Durham E-Theses

Polyfluorinated alkenes and alkynes

Andrew R. Edwards

How to cite:

Edwards, Andrew R. (1997) Polyfluorinated alkenes and alkynes. Doctoral thesis, Durham University.

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a https://etheses.durham.ac.uk/id/eprint/4772/ is made to the metadata record in Durham E-Theses
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the full Durham E-Theses policy for further details.

Academic Support Office, The Palatine Centre, Durham University, Stockton Road, Durham, DH1 3LE
e-mail: e-theses.admin@durham.ac.uk Tel: +44 0191 334 6107
https://etheses.durham.ac.uk

UNIVERSITY OF DURHAM

A THESIS

entitled

POLYFLUORINATED ALKENES AND ALKYNES

submitted by

ANDREW R. EDWARDS B.Sc. (Hons) Dunelm

(Trevelyan College)

The copyright of this thesis rests
with the author. No quotation
from it should be published
without the written consent of the
author and information derived
from it should be acknowledged.

A candidate for the degree of Doctor of Philosophy

Department of Chemistry

1997

23 JAN 1998

Life is a grindstone. Whether it grinds you down or polishes you up depends on what you are made of.

- Anon.

Acknowledgements

I would like to take this opportunity to thank my supervisor, Professor R. D. Chambers, for his continued support and encouragement throughout my years at Durham. Thanks also go to the E.P.S.R.C. for their financial support.

I would also like to thank the many technical staff whose assistance has been invaluable over the past three years and without whom this thesis would have been impossible. Many thanks to Mr. L. W. Lauchlan (gas chromatography), Dr. M. Jones and Miss. L. M. Turner (mass spectrometry), Dr. R. S. Matthews, Dr. A. Kenwright and Mrs. J. Say (NMR spectroscopy), Mrs. J. Dorstal (elemental analysis), Mr. R. Hart and Mr. G. Haswell (glass blowing), Dr. A. Royston (computing), Mr. D. Hunter (high-pressure laboratory), Mr. J. Lincoln and Mr J. Peel (stores), Mrs. E. M. Wood (artwork) and of course anybody else who I've forgotten.

Special thanks need to go to *all* my colleagues from CG115, past and present, and to the many friends that I have made over a memorable six years at Durham. Particular thanks to Phil, Mark and Gary, the original Gilesgaters, and not forgetting Lisa and Sam. Also Rachel, for listening, encouraging, believing, photocopying, making my skiing look good and so much more.

Finally, I must thank my family, especially my parents for their genuine interest, encouragement and for being there when I've needed them.

Thank you.

Memorandum

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

The copyright of this thesis lies solely with the author. No quotation from it should be published without his prior consent and information derived from it should be acknowledged.

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

Richard D. Chambers and Andrew R. Edwards, '*Perfluorocarbons as Solvent Replacements*', UK Pat. Appl. No. 9711588, June 1997.

Richard D. Chambers and Andrew R. Edwards, '*Perfluorocarbons as Solvent Replacements*', accepted for publication in *J. Chem. Soc., Perkin Trans. I.*

and has been presented at:

I.C.I Poster Session
University of Durham
December, 1996

11th Postgraduate Heterocyclic Symposium
University of Keele.
June, 1997

15th International Symposium on Fluorine Chemistry
University of British Columbia, Vancouver, CANADA.
August, 1997

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 this thesis:

CFC	chlorofluorocarbon
DCM	dichloromethane
GLCMS	gas-liquid chromatography-mass spectrometry
IR	infrared
NMP	N-methyl-2-pyrollidone
NMR	nuclear magnetic resonance
PFC	perfluorocarbon
HMPT	hexamethylphosphorous triamide
SMT	sealable metal tube
HFB	hexafluorobut-2-yne

Abstract

Polyfluorinated Alkenes and Alkynes
by A. R. Edwards

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

1) The use of (*Z*)-2*H*-heptafluorobut-2-ene (**10**) as a synthon for hexafluorobut-2-yne (**4**) in Diels-Alder reactions was investigated. Novel 'one-pot' routes to a variety of bis(trifluoromethyl) substituted furan and arene derivatives were discovered, along with the synthesis of the novel diene, bis(trifluoromethyl)cyclopentadiene (**46**), from cyclopentadiene.

2) A variety of nucleophiles were successfully reacted with (**10**), the products of which were identical to those that have been, or would be expected to be, formed from the reaction of the same nucleophile with (**4**). A novel route to a fluorinated quinoline derivative was also discovered.

3) Perfluoroperhydrophenanthrene (**74**) was used as a 'bulking agent' to replace the hydrocarbon solvent used in halogen exchange reactions for the preparation of octafluorocyclopentene (**3**), chlorofluoro -pyridine, -pyrimidine, and -benzene derivatives. New 'one-pot' syntheses of hexafluorobut-2-yne (**4**), octafluorobut-2-ene (**6**) and hexafluorocyclobutene (**2**) were also discovered.

4) Various routes were explored in an attempt to improve the present literature preparations of tetrafluoropropyne (**79**), including pyrolysis and elimination methods. Tetrafluoroallene (**81**), and trace amounts of (**79**), were found to be formed on the elimination of hydrogen fluoride from 2*H*-pentafluoropropene (**5**).

CONTENTS

CHAPTER ONE.. 1

1.I.1. General Introduction into Fluorine Chemistry............................ 1

1.I.2. Industrial Applications... 2

1.II. Synthesis and Reactions of Polyfluorinated Alkenes and Alkynes.. 3

1.II.1 Aims.. 3

1.II.2. Synthesis of Polyfluorinated Alkenes and Alkynes.................... 3

1.II.2.a. Dehalogenations... 3

1.II.2.b.. Dehydrohalogenations.. 5

1.II.2.c. Pyrolytic Eliminations... 6

1.II.2.d. Fluoride Ion Reactions.. 8

1.II.2.e. Other Methods.. 9

1.II.3. Reactions of Polyfluorinated Alkenes and Alkynes.................... 9

1.II.3.a. Nucleophilic Reactions.. 9

1.II.3.b. Electrophilic Reactions... 18

1.II.3.c. Free-Radical Reactions... 19

1.II.3.d. Cycloaddition Reactions... 20

1.II.3.e. Organometallic Chemistry... 23

1.III. Conclusions.. 24

CHAPTER TWO. 25

2.I. Introduction.. 25

2.I.1. The Diels-Alder Reactions of Hexafluorobut-2-yne.................. 25

2.I.1.a. Reactions involving Furan Derivatives..................................... 25

2.I.1.b. Arenes and Other Diels-Alder Reactions.................................. 31

2.II. Reactions of (*Z*)-2*H*-Heptafluorobut-2-ene with Dienes............ 35

Results and Discussion.. 36

2.III. Further Investigation Of The Reaction Of 2*H*-Heptafluorobut-2-ene 36

2.III.1. Furan.. 36

2.III.2. 2,5-Dimethylfuran 37

2.IV. Further Investigation Of The Reaction Of (*Z*)-2*H*-Heptafluorobut-2-ene with Cyclopentadiene............................... 38

2.IV.1.a. Cyclopentadiene.. 38

2.IV.1.b. Dicyclopentadiene.. 40

2.IV.2. Hydrogenation of *Endo*- and *Exo*- 5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene............................. 40

2.IV.3. Dehydrofluorination of *Endo*- and *Exo*- 2-fluoro-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane. 41
2.IV.4. Pyrolysis of 2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene. 42
2.V. Investigation of (*Z*)-2*H*-Heptafluorobut-2-ene with Arenes. 43
2.V.1. 1,2,4,5-Tetramethylbenzene 43
2.V.2. Anthracene 44
2.V.3. Benzene 44
2.V.4. Trifluoromethylbenzene 45
2.V.5. 1,3,5-Trimethylbenzene 45

CHAPTER THREE 49
3.I. Review of Nucleophilic Additions to Hexafluorobut-2-yne and (*Z*)-2*H*-Heptafluorobut-2-ene 49
3.I.1. Oxygen Nucleophiles 49
3.I.2. Nitrogen Nucleophiles 53
3.I.3. Sulfur Nucleophiles 55
Results and Discussion 55
3.II. Novel Nucleophilic Additions to 2*H*-Heptafluorobut-2-ene 55
3.II.1. Oxygen Nucleophiles 55
3.II.1.a. 2,2-Di(4-hydroxyphenol)hexafluoropropane 55
3.II.1.b.i. Allyl alcohol 56
3.II.1.a.ii. Pyrolysis of Allyl alcohol adduct 57
3.II.2. Nitrogen Nucleophiles 58
3.II.2.a. Aniline 58
3.II.2.a.i. 2-Phenylimino-1,1,1,4,4,4-hexafluorobutane and Potassium Hydroxide 60
3.II.2.b. 4-Methylaniline 62
3.II.3. Sulfur Nucleophiles 63
3.II.3.a. Thiophenol. 63
3.III. Elucidation of Stereochemistry 65

CHAPTER FOUR. 66
4.I. Introduction. 66
4.I.1. Perfluorocarbon Fluids. 66
4.I.2. The Halogen Exchange Reaction. 67
4.I.2.a. Iodine 67
4.I.2.b. Fluorine 68

4.I.2.c. Chlorine and Bromine. 69
Results and Discussion 70

CHAPTER FIVE. 77
5.I. Introduction. 77
Results and Discussion 78
5.II. Hexafluoropropene (11) adducts 78
5.II.1. Acetaldehyde 79
5.II.2. Methanol 81
5.II.3. Pyrolysis 84
5.II.4. Cyclohexanone 84
5.III. Other Attempted Routes. 85
5.III.1. 2*H*-Pentafluoropropene 85
5.III.2. Decarboxylation of Isoxazolone derivatives 87
5.III.3. 3,4,6-Trichloro-7-methyl-coumarin 90

Instrumentation and Reagents 92

CHAPTER SIX. 94
Furan Systems 94
Cyclopentadiene 94
Arene Systems 96

CHAPTER SEVEN. 98
General Procedure with Potassium Carbonate. 98
Oxygen Nucleophiles. 98
Nitrogen Nucleophiles. 98
Sulfur Nucleophiles. 99
General Procedure without Potassium Carbonate. 99
Nitrogen Nucleophiles 100
Oxygen Nucleophiles. 100
Formation of 2-Trifluoromethyl-4-(*N*-phenylamino)-quinoline. 100

CHAPTER EIGHT. 102
Reactions using sulpholane 102
Reactions using 18-Crown-6 103

CHAPTER NINE 107
Hexafluoropropene Adducts 107
Other Attempted Routes 109

APPENDICES

Appendix 1. NMR Data **110**
Appendix 2. IR Data **134**
Appendix 3. Mass Spec. Data **145**
Appendix 4. Crystallographic Data **194**
Appendix 5. Requirements of the Board of Studies **198**
    Colloquia, Lectures and Seminars From Invited Speakers 199
    First Year Induction Courses 206
    Research Conferences Attended 206

References. **207**

Chapter 1.

Introduction.

1.I.1. General Introduction into Fluorine Chemistry.

Fluorine chemistry is an interesting and important field within the chemical, pharmaceutical and agrochemical industries. Fluoromethane was the first organofluorine compound to be discovered which was reported by Dumas and Peligot[1] in 1836, some 50 years before Moissan[2] isolated elemental fluorine. However, it was the pioneering work carried out by Swarts[3, 4] at the beginning of this century, that established the foundations of organofluorine chemistry. His work on simple aliphatic fluorine containing molecules was fundamental to Midgley and Henne's[5] work in 1930 to produce the first chlorofluorocarbons (CFCs).

Fluorine is the thirteenth most abundant element,[6] so it is surprising that apart from one or two minor exceptions, fluoroacetate being one, fluorine containing organic compounds are not found in nature.[7] This means that organofluorine chemistry is essentially a synthetic field.

Elemental fluorine is extremely reactive because of the weak fluorine-fluorine bond and the strong bonds that fluorine forms with carbon and other elements.[8] Some bond energies are compared in *Table 1.1* and it is important to note from this table that carbon-fluorine bonds are even stronger than carbon-hydrogen bonds. This increase in bond strength imparts exceptional thermal and chemical stabilities[6] on some fluorocarbon systems.

X	H	Cl	C	F
C-X bond energy (kJ/mol)	416	326	368	485

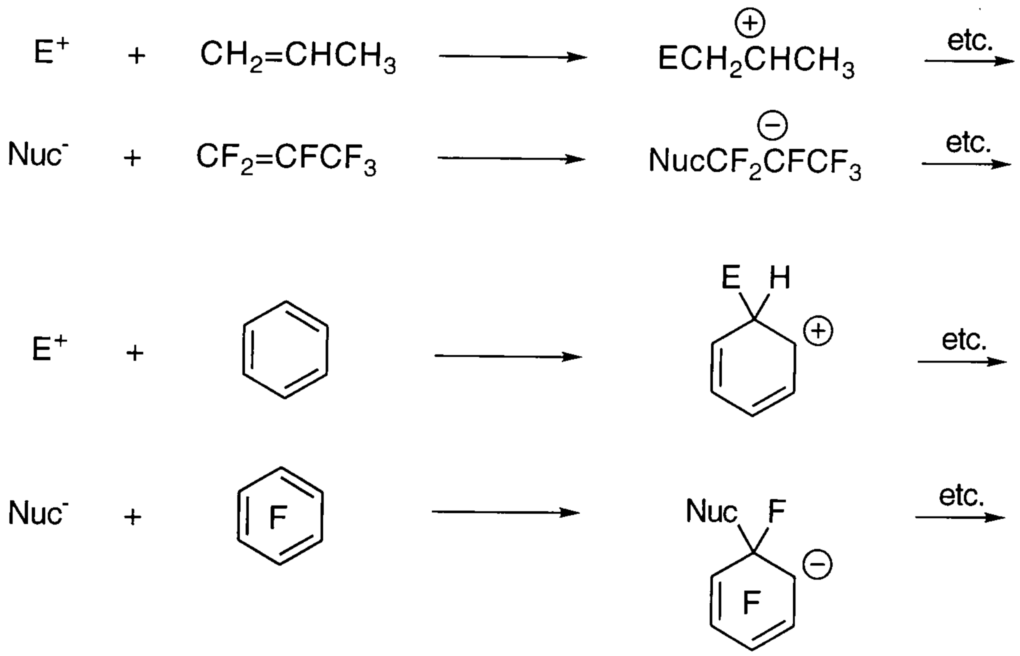
Table 1.1. C-X bond energies.[8]

Volatilities of fluorocarbons are surprisingly similar to the corresponding hydrocarbons, despite the large increase in molecular weight, *Table 1.2*, and this observation demonstrates a decrease in the intermolecular bonding in fluorocarbon systems.

	$CH_3CH_2CH_2CH_3$	$CF_3CF_2CF_2CF_3$
bp (°C)	-0.4	-1.4
RMM	58	238

Table 1.2. A comparison of the volatilities of hydro- and fluoro- carbons.[9]

Fluorine is unique in the fact that it is possible to replace hydrogen by a fluorine in many hydrocarbon molecules, with little overall distortion to the geometry of the system.[10] Since fluorine is the most electronegative element, the introduction of one or more fluorine atoms into a compound creates an entirely different electronic environment, when compared to the hydrocarbon equivalent. Consequently, novel compounds are discovered that have very different properties and reactions to their hydrocarbon analogues. A striking illustration of this difference occurs when comparing the chemistry of simple hydrocarbon arenes and alkenes with the analogous perfluorinated systems. *Scheme 1.1* illustrates the fact that the chemistries of these systems have a 'mirror image' relationship, in that the chemistry of unsaturated hydrocarbon systems is dominated by electrophilic attack, whereas nucleophilic attack is the dominant process in reactions of perfluorinated systems.



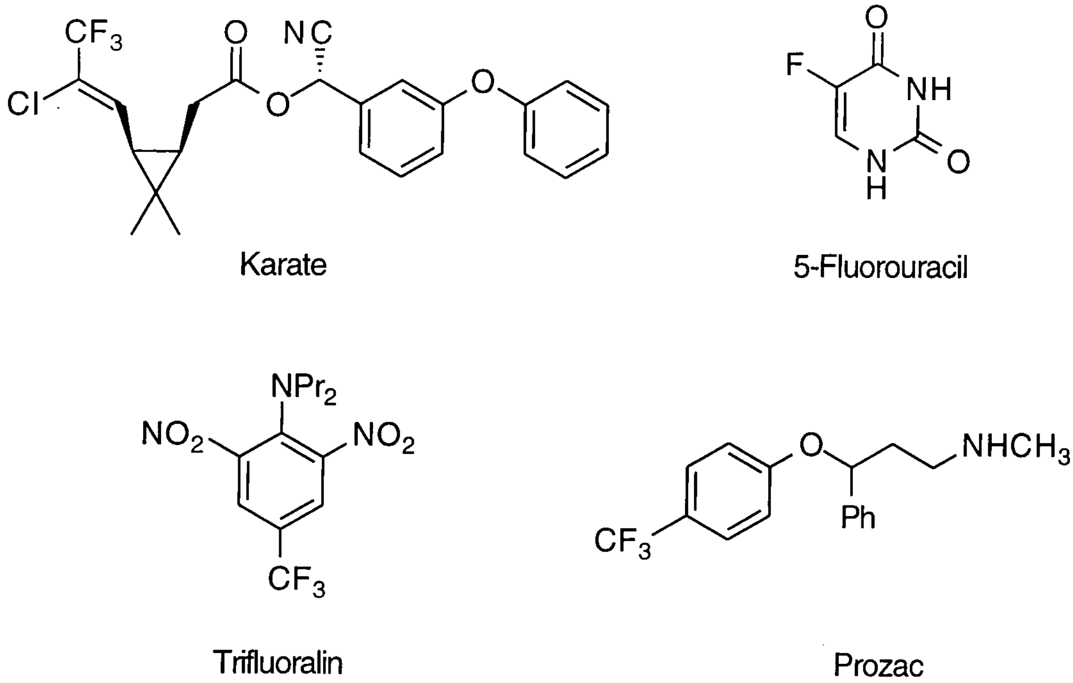
Scheme 1.1. The 'Mirror Image' chemistry of hydrocarbons and perfluorocarbons.

1.1.2. Industrial Applications.

Organofluorine compounds are widely used in society to produce a desired effect or property.[11] Fluorocarbons fluids are used as refrigerants, fire-extinguishers and as fluids in hot-vapour soldering techniques. Polymer chemistry takes advantage of the resistance of fluorinated polymers to bacterial oxidation, and these polymers, such as PVDF and Viton, are used to make inert rubbers used on the space shuttle. Gortex is another well known polymer, which is expanded PTFE.

Fluorocarbon materials have unique surface properties owing to the non-bonding electron pairs and thus show non-stick and oil-repellency, properties that are utilised in stain preventatives and on many kitchen utensils. Also fluorine containing dyes can be made that are colour-fast and brighter than many other dyes.

In the pharmaceutical and agrochemical industries there is a wide range of applications of fluorine containing compounds and some of these are shown in *Scheme 1.2.*


Karate

5-Fluorouracil

Trifluoralin

Prozac

Scheme 1.2. Examples of the uses of fluorine containing compounds in the pharmaceutical and agrochemical industries. 5-Fluorouracil (treatment of breast cancer), Prozac (anti-depressant), Karate and Trifluoralin (weed killers).

1.II. Synthesis and Reactions of Polyfluorinated Alkenes and Alkynes.

1.II.1 Aims.

It is not the intention of this introduction to be a complete and comprehensive text of the syntheses and chemistry of *all* polyfluorinated alkenes and alkynes. The breadth of this field is just too large to write a comprehensive review, however there are a number of excellent review articles[6, 12, 13] that, between them, cover the majority of this area. This introduction will be limited to some of those polyfluorinated alkenes and alkynes that are either commercially available or are, at least, simple to make.

1.II.2. Synthesis of Polyfluorinated Alkenes and Alkynes.

In general there are four methods for synthesising polyfluorinated alkenes and alkynes. These are (i) dehalogenations, (ii) dehydrohalogenations, (iii) pyrolytic eliminations and (iv) fluoride ion halogen exchange reactions.

1.II.2.a. Dehalogenations.

Dehalogenations,[14-20] along with dehydrohalogenations, are one of the most important methods of producing polyfluorinated unsaturated compounds. The precursors required for such eliminations are often synthesised using techniques developed by Swarts,[3, 4] reactions of polychloroalkanes with anhydrous hydrogen fluoride.

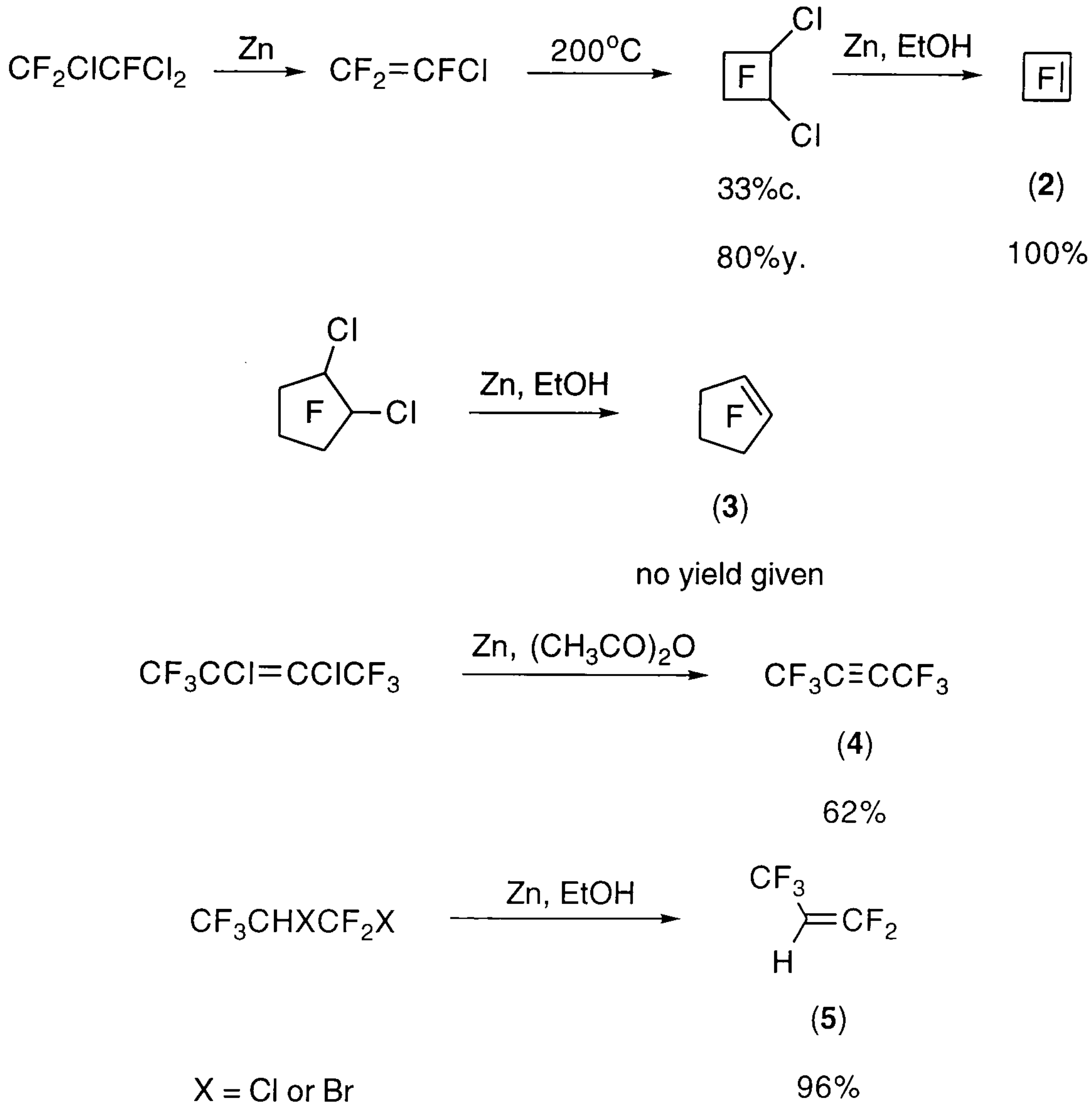
$$CHCl_3 \xrightarrow{HF,\ SbCl_5} CHClF_2 \xrightarrow{700^{\circ}C,\ Pt\ tube} \underset{(\mathbf{1})}{CF_2{=}CF_2}$$

$$CCl_3CCl_3 \xrightarrow{HF,\ SbCl_5} CF_2ClCFCl_2 \xrightarrow{Zn,\ EtOH} CF_2{=}CFCl$$

$$CCl_2{=}CClCCl{=}CCl_2 \xrightarrow{HF,\ SbCl_5} CF_3CCl{=}CClCF_3$$

Scheme 1.3. Example of Swarts reactions to produce fluorinated precursors.[3, 4]

The most common dehalogenations performed are the eliminations of chlorine or bromine and these can be accomplished using zinc in alcohol, *Scheme 1.4*, although electrolytic methods have been applied.[21]



CF2ClCFCl2
Zn
CF2=CFCl
200°C
Cl
F
Cl
Zn, EtOH
F
33%c.
80%y.
(2)
100%
Cl
F
Cl
Zn, EtOH
F
(3)
no yield given
CF3CCl=CClCF3
Zn, (CH3CO)2O
CF3C≡CCF3
(4)
62%
CF3CHXCF2X
Zn, EtOH
CF3
=CF2
H
(5)
X = Cl or Br
96%

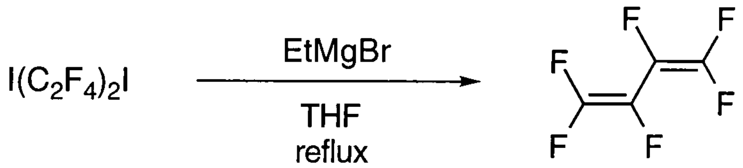
$$CF_3CFXCFXCF_3 \xrightarrow{\text{Zn, EtOH}} CF_3CF{=}CFCF_3$$

(6)

X = Cl (100%) or Br (75%)

Scheme 1.4. Examples of dehalogenations to form perfluorocyclobutene (**2**),[14] perfluorocyclopentene (**3**),[15] hexafluorobut-2-yne (**4**),[9] 2*H*-pentafluoropropene (**5**)[17, 18] and octafluorobut-2-ene (**6**).[19, 20]

It is also possible to eliminate mixed halogens,[22] such as IF to form perfluorodienes, *Scheme 1.5*.

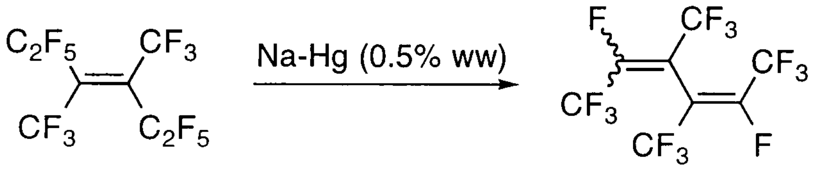


(7)

96%

Scheme 1.5. Elimination of IF.

Defluorination is one technique that has had only limited success, owing mainly to the strength of the carbon-fluorine bond that needs to be broken, and is therefore not widely used. However, sodium amalgams[23] and activated carbon[24] have been applied to this end, but are only good for the synthesis of polyfluorinated dienes and therefore are not a viable general route.



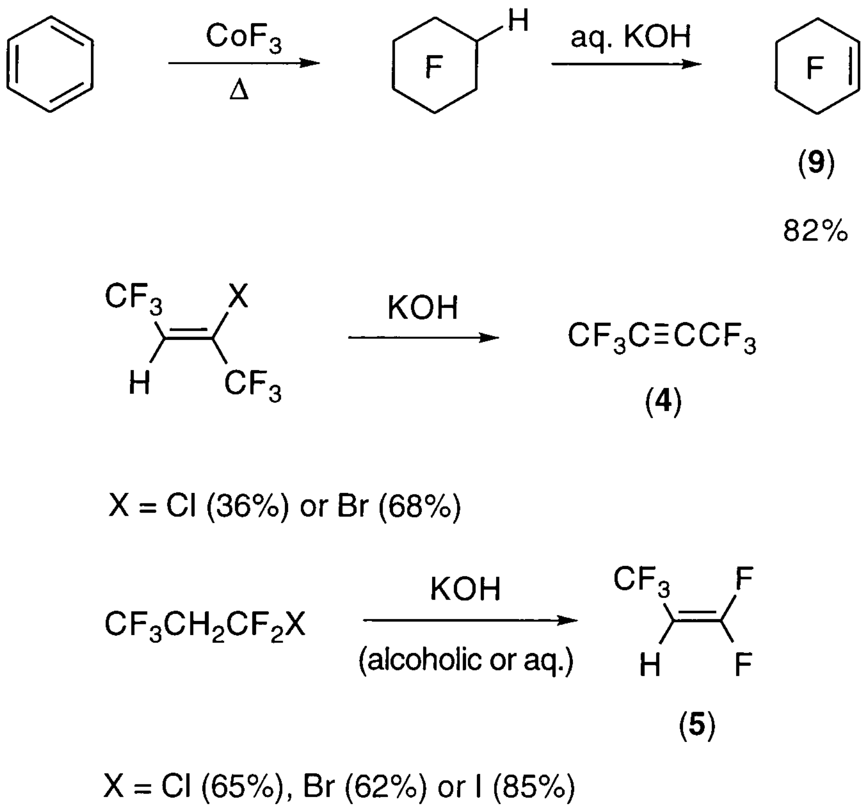
(8)

ZZ 68%
EZ 19%

Scheme 1.6. Sodium amalgam[23] defluorination to produce perfluorinated dienes.

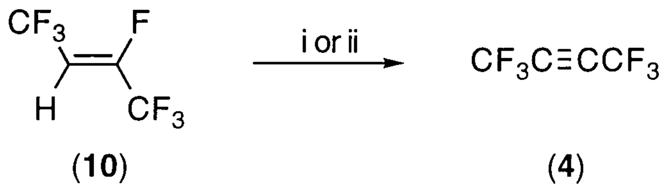
1.II.2.b. Dehydrohalogenations.

β-Elimination of hydrogen halide from polyfluorinated precursors[25-29] is another general method for the synthesis of polyfluorinated alkenes and alkynes. Aqueous potassium hydroxide is the most commonly used base to effect dehydrohalogenation, although many other bases can be utilised.


CoF3
Δ
F
H
aq. KOH
F
(9)
82%
CF3
X
H
CF3
KOH
CF3C≡CCF3
(4)
X = Cl (36%) or Br (68%)
CF3CH2CF2X
KOH
(alcoholic or aq.)
CF3
F
H
F
(5)
X = Cl (65%), Br (62%) or I (85%)

Scheme 1.11. Examples of dehydrohalogenation to form perfluorocyclohexene (**9**),[25] hexafluorobut-2-yne (**4**)[26] and 2*H*-pentafluoropropene (**5**).[27-29]

Stronger bases are sometimes required to carry out elimination such as tertiarybutyl lithium and cesium fluoride; most recently these have shown application in the synthesis of hexafluorobut-2-yne,[30] *Scheme 1.18.*

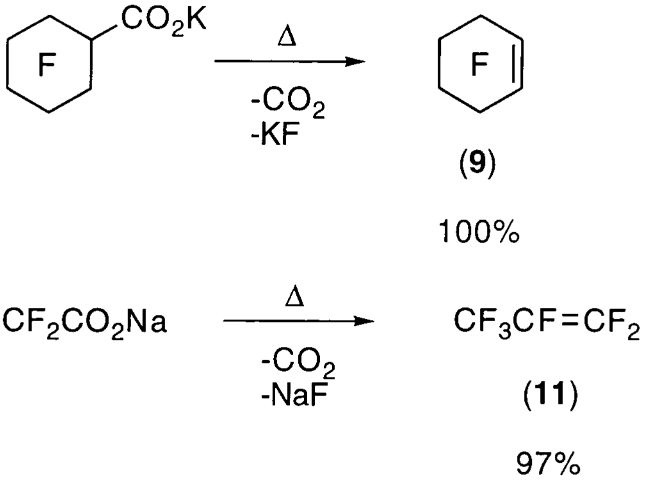

CF3
F
H
CF3
(10)
i or ii
CF3C≡CCF3
(4)

i, CsF, 350°C (36%)
ii, ^{t}BuLi, -196 to 0°C (41%)

Scheme 1.8. Use of stronger bases in the synthesis of hexafluorobut-2-yne.

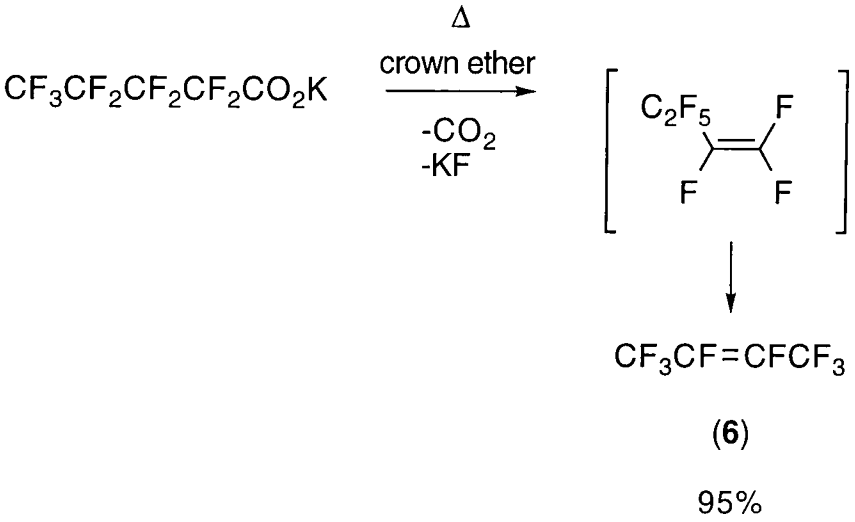
1.II.2.c. Pyrolytic Eliminations.

Pyrolytic elimination[31-33] of carbon dioxide and metal fluoride is another, but less common, technique of forming unsaturated polyfluorinated compounds.


CO2K
Δ
-CO2
-KF
F
(9)
100%
CF3CF2CF2CO2Na
Δ
-CO2
-NaF
CF3CF=CF2
(11)
97%

Scheme 1.9. Examples of pyrolytic elimination to form perfluorocyclohexene (**9**)[31] and hexafluoropropene (**11**).[32]

This is an important technique for the synthesis of terminal alkenes, but contact time is critical. Polyfluorinated terminal alkenes will rearrange at moderate temperatures[33] to the more thermally stable internal alkene.


CF3CF2CF2CF2CO2K
Δ
crown ether
-CO2
-KF
C2F5
F
F
F
CF3CF=CFCF3
(6)
95%

Scheme 1.10. Thermal rearrangement of terminal alkenes.

Pyrolytic elimination may also be used in the synthesis of tetrafluoroethene (**1**), which is formed by the pyrolysis of chlorodifluoromethane to difluorocarbene[3] and its subsequent dimerisation, as shown earlier in *Scheme 1.3.* Further reaction of tetrafluoroethene (**1**) with more carbene is used to produce longer chain polyfluorinated compounds, for example hexafluoropropene (**11**) and perfluoroisobutene (**12**).

$$CF_2{=}CF_2 \quad + \quad :CF_2 \quad \xrightarrow{\Delta} \quad CF_3CF{=}CF_2$$

(**11**)

$$CF_3CF=CF_2 \quad + \quad :CF_2 \xrightarrow{\Delta} (CF_3)_2C=CF_2$$

(12)

Scheme 1.11. A synthesis of hexafluoropropene (**11**) and perfluoroisobutene (**12**).[3]

Tetrafluoroethene (**1**) is also the major product formed when PTFE is pyrolysed under vacuum.[34]

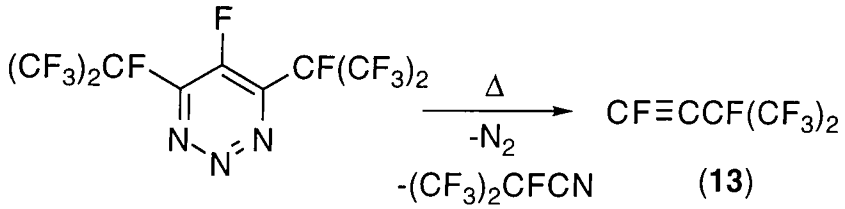
$$\left(CF_2-CF_2\right)_n \xrightarrow[\text{vacuum}]{\sim 600^{\circ}C} CF_2=CF_2$$

(1)

(90%)

Scheme 1.12. Pyrolysis of PTFE.

Another interesting pyrolysis is the decomposition of substituted 1,2,3-triazines,[35] *Scheme 1.13*, to synthesise polyfluorinated alkynes.



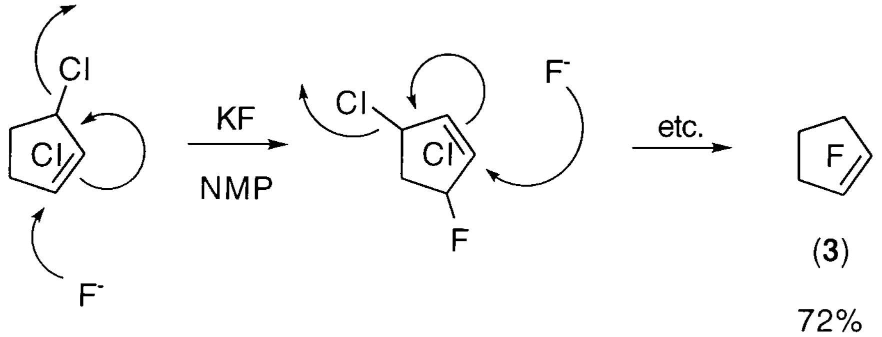
(13)

100%

Scheme 1.13. The pyrolysis of 1,1,1-triazines to form polyfluorinated alkynes.

1.II.2.d. Fluoride Ion Reactions.

Halogen exchange reactions are widely used in the preparation of fluorinated aromatic compounds but their use in the synthesis of alkenes and alkynes is limited. One of the most important examples of this reaction is the allylic displacement of chlorine ions from octachlorocyclopentene[36] to produce perfluorocyclopentene (**3**), *Scheme 1.14*.

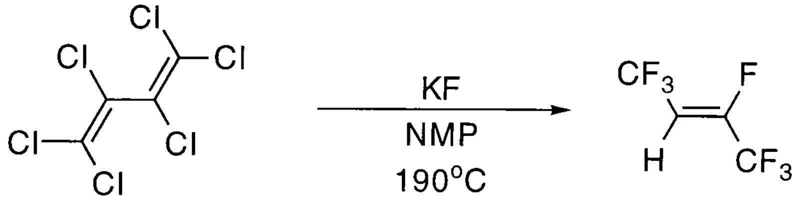


(3)

72%

Scheme 1.14. Allylic displacement of chloride ion.

Important to the work described in this thesis is the direct synthesis of (*Z*)-2*H*-heptafluorobut-2-ene (**10**)[36, 37] from hexachlorobutadiene, *Scheme 1.15*.



(**10**)

65%

Scheme 1.15. The synthesis of (*Z*)-2*H*-heptafluorobut-2-ene (**10**).

1.II.2.e. Other Methods.

There are numerous other examples of synthesising polyfluorinated alkenes and alkynes but two of the most important are illustrated below. Carboxyl groups may be fluorinated[38] to trifluoromethyl groups in the presence of sulfur tetrafluoride, and the addition of aldehydes to 1,1,1-trichlorotrifluoroethane[39] provides a useful synthesis of 1-aryl-3,3,3-trifluoromethylpropynes.

$$HO_2CC{\equiv}CCO_2H \xrightarrow[SF_4]{170^\circ C} CF_3C{\equiv}CCF_3$$

(**4**)

80%

$$RCHO + CCl_3CF_3 \xrightarrow[\text{acetic anhydride}]{Zn} RCH{=}CClCF_3 \xrightarrow{-HCl} RC{\equiv}CCF_3$$

51-95%

Scheme 1.16. Other methods of synthesis.

1.II.3. Reactions of Polyfluorinated Alkenes and Alkynes.

1.II.3.a. Nucleophilic Reactions.

Formation of a Carbanion.

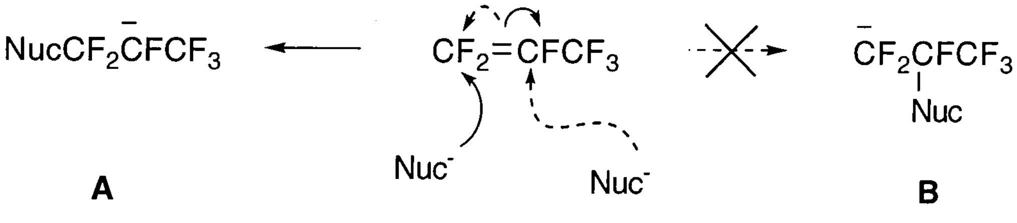
Polyfluorinated alkenes and alkynes are electron deficient species and are thus highly susceptible to nucleophilic attack by a wide range of nucleophiles. Attack can be thought of as occurring in two stages, firstly the addition of a nucleophile to the alkene to produce a carbanion and, secondly, the reaction of the carbanion to form the final product. In this section factors that are important in the formation of a carbanion will be discussed.

$$CF_2{=}CF_2 + Nuc^- \longrightarrow NucCF_2CF_2^- \xrightarrow{etc.}$$

(1)

Scheme 1.17. Nucleophilic attack on tetrafluoroethene (**1**).

For asymmetrical systems there is choice of two sites of attack.

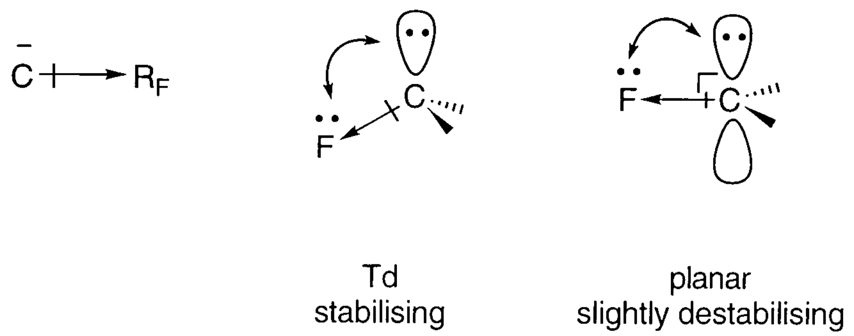


(11)

Scheme 1.18. Nucleophilic attack on hexafluoropropene (**11**).

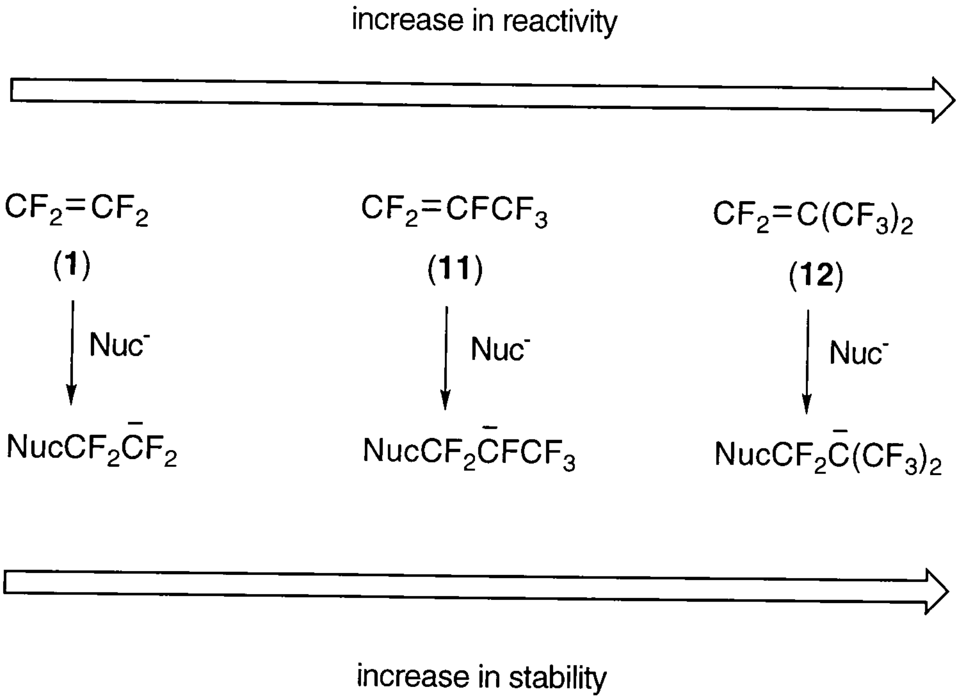
The chemistry of nucleophilic attack on polyfluorinated alkenes can be rationalised by three basic assumptions. (1) There is a significant ion-dipole interaction[40] between carbon and fluorine, this accounts for the fact that terminal difluoromethylenes are very reactive.[41, 42] (2) Fluorine attached to a carbon adjacent to a carbanion centre is strongly stabilising and hence strongly activating. (3) Fluorine attached directly to a carbanion centre is usually stabilising, however to a much lesser extent than for (2). Following these rules it can be seen that **A** will be the preferred site of attack on hexafluoropropene and the carbanion formed will be the most stable.

Perfluoroalkyl groups stabilise adjacent carbanions strongly but the effect of fluorine is more complex and the geometry of the carbanion centre needs to be considered. For a tetrahedral carbanion the inductive effect of the fluorine significantly stabilises the system [CHF_3 is 10^4 more acidic than CH_4][11, 43]. However, if the carbanion is planar there is a destabilising interaction between the carbanion centre and the non-bonding electron pairs of the fluorine. This interaction dominates over the stabilising inductive effect and results in a slight destabilisation of the carbanion.



Scheme 1.19. The effect of fluorine on the stability of carbanion centres.

The effect of fluorine on carbanion stabilities accounts for the reactivity order shown in *Scheme 1.20.*[44] Obviously, fluorine atoms in situations analogous to (2) are the most favourable and it is clear that the number of such stabilising fluorine atoms increases from tetrafluoroethene (**1**) to perfluoroisobutene (**12**).



Scheme 1.20. Reactivity series of some trifluoromethyl substituted fluoroalkenes.[44]

Further evidence is illustrated in the fluoroalkenes reactions with methanol. Tetrafluoroethene[44] requires strong bases and/or high pressures to react with methanol, hexafluoropropene[45] requires only weak bases whereas perfluoroisobutene[46] will react quickly in neutral methanol.

The inductive effect is not, however, sufficient to explain the difference observed between hexafluoropropene (**11**) and octafluorobut-2-ene (**6**). The carbanions produced by nucleophilic attack on the respective alkenes, *Scheme 1.21*, should have only a marginal difference in stability. However, perfluoropropene is much more reactive.

$NucCF_2\bar{C}FCF_3$ $\qquad$ $NucCF(CF_3)\bar{C}FCF_3$

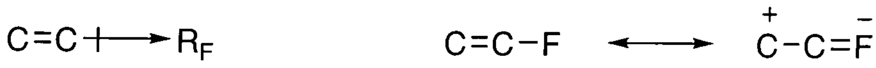
Scheme 1.21. The carbanions produced by nucleophilic attack on hexafluoropropene (**11**) and octafluorobut-2-ene (**6**).

Also the difference observed between the highly reactive perfluoroisobutene (**12**) and octafluorobut-2-ene (**6**) needs to be accounted for.

Consequently, a Frontier Orbital Theory can be used to account for the differences in reactivity and the orientation of nucleophilic attack.[47] Frontier Orbital theory is a method of explaining reaction mechanism considering only *two* molecular orbitals, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). For nucleophilic attack on fluorinated alkenes it is the HOMO of the nucleophile and the LUMO of the alkene that are important. Reaction will only occur if there is sufficient overlap of the two molecular orbitals and increased overlap can be achieved by reducing the energy of the LUMO by having electron-withdrawing groups on the double bond. Increased overlap leads to increased reactivity.

Substituent Effects on Frontier Orbitals

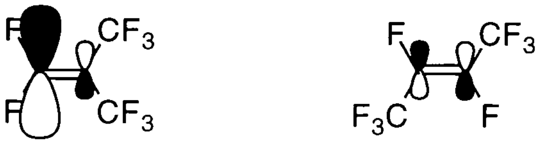
Photo-electron spectroscopic studies[48, 49] on Frontier Orbitals have shown the effects of fluorine and perfluoroalkyl groups on the energy of π-bonds. Perfluoroalkyl groups lower the π-orbital energy, as one would expect for electron withdrawing substituents. However, these studies have shown that fluorine is not all that dissimilar to a hydrogen on a double bond. The inductive effect of fluorine may therefore be off-set by a p-π interaction that causes an increase in the π-electron density.[40, 50, 51]



$$C{=}C \longrightarrow R_F \qquad C{=}C{-}F \longleftrightarrow \overset{+}{C}{-}C{=}\overset{-}{F}$$

Scheme 1.22. Substituent effects of fluorine and perfluoroalkyl groups on double bonds.

Replacing fluorine for a perfluoroalkyl group in a fluorinated alkene lowers the LUMO energy thus increasing the reactivity of the alkene, providing that the perfluoroalkyl groups are on the same carbon atom of the double bond. It appears that coefficients are of significant importance. Trifluoromethyl groups increase the coefficient in the LUMO at the adjacent carbon of the double bond. When two trifluoromethyl groups are attached at adjacent carbons their effect on the coefficient, and hence reactivity, is opposing. Whereas, obviously, for perfluoroisobutene the trifluoromethyl groups are attached to the same carbon, thus their effects are accumulative and the adjacent carbon is highly reactive.



(12) (6)

CF$_3$ groups on the same carbon atom reinforce

CF$_3$ groups on opposite carbon atoms in opposition

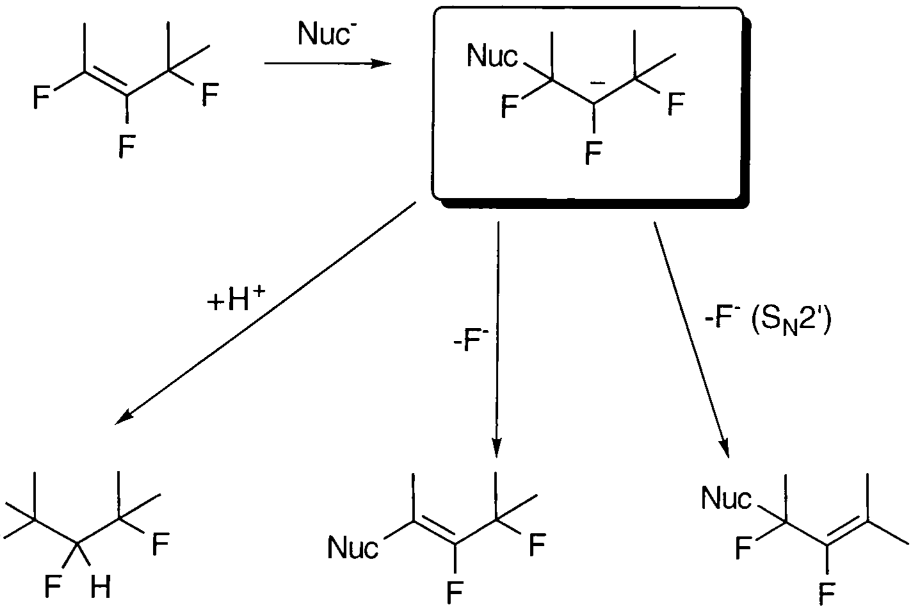
Scheme 1.23. LUMOs of perfluoroisobutene (**12**) and octafluorobut-2-ene (**6**).

The Fate of the Carbanion.

It is the aim of this section to discuss, with examples, what happens to the fluoroalkene after the carbanion has been formed by initial nucleophilic attack.

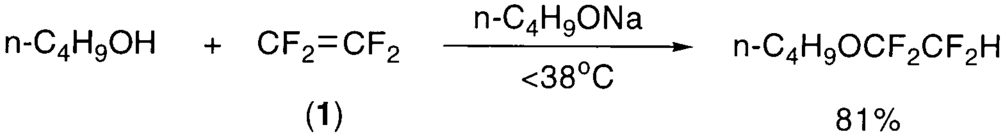
Nucleophilic attack has been shown to proceed via three alternative routes:-

- Direct addition across the double bond
- Vinylic substitution of fluoride ion
- Allylic displacement of fluoride ion (S_N2')



Scheme 1.24. The three possible routes of nucleophilic attack on fluoroalkenes.

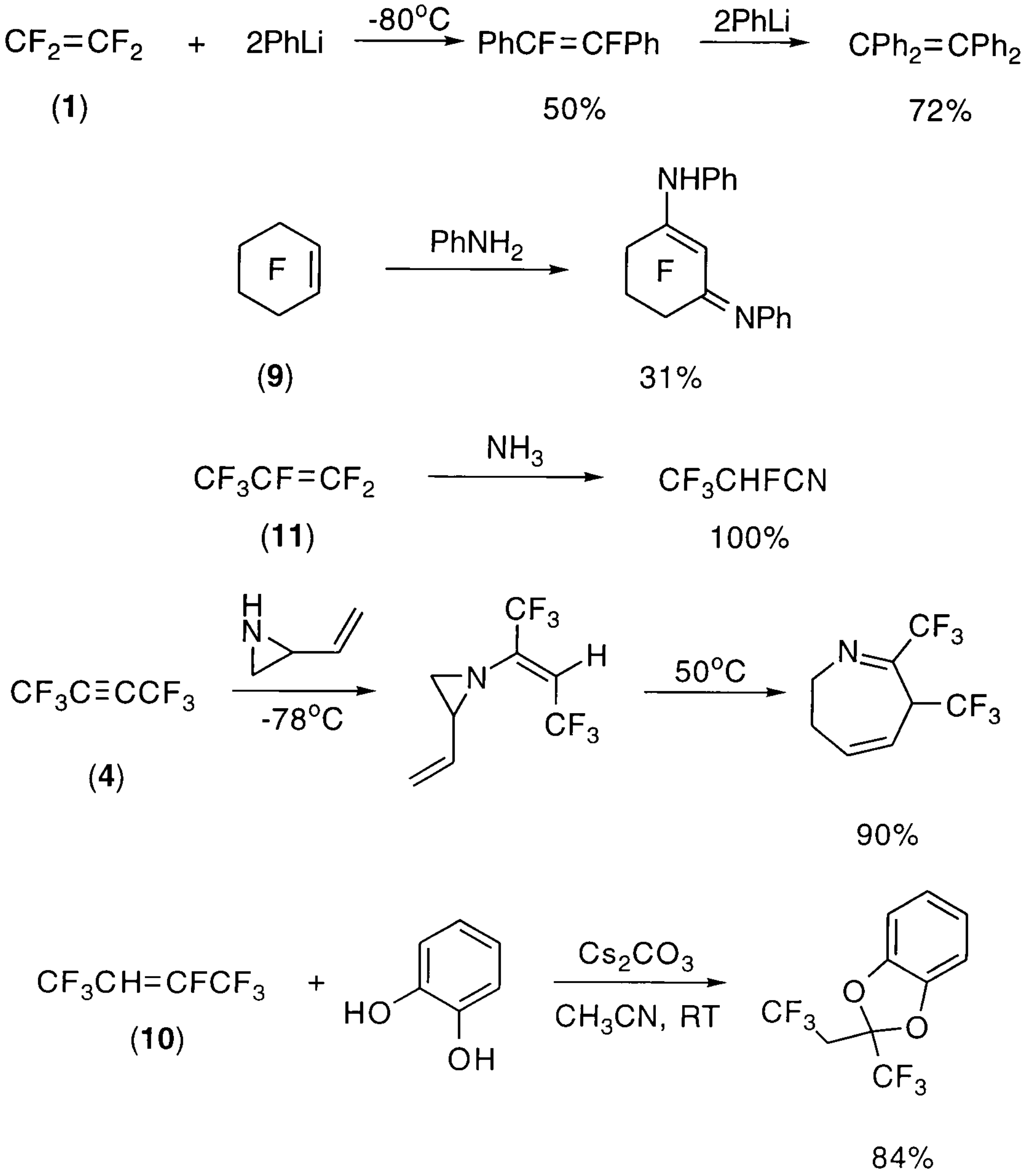
The route followed depends predominantly on the stability of the intermediate carbanion. Carbanions that are very unstable usually abstract a proton from their environment rather than eliminate a fluoride ion. This is exemplified by tetrafluoroethene (**1**). The instability of the $NucCF_2CF_2^-$ carbanion, formed by initial nucleophilic attack on (**1**), is caused by the destabilising effect of two α-fluorine atoms. The result of this is that unsaturated products are rarely formed from the nucleophilic addition to fluoroalkene (**1**),[52] *i.e.* a proton is abstracted in preference to the elimination of fluoride.

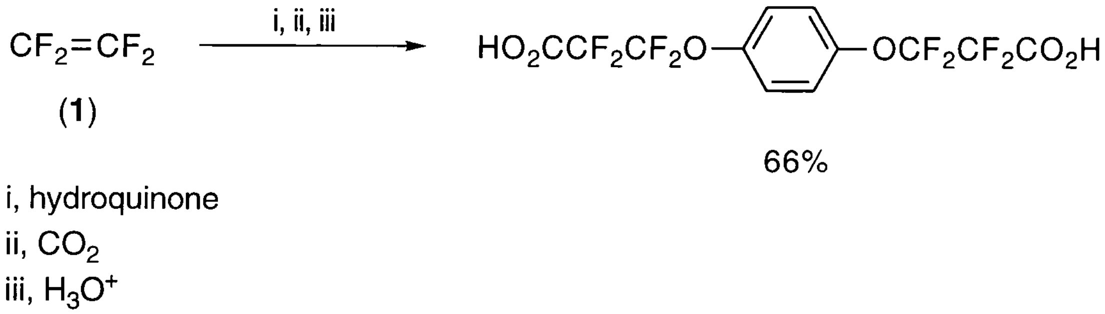


$$\underset{}{n\text{-}C_4H_9OH} + \underset{(\mathbf{1})}{CF_2{=}CF_2} \xrightarrow[<38^{\circ}C]{n\text{-}C_4H_9ONa} \underset{81\%}{n\text{-}C_4H_9OCF_2CF_2H}$$

Scheme 1.25. Saturated products are commonly formed from tetrafluoroethene (**1**).

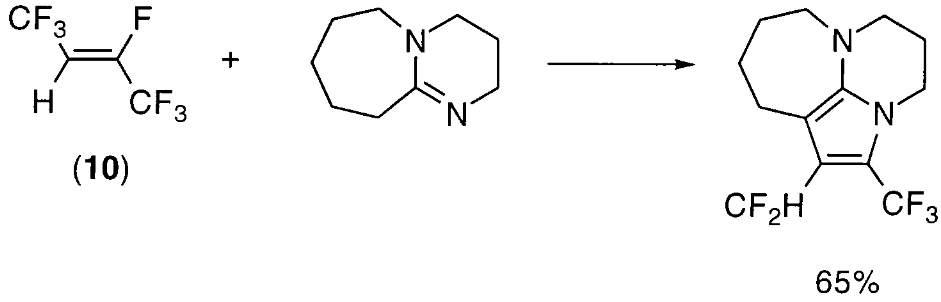
Carbon, nitrogen, oxygen, sulfur and other nucleophiles[53-62] all readily react with polyfluorinated alkenes and alkynes. Examples can be seen in *Scheme 1.26.*


CF2=CF2 + 2PhLi
-80°C
PhCF=CFPh
2PhLi
CPh2=CPh2
(1)
50%
72%
F
PhNH2
NHPh
F
NPh
(9)
31%
CF3CF=CF2
NH3
CF3CHFCN
(11)
100%
CF3C≡CCF3
H
N
-78°C
N
CF3
H
CF3
50°C
N
CF3
CF3
(4)
90%
CF3CH=CFCF3 +
HO
OH
Cs2CO3
CH3CN, RT
O
O
CF3
CF3
(10)
84%


CF2=CF2
(1)
i, ii, iii
HO2CCF2CF2O–C6H4–OCF2CF2CO2H
66%
i, hydroquinone
ii, CO2
iii, H3O+

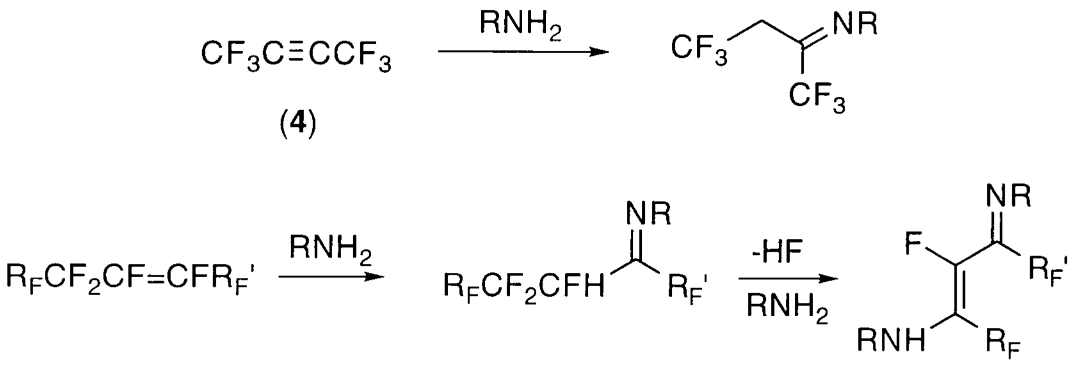
Scheme 1.26. Examples of nucleophilic addition to polyfluoroalkenes and alkynes using phenyl lithium,[58] aniline,[61] ammonia,[62] 2-vinylaziridine,[63] catechol[64] and hydroquinone.[59]

These fluorinated systems are so reactive that, even what are perceived as, non-nucleophilic bases may on occasion react as nucleophiles.


CF3
F
H
CF3
(10)
+
N
N
N
N
CF2H
CF3
65%

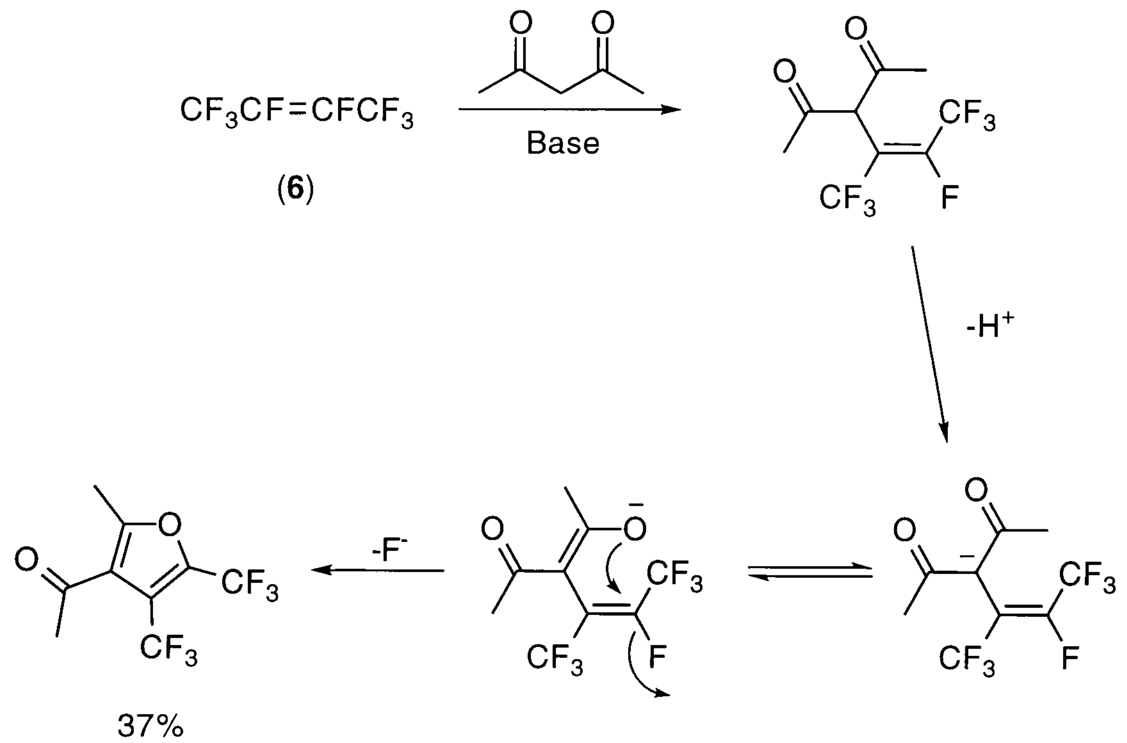
Scheme 1.27. The reaction of DBU with 2*H*-heptafluorobut-2-ene.[65]

Once nucleophilic attack has occurred on a fluoroalkene there is the possibility of further attack, at a position of unsaturation, or the elimination of hydrogen fluoride, as utilised in the synthesis of fluorinated imines.[66]


CF3C≡CCF3
(4)
RNH2
CF3
NR
CF3
RFCF2CF=CFRF'
RNH2
NR
RFCF2CFH
RF'
-HF
RNH2
NR
F
RF'
RNH
RF

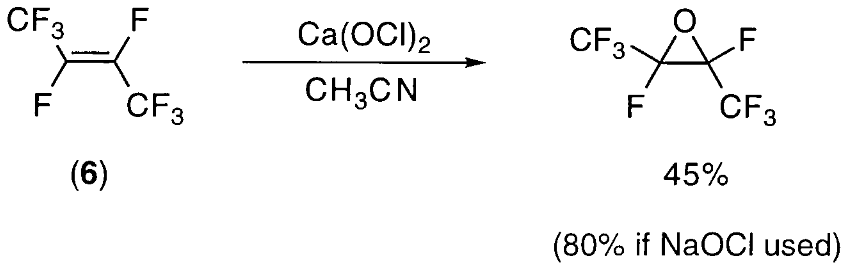
Scheme 1.28. The formation of imines by further nucleophilic attack.

A novel synthesis of a fluorinated furan derivative is observed when 2,4-pentanedione is reacted with octafluorobut-2-ene (**6**),[67] *Scheme 1.29.*



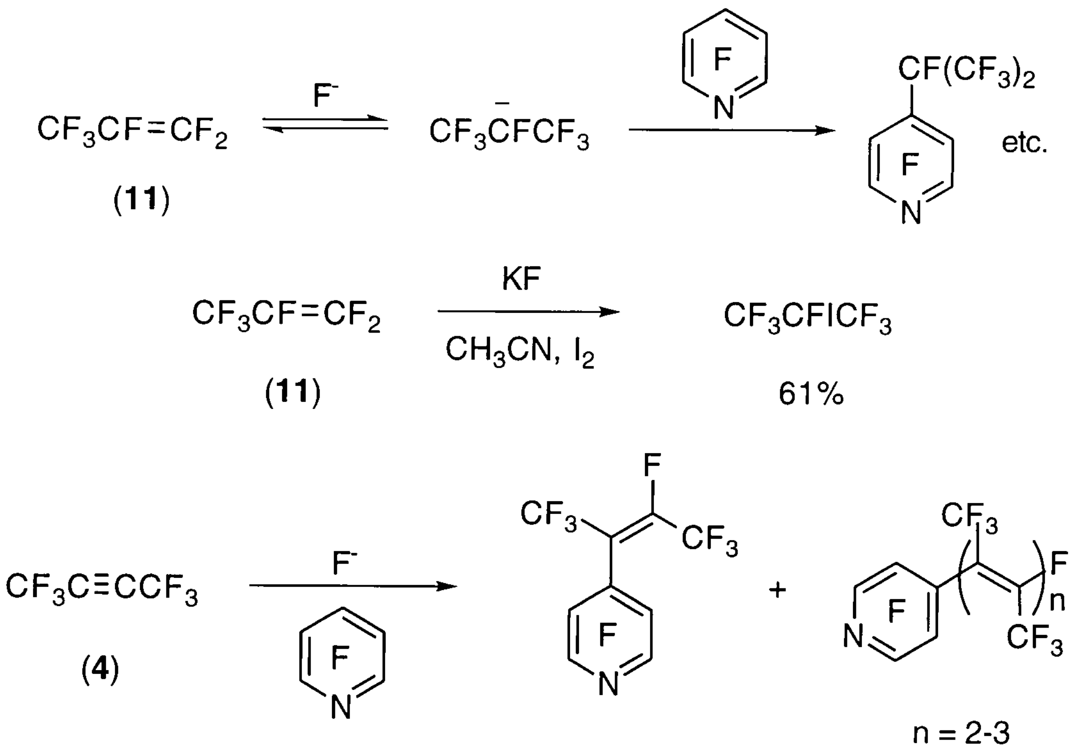
Scheme 1.29. A novel furan synthesis.

Epoxidations of polyfluoroalkenes are industrially important in the synthesis of monomers for the production of fluorinated polyethers. Various reagents can be used to effect efficient epoxidation of these alkenes, including hydrogen peroxide[68] and calcium hypochlorite.[69]



Scheme 1.30. Epoxidation of octafluorobut-2-ene using calcium hypochlorite.

An important area that has not be mentioned so far is the application of fluoride ion to polyfluoroalkenes and alkynes. Carbanions can be generated from fluoroalkenes by the addition of fluoride ion, and these can be trapped by a number of reagents, as shown by Miller[70] in 1960.

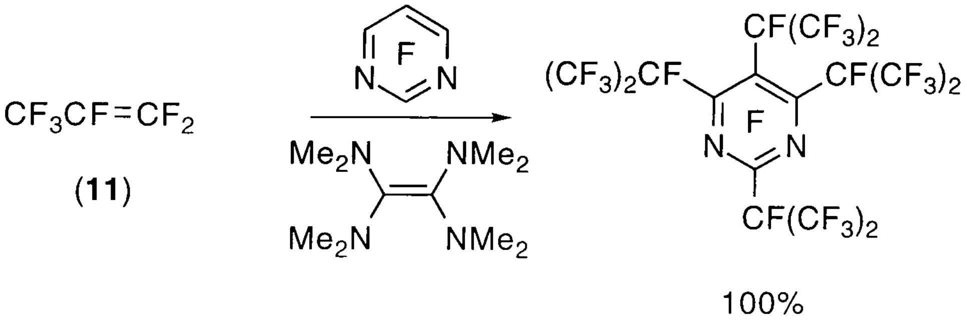


$CF_3CF{=}CF_2$
(11)
F^-
$CF_3\bar{C}FCF_3$
F
N
$CF(CF_3)_2$
etc.
KF
CH_3CN, I_2
CF_3CFICF_3
61%
$CF_3C{\equiv}CCF_3$
(4)
CF_3
CF_3
+
CF_3
n
n = 2-3

Scheme 1.31. Examples of trapping carbanions formed by fluoride ion with hexafluoropropene (**11**) and perfluoropyridine,[71] hexafluoropropene (**11**) and iodine,[72] and hexafluorobut-2-yne (**4**) and perfluoropyridine.[73]

A whole range of fluoroalkyl groups may be added by this method such as C_2F_5, $(CF_3)_2CF$ and larger.[6, 43, 71] Given the right conditions polysubstitution can also be achieved.[71]

Cesium and potassium fluorides are the most commonly used sources of fluoride ion, however more recently tetrakis(dimethylamino)ethene (TDAE) has been used to form a powerful, '*in situ*', source of fluoride when used with unsaturated fluorocarbons,[74] as shown in *Scheme 1.32.*

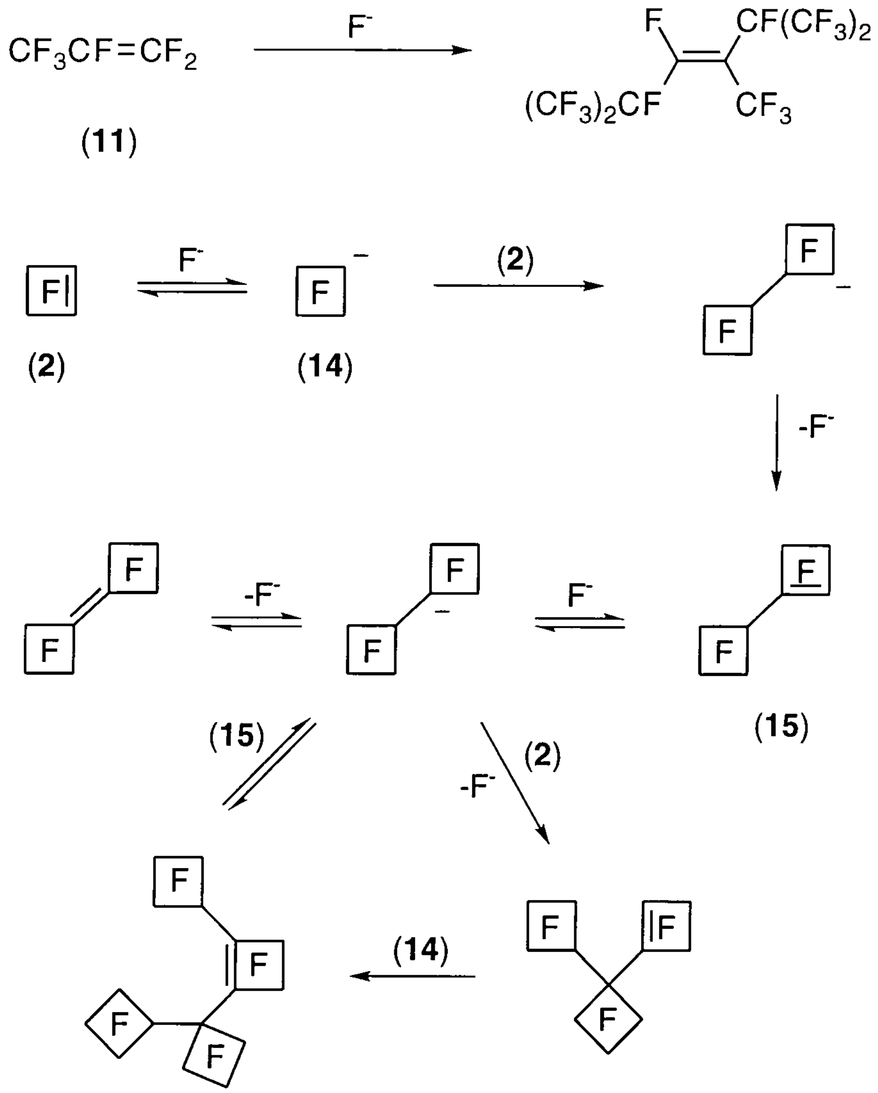


$CF_3CF{=}CF_2$
(11)
F
N
Me_2N
NMe_2
Me_2N
NMe_2
$(CF_3)_2CF$
$CF(CF_3)_2$
$CF(CF_3)_2$
$CF(CF_3)_2$
100%

Scheme 1.32. TDAE as a source of fluoride ion.

Other examples of fluoride sources are proton sponge,[75] alkylamine hydrogen fluorides[76-80] and trisdimethylaminosulfonium difluorotrimethylsilicate (TAS-F).[81]

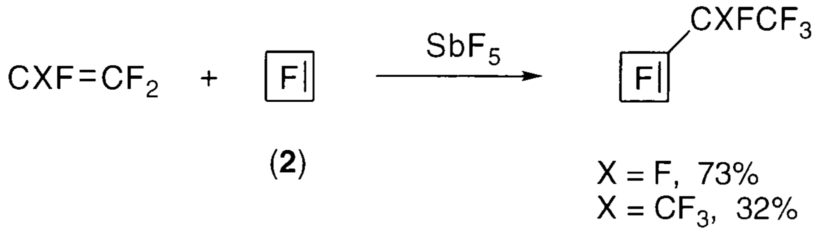
Complex fluorinated alkenes can be formed by the fluoride initiated oligomerisation of simple alkenes. The distance the reaction proceeds varies with the alkene used, for example, tetrafluoroethene (**1**) will produce a hexamer whilst hexafluoropropene (**11**) gives mainly the dimer and only some trimer.[82]


CF3CF=CF2
F-
(11)
F
CF(CF3)2
(CF3)2CF
CF3
F
(2)
(14)
-F-
(15)
(14)

Scheme 1.33. Fluoride ion initiated oligomerisations.[82, 83]

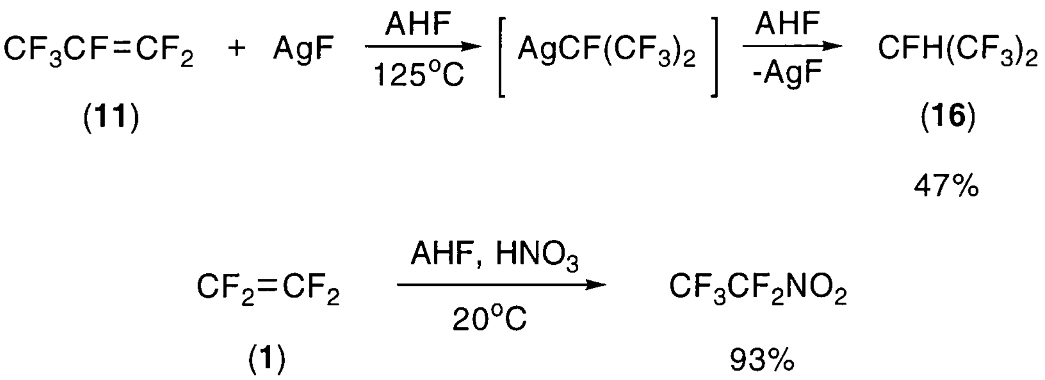
1.II.3.b. Electrophilic Reactions.

Polyfluoroalkenes are fairly resistant to attack by electrophiles, owing to their electron deficiency, however there are a few exceptions. Hexafluorocyclobutene (**2**) does not react with antimony pentafluoride to produce its dimer,[84] however under exactly the same conditions cycloalkene (**2**) will add to tetrafluoroethene (**1**) in good yields.[85]


CXF=CF2
+
F
SbF5
CXFCF3
(2)
X = F, 73%
X = CF3, 32%

Scheme 1.34. A rare example of electrophilic addition.

Hexafluoropropene (**11**) is unreactive with anhydrous hydrogen fluoride, even at 200°C, however in the presence of silver fluoride at 125°C fluoroalkene (**11**) will react readily.[86] Theoretical studies propose that this reaction must go via initial electrophilic addition of hydrogen fluoride. Further examples of similar systems have been observed.



$$\underset{(\mathbf{11})}{CF_3CF{=}CF_2} + AgF \xrightarrow[125^\circ C]{AHF} \left[AgCF(CF_3)_2\right] \xrightarrow[-AgF]{AHF} \underset{\substack{(\mathbf{16})\\47\%}}{CFH(CF_3)_2}$$

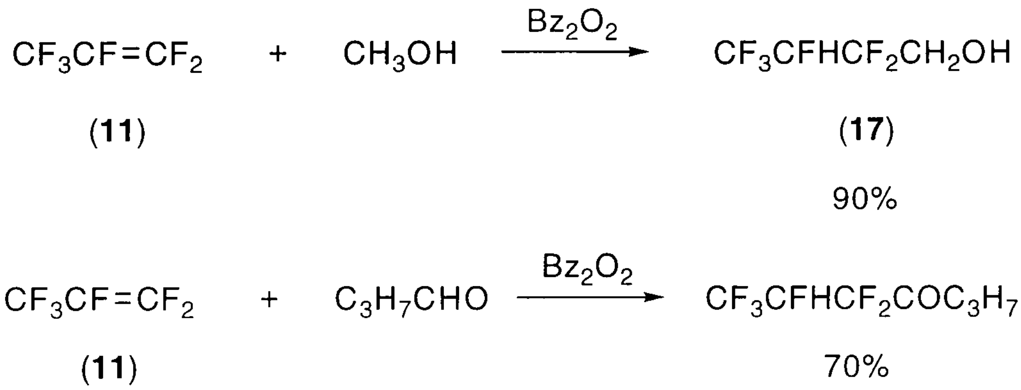
$$\underset{(\mathbf{1})}{CF_2{=}CF_2} \xrightarrow[20^\circ C]{AHF,\ HNO_3} \underset{93\%}{CF_3CF_2NO_2}$$

Scheme 1.35. Examples of electrophilic addition to hexafluoropropene (**11**)[86] and tetrafluoroethene (**1**).[87]

1.II.3.c. Free-Radical Reactions.

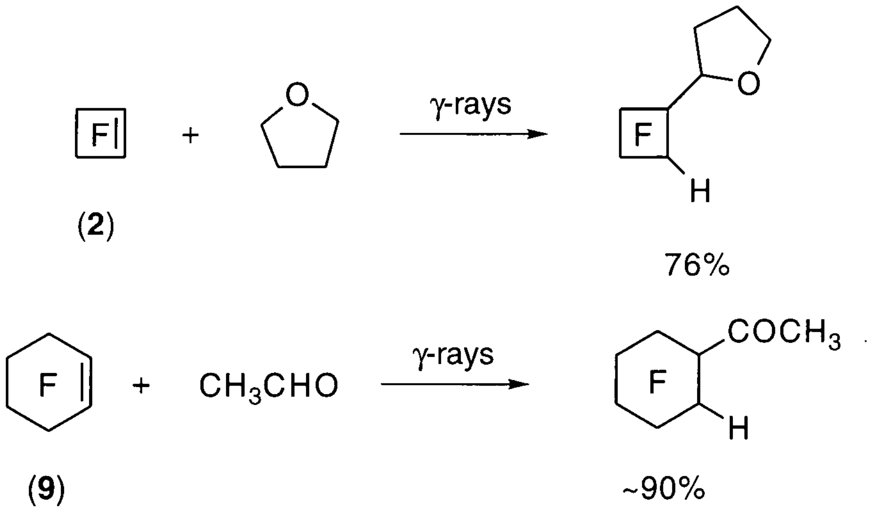
Free-radicals react readily across the double bond of polyfluorinated alkenes. In contrast to their reactions with nucleophiles, the reactions of fluoroalkenes with free-radicals proceeds with low regioselectivity. The orientation of addition is governed by polar effects, steric effects, bond strengths and the stability of the radical intermediate.[88]

Hydrocarbons, such as ethers, alcohols and aldehydes, will react readily across perfluorinated double bonds to give high yields of fluorinated ethers, alcohols and ketones under peroxide initiation or gamma ray initiation.[88, 89] Some examples are shown below in *Scheme 1.36.*



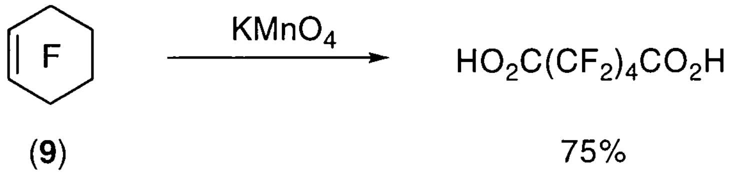
$$\underset{(\mathbf{11})}{CF_3CF{=}CF_2} + CH_3OH \xrightarrow{Bz_2O_2} \underset{\substack{(\mathbf{17})\\90\%}}{CF_3CFHCF_2CH_2OH}$$

$$\underset{(\mathbf{11})}{CF_3CF{=}CF_2} + C_3H_7CHO \xrightarrow{Bz_2O_2} \underset{70\%}{CF_3CFHCF_2COC_3H_7}$$



Scheme 1.36. Examples of free-radical addition to fluoroalkenes using methanol,[90] butanal,[90] THF[91] and acetaldehyde.[90-92]

Halogenation[93-96] and oxidation[97-100] may also be accomplished radically to give saturated mixed halogen compounds or fluorinated carboxylic acids.



Scheme 1.37. Radical oxidation.[101]

There are few examples of radical additions to fluoroalkynes, and these tend to be limited to hexafluorobut-2-yne (**4**).[102]

$$CF_3C{\equiv}CCF_3 \quad + \quad CF_3CH_2OH \longrightarrow CF_3CH{=}C(CF_3)CH(CF_3)OH$$

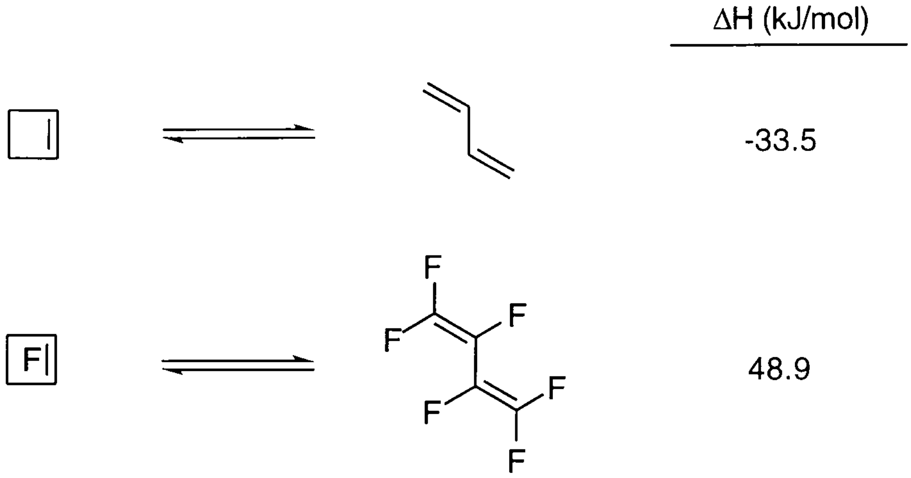
(**4**) 44%

E:Z 1:1

Scheme 1.38. Radical addition to hexafluorobut-2-yne.

1.II.3.d. Cycloaddition Reactions.

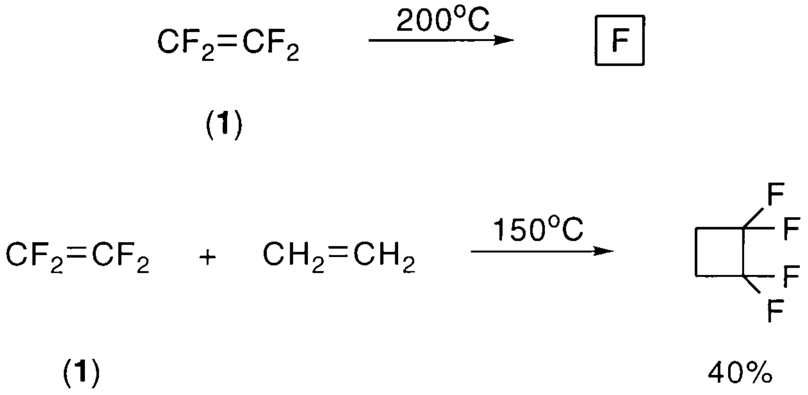
There is a great deal of interest in the cycloadditions of polyfluorinated alkenes and alkynes, owing partly to their ability to form four-membered rings contrasting with their hydrocarbon analogues.[103] This is shown clearly in *Scheme 1.39.*



Scheme 1.39. Contrast between hydrocarbons and fluorocarbons in the formation of ring systems.[103]

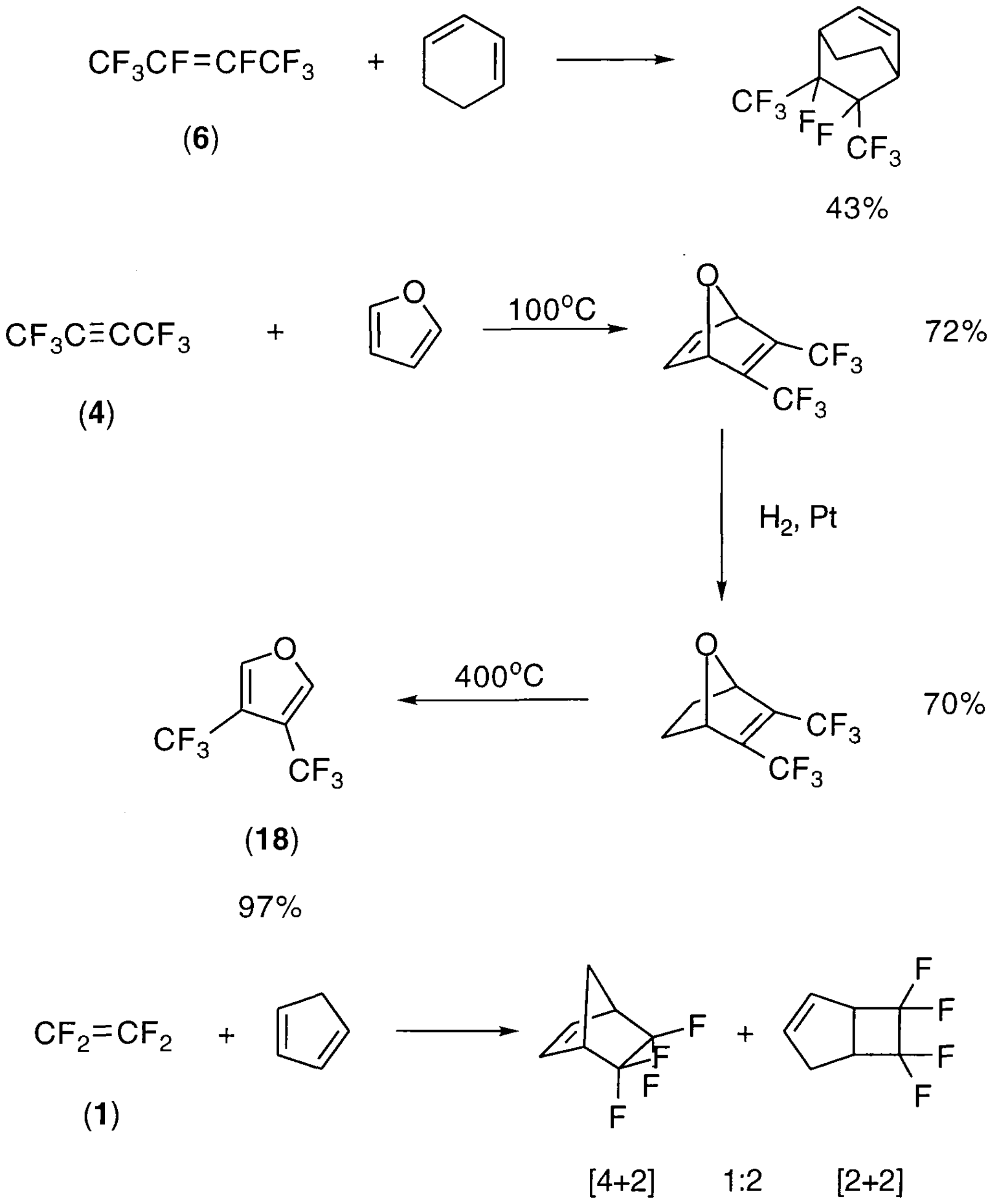
Fluorine destabilises the π-system, as discussed earlier. This means that on cyclisation there are fewer vinylic fluorine and hence the cyclic product is favoured; the energy decrease more than compensates for the energy increase from ring strain. For the hydrocarbon system there is no destabilising effect in the butadiene, however the energy caused by ring strain, that would be present in the cyclobutene, prevents cyclisation.

There are many examples of fluorinated alkenes undergoing [2+2] cycloaddition,[104] and just a few are shown in *Scheme 1.40.* One requirement for [2+2] addition appears to be the need for a terminal $=CF_2$, -CF=CF- systems tend be much less reactive to this type of reaction.



Scheme 1.40. [2+2] cycloadditions.

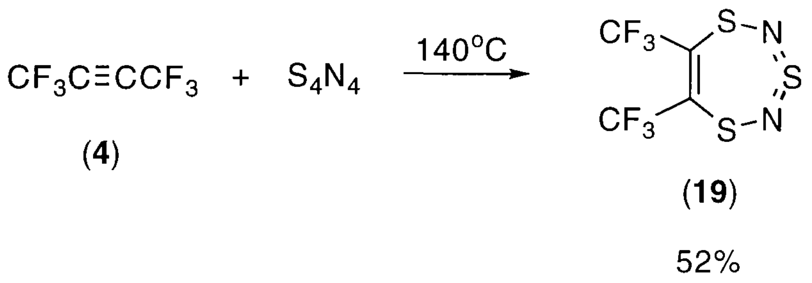
Diels-Alder cycloadditions are another important area in fluoroalkene chemistry. The use of fluorinated heterocycles in pharmaceuticals is widely known and Diels-Alder chemistry is one of the routes used to produce these interesting compounds. Polyfluorinated alkenes are thought to be fairly unreactive as dienophiles, however there are plenty of examples of their Diels-Alder reactions in the literature.[105-107]


CF3CF=CFCF3
+
(6)
CF3
F
F
CF3
43%
CF3C≡CCF3
+
(4)
O
100°C
O
CF3
CF3
72%
H2, Pt
O
400°C
O
CF3
CF3
70%
CF3
CF3
(18)
97%
CF2=CF2
+
(1)
F
F
F
F
+
F
F
F
F
[4+2]
1:2
[2+2]

Scheme 1.41. [4+2] cycloadditions, Diels-Alder reactions of octafluorobut-2-ene (**6**),[105] hexafluorobut-2-yne (**4**)[106] and tetrafluoroethene (**1**).[107]

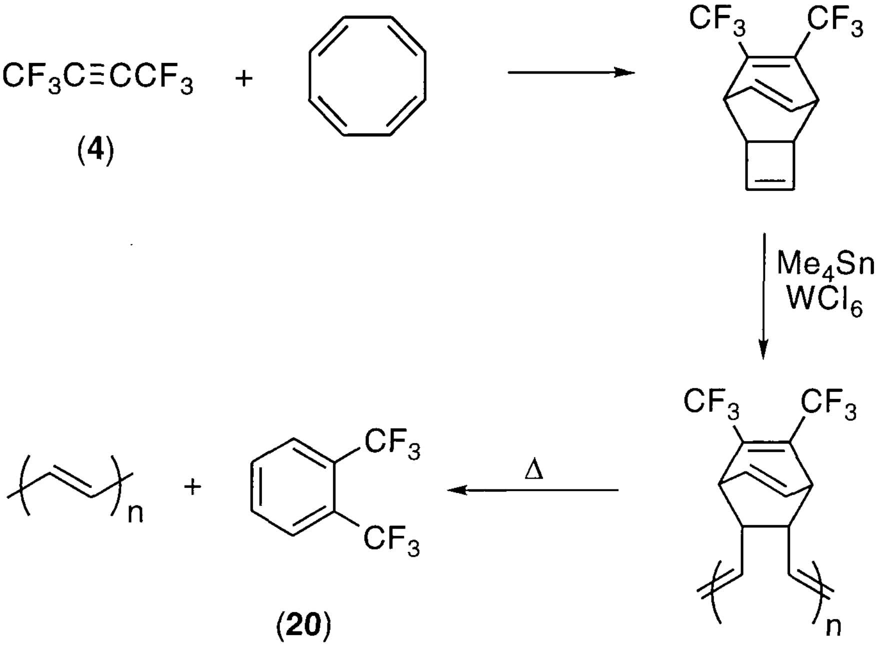
The latter reaction[107] in *Scheme 1.41* is an illustration of the occasional competition that occurs between [2+2] and [4+2] addition.

Hexafluorobut-2-yne (**4**) is a highly reactive dienophile and has been shown to undergo many different cycloaddition reactions.[106] One interesting example is the reaction of (**4**) with tetrasulfur tetranitride to form trithiadiazepine (**19**).[108]



Scheme 1.42. Formation of trithiadiazepine (**19**).

Perfluoroalkyne (**4**) is also used to form polyacetylene from cyclooctatetraene in an example of Ring Opening Metathesis Polymerisation (ROMP), *Scheme 1.43*, commonly known as the 'Durham route'.[109]

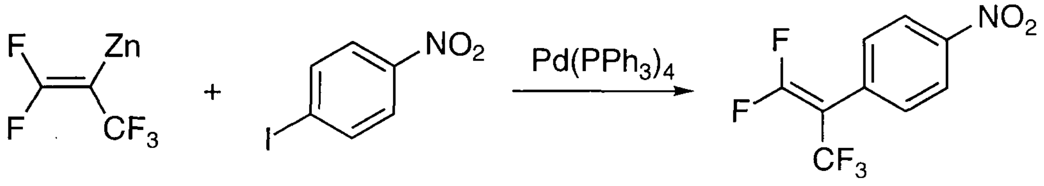


Scheme 1.43. Hexafluorobut-2-yne (**4**) in the synthesis of polyacetylene.

1.II.3.e. Organometallic Chemistry.

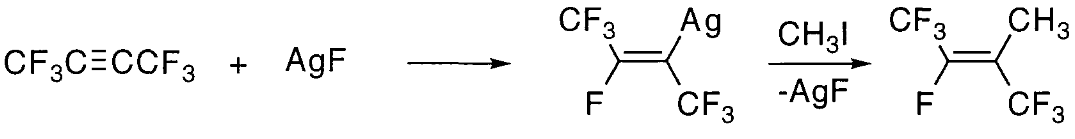
All of the commonly used synthetic techniques may be used to produce polyfluoroalkenyl- and alkynyl- organometallic compounds.

Lithium,[110] cadmium, copper and zinc fluoro-organometallics[111] have been widely investigated as useful synthetic tools. Lithium salts are perhaps the most commonly used, although their reactions tend to require very low temperatures[110] to avoid the elimination of lithium fluoride. Zinc salts are more stable and can be used at temperatures up to 80°C. Good yield of palladium-catalysed coupling products are achieved when zinc salts are used under relatively mild conditions.[112]



Scheme 1.44. Palladium-catalysed coupling using zinc salts.[112]

Silver fluoride[113] has also been used to insert alkyl groups into polyfluorinated alkenes and alkynes.



(4) 100%

Scheme 1.45. Insertion of alkyl groups using silver fluoride.

Polyfluorinated unsaturated compounds have been of considerable interest as ligands for organometallic catalysts. This interest is attributable to their electron deficiency and the effect that this may have when modifying a catalyst.[114]

1.III. Conclusions.

Polyfluorinated compounds, particularly alkenes and alkynes, have a wide range of synthetic and industrial applications. Their uses range from polymers to pharmaceuticals, and from fire extinguishers to blood substitutes. Therefore the drive for discovering more efficient syntheses, novel reactions and new compounds is tremendous and is reflected in the number of publications submitted in this field.

Chapter 2.

Diels-Alder Reactions of (*Z*)-2*H*-Heptafluorobut-2-ene.

2.I. Introduction.

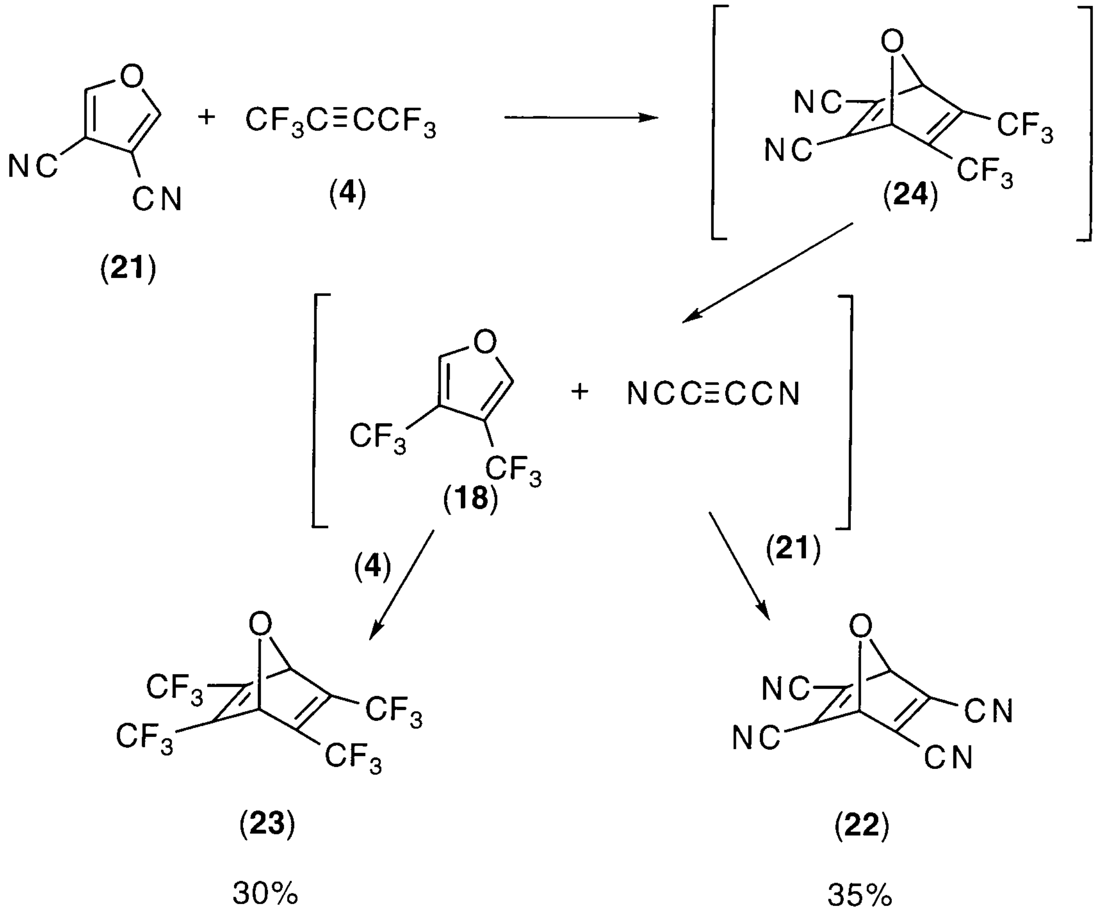
Much attention has been focused on the synthesis of heterocycles and aromatic compounds containing trifluoromethyl groups,[115] owing to their growing use in the medicinal and agrochemical industries, as shown earlier in *Scheme 1.2*. The Diels-Alder reaction is one of the most powerful tools used to synthesise these fluorinated compounds, commonly carried out with hexafluorobut-2-yne (**4**) as the dienophile. Workers in this laboratory have recently shown that (*Z*)-2*H*-heptafluorobut-2-ene (**10**) can be successfully used as a synthon for hexafluorobut-2-yne (**4**) in a number of reactions[30] and in the course of this work many Diels-Alder reactions have been carried out using (**10**). It is the aim of this section to review the Diels-Alder reactions that have been performed with butyne (**4**) and to explore the new work using fluoroalkene (**10**) as the dienophile in analogous reactions.

2.I.1. The Diels-Alder Reactions of Hexafluorobut-2-yne (4).

2.I.1.a. Reactions involving Furan Derivatives.

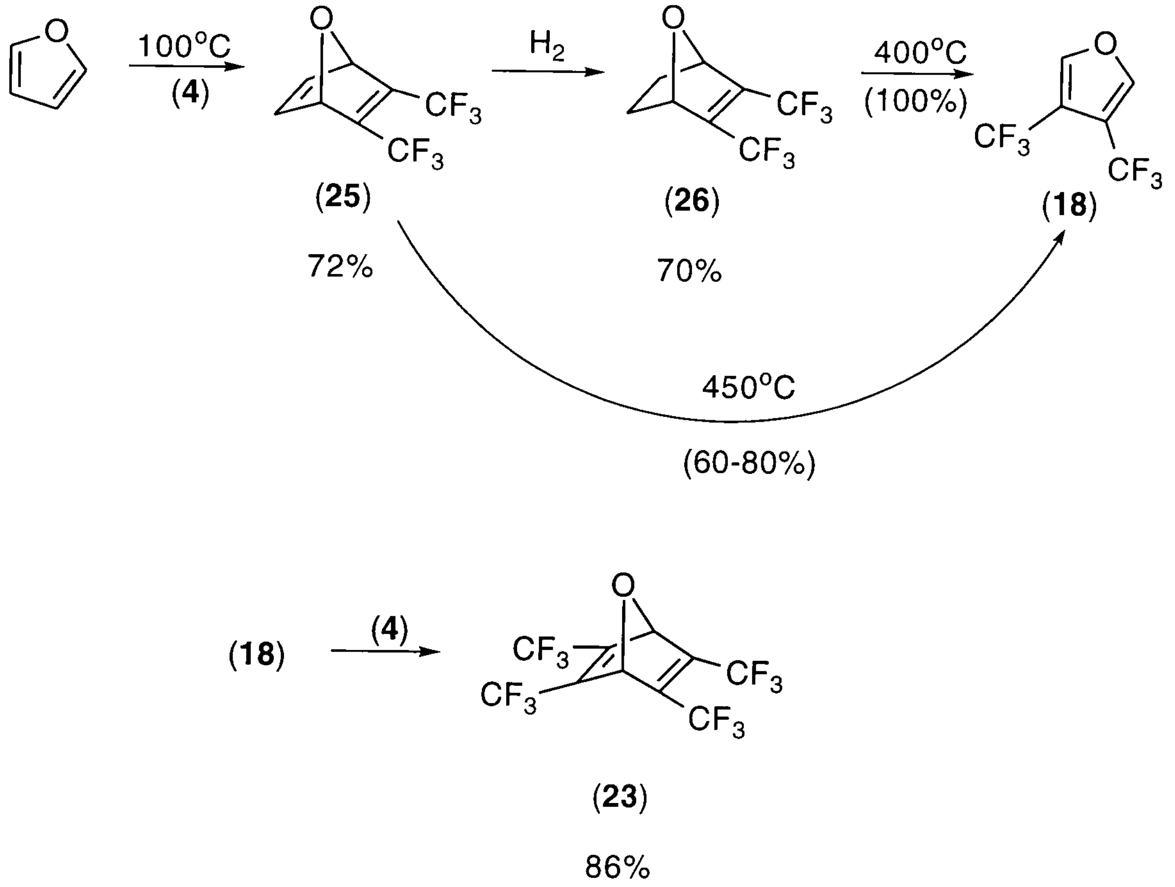
In 1962 Weis[106] studied the Diels-Alder reaction between 3,4-dicyanofuran and hexafluorobut-2-yne, to investigate the retro-Diels-Alder reaction of the 1:1 adduct. On successfully reacting furan (**21**) with hexafluorobut-2-yne at 160 °C two compounds were isolated as the sole products; (**22**) and (**23**). No trace of the expected 2,3-dicyano-5,6-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]-2,5-heptadiene (**24**) was observed.

The formation of (**22**) and (**23**) is illustrated in *Scheme 2.1*. (**24**) is *initially* formed by the Diels-Alder addition of hexafluorobut-2-yne and 3,4-dicyanofuran, however under the reaction conditions, the 1:1 adduct (**24**) decomposes via a retro-Diels-Alder pathway to give dicyanoacetylene and 3,4-bis(trifluoromethyl)furan (**18**), as expected. Further Diels-Alder reactions occur between dicyanoacetylene and 3,4-dicyanofuran, and hexafluorobut-2-yne and 3,4-bis(trifluoromethyl)furan (**18**) to form the stable compounds (**22**) and (**23**).


NC
CN
(21)
+ CF3C≡CCF3
(4)
O
NC
NC
CF3
CF3
(24)
CF3
CF3
(18)
+ NCC≡CCN
(4)
(21)
CF3
CF3
CF3
CF3
(23)
30%
NC
NC
CN
CN
(22)
35%

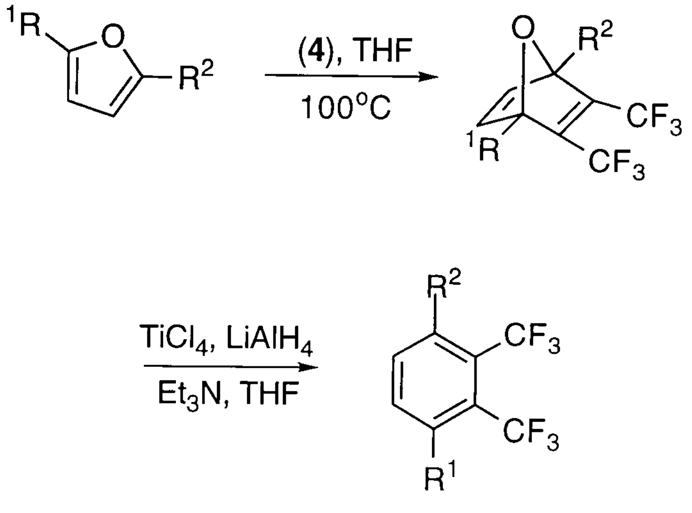
Scheme 2.1. Reaction between hexafluorobut-2-yne and 3,4-dicyanofuran.

Weis[106] also showed that the endoxide (**23**) can be prepared more conveniently by the reaction of excess hexafluorobut-2-yne with 3,4-bis(trifluoromethyl)furan (**18**), *Scheme 2.2*. Also shown in *Scheme 2.2* are the two simplest routes to 3,4-bis(trifluoromethyl)furan (**18**). The first, described by Weis,[106] involves the efficient reaction of furan with hexafluorobut-2-yne (**4**) in THF to give the 1:1 adduct (**25**). Furan (**18**) is obtained in excellent yields by the subsequent hydrogenation and pyrolysis of (**25**). Tipping[116] proposed an alternative, shorter, route in 1991 which neglects the hydrogenation step of Weis's method. Simply by using a higher temperature the pyrolysis proceeds from diene (**25**) in similar overall yield to the first route.


100°C
(4)
H$_2$
400°C
(100%)
(25)
72%
(26)
70%
(18)
450°C
(60-80%)
(18)
(4)
(23)
86%

Scheme 2.2. Formation of 3,4-bis(trifluoromethyl)furan (**18**) and endoxide (**23**).

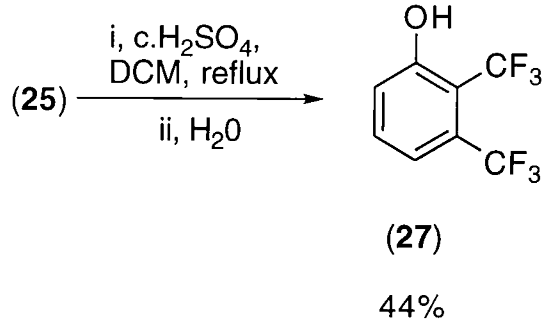
Diels-Alder adducts of hexafluorobut-2-yne and various substituted furan derivatives have been the subject of much interesting research. Wong[16] in 1984 showed that these 1:1 adducts can afford good yields of bis(trifluoromethyl)benzene derivatives when reduced in the presence of titanium chloride catalysts, *Scheme 2.3*.


(4), THF
100°C
TiCl$_4$, LiAlH$_4$
Et$_3$N, THF

$R^1 = R^2 = H$ (60%)
$R^1 = H, R^2 = Me$ (73%)

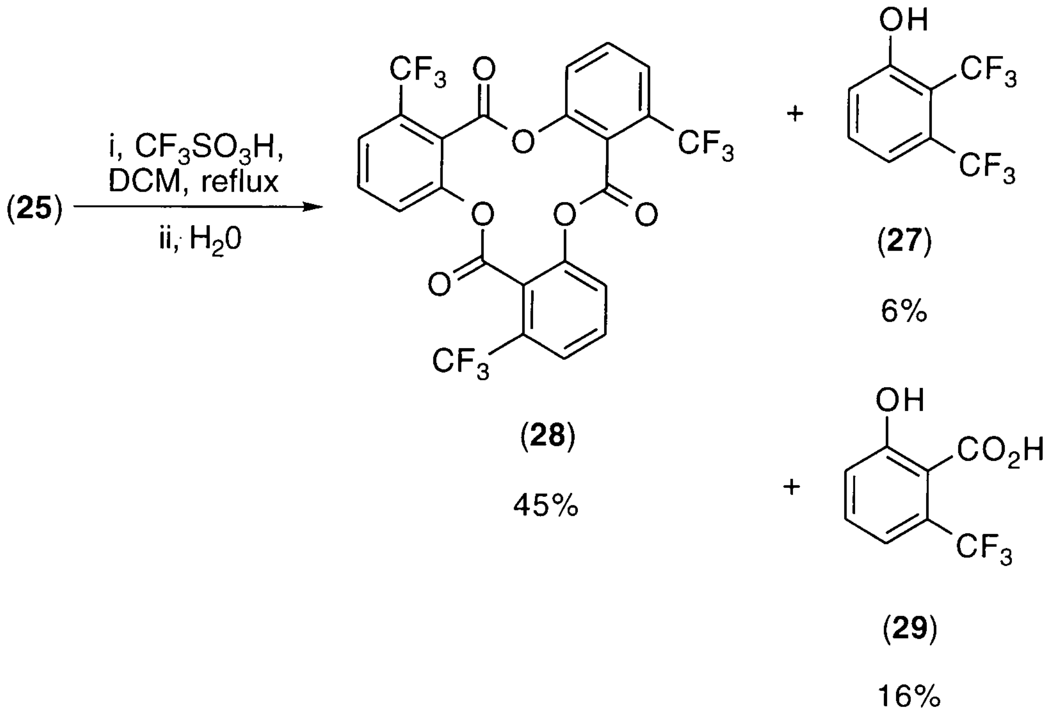
Scheme 2.3. Formation of bis(trifluoromethyl)benzene derivatives.[16]

Bis(trifluoromethyl)phenol derivatives can also be formed from the 1:1 adducts of furan and hexafluorobut-2-yne when refluxed with concentrated sulfuric acid.[116]



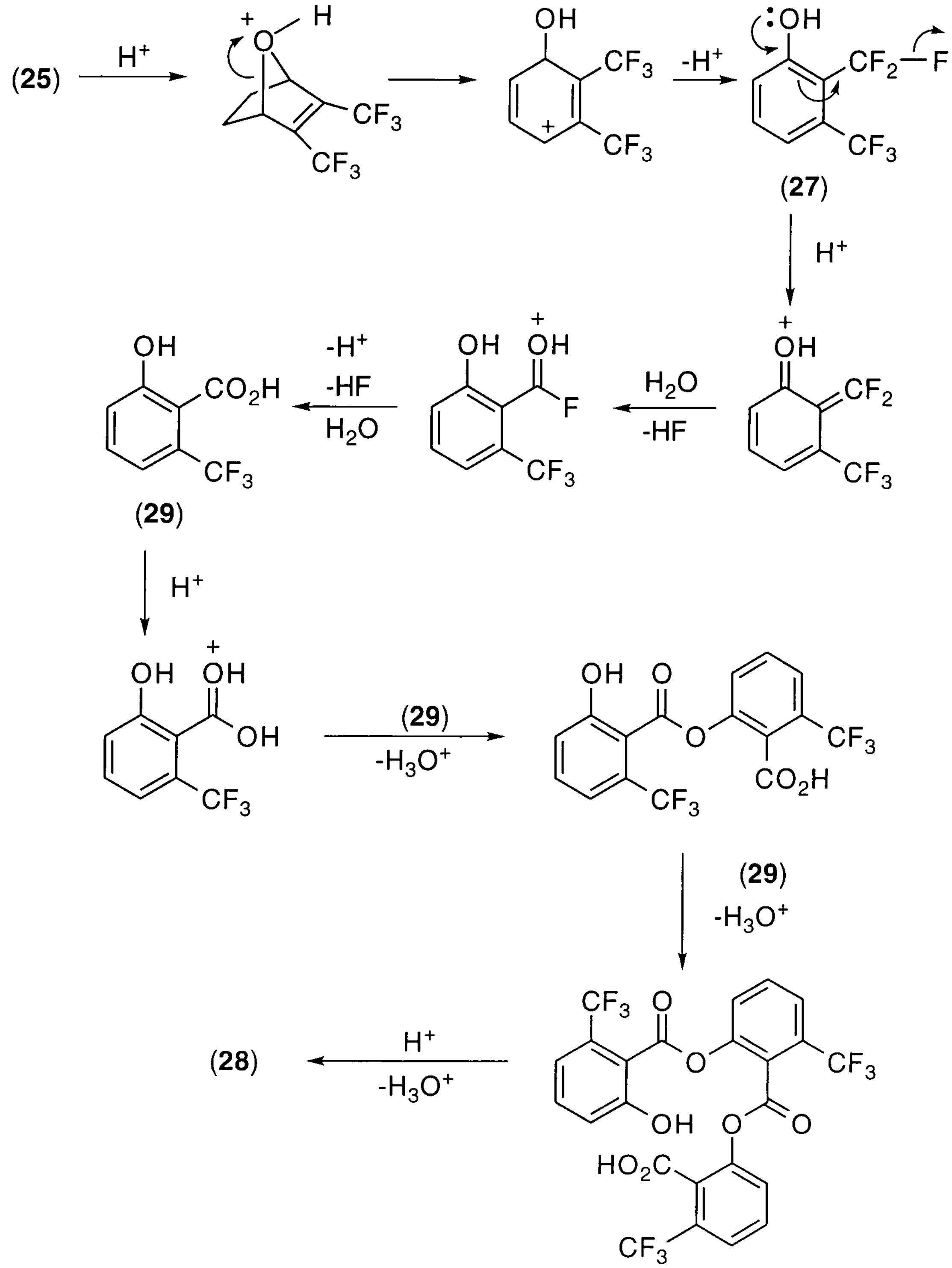
Scheme 2.4.

However when endoxide (**25**) is subjected to triflic acid under similar conditions, tris-(6-trifluoromethylsalicylide) (**28**) is formed in a 45% yield, along with phenol (**27**) and carboxylic acid (**29**) as minor products,[116] *Scheme 2.5.*



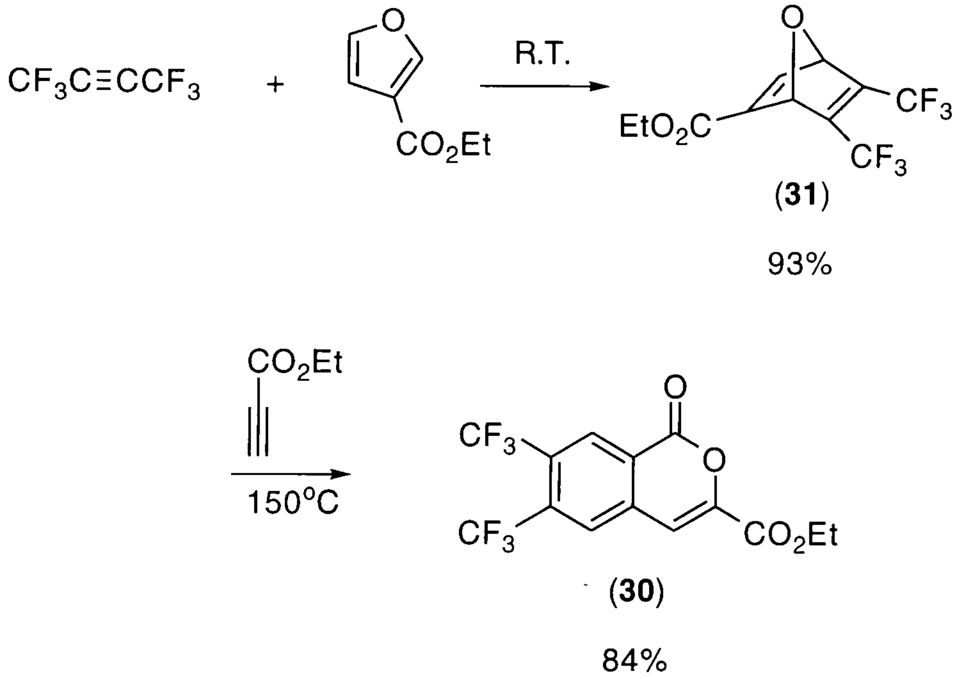
Scheme 2.5. Reaction of triflic acid and oxabicycloheptadiene (**25**).[116]

Formation of these three products is considered to follow *Scheme 2.6*, with phenol (**27**) being formed initially. Trifluoromethylarenes have been shown to require harsh alkaline conditions to undergo hydrolysis,[117] needing electron-releasing substituents *ortho* and/or *para* to the trifluoromethyl group. However, under strongly acid conditions, non-activated trifluoromethyl groups can be hydrolysed to carboxylic acid groups. In this case the trifluoromethyl group that is required to hydrolyse to form the trilactone (**28**) is activated by the hydroxyl group. Sulfuric acid, however, is not strong enough to force the hydrolysis so the reaction terminates at phenol (**27**). Using the much stronger acid, triflic acid, the hydrolysis occurs readily to produce carboxylic acid (**29**), which then undergoes a series of condensation reactions to form trilactone (**28**). It is interesting to note that endoxide (**25**) remains intact if a weaker acid, such as concentrated hydrochloric acid, is used.


(25)
H+
CF3
CF3
OH
CF3
CF3
-H+
CF2
F
(27)
H+
-H+
-HF
H2O
H2O
-HF
CO2H
(29)
(28)
-H3O+
OH
O
CO2H
HO2C

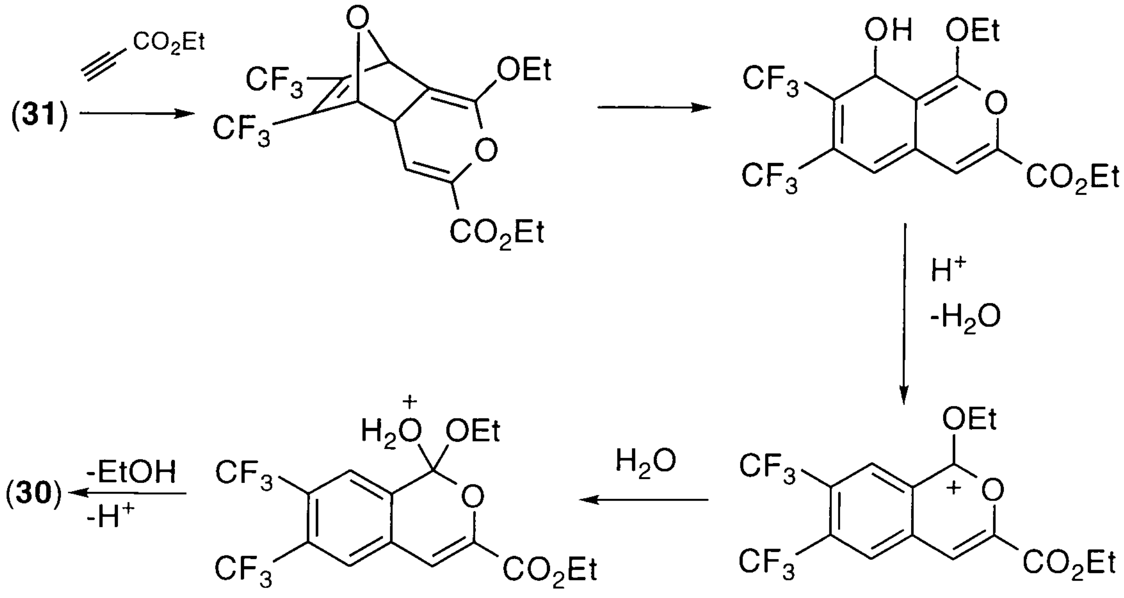
Scheme 2.6. Reaction scheme for the formation of trilactone (**28**).[116]

Another unexpected transformation occurs when endoxide (**31**) of hexafluorobut-2-yne and ethyl 3-furoate is reacted with ethyl propynate, producing high yields of a fluorinated isocoumarin (**30**), *Scheme 2.7.*[116]


CF3C≡CCF3
+
CO2Et
R.T.
EtO2C
CF3
CF3
(31)
93%
CO2Et
150°C
CF3
CF3
CO2Et
(30)
84%

Scheme 2.7. Formation of isocoumarin derivatives.[116]

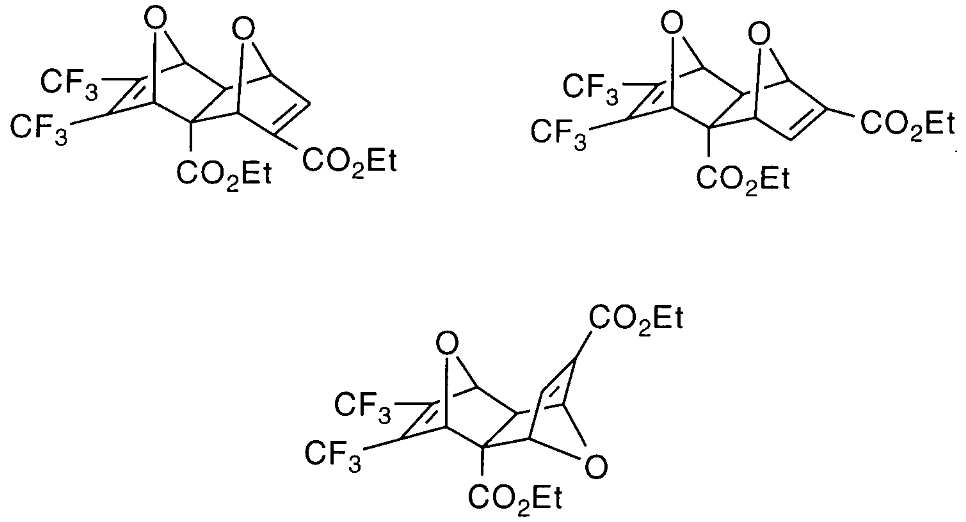
A reaction scheme for this transformation is illustrated in *Scheme 2.8*. Endoxide (**31**) undergoes a further Diels-Alder reaction in which the C=C-C=O system functions as the diene component. Acid-catalysed ring-opening of the oxygen bridge of the 2:1 adduct, followed by elimination of ethanol gives a facile route to a fluorinated coumarin derivative (**30**).


CO2Et
(31)
CF3
CF3
OEt
CO2Et
OH OEt
CF3
CF3
CO2Et
H+
-H2O
OEt
CF3
CF3
CO2Et
H2O
H2O OEt
CF3
CF3
CO2Et
-EtOH
-H+
(30)

Scheme 2.8. Formation of isocoumarin (**30**).

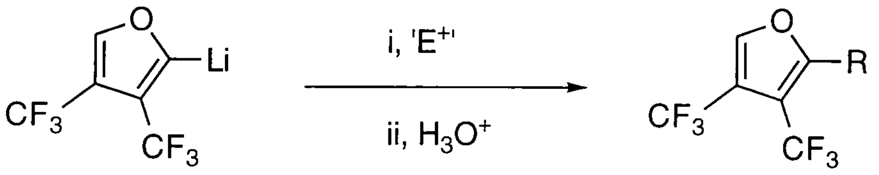
Interestingly, at 60 °C oxanorbornadiene (**31**) undergoes retrocleavage of ethyl propynate to give furan (**18**).

Dioxatetracycloalkene derivatives,[118] *Scheme 2.9*, can be formed in cases where excessive amounts of the furan derivative are used.



Scheme 2.9. Dioxatetracycloalkene derivatives from oxanorbornadiene (**31**).[118]

A large number of 2-substituted 3,4-bis(trifluoromethyl)furan derivatives have been described in the literature[119] synthesised from 2-lithio-3,4-bis(trifluoromethyl)furan (**32**). 2-Lithio-3,4-bis(trifluoromethyl)furan (**32**) is pre-formed by the addition of butyllithium to a solution of 3,4-bis(trifluoromethyl)furan (**18**) at low temperatures. Subsequent reaction of salt (**32**) with electrophiles gives good yields of a variety of furan derivatives, *Scheme 2.10.*



(32)

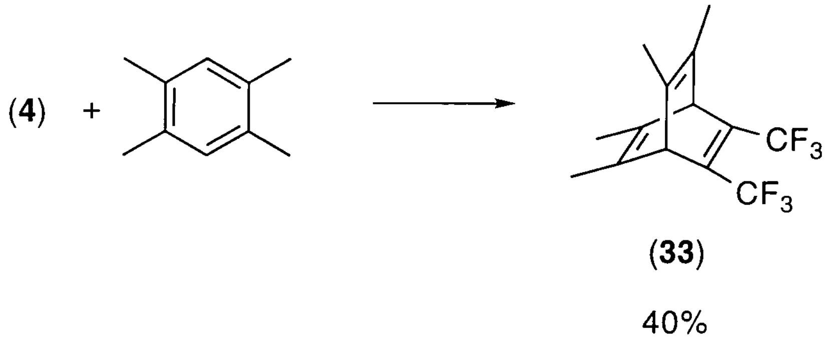
'E^+'	R	Yield (%)
CO_2	CO_2H	82
$CH_2=CHCHO$	$CH(OH)CH=CH_2$	59
DMF	CHO	54
PhCHO	CHPhOH	81
MeCHO	CHMeOH	72

Scheme 2.10. Formation of substituted furan derivatives from 2-lithio-3,4-bis(trifluoromethyl)furan (**32**).[119]

2.I.1.b. Arenes and Other Diels-Alder Reactions.

Normal Diels-Alder reactions of alkenes and alkynes with aromatic compounds have been restricted to very reactive systems such as anthracene and furan. However in 1961

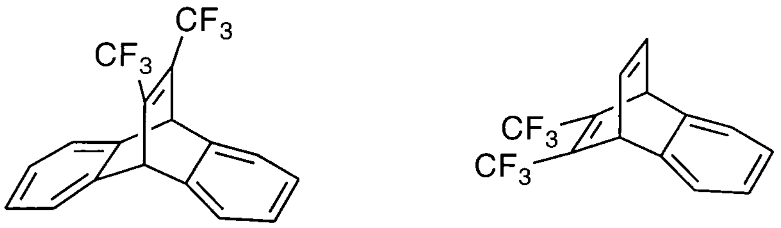
Krespan[120, 121] showed that a Diels-Alder reaction occurs between hexafluorobut-2-yne (**4**) and 1,2,4,5-tetramethylbenzene to yield a fluorinated bicyclooctatriene (**33**).



Scheme 2.11. Reaction of 1,2,4,5-tetramethylbenzene and hexafluorobut-2-yne (**4**).[120, 121]

However, this reaction cannot be accomplished using either acetylene or 1,1,1-trifluoropropyne, indicating the extreme reactivity of hexafluorobut-2-yne as a dienophile. At 250 °C triene (**33**) was found to decompose to give 1,2-dimethyl-4,5-bis(trifluoromethyl)benzene (**34**) as one of the volatile products.

Hexafluorobutyne will also add readily to the 9,10 position of anthracene and even with naphthalene.[121]



Scheme 2.12. Anthracene and naphthalene derivatives.

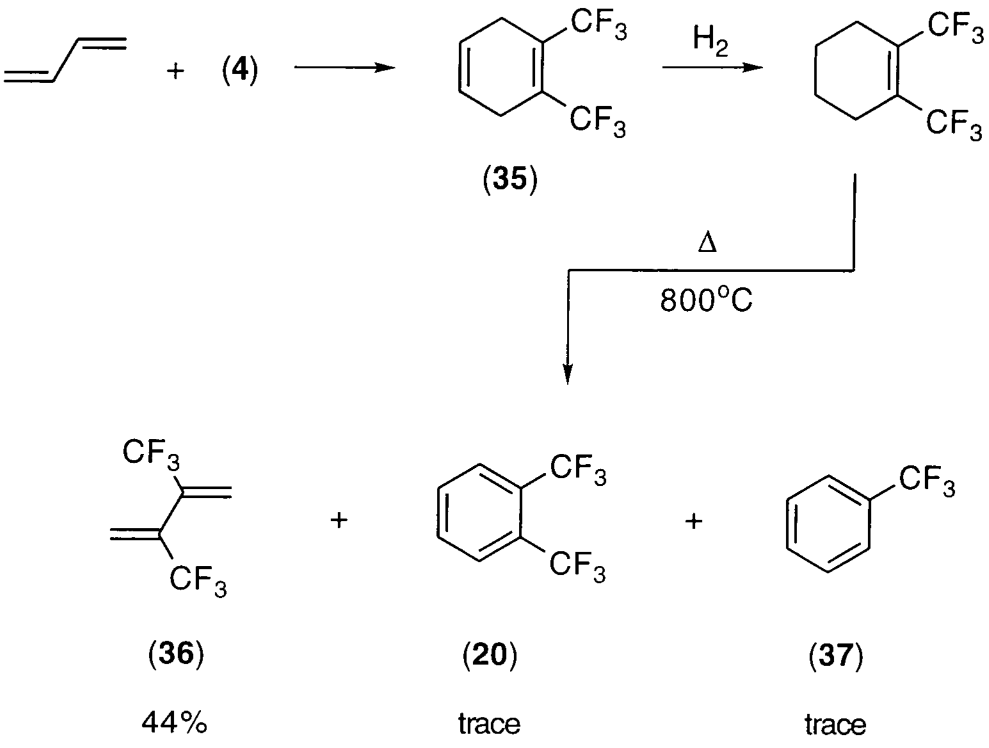
Further studies of the reactions of hexafluorobut-2-yne with arenes[122] showed that other 1,4 adducts can be prepared, however the reactions are often quite poor and the yields relatively low, *Table 2.1.*

Table 2.1. Reaction of (**4**) with arenes.

Reactant	Temperature (°C), time (h)	1,4 adduct (%)
benzene	180, 20	2,3-bis(trifluoromethyl)-bicyclo[2.2.2]octatriene (8)
toluene	180, 12	5-methyl- (21)
1,2-dimethylbenzene	200, 8	5,6-dimethyl- (8)

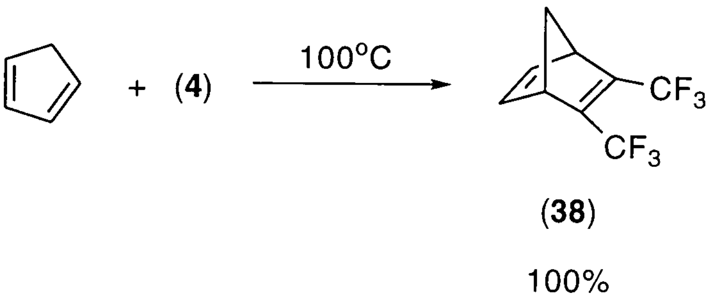
1,3-dimethylbenzene	180, 10	5,8-dimethyl- (7) 1,5-dimethyl- (2)
1,4-dimethylbenzene	200, 10	5,7-dimethyl- (57)
1,2,4-trimethylbenzene	220, 13	NO REACTION
1,2,3-trimethylbenzene	225, 10	NO REACTION
1,2,4,5-tetramethylbenzene	200, 10	5,6,7,8-tetramethyl- (41)

Butadiene, the simplest diene used in Diels-Alder reactions, reacts readily with hexafluorobut-2-yne to form the fluorinated cyclic diene (**35**).[123] Hydrogenation of the Diels-Alder adduct (**35**) and subsequent thermolysis leads to the expected 2,3-bis(trifluoromethyl)butadiene (**36**) and traces of the aromatized products (**20**) and (**37**).



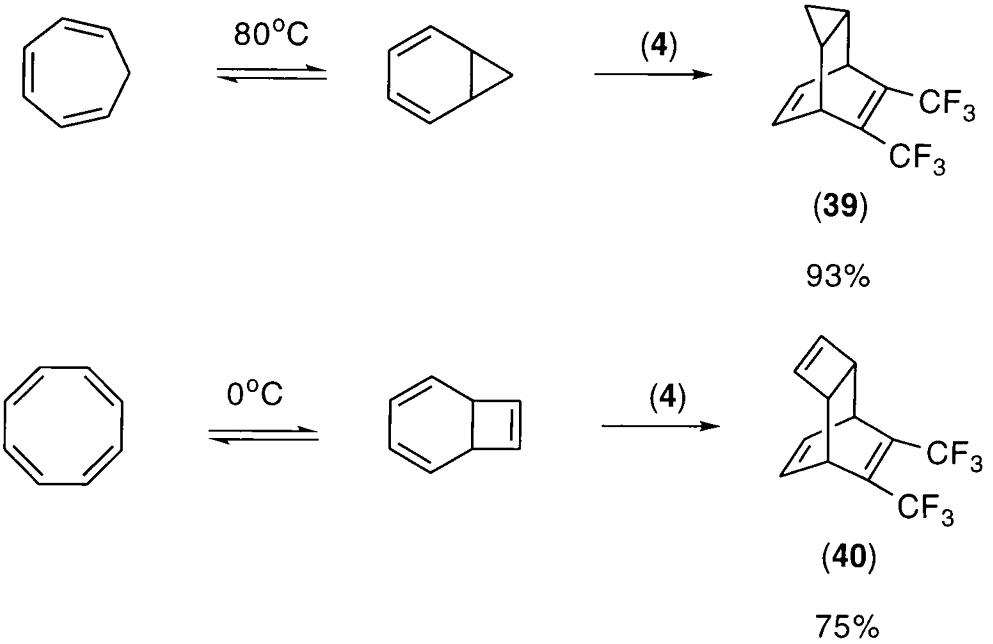
Scheme 2.13. Reaction of butadiene and hexafluorobut-2-yne (**4**).[123]

Reaction of cyclopentadiene and hexafluorobut-2-yne proceeds quantitatively at 100 °C to give bicyclic compound (**38**).[124]


+ (4)
100°C
CF3
CF3
(38)
100%

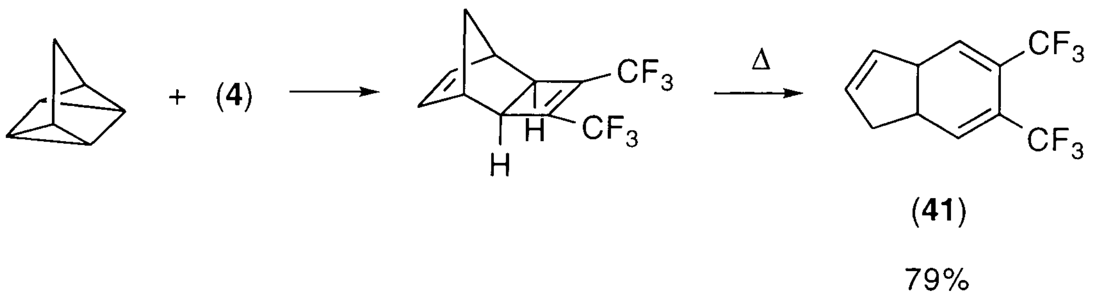
Scheme 2.14. Reaction of cyclopentadiene and hexafluorobut-2-yne (**4**).

Cycloheptatriene and cyclooctatetraene are in equilibrium with bicyclo derivatives at 80 °C and 0 °C, respectively. At these temperatures they will each react with hexafluorobut-2-yne to form Diels-Alder 1:1 adducts (**39**) and (**40**), *Scheme 2.15*.[118, 124]


80°C
(4)
CF3
CF3
(39)
93%
0°C
(4)
CF3
CF3
(40)
75%

Scheme 2.15. Reactions of cycloheptatriene and cyclooctatetraene with hexafluorobut-2-yne (**4**).[118, 124]

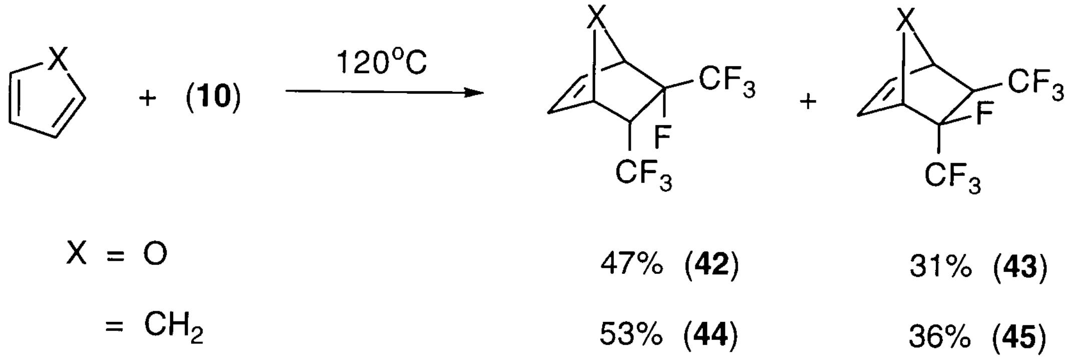
Quadricyclane will react as a diene with hexafluorobut-2-yne and form an interesting tricyclic compound;[125] which on pyrolysis rearranges to bicyclic (**41**) in 79% yield.


+ (4)
CF3
H
CF3
H
Δ
CF3
CF3
(41)
79%

Scheme 2.16. Reaction of quadricyclane and hexafluorobut-2-yne (**4**).[125]

2.II. Reactions of (*Z*)-2*H*-Heptafluorobut-2-ene with Dienes.

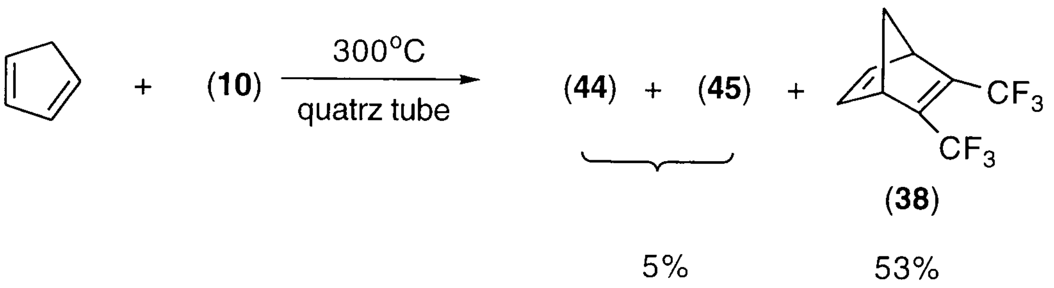
Previous workers[30, 126] in this laboratory have shown the ability of (*Z*)-2*H*-heptafluorobut-2-ene (**10**) to act as a dienophile in its reactions with furan and cyclopentadiene to form the anticipated 1:1 adducts (**42-45**).



Scheme 2.17. Diels-Alder reactions carried out by Rock.[126]

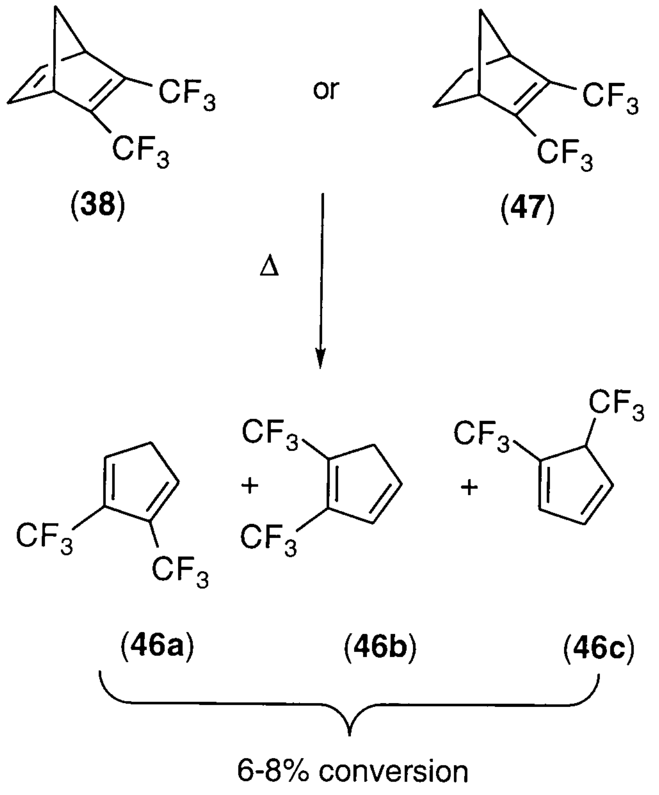
Study of the proton NMR data of the endoxides (**42**) and (**43**)[126] has enabled the correct assignment of the stereoisomers. According to the Karplus Rule[127] the coupling between protons on vicinal carbons in a rigid system depends largely on the dihedral angle between the H-C-C' and C-C'-H' planes. This rule predicts the values of the coupling constant between the bridge head proton and the *endo* proton to be ~0 Hz whilst ~5 Hz should be found for the *exo* proton. The observed values were 0 and 4 Hz respectively, giving clear evidence for the assignment.

Elimination of hydrogen fluoride was a requirement needed to show the effectiveness of (*Z*)-2*H*-heptafluorobut-2-ene as a synthetic equivalent for hexafluorobut-2-yne. However, potassium tertiarybutoxide in butanol only successfully eliminated hydrogen fluoride from the cyclopentadiene adduct, not from the furan adduct. Roche discovered another route to bicyclic diene (**38**);[30] if the initial Diels-Alder reaction is performed at higher temperatures, *c.a.* 300 °C, dehydrofluorination occurs *in situ*, *Scheme 2.19.*



Scheme 2.19. Direct synthesis of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2,5-diene (**38**).

It was believed that the pyrolysis of (**38**) might give a convenient route to fluorinated dienes (**46a-c**), in a similar fashion to *Scheme 2.20.* However evidence obtained by Roche after several attempts was insufficient and isolation of (**46a-c**) was never attempted. Further reactions were carried out to hydrogenate the non-fluorinated double-bond of diene (**38**) in order to simplify the pyrolysis, as was found in the furan case by Weis.[106] However hydrogenation proved difficult and complicated product mixtures were obtained when ethanol was used as the solvent. Pyrolysis of this mixture gave further encouragement that (**46a-c**) could be synthesised by this route but again conversions were too poor to enable isolation.



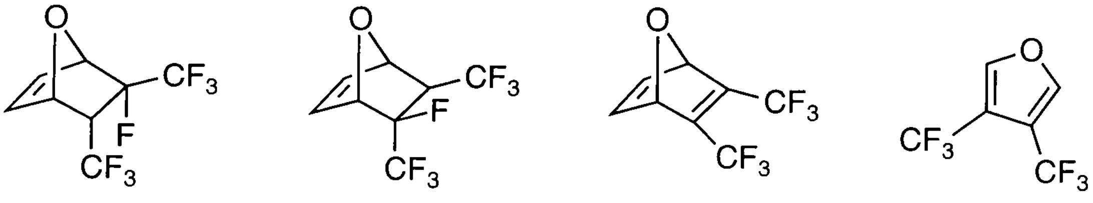
Scheme 2.20. Pyrolysis of norbornenes (**38**) and (**47**).

RESULTS AND DISCUSSION

2.III. Further Investigation Of The Reaction Of 2*H*-Heptafluorobut-2-ene with Furan.

(in collaboration with A.J. Roche)

2.III.1. Furan - It was the aim of this section to continue the research of other members of this laboratory into the Diels-Alder reaction of furan and fluoroalkene (**10**). In an attempt to increase yields of the two 1:1 adducts, (**42**) and (**43**), higher reaction temperatures were used; 190 °C rather than the more usual 120 °C. However, this led to a mixture of products being formed, *Scheme 2.21*.



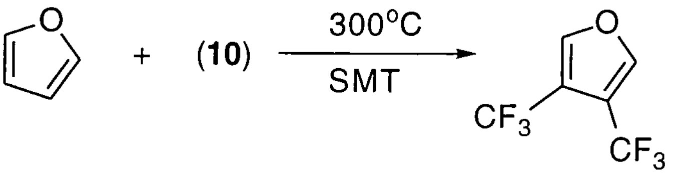
(42) (43) (25) (18)

2% 2% 6% 20%

Scheme 2.21. Reaction of furan and (*Z*)-2*H*-heptafluorobut-2-ene (**10**) at 190 °C.

The four compounds (**18**), (**25**), (**42**) and (**43**) are all known compounds.[106, 116, 119, 126, 128] Isolation of the individual components was not attempted, however they could be identified by comparison of their ^{19}F NMR spectra and GLCMS with literature values.

Exploration of the reaction temperature, remarkably revealed that at 300 °C in a sealable metal tube (**18**) was not only the sole product of the reaction but present in 87% yield.



(18)

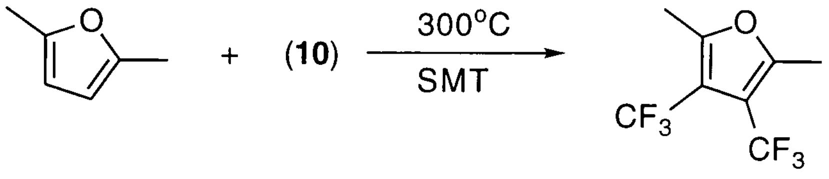
87%

Scheme 2.22. 'One-pot' synthesis of 3,4-bis(trifluoromethyl)furan (**18**).

Furan (**18**) is a known compound;[106] isolation by distillation gave a colourless liquid, shown to be a single product, that was identified as 3,4-bis(trifluoromethyl)furan (**18**) by comparison of its ^{1}H, ^{13}C and ^{19}F NMR spectra and GLCMS with literature values.

This result indicates that a simple 'one-pot' synthesis of furan (**18**) has been discovered, and further investigation into the scope of this reaction was required.

2.III.2. 2,5-Dimethylfuran - When excess fluoroalkene (**10**) was reacted with 2,5-dimethylfuran at 200 °C, high yields of the Diels-Alder-retro-Diels-Alder product 2,5-dimethyl-3,4-bis(trifluoromethyl)furan (**48**) were obtained.



(48)

76%

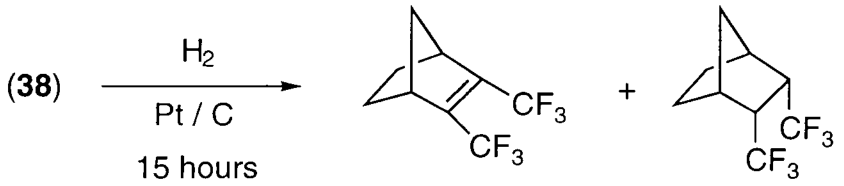
Scheme 2.23. Formation of 2,5-dimethyl-3,4-bis(trifluoromethyl)furan (**48**).

Furan (**48**) is a known compound;[129] isolation by distillation gave a single product that was identified as 2,5-dimethyl-3,4-bis(trifluoromethyl)furan (**48**) by comparison of its ^1H, ^{13}C and ^{19}F NMR spectra and GLCMS with literature values.

2.IV. Further Investigation Of The Reaction Of (*Z*)-2*H*-Heptafluorobut-2-ene with Cyclopentadiene.

Following the discovery of the novel anion pentakis(trifluoromethyl)cyclopentadienide and the inconclusive work started by Roche,[30] attempts were made to synthesise bis(trifluoromethyl)cyclopentadiene.

2.IV.1.a. Cyclopentadiene - It was decided to study more carefully the hydrogenation of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2,5-diene (**38**) in an attempt to isolate 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**) and continue the work started by Roche.[30] Considering the problems encountered when carrying out the hydrogenation in ethanol, including some ethanol addition, dichloromethane was chosen as an alternative solvent. Hydrogenation was carried out in Parr apparatus using a platinum catalyst for 15 hours at room temperature. After this time ^{19}F NMR and GLCMS analysis indicated that there had been quantitative conversion of (**38**) to two compounds; the expected 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**) as the minor component and *endo,endo*-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane (**49**) as the major.



(47) (49)

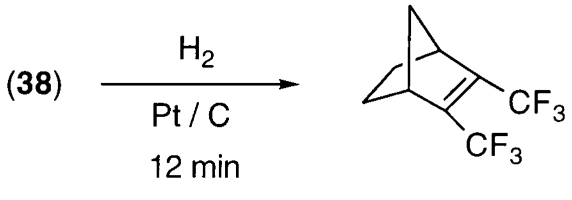
1:9

Scheme 2.24. Hydrogenation of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2,5-diene (**38**).

The reaction mixture was then subjected to further hydrogenation to facilitate isolation of (**49**). After removal of the solvent, distillation gave a colourless oil, analysis of which showed it to be norbornane (**49**). Norbornane (**49**) is a new compound and was identified by its ^{19}F, ^{13}C and ^{1}H NMR and GLCMS spectra. Only one signal was observed in the ^{19}F NMR spectrum at -60.7 ppm indicating the presence of one trifluoromethyl group environment. ^{13}C NMR analysis showed the presence of five distinct carbon environments, and therefore a symmetrical system, and two quartets were observed with coupling of $^{1}J_{C\text{-}F}$ 279 and $^{2}J_{C\text{-}F}$ 29 Hz which are indicative of a CF$_3$ and C-CF$_3$. Owing to complex coupling the ^{1}H NMR spectrum provides little information, however the peaks integrated correctly and a peak at 3.07 ppm (2H) indicated the bridgehead protons. GLCMS gave a mass spectrum with the correct molecular ion of 232 and after distillation at reduced pressure *endo,endo*-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane (**49**) gave a satisfactory elemental analysis.

^{19}F NMR showed the presence of only one fluorine environment indicating either the *endo,endo* or *exo,exo* isomer had been formed. It was impossible to tell which isomer was formed because of complex ^{1}H NMR data, however comparing this compound with similar reactions found in the literature[130, 131] it is assumed that the least hindered face of the norbornene is hydrogenated to give the *endo,endo* isomer.

Since a trace amount of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**) had been observed in this reaction, indicating that the non-fluorinated double bond is hydrogenated first, the period of hydrogenation was investigated. After various trials the time was optimised to give a good yield of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**).



(47)

82%

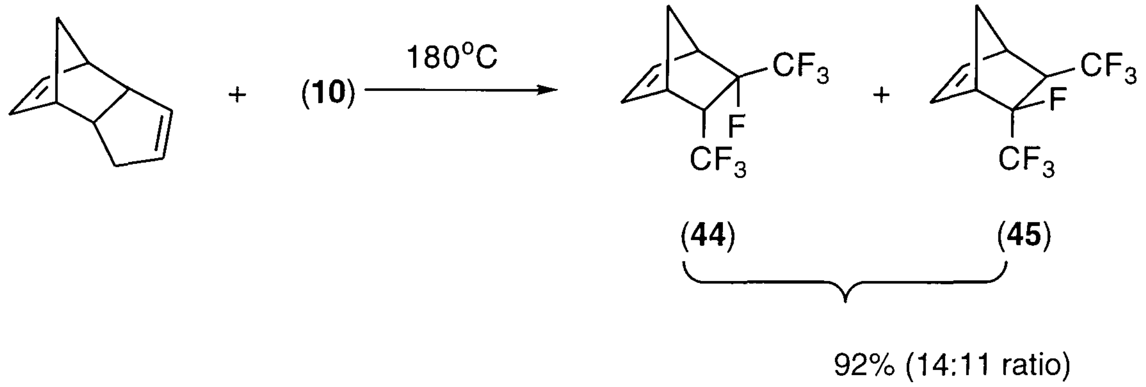
Scheme 2.25. Formation of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**).

Although 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**) has been observed before,[30] it has never been isolated, and was identified by comparison and interpretation of its ^{1}H and ^{19}F NMR spectra and GLCMS with literature data. Only one signal was observed in the ^{19}F NMR spectrum at -60.6 ppm indicating one trifluoromethyl environment. A singlet at 3.30 ppm was observed in the ^{1}H NMR spectrum, indicative of bridgehead protons, and multiplets at 1.28, 1.32, 1.68 and 1.89 ppm confirmed the presence of CH$_2$ protons on the norbornene derivative. ^{13}C NMR data and integration of the ^{1}H NMR were also consistent with compound (**47**), and

HETCOR and COSY NMR analysis confirmed the assignment of the ^1H and ^{13}C NMR spectra (see NMR appendix).

Unfortunately, this reaction is impractical due to the complications found when the reaction goes too far and the reaction can only be successful after several trials to gage the correct period of hydrogenation. For this reason an alternative route to 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**) was investigated.

2.IV.1.b. Dicyclopentadiene - Almost quantitative yields of *endo*- and *exo*- 5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**44**) and (**45**) were obtained when butene (**10**) and dicyclopentadiene were heated at 180 °C for 6 days. This varied from the usual preparation by not pre-forming the cyclopentadiene; instead dicyclopentadiene was used, and higher yields were obtained.

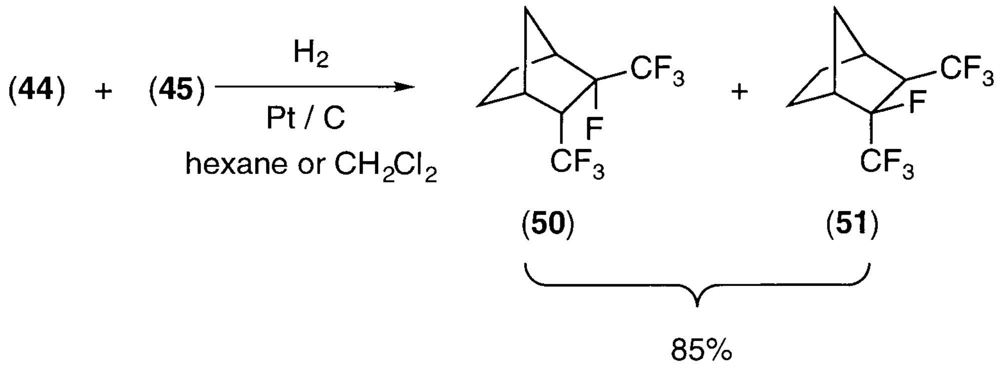


Scheme 2.26. Reaction of dicyclopentadiene and (*Z*)-2*H*-heptafluorobut-2-ene (**10**).

Endo- and *exo*- 5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**44**) and (**45**) are known compounds[128] and were identified by comparison of their ^1H and ^{19}F NMR and GLCMS spectra with literature data. Isolation of the individual components was not attempted, however, after distillation the mixture gave a satisfactory elemental analysis and mass spectrum.

2.IV.2. Hydrogenation of *Endo*- and *Exo*- 5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (44) and (45).

It was at this stage that this new work diverged significantly from those of earlier workers. Considering the difficulty found in hydrogenating (**38**) cleanly at the non-fluorinated double bond it seemed convenient to perform the hydrogenation at this stage in the proceedings to avoid any complications. At room temperature the hydrogenation of (**44**) and (**45**) (combined) was carried out successfully and excellent yields of the saturated derivatives were isolated.

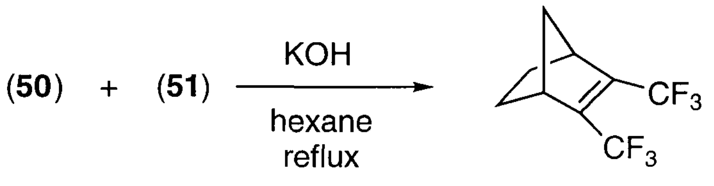


Scheme 2.27. Hydrogenation of norbornenes (**44**) and (**45**).

Endo-2-fluoro-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane (**50**) and *exo*-2-fluoro-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane (**51**) are new compounds and were identified by ^{19}F NMR and GLCMS spectra. Isolation of the individual components was not attempted, owing to the proximity of their peaks on the GC trace. However, after distillation, a colourless oil, shown to be a mixture of (**50**) and (**51**) only, gave a mass spectrum of the correct molecular ion, 250, and a satisfactory elemental analysis. ^{19}F NMR analysis indicated the presence of four trifluoromethyl groups and two tertiary fluorine atoms, furthermore integration enabled these peaks to be assigned to the relevant isomers, since (**50**) is in a slight excess over (**51**). Although good ^{1}H and ^{13}C NMR spectra were obtained they were too complicated to assign and this meant that the isomers were assigned, reasonably, by comparing the chemical shifts in the ^{19}F NMR spectrum with similar compounds (**44**) and (**45**).

2.IV.3. Dehydrofluorination of *Endo*- and *Exo*- 2-fluoro-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane (50) and (51).

Dehydrofluorination of (**50**) and (**51**) would now give a convenient route to the mono-ene (**47**) that Roche had attempted to prepare. Potassium tertiarybutoxide was the first base to be tried, following the success of other dehydrofluorinations carried out using this base. At room temperature, dehydrofluorination of (**50**) occurred overnight, owing to the lower steric demand of the *exo* proton involved in the elimination. Increasing the temperature to 70 °C enabled (**51**) to dehydrofluorinate, thus producing a quantitative conversion of (**50**) and (**51**) to (**47**). However, complete separation from the butanol proved difficult so a further method of dehydrofluorination was required; norbornanes (**50**) and (**51**) were added dropwise to a vigorously stirred suspension of potassium hydroxide in hexane, and then refluxed for 15 hours. After this time the solid base was removed by filtration and the remaining solution distilled to give a quantitative conversion of (**50**) and (**51**) to norbonene (**47**).



(47)

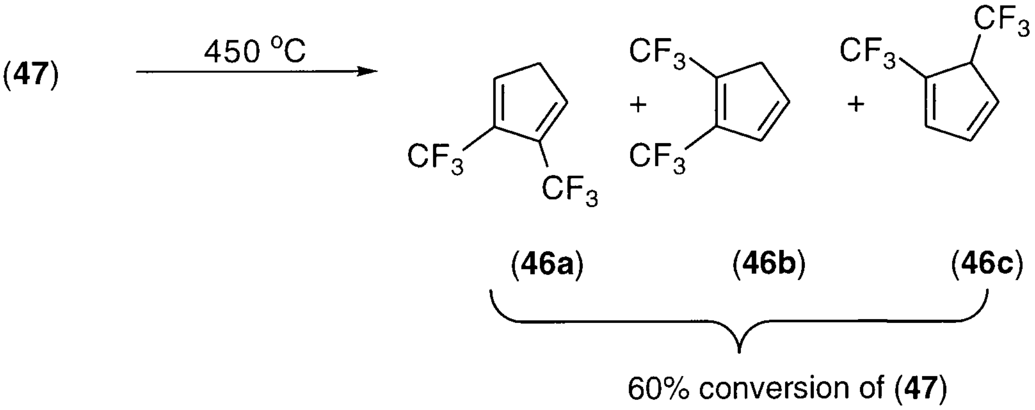
100%

Scheme 2.28. Formation of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**).

2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**) is a known compound[30] and was identified as described in detail earlier.

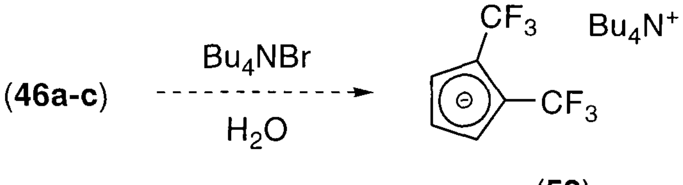
2.IV.4. Pyrolysis of 2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (47).

Norbornene (**47**) was allowed to pass through a glass tube at elevated temperatures in an attempt to facilitate retrocleavage to ethene and bis(trifluoromethyl)cyclopentadiene (**46**). At 300 °C no reaction occurred, however at 450 °C a 60% conversion of norbornene (**47**) to the new compound bis(trifluoromethyl)cyclopentadiene (**46**) was achieved.



Scheme 2.29. Pyrolysis of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**).

Bis(trifluoromethyl)cyclopentadiene was observed as a mixture of olefinic isomers (**46a-c**) by GLCMS, all possessing identical parent ions of 202 and accurate mass analysis was obtained that agreed with the formula $C_7H_4F_6$. ^{19}F NMR gave 5 peaks, indicating all of the possible environments in the three isomers (**46a-c**), at -61.7, -61.8, -61.9, -63.8 and -66.4 ppm. ^{1}H NMR produced a more complex spectrum, however, olefinic protons could be seen between 6.4 and 7.1 ppm, whilst the saturated CH_2 protons gave peaks at 2.7 and 3.3 ppm. Also a well resolved quartet at 4.06 ppm ($^{3}J_{H\text{-}F}$ 9.1 Hz) indicates the presence of the $CHCF_3$ proton in isomer (**46c**). Isolation of the individual dienes was not attempted owing to their volatilities. It was hoped that a pure sample could be isolated by forming the cyclic anion, (**52**), using a tetraalkyl ammonium or metal salt in analogous methods to previous workers in this laboratory.[30, 132] However, time constraints have meant that exploration of this was not possible.



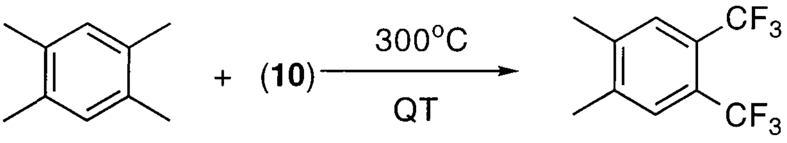
(52)

Scheme 2.30. Proposed formation of tetrabutylammonium 1,2-bis(trifluoromethyl)cyclopentadienide (**52**).

2.V. Investigation of the Reactions of (*Z*)-2*H*-Heptafluorobut-2-ene with Arenes.

As discussed earlier there has been limited success in the Diels-Alder reactions of arenes with alkenes and alkynes. However, owing to the efficiency of the reaction between fluoroalkene (**10**) with furan derivatives and cyclopentadiene it was the aim of this section to investigate the reaction of fluoroalkene (**10**) with arenes.

2.V.1. 1,2,4,5-Tetramethylbenzene - When excess fluoroalkene (**10**) was reacted with 1,2,4,5-tetramethylbenzene in a quartz tube at 300 °C excellent yields of 1,2-bis(trifluoromethyl)-4,5-dimethylbenzene (**34**) were obtained. Surprisingly at this temperature there was no trace of the 1:1 adduct obtained by Krespan.[120]



(34)

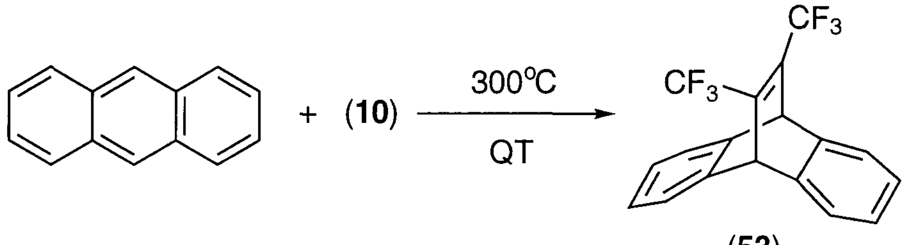
91%

Scheme 2.31. Formation of 1,2-dimethyl-4,5-bis(trifluoromethyl)benzene (**34**).

1,2-Dimethyl-4,5-bis(trifluoromethyl)benzene (**34**) is a known compound[120] and was identified by comparing its ^{1}H and ^{19}F NMR spectra and GLCMS to literature values. It was possible to purify (**34**) by vacuum sublimation, however, a trace of 1,2,4,5-tetramethylbenzene remained in the white crystalline solid that could not be removed by flash column chromatography.

As with the furan derivatives it appears that a 'one-pot' synthesis of 1,2-bis(trifluoromethyl)benzene derivatives has been discovered. Therefore to test the general applicability of this procedure a variety of substituted benzene derivatives were studied.

2.V.2. Anthracene - When excess fluoroalkene (**10**) was reacted with anthracene in a quartz tube at 300 °C quantitative yields of the dehydrofluorinated 1:1 adduct were obtained. In this case further elimination to produce a fluorinated arene does not occur owing to the extreme instability of the resulting benzyne, hence the reaction rests at the norbornatriene type structure (**53**).



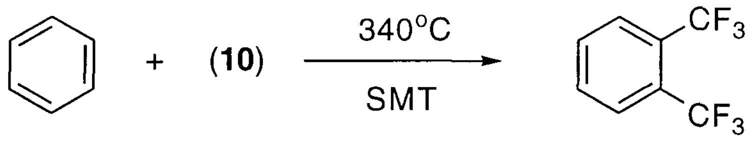
(53)

97%

Scheme 2.32. Formation of 11,12-bis(trifluoromethyl)-9,10-dihydro-9,10-ethenoanthracene (**53**).

11,12-Bis(trifluoromethyl)-9,10-dihydro-9,10-ethenoanthracene (**53**) is a known compound[121] and was identified by its parent peak in GLCMS, and its ^{1}H and ^{19}F NMR spectra by comparison to literature data.

2.V.3. Benzene - The equivalent reaction of benzene and fluoroalkene (**10**) in a quartz tube gave only a 15% conversion of benzene to 1,2-bis(trifluoromethyl)benzene (**20**). In an attempt to increase this conversion the reaction was scaled up in a sealable metal tube and excess benzene used. After various trials using the metal tube it was found that pressure is an important factor in the reaction. When the reaction was carried out at 340 °C and, according to ideal gas calculations, 130 atmospheres, good yields of 1,2-bis(trifluoromethyl)benzene (**20**) were obtained. In comparison to the equivalent reaction carried out by Krespan[120] in 1961 with hexafluorobut-2-yne and benzene this new result is surprisingly uncomplicated.



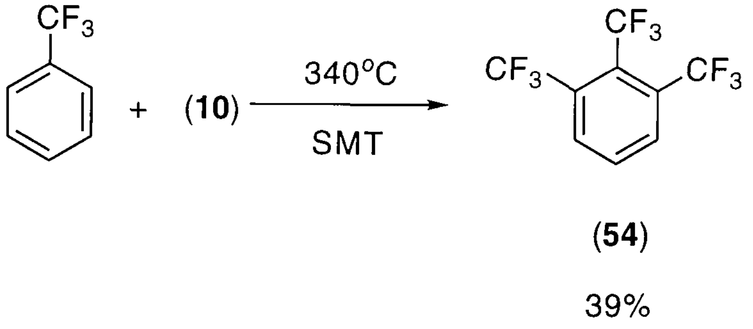
(20)

63%

Scheme 2.33. Formation of 1,2-bis(trifluoromethyl)benzene (**20**).

1,2-Bis(trifluoromethyl)benzene (**20**) is a known compound and was identified by comparing its ^{1}H and ^{19}F NMR spectra and GLCMS to literature values[133] after Spaltrohr distillation.

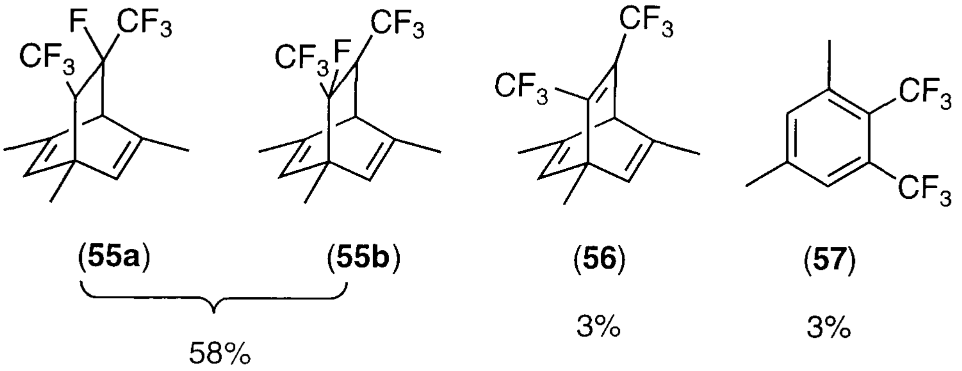
2.V.4. Trifluoromethylbenzene - When excess trifluoromethylbenzene was reacted with fluoroalkene (**10**) in a sealable metal tube at 340 °C and 130 atmospheres, a reasonable conversion to 1,2,3-tris(trifluoromethyl)benzene (**54**) was obtained. Once again the reaction was clean and only traces of the intermediate adducts were seen. However, owing to the low conversion, isolation of a small sample could only be achieved by preparative GLC techniques.



Scheme 2.34. Formation of 1,2,3-tris(trifluoromethyl)benzene (**54**).

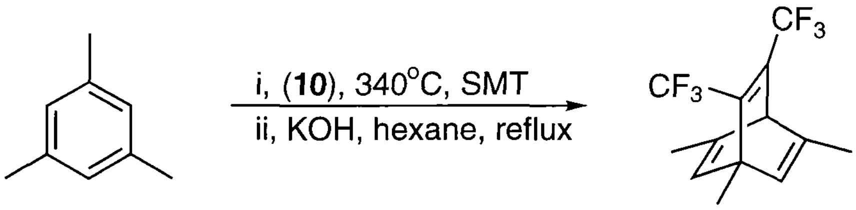
1,2,3-Tris(trifluoromethyl)benzene (**54**) is a known compound and was identified by comparing its ^1H and ^{19}F NMR spectra and GLCMS to literature values[133] after purification of a sample by preparative GLC.

2.V.5. 1,3,5-Trimethylbenzene - A complex product mixture was obtained when excess fluoroalkene (**10**) was reacted with 1,3,5-trimethylbenzene in a quartz tube at 375 °C. Contained within this mixture were two isomers of the 1:1 adduct (**55ab**), dehydrofluorinated adduct (**56**) and retro-Diels-Alder product (**57**), *Scheme 2.35.*



Scheme 2.35. The complex reaction mixture of the reaction between (*Z*)-2*H*-heptafluorobut-2-ene (**10**) and 1,3,5-trimethylbenzene

It was decided to try and isolate (**56**) from this mixture and, to this end, a larger scale reaction in a sealable metal tube was carried out in order to obtain more material. Using excess 1,3,5-trimethylbenzene a similar conversion and product distribution to the quartz tube experiment was achieved. Following the success discovered using potassium hydroxide in hexane, dehydrofluorination of (**55ab**) was carried out to increase the yield of (**56**), and subsequent filtration followed by distillation gave an isolable sample of triene (**56**).



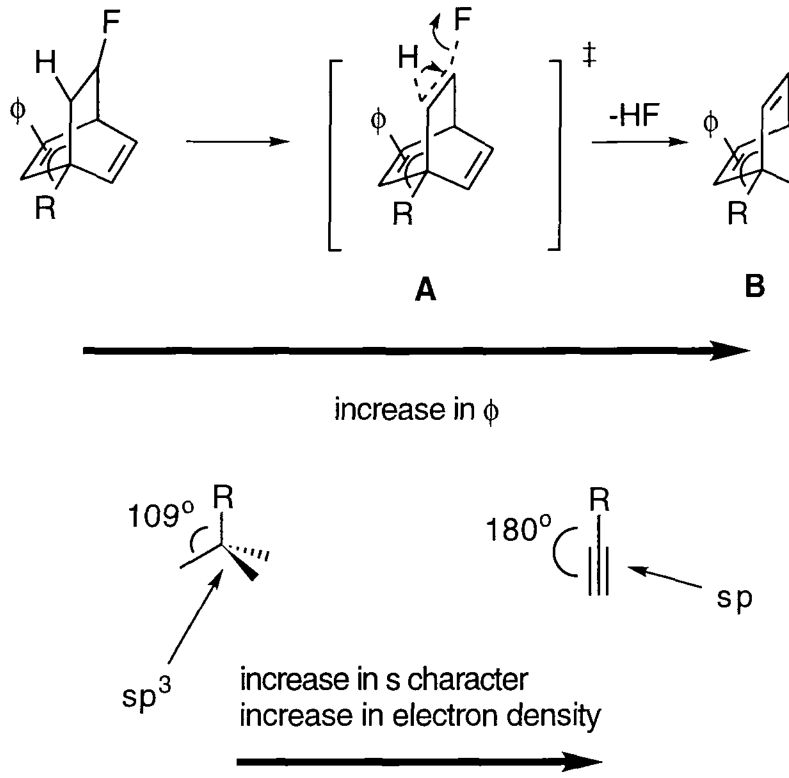
(56)

52%

Scheme 2.36. Formation of 1,3,5-trimethyl-7,8-bis(trifluoromethyl)-bicyclo[2.2.2]-octa-2,5,7-triene (**56**).

1,3,5-Trimethyl-7,8-bis(trifluoromethyl)-bicyclo[2.2.2]-octa-2,5,7-triene (**56**) is a new compound and was identified by its ^{1}H and ^{19}F NMR and GLCMS spectra. Two peaks were observed in the ^{19}F NMR spectrum at -59.0 and -67.8 ppm, indicating two distinct trifluoromethyl environments. Vinylic protons were observed at 6.82 ppm in the ^{1}H NMR spectrum, the bridgehead proton was clearly visible at 3.76 ppm and peaks at 2.29 and 2.30 ppm indicated the presence of two methyl group environments in a 2:1 ratio. Integration was also consistent with compound (**56**). After distillation 1,3,5-trimethyl-7,8-bis(trifluoromethyl)-bicyclo[2.2.2]-octa-2,5,7-triene (**56**) gave a satisfactory mass spectrum and elemental analysis.

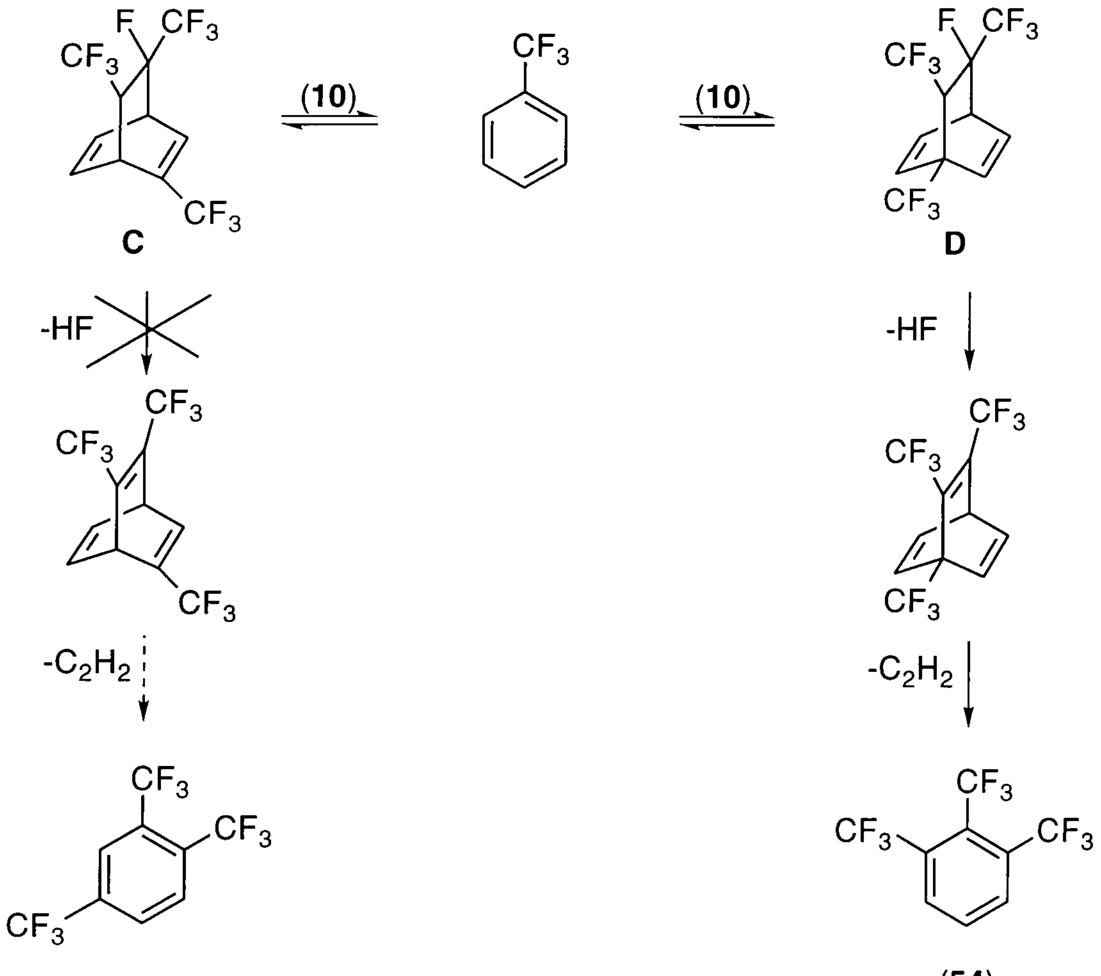
It is of interest that, at the same temperatures as the other benzenoid Diels-Alder reactions, the 1,3,5-trimethylbenzene 1:1 adducts (**55ab**) do not dehydrofluorinate. One plausible explanation of this considers the effect of substituents at the bridge head carbon of the 1:1 adduct, *Scheme 2.37.*



Scheme 2.37. Increase in bond angle going from sp^3 to sp

Assuming that dehydrofluorination is a concerted process, it is reasonable to assume that the transition state, **A**, is similar in character to the barrelene type structure **B**. As the elimination occurs, angle φ at the bridge head carbon increases, and considering the extreme case where angle φ would be 180°, the bridge head carbon would, theoretically be *sp* hybridised. Therefore on elimination of hydrogen fluoride the sp^3 hybridised bridge head carbon becomes more *sp* hybridised, *i.e.* there is an increase in *s* character of the bridge head carbon and hence an increase in electron density. Obviously, electron withdrawing groups would stabilise, and electron releasing groups would destabilise, the transition state. For 1,3,5-trimethylbenzene, R = Me, the methyl group destabilises the transition state and thus inhibits the dehydrofluorination. In the case of trifluoromethylbenzene, R = CF_3, the electron withdrawing group stabilises the transition state and dehydrofluorination occurs.

This theory may also explain why only the 1,2,3-tris(trifluoromethyl) isomer (**54**) is observed in the reaction of fluoroalkene (**10**) and trifluoromethylbenzene.


F
CF3
CF3
(10)
CF3
(10)
F
CF3
CF3
CF3
C
CF3
D
-HF
-HF
CF3
CF3
CF3
CF3
CF3
CF3
-C2H2
-C2H2
CF3
CF3
CF3
CF3
CF3
CF3

(54)

Scheme 2.38. Formation of 1,2,3-tris(trifluoromethyl)benzene (**53**).

Bicyclic **C** must be less stable than **D** following the previous argument. Therefore **D** dehydrofluorinates and undergoes a retro-Diels-Alder reaction to afford 1,2,3-tris(trifluoromethyl)benzene (**54**), whilst **C** does not eliminate hydrogen fluoride. Hence (**54**) is the exclusive isomer seen in this reaction.

Chapter 3.

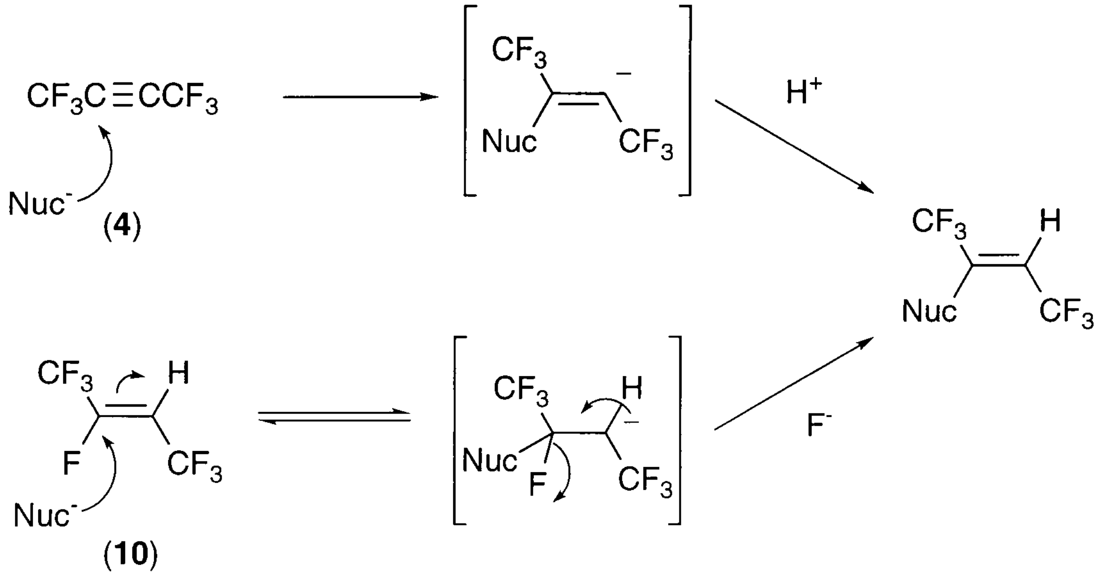
Nucleophilic Additions to (*Z*)-2*H*-Heptafluorobut-2-ene.

3.I. Review of Nucleophilic Additions to Hexafluorobut-2-yne and (*Z*)-2*H*-Heptafluorobut-2-ene

There has been considerable work conducted into the chemistry of both hexafluorobut-2-yne (**4**) and (*Z*)-2*H*-heptafluorobut-2-ene (**10**), especially in this laboratory.[30, 126, 128, 134] It has been shown that fluoroalkene (**10**), produced easily and cheaply on a reasonable laboratory scale, can be effectively used as a synthon for the more expensive hexafluorobut-2-yne.[64, 135] It is therefore the aim of this section to explore some of the analogous reactions between these two fluorocarbon gases and to discuss some new reactions carried out in this area using fluoroalkene (**10**).

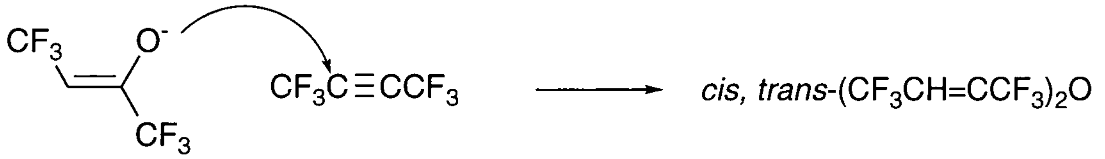
3.I.1. Oxygen Nucleophiles

In general the addition of alcohols to hexafluorobut-2-yne and (*Z*)-2*H*-heptafluorobut-2-ene requires base catalysis at room temperature,[136, 137] and tend to give the *Z* isomer as the major product. However at elevated temperatures the reactions can be carried out without catalysts to give the *E* products.[138] Hexafluorobut-2-yne and (*Z*)-2*H*-heptafluorobut-2-ene usually give identical products; the fluoroalkene (**10**) reactions occur *via* nucleophilic addition elimination type mechanisms, whilst hexafluorobut-2-yne undergoes simple nucleophilic addition across the acetylenic bond, *Scheme 3.1.*



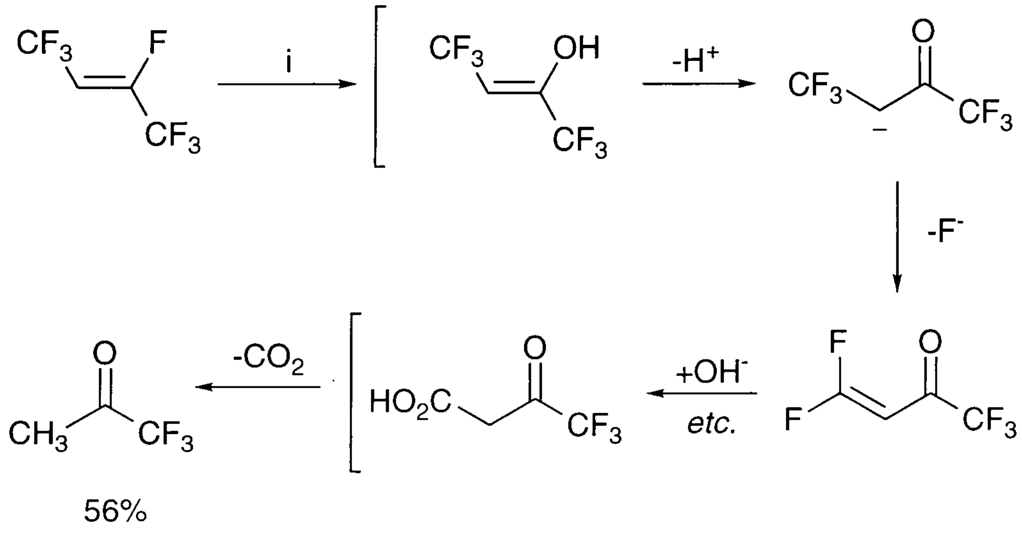
Scheme 3.1. The similarities in nucleophilic addition to hexafluorobut-2-yne and (*Z*)-2*H*-heptafluorobut-2-ene.

Hydration of hexafluorobut-2-yne is difficult in the absence of a basic catalyst. However, in the presence of trimethylamine the fluoroacetylene reacts vigorously with water, although only low yields of the expected butanone are obtained.[139] The main product of the reaction is *cis,trans*-$(CF_3CH{=}CCF_3)_2O$, thought to be formed by attack of the enol form of the butanone on the butyne, *Scheme 3.2.* Other products such as carbon dioxide and *trans*-pentafluorobut-2-ene are also observed that indicate some decomposition of the butyne and catalyst.



Scheme 3.2. Formation of the hydration product of hexafluorobut-2-yne.

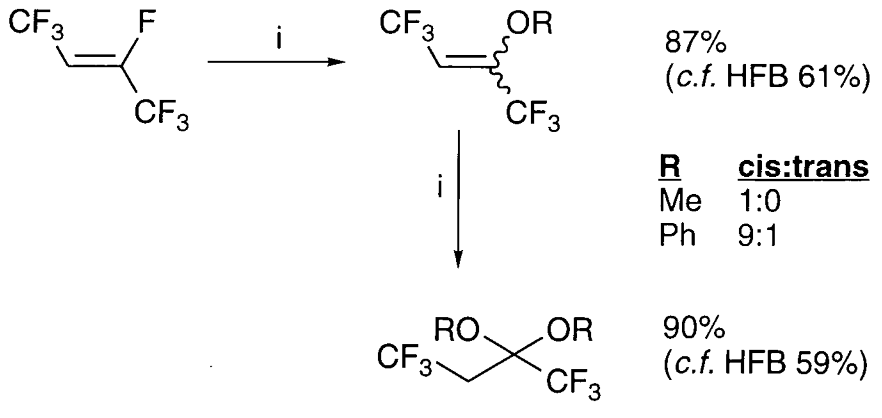
Similarly the reaction of (*Z*)-2*H*-heptafluorobut-2-ene with water is also difficult to carry out. At 80°C 1,1,1-trifluoroacetone is obtained in a 56% yield (isolated as its 2,4-DNP derivative[64]), whilst no reaction was observed below this temperature, using various solvents. It is thought that the 1,1,1-trifluoroacetone is formed in a way analogous to the addition of potassium hydroxide to 2*H*-heptafluorobut-2-ene,[30] *Scheme 3.3.*



i = H_2O, K_2CO_3, CH_3CN, 80°C.

Scheme 3.3. Formation of 1,1,1-trifluoroacetone from (*Z*)-2*H*-heptafluorobut-2-ene.

Sodium salts, such as methoxide and phenoxide, react at room temperature[140] with fluoroalkene (**10**), using cesium carbonate as the basic catalyst, giving excellent yields of the addition-elimination products in 100% and 90% *Z* forms, respectively, *Scheme 3.4.* These products are precisely those that are obtained in reactions carried out with hexafluorobut-2-yne, with similar yields.[136]

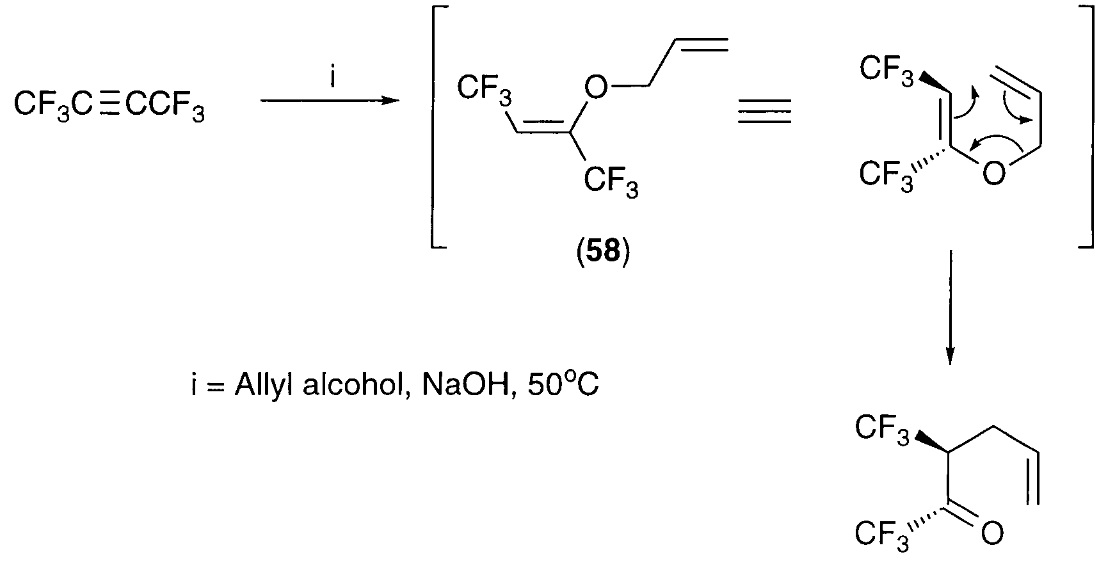

CF3
F
CF3
i
CF3
OR
CF3
i
RO
OR
CF3
CF3
87%
(c.f. HFB 61%)
R cis:trans
Me 1:0
Ph 9:1
90%
(c.f. HFB 59%)

i = NaOR, Tetraglyme, R.T. (yields for R=Me)

Scheme 3.4. Alkoxide addition to (*Z*)-2*H*-heptafluorobut-2-ene.

If more than a two-fold excess of alkoxide is used,[136] further reaction occurs and good yields of the saturated diadducts are obtained.

Allyl alcohol adds to hexafluorobut-2-yne to form 1,1,1-trifluoro-3-trifluoromethylhex-5-ene-2-one (**59**). This occurs by simple nucleophilic addition to the acetylene followed by a facile Claisen rearrangement[141] of the 1:1 adduct, *Scheme 3.5.*


$CF_3C \equiv CCF_3$
i
CF3
O
CF3
CF3
CF3
O
CF3
CF3
O

(58)

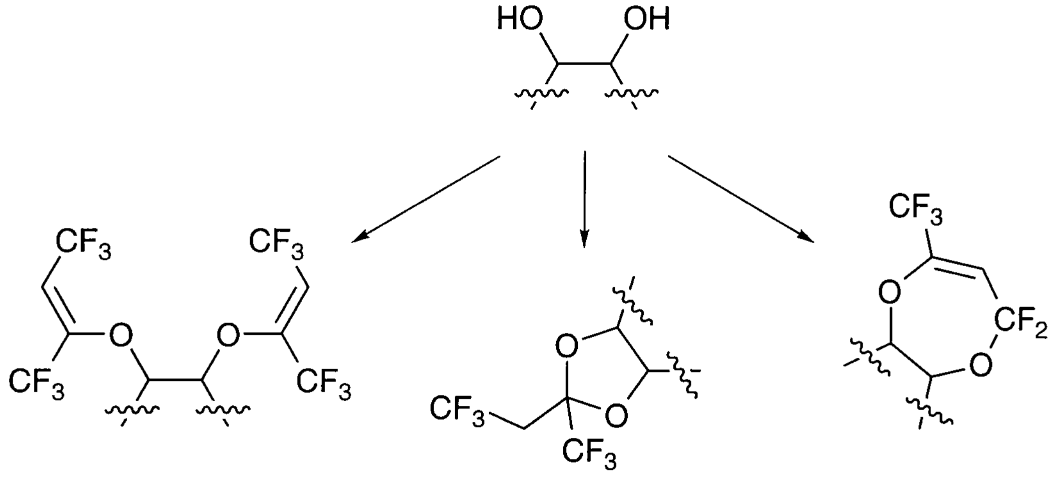
i = Allyl alcohol, NaOH, 50°C

74%

(59)

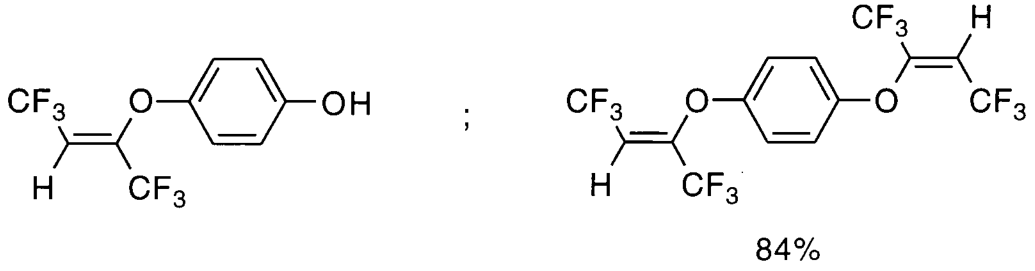
Scheme 3.5. The Claisen rearrangement of the allylic alcohol adduct of hexafluorobut-2-yne.

Diols can be used in some fascinating reactions with these unsaturated fluorocarbons.[64] In these cases the mono- and di- adducts can be formed and also, in the special cases of 1,2-diols, there is the possibility of other interesting addition products, *Scheme 3.6.*



Scheme 3.6. (*Z*)-2*H*-heptafluorobut-2-ene with 1,2-diols.

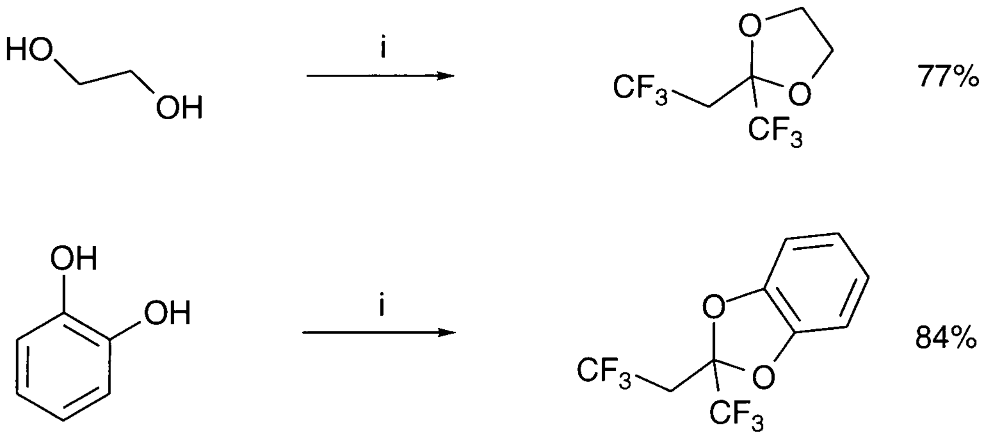
Both the mono- (**60**) and di- (**61**) adducts of hydroquinone with (**10**) have been made.[64]



(60) **(61)**

Scheme 3.7. Mono- and di- adducts of hydroquinone and (*Z*)-2*H*-heptafluorobut-2-ene (**10**).

Catechol and ethylene glycol have been shown to react twice at the same carbon atom, *Scheme 3.8,* in effect producing protected ketones.[64] However, deprotection of these ketals by the usual methods has proven unsuccessful, a difficulty observed in cases of other highly fluorinated systems.[142]



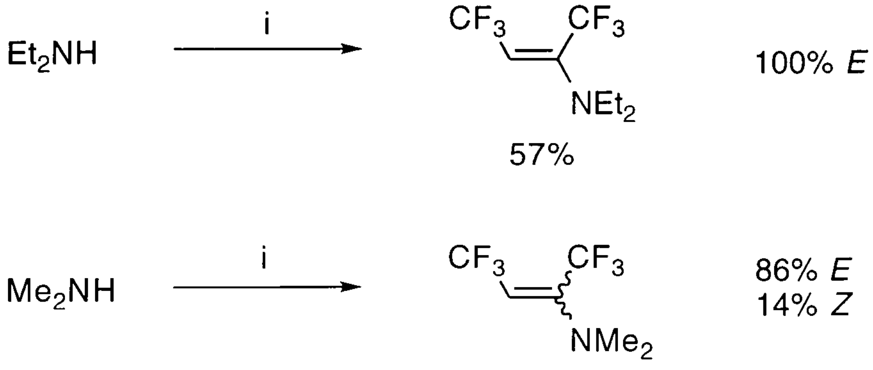
i = (**10**), Cs_2CO_3, CH_3CN or Tetraglyme, R.T.

Scheme 3.8. 1,2-Diol additions to (*Z*)-2*H*-heptafluorobut-2-ene.

3.I.2. Nitrogen Nucleophiles

Nitrogen nucleophiles react in an analogous way to oxygen nucleophiles. Although, for the most part, they do not require the base catalysis of the alcohols due to their greater basicity and nucleophilicity.

Dimethylamine and diethylamine react with hexafluorobut-2-yne to produce 1:1 adducts, *Scheme 3.9.* Diethylamine reacts to give exclusively the *E* form,[136] whilst dimethylamine gives a 6:1 ratio of *trans* to *cis*.[143] Steric factors account for the disparity in the stereochemical outcome; the diethylamine is more sterically demanding than the dimethyl form. Once again, these reactions can be reasonably assumed to proceed *via* nucleophilic attack, promoted by the fluorocarbon groups. In the case of (*Z*)-2*H*-heptafluorobut-2-ene and diethylamine[30] it has been shown that only a very small amount of the adduct is formed (<5%), and this is one of the few differences between hexafluorobut-2-yne and 2*H*-heptafluorobut-2-ene.

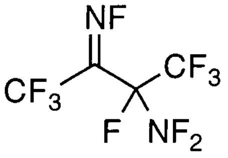


i = (**4**), R.T.

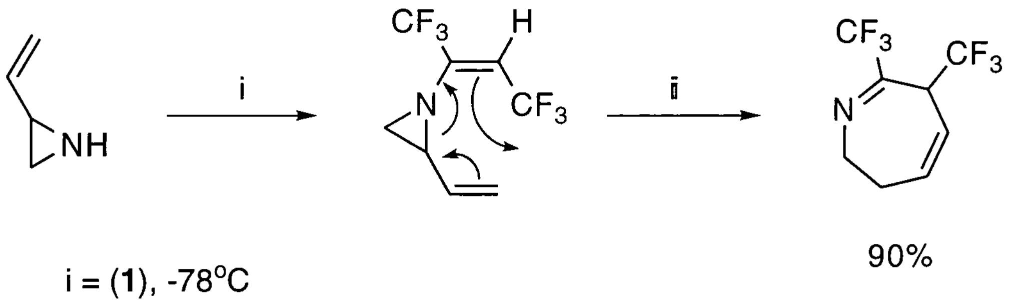
Scheme 3.9. Addition of diethylamine and dimethylamine to hexafluorobut-2-yne.

Cyclohexamine is also found to react with hexafluorobut-2-yne,[144] although the stereochemical outcome is not reported in the literature.

Hexafluorobut-2-yne has been shown to react with N_2F_4[145] to produce *cis* and *trans* isomers of $CF_3C(NF_2)=C(NF_2)CF_3$, which, on heating, rearranges to give the imine, shown below.



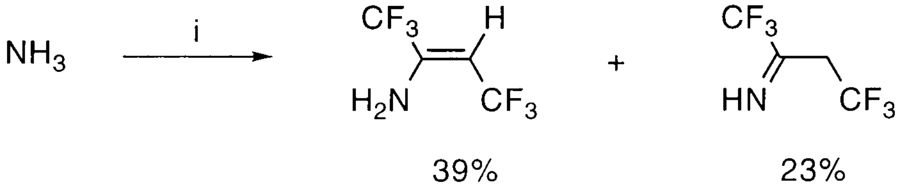
An interesting ring expansion is observed on the addition of 2-vinylaziridine[63] to hexafluorobut-2-yne. At low temperatures the initial mono-adduct is formed, but on heating to 50°C a rearrangement occurs and the ring expands to a seven membered isomer, *Scheme 3.10.*



i = (**1**), -78°C
ii = 50°C

Scheme 3.10. Rearrangement of the 2-vinylaziridine adduct of hexafluorobut-2-yne.

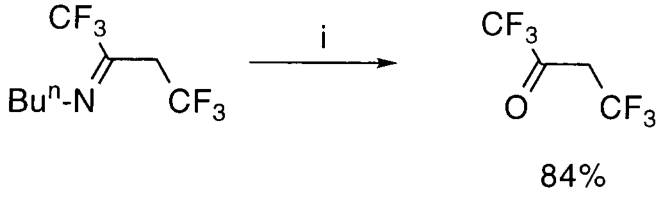
Ammonia affords two products when stirred at 0°C with hexafluorobut-2-yne,[146] *Scheme 3.11*, the first is the expected mono-adduct and the second is an imine, and it has been shown that this is not formed by rearrangement of the mono-adduct at room temperature.[146] With (*Z*)-2*H*-heptafluorobut-2-ene the addition product[64] is observed after one week, at room temperature, although a significant amount of 1,1,1,4,4,4-hexafluorobutan-2-one is also formed. After three weeks this is the sole product, formed by hydrolysis in the aqueous ammonia used by Roche.



i = HFB, 0°C

Scheme 3.11. Addition of ammonia to hexafluorobut-2-yne.

The imine form of the addition product of fluoroalkene (**10**) and n-butylamine[64] is obtained in good yields and is easily hydrolysed in a similar manner to the ammonia product with aqueous sulfuric acid, *Scheme 3.12.*



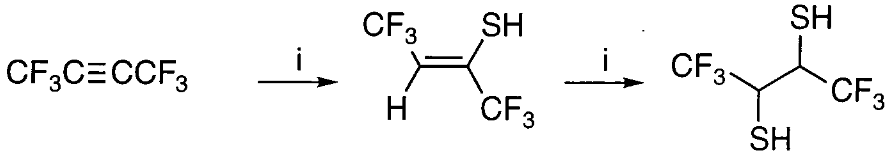
i = aqueous sulfuric acid

Scheme 3.12. Hydrolysis of the n-butylamine product.

3.I.3. Sulfur Nucleophiles

Perhaps surprisingly, little work is documented on the addition of sulfur nucleophiles to hexafluorobut-2-yne, and none on their addition to 2*H*-heptafluorobut-2-ene.

Hexafluorobut-2-yne will react with hydrogen sulfide under X-ray initiation[147] to produce the 1:1 adduct (**62**) in 100% *Z* form. Using excess hydrogen sulfide also gives the diadduct, although the thiol groups are on different carbon atoms, *Scheme 3.13.*



(62)

i = H_2S, X-rays

Scheme 3.13. Hydrogen sulfide addition to hexafluorobut-2-yne.

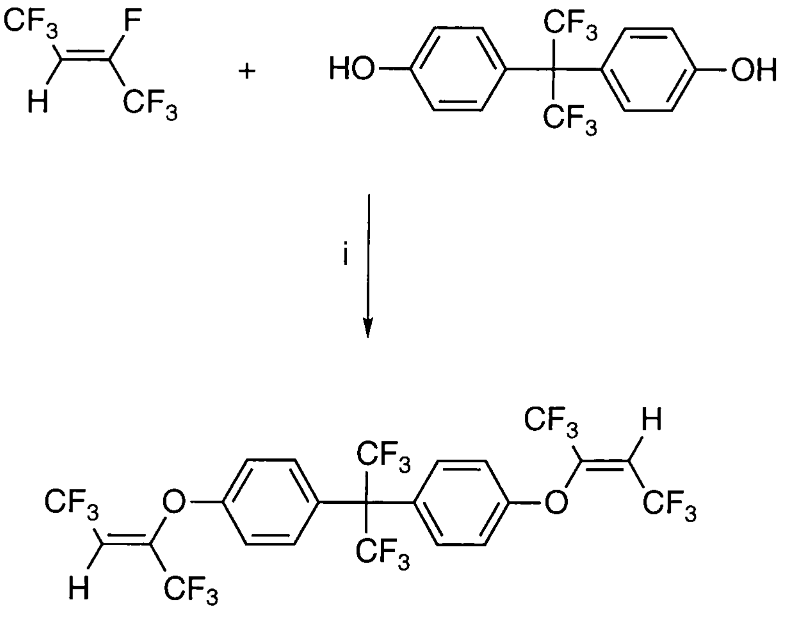
RESULTS AND DISCUSSION

3.II. Novel Nucleophilic Additions to 2*H*-Heptafluorobut-2-ene

It was decided to continue the investigation into the addition of nucleophiles to (**10**) and provide further evidence of the suitability of this fluoroalkene as a synthon for hexafluorobut-2-yne (**4**).

3.II.1. Oxygen Nucleophiles

3.II.1.a. Hexafluoro-2,2-di(4-hydroxyphenyl)propane. - When excess fluoroalkene (**10**) was reacted with hexafluoro-2,2-di(4-hydroxyphenyl)propane, in the presence of base, only the diadduct was observed by ^{19}F NMR. After isolation, this compound was shown to be exclusively in the *Z,Z* conformation, see *Section 3.III* for the elucidation of the stereochemical outcome.



88%

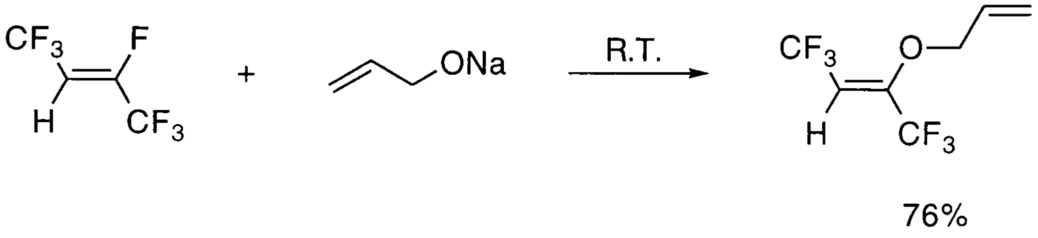
(63)

i = CH_3CN, K_2CO_3, R.T.

Scheme 3.14. Formation of 1,1,1,3,3,3-hexafluoro-2,2-bis[4-(3,3,3-trifluoro-1-trifluoromethylprop-1-enyloxy)phenyl]propane (**63**).

1,1,1,3,3,3-Hexafluoro-2,2-bis[4-(3,3,3-trifluoro-1-trifluoromethylprop-1-enyloxy)phenyl]propane (**63**) is a new compound and was identified by its ^{19}F and ^{1}H NMR spectra and GLCMS. Only three peaks were observed on the ^{19}F NMR spectrum at -59.7, -64.2 and -69.7 which integrated 1:1:1, indicating the presence of three distinct trifluoromethyl environments and there was no trace of the vinylic fluorine at -119 ppm present in the starting fluoroalkene (**10**). A quartet at 6.23 ppm was observed on the ^{1}H NMR spectrum, indicative of a vinylic proton coupling to a trifluoromethyl group, and an AB quartet at 7.03 and 7.37 ppm confirmed the presence of aromatic protons on a *para* substituted benzene ring. Integration of the ^{1}H NMR spectrum and ^{13}C NMR data was also consistent for compound (**63**). GLCMS gave a mass spectrum with the correct molecular ion of 660 and after distillation 1,1,1,3,3,3-hexafluoro-2,2-bis[4-(3,3,3-trifluoro-1-trifluoromethylprop-1-enyloxy)phenyl]propane (**63**) gave a satisfactory elemental analysis.

3.II.1.b.i. Allyl alcohol. - No reaction was observed when excess fluoroalkene (**10**) was stirred with allyl alcohol and potassium carbonate, in acetonitrile, at room temperature. At elevated temperatures complex mixtures of fluorinated products were formed. However when excess (**10**) was added to the sodium salt of allyl alcohol, in the absence of solvent and at room temperature, good yields of the addition product [Z-3,3,3-trifluoro-1-trifluoromethylprop-1-enyl] prop-2-enyl ether were obtained.

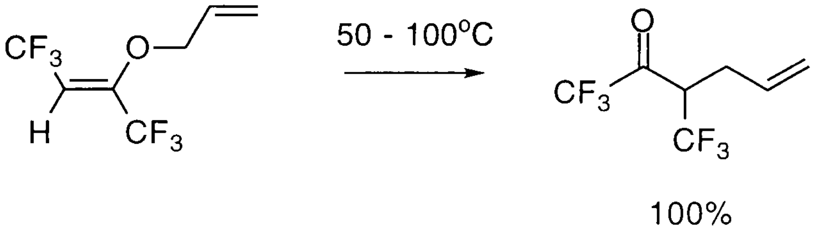


(58)

Scheme 3.15. Formation of [Z-3,3,3-trifluoro-1-trifluoromethylprop-1-enyl] prop-2-enyl ether (**58**).

[Z-3,3,3-Trifluoro-1-trifluoromethylprop-1-enyl] prop-2-enyl ether (**58**) is a new compound and was identified by its ^{19}F and ^{1}H NMR spectra and GLCMS. A ^{19}F NMR spectrum showed two signals of equal intensity at -57.8 and -70.0 ppm indicating two distinct trifluoromethyl groups. On the ^{1}H NMR spectrum a quartet at 5.75 ppm was observed, indicative of a vinylic proton coupling to a trifluoromethyl group, and the allylic $CH_2CH=CH_2$ chain gave appropriate multiplets at 4.58, 5.32, 5.40 and 5.95 ppm. ^{13}C data and integration of the ^{1}H NMR spectrum were also consistent for ether (**58**). GLCMS gave a mass spectrum with the correct molecular ion of 220 and after distillation [Z-3,3,3-trifluoro-1-trifluoromethylprop-1-enyl] prop-2-enyl ether (**58**) gave a satisfactory elemental analysis.

3.II.1.a.ii. Pyrolysis of Allyl alcohol adduct. - Earlier we have seen that diene (**58**) is the intermediate in the Claisen rearrangement shown in the analogous reaction with hexafluorobut-2-yne, *Scheme 3.5,* and has not been isolated before this time. Reaction conditions in the latter reaction cause a thermal rearrangement that does not occur at room temperature. Further, to prove that diene (**58**) is indeed the intermediate in this Claisen rearrangement a pure sample was heated to 80°C for 15 hours. This resulted in a quantitative yield of the ketone (**59**), *Scheme 3.16.*



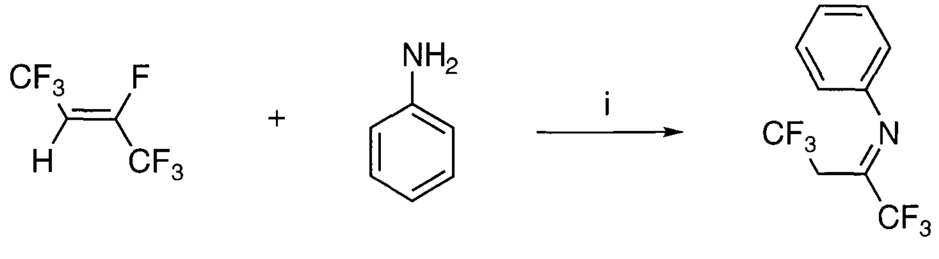
(59)

Scheme 3.16. Formation of 1,1,1-trifluoro-3-trifluoromethyl-5-hexen-2-one (**59**).

1,1,1-Trifluoro-3-trifluoromethyl-5-hexen-2-one (**59**) is a known compound[141] and was identified by comparing its ^{19}F and ^{1}H NMRs and GLCMS data with literature values. The ^{19}F NMR spectrum gave two signals of equal intensity at -66.4 and -79.5 ppm, indicating two distinct trifluoromethyl groups. The allylic chain was still apparent in the ^{1}H NMR spectrum at 2.71, 5.15, 5.19 and 5.67 ppm (2:1:1:1) but more noticeable was the loss of the vinylic proton signal at 5.75 ppm in (**58**), and the gain of a complex multiplet at 3.85 ppm indicating that the vinylic proton is no longer at an unsaturated site and is now coupling to the allylic chain. ^{13}C data and integration of the ^{1}H NMR spectrum were also consistent for ketone (**59**), and agreed with the literature data. After distillation 1,1,1-trifluoro-3-trifluoromethyl-5-hexen-2-one (**59**) gave a satisfactory mass spectrum and elemental analysis.

3.II.2. Nitrogen Nucleophiles

3.II.2.a. Aniline. - When excess fluoroalkene (**10**) was reacted with aniline, in the presence of base, complete conversion of the aniline to one product was observed by GLCMS and ^{1}H NMR. This product was found to be 1,1,1,4,4,4-hexafluoro-2-phenyliminobutane (**64**).



91%

(**64**)

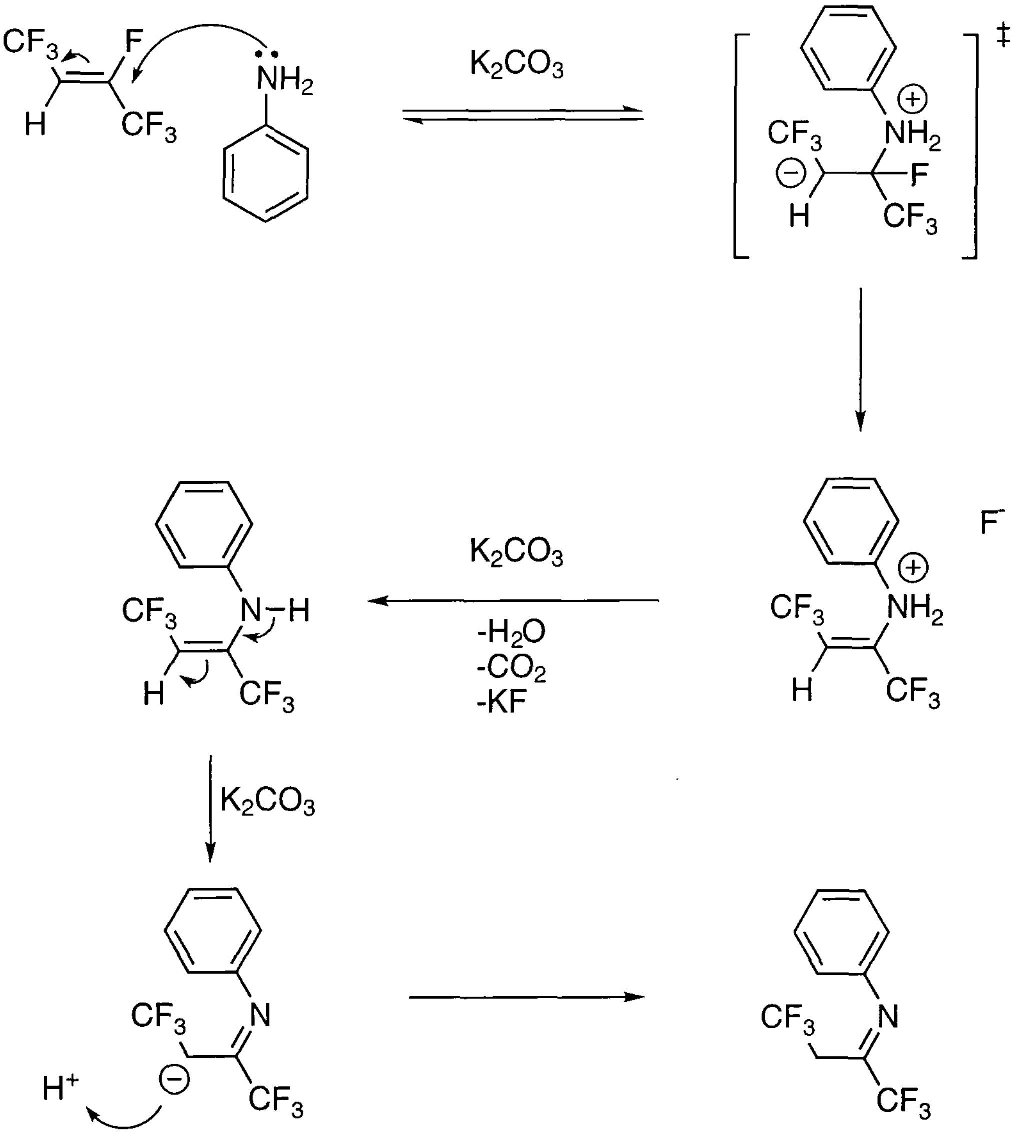
i = CH_3CN, K_2CO_3, R.T.

Scheme 3.17. Formation of 1,1,1,4,4,4-hexafluoro-2-phenyliminobutane (**64**).

1,1,1,4,4,4-Hexafluoro-2-phenyliminobutane (**64**) is a new compound and was identified by its ^{19}F and ^{1}H NMR and GLCMS spectra. Peaks at -60.5 and -71.7 ppm of equal intensity, in the ^{19}F NMR spectrum, indicated the presence of two trifluoromethyl groups. In the ^{1}H NMR spectrum aromatic protons were clearly visible at 6.77, 7.22 and 7.41 ppm and a quartet at 3.33 ppm, a lower chemical shift than vinylic protons, integrated to two protons suggesting a CH_2, therefore illustrating that the imine tautomer of the aniline adduct had been formed. Furthermore, a peak at 150.1 ppm in the ^{13}C spectrum confirmed this conclusion. GLCMS gave a mass spectrum with the correct molecular ion of 255 and after distillation 1,1,1,4,4,4-hexafluoro-2-phenyliminobutane (**64**) gave a satisfactory elemental analysis.

Previously workers[30] had been unsuccessful in the synthesis of this compound, although none had tried using a basic catalyst. At room temperature, in the absence of catalyst, we have shown that there only a small amount of reaction between aniline and (**10**) in acetonitrile.

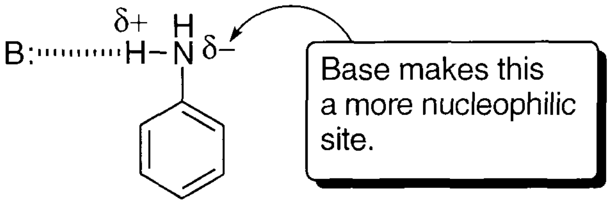
One mechanism is illustrated in *Scheme 3.18.*


K2CO3
K2CO3
-H2O
-CO2
-KF
K2CO3
F⁻

(64)

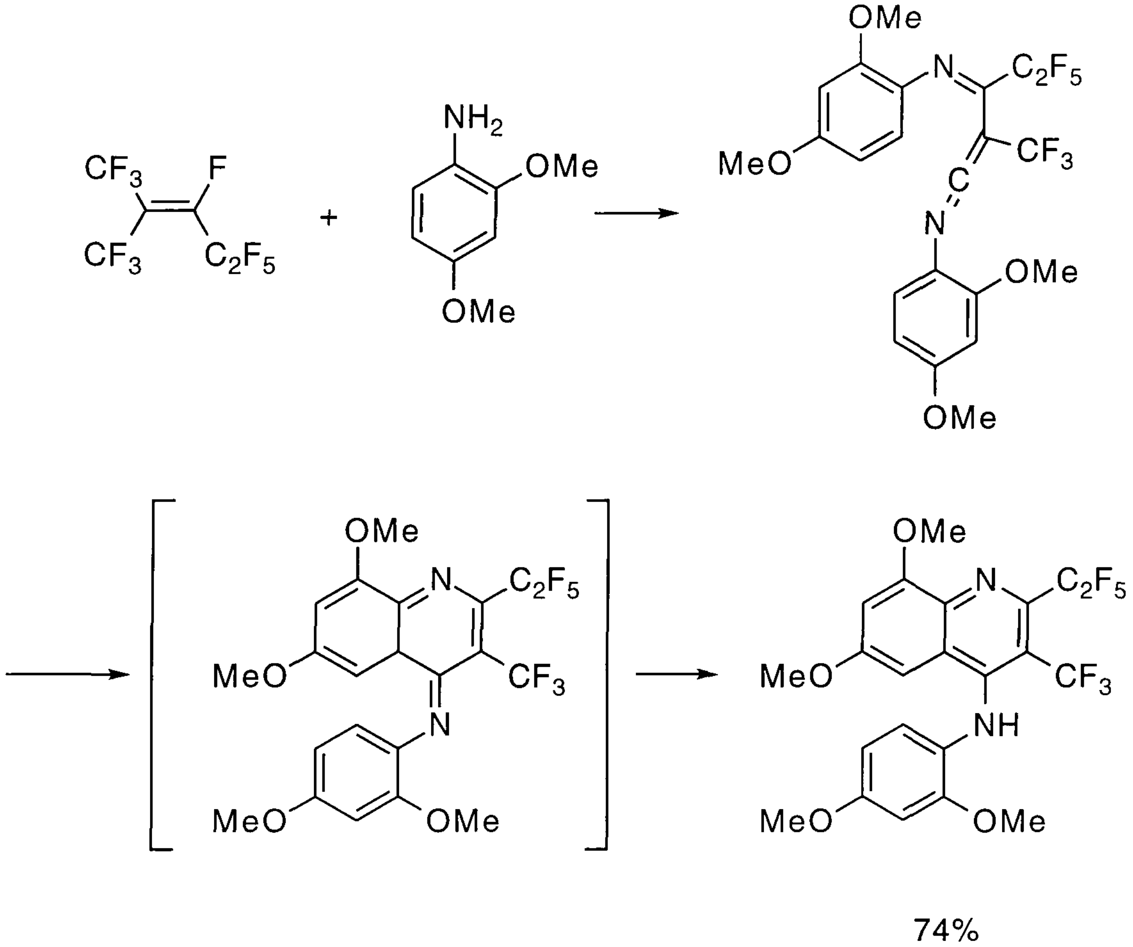
Scheme 3.18. Mechanism of aniline addition?

Of course, this mechanism is also plausible using aniline as the base, instead of potassium carbonate. However, clearly, potassium carbonate must promote nucleophilic attack of the aniline by acting as a Lewis base, *Scheme 3.19.* and this accounts for the huge difference between reactivity of the systems with and without potassium carbonate.


B
δ+
δ−
Base makes this a more nucleophilic site.

Scheme 3.19. Potassium carbonate as a Lewis base?

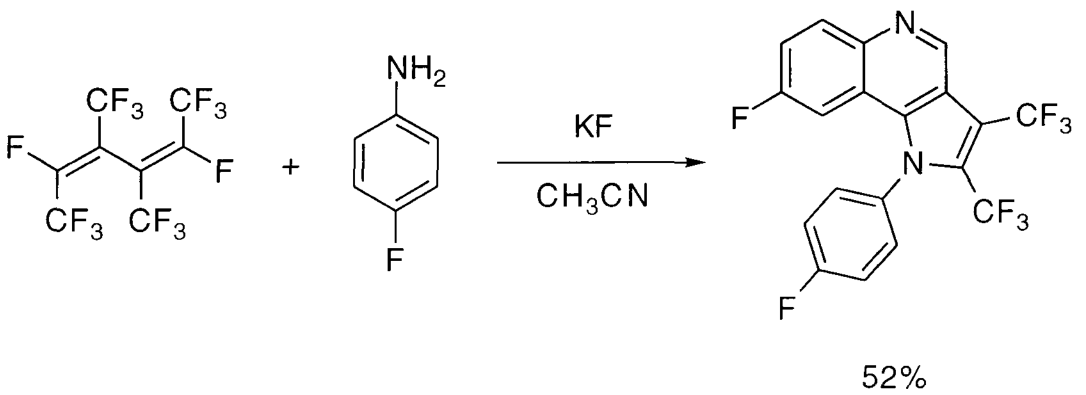
3.II.2.a.i. 1,1,1,4,4,4-Hexafluoro-2-phenyliminobutane (64) and Potassium Hydroxide. - Haszeldine[148] in 1974 showed that aniline derivatives will react with fluoroalkenes, and in the cases where there are hydrogen *ortho* to the amine the reaction can proceed further than the initial adducts,[148-150] *Scheme 3.20.*



Scheme 3.20. Haszeldine's route to fluorinated quinolines.

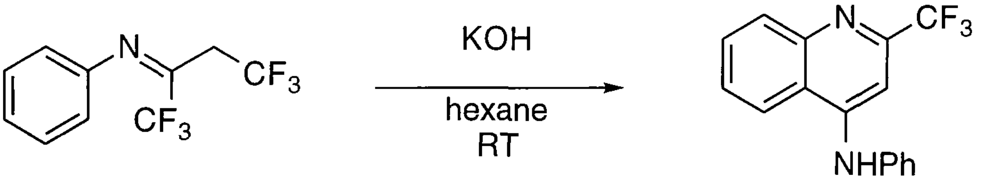
This, therefore, offers a useful route to fluorinated quinoline derivatives.

More recently, work carried out in this laboratory by Mullins[134] again showed the use of primary aromatic amines to form quinolines with fluoroalkenes.



Scheme 3.21. Mullins' route to fluorinated quinolines.

Following these examples it was decided to attempt to synthesise a fluorinated quinoline from 1,1,1,4,4,4-hexafluoro-2-phenyliminobutane (**64**). Imine (**64**) was added to a stirred slurry of a large excess of potassium hydroxide powder in hexane, to give 2-trifluoromethyl-4-(*N*-phenylamino)-quinoline (**65**).



(64)

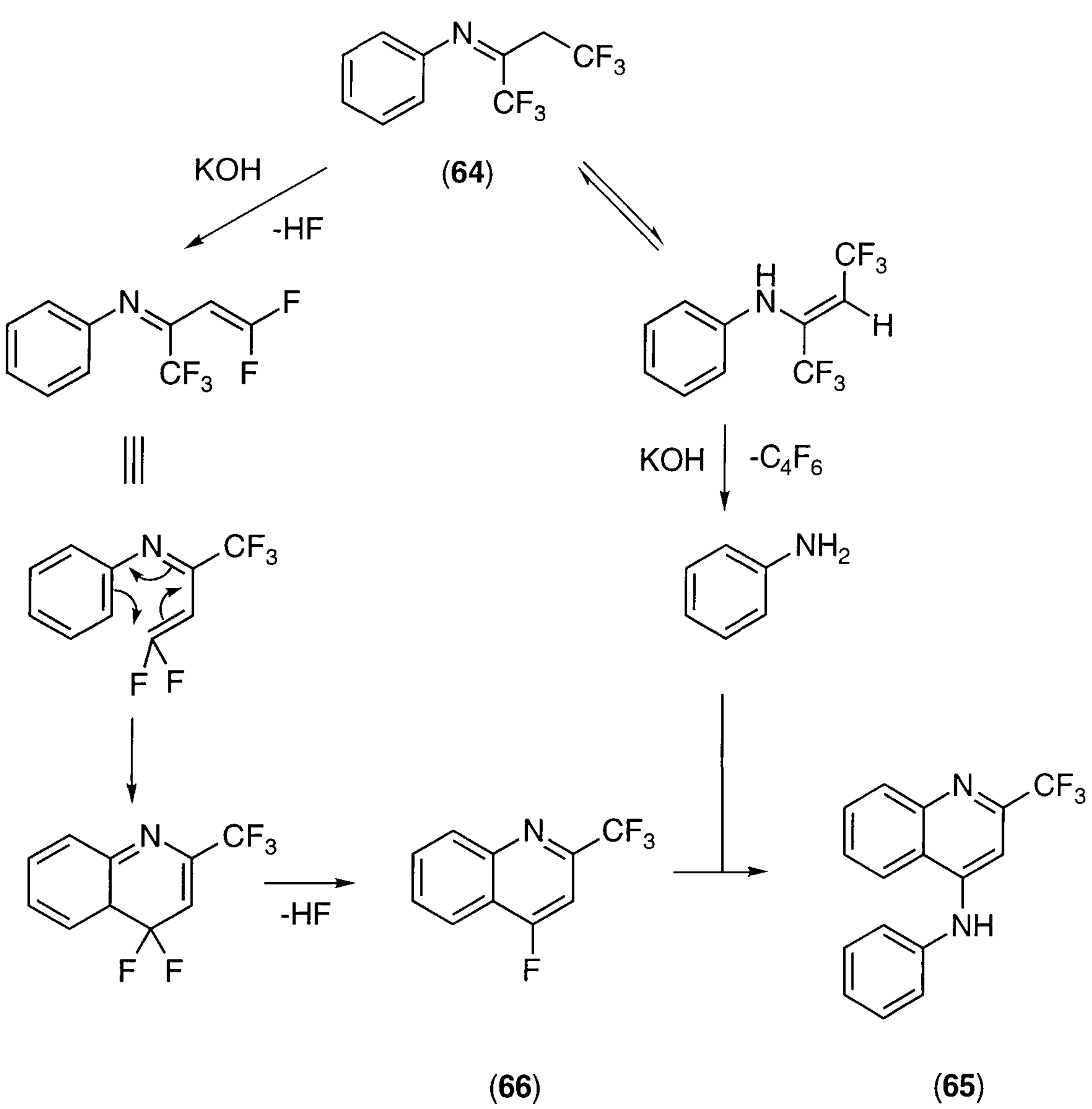
53%

(65)

Scheme 3.22. Formation of 4-(*N*-phenylamino)-2-trifluoromethylquinoline (**65**).

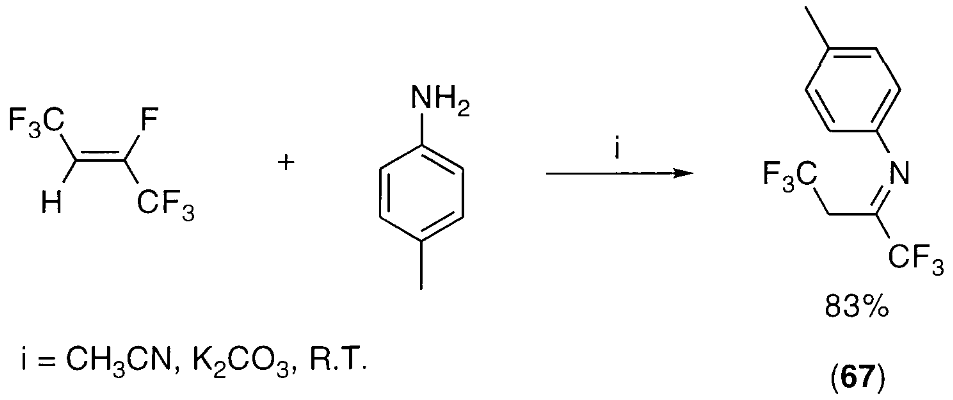
4-(*N*-Phenylamino)-2-trifluoromethylquinoline (**65**) has previously never been synthesised and was identified by its ^{19}F, ^{1}H and ^{13}C NMR and mass spectra. ^{19}F NMR gave a spectrum with only one signal at -67.5 ppm revealing the presence of one trifluoromethyl group. All of the peaks observed in the ^{1}H NMR spectrum were in the aromatic region, between 7.06 and 8.36 ppm and integrated correctly. A singlet at 7.06 ppm was observed, characteristic of a proton at position 3 in a 2,4 substituted quinoline and the other peaks were assigned by comparison with similar compounds in the literature. After vacuum sublimation at 100 °C / 0.1 mmHg a pure sample of 4-(*N*-phenylamino)-2-trifluoromethylquinoline (**65**) gave a satisfactory elemental analysis and mass spectrum.

The formation of quinoline (**65**) can be accounted for by the mechanism illustrated in *Scheme 3.23*. Potassium hydroxide causes a dehydrofluorination from the terminal trifluoromethyl group in imine (**64**), this then undergoes a 6-endo-trig cyclisation followed by a further dehydrofluorination giving 4-fluoro-2-trifluoromethylquinoline (**66**). Simultaneously, aniline is regenerated by the base induced elimination of hexafluorobut-2-yne (**1**) from the amine tautomer of imine (**64**). Aniline then reacts with the quinoline (**66**) to form 4-(*N*-phenylamino)-2-trifluoromethylquinoline (**65**) by nucleophilic displacement of fluorine at position 4.


CF_3
CF_3
KOH
-HF
(64)
F
CF_3 F
H
CF_3
H
CF_3
KOH
$-C_4F_6$
CF_3
NH_2
F F
CF_3
-HF
CF_3
F F
CF_3
F
CF_3
NH
(66)
(65)

Scheme 3.23. Mechanism for the formation of 4-(*N*-phenylamino)-2-trifluoromethylquinoline (**65**).

3.II.2.b. 4-Methylaniline. - When excess fluoroalkene (**10**) was reacted with 4-methylaniline, in the presence of base, complete conversion of the aniline derivative to one product was observed by GLCMS and ^{1}H NMR. This product was found to be 1,1,1,4,4,4-hexafluoro-2-(4-methylphenyl)iminobutane (**67**).

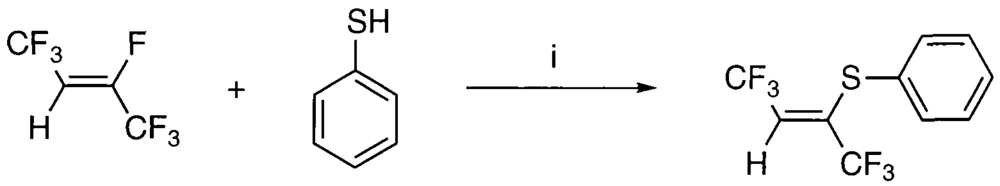

F_3C
F
H
CF_3
+
NH_2
i
F_3C
N
CF_3
83%
i = CH_3CN, K_2CO_3, R.T.
(67)

Scheme 3.24. Formation of 1,1,1,4,4,4-hexafluoro-2-(4-methylphenyl)iminobutane (**67**).

1,1,1,4,4,4-Hexafluoro-2-(4-methylphenyl)iminobutane (**67**) is a new compound and was identified by its ^{19}F, ^{1}H and ^{13}C NMR spectra and GLCMS data, and comparison to (**64**). Peaks at -60.5 and -71.6 ppm of equal intensity, in the ^{19}F NMR spectrum, indicated the presence of two distinct trifluoromethyl groups. Also the vinylic fluorine at -119 ppm, found in the starting fluoroalkene (**10**) had disappeared proving that this fluorine had been replaced by the nitrogen nucleophile in 4-methylaniline. Once again a quartet at 3.33 ppm was observed in the ^{1}H NMR spectrum, integrating to two protons and indicating the formation of the imine. Also a singlet at 2.35 (CH_3) and an AB quartet at 6.67 and 7.21 ppm exposed the *para*-methyl substituted aromatic ring. ^{13}C data were also consistent with compound (**67**) and a quartet of quartets at 149.8 ppm further confirmed the presence of the imine. GLCMS gave a mass spectrum with the correct molecular ion of 269 and after distillation 1,1,1,4,4,4-hexafluoro-2-(4-methylphenyl)iminobutane (**67**) gave a satisfactory elemental analysis.

3.II.3. Sulfur Nucleophiles

3.II.3.a. Thiophenol. - When excess fluoroalkene (**10**) was added to thiophenol at room temperature, in the presence of base, good yields of the addition-elimination product *Z*-1,1,1,4,4,4-hexafluoro-2-phenylthiobut-2-ene (**68**) were obtained.



80%

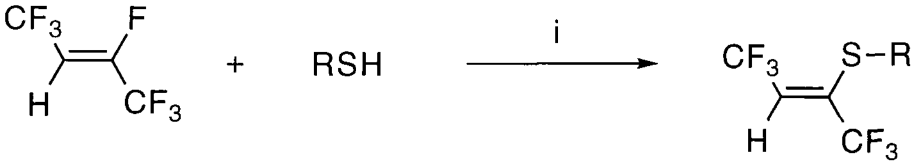
i = CH_3CN, K_2CO_3, R.T.

(68)

Scheme 3.25. Formation of *Z*-1,1,1,4,4,4-hexafluoro-2-phenylthiobut-2-ene (**68**).

Z-1,1,1,4,4,4-Hexafluoro-2-phenylthiobut-2-ene (**68**) is a new compound and was identified by its ^{19}F and ^{1}H NMR spectra and by GLCMS. Two peaks of equal intensity were observed in the ^{19}F NMR spectrum at -58.5 and -64.0 ppm, indicating the presence of two distinct trifluoromethyl environments, again there was no trace of the starting alkene (**10**). A quartet of quartets at 6.65 ppm was observed in the ^{1}H NMR spectrum, indicative of a vinylic proton coupling to two trifluoromethyl groups, and the aromatic protons could be seen as a complex multiplet between 7.3 and 7.5 ppm. ^{13}C NMR data and integration of the ^{1}H NMR spectrum were also consistent for fluoroalkene (**68**). GLCMS gave a mass spectrum with the correct molecular ion of 272 and after distillation *Z*-1,1,1,4,4,4-hexafluoro-2-phenylthiobut-2-ene (**68**) gave a satisfactory elemental analysis.

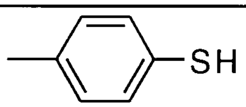
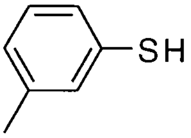
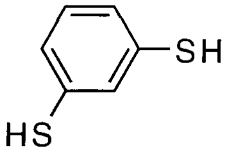
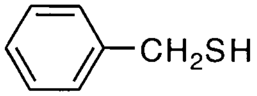
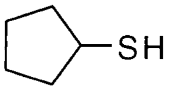
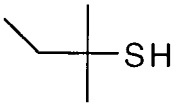
Following the success encountered with thiophenol, and the absence of thiol additions to hexafluorobut-2-yne and (*Z*)-2*H*-heptafluorobut-2-ene in the literature, it was decided to extend this methodology and try different thiols to produce compounds of the type shown in *Scheme 3.26*.



i = CH_3CN, K_2CO_3, R.T.

Scheme 3.26. Reactions of thiols with fluoroalkene (**10**).

Table 3.1. Thiol additions to (**10**) and selected data.

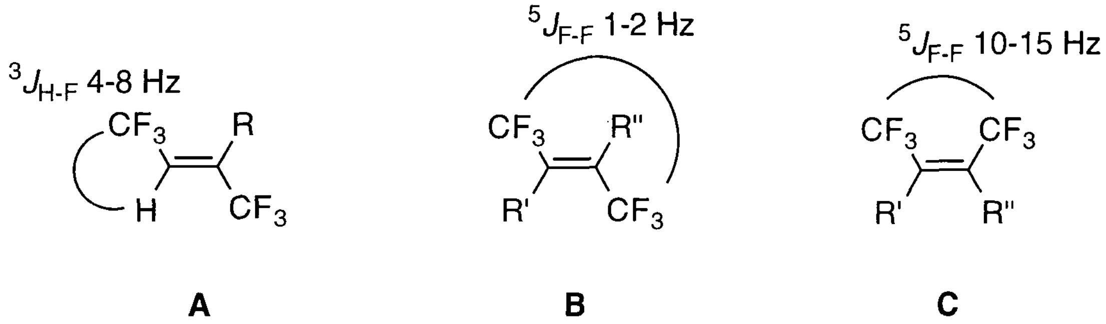
RSH	Yield (%)	δ_F (ppm)	vinylic proton δ_H (ppm)	Compound No.
	78	-58.4, -63.8	6.49	(**69**)
	90	-58.5, -64.0	6.63	(**70**)
	89	-58.6, -64.4	6.72	(**71**)
	86	-59.1, -64.7	6.57	(**72**)
	74c.*	-59.7, -65.5	-*	(**73**)
	NO REACTION	-	-	-

* (**73**) was not isolated therefore the yield given is a conversion based on GCLMS analysis, and no ^1H NMR was obtained.

A convenient route to fluorinated sulfides now exists that is particularly good for phenyl and benzyl thiols. Secondary thiols react less well owing to steric problems during nucleophilic attack, further proved by the complete lack of reaction with the tertiary thiol under these conditions.

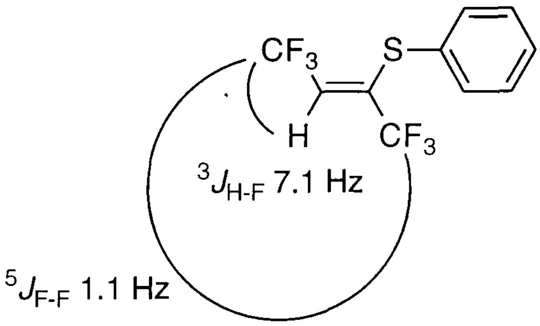
3.III. Elucidation of Stereochemistry

Coupling constants obtained from the ^{19}F and ^{1}H NMR spectra have been used to determine the relationship between the trifluoromethyl groups on the fluoroalkenes synthesised in this section. There has been a significant amount of data compiled in the literature as to the size of these coupling interactions[151] and *Scheme 3.27* illustrates the relevant general trends.



Scheme 3.27. Some general trends in coupling.

All of the fluoroalkenes synthesised in this section show a $^{3}J_{H-F}$ coupling of 7-8 Hz, consistent with published data for systems similar to **A**. However in the ^{19}F spectra there is no evidence of any larger coupling to indicate a *cis* relationship between the trifluoromethyl groups, as in **C**. Fluoroalkenes (**68**) and (**70**) show $^{5}J_{F-F}$ values of 1.1 and 1.5 respectively, *Scheme 3.28*, clearly indicating the *trans* relationship between the trifluoromethyl groups as for **B**. This much smaller coupling is not observed for the other fluoroalkenes in this section, however a coupling of 10-15 Hz (**C**) would be seen if *cis* trifluoromethyl groups were present in the systems. This evidence proves that the trifluoromethyl groups are *trans* to each other in this series of reactions.



Scheme 3.28. Coupling in fluoroalkene (**68**).

Chapter 4.

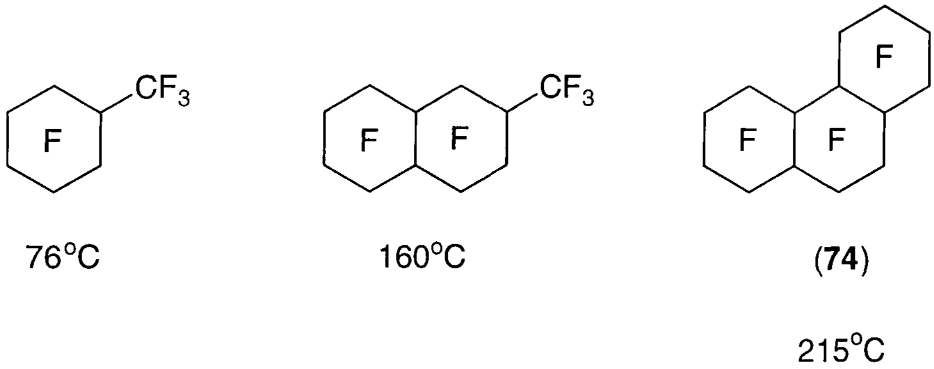
Perfluorocarbon Fluids as Solvent Replacements.

4.I. Introduction.

It is the aim of this chapter to discuss a new, essentially solvent-free methodology in which halogen exchange reactions may be carried out. Perfluorocarbon fluids (PFCs) are used to replace the normal hydrocarbon solvents in efficient halogen exchange reactions involving the replacement of chlorine by fluorine using metal fluorides.

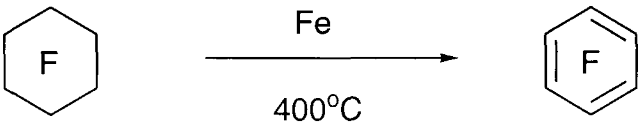
4.I.1. Perfluorocarbon Fluids.

Saturated perfluorocarbons (PFCs), *e.g.* perfluoroperhydrophenanthrene (**74**), are now industrially available over a wide range of boiling-points .



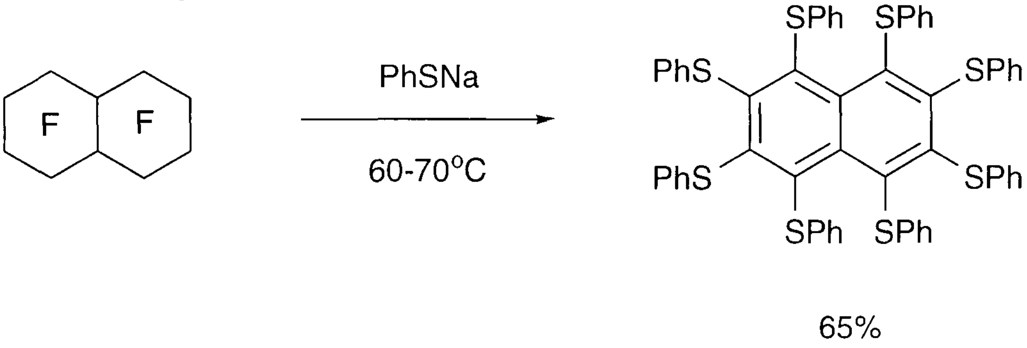
Scheme 4.1. Examples of various perfluorocarbons.

They are essentially chemically inert, with exceptions including defluorinations over hot metal[152]



Scheme 4.2. Defluorination using hot iron.[152]

and the interesting direct reaction with thiophenate.[153]



Scheme 4.3. Reaction of perfluorodecalin with sodium thiophenates.[153]

They are generally regarded as largely immiscible with most organic solvents, although published data is sparse. Low molecular-weight hydrocarbons and some halons have been shown to be soluble in PFCs, together with exceptional solubilities of gases such as oxygen, carbon dioxide and chlorine.[154]

So far, the potential general benefits of using perfluorocarbon fluids in chemistry do not appear to have been recognised. Hydrocarbon solvents could be significantly replaced with a suitable PFC, where the PFC serves to aid efficient mixing of reagents as a 'bulking agent'. Essentially the PFC holds everything in an emulsion, achieved by effective agitation, allowing the reagents to come into contact with each other and hence reaction to occur. Once reaction has taken place any products formed can be easily separated from the PFC which itself can be isolated simply by filtration and/or separation. No further purification would be required, owing to the immiscibility of PFC fluids.

Before discussing the work carried out for this chapter it is important to understand the halogen exchange reaction, and to this end a short review follows.

4.I.2. The Halogen Exchange Reaction.

The halogen exchange reaction, or 'Halex' reaction, is simply a chemical transformation that involves the exchange of one halogen species with another.

$$RX \quad + \quad X'^- \quad \rightleftharpoons \quad RX' \quad + \quad X^-$$

Scheme 4.4. The halogen exchange reaction.

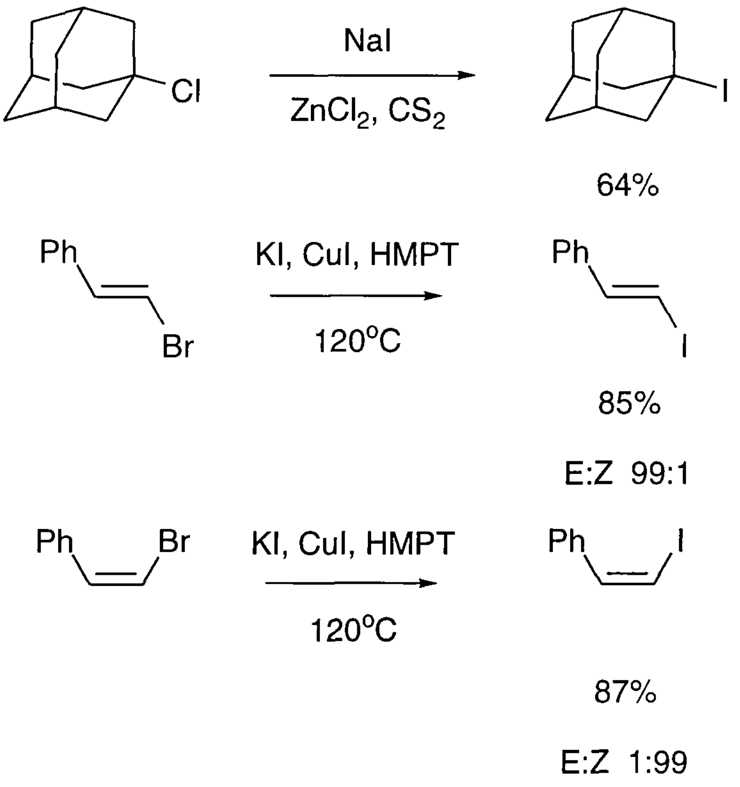
The 'halex' reaction is essentially an equilibrium process and X (and X'), in *Scheme 4.1*, can be fluorine, chlorine, bromine or iodine. The position of equilibrium is relatively easy to shift, for example by using excess halide, therefore it is possible to force the reaction to quantitative conversions. Fluorine and iodine are the most commonly inserted halogens, since there are other generally available methods of inserting chlorine and bromine.

4.I.2.a. Iodine.

Iodine usually replaces chlorine or bromine in a system, commonly using sodium iodide. Sodium iodide is soluble in acetone, unlike the bromide and chloride salts, which provides a convenient method of forcing the equilibrium by precipitation of the chloride or bromide salts when these reactions are carried out in acetone.

The reaction mechanism has been described as an S_N2 reaction, *i.e.* reaction occurs with inversion and proceeds more easily for primary halides than for secondary or tertiary. Reaction of sodium iodide is so effective that it has also found use as a test for primary chlorides and bromides, by the formation of a precipitate in acetone.

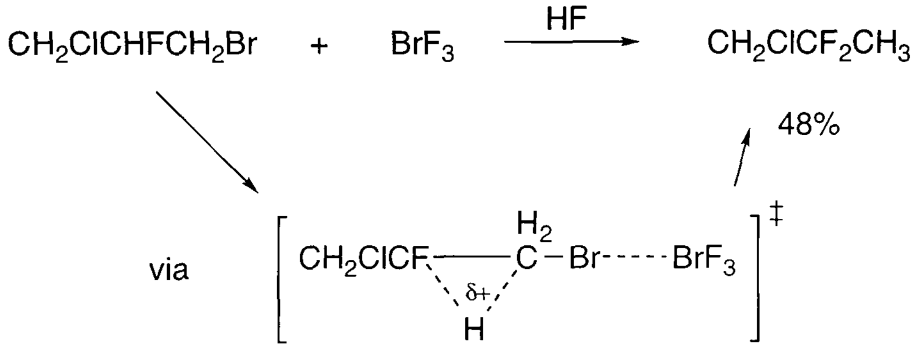
Further methods of iodination via the halogen exchange reaction are shown in *Scheme 4.5*.


Cl
NaI
ZnCl2, CS2
I
64%
Ph
Br
KI, CuI, HMPT
120°C
Ph
I
85%
E:Z 99:1
Ph
Br
KI, CuI, HMPT
120°C
Ph
I
87%
E:Z 1:99

Scheme 4.5. Examples of iodination via halogen exchange reactions of chloro[155] and bromo[156] derivatives.

4.1.2.b. Fluorine

Fluorine-containing compounds can be prepared in an analogous way to that of iodides. Alkyl halides are fluorinated using a variety of fluorinating agents, such as hydrogen fluoride,[157] potassium fluoride,[36] bromine trifluoride,[158] $Et_3N.2HF$[159] and antimony trifluoride with hydrogen fluoride.[160]


CH2ClCHFCH2Br
+
BrF3
HF
CH2ClCF2CH3
48%
via
CH2ClCF
H2
C
Br
BrF3
δ+
H
‡

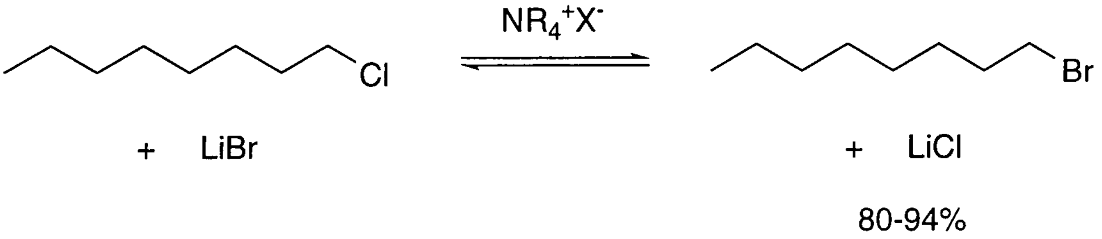
Scheme 4.6. Examples of fluorination using halogen exchange techniques.[158]

For fluoride halo-exchange reactions the equilibrium is shifted towards the fluorinated products, owing to the strong bonds formed by fluorine and consequently its poor ability as a leaving group.

4.I.2.c. Chlorine and Bromine.

Chlorine and bromine containing compounds are readily available from reactions between hydrocarbons and halogen gases.[161] However a number of techniques are available to replace halogens with chlorine or bromine. Primary alkyl bromides can be prepared by converting the equivalent chloride using ethyl bromide and a catalytic amount of sodium bromide.[162] Lithium bromide[163] or tetrabutylammonium bromide[164] will achieve the same transformation whilst gaseous hydrogen bromide[165] can brominate secondary and tertiary alkyl chlorides with anhydrous iron (III) bromide as a catalyst.

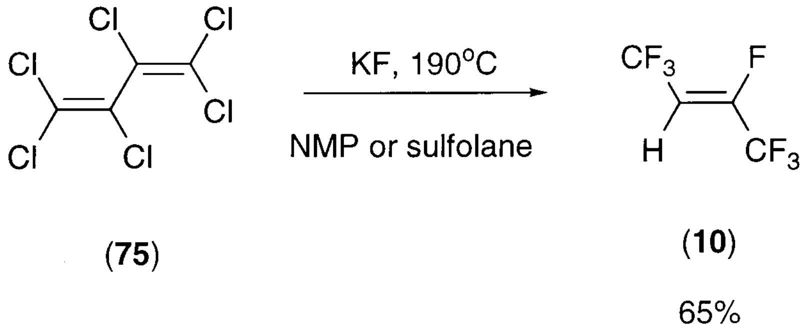
Alkyl bromides and chlorides can also be prepared from alkyl iodides[166] or alkyl fluorides[167] using either hydrogen bromide or hydrogen chloride.



Scheme 4.7. Lithium bromide bromination of 1-chlorooctane.[163]

A number of products are prepared by the Halex process that are operated on industrial scales. Solvent recovery causes serious waste disposal problems and, in the past, established procedures have proven hazardous.[168] Reduced solvent consumption, reduced explosion hazards and simple product isolation are just some of the potential benefits of using PFCs for these processes.

Within this group there is an ongoing interest[64, 65, 135, 169] in the chemistry of (*Z*)-2*H*-heptafluorobut-2-ene (**10**) and hexafluorobut-2-yne (**4**). Fluoroalkene (**10**) is synthesised using a procedure developed by Maynard[36] in 1963 and the overall reaction involves the replacement of chlorine on hexachlorobutadiene (**75**) with fluorine, *Scheme 4.8*, using potassium fluoride in an aprotic solvent.

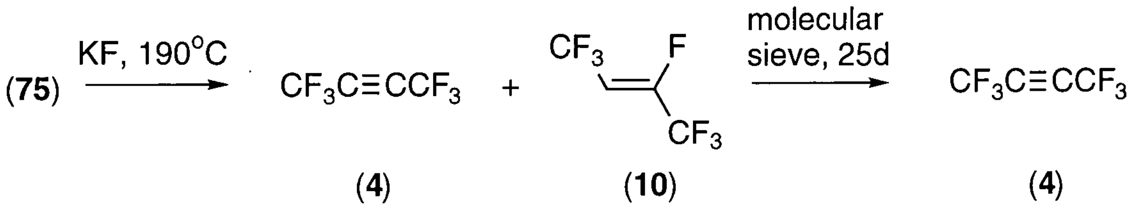


Scheme 4.8. Maynard's route to fluoroalkene (**10**).

It is Maynard's reaction that is used as the starting point for the investigation of the replacement of sulfolane by PFC.

4.II. Results and Discussion

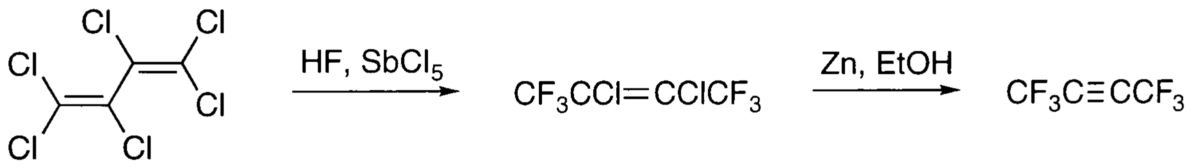
We have taken the halogen exchange system and investigated how far it is possible to replace the hydrocarbon with a perfluorocarbon fluid and retain high conversions and yields. Perfluoroperhydrophenanthrene (**74**) was chosen as the perfluorocarbon to replace sulfolane in these halogen exchange reactions, because owing to its high boiling point (bp 215 °C) there would be limited loss of PFC by evaporation at the reaction temperature 190 °C and no contribution to the pressure in sealed systems. Reaction proceeded efficiently when up to 75% v/v of the normal solvent required[36] was replaced by the equivalent volume of PFC (**74**). For example, in a typical synthesis of fluoroalkene (**10**) where 1500 cm^3 of sulfolane is used reaction could now be accomplished, giving comparable yields, when 375 cm^3 of sulfolane and 1125cm^3 of PFC (**74**) were used. No reaction occurred when 10%, or less, of the normal sulfolane charge was used. Nevertheless, when replacing up to 75% of the normal sulfolane charge, reactions were carried out efficiently using either a Carius tube, or on a larger scale using atmospheric pressure conditions. More remarkable was the observation that the volatile products obtained from fluorination of hexachlorobutadiene contained hexafluorobut-2-yne (**4**) and fluoroalkene (**10**), *Scheme 4.9.*, in a 3:1 ratio.



Scheme 4.9. New convenient synthesis of hexafluorobut-2-yne (**4**).

Hexafluorobut-2-yne (**4**)[9] and (*Z*)-2*H*-heptafluorobut-2-ene (**10**)[36] are both known compounds and, initially, were identified by their characteristic ^{19}F NMR signals. A sharp singlet at -55,6 ppm indicated the presence of the butyne (**4**) and resonances at -62.5, -77.0 and -119.7 ppm (3:3:1) revealed the butene (**10**). After isolation analytical data acquired from the individual fluorinated gases were in agreement with literature data.

Formation of hexafluorobut-2-yne (**4**) was unexpected and coupled with the recent finding that dehydrofluorination of fluoroalkene (**10**) occurs on standing over molecular sieve[65] now provides a simple laboratory synthesis of hexafluorobut-2-yne (**4**). That is, the (**10**) present in the product mixture, was converted quantitatively to butyne (**4**) when the mixture of (**4**) and (**10**) was allowed to stand as a fluid layer, in a sealed system, over 4 Å molecular sieve for 25 days. There have been no previous reports of the direct synthesis of hexafluorobut-2-yne from hexachlorobutadiene (**75**) and the alternative synthesis of (**4**) from (**75**) requires two steps and the use of antimony fluorides and/or hydrogen fluoride.[9]

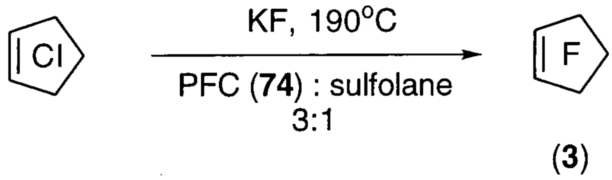


(75) **(76)** **(4)**

Scheme 4.10. The synthesis of hexafluorobut-2-yne using antimony fluorides.[9]

The unique formation of (**4**) can be reasonably explained by the rapid migration of the butyne into the perfluorocarbon layer, where it is protected from further fluoride attack and access to protons, which otherwise would promote the conversion of (**4**) to (**10**).

Along with the synthesis of fluoroalkene (**10**), Maynard also described a convenient laboratory synthesis of octafluorocyclopentene[36] (**3**) from octachlorocyclopentene and potassium fluoride. It is now possible to use only 25% v/v of the normal charge of sulfolane with replacement PFC and still get high conversions to (**3**) using either a Carius tube or atmospheric pressure.



(3)

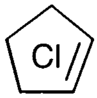
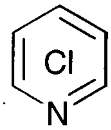
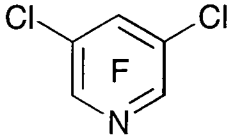
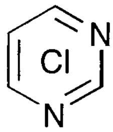
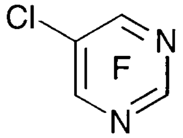
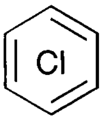
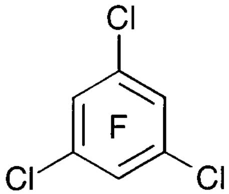
89%

Scheme 4.11. The synthesis of octafluorocyclopentene (**3**).

Perfluorocyclopentene (**3**) is a known compound and was identified by comparing its spectra to literature values,[15] particularly the ^{19}F NMR spectrum. This gave three complex multiplets at -117.6, -129.4 and -148.7 ppm (2:1:1) indicating two CF_2 environments and one vinylic fluorine, in the correct ratio. ^{13}C NMR data were also consistent with (**3**), however they were complicated by second order coupling.

Similarly chlorofluoro-pyridines and -pyrimidines are commercial products and we find that the conditions described above can be equally applied to these systems and also to the synthesis of chlorofluorobenzene derivatives; these results are summarised in *Table 4.1*.

Table 4.1. Fluorination of chlorocarbons using KF and 25% v/v of sulfolane.

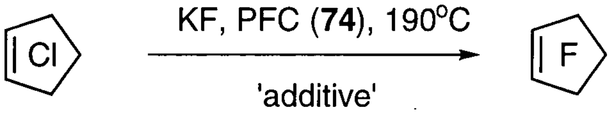
Chlorocarbon	% sulfolane[a]	CT[b]/AP[c]	Products	Yield (%)
75	25	AP	**4**	56[d]
	10	AP	No reaction	-
	KF coated[e]	AP	No reaction	-
	25	CT	**10**	75
	25	AP	**3**	58
	25	CT	**3**	89
	0	CT	No reaction	-
	25	AP		93
	25	CT	"	54
	0	CT	No reaction	-
	25	CT		65
	25	CT		83

[a]Volume % [b]Carius Tube [c]Atmospheric Pressure [d]% After leaving over molecular sieve for 25 days[65] [e]The potassium fluoride used had been soaked in sulfolane and the excess solvent decanted off.

3,5-Dichloroperfluoropyridine,[170] 5-chloroperfluoropyrimidine[171] and 1,3,5-trichloro-2,4,6-trifluorobenzene[36] are all known compounds and were identified by comparison of their spectra with those found in the literature.

Following the successful replacement of up to 75% v/v of the normal charge of sulfolane, the next objective was to reduce the volume of hydrocarbon used further in order to obtain essentially a 'solventless' system. However, it has already been seen that replacing more than 75% of the sulfolane leads to reduced reactivity, and at 90% replacement no reaction occurs. Therefore it was decided to attempt Halex reactions using a series of 'additives' added to the PFC, with complete replacement of the hydrocarbon solvent. It was hoped that the 'additive' would increase the availability of fluoride by co-ordinating to the potassium, or allowing the potassium fluoride to be partially soluble in the PFC. Also ESCA (Electron Spectroscopy for Chemical Analysis) experiments[172] have shown that the surface of analytically pure potassium and cesium fluoride is covered with the equivalent chloride. This implies that all of the chloride impurities in the metal fluoride migrate to the surface. Using 'additives' in the PFC may also aid in the cleaning of the surface, again increasing the availability of fluoride.

The additives examined were water, tetraglyme, tetrabutylammonium bromide, and 18-crown-6 (**77**). Only the latter led to efficient fluorination giving a quantitative yield of cycloalkene (**3**), although tetrabutylammonium bromide showed a significant effect.



'additive' (%)

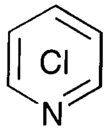
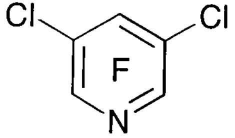
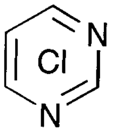
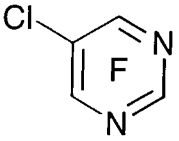
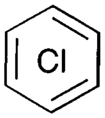
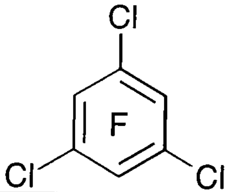
H_2O (0)
tetraglyme (0)
$Bu_4N^+Br^-$ (36)
18-crown-6 (100)

Scheme 4.12. 'Additives' used in the fluorination of octachlorocyclopentene in the absence of hydrocarbon solvent.

Water or tetraglyme did not facilitate fluorination of octachlorocyclopentene. However, in contrast, 18-crown-6 (**77**) was found to be effective down to levels as low as 1% molar ratio, in relation to the chlorinated starting material, thus demonstrating the concept of potentially 'solventless' systems. At these concentrations, however, reaction proceeds slowly and therefore it was necessary to use 10% molar equivalents to effect shorter reaction times in further investigations.

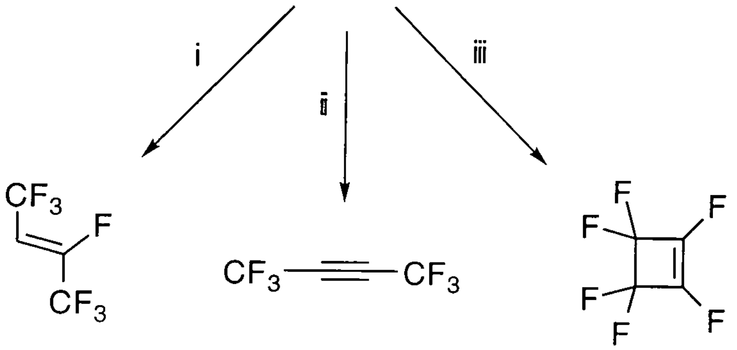
An important factor for this technique to gain general application was the need for the PFC to be recovered unaltered and quantitatively after the reaction. This can be accomplished simply by filtration of the solid material in the perfluorocyclopentene (**3**) synthesis and the PFC requires no further purification before reuse. At this stage the 18-crown-6 remains with the waste inorganic salts but is effectively removed by extraction with acetone. A second cycle reaction was performed using the recovered PFC and 18-crown-6 without further purification with fresh potassium fluoride and octachlorocyclopentene. However, this second cycle reaction gave a lower yield indicating that some decomposition of the crown ether may be occurring during the reaction or that further purification is required to maintain high efficiency in re-use. Examples of the application of this system to the synthesis of fluorinated aromatic compounds are shown in *Table 4.2*.

Table 4.2. Fluorination of aromatics using KF, perfluorocarbon and 18-crown-6 (**77**)

Chlorocarbon	Products	Yield (%)
		84
		91
		60

Returning to the reactions of hexachlorobutadiene, we found that the products obtained from the system containing 18-crown-6 depend on the molar ratio of crown ether used. When a molar ratio of 50% of 18-crown-6 with hexachlorobutadiene was used, the sole product of the reaction was 2*H*-heptafluorobut-2-ene (**10**); a ratio of 10% (**77**) gave hexafluorobut-2-yne (**4**) as the major product (72:10:18; **4**:**10**:**2**), while a 1% ratio and using a sealed system unexpectedly gave hexafluorocyclobutene (**2**) as the product (68%), with traces of (**4**) and (**10**). This leads to a useful route to three interesting compounds from the same starting materials.

(75)



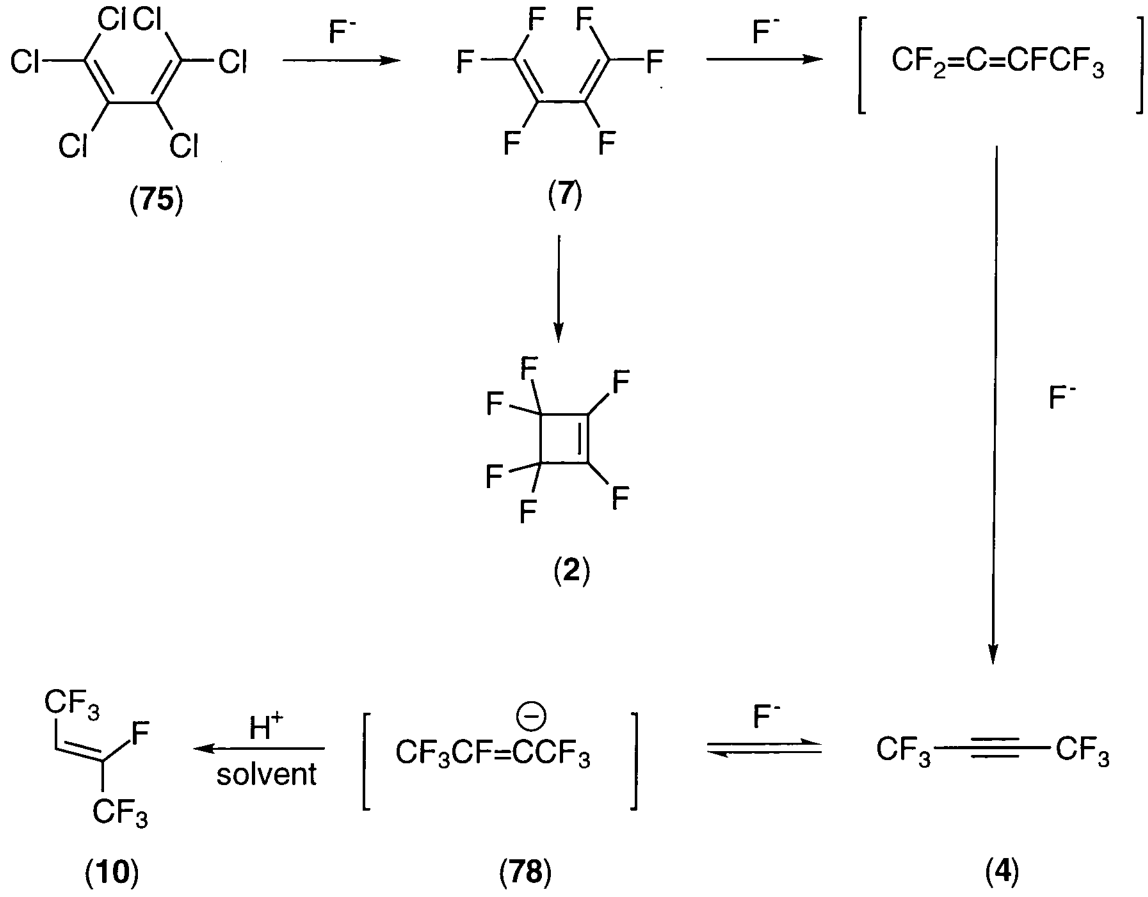
(10) **(4)** **(2)**

18-Crown-6, PFC (**74**), 190°C
i, 50% molar ratio
ii, 10% molar ratio
iii, 1% molar ratio (sealed system)

Scheme 4.13. Three products from hexachlorobutadiene (**75**).

Hexafluorocyclobutene (**2**) is also a known compound and was identified by comparison with published data.[173]

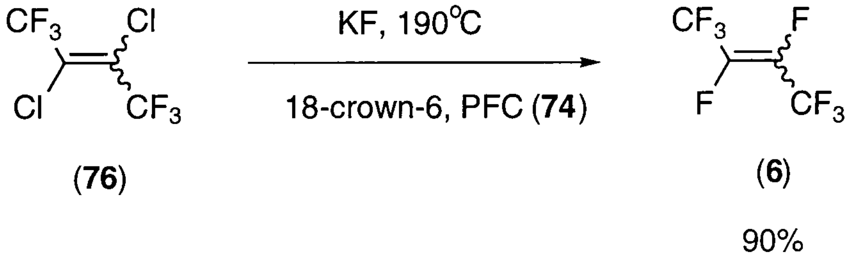
These surprising findings now cast some light onto the previously unestablished mechanism of these processes. If we assume that the availability of fluoride ion in the system is directly related to the concentration of polyether (**77**) used we can conclude that there is only one feasible mechanism that accounts for these observations.



Scheme 4.14. Reaction sequence for the synthesis of hexafluorocyclobutene (**2**), hexafluorobut-2-yne (**4**) and (*Z*)-2*H*-heptafluorobut-2-ene (**10**).

Initial vinylic displacement of chloride by fluoride occurs giving hexafluorobutadiene (**7**) which, at low concentrations of fluoride ion, will be preferentially extracted into the fluorocarbon phase and then undergo the well established electrocyclisation[174] to (**2**). This will also be favoured by the increased pressure associated with the use of a Carius tube. However, in the presence of higher ratios of fluoride, (**7**) is quickly converted to hexafluorobut-2-yne (**4**), again by established processes.[175] This will then be extracted into the perfluorocarbon layer and consequently protected from further reaction. However, at high concentrations of fluoride further reaction *i.e.* (**4**) to (**78**) to (**10**), competes.

The conclusion that the process begins by vinylic displacement of chlorine by fluorine to give (**7**), rather than by attack accompanied by allylic displacement, is further confirmed by the fact that conversion of (**76**) to octafluorobut-2-ene (**6**), is performed with very high efficiency and this perfluoroalkene was previously relatively inaccessible.[176]



Scheme 4.15. Formation of octafluorobut-2-ene (**6**).

Octafluorobut-2-ene (**6**) is a known compound and was identified by comparison of its spectra with literature data.[176] ^{19}F NMR data could be integrated and assigned to show that a 3:1 ratio of the *E* and *Z* isomers, respectively, were produced.

There remains the question of whether the potassium fluoride is actually taken into the perfluorocarbon layer by the 18-crown-6 (**77**), or whether the latter remains solely in suspension. Potassium permanganate and potassium picrate have been used separately with 18-crown-6 (**77**) and the perfluorocarbon (**74**) and in neither case did we have clear evidence of colour generated in the perfluorocarbon layer indicating solubility and it seems unlikely that fluoride salts would be more soluble. On this basis, therefore, we favour the conclusion that the 18-crown-6/potassium fluoride complex is essentially in suspension in the perfluorinated medium, as was described above for sulfolane but that the proportions of (**77**) required for activating the metal fluoride are *substantially* less than for sulfolane.

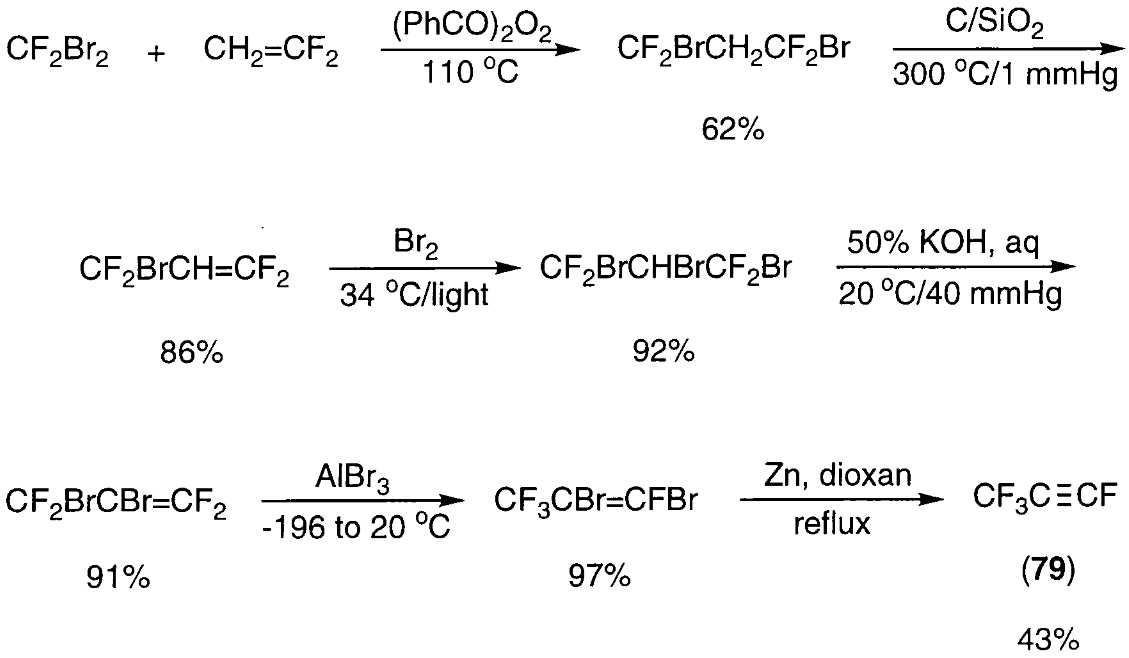
Chapter 5.

Potential Routes to Tetrafluoropropyne.

5.I. Introduction.

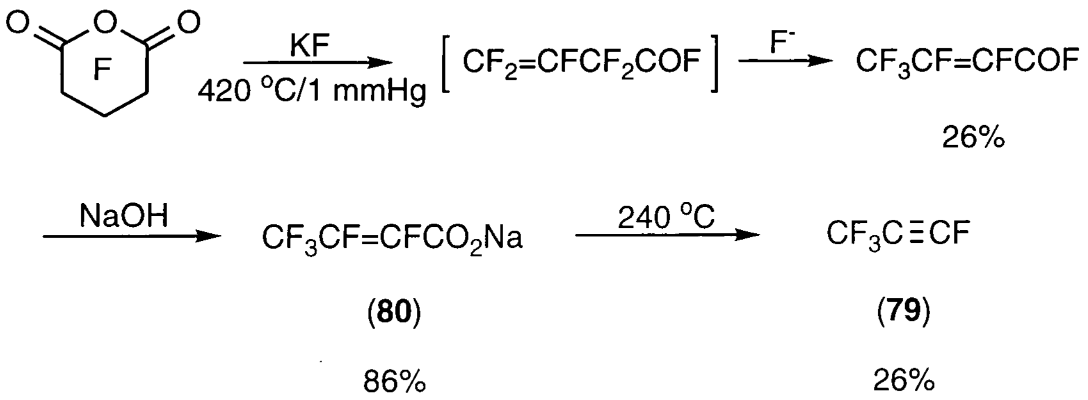
To date, syntheses of the terminal perfluoroalkyne tetrafluoropropyne (**79**) are long, multi-stepped and poor yielding reactions,[177, 178] and this has seriously hindered the studies on the chemistry of this interesting compound.

Tetrafluoropropyne (**79**) was the first 1-perfluoroalkyne to be isolated and it is this work, carried out in 1968 by Banks and Haszeldine,[177] that remains the best method of synthesis today. Their method ends in the debromination of 1,2-dibromotetrafluoropropene, the result of a complicated six step synthesis, *Scheme 5.1*, giving an overall yield of only 19%.


CF_2Br_2 + CH_2=CF_2
$(PhCO)_2O_2$
110 °C
$CF_2BrCH_2CF_2Br$
62%
C/SiO_2
300 °C/1 mmHg
CF_2BrCH=CF_2
86%
Br_2
34 °C/light
$CF_2BrCHBrCF_2Br$
92%
50% KOH, aq
20 °C/40 mmHg
CF_2BrCBr=CF_2
91%
$AlBr_3$
-196 to 20 °C
CF_3CBr=CFBr
97%
Zn, dioxan
reflux
$CF_3C{\equiv}CF$
(79)
43%

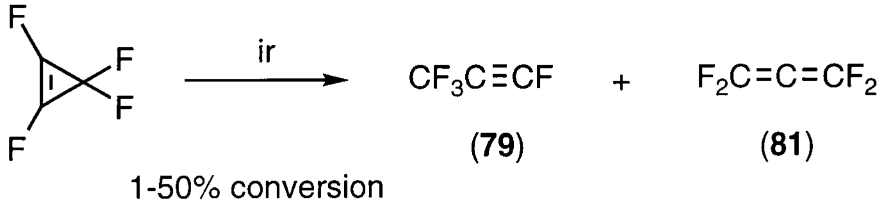
Scheme 5.1. Banks and Haszeldine's synthesis of tetrafluoropropyne (**79**).[177]

The only other usable route to this fluorinated gas, published in the same paper,[177] involves the pyrolysis of sodium pentafluoro-2-butenoate (**80**), *Scheme 5.2*, resulting in low yields, although in fewer steps.



Scheme 5.2. Pyrolysis of sodium pentafluoro-2-butenoate (**80**).[177]

Other examples of the synthesis of tetrafluoropropyne (**79**) are limited and of very poor yields.[178] However one reaction of some interest has been carried out by the group of Burton.[179] Perfluorocyclopropene, synthesised by the route developed by Krespan,[180] gives moderate conversions to tetrafluoropropyne (**79**) and tetrafluoroallene (**81**) when subjected to pulses of infra-red radiation, although the two gases were never separated.

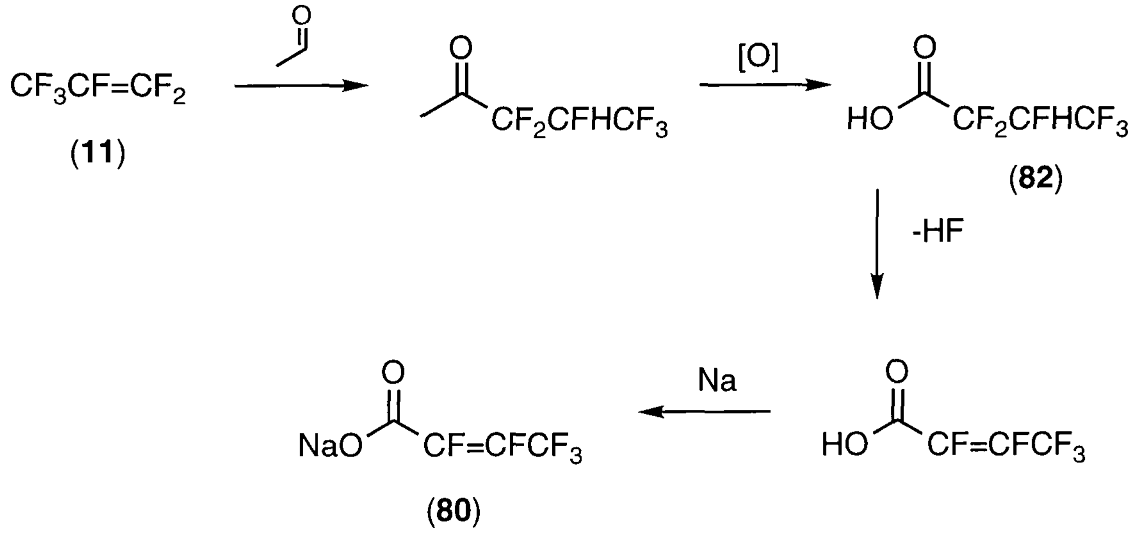


Scheme 5.3. Rearrangement of perfluorocyclopropene.

Obviously, new convenient, higher yielding routes to tetrafluoropropyne (**79**) are required in order for a more thorough investigation of its chemistry. Therefore it was the aim of this section to provide a new practical synthesis of tetrafluoropropyne (**79**).

5.II. Results and Discussion

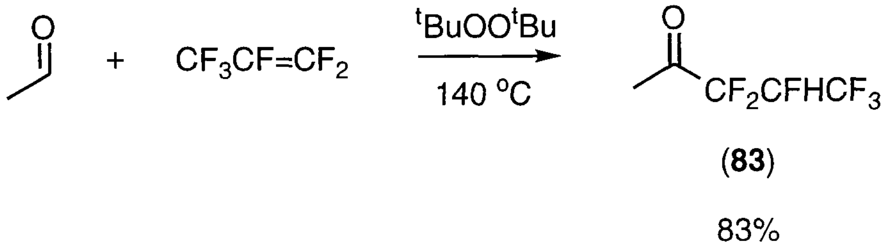
5.II. Hexafluoropropene (11) adducts - Banks and Haszeldine's second route to tetrafluoropropyne (**79**),[177] *Scheme 5.2*, is marred by the low yielding route they employ to produce sodium pentafluoro-2-butenoate (**80**). If an alternative method of synthesising (**80**) could be found then this could become a convenient route to (**79**), and we believed that this could be achieved using hexafluoropropene (**11**) as the starting point for a series of transformations, *Scheme 5.4*.



Scheme 5.4. Proposed route to sodium pentafluoro-2-butenoate (**80**).

Radical additions of hexafluoropropene (**11**) have been the subject of much research recently, especially from within this laboratory.[89, 181, 182] The primary aim of this section was to produce 2,2,3,4,4,4-hexafluorobutanoic acid (**82**) from hexafluoropropene (**11**) in order to effect dehydrofluorination and obtain acid (**80a**).

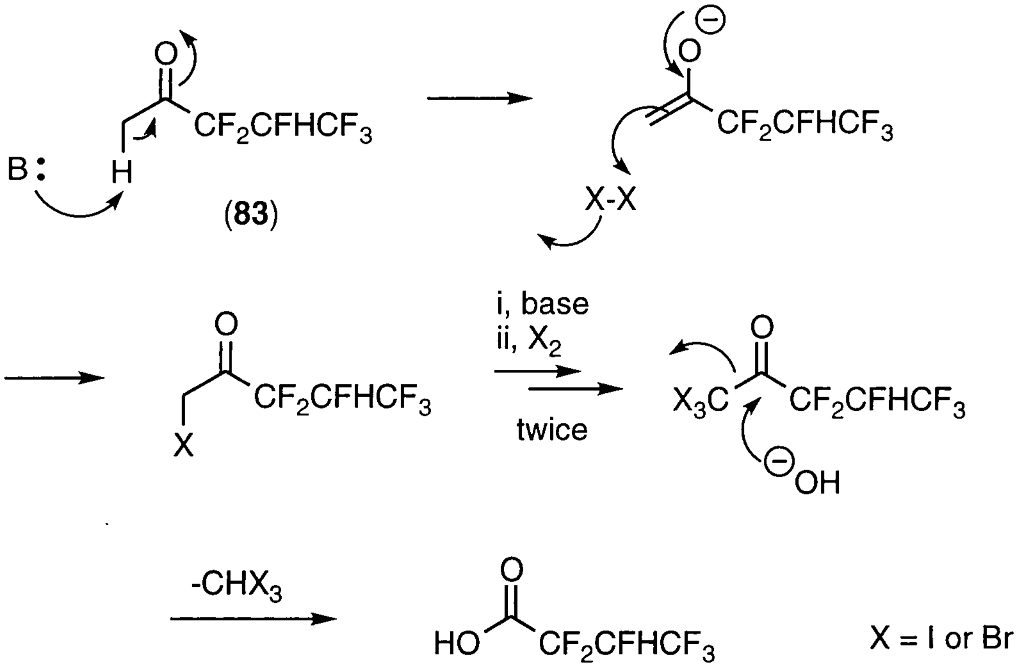
5.II.1. Acetaldehyde - To accomplish the first step outlined in *Scheme 5.4*, peroxide initiated radical addition of hexafluoropropene (**11**) to acetaldehyde was carried out at 140 °C in a sealable metal tube, following procedures developed by LaZerte,[90] and Chambers.[88, 183]



Scheme 5.5. Formation of 3,3,4,5,5,5-hexafluoropentan-2-one (**83**).

Simply washing the resultant material with water removed the excess acetaldehyde used and distillation of the remaining organic layer gave a colourless oil that was identified as 3,3,4,5,5,5-hexafluoropentan-2-one (**83**), a known compound, by comparison of spectra to literature data.[184]

Oxidation of 3,3,4,5,5,5-Hexafluoropentan-2-one (83) - Haloform oxidation of methyl ketones is a commonly used general synthetic transformation for the formation of carboxylic acids. Base induced formation of the enolate allows the addition of halogens to the methyl group, this is repeated until the trihalide is produced which is then eliminated by hydroxide attack to yield the acid, *Scheme 5.6*.



(82)

Scheme 5.6. The haloform mechanism for the formation of 2,2,3,4,4,4-hexafluorobutanoic acid (**82**).

Therefore, when ketone (**83**) was added dropwise to a vigorously stirred suspension of iodine, potassium iodide and sodium hydrogencarbonate in water quantitative conversions of (**83**) to a single compound were seen by ^{19}F NMR analysis.

However problems were encountered on isolation. Sodium metabisulfite was added to the reaction mixture after full conversion, in order to remove the excess iodine, increasing the amount of inorganic material in the already saturated water. It was thought that acid (**82**) could precipitate so filtration was avoided, instead water was added to the slurry to form an aqueous solution. Concentrated hydrochloric acid was then added to the aqueous solution until pH 1 was reached and continuous extraction using dichloromethane was carried out. Unfortunately, continuous extraction only worked efficiently for very small scale reactions (*ca.* 1-2 g); when the reaction was scaled up (*ca.* 10-20 g) the large amounts of aqueous material made the extraction process difficult, even over 7 nights.

A pure sample of (**82**) was isolated, following the above procedure, and is a known compound, identified by comparing its spectra with literature data.[90]

Although 2,2,3,4,4,4-hexafluorobutanoic acid (**82**) had successfully been synthesised, the small amounts of pure material obtained meant that not enough was available to proceed. Therefore an alternative route to (**82**) was explored; oxidation of 2,2,3,4,4,4-hexafluorobutan-1-ol (**17**), the radically formed adduct of methanol and hexafluoropropene.

5.II.2. Methanol - 2,2,3,4,4,4-Hexafluorobutan-1-ol (**17**) was prepared in excellent yields by the peroxide initiated reaction between hexafluoropropene and methanol,[88, 183] carried out at 140 °C in a sealable metal tube.

$$\mathrm{MeOH} \quad + \quad \mathrm{CF_3CF{=}CF_2} \xrightarrow[140\ ^{\circ}\mathrm{C}]{^{t}\mathrm{BuOO}^{t}\mathrm{Bu}} \mathrm{HOCH_2CF_2CFHCF_3}$$

(**17**)

80%

Scheme 5.7. Formation of 2,2,3,4,4,4-hexafluorobutan-1-ol (**17**).

2,2,3,4,4,4-Hexafluorobutan-1-ol (**17**) is a known compound[90] and was identified by comparison of spectra to literature data.

Oxidation of 2,2,3,4,4,4-Hexafluorobutan-1-ol (17) - When 2,2,3,4,4,4-hexafluorobutan-1-ol (**17**) was added to excess potassium dichromate and concentrated sulfuric acid excellent yields of 2,2,3,4,4,4-hexafluorobutanoic acid (**17**) were obtained, as reported by LaZerte.[90]

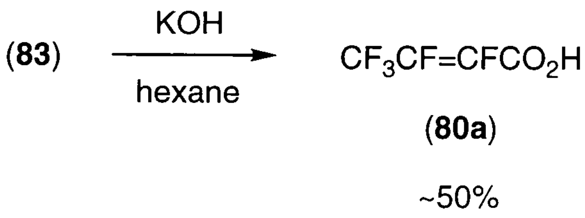
$$\mathrm{HOCH_2CF_2CFHCF_3} \xrightarrow[\substack{\mathrm{H_2SO_4} \\ \mathrm{H_2O}}]{\mathrm{K_2Cr_2O_7}} (\mathbf{82})$$

87%

Scheme 5.8. Formation of 2,2,3,4,4,4-hexafluorobutanoic acid (**82**).

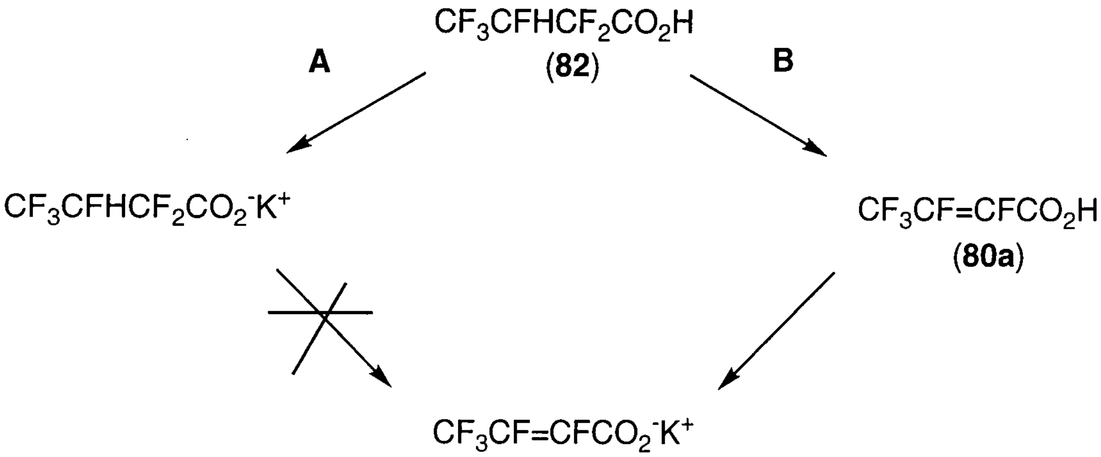
2,2,3,4,4,4-Hexafluorobutanoic acid (**82**) was identified by comparison to the sample produced from 3,3,4,5,5,5-hexafluoropentan-2-one (**83**), after distillation from concentrated sulfuric acid.

Dehydrofluorination of 2,2,3,4,4,4-Hexafluorobutanoic acid (82) - It was now possible, having enough material, to attempt the dehydrofluorination of (**82**), the third step in *Scheme 5.4*. When acid (**82**) was added dropwise to a stirred suspension of powdered potassium hydroxide in hexane at room temperature approximately a 50% conversion of (**82**) was observed, to the *E* and *Z* isomers of pentafluoro-2-butenoic acid (**80a**) (~1:1). To work up this reaction, water was added to the suspension to dissolve the inorganic salts and produce a biphasic mixture. The layers were separated and the hexane layer shown to contain no fluorinated material by ^{19}F NMR. Following this, the remaining aqueous layer was acidified to pH 1 with concentrated sulfuric acid and extracted with dichloromethane. Removal of the solvent by rotary evaporation left a mixture of three compounds; (**82**) and *E* and *Z* isomers of (**80a**), although a poor mass recovery resulted. There was not enough material to distill the components, and both (**82**) and (**80a**) would not pass through the preparative scale GC column intact, so isolation of the unsaturated acid could not be carried out.


(83)
KOH
hexane
$CF_3CF=CFCO_2H$
(80a)
~50%

Scheme 5.9. Formation of pentafluoro-2-butenoic acid (**80a**).

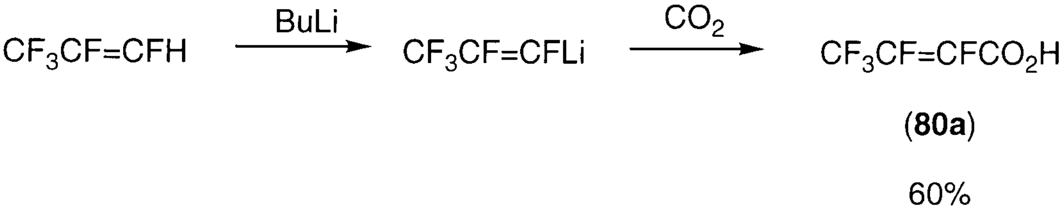
In order to increase the conversion in an attempt to facilitate isolation, the reaction was repeated with different excesses of potassium hydroxide, volumes of hexane and addition rates. However no increase in conversion over the initial conditions could be achieved. This was believed to be caused by 2,2,3,4,4,4-hexafluorobutanoic acid (**82**) undergoing two processes, as outlined in *Scheme 5.10.*


$CF_3CFHCF_2CO_2H$
(82)
A
B
$CF_3CFHCF_2CO_2^-K^+$
$CF_3CF=CFCO_2H$
(80a)
$CF_3CF=CFCO_2^-K^+$

Scheme 5.10. Addition of potassium hydroxide to 2,2,3,4,4,4-hexafluorobutanoic acid (**82**).

In the first process, **A**, the acid forms the potassium salt before dehydrofluorination occurs. Formation of the salt allows the acid to precipitate out of solution and, as a solid, take no further part in the reaction. Secondly, process **B** allows dehydrofluorination to occur before salt formation and it is thus a combination of both **A** and **B** that results in an incomplete conversion.

Pentafluoro-2-butenoic acid (**80a**) is a known compound,[185, 186] made by the addition of carbon dioxide to the lithium salt of 1*H*-pentafluoropropene, *Scheme 5.11.* Despite ineffective isolation due to low conversions, it was possible to obtain a ^{19}F NMR spectrum and thus identify (**80a**).


$CF_3CF=CFH$
BuLi
$CF_3CF=CFLi$
CO_2
$CF_3CF=CFCO_2H$
(80a)
60%

Scheme 5.11. Literature route to pentafluoro-2-butenoic acid (**80a**).[186]

Formation of Esters of 2,2,3,4,4,4-Hexafluorobutanoic acid (82)

Methyl ester - Good yields of methyl 2,2,3,4,4,4-hexafluorobutanoate (**84**) were obtained when (**82**) was refluxed for 15 hours in methanol. Addition of water and distillation led to a lower layer of ester which could then be separated and distilled to give pure samples of the methyl ester (**84**).

$$CF_3CFHCF_2CO_2H \xrightarrow[\text{reflux}]{\text{MeOH}} CF_3CFHCF_2CO_2Me$$

Scheme 5.12. Formation of methyl 2,2,3,4,4,4-hexafluorobutanoate (**84**).

Methyl 2,2,3,4,4,4-hexafluorobutanoate (**84**)[88] is a known compound and was identified by comparison of spectra to literature data.

Ethyl ester - Similarly, the ethyl ether was formed in good yields when (**82**) was refluxed for 15 hours in ethanol, and it was also isolated by the formation of a lower layer by the addition of water and distillation of this lower layer.

Ethyl 2,2,3,4,4,4-hexafluorobutanoate (**85**)[187] is a known compound and was identified by comparison of spectra to literature data.

Dehydrofluorination of Methyl and Ethyl 2,2,3,4,4,4-hexafluorobutanoates (84) and (85) - In an attempt to produce the dehydrofluorinated ester, (**84**) was added dropwise to a stirred slurry of sodium methoxide in hexane at room temperature. However, the results of this reaction were unclear. After filtering off the solid material, ^{19}F NMR analysis of the hexane solution showed only one weak signal indicating a trifluoromethyl group, suggesting that (**84**) had dehydrofluorinated but then undergone further reaction to eliminate both vinylic fluorines. Analysis of the removed solid material by ^{19}F NMR, showed only one strong signal, consistent with fluoride ion, further indicating that the reaction was proceeding beyond the required limit.

$$CF_3CFHCF_2CO_2Me \xrightarrow{MeO^-} CF_3CF{=}CFCO_2Me \xrightarrow{MeO^-}$$

Scheme 5.13.

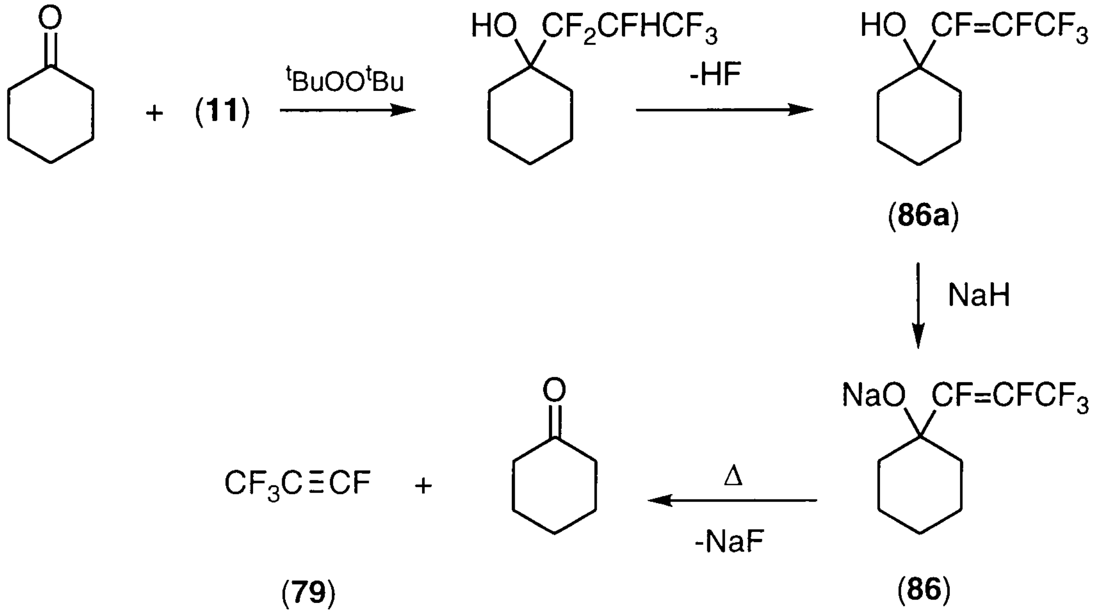
Repeating the reaction at lower temperatures, 0 and -10 °C, produced the same results and isolation of the unidentified compound could not be carried out owing to the small amounts produced.

Using the ethyl ester (**85**) dehydrofluorination was attempted with sodium ethoxide. At room temperature, and even at 60 °C, no reaction was observed, suggesting that the ethoxide is not a strong enough base to effect dehydrofluorination in this system.

5.II.3. Pyrolysis - In the absence of a pure sample of acid (**80a**) the mixture of (**82**) and (**80a**), obtained earlier, was used in a series of pyrolysis experiments to assess the potential of acid (**80a**) pyrolysing to give tetrafluoropropyne. A small amount of the sodium salt of the mixture was heated under reduced pressure in a Wood's Metal bath and any volatile material produced was trapped in two liquid air cooled traps.

Initially 240 °C was used, as reported in the experiments carried out by Banks and Haszeldine,[177] however no volatile material was found in the traps and an intractable material was left in the round bottomed flask. Further reactions carried out at 280 °C produced the same results, however at temperatures below 200 °C there was no reaction. It was at this stage that this proposed route to (**79**) was abandoned and other potential routes investigated.

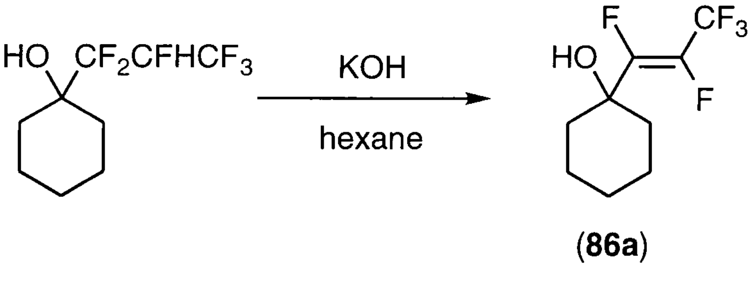
5.II.4. Cyclohexanone (in collaboration with C. Farren) - Another potential route to the fluorinated alkyne (**79**) is outlined in *Scheme 5.13.*



Scheme 5.14. Proposed route to tetrafluoropropyne (**79**).

In this case, pyrolysis of the dehydrofluorinated adduct (**86**) would lead to the elimination of cyclohexanone and the desired fluorinated gas (**79**). So our next aim was to synthesise 1-(pentafluoroprop-1-enyl)-cyclohexanol (**86a**), the dehydrofluorinated hexafluoropropene adduct of cyclohexanone.

A sample of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexanol, prepared by C. Farren, was dehydrofluorinated by adding it dropwise to a stirred suspension of powdered potassium hydroxide in hexane. Reaction was monitored by ^{19}F NMR analysis, and when complete conversion of the adduct was observed the reaction was worked up to give a colourless oil. Identification of this oil by NMR and GLCMS techniques showed it to be a new compound (**86a**).



Scheme 5.15. Formation of 1-(pentafluoroprop-1-enyl)-cyclohexanol (**86a**).

Only one isomer of fluoroalkene (**86a**) was observed and this proved to be the *E* isomer by analysis of the ^{19}F NMR data. For $^3J_{F\text{-}F}$ coupling in alkenes *trans* coupling is always larger than *cis*, generally *trans* values are between 130-150 Hz and *cis* are around 20-40 Hz.[151] Doublets found in the ^{19}F NMR spectrum of fluoroalkene (**86a**) at -149.4 and -170.1 ppm were split by approximately 135 Hz, clearly indicating a trans relationship between the vinylic fluorine atoms. Furthermore, the resonance peak at -149.4 ppm was split into quartet ($J_{F\text{-}F}$ 23 Hz), characteristic of a $^4J_{F\text{-}F}$ (*cis*) relationship between a trifluoromethyl group and a fluorine across a double bond, and *not* a $^3J_{F\text{-}F}$ (CF-CF_3) which would be only about 10 Hz.[151]

Pyrolysis - Pyrolysis of the sodium salt of (**86a**) was performed at 260 and 300 °C under reduced pressure in a Wood's Metal bath with liquid air cooled traps attached: in neither case was tetrafluoropropyne observed. However, GLCMS analysis of the small amount of volatile material collected in the traps indicated the presence of some cyclohexanone, suggesting that the pyrolysis may be working in part. Analysis of the solid matter remaining in the pyrolysis flask showed some starting material, cyclohexanone and an insoluble, charcoal-like solid.

Due to time constraints, further investigation of this route was not carried out, although there is the possibility that by varying the leaving group on the pentafluoroprop-1-enyl system or varying the conditions may lead to a viable synthesis of tetrafluoropropyne (**79**).

5.III. Other Attempted Routes.

5.III.1. 2*H*-Pentafluoropropene - During Roche's work investigating novel syntheses of hexafluorobut-2-yne (**4**) from (*Z*)-2*H*-heptafluorobut-2-ene (**10**), he found that tertiarybutyllithium would dehydrofluorinate (**10**) to give low conversions to (**4**). Following this idea it was decided to use tertiarybutyllithium in analogous reactions with

2*H*-pentafluoropropene (**5**), dehydrofluorination of which could lead to a one-step synthesis of (**79**).

Dehydrofluoroination of (**5**) was investigated using solutions of tertiary butyl lithium at various temperatures in sealable rotaflows, the results of which can be seen in *Table 5.1.*

Table 5.1. Results of dehydrofluorination of 2*H*-pentafluoropropene (**5**).

Ratio (**5**)/BuLi	temperature (°C)	time (hours)	conversion to tetrafluoropropyne (**79**) (%)	conversion to tetrafluoroallene (**81**) (%)
0.5	-78	2	0	0
1	-35	1	0	16.5
1	-78	15	0	0
1.2	RT	1	0	16.6
2	-55 to RT	15	<0.5	16.2

$$CF_3CH=CF_2 \xrightarrow{^tBuLi} CF_2=C=CF_2$$

(5) **(81)**

Scheme 5.16. Formation of tetrafluoroallene (**81**).

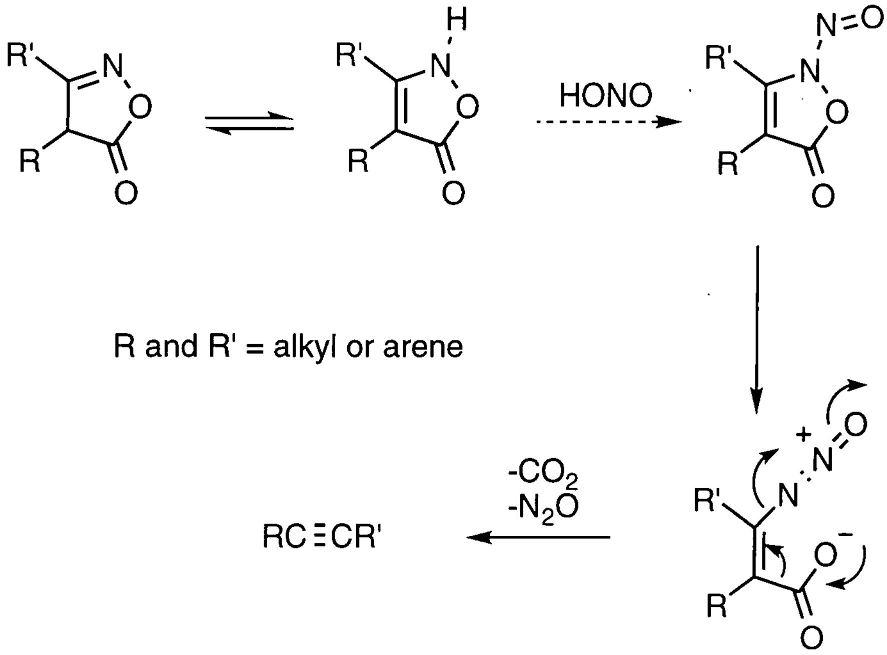
Both tetrafluoropropyne (**79**) and tetrafluoroallene (**81**) are known compounds[178, 188] and were identified by comparison of their ^{19}F NMR spectra with literature data.

These results show that dehydrofluorination occurs from the saturated CF_3 in preference to the unsaturated CF_2 site, producing the allene (**81**) instead of the propyne (**79**). Presumably this is because of the reduced stability of the propyne over the allene caused by the extremely unstable fluorine attached to a triple bond in the latter.[6]

Further attempts were carried out using flow systems, rather than sealed systems. Balloons filled with fluoroalkene (**5**) were allowed to slowly release the gas, bubbling it through a cooled, stirred, solution of tertiarybutyllithium and the evolved gases collected in a series of liquid air cooled traps. Conversion of (**5**) was not increased by this method, and it actually decreased owing to reduced contact time between (**5**) and the base; most of the fluoroalkene simply passed through the solution.

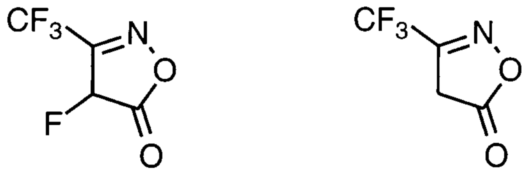
In both cases, sealed and flow systems, mass recovery was never quantitative because of some insoluble polymeric material being formed. It is important to note that since this work has been carried out similar results have been published in the literature[188] although they quote higher conversions using flow systems.

5.III.2. Decarboxylation of Isoxazolone derivatives - Another more recent advance in the synthesis of alkynes was published by Zard in 1991,[189] whose route involves the synthesis of substituted isoxazolones followed by decarboxylation, induced by nitrosation, *Scheme 5.17.*



Scheme 5.17. Formation of alkynes from isoxazolones.

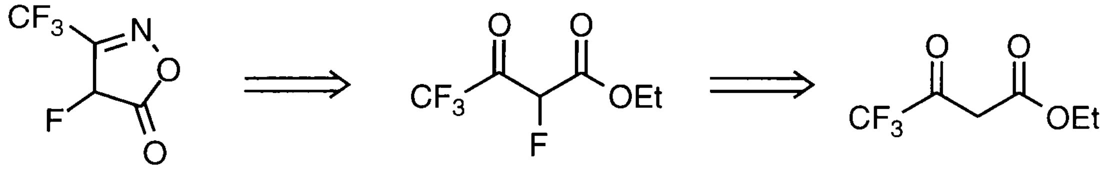
Therefore, if isoxazolone (**87**), *Scheme 5.18*, could be formed easily and the decarboxylation step worked efficiently a new route to (**79**) would be effected.



(87) **(88)**

Scheme 5.18. Target isoxazolones (**87**) and (**88**).

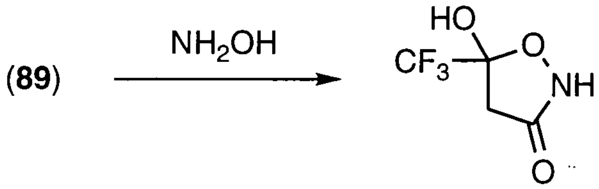
Following the retrosynthetic pathway illustrated in *Scheme 5.19*, it seemed likely that mono fluorination of ethyl trifluoroacetoacetate (**89**) by elemental fluorine, would give a potential precursor to (**87**). However, before fluorination was attempted it was decided to try and form isoxazolone (**88**) from (**89**).



(87) **(89)**

Scheme 5.19. Retrosynthesis of (**87**).

Ethyl trifluoroacetoacetate (**89**) - When ester (**89**) was allowed to react with hydroxylamine hydrochloride and sodium hydroxide in water, good yields of a white crystalline solid were obtained. However this was not our target compound.



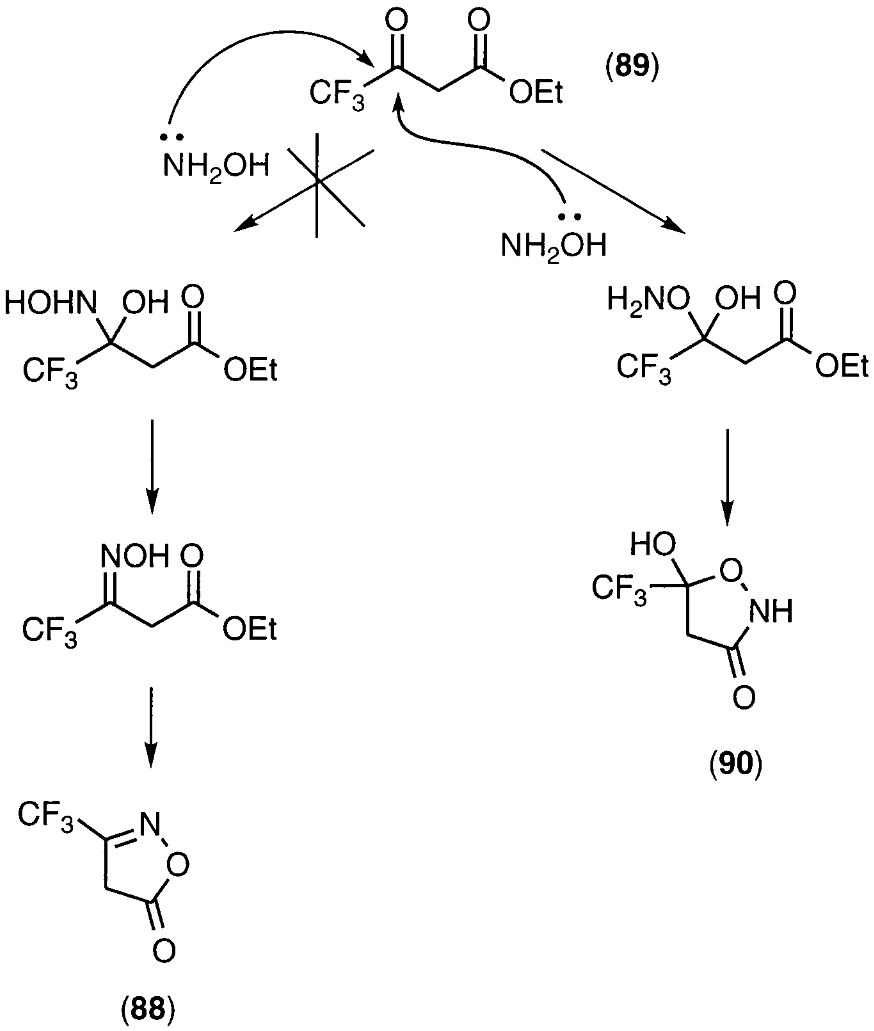
(89) **(90)**

56%

Scheme 5.20. Formation of 5-hydroxy-5-trifluoromethylisoxazolidin-3-one (**90**).

5-Hydroxy-5-trifluoromethylisoxazolidin-3-one (**90**) is a new compound and was identified by NMR and crystallographic data. A single resonance signal in the ^{19}F NMR spectrum at -84.6 ppm indicated one trifluoromethyl group environment. The methylene protons were observed in the ^{1}H NMR spectrum as two doublets at 2.35 and 2.85 ppm and other protons were observed at 8.31 and 11.30 ppm, belonging to the OH and NH (unassigned). ^{13}C data gave four resonances, the methylene carbon was seen at 39.5 ppm, *C*CF3 gave a quartet at 102.5 ($^{2}J_{\text{C-F}}$ 34 Hz), *C*F3 gave a larger quartet at 122.8 ppm ($^{1}J_{\text{C-F}}$ 284 Hz) and the carbonyl carbon gave a characteristic peak at 171.6 ppm.[127] Furthermore crystallographic data was obtained after an adequate crystal was grown from dichloromethane, conclusively proving the structural assignment.

5-Hydroxy-5-trifluoromethylisoxazolidin-3-one (**90**) was formed in preference to isoxazolone (**88**) owing to the hydroxylamine acting as an oxygen nucleophile, rather than a nitrogen nucleophile, illustrated in *Scheme 5.21*.

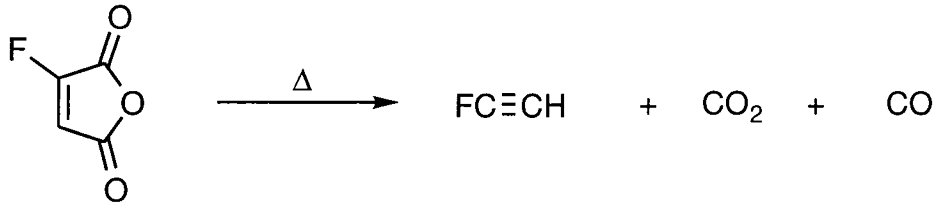


Scheme 5.21. Possible mechanisms for the addition of hydroxylamine hydrochloride to ethyl trifluoroacetoacetate (**89**).

To explain the exclusive attack of oxygen in the bifunctional nucleophile hydroxylamine, the theory of 'hard' and 'soft' acid and bases needs to be considered. This theory works equally well for nucleophiles and electrophiles; a 'hard' nucleophile or electrophile is small and highly charged, while 'soft' are larger and less highly charged. For reactions between nucleophiles and electrophiles 'hard'-'hard' or 'soft'-'soft' interactions dominate *i.e.* a 'hard' nucleophile will preferentially attack a 'hard' electrophile. In (**89**), the trifluoromethyl group pulls electron density away from the carbonyl carbon making it more electropositive and therefore a 'harder' site. In hydroxylamine there is the choice of two nucleophilic sites, 'hard' oxygen or the less 'hard' nitrogen and therefore the 'harder' oxygen nucleophile preferentially attacks the 'hard' carbonyl carbon in (**89**).

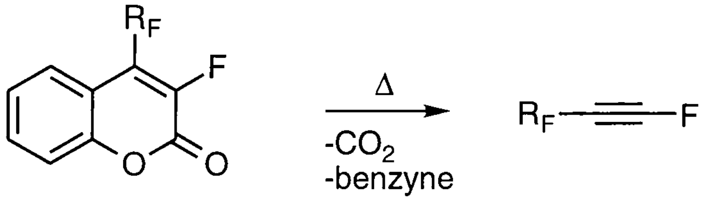
Attempts to produce isoxazolone (**88**) by varying the reaction conditions, including the pH, to alter the mechanistic route were unsuccessful and so efforts to produce isoxazolone (**87**) were abandonned.

5.III.3. 3,4,6-Trichloro-7-methyl-coumarin (91) - Another proposed route to (**79**) was investigated, using substituted coumarin derivatives. In 1959 Middleton and Sharkey[190] provided the first synthesis of a 1-fluoroalkyne, *i.e.* fluorine attached directly to the carbon-carbon triple bond, *Scheme 5.22*, and this reaction was used as the basis for the coumarin work.



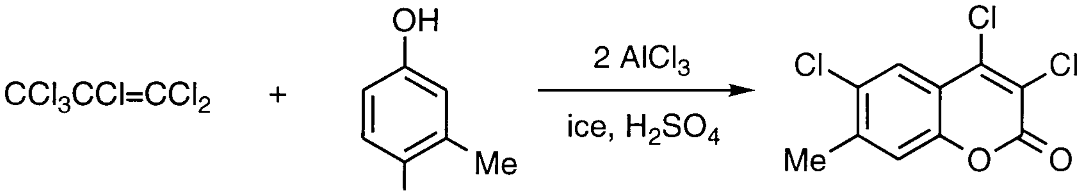
Scheme 5.22. Middleton and Sharkey's route to fluoroacetylene.[190]

Coumarin compounds are prone to decomposition at elevated temperatures,[191] releasing carbon dioxide, therefore it was proposed that if the correct substituents could be put on a coumarin skeleton then decarboxylation could form tetrafluoropropyne or other perfluoro-1-alkynes, *Scheme 5.23.*



Scheme 5.23. Proposed formation of perfluoro-1-alkynes.

In order to synthesise fluorinated coumarin derivatives it was decided to try and perform halogen exchange reactions on a 3,4-dichlorocoumarin, using fluoride ion and/or perfluoroalkyl anions to build the desired structure. 3,4,6-trichloro-7-methyl-coumarin (**91**) was synthesised in high yields following a literature procedure[192, 193] incorporating hexachloropropene and a phenol derivative, *Scheme 5.24.*



(**91**)

85%

Scheme 5.24. Formation of coumarin (**91**).[192, 193]

However, after producing (**91**), it was found to be insoluble in the common organic solvents, including sulfolane and acetonitrile. Therefore the attempted halogen exchange reactions failed using potassium and cesium fluorides, even at elevated temperatures.

Instrumentation and Reagents

Gas Liquid Chromatographic Analysis

GLCMS 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 3 m 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 Brücker 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 Brücker AC250 spectrometer operating at 235.34 MHz or on the Varian VXR400S spectrometer operating at 376.29 MHz. ^{13}C NMR 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 recorded in $CDCl_3$ with TMS and fluorotrichloromethane as internal standards, unless otherwise stated. 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 NaCl 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.

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 4Å molecular sieve. A current of dry nitrogen was maintained for removal of the solvent with a syringe.

Caution: The unsaturated fluorocarbons described in this thesis should be assumed to be highly toxic.

Chapter 6.

Experimental to Chapter 2.

Furan Systems

General Procedure for Sealable Metal Tubes. A sealable metal tube (90 cm^3), charged with 2*H*-heptafluorobut-2-ene (**10**) and furan derivative, was evacuated, sealed and heated in a rocking furnace maintained at 300 °C for 40 h. After the reaction was completed the tube was opened and the contents removed. Distillation under reduced pressure was carried out to afford a single product.

3,4-Bis(trifluoromethyl)furan (**18**). - Furan (3.0 g, 44.1 mmol) and 2*H*-heptafluorobut-2-ene (**10**) (16.0 g, 87.9 mmol) gave *3,4-bis(trifluoromethyl)furan* (**18**) (7.8 g, 87%); bp 87-89°C (lit.,[106] 88-89°C); (Found: C, 35.1; H, 1.1. $C_6H_2F_6O$ requires C, 35.3; H, 1.0%) **NMR spectrum no. 8; IR spectrum no. 7; Mass spectrum no. 7**.

2,5-Dimethyl-3,4-bis(trifluoromethyl)furan (**48**). - 2,5-Dimethylfuran (3.9 g, 40.6 mmol) and 2*H*-heptafluorobut-2-ene (**10**) (14.0 g, 76.9 mmol) gave *2,5-dimethyl-3,4-bis(trifluoromethyl)furan* (**48**) (7.2 g, 76%); bp 52-56 °C / 12 mmHg (lit.,[129] 77-78 °C / 88 mmHg); (Found: C, 41.2; H, 2.7. $C_8H_6F_6O$ requires C, 41.4; H, 2.6%) **NMR spectrum no. 19; IR spectrum no. 11; Mass spectrum no. 19**.

Cyclopentadiene

Endo,endo-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane (**49**). - 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2,5-diene (**38**) (4.0 g, 17.5 mmol) was dissolved in hexane (20 cm^3) and hydrogenated in Parr apparatus for 30 h in the presence of a platinum catalyst on activated carbon (0.6 g). Catalyst was removed by filtration through celite and distillation gave *endo,endo-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane* (**49**) (3.3 g, 81%); bp 34-36 °C / 10 mmHg; (Found: C, 46.4; H, 4.4. $C_9H_{10}F_6$ requires C, 46.6; H, 4.3%) **NMR spectrum no. 20; IR spectrum no. 12; Mass spectrum no. 18.**

2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**). - 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2,5-diene (**38**) (4.0 g, 17.5 mmol) was dissolved in hexane (20 cm^3) and hydrogenated in Parr apparatus for 12 min in the presence of a platinum catalyst on activated carbon (0.6 g). Catalyst was removed by filtration through celite and distillation gave *2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene* (**47**) (3.3 g, 82%); bp 57-59 °C / 44 mmHg; (Found: C, 47.2; H, 3.6. $C_9H_8F_6$ requires C, 47.0; H, 3.5%) **NMR spectrum no. 18; IR spectrum no. 10; Mass spectrum no. 17.**

Endo- and *exo- 5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene* (**44**) and (**45**). - 2*H*-Heptafluorobut-2-ene (**10**) (20.0 g, 0.11 mol) was transferred, under reduced pressure, to a sealable metal tube (40 cm^3) that had previously been charged with dicyclopentadiene (7.9 g, 60 mmol) under a counter current of dry nitrogen. The tube was evacuated, sealed and heated in a rocking furnace maintained at 180 °C for 6 d, under autogeneous pressure. Once reaction was complete the tube was cooled to liquid air temperatures, opened and unreacted fluoroalkene (**10**) removed by distillation at atmospheric pressure. The residue was filtered, redistilled and shown to contain 2 components in approximately a 1:1 ratio, identified as two isomers of *5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene* (**44**) and (**45**) (25.0 g, 92%); bp 24-26 °C / 7 mmHg (lit.,[126] 85.6 °C); (Found: C, 43.2; H, 2.7. $C_9H_7F_7$ requires C, 43.5; H, 2.8%) **NMR spectrum no. 15/16; IR spectrum no. 9; Mass spectrum no. 14/15** by comparison with literature data.[126, 128]

Endo- and *exo- 2-fluoro-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane* (**50**) and (**51**). - A mixture of endo- and exo- 5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**44**) and (**45**) (17.2 g, 69.4 mmol) was dissolved in hexane (20 cm^3) and hydrogenated in Parr apparatus for 15 h in the presence of a platinum catalyst on activated carbon (2 g). Catalyst was removed by filtration through celite and distillation gave a mixture of *endo-* and *exo- 2-fluoro-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane* (**50**) and (**51**) (14.8 g, 85%); bp 38-40 °C / 10 mmHg; (Found: C, 43.4; H, 3.6. $C_9H_9F_7$ requires C, 43.2; H, 3.6%) **NMR spectrum no. 21/22; IR spectrum no. 13; Mass spectrum no. 20/21.**

2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**). - A mixture of *endo-* and *exo-* 2-fluoro-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane (**50**) and (**51**) (14.0 g, 56.0 mmol) was added dropwise to a slurry of powdered potassium hydroxide (10.0 g, 178.6 mmol) in hexane (20 cm^3), stirred and refluxed for 48 h. Reaction could be monitored by ^{19}F NMR, and once reaction was complete the reaction mixture was added to water (100 cm^3) and extracted with dichloromethane (3 x 100 cm^3). Removal of the solvent, followed by redistillation gave a colourless oil identified as *2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene* (**47**) (12.9 g, 100%); bp 57-59 °C / 44 mmHg; see earlier experiment for elemental analysis, **NMR spectrum no. 18; IR spectrum no. 10; Mass spectrum no. 17** by comparison with literature data.[30]

Bis(trifluoromethyl)cyclopentadiene (**46a-c**). - 2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**) (5.0 g, 21.7 mmol) was passed dropwise through a glass tube in a furnace maintained at 450 °C. Volatile material (4.6 g) was collected in a series of traps cooled to liquid air temperatures and was shown to contain an isomeric mixture of *bis(trifluoromethyl)cyclopentadiene* (**46a-c**) (60%); (Found: M^+, 202.0217. $C_7H_4F_6$ requires M^+, 202.0954) **NMR spectrum no. 17; Mass spectrum no. 16**, unreacted 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**) (12%) and unidentified material (28%).

Arene Systems

General Procedure for Quartz Tubes. A quartz tube (1 cm^3), charged with 2*H*-heptafluorobut-2-ene (**10**) and arene derivative, was evacuated, sealed and heated in a furnace maintained at 300 °C for 24 h. After the reaction was completed the tube was opened and the contents removed. Vacuum sublimation was carried out to afford a single product.

1,2-Bis(trifluoromethyl)-4,5-dimethylbenzene (**34**). - 1,2,4,5-Tetramethylbenzene (0.13 g, 1.0 mmol) and 2*H*-heptafluorobut-2-ene (**10**) (0.18 g, 1.0 mmol) gave *1,2-dimethyl-4,5-bis(trifluoromethyl)benzene* (**34**) (0.22 g, 91%); **NMR spectrum no. 11; Mass spectrum no. 10**, identified by comparison with literature data.[123]

11,12-Bis(trifluoromethyl)-9,10-dihydro-9,10-ethenoanthracene (**53**). - Anthracene (0.12 g, 0.7 mmol) and 2*H*-heptafluorobut-2-ene (**10**) (0.18 g, 1.0 mmol) gave *11,12-bis(trifluoromethyl)-9,10-dihydro-9,10-ethenoanthracene* (**53**) (0.23 g, 97%); mp 105-107°C (lit.,[121] 110°C); **NMR spectrum no. 23; Mass spectrum no. 22**, identified by comparison with literature data.[121]

General Procedure for Sealable Metal Tubes. A sealable metal tube (40 or 90 cm^3), charged with 2*H*-heptafluorobut-2-ene (**10**) and arene derivative, was evacuated, sealed and heated in a rocking furnace maintained at 340 °C (~130 atm.) for 60 h. After the reaction was completed the tube was opened and the contents removed. Distillation under reduced pressure was carried out to afford a single product.

1,2-Bis(trifluoromethyl)benzene (**20**). - Benzene (25.0 g, 321 mmol) and 2*H*-heptafluorobut-2-ene (**10**) (9.1 g, 50 mmol) gave *1,2-bis(trifluoromethyl)benzene* (**20**) (6.7 g, 63%); bp 139-141°C (lit.,[38] 143°C); (Found: C, 45.0; H, 2.0. $C_8H_4F_6$ requires C, 44.9; H, 1.9%) **NMR spectrum no. 9; IR spectrum no. 8; Mass spectrum no. 8**, identified by comparison with literature data.[133]

1,2,3-Tris(trifluoromethyl)benzene (**54**). - Trifluoromethylbenzene (29.5 g, 202 mmol) and 2*H*-heptafluorobut-2-ene (**10**) (9.1 g, 50 mmol) gave *1,2,3-tris(trifluoromethyl)benzene* (**54**) (33% conversion of 2*H*-heptafluorobut-2-ene (**10**) by GLCMS); **NMR spectrum no. 24; Mass spectrum no. 23**, identified by comparison with literature data.[133]

1,3,5-Trimethyl-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene (**56**). - 1,3,5-Trimethylbenzene (6.4 g, 53.3 mmol) and 2*H*-heptafluorobut-2-ene (**10**) (5.0 g, 27.5 mmol) gave a mixture of *8-fluoro-1,3,5-trimethyl-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,-diene* (**55a**), *7-fluoro-1,3,5-trimethyl-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,-diene* (**55b**) (58% by GLCMS, (**55ab**) combined), *1,3,5-trimethyl-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene* (**56**) (3%), *1,3-dimethyl-4,5-bis(trifluoromethyl)benzene* (**57**) (3%) and unreacted 1,3,5-trimethylbenzene. The mixture was added to a slurry of powdered potassium hydroxide (9.5 g, 170 mmol) in hexane (50 cm^3) and refluxed for 15 h. After this time the reaction mixture was added to water and extracted with hexane (3 x 70 cm3), removal of the solvent and redistillation gave *1,3,5-trimethyl-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene* (**56**) (4.0 g, 52%); bp 49-52°C / 4 mmHg; (Found: C, 55.6; H, 4.4. $C_{13}H_{12}F_6$ requires C, 55.3; H, 4.3%) **NMR spectrum no. 25; IR spectrum no. 14; Mass spectrum no. 25**.

Chapter 7.

Experimental to Chapter 3.

General Procedure with Potassium Carbonate. A Carius tube (60 cm^3), charged with 2*H*-heptafluorobut-2-ene (**10**), potassium carbonate, acetonitrile and nucleophilic species, was evacuated, sealed and rotated end-over-end at room temperature for 15 h. After the reaction was completed the tube was opened and any volatile material transferred to a cold trap under reduced pressure. The residual solid was then placed in a separating funnel containing water (100 cm^3) and dichloromethane (3 x 50 cm^3) was used to extract the organic layer, which was dried ($MgSO_4$) and the solvent removed by rotatory evaporation. Further distillation under reduced pressure was carried out to afford a single product.

Oxygen Nucleophiles.

1,1,1,3,3,3-Hexafluoro-2,2-bis[4-(3,3,3-trifluoro-1-trifluoromethylprop-1-enyloxy)phenyl]propane (**63**). - Hexafluoro-2,2-di(4-hydroxyphenyl)propane (1.6 g, 4.8 mmol), 2*H*-heptafluorobut-2-ene (**10**) (3.7 g, 20.3 mmol), potassium carbonate (3.5 g, 25.7 mmol) and acetonitrile (20 cm^3) gave *1,1,1,3,3,3-hexafluoro-2,2-bis[4-(3,3,3-trifluoro-1-trifluoromethylprop-1-enyloxy)phenyl]propane* (**63**) (2.8 g, 88%); (Found: C, 42.1; H, 1.5. $C_{23}H_{10}F_{18}O_2$ requires C, 41.8; H, 1.5%) **NMR spectrum no. 26; IR spectrum no. 15; Mass spectrum no. 27**.

Nitrogen Nucleophiles.

1,1,1,4,4,4-Hexafluoro-2-phenyliminobutane (**64**). - Aniline (0.73 g, 7.8 mmol), 2*H*-heptafluorobut-2-ene (**10**) (3.2 g, 17.6 mmol), potassium carbonate (3.3 g, 24.3 mmol) and acetonitrile (10 cm^3) gave *1,1,1,4,4,4-hexafluoro-2-phenyliminobutane* (**64**) (1.8 g, 91%); bp 32-34 °C (5 mmHg); (Found: C, 46.9; H, 2.7; N, 5.4. $C_{10}H_7F_6N$ requires C, 47.1; H, 2.7; N, 5.5%) **NMR spectrum no. 29; IR spectrum no. 18; Mass spectrum no. 30**.

1,1,1,4,4,4-Hexafluoro-2-(4-methylphenylimino)butane (**67**). - *p*-Toluidine (2.1 g, 19.6 mmol), 2*H*-heptafluorobut-2-ene (**10**) (5.6 g, 30.8 mmol), potassium carbonate (4.1 g, 29.7 mmol) and acetonitrile (20 cm^3) gave *1,1,1,4,4,4-hexafluoro-2-(4-methylphenylimino)butane* (**67**) (4.5 g, 83%); bp 48-50 °C (4 mmHg); (Found: C, 48.8; H, 3.1; N, 5.1. $C_{11}H_9F_6N$ requires C, 49.1; H, 3.4; N, 5.2%) **NMR spectrum no. 31; IR spectrum no. 20; Mass spectrum no. 32**.

Sulfur Nucleophiles.

Z-1,1,1,4,4,4-Hexafluoro-2-(3-methylphenylthio)but-2-ene (**70**). - *m*-Thiocresol (1.0 g, 8.1 mmol), 2*H*-heptafluorobut-2-ene (**10**) (3.1 g, 17.0 mmol), potassium carbonate (3.3 g, 24.3 mmol) and acetonitrile (20 cm^3) gave *Z-1,1,1,4,4,4-hexafluoro-2-(3-methylphenylthio)but-2-ene* (**70**) (2.1 g, 90%); bp 42-44 °C (5 mmHg); (Found: C, 46.0; H, 2.7. $C_{11}H_8F_6S$ requires C, 46.2; H, 2.8%) **NMR spectrum no. 34; IR spectrum no. 23; Mass spectrum no. 35**.

1,3-Bis(Z-3,3,3-trifluoro-1-trifluoromethylprop-2-enylthio)benzene (**71**). - 1,3-Dithiolbenzene (1.0 g, 7.0 mmol), 2*H*-heptafluorobut-2-ene (**10**) (3.7 g, 20.3 mmol), potassium carbonate (4.3 g, 31.4 mmol) and acetonitrile (25 cm^3) gave *1,3-bis(Z-3,3,3-trifluoro-1-trifluoromethylprop-2-enylthio)benzene* (**71**) (2.9 g, 89%); bp 58-60 °C (3 mmHg); (Found: C, 35.8; H, 1.2. $C_{14}H_6F_{12}S_2$ requires C, 36.1; H, 1.3%) **NMR spectrum no. 35; IR spectrum no. 24; Mass spectrum no. 36**.

Z-1,1,1,4,4,4-Hexafluoro-2-phenylthiobut-2-ene (**68**). - Thiophenol (1.0 g, 9.1 mmol), 2*H*-heptafluorobut-2-ene (**10**) (2.7 g, 15.0 mmol), potassium carbonate (4.3 g, 31.4 mmol) and acetonitrile (10 cm^3) gave *Z-1,1,1,4,4,4-hexafluoro-2-phenylthiobut-2-ene* (**68**) (2.0 g, 81%); bp 34-36 °C (4 mmHg); (Found: C, 44.0; H, 2.2. $C_{10}H_6F_6S$ requires C, 44.1; H, 2.2%) **NMR spectrum no. 32; IR spectrum no. 21; Mass spectrum no. 33**.

Z-1,1,1,4,4,4-Hexafluoro-2-(4-methylphenylthio)but-2-ene (**69**). - *p*-Thiocresol (1.0 g, 8.1 mmol), 2*H*-heptafluorobut-2-ene (**10**) (3.3 g, 18.1 mmol), potassium carbonate (4.3 g, 31.4 mmol) and acetonitrile (10 cm^3) gave *Z-1,1,1,4,4,4-hexafluoro-2-(4-methylphenylthio)but-2-ene* (**69**) (1.8 g, 78%);bp 51-53 °C (5 mmHg); (Found: C, 45.9; H, 2.7. $C_{11}H_8F_6S$ requires C, 46.2; H, 2.8%) **NMR spectrum no. 33; IR spectrum no. 22; Mass spectrum no. 34**.

Z-1,1,1,4,4,4-Hexafluoro-2-(phenylmethylthio)but-2-ene (**72**). - Benzyl mercaptan (1.5 g, 12.1 mmol), 2*H*-heptafluorobut-2-ene (**10**) (3.3 g, 18.1 mmol), potassium carbonate (4.3 g, 31.4 mmol) and acetonitrile (20 cm^3) gave *Z-1,1,1,4,4,4-hexafluoro-2-(phenylmethylthio)but-2-ene* (**72**) (2.9 g, 84%); bp 52-54 °C (5 mmHg); (Found: C, 45.9; H, 3.0. $C_{11}H_8F_6S$ requires C, 46.2; H, 2.8%) **NMR spectrum no. 36; IR spectrum no. 25; Mass spectrum no. 37**.

Z-2-Cyclopentylthio-1,1,1,4,4,4-hexafluorobut-2-ene (**73**). - Cyclopentyl mercaptan (1.0 g, 9.8 mmol), 2*H*-heptafluorobut-2-ene (**10**) (2.7 g, 15.0 mmol), potassium carbonate (4.3 g, 31.4 mmol) and acetonitrile (20 cm^3) gave *Z-2-cyclopentylthio-1,1,1,4,4,4-hexafluorobut-2-ene* (**73**) (1.8 g, 70%) **NMR spectrum no. 37; Mass spectrum no. 38**.

General Procedure without Potassium Carbonate. A Carius tube (60 cm^3), charged with 2*H*-heptafluorobut-2-ene (**10**), solvent (if required) and nucleophilic species, was evacuated, sealed and rotated end-over-end at room temperature. After the reaction was completed the tube was opened and any volatile material transferred to a cold trap under reduced pressure. The residual solid was then placed in a separating funnel containing water (100 ml) and dichloromethane (3 x 50 cm^3) was used to extract the organic layer, which was dried ($MgSO_4$) and the solvent removed by rotatory evaporation. Further distillation under reduced pressure was carried out to afford a single product.

Nitrogen Nucleophiles.

1,1,1,4,4,4-Hexafluoro-2-phenyliminobutane (**64**). - Aniline (0.7 g, 7.5 mmol), 2*H*-heptafluorobut-2-ene (**10**) (2.6 g, 14.3 mmol) and acetonitrile (10 cm^3) reacted for 60 h gave *1,1,1,4,4,4-hexafluoro-2-phenyliminobutane* (**64**) (0.6 g, 31%); bp 32-34 °C (5 mmHg); see earlier experiment for elemental analysis, **NMR spectrum no. 29; IR spectrum no. 18; Mass spectrum no. 30**.

Oxygen Nucleophiles.

[Z-1-Trifluoromethyl-3,3,3-trifluoroprop-1-enyl] prop-2-enyl ether (**58**). - Allyl alcohol sodium salt (2.4 g, 30.0 mmol) and 2*H*-heptafluorobut-2-ene (**10**) (4.0 g, 22.0 mmol) reacted for 15 h gave *[Z-1-trifluoromethyl-3,3,3-trifluoroprop-1-enyl] prop-2-enyl ether* (**58**) as a volatile product (3.7 g, 76%); bp 40-42 °C; (Found: C, 38.3; H, 2.8. $C_7H_6F_6O$ requires C, 38.2; H, 2.7%) **NMR spectrum no. 27; IR spectrum no. 16; Mass spectrum no. 28**.

1,1,1-Trifluoro-3-trifluoromethyl-5-hexen-2-one (**59**). - A Carius tube (60 cm^3) charged with [Z-1-trifluoromethyl-3,3,3-trifluoroprop-1-enyl] prop-2-enyl ether (**58**) (3.7 g, 16.8 mmol) was evacuated, sealed and heated to 80 °C for 24 h. After the reaction was completed the tube was opened and any volatile material transfered to a cold trap under reduced pressure (0 g). The residual oil was then distilled under reduced pressure to afford a single product identified by comparison with authentic spectra as *1,1,1-trifluoro-3-trifluoromethyl-5-hexen-2-one* (**59**) (3.7 g, 100%); bp 88-90 °C (lit.,[141] 88.5-89 °C); (Found: C, 38.3; H, 2.7. $C_7H_6F_6O$ requires C, 38.2; H, 2.7%) **NMR spectrum no. 28; IR spectrum no. 17; Mass spectrum no. 29**.

Formation of 2-Trifluoromethyl-4-(*N*-phenylamino)-quinoline.

4-(N-Phenylamino)-2-trifluoromethylquinoline (**65**). - 1,1,1,4,4,4-Hexafluoro-2-phenyliminobutane (**64**) (1.0 g, 3.9 mmol) was added dropwise to a stirred slurry of powdered potassium hydroxide (2.0 g, 35.7 mmol) in hexane (50 cm^3) and left at room temperature for 60 h. After the reaction was complete the hexane was removed by rotatory evaporation, the resultant slurry added to water and extracted with dichloromethane (3 x 50 cm^3). Solvent was removed by rotatory evaporation and the resultant solid purified by vacuum sublimation [oil bath temperature 100 °C (<1 mmHg)] to afford a single white crystalline product identified as *4-(N-phenylamino)-2-*

trifluoromethylquinoline (**65**) (0.3 g, 53%); mp 140-142 °C; (Found: C, 66.5; H, 3.8; N, 9.9. $C_{16}H_{11}F_3N_2$ requires C, 66.7; H, 3.8; N, 9.7%) **NMR spectrum no. 30; IR spectrum no. 19; Mass spectrum no. 31**.

Chapter 8.

Experimental to Chapter 4.

Reactions using sulfolane

General Procedure for Reactions in Carius tubes. A Carius tube (60 cm^3), charged with potassium fluoride, PFC (**74**), sulfolane and chlorocarbon, was evacuated, sealed and heated in a rotating oil bath maintained at 190 °C. After the reaction was completed the tube was opened and any volatile material transferred to a cold trap under reduced pressure. Further distillation under reduced pressure was carried out to afford a single product.

2H-Heptafluorobut-2-ene (**10**). - Hexachlorobuta-1,3-diene (**75**) (2.1 g, 8.1 mmol), potassium fluoride (4.7 g, 81 mmol), PFC (**74**) (6.5 cm^3) and sulfolane (2 cm^3), heated for 15 h gave 2*H*-heptafluorobut-2-ene (**10**) (1.1 g, 75%); bp 8-10 °C (lit.,[36] 7-8 °C) **NMR spectrum no. 6; IR spectrum no. 5; Mass spectrum no. 5**.

Octafluorocyclopentene (**3**). - Octachlorocyclopentene (3.4 g, 10 mmol), potassium fluoride (5.8 g, 100 mmol), PFC (**74**) (6.5 cm^3) and sulfolane (2 cm^3), heated for 15 h gave octafluorocyclopentene (**3**) (1.9 g, 89%); bp 26-28 °C (lit.,[15] 25.4-26.5 °C) **NMR spectrum no. 2; IR spectrum no. 2; Mass spectrum no. 2**.

1,3,5-Trichloro-2,4,6-trifluorobenzene. - Hexachlorobenzene (1.0 g, 3.5 mmol), potassium fluoride (1.8 g, 31.6 mmol), PFC (**74**) (10 cm^3) and sulfolane (4.5 cm^3), heated for 200 h gave 1,3,5-trichloro-2,4,6-trifluorobenzene (0.7 g, 83%); mp 59-61 °C (lit.,[36] 57-61 °C); (Found: C, 30.3. $C_6Cl_3F_3$ requires C, 30.6%) **NMR spectrum no. 40; IR spectrum no. 28; Mass spectrum no. 41**.

3,5-Dichlorotrifluoropyridine. - Pentachloropyridine (2.5 g, 10 mmol), potassium fluoride (4.0 g, 70 mmol), PFC (**74**) (6.5 cm^3) and sulfolane (2 cm^3), heated for 15 h gave 3,5-dichlorotrifluoropyridine (1.1 g, 54%); bp 157-159 °C (lit.,[170] 159-160 °C); (Found: C, 29.6; N, 6.9. $C_5Cl_2F_3N$ requires C, 29.7; N, 6.9%) **NMR spectrum no. 38; IR spectrum no. 26; Mass spectrum no. 39**.

5-Chloroperfluoropyrimidine. - Tetrachloropyrimidine (2.2 g, 10 mmol), potassium fluoride (3.5 g, 60 mmol), PFC (**74**) (6.5 cm^3) and sulfolane (2 cm^3), heated for 15 h gave 5-chloroperfluoropyrimidine (1.1 g, 65%); bp 115-116 °C (lit.,[171] 115 °C); (Found: C, 28.5; N, 16.5. $C_4ClF_3N_2$ requires C, 28.5; N, 16.6%) **NMR spectrum no. 39; IR spectrum no. 27; Mass spectrum no. 40**.

General Procedure for Reactions at Atmospheric Pressure. - A round bottomed flask (500 cm^3) fitted with a reflux condenser, charged with potassium fluoride, PFC (**74**) (70 cm^3), sulfolane (30 cm^3) and chlorocarbon was heated to 190 °C and the contents stirred mechanically. After the reaction was complete, the flask was allowed to cool and any volatile material transferred to a cold trap under reduced pressure. Further distillation under reduced pressure afforded a single product.

Octafluorocyclopentene (**3**). - Octachlorocyclopentene (17.2 g, 50 mmol) and potassium fluoride (34.8 g, 600 mmol) heated for 2 d gave octafluorocyclopentene (**3**) (6.1 g, 58%); bp 26-28 °C (lit.,[15] 25.4-26.5 °C) **NMR spectrum no. 2; IR spectrum no. 2; Mass spectrum no. 2**.

3,5-Dichlorotrifluoropyridine. - Pentachloropyridine (6.3 g, 25 mmol) and potassium fluoride (11.6 g, 200 mmol) was heated for 3 d. After this time the flask was allowed to cool and the contents filtered, leaving a bi-phasic mixture; the lower layer (PFC (**74**)) was colourless and the upper (sulfolane) was orange. The layers were separated and worked up independently. The PFC layer was extracted with toluene (3 x 70 cm^3) and the solvent removed by rotatory evaporation yielding a colourless oil which solidified. The sulfolane layer was distilled under reduced pressure and yielded an identical sample of this colourless material. The two samples were combined and gave 3,5-dichlorotrifluoropyridine (4.7 g, 93%); bp 157-159 °C (lit.,[170] 159-160 °C); see earlier experiment for elemental analysis, **NMR spectrum no. 38; IR spectrum no. 26; Mass spectrum no. 39**.

Hexafluorobut-2-yne (**4**). - Hexachlorobuta-1,3-diene (**75**) (261 g, 1 mol) was added dropwise over 2 h to a mechanically stirred suspension of freshly dried potassium fluoride (500 g, 8.5 mol) in anhydrous sulfolane (0.3 l) and PFC (**74**) (1 l), maintained at 190 °C. The reaction was stirred for a further 4 h after the final addition of the diene, whilst volatile products (96 g) were collected in two sequential traps maintained at liquid air temperatures and were identified by comparison to authentic spectra as hexafluorobut-2-yne (**4**) (43% by ^{19}F NMR integration) and 2*H*-heptafluorobut-2-ene (**10**) (14%). The volatiles were condensed over 4 Å molecular sieve[65] under reduced pressure and allowed to stand at room temperature for 25 d. After this time further analysis of a representative sample showed that the volatiles contained only hexafluorobut-2-yne[9] (**4**) (91 g, 56% based on starting diene (**75**)) **NMR spectrum no. 3; IR spectrum no. 3; Mass spectrum no. 3**.

Reactions using 18-Crown-6

General Procedure for Reactions in Carius tubes. A Carius tube (60 cm^3), charged with potassium fluoride, PFC (**74**) (20 cm^3), 18-crown-6 (**77**) and chlorocarbon, was evacuated, sealed and heated in a rotating oil bath maintained at 190 °C. After the reaction was complete, the tube was opened and any volatile material transferred to a cold trap under reduced pressure. Additional distillation under reduced pressure was carried out to effect further purification.

Hexafluorocyclobutene (**2**). - Hexachlorobuta-1,3-diene (**75**) (2.6 g, 10 mmol), potassium fluoride (5.8 g, 100 mmol) and 18-crown-6 (**77**) (0.3 g, 1 mmol), heated for

15 h gave hexafluorocyclobutene (**2**) (1.1 g, 68%); bp 0-2 °C (lit.,[173] 1.1 °C) **NMR spectrum no. 1; IR spectrum no. 1; Mass spectrum no. 1**.

2H-Heptafluorobut-2-ene (**10**). - Hexachlorobuta-1,3-diene (**75**) (2.6 g, 10 mmol), potassium fluoride (4.6 g, 80 mmol) and 18-crown-6 (**77**) (1.3 g, 5 mmol), heated for 15 h gave 2*H*-heptafluorobut-2-ene (**10**).(1.0 g, 55%); bp 8-10 °C (lit.,[36] 7-8 °C) **NMR spectrum no. 6; IR spectrum no. 5; Mass spectrum no. 5**.

Octafluorobut-2-ene (**6**). - 2,3-Dichlorohexafluorobut-2-ene (**76**) (2.3 g, 10 mmol), potassium fluoride (2.3 g, 40 mmol) and 18-crown-6 (**77**) (0.3 g, 1 mmol), heated for 48 h gave *E/Z* octafluorobut-2-ene (**6**) (1.8 g, 90%); bp 0-5 °C (lit.,[176] 0.9 °C) **NMR spectrum no. 4/5; IR spectrum no. 4; Mass spectrum no. 4**.

1,3,5-Trichloro-2,4,6-trifluorobenzene. - Hexachlorobenzene (2.9 g, 10 mmol), potassium fluoride (4.6 g, 80 mmol) and 18-crown-6 (**77**) (0.3 g, 1 mmol), heated for 216 h gave 1,3,5-trichloro-2,4,6-trifluorobenzene (60% by GCMS integration) and, presumably, 1,2,3,5,-tetrachloro-4,6-difluorobenzene (40%) **NMR spectrum no. 40; IR spectrum no. 28; Mass spectrum no. 41**.

3,5-Dichlorotrifluoropyridine. - Pentachloropyridine (2.5 g, 10 mmol), potassium fluoride (4.0 g, 70 mmol) and 18-crown-6 (**77**) (0.3 g, 1 mmol), heated for 15 h gave 3,5-dichlorotrifluoropyridine (1.7 g, 84%); bp 157-159 °C (lit.,[170] 159-160 °C); see earlier experiment for elemental analysis, **NMR spectrum no. 38; IR spectrum no. 26; Mass spectrum no. 39**.

5-Chloroperfluoropyrimidine. - Tetrachloropyrimidine (3.3 g, 15 mmol), potassium fluoride (4.6 g, 80 mmol) and 18-crown-6 (**77**) (0.4 g, 1.5 mmol), heated for 15 h gave 5-chloroperfluoropyrimidine.(2.3 g, 91%); bp 115-116 °C (lit.,[171] 115 °C); see earlier experiment for elemental analysis, **NMR spectrum no. 39; IR spectrum no. 27; Mass spectrum no. 40**.

Octafluorocyclopentene (**3**). - Octachlorocyclopentene (1.7 g, 5 mmol), potassium fluoride (3.5 g, 60 mmol) and 18-crown-6 (**77**) (0.1 g, 0.5 mmol), heated for 15 h gave octafluorocyclopentene (**3**) (1.1 g, 100%). The PFC slurry was then filtered and 18-crown-6 extracted from the inorganic residues using acetone (3 x 10 cm^3). The acetone was removed on a rotatory evaporator and the 18-crown-6 used in a repeat reaction without further purification along with the recovered PFC, as follows. Octachlorocyclopentene (1.5 g, 4.4 mmol), potassium fluoride (3.5 g, 60 mmol) and the recovered material, heated for 15h gave octafluorocyclopentene (**3**) (0.7 g, 75%); bp 26-28 °C (lit.,[15] 25.4-26.5 °C) **NMR spectrum no. 2; IR spectrum no. 2; Mass spectrum no. 2**.

General Procedure for Reactions in Stirred Autoclaves. - A stirred autoclave (500 cm^3), charged with potassium fluoride, PFC (**74**) (50 ml), 18-crown-6 (**77**) and chlorocarbon, was evacuated, sealed and heated in a furnace maintained at 190 °C, whilst being stirred continuously. After the reaction was complete the autoclave was cooled, opened and any volatile material transfered to a cold trap under reduced pressure. Additional distillation under reduced pressure was carried out to effect further purification.

Octafluorocyclopentene (**3**). - Octachlorocyclopentene (5.0 g, 14.4 mmol), potassium fluoride (10.0 g, 172.4 mmol) and 18-crown-6 (**77**) (0.4 g, 1.4 mmol), heated for 120 h gave octafluorocyclopentene (**3**) (2.3 g, 74%); bp 26-28 °C (lit.,[15] 25.4-26.5 °C) **NMR spectrum no. 2; IR spectrum no. 2; Mass spectrum no. 2**.

3,5-Dichlorotrifluoropyridine. - Pentachloropyridine (5.0 g, 20.0 mmol), potassium fluoride (10.0 g, 172.4 mmol) and 18-crown-6 (**77**) (0.5 g, 2.0 mmol), heated for 40 h gave 3,5-dichlorotrifluoropyridine (2.8 g, 69%) after filtration and extraction of the PFC layer with toluene (3 x 70 cm^3), removal of solvent and subsequent distillation; bp 157-159 °C (lit.,[170] 159-160 °C); see earlier experiment for elemental analysis, **NMR spectrum no. 38; IR spectrum no. 26; Mass spectrum no. 39**.

General Procedure for Reactions at Atmospheric Pressure. - A round bottomed flask (250 cm^3) fitted with a reflux condenser, charged with potassium fluoride, PFC (**74**), 18-crown-6 (**77**) and chlorocarbon was heated to 190 °C and the contents stirred mechanically for 4 d. After this time the flask was allowed to cool and any volatile material transferred to a cold trap under reduced pressure. Additional distillation under reduced pressure was carried out to effect further purification.

3,5-Dichlorotrifluoropyridine. - Pentachloropyridine (5.0 g, 20 mmol), potassium fluoride (9.2 g, 159.2 mmol), PFC (**74**) (50cm^3) and 18-crown-6 (**77**) (0.5 g, 2 mmol) gave 3,5-dichlorotrifluoropyridine (2.6 g, 65%) after filtration and extraction of the PFC layer with toluene (3 x 70 cm^3), removal of solvent and subsequent distillation; bp 157-159 °C (lit.,[170] 159-160 °C); see earlier experiment for elemental analysis, **NMR spectrum no. 38; IR spectrum no. 26; Mass spectrum no. 39**.

5-Chloroperfluoropyrimidine. - Tetrachloropyrimidine (3.3 g, 15 mmol), potassium fluoride (5.0 g, 86.2 mmol), PFC (**74**) (20cm^3) and 18-crown-6 (**77**) (0.7 g, 2.8 mmol) gave 3,5-dichlorotrifluoropyridine (1.6 g, 69%); bp 115-116 °C (lit.,[171] 115 °C); see earlier experiment for elemental analysis, **NMR spectrum no. 39; IR spectrum no. 27; Mass spectrum no. 40**.

Hexafluorobut-2-yne (**4**). - Hexachlorobuta-1,3-diene (**75**) (240.0 g, 0.9 mol) was added dropwise over 2 h to a mechanically stirred suspension of freshly dried potassium fluoride (580.0 g, 10.0 mol), 18-crown-6 (**77**) (26.4 g, 0.1 mol) and PFC (**74**) (1.5 l), maintained at 190 °C. The reaction was stirred for a further 4 h after the final addition of the diene. Volatile products (83 g) were collected in two sequential traps maintained at liquid air temperatures and products were identified by comparison to authentic spectra as hexafluorobut-2-yne[194] (**4**) (72% by ^{19}F NMR integration), 2*H*-

heptafluorobut-2-ene[36] (**10**) (10%) and hexafluorocyclobutene[173] (**2**) (18%); see above for spectroscopic data.

Chapter 9.

Experimental to Chapter 5.

Hexafluoropropene (11) Adducts

3,3,4,5,5,5-Hexafluoropentan-2-one (**83**). - Degassed hexafluoropropene (**11**) (16 g, 106.7 mmol) was transferred under reduced pressure to a sealable metal tube that had previously been charged with degassed acetaldehyde (6 g, 136.4 mmol) and di-tertiary butyl peroxide (1 g, 6.8 mmol). The tube was then evacuated, sealed and heated in a rocking furnace maintained at 140 °C for 15 h. After this time the tube was allowed to cool to room temperature and then further cooled to liquid air temperatures before being opened. The resultant liquid was then poured into a separating funnel containing water (300 cm^3) and extracted with dichloromethane (3 x 100 cm^3). Removal of the solvent and distillation under reduced pressure gave a colourless oil (17.2 g), analysis of which identified the oil as *3,3,4,5,5,5-hexafluoropentan-2-one* (**83**) by comparison to literature data[184] (17.2 g, 83%); bp 82-84 °C (lit.,[184] 78 °C); **NMR spectrum no. 46; IR spectrum no. 30; Mass spectrum no. 43**.

2,2,3,4,4,4-Hexafluorobutanoic acid (**82**). - Iodine (14 g, 55.1 mmol) and potassium iodide (3 g, 18.1 mmol) were added to a stirred suspension of fluoroketone (**83**) (3.6 g, 18.6 mmol) and sodium hydrogen carbonate (10 g, 119.0 mmol) in water (100 cm^3) and allowed to react at room temperature for 15 h, monitored by ^{19}F NMR. On completion the reaction was filtered and excess sodium metabisulfite added, the resultant slurry was dissolved in water (200 cm^3) and made to pH 1 with concentrated hydrochloric acid. Continuous extraction with dichloromethane for 15 h, then distillation resulted in a colourless oil (2.3 g). Analysis of the oil, by comparison to literature data,[90] identified it as *2,2,3,4,4,4-hexafluorobutanoic acid* (**82**) (2.3 g, 63%); bp 179-181 °C (lit.,[90] 140 °C / 740 mmHg); (Found: C, 24.6; H, 1.1. $C_4H_2F_6O_2$ requires C, 24.5; H, 1.0%) **NMR spectrum no. 45; IR spectrum no. 29; Mass spectrum no. 42**.

2,2,3,4,4,4-Hexafluorobutan-1-ol (**17**). - Degassed hexafluoropropene (**11**) (45 g, 300.0 mmol) was transferred under reduced pressure to a sealable metal tube that had previously been charged with degassed methanol (8.8 g, 275.0 mmol) and di-tertiary butyl peroxide (1.5 g, 10.3 mmol). The tube was then evacuated, sealed and heated in a rocking furnace maintained at 140 °C for 15 h. After this time the tube was allowed to cool to room temperature and then further cooled to liquid air temperatures before being opened. Unreacted (**11**) was collected in a liquid air cooled trap (3.8 g) and the remaining liquid was transferred to a distillation apparatus. Distillation under reduced pressure gave a colourless oil (40 g), analysis of which identified the oil as *2,2,3,4,4,4-hexafluorobutan-1-ol* (**17**) by comparison to literature data[90] (40.0 g, 80%);

bp 159-161°C (lit.,[90] 114.5 °C / 740 mmHg); (Found: C, 26.2; H, 2.2. $C_4H_4F_6O$ requires C, 26.4; H, 2.2%) **NMR spectrum no. 7; IR spectrum no. 6; Mass spectrum no. 6**.

2,2,3,4,4,4-Hexafluorobutanoic acid (**82**). - A round bottomed flask (250 cm^3) was charged with 2,2,3,4,4,4-hexafluorobutan-1-ol (**17**) (17.4 g, 95.6 mmol), potassium dichromate (28.1 g, 95.6 mmol), concentrated sulfuric acid (38.2 g) and water (80 cm^3) and the contents heated at reflux for 4 h. The reaction mixture was allowed to cool and filtered, the filtrate was then extracted with dichloromethane (4 x 50 cm^3). Removal of the solvent by rotary evaporation followed by distillation from concentrated sulfuric acid (30 cm^3) gave a colourless oil (16.3 g), identified as a single product. Analysis of the oil, by comparison to literature data,[90] indicated it to be *2,2,3,4,4,4-hexafluorobutanoic acid* (**82**) (16.3 g, 87%); bp 179-181 °C (lit.,[90] 140 °C / 740 mmHg); see earlier experiment for elemental analysis, **NMR spectrum no. 45; IR spectrum no. 29; Mass spectrum no. 49**.

E and Z Pentafluoro-2-butenoic acid (**80a**). - Acid (**82**) (1.2 g, 6.1 mmol) was added dropwise to a stirred suspension of powdered potassium hydroxide (1.7 g, 30.4mmol) in hexane (20 cm^3) maintained at 0 °C. On complete addition of (**82**) the suspension was allowed to warm to room temperature and stirred for 40 h. After this time water (100 cm^3) was added and the resultant solution acidified to pH 1 with concentrated sulfuric acid. Extraction of the acidic solution with dichloromethane (4 x 50 cm^3) gave a small amount of material (0.8 g) identified as a mixture of (**82**) and *E and Z pentafluoro-2-butenoic acid* (**80a**) (5:6, 50% conversion of (**82**) by ^{19}F NMR integration of recovered material)**NMR spectrum no. 42/43.**

Methyl 2,2,3,4,4,4-hexafluorobutanoate (**84**). - A round bottomed flask was charged with acid (**82**) (5 g, 25.5 mmol), methanol (20 cm^3) and concentrated sulfuric acid (5 cm^3), the solution was then heated at reflux for 15 h. After this time the solution was allowed to cool to room temperature and a lower layer formed on the addition of water (100 cm^3). Separation and distillation of this lower layer gave a colourless oil (3.6 g) identified as *methyl 2,2,3,4,4,4-hexafluorobutanoate* (**84**) by comparison to literature data[88] (3.6 g, 67%); bp 68-70°C / 740 mmHg (lit.,[88] 116 °C); (Found: C, 28.4; H, 1.9. $C_5H_4F_6O_2$ requires C, 28.6; H, 1.9%) **NMR spectrum no. 47; IR spectrum no. 31; Mass spectrum no. 44**.

Ethyl 2,2,3,4,4,4-hexafluorobutanoate (**85**). - A round bottomed flask was charged with acid (**82**) (5 g, 25.5 mmol), ethanol (20 cm^3) and concentrated sulfuric acid (5 cm^3), the solution was then heated at reflux for 15 h. After this time the solution was allowed to cool to room temperature and a lower layer formed on the addition of water (100 cm^3). Separation and distillation of this lower layer gave a colourless oil (4.3 g) identified as *ethyl 2,2,3,4,4,4-hexafluorobutanoate* (**85**) by comparison to literature data[187] (4.3 g, 75%); bp 104 °C (lit.,[187] 118-119 °C); **NMR spectrum no. 48; IR spectrum no. 32; Mass spectrum no. 45**.

(Z)-1-(Pentafluoroprop-1-enyl)-cyclohexanol (**86a**). - 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexanol (10.0 g, 40.0 mmol) was added dropwise to a stirred suspension of powdered potassium hydroxide (11.2 g, 200 mmol) in hexane (100 cm^3) maintained at 0 °C. On complete addition the suspension was allowed to warm to room temperature and stirred for 40 h. After this time the reaction was filtered and the solvent removed by rotary evaporation to give a pale brown oil (5.6 g). Distillation of the oil gave a colourless liquid identified as *(Z)-1-(pentafluoroprop-1-enyl)-cyclohexanol* (**86a**) (4.9 g, 53%); bp 52-54 °C / 8 mmHg; (Found: C, 47.2; H, 4.9. $C_9H_{11}F_5O$ requires C, 47.0; H, 4.8%) **NMR spectrum no. 49; IR spectrum no. 33; Mass spectrum no. 46**.

Other Attempted Routes

Tetrafluoroallene (**81**). - 2*H*-Pentafluoropropene (**5**) (0.7 g, 5.3 mmol) was transferred, under reduced pressure to a sealable round bottomed flask (250 cm^3) which had previously been charged with a pentane solution of tertiary butyl lithium (1.7 M, 2.1 cm^3) under a counter current of dry nitrogen. The flask was then sealed and allowed to warm to -55 °C and the solution stirred at this temperature for 15 h. After this time the flask was opened and volatile material (0.4 g) collected in a liquid air cooled trap. Analysis of the volatile materials showed it to be a mixture of starting fluoroalkene (**5**) and *tetrafluoropropyne* (**79**) (<0.5% by ^{19}F NMR integration) **NMR spectrum no. 41** and *tetrafluoroallene* (**81**) (16.2%) **NMR spectrum no. 44.**

Tetrafluoroallene (**81**). - 2*H*-Pentafluoropropene (**5**) (0.34 g, 2.6 mmol) was transferred to a sealable bladder which was allowed to bubble the gas through a pentane solution of tertiary butyl lithium (1.7 M, 20 cm^3) cooled to -55 °C. Whilst maintaining this temperature volatile material was trapped in two liquid air cooled traps set up in series over a 6 h period. After this time the volatile material (0.2 g) was collected and analysis showed it to be a mixture of starting fluoroalkene (**5**) and *tetrafluoroallene* (**81**) (10% by ^{19}F NMR integration) **NMR spectrum no. 44.**

5-Hydroxy-5-trifluoromethylisoxazolidin-3-one (**90**). - Ester (**89**) (4.6 g, 25.0 mmol) was added dropwise to a stirred solution of hydroxylamine hydrochloride (1.7 g, 25.0 mmol), sodium hydroxide (1.3 g, 32.5 mmol) and water (20 cm^3) in a round bottomed flask. After complete addition the solution was allowed to stir for 2 h while maintained at room temperature. After this time the solution was acidified to pH 3 with dilute hydrochloric acid added dropwise. Extraction of the aqueous solution with diethyl ether and removal of the solvent by rotary evaporation gave a white crystalline solid. Purification by vacuum sublimation (60 °C / 1 mmHg) gave a single product identified as *5-hydroxy-5-trifluoromethylisoxazolidin-3-one* (**90**) (2.4 g, 56%); mp 140-142 °C; (Found: C, 28.1; H, 2.3; N, 8.0. $C_4H_4F_3NO_3$ requires C, 28.1; H, 2.3; N, 8.2%); **NMR spectrum no. 50** (d_6-DMSO); **Mass spectrum no. 47; Crystal Structure no. 1.**

Appendix 1.

NMR Data

No	Name
1	hexafluorocyclobutene (**2**)
2	octafluorocyclopentene (**3**)
3	hexafluorobut-2-yne (**4**)
4	*trans*-octafluorobut-2-ene (**6**)
5	*cis*-octafluorobut-2-ene (**6**)
6	2*H*-heptafluorobut-2-ene (**10**)
7	2,2,3,4,4,4-hexafluorobutan-1-ol (**17**)
8	3,4-bis(trifluoromethyl)furan (**18**)
9	1,2-bis(trifluoromethyl)benzene (**20**)
10	2,3-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2,5-diene (**25**)
11	1,2-bis(trifluoromethyl)-4,5-dimethylbenzene (**34**)
12	2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2,5-diene (**38**)
13	*endo*-5-fluoro-5,6-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2-ene (**42**)
14	*exo*-5-fluoro-5,6-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2-ene (**43**)
15	*endo*-5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**44**)
16	*exo*-5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**45**)
17	bis(trifluoromethyl)cyclopentadiene (**46a-c**)
18	2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**)
19	2,5-dimethyl-3,4-bis(trifluoromethyl)furan (**48**)
20	*endo,endo*-1,2-bis(trifluoromethyl)bicyclo[2.2.1]heptane (**49**)
21	*endo*-2-fluoro-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane (**50**)
22	*exo*-2-fluoro-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane (**51**)
23	11,12-bis(trifluoromethyl)-9,10-dihydro-9,10-ethenoanthracene (**53**)
24	1,2,3-tris(trifluoromethyl)benzene (**54**)
25	1,3,5-trimethyl-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene (**56**)
26	1,1,1,3,3,3-hexafluoro-2,2-bis[4-(3,3,3-trifluoro-1-trifluoromethylprop-1-enyloxy)phenyl]propane (**63**)
27	[*Z*-1-trifluoromethyl-3,3,3-trifluoroprop-1-enyl] prop-2-enyl ether (**58**)
28	1,1,1-trifluoro-3-trifluoromethyl-5-hexen-2-one (**59**)
29	1,1,1,4,4,4-hexafluoro-2-phenyliminobutane (**64**)
30	4-(*N*-Phenylamino)-2-trifluoromethylquinoline (**65**)
31	1,1,1,4,4,4-hexafluoro-2-(4-methylphenylimino)butane (**67**)
32	*Z*-1,1,1,4,4,4-hexafluoro-2-phenylthiobut-2-ene (**68**)
33	*Z*-1,1,1,4,4,4-hexafluoro-2-(4-methylphenylthio)but-2-ene (**69**)

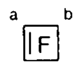
34	*Z*-1,1,1,4,4,4-hexafluoro-2-(3-methylphenylthio)but-2-ene (**70**)
35	1,3-bis(*Z*-3,3,3-trifluoro-1-trifluoromethylprop-2-enylthio)benzene (**71**)
36	*Z*-1,1,1,4,4,4-hexafluoro-2-(phenylmethylthio)but-2-ene (**72**)
37	*Z*-2-cyclopentylthio-1,1,1,4,4,4-hexafluorobut-2-ene (**73**)
38	3,5-dichloroperfluoropyridine
39	5-chloroperfluoropyrimidine
40	1,3,5-trichloro-2,4,6-trifluorobenzene
41	tetrafluoropropyne (**79**)
42	*trans* pentafluoro-2-butenoic acid (**80a**)
43	*cis* pentafluoro-2-butenoic acid (**80a**)
44	tetrafluoroallene (**81**)
45	2,2,3,4,4,4-hexafluorobutanoic acid (**82**)
46	3,3,4,5,5,5-hexafluoropentan-2-one (**83**)
47	methyl 2,2,3,4,4,4-hexafluorobutanoate (**84**)
48	ethyl 2,2,3,4,4,4-hexafluorobutanoate (**85**)
49	1-(pentafluoroprop-1-enyl)-cyclohexanol (**86a**)
50	5-hydroxy-5-trifluoromethylisoxazolidin-3-one (**90**)

Note: ^{19}F NMR spectra are acquired using a machine that records data points every 7 Hz, therefore there is a degree of error in coupling of +/- 7 Hz. This means at times the J_{F-H}, from ^{19}F NMR, does not equal the J_{H-F} obtained in the relevant ^{1}H NMR spectrum, however the two values will be equal within this error.

2D NMR Data

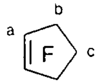
^{1}H-^{1}H COSY NMR	2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**)
^{1}H-^{13}C HETCOR NMR	2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**)

NMR No. 1.



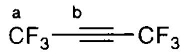
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{13}C	114.1	tm	$^{1}J_{C\text{-}F}$ 285.0	-	b
	135.1	dm	$^{1}J_{C\text{-}F}$ 337.5	-	a
^{19}F	-122.2	m	-	2	b
	-131.4	m	-	1	a

NMR No. 2.



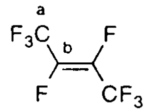
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{13}C	109.1	tpt	$^{1}J_{C\text{-}F}$ 278.0 $^{2}J_{C\text{-}F}$ 23.9 $^{3}J_{C\text{-}F}$ 4.9	-	c
	110.3	tqm	$^{1}J_{C\text{-}F}$ 260.1 $^{2}J_{C\text{-}F}$ 23.7	-	b
	138.6	dm	$^{1}J_{C\text{-}F}$ 297.9	-	a
^{19}F	-117.6	m	-	2	b
	-129.4	m	-	1	c
	-148.7	m	-	1	a

NMR No. 3.



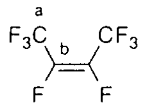
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{13}C	30.0	q	$^{2}J_{C\text{-}F}$ 19.4	-	b
	113.9	q	$^{1}J_{C\text{-}F}$ 259.8	-	a
^{19}F	-55.6	s	-	-	a

NMR No. 4.



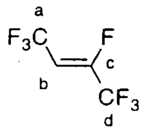
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{13}C	117.7	qdm	$^{1}J_{C\text{-}F}$ 273.1 $^{2}J_{C\text{-}F}$ 30.1	-	a
	142.1	m	-	-	b
^{19}F	-71.9	m	-	3	a
	-162.7	m	-	1	b

NMR No. 5.



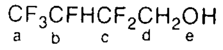
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{13}C	117.2	dqm	$^1J_{C\text{-}F}$ 272.2 $^2J_{C\text{-}F}$ 38.9	-	a
	140-144	br m	-	-	b
^{19}F	-69.3	m	-	3	a
	-145.9	m	-	1	b

NMR No. 6.



Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H	5.57	dq	$^3J_{H\text{-}F}$ 28.4 $^3J_{H\text{-}F}$ 6.9	-	b
^{13}C	102.7	qm	$^2J_{C\text{-}F}$ 38.9	-	b
	117.5	qd	$^1J_{C\text{-}F}$ 272.4 $^2J_{C\text{-}F}$ 38.9	-	d
	120.8	q	$^1J_{C\text{-}F}$ 269.5	-	a
	152.2	dqq	$^1J_{C\text{-}F}$ 282.4 $^2J_{C\text{-}F}$ 39.7 $^3J_{C\text{-}F}$ 5.4	-	c
^{19}F	-62.5	d	$^3J_{F\text{-}H}$ 10.4	3	a
	-77.0	s	-	3	d
	-119.7	br s	-	1	c

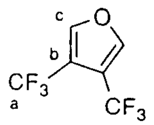
NMR No. 7.



$$\underset{a}{CF_3}\underset{b}{CFH}\underset{c}{CF_2}\underset{d}{CH_2}\underset{e}{OH}$$

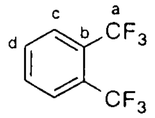
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	2.61	bs	-	1	d
	5.05	ddqd	$^2J_{H\text{-}F}$ 43.2 $^3J_{H\text{-}F}$ 15.2 $^3J_{H\text{-}F}$ 6.0 $^3J_{H\text{-}F}$ 4.8	2	b
	3.8-4.1	m	-	1	e
^{13}C	61.1	dd	$^2J_{C\text{-}F}$ 32.9 $^2J_{C\text{-}F}$ 26.4	-	d
	83.5	dtq	$^1J_{C\text{-}F}$ 194.2 $^2J_{C\text{-}F}$ 35.1 $^2J_{C\text{-}F}$ 26.8	-	b
	117.2	ddd	$^1J_{C\text{-}F}$ 272.8 $^1J_{C\text{-}F}$ 248.0 $^2J_{C\text{-}F}$ 24.8	-	c
	120.7	qd	$^1J_{C\text{-}F}$ 281.9 $^2J_{C\text{-}F}$ 25.1	-	a
^{19}F	-74.3	m	-	3	a
	-119.2 and -122.8	ABm	J_{AB} 287.6	2	c
	-214.0	dm	$^2J_{F\text{-}H}$ 44.0	1	d

NMR No. 8.



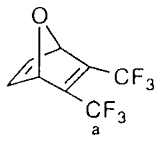
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	7.85	s	-	-	c
^{13}C	115.8	q	$^2J_{C\text{-}F}$ 41.0	-	b
	120.0	q	$^1J_{C\text{-}F}$ 267.8	-	a
	140.4	s	-	-	c
^{19}F	-59.9	s	-	-	a

NMR No. 9.



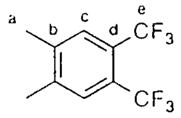
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	7.69	$AA'MM'X_3X'_3$	-	1	c or d
	7.86	$AA'MM'X_3X'_3$		1	c or d
^{19}F	-59.4	s	-	-	a

NMR No. 10.



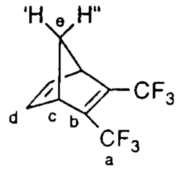
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-66.3	s	-	-	a

NMR No. 11.



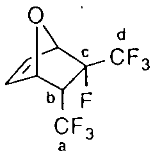
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H	2.37	s	-	3	a
	7.58	s	-	1	c
^{13}C	19.6	s	-	-	a
	123.1	q	$^{1}J_{C-F}$ 274.3	-	e
	129.0	s	-	-	c
	131.5	q	$^{2}J_{C-F}$ 83.6	-	d
	141.2	s	-	-	b
^{19}F	-61.9	s	-	-	e

NMR No. 12.



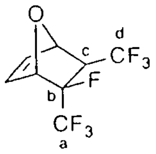
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H	2.10	d	$^{2}J_{H-H}$ 6.8	1	H'
	2.30	dt	$^{2}J_{H-H}$ 6.8 $^{4}J_{H-H}$ 1.6	1	H"
	3.93	s	-	2	c
	6.95	m	-	2	d
^{13}C	52.7	s	-	-	c or e
	73.6	s	-	-	c or e
	122.1	q	$^{1}J_{C-F}$ 269.4	-	a
	142.4	s	-	-	d
	148.4	qm	$^{2}J_{C-F}$ 41.9	-	b
^{19}F	-62.6	s	-	-	a

NMR No. 13.



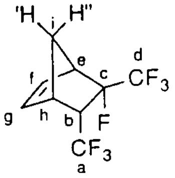
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-68.8	s	-	3	a
	-79.2	s	-	3	b
	-183.8	s	-	1	c

NMR No. 14.



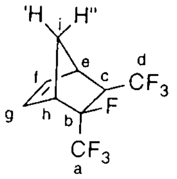
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-65.0	s	-	3	a
	-76.0	s	-	3	c
	-182.9	s	-	1	b

NMR No. 15.



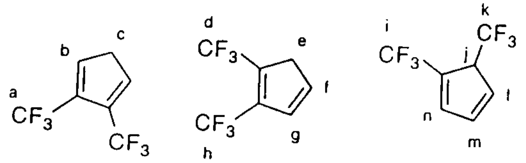
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H	1.70	br s	-	2	i
	3.00	dqd	$^{3}J_{H\text{-}F}$ 12.0 $^{3}J_{H\text{-}F}$ 8.8 $^{4}J_{H\text{-}H}$ 3.2	1	b
	3.19	br s	-	1	e or h
	3.39	br s	-	1	e or h
	6.23	dd	$^{3}J_{H\text{-}H}$ 5.2 $^{4}J_{H\text{-}H}$ 3.6	1	f or g
	6.53	m	-	1	f or g
^{19}F	-63.4	d	$^{3}J_{F\text{-}F}$ 7.9	3	d
	-78.1	d	$^{3}J_{F\text{-}H}$ 4.1	3	a
	-180.3	q	$^{3}J_{F\text{-}F}$ 8.6	1	c

NMR No. 16.


'H
j
H"
e
d
f
c
CF3
g
h
b
F
CF3
a

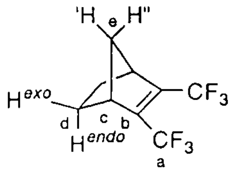
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	1.86	d	$^3J_{H\text{-}H}$ 9.6	1	H' or H"
	2.32	d	$^2J_{H\text{-}H}$ 8.0	1	H' or H"
	2.52	dqd	$^3J_{H\text{-}F}$ 15.2 $^3J_{H\text{-}F}$ 8.8 $^4J_{H\text{-}H}$ 2.0	1	c
	3.19	br s	-	1	e or h
	3.24	br s	-	1	e or h
	6.15	m	-	1	f or g
	6.44	m	-	1	f or g
^{19}F	-64.7	d	$^3J_{F\text{-}F}$ 9.4	3	a
	-76.7	s	-	3	b
	-176.9	m	-	1	d

NMR No. 17.


a
CF3
b
c
CF3
d
CF3
e
f
CF3
h
g
i
CF3
k
CF3
j
l
n
m

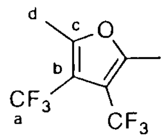
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	2.67	br s	-	-	c or e
	3.29	br s	-	-	c or e
	4.06	q	$^3J_{H\text{-}F}$ 9.1	-	j
	6.4-7.1	m	-	-	b, f, g, l, m and n
^{19}F	-61.7	s	-	-	d, h, i or k
	-61.8	s	-	-	d, h, i or k
	-61.9	s	-	-	d, h, i or k
	-63.8	s	-	-	d, h, i or k
	-66.4	s	-	-	d, h, i or k

NMR No. 18.



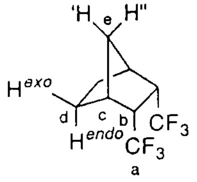
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	1.28	dm	$^2J_{H-H}$ 9.2	1	H'
	1.32	dd	$^2J_{H-H}$ 8.0 $^4J_{H-H}$ 2.8	2	H^{endo}
	1.68	dt	$^2J_{H-H}$ 8.8 $^4J_{H-H}$ 2.1	1	H"
	1.89	d	$^2J_{H-H}$ 8.0	2	H^{exo}
	3.30	s	-	2	c
^{13}C	24.2	s	-	-	d
	44.2	s	-	-	c
	48.1	s	-	-	e
	121.0	q	$^1J_{C-F}$ 271.2	-	a
	139.4	q	$^2J_{C-F}$ 40.0	-	b
^{19}F	-60.6	s	-	-	a

NMR No. 19.



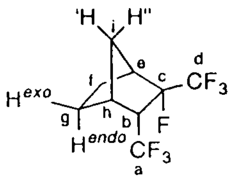
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	2.47	s	-	-	d
^{13}C	12.8	s	-	-	d
	109.8	q	$^2J_{C-F}$ 19.6	-	b
	123.2	q	$^1J_{C-F}$ 264.9	-	a
	152.4	s	-	-	c
^{19}F	-55.7	s	-	-	a

NMR No. 20.


'H
e
H"
H^exo
d
c
b
CF3
H^endo
CF3
a

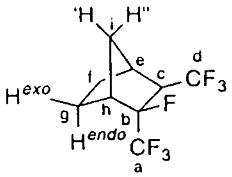
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H	1.53	bs	-	2	H^{exo}
	1.55	bs	-	1	H'
	1.64	dt	$^{2}J_{H-H}$ 10.0 $^{4}J_{H-H}$ 1.6	1	H"
	1.86	dd	$^{2}J_{H-H}$ 10.0 $^{4}J_{H-H}$ 1.6	2	H^{endo}
	2.66	s	-	2	c
	3.07	dm	$^{4}J_{H-H}$ 6.8	2	b
^{13}C	23.0	s	-	-	d
	39.6	s	-	-	c
	40.2	s	-	-	e
	44.4	q	$^{2}J_{C-F}$ 29.0	-	b
	127.6	q	$^{1}J_{C-F}$ 278.7	-	a
^{19}F	-60.7	bs	-	-	a

NMR No. 21.


'H
i
H"
e
d
f
c
CF3
H^exo
g
h
b
F
H^endo
CF3
a

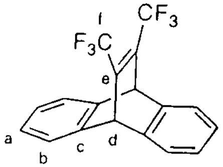
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-61.5	m	-	3	d
	-80.4	m	-	3	a
	-188.6	m	-	1	c

NMR No. 22.


'H
i
H"
e
d
f
c
CF3
H^exo
F
g
h
b
H^endo
CF3
a

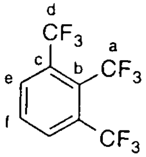
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-64.4	m	-	3	a
	-75.4	s	-	3	d
	-171.8	m	-	1	b

NMR No. 23.



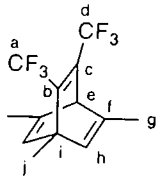
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	5.46	s	-	1	d
	7.07	AA'XX'	-	2	a or b
	7.40	AA'XX'	-	2	a or b
^{13}C	51.1	s	-	-	d
	121.9	q	$^1J_{C\text{-}F}$ 271.6	-	f
	123.9	s	-	-	a or b
	125.9	s	-	-	a or b
	142.8	s	-	-	c
	143.8	q	$^2J_{C\text{-}F}$ 39.5	-	e
^{19}F	-61.7	s	-	-	f

NMR No. 24.



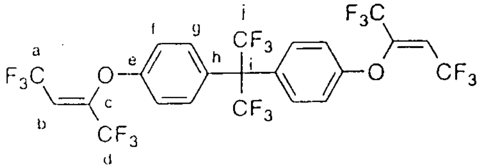
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	8.01	m	$^3J_{H\text{-}H}$ 8.1	2	e
	8.12	br s	-	1	f
^{19}F	-60.1	s	-	2	d
	-63.9	s	-	1	a

NMR No. 25.



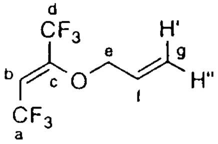
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	2.29	s	-	6	g
	2.30	s	-	3	j
	3.76	s	-	1	e
	6.82	s	-	2	h
^{19}F	-59.0	s	-	1	a or d
	-67.8	s	-	1	a or d

NMR No. 26.



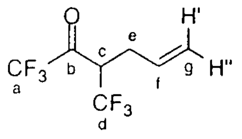
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	6.23	q	$^3J_{H\text{-}F}$ 7.2	1	b
	7.03	d	$^3J_{H\text{-}H}$ 9.2	2	f or g
	7.73	d	$^3J_{H\text{-}H}$ 8.8	2	f or g
^{13}C	63.9	septet	$^2J_{C\text{-}F}$ 25.5	-	i
	112.2	qq	$^2J_{C\text{-}F}$ 37.0 $^3J_{C\text{-}F}$ 3.8	-	b
	116.3	s	-	-	h
	119.1	q	$^1J_{C\text{-}F}$ 278.1	-	a, d or j
	121.1	q	$^1J_{C\text{-}F}$ 271.3	-	a, d or j
	124.1	q	$^1J_{C\text{-}F}$ 287.3	-	a, d or j
	129.5	s	-	-	f
	132.0	s	-	-	g
	146.9	qq	$^2J_{C\text{-}F}$ 36.2 $^3J_{C\text{-}F}$ 4.9	-	c
	156.2	s	-	-	e
^{19}F	-59.7	d	$^3J_{F\text{-}H}$ 7.1	1	a
	-64.2	s	-	1	d or j
	-69.7	s	-	1	d or j

NMR No. 27.



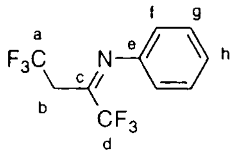
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	4.58	d	$^3J_{H\text{-}H}$ 5.6	2	e
	5.32	dd	$^2J_{H\text{-}H}$ 1.2 $^3J_{H\text{-}H}$ 10.4	1	H"
	5.40	dd	$^3J_{H\text{-}H}$ 17.2 $^2J_{H\text{-}H}$ 1.2	1	H'
	5.75	q	$^3J_{H\text{-}F}$ 7.6	1	b
	5.95	ddt	$^3J_{H\text{-}H}$ 17.2 $^3J_{H\text{-}H}$ 10.4 $^3J_{H\text{-}H}$ 5.6	1	f
^{13}C	74.8	s	-	-	e
	105.2	qq	$^2J_{C\text{-}F}$ 37.0 $^3J_{C\text{-}F}$ 4.6	-	b
	119.2	q	$^1J_{C\text{-}F}$ 278.5	-	a or d
	119.6	s	-	-	g
	121.8	q	$^1J_{C\text{-}F}$ 270.1	-	a or d
	131.2	s	-	-	f
	150.1	qq	$^2J_{C\text{-}F}$ 33.9 $^3J_{C\text{-}F}$ 5.3	-	c
^{19}F	-57.8	d	$^3J_{F\text{-}H}$ 7.5	1	a
	-70.0	s	-	1	d

NMR No. 28.



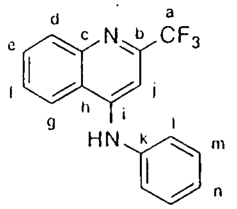
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H	2.71	m	-	2	e
	3.85	dqd	$^{3}J_{H-H}$ 9.6 $^{3}J_{H-F}$ 7.2 $^{3}J_{H-H}$ 5.2	1	c
	5.15	dd	$^{2}J_{H-H}$ 3.2 $^{3}J_{H-H}$ 1.2	1	H''
	5.19	br s	-	1	H'
	5.67	t	$^{3}J_{H-H}$ 10.0	1	f
^{13}C	30.8	s	-	-	e
	49.8	q	$^{2}J_{C-F}$ 27.5	-	c
	114.7	q	$^{1}J_{C-F}$ 291.4	-	a or d
	120.4	s	-	-	g
	123.3	q	$^{1}J_{C-F}$ 281.1	-	a or d
	130.6	s	-	-	f
	185.6	qm	$^{2}J_{C-F}$ 38.1	-	b
^{19}F	-66.4	d	$^{3}J_{F-H}$ 5.3	1	d
	-79.5	s	-	1	a

NMR No. 29.



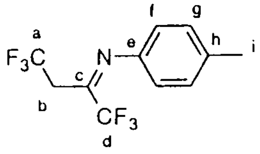
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H	3.33	q	$^{3}J_{H-F}$ 9.6	2	b
	6.77	d	$^{3}J_{H-H}$ 7.6	2	f
	7.22	t	$^{3}J_{H-H}$ 7.2	1	h
	7.41	t	$^{3}J_{H-H}$ 8.0	2	g
^{13}C	33.2	q	$^{2}J_{C-F}$ 32.8	-	b
	117.8	s	-	-	f
	118.8	q	$^{1}J_{C-F}$ 278.5	-	a or d
	122.8	q	$^{1}J_{C-F}$ 278.1	-	a or d
	125.9	s	-	-	h
	129.5	s	-	-	g
	146.4	s	-	-	e
	150.1	q	$^{2}J_{C-F}$ 33.9	-	c
^{19}F	-60.5	tq	$^{3}J_{F-H}$ 9.8 $^{5}J_{F-F}$ 6.0	1	a
	-71.7	q	$^{5}J_{F-F}$ 5.6	1	d

NMR No. 30.



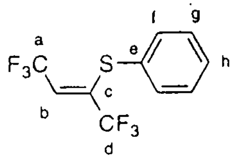
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H	7.06	s	-	1	j
	7.29	m	-	1	n
	7.40	dd	$^3J_{\mathrm{H-H}}$ 8.0 $^4J_{\mathrm{H-H}}$ 0.8	2	l
	7.49	m	-	2	m
	7.64	m	-	1	f
	7.80	m	-	1	e
	8.02	d	$^3J_{\mathrm{H-H}}$ 8.8	1	d
	8.36	d	$^3J_{\mathrm{H-H}}$ 8.4	1	g
^{13}C	97.1	br s	-	-	j
	121.0	s	-	-	g
	122.7	s	-	-	n
	123.2	q	$^1J_{\mathrm{C-F}}$ 274.6	-	a
	125.4	s	-	-	l
	126.9	s	-	-	f
	127.9	s	-	-	d
	130.1	s	-	-	e
	130.9	s	-	-	m
	132.0	s	-	-	h
	140.7	s	-	-	i or k
	149.3	s	-	-	i or k
	149.4	q	$^2J_{\mathrm{C-F}}$ 33.2	-	b
	153.0	s	-	-	c
^{19}F	-67.5	s	-	-	a

NMR No. 31.



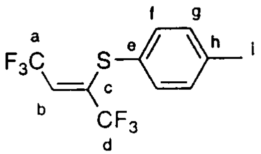
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H	2.35	s	-	3	i
	3.33	q	$^3J_{\mathrm{H-F}}$ 10.0	2	b
	6.67	d	$^3J_{\mathrm{H-H}}$ 8.4	2	g or f
	7.21	d	$^3J_{\mathrm{H-H}}$ 8.0	2	g or f
^{13}C	20.8	s	-	-	i
	33.0	q	$^2J_{\mathrm{C-F}}$ 32.8	-	b
	117.9	s	-	-	h
	118.8	q	$^1J_{\mathrm{C-F}}$ 278.1	-	a or d
	122.9	q	$^1J_{\mathrm{C-F}}$ 278.0	-	a or d
	130.0	s	-	-	f
	135.8	s	-	-	g
	143.8	s	-	-	e
	149.8	qq	$^2J_{\mathrm{C-F}}$ 35.9 $^3J_{\mathrm{C-F}}$ 2.3	-	c
^{19}F	-60.5	tq	$^3J_{\mathrm{F-H}}$ 10.2 $^5J_{\mathrm{F-F}}$ 5.6	1	a
	-71.6	q	$^5J_{\mathrm{F-F}}$ 5.6	1	d

NMR No. 32.



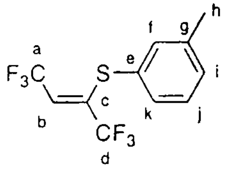
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	6.65	qq	$^3J_{H-F}$ 7.2 $^4J_{H-F}$ 0.8	1	b
	7.3-7.5	m	-	5	f, g, h
^{13}C	121.3	q	$^1J_{C-F}$ 277.0	-	a or d
	121.4	q	$^1J_{C-F}$ 268.6	-	a or d
	127.1	qq	$^2J_{C-F}$ 36.6 $^3J_{C-F}$ 5.3	-	b
	129.3	s	-	-	f
	129.4	s	-	-	h
	130.9	q	$^2J_{C-F}$ 48.0	-	c
	133.4	s	-	-	g
	135.7	s	-	-	e
^{19}F	-58.5	dq	$^3J_{F-H}$ 7.1 $^5J_{F-F}$ 1.1	1	a
	-64.0	bs	-	1	d

NMR No. 33.



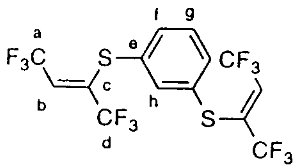
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	2.26	s	-	3	i
	6.49	q	$^3J_{H-F}$ 6.0	1	b
	7.07 and 7.31	AB	J_{AB} 96.0	4	f and g
^{13}C	21.2	s	-	-	i
	121.4	q	$^1J_{C-F}$ 277.3	-	a or d
	121.5	q	$^1J_{C-F}$ 272.0	-	a or d
	125.1	s	-	-	h
	125.9	qq	$^2J_{C-F}$ 36.3 $^3J_{C-F}$ 5.4	-	b
	130.1	s	-	-	f
	133.9	s	-	-	g
	138.8	qq	$^2J_{C-F}$ 32.8 $^3J_{C-F}$ 4.6	-	c
	139.9	s	-	-	e
^{19}F	-58.4	d	$^3J_{F-H}$ 7.1	1	a
	-63.8	s	-	1	d

NMR No. 34.



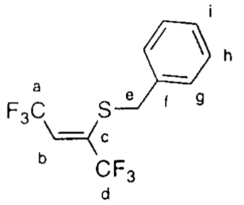
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H	2.33	s	-	3	h
	6.63	qq	$^3J_{H-F}$ 9.6 $^4J_{H-F}$ 0.8	1	b
	7.15	m	-	1	i or k
	7.17	m	-	1	i or k
	7.22	t	$^3J_{H-H}$ 7.4	1	j
	7.29	s	-	1	f
^{13}C	21.1	s	-	-	h
	121.4	q	$^1J_{C-F}$ 272.0	-	a or d
	121.4	q	$^1J_{C-F}$ 277.0	-	a or d
	126.9	qq	$^2J_{C-F}$ 36.3 $^3J_{C-F}$ 4.9	-	b
	127.5	s	-	-	g
	129.1	s	-	-	f, i, j or k
	130.2	s	-	-	f, i, j or k
	130.4	s	-	-	f, i, j or k
	133.8	s	-	-	f, i, j or k
	138.3	qq	$^2J_{C-F}$ 33.2 $^3J_{C-F}$ 4.9	-	c
	139.3	s	-	-	e
^{19}F	-58.5	dq	$^3J_{F-H}$ 7.1 $^4J_{F-F}$ 1.5	1	a
	-64.0	bs	-	1	d

NMR No. 35.



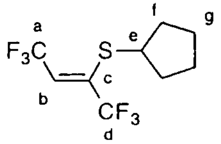
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H	6.72	q	$^3J_{H-F}$ 7.2	1	b
	7.3-7.6	m	-	2	f, g, h
^{13}C	121.2	q	$^1J_{C-F}$ 277.0	-	a or d
	121.2	q	$^1J_{C-F}$ 272.0	-	a or d
	128.6	qq	$^2J_{C-F}$ 36.6 $^3J_{C-F}$ 4.9	-	b
	130.2	s	-	-	h
	130.3	s	-	-	f
	133.9	s	-	-	g
	137.1	s	-	-	e
	139.3	m	-	-	c
^{19}F	-58.6	d	$^3J_{F-H}$ 7.9	1	a
	-64.4	s	-	1	d

NMR No. 36.



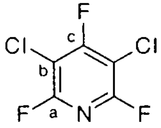
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	4.15	s	-	2	e
	6.57	qq	$^3J_{H\text{-}F}$ 6.8 $^4J_{H\text{-}F}$ 1.6	1	b
	7.32-7.37	m	-	5	g, h, i
^{13}C	38.5	s	-	-	e
	121.4	q	$^1J_{C\text{-}F}$ 272.0	-	a or d
	121.7	q	$^1J_{C\text{-}F}$ 276.6	-	a or d
	126.3	qq	$^2J_{C\text{-}F}$ 36.2 $^3J_{C\text{-}F}$ 5.7	-	b
	128.1	s	-	-	i
	128.8	s	-	-	g
	129.2	s	-	-	h
	135.0	s	-	-	f
	138.0	qq	$^2J_{C\text{-}F}$ 33.6 $^3J_{C\text{-}F}$ 5.0	-	c
^{19}F	-59.1	d	$^3J_{F\text{-}H}$ 7.5	1	a
	-64.7	s	-	1	d

NMR No. 37.



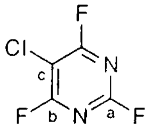
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-59.7	s	-	1	a
	-65.5	s	-	1	d

NMR No. 38.



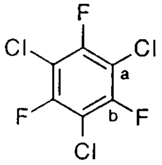
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{13}C	104.4	m	-	-	b
	155.8	ddd	$^1J_{C\text{-}F}$ 246.0 $^3J_{C\text{-}F}$ 17.2 $^3J_{C\text{-}F}$ 10.8	-	a
	164.8	dt	$^1J_{C\text{-}F}$ 265.5 $^3J_{C\text{-}F}$ 5.3	-	c
^{19}F	-70.0	d	$^4J_{F\text{-}F}$ 13.9	2	a
	-93.8	t	$^4J_{F\text{-}F}$ 14.3	1	c

NMR No. 39.



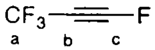
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{13}C	99.5	td	$^2J_{C\text{-}F}$ 30.9 $^4J_{C\text{-}F}$ 10.0	-	c
	158.0	dt	$^1J_{C\text{-}F}$ 230.0 $^3J_{C\text{-}F}$ 21.6	-	a
	168.6	ddd	$^1J_{C\text{-}F}$ 261.0 $^3J_{C\text{-}F}$ 16.4 $^3J_{C\text{-}F}$ 10.3	-	b
^{19}F	-43.1	s	-	1	a
	-55.8	s	-	2	b

NMR No. 40.



Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{13}C	108.7	td	$^2J_{C\text{-}F}$ 22.3 $^4J_{C\text{-}F}$ 4.9	-	a
	154.7	dt	$^1J_{C\text{-}F}$ 249.8 $^3J_{C\text{-}F}$ 4.5	-	b
^{19}F	-114.8	m	-	-	a

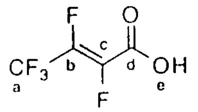
NMR No. 41.



$CF_3C\equiv CF$

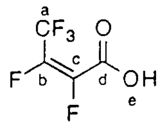
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-51.6	s	-	3	a
	-203.1	s	-	1	c

NMR No. 42.



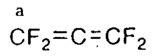
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-69.1	d	$^{4}J_{F\text{-}F}$ 20.2	3	a
	-146.3	d	$^{3}J_{F\text{-}F}$ 138.8	1	b
	-154.3	dq	$^{3}J_{F\text{-}F}$ 137.7 $^{4}J_{F\text{-}F}$ 21.9	1	c

NMR No. 43.



Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-65.7	bs	-	3	a
	-131.7	bs	-	1	b
	-137.9	bs	-	1	c

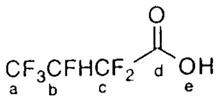
NMR No. 44.



$\overset{a}{CF_2}=C=CF_2$

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-66.9	s	-	-	a

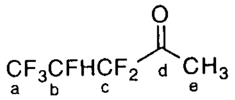
NMR No. 45.



$CF_3CFHCF_2C(=O)OH$

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	5.21	dddq	$^2J_{H\text{-}F}$ 43.2 $^3J_{H\text{-}F}$ 12.8 $^3J_{H\text{-}F}$ 7.2 $^3J_{H\text{-}F}$ 5.6	-	b
	10.58	bs	-	-	e
^{13}C	84.4	dqdd	$^1J_{C\text{-}F}$ 199.1 $^2J_{C\text{-}F}$ 36.2 $^2J_{C\text{-}F}$ 35.5 $^2J_{C\text{-}F}$ 25.5	-	b
	109.4	ddd	$^1J_{C\text{-}F}$ 264.0 $^1J_{C\text{-}F}$ 258.6 $^2J_{C\text{-}F}$ 27.1	-	c
	120.0	qd	$^1J_{C\text{-}F}$ 282.2 $^2J_{C\text{-}F}$ 25.5	-	a
	164.2	t	$^2J_{C\text{-}F}$ 30.7	-	d
^{19}F	-74.8	m	-	3	a
	-116.8 and -121.8	AB	J_{AB} 282.4	2	c
	-214.5	dm	$^2J_{F\text{-}H}$ 43.6	1	b

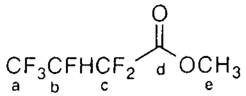
NMR No. 46.



$CF_3CFHCF_2C(=O)CH_3$

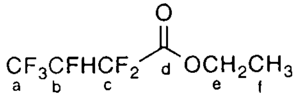
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	2.43	s	-	3	e
	5.25	dddq	$^2J_{H\text{-}F}$ 43.2 $^3J_{H\text{-}F}$ 14.4 $^3J_{H\text{-}F}$ 6.8 $^3J_{H\text{-}F}$ 5.6	1	b
^{13}C	24.3	s	-	-	e
	83.8	dddq	$^1J_{C\text{-}F}$ 196.0 $^2J_{C\text{-}F}$ 31.3 $^2J_{C\text{-}F}$ 24.7 $^2J_{C\text{-}F}$ 24.0	-	b
	110.9	ddd	$^1J_{C\text{-}F}$ 265.9 $^1J_{C\text{-}F}$ 259.4 $^2J_{C\text{-}F}$ 25.5	-	c
	120.6	qd	$^1J_{C\text{-}F}$ 282.6 $^2J_{C\text{-}F}$ 25.2	-	a
	195.5	dd	$^2J_{C\text{-}F}$ 31.3 $^2J_{C\text{-}F}$ 27.2	-	d
^{19}F	-74.3	m	-	3	a
	-116.6 and -122.9	AB	J_{AB} 296.1	2	c
	-216.0	dm	$^2J_{F\text{-}H}$ 43.2	1	b

NMR No. 47.



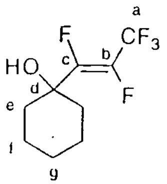
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	3.96	s	-	3	e
	5.19	dddq	$^2J_{H\text{-}F}$ 43.2 $^3J_{H\text{-}F}$ 13.2 $^3J_{H\text{-}F}$ 7.6 $^3J_{H\text{-}F}$ 5.6	1	b
^{13}C	54.3	s	-	-	e
	84.6	dqdd	$^1J_{C\text{-}F}$ 198.7 $^2J_{C\text{-}F}$ 35.5 $^2J_{C\text{-}F}$ 30.9 $^2J_{C\text{-}F}$ 25.9	-	b
	109.6	ddd	$^1J_{C\text{-}F}$ 289.6 $^1J_{C\text{-}F}$ 283.8 $^2J_{C\text{-}F}$ 26.4	-	c
	120.1	qd	$^1J_{C\text{-}F}$ 282.6 $^2J_{C\text{-}F}$ 25.5	-	a
	160.9	t	$^2J_{C\text{-}F}$ 29.8	-	d
^{19}F	-74.6	m	-	3	a
	-116.3 and -120.6	ABm	J_{AB} 263.4	2	c
	-214.5	m	-	1	b

NMR No. 48.



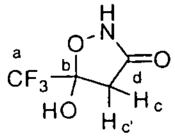
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H	1.39	t	$^3J_{H\text{-}H}$ 7.2	3	f
	4.42	q	$^3J_{H\text{-}H}$ 6.8	2	e
	5.19	dddq	$^2J_{H\text{-}F}$ 43.6 $^3J_{H\text{-}F}$ 13.2 $^3J_{H\text{-}F}$ 7.6 $^3J_{H\text{-}F}$ 6.0	1	b
	13.7	s	-	-	f
^{13}C	64.4	s	-	-	e
	84.6	dqdd	$^1J_{C\text{-}F}$ 199.2 $^2J_{C\text{-}F}$ 35.5 $^2J_{C\text{-}F}$ 30.6 $^2J_{C\text{-}F}$ 25.9	-	b
	109.5	ddd	$^1J_{C\text{-}F}$ 263.2 $^1J_{C\text{-}F}$ 258.3 $^2J_{C\text{-}F}$ 25.9	-	c
	120.1	qdd	$^1J_{C\text{-}F}$ 282.2 $^2J_{C\text{-}F}$ 25.5 $^3J_{C\text{-}F}$ 3.1	-	a
	160.3	t	$^2J_{C\text{-}F}$ 29.4	-	d
^{19}F	-74.3	m	-	3	a
	-116.4 and -120.4	AB	J_{AB} 263.4	2	c
	-214.5	dm	$^2J_{F\text{-}H}$ 43.3	1	b

NMR No. 49.



Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H	1.3-2.2	m	-	-	e, f and g
^{13}C	21.1	s	-	-	e, f or g
	24.9	s	-	-	e, f or g
	34.0	s	-	-	e, f or g
	72.6	dd	$^{2}J_{C\text{-}F}$ 22.5 $^{3}J_{C\text{-}F}$ 4.2	-	d
	119.0	qdm	$^{1}J_{C\text{-}F}$ 270.2 $^{2}J_{C\text{-}F}$ 33.2	-	a
	138.1	ddq	$^{1}J_{C\text{-}F}$ 246.9 $^{3}J_{C\text{-}F}$ 50.4 $^{3}J_{C\text{-}F}$ 39.6	-	b
	157.5	dd	$^{1}J_{C\text{-}F}$ 264.8 $^{3}J_{C\text{-}F}$ 37.8	-	c
^{19}F	-67.6	dd	$^{4}J_{F\text{-}F}$ 22.6 $^{3}J_{F\text{-}F}$ 10.2	3	a
	-149.4	dq	$^{3}J_{F\text{-}F}$ 135.1 $^{4}J_{F\text{-}F}$ 23.0	1	c
	-170.1	d	$^{3}J_{F\text{-}F}$ 133.6	1	b

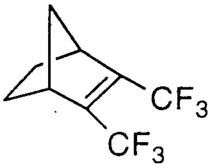
NMR No. 50.



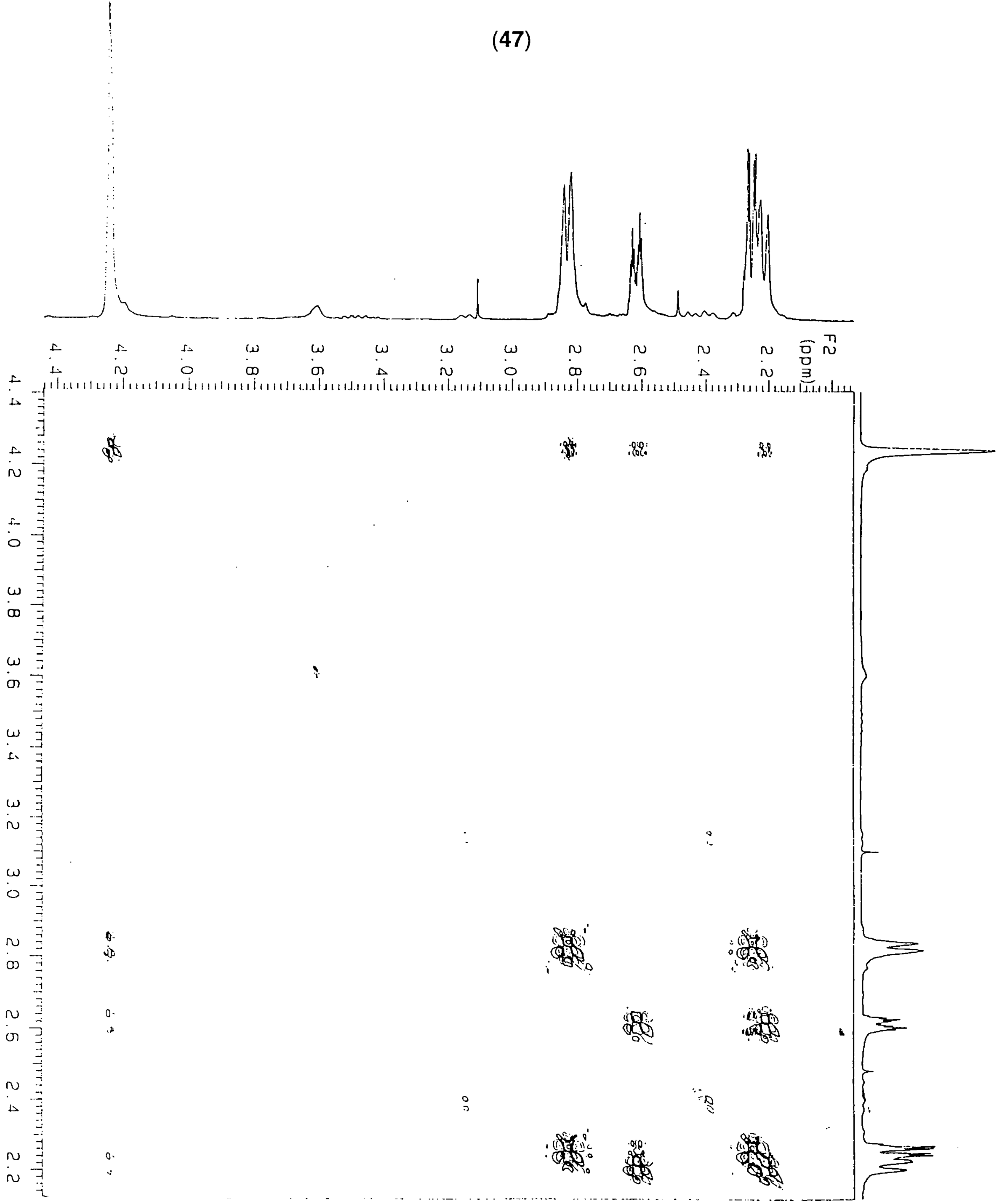
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H	2.35	d	$^{2}J_{H\text{-}H}$ 17.2	1	c or c'
	2.85	d	$^{2}J_{H\text{-}H}$ 17.6	1	c or c'
	8.31	br s	-	1	OH or NH
	11.30	br s	-	1	OH or NH
^{13}C	39.5	s	-	-	c
	102.5	q	$^{2}J_{C\text{-}F}$ 34.3	-	b
	122.8	q	$^{1}J_{C\text{-}F}$ 283.9	-	a
	171.6	s	-	-	d
^{19}F	-84.6	s	-	-	a

^1H-^1H COSY NMR Spectrum

2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**)

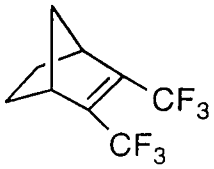


(**47**)

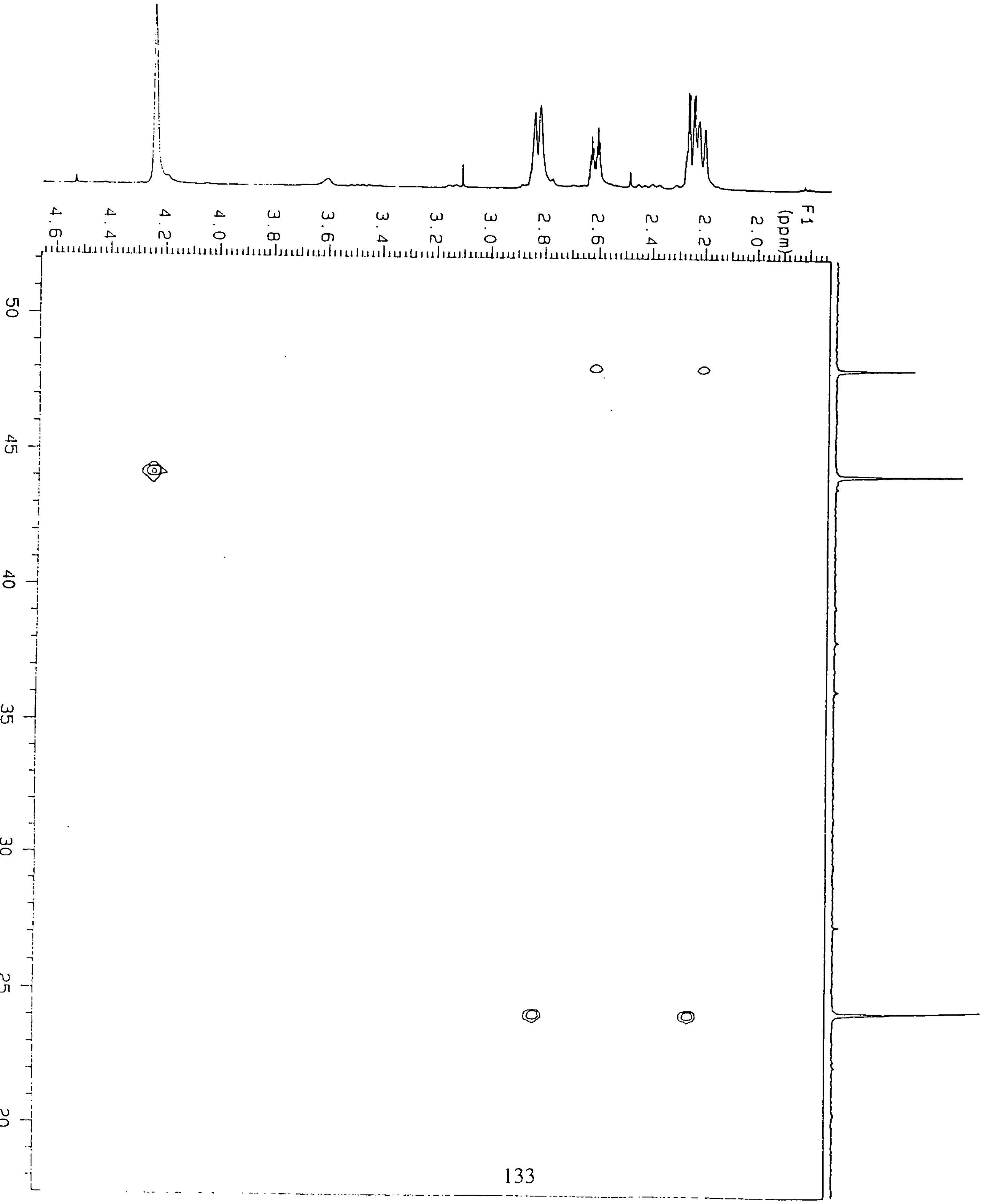


^1H-^{13}C HETCOR NMR Spectrum

2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**)



(**47**)



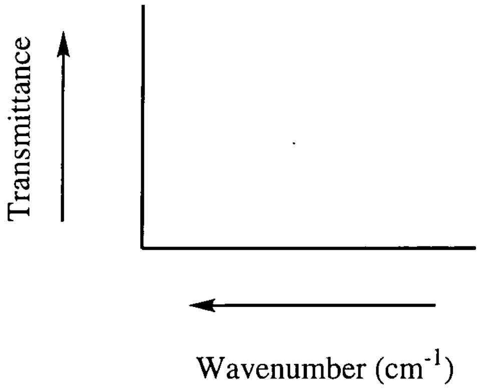
Appendix 2.

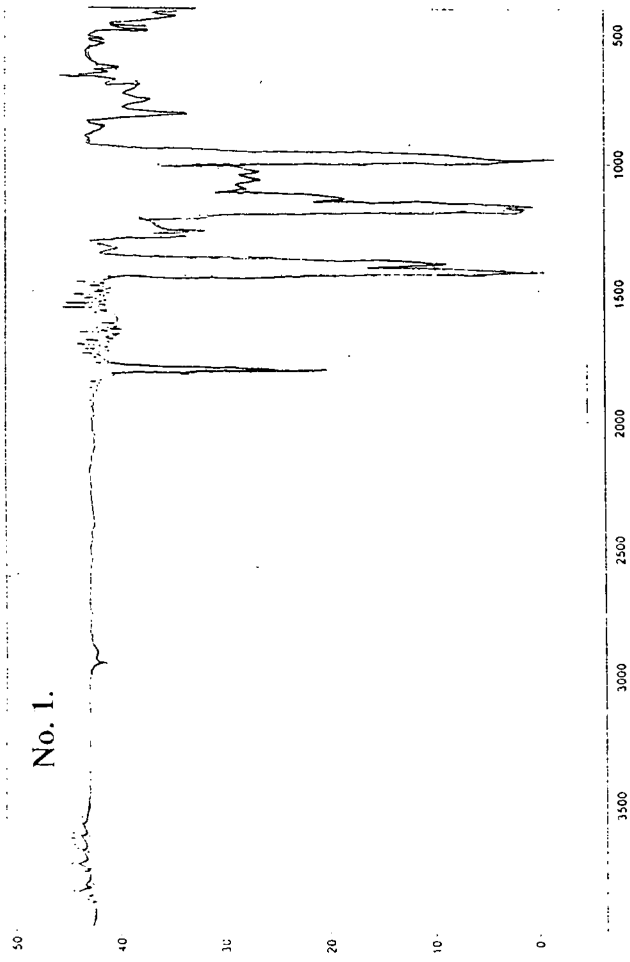
I.R. Data

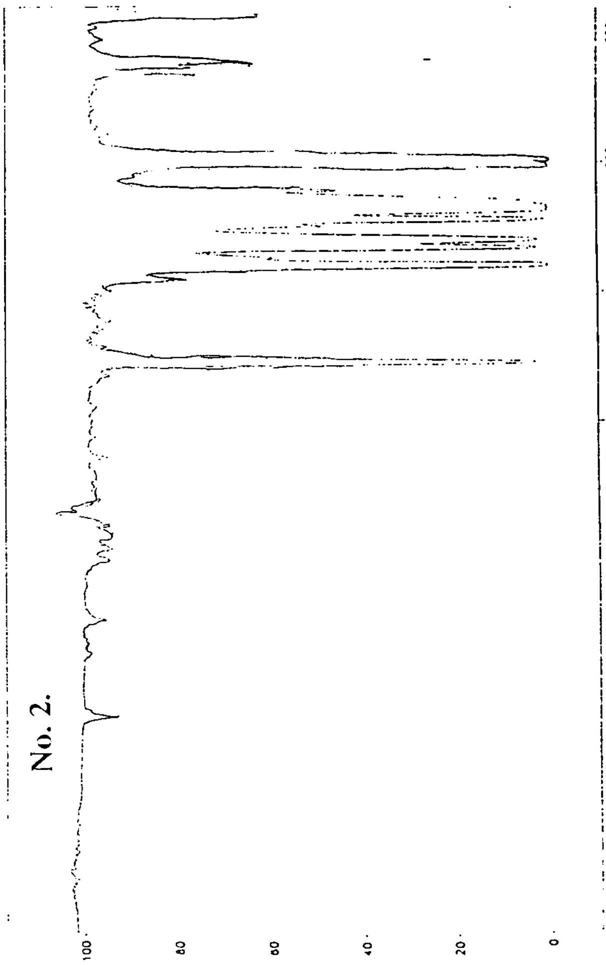
No.	Name
1	hexafluorocyclobutene (**2**)
2	octafluorocyclopentene (**3**)
3	hexafluorobut-2-yne (**4**)
4	*E* and *Z* octafluorobut-2-ene (**6**)
5	2*H*-heptafluorobut-2-ene (**10**)
6	2,2,3,4,4,4-hexafluorobutan-1-ol (**17**)
7	3,4-bis(trifluoromethyl)furan (**18**)
8	1,2-bis(trifluoromethyl)benzene (**20**)
9	*endo* and *exo*-5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**44**) and (**45**)
10	2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**)
11	2,5-dimethyl-3,4-bis(trifluoromethyl)furan (**48**)
12	*endo,endo*-1,2-bis(trifluoromethyl)bicyclo[2.2.1]heptane (**49**)
13	*endo* and *exo*-2-fluoro-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane (**50**) and (**51**)
14	2,4,6-trimethyl-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene (**56**)
15	1,1,1,3,3,3-hexafluoro-2,2-bis[4-(3,3,3-trifluoro-1-trifluoromethylprop-1-enyloxy)phenyl]propane (**63**)
16	[*Z*-1-trifluoromethyl-3,3,3-trifluoroprop-1-enyl] prop-2-enyl ether (**58**)
17	1,1,1-trifluoro-3-trifluoromethyl-5-hexen-2-one (**59**)
18	1,1,1,4,4,4-hexafluoro-2-phenyliminobutane (**64**)
19	4-(*N*-Phenylamino)-2-trifluoromethylquinoline (**65**)
20	1,1,1,4,4,4-hexafluoro-2-(4-methylphenylimino)butane (**67**)
21	*Z*-1,1,1,4,4,4-hexafluoro-2-phenylthiobut-2-ene (**68**)
22	*Z*-1,1,1,4,4,4-hexafluoro-2-(4-methylphenylthio)but-2-ene (**69**)
23	*Z*-1,1,1,4,4,4-hexafluoro-2-(3-methylphenylthio)but-2-ene (**70**)
24	1,3-bis(*Z*-3,3,3-trifluoro-1-trifluoromethylprop-2-enylthio)benzene (**71**)
25	*Z*-1,1,1,4,4,4-hexafluoro-2-(phenylmethylthio)but-2-ene (**72**)
26	3,5-dichloroperfluoropyridine
27	5-chloroperfluoropyrimidine
28	1,3,5-trichloro-2,4,6-trifluorobenzene
29	2,2,3,4,4,4-hexafluorobutanoic acid (**82**)
30	3,3,4,5,5,5-hexafluoropentan-2-one (**83**)
31	methyl 2,2,3,4,4,4-hexafluorobutanoate (**84**)

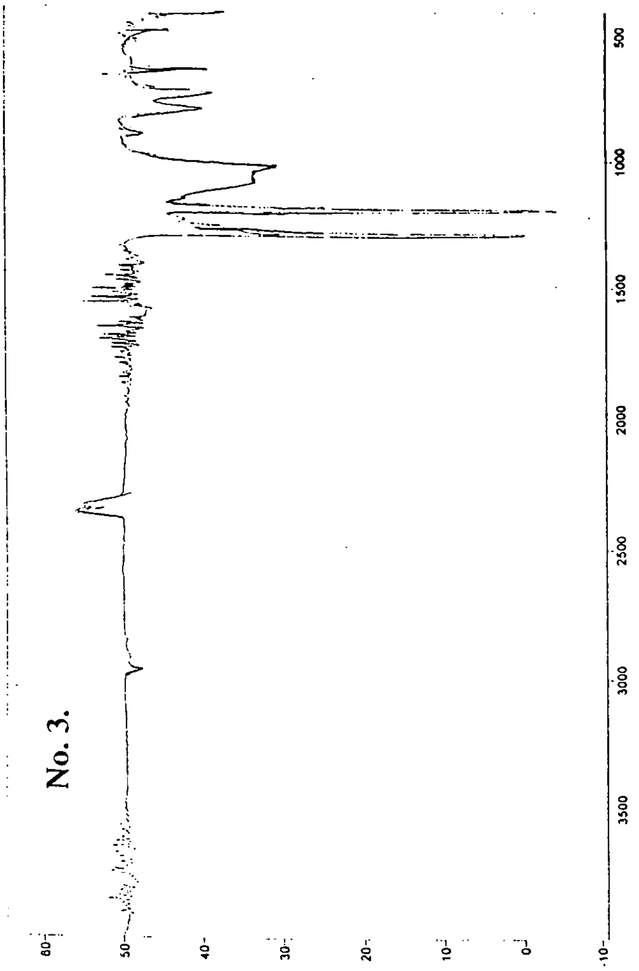
32	ethyl 2,2,3,4,4,4-hexafluorobutanoate (**85**)
33	(*E*)-1-(pentafluoroprop-1-enyl)-cyclohexanol (**86a**)

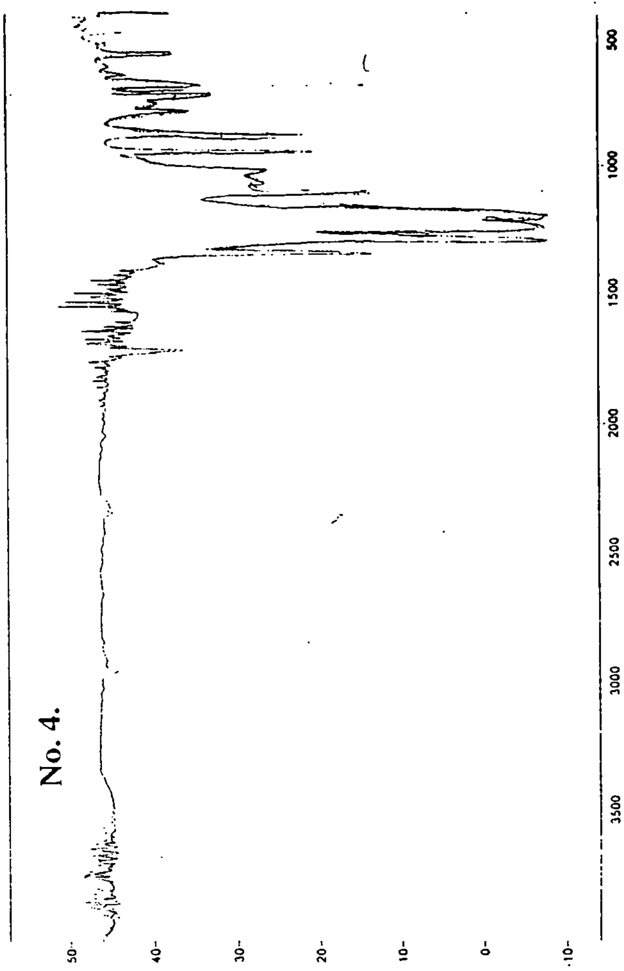
For all of the following IR spectra the axes are as indicated below:-


Transmittance
Wavenumber (cm^{-1})

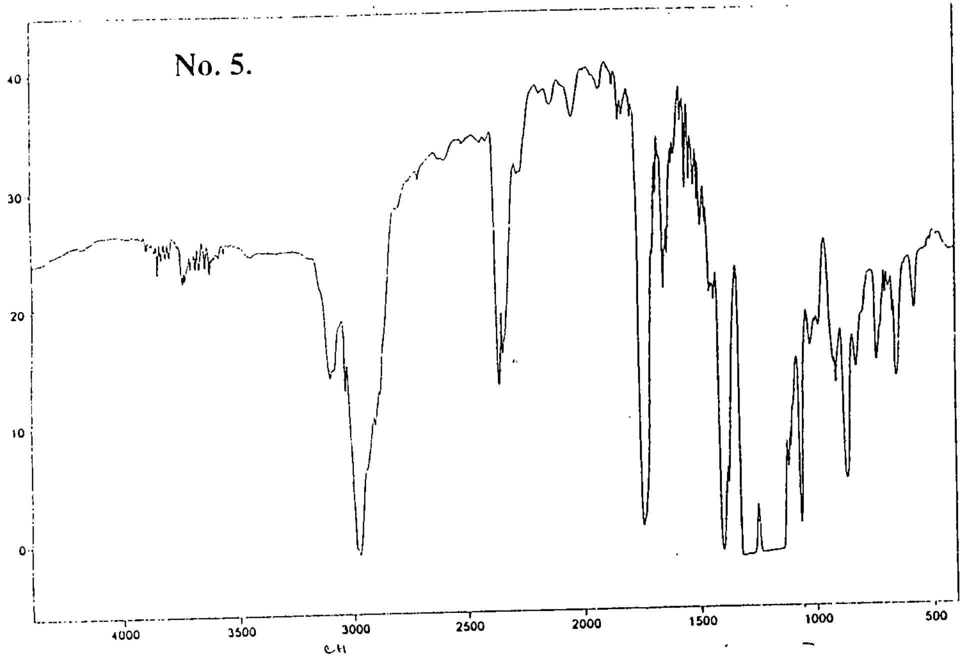

No. 1.


No. 2.

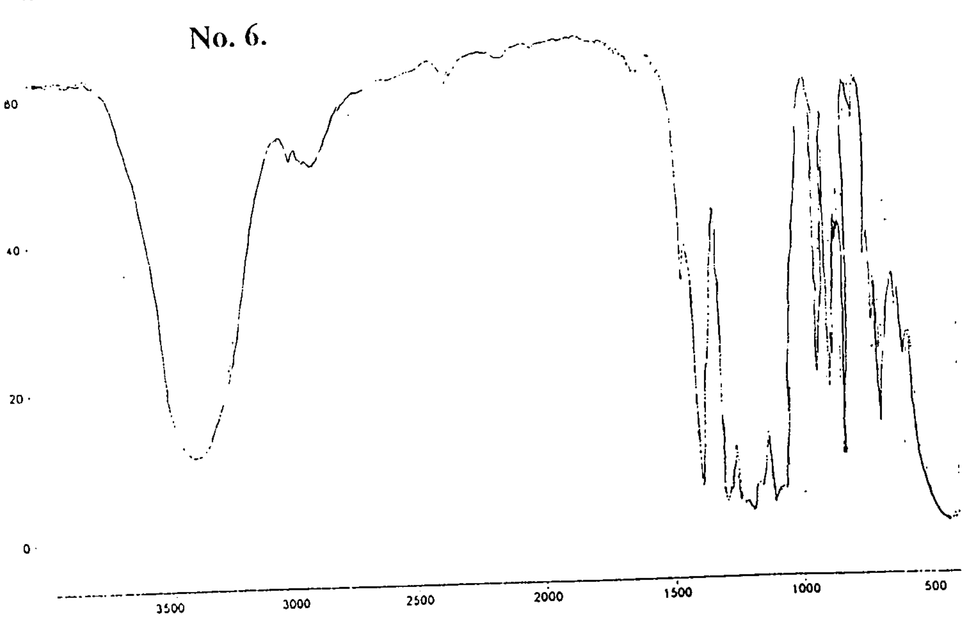

No. 3.


No. 4.

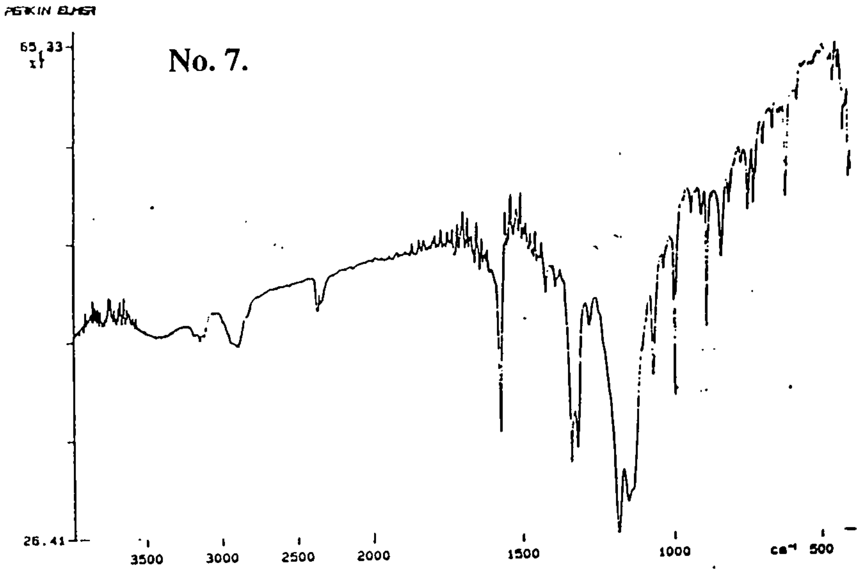
No. 5.



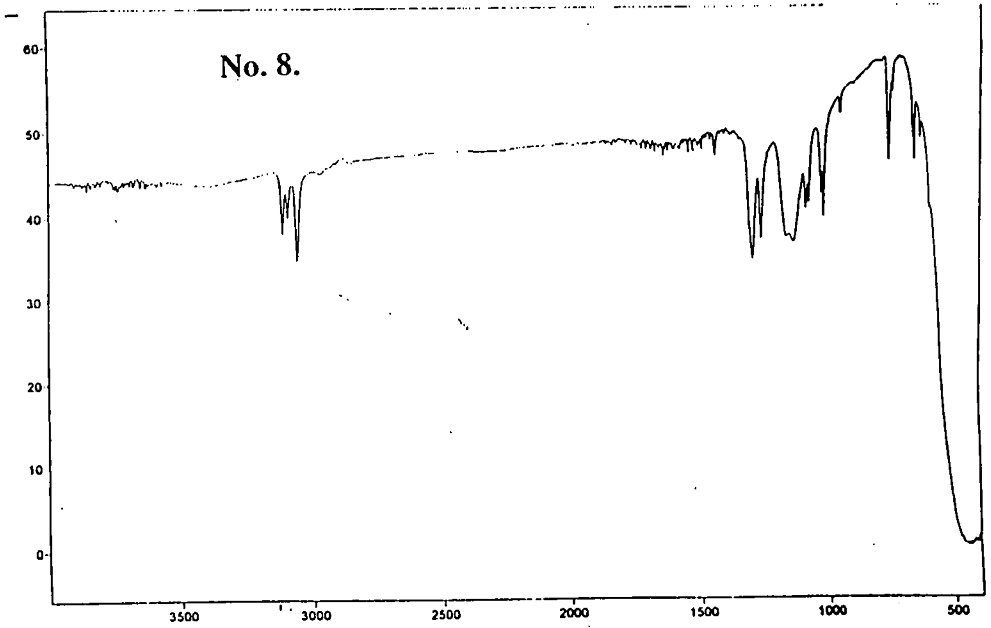
No. 6.



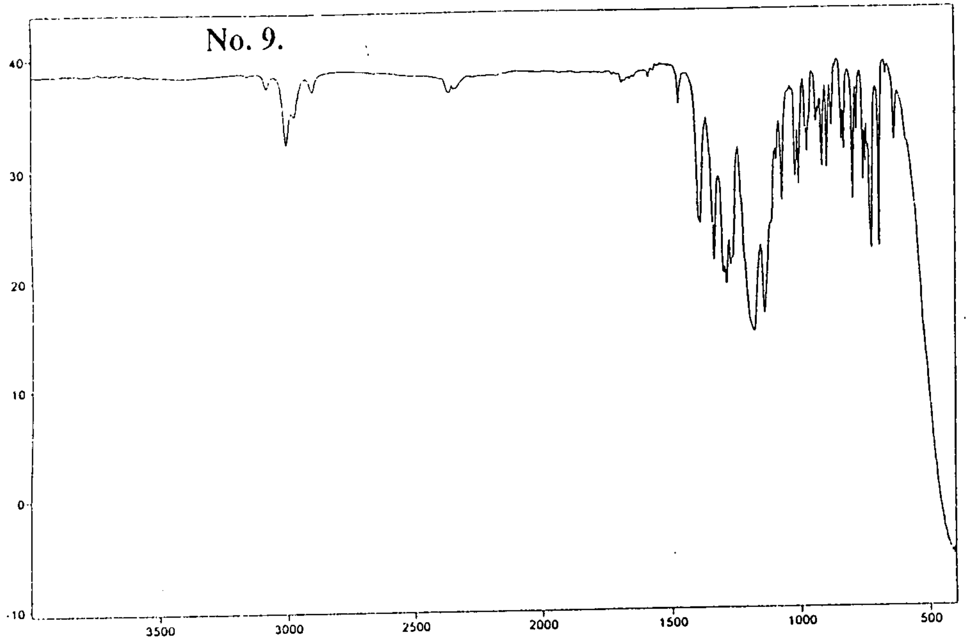
No. 7.



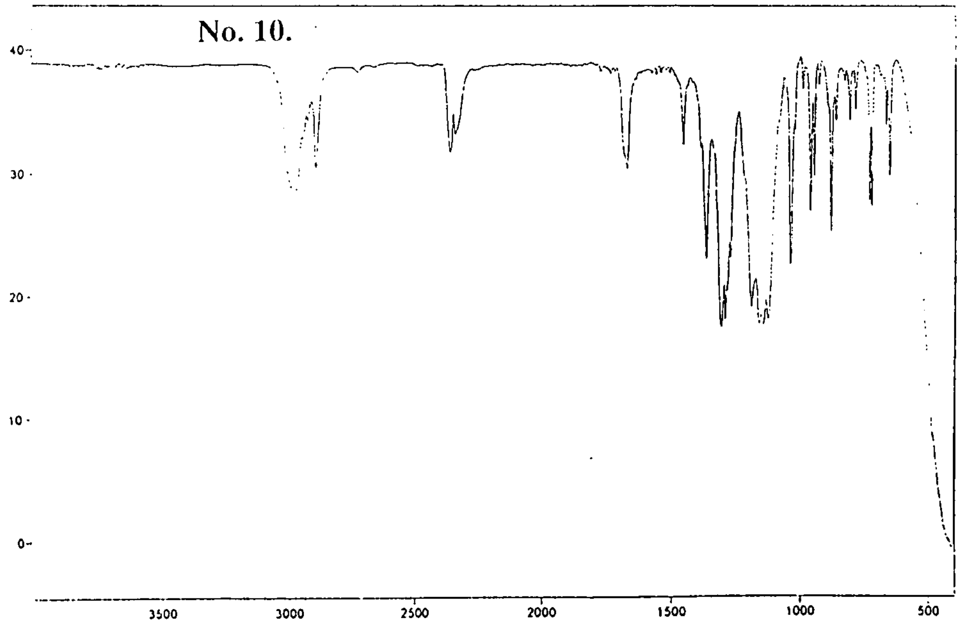
No. 8.



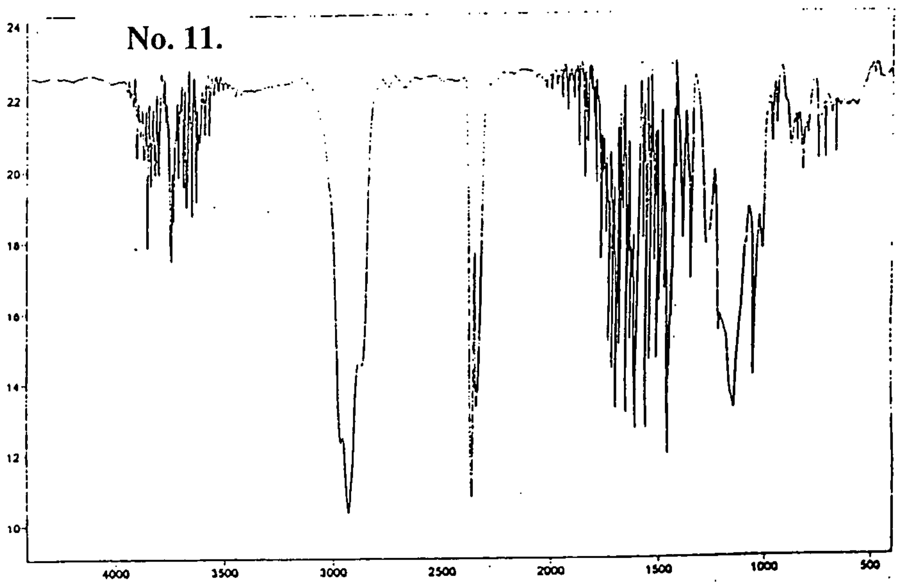
No. 9.



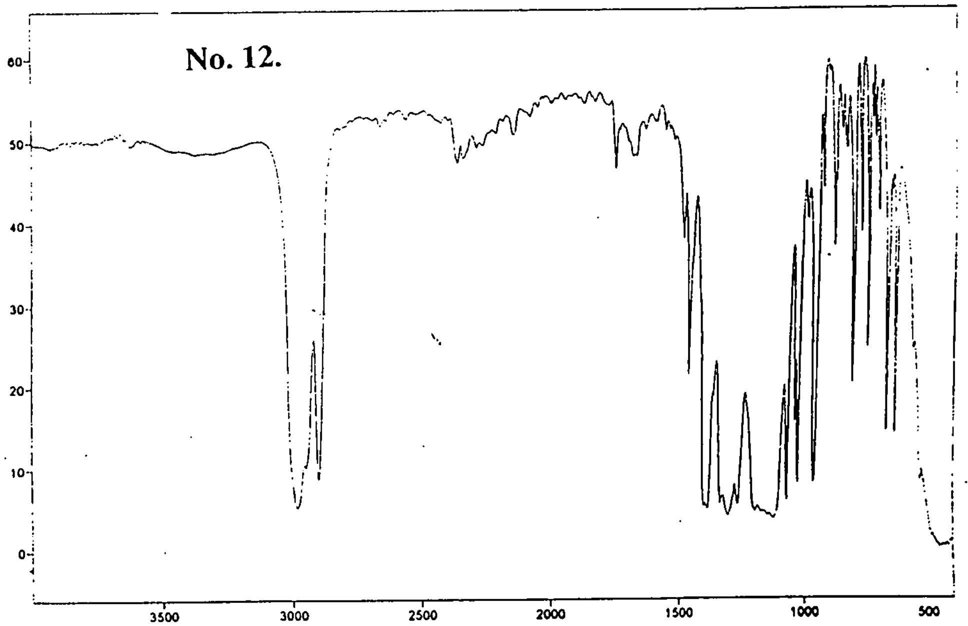
No. 10.

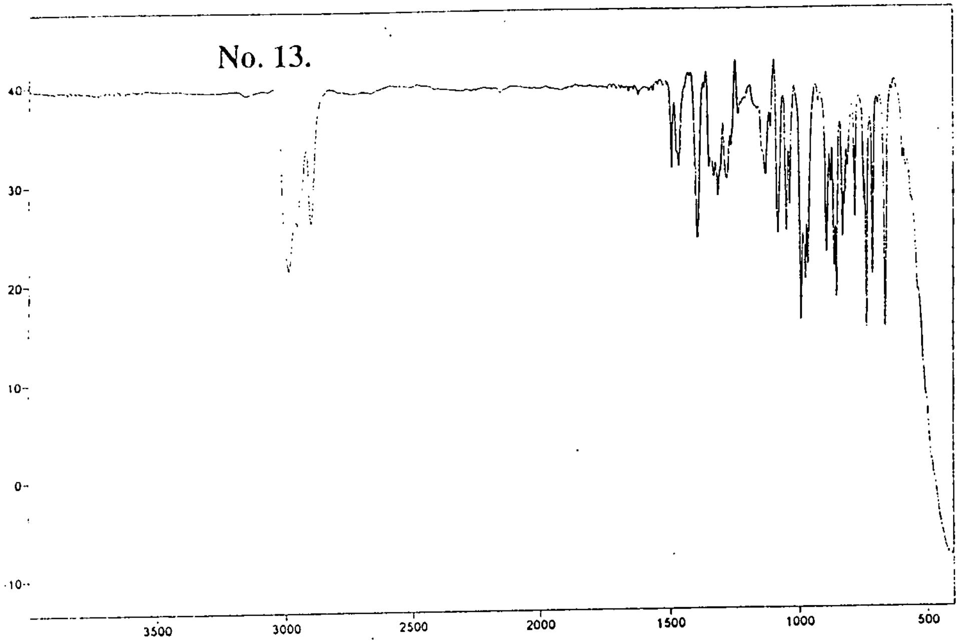


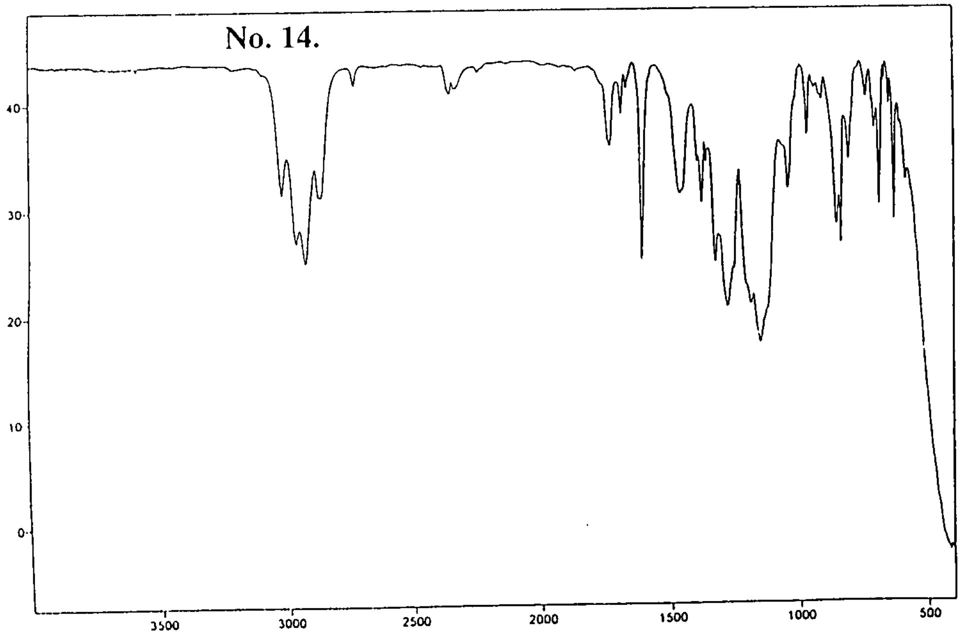
No. 11.

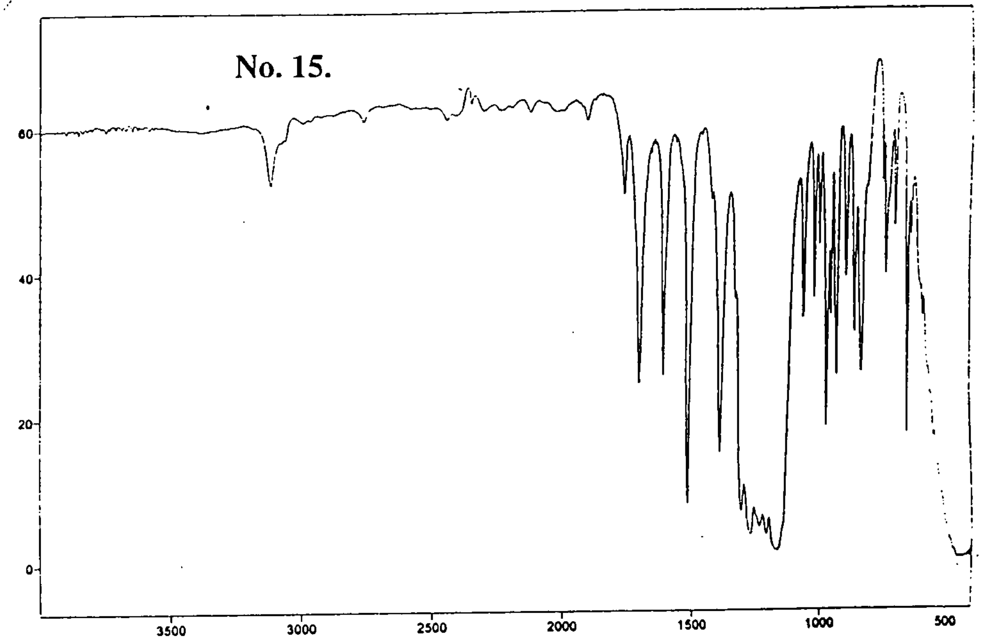


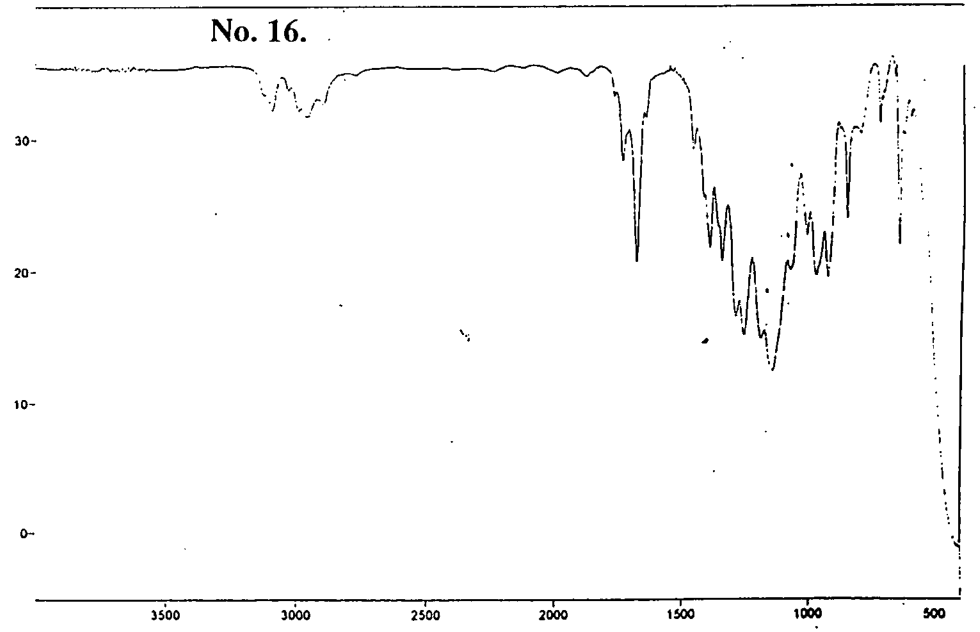
No. 12.



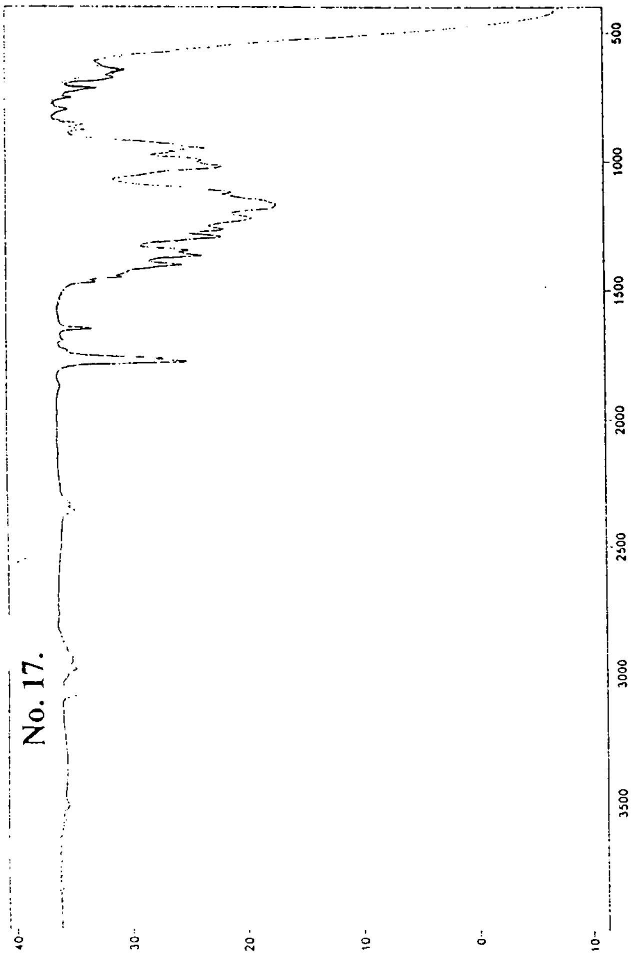

No. 13.


No. 14.

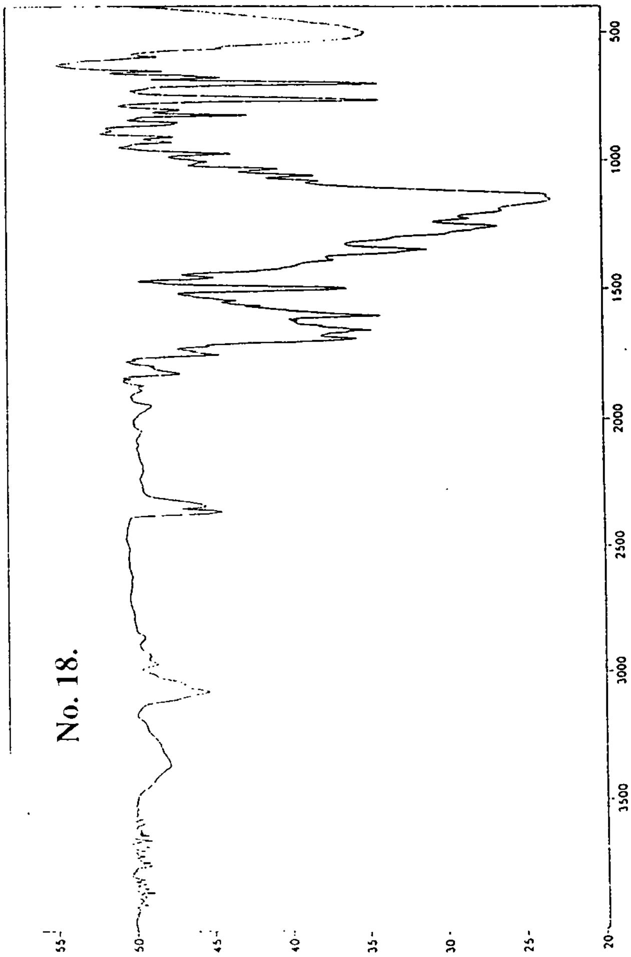

No. 15.


No. 16.

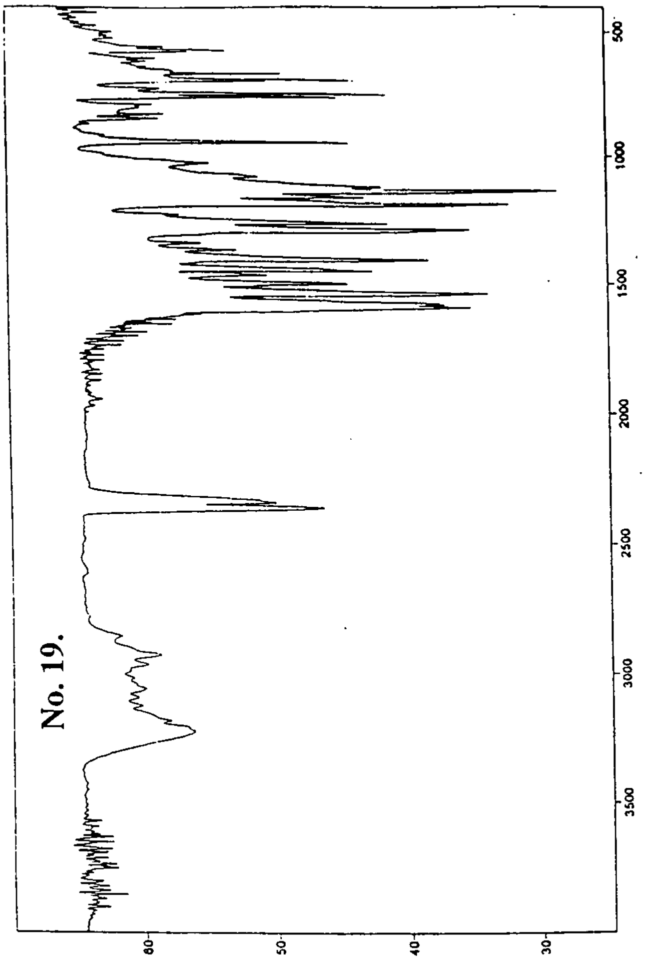
No. 17.



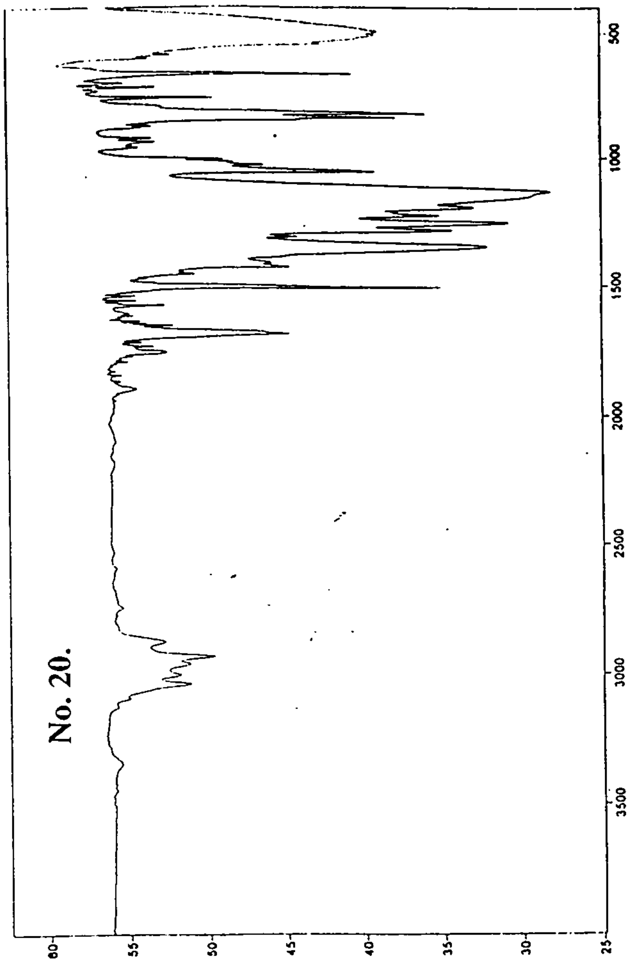
No. 18.

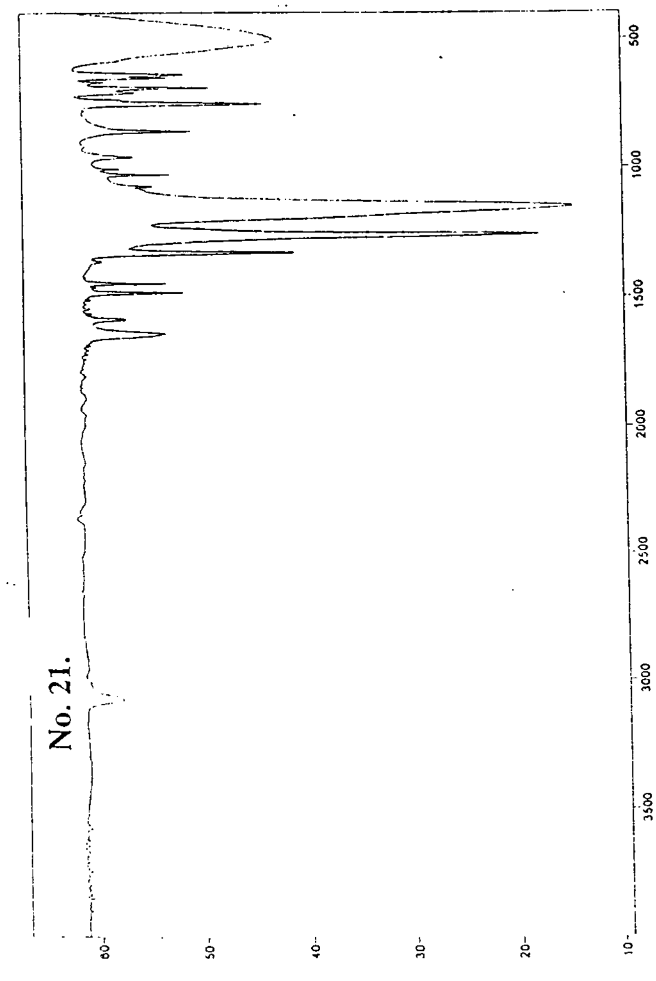


No. 19.

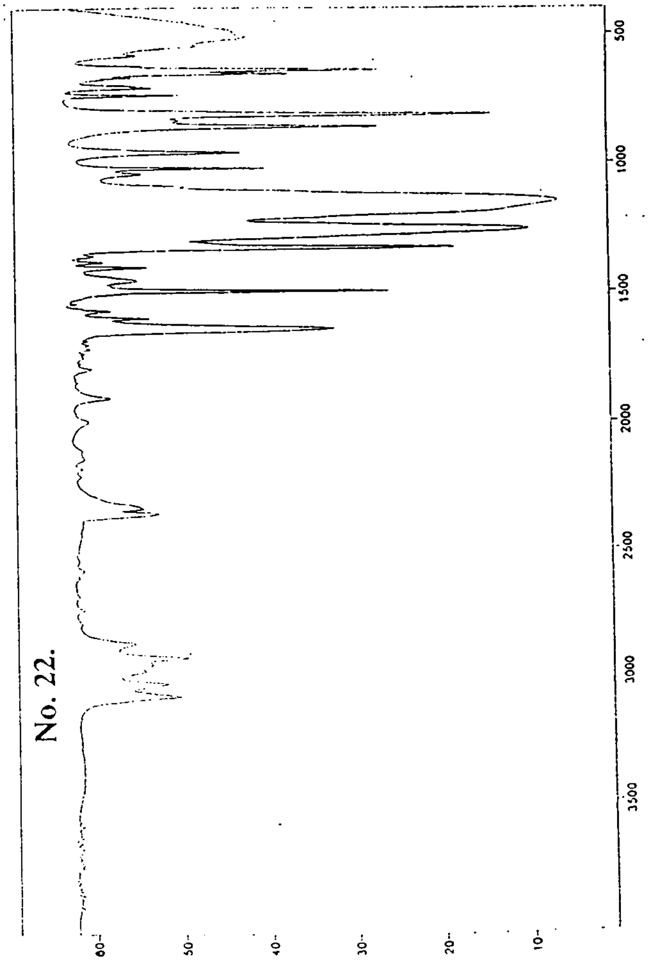


No. 20.

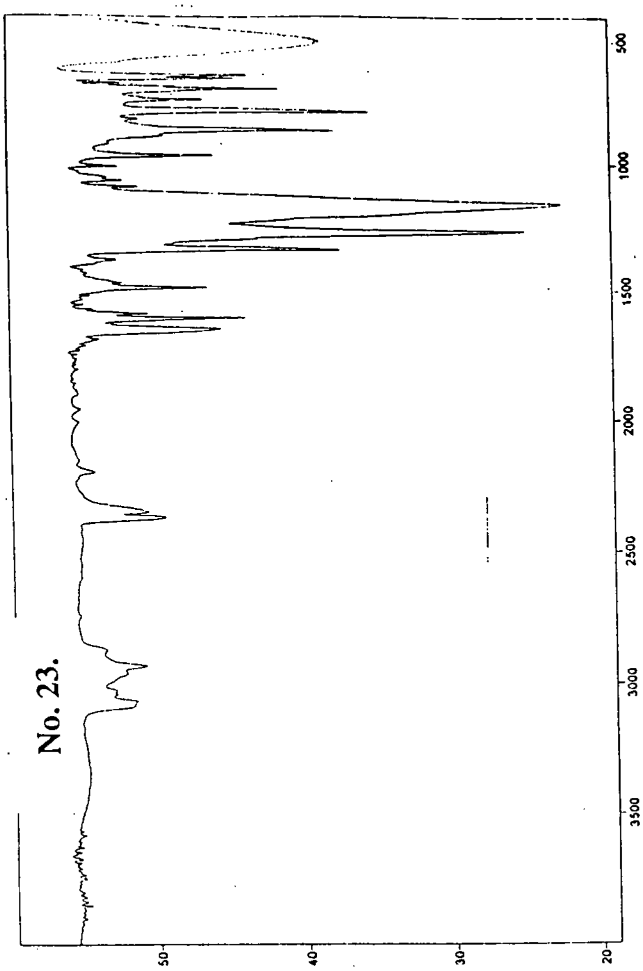




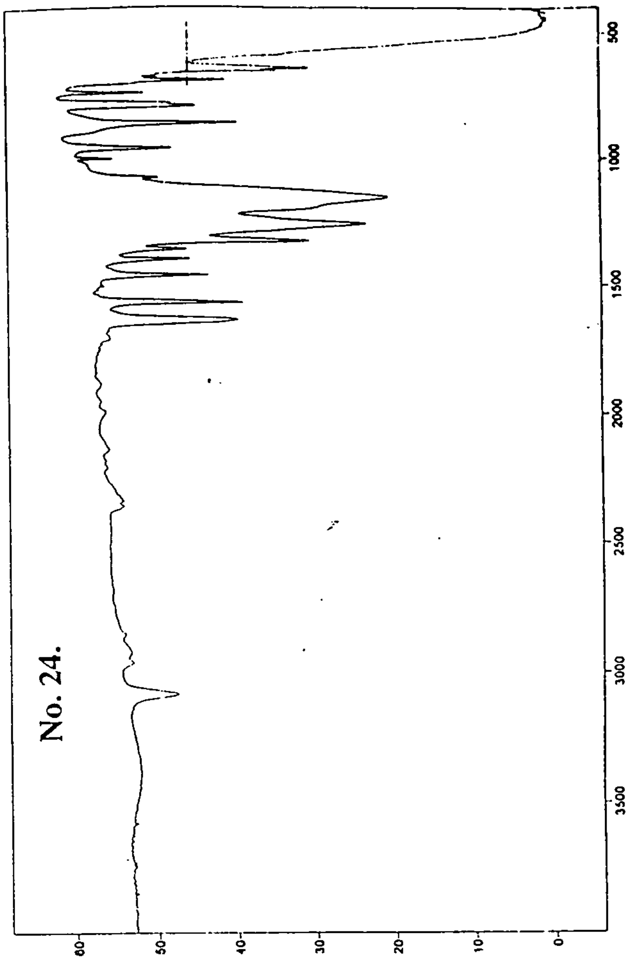
No. 21.



No. 22.

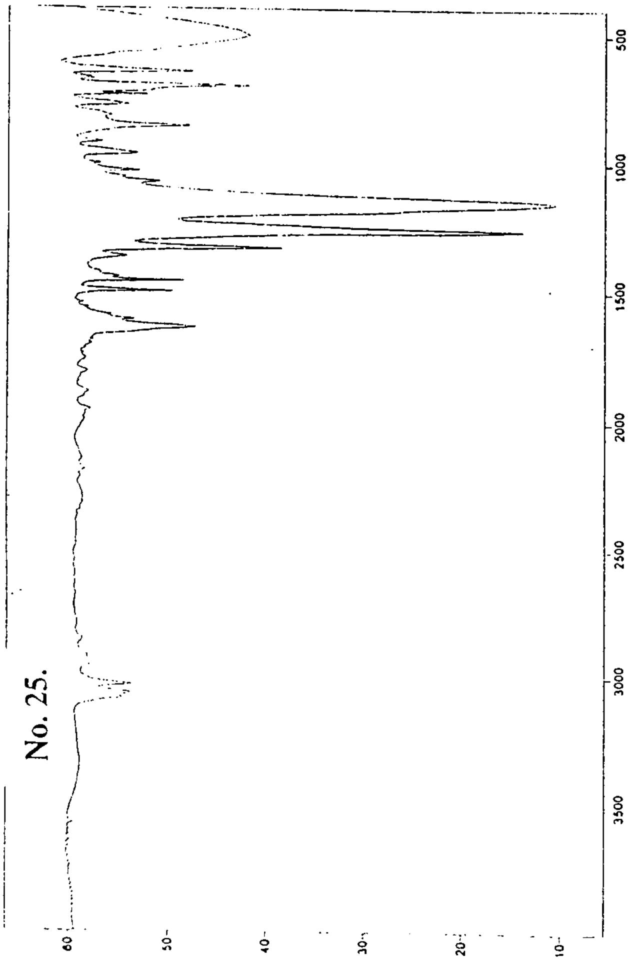


No. 23.

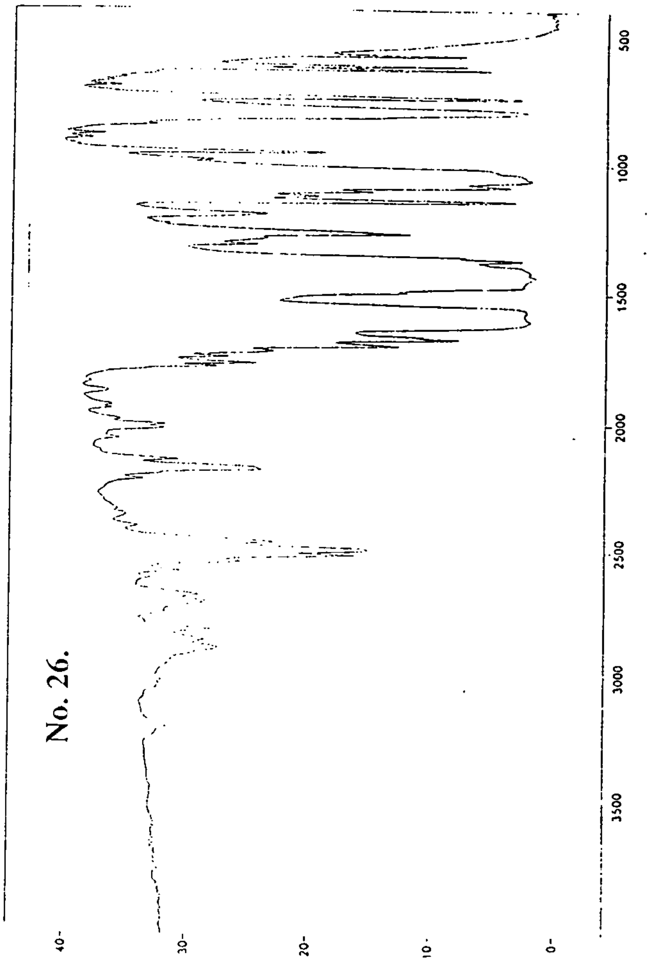


No. 24.

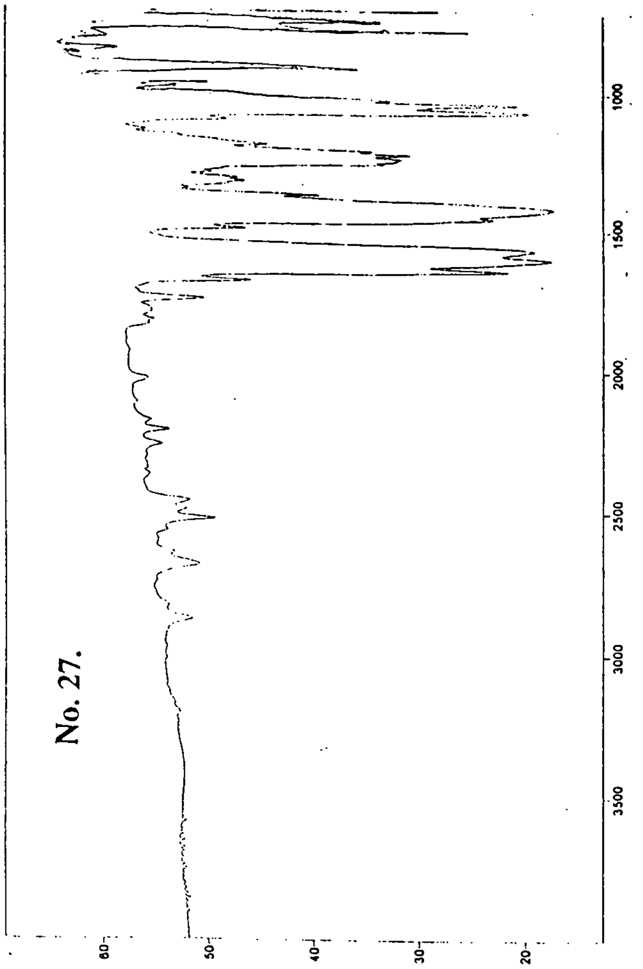
No. 25.



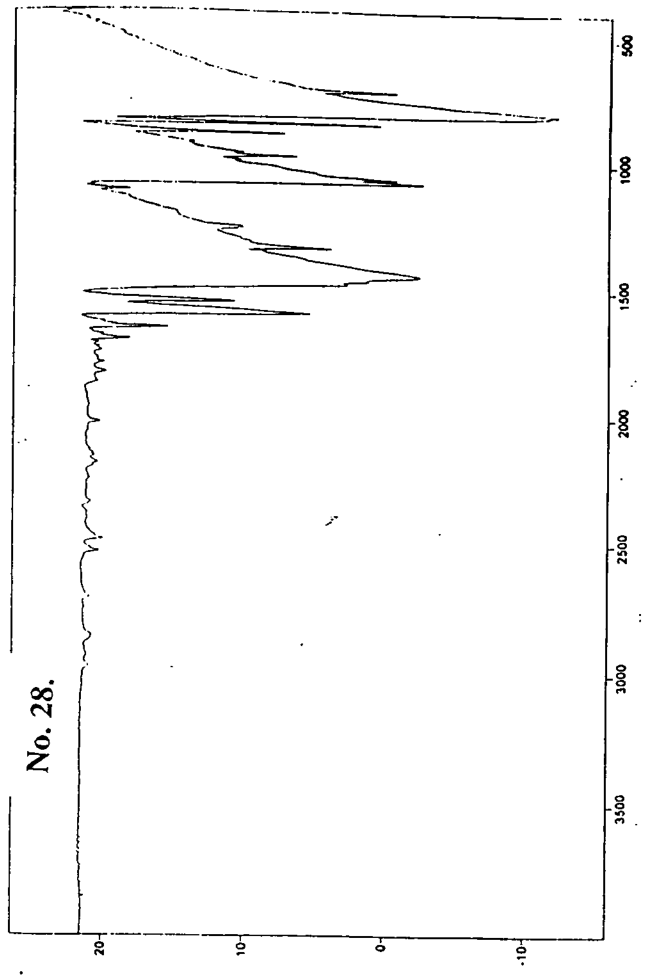
No. 26.



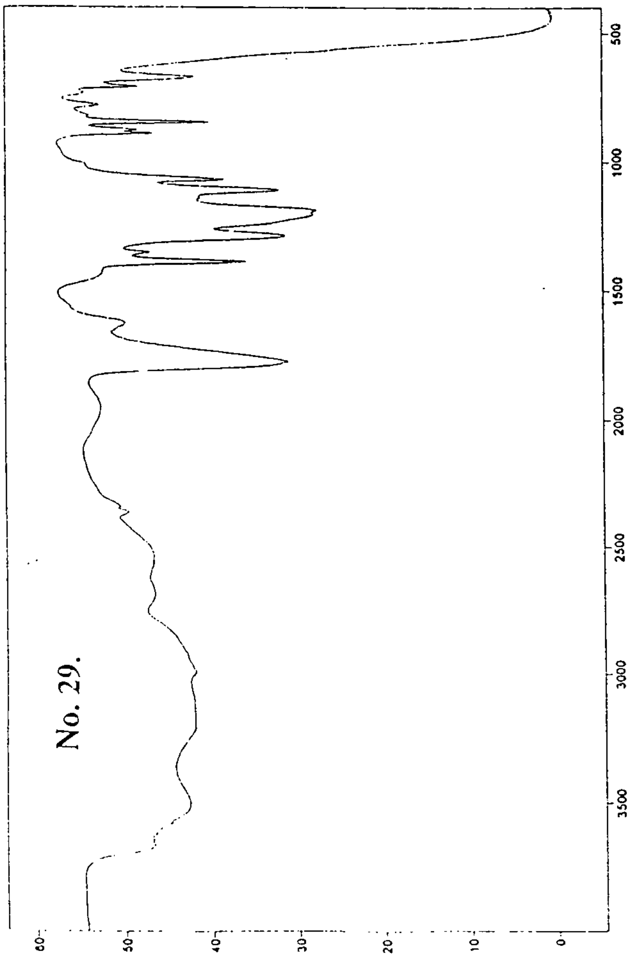
No. 27.



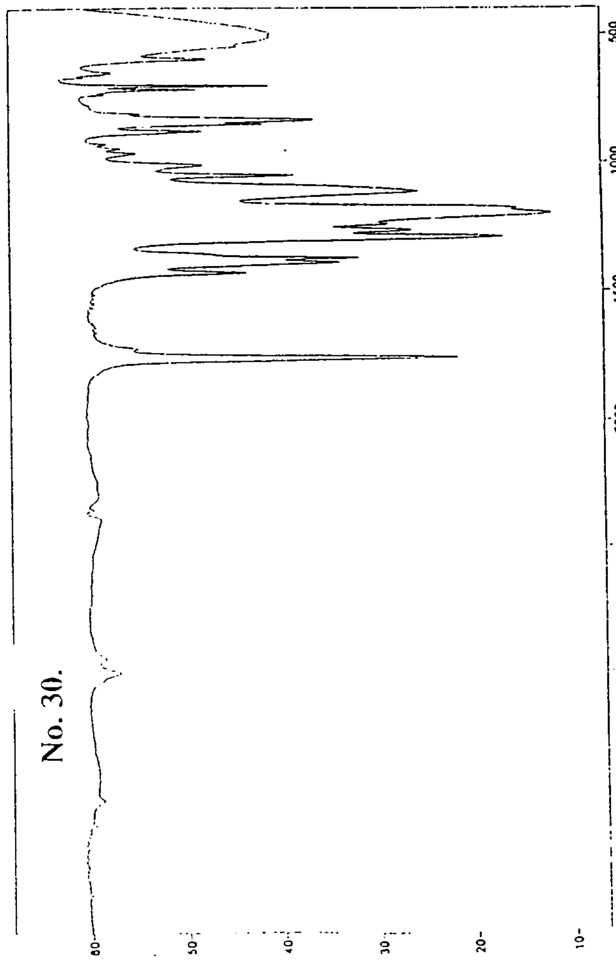
No. 28.



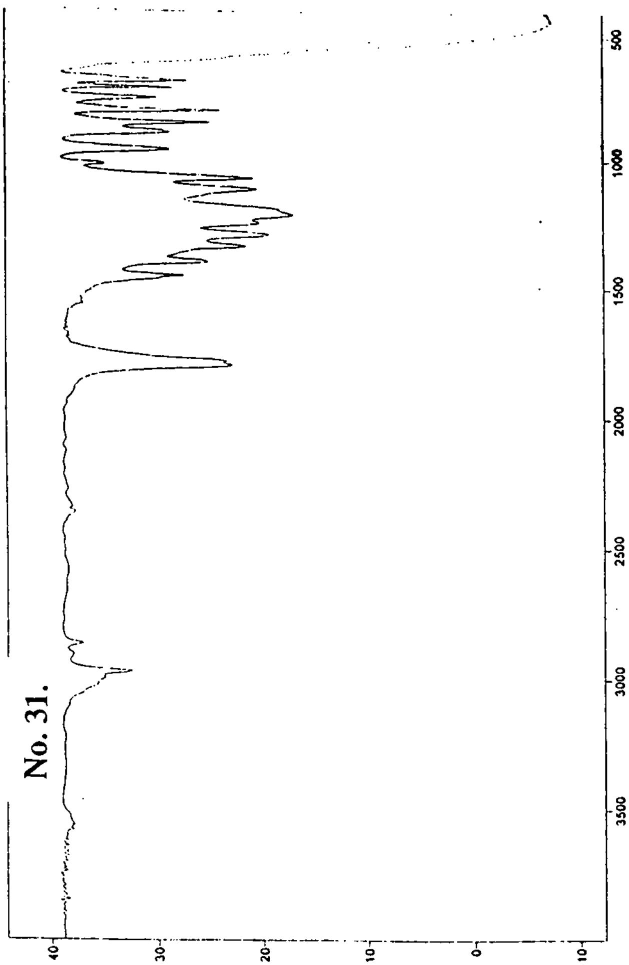
No. 29.



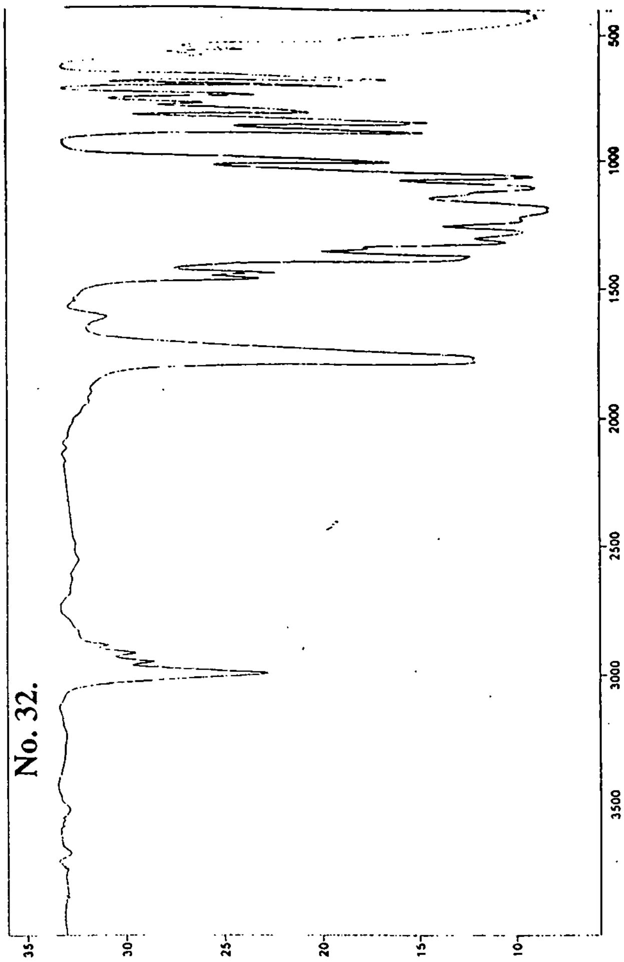
No. 30.



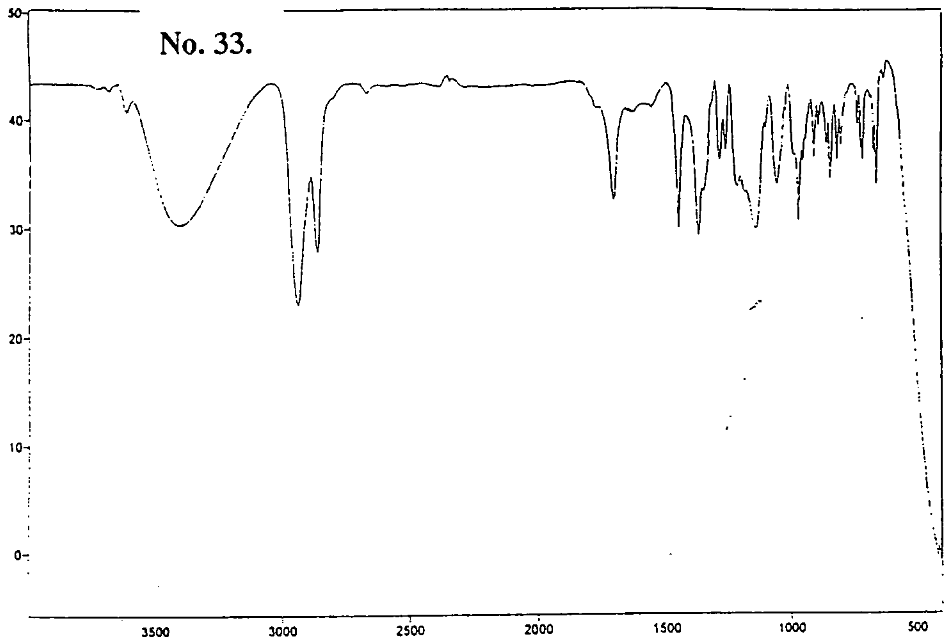
No. 31.



No. 32.



No. 33.

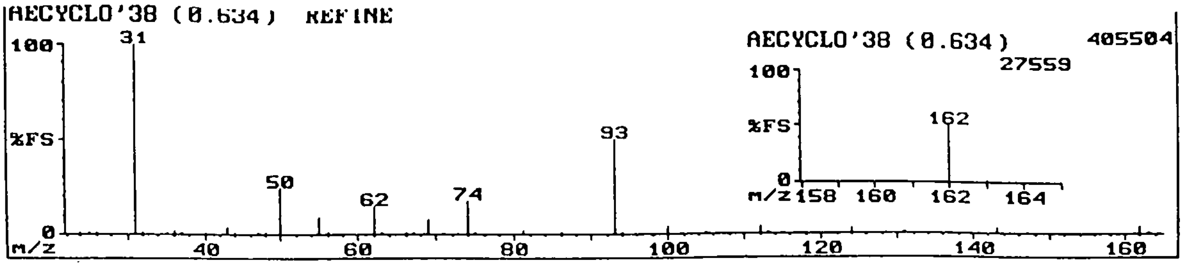


Appendix 3.

Mass Spec. Data

No.	Name
1	hexafluorocyclobutene (**2**)
2	octafluorocyclopentene (**3**)
3	hexafluorobut-2-yne (**4**)
4	*cis- and trans* octafluorobut-2-ene (**6**)
5	2*H*-heptafluorobut-2-ene (**10**)
6	2,2,3,4,4,4-hexafluorobutan-1-ol (**17**)
7	3,4-bis(trifluoromethyl)furan (**18**)
8	1,2-bis(trifluoromethyl)benzene (**20**)
9	2,3-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2,5-diene (**25**)
10	1,2-bis(trifluoromethyl)-4,5-dimethylbenzene (**34**)
11	2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2,5-diene (**38**)
12	*endo*-5-fluoro-5,6-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2-ene (**42**)
13	*exo*-5-fluoro-5,6-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2-ene (**43**)
14	*endo*-5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**44**)
15	*exo*-5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**45**)
16	bis(trifluoromethyl)cyclopentadiene (**46a-c**)
17	2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**47**)
18	*endo,endo*-1,2-bis(trifluoromethyl)bicyclo[2.2.1]heptane (**49**)
19	2,5-dimethyl-3,4-bis(trifluoromethyl)furan (**48**)
20	*endo*-2-fluoro-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane (**50**)
21	*exo*-2-fluoro-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane (**51**)
22	11,12-bis(trifluoromethyl)-9,10-dihydro-9,10-ethenoanthracene (**53**)
23	1,2,3-tris(trifluoromethyl)benzene (**54**)
24	2,4,6-trimethyl-7(or 8)-fluoro-7,8-bis(trifluoromethyl)bicyclo[2.2.1]octa-2,5-diene (**55ab**)
25	2,4,6-trimethyl-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene (**56**)
26	1,2-bis(trifluoromethyl)-3,5-dimethylbenzene (**57**)
27	bis(trifluoromethyl)methylenedi-*p*-phenylenedioxy-2,2'-bis(1,1,1,4,4,4-hexafluorobut-2-ene (**63**)
28	[*Z*-1-trifluoromethyl-3,3,3-trifluoroprop-1-enyl]prop-2-enyl ether (**58**)
29	1,1,1-trifluoro-3-trifluoromethyl-5-hexen-2-one (**59**)
30	1,1,1,4,4,4-hexafluoro-2-phenyliminobutane (**64**)
31	4-(*N*-Phenylamino)-2-trifluoromethylquinoline (**65**)
32	1,1,1,4,4,4-hexafluoro-2-(4-methylphenylimino)butane (**67**)

33	*Z*-1,1,1,4,4,4-hexafluoro-2-phenylthiobut-2-ene (**68**)
34	*Z*-1,1,1,4,4,4-hexafluoro-2-(4-methylphenylthio)but-2-ene (**69**)
35	*Z*-1,1,1,4,4,4-hexafluoro-2-(3-methylphenylthio)but-2-ene (**70**)
36	1,3-bis(*Z*-3,3,3-trifluoro-1-trifluoromethylprop-2-enylthio)benzene (**71**)
37	*Z*-1,1,1,4,4,4-hexafluoro-2-(phenylmethylthio)but-2-ene (**72**)
38	*Z*-2-cyclopentylthio-1,1,1,4,4,4-hexafluorobut-2-ene (**73**)
39	3,5-dichloroperfluoropyridine
40	5-chloroperfluoropyrimidine
41	1,3,5-trichloro-2,4,6-trifluorobenzene
42	2,2,3,4,4,4-hexafluorobutanoic acid (TMS ester) (**82**)
43	3,3,4,5,5,5-hexafluoropentan-2-one (**83**)
44	methyl 2,2,3,4,4,4-hexafluorobutanoate (**84**)
45	ethyl 2,2,3,4,4,4-hexafluorobutanoate (**85**)
46	1-(pentafluoroprop-1-enyl)-cyclohexanol (**86a**)
47	5-hydroxy-5-trifluoromethylisoxazolidin-3-one (**90**)

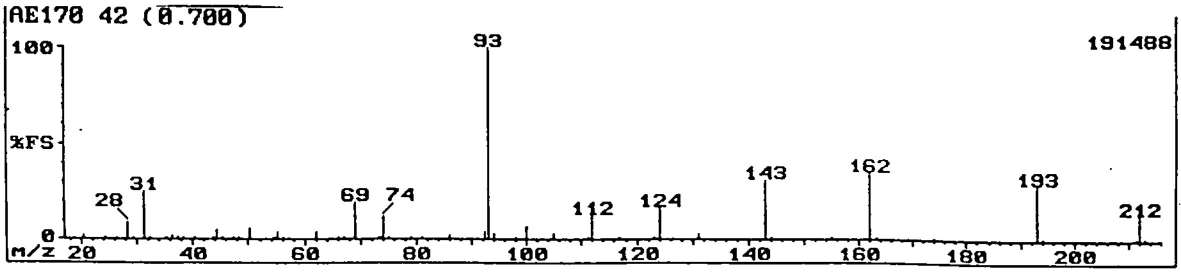


AECYCLO'38 (0.634) REFINE

40

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
24	0.94	43	4.36	66	1.06	100	3.91
25	0.14	44	1.26	67	0.14	105	0.08
26	0.23	47	0.77	69	7.77	112	3.85
31	100.00	48	0.14	74	17.17	113	0.08
32	0.73	50	23.99	75	0.40	124	2.76
35	0.28	55	8.84	81	1.47	131	0.35
36	1.82	56	0.27	86	0.34	143	3.35
37	0.17	62	14.52	93	49.24	162	3.44
40	0.13	63	0.16	94	1.45	163	0.03

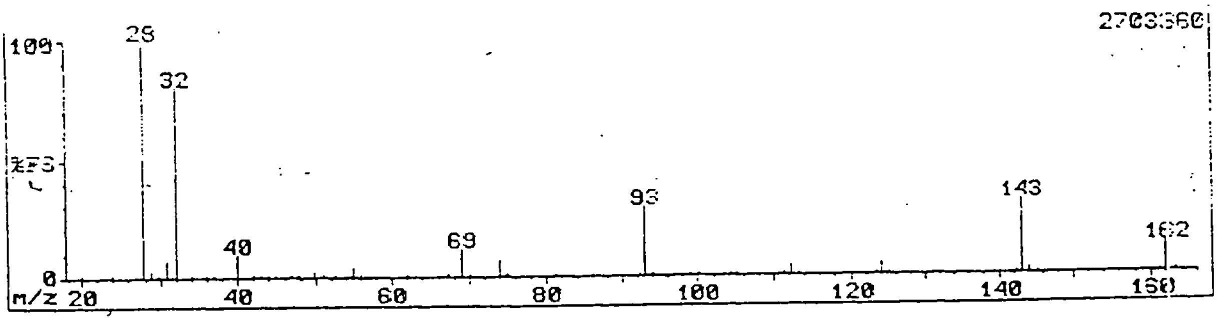
No. 2.



AE170 42 (0.700) 1914

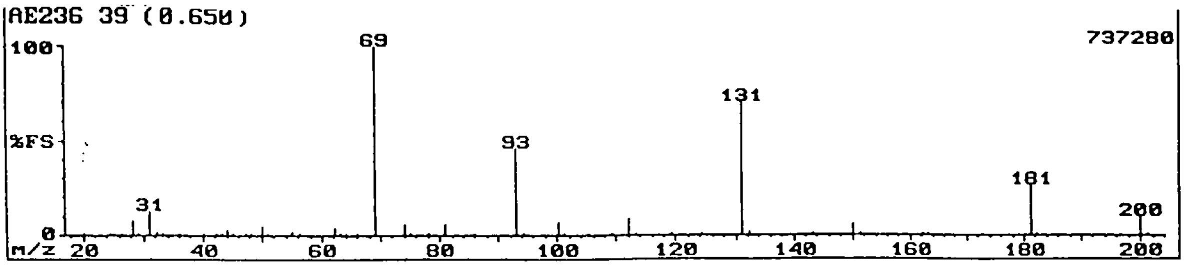
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.55	45	0.16	79	0.22	131	3.28
24	0.17	47	0.73	81	1.45	143	31.42
26	0.22	48	0.21	86	1.68	144	0.57
28	9.09	50	5.55	92	4.11	155	0.88
29	0.22	54	0.29	93	100.00	162	35.29
31	25.27	55	4.21	94	3.18	163	1.31
32	1.30	56	0.18	98	0.36	174	0.67
35	1.01	62	3.64	100	6.45	193	28.74
36	1.46	66	0.22	105	2.44	194	1.18
37	0.35	67	0.24	111	0.62	211	0.89
38	0.48	69	19.65	112	13.10	212	13.37
40	0.18	73	0.50	117	0.62	213	0.59
43	0.58	74	11.23	123	0.57		
44	5.08	75	0.55	124	16.31		

No. 3.



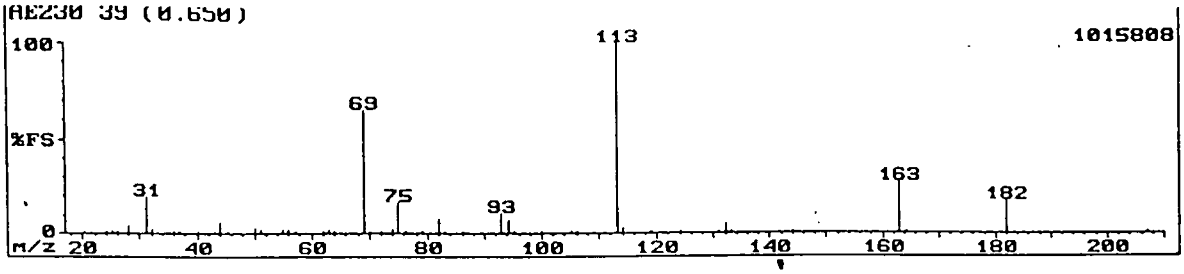
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.05	32	80.61	43	0.32	51	0.04	69	11.97	92	0.42	111	0.05	131	0.14	162	12.58
24	0.14	34	0.49	44	1.08	52	0.03	70	0.15	93	28.94	112	3.90	142	0.57	163	0.58
28	100.00	36	0.96	45	0.02	55	3.98	74	6.86	94	0.99	113	0.14	143	31.06		
29	2.55	37	0.05	47	0.02	56	0.14	75	0.35	100	0.02	123	0.07	144	1.51		
30	0.27	40	9.36	48	0.09	52	0.39	81	0.22	104	0.01	124	5.00	145	0.04		
31	6.57	42	0.13	50	2.23	57	3.32	86	0.22	105	0.20	125	0.22	161	0.37		

No. 4.

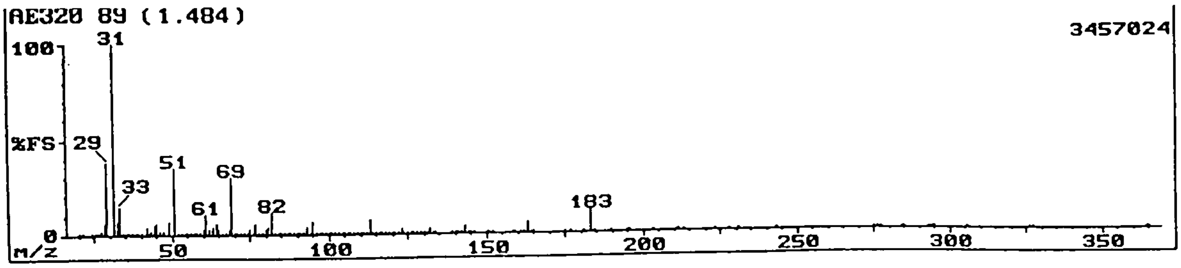


```
                  -----------------------------------------------------------------
AE236 39 (0.650)                                                                 737
----------------+------------------+------------------+----------------
Mass    Rel Int  | Mass    Rel Int  | Mass    Rel Int  | Mass    Rel Int
----------------+------------------+------------------+----------------
  20       0.20  |  44        2.47  |  74        6.25  |  119       0.12
  24       0.05  |  45        0.09  |  75        0.33  |  124       0.25
  25       0.04  |  47        0.24  |  78        0.03  |  131      70.00
  26       0.07  |  48        0.03  |  81        6.18  |  132       2.08
  28       7.64  |  50        5.10  |  86        0.13  |  143       0.39
  29       0.15  |  51        0.14  |  93       45.56  |  150       6.22
  31      12.50  |  55        2.01  |  94        0.60  |  151       0.18
  32       1.80  |  56        0.07  | 100        6.91  |  162       0.46
  33       0.02  |  62        3.82  | 101        0.18  |  163       0.07
  36       0.26  |  63        0.15  | 105        0.04  |  181      26.25
  40       0.18  |  64        0.05  | 109        0.06  |  182       0.94
  42       0.05  |  66        0.08  | 112        8.33  |  200      10.14
  43       0.95  |  69      100.00  | 113        0.39  |  201       0.35
```

No. 5.

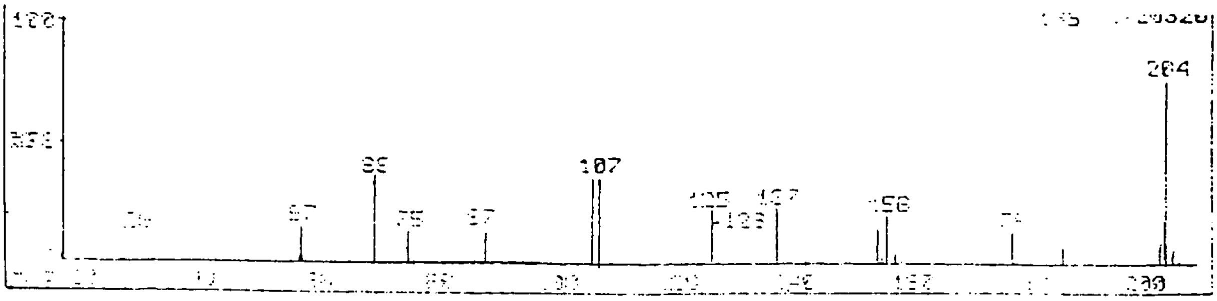


```
AE230 39 (0.650)                                                                        101
-----------------+-----------------+-----------------+-----------------
Mass    Rel Int  | Mass    Rel Int | Mass    Rel Int | Mass    Rel Int
-----------------+-----------------+-----------------+-----------------
 20      0.07    |  50      3.07   |  76      0.49   | 119      0.24
 24      0.23    |  51      2.27   |  79      0.02   | 124      0.29
 25      0.59    |  55      1.47   |  82      7.76   | 131      0.86
 26      0.07    |  56      1.66   |  83      0.17   | 132      4.46
 28      3.40    |  57      0.05   |  86      0.09   | 133      0.51
 31     19.56    |  62      0.38   |  93     10.79   | 144      0.72
 32      1.59    |  63      1.57   |  94      6.55   | 163     27.02
 36      0.25    |  64      0.25   |  95      0.45   | 164      0.75
 37      0.59    |  69     64.92   | 100      0.57   | 182     17.24
 40      0.07    |  70      0.69   | 105      0.05   | 207      0.09
 43      0.47    |  72      0.66   | 106      0.04   |
 44      5.75    |  74      2.19   | 113    100.00   |
 45      0.20    |  75     16.33   | 114      2.77   |
-----------------+-----------------+-----------------+-----------------
```



AE320 89 (1.484) 3457

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.42	65	2.67	104	0.01	150	0.31
21	0.04	66	0.19	105	0.04	151	0.56
24	0.20	67	0.71	106	0.02	152	0.02
25	0.41	68	3.26	107	0.02	158	0.00
26	1.16	69	0.33	108	0.01	159	0.03
27	1.98	70	0.40	109	0.06	161	0.19
28	5.98	71	0.27	110	0.09	162	0.65
29	37.91	72	0.21	111	0.22	163	5.60
31	100.00	73	1.44	112	0.99	164	0.15
32	6.34	74	0.82	113	7.49	165	0.47
33	14.69	75	2.87	114	0.63	175	0.01
34	0.31	76	0.96	115	0.87	177	0.02
35	0.04	77	5.39	116	0.03	181	0.04
36	0.10	78	0.36	117	0.01	183	11.49
37	0.36	79	0.47	118	0.01	184	0.21
38	0.43	80	2.99	119	0.04	190	0.01
39	0.39	81	3.85	120	0.00	195	0.22
40	0.09	82	11.85	121	0.02	195	0.20
42	3.88	83	1.18	122	0.29	203	0.02
43	1.50	84	0.02	123	3.14	211	0.01
44	4.59	85	0.05	124	0.17	211	0.01
45	5.57	86	0.01	125	0.03	213	0.12
46	2.25	87	0.03	126	0.04	223	0.11
47	1.73	88	0.03	127	0.16	228	0.01
49	6.43	89	0.02	128	0.11	231	0.01
51	34.60	90	0.11	129	0.02	243	0.11
52	0.59	91	0.97	130	0.07	275	0.02
53	0.50	92	0.41	131	0.50	276	0.01
54	0.08	93	3.41	132	2.43	277	0.03
55	0.58	94	1.34	133	0.44	284	0.01
56	0.59	95	6.87	134	0.01	285	0.06
57	1.12	96	0.28	139	0.01	293	0.00
58	0.16	97	0.02	140	0.04	294	0.03
59	0.16	98	0.06	141	0.37	295	0.03
60	2.46	99	0.13	142	0.43	305	0.01
61	10.43	100	0.72	143	4.24	326	0.01
62	2.67	101	0.67	144	0.18	327	0.04
63	4.32	102	0.01	145	0.17	364	0.01
64	6.04	103	0.03	146	0.03	365	0.08

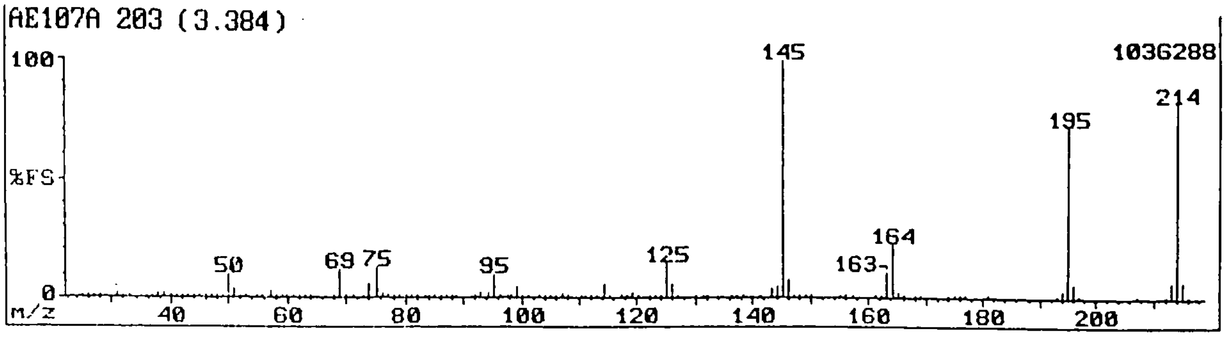


[illegible]

172032[illegible]

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
[illegible]	[illegible]	[illegible]	[illegible]	61	0.15	77	0.03	95	1.01	112	1.62	130	0.01	153	1.58	184	4.17
[illegible]	[illegible]	[illegible]	[illegible]	62	0.32	79	0.31	96	0.05	113	3.29	131	0.13	154	14.82	185	100.00
[illegible]	[illegible]	[illegible]	[illegible]	63	0.75	80	0.23	97	0.01	114	0.23	133	0.04	155	2.26	186	7.00
[illegible]	[illegible]	[illegible]	[illegible]	64	1.35	81	0.32	98	0.40	115	1.32	134	0.51	156	21.43	187	0.46
[illegible]	[illegible]	[illegible]	[illegible]	65	0.19	82	2.23	99	1.44	116	0.71	135	0.21	157	4.05	202	0.17
[illegible]	[illegible]	[illegible]	[illegible]	66	0.15	83	1.52	100	0.32	117	2.16	136	1.52	158	0.21	203	0.51
[illegible]	[illegible]	[illegible]	[illegible]	67	0.46	85	0.05	102	0.04	118	0.39	137	34.05	159	0.05	204	79.05
[illegible]	[illegible]	[illegible]	[illegible]	68	5.60	86	1.41	103	0.03	119	0.46	138	1.55	163	0.03	205	5.65
[illegible]	[illegible]	[illegible]	[illegible]	69	35.43	87	15.95	104	0.19	120	0.03	139	0.24	165	0.11	206	0.38
[illegible]	[illegible]	[illegible]	[illegible]	70	0.55	88	12.52	105	1.93	121	0.22	140	0.45	166	0.14		
[illegible]	[illegible]	[illegible]	[illegible]	71	1.41	89	0.22	106	34.52	122	0.02	141	0.05	167	0.02		
[illegible]	[illegible]	[illegible]	[illegible]	72	0.10	90	2.68	107	33.10	123	0.03	142	0.04	174	0.35		
[illegible]	[illegible]	[illegible]	[illegible]	73	0.03	91	1.12	108	1.76	124	1.26	143	0.95	175	9.23		
[illegible]	[illegible]	[illegible]	[illegible]	74	1.26	92	0.05	109	0.06	125	22.66	144	0.06	176	14.23		
[illegible]	[illegible]	[illegible]	[illegible]	75	14.70	93	5.60	110	0.81	126	14.46	145	0.03	177	0.01		
[illegible]	[illegible]	[illegible]	[illegible]	76	0.75	94	0.92	111	0.06	127	0.67	152	0.05	183	0.04		

No. 8.

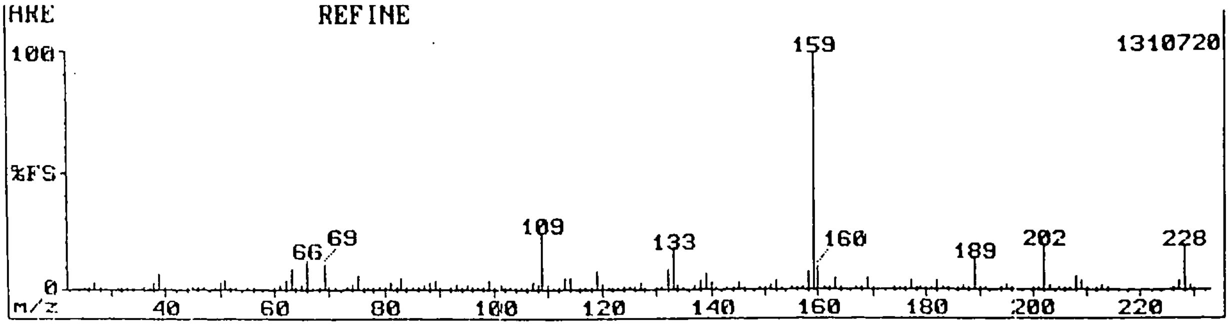


AE107A 203 (3.384)

103

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	43	0.10	59	0.03	78	0.05	95	9.98	112	0.39	131	0.03	156	0.26	193	0.13
26	0.30	44	0.26	60	0.07	79	0.38	96	0.68	113	1.08	132	0.10	157	0.06	194	2.67
27	0.46	45	0.12	61	0.91	80	0.86	97	0.72	114	5.73	136	0.04	161	0.11	195	71.54
28	0.81	46	0.03	62	1.24	81	1.35	98	0.08	115	0.39	137	0.38	162	0.31	196	5.76
29	0.04	47	0.04	63	0.94	82	0.08	99	5.19	117	0.36	138	0.09	163	10.38	197	0.23
31	1.93	48	0.07	64	0.11	83	0.04	100	1.30	118	0.52	141	0.05	164	22.43	207	0.04
32	0.36	49	0.91	68	0.99	84	0.08	101	0.48	119	2.32	143	4.13	165	1.63	212	0.05
33	0.07	50	9.39	69	11.26	85	0.41	103	0.21	120	0.15	144	4.72	166	0.07	213	6.72
36	0.09	51	4.32	70	0.44	86	0.37	104	0.43	122	0.04	145	100.00	168	0.05	214	81.42
37	1.27	52	0.36	71	0.05	87	0.80	105	0.65	123	1.09	146	7.61	169	0.08	215	6.32
38	1.95	53	0.10	73	1.15	88	1.17	106	0.59	124	0.50	147	0.30	174	0.26	216	0.27
39	2.00	55	0.23	74	5.36	89	0.04	107	1.83	125	14.53	148	0.06	175	0.32		
40	0.12	56	0.69	75	12.85	92	0.43	108	0.15	126	6.23	149	0.86	176	0.93		
41	0.07	57	2.64	76	2.40	93	1.61	110	0.03	127	0.48	150	0.11	177	0.09		
42	0.04	58	0.10	77	0.36	94	1.70	111	0.17	130	0.10	155	0.39	181	0.08		

No. 9.

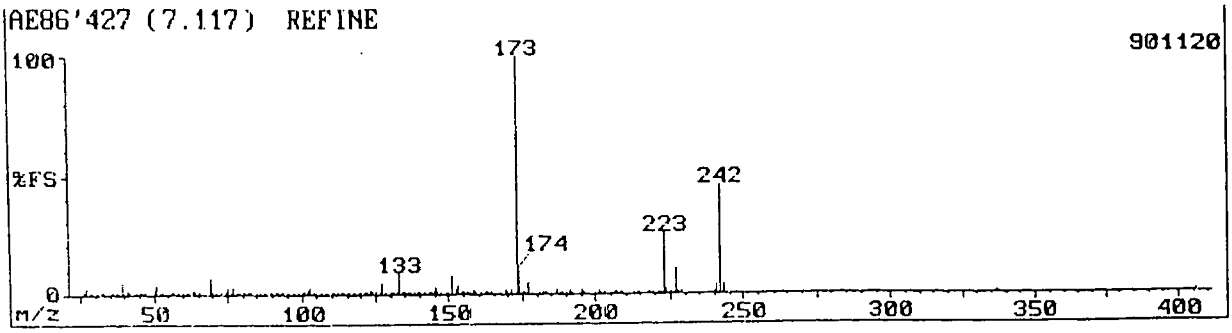


ARELIN'147 (2.450) REFINE

1

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	0.08	51	4.24	74	1.72	93	1.84	111	0.47	131	0.74	153	0.30	177	3.85	201	0.97
26	0.92	52	0.58	75	5.86	94	0.82	112	1.16	132	8.91	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	0.79	179	0.04	203	1.48
28	0.30	55	0.12	77	1.00	96	0.35	114	4.82	134	1.89	157	1.37	180	0.05	205	0.09
31	0.93	56	0.63	78	0.15	97	0.08	116	0.06	135	0.13	158	7.73	181	1.35	206	0.06
32	0.09	60	0.20	79	0.79	98	0.19	117	0.31	137	1.89	159	100.00	182	4.02	207	1.14
33	0.23	61	1.50	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	3.89	81	2.48	100	0.63	119	0.13	139	6.41	161	0.59	184	0.11	209	3.89
37	0.94	63	8.44	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	5.08	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	0.70	188	0.74	213	1.72
40	1.41	66	12.89	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	10.47	88	2.68	107	2.62	126	0.65	149	0.09	170	0.49	194	0.11	228	10.91
47	0.04	70	1.04	89	3.40	108	1.86	127	2.54	150	0.38	174	0.05	195	1.89	229	2.01
49	0.27	71	0.17	90	1.03	109	23.75	128	0.23	151	1.68	175	0.12	196	0.19	230	0.11
50	2.81	73	0.24	92	0.37	110	1.97	130	0.13	152	4.10	176	0.62	200	0.03		

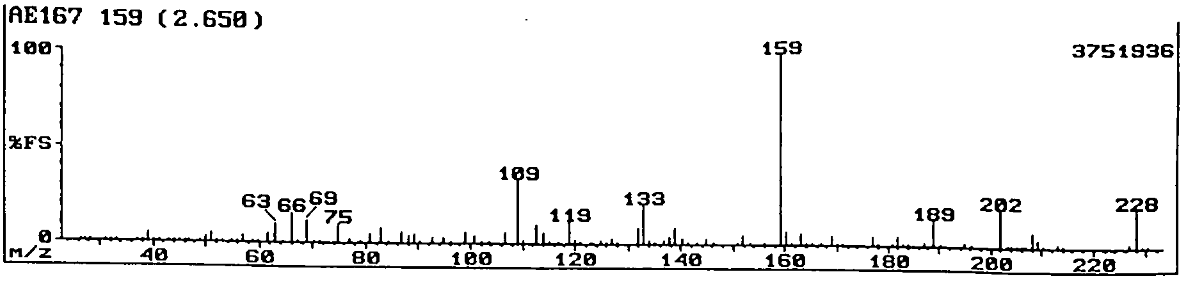
No. 10.



AE86'427 (7.117) REFINE 98

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	0.13	52	0.84	76	0.99	97	0.23	117	0.12	138	1.22	161	0.14	190	0.21	223	25.45
27	2.53	53	0.51	77	2.93	98	0.26	118	0.12	139	0.65	162	0.10	191	1.56	224	2.27
28	0.08	54	0.05	78	0.86	99	1.34	119	0.81	140	0.35	163	1.07	192	0.21	225	0.12
29	0.07	56	0.19	79	0.45	100	0.31	120	0.69	141	0.18	164	0.29	195	2.07	227	10.34
31	0.27	57	1.00	80	0.21	101	1.66	121	0.67	143	0.45	167	0.08	196	0.18	228	0.65
32	0.36	58	0.06	81	0.86	102	1.64	122	0.75	144	0.21	169	2.27	200	0.52	229	0.06
33	0.28	59	0.50	82	0.11	103	2.81	123	2.19	145	3.21	170	0.42	201	1.55	240	0.46
36	0.04	60	0.13	83	0.60	104	1.09	124	0.29	146	0.50	171	2.39	202	0.14	241	3.81
37	0.24	61	0.34	85	0.47	105	0.32	125	1.88	147	0.12	173	100.00	203	0.13	242	45.45
38	0.45	62	1.04	86	0.48	106	0.17	126	0.35	149	0.25	174	10.00	205	0.16	243	4.35
39	4.77	63	2.13	87	0.83	107	0.85	127	4.49	150	0.12	175	0.45	206	0.08	337	0.19
40	0.29	64	0.36	88	0.77	108	0.34	128	0.37	151	0.07	176	0.37	207	0.87	406	0.07
41	1.69	65	0.48	89	0.56	109	1.07	130	0.07	152	1.73	177	5.03	208	0.88		
42	0.08	66	0.09	90	0.08	110	0.08	131	0.34	153	3.44	178	0.45	209	0.40		
44	0.09	69	6.48	91	0.17	111	0.22	132	0.08	154	1.15	181	0.40	213	0.17		
45	0.13	70	0.31	92	0.14	112	0.45	133	9.20	155	0.18	182	0.59	214	0.17		
46	0.06	71	0.13	93	0.48	113	0.57	134	1.19	156	0.52	183	0.33	218	0.09		
47	0.12	73	0.12	94	0.21	114	0.57	135	0.16	157	0.60	187	1.88	219	0.36		
50	2.19	74	1.20	95	0.92	115	0.15	136	0.07	158	2.05	188	0.28	221	0.54		
51	4.06	75	3.21	96	0.63	116	0.02	137	0.65	159	0.56	189	0.35	222	0.38		

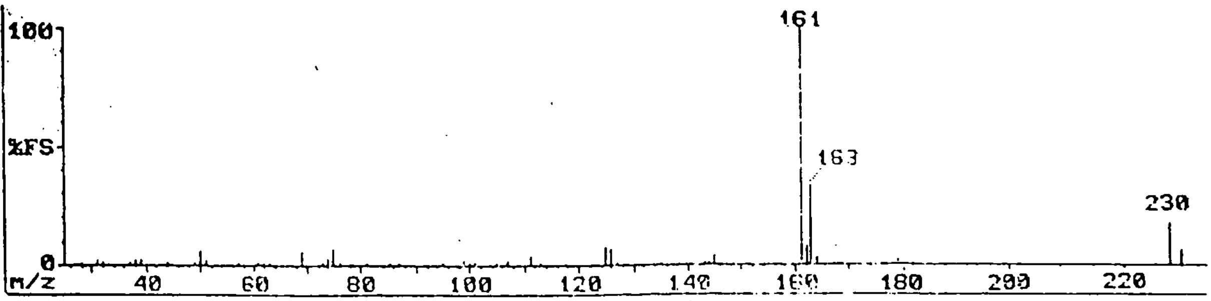
No. 11.



AE167 159 (2.650) 375

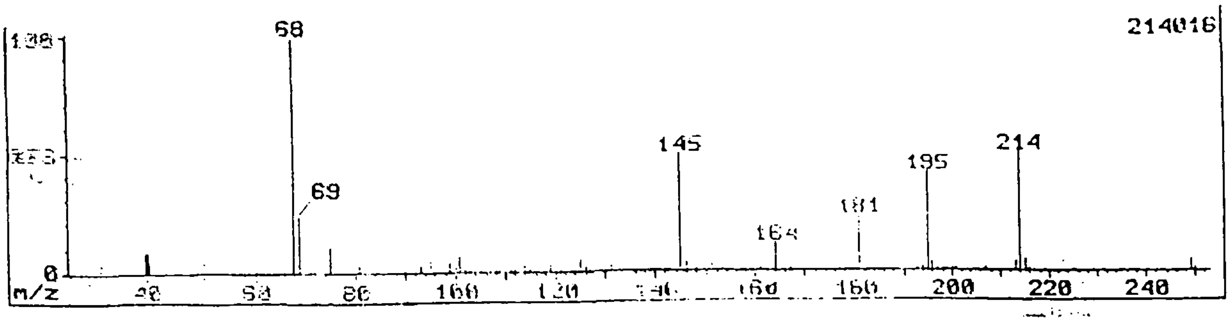
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.18	67	0.73	121	0.35	170	0.34
27	0.80	69	11.35	123	0.39	171	0.03
28	0.09	70	0.98	125	1.88	177	4.67
31	0.34	71	0.16	126	0.33	178	0.57
32	0.04	75	9.28	127	3.38	181	0.91
33	0.10	77	1.50	128	0.19	182	5.08
37	0.50	79	1.29	132	9.06	183	1.18
38	1.39	81	4.42	133	20.20	184	0.08
39	4.59	83	7.31	134	1.60	187	2.37
40	0.91	84	0.76	135	0.06	189	13.97
41	0.17	87	5.49	137	1.46	190	1.04
43	0.06	88	3.55	138	3.63	195	2.24
44	0.13	89	4.86	139	8.41	196	0.14
45	0.16	90	1.21	140	2.84	202	19.54
46	0.04	93	3.33	141	0.22	203	1.06
47	0.02	95	3.33	143	1.15	204	0.02
49	0.17	96	0.42	145	3.17	205	0.12
50	2.84	99	5.65	146	0.25	206	0.02
51	4.42	101	3.96	151	1.17	207	0.61
52	0.49	102	0.35	152	4.91	208	7.75
53	0.16	104	0.24	153	0.20	209	3.52
55	0.09	107	5.54	156	1.08	210	0.27
56	0.44	109	33.19	159	100.00	213	1.91
57	3.79	110	1.94	160	6.93	214	0.13
59	0.28	113	9.50	161	0.42	227	2.18
60	0.08	114	6.03	163	5.40	228	20.52
62	5.32	115	0.44	164	0.53	229	1.33
63	9.50	117	0.49	165	0.03	230	0.06
64	1.33	119	11.68	167	0.14		
66	15.94	120	1.97	169	4.91		

No. 12.



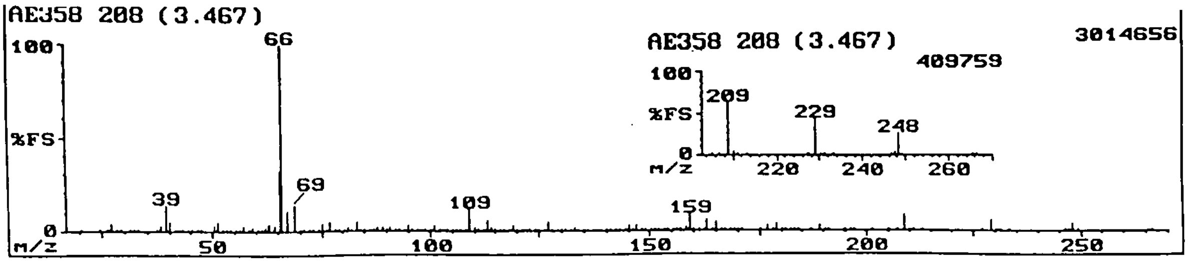
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	75	[illegible]	100	0.34	125	7.70	144	0.34	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	101	0.74	126	5.67	145	4.07	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.31	[illegible]	[illegible]	105	0.54	127	0.77	161	100.00	230	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.35	107	[illegible]	[illegible]	0.78	162	[illegible]	231	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.39	[illegible]	[illegible]	[illegible]	0.72	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.73	[illegible]	[illegible]	[illegible]	[illegible]

No. 13.



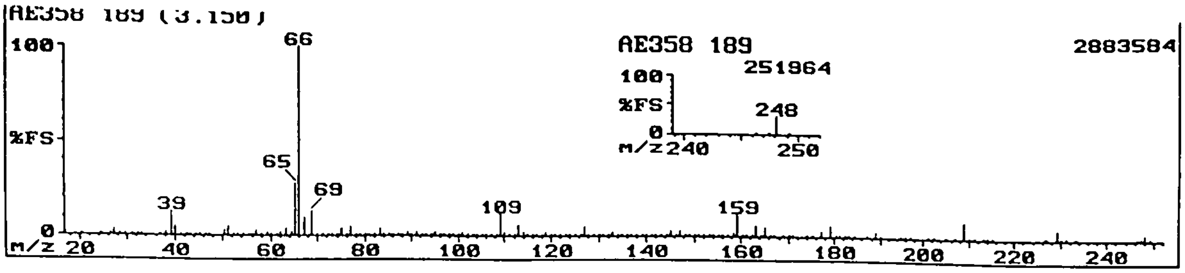
[illegible] REFINE

l Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rei Int	Mass	Rel Int	Mass	Rel Int	Mass	Rei Int
0.55	44	0.35	62	1.52	80	0.83	98	0.21	115	0.23	138	0.22	159	0.30	194	1.77
0.37	45	0.45	63	1.89	81	2.75	99	[illegible]	117	0.47	139	0.58	161	0.17	195	41.63
[illegible]	46	0.10	64	0.38	82	0.57	100	1.31	118	0.30	143	2.03	162	0.27	196	3.22
[illegible]	47	0.12	65	0.16	83	[illegible]	101	5.51	119	2.31	144	2.57	164	12.88	197	0.21
[illegible]	49	0.36	66	0.15	85	0.25	102	1.35	120	0.56	145	45.75	165	1.05	198	[illegible]
[illegible]	50	7.24	67	0.13	86	0.30	103	0.19	121	0.78	146	4.34	167	0.50	199	[illegible]
[illegible]	51	6.91	68	100.00	87	[illegible]	104	0.38	122	[illegible]	147	0.34	[illegible]	0.52	200	[illegible]
[illegible]	52	0.57	69	[illegible]	88	[illegible]	105	0.40	[illegible]	[illegible]	148	[illegible]	170	[illegible]	[illegible]	[illegible]
[illegible]	53	[illegible]	70	[illegible]	[illegible]	0.56	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	54	0.33	71	0.42	90	0.33	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		



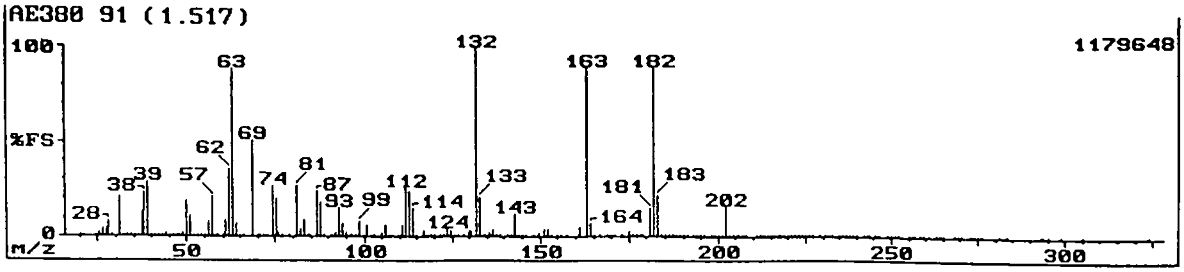
AE358 208 (3.467) 301

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.04	75	3.74	119	2.45	163	5.54
24	0.01	76	0.85	120	0.44	164	0.76
26	0.95	77	4.86	121	0.31	165	4.65
27	3.70	78	0.79	122	0.06	166	0.33
28	0.47	79	0.51	123	0.06	167	0.03
29	0.06	80	0.96	124	0.10	168	0.11
31	0.98	81	1.48	125	0.51	169	1.20
32	0.10	82	0.87	126	0.65	170	0.12
33	0.53	83	4.69	127	4.86	171	0.04
37	0.55	84	0.93	128	0.59	175	0.06
38	2.65	85	0.35	129	0.17	177	2.55
39	13.59	86	0.24	130	0.07	178	0.71
40	4.65	87	0.61	131	0.31	179	3.94
41	1.09	88	1.53	132	1.30	180	0.31
42	0.06	89	1.66	133	1.60	181	0.25
43	0.04	90	0.64	134	0.18	182	0.21
44	0.22	91	1.85	135	0.03	183	0.50
45	0.23	92	0.27	136	0.09	184	0.03
46	0.14	93	0.66	137	0.70	187	0.44
47	0.32	94	0.63	138	0.74	189	3.06
50	3.19	95	2.45	139	1.44	190	0.23
51	5.30	96	0.94	140	0.55	191	0.02
52	0.85	97	1.25	141	0.28	195	0.37
53	0.46	98	0.17	142	0.05	196	0.05
54	0.07	99	0.81	143	0.24	197	0.08
55	0.17	100	0.43	144	0.37	201	0.11
56	0.92	101	2.55	145	3.02	205	0.01
57	3.33	102	0.40	146	0.56	207	0.35
58	0.48	103	0.25	147	3.02	209	8.29
59	1.51	104	0.06	148	0.24	210	0.58
60	0.19	105	0.14	149	0.05	211	0.02
61	0.64	106	0.33	150	0.22	213	0.10
62	1.71	107	1.04	151	0.58	227	0.37
63	3.97	108	1.27	152	0.21	229	5.71
64	2.51	109	11.55	153	0.19	230	0.37
65	32.20	110	1.99	154	0.02	231	0.02
66	100.00	111	0.19	155	0.05	233	0.04
67	10.60	112	0.79	156	0.19	246	0.02
69	13.72	113	6.22	157	0.47	247	0.55
70	1.06	114	1.46	158	1.49	248	3.43
71	0.43	115	1.20	159	9.10	249	0.30
72	0.14	116	0.09	160	0.99	265	0.01
73	0.14	117	0.08	161	0.10	266	0.06
74	0.86	118	0.29	162	0.44		



AE358 189 (3.150) 2883

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
21	0.03	75	3.48	119	2.41	163	5.43
24	0.01	76	0.74	120	0.46	164	0.78
26	0.73	77	4.87	121	0.33	165	4.55
27	3.37	78	0.74	122	0.07	166	0.38
28	0.49	79	0.46	123	0.06	167	0.04
29	0.04	80	0.82	124	0.08	169	1.35
31	0.88	81	1.34	125	0.50	170	0.15
32	0.11	82	0.83	126	0.50	171	0.05
33	0.48	83	4.26	127	4.62	174	0.01
37	0.64	84	0.84	128	0.56	175	0.05
38	2.21	85	0.32	129	0.20	177	2.56
39	12.22	86	0.21	130	0.07	179	5.43
40	4.40	87	0.56	131	0.28	180	0.40
41	1.09	88	1.40	132	1.15	181	0.23
42	0.06	89	1.49	133	1.70	182	0.23
43	0.04	90	0.59	134	0.23	183	0.58
44	0.19	91	1.81	135	0.03	184	0.04
45	0.22	92	0.26	136	0.06	187	0.44
46	0.16	93	0.62	137	0.69	189	3.27
47	0.38	94	0.59	138	0.69	190	0.27
50	2.95	95	2.38	139	1.42	195	0.38
51	5.22	96	0.87	140	0.59	196	0.06
52	0.79	97	1.29	141	0.33	197	0.04
53	0.46	98	0.16	142	0.05	201	0.11
54	0.06	99	0.74	143	0.26	202	0.03
55	0.12	100	0.36	144	0.33	205	0.02
56	0.77	101	2.31	145	2.95	207	0.30
57	3.13	102	0.36	146	0.50	209	8.49
58	0.44	103	0.25	147	2.45	210	0.68
59	1.46	104	0.05	148	0.20	211	0.03
60	0.15	105	0.12	149	0.05	213	0.10
61	0.58	106	0.29	150	0.20	214	0.02
62	1.62	107	1.03	151	0.55	215	0.02
63	3.84	108	1.18	152	0.23	226	0.05
64	2.10	109	11.79	153	0.32	227	0.35
65	26.85	110	2.27	154	0.03	229	4.83
66	100.00	111	0.21	155	0.05	230	0.41
67	9.94	112	0.66	156	0.18	231	0.03
69	12.36	113	5.93	157	0.46	233	0.04
70	0.98	114	1.52	158	1.60	246	0.01
71	0.40	115	1.06	159	11.36	247	0.40
72	0.14	116	0.09	160	1.23	248	2.77
73	0.12	117	0.08	161	0.11	249	0.26
74	0.75	118	0.24	162	0.36		



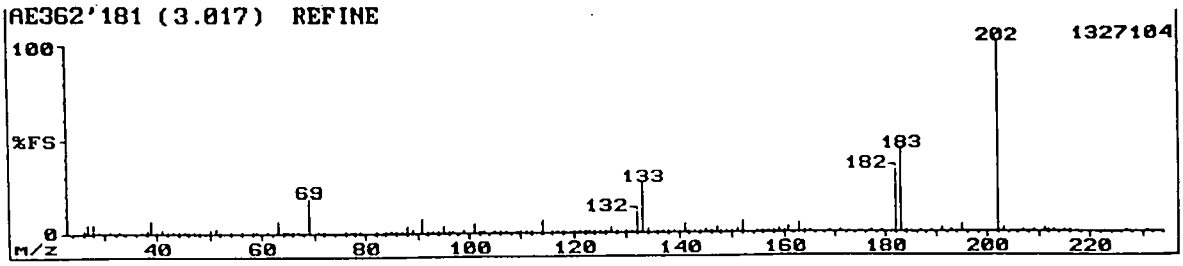
AE380 91 (1.517) 11

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.05	81	26.04	143	11.81	213	0.37
21	0.03	82	3.91	144	1.41	214	0.15
24	1.12	83	9.11	145	1.00	215	0.05
25	1.97	84	0.65	146	0.09	216	0.01
26	4.19	85	0.38	148	0.06	217	0.03
27	3.45	87	22.92	150	1.82	218	0.16
28	7.99	88	17.71	151	3.67	219	0.93
29	0.94	89	0.94	152	3.62	220	0.17
31	20.66	91	0.90	153	0.25	221	0.09
32	1.10	92	1.97	155	0.79	222	0.05
33	1.12	93	14.67	156	0.50	223	0.03
34	0.01	94	6.86	157	0.04	224	0.49
35	0.26	95	1.56	161	4.41	225	0.69
36	1.27	96	0.11	163	88.89	226	0.20
37	12.93	97	0.02	164	6.34	227	0.05
38	22.22	97	0.16	165	0.23	229	0.03
39	27.78	99	7.29	167	0.04	231	0.28
40	1.20	100	1.08	169	1.04	232	0.06
41	0.94	101	5.82	170	0.40	233	0.10
42	0.33	102	0.63	171	0.25	235	0.04
43	0.76	103	0.13	173	0.05	236	0.02
44	1.71	105	1.48	175	2.82	237	0.70
45	1.04	106	5.99	176	0.46	238	0.09
46	0.09	107	1.43	177	0.12	239	0.22
47	0.43	108	0.21	178	0.03	240	0.07
48	0.96	110	0.10	179	0.05	242	0.10
49	2.28	111	5.64	181	14.41	243	0.42
50	18.14	112	25.69	182	88.89	244	0.40
51	10.76	113	22.92	183	21.35	245	0.82
52	0.40	114	15.02	184	1.39	246	0.06
53	0.24	115	1.03	185	0.09	249	0.17
54	0.08	117	3.19	186	0.08	250	0.03
55	1.41	118	0.82	187	0.34	251	0.21
56	7.38	119	0.94	188	0.63	252	0.03
57	20.14	120	0.15	189	0.24	255	0.46
58	0.72	121	0.06	190	0.03	256	0.15
59	0.09	123	1.20	191	0.04	257	0.62
60	0.23	124	3.60	193	0.57	258	0.07
61	9.20	125	3.23	194	0.27	259	0.03
62	34.72	126	0.33	195	1.09	261	0.04
63	88.19	127	0.45	196	0.22	263	0.35
64	6.77	128	0.09	198	0.03	264	0.08
65	0.34	130	2.56	199	0.10	265	0.09
66	0.37	131	3.15	200	0.99	268	0.03
69	50.00	132	100.00	201	0.84	269	0.03
70	1.16	133	20.49	202	15.10	270	0.02
71	0.08	134	1.23	203	1.05	273	0.06
72	0.09	135	0.05	204	0.09	274	0.11
73	0.56	136	2.13	205	0.10	275	0.25
74	26.04	137	3.86	206	0.47	276	0.04
75	19.36	138	0.42	207	0.24	281	0.04
76	1.78	139	0.03	208	0.05	283	0.02
77	0.45	141	0.40	211	0.09	293	0.05
79	0.71	142	0.07	212	0.03	294	0.06

AE380 91 (1.517) 117

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
295	0.05	299	0.02	305	0.02	324	0.03

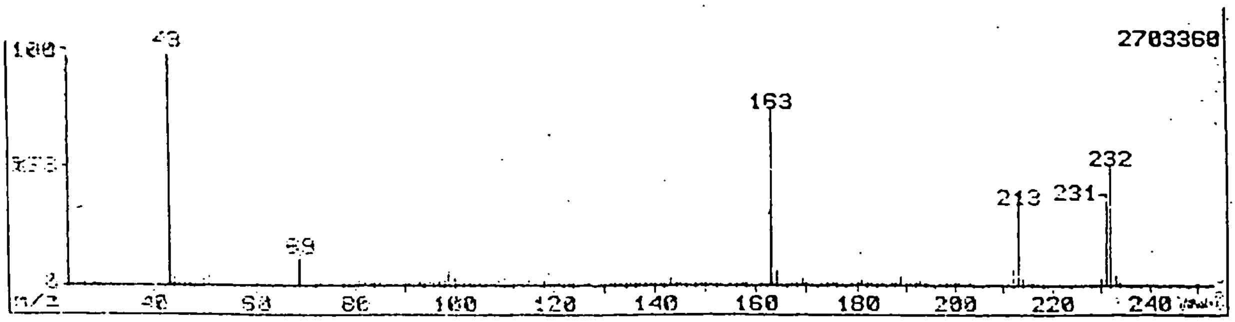
No. 17.

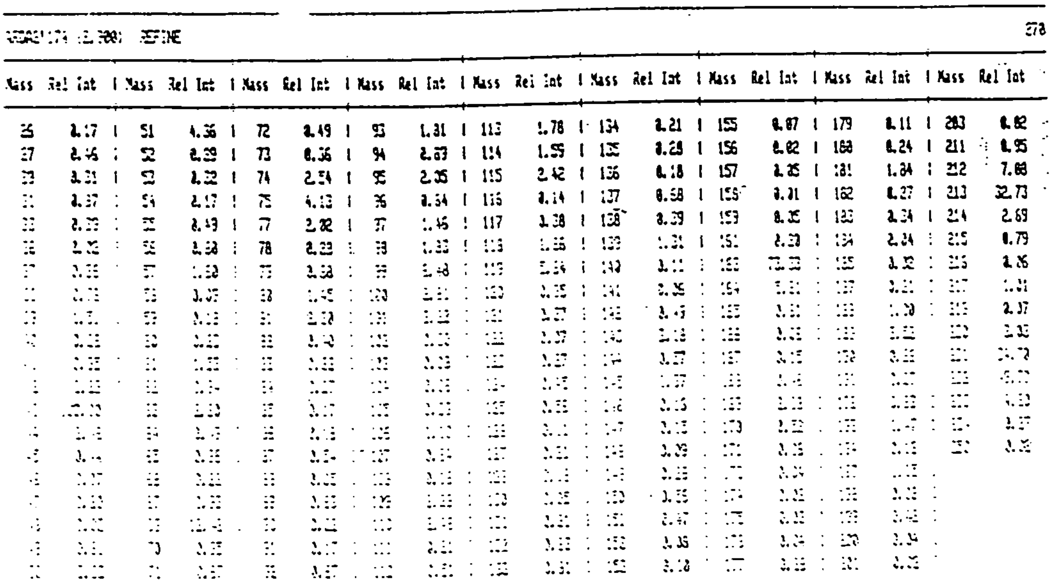


AE362'181 (3.017) REFINE 1327

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	2.20	72	0.17	118	0.10	156	0.16
27	4.90	76	0.50	120	0.31	157	0.15
28	4.57	77	1.03	121	0.54	158	0.51
29	0.81	78	0.56	122	0.09	159	1.49
31	0.81	79	0.27	123	0.13	160	0.58
33	0.82	82	0.51	124	0.20	161	2.66
37	0.77	84	0.68	125	0.88	163	4.55
38	2.14	85	0.33	126	0.25	164	0.53
39	6.87	86	0.28	127	3.40	165	0.39
40	0.95	87	0.53	128	0.31	169	0.82
41	1.81	88	4.01	130	0.05	171	0.74
42	0.17	89	1.66	131	1.03	177	0.35
43	0.07	91	7.56	132	10.57	179	0.04
44	0.12	92	0.98	133	26.54	182	33.02
45	0.29	93	0.47	134	1.56	183	44.14
46	0.30	94	0.28	136	0.09	184	0.26
47	0.63	95	3.72	137	0.44	187	0.32
48	0.03	96	0.82	138	0.58	189	0.60
50	1.89	97	0.37	139	0.71	191	1.62
51	3.26	99	2.04	140	1.39	193	0.01
52	0.36	101	4.82	141	5.25	195	3.57
54	0.15	102	0.47	142	0.63	202	100.00
56	0.35	103	0.14	143	0.61	203	1.81
58	0.16	105	0.21	144	0.67	207	0.08
59	1.22	106	0.46	145	2.16	209	0.35
61	0.22	107	0.88	146	0.79	211	2.12
63	6.64	109	0.80	147	2.55	212	0.38
64	0.92	110	0.27	148	0.15	213	0.07
65	1.22	111	0.24	149	0.07	215	0.30
66	0.39	112	0.85	150	0.55	216	0.03
67	0.59	114	6.87	151	2.33	227	0.07
69	18.29	116	0.11	152	6.17	231	0.32
71	0.47	117	0.16	155	0.07		

No. 18.

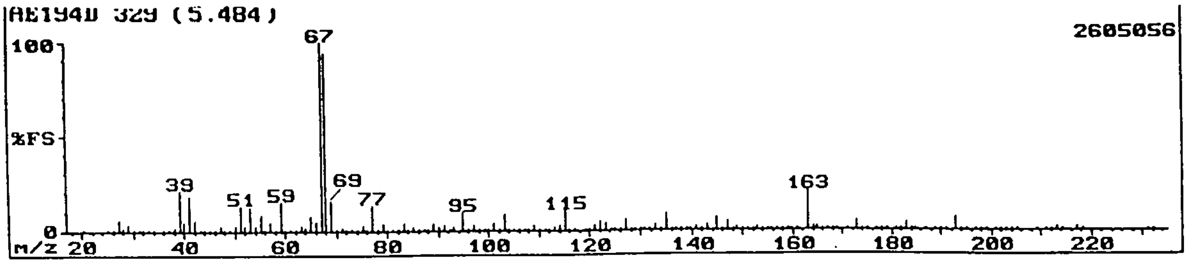




[illegible] 278

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	0.17	51	4.36	72	0.49	93	1.31	113	1.78	134	0.21	155	0.07	179	0.11	203	0.02
27	0.46	52	0.29	73	0.36	94	0.63	114	1.59	135	0.28	156	0.02	180	0.24	211	0.95
[illegible]	0.31	53	0.22	74	2.54	95	2.05	115	2.42	136	0.18	157	0.25	181	1.04	212	7.08
[illegible]	0.37	54	2.17	75	4.13	96	0.54	116	0.14	137	0.58	158	0.01	182	0.27	213	32.73
[illegible]	0.39	55	0.49	77	2.02	97	1.46	117	1.38	138	0.39	159	0.25	183	0.34	214	2.69
[illegible]	1.52	56	0.58	78	0.23	[illegible]	1.33	[illegible]	1.66	139	1.31	[illegible]	0.30	184	2.24	215	0.79
[illegible]	[illegible]	57	1.50	[illegible]	0.58	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.11	[illegible]	[illegible]	[illegible]	0.32	[illegible]	0.86
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.45	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	2.07
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.09	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		

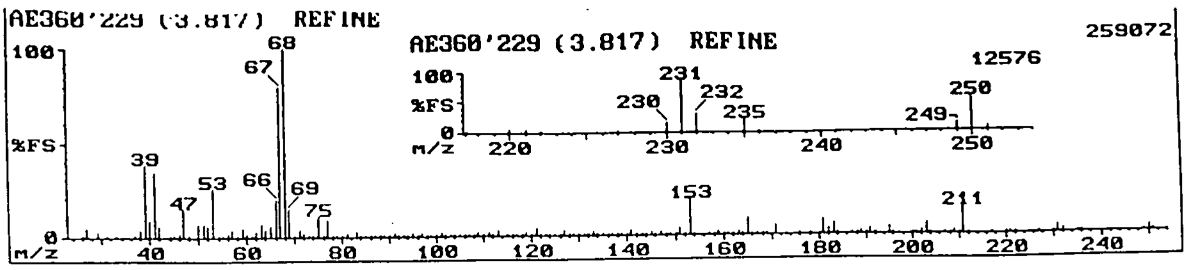
No. 19.



AE194D 329 (5.484) 2605

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	70	0.90	116	0.95	164	1.78
25	0.03	71	1.62	117	0.24	165	2.11
26	0.84	72	1.33	119	0.78	166	0.17
27	6.05	73	0.99	120	0.19	167	0.54
28	2.18	74	0.24	121	2.83	168	0.05
29	3.85	75	3.14	122	4.40	169	0.16
30	0.10	76	0.64	123	4.21	171	0.56
31	0.45	77	13.21	124	0.38	173	4.76
32	0.11	78	1.15	125	0.28	174	0.42
33	0.83	79	4.01	126	0.21	175	0.03
34	0.04	80	0.47	127	6.21	177	1.29
36	0.02	81	0.42	128	0.76	178	0.11
37	0.43	82	0.21	129	0.91	179	0.05
38	2.15	83	3.42	130	0.08	181	0.08
39	21.70	84	1.04	131	0.04	182	0.13
40	4.44	85	1.70	132	0.69	183	3.62
41	18.87	86	0.25	133	2.59	184	0.33
42	5.94	87	1.08	134	1.14	185	0.20
43	0.39	88	1.26	135	8.45	187	0.02
44	0.16	89	3.50	136	1.04	189	0.10
45	0.46	90	1.51	137	0.22	190	0.13
46	0.54	91	3.07	138	0.08	191	0.36
47	3.14	92	0.45	139	0.73	193	6.60
48	0.09	93	1.58	140	0.26	194	0.54
49	0.13	95	9.87	141	2.35	195	0.18
50	2.87	96	1.20	142	0.26	197	1.10
51	13.84	97	3.03	143	2.45	198	0.09
52	2.79	98	0.28	145	6.41	199	0.02
53	12.42	99	1.26	146	0.39	201	0.02
54	3.38	100	0.18	147	4.60	202	0.51
55	9.20	101	3.85	148	0.65	203	1.43
56	0.72	102	0.87	149	1.57	204	0.63
57	5.11	103	8.37	150	0.15	205	0.04
58	0.51	104	0.60	151	1.16	209	0.05
59	15.09	105	0.07	152	0.27	211	0.20
60	0.68	106	0.11	153	1.63	212	0.12
61	0.62	107	0.44	154	0.12	213	2.06
62	0.88	108	0.37	155	0.02	214	0.18
63	2.91	109	2.71	156	0.03	217	1.83
64	2.28	110	0.25	157	0.15	218	0.14
65	7.70	111	0.10	158	0.16	231	0.30
66	4.95	112	0.10	159	0.39	232	0.13
67	100.00	113	1.94	160	0.05		
68	93.71	114	2.52	161	0.62		
69	15.72	115	10.22	163	20.75		

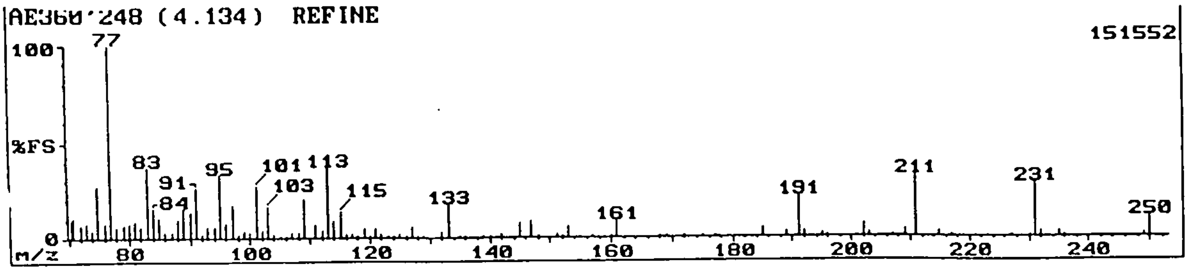
No. 20.



AE360'229 (3.817) REFINE 25

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.81	77	8.50	122	0.38	167	1.20
27	4.82	78	0.57	123	0.23	168	0.39
29	2.96	79	0.61	124	0.13	169	0.54
31	0.17	80	0.72	125	0.31	171	4.97
33	0.24	81	2.10	126	0.51	176	0.28
37	0.77	83	2.82	127	2.92	178	0.12
38	3.51	84	1.26	128	0.34	181	7.51
39	37.55	85	1.03	129	0.22	182	3.06
40	8.40	86	0.62	130	0.11	183	6.18
41	33.99	87	0.75	131	0.29	184	0.78
42	5.81	88	0.85	132	0.69	187	0.28
44	0.47	89	1.45	133	2.42	188	0.08
45	0.38	90	1.14	134	0.52	189	1.90
46	1.57	91	1.61	135	0.73	190	0.61
47	14.72	92	0.26	136	0.14	191	3.16
48	0.43	93	0.40	137	0.35	192	1.06
50	6.32	94	0.41	138	0.41	195	3.41
51	7.21	95	2.12	139	0.54	196	0.44
52	5.68	96	0.66	140	0.61	200	0.09
53	25.30	97	1.73	141	3.29	201	0.29
54	0.81	98	0.18	142	1.20	202	2.10
55	1.18	99	0.26	143	0.42	203	6.05
56	2.00	100	0.17	144	0.36	204	0.40
57	4.00	101	1.83	145	2.05	207	0.17
58	1.14	102	0.37	146	0.29	208	0.25
59	4.84	103	1.14	147	2.35	209	1.46
60	1.80	104	0.38	148	0.82	210	0.34
61	1.04	105	0.08	149	1.30	211	13.14
62	2.45	106	0.12	150	0.48	212	0.85
63	6.62	107	0.28	151	3.75	217	0.19
64	3.46	108	0.19	152	1.31	220	0.24
65	5.81	109	1.73	153	18.68	221	0.32
66	19.07	110	0.40	154	1.26	222	0.12
67	79.84	111	1.70	157	0.72	227	0.16
68	100.00	112	0.32	158	0.30	230	0.68
69	15.02	113	3.11	159	1.47	231	4.08
70	1.03	115	1.25	160	0.88	232	1.49
71	4.00	116	0.17	161	1.26	235	0.98
72	1.50	117	0.18	162	0.48	236	0.16
73	0.70	118	0.07	163	2.12	249	0.57
74	0.75	119	2.25	164	0.96	250	2.62
75	10.97	120	0.30	165	8.30	251	0.36
76	1.40	121	3.83	166	0.84		

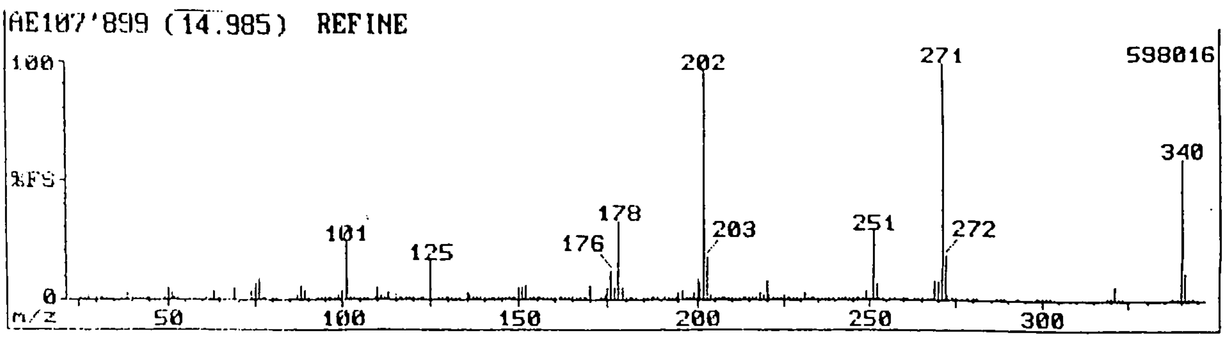
No. 21.



AE360'248 (4.134) REFINE 193

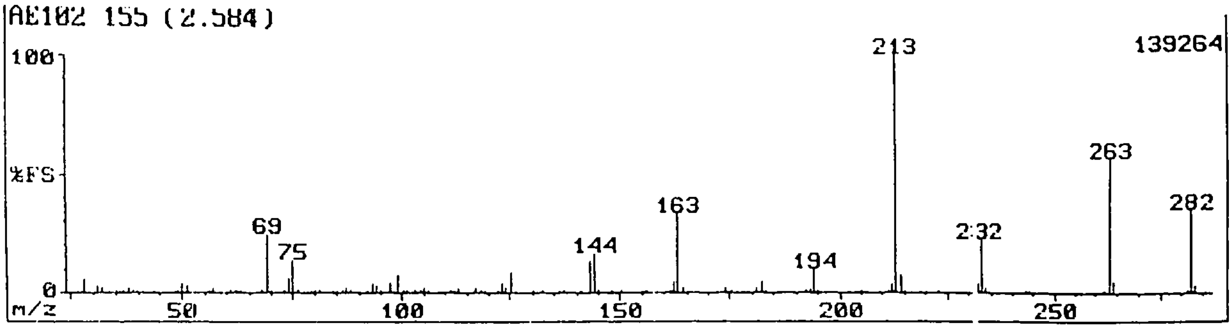
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
70	0.80	96	0.63	123	0.06	175	0.03
71	0.87	97	1.34	124	0.02	177	0.02
72	0.50	98	0.12	125	0.13	185	0.41
73	0.60	99	0.31	126	0.11	189	0.23
74	0.32	100	0.20	127	0.49	191	1.69
75	2.15	101	2.11	128	0.07	192	0.22
76	0.63	102	0.29	129	0.03	195	0.14
77	7.84	103	1.30	132	0.21	196	0.03
78	0.48	104	0.12	133	1.40	202	0.52
79	0.57	105	0.03	135	0.09	203	0.16
80	0.62	106	0.11	136	0.03	207	0.03
81	0.67	107	0.21	139	0.08	209	0.32
82	0.42	108	0.19	140	0.10	211	2.54
83	2.87	109	1.56	142	0.14	215	0.20
84	1.23	111	0.53	145	0.61	217	0.02
85	0.87	112	0.29	147	0.68	227	0.02
86	0.25	113	2.93	148	0.10	230	0.11
87	0.25	114	0.68	151	0.13	231	2.18
88	0.72	115	1.07	152	0.05	232	0.19
89	1.23	116	0.12	153	0.42	235	0.23
90	1.06	117	0.12	157	0.04	236	0.01
91	2.09	118	0.03	160	0.10	249	0.16
92	0.18	119	0.41	161	0.71	250	0.85
93	0.43	120	0.09	168	0.03		
94	0.42	121	0.42	169	0.07		
95	2.61	122	0.12	172	0.03		

No. 22.



AE107'899 (14.985) REFINE 598

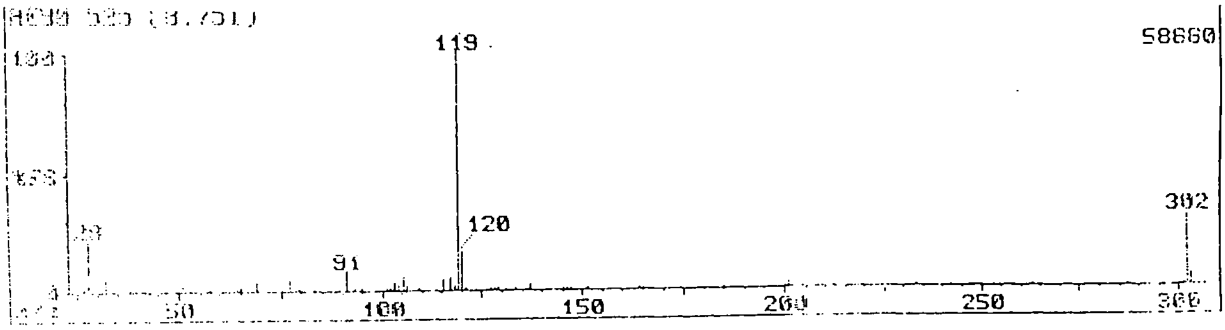
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.17	64	0.29	103	0.21	136	1.99	162	0.64	192	0.53	218	2.58	245	1.33	278	0.09
27	0.47	65	0.17	105	0.71	137	0.61	163	1.06	193	1.42	219	2.01	246	0.92	280	0.23
28	2.34	69	4.41	106	0.57	138	0.31	164	1.03	194	1.00	220	7.66	247	0.62	281	0.11
29	0.33	74	3.64	107	0.37	139	1.02	165	0.40	195	2.70	221	2.04	248	0.36	287	0.24
30	0.07	75	6.42	109	1.46	140	0.56	166	0.09	196	4.15	222	0.41	249	4.11	288	0.27
31	0.28	76	0.30	110	5.22	141	0.17	167	0.26	197	0.09	223	1.04	250	1.09	289	0.13
32	0.62	77	1.03	111	1.49	142	0.88	168	0.63	198	1.16	224	0.87	251	28.42	293	0.04
33	0.05	78	0.16	112	0.34	143	0.68	169	1.11	199	2.40	225	1.47	252	6.64	298	0.21
36	0.06	80	0.10	113	2.56	144	0.75	170	5.52	200	0.39	226	0.28	253	0.08	299	0.16
37	0.14	81	0.25	115	2.00	145	0.96	173	0.51	201	6.98	227	0.26	254	0.15	300	0.12
38	0.52	85	0.20	116	1.21	146	0.37	174	2.19	202	95.89	228	0.14	256	0.36	301	1.32
39	2.56	86	0.88	117	0.37	147	0.28	175	4.54	203	17.47	229	0.89	257	0.09	302	0.29
40	0.18	87	2.14	118	0.28	148	0.16	176	11.64	204	1.78	230	0.57	260	0.10	319	0.73
41	0.51	88	5.91	119	0.46	149	1.25	177	5.31	205	0.93	231	2.72	261	0.13	320	0.40
42	0.17	89	3.72	120	0.23	150	4.73	178	31.68	206	0.53	232	0.75	263	0.44	321	5.39
43	0.64	90	0.24	122	1.40	151	4.92	179	4.97	207	0.39	233	1.25	264	0.36	322	1.00
44	0.85	93	1.15	123	0.94	152	5.65	180	0.66	208	0.08	234	0.38	265	0.13	323	0.11
45	0.14	94	0.22	125	15.41	153	0.79	181	0.65	209	0.08	235	0.10	267	0.98	337	0.07
49	0.14	95	0.10	127	0.88	154	0.12	182	0.48	210	0.20	236	0.26	268	0.33	339	0.40
50	5.09	96	0.22	128	0.89	155	0.32	183	0.20	211	0.40	237	0.23	269	7.45	340	59.59
51	3.04	97	1.11	129	0.15	156	0.26	185	0.05	212	0.36	238	0.55	270	0.18	341	11.64
52	0.47	98	1.23	130	0.22	157	0.34	186	0.33	213	0.07	239	0.14	271	100.00	342	1.02
53	0.10	99	1.93	131	0.33	158	0.14	187	0.49	214	0.97	241	0.28	272	18.49	343	0.08
61	0.22	100	3.77	132	0.20	159	0.19	188	0.36	215	0.18	242	0.28	273	1.66		
62	1.34	101	23.46	133	0.77	160	0.33	189	0.15	216	0.26	243	0.08	274	0.18		
63	3.47	102	0.67	135	2.49	161	0.40	191	0.15	217	0.59	244	0.20	275	0.05		



AE102 155 (2.584) 139

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
28	6.20	51	2.52	76	0.77	95	0.56	113	2.39	137	0.76	164	2.38	212	3.58	264	4.55
31	2.52	56	0.92	79	0.68	97	3.81	117	1.63	141	0.36	174	1.48	213	100.00	281	1.06
32	2.36	57	1.03	80	1.33	98	0.63	118	0.93	143	13.97	175	0.83	214	7.72	282	35.11
35	0.18	61	0.90	81	1.45	99	7.35	119	0.97	144	16.36	181	2.40	215	0.31	283	2.94
36	0.76	62	1.23	84	0.30	100	0.85	122	0.86	145	1.32	182	5.06	223	0.32		
37	1.06	63	0.78	85	0.95	101	0.61	123	3.58	148	0.36	183	0.37	231	3.72		
38	1.55	68	1.26	86	0.90	103	0.53	124	1.92	150	0.24	192	0.40	232	21.88		
39	0.39	69	23.90	87	2.00	104	1.03	125	8.41	155	0.52	193	2.19	233	1.71		
40	0.24	70	0.38	88	1.11	105	2.07	126	0.71	156	0.46	194	9.83	243	0.18		
44	0.42	73	0.88	92	1.21	106	1.40	130	0.35	161	1.19	195	0.86	244	1.39		
49	0.55	74	6.30	93	3.68	111	0.58	132	0.84	162	4.83	205	0.25	262	1.39		
50	4.37	75	13.97	94	2.94	112	1.11	136	0.32	163	33.27	211	0.47	263	56.62		

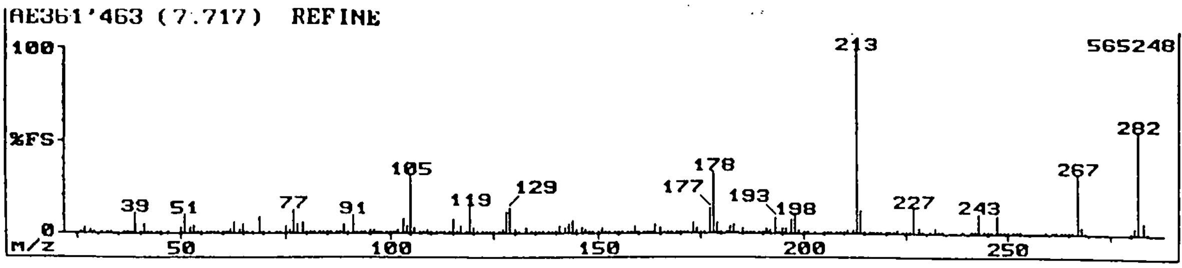
No. 24.



AE30 525 (3.751)

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
27	1.26	44	1.90	65	1.93	91	9.13	105	5.71	120	16.20	137	3.29	200	0.70
28	22.61	50	0.75	69	3.45	92	1.03	106	1.82	121	0.99	145	0.79	201	1.93
29	0.69	51	2.83	75	0.83	93	0.68	109	0.68	123	1.14	146	1.38	233	0.67
32	6.74	52	0.86	77	4.84	95	1.43	115	4.40	127	0.83	147	1.10	263	0.56
38	0.31	53	1.22	78	2.07	101	0.77	116	1.37	128	1.15	151	0.64	287	1.32
39	2.32	58	0.43	79	1.42	102	0.98	117	5.65	129	1.07	164	0.78	301	2.09
40	0.31	63	1.45	83	0.60	103	3.59	118	1.85	131	0.78	165	0.88	302	31.30
41	2.66	64	0.83	89	0.30	104	2.83	119	100.00	133	1.15	185	1.15	303	4.57

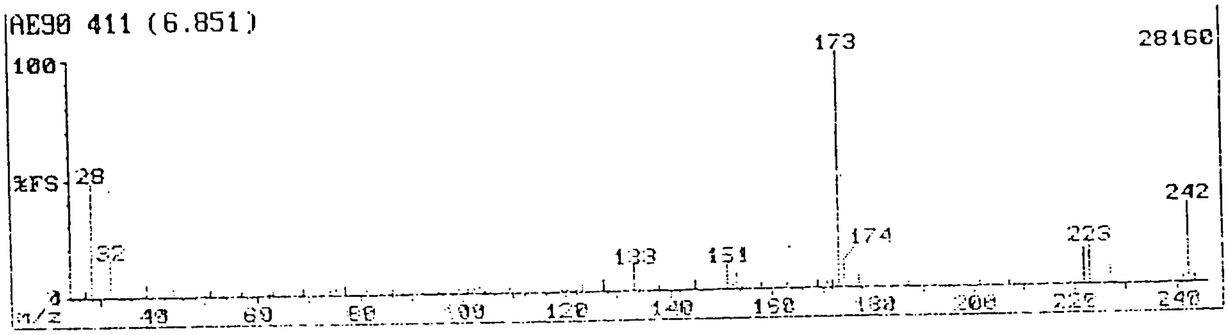
No. 25.



AE361'463 (7.717) REFINE

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.17	88	1.30	143	4.80	197	7.47
27	2.94	89	4.53	144	6.70	198	9.74
28	2.15	90	0.40	145	2.12	199	2.25
29	0.92	91	9.60	146	3.26	200	0.46
31	0.15	92	1.04	147	2.07	201	1.20
32	0.70	93	0.82	148	0.40	203	0.48
33	0.24	94	0.54	149	1.01	205	0.08
36	0.03	95	1.64	150	0.27	206	0.23
37	0.19	96	1.79	151	3.08	207	0.92
38	1.02	97	0.58	152	0.34	208	0.19
39	10.33	98	0.27	153	0.62	209	0.42
40	1.22	99	0.89	154	0.13	210	0.42
41	4.48	100	0.28	155	0.39	211	1.95
42	0.20	101	1.29	156	0.16	212	1.59
43	0.19	102	2.30	157	1.13	213	100.00
44	0.38	103	7.74	158	0.71	214	12.32
45	0.07	104	4.12	159	4.12	215	1.03
47	0.30	105	31.52	160	0.85	216	0.18
50	2.99	106	3.13	161	0.56	217	0.50
51	9.38	107	0.82	162	0.54	218	0.13
52	2.58	108	0.45	163	1.01	219	0.53
53	3.94	109	1.62	164	5.03	220	0.06
54	0.30	110	0.24	165	3.13	221	0.22
55	0.32	111	0.21	166	0.37	222	0.03
56	0.17	112	0.21	167	0.16	223	1.59
57	0.99	113	0.66	168	0.13	224	0.29
58	0.72	114	0.57	169	1.28	225	0.10
59	0.42	115	7.84	170	1.17	226	0.17
60	0.10	116	1.02	171	1.34	227	13.59
61	0.32	117	3.44	172	0.45	228	2.68
62	1.68	118	0.91	173	5.57	229	0.31
63	5.89	119	14.86	174	2.58	231	0.42
64	2.42	120	2.58	175	1.06	232	2.45
65	4.85	121	0.88	176	0.40	233	0.49
66	0.67	122	0.33	177	13.41	234	0.04
67	0.46	123	0.83	178	32.79	239	0.05
69	8.56	124	0.52	179	5.39	241	0.82
70	0.48	125	0.71	180	0.48	242	0.64
71	0.42	126	0.77	181	0.27	243	11.10
73	0.39	127	2.22	182	3.67	244	1.35
74	1.31	128	11.28	183	5.21	245	0.95
75	3.67	129	13.22	184	0.77	246	0.87
76	1.56	130	1.72	185	3.13	247	10.05
77	12.86	131	0.69	186	0.22	248	1.11
78	5.03	133	2.94	187	0.42	249	0.10
79	5.93	134	0.37	188	0.70	250	0.06
80	0.67	135	0.30	189	0.50	251	0.08
81	0.49	136	0.17	190	0.13	252	0.16
82	0.72	137	0.86	191	2.90	253	0.12
83	0.70	138	0.43	192	2.26	259	0.08
84	0.12	139	1.04	193	9.01	261	0.52
85	0.22	140	0.32	194	1.06	262	0.12
86	0.54	141	4.17	195	2.88	263	0.75
87	0.89	142	2.81	196	3.40	264	0.10
265	0.27	268	3.58	281	4.12	284	0.48
266	0.28	269	0.20	282	55.80		
267	32.43	280	0.28	283	7.07		

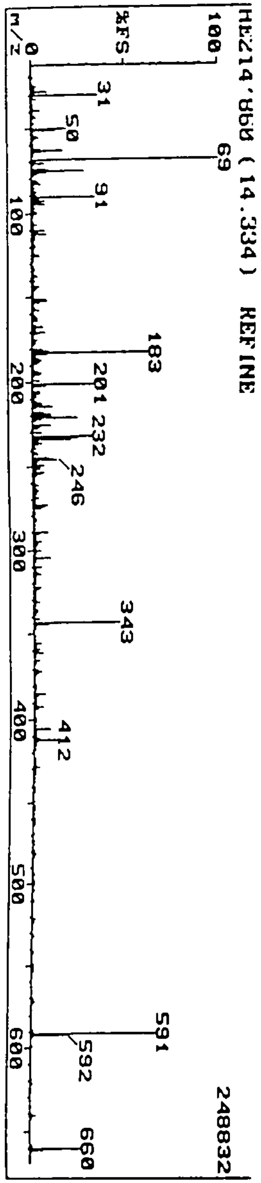
No. 26.



AE90 411 (6.851)

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
27	2.70	50	2.07	75	3.86	95	1.43	119	1.12	145	3.98	171	3.31	201	2.10
28	48.41	51	2.91	77	3.86	96	1.01	120	1.29	151	10.34	172	2.76	207	1.93
32	15.23	52	0.97	78	1.22	99	1.66	122	1.22	152	1.92	173	100.00	222	15.53
38	1.21	57	1.75	79	1.83	101	2.17	123	2.94	153	5.65	174	3.94	223	17.35
39	4.55	62	1.43	91	1.49	102	2.03	127	5.11	154	1.05	177	5.17	227	7.73
40	1.31	63	1.32	[illegible]	1.39	103	3.33	133	10.31	158	2.63	187	2.35	241	2.53
41	1.38	65	3.37	93	1.35	104	1.35	134	1.45	163	1.66	191	1.74	242	34.75
44	3.30	74	1.72	[illegible]	1.33	109	1.46	138	1.52	169	3.13	195	2.12	243	3.73

No. 27.

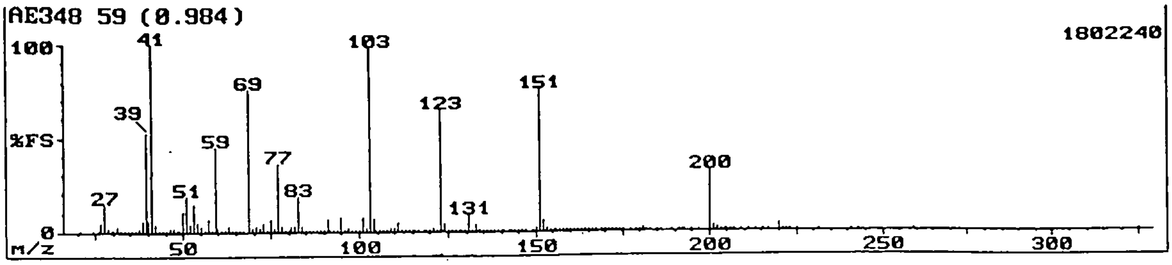


AE214'860 (14.334) REFINE

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.56	84	0.62	140	1.65	199	4.14
21	0.15	85	1.77	141	0.55	201	33.33
24	0.70	86	1.26	142	1.41	202	7.20
25	3.16	87	2.57	143	3.58	203	0.96
26	2.16	88	1.88	144	2.85	205	3.86
27	2.39	89	1.16	145	1.77	206	1.29
28	8.74	90	3.22	146	1.24	207	3.63
29	2.37	91	33.74	147	0.31	208	2.26
31	36.21	92	3.47	149	1.36	209	1.72
32	1.07	93	6.58	150	0.70	210	0.86
33	2.62	94	5.30	151	7.51	211	1.62
35	0.18	95	6.69	152	7.82	212	5.17
36	0.62	96	1.01	153	4.35	213	4.45
37	1.40	97	2.34	154	0.57	214	10.29
38	0.41	98	0.74	155	1.04	215	2.03
39	4.42	99	3.06	156	1.72	217	5.81
40	0.74	100	2.57	157	3.68	219	9.36
41	0.75	101	3.29	158	0.60	220	10.08
42	1.83	102	0.95	159	1.28	221	24.69
43	1.59	103	0.72	160	0.48	222	5.09
44	2.75	105	0.95	161	2.01	223	1.93
45	0.48	106	1.38	162	2.44	225	9.88
47	1.67	107	3.03	163	2.65	226	4.14
48	0.38	108	0.86	164	3.27	227	2.67
50	18.42	109	1.24	166	1.77	229	4.96
51	12.96	110	6.58	167	6.10	230	4.37
52	0.81	111	2.73	168	1.70	232	32.51
53	1.34	112	2.24	169	1.49	233	24.07
55	3.03	113	7.82	170	6.58	234	20.06
56	4.22	114	2.13	171	3.29	235	2.60
57	2.24	115	1.83	172	0.62	236	4.68
58	0.18	116	2.34	173	0.69	237	2.57
59	0.13	117	0.99	174	0.55	238	1.23
60	0.34	118	0.77	175	2.78	239	2.24
61	1.11	119	2.37	176	1.75	241	1.83
62	5.04	120	1.55	177	1.46	242	0.84
63	16.05	121	0.46	178	0.84	243	2.93
64	5.27	122	0.57	180	5.50	245	8.85
65	1.07	123	0.98	181	8.95	246	12.35
66	0.55	124	1.48	183	62.55	247	3.06
67	0.28	125	3.96	184	8.13	248	2.24
69	100.00	126	3.55	185	1.93	249	6.29
70	1.49	127	1.20	186	3.70	250	3.55
71	6.43	128	0.54	187	4.68	251	3.94
72	0.66	129	0.20	188	4.30	252	2.08
74	9.16	131	0.71	189	2.65	254	5.58
75	27.98	132	1.42	190	0.78	255	3.68
76	7.51	133	1.80	191	0.43	256	1.77
77	3.40	134	0.34	192	1.37	257	1.04
78	0.89	135	0.48	193	2.91	258	0.42
79	1.04	136	1.88	194	2.13	259	0.45
81	2.55	137	2.88	195	4.45	260	0.66
82	3.88	138	3.34	196	3.52	261	2.57
83	4.84	139	1.02	197	1.04	262	1.08

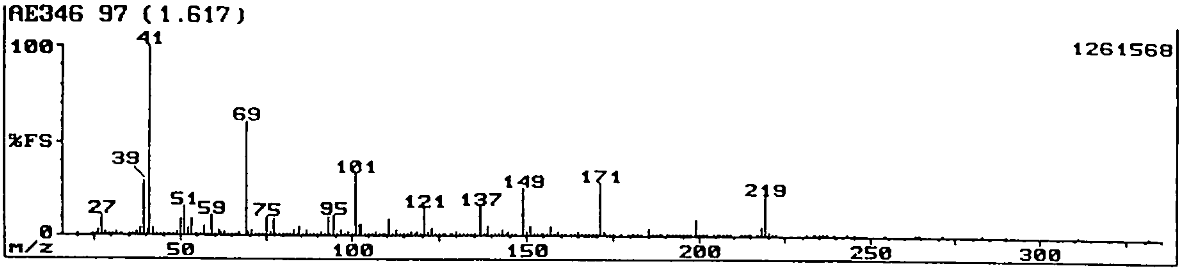
248832 AE214'860 (14.334) REFINE 24

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
263	2.11	326	0.16	399	0.33	482	0.59
264	2.44	327	0.14	400	1.27	483	0.25
265	2.85	328	0.20	401	0.21	493	0.17
266	1.64	329	0.42	403	0.46	494	0.14
267	1.90	330	1.08	405	8.64	497	0.51
268	0.71	331	2.70	406	3.86	498	0.44
269	2.49	332	0.33	407	0.68	499	0.24
270	0.75	333	0.40	408	0.23	500	0.20
271	0.77	335	2.24	409	0.64	501	0.32
272	0.73	336	1.22	410	0.77	503	0.57
273	7.41	337	2.11	411	2.78	504	0.10
274	5.63	338	0.48	412	12.55	509	0.17
275	3.88	339	0.46	413	2.39	511	0.31
278	0.36	341	2.44	414	0.22	521	1.62
279	0.39	343	46.50	415	0.13	522	0.39
281	0.92	344	8.13	417	0.14	523	1.02
282	2.29	345	1.31	423	0.18	524	0.58
283	0.70	346	0.27	424	0.24	531	0.92
285	1.43	347	0.58	425	0.26	532	0.25
287	1.09	351	0.20	426	0.18	541	1.24
290	8.02	353	1.16	427	0.18	542	0.29
291	2.52	355	3.91	428	1.41	549	0.16
292	1.05	356	0.93	429	2.93	550	0.23
293	1.24	357	0.26	430	0.41	551	1.05
294	0.66	359	3.27	431	0.68	552	0.62
295	4.35	360	1.70	432	0.23	553	0.17
296	1.93	361	4.40	433	0.29	570	0.40
297	2.01	362	1.25	435	0.17	571	0.62
298	0.78	363	0.56	437	0.23	572	2.11
299	0.58	365	3.19	441	0.77	573	0.55
300	3.42	366	0.93	442	0.42	589	1.07
302	1.23	367	0.53	443	0.25	590	0.58
303	1.01	371	1.46	444	0.29	591	68.31
305	8.95	372	3.91	449	0.23	592	18.83
306	1.13	373	1.59	451	0.14	593	2.65
307	0.33	374	0.32	453	0.55	594	0.26
310	3.63	379	0.35	454	0.24	599	0.12
312	0.40	380	0.67	455	0.23	619	0.23
313	0.37	381	0.37	457	0.35	621	0.66
314	1.61	383	0.73	459	0.27	622	0.21
315	3.55	385	5.61	460	0.33	640	0.14
316	0.85	386	1.83	461	0.27	641	3.29
317	0.69	387	0.39	462	0.61	642	0.66
318	0.59	388	0.29	463	0.34	643	0.08
319	1.22	389	0.57	469	0.55	658	0.18
320	1.31	390	0.70	473	0.21	659	0.16
322	3.60	391	0.89	475	0.18	660	26.75
323	2.80	392	4.89	479	0.24	661	7.20
324	1.52	393	1.80	480	0.33	662	0.99
325	0.32	394	0.31	481	1.47		



AE348 59 (0.984) 1802

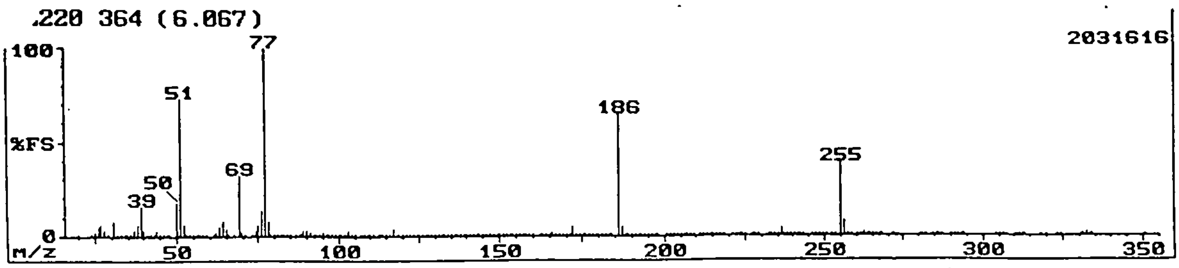
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
21	0.01	71	2.53	118	0.03	166	0.01
24	0.02	72	1.95	119	0.46	167	0.04
26	0.50	73	5.00	120	0.15	169	0.04
27	4.43	74	0.44	121	2.26	170	0.01
27	14.49	75	6.93	122	1.11	171	0.28
28	2.36	76	1.56	123	65.45	172	0.28
29	1.22	77	35.91	124	3.75	173	0.16
30	0.11	78	2.56	125	0.37	174	0.03
31	2.81	79	0.52	126	0.08	175	0.02
32	0.23	80	0.26	127	0.40	177	0.02
33	1.34	81	2.67	128	0.04	179	0.04
34	0.02	82	3.20	129	0.16	180	0.18
35	0.02	83	18.18	130	0.31	181	2.32
36	0.09	84	2.88	131	9.09	182	0.37
37	2.24	85	1.25	132	1.05	183	0.34
38	6.14	86	0.20	133	4.09	185	0.83
39	52.27	87	0.27	134	0.38	186	0.06
40	6.14	88	0.87	135	0.18	189	0.02
41	100.00	89	1.35	136	0.61	191	0.03
42	4.15	90	0.71	137	0.85	192	0.01
43	1.07	91	7.10	138	0.08	193	0.05
44	0.65	92	0.35	139	0.12	195	0.02
45	0.81	93	0.47	140	0.02	197	0.01
46	1.69	94	0.23	141	0.15	200	32.05
47	1.80	95	8.07	142	0.02	201	2.61
48	0.12	96	0.72	143	0.07	202	2.14
49	1.02	97	1.51	144	0.04	203	0.47
50	10.74	98	0.11	145	0.26	204	0.05
51	18.18	99	1.01	146	0.02	205	0.12
52	3.86	100	0.22	147	0.07	206	0.02
53	14.55	101	7.61	149	1.09	207	0.08
54	4.77	102	1.48	150	1.52	209	0.01
55	2.46	103	98.18	151	76.36	211	0.03
56	0.92	104	6.70	152	5.74	213	0.02
57	6.76	105	0.42	153	2.19	215	0.02
58	0.78	106	0.17	154	0.20	217	0.04
59	45.00	107	0.41	155	0.06	220	3.69
60	1.93	108	0.38	156	0.07	221	0.32
61	0.48	109	1.85	157	0.08	222	0.03
62	0.60	110	1.58	158	0.06	223	0.03
63	2.84	111	5.17	159	0.04	225	0.03
64	1.42	112	0.56	160	0.01	231	0.01
65	1.34	113	0.66	161	0.38	241	0.02
66	0.24	114	0.39	162	0.04	243	0.04
67	0.29	115	0.32	163	0.23	259	0.01
69	75.45	116	0.03	164	0.01	325	0.02
70	1.92	117	0.55	165	0.01		



AE346 97 (1.617) 12

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	76	1.68	127	0.56	183	0.07
24	0.02	77	8.77	128	0.02	185	3.47
25	0.17	78	1.23	129	1.44	186	0.46
26	2.48	79	0.51	130	1.46	187	1.19
27	11.12	80	0.53	131	1.12	188	0.15
28	1.95	81	1.27	132	0.50	189	0.12
29	0.65	82	0.32	133	0.34	190	0.03
30	0.04	83	2.64	134	0.02	191	0.08
31	2.17	84	0.42	135	0.65	192	0.17
32	0.21	85	4.50	137	15.10	193	0.20
33	0.48	86	0.26	138	1.01	194	0.08
35	0.45	87	2.90	139	4.81	195	0.14
36	0.36	88	1.24	140	0.34	196	0.01
37	1.64	89	1.23	141	0.18	197	0.02
38	3.73	90	0.63	142	0.07	199	8.77
39	29.55	91	1.46	143	2.76	200	0.66
40	2.88	92	0.12	144	0.76	201	0.11
41	100.00	93	10.15	145	1.79	202	0.03
42	3.71	94	0.62	146	0.31	204	0.03
43	0.85	95	10.88	147	0.38	205	0.43
44	0.36	96	0.41	149	25.32	206	0.18
45	0.74	97	2.86	150	2.09	207	0.09
46	0.62	98	0.17	151	5.28	208	0.06
47	1.05	99	1.62	152	0.40	209	0.02
48	0.17	100	0.35	153	0.06	212	0.02
49	2.31	101	33.12	154	0.03	213	0.04
50	8.60	102	6.17	155	0.38	214	0.05
51	15.34	103	5.60	156	0.32	215	0.06
52	3.47	104	0.43	157	5.17	217	0.75
53	8.69	105	0.27	158	0.38	218	4.73
54	0.75	106	0.35	159	1.66	219	21.43
55	0.89	107	2.23	160	0.11	220	1.58
56	1.15	108	0.31	161	0.12	221	0.16
57	4.99	109	0.85	163	0.18	222	0.02
58	0.48	110	0.13	164	0.04	231	0.02
59	10.23	111	8.44	165	1.83	233	0.02
60	0.84	112	0.37	166	0.15	234	0.17
61	3.10	113	3.02	167	0.93	235	0.03
62	2.09	114	0.27	168	0.34	236	0.06
63	2.11	115	0.31	169	0.31	237	0.02
64	0.94	116	1.42	170	0.24	239	0.02
65	0.88	117	2.11	171	28.57	243	0.12
66	0.36	118	0.79	172	1.72	245	0.01
67	1.91	119	2.19	173	0.32	254	0.02
69	60.06	120	0.56	174	0.03	263	0.05
70	1.64	121	14.94	175	0.05	264	0.02
71	2.84	122	1.97	177	0.02	271	0.09
72	1.44	123	3.57	179	0.34	283	0.05
73	1.32	124	0.50	180	0.06	290	0.02
74	0.44	125	1.02	181	0.10	311	0.06
75	9.58	126	0.10	182	0.03	331	0.05

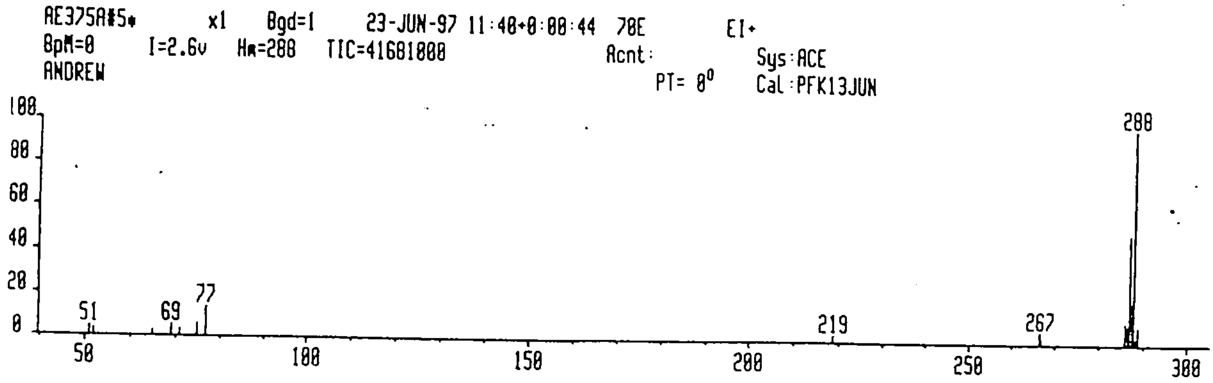
No. 30.



AE220 364 (6.067) 2031616

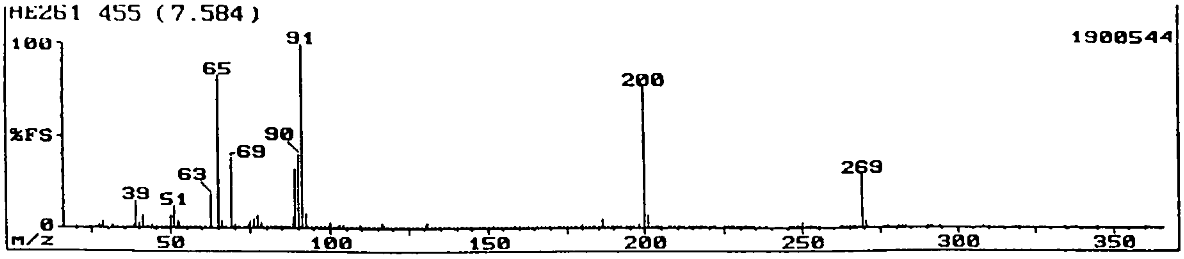
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.46	82	0.28	137	0.10	193	0.10
24	1.23	83	0.32	138	0.53	194	0.58
25	1.76	84	0.11	139	0.34	195	0.04
26	4.74	85	0.12	140	0.28	196	0.35
27	5.39	87	0.20	141	0.04	197	0.10
28	3.07	87	0.41	142	0.02	198	0.07
29	0.18	88	0.38	143	0.07	201	0.03
31	7.36	89	3.16	144	0.28	202	0.07
32	0.61	90	2.75	145	0.95	203	0.16
33	1.45	91	1.56	146	0.86	204	0.38
34	0.03	92	0.33	147	0.14	205	0.06
35	0.05	93	1.10	148	0.12	206	0.01
36	0.20	94	0.53	149	0.03	207	0.10
37	2.61	95	2.29	150	0.05	208	0.03
38	5.70	96	0.78	151	0.11	209	0.03
39	15.93	97	0.17	152	0.27	211	0.04
40	3.23	98	0.08	153	0.20	212	0.05
41	1.10	99	0.56	154	0.55	213	0.06
42	0.18	100	0.35	155	0.08	214	0.77
43	0.31	101	0.31	156	0.03	215	1.25
44	2.52	102	0.43	157	0.17	216	0.78
45	1.17	103	3.05	158	0.18	217	0.20
46	0.36	104	0.64	159	0.18	218	0.03
47	0.11	105	0.07	160	0.04	221	0.02
48	0.64	107	0.41	162	0.02	222	0.19
50	17.14	108	0.36	163	0.14	223	0.08
51	72.58	109	0.72	164	0.52	224	0.07
52	5.44	110	0.38	165	1.05	225	0.03
53	0.32	111	0.07	166	2.14	227	0.01
54	0.14	113	0.18	167	0.29	228	0.11
55	0.16	113	0.21	168	0.12	229	0.12
56	0.40	114	0.45	169	0.10	232	0.01
57	0.74	115	0.66	170	0.16	233	0.07
58	0.42	116	1.00	171	0.26	234	0.30
59	0.08	117	3.48	172	5.24	235	0.59
61	0.25	118	0.39	173	0.41	236	3.83
62	1.64	119	0.92	174	0.05	237	0.54
63	5.19	120	0.30	175	0.01	238	0.06
64	7.66	121	0.24	176	0.13	239	0.01
65	3.93	122	0.17	177	0.09	240	0.19
66	0.67	123	0.02	178	0.09	241	0.03
67	0.05	125	0.16	179	0.02	242	0.20
69	31.85	125	0.18	180	0.16	243	0.04
70	1.94	126	0.84	181	0.04	246	0.07
71	0.14	127	0.29	182	0.03	247	0.11
73	0.58	128	0.35	183	0.22	248	1.22
74	2.66	129	0.03	184	0.77	249	0.31
75	6.30	130	0.03	186	63.71	250	0.06
76	13.91	131	0.03	187	5.09	252	0.03
77	100.00	132	0.07	188	0.32	253	0.06
78	7.36	133	0.04	189	0.04	255	38.91
79	0.32	134	0.26	190	0.30	256	7.91
80	0.07	135	0.29	191	0.04	257	0.63
81	0.25	136	0.04	192	0.05	258	0.04
260	0.04	273	0.02	293	0.05	320	0.01
261	0.14	280	0.05	294	0.06	323	0.02
262	1.54	281	0.04	304	0.04	324	0.19
263	0.34	282	0.03	305	0.09	331	0.03
264	0.06	284	0.04	306	0.84	331	0.32
265	0.03	285	0.03	307	0.12	332	1.97
266	0.24	286	0.29	310	0.03	333	0.31
267	0.05	287	0.04	311	0.01	334	0.03
268	0.04	290	0.04	312	0.05	350	0.03
271	0.01	291	0.03	313	0.02		
272	0.10	292	0.26	318	0.02		

No. 31.



```
Mass       % Base
 51.10       3.73
 52.09       2.26
 65.04       2.04
 68.98       4.33
 71.07       2.49
 74.99       5.30
 77.00      12.85
218.69       2.26
266.58       5.07
266.95       2.10
285.93       9.93
286.51       8.24 F
286.92      51.33 F
287.51      19.01 F
287.94     100.00 F
288.53       2.65
288.81       7.94 F
288.98       4.11 F
```

No. 32.

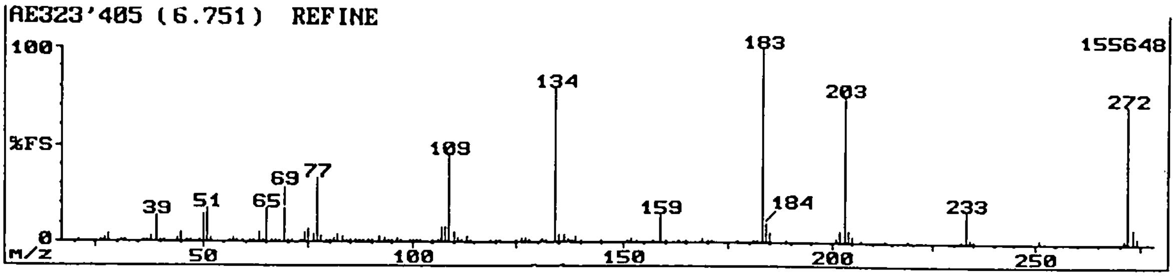


AE261 455 (7.584) 190C

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.04	84	0.19	138	0.26	192	0.02
24	0.13	85	0.19	139	0.29	194	0.08
25	0.27	86	0.61	140	0.49	195	0.02
26	1.27	87	0.92	141	0.18	196	0.19
27	1.51	88	6.30	142	0.08	198	1.71
28	3.61	89	32.11	143	0.05	200	76.72
29	0.10	90	40.09	144	0.20	201	6.79
31	2.24	91	100.00	145	0.32	202	0.40
32	0.88	92	7.92	146	0.26	203	0.07
33	0.65	93	0.64	147	0.16	204	0.30
35	0.03	94	0.44	148	0.29	205	0.04
36	0.10	95	0.76	149	0.13	207	0.09
37	0.82	96	0.30	150	0.20	208	0.22
38	2.36	97	0.10	151	0.71	209	0.55
39	14.87	98	0.11	152	0.47	210	0.25
40	2.63	99	1.23	153	0.20	211	0.06
41	7.06	100	3.39	154	0.14	212	0.03
42	0.34	101	0.63	155	0.04	214	0.11
43	0.17	102	1.04	156	0.07	215	0.04
44	1.68	103	1.85	157	0.32	216	0.06
45	0.97	104	1.68	158	0.86	217	0.04
46	0.62	105	0.42	159	0.55	218	0.26
47	0.20	106	0.26	160	0.34	219	0.03
48	0.24	107	0.52	161	0.13	220	0.02
49	0.46	108	0.64	162	0.17	221	0.02
50	7.11	109	1.95	163	0.10	222	0.01
51	12.12	110	0.89	164	0.28	225	0.02
52	4.15	111	0.17	165	0.44	226	0.03
53	2.65	112	0.12	166	0.24	227	0.04
54	0.41	113	0.38	167	0.08	228	0.46
55	0.17	114	0.51	168	0.06	229	0.98
56	0.35	115	0.98	169	0.09	230	0.57
57	0.60	116	3.30	170	0.10	231	0.09
58	0.37	117	1.98	171	0.11	232	0.04
59	0.14	118	0.35	172	0.10	233	0.13
61	0.61	119	0.26	173	0.07	234	0.07
63	17.67	120	0.25	174	0.03	236	0.03
65	82.76	121	0.22	175	0.04	238	0.01
66	3.61	122	0.26	176	0.14	246	0.13
67	0.22	123	0.25	177	0.29	247	0.03
69	38.15	124	0.15	178	0.94	248	0.16
70	1.66	125	0.23	179	0.74	249	0.46
71	0.15	126	0.24	180	1.79	250	2.52
73	0.47	127	0.58	181	0.31	251	0.28
74	1.86	128	0.82	182	0.21	252	0.02
75	3.88	129	0.98	183	0.29	253	0.05
76	4.53	130	3.34	184	0.22	254	0.08
77	7.17	131	2.45	185	1.25	255	0.02
78	3.10	132	0.66	186	4.53	262	0.03
79	0.84	133	1.13	187	0.44	263	0.01
80	0.22	134	1.16	188	0.09	264	0.02
81	0.32	135	0.26	189	0.08	265	0.02
82	0.58	136	0.15	190	0.11	266	0.05
83	1.35	137	0.20	191	0.02	267	0.16

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
268	0.80	281	0.04	308	0.01	345	0.01
269	29.31	282	0.02	310	0.01	360	0.06
270	3.56	283	0.01	319	0.01	361	0.01
271	0.19	290	0.05	320	0.01		
276	0.06	291	0.02	334	0.02		
277	0.02	294	0.01	338	0.02		

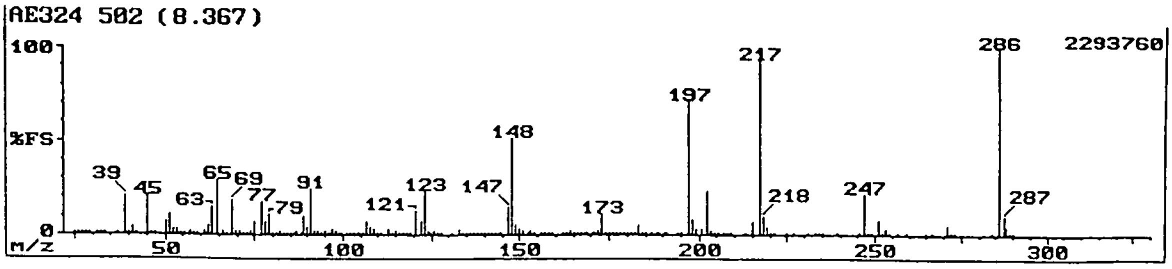
No. 33.



AE323'405 (6.751) REFINE 155648

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
21	0.09	69	17.76	106	0.81	163	0.59
26	0.48	70	1.12	107	8.10	165	0.24
27	2.32	71	0.84	108	7.57	169	1.66
28	3.74	73	0.90	109	44.74	170	0.77
31	1.18	74	5.14	110	4.40	171	0.27
32	1.15	75	7.24	111	1.49	177	0.26
36	0.31	76	3.74	112	0.21	181	0.34
37	1.11	77	33.06	113	2.67	182	1.04
38	3.21	78	2.59	114	0.15	183	100.00
39	13.98	79	0.17	119	0.74	184	9.29
40	0.73	80	0.12	120	0.42	185	4.44
41	0.18	81	1.94	121	0.56	189	0.38
44	1.79	82	4.07	125	0.37	201	2.22
45	5.30	83	2.54	126	1.91	202	6.21
46	0.19	84	1.16	127	1.89	203	74.34
47	0.41	85	0.23	128	0.31	204	5.92
49	0.52	86	0.20	131	0.29	205	3.00
50	14.97	87	1.11	132	0.34	207	0.32
51	17.27	88	0.19	134	78.95	213	0.18
52	1.89	89	1.11	135	4.24	219	0.52
56	0.32	90	0.76	136	3.70	232	0.34
57	2.41	92	3.08	137	0.54	233	16.28
58	0.96	93	1.96	138	0.53	234	1.67
59	0.53	94	0.96	139	2.60	235	0.58
61	0.31	95	0.82	140	0.42	251	2.09
62	1.01	96	1.58	145	1.00	271	2.40
63	4.69	97	0.16	151	1.43	272	70.39
64	0.67	99	0.17	152	1.56	273	7.65
65	17.76	100	0.25	153	0.58	274	3.33
66	1.31	101	0.64	157	0.60		
67	0.32	102	0.23	159	14.47		
68	0.70	105	0.25	160	1.14		

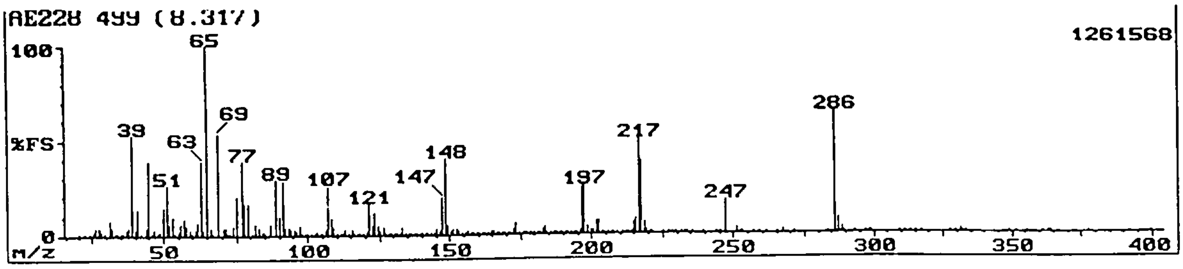
No. 34.



AE324 502 (8.367) 229376(

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
25	0.03	87	1.54	140	0.09	195	0.33
26	0.19	88	0.71	141	0.56	197	70.71
27	1.24	89	9.82	142	0.06	198	7.37
28	0.76	90	3.71	143	0.11	199	3.13
29	0.05	91	24.64	144	0.17	201	2.90
31	0.27	92	2.21	145	0.87	202	23.39
32	0.32	93	2.10	147	14.11	203	2.41
33	0.07	94	1.07	148	51.43	204	1.00
37	0.59	95	2.00	149	5.18	205	0.11
39	20.54	96	0.93	150	2.53	207	0.35
40	1.41	97	2.66	151	1.46	208	0.04
41	3.84	98	2.23	152	0.63	209	0.06
42	0.13	99	0.64	153	2.08	213	0.67
45	20.71	100	0.07	154	0.25	215	7.23
46	0.24	101	0.29	156	0.04	217	93.57
47	1.18	102	0.18	157	0.37	218	9.24
50	6.83	103	0.63	158	0.14	219	3.93
51	10.63	104	0.24	159	0.25	220	0.47
52	2.76	105	0.17	162	0.04	221	0.26
53	2.86	106	0.71	163	0.39	225	0.13
54	0.17	107	7.28	164	2.01	227	0.18
55	0.06	108	4.29	165	1.26	231	0.04
57	2.14	109	2.70	166	0.32	233	0.80
58	1.25	110	0.59	167	0.13	234	0.12
59	0.68	111	0.08	168	0.03	235	0.13
61	1.72	113	3.30	169	0.42	239	0.04
62	5.27	114	0.30	170	0.11	245	0.06
63	14.82	115	1.60	171	0.35	247	21.07
65	29.46	116	0.20	172	1.86	248	1.05
66	1.56	117	0.16	173	10.58	249	0.92
67	0.05	118	0.03	174	0.87	251	7.95
69	18.21	119	0.31	175	0.10	252	0.86
70	2.06	121	12.50	176	0.24	253	3.26
71	2.19	122	6.38	177	0.55	254	0.28
72	0.25	123	22.86	178	0.29	257	0.02
73	0.45	124	2.40	179	0.14	259	0.04
74	2.05	125	1.06	180	0.02	265	1.36
75	6.61	126	1.82	181	0.10	266	0.07
77	17.14	127	0.42	182	0.71	267	0.45
78	6.83	128	0.12	183	4.51	271	5.04
79	10.80	131	0.12	184	1.38	272	0.33
80	0.83	133	3.17	185	0.25	273	0.09
81	0.84	134	1.02	187	0.12	284	0.24
82	2.06	135	0.25	188	0.06	286	100.00
83	1.32	136	0.05	189	0.45	287	9.78
84	0.61	137	0.12	190	0.08	288	4.11
85	0.56	138	0.10	191	0.06	289	0.39
86	1.12	139	0.29	194	0.11	290	0.05

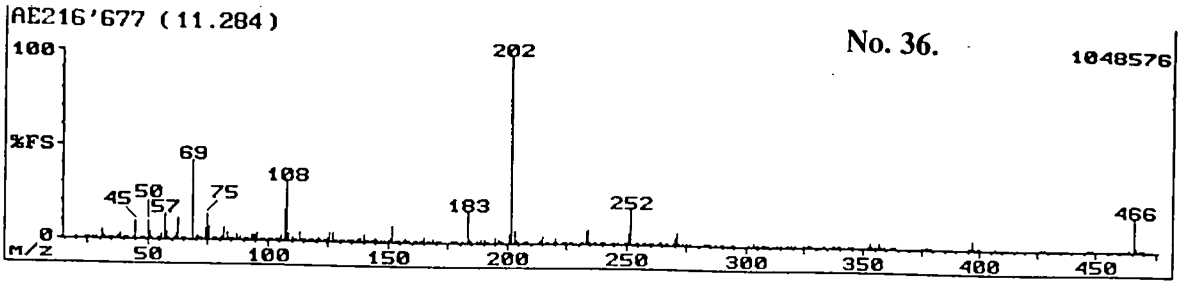
No. 35.



AE228 499 (8.317) 126156

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.12	80	1.44	137	0.30	191	0.07
22	0.02	82	5.68	138	0.53	193	0.06
24	1.44	83	4.36	139	0.83	194	0.19
25	2.37	84	1.68	140	0.42	195	0.63
26	3.53	85	0.60	141	1.23	196	1.66
27	3.84	87	5.84	142	0.92	197	24.35
28	1.87	89	29.55	143	0.71	197	25.00
29	0.24	90	9.66	144	0.85	199	4.32
31	7.47	91	28.57	145	2.56	200	1.66
32	4.08	92	3.49	146	2.25	201	1.75
33	1.07	93	3.79	147	19.72	202	7.14
34	0.96	94	2.94	148	39.61	202	6.66
35	0.12	95	3.33	149	4.89	204	1.07
36	0.49	96	1.91	150	2.19	204	0.38
37	2.88	97	4.93	151	3.17	205	0.07
38	3.98	98	1.12	152	2.52	207	0.24
39	51.95	99	0.67	153	1.66	207	0.27
40	3.08	100	0.27	154	0.79	209	0.08
41	13.56	101	0.85	155	0.29	211	0.06
42	0.41	102	1.40	156	1.81	212	0.04
44	4.36	103	1.58	157	0.87	213	0.32
45	38.96	104	0.40	158	0.39	214	0.46
46	0.99	105	0.50	159	0.30	215	5.44
47	2.56	106	2.50	161	0.18	216	7.55
48	0.97	107	14.77	162	0.24	217	49.35
49	1.46	108	8.44	162	0.52	218	37.99
50	14.94	109	3.92	164	1.23	219	6.25
51	26.62	110	1.01	165	2.39	219	2.25
52	6.01	111	0.15	165	2.17	220	0.34
53	9.25	112	0.51	166	0.68	221	0.11
54	0.26	113	3.17	168	0.63	225	0.21
55	1.81	114	0.70	169	1.09	227	0.21
56	5.52	115	2.50	169	0.82	228	0.05
57	8.77	116	0.39	170	0.57	230	0.06
58	5.19	117	0.23	171	0.46	231	0.04
59	2.50	118	0.19	173	3.08	233	0.42
60	0.85	119	0.54	173	5.36	233	0.55
61	2.66	120	2.09	174	0.69	235	0.13
62	7.14	121	16.48	176	0.56	239	0.08
63	39.29	122	4.61	177	1.03	244	0.04
64	2.74	123	12.01	177	0.80	245	0.14
65	100.00	124	4.63	179	0.66	247	17.53
66	3.94	125	1.87	179	0.51	251	2.54
67	0.14	126	3.71	181	0.21	252	0.39
69	53.57	127	1.28	182	0.78	253	0.70
70	3.45	128	0.49	183	2.88	257	0.08
71	3.55	129	0.46	183	4.04	259	0.04
72	0.31	130	1.34	185	0.90	261	0.10
73	0.70	131	0.44	186	0.47	265	1.18
74	4.89	132	0.99	187	0.30	267	2.23
75	19.97	133	3.84	188	0.30	271	0.91
77	38.96	134	1.44	189	0.58	283	0.04
78	16.72	135	0.57	189	0.48	286	64.29
79	16.48	136	0.15	190	0.14	287	7.79
288	2.74	309	0.08	329	0.06	355	0.02
289	0.34	311	0.03	331	1.77	361	0.02
293	0.01	313	0.02	332	0.23	363	0.24
297	0.33	315	0.18	333	0.15	364	0.02
298	0.05	317	0.11	349	0.14	377	0.03
299	0.10	327	0.03	351	0.05	399	0.06

No. 36.

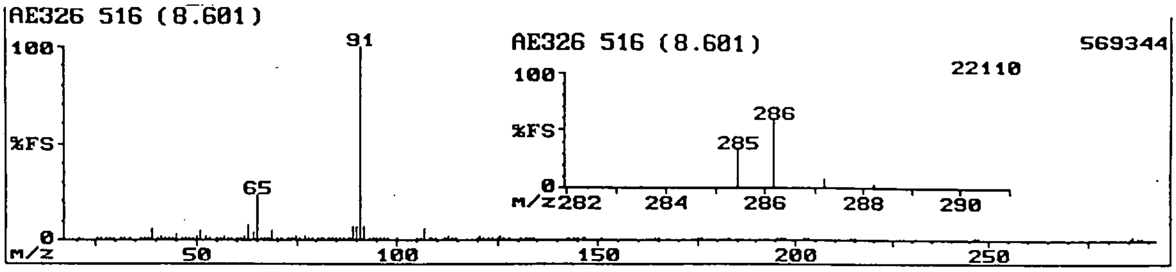


AE216'677 (11.284) REFINE

1048!

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.37	85	0.33	139	2.32	208	0.22
24	0.39	86	0.47	140	4.00	209	0.06
25	0.74	87	2.98	141	0.61	213	0.44
26	0.45	88	0.70	142	0.49	214	2.00
27	0.48	89	2.15	143	0.67	215	4.10
29	0.06	90	0.22	144	0.53	216	0.28
31	5.27	91	0.09	145	1.48	217	0.09
32	1.93	92	0.49	146	0.23	219	0.56
33	0.46	93	2.98	147	0.05	220	2.69
34	0.33	94	2.61	149	0.07	221	0.29
35	0.17	95	3.30	150	0.31	223	0.09
36	0.33	96	3.66	151	2.17	224	0.15
37	1.12	97	0.58	152	8.69	225	0.17
38	1.54	98	0.29	153	0.92	226	0.24
39	2.86	99	0.39	154	0.56	227	0.27
40	0.13	100	0.45	155	0.08	231	0.25
41	0.05	101	1.39	156	0.42	232	0.61
42	0.06	102	0.21	157	1.48	233	6.64
44	1.21	103	0.07	158	0.98	234	8.11
45	9.96	104	0.06	159	0.21	235	0.70
47	0.78	105	0.46	161	0.05	236	0.20
48	0.37	106	2.64	162	0.26	237	0.08
49	0.29	107	16.11	163	0.78	239	1.36
50	9.77	108	30.86	164	1.15	240	0.12
51	3.64	109	3.61	165	2.44	241	0.05
52	0.32	110	1.56	166	0.40	244	0.07
54	0.29	111	0.15	167	0.24	245	0.35
55	1.11	112	0.84	169	1.78	246	0.07
56	3.34	113	5.13	170	1.42	249	0.02
57	13.28	114	0.55	171	0.34	250	0.07
58	3.42	115	0.57	172	0.09	251	5.83
59	0.60	116	0.05	176	0.65	252	18.46
61	1.18	117	0.19	177	0.73	254	1.41
62	3.10	118	0.14	178	0.11	255	0.03
63	11.52	119	0.56	179	0.11	257	0.21
64	1.07	120	0.84	181	1.20	258	1.34
65	1.20	121	2.25	183	16.89	259	1.17
66	0.21	122	0.28	184	1.71	260	0.13
69	41.80	123	0.18	185	0.60	261	0.05
70	1.95	124	0.44	187	0.59	263	0.48
71	1.61	125	1.46	189	1.71	264	1.54
72	0.20	126	4.93	190	2.37	265	0.25
73	0.82	127	4.71	191	0.33	266	0.06
74	5.54	128	0.65	192	0.13	267	0.02
75	13.87	129	0.32	195	2.71	269	0.66
76	6.84	130	0.13	196	1.56	270	3.74
77	0.99	131	0.39	197	0.11	271	6.64
78	0.22	132	1.11	198	0.04	272	0.70
79	0.08	133	0.85	201	4.74	273	0.18
80	0.30	134	0.37	202	100.00	275	0.46
81	2.39	135	0.12	203	7.03	276	0.09
82	6.74	136	0.09	204	2.32	282	0.09
83	4.13	137	0.67	205	0.24	283	0.95
84	0.66	138	1.61	207	0.75	284	0.18
285	0.09	319	0.04	354	0.53	398	0.73
287	0.03	321	0.08	355	0.16	399	0.43
289	0.67	325	0.21	357	2.47	400	0.04
290	0.06	326	0.30	358	0.39	407	0.11
294	0.09	327	0.40	359	0.20	427	0.24
295	0.20	328	0.19	362	0.02	428	0.05
301	0.12	333	0.09	363	0.13	447	0.10
303	1.93	337	0.11	364	0.16	448	0.03
305	0.32	338	0.10	375	0.05	464	0.01
307	0.95	339	0.06	377	0.82	466	17.38
308	0.32	340	0.04	378	0.11	467	2.10
309	0.13	344	0.15	379	0.06	468	1.43
313	0.11	345	0.06	395	0.04	469	0.16
315	0.08	352	0.50	396	0.96	470	0.04
318	0.02	353	3.20	397	4.59		

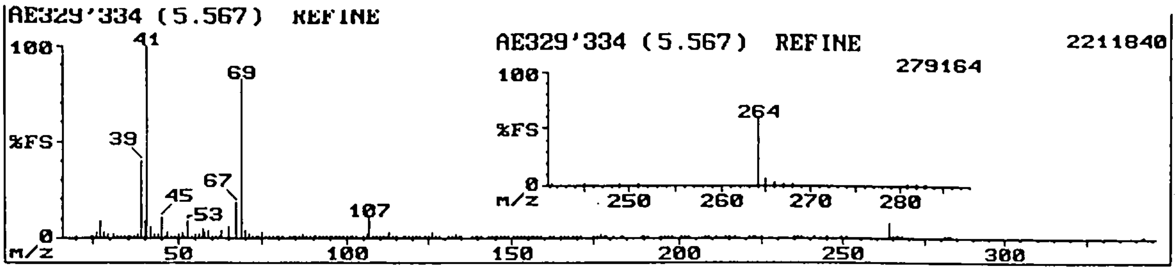
No. 37.



AE326 516 (8.601) 5t

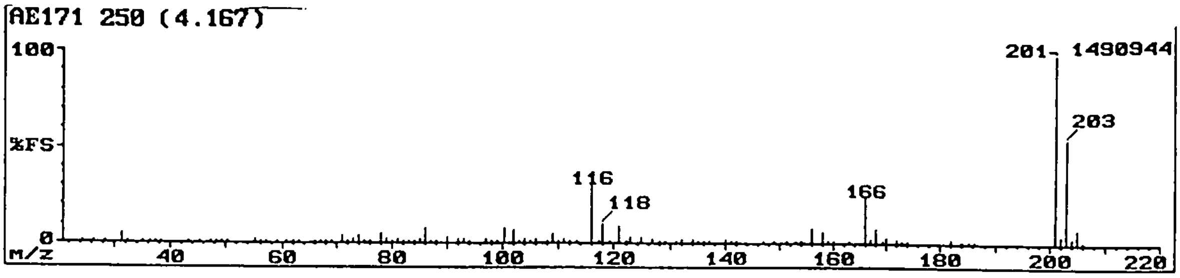
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.08	58	0.24	89	6.47	131	0.11
25	0.08	59	0.10	90	7.01	132	0.04
26	0.17	60	0.07	91	100.00	133	0.39
27	0.19	61	0.48	92	7.15	134	0.05
28	1.10	62	2.17	93	0.78	143	0.07
29	0.04	63	7.91	94	0.44	144	0.06
31	0.35	64	3.73	95	0.32	145	0.35
32	0.48	65	22.84	96	0.10	146	0.04
33	0.06	66	1.33	97	0.12	147	0.18
36	0.05	67	0.08	98	0.19	151	0.07
37	0.20	68	0.62	100	0.08	164	0.09
38	0.84	69	4.77	105	0.04	165	0.10
39	6.12	70	0.09	106	0.68	175	0.03
40	0.62	71	0.16	107	5.67	176	0.17
41	1.51	73	0.08	108	0.23	183	0.10
42	0.09	74	0.67	109	0.94	195	0.37
43	0.14	75	2.00	110	0.14	196	0.17
44	1.26	76	1.16	112	0.15	197	0.13
45	2.71	77	2.05	113	1.82	202	0.02
46	0.14	78	1.05	114	0.06	203	0.07
47	0.31	79	0.41	115	0.13	214	0.04
48	0.11	80	0.03	120	0.13	215	0.20
49	0.35	81	0.08	121	2.06	246	0.04
50	2.32	82	0.43	122	0.23	247	0.26
51	4.72	83	0.29	123	0.25	285	1.29
52	1.72	84	0.06	124	0.05	286	2.28
53	0.39	85	0.24	125	0.21	287	0.34
55	0.20	86	0.32	126	2.20	288	0.12
56	0.62	87	1.30	127	0.09		
57	1.70	88	0.49	128	0.07		

No. 38.



AE329'334 (5.567) REFINE 221184C

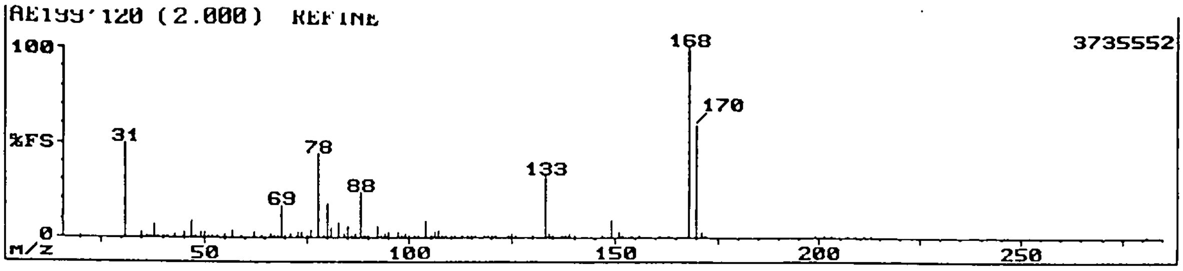
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.16	71	1.74	118	0.01	176	0.57
24	0.34	72	0.81	119	0.06	177	1.69
25	0.75	73	0.74	120	0.06	178	0.12
26	2.72	74	0.82	121	0.03	179	0.09
27	8.29	75	2.96	122	0.03	181	0.03
28	3.33	76	0.86	124	0.14	183	0.17
29	2.19	77	0.32	125	0.54	184	0.02
31	2.14	78	0.10	126	2.66	189	0.10
32	1.15	79	0.07	127	0.65	190	0.02
33	0.66	80	0.02	128	0.15	191	0.06
34	0.28	81	0.24	131	0.08	195	1.10
35	0.18	83	0.14	132	0.13	196	0.95
36	0.19	84	0.30	133	1.47	197	0.14
37	1.22	85	0.43	134	0.08	198	0.05
38	2.28	86	0.28	135	0.08	201	0.13
39	39.63	87	1.77	138	0.02	202	0.06
40	8.47	88	0.10	139	0.24	203	0.08
41	100.00	89	0.25	140	0.04	208	0.06
42	6.30	90	0.04	141	0.03	209	0.16
43	1.85	91	0.08	143	0.11	211	0.03
44	1.76	92	0.08	144	0.08	214	0.01
45	11.16	93	0.65	145	0.56	215	0.12
46	0.75	94	0.63	146	0.08	217	0.04
47	2.71	95	0.46	147	0.18	221	0.04
48	0.14	96	0.05	148	0.02	222	0.14
49	0.30	97	0.46	149	0.02	223	0.03
50	1.88	98	0.10	151	0.23	225	0.03
51	2.85	99	0.16	152	0.10	235	0.13
52	0.91	100	0.21	153	0.90	236	0.08
53	9.12	101	0.17	154	0.06	237	0.14
54	1.13	102	0.05	155	0.03	241	0.05
55	1.53	103	0.07	156	0.02	245	0.07
56	1.77	105	0.06	157	0.27	249	0.02
57	4.49	106	1.47	158	0.06	251	0.02
58	3.19	107	10.23	159	0.08	264	7.50
59	4.21	108	0.54	162	0.05	265	0.79
60	0.66	109	0.52	163	0.09	266	0.37
61	0.45	110	0.03	165	0.34	267	0.04
62	0.23	111	0.01	166	0.04	268	0.01
63	4.35	112	0.30	167	0.25	281	0.00
65	5.42	113	2.94	169	0.07	282	0.03
67	18.70	114	0.14	170	0.03	283	0.02
69	82.96	115	0.18	171	0.05	342	0.02
70	3.89	117	0.01	175	0.07		



AE171 250 (4.167) 149094

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
24	0.03	73	1.73	108	1.43	151	0.03
26	0.01	74	3.42	109	5.29	153	0.04
28	0.06	75	0.23	110	0.39	154	0.15
31	4.46	76	0.09	111	1.75	156	8.24
32	0.08	78	4.74	112	1.30	158	5.63
35	1.03	79	2.06	113	0.12	159	0.21
36	0.40	80	1.03	116	29.95	160	0.84
37	0.32	81	1.79	117	1.37	163	0.04
38	0.21	82	0.23	118	9.62	166	24.18
43	0.12	83	0.19	119	0.46	167	1.46
45	0.11	84	0.09	121	8.38	168	7.69
47	1.01	85	1.91	122	0.13	169	0.17
48	0.21	86	8.10	123	2.82	170	2.61
49	0.35	87	0.94	125	2.46	172	1.87
50	0.17	88	0.13	127	1.58	173	0.09
55	1.53	90	3.21	128	0.39	174	0.29
56	0.06	92	1.68	129	0.28	182	1.82
57	0.15	93	1.68	131	1.30	184	1.20
59	0.13	94	0.33	132	2.42	185	0.08
61	0.06	97	2.20	134	1.60	186	0.19
62	1.27	98	0.17	135	0.27	201	100.00
63	0.06	99	0.81	136	0.27	202	3.50
66	0.47	100	7.69	137	0.39	203	55.22
67	0.59	102	7.28	140	2.03	204	2.95
68	0.20	103	0.55	141	0.13	205	7.83
69	0.73	104	1.58	142	0.66	206	0.44
71	3.95	105	0.78	147	1.02		
72	0.12	106	1.96	149	0.32		

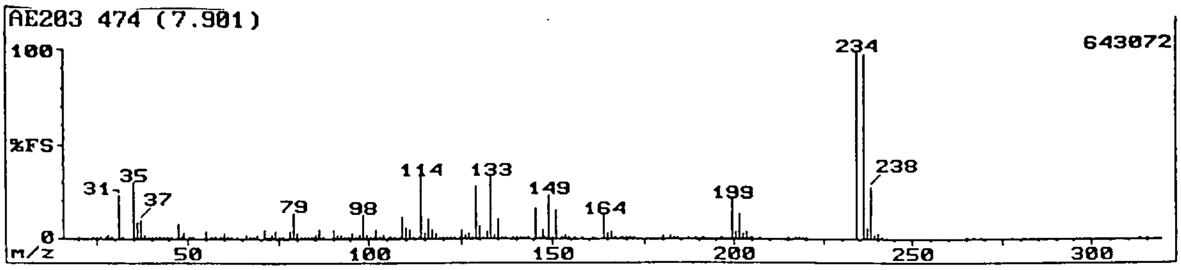
No. 40.



AE199'120 (2.000) REFINE 373

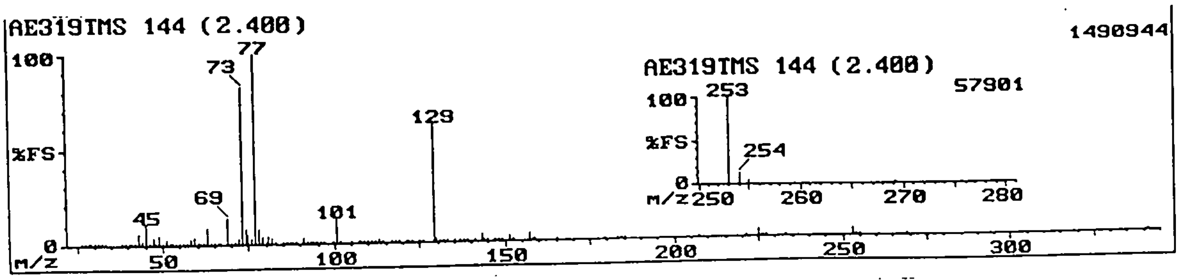
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.00	69	16.23	100	0.08	137	0.90
31	49.12	70	0.57	101	0.18	138	0.16
35	3.34	71	2.08	102	0.79	139	1.67
36	0.87	73	3.07	104	8.33	140	0.04
37	1.25	74	3.21	105	0.32	147	0.01
38	6.91	75	0.79	106	2.88	149	8.66
39	0.21	76	3.81	107	3.62	151	3.32
40	0.09	78	43.86	108	0.12	152	0.14
41	0.02	79	0.78	109	0.55	154	0.07
43	2.14	80	17.32	110	0.01	156	0.03
45	2.58	81	4.99	111	0.39	161	0.02
47	8.55	83	7.35	113	0.07	163	0.01
48	0.10	84	2.28	114	0.64	168	100.00
49	2.71	85	5.73	115	0.04	170	58.33
50	2.99	86	0.11	116	0.75	171	3.10
51	0.12	87	1.84	118	0.47	172	0.08
52	0.39	88	23.57	119	0.02	199	0.09
53	0.01	89	0.84	120	0.04	201	0.05
55	1.47	90	0.41	121	0.07	203	0.01
57	4.22	92	5.95	124	0.94	207	0.02
59	0.65	93	0.17	125	1.97	209	0.01
62	3.23	94	1.95	126	0.34	211	0.06
64	0.53	95	2.69	130	0.08	213	0.02
66	1.47	97	3.02	133	31.58	281	0.01
67	0.02	98	0.01	134	1.70		
68	0.45	99	1.51	135	0.04		

No. 41.



AE203 474 (7.901) 64.

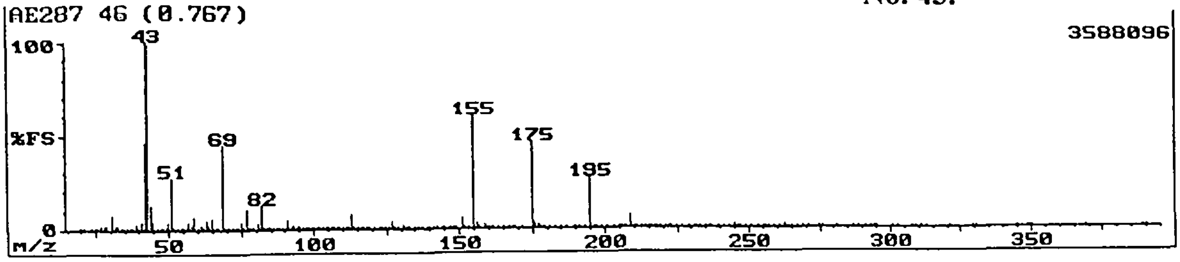
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.66	75	0.43	119	0.72	168	0.15
24	0.43	76	0.03	120	0.49	169	0.40
25	0.13	78	3.54	121	1.43	170	0.11
26	0.20	79	14.01	122	0.12	171	0.09
27	0.10	80	2.79	123	0.47	172	0.05
28	2.26	81	0.25	124	0.19	180	2.08
29	0.13	82	1.24	125	4.86	182	1.49
31	23.25	83	0.67	126	1.72	183	0.15
32	0.45	84	0.37	127	3.30	184	0.26
35	29.62	85	1.91	128	0.42	187	1.20
36	8.56	86	5.33	129	28.34	189	0.80
37	9.83	87	0.80	130	6.61	191	0.15
38	2.11	90	5.18	131	0.52	196	0.04
39	0.12	91	1.92	132	4.34	199	21.82
40	0.05	92	1.93	133	32.96	200	4.34
41	0.05	93	1.26	134	1.94	201	13.85
42	0.10	94	0.51	135	10.83	202	2.67
43	0.74	95	3.30	136	0.60	203	3.62
44	0.67	96	0.75	137	0.32	204	0.59
45	0.07	97	1.64	139	0.23	205	1.41
47	7.60	98	12.58	140	0.34	207	0.54
48	0.93	99	1.69	141	0.12	215	0.40
49	2.55	100	0.22	142	0.17	217	0.39
50	0.51	101	0.61	143	0.06	218	0.10
51	0.10	102	4.58	145	16.40	219	0.14
55	3.54	103	0.54	146	1.29	220	0.06
56	0.24	104	1.56	147	5.21	234	100.00
57	0.10	105	0.27	148	0.20	236	98.73
59	0.44	106	1.14	149	22.93	237	5.61
60	2.59	107	0.26	150	0.83	238	28.50
61	0.73	108	1.12	151	15.13	239	1.75
62	0.27	109	12.10	152	1.04	240	3.11
63	0.05	110	6.05	153	2.41	241	0.18
66	2.36	111	4.50	154	0.19	265	0.14
67	0.48	112	0.22	156	0.52	267	0.14
68	0.94	113	1.14	158	0.36	269	0.06
69	1.73	114	33.28	161	0.39	313	0.09
71	4.38	115	3.03	164	12.90	315	0.06
72	0.75	116	10.99	165	2.45		
73	1.52	117	5.18	166	4.18		
74	4.14	118	2.83	167	1.25		



AE319TMS 144 (2.400) 149

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.06	61	0.70	95	0.35	139	0.02
27	0.27	62	0.99	96	0.06	141	0.05
28	0.31	63	8.93	97	0.03	143	4.09
29	0.70	64	0.60	100	0.23	144	0.34
30	0.09	65	0.39	101	12.43	145	0.17
31	0.48	66	0.12	102	0.32	147	0.39
32	0.08	67	0.29	105	0.05	148	0.08
33	0.03	69	14.01	107	0.05	149	0.04
38	0.03	70	0.59	108	0.04	151	2.95
39	0.16	71	0.63	109	0.39	152	0.07
40	0.03	72	2.83	110	0.07	157	3.49
41	0.12	73	82.42	111	0.06	158	0.16
42	0.97	74	7.55	112	0.17	159	0.17
43	5.77	75	4.46	113	1.75	165	0.11
44	2.09	76	2.76	114	0.06	179	0.03
45	10.71	77	100.00	117	1.17	183	0.61
46	0.82	78	7.69	118	0.11	184	0.07
47	4.31	79	3.86	119	0.10	185	0.03
48	0.33	80	0.26	121	0.19	207	0.03
49	4.46	81	3.85	122	0.02	221	0.02
50	0.47	82	2.64	123	0.05	225	3.54
51	2.63	83	0.26	125	0.17	226	0.37
52	0.08	85	0.15	126	0.02	227	0.10
53	0.52	86	0.02	129	62.09	233	0.04
54	0.27	87	0.15	130	2.04	253	4.22
55	1.37	88	0.07	131	0.97	254	0.48
56	0.40	89	0.20	132	0.33	255	0.19
57	1.18	91	2.94	133	0.05	269	0.02
58	2.95	92	0.20	135	0.01	341	0.03
59	3.66	93	0.55	137	1.39		
60	0.60	94	0.18	138	0.07		

No. 43.



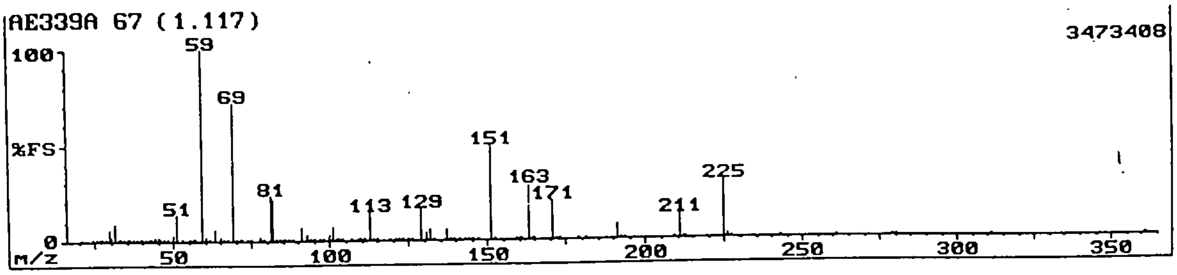
AE287 46 (0.767) 358.

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.12	78	1.02	137	0.40	217	0.09
21	0.01	79	0.09	139	0.41	218	0.01
24	0.13	81	2.65	140	0.04	219	0.02
25	0.32	82	12.44	141	0.46	221	0.07
26	0.90	83	0.61	142	0.03	222	0.01
27	2.28	84	0.04	144	0.40	223	0.02
28	1.91	85	0.06	145	0.21	225	0.10
29	1.91	86	0.03	147	0.66	227	0.19
31	8.11	87	0.11	148	0.02	229	0.02
32	1.64	88	0.23	149	0.06	231	0.02
33	2.31	89	0.41	151	6.28	232	0.04
34	0.08	90	0.50	152	0.19	233	0.09
35	0.09	91	4.91	153	0.18	235	0.02
36	0.12	92	0.19	155	61.64	236	0.01
37	0.56	93	1.78	156	3.25	237	0.18
38	0.76	94	0.34	157	0.93	239	0.05
39	2.63	95	1.61	159	1.81	241	0.03
40	0.52	96	0.15	160	0.12	243	0.31
41	4.11	97	0.03	161	0.07	245	1.48
42	45.21	98	0.01	163	0.10	246	0.09
43	100.00	99	0.11	165	0.01	247	0.02
44	12.44	100	0.74	167	0.04	249	0.03
45	3.80	101	0.73	168	0.15	251	0.07
46	0.66	102	0.04	169	0.11	253	0.04
47	1.19	103	0.04	171	0.06	255	0.02
48	0.11	104	0.07	175	47.03	256	0.04
49	0.66	105	0.05	176	2.48	257	0.01
50	3.91	106	0.16	177	1.48	259	0.01
51	27.17	107	0.57	178	0.10	261	0.01
52	0.42	108	0.39	179	0.21	263	1.47
53	0.86	109	1.03	181	0.06	264	0.09
54	0.09	110	0.09	183	0.02	265	0.05
55	0.83	111	0.10	185	0.06	267	0.02
56	1.02	112	0.85	187	0.05	269	0.02
57	3.82	113	7.99	189	0.45	271	0.03
58	2.11	114	0.30	190	0.05	275	0.02
59	6.65	115	0.08	191	0.04	276	0.01
60	0.79	116	0.01	193	0.09	281	0.01
61	2.28	117	0.08	195	26.71	287	0.05
62	0.67	118	0.01	196	1.29	289	0.02
63	4.88	119	0.13	197	0.16	291	0.01
64	1.50	121	0.18	199	0.04	293	0.01
65	5.45	123	0.04	201	0.03	294	0.01
66	0.19	124	0.07	203	0.02	295	0.08
67	0.36	125	0.34	205	0.04	301	0.02
69	44.75	126	0.42	206	0.02	303	0.01
70	0.66	127	3.74	207	0.02	308	0.02
71	1.13	128	0.21	209	6.39	309	0.03
72	0.19	129	0.10	210	0.37	311	0.02
73	0.53	131	2.11	211	0.04	313	0.01
74	0.56	132	0.42	213	0.09	321	0.04
75	4.05	133	0.23	214	0.01	329	0.03
76	0.63	135	0.84	215	0.02	331	0.01
77	10.73	136	0.05	216	0.01	345	0.05

AE287 46 (0.767)

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
349	0.18	369	0.02	390	0.01
350	0.02	389	0.12		

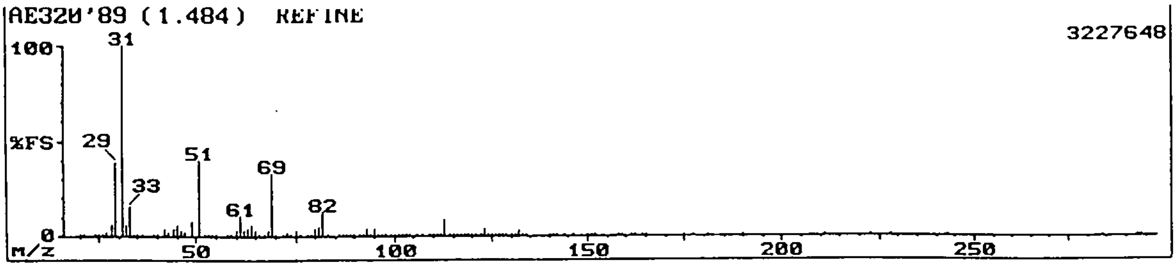
No. 44.



AE339A 67 (1.117) 347

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	56	0.21	98	0.11	147	0.02
24	0.01	57	0.10	100	2.92	151	49.06
25	0.03	59	100.00	101	6.78	152	1.39
26	0.03	60	2.39	102	0.17	159	0.58
27	0.08	61	0.63	103	0.07	160	0.43
28	0.35	63	5.96	104	0.02	161	0.10
29	5.81	65	2.24	107	0.02	163	17.10
30	1.54	66	0.11	109	1.19	164	0.58
31	8.96	67	0.04	110	0.09	165	0.05
32	0.97	69	72.17	111	0.16	171	20.87
33	0.33	70	0.78	113	14.86	172	0.87
34	0.01	71	0.38	114	0.44	173	0.09
35	0.11	72	0.23	115	0.01	179	0.52
36	0.02	74	0.66	119	0.07	181	0.83
37	0.04	75	0.99	121	0.11	191	8.14
38	0.01	78	1.50	122	0.03	192	0.35
39	0.05	79	0.12	123	0.01	193	0.03
40	0.03	81	22.88	125	0.11	209	0.04
41	0.03	82	21.34	126	0.03	211	12.74
42	0.09	83	0.57	129	16.86	212	0.55
43	0.56	84	0.04	131	3.80	213	0.05
44	2.30	85	0.02	132	6.04	225	29.72
45	1.67	86	0.03	133	0.34	226	1.61
46	0.04	87	0.02	137	6.28	227	0.15
47	1.30	88	0.02	138	0.24	243	0.01
48	0.03	91	6.34	139	0.02	261	0.01
50	3.15	93	2.68	141	0.44	279	0.56
51	13.56	94	0.41	143	0.55	280	0.03
53	0.57	95	0.10	144	0.02	311	0.11
55	0.19	97	0.04	145	0.02	361	0.01

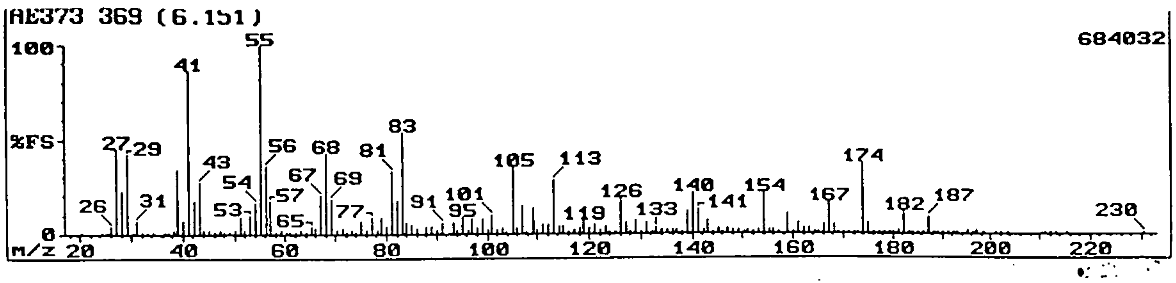
No. 45.



AE320'89 (1.484) REFINE 322

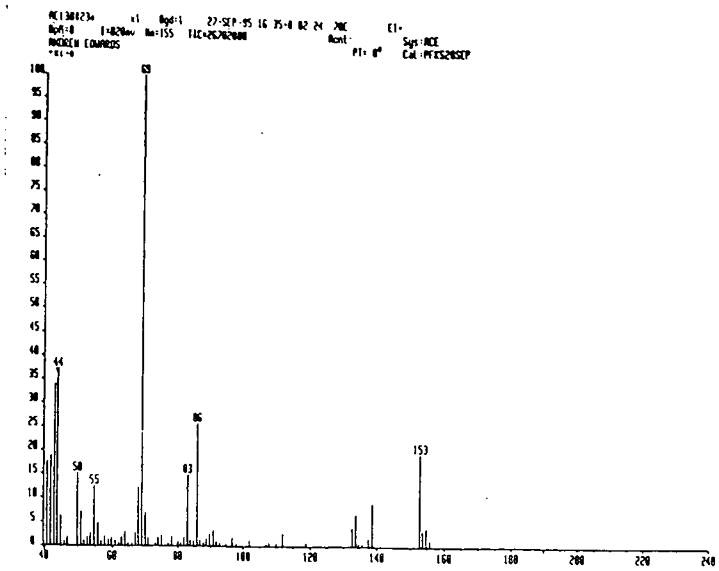
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.33	61	11.04	96	0.30	129	0.02
21	0.05	62	2.70	97	0.06	130	0.08
24	0.22	63	3.97	98	0.08	131	0.85
25	0.37	64	6.12	99	0.16	132	3.05
26	1.12	65	2.70	100	0.94	133	0.60
27	1.98	66	0.16	101	0.83	134	0.02
28	6.03	67	0.69	102	0.03	140	0.05
29	38.58	68	3.39	103	0.04	141	0.29
31	100.00	69	32.99	104	0.01	142	0.46
32	6.22	70	0.45	106	0.02	144	0.12
33	15.36	72	0.16	107	0.02	146	0.03
34	0.30	73	1.49	109	0.06	150	0.42
35	0.06	74	0.33	110	0.12	151	0.77
36	0.11	75	2.92	111	0.24	152	0.02
39	0.23	76	0.52	112	0.97	158	0.00
40	0.09	78	0.36	113	8.88	159	0.04
42	3.90	79	0.50	114	0.74	161	0.11
43	1.47	80	3.46	115	0.85	162	0.69
44	4.16	81	4.47	116	0.03	164	0.16
45	6.06	82	13.07	117	0.01	165	0.67
46	2.44	83	1.33	118	0.01	175	0.01
47	1.65	86	0.01	119	0.04	177	0.02
49	7.58	87	0.03	120	0.00	181	0.06
51	39.59	88	0.03	121	0.01	190	0.02
52	0.70	89	0.02	122	0.27	211	0.02
53	0.49	90	0.12	123	3.43	223	0.11
54	0.04	91	1.10	124	0.16	228	0.02
55	0.54	92	0.49	125	0.02	243	0.08
58	0.13	93	3.84	126	0.10	284	0.01
59	0.14	94	1.40	127	0.19	293	0.00
60	2.70	95	4.03	128	0.18	294	0.02

No. 46.



AE373 369 (6.151) 68

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.21	69	17.96	116	1.30	162	3.26
24	0.03	70	1.86	117	2.10	163	2.96
25	0.16	71	2.66	118	2.54	164	0.53
26	4.19	72	1.09	119	6.74	165	0.83
27	44.91	73	2.40	120	2.73	166	5.28
28	22.31	74	0.83	121	4.87	167	16.17
29	41.32	75	7.11	122	1.54	168	4.38
30	1.02	76	2.07	123	4.23	169	1.16
31	6.62	77	8.87	124	0.62	170	0.91
32	0.68	78	1.55	125	1.22	171	1.11
33	0.94	79	8.42	126	18.56	172	0.31
34	0.07	80	3.71	127	5.80	173	0.85
36	0.02	81	33.08	128	1.29	174	38.32
37	0.52	82	17.07	129	6.44	175	6.21
38	2.06	83	53.29	130	0.53	176	0.93
39	34.13	84	5.35	131	5.88	177	0.74
40	6.55	85	5.28	132	1.07	178	0.06
41	86.83	86	2.62	133	2.92	179	0.17
42	17.66	88	3.41	134	2.03	180	0.08
43	27.54	89	3.52	135	1.67	181	2.26
44	2.03	90	2.30	136	1.94	182	11.83
45	1.47	91	5.43	137	2.23	183	1.24
46	0.36	93	5.91	138	0.33	184	0.39
47	1.88	94	1.65	139	12.13	185	0.07
48	0.25	95	9.09	140	21.41	186	0.15
49	0.74	96	2.28	141	12.28	187	8.76
50	2.01	97	7.86	142	1.87	188	1.05
51	8.98	98	2.47	143	6.40	189	0.50
52	1.72	99	7.37	144	0.65	190	1.14
53	9.43	100	1.85	145	2.43	191	0.40
54	16.32	101	9.36	146	0.48	192	0.38
55	100.00	102	2.03	147	2.84	193	0.49
56	35.93	103	2.62	148	1.46	195	1.62
57	17.22	104	0.60	149	1.70	196	0.12
58	1.15	105	34.58	150	0.70	197	1.60
59	2.37	106	2.73	151	2.16	198	0.12
60	0.52	107	14.37	152	0.36	201	0.48
61	0.62	108	1.28	153	1.69	202	1.27
62	0.88	109	13.92	154	20.96	203	0.08
63	1.90	110	1.67	155	2.40	210	0.66
64	0.72	111	5.01	156	2.23	211	0.37
65	3.63	112	4.98	157	0.46	212	0.93
66	2.62	113	27.99	159	10.63	213	0.14
67	20.06	114	3.78	160	0.60	215	0.06
68	43.11	115	3.82	161	5.43	230	0.04



No. 47.

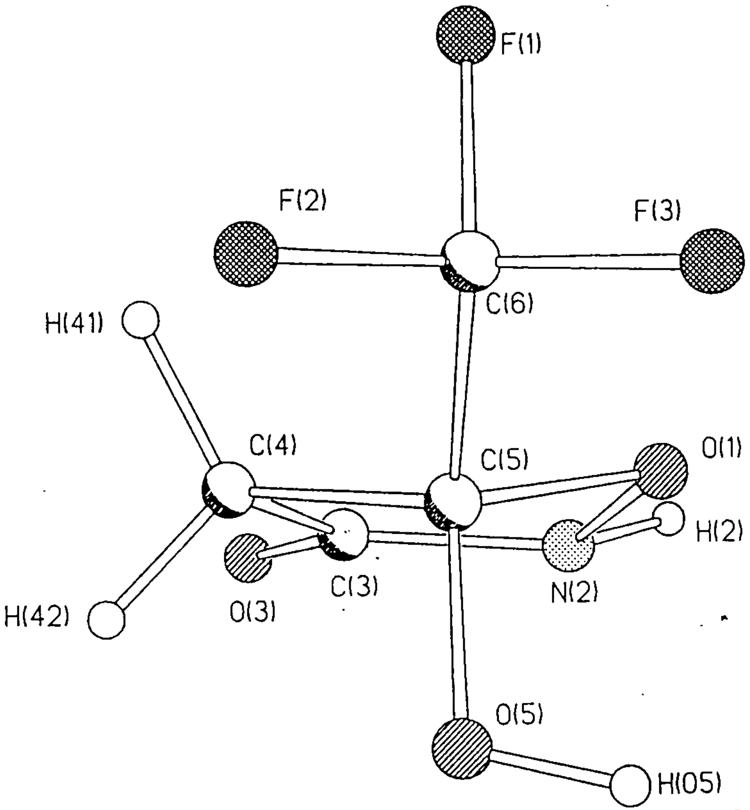
```
BpM=0      I=820mv  Hm=155   TIC=26782000                   Acnt:            Sys:ACE
ANDREW EDWARDS                                                     PT= 0     Cal:PFKS20:
        Mass      % Base                      Mass      % Base
          40 94       17 51                    135.81       0.37
          41.94       18.70                    137.79       1.60
          42 94       33.80                    138.79       8.98
          43 91       37.05 F                  152.77      19.46
          43 94       32.61 F                  153.78       3.18
          44 93        6.10                    154.78       3.81
          45 93        0.93                    155.80       1.19
          46 92        1 77
          49 92       15 08
          50 92        7 06
          51 93        1.02
          52 92        1.75
          53.91        2.58
          54 92       12.36
          55 92        4.65
          56 92        0.93
          57 92        1.84
          58.93        1 19
          59 91        1.64
          60 91        1.02
          61.91        0.61
          62 91        1.78
          63 91        2.97
          64.92        0.45
          65 91        0 39
          66 90        2.60
          67 90       12 23
          68.89      100.00
          69.90        6.84
          70 89        1.62
          72.91        0.41
          73.89        1.78
          74.89        2.21
          76.89        0.50
          77.87        1.88
          79.88        0.74
          80 86        0.63
          81 67        1 77
          82 87       14 80
          83 87        0 97
          84 87        0 93
          85 89       25 58
          86 89        1 15
          87 87        0 56
          86 86        1 49
          89 87        2.42
          90 96        3 27
          91 86        0 69
          92 26        0 63
          94 86        0 39
          96 84        1 95
          97 65        0 43
         101 86        1 10
         107 83        0 75
         109 85        0 63
         111 84        2 70
         116 81        0 80
         132 79        3 90
         133 81        6 67
         134 82        0 59
```

Appendix 4.

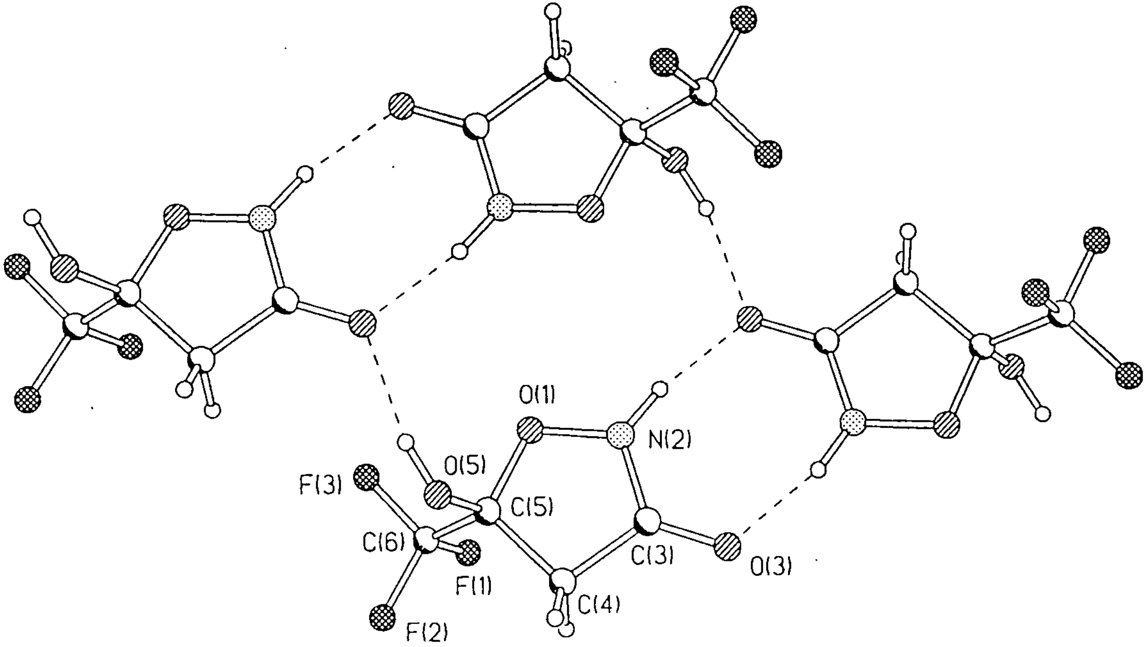
Crystallographic Data.

No.	Name
1	5-hydroxy-5-trifluoromethylisoxazolidin-3-one (**90**)

No. 1.



F(1)
F(2)
F(3)
C(6)
H(41)
C(4)
C(5)
O(1)
H(2)
C(3)
N(2)
O(3)
H(42)
O(5)
H(05)



O(1)
N(2)
O(5)
F(3)
C(5)
C(6)
C(3)
O(3)
F(1)
C(4)
F(2)

Table 1. Crystal data and structure refinement for 1.

Identification code	96srv051
Empirical formula	C4 H4 F3 N O3
Formula weight	171.08
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 5.431(1) A alpha = 90 deg. b = 21.709(3) A beta = 110.81(1) de c = 5.493(1) A gamma = 90 deg.
Volume	605.4(2) A^3
Z	4
Density (calculated)	1.877 Mg/m^3
Absorption coefficient	0.211 mm^-1
F(000)	344
Crystal size	0.30 x 0.20 x 0.06 mm
Theta range for data collection	1.88 to 25.61 deg.
Index ranges	-3<=h<=6, -24<=k<=24, -6<=l<=6
Reflections collected	2625
Independent reflections	1037 [R(int) = 0.0388]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1032 / 0 / 117
Goodness-of-fit on F^2	1.159
Final R indices [I>2sigma(I)]	R1 = 0.0381, wR2 = 0.0852
R indices (all data)	R1 = 0.0542, wR2 = 0.0991
Extinction coefficient	0.031(6)
Largest diff. peak and hole	0.240 and -0.217 e.A^-3

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)
O(1)	1248(3)	756.7(7)	5319(3)	26(1)
N(2)	3276(4)	383.1(9)	7041(4)	24(1)
C(3)	5639(4)	649(1)	7762(4)	23(1)
O(3)	7658(3)	453.3(7)	9475(3)	27(1)
C(4)	5425(5)	1212(1)	6092(5)	29(1)
C(5)	2601(5)	1174(1)	4167(5)	23(1)
O(5)	2556(4)	961.4(8)	1783(3)	29(1)
C(6)	1101(5)	1782(1)	3845(5)	28(1)
F(1)	1049(3)	1997.1(7)	6101(3)	43(1)
F(2)	2234(3)	2213.5(7)	2845(3)	41(1)
F(3)	-1405(3)	1723.8(7)	2229(3)	36(1)

Table 3. Bond lengths [A] and angles [deg] for 1.

O(1)-N(2)	1.423(2)	O(1)-C(5)	1.446(3)
N(2)-C(3)	1.333(3)	N(2)-H(2)	0.98(4)
C(3)-O(3)	1.239(3)	C(3)-C(4)	1.507(3)
C(4)-C(5)	1.525(3)	C(4)-H(41)	1.04(3)
C(4)-H(42)	0.97(3)	C(5)-O(5)	1.381(3)
C(5)-C(6)	1.529(3)	O(5)-H(05)	0.89(4)
C(6)-F(1)	1.334(3)	C(6)-F(3)	1.341(3)
C(6)-F(2)	1.341(3)		
N(2)-O(1)-C(5)	104.7(2)	C(3)-N(2)-O(1)	112.7(2)
C(3)-N(2)-H(2)	125(2)	O(1)-N(2)-H(2)	114(2)
O(3)-C(3)-N(2)	125.1(2)	O(3)-C(3)-C(4)	126.6(2)
N(2)-C(3)-C(4)	108.2(2)	C(3)-C(4)-C(5)	102.7(2)
C(3)-C(4)-H(41)	111(2)	C(5)-C(4)-H(41)	113(2)
C(3)-C(4)-H(42)	110(2)	C(5)-C(4)-H(42)	111(2)
H(41)-C(4)-H(42)	109(3)	O(5)-C(5)-O(1)	111.4(2)
O(5)-C(5)-C(4)	110.5(2)	O(1)-C(5)-C(4)	105.8(2)
O(5)-C(5)-C(6)	110.5(2)	O(1)-C(5)-C(6)	105.0(2)
C(4)-C(5)-C(6)	113.4(2)	C(5)-O(5)-H(05)	111(2)
F(1)-C(6)-F(3)	107.3(2)	F(1)-C(6)-F(2)	107.5(2)
F(3)-C(6)-F(2)	107.5(2)	F(1)-C(6)-C(5)	112.4(2)
F(3)-C(6)-C(5)	111.6(2)	F(2)-C(6)-C(5)	110.3(2)

able 4. Anisotropic displacement parameters (A^2 x 10^3) for 1.
he 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
(1)	18(1)	28(1)	28(1)	8(1)	5(1)	0(1)
(2)	19(1)	25(1)	25(1)	6(1)	2(1)	2(1)
(3)	21(1)	23(1)	24(1)	-3(1)	6(1)	-1(1)
(3)	22(1)	26(1)	29(1)	1(1)	3(1)	0(1)
(4)	22(1)	29(1)	31(2)	5(1)	5(1)	-4(1)
(5)	21(1)	24(1)	24(1)	2(1)	7(1)	-3(1)
(5)	25(1)	33(1)	28(1)	-3(1)	9(1)	-4(1)
(6)	29(1)	27(1)	29(1)	1(1)	9(1)	-3(1)
(1)	48(1)	37(1)	44(1)	-11(1)	18(1)	1(1)
(2)	42(1)	27(1)	56(1)	11(1)	17(1)	-3(1)
(3)	26(1)	33(1)	42(1)	6(1)	5(1)	6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 1.

	x	y	z	U(eq)
H(2)	2683(72)	103(17)	8128(69)	64(10)
H(41)	5785(65)	1610(14)	7205(64)	50(9)
H(42)	6684(62)	1189(13)	5211(56)	42(8)
H(05)	965(78)	826(15)	832(68)	57(10)

Appendix 5.

Requirements of the Board of Studies

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing:-

(A) all research colloquia, seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student;

(B) lectures organised by Durham University Chemical Society;

(C) details of postgraduate induction courses;

(D) all research conferences attended and papers presented by the author during the period when research for the thesis was carried out.

Colloquia, Lectures and Seminars From Invited Speakers 1994-1997

1994

October 5	Prof. N. L. Owen, Brigham Young University, Utah, USA* *Determining Molecular Structure - the INADEQUATE NMR way*
October 19	Prof. N. Bartlett, University of California* *Some Aspects of Ag(II) and Ag(III) Chemistry*
November 2	Dr P. G. Edwards, University of Wales, Cardiff *The Manipulation of Electronic and Structural Diversity in Metal Complexes - New Ligands*
November 3	Prof. B. F. G. Johnson, Edinburgh University* *Arene-metal Clusters*
November 9	Dr G. Hogarth, University College, London *New Vistas in Metal-imido Chemistry*
November 10	Dr M. Block, Zeneca Pharmaceuticals, Macclesfield* *Large-scale Manufacture of ZD 1542, a Thromboxane Antagonist Synthase Inhibitor*
November 16	Prof. M. Page, University of Huddersfield* *Four-membered Rings and b-Lactamase*
November 23	Dr J. M. J. Williams, University of Loughborough* *New Approaches to Asymmetric Catalysis*
December 7	Prof. D. Briggs, ICI and University of Durham* *Surface Mass Spectrometry*

1995

January 11	Prof. P. Parsons, University of Reading* *Applications of Tandem Reactions in Organic Synthesis*
January 18	Dr G. Rumbles, Imperial College, London

	Real or Imaginary Third Order Non-linear Optical Materials
January 25	Dr D. A. Roberts, Zeneca Pharmaceuticals* *The Design and Synthesis of Inhibitors of the Renin-angiotensin System*
February 1	Dr T. Cosgrove, Bristol University* *Polymers do it at Interfaces*
February 8	Dr D. O'Hare, Oxford University* *Synthesis and Solid-state Properties of Poly-, Oligo- and Multidecker Metallocenes*
February 22	Prof. E. Schaumann, University of Clausthal* *Silicon- and Sulphur-mediated Ring-opening Reactions of Epoxide*
March 1	Dr M. Rosseinsky, Oxford University *Fullerene Intercalation Chemistry*
March 22	Dr M. Taylor, University of Auckland, New Zealand *Structural Methods in Main-group Chemistry*
April 26	Dr M. Schroder, University of Edinburgh *Redox-active Macrocyclic Complexes : Rings, Stacks and Liquid Crystals*
May 4	Prof. A. J. Kresge, University of Toronto *The Ingold Lecture Reactive Intermediates : Carboxylic-acid Enols and Other Unstable Species*
October 11	Prof. P. Lugar, Frei Univ Berlin, FRG *Low Temperature Crystallography*
October 13	Prof. R. Schmutzler, Univ Braunschweig, FRG. *Calixarene-Phosphorus Chemistry: A New Dimension in Phosphorus Chemistry*
October 18	Prof. A. Alexakis, Univ. Pierre et Marie Curie, Paris* *Synthetic and Analytical Uses of Chiral Diamines*
October 25	Dr.D.Martin Davies, University of Northumbria *Chemical reactions in organised systems.*

November 1	Prof. W. Motherwell, UCL London* *New Reactions for Organic Synthesis*
November 3	Dr B. Langlois, University Claude Bernard-Lyon* *Radical Anionic and Psuedo Cationic Trifluoromethylation*
November 8	Dr. D. Craig, Imperial College, London* *New Stategies for the Assembly of Heterocyclic Systems*
November 15	Dr Andrea Sella, UCL, London *Chemistry of Lanthanides with Polypyrazoylborate Ligands*
November 17	Prof. David Bergbreiter, Texas A&M, USA* *Design of Smart Catalysts, Substrates and Surfaces from Simple Polymers*
November 22	Prof. I Soutar, Lancaster University *A Water of Glass? Luminescence Studies of Water-Soluble Polymers.*
November 29	Prof. Dennis Tuck, University of Windsor, Ontario, Canada *New Indium Coordination Chemistry*
December 8	Professor M.T. Reetz, Max Planck Institut, Mulheim *Perkin Regional Meeting*

1996

January 10	Dr Bill Henderson, Waikato University, NZ *Electrospray Mass Spectrometry - a new sporting technique*
January 17	Prof. J. W. Emsley , Southampton University* *Liquid Crystals: More than Meets the Eye*
January 24	Dr Alan Armstrong, Nottingham Univesity* *Alkene Oxidation and Natural Product Synthesis*
January 31	Dr J. Penfold, Rutherford Appleton Laboratory, *Soft Soap and Surfaces*

February 7	Dr R.B. Moody, Exeter University *Nitrosations, Nitrations and Oxidations with Nitrous Acid*
February 12	Dr Paul Pringle, University of Bristol *Catalytic Self-Replication of Phosphines on Platinum(O)*
February 14	Dr J. Rohr, Univ Gottingen, FRG *Goals and Aspects of Biosynthetic Studies on Low Molecular Weight Natural Products*
February 21	Dr C R Pulham , Univ. Edinburgh *Heavy Metal Hydrides - an exploration of the chemistry of stannanes and plumbanes*
February 28	Prof. E. W. Randall, Queen Mary & Westfield College *New Perspectives in NMR Imaging*
March 6	Dr Richard Whitby, Univ of Southampton* *New approaches to chiral catalysts: Induction of planar and metal centred asymmetry*
March 7	Dr D.S. Wright, University of Cambridge *Synthetic Applications of* Me_2N*-p-Block Metal Reagents*
March 12	RSC Endowed Lecture - Prof. V. Balzani, Univ of Bologna *Supramolecular Photochemistry*
March 13	Prof. Dave Garner, Manchester University* *Mushrooming in Chemistry*
April 30	Dr L.D.Pettit, Chairman, IUPAC Commission of Equilibrium Data *pH-metric studies using very small quantities of uncertain purity*
October 9	Professor G. Bowmaker, University Aukland, NZ *Coordination and Materials Chemistry of the Group 11 and Group 12 Metals : Some Recent Vibrational and Solid State NMR Studies*
October 14	Professor A. R. Katritzky, University of Gainesville,University of Florida, USA*

	Recent Advances in Benzotriazole Mediated Synthetic Methodology
October 16	Professor Ojima, Guggenheim Fellow, State University of New York at Stony Brook* *Silylformylation and Silylcarbocyclisations in Organic Synthesis*
October 22	Professor Lutz Gade, Univ. Wurzburg, Germany* *Organic transformations with Early-Late Heterobimetallics: Synergism and Selectivity*
October 22	Professor B. J. Tighe, Department of Molecular Sciences and Chemistry, University of Aston *Making Polymers for Biomedical Application - can we meet Nature's Challenge?* Joint lecture with the Institute of Materials
October 23	Professor H. Ringsdorf (Perkin Centenary Lecture), Johannes Gutenberg-Universitat, Mainz, Germany *Function Based on Organisation*
October 29	Professor D. M. Knight, Department of Philosophy, University of Durham. *The Purpose of Experiment - A Look at Davy and Faraday*
October 30	Dr Phillip Mountford, Nottingham University *Recent Developments in Group IV Imido Chemistry*
November 6	Dr Melinda Duer, Chemistry Department, Cambridge *Solid-state NMR Studies of Organic Solid to Liquid-crystalline Phase Transitions*
November 12	Professor R. J. Young, Manchester Materials Centre, UMIST* *New Materials - Fact or Fantasy?* Joint Lecture with Zeneca & RSC
November 13	Dr G. Resnati, Milan* *Perfluorinated Oxaziridines: Mild Yet Powerful Oxidising Agents*
November 18	Professor G. A. Olah, University of Southern California, USA* *Crossing Conventional Lines in my Chemistry of the Elements*

November 19 Professor R. E. Grigg, University of Leeds*
Assembly of Complex Molecules by Palladium-Catalysed Queueing Processes

November 20 Professor J. Earnshaw, Deptartment of Physics, Belfast
Surface Light Scattering: Ripples and Relaxation

November 27 Dr Richard Templer, Imperial College, London
Molecular Tubes and Sponges

December 3 Professor D. Phillips, Imperial College, London
"A Little Light Relief"

December 4 Professor K. Muller-Dethlefs, York University
Chemical Applications of Very High Resolution ZEKE Photoelectron Spectroscopy

December 11 Dr Chris Richards, Cardiff University*
Stereochemical Games with Metallocenes

1997

January 15 Dr V. K. Aggarwal, University of Sheffield*
Sulfur Mediated Asymmetric Synthesis

January 16 Dr Sally Brooker, University of Otago, NZ
Macrocycles: Exciting yet Controlled Thiolate Coordination Chemistry

January 21 Mr D. Rudge, Zeneca Pharmaceuticals*
High Speed Automation of Chemical Reactions

January 22 Dr Neil Cooley, BP Chemicals, Sunbury
Synthesis and Properties of Alternating Polyketones

January 29 Dr Julian Clarke, UMIST
What can we learn about polymers and biopolymers from computer-generated nanosecond movie-clips?

February 4 Dr A. J. Banister, University of Durham

	From Runways to Non-metallic Metals - A New Chemistry Based on Sulphur
February 5	Dr A. Haynes, University of Sheffield *Mechanism in Homogeneous Catalytic Carbonylation*
February 12	Dr Geert-Jan Boons, University of Birmingham* *New Developments in Carbohydrate Chemistry*
February 18	Professor Sir James Black, Foundation/King's College London* *My Dialogues with Medicinal Chemists*
February 19	Professor Brian Hayden, University of Southampton *The Dynamics of Dissociation at Surfaces and Fuel Cell Catalysts*
February 25	Professor A. G. Sykes, University of Newcastle *The Synthesis, Structures and Properties of Blue Copper Proteins*
February 26	Dr Tony Ryan, UMIST* *Making Hairpins from Rings and Chains*
March 4	Professor C. W. Rees, Imperial College* *Some Very Heterocyclic Chemistry*
March 5	Dr J. Staunton FRS, Cambridge University* *Tinkering with biosynthesis: towards a new generation of antibiotics*
March 11	Dr A. D. Taylor, ISIS Facility, Rutherford Appleton Laboratory *Expanding the Frontiers of Neutron Scattering*
March 19	Dr Katharine Reid, University of Nottingham *Probing Dynamical Processes with Photoelectrons*

* lectures attended

First Year Induction Courses

This course consists of a series of one hour lectures on the services available in the department.

Departmental Organisations -	Dr. E. J. F. Ross
Safety Matters -	Dr. G. M. Brooke
Electrical Appliances -	Mr. B. T. Barker
Chromatography and Microanalysis -	Mr. T. F. Holmes
Atomic Absorptiometry and Inorganic Analysis -	Mr. R. Coult
Library Facilities -	Mrs. M. Hird
Mass Spectroscopy -	Dr. M. Jones
NMR Spectroscopy -	Dr. A. Kenwright
Glass-blowing Techniques -	Mr. R. Hart Mr. G. Haswell

Research Conferences Attended

April 1995	North Eastern Graduate Symposium, University of Durham.
June 1997	11th Postgraduate Heterocyclic Symposium, University of Keele.
August 1997	15th International Symposium on Fluorine Chemistry, University of British Columbia, Vancouver, CANADA.

References.

1. H. Moissan, *Le Fluor et ses Composes,* Steinheil, Paris, 1900.
2. H. Moissan, *Compt. Rend.,* 1890, **110**, 276.
3. F. Swarts, *Bull. Acad. Roy. Belg.,* 1892, **24**, 474.
4. A. K. Barbour, L. J. Belf and M. W. Buxton, *Adv. Fluorine Chem.,* 1963, **3**, 181.
5. T. Midgley and A. L. Henne, *Ind. Eng. Chem.,* 1930, **22**, 542.
6. R. D. Chambers, *Fluorine in Organic Chemistry,* Wiley and Sons Inc., New York, 1973.
7. D. B. Harper and D. O'Hagan, *Nat. Prod. Rep.,* 1994, **11**, 123.
8. B. E. Smart, in *Molecular Structure and Energetics,* ed. J. F. Liebman and A. Greenberg, VCH, Deerfield Beach, 1986, vol. 3, p. 141.
9. A. L. Henne and W. G. Finnegan, *J. Am. Chem. Soc.,* 1949, **71**, 298.
10. D. O'Hagan and H. S. Rzepa, *J. Chem. Soc. Chem. Commun.,* 1997, 645.
11. B. E. Smart, in *Organofluorine Chemistry. Principles and Commercial Applications,* ed. R. E. Banks, B. E. Smart and J. C. Tatlow, Plenum, New York, 1994, p. 57.
12. M. J. Silvester, *Aldrichimica Acta,* 1995, **28**, 45.
13. M. Stacey, J. C. Tatlow and A. G. Sharpe, Eds., *Advances in Fluorine Chemistry*, Butterworths, London, 1960 onwards.
14. A. L. Henne and R. P. Puh, *J. Am. Chem. Soc.,* 1947, **69**, 279.
15. A. L. Henne and K. A. Latif, *J. Am. Chem. Soc.,* 1954, **76**, 610.
16. N. C. Wong, Y. D. Xing, Y. F. Zhou, Q. Q. Gong and C. Zhang, *Synthesis,* 1984, 787.
17. E. T. McBee, A. Truchan and R. O. Bolt, *J. Am. Chem. Soc.,* 1948, **70**, 2023.
18. du Pont de Nemours & Co., 1943, US Pat. No. 2404374.
19. A. L. Henne and T. H. Newby, *J. Am. Chem. Soc.,* 1948, **70**, 130.
20. T. I. Filyakova, M. I. Kodess, N. V. Peschanskii, A. Y. Zapevalov and I. P. Kolenko, *J. Org. Chem. USSR (Engl. Transl.),* 1987, **23**, 1651.
21. L. G. Feoktistov and M. M. Gol'din, *J. Gen. Chem. USSR,* 1973, **43**, 524.
22. G. Bargigia, V. Tortelli and C. Tonnelli, 1987, Eur. Pat. Appl. EP 205 892.
23. M. W. Briscoe, R. D. Chambers, S. J. Mullins, T. Nakamura, J. F. S. Vaughan and F. G. Drakesmith, *J. Chem. Soc. Perkin Trans. I,* 1994, 3115.
24. F. J. Weigert, *J. Fluorine Chem.,* 1993, **65**, 67.
25. J. C. Tatlow and R. E. Worthington, *J. Chem. Soc.,* 1952, 1251.
26. R. N. Haszeldine, *J. Chem. Soc.,* 1952, 2504.
27. A. L. Henne and T. P. Waalkes, *J. Am. Chem. Soc.,* 1946, **68**, 496.
28. R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.,* 1954, 923.

29. P. Tarrant, A. M. Lovelace and M. R. Lilyquist, *J. Am. Chem. Soc.,* 1955, **77**, 2783.
30. A. J. Roche, Ph.D. Thesis, Univ. of Durham, 1995.
31. 3M Co., 1951, US Pat. No. 2746997.
32. J. D. LaZerte, L. J. Hols, T. S. Reid and G. H. Smith, *J. Am. Chem. Soc.,* 1953, **75**, 4525.
33. A. V. Podol'skii, T. G. Khonina, T. I. Filyakova, M. I. Kachalkova and M. I. Kodess, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.),* 1991, **40**, 1977.
34. E. A. Belmore, W. M. Ewalt and B. H. Wojcik, *Ind. Eng. Chem.,* 1947, **39**, 338.
35. R. D. Chambers, T. Shepherd, M. Tamura and M. R. Bryce, *J. Chem. Soc. Chem. Comm.,* 1989, 1657.
36. J. T. Maynard, *J. Org. Chem.,* 1963, **28**, 112.
37. R. D. Chambers and A. J. Palmer, *Tet. Lett.,* 1968, 2799.
38. W. R. Hasek, W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.,* 1960, **82**, 543.
39. T. Hiyama, K. Sato and M. Fujita, *Bull. Chem. Soc. Jpn.,* 1989, **62**, 1352.
40. I. N. Rozhkov and T. A. Borisov, *Izv. Akad. Nauk. SSSr Ser. Khim. (Engl. Transl.),* 1990, 1649.
41. H. F. Koch, in *Comprehensive Carbanion Chemistry,* ed. E. Duricel and T. Durst, Elsevier, Amsterdam, 1987, p. 321.
42. H. F. Koch, J. G. Koch, D. B. Donovan, A. G. Toczko and A. J. Kielbania, *J. Am. Chem. Soc.,* 1981, **103**, 5417.
43. M. R. Bryce and R. D. Chambers, in *Comprehensive Carbanion Chemistry,* ed. E. Duricel and T. Durst, Elsevier, Amsterdam, 1987, p. 271.
44. R. D. Chambers and R. H. Hobbs, *Adv. Fluorine Chem.,* 1965, **4**, 50.
45. J. D. Park, W. M. Sweeney, S. L. Hopwood and J. R. Lacher, *J. Am. Chem. Soc.,* 1956, **78**, 1685.
46. R. J. Koshar, T. C. Simmons and F. W. Hoffman, *J. Am. Chem. Soc.,* 1957, **79**, 1741.
47. M. R. Bryce, R. D. Chambers and G. Taylor, *J. Chem. Soc., Perkin Trans. I,* 1984, 509.
48. E. Heilbronner, presented at the Proc. Inst. Petroleum Conf., London, 1977.
49. L. M. Domelsmith, K. N. Piedrahita and W. R. Dolbier, *J. Am. Chem. Soc.,* 1978, **100**, 6908.
50. I. N. Rozhkov and T. A. Borisov, *Izv. Akad. Nauk. SSSr Ser. Khim. (Engl. Transl.),* 1993, 1041.
51. D. A. Dixon and B. E. Smart, *J. Phys. Chem.,* 1989, **93**, 7780.
52. J. D. Park, M. L. Sharrer, W. H. Breen and J. R. Lacher, *J. Am. Chem. Soc.,* 1951, **73**, 1329.

53. E. T. McBee, J. J. Turner, C. J. Morton and A. P. Stefani, *J. Org. Chem.,* 1965, **30**, 3698.

54. R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson and R. H. Lafferty, *J. Am. Chem. Soc.,* 1950, **72**, 3646.

55. P. Robson, J. Roylance, A. Stephens, J. C. Tatlow and R. E. Worthington, *J. Chem. Soc.,* 1964, 5748.

56. J. A. Oliver, R. Stephens, J. C. Tatlow and J. R. Taylor, *J. Fluorine Chem.,* 1976, **7**, 555.

57. C. O. Parker, *J. Am. Chem. Soc.,* 1959, **81**, 2183.

58. S. Dixon, *J. Org. Chem.,* 1956, **21**, 400.

59. R. Arnold-Stanton and D. M. Lemal, *J. Org. Chem.,* 1991, **56**, 151.

60. G. Camaggi and F. Gozzo, *J. Chem. Soc. (C),* 1971, 2382.

61. P. L. Coe, D. Oldfield and J. C. Tatlow, *J. Fluorine Chem.,* 1985, **28**, 453.

62. J. D. LaZerte, 1955, US Pat. No. 2704769.

63. E. L. Stogryn and S. J. Bois, *J. Am. Chem. Soc.,* 1967, **89**, 605.

64. R. D. Chambers and A. J. Roche, *J. Fluorine Chem.,* 1996, **79**, 139.

65. R. D. Chambers and A. J. Roche, *J. Fluorine Chem.,* 1996, **79**, 121.

66. A. V. Fokin, A. F. Kolomiets and N. V. Vasil'ev, *Russ. Chem. Rev.,* 1984, **53**, 238.

67. R. D. Chambers, J. R. Kirk and R. L. Powell, *J. Chem. Soc., Perkin Trans. I,* 1983, 1239.

68. Du Pont & Co., 1962, Brit. Pat. No. 964877.

69. I. P. Kolenko, T. I. Filyakova, A. Y. Zapevalov and E. P. Lur'e, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.),* 1979, **28**, 2323.

70. W. T. Miller, J. H. Fried and H. Goldwhite, *J. Am. Chem. Soc.,* 1960, **82**, 3091.

71. R. D. Chambers, M. P. Greenhall and M. J. Seabury, *J. Chem. Soc., Perkin Trans. I,* 1991, 2061.

72. C. G. Krespan, *J. Org. Chem.,* 1962, **27**, 1813.

73. R. D. Chambers, W. K. R. Musgrave and S. Partington, *J. Chem. Soc., Chem. Commun.,* 1970, 1050.

74. R. D. Chambers, W. K. Gray and S. R. Korn, *Tetrahedron,* 1995, **51**, 13167.

75. R. D. Chambers, S. R. Korn and G. Sandford, *J. Fluorine Chem.,* 1994, **69**, 103.

76. G. Resnati, *Tetrahedron,* 1993, **49**, 9445.

77. J. A. Wilkinson, *Chem. Rev.,* 1992, **92**, 505.

78. W. R. Dolbier, T. A. Gray and K. Ohnishi, *Synthesis,* 1987, 956.

79. W. R. Dolbier, L. Celewicz and K. Ohnishi, *Tet. Lett.,* 1989, **30**, 4929.

80. P. Bravo and G. Resnati, *Tetrahedron,* 1990, **1**, 661.

81. B. E. Smart, W. J. Middleton and W. B. Farnham, *J. Am. Chem. Soc.,* 1986, **108**, 4905.

82. J. A. Young, *Fluorine Chem. Rev.,* 1967, **1**, 359.

83. R. D. Chambers, G. Taylor and R. L. Powell, *J. Chem. Soc., Perkin Trans. I,* 1980, 426.

84. R. D. Chambers, A. Parkin and R. S. Matthews, *J. Chem. Soc., Perkin Trans. I,* 1976, 2107.

85. G. G. Belen'kii, E. P. Lur'e and L. S. German, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.),* 1976, **25**, 2208.

86. W. T. Miller, M. B. Freedman, J. H. Fried and H. F. Kock, *J. Am. Chem. Soc.,* 1961, **83**, 4105.

87. I. L. Knunyants and L. S. German, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.),* 1963,**11**, 1794.

88. R. D. Chambers, G. Grievson and N. M. Kelly, *J. Chem. Soc., Perkin Trans. I,* 1985, 2209.

89. S. N. Dunn, Ph.D. Thesis, Univ. of Durham, 1996.

90. J. D. LaZerte and R. J. Kosher, *J. Am. Chem. Soc.,* 1955, **77**, 910.

91. M. Muramatsu, S. Moriguchi and K. Inukai, *J. Org. Chem.,* 1966, **31**, 1306.

92. J. Cortieu, J. Jullien and N. T. Lai, *Tetrahedron,* 1976, **32**, 669.

93. M. G. Barlow, R. N. Haszeldine, W. D. Morton and D. R. Woodward, *J. Chem. Soc., Perkin Trans. I,* 1972, 2170.

94. G. Camaggi and F. Gozzo, *J. Chem. Soc. (C),* 1969, 489.

95. D. E. M. Evans and J. C. Tatlow, *J. Fluorine Chem.,* 1973, **3**, 259.

96. G. Gambaretto and M. Napoli, *Chem. Abstr.,* 1971, **74**, 31370c.

97. J. Burdon and J. C. Tatlow, *J. Appl. Chem.,* 1958, **8**, 293.

98. M. W. Buxton, D. W. Ingram, F. Smith, M. Stacey and J. C. Tatlow, *J. Chem. Soc.,* 1952, 3830.

99. G. Camaggi and F. Gozzo, *J. Chem. Soc. (C),* 1970, 178.

100. E. T. McBee, P. A. Wiseman and G. B. Bachman, *Ind. Eng. Chem.,* 1947, **39**, 415.

101. J. C. Tatlow and R. E. Worthington, *J. Chem. Soc.,* 1952, 1251.

102. R. D. Chambers, C. G. P. Jones and M. J. Silvester, *J. Fluorine Chem.,* 1986, **32**, 309.

103. J. P. Cheswick, *J. Am. Chem. Soc.,* 1966, **88**, 4800.

104. W. H. Sharkey, *Fluorine Chem. Rev.,* 1968, **2**, 1.

105. V. A. Al'bekov, A. F. Benda, A. F. Gonta', G. A. Sokol'skii and I. L. Knunyants, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.),* 1988, **37**, 765.

106. C. D. Weis, *J. Org. Chem.,* 1962, **27**, 3693.

107. J. J. Drysdale, W. W. Gilbert, H. K. Sinclair and W. H. Sharkey, *J. Am. Chem. Soc.,* 1958, **80**, 3672.

108. P. J. Dunn and C. W. Rees, *J. Chem. Soc., Chem. Commun.,* 1987, 59.

109. J. H. Edwards, W. J. Feast and D. C. Bott, *Polymer,* 1984, **25**, 395.

110. P. Tarrant, P. Johncock and J. Savory, *J. Org. Chem.,* 1963, **28**, 1963, 839.

111. D. J. Burton, in *Synthetic Fluorine Chemistry,* ed. G. A. Olah, R. D. Chambers and G. K. S. Prakash, Wiley Interscience, New York, 1992, p. 205.

112. D. J. Burton, in *Fluorine Containing Molecules,* ed. J. F. Liebman, A. Greenberg and W. R. Dolbier, VCH, New York, 1988, p. 149.

113. W. T. Miller, R. H. Snider and R. J. Hummel, *J. Am. Chem. Soc.,* 1969, **91**, 6532.

114. R. P. Hughes, O. J. Curnow, P. R. Rose, X. Zheng, E. N. Mairs and A. L. Rheingold, *ACS Symp. Ser.,* 1994, **555**, 252.

115. D. Cartwright, in *Organofluorine Chemistry. Principles and Commercial Applications.,* ed. R. E. Banks, B. E. Smart and J. C. Tatlow, Plenium Press, New York, 1994, p. 237.

116. A. B. Abubakar, B. L. Booth, N. N. E. Suliman and A. E. Tipping, *J. Fluorine Chem.,* 1992, **56**, 359.

117. M. Hudlicky, *Chemistry of Organic Fluorine Compounds*, Ellis Horwood, Chichester, 1992, p. 274.

118. M. G. Barlow, N. N. E. Suliman and A. Tipping, *J. Fluorine Chem.,* 1995, **70**, 95.

119. A. B. Abubakar, B. L. Booth and A. Tipping, *J. Fluorine Chem.,* 1991, **55**, 189.

120. C. G. Krespan, B. C. McKusick and T. L. Cairns, *J. Am. Chem. Soc.,* 1961, **83**, 3428.

121. C. G. Krespan, 1961, US Pat. No. 2977394.

122. R. S. H. Liu and C. G. Krespan, *J. Org. Chem.,* 1969, **34**, 1271.

123. R. E. Putman, R. J. Harder and J. E. Castle, *J. Am. Chem. Soc.,* 1961, **83**, 391.

124. A. R. L. Bursics, E. Bursics-Skekeres, M. Murray and F. G. A. Stone, *J. Fluorine Chem.,* 1976, **7**, 619.

125. M. G. Barlow, N. N. E. Suliman and A. Tipping, *J. Fluorine Chem.,* 1995, **73**, 61.

126. M. H. Rock, Ph.D. Thesis, Univ. of Durham, 1990.

127. R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compounds,* John Wiley and Sons, London, 1981.

128. P. Odello, Ph.D. Thesis, Univ. of Durham, 1993.

129. M. Nishida, Y. Hayakawa, M. Matsui, K. Shibata and H. Muramatsu, *J. Heterocyclic Chem.,* 1992, **29**, 113.

130. K. Alder and H. J. Ache, *Chem. Ber.,* 1962, **95**, 503.

131. D. C. Tabor, F. H. White, L. W. Collier and S. A. Evans, *J. Org. Chem.,* 1983, **48**, 1638.

132. W. K. Gray, Ph.D. Thesis, Univ. of Durham, 1996.

133. K. Takahashi, A. Yoshino, K. Hosokawa and H. Muramatsu, *Bull. Chem. Soc. Jpn.,* 1985, **58**, 755.

134. S. J. Mullins, Ph.D. Thesis, Univ. of Durham, 1992.

135. R. D. Chambers, A. J. Roche and M. H. Rock, *J. Chem. Soc., Perkin Trans. 1,* 1996, 1095.
136. R. N. Haszeldine, *J. Chem. Soc.,* 1952, 3490.
137. A. L. Henne and M. Nager, *J. Am. Chem. Soc.,* 1952, **74**, 650.
138. R. D. Chambers, C. G. P. Jones, M. J. Silvester and D. B. Speight, *J. Fluorine Chem.,* 1984, **25**, 47.
139. W. R. Cullen and P. S. Dhaliwal, *Can. J. Chem.,* 1967, **45**, 2887.
140. D. B. Speight, Ph.D. Thesis, Univ. of Durham, 1974.
141. C. G. Krespan, *Tetrahedron,* 1967, **23**, 4243.
142. A. E. Bayliff, M. R. Bryce and R. D. Chambers, *J. Chem. Soc., Perkin Trans. I,* 1987, 763.
143. W. R. Cullen, D. J. Dawson and G. E. Styan, *Can. J. Chem.,* 1965, **43**, 3392.
144. F. G. Pearson, US Pat. 2558875, 1952.
145. A. L. Logothesis and G. N. Sausen, *J. Org. Chem.,* 1967, **32**, 2261.
146. C. G. Krespan, *J. Org. Chem.,* 1969, **34**, 42.
147. F. W. Stacey and J. F. Harris, *J. Am. Chem. Soc.,* 1963, **85**, 963.
148. W. T. Flowers, R. N. Haszeldine, C. R. Owen and A. Thomas, *J. Chem. Soc. Chem. Commun.,* 1974, 134.
149. N. Ishikawa, A. Nagashima and A. Sekiya, *Chem. Lett.,* 1974, 1225.
150. N. Ishikawa and A. Nagashima, *Bull Chem. Soc. Jpn.,* 1976, **49**, 1085.
151. J. W. Emsley, L. Phillips and V. Wray, Eds., *Fluorine Coupling Constants,* Pergamon Press, Oxford, 1977.
152. J. S. Moilliet, in *Organofluorine Chemistry. Principles and Commercial Applications.,* ed. R. E. Banks, B. E. Smart and J. C. Tatlow, Plenium Press, New York, 1994, p. 195.
153. D. D. MacNicol and C. D. Robertson, *Nature,* 1988, **332**, 59.
154. D. S. L. Slinn and S. W. Green, in *Preparation, Properties and Industrial Applications of Organofluorine Compounds,* ed. R. E. Banks, Ellis Horwood, Chichester, 1982, p. 45.
155. J. A. Miller and M. J. Nunn, *J. Chem. Soc., Perkin Trans. I,* 1976, 416.
156. H. Suzuki, M. Aihara, H. Yamamoto, Y. Takamoto and T. Ogawa, *Synthesis,* 1988, 236.
157. M. Hudlicky, *Chemistry of Organic Fluorine Compounds*, Ellis Horwood, Chichester, 1992, p. 24.
158. A. V. Kartashov, N. N. Chuvatkin, Y. A. Kurskii and L. S. Boguslavskava, *J. Org. Chem. USSR,* 1988, **24**, 2279.
159. M. B. Giudicelli, D. Picq and B. Veyron, *Tet. Letters,* 1990, **31**, 6527.
160. M. Hudlicky, *Chemistry of Organic Fluorine Compounds*, Ellis Horwood, Chichester, 1992, p. 91.

161. E. S. Huyser, in *The Chemistry of the Carbon-Halogen Bond,* ed. S. Patai, Wiley, New York, 1973, p. 549.

162. W. E. Willy, D. R. McKean and B. A. Garcia, *Bull. Chem. Soc. Jpn.,* 1976, **49**, 1989.

163. Y. Sasson, M. Weiss, A. Loupy, G. Bram and C. Pardo, *J. Chem. Soc., Perkin Trans. I,* 1986, 1250.

164. I. Bidd and M. C. Whiting, *Tet. Letters,* 1984, **25**, 5949.

165. K. B. Yoon and J. K. Kochi, *J. Org. Chem.,* 1989, **54**, 3028.

166. N. V. Svetlakov, I. E. Moisak and I. G. Averko-Antonovich, *J. Org. Chem. USSR,* 1969, **5**, 971.

167. M. Namavari, N. Satyamurthy, M. E. Phelps and J. R. Barrio, *Tet. Letters,* 1990, **31**, 4973.

168. A. T. Cates, *J. Hazard. Mater.,* 1992, 1.

169. R. D. Chambers, A. J. Roche and J. F. S. Vaughan, *Can. J. Chem.,* 1996, **74**, 1925.

170. R. D. Chambers, J. Hutchinson and W. K. R. Musgrave, *J. Chem. Soc.,* 1964, 3573.

171. E. Klauke, L. Oehlmann and B. Baasner, *J. Fluorine Chem.,* 1982, **21**, 495.

172. R. D. Chambers and D. T. Clark, *unpublished results.*

173. A. L. Henne and R. P. Ruh, *J. Am. Chem. Soc.,* 1947, **69**, 279.

174. E. W. Schlag and W. B. Peatman, *J. Am. Chem. Soc.,* 1964, **86**, 1676.

175. W. T. Miller, W. Frass and P. R. Resnick, *J. Am. Chem. Soc.,* 1961, **83**, 1767.

176. R. N. Haszeldine, *J. Chem. Soc.,* 1952, 4423.

177. R. E. Banks, M. G. Barlow, W. D. Davies, R. N. Haszeldine, K. Mullen and D. R. Taylor, *Tett. Lett.,* 1968, **36**, 3909.

178. R. E. Banks, W. D. Davies, R. N. Haszeldine and D. R. Taylor, *J. Fluorine Chem.,* 1977, **10**, 487.

179. H. B. Friedrich, D. J. Burton and D. C. Tardy, *J. Phys. Chem.,* 1987, **91**, 6334.

180. P. B. Krespan and C. G. Krespan, *J. Am. Chem. Soc.,* 1969, **91**, 415.

181. R. C. H. Spink, Ph.D. Thesis, Univ. of Durham, 1996.

182. C. Farren, Ph.D. Thesis, Univ. of Durham, to be completed 1998.

183. R. D. Chambers and B. Grievson, *J. Chem. Soc. Perkin Trans. I,* 1985, 2215.

184. H. Muramatsu, J. Inukai and T. Veda, *Bull. Chem. Soc. Jpn.,* 1967, **40**, 903.

185. P. Tarrant, R. W. Whitfield and R. H. Summerville, *J. Fluorine Chem.,* 1971, **1**, 31.

186. J. L. Hahnfield and D. J. Burton, *Tett. Lett.,* 1975, **10**, 773.

187. D. Sianesi and R. Fontanelli, *Ann. Chim. (Rome),* 1965, **55**, 872.

188. H. Lu, B. Friedrich and D. J. Burton, *J. Fluorine Chem.,* 1995, **75**, 83.

189. J. Boivin, L. Elkaim, P. G. Ferro and S. Z. Zard, *Tett. Lett.,* 1991, 5321.

190. W. J. Middleton and W. H. Sharkey, *J. Am. Chem. Soc.,* 1959, **81**, 803.

191. R. E. Lenga, *The Sigma-Aldrich Library of Chemical Safety Data,* Sigma-Aldrich Corporation, 1988.

192. M. S. Newman and S. Schiff, *J. Am. Chem. Soc.*, 1959, **81**, 2266.

193. M. S. Newman and C. Y. Perry, *J. Org. Chem.*, 1963, **28**, 116.

194. as obtained from Aldrich.