The generation and chemistry of some novel perfluorinated dienes

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UNIVERSITY OF DURHAM

A THESIS

entitled

THE GENERATION AND CHEMISTRY OF SOME NOVEL PERFLUORINATED DIENES

submitted by

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A candidate for the degree of Doctor of Philosophy

Department of Chemistry

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'Go back?' he thought. 'No good at all! Go sideways! Impossible! Go forward? Only thing to do! On we go!' So up he got and trotted along with his little sword held in front of him and one hand feeling the wall, and his heart all of a patter and a pitter.

J. R. R. Tolkein, *The Hobbit.*

To my Mum, Dad,

Family and Friends.

March 1992.

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Memorandum

The work described in this thesis was carried out in the University of Durham between October 1988 and September 1991. This thesis is the work of the author, except where acknowledged by reference, and has not been submitted for any other degree.

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

M. W. Briscoe, R. D. Chambers, S. J. Mullins, T. Nakamura, and F. G. Drakesmith, *J. Chem. Soc., Chem. Commun.*, 1990, 1127.

R. D. Chambers, S. L. Jones, S. J. Mullins, A. Swales, P. Telford, and M. W. H. West, in *Selective Fluorination in Organic and Bioorganic Chemistry*, ed. J. T. Welch, A.C.S. Symposium Series 456, 1991, ch.5.

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13th International Symposium on Fluorine Chemistry,
Ruhr Universität, Bochum, Germany,
September 1991.

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

The Generation and Chemistry of some Novel Perfluorinated Dienes

by Steven J. Mullins

Abstract

The work contained in this thesis is divided into three sections detailing the formation of fluorinated dienes and some aspects of their chemistry:

a) Through cyclic voltammetry, an electrochemical investigation was carried out to determine the reduction potentials of several easily accessible perfluorinated alkenes. Following this, sodium amalgam was successfully used as a single electron transfer agent in order to reduce a number of these fluoroalkenes by means of selective defluorination. This has enabled a series of perfluorinated alkadienes to be prepared cleanly in good yield. A study of a variety of other means of defluorination was also investigated.

b) These dienes have been subjected to attack by mono- and bi- functional nucleophiles in high yielding reactions. This has enabled an unusual perfluorinated diepoxide to be synthesised which displays remarkable thermal stability. A number of novel pyrrole and pyrrolo-quinoline derivatives have also been made from a series of substituted anilines and these are discussed within a mechanistic framework in order to justify the product distributions. Finally, the reaction between potentially bi- functional carbon nucleophiles and these perfluorinated dienes has been used as a means of synthesising a series of poly(perfluoroalkyl)- substituted cyclopentadienyl anions including the pentakis(trifluoromethyl)-cyclopentadienyl anion, the formation of which could proceed by an unusual cyclisation and elimination mechanism.

c) Charge transfer salts have been prepared by complexation of decamethylferrocene with various fluorinated dienes. These salts have been the subject of X-ray crystallographic and molecular magnetic susceptibility studies. No signs of organic ferromagnetism were observed.

Contents

INTRODUCTION
AND
DISCUSSION

Chapter One

Introduction

1.1 General Introduction

The most electronegative element[1], fluorine is uniquely capable of replacing hydrogen at any site in any organic system[2], creating an alternative, complementary field of organic chemistry[3,4,5,6]. However, despite the carbon-fluorine bond being the strongest of any single covalent bond to carbon[7] and considering the remarkable geological abundance of fluorine, fluorocarbons are found only very rarely in nature; the best known example being potassium monofluoroacetate found in the South African plant "Gifblaar" (*Dichapetalum cymosum*)[8]; therefore the field of organofluorine chemistry is essentially entirely synthetic.

The foundations of organic fluorine chemistry have recently been reviewed[9,10,11] and more recent work has been reported in treatises elsewhere; for examples see refs: [3,4,5,6].

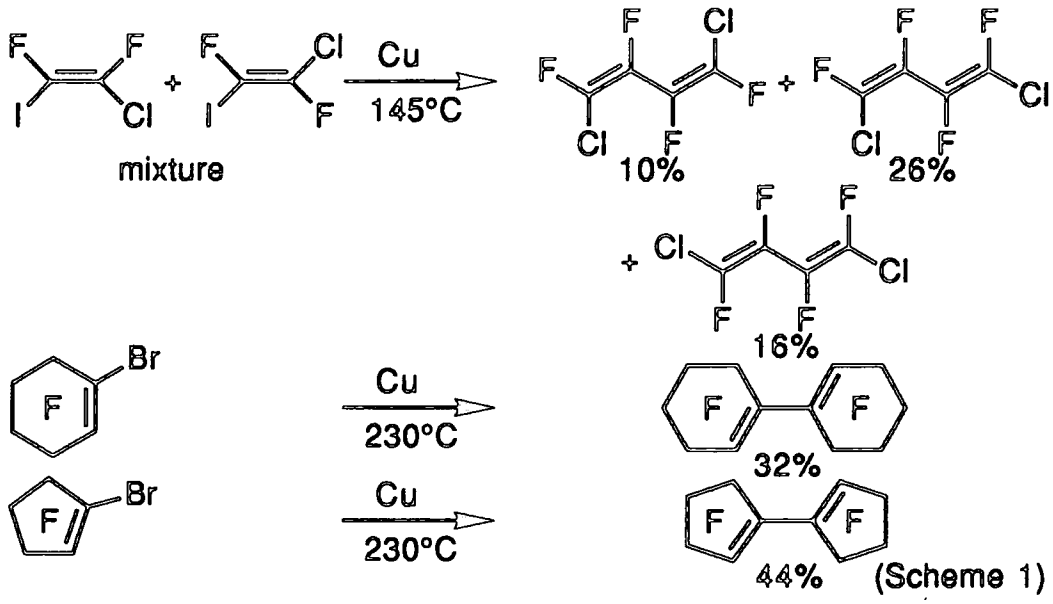
The aim of this review is not to discuss these topics but instead to concentrate specifically upon the subject of fluorinated dienes, their syntheses and chemistry.

1.2 The Synthesis of Fluorinated Dienes

1.2.1 Coupling Reactions

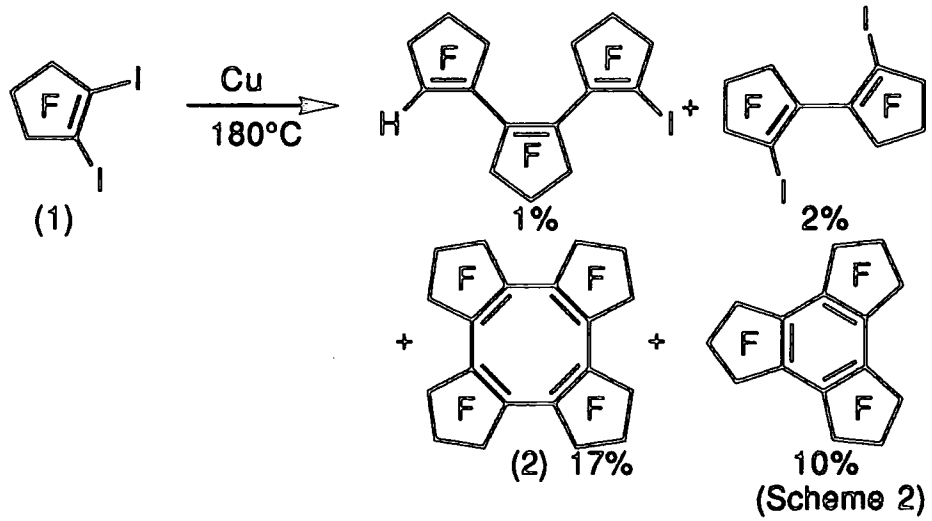
1.2.1.1 Coupling of Fluoroalkenes

One of the methods for the preparation of fluorinated dienes is by simply joining together two fluoroalkene units. This idea was first used by Camaggi and co-workers[12] with the reductive coupling over hot copper-bronze of various polyfluorovinyl halides. In this way, some interesting straight-chain[13] polyfluoro-1,3-dienes and perfluorinated bicyclic dienes were made (Scheme 1).



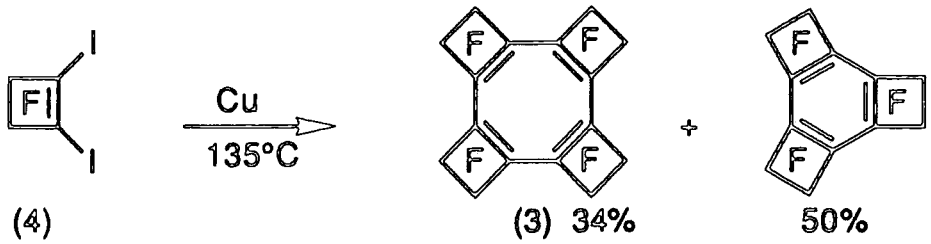
(Scheme 1)

In 1971, Camaggi further reported[14] the reaction of hexafluoro-1,2-di-iodocyclopentene (1) over copper-bronze, a process which afforded several coupled products including the novel cyclo-octatetraene (2) (Scheme 2).



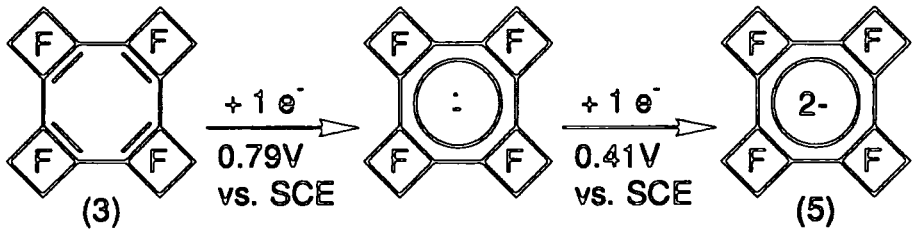
(Scheme 2)

An analogous cyclo-octatetraene to (2), (3), was made in a similar manner[15] by the reductive coupling of 1,2-di-iodotetrafluorocyclobutene (4) over hot copper (Scheme 3).



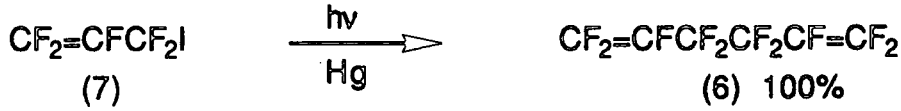
(Scheme 3)

It is worthy of note that although the cyclo-octatetraene (2) has been shown[16] to adopt the expected tub shape, tetraene (3) was demonstrated by X-ray crystallography to possess a planar ring system[17]. This compound is also one of the most powerful neutral oxidants known[18], showing two reversible one-electron reductions to give the 10π aromatic system (5) (Scheme 4).



(Scheme 4)

Using the copper-induced reductive coupling methodology, various other substituted bicyclic dienes have also been formed and reported[15,19] but this technique is not restricted only to the formation of 1,3-dienes; a recent patent[20] of the synthesis of decafluorohexa-1,5-diene (6) by the coupling of 3-iodoperfluoropropene (7) appeared in the literature lately and in the case of this non-vinyl iodide, the reaction became quantitative under UV irradiation when in the presence of mercury (Scheme 5).



(Scheme 5)

1.2.1.2 Step-Wise Couplings

In those copper promoted couplings[12,14,15,19], it was inferred[12] that the reaction itself is a two-step process starting with an attack by copper at the carbon bearing the bromine or iodine to form an activated complex at the metal surface. This complex would then react with a second molecule of the bromide or iodide at the surface to give the final di- or poly- ene.

Indeed, Burton and co-workers[21] observed only the simple coupled symmetrical dienes when trying to generate fluorovinyl copper reagents by this route (Scheme 6).

e.g.

$$2\ CF_2{=}CFI + 2\ Cu \longrightarrow CF_2{=}CFCF{=}CF_2 + 2\ CuI$$

(Scheme 6)

Apparently any vinyl copper intermediates which are formed react rapidly with additional vinyl halide giving the coupled product. Attempts, however, to make fluoroalkenyl cadmium reagents were successful[21] *via* the direct reaction of fluorovinyl iodides or bromides in DMF under mild conditions (Scheme 7).

e.g.

$$R_FCF{=}CFX\ (X = Br, I) + Cd \xrightarrow[RT - 60°C]{DMF} R_FCF{=}CFCdX + (R_FCF{=}CF)_2Cd + CdX_2$$

(Scheme 7)

These reactions proceeded with a total retention on configuration making the cadmium reagents invaluable in the further reaction with copper to give the corresponding fluorovinylcopper reagents[22] (Scheme 8).

e.g.

$$R_FCF{=}CFCdX\ (X = Br, I) + (R_FCF{=}CF)_2Cd \xrightarrow[RT]{Cu^IX} R_FCF{=}CFCu\ \ 68\text{-}99\%$$

(Scheme 8)

Again, this metathesis occurred stereospecifically and, as the route avoided the presence of any vinyl iodides or bromides at the stage when vinyl copper species were present, the resulting organo-copper reagents were prepared unequivocally. These vinyl copper compounds are very versatile and have

been further shown by Dolbier and co-workers[23] to be a good source of fluorinated dienes (Scheme 9).

e.g.

$$R_FCF{=}CFCu + R_F^{I}R_F^{II}C{=}CFI \longrightarrow R_F^{I}R_F^{II}C{=}CFCF{=}CR_F^{I}R_F^{II}$$

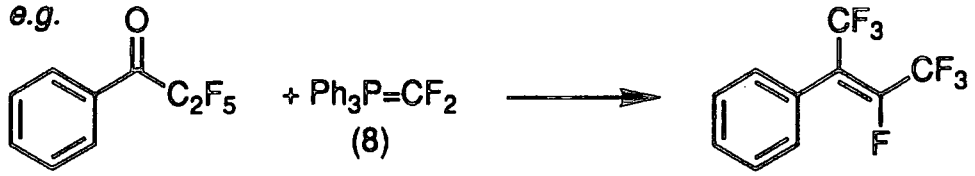
(Scheme 9)

Using a similar methodology, this paper also reported the synthesis of fluorinated dienes *via* the coupling of perfluoropropenylzinc reagents[24] with trifluorovinyl iodide in the presence of tetrakis(triphenylphosphine)palladium.

1.2.1.3 Difluoromethylene Chain-Extension

An intriguing variation on the coupling theme is that of chain-extension or homologation. The initial work in this area, like many of the other methods of diene formation, started with the formation of fluorinated alkenes. It was first reported[25] that for the case of difluoromethylenetriphenylphosphorane (8), prepared *in situ* by the reaction of triphenylphosphine with alkali metal salts of chlorodifluoroacetic acid, in reaction with aldehydes and perfluoroalkyl substituted ketones gave terminal fluoro-alkenes[26]. However this method is often complicated by HF addition and fluoride ion induced isomerisations to give internal fluoroalkenes whenever this is possible[27] (Scheme 10).

e.g.



(Scheme 10)

The generation of the ylide (8) by reaction of triphenylphosphine with dibromodifluoromethane (9) obviated these difficulties and allowed the synthesis of the terminal fluoroalkene in high yield (Scheme 11).

$$\underset{(9)}{CF_2Br_2} + 2\,Ph_3P + RCOR_F \longrightarrow RR_FC{=}CF_2 + Ph_3PO + Ph_3PBr_2$$

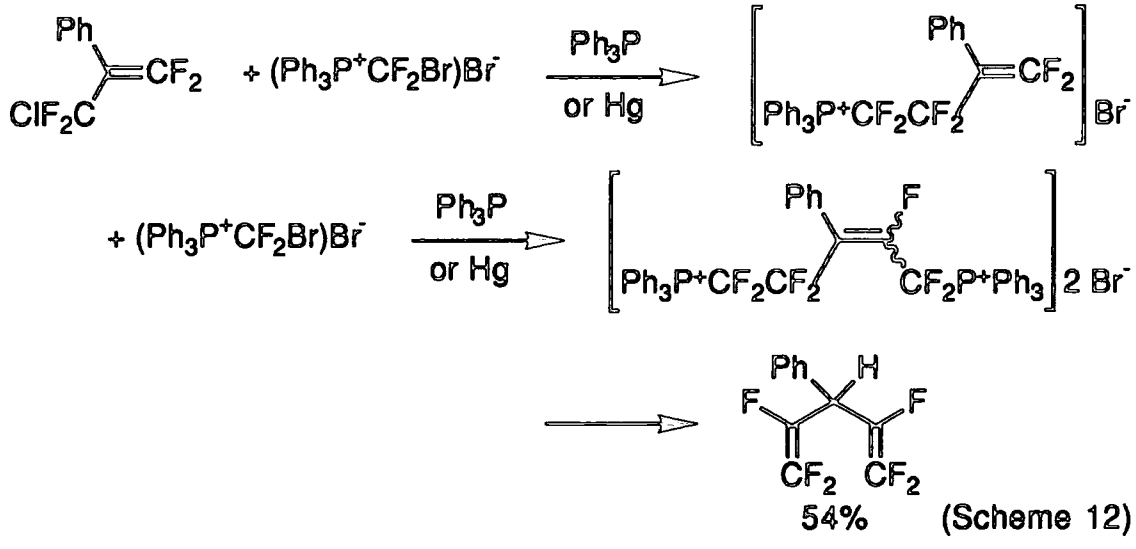
(Scheme 11)

e.g. R = Ph 82% yield

(<1% internal fluoroalkene, 0% HF addition product.)

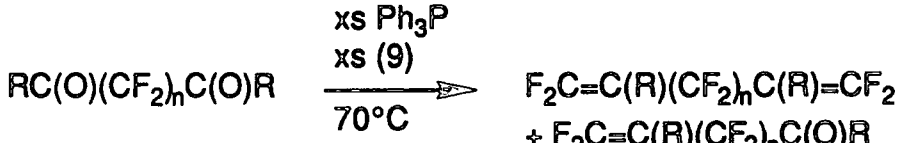
The use of a metal, such as cadmium, zinc or mercury as a dehalogenator, minimised the use of the phosphine[28] and also eliminated the formation of the halogenated phosphorane by-product.

This method, however, initially proved to be unsuitable for the preparation of fluorinated dienes as it was found[29] that the polyfluorinated diketones which were formed, cyclised *via* an intramolecular aldol-type condensation route giving α,β-unsaturated cyclic ketones. This process was found to be promoted by the basic dimethylamine produced by decomposition of the solvent DMF. However, in 1980, Burton and co-workers published a similar route[30] to fluorinated terminal alkadienes by the chain-extension of fluorinated alkenes (Scheme 12).



(Scheme 12)

Subsequent work by Burton and co-workers[31] revealed that fluorinated dienes could be synthesised utilising this methodology by reacting various polyfluorinated diketones with an excess of triphenylphosphine and dibromodifluoromethane (9) in triglyme (Scheme 13).



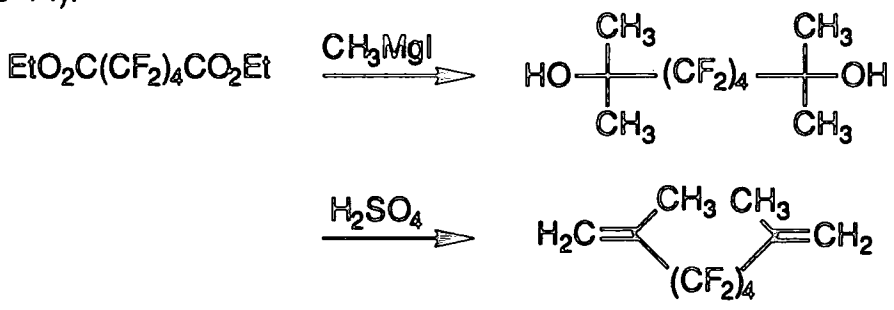
(Scheme 13)

Where R = Ph, Et; n = 2,3. Yields: diene:enone 50-60%:10-20%.

The absence of DMF coupled with the milder reaction conditions circumvented the aldol cyclisation problem giving various fluorinated dienes in modest yields in a mixture with the corresponding enone.

1.2.2 Dehydration

Dehydration was one of the early methods be considered as a reasonable route to fluorinated dienes. The first paper with this theme was published in 1953[32] and used sulphuric acid to dehydrate tertiary alcohols (Scheme 14).

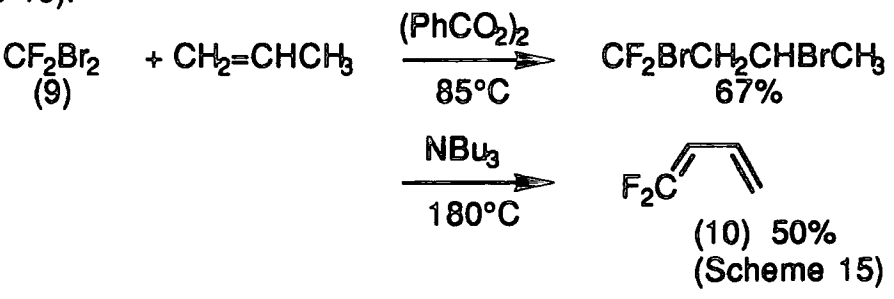


(Scheme 14)

However, interest in such a method is diminished by its very limited scope.

1.2.3 Dehydrohalogenation

A more widely used method for the production of fluorinated alkadienes has been that of dehydrohalogenation. Tarrant and Lovelace utilised this technique[33] in the preparation of 1,1-difluorobuta-1,3-diene (10) (Scheme 15).



(10) 50%
(Scheme 15)

An analogous synthesis for diene (10) and 1,1-difluoroisoprene also appeared in the patent literature[34].

More interestingly, a synthesis of perfluoro-2,3-dimethylbutadiene (11) was reported by some Soviet workers in 1973[35] *via* the aqueous electrolysis

of α-hydro-perfluoroisobutanoic acid (12) containing a little of its potassium salt (Scheme 16).

$$2\,(CF_3)_2CHCO_2H \xrightarrow[\text{electrolysis}]{\text{Kolbe}} (CF_3)_2CHCH(CF_3)_2 + CO_2 + H_2$$

(12) — 67%

(Scheme 16)

This was then dehydrofluorinated to give the diene (11) (Scheme 17).

$$(CF_3)_2CHCH(CF_3)_2 \xrightarrow[Bu_2O]{KOH} \text{(11)}$$

(11) 39%

(Scheme 17)

1.2.4 Decarboxylation

A further method which has been reported in the literature for the formation of fluorinated dienes is the thermolytic decarboxylation of the alkali metal salts of fluorinated dicarboxylic acids. This was first reported in 1954[36] as a viable route to hexafluorobutadiene (13) from the pyrolysis of anhydrous disodium octafluorohexane-1,6-dioate (14) (Scheme 18).

$$NaO_2C(CF_2)_4CO_2Na \xrightarrow{450°C} \text{(13)}$$

(14)

(13) 30%

(Scheme 18)

A more recent development of this process[37] is the decarboxylation of the salts of polyfluorinated carboxylic acids which already contain a terminal double bond[38] (Scheme 19).

$$CXH{=}CF(CF_2)_3CO_2Na \longrightarrow CXH{=}CFCF_2CF{=}CF_2$$

(X = Cl, F)

76% X = Cl

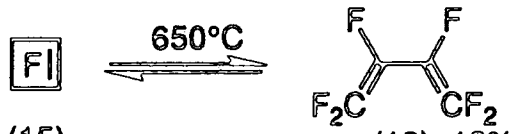
95% X = F

(Scheme 19)

However, at the elevated temperatures needed to achieve thermolysis, a small amount of the cyclic isomers[37] was formed as an impurity.

1.2.5 Isomerisation

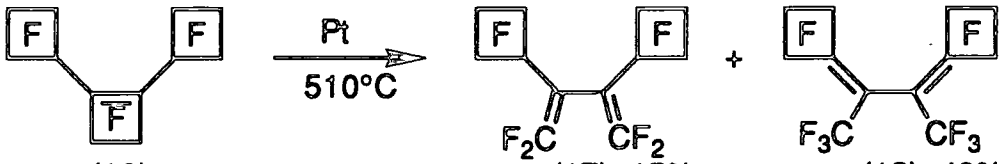
In 1955, Haszeldine and Osbourne suggested[39] that hexafluorobutadiene (13) could be made, in an equilibrium, by simply heating hexafluorocyclobutene (15) (Scheme 20).



(15) (13) 12%

(Scheme 20)

The theory[40], kinetics and thermodynamics of this and related systems[41,42] have been studied more recently but, as the equilibrium lies predominantly on the side of the cyclic compounds, this method has not been proven to be a satisfactory synthesis of perfluorinated dienes with a few notable exceptions which were published by Chambers and co-workers[43]. Starting from the pyridine-formed[44,45] trimer (16) of cyclobutene (15), pyrolysis yielded two isomeric dienes[46] (Scheme 21).



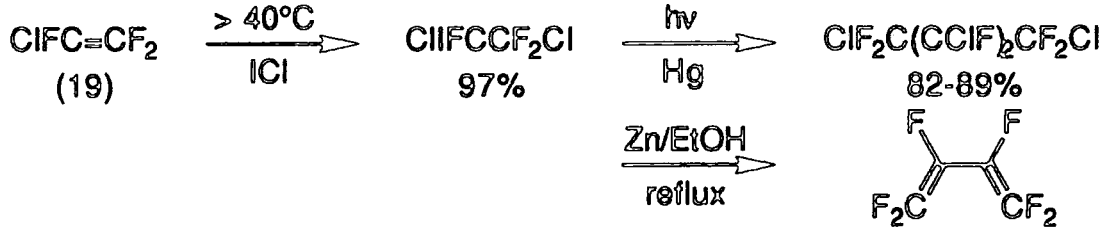
(16) (17) 15% (18) 40%

(Scheme 21)

Diene (18) has been formed by fluoride ion isomerisation from (17).

1.2.6 Dehalogenation

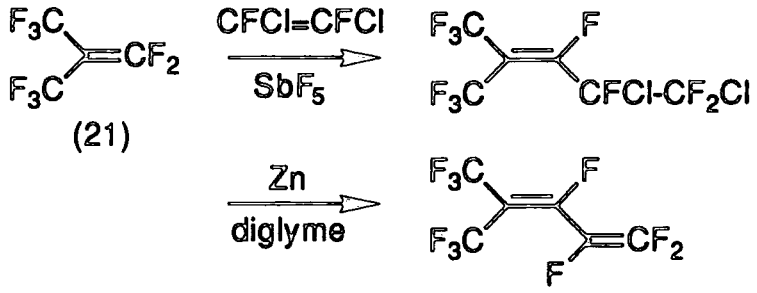
The major route to fluorinated dienes, in the literature, is that of dehalogenation. Haszeldine, in 1952, was the first to report[47] a dechlorination route to a diene. Starting from chlorotrifluoroethene (19), hexafluorobutadiene (13) was made in good yield overall (Scheme 22).



(13) 98%

(Scheme 22)

More recently, zinc dechlorination has been used in the formation of perfluoro-2-methyl-penta-2,4-diene[48] (20) (Scheme 23).



(20) 40%

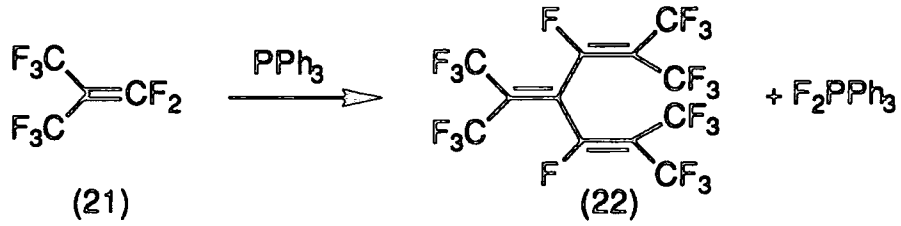
(Scheme 23)

Other zinc dehalogenations have also appeared in the patent literature[49,50] and elsewhere[51,52,53] (Table 1).

Table 1		Reference
$H(CFCl)_4CO_2Me$	$\xrightarrow[-Cl_2]{Zn}$ $HCF=CF-CF=CFCO_2Me$	49
$(BrCF_2-CFCl)_2$	$\xrightarrow[-BrCl]{Zn}$ $F_2C=CF-CF=CF_2$ (13)	50
$ClF_2CCClFCF_2CF=CF_2$	$\xrightarrow[-Cl_2]{Zn}$ $CF_2=CFCF_2CF=CF_2$	51
$CF_2ClCFCl(CF_2)_4Cl$	$\xrightarrow[-Cl_2]{Zn}$ $CF_2=CF(CF_2)_4Cl$ 54%	52
$CF_2=CF(CF_2)_4Cl$	$\xrightarrow[-FCl]{Zn}$ $CF_2=CF(CF_2)_2CF=CF_2$ 50%	52
$CF_2=CF(CF_2CFCl)_2CF_2Cl$	$\xrightarrow[-Cl_2]{Zn}$ $(CF_2=CFCF_2)_2CFCl$	53
$(CF_2=CFCF_2)_2CFCl$	$\xrightarrow[-FCl]{Zn}$ $CF_2=CF-CF=CF-CF_2-CF=CF_2$	53

1.2.7 Phosphorus induced Defluorination-Coupling

In a category of its own lies some particularly interesting Soviet work. Knunyants and co-workers reported[54] the reaction of perfluoroisobutene (21) with triphenylphosphine to give the cross-conjugated perfluorotriene (22) through a defluorination-coupling (Scheme 24).



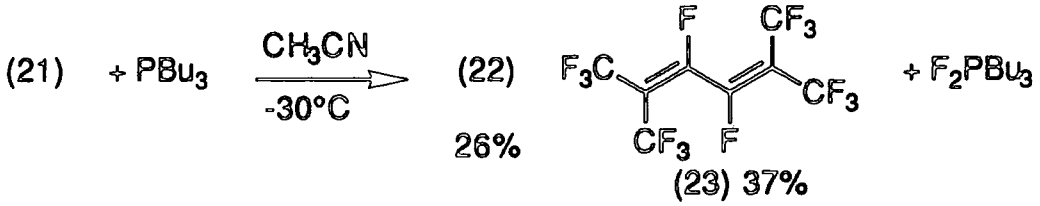
(21) (22)

(Scheme 24)

(It should be noted here that although this method can provide a good route to some relatively inaccessible dienes, the starting material perfluoroisobutene (21) is known to be highly toxic and the by-products which contain phosphorous-fluorine bonds are even more so.)

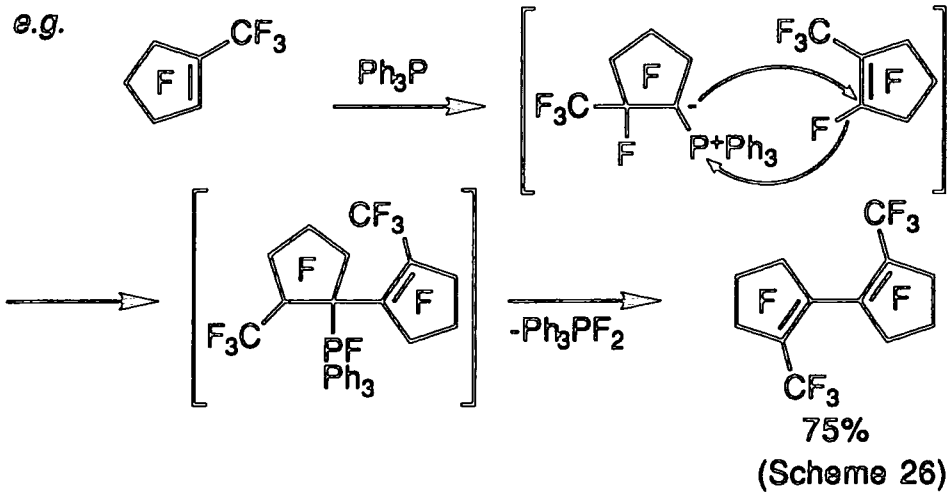
The assumption that the ylide $Ph_3P=C=C(CF_3)_2$ is formed as an intermediate in this reaction was confirmed in a later paper[55] as well as the

result that if fluoroalkene (21) was reacted with tributylphosphine in acetonitrile, triene (22) was made along with a substantial amount of perfluoro-2,5-dimethyl-hexa-2,4-diene (23) (Scheme 25).



(Scheme 25)

These findings were expanded further[56] for various cyclic and acyclic fluoroalkenes (Scheme 26).

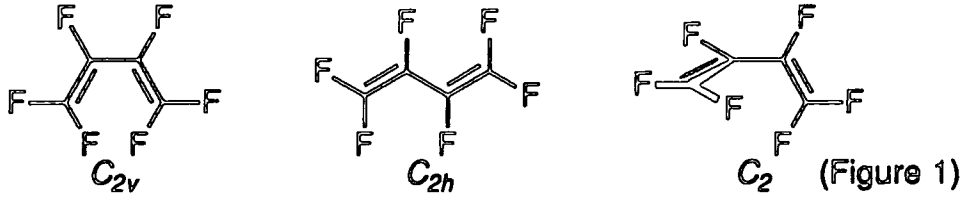


(Scheme 26)

1.3 The Structure of Fluorinated Dienes

Butadiene itself has been shown to exist in the gas phase primarily in the *trans*-planar (C_{2h}) conformation[57] but a small amount of the *gauche* form (C_2) has also recently been predicted[58] to be present. It has likewise been established by Raman, infrared[59] and microwave[60] spectra that 1,1,4,4-tetrafluorobutadiene also adopts the C_{2h} conformation.

The vibrational spectra of hexafluorobutadiene (13), however, were demonstrated[61] to be inconsistent with the C_{2h} conformation. These spectral data were consistent with the C_{2v} symmetry, but the *gauche* conformation or a mixture of several configurations could not be ruled out (Figure 1).



(Figure 1)

Photoelectron and optical spectroscopy studies[62] have since determined that hexafluorobutadiene (13) exists in a non-planar skew cisoid conformation with a dihedral angle from the *cis* structure of 42°±15° which is in good agreement with an angle of 47.4°±2.4° obtained from gas-phase electron diffraction[63]. From NMR studies too, the apparent angular dependence of five bond fluorine-fluorine coupling of diene (13) also supports this non-planarity[64] and more recently, the vibrational spectrum was assigned[65] and was shown to be consistent with the skew C_2 structure.

An interesting theoretical paper has recently been published[66] outlining the determination of the electronic structure of hexafluorobutadiene (13) from *ab initio* molecular orbital calculations. This gave the minimum energy structure to be a skew-*cis* conformation with an optimised dihedral torsion angle, ψ_{opt}, of 58.4°. Analysis of the theoretical molecular orbitals proved to be consistent with the majority of the previous spectroscopic results implying that, if the theoretical modelling was correct, some of the minor spectral data for diene (13) had been misinterpreted and that this was the reason for the differences in the value of ψ.

1.4 Reactions of Fluorinated Dienes

Comparatively few papers detailing examples of reactions of fluorinated dienes can be found in the literature. For the most part, those that do appear outline reactions in which the dienes are considered as simple fluorinated alkenes and treated accordingly.

1.4.1 Reactions with Oxygen Nucleophiles

Knunyants and co-workers[67] were among the first to report their findings between hexafluorobutadiene (13) and various alcohols (Scheme 27).

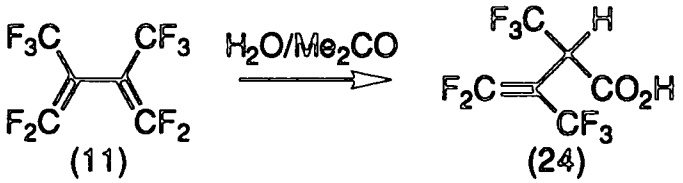
$$\underset{(13)}{CF_2{=}CF\text{-}CF{=}CF_2} + \underset{(R = Me, Et)}{ROH} \xrightarrow{Et_3N} CF_2{=}CF\text{-}CFH\text{-}CF_2OR$$

$$\longrightarrow \quad CF_3\text{-}CF{=}CH\text{-}CF_2OR$$

(Scheme 27)

In the presence of a base, the intermediate terminal fluoroalkene rearranged to give the final, more stable, internal fluoroalkene.

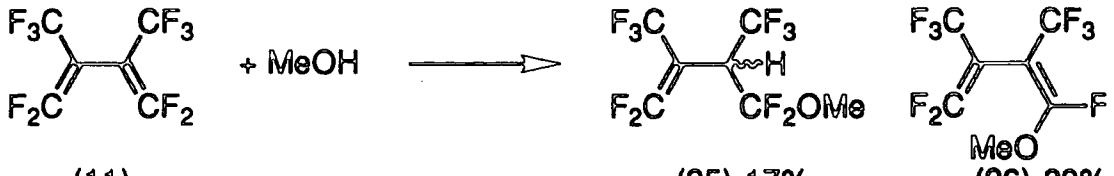
Perfluoro-2,3-dimethylbutadiene (11) has received some attention in the literature. The hydration of diene(11) proceeds in acetone[68] to give mainly the carboxylic acid (24) plus a few minor products (Scheme 28).



(11) (24)

(Scheme 28)

Diene (11) reacts slowly with neutral methanol[69] at room temperature to give a mixture of the 1,2-addition product (25) and a substitution product (26) (Scheme 29).

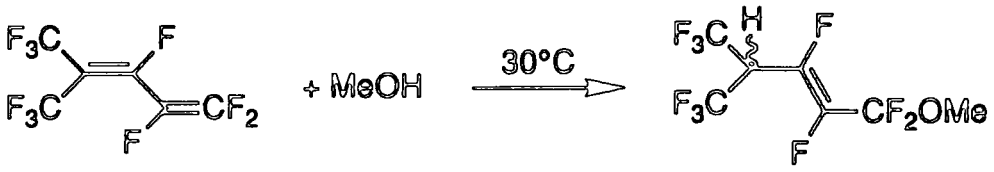


(11) (25) 17% (26) 39%

(Scheme 29)

Stronger nucleophilic conditions using sodium methoxide were needed to bring about a second substitution of diene (11) or substitution product (26)[69].

Interestingly, perfluoro-2-methylpenta-2,4-diene (20)[48] reacts with neutral methanol to give the 1,4-addition product (27) (Scheme 30).



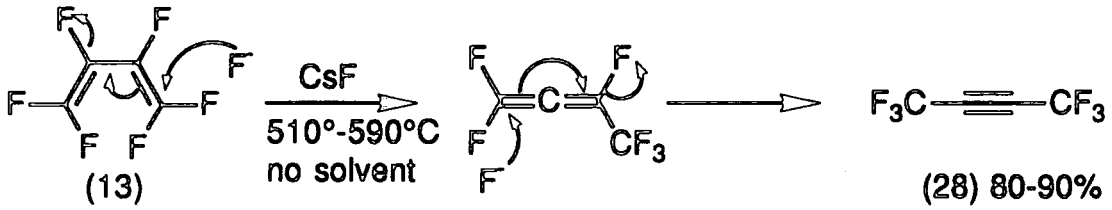
(20) (27) 89%

(Scheme 30)

whereas hexafluorobutadiene (13) adds alcohols only under nucleophilic catalysis[70].

1.4.2 Reactions with Fluoride Ion

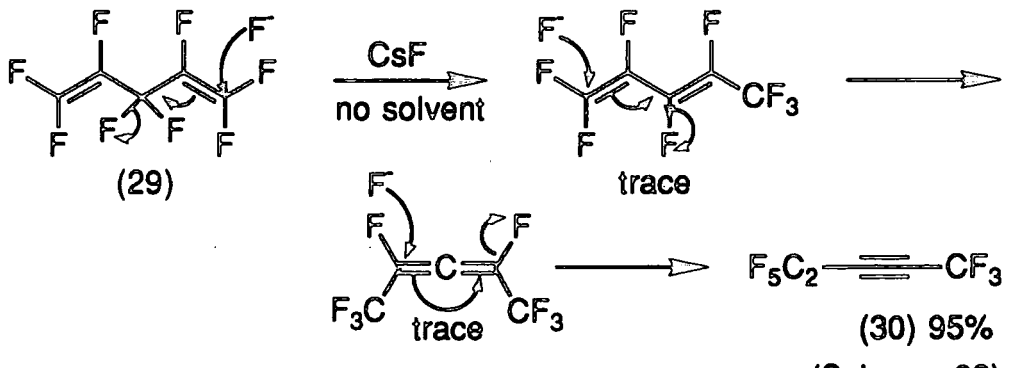
Very few reactions of fluorinated dienes with fluoride ion have been published. The simplest case, hexafluorobutadiene (13) was shown[71] to rearrange to give the alkyne hexafluorobut-2-yne (28) by the passage, in the vapour phase, over caesium fluoride (Scheme 31).



(13) (28) 80-90% (optimum)

(Scheme 31)

Analogously, octafluoropentadiene (29)[51] was isomerised[71] to give its more stable internal isomers and ultimately the alkyne (30) (Scheme 32).

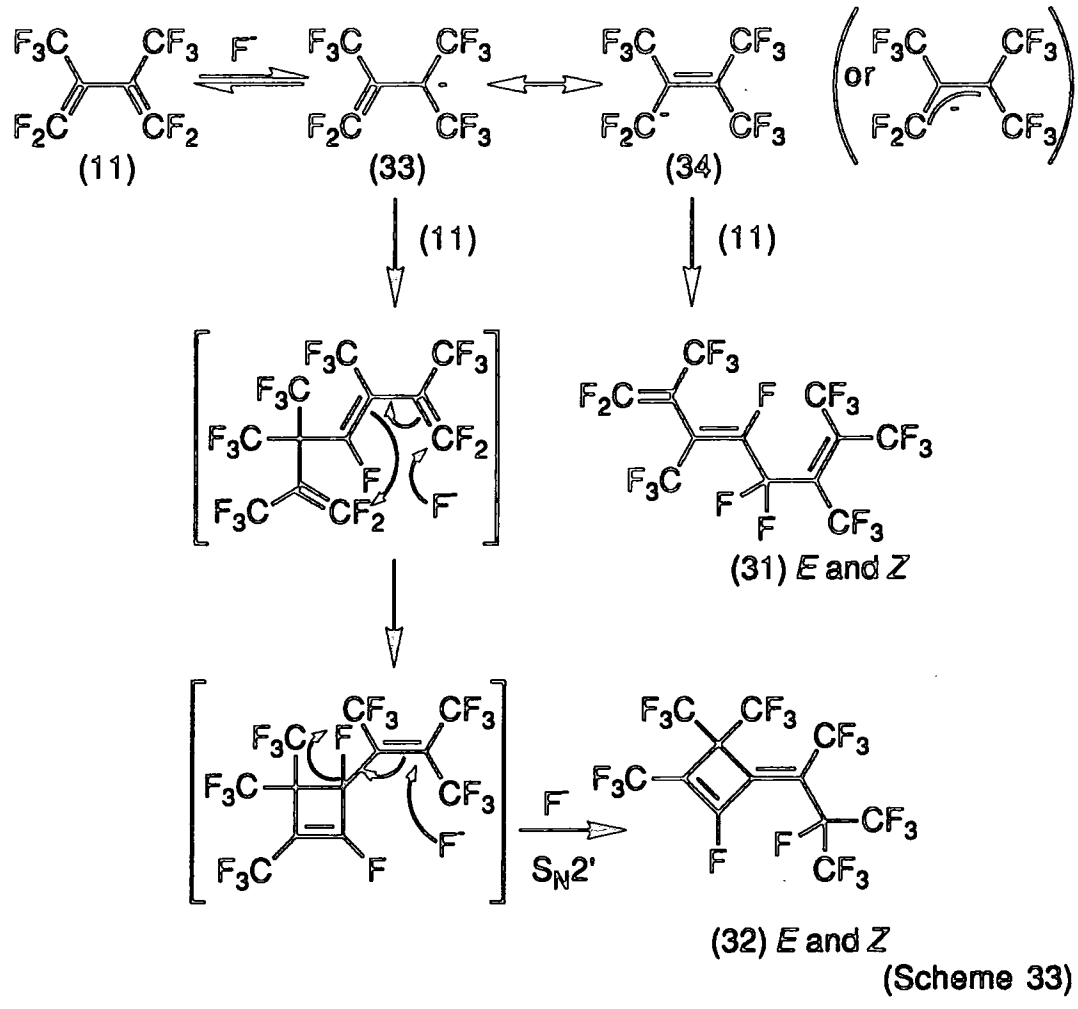


(29) (30) 95%

(Scheme 32)

In a similar vein, terminal diene decafluorohexa-1,5-diene (6)[20] was reported[72] to react with fluoride ion to give the more stable internal diene, decafluorohexa-2,4-diene.

However, in the case of diene (11), preferential isomerisation does not occur, instead fluoride ion induces an oligomerisation to give two dimers (31) and (32)[73] (Scheme 33).



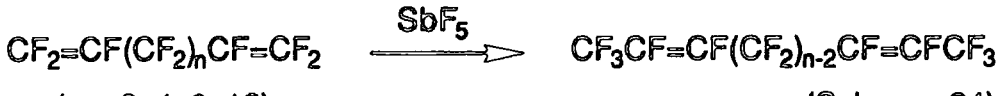
(Scheme 33)

The ratio of the dimers was found to be temperature dependent; attack through the more sterically hindered contributor anion (33) rather than (34) was increased with an increase in temperature leading to an increase in the proportion of diene (32).

1.4.3 Reactions with Antimony Pentafluoride

Antimony pentafluoride, like fluoride ion, can isomerise fluorinated dienes. It has been shown[74] that contacting various terminal dienes with a

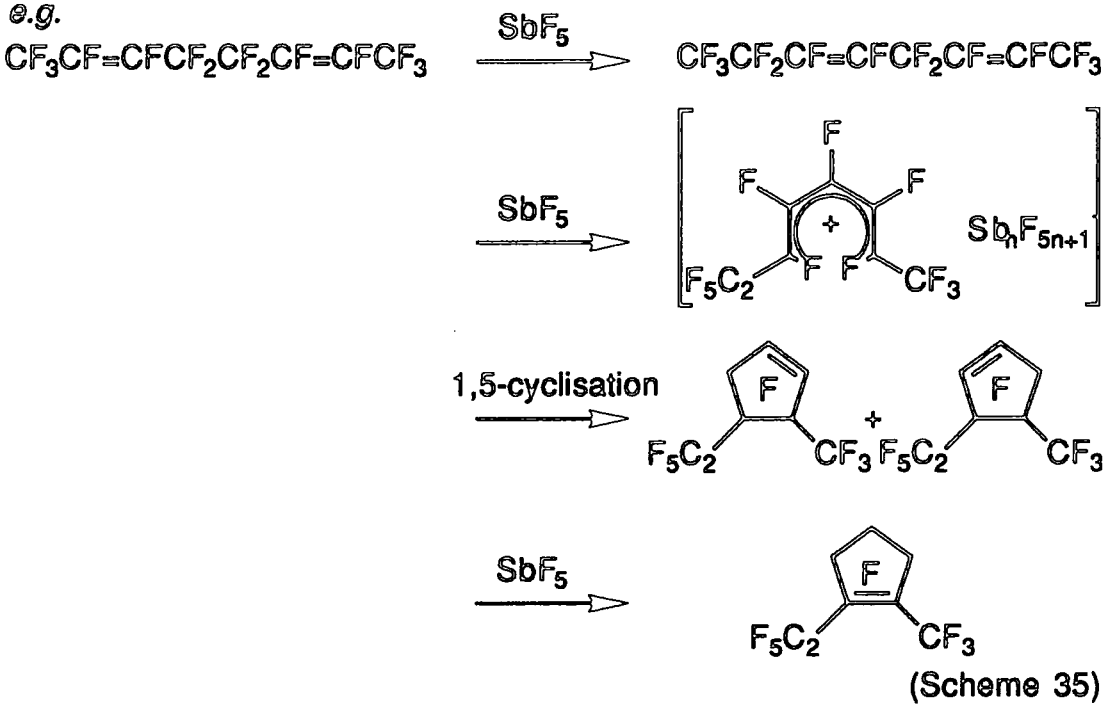
catalytic amount of antimony pentafluoride resulted in the exothermic isomerisation to their corresponding internal dienes (Scheme 34).



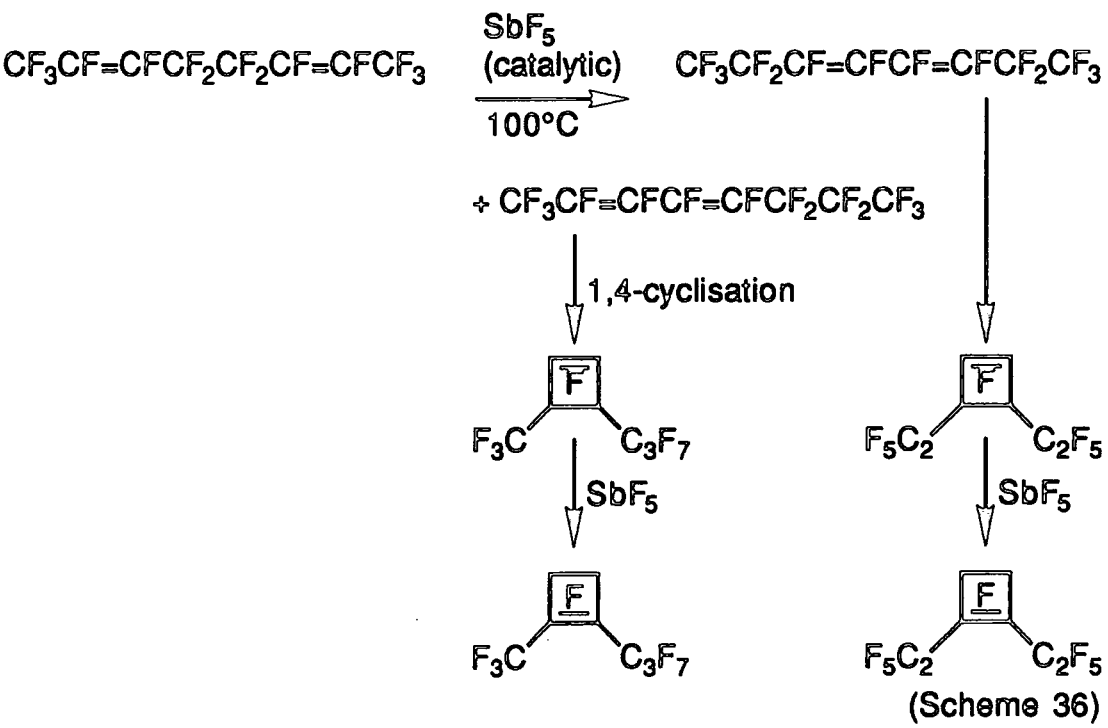
(Scheme 34)

Heating some of these internal dienes with antimony pentafluoride gave a mixture of cyclic products (Schemes 35 and 36).

e.g.

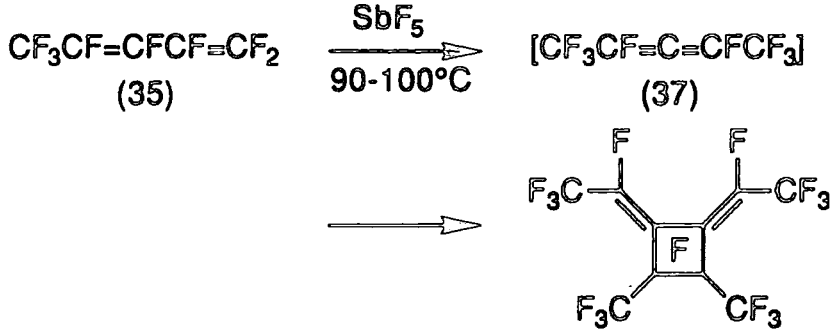


(Scheme 35)



(Scheme 36)

However, in the case of perfluoropenta-1,3-diene (35), heating with excess antimony pentafluoride[75] forced a cyclodimerisation to give the cyclic diene (36) presumed to proceed *via* the allene (37) (Scheme 37).

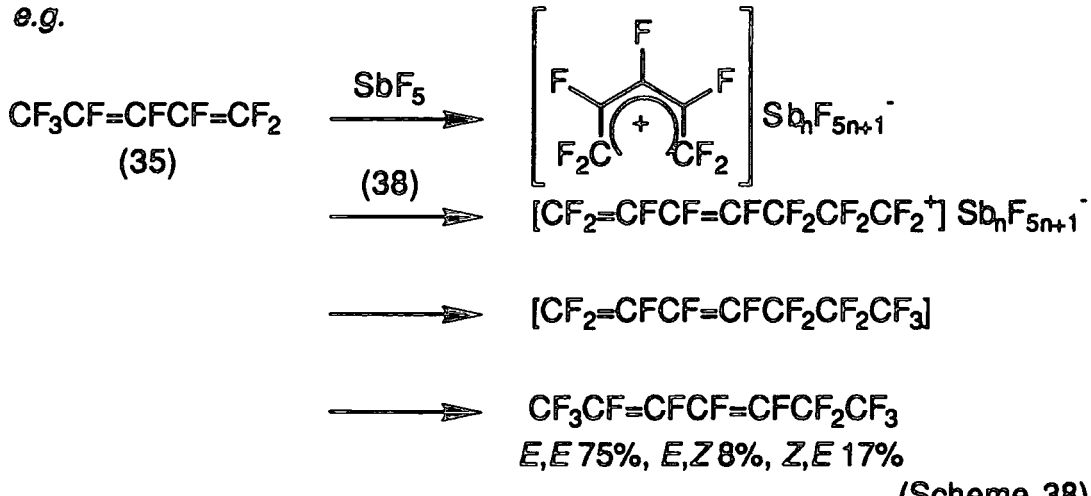


(36) 80-90%

(Scheme 37)

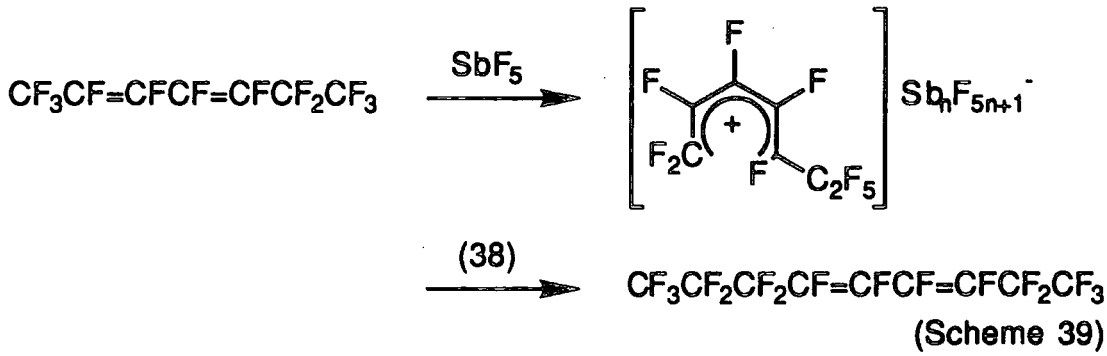
Very recently[76], it has been shown that some perfluorinated dienes can be electrophilically co-oligomerised with tetrafluoroethene (38) under the action of antimony pentafluoride. (Scheme 38).

e.g.



(Scheme 38)

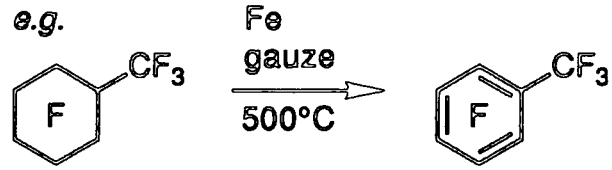
The resulting diene can further add another tetrafluoroethene (38) unit under these conditions (Scheme 39).



(Scheme 39)

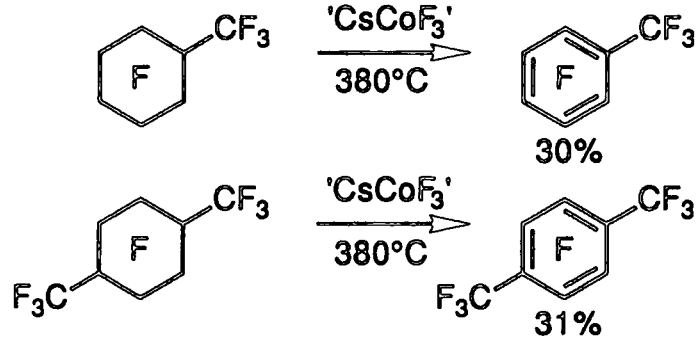
1.5 Defluorination

The great strength of the carbon-fluorine bond (545 kJmol^{-1} for C-F in CF_4 versus 436 kJmol^{-1} for C-H in CH_4 and 293 kJmol^{-1} for C-Cl in CCl_4[1]) accounts for the remarkable thermal stability of fluorocarbon compounds. Indeed, high temperature thermolyses have proven to be one of the more widely used synthetic procedures for the convenient formation of some otherwise difficult to obtain compounds[5,6,77]. Various thermal decompositions and fragmentations involving the elimination of difluoromethylene or tetrafluoroethene moieties have been reported[78,79,80,81] but it is the metal-induced pyrolytic defluorination of cyclic and polycyclic perfluoroalkanes to perfluoroaromatics[82,83] which has been the most widely used process to date (Scheme 40).



(Scheme 40)

As well as iron, analogous defluorinations have also been reported over nickel turnings[84] and activated carbon[85]. More recently, a similar defluorination has been reported[86] using exhausted caesium tetrafluorocobaltate(III) - assumed to be caesium trifluorocobaltate(II) (Scheme 41).



(Scheme 41)

The initial step in these defluorinations is presumably the removal of one of the tertiary fluorines but as the reaction proceeds, the extra stability arising from aromaticity has enabled these products to be isolated from the

reaction mixture rather than mineralisation occurring. However, when there is no aromatic product along the reaction pathway, milder conditions are required in order to avoid the complete decomposition of the fluorocarbons.

The reaction directly between fluorinated organics and alkali metals is known to be very vigorous to the extent of being potentially explosive[3], indeed this reaction remains a valuable tool for the analysis of fluorinated compounds[87]. Milder variations on this theme are the analytical techniques of using sodium in an ammonia solution[88] or as a biphenyl-sodium-dimethoxyethane complex[89,90] both again for use in the semimicro determination of fluorine (and chlorine) in organic compounds.

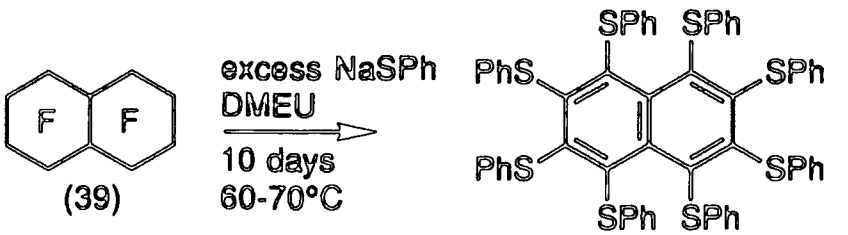
Recently, under relatively mild conditions, the sodium radical anion of naphthalene has been used to completely defluorinate 1,2,4,5-tetrafluoro-benzene and perfluorotoluene[91]. This followed earlier work in which the same naphthalene radical anion was used to partially defluorinate the surface of poly(tetrafluoroethene) (PTFE) in order to bring about effective bonded using commercial resins[92,93].

In fact, surface modification of PTFE has long been a target of interest in research. Dousek and Jansta[94,95] reported the electrochemical surface corrosion by various alkali metal amalgams to give black-coloured carbonaceous products which are typical of the chemical reduction of PTFE and in the recent literature[96], even non-polymers including hexafluorobenzene and tetradecafluorohexane, reduced in the gas phase by the action of a lithium amalgam.

More recently, however, the surface of PTFE has been modified reductively by the action of the potassium benzoin dianion[97,98] giving a reflective metallic lustre (silver or gold). Chakrabarti and Jacobus were also able to report[99] the chemical reduction of bulk PTFE into high density polyethene by the action of lithium in liquid ammonia.

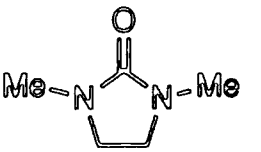
An intriguing paper from MacNicol and Robertson appeared in the literature recently[100]. The authors reported that perfluorodecalin (39) was

completely defluorinated and aromatised by the action of sodium thiophenate under fairly mild conditions (Scheme 42).

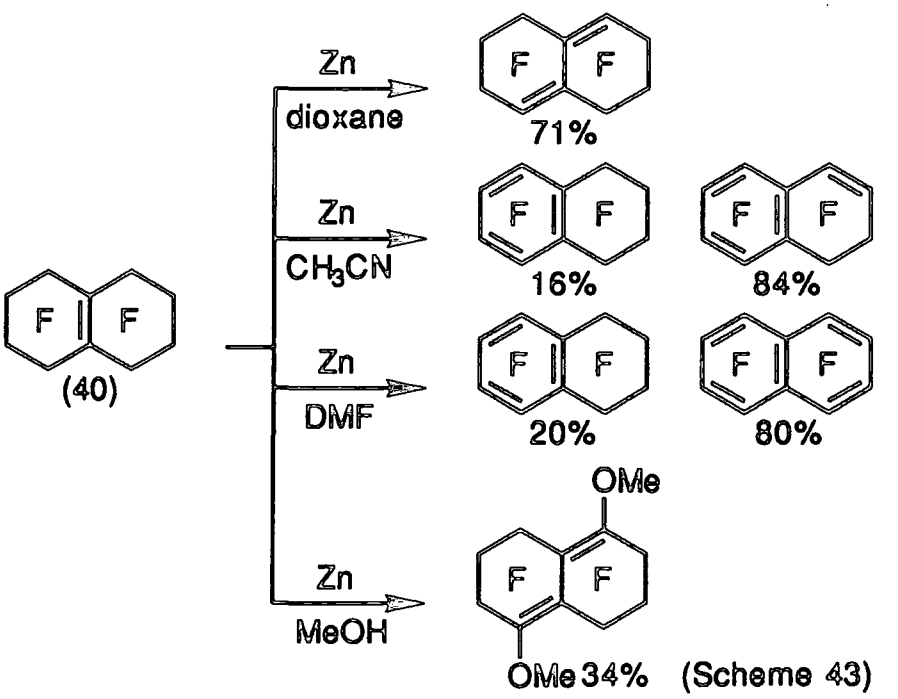


(Scheme 42)

DMEU = 1,3-dimethylimidazolidin-2-one



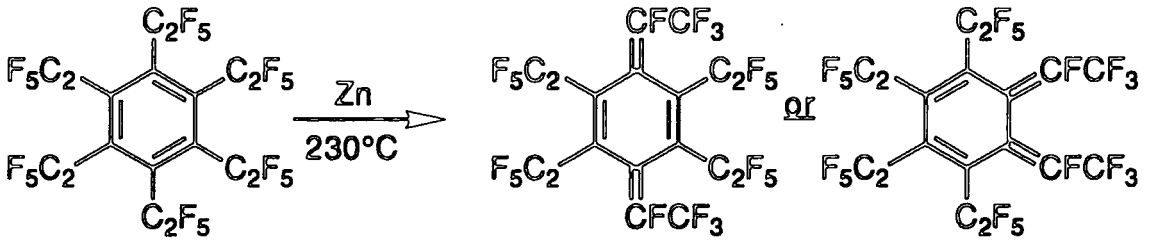
It is worthy of note here, that only model systems in which a tertiary fluorine site or a site of unsaturation was present, underwent this type of reaction[98] suggesting that it is at these positions that the initial reduction takes place. In a similar vein, a very recent paper[101] reported the reduction of perfluorobicyclo[4.4.0]dec-1(6)-ene (40) by activated zinc to give various defluorinated products depending upon the polarity of the solvent present (Scheme 43).



(Scheme 43)

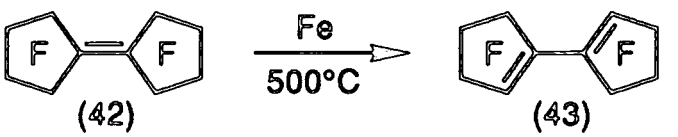
Under these circumstances, however, perfluorodecalin (39) could not be defluorinated[101].

A few papers have been published which outline thermolytic defluorination of perfluorinated alkenes over activated metal surfaces as a viable route to non-aromatic unsaturated fluorocarbons. Among the first was a communication released by Haszeldine and co-workers[102] wherein hexakis(pentafluoroethyl)benzene (41) was defluorinated over activated zinc to give a stable xylylene, the structure of which was not unequivocally assigned (Scheme 44).



(41) (unassigned) (Scheme 44)

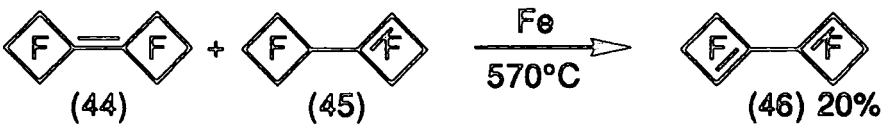
Thermolytic defluorination has been used to good effect in these laboratories; Marper found[5,103] that perfluorobicyclopentylidene (42) could be reductively defluorinated over hot iron to give the diene perfluorobicyclopent-1,1'-enyl (43) (Scheme 45).



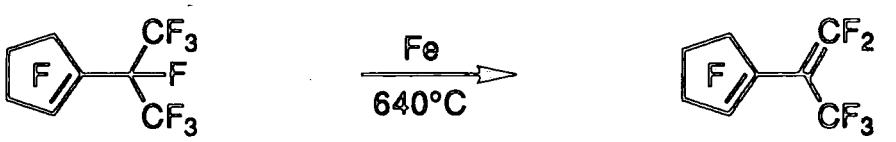
(42) (43)

(Scheme 45)

whilst Taylor[46] performed similar thermolyses on perfluorobicyclobutylidene (44) and perfluoro-1-cyclobutylcyclobutene (45) to give the similar diene (46) and perfluoro-1-(methylethyl)-cyclopentene (47) to give the diene (48) in modest yields (Scheme 46).



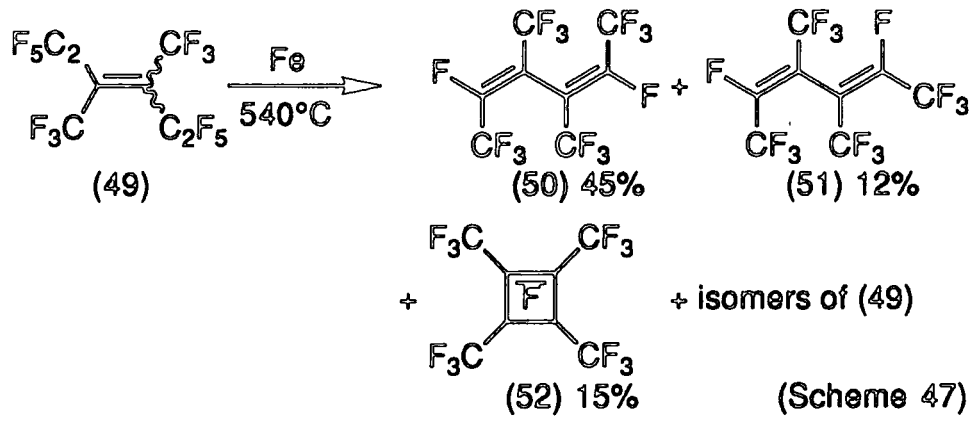
(44) (45) (46) 20%



(47) (48) 35%

(Scheme 46)

Perfluoro-3,4-dimethylhex-3-ene (both *E*- and *Z*-) (49), the readily available[104,105,106] tetramer of tetrafluoroethene (38), has also been thermolytically defluorinated[81,107] over iron to give the isomeric dienes (50) and (51) in good yield along with some of the thermally cyclised product (52) (Scheme 47).



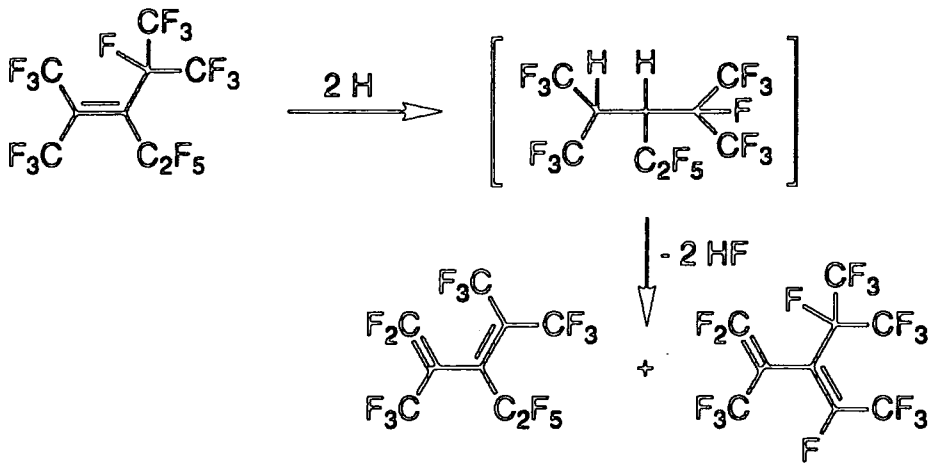
(Scheme 47)

It is significant to note that pyrolysis of the tetramer (49) over caesium fluoride resulted in appreciable defluorination[81] [*ca.* 30% yield for (50), (51) and (52) combined] possibly through the formation of caesium polyfluorides. A similar defluorination over activated carbon has recently appeared in the patent literature[108] whereby tetramer (49) was reduced to the diene (50) at 400°C. The absence of any reference to the thermally cyclised isomer, cyclobutene derivative (52), among the products is noteworthy considering the high temperature of the reaction.

A certain amount of interest has been generated in the chemical literature recently over the activation of carbon-fluorine bonds by the oxidative addition to a metal centre in the cases of fluorinated aromatic systems[109] and perfluoroalkenes[110]. In a paper by Jones and McDonald[111], this idea of metal insertion was extended and the alkane hexafluoroethane was successfully (if slowly) defluorinated in the gas phase by $[Mn(CO)_3]$, a fragment generated by dissociative electron attachment to $Mn_2(CO)_{10}$.

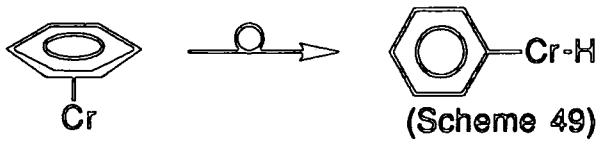
When zero-valent bis(arene)chromium complexes were used as initiators for hexafluoropropene oligomerisation, two of the trimerisation products were found to have been defluorinated[112] although no yields are

given for the process. The authors attributed the apparent defluorination to hydrogenation followed by dehydrofluorination (Scheme 48).



(Scheme 48)

This idea was reinforced through deuterium labelling in that the source of hydrogen was found to be from the aryl ligand upon chromium[113] and presumed to react after η^6-η^1 rearrangement (Scheme 49).



(Scheme 49)

In a more recent example of defluorination of perfluoroalkenes by organometallic reagents, Watson and co-workers reported[114] fluorine abstraction by various divalent lanthanoid complexes to give trivalent lanthanoid fluorides $M(C_5Me_5)_2F.L$ (M = Yb, Eu, Sm; L = diethyl ether, tetrahydrofuran). The driving force for these reactions was the negative reduction potentials of the metal ions [M(III) → M(II)] and the ultimate formation of very strong lanthanoid fluoride bonds.

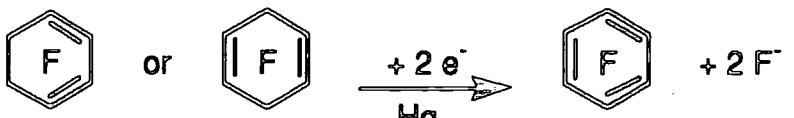
Chapter Two

Electrochemical Generation of Some Perfluorinated Dienes

2.1 Background

Previous attempts in our laboratories to electrochemically reduce fluorinated alkenes to their corresponding dienes have not met with general success[115,116,117]. The major problems with electrochemical reductions of fluorinated substrates have involved complicating side reactions; namely reaction of the substrate with the bulk solvent or the supporting electrolyte, or with fluoride ion formed by elimination which may induce isomerisation or dimerisation with further fluorinated material.

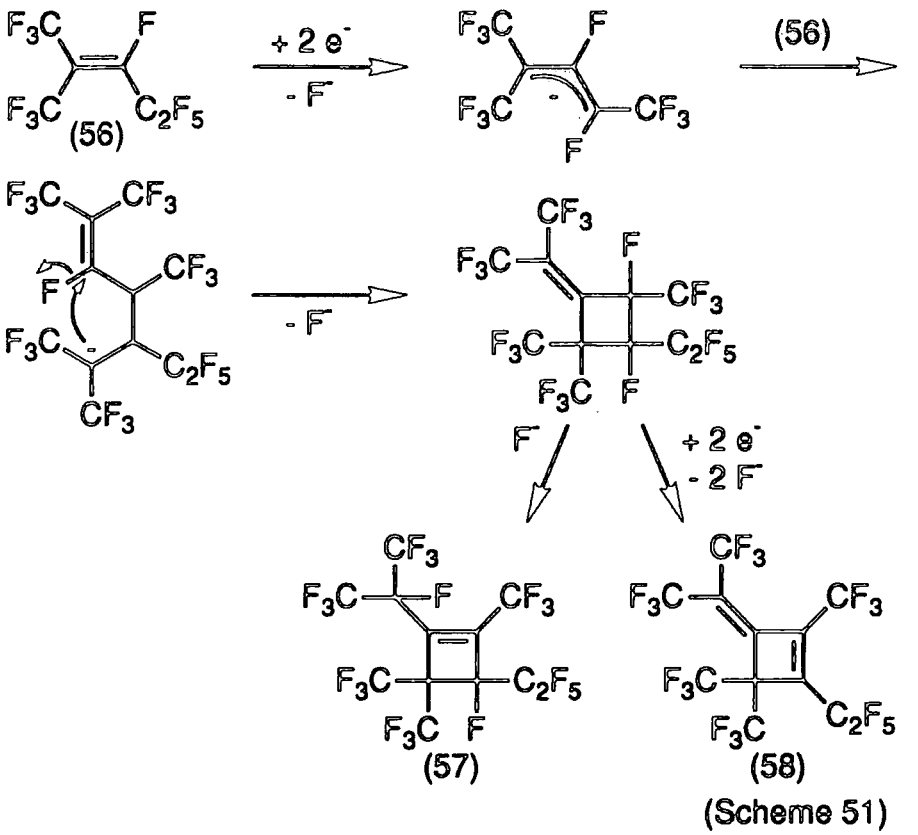
However, some successful electrochemical reductions of perfluorinated alkenes have been published in the literature. For example, fluorinated aromatics have been generated by the reduction of some fluorinated cyclohexadienes[118,119,120]. Thus, octafluorocyclohexa-1,3- and -1,4-diene (53) and (54)[121] were electrochemically defluorinated to give hexafluoro-benzene (55) *via* a step-wise mechanism (Scheme 50).



(53) (54) (55)

(Scheme 50)

Soviet workers[122] reported the electrochemical reduction of perfluoro-4-methylpent-3-ene (56), the thermodynamic dimer of hexafluoro-propene[103,123]. The result of this reduction was the formation of two unusual cyclic dimerisation products (57) and (58) (Scheme 51).



(Scheme 51)

However, the range of clean electrochemical defluorinations is still quite small.

Due to the relative strength of the carbon-fluorine bond[1], a further limiting factor is the size of the applied potential which is needed to reduce fluorinated organics. In order to determine the reductions of some fluorocarbon derivatives, cyclic voltammetry was used.

2.2 Cyclic Voltammetry of some Perfluorinated Alkenes and Dienes

2.2.1 Introduction

Cyclic voltammetry (C.V.) is a useful analytical technique in the investigation of the mechanistic aspects of some electrochemical processes. In C.V. an electrode potential is swept between the limits E_1 and E_2 at a constant sweep rate v which can be either positive or negative. Upon reaching E_2 the sweep is reversed (usually, but not necessarily, at the same sweep rate) until the potential reaches the initial value of E_1. After this, the process may be stopped, repeated or continued further to a value E_3.

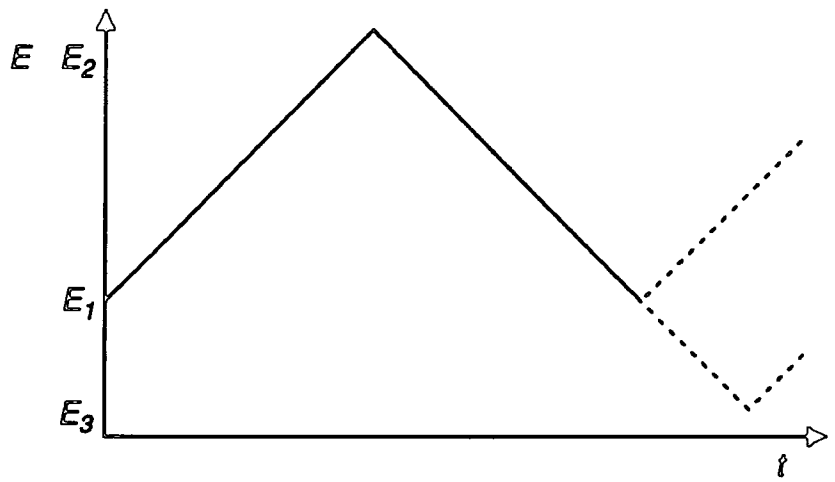


Figure 2. A C.V. potential-time profile.

The current is recorded as a function of the potential applied across the cell. In the simplest case for a reduction, oxidised species O is converted to the reduced species R (Scheme 52).

$$O + e^- \rightleftharpoons R \qquad \text{(Scheme 52)}$$

Initially, only O is present in solution and, if a very slow linear potential ramp is applied, the resultant voltammogram would be a steady state *I versus E* curve. By increasing the sweep rate v, a peak of increasing size develops. This is shown overleaf in Figure 3.

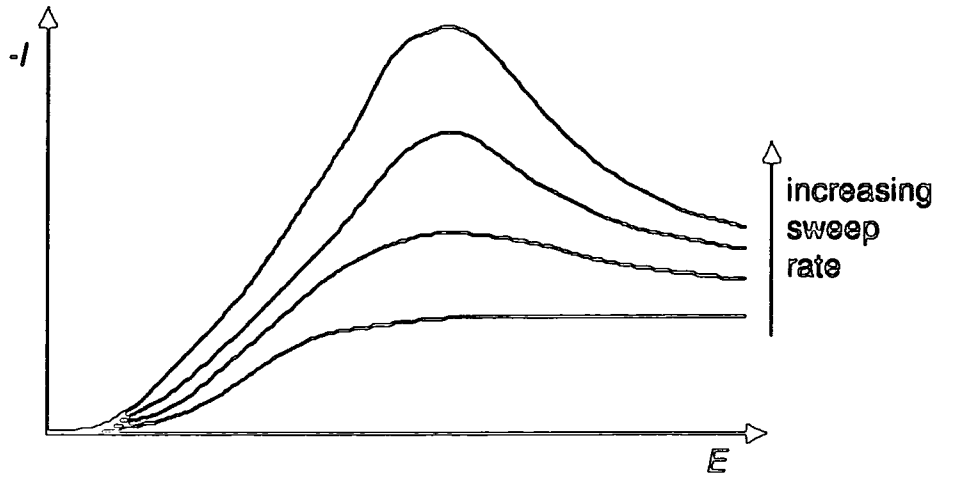


Figure 3. A series of linear sweep voltammograms at various sweep rates.

To understand this, we must consider the steady state conditions for the system when the concentrations of the electroactive substrate O are uniform throughout the bulk solution and are maintained that way by natural convection. However, in the region immediately next to the electrode - known as the Nernst diffusion layer - the concentration gradients are approximately linear, with the ratio of $[O\sigma]/[R\sigma]$ given by the Nernst equation.

$$E = E^o - \frac{RT}{nF} \ln \frac{[R\sigma]}{[O\sigma]}$$

Where E^o is the standard potential of the system, $[R\sigma]$ is the concentration of R at a small distance σ from the electrode and $[O\sigma]$ is the concentration of O at the same distance.

This means that, for this system, as the potential E is made more negative, the surface concentration [O] will be decreased, thereby increasing the concentration gradient and thus the resulting current. The current will reach a plateau value when the surface concentration reaches zero.

If the sweep rate v is increased, the diffusion layer cannot relax to its equilibrium state so it leads to a non-linear concentration gradient. Once the potential is able to reduce O, its concentration decreases in order to satisfy the Nernst equation. This causes a current proportional to the concentration gradient created to flow in the circuit. Diffusion will decrease this gradient but the changing electrode potential in turn decreases the amount of O at the

electrode. It can therefore be seen that, for any given potential, the concentration gradient at the surface is greater than for the steady state case and therefore the current is larger. Once the concentration of O at the surface reaches zero, the gradient will decrease through diffusion thereby relaxing the system hence the current will also decrease leaving a peak in the cyclic voltammogram.

For a very slow sweep (i.e. *pseudo* steady state) the current for the reverse sweep should track the forward one but for faster sweeps, a significant amount of R has been formed in the diffusion layer and continues to be generated until the potential reaches E^o. As the potential approaches this value it starts to be oxidised back to O causing a reverse current to flow. Eventually all the R in the region will be consumed and, in an analogous way to the reductive process, a peaked response will be given in the voltammogram (in the opposite direction). The charge associated with the oxidative peak will be smaller than the reductive case as the concentration differences will have driven most of the R produced into the bulk solution.

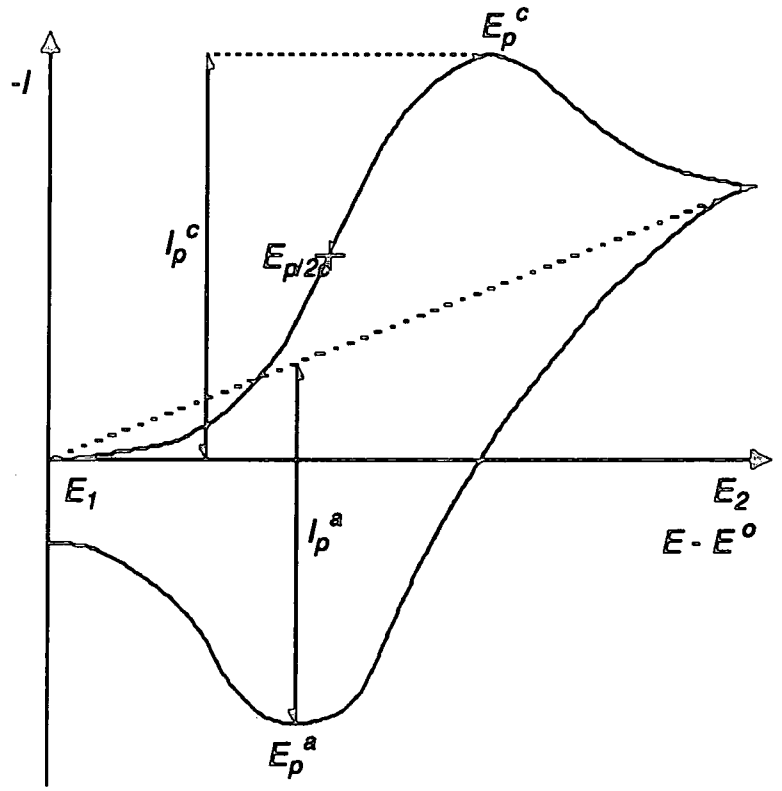


Figure 4. A cyclic voltammogram for a reversible process.

The peak potentials, E_p^c and E_p^a, obtained from such a cyclic voltammogram will be independent of the sweep rate[124], as it is the applied potential and not the rate of change which dictates the actual electrochemical processes occurring.

For the simple case of reduction / oxidation, it is found[124] that the ratio of peak current flowing, I_p^a/I_p^c, is equal to unity. In some cases, however, the intermediate produced at the electrode is unstable on the sweep timescale with respect to further reaction giving a more favourable product P (Scheme 53).

$$O + e^- \rightleftharpoons R \rightarrow P \qquad \text{(Scheme 53)}$$

This means that, for the reverse sweep, the concentration of R is lower than for the simple reversible process and the current arising from the oxidation of R in the electric double layer is decreased. This gives the result that the ratio I_p^a/I_p^c <1 and that the separation between the forward and reverse peaks increases. In the extreme case the reverse peak may not be present.

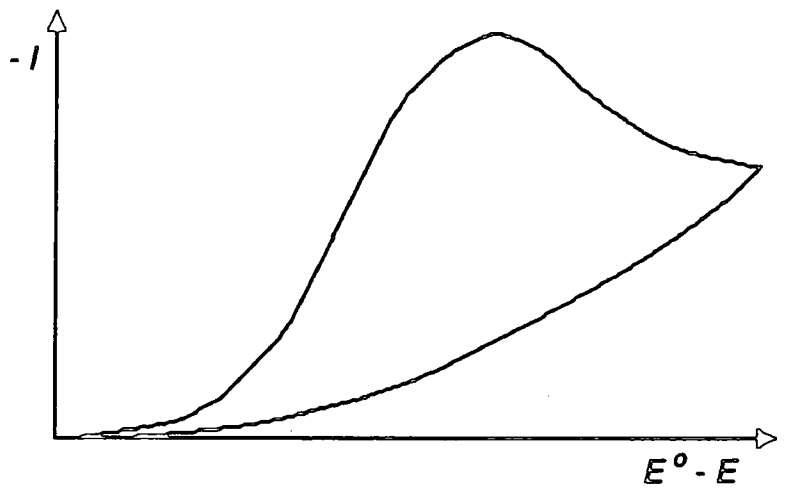


Figure 5. A cyclic voltammogram for a simple irreversible reduction.

By increasing the sweep rate v, for such irreversible systems, the reaction which happens after the first electron transfer occurs to a lesser extent and so the ratio I_p^a/I_p^c increases to such a degree that for very fast scanning the system appears to be totally reversible. Conversely, slowing the speed of the cycles down causes the system to assume a more steady state type of

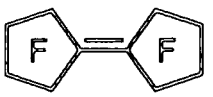
behaviour except that further anomalous peaks may appear from the reduction of the products.

Various studies have been made into the investigation of how some reaction parameters change with a change in sweep rate[124,125] and using C.V. on a qualitative basis, information on reaction mechanisms and sequences has been obtained.

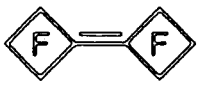
2.2.2 Discussion

Table 2 shows the resulting reduction potentials (*vs.* S.C.E.) from the cyclic voltammetric study of some relatively easily available perfluorinated alkenes and dienes. The fluorocarbons are either oligomers of simple alkenes or dienes obtained by the reduction of these oligomers (see Section 2.3).

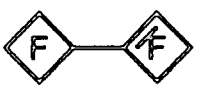
Table 2



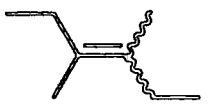
(42)
-1.06 ± 0.03V
(*quasi*-reversible)



(44)
-1.10 ± 0.03V
(*quasi*-reversible)

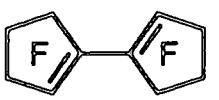


(45)
-1.23 ± 0.03V

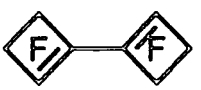


(49)
-1.62 ± 0.05V
(*quasi*-reversible)

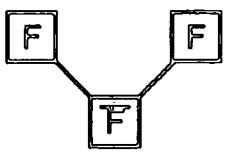
(56)
-1.76 ± 0.08V



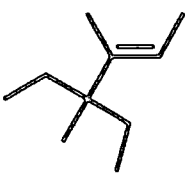
(43)
-2.03 ± 0.01V



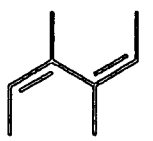
(46)
-2.25 ± 0.01V



(16)
-2.30 ± 0.10V



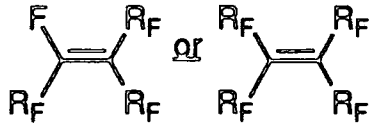
(59)
-2.30 ± 0.05V



(50)
-2.35 ± 0.10V

(All unmarked bonds are to fluorine)

We now possess the reduction potentials for a series of perfluoroalkene derivatives which may be represented by the general formulae:



where R_F = perfluoroalkyl

The replacement of a vinylic fluorine atom in such compounds by a perfluoroalkyl group, R_F, is known to lower the L.U.M.O. energies of the alkene derivative[5]; this is a specific example of the commonly observed phenomenon of electron withdrawing substituents lowering alkene orbital energies[126] and this effect is born out directly in the table. The initial process in the electrochemical reduction of such fluorinated alkenes is the transfer of an electron to the L.U.M.O. of the molecule and so, the lower the energy of this transfer, the less the potential that needs to be applied across the cell to accomplish this reduction.

On the whole, the substrates with the lowest reduction potentials are those which are tetra-substituted and, conversely, those which are harder to reduce tend to possess only three R_F groups on the double bonds. If this trend was continued, those perfluoroalkenes with fewer R_F groups would display still higher reduction potentials than those shown in the table. It must be pointed out here that none of the C.V. experiments that were carried out were reversible; indeed most of the compounds tested in Table 2 did not show any sign of reversibility. Therefore these compounds cannot be considered as behaving in an ideal manner and that electron transfer is very quickly followed by a further reaction such as the elimination of fluoride ion (see Section 2.2.1).

Perfluoroalkenes (42) and (44), both of which could be considered to be tetra-perfluoroalkyl substituted alkenes, display the lowest reduction potentials in the table. One of the reasons for this could be the result of a favourable relief in angle strain in the rings of the two systems which would occur upon the addition of an electron. The resulting radical anions would then be able to

rearrange from their initial high energy probable planar conformations thus decreasing the amount of ring strain present.

Perfluoroalkene (45), an isomer of (44), has a surprisingly low reduction potential for such a trialkyl substituted fluoroalkene. The presence of a vinylic fluorine atom would normally be expected to result in a significantly higher potential than that which is shown. However, unlike for the isomeric perfluorinated alkene (44), the cyclic voltammogram for (45) showed no sign of reversibility and so it is possible that, in this case, the addition of an electron to this system could be coupled with the loss of the tertiary allylic fluorine in a concerted process. It is known that a carbon-fluorine bond in such a site is relatively weak and so the elimination of this fluoride ion linked with the favourable relief of angle strain in the cyclobutenyl ring could result in an overall lowering of the reduction potential for the molecule.

The fluoroalkene (49) possesses four R_F groups around the double bond and therefore its reduction potential is relatively low. However, the fluorinated alkene (56), which has a similar structure to (49) but only bears three R_F groups and a vinylic fluorine, displays a reduction potential which is not very much higher than that for (49) and so since fluoroalkene (56) has no obvious means of lowering its reduction potential, it remains as an anomaly.

Perfluorinated dienes (43) and (46) can be considered as consisting of two tri-alkyl substituted double bonds if the double bonds are not conjugated. This idea helps to explain why the reduction potentials are much higher than those of their precursors (42) and the two isomers (44) and (45) respectively. The difference of approximately a volt in the reduction potentials between these precursors and the dienes is significant and could help to justify how the dienes can be isolated as a result of reduction.

The fluorinated trimer (16)[44,45] possesses four R_F groups on the double bond and also has two tertiary fluorines in adjacent allylic sites and so it should have a low reduction potential. However, its potential is fairly high and is difficult to account for. It is possible that the substantial steric bulk of the two

pendant perfluorocyclobutyl groups could hinder the initial electron transfer in this case and so, although considerable ring strain relief and fluoride ion elimination could occur, it is still quite difficult to accomplish electron transfer to this fluoroalkene.

Perfluoroalkene (59) is a more simple example; it possesses three R_F groups and a vinylic fluorine and so has a high value for its reduction potential. The large perfluoro-1'-ethyl-1'-methyl-propyl group is quite sterically demanding and so the large potential given in Table 2 could quite easily reflect this influence to the reduction of this fluorinated alkene.

Finally, diene (50), if there is no conjugation between the double bonds, can be considered as comprising two tri- alkyl substituted fluoroalkenes in a similar manner to the dienes (43) and (46) and so the high value for its reduction potential can be explained in this way. It is also likely that, again, the large difference in reduction potentials between diene (50) and its precursor (49) is the dominating factor which explains how the diene can be isolated by the reduction of (49).

2.3 Sodium Amalgam Reductions (With M. W. Briscoe)

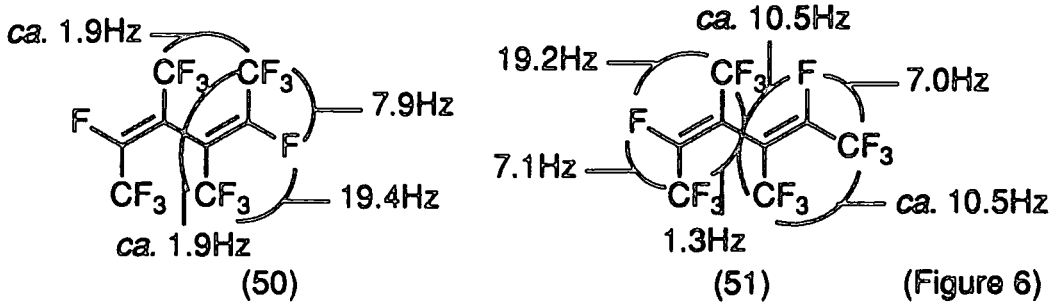
2.3.1 Introduction

Following successful work on the electrochemical polymerisation of octafluorocyclopentene[127], analogous studies were made at the Electricity Council Research Centre Laboratories at Capenhurst (now known as E. A. Technology) using potassium amalgam as a single electron transfer (S.E.T.) agent. These studies resulted in the formation of a similar blue-black polymer. We have used the term 'electromimetic' to describe the effect of such amalgams and the action of sodium amalgam as an S.E.T. agent to be used interchangeably with electrochemical reduction was first used in these laboratories by Mark Briscoe[117].

The following sections describes various attempts to reduce some fluorocarbon derivatives through the action of sodium amalgam.

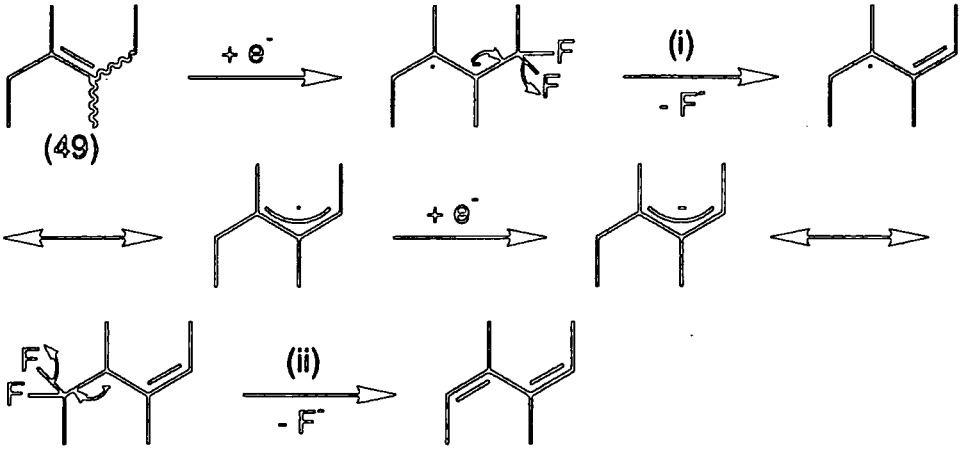
2.3.2 *E*- and *Z*-Perfluoro-3,4-dimethylhex-3-ene (49)

The reduction of perfluorinated alkene (49), the tetramer of tetrafluoroethene[104,105,106], by sodium amalgam produced a mixture of isomeric dienes, *Z,Z*- and *E,Z*- perfluoro-3,4-dimethylhexa-2,4-diene (50) and (51) in 74% and 20% yields respectively. The stereochemistry around the double bonds was confirmed by the ^{19}F NMR coupling constant data of the dienes since it is known that $^{5}J(cis\text{-}CF_3,CF_3)$ values are greater than 10Hz and $^{5}J(trans\text{-}CF_3,CF_3)$ values are typically less than 2Hz and also that $^{4}J(trans\text{-}CF_3,F)$ coupling constants are less than for $^{4}J(cis\text{-}CF_3,F)$[128,129]. Interestingly, *Z,Z*-diene (50) displays a *pseudo*-septet generated by the $(A_3)_2(X_3)_2$ system with a coupling constant of 1.9Hz indicative of a *trans,trans*- diene.(Figure 6).



(Figure 6)

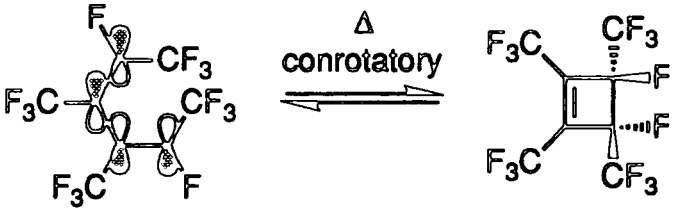
The mechanism for this reduction is presumed to proceed *via* two S.E.T. steps (Scheme 54).



All unmarked bonds to fluorine (50) (Scheme 54)

A similar mechanism may be invoked to explain the formation of diene (51), with a different structural geometry arising after the elimination of fluoride ion after either step (i) or (ii).

This reduction is probably analogous to the thermolytic defluorination of (49) over hot iron[81,107]. However, with the amalgam, the temperature never rose high enough to form cyclobutene derivative (52). Indeed, when diene (50) was heated in a furnace at 100°C, (52) was formed with *ca.* 50% conversion demonstrating that it is, in fact, formed through a thermal cyclisation[40] of diene (50) (Scheme 55).

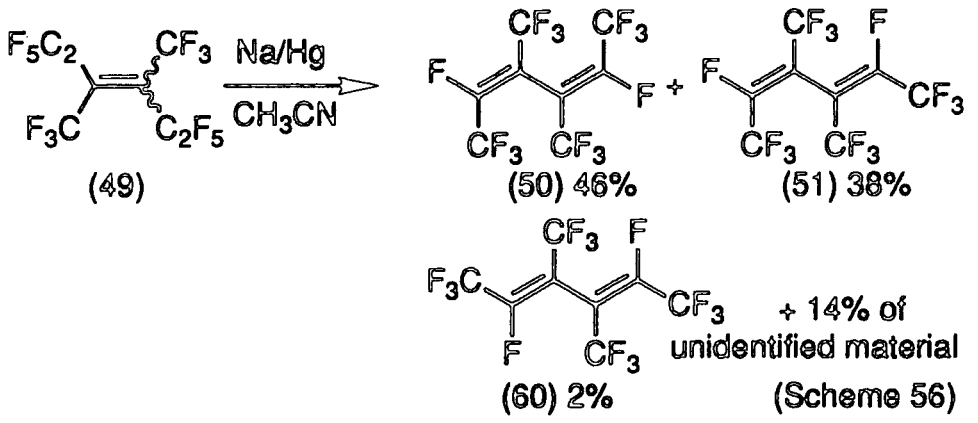


(50) (52) *ca.* 50%

(Scheme 55)

However, when tetramer (49) and sodium amalgam were reacted in the presence of acetonitrile, which was added to act as a heat sink, ^{19}F NMR spectroscopy and G.C. mass spectrometry determined that the two dienes (50) and (51) were formed in *ca.* 46% and 38% yields respectively along with *ca.* 2% of the *E,E*- isomer (60) and some 14% of various unidentified fluorinated

components. There was no evidence for the presence of the cyclobutene derivative (52) (Scheme 56).



This demonstrates that the predominant formation of the *Z,Z*-isomer (50) is through thermodynamic effects and that milder conditions, created with a heat sink like a solvent, allows the production of greater amounts of the less thermodynamically favourable isomers.

Indeed, when a mixture of the isomers (50) and (51) was heated under reflux with caesium fluoride, it was shown by ^{19}F NMR spectroscopy that the less energetically favourable isomer, (51) was converted into the *Z,Z*- isomer, (50) confirming diene (50) as the most stable isomer. There was no evidence for the formation of a stable anion of the diene in the spectra although it may be assumed that the stereochemistry around the double bonds is altered *via* such a transient carbanion. More importantly, this shows that the stereochemistry at the double bonds in the dienes can be interconverted in the presence of fluoride ion and that the mixture of dienes (50) and (51) is a good source of the more stable isomer, (50).

In the dienes (50), (51) and (60), the trifluoromethyl groups impose considerable steric demands around the 1,3-diene skeletons and so the structures of the dienes are very probably twisted out of the *trans*- planar conformations which such dienes would prefer to exist in if allowed to do so in the gas phase. As an exercise, the structures of these dienes were studied by molecular modelling using the COSMIC package on a MicroVAX 2 minicomputer. By an iterative process of minimising the strain energies and

steric hindrance effects between non-bonded atoms, an estimate of the most stable conformer was made for each example starting in each case from the *trans*- planar conformation.

The resulting structures and angles can only be taken as estimates as the package does not deal with the distribution of electon density within the molecules nor all possible bonding arrangements; it makes slight changes in local geometry in order to reduce the energy and so it is possible that the program gives a local minimum and not the thermodynamically most favourable conformer. Indeed, in order to demonstrate this point, the diene hexafluorobut-1,3-diene (13) was modelled using this program and the resulting torsion angle, ψ, was given as 30.1° - which is significantly different to the results found for example through electron diffraction[63] and *ab initio* molecular orbital calculations[66] of $\psi = 47.4° \pm 2.4°$ and $\psi = 58.4°$ respectively (see Section 1.3), implying that a significant error could be involved in the possible outcome. Nonetheless, the resulting conformer is an estimate which would be difficult to obtain by other means and it is important to note that the general structure will be fairly close to that which is actually adopted by the molecule.

In the case of the *Z,Z*- isomer (50), the resulting model was shown by COSMIC to possess a skew structure with a torsion angle, ψ, of 103.0° from the *cis*- planar form (Figure 7).

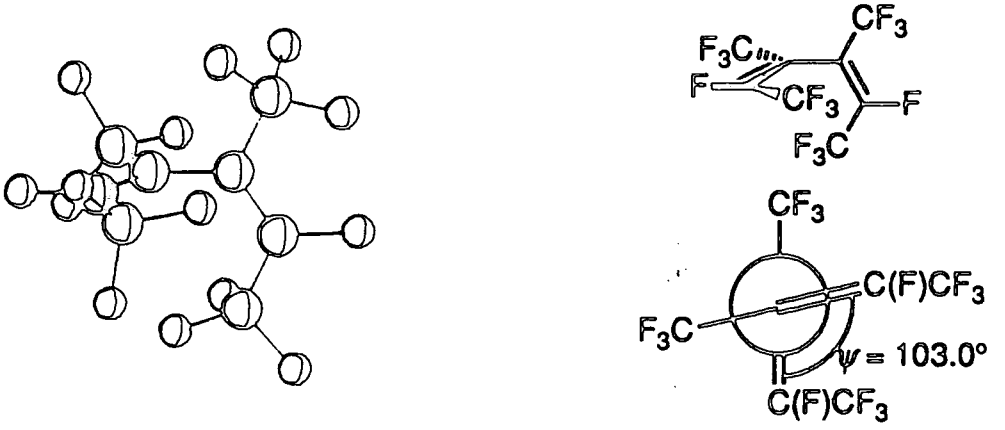
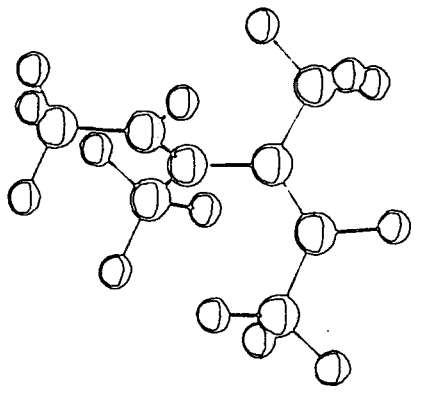


Figure 7. *Z,Z*-Perfluoro-3,4-dimethylhexa-2,4-diene (50).

For the *E,Z*- isomer (51), the modelling gave a larger resulting torsion angle of 117.1° (Figure 8).



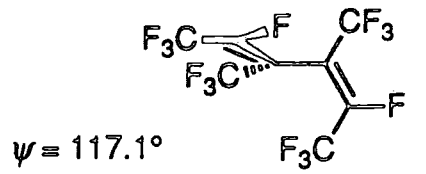
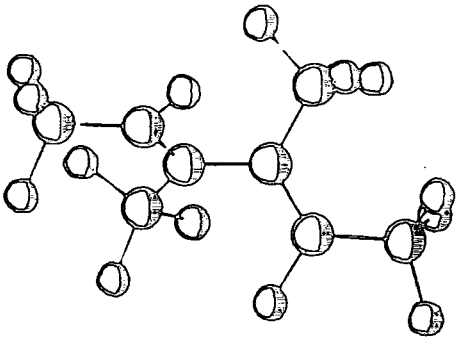


Figure 8. *E,Z*-Perfluoro-3,4-dimethylhexa-2,4-diene (51).

Indeed, this trend in the value of ψ was continued for the *E,E*- isomer (60) in which the calculated lowest energy conformation was shown to be even more aligned to the *trans*-planar structure, displaying a torsion angle of 129.0° (Figure 9).



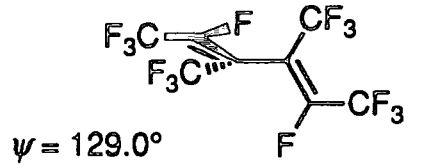


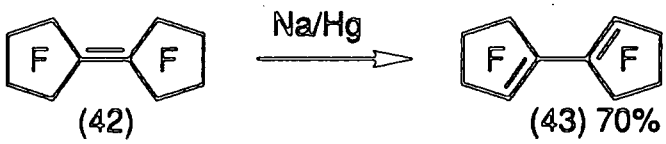
Figure 9. *E,E*-Perfluoro-3,4-dimethylhexa-2,4-diene (60).

It must be pointed out that the COSMIC package, like the more powerful programs of its ilk, also takes no account of any intermolecular considerations. More sophisticated *ab initio* calculations could be carried out but the structures already given in Figures 6,7 and 8 show the general trend that the bulky trifluoromethyl groups, present in the molecules, deviate the geometry of the systems quite considerably away from the possible planar conformations into

the skew structures in which little conjugation would be assumed to exist between the double bonds.

2.3.3 Perfluorobicyclopentylidene (42)

The reduction of the title fluoroalkene (42), the dimer of octafluorocyclopentene[130], by the action of a sodium amalgam gave perfluorobicyclopent-1,1'-enyl (43) in a yield of 70% (Scheme 57).



(42) (43) 70%

(Scheme 57)

Isolation of the diene from remaining (42) was carried out by a simple fractional crystallisation in a refrigerator[131] and its structure was determined by ^{19}F NMR spectroscopy, mass spectrometry and IR spectroscopy. The mechanism for the formation of diene (43) is probably analogous to that in Scheme 54.

The isolated yield of 70% for diene (43) is favourable when compared to 60% which was obtained by the thermolytic defluorination of (42) over hot iron[103] but, more importantly, it is easier to reproduce.

When this diene (43) was modelled on the COSMIC package, the resulting structure was given as a *cis*- conformer with a torsion angle of 25.2° from the *cis*- planar form (Figure 10).

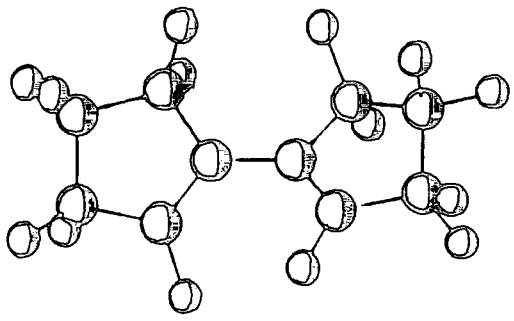
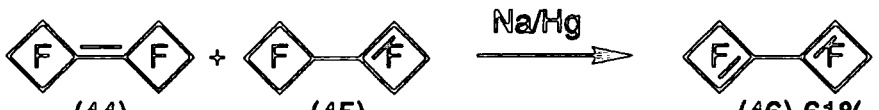


Figure 10. Perfluorobicyclopent-1,1'-enyl (43).

This emphasises the differences between this diene (43) and the isomeric dienes (50), (51) and (60) where bulky trifluoromethyl groups and less geometric restraint force the molecules to adopt structures which are far from planar.

2.3.4 A Mixture of Perfluorobicyclobutylidene (44) and Perfluoro-1-cyclobutylcyclobutene (45)

The reduction of a mixture (*ca.* 1:1) of the isomeric fluoroalkenes (44) and (45), the dimers of hexafluorocyclobutene[44,45], by a sodium amalgam gave perfluorobicyclobut-1,1'-enyl (46) in a yield of 61%. Isolation of the diene was also carried out by crystallisation in a refrigerator and, again, the mechanism probably proceeds *via* a route which is analogous to that in Scheme 54[117] (Scheme 58).



(44) (45) (46) 61%

(Scheme 58)

The structure of diene (46) was identified by ^{19}F NMR spectroscopy, mass spectrometry and IR spectroscopy. In this case, the isolated yield of 61% for the amalgam reduction compares very favourably with 20% which was obtained for the analogous pyrolysis over iron[46].

Diene (46) was also modelled with the graphics package and the resulting low-energy conformer also gave a *cis*- structure. In this case, ψ, the torsion angle, was given as only 18.2° demonstrating that the small rings impose such geometric constraint upon the molecule that the allylic fluorine atoms at the 4 and 4' sites only interact to a fairly minor degree thus forcing the diene out of planarity by a small amount (Figure 11).

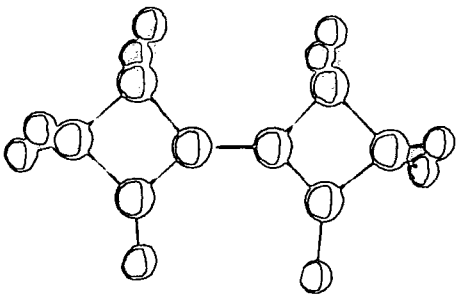


Figure 11. Perfluorobicyclobut-1,1'-enyl (46).

Again, this is in contrast to the dienes (50), (51) and (60) in which the trifluoromethyl groups force the dienes into more skew conformations.

2.3.5 1,4-Dibromo-2,3-dichlorohexafluorobutane (61)

The title halocarbon (61)[132] is known as a precursor in the formation of hexafluorobutadiene (13) *via* zinc dehalogenation[50] (see Table 1; Section 1.2.6). When reacted with only a slight stoichiometric excess of sodium amalgam (2.6:1 molar ratio), the recovered volatile fraction was found by ^{19}F NMR spectroscopy and G.C. mass spectrometry to contain a mixture of products (Scheme 59).

$BrCF_2CFClCFClCF_2Br$ (61) $\xrightarrow{Na/Hg}$ $BrCF_2CFClCF{=}CF_2$ (62) 28%; $BrCF_2CFClCF{=}CFCl$ *E*-(63) 3% and *Z*-(64) 3%; $CF_2{=}CFCF{=}CF_2$ (13) 2% + (61) 64%

(Scheme 59)

As the starting material (61) can be recovered from the products, recycling becomes possible and this method of selective reduction of the halocarbon (61) appears as a favourable process for the generation of highly functionalised fluoroalkene derivatives such as (62). The formation of the unexpected products (63) and (64) is probably due to the nucleophilic attack of

chloride (from resulting sodium chloride powder) on the highly reactive terminal difluoromethylene site in alkene (62) (Scheme 60).

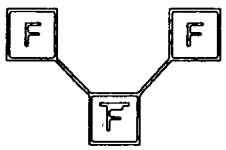
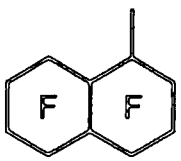
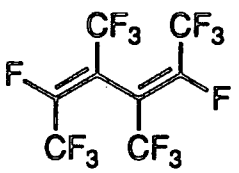
$$\underset{(62)}{BrCF_2CFClCF{=}CF_2} \xrightarrow{Cl^-} \underset{(63)\text{ and }(64)}{BrCF_2CFClCF{=}CFCl} + F^-$$

(Scheme 60)

2.3.6 Other Sodium Amalgam Reductions

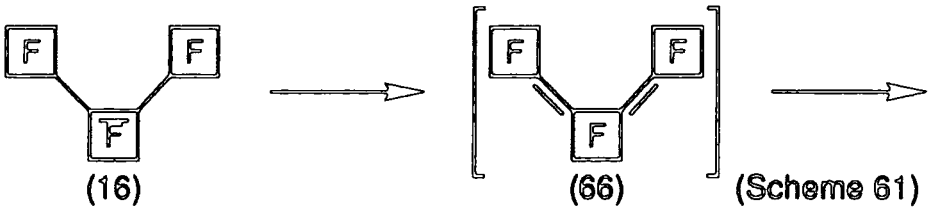
Various other experiments were carried out in which sodium amalgam was used to reduce fluorocarbon derivatives. The results are summarised in Table 3.

Table 3

Fluorocarbon	Percentage recovery of starting material
 (16)	73%
 (65)	34%
 (50)	64%

As in all the examples of amalgam reductions, the reactions were very exothermic and the residual mercuric waste was found to be mixed with a very dark gray to black powder reminiscent of the results of reduction of PTFE with alkali metal amalgams[94,95,96]. Also, in each of the above experiments, no volatile material, other than the starting material, could be obtained from these residues after the reaction. This was especially surprising in the case of perfluoro-1,2-cyclo-butylcyclobutene (16), which appeared to be ideal for

reduction to the related diene (66) as it possesses two allylic tertiary fluorine sites (Scheme 61).



(16) (66) (Scheme 61)

[The formation of diene (66) is a process which has been claimed to occur in the patent literature[108].]

Diene (66), if formed, is probably reduced further by the action of the amalgam until complete decomposition of these products occurs rather than the amalgam reducing more of the alkene (16) to the diene (66). This is a consequence of the relative energies of the L.U.M.O.'s of (16) and (66); fluoroalkene (16) having been shown to possess a relatively high reduction potential in Section 2.2.2.

2.4 Potassium Amalgam

2.4.1 Introduction

As the initial studies into the reduction of octafluorocyclopentene were carried out using potassium amalgam and as potassium is a viable alternative to sodium in amalgam, it was decided to carry out a reduction using a potassium amalgam in order to determine any possible differences. Potassium is a stronger reducing agent than sodium - a fact born out in a comparison of the aqueous oxidation potentials with +2.924V for potassium compared to +2.711V for sodium[1].

2.4.2 Reduction of Alkene (49) (With J. F. S. Vaughan)

The reduction of tetrafluoroethene tetramer (49) by potassium amalgam gave an almost identical mixture of dienes (50) and (51) to that produced by sodium amalgam (see Section 2.3.2) in overall yields of 40% and 12% respectively. Despite this success, it must be noted that potassium is harder to

dissolve in amalgams than sodium and, since the yields are lower using potassium amalgam than for sodium amalgam, no further reductions were performed with potassium amalgams.

2.5 Alkali Metals in Solution

2.5.1 Introduction

There are several reported cases in which alkali metals in complex solutions have been used to defluorinate organic compounds, either for analysis[88,89,90] or in order to facilitate bonding to PTFE and other highly fluorinated polymers[92,93]. In this section, a similar idea is tried in which only a stoichiometric amount of alkali metal is present in an attempt to bring about selective reduction.

2.5.2 Reduction of Alkene (49) with Sodium Biphenyl

A biphenyl - sodium - dimethoxyethane complex[89] was prepared according to the literature[90] and was slowly added to the tetrafluoroethene tetramer (49) under nitrogen. The complex reacted with alkene (49) and the purple colouration slowly disappeared. Analysis, however, showed only the presence of starting material (49), decomposition of any products having presumably occurred rather than selective reduction.

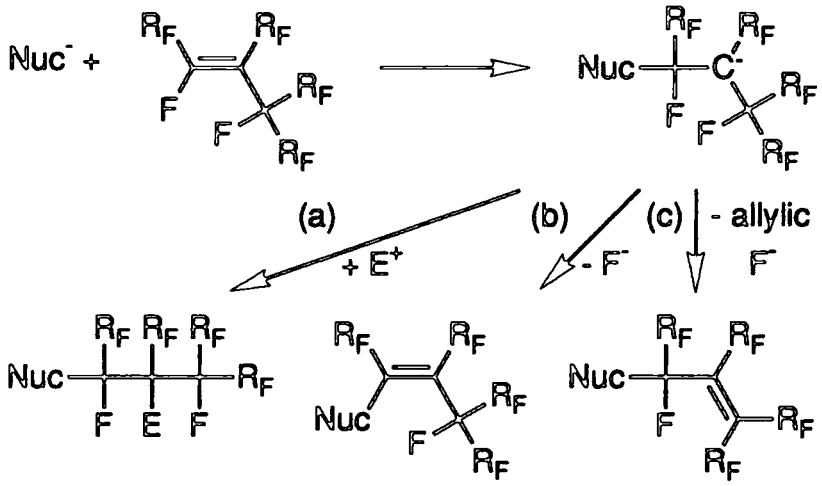
2.5.3 Reduction of Alkene (49) by Potassium in Hexamethylphosphoramide

Potassium dissolves in HMPA to give a solution with a deep blue hue. Tetrafluoroethene tetramer (49) was reduced by this solution but analysis of the solution after reaction shows that a vast mixture of fluorinated compounds was created and that there was no evidence for any selectivity in the process.

3.1 Introduction

The replacement of hydrogen in an alkene by electron withdrawing substituents as fluorine or perfluoroalkyl groups results in the removal of electron density from the double bond. A consequence of this is that such electron deficient π -systems become more susceptible towards nucleophilic attack[5,133] than electrophilic attack[134].

A general scheme for the nucleophilic attack upon a perfluorinated alkene can be shown as follows (Scheme 62):



(base catalysed addition) (nucleophilic displacement) (substitution with rearrangement - S_N2')

(Scheme 62)

There are many influencing factors which must be taken into account in order to determine the reaction pathway which is followed[133].

Pathway (a) is prefered by the simpler fluoroalkenes and the more basic intermediate carbanions and involves an overall addition of a nucleophile Nuc- followed by combination with an electrophile E+ (*e.g.* H+).

Pathway (b) is more often followed by cyclic perfluorinated alkenes and those fluoroalkenes which give intermediate carbanions possessing more stabilising perfluoroalkyl substituents and so allow a more long-lived

intermediate. This route involves an overall substitution of a vinylic fluorine by a nucleophile.

Pathway (c) is not usually preferred as a major route but rather as a competing reaction occurring alongside (a) or (b). Overall, route (c) involves addition, allylic rearrangement and displacement of an allylic fluorine.

3.2 Fluorinated Carbanions

It has been previously stated[5,133] that carbanions are intermediates in nucleophilic reactions of fluoroalkenes. In order to understand the ultimate outcome of such nucleophilic reactions, it is important to appreciate the effects of fluorine in the intermediate carbanions.

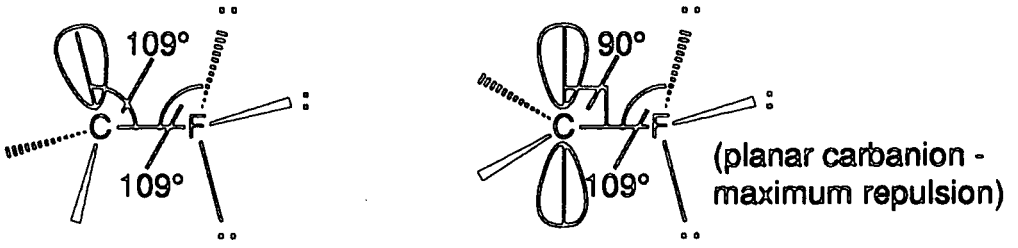
3.2.1 Fluorine Attached to the Carbanionic Site

In the case where fluorine is bonded directly to a carbanionic site, there are two opposing influences affecting stability[5,135]. A stabilising σ-inductive effect ($-I_\sigma$) competes with a potentially destabilising π-field polarisation effect ($+I_\pi$) (Figure 12).

$-I_\sigma$ (stabilising) $+I_\pi$ (destabilising)

(Figure 12)

The magnitude of the electron-pair repulsion ($+I_\pi$) depends upon the geometry of the system[2] with the greatest repulsion arising from a planar system in which the destabilising overlap is maximised (Figure 13).



sp^3 C sp^2 C (Figure 13)

This results in a preference for a developing carbanionic site which bears a fluorine atom to prefer a more pyramidal geometry[2].

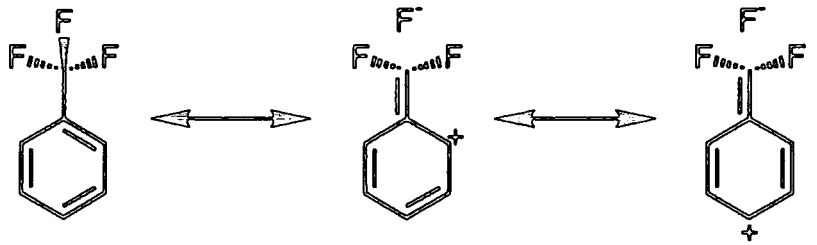
3.2.2 Fluorine Adjacent to the Carbanionic Site

If a fluorine atom is located adjacent to the carbanionic site, however, the carbanion is always more stabilised than the situation in which hydrogen is the substituent[2]. The dominant factor is the inductive effect ($-I_\sigma$) which increases with the number of fluorine substituents present (Figure 14).

(potentially destabilising) (always stabilising)

(Figure 14)

Part of the stabilising influence of a perfluoroalkyl group has been attributed to a resonance effect known as 'negative hyperconjugation' which was first proposed in 1950[136] to help explain the anomalies in measured dipole moments and relative reactivities of various trifluoromethyl substituted benzene derivatives (Scheme 68).



(Scheme 68)

This "no-bond resonance" was also invoked to explain the dependence of protium-deuterium exchange rates in monohydro-fluorocarbons upon the number of β-fluorines[137] (Scheme 69).

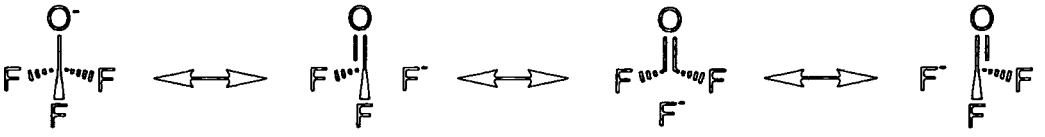
(Scheme 69)

There has been considerable debate as to whether hyperconjugation is required in order to explain the extra carbanion stability which is

displayed[138,139], but, through both experimental and theoretical work[140,141], it now rests upon a solid foundation as a generalised form of the anomeric effect.

Especially dramatic evidence for negative hyperconjugation was given by the X-ray crystal structure of tris(dimethylamino)sulphonium trifluoro-methoxide (TAS^+ CF_3O^-) (67)[142]. In the anion, the carbon-fluorine bond lengths were unusually long and the carbon-oxygen bond was especially short.

Molecular orbital calculations on this anion showed that each fluorine atom also carried more charge (an extra 0.2*e*) than would have been predicted by comparison with the isoelectronic molecule CF_4 and also that the negative hyperconjugation resonance structures (67b-d) were thereby predicted to contribute approximately 20% of the bonding in the anion (Scheme 70).



(67a) (67b) (67c) (67d)

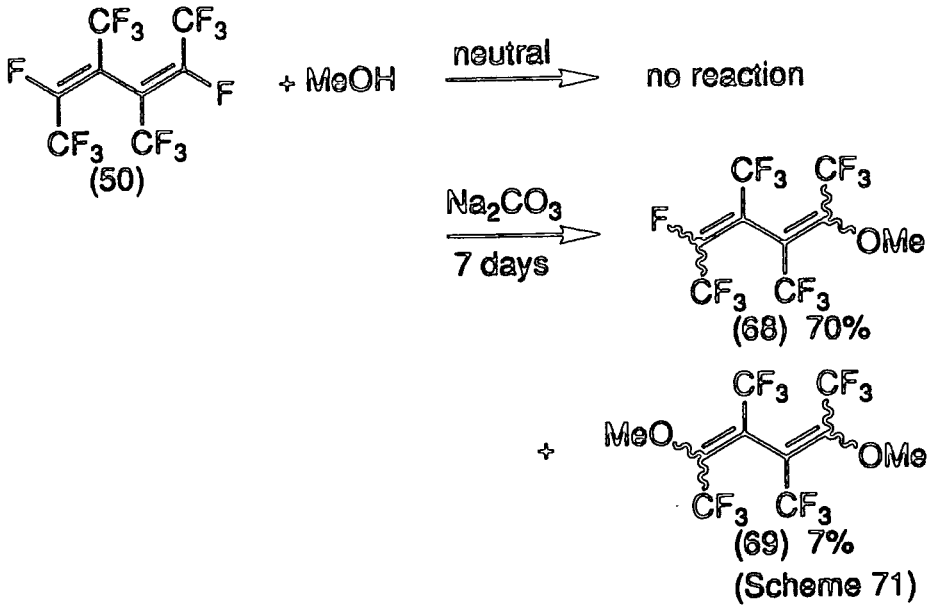
(Scheme 70)

3.3 Reactions with Oxygen Nucleophiles

3.3.1 Background

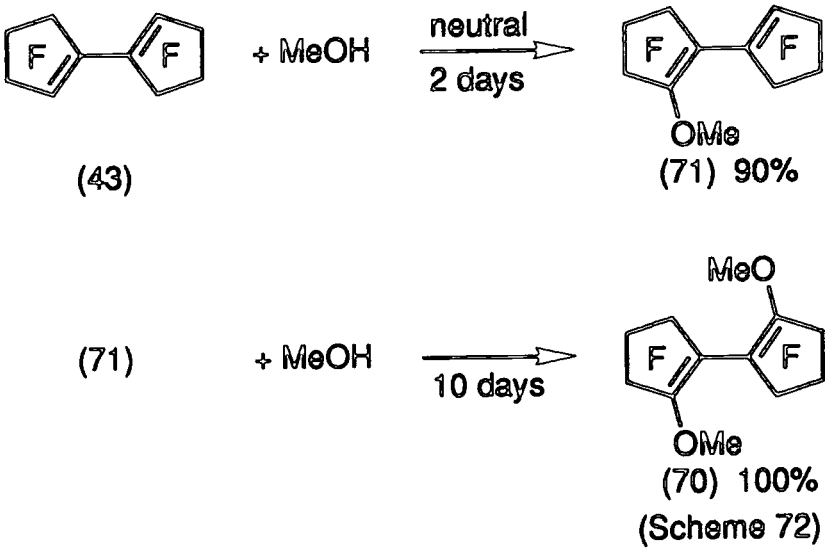
Earlier work in these laboratories[117] on investigating the chemistry of our novel fluorinated diene systems (43), (46), and (50) revealed a remarkable difference in the reactivities of these dienes with oxygen nucleophiles such as methanol.

Diene (50) failed to react with neutral methanol but, under basic conditions, a mixture of the monomethoxy- (68) and dimethoxy- (69) derivatives could be isolated (Scheme 71).



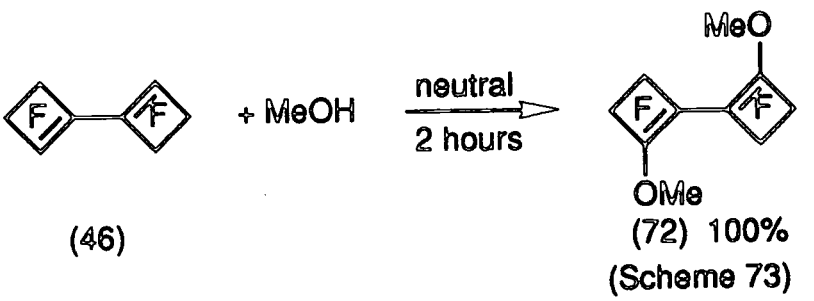
(Scheme 71)

Diene (43) reacted steadily with neutral methanol to ultimately yield the dimethoxy derivative (70) *via* the monomethoxy intermediate (71)[117] (Scheme 72).



(Scheme 72)

Diene (46) reacted rapidly with neutral methanol in an exothermic process yielding the disubstituted product (72) within two hours[117] (Scheme 73).



(Scheme 73)

The conclusions which may be drawn from this information is the obvious reactivity order of:

(46) > (43) >> (50)

The differences in reactivity of these perfluorinated dienes can be assigned to a number of factors[117]:

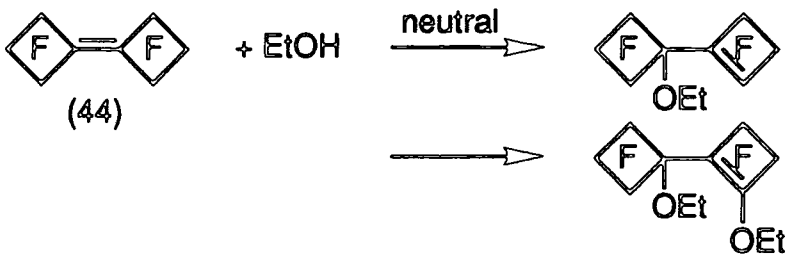
a) Ring strain - in an analogous way to the increase in reactivity[143,144] in perfluorobicyclobutylidene (44) over perfluorobicyclopentylidene (42) through the release of ring strain, a similar argument can be applied for dienes (46) and (43) in which nucleophilic attack alleviates some of the angle strain present in the rings. Diene (50) has no such strain and so there is no aid to promoting nucleophilic attack.

b) Intermediate carbanion stability - the carbanions which result from the initial nucleophilic attack of the dienes differ in nature for the two cyclic dienes (43) and (46) to diene (50). In the case of the cyclic dienes, the orbitals which constitute the carbon skeleton, although formally sp^3 hybridised, will have mainly p character due to the strain imposed by the rings[145]; hence the lone pair on the carbanionic centre which bears the charge will have more s orbital character and will therefore be of a lower energy. This argument cannot be applied to the cases of diene (50) in which no such lowering of orbital energy occurs.

c) Steric hindrance - the acyclic system (50) possesses sterically demanding trifluoromethyl groups around the double bonds. These provide much more steric hindrance than the cyclic arrangements in (43) and (46) which are essentially held in place thus unhindering the reactive double bonds in these systems.

The fact that for all three dienes (43), (46) and (50), a second equivalent of the nucleophile can react without having to impose very forcing conditions upon the reaction mixture implies that the double bonds are not conjugated and that the dienes are behaving more like simple fluorinated alkenes than other known perfluorodienes like hexafluorobutadiene (13)[68] and perfluoro-2,3-dimethylbutadiene (11)[69] (see Section 1.4.1; Schemes 28 and 29).

It is also worth pointing out here that the dienes (43) and (46) are unusual in their reactivity towards aliphatic alcohols in neutral conditions. The few other fluorocarbons which are known to react with neutral alcohols are the highly reactive perfluoro-2,3-dimethylbuta-1,3-diene (11)[69], perfluoro-2-methylpenta-2,4-diene (20)[48], perfluorobicyclobutylidene (44)[146] and perfluoroisobutene (21)[147]. However, it was only in the case of (44) that the perfluoroalkene was subjected to attack by two equivalents of the nucleophile (Scheme 74).

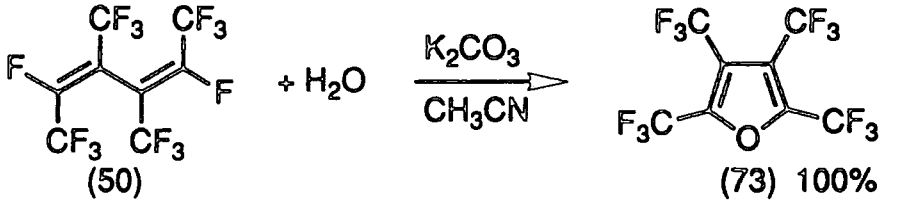


(Scheme 74)

(see also Section 1.4.1; Schemes 29 and 30)

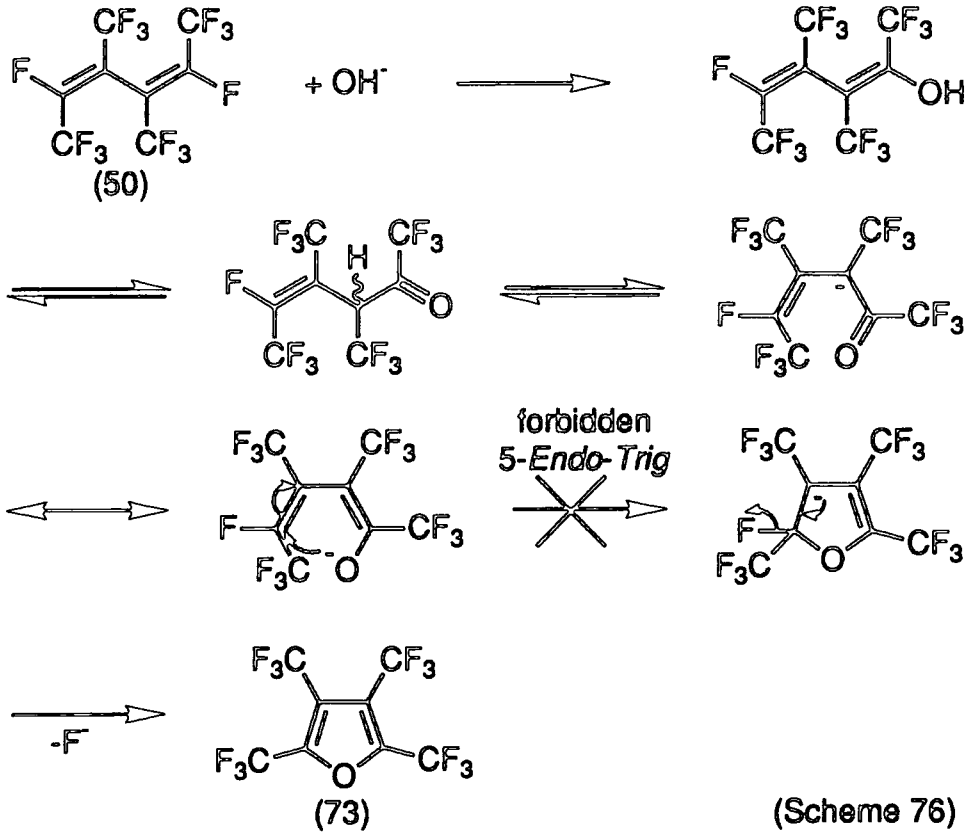
3.3.2 Diene (50) with Water

Diene (50) reacted with moisture present in basic acetonitrile to give tetrakis(trifluoromethyl)furan (73) as the only product (Scheme 75).



(Scheme 75)

The formation of (73) *via* a 5-*Endo-Trig* cyclisation is formally forbidden[148] (Scheme 76).

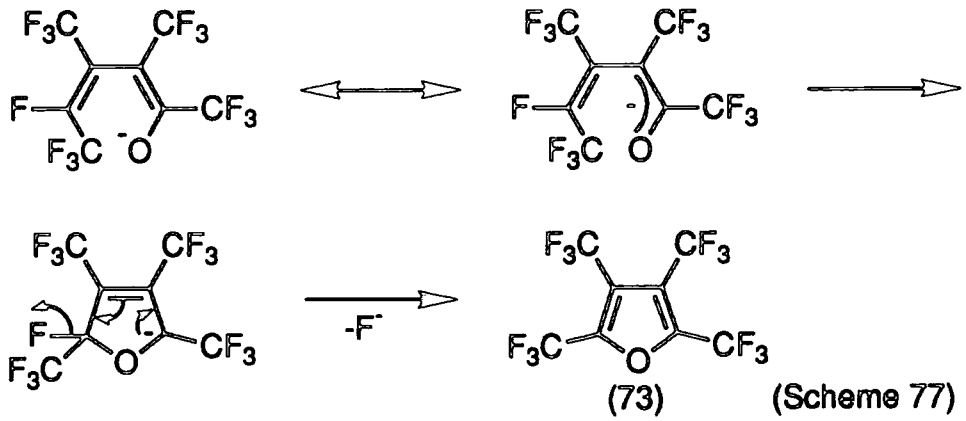


(50)

(73)

(Scheme 76)

If, instead, a 1,5-electrocyclisation mechanism[149] is invoked, the cyclisation not only becomes 'allowed', but rather it actually becomes a favourable process (Scheme 77).



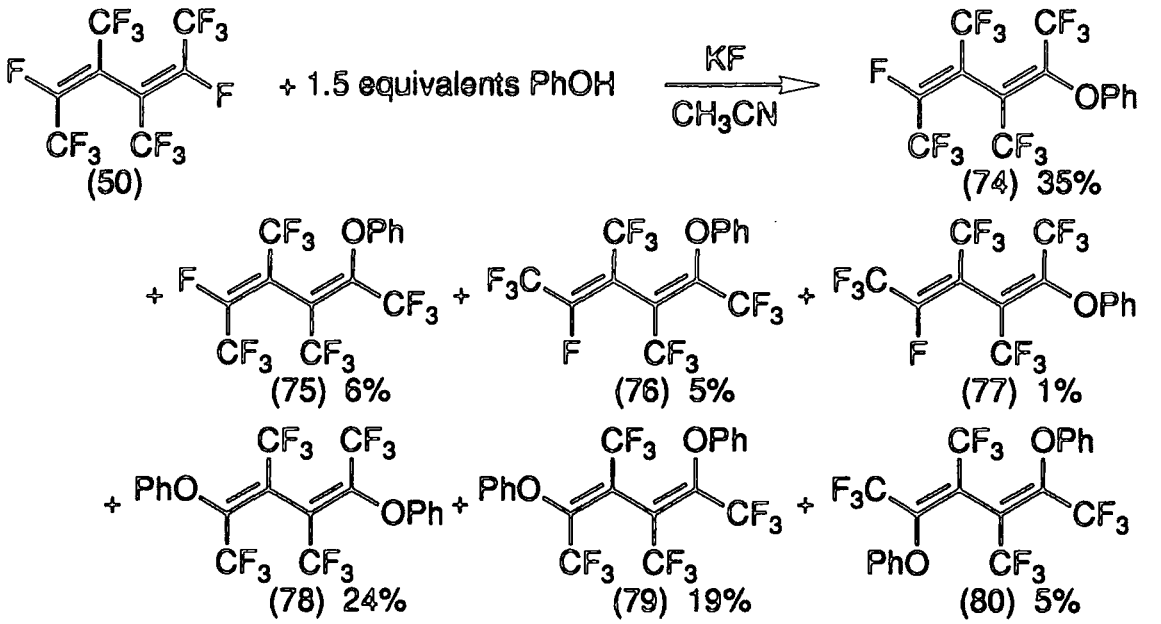
(73)

(Scheme 77)

This compound had previously been made by other methods[150,151] involving somewhat convoluted routes. Our method of synthesis is complete in terms of conversion and, as will be seen later, is quite difficult to avoid unless solvents and reagents are kept extremely dry.

3.3.3 Diene (50) with Phenol

Diene (50) reacted with phenol in the presence of potassium fluoride to give a mixture of the mono- (74), (75), (76) and (77) and di- (78), (79) and (80) substituted products (Scheme 78).



(Scheme 78)

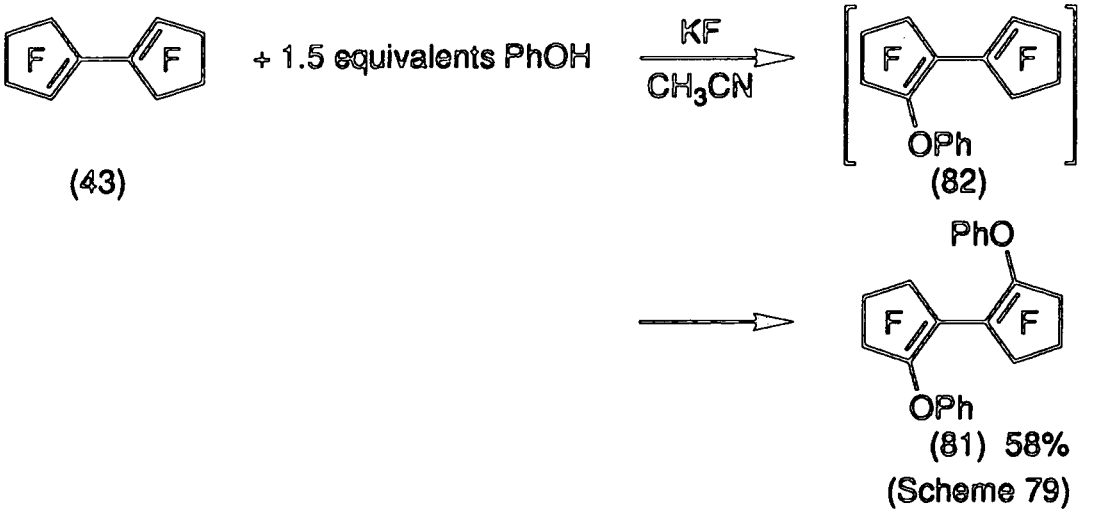
The reaction was carried out with fluoride ion present and therefore the breakdown ratios of the products are dependent upon the thermodynamic stabilities of the individual substituted dienes. Distillation separated the mono-substituted isomers (74), (75), (76) and (77) from the di-substituted isomers (78), (79) and (80) and each individual isomer was subsequently identified by G.C. mass spectrometry and ^{1}H and ^{19}F NMR spectroscopy. The stereochemistry around the double bonds was determined in each case by comparing the fluorine coupling constant data with fluorinated alkenes with known configurations[129].

The reactivity of diene (50) is in marked contrast to that of the similar diene perfluoro-2,3-dimethylbut-1,3-diene (11) which reacts readily with methanol to give a mono-substituted product (26) (see Section 1.4.1) but requires much more forcing conditions to react with a second equivalent of the nucleophile[69]. This infers that, unlike diene (11), diene (50) acts as two connected fluoroalkenes rather than a conjugated diene towards nucleophilic

attack and that the reactivity of each double bond is not dictated by the presence of substituents on the second double bond.

3.3.4 Diene (43) with Phenol

The reaction of diene (43) with phenol in the presence of a base gave only the disubstituted product (81) in the reaction mixture (Scheme 79).



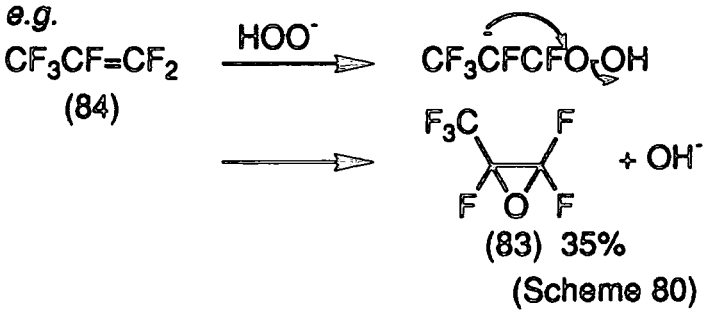
(43) (82) (81) 58%

(Scheme 79)

The assumption is that the mono-substituted intermediate (82) is at least as reactive as the starting material (43) and so too little of the mono-substituted material (82) was left at the end of the reaction to be isolated.

3.3.5 Fluorinated Epoxides

A considerable amount of work has been carried out with perfluorinated epoxides[152,153]. The key material and origin of most of the interest has been hexafluoropropene oxide HFPO (83)[154,155] formed from the readily available hexafluoropropene (84) (Scheme 80).

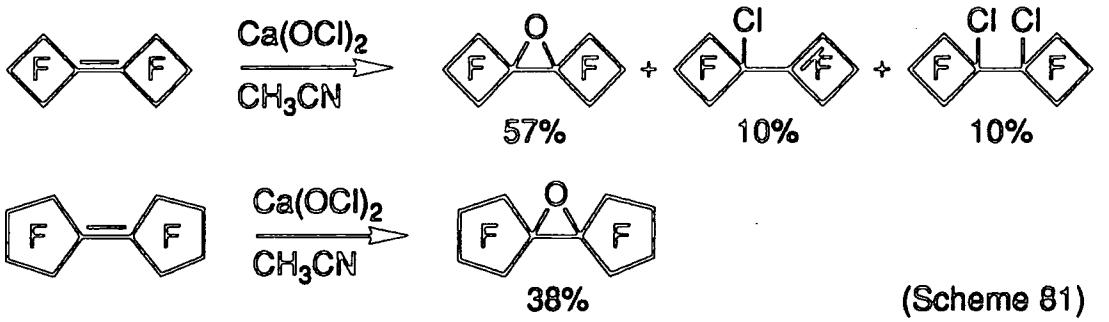


(83) 35%

(Scheme 80)

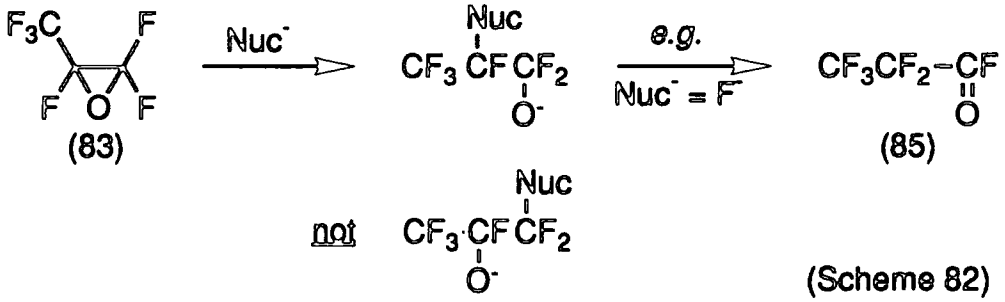
Better yields are possible by a variety of routes[155].

Higher fluorinated epoxides can generally be formed from perfluoroalkene oligomers by the action of aqueous sodium hypochlorite in acetonitrile[156,157] or of anhydrous calcium hypochlorite also in acetonitrile[144,153] (Scheme 81).



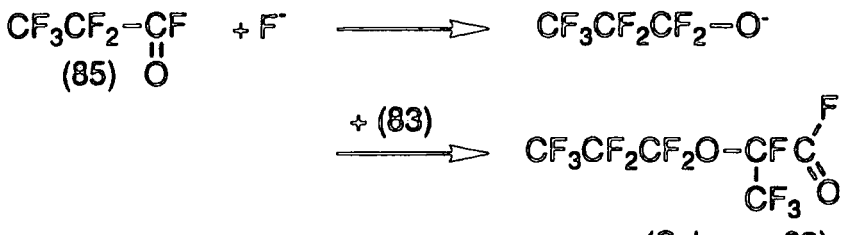
(Scheme 81)

Fluorinated epoxides such as these and HFPO (83) demonstrate remarkable thermal stability[152,103] possibly because of the effect of the bulky electronegative perfluoroalkyl groups which are present[145,157]. However, they are susceptible towards nucleophilic attack. HFPO (83) can be isomerised exothermically[158] by caesium fluoride to give perfluoropropanoyl fluoride (85) (Scheme 82).



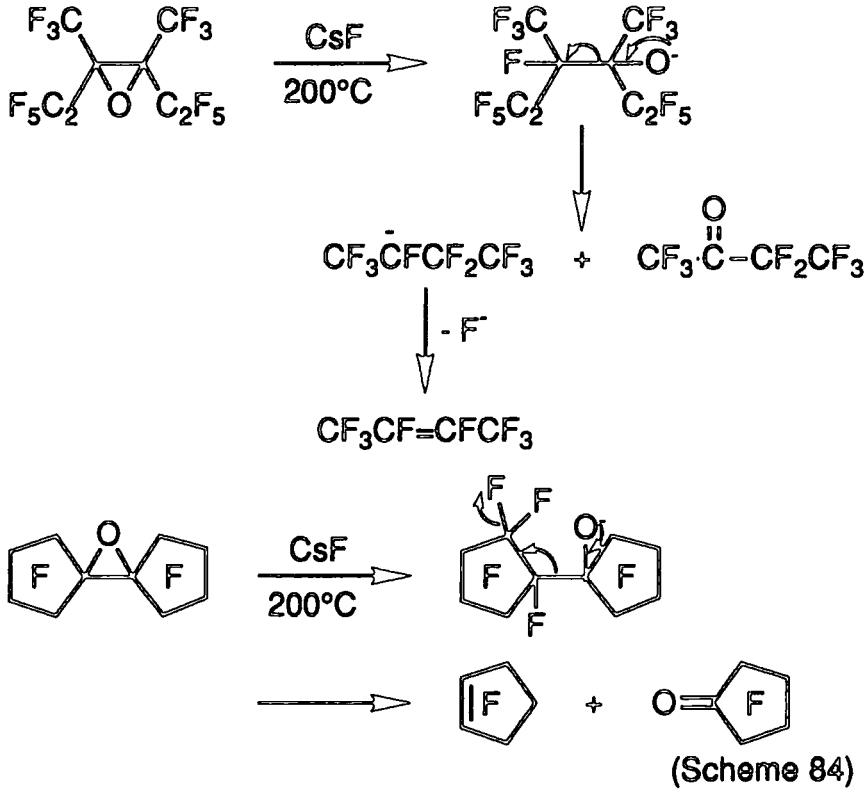
(Scheme 82)

It remains as a slight enigma that the CF_2-O^- oxyanion is formed much more readily than the alternative anion CF_3CF-O^- possibly due to the reinforcing effect of geminal fluorine atoms[157] and, although nucleophilic attack occurs at the most sterically hindered site[155], the stability of this intermediate anion dictates that it is this route which is still followed preferentially. However, perfluoroalkyl acid fluorides are strong electrophiles and so these may react further with more HFPO (83) in oligomerisation and polymerisation processes (Scheme 83).



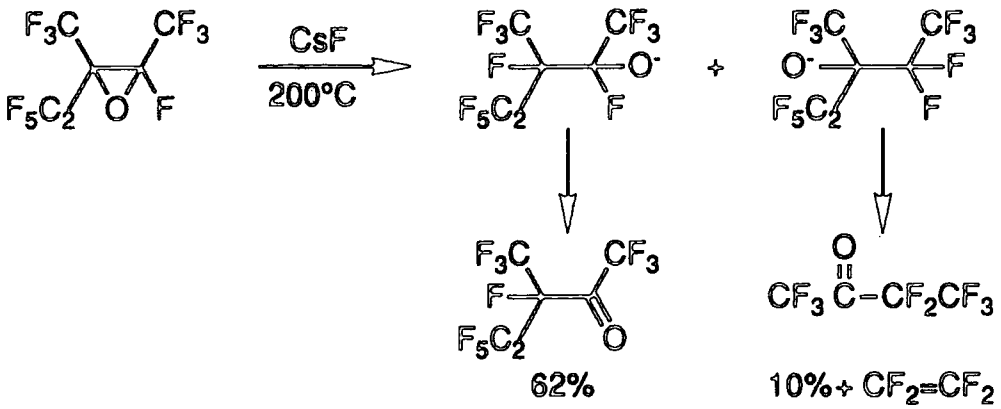
(Scheme 83)

Interesting cleavage reactions have occurred with some of the higher perfluorinated epoxides. In some cases, ring opening of the epoxides by fluoride ion followed by asymmetric scission of the carbon skeleton has been observed[144,157] (Scheme 84).



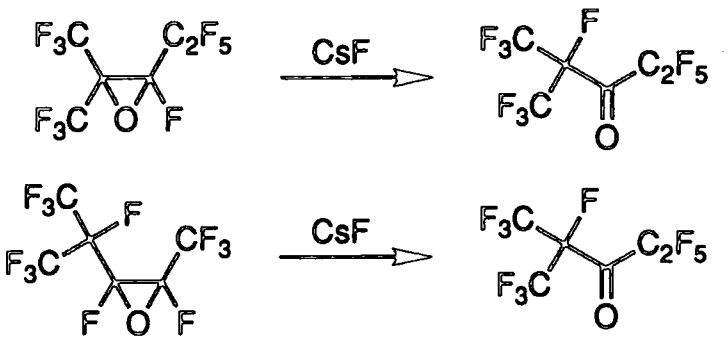
(Scheme 84)

Unsymmetrical perfluorinated epoxides have been found to generally give mixtures of products[157] determined by the possibility of two different reaction pathways (Scheme 85).



(Scheme 85)

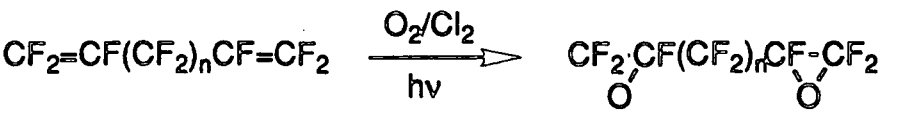
The product breakdown also helps to reassert the point of the stabilisation imparted by the intermediate oxyanion and demonstrates that, once again, nucleophilic attack by fluoride ion has occurred at the most sterically hindered site. However, when the only difference in environment of the two carbons in the oxirane ring is the presence of two slightly different perfluoroalkyl groups, steric effects will start to be introduced and minor differences in electronic effects will cease to be of importance[160] (Scheme 86).



- Nucleophilic attack at the least sterically crowded site

(Scheme 86)

Only two perfluorinated diepoxides have been reported in the literature. Soviet workers succeeded in oxidising two long chain terminal dienes with oxygen in the presence of a catalytic amount of chlorine under UV irradiation[161] (Scheme 87).

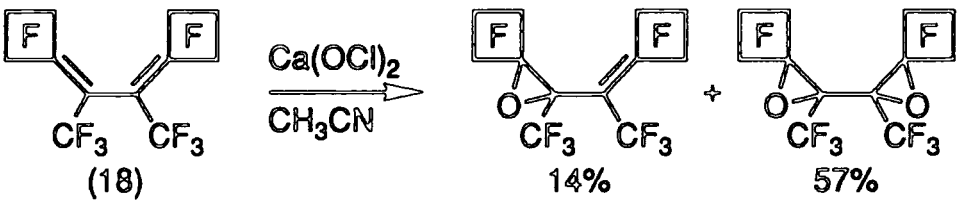


n = 4, 30%; n = 8, 10% yield

(Scheme 87)

Separation of the diepoxides from the dienes and intermediate epoxyalkenes was achieved by bromination of the double bonds followed by fractional distillation[161].

Attempts have been made in these laboratories to generate a perfluorinated diepoxide from diene (18) with limited success[153]. The action of calcium hypochlorite upon the diene created a complex mixture of products which may be derived from various reaction pathways (Scheme 88).

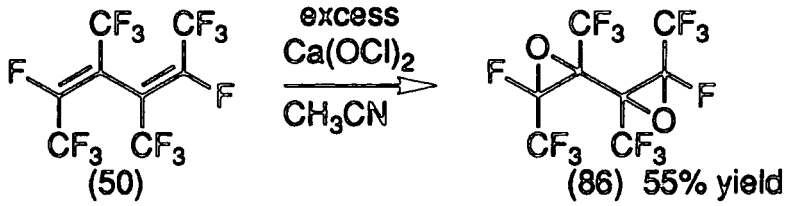


+ unidentified $C_{12}F_{18}O$ isomer
17%

(Scheme 88)

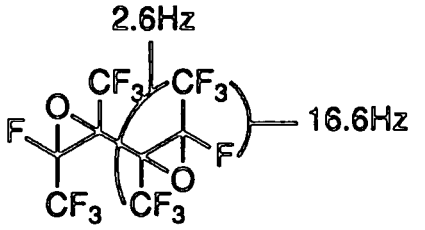
3.3.5.1 Epoxidation of Diene (50)

Diene (50) reacted with a large excess of calcium hypochlorite in suspension in acetonitrile to produce the diepoxide perfluoro-2,2',3,3'-tetramethyl-bi-2,2'-oxiranyl (86) as the sole product (Scheme 89).



(Scheme 89)

^{19}F NMR spectroscopy and G.C. indicated that diepoxide (86) was formed selectively as a single pair of enantiomers(Figure 15).



(Figure 15)

The actual configuration could not be determined by comparison of fluorine coupling constant data because there are no real 'ground rules' for such an

exercise. However, the *trans,trans-* structure can be tentatively suggested on the grounds of minimising the repulsive interactions of the trifluoromethyl groups in any intermediate anion and the lack of contradiction between these coupling constant data and those already established for perfluorinated epoxides[162,163].

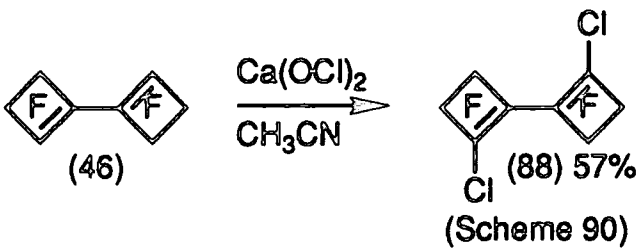
3.3.5.2 Attempted Epoxidation of Diene (43)

Diene (43) also reacted with an excess of calcium hypochlorite in acetonitrile but, after the reaction, analysis of the volatile material showed a complex mixture of products had been made which was presumably a combination of epoxides, chlorinated material[153] and intermediate products. This mixture could not be separated and the reaction was not investigated any further.

3.3.5.3 Attempted Epoxidation of Diene (46)

Similarly, diene (46) also reacted with an excess of calcium hypochlorite in acetonitrile. After fourteen days at room temperature, ^{19}F NMR spectroscopy showed that a mixture of products had been made. Subsequently, the mixture was heated under reflux and ^{19}F NMR spectroscopy showed that the mixture had been mostly converted to give the known diene 2,2'-dichloro-perfluorobicyclobut-1,1'-enyl (88)[15] in 57% conversion.

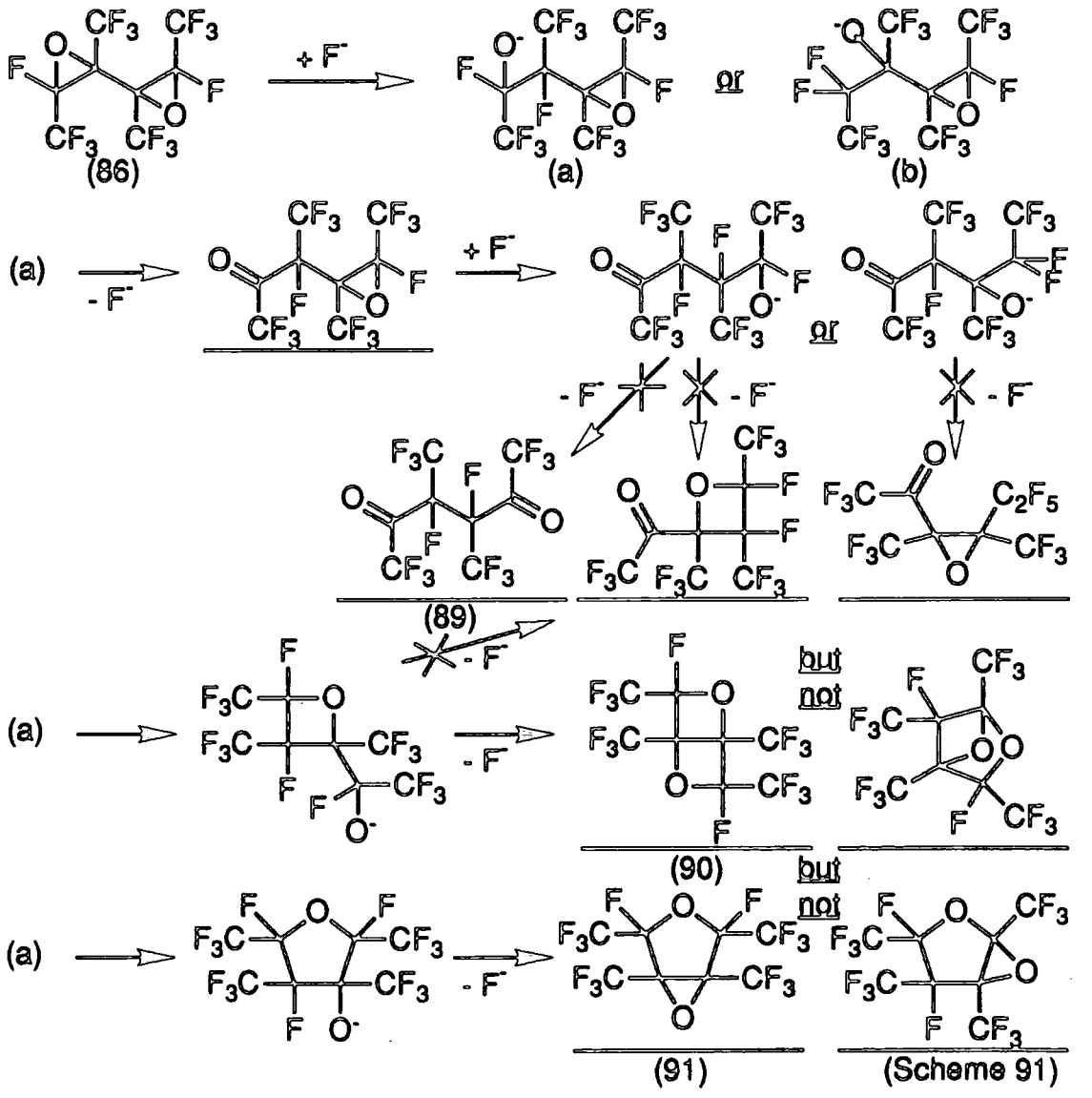
This remarkable result implies that if the reagent is not free chloride ion, then the hypochlorite anion, OCl^-, has reacted with the softer chloro end of the molecule rather than with the oxygen (Scheme 90).



(Scheme 90)

3.3.5.4 Isomerisation of Diepoxide (86)

It is known that fluoride ion can induce the isomerisation of perfluoro-alkyl- substituted epoxides[152,153] to give mainly the ketone and acid fluoride derivatives. With this in mind, diepoxide (86) and a catalytic amount of caesium fluoride were sealed in a Carius tube and heated in a furnace. Diepoxide (86) proved remarkably stable at 100°C but when the temperature was raised to 200°C, complete isomerisation of the diepoxide occurred. ^{19}F NMR and G.C. mass spectrometry showed that the volatile material contained only one product in 80% yield. The structure of the product was not immediately obvious as isomerisation could have occurred *via* several different routes (Scheme 91).



The formation of oxyanion (b) is less likely than that of (a) because of the innate stability of (a) (see earlier: Section 3.3.5). The ^{19}F NMR spectroscopy data also show that a symmetrical product was formed by the isomerisation. No symmetrical product can be made by the rearrangement of the oxyanion (b) and so this anion is rejected as a possible intermediate. The product of isomerisation gave ^{19}F NMR chemical shifts of -66.76 and -77.33ppm suggesting two possible different environments for trifluoromethyl groups and the chemical shift of -151.26ppm also indicates that there is only one environment in the molecule with a tertiary fluorine adjacent to oxygen.

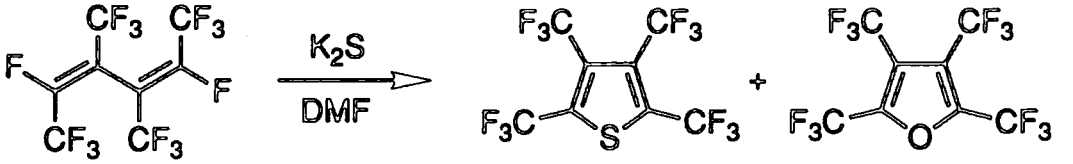
The only species in Scheme 93 which could give such a pattern are the diketone (89), the fused di-oxetane (90) and the saturated furan derivative (91). IR spectroscopy did not show the presence of a carbonyl stretch so (89) can be eliminated as a possibility but it is more difficult to positively determine whether the product is either (90) or (91). The ^{19}F NMR chemical shifts of the the product are within the limits for both perfluorinated epoxides[157,163,164] and perfluoro-oxetanes[165] and the coupling constant data do not set a precedent for determining which possible isomer has been formed. Therefore, there is not enough evidence to confirm or dismiss either structures (90) or (91) as the product resulting from the isomerisation of diepoxide (86).

3.4 Reactions with Sulphur Nucleophiles

In general, sulphur nucleophiles, RS^-, are much more reactive than the equivalent oxygen nucleophile, RO^-. An explanation for this phenomenon is that the sulphur atom has a greater polarisability than oxygen and also possesses d orbitals which may assist in the reaction. Displacements are usually fast and, because sulphur nucleophiles have low basicities, the reactions proceed cleanly with little or no other side reactions such as elimination.

3.4.1 Diene (50) with Potassium Sulphide (With M. W. Briscoe)

Diene (50) reacted with potassium sulphide in DMF at room temperature to give a mixture of tetrakis(trifluoromethyl)thiophene (92) and tetrakis-(trifluoromethyl)furan (73), the result of hydrolysis (Scheme 92).



(50) (92) 72% (73) 28%

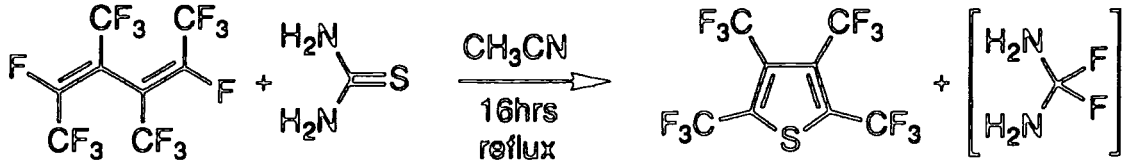
38% isolated yield (Scheme 92)

These compounds were identified by comparison of ^{19}F NMR, mass spectral and IR data with previously made samples. The thiophene derivative (92) has been made previously[166] from the expensive hexafluorobut-2-yne (28) and so our route seems quite favourable as this alkyne is not easily accessible.

It should be noted here that, whereas the furan derivative (73) must be formed as a result of a 1,5-electrocyclisation, the formation of (92) can proceed *via* a 5-*Endo-Trig* cyclisation[167] because, being a second-row element, sulphur is considerably larger than oxygen and so the geometric constraints imposed by the size of the ring are reduced[167]. This process is also aided by back-donation of electron density from the occupied π-orbitals of the double bond to the unoccupied 3d orbitals of sulphur[167].

3.4.2 Diene (50) with Thiourea

The reaction of diene (50) with thiourea also gave tetrakis-(trifluoromethyl)thiophene (92) (Scheme 93).

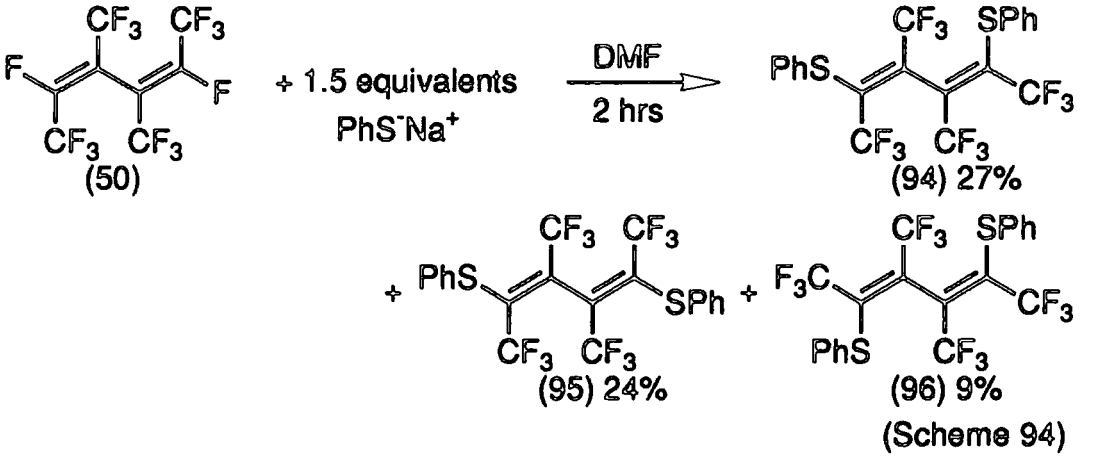


(Scheme 93)

The reaction was slower but a higher overall yield could be obtained by this route. The possible side product (93) was not looked for nor was it observed by ^{19}F NMR spectroscopy.

3.4.3 Diene (50) with Sodium Thiophenate

The reaction of diene (50) with a solution of sodium thiophenate quickly gave a mixture of di-substituted products (94), (95) and (96) (Scheme 94).



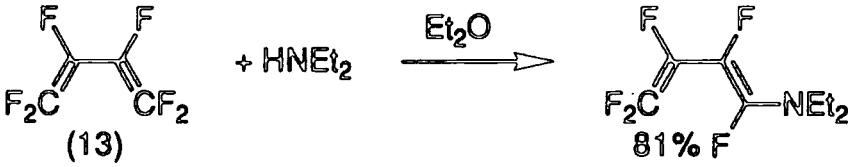
(Scheme 94)

The stereochemistry of the diene systems within isomers (94), (95) and (96) was determined by comparing the fluorine coupling constant data with fluorinated alkenes with known configurations[129]. There was no evidence in the ^{19}F NMR spectroscopy or G.C. mass spectrometry data to indicate the presence of the mono-substituted products. This suggests that the mono-substituted products are at least as reactive towards thiophenate as is the diene (50).

3.5 Reactions with Nitrogen Nucleophiles

3.5.1 Background

Only one paper concerning reactions of fluorinated dienes with nitrogen nucleophiles has appeared in the literature. Early Soviet workers reported[168] the reaction of hexafluorobutadiene (13) with diethylamine which gave a monosubstituted diene (Scheme 95).

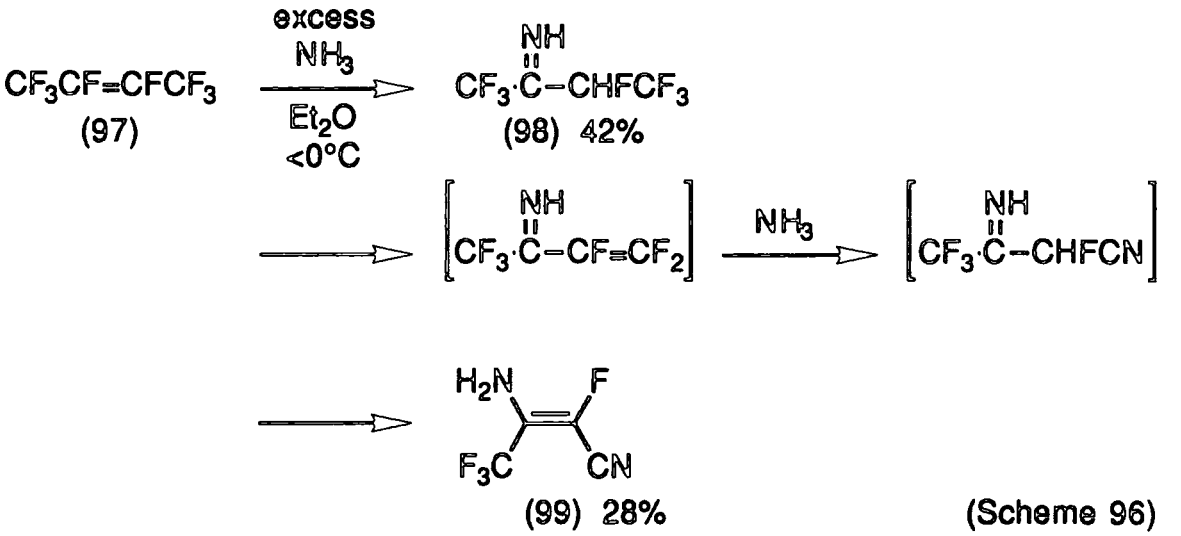


(13) 81% F

(Scheme 95)

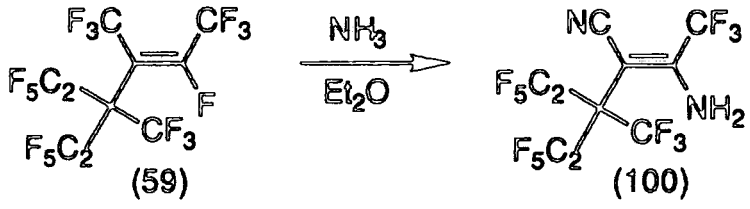
However, there have been several reactions of nitrogen nucleophiles with perfluorinated alkenes published in the literature[133].

Krespan reported[169] the reaction of ammonia with octafluorobut-2-ene (97) which gave the imine (98) below 0°C and the cyanoenamine (99) at slightly higher temperatures (Scheme 96).



(Scheme 96)

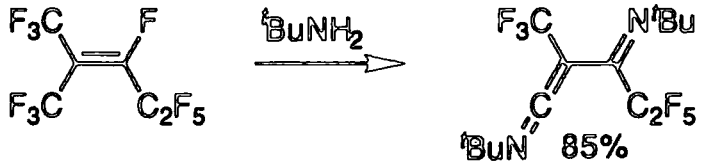
This idea of sequential allylic displacement in perfluorinated alkenes has also been used in the patent literature[170,171]. For example, tetrafluoroethene pentamer (59) reacted with excess ammonia in an analogous process to give the equivalent cyanoenamine[171] (Scheme 97).



(59) (100)

(Scheme 97)

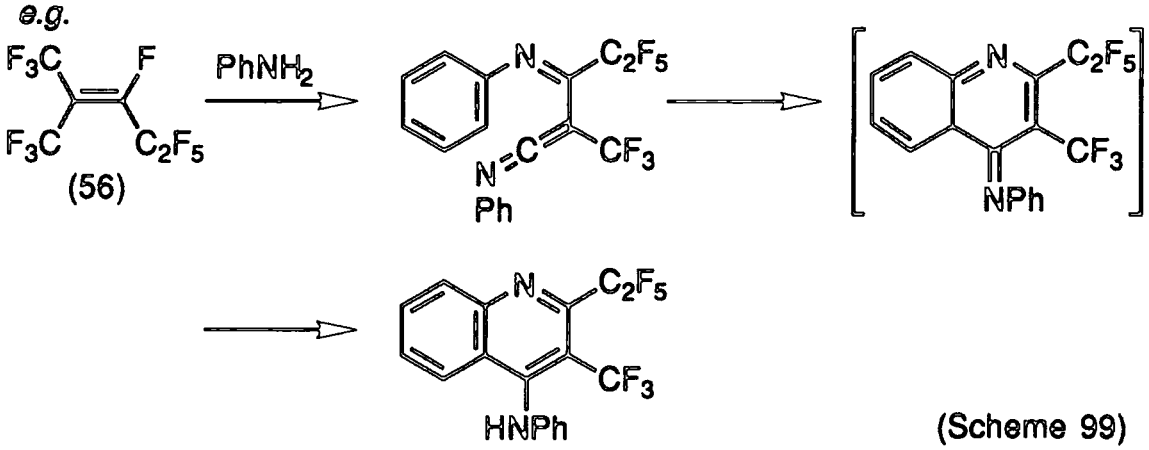
Primary aliphatic amines have often been found to give complex products[172] with fluoroalkenes depending upon the structure of the fluorocarbon. The reaction of hexafluoropropene dimer (56) with *tert*-butylamine gave a ketenimine as the product in good yield[173] (Scheme 98).



(Scheme 98)

Secondary amines, upon reaction with fluoroalkenes, gave the saturated adducts under mild conditions but vinyl amines with excess amine and at higher temperature[133,172].

Primary aromatic nitrogen nucleophiles were found to react with fluoroalkene in a similar manner to primary aliphatic amines if there is no hydrogen in the *ortho*- position[173]. If, however, there is an *ortho*- hydrogen present, the reaction proceeded further[173,174,175] (Scheme 99).

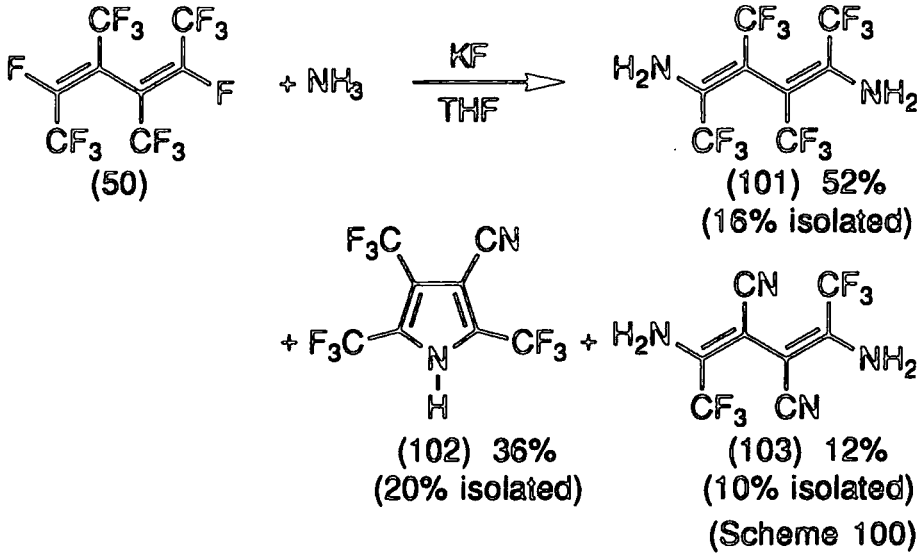


(Scheme 99)

Therefore, this is a good route to fluorinated quinoline systems.

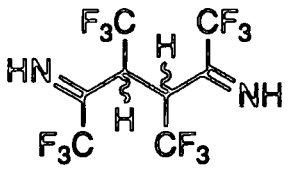
3.5.2 Diene (50) with Ammonia

Diene (50) reacted steadily with ammonia in THF to give a mixture of three compounds (101), (102) and (103), each of which was isolated and purified. The structures were subsequently determined by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy, mass spectrometry and IR spectroscopy (Scheme 100).



(Scheme 100)

The formation of dienamine (101) can be explained by means of two consecutive nucleophilic displacements of vinylic fluorine by ammonia. Only one isomer of dienamine (101) was detected by ^{19}F NMR and none of the di-imino tautomer (104) was found (Figure 16).

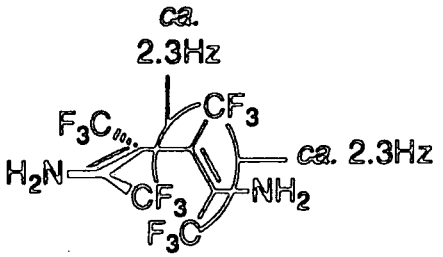


(104) (Figure 16)

The dienamine structure of compound (101) is noteworthy considering that none of its tautomer (104) was present. Analogous hydrocarbon derivatives are observed almost exclusively in their di-imino configurations[176]. The dienamine structure can be explained by means of the extra stabilisation imparted by the electron withdrawing trifluoromethyl groups. These are known[126] to lower the orbital energies of the double bonds in alkenes.

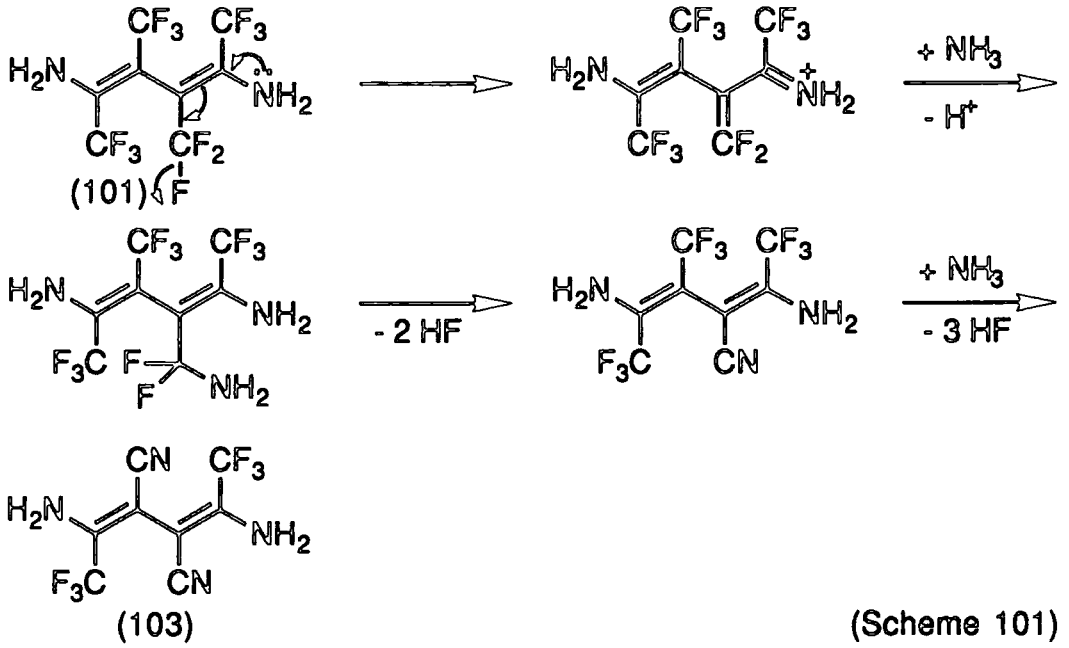
The *Z,Z*- configuration of dienamine (101) was assigned on the basis of the ^{19}F NMR data which showed the presence of two *pseudo*- septets,

generated by the $(A_3)_2(X_3)_2$ system, possessing coupling constants of 2.3Hz indicative of *trans*- coupling (Figure 17).



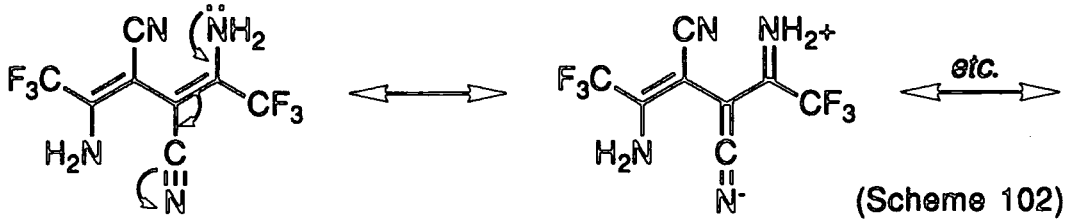
(101) (Figure 17)

Likewise, a dienamine (103) could probably be generated from (101) in excess ammonia *via* the allylic displacement of fluoride (Scheme 101).



(103) (Scheme 101)

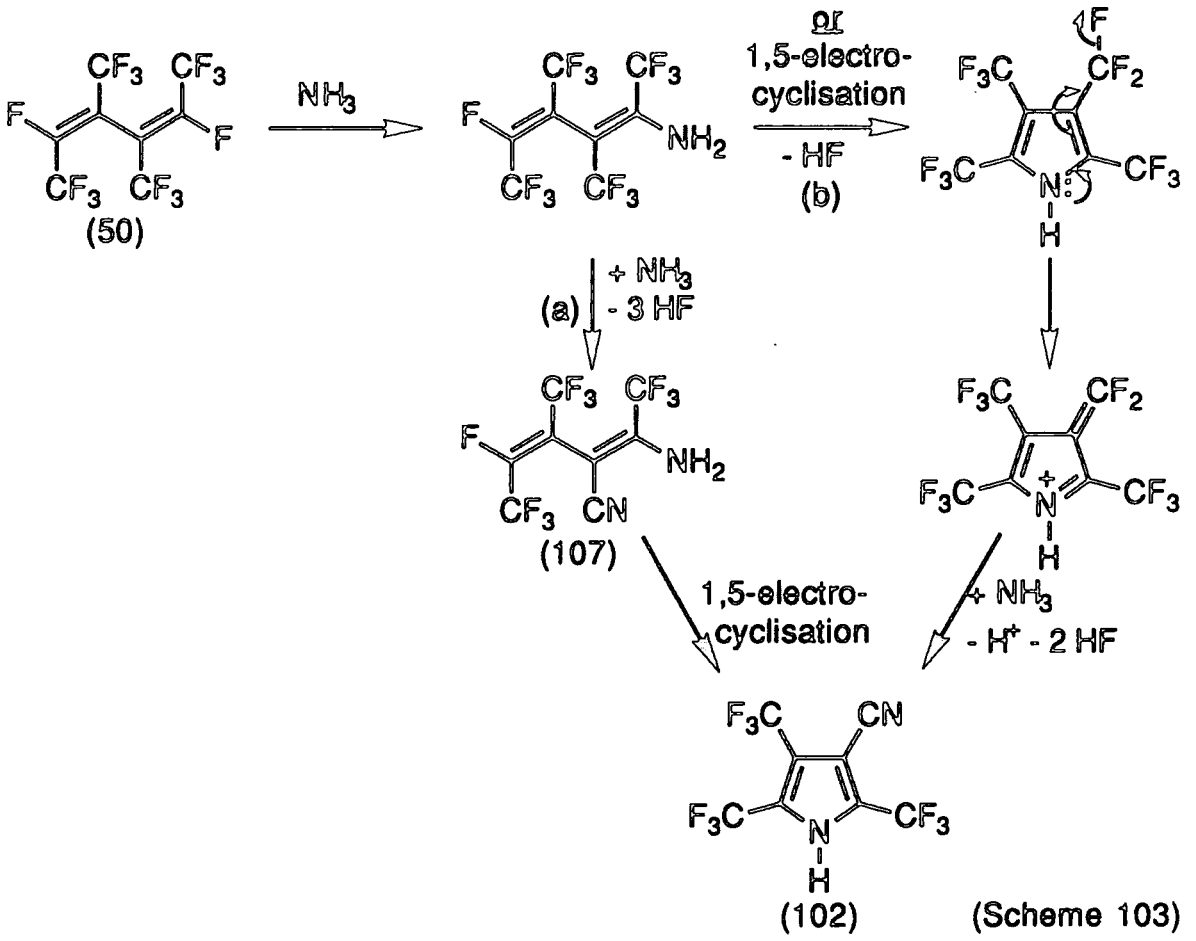
.However, we were unable to conclusively establish the *E*- or *Z*- configuration about the double bonds in (103). Although the similar dienamine (101) possesses a *Z,Z*- configuration, an *E,E*- structure might allow a more extended conjugation to exist[169] (Scheme 102).



(Scheme 102)

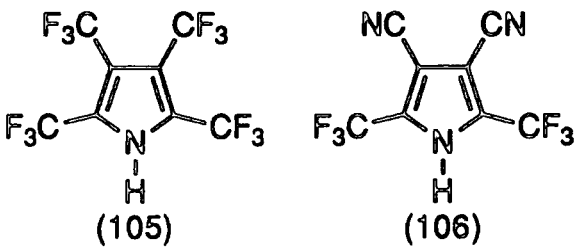
The formation of pyrrole derivative (102) may proceed *via* a single displacement of vinylic fluorine and subsequent allylic displacement before the cyclisation, *i.e.* pathway (a), rather than the cyclisation occurring

the cyclisation, *i.e.* pathway (a), rather than the cyclisation occurring before the allylic displacement - pathway (b) (Scheme 103).



(Scheme 103)

The absence of the pyrrole derivative (105) and also derivative (106) from the reaction mixture indicates that in order for the reaction to proceed *via* pathway (b), an allylic displacement from (105) is relatively easy but a second analogous displacement from (102) is very difficult. This is difficult to justify and so it reinforces the idea that pyrrole derivative (102) is formed by route (a) (Figure 18).

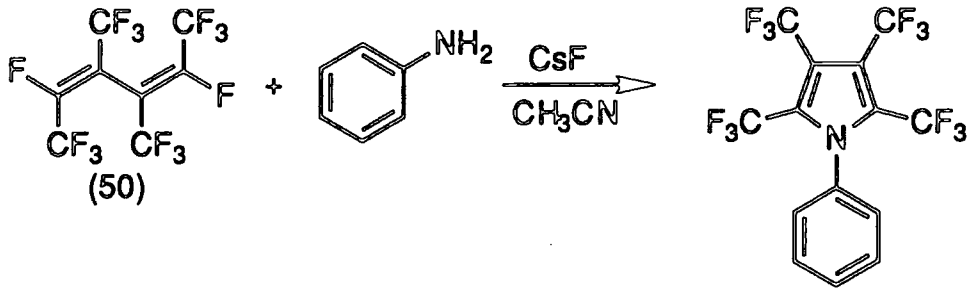


(Figure 18)

The presence of an intermediate such as (107) would also aid the electrocyclisation process because of the increase in electronegativity of carbonitrile over a trifluoromethyl group.

3.5.3 Diene (50) with Aniline

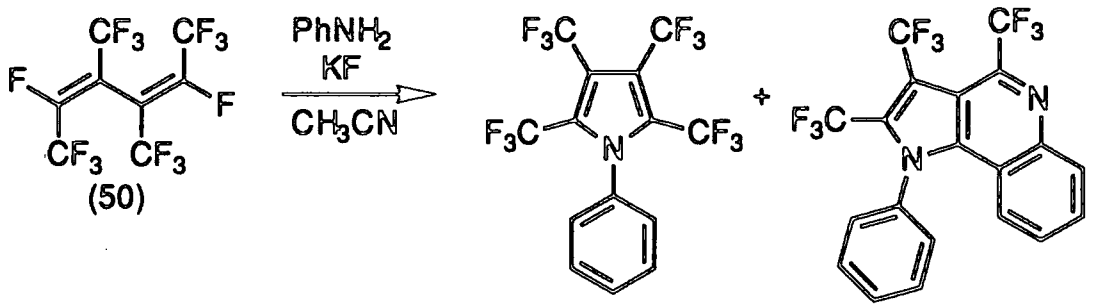
The aim of this reaction was to synthesise the *N*-phenyl pyrrole derivative (108) *via* a simple cyclisation and, indeed, the pyrrole was formed in the presence of caesium fluoride in good yield (Scheme 104).



(108) 72% yield
(Scheme 104)

Pyrrole (108) has been previously made[177] by a route which involves a valence isomer of thiophene derivative (92).

However, when diene (50) and aniline were allowed to react in the presence of potassium fluoride, pyrrole (108) was formed alongside the unexpected pyrrolo-quinoline (109) (Scheme 105).

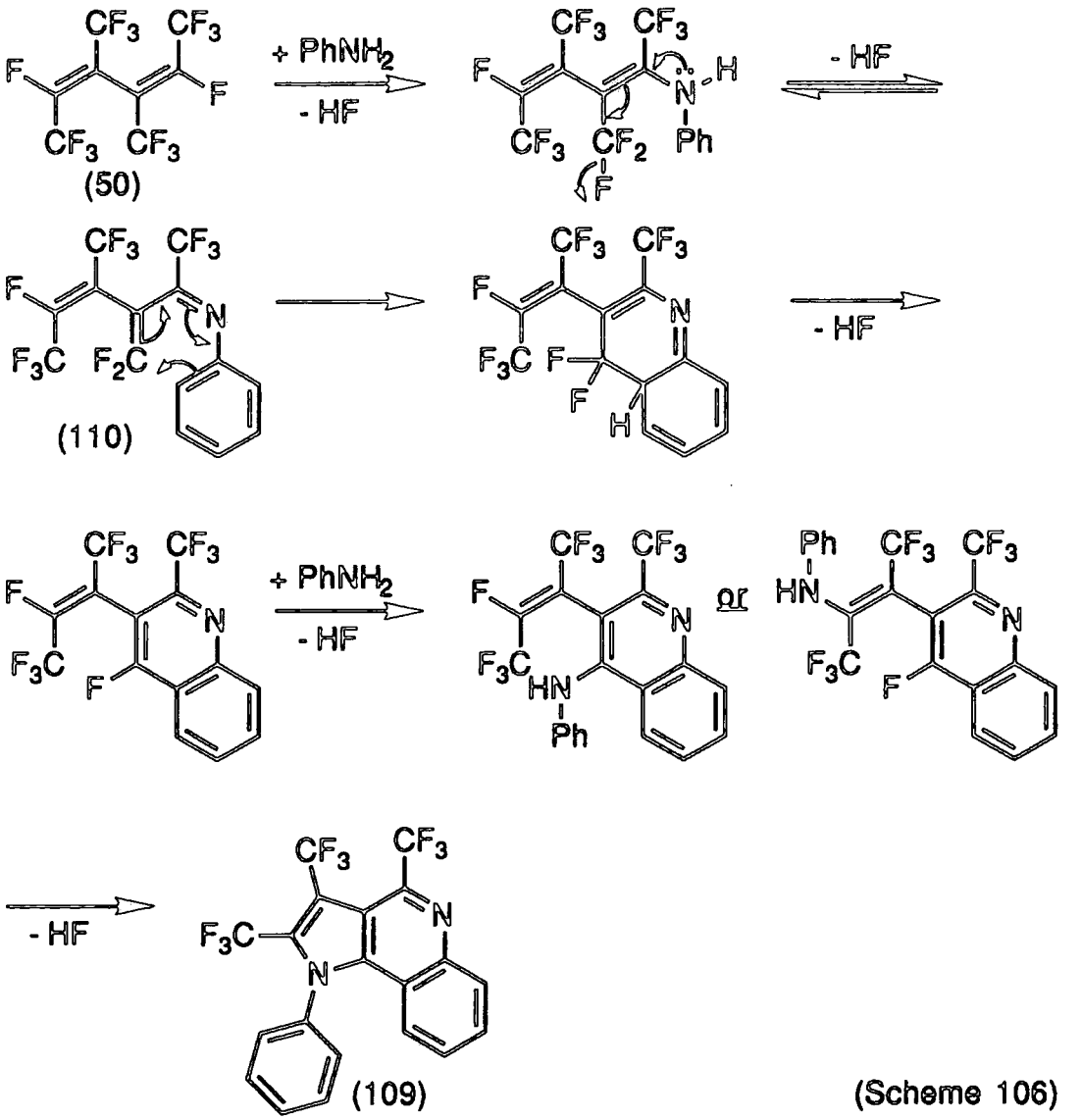


(108) 67% conversion

(109) 27% by NMR integration

(Scheme 105)

The formation of pyrrolo-quinoline (109) can be justified by means of an allylic displacement and subsequent cyclisation (Scheme 106).



(Scheme 106)

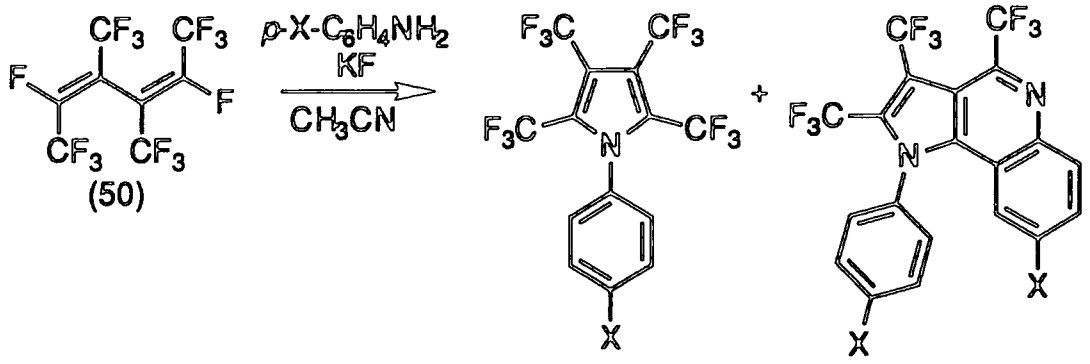
The idea of this mechanism is strengthened by the fact that only the pyrrole (108) was formed when the reaction was carried out in the presence of caesium fluoride. Such an effective source of fluoride ion could add to intermediate (110) forcing the equilibrium back and so ultimately encouraging the formation of pyrrole derivative (108).

Therefore, a series of substituted anilines were used to investigate this reaction.

3.5.4 Diene (50) with 4-Substituted Anilines

The anilines chosen for this study have either an electron donating or electron withdrawing substituent in the 4- position of the phenyl ring.

Upon reaction with a two-fold excess of the 4-substituted anilines in the presence of potassium fluoride, diene (50) gave mixtures of the respective pyrrole and pyrrolo-quinoline derivatives (Scheme 107).



(Scheme 107)

The distributions of the products are collated in Table 4.

Table 4

Substituent X	Proportion pyrrole derivative‡	Proportion pyrrolo-quinoline derivative‡
NMe_2	81% (111)	0%
OMe	73% (112)	21% (113)
H	67% (108)	27% (109)
F	45% (114)	52% (115)
Cl	18% (116)	§
NO_2	79% (117)	0%

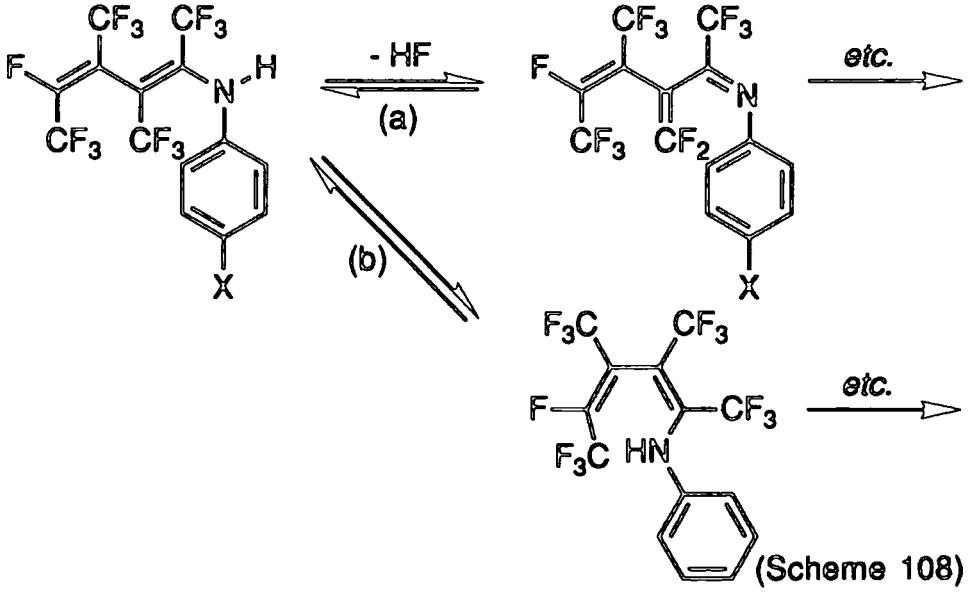
‡ - proportions were obtained from NMR integrations.

§ - the reaction with 4-chloroaniline gave a complex mixture of products and the presence of the pyrrolo-quinoline derivative could not be unequivocally proven.

The shortfall in yields from 100% was made up by the presence of the hydrolysis product tetrakis(trifluoromethyl)furan (73).

It is interesting to note that the pyrrolo-quinoline ring system formed with both electron withdrawing (115) and electron donating (113) substituents whereas none was formed for the two extreme cases of *N,N*-dimethylamino-4-aminoaniline and 4-nitroaniline. The reaction occurs with the liberation of hydrogen fluoride and it is assumed that potassium fluoride removes this by complexation. However, the dimethylamino group is also an effective base[176] and could easily be protonated during the reaction. A dimethyl ammonium group is electron withdrawing and the presence of such a substituent could very well produce the anomalous result given in Table 4.

The electron withdrawing groups reduce the basicities of the aniline derivatives[176] and, in turn, the initial rates of reaction. However, once the aniline has reacted with diene (50), the choice of reaction pathway is determined by a combination of the ease of allylic displacement and the kinetics of the electrocyclisation to generate the pyrrole derivatives (Scheme 108).



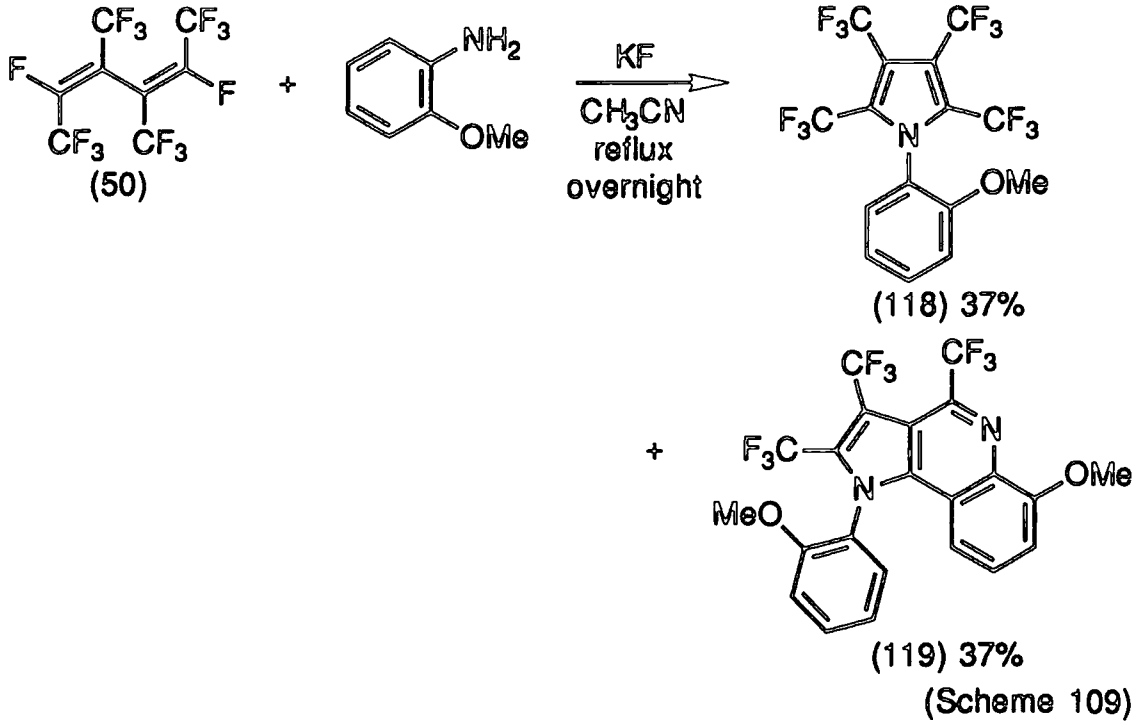
(Scheme 108)

In order to form the pyrrolo-quinoline derivatives, the equilibrium for route (a), although not necessarily lying towards the right, must at least allow allow the formation of some of the azadiene. Conversely, the formation of the pyrrole derivatives demands an interconversion, (b), of the stereochemistry of the double bond bearing the nitrogen.

Therefore, the product breakdown is probably dependent upon the relative positions of the two equilibria (a) and (b). The extremely electron withdrawing *para*- nitro group suppresses allylic displacement but allows the fluoride ion-induced interconversion of stereochemistry, whereas the mildly electron withdrawing *para*- fluorine may suppress the stereochemical interconversion leading ultimately to the formation of an excess of the pyrrolo-quinoline (115).

3.5.5 Diene (50) with 2-Methoxyaniline

Diene (50) reacted slowly with 2-methoxyaniline to give a pyrrole (118) and a pyrrolo-quinoline derivative (119) in an analogous way to the reaction with aniline (Scheme 109).

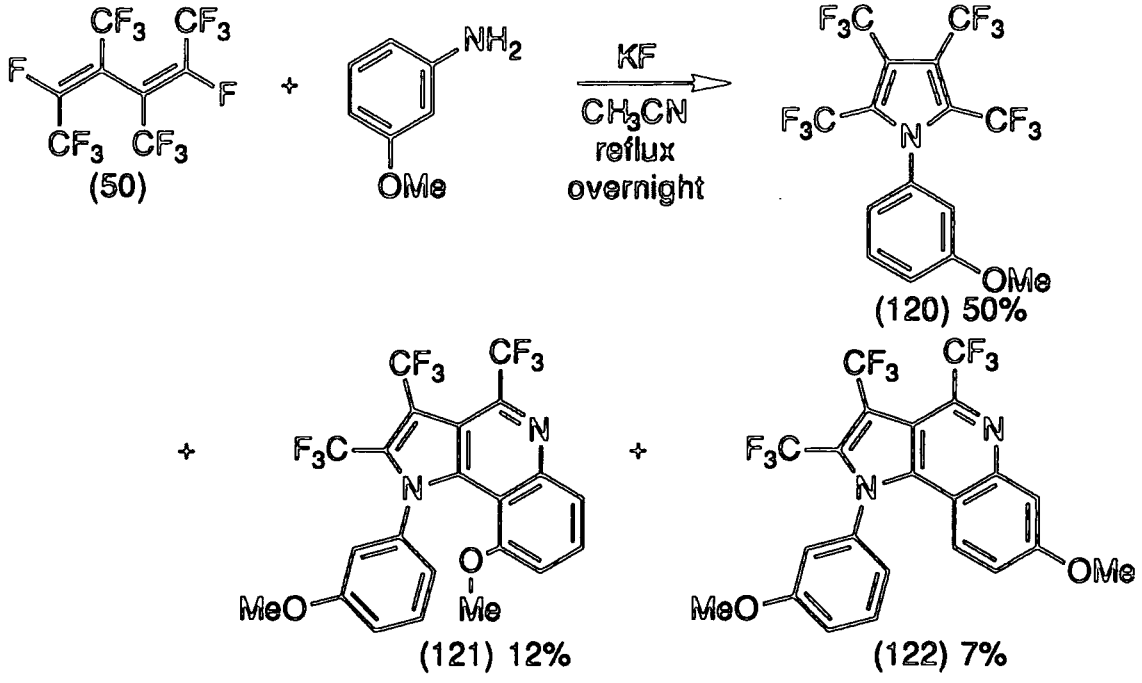


(Scheme 109)

The formation of a large amount of (119) was not expected and may result from the complications involved in the presence of an *ortho*- methoxy group which is not known as an effective electron donor[176].

3.5.6 Diene (50) with 3-Methoxyaniline

Similarly, diene (50) also reacted slowly with 3-methoxyaniline giving a mixture of a pyrrole (120) and two inseparable isomeric pyrrolo-quinolines (121) and (122) Scheme 110).



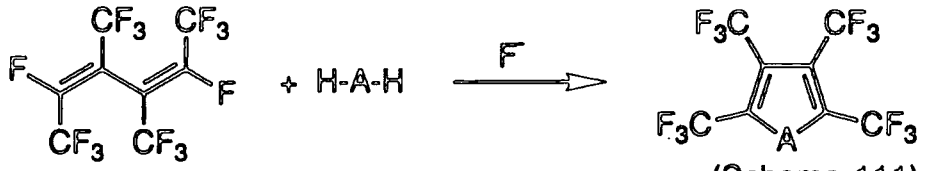
(Scheme 110)

In this case, the *meta*- methoxy group acts as an electron withdrawing group[176] and the distribution of products is in line with previous experiments.

3.6 Reactions with Carbon Nucleophiles

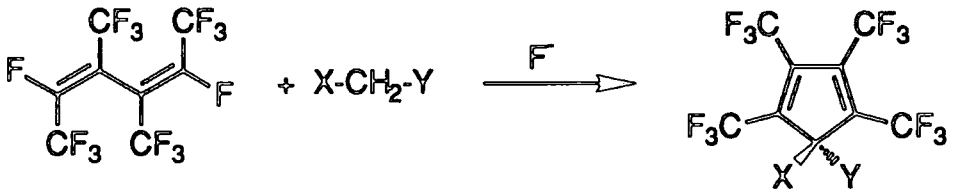
3.6.1 Background

We may now propose a generalised scheme for the cyclisation of the perfluorinated diene (50) with potentially bifunctional nucleophiles (Scheme 111).



(Scheme 111)

If this strategy is extended to include carbon nucleophiles, we obtain a direct route to tetrakis(trifluoromethyl)- substituted cyclopentadienes and other related systems (Scheme 112).



(Scheme 112)

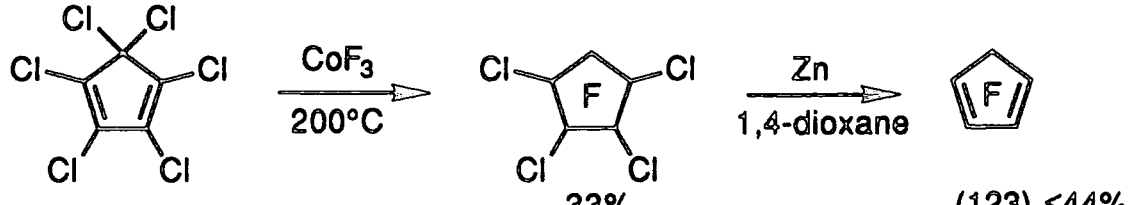
Where X and Y are electron withdrawing groups.

It would therefore be useful to consider the background of this type of cyclic compound.

3.6.2 Fluorinated Cyclopentadienes and Cyclopentadienide Systems

3.6.2.1 Hexafluorocyclopentadiene (123)

The synthesis of diene (123) was first reported in 1963[178] *via* a route starting from hexachlorocyclopentadiene (Scheme 113).



33%

(123) ≤44%

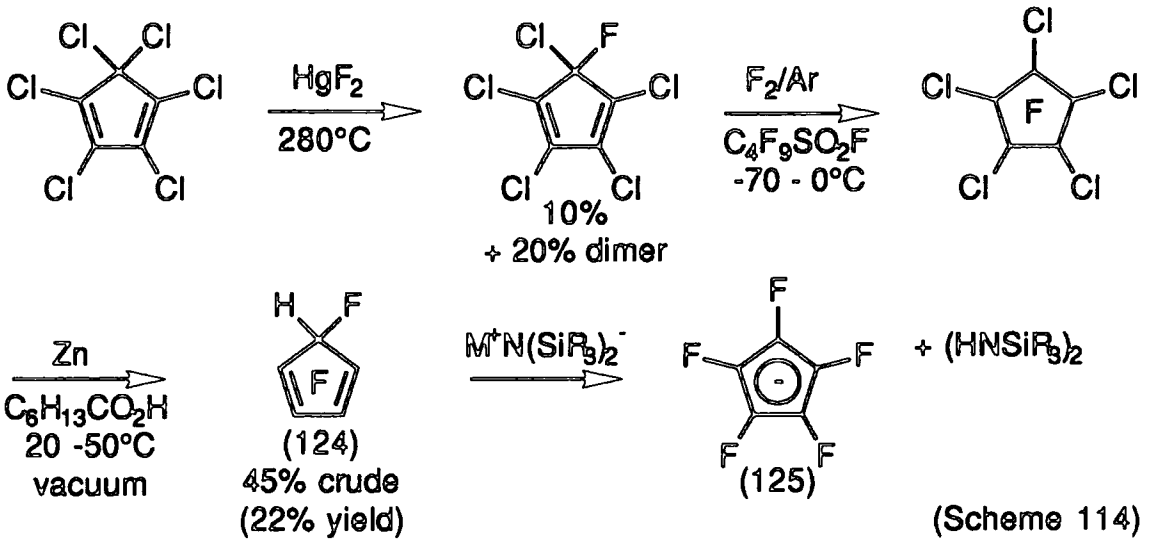
(Scheme 113)

Other, higher yielding routes have also been published[179,180] over the years.

Hexafluorocyclopentadiene (123) dimerised spontaneously[178] even at -22°C to give the Diels-Alder adduct in a similar way to cyclopentadiene itself. Indeed, cyclic diene (123) has been proven to act as both a diene and a dienophile with different reagents in some interesting Diels-Alder chemistry[181].

3.6.2.2 1,2,3,4,5-Pentafluorocyclopentadiene (124)

A similar compound, diene (124), was synthesised by German workers[182,183,184] as a means of obtaining the pentafluorocyclopentadienyl anion (125) (Scheme 114).

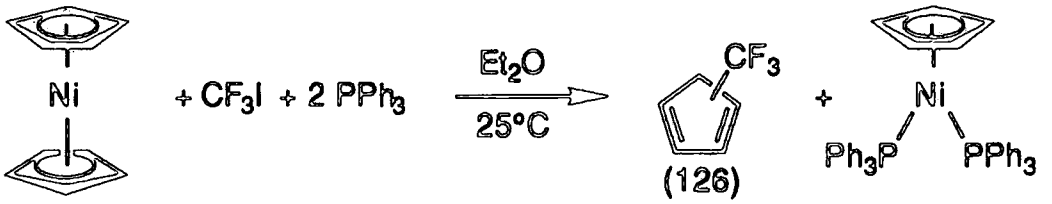


(Scheme 114)

THF solutions of the metal salts of anion (125) are unstable[183]. The lithium salt decomposed within minutes even at -110°C, the sodium salt within hours at -78°C and both the thallium and caesium salts at -30°C. The most stable salt reported was Na+(18-crown-6) $C_5F_5^-$ in THF which could be observed at 22°C for several hours[183]. Decomposition occurred through the loss of metal fluoride coupled with polymerisation. Binding the anion (125) to transition metal centres in 'sandwich' type complexes proved to be unsuccessful[184].

3.6.2.3 Trifluoromethylcyclopentadiene (126)

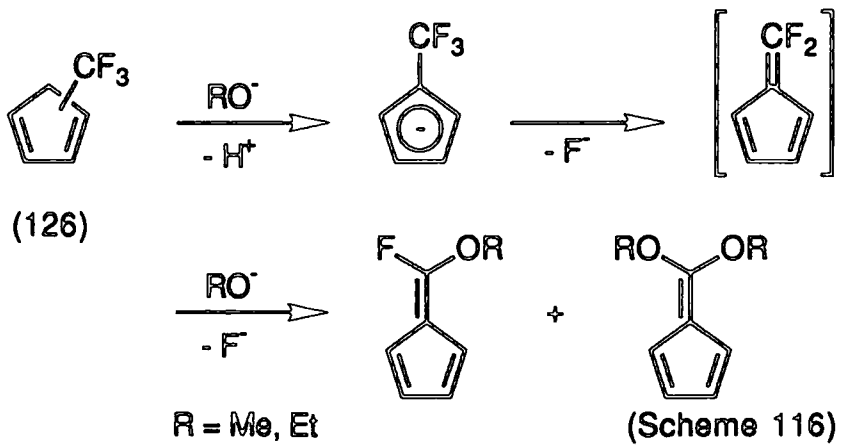
The cyclopentadiene derivative (126) was first prepared by Ollson and Wennerström[185] as a mixture of its 1- and 2- isomers (Scheme 115).



(126)
7:3
1- and 2-
isomers

(Scheme 115)

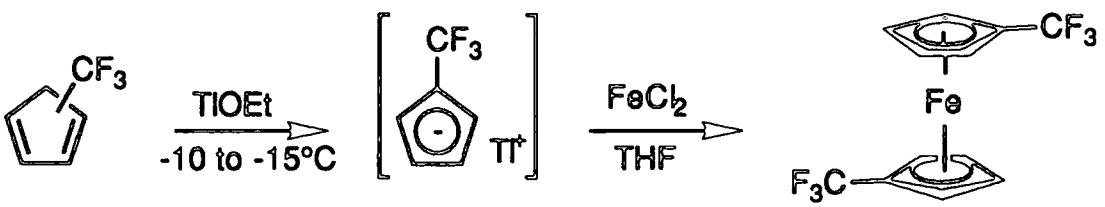
Reaction of diene (126) with alkoxide ultimately gave 6-substituted fulvenes (Scheme 116).



R = Me, Et

(Scheme 116)

Trifluoromethylcyclopentadiene (126) has been successfully bound to a number of transition metal centres[186,187,188]. For example, bis(trifluoromethyl)ferrocene (127) was prepared[186] by the reaction of ferrous chloride with the thallium salt of diene (126) (Scheme 117).



(126) 55 - 60% (127) 43%

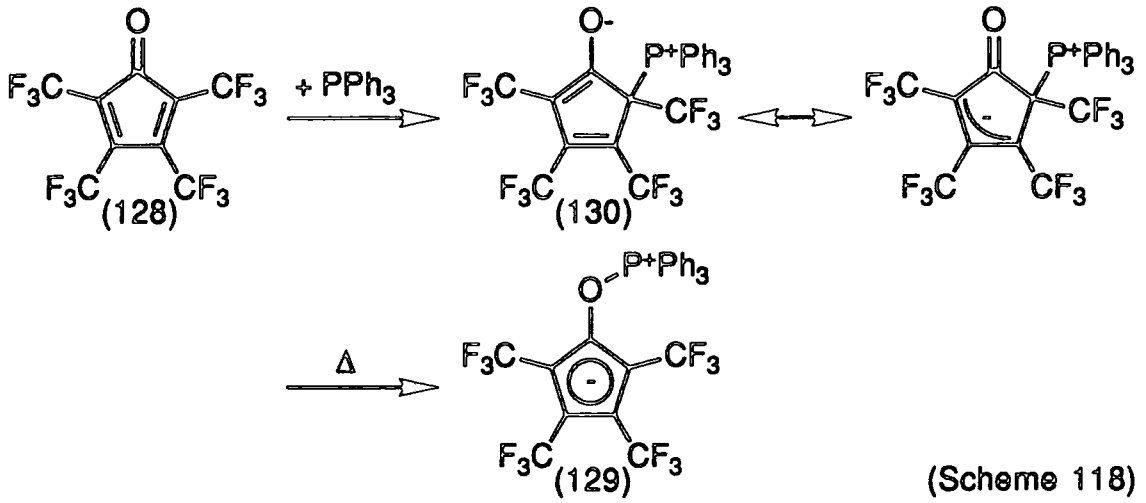
(Scheme 117)

E.S.C.A. measurements[186] on the ferrocene (127) illustrated that the strong electron withdrawing effect of the trifluoromethyl groups increases the binding energy of the inner-shell electrons of iron.

3.6.2.4 Tetrakis(trifluoromethyl)cyclopentadienone (128)

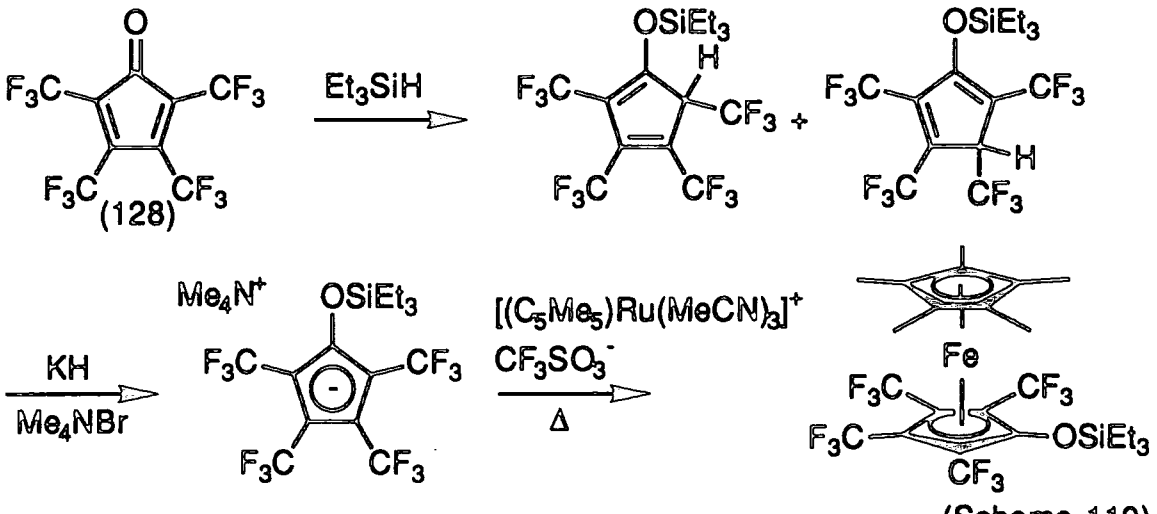
The unequivocal synthesis of dienone (128) was first reported in 1963[189] as a result of the coupling of hexafluorobut-2-yne (28) and carbon monoxide in the presence of $[Rh(CO)_2Cl]_2$ under high pressure. Lemal and co-workers have demonstrated[190] that dienone (128) is a highly versatile inverse electron demand Diels-Alder diene.

Interestingly, the reaction between dienone (128) and triphenylphosphine has recently been found to give the ylide (129)[191] *via* the kinetic isomer (130)[192] (Scheme 118).



(Scheme 118)

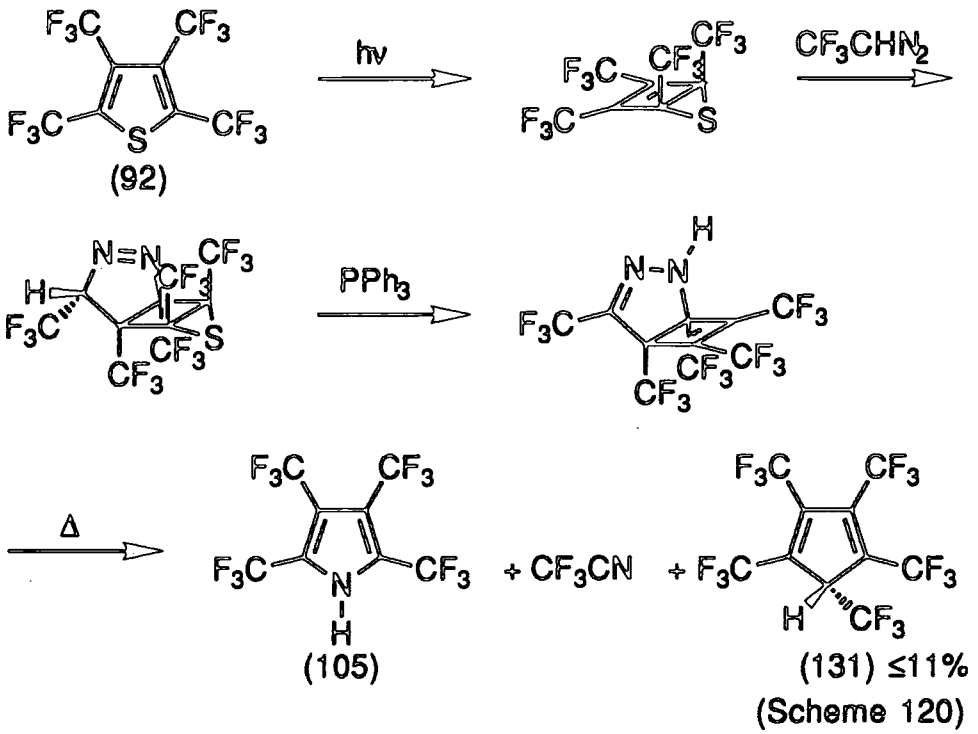
Dienone (128) can be reduced by the addition of trialkylsilanes to give cyclopentadienes[192,193] which have been successfully used as a source of ligands for transition metals[193] (Scheme 119).



(Scheme 119)

3.6.2.5 Pentakis(trifluoromethyl)cyclopentadiene (131)

In 1980, Laganis and Lemal published[194] a low yielding route to the interesting diene system 5-*H*-pentakis(trifluoromethyl)cyclopentadiene (131) starting from the Dewar valence isomer of thiophene derivative (92) (Scheme 120).



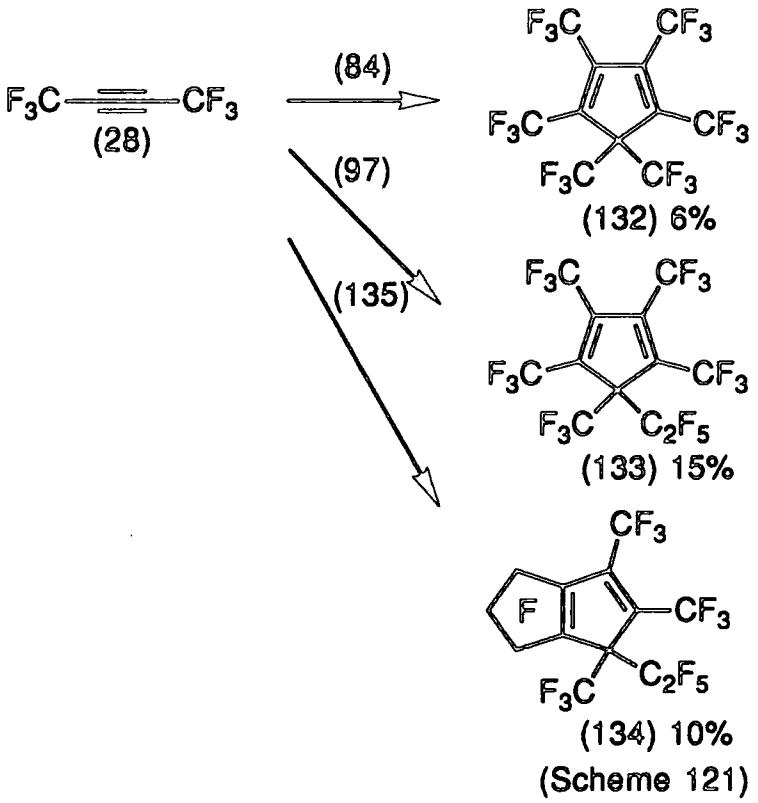
(Scheme 120)

Diene (131) was shown to be a remarkably powerful carbon acid[194] ($pK_a \leq -2$) which is stronger than nitric acid despite its lack of conjugating substituents. This is in contrast to cyclopentadiene derivative (124)[182] ($12.8 < pK_a < 15.5$) and demonstrates the differences in effects fluorine has depending upon whether it is located upon, or adjacent to, the carbanionic centre (see Section 3.2).

A similar route to this has been used by Janulis and Arduengo[195] to prepare derivatives of diene (131) as a source of electrophilic carbenes and ultimately a stabilised carbonyl ylide[196].

3.6.2.6 Cyclopentadienes from Hexafluorobut-2-yne (28)

Work in these laboratories has resulted in the formation of perfluoroalkyl- substituted cyclopentadienes (132), (133) and (134)[197] *via* fluoride ion induced co-oligomerisations of hexafluorobut-2-yne (28) with hexafluoropropene (84)[198], octafluorobut-2-ene (97)[172] and octafluorocyclopentene (135)[198] respectively (Scheme 121).



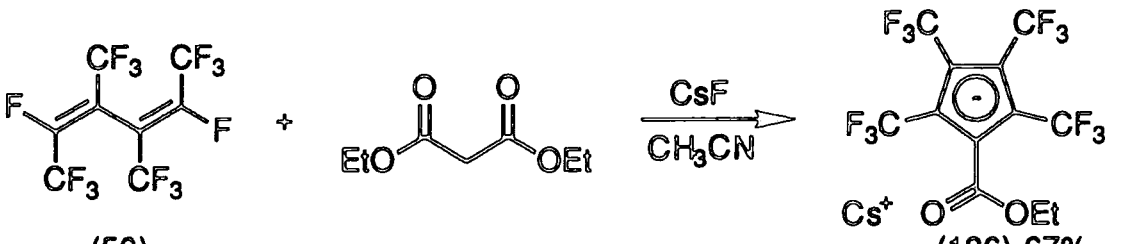
(Scheme 121)

The syntheses are quite complex involving the formation of several other co-oligomers[197] and there is a very poor mass recovery in each case[198].

3.6.3 Reactions with Diethyl Malonate

3.6.3.1 Diene (50)

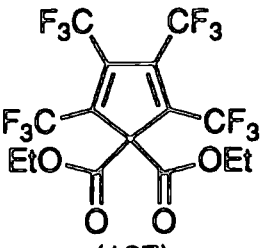
The reaction of diethyl malonate with diene (50) in the presence of caesium fluoride gave the cyclopentadienyl salt (136) directly in good yield (Scheme 122).



(50) (136) 67%

(Scheme 122)

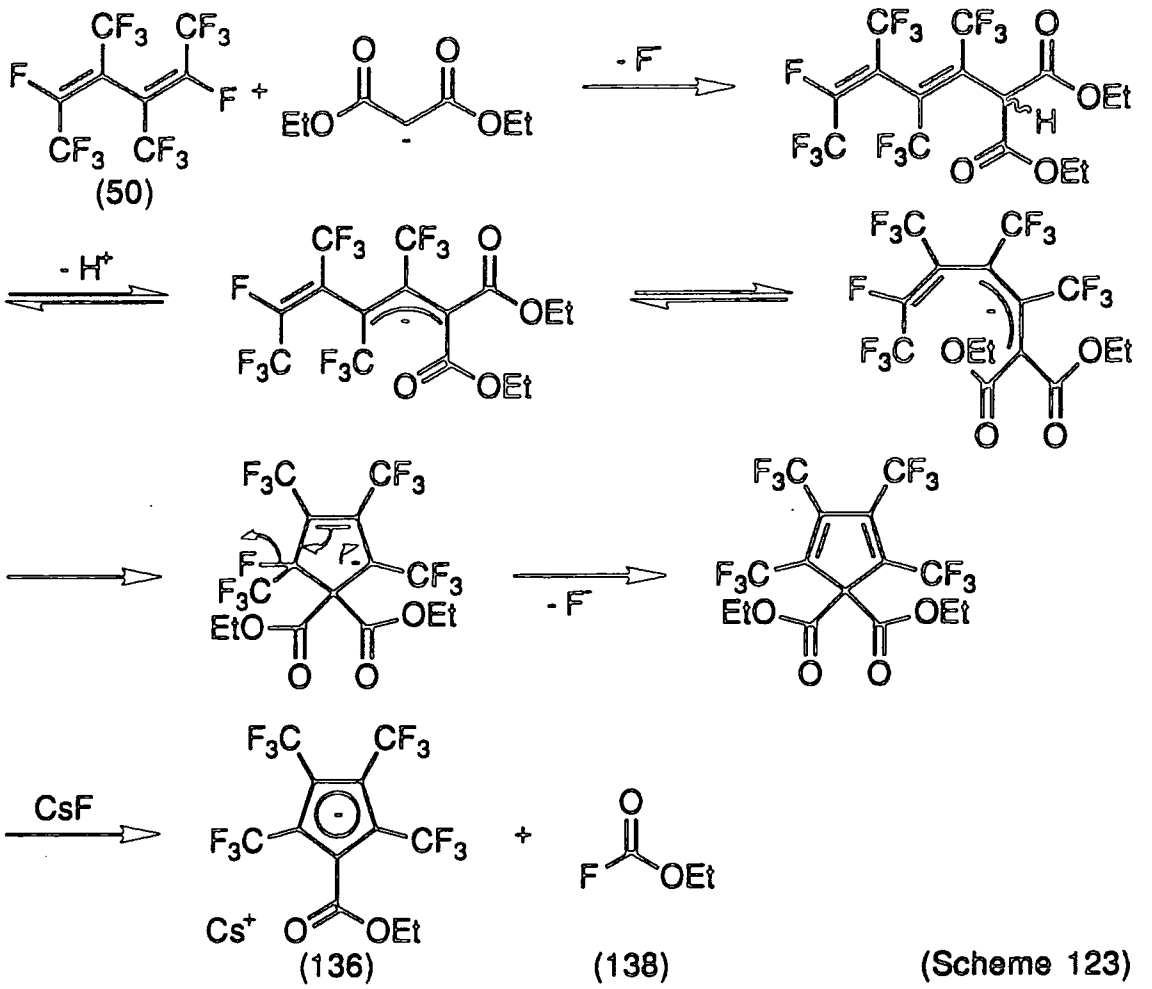
The salt was identified by ^{19}F NMR spectroscopy, F.A.B. mass spectrometry and IR spectroscopy. By following the progress by ^{19}F NMR, the reaction was observed to proceed *via* the precursor diene (137) which, although identified by ^{19}F NMR and G.C. mass spectrometry, could not be isolated (Figure 19).



(137)

(Figure 19)

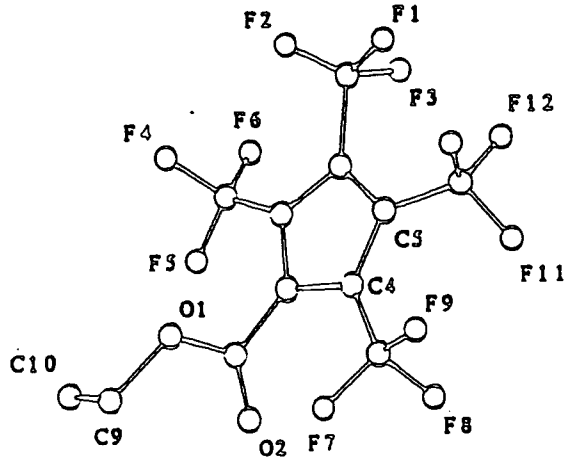
It is also worthy of note here that ^{19}F NMR spectroscopy of the reaction mixture showed a resonance at -17.64ppm which is very close to -17.5ppm which has been reported[199] for the fluorine atom resonance in ethylfluoroformate (138). Therefore it could be postulated that the reaction mechanism may be written as overleaf (Scheme 123).



(50) (136) (138) (Scheme 123)

In similar examples using different nucleophiles, some of the other analogous intermediates have been observed and identified by ^{19}F NMR and mass spectrometry[200,201].

Crystals of salt (136) were suitable for X-ray analysis and a single crystal X-ray structure study was subsequently carried out by Prof. M. B. Hursthouse at Queen Mary and Westfield College, London (X-ray Plot 1).



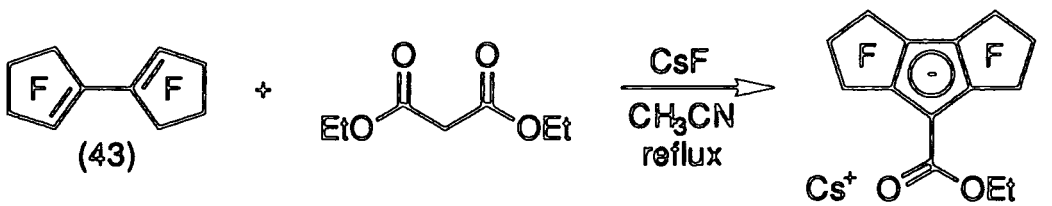
X-ray Plot 1.

Caesium Tetrakis(trifluoromethyl)ethoxycarbonylcyclopentadienide (136)

The final R value of 0.092 demonstrates that there may be considerable errors involved in the values of bond lengths and bond angles but the X-ray crystal structure clearly shows a planar cyclopentadienyl ring system and the presence of the substituents upon it.

3.6.3.2 Diene (43)

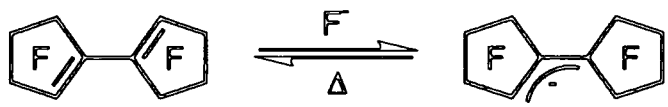
In an analogous manner, diethyl malonate reacted with diene (43) in the presence of caesium fluoride to form the tricyclic cyclopentadienyl salt (138) (Scheme 124).



(138) 68%

(Scheme 124)

The reaction was carried out at reflux temperature to disfavour the formation of anion (139)[131] (Scheme 125).

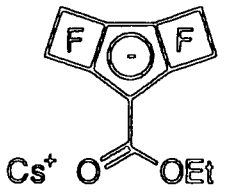


(Scheme 125)

The formation of the tricyclic cyclopentadienyl salt (138) proceeds *via* a mechanism which is analogous to the formation of salt (136).

3.6.3.3 Diene (46)

The reaction of diene (46) with diethyl malonate in the presence of caesium fluoride did not form the highly strained tricyclic cyclopentadienyl salt (140) (Figure 20).



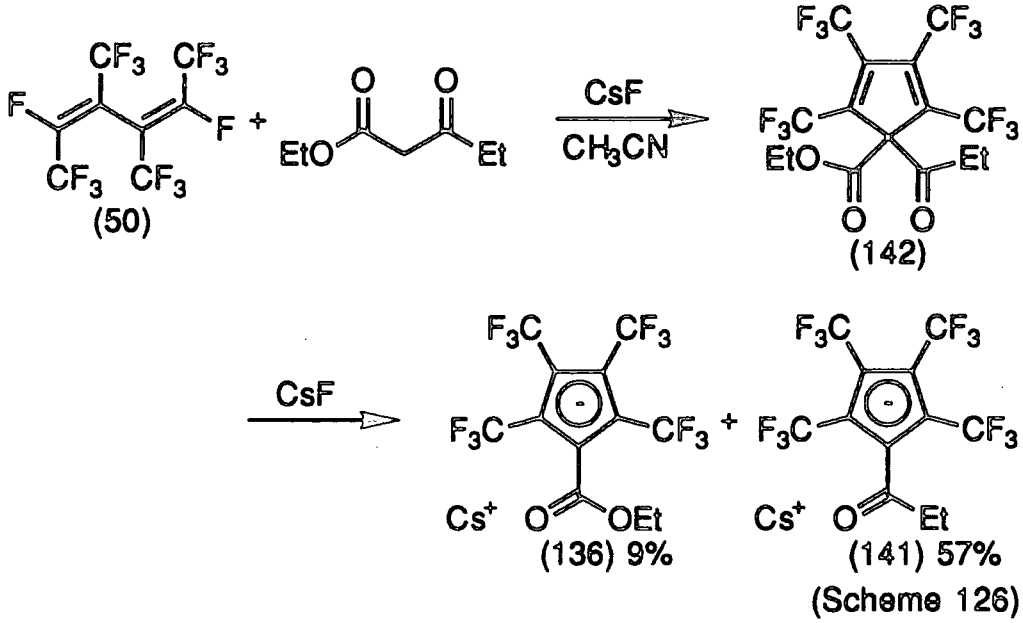
(140)

(Figure 20)

Instead, it resulted in the production of an intractable polymeric tar. This suggests that intermolecular reactions *via* S_N2' processes within the cyclobutene rings have occurred rather than intramolecular coupling. Therefore this experiment was not carried any further.

3.6.4 Diene (50) with Ethyl 3-Oxopentanoate

In a comparable way, diene (50) was treated with the unsymmetrical nucleophile ethyl 3-oxopentanoate in the presence of caesium fluoride and was observed by ^{19}F NMR spectroscopy. The subsequent reaction proceeded to give cyclopentadiene derivative (142) and thence an inseparable mixture of the two cyclopentadienyl salts (136) and (141) (Scheme 126).

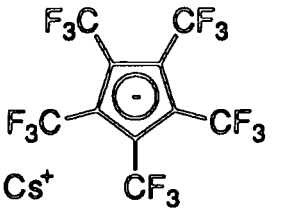


(Scheme 126)

Diene (142) and the two salts (136) and (141) could not be isolated and their assignment is from NMR and mass spectral data.

3.6.5 Diene (50) with 2,2,2-Trifluoroethylphenylsulphone (143)

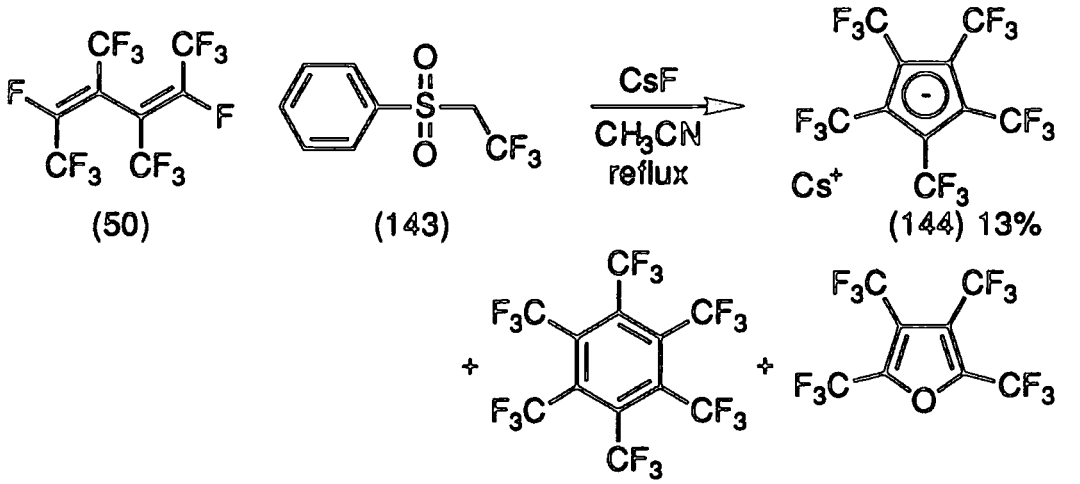
The aim of this experiment was to attempt to synthesise the pentakis(trifluoromethyl)cyclopentadienyl salt (144) - a very interesting target compound (Figure 21).



(144)

(Figure 21)

However, the treatment of diene (50) with the sulphone (143), a potential source of '$X\text{-}CH_2CF_3$', in the presence of caesium fluoride gave a slow reaction which produced a mixture of compounds identified by ^{19}F NMR spectroscopy (Scheme 127).



(50) (143) (144) 13%

(145) 17% (73) 70%

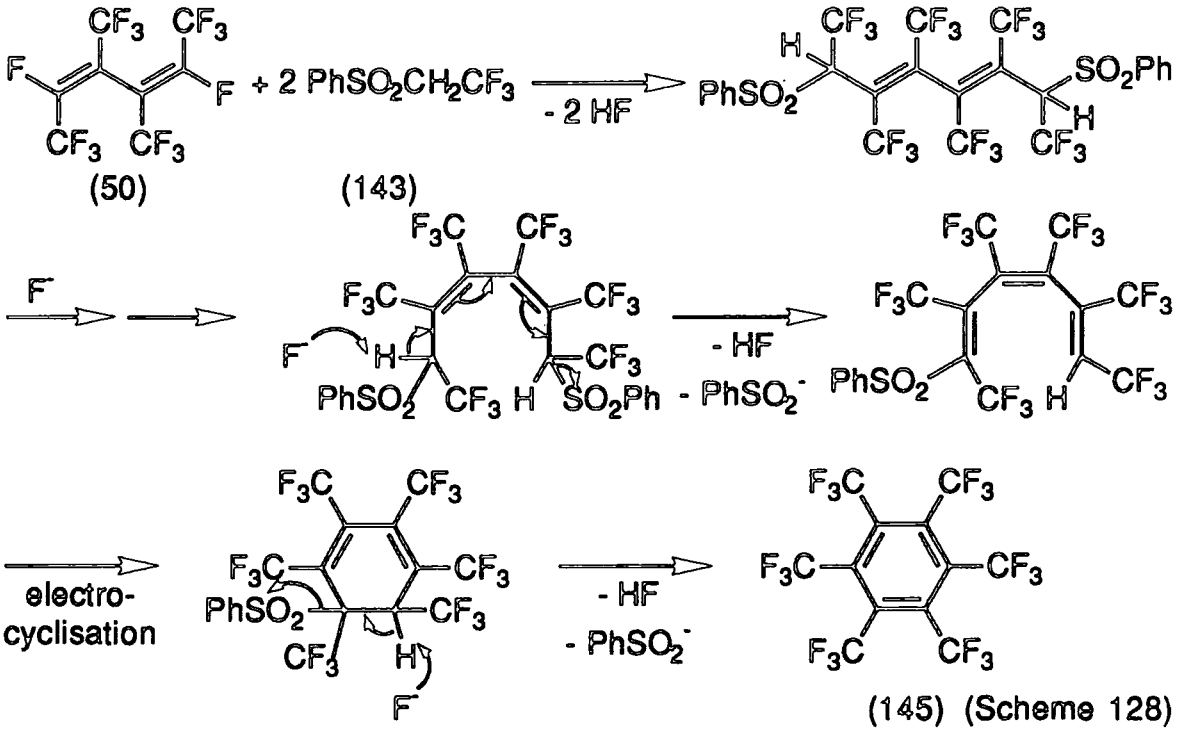
(Scheme 127)

Hydrolysis of diene (50) to give the furan derivative (73) was very difficult to avoid despite attempts to keep all reagents and the solvent scrupulously dry.

Although cyclopentadienyl salt (144) could not be isolated from the mixture, the benzene derivative (145) could be and was subsequently

characterised by ^{19}F NMR spectroscopy, mass spectrometry and IR spectroscopy.

The formation of hexakis(trifluoromethyl)benzene (145) was not expected but it may be explained by the nucleophilic attack of two equivalents of the sulphone (143) and the sequential loss of phenyl sulphinic acid (Scheme 128).



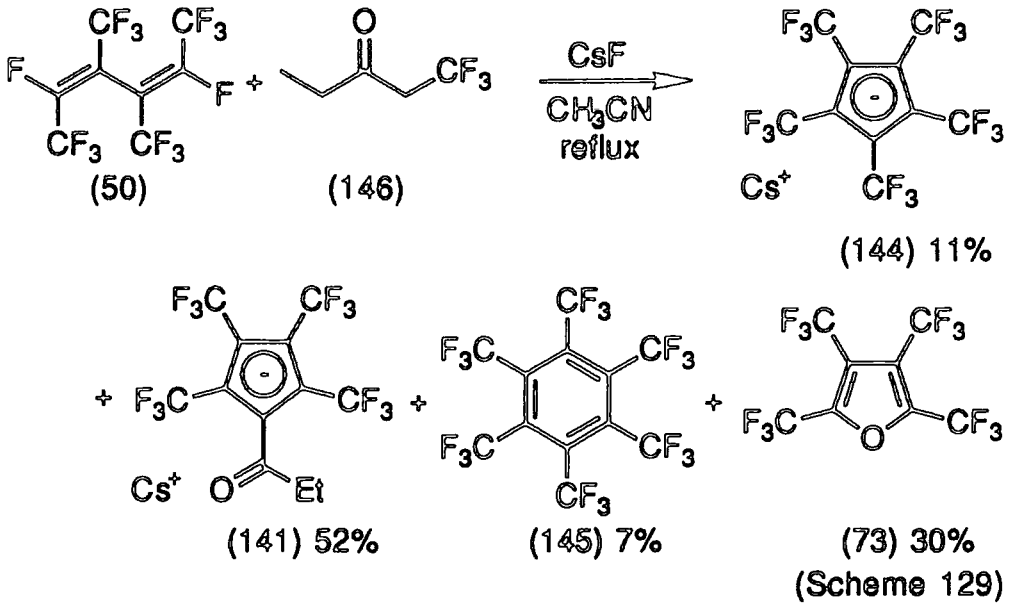
(145) (Scheme 128)

This provides an alternative route to benzene derivative (145) which has been previously made[202,203] starting from the expensive alkyne hexafluorobut-2-yne (28).

3.6.6 Diene (50) with 1,1,1-Trifluoropentan-3-one (146)

As an alternative more acidic source of the nucleophile 'X-CH_2CF_3', the partially fluorinated ketone (146) was synthesised (see Section 6.1.2) and reacted with diene (50) in the presence of an excess of caesium fluoride.

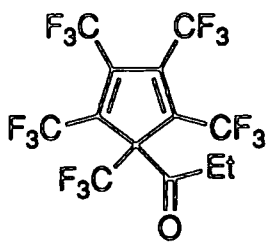
By following the progress of the reaction by ^{19}F NMR spectroscopy, the formation of a mixture of products could be observed (Scheme 129).



(Scheme 129)

The formation of furan (73) and benzene derivatives (145) can be explained by means of hydrolysis of diene (50) and by the nucleophilic attack of two equivalents of ketone (146) respectively, but accounting for the formation and distribution of the two cyclopentadienyl salts (141) and (144) is more complex.

It may be assumed that the two salts, (141) and (144), are derived from the common diene precursor (147) which could not be identified in the ^{19}F NMR spectra (Figure 22).



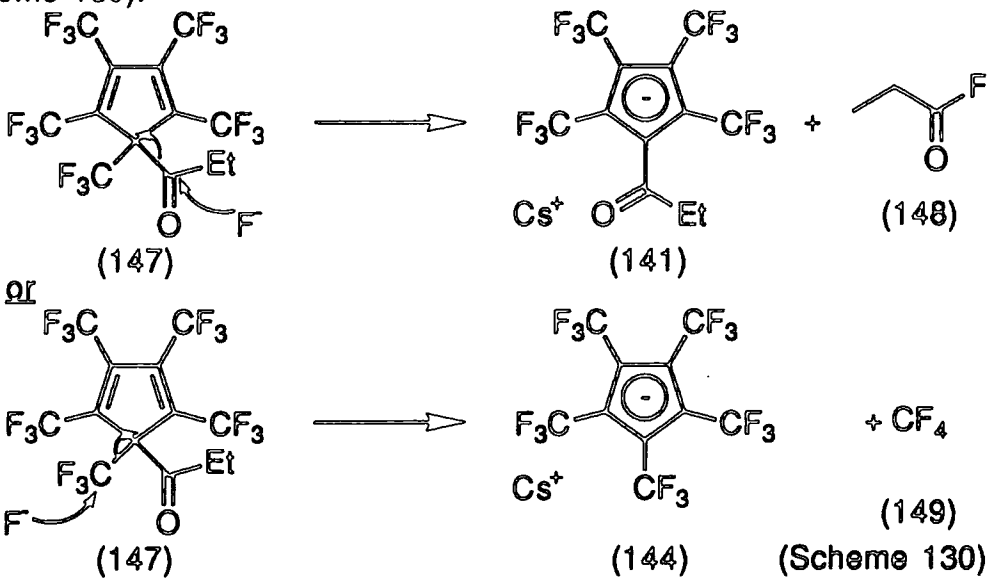
(147)

(Figure 22)

According to the ratios of salts (141) and (144), the trifluoromethyl group is easier to displace by fluoride ion than the propanoyl group.

In order for salt (144) to be generated, fluoride ion must attack the carbon of the carbonyl group in diene (147) and salt (144) would then act as a 'leaving group'. However, if the analogous argument was to be used to explain the generation of the alternative salt (141), we need to invoke an S_N2

type of nucleophilic attack by fluoride ion upon a trifluoromethyl group first (Scheme 130).



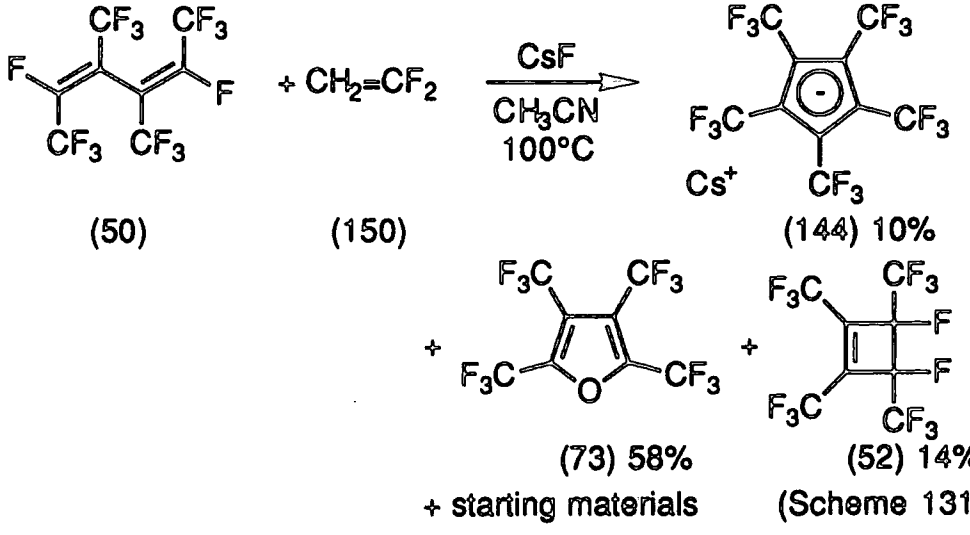
(147) (144) (Scheme 130)

This is made all the more remarkable considering that salt (141) is formed preferentially over salt (144). Neither (148) nor (149) were observed.

3.6.7 Diene (50) with Vinylidene Fluoride (150)

In order to try to avoid the problems involved with mixtures arising from using unsymmetrical nucleophiles, vinylidene fluoride (150) was used as a source of the nucleophile $CF_3CH_2^-$ which can be generated *in situ*.

Heating diene (50), vinylidene fluoride (150) and an excess of caesium fluoride in acetonitrile together in an autoclave resulted in the formation of a mixture of compounds which could be identified by ^{19}F NMR (Scheme 131).



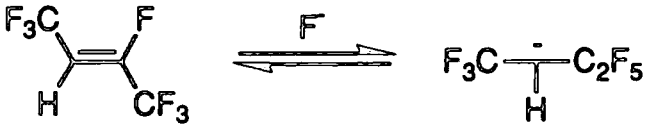
+ starting materials (Scheme 131)

Unfortunately, the cyclopentadienyl salt (144) could not be isolated from the mixture.

We now have an empirical order for the ease of displacement from the derived cyclopentadienes of the various electron-withdrawing groups 'X' in X-CH_2-Y of:

$$SO_2Ph > CO_2Et > CF_3 > COEt > C_6F_5^{201} \sim CN^{201} > C_5F_4N^{201}$$

The more ideal symmetrical nucleophile 1,1,1,3,3,3-hexafluoropropane is too prone to lose hydrofluoric acid and the derivative 2-*H*-pentafluoropropene was observed[204] to co-oligomerise with diene (50) in the presence of caesium fluoride to give a very complex mixture. The next homologue to 2-*H*-pentafluoropropene is 2-*H*-heptafluorobut-2-ene (151) which is a means of generating the possible nucleophilic anion $CF_3CF_2(CF_3)CH^-$ *in situ*[205] (Scheme 132).

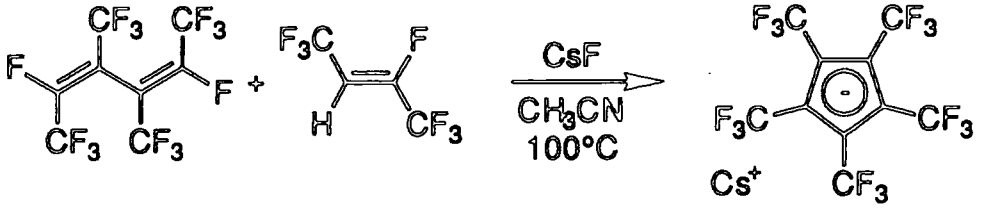


(151) (Scheme 132)

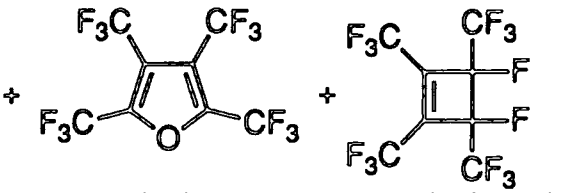
3.6.8 Reactions with *E*-2-*H*-Heptafluorobut-2-ene (151)

3.6.8.1 Diene (50)

Heating a mixture of diene (50), polyfluorinated alkene (151) and an excess of caesium fluoride in acetonitrile together in a rocking autoclave at 100°C yielded a mixture of products which were analysed by ^{19}F NMR spectroscopy (Scheme 133).



(50) (151) (144) 50%

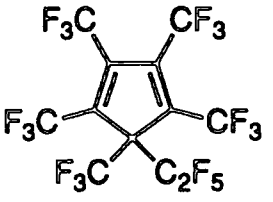


(73) 26% (52) 13%

\+ starting materials (Scheme 133)

The concentration of salt (144) was much higher than for the reaction with vinylidene fluoride (see Section 3.6.7) or the other nucleophiles tested and it could be isolated from the mixture as an off-white powder. Characterisation of salt (144) was by ^{19}F and ^{13}C NMR spectroscopy, FAB mass spectrometry and IR spectroscopy.

The formation of salt (144) probably proceeds *via* the cyclopentadiene derivative (133)[197] (Figure 23).

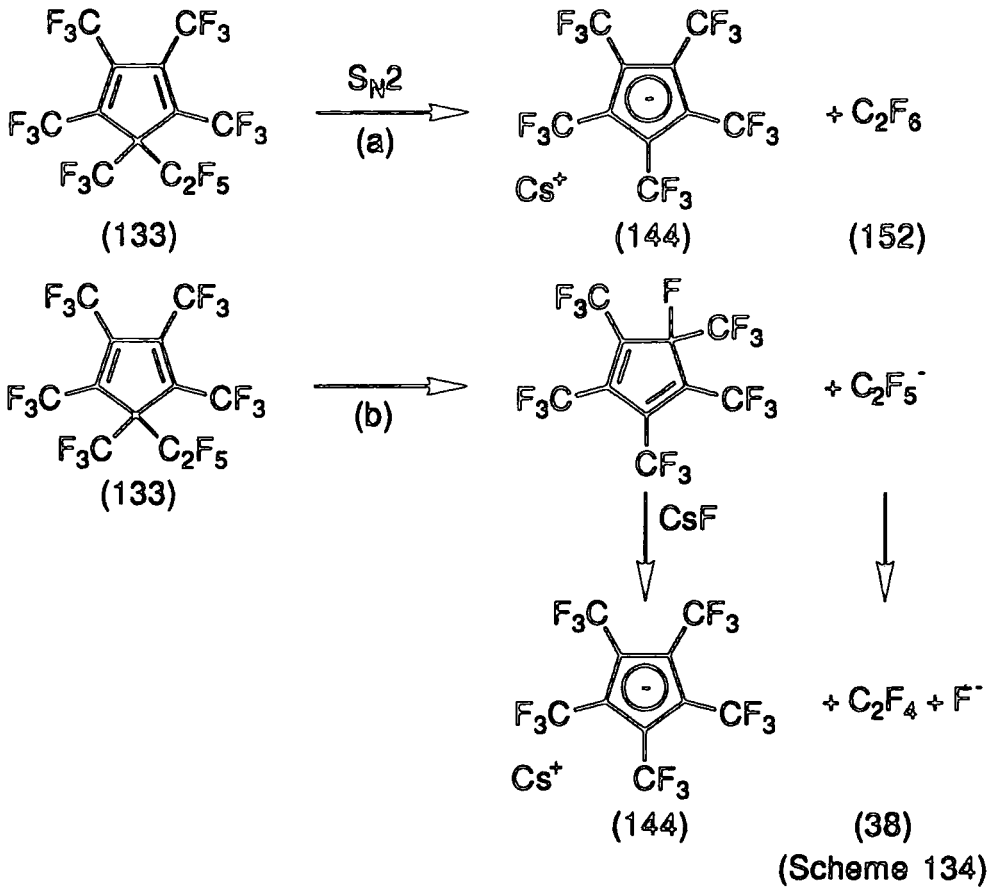


(133)

(Figure 23)

In order for cyclopentadiene derivative (133) to give the salt (144), the elimination of the 5-pentafluoroethyl group over the 5-trifluoromethyl group

occurred selectively but the means to perform such an elimination appear as a quandary (Scheme 134).



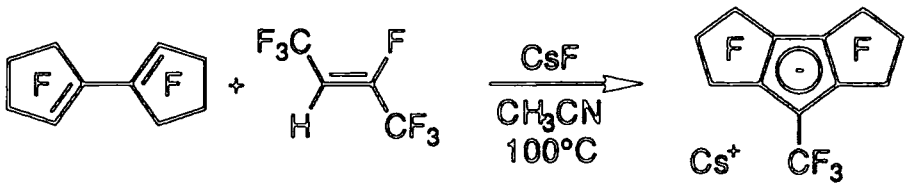
(Scheme 134)

Although pathway (b) is feasible - caesium fluoride induced defluorinations are known[81], the stabilisation of salt (144) will probably mean that it will act as an efficient leaving group for an S_N2 type process, *i.e.* route (a), despite how unusual a nucleophilic attack by fluoride ion upon a saturated perfluoroalkyl group at first appears (see Section 3.6.6). Neither hexafluoroethane (152) nor tetrafluoroethene (38) could be observed by G.C. mass spectrometry although either or both could be assigned to anomalous resonances in the ^{19}F NMR spectra of the volatiles from this experiment.

3.6.8.2 Diene (43)

In an analogous way, an autoclave containing a mixture of diene (43), polyfluorinated alkene (151) and caesium fluoride in acetonitrile was heated at 100°C in a rocking furnace. ^{19}F NMR spectroscopy of the mixture indicated

the presence of the tricyclic cyclopentadienyl salt (153) which was probably formed by an similar route to salt (144) (see Section 3.6.8.1) (Scheme 135).



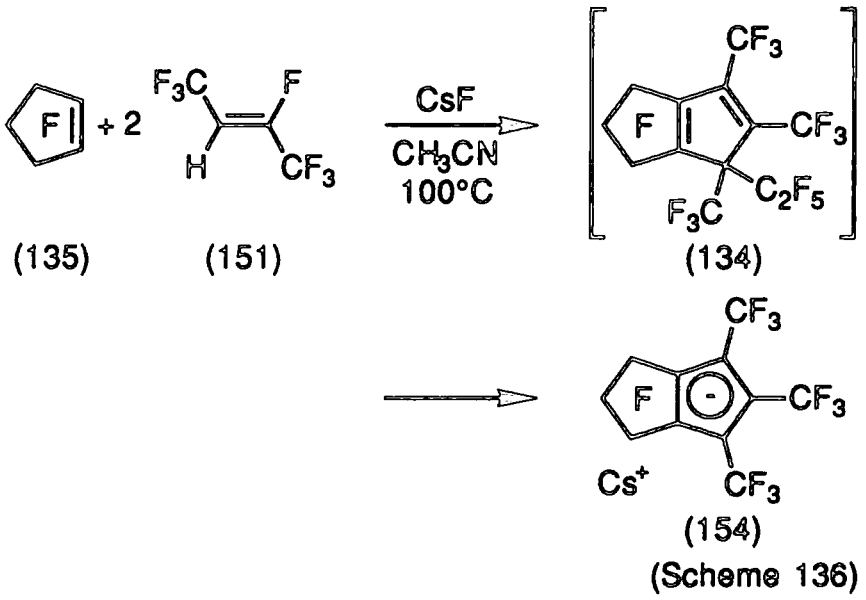
(43) (151) (153)

(Scheme 135)

This salt did not prove to very stable and soon deteriorated after isolation and so could not be properly identified.

3.6.8.3 Octafluorocyclopentene (135)

In order to prove a general point in these reactions, *E*-2-*H*-heptafluorobut-2-ene (151) was treated with octafluorocyclopentene (135) in a similar way. ^{19}F NMR spectroscopy of the mixture indicated the formation of the cyclopentadienyl salt (154) presumably formed from the cyclopentadiene derivative (134)[197] (Scheme 136).



(135) (151) (134) (154)

(Scheme 136)

Again, salt (154) is unstable and so could only be identified by ^{19}F NMR spectroscopy. However, such a species was not looked for in previous experiments in these laboratories[172,197,198] and its presence could explain the low mass recoveries observed in these experiments.

Chapter Four

Formation of Some Charge Transfer Complexes

4.1 Introduction

There has been considerable interest in the area of charge transfer (CT) salts over the past two decades. Recent appeal stemmed initially from the discovery that various 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) salts demonstrated some interesting electrical[206,207] and magnetic[208] properties. The present surge in research today lies in the remarkable result that the CT salt, decamethylferrocenium tetracyanoethanide, $[Fe(C_5Me_5)_2]^{\cdot+}$ $[TCNE]^{\cdot-}$, displayed ferromagnetism below 5K[209] - the first so-called "organic magnet"[210].

Decamethylferrocene has a standard potential, E^o, of -0.1V[211] demonstrating how easily it is to be oxidised. When we compared the standard potentials for TCNQ and TCNE, 0.19V and 0.24V respectively[212], with those of the various fluorocarbon derivatives that we have investigated (see Section 2.2.2), it seemed probable that decamethylferrocene could be capable of reducing the fluorinated alkenes and dienes and that stable CT salts of the dienes with decamethylferrocene might be formed. There was no previous report of any such CT complexes between metallocene donors and fluorocarbon acceptors in the literature.

4.2 Discussion

4.2.1 Reaction of Decamethylferrocene and Diene (43) (With M. W. Briscoe)

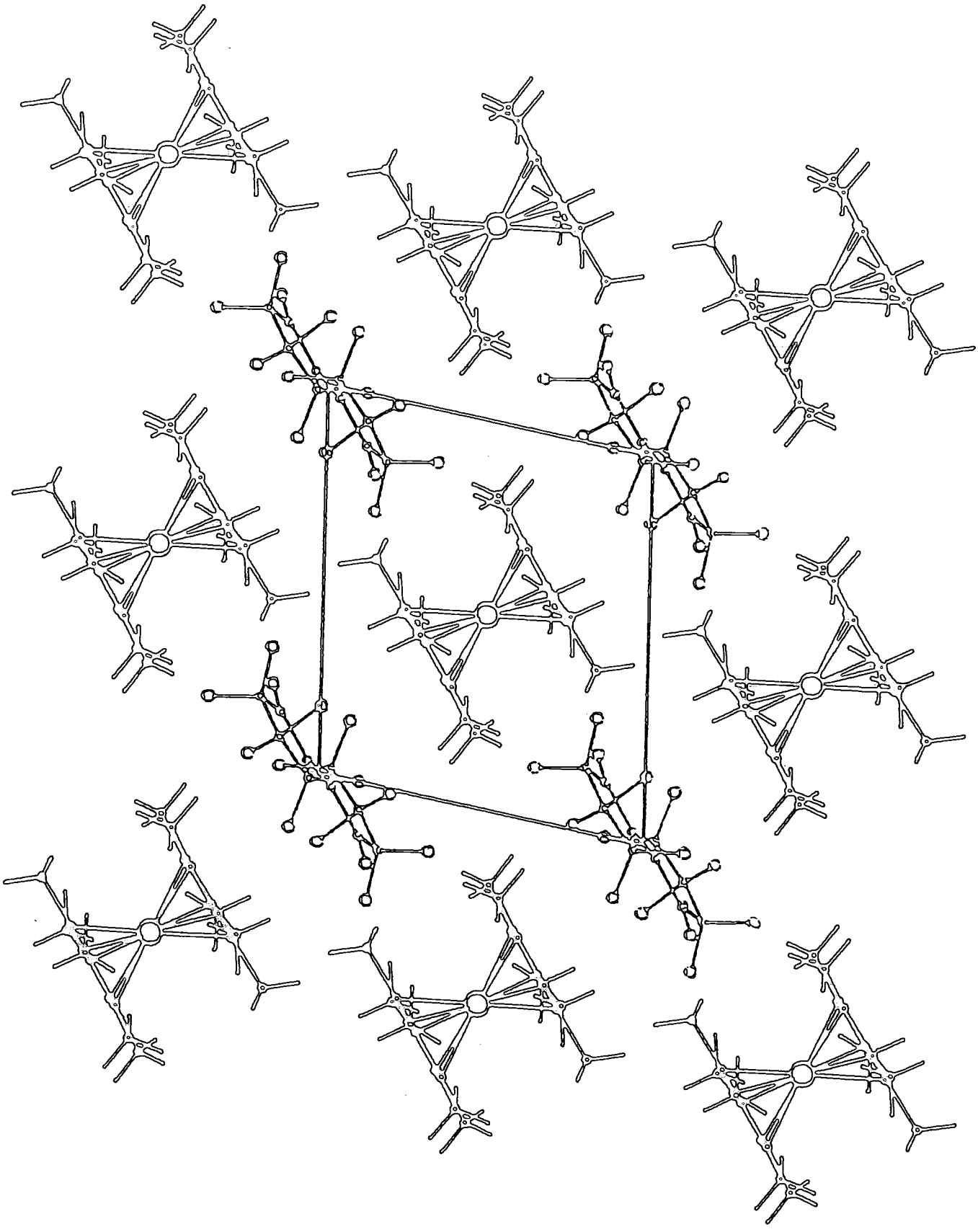
The addition of diene (43) to decamethylferrocene in acetonitrile caused an immediate colour change from orange to dark green indicating the possibility of formation of a CT complex. A very dark green to black crystalline solid could be isolated in 33% yield, which was shown by elemental analysis and IR spectroscopy to be the CT salt $[Fe(C_5Me_5)_2]^{\cdot+}$ $[C_{10}F_{14}]^{\cdot-}$ (155). This had previously been prepared[117] by the reaction of decamethylferrocene and the fluoroalkene perfluorobicyclopentylidene (42). The X-ray crystallographic data of this salt are summarised here (X-ray Plots 2,3,4).

4.2.1.1 X-Ray Crystal Structure of (155)

The structural data for (155) (see X-Ray Plots 2 and 3) indicate a three-dimensional array of alternating radical cations and radical anions in a manner similar to Miller and co-workers' $[Fe(C_5Me_5)_2]^{\cdot+}$ $[TCNE]^{\cdot-}$ complex[209]. However, while this TCNE salt has the donors and acceptors in discrete chains approximately parallel to the major axes of symmetry of the components, when salt (155) is also viewed along the major axis of symmetry of the decamethylferrocenium units, each pair of radical ions is out of register with its neighbouring pairs by approximately half a unit of the radical anion (see X-ray Plot 3) resulting in a secondary structure which does not have any major axis of symmetry along the chains of radical ion pairs. Indeed, if the salt is viewed along a line perpendicular to this major axis, the radical ions also appear in alternating pairs in which each pair is only slightly out of line with the next by a small amount.

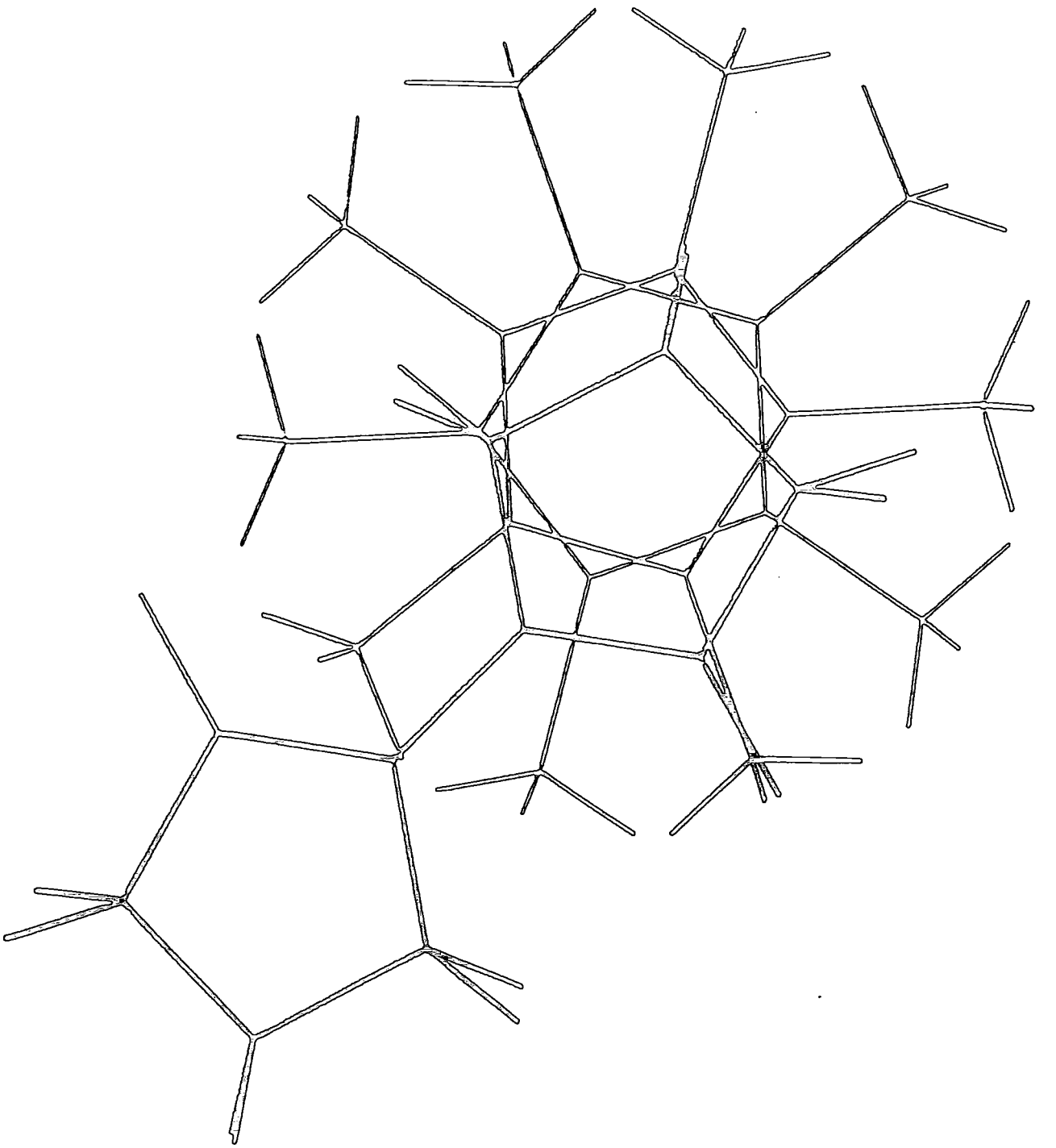
X-ray Plot 2

The solid-state stacking of $[Fe(C_5Me_5)_2]^{\cdot+}$ $[C_{10}F_{14}]^{\cdot-}$



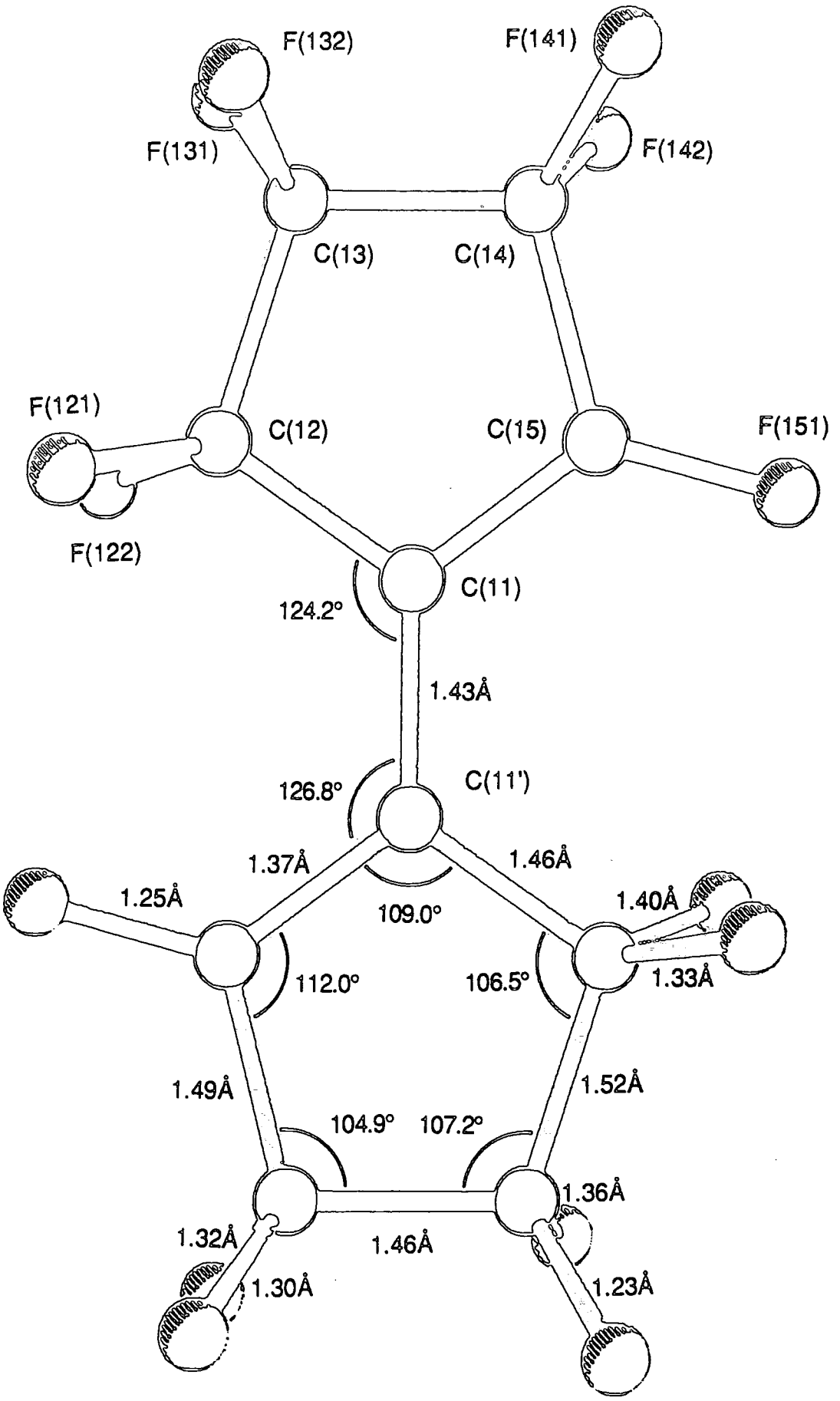
X-ray Plot 3

The relative positioning of the $[Fe(C_5Me_5)_2]^{\cdot+}$ radical cation with respect to the $[C_{10}F_{14}]^{\cdot-}$ radical anion



X-ray Plot 4

The $[C_{10}F_{14}]^{\cdot-}$ radical anion



4.2.1.2 The $[Fe(C_5Me_5)_2]\cdot+$ Radical Cation

The decamethylferrocenium radical cation has its two pentamethylcyclopentadienyl rings arranged in a staggered conformation and possesses a molecular symmetry of D_{5d}. This is the same conformation which has been observed in the X-ray crystal structure analyses for both decamethylferrocene itself[213] and for the decamethylferrocenium radical cation in Miller and co-workers' $[Fe(C_5Me_5)_2]\cdot+$ $[TCNE]\cdot-$ CT complex[209].

4.2.1.3 The $[C_{10}F_{14}]\cdot-$ Radical Anion (156) (X-ray Plot 4)

The perfluorobicyclopentenyl radical anion (156) exists, in this crystal lattice, with a planar structure. The double bonds are arranged in a *trans* conformation with respect to each other and the radical anion possesses C_{2h} symmetry overall.

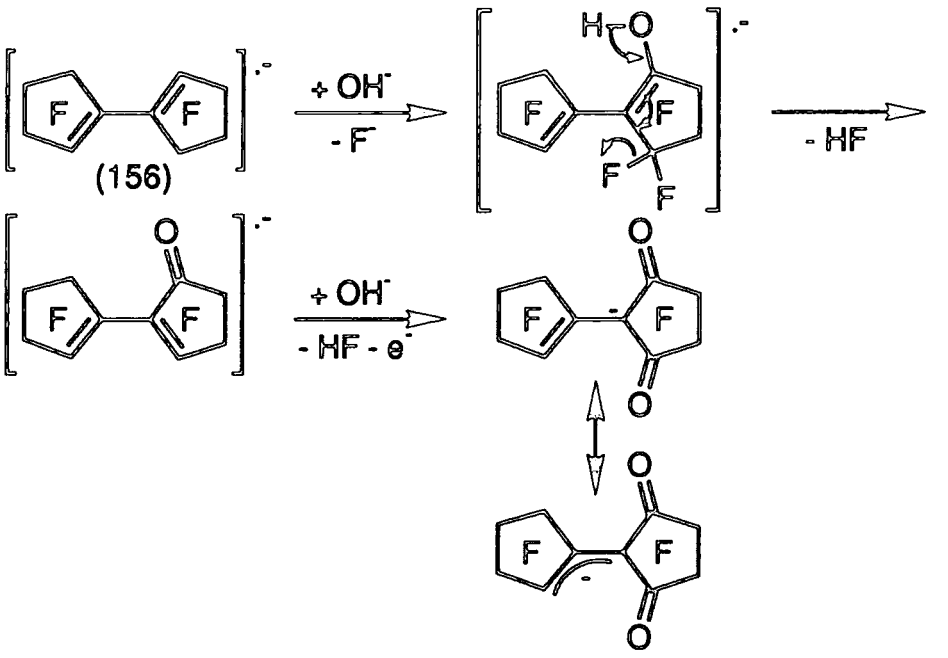
The lengths of the carbon-carbon double bonds [C(11)C(15)] are shown to be about 1.37Å which is longer than the values usually taken for such bonds i.e. 1.31Å in tetrafluoroethene (38)[214] and the carbon-carbon single bond joining the rings [C(11)C(11')] is, at 1.43Å, shorter than for the carbon-carbon single bond found in hexafluoroethane[215] at 1.51Å. This evidence could mean that a certain degree of conjugation occurs between the double bonds.

The length of the vinylic carbon-fluorine bond [C(15)F(151)], at 1.25Å, is notably shorter than the equivalent bond in (38) at 1.31Å[214] but no clear trend appears in the variation of bond lengths for the remaining allylic and aliphatic carbon-fluorine bonds. The geometrical constraints imposed upon the skeleton of the anion by the simultaneous demands of five-membered rings and internal double bonds result in bond angles which deviate significantly from the 108° and 120° ideals. The angle ∠C(12)C(11)C(15) is especially noteworthy in being particularly small at 109.0° for an sp^2 atom.

However, it must be noted that the final *R* value for this X-ray crystal structure analysis is 0.023 (see Appendix 4.2) which is quite high and

represents the effects of thermal vibrations within the molecule. This means that the atomic coordinates are prone to errors which are large enough to make the values of bond lengths and angles subject to a little doubt.

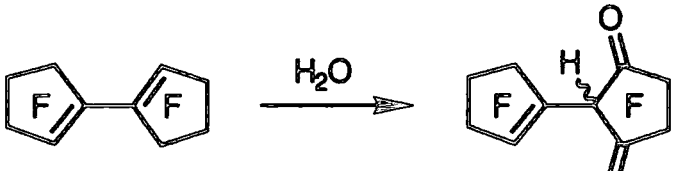
Salt (155) is hygroscopic although the products of hydrolysis are as yet unclear. ^{19}F NMR spectroscopy suggests that the radical anion may be hydrolysed to the diketone anion (157) (Scheme 137).



(156)

(157) (Scheme 137)

This is analogous to the similar hydrolysis of diene (43) to diketone (158)[131] (Scheme 138).



(43) (158) O

(Scheme 138)

A comparison of the ^{19}F NMR data of the resulting salt (159) with those of the sodium salt of (158), (160), also reinforces this idea (Figure 25).

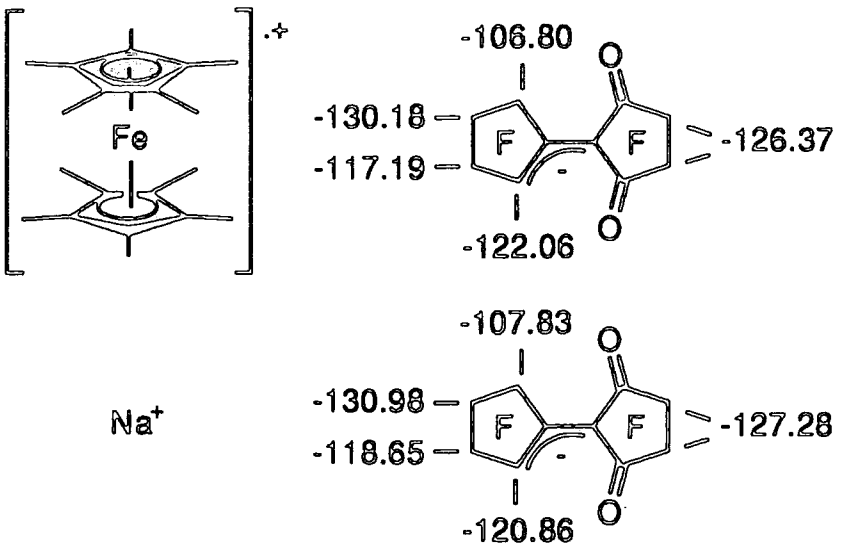


Figure 25. The ^{19}F chemical shifts of salts (159) and (160).

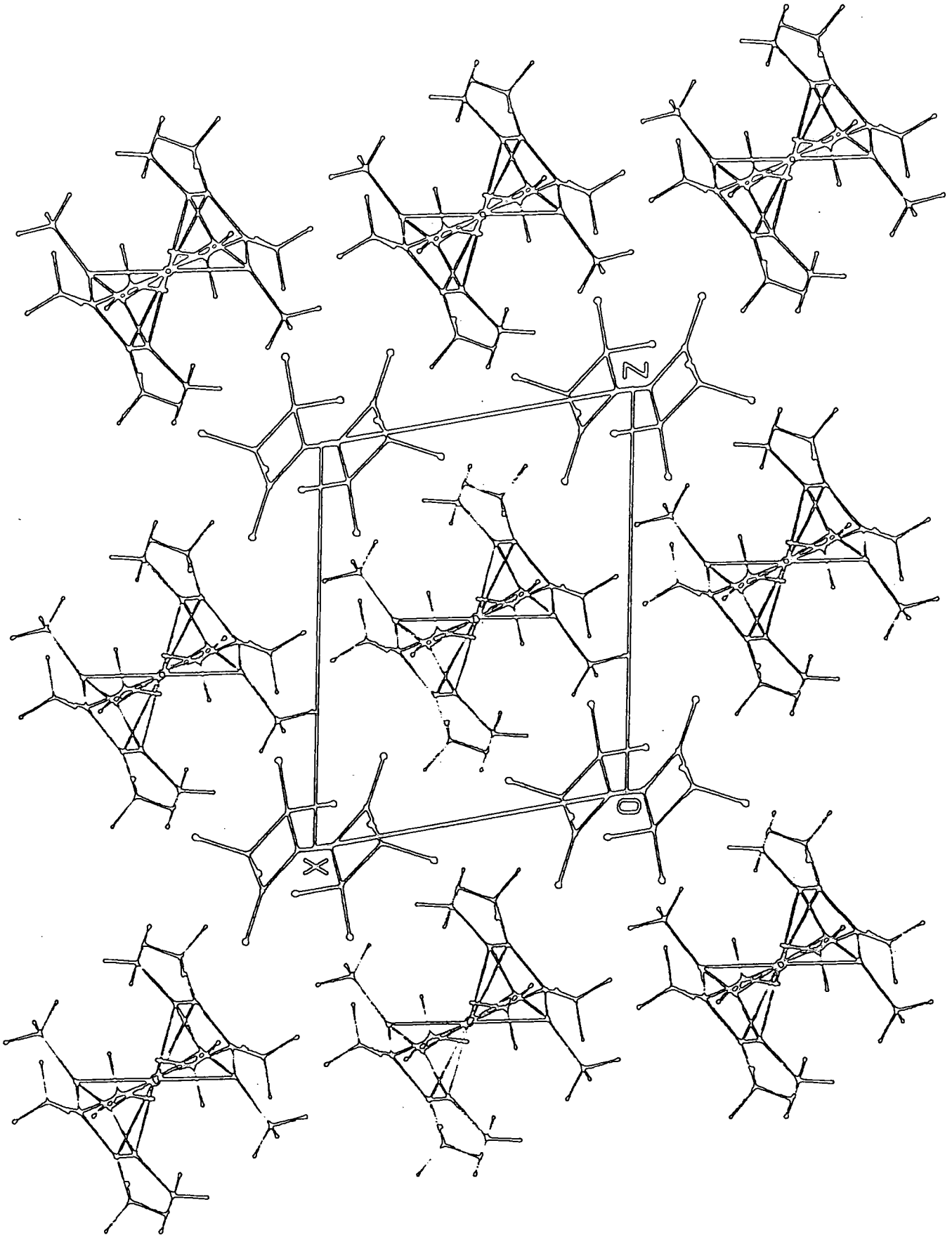
The change in counter cation from sodium to decamethylferrocenium has a notable effect upon the values of the ^{19}F chemical shifts of the anion but the general impression is that the two anions are probably the same.

4.2.2 Reaction of Decamethylferrocene and Diene (46)

The addition of diene (46) to decamethylferrocene in acetonitrile again caused an immediate colour change from orange to dark green indicating the possible formation of a CT salt. Dark green crystals could be isolated from this mixture in 38% yield, which were later identified as the 1:1 CT complex of $[Fe(C_5Me_5)_2]^{\cdot+}$ $[C_8F_{10}]^{\cdot-}$ (161). This salt was the subject of a single crystal X-ray study by Dr. W. Clegg at the University of Newcastle-upon-Tyne and the resulting data are presented here (X-ray Plots 5 and 6).

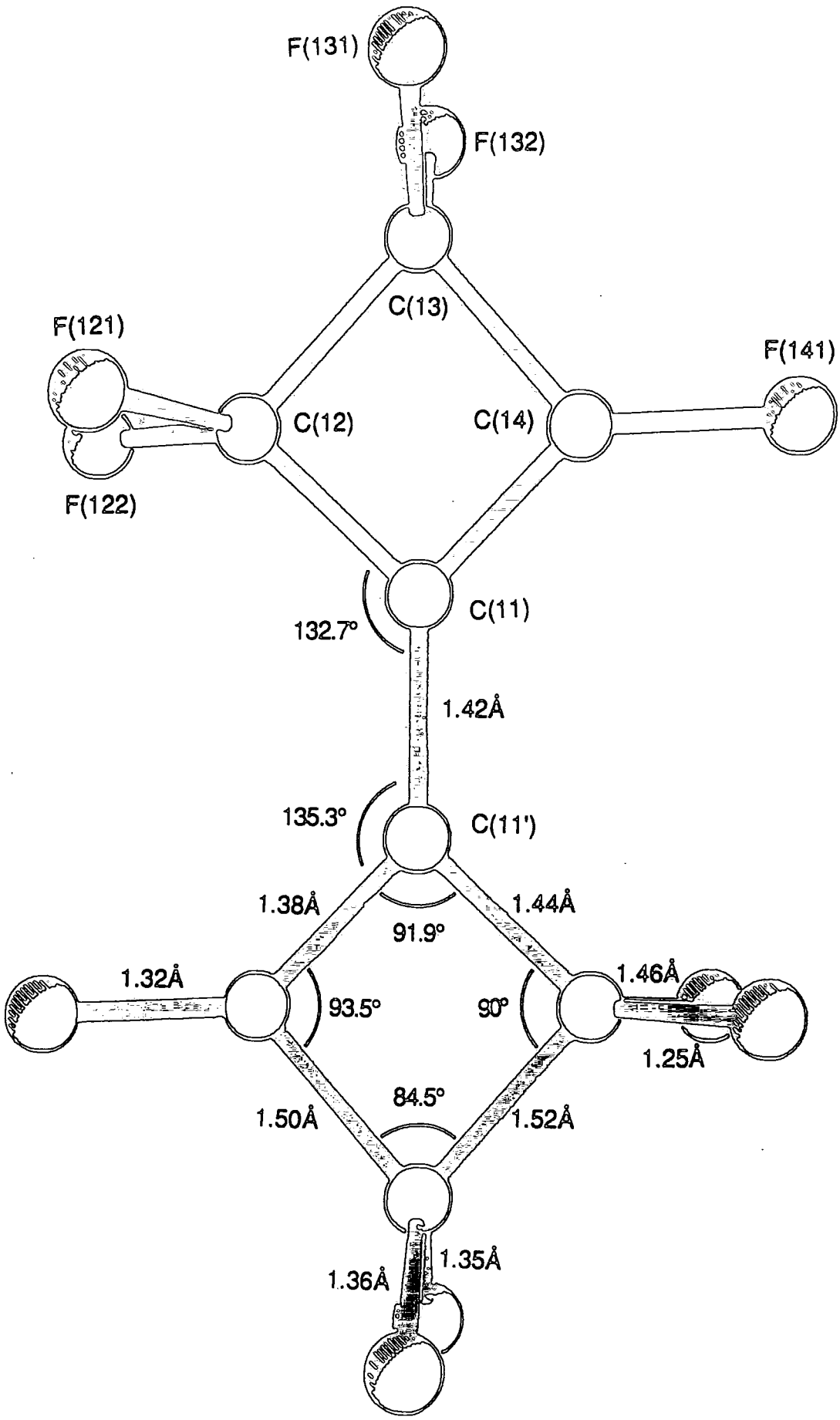
X-ray Plot 5

The solid-state stacking of $[Fe(C_5Me_5)_2]^{\cdot+}$ $[C_8F_{10}]^{\cdot-}$



X-ray Plot 6

The $[C_8F_{10}]^{\cdot-}$ radical anion



4.2.2.1 X-Ray Crystal Structure of (161)

The structural data for (161) (see X-ray Plot 5) are very different to those of both salt (155) and $[Fe(C_5Me_5)_2]^{\cdot+}$ $[TCNE]^{\cdot-}$ [209]. The radical ions lay in two interlocking lattices with the anions skew to the cations. The salt (161) may be viewed along an axis perpendicular to the major axis of symmetry of the decamethylferrocenium radical cations (see X-ray Plot 5; top left to bottom right) and the ions appear in an alternating sequence. No other chains which lie parallel with, or perpendicular to, any major molecular axis of symmetry can be easily envisaged although it can be clearly seen that chains of alternating radical ions can be easily made in which the components are both skew to the axis of these rows such as the one lying in the plane of the page (see X-ray Plot 5; bottom left to top right).

The difference in the solid state structures of this complex with salt (155) is remarkable considering the subtle differences between the dienes (43) and (46). The main conclusion that can be drawn from these results is that it takes only a very small difference in molecular structure to alter the minimum energy stacking arrangements and so change the overall bulk structure.

4.2.2.2 The $[Fe(C_5Me_5)_2]^{\cdot+}$ Radical Cation

The decamethylferrocenium radical cation in this CT salt also possesses D_{5d} symmetry, showing staggered pentamethylcyclopentadienyl rings arranged in that way in order to minimise any possible steric interactions between the methyl groups on opposing rings.

4.2.2.3 The $[C_8F_{10}]^{\cdot-}$ Radical Anion (162) (X-ray Plot 6)

The perfluorobicyclobutenyl radical anion (162) also exhibits a *trans* arrangement with respect to the double bonds and again it possesses C_{2h} symmetry.

The lengths of the carbon-carbon double bonds [C(11)C(14)] are shown to be 1.38Å and the length of the carbon-carbon single bond which

joins the rings [C(11)C(11')] is 1.42Å. These values are almost identical to those in the radical anion $[C_{10}F_{14}]^{\cdot-}$ (156) demonstrating that, once more, only a small degree of conjugation must exist between the double bonds.

The length of the vinylic carbon-fluorine bond [C(14)F(141)] is given as 1.32Å which is a more typical value for such a bond length being very close to the similar bond in (38) at 1.31Å[214]. The remaining carbon-fluorine bonds vary in length depending upon their position on the rings. The most notable difference, from 1.46Å for [C(12)F(121)] to 1.25Å for [C(12)F(122)] is possibly due primarily to interactions with the decamethylferrocenium radical cation.

The perfluorobicyclobutenyl radical anion (162) imposes even more demanding constraints upon the geometry of the carbon skeleton than the perfluorobicyclopentenyl radical anion (156), due to the presence of a highly strained four-membered ring as well as an internal double bond. The resulting bond angles show that it is the angles around the double bond which are forced further from their ideal of 120° than the remaining bonds deviating from their 90° optimum.

It is also worthy of note, here, to point out that the final *R* value for this X-ray crystal structure analysis is 0.017, which is again fairly high and that the values given for the bond lengths and angles are subject to some error.

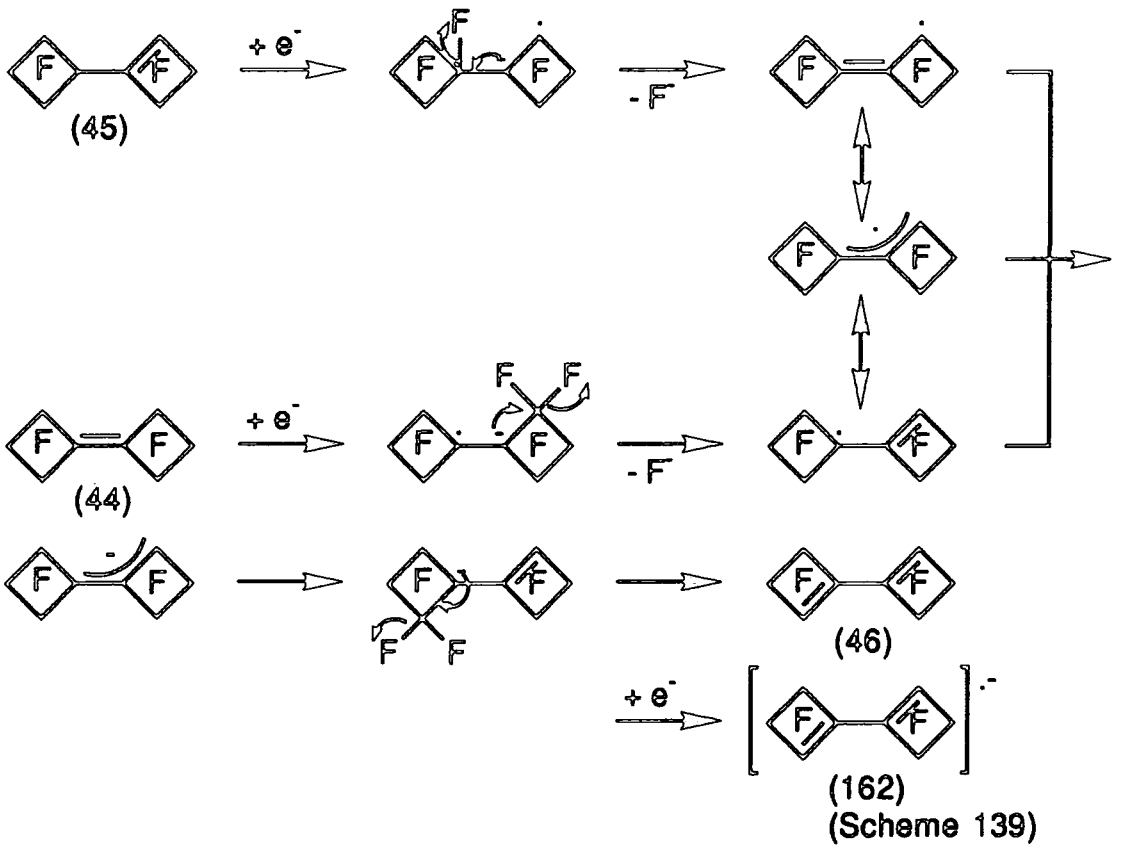
Salt (161) also proved to be hygroscopic but the structures of the complex hydrolysis products have not been elucidated.

4.2.3 Reaction of Decamethylferrocene and Diene (50)

The addition of diene (50) to decamethylferrocene in acetonitrile once again caused an immediate colour change from orange to dark green but no single product could be isolated from the resulting dark green crystals.

4.2.4 Reaction of Decamethylferrocene with Fluoroalkenes (44) and (45)

The addition of a 1:1 mixture of perfluorinated alkenes (44) and (45) to decamethylferrocene in acetonitrile again resulted in an immediate colour change from orange to dark green indicative of the formation of a CT complex with decamethylferrocene. Dark green crystals were isolated from this solution which were subsequently identified as the CT complex $[Fe(C_5Me_5)_2]^{+}$ $[C_8F_{10}]^{-}$ (161), showing that the fluoroalkenes (44) and (45) have undergone a 3e- reduction to give the perfluorobicyclobutenyl radical anion (162) (Scheme 139).



(Scheme 139)

This is analogous to the reduction of perfluorobicyclopenylidene (42) by decamethylferrocene to give the CT salt (155)[117]. This further demonstrates the abilities of decamethylferrocene as a mild reducing agent and the ease of reduction of such fluorinated alkenes (see Chapter 2).

4.2.5 Molecular Magnetic Susceptibility

4.2.5.1 Background

Several theoretical models have been proposed for the stabilisation of ferromagnetic coupling of spins. McConnell first published[216] a model based on Heitler-London spin exchange between positive spin density on one radical and negative spin density on another. He later expanded this model[217] to describe configurational mixing (Hubbard mixing) of a virtual triplet excited state with the ground state for a one-dimensional ...D·+A·-D·+A·-... chain. Breslow and co-workers[218,219,220,221] elaborated upon this idea with the proposal of various highly symmetric hexa-aminobenzene derivatives as approaches to organic ferromagnets. Very high spin multiplicity radicals have also been suggested[222,223] as has ferromagnetic superexchange through a degenerate orbital of a closed-shell molecule or ion[224]. More recently, following the magnetic susceptibility measurements on the $[Fe(C_5Me_5)_2]^{\cdot+}$ $[TCNE]^{\cdot-}$ CT salt[209], Miller and co-workers have developed an extension[225,226,227] which necessitates spin alignment throughout the bulk solid for the stabilisation of bulk ferromagnetism.

Using these theoretical models as a background, current experimental programmes are concentrated on the search for new donors and acceptors[228,229] for the formation of novel molecular ferromagnets.

It may be assumed that, in a compound which is to exhibit ferromagnetic coupling, the virtual charge transfer excitation involves only the highest energy partially occupied molecular orbital (P.O.M.O.). At least one of the stable radicals must possess a non half-filled degenerate P.O.M.O. and the lowest excited state, formed by the virtual charge transfer process, has to have the same spin multiplicity and must mix with the ground state in order to stabilise the ferromagnetically coupled ground state.

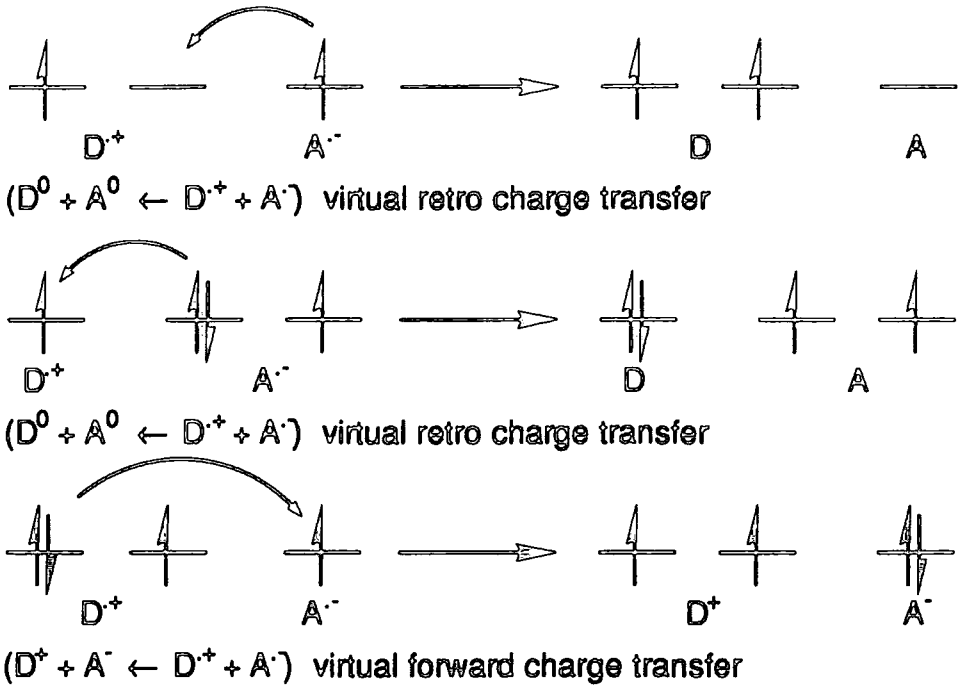


Figure 26. A schematic illustration of the stabilisation of ferromagnetic coupling.

The necessity of a degenerate P.O.M.O. determines[225] that D_{2d}, C_3 or higher symmetry in the radicals is required and that structural or electronic distortions such as the Jahn-Teller effect do not occur. However, accidental or intrinsic degeneracies will suffice.

The X-ray crystal structure analyses performed on the CT salts (155) and (161) have revealed that although the decamethylferrocenium radical cations possess D_{5d} symmetry, both the radical anions (156) and (162) possess a molecular symmetry of C_{2h} (X-ray Plots 4 and 6). These salts can still give a bulk ferromagnet as only one degenerate P.O.M.O. is needed. The magnetic susceptibilities of these two salts were therefore investigated at the University of Cambridge[230].

4.2.5.2 The Theory of Magnetic Susceptibility

All substances exhibit a magnetic moment M upon the application of a magnetic field H which are linked by χ, the magnetic susceptibility per mole thus:

$$\chi = \frac{M}{H} = \frac{\text{Magnetic dipole moment per mole}}{\text{Magnetic field strength}}$$

This total susceptibility can be simply subdivided as:

$$\chi_{tot} = \chi_{core} + \chi_{spin}$$

where χ_{core} is the core diamagnetism, and χ_{spin} is the spin paramagnetism.

χ_{core} is a molecular property, reflecting the response of inner (filled) electronic orbitals and can be estimated from tables of Pascal's constants[231] by adding the contributions from each atom and bonding arrangement within the molecule.

In an insulator which has non-interacting independent spins, χ_{spin} will be due only to localised spins which have a random orientation in zero field but which line up in an applied magnetic field thus inducing a magnetic moment and a positive susceptibility upon the sample. In this case, the effect is that of a Curie paramagnet, which can be described by the Curie expression:

$$\chi_{spin} = C/T$$

where C is the Curie constant that depends upon the number and size of the free spins in the sample and T is the temperature in Kelvin. If the spins have magnetic interactions with each other, such that in zero field, the spins tend to align parallel (ferromagnetically) or antiparallel (antiferromagnetically), then the susceptibility obeys a Curie-Weiss law:

$$\chi_{spin} = C/(T-\theta)$$

where θ is a constant which is positive for ferromagnetic and negative for antiferromagnetic coupling. θ is approximately the temperature at which the

material has a spontaneous magnetic moment and starts to behave like a bulk ferromagnet

The easiest way of observing deviations from Curie law behaviour, is to plot $\{\chi_{spin}T\}$ vs. T on a graph. This plot gives the value of C and thus the effective spin at each temperature, since the Brillouin expression gives:

$$C = \frac{Ng^2\mu_B^2 s(s+1)}{3k_B T} = \frac{N\mu_{eff}^2}{3k_B T}$$

where N is Avogadro's number, g is the Landé factor, μ_B is the Bohr magneton, s is the spin quantum number and k_B is the Boltzmann constant.

A paramagnet will give a constant $\{\chi_{spin}T\}$ with temperature. A ferromagnet will be flat at high temperatures, where thermal fluctuations are most important, but at low temperatures, $\{\chi_{spin}T\}$ will get progressively larger as the susceptibility increases above that of a paramagnet. Similarly at low temperatures $\{\chi_{spin}T\}$ of an antiferromagnet will get progressively smaller.

4.2.5.3 Magnetic Susceptibility Measurements of the Charge Transfer Salts (155) and (161)

The following work was carried out by Margaret Allen under the supervision of Dr. R. Friend at the Cavendish Laboratories of the University of Cambridge and is largely taken from her account which is contained in full in her thesis[230].

The magnetic susceptibilities of randomly oriented crystals of the CT complexes (155) and (161) were measured over a temperature range of 5 to 300K in fields up to 0.9T using a Faraday Balance. Analysis of the field dependence of the susceptibilities at room temperature showed that only very small amounts (<5 ppm by weight) of ferromagnetic impurity were present in the samples. The magnetic susceptibilities of the core electrons were estimated using Pascal's constants to gave $\chi_{TIP} = -248 \times 10^{-6}$ and -211×10^{-6} emu/mol for (155) and (161) respectively. The data shown in Graphs 1, 2 and

3 were corrected for both ferromagnetic impurities and for the core electron contribution.

The susceptibility χ of the salts (155) and (161) proved similar to the response of a Curie-Weiss material, but could be fitted by a single Curie-Weiss law over the whole temperature range. Graph 1 shows $\{\chi_{spin}T\}$ for both (155) and (161); the two compounds show a smaller effective spin (μ_{eff}) at low temperatures. Unfortunately, the low temperature data of (155) are unreliable and much of the decrease in μ_{eff} at low temperatures is spurious.

Salt (161) was well characterised and is shown in more detail on Graphs 2 and 3. Below ~30K the data are comparatively flat, indicating that magnetic coupling between spins is relatively unimportant at low temperatures. (A Curie-Weiss fit in this region gives θ~ -0.2K.) The increase in $\{\chi_{spin}T\}$ with temperature between 30K and 150K is therefore most likely to be due to an increase in the local magnetic moment, and not to antiferromagnetic coupling between the spins. Above 150K, $\{\chi_{spin}T\}$ has a larger value on warming than on cooling, which will probably be due to the crystals having an anisotropic susceptibility. In an applied field, a material with an anisotropic susceptibility will experience a turning force that will try to align the axis with the largest susceptibility parallel to the field direction. The largest force on the crystal is at low temperatures, so the initial cooling data may give the larger susceptibility value and the value at the end of the experiment will approximate to the larger susceptibility direction.

The susceptibility of salt (155) was measured a number of times with different masses of material, and in larger fields than for (161). The susceptibility of each run was markedly different, but had no distinct trend with time, so the change cannot be explained by decomposition of the complex. Again the susceptibility was larger on warming than cooling, which can be explained again by an anisotropic magnetic susceptibility of the crystal. A large jump occurs in one set of data. This measurement was made on a much smaller amount of material, so the jump could be due to one large crystal

suddenly orientating itself in the applied field and causing a large percentage increase in the susceptibility. The decrease in effective moment at low temperatures can be fitted by a Curie-Weiss law with $\theta \sim -2K$, indicating some degree of antiferromagnetic coupling between the spins.

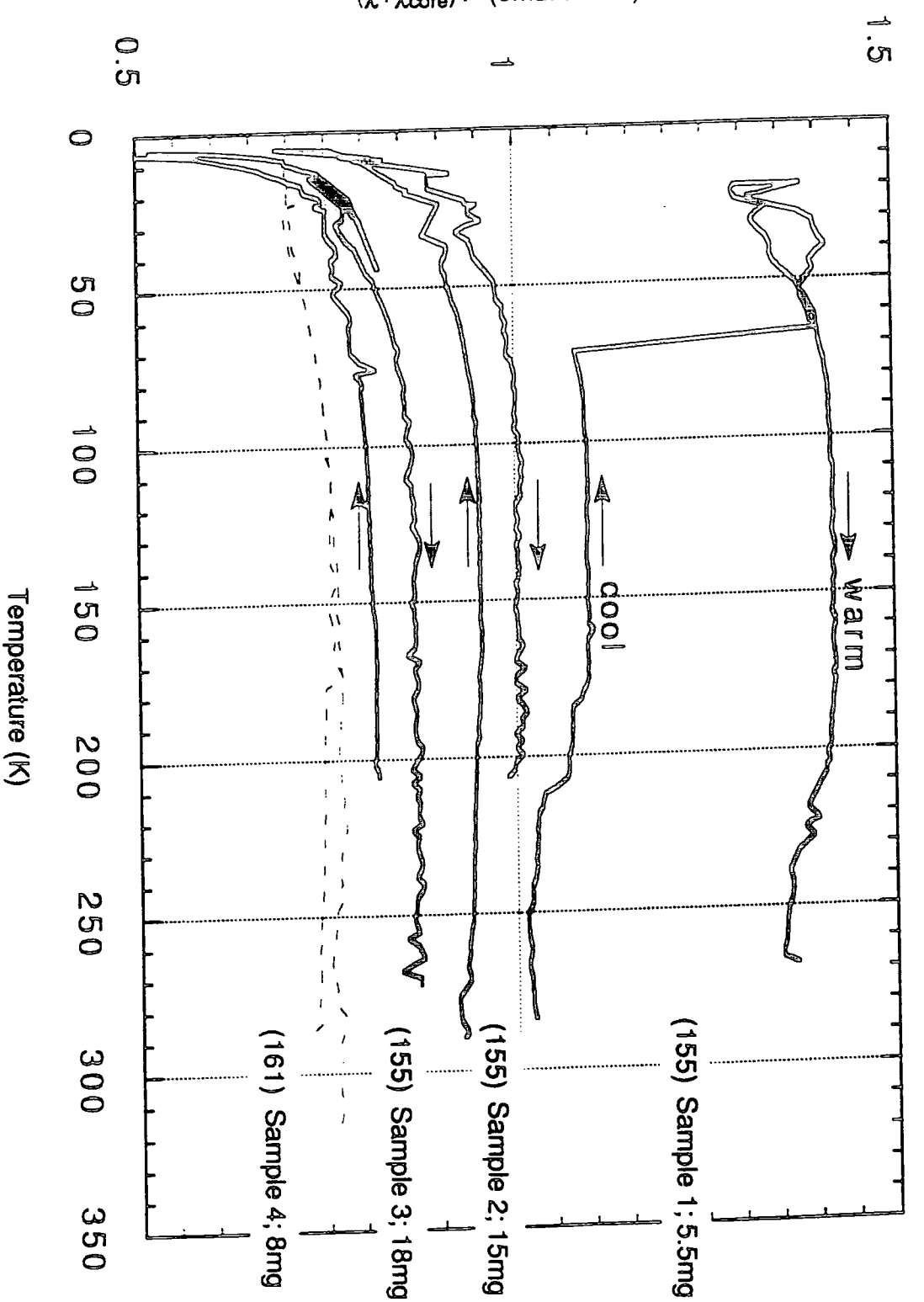
A large anisotropy is predicted in the susceptibility of both compounds from electron spin resonance (ESR) measurements on the $[Fe(C_5Me_5)_2]^{\cdot+}$ radical cation[106:50386h], that give $g_\perp = 4.4\mu_B$ and $g_{||} = 1.3\mu_B$ ($s = 1/2$). The calculated effective moment, μ, for a random collection of $[Fe(C_5Me_5)_2]^{\cdot+}$ radical cations would give $\mu = \{\langle g^2 \rangle s(s+1)\}^{1/2} = 2.95\mu_B$. The moment of the whole complex can be calculated by assuming that the radical anions (156) and (162) have $s = 1/2$ and $g = 2$. Randomly orientated crystals of CT salts (155) and (161) should have an average effective spin of $2.95\mu_B$, although this value could range from the extremes of $4.19\mu_B$ to $2.02\mu_B$ depending upon how the crystals happened to be aligned.

The experimental effective spin ($\mu eff = 2.83\{\chi_{spin}T\}^{1/2}$) at high temperatures range from ~ $2.4\mu_B$ to ~ $3.3\mu_B$ for the salt (155) and is ~ $2.4\mu_B$ for salt (161). These values must be compared with the expected μ_{eff} for these complexes of $2.95\mu_B$. For salt (161), μ_{eff} is close to the value of pure $[Fe(C_5Me_5)_2]^{\cdot+}$ radical cations ($2.38\mu_B$), so it is possible that the radical anion (162) has somehow lost its spin by hydrolysis but tested samples were not returned and the integrity of the complex (161) could not be confirmed. However, the experimental values for both compounds remain well within the potential range of calculated effective spin values given by the anisotropy of g, so it is possible that the crystals were partially aligned in the measured sample.

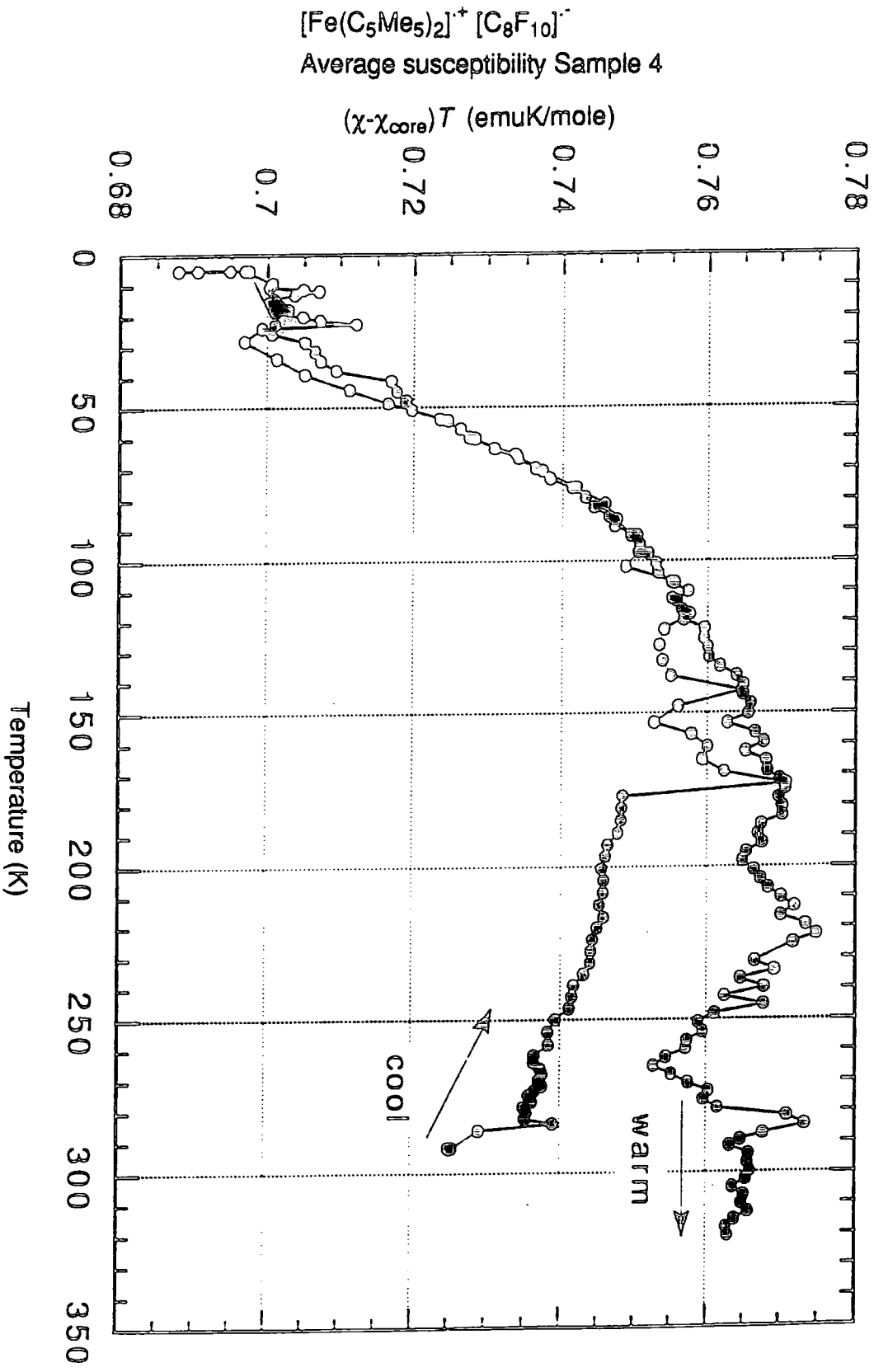
Graph 1

$[Fe(C_5Me_5)_2]^{\cdot+}$ $[C_{10}F_{14}]^{\cdot-}$ and $[Fe(C_5Me_5)_2]^{\cdot+}$ $[C_8F_{10}]^{\cdot-}$

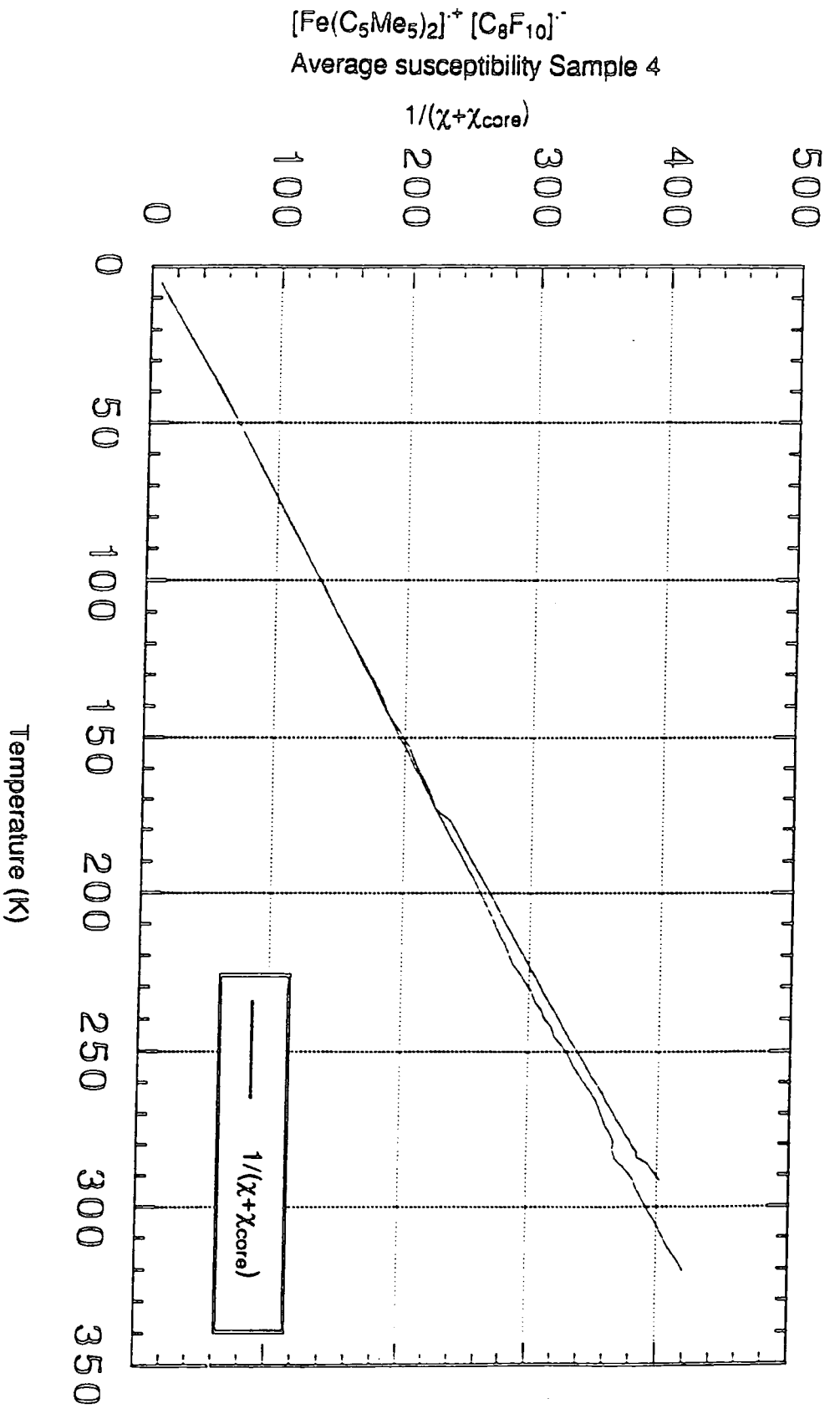
Magnetic susceptibilty



Graph 2


[Fe(C5Me5)2]·+ [C8F10]·-
Average susceptibility Sample 4
(χ-χcore)T (emuK/mole)
0.68
0.7
0.72
0.74
0.76
0.78
0
50
100
150
200
250
300
350
Temperature (K)
cool
warm

Graph 3


[Fe(C5Me5)2]·+ [C8F10]·-
Average susceptibility Sample 4
1/(χ+χcore)
0
100
200
300
400
500
Temperature (K)
0
50
100
150
200
250
300
350
1/(χ+χcore)

4.2.5.4 Conclusions

Both CT salts (155) and (161) behave approximately according to the Curie-Weiss law. The measured effective spin was always larger at the end of an experiment and this is taken as evidence for anisotropy in the susceptibility of the crystals. Further evidence for anisotropy comes from different measurements of complex (155) where there is a large variation in the effective spin (~ 2.4μ_B to ~ 3.3μ_B). These values are well within the calculated range of possible values for partially aligned anisotropic crystals (2.02μ_B to 4.19μ_B) as is the effective spin of (161) at ~2.4μ_B. Complex (155) shows signs of antiferromagnetic coupling with a Weiss constant θ ~ -2K, whereas (161) behaves as a paramagnet with a temperature dependent effective spin that varies from ~ 2.48μ_B at room temperature to ~ 2.37μ_B at low temperatures. The possible antiferromagnetic coupling between the spins in (161) is very small, with a Weiss constant less than -0.2K at low temperatures. No evidence for ferromagnetic coupling was seen in either compound.

INSTRUMENTATION AND EXPERIMENTAL

Instrumentation

Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H NMR spectra were recorded on a Hitachi Perkin-Elmer R-24B (60MHz), a Bruker AC250 (250.13MHz) and a Varian VXR400S (399.95MHz) NMR spectrometer.

^{19}F NMR spectra were recorded on a Varian EM360l (56.45MHz), the Bruker AC250 (235.34MHz) and the Varian VXR400S (376.29MHz) NMR spectrometer.

^{13}C NMR were recorded on the Bruker AC250 (62.9MHz) and the Varian VXR400S (100.58MHz) NMR spectrometer.

Infra Red (IR)

Infra red spectra were recorded on a Perkin-Elmer 577 Grating Spectrophotometer. Solid samples were run as a KBr disc, liquid samples were run as a thin film between two polished KBr plates and gases and very volatile liquids were run in a sealed gas cell fitted with KBr plates.

Mass Spectrometry

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

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. Analysis for halogens were performed as described in the literature[87].

Gas Chromatography (G.C.)

Gas chromatography analysis was carried out on a Hewlett Packard 5890A gas chromatograph fitted with a 25m cross-linked methyl silicone capillary column.

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

Distillation

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

Melting Points

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

Reagents and Solvents

Unless otherwise stated, reagents were used as supplied by the manufacturers. Solvents were predried by standard methods and stored over molecular seive (type 4A) under dry nitrogen. A current of dry nitrogen was maintained for removal of the solvent with a syringe.

Chapter Five

Experimental to Chapter Two

5.1 Cyclic Voltammetry of some Perfluorinated Alkenes and Dienes

All the work on cyclic voltammetry was carried out at the Electricity Research and Development Centre at Capenhurst in Cheshire.

5.1.1 Instrumentation

The cyclic voltammetric studies were carried out in an "H" type preparative electrochemical cell of the type shown in Figure 27.

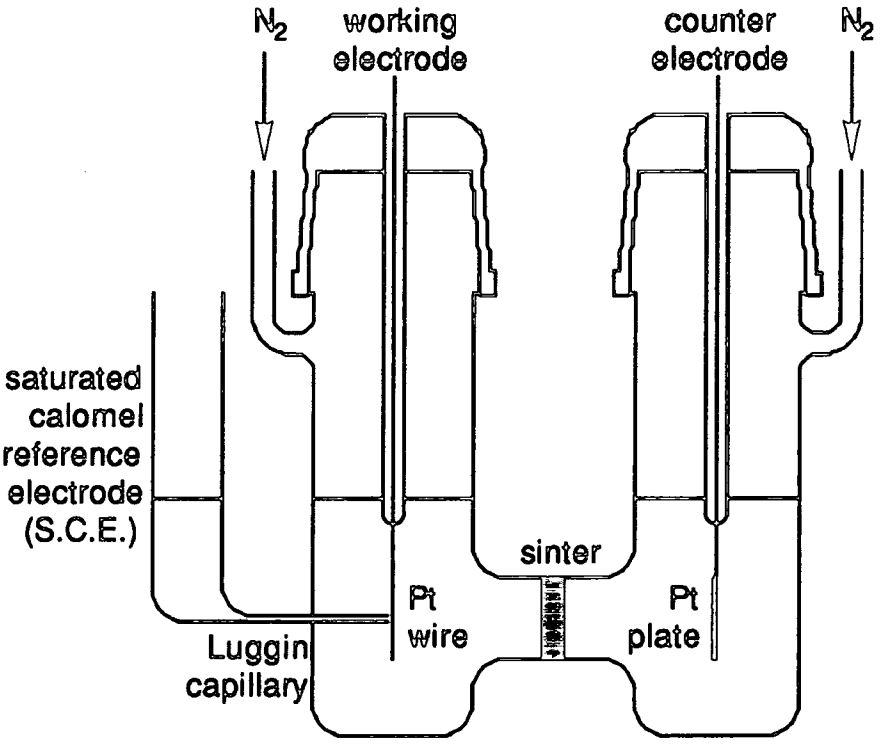


Figure 27. A preparative electrochemical cell.

The ramps were generated by a HI-TEK Instruments Waveform Generator type PPR1, the potential was applied through a Wenking Standard Potentiostat type ST72 and the voltammograms were recorded on a calibrated Advance HR2000 X/Y Recorder.

5.1.2 General Procedure

A solution of tetrabutylammonium tetrafluoroborate (0.5g, 1.52mmol, 30mM) in anhydrous acetonitrile (50 ml) was degassed with dry nitrogen in the cell and the cyclic voltammogram of this electrolyte was recorded as a base line. A few drops of the fluoroalkene under study was added to the working half of the cell and the solution was agitated by the bubbling of dry nitrogen until it became saturated with the fluorocarbon.

In each case, the cyclic voltammogram of the substrate was obtained without agitation between +0.5 V and -2.5 V at 0.1 Vs^{-1} for the first sweep and also for the fifth and thirtieth sweeps to observe the stable cycle. Cyclic voltammograms were also obtained at 1 Vs^{-1} and 0.01 Vs^{-1} after prior agitation to notice if any differences were apparent.

5.2 Sodium Amalgam Reductions

5.2.1 General procedure

As a necessary safety precaution, all the following operations were performed in an efficient fume cupboard due to the toxicity of the substances used and to the potentially explosive nature of the reaction.

Sodium was worked with a knife, under dry diethyl ether, into small lumps of milligram proportions. These lumps were then added, under an atmosphere of dry nitrogen, to some mercury which had been pre-weighed in a Schlenk tube. The open Schlenk tube (still under a flow of dry nitrogen) was then shaken lightly until the sodium dissolved in the mercury. This was repeated usually until the concentration of the amalgams reached about 0.5% w/w. The formation of these amalgams is exothermic and the addition of too much sodium at a time can be dangerous due to the formation of localised hot-spots which can cause the mercury to vaporise. Therefore the Schlenk tube had to be carefully cooled in a flow of cold water at periodic intervals during the amalgam formation in order to prevent this overheating from occurring.

The reactant was carefully added to the amalgam (again under a flow of dry nitrogen) and left to lie on the surface. A rubber blow-off 'Suba-seal' type bung was used to seal the top of the Schlenk tube as a safety measure for these potentially highly exothermic reactions (in order to act as a weak point in the event of an explosion). The tap on the Schlenk tube was then closed to seal it from the nitrogen supply.

The reaction mixture was then vigorously shaken whilst the tube was kept under a flow of cold water to remove any heat generated by the reaction. During the reaction, the consistency of the mercury became very viscous and shaking became difficult. The reaction was judged to have finished when a dark grey dust (sodium fluoride and mercury dust) formed and elemental mercury reformed in the bottom of the Schlenk. The organic product was normally recovered by transferring *in vacuo* into a cold trap.

5.2.2 Reduction of Fluoroalkene (49)

A sodium amalgam (0.58%w/w) (Na 2.9g, 126mmol; Hg 500g) was prepared in a Schlenk tube. The fluoroalkene (49) (20.0g, 50.0mmol) was slowly added to this and the vessel was sealed and shaken vigorously in a stream of cold water until the reaction was complete. The volatile components (15.8g) were transferred *in vacuo* to a cold trap and were found to be an inseparable mixture of two isomeric dienes (50) and (51).

Z,Z-Perfluoro-3,4-dimethylhexa-2,4-diene (50)[81], 74% yield NMR number 1, mass spectrum number 1.

E,Z-Perfluoro-3,4-dimethylhexa-2,4-diene (51)[81], 20% yield NMR number 2, mass spectrum number 2.

For the mixture: b.p. 73-74°C. (Found: C, 26.3; F, 72.8. C_8F_{14} requires C, 26.5; F, 73.5%), IR number 1.

5.2.2.1 Thermal Isomerisation of Diene (50)

A Carius tube was charged with diene (50) (1.0g, 2.8mmol) and then evacuated and sealed. The tube was heated, without agitation, in a furnace at 100°C for three hours. The volatile components (1.0g, 100%) were transferred *in vacuo* to a cold trap and were subsequently shown by ^{19}F NMR spectroscopy and G.C. mass spectrometry to be a mixture (1:1) of diene (50) and:

Perfluoro-1,2,3,4-tetramethylcyclobutene (52)[81]. NMR number 3, mass spectrum number 3.

5.2.2.2 Reduction of Fluoroalkene (49) using Acetonitrile as a Heat Sink

A sodium amalgam (0.50%w/w) (Na 1.4g, 60.9mmol; Hg 280g) was prepared in a Schlenk tube. The fluoroalkene (49) (10.0g, 25.0mmol) and anhydrous acetonitrile (50ml) were added to this and the vessel was sealed and shaken vigorously in a stream of cold water until the reaction was complete. The volatile components were transferred *in vacuo* to a cold trap and allowed to warm to room temperature whereupon water (100ml) was added. The lower fluorocarbon layer (5.8g) was removed and subsequently shown by ^{19}F NMR spectroscopy to be a mixture (23:19:1) of:

Z,Z-Perfluoro-3,4-dimethylhexa-2,4-diene (50) (*ca* 46%) (see Section 5.2.2),

E,Z-Perfluoro-3,4-dimethylhexa-2,4-diene (51) (*ca* 38%) (see Section 5.2.2),

E,E-Perfluoro-3,4-dimethylhexa-2,4-diene (60) (*ca* 2%) NMR number 4; mass spectrum number 4 and some 14% of various unknown fluorinated components.

5.2.2.3 Reaction of Diene Isomers (50) and (51) with Fluoride Ion

A mixture of the diene isomers (50) and (51) (for the mixture 1.0g, 2.8mmol) and dry caesium fluoride (0.5g, 3.3mmol) in anhydrous acetonitrile (30ml) was heated under reflux with continuous stirring for four hours. ^{19}F

NMR spectroscopy showed the presence of only one isomer (50) after this time.

5.2.3 Reduction of Fluoroalkene.(42)

A sodium amalgam (0.55%w/w) (Na 1.0g, 43.5mmol; Hg 180g) was prepared in a Schlenk tube. The fluoroalkene (42) (6.0g, 14.1mmol) was slowly added to this and the vessel was sealed and shaken vigorously in a stream of cold water until the reaction was complete. The volatile components (3.8g) were transferred *in vacuo* to a cold trap after which they were analysed. Diene (43) was purified by crystallising it out at 0°C in a refrigerator.

Perfluorobicyclopent-1,1'-enyl (43)[103], 3.6g, 66%. b.p. 130°C. (Found: C, 31.0; F, 68.5. $C_{10}F_{14}$ requires C, 31.1; F, 68.9%). NMR number 5, IR number 2, mass spectrum number 5.

5.2.4 Reduction of a Mixture of Fluoroalkenes.(44) and (45)

A sodium amalgam (0.46%w/w) (Na 1.1g, 47.8mmol; Hg 240g) was prepared in a Schlenk tube. The isomeric fluoroalkenes (44) and (45) (6.0g, 18.5mmol of the mixture) were slowly added to this and the vessel was sealed and shaken vigorously in a stream of cold water until the reaction was complete. The volatile components (4.5g) were transferred *in vacuo* to a cold trap where they were analysed. Diene (46) was purified by crystallising it out at 0°C in a refrigerator.

Perfluorobicyclobut-1,1'-enyl (46)[46], 4.2g, 79%. b.p. 90-95°C. (Found: C, 33.9; F, 66.2. C_8F_{10} requires C, 33.6; F, 66.4%). NMR number 6, IR number 3, mass spectrum number 6.

5.2.5 Reduction of Haloalkane (61)

A sodium amalgam (0.54%w/w) (Na 0.6g, 26.1mmol; Hg 110g) was prepared in a Schlenk tube. Halocarbon (61) (4.0g, 10.2mmol) was slowly added to this and the vessel was sealed and shaken vigorously in a stream of

cold water until the reaction was complete. The volatile components (3.7g) were transferred *in vacuo* (with additional heating) to a cold trap and were later analysed. The individual components were separated by preparative scale G.C. (10% S.E. 30 column, 80°C).

4-Bromo-3-chlorohexafluorobut-1-ene (62) 0.6g, 21%. (Found: C, 17.1. C_4BrClF_6 requires C, 17.3; Br, 28.8; Cl, 12.8; F, 41.1%). NMR number 7, IR number 4, mass spectrum number 7.

E- and *Z*-4-Bromo-1,3-dichloropentafluorobut-1-ene (63) and (64) 0.3g, 10%. (Found: C, 16.2. $C_4BrCl_2F_5$ requires C, 16.4; Br, 27.2; Cl, 24.1; F, 32.3%). NMR numbers 8 and 9, IR number 5, mass spectrum number 8.

The remaining material was found to compose mainly of starting material.

5.2.6 Reduction of Perfluoro-1,2-cyclobutylcyclobutene (16)

A sodium amalgam (0.50%w/w) (Na 0.4g, 17.4mmol; Hg 80g) was prepared in a Schlenk tube. The fluoroalkene (16) (3.0g, 6.2mmol) was slowly added to this and the vessel was sealed and shaken vigorously in a stream of cold water until the reaction was complete. The volatile components (2.2g 73% recovery) were transferred *in vacuo* to a cold trap but were later shown by ^{19}F NMR spectroscopy and G.C. mass spectrometry to be starting material.

5.2.7 Reduction of Perfluoro-2-methylbicyclo[4.4.0]decane (65)

A sodium amalgam (0.58%w/w) (Na 1.7g, 73.9mmol; Hg 290g) was prepared in a Schlenk tube. The title bicyclic alkane (65) (3.0g, 5.8mmol) was slowly added to this and the vessel was sealed and shaken vigorously in a stream of cold water until the reaction was complete. The volatile components (1.0g 34% recovery) were transferred *in vacuo* to a cold trap but were later shown by ^{19}F NMR spectroscopy and G.C. mass spectrometry to be starting material.

5.2.8 Reduction of Diene (50)

A sodium amalgam (0.52%w/w) (Na 1.0g, 43.5mmol; Hg 190g) was prepared in a Schlenk tube. The diene (50) (5.0g, 13.8mmol) was slowly added to this and the vessel was sealed and shaken vigorously in a stream of cold water until the reaction was complete. The volatile components (3.2g, 64% recovery) were transferred *in vacuo* to a cold trap but were later shown by ^{19}F NMR spectroscopy and G.C. mass spectrometry to be starting material.

5.3 Potassium Amalgam

5.3.1 Reduction of Fluoroalkene (49)

A potassium amalgam (0.40%w/w) (K 0.8g, 20.5mmol; Hg 200g) was prepared in a Schlenk tube. The fluoroalkene (49) (3.2g, 8.0mmol) was slowly added to this and the vessel was sealed and shaken vigorously in a stream of cold water until the reaction was complete. The volatile components (1.6g, 55% yield) were transferred *in vacuo* to a cold trap and were subsequently analysed and found to be an inseparable mixture (3:1) of the two isomeric dienes (50) and (51) (Yields 40% and 12% respectively) (see Section 5.2.2).

5.4 Alkali Metals in Solution

5.4.1 Reduction of Fluoroalkene (49) with Sodium Biphenyl

Sodium (1.2g, 52.2mmol) was heated in toluene (5ml) to reflux temperature when it was stirred vigorously using a high-speed stirrer to make a sand. This was allowed to cool to 5°C and monoglyme (82.5ml) was added. Biphenyl (8.0g, 51.9mmol) in monoglyme (12.5ml) was finally added and the solution was stirred under an atmosphere of dry nitrogen. Fluoroalkene (49) (10.0g, 25.0mmol) was slowly added and the mixture was stirred for thirty minutes. Analysis of the final products by ^{19}F NMR spectroscopy showed only the presence of unreacted fluoroalkene (49).

5.4.2 Reduction of Fluoroalkene (49) by Potassium in HMPA

Under an atmosphere of dry nitrogen, potassium (0.5g, 12.8mmol) was dissolved in HMPA (50g) contained in a Schlenk tube to give a dark blue solution. Fluoroalkene (49) (2.0g, 5.0mmol) was added to this mixture and the tube was sealed and shaken. The colour of the solution changed to yellow and a white powder precipitated out as a lower layer. ^{19}F NMR spectroscopy showed that a complicated mixture of compounds had formed.

Chapter Six

Experimental to Chapter Three

6.1 Preparation of Starting Materials

6.1.1 2,2,2-Trifluoroethylphenylsulphone (143)

6.1.1.1 2,2,2-Trifluoroethyl-*p*-toluenesulphonate

A mixture of trifluoroethanol (50.0g, 500mmol) and *p*-toluenesulphonyl chloride (100.0g, 525mmol) were stirred together in water (225ml) at 40°C. Sodium hydroxide (20.0g, 500mmol) in water (80ml) was added over forty-five minutes whilst keeping the temperature below 50°C. This mixture was left for two hours stirring constantly before 1,4-dioxane (100ml) was added. This was further stirred for three hours and left to stand at room temperature overnight. Ammonia solution (*ca.* 30% w/w) (200ml) was added to the mixture and the resulting crystals were filtered to give crude:

2,2,2-Trifluoroethyl-*p*-toluenesulphonate (88.3g, 70%).

δ_H(250MHz; $CDCl_3$) 2.47 (3H, s, CH_3), 4.35 (2H, q *J* 8.0Hz, CH_2), 7.39 (2H, AB *J* 7.9Hz, Ar-H), 7.82 (2H, AB *J* 7.9Hz, Ar-H); δ_F(235MHz; $CDCl_3$) -74.32 (1F, t *J* 8.0Hz, CF_3).

NMR data in agreement with literature[232]:

δ_H(80MHz; $CDCl_3$) 2.47 (3H, s), 4.36 (2H, q *J* 8.0Hz), 7.39 (2H, d *J* 8.6Hz), 7.83 (2H, d J 8.6Hz).

6.1.1.2 2,2,2-Trifluoroethylphenylsulphide

By using a variation to a literature preparation[233], thiophenol (8.0g, 72.7mmol) was added dropwise to a suspension of sodium hydride (1.8g, 75.0mmol) in DMF (30ml) and stirred for thirty minutes. Over the next thirty minutes, a solution of 2,2,2-trifluoroethyl-*p*-toluene-sulphonate (15.4g, 60.6mmol) in DMF (10ml) was added and this mixture was left stirring for two hours at room temperature. This mixture was poured into water (100ml) in a

separating funnel. The organic products were extracted into diethyl ether (50ml), dried with $MgSO_4$, filtered and purified by distillation to give:

2,2,2-Trifluoroethylphenylsulphide (8.0g, 69%).

δ_H(250MHz; $CDCl_3$) 3.37 (2H, q *J* 10.0Hz, CH_2), 7.1-7.5 (5H, m, Ar-H); δ_F(235MHz; $CDCl_3$) -62.32 (1F, t *J* 10.0Hz, CF_3); m/z 192 (M^+, 100%) and 123 (M^+ -69, 70%).

NMR data in agreement with literature[233]:

δ_H(CCl_4) 3.35 (2H, q *J* 9Hz), 7.1-7.6 (5H, m); δ_F(CCl_4) -65.1 (1F, t *J* 9Hz).

6.1.1.3 2,2,2-Trifluoroethylphenylsulphone (143)

A mixture of 2,2,2-trifluoroethylphenylsulphide (6.0g, 31.2mmol) and potassium dichromate (12.2g, 40.8mmol) in dilute sulphuric acid (200ml, 10% w/w) was stirred at room temperature for three days. The organic components were extracted into dichloromethane (50ml), dried with $MgSO_4$, filtered and the solvent was removed under reduced pressure. The remaining solid was recrystallised from diethyl ether to give:

2,2,2-Trifluoroethylphenylsulphone (143) (4.2g, 60%).

δ_H(250MHz; $CDCl_3$) 3.92 (2H, q *J* 8.9Hz, CH_2), 7.6-8.0 (5H, m, Ar-H); δ_F(235MHz; $CDCl_3$) -61.79 (1F, t *J* 9.0Hz, CF_3); m/z 224 (M^+, 7%) and 141 (M^+ -83, 52%).

NMR data in agreement with literature[234]:

δ_H(60MHz; $CDCl_3$) 3.93 (2H, q), 7.4-8.2 (5H, m).

6.1.2 1,1,1-Trifluoropentan-3-one (146)

6.1.2.1 1-Chloro-1,1-Difluoropentan-3-one

Using a variation of literature preparations[235,236,237], propanoyl chloride (23.0g, 248.7mmol) was added to a stirred suspension of aluminium chloride (34.0g, 255.0mmol) in dichloromethane (250ml) at 0°C. Vinylidene fluoride (150) was added over three hours to this *via* a flexible gas reservoir until no further reaction occurred. The mixture was washed twice with dilute

hydrochloric acid (2 x 250ml 10% w/w) and once with dilute sodium carbonate solution (250ml) before being extracted from water (250ml). The solution was dried with $MgSO_4$ and the solvent distilled off to give:

1-Chloro-2,2-difluoropentan-3-one (17.5g, 45%) b.p.^{15mm} 36-38°C.

δ_H(250MHz; $CDCl_3$) 1.10 (3H, t *J* 7.2Hz, CH_3), 2.58 (2H, q *J* 7.2Hz, $\underline{CH_2}CH_3$), 3.43 (2H, t *J* 12.8Hz, $\underline{CH_2}CF_3$); δ_F(235MHz; $CDCl_3$) -49.19 (1F, t *J* 13.7Hz, CF_2Cl); m/z 156 (M+, 2%) and (M+ +2, 0.6%).

NMR data in agreement with literature[236]:

δ_H($CDCl_3$) 3.40; δ_F($CDCl_3$) -46.6.

6.1.2.2 1,1,1-Trifluoropentan-3-one (146)

1-Chloro-1,1-difluoro-pentan-3-one(10.6g, 67.7mmol) was added to a mixture of dry potassium fluoride (10.0g, 172.4mmol) and benzyl triethylammonium chloride (0.5g, 2.2mmol) in anhydrous acetonitrile (50ml) and left stirring at room temperature for three days. This was then poured into water (150ml) in a separating funnel and the organic products were extracted twice with diethyl ether (2 x 50ml). The extracts were combined, dried with $MgSO_4$ and the ether distilled off. The residue was purified by distillation (b.p. 116°C) to yield:

1,1,1-Trifluoro-pentan-3-one (146) (5.7g, 60%) b.p. 114-116°C.

NMR spectrum number 10; mass spectrum number 9.

6.1.3 *E*-2-*H*-Heptafluorobut-2-ene (151)

By following published syntheses[205,238,239], hexachloro-1,3-butadiene (133g, 0.51mol) was added over a period of three hours to a mixture of anhydrous *N*-methyl-2-pyrrolidinone (750ml) and dry potassium fluoride (270g, 4.7mol) contained in a flask at 200°C which was fitted with an overhead stirrer and a reflux condenser connected to a trap held in liquid air (*ca.* -183°C). The temperature was maintained for a further four hours while the

product was collected in the trap. Fractional distillation of the product (b.p. 8-10°C) gave:

E-2-*H*-Heptafluorobut-2-ene (151) (55.0g, 59%).

δ_F(235MHz; CH_3CN) -57.07 [3F, dd *J* 17.9, 7.4Hz, $CF_3C(H)$], -73.28 [3F, d *J* 9.5Hz, $CF_3C(F)$], -120.17 (1F, ddq *J* 30.7, 18.2, 9.1Hz, CF); m/z 182 (M+, 100%) and (M+ -19, 100%).

NMR data in agreement with literature[205]:

δ_F(neat) -60.4 (3F), -74.6 (3F), -117.2 (1F).

6.2 Reactions with Oxygen Nucleophiles

6.2.1 Diene (50) with Water

A mixture of diene (50) (3.0g, 8.3mmol), water (0.2g, 11.1mmol) and potassium carbonate (2.3g, 16.7mmol), in acetonitrile (20ml) was stirred at room temperature for fourteen days. Volatile material was transfered *in vacuo* to a cold trap and more water (20ml) was added. The lower layer was removed and purified by distillation to yield:

Tetrakis(trifluoromethyl)furan (73)[150,151] (2.3g, 54%).

b.p. 101-103°C (lit.: 104-105°C[150]); NMR number 11; IR number 6; mass spectrum number 10.

6.2.2 Diene (50) with Phenol

A mixture of diene (50) (5.0g, 13.8mmol), freshly sublimed phenol (1.9g, 20.2mmol), and dry potassium fluoride (4.8g, 82.8mmol) in anhydrous acetonitrile (75ml) was stirred at room temperature for seven days. This was then poured into 200ml of water in a separating funnel. The organic products were extracted using diethyl ether (100ml), dried with $MgSO_4$, filtered and the solvent was removed using rotary evaporation. The more volatile components were separated from the resulting oil by distillation (b.p.^{10mm} 52-54°C) (2.8g, 46%) and shown to be a 38:6:5:1 mixture of:

Z,Z-2-Phenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (74).

NMR number 12; mass spectrum number 11,

Z,E-2-Phenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (75).

NMR number 13; mass spectrum number 12,

E,E-2-Phenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (76).

NMR number 14; mass spectrum number 13 and

E,Z-2-Phenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (77).

NMR number 15; mass spectrum number 14.

For the mixture: (Found: C, 38.7; H, 1.1; F, 56.9. $C_{14}H_5F_{13}O$ requires C, 38.6; H, 1.2; F, 56.6%); IR number 7.

The residual waxy solid was purified by sublimation onto a cold finger and recrystallisation from diethyl ether and *n*-hexane (3.3g, 47%) and shown to be a 5:4:1 mixture of:

Z,Z-2,5-Diphenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (78).

NMR number 16; mass spectrum number 15,

E,Z-2,5-Diphenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (79).

NMR number 17; mass spectrum number 16 and

E,E-2,5-Diphenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (80).

NMR number 18; mass spectrum number 17.

For the mixture: (Found: C, 47.0; H, 2.0; F, 44.2. $C_{20}H_{10}F_{12}O_2$ requires C, 47.1; H, 2.0; F, 44.7%); IR number 8.

6.2.3 Diene (43) with Phenol

A mixture of diene (43) (1.0g, 2.6mmol), some freshly sublimed phenol (0.4g, 4.3mmol) and dry potassium fluoride (1.0g, 17.2mmol) in anhydrous acetonitrile (20ml) was stirred at room temperature for seven days. This was then poured into water (100ml) in a separating funnel and the organic components were extracted using diethyl ether (50ml), dried with $MgSO_4$, filtered and the solvent was removed using rotary evaporation. The residue was purified by sublimation onto a cold finger to give:

2,2'-Diphenoxy-perfluorobicyclopent-1,1'-enyl (81) (0.8g, 58%).

m.p. 79-82°C (Found: C, 49.8; H, 2.1, F, 43.1. $C_{22}H_{10}F_{12}O_2$ requires C, 49.5; H, 1.9; F, 42.7%); NMR number 19; IR number 9; mass spectrum number 18.

6.2.4 Fluorinated Epoxides

6.2.4.1 Epoxidation of Diene (50)

A mixture of the diene (50) (5.0g, 13.8mmol), dry calcium hypochlorite (6.8g, 47.6mmol) and anhydrous acetonitrile (20ml) was stirred at room temperature for seven days. Volatile material was transferred *in vacuo* to a cold trap, washed with water (20ml) and the subsequent lower layer removed and subsequently identified as:

Perfluoro-2,2',3,3'-tetramethyl-bi-2,2'-oxiranyl (86) (3.0g, 55%).

(Found: C, 24.2; F, 68.1. $C_8F_{14}O_2$ requires C, 24.4; F, 67.5%.) NMR number 20; IR number 10; mass spectrum number 19.

6.2.4.2 Attempted Epoxidation of Diene (43)

A mixture of the diene (43) (1.0g, 2.6mmol), dry calcium hypochlorite (1.3g, 9.1mmol) and anhydrous acetonitrile (5ml) was stirred at room temperature for seven days. Volatile material was transferred *in vacuo* to a cold trap and shown by ^{19}F NMR spectroscopy to be a complicated mixture. The mixture could not be purified and was not pursued further.

6.2.4.3 Attempted Epoxidation of Diene (46)

A mixture of the diene (46) (1.0g, 3.5mmol), dry calcium hypochlorite (1.7g, 11.9mmol) and anhydrous acetonitrile (10ml) was stirred at room temperature for fourteen days. ^{19}F NMR spectroscopy showed the presence of several compounds at this time but after heating the mixture under reflux for two hours most of the resonances had disappeared only to be converted to: Perfluoro-2,2'-dichloro-bicyclobut-1,1'-enyl (88)[15] (57% by NMR integration only).

NMR number 21. This material was not isolated from solution.

6.2.4.4 Isomerisation of Diepoxide (86)

A Carius tube was charged with diepoxide (86) (1.0g, 2.54mmol) and dry caesium fluoride and subsequently heated in a furnace at 200°C for twenty-four hours. Volatile material was transfered *in vacuo* to a cold trap and was found to be either:

Perfluoro-1,3,4,6-tetramethyl-2,5-dioxabicyclo[2.2.0]hexane (90) or Perfluoro-1,2,4,5-tetramethyl-3,6-dioxabicyclo[3.1.0]hexane (91) (0.8g, 80%). (Found: C, 24.2; F, 68.3. $C_8F_{14}O_2$ requires C, 24.4; F, 67.5%); NMR number 22; IR number 11; mass spectrum number 20.

6.3 Reactions with Sulphur Nucleophiles

6.3.1 Diene (50) with Potassium Sulphide

A mixture of diene (50) (10.0g, 27.6mmol) and dry potassium sulphide (4.5g, 40.9mmol) in anhydrous DMF (25ml) was stirred at room temperature for fourteen days. Volatile material was transfered *in vacuo* to a cold trap and water (25ml) was added. The lower layer was removed and subsequent analysis (^{19}F NMR spectroscopy and G.C. mass spectrometry) demonstrated the presence of a mixture (18:7) of thiophene derivative (92) and furan derrivative (73). Distillation of this mixture afforded:

Tetrakis(trifluoromethyl)thiophene (92)[166] (3.7g, 38%).

b.p. 134-135°C (lit.: 134-135°C[166]); NMR number 23; IR number 12; mass spectrum number 21.

6.3.2 Diene (50) with Thiourea

A mixture of diene (50) (2.0g, 5.5mmol) and thiourea (0.5g, 6.6mmol) in anhydrous acetonitrile (20ml) was heated under reflux overnight with continuous stirring. Volatile material was then transfered *in vacuo* to a cold

trap and water (30ml) was added. The lower layer was removed and purified by distillation to give:

Tetrakis(trifluoromethyl)thiophene (92) (1.0g, 51%) (see Section 6.3.1).

6.3.3 Diene (50) with Sodium Thiophenate

To a stirred suspension of sodium hydride (0.2g, 8.3mmol) in DMF (20ml), thiophenol (0.9g, 8.2mmol) was slowly added and the solution was left at room temperature for thirty minutes. The diene (50) (2.0g, 5.5mmol) was then added and was allowed to stir for two hours. This mixture was poured into slightly alkaline water (100ml) in a separating funnel and the organic components were extracted into diethyl ether (50ml), dried with $MgSO_4$, filtered and the ether was distilled off. The resulting solid was purified by sublimation onto a cold finger and recrystallisation from acetone (1.3g, 59%) to give a 45:40:15 mixture of:

E,Z-2,5-Dithiophenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (94).

NMR number 24; mass spectrum number 22,

Z,Z-2,5-Dithiophenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (95).

NMR number 25; mass spectrum number 23 and

E,E-2,5-Dithiophenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (96).

NMR number 26; mass spectrum number 24.

For the mixture: (Found: C, 44.0; H, 2.2; F, 41.5; S, 13.7. $C_{20}H_{10}F_{12}S_2$ requires C, 44.3; H, 1.9; F, 42.0; S, 11.8%); IR number 13.

6.4 Reactions with Nitrogen Nucleophiles

6.4.1 Diene (50) with Ammonia

A mixture of the diene (50) (10.0g, 27.6mmol) and dry potassium fluoride (9.8g, 169.0mmol) in anhydrous THF (50ml) was stirred for seven days at room temperature while ammonia (2.0g, 117.6mol) was introduced to the flask *via* a flexible gas reservoir. The mixture was filtered and the filtrate washed with more THF (50ml). The solutions were combined and the solvent

was removed under reduced pressure. Chromatography on alumina with dichloromethane as the eluent yielded:

Z,Z-2,5-Diamino-perfluoro-3,4-dimethyl-hexa-2,4-diene (101) (1.5g, 16%).

m.p. 21-23°C (Found: C, 26.7; H, 1.1; F, 66.1; N, 8.0. $C_8H_4F_{12}N_2$ requires C, 27.0; H, 1.1; F, 64.0; N, 7.9%); NMR number 27; IR number 14; mass spectrum number 25.

The remaining solid was separated by Kugelrohr distillation to give:

2,4,5-Tris(trifluoromethyl)-3-cyano-pyrrole (102) (1.6g, 20%).

m.p. 169-171°C (Found: C, 32.4; H, 0.4; F, 58.7; N, 8.0. $C_8HF_9N_2$ requires C, 32.5; H, 0.3; F, 57.7; N, 9.5%); NMR number 28; IR number 15; mass spectrum number 26 and

2,5-Diamino-3,4-dicyano-1,1,1,6,6,6-hexafluorohex-2,4-diene (103) (0.7g, 10%).

m.p. 207-209°C (dec.) (Found: C, 35.1; H, 1.4; F, 41.2; N, 20.4. $C_8H_4F_6N_4$ requires C, 35.6; H, 1.5; F, 42.2; N, 20.7%); NMR number 29; IR number 16; mass spectrum number 27.

6.4.2 Diene (50) with Aniline using Caesium Fluoride as a Base

A mixture of diene (50) (3.0g, 8.3mmol), freshly distilled aniline (1.5g, 16.1mmol) and dry caesium fluoride (3.9g, 25.7mmol) in anhydrous acetonitrile (50ml) was stirred at room temperature for seven days. This was then poured into water (150ml) in a separating funnel. The organic products were extracted twice with diethyl ether (2 x 50ml). The ethereal solutions were combined, dried with $MgSO_4$, filtered and the solvent removed under reduced pressure. Sublimation of the solid residue onto a cold finger yielded:

1-Phenyl-tetrakis(trifluoromethyl)pyrrole (108)[177] (2.5g, 72%).

m.p. 99-100°C (lit.: 98-99°C[177]); (Found: C, 40.4; H, 1.0; F, 54.7; N, 3.2. $C_{14}H_5F_{12}N$ requires C, 40.5; H, 1.2; F, 54.9; N, 3.4%); NMR number 30; IR number 17; mass spectrum number 28.

6.4.3 Diene (50) with Aniline using Potassium Fluoride as a Base

A mixture of diene (50) (3.0g, 8.3mmol), freshly distilled aniline (1.5g, 16.1mmol) and dry potassium fluoride (2.0g, 34.5mmol) in anhydrous acetonitrile (50ml) was stirred at room temperature for fourteen days. This was then poured into water (150ml) in a separating funnel. The organic products were extracted twice with diethyl ether (2 x 50ml). The ethereal solutions were combined, dried with $MgSO_4$, filtered and the solvent removed under reduced pressure. Sublimation of the solid residue onto a cold finger yielded: 1-Phenyl-tetrakis(trifluoromethyl)pyrrole (108) (2.2g, 63%) (see Section 6.4.2). The remaining solid was purified by recrystallisation from diethyl ether to give: 1-*H*-1-Phenyl-2,3,4-tris(trifluoromethyl)pyrrolo[3,2-*c*]quinoline (109) (0.3g, 8%).

m.p. 229-230°C (Found: C, 53.7; H, 2.0; F, 39.7; N; 6.0. $C_{20}H_9F_9N_2$ requires C, 53.6; H, 2.0; F, 38.1; N, 6.2%); NMR number 31; IR number 18; mass spectrum number 29.

6.4.4 Diene (50) with 4-Substituted Anilines

6.4.4.1 With *N,N*-Dimethyl-4-aminoaniline

A mixture of diene (50) (3.0g, 8.3mmol), *N,N*-dimethyl-4-aminoaniline (2.2g, 16.5mmol) and dry potassium fluoride (2.0g, 34.5mmol) in anhydrous acetonitrile (50ml) was stirred at room temperature for two days. This was then poured into water (150ml) in a separating funnel. The organic products were then extracted twice with diethyl ether (2 x 50ml). The ethereal solutions were combined, dried with $MgSO_4$, filtered and the solvent removed under reduced pressure. Sublimation onto a cold finger yielded: 1-(4'-Dimethylaminophenyl)-tetrakis(trifluoromethyl)pyrrole (111) (1.7g, 45%).

m.p. 101-103°C. (Found: C, 42.0; H, 2.3; F, 50.1; N, 5.9. $C_{16}H_{10}F_{12}N_2$ requires C, 41.9; H, 2.2; F, 49.8; N, 6.1%); NMR number 32; IR number 19; mass spectrum number 30.

6.4.4.2 With 4-Methoxyaniline

A mixture of diene (50), (3.0g, 8.3mmol), freshly sublimed 4-methoxyaniline (2.0g, 16.3mmol), and dry potassium fluoride (2.0g, 34.5mmol) in anhydrous acetonitrile (50ml) was stirred at room temperature for seven days. This was then poured into water (150ml) in a separating funnel. The organic products were then extracted with diethyl ether (50ml) which was dried with $MgSO_4$, filtered and the solvent removed under reduced pressure. Sublimation of the solid residue onto a cold finger yielded:

1-(4'-Methoxyphenyl)-tetrakis(trifluoromethyl)pyrrole (112) (2.6g, 71%).

m.p. 59-61°C. (Found: C, 40.2; H, 1.6; F, 50.8; N, 2.7. $C_{15}H_7F_{12}NO$ requires C, 40.5; H, 1.6; F, 51.2; N, 3.1%); NMR number 33; IR number 20; mass spectrum number 31.

The remaining solid was purified by recrystallisation from acetone/water.to give:

1-*H*-1-(4'-Methoxyphenyl)-2,3,4-tris(trifluoromethyl)-8-methoxy-pyrrolo[3,2-*c*]-quinoline (113) (0.5g, 12%).

m.p. 200-201°C. (Found: C, 51.9; H, 2.5; F, 33.7; N, 5.3. $C_{22}H_{13}F_9N_2O_2$ requires C, 52.0; H, 2.6; F, 33.6; N, 5.5%); NMR number 34; IR number 21; mass spectrum number 32.

6.4.4.3 With 4-Fluoroaniline

A mixture of diene (50), (3.0g, 8.3mmol), some 4-fluoroaniline (1.8g, 16.2mmol), and dry potassium fluoride (2.0g, 34.5mmol) in anhydrous acetonitrile (50ml) was heated under reflux for four hours with continuous stirring. This was poured into water (150ml) in a separating funnel and acidified with hydrochloric acid. The organic products were then extracted with diethyl ether (50ml), dried with $MgSO_4$, filtered and the solvent removed under reduced pressure. Sublimation onto a cold finger yielded:

1-(4'-Fluorophenyl)-tetrakis(trifluoromethyl)pyrrole (114) (0.5g, 14%).

m.p. 174-178°C. (Found: C, 38.6; H, 0.9; F, 57.5; N, 3.2. $C_{14}H_4F_{13}N$ requires C, 38.8; H, 0.9; F, 57.0; N, 3.2%). N.M.R. number 35; IR number 22; mass spectrum number 33.

The remaining solid was purified by recrystallisation from acetone/water.to give:

1-*H*-1-(4'-Fluorophenyl)-2,3,4-tris(trifluoromethyl)-8-fluoro-pyrrolo[3,2-*c*]-quinoline (115) (0.5g, 12%).

m.p. 217-218°C. (Found: C, 49.7; H, 1.3; F, 42.5; N, 5.6. $C_{20}H_7F_{11}N_2$ requires C, 49.6; H, 1.5; F, 43.2; N, 5.8%). N.M.R. number 36; IR number 23; mass spectrum number 34.

6.4.4.4 With 4-Chloroaniline

A mixture of diene (50) (3.0g, 8.3mmol), freshly sublimed 4-chloro-aniline (2.1g, 16.5mmol) and dry potassium fluoride (2.0g, 34.5mmol) in anhydrous acetonitrile (50ml) was heated under reflux for three hours with continual stirring. This was then poured into water (150ml) in a separating funnel. The organic products were than extracted twice with diethyl ether (2 x 50ml). The ethereal solutions were combined, dried with $MgSO_4$, filtered and the solvent removed under reduced pressure. Chromatography on silica gel with light petroleum (b.p. 40-60°C), diethyl ether and methanol (90:9:1) as the eluent followed by recrystallisation from *n*-hexane/diethyl ether yielded:

1-(4'-Chlorophenyl)-tetrakis(trifluoromethyl)pyrrole (116) (0.3g, 7%).

m.p. 136-137°C (Found: C, 36.9; H, 0.8; Cl, 7.2; F, 50.0; N; 2.9. $C_{14}H_4ClF_{12}N$ requires C, 37.4; H, 0.9; Cl, 7.9; F, 50.7%); NMR number 37; IR number 24; mass spectrum number 35.

6.4.4.5 With 4-Nitroaniline

A mixture of diene (50) (3.0g, 8.3mmol), freshly sublimed 4-nitroaniline (2.3g, 16.7mmol) and dry potassium fluoride (2.0g, 34.5mmol) in anhydrous acetonitrile (50ml) was heated under reflux for four hours with continual stirring. This was then poured into water (150ml) in a separating funnel. The organic products were then extracted twice with diethyl ether (2 x 50ml). The ethereal solutions were combined, dried with $MgSO_4$, filtered and the solvent removed under reduced pressure. Chromatography on silica gel with light petroleum (b.p. 40-60°C), diethyl ether and methanol (90:9:1) followed by recrystallisation from diethyl ether yielded:

1-(4'-Nitrophenyl)-tetrakis(trifluoromethyl)pyrrole (117) (0.3g, 9%).

m.p. 171-172°C. (Found: C, 35.9; H, 0.7; F, 48.8; N, 5.9. $C_{14}H_4F_{12}N_2O_2$ requires C, 36.5; H, 0.9; F, 49.5; N, 6.1%.); NMR number 38; IR number 25; mass spectrum number 36.

6.4.5 Diene (50) with 2-Methoxyaniline

A mixture of diene (50), (3.0g, 8.3mmol), some 2-methoxyaniline (2.0g, 16.3mmol), and dry potassium fluoride (2.0g, 34.5mmol) in anhydrous acetonitrile (50ml) was heated under reflux overnight with continuous stirring. This was poured into water (150ml) in a separating funnel and acidified with hydrochloric acid. The organic products were then extracted with diethyl ether (50ml), dried with $MgSO_4$, filtered and the solvent removed under reduced pressure. Sublimation onto a cold finger yielded:

1-(2'-Methoxyphenyl)-tetrakis(trifluoromethyl)-pyrrole (118) (0.5g, 14%).

m.p. 94-96°C. (Found: C, 41.0; H, 1.6; F, 50.3; N, 3.1. $C_{15}H_7F_{12}NO$ requires C, 40.5; H, 1.6; F, 51.2; N, 3.1%). N.M.R. number 39; IR number 26; mass spectrum number 37.

The remaining solid was purified by recrystallisation from acetone/water to give:

1-*H*-1-(2'-Methoxyphenyl)-2,3,4-tris(trifluoromethyl)-6-methoxy-pyrrolo[3,2-*c*]-quinoline (119) (0.6g, 14%).

m.p. 201-202°C. (Found: C, 51.7; H, 2.4; F, 33.2; N, 5.2. $C_{22}H_{13}F_9N_2O_2$ requires C, 52.0; H, 2.6; F, 33.6; N, 5.5%). N.M.R. number 40; IR number 27; mass spectrum number 38.

6.4.6 Diene (50) with 3-Methoxyaniline

A mixture of diene (50), (3.0g, 8.3mmol), some 3-methoxyaniline (2.0g, 16.3mmol), and dry potassium fluoride (2.0g, 34.5mmol) in anhydrous acetonitrile (50ml) was heated under reflux overnight with continuous stirring. This was poured into water (150ml) in a separating funnel and acidified with hydrochloric acid. The organic products were then extracted with diethyl ether (50ml), dried with $MgSO_4$, filtered and the solvent removed under reduced pressure. Sublimation onto a cold finger yielded:

1-(3'-Methoxyphenyl)-tetrakis(trifluoromethyl)-pyrrole (120) (1.0g, 27%).

m.p. 65-66°C. (Found: C, 40.5; H, 1.5; F, 50.9; N, 2.9. $C_{15}H_7F_{12}NO$ requires C, 40.5; H, 1.6; F, 51.2; N, 3.1%). N.M.R. number 41; IR number 28; mass spectrum number 39.

The remaining solid was purified by recrystallisation from acetone/water to give a mixture (16:9) (1.0g, 24%) of:

1-*H*-1-(3'-Methoxyphenyl)-2,3,4-tris(trifluoromethyl)-9-methoxy-pyrrolo[3,2-*c*]-quinoline (121) (*ca.*15%).

NMR number 42 and

1-*H*-1-(3'-Methoxyphenyl)-2,3,4-tris(trifluoromethyl)-7-methoxy-pyrrolo[3,2-*c*]-quinoline (122) (*ca.*9%).

NMR number 43.

For the mixture (Found: C, 51.7; H, 2.6; F, 34.1; N, 5.4. $C_{22}H_{13}F_9N_2O_2$ requires C, 52.0; H, 2.6; F, 33.6; N, 5.5%); IR number 29; mass spectrum number 40.

6.5 Reactions with Carbon Nucleophiles

6.5.1 With Diethyl Malonate

6.5.1.1 Diene (50)

A mixture of diene (50) (5.0g, 13.8mmol), diethyl malonate (2.2g, 15.7mmol), and dry caesium fluoride (6.3g, 41.4mmol) in anhydrous acetonitrile (50ml) was stirred at room temperature for twenty-four hours. At this stage, a small aliquot was taken and transfered *in vacuo* to a cold trap. Analysis by NMR and G.C. mass spectrometry revealed the presence of:

5,5-Bis(ethoxycarbonyl)tetrakis(trifluoromethyl)cyclopentadiene (137)

NMR number 44; mass spectrum number 41.

After a further twenty-four hours, the remaining mixture was then filtered and the solvent removed by rotary evaporation and an applied vacuum. The resulting tar was washed with a little cold dichloromethane (20ml) and the remaining crystals were purified by recrystallisation from dichloromethane and were subsequently shown to be:

Caesium tetrakis(trifluoromethyl)ethoxycarbonylcyclopentadienide (136) (5.0g, 67%).

(Found: C, 26.6; H, 0.9; F, 42.1; Cs, 25.9. $C_{11}H_5F_{12}O_2Cs$ requires C,26.6; H, 0.9; F, 42.1; Cs, 24.5%); NMR number 45; IR number 30; mass spectrum number 42.

6.5.1.2 Diene (43)

A mixture of diene (43) (1.0g, 2.6mmol), diethyl malonate (0.4g, 2.5mmol) and dry caesium fluoride (1.6g, 10.5mmol) in anhydrous acetonitrile (50ml) was heated under reflux for three hours whilst being stirred continuously. After filtration, the solvent was removed under reduced pressure. The product was then washed with a little cold dichloromethane (20ml) to give a light yellow powder which was identified as:

Caesium 1-ethoxycarbonylperfluoro-2,3,4,5,6-hexahydrodicyclopenta[*b,d*]-cyclopentadienide (138) (1.0g, 68%).

(Found: C, 29.9; H, 1.0; F, 39.8; Cs, 23.2. $C_{13}H_5F_{12}O_2Cs$ requires C, 29.7; H, 0.9; F, 40.3; Cs 23.4%.); NMR number 46; IR number 31; mass spectrum number 43.

6.5.1.3 Diene (46)

A mixture of diene (46) (1.0g, 3.5mmol), diethyl malonate (0.6g, 3.8mmol) and dry caesium fluoride (2.1g, 13.1mmol) in anhydrous acetonitrile (50ml) was heated under reflux for three hours whilst being stirred continuously. The ^{19}F N.M.R. spectrum of the reaction mixture was obtained at this time and showed the presence of a vast mixture of fluorinated compounds present. A similar work up to that mentioned before was adopted but the only product was an intractable tar.

6.5.2 Diene (50) with Ethyl 3-Oxopentanoate

A mixture of diene (50) (1.0g, 2.8mmol), some ethyl 3-oxopentanoate (0.4g, 2.8mmol) and dry caesium fluoride (2.1g, 13.8mmol) in anhydrous acetonitrile (50ml) was heated under reflux for one hour whilst being stirred continuously. At this stage, a small aliquot was taken and transfered *in vacuo* to a cold trap. Analysis by NMR and G.C. mass spectrometry revealed the presence of:

5-Ethoxycarbonyl-5-propanoyl-tetrakis(trifluoromethyl)cyclopentadiene (142) NMR number 47; mass spectrum number 44.

After a further two hours' reflux, the remaining mixture was shown by ^{19}F NMR to be a mixture of three products:

Caesium tetrakis(trifluoromethyl)ethoxycarbonylcyclopentadienide (136) (*ca.* 9%) (see Section 6.5.1.1) and

Caesium tetrakis(trifluoromethyl)propanoylcyclopentadienide (141) (*ca.* 57%) (see Section 6.5.4)

along with some of the furan derivative (73) (*ca.* 34%).

6.5.3 Diene (50) with 2,2,2-Trifluoroethylphenylsulphone (143)

A mixture of diene (50) (4.0g, 11.0mmol), some 2,2,2-trifluoroethylphenylsulphone (143) (2.5g, 11.2mmol) and dry caesium fluoride (8.5g, 55.9mmol) in anhydrous acetonitrile (50ml) was heated under reflux overnight with continuous stirring. Analysis (^{19}F NMR spectroscopy) demonstrated the presence of a complex mixture (*ca.* 13:17:70) of salt (144), benzene derivative (145) and furan derivative (73) along with some remaining starting material. The mixture was then filtered and the solvent was removed under reduced pressure. The residue was washed with a little diethyl ether (20ml), filtered again and the ether was removed by rotary evaporation. Recrystallisation from dichloromethane afforded:

Hexakis(trifluoromethyl)benzene (145) (0.4g, 7%).

NMR number 48; IR number 32; mass spectrum number 45.

6.5.4 Diene (50) with 1,1,1-Trifluoropentan-3-one (146)

A mixture of diene (50) (1.0g, 2.8mmol), some 1,1,1-trifluoropentan-3-one (146) (0.4g, 2.9mmol) and dry caesium fluoride in anhydrous acetonitrile (50ml) was heated under reflux for four hours with continuous stirring. The ^{19}F N.M.R. spectrum was obtained at this time and showed that a mixture of products had been made which were subsequently identified as:

Caesium pentakis(trifluoromethyl)cyclopentadienide (144) (*ca.* 11%) (see Section 6.5.6.1) and

Caesium tetrakis(trifluoromethyl)propanoyl-cyclopentadienide (141) (*ca.* 52%).

NMR number 49; mass spectrum number 46.

and also the presence of the benzene derivative (145) (*ca.* 7%) and furan derivative (73) (*ca.* 30%).

6.5.5 Reaction of Diene (50) with Vinylidene Fluoride (150)

A stainless steel autoclave was charged with a mixture of diene (50) (8.0g,. 22.1mmol), vinylidene fluoride (150) (1.4g, 21.9mmol) and dry caesium fluoride (10.1g, 66.4mmol) in anhydrous acetonitrile (35ml). The autoclave was then subsequently heated in a rocking furnace at 100°C for twenty hours. Analysis (^{19}F NMR spectroscopy) demonstrated the presence of a complex mixture (*ca.* 5:7:29) of salt (144), cyclobutene derivative (52) and furan derivative (73) along with some starting material. The resulting mixture was filtered and the solvent removed under reduced pressure but nothing could be extracted from the remaining tar although ^{19}F NMR spectroscopy still showed the presence of:

Caesium pentakis(trifluoromethyl)cyclopentadienide (144) (*ca*, 10%) in the mixture (see Section 6.5.6.1).

6.5.6 With *E*-2-*H*-Heptafluorobut-2-ene (151)

6.5.6.1 Diene (50)

A stainless steel autoclave was charged with a mixture of diene (50) (3.0g,. 8.3mmol), 2-*H*-heptafluorobut-2-ene (151) (1.5g, 8.2mmol) and dry caesium fluoride (5.1g, 33.6mmol) in anhydrous acetonitrile (25ml). The autoclave was then subsequently heated in a rocking furnace at 100°C for forty-eight hours. Analysis (^{19}F NMR spectroscopy) demonstrated the presence of a complex mixture (*ca.* 50:13:26) of salt (144), cyclobutene derivative (52) and furan derivative (73) along with some starting material. The resulting mixture was then filtered and any volatile components were removed under reduced pressure. The remaining brown oil was allowed to crystallise over fourteen days. Washing the partially crystalline oil with a little chloroform (20ml) gave an off-white powder which was suitable for FAB mass spectrometry analysis. The powder was identified as:

Caesium pentakis(trifluoromethyl)cyclopentadienide (144) (1.8g, 41%).

NMR number 50; IR number 33; mass spectrum number 47.

6.5.6.2 Diene (43)

A stainless steel autoclave was charged with a mixture of diene (43) (1.4g,. 3.6mmol), 2-*H*-heptafluorobut-2-ene (151) (1.8g, 9.9mmol) and dry caesium fluoride (4.7g, 30.9mmol) in anhydrous acetonitrile (25ml). The autoclave was then subsequently heated in a rocking furnace at 100°C for forty-eight hours. The resulting mixture was then filtered and any volatile components were removed under reduced pressure. The remaining brown oil was allowed to crystallise over seven days. Washing the partially crystalline oil with a little dichloromethane (20ml) gave a light brown powder which was suitable for FAB mass spectrometry analysis. The powder was identified as:

Caesium perfluoro-1-methyl-2,3,4,5,6,7-hexahydro-dicyclopenta[*b*,*d*]cyclopentadienide (153) (0.5g, 25%).

NMR number 51; mass spectrum number 48.

6.5.6.3 Octafluorocyclopentene (135)

A stainless steel autoclave was charged with a mixture of fluoroalkene (135) (2.2g, 10.4mmol), 2-*H*-heptafluorobut-2-ene (151) (3.7g, 20.3mmol) and dry caesium fluoride (7.9g, 52.0mmol) in anhydrous acetonitrile (25ml). The autoclave was then subsequently heated in a rocking furnace at 100°C for forty-eight hours. The resulting mixture was then filtered and any volatile components were removed under reduced pressure. The remaining dark brown oil was allowed to crystallise over fourteen days. Washing the partially crystalline oil with a little dichloromethane (20ml) gave a light brown powder which was suitable for FAB mass spectrometry analysis. The powder was identified as:

Caesium perfluoro-1,2,3-trihydro-4,5,6-trimethyl-pentalenide (154) (1.2g, 21%).

NMR number 52; mass spectrum number 49.

Chapter Seven

Experimental to Chapter Four

7.1 Reagents

Decamethylferrocene was kindly provided by Dr. V. C. Gibson and was sublimed onto a cold finger prior to use.

7.2 Reaction of Decamethylferrocene with Diene (43)

Diene (43) (0.30g, 0.777mmol) was added to a stirred suspension of decamethylferrocene (0.25g, 0.767mmol) in anhydrous acetonitrile (30ml). The mixture was stirred at room temperature for seven days. Any solid material was removed by filtration and the solvent subsequently removed by rotary evaporation. The residual material was recrystallised from acetone and light petroleum (b.p. 40-60°C) to give:

$[Fe(C_5Me_5)_2]^+ [C_{10}F_{14}]^-$ (155) (0.18g, 33%) (Found: C, 50.8; H, 4.3; Fe, 6.9. $C_{30}H_{30}F_{14}Fe$ requires C, 50.6; H, 4.3; Fe, 7.8%.); IR number 34.

Hydrolysis of this gave the salt $[Fe(C_5Me_5)_2]^+ [C_{10}F_{11}O_2]^-$ (159)

N.M.R. number 53.

7.3 Reaction of Decamethylferrocene with Diene (46)

Diene (46) (0.22g, 0.769mmol) was added to a stirred suspension of decamethylferrocene (0.25g, 0.767mmol) in anhydrous acetonitrile (30ml). The mixture was stirred at room temperature for seven days. Any solid material was removed by filtration and the solvent subsequently removed by rotary evaporation. The residual material was recrystallised from acetone and light petroleum (b.p. 40-60°C) to give:

$[Fe(\eta\text{-}C_5Me_5)_2]^+ (C_8F_{10})^-$ (161) (0.18g, 38%) (Found: C, 54.5; H, 4.7; F, 22.6; Fe, 9.2. $C_{28}H_{30}F_{10}Fe$ requires C, 54.9; H, 4.9; F, 31.0; Fe, 9.1%.); IR number 35.

7.4 Reaction of Decamethylferrocene with Diene (50)

Diene (50) (0.25g, 0.773mmol) was added to a stirred suspension of decamethylferrocene (0.25g, 0.767mmol) in anhydrous acetonitrile (30ml). The mixture was stirred at room temperature for seven days. Any solid material was removed by filtration and the solvent subsequently removed by rotary evaporation. The residual material was recrystallised from acetone and light petroleum (b.p. 40-60°C) to give 0.05g of a mixture of unidentified dark green crystals.

7.5 Reaction of Decamethylferrocene with Fluoroalkenes (44) and (45)

A mixture of perfluorinated alkenes (44) and (45) (0.25g, 0.590mmol) was added to a stirred suspension of decamethylferrocene (0.25g, 0.767mmol) in anhydrous acetonitrile (30ml). The mixture was stirred at room temperature for seven days. Any solid material was removed by filtration and the solvent subsequently removed by rotary evaporation. The residual material was recrystallised from acetone and light petroleum (b.p. 40-60°C) to give:

$[Fe(\eta\text{-}C_5Me_5)_2]^+ (C_8F_{10})^-$ (161) (0.10g, 64% based on decamethylferrocene).

APPENDICES

AND

REFERENCES

Appendix I

NMR Spectra

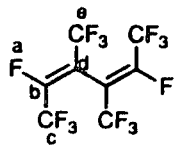
1. *Z,Z*-Perfluoro-3,4-dimethyl-hexa-2,4-diene (50)
2. *E,Z*-Perfluoro-3,4-dimethyl-hexa-2,4-diene (51)
3. Perfluoro-1,2,3,4-tetramethylcyclobutene (52)
4. *E,E*-Perfluoro-3,4-dimethyl-hexa-2,4-diene (60)
5. Perfluorobicyclopent-1,1'-enyl (43)
6. Perfluorobicyclobut-1,1'-enyl (46)
7. 4-Bromo-3-chlorohexafluorobut-1-ene (62)
8. *E*-4-Bromo-1,3-dichloropentafluorobut-1-ene (63)
9. *Z*-4-Bromo-1,3-dichloropentafluorobut-1-ene (64)
10. 1,1,1-Trifluoropentan-3-one (146)
11. Tetrakis(trifluoromethyl)furan (73)
12. *Z,Z*-2-Phenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (74)
13. *Z,E*-2-Phenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (75)
14. *E,E*-2-Phenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (76)
15. *E,Z*-2-Phenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (77)
16. *Z,Z*-2,5-Diphenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (78)
17. *E,Z*-2,5-Diphenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (79)
18. *E,E*-2,5-Diphenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (80)
19. 2,2'-Diphenoxy-perfluorobicyclopent-1,1'-enyl (81)
20. Perfluoro-2,2',3,3'-tetramethyl-bi-2,2'-oxiranyl (86)
21. Perfluoro-2,2'-dichloro-bicyclobut-1,1'-enyl (88)
22. Perfluoro-1,3,4,6-tetramethyl-2,5-dioxabicyclo[2.2.0]hexane (90) or Perfluoro-1,2,4,5-tetramethyl-3,6-dioxabicyclo[3.1.0]hexane (91)
23. Tetrakis(trifluoromethyl)thiophene (92)
24. *E,Z*-2,5-Dithiophenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (94)
25. *Z,Z*-2,5-Dithiophenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (95)
26. *E,E*-2,5-Dithiophenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (96)

27. *Z,Z*-2,5-Diamino-perfluoro-3,4-dimethyl-hexa-2,4-diene (101)
28. 2,4,5-Tris(trifluoromethyl)-3-cyano-pyrrole (102)
29. 2,5-Diamino-3,4-dicyano-1,1,1,6,6,6-hexafluorohexa-2,4-diene (103)
30. 1-Phenyl-tetrakis(trifluoromethyl)pyrrole (108)
31. 1-*H*-1-Phenyl-2,3,4-tris(trifluoromethyl)pyrrolo[3,2-*c*]quinoline (109)
32. 1-(4'-Dimethylaminophenyl)-tetrakis(trifluoromethyl)pyrrole (111)
33. 1-(4'-Methoxyphenyl)-tetrakis(trifluoromethyl)pyrrole (112)
34. 1-*H*-1-(4'-Methoxyphenyl)-2,3,4-tris(trifluoromethyl)-8-methoxy-pyrrolo-[3,2-*c*]quinoline (113)
35. 1-(4'-Fluorophenyl)-tetrakis(trifluoromethyl)pyrrole (114)
36. 1-*H*-1-(4'-Fluorophenyl)-2,3,4-tris(trifluoromethyl)-8-fluoro-pyrrolo[3,2-*c*]quinoline (115)
37. 1-(4'-Chlorophenyl)-tetrakis(trifluoromethyl)pyrrole (116)
38. 1-(4'-Nitrophenyl)-tetrakis(trifluoromethyl)pyrrole (117)
39. 1-(2'-Methoxyphenyl)-tetrakis(trifluoromethyl)pyrrole (118)
40. 1-*H*-1-(2'-Methoxyphenyl)-2,3,4-tris(trifluoromethyl)-6-methoxy-pyrrolo-[3,2-*c*]quinoline (119)
41. 1-(3'-Methoxyphenyl)-tetrakis(trifluoromethyl)pyrrole (120)
42. 1-*H*-1-(3'-Methoxyphenyl)-2,3,4-tris(trifluoromethyl)-9-methoxy-pyrrolo-[3,2-*c*]quinoline (121)
43. 1-*H*-1-(3'-Methoxyphenyl)-2,3,4-tris(trifluoromethyl)-7-methoxy-pyrrolo-[3,2-*c*]quinoline (122)
44. 5,5-Bis(ethoxycarbonyl)tetrakis(trifluoromethyl)cyclopentadiene (137)
45. Caesium tetrakis(trifluoromethyl)ethoxycarbonylcyclopentadienide (136)
46. Caesium 1-ethoxycarbonylperfluoro-2,3,4,5,6-hexahydrodicyclo-penta[*b,d*]cyclopentadienide (138)
47. 5-Ethoxycarbonyl-5-propanoyl-tetrakis(trifluoromethyl)cyclopentadiene (142)
48. Hexakis(trifluoromethyl)benzene (145)

49. Caesium tetrakis(trifluoromethyl)propanoylcyclopentadienide (141)
50. Caesium pentakis(trifluoromethyl)cyclopentadienide (144)
51. Caesium perfluoro-1-methyl-2,3,4,5,6,7-hexahydro-dicyclopenta[*b*,*d*]-cyclopentadienide (153)
52. Caesium perfluoro-1,2,3-trihydro-4,5,6-trimethyl-pentalenide (154)
53. Decamethylferrocenium perfluoro-1-cyclopenenylcyclopenta-2,5-dionide (159)

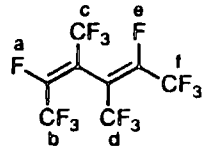
NMR spectra were recorded in *d*-chloroform whenever possible. Spectra 27, 28, 29 and 48 were recorded in d_6-acetone, spectra 45, 46, 50, 51 and 52 were recorded in d_3-acetonitrile and spectra 44, 47 and 53 were recorded in acetonitrile. All spectra were internally referenced using $CFCl_3$ and Me_4Si.

NMR Number 1.



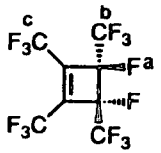
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
19F data				
-60.46	d *pseudo* sept [A3]2[X3]2	$J_{e,a}$19.4, $J_{e,c+e'}$1.9	3	e
-68.24	d *pseudo* sept	$J_{c,a}$7.9, $J_{c,e+e'}$1.9	3	c
-100.94	qq	$J_{a,e}$19.4, $J_{a,c}$7.7	1	a
13C data				
109.5	qd	$J_{CF(e)}$37, $J_{d,a}$18	-	d
118.9	qd	J_{CF}250, $J_{e,a}$38	-	e
121.9	q	J_{CF}276	-	c
154.7	dq	$J_{b,a}$291, $J_{CF(c)}$40	-	b

NMR Number 2.



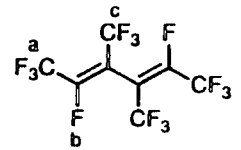
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
19F data				
-56.56	dqq	$J_{d,e}$10.5, $J_{d,f}$10.5, $J_{d,c}$2.3	3	d
-60.27	dqq	$J_{c,a}$19.2, $J_{c,b}$2.6, $J_{c,d}$1.3	3	c
-67.94	qd	$J_{f,d}$10.3, $J_{f,e}$7.0	3	f
-68.80	dqq	$J_{b,a}$7.1, $J_{b,c}$2.4, $J_{b,d}$1.2	3	b
-97.45	qq	$J_{e,d}$10.6, $J_{e,f}$7.0	1	e
-102.22	qq	$J_{a,c}$19.2, $J_{a,b}$6.8	1	a

NMR Number 3.



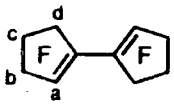
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-63.00	m	-	3	c
-71.84	d	$J_{b,a}$6.4	3	b
-165.84	m	-	1	a

NMR Number 4.



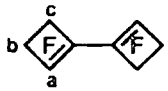
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-58.24	dqq	$J_{c,b}$10.3, $J_{c,a}$10.3, $J_{c,c'}$1.5	3	c
-67.60	qd	$J_{a,c}$10.7, $J_{a,b}$6.3	3	a
-101.38	m	-	1	b

NMR Number 5..



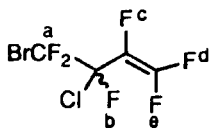
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-107.52	m	-	2	d
-107.81	m	-	1	a
-119.63	m	-	2	b
-130.34	m	-	2	c

NMR Number 6.



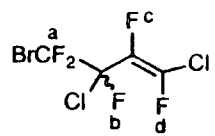
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-95.68	m	-	1	a
-115.68	m	-	2	c
-117.21	m	-	2	b

NMR Number 7.



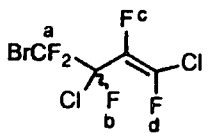
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-60.97	ABdd	J_{AB}64.1, $J_{a,b}$11.3, $J_{a,c}$11.3	1	a
-62.46	ABdd	J_{AB}64.1, $J_{a,b}$14.7, $J_{a,c}$5.9	1	a
-89.35	dd	$J_{d,e}$49.9, $J_{d,c}$38.1	1	d
-103.58	ddd	$J_{e,c}$115.8, $J_{e,b}$94.6, $J_{e,d}$47.2	1	e
-128.51	m	-	1	b
-177.60	dm	$J_{c,e}$110.4	1	c

N.M.R. Number 8.



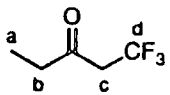
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-60.09	ABdd	J_{AB}89.0, $J_{a,b}$13.4, $J_{a,c}$13.4	1	a
-61.58	AB	J_{AB}89.0	1	a
-105.94	dd	$J_{d,c}$132.0, $J_{d,b}$48.0	1	d
-126.74	m	-	1	b
-149.33	dm	$J_{c,d}$129.0	1	c

NMR Number 9.



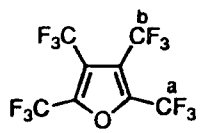
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-60.09	ABdd	J_{AB}89.0, $J_{a,b}$13.4, $J_{a,c}$13.4	1	a
-61.58	AB	J_{AB}89.0	1	a
-105.94	dd	$J_{d,c}$132.0, $J_{d,b}$48.0	1	d
-126.74	m	-	1	b
-149.33	dm	$J_{c,d}$129.0	1	c

NMR Number 10.



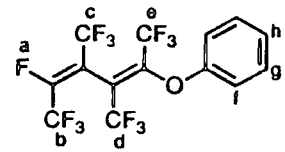
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
1.10	t	$J_{a,b}$7.2	3	a
2.57	q	$J_{b,a}$7.2	2	b
3.27	q	$J_{c,d}$10.3	2	c
^{19}F data				
-62.38	t	$J_{d,c}$10.4	1	d

NMR Number 11.



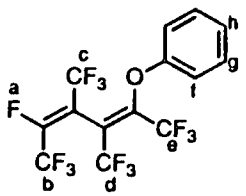
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-57.62	m	-	1	a or b
-62.40	m	-	1	a or b

NMR Number 12.



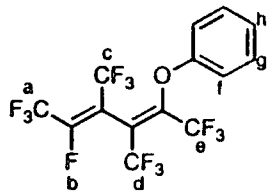
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
6.89	d	$J_{f,g}$8.0	2	f
7.09	t	$J_{h,g}$1.4	1	h
7.25	d	$J_{g,f}$6.8	2	g
^{19}F data				
-61.10	s	-	3	e
-61.12	d	$J_{c,a}$20.3	3	c
-62.31	q	$J_{d,e}$1.9	3	d
-69.59	dq	$J_{b,a}$4.9, $J_{b,c}$1.9	3	b
-105.19	qq	$J_{a,c}$15.5, $J_{a,b}$8.1	1	a

NMR Number 13.



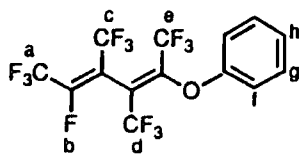
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
6.82	d	$J_{f,g}$8.0	2	f
7.11	t	$J_{h,g}$1.2	1	h
7.27	d	$J_{g,f}$8.8	2	g
^{19}F data				
-60.48	d	$J_{c,a}$15.4	3	c
-60.99	s	-	3	e
-62.70	q	$J_{d,e}$11.9	3	d
-70.49	d	$J_{b,a}$8.6	3	b
-107.08	qq	$J_{a,c}$14.7, $J_{a,b}$8.7	1	a

NMR Number 14.



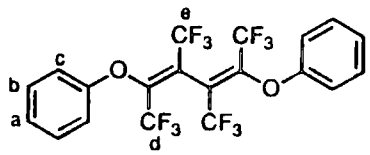
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
6.89	d	$J_{f,g}$7.8	2	f
7.07	t	$J_{h,g}$1.0	1	h
7.26	d	$J_{g,f}$4.4	2	g
^{19}F data				
-57.21	dqq	$J_{c,b}$10.4, $J_{c,a}$10.4, $J_{c,d}$2.6	3	c
-58.29	qq	$J_{e,d}$11.7, $J_{e,c}$1.9	3	e
-63.39	s	-	3	d
-69.23	qd	$J_{a,c}$10.7, $J_{a,b}$7.7	3	a
-101.33	m	-	1	b

NMR Number 15.



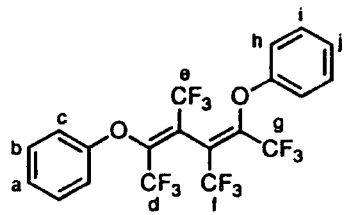
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
6.91	d	$J_{f,g}$8.0	2	f
7.06	t	$J_{h,g}$1.2	1	h
7.23	d	$J_{g,f}$7.6	2	g
^{19}F data				
-56.94	dqq	$J_{c,b}$10.7, $J_{c,a}$10.7, $J_{c,d}$2.9	3	c
-58.29	s	-	3	e
-58.33	q	$J_{d,e}$2.5	3	d
-69.11	qd	$J_{a,c}$10.5, $J_{a,b}$7.5	3	a
-102.49	m	-	1	b

NMR Number 16.



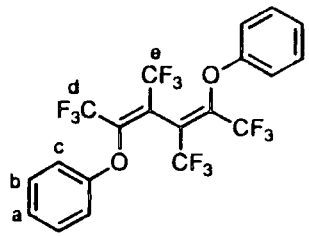
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
6.95	d	$J_{c,b}$8.0	2	c
7.10	t	$J_{a,b}$1.2	1	a
7.29	d	$J_{b,c}$8.4	2	b
^{19}F data				
-60.25	q	$J_{e,d}$2.3	1	e
-61.80	q	$J_{d,e}$1.9	1	d

NMR Number 17.



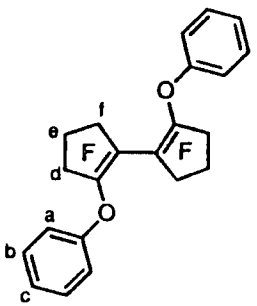
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
6.77	d	$J_{c \text{ or } h,b \text{ or } i}$8.0	2	c or h
6.92	d	$J_{c \text{ or } h,b \text{ or } i}$8.0	2	c or h
7.12	t	$J_{a \text{ or } j,b \text{ or } i}$1.0	1	a or j
7.15	t	$J_{a \text{ or } j,b \text{ or } i}$1.0	1	a or j
7.27	d	$J_{b \text{ or } i,c \text{ or } h}$8.4	2	b or i
7.27	d	$J_{b \text{ or } i,c \text{ or } h}$6.4	2	b or i
^{19}F data				
-57.15	qq	$J_{i,g}$10.9, $J_{i,d}$2.3	1	f
-59.56	s	-	1	e
-62.04	q	$J_{g,f}$12.0	1	g
-63.34	q	$J_{d,f}$3.0	1	d

NMR Number 18.



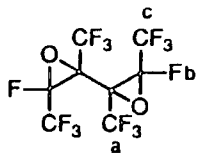
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
6.87	d	$J_{c,b}$8.0	2	c
7.02	t	$J_{a,b}$1.2	1	a
7.24	d	$J_{b,c}$8.8	2	b
^{19}F data				
-56.43	q	$J_{e,d}$11.3	1	e
-62.31	q	$J_{e,d}$12.0	1	d

NMR Number 19.



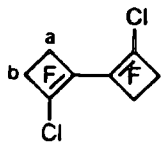
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
7.25	m	-	1	a, b and c
^{19}F data				
-106.90	s	-	1	d, e, or f
-116.93	s	-	1	d, e, or f
-131.13	s	-	1	d, e, or f

NMR Number 20.



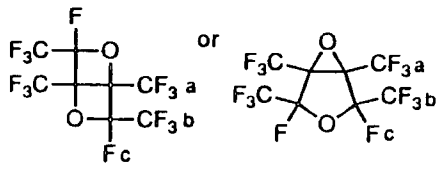
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-66.10	dq	$J_{c,b}$16.6, $J_{c,a}$2.6	3	c
-76.36	s	-	3	a
-154.66	q	$J_{b,c}$16.6	1	b

NMR Number 21.



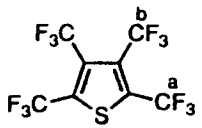
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-113.21	s	-	1	a
-116.26	s	-	1	b

NMR Number 22.



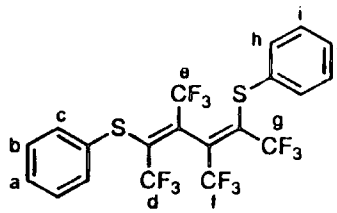
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-66.76	dq	$J_{b,c}$7.7, $J_{b,a}$3.8	3	b
-77.33	qd	$J_{a,b}$4.8, $J_{a,c}$2.4	3	a
-151.26	qq	$J_{c,b}$7.8, $J_{c,a}$4.8	1	c

NMR Number 23.



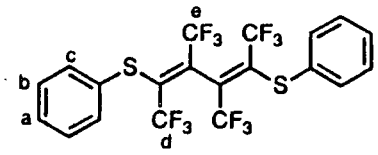
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
19F data				
-54.12	m	-	1	a or b
-56.00	m	-	1	a or b

NMR Number 24.



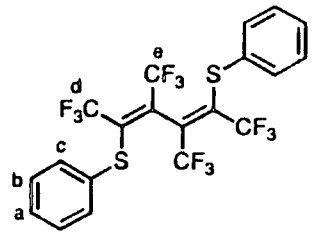
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
1H data				
7.22	t	$J_{a \text{ or } j,b \text{ or } i}$ 2.1	1	a or j
7.23	t	$J_{a \text{ or } j,b \text{ or } i}$ 2.1	1	a or j
7.30	d	$J_{b \text{ or } i,c \text{ or } h}$ 7.4	2	b or i
7.37	d	$J_{b \text{ or } i,c \text{ or } h}$ 6.0	2	b or i
7.49	d	$J_{c \text{ or } h,b \text{ or } i}$ 8.4	2	c or h
7.50	d	$J_{c \text{ or } h,b \text{ or } i}$ 9.6	2	c or h
19F data				
-56.43	q	$J_{g,f}$ 13.4	1	g
-56.57	s	-	1	e
-57.31	qqq	$J_{f,g}$ 13.6, $J_{f,d}$ 4.2, $J_{f,e}$ 1.6	1	f
-57.75	q	$J_{d,f}$ 4.1	1	d

NMR Number 25.



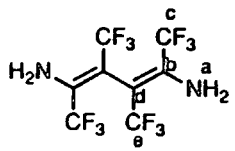
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
7.21	t	$J_{a,b}$2.2	1	a
7.36	d	$J_{b,c}$7.6	2	b
7.46	d	$J_{c,b}$7.6	2	c
^{19}F data				
-57.27	*pseudo* sept	$J_{e,d+e}$2.4	1	e
-57.88	*pseudo* sept	$J_{d,e+e}$2.4	1	d

NMR Number 26.



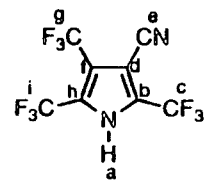
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
7.24	t	$J_{a,b}$2.8	1	a
7.40	d	$J_{b,c}$6.8	2	b
7.50	d	$J_{c,b}$8.0	2	c
^{19}F data				
-56.11	q	$J_{d,e}$13.3	1	d
-56.45	q	$J_{e,d}$13.3	1	e

NMR Number 27.



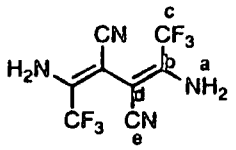
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
4.66	s (broad)	-	1	a
^{19}F data				
-61.59	*pseudo* sept	$J_{c,e+e'}$2.3	1	c or e
-67.07	*pseudo* sept	$J_{c,e+e'}$2.3	1	c or e
^{13}C data				
90.6	q	$J_{CF(c)}$34	-	b
119.2	q	J_{CF}278	-	c
122.9	q	J_{CF}274	-	e
140.1	q	$J_{CF(e)}$32	-	d

NMR Number 28.



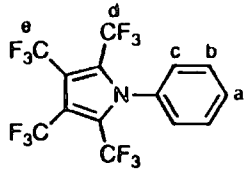
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
7.86	s (broad)	-	1	a
^{19}F data				
-55.80	q	$J_{g,i}$7.3	1	g or i
-58.75	q	$J_{g,i}$7.3	1	g or i
-59.79	s	-	1	c
^{13}C data				
110.5	s	-	-	e
117.56	q	$J_{CF(c,g\ or\ i)}$39	-	b, f or h
117.58	q	$J_{CF(c,g\ or\ i)}$39	-	b, f or h
119.9	q	J_{CF}270	-	c, g or i
121.7	q	J_{CF}269	-	c, g or i
124.3	q	J_{CF}268	-	c, g or i
129.8	q	$J_{CF(c,g\ or\ i)}$41	-	b, f or h

NMR Number 29.



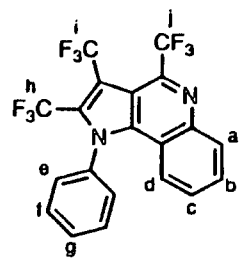
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
7.09	s (broad)	-	1	a
^{19}F data				
-65.91	s	-	1	c
^{13}C data				
116.4	s	-	-	e
121.	q	J_{CF}278	-	c
ca.147.3	q	$J_{CF(c\ or\ e)}$ca.32	-	b or d
147.4	q	$J_{CF(c\ or\ e)}$ca 32	-	b or d

NMR Number 30.



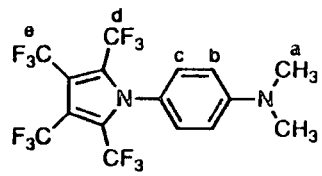
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
7.48	m	-	1	a, b and c
^{19}F data				
-54.34	s	-	1	d or e
-54.72	s	-	1	d or e

NMR Number 31.



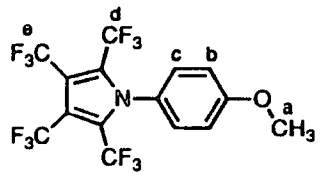
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
6.83	d	$J_{d,c}$8.7	1	d
7.47	d	$J_{a,b}$7.7	1	a
7.82	m	-	6	e, f, g and c
8.27	d	$J_{b,a}$8.1	1	b
^{19}F data				
-51.63	qq	$J_{i,j}$17.9, $J_{i,h}$11.1	1	i
-52.93	q	$J_{h,i}$11.1	1	h
-63.88	q	$J_{j,i}$17.9	1	j

NMR Number 32.



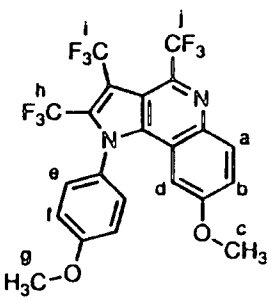
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
3.04	s	-	3	a
6.69	AB	J_{AB}9.1	1	b
7.12	AB	J_{AB}9.1	1	c
^{19}F data				
-54.56	s	-	1	d or e
-54.85	s	-	1	d or e

NMR Number 33.



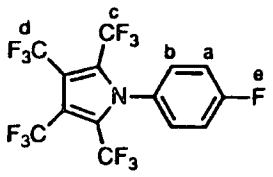
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
3.89	s	-	3	a
7.00	AB	J_{AB}8.8	2	b
7.25	AB	J_{AB}8.8	2	c
^{19}F data				
-53.49	s	-	1	d or e
-53.74	s	-	1	d or e

NMR Number 34.



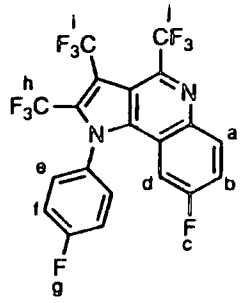
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
3.43	s	-	3	c
3.95	s	-	3	g
6.23	s	-	1	d
7.18	AB	J_{AB}7.4	2	f
7.26	s	-	1	a
7.44	AB	J_{AB}7.4	2	e
8.15	d	$J_{b,a}$8.8	1	b
^{19}F data				
-52.96	qq	$J_{i,j}$17.7, $J_{i,h}$11.2	1	i
-54.07	q	$J_{h,i}$11.2	1	h
-64.70	q	$J_{j,i}$17.7	1	j

NMR Number 35.



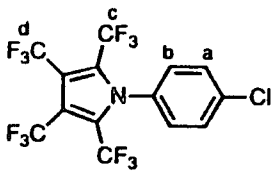
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
7.43	ABX	J_{AB}9.3, $J_{a,e}$8.2	1	a
7.57	ABX	J_{AB}9.3, $J_{b,e}$4.7	1	b
^{19}F data				
-54.36	s	-	6	c or d
-54.78	s	-	6	c or d
-108.41	tt	$J_{e,a}$7.8, $J_{e,b}$4.6	1	e

NMR Number 36.



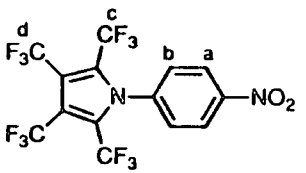
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
6.55	dd	$J_{d,c}$11.0, $J_{d,b}$2.9	1	d
7.64	ABX	J_{AB}9.2, $J_{f,g}$4.8	2	f
7.71	dd	$J_{a,b}$8.8, $J_{a,c}$8.8	1	a
7.74	ABX	J_{AB}9.2, $J_{e,g}$8.5	2	e
8.58	dd	$J_{b,a}$9.5, $J_{b,c}$5.9	1	b
^{19}F data				
-53.03	qq	$J_{i,j}$17.6, $J_{i,h}$10.8	3	i
-53.97	q	$J_{h,i}$11.0	3	h
-65.06	q	$J_{j,i}$17.5	3	j
-106.75	m	-	1	c
-107.05	t	$J_{g,f}$4.9	1	g

NMR Number 37.



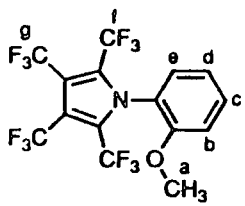
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
7.30	AB	J_{AB}8.6	1	a
7.52	AB	J_{AB}8.6	1	b
^{19}F data				
-54.22	s	-	1	c or d
-54.79	s	-	1	c or d

NMR Number 38.



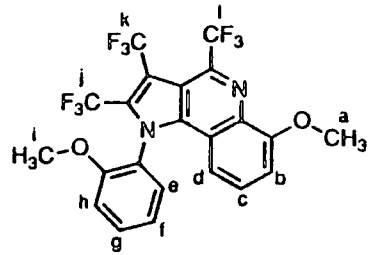
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
7.60	AB	J_{AB}8.6	1	b
8.44	AB	J_{AB}8.6	1	a
^{19}F data				
-53.86	s	-	1	c or d
-54.96	s	-	1	c or d

NMR Number 39.



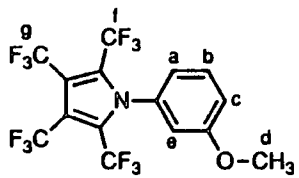
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
3.82	s	-	3	a
7.04	d	$J_{b,c}$8.2	1	b
7.06	dd	$J_{d,c}$7.8, $J_{d,e}$7.8	1	d
7.26	d	$J_{e,d}$7.8	1	e
7.53	ddd	$J_{c,b}$7.9, $J_{c,d}$7.9, $J_{c,e}$1.6	1	c
^{19}F data				
-54.78	s	-	1	f or g
-56.33	s	-	1	f or g

NMR Number 40.



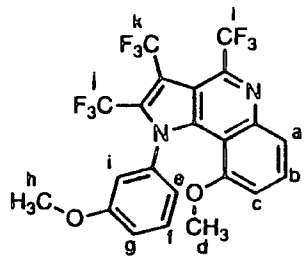
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
3.67	s	-	3	a
4.09	s	-	3	i
6.49	d	$J_{d,c}$8.3	1	d
7.07	d	$J_{h,g}$7.7	1	h
7.19	dd	$J_{f,g}$8.1, $J_{f,e}$8.1	1	f
7.24	d	$J_{c,d}$3.6	1	c
7.28	d	$J_{e,f}$9.4	1	e
7.44	d	$J_{b,c}$6.7	1	b
7.70	dd	$J_{g,h}$8.0, $J_{g,f}$8.0	1	g
^{19}F data				
-52.89	qq	$J_{k,l}$17.9, $J_{k,j}$11.3	1	k
-55.69	q	$J_{j,k}$11.4	1	j
-64.58	q	$J_{l,k}$17.9	1	l

NMR Number 41.



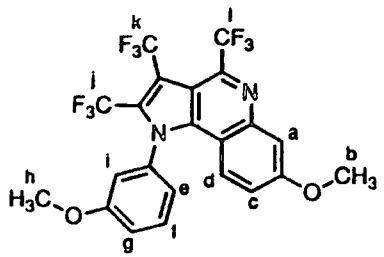
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
3.99	s	-	3	d
7.12	s	-	1	e
7.19	d	$J_{c,b}$7.9	1	c
7.37	dd	$J_{a,b}$9.4, $J_{a,c}$1.5	1	a
7.70	dd	$J_{b,a}$8.4, $J_{b,c}$8.4	1	b
^{19}F data				
-54.92	s	-	1	f or g
-55.17	s	-	1	f or g

NMR Number 42.



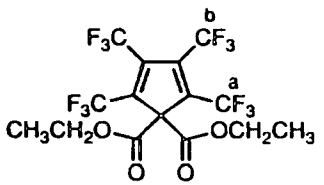
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
3.19	s	-	3	d
3.80	s	-	3	h
6.80	s	-	1	a or i
6.84	s	-	1	a or i
6.98	s	-	1	c or g
7.02	d	$J_{e,f}$8.3	1	e
7.07	s	-	1	c or g
7.39	dd	$J_{i,e}$8.1, $J_{i,g}$8.1	1	f
7.91	d	$J_{a,b}$8.5	1	b
^{19}F data				
-52.05	qq	$J_{k,l}$17.7, $J_{k,j}$11.3	1	k
-53.83	q	$J_{j,k}$11.3	1	j
-65.12	q	$J_{l,k}$17.7	1	l

NMR Number 43.



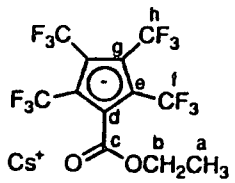
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
3.86	s	-	3	b
3.93	s	-	3	h
6.72	d	$J_{d,c}$9.3	1	d
6.88	s	-	2	a and i
7.03	m	-	1	c or g
7.09	s	-	1	c or g
7.58	dd	$J_{f,e}$8.2, $J_{f,g}$8.2	1	f
7.67	d	$J_{e,f}$14.3	1	e
^{19}F data				
-52.94	qq	$J_{k,l}$17.6, $J_{k,j}$11.2	1	k
-53.97	q	$J_{j,k}$11.2	1	j
-65.02	q	$J_{l,k}$17.7	1	l

NMR Number 44.



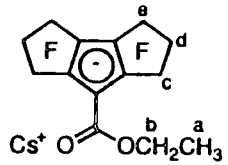
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-55.82	s	-	1	a or b
-60.09	s	-	1	a or b

NMR Number 45.



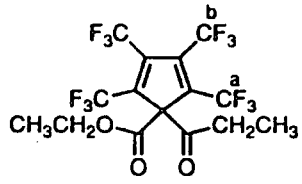
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
1.25	t	$J_{a,b}$7.1	3	a
4.17	q	$J_{b,a}$7.1	2	b
^{19}F data				
-50.64	s	-	1	f or h
-50.96	s	-	1	f or h
^{13}C data				
14.2	s	-	-	a
61.1	s	-	-	b
108.0	s	-	-	e or g
109.0	s	-	-	e or g
118.5	s	-	-	c
124.9	q	J_{CF269}	-	f or h
125.4	q	J_{CF267}	-	f or h

NMR Number 46.



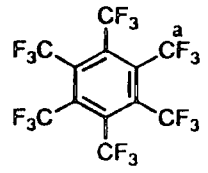
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
1.28	t	$J_{a,b}$7.1	3	a
4.18	q	$J_{b,a}$7.1	2	b
^{19}F data				
-97.55	s	-	1	c or e
-99.84	s	-	1	c or e
-121.61	s	-	1	d

NMR Number 47.



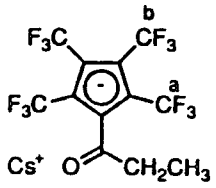
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
19F data				
-54.80	s	-	1	a or b
-60.09	s	-	1	a or b

NMR Number 48.



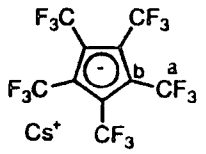
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
19F data				
-51.54	s	-	1	a

NMR Number 49.



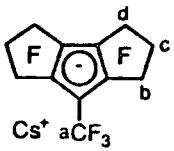
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-48.83	s	-	1	a or b
-49.20	s	-	1	a or b

NMR Number 50.



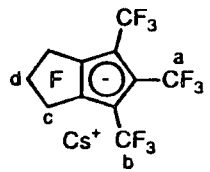
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-49.73	s	-	1	a
^{13}C data				
110.6	q	$J_{CF(a)19}$	-	b
124.7	q	J_{CF271}	-	a

NMR Number 51.



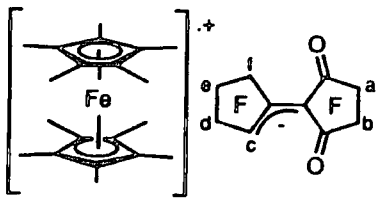
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-53.23	s	-	3	a
-97.24	s	-	4	b or d
-98.94	s	-	4	b or d
-121.76	s	-	4	c

NMR Number 52.



Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-53.03	s	-	6	b
-53.95	s	-	3	a
-117.60	s	-	4	c
-149.17	m	-	2	d

NMR Number 53.



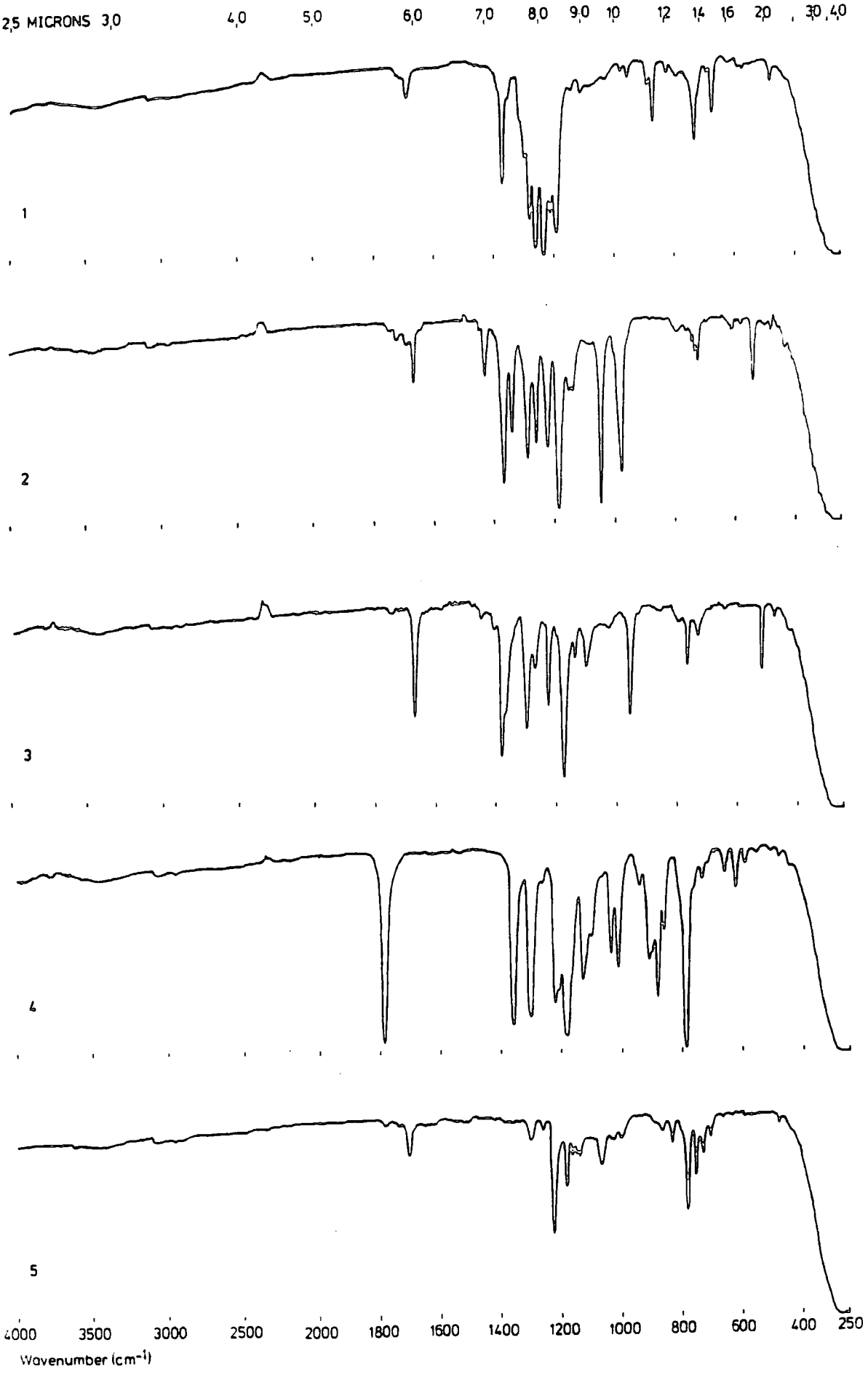
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-106.80	s	-	2	f
-117.19	s	-	2	f
-122.06	s	-	1	c
-126.37	s	-	4	a and b
-130.18	s	-	2	e

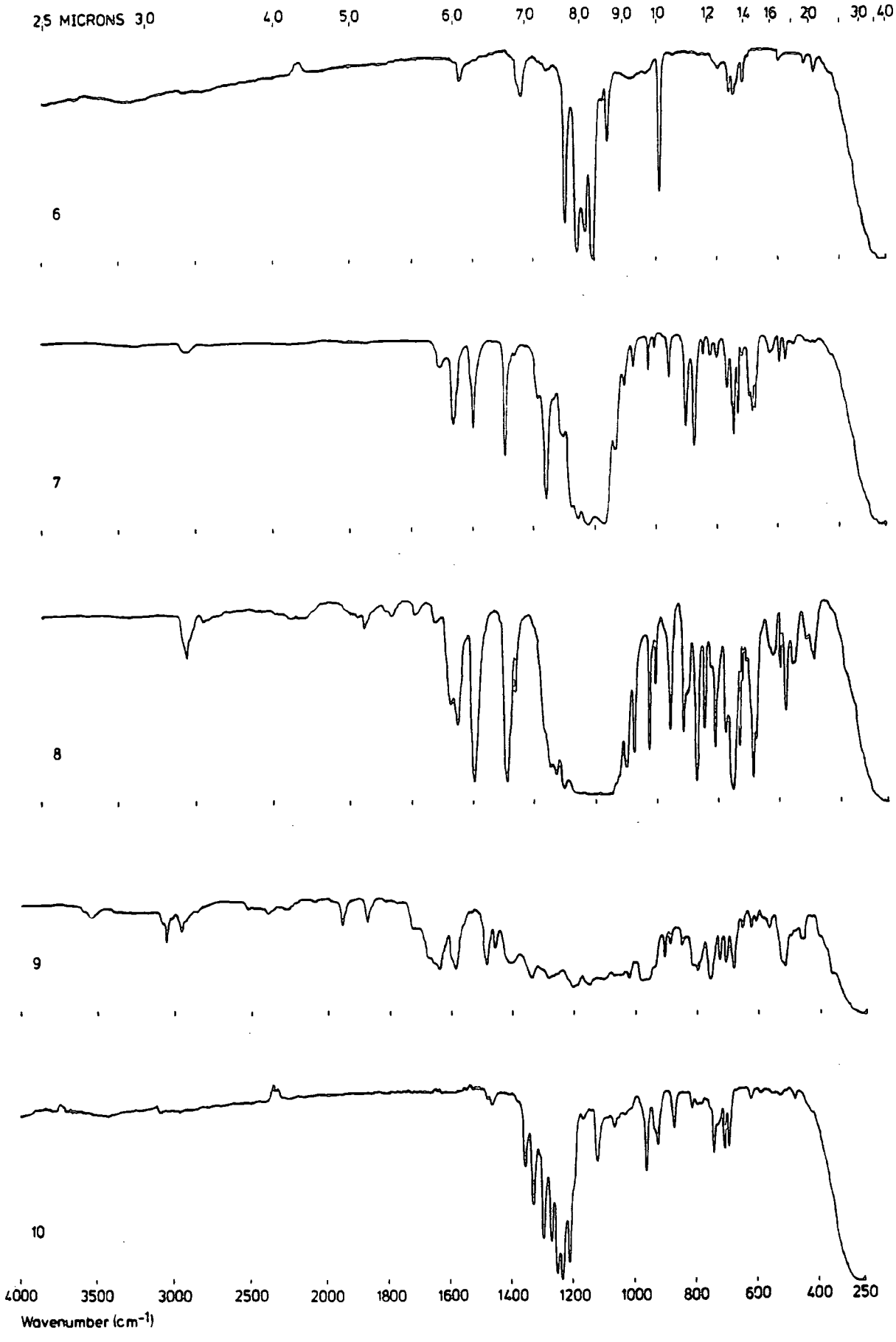
Appendix II

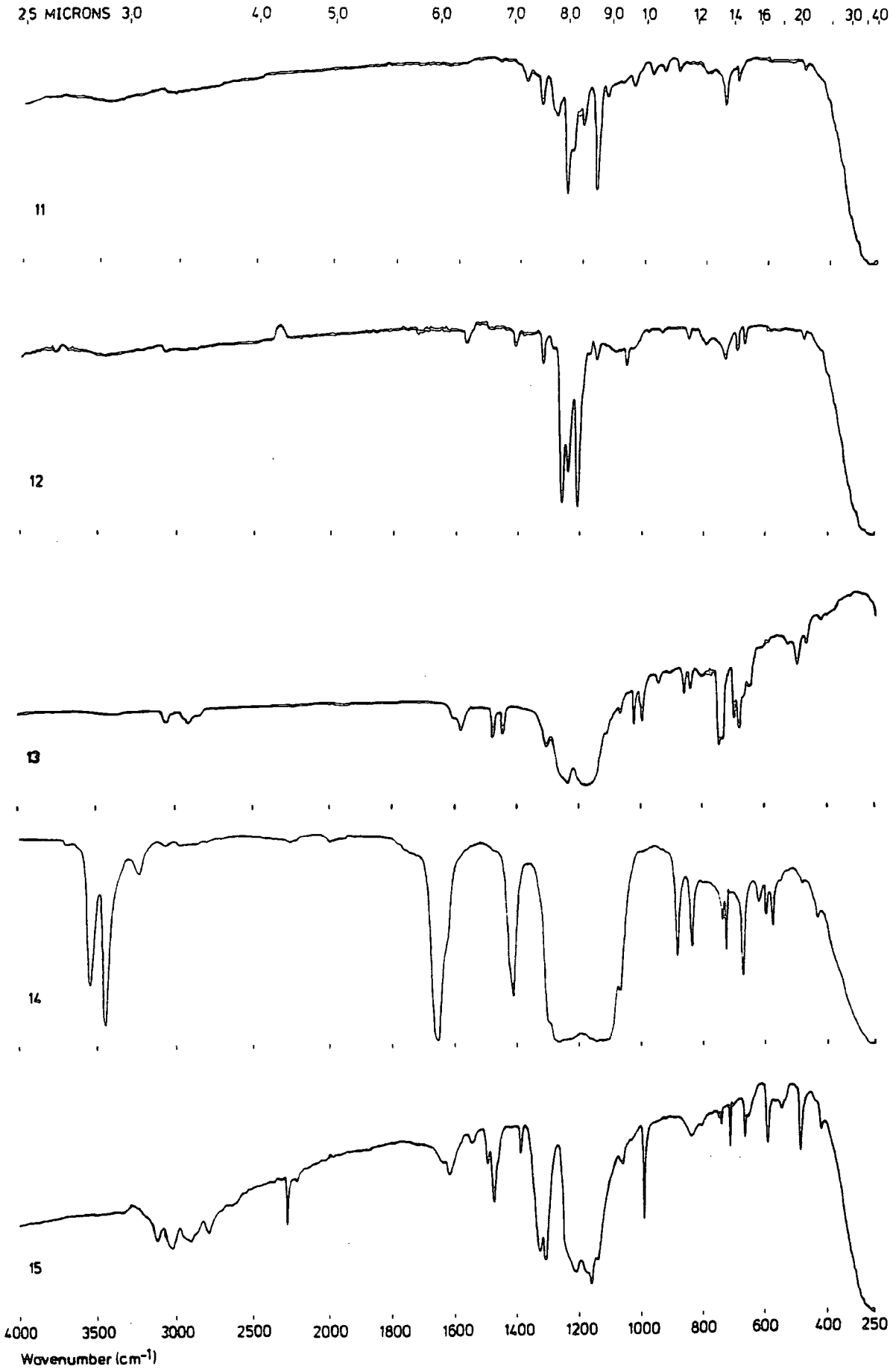
Infra Red Spectra

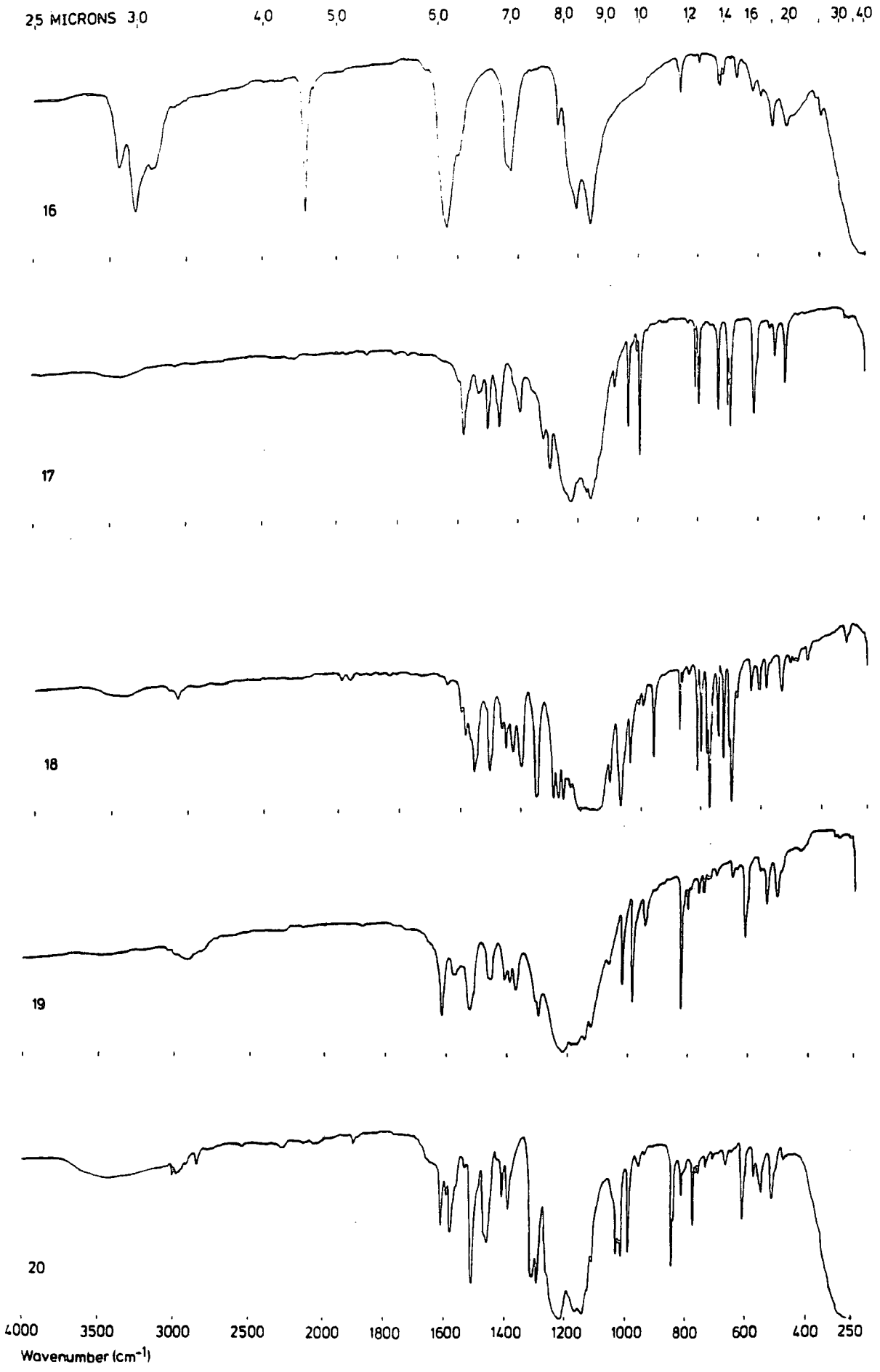
1. *Z,Z*- and *E,Z*-Perfluoro-3,4-dimethyl-hexa-2,4-diene (50) and (51)
2. Perfluorobicyclopent-1,1'-enyl (43)
3. Perfluorobicyclobut-1,1'-enyl (46)
4. 4-Bromo-3-chlorohexafluorobut-1-ene (62)
5. *E*- and *Z*-4-Bromo-1,3-dichloropentafluorobut-1-ene (63) and (64)
6. Tetrakis(trifluoromethyl)furan (73)
7. *Z,Z*-, *Z,E*-, *E,E*- and *E,Z*-2-Phenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (74), (75), (76) and (77)
8. *Z,Z*-, *E,Z*- and *E,E*-2,5-Diphenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (78), (79) and (80)
9. 2,2'-Diphenoxy-perfluorobicyclopent-1,1'-enyl (81)
10. Perfluoro-2,2',3,3'-tetramethyl-bi-2,2'-oxiranyl (86)
11. Perfluoro-1,3,4,6-tetramethyl-2,5-dioxabicyclo[2.2.0]hexane (90) or Perfluoro-1,2,4,5-tetramethyl-3,6-dioxabicyclo[3.1.0]hexane (91)
12. Tetrakis(trifluoromethyl)thiophene (92)
13. *E,Z*-, *Z,Z*- and *E,E*-2,5-Dithiophenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (94), (95) and (96)
14. Z,Z-2,5-Diamino-perfluoro-3,4-dimethyl-hexa-2,4-diene (101)
15. 2,4,5-Tris(trifluoromethyl)-3-cyano-pyrrole (102)
16. 2,5-Diamino-3,4-dicyano-1,1,1,6,6,6-hexafluorohexa-2,4-diene (103)
17. 1-Phenyl-tetrakis(trifluoromethyl)pyrrole (108)
18. 1-*H*-1-Phenyl-2,3,4-tris(trifluoromethyl)pyrrolo[3,2-*c*]quinoline (109)
19. 1-(4'-Dimethylaminophenyl)-tetrakis(trifluoromethyl)pyrrole (111)
20. 1-(4'-Methoxyphenyl)-tetrakis(trifluoromethyl)pyrrole (112)
21. 1-*H*-1-(4'-Methoxyphenyl)-2,3,4-tris(trifluoromethyl)-8-methoxy-pyrrolo-[3,2-*c*]quinoline (113)
22. 1-(4'-Fluorophenyl)-tetrakis(trifluoromethyl)pyrrole (114)

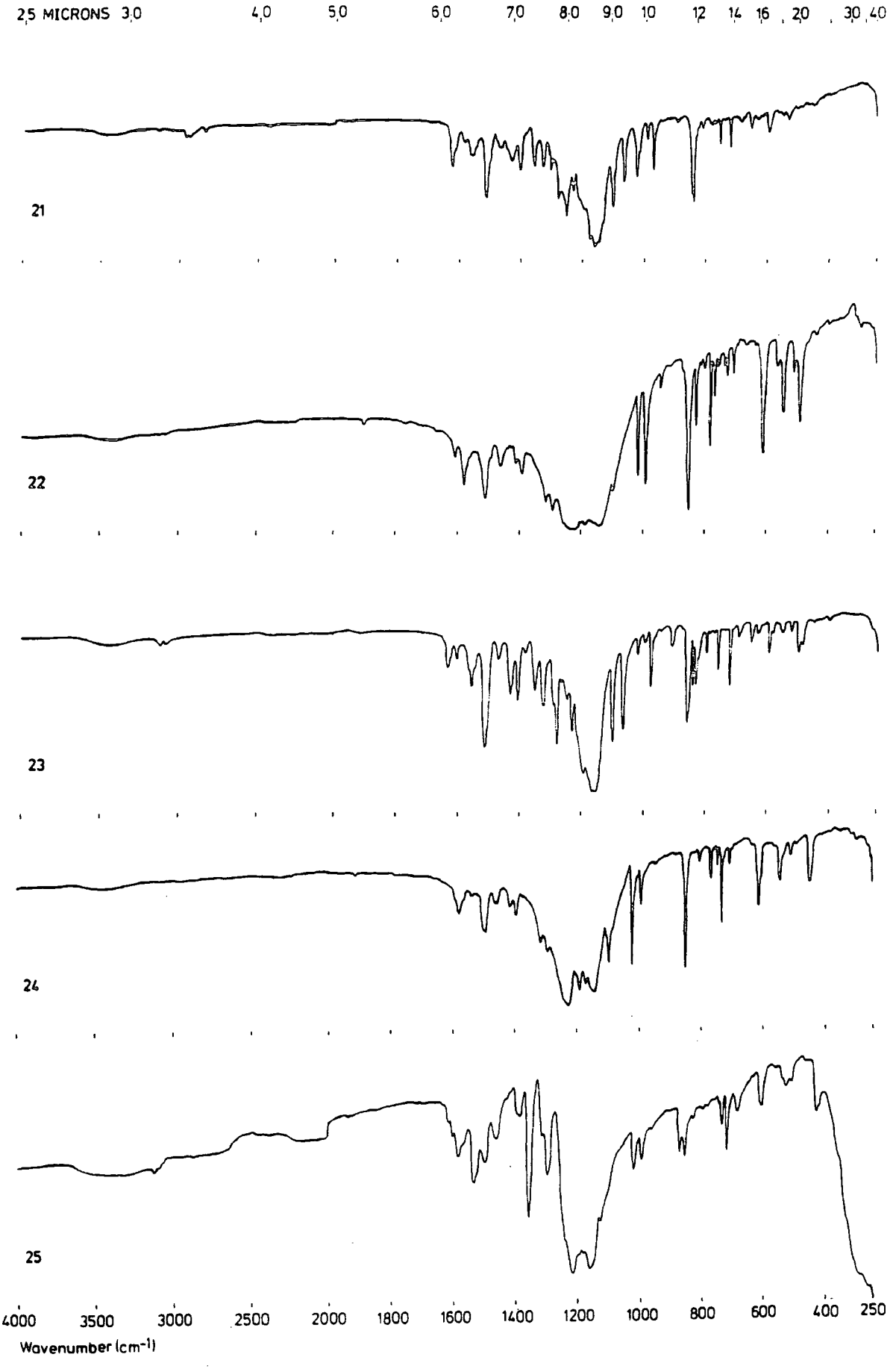
23. 1-*H*-1-(4'-Fluorophenyl)-2,3,4-tris(trifluoromethyl)-8-fluoro-pyrrolo[3,2-*c*]quinoline (115)
24. 1-(4'-Chlorophenyl)-tetrakis(trifluoromethyl)pyrrole (116)
25. 1-(4'-Nitrophenyl)-tetrakis(trifluoromethyl)pyrrole (117)
26. 1-(2'-Methoxyphenyl)-tetrakis(trifluoromethyl)pyrrole (118)
27. 1-*H*-1-(2'-Methoxyphenyl)-2,3,4-tris(trifluoromethyl)-6-methoxy-pyrrolo-[3,2-*c*]quinoline (119)
28. 1-(3'-Methoxyphenyl)-tetrakis(trifluoromethyl)pyrrole (120)
29. 1-*H*-1-(3'-Methoxyphenyl)-2,3,4-tris(trifluoromethyl)-9-methoxy-pyrrolo-[3,2-*c*]quinoline (121) and
    1-*H*-1-(3'-Methoxyphenyl)-2,3,4-tris(trifluoromethyl)-7-methoxy-pyrrolo-[3,2-*c*]quinoline (122)
30. Caesium tetrakis(trifluoromethyl)ethoxycarbonylcyclopentadienide (136)
31. Caesium 1-ethoxycarbonylperfluoro-2,3,4,5,6-hexahydrodicyclo-penta[*b*,*d*]cyclopentadienide (138)
32. Hexakis(trifluoromethyl)benzene (145)
33. Caesium pentakis(trifluoromethyl)cyclopentadienide (144)
34. Decamethylferrocenium perfluorobicyclopent-1,1'-enylide (155)
35. Decamethylferrocenium perfluorobicyclobut-1,1'-enylide (161)

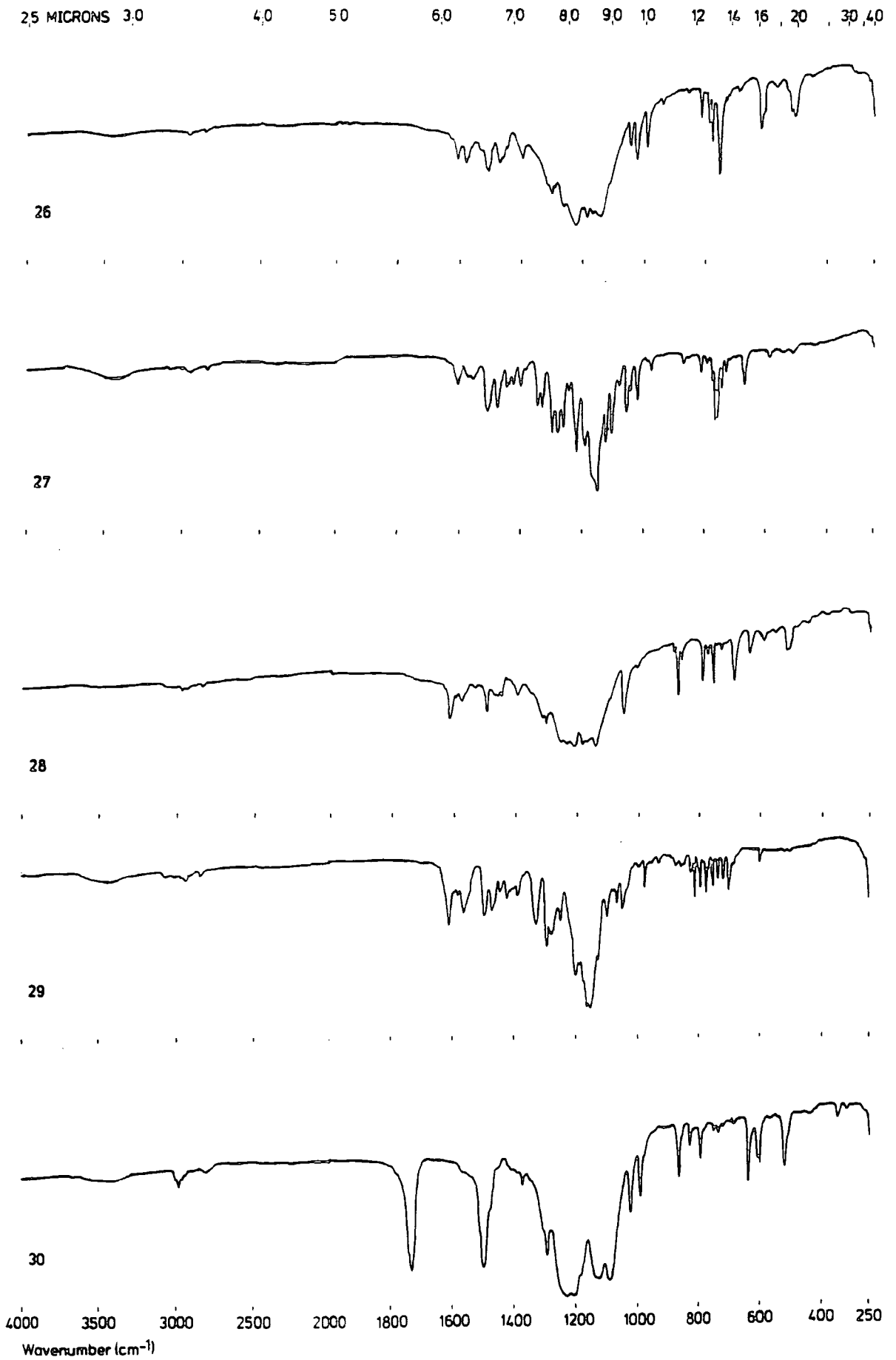

2,5 MICRONS 3,0
4,0
5,0
6,0
7,0
8,0
9,0
10
12
14
16
20
30
40
1
2
3
4
5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm⁻¹)

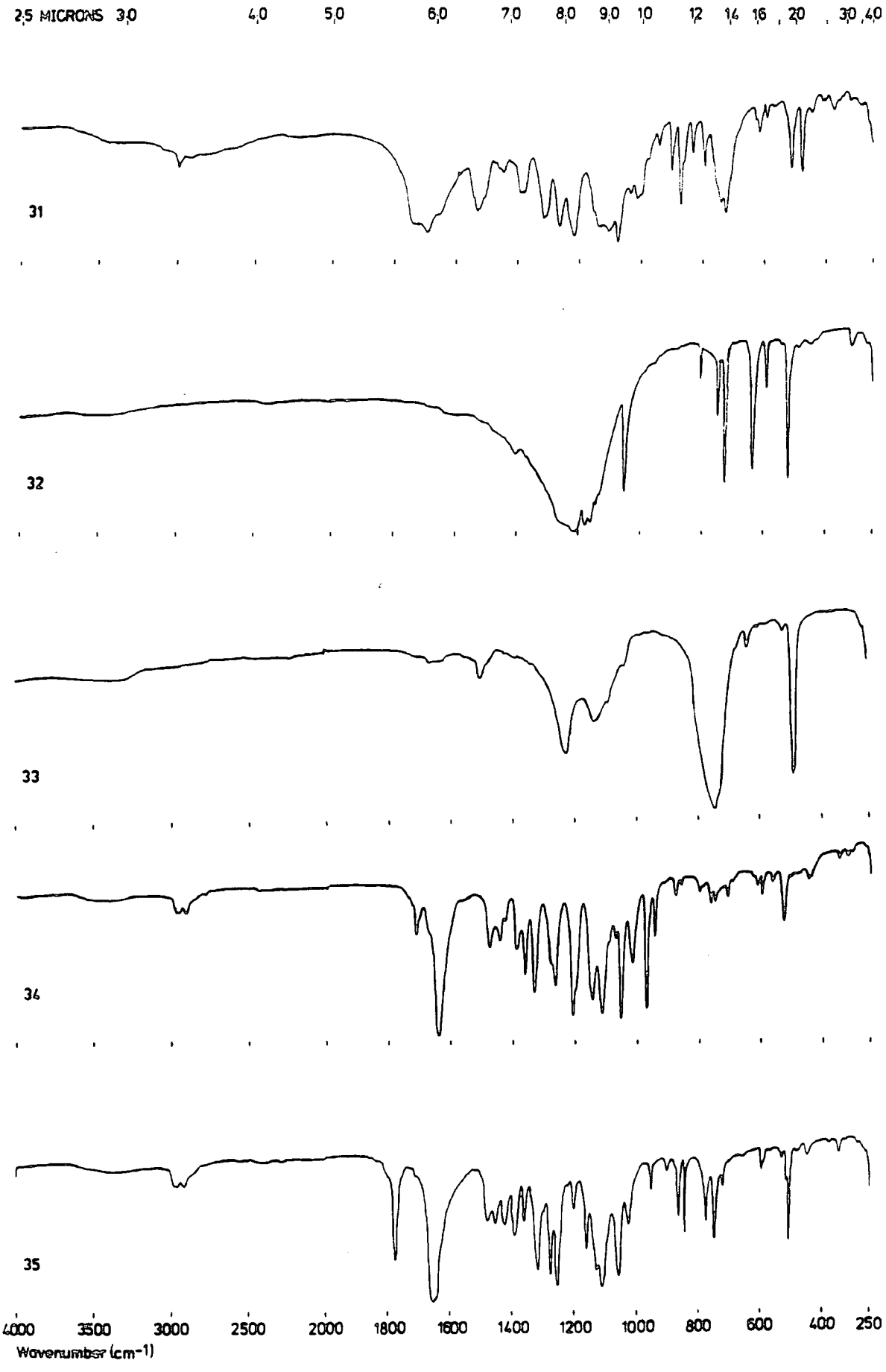

2,5 MICRONS 3,0 4,0 5,0 6,0 7,0 8,0 9,0 10 12 14 16 20 30 40
6
7
8
9
10
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250
Wavenumber (cm⁻¹)


2,5 MICRONS 3,0 4,0 5,0 6,0 7,0 8,0 9,0 1,0 1,2 1,4 1,6 2,0 3,0 4,0
11
12
13
14
15
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250
Wavenumber (cm-1)


2,5 MICRONS 3,0 4,0 5,0 6,0 7,0 8,0 9,0 10 12 14 16 20 30 40
16
17
18
19
20
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250
Wavenumber (cm-1)


2,5 MICRONS 3,0 4,0 5,0 6,0 7,0 8,0 9,0 10 12 14 16 20 30 40
21
22
23
24
25
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250
Wavenumber (cm⁻¹)


2.5 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10 12 14 16 20 30 40
26
27
28
29
30
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250
Wavenumber (cm⁻¹)


2,5 MICRONS 3,0 4,0 5,0 6,0 7,0 8,0 9,0 10 12 14 16 20 30 40
31
32
33
34
35
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250
Wavenumber (cm-1)

Appendix III

Mass Spectra

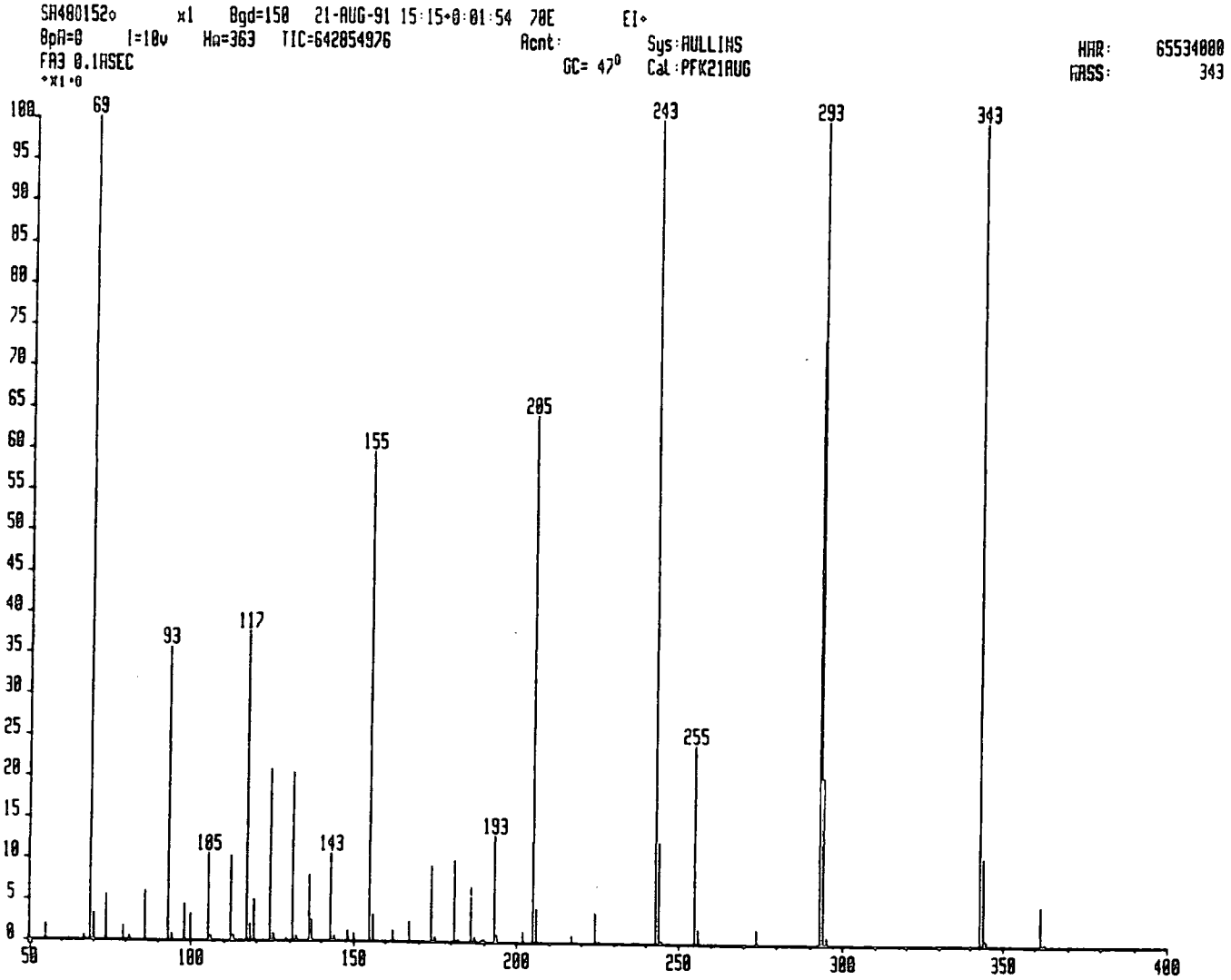
1. *Z,Z*-Perfluoro-3,4-dimethyl-hexa-2,4-diene (50)
2. *E,Z*-Perfluoro-3,4-dimethyl-hexa-2,4-diene (51)
3. Perfluoro-1,2,3,4-tetramethylcyclobutene (52)
4. *E,E*-Perfluoro-3,4-dimethyl-hexa-2,4-diene (60)
5. Perfluorobicyclopent-1,1'-enyl (43)
6. Perfluorobicyclobut-1,1'-enyl (46)
7. 4-Bromo-3-chlorohexafluorobut-1-ene (62)
8. *E*- and *Z*-4-Bromo-1,3-dichloropentafluorobut-1-ene (63) and (64)
9. 1,1,1-Trifluoropentan-3-one (146)
10. Tetrakis(trifluoromethyl)furan (73)
11. *Z,Z*-2-Phenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (74)
12. *Z,E*-2-Phenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (75)
13. *E,E*-2-Phenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (76)
14. *E,Z*-2-Phenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (77)
15. *Z,Z*-2,5-Diphenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (78)
16. *E,Z*-2,5-Diphenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (79)
17. *E,E*-2,5-Diphenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (80)
18. 2,2'-Diphenoxy-perfluorobicyclopent-1,1'-enyl (81)
19. Perfluoro-2,2',3,3'-tetramethyl-bi-2,2'-oxiranyl (86)
20. Perfluoro-1,3,4,6-tetramethyl-2,5-dioxabicyclo[2.2.0]hexane (90) or
    Perfluoro-1,2,4,5-tetramethyl-3,6-dioxabicyclo[3.1.0]hexane (91)
21. Tetrakis(trifluoromethyl)thiophene (92)
22. *E,Z*-2,5-Dithiophenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (94)
23. *Z,Z*-2,5-Dithiophenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (95)
24. *E,E*-2,5-Dithiophenoxy-perfluoro-3,4-dimethyl-hexa-2,4-diene (96)
25. Z,Z-2,5-Diamino-perfluoro-3,4-dimethyl-hexa-2,4-diene (101)
26. 2,4,5-Tris(trifluoromethyl)-3-cyano-pyrrole (102)

27. 2,5-Diamino-3,4-dicyano-1,1,1,6,6,6-hexafluorohexa-2,4-diene (103)
28. 1-Phenyl-tetrakis(trifluoromethyl)pyrrole (108)
29. 1-*H*-1-Phenyl-2,3,4-tris(trifluoromethyl)pyrrolo[3,2-*c*]quinoline (109)
30. 1-(4'-Dimethylaminophenyl)-tetrakis(trifluoromethyl)pyrrole (111)
31. 1-(4'-Methoxyphenyl)-tetrakis(trifluoromethyl)pyrrole (112)
32. 1-*H*-1-(4'-Methoxyphenyl)-2,3,4-tris(trifluoromethyl)-8-methoxy-pyrrolo-[3,2-*c*]quinoline (113)
33. 1-(4'-Fluorophenyl)-tetrakis(trifluoromethyl)pyrrole (114)
34. 1-*H*-1-(4'-Fluorophenyl)-2,3,4-tris(trifluoromethyl)-8-fluoro-pyrrolo[3,2-*c*]quinoline (115)
35. 1-(4'-Chlorophenyl)-tetrakis(trifluoromethyl)pyrrole (116)
36. 1-(4'-Nitrophenyl)-tetrakis(trifluoromethyl)pyrrole (117)
37. 1-(2'-Methoxyphenyl)-tetrakis(trifluoromethyl)pyrrole (118)
38. 1-*H*-1-(2'-Methoxyphenyl)-2,3,4-tris(trifluoromethyl)-6-methoxy-pyrrolo-[3,2-*c*]quinoline (119)
39. 1-(3'-Methoxyphenyl)-tetrakis(trifluoromethyl)pyrrole (120)
40. 1-*H*-1-(3'-Methoxyphenyl)-2,3,4-tris(trifluoromethyl)-9-methoxy-pyrrolo-[3,2-*c*]quinoline (121) and
    1-*H*-1-(3'-Methoxyphenyl)-2,3,4-tris(trifluoromethyl)-7-methoxy-pyrrolo-[3,2-*c*]quinoline (122)
41. 5,5-Bis(ethoxycarbonyl)tetrakis(trifluoromethyl)cyclopentadiene (137)
42. Caesium tetrakis(trifluoromethyl)ethoxycarbonylcyclopentadienide (136)
43. Caesium 1-ethoxycarbonylperfluoro-2,3,4,5,6-hexahydrodicyclo-penta[*b*,*d*]cyclopentadienide (138)
44. 5-Ethoxycarbonyl-5-propanoyl-tetrakis(trifluoromethyl)cyclopentadiene (142)
45. Hexakis(trifluoromethyl)benzene (145)
46. Caesium tetrakis(trifluoromethyl)propanoylcyclopentadienide (141)
47. Caesium pentakis(trifluoromethyl)cyclopentadienide (144)

48. Caesium perfluoro-1-methyl-2,3,4,5,6,7-hexahydro-dicyclopenta[*b*,*d*]-cyclopentadienide (153)

49. Caesium perfluoro-1,2,3-trihydro-4,5,6-trimethyl-pentalenide (154)

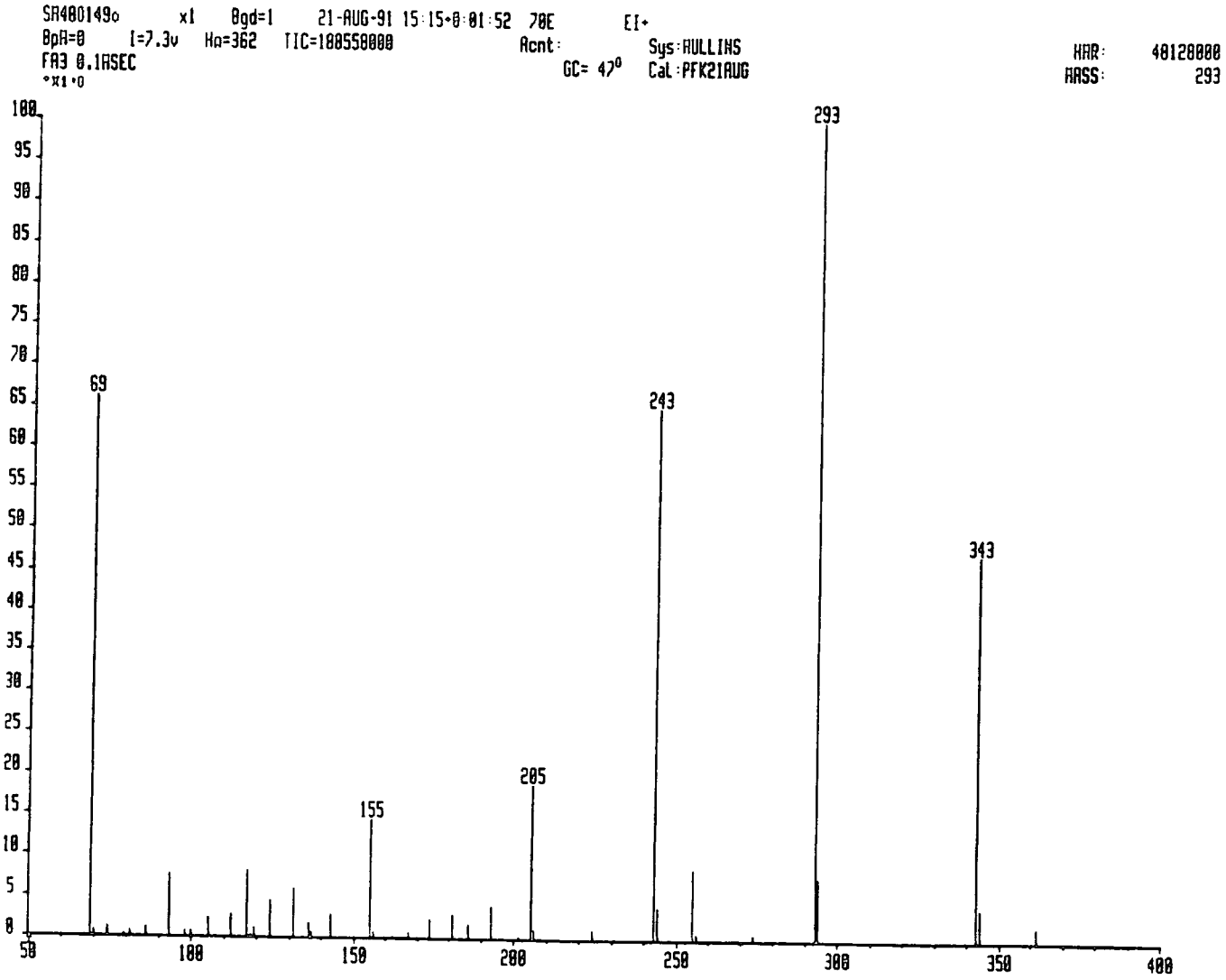
Mass spectrum number 1.



EI+ data

Mass	% Base		Mass	% Base	
49.81	3.55		154.98	59.57	
54.85	1.69		155.99	3.13	
66.95	0.39		161.99	1.17	
68.94	100.00	O	166.99	2.34	
69.96	3.13		173.99	8.98	
73.97	5.47		175.02	0.39	
78.99	1.61		180.98	9.77	
81.01	0.39		185.99	6.64	
86.00	5.86		187.01	0.39	
92.99	35.56		192.98	12.89	
94.01	0.79		194.01	0.78	
98.00	4.30		201.63	1.17	
99.99	3.13		204.98	64.09	
104.99	10.55		205.98	3.91	
106.01	0.39		217.01	0.78	
111.98	10.16		223.98	3.55	
112.50	0.39		242.75	53.64	F
117.00	37.55		243.00	100.00	FO
118.00	1.95		243.96	12.19	
118.99	4.77		254.95	23.88	
123.99	20.70		255.98	1.57	
125.01	0.78		273.96	1.58	
130.98	20.36		292.68	73.44	F
132.01	0.39		292.99	100.00	FO
135.99	7.84		293.95	20.20	F
136.88	0.78	F	295.01	0.78	
137.00	2.34	F	342.94	100.00	FO
142.98	10.55	.	343.95	10.55	F
144.01	0.39		345.03	0.39	
148.01	1.17		361.95	4.69	
150.00	0.78				

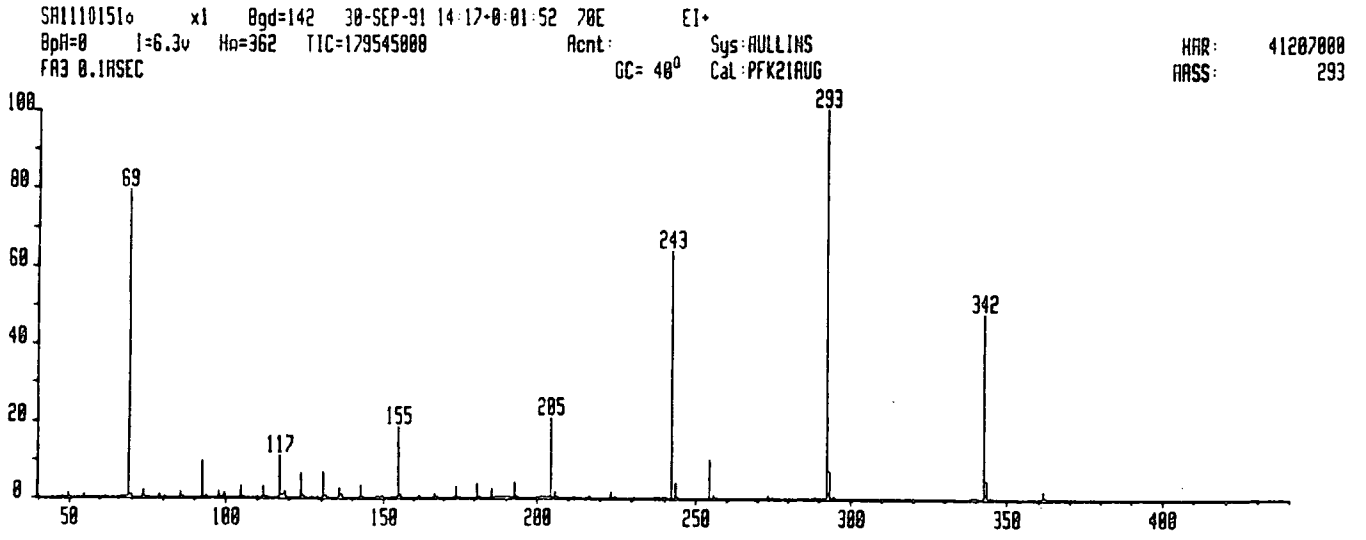
Mass spectrum number 2.



EI+ data

Mass	% Base		
68.96	65.96	274.02	0.53
69.97	0.53	293.01	100.00
73.98	1.06	294.02	7.45
81.01	0.53	343.02	47.34
86.01	1.06	344.03	3.72
93.01	7.51	362.00	1.60
98.02	0.55		
100.01	0.53		
105.01	2.13		
112.01	2.66		
117.01	7.99		
119.01	1.06		
124.01	4.37		
131.01	5.85		
136.01	1.60		
137.02	0.53		
143.00	2.66		
155.01	14.36		
156.01	0.53		
167.02	0.53		
174.02	2.13		
181.02	2.70		
186.02	1.60		
193.02	3.72		
205.02	18.66		
206.02	1.06		
224.02	1.06		
243.01	64.89		
244.01	3.72		
255.01	8.51		
256.02	0.53		

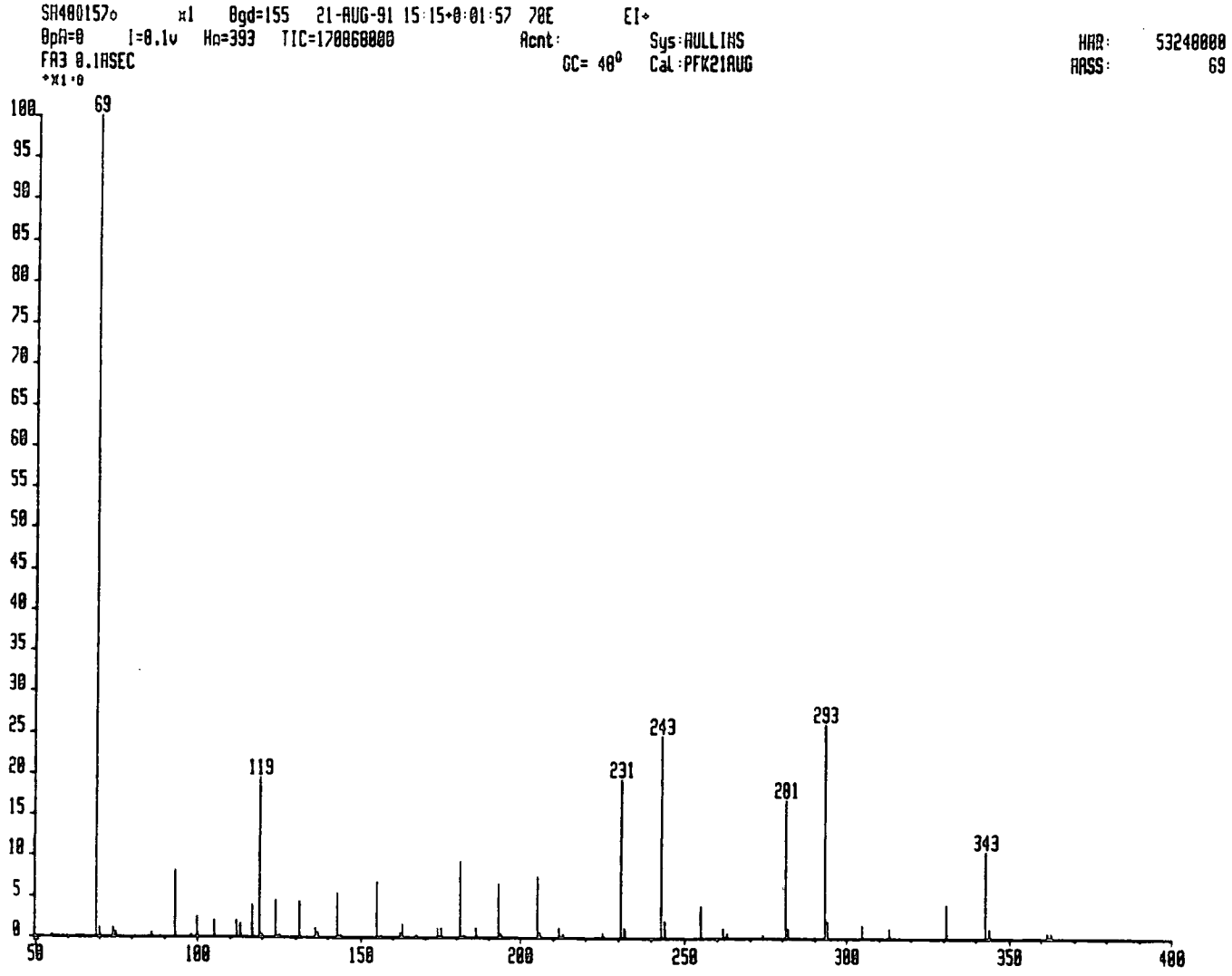
Mass spectrum number 3.



EI+ data

Mass	% Base	
49.64	0.89	
54.67	0.62	
68.75	79.11	
69.75	0.76	
73.76	1.58	
78.77	0.63	
85.76	1.46	
92.75	9.16	
97.74	1.33	
99.74	0.91	
104.73	2.82	
111.71	2.86	
116.71	10.56	
117.72	0.62	
118.71	1.24	
123.70	6.04	
130.69	6.36	
135.68	2.49	
136.68	0.69	
142.67	2.91	
147.66	0.43	
154.65	18.19	
155.65	0.77	
161.65	0.36	
166.65	0.92	
173.63	2.77	
180.62	3.35	
185.61	2.17	
192.59	3.82	
204.59	20.61	
205.60	1.33	
216.59	0.32	
223.57	1.42	
242.54	63.67	
243.55	3.84	
254.53	9.95	
255.54	0.68	
273.54	0.73	
292.52	100.00	F
293.50	6.95	F
342.46	47.65	
343.49	4.35	
361.45	1.86	

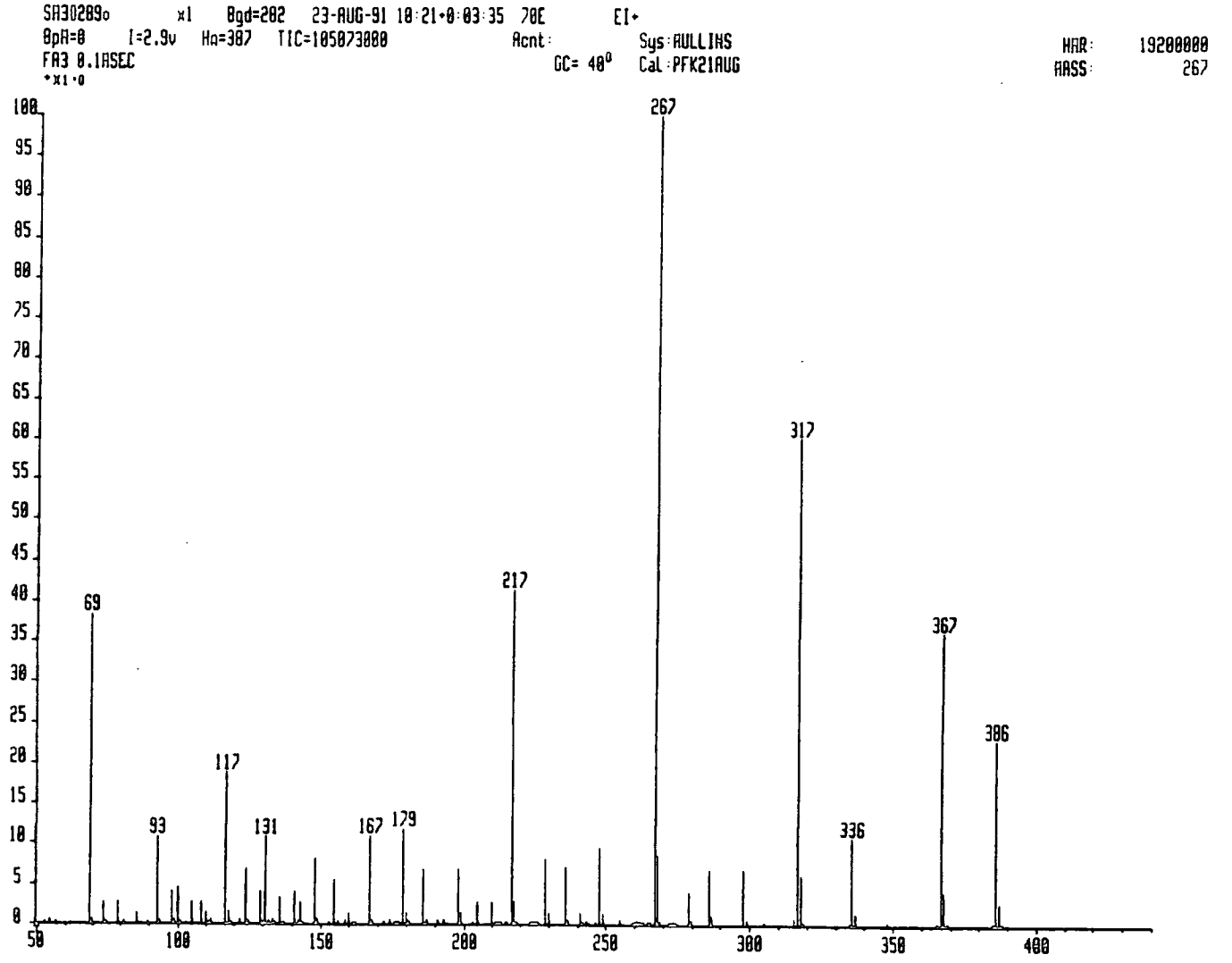
Mass spectrum number 4.



EI+ data

Mass	% Base		
49.82	0.96	231.01	19.30
68.96	100.00	232.01	0.96
69.97	0.96	243.00	24.52
73.98	0.99	244.00	1.92
75.00	0.48	255.00	3.85
86.01	0.48	261.99	0.96
93.01	8.02	263.01	0.48
100.01	2.40	274.00	0.32
105.01	1.92	281.01	16.83
112.01	1.92	282.01	0.96
113.01	1.46	293.01	25.96
117.01	3.85	294.01	1.92
119.01	19.36	305.02	1.44
124.01	4.33	313.01	0.96
131.01	4.19	331.02	3.88
136.01	0.96	343.01	10.58
137.02	0.48	344.02	0.96
143.00	5.29	362.00	0.48
155.01	6.73	363.01	0.48
162.01	0.48		
163.02	1.44		
174.01	0.96		
175.02	0.96		
181.01	9.13		
186.01	0.96		
193.02	6.36		
194.02	0.32		
205.02	7.26		
206.03	0.48		
212.01	0.96		
213.03	0.34		
225.03	0.48		

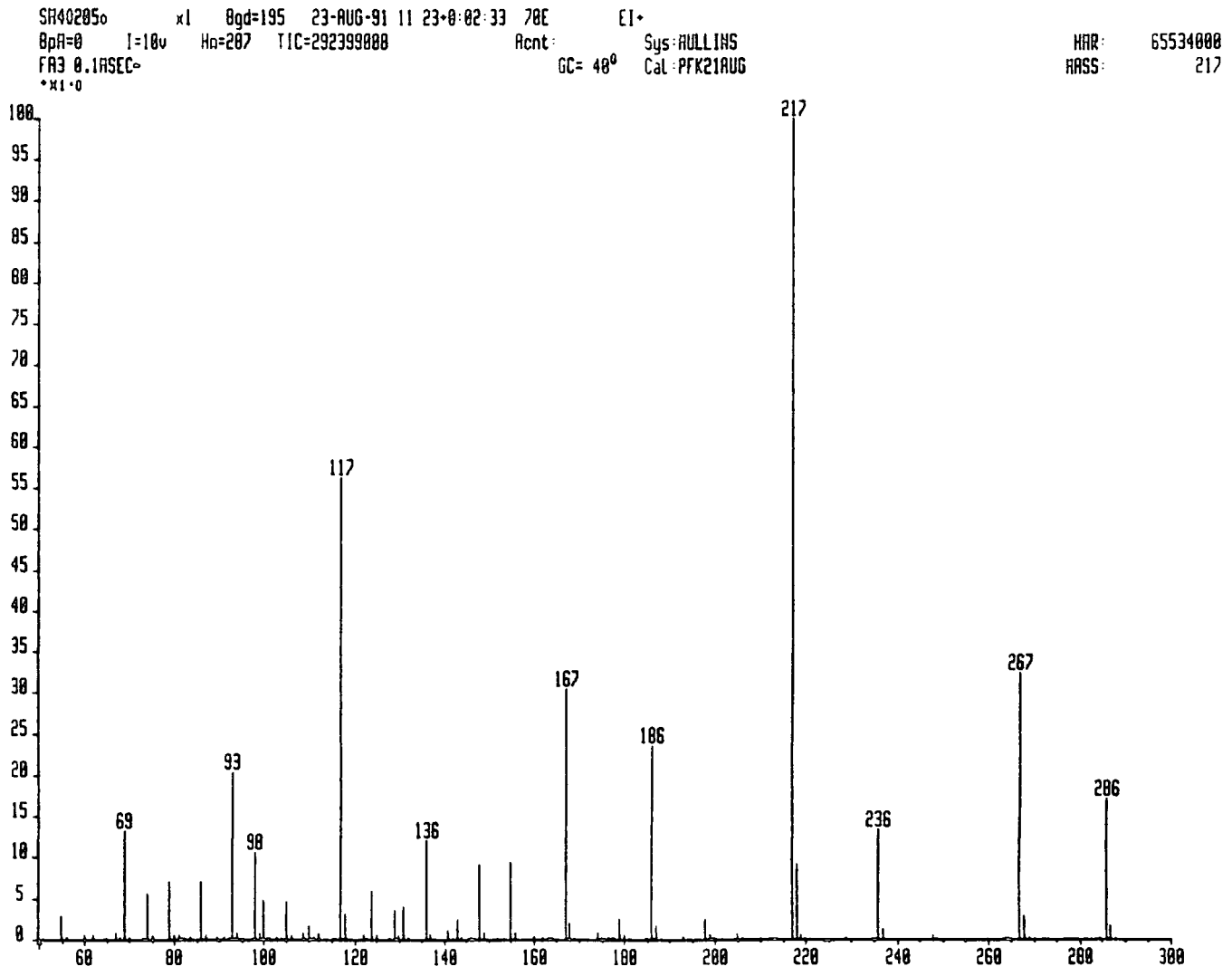
Mass spectrum number 5.



EI+ data

Mass	% Base				
49.79	1.33	158.44	0.42	285.89	6.67
54.84	0.49	159.94	1.33	286.92	1.01
68.92	38.30	166.93	10.74	297.88	6.67
69.93	0.48	167.95	0.43	298.89	0.41
73.94	2.67	173.95	0.51	315.48	0.71
78.96	2.67	178.93	11.67	316.87	60.09
80.97	0.33	179.94	1.33	317.88	5.92
85.96	1.33	180.94	0.35	335.86	10.67
92.96	10.67	185.93	6.67	336.86	1.33
97.96	4.00	186.95	0.43	347.84	0.36
98.96	0.49	190.93	0.44	366.82	36.19
99.96	4.45	192.93	0.48	367.82	4.00
104.96	2.67	197.93	6.76	385.83	22.93
108.46	2.67	198.94	1.33	386.82	2.67
109.95	1.33	204.92	2.67		
111.96	0.43	209.92	2.67		
116.95	18.67	216.91	41.33		
117.96	1.44	217.91	2.83		
121.97	0.37	228.89	8.00		
123.95	6.67	229.92	1.33		
124.96	0.30	235.90	6.94		
128.95	4.00	236.91	0.40		
129.96	0.31	240.91	1.33		
130.95	10.67	247.90	9.33		
133.45	0.47	248.90	1.33		
135.94	3.22	254.89	0.49		
140.94	4.00	259.95	0.31		
142.94	2.67	266.89	100.00		
147.94	8.02	267.90	8.40		
148.95	0.62	278.88	4.00		
154.94	5.33	279.89	0.45		

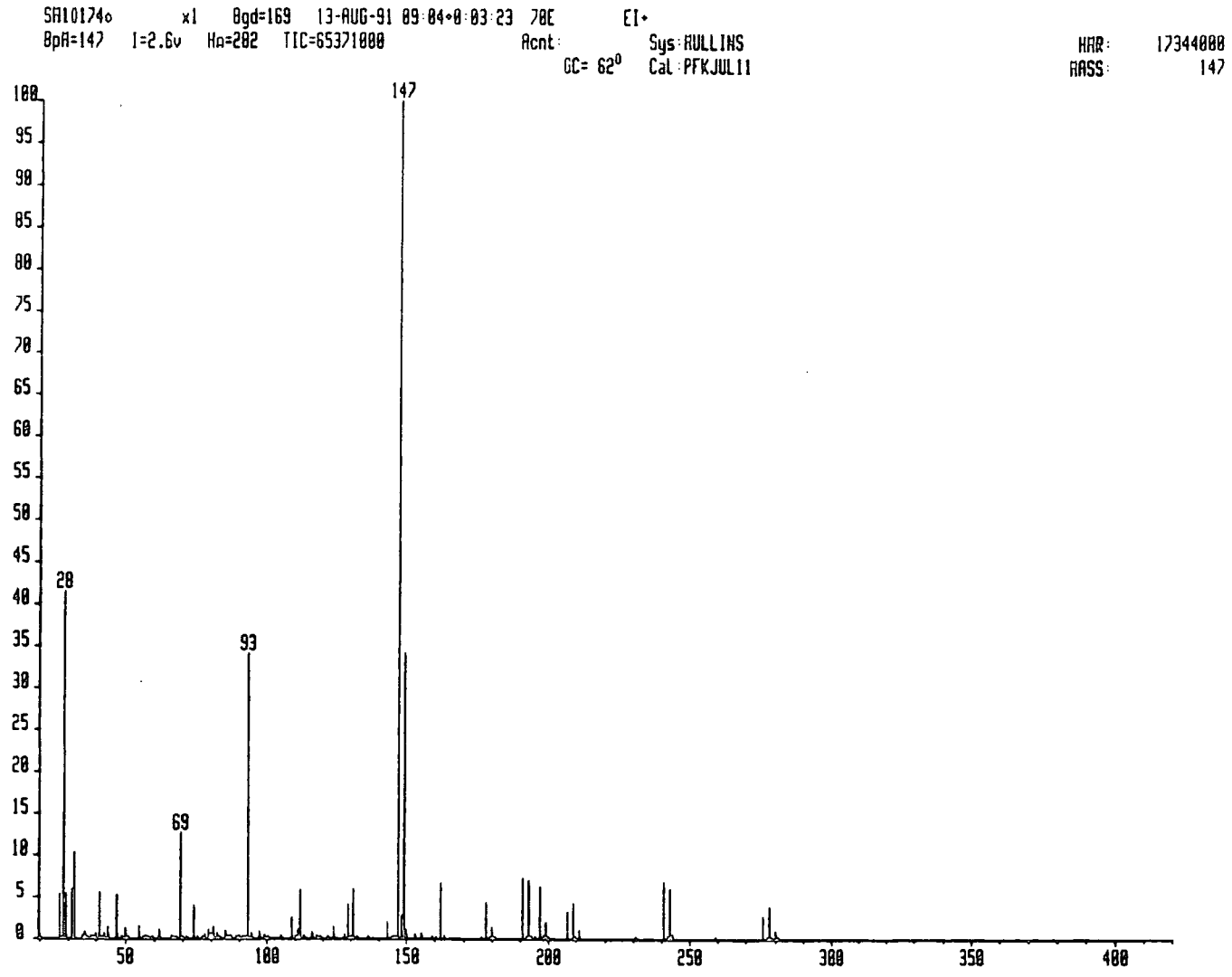
Mass spectrum number 6.



EI+ data

Mass	% Base			
49.79	3.22	140.94	1.07	
54.82	2.73	142.93	2.34	
59.86	0.39	147.92	9.03	
61.87	0.39	148.94	0.78	
66.91	0.78	154.93	9.38	
68.92	13.14	155.94	0.78	
73.94	5.52	166.94	30.40	
74.95	0.39	167.94	1.96	
78.96	7.03	173.94	0.78	
79.97	0.39	178.92	2.46	
80.97	0.39	179.92	0.39	
85.96	7.03	185.92	23.44	
86.97	0.39	186.93	1.56	
92.96	20.31	197.92	2.34	
93.96	0.78	198.92	0.39	
97.96	10.56	204.91	0.65	
98.97	0.78	216.91	100.00	FO
99.95	4.69	217.89	8.98	F
104.95	4.48	218.90	0.39	
105.96	0.39	235.90	13.28	
108.46	0.78	236.90	1.23	
109.95	1.56	247.89	0.47	
111.95	0.78	266.88	32.42	F
116.96	56.25	267.88	2.78	F
117.96	3.13	285.87	17.13	
121.95	0.39	286.88	1.57	
123.95	5.86			
124.96	0.39			
128.88	3.52			
129.95	0.39			
130.95	3.98			
135.94	11.99			
136.95	0.62			

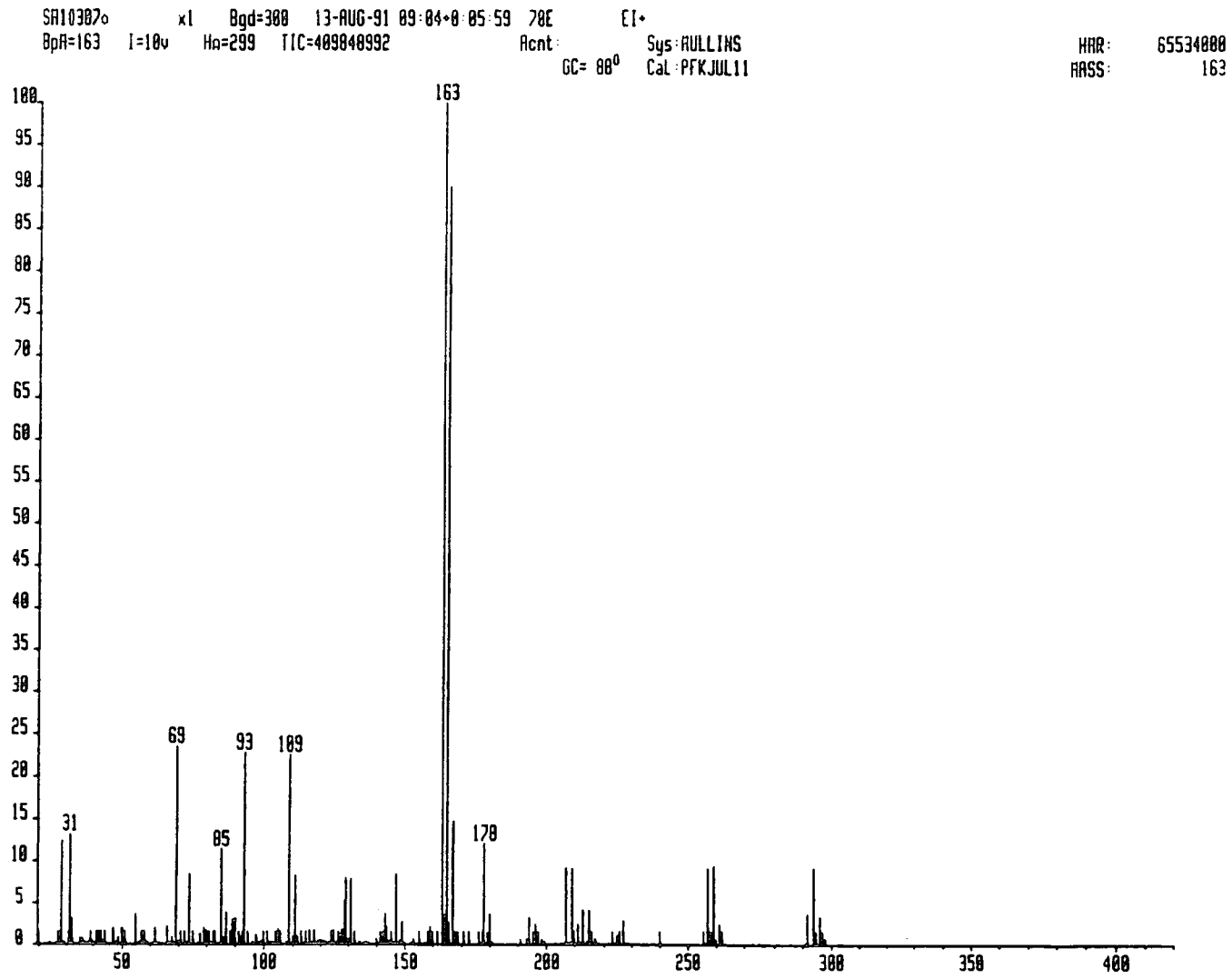
Mass spectrum number 7.



EI+ data

Mass	% Base		
41.07	5.39	147.06	100.00
43.07	0.58	148.07	2.73
44.02	1.22	149.07	33.95
47.02	5.17	150.08	0.99
50.04	1.15	153.02	0.40
55.05	1.39	155.02	0.53
57.12	0.32	162.10	6.56
62.05	1.00	178.09	4.35
69.05	12.59	180.08	1.34
74.05	3.87	191.05	7.12
78.03	0.36	193.05	6.81
78.99	0.97	197.10	6.15
79.99	0.57	199.10	1.83
81.03	1.33	207.03	3.15
81.98	0.55	209.03	4.09
85.03	0.81	211.04	1.03
87.04	0.31	241.07	6.65
93.06	33.95	243.07	5.92
94.07	0.59	244.09	0.36
97.04	0.66	276.06	2.57
109.05	2.38	278.05	3.66
111.05	1.01	280.04	0.87
112.07	5.67		
116.05	0.72		
118.05	0.33		
124.08	1.23		
128.06	0.45		
129.01	4.04		
131.05	5.92		
143.09	1.89		

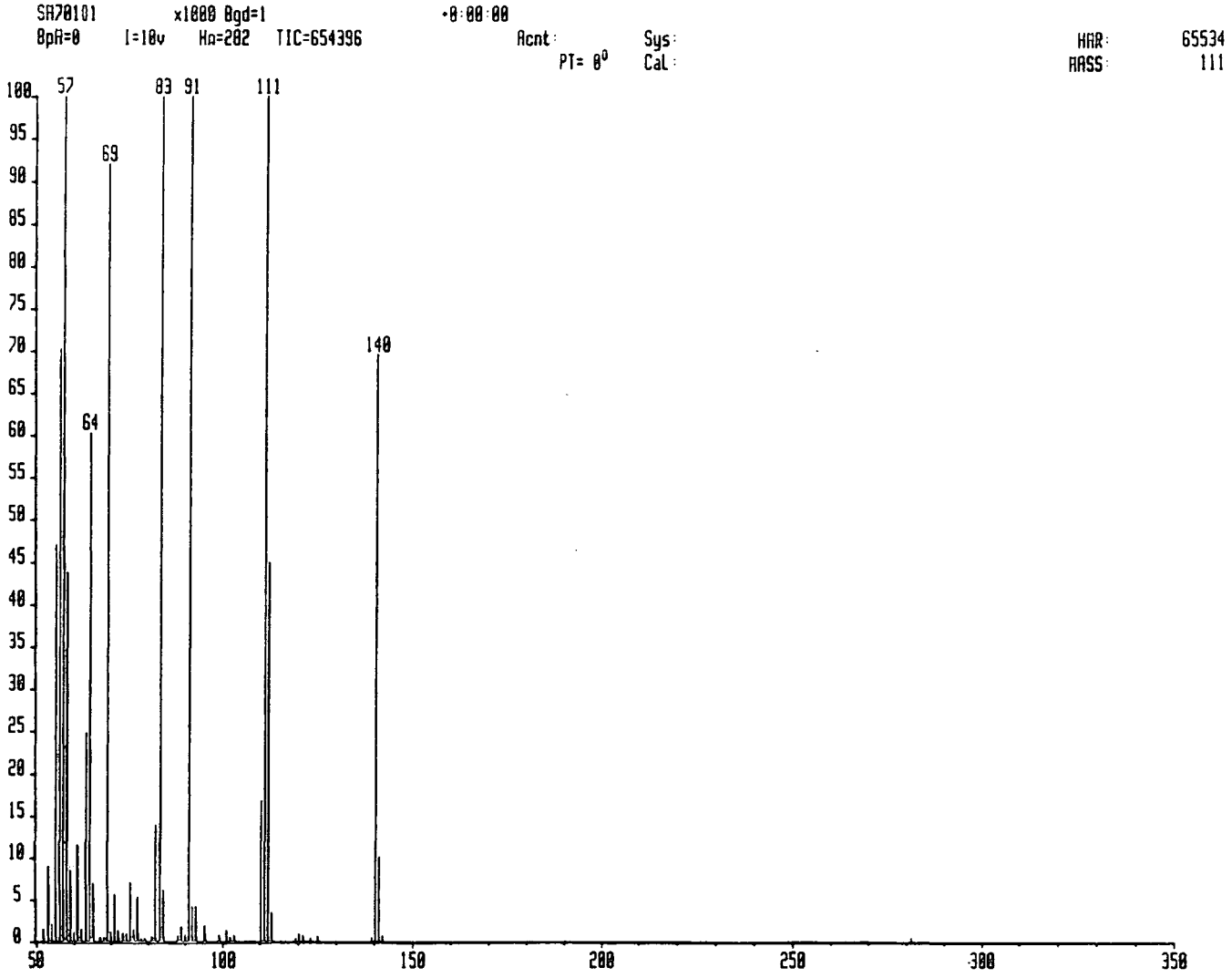
Mass spectrum number 8.



EI+ data

Mass	% Base						
28.00	1.08		158.91	1.06		212.67	0.07
30.98	9.33		161.78	4.38		212.87	4.58
46.96	1.28		161.90	4.38		213.88	0.21
54.98	4 38		162.10	4.38		214.86	2.96
65.95	1.88		162.19	4.38		215.86	0.17
68.97	18.48	F	162.88	100.00		216.86	0.49
69.00	9.31	F	163.89	3.23		222.78	0.49
73.97	4.23		164.87	66.51	F	224.80	4.38
78.97	4.38		164.96	6.73	F	226.78	0.31
84.86	4.38		165.88	2.11		228.79	0.06
84.94	7.75		166.65	4.38		256.54	0.06
86.94	2.72		166.88	11.03		256.81	5.04
88.96	2.56		167.87	4.38		257.77	4.38
89.95	1.84		177.90	7.85		258.81	6.04
92.97	12.65		179.89	4.38		259.81	4.38
93.98	4.38		180.88	0.14		260.80	1.57
98.94	4.38		185.84	0.05		261.80	0.07
100.93	4.38		190.83	0.38		291.77	3.39
104.95	4.38		192.82	0.46		292.75	4.38
108.82	4.38		193.84	4.38	F	293.50	0.07
108.93	12.87		193.90	4.38	F	293.77	5.94
110.93	4.12		194.87	0.16		294.76	0.23
115.93	1.19		195.87	1.42		295.76	4.38
117.93	4.38		196.84	0.18		296.76	0.12
123.96	4.38		197.86	0.31		296.85	0.05
127.92	1.08		198.85	0.05		297.76	0.35
128.88	4.27		206.82	4.31			
130.86	4.48	F	207.82	0.19			
130.92	4.38	F	208.64	0.07			
142.95	2.06		208.82	6.08			
146.91	5.10		209.81	0.20			
147.94	4.38		210.81	1.39			
148.91	1.73		212.64	0.08			

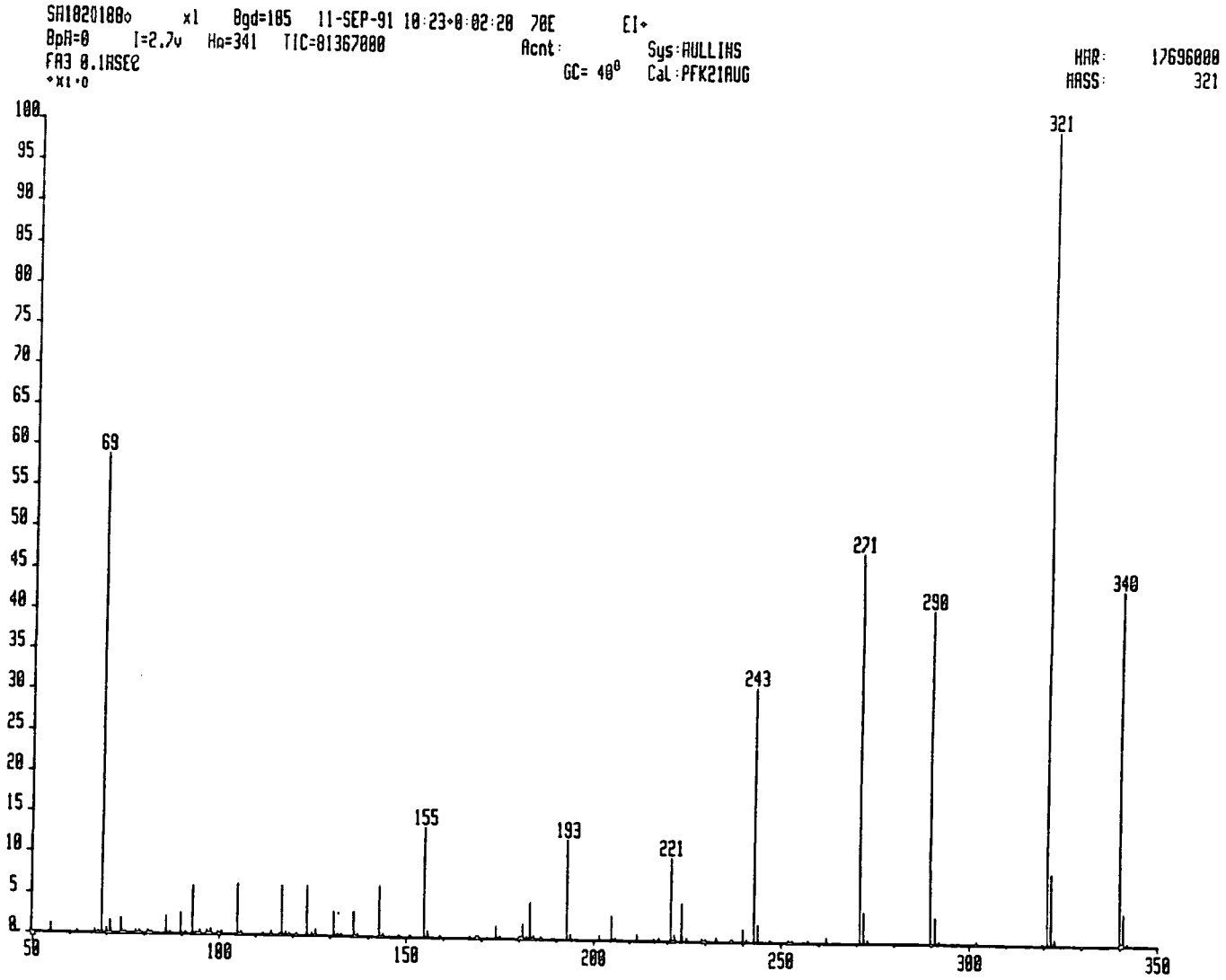
Mass spectrum number 9.



EI+ data

Mass	% Base		
52.10	1.40	89.18	1.67
53.08	7.45	90.17	0.91
53.12	8.86	91.17	100.00
54.09	2.01	92.17	4.20
54.13	0.82	93.18	4.20
55.11	47.00	95.18	1.80
56.11	70.20	99.18	0.67
57.14	100.00	101.20	1.30
58.13	43.70	102.20	0.43
59.13	8.44	103.21	0.68
60.13	0.97	110.18	16.75
61.11	11.45	111.22	100.00
62.11	1.38	112.19	44.90
63.11	24.72	113.19	3.46
64.12	60.35	120.21	0.89
65.13	6.87	121.21	0.66
67.12	0.42	125.20	0.55
68.13	0.45	139.24	0.40
69.11	92.01	140.24	69.62
70.13	1.19	141.25	9.99
71.13	5.64	142.26	0.71
72.16	1.25	281.36	0.38
73.16	1.02		
74.14	0.87		
75.15	6.94		
76.15	1.38		
77.16	5.26		
79.16	0.30		
81.15	0.63		
82.14	13.85		
83.18	100.00		
84.16	6.08		
88.17	0.65		

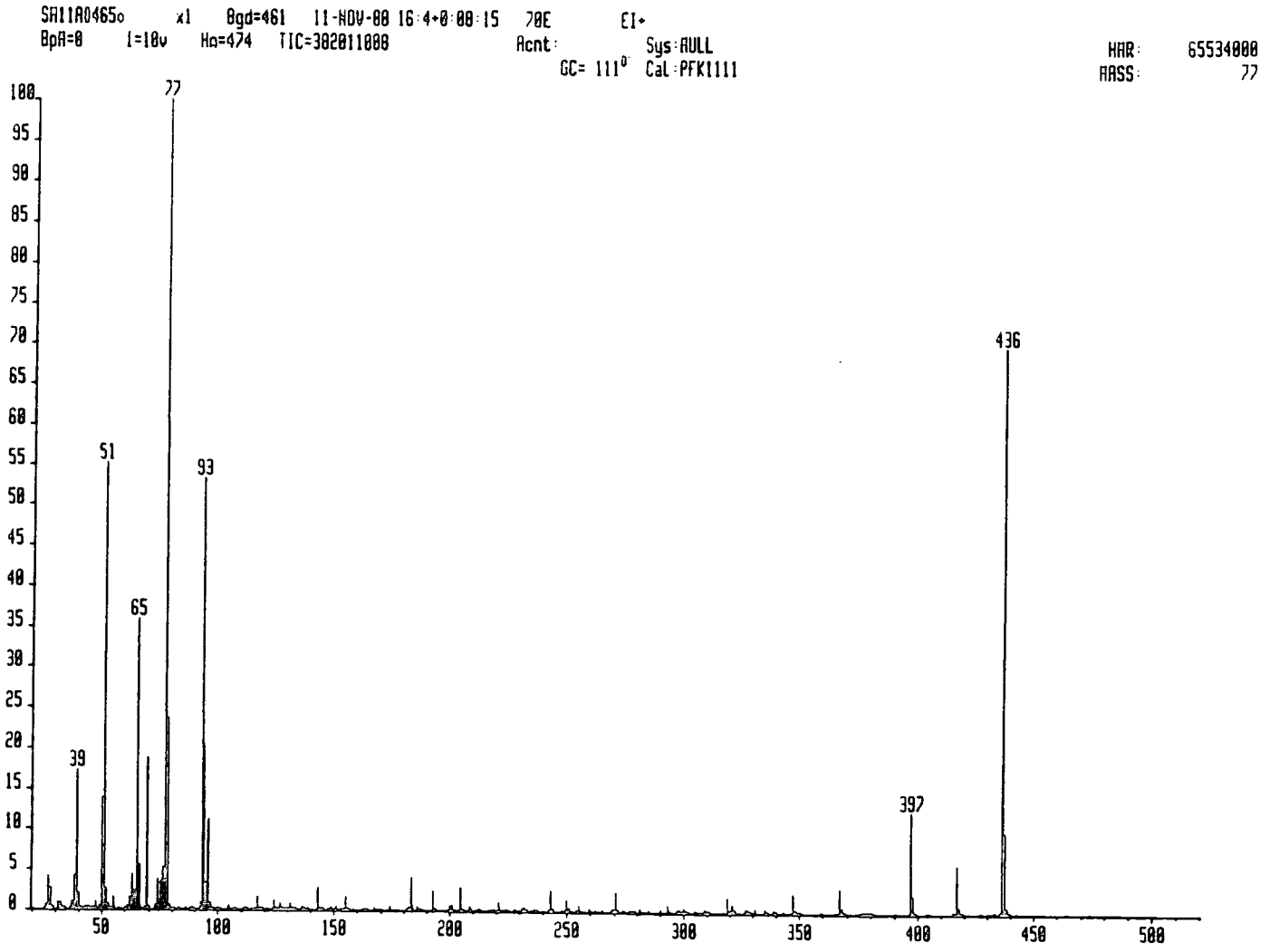
Mass spectrum number 10.



EI+ data

Mass	% Base		
49.77	1.48	211.93	0.75
54.81	1.05	217.78	0.32
66.90	0.33	220.92	10.13
68.91	58.70	221.94	0.68
69.91	0.65	223.94	4.59
70.91	1.45	224.95	0.34
73.93	1.72	232.94	0.40
78.95	0.31	239.93	1.45
80.95	0.35	242.93	31.14
85.95	2.00	243.94	2.02
89.94	2.51	261.94	0.61
92.95	5.79	270.94	47.78
94.94	0.42	271.94	3.63
96.94	0.51	289.94	40.81
97.95	0.63	290.94	3.13
104.94	6.08	320.94	100.00 F
113.94	0.47	321.95	8.68 F
116.94	5.95	322.97	0.54
117.95	0.31	339.95	43.54
123.94	5.97	340.95	3.79
125.94	0.75		
130.94	2.91		
135.94	2.89		
142.93	6.09		
154.94	13.44		
155.94	0.72		
173.94	1.50		
180.94	1.82		
182.94	4.34		
192.94	12.18		
193.95	0.63		
201.94	0.50		
204.94	2.89		

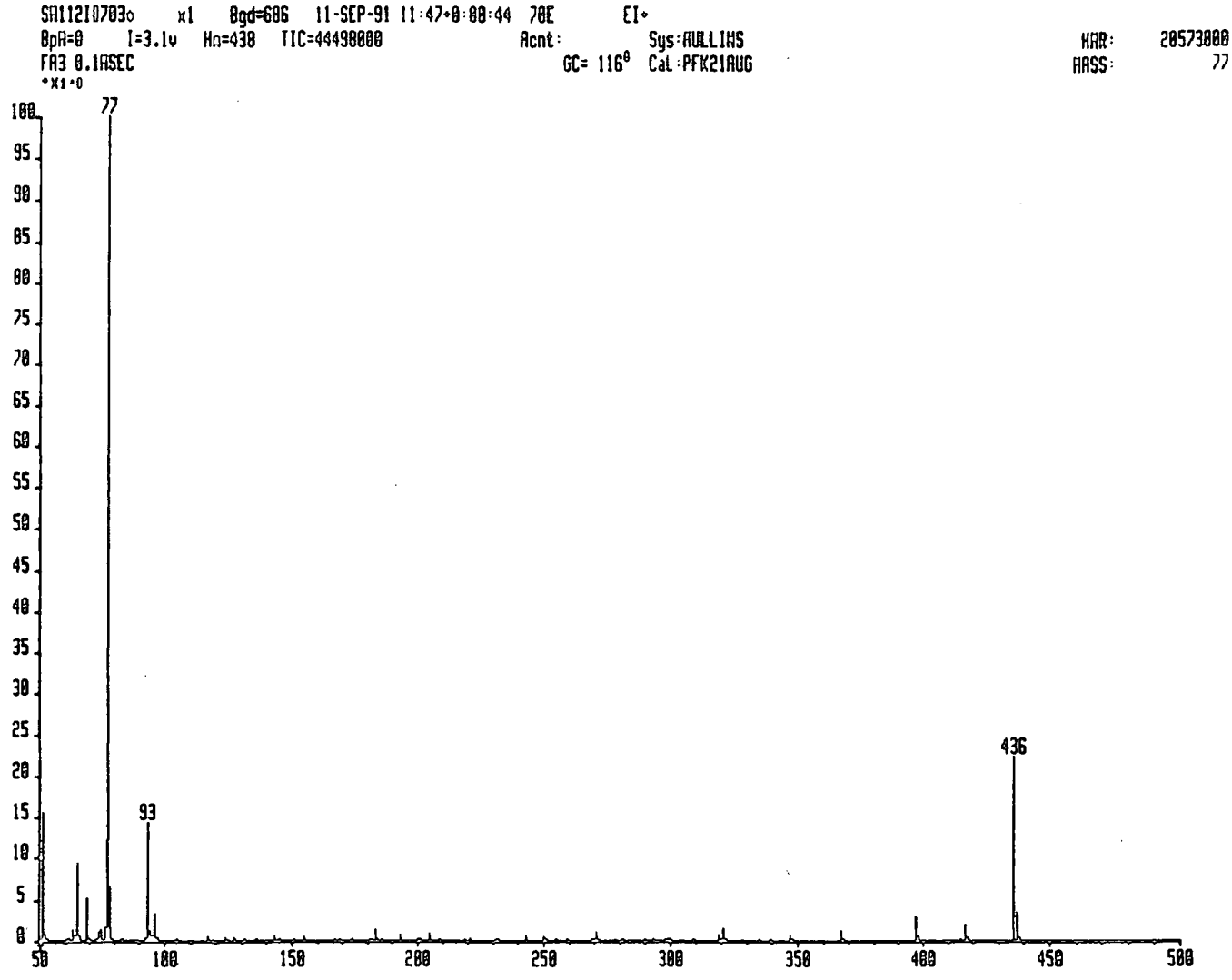
Mass spectrum number 11.



EI+ data

Mass	% Base	Mass	% Base
27.03	4.05	208.55	0.52
28.01	2.58	221.02	1.06
37.02	1.06	231.07	0.38
38.02	4.11	232.07	0.45
39.03	17.23	243.02	2.46
40.04	1.86	250.06	1.28
50.02	13.80	255.02	0.77
51.03	55.13	271.02	2.42
52.03	2.51	290.02	0.37
55.03	1.51	293.04	0.95
62.03	1.43	300.06	0.50
63.04	4.23	319.07	1.79
64.04	2.37	320.07	0.32
65.05	35.91	321.03	0.93
66.06	5.44	322.04	0.37
69.01	18.71	331.06	0.39
74.03	3.73	335.05	0.43
75.03	3.56	336.06	0.12
76.04	5.21	339.09	0.37
76.98	2.67	347.06	2.15
77.05	100.00 0	367.08	2.97
78.05	23.55	368.09	0.63
93.05	53.22	397.08	12.48
94.06	20.08	398.08	2.08
95.05	3.28	417.08	5.91
96.05	11.09	418.08	0.76
117.01	1.55	435.25	0.60
124.01	1.06	436.09	70.07
143.01	2.65	437.09	9.94
155.02	1.69	438.10	0.78
183.53	4.06		
193.00	2.34		
200.06	0.57		
201.07	0.60		
205.03	2.77		

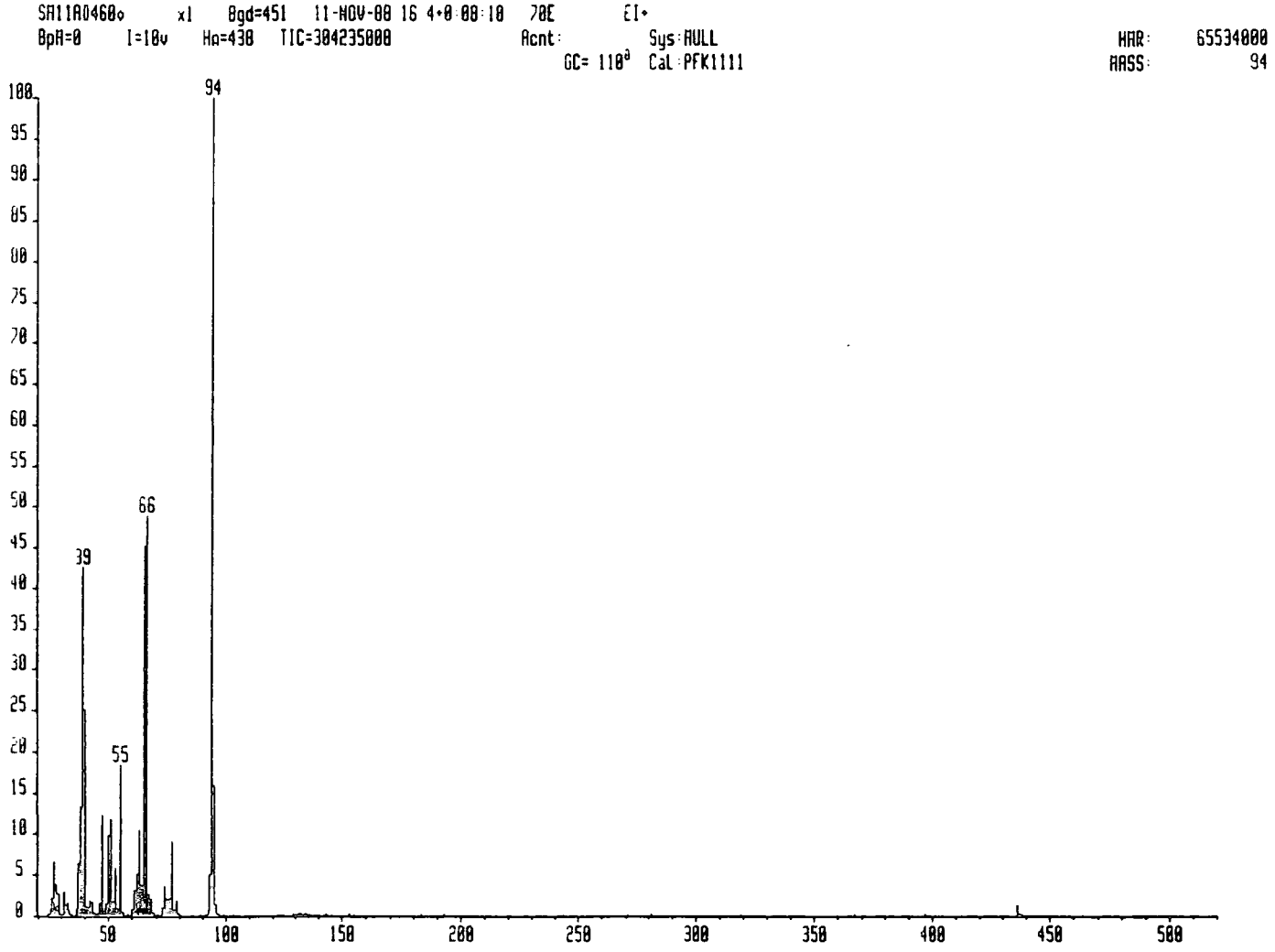
Mass spectrum number 12.



EI+ data

Mass	% Base		
49.80	3.74	397.11	2.94
50.82	15.40	398.12	0.39
51.83	0.70	417.11	1.95
61.89	0.35	436.13	22.40
62.91	1.24	437.14	3.35
63.92	0.66		
64.94	9.32		
65.95	0.53		
68.92	5.10		
73.97	1.09		
74.98	1.24		
75.99	1.57		
77.00	100.00		
78.01	6.43		
93.01	14.36		
94.02	1.14		
95.01	0.65		
96.02	3.18		
116.98	0.38		
123.98	0.32		
142.97	0.61		
154.98	0.48		
183.52	1.24		
192.99	0.68		
204.99	0.87		
220.98	0.34		
243.00	0.58		
250.04	0.46		
271.02	0.95		
319.08	0.70		
321.05	1.47		
347.08	0.60		
367.08	1.14		

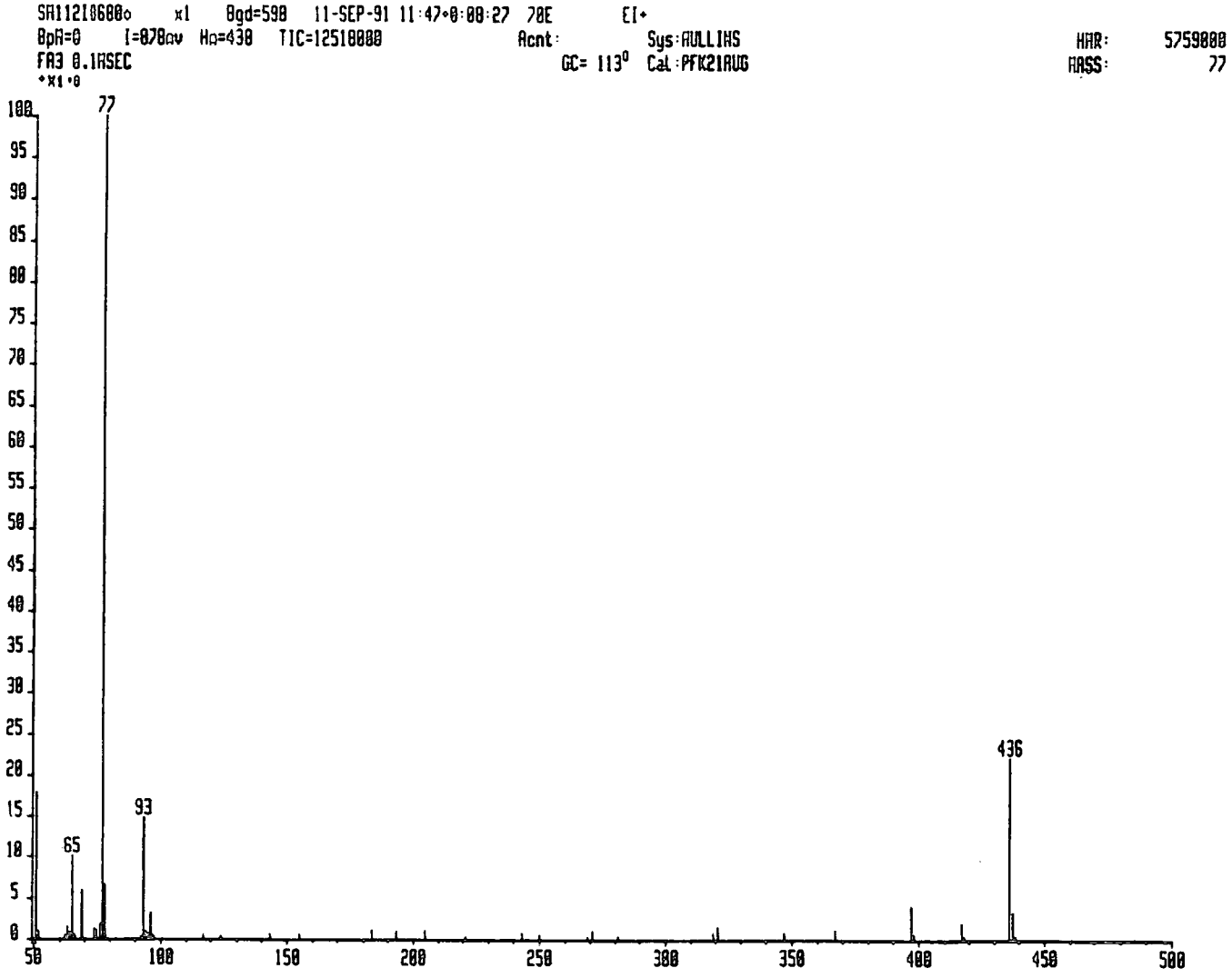
Mass spectrum number 13.



EI+ data

Mass	% Base			
26.02	2.28	75.03	2.04	
27.03	6.48	76.04	2.11	
28.01	3.75	77.05	8.97	
29.01	2.64	79.03	1.72	
31.01	2.76	93.03	4.99	F
31.52	1.01	93.97	1.93	F
31.99	1.07	94.05	100.00	0
32.02	1.13	95.06	15.86	
32.52	1.42	96.06	1.28	
37.01	6.33	206.01	0.06	
38.02	13.34	220.08	0.04	
39.03	42.52	233.08	0.05	
40.04	25.10	243.03	0.06	
41.04	1.02	271.03	0.08	
42.02	1.74	281.07	0.09	
43.03	1.61	319.03	0.07	
46.02	1.54	319.11	0.04	
47.03	12.16	367.05	0.11	
49.02	1.52	397.09	0.21	
50.02	9.79	415.12	0.04	
51.03	11.70	417.05	0.06	
52.04	1.75	418.08	0.04	
53.01	5.84	436.09	1.18	
55.03	18.40	437.08	0.17	
61.02	3.13	438.14	0.07	
62.03	5.09			
63.04	10.37			
64.05	3.81			
65.05	45.19			
66.06	48.83			
67.05	2.50			
68.04	1.88			
73.02	1.03			
74.03	3.55			

Mass spectrum number 14.

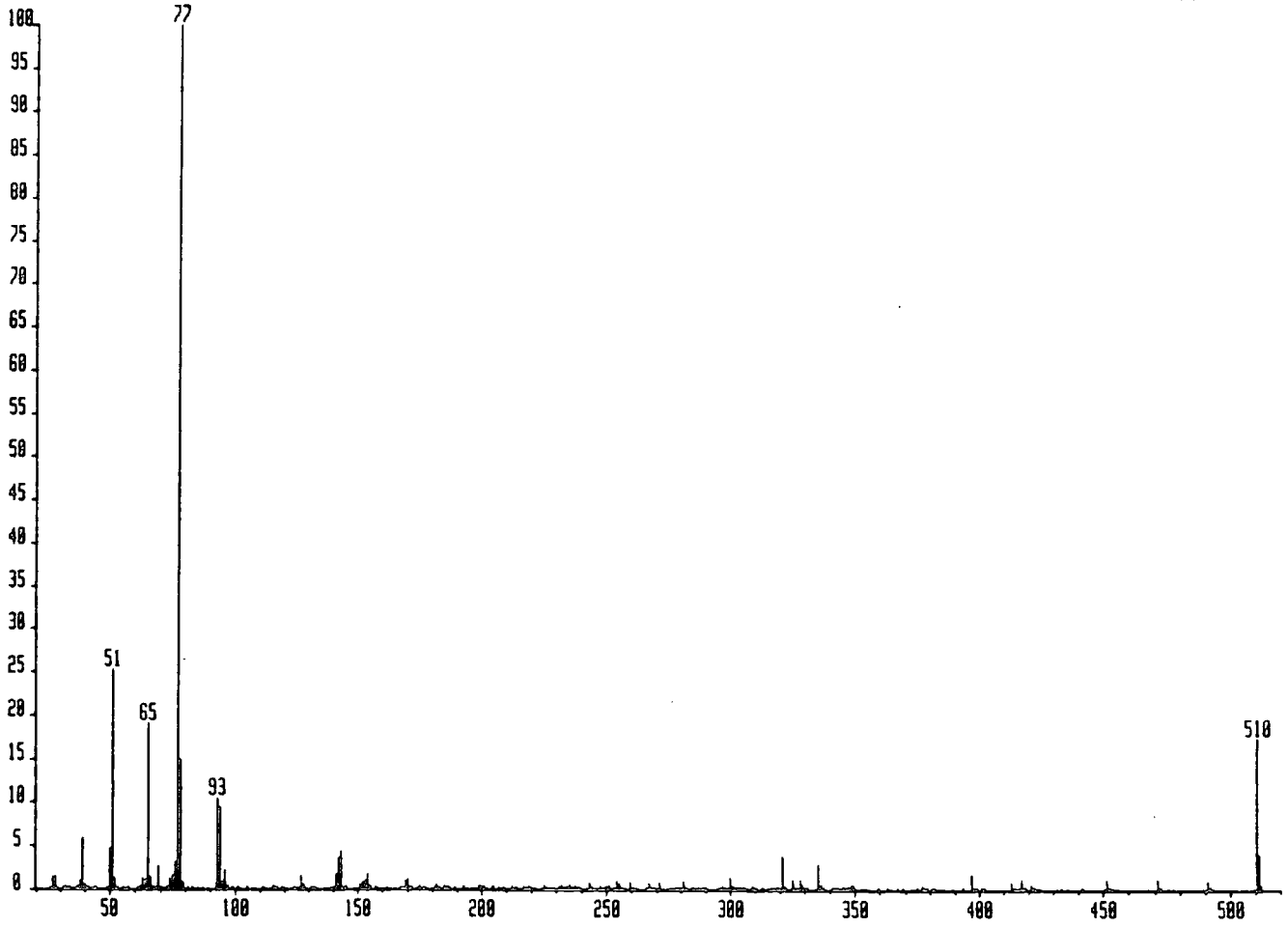


EI+ data

Mass	% Base
49.81	4.45
50.82	17.78
51.83	0.92
61.89	0.47
62.91	1.39
63.92	0.73
64.94	10.11
65.95	0.50
68.93	5.90
73.97	1.22
74.98	1.08
75.99	1.72
77.00	100.00
78.01	6.55
93.01	14.67
94.02	0.94
95.02	0.61
96.02	3.00
116.99	0.47
123.99	0.36
142.99	0.64
154.99	0.54
183.53	1.08
193.00	0.87
205.00	1.06
220.98	0.36
243.01	0.68
250.06	0.47
271.04	1.01
281.10	0.33
319.12	0.78
321.06	1.39
347.10	0.69
367.10	1.02
397.12	3.96
398.15	0.54
417.13	1.88
418.16	0.35
436.14	22.23
437.16	3.23
438.19	0.31

Mass spectrum number 15.

SA11B01020o x1 Bgd=1016 24-NOV-88 14:2+0:18:07 70E EI+
BpA=0 I=10v Ha=513 TIC=285518888 Acnt: Sys:AULL HAR: 65534000
GC= 210° Cal:PFK1111 MASS: 77

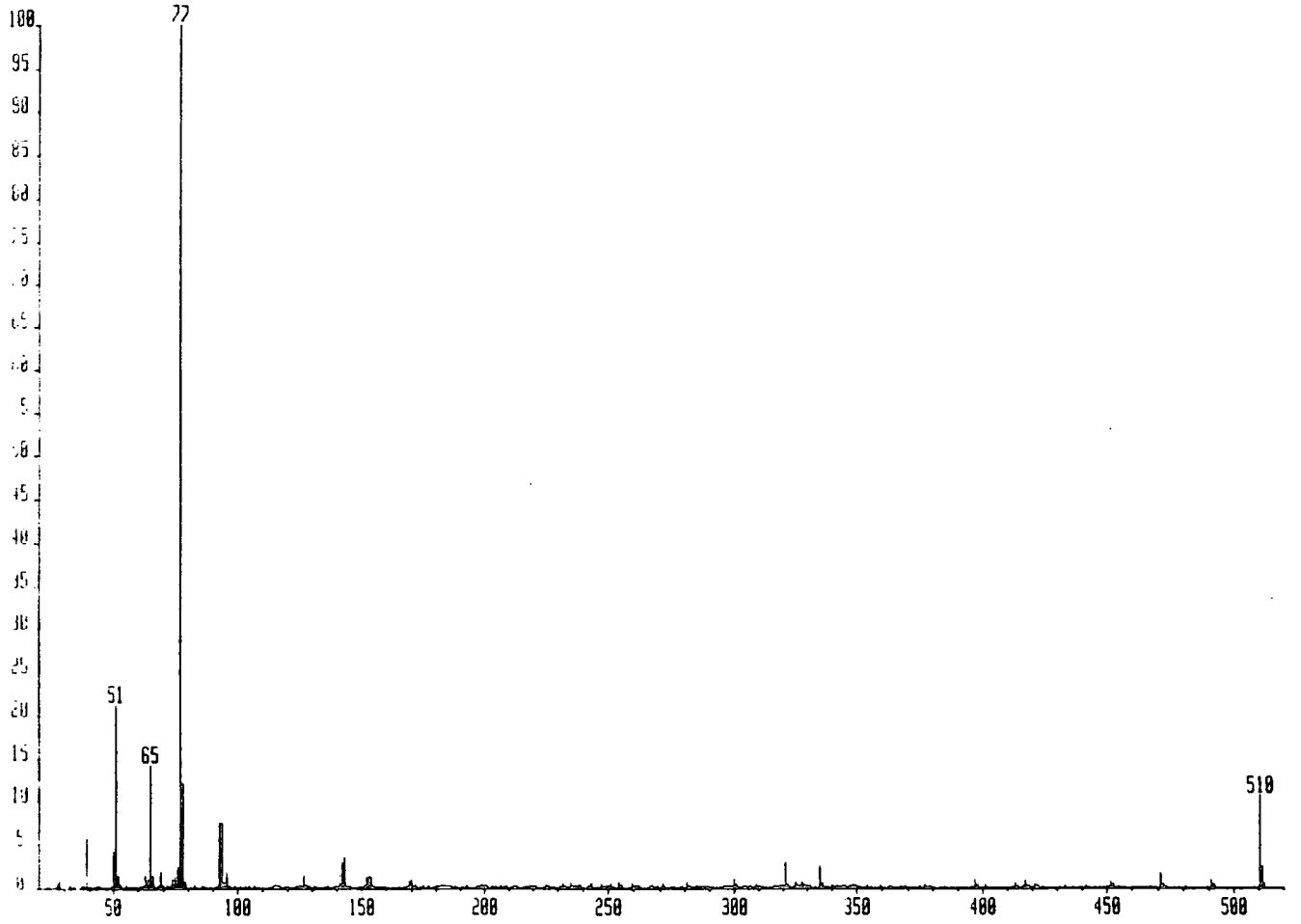


EI+ data

Mass	% Base		Mass	% Base	
27.01	1.34		325.12	1.11	
28.00	1.36		328.12	0.99	
39.01	5.76		329.12	0.45	
50.00	4.64		335.13	2.83	
51.01	25.12		336.13	0.46	
52.02	1.16		397.18	1.60	
63.02	1.25		413.22	0.74	
64.02	1.03		417 21	1.08	
65.03	18.96		451.29	1.10	
66.03	1.29		471.30	1.00	
68.98	2.50		510.36	17 26	
74.01	1.23		511.37	3.94	
75.01	1.52		512.36	0.40	
76.02	3.18				
76.95	1.07	F			
77.03	100.00	FO			
78.03	14.88				
93.02	10.40				
94.03	9.36				
96.03	2.05				
127.03	1.52				
141.07	1.56				
142.08	3.61				
143.00	4.23				
154.09	1.67				
235.06	0.51				
243.05	0.55				
254.06	0.91				
255.06	0.54				
259.07	0.77				
267.10	0 60				
271.05	0 74				
281.10	0.89				
300.10	1 13				
321.09	3.67				

Mass spectrum number 16.

SA1180961o x1 Bgd=955 24-NOV-88 14:2+8:17.84 70E EI+
BpA=8 I=10v Ha=512 TIC=175086000 Acnt: Sys:NULL HAR: 65452000
GC= 200° Cal:PFK1111 MASS: 77

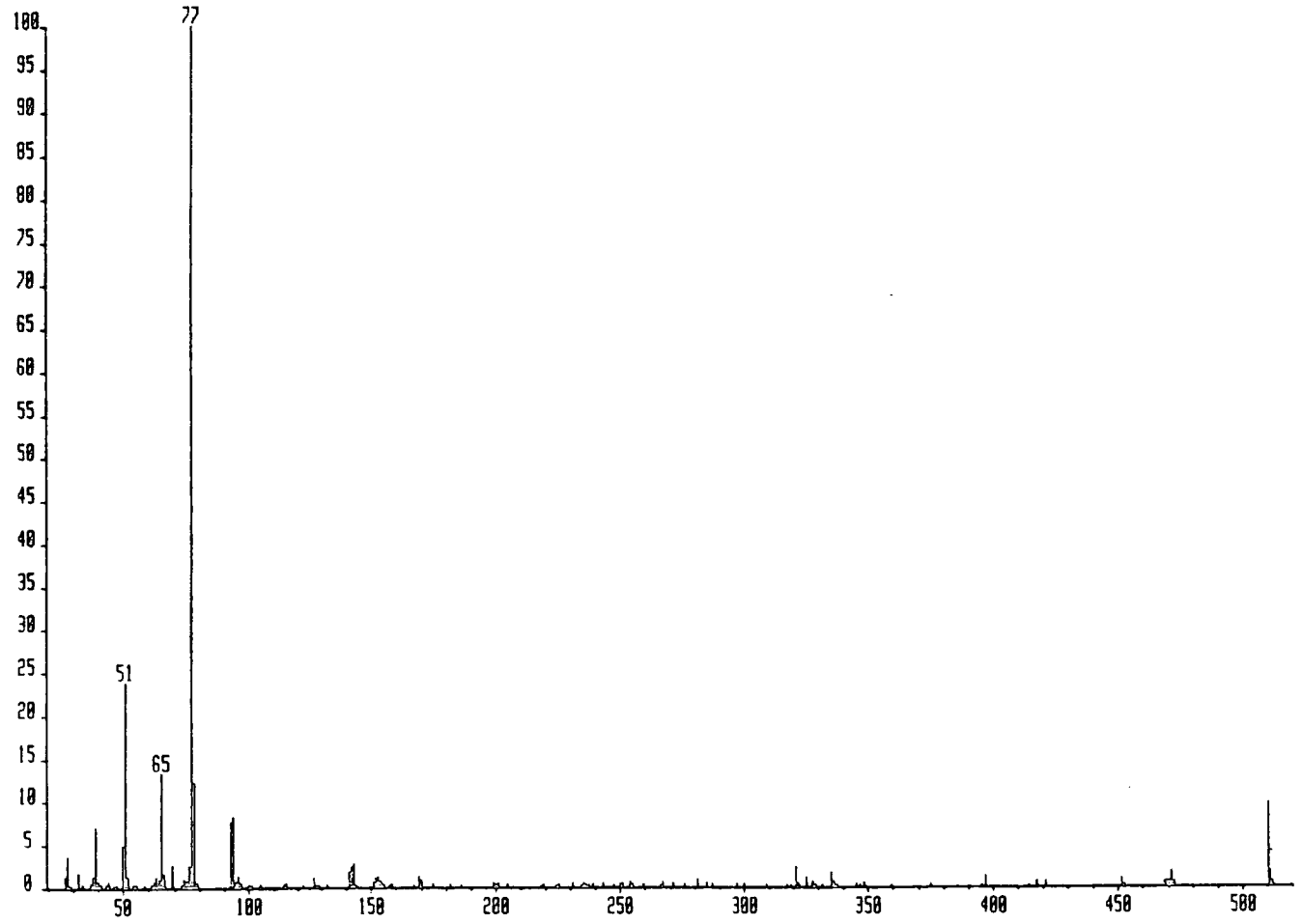


EI+ data

Mass	% Base		
28.00	1.02	281.08	0.61
39.01	5.69	321.09	2.87
50.00	4.19	325.13	0.62
51.01	21.00	328.12	0.59
52.02	1.27	329.15	0.36
63.02	1.30	335.12	2.33
65.03	14.05	336.12	0.48
66.03	1.35	397.19	0.88
68.98	1.74	413.22	0.47
75.01	1.25	417.21	0.77
76.02	2.33	451.28	0.64
77.03	100.00	452.26	0.33
78.03	11.93	471.31	1.47
93.02	7.41	491.33	0.81
94.03	7.41	510.37	10.47
96.03	1.65	511.37	2.39
127.03	1.34	512.38	0.47
141.07	1.56		
142.08	2.84		
143.00	3.44		
152.06	1.23		
153.07	1.28		
154.08	1.13		
232.08	0.39		
235.06	0.42		
243.04	0.41		
251.07	0.44		
254.08	0.65		
255.08	0.22		
259.07	0.41		
271.06	0.50		

Mass spectrum number 17.

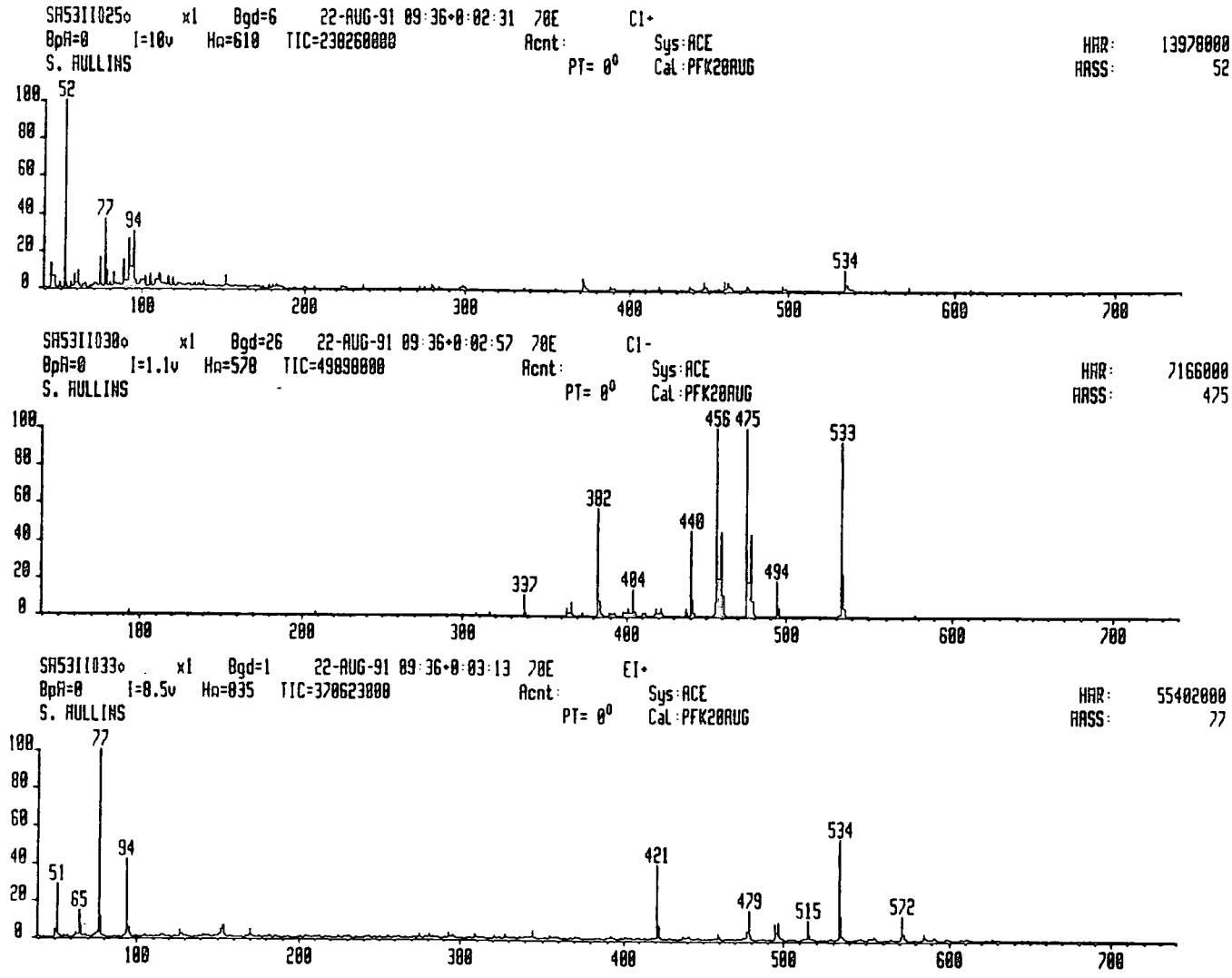
SA1180930o x1 Bgd=927 24-NOV-88 14:2+0:16:31 70E EI+
BpA=0 I=2.4v Ha=512 TIC=41970000 Acnt: Sys:AULL HAR: 16048000
GC= 194° Cal:PFK1111 MASS: 77



EI+ data

Mass	% Base				
27.01	1.13	235.06	0.40	337.12	0.19
28.00	3.63	236.06	0.24	345.23	0.24
31.98	1.59	237.09	0.19	346.72	0.19
38.01	1.17	239.05	0.26	348.10	0.44
39.01	6.92	243.04	0.40	359.14	0.16
50.00	4.84	247.05	0.14	375.12	0.34
51.01	23.72	247.09	0.19	395.15	0.20
52.02	1.23	250.10	0.22	397.17	1.13
63.01	1.21	251.07	0.46	414.17	0.14
65.03	13.15	254.04	0.54	417.21	0.62
66.04	1.54	255.07	0.24	421.24	0.59
68.98	2.50	255.15	0.14	451.26	0.86
76.02	2.52	259.03	0.30	452.30	0.19
77.03	100.00	259.13	0.24	471.30	1.63
78.03	12.13	266.12	0.14	472.25	0.44
93.02	7.54	267.09	0.64	510.34	9.61
94.03	8.21	271.06	0.44	511.36	1.57
96.03	1.21	276.18	0.24	512.34	0.39
127.04	1.11	281.08	0.88		
141.07	1.83	285.11	0.42		
142.08	2.42	287.06	0.24		
142.99	2.64	297.08	0.27		
152.06	1.02	300.09	0.34		
153.07	1.26	309.09	0.31		
169.07	1.23	317.13	0.29		
200.03	0.29	319.13	0.21		
201.04	0.40	321.07	2.24		
205.03	0.31	322.10	0.31		
218.07	0.21	325.12	1.00		
219.05	0.34	327.08	0.31		
223.99	0.19	328.09	0.61		
225.05	0.29	329.12	0.17		
231.07	0.44	331.73	0.11		
234.07	0.19	335.12	1.57		
234.11	0.19	336.12	0.59		

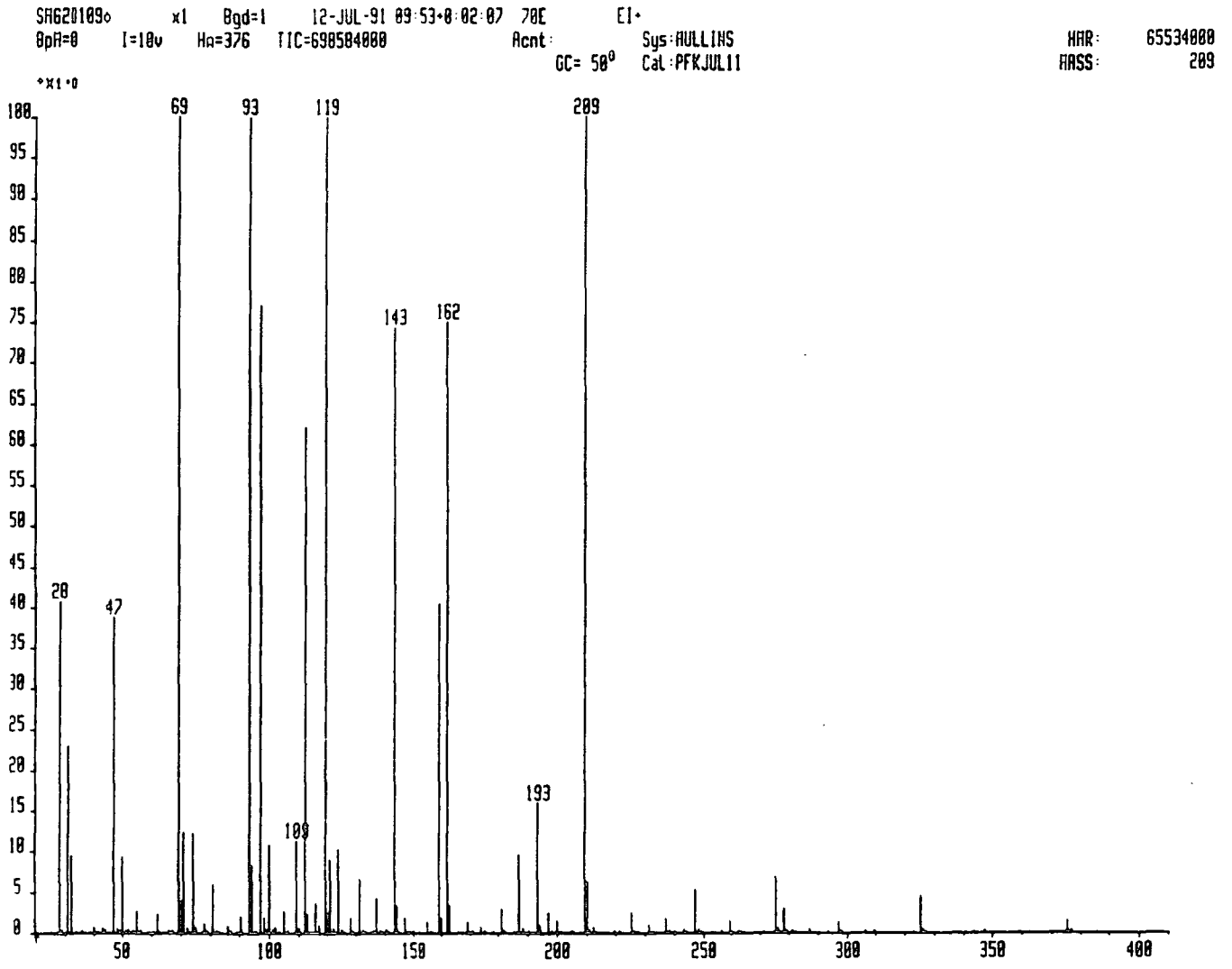
Mass spectrum number 18.



EI+ data

Mass	% Base				
49.99	3.71	230.91	1.39	498.87	0.46
50.99	28.52	254.90	1.37	512.86	0.60
52.00	1.41	274.88	2.88	513.85	0.92 F
62.99	2.78	280.91	2.31	514.85	10.30 F
64.00	1.13	292.88	3.23	515.87	2.50 F
65.00	13.86	294.88	1.85	516.87	0.92
66.01	5.57	308.87	2.38	528.82	0.46
74.98	2.08	309.87	1.01	532.64	0.68 F
75.99	3.23	320.87	1.62	533.85	53.60 F
77.00	100.00	327.86	2.37	534.85	13.01 F
78.00	10.76	336.86	1.39	535.88	1.85 F
92.98	3.23	340.86	1.39	536.89	0.46
93.99	41.63	342.85	1.45 F	544.90	0.46
94.99	5.30	344.63	4.62 F	546.88	0.41
95.99	2.10	354.89	1.85	550.90	0.48
104.97	1.50	358.86	1.41	552.89	1.56
114.99	1.39	370.86	1.39	553.88	0.49
116.00	1.06	392.85	1.86	554.88	1.85
126.97	3.70	400.84	1.39 F	555.88	0.46
127.99	1.95	420.81	39.74 F	564.90	0.93
140.99	1.51	421.84	7.05 F	570.89	1.85 F
142.00	1.08	436.83	2.07	571.85	12.54 F
143.97	1.31	440.84	2.06	572.89	3.34 F
150.96	2.20	458.83	3.23	573.89	0.47
151.98	4.71	459.84	1.37	584.91	3.25
152.99	6.26	474.85	1.39	585.92	0.96
154.00	6.69	476.84	4.62	586.92	0.92
154.96	1.05	477.83	1.16 F	590.93	1.46
168.96	1.37	478.83	15.33 F	591.93	0.46
169.98	4.22	479.83	2.77	598.93	0.92
170.99	1.39	494.84	8.32 F	610.93	0.92
181.94	1.59	495.83	4.13 F	626.93	0.47
212.92	1.43	496.86	9.25 F		
223.91	1.07	497.87	2.40		

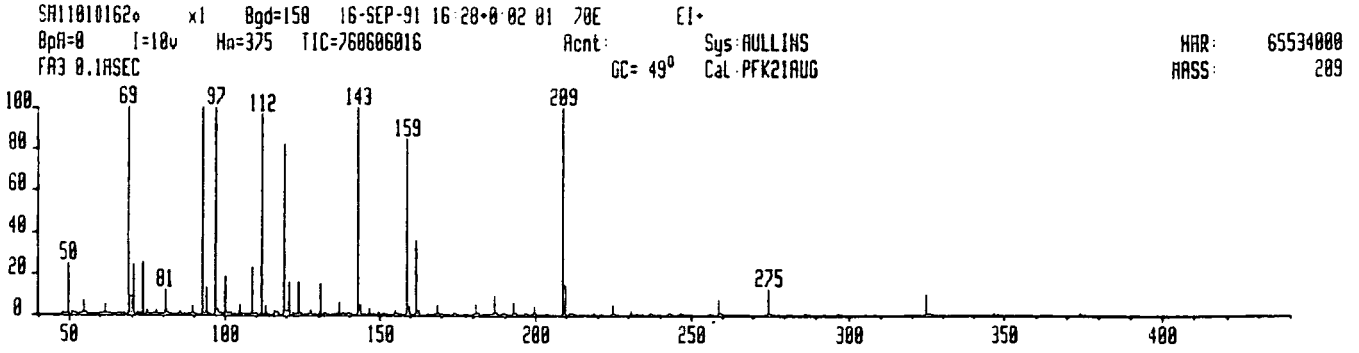
Mass spectrum number 19.



EI+ data

Mass	% Base		Mass	% Base		Mass	% Base	
43.04	0.45		122.11	0.40		259.24	1.28	
47.04	38.75		124.12	10.26		275.24	6.73	
48.04	0.48		125.12	0.33		276.24	0.46	
50.04	9.13		128.12	1.73		278.24	2.84	
52.05	0.31		131.12	6.52		297.28	1.13	
55.05	2.48		137.12	4.15		325.28	4.40	
62.06	2.19		140.13	0.32		326.29	0.36	
69.08	100.00	O	143.13	74.35		375.67	1.26	
70.07	3.86		144.13	3.16				
71.06	12.31		147.13	1.80				
72.07	0.40		155.15	1.37				
74.07	12.15		159.16	40.40				
75.07	0.62		160.15	1.74	F			
78.07	1.00		162.16	75.10	F			
81.07	5.91		163.15	3.18				
86.08	0.73		169.16	1.15				
90.08	1.95		174.17	0.52				
93.10	100.00	O	181.17	2.71				
94.09	8.18		187.17	9.50				
97.08	76.87		188.18	0.51				
98.09	1.79		193.18	15.88				
100.09	10.69		194.18	0.88				
102.09	0.53		197.18	2.35				
105.10	2.45		200.18	1.27				
109.10	11.22		209.21	100.00	FO			
110.10	0.40		210.20	6.17	F			
112.11	62.11		211.20	0.36				
113.11	2.15		212.20	0.54				
116.10	3.49		225.22	2.37				
117.11	0.93		231.24	0.92				
119.12	100.00	O	237.23	1.65				
120.12	2.39		243.25	0.34				
121.11	8.88		247.24	5.17				

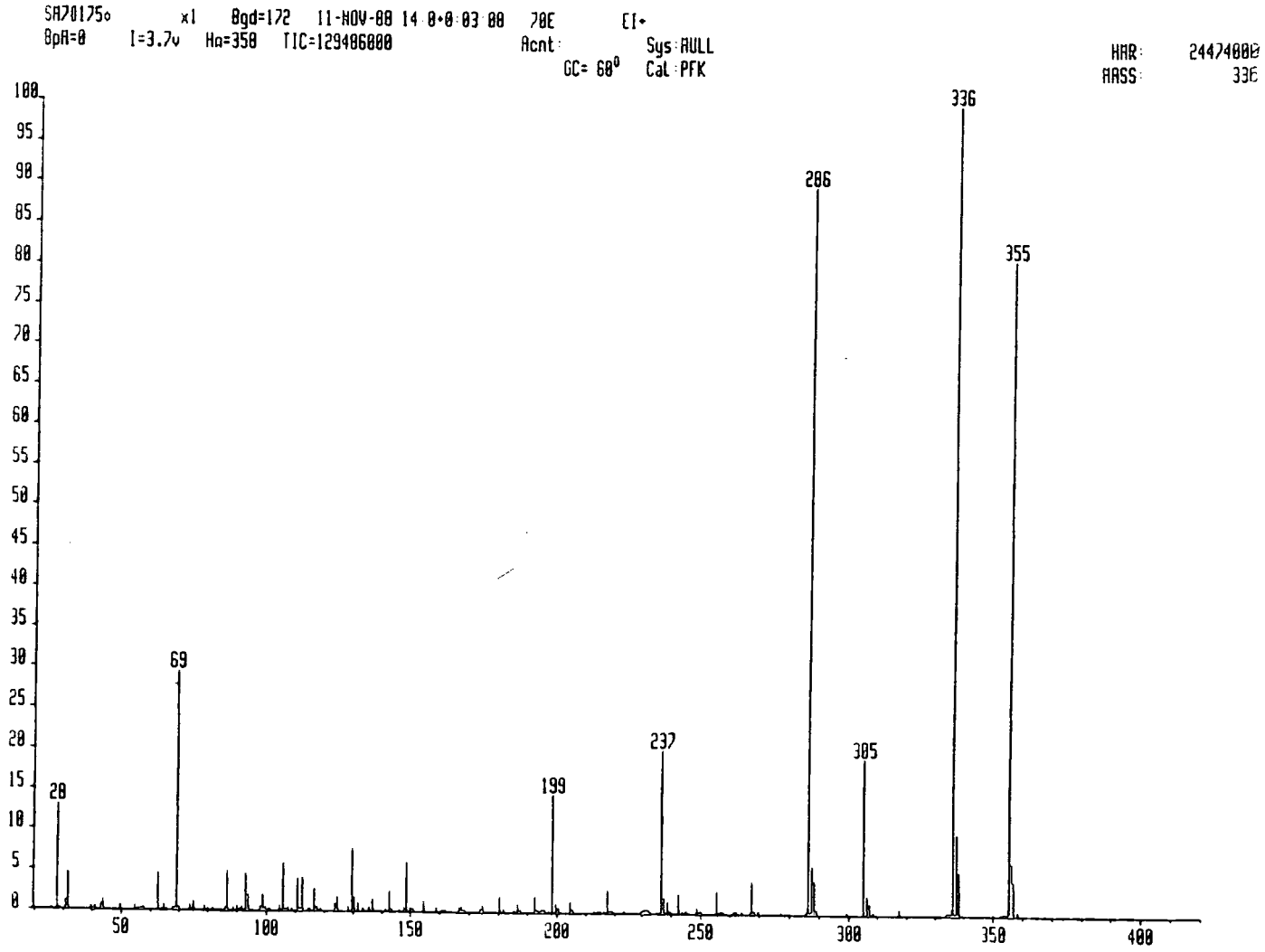
Mass spectrum number 20.



EI+ data

Mass	% Base		Mass	% Base	
47.69	0.89		162.74	1.76	
48.70	0.19		168.70	4.56	
49.70	24.61		169.73	0.20	
50.71	0.99		170.72	0.11	
51.71	0.78		173.72	0.60	
52.73	0.14		174.72	0.12	
54.73	6.26		180.70	5.08	
55.74	0.39		181.71	0.39	
58.75	0.14		184.71	0.23	
61.77	4.46		186.69	9.01	
62.78	0.14		187.70	0.39	
65.79	0.39		189.70	0.34	
67.81	0.78	F	192.69	6.06	
68.84	100.00	FO	193.70	0.39	
69.82	8.40		196.68	0.78	
70.81	23.76		199.68	3.91	
71.82	0.85		200.68	0.19	
73.82	25.01		208.69	100.00	FO
74.83	1.75		209.65	14.10	F
77.83	2.16		210.66	0.78	
78.84	0.13		211.66	0.81	
80.84	11.66		218.68	0.40	
81.84	0.39		220.66	0.27	
85.83	1.17		224.65	4.25	
86.84	0.12		225.66	0.15	
89.82	4.03		230.65	2.07	
92.85	100.00	O	236.64	0.59	
93.83	12.89		242.64	0.39	
94.83	0.27		246.62	0.39	
96.82	100.00	O	255.62	0.12	
97.82	2.73		258.60	7.19	
98.82	0.39		259.61	0.48	
99.81	17.97		261.63	0.12	
100.81	0.52		274.60	12.15	
101.81	0.92		275.61	0.89	
104.80	4.17		277.62	0.26	
105.81	0.21		280.60	0.15	
108.79	22.23		286.59	0.39	
109.80	0.78		296.59	0.86	
111.80	97.02		305.58	0.21	
112.80	3.91		324.55	9.61	
115.79	1.76		325.56	0.78	
116.79	1.20		346.54	0.40	
118.79	81.88		374.51	0.78	
119.79	1.70		375.51	0.11	
120.78	15.27	F			
121.79	0.52	F			
123.78	15.28				
124.78	0.78				
127.77	2.13				
128.77	0.12				
130.77	14.66				
131.77	0.55				
135.77	0.22				
136.75	6.07				
137.76	0.39				
139.75	0.39				
142.75	100.00	O			
143.75	4.41				
146.74	2.73				
149.74	0.79				
154.74	1.72				
155.75	0.16				
158.73	84.84				
159.73	3.71				
161.73	35.98				

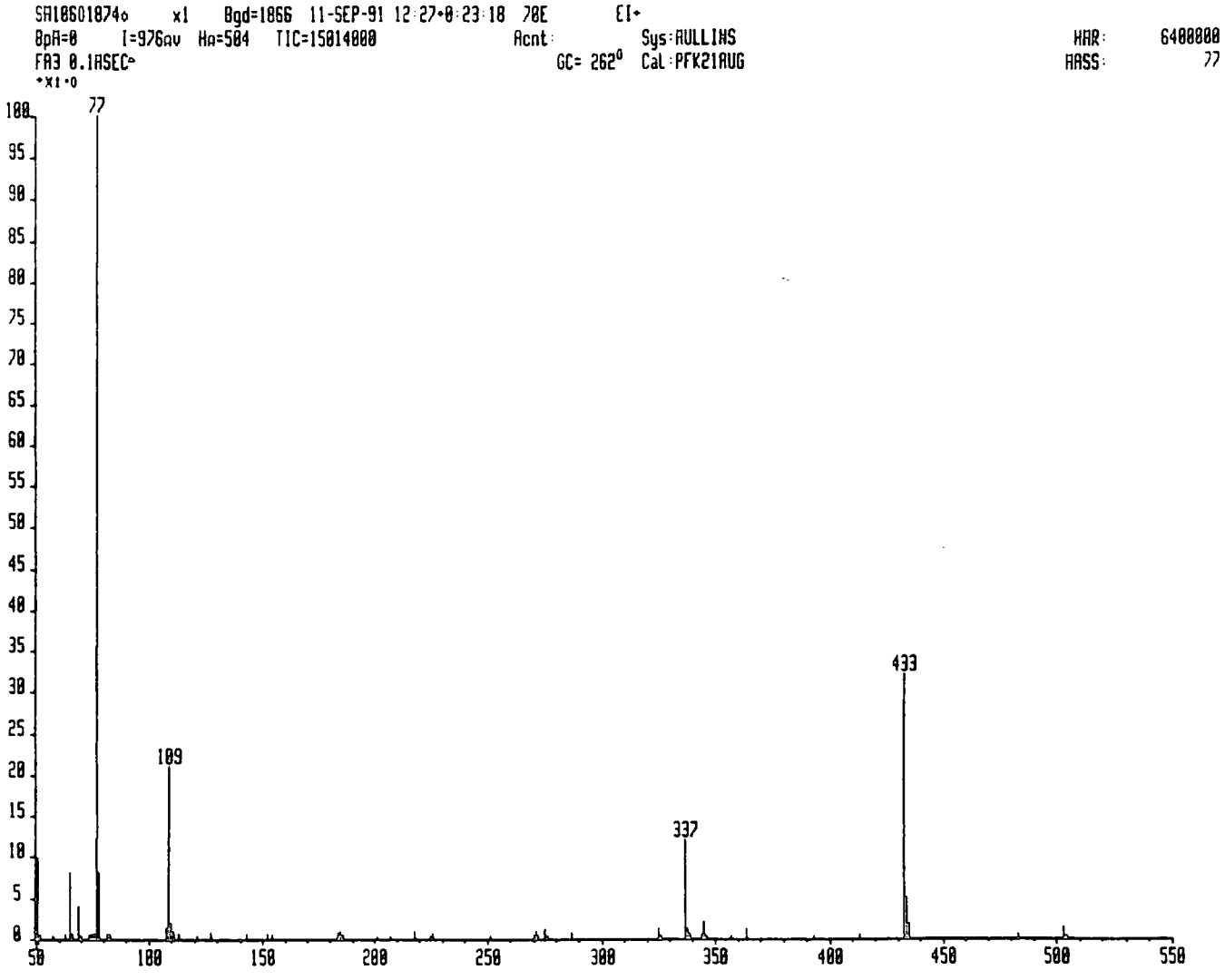
Mass spectrum number 21.



EI+ data

Mass	% Base				
27.92	12.89	150.63	0.35	335.97	0.81
30.90	1.01	154.66	1.24	336.40	100.00
31.88	4.38	158.64	0.47	337.11	0.11
43.86	1.23	166.64	0.45	337.41	9.93
62.80	4.41	167.61	0.65	338.40	5.30
68.82	29.38	174.59	0.71	339.39	0.32
74.78	1.01	180.60	1.79	354.98	0.79
86.76	4.77	186.58	0.91	355.39	81.00
92.78	4.49	192.60	1.86	355.90	0.12
93.75	1.79	193.60	0.35	356.11	0.11
98.73	1.78	198.57	14.34	356.39	6.37
104.75	0.55	199.57	0.98	357.38	4.15
105.72	5.74	200.56	0.60	358.38	0.39
110.72	3.78	204.58	1.30		
111.73	0.27	217.54	2.73		
112.70	4.01	236.51	20.07		
116.73	2.67	237.52	1.79		
117.71	0.51	238.52	1.27		
118.71	0.16	239.54	0.13		
123.72	0.86	242.53	2.18		
124.68	1.59	255.49	2.64		
128.61	0.61	267.49	3.87		
129.68	7.53	268.48	0.27		
130.67	1.60	269.46	0.29		
131.63	1.10	286.10	0.73		
133.64	0.29	286.46	89.74		
135.61	0.36	287.46	5.96		
135.69	0.46	288.45	4.05		
136.67	1.30	289.47	0.54		
141.64	0.12	305.43	19.18		
142.65	2.38	306.44	2.18		
147.68	0.52	307.43	1.15		
148.64	5.97	308.43	0.15		
149.64	0.47	317.42	0.54		

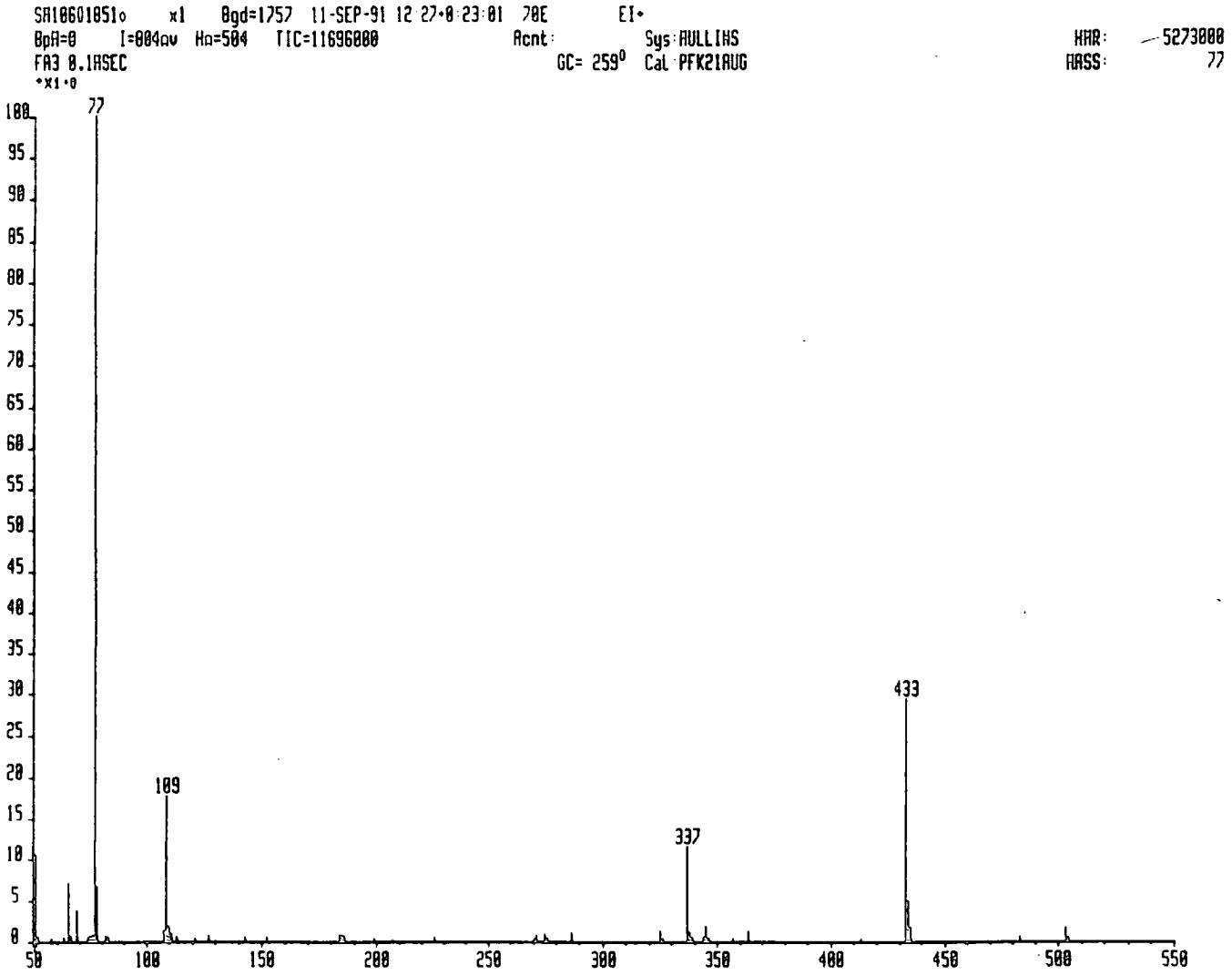
Mass spectrum number 22.



EI+ data

Mass	% Base		
49.79	1.67	286.95	0.80
50.80	9.77	325.01	1.19
51.82	0.45	336.97	12.00
57.82	0.33	337.97	1.14
62.89	0.55	338.98	0.56
64.92	8.00	344 02	0.37
65.94	0.61	345.01	1.98
68.90	4.00	346.03	0.31
73.95	0.47	357.00	0.34
74.96	0.63	364.01	1.19
75.97	0.64	393.07	0.34
76.98	100.00	413.04	0.37
77.99	8.00	433.05	32.14
81.95	0.63	434.06	4.98
82.96	0.52	435.06	1.80
107.96	1.38	483.07	0.50
108.96	21.06	503.07	1.28
109.97	1.91	504.11	0.31
110.97	0.92		
112.92	0.56		
126.99	0.69		
142.95	0.56		
152.02	0.52		
154.04	0.37		
184.00	0.70		
185.01	0.81		
186.02	0.50		
200.99	0.31		
217.99	0.89		
224.97	0.33		
225.97	0.52		
270.00	0.44		
271.00	0.94		
274.99	1.16		

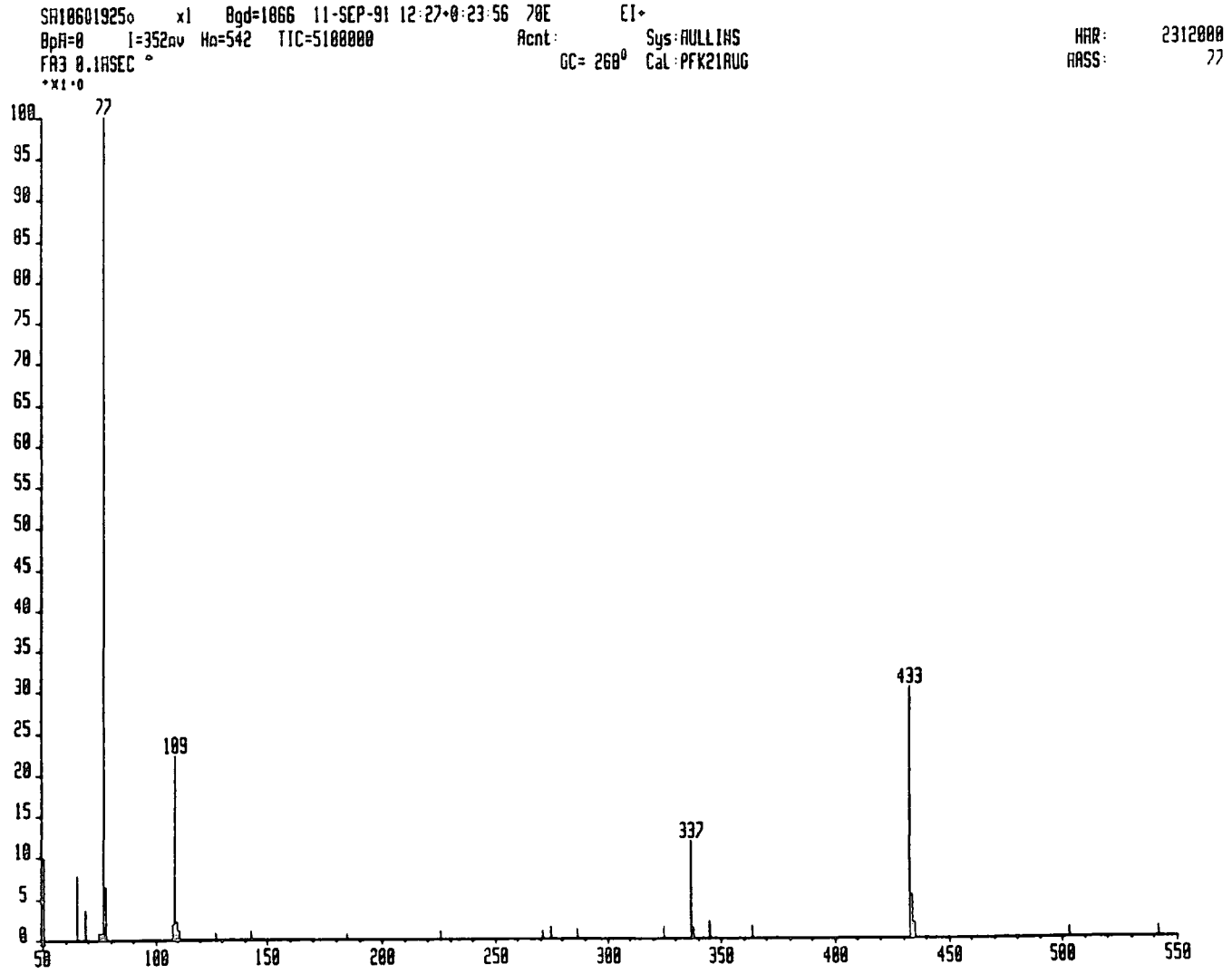
Mass spectrum number 23.



EI+ data

Mass	% Base		
49.79	1.74	336.97	11.55
50.80	10.58	337.98	1.08
51.82	0.47	338.99	0.49
57.82	0.30	344.04	0.38
62.89	0.49	345.01	1.73
64.92	7.02	346.02	0.32
65.93	0.61	356.99	0.32
68.90	3.58	364.01	1.14
73.95	0.42	413.07	0.32
74.96	0.53	433.04	29.41
75.97	0.83	434.04	4.87
76.98	100.00	435.05	1.63
77.99	6.56	483.09	0.49
81.95	0.53	503.08	1.65
82.94	0.36	504.06	0.38
82.97	0.40		
107.96	1.31		
108.97	17.73		
109.97	1.78		
110.97	0.83		
112.93	0.49		
127.00	0.72		
142.95	0.42		
152.02	0.46		
184.01	0.78		
185.02	0.68		
186.03	0.53		
225.99	0.46		
269.99	0.32		
271.00	0.78		
274.98	0.91		
286.96	1.01		
325.01	1.10		

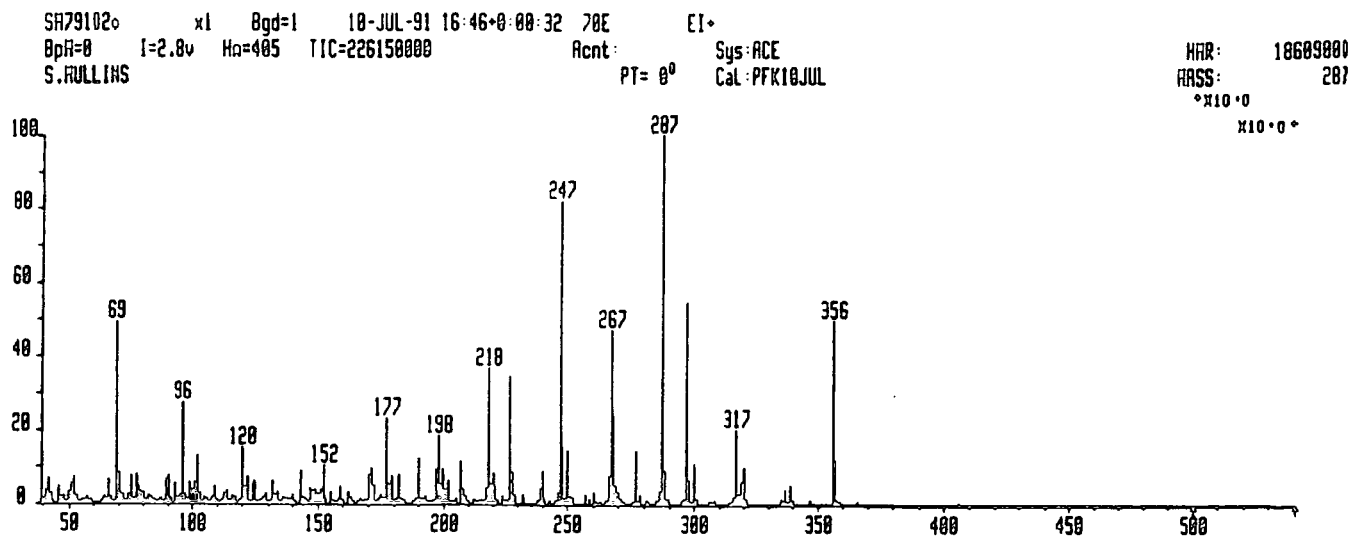
Mass spectrum number 24.



EI+ data

Mass	% Base
49.79	1.77
50.80	9.73
64.92	7.74
68.90	3.55
74.95	0.78
75.97	0.78
76.98	100.00
77.99	6.27
107.96	1.77
108.96	22.15
109.97	2.08
110.96	1.04
127.00	0.69
142.96	0.82
185.01	0.65
225.98	0.82
271.00	0.91
274.99	1.34
286.96	0.95
325.01	1.30
336.97	11.63
337.99	1.12
345.01	1.90
364.03	1.25
433.03	30.36
434.04	5.15
435.06	1.82
503.07	0.99
542.12	1.21

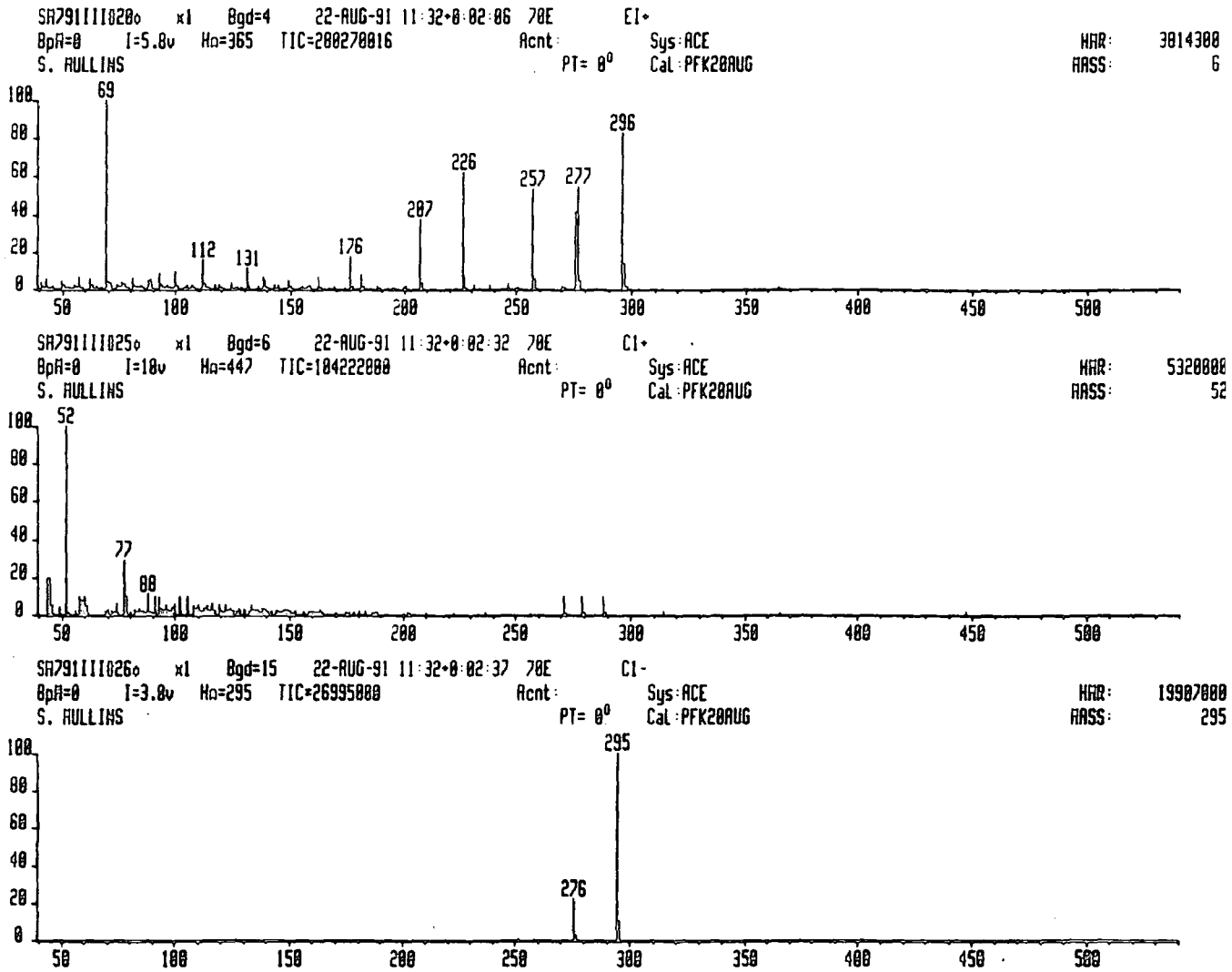
Mass spectrum number 25.



EI+ data

Mass	% Base							
40.00	1.10	107.94	1.50	178.92	7.07	267.88	23.91	
41.01	3.39	108.96	4.24	179.91	0.77	268.86	4.53	
42.02	6.34	109.96	0.60	180.89	1.23	269.86	2.88	
43.01	2.51	111.93	0.63	181.90	7.60	270.86	0.91	
43.99	0.51	112.94	2.42	182.91	0.96	276.84	14.07	
45.98	4.24	113.95	3.40	183.86	0.55	278.14	2.05	
46.99	1.85	114.95	0.60	188.89	1.26	280.84	0.55	
48.00	1.70	115.95	1.66	189.90	11.80	284.85	0.80	
49.97	3.03	116.93	1.52	190.90	0.91	285.85	3.11	F
50.97	5.17	118.93	0.75	191.93	1.00	286.86	100.00	F
51.99	6.78	119.94	14.90	192.89	1.91	287.87	8.54	
52.99	1.83	120.94	4.29	195.91	0.66	288.85	1.04	
54.99	0.66	121.95	6.70	196.90	9.16	289.85	1.16	
55.99	0.88	123.94	5.17	197.91	18.06	294.86	0.63	
56.99	1.50	124.94	5.83	198.91	5.04	295.88	1.07	
58.99	0.87	126.95	0.83	199.88	9.02	296.85	54.54	
62.97	0.52	127.95	1.29	200.89	3.71	297.86	6.00	
63.98	1.24	128.95	2.55	201.88	5.89	298.87	0.51	
64.48	1.98	130.92	0.68	204.88	1.05	299.84	10.42	
64.99	1.00	131.93	5.62	206.88	11.04	300.84	1.14	
65.98	6.29	132.94	1.99	207.88	3.55	F 314.84	0.66	
66.99	1.47	133.44	0.92	208.72	1.83	F 315.87	1.74	
68.96	49.06	133.95	3.06	211.88	0.55	316.84	19.92	
69.97	8.00	135.94	1.54	212.87	0.56	317.83	2.64	
71.00	2.44	136.93	1.06	214.89	0.84	318.81	5.69	
72.00	2.29	137.92	1.19	215.90	0.64	319.82	9.68	
73.01	0.65	138.93	0.81	216.90	3.89	320.84	1.01	
73.96	2.19	139.93	2.27	217.91	36.53	334.84	1.24	
74.48	0.63	140.92	0.44	218.90	5.15	335.83	0.61	
74.96	7.23	142.91	8.81	219.88	8.08	336.85	3.44	
75.97	1.22	143.92	1.27	220.89	4.35	338.83	4.55	
76.97	7.75	144.93	0.97	221.89	0.66	339.84	0.68	
77.97	4.28	146.93	4.03	223.87	1.70	346.80	0.55	
78.98	2.97	147.93	3.07	224.89	0.54	355.82	49.62	
79.99	2.60	148.94	3.73	225.88	0.84	356.83	11.39	
80.95	0.55	149.92	2.35	226.88	34.30	357.85	0.83	
81.96	1.78	150.92	3.48	227.92	8.46	F		
82.97	1.59	151.93	10.27	228.83	2.25	F		
83.97	0.77	152.93	1.02	232.18	2.33	F		
88.96	6.17	154.91	2.83	237.88	0.54			
89.46	0.80	155.91	0.71	238.88	4.08			
89.96	7.07	157.91	0.97	239.88	8.60			
90.97	1.15	158.92	4.21	240.89	1.02			
92.94	5.17	159.93	0.59	242.87	0.70			
93.95	1.39	161.90	3.07	244.89	0.83			
94.96	2.00	162.91	1.33	245.88	2.77			
95.95	27.07	165.92	0.31	246.87	82.05	F		
96.96	2.10	166.90	1.01	247.90	15.16	F		
97.97	1.13	168.42	0.54	248.87	1.60			
98.96	5.58	168.90	0.84	249.86	14.14			
99.46	0.92	169.91	7.49	250.87	1.93			
99.94	3.71	170.92	9.52	251.87	1.46			
100.95	5.27	171.93	4.82	256.86	2.18			
101.95	12.62	173.90	1.00	258.27	1.05			
102.96	2.46	174.91	2.14	259.87	2.80			
104.94	1.41	175.90	1.32	264.86	0.64			
105.94	1.19	176.91	22.90	265.86	7.23	F		
106.95	0.54	177.91	5.03	266.87	46.83	F		

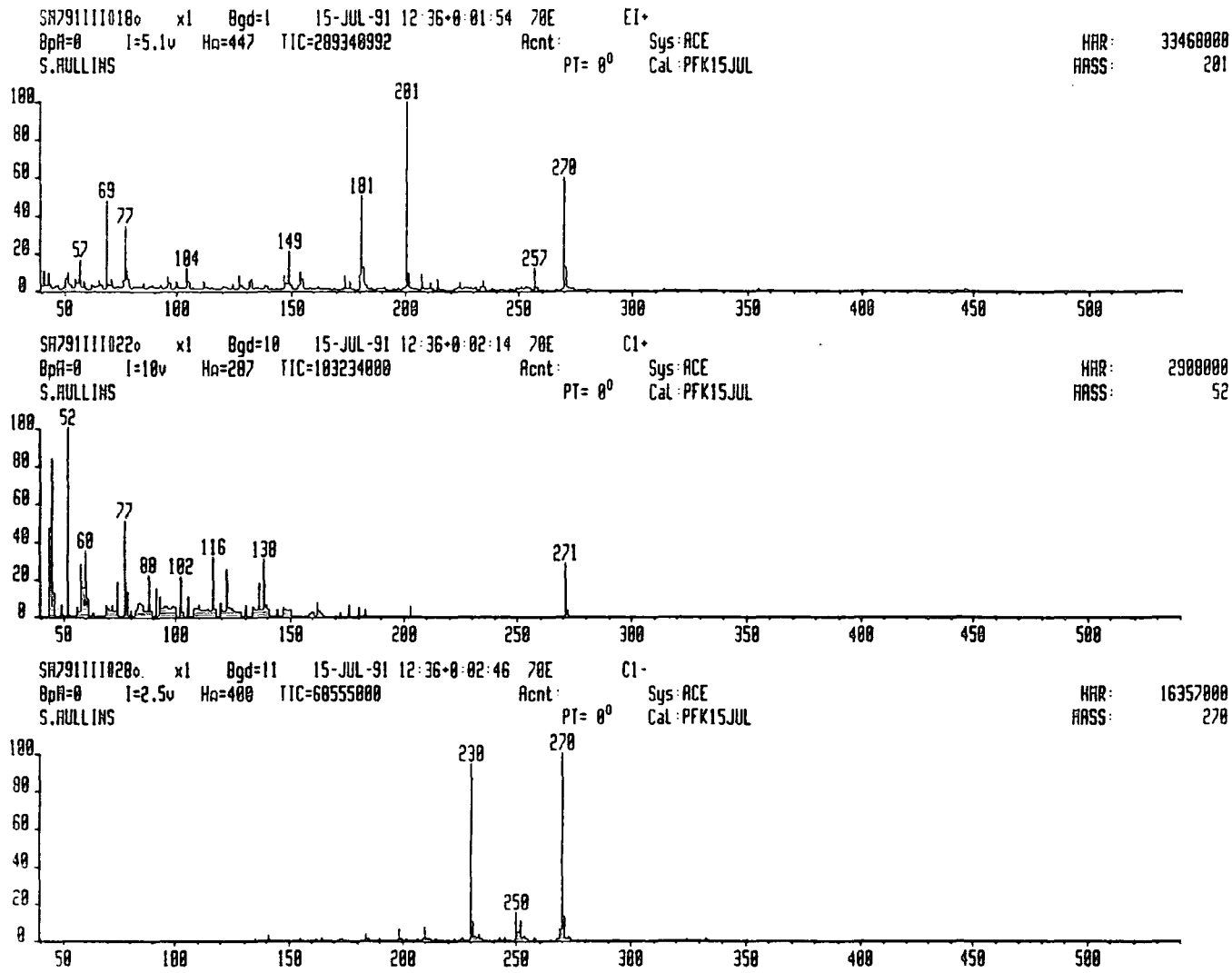
Mass spectrum number 26.



EI+ data

Mass	% Base								
41.00	3.22		80.94	5.58	128.41	0.33	227.87	0.50	
42.00	1.34		81.95	1.48	130.91	10.98	230.85	2.17	
42.97	1.34	F	83.02	1.22	131.92	1.34	238.19	1.97	
43.01	5.29	F	84.03	0.36	135.90	1.34	245.85	2.96	
43.97	0.63		85.04	2.16	137.91	6.58	249.84	0.71	
44.99	0.83		85.94	0.84	138.40	0.58	250.85	0.36	
45.97	1.34		87.94	4.70	138.92	4.19	256.85	53.06	F
49.96	4.08		88.94	4.90	139.92	0.37	257.85	5.37	F
50.97	1.66		92.93	8.30	142.90	1.76	269.87	1.38	
51.98	0.36		93.94	2.01	144.91	1.88	270.87	0.57	
52.98	0.35		94.94	0.36	148.92	4.64	275.81	40.83	F
54.96	1.24	F	95.94	1.93	149.90	1.53	276.83	54.42	F
55.01	2.18	F	97.03	0.69	154.92	1.43	277.84	4.72	
56.01	1.35		97.93	0.67	156.90	1.35	295.82	82.54	
57.03	6.27		99.04	0.75	157.91	2.01	296.83	13.31	
57.97	0.76		99.93	8.95	161.89	6.72	297.84	1.23	
58.03	0.35		100.93	1.34	162.90	0.67	364.81	1.34	
59.00	0.67		103.95	0.81	166.90	0.32			
61.96	5.37		104.93	1.93	168.89	1.34			
62.97	1.62		106.93	2.15	173.90	0.40			
63.97	0.30		107.93	0.67	175.89	17.48			
64.97	1.37		111.04	0.39	176.89	1.48			
66.99	0.34		111.92	15.38	180.89	7.98			
68.94	100.00	F	112.93	2.25	181.89	1.34			
69.02	1.34	F	113.05	0.67	187.88	2.01			
69.95	4.03	F	113.92	0.67	188.88	0.38			
70.03	0.72	F	116.92	2.01	194.87	0.39			
71.03	3.37		118.92	2.03	199.86	1.38			
73.95	2.01		119.93	0.33	200.91	2.70			
74.95	1.34		123.91	2.97	206.86	36.90			
75.95	3.44		124.92	0.32	207.87	3.34			
76.96	2.80		125.05	0.31	222.95	0.35			
77.96	0.52		126.93	0.37	225.85	62.45			
78.95	0.67		127.06	0.41	226.86	7.34			

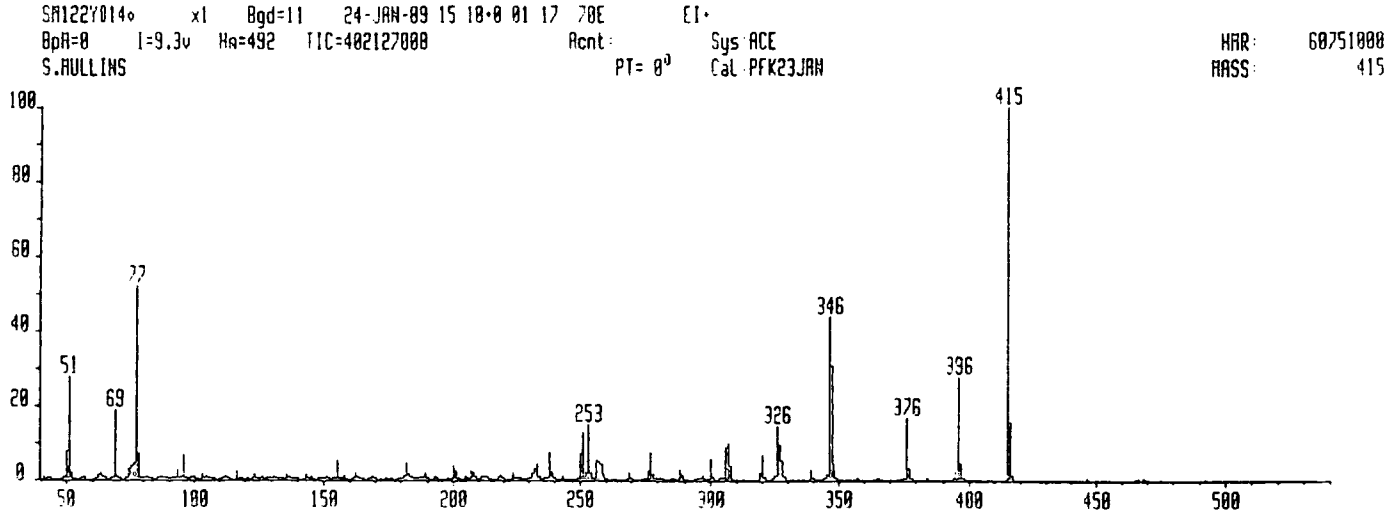
Mass spectrum number 27.



EI+ data

Mass	% Base		Mass	% Base		Mass	% Base		Mass	% Base	
40.02	1.68		79.01	5.70		132.01	5.75		230.96	1.57	
41.03	10.18		80.98	2.17	F	134.04	1.50		232.94	1.65	
42.03	2.55		81.05	1.57	F	135.03	1.43		233.95	4.90	
43.01	3.73	F	81.98	1.31	F	137.97	2.24		234.94	1.32	
43.04	8.94	F	82.05	1.11	F	138.99	1.75		252.94	1.75	
44.00	2.45		83.05	2.13		146.98	7.74		253.95	1.54	
45.01	1.56		84.06	1.01		147.99	3.61		256.92	11.65	
46.00	1.77		85.06	3.74		148.98	20.19		257.93	1.28	
47.01	2.46		87.02	1.05		149.99	2.65		269.96	59.65	
49.99	3.90		87.99	2.11		152.98	2.58		270.96	12.39	
51.00	6.18		88.99	2.75		153.98	9.64				
52.01	8.95		90.00	1.56		154.99	5.73				
53.01	2.56		92.99	2.44		161.98	2.24				
54.02	1.08		95.04	1.03		172.98	1.16				
55.04	5.48		95.98	7.05	F	173.99	7.50				
56.05	3.94		96.99	4.09	F	175.00	1.55				
57.06	16.32		97.07	1.68	F	175.96	4.53				
58.04	1.32		99.07	1.41		179.98	8.29				
59.03	4.33		99.98	4.57		180.98	49.85				
61.99	2.36		100.99	1.37		181.99	12.09				
63.00	1.66		101.99	1.04		182.97	2.60				
66.01	5.07		103.00	1.58		198.97	1.37				
67.02	2.75		104.00	11.38		199.98	2.39				
68.98	47.70	F	105.00	4.26		200.98	100.00				
69.05	3.07	F	111.97	4.29		201.98	8.95				
69.99	2.59	F	112.98	1.37	F	206.94	8.43				
70.06	1.79	F	113.10	1.02	F	207.95	1.24				
71.06	5.79		119.99	1.75		210.96	3.64				
72.04	1.20		121.03	1.90		213.95	5.59				
73.02	1.23		122.04	1.22		224.97	0.51				
74.01	1.61		124.00	2.93		225.94	5.12				
75.00	1.07		126.98	7.96		226.95	1.80				
75.99	5.25		127.99	2.26		227.96	0.40				
77.00	34.15		129.00	1.06		228.96	1.59				
78.00	10.28		130.98	4.41		229.96	0.84				

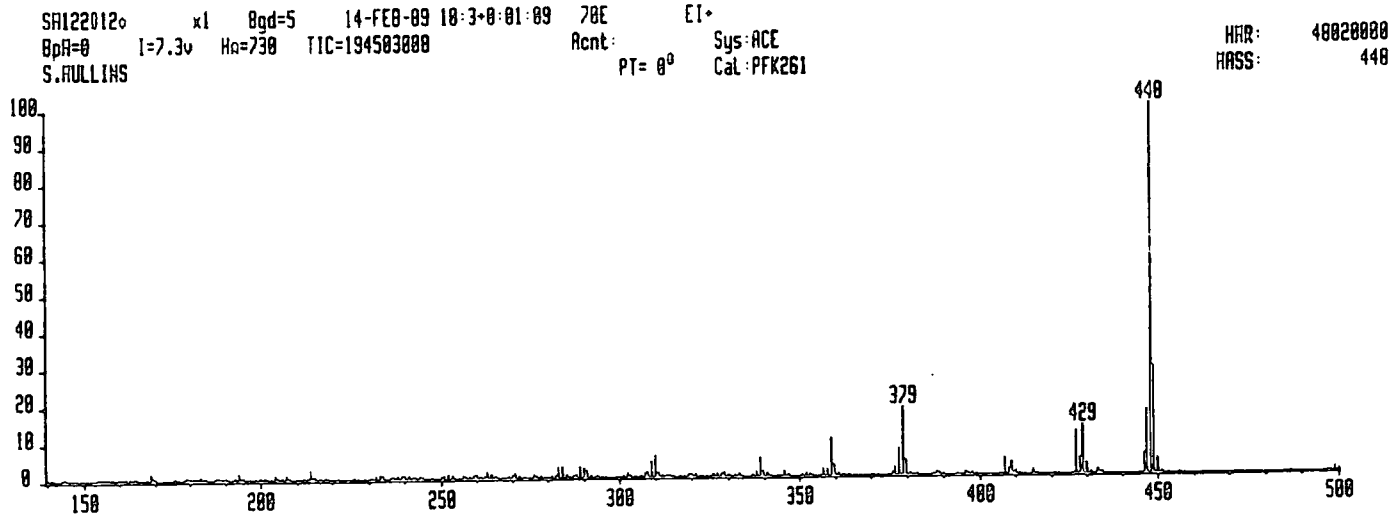
Mass spectrum number 28.



EI+ data

Mass	% Base				
40.84	0.63	165.05	0.47	306.06	8.56 F
42.86	0.51	167.01	0.41	307.09	9.78 F
48.86	0.63	169.02	0.72	308.12	3.53 F
49.87	7.47	174.00	0.50	319.05	1.95
50.89	27.52	181.01	1.15	320.06	6.59
51.90	1.82	182.04	4.28	321.07	0.72
54.93	0.53	183.04	1.60	325.07	1.13
56.95	0.55	184.05	0.55	326.08	14.44
60.94	0.40	188.05	0.67	327.09	9.32
61.95	0.90	189.06	1.65	328.10	4.90
62.97	1.79	190.07	0.39	329.11	0.70
63.97	0.68	193.04	0.57	339.06	2.37
68.99	18.42	200.04	3.55	344.09	0.43
70.05	0.69	201.06	1.98	345.08	1.50 F
74.17	2.96	205.03	0.66	346.09	43.47 F
75.21	3.61	206.05	0.43	347.10	30.29 F
76.26	4.24	207.06	2.07	348.10	3.90
77.30	51.93	208.07	1.61	357.09	0.51
78.35	6.96	209.08	0.56	376.11	16.34
79.38	0.46	211.05	0.54	377.12	2.81
81.41	0.65	212.05	0.82	394.09	0.85
86.33	0.49	213.07	0.62	395.09	2.21
87.33	0.58	214.07	0.51	396.10	27.55
88.31	0.48	218.06	0.73	397.11	4.28
93.22	2.49	219.05	1.24	398.11	0.36
94.22	0.47	220.07	0.38	415.09	100.00 F
95.23	0.88	224.02	1.61	416.11	15.28 F
96.21	6.50	225.04	0.35	417.11	1.15
97.22	0.42	226.05	0.43	446.19	0.34
99.15	0.78	227.05	0.40		
100.13	0.63	231.03	1.95		
103.14	1.27	232.03	2.81		
105.09	0.96	233.04	4.07		
111.06	0.41	234.05	0.61		
112.03	0.85	238.05	6.98		
113.03	0.54	239.06	1.63		
116.99	2.13	243.03	0.62		
123.00	0.47	250.02	6.88		
123.99	1.51	251.05	12.42		
125.00	0.34	252.05	1.91		
126.02	0.32	253.06	14.79		
127.03	0.85	254.08	1.68		
131.00	0.83	256.06	4.84		
132.02	0.49	257.07	4.62		
136.00	1.45	258.08	3.95		
137.02	0.55	259.08	0.91		
138.03	0.45	269.05	1.95		
143.03	1.29	270.06	0.52		
144.05	0.41	275.07	0.44		
145.06	0.56	276.08	2.06		
151.06	0.68	277.08	7.07		
153.54	0.49	278.08	1.38		
155.02	5.02	288.09	2.66 F		
156.03	0.50	289.09	0.91 F		
158.06	1.24	297.08	0.95		
162.02	1.79	300.06	5.41		
163.04	0.68	301.07	0.72		
164.05	0.46	305.07	0.47		

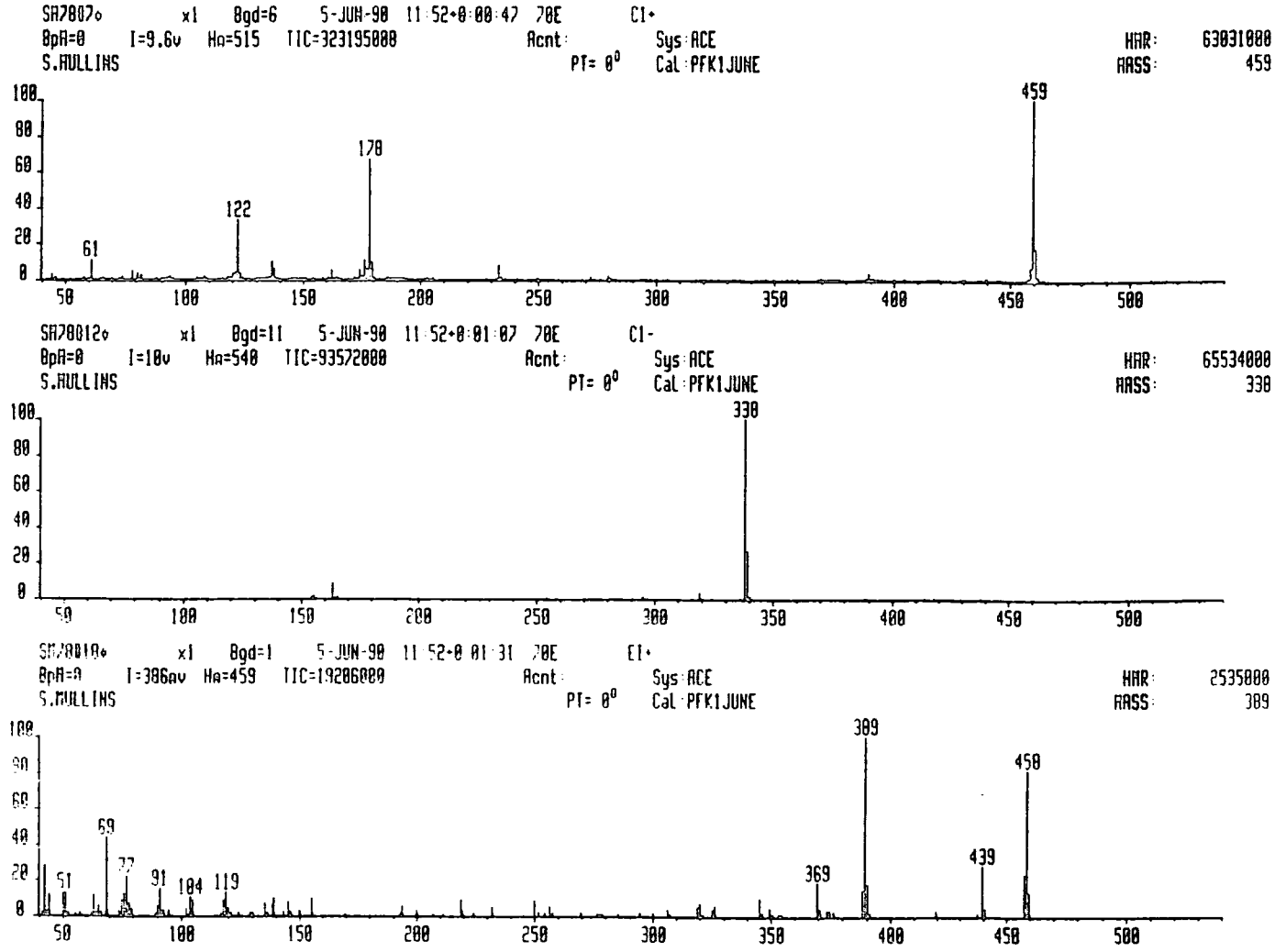
Mass spectrum number 29.



EI+ data

Mass	% Base			
49.99	1.35	320.92	0.70	
51.00	8.77	325.90	0.61	
62.99	0.56	326.93	0.71	
68.95	2.02	327.94	0.67	
74.98	0.80	328.95	1.03	
75.99	0.95	332.91	0.57	
77.00	14.47	337.86	1.36	
78.00	1.03	338.86	5.14	
126.99	0.50	339.86	1.59	
163.99	0.52	340.86	0.71	
168.97	1.67	345.82	1.38	
169.47	0.70	351.87	0.79	
178.97	0.56	356.91	1.74	
180.96	0.52	357.91	1.88	
182.98	0.67	358.92	9.90	
187.98	0.73	359.93	2.97	
193.96	1.66	375.87	0.79	
203.95	0.90	376.90	2.29	
206.95	1.22	377.91	7.03	
212.96	0.51	378.91	18.36	
213.97	2.40	379.92	4.06	
214.98	0.59	387.88	0.55	
225.95	0.52	395.86	0.77	
231.96	0.68	406.87	4.22	F
232.96	1.23	407.89	1.52	F
233.98	0.70	408.88	3.36	F
237.96	0.61	409.88	0.73	
238.97	0.68	414.84	0.99	
239.99	0.71	426.85	11.25	
240.99	0.63	427.86	4.25	
250.94	0.65	428.87	13.08	
251.94	0.96	429.87	2.95	
252.94	0.54	432.85	1.24	
255.93	0.87	445.91	5.21	F
256.95	0.54	446.85	17.11	F
258.97	0.57	447.86	100.00	F
259.98	0.62	448.87	28.53	F
262.95	1.76	449.88	3.88	
263.96	0.92	498.84	1.22	
269.96	0.58	524.84	1.28	
270.96	1.29			
275.93	0.66			
281.94	0.54			
282.93	2.84			
283.96	2.74			
284.96	0.62			
287.94	0.69			
288.95	2.77			
289.95	2.51			
290.96	1.67			
301.92	1.02			
306.92	0.91			
307.93	1.26			
308.94	4.30			
309.94	5.58			
310.94	1.12			
318.92	0.66			
319.93	0.89			

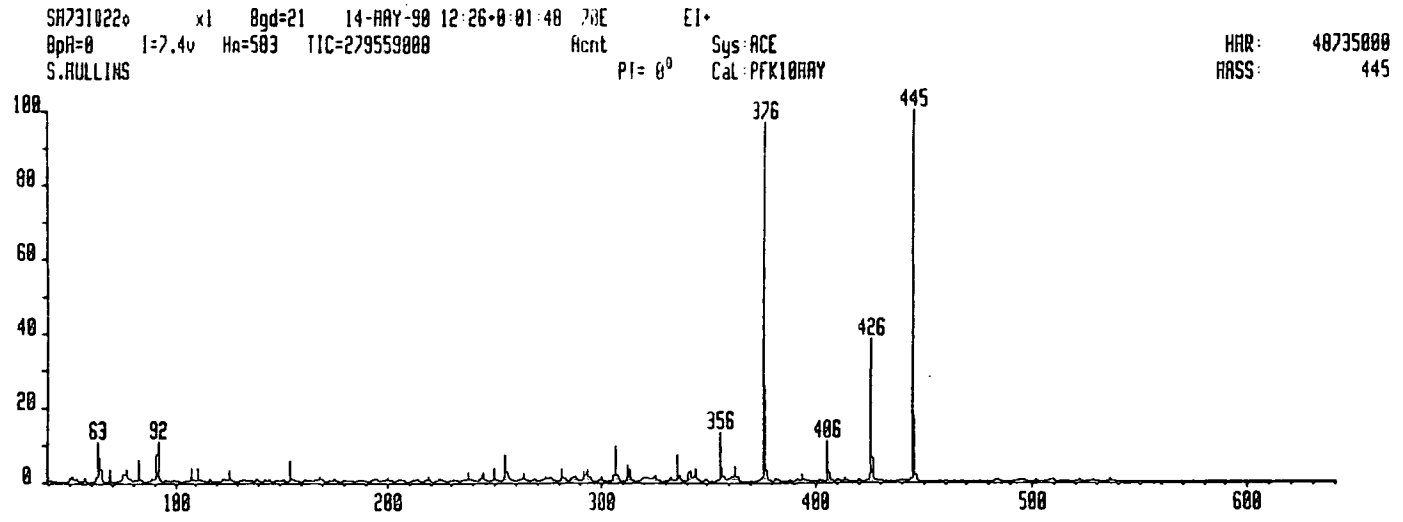
Mass spectrum number 30.



EI+ data

Mass	% Base				
40.96	1.97	118.16	8.36	285.27	0.59
41.97	27.85	119.16	12.58	294.29	1.46
42.98	2.96	120.17	4.30	300.22	1.18
43.99	11.32	121.18	1.58	306.25	3.16
49.98	12.03	124.09	1.10	307.24	0.95
51.00	12.58	129.15	1.26	319.26	4.81
52.00	1.66	130.16	1.22	320.29	7.02
55.04	0.67	135.20	6.86	321.31	0.91
57.06	1.07	136.21	1.46	325.26	3.71
62.03	2.05	138.18	6.07	326.26	5.21
63.04	11.40	139.19	9.55	345.29	9.19
64.04	2.13	143.11	1.70	346.30	1.22
65.06	5.64	145.19	7.42	349.33	4.14
66.06	2.17	146.20	1.74	350.33	0.95
68.08	1.54	150.15	2.52	353.31	0.63
69.04	43.12	155.12	9.23	354.30	0.87
74.07	2.92	169.16	0.79	369.35	18.26
75.08	8.72	193.13	1.10	370.36	4.06
76.08	11.83	194.18	5.52	373.33	3.04
77.10	21.85	200.15	3.04	374.33	2.45
78.10	6.98	207.19	0.83	376.31	2.05
79.11	3.39	211.18	0.79	388.35	13.96
89.11	1.50	219.19	8.56	389.36	100.00
90.11	5.21	219.70	2.41	390.37	17.63
91.13	14.60	224.16	1.07	391.38	1.03
92.13	2.68	232.25	4.97	419.39	2.41
93.07	2.60	250.19	8.36	437.38	1.38
93.13	1.34	251.27	1.70	439.41	27.81
95.10	2.68	254.22	1.46	440.41	3.83
102.11	3.83	256.22	4.93	457.41	22.96
103.12	0.63	257.21	1.18	458.42	80.75
104.13	10.30	269.19	1.74	459.43	12.74
105.14	8.36	276.23	1.58		
117.09	1.34	277.24	0.75		
117.14	1.50	278.25	0.79		

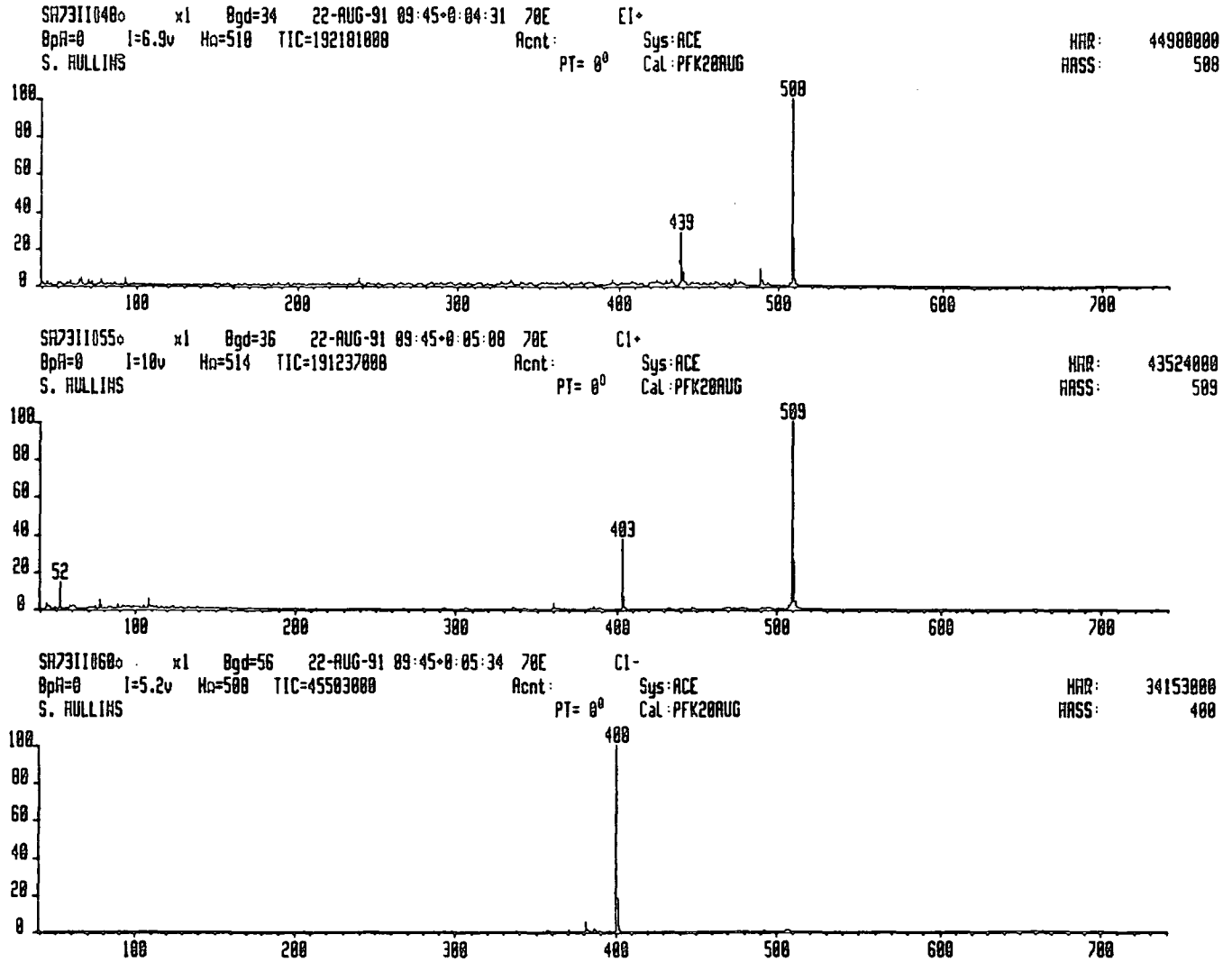
Mass spectrum number 31.



EI+ data

Mass	% Base				
50.00	1.00	236.95	0.47	340.93	2.64
51.01	1.51	237.96	2.50	341.94	2.87
52.02	0.33	238.97	0.50	342.94	0.59
52.99	0.60	239.96	0.43	343.94	1.57
53.02	0.41	242.93	0.67	344.95	3.54
57.00	0.94	243.95	1.74	345.96	0.82
61.99	0.96	244.96	2.42	348.96	0.50
63.00	10.76	249.92	3.55	355.96	13.39
64.00	6.35	250.94	0.37	356.96	3.42
65.01	3.06	253.95	1.12	357.97	1.37
68.96	3.32	254.95	7.01	359.94	0.68
73.99	0.33	255.95	2.50	360.95	0.99
74.99	2.17	256.95	0.91	361.94	1.06
76.00	1.66	261.94	0.36	362.94	3.77
77.01	3.19	262.95	0.89	363.95	1.22
78.02	0.56	263.95	2.15	374.95	0.85
79.02	0.82	264.96	0.40	375.96	96.61
80.99	0.42	267.95	0.34	376.97	25.50
83.00	5.76	268.94	0.55	377.98	2.96
89.01	1.08	272.95	0.43	381.95	0.70
90.01	0.68	273.94	1.06	382.96	0.31
91.02	7.29	274.95	0.77	390.96	0.45
92.00	10.83	275.96	1.19	391.96	0.32
92.99	0.79	276.97	0.33	393.94	1.67
95.00	0.46	280.98	3.37	394.97	0.45
107.02	1.01	281.98	0.75	405.96	10.83
108.02	3.59	282.98	0.61	406.97	1.99
109.02	0.46	285.96	0.65	409.95	0.52
110.99	3.54	286.97	1.08	410.96	0.35
111.99	0.31	287.97	1.51	413.97	0.77
116.96	0.67	288.97	0.40	424.97	1.74
123.01	0.60	291.94	2.96	425.97	38.35
126.01	3.02	292.93	2.27	426.98	6.21
133.01	0.32	293.94	3.06	427.99	0.51
138.98	0.77	294.95	1.15	443.96	0.70
144.98	0.44	299.91	1.12	444.98	100.00
154.96	5.35	305.94	1.61	445.98	17.57
155.97	0.44	306.96	9.63	446.99	1.66
156.98	0.50	307.97	1.84	483.01	0.45
161.95	0.38	311.93	0.79	484.02	0.40
166.94	0.41	312.93	4.11	496.04	0.46
168.97	0.90	313.94	3.10	508.03	0.46
175.98	0.59	314.95	0.37	522.06	0.31
186.96	0.39	318.92	0 86	536.07	0.64
187.98	0.46	319.92	1.12		
193.96	0.81	320.93	1.16		
194.97	0.61	321.94	0.99		
199.94	1.14	322.95	0.62		
204.94	0.45	323.94	0.80		
211.97	0.45	324.94	1.41		
213.97	0.88	325.94	1.95		
217.95	0.48	326.96	0.32		
218.97	1.42	331.94	0.71		
223.93	0.40	332.94	1.73		
224.95	0.73	333.96	0.46		
225.96	0.52	335.95	7.24		
230.97	0.52	336.95	1.68		
231.96	0.31	337.96	0.54		

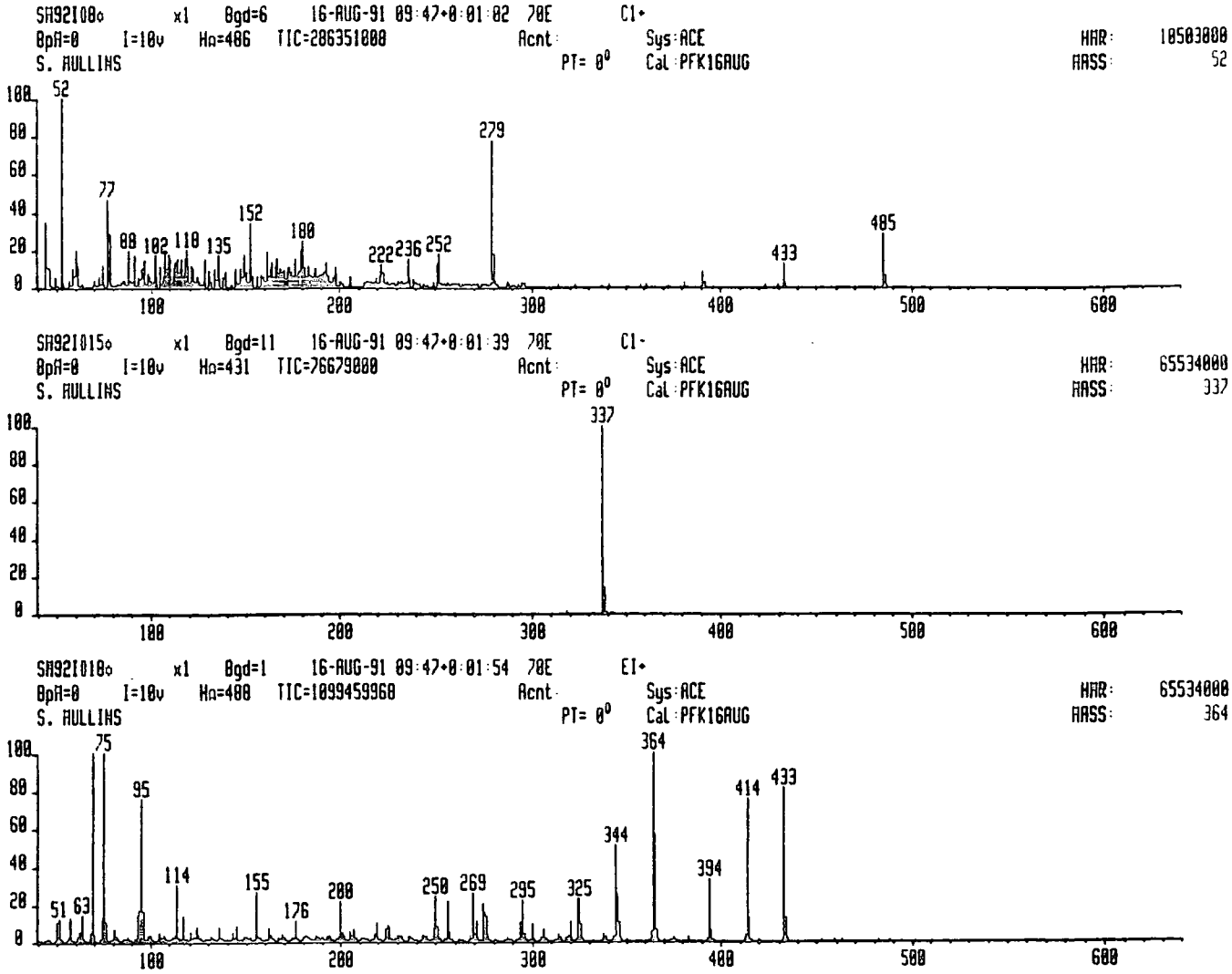
Mass spectrum number 32.



EI+ data

Mass	% Base								
41.01	1.20	344.86	1.26	437.81	1.14 F
43.02	1.87	350.86	1.14	438.84	29.05 F
49.98	1.14	351.85	1.14	439.86	7.24 F
50.99	1.22	352.86	1.18	440.84	1.21
55.02	1.14	354.88	1.69	441.82	1.69
57.03	2.35	356.86	1.10	444.82	1.14
62.99	2.88	360.85	1.15	445.90	1.72
64.00	3.74	363.85	1.21	448.80	1.14
68.96	2.39 F	364.86	2.10	449.82	1.14
69.03	1.14 F	375.86	1.71	452.83	1.15
71.05	1.71	376.86	1.21	457.81	1.14
76.99	3.09	379.11	1.14 F	460.80	1.71
85.05	1.14	380.89	2.48 F	461.81	1.14
91.97	3.93	381.85	1.39	468.85	1.27
187.93	1.14	382.84	1.26	472.82	2.90
193.91	1.03	394.84	1.14	473.81	1.14
219.41	1.14	395.87	2.96	475.82	1.48
236.39	1.14	396.87	1.14	476.84	1.16
237.89	3.47	400.83	1.37	488.85	8.88
257.91	1.14	401.84	1.32	489.85	2.31
263.90	1.14	406.85	1.14	492.82	1.16
282.88	1.22	407.86	1.74	506.51	1.09 F
283.90	1.52	408.84	1.71	507.81	100.00 F
288.86	1.50	409.86	1.14	508.84	25.42 F
294.88	1.14	418.87	1.29	509.84	3.43
300.90	1.23	419.87	1.14
306.88	1.14	420.83	1.06
312.87	1.14	421.83	1.00
313.87	1.23	422.84	1.14
326.88	1.71	423.85	2.85
331.86	1.14	424.84	1.23
332.87	2.63	425.84	1.21
333.86	1.14	429.81	2.28
338.85	1.59	432.82	3.19
343.88	1.14	433.83	1.27

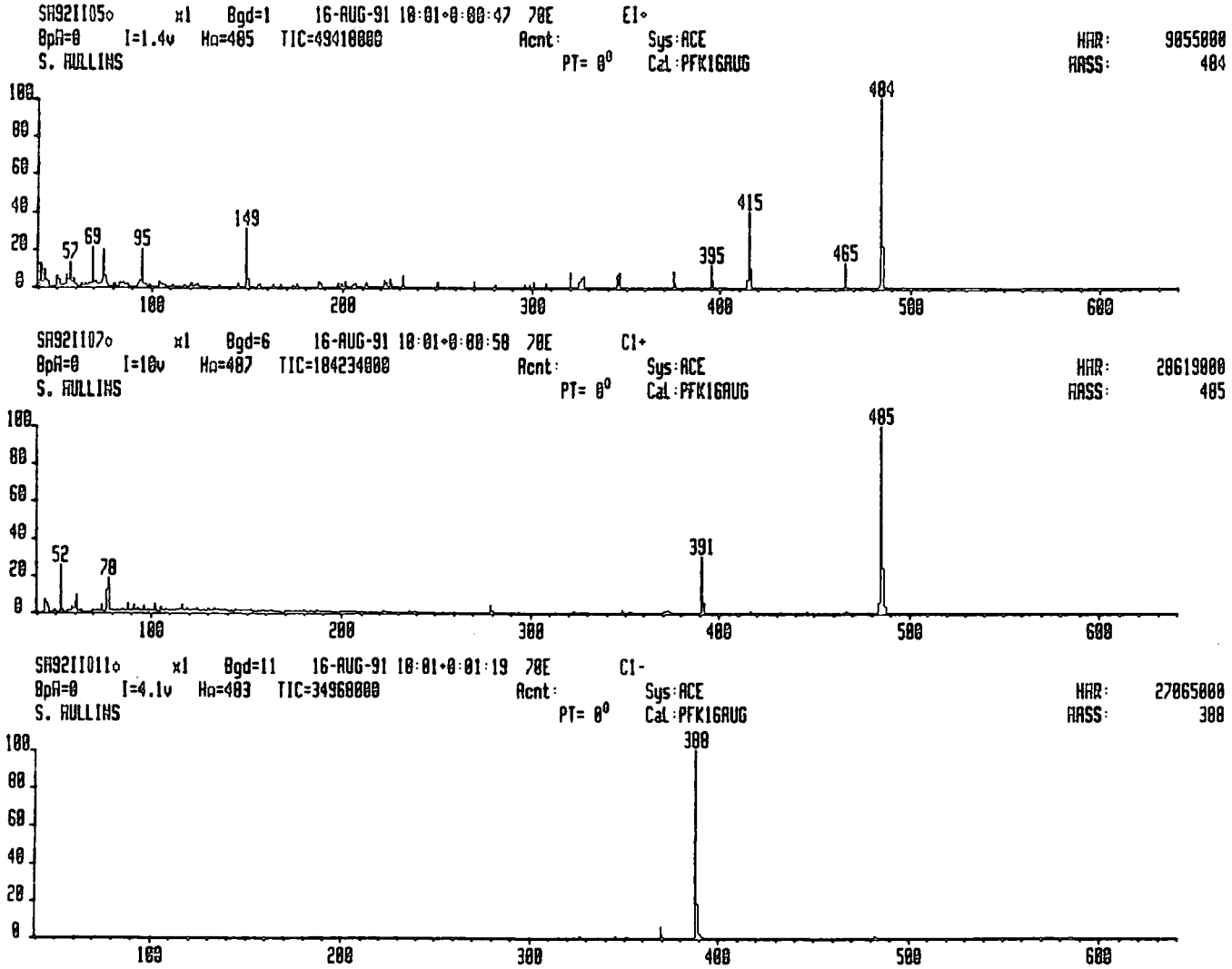
Mass spectrum number 33.



EI+ data

Mass	% Base								
49.98	7.05 F	116.99	13.71	199.00	2.75	296.01	3.91		
50.01	10.51 F	121.02	4.89	199.99	21.35	299.97	8.95		
51.01	12.20	122.02	1.83	201.00	4.55	305.98	6.51	F	
56.00	2.25	123.00	2.25	202.01	2.39	314.00	3.91		
57.01	12.59	123.99	7.51	204.98	4.82	318.97	2.40		
61.00	2.34	125.01	3.00	206.00	2.73	319.97	10.61		
62.01	5.04	126.02	2.12	207.01	6.57	323.96	22.43	F	
63.02	13.99	130.99	2.73	218.00	3.81	324.98	22.48	F	
64.02	1.56	132.01	1.84	219.00	9.43	326.02	8.67	F	
68.00	4.55	135.98	7.88	223.97	6.61	337.99	3.85		
68.99	100.00 O	136.99	1.73	225.00	8.05	338.98	2.41		
70.01	3.20	142.98	5.43	226.01	7.32	342.97	2.76	F	
73.00	1.17	144.00	1.96	230.00	2.55	343.97	50.56	F	
74.00	12.92	145.01	8.49	231.00	2.70	345.00	24.45	F	
75.01	100.00 O	149.01	2.63	232.00	2.34	346.01	10.51		
76.01	10.17	150.00	2.37	235.99	2.34	362.95	5.11	F	
81.00	6.16	152.02	2.01	242.97	3.32	363.97	100.00	FO	
82.00	2.34	154.98	26.35	244.00	2.37	365.00	56.46	F	
88.00	2.70	156.00	2.77	245.01	2.25	366.01	6.33		
92.00	2.01	157.01	2.01	249.00	6.75	383.00	2.30		
92.99	14.06	161.99	7.33	249.98	23.49	393.99	32.72		
94.01	16.71	163.00	3.24	250.99	7.86	395.00	5.52		
95.02	75.37	166.98	2.01	256.00	21.14	412.97	3.22	F	
96.02	16.30	169.01	4 09	257.00	4.43	413.98	75.84	F	
99 00	3.52	173.99	1.89	268.00	3.22	415.01	12.14	F	
99.99	3.10	175.00	1.91	269.00	25.75	432.98	81.67	F	
104.99	4.64	176.01	10.64	270.00	4.17	434.00	12.27	F	
106.00	1.95	180.00	2.81	271.01	10.62				
107.02	3.03	181.00	3 19	273.99	19.93				
108.01	1.89	182.00	2.73	275.00	15.10				
112.00	2.84	183.01	2.17	276.01	13.35				
113.00	3.17	187.00	2.90	277.01	2.45				
114.02	29.92	192.98	2.61	294.00	10.31				
115.02	2.21	194.00	2.34	295.00	22.05				

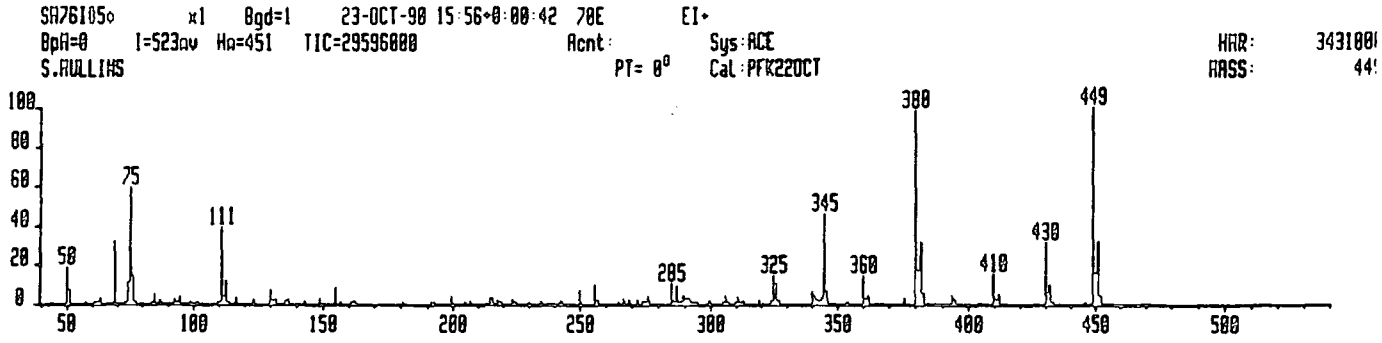
Mass spectrum number 34.

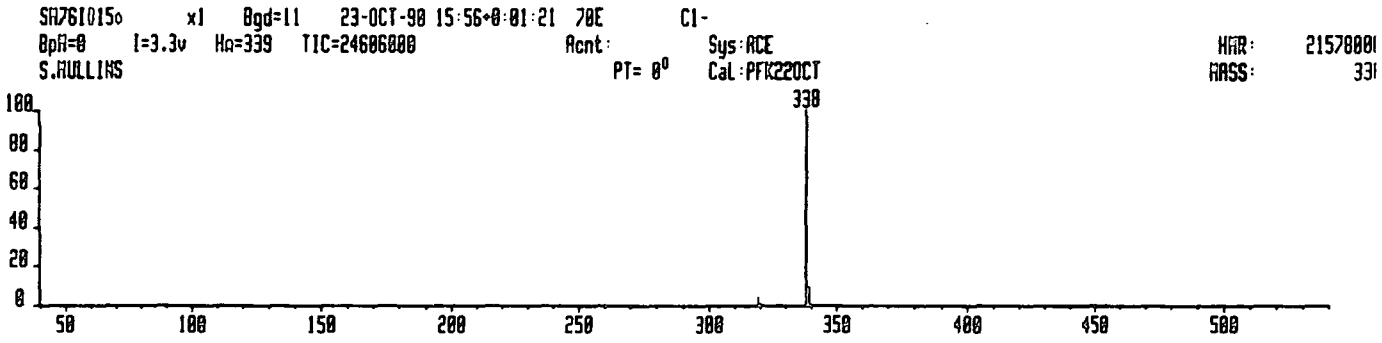


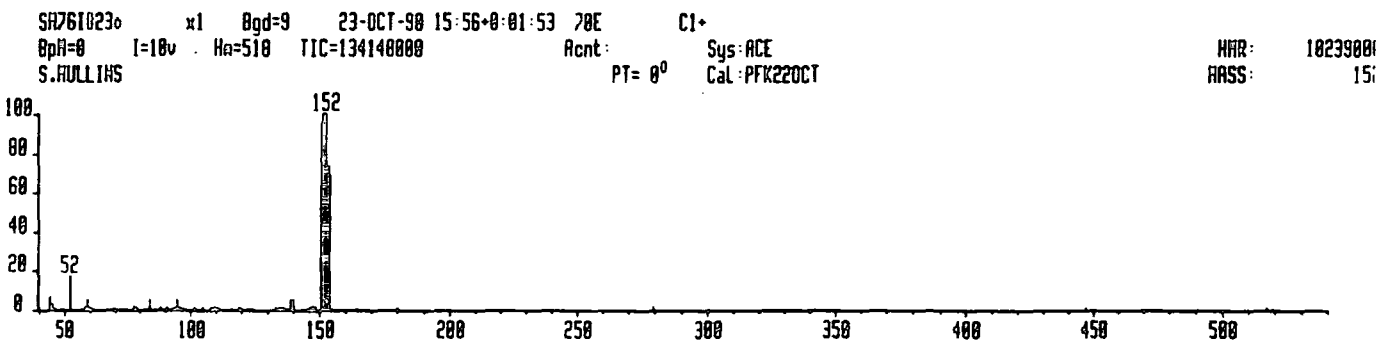
EI+ data

Mass	% Base				
41.05	11.97	93.03	1.54	206.07	1.42
42.05	1.84	94.04	3.40	212.06	2.12
43.03	5.65	95.05	19.79	222.06	3.11
43.06	8.98	96.05	1.49	223.13	1.83
44.02	2.90	97.12	1.12	225.07	3.79
45.03	2.55	99.03	0.85	226.08	1.49
50.02	5.14	104.04	2.88	232.07	5.65
51.03	3.25	105.05	1.51	250.09	1.84
53.05	0.78	106.04	0.74	251.08	2.83
54.06	0.70	107.06	0.63	270.10	2.85
55.06	5.78	111.04	0.87	281.09	1.36
56.07	3.46	111.14	0.54	296.11	1.02
57.07	12.97	117.02	0.89	299.10	1.04
59.05	3.68	120.05	1.36	301.09	2.83
60.04	0.82	121.06	1.93	307.11	1.98
63.03	1.17	123.04	0.73	320.11	7.58
65.05	1.35	124.03	1.02	325.10	2.44
67.07	1.41	135.11	0.87	326.11	4.36
68.02	1.02	145.06	2.16	327.12	5.57
69.01	20.29	149.05	30.55	345.11	6.64
69.08	2.79	150.05	3.57	346.12	7.98
70.03	0.86	155.04	0.73	375.11	8.14
70.09	1.69	156.06	1.45	376.12	1.78
71.10	2.87	163.06	1.28	395.13	11.33
72.06	0.94	167.06	1.04	396.14	3.67
73.05	1.03	173.06	0.83	414.13	3.81
74.04	3.19	175.06	1.37	415.14	39.49
75.04	19.44	187.06	2.83	416.15	9.41
76.04	4.93	187.56	1.65	465.07	12.90
77.05	1.48	188.07	1.16	483.14	1.50
81.08	1.15	197.06	2.02	484.16	100.00
83.10	1.72	199.06	0.99	485.17	20.87
85.11	1.95	201.07	2.35		
87.06	1.16	205.08	0.72		

Mass spectrum number 35.



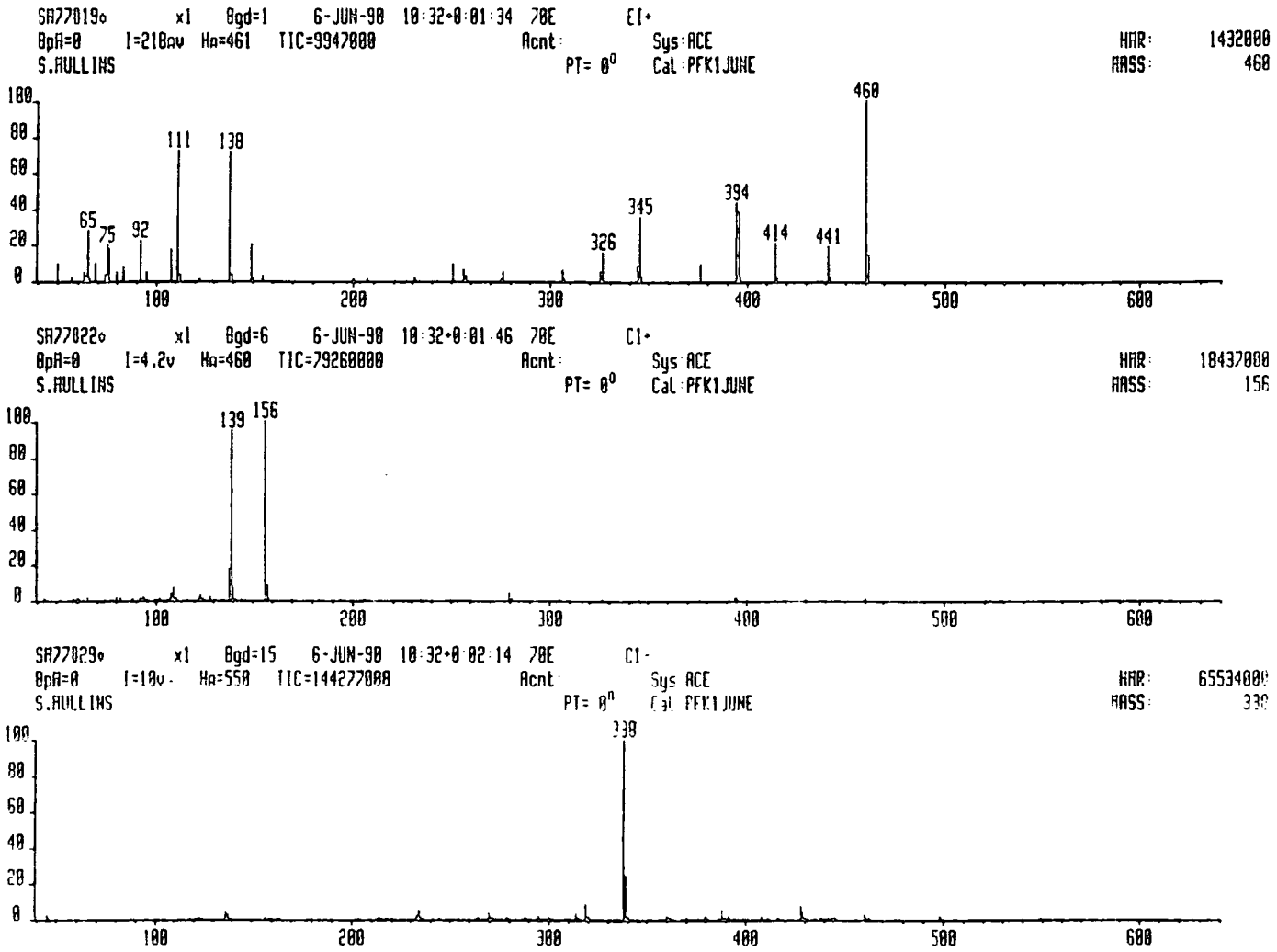




EI+ data

Mass	% Base						
50.00	18.27	154.91	8.07	287.87	0.67	381.82	30.81
51.00	7.05	156.95	0.70	288.87	1.02	382.82	5.10
57.05	0.82	160.91	0.96	289.86	3.99	393.84	4.20
60.96	0.61	161.92	1.08	290.87	2.39	394.84	2.13
61.99	0.67	162.43	0.87	291.87	2.59	409.80	15.01
63.00	2.59	180.92	0.47	292.87	0.85	410.80	1.81
68.96	32.09	191.90	0.99	293.89	0.61	411.80	4.75
72.95	0.61	192.89	0.61	294.90	0.96	429.80	31.22
72.97	0.41	199.89	3.15	299.86	1.17	430.81	5.19
73.98	10.70	204.89	0.90	304.87	0.58	431.79	9.53
74.99	58.90	206.92	1.08	305.87	4.26	432.80	0.76
75.99	14.08	214.88	2.62	306.88	0.67	445.97	0.79
77.00	0.90	215.89	2.80	309.84	0.99	448.80	100.00
83.94	0.55	217.89	1.31	310.85	3.35	449.80	15.36
84.94	4.46	218.89	0.79	311.85	0.79	450.80	31.77
86.94	1.54	223.88	2.04	312.85	1.31	451.80	4.34
92.95	2.19	224.38	0.35	318.85	2.16		
93.98	0.58	224.90	0.61	323.85	1.31		
94.98	3.21	229.90	0.55	324.86	14.31		
98.96	0.44	234.88	1.37	325.87	10.14		
101.99	0.61	241.88	0.64	326.88	1.02		
109.94	0.55	242.87	1.49	339.82	6.00		
110.95	38.36	249.85	6.62	340.83	3.50		
111.95	3.70	255.89	9.53	341.82	2.01		
112.94	11.66	256.89	1.81	342.83	1.25		
113.95	0.52	264.86	0.61	343.85	2.42		
116.94	2.56	266.86	2.71	344.86	45.18		
123.94	1.72	268.86	1.92	345.87	5.95		
129.94	6.56	271.86	2.04	353.83	0.76		
130.93	1.14	273.87	1.08	359.82	14.51		
131.94	1.89	274.88	1.60	360.83	2.54		
135.93	1.14	275.89	4.23	361.82	3.99		
136.94	1.95	284.87	10.29	375.85	2.71		
142.92	1.08	285.87	1.17	379.82	97.70		
148.95	2.74	286.87	8.51	380.83	16.79		

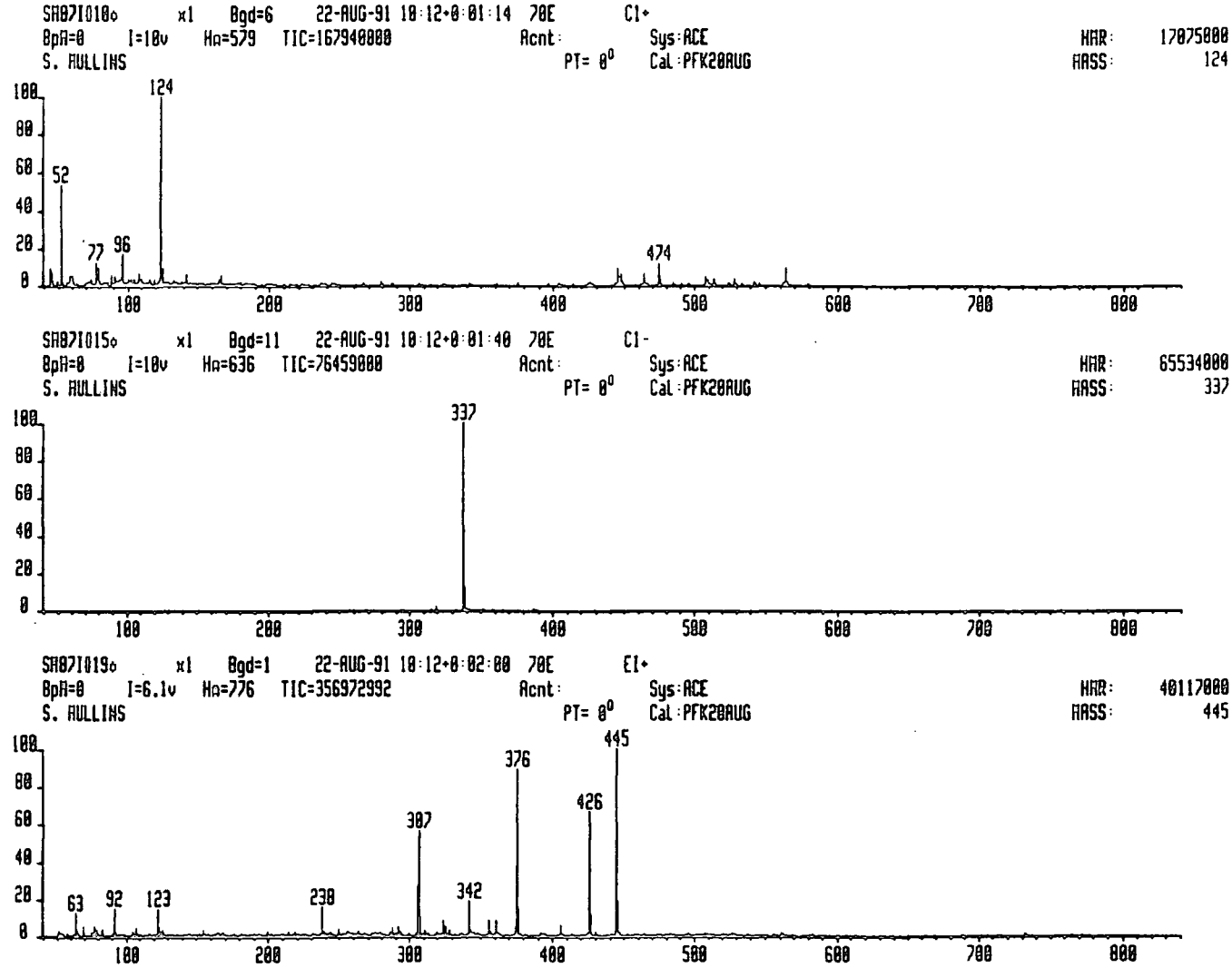
Mass spectrum number 36.



EI+ data

Mass	% Base		
49.98	9.36	344.26	8.66
57.05	2.09	345.26	35.68
63.03	4.54	346.26	2.93
64.04	3.00	376.28	9.15
65.05	27.79	394.29	43.16
66.05	1.05	395.29	37 50
69.02	9.15	396.30	2.65
74.05	3.28	414.31	21.16
75.07	19.62	415.31	1.82
76.07	17.60	441.33	18.72
80.10	4.40	442.32	2.23
83.08	7.26	460.35	100.00
92.11	22.00	461.36	14.04
95.09	4.82		
108.12	17.46		
111.09	72.07		
112.10	3.35		
122.12	1.33		
138.13	71.51		
139.13	3.56		
149.12	20.25		
150.12	1.33		
155.09	3.00		
200.13	1.68		
207.15	1.47		
231.18	2.16		
250.17	9.71		
256.19	6.28		
257.19	2.37		
275.19	1.47		
276.20	5.66		
306.20	5.80		
307.20	1.54		
325.23	5.24		
326.24	16.27		

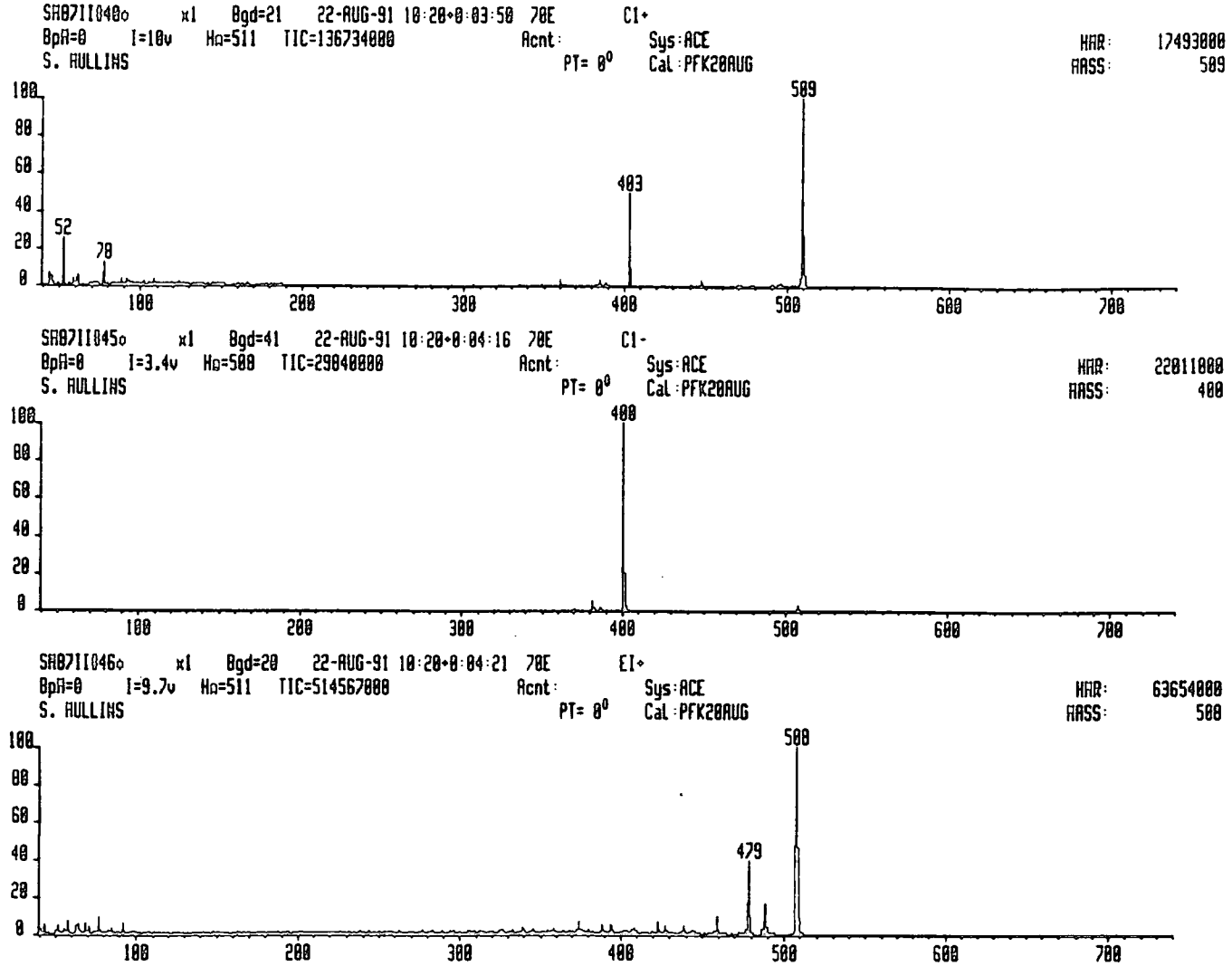
Mass spectrum number 37.



EI+ data

Mass	% Base				
51.00	2.55	255.91	2.74	360.88	8.45
63.00	12.17	256.92	1.62	361.88	1.97
64.00	3.28	257.92	1.43	374.88	5.11 F
68.97	5.11	258.93	1.52	375.88	89.08 F
74.99	2.18	263.91	2.86	376.89	14.68 F
75.99	1.46	273.90	1.45	377.90	1.49 F
77.00	5.32	275.91	1.91	391.88	1.91
78.00	2.55	276.91	1.44	405.89	5.84
78.99	3.12	278.93	1.91	423.87	1.91 F
82.99	3.83	285.91	1.91	424.87	1.69 F
91.98	14.68	286.91	1.91	425.87	66.61 F
92.98	1.89	287.92	4.58	426.87	11.49 F
104.99	2.55	291.90	5.06	429.87	2.55
107.00	4.56	292.90	2.55	443.73	2.55 F
108.00	1.31	293.89	1.91	444.88	100.00 F
123.01	14.68	305.89	26.72 F	445.89	18.51 F
124.01	4.47	306.90	56.16 F	446.91	2.02 F
124.99	2.27	307.92	10.41 F	464.91	1.31
125.99	3.90	308.92	1.43	495.93	1.99
144.96	1.34	310.90	3.44	507.93	1.53
154.93	2.94	319.87	1.91	527.93	1.91
165.00	1.91	323.90	8.34	560.87	1.91 F
168.95	1.91	324.90	2.13		
175.95	1.44	325.89	5.18		
199.92	2.55	326.90	1.38		
213.93	2.55	327.91	3.23		
217.93	1.51	341.88	18.59		
218.94	2.87	342.89	3.42		
237.94	15.28	343.88	1.87		
238.94	2.71	345.89	1.91		
243.92	1.91	347.91	1.31		
244.92	1.46	355.90	8.31		
249.89	3.83	356.90	2.60		

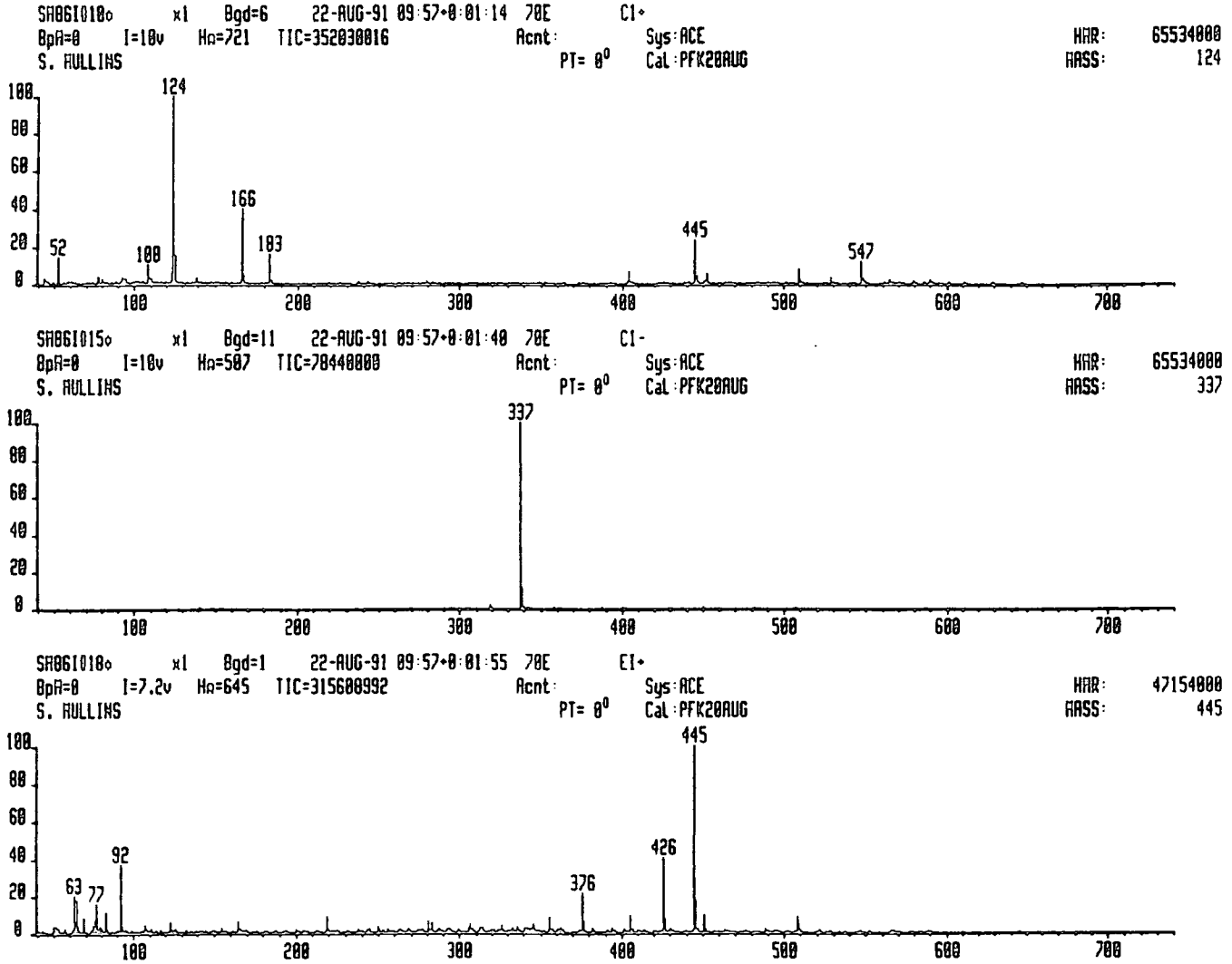
Mass spectrum number 38.



EI+ data

Mass	% Base										
41.01	2.68	305.83	1.32	388.77	4.83 F	487.73	7.31 F
43.02	5.20	306.84	1.78	389.78	2.45 F	488.74	16.36 F
49.98	1.62	307.84	1.31	393.78	4.81 F	489.77	3.83 F
50.99	4.60	308.86	1.73	394.80	4.78 F	506.72	47.40 F
55.01	2.70	312.82	1.62	395.79	1.77	507.73	100.00 F
57.03	6.81	313.83	1.33	402.78	2.10	508.74	46.44 F
62.98	4.53	319.83	1.40	403.79	2.11	509.75	8.58 F
63.99	5.20	324.82	2.28	406.79	2.76		
64.99	1.61	325.82	2.71	407.78	2.00		
68.95	5.63 F	326.83	2.82	408.80	3.22		
69.02	2.20 F	332.81	2.52	409.79	1.61		
71.03	4.03	338.82	3.80	422.77	6.65 F		
74.96	1.50	339.84	2.35	423.76	2.82		
76.98	8.82	340.84	1.66	424.75	1.33		
77.98	1.78	344.81	2.25	427.74	4.34		
83.01	1.61	345.81	2.79	428.74	1.80		
85.04	2.96	346.81	1.50	437.74	1.65 F		
91.96	5.86	354.81	2.34	438.76	4.66 F		
97.02	1.31	356.80	2.04	439.76	1.61 F		
238.88	1.72	358.82	2.98	442.74	1.58		
243.86	1.61	359.81	1.31	443.76	2.42		
253.85	2.13	363.80	1.35	445.82	1.61		
262.85	1.76	364.82	1.93	456.77	1.98		
263.86	1.34	368.82	1.63	457.75	1.63 F		
276.86	2.78	372.79	2.42	458.74	9.58 F		
281.83	1.49	373.80	2.82	459.74	2.82 F		
282.84	2.42	374.79	6.41	472.75	1.32		
288.84	1.64	375.80	2.42	476.71	3.38 F		
294.85	1.96	376.79	1.63	477.73	17.26 F		
295.85	1.98	377.80	1.54	478.74	39.16 F		
296.85	1.61	380.78	2.41	479.77	8.86 F		
304.84	1.88	387.77	1.33 F	486.62	3.11 F		

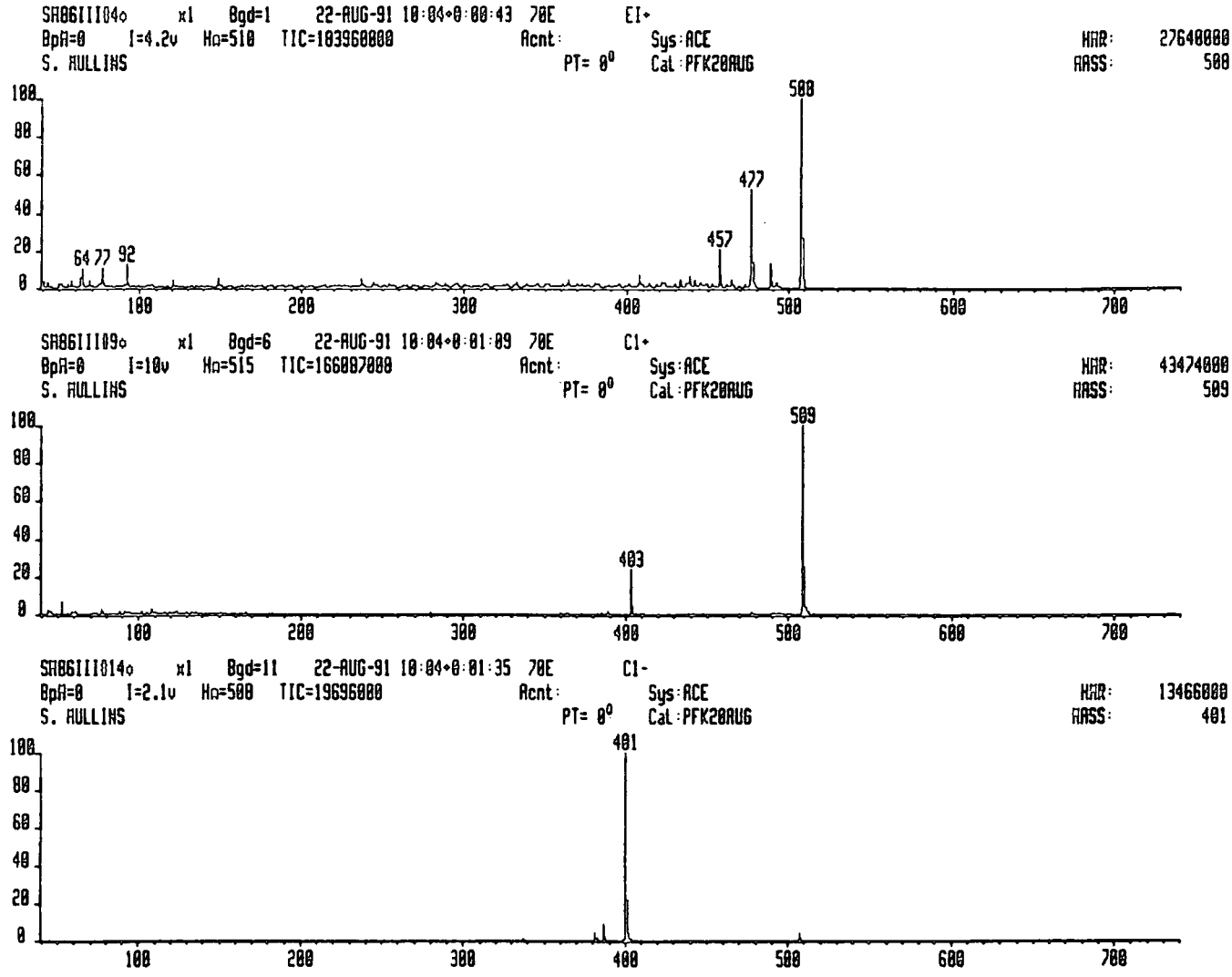
Mass spectrum number 39.



EI+ data

Mass	% Base								
49.98	3.26		168.92	1.09		307.84	1.74		394.79	1.09	
50.98	3.38		193.89	1.09		312.82	2.85		401.79	2.17	
51.99	1.09		199.87	1.70		313.83	2.71		405.80	8.75	
52.96	1.09	F	204.86	1.09		319.80	1.11		406.81	1.63	
53.00	1.63	F	218.90	8.51		321.81	1.09		409.77	1.23	
56.98	2.15		219.90	1.77		323.82	1.09		413.79	1.09	
61.97	2.17		224.87	1.09		324.82	1.13		424.77	1.09	F
62.98	20.17		237.88	1.63		325.83	3.80		425.80	40.53	F
63.99	17.29		242.85	1.09		326.83	1.09		426.80	7.05	
64.99	3.29		243.86	1.63		331.81	1.09		430.77	1.76	
68.95	7.63		244.87	1.63		332.82	2.40		443.76	1.31	F
73.96	1.27		249.84	2.89		335.82	3.26		444.78	100.00	F
74.97	3.98		250.87	1.16		336.82	1.06		445.80	17.35	F
75.98	6.57		252.87	1.09		340.80	2.44		446.81	1.75	
76.98	15.67		255.86	1.74		341.81	2.28		450.79	8.72	
77.99	2.17		262.86	1.09		343.81	1.63		451.80	1.86	
78.99	3.26		263.86	1.63		344.81	2.24		463.80	1.09	
79.99	1.77		267.85	1.09		345.82	4.53		488.78	1.65	
80.96	1.15		268.85	1.63		346.82	1.09		507.83	8.14	
82.97	10.76		273.84	1.09		355.82	8.10		508.84	4.32	
91.96	36.73		275.85	1.18		356.83	1.81		509.85	1.09	
92.96	3.00		276.85	1.63		357.82	1.09		521.82	1.09	
94.97	1.32		280.86	5.90		359.80	1.09		565.83	1.59	
106.97	3.80		281.86	1.33		360.81	1.76				
107.98	2.22		282.86	4.82		361.80	1.24				
110.95	1.79		286.84	1.09		362.80	2.44				
116.92	1.13		287.85	1.63		363.81	1.09				
122.98	5.47		291.84	1.11		374.81	1.09				
123.96	1.09		292.83	1.63		375.82	21.31				
125.96	1.66		293.83	2.17		376.82	5.59				
132.96	1.09		294.84	1.09		381.79	2.87				
154.89	2.74		299.81	1.18		382.80	1.12				
164.97	5.63		305.83	2.47		390.79	1.09				
165.97	1.70		306.85	4.35		393.78	2.47				

Mass spectrum number 40.

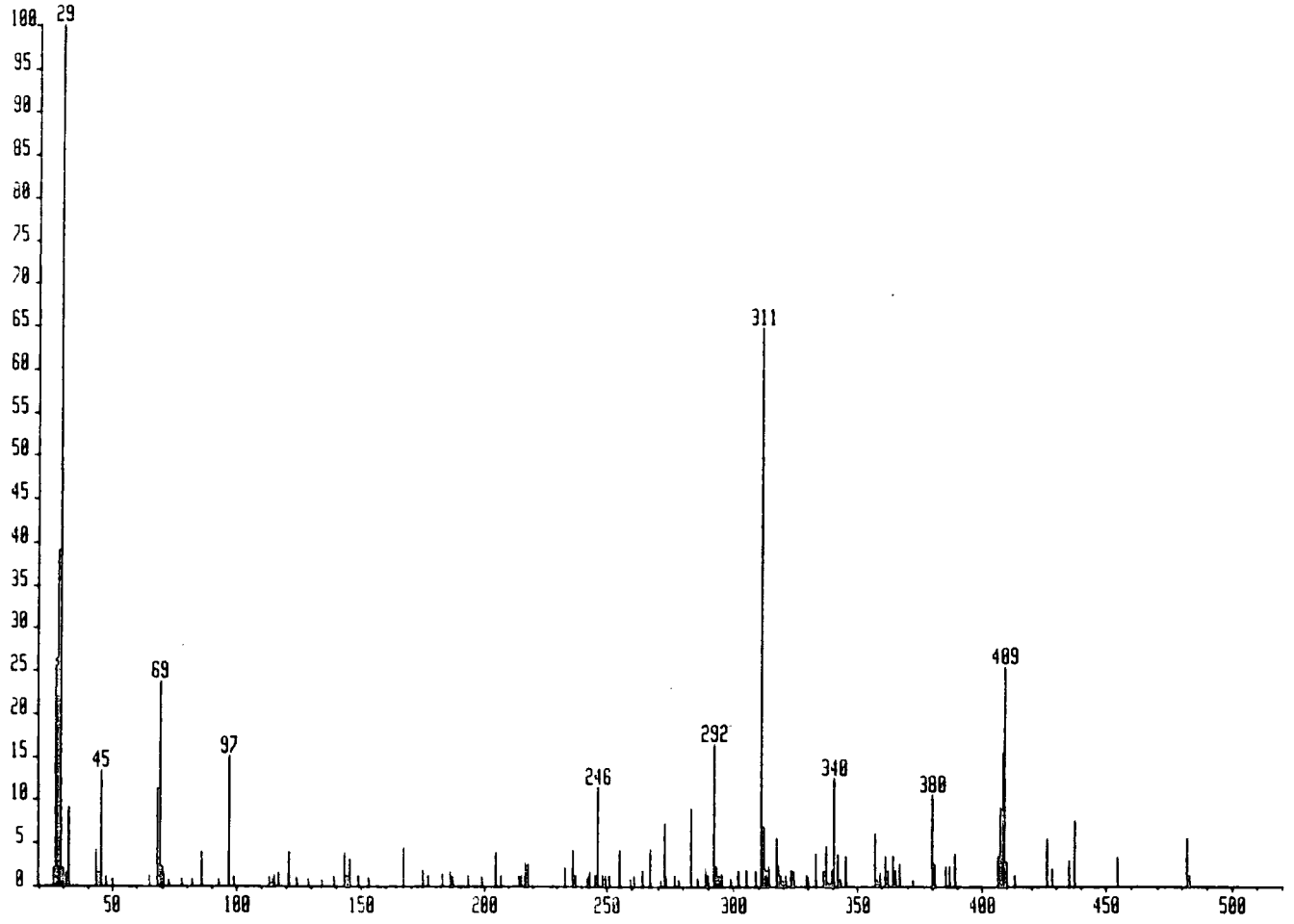


EI+ data

Mass	% Base		Mass	% Base		Mass	% Base	
40.99	3.00		332.71	2.78		429.60	1.85	
42.96	2.05	F	338.69	1.85		432.62	4.53	
43.00	2.78	F	344.70	1.85		433.62	3.67	
49.96	1.89		345.71	1.73		436.47	2.86	F
50.97	1.88		350.69	1.85		437.56	2.16	F
54.99	1.86		351.69	1.72		438.63	6.49	F
57.01	3.70		352.69	1.85		439.63	1.85	F
62.96	5.39		360.69	1.85		441.60	3.70	
63.97	10.09		363.68	1.85		442.61	1.07	
64.97	1.86		364.69	4.20		444.63	2.05	
68.93	3.80	F	365.69	1.58		445.62	2.78	
74.95	1.85		369.72	2.16		447.33	1.14	F
75.95	3.54		370.71	1.05		448.68	1.85	F
76.96	10.20		372.67	1.85		449.60	1.85	F
77.96	1.85		375.69	1.05		452.61	1.85	
90.95	1.03		376.69	1.55		456.61	20.49	
91.93	12.10		380.67	2.85		457.62	6.28	
92.93	1.62		381.67	1.85		458.61	1.05	
120.94	3.70		382.66	1.85		461.60	1.85	
148.87	4.71		392.66	1.55		464.61	4.67	
214.81	1.55		394.67	1.85		465.62	1.03	
236.29	4.63		395.67	1.85		472.59	1.62	
236.79	1.85		400.64	1.85		475.58	6.62	F
243.79	2.78		401.65	1.91		476.58	51.85	F
244.29	1.45		406.66	1.85		477.61	13.42	F
253.78	1.85		407.66	6.86		478.61	2.78	
282.76	2.60		408.66	2.96		488.61	12.89	
283.77	1.85		409.65	1.85		489.61	2.95	
288.74	1.85		413.64	2.50		492.59	2.68	
294.75	1.85		414.65	1.46		506.41	5.56	F
295.76	1.81		418.66	1.85		507.57	100.00	F
311.74	1.52		420.63	1.16		508.60	25.98	F
312.72	1.85		421.63	3.30		509.61	3.70	
313.74	1.85		422.62	2.48				
326.73	1.85		423.65	2.68				

Mass spectrum number 41.

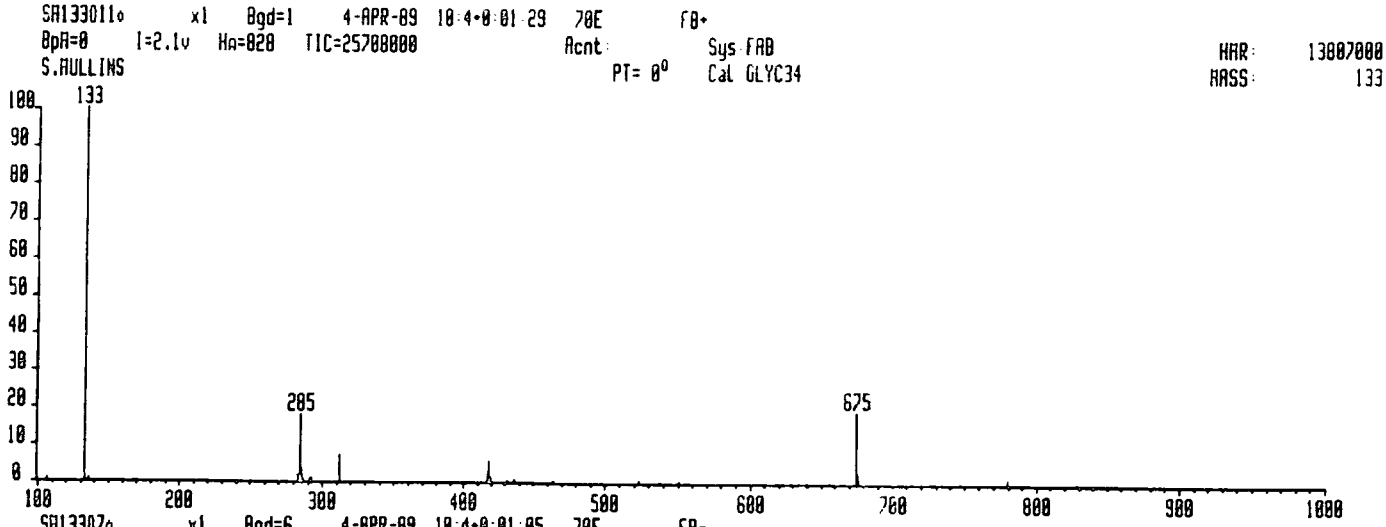
SA130661o x1 Bgd=658 25-NOV-88 12 8:8:11:45 70E EI+
BpA=0 I=464av Ha=483 TIC=20557888 Acnt: Sys:AULL HAR: 3046888
GC= 146° Cal:PFK1111 AASS: 29

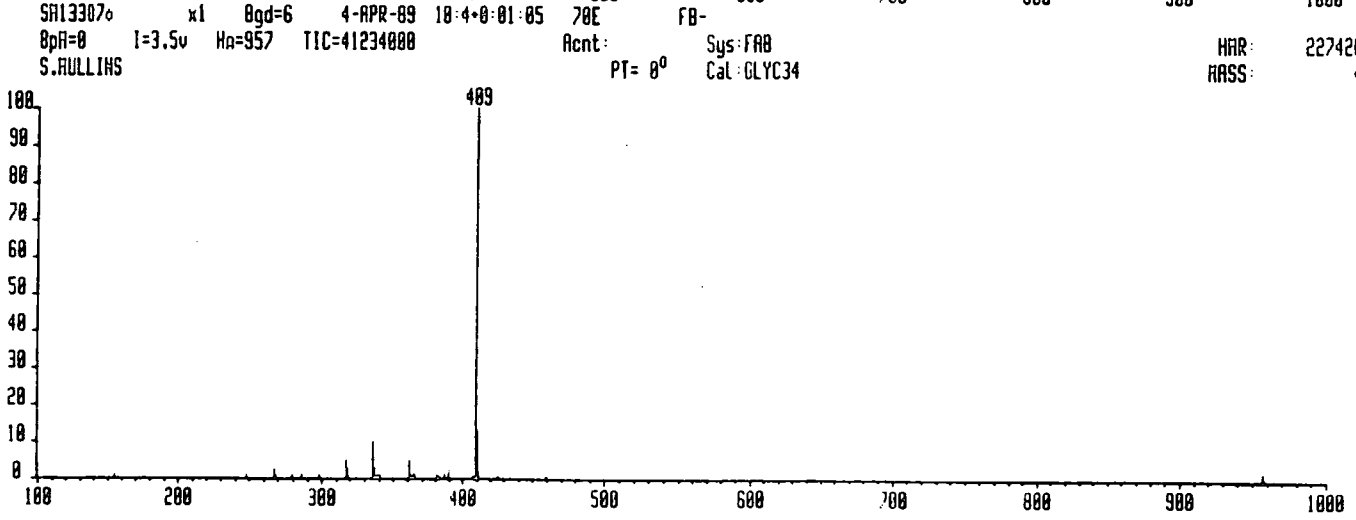


EI+ data

Mass	% Base						
26.01	2.10	205.06	3.87	313.15	2.10	409.26	25.41
27.02	26.46	207.03	1.12	314.11	2.30	410.27	2.82
28.00	39.07	214.09	1.12	314.20	1.12	413.31	1.25
28.03	5.19	215.04	1.51	314.24	1.25	426.31	5.45
29.00	2.30	217.09	2.63	317.17	5.45	428.46	1.97
29.04	100.00	219.09	2.56	318.16	2.30	435.34	3.02
30.01	1.64	233.09	2.10	319.17	1.25	437.33	7.55
30.04	2.10	236.09	4.20	321.15	1.12	454.34	3.22
31.02	1.51	237.08	1.25	323.17	1.77	482.45	5.45
31.99	9.00	242.07	1.25	324.20	1.58	483.46	1.25
43.02	4.14	243.09	1.58	329.20	1.18		
44.00	1.51	243.20	1.12	333.17	3.74		
45.00	2.82	245.10	1.38	336.17	1.77		
45.04	13.33	246.09	11.36	337.20	4.66		
65.01	1.25	248.10	1.12	338.23	1.12		
68.00	11.23	249.14	1.38	339.18	2.10		
69.00	23.64	251.10	1.25	340.19	12.48		
69.04	1.12	255.10	4.27	342.19	3.74		
70.07	2.17	261.09	1.25	345.20	3.35		
71.01	1.44	264.11	1.77	357.24	6.01		
86.02	3.91	267.11	4.27	359.24	1.58		
97.00	14.90	273.12	7.22	361.22	3.38		
115.08	1.25	277.17	1.25	362.21	1.77		
117.01	1.51	283.12	8.86	364.26	3.35		
121.02	3.81	289.11	2.10	365.31	1.77		
143.02	3.68	290.13	1.25	367.24	2.56		
144.01	1.12	292.13	16.48	372.53	0.59		
145.03	3.15	293.16	2.20	380.23	10.57		
149.05	1.12	294.18	1.25	381.21	2.50		
167.05	4.27	295.15	1.38	385.29	2.17		
175.06	1.77	302.14	1.77	387.22	2.17		
177.08	1.25	305.16	1.77	389.25	3.74		
183.09	1.28	309.16	1.77	406.25	3.87		
186.02	1.64	311.15	64.84	407.26	9.13		
193.04	1.12	312.16	6.76	408.25	15.43		

Mass spectrum number 42.





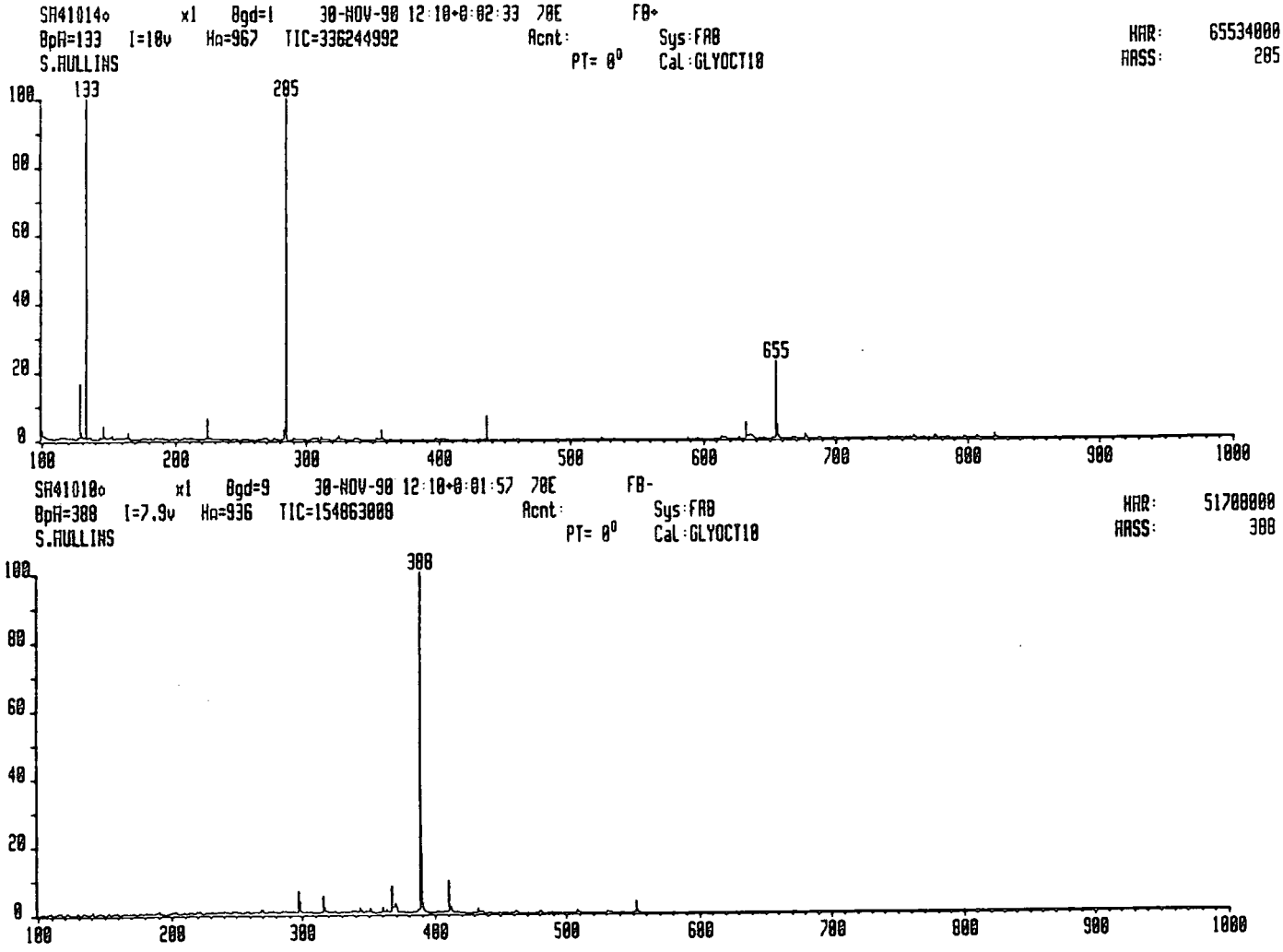
FAB+ data

Mass	% Base
89.03	2.93
132.88	100.00
282.72	1.38
284.71	17.86
285.84	3.24
286.77	0.33
286.93	0.52
291.65	0.46
291.69	0.47
291.75	0.54
291.80	0.85
307.66	0.28
311.69	7.19
416.60	0.33
416.71	0.26
416.79	0.77
416.85	0.69
417.73	2.08
417.93	0.22
418.73	5.65
419.63	0.45
419.74	0.93
419.84	0.90
431.68	0.31
436.46	0.48
436.57	0.38
436.63	0.65
463.60	0.44
523.09	0.72
537.13	0.52
550.69	0.46
550.75	0.31
674.82	18.95
675.85	2.42
779.87	1.14
828.74	0.33

FAB- data

Mass	% Base		Mass	% Base
266.76	2.31		358.73	0.30
267.76	0.63		358.84	0.33
267.83	0.33		360.70	4.69
278.72	0.58		361.73	0.61
278.79	0.70		363.71	1.07
285.67	0.26		364.61	0.51
285.73	0.56		364.75	0.69
294.73	0.22		365.75	0.17
295.72	0.18		380.57	0.30
297.64	0.19		380.69	0.68
297.74	0.73		380.79	0.39
313.76	0.49		382.63	0.44
314.73	0.18		382.70	0.26
316.55	0.16		382.75	0.31
316.72	4.67		382.80	0.51
317.73	2.21		386.74	1.05
318.78	0.21		389.72	2.13
332.72	0.29		390.60	0.33
335.62	8.86	F	390.72	0.29
335.74	9.63	F	390.81	0.25
336.72	2.59		406.68	1.17
336.87	0.17		407.75	0.16
338.71	0.78		408.04	0.19
339.72	0.21		408.70	100.00
339.78	0.32		409.70	12.71
340.69	0.18		410.70	1.53
340.73	0.54		424.66	0.13
340.79	0.24		424.77	0.26
344.73	0.19		456.67	0.36
344.77	0.17		456.78	0.47
349.66	0.34		956.54	1.75
349.71	0.14		957.36	0.40
349.77	0.29		957.53	0.26
351.64	0.38		957.65	0.49
351.73	0.31		957.74	0.27
385.69	0.25		957.84	0.39

Mass spectrum number 43.



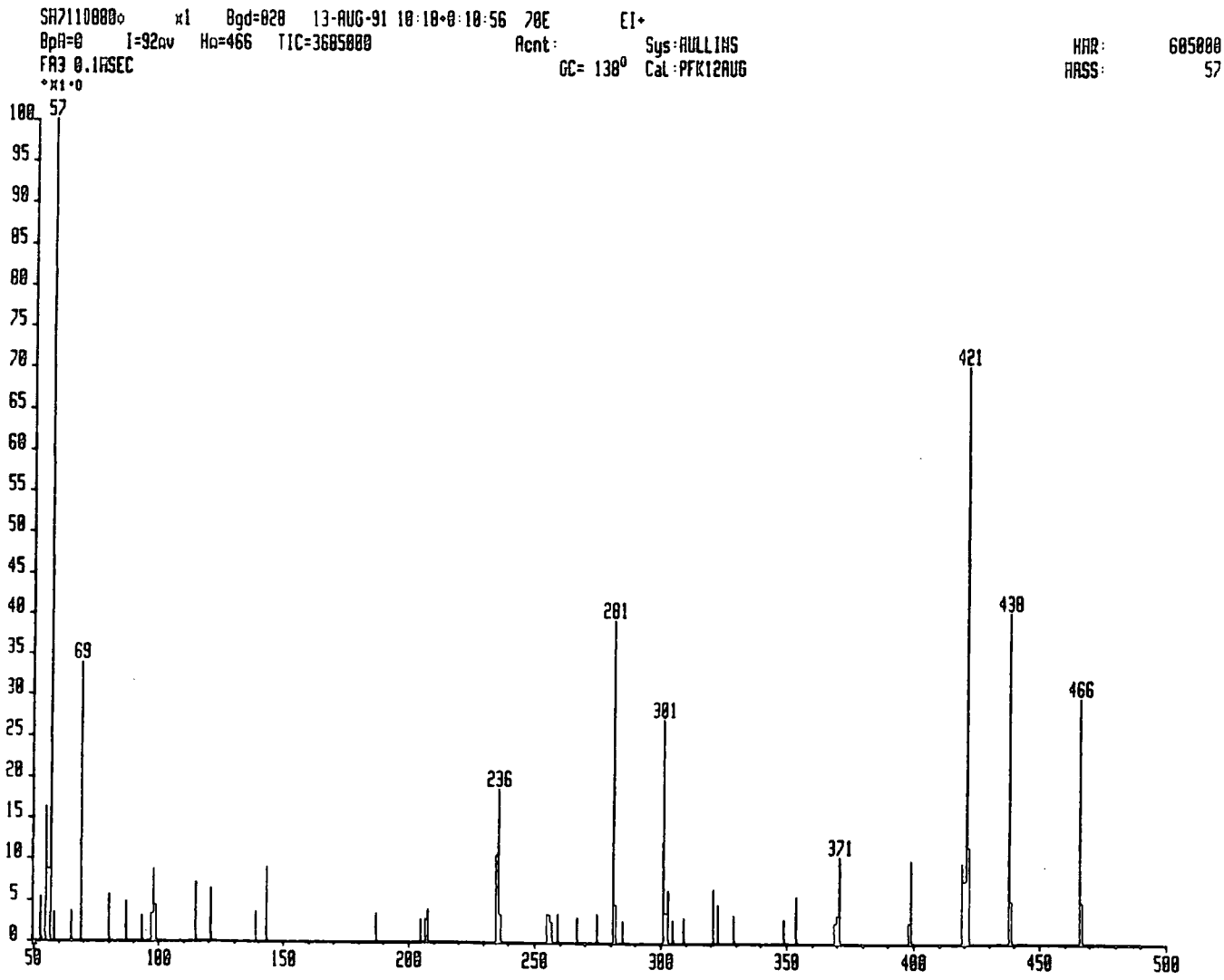
FAB+ data

Mass	% Base		Mass	% Base	
100.01	2.82		636.74	0.61	
102.06	1.14		654.70	22.52	F
102.97	0.80		655.72	3.78	F
114.01	0.76		656.74	0.64	
114.98	0.63		676.76	1.24	
116.99	0.79		758.63	0.69	
126.01	0.63		774.75	0.88	
127.00	0.81		819.82	1.07	
128.02	16.57				
129.02	1.97				
130.00	0.68				
130.96	0.51				
132.01	0.55				
132.89	100.00	O			
136.01	0.57				
143.05	0.76				
146.02	3.94				
147.00	0.61				
150.83	0.64				
152.82	1.05				
162.82	0.72				
165.03	2.23				
184.99	0.79				
224.82	6.05				
282.66	2.86				
284.76	100.00	O			
308.66	0.54				
310.67	0.74				
324.67	0.94				
396.68	2.90				
436.55	6.90				
613.67	0.79				
632.69	4.80				
633.71	0.75				
635.70	1.13				

FAB- data

Mass	% Base		Mass	% Base	
140.77	0.79		347.53	0.80	
190.72	0.57		348.52	0.50	
202.69	0.77		350.52	1.54	
218.69	0.80		359.55	0.50	
221.69	0.79		360.55	1.79	
237.65	0.52		361.55	0.50	
240.64	0.84		362.55	0.91	
246.62	0.61		366.56	7.76	
249.62	0.64		367.56	1.67	
258.65	0.72		368.58	0.50	
259.64	0.51		369.56	2.91	
268.62	1.07		370.55	1.64	
269.63	1.24		371.56	0.38	
274.60	0.82		372.54	0.51	
277.61	0.82		373.53	0.50	
281.59	0.52		386.52	1.11	
284.59	0.64		388.50	100.00	F
287.57	0.64		389.53	17.16	F
293.55	0.73		390.53	2.74	
296.55	6.39		391.52	0.91	
297.55	3.58		410.47	9.43	
298.55	0.58		411.48	1.66	
315.46	3.74	F	432.53	1.60	
315.64	5.14	F	508.53	0.62	
316.59	1.68		530.49	0.50	
317.57	0.80		992.46	3.27	
318.58	0.74		993.44	0.75	
319.58	0.50				
324.57	0.71				
335.54	0.53				
337.54	0.74				
338.54	0.70				
340.52	0.60				
343.52	1.79				
344.53	1.01				

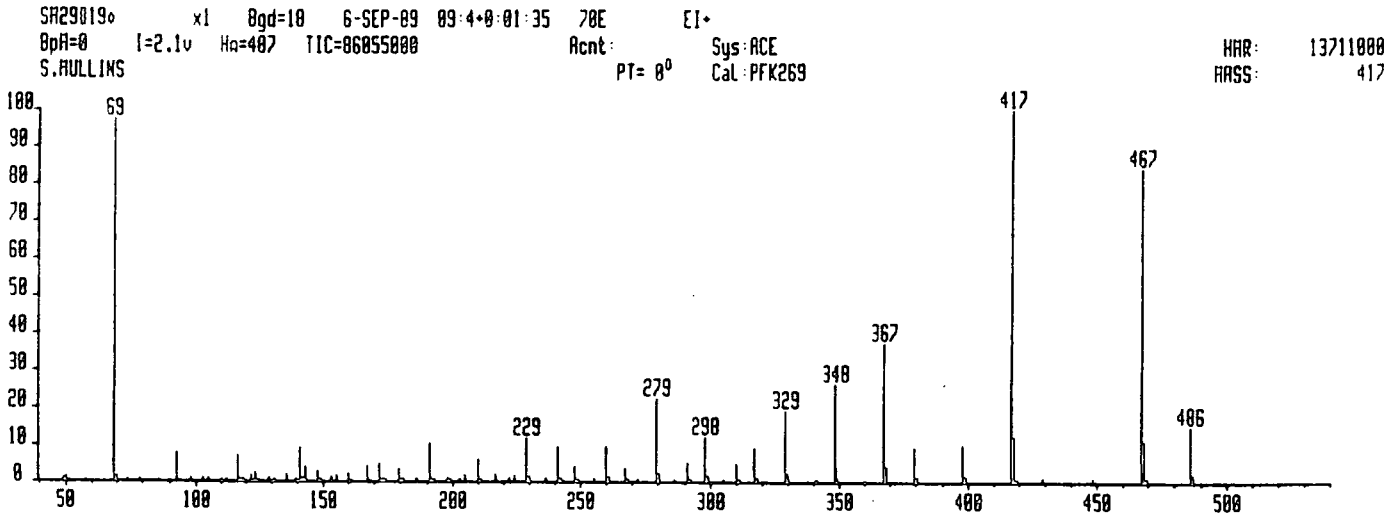
Mass spectrum number 44.



EI+ data

Mass	% Base		
53.03	5.29	284.96	2.48
55.02	16.20	285.04	2.48
56.03	8.60	300.97	26.94
57.03	100.00	301.98	3.47
58.04	3.31	302.97	6.28
65.02	3.47	304.98	2.64
68.99	33.88	308.98	2.98
80.02	5.62	320.96	6.45
87.00	4.63	322.96	4.46
92.98	2.98	328.97	3.14
97.01	3.14	348.95	2.81
98.03	8.60	353.93	5.62
99.03	4 30	368.96	2.31
115.03	6.94	369.94	3.14
120.99	6.28	370.96	10.41
139.01	3.47	397.94	2.31
142.98	8.93	398.94	9.92
187.00	3.31	418.94	9.59
204.98	2.64	419.95	7.44
207.00	2.64	420.94	70.41
208.00	3.80	421.96	11.57
234.98	10.58	437.94	40.33
235.98	18.51	438.96	4.96
237.01	3.14	465.96	29.75
284.97	3.31	466.99	4.79
255.99	3.14		
256.97	2.31		
259.01	3.31		
266.96	2.98		
274.99	3.31		
280.96	39.34		
281.97	4.46		

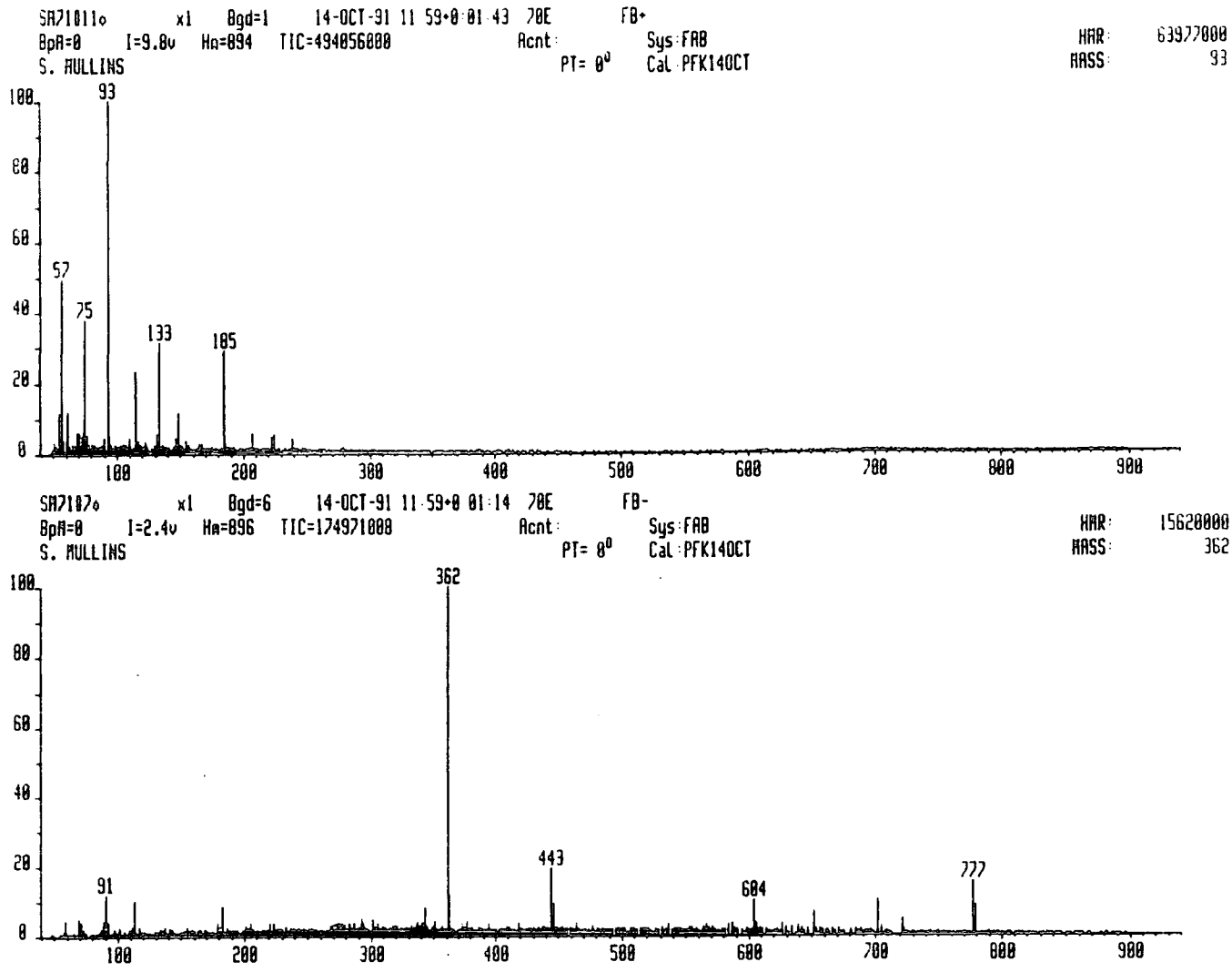
Mass spectrum number 45.



EI+ data

Mass	% Base		
30.99	1.91	261.09	0.90
48.98	0.59	267.08	3.37
50.00	1.11	268.09	0.20
68.99	97.01	272.09	0.50
69.99	0.90	279.09	21.97
74.00	0.49	280.09	2.15
79.00	0.35	286.08	0.32
93.01	7.61	291.10	5.00
98.02	0.80	292.10	0.44
103.02	0.69	298.10	11.93
105.02	0.77	299.10	1.29
110.02	0.39	305.09	0.20
112.02	0.20	310.11	4.57
117.02	6.83	311.11	0.50
118.02	0.25	317.12	8.97
122.02	1.60	318.12	0.82
124.02	2.30	329.10	18.82
129.02	0.85	330.10	2.03
131.02	0.42	341.12	0.23
136.03	1.77	348.12	25.95
139.53	0.24	349.12	3.41
141.03	9.04	367.12	37.28
142.04	0.65	368.13	3.91
143.03	3.46	379.14	8.80
148.04	2.63	380.14	1.02
149.06	0.53	398.14	9.67
153.04	0.96	399.15	1.50
155.04	1.47	417.16	100.00
160.04	1.98	418.16	11.68
167.05	3.79	419.16	0.50
172.05	4.76	429.16	0.68
173.06	0.32	448.17	0.82
174.05	0.21	467.19	84.39
179.05	3.33	468.19	10.68
180.06	0.24	469.20	0.58
181.05	0.79	486.19	14.59
186.05	0.65	487.19	1.68
191.06	9.93		
192.07	0.87		
193.06	0.35		
198.06	0.85		
199.06	0.41		
203.07	0.53		
205.06	1.73		
210.07	5.81		
211.07	0.47		
217.07	1.79		
222.07	0.63		
224.07	1.55		
229.07	11.45		
230.08	1.00		
236.08	0.88		
241.08	9.18		
242.08	0.75		
248.08	3.81		
249.09	0.33		
255.08	0.69		
260.08	9.28		

Mass spectrum number 46.



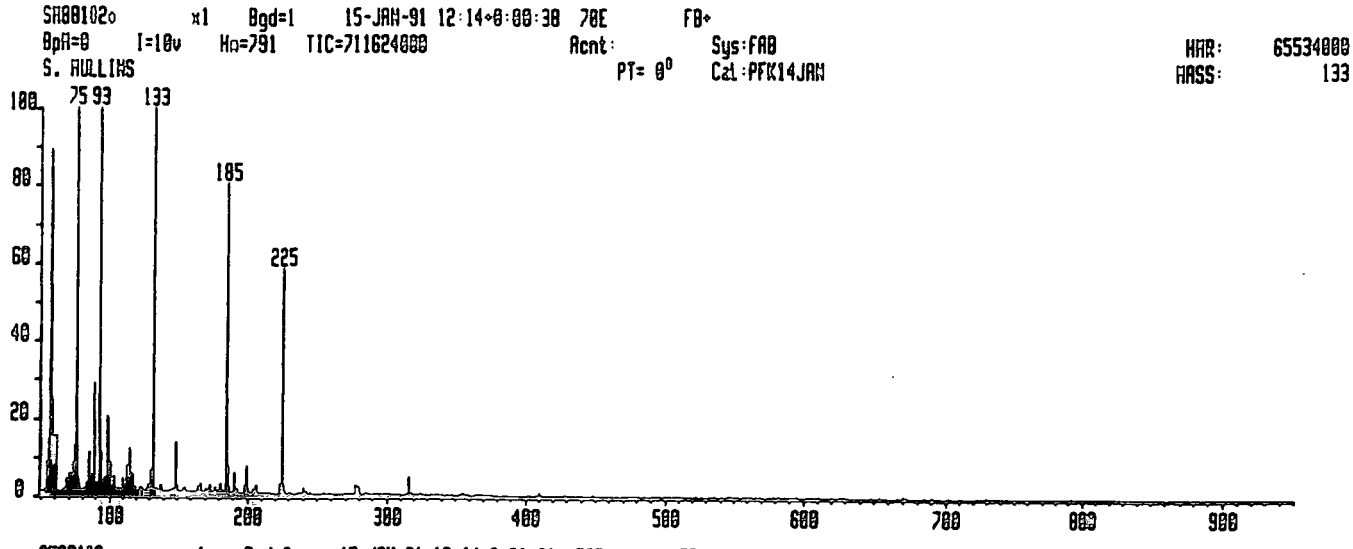
FAB+ data

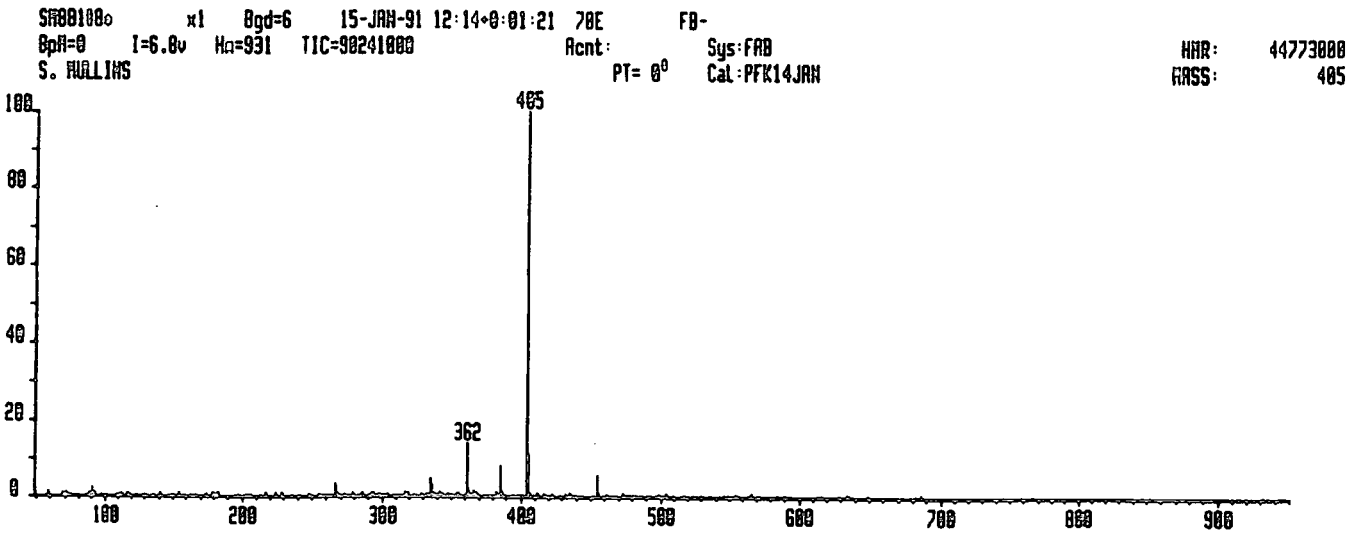
Mass	% Base	
54.91	11.45	
56.92	49.21	
60.91	11.61	
68.95	5.85	
70.98	5.99	
73.96	5.76	
74.96	37.72	
76.96	5.20	
92.96	100.00	
114.93	23.03	
130.89	5.63	
132.78	31.12	
148.88	11.22	
184.89	28.70	F
206.83	5.60	
224.73	5.04	

FAB- data

Mass	% Base	
90.92	11.69	
112.95	9.85	
182.86	8.19	
342.49	7.73	
361.61	100.00	F
362.62	11.60	F
443.42	19.13	
445.51	9.19	F
604.47	10.04	F
651.95	6.56	F
702.11	9.83	F
776.75	15.08	F
778.53	8.60	F

Mass spectrum number 47.



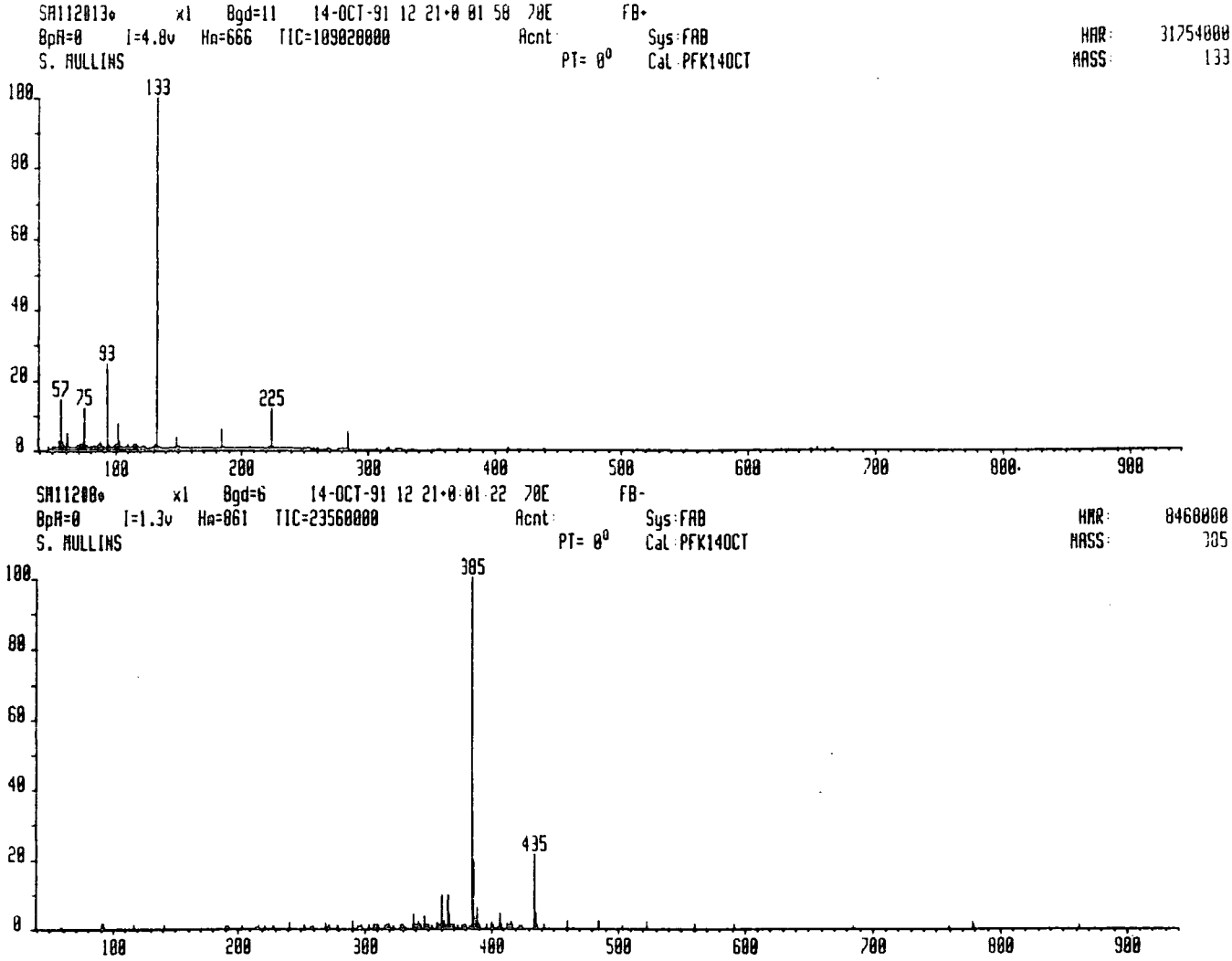


FAB+ data

Mass	% Base		Mass	% Base		Mass	% Base	
54.93	8.67		112.90	7.55		58.91	1.14	
55.93	14.52		114.85	11.85		90.90	1.93	
56.93	89.07		116.87	5.57		182.87	1.14	
57.95	24.70		130.81	6.64		266.71	3.09	
58.95	7.60		132.68	100.00	O	316.74	1.19	
59.93	5.47		148.80	13.71		335.70	4.57	F
60.92	15.34	F	149.80	2.34		336.71	2.86	F
68.91	3.97		166.82	3.13		342.69	1.14	
69.94	5.47		180.85	3.13		361.62	13.73	F
70.92	5.04		184.80	80.47	F	362.66	1.72	F
71.93	5.47		185.81	7.50	F	366.66	1.24	
72.91	8.27		186.80	2.17		382.67	1.14	
73.91	12.68		190.79	5.90		385.66	8.04	F
74.91	100.00	O	198.84	2.80		386.68	1.36	F
75.91	4.43		199.87	7.46		404.65	100.00	F
76.90	2.62		222.70	3.11		405.66	10.86	F
82.90	3.13		224.60	58.60	F	454.68	5.31	F
84.92	10.95		225.61	2.73				
85.92	4.35		316.49	4.90				
86.92	5.09							
88.94	28.69							
89.90	3.25							
90.88	3.13							
92.94	100.00	O						
93.89	10.94							
94.89	3.13							
96.90	4.43							
97.90	3.86							
98.89	20.30							
99.91	3.19							
100.92	8.33							
102.91	4.89							
109.88	4.00							
110.87	2.34							

FAB- data

Mass spectrum number 48.



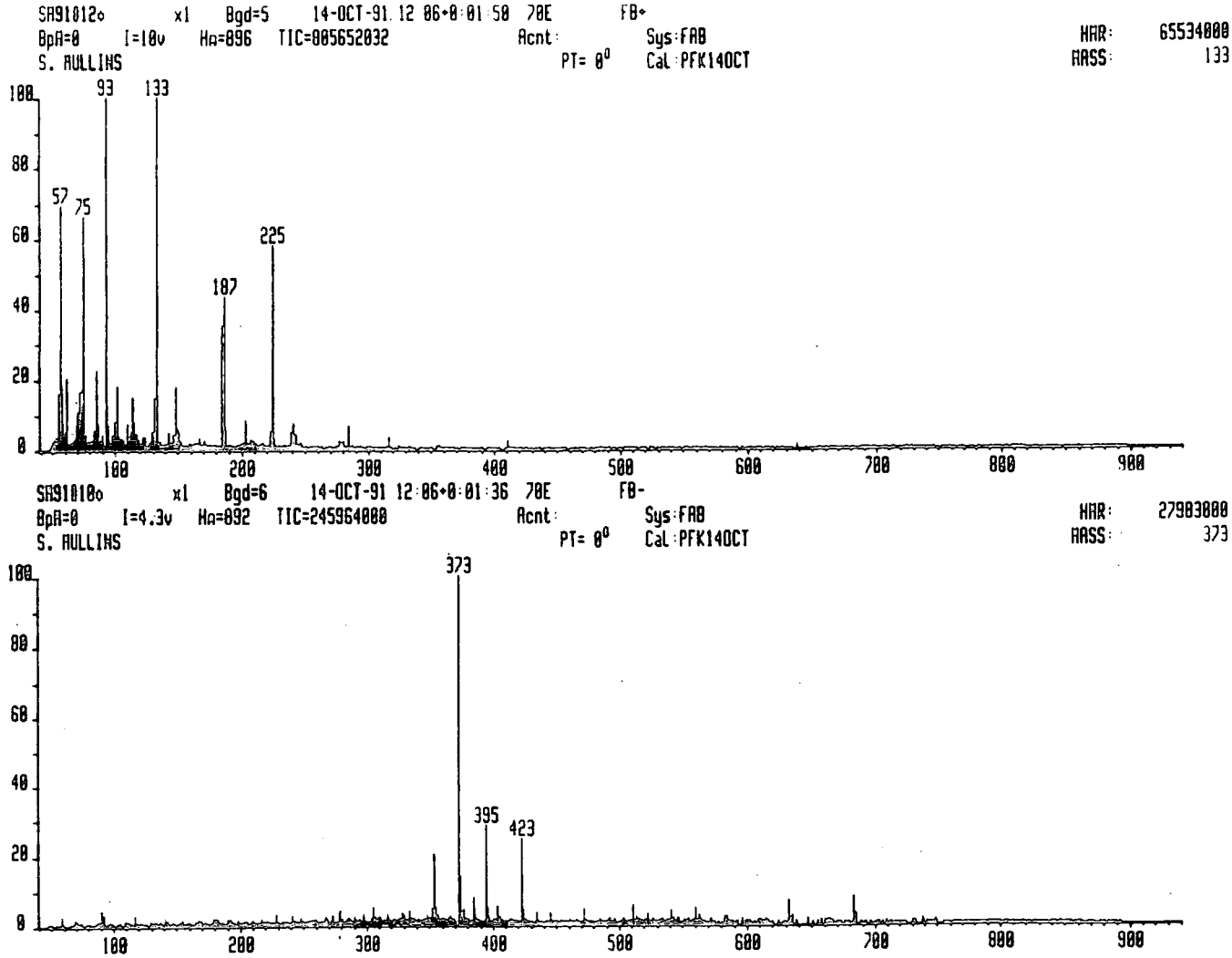
FAB+ data

Mass	% Base			
46.87	1.13		224.74	11.51
54.90	2.30		284.44	5.17 F
55.91	1.91		284.69	4.25 F
56.91	14.39			
57.92	2.34	F		
57.98	1.61	F		
58.92	1.61			
59.91	1.71			
60.91	4.85			
68.94	1.88			
69.96	1.07			
70.96	1.68			
71.98	1.61			
72.95	1.68			
73.98	2.52			
74.96	11.97			
87.94	2.59	F		
88.00	2.54	F		
88.06	1.61	F		
92.96	24.77			
93.97	1.61			
98.95	1.28			
99.95	1.61	F		
100.05	1.23	F		
102.03	7.38			
102.96	2.33			
109.98	1.86			
114.90	2.14	F		
115.01	1.45	F		
116.94	1.61			
117.96	1.03			
130.91	1.88			
132.79	100.00			
148.90	3.46			
184.91	5.76			

FAB- data

Mass	% Base		
90.93	1.20	484.60	1.97
92.88	1.29	522.60	2.09
240.76	1.83	560.56	1.36
268.73	1.56	777.72	2.03
271.70	1.17		
290.72	1.98		
330.69	1.09		
337.68	4.00		
338.68	1.42		
341.68	1.95		
342.69	1.07		
346.67	3.28		
356.66	1.72		
357.66	1.41		
359.67	0.94		
360.65	9.48		
361.68	1.41		
362.66	2.28		
365.65	9.47		
366.65	3.79		
384.62	100.00		
385.63	19.36		
386.64	3.16		
387.62	1.38		
388.66	6.05		
389.65	1.75		
396.66	1.12		
400.67	1.62		
406.63	4.37		
415.61	2.21		
434.61	21.17		
435.61	4.33		
436.57	1.03		
441.60	1.13		
460.61	2.10		

Mass spectrum number 49.



FAB+ data

Mass	% Base	
54.91	15.66	
55.91	13.66	
56.89	69.06	
57.93	17.94	
58.93	7.03	
59.91	5.31	
60.91	20.31	F
68.95	6.76	
69.98	10.63	
70.98	6.35	
71.99	16.38	
72.96	6.79	
73.99	16.87	
74.96	66.02	
86.01	22.26	
86.99	7.03	
92.97	100.00	O
93.97	6.72	
100.01	8.04	
102.04	17.85	
109.98	7.03	
114.02	14.84	
114.95	7.57	
130.98	14.67	
132.92	100.00	FO
148.90	17.98	
149.87	5.94	
184.92	35.27	F
187.04	43.44	F
188.03	6.06	F
203.01	8.28	
222.83	5.06	F
224.74	57.80	F
240.81	7.03	F
284.55	6.58	F

FAB- data

Mass	% Base	
90.92	4.05	
278.71	4.06	
304.68	5.11	
334.66	4.18	
351.65	4.71	
353.62	20.13	F
354.62	5.12	
372.57	100.00	F
373.60	13.71	F
375.62	4.16	F
376.62	4.38	F
384.61	7.80	F
394.58	28.44	F
395.61	5.13	F
403.59	5.54	
422.51	24.75	F
423.56	4.61	F
472.40	4.38	F
510.40	5.31	F
541.30	4.03	F
560.36	4.71	F
632.38	6.79	F
682.40	7.82	F

Appendix IV

X-Ray Data

1) Crystal Structure of $C_{12}H_5O_2F_{12}Cs$ (136)

Crystal Data

$C_{12}H_5O_2F_{12}Cs$	M.w. 542.06
Crystal system:	monoclinic
Space group:	*C2/c*
Cell dimensions:	a = 20.466(2)Å
	b = 13.851(2)Å
	c = 12.674(1)Å
	$\alpha = 90°$
	$\beta = 111.55(7)°$
	$\gamma = 90°$
	$U = 3341.61Å^3$
	Z = 8
	$D_C = 2.15gcm^{-3}$
	F(000) = 2040
radiation:	Mo-Kα
	$\mu = 23.26cm^{-1}$

Data collection

temperature:	room temperature
total data measured:	2927
total data unique:	2323
total data observed:	1448 [F > 3(F)]
	$(1.5° \leq \theta \leq 23°)$
Final R value	0.07 ($R_W = 0.09$)

Table 5 Fractional atomic co-ordinates ($x10^4$)

Atom	x	y	z
Cs(1)	1573(1)	9061(1)	1310(1)
C(1)	1341(9)	1426(12)	167(12)
C(2)	2058(9)	1250(11)	670(12)
C(3)	2291(9)	1478(11)	1827(12)
C(4)	1687(9)	1804(12)	2021(13)
C(5)	1112(8)	1768(12)	978(13)
C(6)	900(9)	1144(16)	-1086(18)
C(7)	2550(12)	986(12)	125(15)
C(8)	2981(8)	1367(15)	2674(15)
C(9)	3872(14)	165(20)	3702(24)
C(10)	4367(19)	210(24)	3123(28)
C(11)	1701(10)	2106(15)	3146(19)
C(12)	357(16)	2080(16)	775(21)
O(1)	3170(6)	435(10)	2789(10)
O(2)	3351(7)	1999(10)	3200(12)
F(1)	249(6)	916(8)	-1162(9)
F(2)	1160(6)	443(9)	-1436(10)
F(3)	775(8)	1958(11)	-1726(12)
F(4)	2594(6)	10(8)	-8(9)
F(5)	3217(6)	1237(8)	691(9)
F(6)	2398(6)	1347(8)	-928(9)
F(7)	2258(6)	1767(8)	3996(10)
F(8)	1732(6)	3073(8)	3288(9)
F(9)	1104(9)	1868(13)	3308(14)
F(10)	-34(7)	1354(10)	849(10)
F(11)	346(8)	2789(12)	1424(14)
F(12)	59(7)	2499(10)	-210(12)

Table 6 Anisotropic thermal parameters (Å x 10^3)

	U11	U22	U33	U23	U13	U12
Cs(1)	99(1)	63(1)	70(1)	13(1)	28(1)	-10(1)
C(1)	58(11)	49(10)	45(9)	13(8)	10(8)	-5(9)
C(2)	76(12)	47(9)	46(8)	5(7)	30(9)	-4(8)
C(3)	61(11)	40(9)	42(9)	-3(7)	18(8)	-7(8)
C(4)	66(12)	45(10)	48(10)	4(8)	17(10)	1(9)
C(5)	35(9)	65(11)	57(10)	1(8)	16(9)	-7(8)
C(6)	60(12)	102(16)	109(16)	64(14)	32(11)	38(11)
C(7)	122(18)	44(9)	66(10)	11(9)	28(12)	-2(12)
C(8)	42(10)	58(12)	65(11)	-8(10)	-4(9)	1(10)
C(9)	80(20)	131(22)	139(21)	17(17)	21(18)	9(17)
C(10)	137(29)	149(26)	173(29)	38(21)	43(24)	36(23)
C(11)	60(13)	79(14)	128(17)	-36(13)	41(13)	-25(11)
C(12)	218(29)	70(14)	110(18)	-21(13)	99(19)	-17(17)
O(1)	65(8)	69(9)	75(8)	9(7)	2(7)	13(7)
O(2)	73(9)	64(9)	95(9)	-21(7)	-7(8)	-8(8)

Table 7 Bond lengths (Å)

C(2)-C(1)	1.390(11)	C(5)-C(1)	1.362(11)
C(6)-C(1)	1.561(14)	C(3)-C(2)	1.401(10)
C(7)-C(1)	1.462(13)	C(4)-C(3)	1.413(12)
C(8)-C(3)	1.435(11)	C(5)-C(4)	1.531(17)
C(11)-C(4)	1.487(13)	C(12)-C(5)	1.531(17)
F(1)-C(6)	1.339(11)	F(2)-C(6)	1.264(12)
F(3)-C(6)	1.356(11)	F(4)-C(7)	1.369(10)
F(5)-C(7)	1.334(11)	F(6)-C(7)	1.350(10)
O(1)-C(8)	1.340(12)	O(2)-C(8)	1.188(10)
C(10)-C(9)	1.454(19)	O(1)-C(9)	1.525(14)
F(7)-C(11)	1.334(12)	F(8)-C(11)	1.350(11)
F(9)-C(11)	1.352(13)	F(10)-C(12)	1.309(12)
F(11)-C(12)	1.287(25)	F(12)-C(12)	1.307(13)

Table 8 Selected non-bonded distances (Å)

Intermolecular:

C(1)-Cs(1a)	3.543	C(2)-Cs(1a)	3.380
C(3)-Cs(1a)	3.618	C(4)-Cs(1a)	3.890
C(5)-Cs(1a)	3.853		

Table 9 Bond angles (°)

C(5)-C(1)-C(2)	108.3(7)	C(6)-C(1)-C(2)	122.7(8)
C(6)-C(1)-C(5)	128.6(8)	C(3)-C(2)-C(1)	109.7(8)
C(7)-C(2)-C(1)	128.5(8)	C(7)-C(2)-C(3)	121.5(8)
C(4)-C(3)-C(2)	105.3(8)	C(8)-C(3)-C(2)	128.5(8)
C(8)-C(3)-C(4)	126.2(8)	C(5)-C(4)-C(3)	108.6(7)
C(11)-C(4)-C(3)	122.9(8)	C(11)-C(4)-C(5)	128.5(8)
C(4)-C(5)-C(1)	108.2(8)	C(12)-C(5)-C(1)	125.2(8)
C(12)-C(5)-C(4)	126.6(9)	F(1)-C(6)-C(1)	108.7(9)
F(2)-C(6)-C(1)	112.9(7)	F(2)-C(6)-F(1)	109.3(10)
F(3)-C(6)-C(1)	108.2(10)	F(3)-C(6)-F(1)	100.8(7)
F(3)-C(6)-F(2)	116.2(10)	F(4)-C(7)-C(2)	113.1(8)
F(5)-C(7)-C(2)	115.3(8)	F(5)-C(7)-F(4)	102.9(8)
F(6)-C(7)-C(2)	115.2(9)	F(6)-C(7)-F(4)	104.3(7)
F(6)-C(7)-F(5)	104.7(8)	O(1)-C(8)-C(3)	110.4(8)
O(2)-C(8)-C(3)	126.2(10)	O(2)-C(8)-O(1)	123.4(8)
O(1)-C(9)-C(10)	104.1(12)	F(7)-C(11)-C(4)	112.8(8)
F(8)-C(11)-C(4)	113.0(10)	F(8)-C(11)-F(7)	104.9(8)
F(9)-C(11)-C(4)	112.4(9)	F(9)-C(11)-F(7)	110.1(10)
F(9)-C(11)-F(8)	102.9(9)	F(10)-C(12)-C(5)	112.1(10)
F(11)-C(12)-C(5)	111.2(11)	F(11)-C(12)-F(10)	112.7(11)
F(12)-C(12)-C(5)	112.0(10)	F(12)-C(12)-F(10)	109.0(11)
F(12)-C(12)-F(11)	99.2(10)	C(9)-O(1)-C(8)	118.2(8)

2) Crystal Structure of $Fe(C_5Me_5)_2 C_8F_{10}$ (161)

Crystal Data

$C_{28}H_{30}F_{10}Fe$	M.w. 612.38
Crystal system:	triclinic
Space group:	$\bar{P}1$
Cell dimensions:	a = 8.222(1)Å
	b = 9.150(2)Å
	c = 9.650(2)Å
	α = 96.67(1)°
	β = 97.34(1)°
	γ = 108.38(1)°
	U = 673.80Å^3
	Z = 1
	D_c = 1.509gcm^{-3}
	F(000) = 314
radiation:	Mo-Kα
	μ = 0.064cm^{-1}

Data collection

temperature:	295K
total data measured:	3692
total data unique:	2360
total data observed:	2079 [$F > 4\sigma_c(F)$]
	($1.5° \leq \theta \leq 25°$)
Final R value	0.017 (R_w = 0.017)

Table 10 Fractional atomic co-ordinates ($x10^4$)

Atom	x	y	z
Fe	5000	5000	5000
C(1)	7445(3)	6216(3)	4524(2)
C(2)	7577(3)	5009(9)	5301(2)
C(3)	6454(3)	3566(3)	4489(3)
C(4)	5620(3)	3866(3)	3225(2)
C(5)	6235(3)	5513(3)	3246(2)
C(6)	8467(4)	7922(3)	4946(4)
C(7)	8761(4)	5217(5)	6672(3)
C(8)	6208(5)	1967(4)	4847(5)
C(9)	4349(4)	2679(4)	2056(3)
C(10)	5746(5)	6335(5)	2095(3)
C(11)	9474(3)	487(3)	-26(2)
C(12)	9136(4)	1455(4)	-1029(3)
C(13)	7877(3)	1877(3)	-162(3)
C(14)	8371(3)	862(3)	807(2)
F(121)	8824(7)	1130(6)	-2352(3)
F(122)	10587(6)	2873(5)	-1028(6)
F(131)	6182(2)	1380(3)	-821(2)
F(132)	8230(3)	3399(2)	361(3)
F(141)	7846(3)	511(3)	1997(2)

Table 11 Anisotropic thermal parameters (Å x 10^3)

	U11	U22	U33	U23	U13	U12
Fe	39(1)	38(1)	39(1)	10(1)	8(1)	11(1)
C(1)	43(1)	57(1)	58(1)	11(1)	19(1)	8(1)
C(2)	47(1)	68(1)	57(1)	11(1)	12(1)	24(1)
C(3)	60(1)	56(1)	69(1)	15(1)	23(1)	28(1)
C(4)	57(1)	61(1)	50(1)	1(1)	18(1)	17(1)
C(5)	57(1)	65(1)	47(1)	18(1)	20(1)	17(1)
C(6)	68(2)	62(1)	95(1)	10(1)	26(1)	-3(1)
C(7)	63(1)	124(3)	71(1)	17(2)	1(1)	41(2)
C(8)	108(2)	67(2)	117(2)	28(2)	33(2)	48(2)
C(9)	82(2)	89(2)	72(2)	-21(1)	14(1)	12(2)
C(10)	101(2)	109(2)	66(1)	47(2)	24(1)	33(2)
C(11)	48(1)	57(1)	54(1)	12(1)	0(1)	16(1)
C(12)	68(1)	89(2)	61(2)	29(1)	9(1)	35(1)
C(13)	61(1)	64(1)	76(1)	7(1)	-4(1)	28(1)
C(14)	56(1)	67(1)	56(1)	8(1)	9(1)	19(1)
F(121)	255(4)	197(3)	80(2)	56(2)	40(2)	163(4)
F(122)	137(2)	124(2)	217(4)	73(3)	59(3)	47(2)
F(131)	67(1)	108(1)	109(1)	8(1)	-9(1)	47(2)
F(132)	112(1)	72(1)	124(2)	7(1)	2(1)	43(1)
F(141)	105(1)	116(1)	82(1)	28(1)	28(1)	46(1)

Table 12 Bond lengths (Å)

Fe-C(1)	2.106(2)	Fe-C(2)	2.099(3)
Fe-C(3)	2.093(3)	Fe-C(4)	2.101(3)
Fe-C(5)	2.107(3)	C(1)-C(2)	1.429(4)
C(1)-C(5)	1.423(3)	C(1)-C(6)	1.499(4)
C(2)-C(3)	1.420(3)	C(2)-C(7)	1.493(4)
C(3)-C(4)	1.420(4)	C(3)-C(8)	1.500(5)
C(4)-C(5)	1.427(4)	C(4)-C(9)	1.498(4)
C(5)-C(10)	1.494(5)	C(11)-C(12)	1.443(5)
C(11)-C(14)	1.381(4)	C(11)-C(11')	1.425(6)
C(12)-C(13)	1.523(5)	C(12)-F(121)	1.251(4)
C(12)-F(122)	1.459(5)	C(13)-C(14)	1.498(4)
C(13)-F(131)	1.364(3)	C(13)-F(132)	1.350(3)
C(14)-F(141)	1.316(3)		

Table 13 Bond angles (°)

C(1)-Fe-C(2)	39.7(1)	C(1)-Fe-C(3)	66.3(1)
C(2)-Fe-C(3)	39.6(1)	C(1)-Fe-C(4)	66.4(1)
C(2)-Fe-C(4)	66.7(1)	C(3)-Fe-C(4)	39.6(1)
C(1)-Fe-C(5)	39.5(1)	C(2)-Fe-C(5)	66.6(1)
C(3)-Fe-C(5)	66.4(1)	C(4)-Fe-C(5)	39.6(1)
Fe-C(1)-C(2)	69.9(1)	Fe-C(1)-C(5)	70.3(1)
C(2)-C(1)-C(5)	108.3(2)	Fe-C(1)-C(6)	127.7(2)
C(2)-C(1)-C(6)	126.0(2)	C(5)-C(1)-C(6)	125.7(2)
Fe-C(2)-C(1)	70.4(1)	Fe-C(2)-C(3)	70.0(1)
C(1)-C(2)-C(3)	107.4(2)	Fe-C(2)-C(7)	127.7(2)
C(1)-C(2)-C(7)	126.3(2)	C(3)-C(2)-C(7)	126.2(3)
Fe-C(3)-C(2)	70.4(2)	Fe-C(3)-C(4)	70.5(2)
C(2)-C(3)-C(4)	108.7(2)	Fe-C(3)-C(8)	126.8(2)
C(2)-C(3)-C(8)	126.9(3)	C(4)-C(3)-C(8)	124.4(2)
Fe-C(4)-C(3)	69.9(1)	Fe-C(4)-C(5)	70.4(1)
C(3)-C(4)-C(5)	107.8(2)	Fe-C(4)-C(9)	126.1(2)
C(3)-C(4)-C(9)	126.7(3)	C(5)-C(4)-C(9)	125.6(3)
Fe-C(5)-C(1)	70.2(1)	Fe-C(5)-C(4)	69.9(1)
C(1)-C(5)-C(4)	107.8(2)	Fe-C(5)-C(10)	127.3(2)
C(1)-C(5)-C(10)	126.4(2)	C(4)-C(5)-C(10)	125.7(2)
C(12)-C(11)-C(14)	91.9(2)	C(12)-C(11)-C(11')	132.7(3)
C(14)-C(11)-C(11')	135.3(3)	C(11)-C(12)-C(13)	90.0(2)
C(11)-C(12)-F(121)	127.9(4)	C(13)-C(12)-F(121)	123.1(4)
C(11)-C(12)-F(122)	115.0(3)	C(13)-C(12)-F(122)	108.6(3)
F(121)-C(12)-F(122)	92.8(4)	C(12)-C(13)-C(14)	84.5(2)
C(12)-C(13)-F(131)	115.5(2)	C(14)-C(13)-F(131)	116.4(2)
C(12)-C(13)-F(132)	117.7(2)	C(14)-C(13)-F(132)	118.1(2)
F(131)-C(13)-F(132)	104.5(3)	C(11)-C(14)-C(13)	93.5(2)
C(11)-C(14)-F(141)	136.6(4)	C(13)-C(14)-F(141)	129.8(3)

3) Crystal Structure of $Fe(C_5Me_5)_2$ $C_{10}F_{14}$ (155)

Crystal Data

$C_{30}H_{30}F_{14}Fe$	M.w. 712.4
Crystal system:	triclinic
Space group:	$\bar{P}1$
Cell dimensions:	a = 9.122(1)Å
	b = 9.640(1)Å
	c = 9.706(2)Å
	α = 97.81(1)°
	β = 95.04(1)°
	γ = 115.83(1)°
	U = 750.7Å^3
	Z = 1
	D_c = 1.576gcm^{-3}
	F(000) = 362
radiation:	Mo-Kα
	μ = 0.061cm^{-1}

Data collection

temperature:	295K
total data measured:	2685
total data unique:	2657
total data observed:	2252 [$F > 4\sigma_c(F)$]
	($1.5° \leq \theta \leq 25°$)
Final R value	0.065 (R_w = 0.074)

Table 14 Fractional atomic co-ordinates ($x10^4$)

Atom	x	y	z
Fe	5000	5000	5000
C(1)	7180(6)	7052(5)	5846(5)
C(2)	6602(7)	6172(5)	6914(5)
C(3)	4998(7)	6019(6)	7057(4)
C(4)	4594(7)	6810(5)	6058(5)
C(5)	5931(7)	7444(5)	5315(5)
C(6)	8849(8)	7561(9)	5413(9)
C(7)	7527(10)	5564(9)	7811(7)
C(8)	3971(11)	5255(9)	8107(6)
C(9)	3039(10)	6997(9)	5890(8)
C(10)	6050(10)	8424(7)	4206(7)
C(11)	9552(5)	377(5)	-287(5)
C(12)	8053(7)	337(8)	173(6)
C(13)	7492(10)	1236(12)	-742(9)
C(14)	8734(9)	1867(8)	-1647(8)
C(15)	9913(8)	1209(8)	-1352(7)
F(121)	8167(6)	889(6)	1526(4)
F(122)	6808(6)	-1203(6)	12(8)
F(131)	6066(8)	179(14)	-1614(12)
F(132)	7107(17)	2186(14)	-100(10)
F(141)	9473(9)	1530(13)	-1349(13)
F(142)	8066(12)	1530(13)	-2960(6)
F(151)	11081(10)	1505(11)	-2027(10)

Table 15 Anisotropic thermal parameters (Å x 10^3)

	U11	U22	U33	U23	U13	U12
Fe	50(1)	42(1)	38(1)	8(1)	7(1)	25(1)
C(1)	64(3)	53(2)	65(3)	8(2)	1(2)	19(2)
C(2)	80(3)	56(2)	49(2)	4(2)	-9(2)	29(2)
C(3)	93(3)	61(2)	43(2)	6(2)	14(2)	41(2)
C(4)	92(3)	58(2)	58(2)	7(2)	16(2)	47(2)
C(5)	89(3)	46(2)	59(2)	10(2)	8(2)	34(2)
C(6)	64(3)	98(4)	114(5)	31(4)	8(3)	19(3)
C(7)	112(5)	99(4)	75(3)	15(3)	-22(3)	53(4)
C(8)	130(6)	100(4)	62(3)	24(3)	40(3)	55(4)
C(9)	114(5)	108(5)	99(4)	22(4)	30(4)	83(4)
C(10)	121(5)	61(3)	84(3)	29(3)	18(3)	46(3)
C(11)	51(2)	54(2)	60(2)	13(2)	13(2)	25(2)
C(12)	71(3)	103(4)	78(3)	26(3)	25(3)	51(3)
C(13)	108(5)	176(8)	114(5)	46(5)	28(4)	112(6)
C(14)	98(4)	94(4)	101(4)	39(3)	15(3)	62(4)
C(15)	82(4)	88(4)	104(4)	50(3)	39(3)	52(3)
F(121)	120(3)	165(4)	77(2)	13(2)	30(2)	93(3)
F(122)	73(3)	116(4)	212(6)	20(4)	44(3)	25(2)
F(131)	90(4)	320(12)	279(10)	147(9)	-28(5)	62(5)
F(132)	483(15)	358(11)	227(8)	153(8)	203(9)	385(12)
F(141)	149(5)	92(3)	462(15)	94(6)	15(7)	67(4)
F(142)	261(8)	348(11)	97(4)	80(5)	24(4)	225(9)
F(151)	228(7)	290(9)	293(9)	240(8)	200(7)	203(7)

Table 16 Bond lengths (Å)

Fe-C(1)	2.094(4)	Fe-C(2)	2.092(4)
Fe-C(3)	2.102(5)	Fe-C(4)	2.093(6)
Fe-C(5)	2.093(5)	C(1)-C(2)	1.420(7)
C(1)-C(5)	1.425(9)	C(1)-C(6)	1.498(9)
C(2)-C(3)	1.427(9)	C(2)-C(7)	1.501(11)
C(3)-C(4)	1.429(8)	C(3)-C(8)	1.493(9)
C(4)-C(5)	1.416(8)	C(4)-C(9)	1.504(12)
C(5)-C(10)	1.506(9)	C(11)-C(12)	1.426(9)
C(11)-C(15)	1.369(9)	C(11)-C(11')	1.434(11)
C(12)-C(13)	1.522(15)	C(12)-F(121)	1.326(7)
C(12)-F(122)	1.398(8)	C(13)-C(14)	1.465(12)
C(13)-F(131)	1.365(10)	C(13)-F(132)	1.231(20)
C(14)-C(15)	1.493(13)	C(14)-F(141)	1.320(9)
C(14)-F(142)	1.295(10)	C(15)-F(151)	1.247(12)

Table 17 Bond angles (°)

C(1)-Fe-C(2)	39.6(2)	C(1)-Fe-C(3)	66.8(2)
C(2)-Fe-C(3)	39.8(2)	C(1)-Fe-C(4)	66.6(2)
C(2)-Fe-C(4)	66.6(2)	C(3)-Fe-C(4)	39.8(2)
C(1)-Fe-C(5)	39.8(2)	C(2)-Fe-C(5)	66.7(2)
C(3)-Fe-C(5)	66.8(2)	C(4)-Fe-C(5)	39.6(2)
Fe-C(1)-C(2)	70.1(2)	Fe-C(1)-C(5)	70.0(2)
C(2)-C(1)-C(5)	107.9(5)	Fe-C(1)-C(6)	128.1(4)
C(2)-C(1)-C(6)	126.1(6)	C(5)-C(1)-C(6)	125.9(6)
Fe-C(2)-C(1)	70.3(2)	Fe-C(2)-C(3)	70.5(3)
C(1)-C(2)-C(3)	108.5(5)	Fe-C(2)-C(7)	127.5(4)
C(1)-C(2)-C(7)	126.9(6)	C(3)-C(2)-C(7)	124.6(5)
Fe-C(3)-C(2)	69.7(3)	Fe-C(3)-C(4)	69.7(3)
C(2)-C(3)-C(4)	107.1(5)	Fe-C(3)-C(8)	128.2(4)
C(2)-C(3)-C(8)	126.6(6)	C(4)-C(3)-C(8)	126.2(7)
Fe-C(4)-C(3)	70.4(3)	Fe-C(4)-C(5)	70.2(3)
C(3)-C(4)-C(5)	108.6(6)	Fe-C(4)-C(9)	127.5(4)
C(3)-C(4)-C(9)	125.0(5)	C(5)-C(4)-C(9)	126.3(6)
Fe-C(5)-C(1)	70.1(3)	Fe-C(5)-C(4)	70.2(3)
C(1)-C(5)-C(4)	107.9(5)	Fe-C(5)-C(10)	127.3(3)
C(1)-C(5)-C(10)	125.8(6)	C(4)-C(5)-C(10)	126.2(7)
C(12)-C(11)-C(15)	109.0(6)	C(12)-C(11)-C(11')	124.2(6)
C(15)-C(11)-C(11')	126.8(6)	C(11)-C(12)-C(13)	106.5(6)
C(11)-C(12)-F(121)	116.7(5)	C(13)-C(12)-F(121)	110.4(7)
C(11)-C(12)-F(122)	111.6(6)	C(13)-C(12)-F(122)	109.9(6)
F(121)-C(12)-F(122)	101.6(6)	C(12)-C(13)-C(14)	107.2(8)
C(12)-C(13)-F(131)	107.8(9)	C(14)-C(13)-F(131)	106.6(8)
C(12)-C(13)-F(132)	115.1(9)	C(14)-C(13)-F(132)	115.6(10)
F(131)-C(13)-F(132)	103.9(9)	C(13)-C(14)-C(15)	104.9(8)

C(13)-C(14)-F(141)	110.6(9)	C(15)-C(14)-F(141)	111.8(6)
C(13)-C(14)-F(142)	111.7(7)	C(15)-C(14)-F(142)	114.1(9)
F(141)-C(14)-F(142)	103.9(9)	C(11)-C(15)-C(14)	112.0(6)
C(11)-C(15)-F(151)	128.8(9)	C(14)-C(15)-F(151)	119.1(8)

Appendix V

Colloquia, Conferences and Induction Course

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

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

2) all research conferences attended and papers presented by the author during the period in which the research for the thesis was carried out.

3) details of the postgraduate induction course.

1) Research Colloquia, Seminars and Lectures

(Those attended are marked *)

6.10.88 Prof. R. Schmutzler (Technische Univerität, Braunschweig),
* *'Fluorophosphines Revisited - New Contributions to an Old Theme'*.

18.10.88 Dr. J. Dingwall (Ciba Geigy),
* *'Phosphorus-containing Amino Acids: Biologically Active Natural and Unnatural Products'*.

18.10.88 Dr. C. J. Ludman (Durham University),
'The Energetics of Explosives'.

21.10.88 Prof. P. von Rague Schleyer (Universität Erlangen Nürnberg),
'The Fruitful Interplay Between Calculational and Experimental Chemistry'.

27.10.88 Prof. W. C. Rees (Imperial College),
* *'Some very Heterocyclic Compounds'.*

9.11.88 Dr. G. Singh (Teesside Polytechnic),
* *'Towards Third Generation Anti-Leukaemics'.*

10.11.88 Prof. J. I. G. Cadogan (British Petroleum),
* *'From Pure Science to Profit'.*

16.11.88 Dr. K. A. McLauchlan (Oxford University),
'The Effect of Magnetic Fields on Chemical Reactions'.

24.11.88 Dr. R. R. Baldwin and Dr. R. W. Walker (Hull University),
'Combustion - Some Burning Problem'.

1.12.88 Dr. R. Snaith (Cambridge University),
'Egyptian Mummies: What, Where, Why and How'.

2.12.88 Dr. G. Hardgrove (St. Olaf College, U.S.A.),
'Polymers in the Physical Chemistry Laboratory'.

9.12.88 Dr. C. Jäger (Friedrich-Schiller University G.D.R.),
'N.M.R. Investigations of Fast Ion Conductors of the NASICON Type'.

25.1.89 Dr. L. Harwood (Oxford University),
'Synthetic Approaches to Phorbols Via Intramolecular Furan Diels-Alder Reactions: Chemistry under Pressure'.

26.1.89 Prof. R. R. Jennings (Warwick University),
'Chemistry of the Masses'.

2.2.89 Prof. L. D. Hall (Addenbrooke's Hospital, Cambridge),
* *'N.M.R. - A Window to the Human Body'*.

9.2.89 Prof. J. E. Baldwin (Oxford University),
* *'Recent Advances in the Bioorganic Chemistry of Penicillin Biosynthesis'*.

13.2.89 Prof. R. R. Schrock (Massachusetts Institute of Technology),
'Recent Advances in Living Metathesis'.

15.2.89 Dr. A. R. Butler (St. Andrews University),
* *'Cancer in Linxiam: The Chemical Dimension'*.

16.2.89 Prof. J. B. Aylett (Queen Mary College),
'Silicon-Based Chips:- The Chemist's Contribution'.

22.2.89 Dr. G. MacDougall (Edinburgh University),
'Vibrational Spectroscopy of Model Catalytic Systems'.

23.2.89 Dr. B. F. G. Johnson (Cambridge University),
'The Binary Carbonyls'.

1.3.89 Dr. R. J. Errington (Newcastle University),
'Polymetallate Assembly in Organic Solvents'.

9.3.89 Dr. I. Marko (Sheffield University),
'Catalytic Asymmetric Osmylation of Olefins'.

15.3.89 Dr. R. Aveyard (Hull University),
'Surfactants at your Surface'.

20.4.89 Dr. M. Casey (Salford University),
* *'Sulphoxides in Stereoselective Synthesis'*.

27.4.89 Dr. D. Crich (University College, London),
* *'Some Novel Uses of Free Radicals in Organic Synthesis'*.

3.5.89 Dr. P. C. B. Page (Liverpool University),
* *'Stereocontrol of Organic Reactions Using 1,3-dithiane-1-oxides'*.

10.5.89 Prof. P. B. Wells (Hull University),
'Catalyst Characterisation and Activity'.

11.5.89 Dr. J. Frey (Southampton University),
'Spectroscopy of the Reaction Path: Photodissociation Raman Spectra of NOCl'.

16.5.89 Dr. R. Stibr (Czechoslovak Academy of Sciences),
'Recent Developments in the Chemistry of Intermediate-Sited Carboranes'.

17.5.89 Dr. C. J. Moody (Imperial College),

* *'Reactive Intermediates in Heterocyclic Synthesis'.*

23.5.89 Prof. P. Paetzold (Aachen),

'Iminoboranes XB≡NR: Inorganic Acetylenes?'.

15.6.89 Prof. J. Pola (Czechoslovak Academy of Sciences),

'Carbon Dioxide Laser Induced Chemical Reactions - New Pathways in Gas-Phase Chemistry'.

17.10.89 Dr. F. Palmer (Nottingham University).

'Thunder and Lightning'.

25.10.89 Prof. C. Floriani (University of Lausanne, Switzerland),

'Molecular Aggregates - A Bridge between Homogeneous and Heterogeneous Systems'.

1.11.89 Dr. J. P. S. Badyal (Durham University),

'Breakthroughs in Heterogeneous Catalysis'.

9.11.89 Prof. N. N. Greenwood (Leeds University),

'Novel Cluster Geometries in Metalloborane Chemistry'.

10.11.89 Prof. J. E. Bercaw (California Institute of Technology),

'Synthetic and Mechanistic Approaches to Ziegler-Natta Polymerisation Of Olefins'.

13.11.89 Dr. J. Becher (Odense University),

* *'Synthesis of New Macrocyclic Systems using Heterocyclic Building Blocks'.*

16.11.89 Dr. D. Parker (Durham University),

'Macrocycles, Drugs and Rock 'n' Roll'.

29.11.89 Prof. D. J. Cole-Hamilton (St. Andrews University),

'New Polymers from Homogeneous Catalysis'.

30.11.89 Dr. M. N. Hughes (King's College London),

'A Bug's Eye View of the Periodic Table'.

4.12.89 Dr. D. Graham (British Petroleum),

'How Proteins Absorb to Interfaces'.

6.12.89 Dr. R. L. Powell (I.C.I),

* *'The Development of C.F.C. Replacements'.*

7.12.89 Dr. A. Butler (St. Andrews University),

'The Discovery of Penicillin: Facts and Fancies'.

13.12.89 Dr. J. Klinowski (Cambridge University),

'Solid State N.M.R. Studies of Zeolite Catalysts'.

15.12.89 Prof. R. Huisgen (Universität München),

* *'Recent Mechanistic Studies of [2+2] Additions'.*

24.1.90 Dr. R. N. Perutz (York University),

* *'Plotting the Course of C-H Activations with Organometallics'.*

31.1.90 Dr. U. Dyer (Glaxo),

'Synthesis and Conformation of C-Glycosides'.

1.2.90 Prof. J. H. Holloway (Leicester University),
'Noble Gas Chemistry'.

7.2.90 Dr. D. P. Thompson (Newcastle University),
'The Role of Nitrogen in Extending Silicate Crystal Chemistry'.

8.2.90 Rev. R. Lancaster (Kimbolton Fireworks),
'Fireworks - Principles and Practice'.

12.2.90 Prof. L. Lunazzi (University of Bologna),
'Application of Dynamic N.M.R. to the Study of Conformational Enantiomerism'.

14.2.90 Prof. D. Sutton (Simon Fraser University, Vancouver B.C.),
'Synthesis and Applications of Dinitrogen and Diazo Compounds of Rhenium and Iridium'.

15.2.90 Prof. L. Crombie (Nottingham University),
'The Chemistry of Cannabis and Khat'.

21.2.90 Dr. C. Bleasdale (Newcastle University),
'The Mode of Action of some Anti-tumour Agents'.

22.2.90 Prof D. T. Clark (I.C.I. Wilton),
'Spatially Resolved Chemistry (using Nature's Paradigm in the Advanced Materials Area)'.

28.2.90 Dr. R. K. Thomas (Oxford University),
'Neutron Reflectometry from Surfaces'.

1.3.90 Dr. J. F. Stoddart (Sheffield University),
'*Molecular Lego*'.

8.3.90 Dr. A. K. Cheetham (Oxford University),
'*Chemistry of Zeolite Cages*'.

21.3.90 Dr. I. Powis (Nottingham University),
'*Spinning off in a huff: Photodissociation of Methyl Iodide*'.

23.3.90 Prof. J. M. Bowman (Emory University),
'*Fitting Experiment with Theory In Ar-OH*'.

9.7.90 Prof. L. S. German (U.S.S.R. Academy of Sciences, Moscow),
* '*New Syntheses in Fluoroaliphatic Chemistry: Recent Advances in the Chemistry of Fluorinated Oxiranes*'.

9.7.90 Prof. V. E. Platonov (U.S.S.R. Academy of Sciences, Novosibirsk),
* '*Polyfluoroindanes: Synthesis and Transformation*'.

9.7.90 Prof. I. N. Rozhkov (U.S.S.R. Academy of Sciences, Moscow),
* '*Reactivity of Perfluoroalkyl Bromides*'.

11.10.90 Dr. W. A. Macdonald (I.C.I. Wilton),
'*Materials for the Space Age*'.

24.10.90 Dr. M. Bochmann (University of East Anglia),
* '*Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyls*'.

26.10.90 Prof. R. Soulen (South Western University, Texas),

* *'Preparation and Reactions of Bicycloalkenes'.*

31.10.90 Dr. R. Jackson (Newcastle University),

* *'New Synthetic Methods: α-aminoacids and Small Rings'.*

1.11.90 Dr. N. Logan (Nottingham University),

'Rocket Propellants'.

6.11.90 Dr. P. Kocovsky (Uppsala),

* *'Stereo-controlled Reactions Mediated by Transition and Non-Transition Metals'.*

7.11.90 Dr. D. Gerrard (British Petroleum),

'Raman Spectroscopy for Industrial Analysis'.

8.11.90 Dr. S. K. Scott (Leeds University),

'Clocks, Oscillations and Chaos'.

14.11.90 Prof. T. Bell (SUNY, Stoney Brook, U.S.A.),

* *'Functional Molecular Architecture and Molecular Recognition'.*

21.11.90 Prof. J. Pritchard (Queen Mary & Westfield College, London),

'Copper Surfaces and Catalysts'.

28.11.90 Dr. B. J. Whitaker (Leeds University),

'Two-Dimentional Velocity Imaging of State-Selected Reaction Products'.

29.11.90 Prof. D. Crout (Warwick University),

* *'Enzymes in Organic Synthesis'.*

5.12.90 Dr. P. G. Pringle (Bristol University),

☆ *'Metal Complexes with Functionalised Phosphines'.*

13.12.90 Prof. A. H. Cowley (University of Texas),

'New Organometallic Routes to Electronic Materials'.

15.1.91 Dr. B. J. Alder (Lawrence Livermore Laboratories, California),

'Hydrogen in all its Glory'.

17.1.91 Dr. P. Sarre (Nottingham University),

'Comet Chemistry'.

24.1.91 Dr. P. J. Sadler (Birkbeck College, London),

'Design of Inorganic Drugs: Precious Metals, Hypertension + H.I.V.'.

30.1.91 Prof. E. Sinn (Hull University),

'New Results in High T_c Superconductivity'.

31.1.91 Dr. D. Lacey (Hull University),

'Liquid Crystals'.

6.2.91 Dr. R. Bushby (Leeds University),

☆ *'Biradicals and Organic Magnets'.*

14.2.91 Dr. M. C. Petty (Durham University),

'Molecular Electronics'.

20.2.91 Prof B. L. Shaw (Leeds University),

☆ *'Syntheses with Coordinated, Unsaturated Phosphine Ligands'.*

28.2.91 Dr. J. Brown (Oxford University),

'Can Chemistry Provide Catalysts Superior to Enzymes?.

6.3.91 Dr. C. M. Dobson (Oxford University),

'N.M.R. Studies of Dynamics in Molecular Crystals'.

7.2.91 Dr. J. Markham (I.C.I. Pharmaceuticals),

'D.N.A. Fingerprinting'.

24.4.91 Prof. R. R. Schrock (Massachusetts Institute of Technology),

'Metal-Ligand Multiple Bonds and Metathesis Initiators'.

25.4.91 Prof. T. Hudlicky (Virginia Polytechnic Institute),

* *'Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products'.*

20.6.91 Prof. M. S. Brookhart (University of North Carolina),

'Olefin Polymerisations, Oligomerisations and Dimerisations using Electrophilic Late Transition Metal Catalysts'.

29.7.91 Dr. M. A. Brimble (Massey University, New Zealand),

* *'Synthetic Studies Towards the Antibiotic Griseusin-A'.*

2) Research Conferences Attended

December 1988.
Royal Society of Chemistry Perkin Division,
One Day Meeting.
York University.

April 1989.
North East Graduate Symposium.
Durham University.

May 1989.
Royal Society of Chemistry Heterocyclic Group,
9th Lakeland Heterocyclic Symposium.
Grasmere.

July 1989.
Royal Society of Chemistry Heterocyclic Group,
Postgraduate Heterocyclic Symposium.
Sheffield University.

December 1989.
Royal Society of Chemistry Perkin Division,
One Day Meeting.
Durham University.

April 1990.

North East Graduate Symposium.

Newcastle University.

July 1991.

Royal Society of Chemistry Heterocyclic Group,

Postgraduate Heterocyclic Symposium.

Leeds University.

September 1991.

13th International Symposium on Fluorine Chemistry,

Ruhr Universität,

Bochum, Federal Republic of Germany.

3) Postgraduate Induction Course

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

Department organisation	Dr. E. J. F. Ross.
Safety matters	Dr. M. R. Crampton.
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 spectrometry	Dr. M. Jones.
Nuclear magnetic resonance spectroscopy	Dr. R. S. Matthews.
Glassblowing techniques	Mr. R. Hart and Mr. G. Haswell.

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