Chemistry of (Z)-2H-Heptafluorobut-2-ENE

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A THESIS
entitled

CHEMISTRY OF (Z)-2*H*-HEPTAFLUOROBUT-2-ENE

submitted by

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Department of Chemistry

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" People must be amused.

They can't be always a learning, nor yet they can't be always a working."

CHARLES DICKENS

"*Hard Times*"

Acknowledgements

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A special mention must go to the late Tom Holmes, who will be greatly missed.

Memorandum

The work described in this thesis was carried out in 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.

Part of this work has been the subject of the following:

Richard D. Chambers, Alex J. Roche, Andrei S. Batsanov and Judith A. K. Howard, *"1,8-Diazabicyclo[5.4.0]undec-7-ene as a Difunctional Nucleophile"*, J. Chem. Soc., Chem. Commun., 1994, 2055.

Richard D. Chambers, Steven J. Mullins, Alex J. Roche and Julian F. S. Vaughan, *"Direct Syntheses of Pentakis(trifluoromethyl)cyclopentadienide Salts and related Dienes"*, *J. Chem. Soc., Chem. Commun.*, 1995, 841.

R. D. Chambers, J. F. S. Vaughan, S. J. Mullins, T. Nakamura and A. J. Roche, *"Fluorinated Dienes"*, *Journal of Fluorine Chemistry*, 72, 1995, 231.

Richard D. Chambers and Alex J. Roche, *"Novel By-Products in the Synthesis of (Z)-2H-Heptafluorobut-2-ene"*, submitted for publication in *Canadian Journal of Chemistry.*

Richard D. Chambers and Alex J. Roche, *"Eliminations from (Z)-2H-Heptafluorobut-2-ene"*, submitted for publication in *Journal of Fluorine Chemistry.*

Richard D. Chambers, Alex J. Roche and Michael H. Rock, *"Cycloaddition reactions involving Hexafluorobut-2-yne and (Z)-2H-Heptafluorobut-2-ene"*, submitted for publication in *Journal of the Chemical Society, Perkin Trans. 1.*

Richard D. Chambers and Alex J. Roche, *"(Z)-2H-Heptafluorobut-2-ene as a Synthon for the Corresponding -Butyne"*, submitted for publication in *Journal of Fluorine Chemistry.*

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9th Postgraduate Heterocyclic Symposium
University of Leicester
July 1994

I.C.I. Poster Session
University of Durham
December, 1994.

North Eastern Graduate Symposium
University of Durham
April, 1995.

11th European Symposium on Fluorine Chemistry
Bled, Slovenia
September 17th-22nd1995.

Nomenclature

Throughout this work, an 'F' in the centre of a ring denotes that all the unmarked bonds are to fluorine.

Abbreviations

The following are used throughout the thesis.

HFP	hexafluoropropene
PFIB	perfluoroisobutene
TFE	tetrafluoroethene
CFC	chlorofluorocarbon
HCFC	hydrochlorofluorocarbon
PFOB	perfluorooctylbromide
FTPA	perfluorotripropylamine
THF	tetrahydrofuran
NMP	N-methyl-2-pyrollidone
GLCMS	gas-liquid chromatography-mass spectrometry
NMR	nuclear magnetic resonance
IR	infrared
FAB	fast atom bombardment
UV	ultraviolet
DCM	dichloromethane

Abstract

Chemistry of (*Z*)-2*H*-Heptafluorobut-2-ene (**8**)
by A.J. Roche

The research described within this thesis may be divided into four areas:

1) The synthesis of (**8**) was investigated, and was shown to produce some novel by-products, including highly fluorinated dienes and even a triene. Perhaps most remarkable, was the presence of potassium pentakis(trifluoromethyl)cyclopentadienide in the reaction residue, since this constitutes a one step synthesis of this system from non-fluorinated precursors. The isolation of this salt proved challenging, but a variety of these salts have been isolated via the formation of 5*H*-pentakis(trifluoromethyl)cyclopentadiene, which is reported to be the strongest non-conjugated organic acid.

2) The elimination of HF from (**8**) to give hexafluorobut-2-yne was explored, and several successful routes have been found. Equally interesting was the variety of products formed with bases. The 'non-nucleophilic' base DBU, was even shown to behave as a difunctional nucleophile with (**8**), resulting in a novel tricyclic pyrrole product, and the product structure was confirmed by a single X-ray crystallographic study.

3) The use of (**8**) as a synthon for hexafluorobut-2-yne in Diels Alder reactions was investigated. This resulted in the discovery of a novel one pot route to a variety of bis(trifluoromethylated) furans.

4) The reactions of (**8**) with a variety of nucleophiles was explored. The products obtained were identical to those that have been formed, or would be expected to be formed, from the reaction of the same nucleophile with hexafluorobutyne.

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Chapter One

I. General Introduction

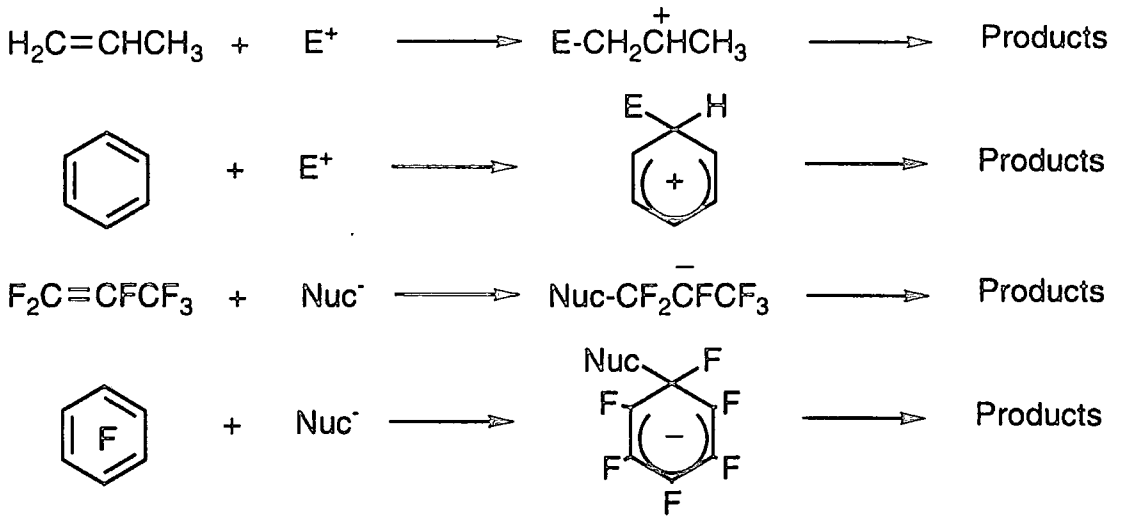
The first reported synthesis of a fluorine containing compound is attributed to Dumas and Peligot[1], when in 1836 they reported a synthesis of fluoromethane. Moissan[2], in 1890, erroneously claimed to have isolated carbon tetrafluoride from the reaction of carbon and fluorine. However, it was Swarts' work[3, 4] on simple aliphatic fluorine containing compounds, between the years of 1890 and 1938, which, it could be argued, established the foundations of organofluorine chemistry. Swarts' studies on the preparation of fluorocarbons using exchange reactions, was used as the basis for Midgley and Henne's work[5], which promoted the introduction of chlorofluorocarbons (CFC's) as refrigerants.

The chemistry of perfluorinated compounds began with the synthesis of carbon tetrafluoride in 1926 by Lebeau and Damiens[6], however it was not fully characterised by these workers until 1930[7], and also in the same year by Ruff and Keim[8]. Since then, varied methodology has been devised to produce a wide range of fully fluorinated compounds[9].

In addition to their application as refrigerants, fluorocarbons find uses in areas as diverse as fire extinguishers, blood substitutes, propellants, anaesthetics, dyes, pharmaceuticals and surfactants[10].

The value of studying fluorocarbon chemistry lies not only in the industrial applications of new materials, but also in new areas of chemistry which display novel types of reaction mechanism. The substitution of hydrogen for fluorine creates an entirely different electronic environment for functionalities, which may modify or drastically alter their reactivity.

An excellent example of this difference in behaviour between hydrocarbon and fluorocarbon analogues can be illustrated by considering the reaction of olefinic and aromatic systems[9]. The chemistry of hydrocarbon aromatic and olefinic systems is dominated by electrophilic attack, resulting in carbonium ion transition states. Fluorocarbon aromatic and olefinic systems are dominated by nucleophilic attack, resulting in carbanionic transition states.



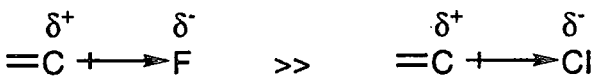
It is therefore, easy to appreciate the so called 'mirror image' chemistry displayed between hydrocarbon and fluorocarbon systems.

I.1. Nucleophilic Attack on Fluoroalkenes

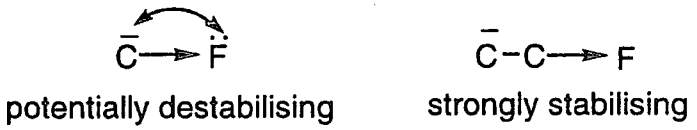
I.1.A. Factors affecting Reactivity and Orientation

As stated previously, the chemistry of fluoroalkenes is dominated by nucleophilic attack, and there are several factors which govern their reactivity, and the orientation of attack[11].

There is a greater reactivity in alkenes bearing fluorine versus chlorine because of an activating polar contribution, due to fluorine's greater electronegativity.

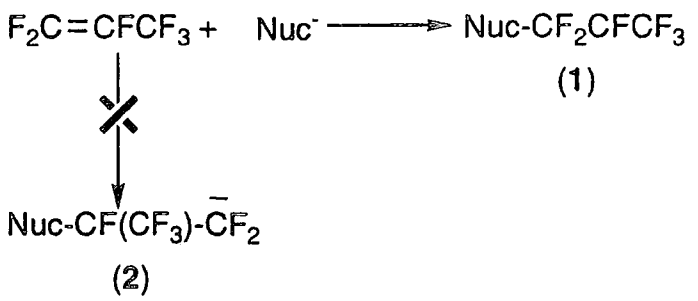


When a fluorine is attached directly to a carbanionic centre, the electron withdrawal effect (stabilising) is offset by electron pair repulsions (destabilising), and the net effect may even be overall destabilisation with respect to hydrogen.

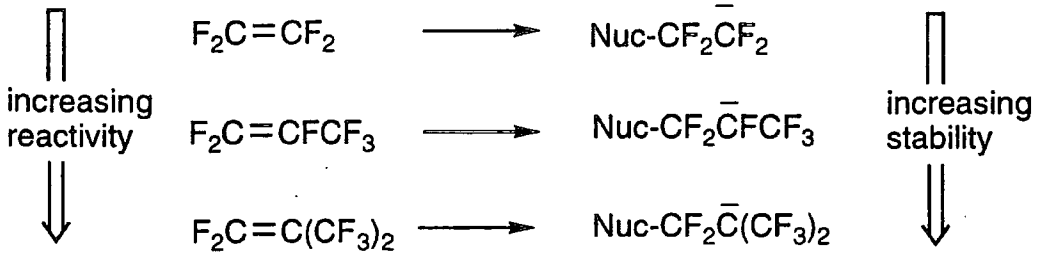


However, fluorine attached to carbon adjacent to a carbanionic centre is always strongly stabilising.

From these effects, it may be predicted that the preferred nucleophilic attack on a fluorinated alkene will occur at the least substituted end, in order to generate an intermediate carbanion with the minimum number of fluorines attached directly to the carbanionic centre, i.e. (1) is favoured over (2).

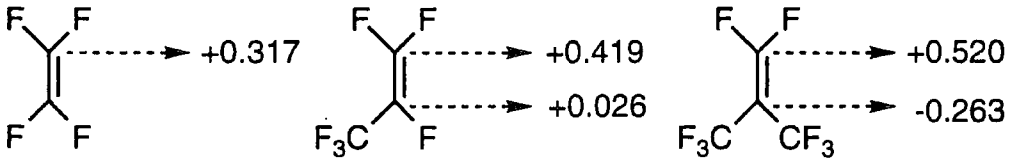


It is also possible to predict a reactivity order for the attack of nucleophiles, based on increasing perfluoroalkyl substitution at one of the sp^2 carbons leading to greater stabilisation of negative charge, and so more stable intermediates.



This order has been established experimentally[12], for it is known that while perfluoroisobutene reacts with neutral methanol[13], hexafluoropropene requires the presence of base for reaction[14], and tetrafluoroethene needs either a strong base[12] or elevated pressures[15] for reaction to occur.

In 1982, Russian workers[16] published theoretical work showing that initial state electron distributions may also be used to predict reactivity order and regioselectivity.



The more reactive alkene contains the vinyl carbon with the largest ground state positive charge, and so most reactive towards the nucleophile.

In 1993, Rozhkov and Borisov[17] published more detailed quantum mechanical calculations on tetrafluoroethene and higher perfluorinated alkenes, probing their electronic structure, which seems to support previous work.

However, these simple 'ground rules' are not totally sufficient, because they do not explain the observation that hexafluoropropene is much more reactive than perfluorobut-2-ene[11, 18].

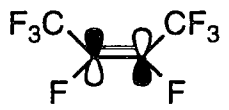
$$F_2C{=}CFCF_3 \;+\; Nuc^- \longrightarrow Nuc\text{-}CF_2\bar{C}FCF_3$$

$$F_3CFC{=}CFCF_3 \;+\; Nuc^- \longrightarrow Nuc\text{-}CF(CF_3)\bar{C}FCF_3$$

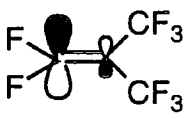
The intermediates formed from these two systems only have a small difference in stability, since fluorine and perfluoroalkyl substituents exert similar stabilising influences when adjacent to a carbanionic centre[19].

Consequently, a frontier-orbital approach has been advanced to explain this observation[20]. This initial state rationalisation proposes that the LUMO of the fluoroalkene interacts with the HOMO of the nucleophile. Electronegative substituents are known to lower orbital energies[21], and so the replacement of fluorine for a trifluoromethyl group reduces the LUMO energy of the fluoroalkene, and so makes it more reactive. i.e. hexafluoropropene is more reactive than tetrafluoroethene[22].

It also becomes apparent that the positioning of the trifluoromethyl groups is important, because perfluoroisobutene is more reactive than perfluorobut-2-ene, yet both have two vinylic fluorines and two vinylic trifluoromethyl groups. This promotes the importance of the relative coefficients of the LUMO. It is known that the introduction of a trifluoromethyl for fluorine increases the LUMO coefficient at the opposite side of the double bond.



Effects of CF_3's in opposition

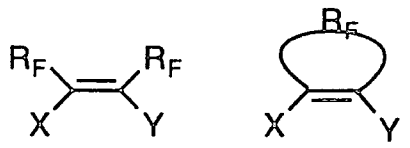


Effects of CF_3's reinforce

Thus, two trifluoromethyl groups on the same side of a double bond will have a doubly enhancing effect on the LUMO coefficient of the adjacent carbon, whereas two trifluoromethyl groups placed one either side of the unsaturation, will only enhance the carbons on both sides of the unsaturation by a single amount. Hence, it is easy to rationalise why less symmetrical and more polarised alkenes are more reactive to nucleophiles than symmetrically substituted alkenes.

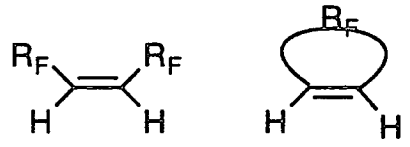
I.2. Some Chemistry of Polyfluorinated Alkenes

This thesis is concerned with the chemistry of 2*H*-heptafluorobut-2-ene, and its application as a building block for fluorine containing compounds. It seems appropriate, therefore, to give the reader an overview of the predicted chemistry of 2*H*-heptafluorobut-2-ene, by means of a review of related systems, which will include both acyclic and cyclic derivatives, where X=Y=H, X=Y=F and X,Y=F,H.



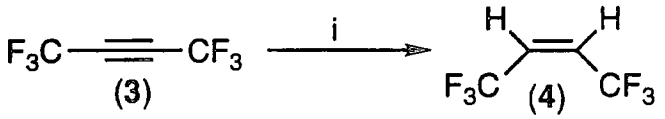
There is no chemical literature bringing these topics together.

I.2.A. Polyfluorinated Internal Alkenes with Two Vicinal Vinylic Hydrogens (X=Y=H)



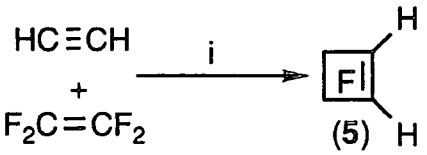
I.2.A.1. Synthesis

The first compound of this type to be synthesised was 1,1,1,4,4,4-hexafluorobut-2-ene (4) in 1949, by Henne and Finnegan[23]. They found that hexafluorobut-2-yne (3) would readily accept one mole of hydrogen to produce butene (4).



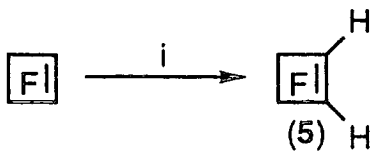
i = H_2, Raney Nickel (42%)

Sharkey and co-workers[24] synthesised 3,3,4,4-tetrafluorocyclobutene (5) in 1960, via the [2+2] cycloaddition of tetrafluoroethene and ethyne at 225°C.



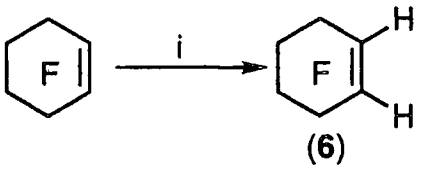
i = 225°C (35%)

In 1961, it was established[25] that vinylic fluorine could be converted in to vinylic hydrogen by the action of lithium aluminium hydride in ether. They demonstrated that (5) could be synthesised from hexafluorocyclobutene



i = $LiAlH_4$, ether, -20°C (37%)

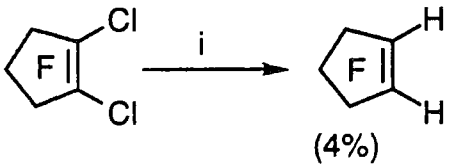
Later work[26] showed the reaction of perfluorocyclohexene under identical conditions gave eight reduction products, which had to be separated by preparative scale gas chromatography. Of these, one of the major products was 1,2 dihydro-octafluorocyclohexene (**6**).



(**6**)

i = $LiAlH_4$, ether, -20°C (24%)

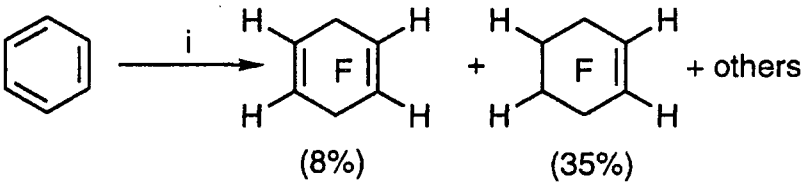
Burton and co-workers[27] later demonstrated that a polyhalogenated olefin would react with sodium borohydride in diglyme, to produce compounds containing one or two vinylic hydrogens. This methodology was superior to that reported previously[25] because it was a cleaner reaction.



(4%)

i = $NaBH_4$, diglyme, -15°C

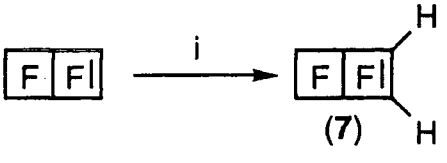
Further work from Birmingham[28] in 1969 reported that benzene could be fluorinated by $KCoF_4$, to produce a mixture of four compounds, two of which are shown below.



(8%) (35%)

i = $KCoF_4$, 280°C

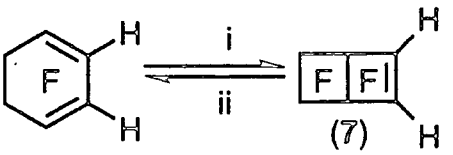
Musgrave and co-workers[29] published work in 1971 concerning the synthesis of several perfluorobicyclo[2.2.0]hex-2-ene derivatives, including (**7**), which was produced from perfluorobicyclo[2.2.0]hex-2-ene using Burton's[27] methodology.



(**7**)

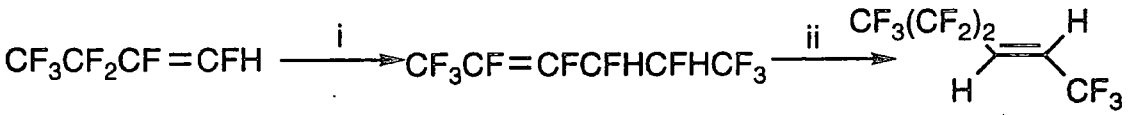
i = $NaBH_4$, diglyme, -15°C

They also showed that (7) was interconvertable with 1,4,5,6-tetrafluorocyclohexa-1,3-diene.



i = hv; ii = heat

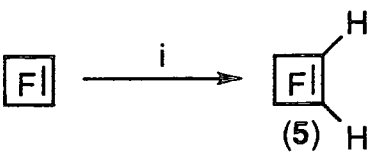
Russian workers have reported the co-oligomerisation of tetrafluoroethene and polyfluorinated alkenes using antimony pentafluoride.



i = SbF_5, CF_2=CF_2
ii = SbF_6^-

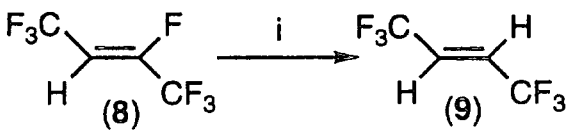
(60%)

Workers[30] wishing to study the microwave spectrum and structure of (5), have synthesised it in modest yield using Burton's[27] methodology, via reaction of perfluorocyclobutene and sodium borohydride.



i = $NaBH_4$, diglyme, -15°C

Recent work from this laboratory[31] has shown that the trans isomer of 1,1,1,4,4,4-hexafluorobut-2-ene (9) can be produced by the reaction of tributyltin hydride and 2*H*-heptafluorobut-2-ene (8), under free radical conditions.



i = Bu_3SnH, hv

(90%)

The synthesis of (9) has also been the subject of a number of recent patents[32, 33], where 1,1,1-trifluoro-2,2-dichloroethane is reacted with an amine and metallic copper.

I.2.B. Reactivity

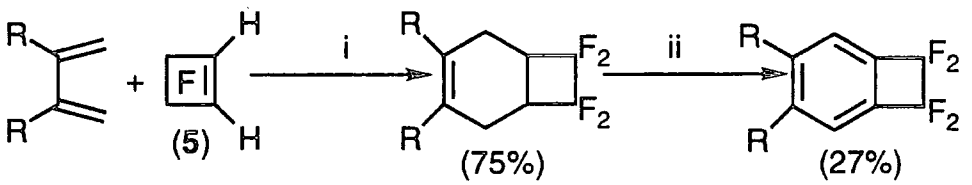
I.2.B.1. Reactions with Nucleophiles

One year after publishing the synthesis of 1,1,1,4,4,4-hexafluorobut-2-ene, the same workers[23] published a paper which reported their inability to add acetic acid to the butene in the presence of base, and their paper contains a quote from an American Chemical Society meeting, claiming 'trifluoromethyl olefins, $CF_3CH=CHR$ were not attacked by nucleophilic reagents...'. This lack of reactivity towards nucleophiles is indeed true for systems of the type $R_FCH=CHR_F$, and there are no literature examples of nucleophilic reactions to this type of systems.

In fact, apart from two examples of fluorination and hydrogenation, the only reactivity that is displayed by these systems is a strong dienophilic (or dipolarophilic) nature.

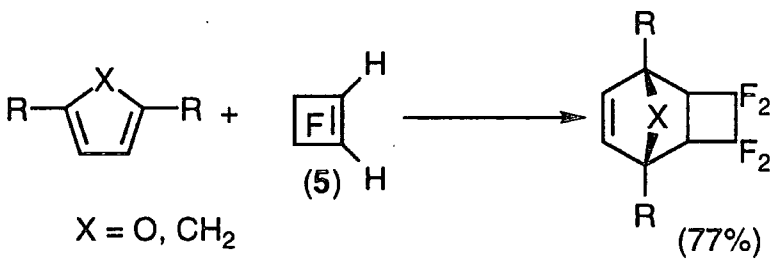
I.2.B.2. Cycloadditions

The first reported example of a cycloaddition reaction involving an $R_FCH=CHR_F$ system was in 1962, when Shozda and Putnam[34] reacted (5) with butadiene to form the diels alder adduct, which was then dehydrogenated to form the corresponding tetrafluorobenzocyclobutene.



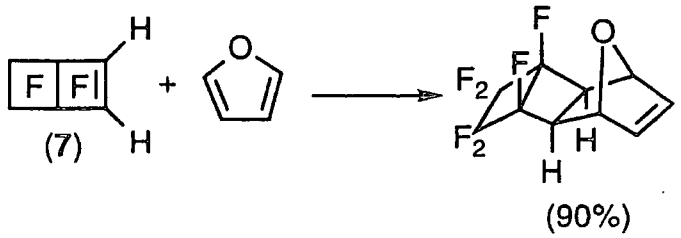
i = 100°C
ii = Pd-C

They also performed reactions using cyclopentadiene and furan (and simple derivatives of these), and obtained Diels Alder adducts.

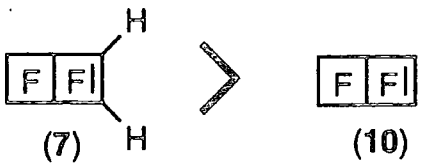


X = O, CH_2

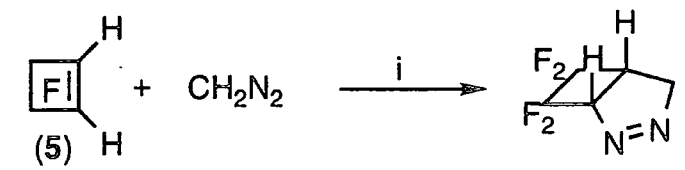
In 1971, workers in Durham[29] published an excellent paper where they describe the cycloaddition chemistry of 1,2-dihydro-perfluorobicyclo[2.2.0]hex-2-ene (7).



They compared its reactivity to other related systems, and proved, by means of a competition reaction that the dihydro- analogue is more dienophilic than the perfluorobicyclo[2.2.0]hex-2-ene.



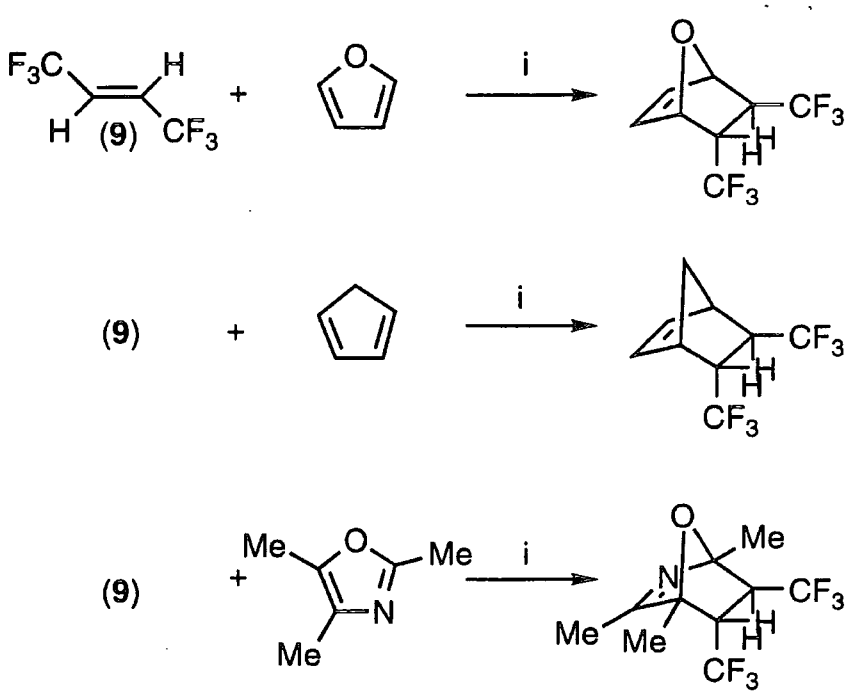
Dolbier Jr. and co-workers[35, 36] in the course of studying the effect of fluorine on the thermal behaviour of molecules, have shown that (5) will react readily with diazomethane, producing 6,6,7,7-tetrafluoro-2,3-diazabicyclo[3.2.0]hept-2-ene.



i = RT, 15 min

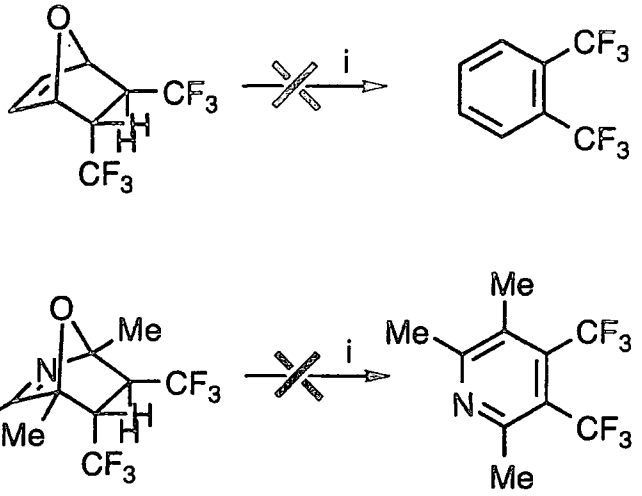
(71%)

Recent unpublished work from this laboratory[31], has shown that hexafluorobut-2-ene (9) will undergo cycloaddition with furan, cyclopentadiene and trimethyl oxazole.



i = THF, 130°C

The stimulus behind this work was a potential direct route into bis(trifluoromethylated) aromatic compounds. However, the adducts did not dehydrate with acid, in the desired aromatisation step.

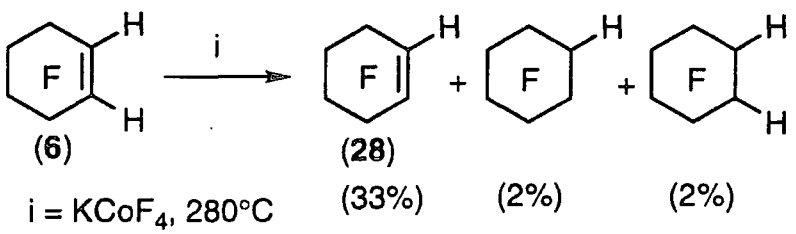


i = THF, p-toluenesulphonic acid, 130°C

I.2.C. Other Reactions

I.2.C.1. Fluorination

In 1981, Burdon and co-workers[37] showed that $KCoF_4$ would fluorinate (**6**), and that this method of fluorination was milder than using CoF_3[28, 38, 39]. They were able to demonstrate that the reaction proceeds via saturation followed by dehydrofluorination, and not by direct replacement of vinylic hydrogen.

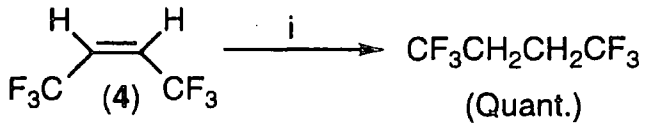


(6) (28) (33%) (2%) (2%)

i = $KCoF_4$, 280°C

I.2.C.2. Hydrogenation

Hexafluorobutene (**4**) was found to readily accept a mole of hydrogen[23, 40] to produce the saturated hexafluorobutane .



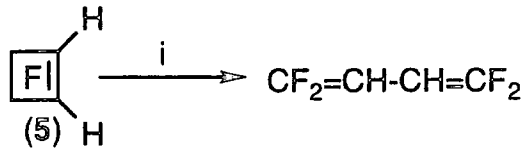
i = H_2, Raney Nickel

Recent work by Daikin Industries has been published also concerning the production of hexafluorobutane[32, 33]. Their interest lies in the application of

hexafluorobutane as a refrigerant, a blowing agent and a cleaning agent. This highlights the fact that saturated linear hydrofluorocarbons (HFC's) are being viewed as new environmentally friendly CFC replacements[41]. HFC's possess similar performance properties to CFC's, but because they do not contain chlorine atoms, they will not cause ozone depletion[42].

I.2.C.3. Ring Opening of Cyclobutenes

1,2-Dihydro-perfluorocyclobut-1-ene is relatively stable, but will ring open to form 1,1,4,4-tetrafluorobutadiene[24] quantitatively at 550°C.

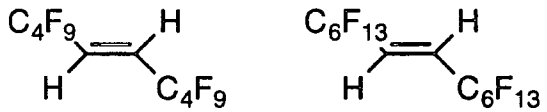


i = 550-750°C

This is in comparison to the perfluoro-analogue which is resistant to thermal isomerism[9], and the hydrocarbon analogues where thermal scission of allylic carbon-carbon bonds of cyclobutenes to give 1,3-dienes occurs readily at lower temperatures[43].

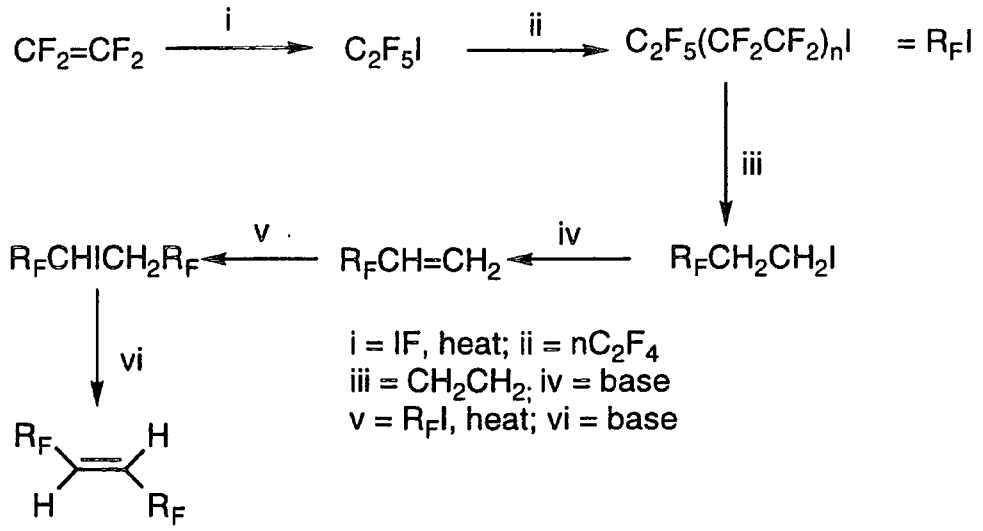
I.2.D. Industrial Applicability

The general lack of reactivity with nucleophiles and electrophiles, and the high stability of compounds of the type $R_FCH=CHR_F$, have been factors in their advancement as potential media for oxygen transport[44-49], such as the trans-1,2-bis(perfluoro-n-alkyl)ethenes[41] F-44E and F-66E below.



F-44E F-66E

The industrial syntheses[41] of these two compounds is summarised below.



I.2.D.1. Fluorocarbons as Vehicles for Respiratory Gas Transport

Over the past twenty years, emulsified fluorocarbons have received much attention concerning their biological and medical applications. One special area of interest, is that of a medium for respiratory gas transport[44-49]. Conventional blood transfusion can be supplemented by these oxygen containing resuscitation fluids, and this has seen the rise of the slightly misdirecting term ' blood substitute'.

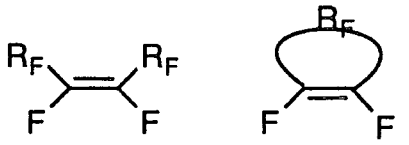
The fluorocarbons used in this field are generally perfluorinated, although some do contain other atoms (e.g. PFOB, FTPA). All these compounds must have certain basic requirements to be successful in this application. High chemical and thermal stabilities are obviously critical, and this is provided by the strength of the carbon fluorine bonds, coupled with the electronic and steric protection provided for the carbon skeleton by the fluorine containing substituents. Also, they must display a high capability to dissolve gases, and fluorocarbons seem excellent at this, especially the F-44E, which has the best results[41], as shown in table 1.

Table 1: Solubilities (vol% at 1atm and 37°C) of O_2 and CO_2 in Water and Selected fluorocarbons.

Compound	Formula	O_2	CO_2
Water	H_2O	2.5	65
Perfluorotributylamine (FTBA)	$(C_4F_9)_3N$	40.0	140
Perfluorodecalin (FDC)	$C_{10}F_{18}$	40.3	142
Bis(perfluorohexyl) ethene (F-66E)	$\mathbf{C_6F_{13}CH=CHC_6F_{13}}$	**43.0**	**180**
Perfluorotripropyl amine(FTPA)	$(C_3F_7)_3N$	45.0	166

Perfluoro-octyl bromine (PFOB)	$C_8F_{17}Br$	50.0	210
Bis(perfluorobutyl) ethene (F-44E)	**$C_4F_9CH=CHC_4F_9$**	**50.0**	**230**

I.3. Polyfluorinated Internal Alkenes with Two Vicinal Vinylic Fluorines (X=Y=F)

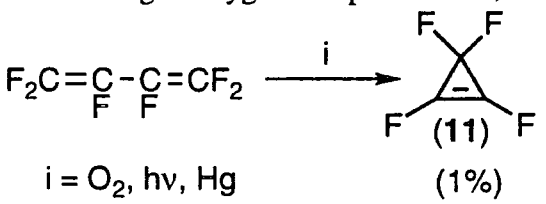


This type of compound is very well known, and for convenience, this review will be separated into two classes. The first is the polyfluorocycloalkene family, on which most work has been reported, and the second class is the acyclic derivatives.

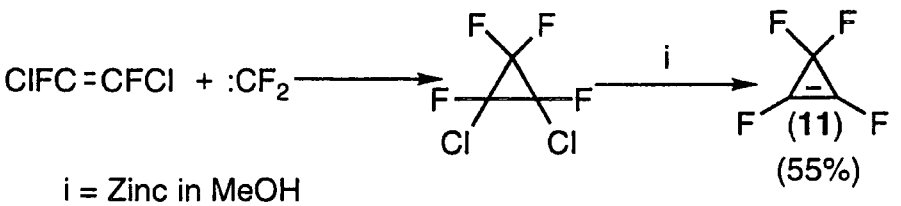
I.3.A. Synthesis of Polyfluorocycloalkenes

I.3.A.1. Cyclopropenes

In 1968, it was reported that perfluorocyclopropene (**11**) was produced as a minor product in the reaction between singlet oxygen and perfluoro-1,3-butadiene[50].

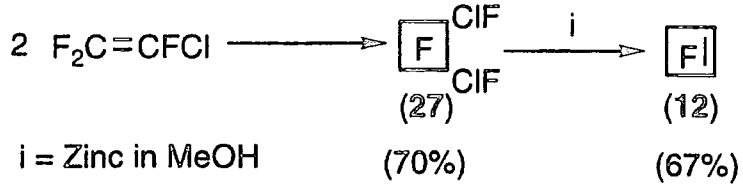


Perfluorocyclopropene (**11**) was prepared in 1969 via the addition difluorocarbene (from HFP oxide) to 1,2-dichlorodifluoroethene, followed by dechlorination[51-54].



I.3.A.2. Cyclobutenes

The four membered ring system is perhaps the most accessible to the fluorine chemist due to the (2+2) cycloadditions that many fluoroethenes will undergo[55]. It is probably no surprise that the first of these polyfluorocycloalkenes to be synthesised was perfluorocyclobutene (**12**) in 1947. The methodology involved the dimerisation of chlorotrifluoroethene, followed by dechlorination of the resultant cyclobutane (**27**)[56].

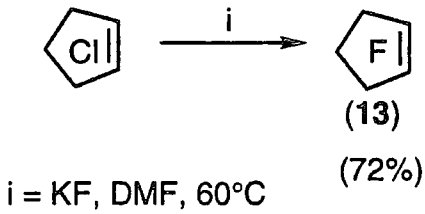


There are also several variations on this general route[57-59]. This compound can also be synthesised via the thermal dimerisation of iodotrifluoroethene in the presence of phosphorous[60], by the debromination of 1,2-dibromoperfluorocyclobutane[61], and by reaction of hexachloro-1,3-butadiene and HF over a zinc fluoride/alumina catalyst[62].

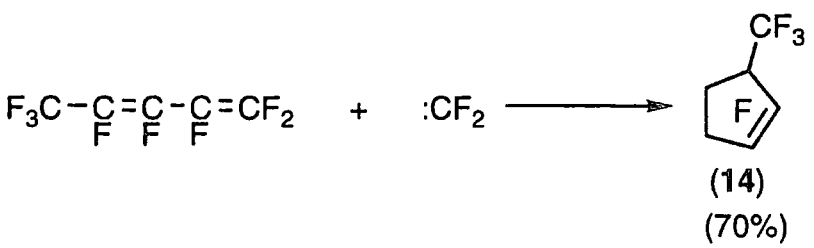
I.3.A.3. Cyclopentenes

The first synthesis of perfluorocyclopentene (**13**) was reported in 1945. Octachlorocyclopentene was fluorinated by antinomy pentafluoride to produce 1,2-dichloroperfluorocyclopentene, which in turn was reacted with fluoride ion to produce (**13**)[63, 64].

Later work showed that this synthesis could be achieved in one step, as octachlorocyclopentene will react with fluoride ion in an aprotic solvent, via a series of Sn2' allylic displacements of chlorine by fluorine[65].

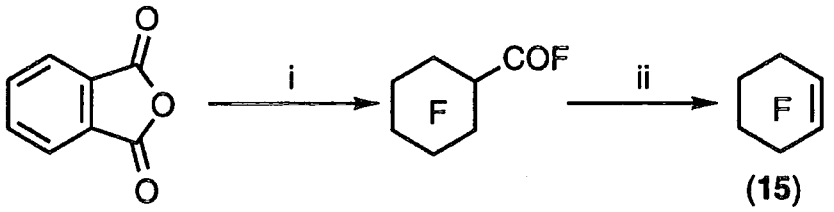


More recently, it has been reported that difluorocarbene (from difluoroaziridine) will react with perfluoropenta-1,3-diene to produce perfluoro-2-methylcyclopent-1-ene (**14**)[66].



I.3.A.4. Cyclohexenes

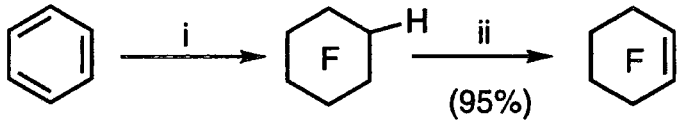
Perfluorocyclohexene (**15**) can be obtained via the acid fluoride derivative, which then undergoes quantitative pyrolysis[67].The acid fluorides are produced from hydrocarbon precursors, via electrochemical fluorination in liquid HF[68-71].



(15)

i = ECF
ii = Pyrolysis

It has also been shown by Tatlow and co-workers[72, 73], that the fluorination of benzene by cobalt trifluoride, gives a range of products, one of which is the undecafluorocyclohexane. This compound, when treated with bases such as KOH[72, 73], anion exchange resins[74] or thermally[75], will produce (15).



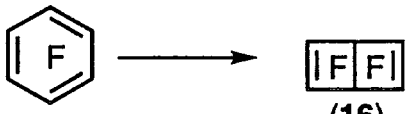
(15)

i = CoF_3
ii = Base

Other work has shown that fluorinations of benzene using cobalt trifluoride[76] and silver difluoride[77] also results in the formation of perfluorohexenes.

I.3.A.4.a. Polycyclic Cyclohexenes

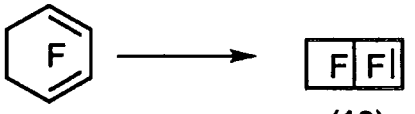
Fluorobenzene can be isomerised by irradiation to produce perfluorobicyclo[2.2.0] hexadiene (16)[78].



(16)

(60%)

Similarly, (10) can be produced from perfluorocyclohexa-1,3-diene[79].

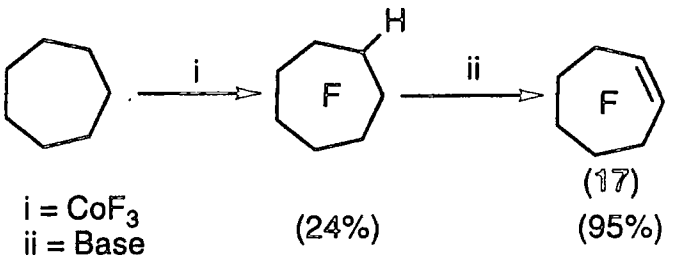


(10)

I.3.A.5. Cycloheptenes

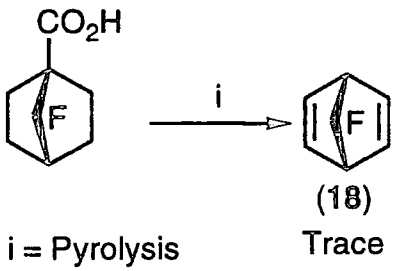
Even though reactions of perfluorocycloheptene were reported[80] in 1977, a synthesis of perfluorocycloheptene was not published until 1983. Tatlow and co-workers[81] fluorinated cycloheptane using cobalt trifluoride, and recovered tridecafluorocycloheptane,

which would eliminate hydrogen fluoride on treatment with base, to produce perfluorocycloheptene (17).

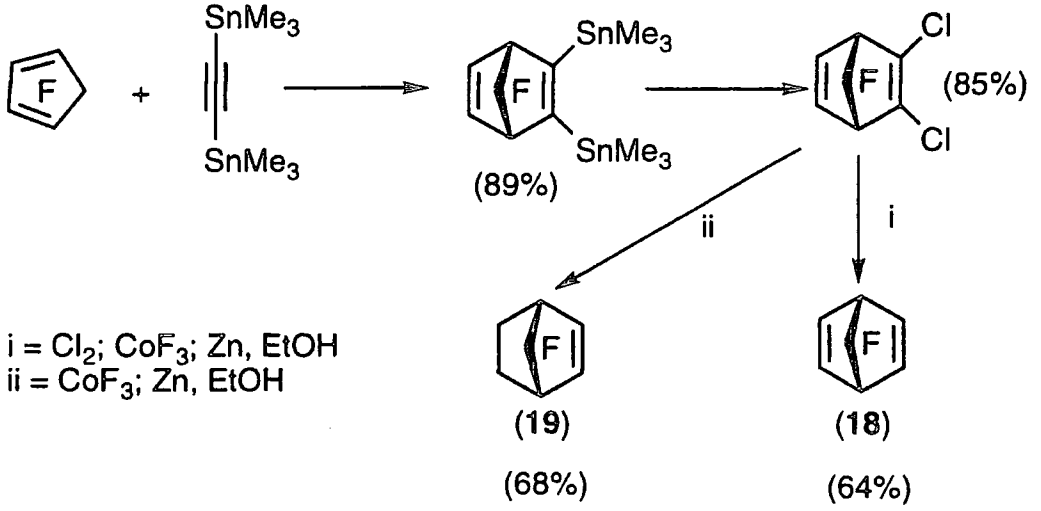


I.3.A.5.b. Bicycloheptenes

The first reported synthesis of perfluoronorbornadiene (18) is as a minor product from the pyrolysis of perfluorobicyclo[2.2.1]heptane-1-carboxylate[82].



It is also possible to prepare perfluoronorbornene (19) and perfluoronorbornadiene (18) via a slightly arduous route starting from perfluorocyclopentadiene[83]. The product from the cycloaddition between the cyclopentadiene and bis(trimethyltin)ethyne, can be halogenated to form a variety of 1,2 disubstituted perfluorinated norbornadienes. The dichloro- compound can be converted into (18) by a chlorination, fluorination and dechlorination procedure, whilst (19) is produced via fluorination and dechlorination steps.

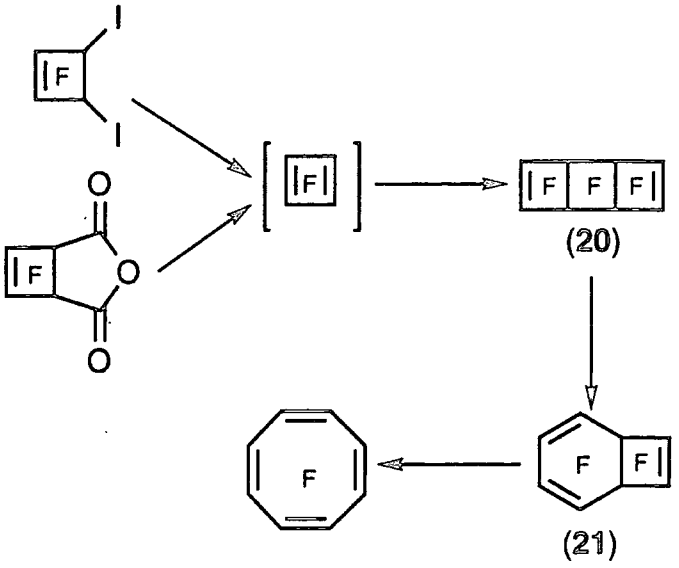


I.3.A.6. Octenes

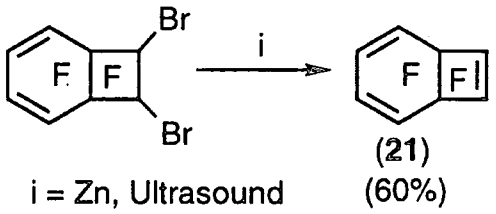
None are reported in the literature.

I.3.A.6.b. Polycyclic Octenes

In 1980, Lemal[84] and Haszeldine[85] reported routes to perfluorobicyclo[4.2.0]octa-2,4,7-triene (20), involving the formation of the perfluorocyclobutadiene[86], and this dimerises to give isolable (20), which can be smoothly converted into the bicyclic triene (21), and this compound will rearrange to produce perfluorocyclooctatetraene quantitatively.



In 1984, a more useful synthetic route to (21) was reported by Lemal and co-workers[87], and this synthesis involved the first examples of vicinal ultrasonic zinc dehalogenations.



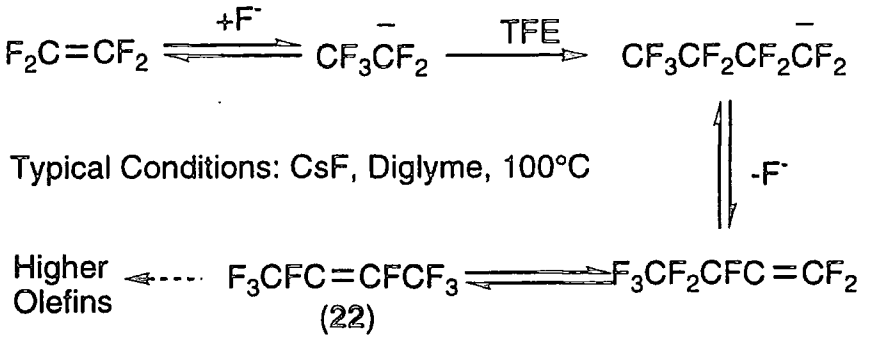
I.4. Synthesis of Acyclic Systems

Perhaps the best route to a large number and variety of higher fluoroalkenes is the 'building block' approach, where simple fluoroalkenes are oligomerised, usually by fluoride ion. The two most commonly used starting alkenes are tetrafluoroethene and hexafluoropropene.

I.4.A. Oligomerisation of Tetrafluoroethene[88-90]

The oligomerisation of tetrafluoroethene can produce hexamers and even higher oligomers, and can be difficult to limit to lower mass alkenes. The desired alkene which

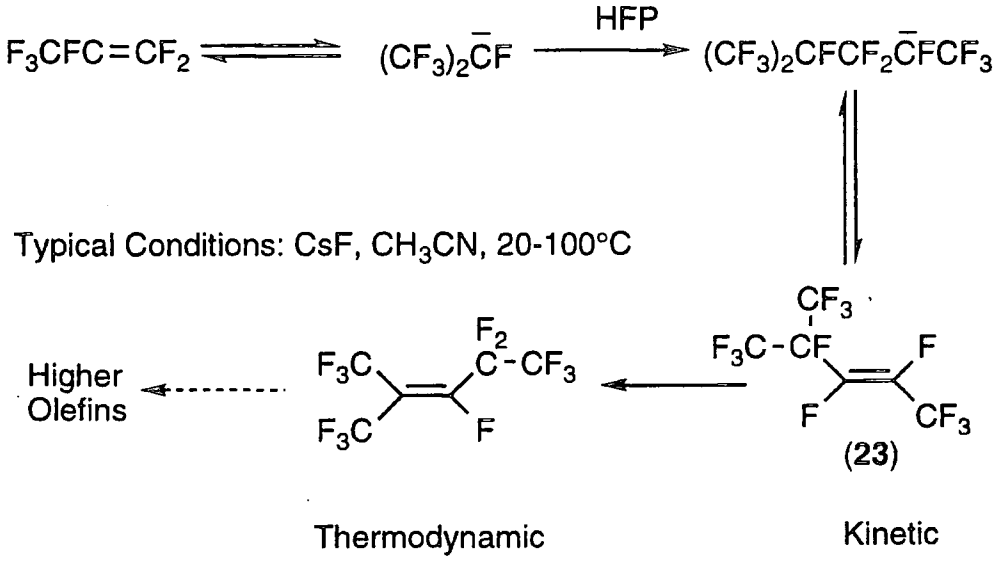
falls into this category is octafluorobut-2-ene (22), which is produced via a fluoride ion rearrangement of a TFE dimer .



(22)

I.4.B. Oligomerisation of Hexafluoropropene[91-95]

This oligomerisation is easier to control, and subtle variations in the reaction conditions can produce selected oligomers in high yields. The alkene of interest to this review is the kinetic dimer (23).

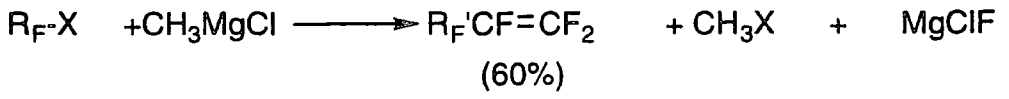


(23)

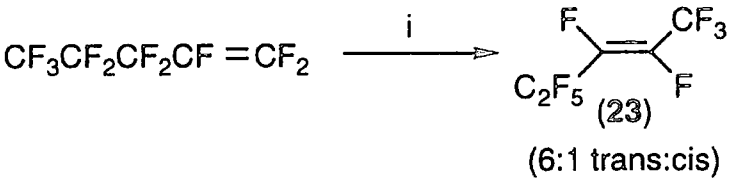
I.4.C. Other Methods

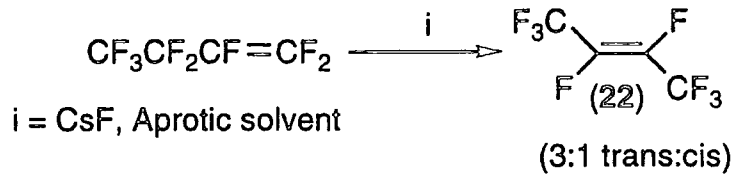
I.4.C.1 Fluoride ion Isomerisation

One of the easiest methods for producing an internal olefin is a fluoride ion induced isomerisation of a terminal alkene. The terminal alkene can be made by reacting a perfluoroalkyl halide with a Grignard reagent[96].

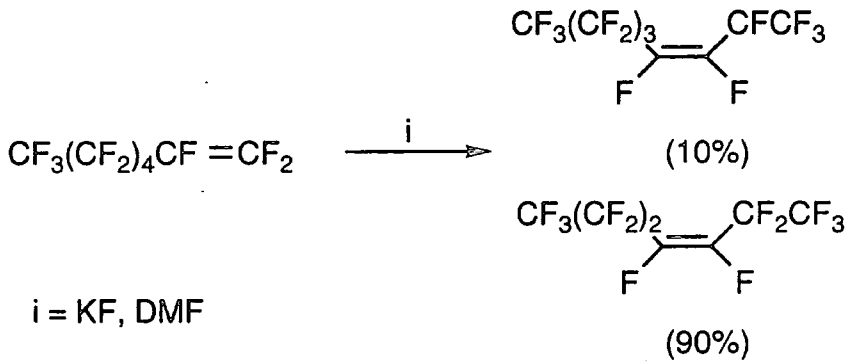


Fluoride ion induced isomerisation usually produces olefins with the perfluoroalkyl groups lying trans to one another, in order to minimise steric crowding[97, 98].





However, workers at Montpellier[99], have shown by NMR that it is possible to produce higher, straight chain perfluoroalkenes, in cis configurations.



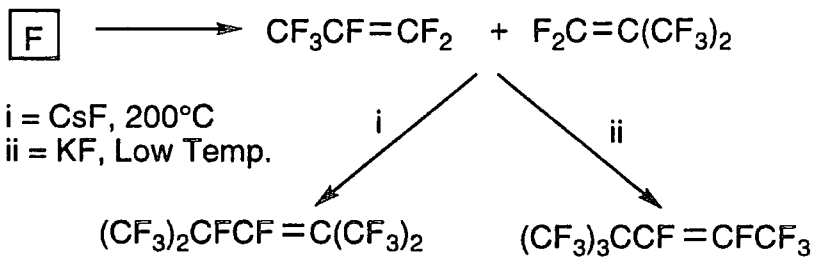
I.4.C.2. Co-oligomerisation

As well as oligomerising a single fluoroalkene, it is also possible to co-oligomerise two (or more) fluoroalkenes to produce members of this class of fluoroalkene.

I.4.C.2.a. Nucleophilic Co-oligomerisation

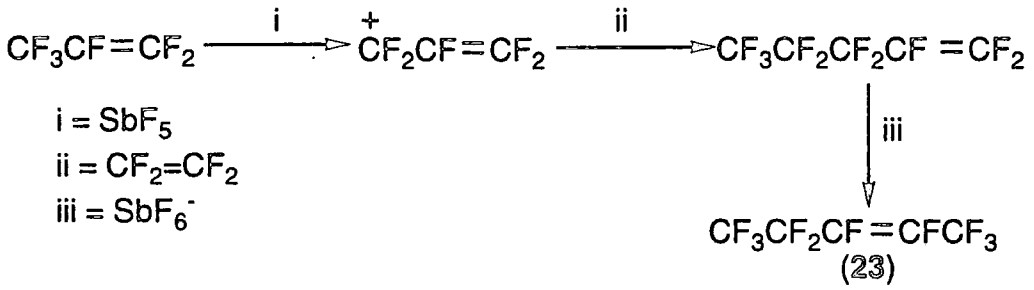
Generally, fluoride ion induced reactions of this type involve the reaction of the anion derived from the least substituted alkene, with the most substituted alkene. This is must be attributable to steric factors and final product stability, because it relies on the formation of the more unstable anion[100].

Despite this, other workers[101, 102] have shown that HFP and PFIB can indeed react with alternative regiochemistry to produce an internal alkene with two vinylic fluorines.



I.4.C.2.b. Electrophilic Co-oligomerisation

It is also possible to co-oligomerise TFE and HFP using antimony pentafluoride[103]. The terminal alkene is isomerised to the more stable internal alkene.



There has also been a recent patent from the Du Pont company[104] published where the same reaction occurs, but in the presence of Aluminium trihalides.

I.5. Reactivity

Generally, the cyclic fluoroalkenes are more reactive than their acyclic counterparts, and the reactivity tends to decrease with the increase in ring size. It is therefore tempting to attribute this extra reactivity to ring strain. Generally, both the cyclic and acyclic systems of this class undergo the same types of reaction, and wherever possible examples of both systems will be cited. However, the unique reactivity of the smaller ring systems, especially the perfluoro-cyclopropene and -butene, does give rise to some interesting reactions, and these will be commented on. It must also be pointed out that this overview is not comprehensive, and just intends to give the reader an introduction to the general reactivity of these systems.

I.5.A. Reaction with Nucleophiles

In contrast to their di-hydro analogues, perfluoroalkenes of this type are very reactive towards nucleophiles, and this area has been extensively reviewed in many books[9, 105, 106] and articles[107-110].

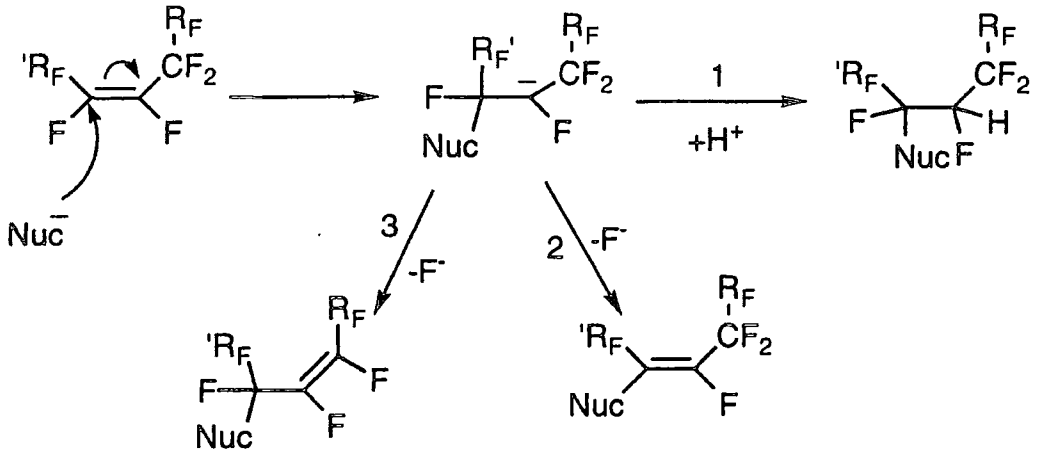
I.5.A.1. Reaction Pathways

There are three basic routes that a reaction between a fluoroalkene and a nucleophile can follow[9].

(1) Overall addition of the nucleophile across the double bond.

(2) Vinylic substitution of fluorine by the nucleophile.

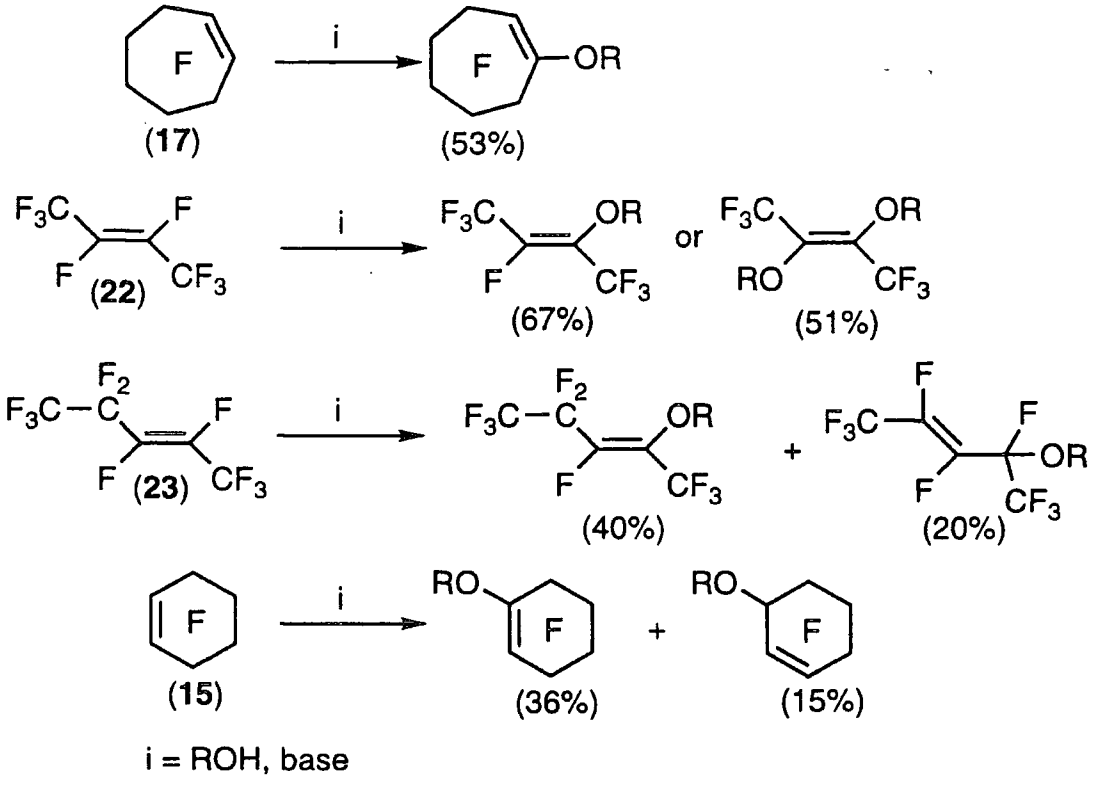
(3) Attack of the nucleophile accompanied by allylic displacement (S_N2') of fluoride.



Generally, it is observed that route (2) dominates[108].

I.5.A.2. Reaction with Oxygen Nucleophiles

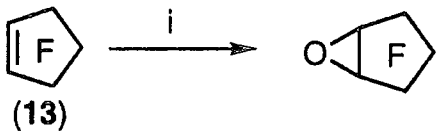
There are many examples of fluoroalkenes of this type reacting with oxygen nucleophiles[78, 111-114]. Generally, these systems are not reactive enough to react with neutral methanol, but require a base. Most reactions display simple vinylic substitution of fluorine, although a few examples show some evidence of allylic displacement of fluorine occurring, and it is possible to replace either one or both of the vinylic fluorines, as shown in the illustrative examples below[115-118].



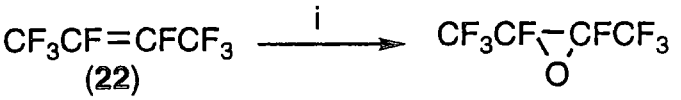
I.5.A.2.a. Epoxidations

Fluorinated epoxides are industrially useful as monomers for fluorinated polyethers[41, 119], and because of this, the early literature is dominated by patents. There are many methods of epoxidation for fluorinated systems, including the use of molecular oxygen[119, 120], potassium permanganate-liquid hydrogen fluoride[121, 122], and oxygen difluoride[123, 124] routes to name but a few. The two methods which shall be discussed are, perhaps, the most common and most applicable on a laboratory scale.

The first general route to fluorinated epoxides was published by Du Pont[125] in 1962. They reported the use of alkaline hydrogen peroxide at low temperatures. This methodology has been used by other workers[126, 127].



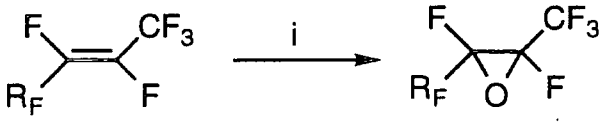
(13)



(22)

i = H_2O_2, KOH, -40°C

Later work[128, 129] in 1979, involved the use of metal hypohalites, for example, calcium hypochlorite, which were found to give best results in polar aprotic solvents, such as diglyme and acetonitrile[130, 131]. It has been shown that these epoxidations proceed with retention of stereochemistry[128].



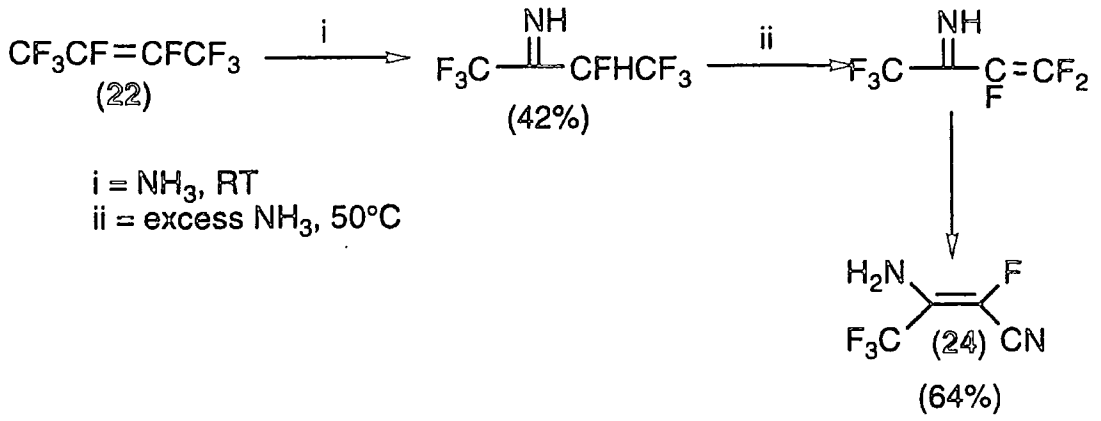
i = $Ca(OCl)_2$, CH_3CN (93%)

I.5.A.3. Reaction with Nitrogen Nucleophiles

There are again many literature examples showing that fluoroalkenes of this type will react readily with nitrogen nucleophiles, and several illustrative examples are cited.

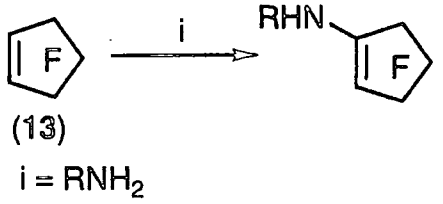
I.5.A.3.a. Reaction with Ammonia

Perfluorobut-2-ene (**22**)[132] and other fluoroalkenes[133-135], will react with ammonia to produce imines at room temperature, Above 50°C, further reaction occurs with (**22**), resulting in the formation of an amino-butene nitrile (**24**).



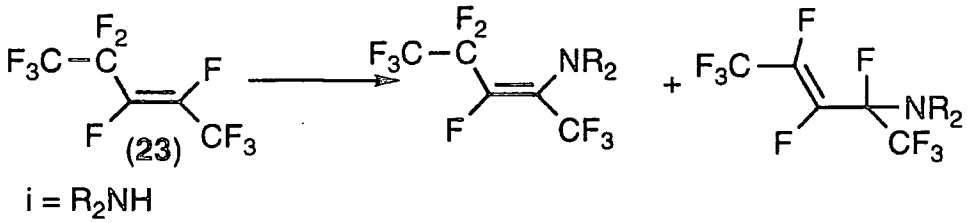
I.5.A.3.b. Reaction with Primary Amines

It has been shown that perfluorocyclopentene[136], and other fluoroalkenes[133, 135, 137-139], will react with primary amines to produce the corresponding vinylamines.



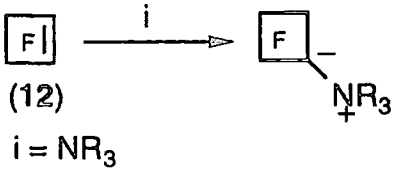
I.5.A.3.c. Reaction with Secondary Amines

Perfluoropent-2-ene (23)[140] and other fluoroalkenes[135, 138, 139, 141-145], will react with dimethylamine to produce a mixture of products formed by vinylic and allylic displacement of fluoride ion.

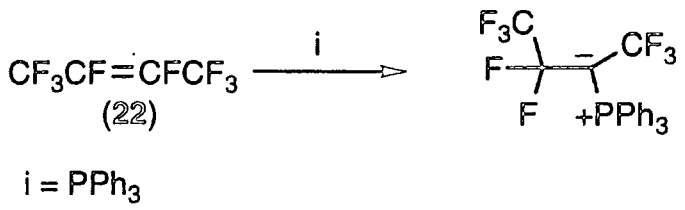


I.5.A.3.d. Reaction with Tertiary Amines

It was generally believed that fluoroalkenes of this type were unreactive towards tertiary amines, until most cyclic members were shown to form stable ylids[146, 147]. The first observed was the reaction between (12) and triethylamine[148] in 1951.



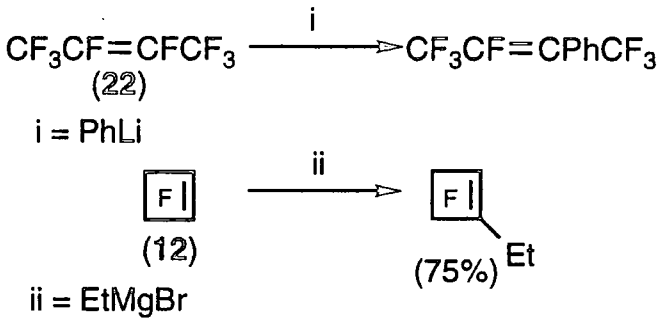
Later work has shown that triphenyl phosphine will also produce ylids from cyclic[149, 150] and acyclic[151] systems, and the ylid structure has been confirmed by an X-ray crystal structure[149].



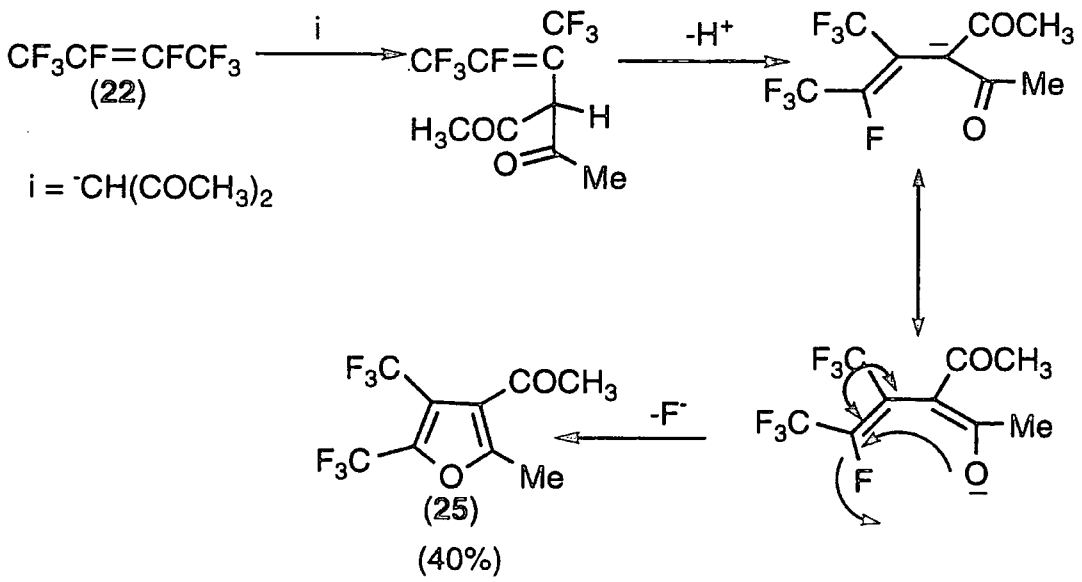
I.5.A.4. Reaction with Other Nucleophiles

I.5.A.4.a. Reaction with Carbon Nucleophiles

Organometallic reagents[29, 78, 143, 152-155] and enolate anions[156] will react with fluoroalkenes of this type.



An interesting production of furan (25) occurs in the reaction between diethylmalonate and (22)[156].



I.5.A.4.b. Reaction with Hydrides

Fluoroalkenes of this type react with sodium borohydride[27, 29, 78, 143] and lithium aluminium hydride[25, 26, 157] to form either monohydro- or dihydroalkenes. These reactions

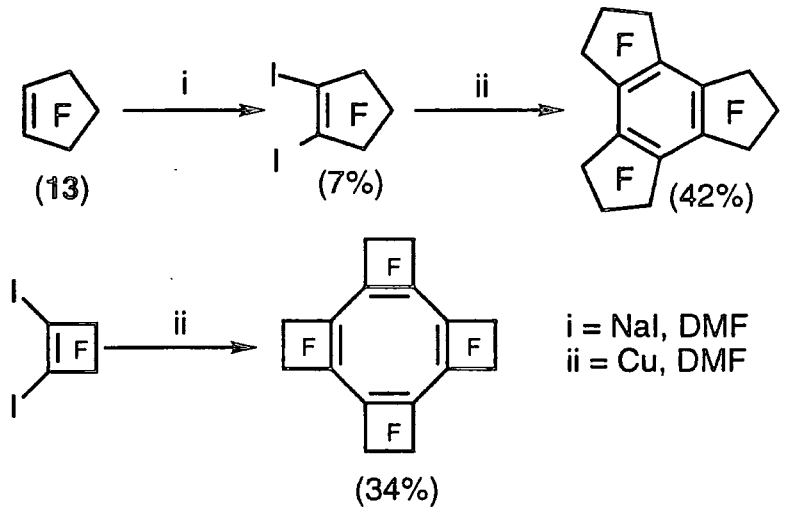
have either been discussed in section earlier concerning the syntheses of X=Y=H systems, or will be mentioned in the synthesis of systems where X=F, Y=H later.

I.5.A.4.c. Reaction with Thiols

The reactions of thiols[158, 159] can be considered analogous to those for alcohols.

I.5.A.4.d. Reaction with Iodide

Iodide ion will replace vinylic fluorine[160] to yield products that are ideal for coupling reactions, and this methodology has seen the development of some interesting large perfluorinated cyclic systems[161-163].



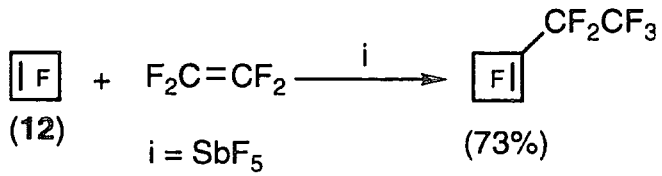
A crystal structure of the tetra-ene has been published[161], and shows that the eight membered ring is planar, and that there is substantial delocalisation of electron density in the ring.

I.5.B. Reaction with Electrophiles

Generally, perfluorinated alkenes of this type will not react with electrophiles[9].

I.5.B.1. Reaction with Antimony Pentafluoride

The only exception found is with (12), which is not dimerised by antimony pentafluoride[164], but under the same conditions, reacts with tetra- and tri-fluoroethanes (and HFP) to produce 1:1 adducts[165].



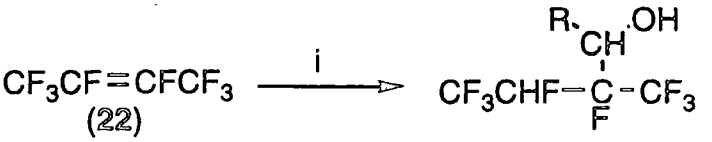
I.5.C. Addition Reactions

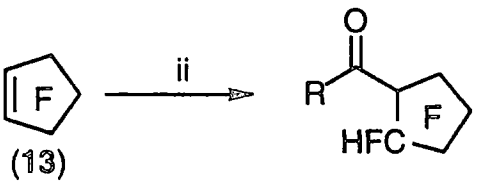
This will include free radical additions and oxidation reactions.

I.5.C.1. Free Radical Reactions

I.5.C.1.a. Hydrocarbons

Reagents such as alcohols, aldehydes and ethers will readily add across the double bonds of this class of perfluoroalkenes, via initiation by gamma rays[166, 167].





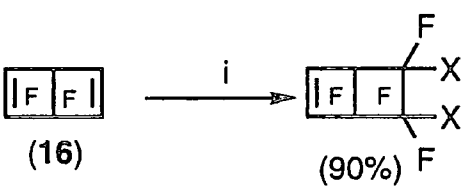
(13)

(87%)

i = RCH_2OH, γ
ii = RC(O)H, γ

I.5.C.1.b. Halogens

Systems of his type will add halogens across their double bonds[78, 143, 168, 169] under free radical conditions.



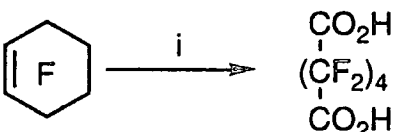
(16)

(90%)

i = X_2, hν
X = Cl, Br

I.5.C.2. Oxidations

The oxidation of the double bond of these type of compounds contains numerous reports in the literature[51, 63, 170, 171], and results in a dicarboxylic acid in the case of cyclic derivatives.

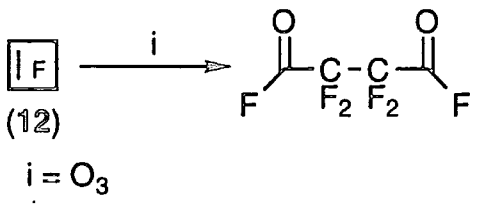


(15)

(75%)

i = MnO_4^-

Oxidation with ozone occurs with (12) to yield a diacid fluoride[172].

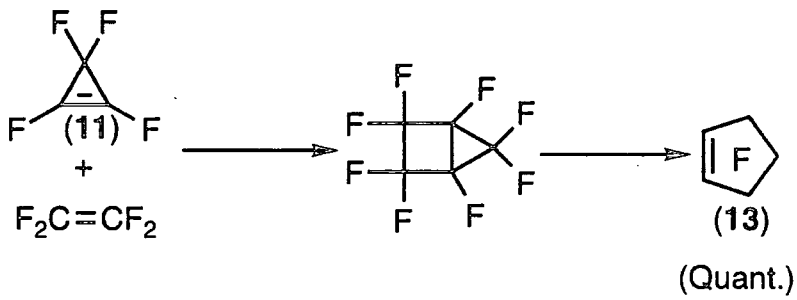


I.5.D. Cycloadditions

These reactions are divided into three classes: (2+2) cycloadditions; (4+2) cycloadditions and reactions involving 1,3 dipolar species

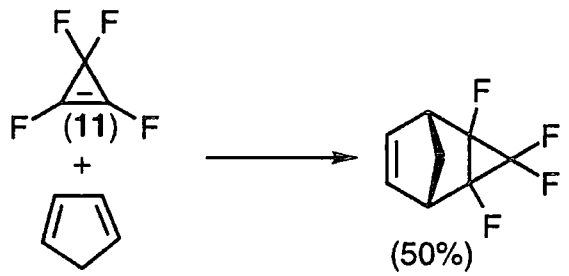
I.5.D.1. (2+2) Cycloadditions

Generally this type of cycloaddition do not occur with this class of fluoroalkene[9]. However, one example is the reaction of TFE and (**11**), which eventually results in the quantitative formation of (**13**)[54].

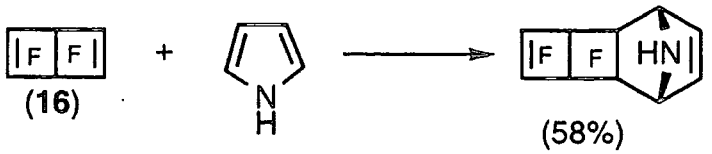


I.5.D.2. (4+2) Cycloadditions

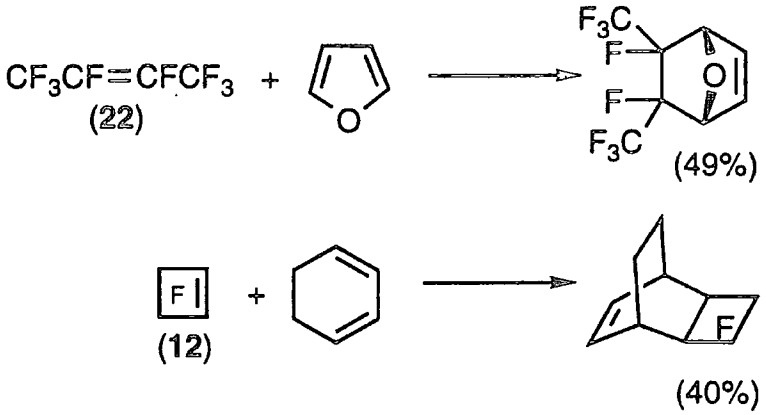
It was generally believed that alkenes of this class were unreactive as dienophiles, with only the more strained cycloalkenes displaying any reactivity[173].



An especially reactive dienophile is (**16**), which even forms a cycloadduct with pyrrole[174].

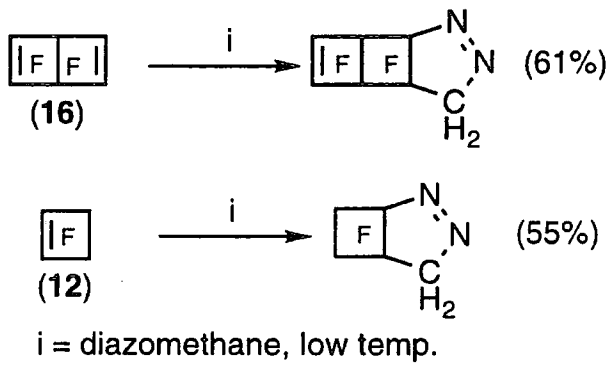


However, recent Russian work[175, 176] has shown that both (22) and (12) will react with classical dienes such as furan and cyclohexadiene at moderate temperatures.



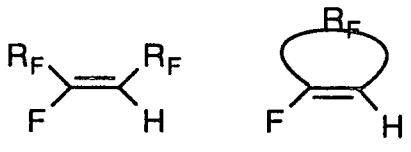
I.5.D.3. (1,3) Dipolar Reactions

A reactivity order of $(R_F)_2C=C(R_F)_2$ >> $(R_F)_2C=CFR_F$ >> $(R_F)_2C=CF_2$, $R_FCF=CFR_F$, $CF_3CH=CHCF_3$ > $CF_3CH=CFCF_3$ >> $CF_3CF=CFCF_3$ has been established for polyfluoro olefins reacting with diazomethane by Chambers and co-workers[20]. Thus, it is not surprising that only the smaller perfluoro (poly)cycloalkenes display any reactivity with 1,3 dipoles[177-179]. Perfluorocyclohexene and perfluorobutene do not react, and perfluorocyclopentene will only react on long exposure to dipoles[20].



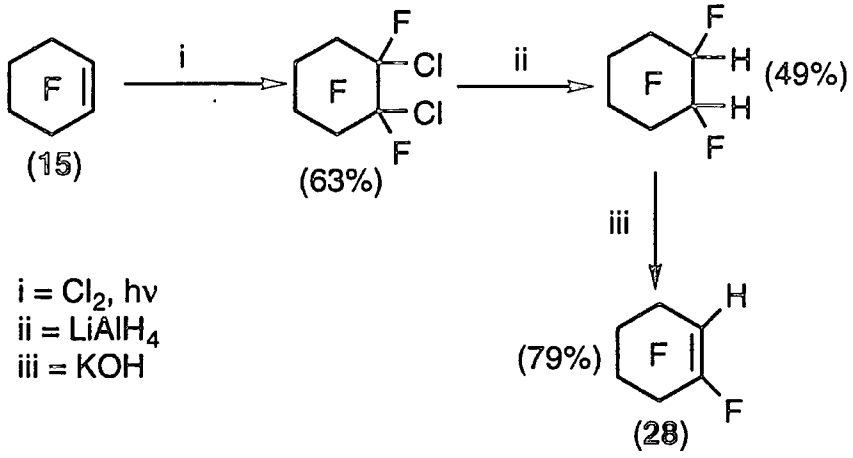
The fact that diazomethane is more reactive towards 3,3,4,4-tetrafluorocyclobutene than perfluorocyclobutene confirms that vinylic fluorine atoms are not enhancing to dipolarity[180].

I.6. Polyfluorinated Internal Alkenes with Vicinal Vinylic Fluorine and Hydrogen (X = F, Y = H)

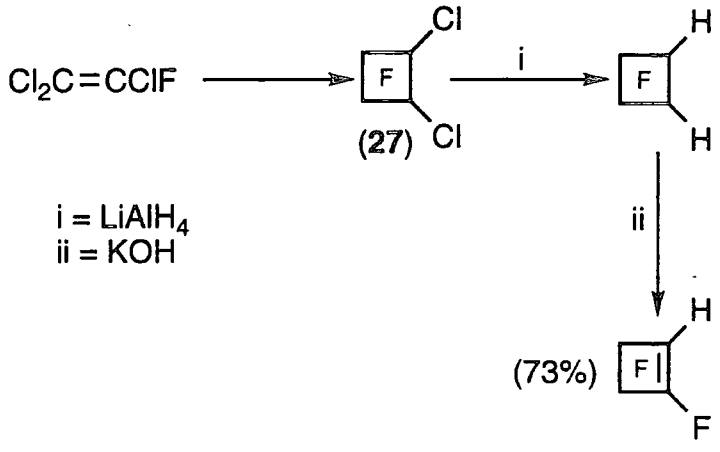


I.6.A. Synthesis

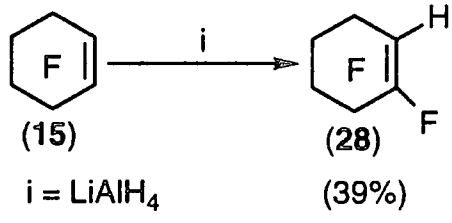
The first reported synthesis was in 1954, starting from (15)[181].



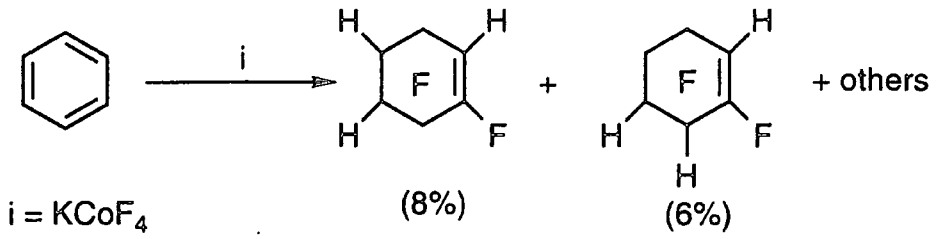
The next synthesis was in 1961, using identical methodology, starting with the trifluorochloroethene dimer (27)[25].



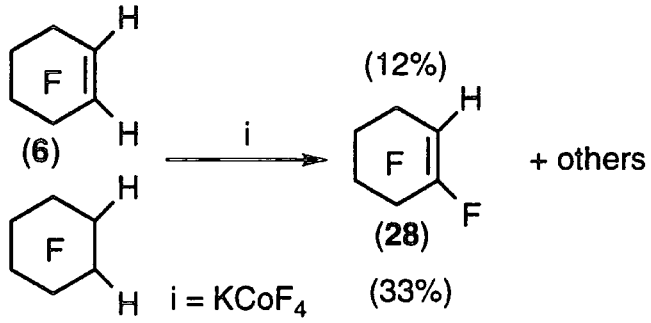
Later work in 1963 showed that vinylic fluorine in (15) could be replaced by hydrogen via reaction with lithium aluminium hydride[26].



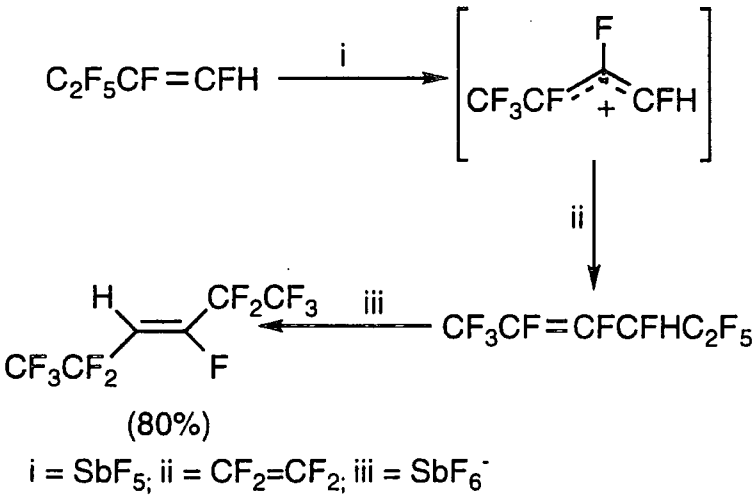
The fluorination of benzene by potassium tetrafluorocolbaltate results in numerous products[28], two of which are shown below.

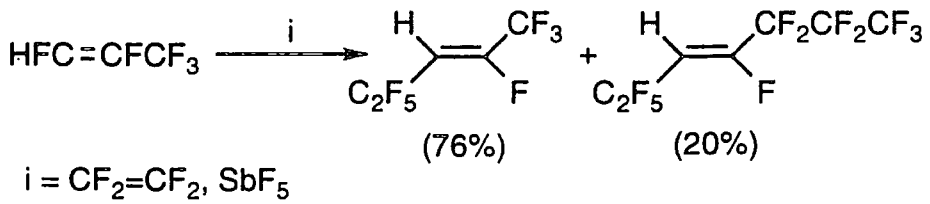


In 1982, other workers[37] showed that the further fluorination of other products from the above reaction, would afford fluoroalkenes of this class.

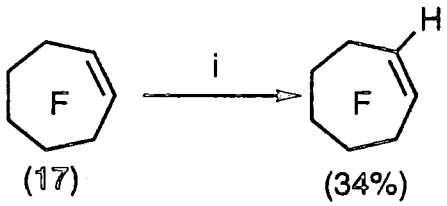


In the same year, Russian workers[182] published a general route to alkenes of this type, by electrophilic co-oligomerisation using polyfluorinated starting alkenes, antimony pentafluoride and TFE.





Workers continued to demonstrate the applicability of the $LiAlH_4$ reaction, and in 1983 they published a route starting from (**17**)[81].



(17) (34%)

i = $LiAlH_4$

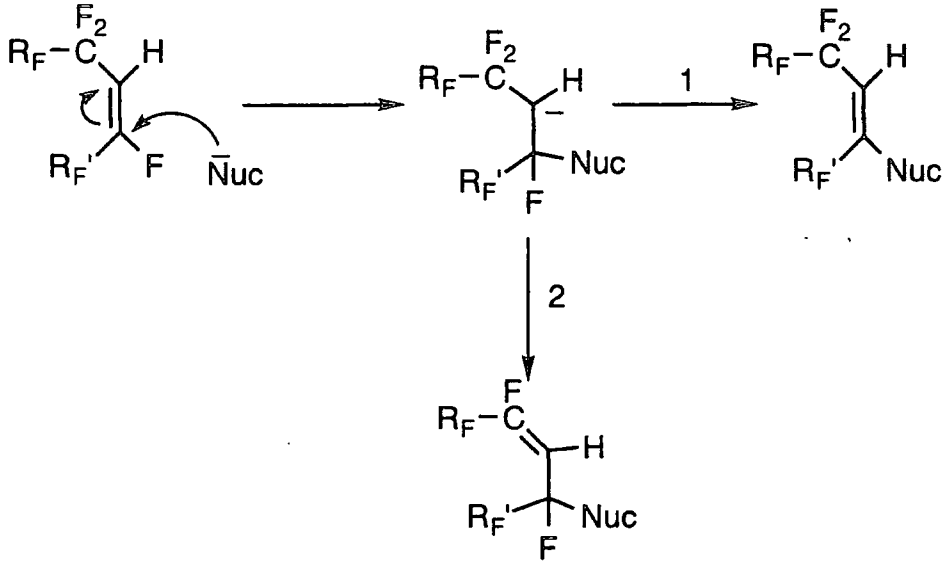
I.6.B. Reactivity

I.6.B.1. Reactions with Nucleophiles

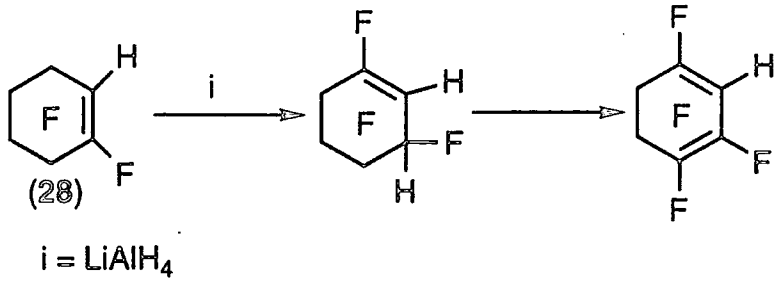
From the previous two reviews of alkene reactivity, we may expect that this class of alkene will be susceptible to nucleophilic attack at the site of the vinylic fluorine. The anion produced can then follow two pathways:

(1) The fluorine at the site of attack can be eliminated, resulting in overall vinylic fluorine substitution.

(2) An allylic fluorine can be eliminated, resulting in S_N2' fluorine substitution.

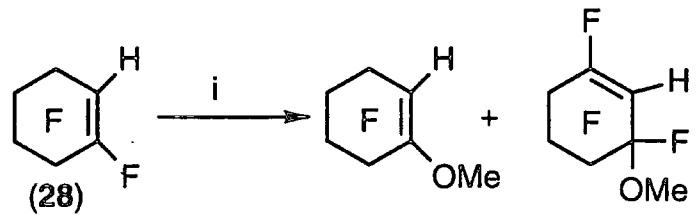


The first reported reaction of this class of alkene was reported in 1963[26]. In the reaction of perfluorocyclohexene with $LiAlH_4$, further reaction of hydride with (**28**) results in a diene, which is formed by initial hydride attack on the site of vinylic fluorine, followed by elimination of allylic fluorine producing a compound containing two hydrogens. This compound will eliminate hydrogen fluoride to produce the diene.



i = $LiAlH_4$

Two years later, (28) was reacted with methoxide ion, and the products were shown to be a 1:1 mixture of products formed from vinylic and allylic displacement of fluorine[183].

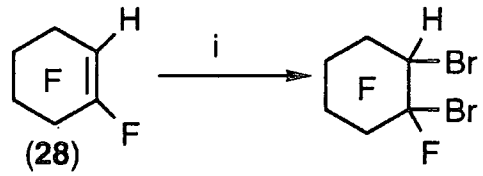


i = MeO^-

I.6.C. Free Radical Reactions

I.6.C.1. Halogenations

In 1965, bromination of (28) under free radical conditions was reported[184]. The reaction of the product with potassium hydroxide gave seven products, one of which was the desired 1,2-dibromoperfluorocylohexene.



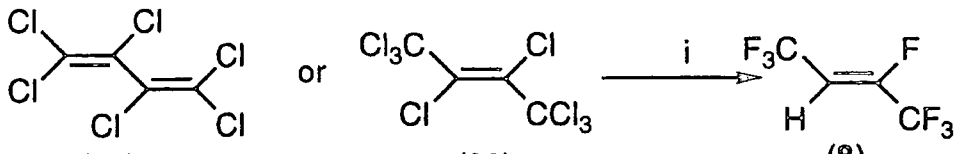
i = Br_2, hv

I.7. Literature Review on 2*H*-Heptafluorobut-2-ene (8)

Due to its obvious relevance to this thesis, this review merits a section of its own.

I.7.A. Synthesis of (8)

The synthesis was reported by Maynard in 1963. Both hexachlorobutadiene (29) and octachlorobutene (30) would produce (8) by reaction with potassium fluoride in NMP.



(29) (30) (8) (65%) (20%)

i = KF, NMP

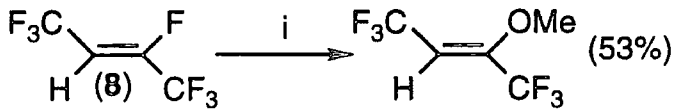
Later work from these laboratories, showed that better yields (85%) could be achieved by the use of sulpholane.

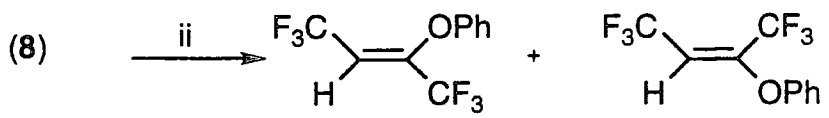
I.7.B. Reactivity

I.7.B.1. Reactions with Nucleophiles

I.7.B.1.a. Oxygen Nucleophiles

The reaction of (8) with methoxide and phenoxide were performed in these laboratories[185]., and the products were shown to be exclusively formed via vinylic substitution of fluorine.





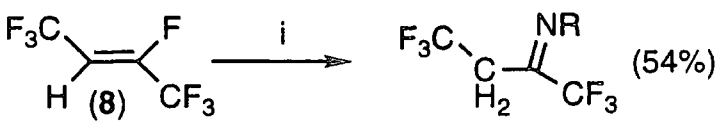
(55%) (18%)

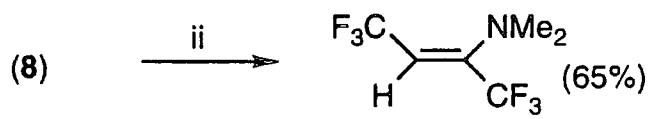
i = MeOH, base
ii = PhOH, base

The phenoxide reaction gives a mixture of (Z) and (E) isomers.

I.7.B.1.b. Nitrogen Nucleophiles

Later work in these laboratories investigated the reaction of (8) with nitrogen nucleophiles, in an attempt to synthesis some compounds for electrochemical studies[186].



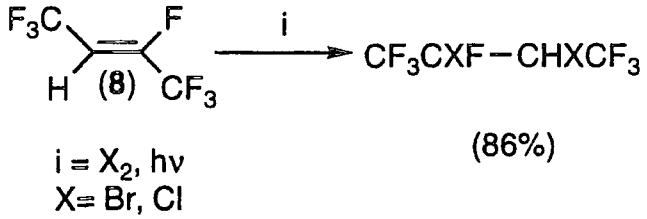


i = RNH_2
ii = Me_2NH

I.7.C. Free Radical Reactions

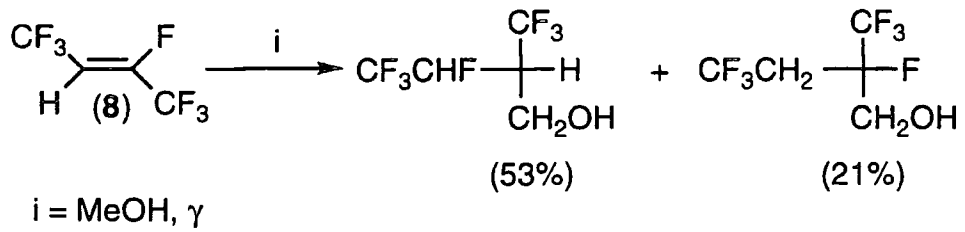
I.7.C.1. Halogenation

Addition of chlorine and bromine have been performed under free radical conditions[187].



I.7.C.2. Hydrocarbons

Also in 1967, methanol was added free radically, and a mixture of products was observed[187].



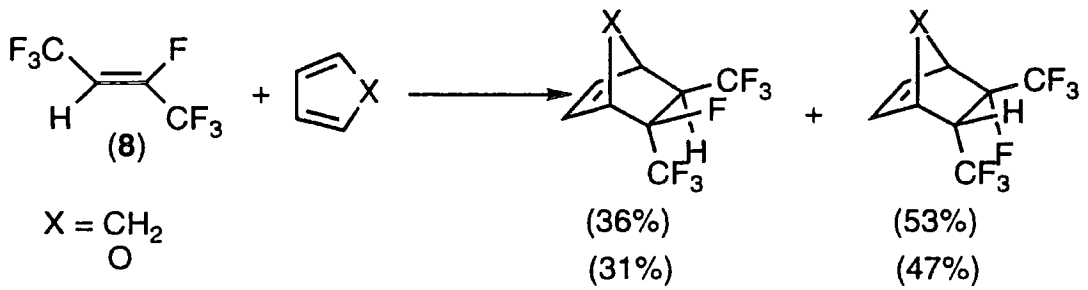
Recently, as described earlier, Odello[31] has shown that tributyltin hydride will convert (**8**) into hexafluorobutene (**9**).

I.7.D. Cycloadditions

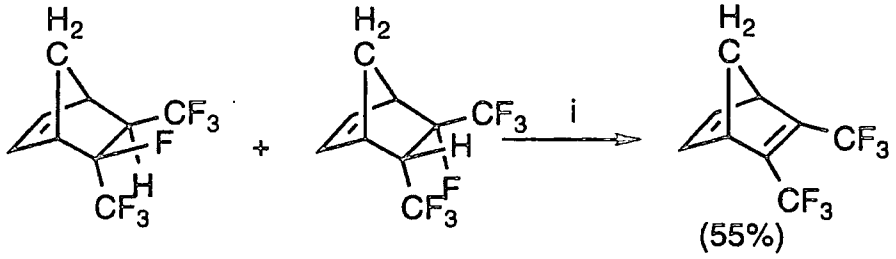
These include (4+2) and 1,3 dipolar cycloadditions.

I.7.D.1. (4+2) Cycloadditions

Recent work in this laboratory[31, 188] has shown that (**8**) will undergo cycloaddition with furan and cyclopentadiene to give mixtures of isomers, with either fluorine or hydrogen occupying the exo position.



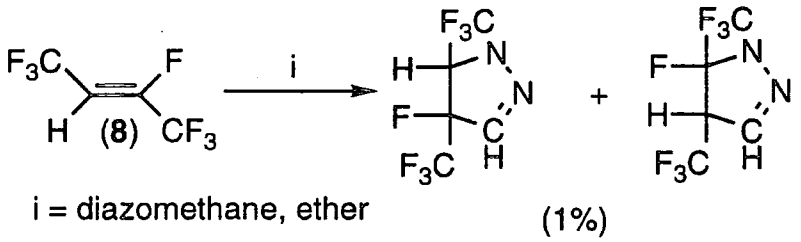
The elimination of HF from these adducts was only successful in the case of the cyclopentadiene adducts.



This was attributed to ring opening complications of the oxygen bridge in the furan adducts.

I.7.D.2. 1,3 Dipolar Cycloadditions

As mentioned briefly previously, (**8**) reacted in poor yield with diazomethane, to give products tentatively identified as two Δ^2-dihydropyrazoles[20].



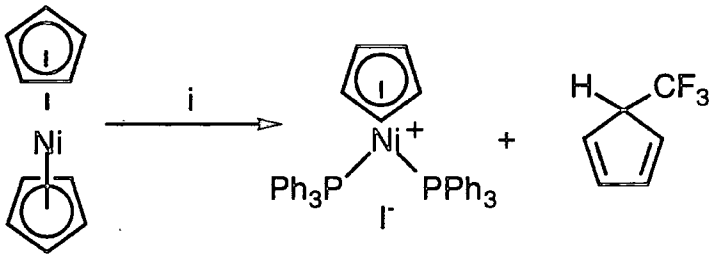
Chapter Two

This chapter is concerned with the synthesis of 2*H*-heptafluorobut-2-ene (8), and during this study, several interesting polytrifluoromethylated-cyclopentadienes and -cyclopentadienides have been synthesised. The following is a review of the sparse literature on polytrifluoromethylated cyclopentadienes and cylopentadienides.

II.1. Review of Cyclopentadienes Bearing Trifluoromethyl Groups

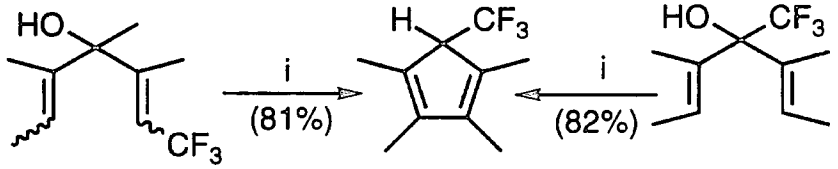
II.1.A. One Trifluoromethyl Group

There are two reported syntheses in the literature. The first was observed in 1978 as an ether solution, but never isolated[189].



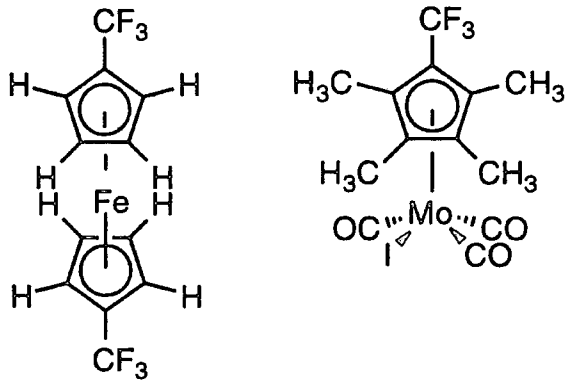
i = CF_3I, $2PPh_3$

The second was by Gassman[190] in 1992, using a route based on the ring closure of a pentadienyl cation.



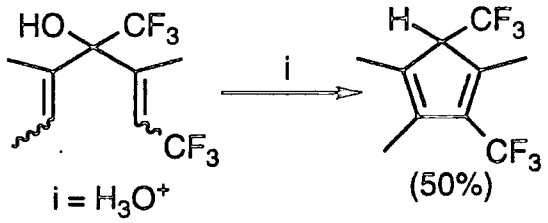
i = H_3O^+

Transition metal complexes have been produced from both ligands[190, 191].



II.1.B. Two Trifluoromethyl Groups

Similar methodology by Gassman[190] provides the only example.



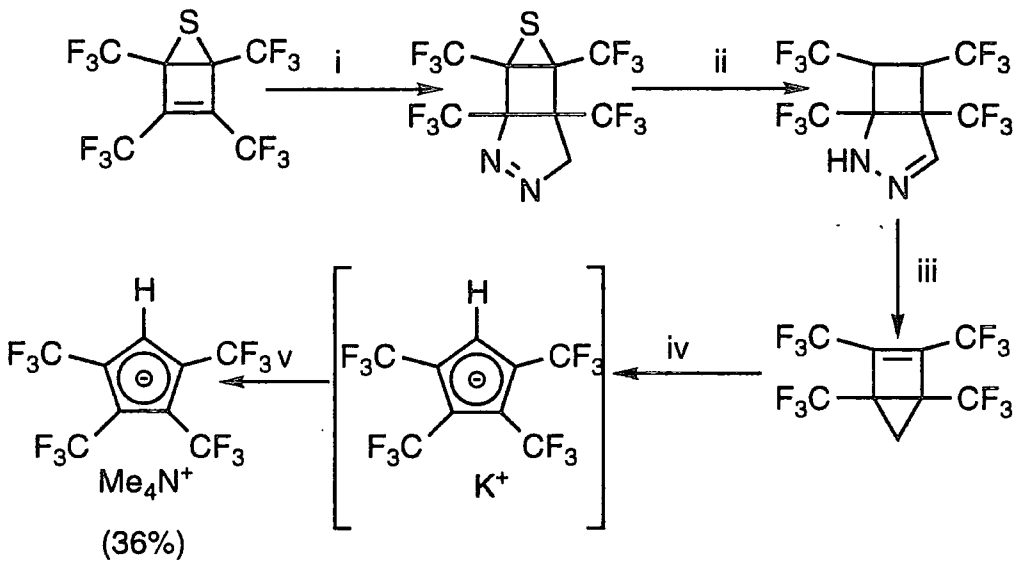
No transition metal complexes have been described.

II.1.C. Three Trifluoromethyl Groups

There are no direct syntheses published, but several examples are reported via tetrakis(trifluoromethyl) cyclopentadienes, and discussed later.

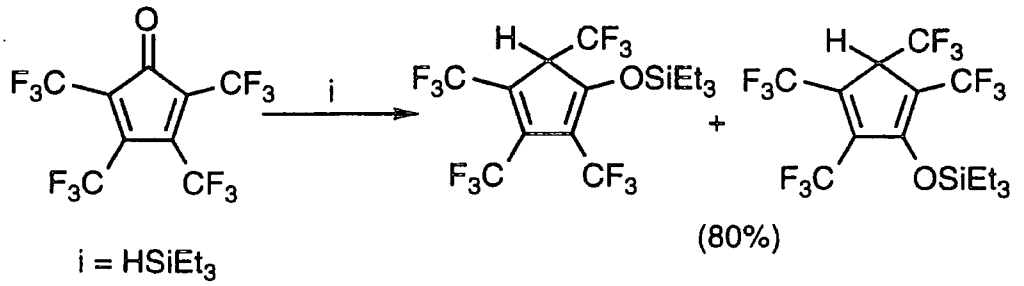
II.1.D. Four Trifluoromethyl Groups

The first route[192] was reported in 1983 using a strategy previously devised by Lemal[193].

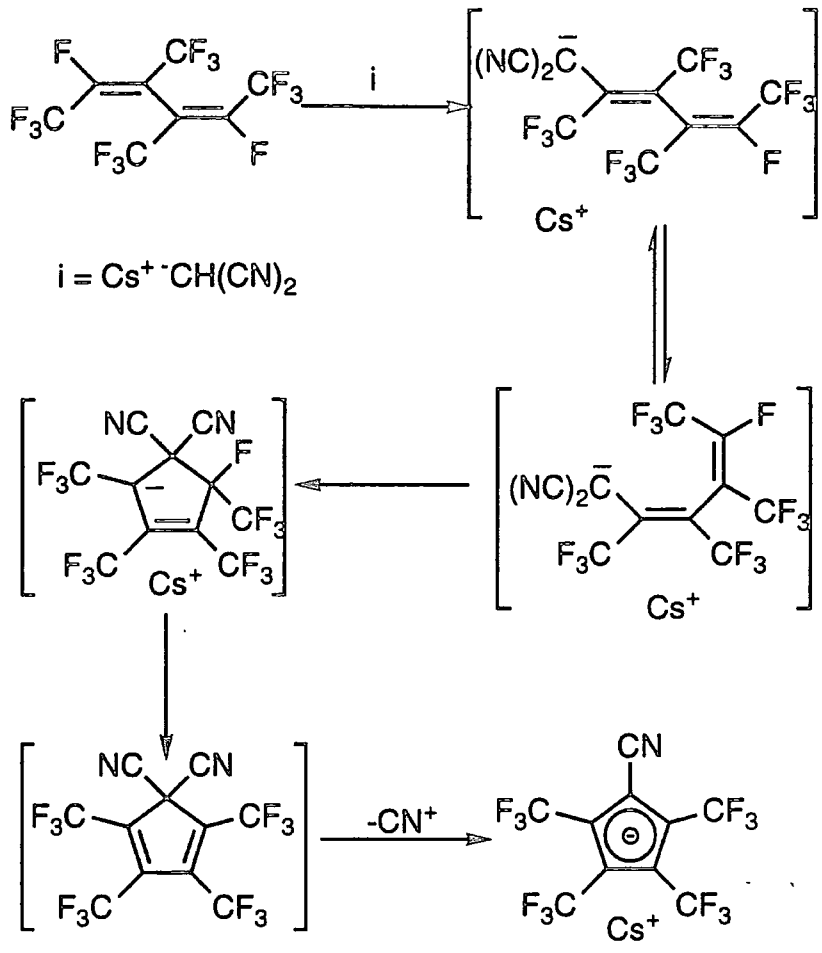


i = CH_2N_2; ii = PPh_3; iii = hν, iv = hν, K_2CO_3; Me_4NBr

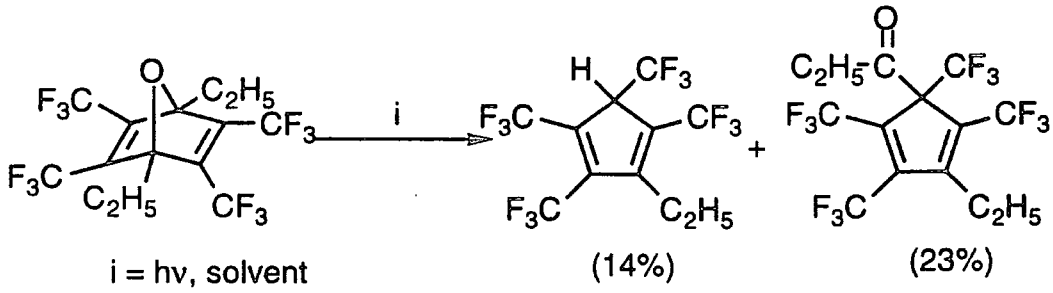
The next report was in 1989, concerning the addition of triethylsilane to tetrakis(trifluoromethyl) cyclopentadienone[194].



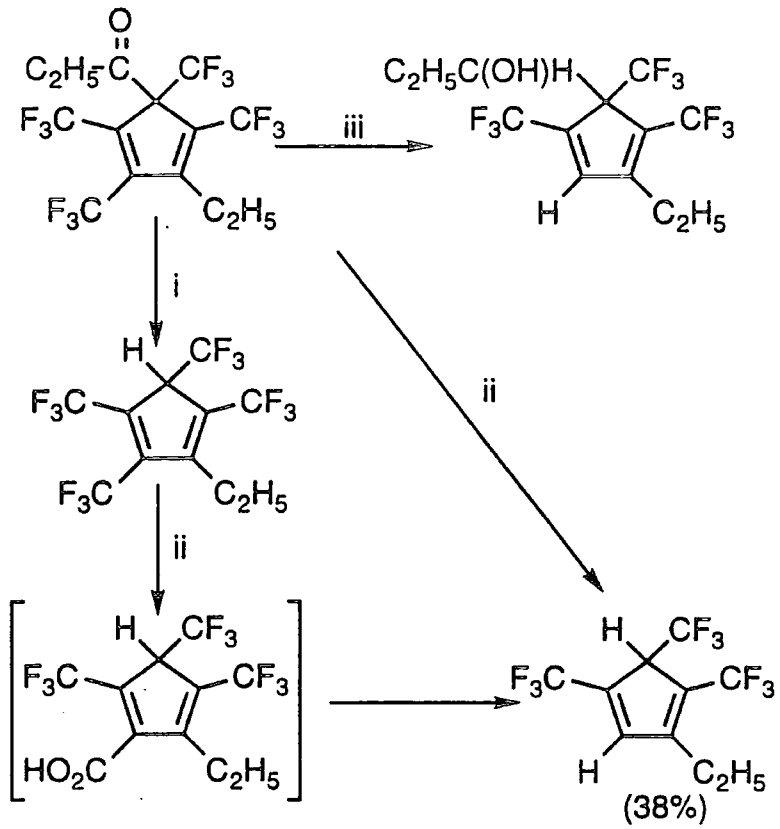
Workers from this laboratory[195] reported the synthesis of tetrakis(trifluoromethyl)cyano cyclopentadienide in 1990.



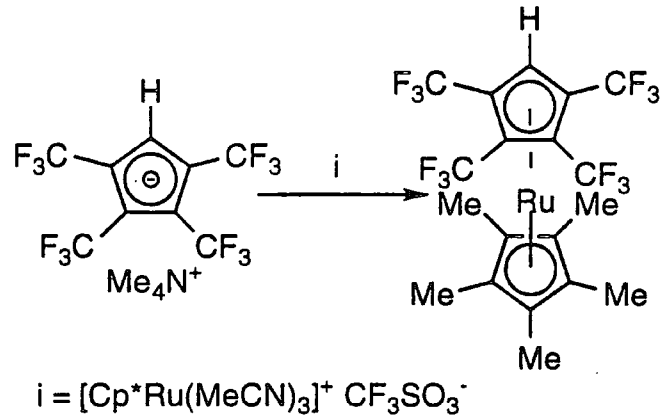
Muramatsu and co-workers[196] showed in 1992 that the photolysis of the polyfluorinated endoxide would produce two new tetrakis(trifluoromethyl)cyclopentadienes.



It was possible to hydrolyse a trifluoromethyl group from both of these new cyclopentadienes, to produce two novel tris(trifluoromethyl) cyclopentadienes.



Burk and co-workers[194, 197] have been successful in producing several tetrakis(trifluoromethyl)cyclopentadienyl complexes.

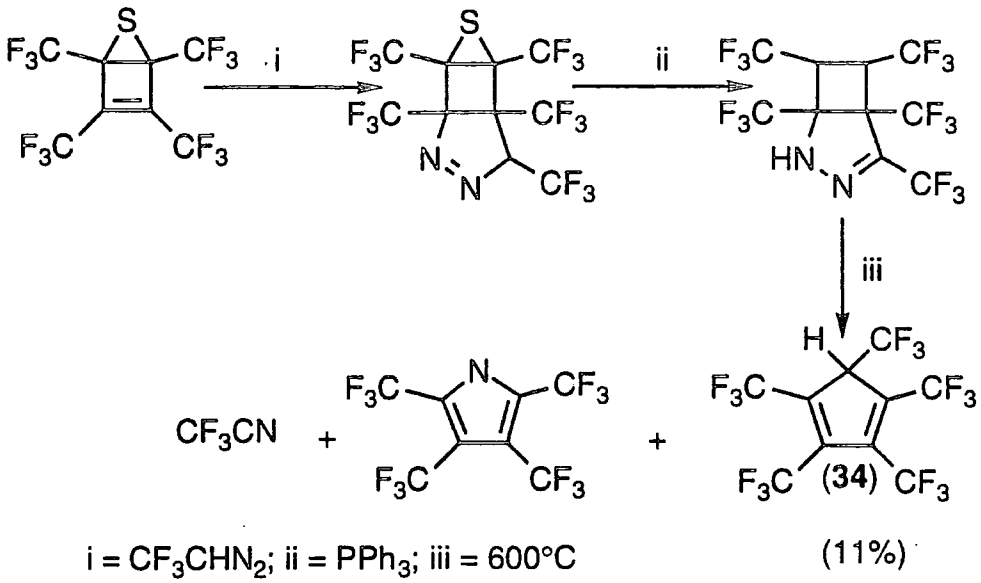


They reported that these ligands would not displace normal metal halides (e.g. $FeCl_2$) because the trifluoromethyl groups render the ligands too un-nucleophilic. They therefore had to employ cationic metal centres with loosely bound solvent molecules to achieve displacement.

II.1.E. Five Trifluoromethyl Groups

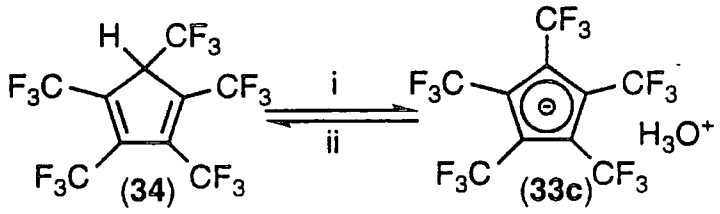
There is only one example of a synthesis of this type of compound in the literature[193], and the compounds were not isolated. The lengthy synthesis started from a

tetrakis(trifluoromethyl)thiophene derivative, and the final pyrolysis step was " performed successfully on several occasions, but on others. minuscule amounts of cyclopentadiene (**34**) were obtained."



i = CF_3CHN_2; ii = PPh_3; iii = 600°C

They showed that (**34**) was deprotonated in aqueous solution. Acidity calculations provided a pKa value of -2, which is stronger than nitric acid, and they reported (**34**) to be the strongest organic acid without the aid of conjugating substituents.



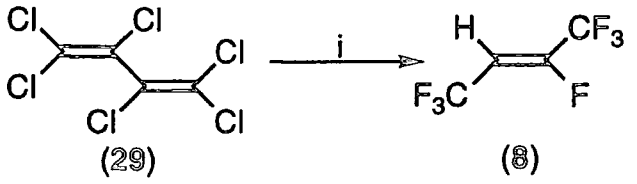
i = H_2O; ii = H_3O^+

II.1.F. Conclusions

From this brief overview, it can be seen that there are no general synthetic routes to polytrifluoromethylated cyclopentadienes. The transition metal chemistry employing trifluoromethyl containing cyclopentadienyl ligands is also very scarce, despite the fact that many transition metal catalysed reactions have been shown to benefit from electron withdrawing substituents on the cyclopentadienyl ligand.

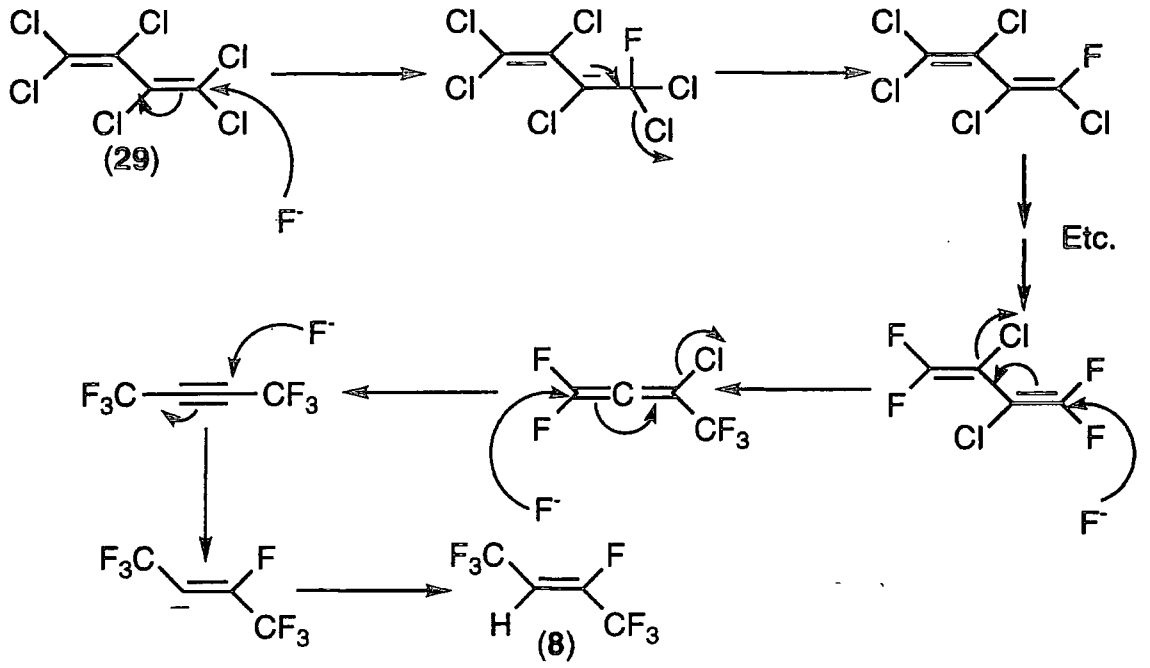
II.2. The Synthesis of 2*H*-Heptafluorobut-2-ene (8)

The synthesis of (**8**) in 65% yield via the treatment of (**29**) with anhydrous potassium fluoride in NMP at 200°C, was first reported by Maynard[65] in 1963. Later work from these laboratories has published yields of up to 85% in sulpholane[198].



i = KF, 190°C, Sulpholane or NMP

The mechanism of the reaction is not fully understood[65, 198], although it is likely to proceed via a succession of vinylic substitutions of chlorine by fluorine.



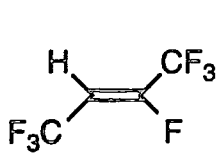
Since the aim of this work was to explore the chemistry of (**8**), this synthesis became a regular task, and it was surprising that even after many runs of this experiment, yields of only 45-50% could be obtained using sulpholane as the solvent, and worse in NMP. These phenomena have also been observed by a recent worker in this laboratory[31], and because of the fundamental importance of the synthesis of (**8**) to this project, an investigation into the missing mass balance was performed.

Results and Discussion

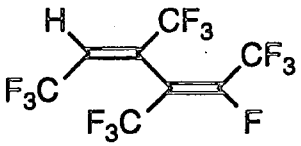
II.3. Investigation of By-Products

II.3.A. Volatile Components

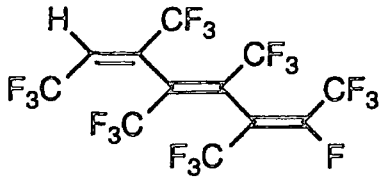
A closer examination of the volatiles produced in this reaction revealed the presence of three components. The first was identified as (**8**). The second was shown to consist of a mixture of isomers of (**31**), and the final component was identified as (**32**).



(8)
(45%)



(31)
(6%)



(32)
(trace)

These compounds were separated from (8) by distillation. The diene mixture distilled at 78°C, and was shown by GLCMS to contain 99% of dienes (31) and 1% triene (32). Dienes (31) were isolated pure by preparative scale GLC.

II.3.A.1. Identification - The mixture of dienes (31) were identified by their (M^+-1) parent peaks in GLCMS, and elemental analysis. ^{19}F and ^1H NMRs and GLC analysis confirmed the presence of two isomeric forms, in a 4:1 ratio. Both isomers displayed a set of four trifluoromethyl signals ($-\delta_F$ = 60-70ppm) and a vinylic fluorine signal ($-\delta_F$ = ~104ppm).

The triene (32) existed as a minor impurity in the diene mixture, and was identified by its parent (M^+-1) peak in the GLCMS data. The ^{19}F NMR spectrum showed numerous resonances in the region of $-\delta_F$ = 60-70ppm, which is characteristic of trifluoromethyl groups on double bonds. However, no assignments were possible due to the trace amounts available.

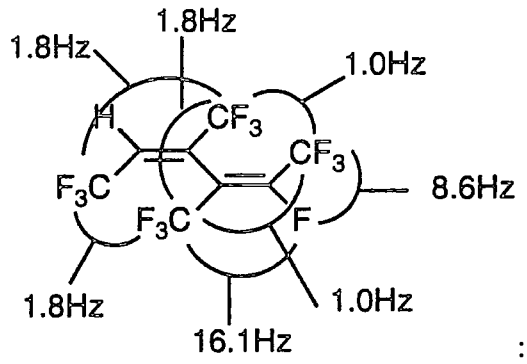
The mass spectrums of both (31) and (32) have been reported in the literature[199], by workers who heated samples of poly(hexafluorobutyne) inside a mass spectrometer.

II.3.A.2. Stereochemistry - Since it is known[200, 201] that ^5J(*cis*-CF_3, CF_3) values are generally greater than 10Hz, ^5J(*trans*-CF_3, CF_3) values are typically less than 2Hz, and ^4J(*trans*-CF_3, F) coupling constants are usually less than ^4J(*cis*-CF_3, F), the stereochemistry of the major isomer of (31) has been elucidated from the ^{19}F NMR coupling constant data. The observed results are displayed below.

δ_F /ppm	Mult.
-68.71	m 1.8Hz
-70.36	d, sept 8.6, 1.0Hz
-60.86	d, t, t 16.1, 1.8, 1.0Hz
-62.27	sept 1.8Hz

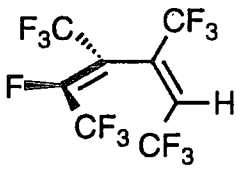
-105.59	q, q 16.1, 8.6Hz

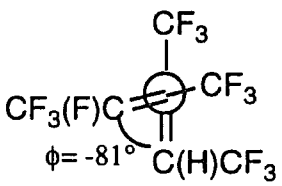
From these results the major isomer can be attributed (Z,E) stereochemistry.



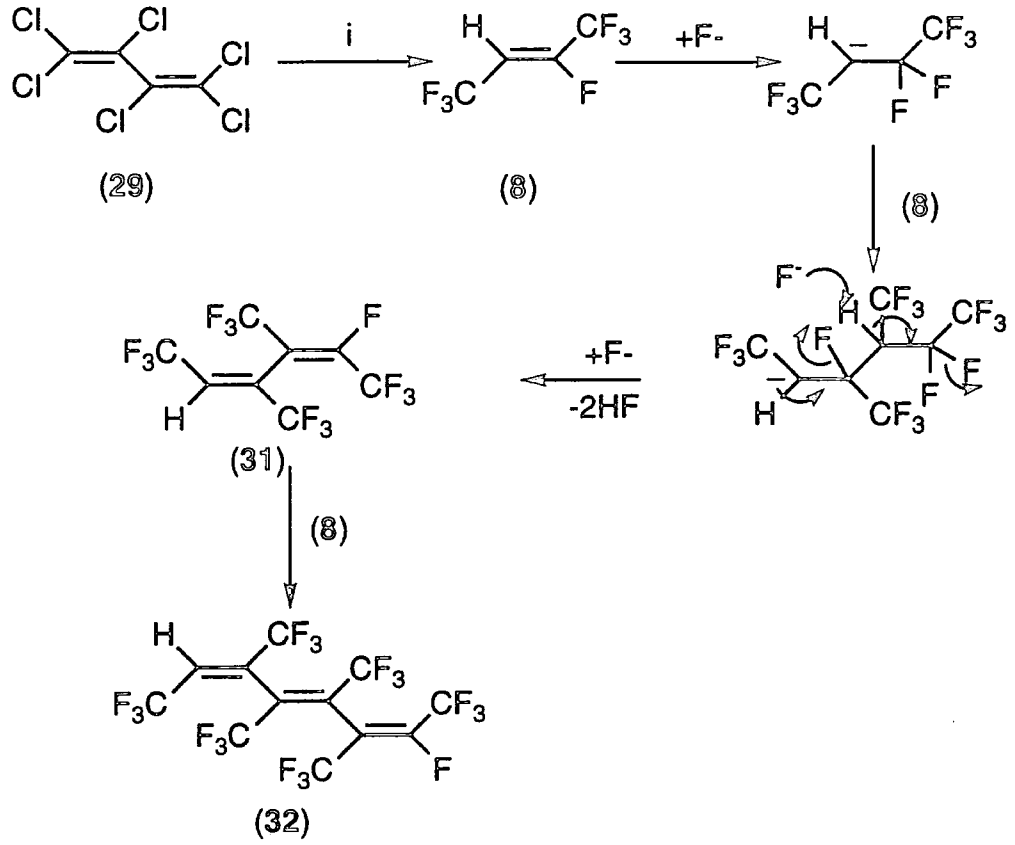
The stereochemistry of the minor isomer has not yet been elucidated due to a lack of resolution of the appropriate peaks in the ^{19}F NMR spectrum.

II.3.A.3. U.V Data - The u.v. extinction coefficient (ε_{max}) for this mixture of (**31**) has been measured as 1148 $mol^{-1}cm^{-1}$, showing absorption at λ_{max} at 295nm. The relatively low value of ε_{max} indicates that the double bonds are not conjugated, and this is in accordance with data recorded for other dienes bearing trifluoromethyl groups[202]. The trifluoromethyl groups impose a large steric demand due to the unpaired electrons on the fluorine atoms, and this forces a deviation from planarity. Computer modelling using the COSMIC package (MOPAC) has predicted a skew conformation to have the minimum energy, with the dihedral angle between the double bonds as 81°. This is consistent with data for other dienes containing trifluoromethyl groups[203].





II.3.A.4. Mechanism of Formation of By-Products - These previously unobserved unusual by-products can be rationalised by the fluoride ion initiated oligomerisation of (**8**).



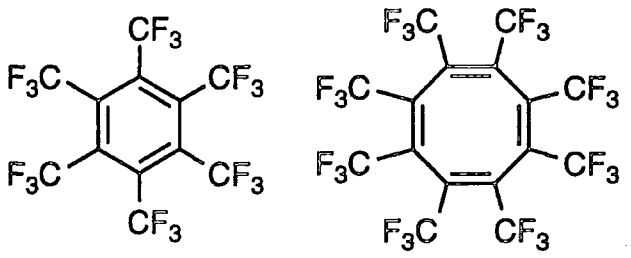
i = KF, Sulpholane, 190°C.

Fluoride ion attacks (**8**) to produce the most stable anion, which then attacks another molecule of (**8**), and fluoride ion is eliminated. Hydrogen fluoride is eliminated via the action of fluoride ion acting as a base. This results in the formation of (**31**), and an analogous reaction between the (**31**) and (**8**) results in the production of the (**32**).

II.3.B. Reaction Residue

The sulpholane residue from the synthesis of (**8**) was also examined. It was remarkable that a filtered sample of this black liquid gave only one resonance in the ^{19}F NMR spectrum, at δ_F = -50ppm. The single resonance indicated either a highly symmetrical i.e. cyclic structure. Also, the involatility points to either a high molecular mass or ionic solid of some description.

Due to the confirmed existence of the (**31**) and (**32**), it seemed logical that this compound is a higher oligomer, but the need for a single fluorine environment would imply that some type of cyclisation to have occurred. Two feasible candidates were the known compounds hexakis(trifluoromethyl)benzene and octakis(trifluoromethyl)cyclooctatetraene.



However, their δ_F values[204, 205] (-54 and -60ppm respectively) are too far upfield, and with the knowledge that charge shifts signals to higher frequency[206], an anion of some description was the next proposal. It was known that δ_F of pentakis(trifluoromethyl)cyclopentadienide[193] is around -50ppm.

When water was added to an aliquot of the residue, a black solid was isolated by filtration, and FAB mass spectrometry confirmed the presence of potassium (m/z 39, 100% in the positive ion spectrum), and only m/z 405 (100%) in the negative ion spectrum, which corresponds to the pentakis(trifluoromethyl)cyclopentadienide moiety. Thus, it is confirmed that potassium pentakis(trifluoromethyl) cyclopentadienide (**33a**) had been obtained from hexachlorobutadiene and KF in one step!

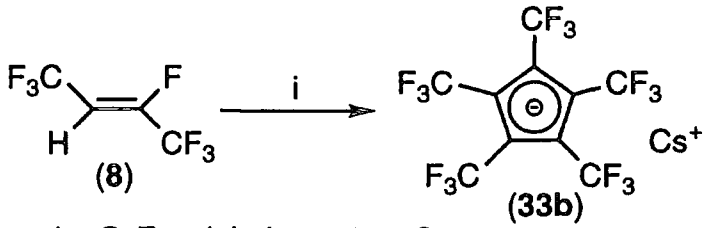
The yield of (**33a**) was calculated by ^{19}F NMR (integrating against an internal marker) as 3%. Although this may seem a poor yield, the large scale of the reaction means, on average, there would be 12.9 mmol (~6g) of (**33a**) in the residue, which is remarkable considering the previous laborious route to this moiety, described earlier.

By performing the reaction in a sealed system, higher yields of (**33a** or **b**) are produced.

Reagent	Source of F-	Vessel	Yield	Product
(**29**)	KF	a	11%	(**33a**)
(**29**)	CsF	a	10%	(**33b**)

a = Round bottomed flask sealed with a Young's tap, stirred by a magnetic follower.

It has also been shown that (**33b**) can be obtained in higher yields if (**8**) is heated with fluoride ion.



(**8**) (**33b**)

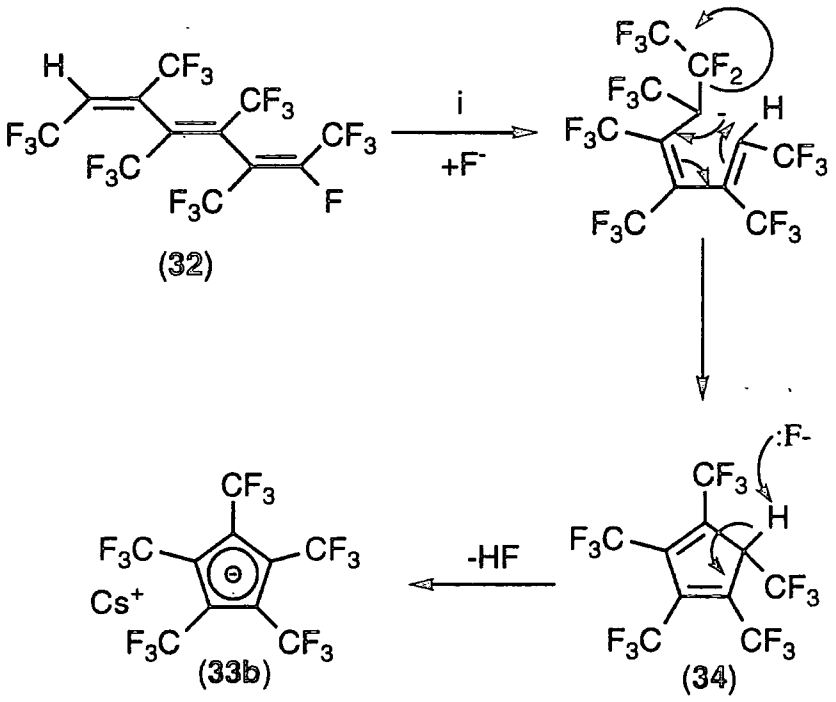
i = CsF, sulpholane, 190°C

The reaction vessel and method of agitation seem to effect the yield of (33b).

Reagent	Source of F^-	Vessel	Yield of (33b)
(8)	CsF	b	13%
(8)	CsF	a	20%

a = Round bottom flask sealed via a Young's tap, stirred by magnetic follower.
b = Carius tube, agitated by horizontal rotation.

II.3.B.1. Mechanism for Formation of (33) - The mechanism of such a remarkable transformation merits discussion, and can be rationalised by considering the action of fluoride ion on triene (32).



i, CsF, Sulpholane, 190°C.

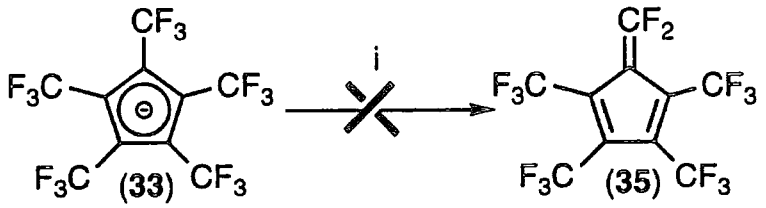
The cyclisation step is extremely interesting, because, as a 5-*endo-trig* process, it is formally 'disallowed' by the Baldwin rules[207]. It seems more appropriate, therefore, to regard this process as a 1,5 electrocyclic ring closure[208], to produce (34), followed by the elimination of the acidic proton by fluoride ion acting as a base.

II.3.C. Isolation of Salt (33)

The isolation of the salt initially proved a problem, bearing in mind the pursuit of ~6g of (33a) in typically 3 litres of sulpholane.

II.3.C.1. Precipitation using Water - The large scale precipitation using water was unacceptable due to the large amount of black tars produced.

II.3.C.2. Reaction with BoronTrifluoride-Etherate - Another proposal was the addition of BF_3-Et_2O, in an attempt to produce (35), which would be volatile and so could be distilled from the sulpholane solution.

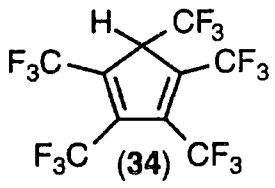


i = BF_3-Et_2O

However, no reaction occurred.

II.3.C.3. Reaction with Strong Acid - It has been reported earlier, it is possible to protonate (**33**) using concentrated sulphuric acid, thus producing the acidic cyclopentadiene (**34**), which was observed but not isolated[193]. It has been possible to apply this reaction in the isolation of (**33**).

The addition of 98% sulphuric acid to the filtered residue from the synthesis of (**8**) results in the formation of (**34**), and it is possible to distill (**34**) from the sulpholane solution. Best results were achieved performing the whole reaction under vacuum, and collecting (**34**) in liquid air traps as it is formed.



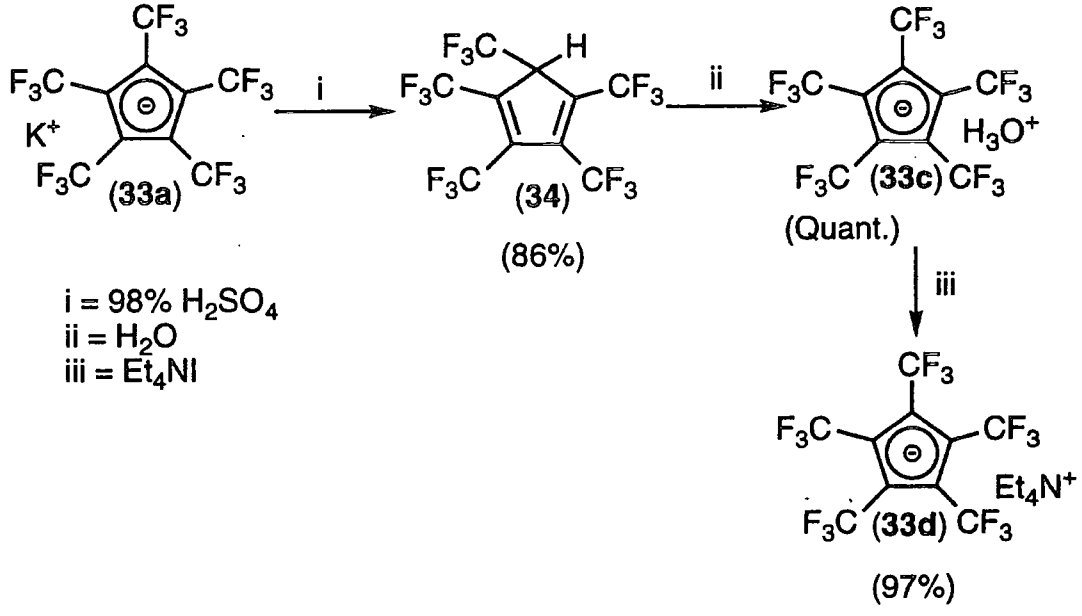
Compound (**34**) was isolated by the above procedure in 86% yield, and was identified by the reported[193] 2:1:2 set of CF_3 resonances in the ^{19}F NMR spectrum. Also observed was a quartet at 4.80ppm in the ^{1}H NMR and six quartets in the ^{13}C NMR, and its parent ion in GLCMS. However (**34**) is very reactive and will decompose on standing in sample bottles with vigorous etching of the glass surface.

Lemal and co-workers[193] calculated that the pKa value of (**34**) was -2, (c.f. pKa Nitric Acid -1.2), and claimed that (**34**) was the 'strongest organic acid without conjugating substituents'.

They also demonstrated that (**34**) will deprotonate in aqueous solution to regenerate (**33c**), presumably with H_3O^+ as the cation, and our work has also shown this to be so. Compound (**33c**) is stable for months in aqueous solution, but heating to 50°C

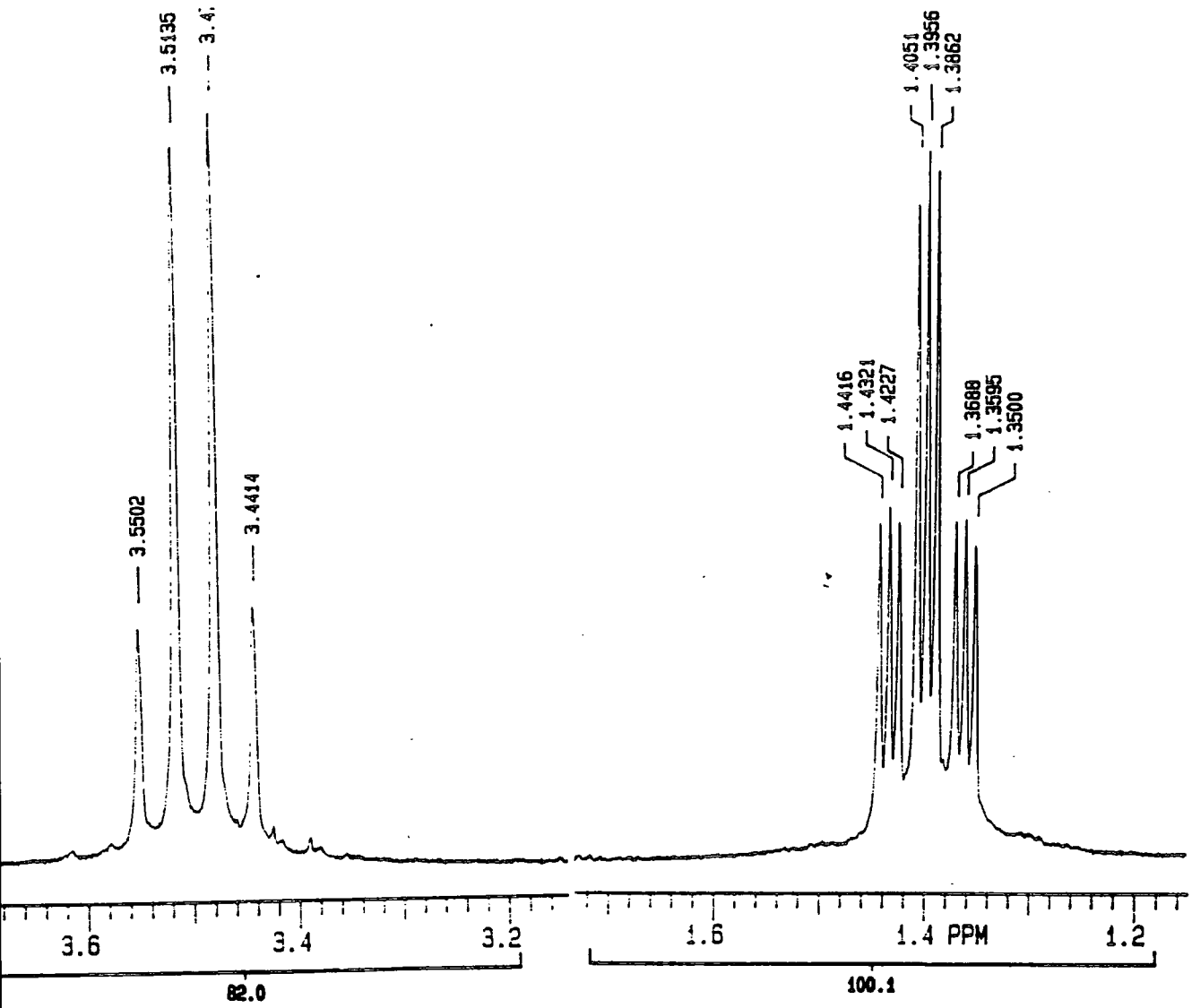
resulted in slow decomposition, liberating fluoride ion. This is in comparison to the tetrakis(trifluoromethyl)cyanocyclopentadienide which is very water sensitive[195].

II.3.C.4. Precipitation of (33) - In an attempt to produce an isolable salt of (33), tetraethyl ammonium iodide was added to the aqueous solution. This iodide was chosen for it is known to be water soluble, but it was hoped that the tetraethylammonium salt of (33) would not be. The addition of tetraethyl ammonium iodide to the aqueous solution containing (33c) resulted in immediate precipitation of a dark yellow/brown solid. This solid was recrystallised from ether and hexane using the method of incipient turgidity, producing colourless needles of tetraethylammonium pentakis(trifluoromethyl)cyclopentadienide (**33d**).



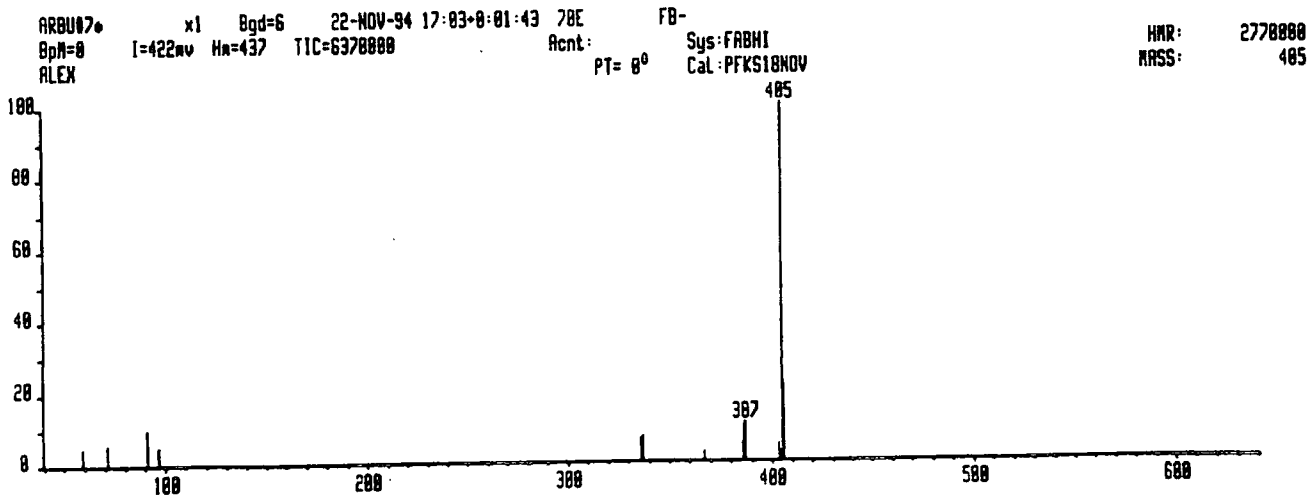
II.3.C.5. Characterisation of (33d) - The characterisation of (**33d**) led to several notable features. The first being that in the negative ion FAB mass spectrum, the parent ion of 405 shows little or no fragmentation.

The second observation is that in the ^{1}H NMR, it is possible to observe the $^{3}J_{N\text{-}H}$ coupling between the nitrogen and the protons on the CH_3 groups, whereas the $^{2}J_{N\text{-}H}$ coupling between the nitrogen and the CH_2 protons is not observed. (This effect is not observed in Et_4NI).



CH_2 Protons not Split

CH_3 Protons Split



FAB Mass Spectrum of (33)

A possible explanation for this phenominum is that because of its electric quadrupole, the nitrogen can rapidly flip between its spin states, thus providing a mechanism for relaxation[209]. This would have the effect of relaxing the protons on the CH_2 quicker than the CH_3, because the CH_2 protons are nearer. So the CH_3 protons are split whilst the CH_2 protons are not. The reason why this effect is not observed in Et_4NI is unclear, but the observation of such effects is rare, and is believed to depend on solvent, concentration and cation environment.

II.3.C.6. Salts of (33) with Different Cations - It has been possible to produce a range of salts containing (**33**) by this methodology, and they are summarised below.

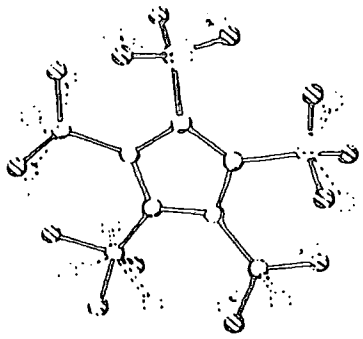
Salt Used	Product	Yield
Et_4NI	$Et_4N^+ C_5(CF_3)_5^-$	83%
Et_4NBr	$Et_4N^+ C_5(CF_3)_5^-$	80%
Pr_4NI	$Pr_4N^+ C_5(CF_3)_5^-$	80%
Bu_4NI	$Bu_4N^+ C_5(CF_3)_5^-$	86%
KI	$K^+ C_5(CF_3)_5^-$	15%
CsF	$Cs^+ C_5(CF_3)_5^-$	12%
$Tl(CH_3CO_2)$	$Tl^+ C_5(CF_3)_5^-$	15%
$BaCl_2$	$Ba^{2+} (C_5(CF_3)_5^-)_2$	40%

The tetra-alkyl ammonium salts are produced identically as described previously, using either the appropriate bromide or iodide.

The formation of metal salts was slightly more difficult, as the potassium, caesium and thallium product salts had a degree of solubility in water. and so would not simply precipitate out, and continuous extraction with DCM had to be used. This had the unfortunate effect of lowering the yield, since moderate amounts of decomposition occurred due to the heating of the salts in aqueous media.

The barium salt did not need to be continuously extracted. However, despite showing only the characteristic ^{19}F NMR shift and m/z 405 peak in the FAB spectrum, a correct elemental analysis could not be obtained for $Ba(C_{10}F_{15})_2$ or $Ba(C_{10}F_{15})Cl$. Recrystallisation proved difficult due to the vast insolubility of the product and other barium compounds.

II.3.C.7. Crystal Structure Analysis - A sample of (**33d**) was submitted for crystal structure, and although a full structural analysis could not be obtained, the structure of the cyclopentadienide was resolved, and is shown below. The reasons why a full analysis could not be obtained are not fully understood, but there seems to be too much disorder in the cation structure[210], which is probably due to the ethyl groups adopting many conformations in the crystal.



(33)

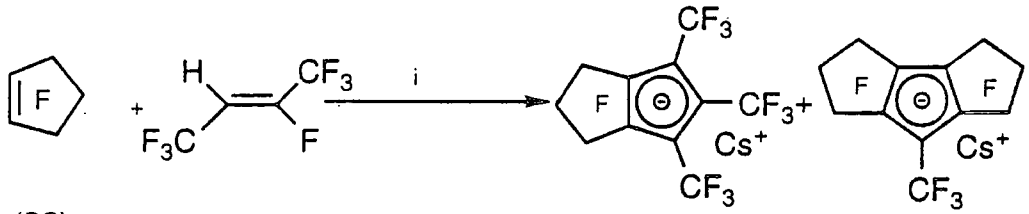
II.3.C.8. Conclusion

These two routes (one directly from (29), the other from (8)), provide a realistic pursuit of the chemistry of (33).

II.4. Extension of Methodology

The synthetic methodology used in the synthesis of (33) can be used to create more elaborate ring systems.

II.4.A. Reaction between perfluorocyclopentene and (8) - The reaction of (8) with perfluorocyclopentene (36) at 110°C produces novel bicyclic (37) and tricyclic (38) anions.



(36) (8) (37) (38)

(37) (20%) (38) (7%)

i = Sulpholane, CsF, 110°C.

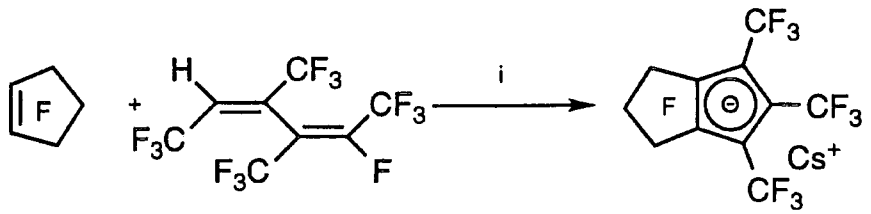
The mechanisms of formation are analogous as for (33), except that for (37) two units of (8) and one of (36) combine, whereas the production of (38) results from two units of (36) and one of (8).

II.4.A.1. Identification - Product (37) was identified using ^{19}F NMR by its pair of CF_3 resonances in a 6:3 ratio, and its pair of CF_2 resonances in a 4:2 ratio. It also gave a parent ion in the negative FAB mass spectrum, which again showed very little fragmentation.

Product (**38**) was similarly identified using ^{19}F NMR by the observation of a single CF_3 resonance and three CF_2 signals in the ratio of 3:4:4:4. Again, a parent ion was observed in the negative ion FAB mass spectrum. However, considerable fragmentation occurred, which reflects the strain of the tricyclic system. Yields were calculated by integration against an internal marker.

II.4.B. Reaction between perfluorocyclopentene and (31)

It has been possible to produce (**37**) in a higher yielding and cleaner reaction using diene (**31**) and (**36**).

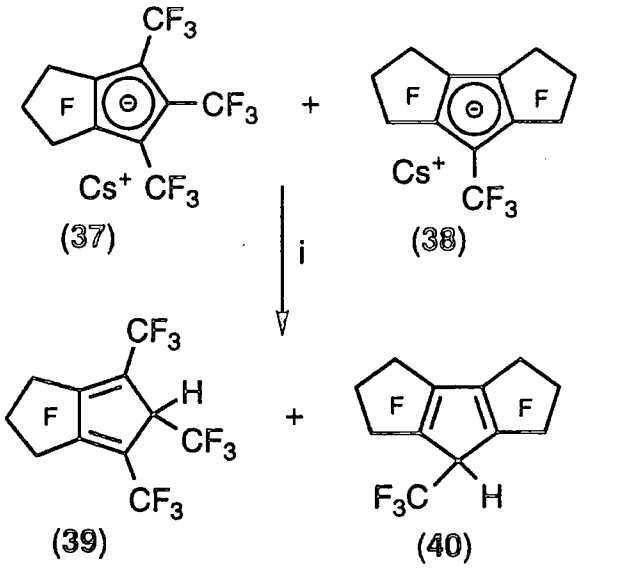


(**36**) (**31**) (**37**)

i , Sulpholane, CsF, 110°C. (41%)

II.4.C. Isolation of (37) and (38) - It was hoped that the protonation-distillation-recrystalisation procedure reported for isolation of (**33d**), would be equally successful for (**37**) and (**38**), and so their protonation was attempted.

II.4.C.1. Protonation of (37) and (38) - Using identical techniques as outlined earlier, concentrated sulphuric acid was added to a sulpholane solution containing (**37**) and (**38**).



i = 98% H_2SO_4

The volatile products collected in this reaction contained many products. Two of the components were identified as (**39**) and (**40**) on the basis of their GLCMS data. However, further characterisation was unable to be obtained due to the complexity of the product mixture.

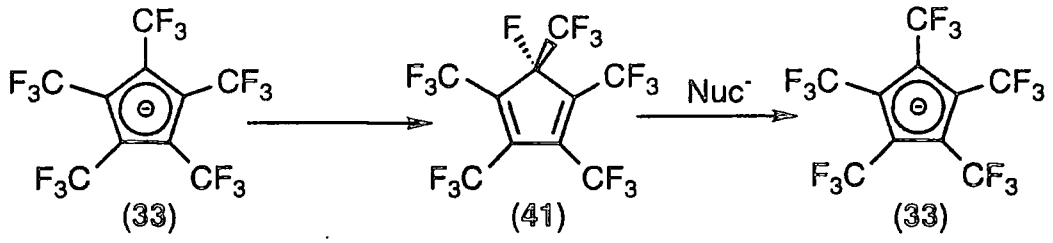
II.4.C.2. Attempted Regeneration of (37) and (38) - The volatiles from the above protonation were added to water in an attempt to regenerate anions (**37**) and (**38**). However, ^{19}F NMR showed that extensive decomposition had occurred.

II.5. Reactions of Pentakis(Trifluoromethyl) Cyclopentadienide

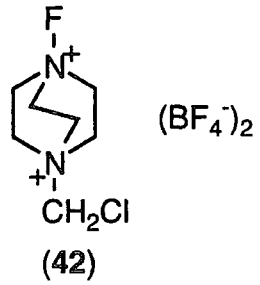
Preliminary reactions of (**33d**) with classical electrophiles and transition metals were studied.

II.5.A. Electrophiles - There was no observable reaction by ^{19}F NMR when acetonitrile and sulpholane solutions of (**33d**) were stirred at room temperature with ethanoyl chloride or methyl iodide.

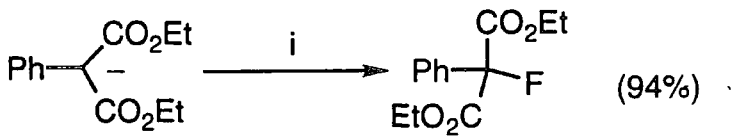
II.5.B. SelectFluor™ F-TEDA-BF_4 - The fluorination of (**33d**) would lead to the interesting cyclopentadiene (**41**), and this compound could behave as an electrophilic fluorinating agent (i.e. source of F^+).



SelectFluor™ F-TEDA-BF_4 (42) is marketed as a safe and convenient laboratory electrophilic fluorinating agent[211, 212].



One of the many areas where this type of reagent has found application is the fluorination of stabilised carbanions.



i = Selectfluor™ F-TEDA-BF_4, THF, 30 mins, r.t.

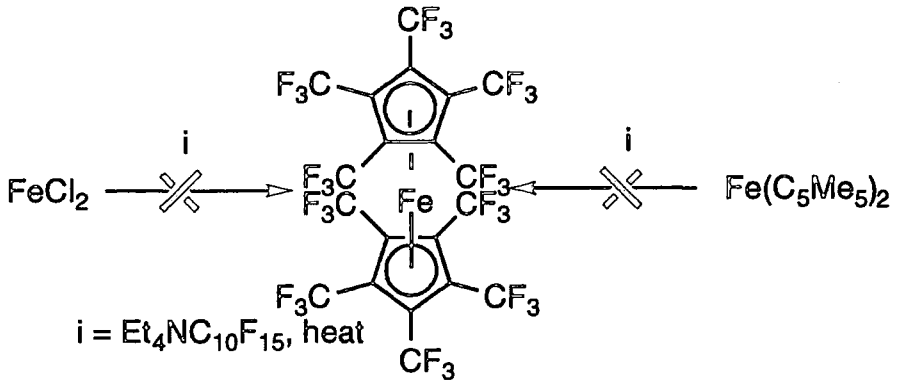
The reaction between (**33d**) and (**42**) in DMF proceeded to complete conversion of (**33d**) after 1 day at room temperature. Volatile products were removed, and shown by GLCMS to contain four components in approximately equal proportions. The third compound gave a parent peak in the mass spectrum of 424, which corresponds to the formation of (**41**). Further characterisation and isolation was not pursued because of the complexity of the mixture and the expense of (**42**).

II.5.C. Transition Metals

The potential application of (**33**) as a transition metal ligand merits investigation, and since viable synthetic routes have been discovered, elementary attempts to coordinate (**33**) to a transition metal centre have been explored.

II.5.C.1. Iron (II) Chloride - In an analogous reaction to the formation of ferrocene, (**33d**) was heated with iron (II) chloride. Analysis by ^{19}F NMR showed no evidence of reaction, except for a few decomposition products. (If (**33**) had become coordinated to the

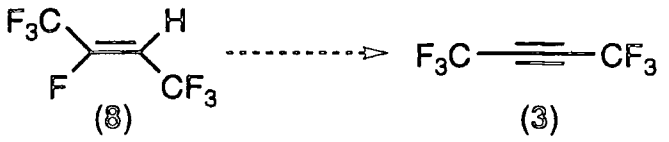
metal, then a characteristic shift in δ_F would have been observed, and none was observed).



II.5.C.2. Decamethylferrocene - A similar reaction was attempted using (33d) and decamethylferrocene, and again no reaction was observed. This is in keeping with the observations of other workers[194] who experienced similar difficulties with 1,2,3,4-tetrakis(trifluoromethyl)cyclopentadienide. They reasoned that because the trifluoromethyl groups are so electron withdrawing, the anion is rendered sufficiently 'un-nucleophilic', that these simple nucleophilic displacements will not proceed.

III. Introduction

This chapter is concerned with the use of (8) as either a synthetic equivalent for, or a precursor to, hexaflurobut-2-yne (3).



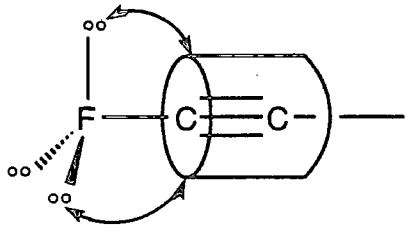
(8) (3)

As way of an introduction, the following is a brief overview of fluoro- and perfluoroalkyl-alkynes.

III.1. Alkynes containing Fluorine

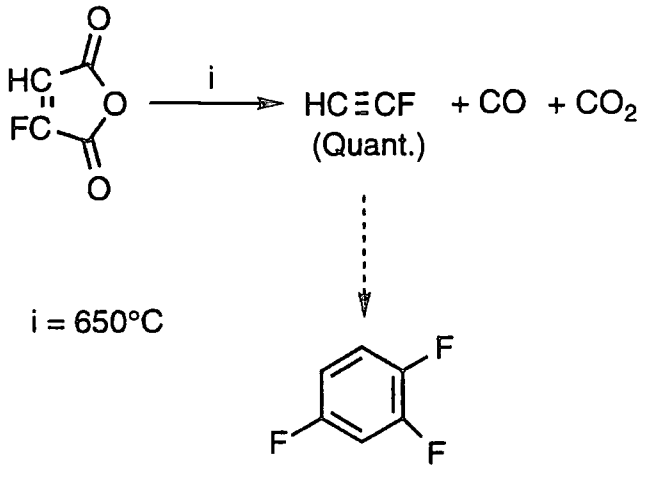
III.1.A. Fluoroalkynes

Fluorine, despite being the most electronegative element, when attached directly to a triple bond, tends to raise the energy of the system relative to hydrogen, and this can be attributed to electron pair repulsions between the lone pairs on fluorine and the π-system[9].



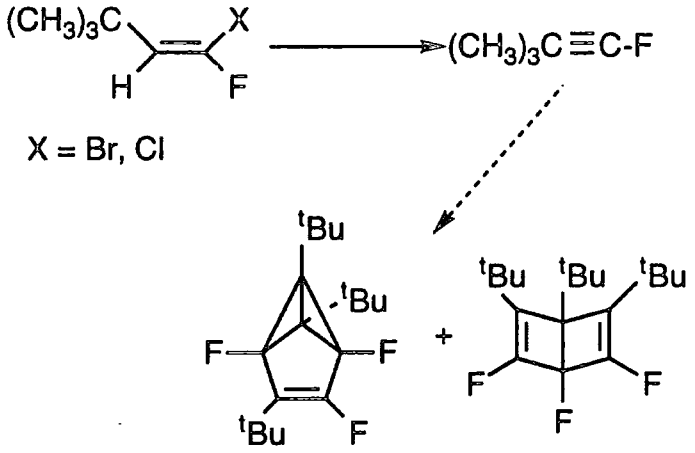
III.1.B. Syntheses

Monofluoroalkyne, which is explosive, has been obtained quantitatively via the pyrolysis of monofluoromaleic anhydride[213].



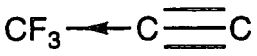
Difluoroalkyne has not been isolated, but is claimed to be an intermediate from the analogous pyrolysis of difluoromaleic anhydride[214].

^{t}Butylfluoroalkyne can be prepared via a dehydrohalogenation reaction, and is very reactive[215, 216]. It will oligomerise below 0°C, yielding unusual products such as Dewar benzenes and benzvalenes.



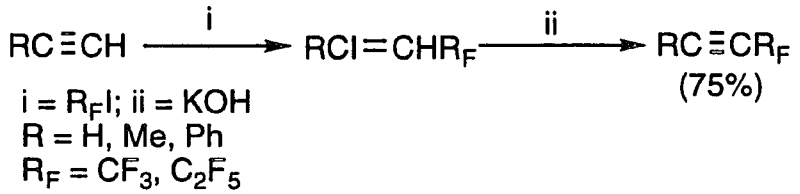
III.1.C. Perfluoroalkyl-Derivatives

In contrast to the fluoroalkynes, the electron withdrawing perfluoroalkyl group pulls electron density away from the triple bond, and thus stabilisation relative to hydrogen is observed[9].

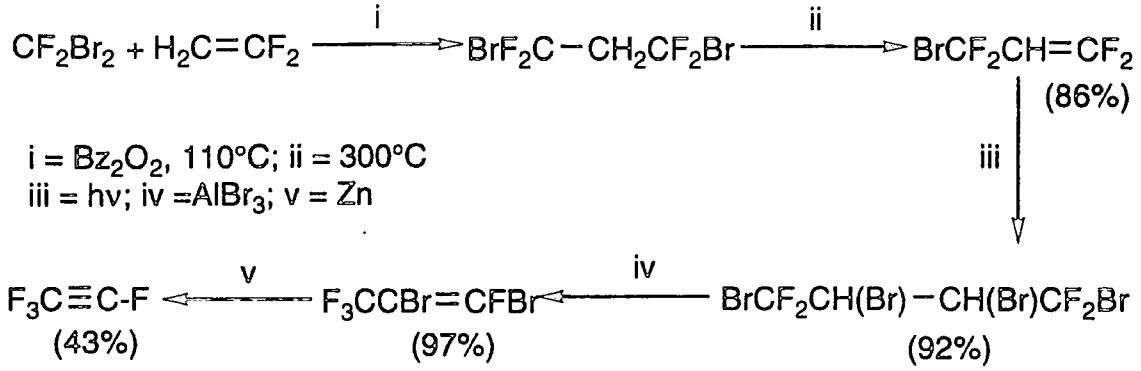


III.1.D. Syntheses

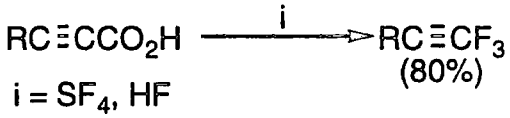
There are several examples of synthesis of these systems, and most involve dehydrohalogenation or dehalogenation from appropriately substituted alkenes. Addition of a perfluoroalkyl iodide to a hydrocarbon alkyne, followed by elimination of HI, also provides a general route to fluoroalkyl alkynes[217, 218].



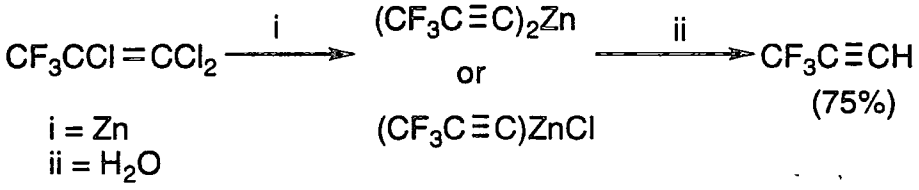
Perfluoropropyne, may be synthesised in five steps from simple precursors[219].



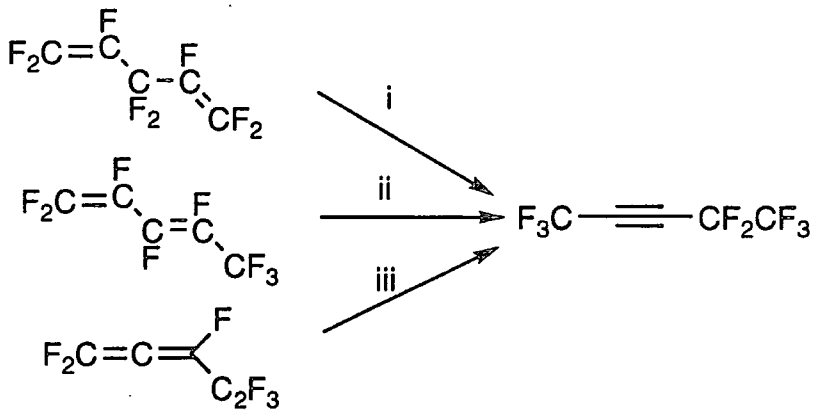
Other methodology involves the action of sulphur tetrafluoride on alkynes bearing carboxylic acid functionality[220, 221].



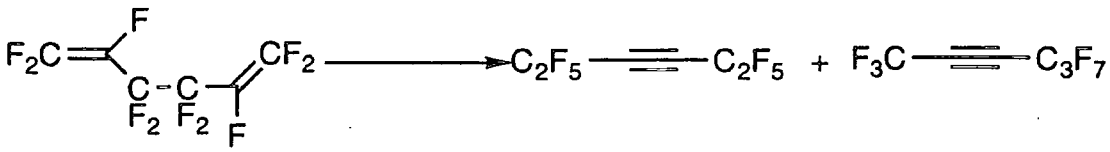
Hydrolysis of zinc acetylides also results in the formation of polyfluoroalkyl alkynes[222, 223].



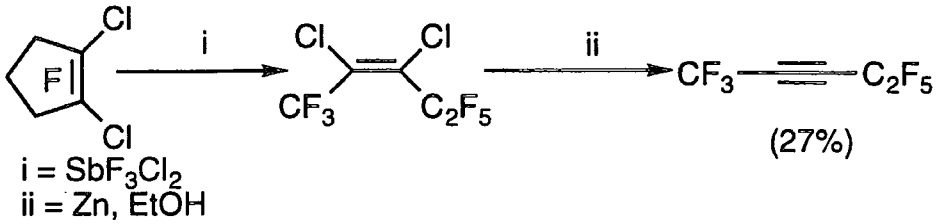
Fluoride ion isomerisation has produced a number of routes to fluoroalkyl acetylenes[224-226].



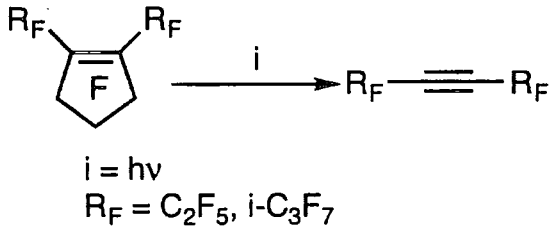
Similarly, a mixture of isomeric hexynes can be produced from perfluorohexa-1,5-diene[226].



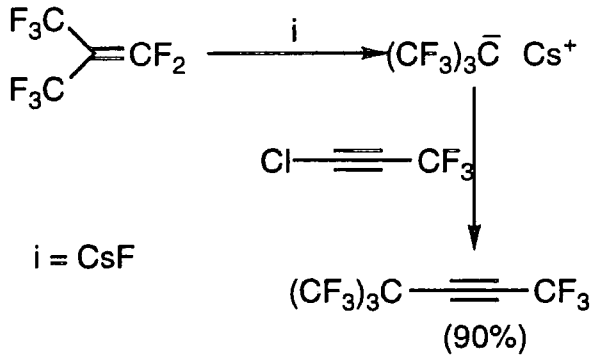
Octafluoropent-2-yne can also be prepared by ring opening of 1,2-dichloroperfluorocyclopentene with SbF_3Cl_2, followed by dechlorination with zinc[227].



It is possible to obtain several perfluoroalkynes as minor products from photolyses of perfluoroalkenes[228].



Perfluoro-(2,2-dimethylpent-3-yne) can be prepared via reaction of 1-chloroperfluoropropyne and the anion derived from PFIB[229].

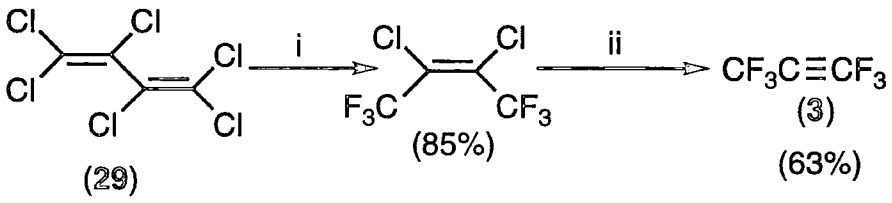


III.1.E. Hexafluorobut-2-yne (3)

Without doubt, the most important member of this class of compounds is hexafluorobut-2-yne (**3**), which was the first perfluoroalkyne synthesised. It is the only perfluoroalkylalkyne that is commercially available , and may be obtained via a variety of methodology.

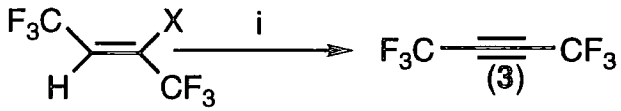
III.1.F. Syntheses

The most common general synthesis is the reaction of (29) with antimony trifluoride, followed by zinc dechlorination[23].



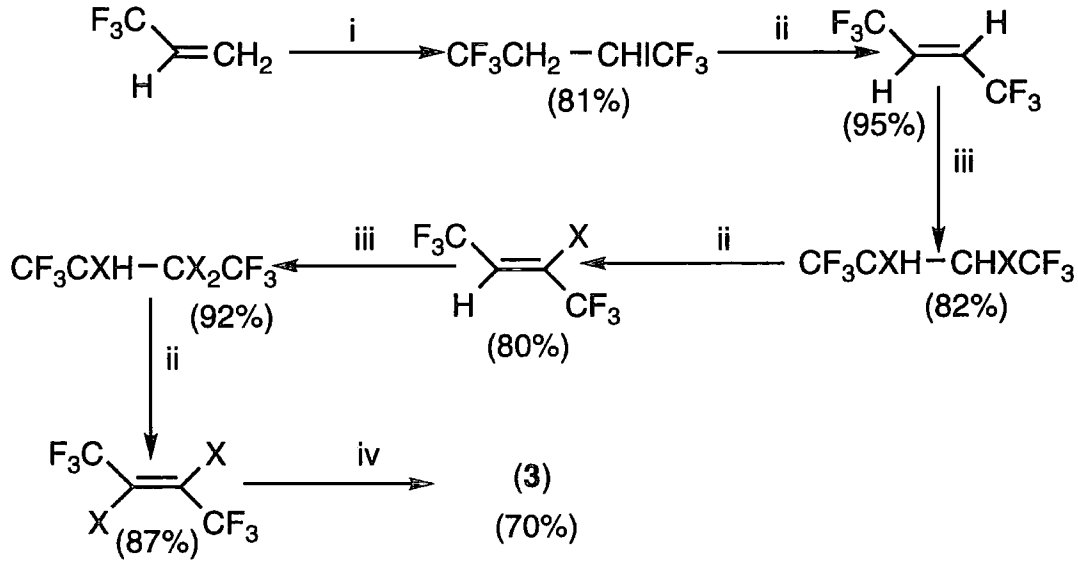
i = SbF_3, SbF_3Cl_2
ii = Zn

There have been reports of (3) also being produced via dehydrohalogenation of 2-halogenobut-2-enes[40].



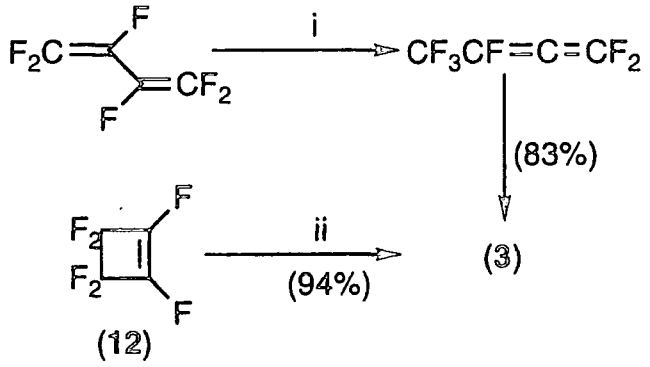
i = KOH,10°C; X = Cl (46) (36%)
= Br (47) (68%)

Haszeldine reports that better routes to (3) are obtained by dehalogenation of dihalogenobut-2-enes, as opposed to dehydrohalogenation of 2-halogenobut-2-enes. The route to these compounds is arduous, starting with the addition of trifluoromethyl iodide to trifluoropropene, followed by a succession of addition and elimination reactions[40].



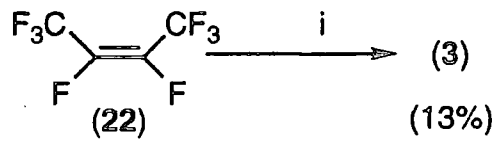
i = CF_3I, hv; ii = KOH, 10°C; iii = X_2 ,hv; iv = Zn

Hexafluorobuta-1,3-diene[226] and perfluorocyclobutene [230] (12) have been shown to isomerise to (3) in the presence of fluoride ion.



i = CsF, 100°C, flow system
ii = KF, 600°C, flow system

Condensation of (22) and calcium vapour onto a liquid nitrogen cooled surface results in defluorination[231].

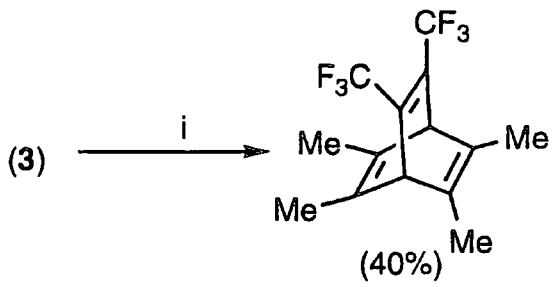


i = Ca, low temp.

III.1.G. Reactions of (3)

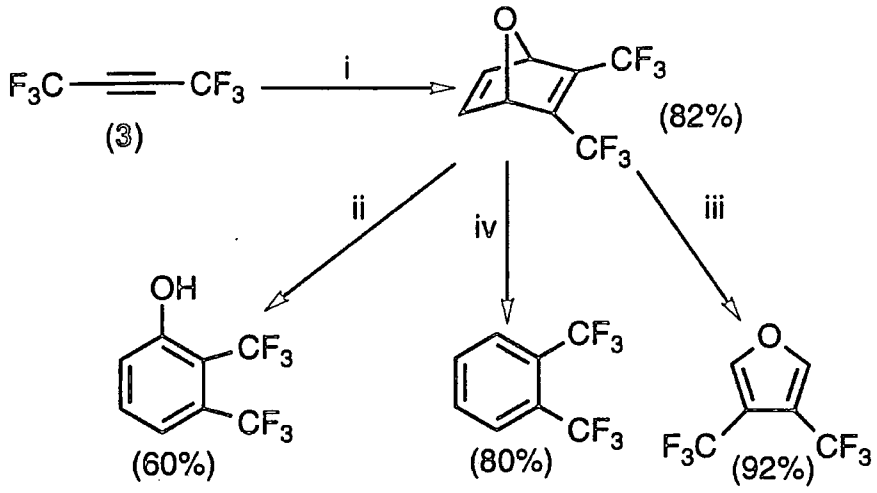
The two electron withdrawing trifluoromethyl groups render the triple bond electron deficient, and therefore very electrophilic in nature[232].

III.1.G.1. Cycloadditions - Hexafluorobut-2-yne (3) is a reactive dienophile[233], and will even undergo cycloaddition with benzene and durene[234].



i = durene, 200°C

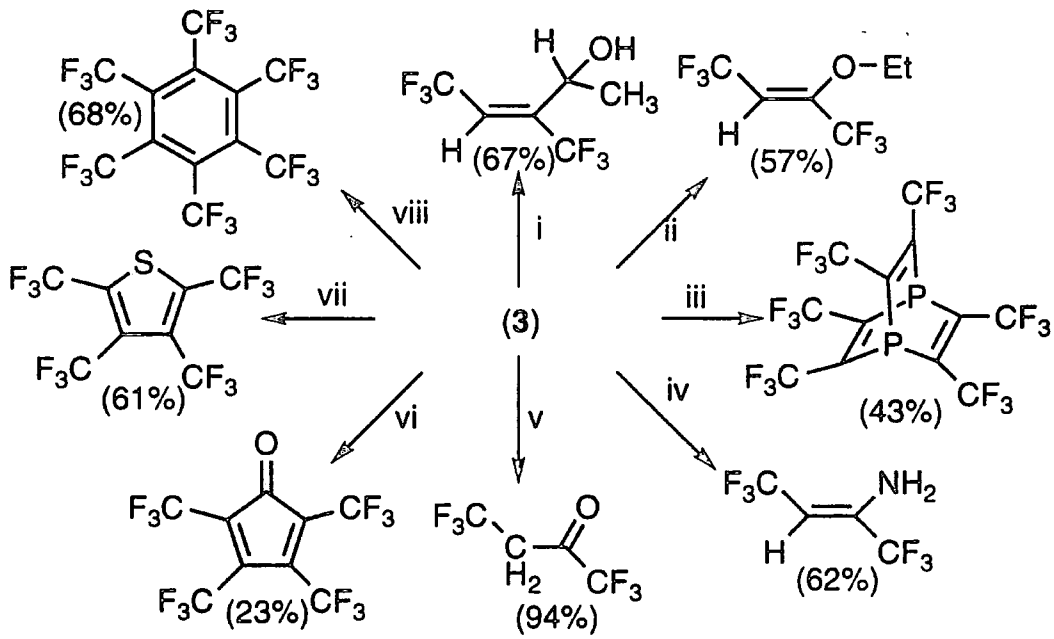
Cycloaddition with furan[235], provides the starting point for a versatile synthesis of benzenes[236], phenols[188] and furans[235] containing two vicinal trifluoromethyl groups.



i = furan, 100°C
ii = BF_3-Et_2O
iii = H_2/Pt; 400°C
iv = $TiCl_4$, $LiAlH_4$, Et_3N

This methodology has been shown to tolerate a variety of different furans[188].

III.1.G.2. Other Selected Examples - Due to its electrophilic character, (3) will react readily with nucleophiles[232], and free radical reactions may also occur[40, 222, 232, 237, 238]. Therefore, (3) has proved to be a versatile building block for a wide variety of organic compounds containing trifluoromethyl groups[237-244].



i = EtOH, γ; ii = EtOH, base; iii = P, I_2, 200°C; iv = NH_3; v = H_2O, 110°C
vi = $Rh(CO)_2Cl$, CO, 150°C; vii = S_8, I_2, 200°C; viii = 375°C

III.1.H. Problems with Hexafluorobut-2-yne (3) - Despite the obvious utility of (3), no easy laboratory scale syntheses have been developed, and low industrial demand means (3) is expensive commercially.

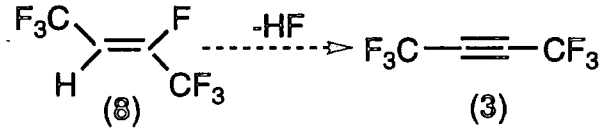
Results and Discussion

III.2. Aims of this Project

The above reasons prompted the desirability of either developing a synthon for, or a new convenient route to, (3).

III.3. New Routes to Hexafluorobut-2-yne (3)

As discussed in detail in the previous chapter, the fluoroalkene (8) can be made easily in the laboratory from cheap, non-fluorinated precursors[65], and the seemingly facile elimination of hydrogen fluoride from (8), should provide a convenient route to (3).



(8) (3)

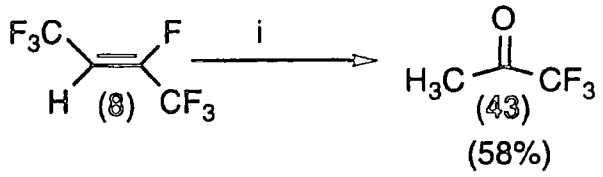
This elimination has been achieved by a recent worker from this laboratory[31], who used molecular sieves as a recyclable source of dehydrofluorinating agent. However, this only works if the reagent is in a liquid form, since the reaction is highly dependant on the surface contact between the reagent and the molecular sieve. Since (8) is a gas, this can be difficult to achieve if small quantities are to be used, and so alternative methods of dehydrofluorination were investigated.

III.3.A. Thermal Dehydrofluorination - A sample of (8) was heated at 400°C in an attempt to 'crack out' HF. However, (8) was retrieved unchanged after 7 days.

III.3.B. Photochemical Dehydrofluorination - A sealed quartz tube containing (8) was left in sunlight for three months, and again, (8) was recovered unchanged.

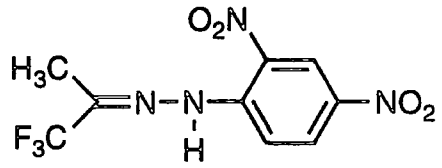
III.3.C. Caesium Carbonate - The reactions of (8) with nucleophiles has been studied (see chapter five), and often caesium carbonate was used to generate the nucleophilic anion. To confirm that these reactions are proceeding directly from (8), and not via preformation of butyne (3), a sample of (8) was stirred in both acetonitrile and sulpholane solutions containing excess caesium carbonate. No reaction was observed.

III.3.D. Potassium Hydroxide - Attempts to emulate the successful dehydrohalogenations using KOH reported by Haszeldine[40] produced unexpected results. The only volatile product observed in this reaction was 1,1,1-trifluoroacetone (43)!

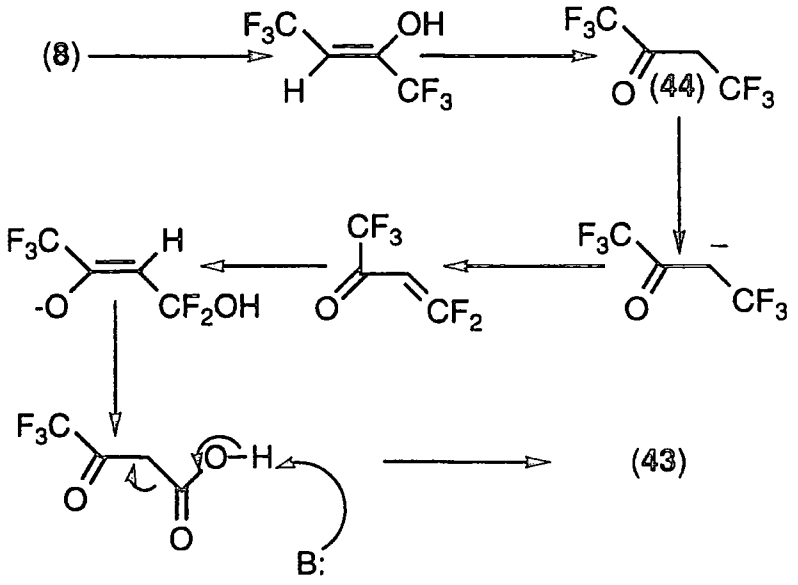


i = KOH, 0°C, sulpholane or CH_3CN

Identification of Product - Product (43) was identified by its characteristic singlets in ^1H and ^{19}F NMRs, and three signals in the ^{13}C NMR. It did not give a parent peak in GLCMS, but gave two simple fragments of 69 (CF_3) and 43 ($CH_3C{=}O$). The product was too volatile for satisfactory elemental analysis. Therefore, further confirmation was achieved via the formation of the known 2,4-DNP derivative, which, when recrystallised from hot ethanol, gave orange needles that gave a satisfactory melting point[245], mass spectrum and elemental analysis.

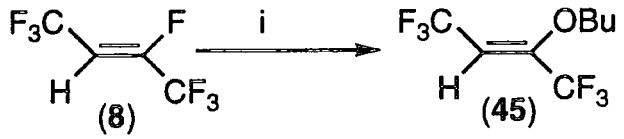


Mechanism of Formation of (43) - Initial nucleophilic attack must occur on (8) by hydroxide ion, leading to vinylic substitution of fluorine. No traces of the known hexafluorobutan-2-one (44) were observed. Butanone (44) must then lose fluoride from the trifluoromethyl adjacent to the acidic protons, producing a β keto acid, which readily decarboxylates in the basic conditions to produce (43). Similar observations have been reported in the literature[245].



III.3.E. Potassium ^{t}Butoxide - Several workers[188, 246] in this laboratory have performed many successful dehydrofluorinations from fluorinated systems, using potassium ^{t}butoxide.

The reaction between (**8**) and potassium ^{t}butoxide in di-isopropyl ether was allowed to warm from liquid air temperatures up to 0°C. This was an attempt to distill out any (**3**) formed from the reaction mixture, before it reacted further. However, no volatile products were collected in the liquid air trap. An examination of the ether layer showed the presence of (*Z*)-2-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (**45**), in 79% yield, which must be produced via vinylic substitution of fluorine by the ^{t}butoxide ion.

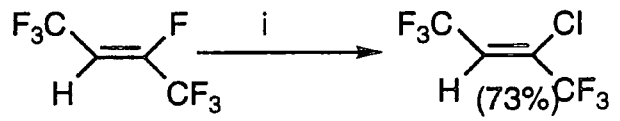


i = tBuOK, di-isopropyl ether, 0°C

Identification of Product - Product (**45**) was identified by ^{19}F and ^{1}H NMRs via comparison with literature data[241], and its parent peak in GLCMS. Attempts to isolate (**45**) by distillation resulted in product decomposition, with the liberation of fluoride ion. Addition of water and ether extraction also resulted in the decomposition of the (**45**). The yield was calculated by integration of ^{19}F signals against an internal standard of 1,1,1-trifluorotoluene.

III.3.F. Lithium Chloride - The action of lithium chloride in refluxing DMF is reported as a useful method for dehydrohalogenations[247] .

The reaction of (**8**) and LiCl in DMF at 150°C resulted in the formation of (*Z*)-2-chloro-1,1,1,4,4,4-hexafluorobut-2-ene (**46**) in 73% yield.



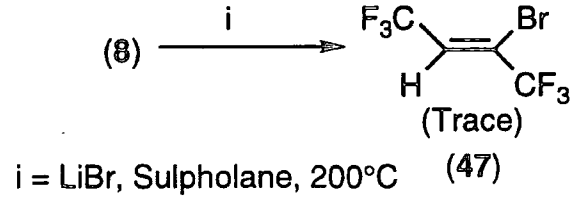
i = LiCl, DMF, 150°C

Again this reaction proceeds via vinylic substitution of fluorine, this time by chlorine.

Identification of Product - The reaction volatiles were distilled at 0°C/0.1mbar, and then -78°C/0.1mbar. The product was identified by ^{19}F and ^{1}H NMRs, its parent peak in GLCMS and IR spectrum, by comparison with literature data[40]. The product proved too volatile for a satisfactory elemental analysis.

As reported previously, Haszeldine[40] has shown that (46) will react with KOH to form (3) in 36%. Better yields of (3) are reported via the dehydrobromination of the corresponding 2-bromohexafluorobutene (47), and this led to the proposal that the bromine containing butene could be synthesised using a similar reaction as the LiCl/DMF reaction.

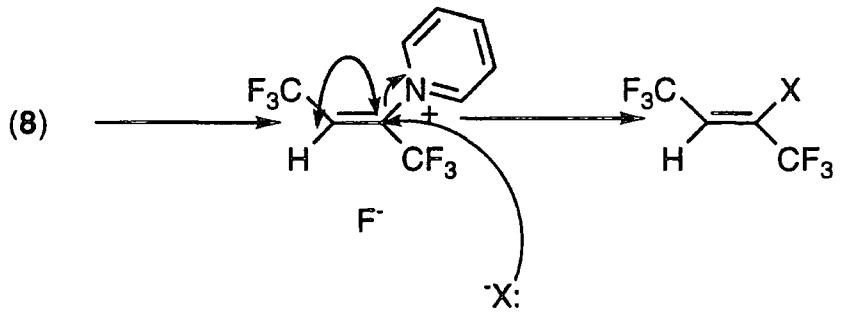
III.3.G. Lithium Bromide - Using identical conditions as above, the reaction of LiBr in DMF with (8) at 150°C resulted in almost quantitative recovery of (8). In an attempt to promote reaction, sulpholane was used as a solvent, and the temperature was increased to 200°C for 1 week. This time, the volatiles were shown to contain unreacted (8) and (Z)-2-bromo-1,1,1,4,4,4-hexafluorobut-2-ene(47) in a 90:1 ratio.



Identification of Product - The product was identified by ^{19}F and ^{1}H NMRs and its parent peak in GLCMS by comparison with literature data[40]. No isolation was attempted.

III.3.H. Lithium Iodide - No reaction was observed between (8) and lithium iodide in DMF at 150°C or in sulpholane at 200°C.

III.3.I. Addition of Pyridine - In an attempt to promote the reactions with LiBr and LiI to synthetically viable routes, a catalytic amount of pyridine was added to the reactions. It was hoped that pyridine would initially displace the vinylic fluorine, thus producing the pyridinium salt[248]. Then the displacement of pyridine by halide should be facile.



However, starting alkene (8) was observed as the only volatile product in both cases. The residues were examined by ^{19}F NMR for any indication of the pyridinium salt, but there was no evidence of this salt.

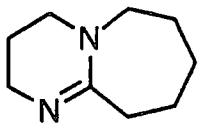
Choice of Metal Halides - The lithium salts were used for two reasons. The first is because this is the best cation for 'free' bromide or chloride. The second reason is to effectively remove the generated fluoride since lithium fluoride is not a source of active fluoride ion, and so prevent any back reaction to regenerate (**8**).

III.3.J. Rationale of Observed Products - The double bond in (**8**) is flanked by electron withdrawing trifluoromethyl groups, and this renders it electron deficient, and thus susceptible to nucleophilic attack[9]. This explains the difficulties experienced in the above attempts to eliminate HF from (**8**), because products resulting from nucleophilic attack rather than elimination, have been produced.

The next logical step, therefore, was to try to perform the elimination of HF from (**8**) using 'non-nucleophilic bases'.

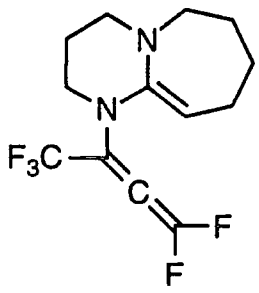
III.4. Reaction with Non Nucleophilic Bases

II.4.A. DBU - The 'non-nucleophilic' base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is perhaps the most common hindered base[249] used for dehydrohalogenations[250].



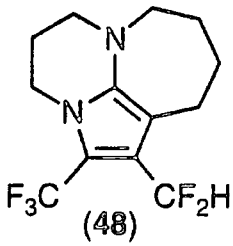
DBU

A tube containing excess DBU and (**8**) was agitated overnight, and then it was observed that no volatile material was present. The residual black oily solid was dissolved in hexane, and evaporation led to a pale yellow solid that only gave two ^{19}F NMR resonances, in a 3:2 ratio. The mass spectrum indicated a mass of 294, which is the equivalent of the mass of (**8**) plus the mass of DBU, less two equivalents of HF. Initial proposals were of an allene type product, which could be formed by initial nucleophilic attack on (**8**), resulting in vinylic substitution of fluorine, followed by elimination of fluoride from the activated trifluoromethyl group.



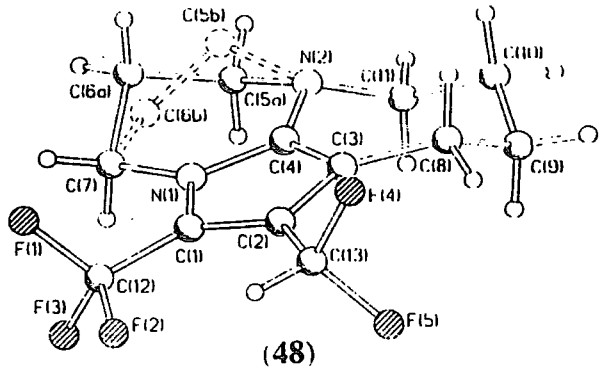
A closer examination of NMR and IR data, especially the lack of an allenic carbon in the ^{13}C spectrum (~200ppm)[251] and the lack of allenic stretch in the IR (~2000cm^{-1})[251], cast

doubts on the credibility of this proposal. Further ponderance led to the proposal of a tricyclic fused pyrrole (48), which seemed to fit all the spectroscopic data.



(48)

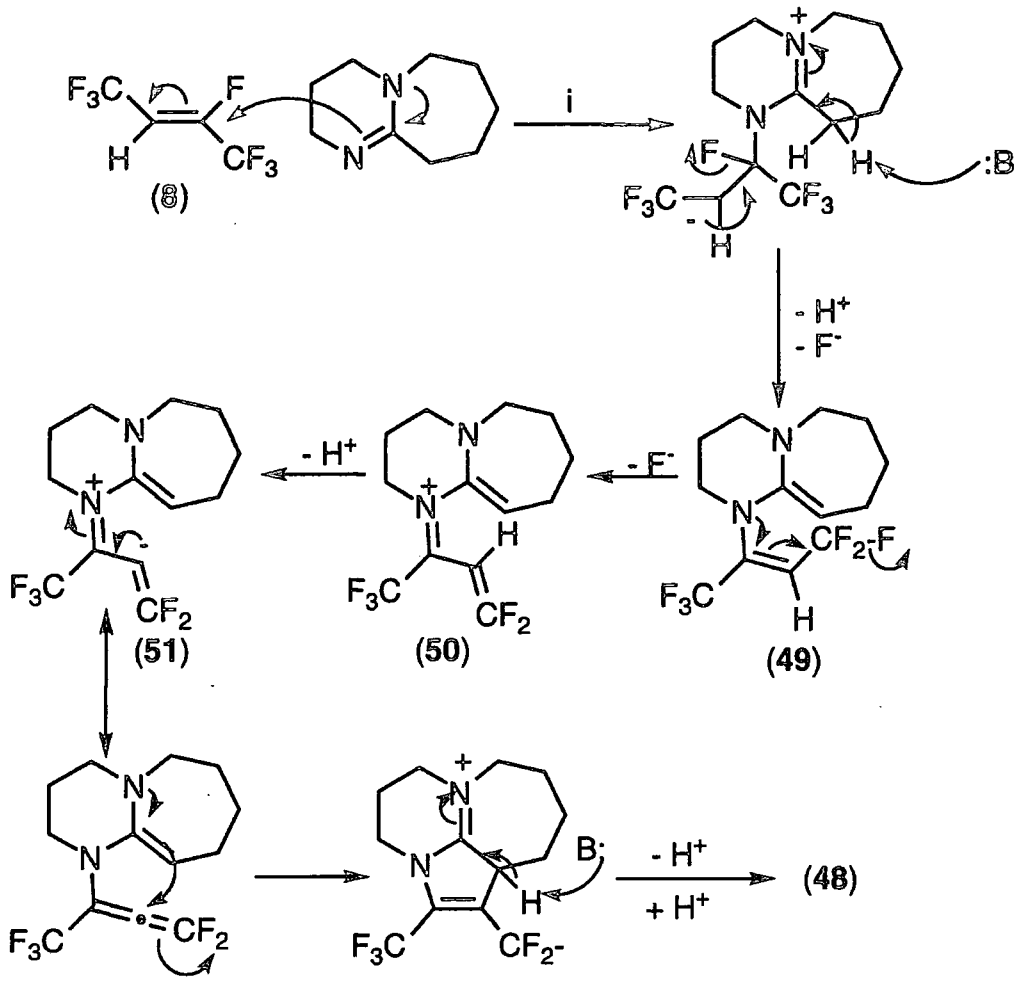
Further repetitions of this reaction under various conditions showed that if hexane was used as the reaction solvent, and a ratio of DBU to (8) of 4:1, yields of 85% of the product with the formula $C_{13}H_{15}N_2F_5$ (established by elemental analysis) could be produced. Following further recrystallisations from hexane, it was possible to grow single crystals of the product, that were suitable for a single-crystal X-ray diffraction study, and thus the proposal of the unusual tricyclic pyrrole structure for (48) was confirmed.



(48)

The five membered ring is planar. The seven membered ring adopts a distorted chair conformation, and the six membered ring has a non-symmetrical twist conformation. The carbon atoms C(5) and C(6) are disordered over the two positions with occupancies of 75% (a) and 25% (b, dashed, hydrogen atoms omitted).

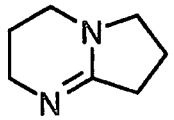
II.4.B. Mechanism - The formation of (**48**) probably begins with nucleophilic attack by DBU on (**8**), leading to vinylic displacement of fluoride ion, followed by proton loss to give (**49**). The further loss of fluoride must occur from trifluoromethyl, and (**49**) to (**50**) seems reasonable as related systems have shown similar examples of fluoride loss[203, 252, 253]. The cyclisation step commences with the generation of anion (**51**), which is facilitated by the adjacent positively charged nitrogen. Cyclisation occurs via nucleophilic attack by the ketimine on the middle carbon of the allene. Proton transfer to the anion creates the CF_2H group, which would be difficult to account for, other by than the process shown.



i = DBU : (8) = 4:1, hexane , sealed tube , room temp, 2 days .

Thus, it has been shown that a 'non-nucleophilic' base has been shown to react a difunctional nucleophile! There are three reports of similar observations in the literature[254-256].

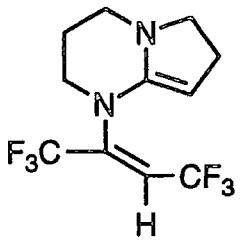
II.4.C. DBN - In most of the reported examples of nucleophilic behaviour of DBU, similar behaviour was also reported for the more reactive hindered base, DBN.



DBN

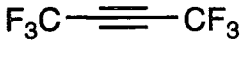
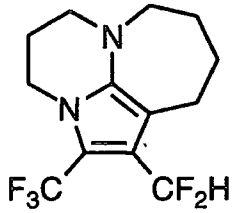
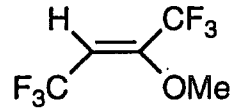
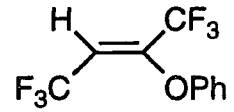
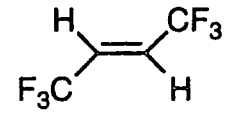
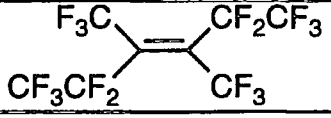
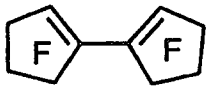
So, DBN was reacted with (**8**), using identical conditions as above. However, after two days, only a mixture of unidentifiable products was observed. A ^{19}F NMR of the reaction solution after 10 minutes gave only signals corresponding to (**8**) and two other CF_3 signals (-60 and -65ppm). This pair of CF_3 resonances, shifted to higher frequency

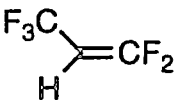
from the CF_3's in (8), are characteristic of a simple substitution product of (8), where the vinylic fluorine has been replaced. This is attributed to an intermediate formed via nucleophilic attack on (8) by the imine functionality of DBN, resulting in vinylic substitution of fluorine.



So it can be proposed that in the reaction with DBN, although initial attack occurs in a similar fashion to the reaction with DBU, further reaction does not proceed cleanly.

II.4.D. DBU and other Fluorinated Systems - In an attempt to probe the applicability of DBU as a difunctional nucleophile, several different fluorinated systems were reacted with DBU, and the results are tabulated.

Compound	Conditions	Product
	RT	 (65%)
	RT-100°C	None
	RT-100°C	None
	RT-100°C	None
	RT	100% Conversion to unidentified products
	RT	100% Conversion to unidentified products
	RT	100% Conversion to unidentified products

	RT	100% Conversion to unidentified products

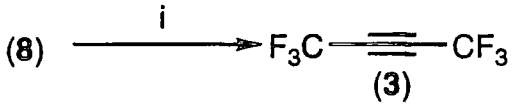
These reactions raise several points worthy of discussion. The first is that because the same product is formed using butyne (3) as (8), it could be argued that the initial step in the reaction between (8) and DBU must be elimination of HF to produce (3). However, this theory can be disproved, since the yield using (3) is lower than when (8) is used.

Secondly, these results show conclusively that DBU will attack terminal CF_2 and vinylic fluorine functionalities (even if in an uncontrollable fashion), thus proving DBU is reacting as a nucleophile. The main implication of these reactions, and the DBN reaction, is that the use of DBU as a difunctional nucleophile is very limited, and the reactions with (8) and (3) are a special case.

III.5. Successful Routes To Hexafluorobut-2-yne (3)

Despite the (interesting) difficulties described in this chapter, two successful methods of eliminating HF from (8) to form (3) have been developed.

III.5.A. Caesium Fluoride as a Base - When (8) was passed through a hot glass pyrolysis tube containing caesium fluoride, mixtures of unreacted (8) and (3) were recovered. These compounds could be separated by repeated distillation at 0°C.



i = CsF, pyrolysis

Optimum conditions are shown below.

Temperature /°C	N_2 Flow /ml min^{-1}	Length of CsF Plug /cm	Hexafluorobut-2-yne (3)*	Recovered (8)
300	100	1	23%	37%
350	150	1	36%	50%
300	150	2	8%	77%

(* isolated yield)

Identification of Product - The product was identified by its singlet in the ^{19}F NMR spectrum and its pair of quartets in the ^{13}C NMR spectrum, its parent ion in GLCMS and

IR spectra, by comparison with literature data[23, 257] and comparison with an authentic sample.

The caesium fluoride plugs were coated in black tars after each run. It was possible that these tars could have contained caesium pentakis(trifluoromethyl) cyclopentadienide (33b), so after several runs, the plug was removed, and stirred with DCM in an attempt to dissolve any (33b), and filtration removed the caesium fluoride. However, a ^{19}F NMR of the DCM solution showed only a weak fluoride ion signal.

III.5.B. ^{t}Butyl Lithium - A 1:1 mixture of ^{t}butyl lithium in pentane and (**8**) was allowed to warm from liquid air temperatures to 0°C, and the volatiles collected, were shown to contain only (**3**), in 41% yield.

A variety of different procedures for this reaction were used, and the results are tabulated below.

Method	Isolated Yield of Hexafluorobut-2-yne
a	16%
b	41%
c	19%
d	28%
e	22%

Where **a** = The reaction mixture was allowed to warm from liquid air temperatures to -78°C, kept at this temperature for 1 hour, and then allowed to warm to 0°C, thus distilling (**3**).

b = The reaction mixture was allowed to warm from liquid air temperatures to 0°C, and any product distilled was caught in a liquid air temperature trap.

c = The tbutyl lithium was added dropwise to the reaction mixture, cooled to -10°C, and any product distilled was caught in a liquid air temperature trap.

d = The reaction mixture was allowed to warm from liquid air temperatures to room temperature, and agitated overnight. The product was then distilled at 0°C.

e = The reaction was performed as (**b**), but using a 400% excess of tBuLi.

III.6. Conclusions

(1) New routes to hexafluorobutyne have been found starting from (**8**), and they are simple, practical laboratory preparations.

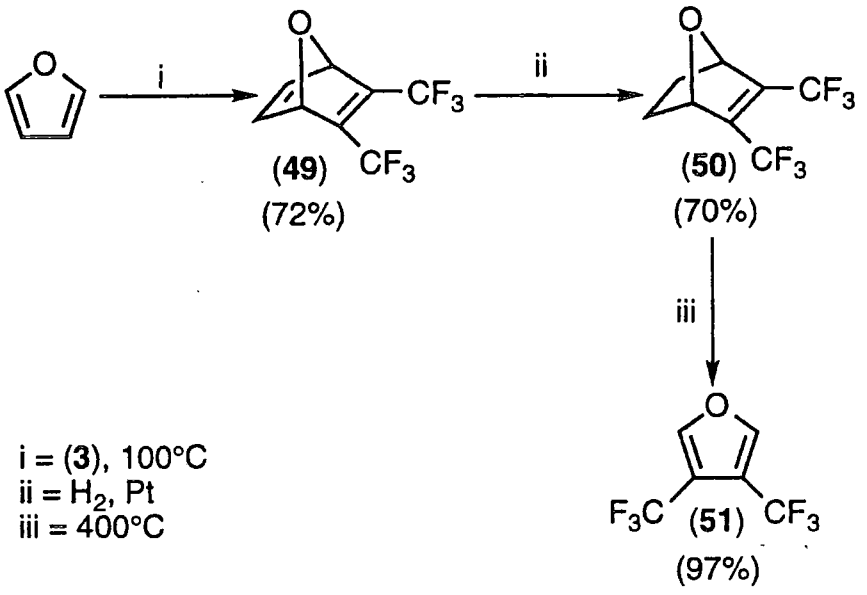
(2) DBU has been shown to react as a difunctional nucleophile with (**8**), producing a tricyclic pyrrole (**48**), and its structure has been confirmed by a single crystal X-ray study.

Chapter Four

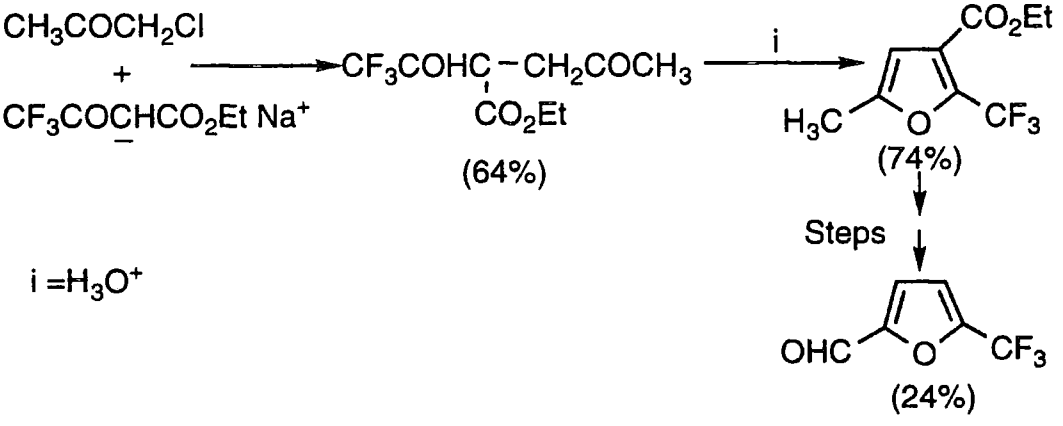
In the course of this work, many bis(trifluoromethyl) containing furans have been produced, and the following is a overview of the literature concerning these and related compounds.

IV.1. Poly-trifluoromethylated Furans

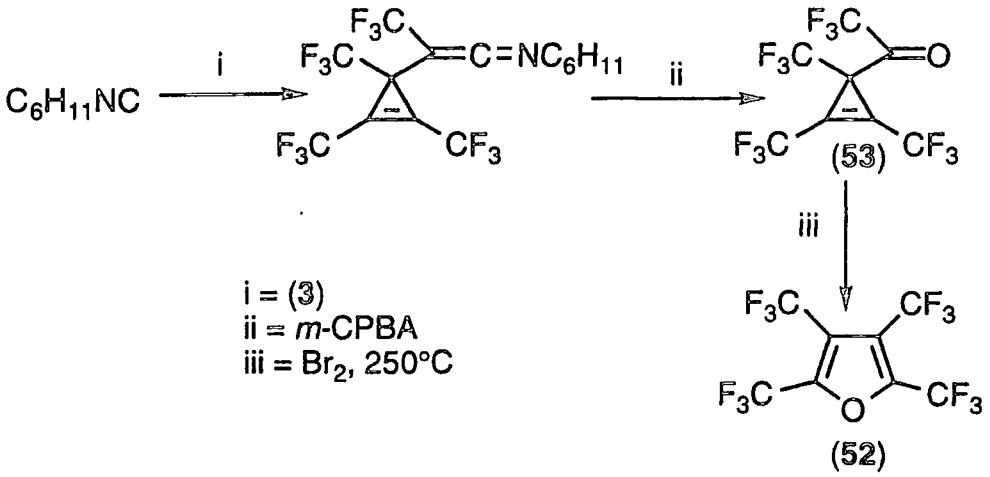
In 1962, Weis[235] showed that hexafluorobutyne (**3**) would react with furan to produce (**49**) in good yield. Compound (**49**) was readily reduced, producing (**50**), and pyrolysis of (**50**) resulted in furan (**51**).



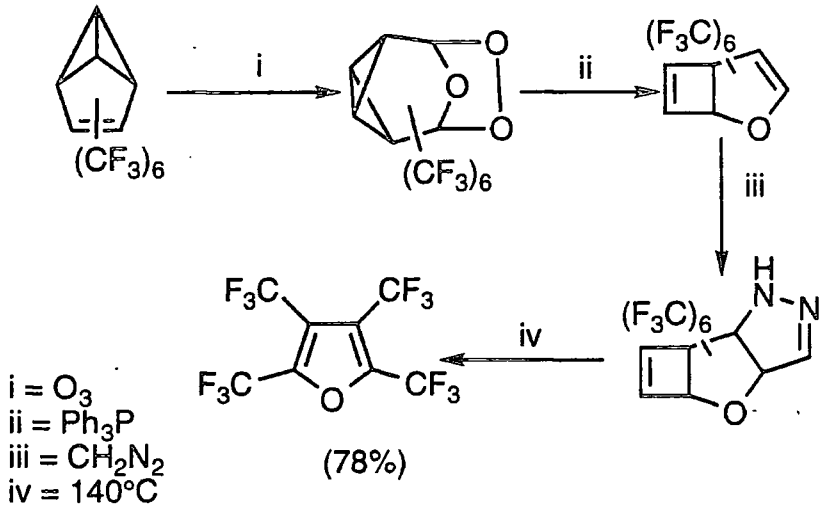
In 1968, workers, reported the synthesis of 5-trifluoromethyl-2-furancarbaldehyde, and simple derivatives of it[258]. Two years later, they also published work concerning the production of a variety of 4-trifluoromethyl furans by similar methodology[259].



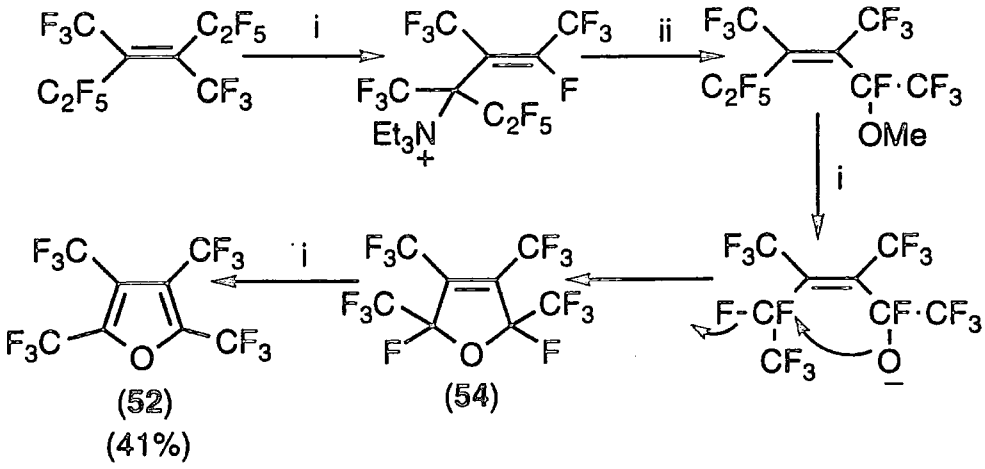
In 1978, four different routes to tetrakis(trifluoromethyl) furan (**52**) appeared in the literature. The first involved hexafluorobutyne (**3**) and cyclopropenyl ketone (**53**)[260].



The second was via the ozonolysis of hexakis(trifluoromethyl)benzvalene[261].

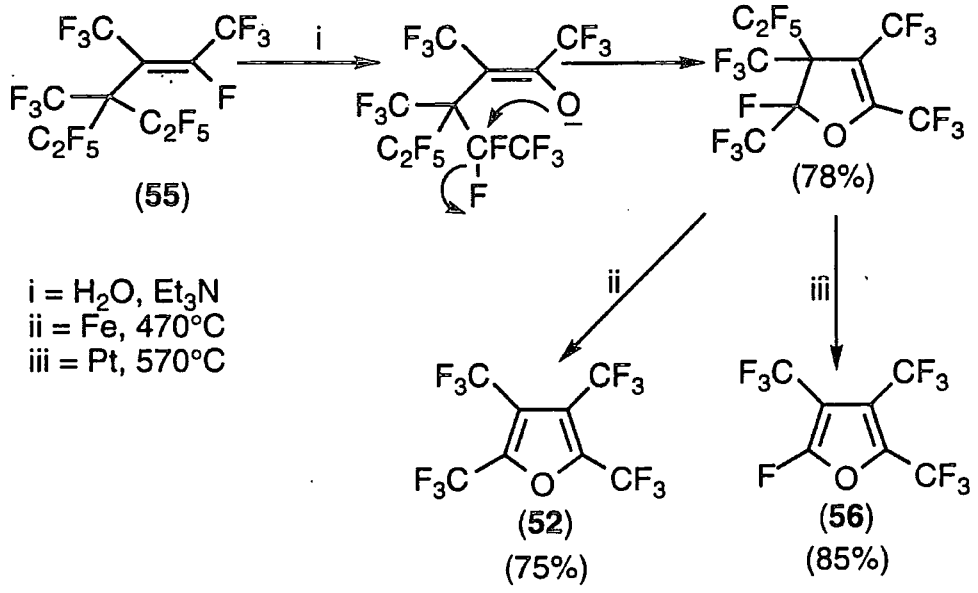


Chambers and co-workers[262]have reported a remarkable reaction, where a tetramer of TFE reacts with base and methanol, to form the isolable intermediate (**54**), and this defluorinates to produce (**52**).



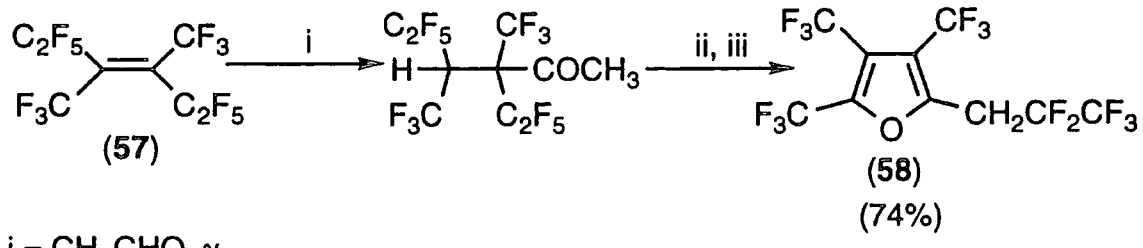
i = Et_3N, tetraglyme
ii = MeOH

Fluoroalkene (55) may also be converted into (52)[262, 263] or, under different conditions, (56).



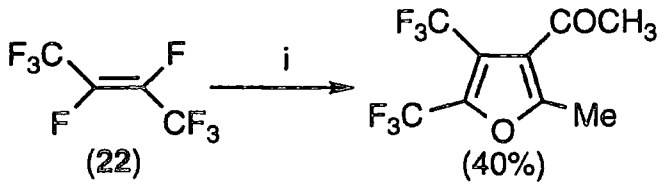
i = H_2O, Et_3N
ii = Fe, 470°C
iii = Pt, 570°C

In 1980, it was reported that the free radical addition of acetaldehyde to (57) gave a product which would react further with base to give a novel cyclisation, leading to furan (58)[264].



i = CH_3CHO, γ
ii = Base
iii = 600°C, Pt

As reported previously, perfluorobut-2-ene (22) and diethylmalonate produce (25)[156].



(22) (40%) (25)

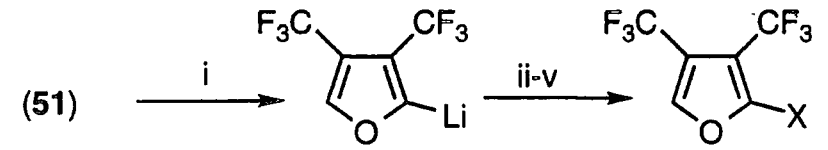
i = $CH_2(COCH_3)_2$, base

The trifluoromethylation of electron rich aromatics using bis(trifluoroacetyl) peroxide was reported in 1990[265], and this produced furan (**59**) in 53%.

(**59**)
(53%)

i = $(CF_3CO_2)_2$, 60°C

In 1991, two routes to bis(trifluoromethyl)-ated furans were published. The first was by workers in Manchester[266], who used Weis'[235] methodology to produce furan (**51**). This compound was then lithiated, using previously reported methodology[267], and reacted with a variety of electrophiles to produce a selection of 3,4-bis(trifluoromethylated) furans.

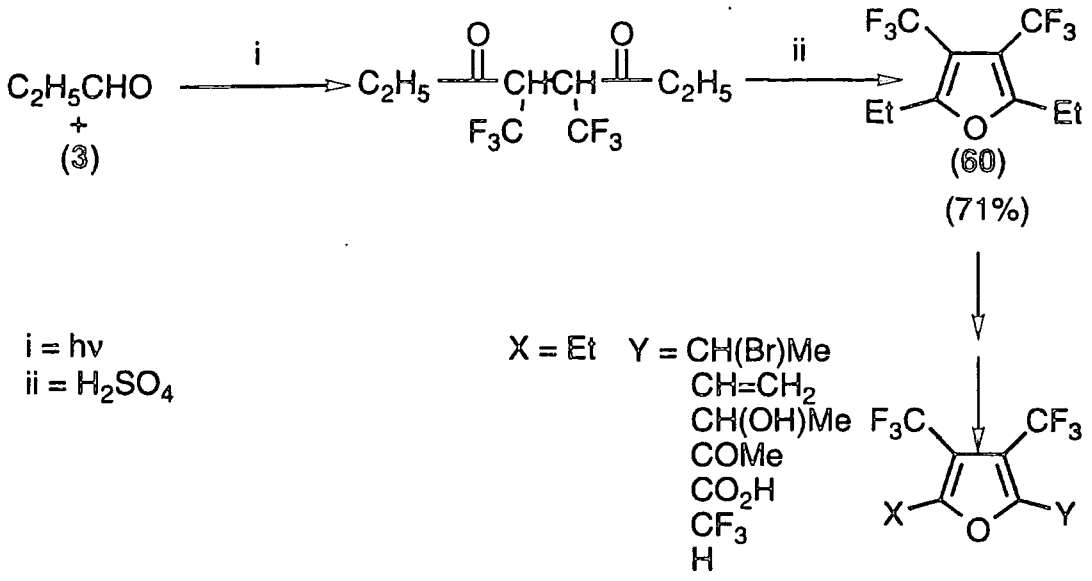


i = ^{n}BuLi, -70°C
ii = CO_2, H_3O^+
iii = DMF, H_3O^+
iv = MeCHO,H_3O^+
v = CH_2=CHCHO, H_3O^+

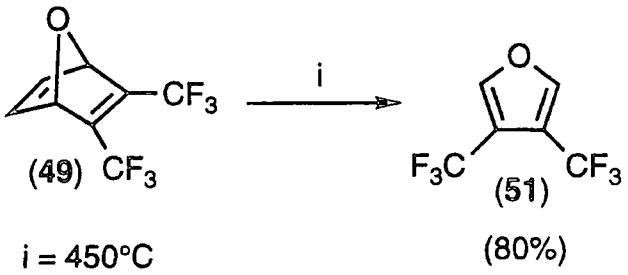
(54-82%)

X = CO_2H, CHO,
CH(OH)Me, CH(OH)CH=CH_2

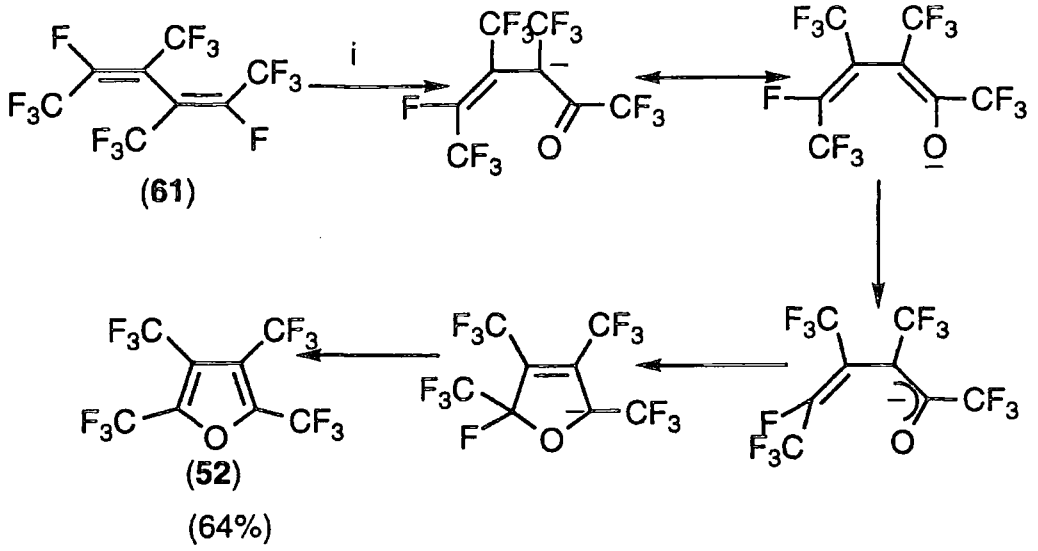
The second route was reported by Japanese workers[268], and concerns the free radical addition of propionaldehyde with (**3**), and the di-adduct from this reaction cyclises in acidic media to give furan (**60**) in good yield. Chemistry performed on the ethyl groups of (**60**) produced a variety of derivatives.



Interestingly, the Manchester workers reported that the pyrolysis of endoxide (49) at 450°C gave furan (51)[269], but they claim that this experiment did not give consistent results, and that partial hydrogenation and pyrolysis, as reported by Weis[235], is the preferred route to furan (51).



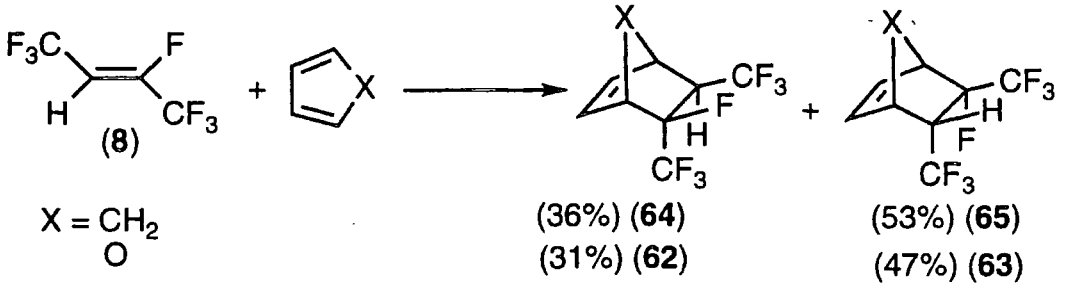
Workers in these laboratories have shown that the perfluorinated diene (**61**), which is obtained via defluorination of a TFE tetramer, will react with water in the presence of base to produce (52)[252]. Again, this is an example where Baldwin's rules[207] indicate that the reaction probably proceeds via a 1,5-electrocyclisation, and not via a disallowed 5-*Endo-trig* cyclisation.



The following is a more detailed description of the previous work performed in these laboratories concerning (**8**) with furan or cyclopentadiene.

IV.2. Reaction of (8) with Furan and Cyclopentadiene.

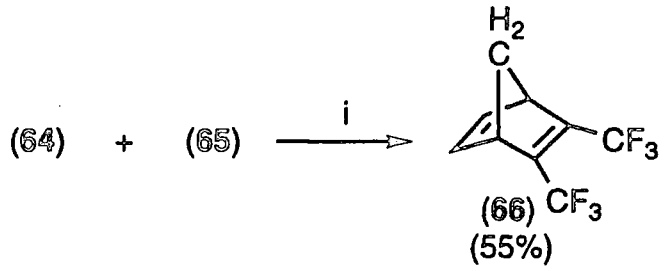
Workers in this laboratory have shown that (**8**) will react with furan and cyclopentadiene, to produce the expected Diels Alder adducts (**62**) - (**65**)[31, 188].



Odello[31] separated (**62**) and (**63**) via preparative scale GLC, and assigned the stereochemistry of the isomers via a close study of the ^1H NMR spectrum. The assignments were based on the knowledge that coupling between protons on vicinal carbons in rigid systems, depends largely on the dihedral angle between the H-C-C' and C-C'-H' planes. This is Karplus' Rule[251], and it allows the prediction of the coupling constant between the bridge head proton and the endo proton to be ~0Hz, and between the bridge head proton and the exo proton as ~5Hz. This difference was notable, with observed values of 0Hz and 4Hz respectively.

The elimination of HF from (**62**)-(**65**) was a main objective, since this would demonstrate the utility of (**8**) as a synthon for hexafluorobutyne (**3**). However, using potassium ^{t}butoxide in butanol, this reaction was only successful for the cyclopentadiene adducts[188], producing 2,3-bis(trifluoromethyl) norbornadiene (**66**), which is a popular

monomer for ROMP polymerisations[270, 271]. Literature preparations of (66) involve the use of expensive hexafluorobutyne (3) and cyclopentadiene[271].

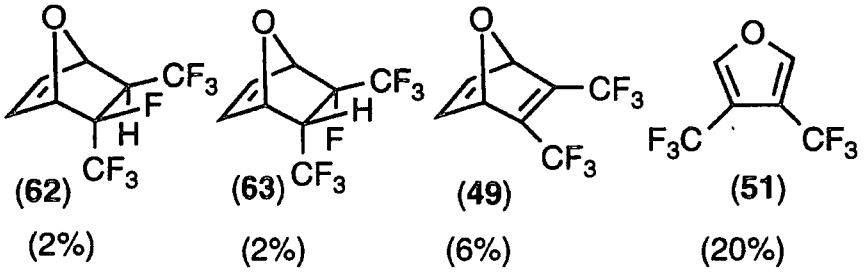


i = ^{t}BuOH, KO^{t}Bu, Reflux

Results and Discussion

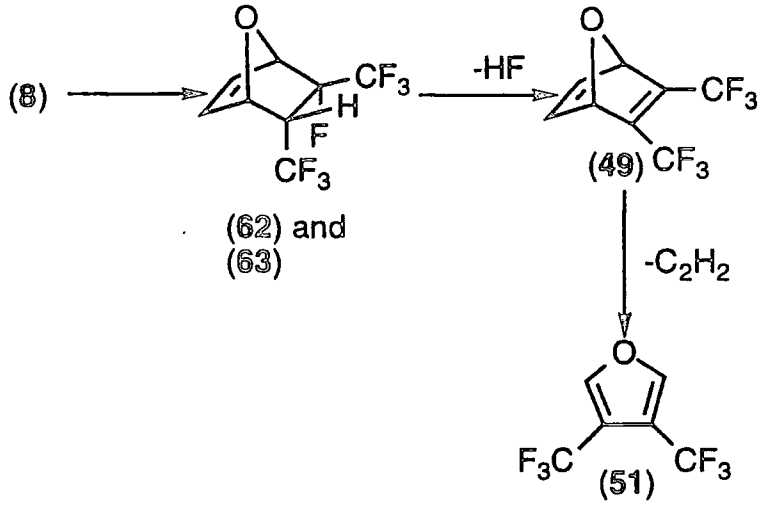
IV.3. Further Investigation of the Reaction of (8) with Furan

In an attempt to explore further the elimination of hydrogen fluoride from (62) and (63), more was synthesised by the reaction between furan and (8). The reaction was performed at a higher temperature (200°C) than previously (120°C), with a view to increase the conversion. However, at this temperature a mixture of four compounds was obtained.



Identification of Products - These products are all known compounds[31, 188, 235, 266, 269], and were identified by their parent ions in GLCMS, and confirmed by their ^{19}F NMR and ^{1}H data by comparison with literature data or authentic samples. The formation of (51) was unexpected, and the structure followed from the above techniques, and later from ^{13}C NMR, which only displayed two quartets and a singlet.

Mechanism - The presence of all four products confirms the reaction pathway. The Diels Alder adduct is formed initially, and at this temperature, hydrogen fluoride is thermally 'cracked out', to produce endoxide (49). Also at these elevated temperatures, (49) under goes a retro Diels Alder reaction, to produce (51). Also, in the previous chapter, it has been shown that (8) does not eliminate hydrogen fluoride to give (3) at these temperatures.

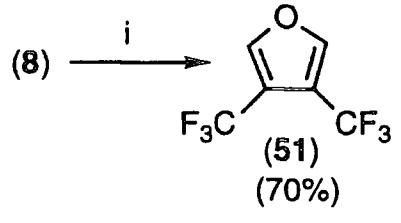


It was hoped that it would be possible to find conditions where (**49**) was the major product, since it is possible to easily prepare trifluoromethylated benzenes, phenols and furans from this compound[188, 235].

Conditions	Temperature	(62) and (63)	(49)	(51)
a	120°C	78%		
b	150°C	5%	19%	
c	150°C	8%	4%	
d	200°C			25%
e	300°C			70%

Where a = Carius tube, agitated by horizontal rotation, for 4 days.
b = Quartz tube (~5ml volume), no agitation.
c = As a, but with water as solvent.
d = Rocked sealed metal tube, 1 week.
e = Rocked sealed metal tube, 8 hours.

As shown above, the promotion of (**49**) as a major product was unsuccessful under these conditions. The best temperature for the synthesis of furan (**51**) was found to be 300°C, which resulted in a 70% isolated yield.



i = Furan, 300°C, Sealed metal tube

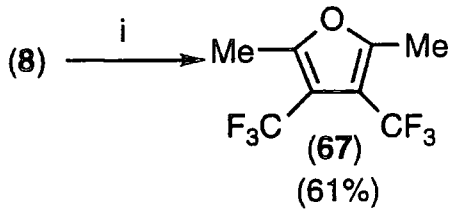
Thus, a very efficient synthesis to 3,4-bis(trifluoromethyl) furan (51) had been discovered. One large advantage with this reaction is the simple work-up procedure.

Procedure - The reaction was performed in a sealed metal tube for three days at 300°C. The tube was allowed to cool, and unreacted (8) was removed by distillation at room temperature and atmospheric pressure. The residual mixture was filtered, and the filtrate was shown to consist of (51) in ~95% purity . This was ample purity for ^{13}C NMR analysis. Distillation (bp 87-89°C) produced ~6g of product that gave a satisfactory elemental analysis.

IV.4. Extension of Methodology

To test the general applicability of this reaction where (8) essentially bis(trifluoromethyl)-ates a furan, the reaction between (8) and a variety of furans was studied.

IV.4.A. Dimethyl Furan - The reaction between dimethyl furan and (8) was performed at 200°C and 300°C, giving (67) in yields of 61 and 24% respectively.

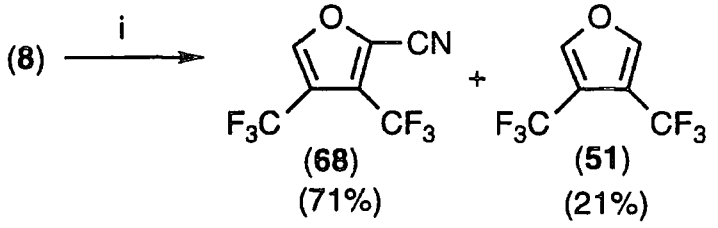


(67)
(61%)

i = Dimethylfuran, 200°C, Sealed metal tube

Identification of Product - The product was isolated by distillation (52-56°C /12mmHg). It is a known compound[268], and was identified by its parent peak in GLCMS, and by ^{1}H and 19F NMRs by comparison with literature data. It was also possible to obtain the ^{13}C NMR spectrum, which consisted of two quartets and two singlets.

IV.4.B. 2-Furonitrile - The reaction of (8) and 2-furonitrile at 250°C gave a mixture of two products, identified as (68) and (51).



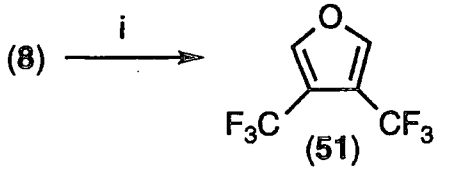
(68)
(71%)

(51)
(21%)

i = 2-Furonitrile, 250°C, Quartz tube

Identification of Product - It was possible to distill apart (**51**) and (**68**). Product (**68**) is a new compound, and was identified by elemental analysis, its parent peak in the GLCMS spectrum, its single ^{1}H resonance at 8.48ppm, two CF_3 resonances in the ^{19}F spectrum, and its ^{13}C spectrum which showed the seven different carbon resonances.

IV.4.C. 2-Furoic Acid - The reaction of 2-furoic acid with (**8**) at 200°C and 300°C gave moderate yields of (**51**). There was no evidence of 3,4-bis(trifluoromethyl)-2-furoic acid (**69**)[266, 268].



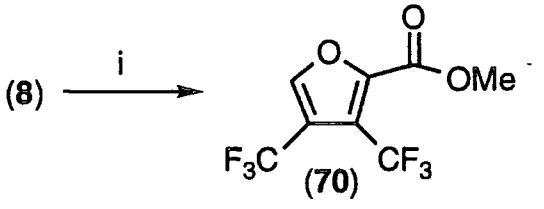
(**51**)

(39%)

i = 2-Furoic Acid, 300°C, Sealed metal tube

Presumably, the decarboxylation is caused by the high temperature.

IV.4.D. Methyl 2-Furanoate - The reaction of methyl 2-furanoate with (**8**) at 250°C gave product (**70**) in 85% yield.



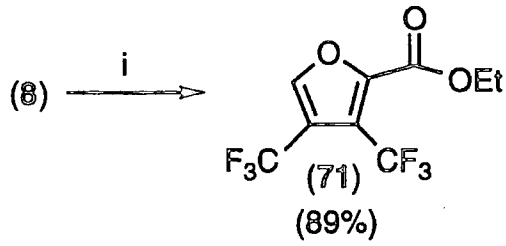
(**70**)

(85%)

i = Methyl 2-furanoate, 250°C, quartz tube

Identification of Product - Product (**70**) is a known compound[266], and was identified by its parent peak in GLCMS, and its ^{1}H, ^{19}F and ^{13}C NMR spectra by comparison with literature data.

IV.4.E. Ethyl 2-Furanoate - The reaction of ethyl 2-furanoate with (**8**) at 250°C gave product (**71**) in 89% yield.

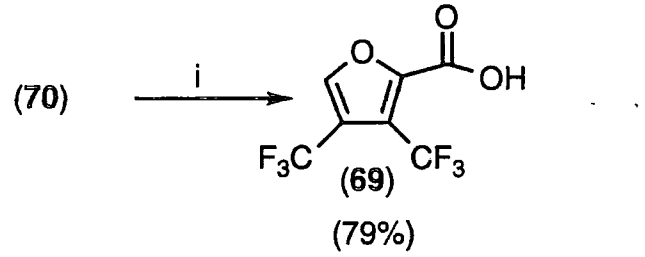


i = Ethyl 2-furanoate, 250°C, quartz tube

Identification of Product - Product (71) is also a known compound[266], and was similarly identified by its parent peak in GLCMS, and its ^{1}H, ^{19}F and ^{13}C NMR spectra by comparison with literature data.

The idea behind making the esters, was because they should provide a route to the otherwise unobtainable bis(trifluoromethyl) furoic acid(**69**).

IV.4.F. Hydrolysis of (70) - Both (**70**) and (**71**) were found to be resistant to acid hydrolysis. However, the desired transformation could be performed by a literature method for basic hydrolysis[106], using moist potassium ^{t}butoxide. This resulted in the production of (**69**) in 79% yield.

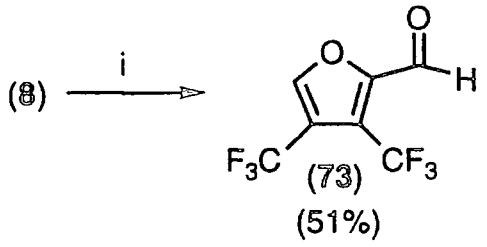


i = potassium ^{t}butoxide, water, acetonitrile, room temp.

Identification of Product - Product (**69**) was recrystallised from ether/chloroform, and obtained as pale yellow needles. Product (**69**) is a known compound[266, 268], and was identified by its parent peak in mass spectrum, and its ^{1}H, ^{19}F and ^{13}C NMR spectra by comparison with literature data.

(It is possible that hydrolysis of (**68**) could also result in the formation of (**69**), however due to the expense of the starting furonitrile, the above method was used in preference).

IV.4.G. 2-Furancarbaldehyde - The reaction of 2-furancarbaldehyde with (**8**) at 225°C gave product (**73**) in 51% yield.



(73)
(51%)

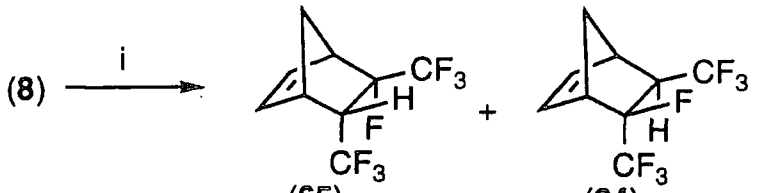
i = 2-Furancarbaldehyde, 225°C, quartz tube

Identification of Product - Product (73) is a known compound[266], and was similarly identified by its parent peak in GLCMS, and its ^{1}H, ^{19}F and ^{13}C NMR spectra by comparison with literature data.

IV.5. Reaction of (8) with Cyclopentadiene

Bearing in mind the reaction with (8) and furan yielding 3,4-bis(trifluoromethyl) furan (51), it was hoped that the reaction with (8) and cyclopentadiene at elevated temperatures, would provide a route to bis(trifluoromethyl) cyclopentadiene (72), and as explained earlier, in the literature there is only one other example of a cyclopentadiene bearing two trifluoromethyl groups. Therefore the reaction between (8) and cyclopentadiene was investigated at a variety of temperatures.

IV.5.A. Reaction at room temp.- 200°C - The reaction between (8) and cyclopentadiene, performed at temperatures varying from room temperature to 200°C, produced only the simple Diels Alder adducts (64) and (65), in a 1:1 ratio.

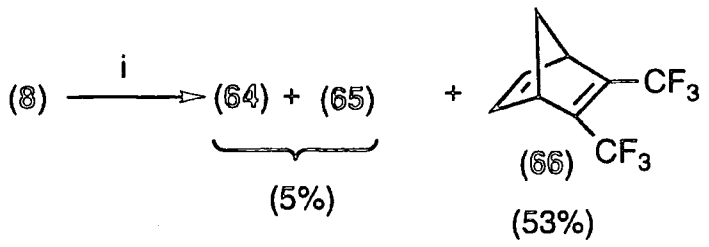


(65) (41%) (64) (40%)

i = Cyclopentadiene, 200°C, quartz tube

Identification of Products - Both isomers gave parent peaks in GLCMS. It was possible to isolate each isomer by preparative scale GLC, and determine the stereochemistry of each isomer, by comparison of ^{1}H and ^{19}F NMR data with similar data for (62) and (63), whose stereochemistry was assigned by a previous worker[31].

IV.5.B. Reaction at 300°C - The reaction between (8) and cyclopentadiene at 300°C gave a mixture of three products.



i = Cyclopentadiene, 300°C, quartz tube

Identification of Products - Product (66) is a known compound, and was identified by its parent peak in GLCMS, and ^{1}H, ^{19}F and ^{13}C NMR data, by comparison with literature data.

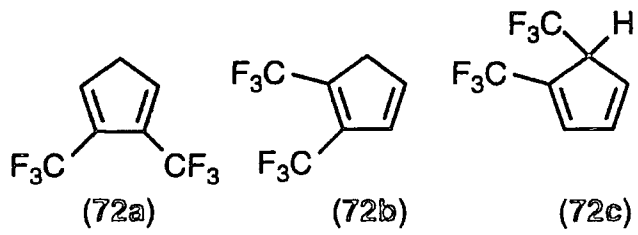
IV.5.C. Reaction at 400°C - The reaction between (8) and cyclopentadiene at 400°C gave an unidentifiable tarry mixture.

IV.5.D. Pyrolysis of Products - In an attempt to facilitate elimination of hydrogen fluoride and retro Diels Alder cleavage of ethyne, (64) and (65) were heated in a sealed tube at 250°C for 1 week, but no elimination was observed. After heating at 300°C for four days, trace amounts of (66) were observed. It was then proposed that pyrolysis through a flow system may produce better results, and (64) and (65) were passed through a glass tube at elevated temperatures, containing glass wool.

Temperature	(64), (65)	(66)	(72)
400°C	40%		
450°C	6%	18%	6%
500°C	7%	17%	5%

Identification of Product - Bis(trifluoromethyl) cyclopentadiene (72) was observed as a mixture of olefinic isomers (72a-c), which gave a very broad GLC peak, all of which gave the same parent ion of 202. The ^{19}F NMR gave numerous resonances in the region $-\delta_F$ = 50-75ppm, however no assignments were possible on the small of compound produced.

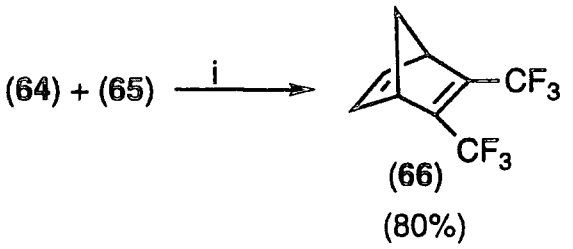
Olefinic Isomers of bis(trifluoromethyl)cyclopentadiene



(72a) (72b) (72c)

IV.5.E. Elimination of HF from (64) and (65)

It was proposed that a better route to (72) would be the production of (66), followed by partial hydrogenation, and then pyrolysed[235, 269]. Therefore, a mixture of (64) and (65) was treated with potassium ^{t}butoxide in butanol[188], to eliminate hydrogen fluoride, and diene (66) was isolated in 80% yield.



(66)

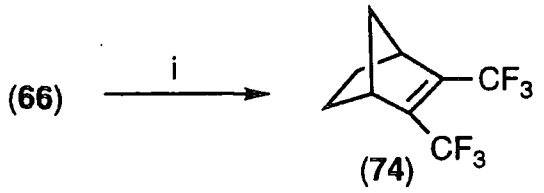
(80%)

i = ^{t}BuOK, ^{t}BuOH, room temp.

This reaction is reported to proceed to completion in hour at reflux[188]. However, it was interesting to observe that at room temperature, after one hour, all of (65) had reacted, whereas approximately one third of (64) remained. The reaction was found to proceed to completion at room temperature overnight. This can be rationalised by the *exo* hydrogen in (65) being less sterically hindered than the corresponding proton in (64), and so the more accessible to the butoxide anion.

IV.5.F Hydrogenation of (66)

Hydrogenation of (66) was performed using Parr apparatus, with a platinum catalyst on activated carbon.



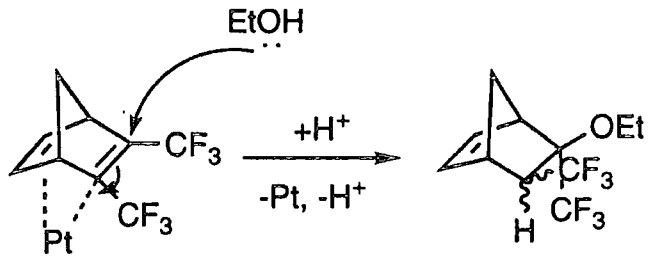
(74)

i = H_2, Pt/C, EtOH

However, despite compound (74) being the major component of the product mixture, the reaction did not proceed as cleanly as expected, with at least five other products produced.

Identification of Product - Compound (74) is a new compound, and was identified by its molecular ion in GLCMS, its single ^{19}F NMR resonance and its ^{1}H NMR which consisted of four equal intensity signals. Due to the complexity of the product mixture, this compound was not isolated. Mass spectrometry of the product mixture indicates that several of the products have incorporated ethoxide. This was unexpected, and a possible

explanation may be that ethanol, the reaction solvent, attacks complex (75), where the platinum is activating one or both of the double bonds towards nucleophilic attack.

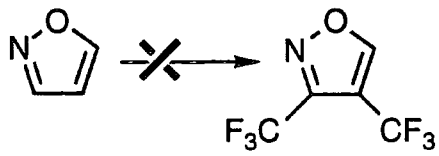


(75)

IV.5.G. Pyrolysis - The product mixture from the above reaction was pyrolysed at 400°C in an attempt to produce (**72a-c**). However, despite small amounts of (**72a-c**) being observed in the product mixture, the mixture contained many products, and was not synthetically viable. Time limitations have prevented the further repetition of the hydrogenation step in a different solvent (e.g. THF), and the subsequent pyrolysis of (**74**).

IV.5.H. Reaction of (8) with Isoxazole

In an attempt to form bis(trifluoromethyl)isoxazole, the reaction of (**8**) with isoxazole performed.



However, at 200°C and 300°C only intractable mixtures of unidentified products were produced. This was not too surprising as isoxazoles are known to not react as dienes in classical Diels Alder reactions[272].

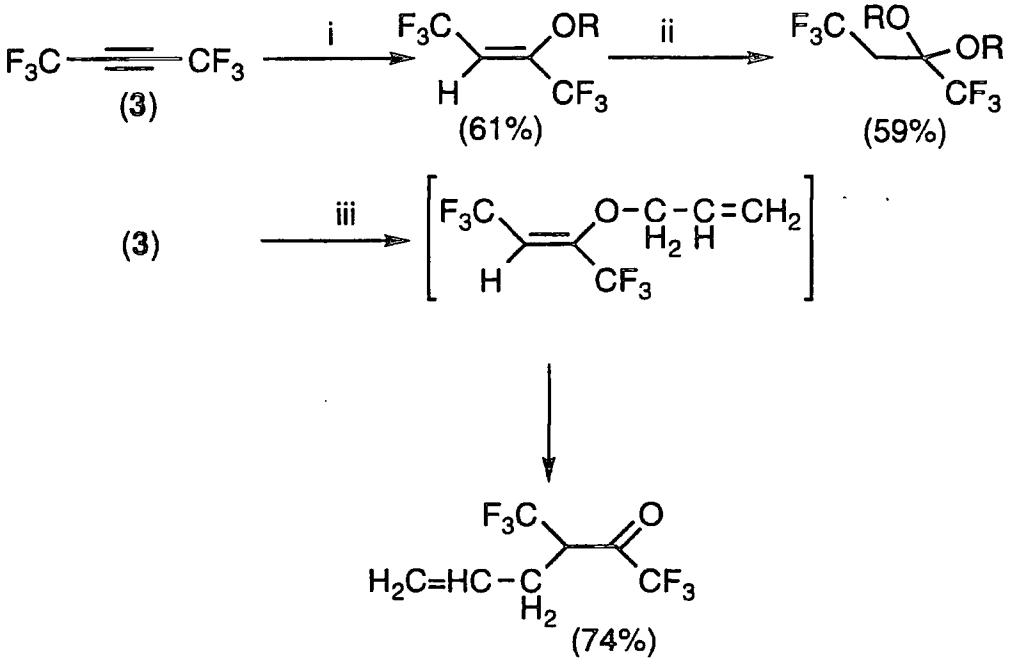
V. Reaction of 2*H*-Heptafluorobut-2-ene (8) with Nucleophiles

As shown in chapter one, heptafluorobut-2-ene (8) will react readily with oxygen and nitrogen nucleophiles, and generally, the products are the same as the products formed when the same nucleophile reacts with hexafluorobutyne (3). Therefore, the following is a brief summary of the reported reactions between (3) and oxygen and nitrogen nucleophiles.

V.1. Review of (3) with Nucleophiles

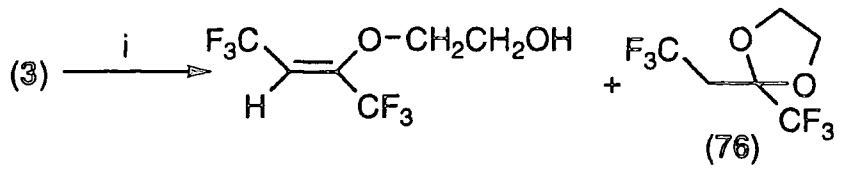
V.1.A. Oxygen Nucleophiles

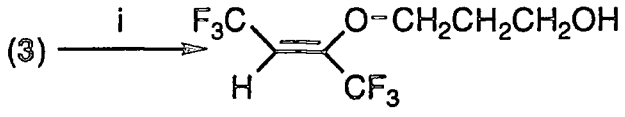
Methanol and ethanol addition at room temperature requires the presence of a base, and at higher temperatures, diaddition occurs[240]. Work from these laboratories has explored the reaction of (3) with different alcohols under various conditions, and report that base catalysed reactions generally give trans addition, whereas uncatalysed reactions performed at elevated temperatures mainly give cis addition[241]. The addition of allyl alcohol is accompanied by a Claisen rearrangement[273].



i = RONa, Room temperature; ii = RONa, 70°C
iii = Allyl alcohol, NaOH, 50°C

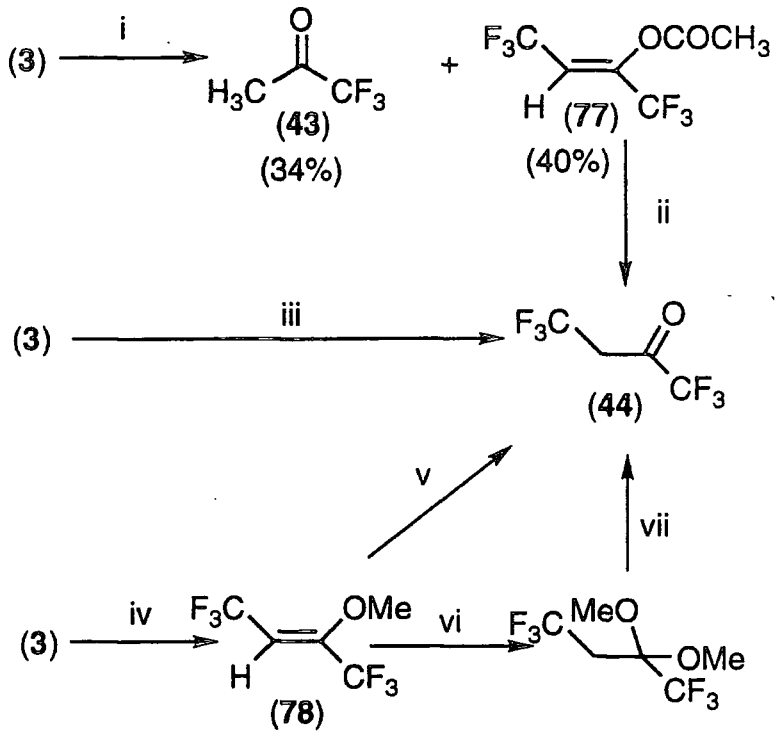
Dihydric alcohols are reported to give both cyclic and acyclic products[274].





i = ROH, NaOR,50°C

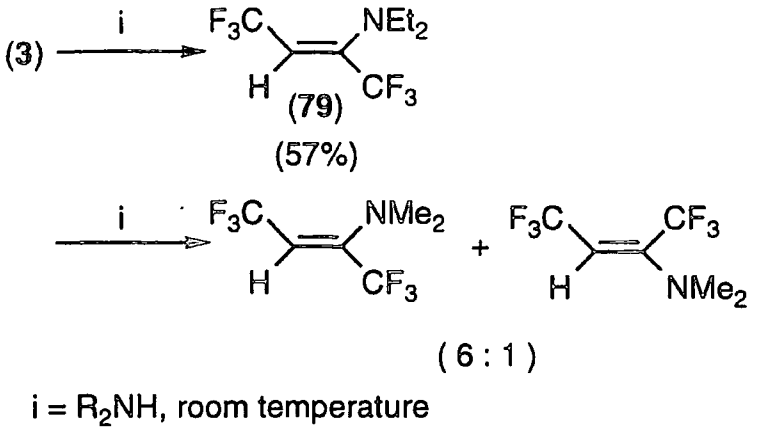
Acetic acid adds to (3) to give (43) and enol acetate (77), and (77) can be hydrolysed by acid to give (44)[245]. Ketone (44) has also been produced by a variety of routes[240], with perhaps the most direct being the reaction between (3) and water at 110°C[241].



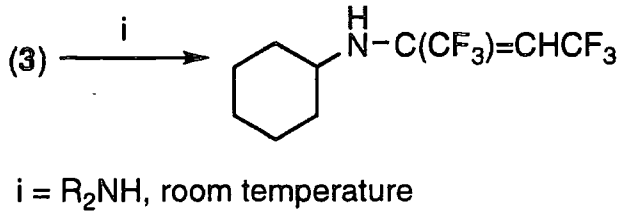
i =CH_3CO_2H, CH_3CO_2Na, 60°C; ii = H_3O^+; iii = H_2O, 110°C, Sulpholane; iv = MeONa, MeOH; v = HI, or [H]; vi = MeONa, 70°C; vii = H_3O^+

V.1.B. Nitrogen Nucleophiles

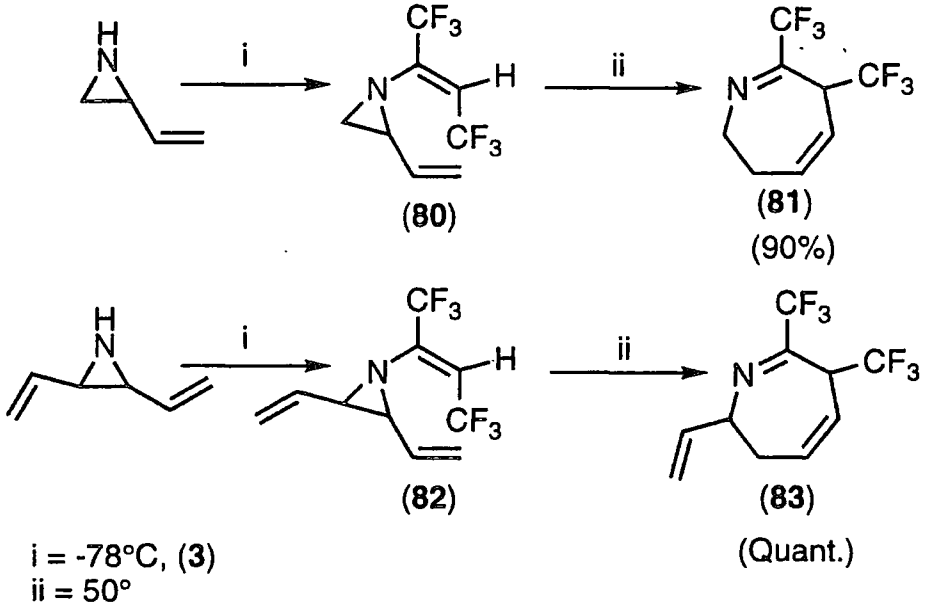
Diethylamine reacts with (3) to give a 1:1 adduct (79) which is 100% trans[240], whereas dimethylamine gives a mixture of trans and cis addition products (6:1)[275].



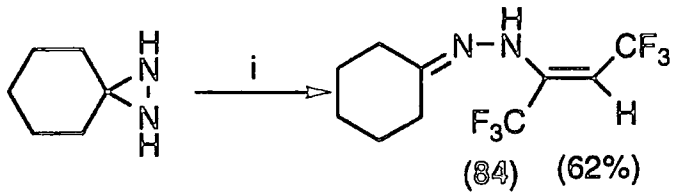
Cyclohexamine also produces a 1:1 adduct, but the stereochemistry was not reported[276].



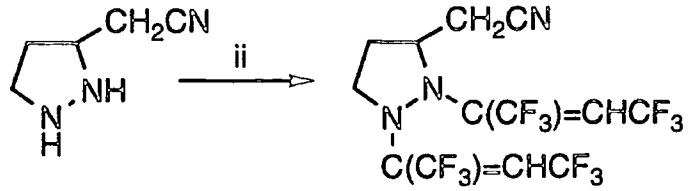
The addition of 2-vinylaziridine to (3) at low temperature gave (**80**), which on standing, isomerised to (**81**)[277]. Similarly, the divinylaziridine gave (**82**) and (**83**)[277].



A further example of ring opened products from cyclic amines is the production of (**84**)[278], whereas the less strained pyrazolidine gives a simple 2:1 adduct (**85**)[279].



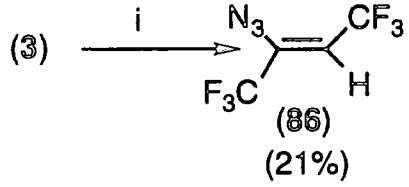
(84) (62%)



(85) (68%)

i = (3), DCM, -70°C
ii = (3), THF, 50°C

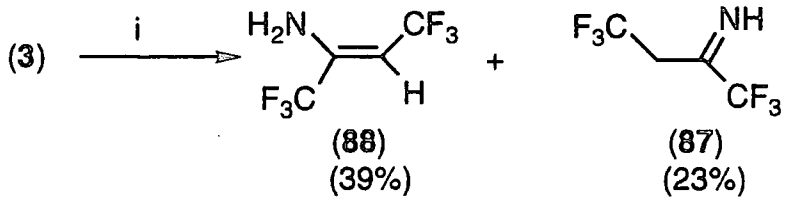
Triethylammonium azide reacts with (3) to give (86)[280].



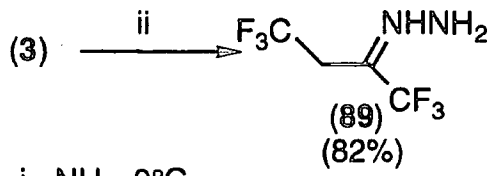
(86)
(21%)

i = $Et_3NH^+ N_3^-$, 0°C

Ammonia reacts with (3) to give both imine (87) and vinylamine (88), whereas hydrazine gives imine (89). Compounds (87) and (88) where shown not to interconvert at 25°C[132].



(88) (39%) (87) (23%)



(89)
(82%)

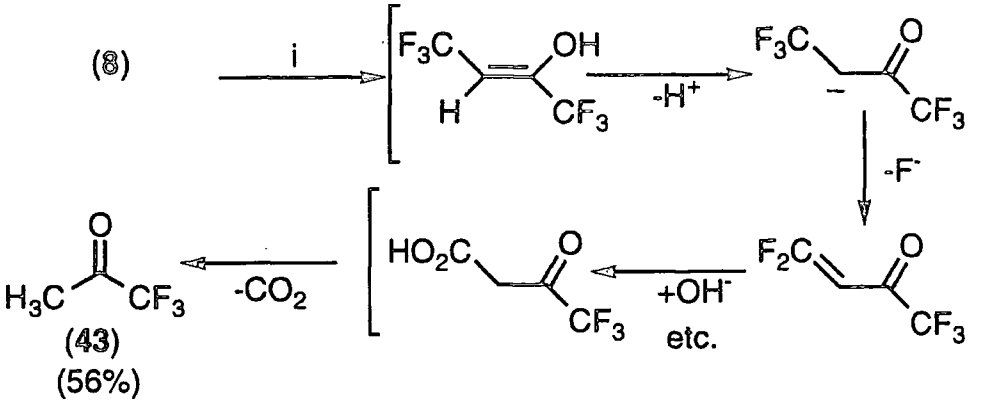
i =NH_3, 0°C
ii NH_2NH_2, 0°C

V.2. Reaction of 2*H*-Heptafluorobut-2-ene (8) with Nucleophiles

V.2.A. Oxygen Nucleophiles

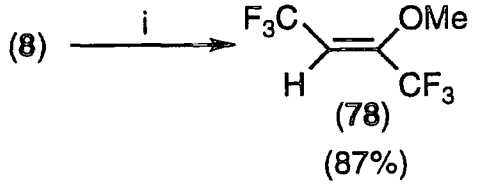
V.2.A.1. Water - No reaction was found to occur between (8) and water in acetonitrile at 50°C, or at 110°C in sulpholane. When base was added (caesium carbonate), no reaction was observed at room temperature or 50°C. At 80°C 1,1,1-trifluoroacetone (43) was

produced in 56% yield. As previously, (43) was isolated as its 2,4-DNP derivative. The production of (43) is analogous to its formation in the reaction between (8) and sodium hydroxide.(Chapter 3).



i = H_2O, Na_2CO_3, Acetonitrile, 80°C

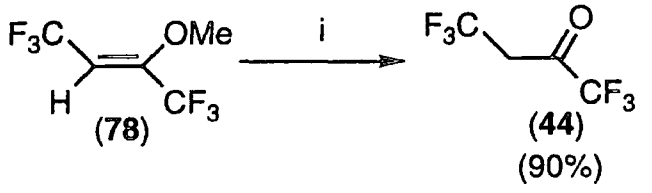
V.2.A.2. Methoxide Ion - This reaction has been performed previously by a worker in this laboratory, and similar results were obtained[185]. Product (78) was only observed as one isomer, with the CF_3 groups lying trans to each other.



i = NaOMe, Tetraglyme, Room Temp.

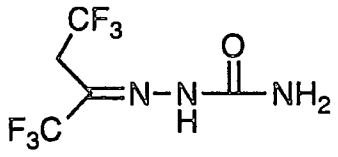
Identification of Product - Compound (78) is a known compound, and was identified by its ^1H and ^{19}F NMR, and its parent peak in GLCMS, by comparison with literature data[240, 241].

V.2.A.3. Reaction of (78) with aqueous Triflic Acid - As reported earlier in this chapter, compound (78) has been used in several routes to produce butanone (44). However, it has been discovered that it is also possible to convert (78) into (44) by the addition of aqueous triflic acid.



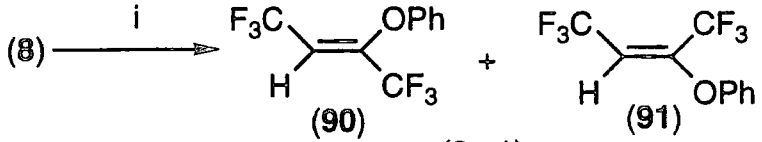
i = Aqueous TriflicAcid

Identification of Product - Butanone (44) is a known compound, and was identified by its ^{1}H and ^{19}F NMRs by comparison with literature data[240, 241]. It did not give a parent peak in GLCMS, but simple fragments of 69 (CF_3), and 111 (CF_3CH_2CO). The semi-carbazone derivative was made by standard procedures, and resulted in a white solid that gave a satisfactory elemental analysis, melting point[240] and mass spectrum.



It is interesting to note that it was not possible to form the corresponding 2,4-DNP derivative by standard procedures, and this has also been observed by other workers[240].

V.2.A.4. Phenoxide Ion - This reaction has been performed previously by a worker in this laboratory, and similar results were obtained[185]. Products (**90**) and (**91**) were observed as a pair of isomers, in a 9:1 ratio.



(**90**) + (**91**)

(9 : 1)

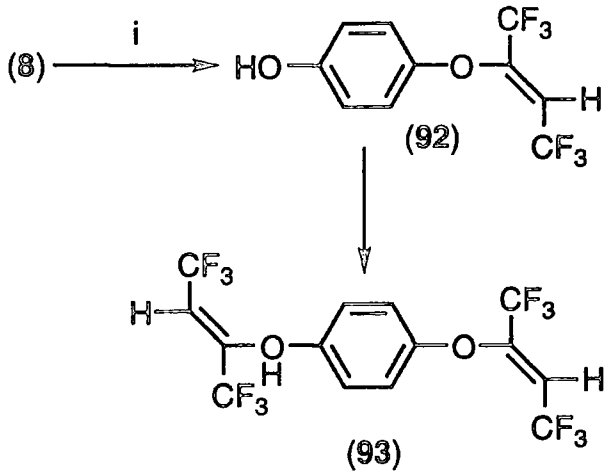
(80% total)

i = PhOH, CsF, Acetontitrile, Room Temp.

Identification of Product - Compounds (**90**) and (**91**) are known compounds, and were identified by their ^{1}H and ^{19}F NMR, and parent peaks in GLCMS, by comparison with literature data[185]. The fact that reaction with phenoxide gives a pair of isomers, whereas the reaction with methoxide gives only one isomer, implies that phenoxy has a larger steric demand than methoxy.

Aqueous triflic acid was added to a mixture of (**90**) and (**91**), but no production of butanone (**44**) was observed.

V.2.A.5. Hydroquinone - When (**8**) was reacted with hydroquinone in the presence of base, initially it was possible to identify both the mono- and the di-addition products by ^{1}H and ^{19}F NMRs. To aid isolation, all (**92**) was converted to (**93**) using an excess of (**8**).

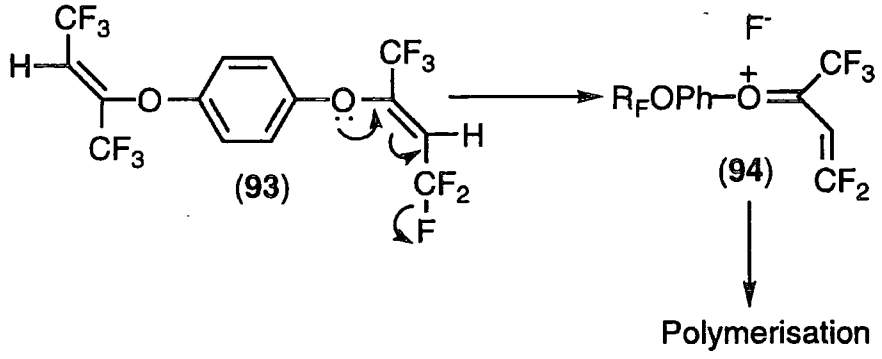


(84%)

i = Hydroquinone, Cs_2CO_3, Acetonitrile, Room temperature

Identification of Products - Compounds (**92**) and (**93**) were identified by their ^{19}F and ^{1}H NMRs which were similar to those for product (**90**), from the reaction with phenoxide ion. Diaddition product (**93**) was a solid which was recrystallised from DCM/hexane to give a satisfactory elemental analysis and mass spectrum.

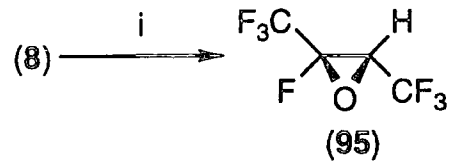
Product (**93**) was suprisingly unstable, and gave high molecular weight products on standing at room temperature for a week. It seems likely that fluoride ion is being expelled from one of the CF_3 groups, giving (**94**), which undergoes some polymerisation process.



Epoxidation

As reported in chapter one, there are various methods for nucleophilic epoxidation of fluoroalkenes.

V.2.A.6. ^{t}Butylhydroperoxide - Butene (**8**) was shown to react at room temperature with a THF solution of ^{t}butylhydroperoxide and butyl lithium, to produce the epoxide (**95**).



(95)

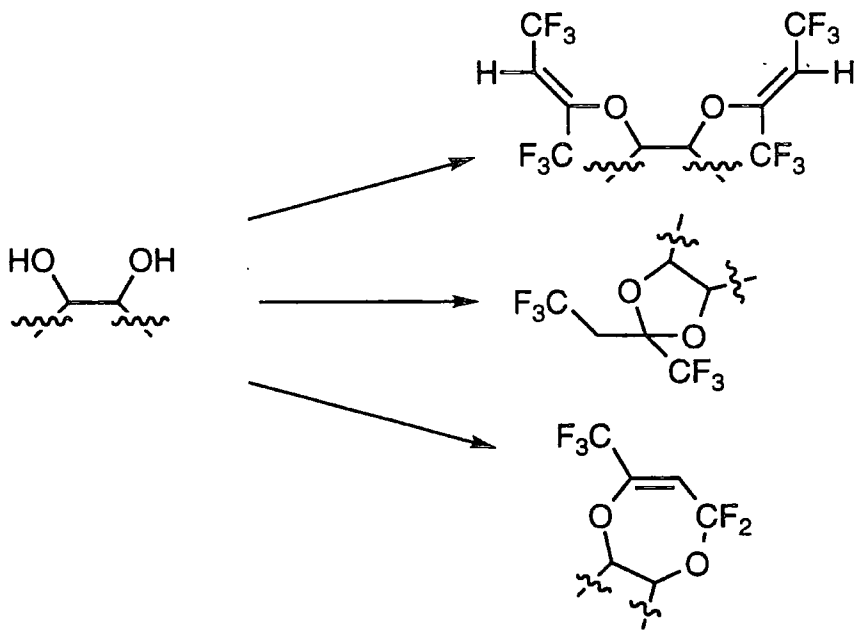
i = tButylhdroperoxide, BuLi, THF, -78°C-room temperature

Identification of Product - The product was not isolated from THF, but ^{19}F NMR shifts of -70.59, -81.63 and -169.32ppm are consistent with trifluoromethyl groups and tertiary fluorine on an epoxide ring. Also, compound (**95**) gave a parent peak in GLCMS. In an attempt to make the isolation of (**95**) easier, the reaction was repeated using tetraglyme instead of THF as the solvent. Despite using identical conditions, none of (**95**) was observed, although all (**8**) had reacted.

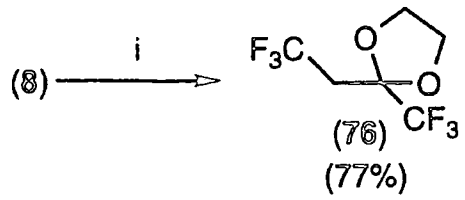
V.2.A.7. Calcium Hypochlorite - The reaction of (**8**) with both acetonitrile and sulpholane solutions of calcium hypochlorite, gave none of product (**95**), although all (**8**) had reacted.

V.2.B. Reaction with 1,2-Diols

The reaction of (**8**) with 1,2-diols with (**8**) leads to the possibility of inter- or intra-molecular reactions.



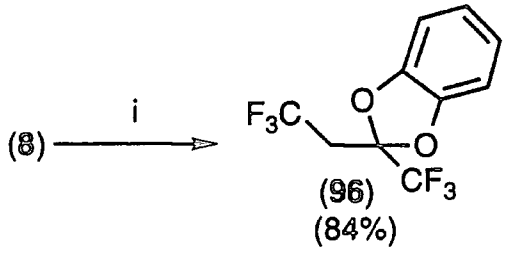
V.2.B.1. Ethylene Glycol - The reaction between ethylene glycol and (**8**) in the presence of base leads to the formation of dioxolane (**76**) in good yield.



i = Ethylene Glycol, Cs_2CO_3, Tetraglyme, Room temperature

Identification of Product - Product (76) has been previously reported from hexafluorobutyne (3), but no analytical or spectroscopic data were reported. Compound (76) gave a parent peak in GLCMS, and the expected ^{19}F NMR spectra with CF_3 resonances at -62.23 and -85.40ppm. There was only two ^{1}H NMR resonances at 4.28 and 2.73ppm, in 4:2 ratio, and ^{13}C NMR confirms the structure, especially the CF_3CH_2 resonance at 36.04ppm, which demonstrates that di-addition has occurred. An analytical sample prepared by preparative scale GLC gave a satisfactory elemental analysis.

V.2.B.2. Catechol - Similarly, the reaction between catechol and (8) produces benzodioxole (96) in good yield.



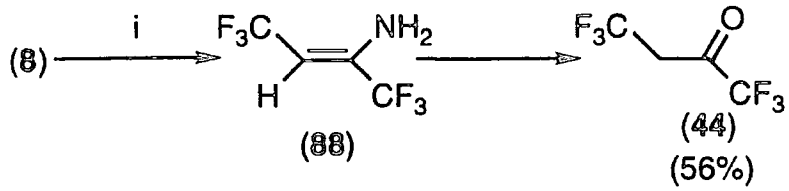
i =Catechol, Cs_2CO_3, Acetonitrile, Room temperature

Identification of Product - Product (96) gave a parent peak in the GLCMS, and the ^{1}H and ^{19}F NMRs were very similar to those for (76), and a satisfactory elemental analysis was obtained.

V.2.B.3. Acid with (76) and (96) - It is possible to regard (76) and (96) as protected ketals of ketone (44). However, treatment of (76) and (96) with acid, ranging from 0.01M HCl to neat triflic acid, even on warming, left the dioxolane derivatives intact. This effect has been previously observed in perfluorinated systems by workers in this laboratory[281].

V.3. Nitrogen Nucleophiles

V.3.A. Aqueous Ammonia - After 1 week , the reaction of (8) and aqueous ammonia gave 2 products identified as vinylamine (88) and ketone (44) in a 7:3 ratio.

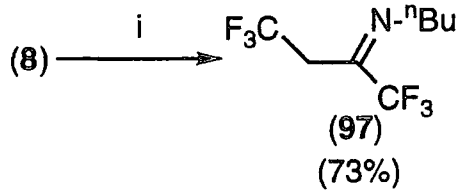


i = Aq.NH_3, 3 weeks.

The reaction was left to continue for two weeks, and then the only identifiable product was (44), which was again isolated as its semicarbazone derivative, in 56% yield. None of imine tautomer (87) was observed, although it seems probable that the hydrolysis of (88) to (44) proceeds via (87) as an intermediate.

Identification of Products - Vinylamine (88) is a known compound, and () was identified by its parent peak in GLCMS, and by its ^{1}H and ^{19}F NMRs by comparison with literature data[132].

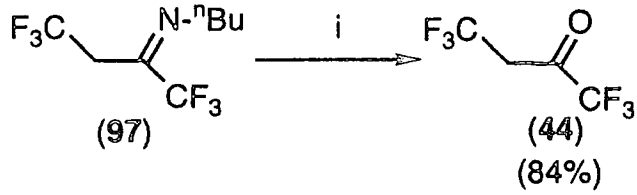
V.3.B. ^{n}Butylamine - The reaction with ^{n}butylamine and (8) at room temperature gave imine (97) in 73% yield.



i = ^{n}Butylamine, room temp., 1 week

Identification of Product - The structure of (97) followed from its parent peak in GLCMS, the two ^{19}F resonances at -62.42 and -73.57ppm, the ^{1}H spectrum, but especially the ^{13}C spectrum resonances at 31.7ppm (q) and 148.4ppm (q), which correspond to the CF_3CH_2 and C=N carbons respectively, and thus confirm the imine structure of (97). An analytical sample was obtained by preparative scale GLC that gave a satisfactory elemental analysis.
Product (97) was found to be unstable, and the colourless analytical sample changed on standing for 2 weeks, to a deep yellow oil which contained unidentifiable products.

V.3.C. Hydrolysis of (97) - The hydrolysis of imines is well known, and it was shown that in the presence of water acidified to pH1, (97) was smoothly converted into ketone (44).

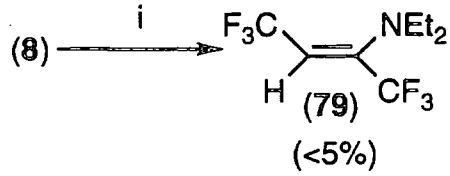


(97) (44) (84%)

i = Aqueous sulphuric acid

V.3.D. Aniline - Butene (8) was found not to react with aniline at room temperature, and even at elevated temperatures only trace amounts of a simple vinylic substitution product were observed, identified by two new CF_3 resonances at -59 and -65ppm, which are shifted characteristically to higher frequency than the CF_3 groups in (8). Attempts to promote reaction using the more reactive 4-methoxyaniline did not give any improvement.

V.3.E. Diethylamine - The reaction of (8) with diethylamine in sulpholane has been reported by a previous worker from this laboratory to give (79) in less than 5% yield[186].



(79) (<5%)

i = Et_2NH, Room temp. Sulpholane

Attempts to increase the yield by using either acetonitrile, no solvent, or increased temperature gave no improvement.

V.3.F. Triethylamine - It was hoped that this tertiary amine would promote either dehydrofluorination[106] or base induced dimerisation[248], both of which are desirable processes. However, no reaction was observed when (8) was stirred with triethlamine at room temperature for 1 week.

V.4. Conclusions

It has been shown successfully that butene (8) acts as a synthon for hexafluorobutyne (3) with a variety of nucleophiles, producing some simple organic molecules containing two trifluoromethyl group

Instrumentation and Reagents

Gas Liquid Chromatographic Analysis

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

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

Elemental Analysis

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

NMR Spectra

^{1}H NMR spectra were recorded on a Bruker AC250 spectrometer operating at 250.13 MHz, a Varian Gemini VXR200 spectrometer operating at 199.98 MHz, or a Varian VXR400S spectrometer operating at 399.96 MHz. ^{19}F NMR spectra were recorded on the Bruker AC250 spectrometer operating at 235.34 MHz or on the Varian VXR400S spectrometer operating at 376.29 MHz. ^{13}C spectra were recorded on the Varian VXR400S spectrometer operating at 100.58 MHz, or the Varian Gemini VXR200 spectrometer operating at 50.29 MHz. All spectra were recored with TMS and fluorotrichloromethane as internal references. *J* Values are given in Hz.

FT / IR Spectra

Infrared spectra were recorded on a Perkin-Elmer 1600 FT/IR spectrometer using KBr discs (solid samples) or thin films between two KBr plates (liquid samples), or volatile compounds were run in a sealed gas cell fitted with KBr plates

Mass Spectra

Mass spectra of solid samples were recorded on a VG7070E spectrometer. Fast atom bombardment (FAB) mass spectrometry were performed on the same machine, with glycerol or glycerol/H_2O as a solvent.

Distillation

Fractional distillation of product mixtures was carried out using a Fischer Spahltroh MMS255 small concentric tube apparatus. Boiling points were recorded during the distillation.

Melting Points

Melting points were carried out at atmospheric pressure, using a Gallenkamp apparatus, and are uncorrected.

Reagents and Solvents

Unless otherwise stated, chemicals were used as received from suppliers (Aldrich, Fluorochem, Fluka, Jansen, BDH). Solvents were dried by standard methods and stored over a molecular sieve (type 4A). A current of dry nitrogen was maintained for removal of the solvent with a syringe.

Chapter Six
Experimental to Chapter Two

VI.1. Synthesis of (*Z*)-2*H*-Heptafluorobut-2-ene (8)

Hexachlorobuta-1,3-diene (334g, 1.28mol) was added dropwise for approximately thirty seconds every five minutes to a suspension of freshly dried potassium fluoride (600g, 10.17mol) in anhydrous sulpholane (2.5l), maintained at 190°C. The reaction was stirred for a further three hours after the final addition of hexachlorobutadiene, while volatile products were collected in two sequential traps maintained at liquid air temperatures. Distillation at room temperature and atmospheric pressure gave :

(Z)-2H-Heptafluorobut-2-ene (8) (105.1g, 45%); b.p. 8°C (lit.,[65, 198] 7-10°C); **IR spectrum no 1; NMR spectrum no 1; Mass spectrum no 1.**

Distillation of the volatile residue using the Spaltrohr (Column A) gave a 4:1 mixture of two isomers of *5-H-perfluoro-3,4-bis(trifluoromethyl)hexa-2,4-diene* (31) (13.2g, 6%); and trace amounts of a component identified as *7-H-perfluoro-Z,E,E-3,4,5,6-tetramethylocta-2,4,6-triene* (32) on the basis of the GLCMS data[199] (**Mass spectrum no 2**). Preparative scale GC (SE30/40°C) was used to isolate the isomers of (31). For the isomers of (31), (Found: C, 28.0; H, 0.2. C_8HF_{13} requires C, 27.9; H, 0.3%); b.p. 78-80°C; $\lambda_{max}(CH_3CN)$/nm 295; ε/dm^{3}mol^{-1}cm^{-1} 1148; **IR spectrum no 2; Mass Spectrum no 3.** The major isomer was confirmed as the (Z,E) isomer by examining the small fluorine-fluorine coupling constants; **NMR spectrum no 2 .** The geometry of the other isomer has not yet been confirmed; **NMR spectrum no 3.**

Reaction Residue - The residual sulpholane solution was shown to contain *potassium pentakis(trifluoromethyl)cyclopentadienide* (**33a**) (12.9mmol, 3%);(**NMR spectrum no 4**), as shown by ^{19}F NMR integrated against an internal standard of 1,1,1-trifluorotoluene. Dilution of a 10ml aliquot of this solution with 100ml of water, followed by filtration gave a crude black solid which gave FAB mass spectroscopy data corresponding to *potassium pentakis(trifluoromethyl)cyclopentadienide* (**33a**), **Mass spectrum no 4.**

The residual sulpholane solution was filtered, and the solid filtered off was washed with acetonitrile (200ml). These washings were combined with the sulpholane filtrate, and the acetonitrile was removed by rotary evaporation. The residue was placed in a 2 necked round bottomed flask, which was fitted with a pressure equalising dropping funnel containing 98% sulphuric acid (750ml, 14.1mol), and the other neck was connected to a vacuum pump via three liquid air temperature traps. The system was evacuated and the sulphuric acid was added dropwise to the stirred sulpholane mixture, and volatile products were collected in the traps. Water (100ml) was added to the volatile products and stirred for 1 hour, producing *hydronium pentakis(trifluoromethyl)cyclopentadienide* (**33c**) (12.1mmol, 94%)[193], **NMR spectrum no 5.** Then an aqueous solution (50ml) of tetraethyl ammonium iodide (15.9g, 64.4mmol) was added. After stirring for 1 hour,

extraction with dichloromethane (3x50ml), followed by rotary evaporation, gave a crude solid, which was recrystallised from hexane and diethyl ether using the point of incipient turgidity, giving colourless crystals identified as *tetra-ethyl ammonium pentakis(trifluoromethyl) cyclopentadienide* (33d) (5.7g, 83% from (33a); mp 229-232°C; (Found: C, 40.1; H, 3.9; N, 2.9. $C_{18}H_{20}F_{15}N$ requires C, 40.4; H, 3.7; N, 2.6%); IR spectrum no 3; NMR spectrum no 6; Mass spectrum no 5.

VI.2. General Procedure for Salt Formation.

As above, an aqueous solution of the desired halide salt (typically 500% excess) was added to the aqueous (33c) solution. This mixture was stirred for 1 hour, before dichloromethane extraction and recrystallisation.

Salt Used	Product	Yield
Et_4NI	$Et_4N^+ C_5(CF_3)_5^-$	83%
Et_4NBr	$Et_4N^+ C_5(CF_3)_5^-$	80%
Pr_4NI	$Pr_4N^+ C_5(CF_3)_5^-$	80%
Bu_4NI	$Bu_4N^+ C_5(CF_3)_5^-$	86%
$Ba(Cl)_2.2H_2O$	$Ba^{2+} [C_5(CF_3)_5^-]_2$[a]	40%[a]
KI	$K^+ C_5(CF_3)_5^-$	15%*
CsF	$Cs^+ C_5(CF_3)_5^-$	12%*
$Tl(CH_3CO_2)$	$Tl^+ C_5(CF_3)_5^-$	15%*

* Products were continuously extracted (dichloromethane) due to some solubility of these products in water, and this resulted in lower yields.

[a] Despite consistent FAB and ^{19}F NMR data, satisfactory elemental analysis were not obtained.

Tetraethylammonium pentakis(trifluoromethyl)cyclopentadienide(33d) m.p. 229-232°C; (Found: C, 40.1; H, 3.9; N, 2.9. $C_{18}H_{20}F_{15}N$ requires C, 40.4; H, 3.7; N, 2.6%); IR spectrum no 3; NMR spectrum no 6; Mass spectrum no 5.

Tetrapropylammonium pentakis(trifluoromethyl)cyclopentadienide (33e)m.p. 128-131°C; (Found: C, 44.8; H, 4.6; N, 2.4. $C_{22}H_{28}F_{15}N$ requires C, 44.7; H, 4.7; N, 2.4%); IR spectrum no 4; NMR spectrum no 7; Mass spectrum no 6.

Tetrabutylammonium pentakis(trifluoromethyl)cyclopentadienide(33f)m.p. 139-141°C; (Found: C, 48.2; H, 5.7; N, 2.0. $C_{26}H_{36}F_{15}N$ requires C, 48.2; H, 5.6; N, 2.2%); IR spectrum no 5; NMR spectrum no 8;Mass spectrum no 7.

Barium pentakis(trifluoromethyl)cyclopentadienide(33g)m.p. >330°C; (Found: C, 11.4. $BaC_{20}F_{30}$ requires C, 25.3. $BaC_{10}F_{15}Cl$ requires C, 20.8%); IR spectrum no 6; NMR spectrum no 9; Mass spectrum no 8.

Potassium pentakis(trifluoromethyl)cyclopentadienide(33a)m.p. >330°C; (Found: C, 27.1;. $KC_{10}F_{15}$ requires C, 27.0%;); **IR spectrum no 7; NMR spectrum no 4; Mass spectrum no 4.**

Caesium pentakis(trifluoromethyl)cyclopentadienide (33b)m.p. >330°C; (Found: C, 22.3. $CsC_{10}F_{15}$ requires C, 22.3%); **IR spectrum no 8; NMR spectrum no 10; Mass spectrum no 9.**

Thallium pentakis(trifluoromethyl)cyclopentadienide (33h) m.p. >330°C; (Found: C, 19.6. $TlC_{10}F_{15}$ requires C, 19.7%); **IR spectrum no 9; NMR spectrum no 11; Mass spectrum no 10.**

VI.3. *5H*-Pentakis(trifluoromethyl)cyclopenta-1,3-diene (34)

A two necked round bottomed flask was charged with a sulpholane solution (10ml) containing caesium pentakis(trifluoromethyl)cyclopentadienide (0.43mmol). The system was evacuated, and 98% sulphuric acid (110ml) was added dropwise to the stirred solution. Volatile material was continuously condensed into two sequential traps maintained at liquid air temperatures, and was shown to contain 1 component by GLCMS, which was identified[193] as *5H-pentakis(trifluoromethyl)cyclopenta-1,3-diene* (34) (0.15g, 86%); **IR spectrum no 10; NMR spectrum no 12; Mass spectrum no 11.**

VI.4. (33a): Hexachlorobutadiene and KF in a Sealed System

A round bottomed glass vessel (sealable via an integral Young's tap) was charged with hexachloro-1,3-butadiene (1.26g,4.9mmol), potassium fluoride (3.46g,58.6mmol) and sulpholane (10ml) under a counter current of dry nitrogen. The vessel was cooled to liquid air temperature, evacuated, sealed and stirred at 190°C for 3 days. Volatile material was removed under reduced pressure, and shown to contain butene (8) (0.3g, 35%); **IR spectrum no 1; NMR spectrum no 1; Mass spectrum no 1.** The sulpholane residue was shown by ^{19}F NMR (integrated against an internal standard of 1,1,1 trifluorotoluene) to contain *potassium pentakis(trifluoromethyl) cyclopentadienide* (**33a**) (0.18mmol, 11%); **NMR spectrum no 4 .**

VI.5. (33b): Hexachlorobutadiene and CsF in a sealed System

A round bottomed glass vessel (sealable via an integral Young's tap) was charged with hexachloro-1,3-butadiene (1.34g, 4.9mmol), caesium fluoride (7.60g, 50.0mmol) and sulpholane (10ml) under a counter current of dry nitrogen. The vessel was cooled to liquid air temperature, evacuated, sealed and stirred at 190°C for 3 days. Volatile material was removed under reduced pressure, and found to contain no evidence of (**8**). The sulpholane residue was shown by ^{19}F NMR (integrated against an internal standard of 1,1,1 trifluorotoluene) to contain *caesium pentakis(trifluoromethyl)cyclopentadienide* (**33b**) (0.16mmol, 10%); **NMR spectrum no 10.**

VI.6. (33b): (8) and CsF in a sealed system (i)

Butene (8) (1.18g, 4.68mmol) was transferred under reduced pressure into a round bottomed glass vessel (sealable via an integral Young's tap) previously charged with caesium fluoride (6.00g, 39.47mmol) and sulpholane (10ml) under a counter current of dry nitrogen. The vessel was cooled to liquid air temperature, evacuated, sealed and stirred at 190°C for 3 days. Volatile material was removed under reduced pressure, and the sulpholane residue was shown by ^{19}F NMR (integrated against an internal standard of 1,1,1 trifluorotoluene) to contain *caesium pentakis(trifluoromethyl)cyclopentadienide* (33b) (0.43mmol, 20%); NMR spectrum no 10 .

VI.7. (33b): (8) and CsF in a sealed system (ii)

Butene (8) (1.18g, 4.68mmol) was transferred under reduced pressure into a carius tube previously charged with caesium fluoride (6.00g, 39.47mmol) and sulpholane (10ml) under a counter current of dry nitrogen. The flask was cooled to liquid air temperature, evacuated, sealed and rotated at 190°C for 3 days. The volatiles were removed under reduced pressure, and the sulpholane residue was shown by ^{19}F NMR (integrated against an internal standard of 1,1,1 trifluorotoluene) to contain *caesium pentakis(trifluoromethyl)cyclopentadienide* (33b) (0.28mmol, 13%); NMR spectrum no 10.

VI.8. (41): Fluorination of (33d)

A round bottomed glass vessel (sealable via an integral Young's tap) was charged with Selectfluor^{TM}F-TEDA-BF_4 (1.7g, 4.77mmol of "F^+"), tetraethylammonium pentakis(trifluoromethyl) cyclopentadienide (33d) (1.2g, 2.2mmol), and dimethylformamide (10ml) under a counter current of dry nitrogen. The flask was cooled to liquid air temperatures, evacuated, sealed and stirred at room temperature for 1 day. The volatiles were removed under reduced pressure, and were shown by GLCMS to contain four major components of almost equal proportions. The third of which is proposed, on the basis of its M^+ in the GLCMS data as *perfluoro-1,2,3,4,5-pentamethylcyclopenta-2,4-diene* (41), Mass spectrum no 12.

VI.9. Synthesis of (37) and (38)

Butene (8) (0.7g,3.8mmol) and perfluorocyclohexene (36) (1.04g, 4.9mmol) were transferred under reduced pressure into a round bottomed glass vessel (sealable via an integral Young's tap) previously charged with caesium fluoride (2.00g, 13.2mmol) and sulpholane (20ml) under a counter current of dry nitrogen. The vessel was cooled to liquid air temperature, evacuated, sealed and stirred at 110°C for 5 days. Volatile material was removed under reduced pressure, and the sulpholane residue was shown by ^{19}F NMR (integrated against an internal standard of 1,1,1 trifluorotoluene) and FAB mass spectrometry to contain *caesium perfluoro1,2,3-trihydro-4,5,6-trimethylpentalenide* (37) (0.4mmol, 20%); NMR spectrum no 13, Mass spectrum no 13 ; and *caesium*

perfluoro-1-methyl-2,3,4,5,6,7-hexahydrodicyclopenta[b,d]cyclopentadienide (**38**) (0.2mmol, 7%); **NMR spectrum no 14, Mass spectrum no 14.**

VI.10. Synthesis of (37)

Perfluorocyclohexene (**36**) (1.04g, 4.9mmol) was transferred under reduced pressure into a round bottomed glass vessel (sealable via an integral Young's tap) previously charged with caesium fluoride (2.00g, 13.2mmol), (Z,E) and (Z,Z)-5-H-perfluoro-3,4-dimethyl-2,4-diene (**31**) (1.6g, 4.7mmol) and sulpholane (20ml) under a counter current of dry nitrogen. The flask was cooled to liquid air temperature, evacuated, sealed and stirred at 110°C for 5 days. The volatiles were removed under reduced pressure, and the sulpholane residue was shown by ^{19}F NMR (integrated against an internal standard of 1,1,1 trifluorotoluene) and FAB mass spectrometry to contain *caesium perfluoro-1-methyl-2,3,4,5,6,7-hexahydrodicyclopenta[b,d]cyclopentadienide* (**37**) (1.9mmol,41%); **NMR spectrum no 13, Mass spectrum no 13.**

VI.11. (39) and (40): Protonation of (37) and (38)

Sulphuric acid (98%, 50ml) was added dropwise to a sulpholane (20ml) solution containing caesium perfluoro-1,2,3-trihydro-4,5,6-trimethylpentalenide (**37**) (0.98mmol) and caesium perfluoro-1-methyl-2,3,4,5,6,7-hexahydrodicyclopenta [b,d]cyclopentadienide (**38**) (0.34mmol) under reduced pressure. The volatile products were collected in a trap maintained at liquid air temperatures, and were shown by GLCMS to contain greater than 10 different compounds, two of which have been proposed as *5-H-perfluoro-1,2,3-trihydro-4,5,6-trimethylpentalena-4,6-diene* (**39**) and *1-H-perfluoro-1-methyl-2,3,4,5,6,7-hexahydrodicyclopenta[b,d]cyclopenta-8,9-diene* (**40**) on the basis of their GLCMS data; **Mass spectrum no 15; Mass spectrum no 16.**

Chapter Seven
Experimental to Chapter Three

VII.1. (43): Potassium Hydroxide and (8)

Fluoroalkene (8) (0.9g,5.0mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with sodium hydroxide (0.6g,15.0mmol), water (5ml) and acetonitrile (7ml). The tube was evacuated, sealed and rotated end over end for 48 hours at room temperature. It was then cooled to liquid air temperatures and opened. Volatile material was removed under reduced pressure, and shown by NMR (NMR spectrum no 15) and GLCMS (Mass spectrum no 17) to contain *1,1,1-trifluoroacetone* (43) as the major component. The volatiles were transferred into a round bottom flask charged with 2,4 diphenylhydrazine (2.1g,11.1mmol), ethanol (15ml), and sufficient conc. hydrochloric acid to dissolve the 2,4 dinitrophenylhydrazine. The flask was warmed for 10 minutes and then placed in a freezer (-15°C). The precipitate was filtered, recrystallised from hot EtOH and identified as the *2,4 dinitrophenylhydrazone of 1,1,1-trifluoroacetone* (0.9g,60%); mp 136-137°C, (lit.,[282] 139°C); (Found: C,37.1; H, 2.3; N,19.0. Calc for $C_9H_7F_3N_4O_4$: C,37.0; H, 2.4; N,19.2%); IR spectrum no 11; Mass spectrum no 18 .

VII.2. (48): DBU and (8)

Fluoroalkene (8) (0.82g,4.5mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with 1,8-diazabicyclo[5.4.0]undec-7-ene (3.04g,20.0mmol) and hexane (10ml) under a counter current of dry nitrogen. The tube was evacuated, sealed and rotated end over end for 3 days at room temperature. It was then cooled to liquid air temperatures and volatile material was removed under reduced pressure, and acetonitrile (3ml) was added to the residual brown solution. This produced two layers, and the upper golden hexane layer was removed, and the lower layer was extracted by more hexane (2x10ml). The hexane solutions were combined, and the hexane was removed by rotary evaporation to yield a pale yellow solid, which was recrystallised from hot hexane to yield colourless crystals identified as *1,9-diazabicyclo[5.4.0]undecano-a,b-2-difluoromethyl-3-trifluoromethylpyrrole* (48) (1.12g,85%) crystal structure no 1; mp 63°C. (Found C, 53.0; H, 5.2; N, 9.4. $C_{13}H_{15}N_2F_5$ requires C, 53.1;H, 5.1;N, 9.5%); IR spectrum no 12; NMR spectrum no 16; Mass spectrum no 19.

VII.3. (48): DBU and (3)

Hexafluorobut-2-yne (3) (0.6g,3.7mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with 1,8-diazabicyclo[5.4.0]undec-7-ene (2.9g,19.1mmol) and hexane (10ml) under a counter current of dry nitrogen. The tube was evacuated, sealed and rotated end over end for 3 days at room temperature. It was then cooled to liquid air temperatures and volatile material was removed under reduced

pressure, and acetonitrile (3ml) was added to the residual brown solution. This produced two layers, and the upper golden hexane layer was removed, and the lower layer was extracted by more hexane (2x10ml). The hexane solutions were combined, and the hexane was removed by rotary evaporation to yield a pale yellow solid, which was recrystallised from hot hexane to yield colourless crystals identified as *1,9-diazabicyclo[5.4.0]undecano-a,b-2-difluoromethyl-3-trifluoromethylpyrrole* (48) (0.7g,65%), which were identical to those described above.

Crystal Structure Data No 1

Crystal data for (48): $C_{13}H_{15}F_5N_2$, M = 294.27, monoclinic, space group $P2_1/c$, a = 8.752(2), b = 15.637(6), c = 9.559(4) Å, b = 102.15(3)°, V = 1278.9(8) $Å^3$ (at 150 K, from 20 reflections with 12.7 < q < 15.0°), Z = 4, F(000) = 608, m(U_0-K_a) =1.42 cm^{-1}, D_c = 1.53 gcm^{-3}, crystal size 0.11 x 0.38 x 0.50 mm. 1754 total (1629 independent) reflections were collected on a Rigaku AFC6S diffractometer at 150 K (graphite-monochromated U_0-K_a radiation, $\overline{\lambda}$ = 0.71073 Å, 2q/w scan mode, 2q <= 45°). The structure was solved by direct methods (using SHELXS-86 programs) and refined by full-matrix least squares (using SHELXL-93 programs) in the anisotropic approximation (176 variables, H atoms in riding model) on F^2 of 1628 reflections with Chebushev weighting scheme to R(F) = 0.052 and wR(F^2) = 0.102 for all data, with maximum residual peak in the final Fourier difference synthesis of 0.25 $eÅ^{-3}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

The 5-membered ring is planar; the 7-membered ring adopts a distorted chair conformation, with atoms N(2), C(4) and C(9) deviating by 0.76, 0.38 and -0.72Å from the C(3)C(8)C(10)C(11) plane. In the 6 membered ring, atoms C(5) and C(6) are disordered over two positions, A and B, with occupancies of 75% and 25% respectively. In both cases, the ring adopts a non-symmetrical twist conformation, with the essentially planar C(7)N(1)C(4)N(2) moiety, from which C(5A) and C(6A) deviate by -0.21 and 0.58Å, and C(5B) and C(6B) by 0.46 and -0.19Å respectively.

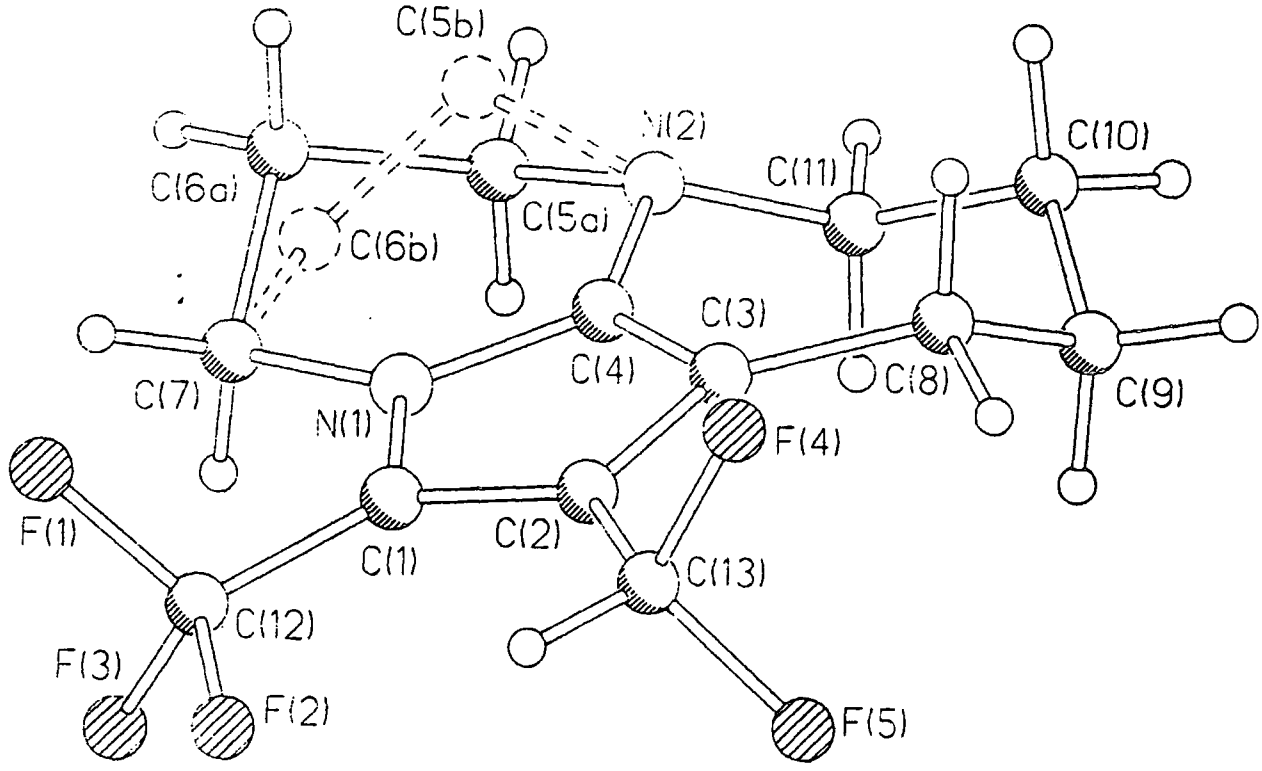


Table 1. Bond lengths [A] and angles [deg] for 1.

F(1)-C(12)	1.345(3)
F(2)-C(12)	1.337(3)
F(3)-C(12)	1.346(3)
F(4)-C(13)	1.373(3)
F(5)-C(13)	1.375(3)
N(1)-C(4)	1.383(3)
N(1)-C(1)	1.385(3)
N(1)-C(7)	1.472(3)
N(2)-C(4)	1.393(3)
N(2)-C(11)	1.471(3)
N(2)-C(5A)	1.483(4)
N(2)-C(5B)	1.485(8)
C(1)-C(2)	1.376(4)
C(1)-C(12)	1.476(4)
C(2)-C(3)	1.424(4)
C(2)-C(13)	1.493(4)
C(3)-C(4)	1.389(3)
C(3)-C(8)	1.501(3)
C(5A)-C(6A)	1.541(5)
C(6A)-C(7)	1.518(4)
C(5B)-C(6B)	1.447(12)
C(6B)-C(7)	1.504(8)
C(8)-C(9)	1.516(3)
C(9)-C(10)	1.513(4)
C(10)-C(11)	1.512(4)

C(4)-N(1)-C(1)	108.8(2)
C(4)-N(1)-C(7)	124.0(2)
C(1)-N(1)-C(7)	127.2(2)
C(4)-N(2)-C(11)	117.0(2)
C(4)-N(2)-C(5A)	115.9(2)
C(11)-N(2)-C(5A)	106.4(2)
C(4)-N(2)-C(5B)	114.4(4)
C(11)-N(2)-C(5B)	123.6(5)
C(2)-C(1)-N(1)	107.7(2)
C(2)-C(1)-C(12)	131.9(2)
N(1)-C(1)-C(12)	120.4(2)
C(1)-C(2)-C(3)	108.6(2)
C(1)-C(2)-C(13)	127.0(2)
C(3)-C(2)-C(13)	124.3(2)
C(4)-C(3)-C(2)	106.2(2)
C(4)-C(3)-C(8)	127.5(2)
C(2)-C(3)-C(8)	126.2(2)
N(1)-C(4)-C(3)	108.7(2)
N(1)-C(4)-N(2)	121.3(2)
C(3)-C(4)-N(2)	130.0(2)
N(2)-C(5A)-C(6A)	109.4(3)
C(7)-C(6A)-C(5A)	107.7(3)
C(6B)-C(5B)-N(2)	111.6(9)
C(5B)-C(6B)-C(7)	114.8(9)
N(1)-C(7)-C(6B)	110.7(5)
N(1)-C(7)-C(6A)	107.8(2)
C(3)-C(8)-C(9)	115.4(2)
C(10)-C(9)-C(8)	113.5(2)
C(11)-C(10)-C(9)	115.0(2)
N(2)-C(11)-C(10)	116.5(2)
F(2)-C(12)-F(1)	105.7(2)
F(2)-C(12)-F(3)	106.5(2)
F(1)-C(12)-F(3)	105.1(2)
F(2)-C(12)-C(1)	112.1(2)
F(1)-C(12)-C(1)	113.9(2)
F(3)-C(12)-C(1)	112.9(2)
F(4)-C(13)-F(5)	104.3(2)
F(4)-C(13)-C(2)	110.3(2)
F(5)-C(13)-C(2)	110.9(2)

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
F(1)	8892(2)	2037(1)	7179(2)	45(1)
F(2)	10157(2)	3215(1)	7380(2)	49(1)
F(3)	8988(2)	2763(1)	5308(2)	59(1)
F(4)	8026(2)	4511(1)	10001(2)	48(1)
F(5)	8596(2)	5315(1)	8334(2)	60(1)
N(1)	5983(2)	3095(1)	6025(2)	24(1)
N(2)	3397(2)	3561(1)	5714(2)	29(1)
C(1)	7435(3)	3322(2)	6823(3)	27(1)
C(2)	7236(3)	4028(2)	7627(3)	27(1)
C(3)	5624(3)	4252(2)	7322(2)	25(1)
C(4)	4679(3)	3661(2)	6321(2)	24(1)
C(5A)	2917(4)	2934(2)	4528(4)	28(1)
C(6A)	3331(4)	2128(2)	4913(4)	29(1)
C(5B)	2866(12)	2698(6)	5109(13)	32(2)
C(6B)	3933(9)	2406(10)	4243(14)	56(4)
C(7)	5622(2)	2383(1)	5001(2)	31(1)
C(8)	4886(2)	4960(1)	8010(2)	33(1)
C(9)	3666(3)	5481(2)	7003(3)	35(1)
C(10)	2212(3)	4977(2)	6359(3)	41(1)
C(11)	2406(3)	4341(2)	5218(3)	36(1)
C(12)	3845(3)	2842(2)	6676(3)	34(1)
C(13)	3461(3)	4473(2)	8703(3)	39(1)

Table 3. Anisotropic displacement parameters (A^2 x 10^3) for 1. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
F(1)	36(1)	34(1)	65(1)	6(1)	10(1)	6(1)
F(2)	22(1)	46(1)	76(1)	4(1)	3(1)	-1(1)
F(3)	42(1)	96(2)	45(1)	10(1)	21(1)	25(1)
F(4)	47(1)	66(1)	29(1)	-6(1)	-1(1)	-9(1)
F(5)	67(1)	54(1)	51(1)	-1(1)	-7(1)	-36(1)
N(1)	21(1)	26(1)	26(1)	-1(1)	4(1)	0(1)
N(2)	21(1)	25(1)	39(1)	-7(1)	0(1)	0(1)
C(1)	20(2)	32(2)	28(1)	6(1)	5(1)	0(1)
C(2)	25(2)	32(2)	23(1)	5(1)	2(1)	-6(1)
C(3)	27(2)	24(1)	24(1)	1(1)	4(1)	-3(1)
C(4)	22(2)	24(1)	26(1)	3(1)	6(1)	1(1)
C(7)	35(2)	25(1)	33(2)	-4(1)	6(1)	4(1)
C(8)	42(2)	28(1)	30(2)	-6(1)	9(1)	-3(1)
C(9)	37(2)	35(2)	46(2)	-1(1)	16(1)	5(1)
C(10)	32(2)	32(2)	62(2)	-2(1)	12(1)	9(1)
C(11)	24(2)	42(2)	40(2)	5(1)	-1(1)	3(1)
C(12)	26(2)	40(2)	36(2)	8(1)	7(1)	0(1)
C(13)	35(2)	43(2)	36(2)	1(1)	2(1)	-9(1)

Table 4. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 1.

	x	y	z	U(eq)
H(51A)	3108(4)	3190(2)	3633(4)	34
H(52A)	1799(4)	2776(2)	4372(4)	34
H(61A)	3796(4)	1890(2)	5839(4)	34
H(62A)	3620(4)	1686(2)	4166(4)	34
H(51B)	3974(12)	2288(6)	5900(13)	39
H(52B)	1792(12)	2716(6)	4517(13)	39
H(61B)	3830(9)	2785(10)	3399(14)	67
H(62B)	3617(9)	1824(10)	3889(14)	67
H(71)	6294(2)	1885(1)	5347(2)	37
H(72)	5819(2)	2557(1)	4059(2)	37
H(81)	5720(2)	5352(1)	8492(2)	40
H(82)	4393(2)	4708(1)	8757(2)	40
H(91)	3364(3)	5976(2)	7531(3)	42
H(92)	4132(3)	5706(2)	6219(3)	42
H(101)	1373(3)	5383(2)	5941(3)	50
H(102)	1863(3)	4664(2)	7138(3)	50
H(111)	1054(3)	4169(2)	4689(3)	44
H(112)	2231(3)	4635(2)	4531(3)	44
H(13)	3488(3)	4173(2)	8800(3)	47

VII.4. (46): LiCl and (8)

Fluoroalkene (8) (3.0g,16.5mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with lithium chloride (2.2g/51.8mmol) and dimethylformamide (8ml) under a counter current of dry nitrogen. The tube was evacuated, sealed and rotated in an oil bath maintained at 140°C for 1 week. It was then cooled to liquid air temperatures and volatile material was removed under reduced pressure, and then distilled at 0°C/0.1mbar. The distillate was distilled further (-78°C/0.1mbar) to leave a clear volatile liquid containing one component by GLCMS, identified as *(Z)-2-chloro-1,1,1,4,4,4-hexafluorobut-2-ene* (46) (2.4g/73%) by comparison with literature data[40]; **IR spectrum no 13; NMR spectrum no 17; Mass spectrum no 20.**

VII.5. (47): LiBr and (8)

Fluoroalkene (8) (2.7g,14.8mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with lithium bromide (3.3g/38.0mmol) and sulpholane (15ml) under a counter current of dry nitrogen. The tube was evacuated, sealed and rotated in an oil bath maintained at 200°C for 1 week. It was then cooled to liquid air temperatures and volatile material was removed under reduced pressure, and shown by GLCMS to contain 2 components in a 90:1 ratio, identified as unreacted (8) and *(Z)-2-bromo-1,1,1,4,4,4-hexafluorobut-2-ene* [40] (47) (**NMR spectrum no 18 ; Mass spectrum no 21**).

VII.6. (3): (8) and CsF in hot Tube (Typical Run)

Fluoroalkene (8) (1.77g,9.73mmol) was passed through a glass pyrolysis tube (15mm o.d.) packed with a 1cm length plug of caesium fluoride at 300°C, by bubbling a slow current (100ml/min) of nitrogen through (8) cooled to 0°C. The products were collected in a trap maintained at liquid air temperatures, and were shown by GLCMS and NMR to contain unreacted (8) (37%) and *hexafluorobut-2-yne* (3) (23%). The products were separated by repeated distillation at 0°C. **IR spectrum no 14; NMR spectrum no 19; Mass spectrum no 22.**

Temperature /°C	N_2 Flow /ml min^{-1}	Length of CsF Plug /cm	Yield of Hexafluorobut-2-yne	Recovered (8)
300	100	1	23%	37%
350	150	1	36%	50%
300	150	2	8%	77%

VII.7. (3): ^{t}Butyl Lithium and (8)

Fluoroalkene (8) (1.6g,8.8mmol) was transferred, under reduced pressure, into a round bottomed flask which had previously been charged with a pentane solution of ^{t}butyl lithium (1.7M, 5ml) under a counter current of dry nitrogen. The flask was stirred and allowed to warm from liquid air temperatures to 0°C. Volatile material was collected in a trap maintained at liquid air temperatures, and was shown to only contain *hexafluorobut-2-yne* (3) (0.58g,41%). **IR spectrum no 14; NMR spectrum no 19; Mass spectrum no 22.**

VII.8. (45): Potassium ^{t}Butoxide and (8)

Fluoroalkene (8) (4.2g,23.1mmol) was transferred, under reduced pressure, into a round bottomed flask which had previously been charged with potassium ^{t}butoxide (5.28g,47.0mmol) and di-isopropyl ether (20ml) against a counter current of dry nitrogen. The flask was allowed to warm from liquid air temperatures to 0°C, and volatile material was collected in a liquid air temperature trap. However, none was recovered. The residual ether layer was filtered, and shown by GLCMS and NMR to contain *(Z)-2-^{t}butoxy-1,1,1,4,4,4-hexafluorobut-2-ene* (45) (18.2mmol,79%); **(NMR spectrum no 20, Mass spectrum no 23)**, by comparison with literature data[241]. (^{19}F NMR integrated against an internal standard of 1,1,1 trifluorotoluene).

Chapter Eight
Experimental to Chapter Four

VIII.1. (51): Furan and (8) (200°C)

Fluoroalkene (8) (2.1g,11.5mmol) was transferred, under reduced pressure, into a carius tube which had previously been charged with furan (0.3g,4.4mmol) under a counter current of dry nitrogen. The tube was evacuated, sealed and rotated in an oil bath maintained at 200°C for 1 week. Volatile material was removed under reduced pressure, and shown by GLCMS and NMR to contain *3,4 bis(trifluoromethyl)furan* (**51**) (20%); **NMR spectrum no 21, Mass Spectrum no 24**; *2,3-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene* (**49**) (6%); **NMR spectrum no 22, Mass Spectrum no 25**; *exo-5-fluoro-5,6-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2-ene* (**62**); **NMR spectrum no 23, Mass Spectrum no 26**; and *endo-5-fluoro-5,6-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2-ene* (**63**) (4% combined); **NMR spectrum no 24, Mass Spectrum no 27**; by comparison with literature data[31, 188, 235, 236].

VIII.2. (51): Furan and (8) (300°C)

Fluoroalkene (**8**) (12.0g,65.9mmol) was transferred, under reduced pressure, into a sealed metal tube which had previously been charged with furan (2.8g,41.2mmol) under a counter current of dry nitrogen. The tube was evacuated, sealed and rocked in a furnace maintained at 300°C for 3 days. It was then cooled to liquid air temperatures, opened and excess (**8**) was removed by distillation at room temperature and atmospheric pressure. The residual solution was filtered and distilled using the Spaltrohr (Column A) to give *3,4-bis(trifluoromethyl)furan* (**51**) (5.9g,70%) b.p. 87-89 °C (lit.,[235] 88-89°C); (Found: C, 35.2; H, 1.1. Calc. for $C_6H_2OF_6$: C, 35.3; H, 1.0%); **IR spectrum no 15; NMR spectrum no 21; Mass spectrum no 24.**

VIII.3. (67): Dimethyl Furan and (8)

Fluoroalkene (**8**) (6.8g, 37.4mmol) was transferred, under reduced pressure, into a sealed metal tube which had previously been charged with 2,5-dimethylfuran (2.0g, 20.8mmol) under a counter current of dry nitrogen. The tube was evacuated, sealed and heated in a furnace maintained at 200°C for 2 days. It was then cooled to liquid air temperatures, opened and excess (**8**) was removed by distillation at room temperature and atmospheric pressure. The residual solution was filtered and distilled using the Spaltrohr (Column A) to give *2,5-dimethyl-3,4-bis(trifluoromethyl)furan* (**67**) (2.96g, 61%) b.p. 52-56°C/12mm Hg; (lit., [196]77-78°C/88mm Hg); **IR spectrum no 16; NMR spectrum no 25; Mass spectrum no 28.**

VIII.4. (68): 2-Furonitrile and(8)

Fluoroalkene (8) (1.2g,6.6mmol) was transferred, under reduced pressure, into a quartz tube which had previously been charged with 2-furonitrile (0.4g,4.3mmol) under a counter current of dry nitrogen. The tube was evacuated, sealed and heated in a furnace maintained at 250°C for 24 hours. It was then cooled to liquid air temperatures, opened and excess (8) was removed by distillation at room temperature and atmospheric pressure. The residual solution was filtered and was shown by GLCMS to comprise of two components in a 7:2 ratio. Distillation of this mixture at 0°C/0.1mbar gave *3,4-bis(trifluoromethyl)furan* (51) 0.2g,21%), as above. This left a pale brown liquid identified as *3,4-bis(trifluoromethyl)-2-furonitrile* (68) (0.7g,71%). An analytical sample was prepared by preparative GLC (SE30/50°C), (Found: C, 36.9; H, 0.5; N, 6.3. C_7HF_6NO requires C, 36.7; H, 0.4; N, 6.1%); **IR spectrum no 17, NMR spectrum no 26; Mass spectrum no 29.**

VIII.5. (51): 2-Furoic acid and (8)

Fluoroalkene (8) (11.1g,61.0mmol) was transferred, under reduced pressure, into a sealed metal tube which had previously been charged with 2-furoic acid (4.5g,40.1mmol) under a counter current of dry nitrogen. The tube was evacuated, sealed and rocked in a furnace maintained at 300°C for 24 hours. It was then cooled to liquid air temperatures, opened, and excess (8) was removed by distillation at room temperature and atmospheric pressure. The residual solution was filtered and distilled using the Spaltrohr (Column A) to give *3,4-bis(trifluoromethyl)furan* (51) (3.2g, 39%) as above. (There was no evidence of 3,4-bis(trifluoromethyl)-2-furoic acid[266, 268] (69)).

VIII.6. (70): Methyl 2-furanoate and (8)

Fluoroalkene (8) (1.6g, 8.8mmol) was transferred, under reduced pressure, into a quartz tube which had previously been charged with methyl 2-furanoate (0.8g, 6.3mmol) under a counter current of dry nitrogen. The tube was evacuated, sealed and heated in a furnace maintained at 250°C for 24 hours. It was then cooled to liquid air temperatures, opened, and excess (8) was removed by distillation at room temperature and atmospheric pressure. The residual solution was filtered and identified as *methyl-3,4-bis(trifluoromethyl)furan-2-oate* (70) (1.2g, 85%); **IR spectrum no 18; NMR spectrum no 27; Mass spectrum no 30,** by comparison with literature data[266].

VIII.7. (71): Ethyl 2-furanoate and (8)

Fluoroalkene (8) (1.6g, 8.8mmol) was transferred, under reduced pressure, into a quartz tube which had previously been charged with ethyl 2-furanoate (0.8g, 5.7mmol) under a counter current of dry nitrogen. The tube was evacuated, sealed and heated in a furnace maintained at 250°C for 24 hours. It was then cooled to liquid air temperatures, opened, and excess (8) was removed by distillation at room temperature and atmospheric pressure. Ether (20ml) was added to the residual pale yellow oil, which was filtered. Rotary evaporation produced a pale yellow oil which was partially crystalline, identified as

ethyl-3,4-bis(trifluoromethyl)furan-2-oate (71) (1.4g, 89%) ; **IR spectrum no 19; NMR spectrum no 28; Mass spectrum no 31**, by comparison with literature data[266].

VIII.8. Preparation of 3,4-bis(trifluoromethyl)-2-furoic acid (69)

Methyl-3,4-bis(trifluoromethyl)furan-2-oate (70) (0.8g, 3.05mmol) was added to a round bottomed flask which had previously been charged with potassium ^{t}butoxide (2.7g, 24.1mmol), water (0.2g, 11.1mmol) and acetonitrile (10ml). The reaction was stirred vigorously for 16 hours, and then water (20ml) was added, and the solution was acidified to pH1 using H_2SO_4. Ether (30ml) was added , and the ethereal layer was separated and evaporated to produce a yellow oil. This oil was dissolved in pet ether/chloroform (4:1), filtered and evaporated to give pale yellow needles identified as *3,4-bis(trifluoromethyl)-2-furoic acid* (**69**) (0.6g, 79%); m.p. 123-124°C, (Lit.,[266, 268] 124-127°C); (Found: C, 33.9; H, 0.90. Calc. for $C_7H_2F_6O_3$ C, 33.87; H, 0.81%); **IR spectrum no 20; NMR spectrum no 29; Mass spectrum 32**, by comparison with literature data[266, 268].

VIII.9. (73): 2-Furancarbaldehyde and (8)

Fluoroalkene (**8**) (1.5g,8.2mmol) was transferred, under reduced pressure, into a quartz tube which had previously been charged with 2-furancarbaldehyde (0.5g,5.2mmol) under a counter current of dry nitrogen. The tube was evacuated, sealed and heated in a furnace maintained at 225°C for 24 hours. It was then cooled to liquid air temperatures, opened, and excess (**8**) was removed by distillation at room temperature and atmospheric pressure. The residue was filtered and was shown by GLCMS and NMR to contain a mixture of unreacted starting aldehyde (43%) and *3,4-bis(trifluoromethyl)-2-furancarbaldehyde* (73) (51%); **NMR spectrum no 30; Mass spectrum no 33**, by comparison with literature data[266].

VIII.10. (64) and (65): Cyclopentadiene and (8) (200°C)

Fluoroalkene (**8**) (2.5g,13.7mmol) was transferred, under reduced pressure, into a quartz tube which had previously been charged with cyclopentadiene (0.7g,10.6mmol) under a counter current of dry nitrogen. The tube was evacuated, sealed and heated in a furnace maintained at 200°C for 24 hours. It was then cooled to liquid air temperatures, opened, and excess (**8**) was removed by distillation at room temperature and atmospheric pressure. The residue was filtered and was shown to contain 2 major components in a 1:1 ratio, identified as two isomers of *5-fluoro-5,6-bis(trifluoromethyl)-7-bicyclo[2.2.1]hept-2-ene* (**64** and **65**) (**Mass Spectrum no 34 and 35; IR spectrum no 21**) (2.1g, 81% combined), by comparison with authentic samples[31, 188]. It was possible to separate the isomers by preparative scale GC(SE30/50°C) and determine the stereochemistry of each isomer by an examination of the NMR data.

Exo-5-fluoro-5,6-bis(trifluoromethyl)-7-bicyclo[2.2.1]hept-2-ene (**64**), **NMR spectrum no 31**.

Endo-5-fluoro-5,6-bis(trifluoromethyl)-7-bicyclo[2.2.1]hept-2-ene (**65**), NMR **spectrum no 32.**

VIII.11. (66): Cyclopentadiene and (8) (300°C)

Fluoroalkene (**8**) (1.4g,7.7mmol) was transferred, under reduced pressure, into a quartz tube which had previously been charged with cyclopentadiene (0.3g,4.5mmol) under a counter current of dry nitrogen. The tube was evacuated, sealed and heated in a furnace maintained at 300°C for 24 hours. It was then cooled to liquid air temperatures, opened and excess (**8**) was removed by distillation at room temperature and atmospheric pressure. The residue was filtered and was shown to be a mixture of *2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene* (**66**)[271](53% by ^{19}F NMR integration against an internal standard of 1,1,1 trifluorotoluene); (**NMR spectrum no 33; Mass spectrum no 36**), and a 1:1 mixture of *exo-* and *endo-5-fluoro-5,6-bis(trifluoromethyl)-7-bicyclo[2.2.1]hept-2-ene* (**64** and **65**) [31, 188](5% by ^{19}F NMR integration against an internal standard of 1,1,1 trifluorotoluene).

VIII.12. (66) and (72): Pyrolysis of (64) and (65)

A mixture of (**64**) and (**65**) was passed dropwise through a glass tube packed with glass wool at 450°C under a slow current of nitrogen. Volatile material was collected in a trap maintained at liquid air temperatures, and was shown by GLCMS to contain unreacted (**64**) and (**65**) (6%), *2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene* (**66**) (18%), and a mixture of olefinic isomers of *bis(trifluoromethyl)cyclopentadiene* (**72a-c**) (8%) **(Mass spectrum no 37)**

VIII.13. (66): Potassium ^{t}Butoxide with (64) and (65)

A mixture of (**64**) and (**65**) (4.1g,16.5mmol) was added dropwise to a 1.0M ^{t}butanol solution of potassium ^{t}butoxide (50ml), and stirred at room temperature for 10 hours. The reaction mixture was then poured into water (50ml). Ether (3x30ml) extraction followed by distillation gave *2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene* (**66**) (3.0g,80%); b.p. 119-123°C; (lit.,[271] 120-122°C); **IR spectrum no 22; NMR spectrum no 33; Mass spectrum no 36.**

VIII.14. (74): Hydrogenation of (66)

2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (**66**) (3.0g, 13.3mmol) was dissolved in ethanol (100ml) and hydrogenated in the presence of a platinum catalyst on activated carbon (0.1g) in a Parr apparatus for 36 hours. The reaction mixture was filtered through a bed of celite, and the brown filtrate was added to water (50ml), and extracted with DCM (3x30ml). The solvent was evaporated to leave a brown liquid (1.9g), which was shown to contain at least 6 components by GLCMS, one of which was proposed as *2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene* (**74**) **NMR spectrum no 34 ; Mass spectrum no 38.**

Chapter Nine
Experimental to Chapter Five

IX.1. (43): Water and (8)

Fluoroalkene (8) (1.1g, 6.0mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with water (5.7g, 316mmol), sodium carbonate (1.1g, 10.4mmol) and acetonitrile (7ml). The tube was then evacuated, sealed and rotated in an oil bath maintained at 80°C for 24 hours. It was then cooled to liquid air temperatures and opened. Volatile material was removed under reduced pressure, and shown by NMR (**NMR spectrum no 15**) and GLCMS (**Mass spectrum no 17**) to contain *1,1,1-trifluoroacetone* (**43**) as the major component. As before, the 2,4 DNP derivative was prepared, yielding yellow needles of the 2,4 *dinitrophenylhydrazone of 1,1,1-trifluoroacetone* (0.8g,56%), mp 136-137°C, (lit.,[282] 139°C); (Found: C, 37.1; H, 2.3; N, 19.0. Calc for $C_9H_7F_3N_4O_4$: C, 37.0; H, 2.4; N, 19.2%); **IR spectrum no 11**; **Mass spectrum no 18** .

IX.2. (78): Sodium Methoxide and (8)

Fluoroalkene (**8**) (3.6g, 19.8mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with sodium methoxide (1.55g, 28.7mmol) and tetraglyme (10ml) against a counter current of dry nitrogen. The tube was then evacuated, sealed and rotated end over end for 2 weeks at room temperature. It was then cooled to liquid air temperatures and opened. Volatile material was removed under reduced pressure, and distilled at -78°C/0.1mbar and then 0°C/0.1mbar to leave a clear volatile liquid identified as *(Z)-2-methoxy 1,1,1,4,4,4 hexafluorobut-2-ene* (**78**) (3.3g, 87%) by comparison with literature data[185, 241, 257]. **IR spectrum no 23 ;NMR spectrum no 35; Mass spectrum no 39** .

IX.3. (90) and (91): Caesium Phenoxide and (8)

Fluoroalkene (**8**) (0.94g, 5.1mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with freshly sublimed phenol (0.47g,5.0mmol), dry caesium fluoride (0.88g, 5.8mmol) and acetonitrile (9ml) against a counter current of dry nitrogen. The tube was then evacuated, sealed and rotated end over end for 2 weeks at room temperature. It was then cooled to liquid air temperatures and opened. Volatile material was removed under reduced pressure. The residual white suspension was poured into a separating funnel containing water (125ml). Ether (3x50ml) was used to extract the organic layer. The ether layer was dried ($MgSO_4$) and evaporated. The residual clear oil was identified[185] as a 9:1 mixture of (*Z*) and (*E*) isomers of *2-phenoxy-1,1,1,4,4,4-hexafluorobut-2-ene* (**90**), (**91**) (1.0g, 80%); (Found C, 47.0; H, 2.3. Calc. for $C_{10}H_6F_6O$, C, 46.9; H, 2.3%). **IR spectrum no 24.**

The isomers were separated by preparative scale GLC (SE30/50°C).

(*Z*) isomer: NMR spectrum no 36 ; Mass spectrum no 40.
(*E*) isomer: NMR spectrum no 37 ; Mass spectrum no 41.

IX.4. (76): Ethylene Glycol and (8)

Fluoroalkene (8) (4.2g, 23.1mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with ethylene glycol (1.5g, 24.2mmol), sodium carbonate (6.2g, 58.5mmol) and tetraglyme (15ml) against a counter current of dry nitrogen. The tube was then evacuated, sealed and rotated end over end for 2 weeks at room temperature. It was then cooled to liquid air temperatures and opened. Volatile material was removed under reduced pressure, and shown to contain a major product, which was isolated by preparative scale GLC (SE30/40°C), giving *2-trifluoromethyl-2-(1,1,1-trifluoroethyl)-1,3-dioxole* (76) (4.0g, 77%). (Found: C, 32.4; H, 3.0. $C_6H_6F_6O_2$ requires C, 32.1; H, 2.7%). IR spectrum no 25; NMR spectrum no 38; Mass spectrum no 42.

IX.5. (96): Catechol and (8)

Fluoroalkene (8) (1.82g, 10.0mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with catechol (1.08g, 9.8mmol), caesium carbonate (6.4g, 19.7mmol), and acetonitrile (10ml) against a counter current of dry nitrogen. The tube was then evacuated, sealed and rotated end over end for 2 weeks at room temperature. It was then cooled to liquid air temperatures and opened. Volatile material was removed under reduced pressure, and the residual white suspension was poured into a separating funnel containing water (125ml). Ether (3x50ml) was used to extract the organic layer, which was dried ($MgSO_4$) and distilled to remove solvent. The residual clear oil was identified as *2-trifluoromethyl-2-(1,1,1-trifluoroethyl)-1,3-benzodioxole* (96) (2.3g,84%). (Found: C, 44.1; H, 2.4. $C_{10}H_6F_6O_2$ requires C, 44.1; H, 2.2%); IR spectrum no 26; NMR spectrum no 39; Mass spectrum no 43.

IX.6. (92) and (93): Hydroquinone and (8)

Fluoroalkene (8) (1.80g, 9.9mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with hydroquinone (0.56g, 5.1mmol), caesium carbonate (3.68g, 11.3mmol) and acetonitrile (10ml) against a counter current of dry nitrogen. The tube was then evacuated, sealed and rotated end over end for 5 days at room temperature. It was then cooled to liquid air temperatures, opened, and volatile material was removed under reduced pressure. The residue was shown by NMR to contain a mixture of *(Z)-2-(4-hydroxyphenoxy)-1,1,1,4,4,4-hexafluorobut-2-ene* (92) and *p-phenylenedioxy-2-2'-bis-(Z-1,1,1,4,4,4-hexafluorobut-2-ene)* (93) (NMR spectrum no 40 and NMR spectrum no 41).

Fluoroalkene (8) (0.90g, 5.0mmol) was then transferred, under reduced pressure, into a Carius tube which had been previously charged with the above residue, caesium carbonate (3.34g, 5.7mmol) and acetonitrile (10ml) against a counter current of dry

nitrogen. The tube was then evacuated, sealed and rotated end over end for 5 days at room temperature. It was then cooled to liquid air temperatures, opened, and volatile material was removed under reduced pressure and the residual white suspension was poured into a separating funnel containing water (125ml). Ether (3x50ml) was used to extract the organic layer, which was dried ($MgSO_4$) and distilled to remove solvent. The residual solid was recrystallised from DCM/hexane, to give a white solid identified as *p-phenylenedioxy-2-2'-bis-(Z-1,1,1,4,4,4-hexafluorobut-2-ene)* (93) (2.3g, 84%). (Found: C, 38.9; H, 1.6. $C_{14}H_6F_{12}O_2$ requires C, 38.7; H, 1.4%); **IR spectrum no 27; NMR spectrum no 41; Mass spectrum no 44.**

IX.7. (88) and (44): Ammonia and (8)

Fluoroalkene (8) (1.90g, 10.2mmol) was transferred under reduced pressure into a round bottomed glass vessel (sealable via an integral Young's tap) , which had previously been charged with 33%w/w aqueous ammonia solution (1.56g, 30.6mmol of NH_3). The flask was evacuated, sealed and stirred for 1 week at room temperature. It was then cooled to liquid air temperatures and volatile material was removed under reduced pressure, and shown by GLCMS and NMR to contain two major components in a 7:3 ratio. The first was identified as *2-amino-1,1,1,4,4,4-hexafluorobut-2-ene*, (88) (**NMR spectrum no 42; Mass spectrum no 45**) by comparison with data from an authentic sample. The second was identified as *1,1,1,4,4,4-hexafluorobutan-2-one* (44) [132], **NMR spectrum no 43; Mass spectrum no 46**. Volatile material was recondensed into the flask still containing the original mixture, which was then evacuated, resealed and stirred for two weeks. Volatile material was again removed under reduced pressure and were shown to contain *1,1,1,4,4,4 hexafluorobutan-2-one* (44) [241]as the major component by GLCMS. The volatile material was transferred into a round bottomed flask containing a solution of semicarbazide hydrogen chloride (1.5g,19.1mmol) and sodium acetate (6.75g, 82.3mmol) in water (15ml). The flask was stirred for 1 hour at room temperature and then placed into a fridge and left overnight. The resulting pale yellow crystals were filtered and recrystallised from hot EtOH, yielding *1,1,1,4,4,4-hexafluorobutan-2-one semicarbazone* (1.4g, 56%); mp 122-123°C, (lit.[245],122°C (EtOH). (Found: C, 25.2;H, 2.1; N, 17.9. Calc. for $C_5H_5N_3O$: C, 25.3; H, 2.1; N, 17.7%); **IR spectrum no 28; Mass spectrum no 48.**

IX.8. (97): n-Butylamine and (8)

Fluoroalkene (8) (3.4g, 18.7mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with n-butylamine (4.5g, 60.8mmol) under a counter current of dry nitrogen. The tube was evacuated, sealed and rotated end over end for 2 days at room temperature. It was then cooled to liquid air temperatures and the volatile material was removed under reduced pressure, and ether (3x15ml) was added to the residual orange mixture, and stirred for 30 minutes. This slurry was then filtered, and the solid filtered was washed with more ether (2x10ml). These washings were added to the original filtrate, and the ether and unreacted n-butylamine removed by distillation, leaving

an oil which contained one major component, which was isolated by preparative scale GLC (SE30/70°C) and identified as *2-^{n}Butylimino-1,1,1,4,4,4-hexafluorobutane* (**97**) (3.4g, 73%). (Found: C, 35.9; H, 4.4; N, 5.9. $C_7H_{11}NF_6$ requires C, 35.7; H, 4.7; N, 6.0%); **IR spectrum no 29; NMR spectrum no 44; Mass spectrum no 47.**

IX.9. Formation of Butan-2-one (44) - (ii)

(Z)-2-Methoxy-1,1,1,4,4,4-hexafluorobut-2-ene (**78**) (0.4g, 2.1mmol) was transferred under reduced pressure into a round bottomed glass vessel (sealable via an integral Young's tap), which had previously been charged with water (7ml) and triflic acid (1ml).The flask was evacuated, sealed and stirred for 2 days at room temperature. It was then cooled to liquid air temperatures and opened. Ether (10ml) was added and the ethereal layer was separated, washed with more water (2x10ml), dried (MgSO4) and was shown to contain *1,1,1,4,4,4 hexafluorobutan-2-one* (**44**) by NMR and GLCMS. (**NMR spectrum no 43; Mass spectrum no 46**). The product was isolated as *1,1,1,4,4,4 hexfluorobutan-2-one semicarbazone* (0.44g, 90%) by standard procedures as reported earlier.

IX.10. Formation of Butan-2-one (44) - (iii)

2-^{n}Butylimino-1,1,1,4,4,4-hexafluorobutane (**97**) (0.5g, 2.1mmol) was transferred into a round bottomed flask which had been previously charged with water (5ml) which had been acidified to pH1 using 98% sulphuric acid. The flask was stirred for 1 day at room temperature. Ether (10ml) was then added and the ethereal layer was separated, washed with more water (2x10ml), dried (MgSO4) and was shown to contain *1,1,1,4,4,4 hexafluorobutan-2-one* (**44**) by NMR and GLCMS. (**NMR spectrum no 43; Mass spectrum no 46**). The product was isolated as *1,1,1,4,4,4 hexfluorobutan-2-one semicarbazone* (0.42g, 84%) by standard procedures as reported earlier.

Appendix One
Nuclear Magentic Resonance Data

No.1	2*H*-Heptafluorobut-2-ene (**8**)
No. 2	(Z, E)-5*H*-perfluoro-3,4-bis(trifluoromethyl)hexa-2,4-diene (**31a**)
No. 3	5*H*-perfluoro-3,4-bis(trifluoromethyl)hexa-2,4-diene (**31b**)
No. 4	Potassium pentakis(trifluoromethyl)cyclopentadienide (**33a**)
No. 5	Hydronium pentakis(trifluoromethyl)cyclopentadienide (**33c**)
No. 6	Tetraethylammonium pentakis(trifluoromethyl) cyclopentadienide (**33d**)
No. 7	Tetrapropylammonium pentakis(trifluoromethyl)cyclopentadienide (**33e**)
No. 8	Tetrabutylammoniumpentakis(trifluoromethyl)cyclopentadienide(**33f**)
No. 9	Barium pentakis(trifluoromethyl)cyclopentadienide(**33g**)
No. 10	Caesium pentakis(trifluoromethyl)cyclopentadienide (**33b**)
No. 11	Thallium pentakis(trifluoromethyl)cyclopentadienide (**33h**)
No. 12	5*H*-pentakis(trifluoromethyl)cyclopenta-1,3-diene (**34**)
No. 13	Caesium perfluoro1,2,3-trihydro-4,5,6-trimethylpentalenide (**37**)
No. 14	Caesium perfluoro-1-methyl-2,3,4,5,6,7-hexahydrodicyclopenta[b,d]cyclopentadienide (**38**)
No. 15	1,1,1-Trifluoroacetone (**43**)
No. 16	1,9-diazabicyclo[5.4.0]undecano-a,b-2-difluoromethyl-3-trifluoromethylpyrrole (**48**)
No. 17	(*Z*)-2-Chloro-1,1,1,4,4,4-hexafluorobut-2-ene (**46**)
No. 18	(*Z*)-2-Bromo-1,1,1,4,4,4-hexafluorobut-2-ene (**47**)
No. 19	Hexafluorobut-2-yne (**3**)
No. 20	(*Z*)-2-^{t}Butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (**45**)
No. 21	3,4-bis(trifluoromethyl)furan (**51**)
No. 22	2,3-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene (**49**)
No. 23	*exo*-5-fluoro-5,6-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2-ene (**62**)
No. 24	*endo*-5-fluoro-5,6-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2-ene (**63**)
No. 25	2,5-dimethyl-3,4-bis(trifluoromethyl)furan (**67**)
No. 26	3,4-bis(trifluoromethyl)-2-furonitrile (**68**)
No. 27	methyl-3,4-bis(trifluoromethyl)furan-2-oate (**70**)
No. 28	ethyl-3,4-bis(trifluoromethyl)furan-2-oate (**71**)
No. 29	3,4-bis(trifluoromethyl)-2-furoic acid (**69**)
No. 30	3,4-bis(trifluoromethyl)-2-furancarbaldehyde (**73**)
No. 31	*Exo*-5-fluoro-5,6-bis(trifluoromethyl)-7-bicyclo[2.2.1]hept-2-ene (**64**)

No. 32 *Endo*-5-fluoro-5,6-bis(trifluoromethyl)-7-bicyclo[2.2.1]hept-2-ene (65)

No. 33 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (66)

No. 34 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (74)

No. 35 (*Z*)-2-methoxy 1,1,1,4,4,4 hexafluorobut-2-ene (78)

No. 36 (*Z*)-2-phenoxy-1,1,1,4,4,4-hexafluorobut-2-ene (90)

No. 37 (*E*)-2-phenoxy-1,1,1,4,4,4-hexafluorobut-2-ene (91)

No. 38 2-trifluoromethyl-2-(1,1,1-trifluoroethyl)-1,3-dioxole (76)

No. 39 2-trifluoromethyl-2-(1,1,1-trifluoroethyl)-1,3-benzodioxole (96)

No. 40 (*Z*)-2-(4-hydroxyphenoxy)-1,1,1,4,4,4-hexafluorobut-2-ene (92)

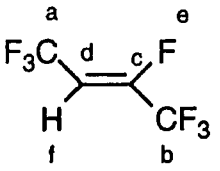
No. 41 *p*-phenylenedioxy-2-2'-bis-(Z-1,1,1,4,4,4-hexafluorobut-2-ene) (93)

No. 42 2-amino-1,1,1,4,4,4-hexafluorobut-2-ene, (88)

No. 43 1,1,1,4,4,4-hexafluorobutan-2-one (44)

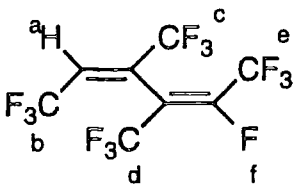
No. 44 2-^{n}Butylimino-1,1,1,4,4,4-hexafluorobutane (97)

NMR No 1



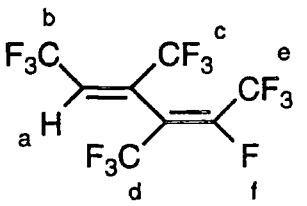
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-61.60	s		3	a
	-76.22	s		3	b
	-119.86	s		1	e
^{1}H	5.45	d q	$^{3}J_{f-e}$=28.3 $^{3}J_{f-a}$=5.3		f
^{13}C	101.31	q	$^{2}J_{d-a}$=39.1		d
	116.17	q d	^{1}J=272.5 $^{2}J_{b-e}$=38.3		b
	119.45	q	^{1}J=269.5		a
	150.82	d q q	$^{1}J_{c-e}$=283.3 $^{2}J_{c-b}$=41.2 $^{3}J_{c-a}$=5.9		c

NMR No 2



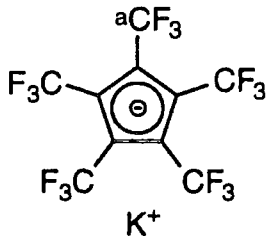
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-60.81	d q q	$^{4}J_{d-f}$=16.1 $^{5}J_{d-c}$=1.8 $^{5}J_{d-e}$=1.0	3	d
	-62.33	Pseudo 7	$^{5}J_{c-b}$=1.8 $^{5}J_{c-d}$=1.8	3	c
	-68.74	m	$^{5}J_{b-c}$=1.8	3	b
	-70.41	d pseudo7	$^{3}J_{e-f}$=8.6 $^{5}J_{e-d}$=1.0 $^{6}J_{e-c}$=1.0	3	e
	-104.96	q q	$^{4}J_{f-d}$=16.1 $^{3}J_{f-e}$=8.6	1	f

NMR No 3



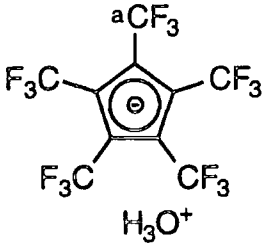
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-62.13	s		3	d
	-56.65	s		3	c
	-64.62	s		3	b
	-68.28	s		3	e
	-101.76	s		1	f

NMR No 4



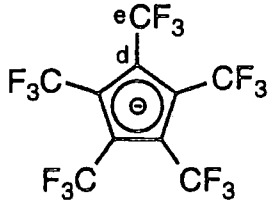
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-49.82	s			a

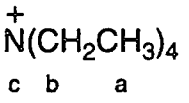
NMR No 5



Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-51.40	s			a

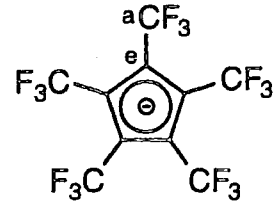
NMR No 6

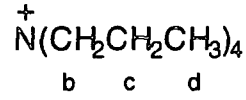




Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-50.87	s			e
^{1}H	1.42	t t(1:1:1)	$^{3}J_{a-b}=7.2$ $^{3}J_{a-c}=1.9$	3	a
	3.51	q	$^{3}J_{b-a}=7.2$	2	b
^{13}C	15.70	s			a
	53.11	t	$^{1}J_{b-c}=2.6$		b
	110.21	q	$^{2}J_{d-e}=19.2$		d
	124.65	q	$^{1}J=271.3$		e

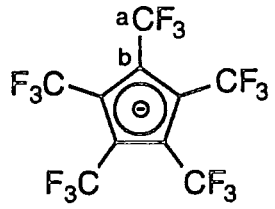
NMR No 7

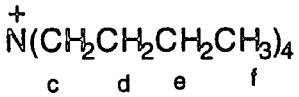




Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-50.91	s			a
^{1}H	0.96	t	$^{3}J_{d-c}=7.2$	3	d
	1.70	sextet	$^{3}J_{c-b+d}=7.2$	2	c
	3.01	m		2	b
^{13}C	15.30	s			d
	30.99	s			c
	55.20	s			b
	110.11	q	$^{2}J_{e-a}=19.0$		e
	123.33	q	$^{1}J=270.5$		a

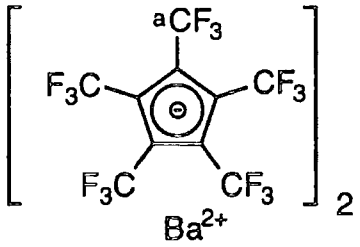
NMR No 8





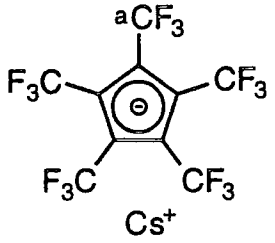
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-50.11	s			a
^{1}H	0.95	t	$^{3}J_{f-e}=7.2$	3	f
	1.33	sextet	$^{3}J_{c-b+d}=7.2$	2	e
	1.60	quintet	$^{3}J_{d-c+e}=8.4$	2	d
	3.11	m		2	c
^{13}C	13.11	s			f
	19.20	s			e
	23.44	s			d
	58.50	s			c
	109.62	q	$^{2}J_{b-a}=18.5$		b
	123.69	q	$^{1}J=269.9$		a

NMR No 9



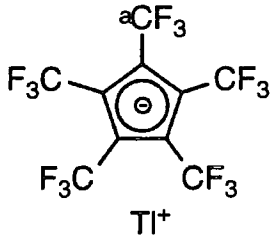
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-49.99	s			a

NMR No 10



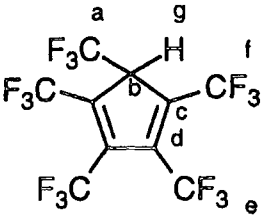
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-49.91	s			a

NMR No 11



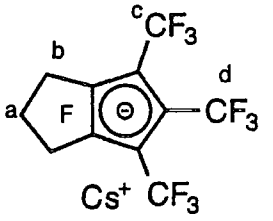
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-50.10	s			a

NMR No 12



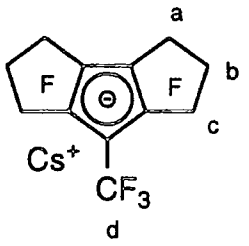
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-57.12	s		6	f
	-60.18	s		3	a
	-60.86	s		6	e
^{1}H	4.80	q	$^{3}J_{g-a}=5.6$		g
^{13}C	58.44	q	$^{2}J_{b-a}=32.1$		b
	119.22	q	$^{1}J=275.1$		a,e or f
	120.20	q	$^{1}J=272.4$		a,e or f
	122.56	q	$^{1}J=284.1$		a,e or f
	139.65	q	$^{2}J_{c-f}=40.4$		c or d
	139.80	q	$^{2}J_{d-e}=40.3$		c or d

NMR No 13



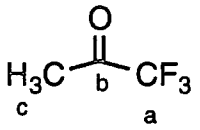
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-49.71	s		3	d
	-52.53	s		6	c
	-97.68	s		4	b
	-121.10	s		2	a

NMR No 14



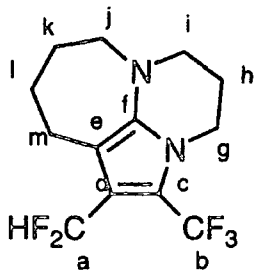
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-54.39	s		3	d
	-98.35	s		4	a or c
	-100.12	s		4	a or c
	-122.19	s		4	b

NMR No 15



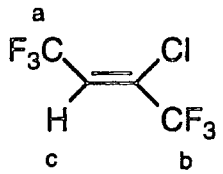
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-85.54	s			a
^{1}H	2.46	s			c
^{13}C	23.5	s			c
	120.1	q	$^{1}J=291.0$		a
	188.7	q	$^{2}J_{a-b}=36.2$		b

NMR No 16



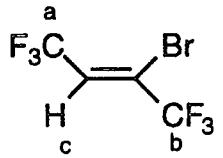
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-58.87	t	$^{5}J_{b-a}$=4.9	3	b
	-106.47	d q	^{2}J=54.6 $^{5}J_{a-b}$=4.9	2	a
^{1}H	1.51	m		2	h,k or l
	1.75	m		2	h,k or l
	2.07	m		2	h,k or l
	2.66	m		2	g,i or j
	2.98	m		2	g,i or j
	3.08	m		2	g,i or j
	3.87	m		2	m
	6.75	t	^{2}J=54.5	1	a
^{13}C	21.95	s			h,k or l
	25.08	s			h,k or l
	26.74	s			h,k or l
	31.13	s			g,i,j or m
	42.47	s			g,i,j or m
	50.14	s			g,i,j or m
	56.67	s			g,i,j or m
	104.55	s			e
	109.83	q t	$^{2}J_{c-b}$=37.6 $^{3}J_{c-a}$=8.8		c
	115.56	t q	^{1}J=229.5 $^{4}J_{a-b}$=5.0		a
	117.58	t	$^{2}J_{d-a}$=25.6		d
	122.04	q	^{1}J=266.4		b
	141.63	s			f

NMR No 17



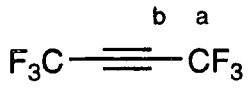
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-64.15	s		3	a
	-74.03	s		3	b
^{1}H	6.32	q	$^{3}J_{c-a}$=6.3		c

NMR No 18



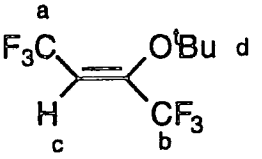
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-63.47	s		3	a
	-71.24	s		3	b
^{1}H	6.63	q	$^{3}J_{a-c}$=6.4		c

NMR No 19



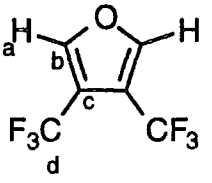
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-54.21	s			a
^{13}C	30.02	q	$^{2}J_{b-a}$=19.4		b
	113.86	q	^{1}J=259.8		a

NMR No 20



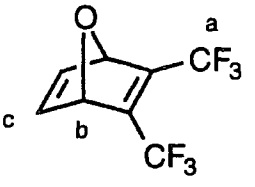
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-57.13	s		3	a
	-67.75	s		3	b
^{1}H	1.44	s		9	d
	6.05	q	$^{3}J_{C-a}=6.5$	1	c

NMR No 21



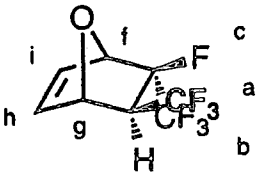
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-59.87	s			d
^{1}H	7.85	s			a
^{13}C	115.8	q	$^{2}J_{C-d}=41.0$		c
	120.0	q	$^{1}J=267.8$		d
	140.4	s			b

NMR No 22



Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-66.25	s			a
^{1}H	5.70	s		2	b
	7.28	s		2	c

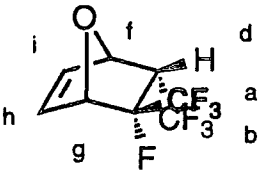
NMR No 23



d

Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-64.96	s		3	a
	-75.99	s		3	b
	-182.91	s		1	c
^{1}H	3.17	d q	$^{3}J_{d-c}$=12.2 $^{3}J_{d-a}$=9.0	1	d
	5.42	m		2	f,g
	6.42	m		1	h or i
	6.74	m		1	h or i

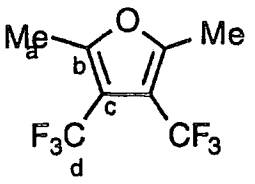
NMR No 24



c

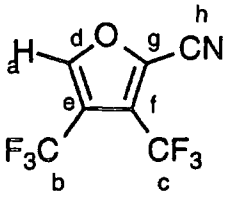
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-68.81	s		3	a
	-79.23	s		3	b
	-183.75	s		1	c
^{1}H	3.62	d q d	$^{3}J_{d-c}$=12.6 $^{3}J_{d-b}$=8.9 $^{3}J_{d-f}$=4.3	1	d
	5.40	m		2	f, g
	6.68	m		1	h or i
	6.91	m		1	h or i

NMR No 25



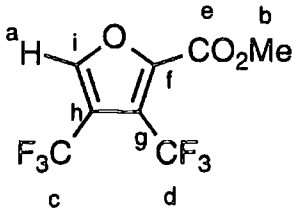
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-55.72	s			d
^{1}H	2.47	s			a
^{13}C	12.8	s			a
	109.8	q	$^{2}J_{c-d}$=19.6		c
	123.2	q	^{1}J=264.9		d
	152.4	s			b

NMR No 26



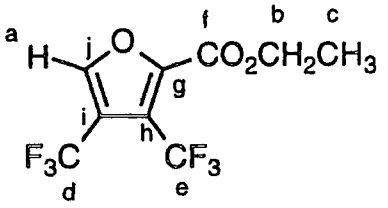
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-59.37	s		3	b
	-64.32	s		3	c
^{1}H	7.62	s			a
^{13}C	115.17	s			g
	117.44	q	$^{2}J_{e-b}$=39.7		e or f
	118.24	q	$^{2}J_{f-c}$=40.3		e or f
	120.49	q	^{1}J=269.7		b or c
	121.33	q	^{1}J=269.6		b or c
	121.54	s			h
	146.24	s			d

NMR No 27



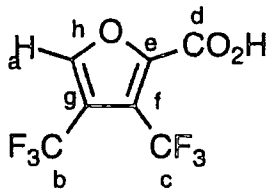
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-55.75	s		3	c or d
	-58.40	s		3	c or d
^{1}H	3.82	s		3	b
	7.91	s		1	a
^{13}C	52.95	s			b
	117.89	q	$^{2}J_{g-d}$=41.1		g or h
	119.01	q	$^{2}J_{h-c}$=39.8		g or h
	120.55	q	^{1}J=270.1		c or d
	121.09	q	^{1}J=269.8		c or d
	145.43	s			f
	146.06	s			i
	156.56	s			e

NMR No 28



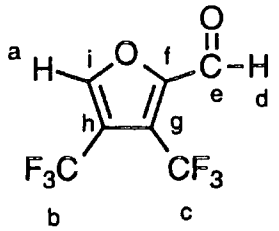
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-55.89	s		3	d or e
	-59.50	s		3	d or e
^{1}H	1.00	t	$^{3}J_{c-b}=7.0$	3	c
	3.97	q	$^{3}J_{b-c}=7.0$	2	b
	8.18	s		1	a
^{13}C	17.38	s			c
	66.11	s			b
	118.19	q	$^{2}J_{h-e}=41.2$		h or i
	119.21	q	$^{2}J_{i-d}=42.0$		h or i
	120.23	q	$^{1}J=269.5$		d or e
	121.01	q	$^{1}J=270.2$		d or e
	145.89	s			j
	146.06	s			g
	157.90	s			f

NMR No 29



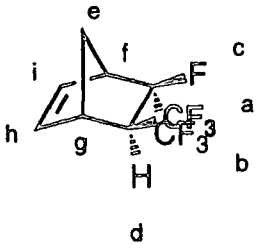
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-58.27	s		3	b
	-60.14	s		3	c
^{1}H	7.75	s			a
^{13}C	118.27	q	$^{2}J_{f\text{-}c}$=40.1		f or g
	119.41	q	$^{2}J_{g\text{-}b}$=40.2		f or g
	120.29	q	^{1}J=270.2		b or c
	121.21	q	^{1}J=269.6		b or c
	146.80	s			e
	147.29	s			h
	173.27	s			d

NMR No 30



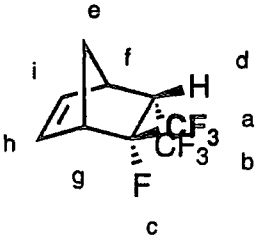
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-55.82	s		3	a or b
	-58.29	s		3	a or b
^{1}H	8.07	s		1	a
	9.88	s		1	d
^{13}C	118.47	q	$^{2}J_{g-c}$=40.1		g or h
	119.62	q	$^{2}J_{h-b}$=40.0		g or h
	120.42	q	^{1}J=269.5		b or c
	121.68	q	^{1}J=270.1		b or c
	148.75	s			i or f
	151.66	s			i or f
	178.45	s			e

NMR No 31



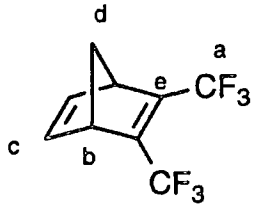
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-65.16	s		3	a
	-77.18	s		3	b
	-176.86	s		1	c
^{1}H	1.30 & 1.48	AB	J=7.9	2	e
	2.55	m		1	d
	3.23	m		2	f,g
	5.96	m		1	h or i
	6.20	m		1	h or i

NMR No 32



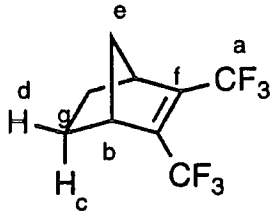
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-65.16	s		3	a
	-78.73	s		3	b
	-180.26	s		1	c
^{1}H	1.80 & 2.20	AB	J=7.9	2	e
	2.77	m		1	d
	3.40	m		2	f, g
	6.22	m		1	h or i
	6.43	m		1	h or i

NMR No 33



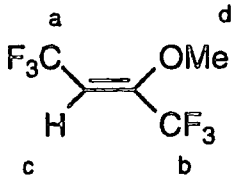
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-62.04	s			a
^{1}H	2.29	m		2	d
	3.93	s		2	b
	6.96	s		2	c
^{13}C	53.07	s			d
	74.12	s			b
	122.8	q	^{1}J=269.4		a
	143.04	s			c
	149.55	q	$^{2}J_{e-a}$=17.9		e

NMR No 34



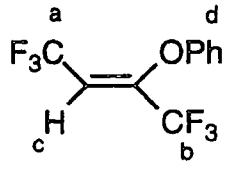
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-60.45	s			a
^{1}H	1.41	m		2	c or d
	1.73	m		2	c or d
	3.13	m		2	e
	4.08	m		2	b

NMR No 35



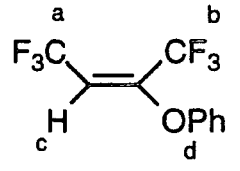
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-58.83	s		3	a
	-71.64	s		3	b
^{1}H	3.50	s		3	d
	5.25	q	$^{3}J_{c-a}$=7.5	1	c

NMR No 36



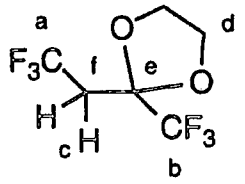
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-60.17	s		3	a
	-69.94	s		3	b
^{1}H	6.50	q	$^{3}J_{c-a}$=7.8	1	c
	7.28 - 6.98	m		5	d

NMR No 37



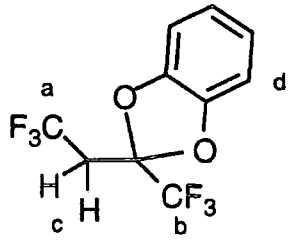
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-54.72	s		3	a
	-68.89	s		3	b
^{1}H	5.70	q	$^{3}J_{c-a}$=7.8	1	c
	7.26 - 6.98	m		5	d

NMR No 38



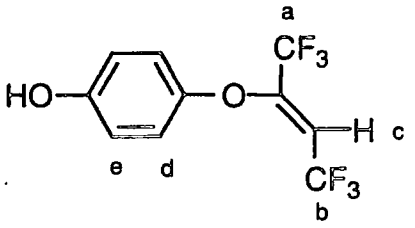
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-62.23	s		3	a
	-85.40	s		3	b
^{1}H	4.28	s		4	d
	2.73	q	$^{3}J_{c-a}$=9.9	2	c
^{13}C	36.04	q	$^{2}J_{f-a}$=29.0		f
	67.52	s			d
	103.35	q	$^{2}J_{e-b}$=28.7		e
	122.93	q	^{1}J=290.2		a or b
	124.70	q	^{1}J=272.2		a orb

NMR No 39



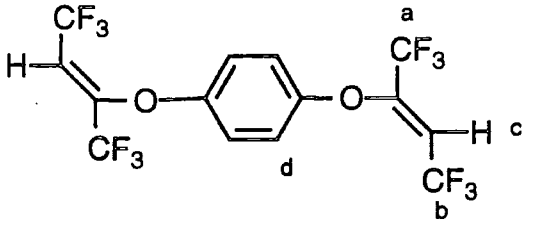
Nucleus	Shift (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
^{19}F	-61.15	s		3	a
	-86.86	s		3	b
^{1}H	3.10	q	$^{3}J_{c-a}$=9.6	2	c
	7.41 - 6.88	m		4	d

NMR No 40



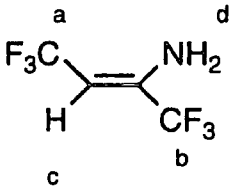
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-54.57	s		3	b
	-69.03	s		3	a
^{1}H	6.13	q	$^{3}J_{c-b}$=6.8	1	c
	7.00 - 7.26	m		4	d+e

NMR No 41



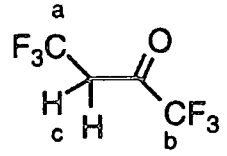
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-59.89	s		3	b
	-69.74	s		3	a
^{1}H	6.18	q	$^{3}J_{c-b}$=6.8	2	c
	7.08	s		4	d

NMR No 42



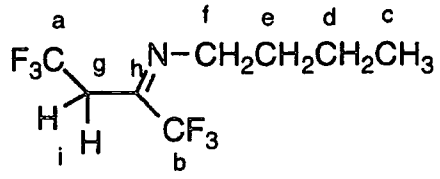
Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-58.08	s		3	a
	-71.98	s		3	b
^{1}H	4.89	q	$^{3}J_{c-a}$=8.4	1	c
	4.33	br		2	d

NMR No 43



Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-60.97	s		3	a
	-86.92	s		3	b
^{1}H	3.25	q	$^{3}J_{c-a}$=9.3		c

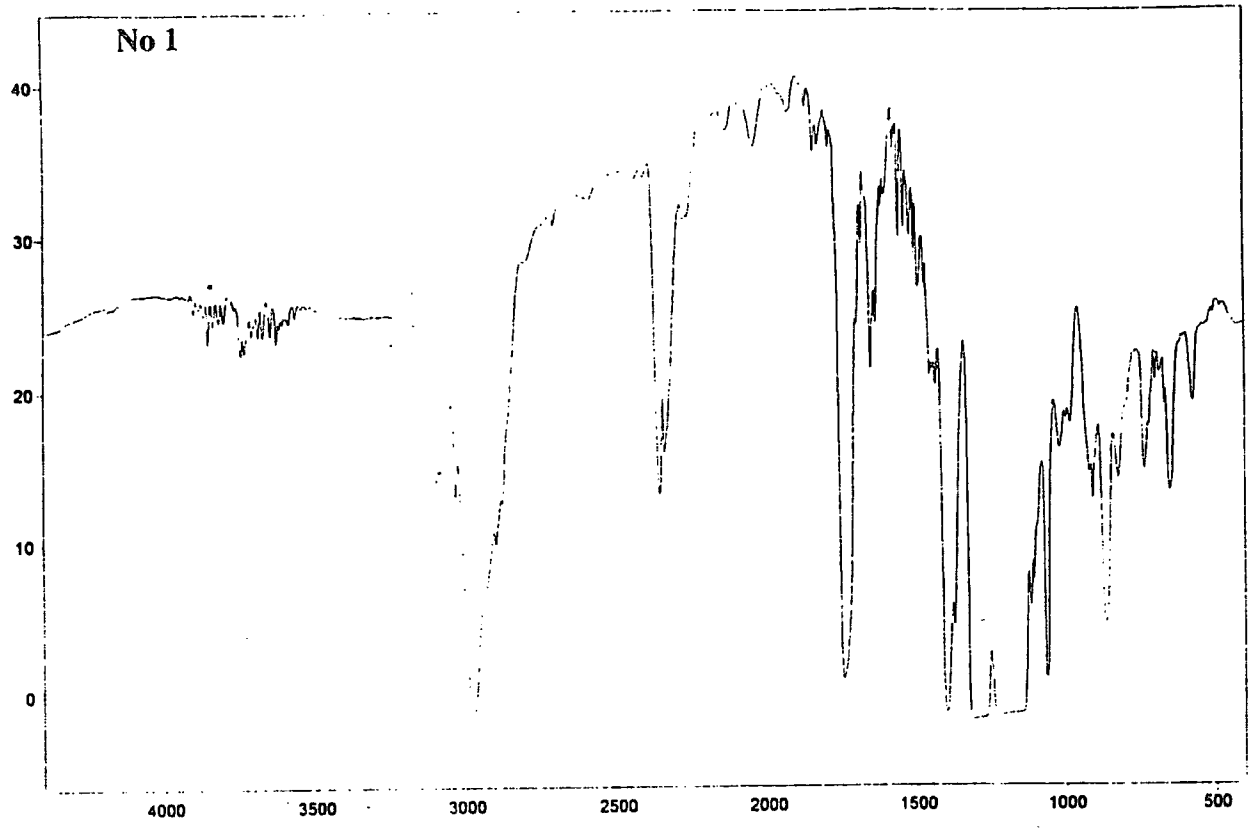
NMR No 44



Nucleus	Shift	Multiplicity	Coupling	Integral	Assignment
	(ppm)		(Hz)		
^{19}F	-62.42	s		3	b
	-73.57	s		3	a
^{1}H	0.93	t	$^{3}J_{c-d}$=7.5	3	c
	1.44	q	$^{3}J_{d-c}$=7.5	2	d
	1.72	t	$^{3}J_{e-f}$=6.5	2	e
	3.68	m		2	f
	3.38	q	$^{3}J_{i-a}$=10.1	2	i
^{13}C	14.18	s			c
	20.94	s			d
	32.47	s			e
	53.36	s			f
	31.77	q	$^{2}J_{g-a}$=32.5		g
	148.43	q	$^{2}J_{h-b}$=35.1		h
	119.57	q	^{1}J=220.5		a or b
	123.89	q	^{1}J=270.8		a or b

Appendix Two
Infrared Red Data

No.1	2*H*-Heptafluorobut-2-ene (**8**)
No. 2	5*H*-perfluoro-3,4-bis(trifluoromethyl)hexa-2,4-diene (**31**)
No. 3	Tetraethylammonium pentakis(trifluoromethyl) cyclopentadienide (**33d**)
No. 4	Tetrapropylammonium pentakis(trifluoromethyl)cyclopentadienide (**33e**)
No. 5	Tetrabutylammoniumpentakis(trifluoromethyl)cyclopentadienide(**33f**)
No. 6	Barium pentakis(trifluoromethyl)cyclopentadienide(**33g**)
No. 7	Potassium pentakis(trifluoromethyl)cyclopentadienide(**33a**)
No. 8	Caesium pentakis(trifluoromethyl)cyclopentadienide (**33b**)
No. 9	Thallium pentakis(trifluoromethyl)cyclopentadienide (**33h**)
No. 10	5*H*-pentakis(trifluoromethyl)cyclopenta-1,3-diene (**34**)
No. 11	2,4 dinitrophenylhydrazone of 1,1,1-trifluoroacetone
No. 12	1,9-diazabicyclo[5.4.0]undecano-a,b-2-difluoromethyl-3-trifluoromethylpyrrole (**48**)
No. 13	(*Z*)-2-chloro-1,1,1,4,4,4-hexafluorobut-2-ene (**46**)
No. 14	hexafluorobut-2-yne (**3**)
No. 15	3,4 bis(trifluoromethyl)furan (**51**)
No. 16	2,5-dimethyl-3,4-bis(trifluoromethyl)furan (**67**)
No. 17	3,4-bis(trifluoromethyl)-2-furonitrile (**68**)
No. 18	methyl-3,4-bis(trifluoromethyl)furan-2-oate (**70**)
No. 19	ethyl-3,4-bis(trifluoromethyl)furan-2-oate (**71**)
No. 20	3,4-bis(trifluoromethyl)-2-furoic acid (**69**)
No. 21	5-fluoro-5,6-bis(trifluoromethyl)-7-bicyclo[2.2.1]hept-2-ene (**64**), (**65**)
No. 22	2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (**66**)
No. 23	(*Z*)-2-methoxy 1,1,1,4,4,4 hexafluorobut-2-ene (**78**)
No. 24	2-phenoxy-1,1,1,4,4,4-hexafluorobut-2-ene (**90**), (**91**)
No. 25	2-trifluoromethyl-2-(1,1,1-trifluoroethyl)-1,3-dioxole (**76**)
No. 26	2-trifluoromethyl-2-(1,1,1-trifluoroethyl)-1,3-benzodioxole (**96**)
No. 27	*p*-phenylenedioxy-2-2'-bis-(Z-1,1,1,4,4,4-hexafluorobut-2-ene) (**93**)
No. 28	1,1,1,4,4,4-hexfluorobutan-2-one semicarbazone
No. 29	2-^{n}Butylimino-1,1,1,4,4,4-hexafluorobutane (**97**)

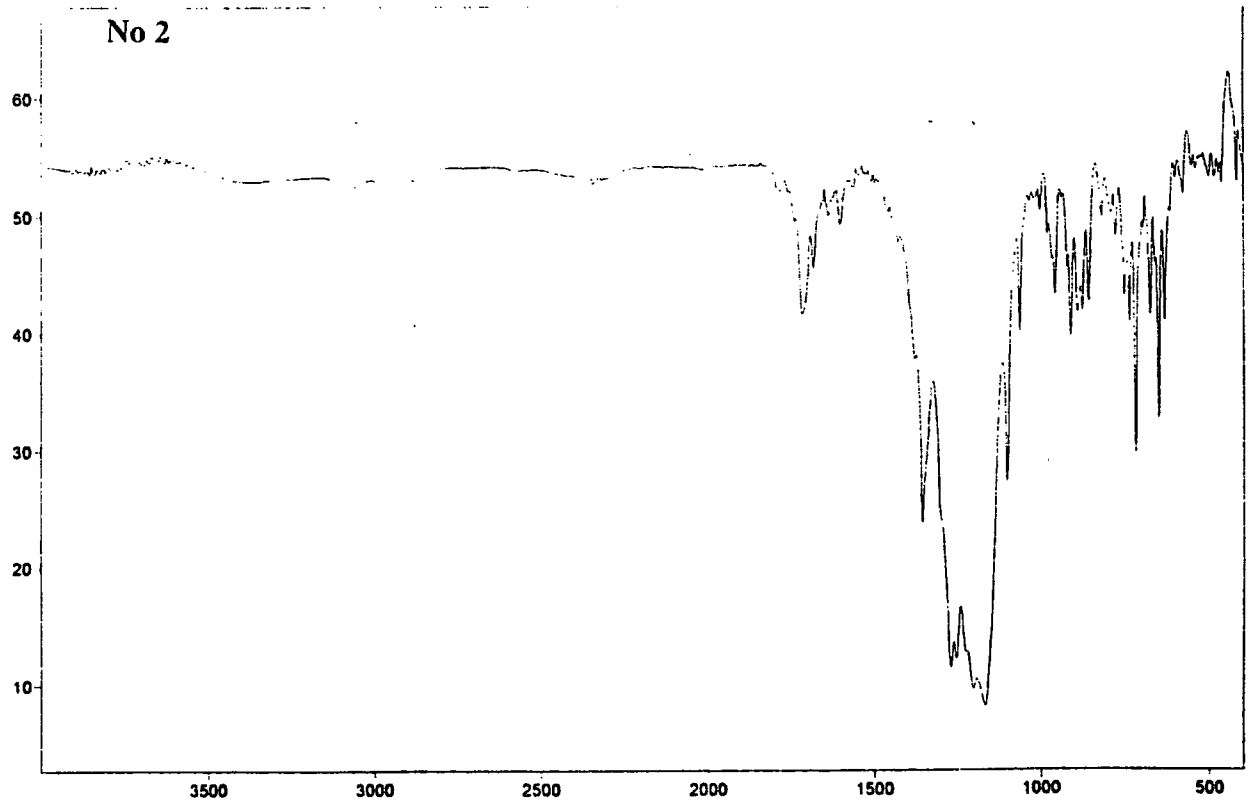


Arbitrary Y / Wavenumber (cm-1)

File # 1 : PC

Number of Scans= 4 Apodization= Strong

04/01/95 12:19 Res=4 cm-1



Transmittance / Wavenumber (cm-1)

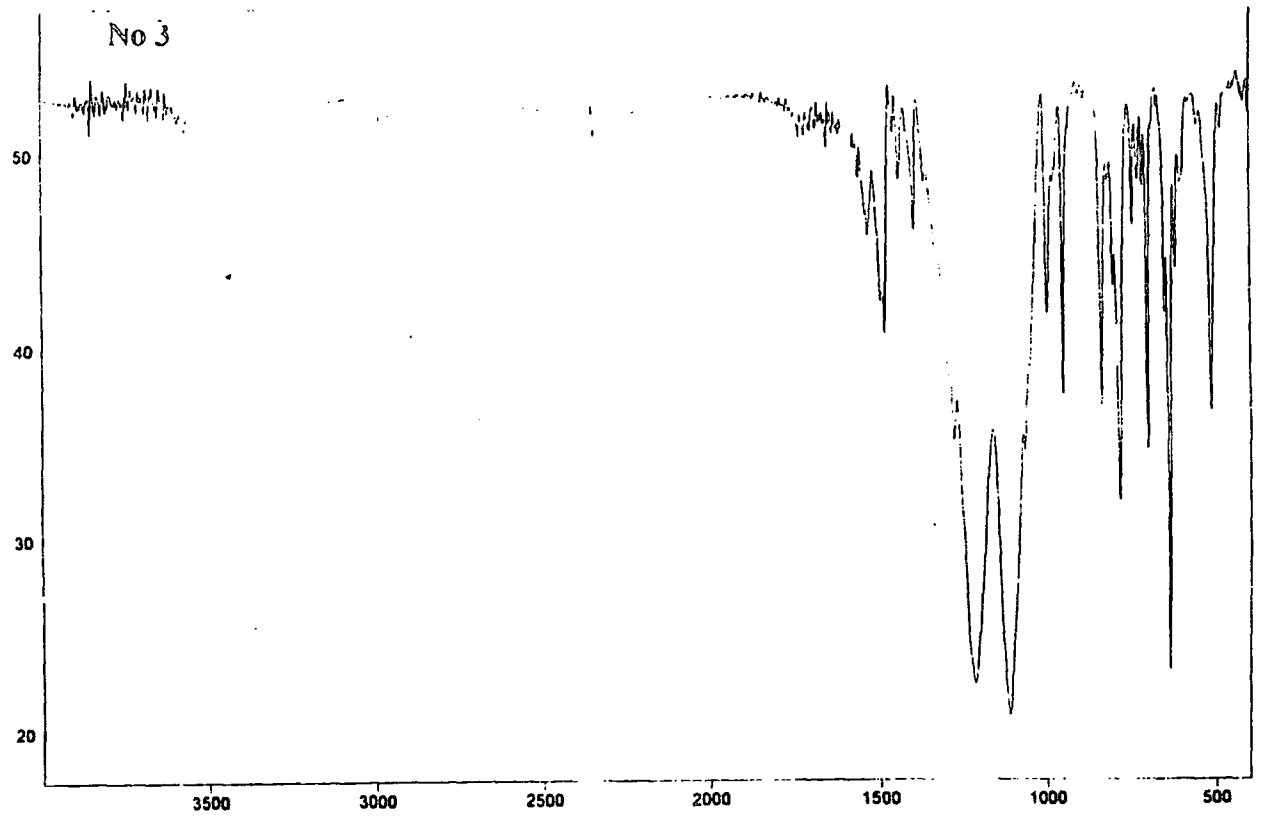
File # 2 : 431

diene

Number of Scans= 4 Apodization= Strong

24/01/95 14:14 Res=4 cm-1

No 3



Transmittance / Wavenumber (cm-1)

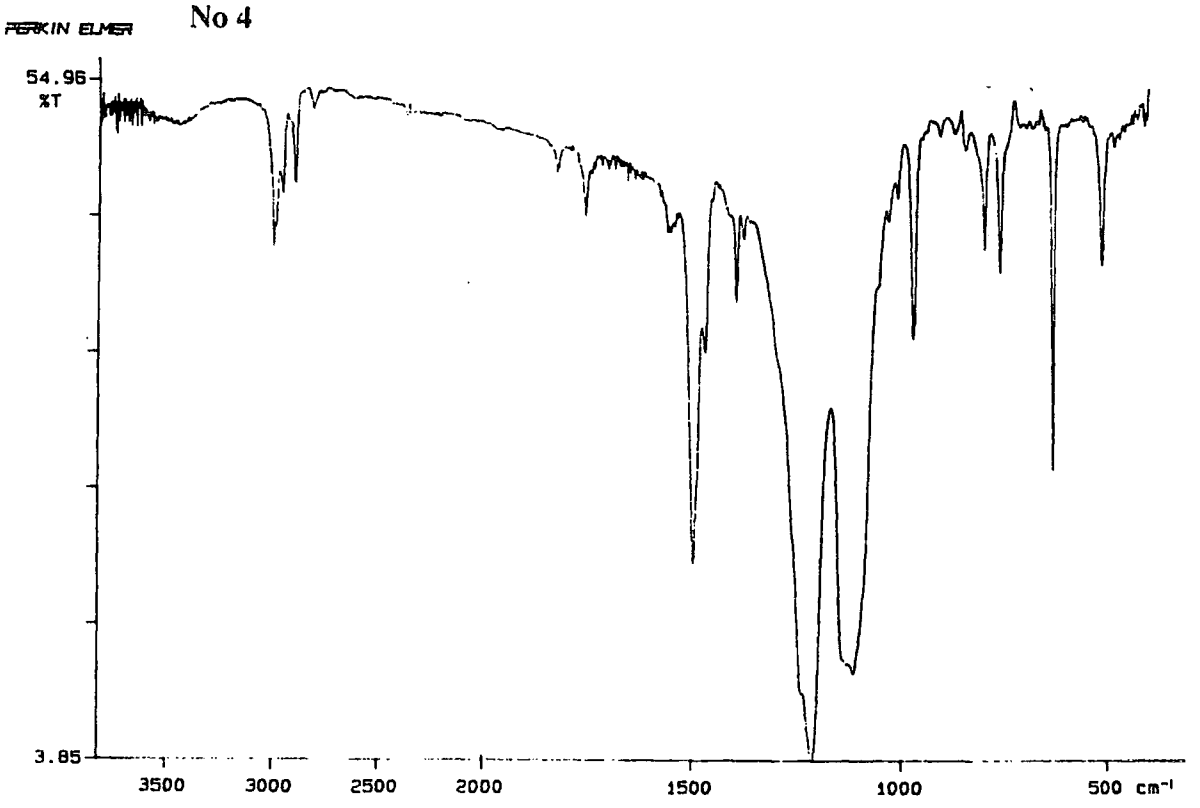
Number of Scans= 4 Apodization= Strong

File # 1 : PC

07/04/95 10:23 Res=4 cm-1

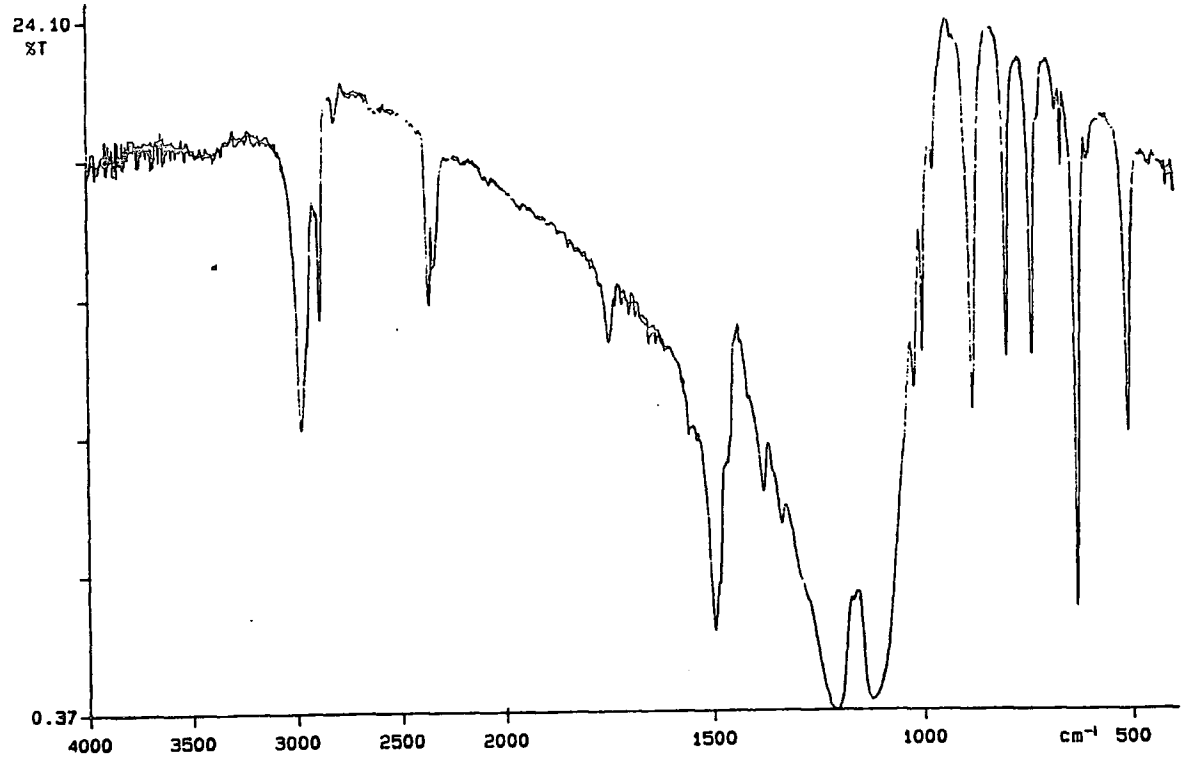
pt -49

No 4



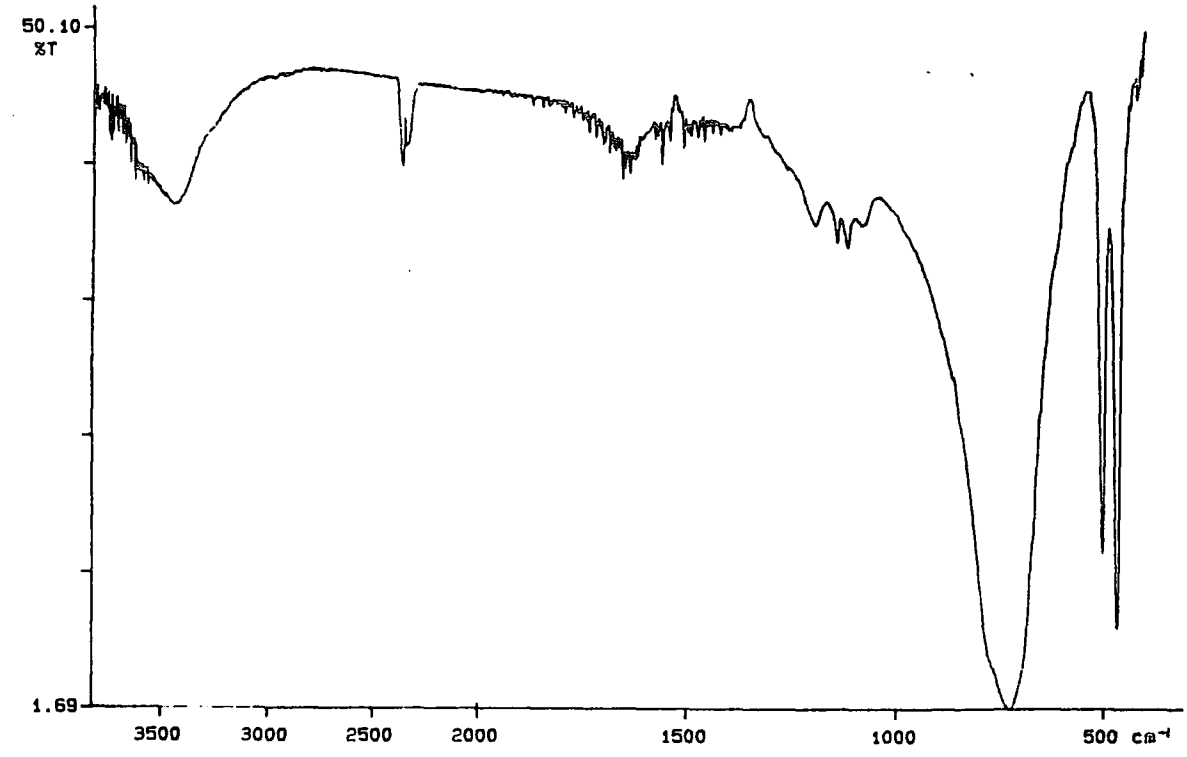
94/11/24 14:24
Y; 1 scan, 4.0cm-1, flat
prop-49

PERKIN ELMER No 5

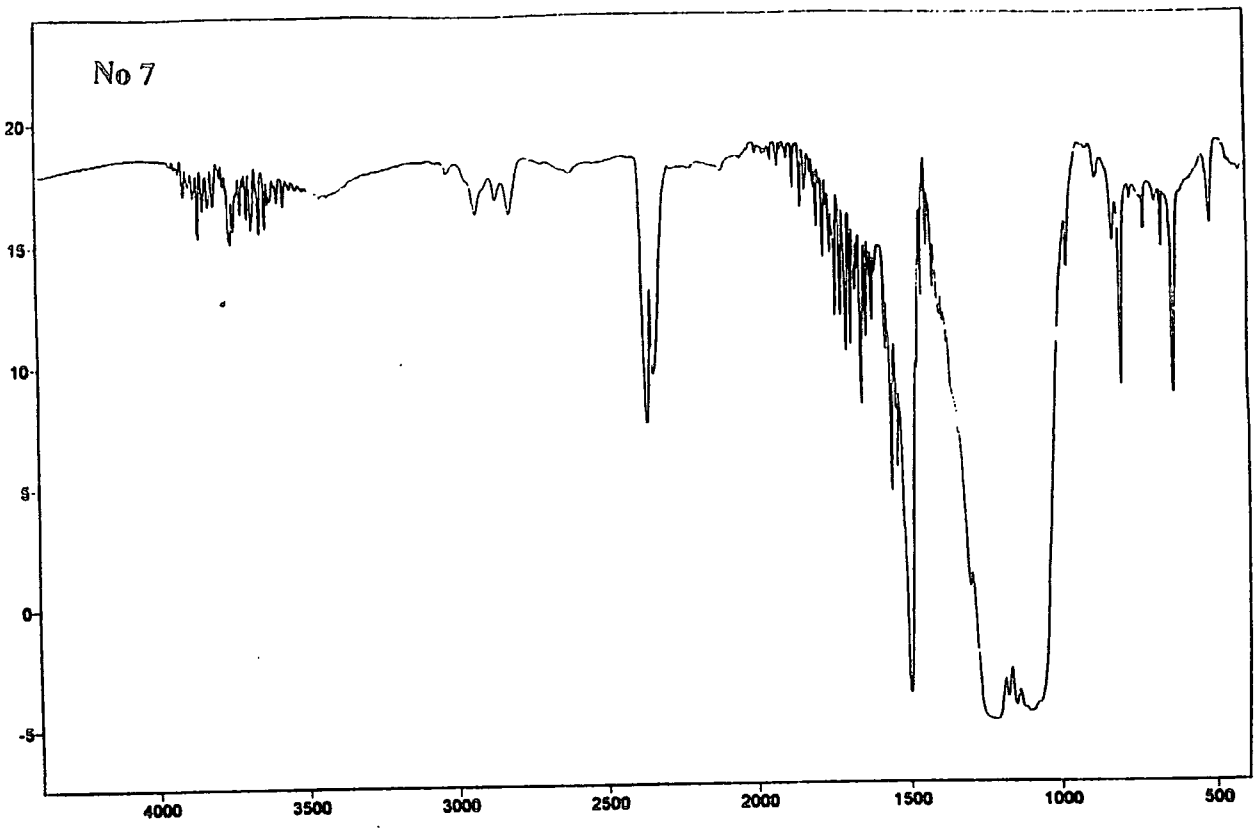


94/11/24 14:10
X: 1 scan, 4.0cm-1, flat, deriv
butyl-49

PERKIN ELMER No 6



94/11/24 14:35
X: 1 scan, 4.0cm-1, flat
Ba salt -49



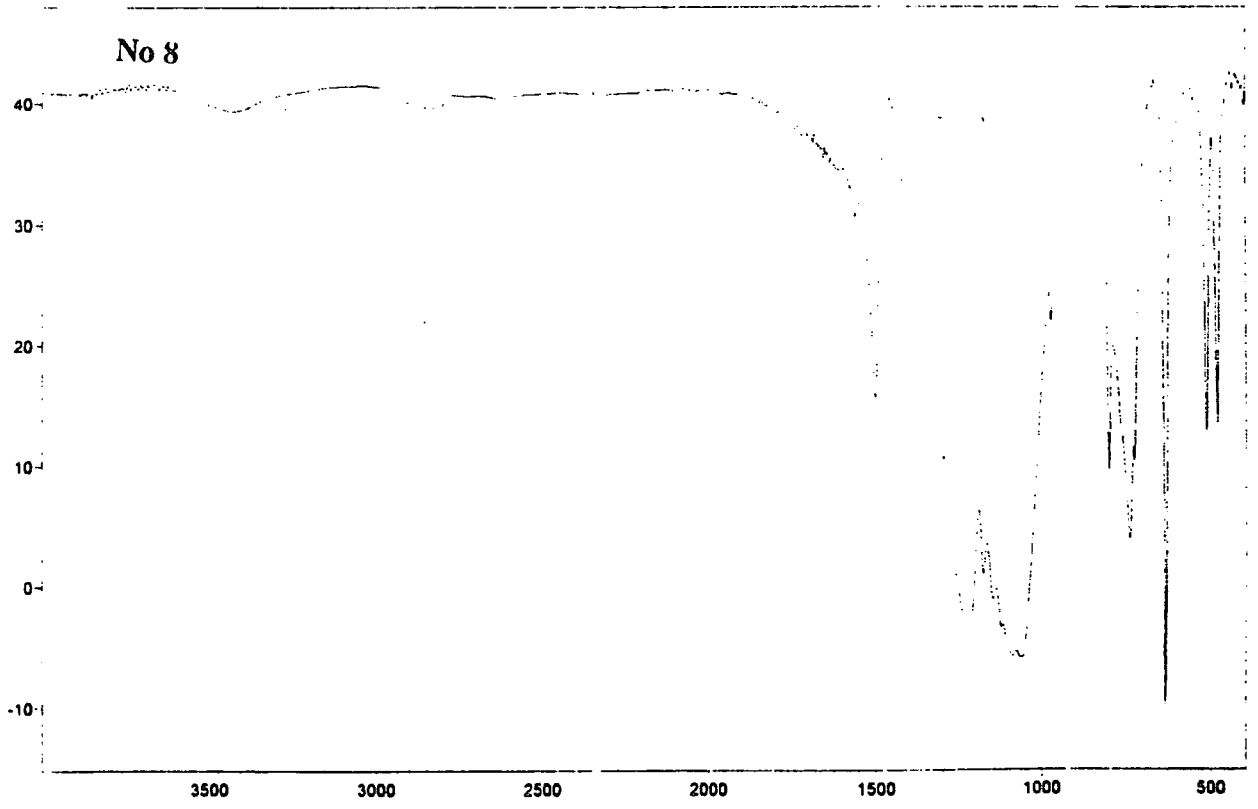
Number of Scans= 4 Apodization= Strong

05/01/95 16:07 Res=4 cm-1

Library Y / Wavenumber (cm-1)

File # 1 : PC

$K^+ \; Cp^{\ominus}$



Transmittance / Wavenumber (cm-1)

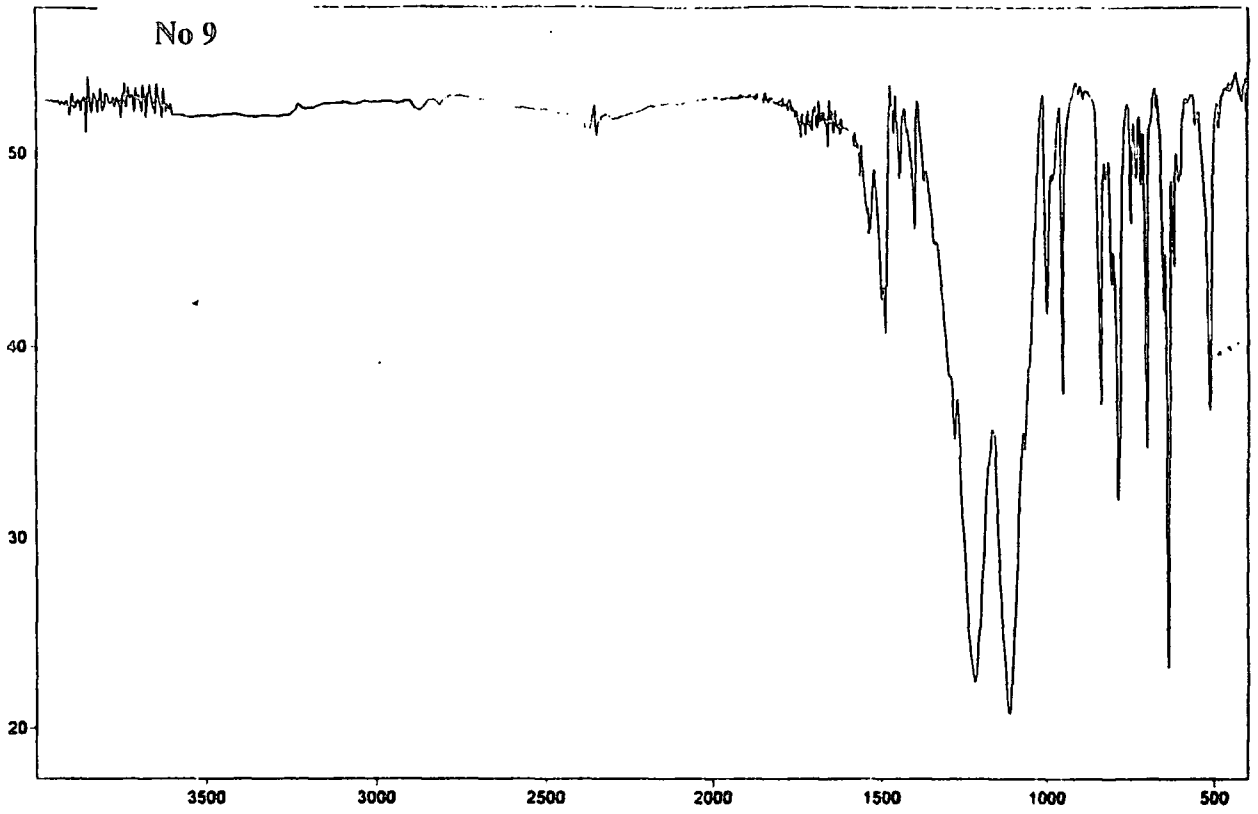
Number of Scans= 4 Apodization= Strong

File # 2 : PC

23/05/95 15:35 Res=4 cm-1

Cs salt

No 9



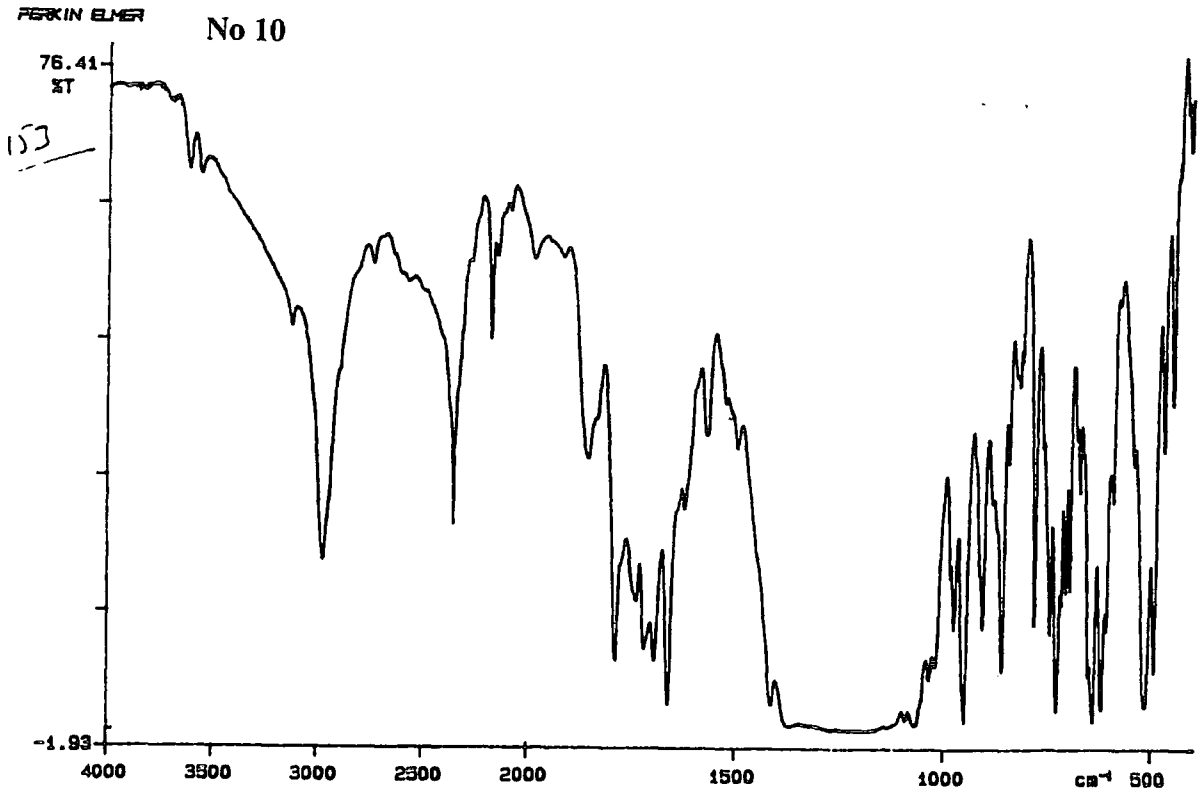
Transmittance / Wavenumber (cm-1)

File # 1 : PC

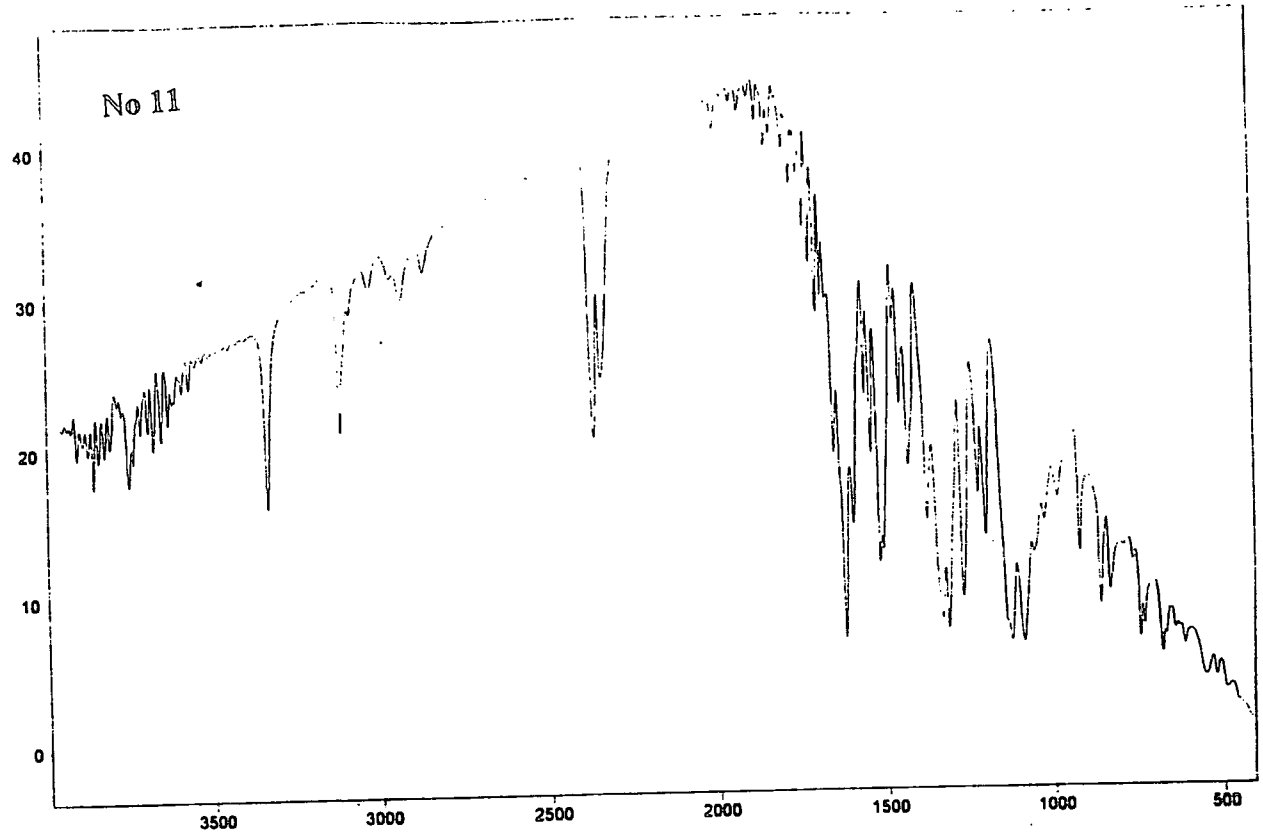
Number of Scans= 4 Apodization= Strong

07/04/95 10:23 Res=4 cm-1

No 10



94/01/28 10:08
X: 4 scans, 4.0cm-1

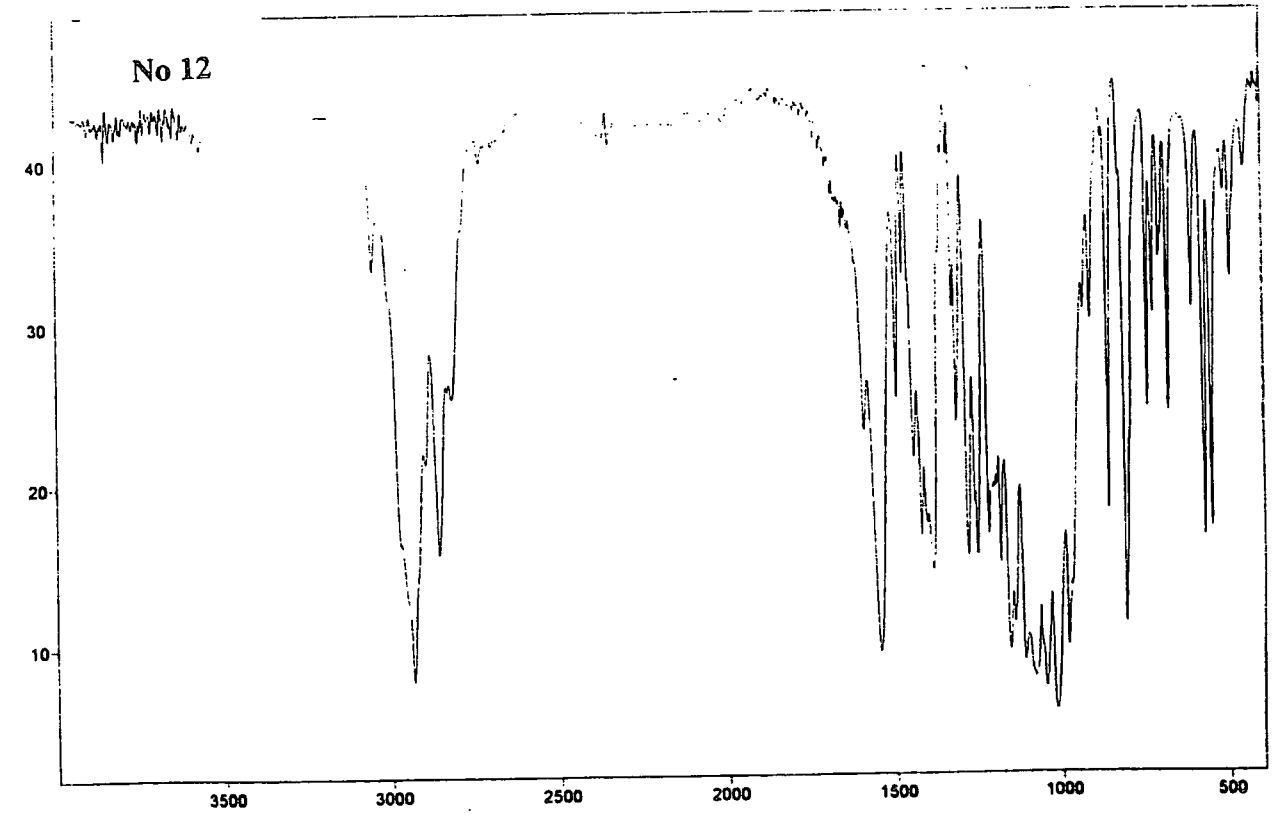


Arbitrary Y / Wavenumber (cm-1)

File # 2 : SMOOTH

Number of Scans= 4 Apodization= Strong

13/12/94 10:31 Res=4 cm-1

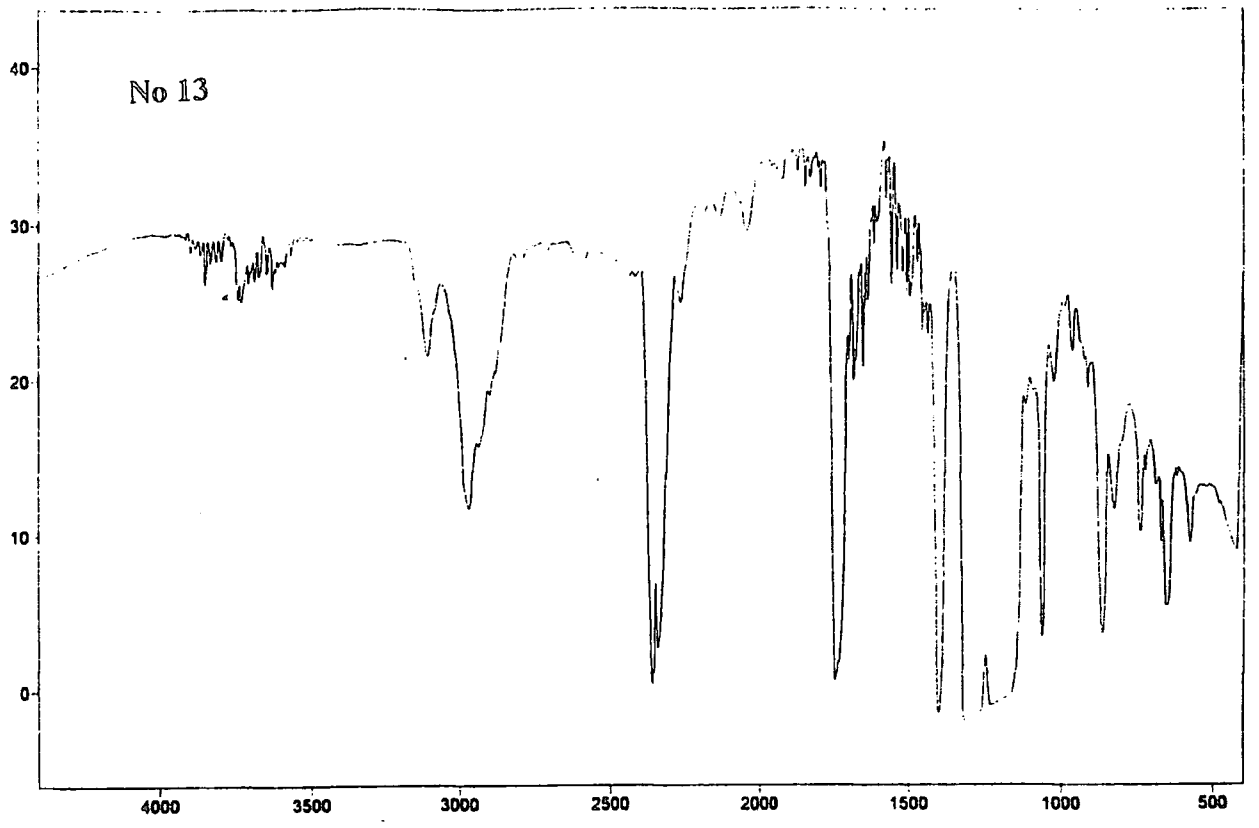


Transmittance / Wavenumber (cm-1)

File # 1 : PC

Number of Scans= 4 Apodization= Stron

12/04/95 14:37 Res=4 cm-



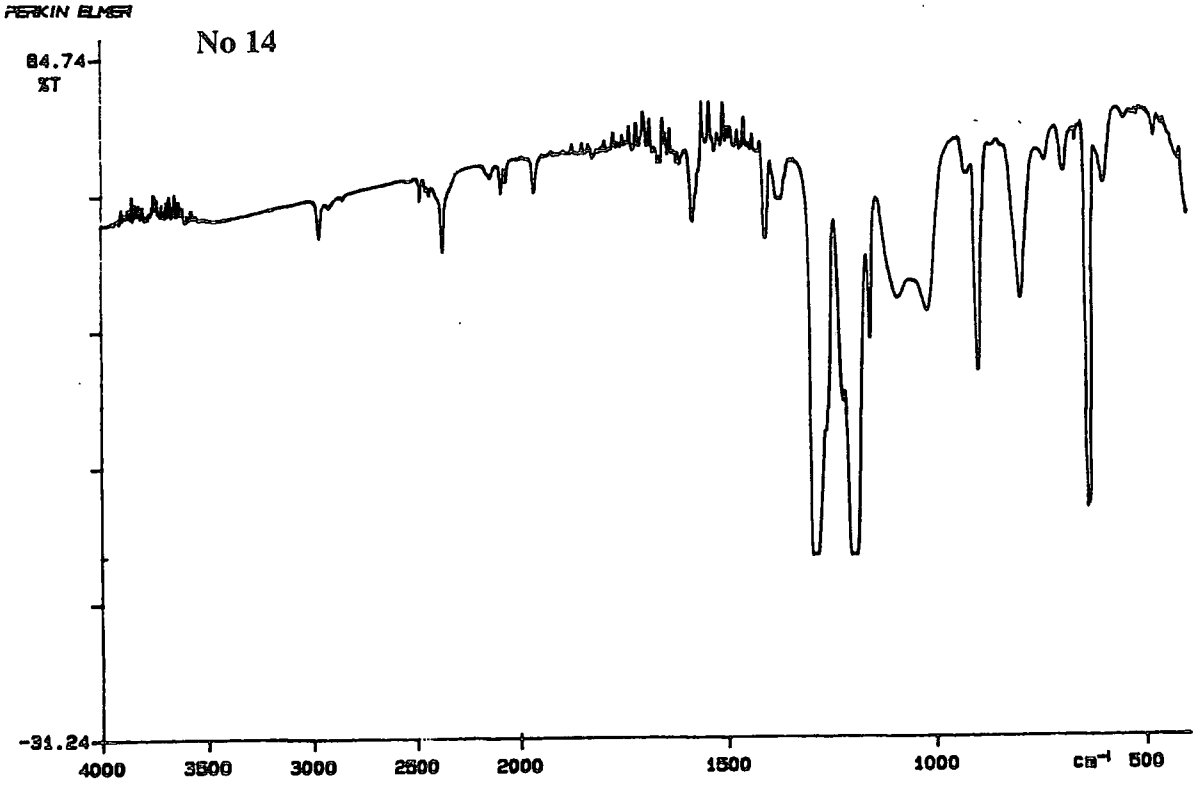
Arbitrary Y / Wavenumber (cm-1)

File # 1 : PC

chlorm cnd

Number of Scans= 4 Apodization= Strong

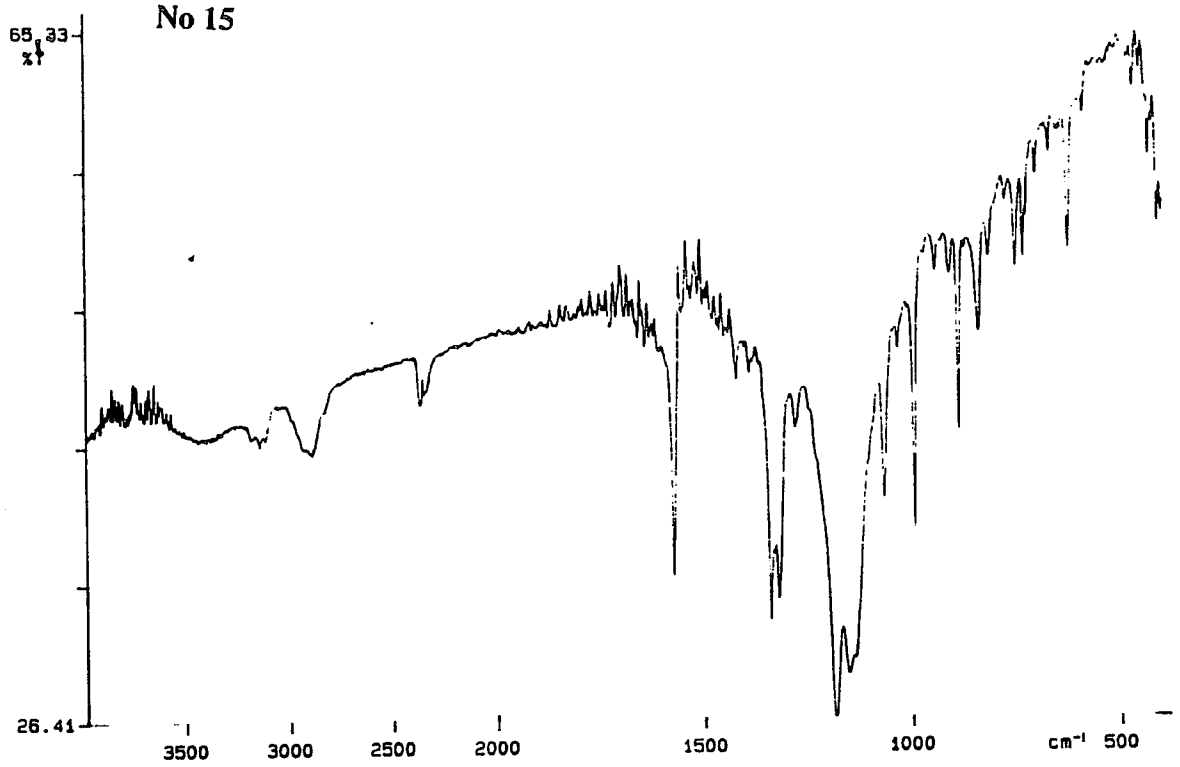
04/01/95 16:00 Res=4 cm-1



94/08/07 17:38
X: 4 scans, 4.0cm-1

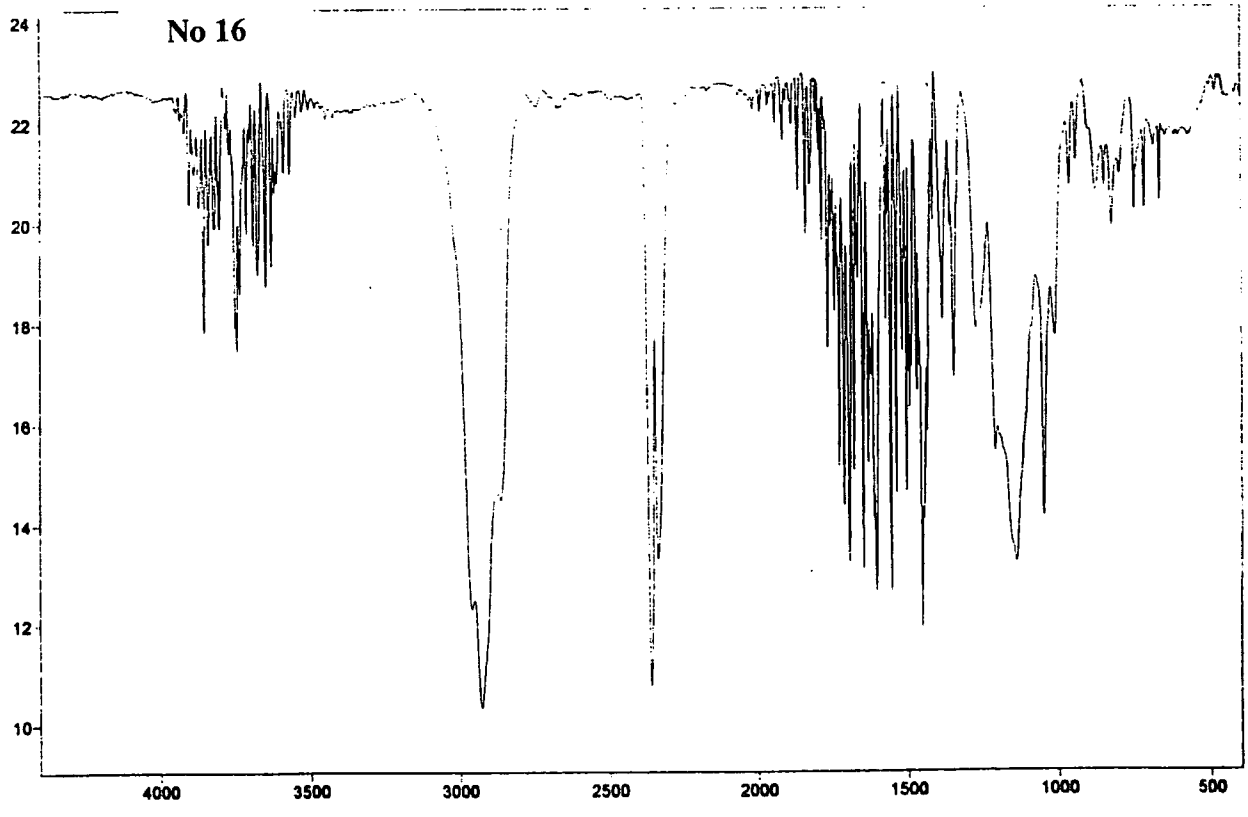
PERKIN ELMER

No 15



94/11/24 09:39
X: 1 scan, 4.0cm-1
bis-cf3-furan

No 16



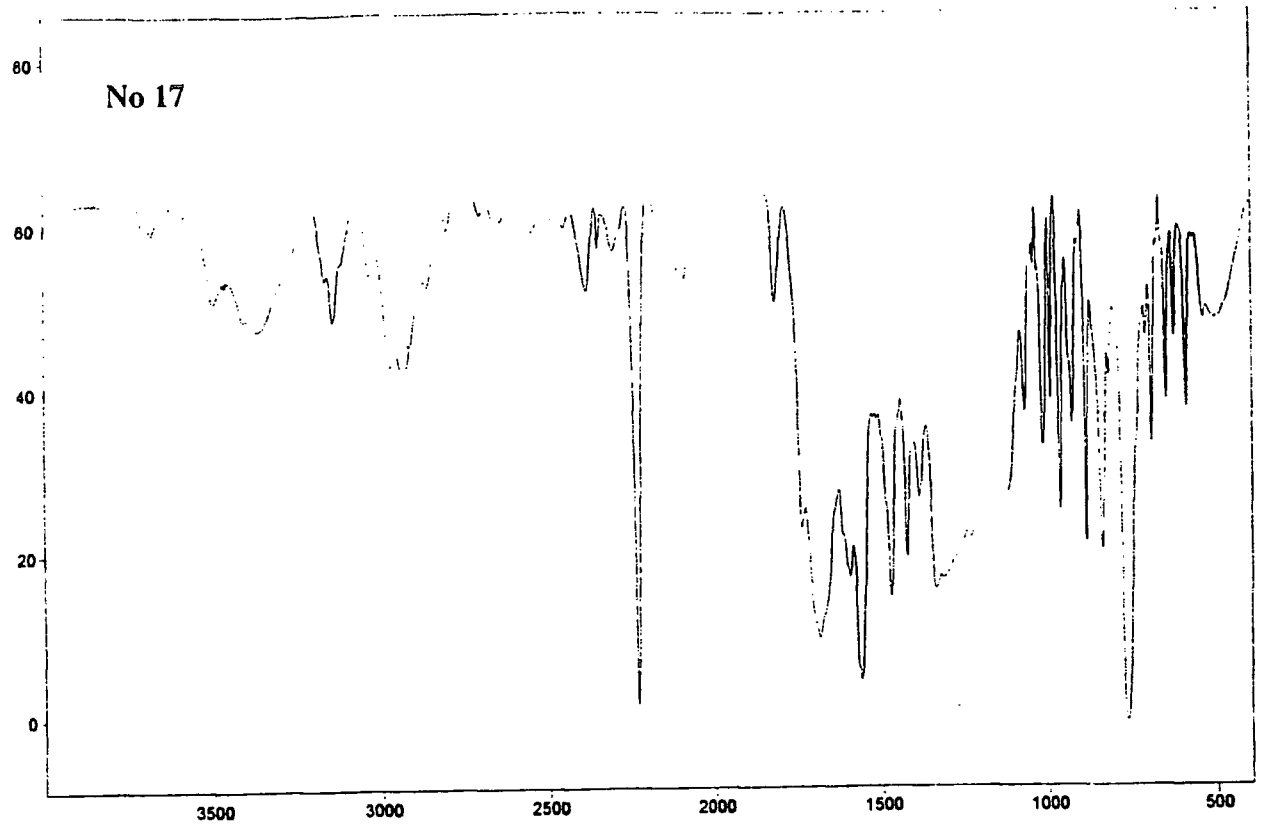
Arbitrary Y / Wavenumber (cm-1)

File # 1 : PC

AR dimethyl furan

Number of Scans= 4 Apodization= Stro:

09/01/95 14:18 Res=4 cm.

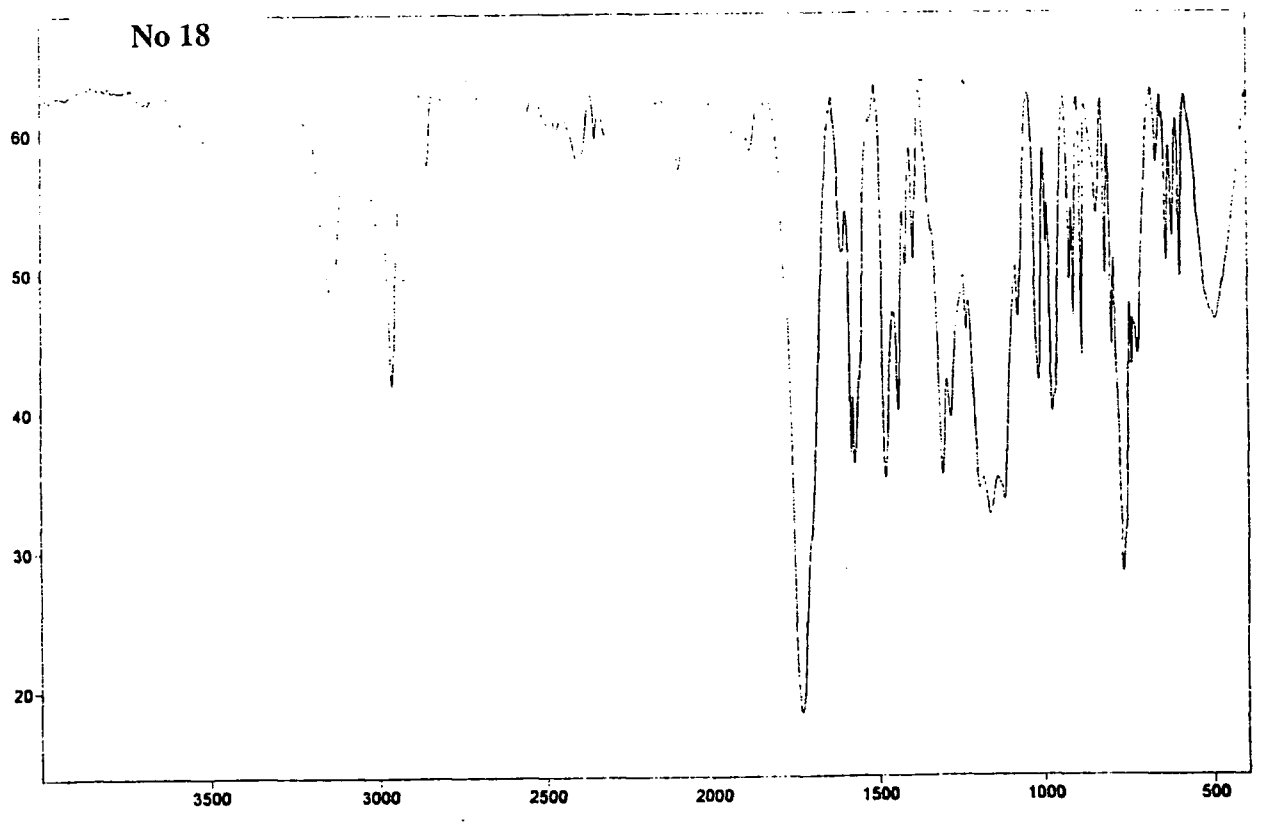


Transmittance / Wavenumber (cm-1)

File # 3 : ALEXCN

Number of Scans= 4 Apodization= Strong

31/01/95 12:23 Res=4 cm-1

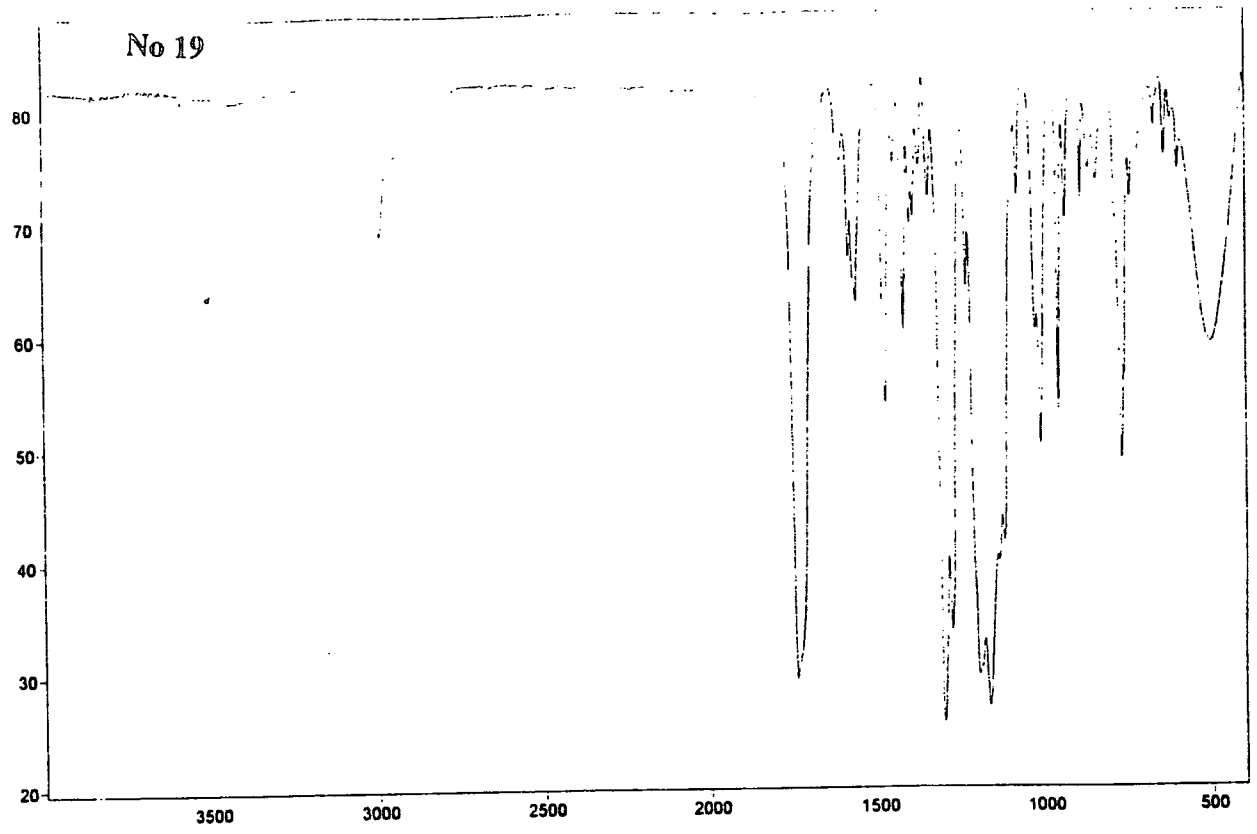


Transmittance / Wavenumber (cm-1)

File # 2 : RJPB9

Number of Scans= 4 Apodization= Strong

10/02/95 14:05 Res=4 cm-1

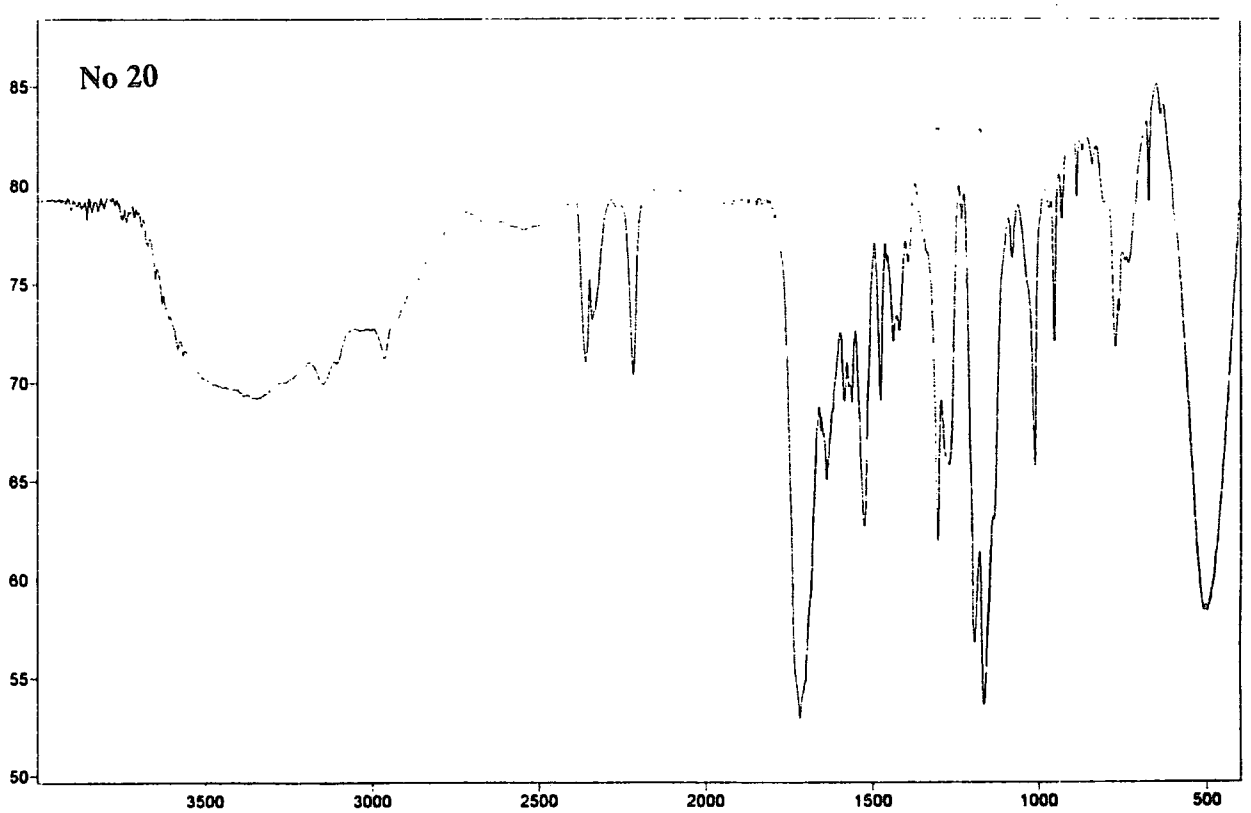


Transmittance / Wavenumber (cm-1)

File # 5 : DC4

Number of Scans= 4 Apodization= Strong

24/02/95 16:26 Res=4 cm-1



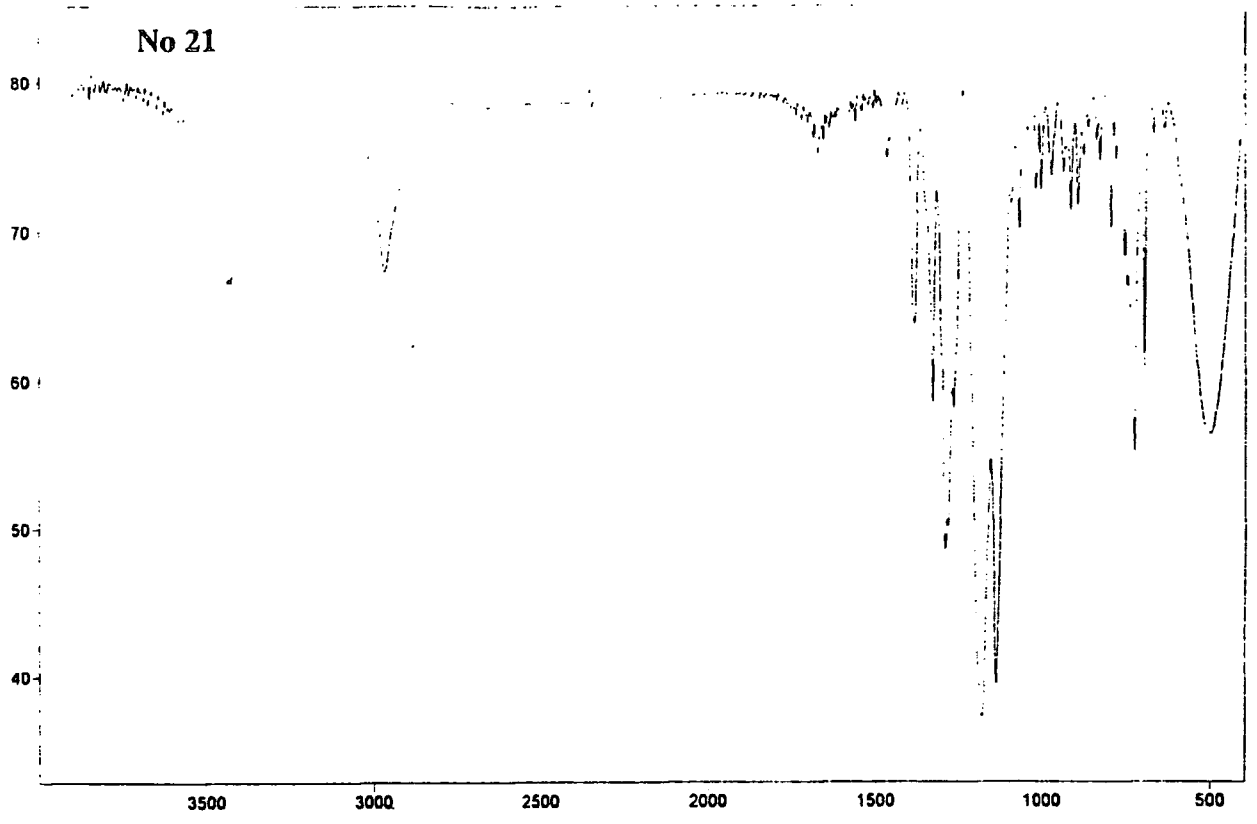
Transmittance / Wavenumber (cm-1)

File # 1 : PC

Number of Scans= 4 Apodization= Strong

27/02/95 16:43 Res=4 cm-1

No 21



Transmittance / Wavenumber (cm-1)

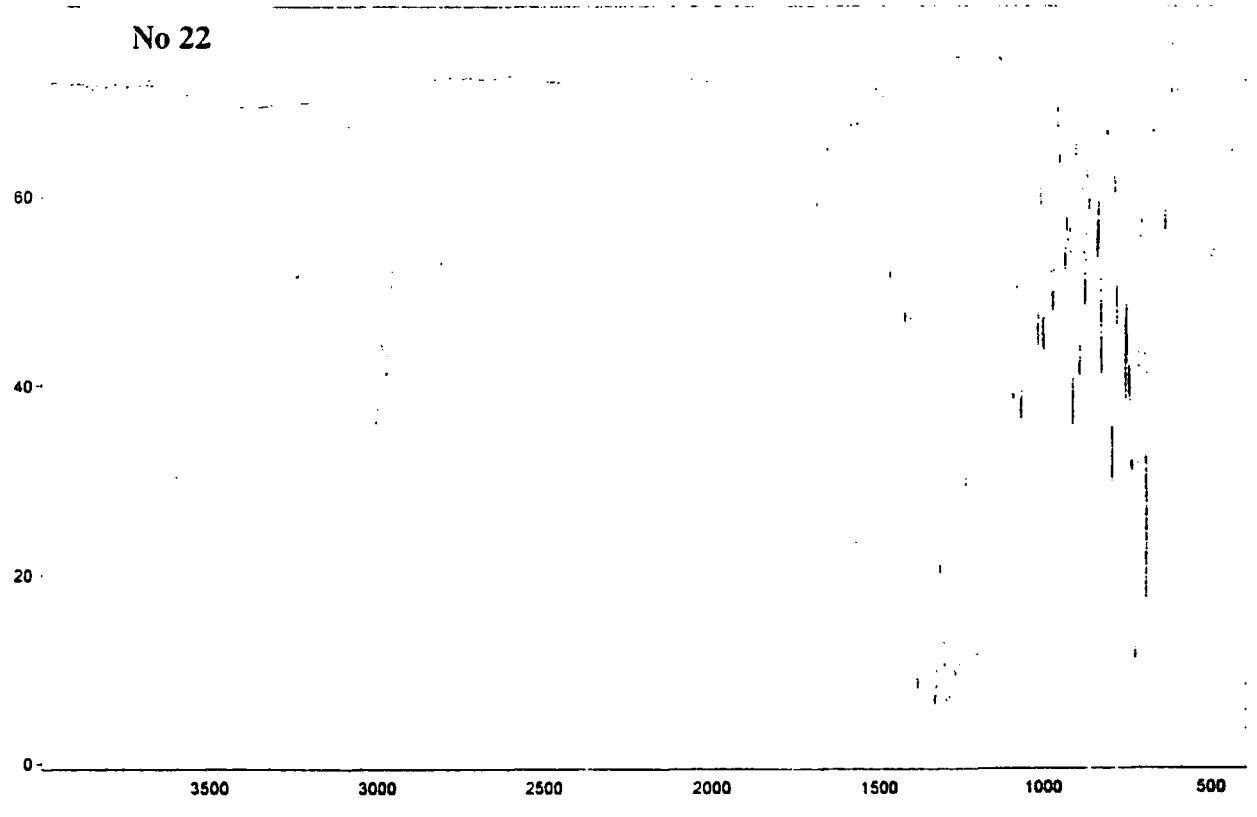
Number of Scans= 4 Apodization= Strong

File # 2 : PC

20/02/95 11:40 Res=4 cm-1

In reaction 2 isomers

No 22



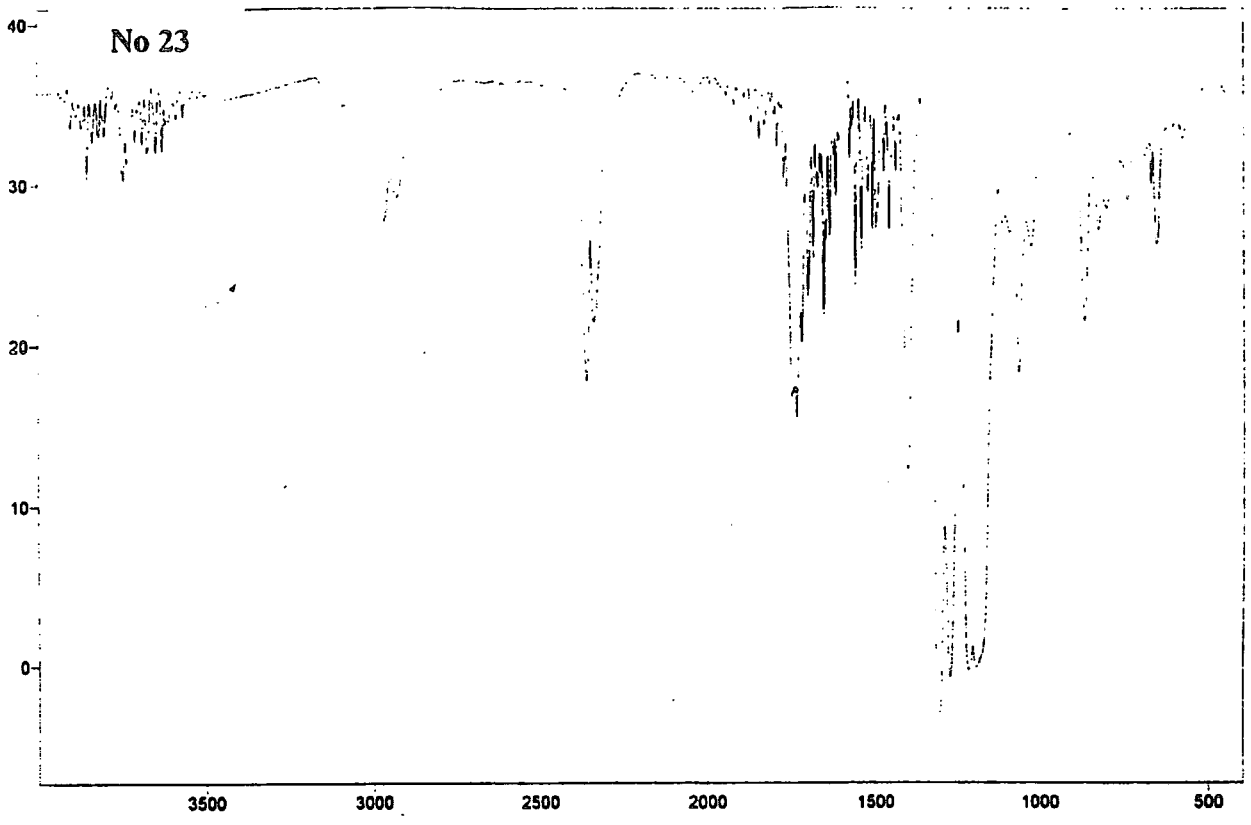
Transmittance / Wavenumber (cm-1)

Number of Scans= 4 Apodization= Strong

File # 1 : RJPD8O

13/03/95 09:20 Res=4 cm-1

P at 300 volts vented

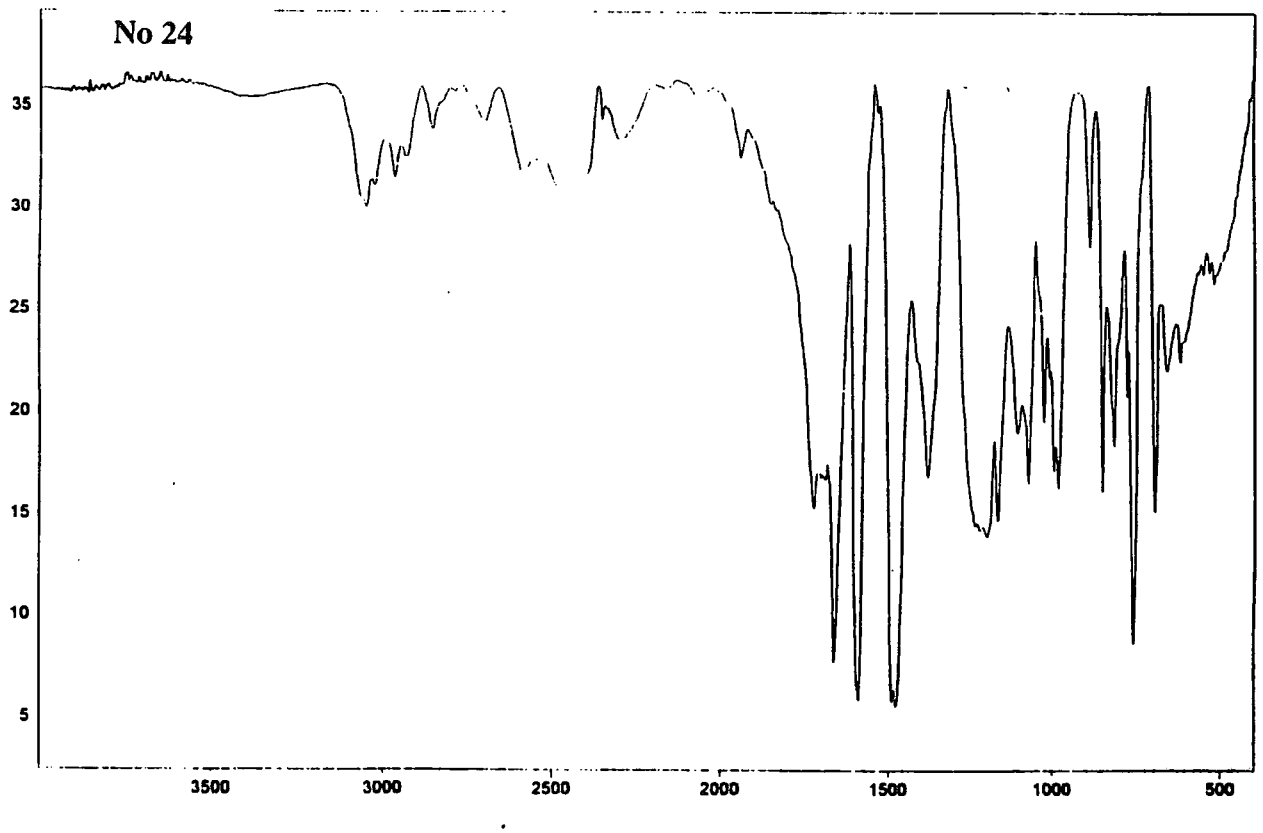


rbitrary Y / Wavenumber (cm-1)

ile # 1 : PC

Number of Scans= 4 Apodization= Strong

10/04/95 10:46 Res=4 cm-1



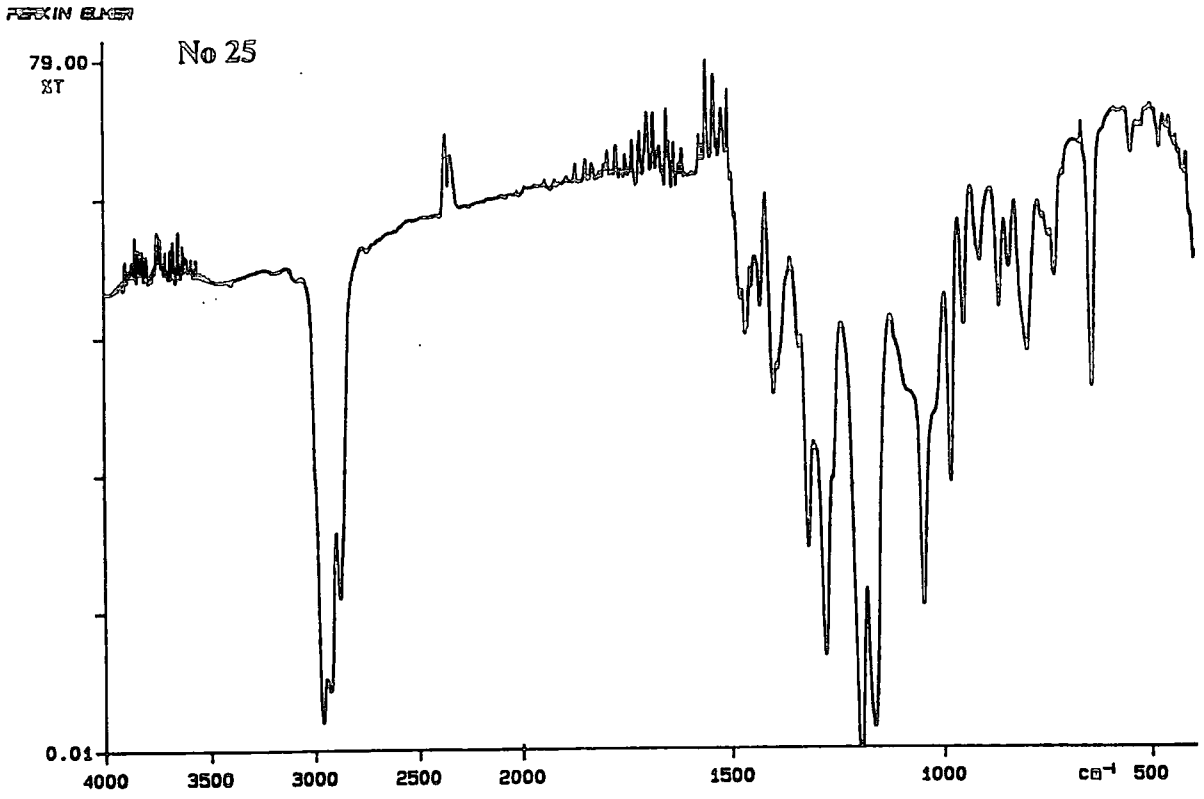
ansmittance / Wavenumber (cm-1)

1 : PC

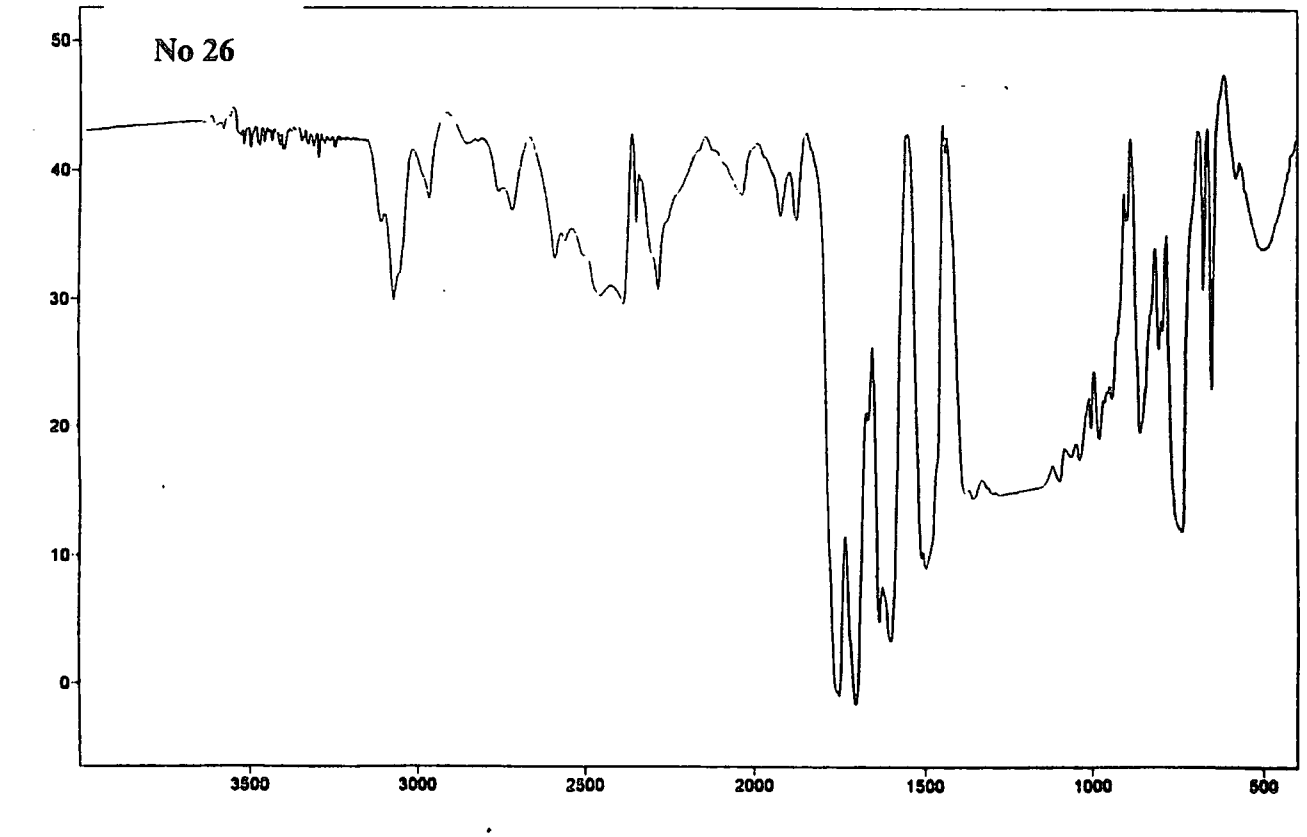
prods

Number of Scans= 4 Apodization= Strong

19/04/95 08:14 Res=4 cm-1



94/06/13 15: 11
X: 4 scans, 4.0cm-1

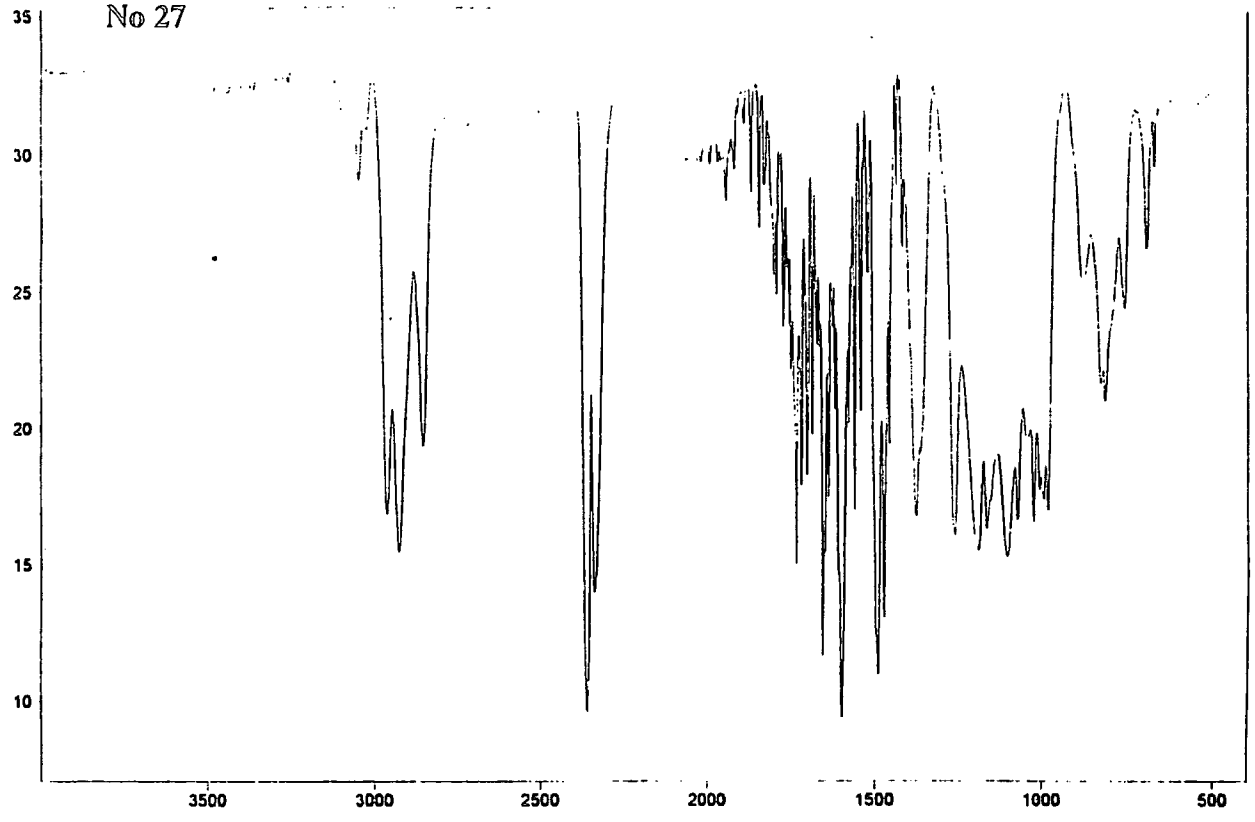


Transmittance / Wavenumber (cm-1)

File @ 1 : PC

Number of Scans= 4 Apodization= Strong

04/05/95 16:43 Res=4 cm-1

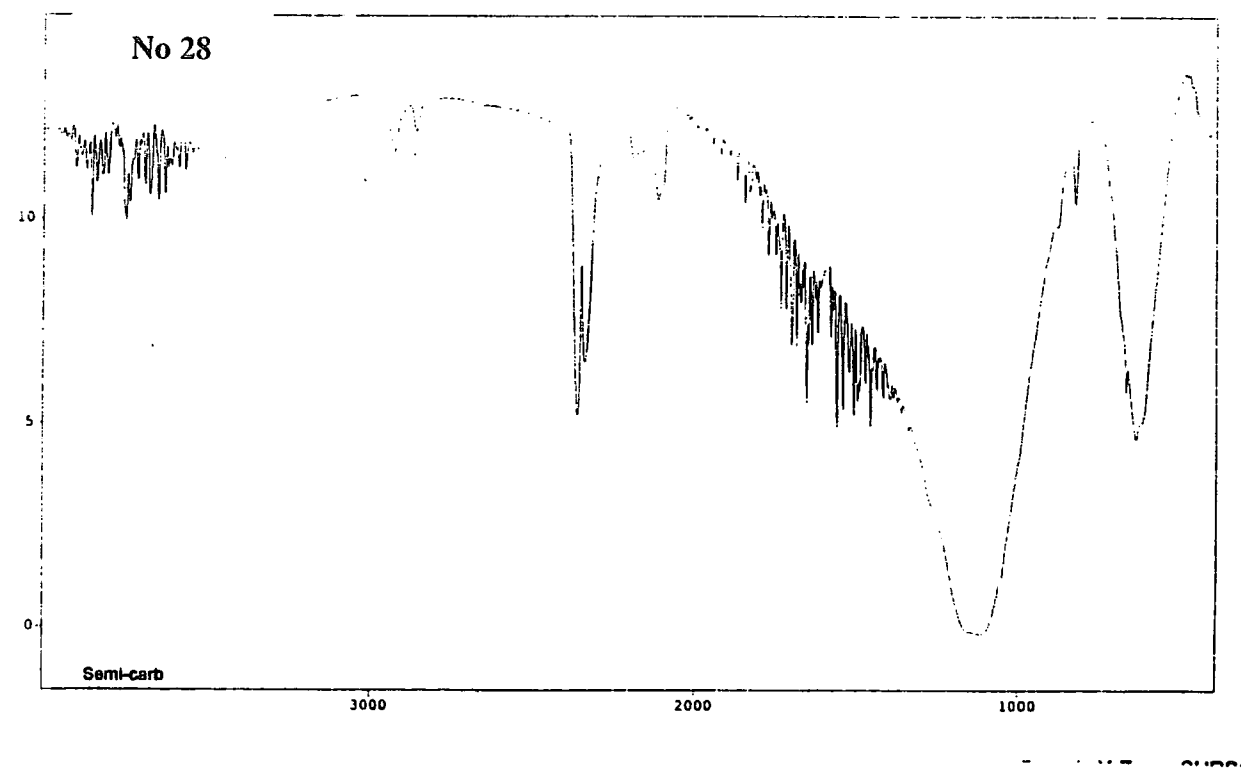


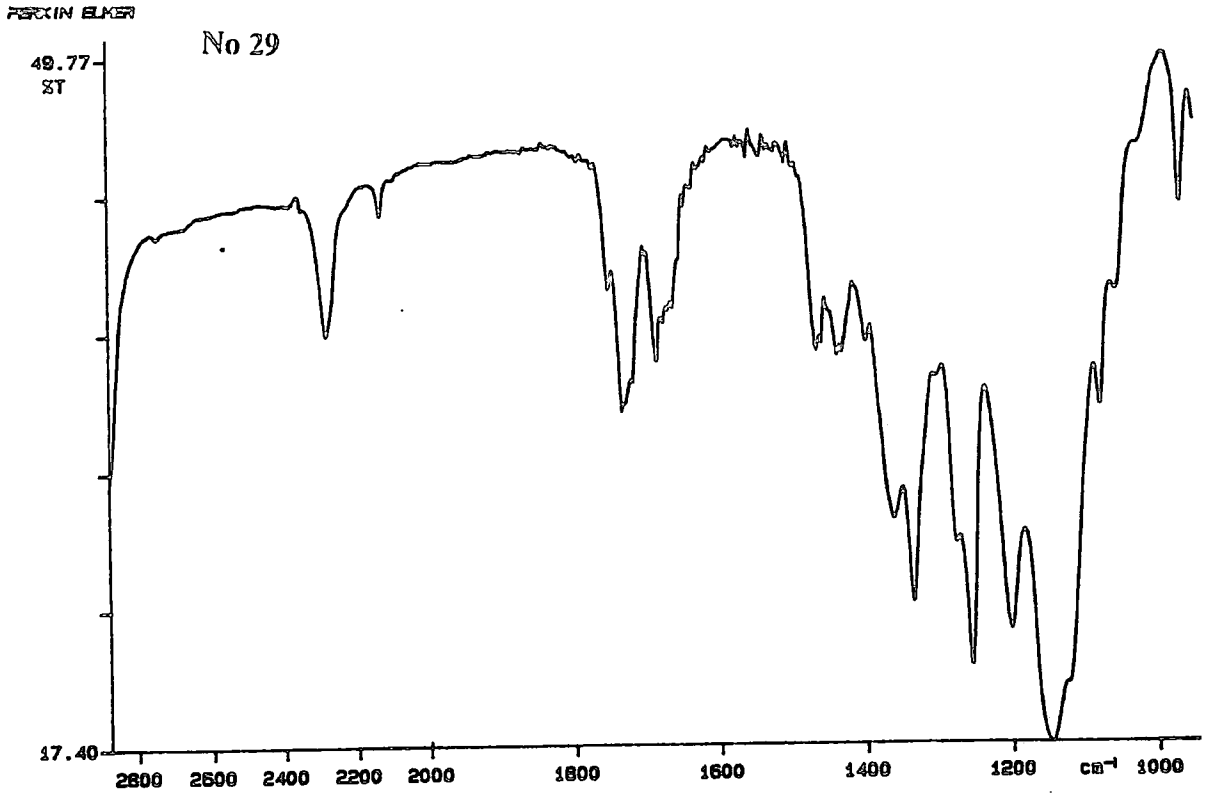
rbitrary Y / Wavenumber (cm-1)

ile # 2 : PC

Number of Scans= 4 Apodization= Strong

01/05/95 10:59 Res=4 cm-1





94/06/02 16:57
X: 4 scans, 4.0cm-1

Appendix Three
Mass Spectrometry Data

No.1	2*H*-Heptafluorobut-2-ene (8)
No. 2	7*H*-perfluoro-Z,E,E-3,4,5,6-tetramethylocta-2,4,6-triene (32)
No. 3	5*H*-perfluoro-3,4-bis(trifluoromethyl)hexa-2,4-dienes (31)
No. 4	Potassium pentakis(trifluoromethyl)cyclopentadienide (33a)
No. 5	Tetraethylammonium pentakis(trifluoromethyl) cyclopentadienide (33d)
No. 6	Tetrapropylammonium pentakis(trifluoromethyl)cyclopentadienide (33e)
No. 7	Tetrabutylammoniumpentakis(trifluoromethyl)cyclopentadienide(33f)
No. 8	Barium pentakis(trifluoromethyl)cyclopentadienide(33g)
No. 9	Caesium pentakis(trifluoromethyl)cyclopentadienide (33b)
No. 10	Thallium pentakis(trifluoromethyl)cyclopentadienide (33h)
No. 11	5*H*-pentakis(trifluoromethyl)cyclopenta-1,3-diene (34)
No. 12	Perfluoro-1,2,3,4,5-pentamethylcyclopenta-2,4-diene (34),
No. 13	Caesium perfluoro1,2,3-trihydro-4,5,6-trimethylpentalenide (37)
No. 14	Caesium perfluoro-1-methyl-2,3,4,5,6,7-hexahydrodicyclopenta[b,d]cyclopentadienide (38)
No. 15	5*H*-Perfluoro-1,2,3-trihydro-4,5,6-trimethylpentalena-4,6-diene (39)
No. 16	1*H*-Perfluoro-1-methyl-2,3,4,5,6,7-hexahydrodicyclopenta[b,d]cyclopenta-8,9-diene (40)
No. 17	1,1,1-Trifluoroacetone (43)
No. 18	2,4 Dinitrophenylhydrazone of 1,1,1-trifluoroacetone
No. 19	1,9-diazabicyclo[5.4.0]undecano-a,b-2-difluoromethyl-3-trifluoromethylpyrrole (48)
No. 20	(Z)-2-Chloro-1,1,1,4,4,4-hexafluorobut-2-ene (46)
No. 21	(Z)-2-Bromo-1,1,1,4,4,4-hexafluorobut-2-ene (47)
No. 22	Hexafluorobut-2-yne (3)
No. 23	(Z)-2-^{t}Butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (45)
No. 24	3,4-bis(trifluoromethyl)furan (51)
No. 25	2,3-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene (49)
No. 26	*exo*-5-fluoro-5,6-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2-ene (62)
No. 27	*endo*-5-fluoro-5,6-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2-ene (63)
No. 28	2,5-dimethyl-3,4-bis(trifluoromethyl)furan (67)
No. 29	3,4-bis(trifluoromethyl)-2-furonitrile (68)
No. 30	methyl-3,4-bis(trifluoromethyl)furan-2-oate (70)

No. 31 ethyl-3,4-bis(trifluoromethyl)furan-2-oate (**71**)

No. 32 3,4-bis(trifluoromethyl)-2-furoic acid (**69**)

No. 33 3,4-bis(trifluoromethyl)-2-furancarbaldehyde (**73**)

No. 34 *Exo*-5-fluoro-5,6-bis(trifluoromethyl)-7-bicyclo[2.2.1]hept-2-ene (**64**)

No. 35 *Endo*-5-fluoro-5,6-bis(trifluoromethyl)-7-bicyclo[2.2.1]hept-2-ene (**65**)

No. 36 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (**66**)

No. 37 bis(trifluoromethyl)cyclopentadiene (**72a-c**)

No. 38 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**74**)

No. 39 (*Z*)-2-methoxy 1,1,1,4,4,4 hexafluorobut-2-ene (**78**)

No. 40 (*Z*) -2-phenoxy-1,1,1,4,4,4-hexafluorobut-2-ene (**90**)

No. 41 (*E*)-2-phenoxy-1,1,1,4,4,4-hexafluorobut-2-ene (**91**)

No. 42 2-trifluoromethyl-2-(1,1,1-trifluoroethyl)-1,3-dioxole (**76**)

No. 43 trifluoromethyl-2-(1,1,1-trifluoroethyl)-1,3-benzodioxole (**96**)

No. 44 *p*-phenylenedioxy-2-2'-bis-(Z-1,1,1,4,4,4-hexafluorobut-2-ene) (**93**)

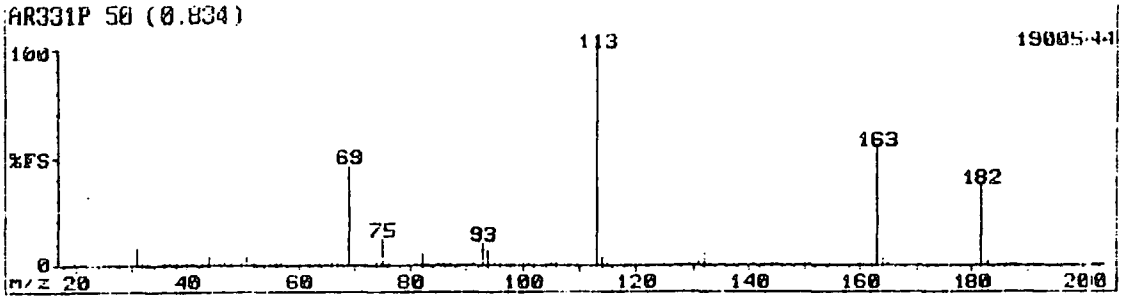
No. 45 2-amino-1,1,1,4,4,4-hexafluorobut-2-ene (**88**)

No. 46 1,1,1,4,4,4-hexafluorobutan-2-one (**44**)

No. 47 2-^{n}Butylimino-1,1,1,4,4,4-hexafluorobutane (**97**)

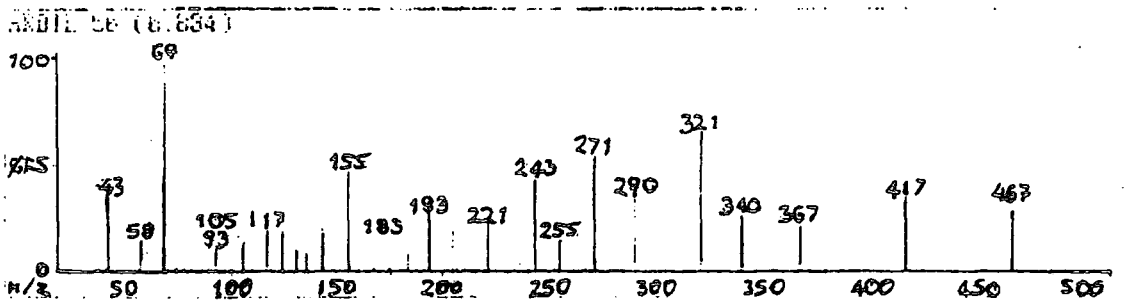
No. 48 1,1,1,4,4,4 hexfluorobutan-2-one semicarbazone

Spectrum 1



AR331P 50 (0.834)																							139544
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	Mass	Rel Int		
20	0.02	33	0.12	47	0.03	64	0.11	81	0.18	96	0.02	119	0.15	145	0.26	183	1.60						
22	0.01	35	0.18	48	0.05	65	0.03	82	5.58	100	0.74	124	0.44	150	0.05	200	0.06						
24	0.07	37	0.28	50	2.28	66	0.02	83	0.16	101	1.37	125	0.03	151	0.02								
25	0.19	38	0.01	51	4.31	67	0.01	85	1.29	102	0.04	129	0.02	160	0.02								
26	0.02	40	0.03	52	0.05	69	46.12	86	0.14	104	0.03	131	1.72	162	0.08								
27	0.01	41	0.04	55	1.19	70	0.62	87	0.07	105	0.09	132	5.07	163	54.99								
28	0.93	43	0.33	56	1.35	72	0.45	91	0.04	106	0.05	133	0.21	164	2.49								
29	0.03	44	4.65	57	0.05	74	2.25	93	10.34	113	100.00	141	0.01	165	0.07								
31	7.97	45	0.11	62	0.33	75	12.38	94	6.41	114	3.59	143	0.55	181	0.53								
32	0.78	46	0.01	63	1.23	76	0.45	95	0.49	115	0.09	144	1.21	182	35.64								

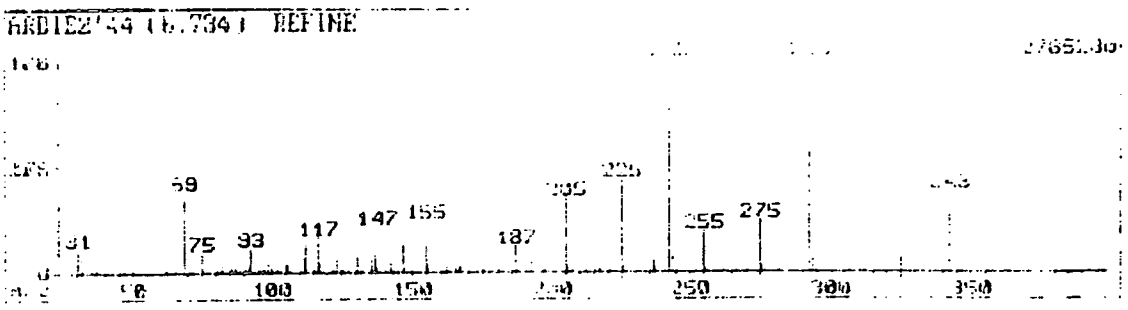
Spectrum 2



No 2

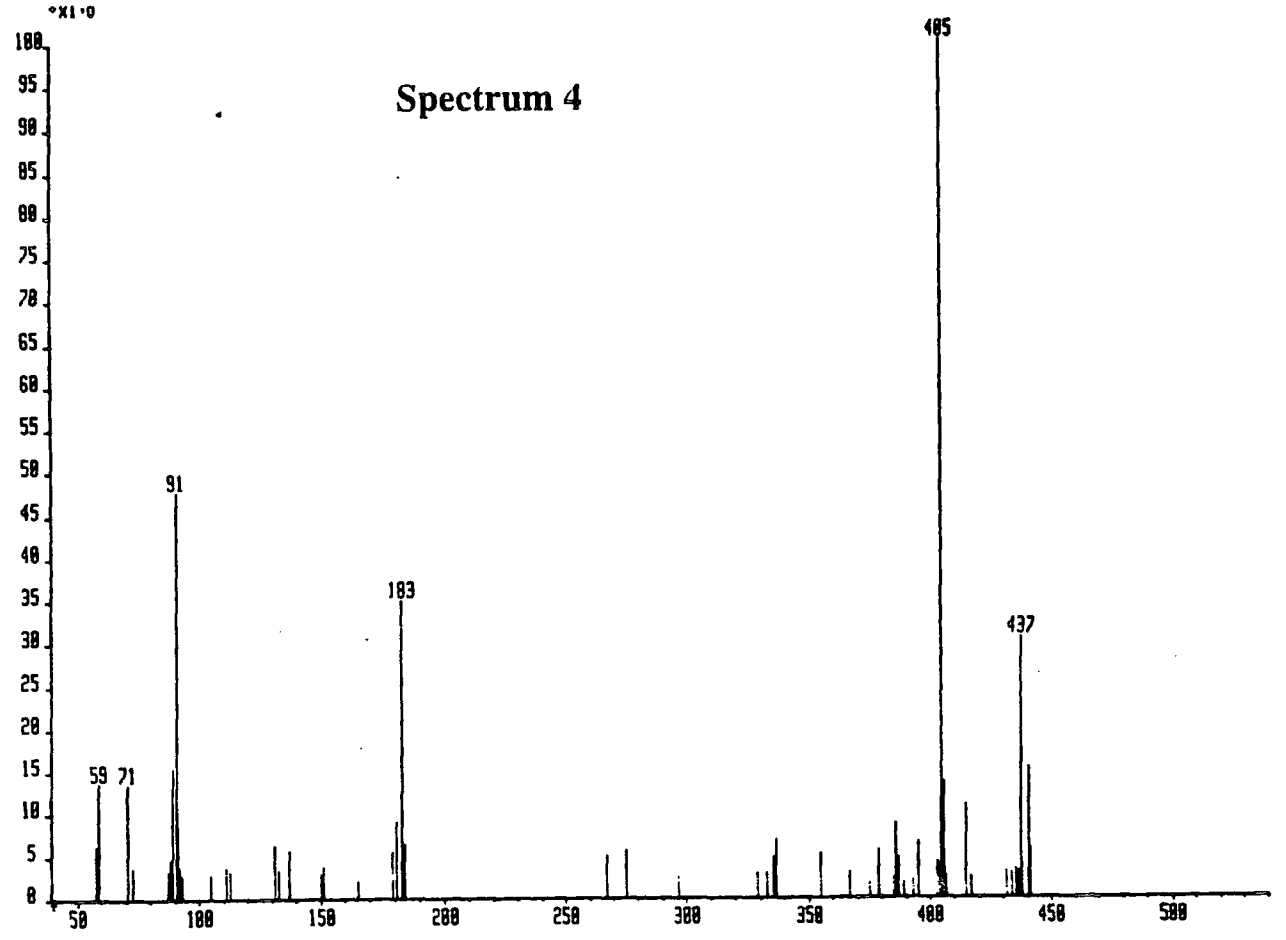
Mass	Rel. Int.
43	36.87
58	15.44
69	100.00
93	11.75
105	12.44
117	20.62
155	47.47
183	9.79
193	26.96
221	22.00
243	44.24
255	16.01
271	55.30
290	36.87
321	65.90
340	26.84
367	23.39
417	34.56
467	32.72

Spectrum 3



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
39	4.41	95	0.14	150	0.43	205	0.71
41	12.06	96	0.11	155	11.82	207	0.09
42	6.51	97	1.20	156	1.66	209	0.01
43	0.58	98	3.53	157	0.10	221	0.01
44	0.02	99	4.08	161	0.33	235	0.01
45	0.09	100	2.72	163	1.46	237	0.12
46	0.12	101	0.16	164	0.31	239	0.67
47	0.28	102	0.23	166	0.11	249	0.07
48	0.02	103	0.16	167	0.50	251	0.02
41	0.04	104	0.35	186	0.90	267	100.00
43	0.13	105	4.04	169	0.45	269	0.01
45	0.37	106	3.42	170	0.02	281	0.25
47	0.50	107	0.15	174	0.79	283	0.01
50	3.64	110	0.81	175	0.20	285	10.97
51	1.76	111	7.46	176	0.19	286	0.01
50	0.09	112	6.69	179	0.26	287	0.01
51	0.34	113	13.68	181	5.46	299	0.01
53	0.91	114	1.26	182	0.25	301	0.09
54	0.91	115	0.06	185	0.68	307	0.01
56	0.09	116	1.04	187	12.50	311	0.01
57	37.65	117	16.19	188	0.97	317	0.01
58	1.40	118	3.79	189	0.08	329	0.01
59	0.36	119	2.63	191	0.01	347	0.01
61	0.04	120	0.08	193	1.11	365	0.01
62	2.72	122	0.03	194	0.35	377	0.04
63	9.34	123	0.61	195	0.05	393	100.00
65	0.33	124	5.95	199	0.54	395	0.01
66	0.61	125	1.17	199	0.31	399	0.01
67	0.81	126	0.05	199	0.01	309	0.01
69	1.21	128	0.46	200	0.12	307	0.01
70	0.83	130	0.72	205	34.71	209	0.01
71	1.18	131	7.57	206	4.87	211	0.01
73	3.79	132	0.50	207	0.15	217	0.01
75	0.17	133	0.03	208	0.02	225	0.01
77	0.21	136	5.40	213	0.60	241	10.00
78	2.25	137	10.15	217	0.23	243	0.01
79	2.38	139	1.65	219	0.01	245	0.01
81	0.13	141	0.07	225	0.03	265	0.01
83	0.07	142	0.19	227	0.01	271	0.01
85	0.28	144	0.31	229	0.01	283	0.01
87	2.10	145	0.61	233	0.01	285	0.01
89	2.68	147	10.14	235	0.12	287	0.01
91	11.76	148	1.01	241	0.01	289	0.01
93	0.69	149	4.52	245	0.07	291	0.01

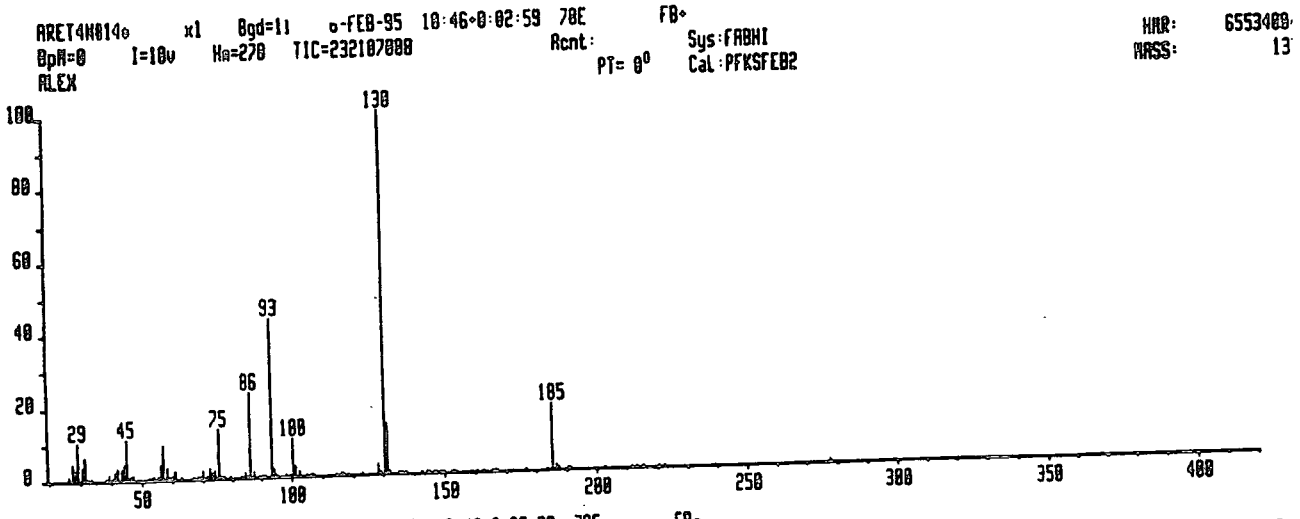
ARK#9 x1 Bgd=6 22-NOV-94 16:08+0:02:05 70E FB-
BpM=0 I=574mv Hm=441 TIC=20177000 Acnt: Sys:FABHI
ALEX PT= 0° Cal:PFKS18NOV
°x1·0

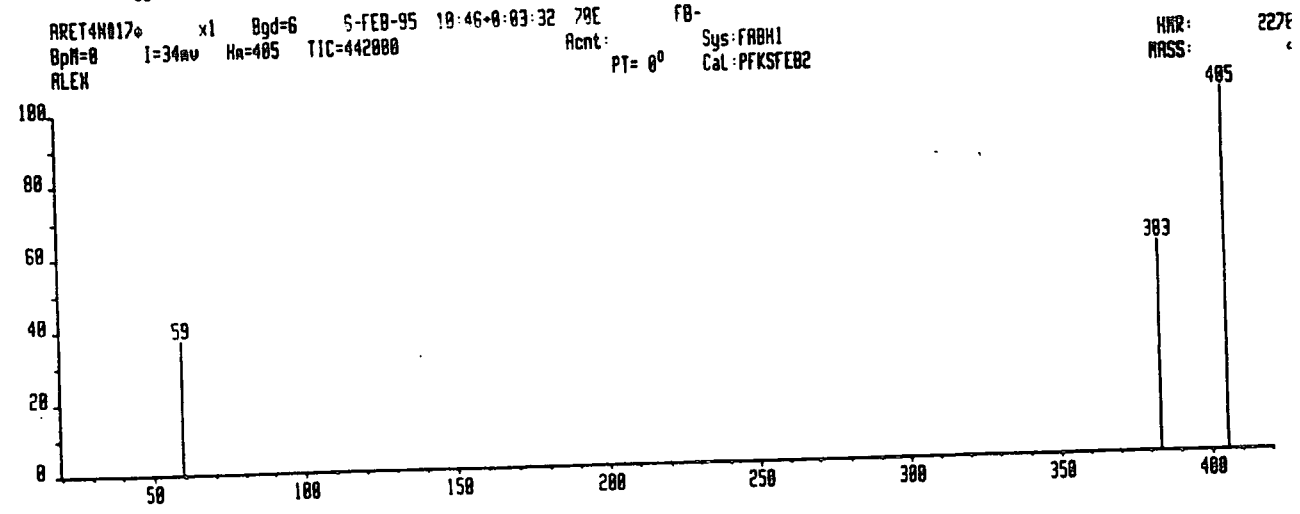


ARK#9 x1 Bgd=6 22-NO
BpM=0 I=574mv Hm=441 TIC=2017
ALEX

Mass	% Base	
57.95	3.85	
57.97	6.11	
58.97	13.60	
70.96	13.44	
72.96	3.53	
86.94	3.27	
87.95	4.57	
88.95	15.33	
90.96	47.61	F
91.02	8.40	F
91.96	3.61	
92.95	2.58	
104.96	2.84	
110.98	3.61	
112.85	1.43	
112.92	3.13	
130.94	6.19	
132.95	3.21	
136.99	5.53	
149.91	2.74	
150.98	3.69	
164.98	1.91	
178.94	5.37	
180.97	8.93	
182.99	34.91	
183.99	6.35	
266.87	4.86	
275.00	5.55	
298.83	2.31	
328.89	2.84	
332.97	2.79	
335.84	4.73	
336.86	6.70	
354.85	5.07	
366.87	2.98	
368.97	2.34	
374.89	1.65	
378.89	5.45	
384.88	2.15	
385.81	8.63	
386.83	4.57	
388.92	1.67	
392.81	1.86	
394.86	6.40	
402.50	1.46	
402.95	4.04	
403.70	3.83	
404.82	100.00	
405.87	13.42	
406.36	3.21	
406.54	2.31	
407.03	1.25	
414.90	10.76	
415.08	2.84	
416.95	2.31	
431.33	2.92	
433.97	2.74	
435.23	3.24	
436.29	2.95	
437.27	30.37	F
mass	% Base	
437.32	22.13	F
437.47	5.95	
437.64	3.88	
437.96	3.83	
437.99	3.40	
438.32	1.59	
440.66	15.17	
440.80	1.49	
441.31	5.66	

Spectrum 5

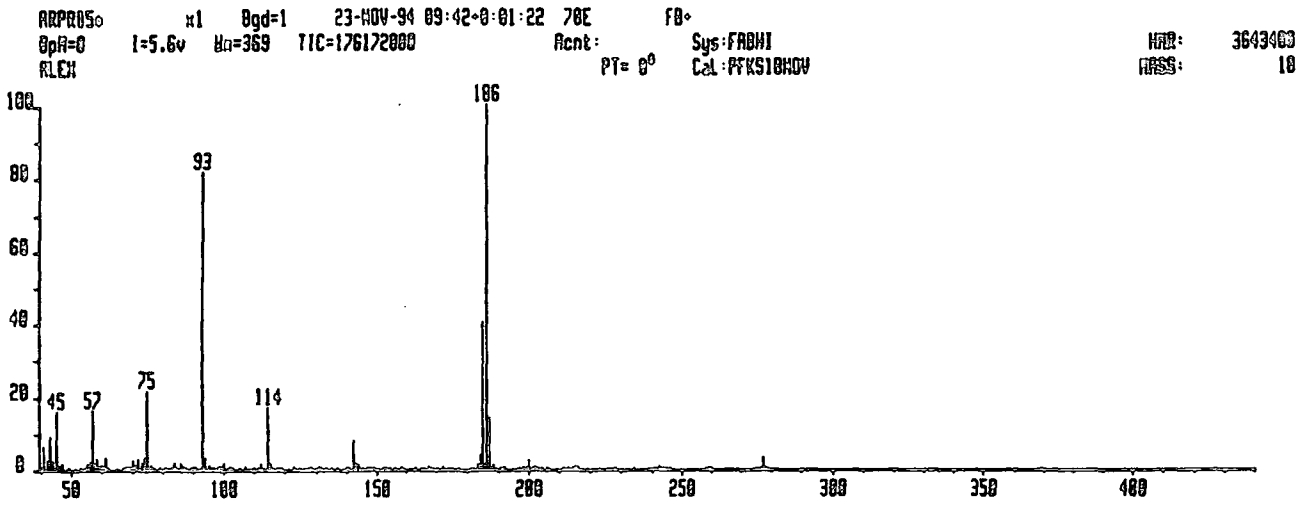


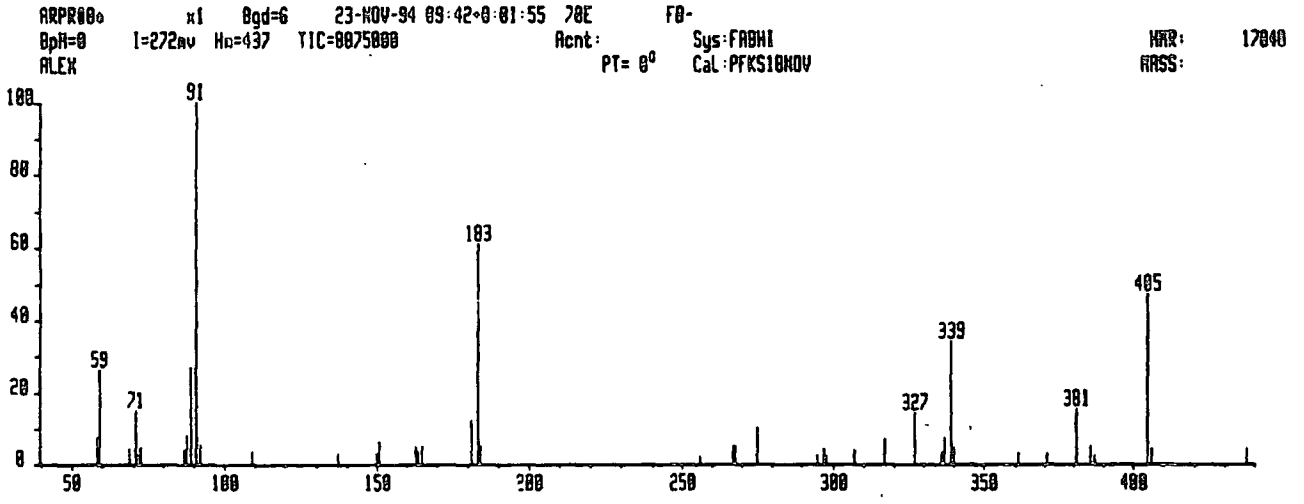


ARET4N817e x1 Bgd=6 6-FEB-95 10:46+0:03:32 70E FB- 2.1
BpM=0 I=34mv Hm=405 TIC=442000 Acnt: Sys:FABH1
ALEX PT= 0 Cal:PFKSFEB2

Mass	% Base
59.14	37.00
383.48	57.71
405.45	100.00

Spectrum 6

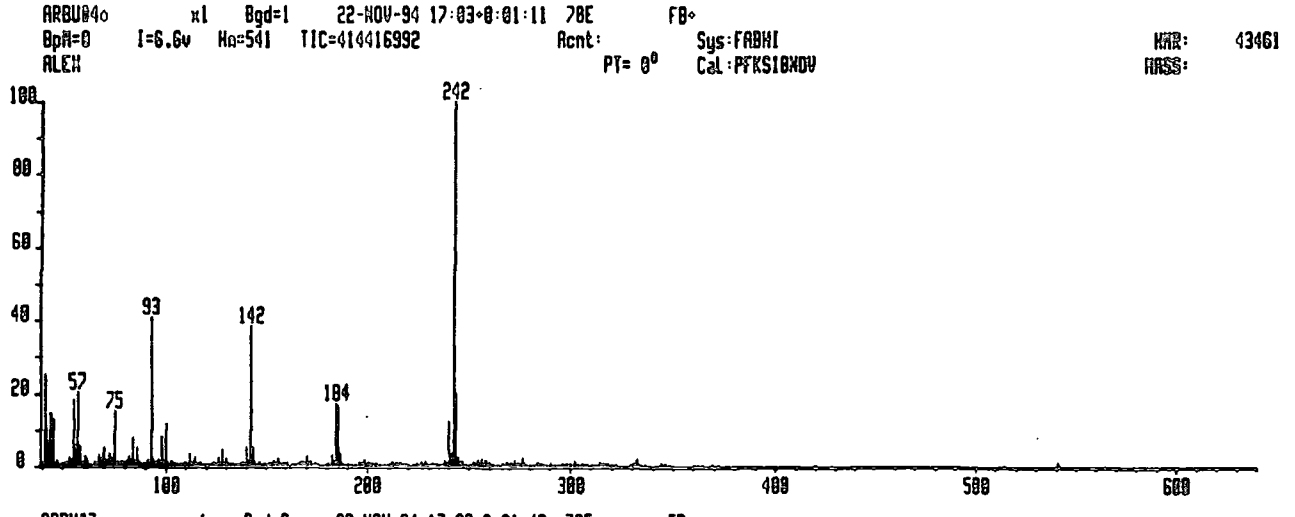


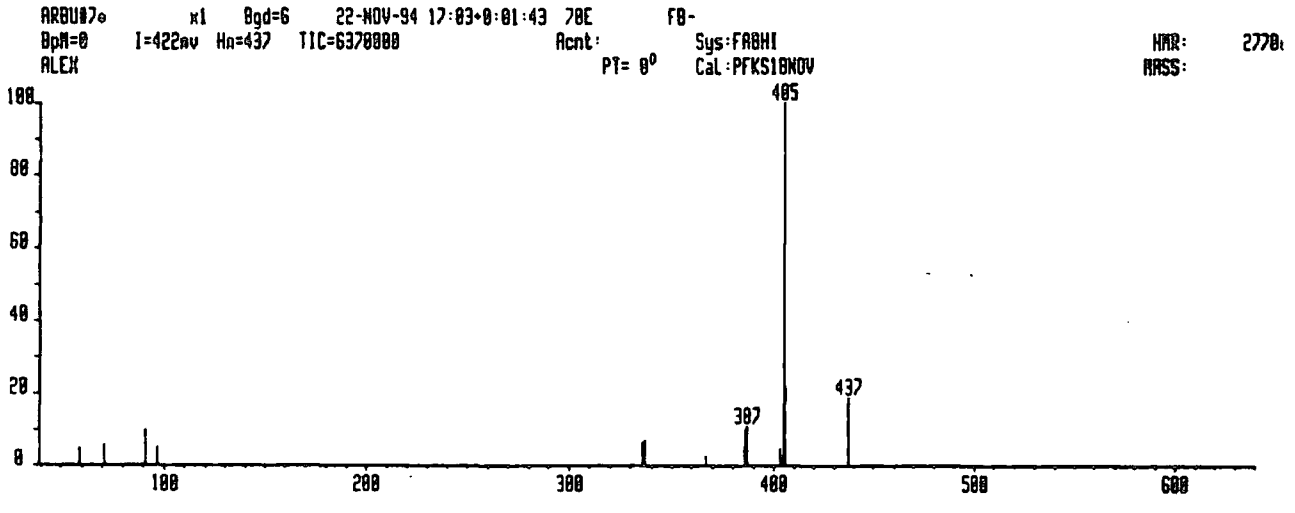


ARPR88# x1 Bgd=6 23-NOV-94 09:42+0:01:55 70E FB- 2.1
BpM=0 I=272mv Hm=437 TIC=8875000 Acnt: Sys:FABHI
ALEX PT= 0 Cal:PFKS18NOV

Mass	% Base	Mass	% Base
57.96	7.23	294.97	2.52
58.97	26.12	296.96	4.15
68.97	4.20	297.99	1.91
70.98	14.80	306.90	3.70
71.99	2.35	307.04	3.42
73.00	4.37	316.95	6.78
86.97	3.70	326.93	14.18
87.98	8.02	335.86	3.25
88.98	26.63	336.86	7.23
90.99	100.00	338.84	33.80
92.00	4.99	339.85	4.60
108.98	3.59	360.86	2.91
136.96	2.80	370.79	2.58
149.94	2.80	380.83	15.13
150.95	6.11	385.78	4.76
162.95	4.88	386.92	1.96
163.98	3.36	404.81	47.03
164.97	4.88	405.80	4.04
181.03	12.11	437.32	3.98
183.05	60.48		
184.05	4.88		
256.05	1.91		
266.94	4.71		
267.95	4.65		
275.04	9.98		

Spectrum 7

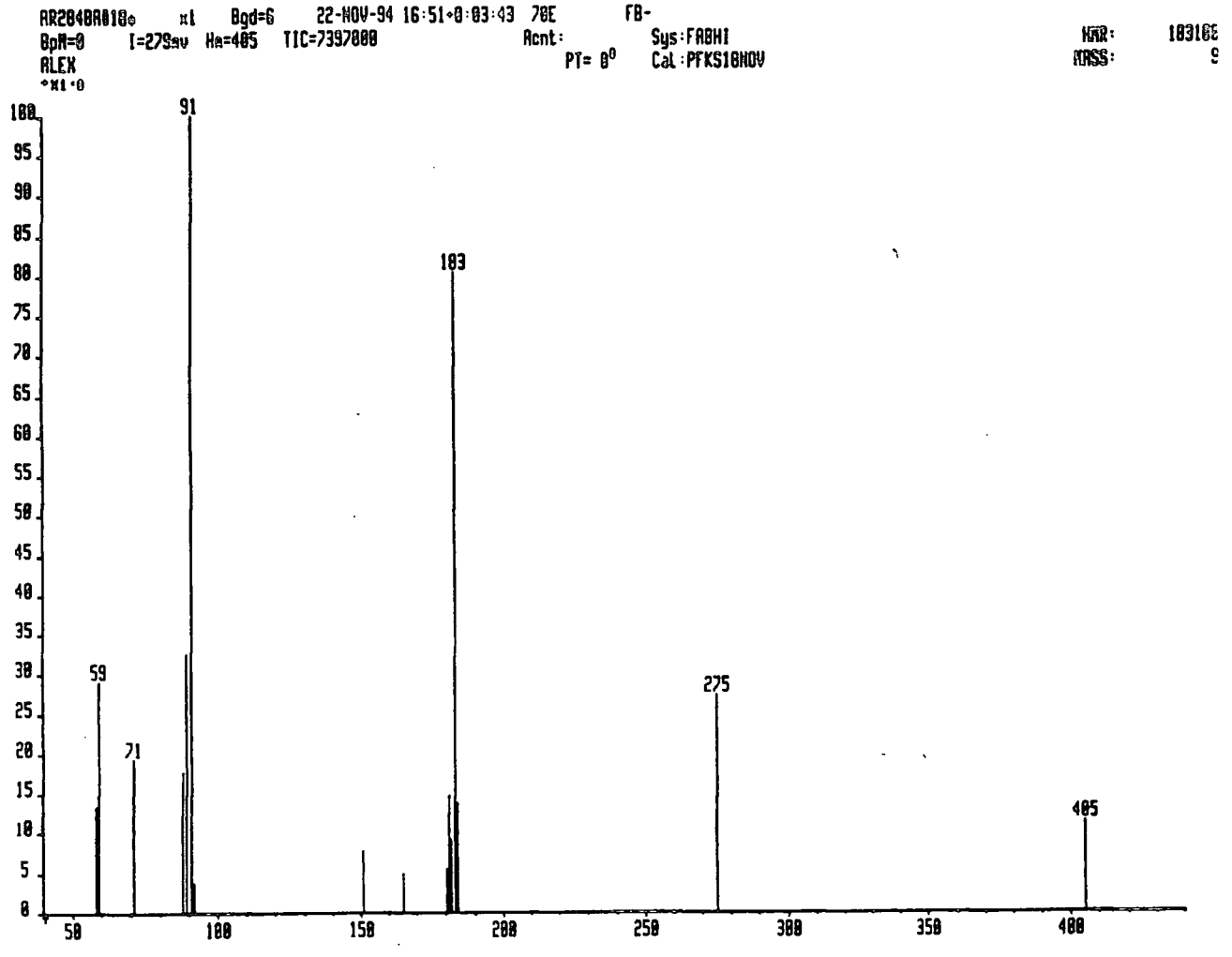




BpM=0 I=422mv Hm=437
ALEX

Mass	% Base	
58.98	4.55	
70.99	5.34	
91.01	9.42	
96.93	4.77	
336.08	6.14	
336.92	6.75	
337.12	4.12	
366.98	2.49	
385.75	5.09	
386.01	9.68	
387.05	10.76	
403.17	4.58	
403.44	2.56	
404.91	100.00	F
405.37	10.61	F
405.99	21.88	
437.32	18.48	
437.49	2.74	

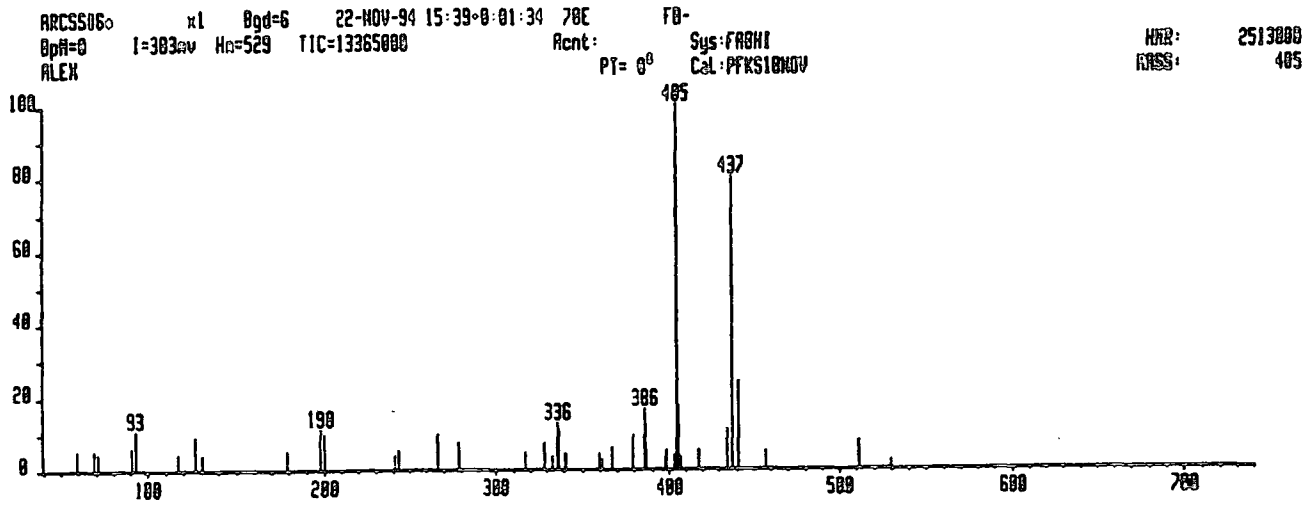
Spectrum 8

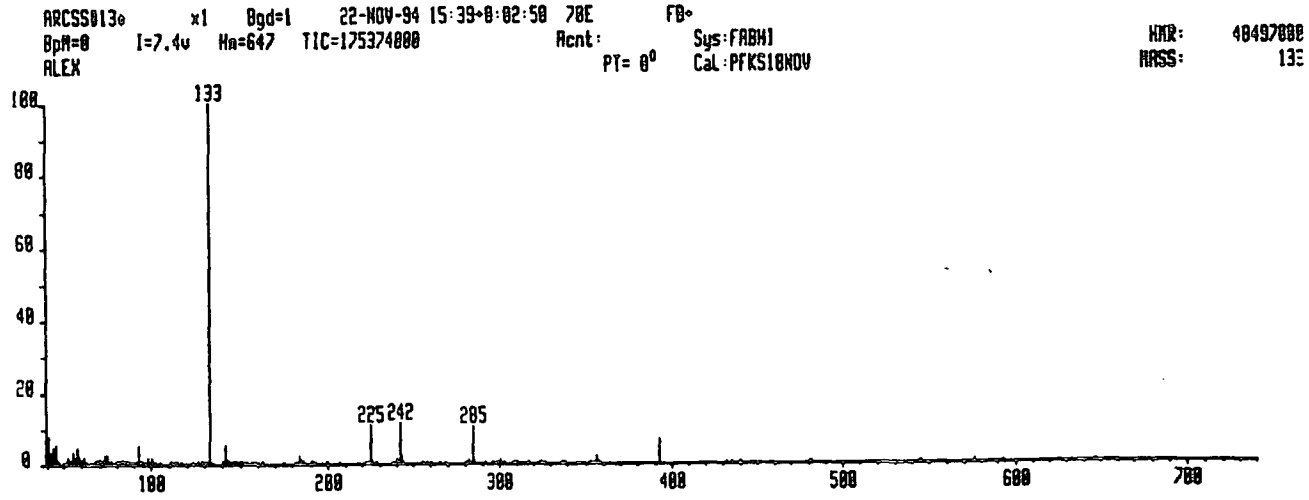


ALEX PT= 0 Cal:PFKS18NOV

Mass	% Base
57.98	13.22
58.98	29.00
70.99	19.28
87.97	17.70
88.99	32.55
91.00	100.00
91.06	14.64
91.99	3.71
151.00	7.59
165.00	4.81
180.03	5.41
181.03	14.64
182.05	9.01
183.04	80.28
184.02	13.76
275.13	27.14
405.01	11.25

Spectrum 9

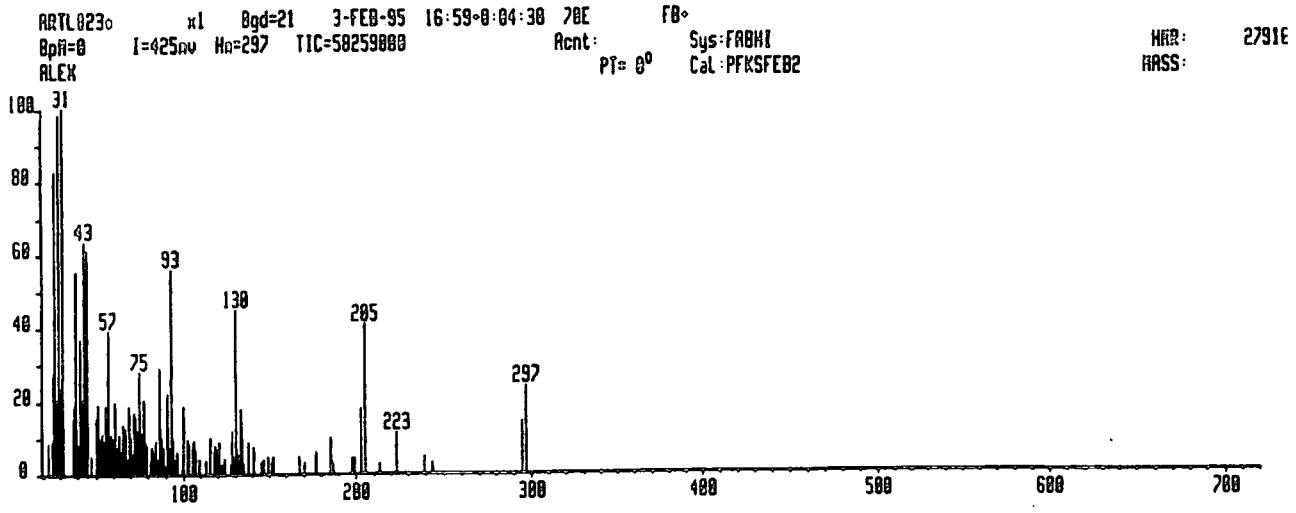


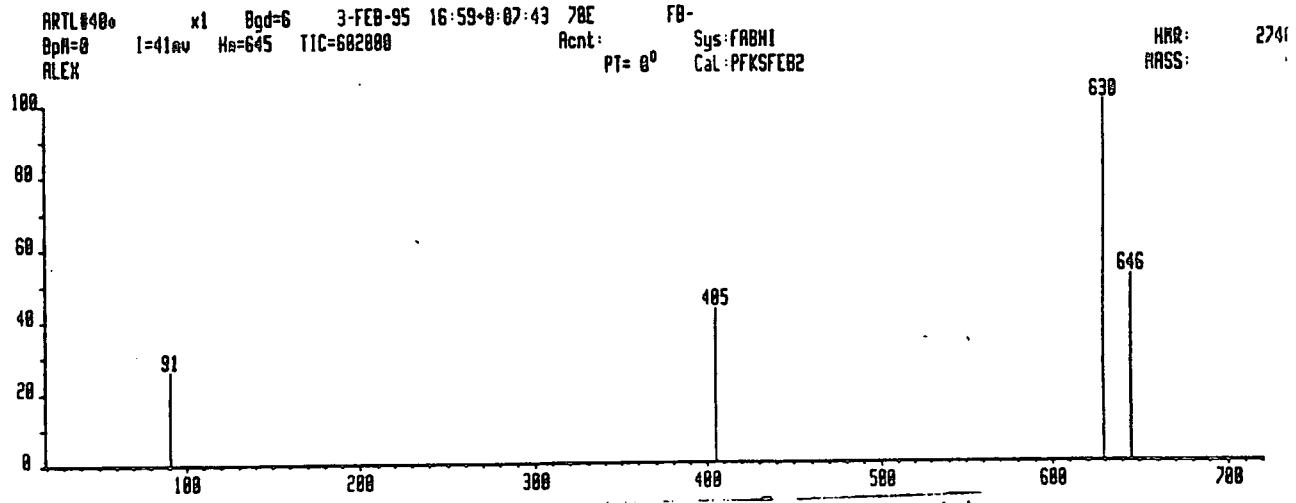


ARCSS06# x1 Bgd=6 22-NOV-94 15:39+0:01:34 70E FB- 1.1
BpM=0 I=383mv Hm=529 TIC=13365000 Acnt: Sys:FABHI
ALEX PT= 0 Cal:PFKS18NOV

Mass	% Base
58.97	4.81
68.95	5.21
70.97	4.26
90.96	5.77
92.89	2.51
92.93	10.58
116.90	4.14
126.81	8.91
130.88	3.90
178.86	4.66
197.81	11.06
199.85	9.43
240.75	3.82
242.85	5.09
266.78	9.71
278.83	7.16
316.95	4.46
328.82	7.12
332.76	3.54
335.83	12.81
336.78	10.35
340.76	4.06
359.68	4.06
360.63	2.27
366.72	5.81
378.79	9.35
385.79	16.51
386.61	4.85
386.83	6.41
397.89	2.98
398.69	5.13
403.13	3.70
404.72	100.00 F
405.03	25.67 F
405.68	17.59 F
406.65	3.02
417.75	4.97
433.98	10.90
434.15	5.13
437.27	80.26 F
437.43	21.37 F
437.48	14.84 F
440.63	24.11
440.79	5.25
456.90	4.70
511.53	7.44
929.06	2.11

Spectrum 10



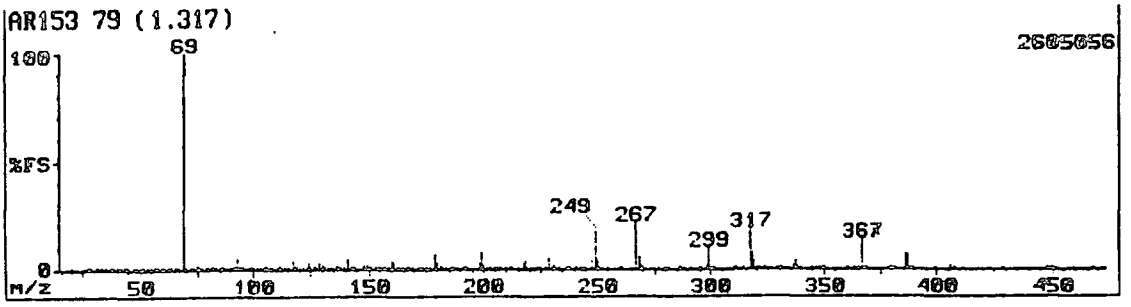


ARTL823o x1 Bgd=21 3-FEB-95 16:59+0:04:30 70E FB+ 1.1
BpM=0 I=425mv Hm=297 TIC=58259000 Acnt: Sys:FABHI
ALEX PT= 0 Cal:PFKSFEB2

ARTL840o x1 Bgd=6 3-FEB-95 16:59+0:07:43 70E FB- 2.1
BpM=0 I=41mv Hm=645 TIC=602000 Acnt: Sys:FABHI
ALEX PT= 0 Cal:PFKSFEB2

Mass	% Base
91.14	25.55
405.38	42.34
629.62	100.00
645.93	51.82

Spectrum 11

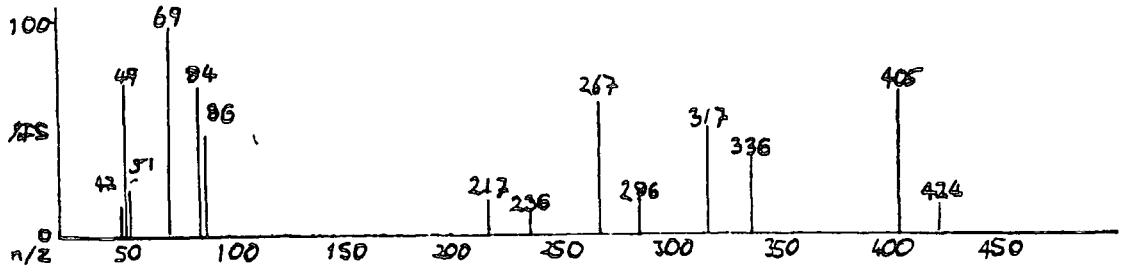


AR153 79 (1.317) 2605056

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.39	86	0.41	155	0.98	237	0.18
26	0.01	87	0.50	156	0.12	238	0.02
27	0.02	88	0.07	157	0.03	241	0.13
28	0.13	90	0.04	159	0.02	242	0.03
29	0.02	91	0.30	160	4.25	243	0.02
31	1.38	92	0.47	161	2.79	245	0.04
32	0.06	93	4.64	162	0.27	248	3.97
33	0.01	94	0.19	163	0.04	249	17.61
35	0.02	95	0.05	165	0.01	250	3.66
36	0.08	96	0.01	167	1.13	251	0.24
37	0.18	97	0.02	168	0.95	255	0.02
38	0.07	98	0.72	169	0.12	260	0.05
39	0.04	99	1.44	172	0.16	261	0.05
40	0.01	100	0.17	173	0.01	267	31.70
41	0.03	101	0.02	174	0.16	268	6.29
42	0.03	103	0.34	175	0.06	269	1.78
43	0.03	104	0.07	177	0.03	270	0.13
44	0.14	105	1.48	179	6.84	277	0.02
45	0.02	106	0.46	180	2.56	279	0.59
47	0.04	107	0.04	181	1.96	280	0.20
48	0.02	108	0.03	182	0.14	281	0.03
49	0.02	110	1.02	184	0.22	286	1.76
50	1.00	111	1.76	186	0.13	287	0.26
51	0.48	112	0.70	187	0.16	288	0.04
52	0.01	113	0.47	188	0.01	291	0.02
53	0.01	115	0.63	191	0.31	295	0.16
55	0.24	117	4.01	192	0.10	296	0.03
56	0.25	118	0.27	193	0.09	298	1.86
57	0.09	119	0.18	198	2.71	299	10.06
58	0.01	120	0.01	199	8.10	300	0.86
59	0.01	122	0.74	200	2.01	301	0.04
60	0.10	123	0.37	201	0.14	310	0.01
61	0.77	124	3.11	203	0.04	311	0.04
62	0.27	125	0.24	205	0.38	314	0.03
63	0.05	126	0.02	206	0.03	317	18.71
64	0.03	127	0.02	207	0.04	318	7.98
65	0.03	129	3.26	210	0.50	319	3.62
66	0.01	130	1.71	211	0.26	320	0.29
67	0.08	131	0.38	212	0.03	321	0.02
69	100.00	132	0.04	217	3.34	323	0.01
70	1.34	134	0.08	218	3.58	329	0.02
72	0.04	136	1.92	219	0.33	330	0.02
73	0.06	137	0.56	220	0.02	331	0.01
74	0.95	138	0.07	222	0.01	336	2.12
75	2.12	140	0.25	223	0.03	337	3.81
76	0.08	141	4.44	224	0.02	338	1.40
77	0.04	142	0.39	225	0.01	339	0.12
79	1.29	143	0.97	227	0.01	345	0.59
80	0.98	144	0.05	229	5.31	346	0.06
81	0.47	148	1.63	230	1.39	348	0.16
82	0.08	149	1.55	231	2.20	349	0.15
83	0.04	150	0.75	232	0.16	350	0.02
84	0.04	151	0.05	233	0.01	360	0.01
85	0.15	153	0.04	236	0.90	361	0.01

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
364	0.34	379	0.03	388	0.62	429	0.02
365	0.04	380	0.03	389	0.03	448	0.01
367	13.84	381	0.01	399	0.04	449	0.04
368	1.37	386	6.84	406	1.73	450	0.01
369	0.07	387	6.84	407	0.16	468	0.02

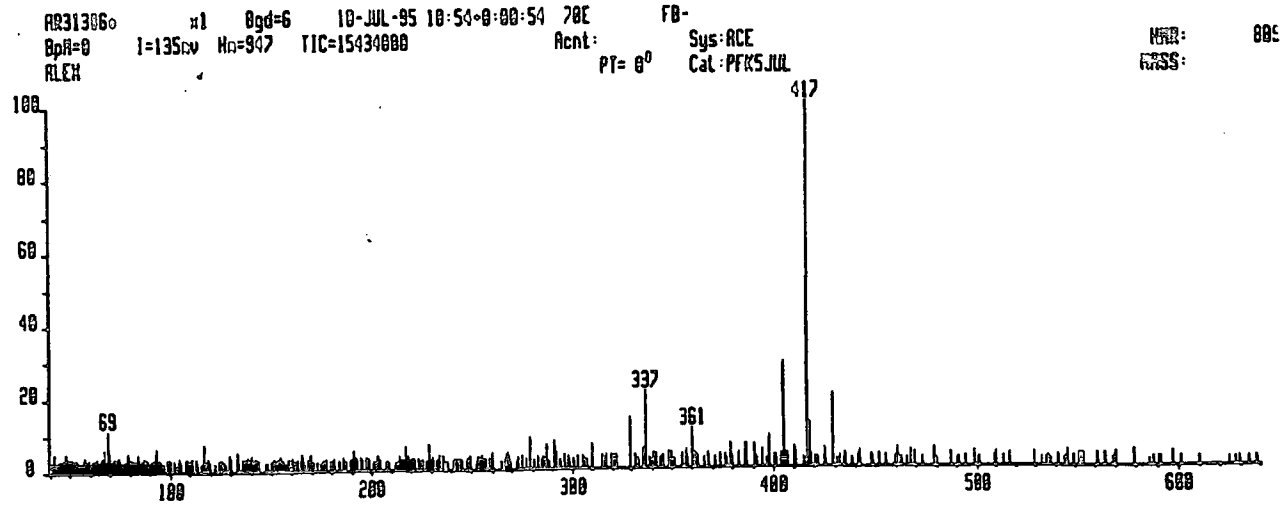
Spectrum 12



No 12

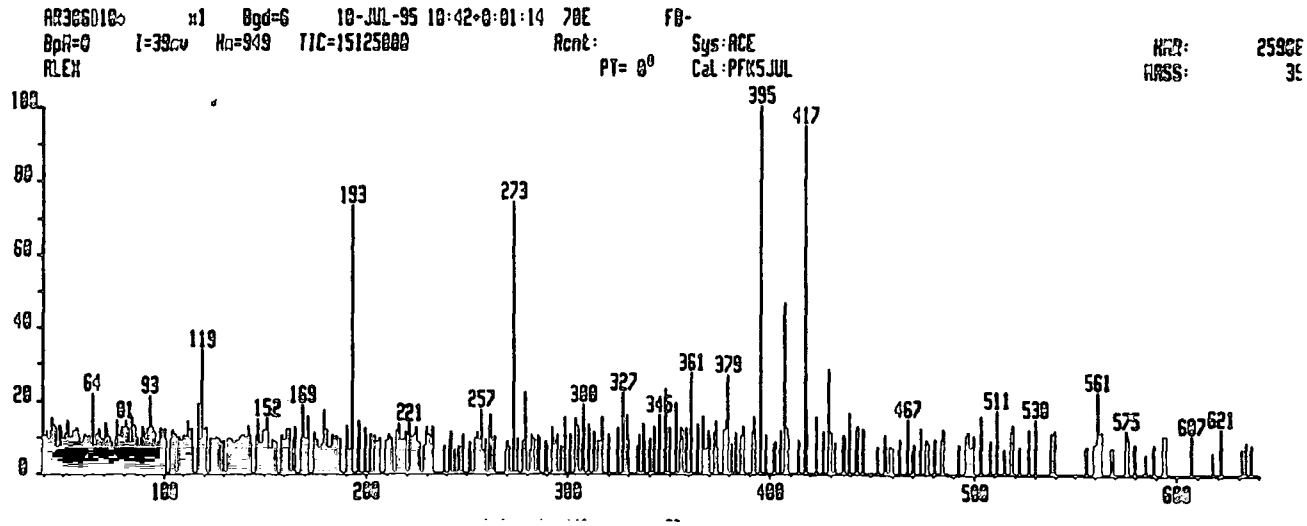
Mass	Rel. Int.
47	13.17
49	70.73
51	21.83
69	100.00
84	71.71
86	46.34
217	18.99
236	10.98
267	66.34
286	16.59
317	49.27
336	36.10
405	67.80
424	15.85

Spectrum 13



Mass	% Base	Mass	% Base	Mass	% Base	Mass	% Base	Mass	% Base
134.01	1.91	195.64	2.59	268.42	3.26	363.15	3.26	487.08	3.
136.04	3.15	197.00	3.37	268.94	1.80	366.02	2.59	490.63	1.
137.04	3.04	198.60	2.92	272.98	2.14	368.20	4.05	491.07	2.
137.22	2.47	201.16	1.91	272.98	2.92	371.42	2.81	494.50	2.
138.22	3.71	201.52	1.57	274.70	3.82	374.06	3.71	499.03	4.
139.03	3.04	202.93	3.82	277.09	2.70	376.84	3.49	500.91	2.
139.14	2.25	204.50	2.70	278.98	8.66	377.45	2.25	501.51	2.
140.26	4.27	207.38	2.02	281.04	2.47	378.86	6.41	509.22	2.
141.02	2.25	209.21	2.02	283.04	3.49	379.95	3.04	509.63	1.
141.46	2.25	212.31	1.80	284.85	2.36	383.00	4.27	510.10	3.
142.26	3.04	213.70	2.14	285.16	3.49	385.97	6.30	514.07	2.
142.63	1.80	214.07	3.82	285.55	2.14	387.04	6.30	517.15	3.
143.02	2.25	215.58	2.59	285.80	2.70	390.99	6.30	529.49	3.
143.38	2.59	215.78	2.25	287.18	6.41	391.65	2.81	533.29	2.
147.72	2.14	215.96	2.14	288.38	2.02	392.14	2.36	535.00	2.
148.09	1.91	217.03	6.19	291.01	7.65	394.43	2.02	536.64	2.
149.94	2.25	217.37	1.80	291.66	2.59	395.00	4.84	537.75	2.
151.04	2.92	218.93	3.60	292.03	4.50	396.93	2.36	541.90	2.
152.20	2.36	220.06	2.81	293.68	2.47	397.97	8.44	544.67	1.
153.48	2.92	221.05	3.15	294.32	2.02	400.59	3.37	546.00	4.
153.70	2.70	222.18	2.59	296.08	3.94	400.98	2.92	549.08	2.
154.32	2.81	223.80	3.15	297.97	3.26	403.50	3.60	552.29	3.
154.73	3.82	225.02	2.14	298.49	2.25	404.04	2.25	552.72	3.
155.61	2.02	225.15	2.02	298.74	1.80	404.94	28.91	553.77	3.
155.90	2.81	225.63	2.47	300.67	2.81	406.02	3.71	561.08	3.
156.87	1.80	225.96	2.70	303.00	3.49	406.78	3.60	564.94	3.
158.31	3.15	227.53	2.14	305.07	3.26	409.93	5.51	568.73	1.
160.41	1.80	229.01	6.97	306.68	2.47	411.00	4.50	570.10	3.
160.61	3.37	229.53	2.36	307.56	2.47	414.59	2.70	579.05	4.
161.86	2.36	230.05	2.02	309.98	6.64	415.96	2.14	585.99	1.
162.92	2.81	230.91	3.49	314.83	3.71	416.92	100.00	588.37	2.
163.17	2.36	232.78	2.25	315.91	2.70	417.99	12.15	590.78	2.
165.02	4.50	234.00	3.94	317.03	3.82	418.78	3.26	591.75	2.
165.79	3.26	235.97	3.82	319.41	3.60	420.88	2.70	597.07	3.
166.28	1.80	238.27	2.14	319.75	2.36	422.02	2.59		
167.98	2.81	241.13	1.69	321.01	3.37	425.14	5.06		
169.24	4.05	241.52	2.47	321.49	1.80	425.93	1.57		
170.09	2.02	241.81	2.25	321.93	3.94	428.98	19.80		
170.85	2.14	242.08	2.81	329.02	13.84	430.73	1.91		
172.66	1.91	243.29	2.59	331.82	3.60	432.09	3.04		
174.60	1.69	244.35	2.70	333.34	2.59	433.90	2.14		
174.74	1.69	245.49	2.47	333.98	2.02	435.04	3.71		
175.31	2.14	248.06	2.70	335.94	5.17	437.91	2.25		
176.07	2.47	249.00	3.94	336.97	21.03	441.01	3.49		
177.25	3.15	252.52	1.46	338.97	2.70	441.84	4.61		
179.89	2.36	252.74	3.26	339.62	2.14	447.80	3.49		
181.07	3.04	253.00	2.25	340.86	4.05	448.18	2.25		
181.25	2.36	254.50	3.04	341.23	3.37	451.93	3.49		
183.75	2.25	254.98	3.71	341.98	3.71	455.05	3.04		
185.46	3.37	256.16	2.81	344.09	2.25	459.49	2.25		
185.71	3.26	256.35	2.14	344.43	2.14	459.89	2.59		
186.92	2.25	256.72	2.81	345.67	3.26	460.88	5.17		
189.69	2.70	257.00	1.91	348.94	4.50	461.98	2.25		
191.01	5.17	258.59	2.81	349.99	4.27	462.76	2.47		
191.34	2.70	260.06	4.39	351.35	2.25	465.43	2.25		
191.96	3.37	264.44	2.14	355.10	3.94	466.92	4.61		
192.42	2.47	266.29	2.70	357.09	4.95	469.09	3.71		
192.95	2.70	266.93	4.05	357.82	2.81	472.81	2.36		
194.84	2.59	267.67	2.02	360.64	10.46	478.98	5.29		
194.99	3.49	268.01	4.61	361.94	4.27				

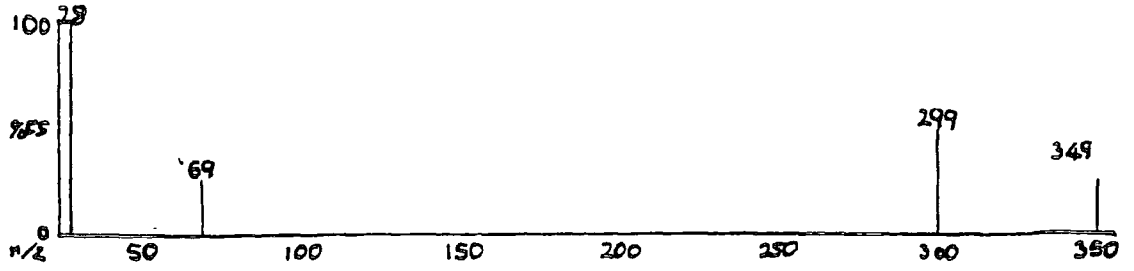
Spectrum 14



AR3G6010▷ x1 Bgd=6 10-JUL-95 10:42÷0:01:14 70E FQ= 1.1
BpM=0 I=39mv Hm=949 TIC=15125000 Acnt: Sys:ACE
ALEX PT= 0 Cal:PFK9JUL

Mass	% Base	Mass	% Base	Mass	% Base	Mass	% Base	Mass	% Base
146.08	10.04	212.81	6.95	295.14	10.42	392.69	8.49	530.11	14.67
147.07	14.29	214.62	11.20	296.99	7.34	392.96	5.41	537.42	10.81
147.19	8.49	215.81	8.11	298.98	19.06	399.28	100.00	939.91	11.98
148.14	7.72	216.12	13.13	301.20	10.42	398.02	10.42	555.18	7.34
149.34	11.20	216.48	8.49	304.04	14.67	401.93	7.72	995.74	7.34
150.35	11.20	217.64	8.49	305.23	12.74	402.26	8.49	559.33	7.72
151.57	14.67	218.03	8.88	307.15	8.88	405.07	11.58	560.12	9.27
152.70	6.56	219.37	8.49	308.16	18.53	407.17	46.72	561.23	22.39
153.98	8.88	219.58	10.81	310.79	13.13	408.18	12.36	562.26	9.65
155.10	8.49	221.05	13.51	313.14	10.81	409.13	9.65	563.11	11.20
156.09	8.11	222.84	9.65	313.43	6.95	414.05	8.88	568.19	6.95
158.58	10.42	224.06	10.42	315.19	8.49	417.05	94.59	568.60	6.85
158.75	8.49	224.31	12.36	315.90	6.18	418.20	16.99	579.13	11.98
158.90	6.18	226.07	8.11	316.52	8.11	423.18	19.44	579.89	10.42
159.79	8.88	226.30	7.72	317.25	18.06	426.29	10.42	576.49	8.49
159.94	6.56	228.30	7.34	320.10	10.42	426.65	11.20	579.91	7.72
161.03	11.97	229.56	12.36	320.43	6.95	429.16	28.97	584.95	5.02
162.22	11.97	230.86	8.11	324.97	12.36	430.10	10.81	589.10	7.72
164.27	8.88	231.11	10.42	327.15	22.01	432.11	8.11	593.63	10.42
164.69	5.41	231.36	7.34	329.22	19.83	435.83	7.34	594.74	10.42
164.81	12.74	233.20	12.36	329.83	8.88	436.25	10.42		
165.00	9.27	238.60	6.95	330.10	7.72	436.72	9.65		
167.99	9.27	238.91	7.34	334.24	7.34	439.30	16.60		
168.34	9.27	241.19	8.11	334.95	9.27	442.44	11.58		
168.51	8.49	241.40	8.88	335.21	10.42	443.00	12.74		
169.08	18.53	241.99	10.81	337.15	13.51	446.06	11.97		
169.67	8.11	243.98	6.18	337.99	8.11	452.98	7.34		
169.85	9.27	245.53	7.34	340.20	7.72	455.92	10.42		
171.08	15.44	247.73	10.42	340.59	9.27	456.45	6.95		
171.32	8.88	251.18	8.11	342.22	12.74	456.90	7.34		
174.84	10.81	251.44	5.79	342.47	9.65	458.98	7.34		
176.14	8.88	253.47	9.27	345.12	19.83	459.44	6.18		
176.34	6.95	259.10	11.20	348.12	22.78	459.97	6.95		
177.72	7.72	255.37	8.88	350.32	12.36	463.14	9.27		
179.01	16.99	256.94	16.99	353.12	19.31	467.06	14.67		
179.92	9.65	257.38	5.79	355.19	8.49	469.78	5.41		
180.40	11.58	259.05	9.27	355.54	9.65	470.37	7.72		
181.74	6.95	260.86	12.74	355.93	12.36	473.44	6.18		
182.73	10.42	261.14	15.83	356.28	11.58	473.84	12.36		
184.37	8.49	263.07	10.04	358.17	12.36	476.00	8.88		
184.95	8.88	269.03	5.41	361.11	27.41	476.40	7.72		
184.76	10.04	269.57	8.49	364.24	13.51	476.97	8.49		
187.22	9.27	271.13	6.95	366.78	11.20	477.36	7.72		
189.95	13.13	273.07	74.13	367.12	19.44	480.76	9.27		
190.16	10.04	275.05	9.27	368.39	6.56	484.04	8.88		
190.37	8.49	277.52	8.49	369.14	11.20	484.73	11.97		
191.20	6.18	279.14	22.01	370.01	10.04	492.16	7.72		
192.46	8.88	279.43	5.79	372.42	10.81	492.67	7.34		
193.03	72.97	281.53	6.18	373.11	13.90	495.50	10.42		
195.82	13.90	281.76	10.04	374.07	6.95	497.11	11.20		
199.02	11.97	282.13	10.42	377.19	11.90	498.19	6.95		
202.12	10.42	283.09	9.27	378.34	13.90	499.27	10.42		
203.43	10.04	285.12	10.04	379.19	26.64	503.32	19.83		
205.03	8.11	289.70	7.72	380.90	7.72	508.12	8.08		
206.61	9.27	286.03	9.27	382.92	9.27	511.11	16.99		
209.86	8.49	288.94	8.49	383.32	10.81	514.86	6.96		
210.03	7.72	289.87	7.34	385.46	10.04	518.33	11.20		
211.12	10.42	292.29	12.36	386.72	12.74	519.03	13.13		
211.39	8.11	293.67	7.34	391.24	10.81	521.90	7.34		
212.39	9.27	294.31	8.49	392.25	19.44	526.43	11.97		

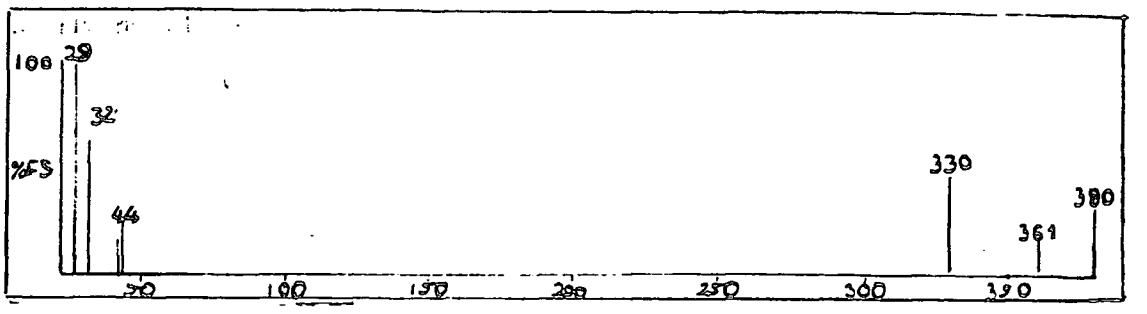
Spectrum 15



No 15

Mass	Rel. Int.
28	100.00
69	27.58
299	50.23
349	27.58

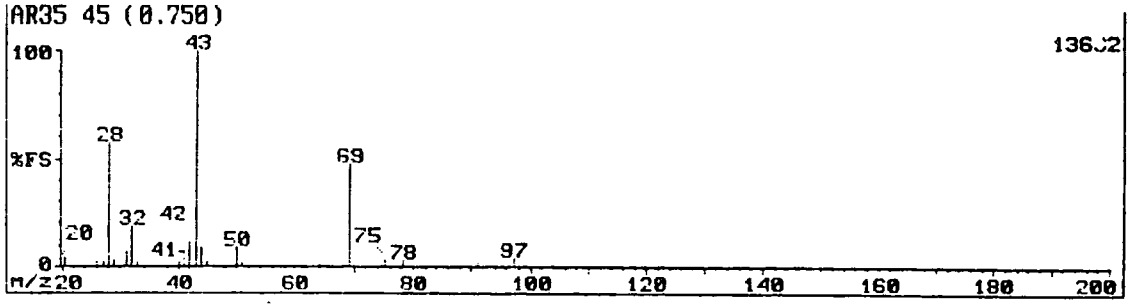
Spectrum 16



No 16

Mass	Rel. Int.
28	100
32	63.33
43	17.29
44	24.38
330	48.54
361	16.46
380	33.74

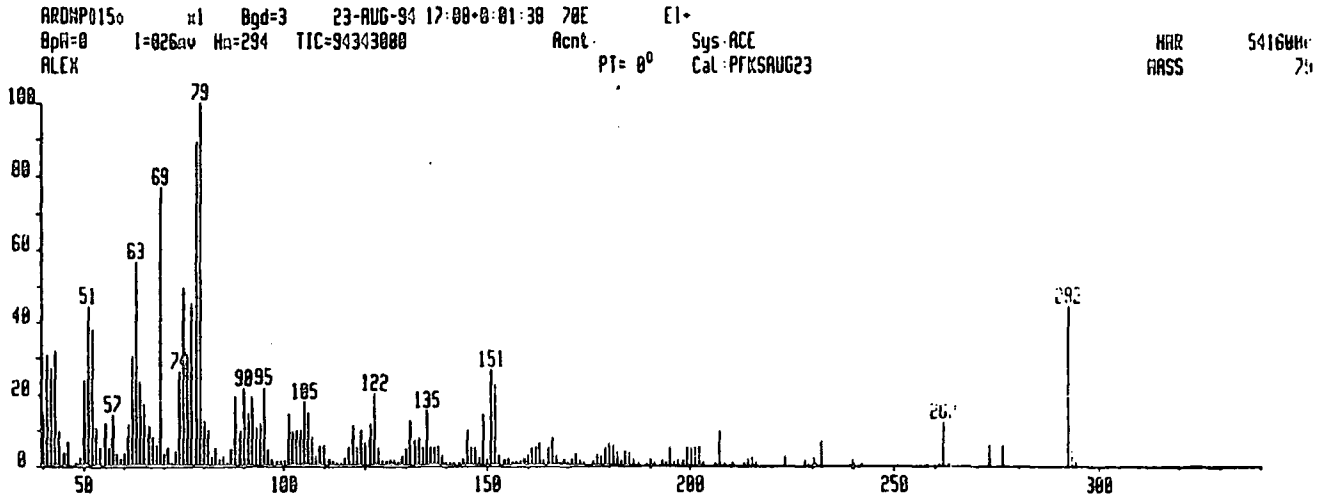
Spectrum 17

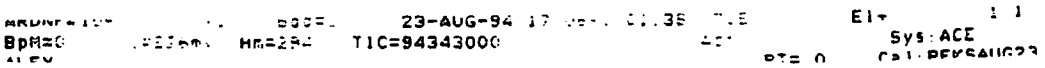


AR35 45 (0.750) 13632

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	4.11	32	18.31	44	8.45	75	3.82
26	2.08	33	2.05	45	1.64	78	3.17
27	2.14	40	2.26	50	9.04	91	1.57
28	56.81	41	3.64	51	2.08	95	1.40
29	3.29	42	12.32	64	1.94	97	3.58
31	6.57	43	100.00	69	47.89		

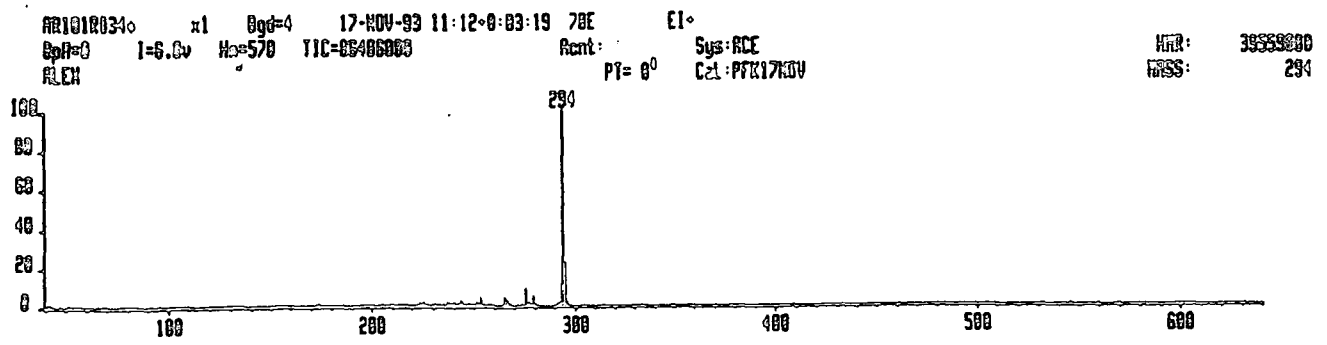
Spectrum 18





Mass	% Base	Mass	% Base	Mass	% Base	Mass	% Base
40 01	14.18	99 10	0 95	159.09	1 57	262.12	11.96
41 04	30.69	100.05	1 35	160 10	2 68	263.15	1 27
42 04	27 01	101 06	14 15	161 11	4 80	273 11	5 82
43 02	31.92 F	102 06	8 34	162 10	4 73	276.12	5 76
43 06	13 28 F	103.06	9 45	163.08	6.17	292.09	44 24
44 01	9 45	104 06	9 45	164.09	1.53	293.11	5.02
45 03	3 43	105 06	17 41	165.09	4 75	294.13	0 87
47 02	6 54	106 06	14 3.	166 08	7.70		
48 02	0 54	107 03	7 75	167 10	2.68		
49 02	1.90	108 08	2 55	168 09	1 81		
50 02	23 56	109 09	5 08	169 07	1 83		
51 03	44 26	110 06	5 47	170 11	0 78		
52 03	17 8.	111 09	F	171 09	1 82		
53 04	10.19	112 10	1 02	172 09	3 18		
54 04	4 72	113 11	0 85	173.10	1 53		
55 06	11 76	114 07	0 6.	174 13	0 57		
56 07	4 95	115.06	2.01	176 11	1 16		
57 08	14 20	116 06	5 04	177 13	2 66		
58 08	2.94	117 02	11 12	178 09	2 44		
59.05	1 72	118 09	4 89	179 11	4 73		
60 04	3.03	119.07	9 45	180 08	6.09		
61 03	11.21	120.08	6 07	181 07	5 34		
62 03	30 08	121 08	11 32	182 08	3 69		
63 04	56 63	122 06	19 94	183 09	1 28		
64 04	23.56	123 08	4 75	184 10	2 66		
65 05	16 86	124 10	1.03	185 08	3 31		
66 06	11 00	125 10	1 14	186 10	1 85		
67 06	8 01	126 06	1 42	187 11	0 79		
68 06	8 38	127 11	1 36	188 11	2 39		
69 01	77 10 F	128 08	1 7.	189 11	1 55		
69 08	20 11 F	129 08	2 34	190 10	0 63		
70 08	3 01	130 09	4 61	191 12	1 20		
71 10	4 73	131 08	12 19	192 12	0 85		
72 06	0 81	132.06	6 98	193 09	4 73		
73 05	2 90	133 08	7 46	194 12	0 89		
74 04	25 87	134 08	4 73	195 09	1 61		
75 04	49 35	135.06	15 20	196 10	1 46		
76 04	30 80	136 05	4 93	197 10	4 73		
77 04	45 19	137 10	4 73	200 10	4 73		
78 05	89 44	138 06	5 08	201 10	4 87		
79 04	100 00	139 07	1 90	202 12	5 26		
80 06	12 32	140 08	3 68	203 13	0 87		
81 08	9 47	141 09	0 85	204 12	0 52		
82 06	2 20	142 10	1 51	205 10	5 45		
83 08	4 73	143 09	1 8.	206 13	0 52		
84 08	1 85	144 08	. 82	211 11	1 11		
85 11	2 44	145 07	0 48	212 14	0 63		
86 05	1 73	146 08	1 73	214 11	1 88		
87 F	4 01	147 11	4 73	215 11	2 31		
88 -	18 1	148 13	1 81	216 11	1 13		
89 1	3 15	149 04	14 11	223 12	2 64		
90 13	21 27	150 08	2 14	228 12	1 42		
91 -	17 9	151 06	28 47	229 14	0 48		
92 -	18 7.	152 07	21 2	230 13	1 82		
93 13	11 14	153 05	3 0	231 09	0 54		
94 0	11 61	154 08	1 27	232 09	6 48		
95 05	2. 04	155 05	1 6-	241 11	1 68		
96 06	4 82	156 09	0 6.	244 13	0 63		
97 10	1 71	157 09	1 72	245 11	1 55		
98 10	1 16	158 08	1 22	246 -	1 64		

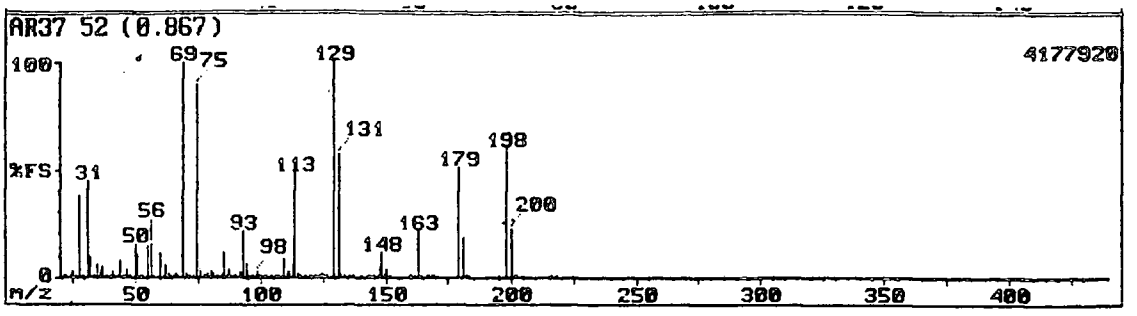
Spectrum 19



101R029# x1 Bgd=26 17-NOV-93 11:12:0:02:53 70E CI- 1.1
M=0 I=1.0v Ma=900 TIC=25689000 Acnt: Sys:ACE
EX PT= 0 Cal:PFK17N0v

Mass	% Base	
41.01	1.29	
42.01	0.96	
90.97	0.74	
183.03	0.65	
186.95	0.32	
172.99	0.91	
174.00	0.44	
182.96	0.30	
194.96	0.36	
196.96	0.86	
197.95	0.36	
204.95	0.52	
208.96	0.94	
209.96	0.39	
210.93	0.40	
212.94	0.33	
214.96	1.01	
216.92	0.61	
222.96	0.99	
223.97	1.53	
224.97	1.91	
225.98	1.30	
226.96	0.74	
230.92	0.51	
232.94	0.32	
236.90	1.83	
237.92	1.03	
238.93	0.45	
239.92	1.06	
240.94	0.68	
241.96	0.75	
242.96	2.37	
243.96	0.67	
244.94	0.66	
246.93	1.29	
248.90	0.49	
250.91	1.74	
251.92	0.69	
252.92	3.65	
253.93	0.60	
262.91	0.32	
264.86	4.07	F
265.92	2.71	F
266.93	0.69	
272.94	0.36	
274.91	8.21	
275.95	1.37	
276.91	1.63	
277.92	0.47	
278.92	4.99	
279.92	0.61	
290.91	0.79	F
291.92	1.56	F
292.93	10.70	F
293.84	100.00	F
294.95	21.91	F
295.96	2.18	F
545.80	0.47	
959.22	0.46	

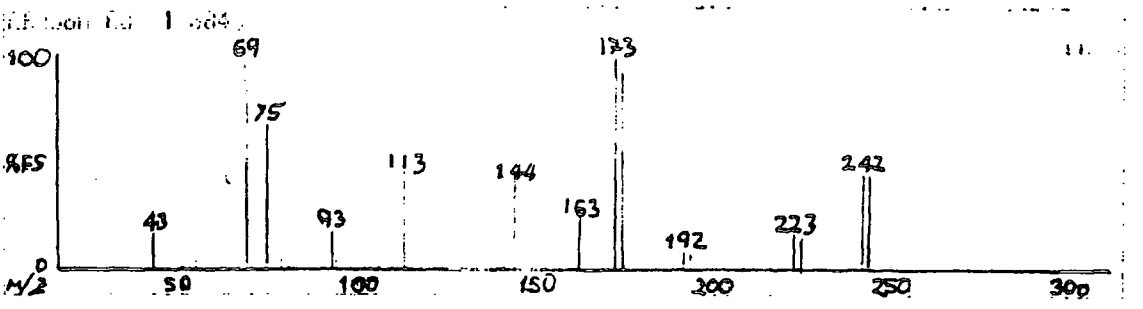
Spectrum 20



AR37 52 (0.867) 4177920

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.15	63	1.56	98	3.01	137	0.04
22	0.01	64	0.13	99	0.31	140	0.03
24	0.70	65	0.17	100	1.32	142	0.08
25	2.82	66	1.89	101	0.06	143	1.08
26	0.39	67	0.68	102	0.02	144	0.74
28	37.65	69	100.00	104	0.04	145	0.07
29	0.62	70	2.08	105	0.42	146	0.34
31	44.71	71	0.67	106	0.23	147	5.10
32	9.80	72	0.67	107	0.02	148	12.06
33	0.05	73	1.15	108	0.53	149	1.94
35	5.66	75	89.02	109	8.33	150	3.77
36	2.48	76	2.65	110	3.28	151	0.12
37	5.17	77	0.42	111	2.92	159	0.29
38	0.40	78	0.83	112	5.61	160	0.24
39	1.36	79	1.76	113	48.24	161	0.10
40	0.83	80	3.16	114	1.59	163	30.98
41	2.67	81	1.72	115	0.08	164	0.71
42	0.16	82	1.07	116	0.78	166	0.16
43	1.23	83	0.05	117	0.04	167	0.09
44	7.55	84	0.96	118	0.27	168	0.06
45	0.50	85	11.96	119	0.08	169	0.03
47	4.00	86	0.94	120	0.01	179	51.37
48	0.44	87	3.90	121	0.03	181	18.24
50	15.10	88	0.06	122	0.01	182	1.05
51	10.20	89	0.14	123	0.15	183	0.05
52	0.22	90	1.37	124	2.08	195	0.02
53	0.48	91	2.94	125	0.40	198	60.00
55	14.51	92	2.13	126	0.03	200	22.45
56	15.10	93	20.98	129	100.00	201	0.66
57	0.47	94	7.06	131	57.25	202	0.02
60	11.37	95	0.47	132	1.57	216	0.26
61	0.97	96	0.06	133	0.08	218	0.08
62	5.47	97	0.66	135	0.10		

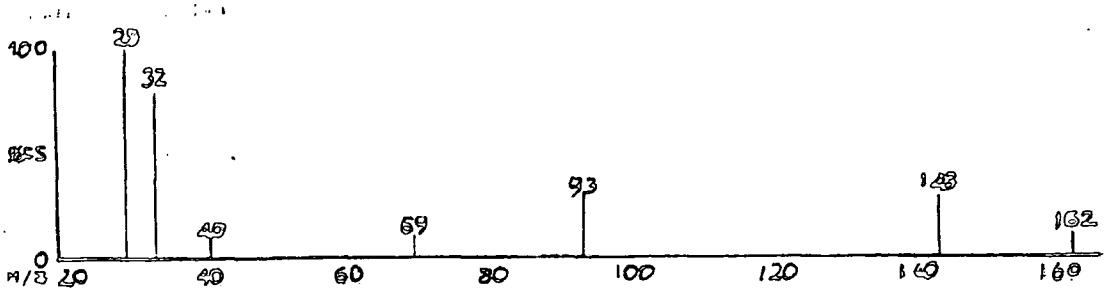
Spectrum 21



No 21

Mass	Rel. Int.
43	18.72
69	100.00
75	70.21
93	19.57
113	46.81
144	41.70
163	25.64
173	99.57
175	95.32
192	9.68
223	18.51
225	17.45
242	45.81
244	45.53

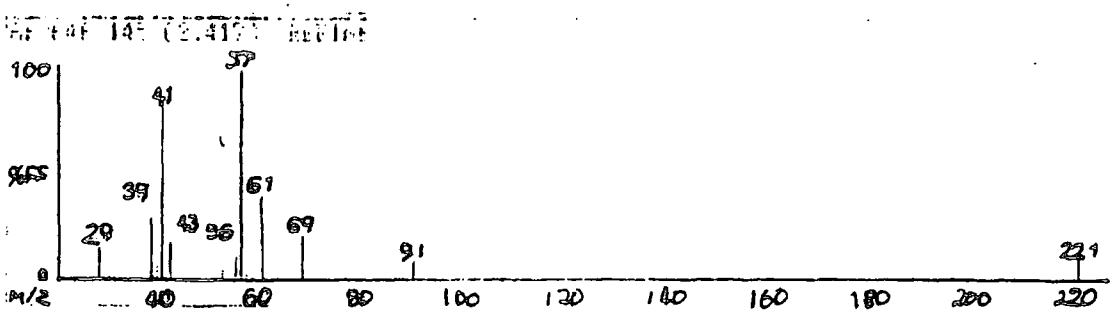
Spectrum 22



No 22

Mass.	Rel Int.
28	100.00
32	80.61
40	8.29
69	11.97
93	28.94
143	31.26
162	12.58

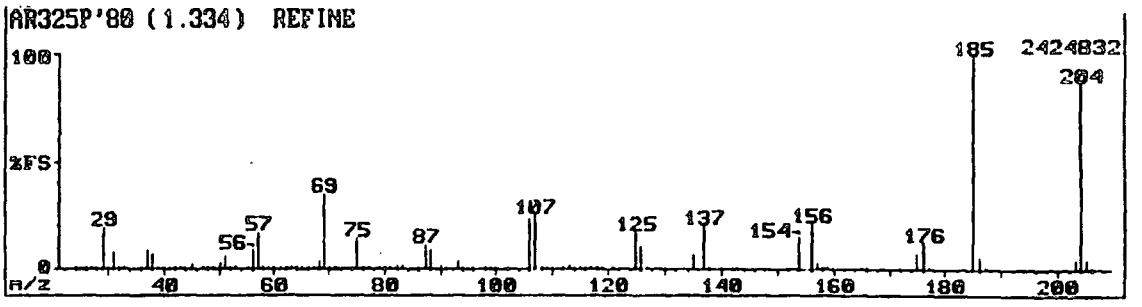
Spectrum 23



No 23

Mass	Rel. Int.
29	18.65
39	30.47
41	83.59
43	15.92
56	11.62
57	100.00
61	41.41
69	22.46
91	10.16
221	10.35

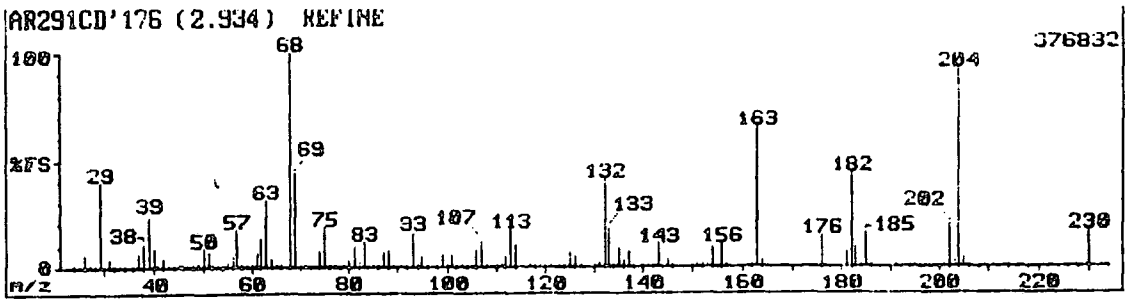
Spectrum 24



AR325P'80 (1.334) REFINE

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.
24	0.05	38	6.88	51	5.79	64	1.24	77	0.38	90	0.64	112	1.05	125	7.01	166			
25	0.12	39	0.27	52	0.15	65	0.15	80	0.22	91	0.70	113	2.03	127	19.93	175			
26	0.07	40	0.05	53	0.19	66	0.12	81	0.23	95	0.04	114	0.08	138	1.18	176			
27	0.25	41	0.35	55	1.35	67	0.29	82	1.91	98	0.27	115	0.59	140	0.39	177			
28	0.27	42	1.35	56	9.16	68	4.18	83	1.62	99	0.92	116	0.42	143	0.02	185			
29	19.76	43	0.47	57	17.40	69	34.97	86	0.78	100	0.28	117	1.44	144	0.04	186			
30	0.28	44	0.04	58	0.62	70	0.48	87	11.49	102	0.03	118	0.24	154	14.53	187			
31	7.69	45	2.79	59	0.58	71	1.38	88	0.78	105	23.48	119	0.31	155	21.45	203			
32	0.28	47	0.14	60	0.08	74	0.75	89	0.42	107	25.68	121	0.17	157	3.34	204			
33	0.13	48	0.25	61	0.09	75	14.86	90	1.92	108	1.14	123	17.06	158	0.17	205			
36	0.71	49	1.15	62	0.31	76	0.72	91	0.76	109	0.07	126	10.22	159	0.04	206			
37	0.07	50	3.21	63	0.73	77	0.10	93	3.09	110	0.56	127	0.45	165	0.10				

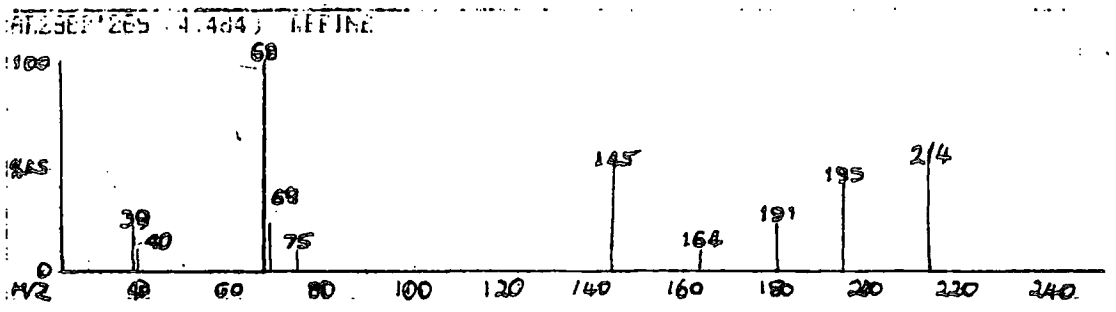
Spectrum 25



AR291CD'176 (2.934) REFINE

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
24	0.09	42	4.21	55	0.16	79	0.62	96	0.25	115	0.82	132	1.50	151	1.23	201	0.47
25	0.37	43	0.38	60	0.24	80	2.22	99	0.17	117	1.03	137	1.50	152	1.50	221	15.04
26	0.05	44	0.28	61	0.59	81	1.76	95	5.64	118	2.32	138	2.44	153	54.95	227	0.15
27	1.15	45	0.37	62	13.45	82	1.99	100	0.62	119	1.41	140	0.18	154	4.21	224	32.23
28	1.22	46	0.07	63	38.96	83	11.62	101	5.43	122	0.13	141	0.68	162	0.13	205	0.13
29	33.48	47	0.17	64	3.80	84	0.68	102	0.76	123	0.44	143	11.87	165	0.15	206	0.16
30	0.24	48	0.12	65	0.38	85	0.28	103	0.13	123	0.59	144	0.71	177	1.69	207	0.14
31	4.11	49	1.70	66	0.45	86	0.73	104	0.17	124	1.38	145	1.75	178	14.81	211	0.56
32	0.34	50	9.17	68	100.00	87	6.79	105	0.61	125	0.66	146	0.23	177	0.61	213	0.15
33	0.24	51	0.73	69	43.21	88	7.54	106	7.54	126	0.52	150	0.93	181	7.56	214	0.15
34	0.05	52	0.37	70	1.41	89	0.42	107	12.02	127	0.13	151	0.31	183	45.46	230	15.21
36	0.78	53	1.22	71	1.18	90	0.58	108	0.72	130	0.17	152	1.66	183	9.78	231	0.44
37	7.13	54	0.12	73	1.14	91	0.34	110	0.27	131	1.83	153	0.51	184	0.32		
38	11.62	55	2.89	74	0.82	92	1.24	111	1.14	132	48.76	154	5.63	185	15.15		
39	25.54	56	5.10	75	18.21	93	15.92	112	5.16	133	17.55	155	0.36	186	2.73		
40	0.78	57	17.85	76	0.81	94	1.66	113	17.29	134	0.53	156	18.23	191	0.22		
41	0.07	58	0.65	77	0.32	95	4.55	114	18.25	135	0.36	157	1.12	199	0.17		

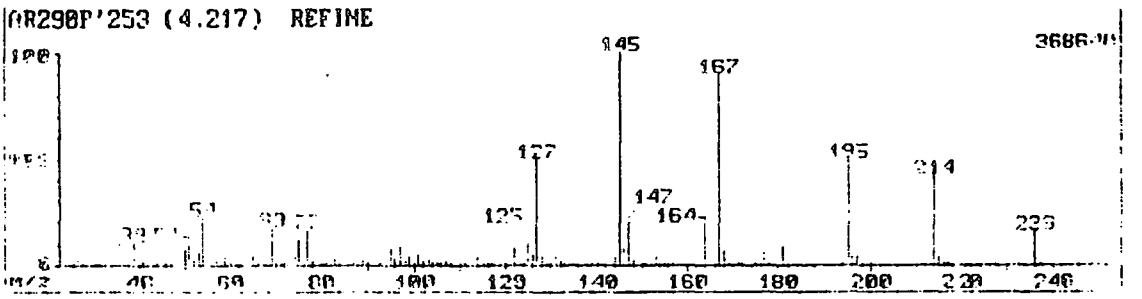
Spectrum 26



No 26

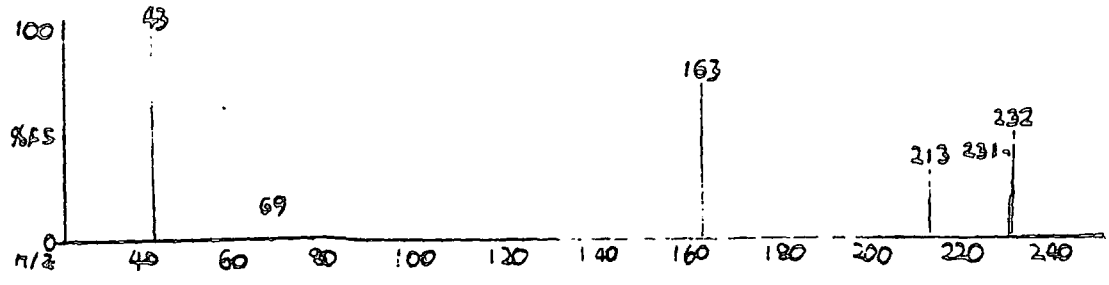
Mass	Rel. Int.
39	21.17
40	10.53
68	100.00
69	23.56
75	11.80
145	49.76
164	12.08
181	23.09
195	41.63
214	50.72

Spectrum 27



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
26	0.65	52	2.33	78	2.80	89	1.67	105	0.46	123	1.81	140	0.85	157	0.33	194	1.10
27	2.89	53	5.45	71	1.32	99	1.11	106	0.46	124	0.37	141	0.15	159	0.05	195	49.72
28	0.57	54	22.22	72	1.27	91	0.28	107	1.55	125	11.66	143	1.51	161	0.15	196	4.13
29	1.85	55	1.27	73	0.56	92	0.31	108	0.30	126	5.09	144	4.16	164	15.17	197	4.22
30	0.43	56	0.67	74	4.29	93	1.27	109	0.82	127	49.73	145	100.00	165	1.07	198	0.46
39	10.97	57	4.27	75	11.32	94	1.23	110	0.10	128	4.06	146	7.57	167	88.89	200	0.24
40	2.28	58	0.42	76	2.20	95	7.95	111	0.12	129	0.15	147	20.28	168	6.35	201	0.33
41	1.77	59	4.31	77	15.60	96	2.90	112	0.31	130	0.25	148	1.73	169	0.46	213	3.43
44	0.14	60	0.47	78	1.91	97	0.47	114	4.27	131	3.66	149	0.14	171	1.00	214	41.94
45	0.54	61	0.78	79	1.82	98	1.61	115	1.18	132	1.52	150	0.74	172	0.10	215	3.47
46	0.39	62	1.16	80	0.72	99	3.56	116	0.21	133	1.98	151	1.21	175	0.14	216	0.13
47	0.72	63	1.51	81	1.25	100	1.00	117	0.49	134	0.26	152	0.62	176	0.06	217	0.09
48	0.04	64	1.29	83	2.88	101	5.00	119	2.17	135	0.13	153	2.96	177	6.04	233	15.65
49	0.53	65	4.24	84	0.55	102	2.05	120	0.42	137	0.47	154	0.32	178	0.56	237	1.35
50	6.32	66	0.58	87	0.69	103	4.03	121	3.11	138	0.16	155	0.23	181	0.65	245	1.22
51	11.11	69	17.58	88	1.41	104	0.35	122	11.39	139	1.25	156	0.32	188	0.13		

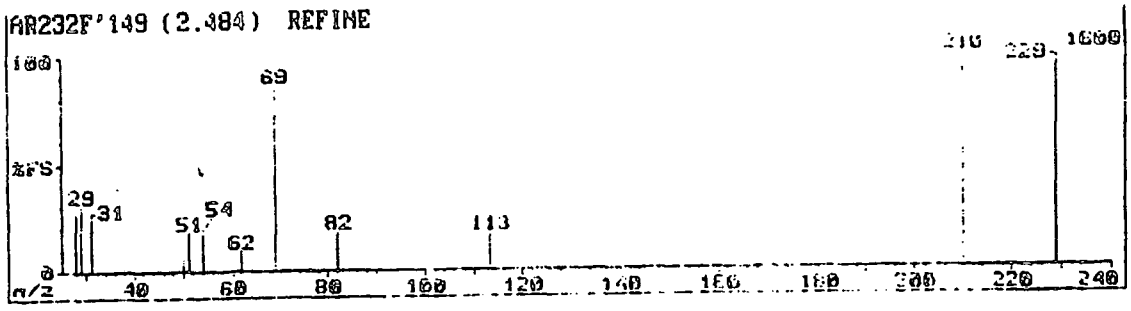
Spectrum 28



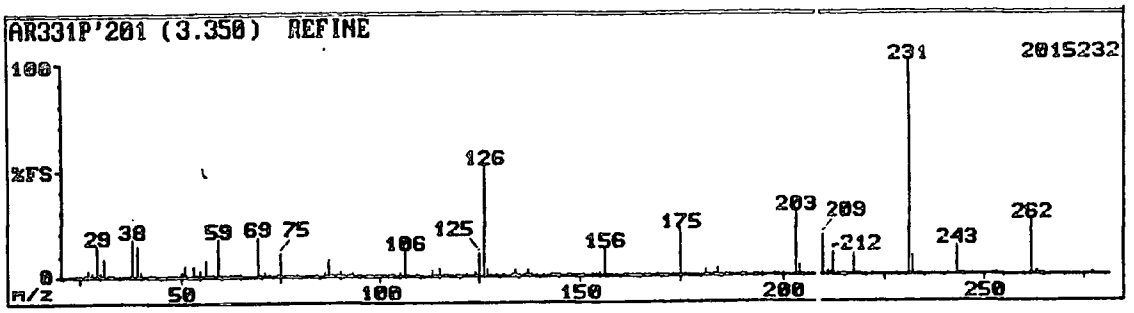
No 28

Mass	Rel. Int.
43	100.00
69	12.43
163	73.33
213	32.73
231	34.70
232	49.70

Spectrum 29


AR232F'149 (2.484) REFINE
100
%FS
0
m/z
29
31
51
54
62
69
82
113
210
229
1000
40
60
80
100
120
140
160
180
200
220
240

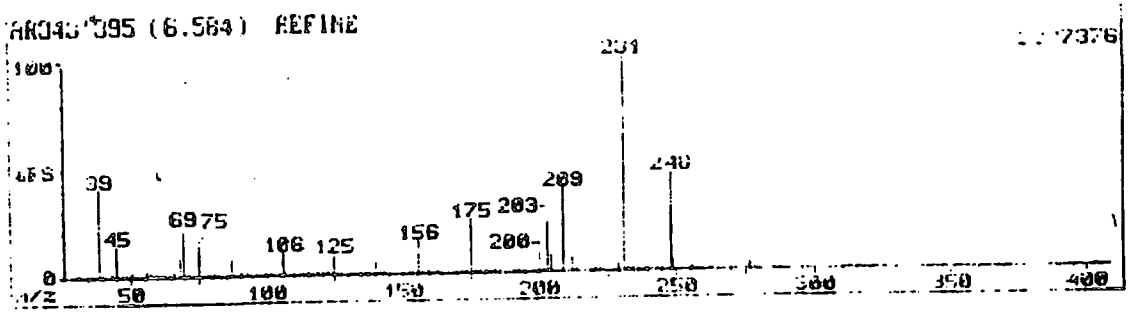
Spectrum 30



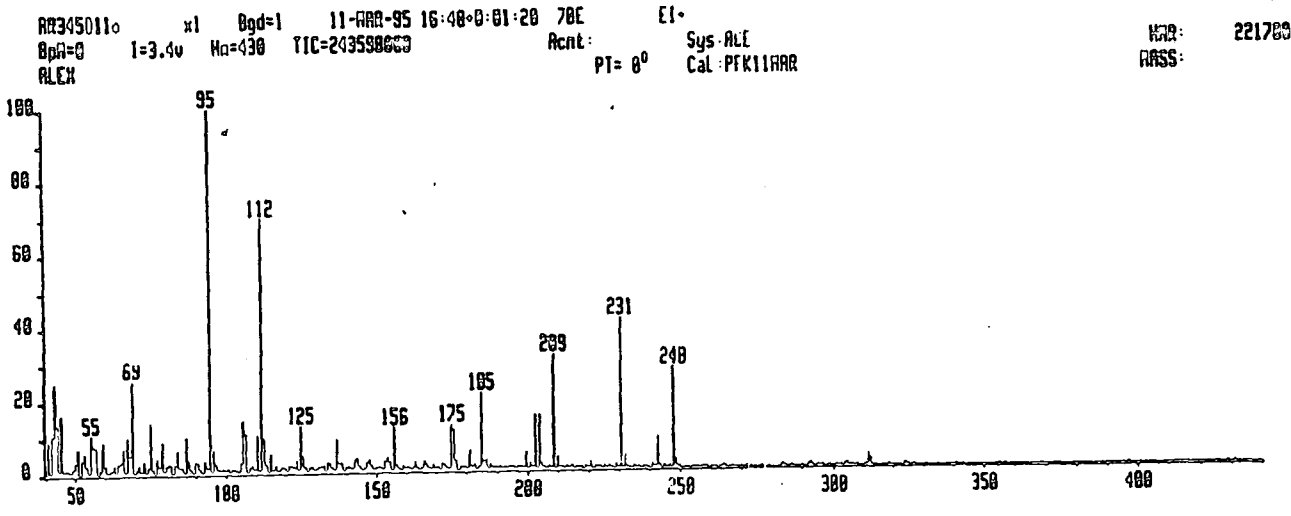
AR331P'201 (3.350) REFINE 2015232

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
24	0.06	53	4.67	76	0.40	103	0.07	128	0.58	153	0.51	175	28.93	203	20.06	233	1.03
25	0.49	54	0.91	77	0.49	105	1.96	129	0.08	154	0.15	176	1.41	204	4.03	234	0.15
26	1.32	55	2.76	78	0.06	106	11.23	131	0.04	155	1.99	177	0.08	205	0.42	241	0.02
27	2.72	56	0.03	79	0.21	107	0.09	133	0.37	156	12.50	178	0.03	206	0.04	243	13.21
28	1.69	57	1.24	84	0.23	109	0.07	134	3.21	157	0.79	181	3.85	209	18.78	244	1.19
29	14.84	58	0.07	86	1.63	113	2.50	135	0.36	158	0.05	182	0.22	210	1.47	245	0.15
30	3.38	59	17.28	87	7.37	114	0.09	136	0.39	159	0.05	183	0.28	211	0.12	247	0.03
31	9.10	60	0.41	88	0.55	115	3.96	137	2.71	161	0.61	184	3.91	212	11.03	253	0.02
32	0.23	61	0.16	89	0.11	116	0.29	138	0.20	162	0.23	185	0.57	213	1.07	262	25.20
33	0.31	62	0.28	90	2.52	117	1.13	139	0.21	163	0.46	186	0.05	214	0.12	263	2.21
38	17.28	63	0.25	91	0.34	118	0.12	141	0.28	164	0.06	187	0.06	215	0.05	264	0.26
39	14.23	64	0.32	92	0.71	119	0.34	143	1.11	165	0.08	190	0.10	217	9.55	265	0.03
40	2.81	65	0.91	93	2.22	120	0.07	144	0.20	166	0.02	191	0.34	218	0.76	277	0.06
42	1.16	69	18.09	97	1.41	121	0.55	145	0.06	167	0.13	193	0.90	219	0.71		
43	0.97	70	0.44	98	0.63	122	0.11	147	0.04	169	0.13	194	0.17	220	0.06		
47	1.21	71	2.23	99	0.32	124	1.46	148	0.05	170	0.02	195	0.06	222	0.03		
48	0.22	72	0.11	100	0.09	125	18.52	149	0.14	171	0.06	198	0.30	228	0.07		
50	1.68	74	0.98	101	0.41	126	51.63	150	0.07	172	0.09	199	0.04	231	100.00		
51	4.42	75	18.37	102	0.23	127	4.07	151	0.04	173	0.10	200	0.07	232	0.79		

Spectrum 31


100
%
0
m/z
50
100
150
200
250
300
350
400
39
45
69
75
106
125
156
175
203
200
209
231
240

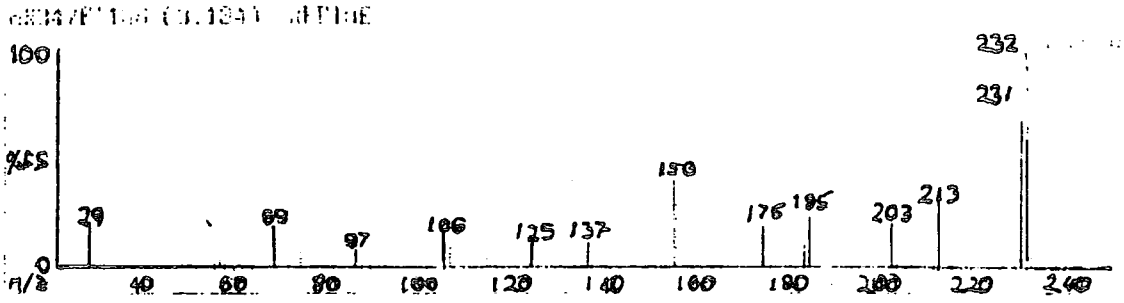
Spectrum 32



AR345011o x1 Bgd=1 11-MAR-95 16:48+0:01:20 70E EI+
BpM=0 I=3.4v MA=430 TIC=243598000 Acnt: Sys:ACE
ALEX PT= 0 Cal:PFK11MAR

MASS	% BASE	MASS	% BASE
41.00	8.89	94.95	100.00
42.00	10.76	95.96	6.25
43.00	24.79	96.99	2.34
43.97	13.32	97.99	0.94
44.97	16.09	98.97	1.15
45.98	0.60	99.96	0.65
46.97	1.15	100.97	1.10
47.02	0.34	101.95	0.72
47.96	0.62	102.95	1.18
48.98	1.46	103.95	0.79
49.98	3.20	104.95	3.10
50.99	6.78	105.93	14 43
51.99	3.87	106.95	10.55
52.98	5.42	107.96	1.37
54.00	2.56	108.97	1.90
55.00	10.47	109.97	0.98
55.99	7.54	110.96	10.40
56.98	7.08 F	111.94	69.46
57.04	4.56 F	112.94	9.40
58.02	1.16	113.94	2.38
58.98	8.54	114.93	5.09
59.99	2.46	115.95	0.85
60.99	0.65	116.94	1.77
61.97	0.82	117.96	0.57
62.98	2.39	118.95	1.25
63.97	2.61	119.95	0.94
64.98	3.34	120.94	1.80
65.98	7.01	121.95	1.88
66.98	10.00	122.96	1.37
67.97	5.20	123.92	3.56
68.95	25.56	124.92	12.70
69.99	0.98	125.93	4.10
70.94	2.44 F	126.95	1.54
71.03	2.12 F	127.93	1.10
71.99	0.92	128.97	1 49
72.98	3.26	129.97	0.60
73.96	1.74	130.94	1.01
74.99	13.91	131.95	1.25
75.96	1.43	132.95	1.61
76.98	4.18	133.93	2.90
77.98	2.15	134.93	2.40
78.99	8.64	135.94	1.05
79.87	0.35	136.93	8.82
79.99	2.19	137.96	2.44
80.96	2.67 F	138.95	2.27
81.02	1.70 F	139.96	0.89
81.97	2.38	140.94	1.26
82.98	2.46	141.89	0 54
83.96	6.60 F	142.93	3.32
84.03	1.61 F	143.91	3.46
85.00	1.68	144.94	1.32
85.95	1.86	145.95	0.65
86.94	9.77	146.95	2 31
87.95	3.38	147.97	2.94
88.97	1.01	148.94	1 70
89.93	3.18	149.93	0.81
90.07	2.85	150.93	1 03
91.97	1.02	151.94	1.15
92.99	3.52	152.91	2.81
93.06	1.63	153.91	3.88
154.91	2.52	214.91	0.99
155.90	11.88	215.90	0.69
156.92	1.83	216.92	0.61
157.94	0.65	217.92	0.55
158.94	1.38	218.90	1.07
159.95	0 78	219.91	0.66
160.92	1.09	220.91	2.34
161 90	0.65	221.92	0.57
162.91	2.41	222.91	0.60
163.92	0.68	223.90	0.74
164 95	0.82	224.91	0.87
165.95	2.61	225.90	0.47
166.95	1.59	226.89	0.87
167.93	0.59	227.92	0.43
168.91	1.57	228.88	1.64
169.92	0 79	229.87	0.82
170 95	0.91	230.85	41.46
171.90	2.11	231.85	3.94
172.93	1.56	232.89	0.62
173.94	0.75	233.92	0.50
174 89	12.70	234.89	1.09
175.93	11.05	235.91	0.46
176.95	2.81	236.91	0.57
177 93	0.86	237.92	0.46
178.93	0.94	238.92	0.52
179.93	0.88	239.91	0.43
180.88	5.63	240.88	1.76
181 91	1.05	241.89	0.96
182.92	1.73	242.86	9.00
183.91	1.06	243.87	1.40
184 89	21.30	244.89	1.17
185.89	2.31	245.90	0.31
186.89	3.04	246.87	0.75
187.89	1.59	247.84	27.68
188.92	0.79	248.85	2.80
189.94	0.68	249.85	0.54
190.93	0.73	250.87	0.38
191.93	0.37	251.92	0.44
192.91	0.66	252.89	0.50
193.91	0.74	253.87	0.49
194.91	0.83	254.88	0.80
195.91	0 92	255.92	0.58
196.93	1.06	256.90	0.51
197.92	0.93	257.88	0.79
198.94	0.65	258.89	0.68
199.87	4.76	259.88	0.62
200.91	1.99	260.89	0.61
201.92	1.15	261.87	0.71
202.86	15.10	262.89	0.36
203.87	15.19	263.87	1.60
204.90	1.57	264.90	0.90
205.90	0.56	265.90	0.46
206.90	1.10	266.89	0.97
207.90	0.66	268.89	0.40
208.85	31.47	269.89	0.83
209.87	3.49	270.87	0.43
210.89	0.80	271.87	1.09
211.90	0.73	272.86	1.00
212.90	1.05	273.86	0.35
213.91	0 42	274.88	0.43
		279.89	1.24
		276.90	0.59
		280.87	1.09
		282.88	0.65
		283.87	2.57
		284.85	0.77
		285.91	0.32
		291.88	1.17
		292.86	1.41
		293.88	0.30
		294.88	0.49
		301.86	0.36
		303.87	0.91
		304.88	1.32
		305.87	0.40
		306.87	0.31
		311.86	3.48
		312.86	1.90
		313.89	0.31
		323.86	1.10
		324.87	0.30
		330.86	0.36
		340.81	0.33
		354.87	0.47
		368.89	0.30
		396.88	0.37

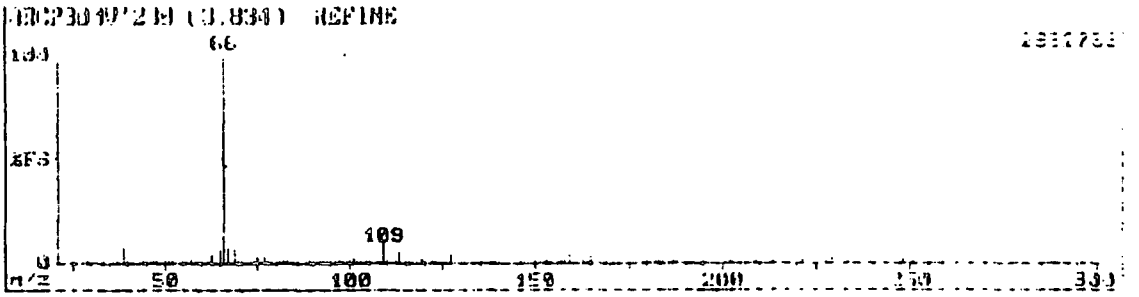
Spectrum 33



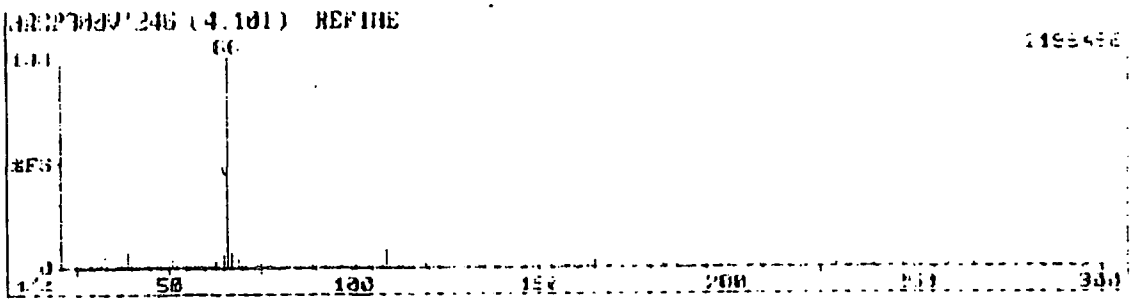
No 33

Mass	Rel. Int.
29	80.00
69	19.77
87	9.09
106	15.91
125	12.39
137	13.75
156	41.82
175	20.91
185	26.41
203	20.91
213	29.77
231	69.09
232	100.00

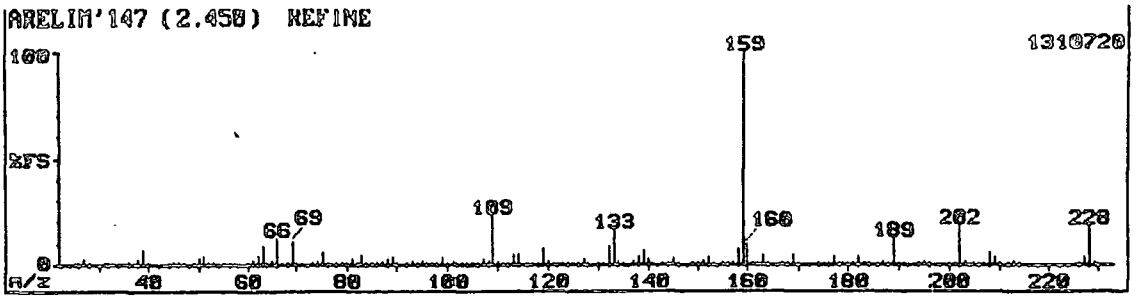
Spectrum 34



Spectrum 35



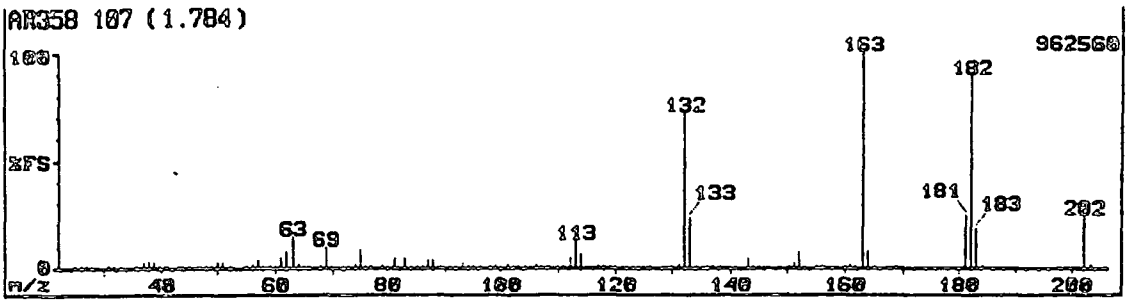
Spectrum 36



ARELIM'147 (2.458) REFINE 1310720

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
25	0.00	51	4.24	74	1.72	93	1.84	111	0.47	131	0.74	153	0.38	177	3.65	201	0.97
26	0.92	52	0.58	75	5.65	94	0.82	112	1.16	132	0.91	155	0.13	178	0.69	202	18.28
27	2.70	53	0.17	76	0.51	95	1.68	113	5.23	133	16.09	156	0.73	179	0.04	203	1.48
28	0.39	55	0.12	77	1.00	96	0.35	114	4.02	134	1.09	157	1.37	189	0.65	205	0.09
31	0.93	56	0.63	78	0.15	97	0.00	115	0.06	135	0.13	158	7.73	181	1.35	206	0.05
32	0.09	69	0.20	79	0.79	98	0.19	117	0.31	137	1.09	159	100.00	182	4.02	207	1.14
33	0.23	61	1.58	80	0.72	99	3.55	118	0.71	138	3.73	160	9.38	183	1.35	208	6.25
36	0.05	62	3.09	81	2.48	100	0.63	119	0.13	139	6.41	161	0.59	184	0.11	209	3.09
37	0.94	63	0.44	82	0.56	101	2.36	120	1.86	140	3.07	162	0.24	186	0.10	210	0.38
38	2.58	64	1.39	83	4.65	102	0.34	121	0.34	141	0.29	163	5.66	187	2.01	212	0.08
39	7.11	65	2.34	84	0.59	103	0.10	122	0.05	143	0.98	164	0.78	188	0.74	213	1.72
40	1.41	66	12.09	85	0.53	104	0.17	123	0.26	144	0.68	167	0.14	189	12.50	214	0.17
44	0.12	67	0.72	86	0.98	105	0.42	124	0.28	145	2.75	168	0.24	190	1.29	226	0.17
45	0.19	68	0.70	87	2.29	106	0.76	125	1.31	146	0.32	169	4.61	191	0.08	227	3.73
46	0.05	69	18.47	88	2.68	107	2.62	126	0.65	149	0.09	170	0.49	194	0.11	228	18.91
47	0.04	70	1.04	89	3.49	108	1.06	127	2.54	150	0.38	174	0.05	195	1.09	229	2.01
49	0.27	71	0.17	90	1.03	109	23.75	128	0.23	151	1.60	175	0.12	196	0.19	230	0.11
50	2.01	73	0.24	92	0.37	110	1.97	130	0.13	152	4.10	176	0.62	200	0.03		

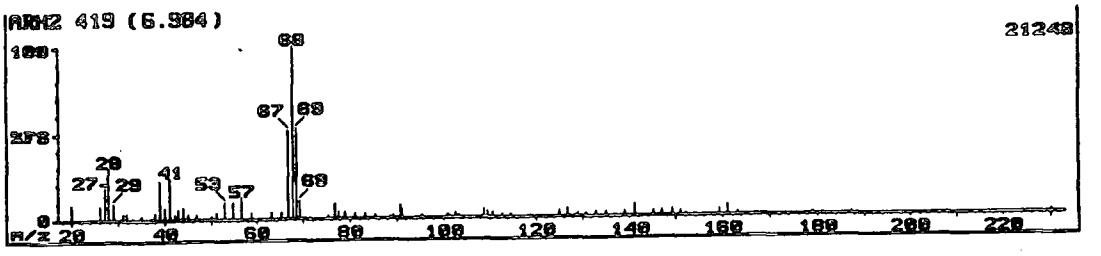
Spectrum 37



AR358 107 (1.784)

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
25	0.03	44	0.54	61	4.68	76	0.47	92	1.02	107	0.43	124	0.52	145	0.14	181	24.47
26	0.10	45	0.17	62	7.93	77	0.19	93	2.82	108	0.14	125	0.32	150	0.39	182	69.35
27	0.12	47	0.09	63	15.60	79	0.62	94	1.82	110	0.14	126	0.10	151	2.59	183	17.98
28	0.25	48	0.09	64	1.48	80	0.93	95	0.75	111	1.18	130	0.37	152	7.34	184	1.17
31	1.60	49	0.61	65	0.89	81	4.44	96	0.85	112	4.41	131	1.09	153	0.53	201	0.72
32	0.20	50	1.35	66	0.57	82	1.34	98	0.12	113	12.77	132	71.91	155	0.19	202	24.65
33	0.07	51	1.01	68	2.21	83	4.39	99	2.13	114	6.54	133	23.62	156	0.47	203	1.73
35	0.15	52	0.69	69	16.88	84	0.23	100	0.23	115	0.45	134	1.45	159	0.11		
37	2.45	55	0.51	70	0.47	85	0.07	101	1.69	117	0.74	135	0.44	161	2.65		
38	1.27	56	2.10	71	0.07	86	0.23	102	0.39	118	0.21	137	1.39	162	0.71		
39	2.61	57	4.35	72	0.05	87	1.78	103	0.09	119	0.40	138	0.27	163	100.00		
40	0.14	58	0.19	73	0.41	88	3.49	104	0.09	120	0.05	141	0.14	164	5.89		
41	0.04	59	0.05	74	1.78	89	0.23	105	0.31	122	0.05	143	4.69	165	0.35		
43	0.07	60	0.49	75	0.94	91	1.32	106	1.04	123	0.31	144	0.45	169	0.20		

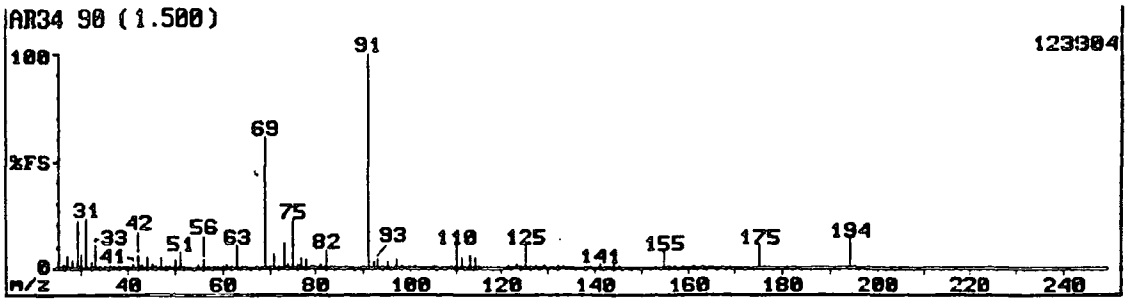
Spectrum 38



ARH2 419 (6.984) 2124

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	9.19	50	2.18	85	1.54	131	1.94
26	7.30	51	4.16	89	0.95	133	2.43
27	18.15	53	9.49	89	2.09	135	3.03
28	29.82	55	9.94	91	7.91	137	1.00
29	9.94	57	12.42	91	4.78	139	2.65
31	4.29	59	4.09	95	2.01	141	6.40
32	3.77	63	3.82	101	2.37	145	3.31
33	0.63	65	4.09	101	2.28	147	3.24
35	1.58	67	51.51	103	2.86	149	3.60
37	1.37	68	100.00	103	2.28	151	2.84
38	4.12	69	52.71	109	4.97	152	1.34
39	22.29	69	10.92	109	3.92	159	4.27
40	7.08	71	0.72	111	3.26	161	5.35
41	24.70	75	1.73	113	1.66	163	1.79
42	3.01	77	8.89	115	2.03	167	0.80
43	5.65	77	3.93	119	1.10	179	1.73
44	6.55	79	4.29	125	3.58	181	1.37
45	2.45	81	2.79	127	4.80	187	1.56
47	3.03	83	2.58	129	1.66	230	1.71

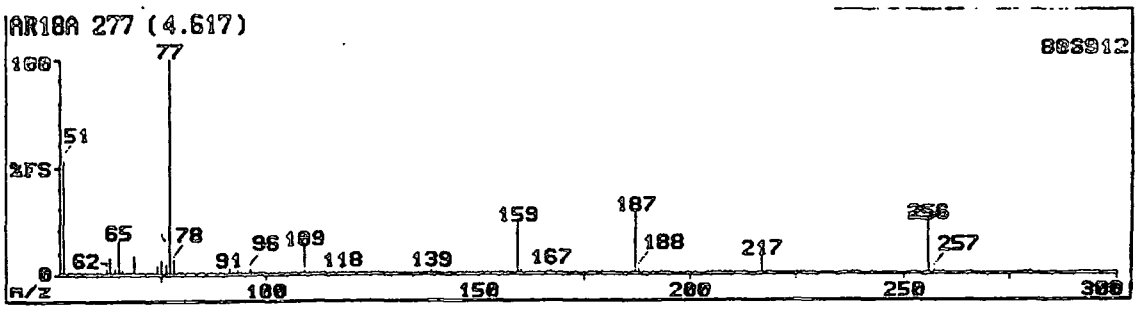
Spectrum 39



AR34 90 (1.500) 123904

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
25	0.84	51	7.95	80	0.36	123	1.46
26	1.83	52	0.29	81	2.21	124	0.85
27	5.37	53	0.90	82	8.78	125	10.80
28	3.62	55	1.89	83	0.40	126	0.74
29	22.52	56	3.41	84	0.12	127	0.70
30	6.35	57	1.12	86	0.19	129	0.19
31	23.14	58	0.16	90	0.67	132	2.26
32	2.48	59	0.79	91	100.00	133	0.16
33	10.85	60	0.62	92	3.28	139	0.41
34	0.24	61	2.16	93	3.56	141	2.32
35	0.15	62	0.93	94	1.11	142	1.07
36	0.36	63	11.00	95	2.49	143	0.37
37	0.85	64	0.74	97	3.51	144	1.67
38	0.36	65	0.24	98	0.14	145	0.29
39	0.67	67	0.17	100	0.21	155	7.64
40	0.33	69	61.16	101	0.45	156	0.99
41	2.04	70	1.07	105	0.33	157	0.60
42	6.10	71	6.51	106	0.19	159	0.08
43	2.35	72	0.54	109	0.33	161	0.39
44	4.49	73	11.88	110	11.00	163	0.15
45	1.76	74	2.38	111	5.27	175	10.80
46	0.33	75	21.90	112	0.36	176	0.58
47	5.27	76	1.81	113	6.30	194	13.84
48	0.26	77	5.32	114	4.91	195	0.70
49	0.72	78	3.67	115	0.22		
50	4.34	79	0.30	121	0.14		

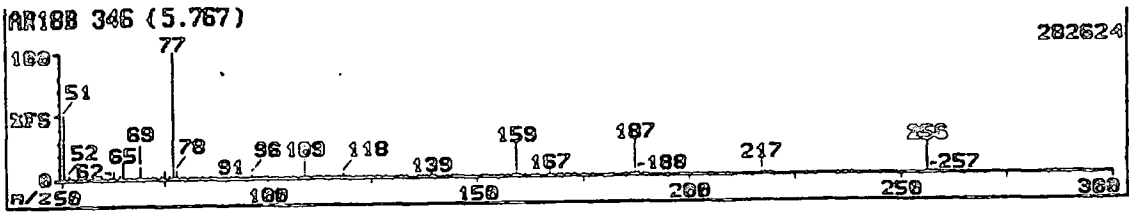
Spectrum 40



AR18A 277 (4.617) 806912

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
51	53.81	93	1.75	136	0.35	185	0.28
52	2.51	94	1.22	137	0.20	186	0.78
53	0.86	95	0.95	138	0.35	187	28.55
54	0.21	96	2.63	139	3.01	188	3.54
55	0.55	97	0.27	140	0.46	189	0.35
56	0.42	98	0.02	141	0.07	190	0.03
57	0.46	99	0.16	143	0.10	191	0.02
58	0.07	100	0.06	144	0.07	193	0.01
59	0.21	101	0.31	145	0.33	194	0.02
60	0.24	102	0.06	146	0.03	195	0.04
61	0.91	103	0.04	147	0.01	200	0.01
62	2.60	104	0.02	148	0.03	201	0.02
63	7.46	105	0.09	149	0.10	204	0.02
64	3.36	106	0.05	150	0.02	205	0.02
65	15.10	107	0.22	151	0.08	207	0.12
66	1.55	108	0.41	152	0.02	208	0.10
67	0.13	109	12.94	154	0.05	209	0.02
68	0.51	110	1.27	155	0.02	213	0.02
69	8.88	111	0.12	156	0.05	216	0.13
70	0.57	112	0.12	157	0.19	217	7.58
71	0.47	113	0.81	158	0.56	218	0.70
72	0.08	114	0.14	159	23.48	219	0.05
73	0.71	115	0.04	160	1.86	227	0.03
74	4.06	116	0.03	161	0.06	228	0.10
75	7.20	117	0.05	162	0.02	229	0.02
76	4.47	118	2.60	163	0.08	235	0.22
77	100.00	119	0.94	164	0.03	236	0.05
78	6.41	120	0.20	165	0.01	237	1.21
79	0.30	121	0.22	166	0.06	238	0.12
80	0.08	122	0.02	167	4.22	239	0.01
81	0.18	123	0.03	168	0.39	243	0.01
82	0.65	124	0.10	169	0.42	248	0.01
83	0.45	125	0.11	170	0.03	255	0.49
84	0.82	126	0.06	171	0.03	256	24.49
85	0.06	127	0.48	173	0.02	257	3.22
86	0.07	128	0.06	175	0.01	258	0.14
87	0.11	129	0.03	176	0.02	259	0.01
88	0.13	130	0.01	177	0.15	265	0.01
89	0.48	131	0.04	178	0.04	266	0.01
90	0.51	132	0.15	179	0.01	279	0.02
91	2.70	133	0.05	181	0.02	280	0.01
92	0.59	134	0.01	182	0.02	300	0.01

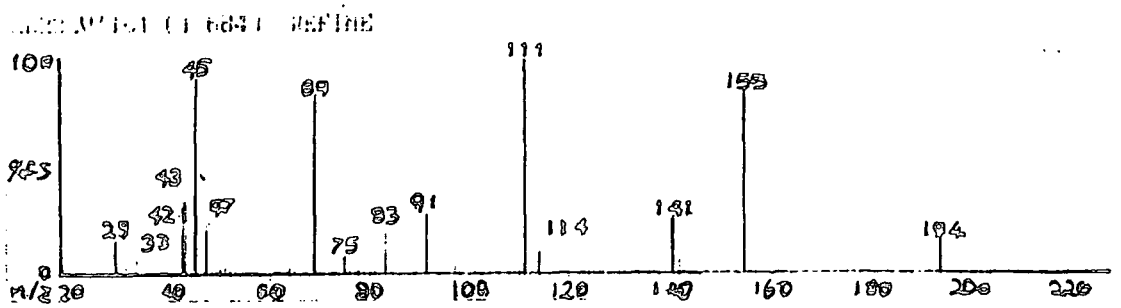
Spectrum 41



AR18B 277 (4.617) 1720320

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
50	12.20	92	0.54	133	0.04	177	0.17
51	44.05	93	1.53	134	0.01	178	0.03
52	2.08	94	1.07	136	0.26	179	0.00
53	0.71	95	0.83	137	0.15	181	0.02
54	0.16	96	2.25	138	0.29	182	0.02
55	0.44	97	0.22	139	2.32	185	0.32
56	0.35	98	0.03	140	0.35	187	32.14
57	0.36	99	0.14	141	0.04	188	2.77
58	0.05	100	0.04	142	0.01	189	0.38
59	0.17	101	0.26	143	0.10	190	0.04
60	0.21	102	0.05	144	0.06	195	0.03
61	0.83	103	0.02	145	0.26	197	0.01
62	2.37	104	0.01	146	0.02	198	0.01
63	6.55	105	0.06	147	0.01	202	0.01
64	3.14	106	0.04	148	0.01	204	0.01
65	13.39	107	0.20	149	0.08	205	0.01
66	1.38	108	0.45	150	0.01	207	0.12
67	0.10	109	11.37	151	0.07	208	0.11
69	8.63	110	1.13	152	0.02	209	0.02
70	0.57	111	0.10	153	0.01	213	0.01
71	0.42	112	0.12	154	0.07	217	3.52
72	0.08	113	0.76	155	0.01	218	0.84
73	0.74	114	0.13	156	0.01	219	0.06
74	4.17	115	0.03	157	0.14	227	0.02
75	7.20	116	0.02	159	26.19	228	0.09
76	5.18	117	0.07	160	1.93	229	0.01
77	100.00	118	2.23	161	0.09	235	0.28
78	6.31	119	0.80	162	0.02	237	1.46
79	0.29	120	0.17	163	0.08	238	0.12
80	0.04	121	0.17	164	0.06	239	0.01
81	0.16	122	0.02	165	0.01	254	0.01
82	0.61	123	0.01	167	4.82	255	0.87
83	0.42	124	0.09	168	0.44	256	29.52
84	0.72	125	0.08	169	0.47	257	2.57
86	0.02	126	0.05	170	0.05	258	0.17
87	0.10	127	0.37	171	0.03	272	0.01
88	0.11	128	0.05	172	0.01	285	0.01
89	0.46	129	0.01	173	0.02	288	0.01
90	0.47	131	0.01	175	0.01		
91	2.44	132	0.11	176	0.03		

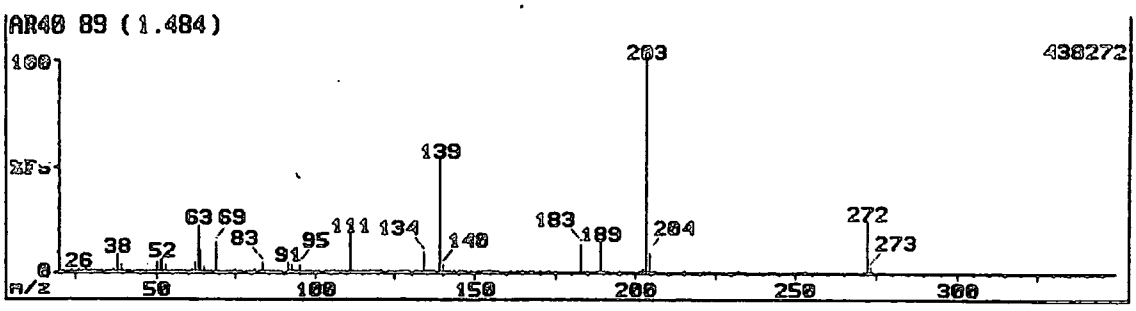
Spectrum 42



No 42

Mass	Rel. Int.
29	17.50
33	11.97
42	24.08
43	34.21
45	92.83
47	20.53
69	82.63
75	9.61
83	23.55
91	28.95
111	100.00
114	9.87
141	25.05
141	26.05
155	84.21
194	15.92

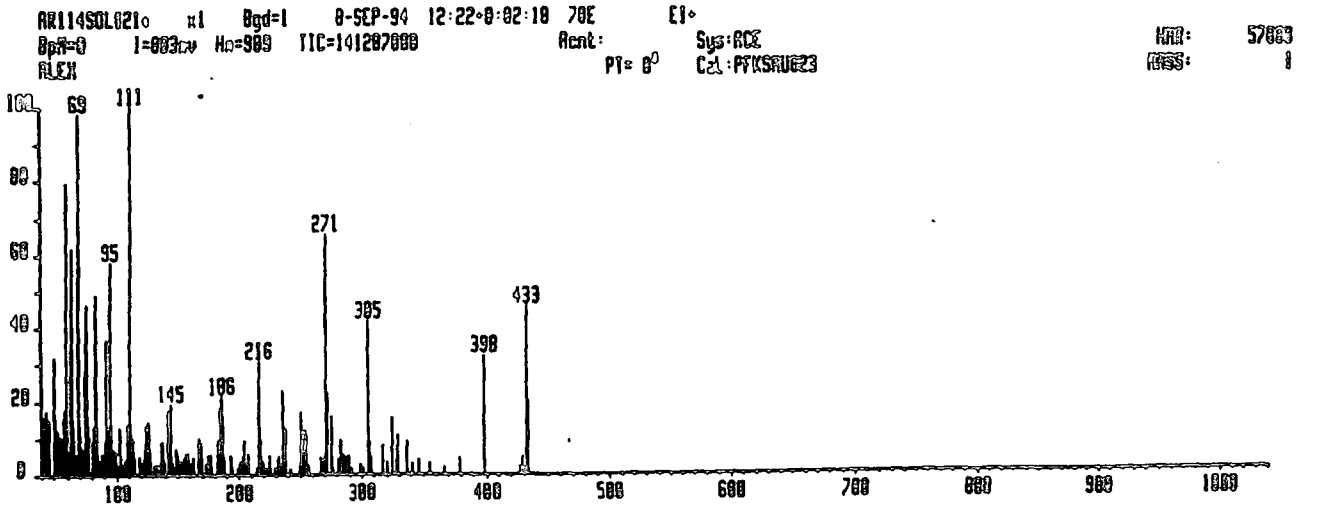
Spectrum 43



AR40 89 (1.484) 438272

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.04	63	21.96	105	0.32	151	0.16
24	0.03	64	10.98	106	0.12	152	0.25
25	0.16	65	2.73	107	0.35	153	0.07
26	2.34	66	0.47	108	0.10	154	0.11
27	1.18	67	0.24	109	0.47	155	0.14
28	1.72	69	14.72	111	18.69	156	0.07
29	0.66	70	0.30	112	0.78	157	0.07
30	0.08	71	0.37	113	0.73	161	0.09
31	0.99	72	0.05	114	0.21	163	0.12
32	0.63	73	0.31	115	0.10	165	0.06
33	1.21	74	0.49	116	0.18	166	0.13
35	0.06	75	2.35	117	0.06	167	0.07
36	0.14	76	0.71	118	0.08	168	0.07
37	2.34	77	0.83	119	0.53	170	0.10
38	8.41	78	0.79	120	0.27	173	0.08
39	3.43	79	0.82	121	0.20	175	0.06
40	0.32	80	1.04	123	0.18	183	13.79
41	1.01	81	1.90	124	0.08	184	1.42
42	0.84	82	0.36	125	0.19	185	0.18
43	0.69	83	4.44	126	0.17	188	0.10
44	1.05	84	0.23	127	1.33	189	14.43
45	0.51	85	0.13	128	0.14	190	1.23
46	0.05	86	0.08	129	0.12	191	0.12
47	0.33	87	0.08	131	0.12	195	0.21
48	0.06	88	0.08	132	0.16	201	0.53
49	0.51	89	0.12	133	0.52	202	2.34
50	4.56	91	4.91	134	9.40	203	100.00
51	5.84	92	4.09	135	0.88	204	9.58
52	6.95	93	0.83	136	0.17	205	0.92
53	3.53	94	0.30	137	0.11	206	0.09
54	0.79	95	4.26	139	53.04	215	0.07
55	0.78	96	0.45	140	4.09	221	0.05
56	0.30	97	0.49	141	0.50	223	0.09
57	0.61	98	0.10	142	0.07	232	0.10
58	0.06	99	0.11	143	0.26	253	0.55
59	0.10	100	0.10	145	0.67	271	0.14
60	0.28	101	0.31	146	0.24	272	24.30
61	1.68	103	0.09	147	0.09	273	2.60
62	5.02	104	0.18	149	0.11	274	0.24

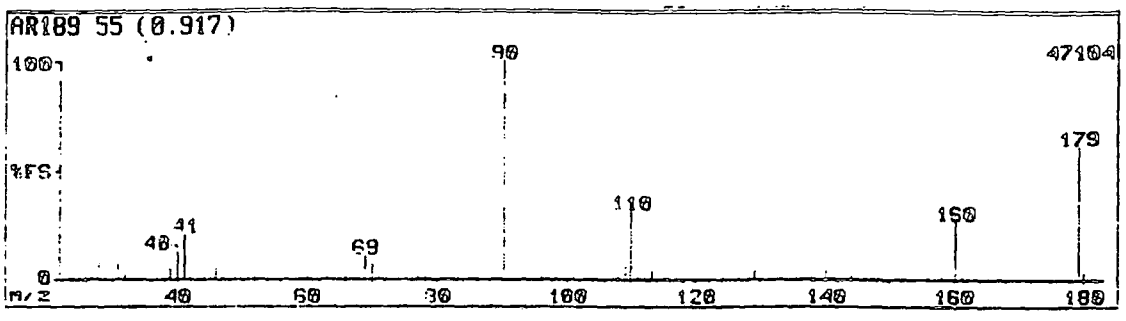
Spectrum 44



:114SOL821o x1 Bgd=1 8-SEP-94 12:22+0:02:18 70E EI+ 3.1
)N=0 I=883av Ha=989 TIC=141287000 Acnt: Sys:ACE
.EX PY= 0 Cal:PFKSAUG23

Mass	% Base		Mass	% Base	Mass	% Base	Mass	% Base
41.00	15.48		103.01	12.20	200.90	3.02	346.84	3.89
42.01	2.00		104.98	2.40	201.91	1.12	354.84	2.76
42.98	9.86		106.95	3.27	202.89	4.91	366.80	1.86
43.02	17.19		107.96	3.61	203.90	8.74	370.82	3.94
43.98	3.63		108.93	13.42	204.88	2.66	397.81	31.93
45.00	14.56		109.95	1.80	206.90	5.37	426.74	1.61
49.98	31.39		110.95	100.00	213.92	1.52	428.77	2.57
50.98	7.79		111.96	6.06	214.90	1.74	429.76	4.34
51.99	11.66		112.93	9.09	215.90	30.43	430.78	0.95
52.96	4.37		113.95	4.04	216.90	8.79	431.76	1.38
53.00	5.67		118.94	4.39	217.88	1.92	432.80	46.21
53.97	9.99		120.93	1.12	218.89	3.11	433.79	19.66
54.01	1.55		121.03	2.61	219.89	1.02		
54.98	2.89		122.95	6.36	220.95	1.31		
55.02	9.42		123.92	13.03	222.89	1.14		
56.02	2.35		124.91	3.01	224.88	4.87		
56.98	3.42		125.95	13.87	228.88	1.36		
57.03	14.96		126.96	6.36	230.89	3.90		
59.00	17.05		128.91	0.85	231.88	4.82		
59.01	79.04		130.92	2.00	232.89	2.33		
60.02	2.45		131.00	1.14	233.87	1.90		
61.98	5.98		133.00	2.25	234.89	22.67		
62.98	33.17		135.95	2.95	235.89	11.58		
63.99	61.54		136.92	8.43	236.87	12.39		
64.99	9.30		137.04	3.11	241.89	0.90		
67.01	5.22		137.94	8.72	248.88	2.23		
68.95	98.05 F		138.95	3.37	249.87	2.49		
69.03	20.63 F		142.91	16.98	250.87	16.71		
69.99	0.97		143.91	1.05	252.85	9.07		
71.00	1.76		144.94	18.68	253.87	11.58		
71.04	6.84		145.95	3.13	254.87	10.26		
72.99	5.95		146.97	1.59	256.86	2.44		
73.98	6.80		148.93	6.55	266.86	4.54		
74.97	28.09		149.02	2.09	268.85	3.65		
75.98	46.06		149.93	4.89	269.85	4.98		
76.98	10.00		150.94	3.44	270.88	64.98		
79.97	8.45		151.96	3.51	271.89	22.06		
80.98	8.69 F		153.93	2.95	274.85	15.50		
81.01	12.70 F		154.92	3.97	275.88	1.45		
81.95	9.31		156.92	4.99	280.89	3.87		
82.96	48.69 F		157.93	4.49	282.87	8.86		
83.02	6.43 F		158.86	5.53	284.86	5.03		
83.98	2.56		160.88	2.61	285.88	2.68		
85.04	3.58		162.91	4.60	286.86	4.39		
86.98	5.20		166.93	9.68	287.88	1.00		
87.98	1.19		167.92	4.73	288.89	4.91		
88.99	5.25		168.92	8.10	290.86	1.31		
90.94	9.36		169.95	2.82	298.85	2.30		
91.97	38.48		172.92	2.38	300.85	1.52		
92.95	11.68		174.92	4.63	304.84	41.60		
93.98	1.87		176.93	5.04	305.84	8.00		
94.98	97.38 F		181.91	8.85	306.82	8.62		
95.02	7.77 F		182.92	2.51	307.85	4.84		
95.97	5.32		184.91	17.90	316.85	7.38		
96.03	2.07		185.92	20.80	320.82	3.02		
96.92	6.39		186.91	15.65	324.82	15.20		
97.03	3.23		187.91	4.06	327.85	3.47		
98.94	5.68		192.91	4.79	328.84	10.40		
99.93	2.11		193.91	1.81	336.83	0.80		
100.97	1.74		198.90	1.21	340.82	2.97		

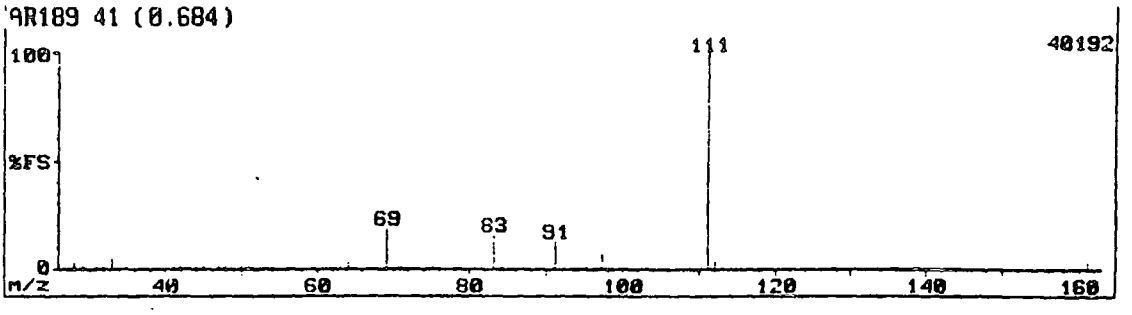
Spectrum 45



AR189 55 (0.917) 47104

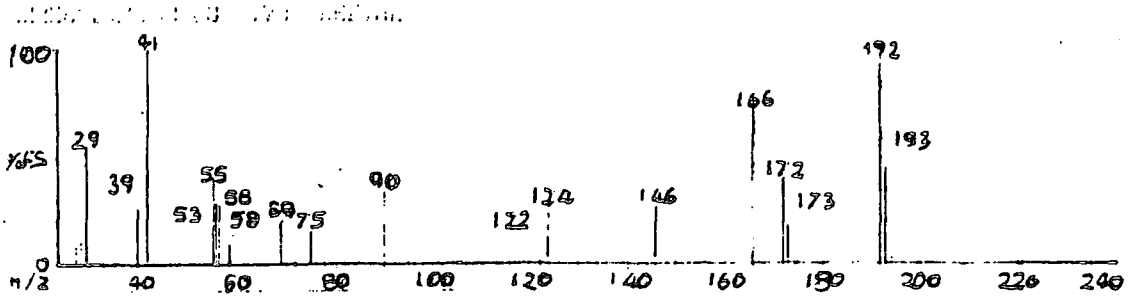
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
25	0.59	47	0.31	78	3.44	120	0.96
26	0.99	50	3.28	82	3.80	124	0.53
27	1.39	51	1.45	83	0.34	128	0.71
28	7.47	52	1.14	89	1.92	129	3.63
29	1.20	29	0.80	90	100.00	138	0.92
31	6.39	60	0.64	91	5.10	140	3.91
38	2.31	63	1.07	93	1.53	144	2.21
39	0.83	65	0.67	96	7.00	146	0.51
38	3.09	66	0.74	97	0.54	158	0.69
39	5.06	69	10.73	98	0.68	160	25.95
40	12.83	70	6.69	108	1.99	161	1.34
41	20.11	71	0.31	109	5.77	179	60.87
42	0.74	72	0.35	110	31.39	180	2.92
44	1.25	74	0.99	111	1.29		
45	1.00	75	1.49	113	3.57		
46	4.55	77	0.91	117	0.58		

Spectrum 46



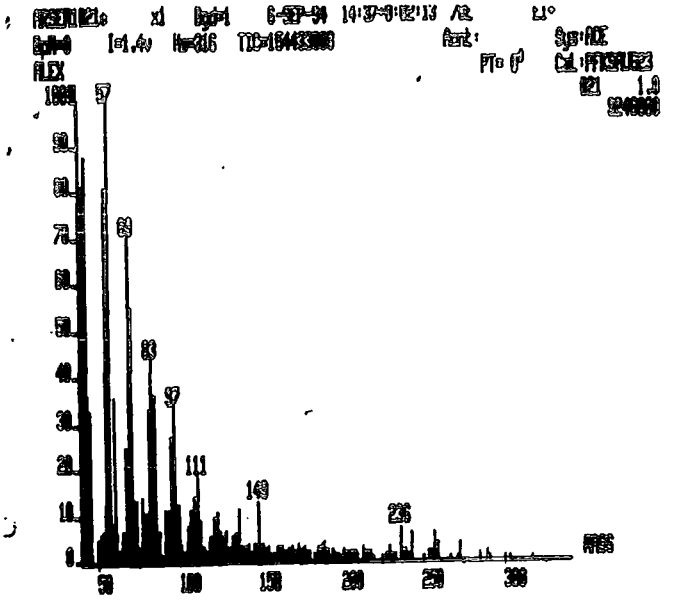
AR189 41 (0.684)								40192
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	
38	3.30	44	3.12	69	18.95	92	0.66	
39	0.31	45	3.19	71	1.04	95	0.58	
41	3.90	47	1.26	75	0.53	97	7.05	
42	2.47	48	1.11	78	0.92	110	0.73	
43	2.85	50	2.33	82	0.72	111	100.00	
41	0.96	51	1.04	83	15.56	112	3.70	
42	2.05	53	3.14	84	3.53	113	1.00	
43	1.38	54	3.34	91	13.69	161	3.11	

Spectrum 47



No 47	
Mass	Rel. Int.
29	55.14
39	25.93
41	100.00
53	11.69
55	37.05
56	26.75
69	21.26
75	16.24
90	34.58
122	16.47
124	27.22
146	27.10
166	71.96
172	39.72
173	17.41
192	95.33
193	45.79

Spectrum 48



Mass	% Base
109.08	3.67
110.08	4.97
111.10	9.81
112.10	3.39
113.09	3.39
114.05	2.14
115.06	12.46
116.06	2.42
117.06	2.14
118.06	1.44
119.09	2.93
120.07	1.44
121.09	4.37
122.11	2.51
123.11	8.46
124.12	3.67
125.11	8.53
126.07	2.37
127.08	5.21
127.92	2.14
128.06	6.65
129.08	7.90
131.03	3.44
133.09	2.65
135.10	3.21
137.12	3.25
138.13	3.35
139.08	6.09
140.07	4.51
141.06	11.02
142.07	1.63
143.09	2.65
145.07	2.46
147.10	4.32
149.09	3.67
151.03	1.07
151.14	1.95
152.15	2.56
153.13	2.56
155.06	2.79
156.06	2.46
157.07	3.02
158.07	1.81
165.13	1.44
167.11	0.93
168.06	9.11
169.04	5.39
171.10	2.65
179.02	1.35
183.05	2.28
184.05	5.53
185.15	1.58
186.06	2.23
199.16	2.70
205.08	1.39
213.18	3.63
223.08	3.07
233.09	4.23
236.22	6.46
237.23	2.70

Mass	% Base
239.25	3.21
255.23	2.56
256.24	2.65
257.25	2.05
260.10	2.84
368.33	4.70
369.36	2.46
446.15	59.04
447.17	22.50
448.18	3.16

Appendix Four

Requirements for the Board of Studies

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing:-

(1) all research colloquia, seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student;

(2) lectures organised by Durham University Chemical Society;

(3) details of the postgraduate induction course;

(4) all research conferences attended and papers presented by the author during the period when research for the thesis was carried out.

Colloquia, Lectures and Seminars From Invited Speakers
1992-1995

1992

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.

1993

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.

1994

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

October 5 Prof. N. L. Owen, Brigham Young University, Utah, USA
Determining Molecular Structure - the INADEQUATE NMR way

October 19 Prof. N. Bartlett, University of California*
Some Aspects of Ag(II) and Ag(III) Chemistry

November 2 Dr P. G. Edwards, University of Wales, Cardiff*
The Manipulation of Electronic and Structural Diversity in Metal Complexes - New Ligands

November 3 Prof. B. F. G. Johnson, Edinburgh University*
Arene - Metal Clusters - DUCS Lecture

November 9 Dr J. P. S. Badyal, University of Durham
Chemistry at Surfaces, A Demonstration Lecture

November 9 Dr G. Hogarth, University College, London
New Vistas in Metal Imido Chemistry

November 10 Dr M. Block, Zeneca Pharmaceuticals, Macclesfield*
Large Scale Manufacture of the Thromboxane Antagonist Synthase Inhibitor ZD 1542

November 16 Prof. M. Page, University of Huddersfield*
Four Membered Rings and β-Lactamase

November 23 Dr J. M. J. Williams, University of Loughborough*
New Approaches to Asymmetric Catalysis

December 7 Prof. D. Briggs, ICI and University of Durham
Surface Mass Spectrometry

1995

January 11 Prof. P. Parsons, University of Reading*
Applications of Tandem Reactions in Organic Synthesis

January 18 Dr G. Rumbles, Imperial College, London
Real or Imaginary 3rd Order non-Linear Optical Materials

January 25 Dr D. A. Roberts, Zeneca Pharmaceuticals*
The Design and Synthesis of Inhibitors of the Renin-Angiotensin System

February 1 Dr T. Cosgrove, Bristol University
Polymers do it at Interfaces

February 8 Dr D. O'Hare, Oxford University*
Synthesis and Solid State Properties of Poly-, Oligo- and Multidecker Metallocenes

February 22 Prof. E. Schaumann, University of Clausthal*
Silicon and Sulphur Mediated Ring-opening Reactions of Epoxide

March 1 Dr M. Rosseinsky, Oxford University*
Fullerene Intercalation Chemistry

† Invited specially for the graduate training programme.
* Those attended,

First Year Induction Courses

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

Research Conferences Attended

July 1993	2nd Anglo-Russian-Ukranian Symposium on Fluorine Chemistry, Durham.
July 1994	9th Postgraduate Heterocyclic Symposium, University of Leicester
April 1995	North Eastern Graduate Symposium Durham
September 1995	11th European Symposium on Fluorine Chemistry Bled, Slovenia.

References

1. H. Moissan, *Le Fluor et ses Composes,* Steinheil, Paris, 1900.
2. H. Moissan, *Compt. Rend.,* 1890, **110**, 276.
3. A. K. Barbour, L. J. Belf and M. X. Buxton, *Adv. Fluorine Chem.,* 1963, **3**, 181.
4. F. Swarts, *Bull. Acad. Roy. Belg.,* 1892, **24**, 474.
5. T. Midgley and A. L. Henne, *Ind. Eng. Chem.,* 1930, **22**, 542.
6. P. Lebeau and A. Damiens, *Compt. Rend.,* 1926, **182**, 1340.
7. P. Lebeau and A. Damiens, *Compt. Rend.,* 1930, **191**, 939.
8. O. Ruff and R. Keim, *Z. Anorg. Allegm. Chem.,* 1930, **192**, 249.
9. R. D. Chambers, *Fluorine in Organic Chemistry,* Wiley, 1973.
10. R. E. Banks, Eds., *Organofluorine Chemicals and their Industrial Applications*, Ellis Horwood, Chichester, 1979
11. E. Buncel and T. Durst, Eds., *Comprehensive Carbanion Chemistry*, Elsevier, 1987
12. R. D. Chambers and R. H. Hobbs, *Adv. Fluorine Chem.,* 1965, **4**, 50.
13. R. J. Koshar, T. C. Simmons and F. W. Hoffman, *J. Am. Chem. Soc.,* 1957, **79**, 1741.
14. J. D. Park, W. M. Sweeney, S. L. Hopwood and J. R. Lacher, *J. Am. Chem. Soc.,* 1956, **78**, 1685.
15. D. C. England, L. R. Melby, M. A. Dietrich and R. V. LIndsey, *J. Am. Chem. Soc.,* 1960, **82**, 5116.
16. A. V. Fokin and M. A. Landau, *Bull. Acad. Sci. USSR. Div. Chem. Sci.,* 1982, **31**, 1553.
17. I. N. Rozhkov and Y. A. Borisov, *Izv. Akad. Nauk. SSSR. Ser. Khim.,* 1993, **6**, 1334.
18. R. D. Chambers, A. A. Lindley and H. C. Fielding, *J. Fluorine Chem.,* 1978, **12**, 85.
19. R. D. Chambers, J. S. Waterhouse and D. H. L. Williams, *Tetrahedron Lett.,* 1974, **9**, 74.
20. M. R. Bryce, R. D. Chambers and G. Taylor, *J. Chem. Soc., Perkin Trans. I,* 1984, 509.
21. I. Fleming, *Frontier Orbitals in Organic Reactions,* Wiley, London, 1976.
22. B. E. Smart, in *The Chemistry of Functional groups Supplement D:,* ed. S. Patai and Z. Rapport, Wiley, Chichester, 1983, vol. Pt 1, Ch 14.
23. A. L. Henne and W. G. Finnegan, *J. Am. Chem. Soc.,* 1949, **71**, 298.
24. J. L. Anderson, R. E. Putnam and W. H. Sharkey, *J. Am. Chem. Soc.,* 1961, **83**, 382.
25. G. Fuller and J. C. Tatlow, *J. Chem. Soc.,* 1961, 3198.

26. D. E. M. Evans, W. J. Feast, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, 1963, 4828.
27. D. J. Burton and R. L. Johnson, *J. Am. Chem. Soc.*, 1964, **86**, 5361.
28. P. L. Coe, R. G. Plevey and J. C. Tatlow, *J. Chem. Soc. (C)*, 1969, 1060.
29. W. J. Feast, W. K. R. Musgrave and R. G. Weston, *J.C.S. Chem.Commun.*, 1971, 709.
30. A. M. Andrews, S. L. Maruca, I. K W Hillig, R. L. Kuczkowski and N. C. Craig, *J. Phys. Chem.*, 1991, **95**, 7714.
31. P. Odello, Ph.D Thesis, Univ. of Durham, 1993.
32. H. Aoyama, T. Aoyama and Osaka, *Process for Producing 1,1,1,4,4,4-hexafluoro-2-butene and 1,1,1,4,4,4-hexafluorobutane*, Int. Appl. WO 94/12454, 1994.
33. T. Nakada, H. Aoyama and S. Takubo, *Process for Producing 1,1,1,4,4,4-hexafluoro-2-butenes and 1,1,1,4,4,4-hexafluorobutane*, PCT Int. Appl. WO 4/17020, 1994.
34. R. J. Shozda and R. E. Putnam, *J. Am. Chem. Soc.*, 1962, **27**, 1557.
35. W. R. DolbierJr and D. M. Al-Fekri, *Tetrahedron Lett.*, 1983, **24**, 4047.
36. W. R. DolbierJr and D. M. Al-Fekri, *Tetrahedron*, 1987, **43**, 39.
37. J. Burdon, I. W. Parsons and A. Shommakhi, *J. Fluorine Chem.*, 1981, **20**, 357-363.
38. J. Burdon, R. Nights, I. W. Parsons and J. C. Tatlow, *Tetrahedron*, 1976, **32**, 10941.
39. J. Burdon, G. E. Chivers and J. C. Tatlow, *J. Chem. Soc. (C)*, 1969, 2585.
40. R. N. Haszeldine, *J. Am. Chem. Soc.*, 1952, 2054-2513.
41. R. E. Banks, B. E. Smart and J. C. Tatlow, Eds., *Organofluorine Chemistry. Principles and Commercial Applications*, Plenum Press, New York and London, 1994
42. J. P. John, *Bioscience*, 1987, **37**, 647.
43. E. Vogel, *Fortschr. Chem. Forsch*, 1955, **3**, 430.
44. J. G. Reiss, *Vox. Sang.*, 1991, **61**, 225.
45. K. C. Lowe, 1987, **87A**, 825.
46. K. C. Lowe, *Ischemic Diseases and the Microcirculation-New Results*, Zuckschwerdt, Munich, 1989.
47. K. C. Lowe, *Vox. Sang.*, 1991, **60**, 129.
48. N. S. Faithfull and K. C. Lowe, *Blood Substitutes: Preparation, Physiology and Medical Applications*, Ellis Horwood, Chichester, 1988.
49. G. P. Biro and P. Blais, *CRC Crit. Rev. Oncol. Haem. 6*, 1987, 311.
50. W. Stuckey and J. Heicklen, *J. Am. Chem. Soc.*, 1968, **90**, 3952.
51. G. Camaggi and F. Gozzo, *J. Chem. Soc. (C)*, 1970, 178.
52. A. E. Barkdoll and P. B. Sargeant, *Chem. Abstr.*, 1972, **77**, 20308.
53. A. E. Barkdoll and P. B. Sargent, *Chem. Abstr.*, 1969, **70**, 38304.

54. P. B. Sargeant and C. G. Krespan, *J. Am. Chem. Soc.*, 1969, **91**, 415.
55. W. H. Sharkey, *Fluorine Chem. Revs.*, 1968, **2**, 1.
56. A. L. Henne and R. P. R. Ruh, *J. Am. Chem. Soc.*, 1947, **69**, 279.
57. L. E. Gardner, *Chem. Abstr.*, 1972, **76**, 71992.
58. C. A. Bordner, *Chem. Abstr.*, 1954, **48**, 8770f.
59. R. M. Mantell, *Chem. Abstr.*, 1956, **50**, 2651a.
60. J. D. Park, R. J. Seffl and J. R. Lacher, *J. Am. Chem. Soc.*, 1956, **78**, 59.
61. W. R. Cullen and P. Singh, *Can. J. Chem.*, 1963, **41**, 2397.
62. J. A. Thoroughgood, *Chem. Abstr.*, 1973, **79**, 31574.
63. E. T. McBee, P. A. Wiseman and G. B. Bachman, *Ind. Eng. Chem. (Lon.)*, 1947, **39**, 415.
64. A. L. Henne and W. J. ZImmerschied, *J. Am. Chem. Soc.*, 1945, **67**, 1235.
65. J. T. Maynard, *J. Org. Chem.*, 1963, **28**, 112.
66. V. A. Petrov, S. D. Chepik, G. G. Belen'kii and L. S. German, *Izv. Akad. Nauk. SSSR. Ser. Khim.*, 1990, **6**, 1430.
67. T. S. Reid, G. H. Smith and W. H. Pearlson, *Chem. Abstr.*, 1957, **51**, 1260i.
68. G. Trolio and G. Gambaretto, *Ann. Chim. (Rom.)*, 1970, **61**, 245.
69. G. Trolio and G. Gambaretto, *Chem. Abstr.*, 1971, **75**, 109901.
70. G. Gambaretto, G. Trolio and M. Napoli, *Chim. Ind. (Milan)*, 1970, **52**, 1097.
71. G. Gambaretto, G. Trolio and M. Napoli, *Chem. Abstr.*, 1971, **75**, 41979.
72. R. P. Smith and J. C. Tatlow, *J. Chem. Soc.*, 1957, 2505.
73. A. K. Barbour, H. D. Mckenzie, M. Stacey and J. C. Tatlow, *J. Appl. Chem.*, 1954, **4**, 347.
74. R. E. Banks, W. I. Bevan and W. K. R. Musgrave, *Chem. and Ind. (Lon.)*, 1959, 296.
75. R. E. Banks and A. E. Tipping, *Chem. and Ind. (Lon.)*, 1959, 1491.
76. J. Riera and R. Stephens, *Tetrahedron*, 1966, 2555.
77. M. P. Stewart and J. C. Tatlow, *J. Fluorine Chem.*, 1973, **3**, 259.
78. G. Camaggi and F. Gozzo, *J Chem. Soc. (C)*, 1969, 489.
79. W. J. Feast, W. K. R. Musgrave and R. G. Weston, *J. Chem. Soc. (D)*, 1970, 1337.
80. R. G. Plevey and R. E. Talbot, *J. Fluorine Chem.*, 1977, **10**, 577.
81. J. A. Oliver, R. Stephens and J. C. Tatlow, *J. Fluorine Chem.*, 1983, **22**, 21.
82. S. Campbell, J. M. Leach, R. Stephens and J. C. Tatlow, *J. Fluorine Chem.*, 1971, **1**, 85.
83. R. E. Banks, R. N. Haszeldine and A. Prodgers, *J. Chem. Soc., Perkin Trans. I*, 1973, 596.
84. D. M. Lemal, J. M. Buzby and A. C. Barefoot, *J. Org. Chem.*, 1980, **45**, 3118.
85. M. G. Barlow, M. W. Crawley and R. N. Haszeldine, *J. Chem. Soc., Perkin Trans. I*, 1980, 122.
86. M. J. Gerace, D. M. Lemal and H. Ertl, *J. Am. Chem. Soc.*, 1975, **97**, 5584.

87. Y. Waldon, A. C. Barefoot and D. M. Lemal, *J. Am. Chem. Soc.*, 1984, 106, 8301.
88. D. P. Graham, *J. Org. Chem.*, 1966, 31, 355.
89. D. P. Graham, 1968, U.S. Patent 3,403,191.
90. H. C. Fielding and A. J. Rudge, 1967, British Patent, 1,082, 127.
91. R. D. Chambers, J. A. Jackson, W. K. R. Musgrave and R. A. Storey, *J. Chem. Soc. (C)*, 1968, 2221.
92. J. A. Young, *Fluorine Chem. Revs.*, 1967, 1, 359.
93. W. J. Brehm, K. G. Bremer, H. S. Eleuterio and R. W. Meschke, 1959, U.S. Patent 2,918,501.
94. W. Brunskill, W. T. Flowers, R. Gregory and R. N. Haszeldine, *Chem. Comms.*, 1970, 1444.
95. W. Dmowski, W. T. Flowers and R. N. Haszeldine, *J. Fluorine Chem.*, 1977, 9, 94.
96. E. S. Lo, *J. Org. Chem.*, 1971, 36, 364.
97. T. Filyakova, A. Y. Zapevalov, I. P. Kolenko and L. S. German, *Izv. Akad. Nauk. SSSR. Ser. Khim.*, 1979, 12, 2789.
98. M. A. Kurykin and L. S. German, *Izv. Akad. Nauk. SSSR. Ser. Khim.*, 1981, 11, 2646.
99. A. Battais, B. Boutevin and P. Moreau, *J. Fluorine Chem.*, 1979, 13, 391.
100. J. A. Young and M. H. Bennet, *J. Org. Chem.*, 1977, 42, 4055.
101. K. V. Scherer and T. F. Terranova, *J. Fluorine Chem.*, 1979, 13, 89.
102. D. C. England and C. G. Krespan, *J. Am. Chem. Soc.*, 1966, 88, 5582.
103. V. A. Petrov, G. G. Belen'kii, L. S. German and E. I. Mysov, *Izv. Akad. Nauk. SSSR. Ser. Khim.*, 1981, 9, 2098.
104. C. G. Krespan and R. C. Siegell In 1992; pp WO 92/06942.
105. R. E. Banks, *Fluorocarbos and their Derivatives*, Oldbourne Press, London, 1964.
106. M. Hudlicky, *Chemistry of Organic Fluorine Compounds*, Ellis-Horwood, London, 1976.
107. J. D. Park, R. J. McMurty and J. H. Adams, *Fluorine Chem. Reviews*, 1968, 2, 55.
108. R. D. Chambers and R. H. Mobbs, *Adv. Fluorine Chem.*, 1965, 4, 50.
109. Y. V. Zeifman, E. G. Tergabrielyan, N. P. Gambaryan and I. L. Knunyants, *Russ. Chem. Rev. (Eng. Transl.)*, 1984, 53, 256.
110. N. Ishikawa and M. Maruta, *Chem. Abstr.*, 1982, 95, 5897u.
111. R. E. Banks and A. Prodgers, *J. Fluorine Chem.*, 1984, 26, 169.
112. J. D. Park, M. L. Sharah and J. R. Lacher, *J. Am. Chem. Soc.*, 1949, 71, 2337.
113. B. E. Smart, *J. Org. Chem.*, 1976, 41, 2377.
114. J. T. Barr, K. E. Rapp, R. L. Pruett, C. T. Bahner, J. D. Gibson and R. H. Lafferty, *J. Am. Chem. Soc.*, 1950, 72, 4480.

115. C. M. Jenkins, R. Stephens and J. C. Tatlow, *J. Fluorine Chem.*, 1984, **25**, 233.
116. C. G. Krespan, 1977, U.S. Patent 4,005,104.
117. M. A. Kurykin and L. S. German, *Bull. Acad. Sci. U.S.S.R. (Eng. Trans.)* 1981, **30**, 2202.
118. A. B. Clayton, J. Roylance, D. R. Sayers, R. Stephens and J. C. Tatlow, *J. Org. Chem.*, 1965, 7358.
119. P. Tarrant, C. G. Allison, K. P. Barthold and J. E. C. Stump, *Fluorine Chemistry Reviews,* Marcel Dekker, New York, 1971.
120. F. Gozzo and G. Camaggi, 1968, U.S. Patent 3,392,097.
121. G. C. Belen'kii, L. S. German and I. L. Knunyants, *Izv. Akad. Nauk. SSSR. Ser. Khim.*, 1968, 554.
122. G. C. Belen'kii, L. S. German and I. L. Knunyants, *Izv. Akad. Nauk. SSSR. Ser. Khim.*, 1967, **12**, 2780.
123. Monsanto, 1966, Brit. Patent 1,036,174.
124. J. W. Dale, 1971, U.S. Patent 3,622,601.
125. E. I. DuPont&Co, 1962, Brit. Patent 904,877.
126. H. H. Evans, R. Fields, R. N. Haszeldine and M. Illingworth, *J. Chem. Soc., Perkin Trans. I,* 1973, 649.
127. H. C. Fielding, 1969, Brit. Patent 1,148,486.
128. I. P. Kolenko, T. I. Filyakova, A. Y. Zapevalov and E. P. Lur'e, *Izv. Akad. Nauk. SSSR. Ser. Khim.*, 1979, **11**, 2509.
129. A. Y. Zapevalov, T. I. Filyakova and I. P. Kolenko, *Izv. Akad. Nauk. SSSR. Ser. Khim.* 1979, **12**, 2812.
130. P. L. Coe, A. Sellars and J. C. Tatlow, *J. Fluorine Chem.*, 1982, **20**, 243.
131. T. I. Filyakova, A. Y. Zapevalov, N. V. Peschanskii, M. I. Kodess and I. P. Kolenko, *Izv. Akad. Nauk. SSSR. Ser. Khim.*, 1981, **11**, 2612.
132. C. G. Krespan, *J. Org. Chem.*, 1969, **34**, 42-45.
133. E. T. McBee, J. J. Turner, C. J. Morton and A. P. Stefani, *J. Org. Chem.*, 1965, **30**, 3698.
134. P. Robson, J. Roylance, R. Stephens, J. C. Tatlow and R. E. Worthington, *J. Chem. Soc.*, 1964, 5748.
135. R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson and R. H. LaffertyJr, *J. Am. Chem. Soc.*, 1950, **72**, 3646.
136. P. L. Coe, D. Oldfield and J. C. Tatlow, *J. Fluorine Chem.*, 1985, **28**, 453.
137. P. Robson, J. Roylance, A. Stephens, J. C. Tatlow and R. E. Worthington, *J. Chem. Soc.*, 1964, 5748.
138. J. A. Oliver, R. Stephens, J. C. Tatlow and J. R. Taylor, *J. Fluorine Chem.*, 1976, **7**, 555.
139. C. O. Parker, *J. Am. Chem. Soc.*, 1959, **81**, 2183.

140. M. A. Kurykin, L. S. German and I. L. Knunyants, *Izv. Akad. Nauk. SSSR. Ser. Khim.* 1980, **9**, 2172.
141. A. F. Gontar, E. G. Bykhovskaya and I. L. Knunyants, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.,* 1975, **24**, 2161.
142. F. Lautenschlager, F. Myhre, F. Hopton and J. Wilson, *J. Heterocyclic Chem.,* 1971, **8**, 241.
143. M. G. Barlow, R. N. Haszeldine, W. D. Morton and D. R. Wodword, *J. Chem. Soc., Perkin Trans. I,* 1972, 2170.
144. A. W. Frank, *J. Org. Chem.,* 1966, **31**, 1917.
145. W. R. Cullen and P. S. Dhaliwal, *Can. J. Chem,* 1967, **45**, 719.
146. D. J. Burton, R. D. Howells and P. V-d-Valk, *J. Am. Chem. Soc.,* 1977, **99**, 4830.
147. R. L. Pruett, C. T. Bahner and H. A. Smith, *J. Am. Chem. Soc.,* 1952, **74**, 1633.
148. K. E. Rapp, *J. Am. Chem. Soc.,* 1951, **74**, 1633.
149. M. A. Howells, R. D. Howells, N. C. Baenziger and D. J. Burton, *J. Am. Chem. Soc.,* 1973, **95**, 5366.
150. R. F. Stockel, F. Megson and M. T. Beachem, *J. Org. Chem.,* 1968, **33**, 4395.
151. D. J. Burton, S. Shinya and R. D. Howells, *J. Am. Chem. Soc.,* 1979, **101**, 3689.
152. J. D. Park, T. S. Croft and R. W. Anderson, *J. Organom.et.Chem.,* 1974, 19.
153. J. D. Park and R. Fontanelli, *J. Org. Chem.,* 1963, **28**, 258.
154. J. D. Park, R. Sullivan and R. J. McMurty, *Tetrahedron Lett.,* 1967, 173.
155. R. D. Sayers, R. Stephens and J. C. Tatlow, *J. Chem. Soc.,* 1964, 3035.
156. R. D. Chambers and J. R. Kirk, *J. Chem. Soc., Perkin Trans. I,* 1983, 1239.
157. W. J. Feast, D. R. Perry and R. Stephens, *Tetrahedron,* 1966, **22**, 433.
158. W. R. Cullen, D. S. Dawson and P. S. Dhaliwall, *Can. J. Chem,* 1967, **45**, 683.
159. K. E. Rapp, R. L. Pruett, J. T. Barr, C. T. Bahner, J. D. Gibson and R. H. Lafferty, *J. Am. Chem. Soc.,* 1950, **72**, 3642.
160. G. Camaggi and F. Gozzo, *J. Chem. Soc. (C),* 1971, 2382.
161. F. W. B. Einstein, A. C. Willis, W. R. Cullen and R. L. Soulen, *J.C.S. Chem. Commun.*, 1981, 526.
162. W. R. Cullen, P. S. Dhaliwall and G. E. Styan, *J. Organomet. Chem.,* 1966, **6**, 364.
163. A. W. Wu, S. K. Choi, J. D. Park and R. L. Soulen, *J. Fluorine Chem.,* 1979, **13**, 379.
164. R. D. Chambers, A. Parkin and R. S. Matthews, *J. Chem. Soc., Perkin Trans. I,* 1976, 2107.
165. G. G. Belen'kii, E. P. Lur'e and L. S. German, *Bull. Acad. Sci. U.S.S.R. (Eng. Trans.)* 1976, **25**, 2208.
166. J. Cortieu, J. Jullien and N. T. Lai, *Tetrahedron,* 1976, **32**, 669.

167. H. Muramatsu, S. Moriguchi and K. Inukai, *J. Org. Chem.*, 1966, 31, 1306.
168. G. Gambaretto and M. Napoli, *Chem. Abstr.*, 1971, 74, 31370.
169. D. E. M. Evans and J. C. Tatlow, *J. Fluorine Chem.*, 1973, 3, 259.
170. M. W. Buxton, D. W. Ingram, F. Smith, M. Stacey and J. C. Tatlow, *J. Chem. Soc.*, 1952, 3830.
171. J. Burdon and J. C. Tatlow, *J. Appl. Chem.*, 1958, 8, 293.
172. I. Watanabe, Y. Yamakoshi, T. Misumi, H. Miyauchi and M. Fukumoto, *Chem. Abstr.*, 1976, 85, 93867.
173. P. B. Sargeant, *J. Am. Chem. Soc.*, 1969, 91, 3061.
174. M. G. Barlow, R. N. Haszeldine and R. Hubbard, *J. Chem. Soc. (C)* 1971, 90.
175. V. A. Al'bekov, A. F. Benda, A. F. Gonta', G. A. Sokol'skii and I. L. Knunyants, *Izv. Akad. Nauk. SSSR. Ser. Khim.*, 1988, 4, 897-900.
176. V. A. Al'bekov, A. F. Benda, A. F. Gonta', G. A. Sokol'skii and I. L. Knunyants, *Izv. Akad. Nauk. SSSR. Ser. Khim.*, 1988, 4, 887-890.
177. W. R. DolbierJr and D. M. Al-Fekri, *J. Org. Chem.*, 1987, 52, 1872.
178. M. G. Barlow, R. N. Haszeldine, W. D. Morton and D. R. Woodward, *J. Chem. Soc., Perkin Trans. I*, 1973, 1798.
179. M. G. Barlow, R. N. Haszeldine and W. D. Morton, *J.C.S. Chem. Commun.*, 1969, 931.
180. W. R. DolbierJr and M. J. Seabury, *Tetrahedron*, 1987, 43, 2437.
181. J. Roylance, J. C. Tatlow and R. E. Worthington, *J. Chem. Soc.*, 1954, 4426.
182. V. A. Petrov, G. G. Belen'kii and L. S. German, *Izv. Akad. Nauk. SSSR. Ser. Khim.* 1982, 7, 1591.
183. A. B. Clayton, J. Roylance, D. R. Sayers, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, 1965, 7358.
184. S. F. Campbell and R. Stephens, *J. Chem. Soc.*, 1965, 7367.
185. D. B. Speight, Ph.D Thesis, Univ. of Durham, 1974.
186. M. J. Silvester, Ph.D Thesis, Univ. of Durham, 1980.
187. A. J. Palmer, Ph.D Thesis, Univ. of Durham, 1967.
188. M. H. Rock, Ph.D. Thesis, Univ. of Durham, 1990.
189. T. Olsson and O. Wennerstrom, *Acta Chem. Scand., Ser B*, 1978, B32, 293.
190. J. W. Mickleson, Ph.D Thesis, Univ. of Minnesota, 1992.
191. P. G. Gassmann and C. H. Winter, *J. Am. Chem. Soc.*, 1986, 108, 4228.
192. E. P. JanulisJr and A. J. A. III, *J. Am. Chem. Soc.*, 1983, 105, 3563-3567.
193. E. D. Laganis and D. M. Lemal, *J. Am. Chem. Soc.*, 1980, 102, 6633.
194. M. J. Burk, M. J. ArduengoIII, J. C. Calabrese and R. L. Harlow, *J. Am. Chem. Soc.*, 1989, 111, 8938-8940.
195. R. D. Chambers and M. P. Greenhall, *J. Chem. Soc., Chem. Commun.*, 1990, 1128.

196. M. Nishida, Y. Hayakawa, M. Matsui, K. Shibata and H. Muramatsu, *J. Heterocyclic Chem.*, 1992, **29**, 113-116.
197. M. J. Burk, J. C. Calabrese, F. Davidson, R. L. Harlow and D. C. Roe, *J. Am. Chem. Soc.*, 1991, **113**, 2209-2222.
198. R. D. Chambers and A. J. Palmer, *Tetrahedron*, 1969, **31**, 3293.
199. W. T. Flowers, R. N. Hasveldine, A. Janik, A. K. Lee, P. G. Marshall and R. D. Sedgwick, *J. Polym. Sci., Polym. Chem. Ed.*, 1972, **10**, 3497-3501.
200. J. W. Emsley, L. Phillips and V. Wray, *Fluorine Coupling Constants*, Pergamon, Oxford, 1977.
201. R. D. Chambers, S. Partington and D. B. Speight, *J. Chem. Soc., Perkin Trans. I* 1974, 2673.
202. T. Nakamura, Ph.D Thesis, Univ. of Durham, 1992.
203. S. T. Mullins, Ph.D Thesis, Univ. of Durham, 1992.
204. R. D. Chambers, A. A. Lindley, P. D. Philpot, H. C. Fielding and J. Hutchinson, *Isr.J. Chem.* 1978, **17**, 150.
205. R. D. Chambers and A. J. Palmer, *Tetrahedron*, 1969, **25**, 4217.
206. A. E. Bayliff and R. D. Chambers, *J. Chem. Soc., Perkin Trans. I*, 1988, 201.
207. J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 1976, 734.
208. R. Huisgen, *Angew. Chem., Int. Ed. Eng.*, 1980, **19**, 947.
209. W. Kemp, *Organic Spectroscopy*, MacMillan, London, 1992.
210. A. S. Batsanov, Personal communication, 1995.
211. R. E. Banks, *J. Chem. Soc, Chem. Commun.*, 1992, 595.
212. G. S. Lal, *J. Org. Chem.*, 1993, **58**, 2791.
213. W. J. Middleton and W. H. Sharkey, *J. Am. Chem. Soc.*, 1959, **81**, 803.
214. W. J. Middleton, U.S. Patent 2,831,835 1958.
215. H. G. Viehe, *Angew. Chem., Int. Ed. Eng.*, 1965, **4**, 746.
216. H. G. Viehe, J. M. F. Oth and P. Valange, *Angew. Chem., Int. Ed. Eng.*, 1964, **3**, 746.
217. R. N. Haszeldine, *J. Chem. Soc.*, 1951, 588.
218. R. N. Haszeldine and K. Leedham, *J. Chem. Soc.*, 1952, 3483.
219. R. E. Banks, M. G. Barlow, W. D. Davies, R. N. Haszeldine and D. R. Taylor, *J. Chem. Soc. (C)* 1969, 1104.
220. W. C. Smith, C. W. Tullock, E. L. Mutterties, W. R. Hasek, F. S. Fawcett, V. A. Engelhardt and D. D. Coffman, *J. Am. Chem. Soc.*, 1959, **81**, 3166.
221. W. C. Smith, *Angew. Chem., Int. Ed. Eng.*, 1962, 1467.
222. W. P. Norris and W. G. Finnegan, *J. Org. Chem.*, 1966, **31**, 3292.
223. W. G. Finnegan and W. P. Norris, *J. Org. Chem.*, 1963, **28**, 1139.
224. R. E. Banks, A. Braithwaite, R. N. Haszeldine and D. R. Taylor, *J. Chem. Soc, Chem. Commun.*, 1969, 454.
225. R. D. Dresdner, F. N. Tuimac and J. A. Young, *J. Org. Chem.*, 1965, **30**, 3524.
226. W. T. Miller, W. Frass and P. R. Resnick, *J. Am. Chem. Soc.*, 1961, **83**, 1767.

227. A. L. Henne and K. A. Latif, *J. Am. Chem. Soc.*, 1954, 76, 610.
228. J. V. Drayton, W. T. Flowers, R. N. Haszeldine and D. R. Taylor, *J. Chem. Soc, Chem. Commun.*, 1976, 490.
229. N. I. Delyagina, B. L. Dyatkin and I. L. Knunyants, *Bull. Acad. Sci. U.S.S.R. (Eng. Trans.)* 1974, 1594.
230. R. D. Chambers, C. G. P. Jones and G. Taylor, *J. Fluorine Chem.*, 1981, 18, 407.
231. K. J. Klabunde, J. F. V. Low and M. S. Key, *J. Fluorine Chem.*, 1972, 2, 207.
232. M. I. Bruce and W. R. Cullen, *Fluorine Chem. Revs.*, 1969, 4, 79.
233. R. E. Putnam, R. J. Harder and J. E. Castle, *J. Am. Chem. Soc.*, 1961, 83, 391.
234. C. G. Krespan, B. C. McKusick and T. L. Cairns, *J. Am. Chem. Soc.*, 1961, 83, 3428.
235. C. D. Weis, *J. Org. Chem.*, 1962, 27, 3693.
236. H. N. C. Wong, *Synthesis*, 1984, 787.
237. C. G. Krespan, *J. Am. Chem. Soc.*, 1961, 83, 3432.
238. C. G. Krespan, *J. Am. Chem. Soc.*, 1961, 83, 3434.
239. H. Muramatsu and H. Kimoto, Jap. Patent 71. 14004, 1971.
240. R. N. Haszeldine, *J. Am. Chem. Soc.*, 1952, 3490-3498.
241. R. D. Chambers, C. G. P. Jones, M. J. Silvester and D. B. Speight, *J. Fluorine Chem.*, 1984, 25(1), 47-56.
242. R. S. Dickson and G. Wilkinson, *J. Chem. Soc.*, 1964, 2699-2704.
243. H. C. Brown, H. L. Gewanter, D. H. White and W. G. Woods, *J. Org. Chem.*, 1960, 25, 634.
244. H. C. Brown, *J. Org. Chem.*, 1957, 22, 1256.
245. A. L. Henne, J. V. Schmitz and W. G. Finnegan, *J. Am. Chem. Soc.*, 1950, 4195.
246. R. C. H. Spink, Personal communication, 1995.
247. R. P. Holysz, *J. Am. Chem. Soc.*, 1953, 75, 4432.
248. R. D. Chambers, G. Taylor and R. L. Powell, *J. Chem. Soc., Perkin Trans. I*, 1980, 426.
249. H. Oediger, F. Moller and K. Eiter, *Synthesis*, 1972, 591.
250. I. Hermecz, *Adv. Heterocycl. Chem.*, 1987, 42, 83.
251. R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compounds.*, John Wiley and Sons, 1981.
252. M. W. Briscoe, R. D. Chambers, S. J. Mullins, T. Nakamura and J. F. S. Vaughan, *J. Chem. Soc., Perkin Trans. I*, 1994, 3119.
253. J. F. S. Vaughan, Ph.D Thesis, Univ. of Durham, 1994.
254. L. L. McCoy and D. Mal, *J. Org. Chem.*, 1981, 46, 1016-1018.
255. H. Lammers, P. Cohen-Fernandes and C.L.Habraken, *Tetrahedron*, 1994, 50, 865-870.

256. R. Reed, R. Reau, F. Dahan and G. Bertrand, *Angew. Chem., Int. Ed. Eng.*, 1993, 32, 399-401.
257. C. G. P. Jones, Ph.D Thesis, Univ. of Durham, 1980.
258. R. E. Bambury, H. K. Yaktin and K. K. Wyckoff, *J. Heterocyclic Chem.*, 1968, 5, 95-100.
259. R. E. Bambury and L. F. Miller, *J. Heterocyclic Chem.*, 1970, 7, 269-273.
260. C. J. Boriack, E. D. Laganis and D. M. Lemal, *Tetrahedron Lett.* 1978, 1015.
261. Y. Kobayashi, Y. Hanzawa, Y. Nakanishi and T. Kashiwagi, *Tetrahedron Lett.* 1978, 1019.
262. R. D. Chambers, A. A. Lindley, H. C. Fielding, J. S. Moilliet and G. Whittaker, *J. Chem. Soc, Chem. Commun.*, 1978, 475.
263. R. D. Chambers, A. A. Lindley, P. D. Philpot, H. C. Fielding, J. Hutchinson and G. Whittaker, *J. Chem. Soc., Perkin Trans. I,* 1979, 214.
264. R. D. Chambers, S. Bartlett and N. Kelly, *Tetrahedron Lett.*, 1980, 1891.
265. H. Sawada, M. Nakayama, M. Yoshida, T. Yoshida and N. Kamigata, *J. Fluorine Chem.*, 1990, **46**, 423-431.
266. A. B. Abubakar, B. L. Booth and A. E. Tipping, *J. Fluorine Chem.*, 1991, 55, 189-198.
267. T. Okano, T. Ueda, K. Ito, K. Kodaira, K. Hosokawa and H. Muramatsu, *J. Fluorine Chem.*, 1986, **31**, 451-459.
268. M. Nishida, Y. Hayakawa, M. Matsui, K. Shibata and H. Muramatsu, *J. Heterocyclic Chem.*, 1991, **28**, 225-229.
269. A. B. Abubakar, B. L. Booth, N. N. E. Suliman and A. E. Tipping, *J. Fluorine Chem.*, 1992, **56**, 359-371.
270. G. C. Bazan, E. Khorsravi, R. R. Schrock, W. J. Feast, V. C. Gibson, M. B. O'Regan, J. K. Thomas and W. M. Davis, *J. Am. Chem. Soc.*, 1990, **112**, 8378-8387.
271. A. B. Alimuniar, P. M. Blackmore, J. H. Edwards, W. J. Feast and B. Wilson, *Polymer,* 1986, **27**, 1281-1288.
272. A. R. Katritzky and C. W. Rees, in *Comprehensive Heterocyclic Chemistry,* ed. K. T. Potts, Pergammon, 1984, vol. 6.
273. C. G. Krespan, *Tetrahedron,* 1967, **23**, 4243.
274. D. W. Chaney, U.S. Patent 2,522,566, 1950.
275. W. R. Cullen, D. J. Dawson and G. E. Styan, *Can. J. Chem.*, 1965, **43**, 3392.
276. F. G. Pearson, U.S. Patent 2,558,875, 1952.
277. E. L. Stogryn and S. J. Bois, *J. Am. Chem. Soc.*, 1967, **89**, 605.
278. H. W. Heine, T. R. Hoye, P. G. Williard and R. C. Hoye, *J. Org. Chem.*, 1973, **38**, 2984.
279. F. J. Weigert, *J. Org. Chem.*, 1978, **43**, 622.
280. R. E. Banks and M. J. McGlinchey, *J. Chem. Soc. (C)*, 1970, 2172.

281. A. E. Bayliff, M. R. Bryce and R. D. Chambers, *J. Chem. Soc., Perkin Trans. I,* 1987, 763.

282. A. L. Henne, M. S. Newman, L. L. Quill and R. A. Staniforth, *J. Amer. Chem. Soc.,* 1947, **69**, 1819.