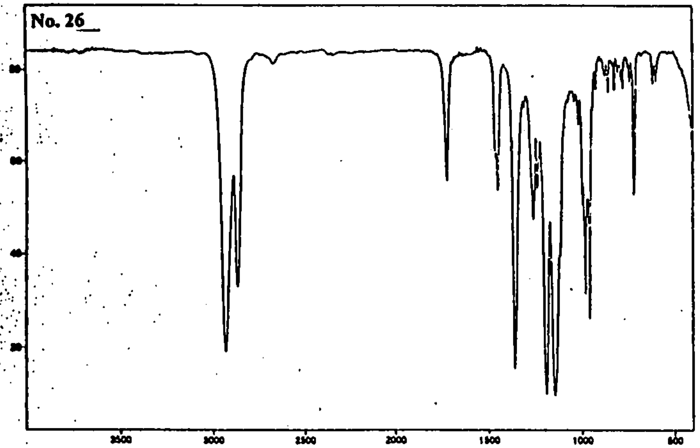
Transmittance / Wavenumber (cm-1)

File # 1 : PC

-(pentafluoroprop-2-enyl)trans-decalin

Number of Scans= 4 Apodization= Strong

Res=4 cm-1



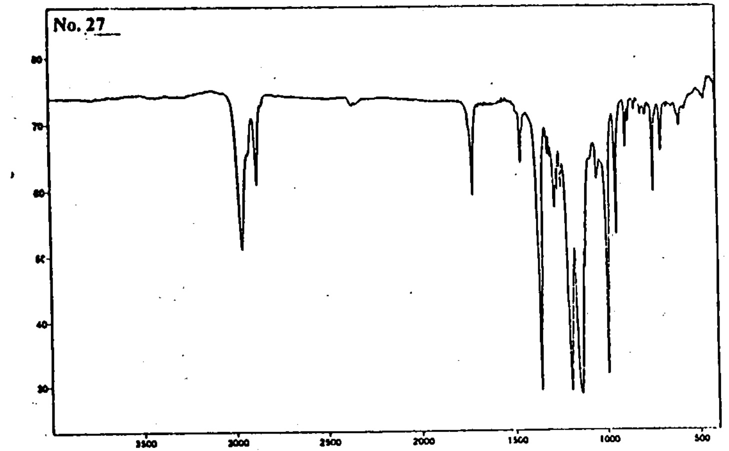
Transmittance / Wavenumber (cm-1)

File # 1 : PC

[illegible]

Number of Scans= 4 Apodization= Strong

Res=4 cm-1



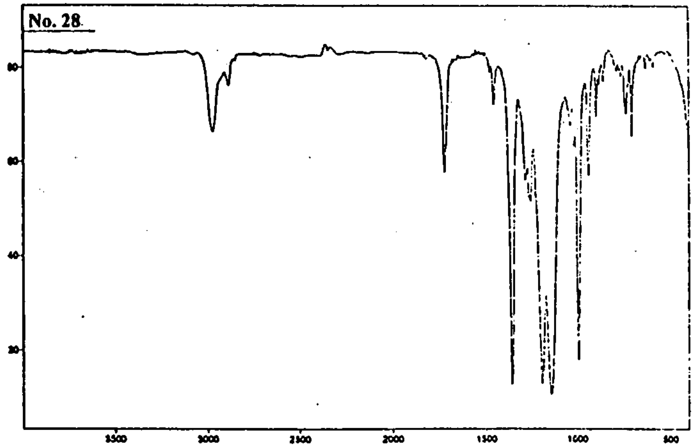
Transmittance / Wavenumber (cm-1)

File # 1 : PC

exo-2-(pentafluoroprop-2-enyl)norbornane

Number of Scans= 4 Apodization= Strong

Res=4 cm-1

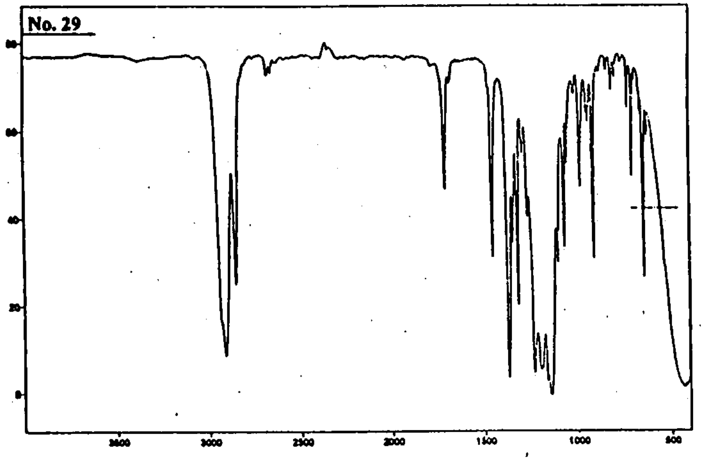


Transmittance / Wavenumber (cm-1)

File # 1 : PC

Number of Scans= 4 Apodization= Strong

Res=4 cm-1



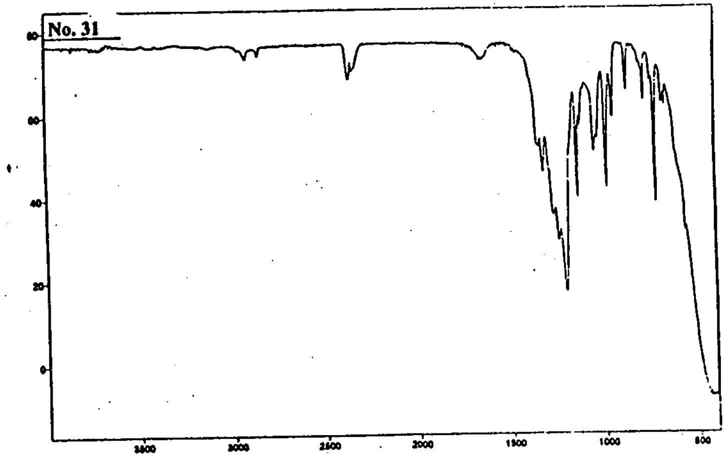
Transmittance / Wavenumber (cm-1)

File # 1 : MP53

1,3,5,7-tetrakis(pentafluoroprop-2-enyl)adamantane

Number of Scans= 4 Apodization= Strong

Res=4 cm-1



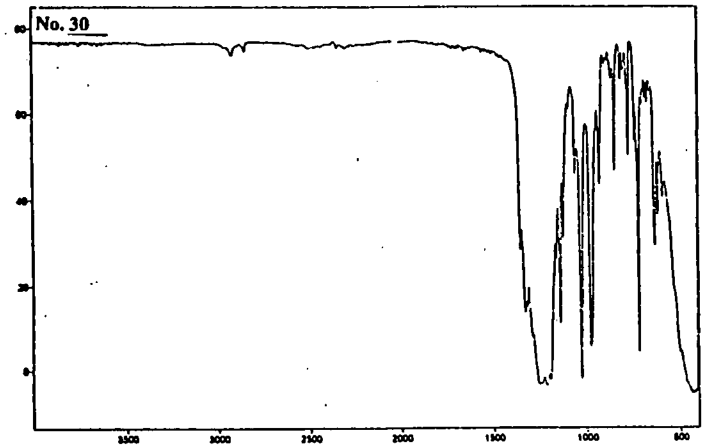
ansmittance / Wavenumber (cm-1)

e # 1 : PD374

rfluoro-propylcyclopentane

Number of Scans= 4 Apodization= Strong

Res=4 cm-1



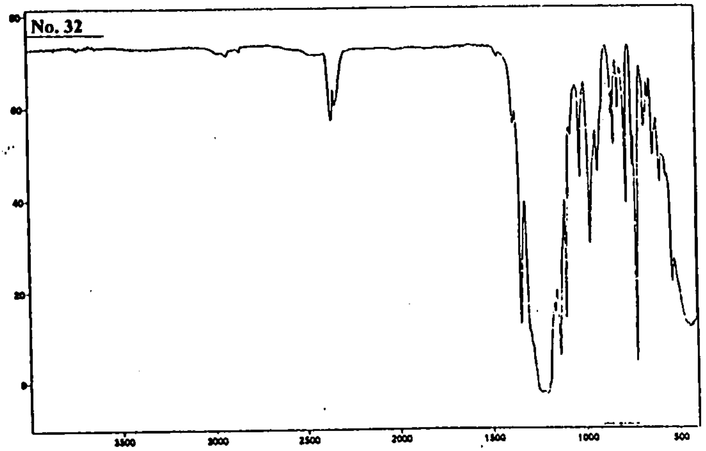
Transmittance / Wavenumber (cm-1)

File # 1 : PD374

[illegible]

Number of Scans= 4 Apodization= Strong

Res=4 cm-1



ansmittance / Wavenumber (cm-1)

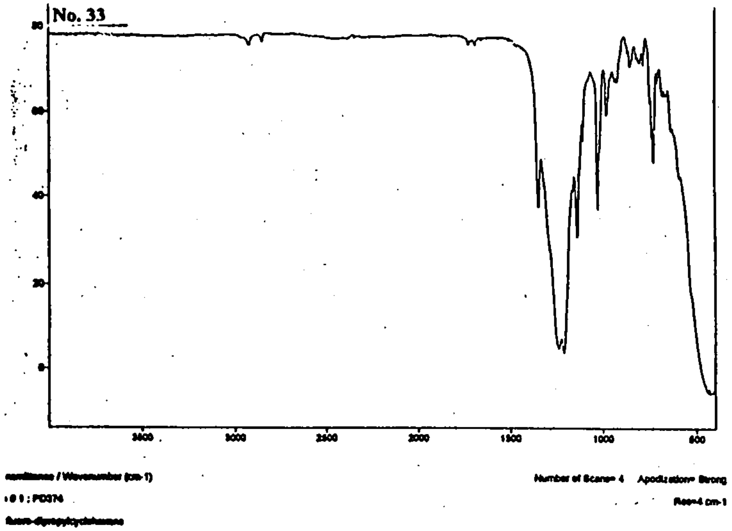
te # 1 : MP53

[illegible]

Number of Scans= 4 Apodization= Strong

Res=4 cm-1

No. 33



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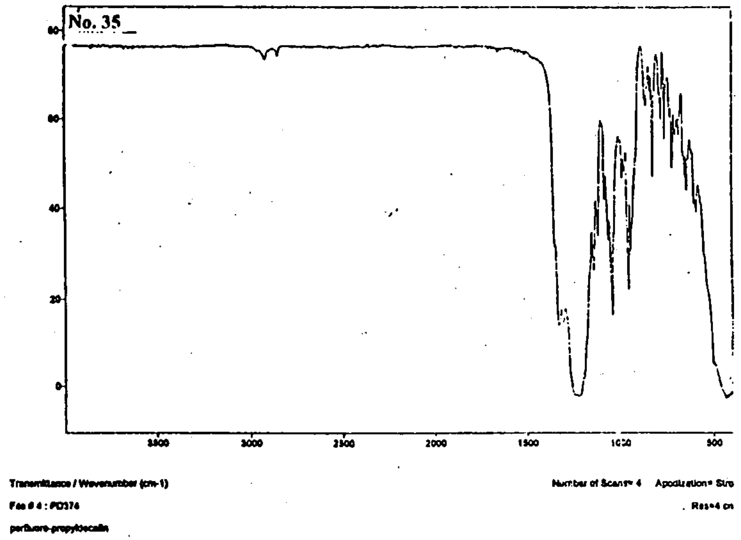

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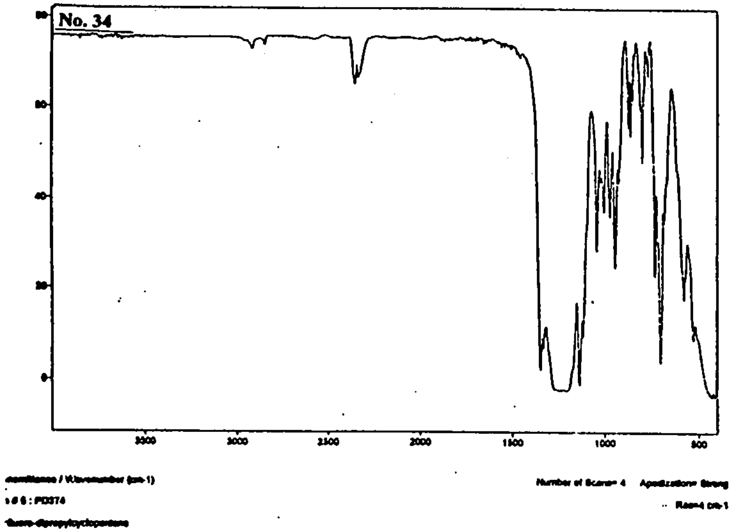

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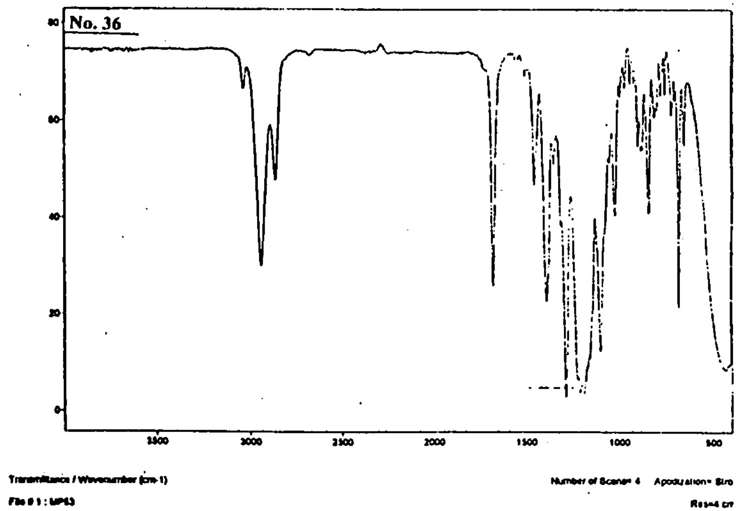

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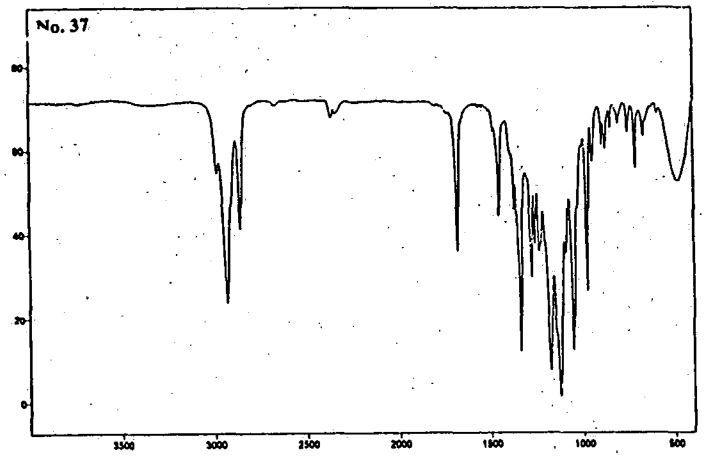


nsmittance / Wavenumber (cm-1)

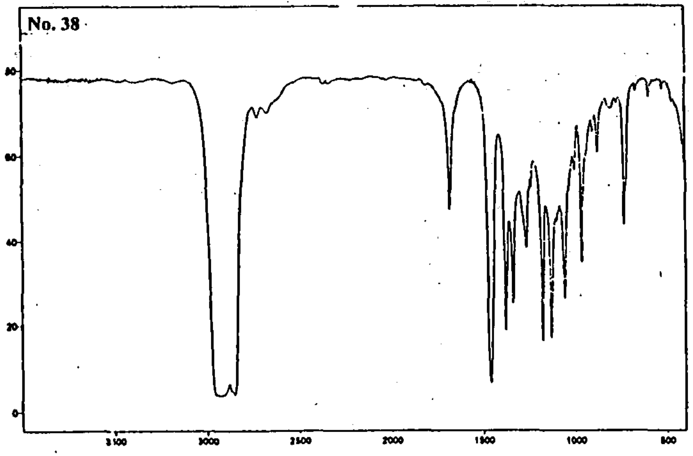
Number of Scans= 4 Apodization= Strong

e # 1 : MP53

Res=4 cm-1

thoxy-tetrafluoroprop-2-enylcyclohexane

No. 38



ansmittance / Wavenumber (cm-1)

Number of Scans= 4 Apodization= Strong

e # 1 : PC

Res=4 cm-1

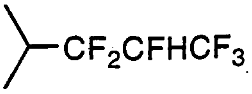
Appendix Four

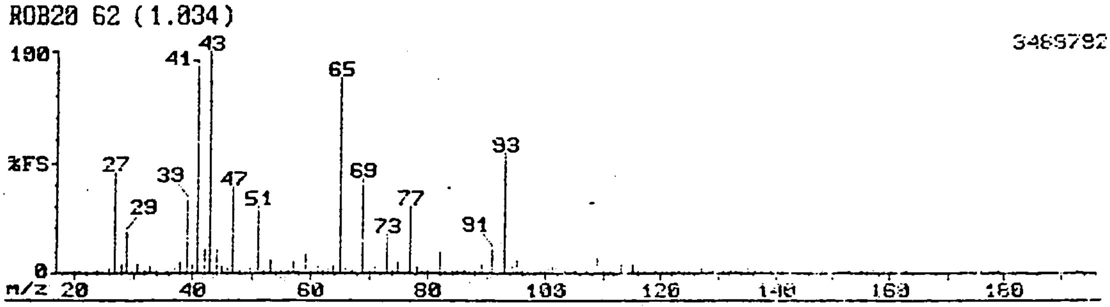
EI$^+$ Mass Spectra

1. 4-methyl-1,1,1,2,3,3-hexafluoropentane (**28**)
2. 1,1,1,2,3,3-hexafluorohexane (**29**)
3. 1,1,1,2,3,3-hexafluoro-4,4-dimethylpentane (**30**)
4. 1,1,1,2,3,3-hexafluoro-5-methylhexane (**31**)
5. 1,1,2,3,3,3-hexafluoropropylcyclopropane (**32**)
6. 1,1,2,3,3,3-hexafluoropropylcyclopentane (**25**)
7. 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclopentane (x=2,3) (**26**)
8. 1,1,2,3,3,3-hexafluoropropylcyclohexane (**24**)
9. 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x=2-4) (**27**)
10. *2R,2'S-trans*-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (**27a**)
11. x-(1,1,2,3,3,3-hexafluoropropyl)*cis*-decalin (x=1,2,9) (**33**)
12. x,y-bis(1,1,2,3,3,3-hexafluoropropyl)*cis*-decalin (x=1,y=2-10, x=2,y=3-10) (**34**)
13. x-(1,1,2,3,3,3-hexafluoropropyl)*trans*-decalin (x=1,2) (**35**)
14. x,y-bis(1,1,2,3,3,3-hexafluoropropyl)*trans*-decalin (x=1,y=2-10, x=2,y=3-10) (**36**)
15. 2-*exo*-(1,1,2,3,3,3-hexafluoropropyl)norbornane (**37**)
16. 2,x-bis(1,1,2,3,3,3-hexafluoropropyl)norbornane (x=5,6) (**38**)
17. 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane (**22**)
18. 1,3-bis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**23**)
19. 1,3,5,-tris(1,1,2,3,3,3-hexafluoropropyl)adamantane (**39**)
20. 1,3,5,7-tetrakis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**40**)
21. Z-Pentafluoroprop-2-enylcyclohexane (**43a**)
22. E-Pentafluoroprop-2-enylcyclohexane (**43b**)
23. 1-(E-pentafluoroprop-2-enyl)adamantane (**45a**)
24. 1-(Z-pentafluoroprop-2-enyl)adamantane (**45b**)
25. *trans*-1,4-bis(Z-pentafluoroprop-2-enyl)cyclohexane (**46**)
26. *cis*-1,3-bis(Z-pentafluoroprop-2-enyl)cyclohexane (**47**)
27. Z-Pentafluoroprop-2-enylcyclopentane (**49**)
28. *trans*-1,3-bis(Z-pentafluoroprop-2-enyl)cyclopentane (**50a**)
29. *cis*-1,3-bis(Z-pentafluoroprop-2-enyl)cyclopentane (**50b**)
30. *trans*-1,2-bis(Z-pentafluoroprop-2-enyl)cyclopentane (**50c**)
31. 2-(Z-pentafluoroprop-2-enyl)*trans*-decalin (**51b**)
32. 1-(Z-pentafluoroprop-2-enyl)*trans*-decalin (**51a**)
33. 1-(Z-Pentafluoroprop-2-enyl)*cis*-decalin (**52a**)
34. 2-(Z-Pentafluoroprop-2-enyl)*cis*-decalin (**52b**)
35. *exo*-2-(Z-Pentafluoroprop-2-enyl)norbornane (**53**)

36. *exo*-2,5-Bis(Z-pentafluoroprop-2-enyl)norbornane (**54a**)
37. *exo*-2,6-Bis(Z-pentafluoroprop-2-enyl)norbornane (**54b**)
38. 1,3,5,7-Tetrakis(E-pentafluoroprop-2-enyl)adamantane (**55**)
39. 1-(Z-Pentafluoroprop-2-enyl)-3,5,7-tris(E-pentafluoroprop-2-enyl)adamantane (**55a**)
40. Perfluoro-2,5-dipropyltetrahydrofuran (59)
41. Perfluoropropylcyclohexane (**60**)
42. Perfluoropropylcyclopentane (**61**)
43. *trans*-perfluoro-1,4-dipropylcyclohexane (**62a**)
44. *cis*-perfluoro-1,4-dipropylcyclohexane (**62b**)
45. *trans*-Perfluoro-1,3-dipropylcyclohexane (**63a**)
46. *cis*-Perfluoro-1,3-dipropylcyclohexane (**63b**)
47. Perfluoro-1,x-dipropylcyclopentane (x=2,3) (**64**)
48. Perfluoro-x-propyldecalin (x=1,2,9) (**66**)
49. Perfluoro-1-propyladamantane (**67**)
50. Perfluorooctane (**68a**)
51. Perfluorohexane (**69a**)
52. 1H-Perfluorohexane (**70**)
53. x-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl chloride (x=2-4) (**74**)
54. x-(1,1,2,3,3,3-hexafluoropropyl)cyclopentyl chloride (x=2,3) (**75**)
55. x-(1,1,2,3,3,3-hexafluoropropyl)cyclohex-1-ene (x=2-4) (**76**)
56. x-(1,1,2,3,3,3-hexafluoropropyl)cyclopent-1-ene (x=2,3) (**78**)
57. Z-1-ethoxy-2,3,3,3-tetrafluoroprop-2-enylcyclohexane (**44a**)
58. E-1-ethoxy-2,3,3,3-tetrafluoroprop-2-enylcyclohexane (**44b**)
59. *trans*-1,4-Bis(Z-1-ethoxy-2,3,3,3-tetrafluoroprop-2-enyl)cyclohexane (**80**)

1. 4-methyl-1,1,1,2,3,3-hexafluoropentane (28)

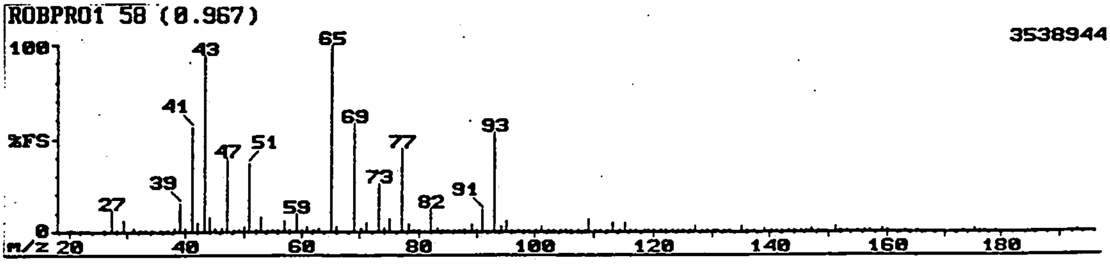




RSPROPS 62 (1.034) 2998272

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	39	21.04	54	0.34	70	0.38	85	0.40	101	2.32	117	0.03	136	0.10	159	1.35
24	0.01	40	3.11	55	0.24	71	2.36	86	0.06	102	0.19	119	0.65	137	0.06	160	0.09
25	0.05	41	85.73	56	0.61	72	0.42	87	0.18	103	0.52	120	0.06	139	1.42	163	0.03
26	1.31	42	7.00	57	4.17	73	12.30	88	0.81	104	0.12	121	0.23	140	0.10	173	0.24
27	23.22	43	100.00	58	0.50	74	0.30	89	2.30	105	0.73	122	0.03	141	0.04	175	0.45
28	3.15	44	7.83	59	5.66	75	3.45	90	1.12	106	0.19	123	0.02	145	0.16	176	0.03
29	8.40	45	2.08	60	0.47	76	0.62	91	9.43	107	0.16	124	0.01	146	0.42	177	0.02
30	0.17	46	1.29	61	1.97	77	22.40	93	46.45	108	0.32	125	0.03	147	1.17	179	0.02
31	1.95	47	21.42	62	0.34	78	2.19	94	2.08	109	5.67	127	2.02	148	0.03	193	0.06
32	2.40	48	0.76	63	1.33	79	0.31	95	5.23	110	0.25	128	0.11	151	2.13		
33	1.54	49	0.23	64	3.24	80	0.08	96	0.21	111	0.13	129	0.40	152	0.06		
34	0.02	50	2.03	65	72.13	81	0.41	97	0.70	113	4.10	131	0.46	153	0.11		
35	0.03	51	25.41	66	1.64	82	7.41	98	0.22	114	0.15	132	0.34	155	0.60		
37	0.87	52	0.75	67	0.07	83	1.15	99	0.22	115	2.86	133	0.49	156	0.04		
38	2.73	53	4.35	69	33.32	84	0.25	100	0.73	116	0.21	135	1.64	157	0.03		

2. 1,1,1,2,3,3-hexafluorohexane (29)



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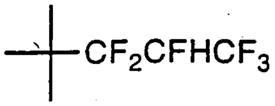
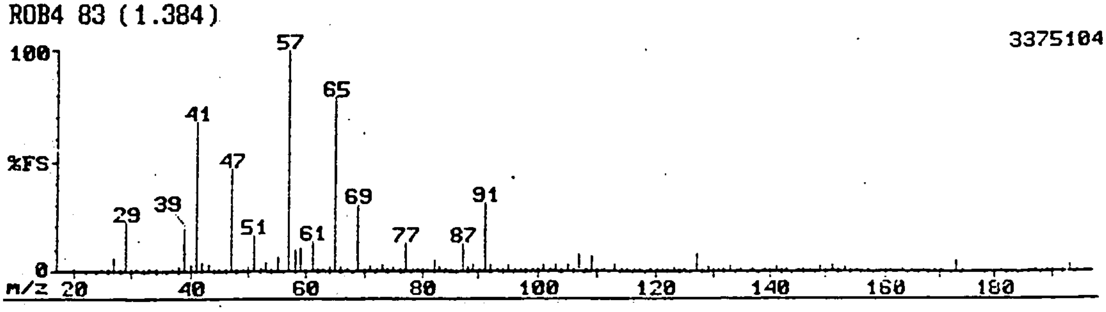
-----------------+-----------------+-----------------+-----------------
   20      0.01  |   60      0.70  |  100      0.88  |  133      0.73
   26      0.74  |   61      2.98  |  101      2.98  |  135      2.60
   27     11.92  |   62      0.48  |  102      0.30  |  136      0.18
   28      1.35  |   63      2.08  |  103      0.63  |  137      0.14
   29      5.87  |   65    100.00  |  104      0.27  |  139      2.23
   31      1.49  |   66      2.60  |  105      0.88  |  140      0.16
   32      0.33  |   69     58.33  |  106      0.26  |  141      0.06
   33      1.15  |   70      1.84  |  107      0.25  |  142      0.01
   34      0.01  |   71      4.75  |  108      1.17  |  143      0.01
   36      0.01  |   73     26.27  |  109      7.06  |  144      0.02
   37      0.70  |   74      1.83  |  110      0.36  |  145      0.28
   38      2.20  |   75      7.03  |  111      0.18  |  146      0.72
   39     15.39  |   77     44.44  |  112      0.60  |  147      1.61
   40      2.11  |   78      4.05  |  113      5.03  |  148      0.08
   41     56.48  |   79      0.57  |  114      0.64  |  151      3.36
   42      4.51  |   80      0.15  |  115      5.06  |  152      0.12
   43     94.44  |   82     13.08  |  116      0.29  |  153      0.15
   44      7.75  |   83      1.79  |  117      0.04  |  155      1.12
   45      2.34  |   84      0.38  |  118      0.11  |  156      0.08
   46      1.46  |   85      0.56  |  119      0.88  |  157      0.05
   47     39.35  |   86      0.09  |  120      0.09  |  159      2.05
   48      1.03  |   87      0.26  |  121      0.34  |  160      0.14
   49      0.35  |   88      1.10  |  122      0.08  |  163      0.08
   50      3.13  |   89      3.76  |  123      0.06  |  165      0.01
   51     37.04  |   90      1.32  |  124      0.02  |  173      0.31
   52      1.16  |   91     11.34  |  125      0.05  |  175      2.08
   53      7.52  |   93     53.70  |  126      0.37  |  176      0.13
   54      0.50  |   94      2.58  |  127      3.07  |  177      0.03
   55      0.38  |   95      6.02  |  128      0.26  |  179      0.02
   56      0.95  |   96      0.26  |  129      0.71  |  193      0.08
   57      6.22  |   97      0.87  |  130      0.07  |
   58      0.76  |   98      0.04  |  131      0.69  |
   59      9.95  |   99      0.30  |  132      0.57  |
-----------------+-----------------+-----------------+-----------------
```

3. 1,1,1,2,3,3-hexafluoro-4,4-dimethylpentane (30)





ROB4 83 (1.384) 3375104

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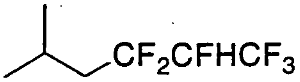
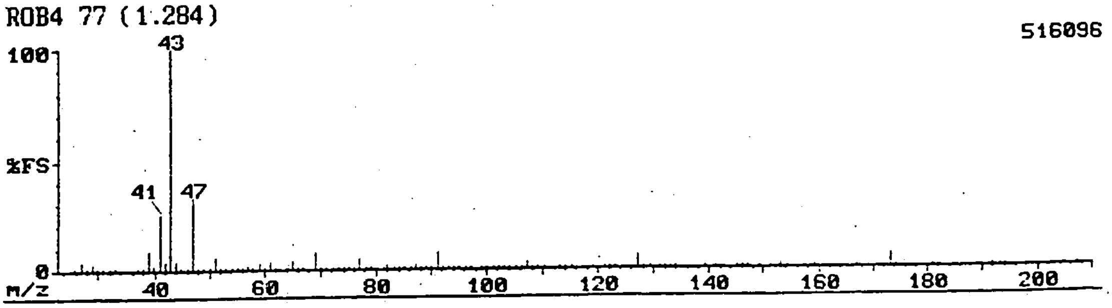
20	0.01	42	3.55	59	10.92	76	0.38	93	0.62	109	7.10	128	0.28	147	0.74	170	0.03
25	0.02	43	2.49	60	0.66	77	12.50	94	0.14	110	0.29	129	1.82	149	1.07	173	5.25
26	0.52	44	0.37	61	13.96	78	0.53	95	2.91	111	0.38	130	0.00	150	0.12	174	0.30
27	6.04	45	1.17	62	0.68	79	0.78	96	0.10	113	3.25	131	0.53	151	2.76	177	0.20
28	1.28	46	0.74	63	1.11	80	0.09	97	0.30	114	0.20	132	0.17	152	0.05	181	0.02
29	22.33	47	46.12	64	2.12	81	0.39	98	0.05	115	0.43	133	2.79	153	2.18	187	0.09
30	0.54	48	1.13	65	78.16	82	5.10	99	0.24	116	0.03	134	0.15	154	0.13	188	0.01
31	0.96	49	0.20	66	1.00	83	1.74	100	0.61	117	0.04	135	0.02	155	0.02	189	0.31
32	0.21	50	2.21	67	1.37	84	0.49	101	2.97	119	0.57	137	0.13	157	0.07	190	0.02
33	0.79	51	16.50	69	30.10	85	1.33	102	0.32	120	0.06	139	0.38	159	0.37	192	0.38
34	0.01	52	0.97	70	0.77	87	12.26	103	2.85	121	0.86	140	0.03	160	0.02	193	2.52
37	0.41	53	4.00	71	1.97	88	1.79	104	0.43	122	0.00	141	1.57	161	0.09	194	0.12
38	1.61	54	0.62	72	0.44	89	3.06	105	3.03	123	1.74	142	0.10	163	0.02		
39	18.33	55	7.22	73	2.43	90	0.06	106	0.27	124	0.09	143	0.27	165	0.07		
40	2.70	57	100.00	74	0.50	31	30.83	107	7.62	125	0.03	145	0.94	167	0.13		
41	57.46	58	9.83	75	2.09	92	2.58	108	0.57	127	7.28	146	0.06	169	0.58		

4. 1,1,1,2,3,3-hexafluoro-4,4-dimethylhexane (30)

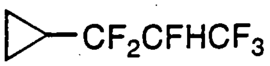


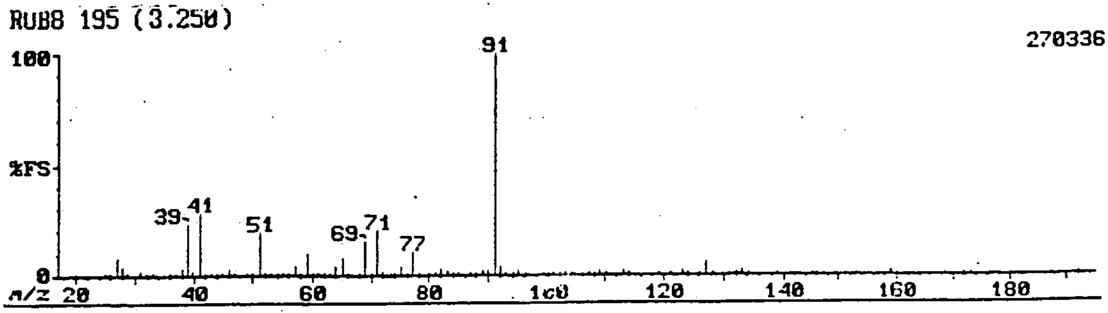


ROB4 77 (1.284) 516096

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
26	0.21	42	4.32	55	1.39	69	0.18	83	0.78	96	0.10	110	0.07	133	1.44	173	5.85
27	4.22	43	100.00	56	0.49	70	0.25	84	0.24	97	0.13	113	1.08	134	0.10	174	0.37
28	0.97	44	3.67	57	2.01	71	1.28	85	0.30	99	0.09	114	0.09	139	0.05	181	0.08
29	2.63	45	0.56	58	0.16	72	0.16	86	0.06	100	0.13	115	0.13	141	0.20	192	0.59
30	0.08	46	0.52	59	3.06	73	0.41	87	1.48	101	1.18	119	0.17	145	0.53	193	1.17
31	0.38	47	33.13	60	0.28	74	0.07	88	0.29	102	0.16	121	0.34	146	0.20	194	0.08
32	0.31	48	0.78	61	3.47	75	0.72	89	0.94	103	0.83	122	0.05	147	0.23	207	0.24
33	0.45	49	0.07	62	0.19	76	0.14	90	0.50	104	0.16	123	0.38	149	0.07		
37	0.21	50	0.45	63	0.29	77	5.01	91	7.99	105	0.28	127	5.75	151	0.78		
38	0.78	51	5.46	64	1.43	78	0.23	92	0.41	106	0.07	128	0.39	153	1.60		
39	0.93	52	0.33	65	3.62	79	0.25	93	0.17	107	2.43	129	0.15	154	0.12		
40	1.46	53	0.81	66	0.08	81	0.08	94	0.04	108	0.21	131	0.26	159	0.27		
41	24.80	54	0.17	67	0.08	82	1.62	95	1.22	109	1.33	132	0.08	167	0.04		

5. 1,1,2,3,3,3-hexafluoropropylcyclopropane (25)

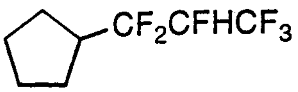


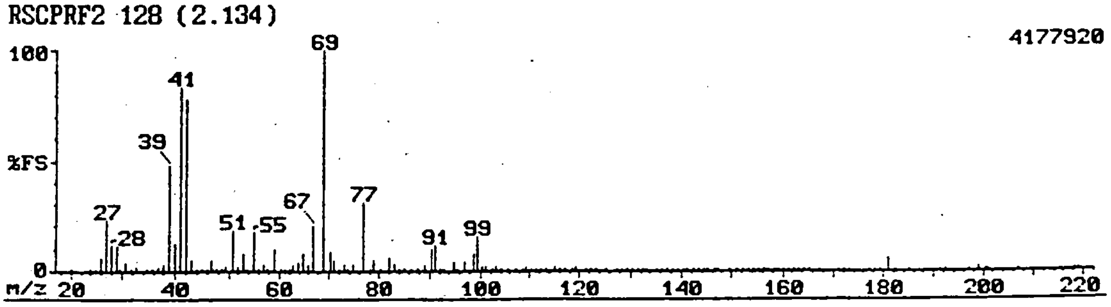


RUB8 195 (3.250) 270336

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	0.08	39	23.58	52	0.86	64	3.40	77	10.51	91	100.00	106	0.11	127	6.06	160	0.13
25	0.09	40	2.18	53	0.90	65	8.24	78	0.26	92	4.33	107	0.15	128	0.57	172	0.11
26	1.21	41	20.03	54	0.16	66	0.24	80	0.11	93	0.50	108	0.23	131	0.14	173	0.15
27	7.29	42	1.10	55	0.12	68	0.43	81	0.48	94	0.11	109	1.05	132	0.12	192	0.66
28	3.81	43	0.15	56	0.63	69	15.06	82	3.24	95	2.23	110	0.08	133	2.39		
29	0.19	44	0.82	57	3.40	70	0.78	83	2.04	96	0.08	113	1.50	134	0.20		
31	2.20	45	1.14	58	0.38	71	20.83	84	0.62	99	0.12	114	0.13	139	0.15		
32	1.32	46	3.01	59	9.38	72	1.66	85	0.13	100	0.25	119	0.20	145	0.53		
33	0.95	47	0.78	60	0.51	73	0.15	87	0.17	101	1.75	121	0.32	146	0.20		
36	0.08	49	0.21	61	0.26	74	0.17	88	0.75	102	0.30	123	1.00	151	0.33		
37	1.17	50	1.38	62	0.32	75	3.46	89	2.11	103	1.02	124	0.13	153	0.60		
38	3.31	51	13.60	63	1.08	76	0.52	90	1.52	104	0.26	126	0.11	159	1.34		

6. 1,1,2,3,3,3-hexafluoropropylcyclopentane (25)

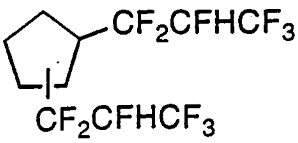


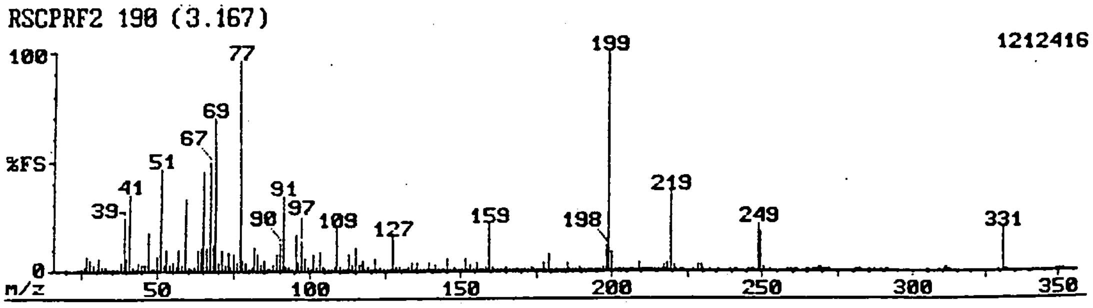


RSCPRF2 128 (2.134) 4177920

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	0.20	41	83.14	58	0.23	77	31.37	97	3.70	116	0.23	137	0.10	156	0.04	181	6.00
24	0.21	42	78.04	59	9.41	78	1.24	99	7.55	117	0.38	138	0.09	157	0.09	182	0.44
25	0.77	43	4.39	60	0.71	79	5.17	99	15.69	119	1.13	139	0.36	158	0.30	185	0.03
26	5.81	44	1.12	61	0.48	80	0.92	100	2.06	119	1.96	140	0.34	159	1.02	191	0.02
27	23.53	45	1.08	62	0.70	82	5.42	101	2.06	121	0.84	141	1.40	160	0.17	192	0.02
28	11.96	46	1.22	63	2.84	83	2.75	102	1.19	122	0.12	142	0.11	161	0.50	197	0.03
29	11.47	47	4.53	64	3.46	84	0.83	103	1.79	123	0.06	143	0.02	162	0.06	199	1.55
30	0.18	48	0.13	65	8.04	85	1.04	104	0.25	125	0.04	144	0.07	163	0.03	200	0.14
31	3.87	49	0.25	66	3.04	86	0.08	105	0.05	127	1.01	145	0.33	164	0.01	201	0.02
32	0.91	50	1.76	67	20.39	88	1.24	107	0.31	128	0.13	146	0.05	165	0.02	207	0.05
33	1.79	51	18.43	69	100.00	89	2.99	108	1.04	129	0.07	147	0.03	167	0.02	218	0.12
35	0.09	52	1.67	70	8.63	90	9.80	109	1.64	130	0.11	149	0.02	171	0.06	219	0.08
36	0.50	53	7.65	71	4.83	91	11.67	110	0.21	131	0.25	151	1.21	172	0.21		
37	1.72	54	1.02	72	0.97	92	0.53	111	0.26	132	0.29	152	0.07	173	0.15		
38	3.11	55	17.55	73	3.04	93	0.55	112	0.80	133	0.45	153	0.17	177	0.10		
39	47.45	56	1.16	74	0.13	95	3.75	113	1.26	135	0.42	154	0.09	178	0.04		
40	12.75	57	3.16	75	3.33	96	0.21	115	2.08	136	0.05	155	0.33	179	0.15		

7. 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclopentane x=2,3 (26)

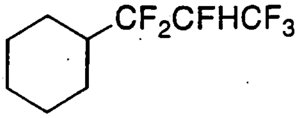


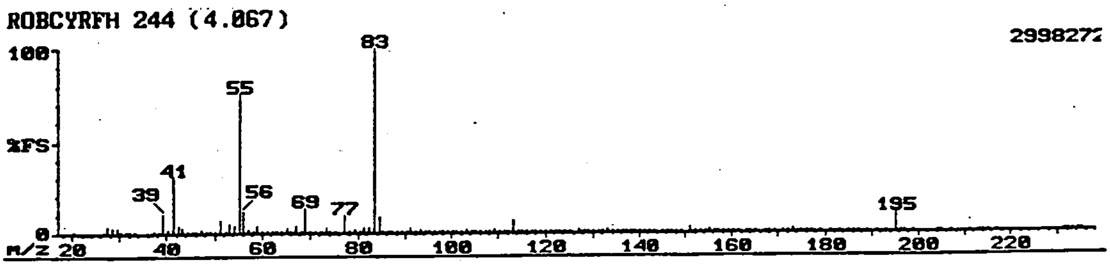


RSCPRF2 190 (3.167) 1212416

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	0.34	51	46.28	79	4.31	107	1.09	135	4.22	163	1.02	191	0.98	219	33.81	267	0.39
24	0.21	52	3.25	80	0.78	108	2.30	136	0.33	164	0.34	192	0.22	220	2.83	269	2.36
25	0.46	53	9.80	81	2.15	109	19.59	137	0.42	165	1.98	193	0.16	221	0.73	269	2.15
26	2.07	54	3.21	82	10.47	110	2.22	138	0.51	166	0.28	194	0.11	223	0.18	271	0.54
27	6.59	55	3.70	83	7.52	111	1.21	139	3.91	167	0.67	195	0.89	223	0.14	271	0.33
28	4.58	56	1.52	84	2.79	112	0.89	140	1.44	168	0.13	196	0.41	227	1.00	272	0.05
29	3.34	57	9.46	85	4.46	113	8.11	141	3.08	169	0.61	197	1.58	229	2.68	281	0.34
30	0.31	58	2.70	86	0.65	114	2.87	142	0.25	170	0.24	198	11.74	229	3.08	281	0.37
31	5.66	59	33.11	87	0.66	115	11.15	143	0.12	171	1.22	199	100.00	230	0.37	282	0.09
32	1.48	60	2.09	88	2.60	116	2.43	144	0.45	172	0.43	200	8.70	233	0.18	285	0.42
33	1.78	61	1.35	89	8.02	117	4.90	145	5.91	173	1.69	201	0.90	235	0.38	287	0.08
34	0.06	62	2.09	90	12.16	118	0.81	146	0.86	174	0.15	202	0.25	239	0.30	289	0.08
35	0.48	63	10.14	91	33.78	119	1.98	147	1.71	175	0.08	203	1.16	241	0.54	291	0.75
36	0.84	64	10.22	92	1.71	120	0.74	148	0.43	176	0.42	204	0.25	241	0.53	291	0.80
37	1.41	65	45.27	93	1.65	121	5.57	149	0.36	177	4.16	205	1.35	245	0.16	305	0.06
38	3.80	66	10.81	94	0.98	122	0.98	150	0.77	178	1.24	206	0.17	247	0.58	309	0.17
39	24.66	67	49.32	95	16.05	123	2.32	151	6.25	179	7.52	207	0.39	247	0.46	311	1.53
40	5.66	68	11.82	96	4.33	124	0.19	152	0.68	180	0.96	208	0.60	249	20.95	311	2.05
41	33.14	69	67.59	97	14.02	125	0.38	153	2.43	181	0.43	209	4.05	249	17.23	312	0.24
42	2.22	70	3.91	98	5.49	126	1.30	154	0.44	182	0.30	210	0.65	250	1.82	329	0.15
43	1.26	71	9.97	99	1.84	127	15.37	155	3.65	183	1.01	211	0.17	253	0.10	331	19.00
44	3.72	72	3.21	100	1.19	128	2.22	156	0.34	184	0.35	212	0.05	259	0.28	332	1.23
45	2.64	73	8.70	101	8.11	129	2.03	157	0.65	185	3.48	213	0.19	259	0.26	349	0.41
46	2.55	74	1.60	102	1.90	130	0.43	158	2.20	186	0.29	214	0.07	261	0.17	350	0.07
47	17.74	75	8.11	103	8.95	131	1.10	159	21.28	187	0.18	215	0.24	261	0.13	351	0.09
48	0.68	76	3.80	104	1.46	132	1.69	160	1.88	188	0.18	216	0.37	265	0.27		
49	0.86	77	95.95	105	0.82	133	4.10	161	0.40	189	1.79	217	3.02	265	0.23		
50	7.26	78	5.13	106	0.33	134	0.90	162	0.13	190	0.42	218	4.16	267	0.43		

8. 1,1,2,3,3,3-hexafluoropropylcyclohexane (24)

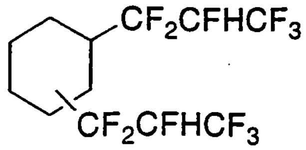


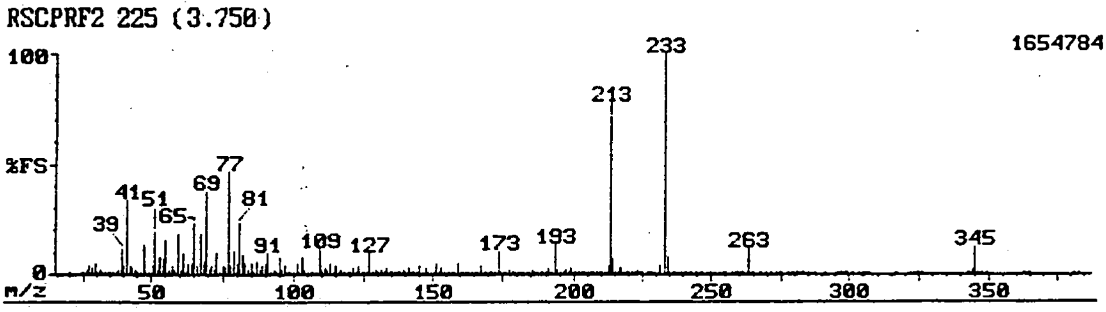


ROBCYRFH 244 (4.067) 2998272

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	71	1.03	115	1.01	161	0.01
27	0.93	72	0.25	116	0.16	163	0.07
27	3.65	73	2.70	117	0.25	164	0.01
28	2.46	74	0.19	118	0.03	165	0.17
29	3.21	75	0.96	119	0.33	167	0.90
30	0.08	77	9.43	120	0.09	168	0.06
31	0.23	78	0.64	121	0.73	169	0.11
32	0.08	79	2.15	122	0.12	171	0.10
33	0.26	80	0.46	123	0.45	172	1.02
37	0.10	81	3.07	124	0.08	173	1.77
38	0.51	82	2.87	125	0.13	174	0.10
39	10.52	83	100.00	127	2.39	175	0.52
40	1.94	84	8.88	128	0.17	176	0.05
41	30.74	85	1.28	129	0.30	177	0.16
42	4.34	86	0.12	130	0.03	179	0.05
43	3.21	87	0.41	131	0.37	181	0.01
44	0.23	88	0.35	132	0.13	183	0.01
45	0.20	89	0.98	133	1.61	185	0.14
46	0.26	90	1.16	134	0.12	186	0.03
47	2.18	91	2.60	135	0.56	187	0.10
48	0.06	92	0.18	136	0.04	189	0.01
49	0.05	93	1.82	137	0.07	191	0.15
50	0.91	94	0.45	138	0.02	193	0.30
51	6.86	95	1.45	139	0.37	195	10.66
52	1.05	96	0.38	140	0.17	196	0.77
53	4.99	97	0.84	141	0.34	197	0.05
54	3.55	98	0.14	142	0.04	199	0.09
55	75.96	99	0.20	143	0.04	204	0.02
56	11.34	100	0.17	145	1.27	205	0.02
57	1.77	101	1.42	146	0.07	207	0.01
58	0.22	102	0.36	147	0.54	211	0.01
59	3.72	103	2.07	148	0.04	213	0.79
60	0.24	104	0.53	149	0.30	214	0.18
61	0.92	105	0.54	151	3.01	215	0.02
62	0.16	106	0.08	152	0.09	217	0.02
63	0.67	107	0.13	153	0.50	231	0.00
64	1.12	108	0.17	154	0.02	232	0.06
65	3.01	109	2.04	155	1.53	233	0.13
66	0.62	110	0.20	156	0.10	234	1.20
67	4.17	111	0.33	157	0.08	235	0.09
68	0.54	112	0.18	158	0.05		
69	13.11	113	7.14	159	0.92		
70	0.42	114	0.73	160	0.06		

9. 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane x=2,3,4 (27)

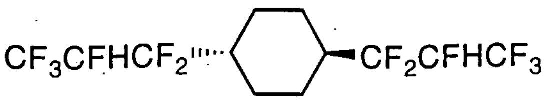


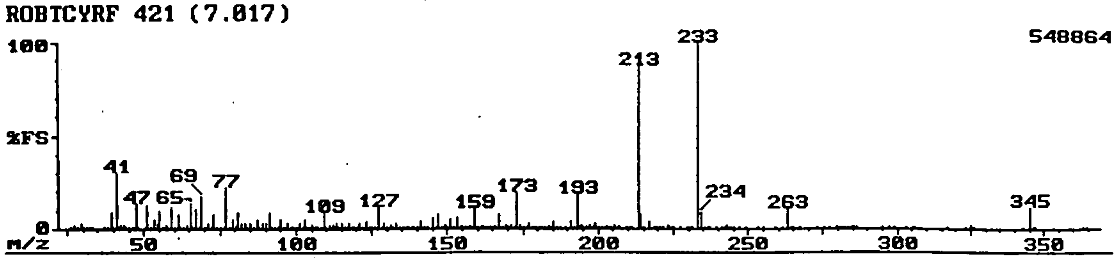


RSCPRF2 225 (3.750) 1654784

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	0.16	55	15.47	87	5.38	119	0.99	151	5.07	183	0.72	215	0.46	250	0.05	296	0.02
24	0.13	56	1.64	88	1.49	120	0.43	152	0.58	184	0.31	216	0.21	251	0.06	297	0.19
25	0.38	57	4.02	89	4.13	121	3.37	153	2.71	185	2.37	217	2.85	252	0.12	298	0.02
26	1.78	58	1.59	90	4.76	122	0.86	154	0.35	186	0.29	218	0.20	253	0.10	299	0.15
27	3.85	59	18.56	91	9.84	123	3.40	155	0.57	187	0.47	219	0.26	254	0.06	301	0.04
28	2.61	60	1.66	92	1.11	124	0.57	156	0.09	188	0.06	220	0.09	255	0.17	303	0.08
29	4.52	61	9.28	93	1.67	125	0.56	157	0.31	189	0.45	221	0.58	257	0.07	304	0.06
30	0.27	62	1.28	94	0.58	126	0.78	158	0.69	190	0.31	222	0.23	258	0.03	305	0.62
31	2.17	63	4.70	95	7.49	127	9.78	159	5.26	191	3.34	223	1.83	259	0.27	306	0.10
32	0.56	64	4.70	96	1.83	128	1.08	160	0.44	192	1.35	224	0.22	260	0.05	307	0.02
33	0.77	65	23.02	97	4.33	129	2.24	161	0.36	193	13.55	225	0.06	261	0.44	316	0.01
34	0.03	66	3.65	98	0.78	130	0.59	162	0.15	194	1.50	227	0.16	263	11.57	317	0.10
35	0.18	67	18.81	99	0.96	131	1.70	163	0.56	195	0.95	227	0.16	264	0.52	322	0.04
36	0.37	68	5.94	100	0.72	132	1.24	164	0.25	196	0.30	228	0.04	265	0.30	323	0.12
37	0.64	69	38.12	101	4.83	133	2.91	165	1.18	197	1.56	229	0.08	267	0.09	324	0.18
38	1.96	70	1.93	102	1.28	134	0.50	166	0.36	198	0.37	231	3.84	269	0.03	325	1.45
39	11.88	71	3.62	103	7.61	135	1.05	167	3.40	199	2.46	233	100.00	271	0.03	326	0.20
40	4.08	72	1.49	104	1.92	136	0.13	168	0.33	200	0.26	234	8.11	273	0.18	342	0.02
41	33.91	73	10.09	105	1.41	137	0.27	169	0.81	201	0.41	235	0.59	274	0.04	343	0.14
42	3.64	74	1.31	106	0.23	138	0.23	170	0.18	202	0.13	236	0.05	275	0.11	345	1.64
43	2.72	75	4.08	107	0.51	139	1.62	171	1.27	203	1.08	237	0.31	277	0.16	345	12.44
44	1.47	76	2.48	108	1.14	140	0.89	172	1.44	204	0.39	238	0.02	278	0.03	346	1.42
45	1.04	77	46.78	109	11.70	141	2.71	173	10.95	205	1.22	239	0.11	279	0.36	347	0.07
46	1.44	78	3.79	110	1.55	142	0.43	174	1.10	206	0.16	240	0.07	280	0.04	349	0.04
47	13.80	79	11.14	111	3.06	143	0.32	175	0.22	207	0.11	241	0.96	281	0.29	363	0.08
48	0.43	80	4.46	112	2.13	144	0.37	176	0.23	208	0.07	242	0.20	282	0.11	363	0.60
49	0.45	81	23.27	113	5.07	145	4.08	177	2.23	209	0.31	243	1.14	283	0.46	364	0.13
50	4.08	82	8.60	114	1.38	146	0.72	178	0.28	210	0.12	244	0.24	285	0.41	365	0.15
51	19.80	83	5.26	115	3.77	147	3.23	179	1.02	211	0.74	245	0.17	286	0.07	381	0.05
52	2.38	84	2.20	116	0.79	148	0.36	180	0.16	212	3.96	246	0.02	287	0.03	383	0.06
53	7.67	85	4.89	117	1.95	149	3.83	181	0.33	213	77.23	247	0.11	291	0.04		
54	6.81	86	0.58	118	0.25	150	0.62	182	0.20	214	6.81	249	0.12	295	0.10		

10. *trans*-1,4-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (27a)



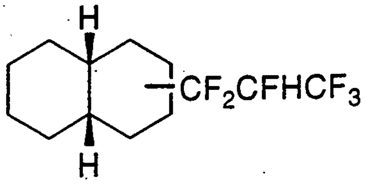


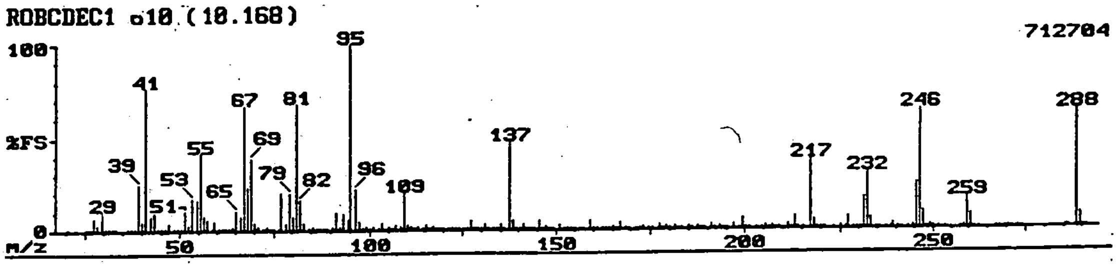
ROBTCYRF 421 (7.017) 5488

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.11	84	0.99	138	0.07	195	0.62
27	1.81	85	2.47	139	1.24	196	0.10
28	1.10	86	0.33	140	0.58	197	1.81
29	2.80	87	4.71	141	3.92	198	0.15
30	0.08	88	0.76	142	0.59	199	3.03
31	0.26	89	2.52	143	0.30	200	0.28
32	0.31	90	3.13	145	6.30	201	0.17
33	0.39	91	8.68	146	0.47	202	0.05
37	0.07	92	0.78	147	7.60	203	1.01
38	0.28	93	0.49	148	0.63	204	0.15
39	8.35	94	0.22	149	1.66	205	2.38
40	1.29	95	4.38	150	0.18	206	0.11
41	29.85	96	0.84	151	4.66	207	0.12
42	1.48	97	2.64	152	0.39	209	0.35
43	1.59	98	0.45	153	5.55	210	0.04
44	0.78	99	0.57	154	0.49	211	0.30
45	0.34	100	0.34	155	1.11	213	87.31
46	0.48	101	3.17	156	0.11	214	7.98
47	13.25	102	0.78	157	0.25	215	0.58
48	0.31	103	4.85	158	0.25	217	3.40
50	0.58	104	0.82	159	10.87	218	0.17
51	12.31	105	2.41	160	0.67	219	0.31
52	1.05	106	0.12	161	0.36	220	0.03
53	4.57	107	0.28	162	0.12	221	0.17
54	3.17	108	0.42	163	0.57	223	1.88
55	9.24	109	9.14	164	0.13	224	0.32
56	0.57	110	0.97	165	0.84	225	0.04
57	1.70	111	1.84	166	0.11	227	0.16
58	0.29	112	1.89	167	8.02	229	0.06
59	11.75	113	2.72	168	0.59	231	0.06
60	0.57	114	0.75	169	1.54	231	1.40
61	7.51	115	2.51	170	0.10	233	100.00
62	0.33	116	0.45	171	1.55	234	9.19
63	0.70	117	2.60	172	0.85	235	0.76
64	2.24	118	0.12	173	19.59	236	0.03
65	13.62	119	0.64	174	1.48	237	0.28
66	1.28	120	0.15	175	0.15	239	0.07
67	11.15	121	2.97	176	0.07	241	0.70
68	0.90	122	0.57	177	2.83	242	0.09
69	17.72	123	3.92	178	0.21	243	1.85
70	0.70	124	0.57	179	1.41	244	0.25
71	2.51	125	0.33	180	0.16	245	0.15
72	0.85	126	0.11	181	0.12	247	0.05
73	7.60	127	11.89	182	0.10	249	0.10
74	0.46	128	0.85	183	0.67	253	0.12
75	1.38	129	2.60	184	0.09	255	0.13
76	0.18	130	0.43	185	3.40	259	0.28
77	22.76	131	1.76	186	0.29	261	0.30
78	1.45	132	0.60	187	0.58	263	10.35
79	4.66	133	3.13	189	0.28	264	1.04
80	1.89	134	0.42	191	4.34	265	0.23
81	8.30	135	1.13	192	0.35	267	0.03
82	2.69	136	0.07	193	18.10	273	0.09
83	2.82	137	0.30	194	1.77	275	0.03

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
277	0.10	285	0.41	306	0.07	346	1.26
279	0.46	286	0.03	317	0.07	347	0.08
280	0.05	295	0.08	323	0.11	363	0.43
281	0.23	297	0.16	325	1.48	364	0.07
282	0.03	299	0.23	326	0.17		
283	0.73	303	0.09	343	0.10		
284	0.04	305	0.60	345	11.94		

11. x-(1,1,2,3,3,3-hexafluoropropyl)*cis*-decalin x=1,2,9 (33)



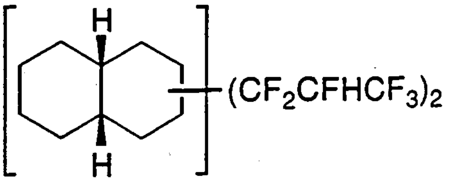


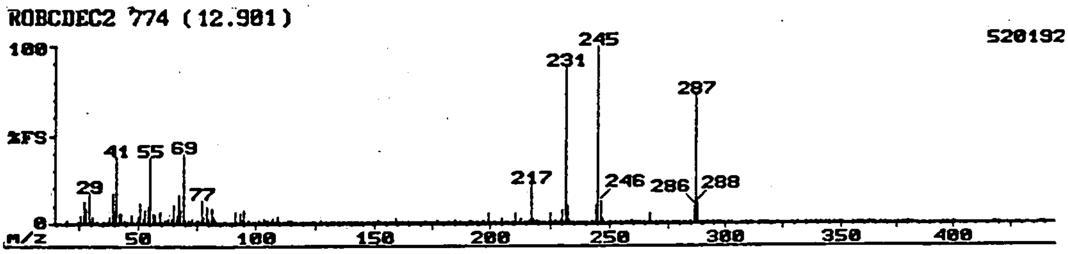
ROBCDEC1 610 (10.168) 7127

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	80	8.12	134	0.25	194	0.25
25	0.03	81	67.82	135	2.77	195	0.51
26	0.37	82	16.67	136	0.38	197	3.23
27	6.68	83	3.84	137	47.13	198	0.62
28	3.02	84	0.90	138	5.21	199	5.85
29	10.78	85	2.18	139	1.06	200	0.54
30	0.27	86	0.28	140	0.34	201	0.16
31	0.21	87	0.61	141	2.62	203	0.48
32	0.34	88	0.35	142	0.43	204	0.45
33	0.39	89	1.28	143	0.54	205	1.80
36	0.04	90	1.64	144	0.23	206	0.26
37	0.16	91	9.48	145	4.49	207	1.60
38	0.62	92	1.67	146	0.55	208	0.18
39	25.72	93	8.55	147	1.83	209	0.23
40	4.81	94	6.21	148	0.25	211	2.95
41	77.01	95	100.00	149	0.32	212	0.46
42	7.61	96	22.41	151	3.38	213	7.11
43	9.91	97	4.49	152	0.24	214	0.66
44	0.75	98	0.79	153	1.02	216	0.04
45	0.26	99	2.01	154	0.12	217	37.93
46	0.31	100	0.32	155	1.00	218	4.56
47	4.27	101	1.90	156	0.15	219	1.39
48	0.14	102	0.62	157	0.37	220	0.17
49	0.07	103	3.70	159	4.89	221	0.23
50	1.03	104	0.70	160	0.41	223	0.15
51	10.34	105	1.51	161	0.65	225	2.33
52	2.87	106	0.41	162	0.09	226	0.75
53	17.96	107	3.34	163	0.39	227	6.39
54	16.81	108	1.46	164	0.24	228	0.68
55	41.38	109	20.83	165	1.54	229	0.29
56	8.08	110	2.73	166	0.16	230	1.33
57	5.71	111	1.55	167	3.95	231	17.39
58	0.76	112	0.26	168	0.41	232	30.75
59	5.32	113	1.77	169	0.23	233	5.93
60	0.46	114	0.62	171	0.91	234	0.43
61	1.17	115	3.16	172	0.19	235	0.04
62	0.27	116	0.84	173	1.86	237	0.04
63	1.13	117	1.76	174	0.16	239	0.13
64	1.66	118	0.27	175	0.10	239	2.69
65	11.06	119	0.75	177	2.51	240	0.34
66	7.51	120	0.12	178	0.20	241	0.07
67	66.67	121	1.37	179	2.17	243	0.13
68	23.28	122	0.40	180	0.19	245	1.87
69	38.51	123	1.30	181	2.24	245	25.43
70	3.45	124	1.03	182	0.24	246	64.94
71	1.83	125	0.59	183	0.37	247	9.34
72	0.60	126	0.16	185	2.06	248	0.78
73	2.27	127	4.81	186	0.21	249	1.82
74	0.26	128	0.76	187	1.57	250	0.26
75	0.86	129	1.14	188	0.18	251	0.03
76	1.34	130	0.57	189	0.11	253	0.10
77	20.55	131	3.05	191	2.77	257	0.17
78	4.02	132	0.67	192	0.28	258	1.98
79	19.97	133	1.25	193	2.26	259	17.82

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
260	8.23	268	0.81	273	0.09	286	0.30
261	0.88	269	0.51	273	1.10	288	64.37
262	0.05	271	0.06	274	0.16	289	7.87
267	0.12	271	0.17	286	0.04	290	0.55

12. x,y-bis(1,1,2,3,3,3-hexafluoropropyl)*cis*-decalin x=1,y=2-10, x=1,y=3-10 (**34**)



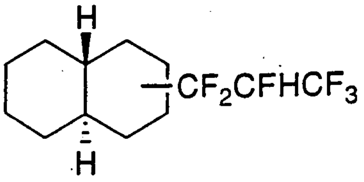


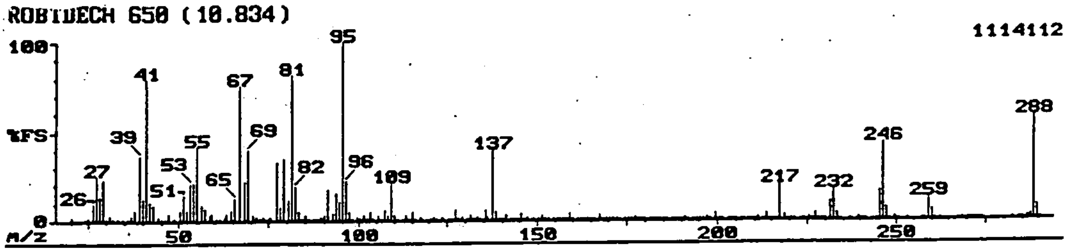
ROBCDEC2 774 (12.901) 5201

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.53	78	3.64	133	0.81	187	0.54
24	0.34	79	9.60	134	0.26	188	0.12
25	1.07	80	3.13	135	1.45	189	0.47
26	4.63	81	8.27	136	0.28	190	0.28
27	12.25	82	3.79	137	0.43	191	2.10
28	8.42	83	2.33	138	0.08	192	0.45
29	17.72	84	0.68	139	0.32	193	0.89
30	0.46	85	1.45	140	0.22	194	0.11
31	3.94	86	0.26	141	1.05	195	0.74
32	0.64	87	0.67	142	0.22	196	0.33
33	1.35	88	0.52	143	0.37	197	1.88
35	0.05	89	1.22	144	0.13	198	0.56
36	0.39	90	1.11	145	1.17	199	6.20
37	1.33	91	6.74	146	0.31	200	0.69
38	3.54	92	1.30	147	0.47	201	0.49
39	17.52	93	5.46	148	0.10	202	0.19
40	6.89	94	1.62	149	0.12	203	0.79
41	37.40	95	7.82	150	0.14	204	0.79
42	6.10	96	1.45	151	2.25	205	2.58
43	6.10	97	1.69	152	0.24	206	0.50
44	1.51	98	0.49	153	0.54	207	0.84
45	0.70	99	1.33	154	0.15	208	0.20
46	0.82	100	0.34	155	0.52	209	1.25
47	4.43	101	1.78	156	0.15	210	0.49
48	0.14	102	0.55	157	0.37	211	5.76
49	0.62	103	2.74	158	0.29	212	0.82
50	3.54	104	0.62	159	2.50	213	2.83
51	11.42	105	1.56	160	0.31	214	0.47
52	2.63	106	0.52	161	0.33	215	0.50
53	7.92	107	2.62	162	0.07	216	1.59
54	9.84	108	0.72	163	0.46	217	22.24
55	37.99	109	3.69	164	0.28	218	2.74
56	5.56	110	0.65	165	0.86	219	1.65
57	4.92	111	0.53	166	0.19	220	0.37
58	1.25	112	0.24	167	0.91	221	0.55
59	6.45	113	1.55	168	0.14	222	0.22
60	0.87	114	0.53	169	0.35	223	1.02
61	1.67	115	1.86	170	0.07	224	0.80
62	1.03	116	0.42	171	0.74	225	6.30
63	3.35	117	0.73	172	0.26	226	1.01
64	3.11	118	0.14	173	0.84	227	1.92
65	10.58	119	0.49	174	0.12	228	0.51
66	4.68	120	0.16	175	0.10	229	2.15
67	16.54	121	0.65	176	0.14	230	7.33
68	8.17	122	0.22	177	1.50	231	88.19
69	39.37	123	0.51	178	0.28	232	10.09
70	1.94	124	0.20	179	1.11	233	1.46
71	1.97	125	0.15	180	0.22	234	0.30
72	1.38	127	1.04	181	1.33	235	0.69
73	2.74	128	0.41	182	0.26	236	0.16
74	0.70	129	0.65	183	0.54	237	0.48
75	1.81	130	0.18	184	0.17	238	0.21
76	2.36	131	0.38	185	1.46	239	0.82
77	13.98	132	0.52	186	0.24	240	0.31

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
241	0.91	268	0.46	296	0.20	358	0.35
243	0.26	270	0.20	296	0.13	359	0.06
243	2.36	270	0.18	297	0.77	360	0.06
244	10.24	272	0.69	298	0.16	362	0.10
245	100.00	272	0.21	300	0.08	363	0.03
246	12.60	273	0.14	301	0.04	364	0.38
247	3.10	274	0.07	303	0.04	365	0.05
248	0.53	275	0.23	308	0.04	368	0.10
249	0.68	276	0.04	309	0.10	370	0.03
250	0.13	277	0.26	312	0.05	376	0.08
251	0.22	278	0.04	316	0.05	378	0.31
252	0.11	280	0.10	316	0.12	379	0.05
253	0.37	280	0.06	318	1.12	380	0.20
254	0.15	281	0.38	319	0.17	381	0.05
255	0.52	282	0.09	324	0.05	382	0.13
256	0.26	283	0.14	330	0.07	396	0.19
257	1.29	284	0.32	332	0.15	398	0.05
258	0.75	285	2.40	336	0.05	400	1.35
259	1.67	286	9.79	338	0.14	401	0.21
260	0.38	287	72.44	340	0.04	418	0.07
261	0.38	288	11.32	342	0.04	419	0.04
262	0.10	290	0.78	344	0.16	420	0.08
263	0.15	290	0.09	346	0.04	438	0.19
264	0.08	292	0.06	348	0.06	439	0.09
265	0.34	292	0.04	350	0.21		
266	0.72	293	0.08	351	0.04		
267	5.71	294	0.07	356	0.05		

13. x-(1,1,2,3,3,3-hexafluoropropyl)*trans*-decalin x=1,2 (35)



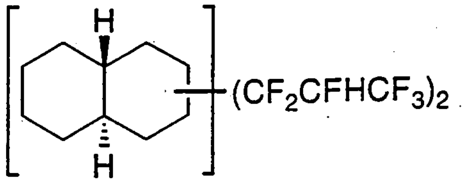


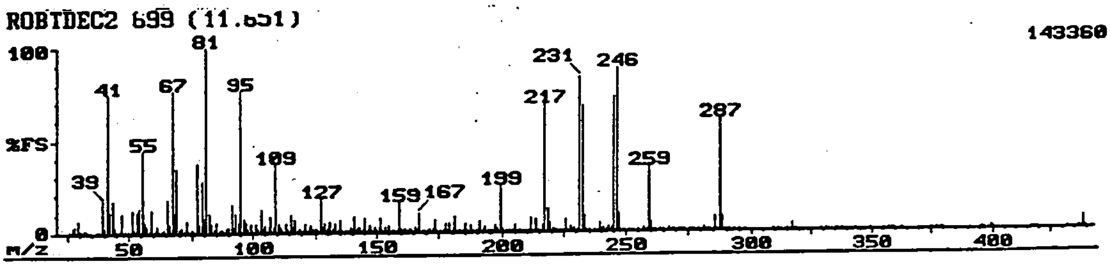
ROBTDECH 650 (10.834) 1114112

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.70	80	12.13	134	0.57	188	0.19
24	0.54	81	81.25	135	6.07	189	0.13
25	2.32	82	19.85	136	1.68	190	0.08
26	10.02	83	5.31	137	39.34	191	1.75
27	25.37	84	1.39	138	4.62	192	0.32
28	14.06	85	2.99	139	1.29	193	1.34
29	23.25	86	0.48	140	0.64	194	0.17
30	0.99	87	0.97	141	2.62	195	0.33
31	3.10	88	0.94	142	0.67	196	0.18
32	0.87	89	2.34	143	0.86	197	1.98
33	1.01	90	3.31	144	0.36	198	0.25
35	0.17	91	17.46	145	4.14	199	3.47
36	1.04	92	3.88	146	0.78	200	0.34
37	2.53	93	15.90	147	1.61	201	0.09
38	5.63	94	11.03	148	0.28	203	0.33
39	37.13	95	100.00	149	0.26	204	0.38
40	12.22	96	22.61	150	0.31	205	1.24
41	79.78	97	5.12	151	3.29	206	0.23
42	10.48	98	1.22	152	0.32	207	1.06
43	8.55	99	2.32	153	0.95	208	0.16
44	1.65	100	0.67	154	0.23	209	0.25
45	0.80	101	2.99	155	0.82	210	0.12
46	0.91	102	1.15	156	0.26	211	1.91
47	4.04	103	5.19	157	0.51	212	0.33
48	0.28	104	1.26	158	0.34	213	3.91
49	0.99	105	2.69	159	3.70	214	0.41
50	5.45	106	0.91	160	0.52	215	0.05
51	14.98	107	5.63	161	0.48	216	0.31
52	5.58	108	3.29	162	0.07	217	20.31
53	21.32	109	21.14	163	0.37	218	2.53
54	21.05	110	3.19	164	0.31	219	0.85
55	41.91	111	1.37	165	1.17	220	0.13
56	8.73	112	0.86	166	0.21	221	0.15
57	6.80	113	3.33	167	2.85	223	0.17
59	2.71	114	1.31	168	0.31	224	0.08
59	4.20	115	4.46	169	0.23	225	1.86
61	0.87	116	1.28	170	0.09	226	0.44
61	1.32	117	2.11	171	0.78	227	3.93
63	1.98	118	0.31	172	0.35	228	0.51
63	3.63	119	1.17	173	1.14	229	0.29
65	6.16	120	0.35	174	0.16	230	0.46
65	12.78	121	1.95	175	0.10	231	10.85
67	75.37	122	0.74	176	0.05	232	17.10
68	22.24	123	1.65	177	1.75	233	3.40
69	40.07	124	0.91	178	0.28	234	0.25
70	3.22	125	1.39	179	1.42	237	0.04
71	1.59	126	0.39	180	0.21	239	1.95
73	1.40	127	6.07	181	1.35	240	0.30
73	2.16	128	0.98	182	0.19	241	0.08
75	1.21	129	1.72	183	0.31	243	0.24
75	1.68	130	0.88	184	0.08	244	0.99
77	33.09	131	3.01	185	1.41	245	16.18
78	7:44	132	1.36	186	0.30	246	43.38
79	35.29	133	2.00	187	1.31	247	6.53

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
248	0.56	260	5.54	271	0.51	286	2.09
249	2.16	261	0.59	272	0.07	287	2.76
250	0.32	262	0.04	273	0.79	288	58.09
253	0.13	267	0.19	274	0.07	289	7.72
257	0.28	268	0.80	282	0.03	290	0.47
258	1.03	269	0.63	284	0.06		
259	12.78	270	0.09	285	0.15		

14. x,y-bis(1,1,2,3,3,3-hexafluoropropyl)*trans*-decalin x=1,y=2-10, x=1,y=3-10 (36)



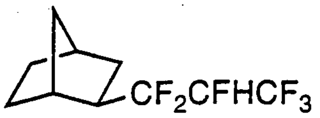


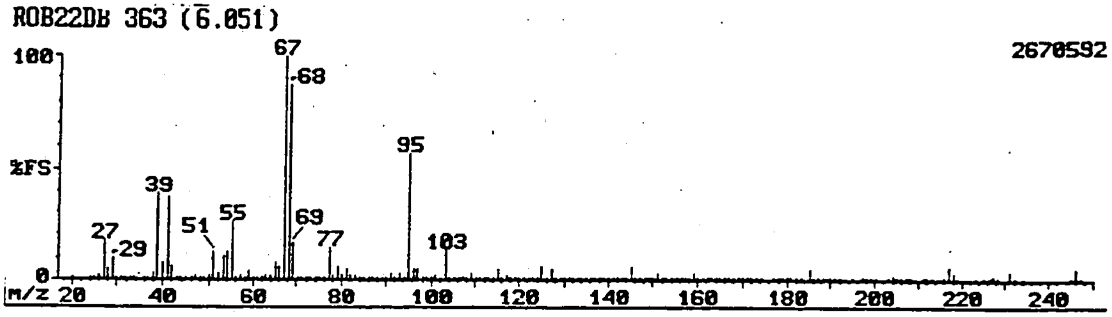
ROBTDEC2 699 (11.651) 143:

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.14	84	1.76	138	0.61	192	0.49
27	2.86	85	6.03	139	3.26	193	2.85
28	3.88	86	0.37	140	1.44	194	0.33
29	7.23	87	1.64	141	8.88	195	1.26
30	0.15	88	0.86	142	1.57	196	0.24
31	0.31	89	2.86	143	2.56	197	4.33
32	1.75	90	3.39	144	0.66	198	1.63
33	0.64	91	15.71	145	7.50	199	25.00
37	0.17	92	2.80	146	1.26	200	2.27
38	0.42	93	10.63	147	3.44	201	1.18
39	17.86	94	5.67	148	0.57	202	0.18
40	3.39	95	77.14	149	3.13	203	1.27
41	75.00	96	7.72	150	0.34	204	1.15
42	11.79	97	6.12	151	7.72	205	4.29
43	17.86	98	1.95	152	0.87	206	0.59
44	3.08	99	5.13	153	3.30	207	1.44
45	0.40	100	0.73	154	0.54	208	0.16
46	0.41	101	4.78	155	3.97	209	1.27
47	10.71	102	1.50	156	0.64	210	0.32
48	0.19	103	12.86	157	1.23	211	7.46
50	0.74	104	2.19	158	0.94	212	1.15
51	12.32	105	3.48	159	16.79	213	7.01
52	1.98	106	1.25	160	1.53	214	0.76
53	11.61	107	8.57	161	1.69	215	0.36
54	13.39	108	2.86	162	0.21	216	3.62
55	45.00	109	36.79	163	2.27	217	68.57
56	5.45	110	5.04	164	0.81	218	12.14
57	3.97	111	2.68	165	3.39	219	4.73
58	0.74	112	0.85	166	0.57	220	2.37
59	12.50	113	4.69	167	11.03	221	1.41
60	0.92	114	1.89	168	0.87	222	0.17
61	3.53	115	10.00	169	1.12	223	1.00
62	0.28	116	2.51	170	0.12	224	0.27
63	1.10	117	6.83	171	2.31	225	6.56
64	1.48	118	1.10	172	1.94	226	1.04
65	18.04	119	2.02	173	6.34	227	3.35
66	4.78	120	0.50	174	0.56	228	0.54
67	76.43	121	5.04	175	0.43	229	2.37
68	10.94	122	1.33	177	0.14	230	0.87
69	34.82	123	3.75	177	5.18	231	83.57
70	1.77	124	2.17	178	0.69	232	67.86
71	2.47	125	1.47	179	5.00	233	8.62
72	1.27	126	0.43	180	0.67	234	0.65
73	6.70	127	18.39	181	8.71	235	0.53
74	0.52	128	3.13	182	1.00	237	0.54
75	1.89	129	4.64	183	1.34	239	5.04
76	0.56	130	2.11	184	0.34	240	0.45
77	37.86	131	6.21	185	5.04	241	2.20
78	4.96	132	1.72	186	0.73	242	0.42
79	28.57	133	4.87	187	3.44	243	2.65
80	7.72	134	1.35	188	0.39	244	2.04
81	100.00	135	6.92	189	0.74	245	72.86
82	10.31	136	1.09	190	0.23	246	88.57
83	4.96	137	1.37	191	5.71	247	9.69

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
248	0.35	272	0.31	297	0.54	363	0.61
249	0.52	273	0.42	309	0.13	375	0.17
251	0.12	275	0.81	311	0.10	377	0.63
253	0.20	277	0.21	315	0.20	379	0.24
255	0.40	279	0.16	317	3.53	395	0.12
257	1.83	281	1.86	318	0.51	396	0.12
258	0.56	282	0.32	329	0.16	399	2.09
259	34.64	283	0.16	331	0.08	400	0.36
260	4.91	285	7.46	335	0.15	417	0.13
261	0.71	286	1.03	337	0.25	418	0.14
263	0.33	287	60.00	343	0.34	419	0.15
265	0.33	288	7.81	349	0.24	432	0.12
267	1.70	289	0.63	355	0.09	436	0.68
268	0.17	291	0.13	357	0.79	437	0.11
269	0.25	293	0.19	358	0.08	438	6.56
271	0.92	295	0.56	359	0.12	439	1.13

15. *exo*-2-(1,1,2,3,3,3-hexafluoropropyl)norbornane (37)

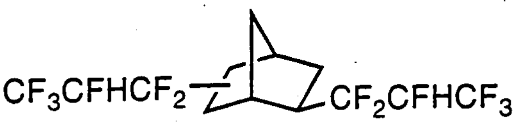


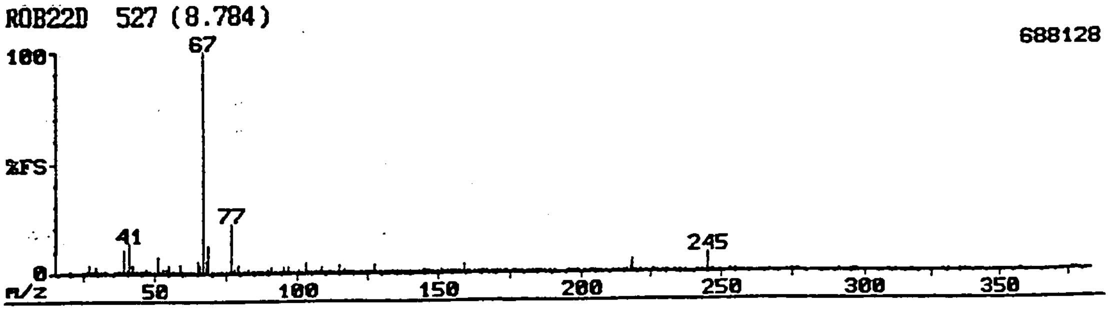


RO822DB 363 (6.051) 2670592

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.05	73	0.63	122	0.19	171	0.24
24	0.02	74	0.17	123	0.80	172	0.13
25	0.07	75	1.39	124	0.31	173	0.71
26	1.63	76	0.29	125	5.83	174	0.03
27	17.79	77	14.57	126	0.57	177	1.24
28	4.64	78	1.50	127	4.41	178	0.11
29	9.32	79	5.60	128	0.68	179	1.16
30	0.23	80	1.48	129	0.65	180	0.09
31	0.92	81	4.56	130	0.16	181	0.45
32	0.27	82	2.04	131	0.26	182	0.03
33	0.96	83	1.96	132	0.22	183	0.09
34	0.02	84	0.71	133	0.76	185	4.83
36	0.03	85	1.42	134	0.13	186	0.42
37	0.50	86	0.23	135	0.72	187	0.41
38	2.45	87	0.72	136	0.10	188	0.03
39	38.80	88	0.64	137	0.26	189	0.03
40	7.48	89	1.29	138	0.08	190	0.02
41	36.50	90	1.42	139	0.49	191	0.26
42	5.44	91	3.22	140	0.21	192	0.03
43	0.76	92	0.42	141	0.91	195	0.03
44	0.23	93	2.53	142	0.13	197	0.95
45	0.41	94	0.81	143	0.18	198	0.10
46	0.41	95	57.06	144	0.06	199	0.40
47	1.71	96	5.25	145	5.56	200	0.04
48	0.03	97	5.14	146	0.47	203	0.03
49	0.09	98	0.52	147	0.51	204	1.88
50	1.98	99	0.64	148	0.07	205	0.42
51	12.88	100	0.45	149	0.08	206	0.03
52	2.53	101	2.36	150	0.06	207	1.32
53	10.89	102	0.42	151	2.53	208	0.14
54	12.27	103	13.34	152	0.11	211	0.27
55	26.38	104	1.31	153	0.46	212	0.03
56	1.34	105	1.12	154	0.05	213	0.02
57	1.84	106	0.21	155	0.12	216	0.18
58	0.20	107	0.29	156	0.02	217	5.98
59	3.49	108	0.21	157	0.20	218	3.34
60	0.21	109	2.76	158	0.09	219	0.24
61	0.66	110	0.51	159	2.49	223	0.01
62	0.56	111	0.22	160	0.19	225	0.11
63	1.75	112	0.10	161	0.20	226	0.37
64	1.52	113	1.37	162	0.01	227	1.93
65	7.94	114	0.82	163	0.23	228	0.19
66	5.98	115	4.79	164	0.06	231	3.72
67	100.00	116	1.16	165	0.64	232	0.33
68	87.12	117	1.98	166	0.06	245	0.65
69	16.41	118	0.14	167	0.91	246	4.52
70	0.70	119	0.43	168	0.07	247	0.44
71	0.66	120	0.11	169	0.03		
72	0.25	121	0.96	170	0.02		

16. 2,x-bis(1,1,2,3,3,3-hexafluoropropyl)norbornane x=5,6 (**38**)



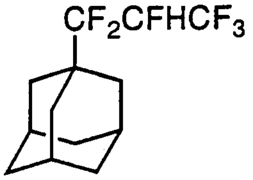


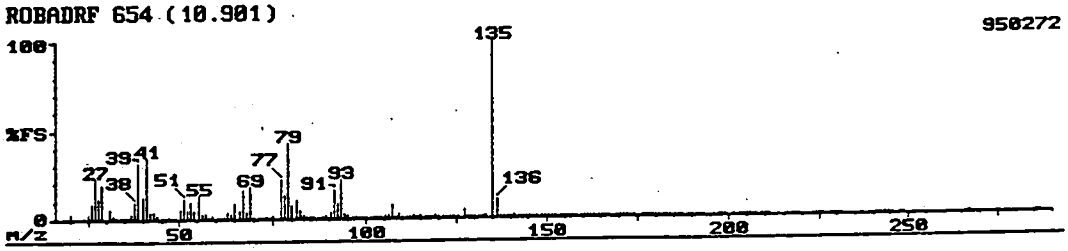
ROB22D 527 (8.784) 688128

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.07	81	0.36	135	0.55	198	0.08
25	0.03	82	1.41	136	0.10	199	0.15
26	0.26	83	1.70	137	0.16	201	0.02
27	4.13	84	0.62	138	0.07	203	0.11
28	1.25	85	0.77	139	0.60	204	0.19
29	3.35	86	0.12	140	0.24	205	0.60
30	0.11	87	0.17	141	1.05	206	0.06
31	0.53	88	0.49	142	0.17	207	0.04
32	0.38	89	1.31	143	0.36	209	0.14
33	0.65	90	1.54	144	0.12	211	0.16
36	0.04	91	2.64	145	1.70	213	0.07
37	0.11	92	0.47	146	0.21	215	0.06
38	0.51	93	1.25	147	0.29	216	0.07
39	10.27	94	0.93	148	0.05	217	3.42
40	1.87	95	2.98	149	0.17	218	6.21
41	13.54	96	1.20	150	0.06	219	0.51
42	3.42	97	3.01	151	2.16	221	0.02
43	0.38	98	0.37	152	0.22	223	0.06
44	0.31	99	1.36	153	0.43	225	0.57
45	0.23	100	0.24	154	0.10	226	0.07
46	0.19	101	2.22	155	0.20	227	0.12
47	1.96	102	0.43	156	0.06	229	0.26
48	0.04	103	5.13	157	0.18	230	0.04
50	0.55	104	0.58	158	0.12	231	0.31
51	7.48	105	0.18	159	3.91	233	0.05
52	0.85	106	0.06	160	0.25	235	0.16
53	2.38	107	0.23	161	0.15	237	0.03
54	1.49	108	0.25	163	0.29	241	0.02
55	3.57	109	2.64	164	0.11	243	0.04
56	0.23	110	0.32	165	0.56	245	9.15
57	1.11	111	0.15	166	0.08	246	0.99
58	0.19	112	0.11	167	0.12	247	0.13
59	3.61	113	1.31	169	0.14	249	0.04
60	0.20	114	0.79	170	0.04	253	0.16
61	0.24	115	4.09	171	0.26	255	0.21
62	0.14	116	0.90	172	0.11	267	0.03
63	0.74	117	1.79	173	0.36	273	0.05
64	0.96	118	0.15	174	0.05	275	0.80
65	5.62	119	0.44	176	0.02	276	0.10
66	3.87	120	0.14	177	1.08	277	0.04
67	100.00	121	1.01	178	0.09	291	0.03
68	5.92	122	0.25	179	0.36	295	0.49
69	12.80	123	0.83	181	0.11	296	0.07
70	0.52	124	0.57	182	0.05	297	0.03
71	0.78	125	0.27	183	0.19	309	0.07
72	0.42	126	0.08	184	0.03	311	0.03
73	0.58	127	4.35	185	0.71	317	0.08
74	0.10	128	0.65	186	0.07	329	0.04
75	1.06	129	0.59	187	0.05	331	0.05
76	0.24	130	0.05	189	0.13	335	0.06
77	22.17	131	0.20	191	0.21	337	0.08
78	1.50	132	0.30	195	0.14	357	0.35
79	3.61	133	0.86	196	0.04	358	0.06
80	0.62	134	0.19	197	0.66	376	0.06

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
377	0.25	378	0.04				

17. 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane (22)

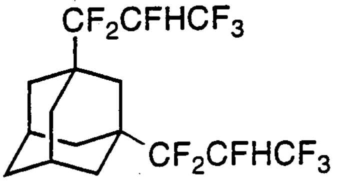


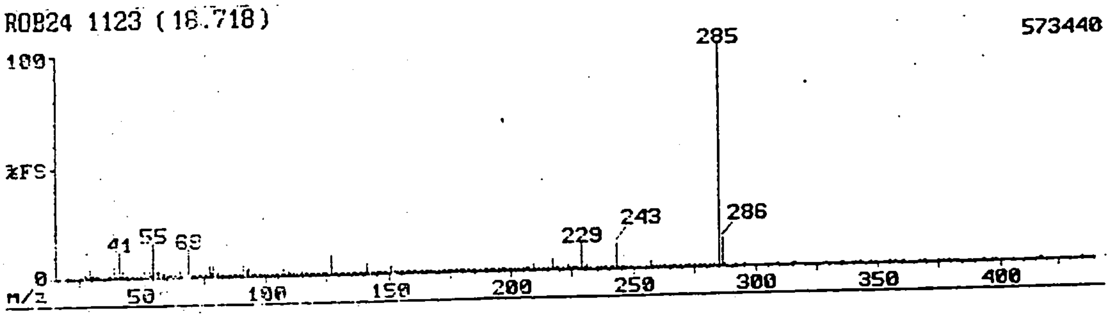


ROBADRF 654 (10.901) 950272

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	2.64	75	2.24	128	1.23	182	0.04
24	1.19	77	22.74	129	1.13	183	0.13
25	2.56	78	13.90	130	0.35	184	0.08
26	8.94	79	43.10	131	0.55	185	0.59
27	23.06	80	7.44	132	1.13	186	0.06
28	11.31	81	10.88	133	2.40	187	0.04
29	19.07	82	5.01	135	100.00	189	0.08
31	5.39	83	1.72	136	10.24	190	0.07
32	1.51	84	0.66	137	0.80	191	0.23
33	1.14	85	0.97	138	0.17	192	0.07
34	0.04	86	0.13	139	0.28	193	0.06
35	0.13	87	0.30	140	0.45	196	0.05
36	0.91	88	0.72	141	1.78	197	0.19
37	2.80	89	1.47	142	0.46	198	0.06
38	9.81	90	3.96	143	0.36	199	0.12
39	31.90	91	16.92	144	0.14	201	0.03
40	12.72	92	8.73	145	0.58	203	0.07
41	34.91	93	22.41	146	0.28	204	0.07
42	4.28	94	3.31	147	0.24	205	0.28
43	3.69	95	2.24	148	0.11	206	0.06
44	1.78	96	1.25	149	0.25	207	0.06
45	0.63	97	1.19	150	0.17	209	0.19
46	0.57	98	0.36	151	1.05	210	0.07
47	1.43	99	0.41	152	0.19	211	0.18
48	0.27	100	0.35	153	0.45	216	0.06
49	1.22	101	1.10	154	0.31	217	0.20
50	5.52	102	0.59	155	0.24	218	0.03
51	11.53	103	1.29	156	0.11	219	0.11
52	4.66	104	0.76	157	0.11	223	0.14
53	10.13	105	2.40	158	0.09	224	0.08
54	4.98	106	1.78	159	0.26	225	0.14
55	13.58	107	7.97	160	0.11	226	0.05
56	2.80	108	1.02	161	0.09	228	0.09
57	2.56	109	2.51	162	0.05	229	0.21
58	0.77	110	0.59	163	0.08	230	0.06
59	2.07	111	0.40	164	0.13	231	0.10
60	0.37	112	0.38	165	0.42	237	0.03
61	0.62	113	2.16	166	0.07	241	0.04
62	1.42	114	0.78	167	0.11	242	0.07
63	4.34	115	2.29	169	0.25	243	0.15
64	2.53	116	0.66	170	0.07	244	0.04
65	8.51	117	1.06	171	0.15	245	0.05
66	5.33	118	0.34	172	0.05	247	0.26
67	16.59	119	1.64	173	0.10	248	0.07
68	4.01	120	0.43	174	0.05	266	0.03
69	18.75	121	0.65	176	0.03	267	0.11
70	1.02	122	0.39	177	0.19	285	0.10
71	0.62	123	0.69	178	0.07	286	0.05
72	0.37	124	0.22	179	0.15		
73	0.89	125	0.35	180	0.03		
74	1.14	127	5.09	181	0.06		

18. 1,3-bis(1,1,2,3,3,3-hexafluoropropyl)adamantane (23)

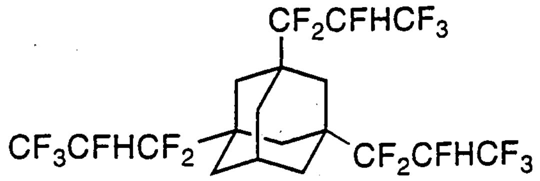


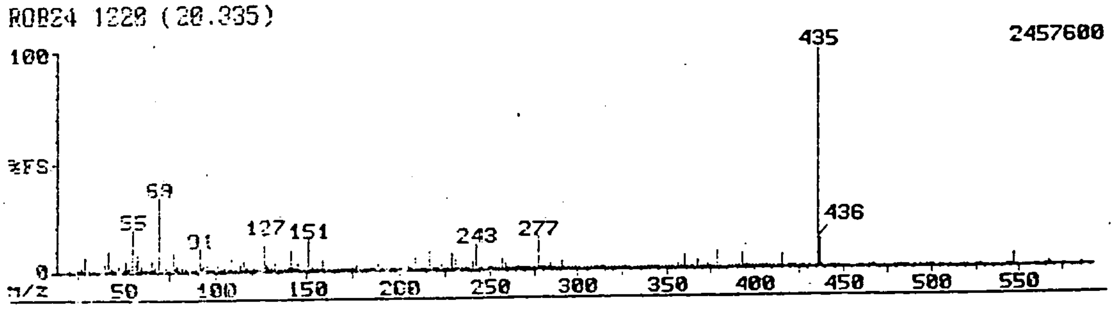


ROB24 1123 (18.718) 573440

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	0.37	57	2.13	85	0.46	115	1.21	144	0.15	175	0.11	209	2.73	247	0.10	329	0.08
26	0.09	58	0.38	86	0.07	116	0.43	145	0.38	176	0.22	210	0.50	249	0.15	335	0.73
27	1.46	59	1.76	87	0.15	117	0.55	146	0.29	177	0.75	211	0.50	255	0.44	336	0.10
28	1.18	60	0.36	88	2.13	118	0.12	147	0.33	178	0.12	213	0.11	257	1.35	341	0.09
29	2.66	61	0.40	89	0.22	119	0.31	148	0.12	179	0.25	215	0.10	258	0.20	343	0.06
30	0.12	62	0.03	90	0.25	120	0.22	149	0.13	180	2.02	217	4.32	259	0.11	347	0.09
31	0.17	63	2.33	91	5.22	121	0.44	151	2.46	181	0.43	218	0.44	261	0.08	349	0.13
32	0.50	64	0.35	92	2.47	122	0.34	152	0.22	182	0.15	219	0.22	263	0.10	355	0.30
33	0.22	65	2.50	93	4.32	123	0.54	153	0.52	183	0.48	221	0.35	265	0.69	357	0.06
37	0.05	66	0.32	94	0.61	124	0.16	154	0.11	184	2.18	223	1.73	266	0.15	361	0.13
38	0.13	67	1.30	95	0.37	125	0.15	155	2.75	185	0.32	224	0.35	267	0.12	367	0.25
39	4.78	68	2.48	96	0.49	127	3.02	156	0.15	187	0.14	225	0.36	269	0.21	369	0.09
40	0.32	69	12.14	97	0.54	128	1.37	157	0.14	189	0.48	226	0.03	271	0.09	375	0.11
41	11.79	70	0.52	98	0.17	129	0.74	158	0.17	190	0.13	227	0.08	273	0.15	377	0.17
42	0.53	71	0.49	99	0.30	130	0.16	159	1.35	191	0.56	229	11.51	275	0.36	379	0.38
43	2.36	72	0.16	101	0.53	131	0.30	160	0.10	192	0.09	230	1.09	277	0.66	385	0.09
44	0.48	73	0.71	102	2.08	132	0.28	161	0.17	193	0.13	231	2.12	278	0.36	397	1.33
45	0.12	74	2.11	103	0.31	133	1.31	163	0.11	195	0.23	232	2.22	279	0.35	399	0.28
46	0.07	75	0.49	104	0.28	134	1.16	164	0.31	196	0.07	235	0.18	281	0.38	417	1.02
47	1.38	76	2.17	105	1.23	135	0.73	165	0.37	197	0.71	237	0.56	283	0.11	419	0.16
48	0.05	77	4.31	106	0.43	136	0.16	166	0.07	198	0.07	238	0.10	285	100.00	435	0.25
50	0.25	78	1.36	107	2.53	137	0.13	167	0.13	199	0.60	239	0.28	286	12.24		
51	2.78	79	4.38	108	0.29	138	0.07	169	0.37	200	0.28	241	0.78	287	0.57		
52	0.53	80	0.33	109	2.22	139	0.30	170	0.09	201	0.12	242	0.34	291	0.27		
53	2.53	81	2.18	110	0.40	140	0.56	171	0.35	203	0.38	243	11.43	295	0.23		
54	0.73	82	0.75	111	0.23	141	4.51	172	0.07	205	0.33	244	1.13	309	0.25		
55	15.71	83	0.58	113	0.74	142	2.34	173	0.32	206	0.12	245	0.40	315	0.63		
56	2.48	84	0.13	114	0.49	143	0.43	174	0.09	207	0.22	246	0.10	316	0.10		

19. 1,3,5,-tris(1,1,2,3,3,3-hexafluoropropyl)adamantane (39)



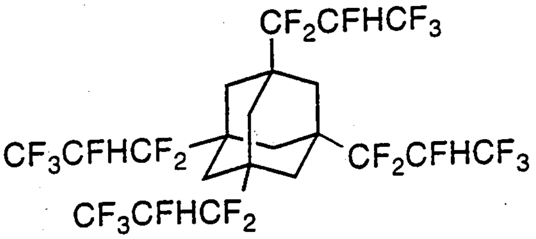


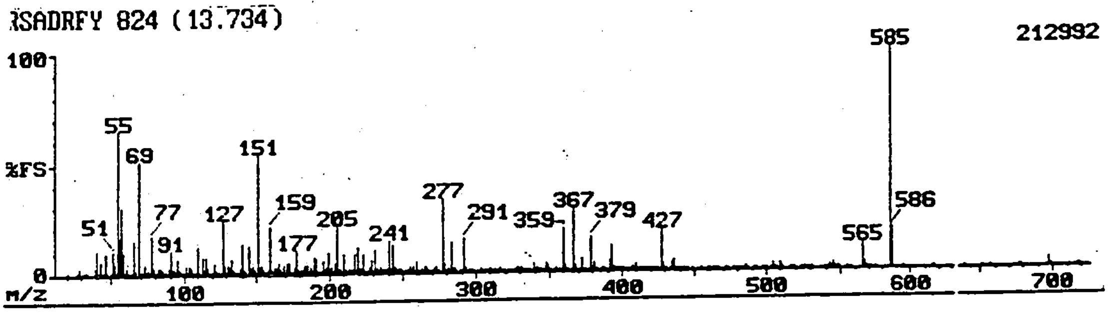
ROB24 1228 (20.335)

2457600

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	Mass	Rel Int
20	0.04	70	0.30	115	4.42	156	0.29	199	0.15	247	[illegible]	301	0.12	373	1.33	461	0.02
24	0.01	71	0.55	116	1.59	157	0.62	200	0.33	249	0.76	303	0.33	375	0.73	463	1.02
25	0.02	73	1.33	117	1.55	158	0.46	201	0.31	250	0.18	305	0.36	376	0.24	465	0.15
26	0.09	74	0.11	118	0.30	159	4.67	202	0.13	251	0.24	307	0.12	377	0.11	467	0.25
27	1.89	75	0.22	119	0.33	160	0.53	203	1.24	252	0.24	309	0.44	379	7.53	471	0.21
28	2.59	77	0.32	120	0.35	161	0.46	205	2.33	255	1.33	310	0.03	381	0.77	473	0.25
29	5.75	78	1.81	121	1.36	163	1.22	206	0.12	257	5.13	311	0.21	385	0.13	481	0.02
30	0.15	79	1.17	122	0.30	164	0.31	207	0.13	259	2.57	313	0.24	387	0.58	483	0.01
31	0.46	80	0.55	123	1.13	165	1.25	209	5.67	260	0.27	314	0.19	389	0.33	485	0.76
32	0.12	81	0.21	124	0.29	166	0.34	210	0.50	261	0.37	315	0.21	391	1.10	489	0.07
33	0.40	82	1.39	125	0.43	167	1.22	211	0.32	262	0.55	317	0.42	393	7.30	487	0.39
37	0.23	83	1.56	127	15.33	168	0.13	212	0.07	265	0.30	319	0.12	394	0.24	491	0.05
39	2.79	84	0.56	128	2.55	169	1.19	213	0.42	266	0.28	321	0.21	395	1.13	493	0.02
40	0.69	85	0.69	129	1.34	170	0.35	214	0.13	267	0.45	323	0.19	396	0.13	497	0.02
41	3.46	86	0.17	130	0.49	171	1.25	215	0.52	269	1.17	325	0.37	397	0.11	499	0.21
42	0.27	87	0.55	131	1.51	172	0.41	217	1.75	270	2.09	326	0.05	399	0.24	500	0.22
43	2.42	88	2.31	132	1.19	173	1.23	218	0.71	271	0.52	327	0.43	401	0.07	501	0.23
44	0.14	89	1.55	133	5.33	174	0.30	219	1.21	272	0.11	329	0.53	403	0.33	505	0.35
45	0.39	91	10.22	134	1.11	175	0.34	220	0.14	273	0.93	331	0.34	405	0.52	507	0.30
47	2.51	92	1.33	135	1.21	176	1.02	221	0.40	274	0.23	333	2.32	407	0.51	511	0.36
48	0.26	93	2.32	136	0.29	177	2.67	222	0.33	275	0.18	335	0.25	409	0.22	517	0.32
50	0.20	94	0.58	137	0.46	178	0.52	224	0.51	277	15.00	337	0.08	411	0.03	519	0.27
51	4.54	95	2.73	138	0.27	179	0.69	225	0.41	278	1.19	339	0.45	413	0.11	521	0.02
52	0.40	96	0.99	139	1.09	181	2.78	226	0.09	279	0.42	341	0.95	415	5.38	525	0.08
53	2.22	97	1.31	140	1.51	182	0.70	227	0.61	280	0.06	343	0.41	419	0.31	527	0.74
55	13.33	98	0.29	141	9.63	183	1.33	229	0.04	281	0.29	345	0.04	421	0.15	529	0.11
56	4.00	99	0.47	142	1.53	184	0.18	230	0.41	283	1.34	347	1.31	423	0.04	543	0.32
57	7.42	101	2.67	143	0.97	185	1.20	231	4.35	284	2.29	349	1.13	425	0.14	545	0.25
58	0.41	102	0.55	144	0.19	186	0.11	232	0.43	285	1.24	351	0.35	427	0.17	547	5.42
59	2.55	103	2.38	145	3.50	187	0.61	233	0.24	286	0.18	353	0.51	429	0.03	548	0.54
60	0.17	104	2.75	146	1.18	189	2.53	235	0.60	287	0.20	355	1.51	431	0.02	565	0.08
61	0.32	105	2.17	147	1.45	190	7.67	237	1.33	289	0.18	357	0.08	435	100.00	567	2.41
62	0.39	106	0.68	148	0.30	191	1.33	238	0.16	291	1.75	359	5.38	436	12.33	568	0.40
63	0.47	107	0.47	149	0.42	192	0.29	239	0.43	292	0.45	361	0.64	437	0.56	585	0.10
64	0.56	109	5.92	151	14.57	193	0.30	241	3.42	293	0.16	363	0.10	441	0.33		
65	4.75	110	0.73	152	0.37	195	1.10	243	11.67	294	0.16	365	0.05	443	0.23		
66	0.23	111	0.40	153	1.57	196	0.25	244	1.13	295	0.26	367	3.71	445	0.26		
67	1.53	113	3.13	154	0.65	197	1.34	245	0.61	297	0.25	369	0.36	447	0.01		
69	34.30	114	1.02	155	1.29	198	0.11	246	0.17	299	0.24	371	0.06	453	0.04		

20. 1,3,5,7-tetrakis(1,1,2,3,3,3-hexafluoropropyl)adamantane (40)

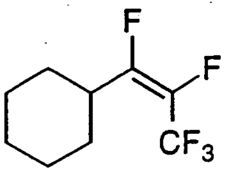


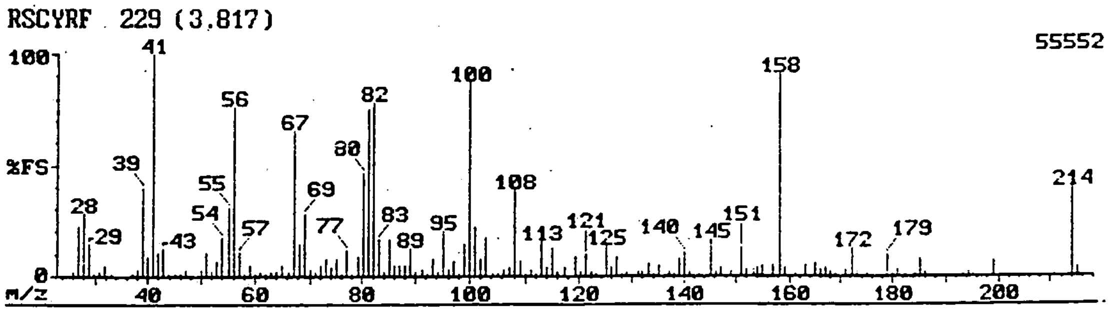


RSADRFY 824 (13.734) 212992

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
26	0.10	86	0.58	138	0.35	191	7.21	242	2.37	296	0.26	353	1.23	416	0.14	510	0.75
27	0.46	87	1.21	139	2.91	192	1.86	243	12.86	297	1.16	354	0.30	417	0.68	511	0.71
28	0.81	88	0.49	140	4.81	193	0.65	244	2.52	298	0.29	355	1.86	418	0.13	517	0.73
29	3.13	89	2.91	141	13.46	194	0.32	245	2.40	299	0.74	356	0.33	419	1.25	518	0.14
31	0.32	90	1.49	142	2.34	195	5.50	246	1.03	301	0.57	357	0.15	420	0.22	519	0.65
32	0.47	91	10.94	143	1.36	196	1.80	247	1.98	303	1.64	359	19.23	421	0.34	523	1.03
33	0.30	92	1.87	145	12.62	197	3.37	248	0.37	304	0.29	360	2.58	423	0.71	524	0.22
39	3.25	93	1.95	146	3.25	198	0.44	249	1.82	305	1.37	361	2.79	424	0.34	525	1.00
40	1.07	94	0.32	147	4.80	199	9.50	250	0.56	306	0.29	362	0.43	425	0.34	526	0.21
41	10.34	95	6.73	148	0.79	200	1.81	251	1.22	307	0.36	363	0.50	427	18.51	527	0.37
42	0.66	96	1.45	149	1.86	201	2.55	252	0.48	308	0.38	365	0.66	428	2.61	529	1.07
43	5.71	97	2.13	151	54.81	202	1.34	253	2.07	309	2.16	367	27.76	429	0.49	530	0.17
44	0.38	98	0.54	152	3.28	203	4.96	254	0.45	310	0.38	368	3.13	431	0.22	531	0.45
45	0.22	99	0.51	153	4.36	204	0.68	255	3.25	311	0.89	369	0.48	433	1.34	537	0.45
47	10.10	100	0.24	154	1.40	205	21.15	256	0.69	312	0.23	371	0.45	434	3.70	539	0.14
48	0.28	101	3.73	155	2.19	206	2.13	257	2.43	313	1.42	373	5.62	435	5.02	541	0.21
50	0.56	102	1.16	156	0.52	207	1.59	258	0.66	314	0.31	374	1.18	436	0.79	543	1.49
51	10.58	103	4.36	157	1.04	208	1.01	259	5.20	315	0.80	375	1.28	437	0.19	544	0.30
52	0.56	104	1.73	158	1.79	209	0.41	260	1.32	317	2.07	377	0.41	439	0.32	545	3.37
53	4.42	105	2.43	159	21.03	210	1.46	261	1.37	318	0.30	379	15.26	441	0.58	546	0.77
54	1.38	106	0.37	160	2.40	211	1.03	262	0.21	319	0.46	380	1.89	442	0.14	547	0.46
55	64.90	107	0.52	161	1.60	212	0.64	263	1.04	321	1.22	381	4.36	443	0.34	549	0.49
56	16.11	108	0.62	162	0.68	213	1.71	264	0.49	322	0.23	382	0.52	444	0.22	555	0.52
57	29.69	109	12.90	163	3.00	214	1.00	265	3.06	323	1.11	383	0.13	445	0.34	557	0.58
58	1.54	110	1.24	164	2.82	215	1.05	266	0.56	324	0.22	385	0.81	449	0.35	565	12.02
59	9.25	111	0.56	165	4.75	216	0.71	267	2.37	325	0.26	387	1.59	455	0.19	566	2.58
60	0.50	113	7.69	166	1.07	217	9.01	268	0.44	326	0.65	388	0.27	459	0.26	567	0.50
61	2.70	114	2.22	167	2.28	218	1.07	269	0.95	327	1.62	389	0.46	461	0.22	569	0.19
62	0.22	115	7.33	168	0.36	219	11.10	270	0.33	328	0.22	391	4.72	463	0.26	571	0.10
63	0.49	116	2.10	169	3.97	220	1.55	271	2.31	329	2.01	392	1.13	464	0.21	575	0.28
64	0.91	117	2.73	170	1.24	221	2.31	272	0.74	330	0.22	393	12.02	465	0.48	585	100.00
65	15.63	118	0.56	171	5.02	222	1.38	273	2.79	331	1.92	394	1.90	467	0.15	586	18.63
66	1.36	119	1.29	172	1.28	223	0.41	274	0.37	332	0.28	395	0.77	471	0.13	587	1.77
67	1.56	120	0.76	173	4.96	224	1.41	275	0.38	333	0.97	396	0.19	473	0.18	595	0.51
69	51.44	121	4.63	174	0.82	225	0.92	277	33.17	334	0.18	397	0.46	477	0.23	615	0.85
70	0.93	122	1.48	175	0.50	226	0.84	278	4.09	335	1.45	399	1.17	479	0.39	616	0.21
71	1.23	123	1.98	176	3.25	227	3.13	279	1.74	336	0.17	400	0.20	481	0.23	635	0.56
72	0.32	124	0.33	177	10.94	228	1.05	280	0.27	337	0.30	401	0.14	483	0.27	651	0.15
73	4.75	125	0.48	178	1.92	229	5.92	281	1.67	339	3.49	403	0.28	485	1.82	657	0.27
74	0.27	126	0.56	179	2.34	230	0.92	282	0.35	340	0.51	404	0.11	486	0.34	677	1.20
75	1.62	127	23.92	180	0.53	231	10.46	283	13.58	341	2.22	405	1.44	487	0.14	678	0.28
76	0.34	128	3.97	181	1.65	232	2.07	284	1.98	342	0.35	406	0.27	491	0.67	697	4.00
77	17.67	129	3.97	182	2.13	233	1.30	285	1.82	343	1.33	407	1.62	493	0.30	698	1.01
78	1.92	130	1.40	183	3.88	234	0.42	286	0.37	344	0.20	408	0.28	497	0.63	717	1.10
79	2.97	131	3.82	184	0.99	235	3.00	287	0.45	345	0.50	409	2.91	499	1.24	718	0.31
80	0.75	132	2.70	185	3.82	236	0.35	289	0.68	346	0.15	410	0.50	500	0.23		
81	0.30	133	6.97	186	0.83	237	1.95	290	0.68	347	3.73	411	0.45	503	0.39		
82	2.82	134	1.77	187	2.76	238	0.68	291	15.99	348	0.48	412	0.14	505	2.46		
83	2.08	135	2.25	188	0.75	239	1.95	292	2.37	349	3.37	413	0.52	506	0.48		
84	0.99	136	0.46	189	7.45	240	0.54	293	1.46	350	0.45	414	0.44	507	0.16		
85	1.09	137	0.67	190	2.82	241	14.42	295	0.74	351	0.24	415	0.74	509	2.58		

21. Z-Pentafluoroprop-2-enylcyclohexane (43a)

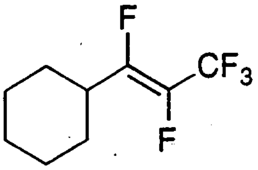


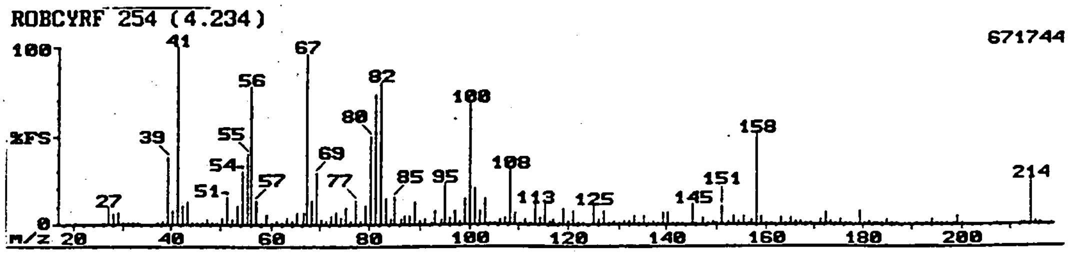


RSCYRF 229 (3.817) 55552

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
26	2.10	45	0.95	63	2.42	79	8.53	95	20.39	111	3.05	129	2.13	151	12.33	172	12.44
27	22.00	46	0.71	64	1.61	80	46.54	96	3.28	112	1.25	131	2.42	152	2.68	173	1.74
28	28.00	47	2.71	65	5.13	81	75.58	97	6.91	113	15.67	132	2.04	153	3.20	175	1.43
29	14.40	50	2.79	66	2.10	82	78.80	98	1.16	114	4.09	133	5.56	154	3.80	179	10.14
30	0.49	51	10.71	67	65.90	83	16.94	99	14.17	115	12.21	134	0.90	155	4.64	180	0.96
31	1.74	52	2.13	68	14.40	84	2.42	100	87.56	116	1.66	135	4.81	157	4.61	181	3.23
32	4.98	53	6.91	69	28.57	85	16.82	101	22.70	117	3.77	137	2.33	158	91.24	184	1.04
33	1.22	54	17.74	70	3.11	86	4.52	102	7.37	119	8.41	138	1.15	159	4.29	185	7.37
37	0.68	55	31.34	71	1.58	87	4.95	103	17.86	120	1.84	139	7.72	161	0.70	186	2.02
38	2.48	56	76.96	72	4.55	88	4.49	104	1.45	121	9.33	140	11.06	163	4.72	193	0.59
39	40.09	57	10.48	73	7.60	89	12.67	105	1.30	122	1.53	141	1.75	165	5.93	194	2.10
40	8.29	58	0.91	74	4.18	90	2.16	106	2.65	123	1.12	143	0.87	166	2.82	199	6.57
41	100.00	59	4.87	75	8.18	91	3.20	107	3.51	125	13.94	145	16.13	167	3.92	214	39.63
42	11.06	60	0.92	76	1.15	92	0.75	108	38.71	126	3.77	146	1.71	168	1.51	215	3.95
43	12.44	61	1.53	77	11.75	93	7.95	109	7.06	127	9.10	147	4.29	169	0.71		
44	1.35	62	0.79	78	1.25	94	1.78	110	0.79	128	1.08	149	1.61	171	3.14		

22. E-Pentafluoroprop-2-enylcyclohexane (43b)





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ROBCYRF 254 (4.234)                                               671744
-----------------+-----------------+-----------------+------------------
Mass   Rel Int   | Mass   Rel Int  | Mass   Rel Int  | Mass   Rel Int
-----------------+-----------------+-----------------+------------------
 20      0.03    |  71       2.15  | 114      3.77   | 159       4.84
 26      1.15    |  72       4.73  | 115     11.28   | 160       0.33
 27      9.76    |  73       6.44  | 116      1.46   | 161       0.42
 28      5.49    |  74       3.96  | 117      3.01   | 163       3.43
 29      7.16    |  75       9.76  | 118      0.76   | 164       0.60
 30      0.20    |  76       1.95  | 119      8.35   | 165       3.43
 31      0.95    |  77      13.57  | 120      1.77   | 166       1.67
 32      0.16    |  78       1.72  | 121      7.85   | 167       1.96
 33      0.67    |  79      10.67  | 122      1.07   | 168       0.85
 37      0.54    |  80      49.39  | 123      0.97   | 169       0.50
 38      2.30    |  81      72.56  | 125     10.82   | 171       3.13
 39     38.26    |  82      79.88  | 126      3.39   | 172       6.63
 40      7.51    |  83      14.94  | 127      7.81   | 173       1.80
 41    100.00    |  84       3.13  | 128      0.81   | 174       0.20
 42     10.37    |  85      15.09  | 129      1.80   | 175       2.78
 43     12.20    |  86       2.59  | 130      0.34   | 176       0.30
 44      0.76    |  87       4.54  | 131      1.95   | 177       0.45
 45      1.01    |  88       5.14  | 132      2.41   | 179       8.00
 46      0.76    |  89      12.35  | 133      4.80   | 180       0.72
 47      3.24    |  90       2.07  | 134      0.91   | 181       2.42
 48      0.12    |  91       3.16  | 135      5.11   | 182       0.22
 49      0.25    |  92       0.90  | 136      0.55   | 183       0.11
 50      3.62    |  93       7.47  | 137      2.09   | 184       0.29
 51     15.24    |  94       2.74  | 138      1.16   | 185       3.32
 52      2.86    |  95      23.02  | 139      6.75   | 186       1.12
 53     10.21    |  96       3.81  | 140      7.05   | 187       0.14
 54     30.03    |  97       7.43  | 141      1.12   | 191       0.10
 55     39.63    |  98       1.57  | 142      0.15   | 193       0.75
 56     78.05    |  99      14.63  | 143      0.61   | 194       2.67
 57     13.57    | 100      67.68  | 145     11.59   | 195       0.57
 58      1.33    | 101      20.73  | 146      0.68   | 196       0.08
 59      6.06    | 102       7.47  | 147      3.70   | 197       0.25
 60      0.95    | 103      14.94  | 148      0.50   | 199       0.28
 61      1.75    | 104       1.10  | 149      1.66   | 199       5.26
 62      1.18    | 105       1.13  | 150      0.49   | 200       0.44
 63      3.43    | 106       2.52  | 151     10.37   | 207       0.08
 64      2.23    | 107       4.04  | 152      2.02   | 212       0.08
 65      6.40    | 108      31.10  | 153      4.65   | 213       0.25
 66      6.94    | 109       6.33  | 154      2.28   | 214      24.85
 67     96.34    | 110       0.72  | 155      5.34   | 215       2.12
 68     13.41    | 111       2.86  | 156      0.78   | 216       0.11
 69     29.27    | 112       1.41  | 157      2.52   |
 70      3.28    | 113      11.59  | 158     51.83   |
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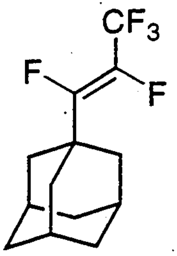
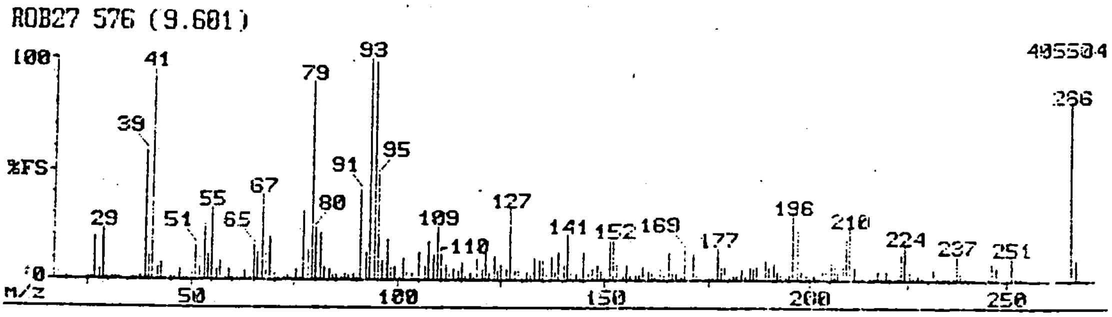
23. 1-(E-pentafluoroprop-2-enyl)adamantane (**44a**)



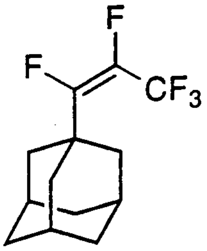


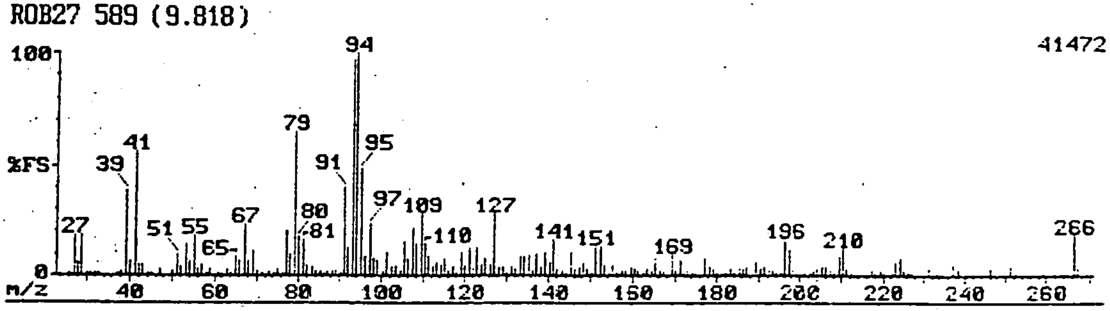
ROB27 576 (9.601) 405504

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.07	80	23.74	134	3.96	188	1.33
25	0.09	81	20.96	135	9.09	189	8.78
26	0.20	82	6.12	136	1.55	190	6.12
27	13.44	83	4.55	137	10.35	191	7.58
28	4.42	84	2.11	138	3.68	192	3.95
29	22.98	85	2.68	139	12.75	193	2.84
30	0.58	86	1.18	140	7.20	194	1.39
31	0.72	87	2.51	141	20.20	195	1.99
32	0.44	88	2.35	142	2.78	196	29.29
33	0.95	89	2.51	143	2.45	197	22.47
36	0.10	90	0.69	144	0.77	198	3.93
37	0.43	91	40.66	145	12.98	199	2.19
38	1.93	92	12.82	146	3.17	200	0.57
39	57.83	93	100.00	147	4.42	201	1.86
40	10.57	94	97.98	148	5.44	202	0.71
41	94.95	95	47.22	149	3.46	203	3.54
42	6.25	96	8.59	150	1.34	204	4.48
43	8.14	97	18.43	151	17.42	205	7.51
44	0.62	98	6.25	152	19.59	206	6.12
45	0.59	99	5.74	153	6.38	207	3.50
46	0.38	100	1.40	154	1.86	208	5.56
47	4.42	101	9.85	155	6.44	209	18.43
48	0.15	102	3.20	156	1.74	210	22.98
49	0.15	103	3.19	157	3.11	211	5.93
50	2.98	104	1.20	158	2.48	212	1.77
51	15.97	105	12.50	159	6.31	213	0.31
52	5.74	106	6.12	160	4.04	215	0.21
53	25.00	107	17.93	161	2.64	216	0.10
54	12.06	108	11.55	162	1.07	217	4.10
55	33.33	109	23.99	163	4.80	218	2.15
56	4.42	110	11.30	164	2.67	219	3.44
57	9.15	111	6.94	165	12.94	220	1.69
58	0.71	112	3.17	166	3.35	221	0.82
59	4.99	113	4.92	167	2.49	222	1.33
60	0.44	114	4.36	168	1.03	223	11.93
61	1.20	115	7.77	169	13.64	224	15.59
62	0.84	116	1.72	170	2.56	225	4.17
63	4.04	117	3.08	171	11.93	226	0.76
64	1.23	118	1.09	172	2.10	227	2.67
65	15.66	119	9.85	173	2.87	228	0.35
66	12.69	120	4.42	174	0.90	231	5.05
67	39.14	121	11.81	175	0.95	232	0.53
68	11.55	122	2.57	176	0.60	233	0.73
69	19.19	123	10.98	177	14.52	234	0.08
70	2.79	124	3.96	178	6.12	235	0.15
71	1.14	125	6.82	179	5.56	236	0.49
72	0.49	126	4.61	180	2.35	237	11.43
73	2.34	127	32.32	181	1.56	238	5.68
74	1.00	128	4.36	182	1.55	239	0.56
75	5.05	129	3.61	183	5.18	245	0.28
76	0.99	130	1.26	184	2.24	246	7.51
77	31.06	131	3.99	185	5.37	247	5.87
78	13.51	132	3.19	186	4.55	248	0.75
79	88.89	133	9.97	187	7.58	251	10.35

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
252	1.20	265	0.56	267	9.60		
253	0.08	266	79.80	268	0.62		

24. 1-(Z-pentafluoro-2-propenyl)adamantane (44b)

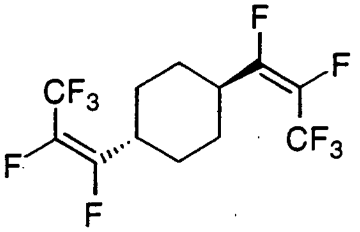


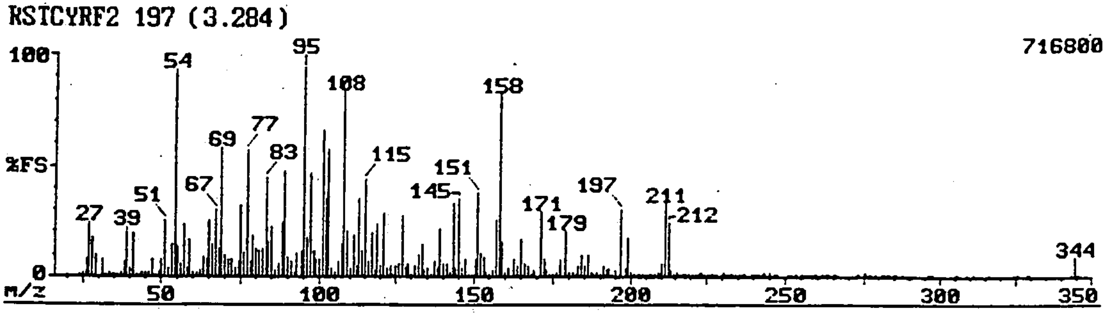


ROB27 589 (9.818) 41472

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.97	84	1.75	134	8.60	185	2.47
27	18.67	85	2.41	135	9.88	186	2.74
28	5.86	86	1.12	136	1.85	187	4.28
29	18.21	87	2.24	137	10.03	188	0.90
30	0.64	88	2.08	138	3.67	189	5.67
31	0.83	89	2.16	139	10.80	190	3.24
32	1.34	90	0.69	140	5.90	191	4.17
33	1.05	91	40.12	141	16.67	192	2.21
37	0.45	92	12.65	142	2.51	193	1.68
38	1.49	93	97.53	143	2.16	194	0.86
39	38.89	94	100.00	144	0.81	195	1.15
40	7.02	95	48.15	145	10.49	196	16.20
41	56.79	96	9.22	146	2.78	197	11.73
42	4.67	97	22.99	147	3.86	198	2.41
43	4.63	98	8.10	148	5.40	199	1.18
44	0.89	99	7.02	149	2.93	201	1.11
45	0.50	100	1.83	150	1.34	202	0.55
47	2.70	101	10.80	151	13.27	203	2.01
50	1.93	102	3.55	152	13.12	204	2.78
51	9.61	103	3.51	153	4.63	205	3.97
52	3.63	104	1.57	154	1.35	206	3.47
53	14.35	105	15.28	155	4.44	207	2.05
54	7.06	106	7.37	156	1.21	208	3.05
55	18.06	107	20.99	157	2.19	209	9.03
56	2.78	108	14.66	158	1.64	210	12.19
57	5.17	109	28.40	159	4.05	211	3.13
58	0.41	110	14.66	160	2.85	212	1.04
59	2.93	111	9.03	161	1.75	217	2.36
61	0.62	112	4.28	162	0.82	218	1.15
62	0.68	113	5.59	163	3.05	219	2.00
63	2.66	114	4.75	164	1.86	220	0.87
64	0.94	115	8.22	165	8.02	221	0.43
65	9.10	116	2.11	166	2.28	222	0.84
66	6.93	117	3.74	167	1.55	223	5.63
67	22.84	118	1.35	168	0.72	224	7.79
68	6.48	119	10.65	169	9.41	225	2.10
69	11.27	120	4.78	170	1.94	226	0.43
70	1.86	121	12.50	171	6.98	227	0.69
71	0.61	122	2.97	172	1.32	231	2.55
73	1.49	123	12.50	173	1.69	233	0.44
74	0.65	124	4.59	174	0.58	237	5.05
75	3.40	125	7.33	175	0.69	238	2.74
76	0.44	126	5.29	177	8.22	246	2.89
77	20.37	127	28.40	178	3.67	247	0.97
78	9.61	128	4.09	179	3.13	251	4.28
79	65.43	129	3.63	180	1.28	252	0.61
80	17.90	130	1.34	181	0.50	266	18.36
81	16.05	131	3.63	182	0.68	267	2.51
82	4.86	132	2.66	183	2.62		
83	3.51	133	8.99	184	1.15		

25. *trans*-1,4-bis(Z-pentafluoroprop-2-enyl)cyclohexane (46)

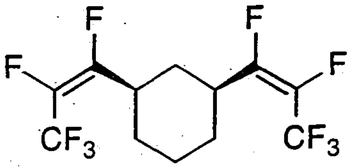


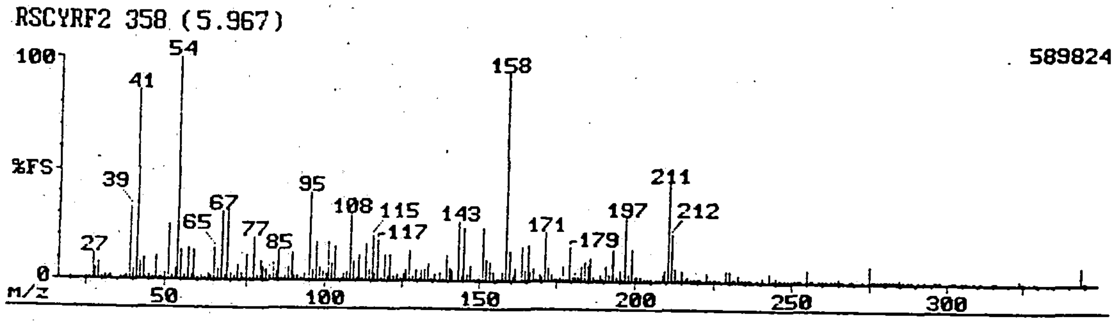


RSTCYRF2 197 (3.284) 716800

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	0.77	53	14.29	82	12.86	111	18.00	140	6.14	171	29.57	202	0.62	231	0.47	265	0.88
24	0.71	54	93.14	83	45.14	112	4.93	141	5.71	172	7.57	203	0.91	233	0.17	273	0.11
25	1.62	55	13.29	84	15.14	113	35.29	142	1.96	173	2.50	204	0.31	233	0.58	273	0.10
26	7.57	56	6.00	85	22.00	114	11.43	143	33.14	174	0.63	205	0.90	234	0.16	275	2.25
27	23.86	57	23.43	86	2.82	115	43.43	144	3.61	175	1.03	206	0.38	235	0.67	275	2.20
28	17.57	58	3.79	87	6.18	116	7.00	145	34.86	176	2.26	207	1.10	236	0.21	277	0.16
29	9.57	59	16.86	88	24.71	117	19.71	146	4.21	177	7.75	208	0.52	237	0.22	277	0.24
31	8.11	60	1.54	89	48.00	118	2.43	147	7.43	179	20.29	209	2.29	239	0.73	279	0.24
32	1.15	61	2.09	90	8.39	119	23.14	148	1.29	180	2.32	210	5.36	240	0.28	281	0.21
33	1.53	62	3.25	91	6.61	120	5.14	149	1.33	181	1.46	211	33.29	241	1.34	281	0.20
34	0.19	63	9.07	92	1.93	121	28.14	151	7.46	182	1.44	212	24.14	242	0.43	283	0.29
35	0.74	64	7.79	93	10.29	122	4.07	151	37.71	183	5.04	213	2.96	243	1.95	283	0.28
36	1.36	65	25.00	94	11.29	123	4.54	152	10.43	184	9.43	214	0.69	245	2.39	285	1.34
37	1.68	66	14.29	95	100.00	124	0.96	153	8.93	185	4.64	215	2.36	246	0.16	285	1.41
38	7.14	67	29.86	96	17.00	125	4.96	154	1.66	186	9.86	216	0.63	247	0.44	288	0.17
39	22.57	68	12.43	97	46.29	126	5.39	155	0.85	187	2.08	217	1.31	251	0.17	296	0.10
40	4.11	69	58.29	98	11.43	127	26.71	156	3.07	188	0.50	218	0.25	251	0.14	297	0.09
41	19.86	70	9.29	99	7.75	128	3.68	158	25.29	189	1.99	219	0.67	253	0.19	305	1.19
42	1.25	71	7.50	100	7.29	129	5.86	158	82.86	190	0.81	220	0.31	255	1.25	305	1.26
43	0.84	72	7.93	101	65.71	130	1.22	159	15.29	191	5.25	221	1.18	255	1.24	309	0.23
44	1.84	73	4.11	102	34.57	131	4.86	160	2.15	192	2.75	222	0.36	257	0.51	311	0.22
45	2.13	74	6.93	103	57.71	132	9.57	161	3.54	193	4.21	223	1.76	257	0.33	316	0.17
46	1.68	75	32.14	104	4.07	133	14.86	163	7.29	194	1.08	224	0.35	259	0.51	324	0.85
47	7.79	76	11.00	105	1.58	134	2.43	164	4.57	195	2.79	225	0.82	259	0.39	325	0.23
48	0.52	77	57.14	106	7.21	135	3.79	165	16.86	197	29.86	226	0.44	261	0.25	329	0.07
49	1.47	78	7.25	107	14.43	136	0.60	166	5.39	198	4.07	227	0.89	261	0.25	329	0.25
50	8.00	79	18.29	108	83.43	137	6.36	167	4.43	199	17.43	228	0.36	263	0.24	344	1.36
51	25.00	80	12.29	109	20.86	138	4.18	168	1.13	200	1.76	229	0.73	263	0.21	344	9.14
52	4.07	81	11.86	110	3.54	139	21.29	169	3.18	201	1.17	230	2.02	265	0.98	345	0.88

26. *cis*-1,3-bis(Z-pentafluoroprop-2-enyl)cyclohexane (47)



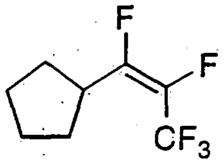


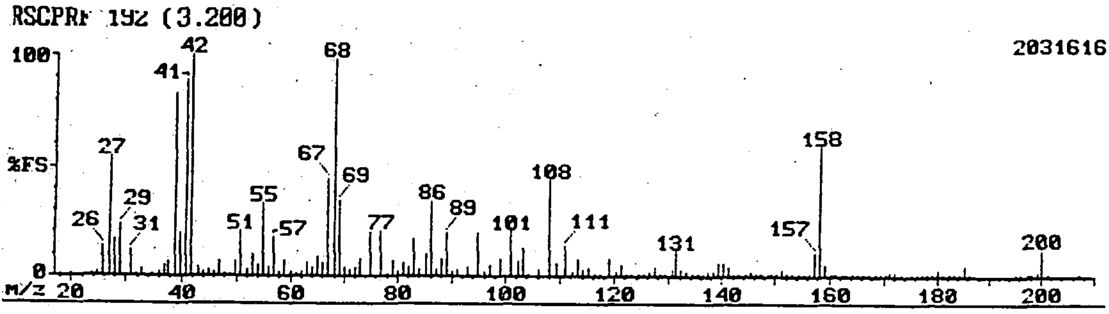
RSCYRF2 358 (5.967)

589824

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	0.07	56	1.69	86	1.13	117	18.23	149	0.98	180	2.32	211	45.14	246	0.36	284	0.73
25	0.03	57	14.24	87	1.51	118	1.14	150	1.11	181	4.17	212	21.01	247	0.68	285	2.03
26	0.73	58	1.70	88	5.73	119	11.28	151	23.96	182	1.66	213	5.82	248	0.09	286	0.25
27	11.28	59	13.72	89	13.02	120	1.83	152	10.03	183	6.68	214	0.77	249	0.13	288	0.09
28	4.82	60	1.18	90	2.22	121	11.28	153	8.59	184	8.94	215	5.08	250	0.15	289	0.17
29	7.90	61	1.55	91	2.26	122	1.46	154	3.60	185	7.20	216	0.99	251	0.54	291	0.16
30	0.18	62	0.73	92	0.21	123	2.59	155	0.73	186	10.68	217	1.84	252	0.16	293	0.32
31	1.74	63	3.21	93	3.04	124	0.33	156	0.68	187	2.24	218	0.19	253	0.17	296	0.36
32	0.99	64	2.00	95	39.93	125	2.54	157	3.69	188	0.31	219	0.64	255	6.03	297	0.24
33	2.13	65	14.58	96	4.38	126	5.25	158	93.75	189	3.13	220	0.14	256	0.69	298	0.17
36	0.06	66	5.03	97	17.19	127	13.72	159	13.72	190	0.63	221	1.38	257	0.75	302	0.21
37	0.44	67	31.08	98	5.38	128	1.89	160	1.64	191	7.12	223	3.43	259	0.97	303	0.15
38	2.09	68	2.08	99	4.04	129	4.86	161	5.90	192	2.63	224	0.40	260	0.21	305	1.42
39	33.16	69	30.73	100	3.39	130	1.17	163	15.80	193	14.24	225	1.19	261	0.49	306	0.16
40	4.64	70	3.17	101	17.36	131	4.95	164	4.86	194	1.91	226	0.20	263	0.52	309	0.51
41	85.42	71	2.33	102	7.29	132	4.51	165	16.15	195	4.56	227	1.36	264	1.18	311	0.34
42	7.94	72	6.47	103	15.10	133	8.16	166	4.30	196	1.04	229	4.47	265	1.82	315	0.10
43	9.90	73	2.64	104	1.25	134	1.30	167	5.90	197	28.65	230	5.25	266	0.22	316	0.25
44	0.80	74	0.64	105	0.65	135	2.95	168	1.40	198	3.08	231	1.20	269	0.14	324	1.74
45	1.54	75	11.63	106	2.52	137	3.91	169	3.34	199	14.58	232	0.60	270	0.12	325	0.29
46	1.10	76	1.04	107	4.04	138	0.99	170	2.39	200	1.71	233	2.95	273	0.11	329	1.12
47	10.76	77	19.10	108	29.86	139	11.46	171	22.40	201	2.40	234	0.40	275	7.55	344	7.55
48	0.28	78	1.63	109	8.68	140	5.90	172	5.95	202	1.80	235	1.39	276	0.95	345	0.89
49	0.19	79	8.33	110	1.30	141	5.12	173	2.48	203	1.30	236	0.34	277	0.67		
50	2.68	80	5.56	111	11.46	143	27.43	174	0.36	204	0.34	237	0.24	278	0.23		
51	25.17	81	4.56	112	1.29	144	1.52	175	0.50	205	0.99	239	0.97	279	0.54		
52	2.26	82	2.14	113	16.15	145	24.48	176	2.04	207	1.11	241	1.58	280	0.14		
53	4.90	83	7.81	114	4.99	146	2.54	177	7.16	208	0.16	243	3.43	281	0.11		
54	100.00	84	4.08	115	20.14	147	6.38	178	0.60	209	3.17	244	0.17	282	0.47		
55	13.89	85	13.37	116	2.78	148	1.06	179	15.45	210	5.12	245	2.37	283	0.72		

27. Z-Pentafluoroprop-2-enylcyclopentane (49)

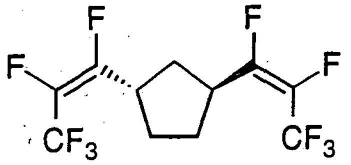


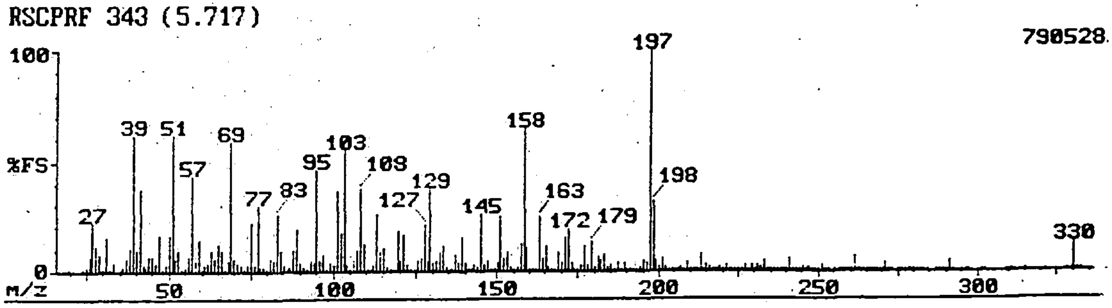


RSCPRF 192 (3.200) 2031616

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	0.86	43	4.03	61	1.45	81	5.90	103	12.15	125	1.16	143	0.18	161	1.32	180	2.70
24	0.70	44	2.09	62	2.26	82	3.68	104	0.60	126	1.90	144	0.52	162	0.18	181	0.82
25	1.94	45	2.56	63	5.90	83	16.73	106	3.07	127	3.78	145	2.15	163	0.36	182	0.09
26	13.31	46	1.94	64	4.23	84	3.05	108	43.35	128	0.65	146	0.29	164	0.26	183	0.05
27	54.03	47	6.60	65	8.32	85	9.53	109	5.59	129	0.63	147	0.25	165	1.40	184	0.46
28	16.94	48	0.34	66	5.85	86	33.67	111	13.71	130	2.95	148	0.13	166	0.18	185	4.44
29	23.19	49	1.30	67	44.15	87	2.60	112	2.42	131	11.49	149	0.61	167	0.54	186	0.26
31	11.19	50	7.11	68	97.58	88	8.11	113	7.51	132	2.82	150	0.81	168	0.05	195	0.03
32	0.76	51	20.77	69	33.67	89	19.35	114	2.78	133	2.07	151	2.95	169	0.07	196	0.06
33	3.04	52	3.38	70	4.18	90	2.34	115	3.68	134	0.57	152	0.92	170	0.24	197	0.04
35	0.48	53	9.78	71	2.71	91	2.87	116	0.58	135	1.22	153	1.05	171	1.54	198	0.22
36	1.70	54	5.19	72	4.08	93	4.08	117	1.05	136	0.92	154	0.89	172	2.26	199	1.69
37	4.54	55	33.47	73	7.86	95	18.95	119	8.01	137	1.68	155	0.11	173	0.10	200	12.80
38	6.50	56	3.63	75	19.35	96	2.02	120	2.21	138	1.83	156	0.51	175	0.03	201	0.61
39	82.26	57	17.74	77	20.77	97	4.59	121	4.89	139	5.90	157	10.53	176	0.05	207	0.05
40	18.95	58	1.69	78	1.34	99	7.61	122	0.64	140	5.90	158	59.68	177	0.12		
41	88.71	59	6.85	79	6.70	101	19.96	123	0.12	141	4.03	159	5.19	178	0.13		
42	100.00	60	2.31	80	1.78	102	6.96	124	0.30	142	0.37	160	0.51	179	0.58		

28. *trans*-1,3-bis(Z-pentafluoroprop-2-enyl)cyclopentane (50a)

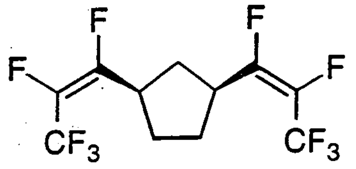


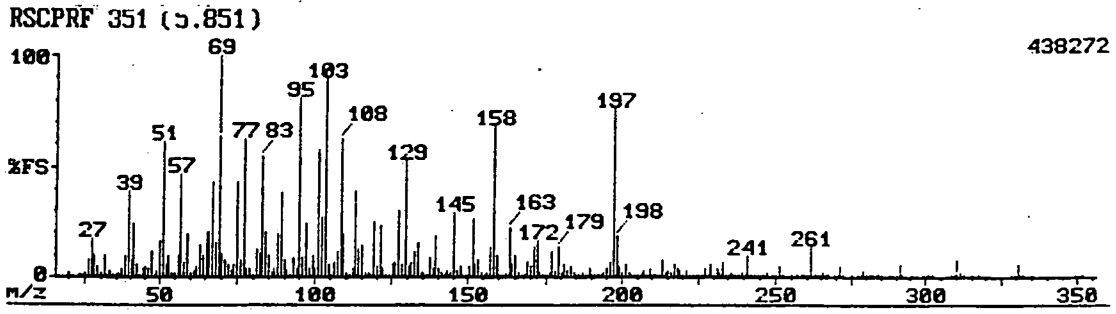


RSCPRF 343 (5.717) 790528

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	1.22	56	6.99	88	9.84	120	4.37	152	5.44	184	2.20	216	2.10	248	0.21	282	0.37
24	0.83	57	43.52	89	19.43	121	16.97	153	8.68	185	2.91	217	0.33	249	0.24	283	0.36
25	1.47	58	4.95	90	4.31	122	2.69	154	1.88	186	0.40	218	0.55	250	0.32	284	0.31
26	6.67	59	14.25	91	1.57	123	0.79	155	0.76	187	3.59	219	2.23	251	2.98	287	0.09
27	22.80	60	1.13	92	0.66	124	0.70	156	1.79	188	1.12	220	0.75	252	0.39	288	0.31
28	11.66	61	2.49	93	5.31	125	4.47	157	12.56	189	3.98	221	2.59	253	0.07	289	0.20
29	7.55	62	3.72	94	3.85	126	5.73	158	64.77	190	1.30	222	0.86	255	0.10	290	0.20
30	0.07	63	9.84	95	46.63	127	21.11	159	10.75	191	0.79	223	0.41	256	0.05	291	5.05
31	15.41	64	6.19	96	4.83	128	4.47	160	0.87	192	0.50	224	0.22	257	0.49	292	0.58
32	1.17	65	13.08	97	7.64	129	37.82	161	1.27	193	1.19	225	0.79	258	0.10	295	0.19
33	4.15	66	9.97	98	0.83	130	3.47	162	1.34	194	1.57	226	0.56	259	0.65	296	0.02
35	1.23	67	1.45	99	4.15	131	5.31	163	25.13	195	4.60	227	3.14	260	0.51	297	0.24
36	2.27	68	5.08	100	2.49	132	8.94	164	5.57	196	4.15	228	0.21	261	6.87	301	0.42
37	5.57	69	59.07	101	37.31	133	11.66	165	11.79	197	100.00	229	3.01	262	0.85	302	0.15
38	10.36	70	5.83	102	17.88	134	1.73	166	2.17	198	32.38	230	0.45	263	0.62	309	0.07
39	61.66	71	3.82	103	54.92	135	1.07	167	1.00	199	4.40	231	3.11	264	0.31	310	0.33
40	9.59	72	2.72	104	3.30	136	0.48	168	0.96	200	2.30	232	1.64	265	1.12	311	1.42
41	38.34	73	0.96	105	0.93	137	7.48	169	8.29	201	5.44	233	4.99	266	0.18	312	0.16
42	2.45	74	2.69	106	5.21	138	3.98	170	4.08	202	1.68	234	0.43	267	0.11	315	0.23
43	1.85	75	22.41	107	9.33	139	15.67	171	15.16	203	1.37	235	0.08	268	0.04	328	0.07
44	6.35	76	3.30	108	38.34	140	3.59	172	19.56	204	0.09	236	0.05	269	0.37	329	0.62
45	7.19	77	29.92	109	12.69	141	1.35	173	4.11	205	1.01	237	0.54	270	0.38	330	12.56
46	4.05	78	1.70	110	1.25	142	0.33	174	0.96	206	0.38	238	0.16	271	3.56	331	1.35
47	16.19	79	1.59	111	0.89	143	2.78	175	1.36	207	1.99	239	1.16	272	0.47	332	0.06
48	1.32	80	0.70	112	2.82	144	2.07	176	2.72	208	0.62	240	0.57	273	0.07		
49	2.95	81	5.83	113	26.42	145	26.42	177	12.05	209	3.63	241	6.02	275	0.14		
50	16.45	82	4.70	114	8.42	146	2.75	178	2.56	210	0.60	242	0.83	276	0.03		
51	62.18	83	26.42	115	10.23	147	4.86	179	13.47	211	0.90	243	0.31	277	0.37		
52	5.63	84	9.46	116	1.46	148	0.57	180	1.68	212	1.14	244	0.37	278	0.06		
53	9.59	85	2.91	117	1.09	149	0.62	181	6.48	213	7.67	245	1.68	279	0.79		
54	1.31	86	0.49	118	1.13	150	4.34	182	5.02	214	1.40	246	0.33	280	0.15		
55	1.86	87	2.17	119	18.01	151	25.39	183	8.16	215	2.66	247	1.89	281	0.26		

29. *cis*-1,3-bis(Z-pentafluoroprop-2-enyl)cyclopentane (50b)

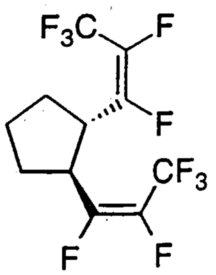


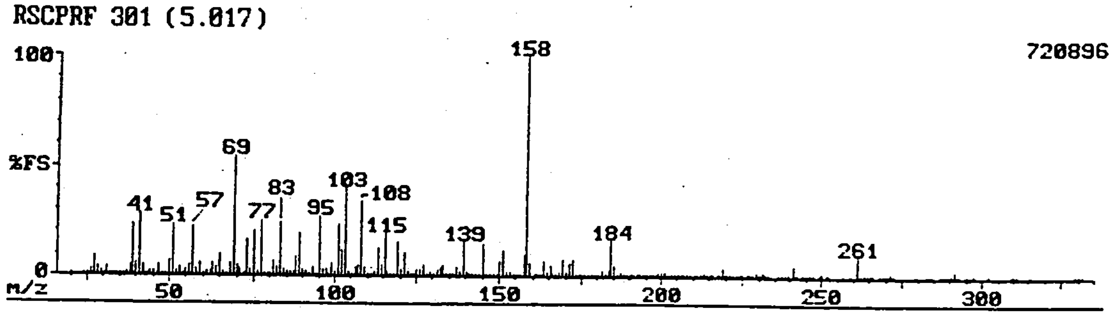


RSCPRF 351 (5.851) 438272

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	1.50	54	2.26	86	1.78	118	1.30	150	4.61	182	2.83	214	1.69	246	0.46	288	0.41
23	0.16	55	2.21	87	4.15	119	25.23	151	26.17	183	4.50	215	3.04	247	1.72	289	0.31
24	0.71	56	9.29	88	19.16	120	5.32	152	5.78	184	1.83	216	2.28	249	0.77	290	0.40
25	1.96	57	46.96	89	37.85	121	23.36	153	8.00	185	0.96	217	5.55	250	0.77	291	5.61
26	8.24	58	6.83	90	7.77	122	3.91	154	1.49	186	0.43	218	3.72	251	5.02	292	0.62
27	17.76	59	19.39	91	3.37	123	1.07	155	0.55	187	1.55	219	2.80	252	0.66	295	0.23
28	9.87	60	2.35	92	1.11	124	0.80	156	1.90	188	1.14	220	0.98	255	0.15	297	0.34
29	5.32	61	2.69	93	8.94	125	5.90	157	13.90	189	3.64	221	3.14	257	0.64	299	0.14
30	2.10	62	5.26	94	3.58	126	6.83	158	68.22	190	1.14	222	0.96	258	0.08	300	0.04
31	9.46	63	14.25	95	80.37	127	30.14	159	10.11	191	0.54	223	0.35	259	1.08	301	0.47
32	1.42	64	9.81	96	8.41	128	5.43	160	0.96	192	0.54	224	0.13	260	0.35	302	0.14
33	2.96	65	20.79	97	24.30	129	52.34	161	1.20	193	0.99	225	0.39	261	13.49	308	0.08
34	0.22	66	20.09	98	3.49	130	4.91	162	2.19	194	1.49	226	0.72	262	0.99	309	0.61
35	1.29	67	42.52	99	9.35	131	6.66	163	22.66	195	4.21	227	3.91	263	0.55	310	7.77
36	2.26	68	15.19	100	3.80	132	11.97	164	5.49	196	6.83	228	0.56	264	0.85	311	2.41
37	3.91	69	100.00	101	57.71	133	15.42	165	10.16	197	75.70	229	5.90	265	1.69	312	0.20
38	9.99	70	10.69	102	26.87	134	2.13	166	2.00	198	18.69	230	0.79	266	0.26	315	0.19
39	39.02	71	7.48	103	89.72	135	1.49	167	0.92	199	5.32	231	3.74	267	0.20	317	0.06
40	7.94	72	6.13	104	5.55	136	0.45	168	1.05	200	2.32	232	2.03	269	0.55	328	0.15
41	24.30	73	3.33	105	1.24	137	8.70	169	7.13	201	5.61	233	6.48	270	0.35	329	0.58
42	6.02	74	5.72	106	7.18	138	4.32	170	4.38	202	1.61	234	0.44	271	4.67	330	6.07
43	1.37	75	42.99	107	11.92	139	18.22	171	13.38	203	1.08	235	0.22	272	0.55	331	1.21
44	4.26	76	7.48	108	62.62	140	3.91	172	16.82	204	0.28	236	1.58	275	0.12	332	0.09
45	4.44	77	62.62	109	19.16	141	2.29	173	1.56	205	1.20	237	0.70	277	0.26	335	0.15
46	3.53	78	3.74	110	2.09	142	0.45	174	0.37	206	0.61	238	0.11	278	0.08	349	0.18
47	11.86	79	4.26	111	1.39	143	3.29	175	0.69	207	3.14	239	1.61	279	3.39	350	1.02
48	1.02	80	1.36	112	3.50	144	2.42	176	1.77	208	0.99	240	0.57	280	0.30	351	0.14
49	2.82	81	12.15	113	38.79	145	29.21	177	11.97	209	3.74	241	9.23	281	1.27		
50	16.59	82	10.63	114	12.27	146	3.23	178	2.92	210	0.72	242	1.14	282	0.61		
51	60.75	83	53.97	115	14.95	147	5.32	179	13.26	211	1.18	243	0.39	283	0.36		
52	5.84	84	20.56	116	2.13	148	0.70	180	2.12	212	1.39	244	0.41	284	1.61		
53	9.81	85	9.58	117	1.68	149	0.74	181	5.84	213	8.24	245	1.15	285	0.39		

30. *trans*-1,2-bis(Z-pentafluoroprop-2-enyl)cyclopentane (50c)



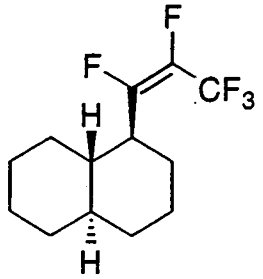


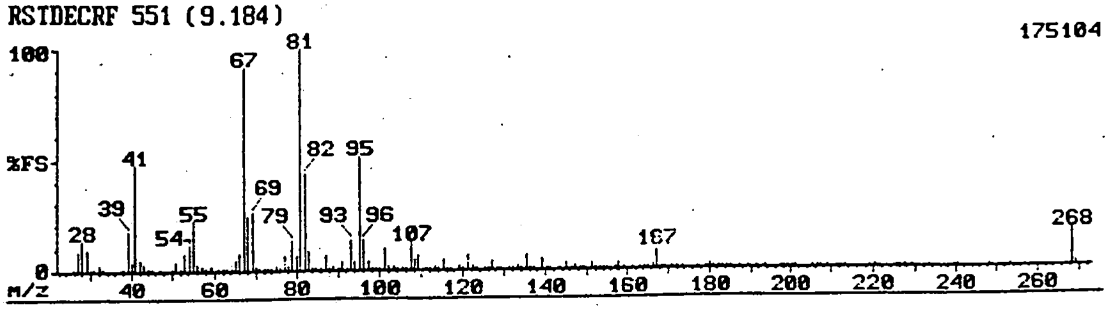
RSCPRF 301 (5.017)

720896

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	0.26	52	2.27	81	6.36	110	0.44	139	15.77	168	1.58	197	0.84	226	0.29	266	0.18
24	0.30	53	3.55	82	3.44	111	0.43	140	2.34	169	7.35	198	0.72	227	1.40	268	0.08
25	0.68	54	0.82	83	23.86	112	1.59	141	0.63	170	1.70	199	2.41	228	0.17	269	0.54
26	3.27	55	2.70	84	3.09	113	12.36	142	0.16	171	5.50	200	1.88	229	1.93	270	1.13
27	8.81	56	4.69	85	1.77	114	4.76	143	1.20	172	7.42	201	1.56	230	0.18	271	1.50
28	3.59	57	21.88	86	2.10	115	19.32	144	1.23	173	0.62	202	0.62	231	1.86	272	0.19
29	1.80	58	2.49	87	1.86	116	2.06	145	14.63	174	0.15	203	0.59	232	0.75	279	0.14
30	0.60	59	6.25	88	8.31	117	1.04	146	1.44	175	0.58	204	0.06	233	0.72	283	0.31
31	3.84	60	1.07	89	19.74	118	0.70	147	0.67	176	0.71	205	0.51	236	0.03	284	0.23
32	0.49	61	1.97	90	3.30	119	15.91	148	0.27	177	1.21	206	0.22	237	0.26	287	0.04
33	1.02	62	2.27	91	1.46	120	2.66	149	0.90	178	0.18	207	0.90	238	0.31	288	0.78
34	0.07	63	5.47	92	0.36	121	10.51	150	6.46	179	0.99	208	0.23	239	0.52	289	0.15
35	0.54	64	3.94	93	4.12	122	1.78	151	11.65	180	0.65	209	0.48	241	4.44	290	0.18
36	0.91	65	9.23	94	1.44	123	0.40	152	1.79	181	2.95	210	0.07	242	0.53	291	3.37
37	1.99	66	2.17	95	26.85	124	0.46	153	1.77	182	0.94	211	0.39	244	0.06	292	0.20
38	4.90	67	1.19	96	3.34	125	2.73	154	0.17	183	2.59	212	0.45	245	0.78	295	0.06
39	23.58	68	5.50	97	2.95	126	3.30	155	0.31	184	16.62	213	1.71	246	0.15	297	0.05
40	5.58	69	53.98	98	0.62	127	4.79	156	0.80	185	4.72	214	0.43	247	0.78	302	0.09
41	28.27	70	4.87	99	6.29	128	0.59	157	9.94	186	0.49	215	1.07	249	0.11	309	0.09
42	5.22	71	3.16	100	1.78	129	2.04	158	100.00	187	1.50	216	0.49	250	1.66	310	1.11
43	0.72	72	1.19	101	23.01	130	1.16	159	6.21	188	0.36	217	0.15	251	1.19	311	0.51
44	1.76	73	16.05	102	11.65	131	3.27	160	0.14	189	1.05	218	0.82	252	0.30	315	0.08
45	1.87	74	3.16	103	39.77	132	4.15	161	0.69	190	0.34	219	4.01	257	0.22	329	0.15
46	1.39	75	20.60	104	2.27	133	5.18	162	0.68	191	0.27	220	0.54	259	0.24	330	1.20
47	5.04	76	1.79	105	0.55	134	0.69	163	6.96	192	0.09	221	1.31	261	9.23	331	0.15
48	0.47	77	25.71	106	3.69	135	0.74	164	1.58	193	0.36	222	0.39	262	0.45		
49	1.27	78	1.31	107	4.76	136	0.27	165	5.33	194	0.54	223	0.18	263	0.27		
50	6.68	79	0.98	108	34.23	137	3.98	166	0.93	195	1.28	224	0.10	264	0.12		
51	23.72	80	1.26	109	3.98	138	2.27	167	0.61	196	0.31	225	1.15	265	0.71		

31. 1-(Z-pentafluoroprop-2-enyl)*trans*-decalin (51a)

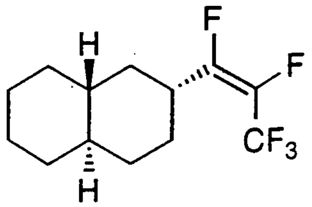


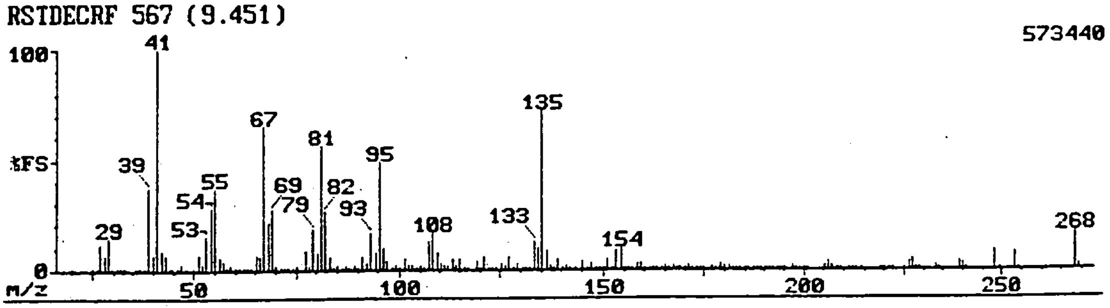


RSTDECRF 551 (9.184) 175104

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
26	0.50	52	1.39	72	0.28	91	3.47	110	1.03	132	0.58	155	0.34	182	0.85	213	0.28
27	8.26	53	7.97	73	0.57	92	0.71	111	0.88	133	1.59	157	0.68	183	0.39	219	0.48
28	13.45	54	11.55	74	0.22	93	13.89	112	0.47	134	0.46	158	3.33	184	0.37	220	0.31
29	9.94	55	22.66	75	1.77	94	4.20	113	1.94	135	6.51	159	1.45	185	0.61	225	0.78
30	0.33	56	2.63	76	0.34	95	51.46	114	1.42	136	0.89	161	0.72	187	0.93	226	0.57
31	0.26	57	1.66	77	6.62	96	13.89	115	4.71	137	1.11	163	0.92	189	0.45	227	1.00
32	3.18	58	0.20	78	1.71	97	3.65	116	0.46	139	4.93	164	0.42	191	0.36	229	0.19
33	0.40	59	1.49	79	13.60	98	0.49	117	0.40	140	0.74	165	1.39	193	0.42	233	0.29
38	0.54	61	0.29	80	6.36	99	1.28	119	2.34	141	1.03	166	1.87	197	0.56	239	0.53
39	17.84	62	0.21	81	100.00	100	1.36	120	0.38	143	0.36	167	9.65	198	0.35	240	0.73
40	3.65	63	0.98	82	43.27	101	9.80	121	6.83	145	2.96	168	1.43	199	0.39	248	0.51
41	47.37	64	0.41	83	8.41	102	2.07	122	2.28	146	0.46	169	0.48	200	1.20	253	0.96
42	5.26	65	4.50	84	0.91	103	1.71	123	1.40	147	2.18	171	1.20	201	0.31	268	16.67
43	3.07	66	7.89	85	0.56	104	0.22	125	1.05	148	0.40	172	0.26	205	0.41	269	2.33
44	1.44	67	91.81	86	1.16	105	0.74	126	0.62	149	0.75	173	0.30	206	0.28		
45	0.24	68	24.12	87	6.51	106	0.34	127	4.28	151	3.29	177	1.21	207	0.67		
47	1.08	69	26.46	88	0.65	107	12.57	128	0.86	152	0.65	179	1.23	209	0.62		
50	0.67	70	1.92	89	1.71	108	4.57	129	0.90	153	0.69	180	1.75	211	0.43		
51	3.76	71	0.44	90	0.37	109	7.16	131	0.56	154	0.37	181	1.23	212	0.36		

32. 2-(Z-pentafluoroprop-2-enyl)*trans*-decalin (**51b**)

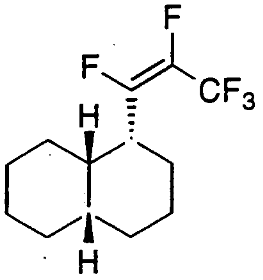


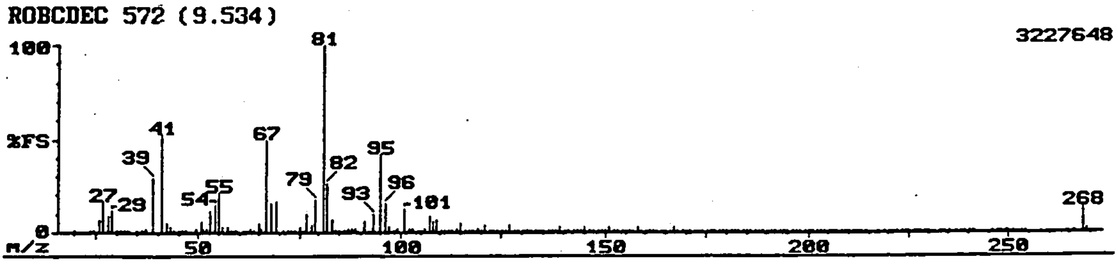


RSTDECRF 567 (9.451) 573440

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	0.05	50	1.19	73	1.08	97	3.79	121	6.03	145	3.84	168	0.16	192	1.05	226	4.24
25	0.06	51	7.05	74	0.24	98	0.76	122	1.04	146	0.52	169	0.84	193	0.77	227	4.60
26	0.25	52	2.72	75	1.75	99	1.93	123	1.36	147	2.99	170	0.23	194	0.56	228	0.23
27	11.61	53	15.71	77	8.35	100	1.28	124	0.24	148	0.41	171	2.05	195	0.10	229	0.41
28	6.88	54	28.21	78	2.40	101	4.42	125	2.62	149	0.75	172	0.33	197	2.06	233	1.75
29	15.00	55	36.96	79	18.39	102	1.72	126	1.64	150	0.22	173	0.73	198	0.44	234	0.12
30	0.39	56	5.76	80	7.95	103	2.02	127	5.80	151	4.38	174	0.15	199	0.71	239	4.24
31	0.38	57	4.24	81	56.43	104	0.28	128	1.03	152	0.77	175	0.23	200	0.22	240	2.90
32	1.04	58	0.37	82	26.43	105	1.46	129	2.99	153	8.79	177	1.94	201	0.21	241	0.21
33	0.41	59	2.27	83	6.21	106	1.16	130	0.33	154	9.69	178	0.81	205	1.84	248	8.88
36	0.06	60	0.15	84	0.97	107	12.68	131	0.66	155	1.34	179	2.77	206	3.53	249	1.10
37	0.15	61	0.46	85	1.52	108	16.96	132	0.71	156	0.22	180	1.50	207	2.24	253	7.99
38	0.71	62	0.24	86	1.10	109	8.13	133	13.04	157	0.76	181	1.70	208	0.32	254	0.97
39	37.32	63	1.13	87	1.51	110	2.43	134	9.73	158	3.17	182	0.25	209	0.35	268	16.79
40	7.01	64	0.56	88	0.90	111	1.98	135	71.43	159	2.85	183	0.57	211	1.35	269	2.15
41	100.00	65	6.83	89	2.11	112	2.25	136	8.26	160	0.33	184	0.24	212	0.62		
42	8.26	66	5.58	90	0.33	113	4.46	137	1.94	161	1.38	185	0.94	213	0.41		
43	7.19	67	65.00	91	5.89	114	1.50	138	0.30	162	0.18	186	0.19	214	0.23		
44	0.36	68	21.25	92	2.95	115	4.69	139	4.69	163	1.03	187	1.14	219	0.83		
45	0.24	69	27.32	93	16.96	116	0.53	140	0.77	164	0.42	188	0.16	220	0.50		
46	0.31	70	1.94	94	7.63	117	0.49	141	1.81	165	2.13	189	0.43	221	0.30		
47	2.54	71	0.49	95	48.57	119	3.75	142	0.31	166	0.75	190	0.12	222	0.28		
48	0.09	72	0.42	96	9.51	120	0.73	143	1.44	167	2.13	191	1.03	225	1.21		

33. 1-(Z-Pentafluoroprop-2-enyl)*cis*-decalin (52a)

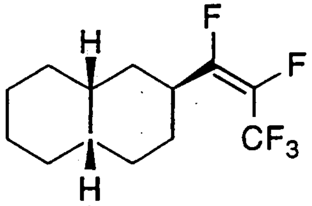


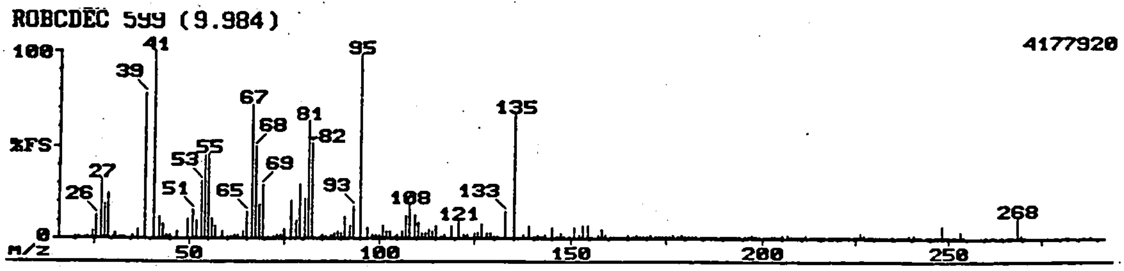


ROBCDEC 572 (9.534) 3227648

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.42	83	6.41	141	0.87	195	0.11
24	0.50	84	0.94	142	0.25	196	0.09
25	0.73	85	0.98	143	0.46	197	0.48
26	7.14	86	0.85	144	0.37	198	0.22
27	16.37	87	2.22	145	2.60	199	0.20
28	9.01	88	1.51	146	0.58	200	0.28
29	11.68	89	2.01	147	1.30	201	0.12
30	0.35	91	6.00	148	0.32	202	0.03
31	1.38	93	10.03	149	0.47	203	0.06
32	0.28	95	41.62	150	0.36	204	0.03
33	0.50	96	15.10	151	2.47	205	0.34
35	0.13	97	2.92	152	0.57	206	0.21
36	0.53	98	0.59	153	0.51	207	0.46
37	1.56	99	1.76	154	0.31	208	0.08
39	28.68	101	12.18	155	0.19	209	0.42
41	52.28	102	2.28	156	0.16	210	0.12
42	5.33	103	1.90	157	0.71	211	0.29
43	2.73	104	0.37	158	2.51	212	0.24
44	0.78	105	1.00	159	0.89	213	0.11
45	0.46	106	2.01	160	0.14	214	0.05
46	0.38	107	8.88	161	0.40	217	0.03
47	1.08	108	5.49	162	0.13	219	0.21
49	2.16	109	6.47	163	0.78	220	0.15
51	5.58	110	1.22	164	0.51	221	0.06
51	2.35	111	0.75	165	1.07	222	0.05
52	2.28	112	0.82	166	1.17	223	0.04
53	11.29	113	1.24	167	3.36	224	0.12
54	14.85	114	2.28	168	0.53	225	0.38
55	21.45	115	4.44	169	0.57	226	0.36
56	2.98	116	0.65	170	0.19	227	0.47
57	2.70	117	0.57	171	1.06	228	0.09
58	0.14	118	0.49	172	0.44	229	0.25
59	1.31	119	2.25	173	0.32	230	0.04
59	0.61	120	1.19	174	0.06	233	0.15
61	0.54	121	3.84	175	0.11	234	0.01
62	0.40	122	1.04	176	0.08	235	0.02
63	2.28	123	0.88	177	0.88	237	0.04
64	0.50	124	0.21	178	0.23	238	0.06
65	4.95	125	0.85	179	0.67	239	0.36
65	1.94	126	1.05	180	0.62	240	0.34
67	49.24	127	3.74	181	0.49	241	0.03
68	15.10	128	0.88	182	0.24	246	0.03
69	16.88	129	0.79	183	0.22	247	0.14
71	0.48	130	0.23	184	0.32	248	0.51
72	0.40	131	0.52	185	0.41	249	0.11
73	0.69	132	0.80	186	0.13	250	0.01
74	0.57	133	1.41	187	0.51	251	0.02
75	2.76	134	0.54	188	0.08	253	0.64
76	1.00	135	1.32	189	0.42	254	0.07
77	9.26	136	0.31	190	0.11	264	0.06
78	3.49	137	0.75	191	0.35	266	0.59
79	17.77	138	0.64	192	0.12	268	13.58
81	100.00	139	3.33	193	0.32	269	1.71
82	26.27	140	0.67	194	0.11		

34. 2-(Z-Pentafluoroprop-2-enyl)*cis*-decalin (**52b**)

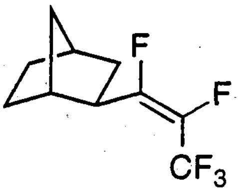


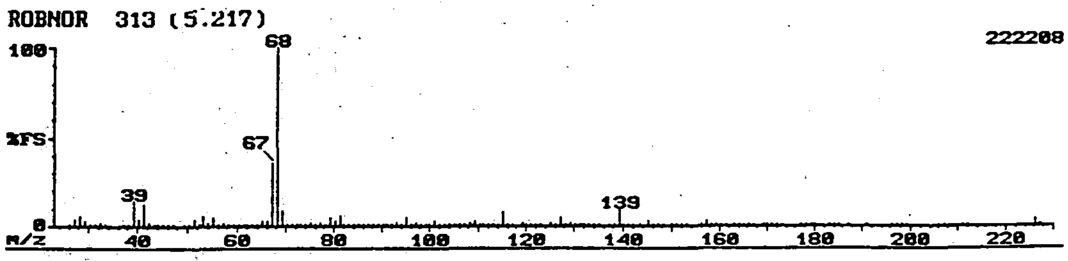


ROBCDEC 599 (9.984) 4177920

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.21	86	1.20	151	5.96	206	2.43
21	0.01	87	1.86	152	2.01	207	1.31
24	1.29	88	3.04	153	7.06	208	0.35
25	3.46	89	4.09	154	6.57	209	0.86
26	12.55	90	2.97	155	0.99	210	0.50
27	32.16	91	11.76	157	2.06	211	1.56
28	18.53	92	6.76	158	4.83	212	0.84
29	24.12	93	17.65	159	2.38	213	0.31
30	0.63	95	98.04	160	0.58	214	0.10
31	3.36	97	5.59	161	1.19	215	0.02
32	0.35	98	1.46	162	0.38	216	0.03
33	1.16	99	2.35	163	1.31	217	0.07
36	2.06	100	2.13	164	1.14	218	0.17
37	4.83	101	6.76	165	2.38	219	0.97
39	77.25	102	3.46	166	1.17	220	0.61
41	100.00	103	3.43	167	1.81	221	0.16
42	11.37	104	1.28	168	0.47	222	0.20
43	8.14	105	1.69	169	1.04	223	0.10
44	1.99	106	3.41	170	0.70	224	0.28
45	1.59	107	12.94	171	2.16	225	1.40
47	4.24	108	18.63	172	0.70	226	2.70
50	10.29	109	12.25	173	0.72	227	2.08
51	15.29	110	8.73	174	0.23	228	0.40
52	9.31	111	3.04	175	0.26	229	0.84
53	30.59	112	3.26	176	0.47	230	0.09
54	44.71	113	5.10	177	2.13	231	0.07
55	45.49	114	3.70	178	1.13	232	0.12
56	10.29	115	7.16	179	2.21	233	1.01
57	7.06	116	1.28	180	1.21	234	0.13
58	1.37	117	1.47	181	1.07	235	0.04
59	3.41	119	6.76	182	0.42	236	0.02
60	0.55	121	9.61	183	0.67	237	0.08
61	1.26	122	1.89	184	0.72	238	0.29
62	1.86	123	2.33	185	0.94	239	2.30
63	2.43	125	3.24	186	0.42	240	1.64
64	4.09	126	2.55	187	0.69	241	0.10
65	14.12	127	7.65	188	0.28	242	0.03
67	72.16	128	2.50	189	0.73	244	0.04
68	49.80	129	3.38	190	0.35	245	0.05
68	18.43	130	0.77	191	1.16	246	0.21
69	29.41	131	0.97	192	0.84	247	0.92
71	0.64	133	14.71	193	0.67	248	6.76
72	0.92	135	67.45	194	0.35	249	0.87
73	1.72	137	2.18	195	0.24	250	0.05
74	1.67	139	7.16	196	0.67	251	0.12
75	4.75	140	1.37	197	2.43	252	0.30
77	20.10	141	2.18	198	1.12	253	4.31
78	9.61	142	0.82	199	0.93	254	0.48
79	29.02	143	1.81	200	0.28	260	0.01
80	21.67	145	5.96	201	0.21	262	0.02
81	62.75	146	0.85	202	0.08	264	0.07
82	51.37	147	2.57	203	0.14	266	0.80
84	0.88	148	0.53	204	0.25	267	1.08
85	2.01	149	0.78	205	1.67	268	11.96

35. *exo*-2-(Z-Pentafluoroprop-2-enyl)norbornane (53)

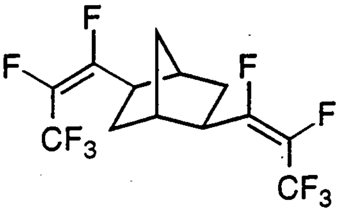


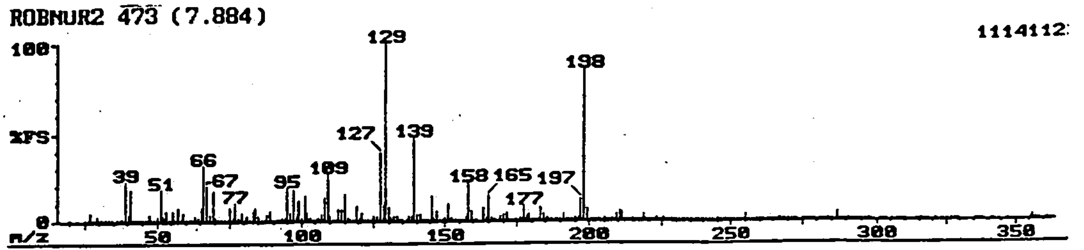


ROBNOR. 313 (5.217) 22220

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.28	69	8.64	108	2.25	152	0.22
27	3.69	70	0.59	109	2.51	153	0.18
28	5.39	71	0.25	110	0.33	156	0.09
29	3.11	72	0.11	111	0.38	157	3.05
30	0.11	73	0.26	112	0.39	158	1.43
31	0.41	74	0.27	113	1.14	159	1.00
32	1.59	75	1.74	114	1.35	160	0.07
33	0.33	76	0.23	115	7.37	161	0.16
37	0.26	77	2.42	116	0.71	163	0.53
38	1.01	78	0.51	117	0.17	164	0.25
39	14.17	79	4.55	119	2.10	165	1.08
40	3.80	80	3.23	120	0.41	166	0.16
41	12.67	81	5.62	121	1.06	167	0.45
42	1.84	82	0.61	122	0.10	169	0.21
43	0.32	83	1.11	123	0.28	170	0.12
44	1.19	84	0.41	125	2.04	171	0.23
45	0.24	85	0.48	126	0.33	172	0.28
46	0.14	86	0.19	127	4.44	173	0.10
47	0.46	87	0.30	128	0.68	177	0.73
49	0.06	88	0.85	129	1.99	178	0.38
50	0.94	89	1.31	130	0.21	179	0.26
51	3.43	90	0.22	131	0.18	180	0.19
52	0.98	91	0.74	132	0.47	183	0.31
53	6.08	92	0.19	133	0.75	184	1.27
54	1.87	93	1.74	134	0.14	185	0.46
55	5.27	94	0.44	135	0.23	187	0.47
56	0.52	95	4.61	137	0.99	191	0.20
57	1.49	96	1.13	138	0.30	196	0.17
58	0.15	97	1.74	139	10.02	197	0.98
59	0.76	98	0.17	140	0.69	198	0.59
60	0.09	99	0.94	141	0.46	199	0.07
61	0.17	100	0.18	142	0.05	206	0.15
62	0.29	101	3.02	143	0.13	207	0.20
63	0.93	102	0.99	145	2.48	211	0.57
64	0.41	103	0.70	146	0.33	212	0.09
65	2.79	104	0.09	147	0.85	226	3.77
66	2.85	105	0.23	148	0.10	227	0.42
67	35.48	106	0.54	150	0.10		
68	100.00	107	0.72	151	1.12		

36. *exo*-2,5-Bis(Z-pentafluoroprop-2-enyl)norbornane (54a)



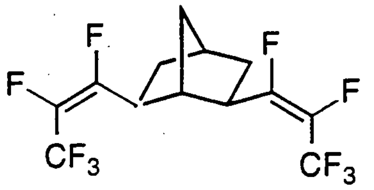


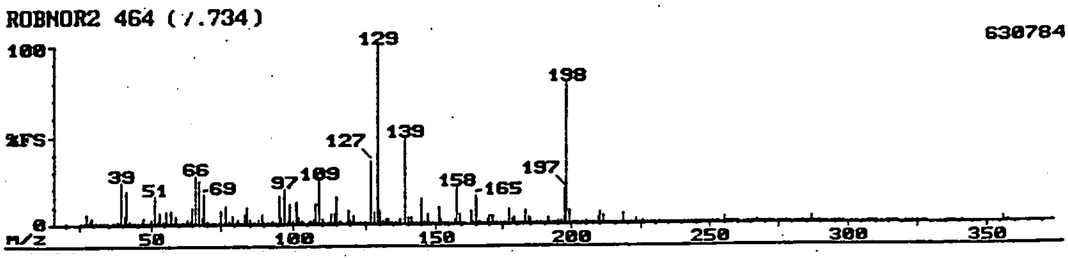
ROBNOR2 473 (7.884) 11141

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	79	5.03	133	3.31	189	1.35
25	0.03	80	1.37	134	0.66	190	0.30
26	0.33	81	2.85	135	0.71	191	4.16
27	5.06	82	1.41	136	0.21	192	1.15
28	0.97	83	5.88	137	2.73	193	0.40
29	2.94	84	8.09	138	2.44	194	0.24
30	0.10	85	2.50	139	47.43	195	2.18
31	0.99	86	0.87	140	3.54	196	1.95
32	0.21	87	0.98	141	4.18	197	12.96
33	1.29	88	3.61	142	0.91	198	85.29
34	0.02	89	6.25	143	1.03	199	6.89
36	0.03	90	0.95	144	0.94	200	0.74
37	0.37	91	1.38	145	14.80	201	0.57
38	1.72	92	0.44	146	1.86	202	0.30
39	23.53	93	1.72	147	6.07	203	0.55
40	4.34	94	1.79	148	0.32	205	2.07
41	18.57	95	19.21	149	0.33	206	0.55
42	1.42	96	5.28	150	1.54	207	0.59
43	0.20	97	18.75	151	10.02	208	0.23
44	0.34	98	2.50	152	2.34	209	4.18
45	0.89	99	11.95	153	1.11	210	6.16
46	0.46	100	2.09	154	0.22	211	4.76
47	4.02	101	14.15	155	0.52	212	0.59
48	0.13	102	4.48	156	1.17	213	0.86
49	0.16	103	1.88	157	3.38	214	0.34
50	2.76	104	0.25	158	21.88	215	0.59
51	18.20	105	0.49	159	5.38	216	0.27
52	2.44	106	1.88	160	0.53	217	1.35
53	6.25	107	3.63	161	0.64	218	4.16
54	1.34	108	13.14	163	8.00	219	0.73
55	5.88	109	26.84	164	2.25	220	0.17
56	1.04	110	3.03	165	14.25	221	0.41
57	8.09	111	0.63	166	1.72	222	0.32
58	0.60	112	1.11	167	0.95	223	2.39
59	4.76	113	6.43	169	3.08	224	0.68
60	0.35	114	6.62	170	4.14	225	2.05
61	0.36	115	15.90	171	5.26	226	0.49
62	0.76	116	1.72	172	1.11	227	1.18
63	3.33	117	0.51	173	0.39	228	0.52
64	1.77	118	0.57	174	0.35	229	1.08
65	8.09	119	8.73	175	0.82	230	0.45
66	31.99	120	2.27	176	1.49	231	1.03
67	20.77	121	5.31	177	9.01	232	0.28
68	3.58	122	0.80	178	2.90	233	0.48
69	17.83	123	0.87	179	3.58	234	0.13
70	2.16	124	0.17	180	0.62	235	0.47
71	1.10	125	2.67	181	0.94	236	0.10
72	0.48	126	2.57	182	1.30	237	0.71
73	0.64	127	38.97	183	7.72	238	0.16
74	1.16	128	8.64	184	3.98	239	0.39
75	8.09	129	100.00	185	2.34	240	0.10
76	1.52	130	7.90	186	0.36	241	0.49
77	10.29	131	1.98	187	1.32	242	0.96
78	2.27	132	3.03	188	0.40	243	0.22

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
245	1.91	267	1.54	291	0.33	321	0.06
246	0.41	268	0.28	292	0.12	323	0.03
247	0.49	269	0.56	293	0.03	325	0.10
248	0.19	270	0.22	294	0.09	327	0.09
249	0.16	271	0.37	295	0.40	328	0.13
251	0.03	272	0.08	296	0.34	329	0.01
251	0.44	273	0.20	297	0.74	336	0.09
252	0.12	275	0.30	298	0.11	336	0.86
253	0.38	276	0.12	301	0.03	337	0.43
255	0.23	277	0.99	302	0.02	338	0.06
255	4.30	278	0.25	303	0.02	341	0.14
256	0.55	279	0.06	305	0.08	342	0.01
257	0.70	281	0.03	307	0.13	347	0.05
258	0.12	282	0.03	308	0.22	356	0.43
259	0.36	283	0.09	309	0.31	356	3.22
260	0.07	284	0.04	310	0.13	357	0.44
261	0.03	285	0.03	314	0.35	358	0.03
263	0.14	287	4.39	315	0.16	361	0.02
264	0.11	288	0.56	316	0.12		
265	0.15	289	0.38	317	1.03		
267	0.13	290	0.12	318	0.13		

37. *exo*-2,6-Bis(Z-pentafluoroprop-2-enyl)norbornane (54b)

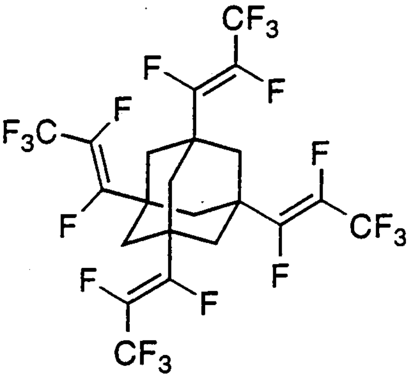


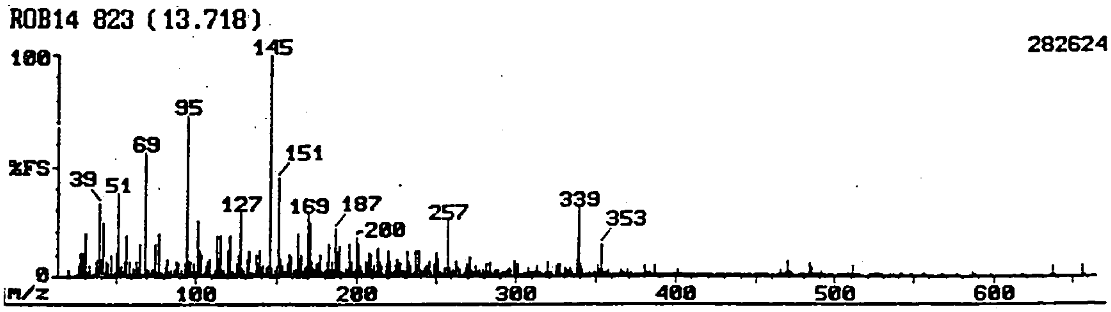


ROBNOR2 464 (7.734) 630

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.05	79	4.91	133	3.00	189	1.33
25	0.03	80	1.32	134	1.01	190	0.49
26	0.54	81	2.64	135	0.70	191	3.61
27	5.97	82	1.22	136	0.19	192	1.15
28	1.90	83	5.52	137	2.60	193	0.37
29	3.94	84	10.06	139	48.70	194	0.23
30	0.12	85	2.76	140	3.57	195	2.22
31	1.10	86	0.76	141	4.02	196	2.14
32	0.48	87	0.81	142	0.92	197	19.97
33	1.38	88	3.00	143	1.00	198	79.87
34	0.03	89	5.60	144	0.66	199	8.08
36	0.04	90	0.83	145	14.29	200	0.81
37	0.36	91	1.25	146	1.78	201	0.61
38	1.72	92	0.21	147	6.17	202	0.31
39	24.51	93	1.54	148	0.69	203	0.61
40	4.55	94	1.18	149	0.30	204	0.23
41	19.16	95	16.88	150	1.27	205	1.86
42	1.52	96	4.30	151	9.38	206	0.50
43	0.23	97	20.45	152	2.64	207	0.59
44	0.57	98	2.17	153	1.13	208	0.41
45	0.90	99	11.20	154	0.14	209	4.22
46	0.46	100	1.51	155	0.57	210	7.14
47	4.22	101	12.34	156	1.13	211	5.07
48	0.13	102	4.18	157	2.92	212	0.33
49	0.14	103	1.94	158	21.43	213	0.87
50	2.58	104	0.16	159	5.56	214	0.35
51	16.72	105	0.22	160	0.29	215	0.61
52	2.31	106	1.67	161	0.70	216	0.23
53	6.45	107	3.04	163	7.75	217	1.22
54	1.82	108	11.36	164	2.41	218	5.52
55	8.20	109	25.32	165	16.40	219	0.86
56	1.07	110	2.76	166	1.87	220	0.17
57	7.63	111	0.38	167	0.95	221	0.42
58	0.77	112	0.89	168	0.21	222	0.31
59	4.83	113	5.76	169	2.84	223	2.53
60	0.41	114	6.05	170	4.46	224	0.67
61	0.37	115	15.42	171	5.24	225	1.77
62	0.80	116	1.61	172	1.14	226	0.42
63	3.13	117	0.55	173	0.43	227	1.11
64	1.65	118	0.27	174	0.31	228	0.53
65	9.38	119	7.63	175	0.75	229	1.23
66	28.41	120	1.97	176	1.34	230	0.61
67	24.84	121	5.07	177	8.48	231	0.89
68	3.86	122	0.80	178	2.92	232	0.27
69	17.37	123	0.41	179	3.65	233	0.46
70	2.07	124	0.18	180	0.68	234	0.08
71	1.08	125	1.37	181	0.98	235	0.46
72	0.51	126	0.90	182	1.30	236	0.12
73	0.68	127	36.20	183	8.12	237	0.56
74	0.83	128	6.57	184	4.22	238	0.13
75	7.95	129	100.00	185	2.45	239	0.39
76	1.19	130	7.95	186	0.35	240	0.09
77	10.39	131	1.81	187	1.24	241	0.50
78	2.26	132	2.68	188	0.37	242	1.18
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
243	0.29	265	0.14	287	0.22	314	0.31
244	0.17	266	0.05	287	3.98	315	0.16
245	1.43	267	1.46	288	0.61	316	0.11
246	0.33	268	0.24	289	0.36	317	0.79
247	0.41	269	0.44	290	0.07	318	0.13
248	0.18	270	0.20	291	0.28	321	0.04
249	0.09	271	0.33	292	0.10	323	0.06
251	0.03	272	0.08	294	0.05	325	0.18
251	0.40	273	0.17	295	0.36	327	0.09
252	0.09	275	0.25	296	0.30	328	0.13
253	0.34	276	0.17	297	0.63	336	0.76
255	3.94	277	0.78	298	0.10	337	0.36
256	0.51	278	0.19	301	0.04	338	0.07
257	0.60	279	0.03	303	0.04	341	0.09
258	0.12	281	0.04	305	0.08	356	2.88
259	0.36	282	0.04	307	0.16	357	0.39
260	0.08	283	0.08	308	0.17	358	0.04
263	0.13	284	0.06	309	0.26		
264	0.10	285	0.09	310	0.13		

38. 1,3,5,7-Tetrakis(E-pentafluoro-2-propenyl)adamantane (55)

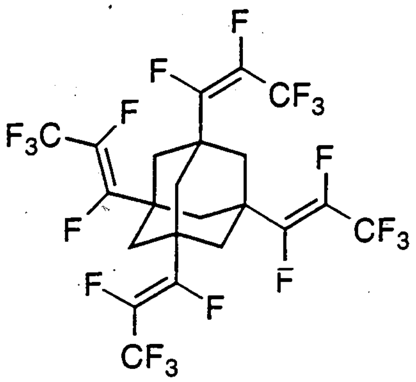


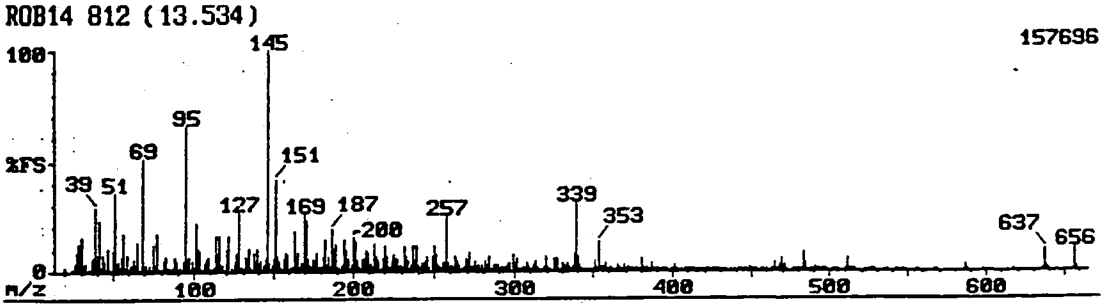


ROB14 823 (13.718) 28262

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	2.99	78	1.63	132	6.52	186	2.67	240	2.54	294	2.56	348	0.46	402	0.09	460	0.07
24	0.00	79	1.47	133	11.59	187	21.29	241	1.72	295	4.00	349	1.56	403	0.52	461	0.00
25	1.34	80	1.34	134	2.15	188	10.87	242	3.07	296	1.37	350	1.05	404	0.11	463	0.72
26	5.05	81	5.19	135	2.22	189	13.86	243	4.42	297	3.37	351	4.44	405	0.33	464	0.46
27	10.87	82	2.45	136	0.95	190	2.42	244	4.76	298	0.71	352	2.55	406	0.10	465	3.03
28	10.69	83	7.97	137	9.60	191	1.01	245	6.97	299	6.97	353	14.31	407	0.40	466	0.65
29	9.23	84	2.25	138	5.53	192	1.01	246	1.92	300	3.78	354	2.36	408	0.19	467	0.27
30	0.23	85	2.67	139	11.23	193	3.56	247	1.26	301	5.41	355	2.42	409	0.76	468	1.92
31	19.20	86	1.00	140	3.89	194	3.37	248	0.34	302	1.13	356	1.86	410	0.30	469	6.61
32	2.22	87	3.00	141	4.82	195	14.76	249	5.98	303	1.06	357	3.31	411	0.40	470	2.22
33	4.37	88	7.25	142	1.00	196	10.60	250	10.07	304	0.44	358	0.91	412	0.17	471	2.36
35	0.33	89	5.43	143	3.55	197	6.34	251	7.43	305	1.74	359	1.25	413	0.65	472	0.59
36	0.96	90	1.14	144	5.23	198	1.60	252	2.36	306	0.52	360	0.73	414	0.13	473	0.35
37	6.43	91	2.67	145	100.00	199	3.31	253	2.26	307	3.99	361	1.31	415	1.14	475	0.10
38	0.24	92	0.95	146	7.70	200	17.12	254	0.79	308	1.56	362	1.18	416	0.20	477	0.35
39	33.33	93	5.77	147	3.99	201	14.95	255	4.26	309	2.06	363	1.10	417	0.12	478	0.17
40	0.24	94	3.42	148	0.91	202	5.07	256	4.10	310	0.66	364	0.63	418	0.5	479	0.03
41	24.28	95	72.83	149	2.55	203	2.28	257	25.36	311	2.29	365	2.54	419	0.61	480	0.27
42	1.83	96	6.34	150	5.12	204	1.05	258	3.96	312	3.37	366	1.74	420	0.18	482	1.42
43	6.61	97	7.16	151	44.20	205	6.61	259	2.00	313	4.62	367	0.98	421	0.57	483	5.00
44	6.16	98	1.63	152	7.34	206	5.71	260	1.72	314	1.95	368	0.25	422	0.34	484	3.49
45	5.39	99	6.25	153	5.32	207	9.63	261	2.67	315	1.95	369	2.05	423	0.32	485	1.45
46	1.15	100	2.31	154	1.70	208	10.24	262	1.03	316	0.2	370	1.10	425	0.04	486	0.23
47	10.14	101	25.36	155	1.99	209	10.05	263	6.00	317	0.07	371	1.47	426	0.31	487	0.10
48	0.86	102	11.60	156	5.07	210	2.92	264	4.21	318	1.30	372	0.40	427	0.45	488	0.20
49	1.52	103	10.14	157	9.51	211	4.62	265	2.51	319	6.00	373	0.52	428	0.10	489	0.34
50	10.42	104	1.18	158	9.33	212	1.37	266	0.70	320	2.33	374	0.12	429	0.75	490	0.07
51	38.04	105	1.77	159	9.06	213	12.95	267	1.30	321	2.24	375	0.74	430	0.22	491	1.92
52	3.96	106	4.57	160	0.69	214	6.43	268	1.95	322	0.76	376	0.73	431	0.02	492	0.46
53	5.30	107	6.61	161	2.51	215	4.51	269	5.00	323	1.25	377	0.00	432	0.25	493	0.13
54	1.72	108	4.78	162	2.47	216	0.99	270	4.05	324	0.39	378	0.36	433	0.45	495	0.20
55	7.16	109	7.00	163	19.29	217	1.35	271	0.42	325	5.00	379	1.21	434	0.13	496	0.16
56	5.64	110	1.81	164	7.34	218	5.98	272	0.79	326	5.00	380	4.78	435	0.00	497	0.92
57	10.21	111	1.10	165	9.33	219	11.32	273	2.45	327	5.43	381	1.92	437	0.36	498	0.40
58	1.25	112	2.74	166	1.60	220	3.99	274	1.60	328	1.22	382	1.05	438	0.17	499	0.10
59	7.25	113	10.40	167	3.94	221	6.52	275	5.07	329	0.38	383	2.00	439	0.46	502	0.15
60	0.65	114	0.15	168	4.46	222	2.26	276	1.99	330	3.60	384	0.55	440	0.13	503	0.00
61	3.58	115	10.12	169	28.62	223	2.38	277	2.74	331	3.10	385	0.40	441	0.50	505	0.19
62	2.90	116	3.33	170	0.33	224	5.12	278	0.52	332	2.06	386	0.40	442	0.22	507	0.25
63	6.34	117	2.90	171	23.91	225	7.79	279	3.13	333	3.78	387	4.60	443	0.30	508	0.00
64	3.44	118	0.85	172	6.43	226	5.00	280	1.74	334	1.01	388	0.76	444	0.11	509	0.44
65	14.06	119	11.07	173	3.44	227	5.00	281	5.40	335	1.74	389	0.52	445	1.12	510	0.27
66	1.44	120	3.49	174	2.47	228	1.55	282	2.15	336	0.53	390	0.16	446	0.20	511	4.62
67	0.91	121	10.75	175	6.25	229	2.60	283	6.52	337	1.45	391	0.38	447	0.31	512	0.77
68	4.64	122	2.06	176	6.07	230	1.79	284	1.74	338	7.34	392	0.19	449	1.40	513	0.11
69	56.16	123	1.99	177	9.42	231	12.59	285	1.18	339	30.30	393	0.50	450	0.07	514	0.00
70	3.10	124	1.05	178	1.95	232	6.34	286	0.96	340	6.25	394	0.37	451	1.21	515	0.23
71	2.74	125	5.57	179	1.77	233	4.57	287	3.31	341	2.79	395	1.03	452	0.37	521	0.09
72	0.82	126	9.07	180	2.51	234	1.24	288	2.03	342	0.53	396	0.46	453	0.34	522	0.14
73	2.81	127	28.35	181	6.79	235	1.10	289	2.69	343	1.03	397	0.63	454	0.09	523	0.17
74	3.40	128	3.62	182	14.76	236	2.36	290	0.51	344	1.17	398	0.27	455	0.00	525	0.70
75	15.04	129	2.49	183	9.60	237	11.60	291	1.74	345	1.47	399	1.10	456	0.31	526	0.36
76	2.40	130	0.59	184	2.03	238	5.00	292	1.63	346	0.90	400	1.05	457	0.45	527	0.21
77	19.66	131	7.52	185	7.07	239	11.59	293	2.29	347	0.91	401	3.00	459	0.30	528	0.13
529	0.09	541	0.11	549	0.06	557	0.03	587	1.52	607	0.20	637	5.32	657	0.75		
535	0.10	542	0.25	555	0.79	568	0.14	588	0.29	618	0.10	638	0.93				
537	0.12	547	0.10	556	0.17	577	0.07	597	0.13	626	0.09	656	4.05				

39. 1-(Z-Pentafluoro-2-propenyl)-3,5,7-tris(E-pentafluoro-2-propenyl)adamantane (55a)

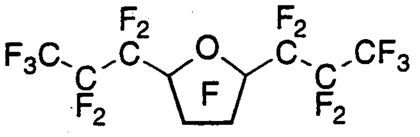


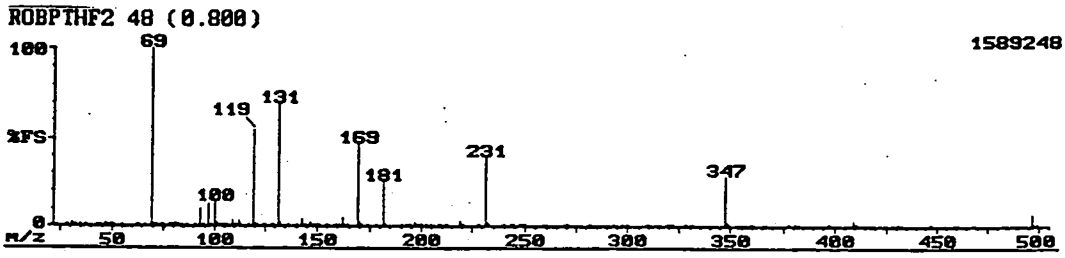


ROB14 812 (13.534) 157636

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	2.33	79	1.33	133	10.55	187	19.64	241	1.59	295	3.94	349	1.44	407	0.44	478	0.25
24	0.43	80	1.09	134	1.72	188	10.27	242	3.61	296	1.35	350	0.88	408	0.18	479	0.09
25	1.20	81	4.55	135	1.97	189	12.99	243	4.02	297	3.81	351	4.42	409	0.61	480	0.30
26	4.30	82	2.16	136	0.55	190	2.26	244	4.55	298	0.72	352	2.33	410	0.12	481	0.15
27	0.89	83	7.22	137	0.81	191	1.49	245	6.94	299	7.31	353	13.64	411	0.42	482	0.77
28	12.66	84	2.00	138	4.87	192	0.59	246	1.77	300	3.86	354	2.41	412	0.14	483	0.55
29	7.91	85	2.13	139	10.71	193	3.25	247	1.20	301	5.40	355	2.34	413	0.60	484	4.10
31	15.10	86	0.94	140	3.57	194	3.04	248	0.49	302	1.03	356	2.10	414	0.44	485	1.09
32	2.54	87	2.37	141	4.42	195	14.29	249	6.41	303	1.03	357	3.69	415	1.32	486	0.26
33	3.73	88	6.37	142	0.91	196	9.74	250	11.85	304	0.41	358	0.66	416	0.28	488	0.41
35	0.38	89	4.87	143	3.00	197	5.93	251	7.83	305	1.73	359	1.25	417	0.18	489	0.62
36	0.38	90	1.18	144	6.21	198	1.43	252	2.44	306	0.55	360	1.01	418	0.46	491	2.40
37	5.80	91	2.34	145	100.00	199	2.72	253	2.14	307	3.77	361	1.55	419	0.56	492	0.61
38	7.22	92	0.60	146	7.63	200	15.23	254	0.85	308	1.43	362	1.29	420	0.10	493	0.24
39	29.86	93	4.79	147	3.69	201	13.00	255	4.14	309	1.95	363	1.30	421	0.56	495	0.32
40	7.67	94	2.96	148	0.57	202	4.91	256	4.34	310	1.31	364	0.31	422	0.44	496	0.14
41	23.05	95	66.23	149	2.49	203	2.21	257	24.84	311	1.31	365	2.76	423	0.44	497	1.10
42	1.82	96	6.05	150	5.72	204	0.78	258	4.02	312	3.00	366	1.65	425	0.71	498	0.59
43	6.25	97	6.37	151	42.21	205	6.17	259	2.18	313	4.63	367	0.94	426	0.23	502	0.24
44	7.91	98	1.41	152	7.14	206	5.40	260	1.59	314	1.89	368	0.34	427	0.47	503	0.11
45	5.15	99	4.99	153	4.99	207	0.89	261	2.58	315	1.27	369	2.00	428	0.27	505	0.14
46	1.16	100	1.03	154	1.53	208	9.42	262	2.24	316	0.43	370	0.76	429	0.52	509	0.30
47	10.71	101	22.73	155	1.44	209	9.05	263	6.74	317	0.65	371	1.54	431	0.78	510	0.23
48	0.72	102	10.39	156	5.72	210	2.64	264	4.67	318	1.82	372	0.38	432	0.15	511	6.13
49	1.38	103	9.38	157	0.85	211	4.14	265	2.60	319	7.02	373	0.61	433	0.47	512	1.11
50	9.70	104	0.95	158	0.85	212	1.92	266	0.67	320	2.32	374	0.38	434	0.10	513	0.15
51	35.04	105	1.42	159	7.95	213	12.18	267	1.31	321	1.19	375	0.94	437	0.27	514	0.13
52	3.94	106	3.98	160	0.79	214	6.45	268	2.34	322	0.72	376	0.65	439	0.43	515	0.22
53	5.03	107	6.13	161	2.09	215	4.75	269	6.01	323	1.20	377	0.97	441	0.56	523	0.18
54	1.61	108	4.26	162	2.22	216	0.94	270	4.79	324	0.45	378	0.42	442	0.24	525	1.21
55	7.10	109	6.82	163	10.51	217	1.11	271	0.52	325	5.44	379	1.20	443	0.20	526	0.20
56	4.79	110	0.90	164	7.02	218	5.93	272	1.32	326	6.05	380	5.00	445	1.09	527	0.19
57	17.53	111	0.85	165	9.05	219	11.20	273	2.21	327	5.44	381	2.11	446	0.33	528	0.16
58	1.65	112	2.30	166	1.66	220	3.94	274	1.40	328	0.99	382	0.95	447	0.34	535	0.25
59	7.51	113	16.80	167	3.57	221	6.41	275	4.91	329	0.37	383	2.01	449	1.07	537	0.16
60	0.77	114	7.31	168	4.06	222	2.16	276	1.97	330	4.18	384	0.65	450	0.81	542	0.40
61	2.96	115	16.56	169	25.81	223	2.21	277	2.59	331	2.64	385	0.56	451	1.31	543	0.12
62	2.40	116	2.92	170	0.04	224	4.30	278	0.92	332	2.22	387	3.81	452	0.42	547	0.18
63	5.60	117	2.44	171	23.05	225	7.79	279	1.21	333	3.94	388	0.70	453	0.40	555	1.29
64	2.84	118	0.53	172	5.64	226	5.76	280	0.66	334	1.14	389	0.44	456	0.24	556	0.28
65	13.96	119	10.39	173	3.04	227	5.60	281	5.24	335	1.70	390	0.27	457	0.14	557	0.95
66	1.39	120	3.25	174	1.00	228	1.50	282	2.00	336	0.59	391	0.30	459	0.28	558	0.16
67	0.52	121	16.72	175	5.64	229	2.49	283	6.57	337	1.56	393	0.46	463	0.74	587	2.72
68	4.55	122	1.13	176	5.32	230	1.72	284	1.65	338	7.35	394	0.23	464	0.46	588	0.46
69	51.30	123	1.57	177	0.56	231	11.20	285	1.02	339	31.49	395	1.00	465	3.73	597	0.15
70	2.60	124	0.81	178	1.76	232	7.02	286	0.84	340	6.74	396	0.37	466	0.79	617	0.28
71	2.64	125	4.79	179	1.54	233	4.71	287	2.96	341	2.90	397	0.07	467	0.39	635	0.26
72	0.36	126	0.81	180	1.73	234	1.39	288	2.64	342	0.86	398	0.19	468	3.29	637	9.52
73	2.64	127	26.95	181	6.57	235	1.15	289	2.00	343	0.81	399	1.22	469	6.29	638	2.00
74	1.02	128	1.55	182	14.12	236	2.51	290	0.57	344	1.22	400	0.94	470	2.14	639	0.21
75	12.82	129	2.11	183	9.05	237	11.53	291	1.66	345	1.34	401	3.17	471	2.60	656	10.27
76	2.60	130	1.10	184	2.60	238	4.95	292	1.67	346	0.94	402	0.91	472	0.67	657	1.46
77	17.86	131	7.06	185	6.66	239	11.63	293	2.09	347	0.95	403	0.51	473	0.37		
78	1.44	132	6.01	186	2.25	240	2.47	294	2.17	348	0.57	405	0.26	477	0.32		

40. Perfluoro-2,5-dipropyltetrahydrofuran (59)

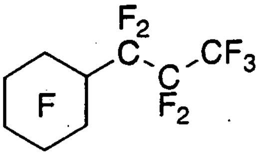


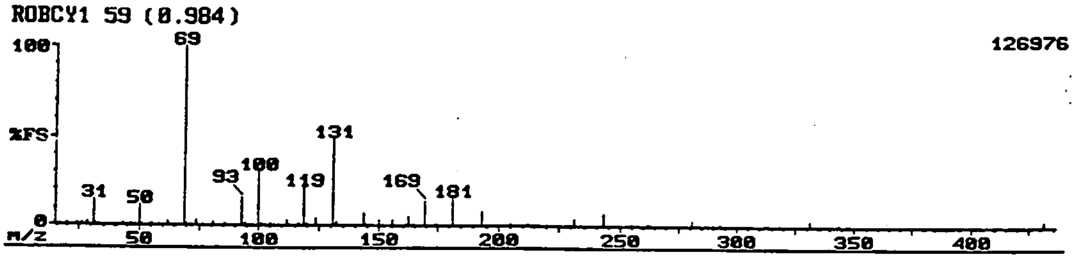


ROBPTHF2 48 (0.800) 1589248

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	0.08	101	2.19	170	1.50	270	0.02
31	2.00	102	0.03	171	0.20	271	0.15
32	0.04	103	1.27	174	0.08	281	0.73
35	0.30	105	0.39	178	0.07	282	0.03
37	0.11	106	0.02	181	25.26	293	0.04
43	0.03	109	2.46	182	1.01	297	0.06
44	0.02	110	0.05	190	0.03	300	0.14
47	2.40	112	2.98	193	0.87	309	0.51
48	0.03	113	0.13	194	0.05	310	0.04
49	0.10	117	0.08	197	2.38	319	1.16
50	1.43	119	54.12	198	0.10	320	0.07
51	0.08	120	1.26	200	0.02	321	0.13
55	0.07	121	0.04	202	0.02	328	0.02
62	0.31	124	0.94	205	0.02	331	0.09
63	0.01	125	0.06	209	0.89	347	28.35
66	0.31	128	0.81	210	0.03	348	1.98
69	100.00	129	0.05	212	0.39	349	0.14
70	1.26	131	69.07	213	0.03	359	1.18
71	0.16	132	2.34	219	2.69	360	0.11
72	0.04	136	0.03	220	0.12	378	0.09
74	0.61	140	0.11	221	0.18	381	0.03
75	0.03	143	3.56	228	0.03	397	0.24
78	0.55	144	0.17	231	39.18	398	0.01
79	0.01	147	2.26	232	2.01	409	2.96
81	1.79	148	0.09	233	0.06	410	0.29
82	0.14	150	1.01	240	0.08	411	0.01
84	0.07	151	0.04	243	0.19	431	0.03
86	0.06	155	0.25	244	0.02	447	0.03
90	0.05	159	1.05	247	0.62	459	0.02
93	9.34	160	0.05	248	0.03	497	6.44
94	0.33	162	4.38	250	0.15	498	0.71
97	12.69	163	0.20	259	0.43	499	0.05
98	0.29	164	0.02	260	0.03		
100	13.34	169	46.13	269	0.34		

41. Perfluoropropylcyclohexane (**60**)

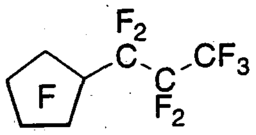


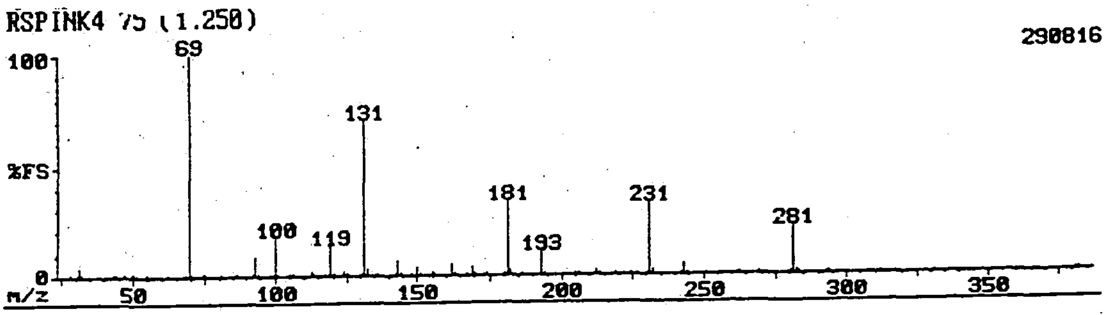


ROBCY1 59 (0.984) 126976

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.26	70	1.17	124	4.03	212	1.45
24	0.16	74	3.13	131	48.99	231	3.78
26	0.27	81	1.81	132	1.58	243	6.70
28	1.46	86	0.29	143	6.60	255	0.34
31	14.92	93	15.93	144	0.31	262	0.58
32	0.59	94	0.45	150	2.92	281	2.52
43	0.95	100	30.24	155	3.23	293	1.32
47	0.83	101	0.70	162	5.29	331	2.73
50	12.10	105	0.84	169	13.91	343	0.54
51	0.45	112	3.10	174	0.79	431	2.68
55	0.88	117	0.59	181	15.32		
62	1.74	119	21.77	193	7.41		
69	100.00	120	0.35	205	0.60		

42. Perfluoropropylcyclopentane (61)

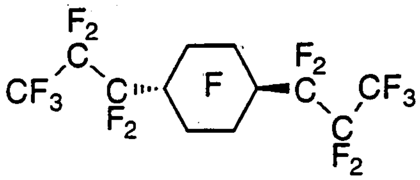


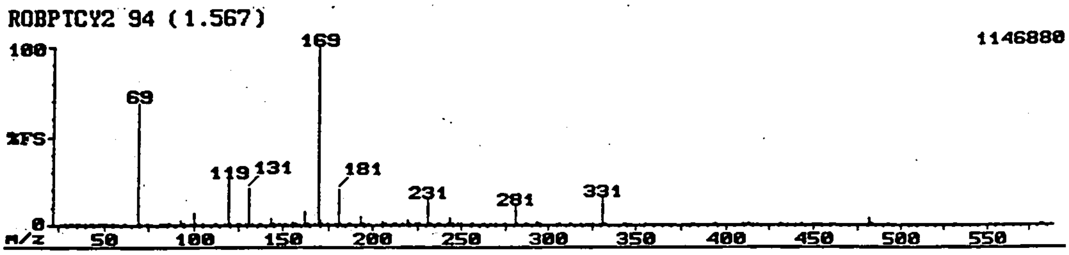


RSPINK4 75 (1.250) 290816

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	0.39	94	0.34	144	0.36	213	0.13
30	0.05	98	0.10	148	0.06	219	0.57
31	4.01	99	0.08	150	3.54	224	0.13
32	0.31	100	17.43	151	0.16	230	0.10
43	0.06	101	0.43	155	2.42	231	32.04
44	0.09	105	0.57	156	0.16	232	1.91
47	0.07	106	0.07	162	5.30	242	0.04
49	0.04	112	1.67	163	0.28	243	5.00
50	1.58	113	0.12	167	0.10	244	0.36
51	0.11	117	0.72	169	3.87	262	0.34
55	0.22	118	0.06	170	0.15	269	0.06
62	0.30	119	13.73	174	0.37	280	0.17
68	0.27	120	0.35	180	0.07	281	21.21
69	100.00	124	2.11	181	33.10	282	1.47
70	1.21	125	0.12	182	1.52	283	0.06
74	1.01	130	0.25	186	0.22	293	1.09
75	0.08	131	70.07	193	10.48	294	0.10
81	0.86	132	2.53	194	0.62	312	0.21
86	0.18	136	0.17	205	0.93	331	0.33
92	0.04	142	0.04	206	0.08	381	0.83
93	8.98	143	7.22	212	1.89	382	0.11

43. *trans*-Perfluoro-1,4-dipropylcyclohexane (62a)

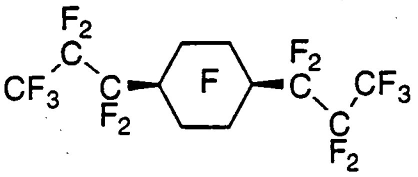


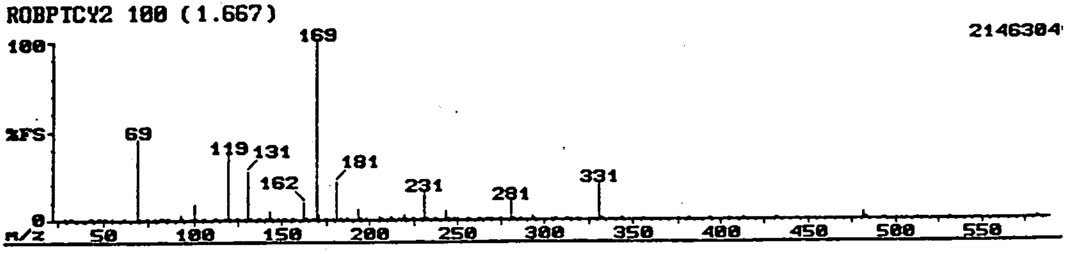


ROBPTCY2 94 (1.567) 1146880

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	0.12	117	0.36	194	0.28	286	0.03
31	0.66	119	26.07	195	0.03	287	0.01
32	0.09	120	0.63	198	0.05	293	1.63
35	0.02	124	0.83	205	1.72	294	0.13
36	0.02	125	0.03	206	0.12	295	0.05
40	0.01	126	0.04	207	0.09	305	0.26
43	0.01	129	0.02	212	1.41	306	0.03
44	0.18	131	21.25	213	0.18	312	0.50
47	0.07	132	0.74	217	0.32	313	0.03
48	0.02	136	0.09	219	3.04	319	0.07
49	0.02	137	0.04	220	0.13	325	0.03
50	0.71	143	3.62	224	0.26	331	15.98
51	0.28	144	0.26	225	0.25	332	1.19
55	0.04	145	0.06	226	0.02	333	0.05
62	0.07	148	0.08	231	14.37	343	0.27
69	68.57	150	0.68	232	0.78	344	0.03
70	0.85	151	0.16	233	0.02	355	0.03
74	0.18	155	1.85	236	0.24	381	0.40
75	0.06	156	0.11	237	0.03	382	0.03
81	0.28	157	0.05	243	0.19	393	0.45
82	0.04	162	7.95	243	3.62	394	0.04
83	0.14	163	0.56	244	0.26	409	0.02
85	0.09	164	0.03	245	0.03	412	0.17
86	0.02	167	0.19	248	0.02	413	0.02
87	0.02	169	100.00	250	0.03	431	0.18
93	0.07	170	3.28	255	0.75	443	0.08
93	3.08	171	0.04	256	0.07	481	3.77
94	0.12	174	0.33	262	0.26	482	0.38
95	0.05	175	0.12	263	0.10	483	0.02
98	0.02	179	0.06	267	0.06	493	0.06
100	7.05	181	20.63	269	0.14	531	0.02
101	0.19	182	0.89	274	0.04	581	0.55
105	0.12	186	0.63	275	0.03	582	0.07
112	0.92	187	0.06	281	10.27		
113	0.31	193	4.98	282	0.61		

44. *cis*-Perfluoro-1,4-dipropylcyclohexane (62b)

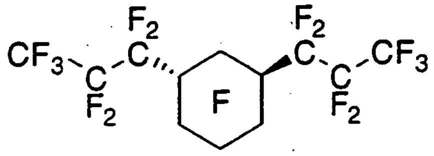


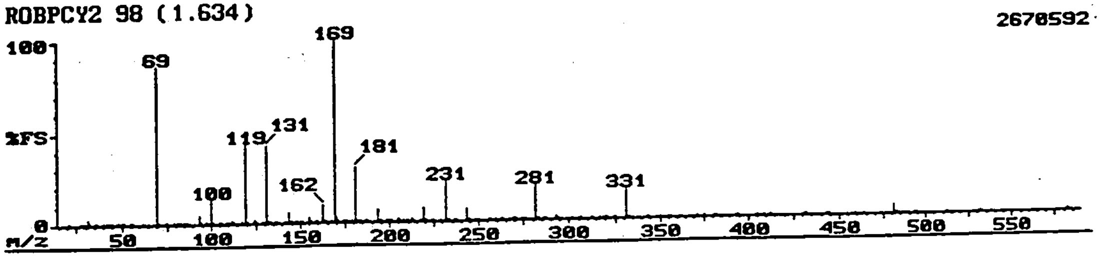


ROBPTCY2 100 (1.667) 2146304

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	0.13	125	0.03	207	0.02	293	1.99
31	0.89	129	0.03	210	0.01	294	0.14
32	0.05	131	27.48	212	1.69	305	0.32
43	0.01	132	0.92	213	0.10	306	0.03
44	0.06	136	0.12	217	0.37	312	0.65
47	0.02	137	0.02	218	0.03	313	0.05
48	0.01	141	0.01	219	2.58	319	0.05
50	0.61	143	4.58	220	0.10	331	20.04
51	0.05	144	0.21	224	0.31	332	1.35
55	0.03	148	0.06	225	0.02	333	0.05
62	0.05	150	0.86	229	0.01	343	0.30
69	45.80	151	0.06	231	15.84	344	0.02
70	0.58	155	1.30	232	0.79	355	0.04
74	0.15	156	0.12	233	0.03	375	0.01
75	0.02	162	9.73	236	0.28	381	0.35
79	0.01	163	0.43	237	0.03	382	0.03
81	0.23	154	0.01	243	4.58	393	0.53
82	0.02	167	0.21	244	0.28	394	0.05
83	0.03	169	100.00	245	0.01	405	0.01
85	0.02	170	2.91	248	0.02	412	0.20
86	0.02	174	0.31	250	0.03	413	0.01
93	3.15	175	0.04	255	0.89	431	0.44
94	0.11	179	0.06	256	0.07	432	0.04
98	0.02	181	21.18	262	0.39	443	0.07
100	8.54	182	0.88	263	0.04	481	4.01
101	0.22	183	0.02	267	0.08	482	0.36
105	0.16	186	0.66	268	0.01	483	0.02
106	0.01	187	0.03	269	0.04	493	0.04
112	1.37	193	5.44	274	0.05	512	0.01
113	0.09	194	0.29	275	0.01	531	0.03
117	0.52	195	0.01	281	10.97	581	0.29
119	37.21	198	0.05	282	0.66	582	0.03
120	0.83	205	2.10	283	0.01		
124	1.23	206	0.14	286	0.04		

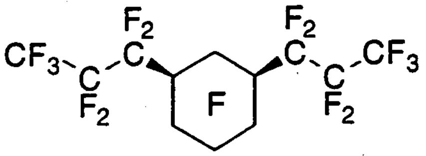
45. *trans*-Perfluoro-1,3-dipropylcyclohexane (**63a**)

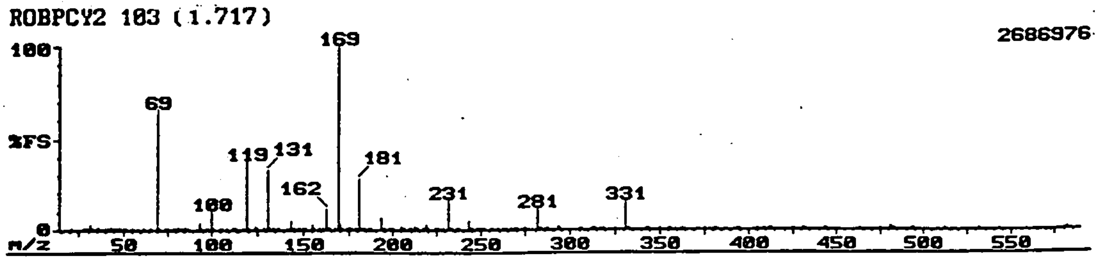




ROBPCY2 98 (1.634) 267059:

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	120	1.04	206	0.15	312	0.42
27	0.01	124	1.67	207	0.02	313	0.08
28	0.70	125	0.08	209	0.01	317	0.01
29	0.02	129	0.03	210	0.01	319	0.20
31	3.11	131	42.33	212	1.74	320	0.01
32	0.20	132	1.43	213	0.14	321	0.01
35	0.01	133	0.03	217	0.46	324	0.01
36	0.01	136	0.17	218	0.03	325	0.01
40	0.02	137	0.04	219	7.32	331	16.87
42	0.01	141	0.02	220	0.31	332	1.17
43	0.03	143	5.87	221	0.02	333	0.05
44	0.40	144	0.27	224	0.36	343	0.46
45	0.01	145	0.01	225	0.06	344	0.04
47	0.08	147	0.02	229	0.02	350	0.03
48	0.01	148	0.11	231	22.24	355	0.07
50	1.33	150	1.05	232	1.16	356	0.01
51	0.10	151	0.09	233	0.04	362	0.01
55	0.06	155	2.88	236	0.36	371	0.01
56	0.01	156	0.17	237	0.04	375	0.02
62	0.10	159	0.04	243	6.48	381	0.99
69	86.50	160	0.01	244	0.41	382	0.08
70	1.16	162	9.51	245	0.02	393	0.70
74	0.28	163	0.48	248	0.02	394	0.07
75	0.04	164	0.02	250	0.07	405	0.03
79	0.02	167	0.28	255	1.05	409	0.04
81	0.45	169	100.00	256	0.08	412	0.17
82	0.01	170	3.34	259	0.01	413	0.02
83	0.03	171	0.09	262	0.22	431	0.42
85	0.02	174	0.46	263	0.06	432	0.04
86	0.02	175	0.06	267	0.11	443	0.14
87	0.00	176	0.00	269	0.65	444	0.01
93	4.56	179	0.08	270	0.04	459	0.02
94	0.17	181	30.06	271	0.01	463	0.02
97	0.01	182	1.25	274	0.07	481	4.52
98	0.03	183	0.04	275	0.03	482	0.43
100	13.80	186	0.81	281	19.17	483	0.03
101	0.32	187	0.07	282	1.26	493	0.08
105	0.22	193	7.02	283	0.03	494	0.01
106	0.01	194	0.39	286	0.04	512	0.01
109	0.03	195	0.01	287	0.01	531	0.03
110	0.01	198	0.06	293	1.49	581	0.52
112	1.58	199	0.02	294	0.11	582	0.07
113	0.15	200	0.01	301	0.01		
117	0.69	201	0.01	305	0.40		
119	44.17	205	2.39	306	0.04		





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ROBPCY2 103 (1.717)                                                    268697(
-----------------+-------------------+-------------------+------------------
 Mass   Rel Int  | Mass   Rel Int    | Mass   Rel Int    | Mass   Rel Int
-----------------+-------------------+-------------------+------------------
   20     0.03   |  120      0.88    |  207      0.03    |  306      0.03
   27     0.01   |  124      1.50    |  209      0.01    |  312      0.48
   28     0.62   |  125      0.10    |  210      0.01    |  313      0.13
   29     0.02   |  129      0.03    |  212      1.90    |  314      0.01
   31     2.67   |  131     32.93    |  213      0.21    |  317      0.01
   32     0.18   |  132      1.08    |  214      0.01    |  319      0.06
   35     0.01   |  133      0.01    |  217      0.41    |  325      0.03
   36     0.01   |  136      0.15    |  218      0.04    |  331     15.24
   40     0.02   |  137      0.06    |  219      3.24    |  332      1.03
   42     0.01   |  141      0.02    |  220      0.14    |  333      0.04
   43     0.03   |  143      5.34    |  224      0.34    |  343      0.27
   44     0.36   |  144      0.39    |  225      0.20    |  344      0.03
   45     0.01   |  145      0.02    |  226      0.02    |  350      0.03
   47     0.05   |  147      0.01    |  229      0.02    |  355      0.05
   48     0.01   |  148      0.11    |  231     16.77    |  356      0.01
   50     1.18   |  150      1.12    |  232      0.87    |  363      0.01
   51     0.21   |  151      0.15    |  233      0.03    |  375      0.07
   55     0.04   |  155      2.55    |  236      0.31    |  381      0.29
   62     0.07   |  156      0.14    |  237      0.05    |  382      0.02
   66     0.01   |  159      0.02    |  243      4.88    |  393      0.40
   69    66.46   |  160      0.01    |  244      0.28    |  394      0.04
   70     0.88   |  162     11.28    |  245      0.01    |  405      0.02
   74     0.22   |  163      0.64    |  248      0.03    |  409      0.00
   75     0.05   |  164      0.02    |  249      0.01    |  412      0.09
   79     0.01   |  167      0.26    |  250      0.08    |  413      0.03
   81     0.31   |  169    100.00    |  251      0.01    |  425      0.01
   82     0.01   |  170      3.35    |  255      0.90    |  431      0.59
   83     0.03   |  171      0.07    |  256      0.07    |  432      0.06
   85     0.02   |  174      0.42    |  259      0.01    |  443      0.07
   86     0.03   |  175      0.11    |  262      0.34    |  444      0.01
   87     0.01   |  176      0.01    |  263      0.14    |  463      0.05
   93     4.15   |  179      0.08    |  264      0.01    |  475      0.01
   94     0.14   |  181     28.20    |  267      0.09    |  481      2.25
   97     0.01   |  182      1.16    |  269      0.13    |  482      0.23
   98     0.03   |  183      0.03    |  270      0.00    |  483      0.01
  100    10.21   |  186      0.85    |  274      0.05    |  493      0.05
  101     0.25   |  187      0.10    |  275      0.06    |  494      0.01
  105     0.18   |  193      6.86    |  281     11.59    |  512      0.01
  106     0.01   |  194      0.36    |  282      0.68    |  531      0.02
  109     0.01   |  195      0.01    |  283      0.03    |  543      0.01
  112     1.43   |  198      0.06    |  286      0.04    |  581      0.23
  113     0.27   |  199      0.01    |  287      0.02    |  582      0.03
  114     0.01   |  200      0.01    |  293      1.64    |
  117     0.55   |  205      2.32    |  294      0.13    |
  119    37.80   |  206      0.15    |  305      0.29    |
-----------------+-------------------+-------------------+------------------
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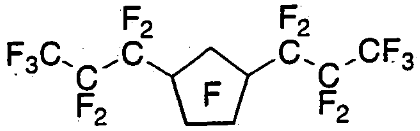
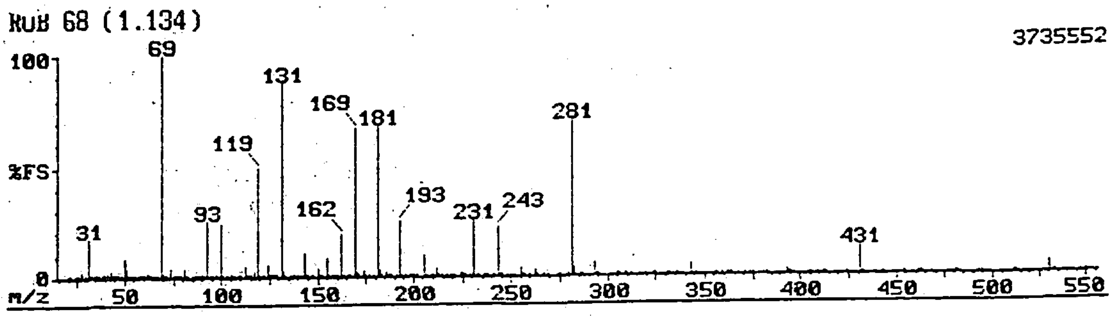
47. Perfluoro-1,x-dipropylcyclopentane x=2,3 (64)



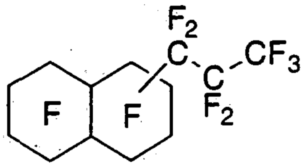


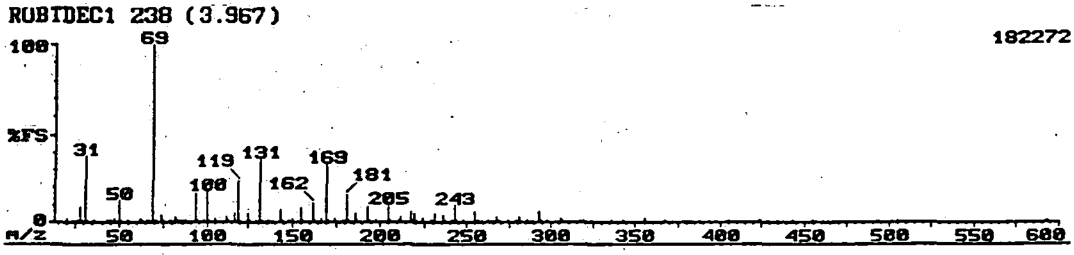
RCB 68 (1.134) 373555

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.35	83	0.05	156	0.46	244	1.32
21	0.00	85	0.26	157	0.02	245	0.05
24	0.11	86	0.61	159	0.07	248	0.03
25	0.09	87	0.10	160	0.02	250	0.54
26	0.25	88	0.03	162	19.52	251	0.04
27	1.21	89	0.02	163	1.01	255	3.70
28	2.47	90	0.03	164	0.04	256	0.26
29	0.49	91	0.07	165	0.01	257	0.01
31	17.00	93	24.78	167	0.50	259	0.01
32	0.43	94	0.94	169	67.11	262	2.69
33	0.05	95	0.07	170	2.03	263	0.27
35	0.02	97	0.08	171	0.04	267	0.16
36	0.08	98	0.28	174	2.49	269	0.06
37	0.15	100	24.67	175	0.40	274	0.37
38	0.22	101	1.15	176	0.03	275	0.09
39	2.25	102	0.04	179	0.10	279	0.01
40	0.32	103	0.02	181	67.98	281	69.74
41	1.78	105	1.67	182	2.66	282	3.56
42	0.34	106	0.26	183	0.07	283	0.11
43	2.88	107	0.03	186	1.95	286	0.08
44	0.51	109	0.07	187	0.20	287	0.02
45	0.10	110	0.03	188	0.02	293	5.87
46	0.03	112	5.26	191	0.01	294	0.39
47	0.33	113	0.86	193	24.78	295	0.02
48	0.06	114	0.04	194	1.27	300	0.01
50	8.33	115	0.02	195	0.04	305	1.19
51	4.06	117	2.60	198	0.07	306	0.09
52	0.11	119	49.12	199	0.03	309	0.01
53	0.16	120	1.04	200	0.06	312	0.09
54	0.04	121	0.03	202	0.01	313	0.03
55	1.32	122	0.02	205	9.43	317	0.03
56	0.30	124	6.06	206	0.58	319	0.03
57	0.66	125	0.39	207	0.03	324	0.09
58	0.10	126	0.03	209	0.03	325	0.03
59	0.05	127	0.04	210	0.01	331	1.36
60	0.03	128	0.02	212	4.00	332	0.09
62	1.86	129	0.06	213	0.29	336	0.01
63	0.27	131	87.28	214	0.02	343	4.80
64	0.07	132	2.99	217	0.73	344	0.36
65	0.07	133	0.07	219	0.77	345	0.02
66	0.09	136	0.64	220	0.04	355	0.18
67	0.10	137	0.23	221	0.03	356	0.02
69	100.00	138	0.02	224	1.67	359	0.01
70	2.41	139	0.01	225	0.29	362	0.02
71	0.13	141	0.02	226	0.02	362	0.18
72	0.04	143	10.86	229	0.02	363	0.03
74	4.25	144	0.58	231	25.55	371	0.01
75	0.97	145	0.04	232	1.22	374	0.01
76	0.06	147	0.03	233	0.04	375	0.01
77	0.09	148	0.21	236	0.63	381	0.61
78	0.03	150	4.06	237	0.08	382	0.05
79	0.18	151	0.36	238	0.01	393	2.11
81	3.70	152	0.02	241	0.01	394	0.18
82	0.57	155	8.44	243	22.81	395	0.01

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int.
405	0.01	431	13.05	463	0.01	531	5.04
405	0.02	432	1.06	481	0.06	532	0.54
409	0.01	433	0.05	482	0.01	533	0.03
409	0.01	443	0.30	493	0.30	547	0.01
412	0.08	444	0.03	494	0.03	550	0.01
413	0.02	455	0.01	512	0.03		
424	0.01	462	0.04	513	0.01		

48. Perfluoro-x-propyldecalin x=1,2,9 (66)

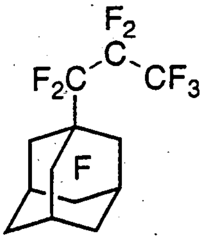


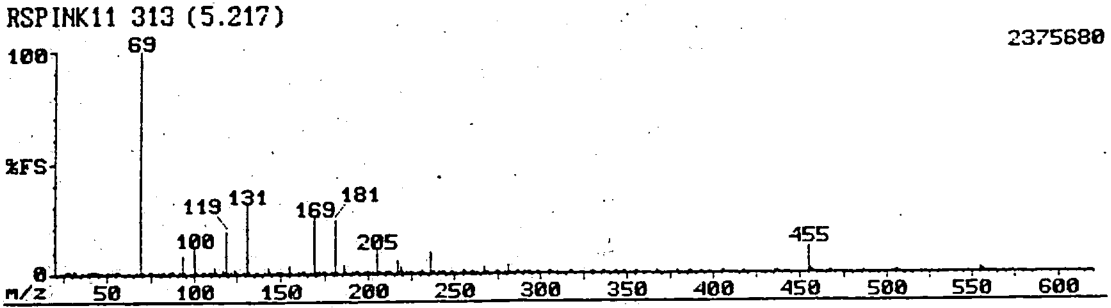


ROBTDEC1 238 (3.967) 182272

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	2.28	86	0.61	170	0.90	262	0.52
24	0.19	87	0.12	174	1.89	267	3.30
26	0.50	93	16.43	179	0.95	268	0.26
27	0.34	94	0.34	181	15.31	274	0.89
28	8.36	98	0.36	182	0.56	279	0.25
29	0.33	100	16.99	186	5.27	281	2.49
31	38.20	101	0.27	187	0.36	286	1.17
32	0.98	105	1.57	193	9.13	293	5.83
36	0.19	112	3.05	194	0.37	294	0.40
43	1.01	113	0.21	198	0.81	298	0.25
44	1.45	117	4.85	205	9.27	305	2.22
45	0.18	119	23.17	206	0.47	306	0.17
47	1.54	120	0.23	210	0.17	317	1.24
50	12.78	124	4.85	212	2.70	319	0.16
51	0.72	125	0.23	217	5.58	324	0.54
55	1.38	129	0.28	218	0.27	336	0.28
62	1.93	131	35.96	219	5.20	343	0.87
63	0.12	132	1.16	220	0.14	355	1.51
66	0.39	136	0.97	224	2.14	367	0.36
67	0.15	143	6.92	229	0.38	405	1.41
69	100.00	144	0.32	231	5.06	424	0.24
70	1.11	148	1.05	236	3.72	443	0.30
71	0.13	150	1.89	237	0.22	455	0.31
74	3.44	155	8.25	241	0.16	493	0.96
75	0.26	156	0.43	243	9.55	505	0.23
79	0.28	162	10.39	244	0.46	593	0.27
81	2.67	163	0.43	248	0.74		
82	0.17	167	1.94	255	6.29		
85	1.15	169	33.29	256	0.36		

49. Perfluoro-1-propyladamantane (67)

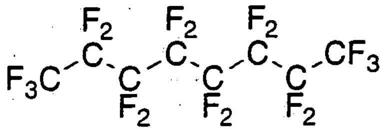


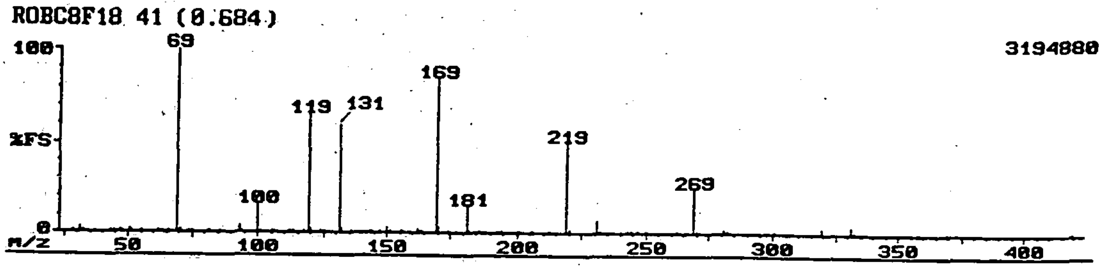


RSPINK11 313 (5.217) 2375680

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.01	113	0.24	205	11.03	299	0.06
27	0.02	117	2.48	206	0.68	305	1.23
28	0.24	118	0.07	207	0.03	306	0.10
29	0.02	119	13.48	210	0.27	310	0.02
31	2.21	120	0.40	211	0.03	317	1.26
32	0.15	122	0.03	212	0.28	318	0.13
36	0.01	124	2.25	213	0.04	329	0.11
39	0.03	125	0.11	217	6.03	330	0.01
40	0.02	129	0.23	218	0.45	331	0.01
41	0.03	131	31.21	219	3.28	336	0.35
42	0.02	132	1.00	220	0.14	337	0.05
43	0.05	136	0.43	222	0.02	343	0.22
44	0.13	137	0.09	224	0.25	344	0.02
45	0.01	141	0.23	225	0.03	348	0.12
47	0.03	143	2.73	229	0.49	349	0.04
50	1.23	144	0.15	230	0.05	355	0.27
51	0.23	148	0.57	231	1.68	356	0.03
53	0.01	149	0.04	232	0.09	367	1.59
55	0.11	150	0.55	236	9.96	368	0.17
56	0.02	151	0.07	237	0.73	379	0.05
57	0.02	153	0.01	238	0.03	386	0.13
62	0.13	155	3.84	241	0.18	387	0.04
63	0.01	156	0.20	243	1.21	393	0.02
67	0.01	160	0.15	244	0.08	398	0.02
69	100.00	162	1.44	248	0.53	405	0.37
70	1.25	163	0.12	249	0.08	406	0.04
74	0.50	167	1.06	255	2.13	417	0.20
75	0.09	169	25.69	256	0.16	418	0.02
79	0.10	170	0.79	260	0.11	436	0.04
81	0.62	172	0.04	261	0.02	437	0.07
82	0.04	174	0.62	263	0.03	455	12.24
85	0.02	175	0.07	267	2.44	456	1.48
86	0.15	179	0.94	268	0.21	457	0.08
87	0.02	181	23.79	269	0.02	467	0.18
91	0.01	182	0.95	274	0.09	468	0.01
93	8.41	186	4.27	275	0.02	486	0.02
94	0.29	187	0.36	279	0.33	505	0.19
98	0.20	191	0.07	281	3.58	506	0.03
100	12.07	193	1.06	282	0.22	555	2.42
101	0.28	194	0.06	286	1.17	556	0.35
105	0.58	198	0.51	287	0.11	557	0.03
106	0.03	199	0.10	291	0.03	574	0.01
109	0.02	200	0.02	293	0.26		
110	0.05	201	0.03	294	0.02		
112	3.06	203	0.02	298	0.37		

50. Perfluorooctane (68a)

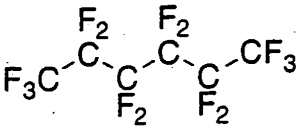


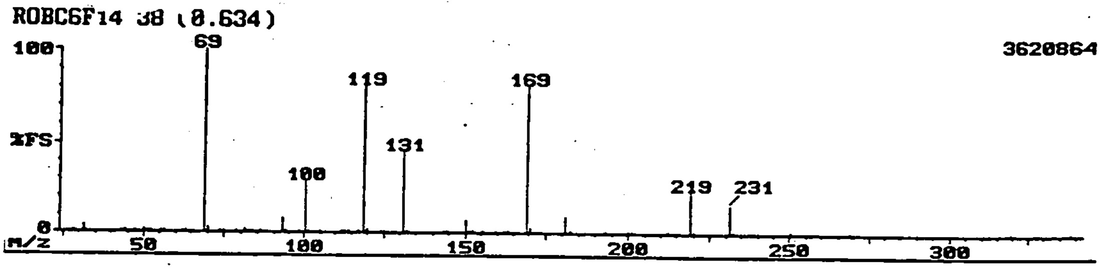


ROBC8F18 41 (0.684) 3194880

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	0.08	93	4.26	150	2.63	220	1.94
31	2.56	94	0.14	151	0.09	231	6.73
32	0.05	100	15.26	155	0.21	232	0.34
43	0.01	101	0.19	156	0.01	243	0.26
44	0.03	105	0.11	162	1.97	244	0.01
47	0.02	106	0.01	163	0.09	247	0.01
50	1.59	112	1.15	169	84.62	250	0.28
51	0.07	113	0.05	170	2.76	262	0.02
55	0.08	117	0.07	174	0.03	269	24.62
62	0.31	119	64.62	181	15.00	270	1.11
63	0.01	120	1.46	182	0.60	281	2.24
66	0.01	124	0.52	186	0.01	282	0.13
69	100.00	125	0.03	193	0.33	300	0.01
70	1.67	131	59.49	194	0.02	319	2.44
74	0.49	132	1.99	200	1.04	331	4.29
75	0.03	136	0.03	201	0.02	332	0.26
81	0.86	143	1.29	205	0.01	369	0.01
82	0.03	144	0.06	212	0.09	419	0.06
86	0.04	147	0.01	219	49.74		

51. Perfluorohexane (69a)

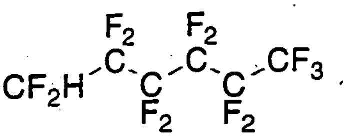


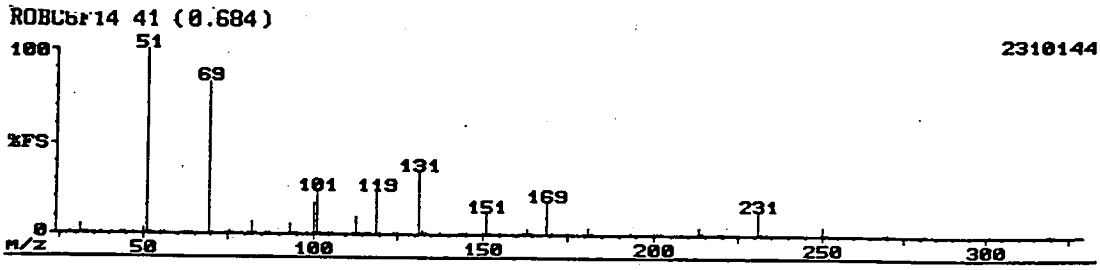


ROBC6F14 38 (0.634) 3620864

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	0.07	75	0.08	119	81.00	181	8.37
31	3.62	79	0.01	120	1.87	182	0.31
32	0.06	81	2.15	124	0.45	193	0.01
43	0.02	82	0.16	125	0.12	200	0.39
44	0.02	83	0.02	131	44.80	201	0.02
47	0.01	86	0.10	132	1.44	212	0.01
50	1.92	93	8.03	143	0.45	219	23.42
51	0.57	94	0.26	144	0.01	220	0.90
52	0.00	98	0.04	150	6.36	231	15.27
55	0.07	100	28.39	151	0.21	232	0.74
56	0.01	101	0.75	152	0.01	250	0.10
62	0.67	105	0.15	155	0.05	269	0.13
63	0.02	112	1.35	162	0.64	319	0.94
69	100.00	113	0.21	163	0.03	338	0.03
70	2.63	114	0.00	169	81.00		
74	0.87	117	0.11	170	2.77		

52. 1H-Perfluorohexane (70)

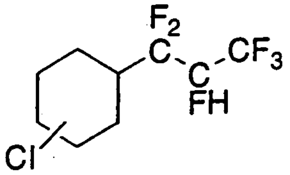


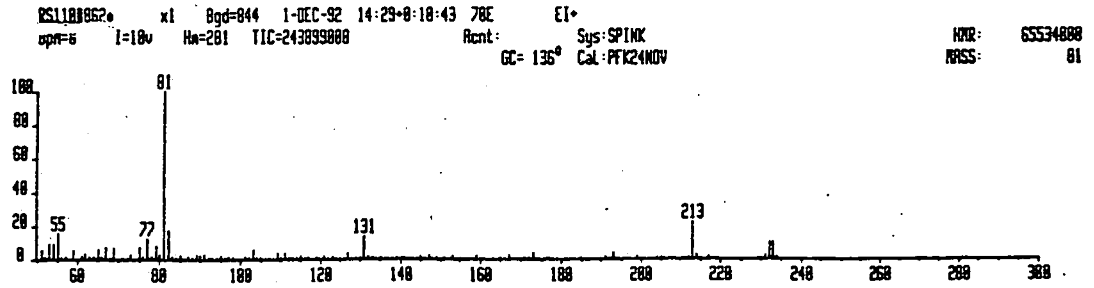


ROBC6F14 41 (0.684) 2310144

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	0.03	79	0.02	120	0.54	182	0.18
31	4.61	81	1.19	124	0.35	193	0.06
32	0.56	82	7.09	125	0.14	200	0.51
33	0.01	83	0.16	131	34.04	201	0.69
37	0.03	86	0.07	132	1.51	202	0.03
43	0.08	87	0.05	133	0.04	213	3.50
44	0.24	93	5.59	137	0.02	214	0.19
47	0.01	94	0.39	143	0.34	219	1.34
50	3.10	95	0.02	144	0.18	220	0.06
51	100.00	98	0.02	145	0.01	231	12.94
52	1.30	100	17.20	150	1.02	232	0.67
55	0.22	101	23.23	151	11.70	233	0.02
56	0.20	102	0.55	152	0.39	250	4.61
62	0.60	105	0.11	155	0.04	251	0.23
63	0.80	106	0.11	162	0.44	269	0.23
64	0.02	112	1.17	163	3.01	270	0.02
69	82.27	113	9.40	164	0.14	281	0.02
70	1.01	114	0.32	169	17.55	301	0.17
74	0.88	116	0.02	170	0.53	319	0.01
75	1.52	117	0.07	175	0.01		
76	0.06	119	22.87	181	3.90		

53. x-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl chloride (x=2-4) (74)





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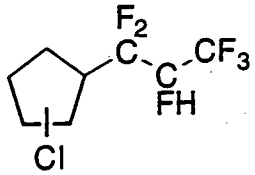
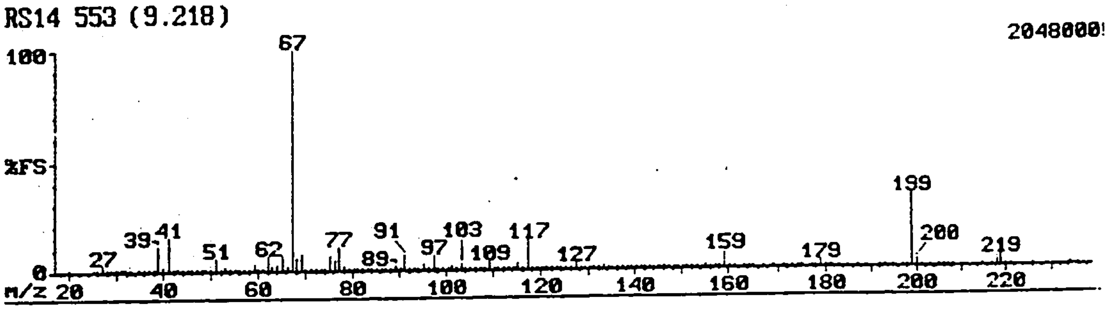
RS110#862*      x1     Bgd=844    1-DEC-92   14:29+0:10:43  70E        EI+        10.1
BpM=0       I=10v     Hm=281    TIC=243899000                 Acnt:          Sys:SPINK
                                                           GC= 136   Cal:PFK24NOV
          Mass      % Base                      Mass      % Base
          48.95       1.33                     128.99      0.78
          49.98       0.78                     130.00      0.38
          50.98       5.34                     131.00     13.27
          52.00       1.31                     132.00      1.02
          53.01       8.80                     132.97      0.70
          54.01       9.08                     134.97      0.46
          55.02      15.09                     138.95      0.40
          56.02       0.80                     140.98      0.85
          56.98       1.14                     144.94      1.14
          58.99       5.04                     146.97      1.65
          61.00       2.14                     148.98      0.35
          61.96       3.07                     150.94      0.85
          62.97       1.52                     152.96      1.16
          63.96       1.39                     158.94      2.24
          64.98       5.46                     164.96      0.35
          66.00       1.44                     166.97      1.62
          67.01       6.85                     168.98      0.31
          68.01       0.47                     170.95      0.45
          68.95       6.50                     171.95      0.64
          70.98       0.89                     172.96      3.44
          72.99       2.34                     176.94      0.45
          74.96       6.74                     184.96      0.73
          75.97       0.99                     190.94      0.98
          76.98      12.13                     192.96      3.39
          77.99       1.07                     198.94      1.31
          79.01       7.86                     203.94      0.56
          79.98       2.85 F                   204.95      0.48
          81.04     100.00 FO                  211.97      0.63 F
          82.03      16.86                     212.97     21.82 F
          83.00       1.32                     213.98      2.15 F
          83.99       0.43                     216.96      1.27
          85.00       1.95                     230.96      1.66
          87.01       1.30                     231.96      9.85 F
          87.97       0.69                     232.97      9.36 F
          88.97       2.30                     233.98      0.90
          89.98       1.86
          90.99       2.79
          91.99       0.46
          92.95       0.38
          94.97       1.81
          95.99       0.49
          97.00       1.03
          98.01       0.40
         100.98       1.51
         101.98       0.37
         103.00       5.23
         104.00       0.78
         105.00       0.78
         108.98       3.42
         109.99       0.78
         111.00       3.50
         112.01       0.96
         112.95       0.84
         113.97       0.38
         114.98       1.65
```

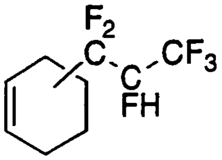
54. x-(1,1,2,3,3,3-hexafluoropropyl)cyclopentyl chloride (x=2,3) (75)

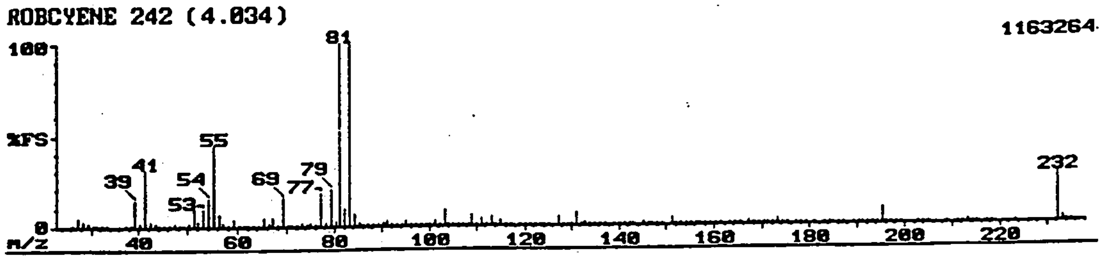




```
RS14 553 (9.218)
---------------
Mass      Rel Int
27          2.3
39         11.5
41         14.9
51          5.7
62          6.9
67        100.0
77         11.0
89          1.8
91          6.9
97          6.9
103         2.2
109         4.1
117        13.8
127         3.4
159         8.0
179         2.3
199        33.3
200         2.5
218         4.1
219         4.8
-------------
```

55. x-(1,1,2,3,3,3-hexafluoropropyl)cyclohex-1-ene (x=2-4) (76)

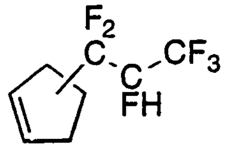


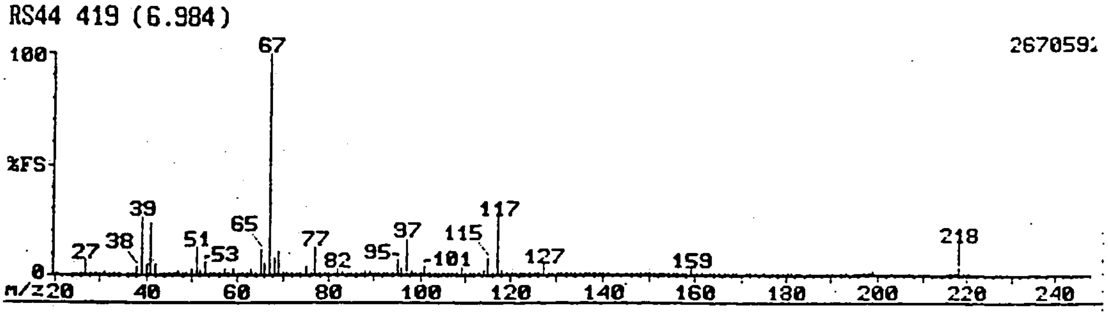


ROBCYENE 242 (4.034) 1163264

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.58	73	2.00	117	0.25	168	0.12
27	5.19	74	0.38	119	0.46	169	0.18
28	2.51	75	1.89	120	0.14	170	0.02
29	2.29	76	0.43	121	1.03	171	0.43
30	0.07	77	18.31	122	0.32	172	0.96
31	0.33	78	2.24	123	1.14	173	2.75
32	0.12	79	20.60	124	0.25	174	0.24
33	0.29	80	3.39	125	0.21	175	0.36
37	0.19	81	100.00	127	4.93	177	0.85
38	0.91	82	9.86	128	0.56	178	0.08
39	14.88	83	100.00	129	0.50	179	0.05
40	2.07	84	7.13	130	0.27	181	0.03
41	31.34	85	2.02	131	6.43	183	0.07
42	2.99	86	0.26	132	0.69	184	0.05
43	1.61	87	0.38	133	1.52	185	0.42
44	0.21	88	0.70	134	0.15	186	0.06
45	0.24	89	1.39	135	0.87	187	0.08
46	0.24	90	1.67	136	0.05	189	0.08
47	1.74	91	3.26	137	0.13	190	0.04
48	0.05	92	0.35	139	0.50	191	0.49
49	0.09	93	1.41	140	0.37	192	0.04
50	1.96	94	0.51	141	1.01	193	1.41
51	9.95	95	2.57	142	0.19	194	0.13
52	2.62	96	1.02	143	0.30	195	8.36
53	10.04	97	1.38	145	1.61	196	0.81
54	15.32	98	0.30	146	0.12	197	0.78
55	44.72	99	0.42	147	1.25	198	0.07
56	6.78	100	0.31	148	0.10	199	0.10
57	2.02	101	3.06	149	0.30	203	0.03
58	0.25	102	1.01	151	3.72	204	0.47
59	3.72	103	8.89	152	0.17	205	0.06
60	0.22	104	0.85	153	1.17	209	0.03
61	0.66	105	0.46	154	0.10	211	0.16
62	0.36	106	0.11	155	0.96	212	0.10
63	1.39	107	0.34	156	0.09	213	2.22
64	1.41	108	0.61	157	0.15	214	0.34
65	5.22	109	5.90	158	0.14	215	0.04
66	2.18	110	1.12	159	1.14	217	1.41
67	5.15	111	4.20	160	0.09	218	0.12
68	0.74	112	0.68	161	0.04	223	0.05
69	15.76	113	5.28	163	0.20	232	27.46
70	0.64	114	1.24	164	0.02	233	2.73
71	0.97	115	3.08	165	0.31	234	1.30
72	0.34	116	0.52	167	1.56	235	0.12

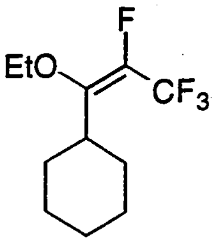
56. x-(1,1,2,3,3,3-hexafluoropropyl)cyclopent-1-ene (x=2,3) (78)

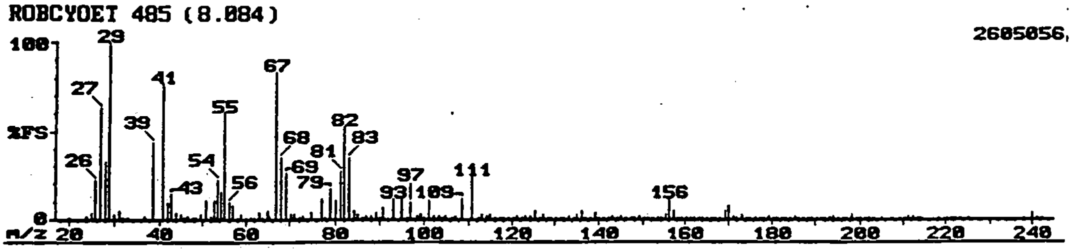




```
RS44 419 (6.984)
---------------
Mass     Rel Int
27          6.9
38          4.6
39         25.3
40         23.0
51         12.6
53          5.7
65         11.5
67        100.0
77         12.6
82          2.9
95          6.9
97         16.1
101         3.4
115         6.9
117        26.4
127         4.6
159         2.3
218        15.0
-------------
```

57. Z-1-ethoxy-2,3,3,3-tetrafluoroprop-2-enylcyclohexane (44a)





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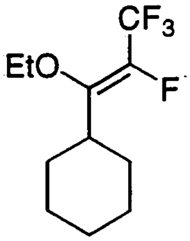
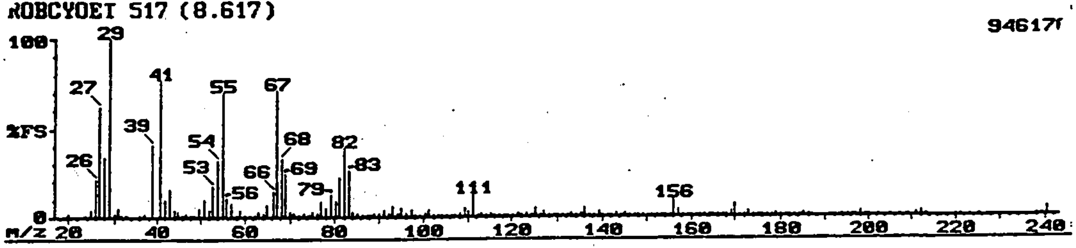
 ROBCYOET 485 (8.084)                                                  2605056
----------------+-----------------+-----------------+-------------------------
 Mass   Rel Int | Mass   Rel Int  | Mass   Rel Int  | Mass   Rel Int
----------------+-----------------+-----------------+-------------------------
  20      1.10  |  77     12.11   | 129     1.21    | 177     0.39
  24      1.59  |  78      1.27   | 130     0.83    | 178     0.20
  25      4.13  |  79     17.92   | 131     0.56    | 179     1.77
  26     22.33  |  80     10.22   | 132     0.88    | 180     0.22
  27     62.89  |  81     27.04   | 133     1.80    | 181     0.27
  28     33.18  |  82     52.83   | 134     0.82    | 182     0.19
  29    100.00  |  83     35.06   | 135     2.56    | 183     0.91
  30      3.03  |  84      4.52   | 136     5.15    | 184     0.40
  31      5.31  |  85      2.87   | 137     1.04    | 185     1.99
  32      0.87  |  86      0.79   | 138     1.36    | 186     0.16
  33      1.00  |  87      1.57   | 139     3.54    | 187     0.05
  37      2.38  |  88      2.03   | 140     1.08    | 188     0.02
  39     43.40  |  89      3.46   | 141     1.22    | 189     0.05
  41     76.73  |  90      0.76   | 142     0.71    | 190     0.06
  42      9.79  |  91      6.96   | 143     2.30    | 191     0.21
  43     14.62  |  93     12.11   | 144     1.26    | 192     0.29
  44      3.50  |  95     11.32   | 145     2.01    | 193     1.09
  45      3.07  |  96      1.35   | 146     0.46    | 194     1.46
  46      0.31  |  97     10.06   | 147     0.82    | 195     0.28
  47      2.16  |  98      1.88   | 148     0.89    | 196     0.10
  48      0.13  |  99      2.59   | 149     1.49    | 197     0.55
  49      0.64  | 100      0.96   | 150     0.50    | 198     2.52
  50      2.75  | 101     10.53   | 151     0.60    | 199     0.22
  51     11.01  | 102      2.00   | 152     0.45    | 200     0.07
  52      1.65  | 103      2.32   | 153     0.95    | 201     0.02
  53     10.53  | 104      0.20   | 154     0.53    | 202     0.02
  54     22.33  | 105      2.37   | 155     2.79    | 203     0.02
  54     15.25  | 106      1.05   | 156    11.32    | 205     0.08
  55     60.38  | 107      1.55   | 157     4.48    | 207     0.04
  56      9.98  | 109     11.48   | 158     0.55    | 209     0.03
  57      7.43  | 111     23.90   | 159     0.63    | 210     0.10
  58      1.25  | 112      1.42   | 160     0.15    | 211     1.55
  59      3.30  | 113      2.67   | 161     0.39    | 212     1.93
  60      0.40  | 114      1.67   | 162     0.51    | 213     0.21
  61      0.80  | 115      2.63   | 163     1.04    | 214     0.01
  62      0.43  | 116      0.80   | 164     0.52    | 218     0.03
  63      3.50  | 117      0.92   | 165     0.58    | 220     0.06
  64      0.81  | 118      0.55   | 166     0.93    | 221     0.18
  65      5.07  | 119      1.14   | 167     0.39    | 222     0.03
  65      2.41  | 120      0.85   | 168     0.70    | 223     0.02
  67     83.65  | 121      2.33   | 169     4.95    | 225     0.06
  68     35.06  | 122      0.98   | 170     7.94    | 238     0.05
  69     26.26  | 123      2.32   | 171     1.50    | 240     3.46
  70      3.11  | 124      2.11   | 172     0.98    | 241     0.32
  71      2.51  | 125      5.27   | 173     3.03    | 242     0.02
  72      0.98  | 126      1.36   | 174     0.47    |
  73      1.71  | 127      2.71   | 175     0.58    |
  75      3.93  | 128      1.13   | 176     0.15    |
----------------+-----------------+-----------------+-------------------------
```

58. E-1-ethoxy-2,3,3,3-tetrafluoroprop-2-enylcyclohexane (44b)

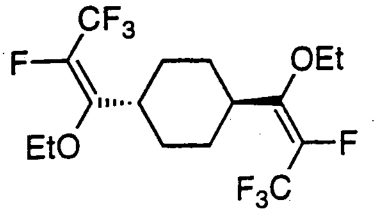


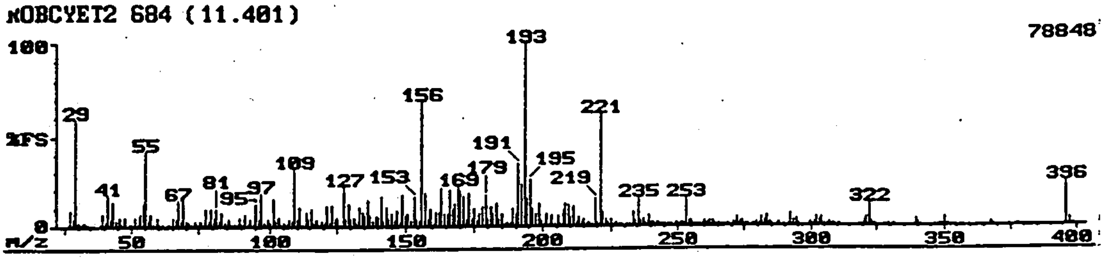


ROBCYOET 517 (8.617) 946176

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.56	73	1.63	119	0.87	165	0.44
24	1.26	74	0.99	120	0.47	166	0.77
25	3.57	75	2.84	121	1.81	167	0.33
26	21.21	76	2.16	122	0.62	168	0.20
27	61.90	77	8.55	123	2.03	169	2.95
28	34.20	78	4.44	124	1.16	170	6.47
29	100.00	79	12.55	125	4.79	171	1.12
30	1.52	80	8.77	126	0.87	172	0.66
31	4.71	81	22.40	127	2.44	173	2.68
32	0.69	82	38.53	128	1.03	174	0.39
33	0.73	83	25.76	129	1.17	175	0.48
36	0.66	84	3.22	130	0.76	176	0.18
37	1.81	85	1.95	131	1.36	177	0.53
39	40.69	86	0.36	132	0.60	178	0.10
41	76.62	87	0.57	133	1.62	179	1.54
42	9.63	88	1.31	134	0.57	180	0.21
43	15.80	89	2.14	135	1.51	181	0.24
44	3.92	90	1.58	136	5.09	182	0.11
45	2.92	91	3.63	137	0.98	183	0.85
46	0.73	92	1.67	138	0.71	184	0.30
47	2.27	93	5.68	139	3.25	185	1.68
48	0.33	94	1.69	140	0.82	186	0.13
49	0.65	95	4.46	141	1.20	187	0.03
50	4.68	96	2.08	142	0.26	191	0.16
51	9.52	97	4.14	143	2.06	192	0.34
52	4.25	98	0.95	144	0.86	193	1.14
53	17.21	99	1.40	145	1.76	194	1.44
54	32.03	100	1.79	146	0.32	195	0.48
55	70.13	101	4.30	147	0.72	196	0.10
56	10.61	102	1.08	148	0.72	197	0.44
57	8.01	103	1.35	149	1.31	198	2.76
58	1.44	104	0.43	150	0.37	199	0.21
59	3.41	105	1.16	151	0.53	200	0.08
60	0.35	106	0.64	152	0.32	202	0.06
61	0.80	107	0.97	153	0.78	205	0.08
62	1.14	108	2.08	154	0.34	207	0.05
63	3.22	109	4.90	155	0.72	209	0.03
64	2.11	110	2.57	156	9.31	211	2.25
65	6.63	111	12.77	157	3.52	212	2.87
66	15.04	112	1.24	158	0.46	213	0.25
67	70.56	113	1.76	159	1.45	220	0.17
68	32.90	114	0.99	160	0.19	221	0.26
69	24.57	115	1.95	161	0.31	225	0.11
70	3.11	116	0.55	162	0.35	238	0.04
71	2.27	117	0.68	163	0.81	239	0.30
72	1.01	118	0.34	164	0.38	240	4.63

59. *trans*-1,4-bis(Z-2,3,3,3-Tetrafluoro-1-ethoxyprop-2-enyl)cylohexane (**80**)





ROBCYET2 684 (11.401) 78848

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.61	86	0.58	140	5.11	194	15.10
27	8.93	87	1.01	141	16.23	195	26.62
28	4.04	88	1.13	142	2.52	196	9.25
29	59.42	89	4.57	143	10.31	197	6.41
30	1.79	90	1.19	144	3.57	198	12.66
31	0.93	91	6.74	145	6.74	199	2.64
32	1.54	92	1.00	146	2.92	200	0.80
33	0.27	93	3.79	147	9.09	201	6.66
38	0.30	94	1.24	148	2.27	202	1.40
39	6.82	95	12.26	149	17.29	203	5.52
40	1.87	96	4.30	150	5.68	204	1.21
41	17.78	97	18.10	151	6.82	205	5.52
42	3.51	98	1.99	152	2.94	206	1.06
43	13.47	99	3.41	153	16.40	207	8.60
44	2.60	100	1.64	154	3.84	208	12.58
45	4.71	101	15.99	155	2.88	209	12.01
46	0.33	102	3.17	156	68.51	210	4.77
47	5.09	103	4.53	157	18.26	211	10.47
49	0.74	104	0.50	158	3.43	212	1.62
50	0.56	105	1.72	159	9.50	213	4.73
51	4.57	106	0.93	160	1.24	214	1.60
52	1.20	107	4.12	161	7.39	215	3.49
53	6.49	108	2.78	162	7.95	216	0.64
54	12.91	109	31.82	163	21.10	217	2.03
55	41.88	110	3.51	164	7.14	218	0.48
56	3.15	111	10.39	165	6.82	219	15.10
57	7.22	112	1.29	166	19.97	220	2.21
58	0.59	113	7.95	167	9.74	221	61.69
59	4.75	114	3.55	168	12.66	222	7.31
60	0.35	115	9.50	169	22.73	223	4.16
61	0.59	116	2.15	170	19.81	224	1.99
63	0.93	117	3.81	171	16.56	225	3.98
64	0.51	118	0.97	172	4.34	226	0.94
65	5.15	119	2.98	173	18.59	227	2.13
66	4.34	120	1.46	174	3.92	228	0.55
67	14.61	121	11.53	175	10.06	229	0.68
68	3.29	122	2.09	176	3.04	231	1.26
69	14.29	123	11.69	177	6.41	232	0.89
70	2.98	124	3.81	178	10.47	233	7.71
71	2.21	125	5.19	179	17.53	234	2.48
72	0.63	126	1.23	180	3.90	235	15.18
73	2.92	127	22.08	181	10.31	236	3.21
74	0.21	128	3.98	182	7.22	237	4.32
75	2.76	129	12.91	183	13.07	238	1.15
76	0.42	130	3.59	184	3.81	239	6.01
77	9.74	131	4.71	185	6.82	240	1.48
78	2.58	132	1.72	186	1.01	241	1.42
79	9.90	133	10.39	187	2.39	242	1.54
80	4.48	134	7.55	188	1.77	243	1.26
81	10.06	135	5.44	189	10.06	244	0.32
82	3.27	136	14.45	190	6.74	245	1.24
83	7.71	137	6.17	191	34.74	246	1.16
84	2.11	138	2.54	192	23.70	247	0.98
85	3.88	139	6.09	193	100.00	249	2.41

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
250	0.29	269	0.46	293	2.54	323	1.85
251	1.70	271	1.56	294	4.08	324	0.77
252	1.50	272	4.73	295	0.78	328	0.22
253	15.99	273	2.35	299	1.68	329	0.24
254	3.39	274	2.92	300	0.82	331	0.63
255	2.72	275	1.05	301	2.03	339	3.71
256	0.38	276	0.38	302	5.03	340	2.39
257	0.49	278	0.67	303	3.31	348	0.38
258	0.46	279	1.56	304	4.75	349	1.04
259	1.44	280	1.15	305	1.00	350	4.85
260	3.31	281	4.59	306	0.50	351	0.66
261	2.17	282	2.74	307	1.70	367	1.48
262	2.50	283	5.52	308	0.39	368	1.40
263	2.94	284	1.91	309	0.31	377	0.54
264	0.62	285	0.97	311	0.30	396	24.03
265	1.06	287	1.99	319	1.11	397	3.94
266	0.28	289	0.51	320	2.98	398	0.44
267	1.30	291	1.26	321	5.28		
268	0.26	292	7.14	322	13.07		

Appendix Five
Colloquia, Induction Courses and Conferences

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 the postgraduate induction course.

d) all research conferences attended and papers presented by the author during the period when research for the thesis was carried out.

*a) Colloquia, Lectures and Seminars From Invited Speakers **1991 - 1994***

<u>1991</u>

October 17	Dr. J. A. Salthouse, University of Manchester* *Son et Lumiere - a demonstration lecture.*
October 31	Dr. R. Keely, Metropolitan Police Forensic Science *Modern Forensic Science.*
November 6	Prof. B. F. G. Johnson†, University of Edinburgh *Cluster-Surface Analogies.*
November 7	Dr. A. R. Butler, St. Andrews University *Traditional Chinese Herbal Drugs.*
November 13	Prof. D. Gani†, St. Andrews University* *The Chemistry of PLP Dependant Enzymes.*
November 20	Dr. R. More O'Ferrall†, Dublin* *Some Acid-Catalysed Rearrangements in Organic Chemistry.*
November 28	Prof. I. M. Ward, Leeds University *The Science & Technology of Orientated Polymers.*
December 4	Prof. R. Grigg†, Leeds University *Palladium Catalysed Cyclisation and Ion Capture Processes.*
December 5	Prof. A. L. Smith, ex Unilever *Soap Detergents and Black Puddings.*
December 11	Dr. W. A. Cooper†, Shell Research *Colloid Science, Theory, and Practice.*

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January 16	Dr. N. J. Long, University of Exeter *Metallocenophanes-Chemical sugar-tongs.*
January 22	Dr. K. D. M. Harris†, University of St. Andrews* *Understanding the Prperties of Solid Inclusion Compounds.*
January 29	Dr. A. Holmes†, University of Cambridge* *Cycloaddition Reactions in the Service of the Synthesis of Piperidine and ndolizidine Natural Products.*
January 30	Dr. M. Anderson, Sittingbourne Research Centre, Shell Research *Recent Advances in the Safe and Selective Chemical Control of Insect Pests.*
February 12	Dr. D. E. Fenton†, University of Sheffield* *Polynuclear Complexes of Molecular Clefts as Models for Copper Biosites.*
February 13	Dr. J. Saunders, Glaxo Group Research Limited *Molecular Modelling in Drug Discovery.*
February 19	Prof. E. J. Thomas†, University of Manchester *Application of Organo-Stannanes to Organic Synthesis.*
February 20	Prof. E. Vogel, University of Cologne* *The Musgrave Lecture: Porrphyrins, Molecules of Interdisciplinary Interest.*
February 25	Prof. J. F. Nixon, University of Sussex *Phosphoalkylenes, New Building Blocks in Inorganic and Organometallic Chemistry.*
February 26	Prof. M. L. Hitchman†, University of Stratheclyde *Chemical Vapour Deposition.*
March 5	Dr. N. C. Billingham, University of Sussex *Degradable Plastics - Myth or Magic ?*
March 11	Dr. S. E. Thomas†, Imperial College London* *Recent Advances in Organoiron Chemistry.*
March 12	Dr. R. A. Hann, ICI Image Data *Electronic Photography - An Image of the Future*
March 18	Dr H. Maskill†, University of Newcastle *Concerted or stepwise fragmentation in a deamination-type reaction.*
April 7	Prof. D. M. Knight, Philosophy Department, University of Durham *Interpreting experiments: the begining of electrochemistry.*
May 13	Dr. J-C. Gehret, Ciba Geigy, Basel* *Some aspects of Industrial Agrochemical Research.*

October 15	Dr M. Glazer & Dr. S. Tarling, Oxford University & Birbeck College, London *It Pays to be British! - The Chemist's Role as an Expert Witness in Patent Litigation.*
October 20	Dr. H. E. Bryndza, Du Pont Central Research *Synthesis, Reactions and Thermochemistry of Metal (Alkyl) Cyanide Complexes and Their Impact on Olefin Hydrocyanation Catalysis.*
October 22	Prof. A. Davies, University College London *The Ingold-Albert Lecture The Behaviour of Hydrogen as a Pseudometal.*
October 28	Dr. J. K . Cockcroft, University of Durham *Recent Developments in Powder Diffraction.*
October 29	Dr. J. Emsley, Imperial College, London *The Shocking History of Phosphorus.*
November 4	Dr. T. P. Kee, University of Leeds *Synthesis and Co-ordination Chemistry of Silylated Phosphites.*
November 5	Dr. C. J. Ludman, University of Durham* *Explosions, A Demonstration Lecture.*
November 11	Prof. D. Robins†, Glasgow University* *Pyrrolizidine Alkaloids : Biological Activity, Biosynthesis and Benefits..*
November 12	Prof. M. R. Truter, University College, London *Luck and Logic in Host - Guest Chemistry.*
November 18	Dr. R. Nix†, Queen Mary College, London *Characterisation of Heterogeneous Catalysts.*
November 25	Prof. Y. Vallee. University of Caen *Reactive Thiocarbonyl Compounds.*
November 25	Prof. L. D. Quin†, University of Massachusetts, Amherst *Fragmentation of Phosphorous Heterocycles as a Route to Phosphoryl Species with Uncommon Bonding.*
November 26	Dr. D. Humber, Glaxo, Greenford *AIDS - The Development of a Novel Series of Inhibitors of HIV.*
December 2	Prof. A. F. Hegarty, University College, Dublin *Highly Reactive Enols Stabilised by Steric Protection.*
December 2	Dr. R. A. Aitken†, University of St. Andrews *The Versatile Cycloaddition Chemistry of* $Bu_3P.CS_2$.
December 3	Prof. P. Edwards, Birmingham University *The SCI Lecture - What is Metal?*
December 9	Dr. A. N. Burgess†, ICI Runcorn* *The Structure of Perfluorinated Ionomer Membranes.*

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January 20	Dr. D. C. Clary†, University of Cambridge *Energy Flow in Chemical Reactions.*
January 21	Prof. L. Hall, Cambridge* *NMR - Window to the Human Body.*
January 27	Dr. W. Kerr, University of Strathclyde* *Development of the Pauson-Khand Annulation Reaction : Organocobalt Mediated Synthesis of Natural and Unnatural Products.*
January 28	Prof. J. Mann, University of Reading *Murder, Magic and Medicine.*
February 3	Prof. S. M. Roberts, University of Exeter *Enzymes in Organic Synthesis.*
February 10	Dr. D. Gillies†, University of Surrey *NMR and Molecular Motion in Solution.*
February 11	Prof. S. Knox, Bristol University *The Tilden Lecture: Organic Chemistry at Polynuclear Metal Centres.*
February 17	Dr. R. W. Kemmitt†, University of Leicester *Oxatrimethylenemethane Metal Complexes.*
February 18	Dr. I. Fraser, ICI Wilton *Reactive Processing of Composite Materials.*
February 22	Prof. D. M. Grant, University of Utah *Single Crystals, Molecular Structure, and Chemical-Shift Anisotropy.*
February 24	Prof. C. J. M. Stirling†, University of Sheffield* *Chemistry on the Flat-Reactivity of Ordered Systems.*
March 10	Dr. P. K. Baker, University College of North Wales, Bangor *'Chemistry of Highly Versatile 7-Coordinate Complexes'.*
March 11	Dr. R. A. Y. Jones, University of East Anglia *The Chemistry of Wine Making.*
March 17	Dr. R. J. K. Taylor†, University of East Anglia* *Adventures in Natural Product Synthesis.*
March 24	Prof. I. O. Sutherland†, University of Liverpool *Chromogenic Reagents for Cations.*
May 13	Prof. J. A. Pople, Carnegie-Mellon University, Pittsburgh, USA* *The Boys-Rahman Lecture: Applications of Molecular Orbital Theory*
May 21	Prof. L. Weber, University of Bielefeld *Metallo-phospha Alkenes as Synthons in Organometallic Chemistry*
June 1	Prof. J. P. Konopelski, University of California, Santa Cruz* *Synthetic Adventures with Enantiomerically Pure Acetals*

June 2	Prof. F. Ciardelli, University of Pisa *Chiral Discrimination in the Stereospecific Polymerisation of Alpha Olefins*
June 7	Prof. R. S. Stein, University of Massachusetts *Scattering Studies of Crystalline and Liquid Crystalline Polymers*
June 16	Prof. A. K. Covington, University of Newcastle *Use of Ion Selective Electrodes as Detectors in Ion Chromatography.*
June 17	Prof. O. F. Nielsen, H. C. Arsted Institute, University of Copenhagen *Low-Frequency IR - and Raman Studies of Hydrogen Bonded Liquids.*
September 13	Prof. Dr. A. D. Schlüter, Freie Universität Berlin, Germany *Synthesis and Characterisation of Molecular Rods and Ribbons.*
September 13	Prof. K. J. Wynne, Office of Naval Research, Washington, U.S.A. *Polymer Surface Design for Minimal Adhesion*
September 14	Prof. J. M. DeSimone, University of North Carolina, Chapel Hill, U.S.A. *Homogeneous and Heterogeneous Polymerisations in Enviromentally Responsible Carbon Dioxide.*
September 28	Prof. H. Ila., North Eastern University, India *Synthetic Strategies for Cyclopentanoids via OxoKetene Dithiacetals.*
October 4	Prof. F. J. Feher†, University of California at Irvine *Bridging the Gap between Surfaces and Solution with Sessilquioxanes.*
October 14	Dr. P. Hubberstey, University of Nottingham *Alkali Metals: Alchemist's Nightmare, Biochemist's Puzzle and Technologist's Dream.*
October 20	Dr. P. Quayle†, Unversity of Manchester *Aspects of Aqueous Romp Chemistry.*
October 23	Prof. R. Adams†, University of S. Carolina *The Chemistry of Metal Carbonyl Cluster Complexes Containing Platinum and Iron, Ruthenium or Osmium and the Development of a Cluster Based Alkyne Hydrogenating Catalyst.*
October 27	Dr. R. A. L. Jones†, Cavendish Laboratory* *'Perambulating Polymers'.*
November 10	Prof. M. N. R. Ashfold†, University of Bristol *High-Resolution Photofragment Translational Spectroscopy: A New Way to Watch Photodissociation.*
November 17	Dr. A. Parker†, Laser Support Facility *Applications of Time Resolved Resonance Raman Spectroscopy to Chemical and Biochemical Problems.*
November 24	Dr. P. G. Bruce†, University of St. Andrews *Synthesis and Applications of Inorganic Materials.*

December 1	Prof. M. A. McKervey†, Queens University, Belfast* *Functionlised Calixerenes.*
December 8	Prof. O. Meth-Cohen, Sunderland University* *Friedel's Folly Revisited.*
December 16	Prof. R. F. Hudson, University of Kent *Close Encounters of the Second Kind.*
January 26	Prof. J. Evans†, University of Southhampton *Shining Light on Catalysts.*
February 2	Dr. A. Masters†, University of Manchester* *Modelling Water Without Using Pair Potentials.*
February 9	Prof. D. Young†, University of Sussex *Chemical and Biological Studies on the Coenzyme Tetrahydrofolic Acid.*
February 16	Prof. K. H. Theopold, University of Delaware, U.S.A *Paramagnetic Chromium Alkyls: Synthesis and Reactivity.*
February 23	Prof. P. M. Maitlis†, University of Sheffield *Why Rodium in Homogenous Catalysis.*
March 2	Dr. C. Hunter†, University of Sheffield* *Non Covalent Interactions between Aromatic Molecules.*
March 9	Prof. F. Wilkinson, Loughborough University of Technology *Nanosecond and Picosecond Laser Flash Photolysis.*
March 10	Prof. S.V. Ley, University of Cambridge* *New Methods for Organic Synthesis.*
March 25	Dr. J. Dilworth, University of Essex *Technetium and Rhenium Compounds with Applications as Imaging Agents.*
April 28	Prof. R. J. Gillespie, McMaster University, Canada* *The Molecular Structure of some Metal Fluorides and OxoFluorides: Apparent Exceptions to the VSEPR Model.*
May 12	Prof. D. A. Humphreys, McMaster University, Canada *Bringing Knowledge to Life*

† Invited specially for the graduate training programme.

* Those attemded.

b) First Year Induction Course

This course consists of a series of one hour lectures on the services available in the department.

Departmental Organisation - Dr. E.J.F. Ross
Safety Matters - Dr. G.M. Brooke
Electrical Appliances - Mr. B.T. Barker
Chromatography and Microanalysis - Mr. T.F. Holmes
Atomic Absorptiometry and Inorganic Analysis - Mr. R. Coult
Library Facilities - Mr. R.B. Woodward
Mass Spectroscopy - Dr. M. Jones
Nuclear Magnetic Resonance Spectroscopy - Dr. R.S. Matthews
Glass-blowing Techniques - Mr. R. Hart / Mr. G. Haswell

c) Research Conferences Attended

July 1993	2nd Anglo-Russian-Ukranian Symposium on Fluorine Chemistry, Durham.
September 1995	11th European Symposium on Fluorine Chemistry, Bled, Slovenia.

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2a. R. E. Banks and J. C. Tatlow, in *Organofluorine Chemistry,* ed. R. E. Banks, B. E. Smart and J. C. Tatlow, Plenum Press, New York, 1994, p. 25.

2b *Selective Fluorination on Organic and Bioorganic Chemistry,* ed J. T. Welch, American Chemical Society, Washington, 1991.

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