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UNIVERSITY OF DURHAM

Department of Chemistry

A THESIS
entitled

PERFLUOROALKYLATION OF AROMATIC SYSTEMS

submitted by

CORINNE MAGRON
(St Mary's College)

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A candidate for the degree of Doctor of Philosophy
1997

21 MAY 1998

"*Un vaste et tendre*
Apaisement
Semble descendre
Du firmament
Que l'astre irise...
C'est l'heure exquise."
Verlaine (La Bonne Chanson, VI)

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I would like to thank Professor R.D. Chambers for his help and encouragement throughout this period of research, and Dr. Geoffrey C. Nicholson of 3M Company for their financial support. Dr. G. Sandford is also acknowledged for his helpful advice and useful discussions

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Particular thanks are due to everyone in lab 115 for a wonderful and enjoyable time over the last three years.

Memorandum

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

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Part of this work has been presented at:

15th International Symposium on Fluorine Chemistry
Vancouver, Canada
August 2-7, 1997.

and will be subject to publication in the near future.

Nomenclature

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

Abbreviations

The following are used throughout the thesis.

GLC	gas-chromatography
GLC-MS	gas-chromatography-mass spectrometry
NMR	nuclear magnetic resonance
IR	infrared
FAB	fast atom bombardment

Perfluorocarbon solvents used throughout the course of this work:

FC-84, bp. 80°C: perfluoroheptane C_7F_{16} commercialised as Fluorinert liquids by 3M company.

PP-11, bp. 215°C: perfluoroperhydrophenanthrene $C_{14}F_{24}$ commercialised as Flutec liquids by F_2 Chemicals Ltd.

Abstract
Perfluoroalkylation of Aromatic Systems
by Corinne Magron

I. We have concentrated on the synthesis of aromatic systems containing CH_2R_F groups, where R_F is a bulky group derived from hexafluoropropene dimer, using fluoride ion induced methodology. A variety of procedures have been explored and methods of synthesis are described. We have made a major advance in this area by the simple expedient of extracting the polyfluoroalkylated products directly into commercially available perfluorinated fluids: FC-84 (bp 80°C), enabling simple purification.

II. This new class of perfluoroalkylated derivatives has allowed us to explore some further chemistry. Synthesis and reactions are presented and the results are discussed in terms of electronic effects of the perfluoroalkyl group on the benzene ring. The unusual miscibility properties of fluorocarbon solvents have also prompted us to investigate the potential utility of these systems for dyes and catalysis.

III. Synthetically useful perfluoroalkylated-s-triazines have been synthesised from 2,4,6-trifluoro-s-triazine, by fluoride ion induced reaction with hexafluoropropene. These systems so produced were extensively studied, and particular attention was paid to reactions with oxygen-centered nucleophiles. Model chemistry to demonstrate that attachment of perfluorocarbon groups to surfaces could be a useful form of treatment by using this methodology and was explored.

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CHAPTER I
INTRODUCTION

I. GENERAL INTRODUCTION
I.1. INTRODUCTION

Fluorine can be found in the earth's crust in high abundance for a halogen (0.065% F; 0.055% Cl). With other elements, it forms concentrated minerals such as fluorspar (CaF_2) or cryolite (Na_3AlF_6) and fluorapitite ($[Ca_3(PO_4)_2Ca(F,Cl)_2]$)[1].

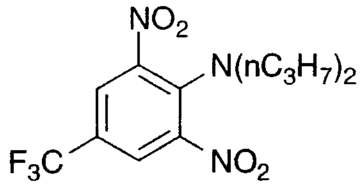
The first fluorine containing organic compound reported was fluoromethane attributed to Dumas and Peligot[2]. However, it was in 1898 that Swarts[3] prepared the first trifluoromethyl-containing molecule, trifluorotoluene, and established the foundations of organofluorine chemistry.

Ever since, the development of techniques for introducing fluorine into organic molecules has increased and has resulted in a vast expansion of this field. The motivating forces behind the development of the area is the interesting and significant change in the physical and chemical properties that compounds containing fluorine exhibit. These compounds have found many industrial applications including those listed in **Table 1**.

Table 1. Uses of fluorinated materials

Industrial Applications	Fluorocarbon components
Coolants and Aerosol propellants	$CFCl_3$, CF_2Cl_2 (CFC's) CF_2HCF_2H, CF_3CF_2H (HFC's)
Anaesthetics	$CF_3CHClBr$ (Halothane)
Surfactants	R_FSO_3H
Blood substitutes	Perfluorodecalin
Pharmaceutical	5-Fluorouracil
Polymers	$(-CF_2-)_n$; PTFE

Furthermore, the influence of trifluoromethyl moieties attached to aromatic systems has found a large number of industrial uses from dyes to pharmaceuticals and agrochemicals. The trifluoromethyl derivatives are the largest subgroup for the preparation of agrochemicals, for example, trifluralin (1), produced by Eli Lilly, is one of the most commercially successful herbicides of the past few decades[4].



(1)

Unique properties of organofluorine systems are due to a number of significant factors:

- High electronegativity of fluorine and, consequently, strong polarisation of the C-F bond.
- Fluorine has non-bonding electron pairs.
- Fluorine is the halogen with the Van der Waals radius most like that of hydrogen (F = 1.35 A, H = 1.10 A) leading to the possibility of multiple substitution of C-H by C-F in carbon chains.
- Fluorine can be readily displaced from fluorocarbon systems as fluoride ion.
- C-F bond is exceedingly strong (107 Kcal/mol) leading to enhanced thermal stability.

I.2. INTRODUCTION OF PERFLUOROALKYL GROUPS

The aim of the project described here, has been to develop methods for introducing perfluoroalkyl groups, specially bulky groups into specific sites in aromatic molecules and to study the subsequent chemistry of the resulting systems.

Before describing methods explored in this work, procedures reported in the literature will be reviewed. Different methodologies including radical, electrophilic or nucleophilic reactions, available for the introduction of perfluoroalkyl groups into aromatic rings will be discussed and recent examples will be given to illustrate the current development of this chemistry, but more extensive reviews of earlier work can be found elsewhere[5, 6, 7, 8, 4].

The synthetic routes can be grouped under the following headings: (1) transformation of functional groups, cycloaddition and cyclisation reactions, (2) radical reactions, (3) electrophilic reactions, (4) use of organometallic reagents to generate perfluoroalkyl species and, (5) fluoroalkylation of activated systems via nucleophilic attack by so-called negative Friedel-Crafts reactions.

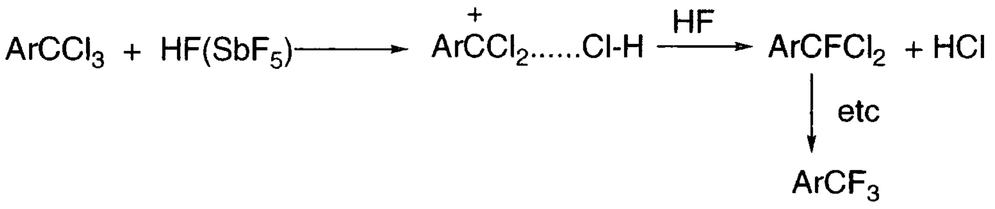
A comprehensive survey of the recent applications of perfluoroalkylated systems will be given in the last section in particular the use of perfluorocarbon fluids.

So far, the trifluoromethylation of aromatic ring has been an active area of chemical research, but the incorporation of higher perfluoroalkyl groups has been less studied.

I.2.A. TRANSFORMATION OF FUNCTIONAL GROUPS

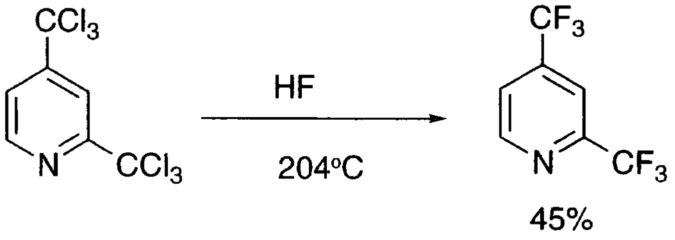
I.2.A.1. HALOGEN EXCHANGE

Antimony pentafluoride as a catalyst with hydrogen fluoride is used to convert trichloromethyl groups to trifluoromethyl. This process is used on an industrial scale for making trifluoromethylated aromatics[3, 5].



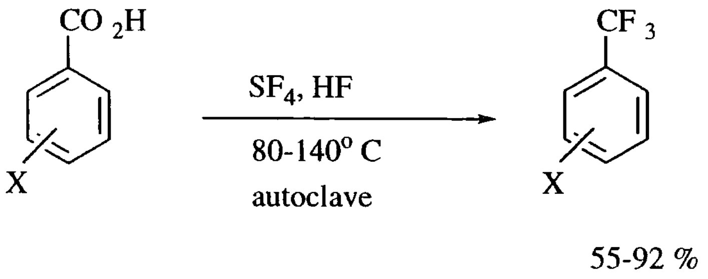
$$ArCCl_3 + HF(SbF_5) \longrightarrow \overset{+}{ArCCl_2}\ldots\ldots Cl\text{-}H \xrightarrow{HF} ArCFCl_2 + HCl \xrightarrow{etc} ArCF_3$$

This well-established process can be applied to heteroaromatic systems[9].



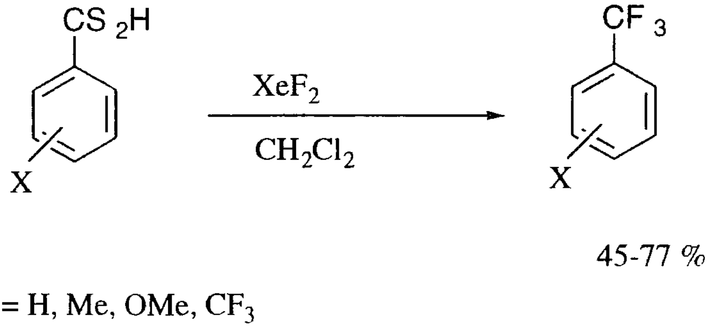
I.2.A.2. CONVERSION OF CARBOXYLIC ACID DERIVATIVES

Conversion of carboxylic groups to trifluoromethyl using sulphur tetrafluoride may be applied to aromatic systems but yields are variable[10, 11].



X= H, Me, OMe, Cl, NO_2

Aromatic dithiocarboxylic acids have also been used as substrates in trifluoromethylation processes[12, 13].


CS2H
XeF2
CH2Cl2
CF3
X
X

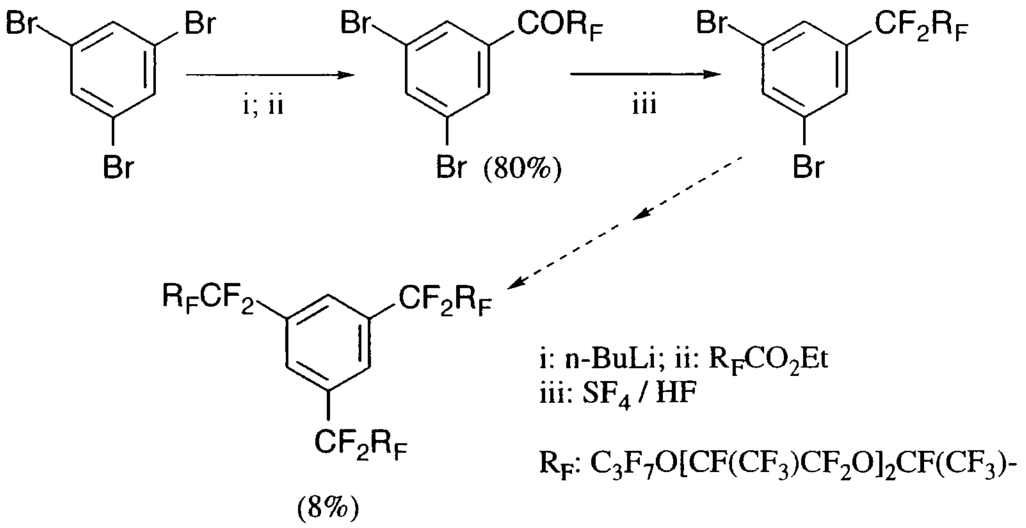
45-77 %

X= H, Me, OMe, CF_3

However the cost of XeF_2 makes the reaction unattractive.

I.2.A.3. CONVERSION OF ARYL KETONES

Chen and co-workers[14] reported the synthesis of aromatic compounds containing perfluoroalkyl (R_F) substituents via organometallic intermediates.

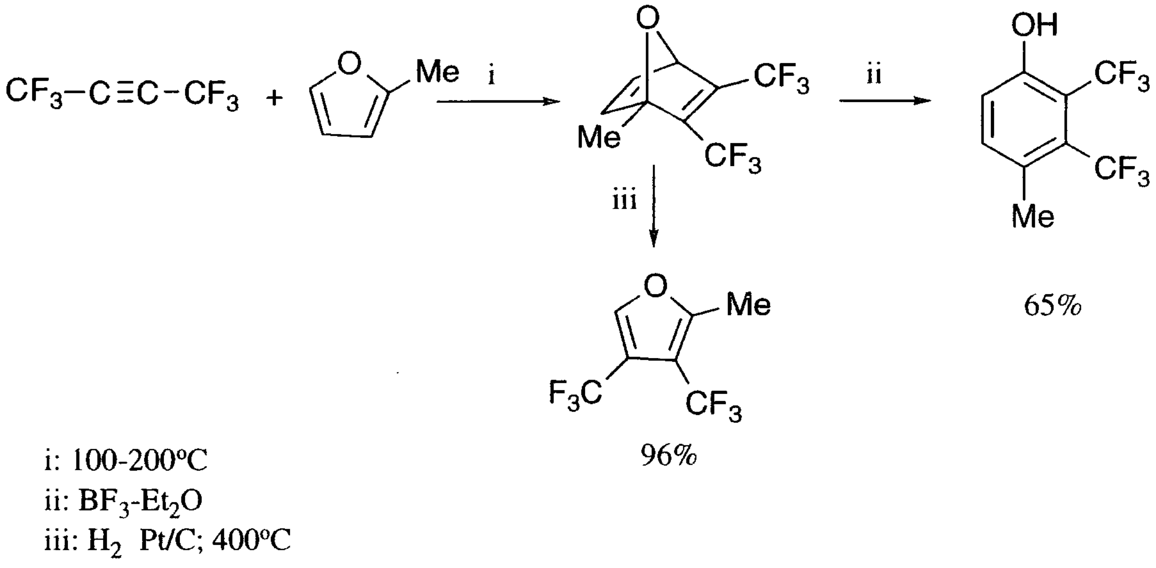

Br
Br
Br
i; ii
Br
CORF
Br (80%)
iii
Br
CF2RF
Br
RFCF2
CF2RF
CF2RF
(8%)

i: n-BuLi; ii: R_FCO_2Et
iii: SF_4 / HF

R_F: $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$-

I.2.B. CYCLOADDITION REACTIONS

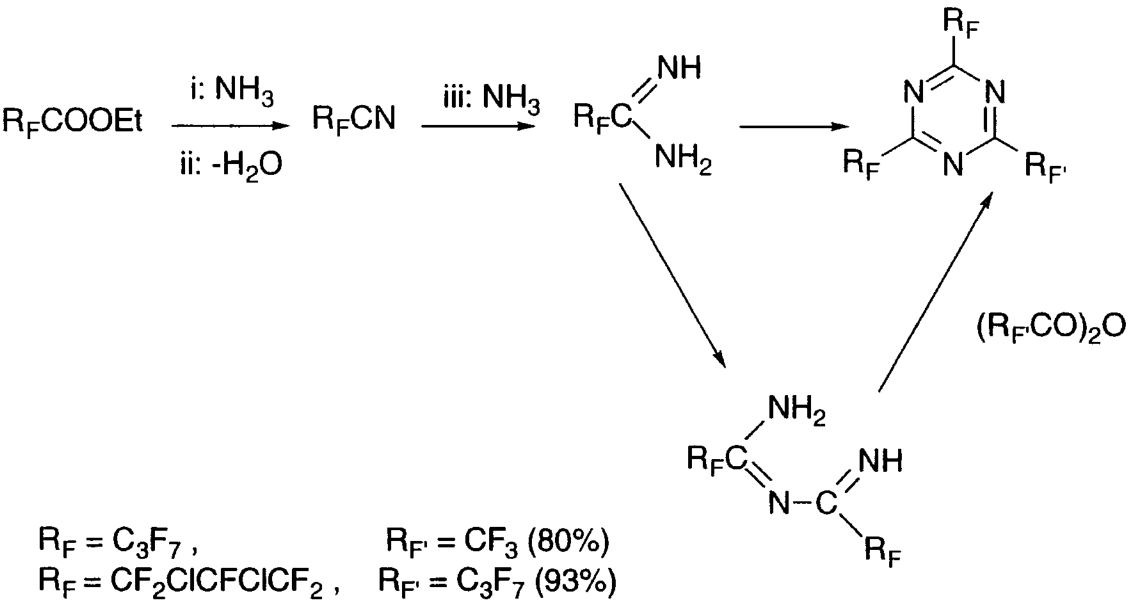
Hexafluorobut-2-yne was shown to be an excellent synthon for introducing trifluoromethyl groups into furan or benzenoid systems[15].


i: 100-200°C
ii: BF_3-Et_2O
iii: H_2 Pt/C; 400°C

I.2.C. CYCLIZATION USING FLUORINATED PRECURSORS

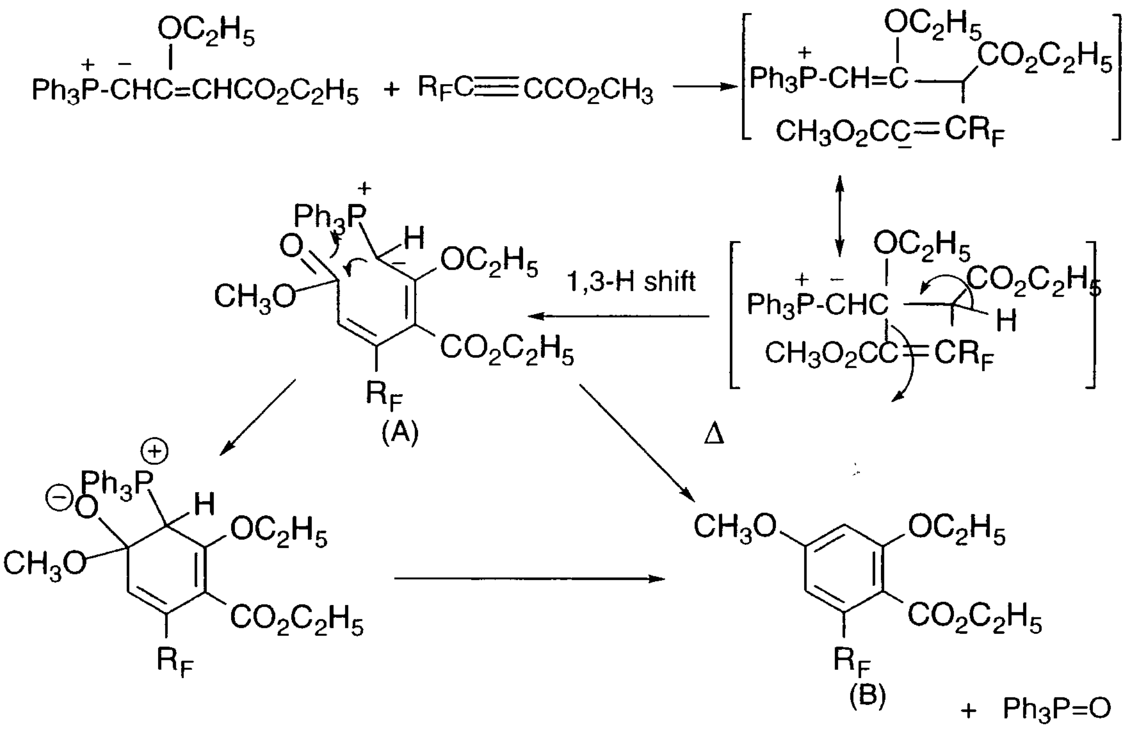
I.2.C.1. TRIMERIZATION

Addition of ammonia to fluorinated nitriles affords the corresponding amidines, themselves obtained from fluorinated esters and 1,3,5-perfluoroalkyl-triazines are formed from the appropriate amidines in high yields, by condensation with perfluoroalkyl anhydrides[16, 17].


$R_F = C_3F_7$, $R_{F'} = CF_3$ (80%)
$R_F = CF_2ClCFClCF_2$, $R_{F'} = C_3F_7$ (93%)

I.2.C.2. INTRAMOLECULAR ELIMINATION

A synthetic methodology was developed by Cao and co-workers[18], the first step involves nucleophilic addition of a phosphorane to an alkyne. Finally, under heating, the acyclic precursor gives the polysubstituted arene via an intramolecular elimination of Ph3P=O.



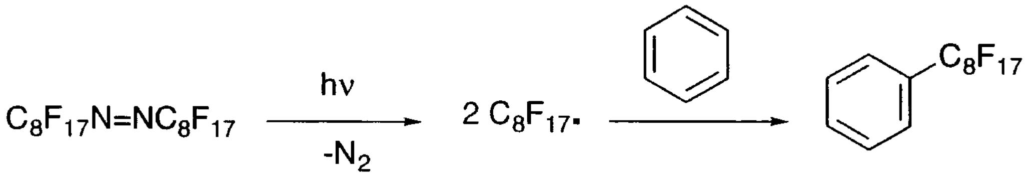
R_F	(A)	(B)
R_F: CF_3	85.8%	84.5%
$(CF_2)_2CF_3$	90.4%	88.7%

I.2.D. RADICAL PERFLUOROALKYLATION

Perfluoroalkyl radicals $R_F\bullet$ can be generated by a number of reactions[19] which involve thermal, photochemical, electrochemical and chemical processes.

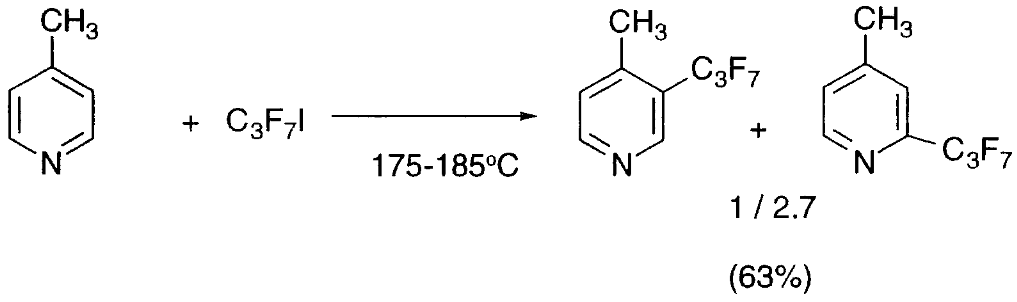
I.2.D.1. PHOTOCHEMICAL PROCESSES

Nakamura[20, 21] has investigated the perfluoroalkylation of organic compounds by photolysis[22] of perfluoroazo compounds.

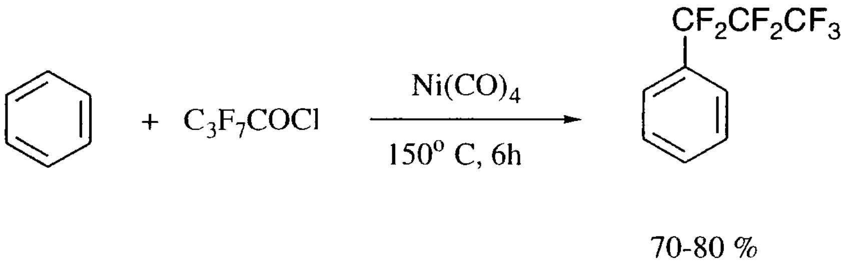


I.2.D.2. THERMAL PROCESSES

Radical species can be formed by thermal reactions which involve homolytic cleavage of the carbon-iodine bond of perfluoroalkyl iodides[23]. Reactions of iodoperfluoroalkanes with aromatic systems have led to perfluoroalkyl derivatives.



Drysdale and co-workers[24] have been successful in producing heptafluoropropylbenzene in the presence of perfluoropropanoyl chloride and nickel carbonyl; substituted benzenes led to the production of isomeric mixtures.

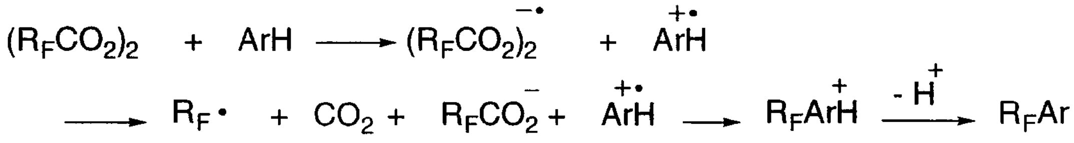


I.2.D.3. SINGLE ELECTRON PROCESSES

Recent developments in this area have proved that the reaction can go through a single electron transfer[25, 19].

I.2.D.3.i. PERFLUORODIACYL PEROXIDES

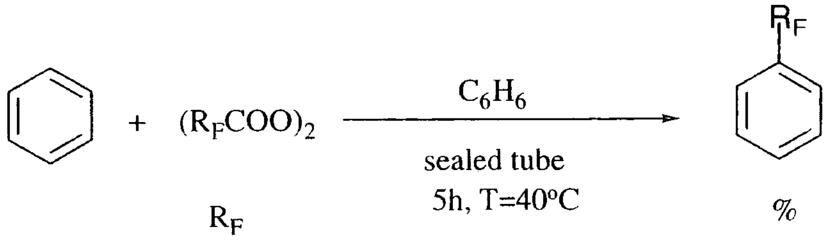
Nakayama[26] has explored the perfluoroalkylation of electron-rich substrates using bis(perfluoroalkyl)peroxide[27].



$$(R_FCO_2)_2 + ArH \longrightarrow \overset{-\bullet}{(R_FCO_2)_2} + \overset{+\bullet}{ArH}$$

$$\longrightarrow R_F\bullet + CO_2 + R_FCO_2^- + \overset{+\bullet}{ArH} \longrightarrow R_F\overset{+}{ArH} \xrightarrow{-H^+} R_FAr$$

As described in this mechanism, electron deficient peroxides undergo electron transfer and decarboxylation to give perfluoroalkyl derivatives in good yield, as illustrated in the following reaction.



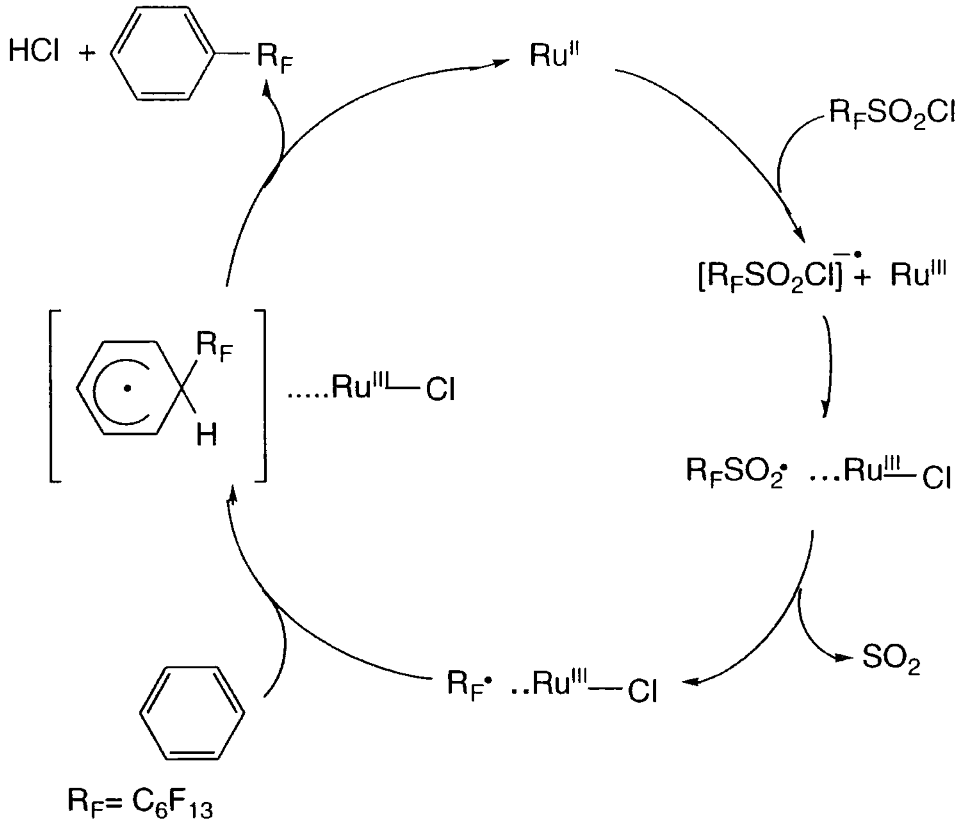
+ $(R_FCOO)_2$
C_6H_6
sealed tube
5h, T=40°C
R_F

R_F	%
C_3F_7	86
C_7F_{15}	97

I.2.D.3.ii. USE OF RUTHENIUM (II)

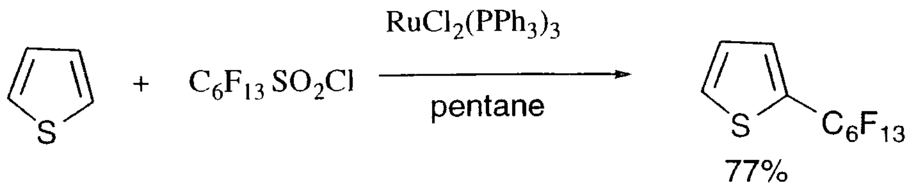
The use of a catalytic amount of dichlorotris(triphenyl-phosphine) ruthenium (II) in the synthesis of perfluoroalkylated compounds was reported by Fukushima[28, 29] and Kamigata[30, 31].

$$ArH + C_6F_{13}SO_2Cl \xrightarrow[\text{120° C, 19h, sealed tube}]{RuCl_2(PPh_3)_3} \underset{44\ \%}{C_6F_{13}Ar} + SO_2$$



HCl +
R_F
Ru^{II}
R_FSO_2Cl
$[R_FSO_2Cl]^{-\bullet}$ + Ru^{III}
R_F
H
.....Ru^{III}—Cl
$R_FSO_2^{\bullet}$ ...Ru^{III}—Cl
SO_2
$R_F^{\bullet}$ ..Ru^{III}—Cl
R_F= C_6F_{13}

The procedure was extended to the perfluoroalkylation of heteroaromatic compounds to afford the corresponding products in high yield[30, 31].



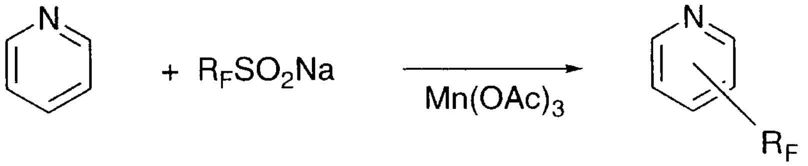
I.2.D.3.iii. PERFLUOROALKYLSULFINATES

Huang[32, 33] proposed a route to accomplish the perfluoroalkylation of aromatics with perfluoroalkanes sulfinate/oxidant systems.

$$R_FSO_2Na + \overset{(III)}{Mn(OAc)_3} \longrightarrow \overset{(II)}{Mn} + \left[R_FSO_2Na\right]^{+\bullet}$$

$$\longrightarrow R_FSO_2\bullet + \overset{+}{Na} \longrightarrow R_F\bullet + SO_2$$

Perfluoroalkyl radicals are easily generated from a sodium sulfinate species in the presence of manganese (III) following this mechanism.



$R_F = (CF_2)_5CF_3$

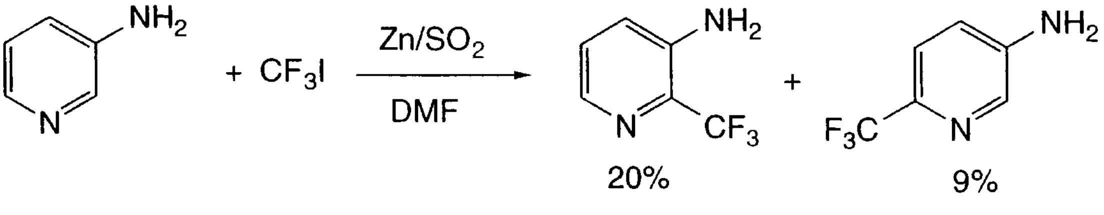
2-, 3-, 4- isomers (6.5/6.7/1)

I.2.D.3.iv. USE OF ZINC METAL

A trifluoromethylated pyridine was prepared using trifluomethyl iodide and zinc in a polar solvent N,N'-dimethylformamide (DMF)[34, 35]. This electron transfer process was suggested in view of the ease of reduction of sulphur dioxide[36].

$$Zn + SO_2 \longrightarrow \overset{+}{Zn} + SO_2^{-\bullet}$$

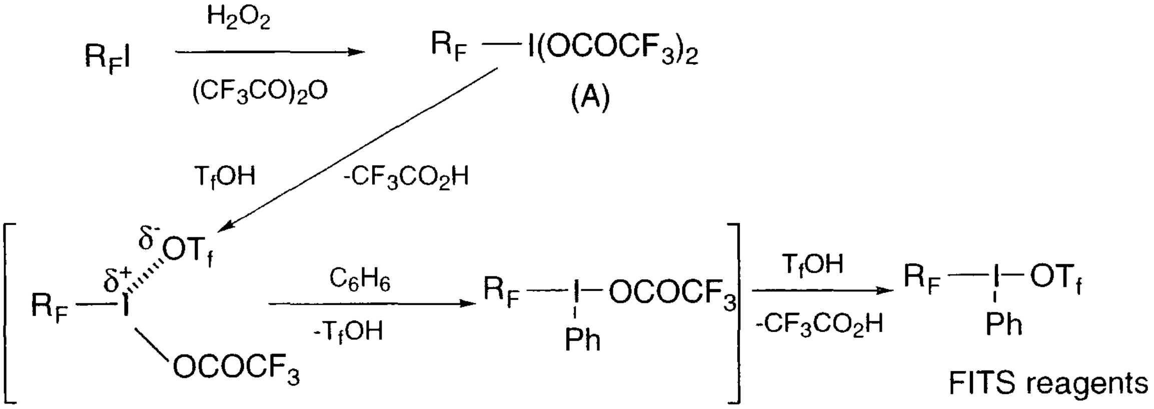
$$\xrightarrow{CF_3I} SO_2 + \left[CF_3I\right]^{-\bullet} \longrightarrow CF_3\bullet + I^{\ominus}$$



I.2.E. ELECTROPHILIC PERFLUOROALKYLATING AGENTS

I.2.E.1. SYNTHESIS OF PERFLUOROALKYLPHENYLIODONIUM TRIFLATES (FITS) REAGENTS

Recently, Umemoto[37] reported an alternative procedure for the preparation of perfluoroalkyl-containing compounds by an electrophilic process. The precursors (A) were prepared by oxidation of perfluoroalkyl iodide using hydrogen peroxide and a large excess of trifluoroacetic anhydride. A series of FITS reagents were synthesized in good yields by treating (A) with benzene in triflic acid.



R_F: n-$C_{10}F_{21}$ (73%)

FITS reagents are highly reactive electrophilic perfluoroalkylating agents which react according to the general scheme shown below[37, 38]. These reactions were carried out using methylene chloride or acetonitrile as solvent and produced *ortho-* and *para-*perfluoroalkylated aromatics as the major products.

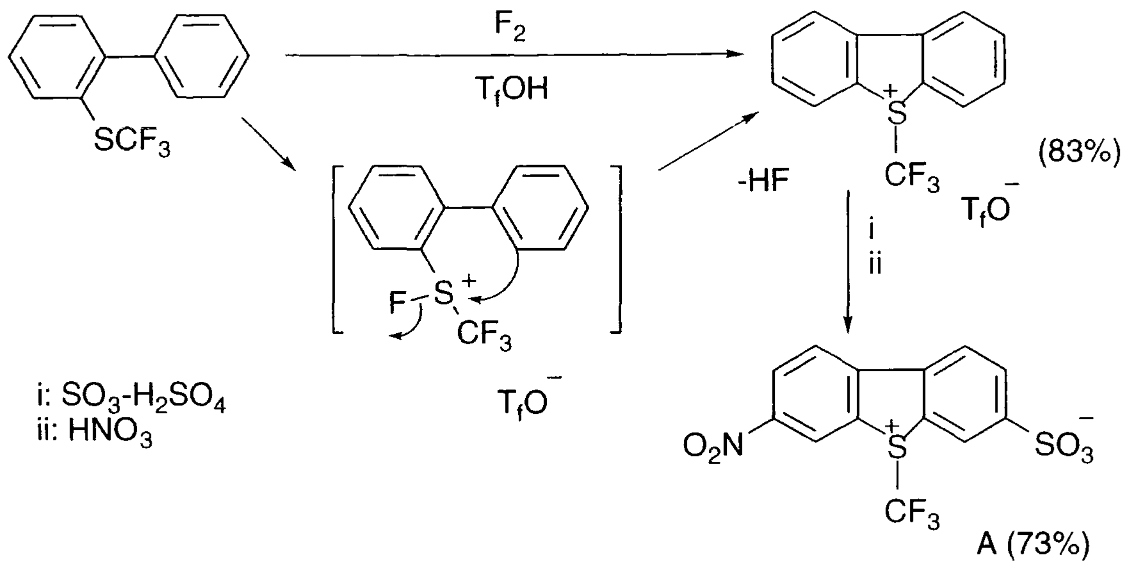
$$\text{FITS} + \text{Ar-H} \longrightarrow R_F\text{-Ar} + \text{PhI} + T_fOH$$

Ar	R_F-Ar	yields (%)
furan	2-R_F-furan	87
C_6H_5	R_F-C_6H_5	97

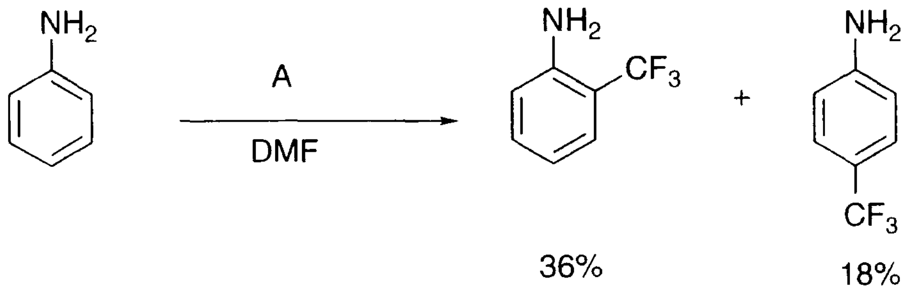
R_F= n-$C_{10}F_{21}$

I.2.E.2. TRIFLUOROMETHYL DIBENZO-SULFONATES

Umemoto[37, 39] have developed a new class of electrophilic trifluoromethylating agents S-, Se-, Te- dibenzo-sulfonates. The dibenzothiocyclic system is obtained by intramolecular cyclisation initiated by the fluorination of the sulfur. The reagent was functionalised by nitration and sulfonation in good yield.


F2
TfOH
SCF3
-HF
(83%)
TfO⁻
i
ii
i: SO3-H2SO4
ii: HNO3
O2N
SO3⁻
CF3
A (73%)

Trifluoromethylation reaction was successfully performed using this electrophilic agent.

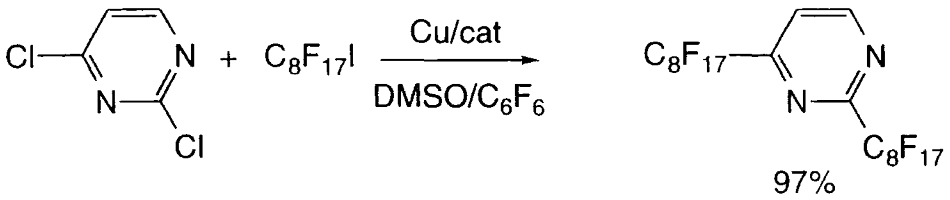

NH2
A
DMF
CF3
+
36%
18%

I.2.F. COPPER REAGENTS AS A SOURCE OF FLUOROALKYL GROUPS

Perfluoroalkylation reactions have been reported via copper coupling mechanism with copper metal or organocopper compounds.

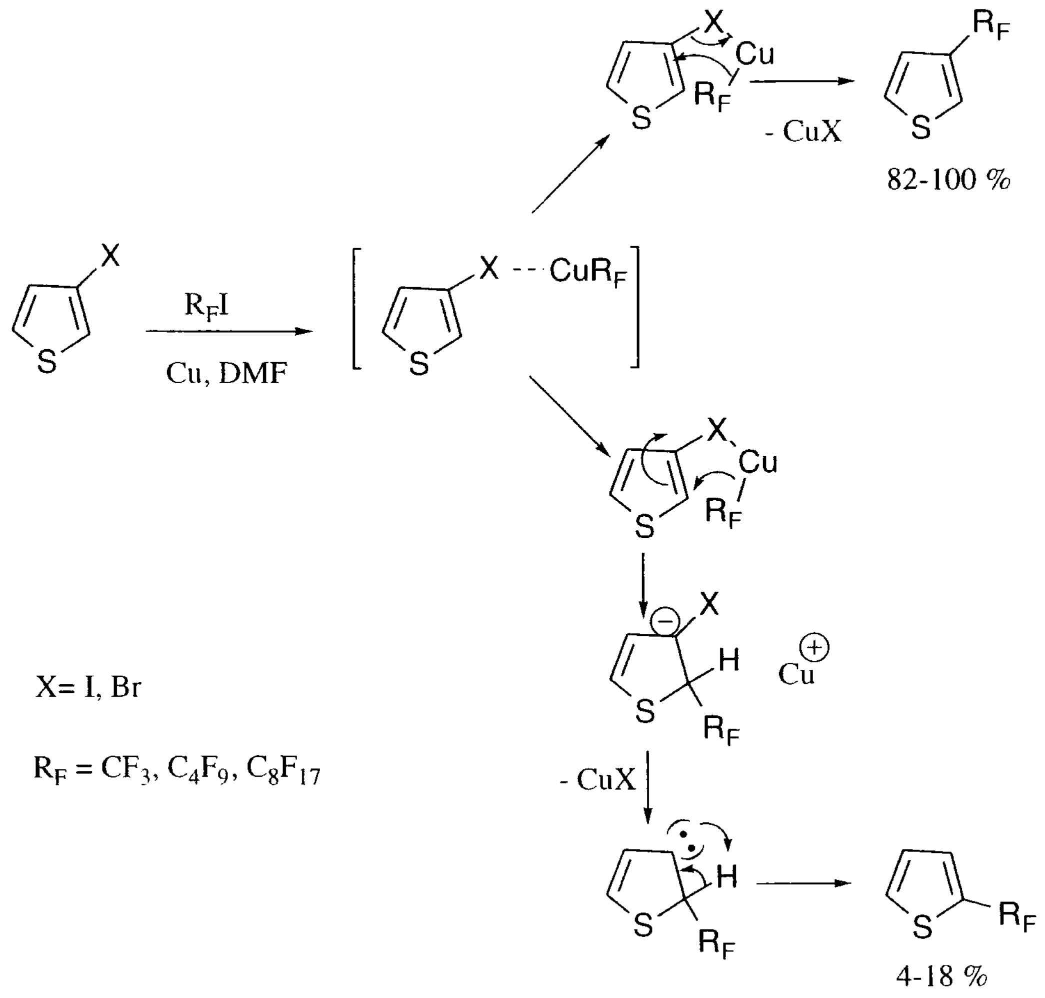
I.2.F.1. USE OF COPPER METAL

Perfluoroalkylation reactions were accomplished by using chloro substituted diazines as substrates[40] with copper metal and perfluoroalkyl iodide in a fluorinated solvent: C_6F_6.


Cl
N
+
C8F17I
Cu/cat
DMSO/C6F6
C8F17
97%

cat: 2,2'-bipyridine

A rearrangement has been observed by Leroy[41] in the perfluoroalkylation of 3-iodo- and bromo-substituted thiophenes.



X= I, Br

$R_F = CF_3, C_4F_9, C_8F_{17}$

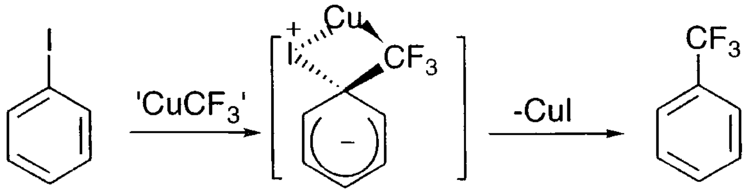
I.2.F.2. USE OF ORGANOCOPPER COMPOUNDS

Cheaper sources of the trifluoromethyl groups have been pursued by several groups of research like the use of trifluoroacetate and copper iodide in polar aprotic solvent. A route was reported in 1988 (Chambers[42]) utilising sodium trifluoroacetate and copper (I) iodide.

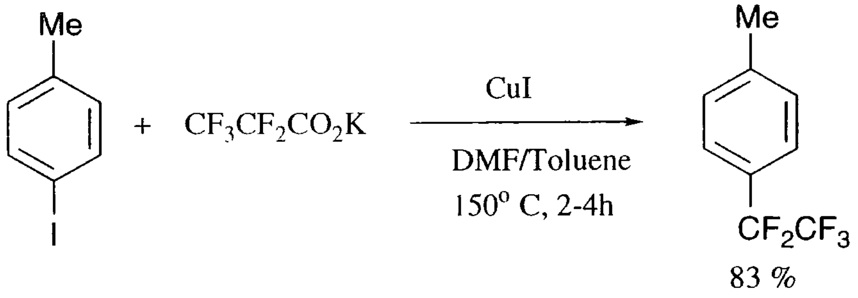
$$\text{ArI} + \text{CF}_3\text{CO}_2\text{Na / CuI} \xrightarrow[\text{140-160° C}]{\text{NMP}} \text{ArCF}_3$$

40-78 %

The mechanism involves a *copper assisted nucleophilic substitution* via decarboxylation of the acetate at high temperature. The nucleophilic character of the reacton was supported by a crude Hammet study[42].



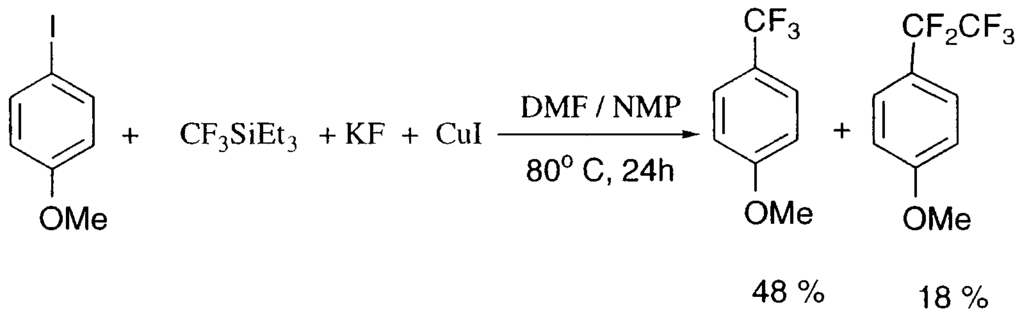
Freskos[43] proposed a convenient synthesis of pentafluoro-ethyl substituted aromatics with potassium pentafluoropropionate and copper (I) iodide based on the same mechanism.



These two categories of reactions involving copper metal and organocopper species require specific conditions such as the reactant, polar aprotic solvent, time and temperature. These parameters play a critical role in determining the yield of the products as well as the by-products formation due to competing reactions.

I.2.F.3. RUPPERT'S REAGENT

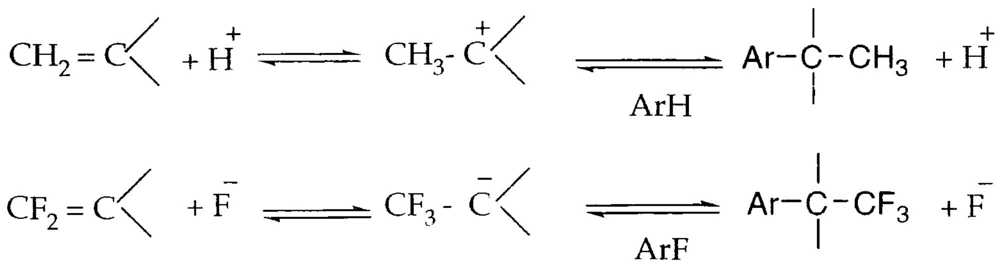
Urata and Fuchikami[44] have reported an interesting approach to the generation and the capture of trifluoromethylcopper of trifluoromethyltrialkylsilane. Potassium fluoride is used as a source of fluoride ion to generate the trifluoromethyl anion species



I.2.G. PERFLUOROALKYLATION OF ACTIVATED AROMATICS

I.2.G.1. NEGATIVE FRIEDEL-CRAFTS REACTIONS

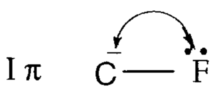
This section concerns the methods available for inserting R_F groups in aromatics which involve the chemistry of polyfluoroalkylanions generated by reaction of fluoro olefins with fluoride ion[45, 46, 47, 48, 49]. These reactions are reminiscent of cationic processes and are called as 'Negative Friedel-Crafts reactions'. The role of fluoride in fluorocarbon chemistry is analogous to the role of the proton in hydrocarbon chemistry. Just as the chemistry of unsaturated hydrocarbons is dominated by carbocation intermediates, produced by electrophilic attack, so the chemistry of unsaturated fluorocarbons is dominated by carbanions, produced by nucleophilic attack[50], as outlined below.



This highlights the unusual effects of fluorine on reactivity. In order to understand nucleophilic attack on fluoro-alkenes, we must consider the mechanistic basis particularly for explaining the regiochemistry of the attack and the relative stability of the carbanion centre.

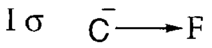
I.2.G.2. CARBANION STABILITY

A fluorine and a perfluorocarbon substituent adjacent to a carbanion centre (A) and (A') respectively are strongly stabilising by inductive effects[51]. Against the inductive electron withdrawal is the presence of the non-bonding electron pairs on fluorine, which tends to return electron density to the π-system and the latter effect is destabilising (B). As a result, there is a competing effect between inductive stabilisation by fluorine and electron-pair repulsions[52].



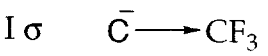
destabilising

(B)



strongly stabilising

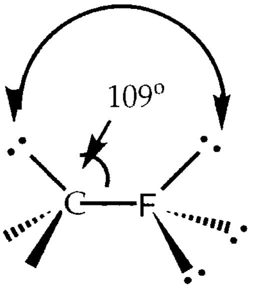
(A)



strongly stabilising

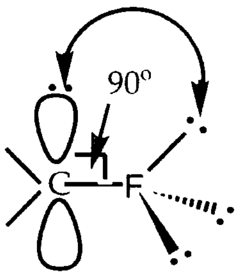
(A')

The resultant is dependant on the geometry of the system. Considering the bond angles, Iπ repulsion is much greater with fluorine attached to sp^2 (planar) centre than to a sp^3 (Td: Tetrahedral) centre.



sp^3

slightly stabilising



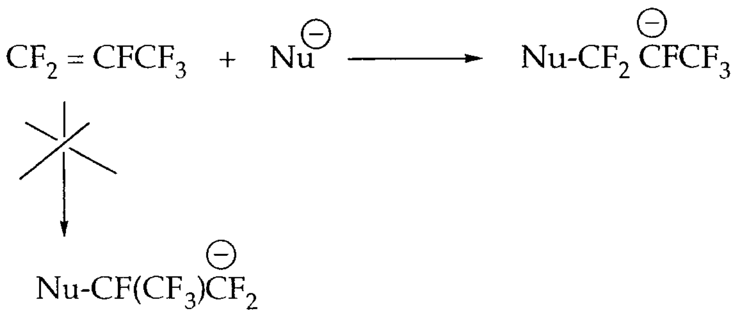
sp^2 (electron-pair repulsion greater)

strongly destabilising

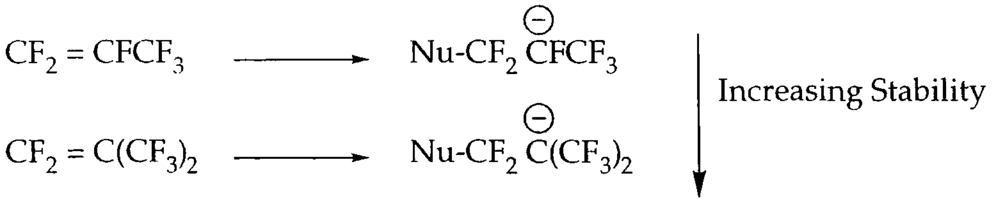
Clearly, fluorine atoms and fluorocarbon groups facilitate carbanion formation at the adjacent position but an attached fluorocarbon chain is much more effective than a fluorine atom at carbanion stabilising, that is, F-C$^-$ is less stable than R_F-C$^-$ [53, 54].

I.2.G.3. NUCLEOPHILIC ATTACK ON FLUOROALKENES

Fluoro-alkenes are usually much more susceptible to nucleophilic attack than electrophilic attack[45, 55].


$CF_2=CFCF_3$ + $Nu^{\ominus}$
$Nu\text{-}CF_2\overset{\ominus}{C}FCF_3$
$Nu\text{-}CF(CF_3)\overset{\ominus}{C}F_2$

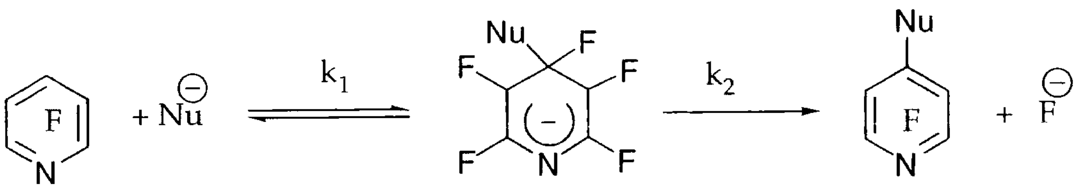
Only one orientation of the attack is observed with hexafluoropropene. It has been shown (section I.2.G.2.) that fluorine directly attached to an anionic site is overall, strongly destabilising, the converse holds for a trifluoromethylated substituent attached to a carbanion centre. Therefore, as the number of perfluoroalkyl groups attached to a carbanion, increases the ability to support the negative charge rises. The stability of these systems can be ordered as followed.


$CF_2=CFCF_3$
$Nu\text{-}CF_2\overset{\ominus}{C}FCF_3$
$CF_2=C(CF_3)_2$
$Nu\text{-}CF_2\overset{\ominus}{C}(CF_3)_2$
Increasing Stability

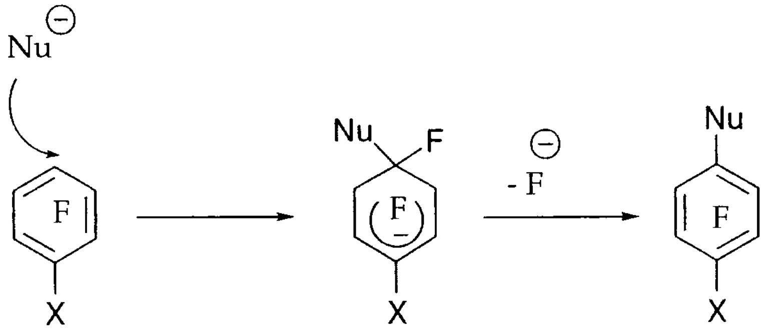
These principles have been developed to rationalize a series of experimental results[45]: perfluoroisobutene is attacked by neutral methanol[56], whereas hexafluoropropene requires the presence of a base[57]; and tetrafluoroethylene reacts only in the presence of a strong base[45] or at elevated temperature[58].

I.2.G.4. NUCLEOPHILIC AROMATIC SUBSTITUTION

With highly fluorinated aromatic systems the nucleophilic aromatic substitution involves a two-step mechanism with the rate limiting on the first step[59, 52, 55].



While hydrocarbon aromatics are activated towards attack from electrophiles, by electron donating groups at the *ortho* and *para* positions, fluoro-aromatics are activated to attack at these positions by electron withdrawing groups[5].



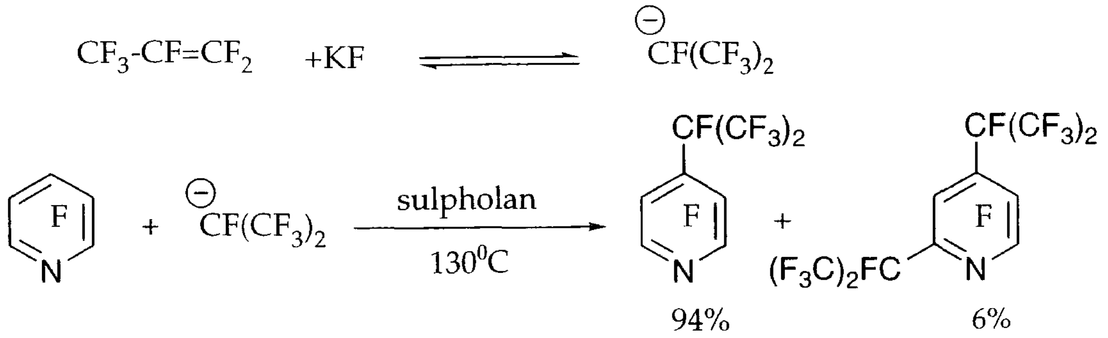
X: R_F, NO_2, Cl

Therefore, it is concluded that the orientation of nucleophilic attack is controlled by the fluorine atoms where fluorine atoms *ortho-* and *meta-* to the position of attack are known to be *strongly activating*, whereas a fluorine atom located *para-* has an effect similar to H, or is *slightly deactivating*. For pentafluoropyridine the position of monosubstitution by nucleophilic reagents is *para* to the nitrogen. In general all the fluoroazabenzenoid systems are activated towards nucleophilic attack, activated by the nitrogen but the orientation is frequently governed by the fluorine substituents.

I.2.G.5. PERFLUOROALKYLATION

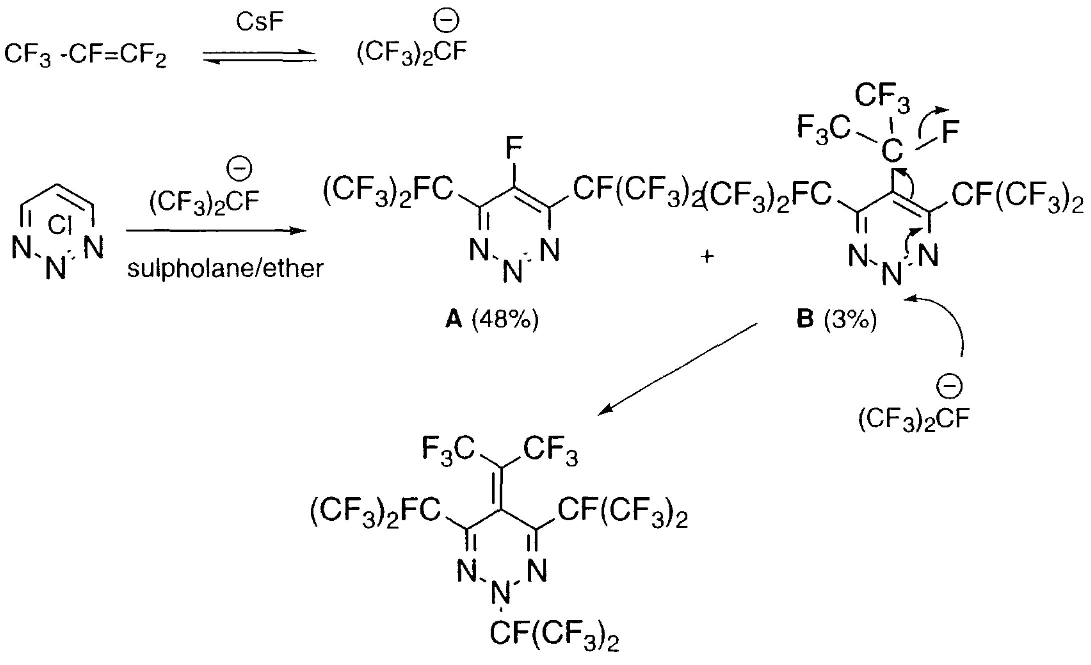
I.2.G.5.i. USE OF POTASSIUM FLUORIDE AND CAESIUM FLUORIDE

The polyfluoroalkylation of pentafluoropyridine was achieved in high yield by Chambers and co-workers[60, 61] using potassium fluoride for initiation and hexafluoropropene.



CF_3-CF=CF_2 +KF
$CF(CF_3)_2$
F
N
$CF(CF_3)_2$
sulpholan
130⁰C
$CF(CF_3)_2$
$CF(CF_3)_2$
$(F_3C)_2FC$
94%
6%

In the case of further attack on the disubstituted compound, the preferential 5-position with the least crowded anions is observed, instead of the more thermodynamicly stable one (with position 6 perfluoroalkylated). Trichloro-1,2,3-triazine is reactive towards nucleophilic aromatic substitution. Furthermore, a novel product (C) is described that arises from nucleophilic attack of a perfluoroisopropyl anion on the ring nitrogen[62, 63].



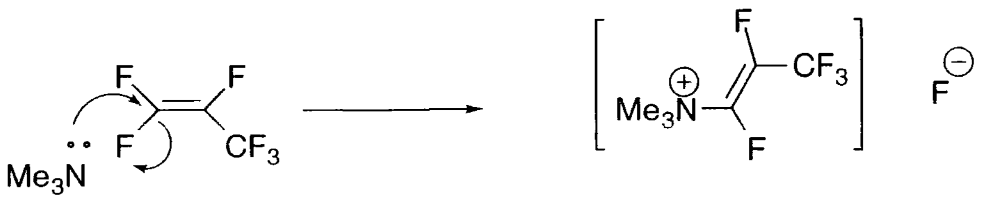
CsF
CF_3 -CF=CF_2
$(CF_3)_2CF$
Cl
N
$(CF_3)_2CF$
sulpholane/ether
F
$(CF_3)_2FC$
$CF(CF_3)_2$
A (48%)
CF_3
F_3C
C
F
$(CF_3)_2FC$
$CF(CF_3)_2$
B (3%)
$(CF_3)_2CF$
F_3C
CF_3
$(CF_3)_2FC$
$CF(CF_3)_2$
$CF(CF_3)_2$

C (2%)

Other fluoride ion sources have been used to generate the carbanion R_F^- that may react with these reactive systems[64, 65].

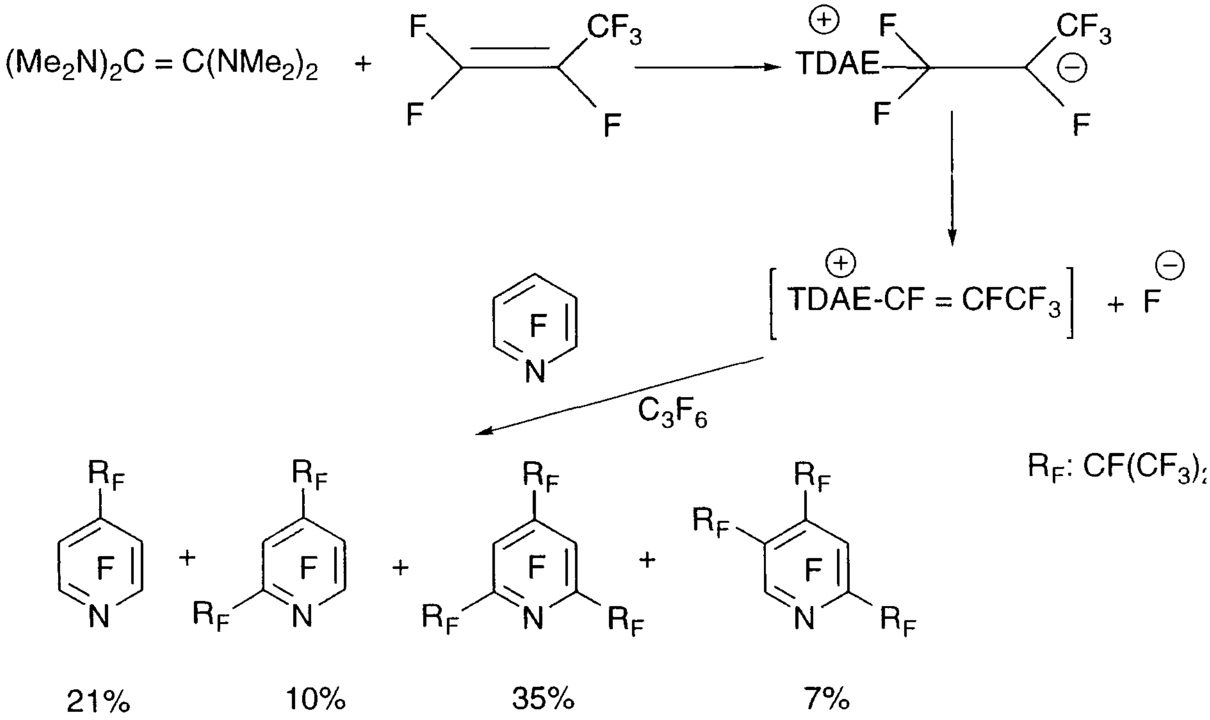
I.2.G.5.ii. REACTIONS WITH OTHER FLUORIDE SOURCES

Haszeldine and co-workers[66] found that hexafluoropropene could be oligomerised by the addition of a small amount of the base trimethylamine[50] to the monomer in an aprotic solvent. The reaction is thought to be initiated by addition and then a displacement mechanism shown below.



The trimethylamine can be thought of as a promoter of fluoride ion. Similarly, Ishikawa[67] has reported an analogous reaction between hexafluoropropene dimer and triethylamine.

Finally, pentafluoropyridine was alkylated successfully with hexafluoropropene using a catalytic amount of tetrakis(dimethylamino)ethene TDAE[68, 69].



TDAE acts as a promoter of fluoride ion. The system has the advantage of being homogeneous, easy to handle and gives high yields at moderate temperature. Finally, such reactions occur without the need of a solvent and this is a major advantage over previous methods reported in the literature, allowing separation of the products.

I.3. "FLUOROUS PHASE": SYNTHESIS AND REACTIONS

Some perfluorinated compounds have now emerged as readily-available products for further synthesis of fluorocarbon derivatives and also for their exploitable applications[70, 71, 4]. Therefore, a survey of their properties and reactions follows.

I.3.A. PERFLUORCARBON FLUIDS

I.3.A.1. INTRODUCTION

Perfluorcarbon fluids[70, 71, 4] (PFC) are saturated aliphatic compounds which include perfluoroalkanes, perfluoroalkylethers and perfluoroalkylamines. Some of their properties[72, 73] are summarised in the **Table 2**.

Table 2

PFC fluids	bp, °C	Density (25°C), g/ml	Viscosity (25°C), cs	Solubility in water, ppm	Surface tension, mN/m
C_6F_{14}	57	1.68	0.40	10	12
C_8F_{18}	103	1.78	0.80	13	14
$(C_4F_9)_3N$	177	1.88	2.8	7.0	16

Perfluorocarbons are very different from their hydrocarbon analogues:. they usually have higher density, lower boiling point, lower heat of vaporisation and lower polarity. They are also able to dissolve large quantities of oxygen, a property which has been found to be useful in oxidation reactions. So far, major uses are as inert fluids for electronics testing, cooling of electronic devices, vapor-phase soldering, lubricants and vacuum fluids for chemically demanding systems. Among the most important characteristics are their extremely low miscibility, excellent thermal stability and chemical inertness with organic compounds.

I.3.B. USE AS REACTION MEDIA

Some recent investigations have led to the development of perfluorocarbons as reaction media for some reactions including bromination[74], photolysis reactions[21], polymerisation[75, 73] as well as oxidation reactions[76, 77]. Pozzi and co-workers[77] showed that fluorocarbons are convenient inert reaction media for olefin epoxidation. The results obtained were similar to those reported in the literature using chlorinated solvents: 1,2-dichloroethane or CCl_4. The nature of the perfluorocarbon has only a slight influence on the reaction.

Yields of cis-cyclooctene epoxide with different perfluorocarbons

Perfluorocarbon	Reaction time (h)	yield (%)
none	4	0
FC-75 (n-perfluoro-butyltetrahydrofuran)	4	95
FC-72 (perfluorohexane)	4	95
FC-43 (perfluoro-tributylamine)	6	92

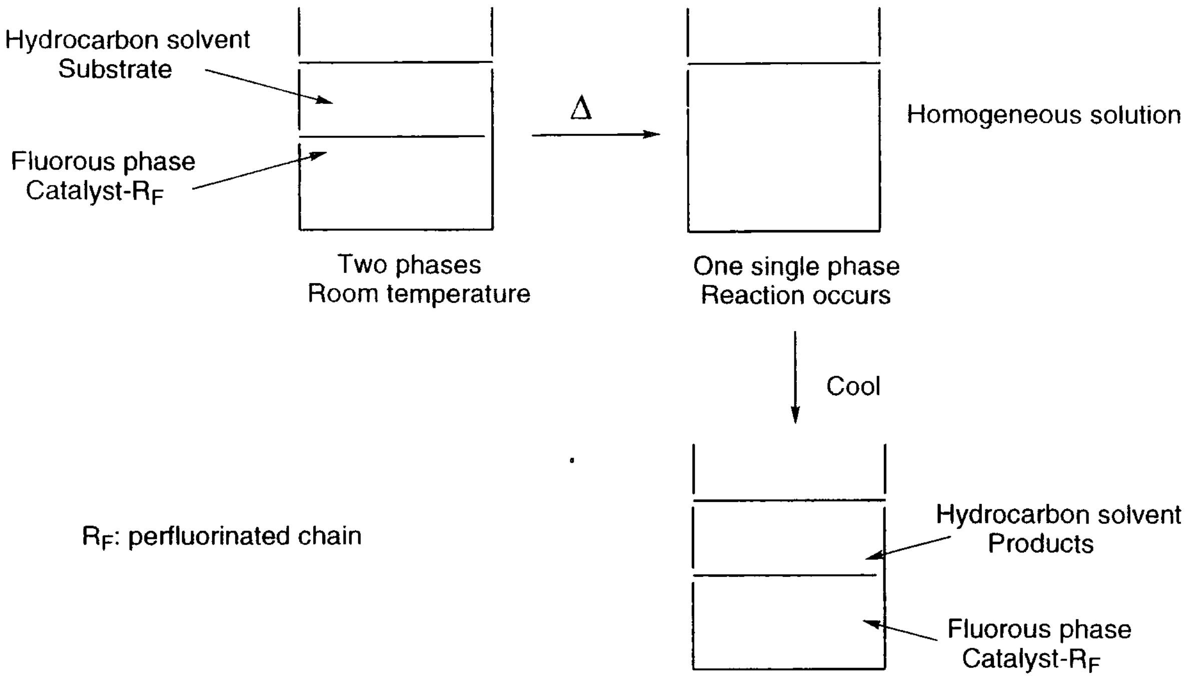
Benzotrifluoride and perfluorocarbon fluids were reported[72, 76, 78] as potentially valuable alternative solvents to chlorinated solvents. Their non-toxicity, the non-ozone depleting property coupled with the wide range of boiling point and the fact that these perfluorocarbons are available, make their use very attractive.

I.3.C. "FLUOROUS BIPHASE SYSTEMS"

The elegant approach to catalyst separation has led to significant attention to industrial applications of two-phase catalysis. The breakthrough of two-phase catalysis[79] has been achieved by arranging the process such that, when the reaction is complete, the catalyst on the one hand, and the reaction product (and residual starting material) on the other hand, are located in different phases, so a simple separation is sufficient for isolating the product from the catalyst, which may be re-used. The most commonly used combinations are aqueous biphase systems[80, 79]. Unfortunately, these processes have some limitions in their uses, such as high sensitivity of some chemical systems which undergo undesired reactions in water, or their low solubility which make the methodology inadequate.

A new approach of two-phase catalysis using fluorinated solvents was suggested by Horvath and Rabai[81, 82, 83]. They introduced for the first time the concept of "fluorous biphase system". The term fluorous is used, as the analogue of the term aqueous, to underline that the reaction will occur in the fluorous phase, requiring reagents which have been specially designed[84].

The methodology takes advantage of labeling the catalyst with a perfluorinated segment that is large enough to force partitioning into the fluorous phase. The two-phase mixture, containing the catalyst phase and the organic product, becomes homogeneous at higher temperature, causing the catalytic process itself to occur with a high rate of reaction in a single phase, such as illustrated in **scheme 1**.


Hydrocarbon solvent
Substrate
Fluorous phase
Catalyst-R_F
Δ
Homogeneous solution
Two phases
Room temperature
One single phase
Reaction occurs
Cool
R_F: perfluorinated chain
Hydrocarbon solvent
Products
Fluorous phase
Catalyst-R_F

Scheme 1

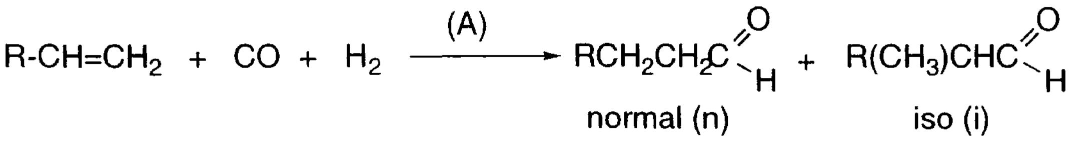
The system is cooled, permitting separation of the reaction product from the catalyst, which then becomes available for immediate re-use.

This strategy relies on designing catalysts which dissolve preferentially in the fluorous phase and the catalyst is synthesized with long carbon chains consisting mainly of perfluoroalkyl segments to allow its solubility in the fluorous phase. It is necessary that these catalysts bearing such segments, or so-called ponytails[84], should retain their electronic properties. In practice, several CH_2 groups, located between the reacting centre and the fluorinated chains, are used to insulate the powerful electron-withdrawing effect of such groups and maintain their reactivity close to their underivatized species.

I.3.C.1. SYNTHESIS OF CATALYSTS AND USE IN REACTIONS

I.3.C.1.i. RHODIUM DERIVATIVES

Horvah and Rabai[82] explored the property of catalysts attached to a partially fluorinated phosphine in the context of the hydroformylation reaction.



$$R\text{-}CH{=}CH_2 + CO + H_2 \xrightarrow{(A)} RCH_2CH_2CHO + R(CH_3)CHCHO$$

normal (n) iso (i)

The hydroformylation of 1-octene was chosen with a rhodium complex catalyst (A). In order to perform the reaction, a new procedure for the preparation of the phosphine $P[CH_2CH_2(C_6F_{13})]_3$ was designed.

$$CF_3(CF_2)_5CH = CH_2 \quad + \quad PH_3 \xrightarrow[\substack{\text{autoclave} \\ 100^{\circ}C}]{AIBN} P(CH_2CH_2R_F)_3 \quad (26\%)$$

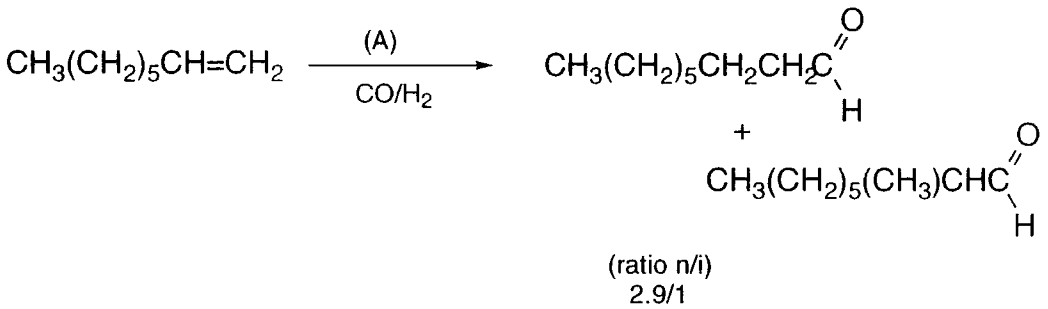
$$R_F = C_6F_{13}$$

The catalyst was prepared in situ from $Rh(CO)_2(acac)$ (acac: acetylacetonate) under 5 atm CO/H_2.

$$\begin{matrix} Rh(CO)_2(CH_3COCHCOCH_3) \\ + \\ P[CH_2CH_2R_F]_3 \end{matrix} \xrightarrow[\substack{C_6H_5CH_3/C_6F_{11}CF_3 \\ 100^{\circ}C,\ 5\ atm}]{CO/H_2} \underset{(A)}{HRh(CO)\{P[CH_2CH_2R_F]_3\}_3}$$

$$R_F = C_6F_{13}$$

The hydroformylation was performed with $C_6F_{11}CF_3$ as the fluorous phase and toluene as the hydrocarbon phase.



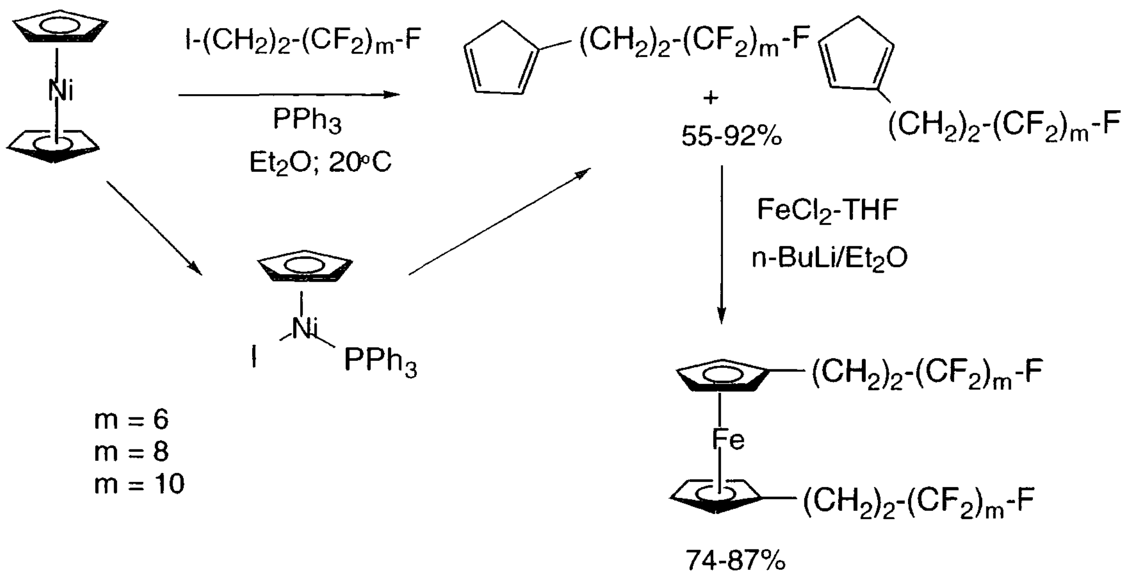
(ratio n/i)
2.9/1
conversion (85%)

The ratio of normal to iso products was not altered when the "fluorous biphase system" was used and it was demonstrated that this procedure was a convenient way to recover the catalyst as well as the ability to re-use it. The application of "fluorous biphase system" for extraction of rhodium from hydrocarbon phase with fluorous soluble ligands is a novel approach and this is important as rhodium is one of the most expensive transition metals used in homogeneous catalytic processes.

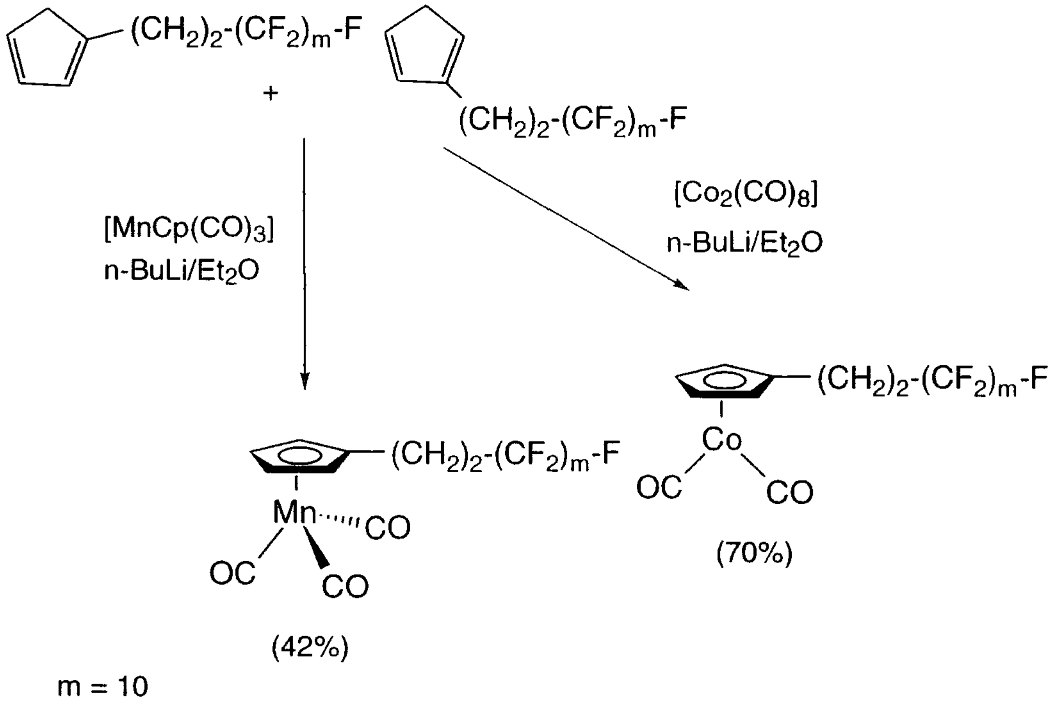
I.3.C.1.ii. METALLOCENES

I.3.C.1.ii.a. VIA PONYTAIL OF CYCLOPENTADIENYLS

Cyclopentadienes bearing fluorinated ponytails have been prepared by reaction of a perfluoroalkyl iodide and triphenylphosphine with nickelocene[85]. The ferrocene derivatives were prepared by reaction of iron (II) chloride with the intermediate lithiated dienes.


Ni
I-(CH2)2-(CF2)m-F
PPh3
Et2O; 20°C
(CH2)2-(CF2)m-F
+
55-92%
(CH2)2-(CF2)m-F
Ni
I
PPh3
FeCl2-THF
n-BuLi/Et2O
m = 6
m = 8
m = 10
(CH2)2-(CF2)m-F
Fe
(CH2)2-(CF2)m-F
74-87%

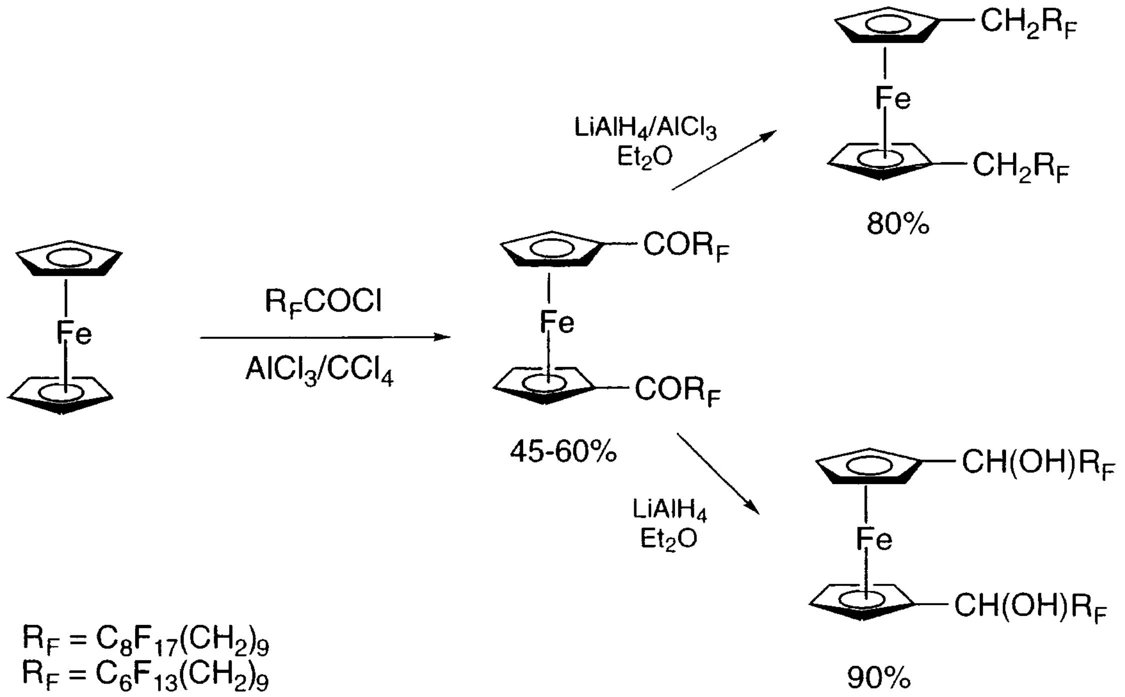
Reactions were also carried out using manganese and cobalt complexes to afford, in reasonably high yield, the corresponding ponytail complexes[85].


(CH2)2-(CF2)m-F
+
(CH2)2-(CF2)m-F
[MnCp(CO)3]
n-BuLi/Et2O
[Co2(CO)8]
n-BuLi/Et2O
(CH2)2-(CF2)m-F
Mn
CO
OC
CO
(42%)
(CH2)2-(CF2)m-F
Co
OC
CO
(70%)
m = 10

In summary, a series of cyclopentadienes bearing perfluorinated chains have been prepared. Some studies have confirmed that the ethylene spacer group is necessary to effectively insulate the cyclopentadienyl ring from the electronic effect of the fluoroalkyl part. It was found that the solubilities and partitioning of these complexes are strongly temperature-dependant and change dramatically with the length of the perfluoroalkyl tail. ***A strong selectivity for fluorous solvents was not observed until the compound bears two $C_{10}F_{21}$ tails***[85].

I.3.C.1.ii.b. DIRECT PERFLUOROALKYLATION OF FERROCENES

Guillon and co-workers[86] have developed new amphiphilic analogues of metal complexes known to have biological or therapeutic properties.



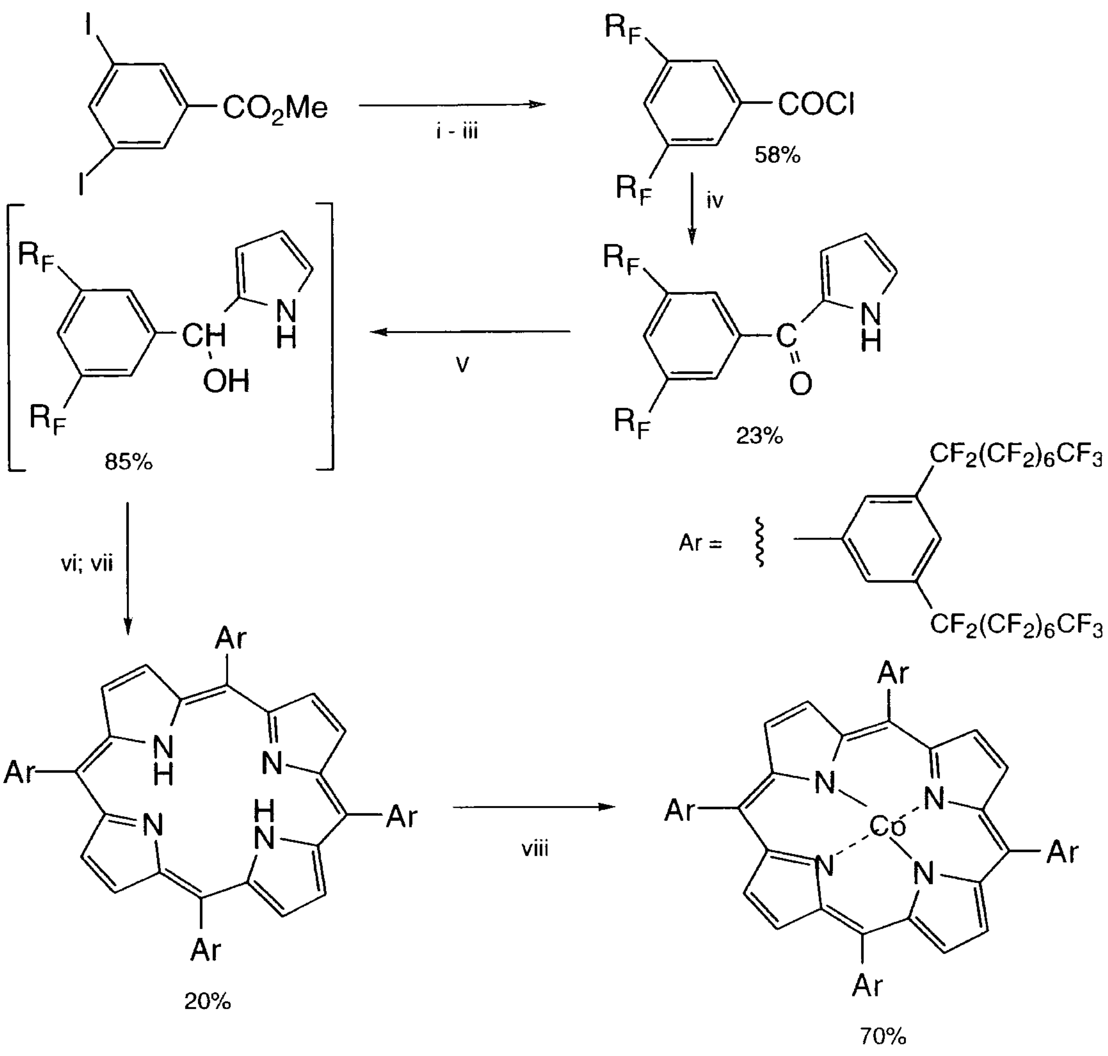
$R_F = C_8F_{17}(CH_2)_9$
$R_F = C_6F_{13}(CH_2)_9$

The acylferrocenes are obtained by Friedel-Crafts acylation in the presence of acyl chloride derivative and aluminium chloride as the Lewis acid. By selective reduction, the general route gives access to various perfluoroalkylated-(hydroxy)ferrocenes with $LiAlH_4$ and perfluoroalkylated-ferrocenes under stronger conditions.

I.3.C.1.iii. TETRAARYLPORPHYRIN CATALYST

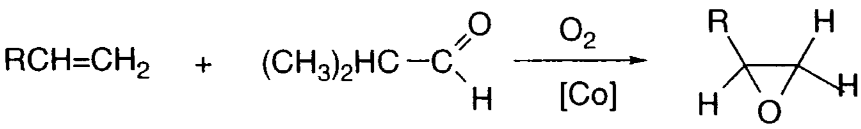
The approach was extended to the synthesis of perfluorocarbon soluble complexes of tetraarylporphyrin as catalyst. Metalloporphyrin complexes are active catalysts for oxidation reactions[87]. In these reactions the high solubility of oxygen in perfluorocarbon fluids are very helpful.

Pozzi[88] and Wijesekera[89, 88] investigated the catalytic activity of these metalloporphyrin complexes bearing R_F groups.


CO2Me
i - iii
RF
COCl
58%
iv
23%
v
85%
CH
OH
NH
Ar =
CF2(CF2)6CF3
vi; vii
Ar
20%
viii
Co
70%

i: $C_8F_{17}I$, Cu, DMF; ii: KOH, H_2O; iii: $SOCl_2$; iv: pyrrole, Et_2O
v: $LiAlH_4$, THF; vi: $Zn(OAc)_2$; vii: CF_3CO_2H, $NaHCO_3$; viii: $Co(OAc)_2$, DMF

The epoxidation of alkenes was carried out under fluorous biphasic conditions in the presence of the perfluorocarbon-soluble cobalt complex of tetraarylporphyrin as a catalyst[88]. The reaction was successfully performed with molecular oxygen and 2-methylpropanal as the reducing agent.

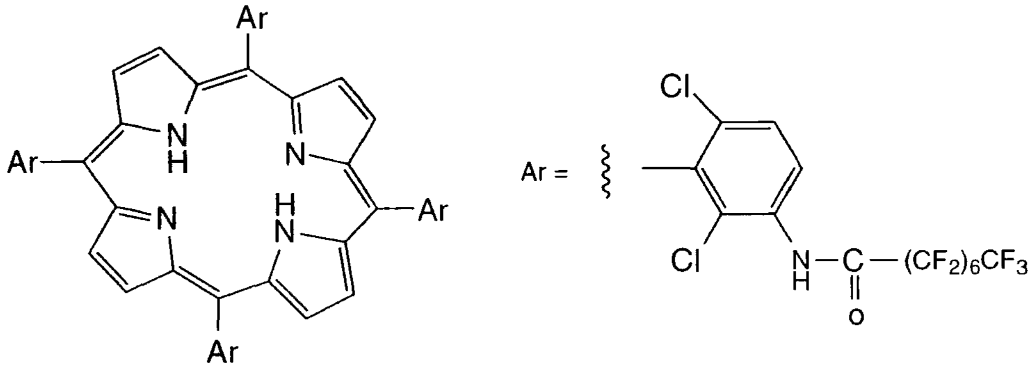

RCH=CH2
+
(CH3)2HC
O
H
O2
[Co]
R
H
O

Substrate	
R: $C_{10}H_{21}$	48%
cis-cyclooctene	95%

The reaction under fluorous phase conditions has been compared with earlier results reported in the literature[88]. This procedure allows a much higher substrate-catalyst ratio (1000:1) than those previously reported (20:1).

Moreover, after completion of the reaction, the perfluorocarbon layer containing the catalyst can both be re-used without decreasing the substrate conversion. This work demonstrated the use of perfluorocarbon fluids but also demonstrated that groups with withdrawing electrons attached to the porphyrin periphery lead to active catalysts for alkene oxidation.

An experiment was carried out by Pozzi and co-workers[90] who synthesized in a similar route Mn-tetraarylporphyrins[91] bearing also 4 perfluoroalkyl groups as shown below.



However, this feature was not sufficient to impart solubility in fluorocarbons. The location of the R_F substituents on the meso-aryl groups strongly affects the behaviour of these compounds, at least in the case of tails tethered through amido bonds.

I.3.C.2. SYNTHESIS OF ORGANIC MOLECULES BEARING FLUOROUS LABEL

The strategy of using "fluorous biphase systems" in organic synthesis[92] relies on two concepts: fluorous synthesis and fluorous-phase switch. In the fluorous synthesis approach, the organic molecules are rendered soluble in fluorocarbon solvents by attachment of a suitable fluorocarbon group. The fluorous-phase switch method concerns the use of perfluorocarbon fluids in organic synthesis as a general procedure for isolating and purifying the products from unreactive substrate and impurities. Simple substantive separations of the different phases with the desired products are achieved without resorting to chromatography.

I.3.C.2.i. FLUOROUS SYNTHESIS

Two classes of organic compounds are chosen; the protecting groups commonly used in organic synthesis: trialkylsilyl derivatives and the popular reducing agent tin hydride. These two categories of reagents are designed to react with the substrate in a further reaction and label the product to conduct solvent partitioning. The fluorous synthesis combines in many respects the features of traditional organic synthesis.

I.3.C.2.i.a. SYNTHESIS OF TIN DERIVATIVES

The fluorous strategy was adopted by Curran and co-workers[93] making fluorous tin hydride reagents and proving that they behave like normal tin hydride reagent in radical reductions. Reaction of a Grignard reagent with phenyltrichlorotin followed by bromonolysis gave the corresponding tin hydride after reduction with lithium aluminium hydride.

$$R_F(CH_2)_2MgI \xrightarrow[\text{ii: } Br_2]{\text{i: } Cl_3SnPh} (R_F(CH_2)_2)_3SnBr \xrightarrow{\text{iii: } LiAlH_4} \underset{\substack{65\% \\ \text{(A)}}}{(R_F(CH_2)_2)_3SnH}$$

$$R_F = C_6F_{13}$$

The tin hydride was immediately used for the radical reaction with perfluorodecyl iodide and provided the corresponding hydro-compound in high yield.

$$C_{10}F_{21}I + A \xrightarrow[C_6F_{11}CF_3]{AIBN} \underset{72\%}{C_{10}F_{21}H}$$

The process of synthesising labelled tin reagents has very significant practical advantages since the most common alkyl derivatives used so far contain methyl or butyl groups. Trimethyltin by-products are easy to remove but toxic and tributyltin by-products are less toxic but difficult to remove.

I.3.C.2.i.b. SYNTHESIS OF SILYL DERIVATIVES

Boutevin and his co-workers[94] focused their interest on synthesising perfluoroalkysilane of high molecular weight following conventional reaction schemes based on magnesium organometallic compounds.

$$C_6F_{13}CH=CH_2 + HSiCl_3 \xrightarrow{H_2PtCl_6} \underset{83\%}{C_6F_{13}CH_2CH_2SiCl_3}$$

$$C_6F_{13}CH_2CH_2MgI + C_6F_{13}CH_2CH_2SiCl_3 \longrightarrow \underset{27\%}{(C_6F_{13}CH_2CH_2)_3SiCl}$$

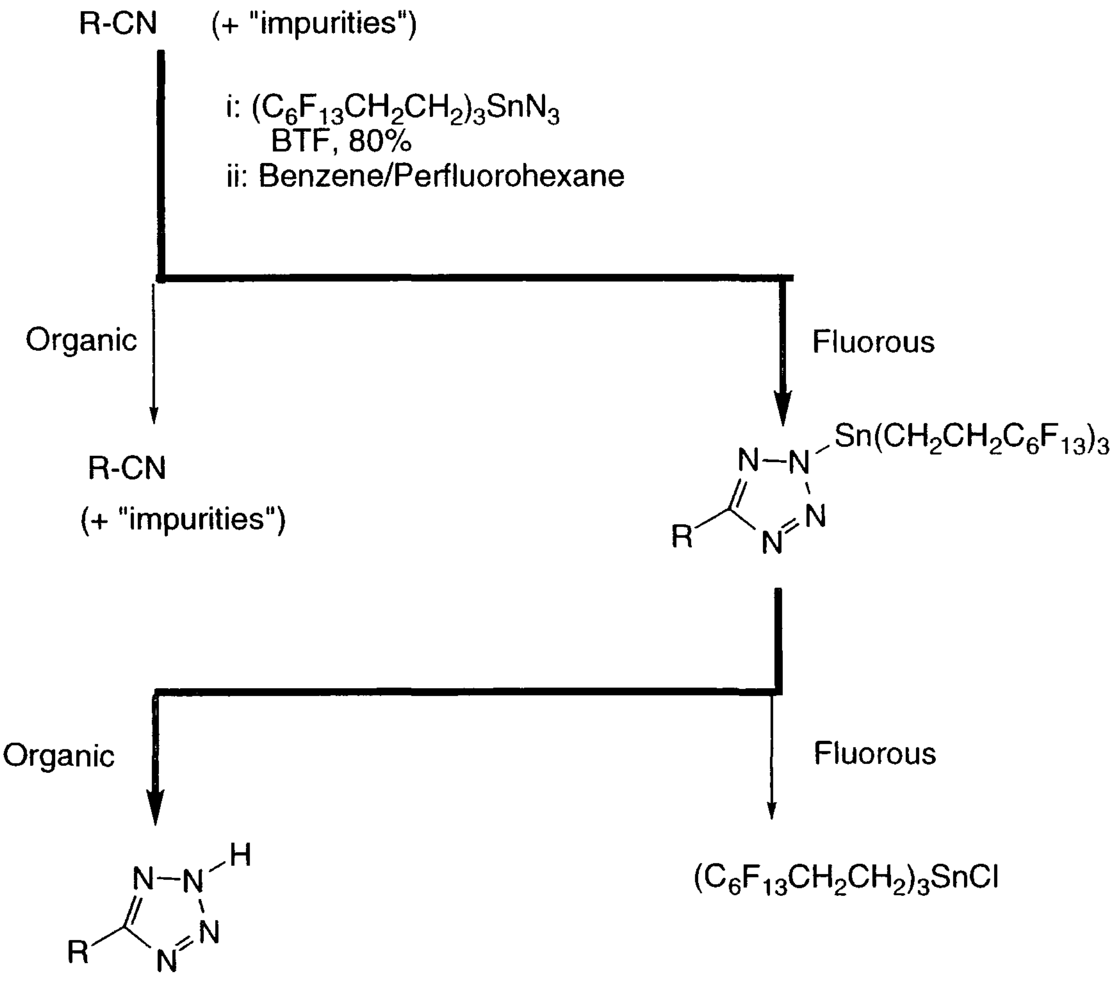
At this stage, these "smart reagents" tin and silyl derivatives allow for ready use of the fluorous phase in organic synthesis[92].

I.3.C.2.ii. FLUOROUS-PHASE SWITCH

The reagents described in the previous section belong to classes of reactions used in organic synthesis to prepare usual compounds. The purpose of these familiar reactions is to demonstrate that the products can be extracted into the fluorous layer if properly labeled and isolated in high yield by applying the "organic-fluorous" switch[92]. The reaction is performed in one single phase, and it is an important advantage if the substrate is completely consumed because it occupies the same phase as the product. Then, by performing an extraction, a selective phase switch is conducted in which the fluorous phase attracts fluorous labeled compounds and the organic phase retains the non-fluorinated residue. After evaporation of the fluorous solvent, the phase is switched back to an organic phase to carry on some further reactions. Furthermore, the final fluorous reagent after reaction can be retrieved from the fluorous layer and reused. The technique reported here is illustrated by some examples.

I.3.C.2.ii.a. USE OF LABELLED TIN REAGENTS

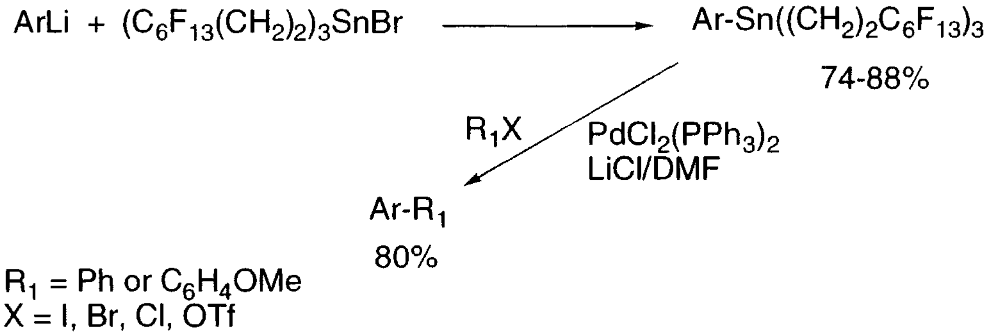
The phase switching method[92] can be used with "impure" starting material so that the transformation of the substrate is designed to remove any impurities and by-products, as illustrated by the reaction of tin azide to afford pure tetrazoles[95, 92].


R-CN (+ "impurities")
i: $(C_6F_{13}CH_2CH_2)_3SnN_3$
BTF, 80%
ii: Benzene/Perfluorohexane
Organic
Fluorous
R-CN
(+ "impurities")
$Sn(CH_2CH_2C_6F_{13})_3$
N
R
Organic
Fluorous
H
$(C_6F_{13}CH_2CH_2)_3SnCl$

R = CH_3, 83%; i-Bu, 87%; $PhCH_2$, 77%

The reaction of an organic nitrile with fluorous azide in benzotrifluoride (BTF) proved to be successful after organic and fluorous extraction (perfluorohexane). This suggests that fluorous tin reagents could be a general stategy to make the organotin repertoire more practical and more environmental friendly.

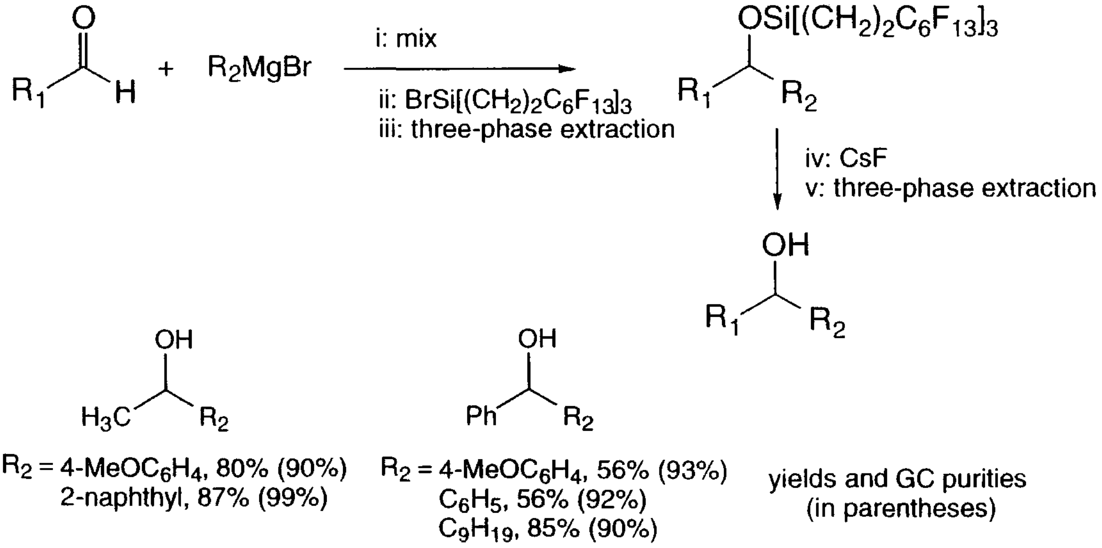
The Stille reaction[96], [97] was selected to probe the potential of the fluorous tin strategy[98]. The reaction involves a catalysed cross-coupling mechanism with Pd^{o}.


ArLi + (C6F13(CH2)2)3SnBr
Ar-Sn((CH2)2C6F13)3
74-88%
R1X
PdCl2(PPh3)2
LiCl/DMF
Ar-R1
80%
R1 = Ph or C6H4OMe
X = I, Br, Cl, OTf

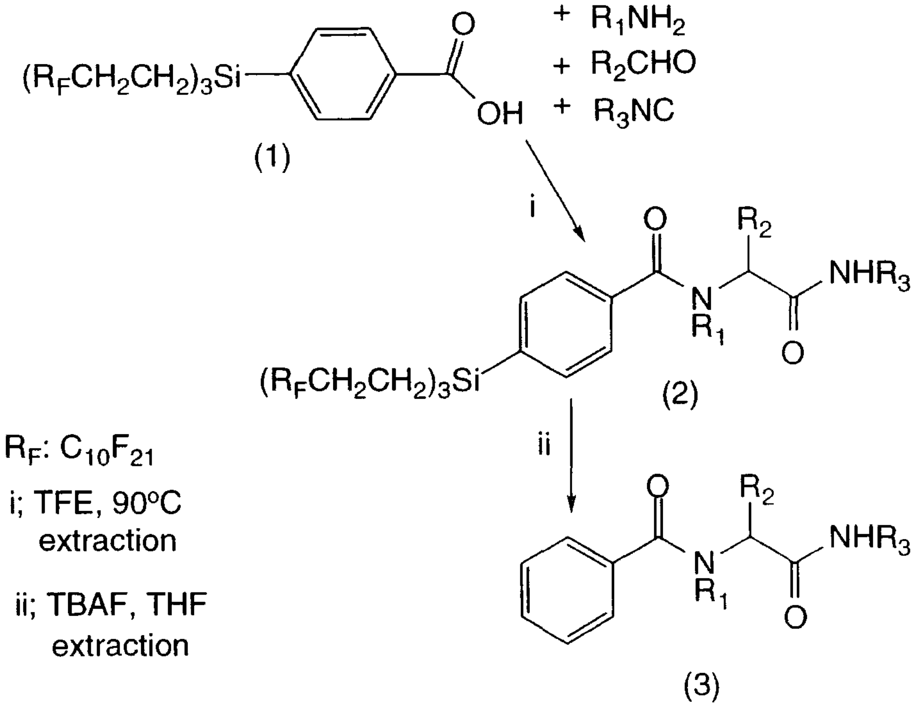
The biaryl product was synthesised in high yield and the ease of separation and reuse of the tin reagent made the procedure very attractive.

I.3.C.2.ii.b. USE OF LABELLED SILYL REAGENTS

The reaction of Grignard is followed by fluorous labelling the corresponding alcohol[92]. The fluorous silyl ether is then separated by three-phase extraction with ether as the organic solvent. Treatment of the crude material from the fluorous phase by CsF was used to remove the silyl group followed by an acidification. A second three-phase extraction was performed to afford the corresponding alcohols which have switched back in the organic phase.


O
R1
H
+ R2MgBr
i: mix
ii: BrSi[(CH2)2C6F13]3
iii: three-phase extraction
OSi[(CH2)2C6F13]3
R1
R2
iv: CsF
v: three-phase extraction
OH
R1
R2
OH
H3C
R2
OH
Ph
R2
R2 = 4-MeOC6H4, 80% (90%)
2-naphthyl, 87% (99%)
R2 = 4-MeOC6H4, 56% (93%)
C6H5, 56% (92%)
C9H19, 85% (90%)
yields and GC purities
(in parentheses)

The development of fluorous reagents provided novel options for combinatorial synthesis. Curran and co-workers have adapted the Ugi multicomponent condensations with the fluorous equivalents. The acid bearing 63 fluorine atoms was reacted with an excess of three components: amine, aldehyde and isonitrile. Trifluoroethanol (TFE) was used as the solvent because it had the ability to solubilize both organic and fluorous components.


(RFCH2CH2)3Si
O
OH
+ R1NH2
+ R2CHO
+ R3NC
(1)
i
O
R2
NHR3
N
R1
O
(RFCH2CH2)3Si
(2)
ii
RF: C10F21
i; TFE, 90°C
extraction
ii; TBAF, THF
extraction
O
R2
NHR3
N
R1
O
(3)

After removal of the solvent, benzene and FC-72 (perfluorocyclohexane) were added. The crude material (2) was extracted with FC-72. Evaporation of the fluorous phase yielded the fluorous Ugi product (2). Finally, the desilylation reaction was carried out with TBAF in tetrahydrofuran and the desired product was purified by phase extraction using benzene and FC-72. The organic layer afforded the pure Ugi product in good yields as shown in the **Table 3**.

R_1	R_2	R_3	Yield(%)	Purity(%) GC data
Bn	Ph	t-Bu	83	85
Bn	c-Hex	c-Hex	99	95
Bn	Et	t-Bu	75	93

Table 3

This illustrates the power of the fluorous approach for conducting and purifying multicomponent reactions, furthermore, it proved valuable in the synthesis of librairies of individual pure organic compounds.

CHAPTER II

SYNTHESIS OF [(PERFLUORO-2-METHYLPENTAN-2-YL)METHYL]BENZENE AND DERIVATIVES

II.1. INTRODUCTION

Our attention has been focussed on the introduction of perfluoroalkyl groups into specific sites in aromatic systems and to investigate the physical and chemical properties which these highly fluorinated molecules exhibit. This chapter deals with the synthesis of perfluoroalkylated aromatic compounds and their characterisation. The synthetic route that we explored involved the use of fluoride ion source and a fluorinated alkene. Various unsaturated fluorocarbons were studied to generate the most suitable and reactive perfluoroalkyl anions to react with electrophiles eg. $ArCH_2Br$. The synthesis and reactions of a range of aromatic systems will be discussed in this chapter.

II.2. PERFLUOROALKYLATING AGENTS

The present work is concerned with the synthesis of new fluorinated materials using a range of fluorinated alkenes as perfluoroalkylating agents: hexafluoropropene, hexafluoropropene dimer, hexafluoropropene trimer and tetrafluoroethylene pentamer. The general procedure is described below which involves the formation of a reactive species: perfluorocarbanion derived from a perfluorinated alkenes using fluoride ion induced methodology.

$$\text{Alkene} + \text{M F} \xrightleftharpoons{K} R_F^{\ominus} M^{\oplus}$$

$$R_F^{\ominus} + ArCH_2Br \xrightarrow{k} ArCH_2R_F$$

Alkenes

MF: CsF, KF

$CF_3\text{-}CF{=}CF_2$

$(CF_3)_2C{=}CFCF_2CF_3$

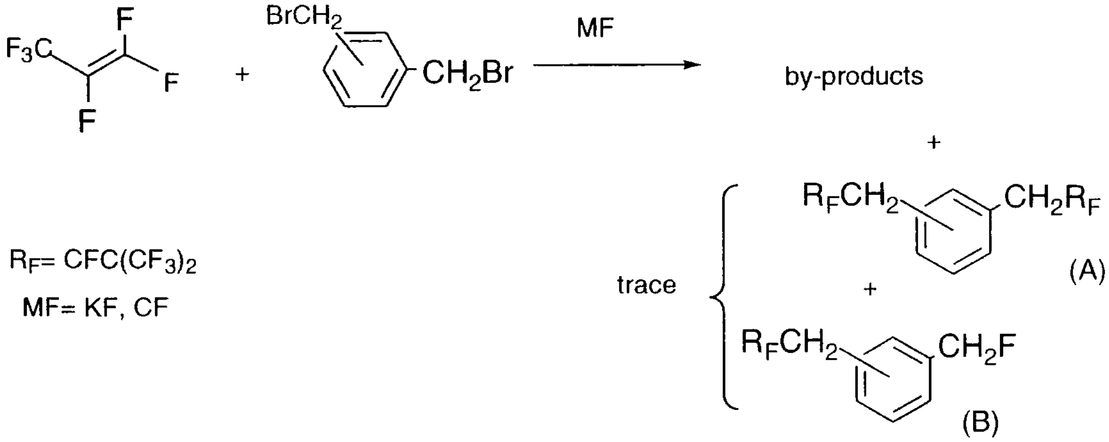
$(CF_3)_2C{=}C(CF_2CF_3)CF(CF_3)_2$

$(C_2F_5)_2C(CF_3)C(CF_3){=}CF(CF_3)$

Fluorinated alkenes have been reported to have a very interesting reactivity[99, 100, 101, 102, 103, 104]. The generation of perfluoroalkyl anions using fluoride ion source in reactions of fluorinated alkenes is well known[105, 106, 52, 103, 107, 108]. Depending on the conditions, long-lived carbanions can perfluoroalkylate directly[103, 61] or promote oligomerisation reactions of the corresponding alkene[105]. As a result, various unsaturated fluorocarbons were investigated to generate the perfluoroalkyl anions and be trapped with electrophiles derived from $ArCH_2Br$. Bearing in mind these observations, the conditions of the experiment are essential and were explored for each alkene.

II.3. PERFLUOROALKYLATION USING HEXAFLUOROPROPENE

The reaction between hexafluoropropene and xylylene dibromide (m- and p-) was carried out in the presence of potassium fluoride at 100°C for a minimum of 12 hours in a sealed vessel in aprotic polar solvent such as DMF, diglyme, NMP and sulpholane.



Only two solvents allowed the reaction to occur: DMF and sulpholane. In both cases, the ^{19}F NMR and glc-ms showed that numerous side-products were formed, in particular, hexafluoropropene dimer and hexafluoropropene trimer. Traces of perfluoalkylated compounds (A) and (B) were observed. There was no noticeable change when the reaction was repeated using a bladder (reaction at 1 atmosphere) instead of a Carius tube. The procedure should have had the advantage of reducing the range of side-products. Nevertheless, the spectrum of products did not simplify. Finally, as high temperature might have had an adverse effect on the stability of the carbanion[61], the reaction was performed in sulpholane at 60°C for different time 16 hours, 4 days and a week, using a sealed system.

Solvent	T °C	time	vessel	products
Supholane	100	24 hours	bladder	trace (A)+(B)
Supholane	60	16 hours	Carius tube	trace (A)+(B)
Supholane	60	4 days	Carius tube	trace (A)+(B)
Supholane	60	1 week	Carius tube	trace (A)+(B)

For each experiment, the conversion of hexafluoropropene was 100%, but only traces of (A) and (B) were obtained. Furthermore, the ^{19}F NMR spectrum still contained a large number of peaks, implying some further complexities in the reaction. The ^{19}F NMR spectrum gave the same chemical shifts as were observed when the reaction was performed with caesium fluoride in sulpholane. There was no noticeable change when the starting material xylylene dibromide was replaced by benzyl bromide; only a trace of benzyl-perfluoroisopropane was detected and again a complex spectrum was obtained. Finally, in order to investigate whether the electrophilic species was important or not , the reaction was carried out in sulpholane with hexafluoropropene and caesium fluoride only. The spectrum did not simplify and glc-ms showed that under these conditions, in the presence of fluoride ion, the hexafluoropropene had oligomerised[109, 110] to give hexafluoropropene dimer and trimer.

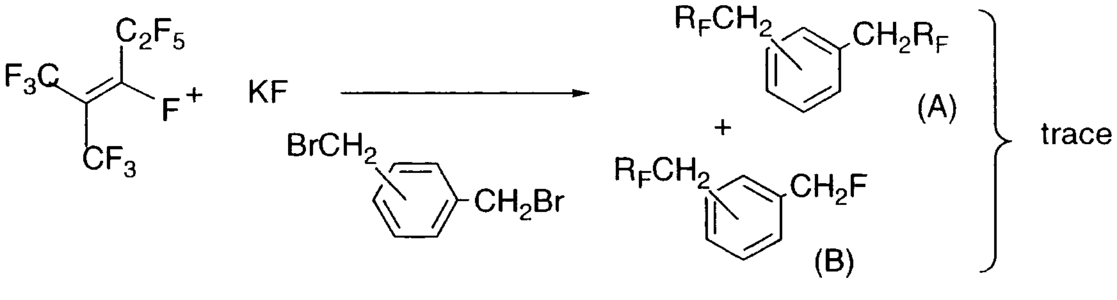
Reaction with hexafluoropropene, using systems such as KF/DMF, KF/sulpholane and CsF/sulpholane did not generate substantial concentration of the perfluoroalkylated product but instead promoted oligomerisation of hexafluoropropene. As a consequence, the perfluoroalkylation approach using hexafluoropropene was abandoned.

II.3. PERFLUOROALKYLATION USING HEXAFLUOROPROPENE DIMER

II.3.A. USE OF KF

Hexafluoropropene dimer was reported by Ikeda[104, 111] and Makarov[103] to have a very interesting reactivity. This alkene reacts with various nucleophiles to give a carbanion, which under appropriate conditions reacts with electrophiles to give addition products[52, 61].

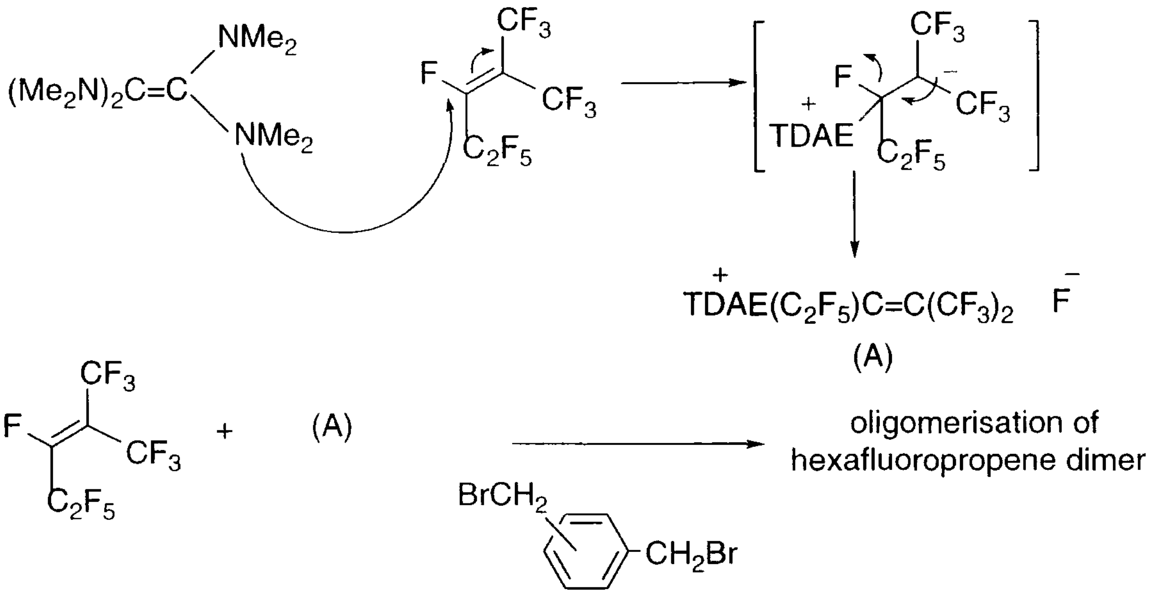
When the reaction was performed in a sealed system, a marked solvent effect was found in the reaction of hexafluoropropene dimer with xylylene dibromide and potassium fluoride as a source of fluoride ion[104, 111]. DMF proved to be successful but afforded a range of products including oligomerisation of hexafluoropropene dimer with a very low yields of the desired products (A) and (B) (less than 5%). The glc-ms spectrum showed the presence of hexafluoropropene trimer. In contrast, in sulpholane, no perfluoroalkyl derivatives were observed even in a trace amount. The reaction was repeated at different temperatures 100°C and 60°C, but no change was observed.



$R_F= CF_3CF_2CF_2C(CF_3)_2$

II.3.B. USE OF TETRAKIS(DIMETHYLAMINO)ETHYLENE (TDAE)

The route we investigated next, involved the use of TDAE as an alternative to KF, reacting as nucleophile to produce fluoride ion$^{66, 68, 69}$.



The effect of solvent was studied by performing the reaction consecutively in acetonitrile, sulpholane and in absence of any solvent^{69}. ^{19}F NMR and glc-ms data showed the presence of a wide range of products in all the cases including hexafluoropropene, hexafluoropropene trimer. Due to the high reactivity of hexafluoropropene dimer under the action of TDAE, no further investigations were carried out. However, these observations confirmed the importance of the solvent and the fluoride ion source used for these kind of reactions. No reaction was observed when the reaction was attempted with potassium fluoride in sulpholane; by replacing potassium fluoride with TDAE the reactivity increased dramatically.

All these one step methods explored in section II.3.A. and II.3.B. using KF or TDAE afforded too low a concentration of perfluorocarbanion to allow the perfluorolkylation to occur.

II.3.C. TWO-STAGE PROCEDURE: USE OF CsF

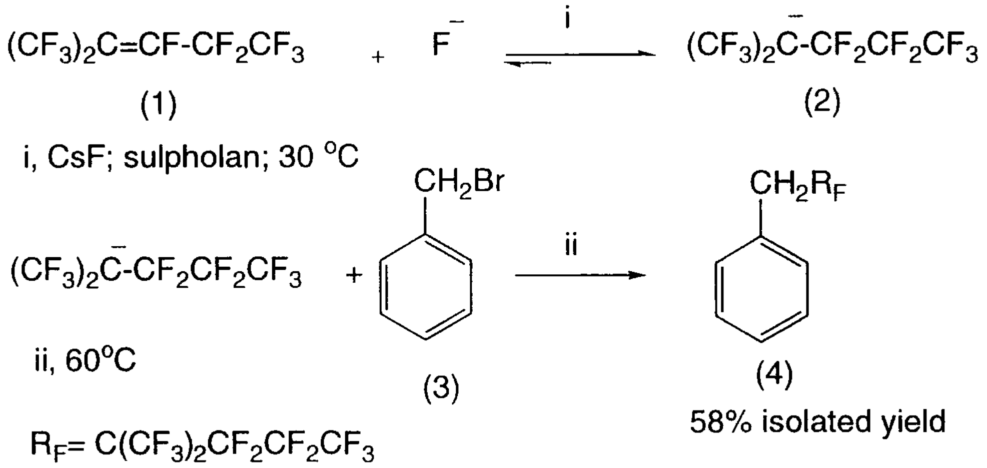
II.3.C.1. MONOPERFLUOROALKYLATION: REACTION WITH BENZYL BROMIDE

The methodology, we investigated next is a two-step reaction where the concentration of perfluoroarbanion was increased dramatically by preforming the anion. Recent work in our laboratories^{61} has shown that some fluorinated alkenes form stable perfluorinated carbanions by reaction with caesium fluoride under certain conditions. This remarkable work^{61}, involving observable fluorinated carbanion and the establishement of threshold temperatures for the onset of fluoride ion exchange, stimulated our approach using hexafluoropropene dimer with caesium fluoride.

The successful procedure to prepare a solution of carbanion was achieved by using the system CsF/sulpholane. In the current investigation, sulpholane was found to be the superior solvent ie. CsF/ DMF did not generate appreciable concentration of the anion to afford any perfluoroalkyl aromatic compounds[104, 111].

CONDITIONS OF THE REACTION

The synthetic route involved a two step procedure where the tertiary perfluorinated carbanion[61] (2) was preformed to react with the appropriate electrophile (3). The perfluorocarbanion was obtained by stirring a mixture containing hexafluoropropene dimer, caesium fluoride and a minimum of sulpholane at 30°C. The generation of the caesium salt was confirmed by ^{19}F NMR. The ^{19}F NMR spectrum, run in sulpholane using trichlorofluoromethane as the reference, showed the presence of four sharp peaks all singlet at -41.2 (6F, s, $(\underline{CF_3})_2C$), -79.7 (3F, s, $\underline{CF_3}CF_2$), -92.0 (2F, s, $\underline{CF_2}CF_2CF_3$), -125.4 (2F, s, $\underline{CF_2}CF_3$).


$(CF_3)_2C{=}CF{-}CF_2CF_3$
+
F^-
i
$(CF_3)_2\bar{C}{-}CF_2CF_2CF_3$
(1)
(2)
i, CsF; sulpholan; 30 °C
CH_2Br
CH_2R_F
$(CF_3)_2\bar{C}{-}CF_2CF_2CF_3$
+
ii
ii, 60°C
(3)
(4)
58% isolated yield
$R_F = C(CF_3)_2CF_2CF_2CF_3$

The reaction was monitored by ^{19}F NMR to check the completion of the reaction before the addition of the electrophile eg. $PhCH_2Br$. In these circumstances, the long-lived fluorocarbanion does not act as a potent source of fluoride ion but as a perfluoroalkylating agent. This is clear evidence of a competing transfer of fluoride ion from the carbanion in addition to the source of fluoride ion present in the solution. This fluoride ion exchange was found to occur predominently when the reaction was carried out at the above temperature of 70°C or alternatively for a short period of time as previously[61]. After addition of the bromo compound to the system, the temperature was raised to 60-69°C for 6 days. The alkylated product was synthesised in a relatively high yield 58%.

It is important to note that the formation of the anion is essential in the procedure to afford the substituted product in high yield; therefore dried and ground caesium fluoride are required as well as dry sulpholane. Yields of the reaction will be directly affected by the moisture present in the solvent and in the fluoride source. The ratio of benzyl fluoride to [(perfluoro-2-methylpentan-2-yl)methyl]benzene formed was found to be 1/6.5 and was separated from the product with a commercially available fluorocarbon solvent (Fluorinert FC-84, bp= 80°C).

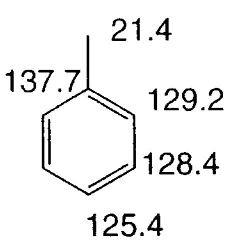
ISOLATION

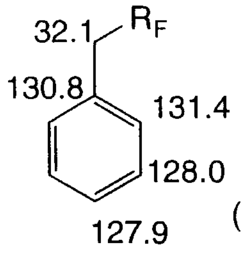
The feature that made our synthetic route very successful comes from the use of fluorocarbon solvents. Fluorocarbon fluids are not miscible with most organic solvents and therefore by simple extraction the required product was isolated and purified. Moreover, the perfluorinated solvent can be removed by distillation and completely recovered to the next extraction. The product: [(perfluoro-2-methylpentan-2-yl)methyl]benzene, was extracted from sulpholane and purified while the benzyl fluoride remained in the sulpholane layer.

This observation not only provides convenient methodology for the isolation step but also emphasises the potential value of these systems in producing a variety of products that are soluble in fluorocarbons.

SPECTROSCOPIC STUDIES: NMR

The ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded for the compound (4) in deuterated acetonitrile. From the ^{1}H spectrum, we can observe the following signals: two singlets at 7.11 ppm in the aromatic region (5H) and 3.36 ppm (2H) (lit.[104] 7.28 ppm and 3.44 ppm). To assign the ^{13}C, we compared the chemical values of toluene with these chemical shifts observed for our system[112].





(4)

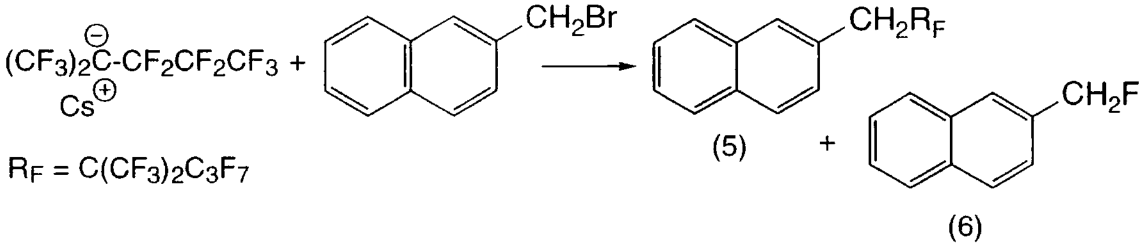
$R_F : C(CF_3)_2CF_2CF_2CF_3$

The chemical shifts did not change dramatically apart from the methylene bearing the perfluoroalkylated group which has a large downfield shift relative to the toluene. This is due to the electron-withdrawing effect of the perfluorinated segment. The ^{13}C NMR spectrum was particularly interesting in the region between 123 ppm and 61 ppm to assign the chemical shifts of the different carbons on the fluorinated aliphatic chain. The quaternary carbon gave a septuplet located upfield at 61.6 ppm (sept, $^{2}J_{CF}$ 25); the CF_3 had their chemical values upfield at 122.1 ppm (q, $^{1}J_{CF}$ 290) and 109.7 ppm (qt, $^{1}J_{CF}$ 290, $^{2}J_{CF}$ 34). Finally, the secondary carbons gave complex signals at 114.9 ppm (tt, $^{1}J_{CF}$ 270, $^{2}J_{CF}$ 33) and 109.7 ppm (tsext, $^{1}J_{CF}$ 271, $^{2}J_{CF}$ 37). The ^{19}F NMR spectrum of structure (4) consisted of four resonances (two CF_3 and two CF_2) of relative intensities 6:3:2:2 with the respectively following chemical shifts: -62.7 ppm

(CF_3), -80.5 ppm (CF_3), -106.4 ppm (CF_2) and -123.4 ppm (CF_2), consistant with the perfluoroalkyl branched segment: $R_F = C(CF_3)_2CF_2CF_2CF_3$.

II.3.C.2. PERFLUOROALKYLATION OF 2-(BROMOMETHYL) NAPHTHALENE

Similar two-step reaction between 2-(bromomethyl)naphthalene and hexafluoropropene dimer in the presence of caesium fluoride gave a mixture of two products 2-[(perfluoro-2-methylpentan-2-yl)methyl]naphthalene (5) and 2-(fluoromethyl)naphthalene (6).



58% isolated yield of (5)

Again the perfluorinated solvent was used to extract 2-[(perfluoro-2-methylpentan-2-yl)methyl]naphthalene (5) from sulpholane and to seperate it from 2-(fluoromethyl)naphthalene (6), as compound (5) was the only material soluble in perfluorocarbon solvent.

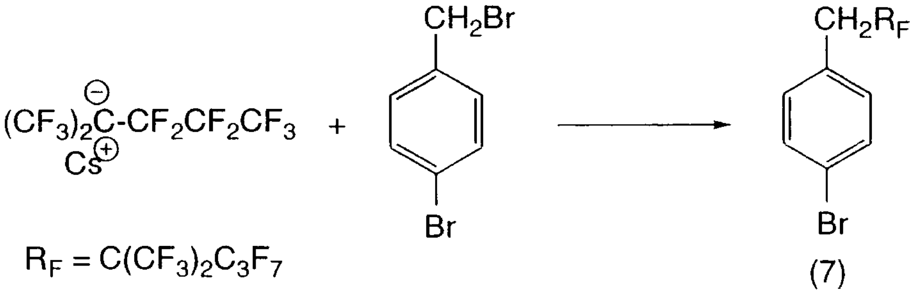
SPECTROSCOPIC STUDIES: NMR AND IR

The ^1H NMR spectra consists of two peaks one multiplet in the range of 7.8-7.3 ppm (protons on the naphthalene ring) and one singlet at 3.67 ppm. The ^{19}F chemical shifts were recorded as expected for the side chain R_F. The result of the complete analysis of the spectra is given in section spectrum No 4. The infra Red spectra was recorded on KBr pastille. The Bolhmann bands at 1602 and 1453 cm^{-1} are due to the presence of double bonds of the aromatic systems, a broad peak is observed between 1263 and 1218 cm^{-1} which is due to C-F bond.

II.3.C.3. PERFLUOROALKYLATION OF 4-BROMOBENZYL BROMIDE

As the introduction of the perfluorohexyl group proved so successful via the two stage fluoride ion induced methodology, the method was extended to other bromomethyl derivatives such as the bromobenzyl bromide.

The alkylated product was synthesised in a relatively high yield by a two-stage process. 4-bromobenzyl fluoride was formed in trace quantities and was separated from the main product (7) with a perfluorinated solvent (Fluorinert: FC-84, bp 80 °C).

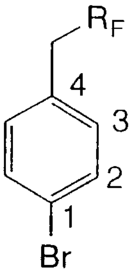


(7)
62% isolated yield

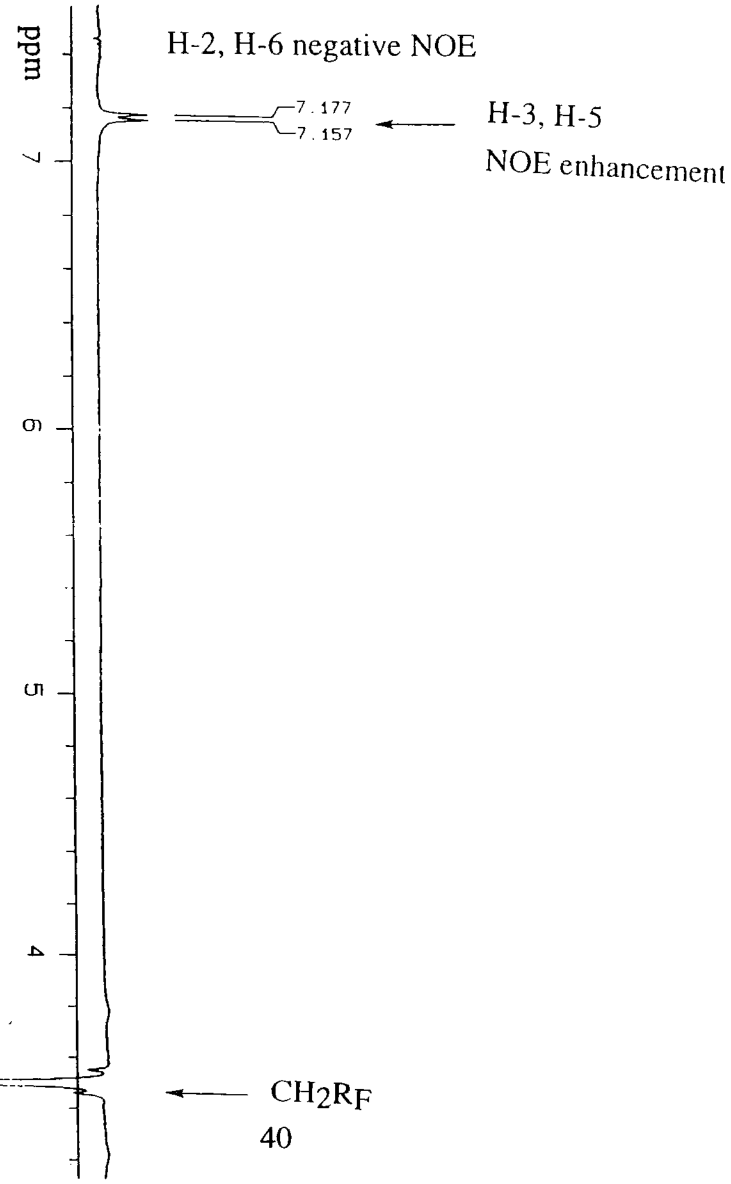
SPECTROSCOPIC STUDIES: NMR

Compound (7) presents two pairs of chemically equivalent protons, H-2/6 and H-3/5 but are magnetically inequivalent; the spectrum is a AA'XX' system.

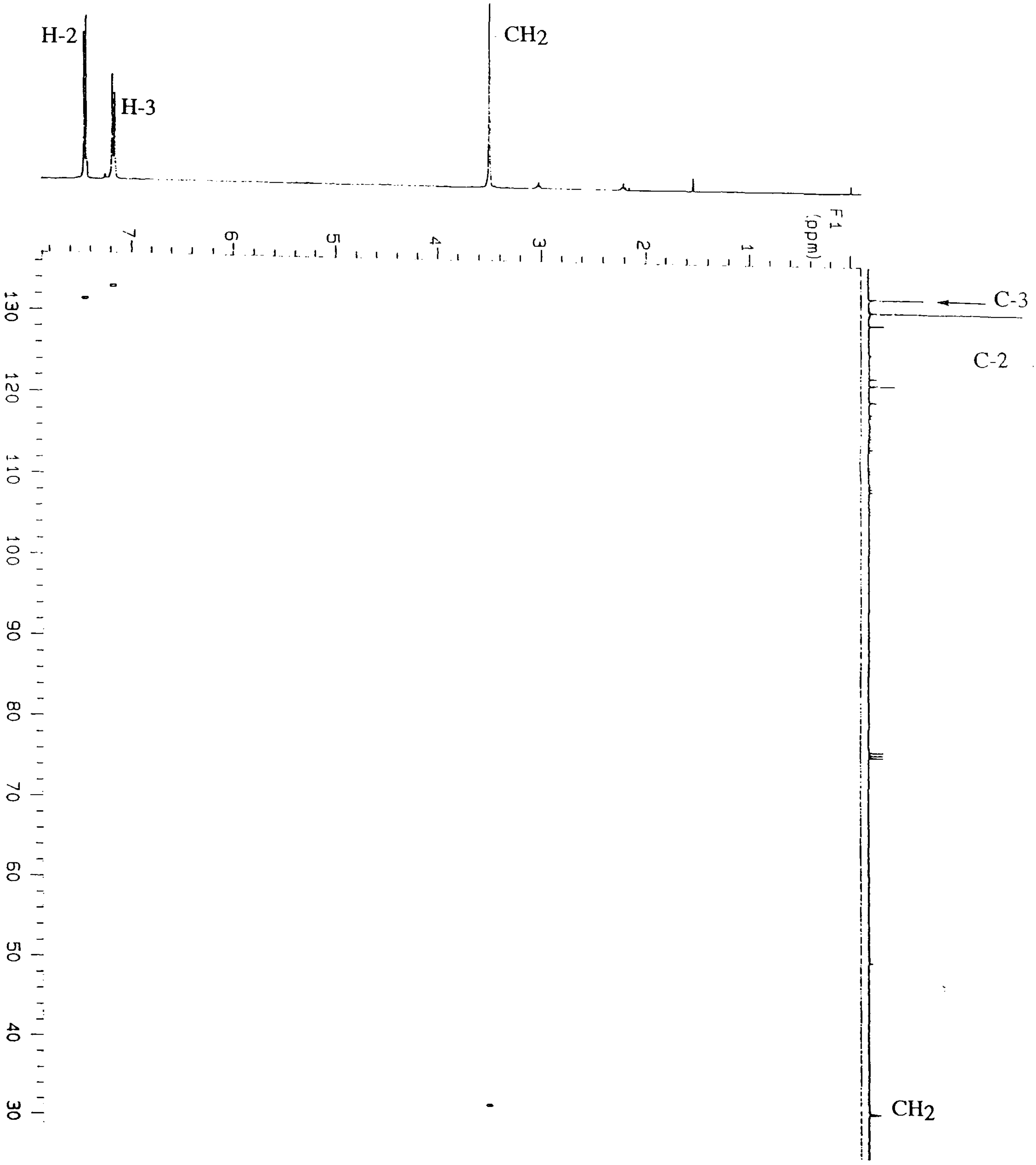
The question of whether the chemical shift δ3= δ5 is higher than δ2=δ6 could not be answered from either the ^1H or the ^{13}C NMR spectrum. A NOE experiment provided a decision in favor of the correct values. Irradiating the CH_2R_F resonance gave an increase in the intensities of the signals of the ring protons H3 and H5. From this we concluded that positions H3 and H5 have the lowest chemical shift δ(H-3, 5)= 7.16 ppm. In contrast, the signals of the ring protons H2 and H6 showed a negative NOE, proving as expected that δ(H-2, 6)= 7.44 ppm (see spectrum below).



$R_F= C(CF_3)_2CF_2CF_2CF_3$



For ^{13}C NMR, the method described below enabled us to decide which of the two ^{1}H NMR signals at δ= 7.16 and 7.44 ppm belongs to C-2 and which to C-3. This was possible from the two dimensional correlated NMR spectroscopy (H,C) COSY spectrum. We proceeded via the correlation peak for δH= 7.16 attributed earlier to (H-3, 5) to δC= 133.1 ppm. The signal was assigned as follow: δ(C-3, 5)= 133.1 ppm.



Introducing substituents extends the range of chemical shifts and to a good approximation the substituent effects are additive. Furthermore, perfluoroalkyl substituted benzene was treated as toluene derivative ($\delta(CH_2R_F)=\delta(CH_3)$). We used the following predicting chemical shifts[112] to predict the chemical shifts for δ(C-1) and δ(C-4) and the empirical equation shown below:.

$$\delta = 128.5 + \Sigma S$$

X	S1	So	Sm	Sp
CH_3	9.2	0.7	-0.1	-3.1
Br	-5.8	3.2	1.6	-1.6
NO_2	19.9	-4.9	0.9	6.1
NH_2	18.2	-13.4	0.8	-10.0

^{13}C Chemical shifts of monosubstituted benzene

$\delta(C\text{-}1) = 128.5 + S1(Br) + Sp(CH_3) = 128.5 - 5.8 - 3.1 = 119.6$ ppm

experimental: 122.5 ppm

$\delta(C\text{-}2) = 128.5 + So(Br) + Sm(CH_3) = 128.5 + 3.2 - 0.1 = 131.6$ ppm

experimental: 131.4 ppm

$\delta(C\text{-}3) = 128.5 + Sm(Br) + So(CH_3) = 128.5 + 1.6 + 0.7 = 130.8$ ppm

experimental: 133.1 ppm

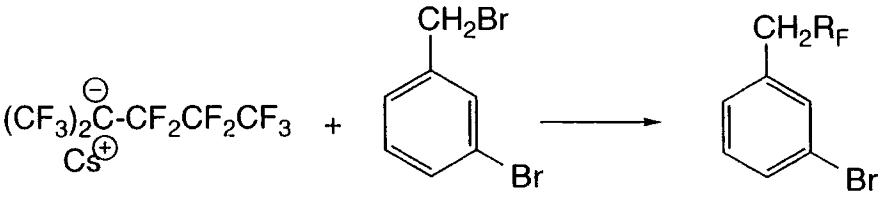
$\delta(C\text{-}4) = 128.5 + Sp(Br) + S1(CH_3) = 128.5 - 1.6 + 9.2 = 136.1$ ppm

experimental: 129.9 ppm

The result of the complete analysis of the spectrum is given in section Spectrum No 5.

II.3.C.4. PERFLUOROALKYLATION OF 3-BROMOBENZYL BROMIDE

Under similar conditions, 3-bromobenzyl bromide was polyfluoroalkylated successfully in good yield to give the corresponding 1-bromo-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene. The 3-bromobenzyl fluoride as a side-product was detected only in a trace amount.


$(CF_3)_2\overset{\ominus}{C}\text{-}CF_2CF_2CF_3$ $Cs^{\oplus}$
+
CH_2Br
Br
CH_2R_F
Br

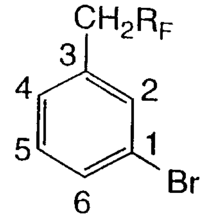
(8)

$R_F = C(CF_3)_2C_3F_7$

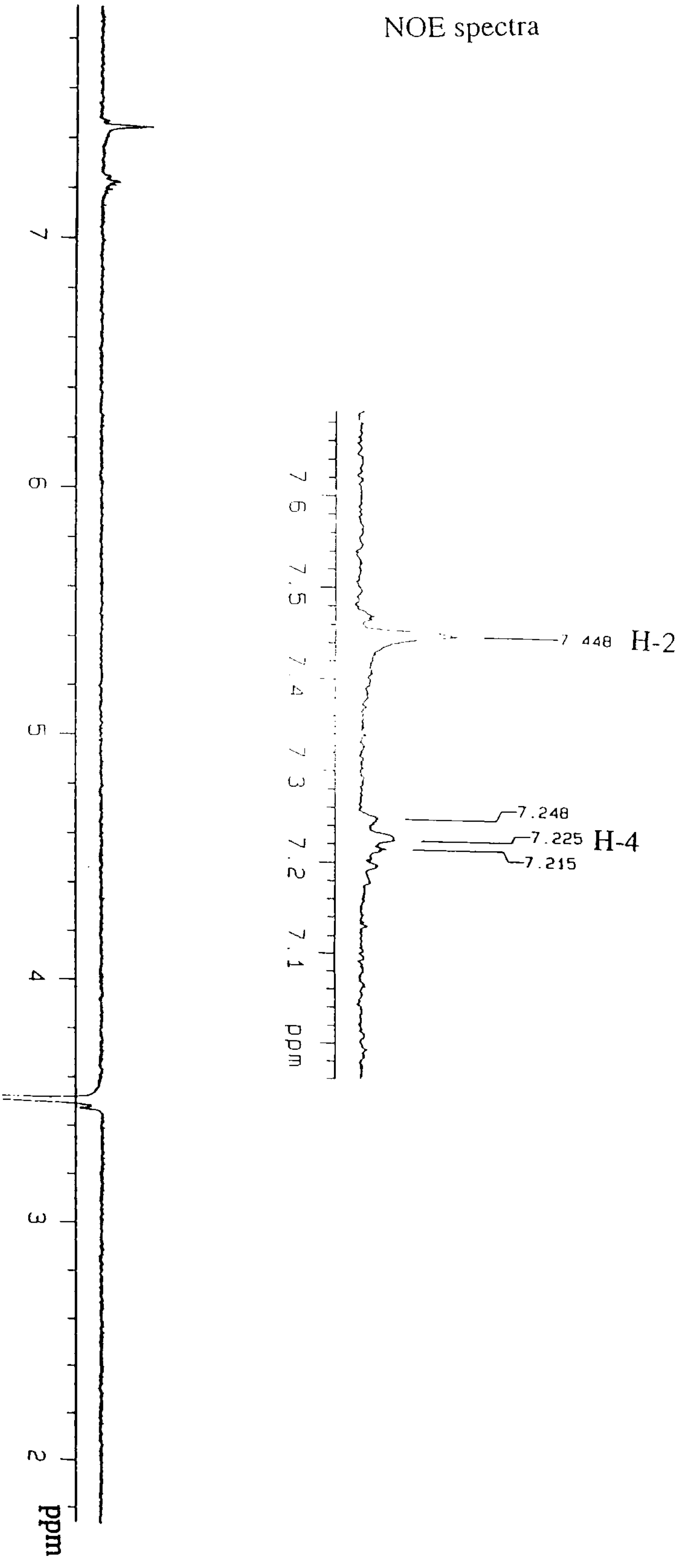
64% isolated yield

SPECTROSCOPICAL STUDIES: NMR

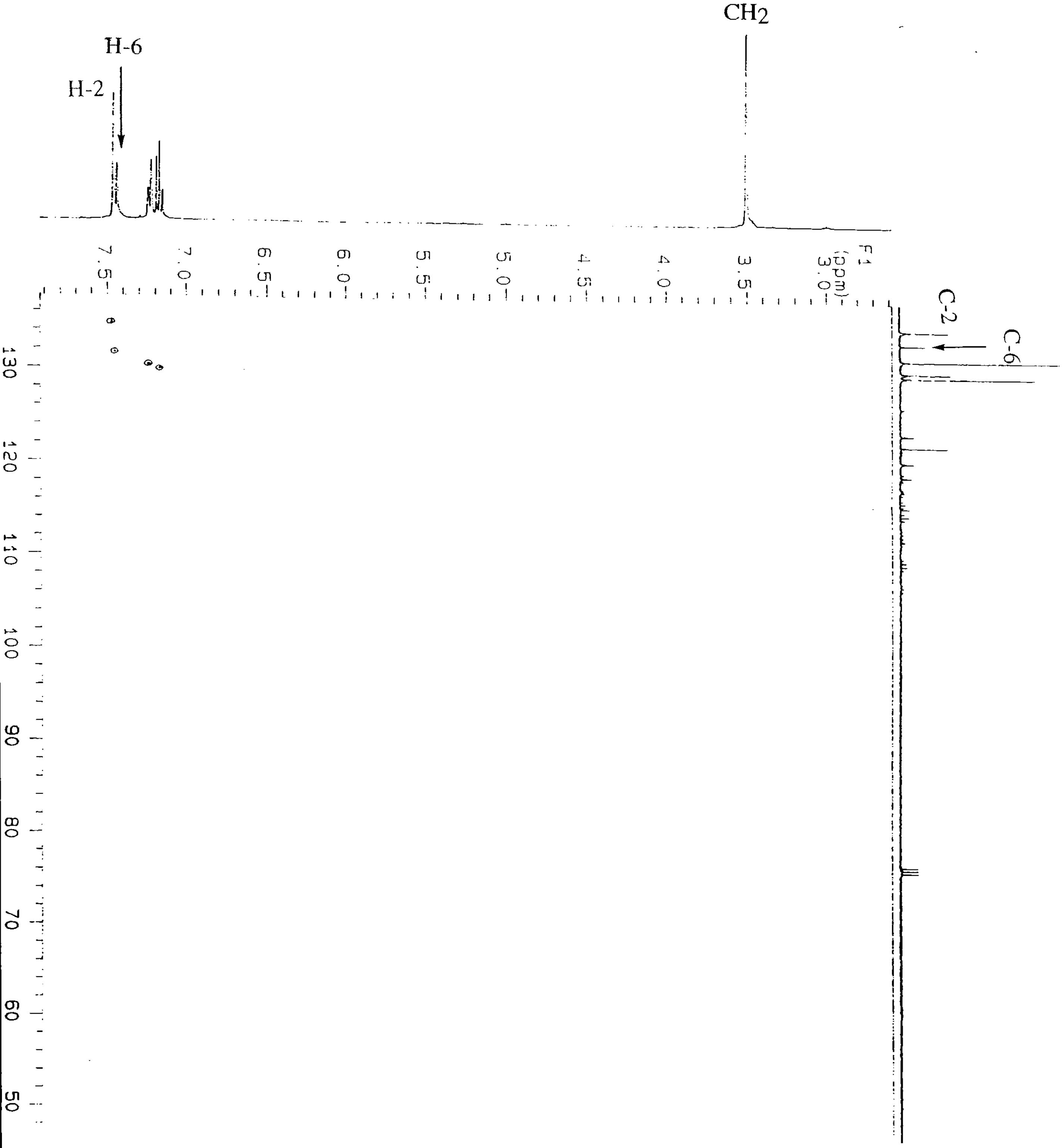
The NOE experiment proved as expected that δ(H-2) and δ(H-4) were respectively 7.45 ppm (s) and 7.22 ppm (d, $^3J_{HH}$ 7.2), as shown below. From these results, δ(H-5) and δ(H-6) could be deduced as followed: δ(H-5)= 7.16 ppm (t, $^3J_{HH}$ 7.6), δ(H-6)= 7.44 ppm (d, $^3J_{HH}$ 8.4).



R_F= $C(CF_3)_2CF_2CF_2CF_3$



The two dimensional correlated NMR spectroscopy (H,C) COSY spectrum provided the proof of our assessment concerning δ(C-2), δ(C-4), δ(C-5) and δ(C-6).



We used the following predicting chemical shifts[112] to predict the chemical shifts for δ(C-1) and δ(C-3), see section II.3.C.3.

δ(C-1)= 128.5 + S1(Br) + Sm(CH_3) = 128.5 - 5.8 - 0.1= 122.6 ppm

experimental: 122.3 ppm

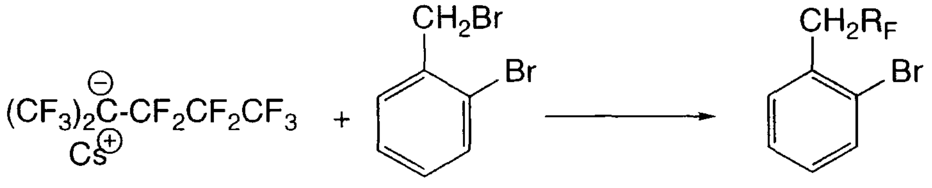
δ(C-3)= 128.5 + Sm(Br) + S1(CH_3) = 128.5 + 1.6 + 9.2= 139.3 ppm

experimental: 129.7 ppm

The result of the complete analysis of the spectrum is given in section Spectrum No 6.

II.3.C.5. PERFLUOROALKYLATION OF 2-BROMOBENZYL BROMIDE

The reaction between 2-bromobenzyl bromide and hexafluoropropene dimer in the presence of caesium fluoride afforded 1-bromo-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene in a relative low yield. The low reactivity of the *o*-isomer towards the nucleophilic substitution is most likely to be due to steric hindrance by the *ortho*-bromine.



$R_F = C(CF_3)_2C_3F_7$

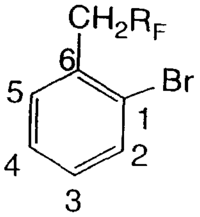
(9)

34% isolated yield

Again, *o*-bromobenzyl fluoride was formed as a trace. The use of Fluorinert (FC-84, bp 80 °C) allowed us to extract the perfluoroalkylated product from sulpholane and to separate it from the benzyl fluoride derivative.

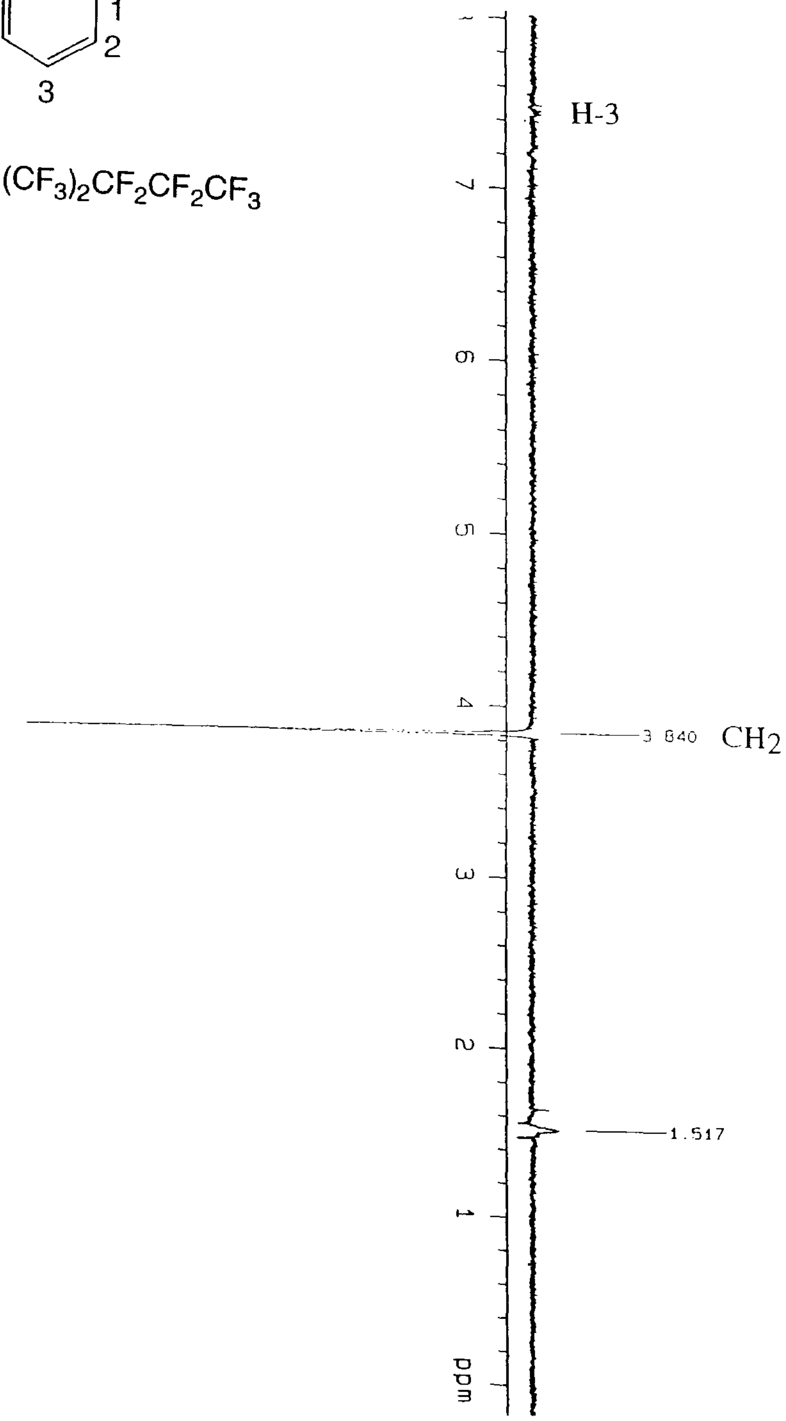
SPECTROSCOPIC STUDIES: NMR

The NOE experiment provided the necessary information to assign δ(H-3)= 7.43 ppm.

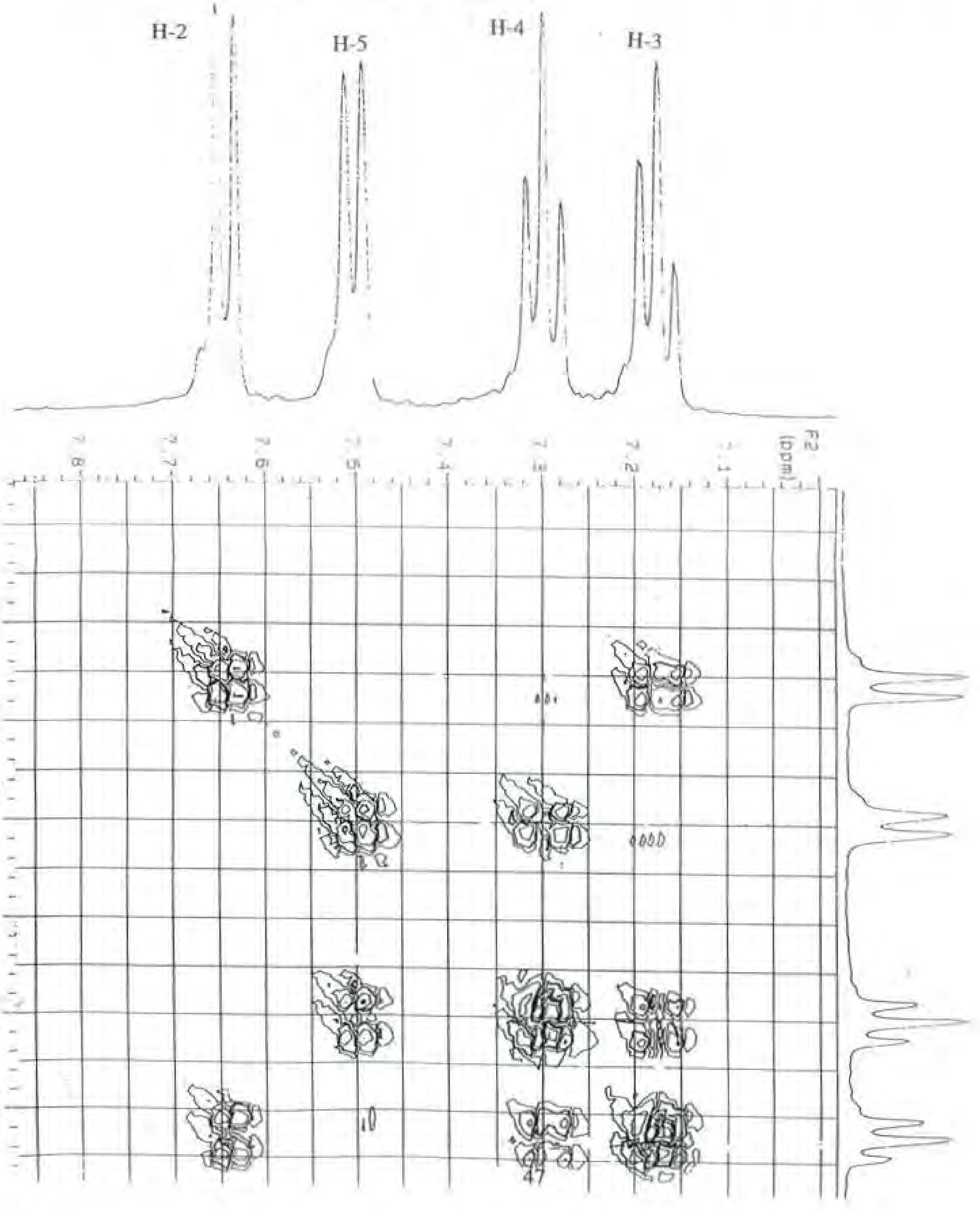

CH2RF
6
Br
1
2
3
4
5

$R_F= C(CF_3)_2CF_2CF_2CF_3$

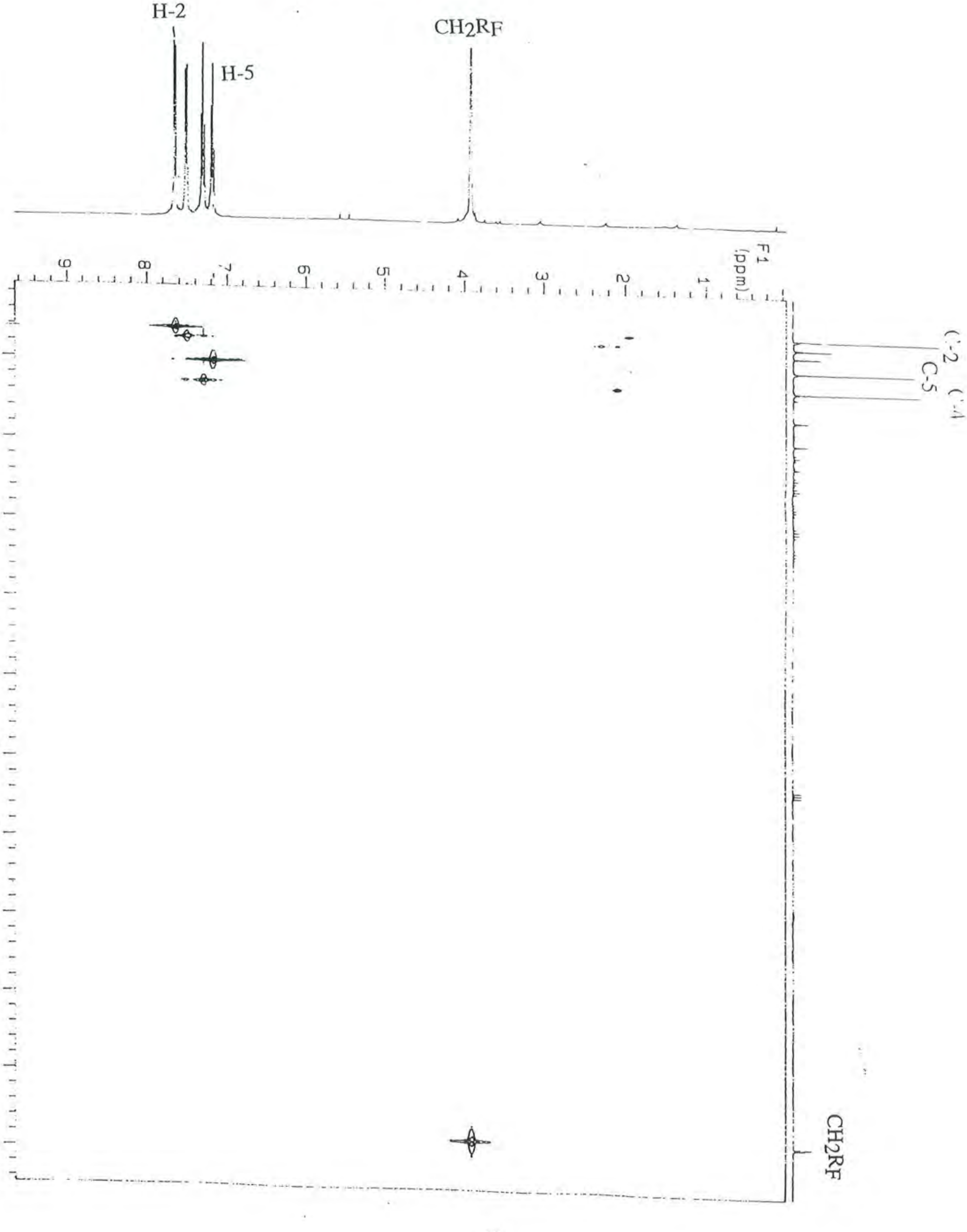
NOE spectra



The two dimensional correlated NMR spectroscopy (H,H) COSY was required to assign the ^{1}H signals. From the unambiguously assigned signal of H-3, the cross peak immediately indicated the position of H-4 as a triplet at 7.25 ppm (t, $^3J_{HH}$ 7.6). From which we determined the position of the signal (H-5) as a triplet 7.13 ppm (t, $^3J_{HH}$ 7.9). To continue the analysis of the spectrum we linked (H-5) to (H-6) which led us to the following assignements: δ(H-4)= 7.25 ppm (t, $^3J_{HH}$ 7.6); δ(H-5)= 7.13 ppm (t, $^3J_{HH}$ 7.9); δ(H-2)= 7.59 ppm (t, $^3J_{HH}$ 7.9).



The two dimensional correlated NMR spectroscopy (H,C) COSY enabled us to determine the following chemical shifts: δ(C-3)= 132.6 ppm, δ(C-4)= 127.2 ppm, δ(C-5)= 129.7 ppm, δ(C-6)= 133.7 ppm.



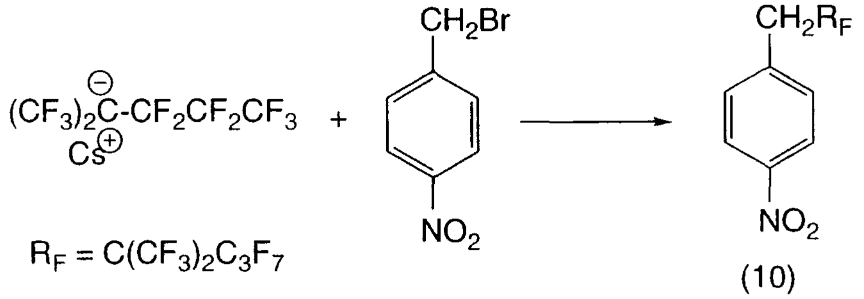
We used the following predicting chemical shifts[112] to assess δ(C-1) and δ(C-2) as described previously section II.3.C.3.

δ(C-1)= 128.5 + S1(Br) + So(CH3) = 128.5 - 5.8 + 0.7= 123.4 ppm
experimental: 127.2 ppm
δ(C-2)= 128.5 + So(Br) + S1(CH3) = 128.5 + 3.2 - 0.1= 140.9 ppm
experimental: 131.5 ppm

The result of the complete analysis of the spectrum is given in section Spectrum No 7.

II.3.C.6. PERFLUOROALKYLATION OF 4-NITROBENZYL BROMIDE

It was found that the reaction between 4-nitrobenzyl bromide and perfluoro-2-methylpentan-2-yl anion, derived from hexafluoropropene dimer and caesium fluoride, afforded the corresponding perfluoroalkylated product 1-nitro-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene in reasonable high yield. No trace of 1-nitro-4-(fluoromethyl)benzene was detected. The method was extended to the *m*- nitro isomer.



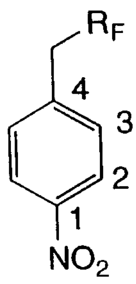
(10)

60% isolated yield

SPECTROSCOPIC STUDIES: NMR

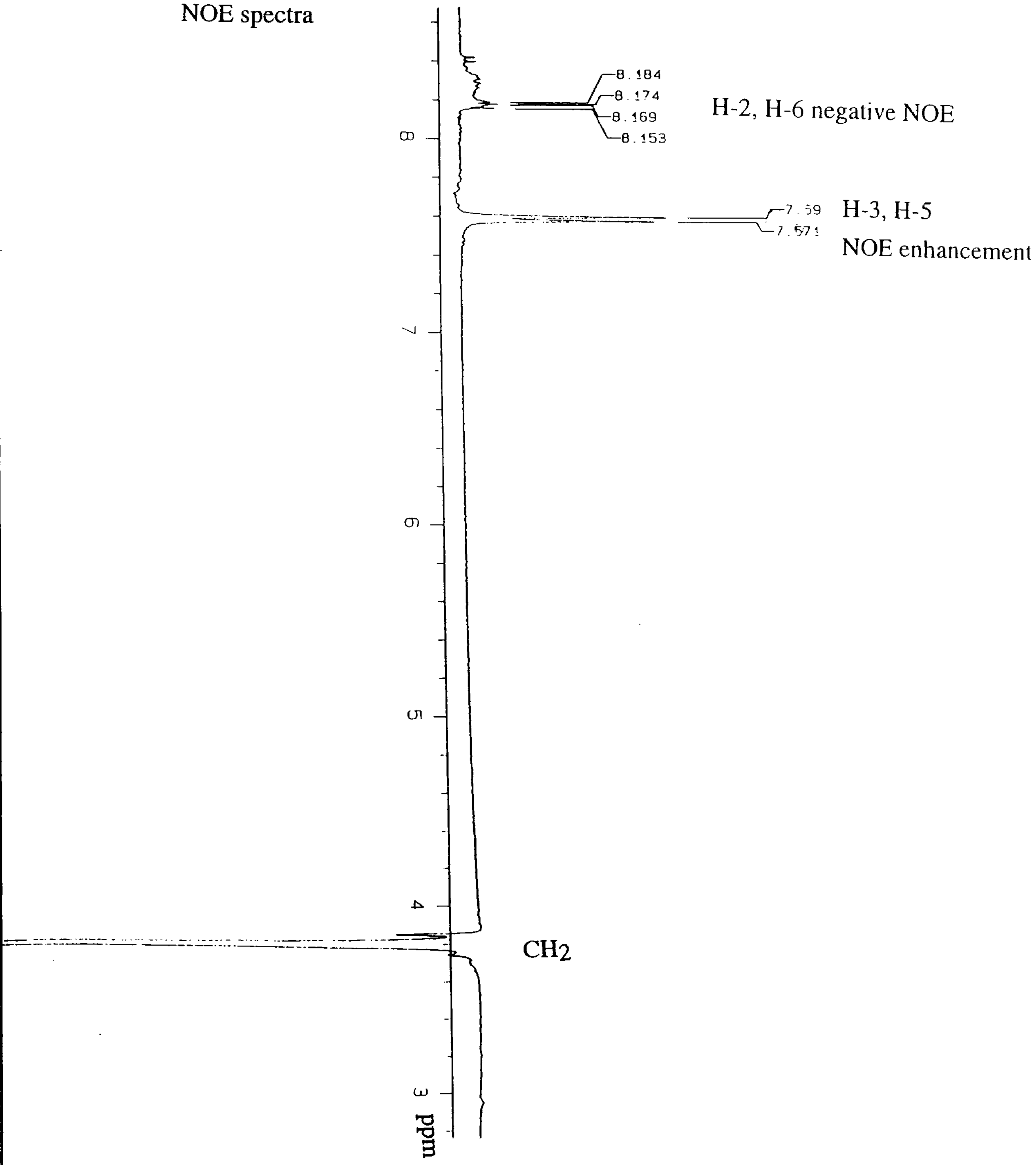
This system present two pairs of chemically equivalent protons, H-2/6 and H-3/5 but magnetically inequivalent: the spectrum is a AA'XX' system.

The NOE experiment provided enough information to assign δ(H-2, 6)= 8.16 ppm and δ(H-3, 5)= 7.58 ppm.

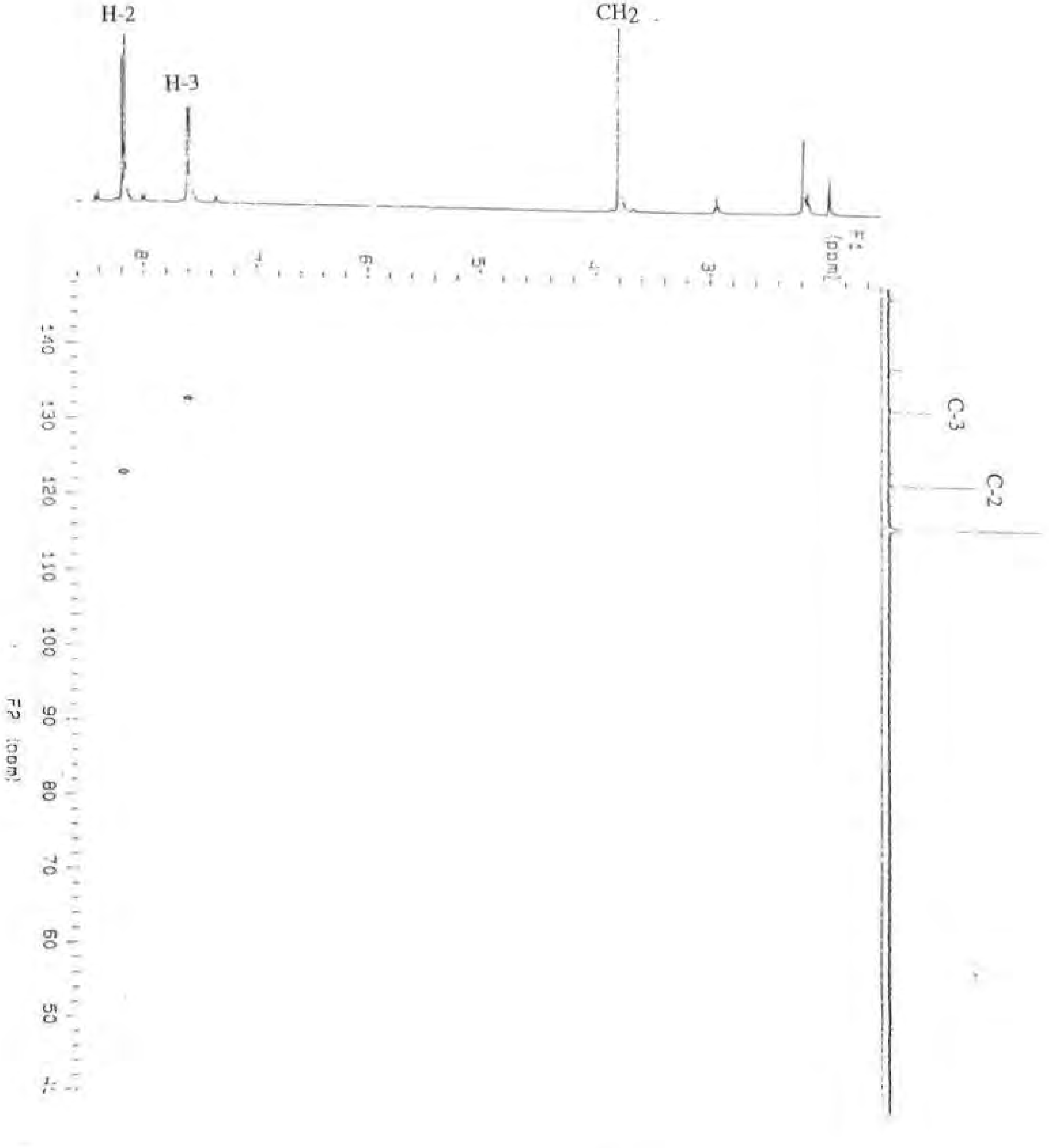


$R_F= C(CF_3)_2CF_2CF_2CF_3$

NOE spectra



A two dimensional correlated NMR spectroscopy (H,C) COSY spectrum was erequired to assign correctly δ(C-3,5)= 133.9 ppm and δ(C-2,6)= 124.1 ppm.



We used the following predicting chemical shifts[112] to assess the chemical shifts for ^{13}C NMR spectra, see section II.3.C.3.

δ(C-1)= 128.5 + S1(NO_2) + Sp(CH_3) = 128.5 + 19.9 - 3.1= 145.3 ppm

experimental: 148.8 ppm

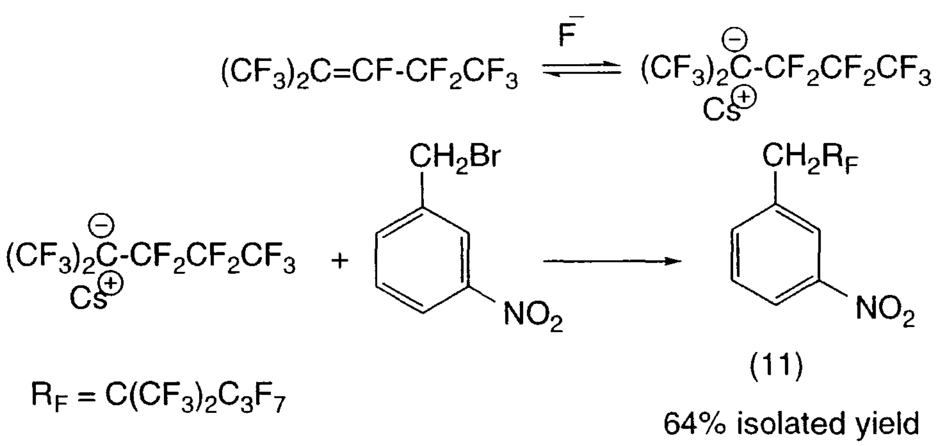
δ(C-4)= 128.5 + Sp(NO_2) + S1(CH_3) = 128.5 - 10 + 9.2= 127.7 ppm

experimental: 139.6 ppm

The result of the complete analysis of the spectrum is given in section Spectrum No 8.

II.3.C.7. PERFLUOROALKYLATION OF 3-NITROBENZYL BROMIDE

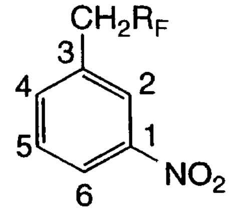
The reaction between 3-nitrobenzyl bromide and hexafluoropropene dimer in the presence of caesium fluoride, afforded the corresponding perfluoroalkylated product 1-nitro-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene in high yield.



The formation of the corresponding nitro benzyl fluoride was not observed. The polyfluorinated products were extracted and isolated with Fluorinert: FC-84, bp=80°C.

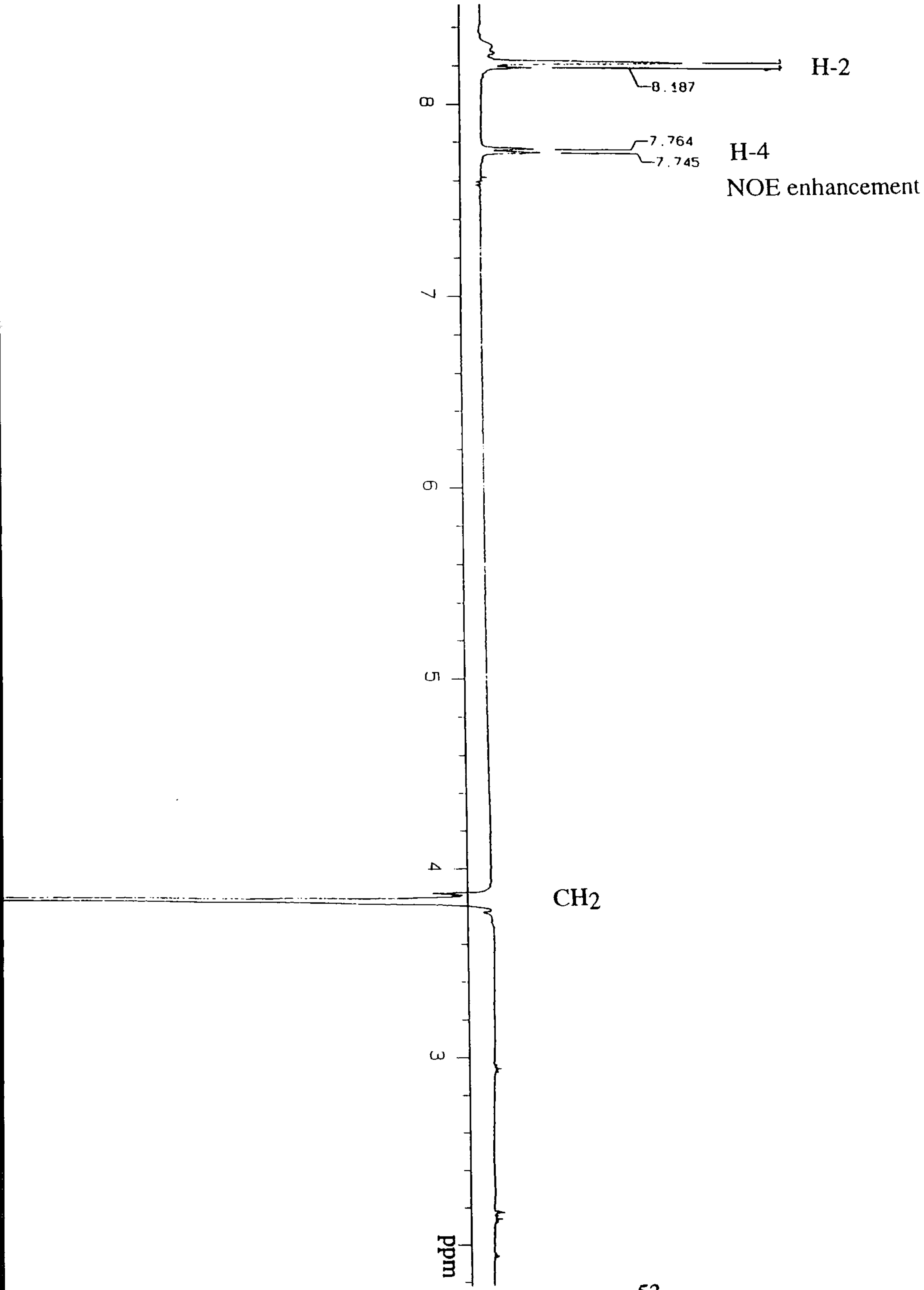
SPECTROSCOPICAL STUDIES: NMR

The NOE experiment proved that δ(H-2) and δ(H-4) were respectively 8.2 ppm (s) and 7.75 ppm (d, $^3J_{HH}$ 7.6). The values of H_5 and H_6 were deduced δ(H-5)= 7.58 ppm (t, $^3J_{HH}$ 8) and δ(H-6)= 8.19 ppm (d, $^3J_{HH}$ 8.8).

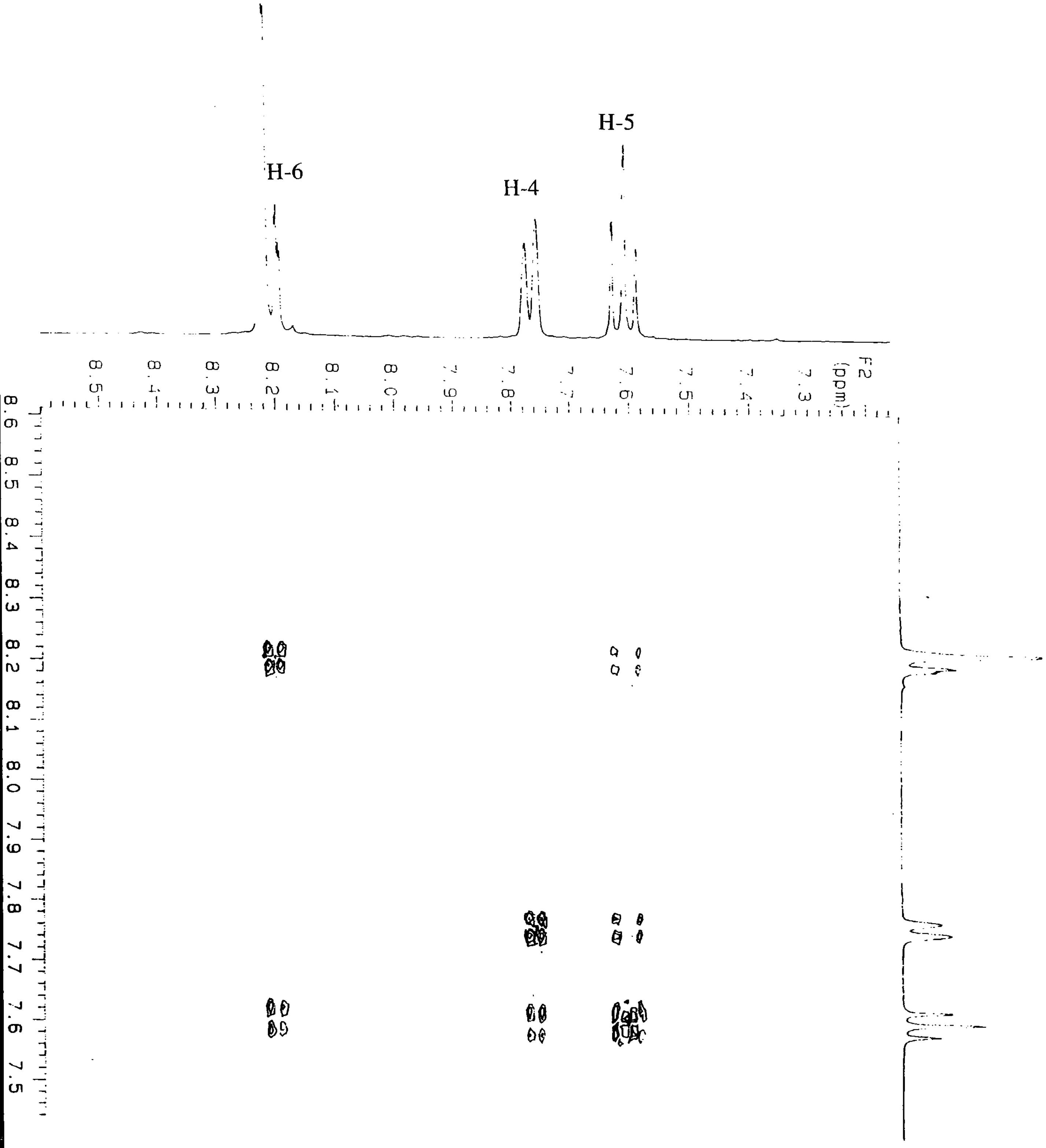

CH2RF
3
2
4
1
5
NO2
6

NOE spectra

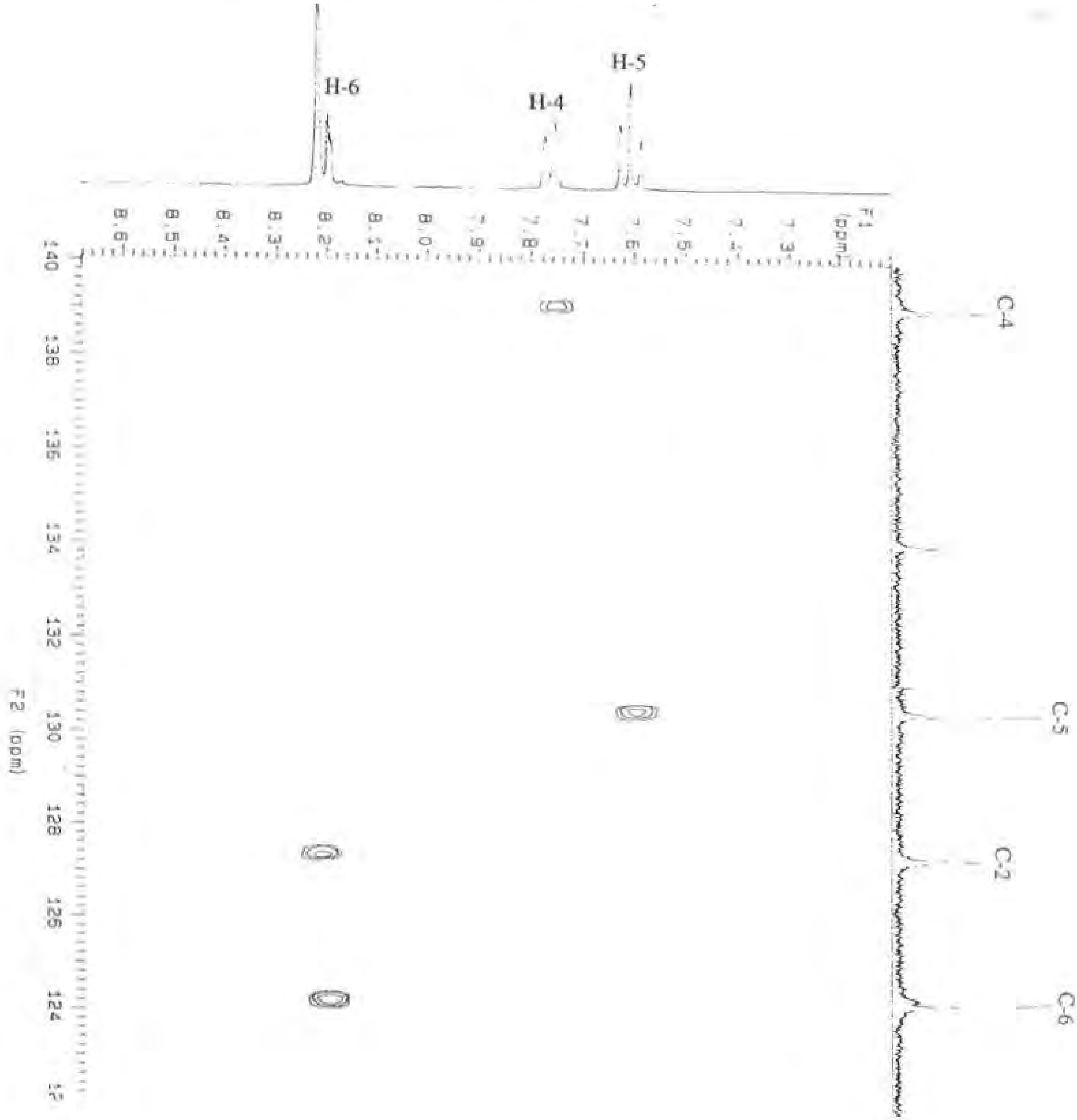
$R_F = C(CF_3)_2CF_2CF_2CF_3$



The two dimensional correlated NMR spectroscopy (H,H) COSY was required to assign the ^{1}H signals. From the unambiguously assigned signal of H-5: δ(H-5)= 7.58 ppm (t, $^3J_{HH}$ 8), the cross peak immediately indicated the position of H-2 and H-4. This information combined with NOE experiment provided enough information to determine the position of the signals and led us to the following assignements: δ(H-2)= 8.2 ppm (s); δ(H-4)= 7.75 ppm (d, $^3J_{HH}$ 7.6); δ(H-5)= 7.58 ppm (t, $^3J_{HH}$ 8); δ(H-6)= 8.19 ppm (d, $^3J_{HH}$ 8.8).



The method described below enabled us to decide which of the two ^{1}H NMR signals at δ= 8.19 and 7.75 ppm belongs to C-4 and which to C-6. This was possible from the two dimensional correlated NMR spectroscopy (H,C) COSY spectrum. We proceeded via the correlation peak for δH= 8.19 attributed earlier to (H-6) to δC= 124.3 ppm. All the signals were assigned as described.



We used the following predicting chemical shifts[112] to assess δ(C-1) and δ(C-3), see section II.3.C.3.

$\delta(C\text{-}1) = 128.5 + S1(NO_2) + Sm(CH_3) = 128.5 - 5.8 - 3.1 = 119.6$ ppm

experimental: 149.0 ppm

$\delta(C\text{-}3) = 128.5 + Sm(NO_2) + S1(CH_3) = 128.5 + 0.9 + 9.2 = 138.6$ ppm

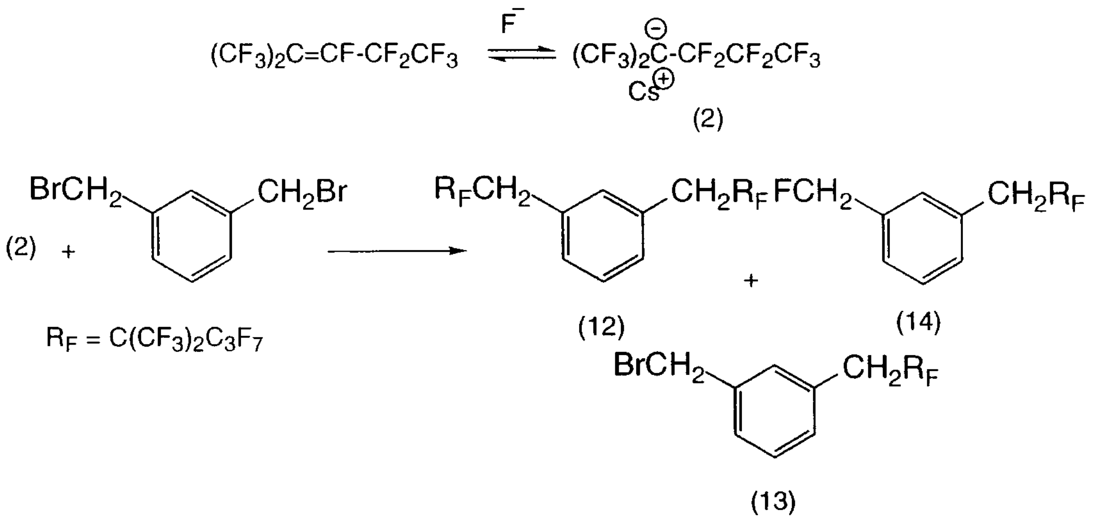
experimental: 134.1 ppm

The result of the complete analysis of the spectrum is given in section Spectrum No 9.

II.3.C.8. DIPERFLUOROALKYLATION: WITH 1,3-XYLYLENE DIBROMIDE

The perfluoroalkylation reaction was extended to more complex systems such as a xylylene dibromide and a bis(bromomethyl)pyridine to give di-perfluoroalkylated products.

The perfluoroalkylation reaction of 1,3-xylylene dibromide was carried out in sulpholane with caesium fluoride and a big excess of hexafluoropropene dimer in the ratio of 1:4.


F^-
$(CF_3)_2C{=}CF\text{-}CF_2CF_3$
$(CF_3)_2\overset{\ominus}{C}\text{-}CF_2CF_2CF_3$
$Cs^{\oplus}$
(2)
$BrCH_2$
CH_2Br
(2) +
$R_F = C(CF_3)_2C_3F_7$
R_FCH_2
CH_2R_F
R_FCH_2
CH_2R_F
+
(12)
(14)
$BrCH_2$
CH_2R_F
(13)

Three major compounds (12), (13), (14) were formed with 100% conversion. The reaction has been carried out varying the time to afford only compounds (12) and (14) as shown next page.

	RATIO		
time after addition of dibromo-compound	(12)	(13)	(14)
15 hours	2.3	1	1.6
24 hours	3.2	1	1.2
48 hours	6.5	1	1.5
5 days	4.2	0	1
8 days	4.2	0	1

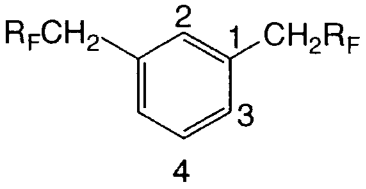
The bromo intermediate (13) disappeared after 5 days. In the case of the di-alkylation reaction, two products were formed and isolated.

ISOLATION

Again, the feature that made our synthetic route very successful comes from the use of fluorocarbon solvents. The two perfluoroalkylated compounds 1,3-xylylene-bis(perfluoro-2-methylpentan-2-yl) (12) and 1-fluoromethyl-3-methyl(perfluoro-2-methylpentan-2-yl)benzene (14) were extracted from sulpholane by a perfluorinated solvent: FC-84, bp. 80°C. Then, by simple column chromatography the two products were purified. A good yield of bis-alkylated product (56% of isolated yield) was formed and the mono-alkylated material was also isolated (21%).

SPECTROSCOPIC STUDIES: NMR

1,3-Xylylene-bis (perfluoro-2-methylpentan-2-yl) (12)



The chemical shifts for ^{13}C NMR spectra were assigned using the following predicting ^{13}C chemical shifts of monosubstituted benzene[112], where to a good approximation the substituent effects are additive. We also used ^{13}C NMR coupled, which indicated the number of carbons directly attached to protons, see section II.3.C.3. This was particularly useful to assign δ(C-1)= 131.5 ppm.

δ(C-1)= 128.5 + S1(CH_3) + Sm(CH_3) = 128.5 + 9.2 - 0.1= 137.6 ppm

experimental: 131.5 ppm

δ(C-2)= 128.5 + So(CH_3)x2 = 128.5 + 0.7x2= 129.9 ppm

experimental: 128.3 ppm

δ(C-3)= 128.5 + Sp(CH_3) + So(CH_3) = 128.5 - 3.1 + 0.7= 126.1 ppm

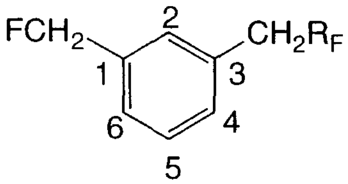
experimental: 131.7 ppm

δ(C-4)= 128.5 + Sm(CH_3)x2 = 128.5 - 0.1x2= 128.3 ppm

experimental: 135.1 ppm

The result of the complete analysis of the spectrum is given in section Spectrum No 10.

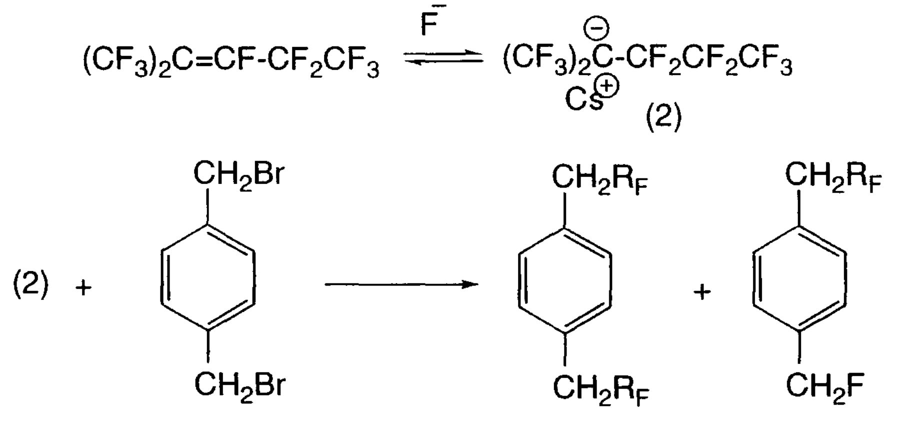
1-Fluoromethyl-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (14)



In order to interprete the ^{13}C NMR spectra, a DEPT (distortionless enhancement by polarization transfer) experiment was required to know which signals belong to quaternary, CH carbon nuclei. This led us to the conclusion that δ(C-1)= 136.5 ppm (d, $^2J_{CF}$ 17) and δ(C-3)= 131.5 ppm (s). The result of the complete analysis of the spectrum is given in section Spectrum No 11.

II.3.C.9. DIPERFLUOROALKYLATION OF WITH 1,4-XYLYLENE DIBROMIDE

In a similar experiment, the perfluoroalkylation reaction of 1,4-xylylene dibromide with hexafluoropropene dimer afforded the bis-alkylated product 1,4-xylylene-bis(perfluoro-2-methylpentan-2-yl) (15) in 59% and the mono-alkylated derivative 1-fluoromethyl-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (16) in 22% yield.



$R_F = C(CF_3)_2C_3F_7$

(15) (16)

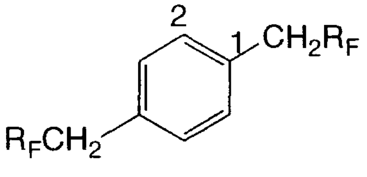
4.8 : 1

59 % isolated yield of (15)

Similarly, the two perfluoroalkylated compounds 1,4-xylylene-bis(perfluoro-2-methylpentan-2-yl) (15) and 1-fluoromethyl-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (16) were extracted from sulpholane by a perfluorinated solvent: FC-84, bp. 80°C. Then, by simple column chromatography the two products were purified. A good yield of bis-alkylated product (59% of isolated yield) was formed and the mono-alkylated material was also synthesised (22%).

SPECTROSCOPIC STUDIES: NMR

1,4-Xylylene-bis(perfluoro-2-methylpentan-2-yl) (15)



From the ^1H spectrum we can observe: a single peak δ= 7.26 ppm with an integration of four hydrogens. The ^{13}C NMR of the aromatic ring gave two sharp peaks corresponding to δ(C-1)= 131.1 ppm (quaternary carbon and therefore lower intensity) and δ(C-2)= 131.4 ppm. The result of the complete analysis of the spectrum is given in section Spectrum No 12.

1-Fluoromethyl-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (16)

The assignements for the carbon chemical shifts were more straight forward due to the different values of coupling constants. The result of the complete analysis of the spectrum is given in section Spectrum No 13.

II.3.C.10. DIPERFLUOROALKYLATION OF WITH 1,2-XYLYLENE DIBROMIDE

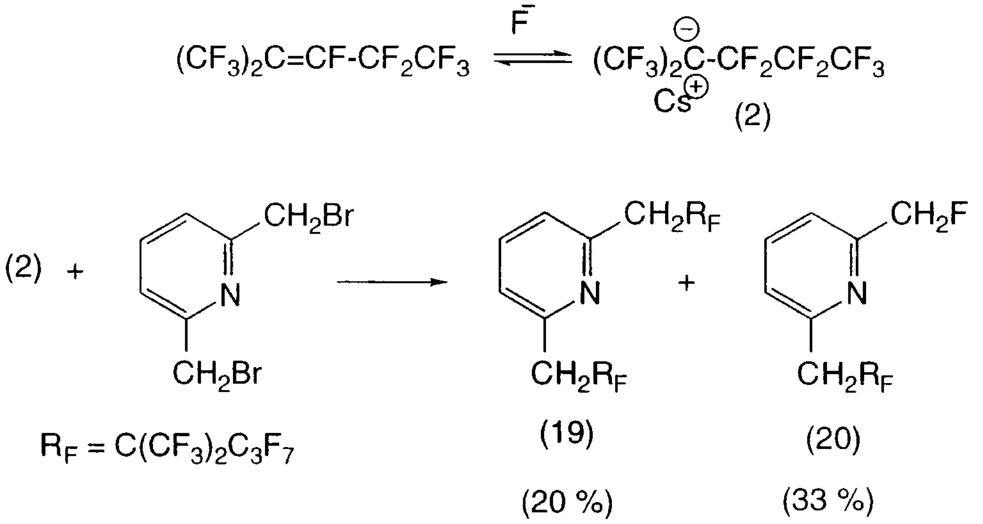
In this case, the reaction between 1,2-xylylene dibromide and hexafluoropropene dimer in the presence of caesium fluoride afforded predominently the mono-alkylated compound 1-fluoromethyl-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (18), the bis-alkylated 1,2-xylylene-bis(perfluoro-2-methylpentan-2-yl) (17) was obtained, after purification, in only 12% yield.

1-Fluoromethyl-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (18)

Simillarly, the chemical shifts of the ^{13}C NMR spectra of structure (18) were determined by comparing intensity and width of the peaks and assessing the right coupling constants. The result of the complete analysis of the spectrum is given in section Spectrum No 15.

II.3.C.11. DIPERFLUOROALKYLATION OF 2,6-BIS(BROMOMETHYL) PYRIDINE

Similar two-step reaction between 2,6-bis(bromomethyl)pyridine and hexafluoropropene dimer in the presence of caesium fluoride gave a mixture of two products 2,6-bis[(perfluoro-2-methylpentan-2-yl)methyl]pyridine (19) and 2-fluoromethyl-6-[(perfluoro-2-methylpentan-2-yl)methyl]pyridine (20).



After extraction using a perfluorinated solvent: FC-84, bp. 80^{o}C and a separartion by column chromatography two compounds 2,6-bis[(perfluoro-2-methylpentan-2-yl)methyl]pyridine (19) and 2-fluoromethyl-6-[(perfluoro-2-methylpentan-2-yl)methyl]pyridine (20) were purified.

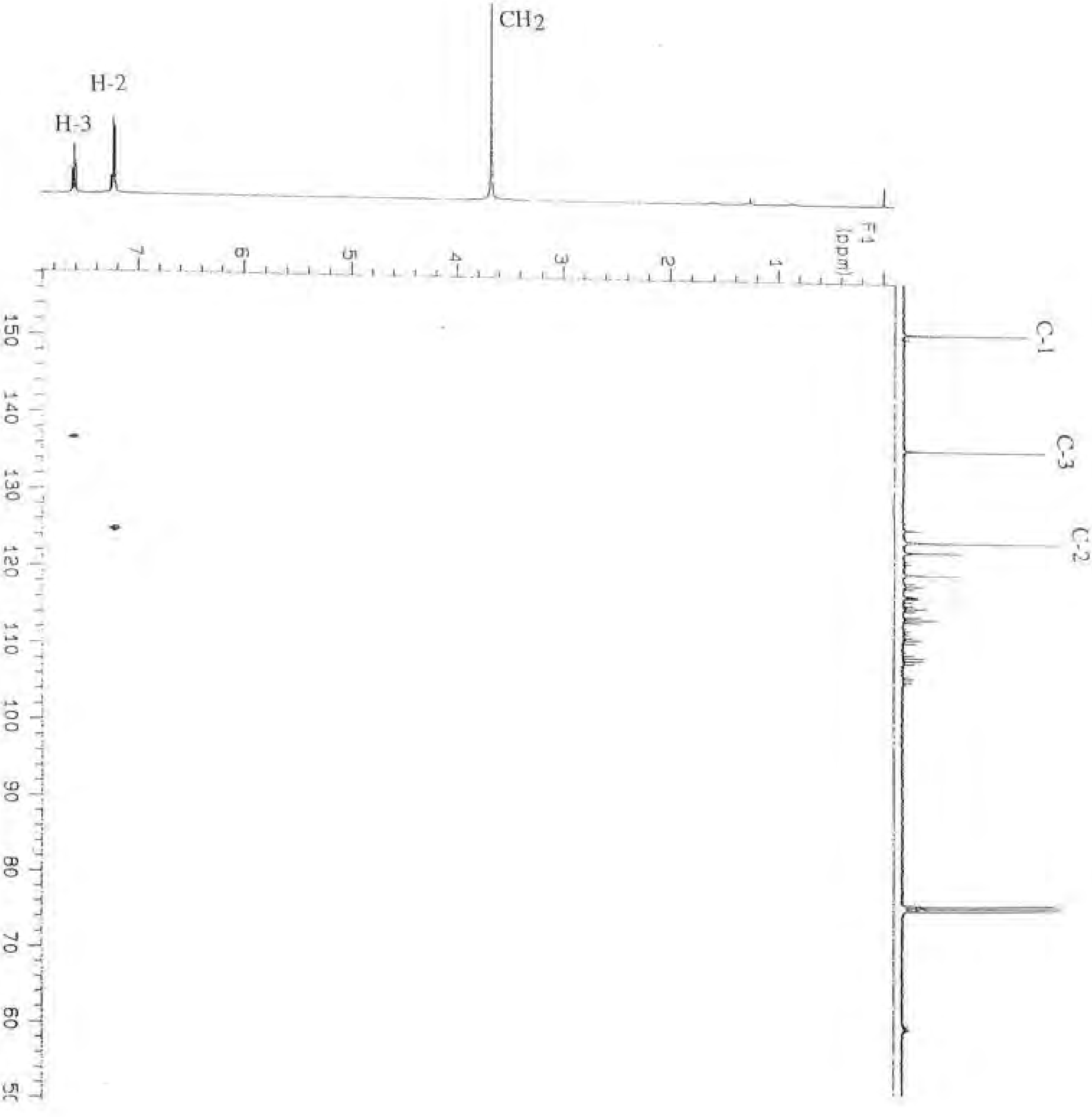
SPECTROSCOPIC STUDIES: NMR

2,6-Bis[(perfluoro-2-methylpentan-2-yl)methyl]pyridine (19)

The result of the complete analysis of the spectrum is given in section Spectrum No 16.

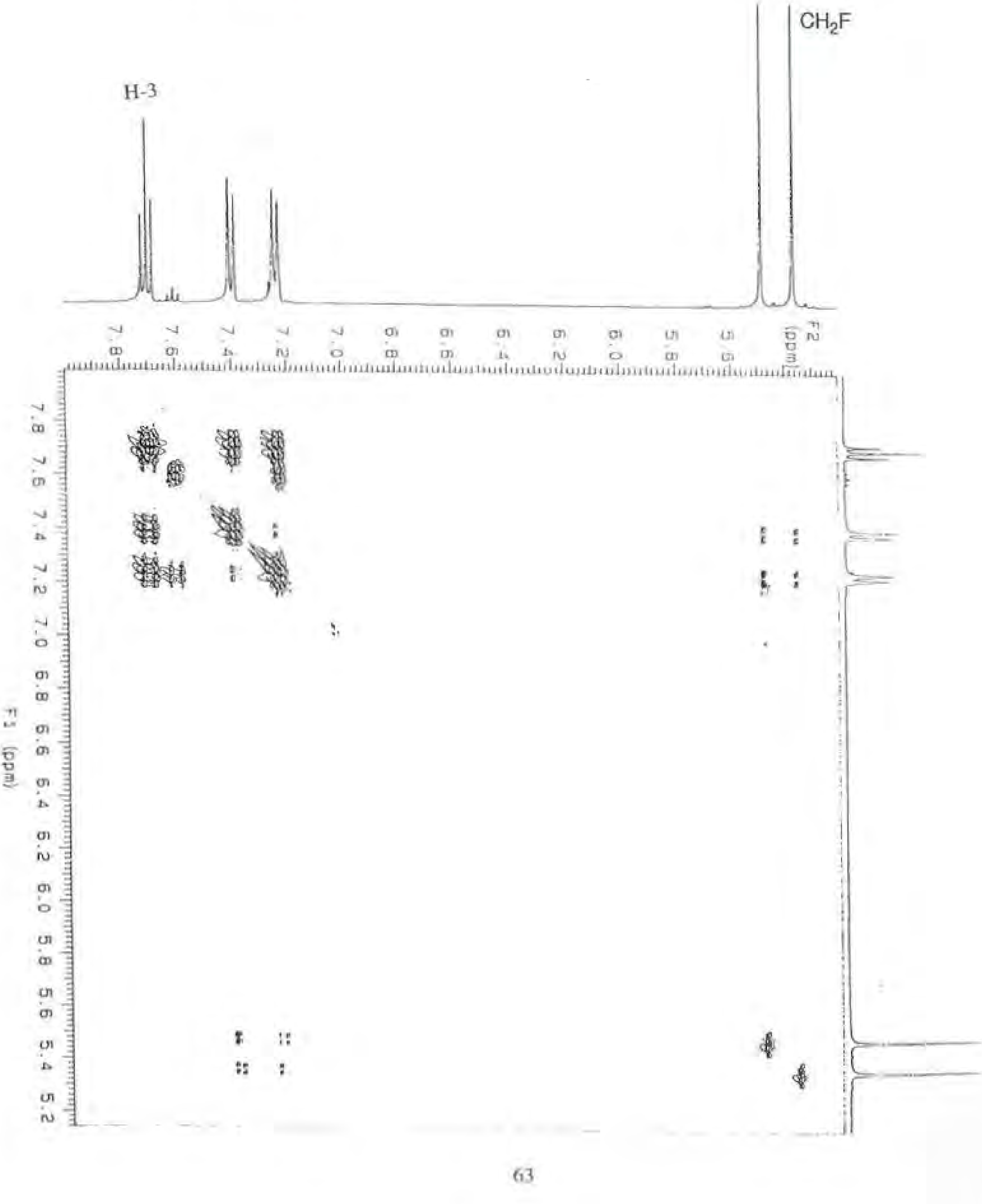
A DEPT (distortionless enhancement by polarization transfer) experiment of structure (19) provided evidence of δ(C-1)= 151.6 ppm and knowing that C-2 has a chemical shift δ(C-2)= 124.6 ppm.

Furthermore, a two dimensional correlated NMR spectroscopy (H,C) COSY unabled us to determine the following chemical shifts from δ(H-3)= 7.61 ppm (t) to δ(C-3)= 136.5 ppm. The other chemical shifts could be deduced from ^{1}H NMR spectra: δ(H-3)= 7.61 ppm (t, $^3J_{HH}$ 8) and δ(H-2)= 7.22 ppm (d, $^3J_{HH}$ 8).

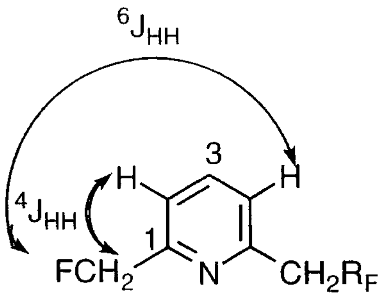


2-Fluoromethyl-6-[(perfluoro-2-methylpentan-2-yl)methyl]pyridine (20).

The chemical shifts of the 13C NMR spectra were assigned and a downfield as expected to C-1 with a C-F coupling δ(C-1)= 156.2 ppm (d, $^2J_{CF}$ 22). A two dimensional correlated NMR spectroscopy (H,H) COSY unabled us to assign δ(H-3)= 7.70 ppm (t, $^3J_{HH}$ 8).

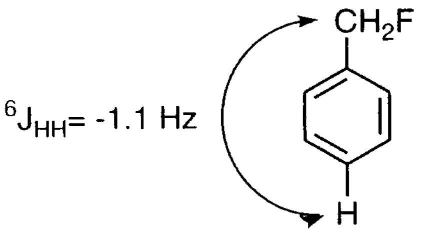


However, an unusual coupling was observed between the two protons CH_2F and H-4 as well as CH_2F and H-2.



$R_F = C(CF_3)_2C_3F_7$

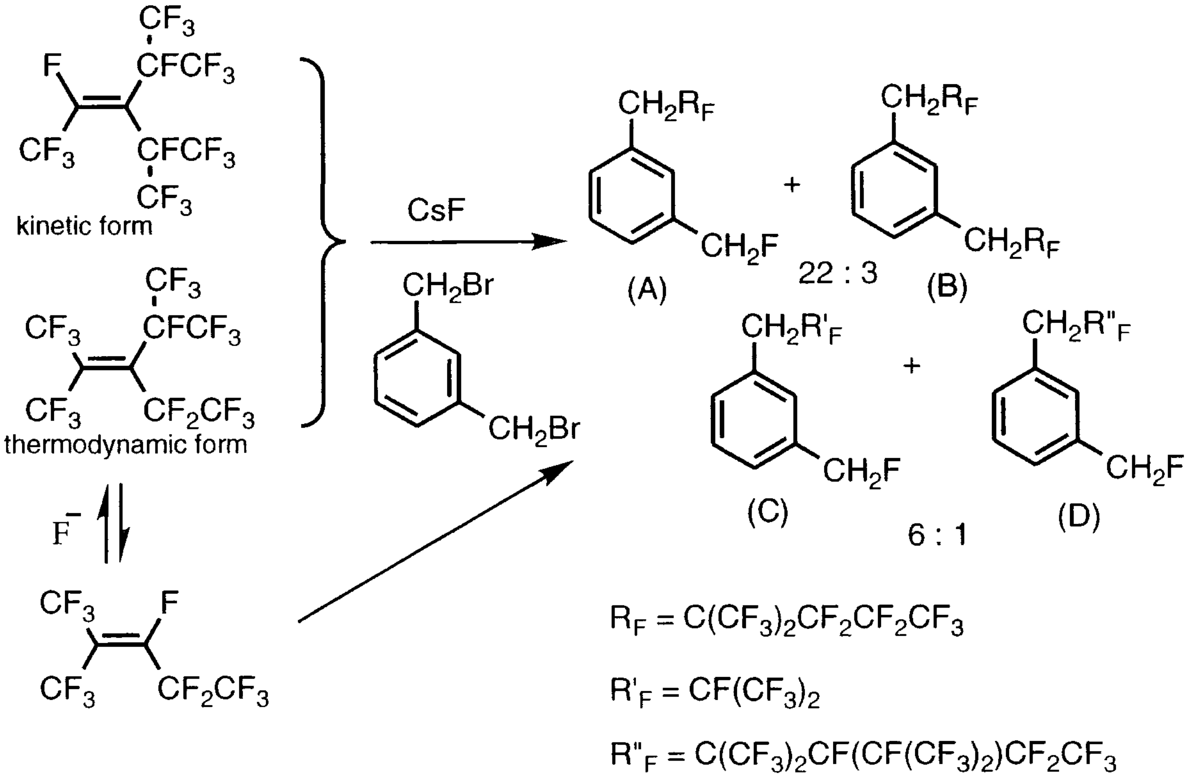
Similar results have been reported by Facelli and co-workers[113], where he observed a $^6J_{HH}$= -1.1 Hz.



The result of the complete analysis of the spectrum is given in section Spectrum No 17.

II.4. USE OF HEXAFLUOROPROPENE TRIMER

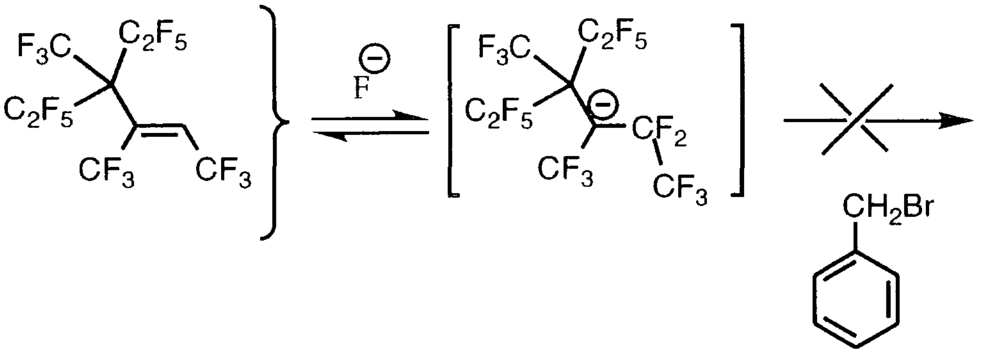
As the reaction was successful with hexafluoropropene, under the same conditions, the reaction was performed in sulpholan in the presence of caesium fluoride with hexafluoropropene trimer.



The ^{19}F NMR data confirmed the formation of the carbanion after 16 hours as the lowest chemical shift was recorded at -40 ppm but the ^{19}F NMR spectra was very complex. After addition of 1,3-xylylene dibromide to the system the temperature was raised to 60-69°C. A mixture of products was formed, the highest yield was observed for the component (A) as if the carbanion had been derived from the hexafluoropropene dimer. These results imply that the carbanion derived from the hexafluoropropene trimer had de-oligomerised. The outcome could be explained by the steric hindrance, as the bulky fluorinated segments are more likely to generate less hindered carbanions.

II.5. USE OF TETRAFLUOROETHYLENE PENTAMER

In the attempt of synthesising an aromatic compound with very long perfluoroalkyl chain, tetrafluoroethylene pentamer was used. Under conditions to those used previously, the derivative perfluorocarbanion was generated after 12 days and quantitative conversion of the fluoro-alkene to the carbanion was confirmed by ^{19}F NMR. The ^{19}F NMR spectrum showed five sharp singlets: -42.1 ppm (3F, s, CF_3CCs), -54 ppm (3F, s, $CF_3C(C_2F_5)$), -69.9 (3F, s, $CCsCF_2CF_3$), -77 ppm (8F, m, $(CF_3CF_2)C(CF_3)CCs(C_2F_5)$), -104.6 ppm (4F, m, $(CF_3CF_2)_2C(CF_3)$). However, after addition of the benzyl bromide to the system no perfluoroalkylated compound was formed. The reaction was left longer, 10 days and the only product, which was detected on the glc-ms, was the benzyl fluoride and the remaining starting material.



The addition of fluoride ion to such a bulky fluoro-alkene produces a carbanion with high steric requirements; consequently, we have been unable to form the corresponding perfluoroalkylated adduct from this system even though the anion generated showed some stability.

II.6. CONCLUSION

This methodology described in this chapter afforded a whole range of new perfluoroalkylated aromatic systems in high yields when hexafluoropropene dimer was used as the source of the perfluoroalkylating agent. A major advance was also made in the area by simply extracting the polyfluoroalkylated products into commercially available perfluorocarbon solvent (FC-84, bp 80°C). The size of the fluorinated segment derived from hexafluoropropene dimer was sufficiently large enough to impart solubility in Fluorinert (FC-84, bp 80°C) and facilitate the isolation and purification processes. This observation not only provides convenient methodology for the isolation step but also emphasises the potential value of these systems in promoting a variety of products that are soluble in perfluorocarbon.

However, this procedure did not show any success when the reaction was performed with longer perfluorinated alkenes such as hexafluoropropene trimer or tetrafluoroethylene pentamer.

CHAPTER III

CHEMISTRY AND REACTIONS OF PERFLUOROALKYLATED AROMATIC SYSTEMS

III.1. INTRODUCTION

A large number of reactions of benzotrifluoride have been reported and considerable effort has been directed towards evaluating the effects of the CF_3 substituent on reactivity. The strong deactivating effect of the trifluoromethyl group attached to the benzene ring has been well recognised[114, 115, 116] and is known to be a strong meta orientating group in electrophilic aromatic substitutions[114, 115, 116]. Quantitative measurements[114, 116] have shown that this effect is attributed mainly to an inductive withdrawal and in aromatic systems a conjugative contribution is also found. Our aim in the first part of this chapter, is to study the effect of such substituent CH_2R_F (where R_F is a bulky group derived from hexafluoropropene dimer) on the ring and understand the reactivity of these novel materials. In practice, we wanted to compare the reactivity of these systems to benzotrifluoride and evaluate the effect of the methylene group between the aromatic ring and the perfluorinated branch. Indeed, the procedures described in chapter II have allowed the synthesis of a range of new perfluoroalkylated aromatic systems and this new class of compounds has provided the opportunity to explore some further chemistry.

In this chapter, functional derivatives[115, 117, 116, 118] have been prepared through a variety of electrophilic substitution reactions: nitration, chlorosulphonation and bromination. The results will be presented and discussed in terms of character effects of the perfluoroalkyl group on the benzene ring, bearing in mind that the nature of the substituent already present on the benzene ring determines the orientation of further substitution.

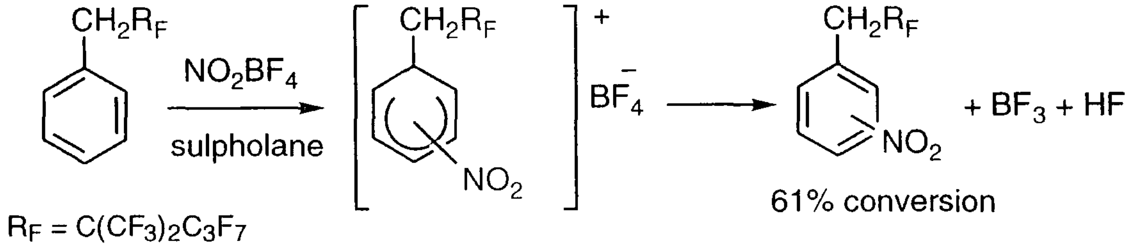
The second part of this chapter will deal with investigating synthetic routes to these diverse compounds. We have prepared corresponding benzoic acids of [(perfluoro-2-methylpentan-2-yl)methyl]benzene and some measurements of the ionisation constants have been carried out to study and confirm the electronic behaviour of CH_2R_F on the aromatic ring[115]. The unusual miscibility properties of fluorocarbon solvents have been recognised recently as having potential utility for synthesis and catalysis[82, 81]. The perfluoroalkylation procedure has prompted us to prepare some derivatives such as fluorine containing dyes[119] and to synthesise triphenyl phosphine derivatives that could lead to novel catalysts.

III.2. ELECTROPHILIC REACTIONS

The most important reaction of aromatic compounds is electrophilic substitution. In the previous chapter, we described the preparation of $ArCH_2R_F$ systems, and here, our main interest has been to evaluate the effects of CH_2R_F on the reactivity of the benzene ring[116, 120] in electrophilic substitution reactions. This relies on the fact that the introduction of one substituent is strongly affected by the directing effect of other substituents. Our effort has been focussed on performing these substitution reactions in the search for a rationale for the electronic effect of CH_2R_F group. Consequently, a number of electrophilic reactions has been accomplished including synthesis of nitro and bromo compounds, sulphonyl chloride derivatives, all valuable because of the further chemistry they undergo.

III.2.A. NITRATION

The preparation[115, 121, 122, 123] of nitro-[(perfluoro-2-methylpentan-2-yl)methyl]benzene isomers is shown below, the sequence is particularly important as the products can be reduced to yield the corresponding aminoarenes (see section III.4.). The reaction between [(perfluoro-2-methylpentan-2-yl)methyl]benzene and a very effective nitrating agent nitronium tetrafluoroborate, was carried out in sulpholane to give three mono-isomers: 1-nitro-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (21), 1-nitro-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (11), 1-nitro-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (10) in the respective ratio 1/3.8/3.8 (in 61% conversion). A ratio of 1 to 1 of reagent to the starting material was used in order to avoid the formation of dinitro-adducts. The experiment was repeated at various temperatures, 30°C and 100°C, and samples were collected at different intervals of time, 2 hours and 4 days but the isomer distribution remained identical.



Extraction with fluorocarbon solvent
FC-84, Bp= 80°C

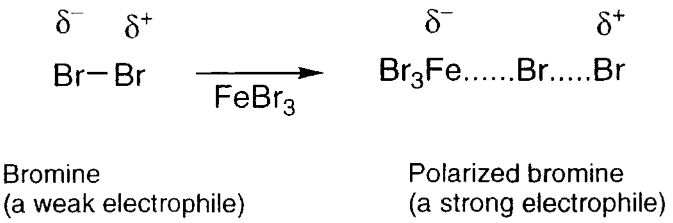
Substituent = NO_2	*ortho* (21)	*meta* (11)	*para* (10)
ratio by gc	1	3.8	3.8

The mixture was successfully extracted from sulpholane using a perfluorocarbon solvent and the three isomers were separated from the starting material by column chromatography using hexane as the eluent. The isomer distribution and the respective structures were attributed after comparing with the data of 1-nitro-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (11), 1-nitro-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (10) prepared in Chapter II (see section II.3.C.6.). Indeed, compounds (10) and (11) were fully characterised in the previous chapter including their respective accurate time retention on the glc chromatogram and their mass spectrometry data. The assignement and the isomeric composition of the mixture was then facilitated. No further purification was attempted.

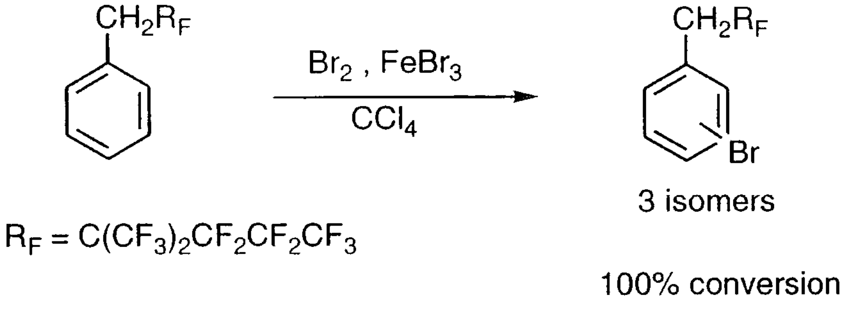
The electrophilic substitution occured at the three positions *ortho*, *meta* and *para* on the benzene ring with formation of mainly the *meta* and *para* isomers.

III.2.B. BROMINATION

The bromination reaction[124, 125, 115] of [(perfluoro-2-methylpentan-2-yl)methyl]benzene was performed in the presence of ferric bromide as the catalyst in tetrachloromethane to yield the substituted product. The catalyst makes the Br_2 molecule more electrophilic by complexing with it to give an $FeBr_4^-Br^+$ species that reacts as as source of bromonium ion.


δ⁻ δ⁺
Br–Br
FeBr3
δ⁻ δ⁺
Br3Fe......Br.....Br
Bromine
(a weak electrophile)
Polarized bromine
(a strong electrophile)

The [(perfluoro-2-methylpentan-2-yl)methyl]benzene (4) was brominated to its monobromo-isomers


CH2RF
Br2 , FeBr3
CCl4
CH2RF
Br
3 isomers
RF = C(CF3)2CF2CF2CF3
100% conversion

Substituent = Br	*ortho* (9)	*meta* (8)	*para* (7)
ratio by gc	1	2	3

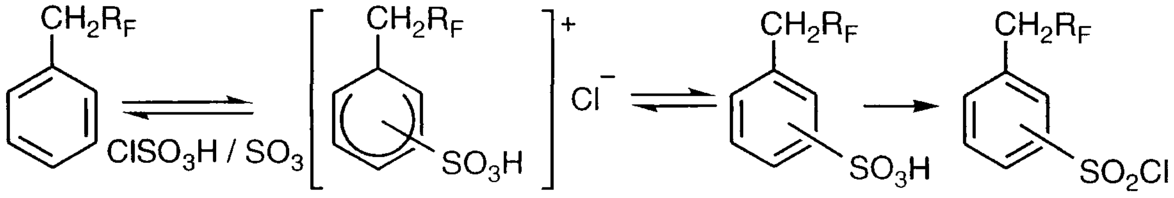
Three monobromo-isomers were detected by glc in a 1/2/3 distribution for the following compounds: 1-bromo-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (7), 1-bromo-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (8) and 1-bromo-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (9). The glc-ms spectrum and glc chromatograms matched exactly with these obtained for the compounds (7), (8), (9) synthesised and described in the Chapter II. No further purification was carried out.

The isomer distribution was again formation of predominantly *para*-bromo compound (7) and *meta*-bromo derivative (9).

III.2.C. CHLOROSULPHONATION

III.2.C.1. PREPARATION OF SULPHONYL CHLORIDE DERIVATIVES

Sulphonation [126], [127] was carried out using an excess of oleum (20%) and chlorosulphonic acid with [(perfluoro-2-methylpentan-2-yl)methyl]benzene (4) as the substrate.



$R_F = C(CF_3)_2C_3F_7$

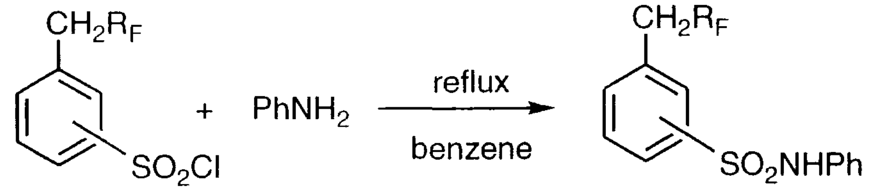
100% conversion

SO_2Cl	*meta* (22)	*para* (23)
ratio	1	1.4

The mixture obtained was composed of two mono-isomers: 3-[(perfluoro-2-methylpentan-2-yl)methyl]benzenesulphonyl chloride (22) and 4-[(perfluoro-2-methylpentan-2-yl)methyl]benzenesulphonyl chloride (23), with 100% conversion of the starting material. The isomer distribution was confirmed by ^1H NMR, section n.m.r. spectra No 18 and No 19. The electrophilic substitution occured only at the *meta* and *para* position, confirming the important effect of CH_2R_F on the benzene ring. These results support the theory that the electronic properties of these compounds might not be as close as the parent species: toluene. The product was characterised as a mixture and attempts have been made to fully characterise each of the two sulphonyl chlorides synthesised (using HPLC), but with little success.

III.2.C.2. PREPARATION OF SULPHONAMIDE COMPOUNDS

These classes of compounds are important and could be suitable precursors for interesting materials such as sulphonamide derivatives[128]. Perfluoroalkylated sulphoanilide compounds were prepared through the reaction of a mixture of sulphonyl chlorides compounds (22) and (23) in the ratio of 1/1.4 with an excess of aniline in benzene. A mixture of isomers 3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene sulphanilide (24) and 4-[(perfluoro-2-methylpentan-2-yl)methyl]benzenesulphanilide (25) was formed in the ratio of 1/1.4, confirmed by ^1H NMR, section Spectra No 20 and No 21.



1 (22)/ 1.4 (23)

1 (24)/ 1.4 (25)

$R_F = C(CF_3)_2C_3F_7$

100% conversion

The separation was accomplished by HPLC using water/methanol as the eluent.

SPECTROSCOPIC STUDIES: NMR

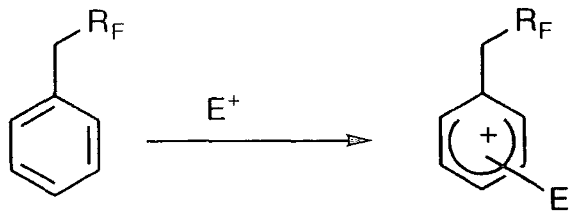
The ^{19}F NMR shifts for compounds (24) and (25) are tabulated below along with the shifts of the unsubstituted [(perfluoro-2-methylpentan-2-yl)methyl]benzene (4) and 3-[(perfluoro-2-methylpentan-2-yl)methyl]benzenesulphonyl chloride (22) with 4-(perfluoro-2-methylpentan-2-yl)methylbenzenesulphonyl chloride (23). The spectra of compounds (24) and (25) can be found in section Spectrum No 20 and No 21.

compounds/ ppm	$C(\underline{CF_3})_2$	$CF_2\underline{CF_3}$	$\underline{CF_2}CF_2CF_3$	$\underline{CF_2}CF_3$
(4)	- 62.7	- 80.5	- 106.4	- 123.4
(22)	- 62.5	- 80.5	- 106.6	- 123.1
(23)	- 62.4	- 80.8	- 106.2	- 123.2
(24)	- 62.2	- 80.5	- 105.6	- 122.8
(25)	- 63.3	- 81.5	- 106.6	- 123.7

Very little difference was observed for the ^{19}F chemical shifts. The deuterated solvents used for each spectrum were different: for (4) CD_3CN, (22) and (23) CD_3COCD_3, finally (24) and (25) CD_3OD. The results of the complete analysis of the spectrum for compounds (24) and (25) is given in section Spectrum No 20 and No 21.

III.2.D. CONCLUSION

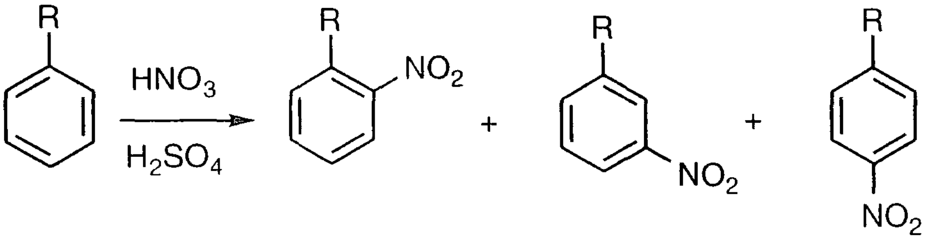
The electrophilic substitution reaction: nitration, bromination and sulphonation occured at the three positions *ortho*, *meta* and *para* positions on the benzene ring with formation mainly of *meta* and *para* derivatives.



$R_F = C(CF_3)_2CF_2CF_2CF_3$

	RATIO OF ISOMERS		
Electrophile E^+	*ORTHO*	*META*	*PARA*
NO_2^+	1	3.8	3.8
Br^+	1	2	3
SO_2Cl^+	0	1	1.4

The nature of the substituent CH_2R_F present on the ring determined the positions of the different groups[120]. Orientation and reactivity effects of each group are explained on the basis of resonance and field effects on the stability of the intermediate arenium ion. To understand these reactions, it is necessary to know that the product is dependant not on the thermodynamic stability of the intermediates, but on the activation energy necessary to form each of them. Therefore, we can predict that any -I group such as CF_3, removing electron density, should destabilise all positions and mostly *ortho* and *para*. In other words, substitution in benzotrifluoride occurs at the least deactivated position and CF_3 groups are **meta-directing deactivators.** Comparing with the effect of a methyl substituent, the nitration of toluene yields predominantly *ortho* and *para* products, showing the strong **ortho and para-directing activator** of such a group.



R= CH_3	(58%)	(5%)	(37%)
t-butyl	(16%)	(11%)	(73%)

Another important factor is the steric effect of the different substituents. As the group on the ring is large, steric hindrance inhibits the formation of the ortho product and increases the amount of para isomer. The example given above shows that under the same conditions the results of the nitration reaction vary. Toluene gives 58% of the ortho compound and 37% of the para, while the more bulky t-butyl group gave 16% of the ortho and 73% of the para. As the group becomes larger it directs almost entirely para. Steric hindrance factors have already been discussed in Chapter II to explain the low reactivity of the 2-bromobenzyl bromide and 1,2-xylylene dibromide towards the nucleophilic substitution for the perfluoroalkylation reaction. However to explain the high ratio of the meta derivatives, we might have to consider that there is also an electronic effect of the perfluoroalkyl group to understand these results.

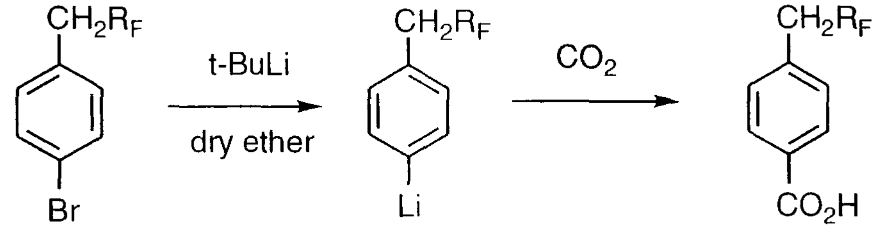
To interpret the outcome of the electrophilic substitution reactions on these systems different factors have to be considered, in particular, the combination of electronic and steric effects. We can conclude that these results may indicate that the two electronic behaviours of the CH_2R_F group: electron-withdrawing and electron-donating are competing and overall cancel each other out. As a result, the three positions on the benzene ring are likely to be reactive towards an electrophile but the orientation and the reactivity of these systems will be mainly under steric control.

III.3. SYNTHESIS OF BENZOIC ACIDS AND DERIVATIVES

Our efforts have been concerned with the preparation of (perfluoro-2-methylpentan-2-yl)methylbenzoic acids as a strategy to evaluate the electronic influence of CH_2R_F onto the aromatic ring[114, 115, 116].

III.3.A. SYNTHESIS OF 4-[(PERFLUORO-2-METHYLPENTAN-2-YL)METHYL]BENZOIC ACID

The 4-[(perfluoro-2-methylpentan-2-yl)methyl]benzoic acid (27) was prepared[118] by a two-step procedure from 1-bromo-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (7), by metallation with t-butyllithium[129, 130, 131] to give (26) followed by quencing with solid carbon dioxide.



(7)

(26)

(27)

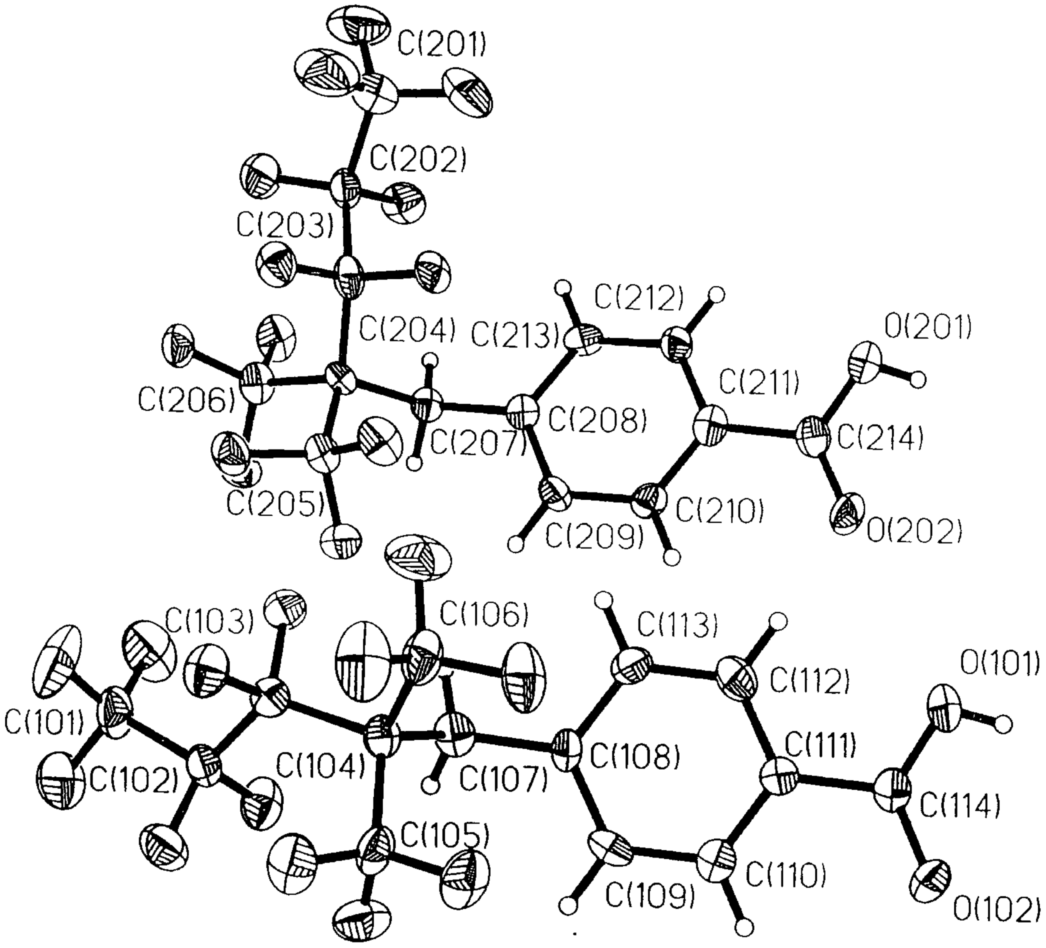
$R_F = C(CF_3)_2C_3F_7$

64% isolated yield

In the first stage, we were quite concerned that the perfluoroalkyl group might promote the deprotonation at the benzylic position. However, a rather regioselective reaction occured and the organolihium intermediate (26) was formed. When the reaction was carried out with n-butyllithium, the formation of the benzoic acid did not occur. The use of a stronger base tert-butyllithium was necessary to generate intermediate (26), which afforded the corresponding benzoic acid (27) in excellent yields[115, 132, 118] 64%.

The crude solid was then recrystallised from hexane and single crystals of (27) were grown over one week at room temperature. An X-ray crystal structure was obtained and gave the following crystallographic structure: Figure I.

CRYSTALLOGRAPHIC STUDY



C(201)
C(202)
C(203)
C(212)
C(204)
C(213)
O(201)
C(211)
C(206)
C(208)
C(214)
C(207)
C(205)
C(210)
O(202)
C(209)
C(106)
C(103)
C(113)
C(112)
O(101)
C(101)
C(111)
C(102)
C(104)
C(107)
C(108)
C(114)
C(105)
C(110)
C(109)
O(102)

Figure I

As we move along the benzene ring which is planar as expected, we can see the arrangement through space of the C_6F_{13} chain, in zig-zag in order to minimise the 1,3-interaction between the fluorine atoms.

This lets us predict that a longer perfluoroalkyl chain will have different conformational isomers depending on the orientation of the helicoid. To our knowledge, this is the first crystal structure of a perfluoroalkylated benzoic acid reported in the literature.

SPECTROSCOPIC STUDIES

IR

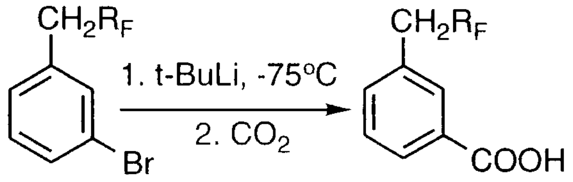
The infra red spectra of compound (27) showed a broad band at 1683 cm^{-1} due to C=O stretch conjugated with the benzene ring as the absorption has moved to the higher frequency; also a very broad band 1334-1176 cm^{-1} which includes C-O and C-F bonds. The hydrogen bonded O-H stretch is a broad peak overlapping with C-H strech absorptions at 3070 cm^{-1} (Spectrum No. 16).

NMR

Different experiments (DEPT, NOE, COSY) were required to complete fully the analysis of the spectrum, section Spectrum No 22.

III.3.B. SYNTHESIS OF 3-[(PERFLUORO-2-METHYLPENTAN-2-YL)METHYL]BENZOIC ACID

Under identical conditions, the two-step reaction was carried out with 1-bromo-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (8) and t-BuLi with solid carbon dioxide to give 3-[(perfluoro-2-methylpentan-2-yl)methyl]benzoic acid (28) in 60 % yield.



(8) (28)

$R_F = C(CF_3)_2C_3F_7$ 60% isolated yield

The crude material was recrystallised from hexane, attempt has been made for growing crystal but with little success.

SPECTROSCOPIC STUDIES

IR

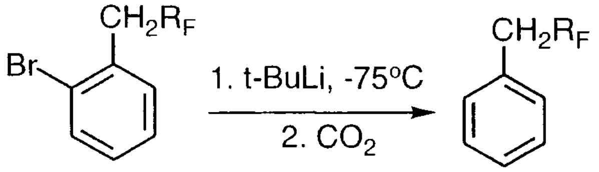
The infra red spectra of compound (28) was recorded and gave similar absoption bands see section IR No 17.

NMR

The result of the complete analysis of the spectrum is given section Spectrum No 23.

III.3.C. ATTEMPT TO SYNTHESISE 2-[(PERFLUORO-2-METHYLPENTAN-2-YL)METHYL]BENZOIC ACID

The metallation reaction was performed using t-BuLi and 1-bromo-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (9) in dry ether at 75°C, followed by the addition of dry ice. The hydrolysed product [(perfluoro-2-methylpentan-2-yl)methyl]benzene (4) was obtained instead with 100% conversion of the starting material. Glc-ms and NMR data matched and confirmed the structure of compound (4), fully characterised Chapter II.



(9)

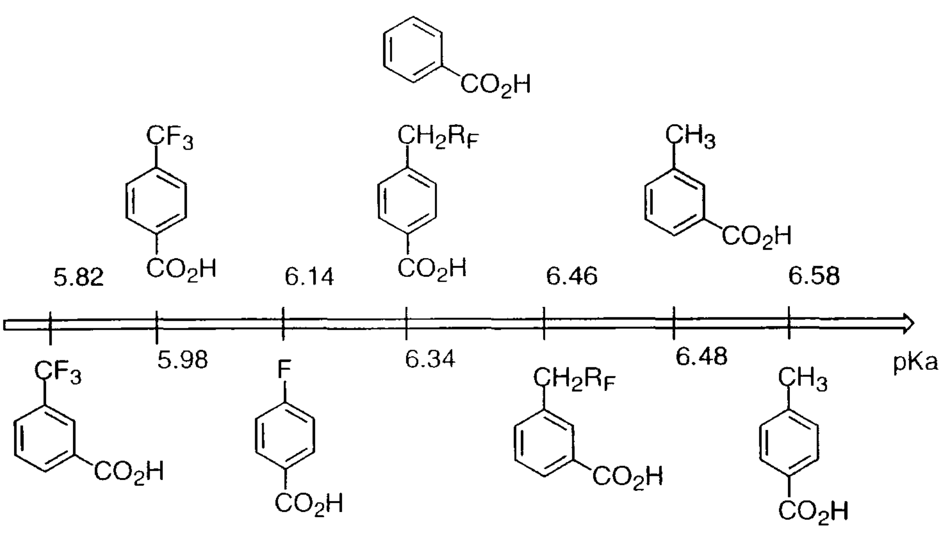
(4)

$R_F = C(CF_3)_2C_3F_7$

The carboxylation process did not occur. These results could be explained in terms of steric effects, due to the close proximity of the perfluorinated group. Furthermore, this explanation might be applied for the preparation of sulphonyl chloride (section III.2.C.1.) where the chlorosuphonation reaction occured at the position *m*- and *p*- but no trace of the *o*- derivative.

III.3.D. IONISATION CONSTANT MEASUREMENTS

The pKa measurements of [(perfluoro-2-methylpentan-2-yl)methyl]benzoic acids have been investigated and the results will be discussed in this section. The procedure used a Beckman research pH meter to determine the ionisation constants of the benzoic acid derivatives[115]. Because of the poor solubility, the pKa measurements of 3-[(perfluoro-2-methylpentan-2-yl)methyl]benzoic acid (28) and 4-[(perfluoro-2-methylpentan-2-yl)methyl]benzoic acid (27) could not be run in water. A solvent of 1,4-dioxane-water (41.7/58.3 in volume) was chosen according to the method of Willi[133]. The pKa of a series of reference benzoic acids were employed under identical conditions at 24°C and are presented below. The substituents can donate (CH_3) or withdraw (F, CF_3) electrons from the aromatic ring; electron-withdrawing groups increase acidity and therefore present a pKa much lower while electron-donating groups act in the opposite way.



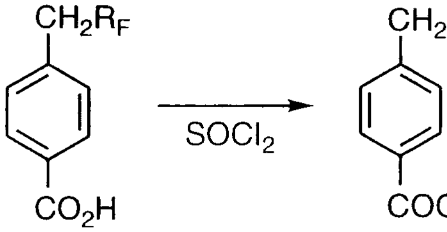
These measurements show that the ionisation constants are influenced by the substituents on the benzene ring and that CH_2R_F does not behave similarly to a CF_3 or a CH_3 group. The pKa measured for [(perfluoro-2-methylpentan-2-yl)methyl]benzoic acids are smaller than the values for the corresponding toluic acids. These results suggest that CH_2R_F in comparison to CH_3 group might have a slight effect -I (inductive effect) and increases the acidity of compounds (27) and (28), but to certain extent as the pKa values obtained for CF_3 are much lower. These measurements indicate also that the electronic effect of CH_2R_F has a little influence, as the pKa of 4-[(perfluoro-2-methylpentan-2-yl)methyl]benzoic acid is identical to benzoic acid. Finally, the small variations between the values of the different pKa's do clearly indicate caution when attributing them to any particular effect. In particular, the interaction of the perfluoroalkyl group with solvents might have interfered and affected the measurements.

III.3.E. PERFLUOROALKYLATED BENZOIC ACIDS: VERSATILE STARTING MATERIALS

We have demonstrated that the carboxylation route in a two-step process is a convenient and effective method to achieve synthesis of [(perfluoro-2-methylpentan-2-yl)methyl]benzoic acids in very good yields. A new class of compounds was prepared using these acids as precursors.

III.3.E.1. SYNTHESIS OF 4-[(PERFLUORO-2-METHYLPENTAN-2-YL)METHYL]BENZOYL CHLORIDE

The reaction between 4-[(perfluoro-2-methylpentan-2-yl)methyl]benzoic acid and an excess of thionyl chloride after two hours reflux afforded the corresponding 4-[(perfluoro-2-methylpentan-2-yl)methyl]benzoyl chloride[134, 120] (29) in 82% yield after removal the by-products which are gases and thionyl chloride. The cautious step for this process concerned the evolution of hydrogen chloride and sulphuric oxyde. The pure product was obtained after simple distillation of the unreacted thionyl chloride.



(27) (29)

$R_F = C(CF_3)_2C_3F_7$ 82 % isolated yield

SPECTROSCOPIC STUDIES

IR

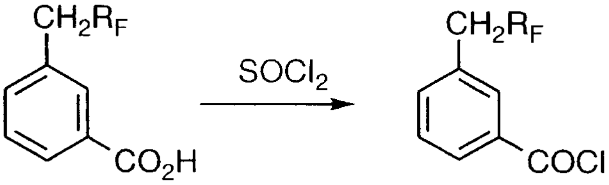
The infra red spectra of compound (29) showed a band at 1770 cm^{-1} due to C=O stretch conjugated with the benzene ring as the absorption has moved to lower wavelengths , also a broad band 1240 cm^{-1} which corresponds to C-F bonds. Finally, the hydrogen bonded O-H stretch observed for compound (29) has disappeared (Spectrum No. 18).

NMR

The ^{1}H, ^{13}C and ^{19}F chemical shifts were recorded by comparing the chemical shifts with the derived 4-[(perfluoro-2-methylpentan-2-yl)methyl]benzoic acid (27). The complete analysis of the spectrum is given section Spectrum No 24.

III.3.E.2. SYNTHESIS OF 3-[(PERFLUORO-2-METHYLPENTAN-2-YL)METHYL]BENZOYL CHLORIDE

Under identical conditions to those used before, the reaction between 3-[(perfluoro-2-methylpentan-2-yl)methyl]benzoic acid (28) and thionyl chloride afforded 3-[(perfluoro-2-methylpentan-2-yl)methyl]benzoyl chloride (30) in 80% yield



(28) (30)

$R_F = C(CF_3)_2C_3F_7$ 80% isolated yield

SPECTROSCOPIC STUDIES

IR

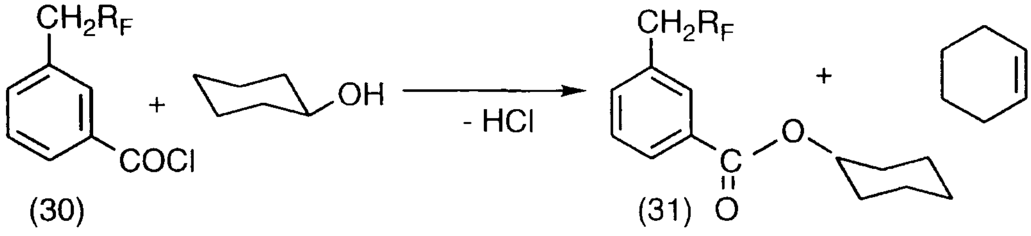
The infra red spectra of compound (30) gave similar absorption bands see section IR Spectrum No 19.

NMR

The ^{1}H, ^{13}C and ^{19}F chemical shifts were recorded by comparing the chemical shifts with the starting material (28). The complete analysis of the spectrum is given section Spectrum No 25.

III.3.E.3. SYNTHESIS OF CYCLOHEXYL3-[(PERFLUORO-2-METHYLPENTAN-2-YL)METHYL]BENZOATE

The esterification reaction of 3-[(perfluoro-2-methylpentan-2-yl)methyl]benzoyl chloride (30) with cyclohexanol occured after 14 hours reflux and afforded cyclohexyl 3-[(perfluoro-2-methylpentan-2-yl)methyl]benzoate (31) in 91% yield after distillation of excess of cyclohexanol and cyclohexene formed by dehydration.



(30)

(31)

$R_F = C(CF_3)_2C_3F_7$

91% isolated yield

SPECTROSCOPIC STUDIES

IR

The infra red spectra of compound (31) showed a broad band at 1721 cm^{-1} due to C=O stretch conjugated with the benzene ring as the absorption has moved to lower wavelengths, also a very broad band 1338-1200 cm^{-1} which includes C-O and C-F bonds (Spectrum No. 20).

NMR

The ^{1}H, ^{13}C and ^{19}F chemical shifts were recorded by comparing the chemical shifts with compound (30). The complete analysis of the spectrum is given section Spectrum No 26.

III.4. DYES SOLUBLE IN FLUOROCARBON FLUIDS

The purpose of this work was to search for a new fragment for use in dye systems where the insertion of a perfluoroalkyl group onto the azo-dyes could affect greatly the properties of the compound in terms of fastness or colours[71]. Previously, interesting behaviour has been observed for azo-dyes containing fluorine atoms or the CF_3 group. It is well known that dyes with fluorine atoms such as C.I. Acid Red 266, an acid dye for nylon dyeing, has excellent lightfastness[71, 4]. This property is due to the electronegativity of the fluorine atom. Also, an -N=N- double bond conjugated with the aromatic systems generates a very strong chromophore that imparts a brillant colour to the system[135, 136]. Functional groups will play an important role in these various phenomena[137].

As a result, we prepared corresponding aniline derivatives ready to be coupled with suitable activated molecules via diazotization reactions[135, 138], as shown in the scheme below.

$$R_FCH_2Ar\text{-}NO_2 \xrightarrow{i} R_FCH_2Ar\text{-}NH_2 \xrightarrow{ii} R_FCH_2Ar\ \overset{+}{N}\equiv N \xrightarrow{iii} R_FCH_2Ar\text{-}N{=}N\text{-}Ar'$$

R_F: $C(CF_3)_2C_3F_7$

Ar' electron rich molecules

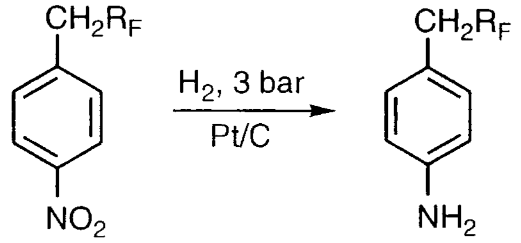
i: reduction
ii: HCl, $NaNO_2$
iii: Ar'

III.4.A. REDUCTION REACTIONS

A range of perfluoroalkylated compounds were synthesised in Chapter II including 1-nitro-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (10) and 1-nitro-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (11). Aromatic nitro groups can be easily reduced chemoselectively to afford primary amines[139].

III.4.A.1. 1-AMINO-4-[(PERFLUORO-2-METHYLPENTAN-2-YL)METHYL] BENZENE

The heterogenous hydrogenation reaction of 1-nitro-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (10) was performed using a catalytic amount of Platinum activated on carbon (over 10%) at room temperature under 3 bar hydrogen pressure[140] to afford 1-amino-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (32) in high yield 82%. This reaction was very clean as a simple filtration was required to remove any impurities coming from the catalyst.



(10)

(32) 82%

$R_F = C(CF_3)_2C_3F_7$

SPECTROSCOPY STUDIES

IR

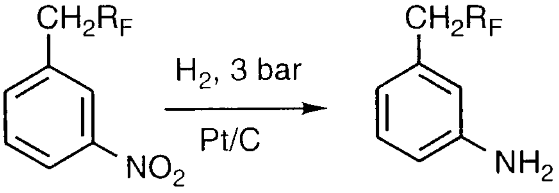
The Infra red spectra of compound (32) showed a stretch broad band at 3370 cm^{-1} and a bend band at 1520 cm^{-1} due to N-H, characteristic to primary amine; a sharp band for the double bond in the aromatic region 1626 cm^{-1} (C=C) and finally a broad band 1261-1221 cm^{-1} for C-F bonds (Spectrum No. 21).

NMR

The ^{19}F NMR spectrum of structure (32) consisted of four resonances (two CF_3 and two CF_2) of relative intensities 6:3:2:2 with the respectively following chemical shifts: -62.7 ppm (CF_3), -80.9 ppm (CF_3), -106.3 ppm (CF_2) and -123.2 ppm (CF_2), consistant with the perfluoroalkyl branched segment: R_F= $C(CF_3)_2CF_2CF_2CF_3$. The result of the complete analysis of the spectrum is given in section Spectrum No 27.

III.4.A.2. 1-AMINO-3-[(PERFLUORO-2-METHYLPENTAN-2-YL)METHYL] BENZENE

In a similar experiment, reduction of 1-nitro-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (11) was carried out and afforded 1-amino-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (33) in 85%yield.



(11)

(33) 85%

$R_F = C(CF_3)_2C_3F_7$

SPECTROSCOPY STUDIES

IR

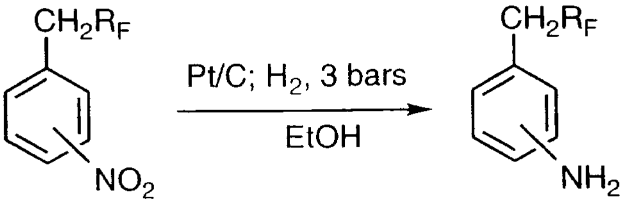
The Infra red spectra of compound (33) showed similar absorption peaks (Spectrum No 22).

NMR

The ^{19}F chemical shifts were recorded as expected for the side chain R_F, as seen in the section III.4.B.1. The result of the complete analysis of the spectrum is given in section Spectrum No 28.

III.4.A.3. REDUCTION OF THE MIXTURE

The hydrogenation reaction was performed with the mixture of nitro compounds (21), (11) and (10) in the ratio 1/3.8/3.8 under identical conditions[140].



$R_F = C(CF_3)_2C_3F_7$

100% conversion

The solution reaction was cautiously filtered to remove the excess of the catalyst and the distillation of ethanol afforded the corresponding amines: 1-amino-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (34) , 1-amino-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (33) and 1-amino-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (32) with 100% conversion in the ratio 1/3.8/3.8, detected by glc. NMR and glc-ms data of compounds (32) and (33) were consistent to those obtained in section III.4.A.1 and III.4.A.2. The product was characterised as a mixture containing compounds (32), (33), (34). No further purification was attempted.

III.4.A.4. SUMMARY

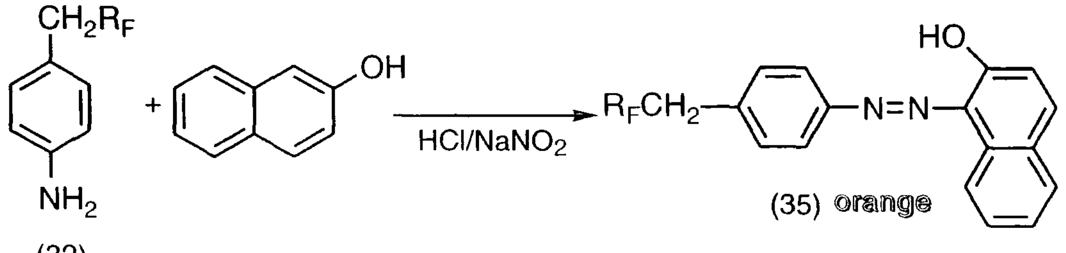
We found that this hydrogenation reaction is very effective with these perfluoroalkylated materials[116, 115] affording the corresponding primary amine in high yield and only mild conditions were required to carry out chemoselectively the reaction. Finally, a simple filtration and distillation of ethanol are necessary to give the pure aniline.

III.4.B. SYNTHESIS OF AZO-DYES

We have now achieved the synthesis of ready to use large, branched perfluoroalkylated aniline derivatives (32) and (33). This section deals with the synthesis of perfluoroalkylated azo-dyes and their characterisations. The synthetic route that we explored involved a two-step process[141, 142]; first, preparation of the reactive species: the diazonium salt from the aniline; then, the coupling reaction between the salt and electron rich compounds such as β-naphthol[136, 143].

III.4.B.1. 1-AMINO-4-[(PERFLUORO-2-METHYLPENTAN-2-YL)METHYL] BENZENE

Compound (35) was synthesised by coupling of diazotized 1-amino-4-[(perfluoro-2-methypentan-2-yl)methyl]benzene (32) with β-naphthol in an alkaline condition[136, 143]. The dye was precipitated from solution and collected as an orange solid: mp. 110-115°C. Problems were encountered during the purification stage; the product was purified by repeated column chromatography with methanol/water as the eluent. Growth of single crystals for X-ray crystallographic structure has been attempted but with little success.



(32)

(35) orange

53%

$R_F = C(CF_3)_2CF_2CF_2CF_3$

Mass spectrometry and accurate mass of compound (35) were consistent with the following molecular formular: $C_{23}H_{13}F_{13}N_2O$.

SPECTROSCOPY STUDIES

ULTROVIOLET

Spectrophotometric measurements have been carried out in acetonitrile to evaluate the extinction coefficients at different wavelengths, at 298 K. This azo-dye can be excited to give two electronic excitations[120]:

$$\pi \longrightarrow \pi^* \quad \text{(high energy)}$$

$$n \longrightarrow \pi^* \quad \text{(low energy)}$$

λ_{max} (nm)	ε_{max} ($dm^3.mol^{-1}.cm^{-1}$)
199	120,359
250	16,249
sh 420	7,999
sh 500	7,999

The intensities and positions of these bands depend on the groups attached to either end of the azo group[144]. The ultraviolet absorption of compound (35) is displaced towards higher wavelengths: a bathochrome shift, as more conjugation.

IR

The infra red spectra of compound (35) showed a peak in the aromatic region at 1622 cm^{-1} for C=C, which has moved to lower wavelengths because of high conjugation; a broad band at 1517-1450 cm^{-1} due to N=N stretch conjugated with the benzene ring and a very strong band at 1330-1145 cm^{-1} which includes N-C and C-F bonds, and finally a strong band at 3412 cm^{-1} for O-H bond (Spectrum No. 23).

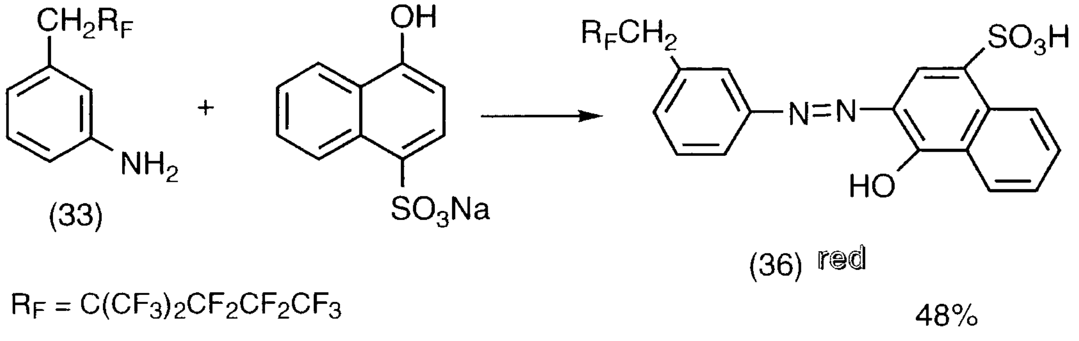
NMR

The ^{19}F NMR spectrum of structure (35) was consistent with the perfluoroalkyl branched segment: R_F= $C(CF_3)_2CF_2CF_2CF_3$. We encountered some problems to dissolve the azo-dyes in an organic solvent to run ^1H and ^{13}C NMR. ^1H NMR spectra showed broad multplet in the range of 8.6-6.6 pm and a singlet at $\delta(CH_2R_F)=3.8$ ppm, ^{13}C NMR spectrum was very complex, the signals were concentrated around 145-113 ppm and the assignement was not successful (Spectrum No. 29).

III.4.B.2. 1-AMINO-3-[(PERFLUORO-2-METHYLPENTAN-2-YL)METHYL] BENZENE

III.4.B.2.i. REACTION WITH α-NAPHTHOL DERIVATIVE

Compound (36) was synthesised by coupling of diazotized 1-amino-3-[(perfluoro-2-methypentan-2-yl)methyl]benzene (33) with sodium salt 4-hydroxy-1-naphthalenesulphonic acid hydrate in an alkaline condition[136, 143]. The dye was precipitated from solution and collected as a red solid: mp. 195-200°C. Problems were again encountered during the purification stage, the product was purified by repeated column chromatography with methanol/water as the eluent. Growth of single crystals for X-ray crystallographic structure has been attempted but with little success.



(33)

(36) red

48%

$R_F = C(CF_3)_2CF_2CF_2CF_3$

Mass spectrometry and accurate mass of compound (36) were consistent with the following molecular formular: $C_{23}H_{13}F_{13}N_2O_4S$.

SPECTROSCOPY STUDIES

ULTROVIOLET AND IR

Spectrophotometric measurements have been carried out in acetonitrile to evaluate the extinction coefficients at different wavelengths, at 298 K.

λ_{max} (nm)	ε_{max} ($dm^3 \cdot mol^{-1}.cm^{-1}$)
198	184,812
sh 235	11,331
350	2,331
490	3,716

The ultraviolet absorption of compound (36) is displaced towards higher wavelengths: a bathochrome shift, as more conjugation[144, 120].

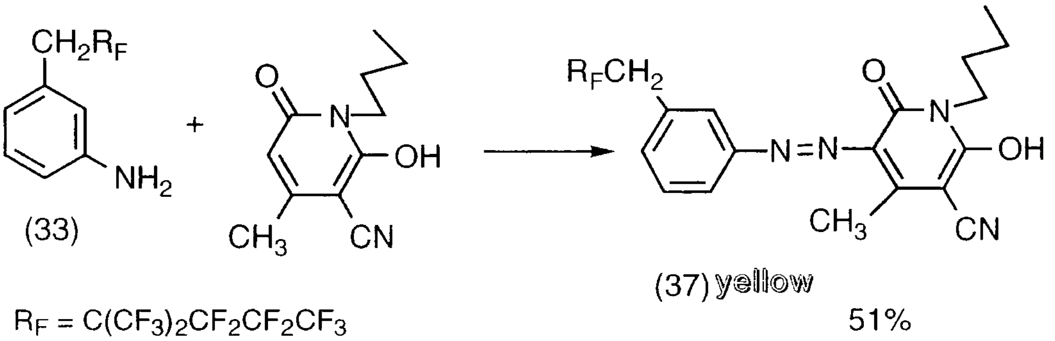
The infra red spectra of compound (36) showed a very broad peak at 3470 cm^{-1} for O-H, a peak at 1630 cm^{-1} for C=C; a resonably sharp band at 1593-1577 cm^{-1} due to N=N stretch conjugated with the benzene ring and a strong band at 1269-1218 cm^{-1} which includes N-C and C-F bonds (Spectrum No. 24).

NMR

The ^{19}F NMR spectrum of structure (36) was consistent with the perfluoroalkyl branched segment: $R_F= C(CF_3)_2CF_2CF_2CF_3$. We encountered some problems to dissolve the azo-dyes in an organic solvent to run ^1H and ^{13}C NMR. ^1H NMR spectra showed broad multplet in the range of 8.6-7.0 pm and a singlet at $\delta(CH_2R_F)=3.8$ ppm, ^{13}C NMR spectrum was very complex and the assignement was not successful (Spectrum No. 30).

III.4.B.2.ii. REACTION WITH PYRIDONE DERIVATIVE

Compound (37) was synthesised by coupling of diazotized 1-amino-3-[(perfluoro-2-methypentan-2-yl)methyl]benzene (33) with 1-*n*-butyl-2-hydroxy-3-cyano-4-methyl-1-pyridone-2 in an alkaline condition[136, 143]. The dye was precipitated from solution and collected as a yellow solid, mp. 75-80°C. Problems were encountered during the purification stage; the product was purified by repeated column chromatography with methanol/water as the eluent. Growth of single crystals for X-ray crystallographic structure has been attempted but with little success.



Mass spectrometry and accurate mass of compound (37) were consistent with the following molecular formular: $C_{24}H_{19}F_{13}N_4O_2$.

SPECTROSCOPY STUDIES

ULTROVIOLET

Spectrophotometric measurements have been carried out in acetonitrile to evaluate the extinction coefficients at different wavelengths, at 298 K.

λ_{max} (nm)	ε_{max} ($dm^3.mol^{-1}.cm^{-1}$)
199	1,369,732
sh 263	55,401
420	7,035

The ultraviolet absorption of compound (37) is displaced towards higher wavelengths: a bathochrome shift, as more conjugation[144, 120].

IR

The infra red spectra of compound (37) showed a small band at 3450 cm^{-1} for O-H, peaks at 2959 cm^{-1} for C-H bonds, the nitrile absorbed at 2235 cm^{-1} and broad peak 1698-1640 cm^{-1} including C=O and C=C. Finally, a broad band was observed at 1525 cm^{-1} due to N=N stretch conjugated with the benzene ring and a wide peak at 1280-1145 cm^{-1} which included N-C and C-F bonds (Spectrum No. 25).

NMR

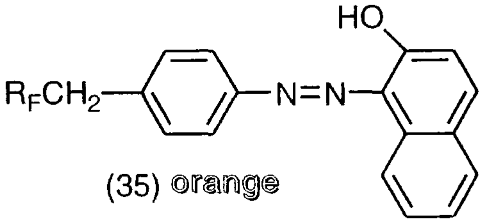
The ^{19}F NMR spectrum of structure (37) was consistent with the perfluoroalkyl branched segment: $R_F = C(CF_3)_2CF_2CF_2CF_3$. We encountered some problems to dissolve the azo-dyes in an organic solvent to run ^1H and ^{13}C NMR. The spectra obtained in both cases were too complex and the assignement was not successful (Spectrum No. 31).

III.4.C. SOLUBILITY OF DYES IN FLUOROCARBON SOLVENT

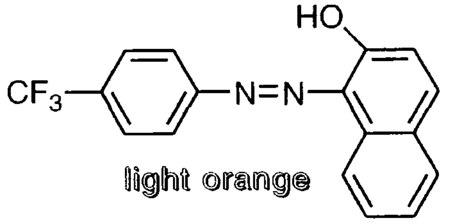
In summary, we have successfully synthesised azo-dyes in the range of colour red, orange and yellow which are soluble in fluorocarbon fluids FC-84, bp. 80°C, due to the presence of the perfluoroalkyl chain. This approach has allowed us to explore the effect of the perfluoroalkyl group on the solubility of these systems in perfluorinated fluids. We have now addressed the significant question of synthesising dyes that are made soluble in fluorocarbon solvent by the presence of the perfluoroalkyl segment.

yellow
orange
red

To our knowledge, these are the first such azo-dyes available. We have also compared the solubility of these systems by replacing CH_2R_F by CF_3.



(35) orange



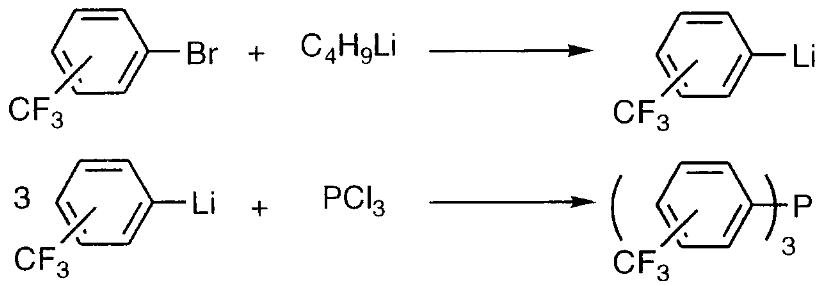
light orange

$R_F = C(CF_3)_2CF_2CF_2CF_3$

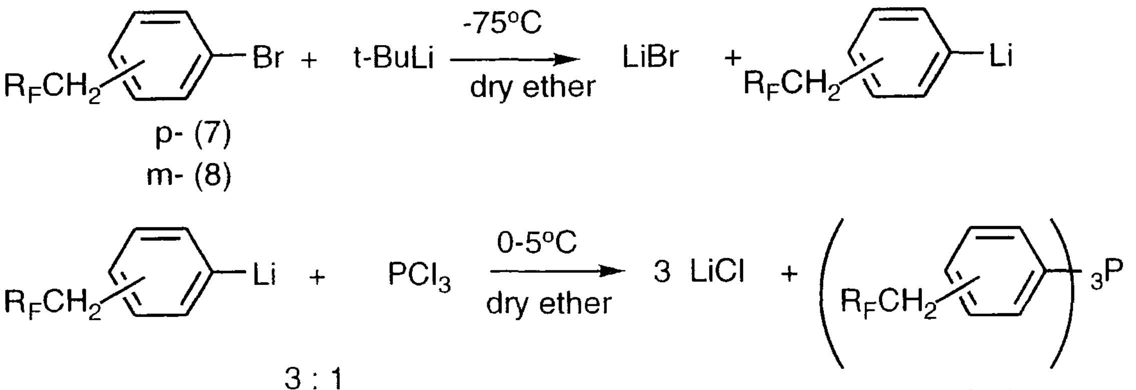
As we replaced C_6F_{13} by a smaller group CF_3 , we observed a dramatic decrease in the solubility of these systems in fluorocarbon solvent: FC-84. These results led us to the conclusion that the C_6F_{13} chain is long enough to force partitioning of the molecule into the fluorocarbon layer. These solubility experiments were easy to follow as the extinction coefficients of these azo-dyes are very high.

III.5. PERFLUOROALKYLATED TRIPHENYL PHOSPHINE DERIVATIVES

Finally, the approach of biphasic catalysis has been exploited for the preparation of triphenyl phosphines derivatives following the methodology that Eapan and co-workers[129] explored. The synthesis of tris-(trifluoromethylphenyl)phosphines has been achieved through the reaction of the appropriate trifluoromethylphosphosphyllithium and phosphorus trichloride.



The procedure involves a two-step reaction, formation of an organolithium reagent and then addition of phosphorus trichloride to form the triphenyl phosphine derivative[145, 118]. The preparation of these perfluoroalkylated derivatives was carried out in very dry diethyl ether under nitrogen, first by adding t-BuLi at -75°C to promote the metal exchange reaction with the bromo-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (7) and (8), then the intermediate was trapped with the electrophile, PCl_3 at a temperature between 0-5°C.



p- (7)
m- (8)

p- (38)
m- (39)

During the course of isolating the phosphine from the reaction mixture, it was noted that the product was air sensitive and was slowly converted to the phosphine oxide[129], [146], [147], as ^{31}P NMR indicated.

		(38) para (ppm)	(39) meta (ppm)
^{31}P	phosphine	-7.6	-5.2
	phosphine oxide	+23	+24.7
^{19}F		-62.8	-62.3
		-81.0	-80.5
		-106.3	-105.8
		-123.4	-122.9

After an additional of two hours, the reaction mixture became turbid and a white solid was deposited at the bottom of the flask. Removal of the solvent by filtration under nitrogen gave a white powder solid.

IR

The Infra red spectra of compound (38) in nujol showed a band at 1638 cm^{-1} due to C=C, a band at 1462 cm^{-1} characteristic to P-Ph bond+ nugol and finally a broad band 1263-1220 cm^{-1} for P-O and C-F bonds.

Furthermore, in the attempt to check the solubility of these phosphines in fluorocarbon solvent, NMR tubes containing compounds (38) and (39) were prepared with fluorocarbon fluids (FC-84, bp. 80°C; PP-11, bp. 215°C) and sealed under vacuum. ^{31}P NMR was run at different temperatures.

The experiment was carried out in FC-84 and repeated in PP-11; similar results were obtained. ^{31}P NMR were collected but no signal was recorded on the spectra. The phosphines (38) and (39) were found to be inmiscible in fluorocarbon solvent FC-84 or PP-11 at room temperature or 80°C. Similar attempts to dissolve (38) and (39) were carried out in organic solvents (THF, benzene, pentane, diethyl ether, acetone); both compounds failed to dissolve. Furthermore, the low solubility of the triphenyl phosphine derivatives caused insuperable problems to record NMR data.

Moreover, the order of oxidative stability of the phosphines (38) and (39) did not vary moving from the *meta* to the *para* isomer. Similarly, oxygen sensitivity was recorded by Eapen and co-workers[129] with tris-(trifluoromethylphenyl)phosphine. He reported that $(4\text{-}CF_3C_6H_4)_3P$, $(2\text{-}CF_3C_6H_4)_3P$ and $(3\text{-}CF_3C_6H_4)_3P$ were easily oxidised and converted into the oxide analogs. These observations towards atmospheric oxidation demonstrate that the introduction of a $C_6F_{13}CH_2$-group into the phenyl ring reduces their oxidative stability, similarly to incorporation of a CF_3 group. However, non-fluorinated analogs such as tris-(toluyl)phosphines have also been classified as air sensitive. This information is noteworthy for the study regarding the electronic effects of CH_2R_F when attributing any electronic properties of these perfluoroalkylated phosphines to air sensitivity.

III.6. CONCLUSION

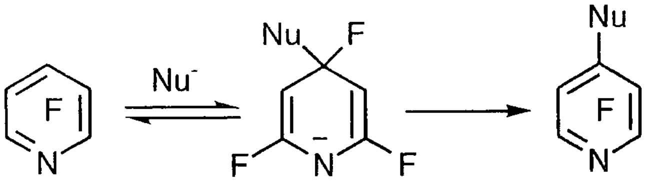
We have explored a range of synthetically useful reactions with these systems and synthesised a number of organic molecules containing a perfluoroalkyl chain: anilines, benzoic acids and azo-dyes. The chemistry of these systems has been investigated towards electrophilic substitution reactions, measurements of ionisation constants and oxidation reactions. It was found that the CH_2R_F group exerts predominantly a steric effect rather than an electronic influence on the reactivity of the benzene ring, these results were confirmed in the light of the electrophilic substitution reactions summarised in section III.2.D. Finally, these observations suggested that one methylene group between the reactive centre and the perfluoroalkyl group might behave as an insulating layer. Moreover, we showed that the perfluoroalkyl segment was long enough in the case of the azo-dyes to impart some solubility in fluorocarbon solvent.

CHAPTER IV

SYNTHESIS OF PERFLUOROALKYLATED TRIAZINES AND NUCLEOPHILIC REACTIONS OF THESE SYSTEMS

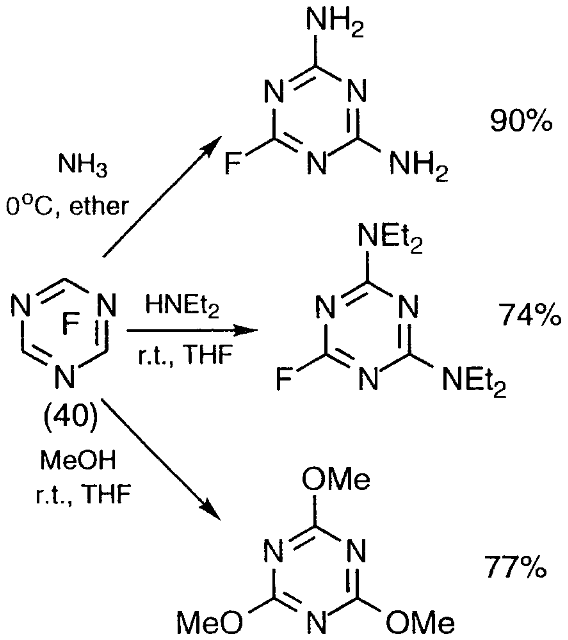
IV.1. INTRODUCTION

Highly fluorinated nitrogen heterocyclic systems are activated towards nucleophilic aromatic substitution. Taking pentafluoropyridine as an example, this system reacts with a wide range of nucleophiles[60, 148, 5, 149] to give the substitution products in high yields.



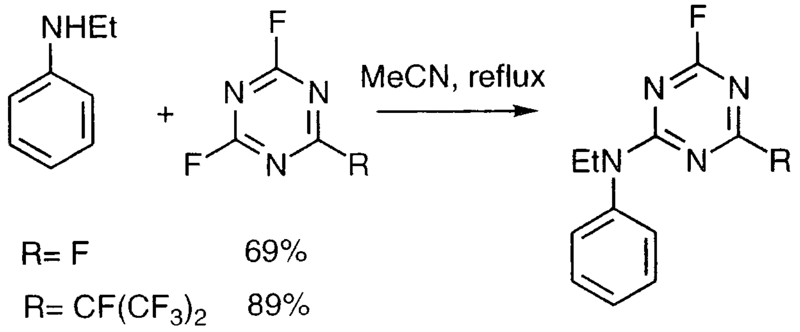
Nu⁻ = O, N, S, C.

The nucleophilc attack occurs exclusively at the 4-position maximising the activating effect of fluorine and nitrogen. On this basis, pyridine and related compounds are activated towards nucleophiles, with 2,4,6-trifluoro-s-triazine (40) the most reactive[150, 5, 151].



Other nucleophiles such as perfluorocarbanions, generated by reactions between fluoro-olefins and fluoride ion react with these highly fluorinated heterocyclic systems to give perfluoroalkylation products, these nucleophilic substitution reactions referred to as Negative Friedel-Crafts reactions[60, 59, 52, 55]. The literature concerning these reactions has been reviewed in Chapter I.

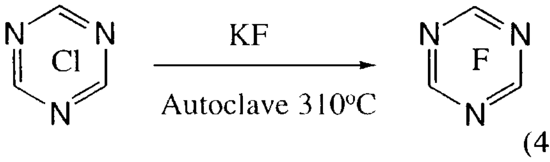
Since the incorporation of perfluoroalkyl groups described in Chapter II appears to be limited to benzylic systems, we have considered exploring alternative systems eg. 2,4,6-trifluoro-s-triazine. Moreover, nucleophilic substitution reactions have been reported in the literature with these perfluoroalkylated-s-triazines using nitrogen nucleophiles[5, 152, 151].



Our approach has been to explore methods for introducing perfluoroalkyl groups derived from hexafluoropropene into 2,4,6-trifluoro-s-triazine. The reactivity of these perfluoroalkylated systems has been investigated and examples of nucleophilic reactions of such materials will be described in this chapter using oxygen nucleophiles. Reactions between amines and perfluoroalkylated triazines have been reported in the literature[5, 152, 151] but we are unaware of any previous detailed investigations of reactions between perfluoroalkylated triazine and alcohols such as cyclohexanol or derivatives. These nucleophilic reactions have been extended to system containing free hydroxy group for surface treatment eg. cellulose.

IV.2. SYNTHESIS OF 2,4,6-TRIFLUORO-S-TRIAZINE

To perform the nucleophilic substitution reactions of 2,4,6-trifluoro-s-triazine the synthesis of the perfluorotriazine had to be carried out from the 2,4,6-trichloro-s-triazine[153, 151]. The reaction between 2,4,6-trichloro-s-triazine and anhydrous potassium fluoride in an autoclave at 310 °C, gave 2,4,6-trifluoro-s-triazine (40) in more than 90 % yield.



(40)

95%

This relatively low temperature (the optimum temperature for the analogous preparation of pentafluoropyridine is 470 °C) reflects the ease of nucleophilic substitution of triazine systems[5].

IV.3. PERFLUOROALKYLATION OF TRIFLUORO-S-TRIAZINE

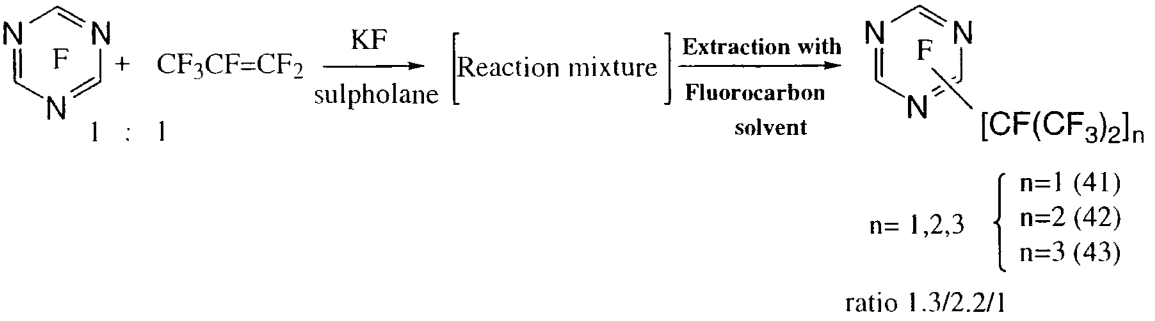
Chambers and other workers[45, 66, 52, 55] have demontrated that fluoride-ion induced formation of carbanions, from reactions with fluorinated alkenes, provides useful methodology for carbon-carbon formation after trapping the carbanion with a fluoroheterocycle.

$$F^{\ominus} + CF_3CF{=}CF_2 \rightleftharpoons (CF_3)_2\overset{\ominus}{C}F \dashrightarrow$$

Two methods of perfluoroalkylation have been investigated. The first procedure used potassium fluoride to initiate the reaction[154] and the second one employed trimethylamine as a reagent[66].

IV.3.A. USE OF POTASSIUM FLUORIDE IN SULPHOLANE

The perfluoroalkylation reaction was carried out in sulpholane at 70°C, a process developed previously in these laboratories[155, 105, 156, 157]. After 19 hours, a mixture containing 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41), 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) and 2,4,6-perfluorotri-isopropyl-s-triazine (43) was obtained, the ratio of products showed predominantly compound (42).

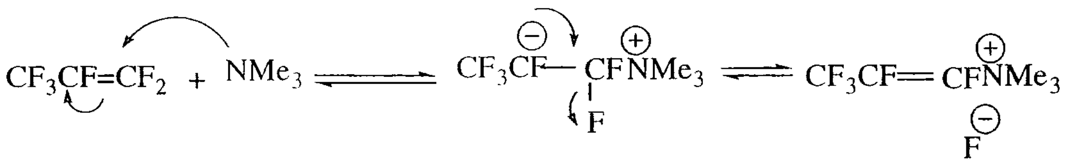


Previously, anhydrous potassium fluoride, largely in suspension in sulpholane has been used effectively, but problems have been encountered in isolation of the products. The extraction of the products (41), (42) and (43) from sulpholane was successful by using a perfluorocarbon solvent: PP-11, bp 215°C. The distillation with a column length distillation of 800 mm and the calculated 75 theoretical plates enabled us to separate the mono-derivative (41) and di-derivative (42) in 90% purity, this experiment was particularly delicate as the boiling points of the respective compounds are very close. The glc-ms and NMR data for 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41) and 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) were consistent with the literature[151] values.

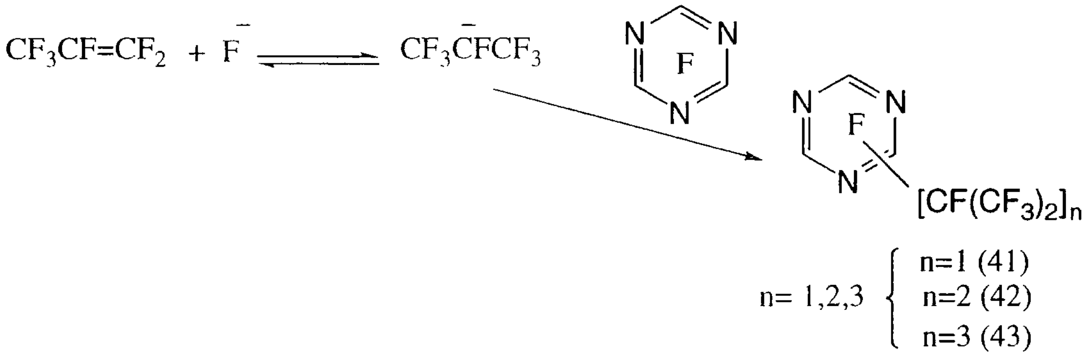
IV.3.B. USE OF TRIMETHYLAMINE

IV.3.B.1. CONDITIONS OF THE REACTION

The use of trimethylamine as a catalyst in perfluoroalkylation reactions was explored as a way to produce fluoride ion *in situ* in the absence of a solvent[158, 66, 109, 68].



It seemed reasonable to consider using a small amount of this amine, with an unsaturated fluorocarbon, to generate a source of fluoride ion, that was very active. This is providing that the starting materials are anhydrous.



The approach was developed to synthesise mainly the 2,4,6-perfluorotri-isopropyl (43) adduct and to determine the conditions for the success of the reaction. For that purpose, different reactions were set up, in particular involving various sealed systems dependent on the pressure required. Sealed tubes were charged with hexafluoropropene and a base in a 3:1 ratio or more to 2,4,6-trifluoro-s-triazine (40). Yields for the synthesis of (43) seemed to vary depending on the proportion of 2,4,6-trifluoro-s-triazine (40) to hexafluoropropene and the volume of material used.

1,3,5-TRIFLUORO-S-TRIAZINE WITH HEXAFLUOROPROPENE

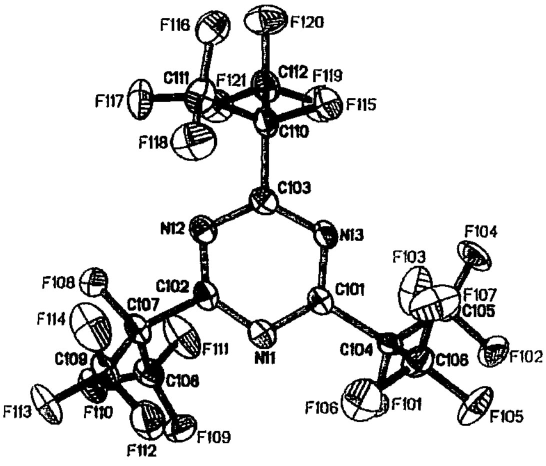
VOLUME OF SEALED TUBE	NB MOLE OF OLEF.	RATIO TRIAZ./OLEF	(41) %	(42) %	(43) %
60 CM3	22.8 MMOL	1:3	10	55	35
	30 MMOL	1:4	19	65	16
20 CM3	68 MMOL	1:3.1	1	14	85
	68.6 MMOL	1:3.8	0	0	100

As the proportion of material increases in the sealed system the perfluoroalkylation reaction occurs selectively to give 2,4,6-perfluorotri-isopropyl-s-triazine (43) as a solid material, using a ratio of triazine/olefin equal to 1:3.8. The important aspect of this procedure was that the products may be isolated essentially pure simply by transfering to a cold trap under reduced pressure. Analyses was carried out after dissolving in a fluorocarbon solvent (FC-84, bp. 80°C) and a single crystal of

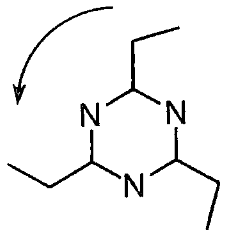
(43) was grown from fluorocarbon (FC-84, bp. 80°C) over a week at -15°C and an X-ray structure was obtained.

IV.3.B.2. CRYSTAL STRUCTURE OF 2,4,6-PERFLUOROTRI-ISOPROPYL-S-TRIAZINE

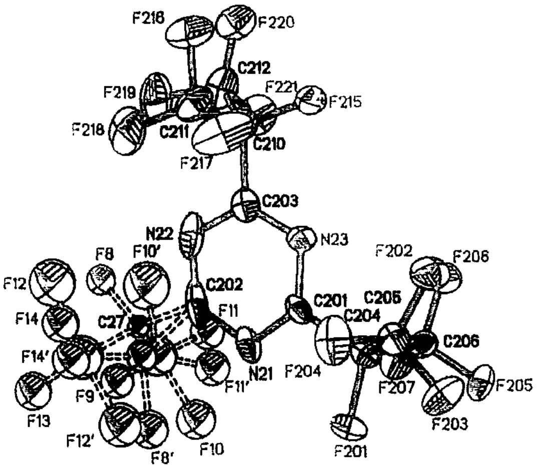
The growth of crystals (in FC-84) allowed us to obtain a crystal structure of the 2,4,6-perfluorotri-isopropyl-s-triazine (43). Two conformational isomers Scheme 1 and 2 [molecule (I), (II)] were identified, arising from the different conformation which the perfluoroisopropyl groups at the 2-, 4- and 6-positions can adopt[159]. The structures are represented Figure I, where the triazine ring and the C-F bonds from the perfluoroisopropyl group are in the same plan. Scheme 3 represents a disordered molecule corresponding to the superposition of molecules (I) and (II). The molecule (I) has the three perfluoroisopropyl groups orientated in clockwise direction as shown in Scheme 1. The second isomer molecule (II) presents two perfluoroisopropyl groups in the same direction while the third one is orientated anticlockwise.


F116
F120
C111
F121
C112
F119
F117
F115
F118
C110
C103
N12
N13
F104
F103
F108
C102
C101
F107
C105
C107
F114
F111
N11
C104
C106
F102
C109
C108
F113
F110
F106
F101
F105
F112
F109

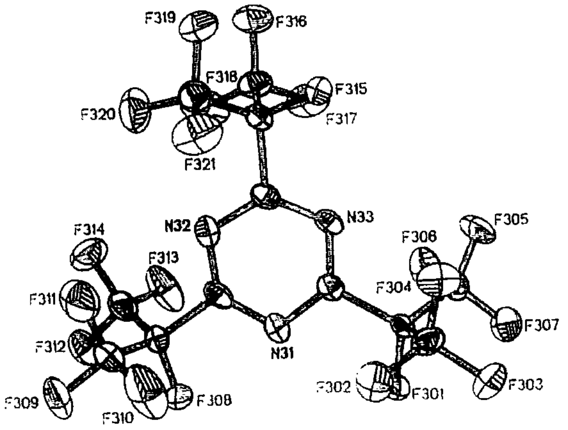
Molecule (I)



Scheme 1


F216
F220
C212
F219
F221
F215
F218
C211
C210
F217
C203
N22
N23
F202
F206
F8
F10'
F12
C202
F11
C201
C205
F14
C27
C204
C206
F14'
F11'
N21
F204
F9
F207
F205
F13
F203
F12'
F8'
F10
F201

Scheme 3


F319
F316
F318
F315
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F317
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N32
N33
F314
F306
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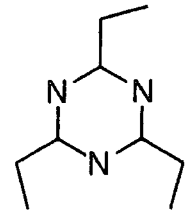
N31
F302
F301
F303
F309
F308
F310

Molecule (II)



Scheme 2

Figure I

SPECTROSCOPIC STUDIES: NMR

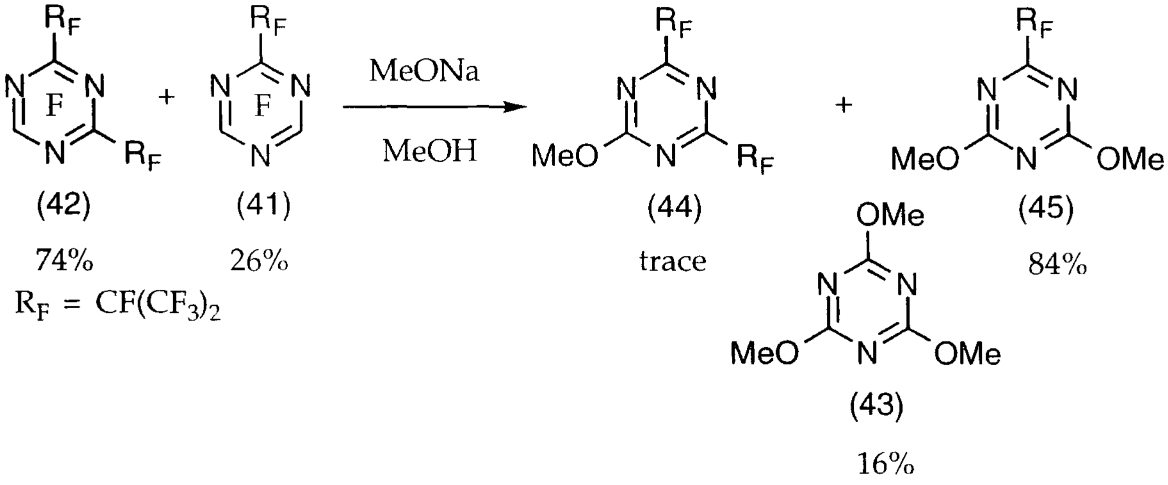
At room temperature, the ^{19}F NMR spectra was run in deuterated chloroform and exhibited two resonance peaks: -73.7 ppm (d, $^{3}J_{FF}$ 7.5, CF_3) and -186.4 ppm (sept, $^{3}J_{FF}$ 7.5, $\underline{CF}(CF_3)_2$) showing an average of the two conformational isomers. Similarly, the ^{13}C NMR spectra was consistent with the structure: 88.8 ppm (dsept, $^{1}J_{CF}$ 215, $^{2}J_{CF}$ 33, $\underline{CF}(CF_3)_2$), 118.3 ppm (qd, $^{1}J_{CF}$ 286, $^{2}J_{CF}$ 26, $CF(\underline{CF_3})_2$), 166.6 ppm (d, $^{2}J_{CF}$ 22, $\underline{C}_{triaz}CF(CF_3)_2$), section n.m.r. spectrum No 34.

IV.4. NUCLEOPHILIC SUBSTITUTION REACTIONS OF PERFLUOROALKYLATED TRIAZINES

In this section, we will be describing nucleophilic substitution reactions using a mixture of 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41) and 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) with a range of alcohols and derivatives. Most of the following nucleophilic reactions were carried out using a mixture containing compounds (41) and (42) as the separation and purification steps were delicate.

IV.4.A. SODIUM METHOXIDE

Reaction between a mixture containing compounds (41) and (42) in the ratio 26% / 74% with sodium methoxide was carried out in methanol at room temperature to give three components the mono, di and trimethoxy derivatives[160].



(42) 74%

(41) 26%

$R_F = CF(CF_3)_2$

(44) trace

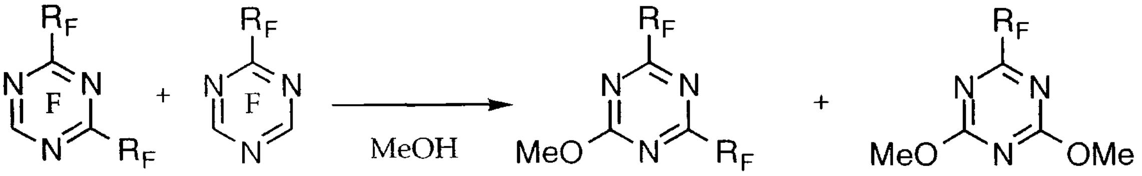
(45) 84%

(43) 16%

During the reaction, displacement of fluorine and perfluoroisopropyl groups were observed. Full replacement of R_F and F substituents by the methoxy group occured at room temperature; 2,4,6-trimethoxy-s-triazine (43) was detected by glc in 16%. The conditions of the reaction showed the ease of the displacement of the perfluoroalkyl group. The results suggested also that the base (sodium methoxide) used was too strong for these very reactive systems. No further purification was attempted.

IV.4.B. METHANOL

Reaction was then performed using a mixture of (41) and (42) in the ratio 26% / 74% in methanol at room temperature. Full conversion of the starting materials was observed and two components, 2-methoxy-4,6-perfluorodi-isopropyl-s-triazine (44) and 2,4-dimethoxy-6-perfluoroisopropyl-s-triazine (45) were formed[160].



(42) 74% (41) 26% (44) 74% (45) 26%

R_F = $CF(CF_3)_2$

Nucleophilic substitution occured at the fluorine positions only. The two compounds 2-methoxy-4,6-perfluorodi-isopropyl-s-triazine (44) and 2,4-methoxy-6-perfluoroisopropyl-s-triazine (45) were characterised as single components after separation using preparative scale chromatography.

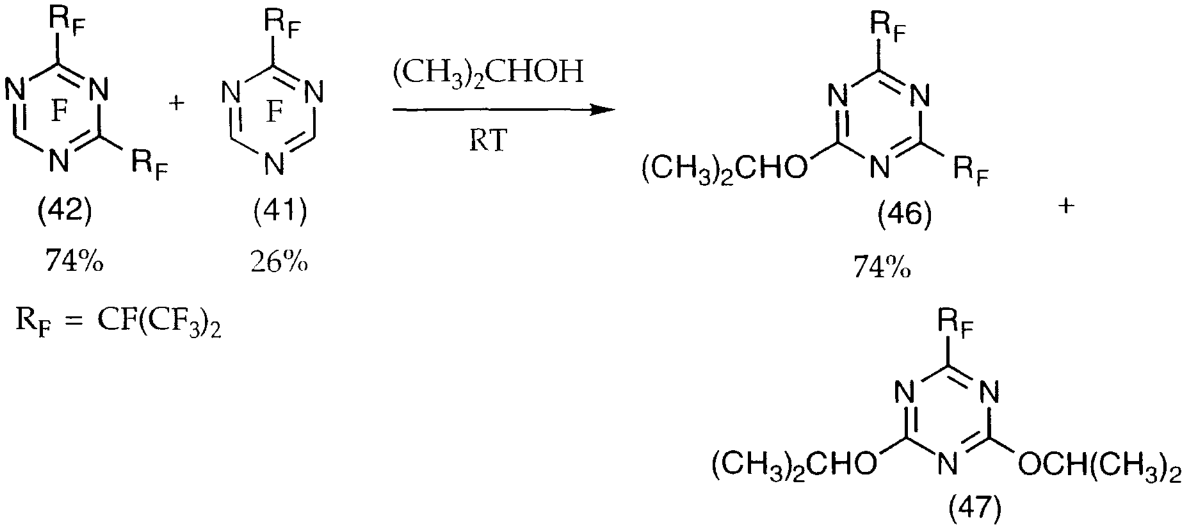
SPECTROSCOPIC STUDIES: NMR

^{1}H NMR spectra were assigned with reference to shifts of similar compounds taken from the literature[160]. Only one singlet was detected for structures (44) and (45) which were respectively 4.26 ppm and 4.12 ppm.

^{19}F NMR gave identical chemical shifts for the compounds (44) and (45): -74.4 (d, $^3J_{FF}$ 7.5, $CF(\underline{CF}_3)_2$) and -184.8 ppm (sept, $^3J_{FF}$ 7.5, $\underline{CF}(CF_3)_2$). The result of the complete analysis of the spectra is given section spectrum No 35 and No 36.

IV.4.C. ISOPROPANOL

A mixture of (41) and (42) in the ratio 26% / 74% reacted with isopropanol at room temperature to give nucleophilic substitution products 2-isopropoxy-4,6-perfluorodi-isopropyl-s-triazine (46) and 2,4-di-isopropoxy-6-perfluoroisopropyl-s-triazine (47).



(42) 74% (41) 26% (46) 74% (47) 26%

R_F = $CF(CF_3)_2$

SPECTROSCOPIC STUDIES: NMR

Structure (46)

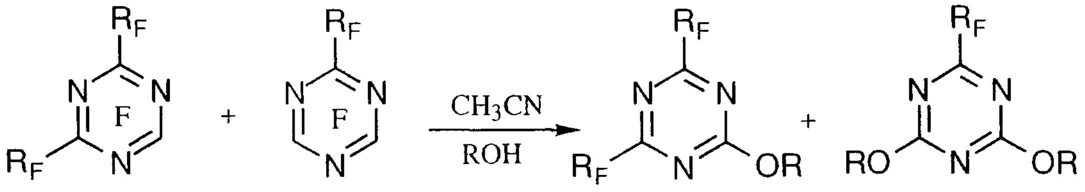
^1H NMR spectra showed a doublet with an integration of 6H at 1.50 ppm ($^3J_{HH}$ 6, CH($\underline{CH}_3$)$_2$) and a septuplet with an integration of 1H at 5.47 ppm ($^3J_{HH}$ 6, $\underline{CH}$(CH_3)$_2$). ^{13}C NMR showed the presence of the isopropoxy substituents as 2 resonances (CH and CH_3) of relative intensities 1:2 at 78 ppm and 21.2 ppm. ^{19}F NMR consisting of 2 resonances (CF_3, CF) of relative intensities 12:2 at respectively 74.4 (d, $^3J_{FF}$ 7.5) and -184.8 ppm (sept, $^3J_{FF}$ 7.5). The result of the complete analysis of the spectra is given section spectrum No 37.

Structure (47)

^1H, ^{13}C and ^{19}F NMR gave very simillar spectra as compounds (46). The result of the complete analysis of the spectra is given section spectrum No 38.

IV.4.D. REACTION WITH PHENOL AND p-CRESOL

A mixture of 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41) and 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) in the ratio 26% / 74% reacted with phenol or p-cresol in acetonitrile at different temperatures to give the corresponding products the mono-derivative (48) and the di-derivative (49).



(42) 74%

(41) 26%

(48)

(49)

R_F= CF(CF_3)$_2$

R= OC_6H_5 (A)	R.T. 2 hours	5%	/
	reflux 12 hours	74%	26%
R= $OC_6H_4(CH_3)$ (B)	reflux 12 hours	74%	26%

At room temperature, the reaction with phenol gave a low conversion. For completion of the reaction, the temperature had to be raised to 80°C and left overnight. The reaction was repeated with p-cresol to afford the desired compounds. The increase in temperature which is required can be explained as we move to less nucleophilic substrate phenol and p-cresol (in comparison to methanol and isopropanol) and also they might be more sterically demanding nucleophiles. In both cases, the purification of compounds 48A and 48B required a column chromatography using CH_2Cl_2/Hexane as the eluent. Furthermore, full characterisation of the mono-substituted products 48A and 48B were carried out.

SPECTROSCOPIC STUDIES: NMR

Comparing the chemical shifts data of ^{19}F NMR for the perfluoroalkylated groups in these compounds (41), (42), (48A) and (48B), in Table 1, it is clear that the shifts are similar.

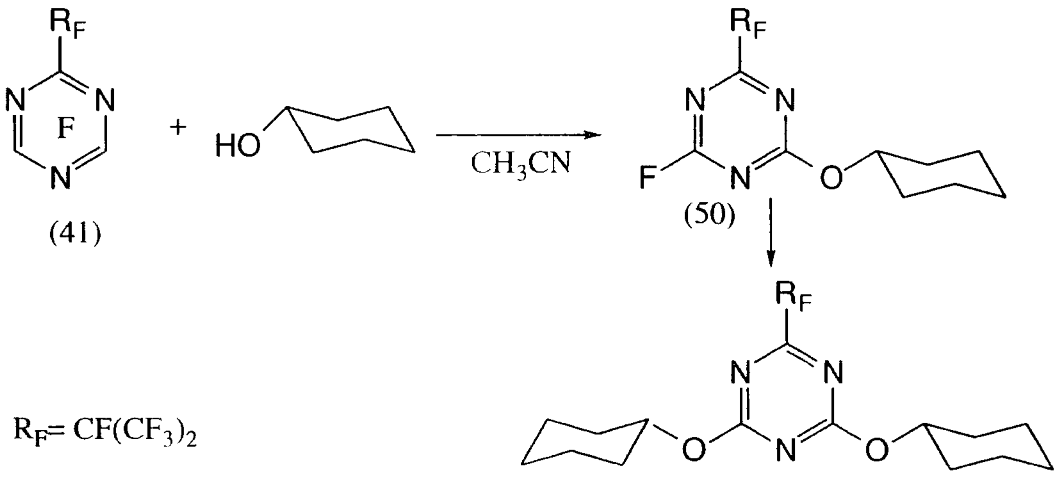
	Ring F (ppm)	CF (ppm)	CF_3 (ppm)
compound (41)	-30.4	-188.8	-74.4
compound (42)	-30.0	-186.8	-75.7
compound (48A)	/	-184.8	-74.4
compound (48B)	/	-184.5	-74.5

Table 1

The result of the complete analysis of the spectra for compounds 48A and 48B is given section spectrum No 39 and No 40.

IV.4.E. REACTION WITH CYCLOHEXANOL 2,4-DIFLUORO-6-PERFLUOROISOPROPYL-S-TRIAZINE

A similar reaction between 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41) and cyclohexanol, was performed in acetonitrile to give the nucleophilic substituted product 2,4-dicyclohexanoxy-6-perfluoroisopropyl-s-triazine (51) in good yield 66%.



(41)

(50)

$R_F = CF(CF_3)_2$

(51) 66% isolated yield

The reaction was followed by glc-ms as an intermediate was formed: 2-cyclohexanoxy-4-fluoro-6-perfluoroisopropyl-s-triazine (50). The product (51) was formed by nucleophilic substitution in good yield, after addition of an excess of cyclohexanol for completion of the reaction.

analysis by glc-ms	addition of 2.5 cyclohexanol 15 hours reflux	excess of cyclohexanol 15 hours reflux	15 hours reflux
ratio (50)/(51)	84%/16%	45%/55%	4%/96%

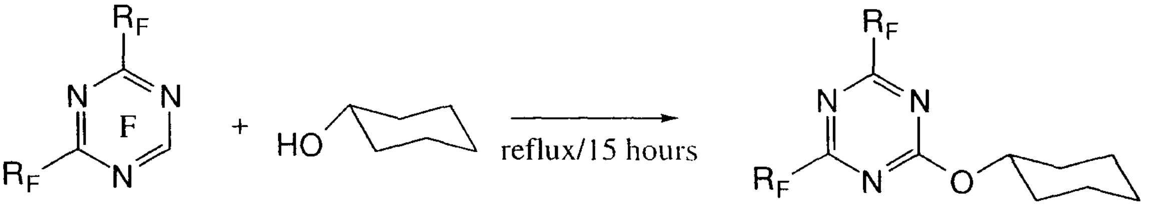
The 2,4-dicyclohexanoxy-6-perfluoroisopropyl-s-triazine (51) was successfully purified by column chromatography using CH_2Cl_2/Hexane as the eluent.

SPECTROSCOPIC STUDIES: NMR

The ^{19}F NMR shifts for compound (51) are tabulated section spectrum No 41. The spectra are as expected by comparaison with the shifts of the parent triazine. The ^{13}C NMR and ^{1}H NMR shifts were also assigned and are given section spectrum No 41.

2-FLUORO-4,6-PERFLUORODI-ISOPROPYL-S-TRIAZINE

The substitution reaction between 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) and cyclohexanol was carried out in acetonitrile and also in perfluorocarbon media to give 2-cyclohexanoxy-4,6-perfluorodi-isopropyl-s-triazine (52) in respectively good yield 63% and 60%.



(42)

(52)

R_F= $CF(CF_3)_2$

Solvent:	
CH_3CN	63%
FC-84	60%

The complete conversion of the 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine was observed in both reactions and the isolated yields recorded were very similar 63% and 60%, using a column chromatography with CH_2Cl_2/Hexane as the eluent.

The success of this nucleophilic substitution reaction demonstrates that perfluorocarbon fluids can be used effectively as a reaction media.

SPECTROSCOPIC STUDIES: NMR

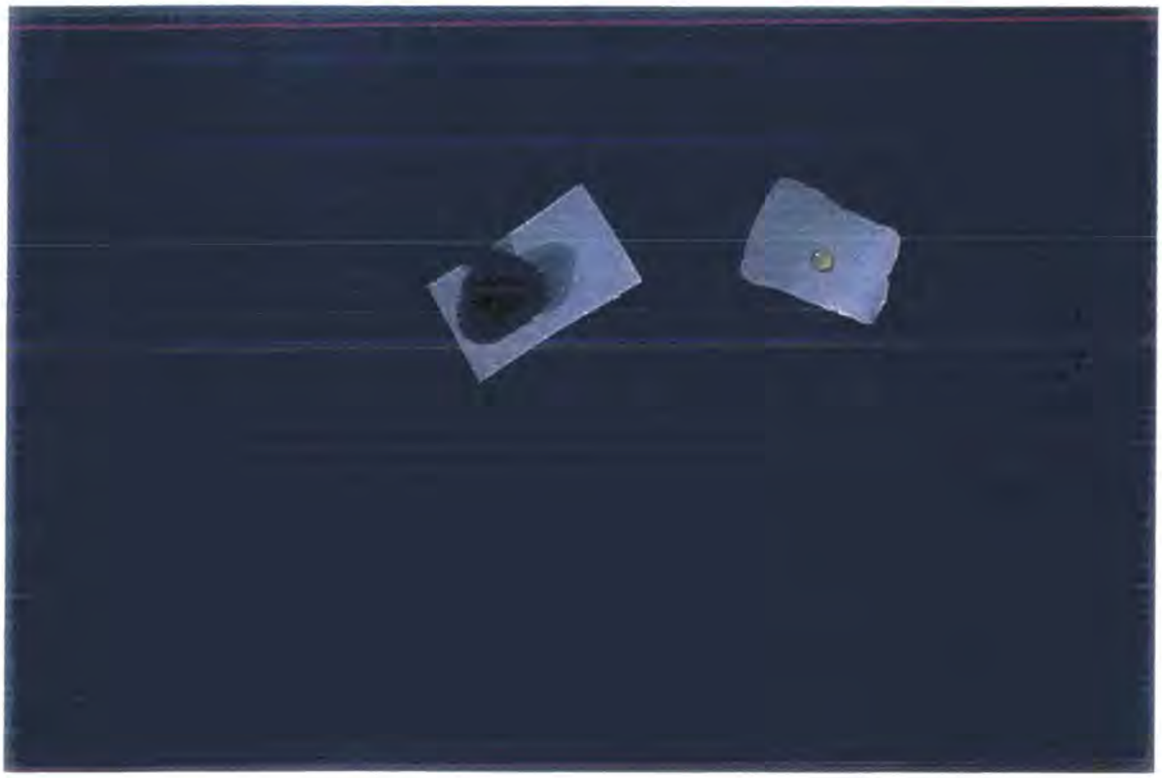
The ^{19}F NMR, ^{13}C NMR and ^{1}H NMR shifts for compound (52) are given section spectrum No 42.

IV.4.F. CELLULOSE DERIVATIVES

We have demonstated that 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41) 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) are reactive towards oxygen nucleophiles. We went further and explored the possibility of reacting these derivatives with cellulose which has free hydroxy groups. A mixture of (41) and (42) in the ratio of 74%/26% was placed in a round bottom flask with some standard filter paperand the mixture was stirred and refluxed in PP-11/acetonitrile (1/4) as the solvent overnight. The progression of the reaction was followed by glc as the concentration of compounds (41) and (42) was calculating by integrating the peak area. Completion of the reaction was determined when no trace of 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41) and 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) were detected by glc. After removal of the solvent, different tests were carried out with the treated filter paper (A). We compared filter paper (A) to standard filter paper (B) and filter paper (C). The filter paper (C) was left overnight in PP-11 solvent and the solvent pumped off.

The filter papers (B) and (C) absorbed water and oil. However, the treated filter paper (A) presented water and oil repellency see the photograph below.

These perfluoroalkylated triazines: 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41) and 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) are reactive towards any compounds bearing a free hydroxy group such as cellulose. This is particularly interesting as fluorochemicals carrying perfluoroalkyl groups modify the surface of the material and hence impart resistance to water, oils and soils. This could find applications with textile finishes, leather and paper finishes.



IV.5. CONCLUSION

We have shown that the 2,4,6-trifluoro-s-triazines are activated systems and undergo easily nucleophilic attack, in particular, the introduction of perfluoroalkyl groups was successful. Two procedures could be quoted to introduce perfluoroalkyl chains into fluorinated heterocycles systems. The method involving the use of trimethylamine at high pressure seems to give predominantly the tri-substituted product. This methodology constitutes a useful procedure to replace all the fluorine atoms by perfluoroalkyl groups in absence of a solvent.

A series of nucleophilic substitution reactions of the perfluoralkylated-s-triazines (41) and (42) were performed successfully. Perfluoroalkylated-s-triazines, similar to trifluoro-s-triazine, were found to be highly reactive towards oxygen nucleophiles. Furthermore, this process did not require any base and occured simply with neutral alcohols at room temperature such as methanol or isopropanol. These perfluoroalkylated triazines could be used as precursor of fibre-reactive dyes as many of them are prepared by simple nucleophilic displacement.

We have also demonstated that compounds bearing a free hydroxy group such as cellulose react with perfluoroalkylated triazine materials. These systems with such valuable properties as water and oil repellency have potential in a wide area of applications.

INSTRUMENTATION AND REAGENTS

NMR Spectra

^1H NMR spectra were recorded on Bruker AC 250 spectrometer operating at 250.13 MHz, a Varian Gemini VXR 200 spectrometer operating at 199.98 MHz, or a Varian VXR 400S spectrometer operating at 399.96 MHz. ^{19}F NMR spectra were recorded on the Brucker AC 250 spectrometer operating at 235.34 MHz or on the Varian VXR 400S spectrometer operating at 376.29 MHz. ^{31}P NMR spectra were recorded on the Brucker AC 250 spectrometer operating at 100.03 MHz. ^{13}C NMR spectra were recorded on the Varian VXR 400S spectrometer operating at 100.58 MHz. Chemical shifts are quoted in ppm relative to internal TMS or $CFCl_3$. The coupling constants (J values) are quoted in Hz.

Infra-Red Spectra

IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrometer using KBr disc (solid samples) or thin films between two KBr plates (liquid samples).

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.

Mass Spectra

The mass spectra of solid samples were recorded on a VG 7070E Spectrometer. Fast atom bombardment (FAB) mass spectrometry were performed on the same machine, with glycerol or glycerol/H_2O as a solvent. Mass spectra of solutions were run on a VG Trio 1000 spectrometer fitted with a Hewlett Packard 5890 Series II Gas Chromtograph (GLC-MS) equipped with a 25m cross-linked methyl silicone Gum (0.2 mm * 0.33 µm film) or fitted with a VG platform II electrospray.

Gas Liquid Chromatographic analysis

Analyses were performed on a VG Trio 1000 spectrometer linked to a Hewlett Packard 5890 Series II gas liquid chromatograph. HPLC (high-performance liquid chromatography) analyses were carried out on a Varian star system incorporating a polychrome diode array detector. Preparative scale GC was performed on a Varian Aerograph Model 920 (catharometer detector) gas liquid chromatograph, fitted with a 3m 10% SE 30 packed columns.

UV Spectra

Analyses were recorded at 25°C on a Perkin-Elmer Lambda 12 spectrophotometer using 1cm path length quartz cells.

Fractional Distillation

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

Melting Points

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

Reagents and Solvents

Unless otherwise stated, chemicals were used as received from suppliers (Aldrich, Fluorochem, Lancaster, Zeneca). Solvents were dried by standard methods and stored over a molecular sieve (type 4A).

CHAPTER V
EXPERIMENTAL TO CHAPTER II

V.1. ATTEMPTED PERFLUOROALKYLATION USING HEXAFLUOROPROPENE

V.1.A. USE OF POTASSIUM FLUORIDE

V.1.A.1. 1,3-Xylylene dibromide

A Carius tube was charged with hexafluoropropene (1.0 g, 6.6 mmol), 1,3-xylylene dibromide (0.56 g, 2.1 mmol), potassium fluoride (0.54 g, 9.3 mmol) and N,N-dimethylformamide (5 ml). The tube was sealed and heated at 100 °C for 18h. The reaction was analysed by glc-ms, glc and ^{19}F NMR. A mixture of products was obtained giving very complex spectra, with complete conversion of hexafluoropropene. Trace of perfluoroalkylated products were detected by glc-ms: 1,3-bis(perfluoro-isopropyl)xylylene m/z (EI$^+$).442 (M$^+$, 4%) 104 (21) 69 (100) and 1-fluoromethyl-3-[(perfluoro-isopropyl)methyl]benzene m/z (EI$^+$).292 (M$^+$, 1%) 123 (100) 69 (32); the glc-ms spectrum also showed oligomers of hexafluoropropene, hexafluoropropene dimer m/z (EI$^+$).300 (M$^+$, 5%) 231 (14) 281(37) 181 (50) 69 (100) and hexafluoropropene trimer m/z (EI$^+$).450 (M$^+$, 1%) 431 (14) 69 (100). No further purification was attempted.

The reaction was repeated at atmospheric pressure with hexafluoropropene added using a bladder with different solvents: DMF and sulpholane. Similar results were recorded as previously. When diglyme or NMP was used as the solvent the starting materials were fully recovered and glc-ms showed no trace of perfluoroalkyl compounds.

V.1.A.2. 1,4-Xylylene dibromide

A Carius tube was charged with hexafluoropropene (1.1 g, 7.3 mmol), 1,4-xylylene dibromide (0.61 g, 2.3 mmol), potassium fluoride (0.5 g, 8.6 mmol) and N,N-dimethylformamide (5 ml). The tube was sealed and heated at 100 °C for 18h. The reaction was analysed by glc-ms, gc and ^{19}F NMR. A mixture of products was obtained giving very complex spectra, with complete conversion of hexafluoropropene. Trace of perfluoroalkylated products were detected by glc-ms: 1,4-bis(perfluoro-isopropyl)xylylene m/z (EI$^+$).442 (M$^+$, 6%) 104 (24) 69 (100) and 1-fluoromethyl-4-[(perfluoro-isopropyl)methyl]benzene m/z (EI$^+$).292 (M$^+$, 1%) 273 (100) 104 (42) 69 (32); the glc-ms spectrum also showed oligomers of hexafluoropropene, hexafluoropropene dimer m/z (EI$^+$).300 (M$^+$, 5%) 231 (14) 281(37) 181 (50) 69 (100) and hexafluoropropene trimer m/z (EI$^+$).450 (M$^+$, 1%) 431 (14) 69 (100). No further purification was attempted.

The reaction was repeated at atmospheric pressure with hexafluoropropene added using a bladder with different solvents: DMF and sulpholane. Similar results were recorded as previously. When diglyme or NMP was used as the solvent the starting materials were fully recovered and glc-ms showed no trace of perfluoroalkyl compounds.

V.1.A.3. Absence of solvent

A Carius tube was charged with hexafluoropropene (0.7 g, 4.6 mmol), 1,3-xylylene dibromide (0.4 g, 1.5 mmol) and potassium fluoride (0.4 g, 6.8 mmol). The reaction was heated at 100 °C for 18h. The mixture was washed with acetonitrile. The solution was analysed by glc-ms and ^{19}F NMR. After 18h heating the starting materials were recovered and ^{19}F NMR data showed no perfluoroalkyl compounds apart from hexafluoropropene (n.m.r. Spectrum No 1) and hexafluoropropene dimer was detected by glc-ms: m/z (EI^+).300 (M^+, 5%) 231 (14) 281(37) 181 (50) 69 (100). The experiment was repeated by using a rotating oil bath at 100 °C but the reaction did not give better results.

V.1.B. USE OF CAESIUM FLUORIDE

General Procedure - A Carius tube was charged with hexafluoropropene, benzyl or xylylene derivative and caesium fluoride in sulpholane. The tube was sealed and heated at 60 °C for at least 16hrs. The volatile materials were isolated by transfer to a cold trap under reduced pressure.

V.1.B.1. Reaction with $ArCH_2Br$ derivatives

Caesium fluoride (0.8 g, 5.2 mmol) was rapidly introduced into a dry Carius tube with 1,3-xylylene dibromide (0.7 g, 2.6 mmol) and sulpholane (7 ml). Hexafluoropropene (1.2 g, 8 mmol) was condensed inside, under vacuum, the tube was then sealed and heated at 60°C for 16 hrs. No volatile material was transfered. After addition of CH_3CN to the residual, the glc-ms did not show the presence of any perfluoroalkylated compounds apart from 1,3-xylylene difluoride m/z (EI^+) 142 (M^+, 20 %) 104 (100). The ^{19}F NMR spectra contained a large number of peaks; no further purification was attempted. Under the same conditions, the reaction was repeated for days and one week without success. No further purification was attempted.

Finally, 1,3-xylylene dibromide was replaced by benzyl bromide and the reaction was performed in supholane at 60°C for 16 hrs. The glc-ms chromatogram showed the presence (trace) of [(perfluoroisopropyl)methyl]benzene m/z (EI^+) 260 (M^+, 6%) 207 (22) 91 (26) and the starting material. The ^{19}F NMR spectra contained a large number of peaks. No further purification was attempted.

V.1.B.2. Reaction of CsF with hexafluoropropene

Caesium fluoride (1.3g, 8.5 mmol) was rapidly introduced into a dry Carius tube with sulpholane (6 ml). Hexafluoropropene (1.3 g, 8.6 mmol) was condensed into the tube, under vacuum and the tube was then sealed. The mixture was heated and agitated at 60 °C for 12hrs. No hexafluoropropene was transfered showing that it was completely consumed. After addition of CH_3CN to the residue, the glc-ms showed the presence of some fairly volatile product: hexafluoropropene trimer m/z (EI^+) 431 (M^+, 0.1 %) 159 (41) 69 (100) and hexafluoropropene dimer m/z (EI^+).300 (M^+, 5%) 231 (14) 281(37) 181 (50) 69 (100). A mixture of products was obtained giving very complex ^{19}F NMR spectra.

V.2. PERFLUOROALKYLATION USING PERFLUORO-2-METHYL-2-PENTENE

V.2.A. USE OF POTASSIUM FLUORIDE

V.2.A.1. 1,3-Xylylene dibromide

Perfluoro-2-methyl-2-pentene (1.79g, 5.9 mmol), potassium fluoride (0.41g, 7 mmol), 1,3-xylylene dibromide (0.5g, 1.9 mmol) and N,N-dimethylformamide (10 ml) were placed in a sealed glass tube and heated at 100 °C for 24h. The reaction was analysed by glc-ms, gc and ^{19}F NMR. A mixture of products was obtained giving very complex spectrum. After 24h heating the ^{19}F NMR data did not show any hexafluoropropene dimer. The glc-ms chromatogram showed traces of 3 compounds as well as the starting material; m/z 1,3-xylylene-bis(perfluoro-2-methyl pentan-2-yl) (12) (EI$^+$) 743 (M$^+$, ~1%) 442 (1) 423 (49) 235 (13) 123 (3)69 (28) 104 (45) 69 (100); 1-bromomethyl-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (13) (EI$^+$) 423 (M$^+$, 70%) 123 (3) 104 (97) 69 (100); 1-fluoromethyl-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (14) (EI$^+$) 442 (M$^+$, 7%) 423 (1) 123 (100); the glc-ms spectrum also showed the presence hexafluoropropene dimer m/z (EI$^+$).300 (M$^+$, 5%) 231 (14) 281(37) 181 (50) 69 (100) and hexafluoropropene trimer m/z (EI$^+$).450 (M$^+$, 1%) 431 (14) 69 (100). No further purification was attempted. Similar reactions were conducted at temperature 100 °C for 3 days and 5 days but no change could be detected by glc-ms, glc or ^{19}F NMR. Sulpholane was also tried to perform the reaction at 100 °C and 60 °C for 14 hours but without any better results.

V.2.A.2. 1,4-Xylylene dibromide

Perfluoro-2-methyl-2-pentene (1.8g, 6 mmol), potassium fluoride (0.5g, 8.6 mmol), 1,4-xylylene dibromide (0.5g, 1.9 mmo) and N,N-dimethylformamide (10 ml) were placed in a sealed glass tube and heated at 100 °C for 5 days. The reaction was analysed by glc-ms, gc and ^{19}F NMR. A mixture of products was obtained giving very complex spectrum. After 24h heating the ^{19}F NMR data did not show any hexafluoropropene dimer. The glc-ms chromatogram showed traces of 3 compounds as well as the starting material; m/z 1,4-xylylene-bis(perfluoro-2-methyl pentan-2-yl) (15) (EI$^+$) 743 (M$^+$, ~1%) 442 (1) 423 (49) 235 (13) 123 (3)69 (28) 104 (45) 69 (100), 1-bromomethyl-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (EI$^+$) 423 (M$^+$, 70%) 123 (3) 104 (97) 69 (100), 1-fluoromethyl-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (16) (EI$^+$) 442 (M$^+$, 7%) 423 (1) 123 (100); the glc-ms spectrum also showed the presence hexafluoropropene dimer m/z (EI$^+$).300 (M$^+$, 5%) 231 (14) 281(37) 181 (50) 69 (100) and hexafluoropropene trimer m/z (EI$^+$).450 (M$^+$, 1%) 431 (14) 69 (100). No further purification was attempted. A similar reaction was conducted at temperature 100 °C for 14 hours in sulpholane but no change could be detected by glc-ms, glc or ^{19}F NMR.

V.2.B TETRAKIS(DIMETHYLAMINO)ETHYLENE (TDAE)

V.2.B.1. Use of sulpholane as solvent

Perfluoro-2-methyl-2-pentene (1.8 g, 6 mmol), TDAE (1.8 ml, 7.7 mmol), 1,3-xylylene dibromide (0.5 g, 1.9 mmol) and sulpholane (10 ml) were placed in a sealed glass tube and heated at 80 °C for 14h. The reaction was analysed by glc-ms, glc and ^{19}F NMR.

A mixture of products was obtained giving a very complex spectrum. The glc-ms chromatogram showed the presence hexafluoropropene dimer m/z (EI$^+$).300 (M$^+$, 5%) 231 (14) 281(37) 181 (50) 69 (100), hexafluoropropene trimer m/z (EI$^+$).450 (M$^+$, 1%) 431 (14) 69 (100), and compound with higher molecular weight m/z (EI$^+$).487 (3%) 349 (16) 119 (10) 69 (100). No further purification was attempted.

V.2.B.2. Use of acetonitrile as solvent

Perfluoro-2-methyl-2-pentene (1.8 g, 6 mmol), TDAE (1.8 ml, 7.7 mmol), 1,3-xylylene dibromide (0.5 g, 1.9 mmol) and acetonitrile (10 ml) were placed in a sealed glass tube. The mixture was heated at 60 °C for 14h in a rotating oil bath. The reaction was analysed by glc-ms, gc and ^{19}F NMR. A mixture of products was obtained giving a very complex spectrum. The glc-ms chromatogram showed the presence hexafluoropropene dimer m/z (EI$^+$).300 (M$^+$, 5%) 231 (14) 281(37) 181 (50) 69 (100), hexafluoropropene trimer m/z (EI$^+$).450 (M$^+$, 1%) 431 (14) 69 (100), and compound with higher molecular weight m/z (EI$^+$).487 (3%) 349 (16) 119 (10) 69 (100). No further purification was attempted.

V.2.B.3. Absence of solvent

Perfluoro-2-methyl-2-pentene (1.9 g, 6.3 mmol), TDAE (1.8 ml, 7.7 mmol) and 1,3-xylylene dibromide (0.5 g, 1.9 mmol) were placed in a sealed glass tube and heated at 80 °C for 14h. The mixture was washed with acetonitrile. The reaction was analysed by glc-ms, gc and ^{19}F NMR. A mixture of products was obtained giving a very complex spectrum. The glc-ms chromatogram showed the presence hexafluoropropene dimer m/z (EI$^+$).300 (M$^+$, 5%) 231 (14) 281(37) 181 (50) 69 (100), hexafluoropropene trimer m/z (EI$^+$).450 (M$^+$, 1%) 431 (14) 69 (100), and compound with higher molecular weight m/z (EI$^+$).487 (3%) 349 (16) 119 (10) 69 (100). No further purification was attempted.

V.2.C. TWO-STAGE REACTION:USE OF CAESIUM FLUORIDE

V.2.C.1. Reaction with benzyl bromide

A flask was charged with perfluoro-2-methylpent-2-ene (16.8 g, 56 mmol) and dry caesium fluoride (7.9 g, 52 mmol) in dry sulpholane (38 cm^3). The solution was stirred continuously at 30-35 °C for 40h until the perfluoro-2-methylpentan-2-yl anion had been formed. Quantitative conversion of the fluoro-alkene to the carbanion[161] (3) was confirmed by ^{19}F NMR; δ_F(235 MHz; sulpholane; CFCl3) -41.2 (6F, s, $(CF_3)_2C$), -79.7 (3F, s, CF_3CF_2), -92.0 (2F, s, $CF_2CF_2CF_3$), -125.4 (2F, s, CF_2CF_3) and compared to literature data[161]. Under nitrogen, benzyl bromide (3.8 cm^3, 33 mmol) was added slowly to the mixture which was then heated with stirring at 65 °C for 6 days. The precipitate was removed by filtration and a perfluorinated solvent (FC-84, bp. 80°C) was added (2x30 cm^3) to the filtrate to extract the products. The solvent was cautiously evaporated to afford the crude material (7.8 g). The residue was purified by column chromatography on silica gel (eluent: Pet. ether 40-60 °C) to give **[(perfluoro-2-methylpentan-2-yl)methyl]benzene** (4) (7.5 g, 58%); as a pale yellow liquid;

ν_{max}/cm^{-1} 3041 (Ar-H), 2964 (C-H), 1263 (C-F); n.m.r. Spectrum No 3 consistent with literature values[103, 104]; m/z (EI$^+$) 410 (M$^+$, 4%) 91 (100) 69 (24).

V.2.C.2. Reaction with 2-(bromomethyl)naphthalene

A flask was charged with perfluoro-2-methylpent-2-ene (7.3 g, 24.3 mmol) and dry caesium fluoride (3.8 g, 25 mmol) in dry sulpholane (40 cm^3). The solution was stirred continuously at 30-35 °C for 40h until the perfluoro-2-methylpentan-2-yl anion had been formed as confirmed by ^{19}F NMR (see section VI.2.C.1.). Under nitrogen, 2-(bromomethyl)naphthalene (3 g, 13.5 mmol) was added slowly to the mixture which was then heated with stirring at 65 °C for 7 days. The precipitate was removed by filtration. A perfluorinated solvent (FC-84, bp. 80°C) was added (2x30 cm^3) to the filtrate to extract and purify 2-[(perfluoro-2-methylpentan-2-yl)-methyl]naphthalene from 2-(fluoromethyl)naphthalene m/z (EI$^+$) 160 (M$^+$, 95%) 159 (100) 133 (21)which was formed as a side product in trace amount. The solvent was cautiously evaporated to afford **2-[(perfluoro-2-methylpentan-2-yl)-methyl]naphthalene** (5) (3.6 g, 58%), as a pale yellow liquid; bp. 284°C, Siwoloboff's method[134]; (Found: C, 44.3; H, 2.0. $C_{17}H_9F_{13}$ requires C, 44.3; H, 1.9%); λ_{max}(n-hexane)/nm 224 (ε/ dm^3 mol^{-1} cm^{-1} 19145), 276 (5744); ν_{max}/cm^{-1} 3064br (C-H), 1602 (C=C), 1453 (C=C), 1263-1218 (C-F), 739 and 701 (C-H); n.m.r. spectrum No 4; m/z (EI$^+$) 460 (M$^+$, 12%) 141 (100) 69 (10); Mass spectrum No 3, IR spectrum No 1.

V.2.C.3. Preparation of 1-bromo-4-[(perfluoro-2-methylpentan-2-yl)methyl] benzene

A flask was charged with perfluoro-2-methylpent-2-ene (162 g, 54 mmol) and dry caesium fluoride (7.9 g, 52 mmol) in dry sulpholane (40 cm^3). The solution was stirred continuously at 30-35 °C for 40h until the perfluoro-2-methylpentan-2-yl anion had been formed as confirmed by ^{19}F NMR (see section VI.2.C.1.). Under nitrogen, 4-bromobenzyl bromide (8.9 g, 36 mmol) was added slowly to the mixture which was then heated with stirring at 65 °C for 6 days. The precipitate was removed by filtration and a perfluorinated solvent (FC-84, bp. 80°C) was added (2x40 cm^3) to the filtrate to extract the product, trace of 4-bromobenzyl fluoride was detected and remained in the sulpholane layer.. The solvent was cautiously evaporated to afford **1-bromo-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene** (7) (10.8 g, 62%); as a pale yellow liquid; bp. 244°C, Siwoloboff's method[134]; (Found: C, 31.9; H, 1.2.$C_{13}H_6F_{13}Br$ requires C, 31.9; H, 1.2%); ν_{max}/cm^{-1} 1269 (C-F), 1220 (C-F), 885 (C-H), 700 (C-Br); n.m.r. spectrum No 5; m/z (EI$^+$) 490 (M$^+$, 3%) 488 (M$^+$, 3%) 169 (100) 69 (85); Mass spectrum No 4, IR spectrum No 2.

V.2.C.4. Preparation of 1-bromo-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene

A flask was charged with perfluoro-2-methylpent-2-ene (16.2 g, 54 mmol) and dry caesium fluoride (7.9 g, 52 mmol) in dry sulpholane (40 cm^3). The solution was stirred continuously at 30-35 °C for 40h until the perfluoro-2-methylpentan-2-yl anion had been formed as confirmed by ^{19}F NMR (see section VI.2.C.1.). Under nitrogen, 3-bromobenzyl bromide (8.5 g, 34.2 mmol) was added slowly to the mixture which was then heated with stirring at 65 °C for 6 days. The precipitate was removed by filtration and a perfluorinated solvent (FC-84, bp. 80°C) was added (2x40 cm^3) to the filtrate to extract the product, trace of 3-bromobenzyl fluoride was detected and remained in the sulpholane layer. The solvent was cautiously evaporated to afford **1-bromo-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene** (8) (13.2 g, 64%); as a pale yellow liquid; bp. 234-236°C, Siwoloboff's method[134]; (Found: C, 31.8; H, 1.2.$C_{13}H_6F_{13}Br$ requires C, 31.9; H, 1.2%); ν_{max}/cm^{-1} 1220-1268 (C-F), 980s (C-H), 880 (C-H), 736 (C-H); n.m.r. spectrum No 6; m/z (EI$^+$) 490 (M$^+$, 10%) 488 (M$^+$, 10%) 169 (100) 69 (65); Mass spectrum No 5, IR spectrum No 3.

V.2.C.5. Preparation of 1-bromo-2-[(perfluoro-2-methylpentan-2-yl) methyl]benzene

A flask was charged with perfluoro-2-methylpent-2-ene (16.2 g, 54 mmol) and dry caesium fluoride (7.9 g, 52 mmol) in dry sulpholane (40 cm^3). The solution was stirred continuously at 30-35 °C for 40h until the perfluoro-2-methylpentan-2-yl anion had been formed as confirmed by ^{19}F NMR (see section VI.2.C.1.). Under nitrogen, 2-bromobenzyl bromide (8.6 g, 34.6 mmol) was added slowly to the mixture which was then heated with stirring at 65°C for 6 days. The precipitate was removed by filtration and a perfluorinated solvent (FC-84, bp. 80°C) was added (2x40 cm^3) to the filtrate to extract the product, trace of 2-bromobenzyl fluoride was detected and remained in the sulpholane layer. The solvent was cautiously evaporated to afford **1-bromo-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene** (9) (5.6 g, 34%); as a pale yellow liquid; bp. 230-233°C, Siwoloboff's method[134]; (Found: C, 31.7; H, 1.2.$C_{13}H_6F_{13}Br$ requires C, 31.9; H, 1.2%); ν_{max}/cm^{-1} 1220-1272 (C-F), 752 (C-H), 737 (C-H); n.m.r. spectrum No 7; m/z (EI$^+$) 490 (M$^+$, 12%) 488 (M$^+$, 13%) 169 (100) 69 (25); Mass spectrum No 6, IR spectrum No 4.

V.2.C.6. Preparation of 1-nitro-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene

A flask was charged with perfluoro-2-methylpent-2-ene (41 g, 141 mmol) and dry caesium fluoride (20 g, 133 mmol) in dry sulpholane (40 cm^3). The solution was stirred continuously at 30-35 °C for 40h until the perfluoro-2-methylpentan-2-yl anion had been formed as confirmed by ^{19}F NMR (see section VI.2.C.1.). Under nitrogen, 4-nitrobenzyl bromide (18.6 g, 86 mmol) was added slowly to the mixture which was then heated with stirring at 65 °C for 6 days. The precipitate was removed by filtration and a perfluorinated solvent (FC-84, bp. 80°C) was added (2x40 cm^3) to the filtrate to extract the products. No trace of 4-nitrobenzyl fluoride was observed by glc-ms. The solvent was cautiously evaporated to afford **1-nitro-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene**[104] (10) (23.4 g, 60%); as a pale yellow liquid; bp. over 250°C and decomposes, Siwoloboff's method[134]; (Found: C, 34.5; H, 1.2; N, 3.1%.$C_{13}H_6F_{13}NO_2$ requires C, 34.3; H, 1.3; N, 3.0%); ν_{max}/cm^{-1} 1609 (C=C), 1530 (N=O), 1351 (N=O), 1242 (br, C-F), 887-860 (C-H); n.m.r. spectrum No 8; m/z (EI^+) 455 (M^+, 27%), 136 (100), 109 (96), 69 (34); Mass spectrum No 7, IR spectrum No 5.

V.2.C.7. Preparation of 1-nitro-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene

A flask was charged with perfluoro-2-methylpent-2-ene (31 g, 107 mmol) and dry caesium fluoride (15 g, 99 mmol) in dry sulpholane (40 cm^3). The solution was stirred continuously at 30-35 °C for 40h until the perfluoro-2-methylpentan-2-yl anion had been formed as confirmed by ^{19}F NMR (see section VI.2.C.1.). Under nitrogen, 3-nitrobenzyl bromide (13.5 g, 62.6 mmol) was added slowly to the mixture which was then heated with stirring at 65 °C for 6 days. The precipitate was removed by filtration and a perfluorinated solvent (FC-84, bp. 80°C) was added (2x40 cm^3) to the filtrate to extract the products. No trace of 3-nitrobenzyl fluoride was observed by glc-ms. The solvent was cautiously evaporated to afford **1-nitro-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene**[104] (11) (18.2 g, 64%); as a pale yellow liquid; bp. over 250°C and decomposes, Siwoloboff's method[134]; (Found: C, 34.5; H, 1.3; N, 3.0%.$C_{13}H_6F_{13}NO_2$ requires C, 34.3; H, 1.3; N, 3.0%); ν_{max}/cm^{-1} 1537s (N=O), 1353 (N=O), 1243br (C-F), 983s (C-H), 881 (C-H), 743-732 (C-H); n.m.r. spectrum No 9; m/z (EI^+) 455 (M^+, 12%) , 136 (62) , 109 (100); Mass spectrum No 8, IR spectrum No 6.

V.2.C.8. Reaction with 1,3-xylylene dibromide

A flask was charged with perfluoro-2-methylpent-2-ene (16 g, 53.3 mmol) and dry caesium fluoride (7.98 g, 52.5 mmol) in dry sulpholane (37 cm^3). The solution was stirred continuously at 30-35 °C for 40h until the perfluoro-2-methylpentan-2-yl anion had been formed as confirmed by ^{19}F NMR (see section VI.2.C.1.). Under nitrogen, 1,3-xylylene dibromide (4.25 g, 16.1 mmol) was added slowly to the mixture which was then heated with stirring at 65 °C. The reaction was followed by glc-ms at different time and showed the formation of three products: 1,3-xylylene-bis(perfluoro-2-methylpentan-2-yl) (12), 1-bromomethyl-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (13) and 1-fluoromethyl-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (14); after 15 hours the ratio of (12)/(13)/(14) was 2.3/1/1.6, after 24 hours 3.2/1/1.2, after 48 hours 6.5/1/1.5, after 5 days and 7 days the ratio of (12) to (14) remained the same and was 4.2/0/1. The completion of the reaction gave two products (12) and (14). The precipitate was removed by filtration and a perfluorinated solvent (FC-84, bp. 80°C) was added was added (2x30 cm^3) to the filtrate to extract the products. The solvent was cautiously evaporated to afford the crude material (7.8 g). The residue was purified by column chromatography on silica gel (eluent: Pet. ether 40-60 °C) to give **1,3-xylylene-bis(perfluoro-2-methylpentan-2-yl)**[104] (12) (6.8 g, 56%); as a pale yellow liquid; bp. 286°C, Siwoloboff's method[134]; (Found: C, 32.0; H, 0.8. $C_{20}H_8F_{26}$ requires C, 32.3; H, 1.0%); $R_f = 0.4$; λ_{max}(n-hexane)/nm 220 (ε/ dm^3 mol^{-1} cm^{-1} 1039), 261 (209); ν_{max}/cm^{-1} 3030br (Ar-H), 1264-1218 (C-F), 983 (C-H), 880 (C-H), 736 (C-H); n.m.r. spectrum No 10; m/z (EI^+) 743 (M^+, 0.3%) 423 (29) 104 (24) 69 (100); Mass spectrum No 9, IR spectrum No 7 and, **1-fluoromethyl-3-[(perfluoro-**

2-methylpentan-2-yl)methyl]benzene (14) (1.5 g, 21%); as a pale yellow liquid; bp. 207°C, Siwoloboff's method[134]; (Found: C, 37.7; H, 1.6. $C_{14}H_8F_{14}$ requires C, 38.0; H, 1.8%); Rf = 0.2; λ_{max}(n-hexane)/nm 222 (ε/ dm^3 mol^{-1} cm^{-1} 1245), 267 (296); ν_{max}/cm^{-1} 3030br (Ar-H), 1263-1218 (C-F), 981 (C-H), 880 (C-H), 734 (C-H); n.m.r. spectrum No 11; m/z (EI^+) 443 (M^+, 0.5%) 123 (100); Mass spectrum No 10, IR spectrum No 8.

V.2.C.9. Reaction with 1,4-xylylene dibromide

A flask was charged with perfluoro-2-methylpent-2-ene (16.2 g, 54 mmol) and dry caesium fluoride (8.1 g, 53.3 mmol) in dry sulpholane (45 cm^3). The solution was stirred continuously at 30-35 °C for 30h until the perfluoro-2-methylpentan-2-yl anion had been formed as confirmed by ^{19}F NMR (see section VI.2.C.1.). Under nitrogen, 1,4-xylylene dibromide (4.25 g, 16.1 mmol) was added slowly to the mixture which was then heated with stirring at 65 °C for a 7 days. The precipitate was removed by filtration and a perfluorinated solvent (FC-84, bp. 80°C) was added (2x30 cm^3) to the filtrate to extract the products. The solvent was cautiously evaporated to afford the crude material (8.4 g). The residue was purified by column chromatography on silica gel (eluant: Pet. ether 40-60 °C,) to give **1,4-xylylene-bis(perfluoro-2-methylpentan-2-yl)**[104] (15) (7.1 g, 59%); as a pale yellow liquid; bp. 294°C, Siwoloboff's method[134]; (Found: C, 32.3; H, 0.9. $C_{20}H_8F_{26}$ requires C, 32.3; H, 1.0%); Rf = 0.4; λ_{max}(n-hexane)/nm 222 (ε/ dm^3 mol^{-1} cm^{-1} 1064), 266 (326); ν_{max}/cm^{-1} 3030br (Ar-H), 1263-1220 (C-F), 882s (C-H); n.m.r. spectrum No 12; m/z (EI^+) 743 (M^+, 0.1%) 423 (64) 104 (100) 69 (74); Mass spectrum No 11, IR spectrum No 9 and, **1-fluoromethyl-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene** (16) (1.5g, 22%), as a pale yellow liquid; bp. 212°C, Siwoloboff's method[134]; (Found: C, 37.4; H, 1.6. $C_{14}H_8F_{14}$ requires C, 38.0; H, 1.8%); Rf = 0.2; ν_{max}/cm^{-1} 3038 (Ar-H), 2964 (C-H), 1263-1220 (C-F), 885s (C-H); n.m.r. spectrum No 13; m/z (EI^+) 443 (M^+, 0.2%) 123 (100); Mass spectrum No 12, IR spectrum No 10.

V.2.C.10. Reaction with 1,2-xylylene dibromide

A flask was charged with perfluoro-2-methylpent-2-ene (12.3 g, 41 mmol) and dry caesium fluoride (6 g, 39.4 mmol) in dry sulpholane (30 cm^3). The solution was stirred continuously at 30-35 °C for 40h until the perfluoro-2-methylpentan-2-yl anion had been formed as confirmed by ^{19}F NMR (see section VI.2.C.1.). Under nitrogen, 1,2-xylylene dibromide (3.23 g, 12.3 mmol) was added slowly to the mixture which was then heated with stirring at 65 °C for a 7 days. The precipitate was removed by filtration and a perfluorinated solvent (FC-84, bp. 80°C) was added (2x30 cm^3) to the filtrate to extract the products. The solvent was cautiously evaporated to afford the crude material (5.2 g). The residue was purified by column chromatography on silica gel (eluant: Pet. ether 40-60 °C) to give **1,2-xylylene-bis(perfluoro-2-methylpentan-2-yl)** (17) (1.1 g, 12%); as a pale yellow liquid; bp. 264°C, Siwoloboff's method[134]; (M^+ 742.021000 $C_{20}H_8F_{26}$ requires M^+ 742.021084); Rf = 0.4; ν_{max}/cm^{-1} 3074 (Ar-H), 1277-1218 (C-F), 737-732 (C-H); n.m.r. spectrum No 14; m/z (EI$^+$) 743 (M$^+$, 0.3%) 423 (52) 123 (100) 69 (17); Mass spectrum No 13, IR spectrum No 11 and, **1-fluoromethyl-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene** (18) (3.6 g, 66%); as a pale yellow liquid; bp. 180°C, Siwoloboff's method[134]; (Found: C, 38.2; H, 1.9.$C_{14}H_8F_{14}$ requires C, 38.0; H, 1.8%); $R_f = 0.2$; λ_{max}(n-hexane)/nm 221 (ε/ dm^3 mol^{-1} cm^{-1} 1331), 267 (285); ν_{max}/cm^{-1} 2960 (C-H), 1275-1220 (C-F), 735 (C-H); n.m.r. spectrum No 15; m/z (EI$^+$) 443 (M$^+$, 0.2%) 123 (100); Mass spectrum No 14, IR spectrum No 12.

V.2.C.11. Reaction with 2,6-bis(bromomethyl)pyridine

A flask was charged with perfluoro-2-methylpent-2-ene (13.2 g, 44 mmol) and dry caesium fluoride (6.5 g, 42.7 mmol) in dry sulpholane (40 cm^3). The solution was stirred continuously at 30-35 °C for 40h until the perfluoro-2-methylpentan-2-yl anion had been formed as confirmed by ^{19}F NMR (see section VI.2.C.1.). Under nitrogen, 2,6-bis(bromomethyl)pyridine (3.6 g, 13.5 mmol) was added slowly to the mixture which was then heated with stirring at 65 °C for 7 days. The precipitate was removed by filtration and a perfluorinated solvent (FC-84, bp. 80°C) was added (2x40 cm^3) to the filtrate to extract the products. The solvent was cautiously evaporated to afford the crude material (5.2 g). The residue was purified by column chromatography on silica gel (eluant: Pet. ether 40-60 °C) to give **2,6-bis[(perfluoro-2-methylpentan-2-yl) methyl]pyridine** (19) (1.9 g, 20%); as a pale yellow liquid; bp. 277°C, Siwoloboff's method[134]; (Found: C, 33.2; H, 1.2; N, 2.3. $C_{19}H_7F_{26}N$ requires C, 33.1; H, 1.0; N, 2.0 %); $R_f = 0.36$; ν_{max}/cm^{-1} 2960 (C-H), 1596 (C=C), 1581 (C=N), 1461 (C=C), 1268-1214 (C-F); n.m.r. spectrum No 16; m/z (EI$^+$) 743 (M$^+$, 0.8%) 424 (100) 169 (82); Mass spectrum No 15, IR spectrum No 13 and, **2-fluoromethyl-6-[(perfluoro-2-methylpentan-2-yl) methyl]pyridine** (20) (1.7 g, 33%); as a pale yellow liquid; bp. 230°C, Siwoloboff's method[134]; (Found: C, 35.2; H, 1.59; N 3.2 %.$C_{13}H_7F_{14}N$ requires C, 35.2; H, 1.6; N, 3.1%); $R_f = 0.16$; ν_{max}/cm^{-1} 2960 (C-H), 1596 (C=C), 1581 (C=N), 1461 (C=C), 1268-1214 (C-F); n.m.r. spectrum No 17; m/z (EI$^+$) 443 (M$^+$, 21%) 124 (100) 69 (15); Mass spectrum No 16, IR spectrum No 14.

V.3. REACTION WITH HEXAFLUOROPROPENE TRIMER

A flask was charged with hexafluoropropene trimer (3.2 g, 7.1 mmol) and dry caesium fluoride (1 g, 6.5 mmol) in dry sulpholane (20 ml). The solution was stirred continuously at 30-35 °C for 16 hours until the corresponding anion had been formed. Quantitative conversion of the fluoro-alkene to the carbanion was confimed by ^{19}F NMR which gave a fairly complicated NMR spectra. Under nitrogen, 1,3-xylylene dibromide (0.55 g, 2 mmol) was added slowly to the mixture which was then heated with stirring at 65 °C for a 7 days. The ^{19}F NMR data did not become clearer however the glc-ms technique showed the presence of different compounds: 1-fluoromethyl-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (A, compound (14)) m/z (EI$^+$) 443 (M$^+$, 0.5%) 123 (100); .1-fluoromethyl-3-[(perfluoro-isopropyl)methyl]benzene (C) m/z (EI^+) 292 (M^+, 8%) 123 (100) 69 (7) (see Mass spectrum No 2), 1-fluoromethyl-3-[(perfluoro-2-methyl-3-isopropylpentan-2yl)methyl]benzene (D) m/z (EI^+) 592 (M^+, 1%) 273 (94) 69 (11) (see Mass spectrum No 1) and finally 1,3-xylylene-bis(perfluoro-2-methyl pentan-2-yl) (B, compound (12)) m/z (EI^+) 743 (M^+, 0.3%) 423 (29) 104 (24) 69 (100) in the ratio 22:6:3:1 (calculated by gc); no further purification was attempted.

V.4. REACTION WITH TETRAFLUOROETHYLENE PENTAMER

A flask was charged with tetrafluoroethylene pentamer (6.3 g, 12.6 mmol) and dry caesium fluoride (1.9 g, 12.5 mmol) in dry sulpholane (25 ml). The solution was stirred continuously at 30-35 °C for 12 days until the corresponding anion had been formed. Quantitative conversion of the fluoro-alkene to the carbanion was confimed by ^{19}F NMR; δ_F(235MHz; sulpholane; $CFCl_3$) -42.1 (3F, s, $\underline{CF}_3CCs$), -54 (3F, s, $\underline{CF}_3C(C_2F_5)$), -69.9 (3F, s, $CCsCF_2\underline{CF}_3$), -77.0 (8F, m, $(\underline{CF}_3CF_2)_2C(CF_3)CCs$ $\underline{CF}_2CF_3$), -104.6 (4F, m, $(CF_3\underline{CF}_2)_2C(CF_3)$) . Under nitrogen, benzyl bromide (1.4 ml, 12 mmol) was added slowly to the mixture which was then heated with stirring at 65 °C for a 10 days. The mixture was analysed by a combination of glc-ms and ^{19}F NMR. No trace of perfluoroalkylated compound was detected, however fluoromethyl benzene was formed; m/z (EI^+) 110 (M^+, 30%) 109 (100) and δ_F (235 MHz; $CDCl_3$, $CFCl_3$) -204.2 (1F, t, $^2J_{HF}$ 47).

CHAPTER VI
EXPERIMENTAL TO CHAPTER III

VI.1. ELECTROPHILIC SUBSTITUTION REACTIONS

VI.1.A. NITRATION

A flask was charged with (perfluoro-2-methylpentan-2-yl)-methylbenzene (4) (2.1 g, 5 mmol) and nitronium tetrafluoroborate (0.7 g, 5 mmol) in dry sulpholane (40 ml) at 30°C. The solution was stirred for 2 hours[162], [122]. A perfluorinated solvent (Fluorinert: FC-84, bp= 80°C) was added (2x30 ml) to extract the products. The solvent was cautiously evaporated to afford the crude material: m= 2.2 g. A mixture of three mono-isomers: **1-nitro-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene** (21), **1-nitro-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene** (11), **1-nitro-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene** (10) was obtained in the respective ratio 1/3.8/3.8 detected by glc. The mixture of mono-isomers was separated from the starting material by column chromatography on alumina (eluent: hexane), 61% conversion of the starting material was recorded. The product was characterised as a mixture of isomers (21), (10), (11): pale yellow liquid, M^+ 455.01910 $C_{13}H_6F_{13}NO_2$ requires M^+ 455.01910; ν_{max}/cm^{-1} 1609 (C=C), 1534 (N=O), 1352 (N=O), 1247 (br C-F); δ_H (400 MHz; CD_3CN, Me_4Si) 8.2 (m), 7.9 (m), 7.6 (m), 7.5 (m), 3.82 (2H, s, CH_2 (compound 21)), 3.80 (2H, s, CH_2 (compound 22)), 3.67 (2H, s, CH_2 (compound 23)); δ_F (235 MHz; CD_3CN, $CFCl_3$) -62 (18F, s, $C(\underline{CF}_3)_2$), -81 (9F, s, $CF_2\underline{CF}_3$), -106 (6F, s, $\underline{CF}_2CF_2CF_3$), -123 (6F, s, $\underline{CF}_2CF_3$); δ_C {H} (100 MHz; CD_3CN, Me_4Si) 148.0 (s), 147.7 (s), 138.2 (s), 137.4 (s), 132.9 (s), 132.5 (s), 132.4 (s), 129.6 (s), 129.3 (s), 126.4 (s), 123.4 (s), 123.3 (s), 121.8 (q, $^1J_{CF}$ 290, $CF(\underline{CF}_3)_2$), 117.4 (qt, $^1J_{CF}$ 290, $^2J_{CF}$ 34, $CF_2\underline{CF}_3$), 114.6 (tt, $^1J_{CF}$ 270, $^2J_{CF}$ 33, $\underline{CF}_2CF_2CF_3$), 109.5 (tsext, $^1J_{CF}$ 272, $^2J_{CF}$ 37, $\underline{CF}_2CF_3$), 61 (m, $\underline{C}(CF_3)_2$), 32.2 (s, CH_2), 31.9 (s, CH_2); m/z of compound 21 (EI^+) 455 (M^+, 1%) 136 (68) 109 (100) 69 (26), Mass spectrum No 17; m/z of compound 11 (EI^+) 455 (M^+, 1%) 136 (100) 109 (50) 69 (9); m/z of compound 10 (EI^+) 455 (M^+, 1%) 136 (100) 109 (61) 69 (13). Compounds (10) and (11) were fully charaterised in Chapter II (II.3.C.6 and II.3.C.7) and the glc-ms and spectroscopy data were identical to the data obtained in Chapter II (II.3.C.6 and II.3.C.7). The reaction was repeated and left for 4 days, the progression of the reaction was followed by gc and samples were collected at days intervals. The ratio of the mixture did not vary. In the last experiment, the reaction was carried out at higher temperature 100°C and left stirring for one week. The proportion of isomers maintained respectively 1/3.8/3.8. No further purification was attempted.

VI.1.B. CHLOROSULPHONATION

VI.1.B.1. Preparation of sulphonyl chloride derivatives

A flask was charged with oleum 20% (1.18 g, 4.6 mmol), chlorosulphonic acid (0.95 g, 8.1 mmol) and [(perfluoro-2-methylpentan-2-yl)methyl]benzene (4) (1 g, 2.4 mmol) was added slowly to maintain the temperature below 10 °C[123, 128, 127, 126]. After the addition was complete , the mixture was allowed to warm to room temperature and stirred for an hour before addition of water. The extraction of the product was carried out using a perfluorinated solvent (Fluorinert: FC-84, bp 80°C). The white solution was then analysed by glc-ms and NMR. The glc-ms showed the presence of 2 mono-isomers with 100% conversion of the starting material, after distillation of the solvent the crude material was obtained (1 g; 81 %). The mixture was identified as **3-[(perfluoro-2-methylpentan-2-yl)methyl]benzenesulphonyl chloride** (22), **4-[(perfluoro-2-methylpentan-2-yl)methyl]benzenesulphonyl chloride** (23) in the ratio 1/1.4 by glc and characterised as a mixture of isomers; very thick pale yellow liquid, M^+ 507.95700 $C_{13}H_6O_2SF_{13}Cl$ requires M^+ 507.95694; v_{max}/cm^{-1} 3080 (C-H), 2917 (C-H), 1477 (CH_2), 1457 (CH_2), 1383 (br S=O), 1332 (S=O), 1220 (S=O), 1270 (br C-F). Analytical samples were obtained by HPLC using water/methanol as the eluent, **3-[(perfluoro-2-methylpentan-2-yl)methyl]benzenesulphonyl chloride** (22): very thick liquid; n.m.r. spectrum No 18, recorded in deuterated acetone; m/z (EI^+) 508 (M^+, 5%) 409 (49) 189 (66) 109 (100) 69 (22), Mass spectrum No 18; **4-[(perfluoro-2-methylpentan-2-yl)methyl]benzenesulphonyl chloride** (23): very thick liquid; n.m.r. spectrum No 19, recorded in deuterated acetone; m/z (EI^+) 508 (M^+, 2%) 409 (40) 189 (38) 109 (100) 69 (20); Mass spectrum No 19; IR spectrum No 15.

VI.1.B.2. Preparation of sulphonamide derivatives

A mixture of 3-[(perfluoro-2-methylpentan-2-yl)methyl]benzenesulphonyl chloride (22) and 4-[(perfluoro-2-methylpentan-2-yl)methyl]benzenesulphonyl chloride (23) in the ratio 1/1.4 (1.2 g, 2.3 mmol) was added to aniline (0.44 g, 4.7 mmol) and 25 ml of benzene[128],. The reaction was refluxed for 1 hour. After filtration, a white solid material was obtained (1.1 g, 84 %). A mixture of the two isomers was identified 3-[(perfluoro-2-methylpentan-2-yl)methyl]benzenesulphanilide (24) and 4-[(perfluoro-2-methylpentan-2-yl)methyl]benzenesulphanilide (25) in the ratio 1/1.4 by glc, with 100% conversion of the starting material and was characterised as a mixture of isomers; very thick paste; analytical samples were obtained by HPLC using water/methanol as the eluent, **3-[(perfluoro-2-methylpentan-2-yl)methyl]benzenesulphanilide** (24), n.m.r. spectrum No 20, recorded in deuterated methanol; m/z (EI^+) 565 (M^+, 1%) 92 (100), Mass spectrum No 20; **4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene sulphanilide** (25), n.m.r. spectrum No 21, recorded in deuterated methanol; m/z (EI^+) 566 (MH^+, 4%) 92 (100); Mass spectrum No 21.

VI.1.C. BROMINATION REACTION

VI.1.C.1. [(Perfluoro-2-methylpentan-2-yl)methyl]benzene

A mixture of [(perfluoro-2-methylpentan-2-yl)methyl]benzene (4) (1 g, 2.4 mmol) and a catalytic amount of iron bromide was stirred and heated to 80 °C followed by slow addition of bromine (0.3 g, 2.3 mmol)[125]. The solution was refluxed until evolution of hydrogen bromide had ceased. After heating for 2 hours, the reaction mixture was cooled, filtered and taken up in pentane. The pentane solution was washed successively with 20 ml of 6N hydrochloric acid, 10% sodium bisulfite, and saturated sodium chloride solution, dried. A mixture of three mono-bromoisomers: 1-bromo-2-

[(perfluoro-2-methylpentan-2-yl)methyl]benzene (9), 1-bromo-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (8), 1-bromo-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (7), was detected by glc in the ratio of 1/2/3, 100 % conversion of the starting material was observed; m/z for compound 9 (EI$^+$) 489 (M$^+$, 15%) 169 (100) 69 (14); m/z for compound 8 (EI$^+$) 489 (M$^+$, 10%) 169 (100) 69 (65); m/z for compound 7 (EI$^+$) 489 (M$^+$, 10%) 169 (100) 69 (56); no further purification was attempted. These bromo materials (7), (8) and (9) were fully charaterised in Chapter II (section II.3.C.3, II.3.C.4 and II.3.C.5).

VI.2. SYNTHESIS OF BENZOIC ACIDS AND DERIVATIVES

VI.2.A. PREPARATION OF 4-[(PERFLUORO-2-METHYLPENTAN-2-YL) METHYL]BENZOIC ACID

Under nitrogen atmosphere at -75 °C, tert-butyllithium (2.4 cm^3, 4 mmol) was added[131] to a solution of 1-bromo-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (7) (1.0 g, 2 mmol) in dry diethyl ether (40 cm^3). After 1h of vigorous stirring at -75 °C, freshly solid CO_2 was added to the mixture[118]. The flask was allowed to stand at room temperature. A white precipitate was formed. The acid was extracted with 2M NaOH (2 x 30 cm^3) and collected as a white powder after acidification with 2M HCl of the aqueous phase. The crude solid was recrystallized from hexaneas identified as **4-[(perfluoro-2-methylpentan-2-yl)methyl]benzoic acid** (27) (0.6 g, 64 %); as white crystal; m.p. 135-138 °C; (Found: C, 36.98; H, 1.52.$C_{14}H_7F_{13}O_2$ requires C, 37.02; H, 1.55%); ν_{max}/cm^{-1} 1683 (C=O), 1176-1326 (C-F and C-O); n.m.r. spectrum No 22, recorded in deuterated acetone; m/z (FAB$^+$) 454 (M$^+$, 8%) 135 (100) 69 (56); Mass spectrum No 22; IR spectrum No 16. Single crystals were grown from hexane at room temperature over one week and an X-ray crystallographic structure was obtained.

VI.2.B. PREPARATION OF 3-[(PERFLUORO-2-METHYLPENTAN-2-YL) METHYL]BENZOIC ACID

Under nitrogen atmosphere at -75 °C, tert-butyllithium (2.6 cm^3, 4.5 mmol) was added to a solution of 1-bromo-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (8) (1.1.g, 2 mmol) in dry diethyl ether (30 cm^3). After 1h of vigorous stirring at -75 °C, freshly freshly solid CO_2 was was added to the mixture[118]. The flask was allowed to stand at room temperature. A white precipitate was formed. The acid was extracted with 2M NaOH (2 x 30 cm^3) and collected as a white powder after acidification with 2M HCl of the aqueous phase. The crude solid was recrystallized from hexane and identified as **3-[(perfluoro-2-methylpentan-2-yl)methyl]benzoic acid** (28) (0.62 g, 60%); as white crystal; m.p. 81-83 °C; (Found: C, 36.81; H, 1.45.$C_{14}H_7F_{13}O_2$ requires C, 37.02; H, 1.55%); ν_{max}/cm^{-1} 1682 (C=O), 1180-1338 (C-F and C-O); n.m.r. spectrum No 23, recorded in deuterated acetone; m/z (FAB$^+$) 454 (M$^+$, 14%) 135 (100) 69 (54); Mass spectrum No 23; IR spectrum No 17.

VI.2.C. ATTEMPT TO PREPARE 2-[(PERFLUORO-2-METHYLPENTAN-2-YL) METHYL]BENZOIC ACID

Under nitrogen atmosphere at -75 °C, tert-butyllithium (2.6 cm^3, 4.5 mmol) was added to a solution of 1-bromo-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (9) (1.1.g, 2 mmol) in dry diethyl ether (30 cm^3). After 1hour of vigorous stirring at -75 °C, freshly freshly solid CO_2 was was added to the mixture[118]. The flask was allowed to stand at room temperature. No precipitate was formed. The extraction with 2M NaOH (2 x 30 cm^3) and the acidification with 2M HCl of the aqueous phase were carried on but no precipitate was formed. The ethereal layer was analysed by glc-ms and showed the presence of [(perfluoro-2-methylpentan-2-yl)methyl]benzene (4) detected by glc-ms, with no starting material left. The data obtained matched with the data collected for compound (4) in Chapter II (section II.3.C.1).

VI.2.D. PREPARATION OF 4-[(PERFLUORO-2-METHYLPENTAN-2-YL) METHYL]BENZOYL CHLORIDE

A flask was charged with 4-[(perfluoro-2-methylpentan-2-yl)methyl]benzoic acid (27) (0.54 g, 1.2 mmol) in an excess of $SOCl_2$ (30 cm^3). The mixture was refluxed for 2 hours until the evolution of hydrogen chloride and sulphur dioxide ceased[132, 120]. The thionyl chloride was then removed by distillation and also the corresponding benzoyl chloride under reduced pressure to give **4-[(perfluoro-2-methylpentan-2-yl)methyl] benzoyl chloride** (29) (0.46 g, 82%); as a liquid; b.p. 70°C (4 mmHg); (Found: C, 35.3; H, 1.3 %.$C_{14}H_6F_{13}OCl$ requires C, 35.5; H, 1.3 %); ν_{max}/cm^{-1} 1783 (C=O), 1609 (C=C), 1268-1216 (br C-F); n.m.r. spectrum No 24, recorded in deuterated acetone; m/z (EI^+) 437 (M^+ - 35, 76%) 109 (70) 69 (100); Mass spectrum No 24; IR spectrum No 18.

VI.2.E. PREPARATION OF 3-[(PERFLUORO-2-METHYLPENTAN-2-YL) METHYL]BENZOYL CHLORIDE

A flask was charged with 3-[(perfluoro-2-methylpentan-2-yl)methyl]benzoic acid (28) (0.51 g, 1.2 mmol) in an excess of $SOCl_2$ (30 cm^3). The mixture was refluxed for 2 hours until the evolution of hydrogen chloride and sulphur dioxide ceased[132, 120]. The thionyl chloride was then removed by distillation and also the corresponding benzoyl chloride under reduced pressure to give **3-[(perfluoro-2-methylpentan-2-yl)methyl] benzoyl chloride** (30) (0.42 g, 80%); as a liquid; b.p. 60°C (4 mmHg); (Found: C, 35.4; H, 1.4 %.$C_{14}H_6F_{13}OCl$ requires C, 35.5; H, 1.3%); ν_{max}/cm^{-1} 1775 (C=O), 1242 (br C-F); n.m.r. spectrum No 25, recorded in deuterated acetone; m/z (EI^+) 437 (M^+ - 35, 100%) 109 (35) 69 (25); Mass spectrum No 25; IR spectrum No 19.

VI.2.F. PREPARATION OF CYCLOHEXYL 3-[(PERFLUORO-2-METHYL PENTAN-2-YL) METHYL]BENZOATE

A flask was charged with 3-[(perfluoro-2-methylpentan-2-yl)methyl]benzoyl chloride (0.50 g, 1.2 mmol) in an excess of cyclohexanol (25 cm^3) with hydrochloric acid (2 cm^3). The mixture was refluxed for 14 hours[120]. Distillation of the reaction mixture gave a fraction of low boiling point (containing cyclohexene) with the excess of cyclohexanol and the ester: **cyclohexyl 3-[(perfluoro-2-methylpentan-2-**

yl)methyl]benzoate (31) (0.58 g, 91%); as a very viscous liquid; b.p. > 200°C; (Found: C, 45.1; H, 3.4 %.$C_{20}H_{17}F_{13}O_2$ requires C, 44.8; H, 3.2 %); ν_{max}/cm^{-1} 2900 (br C-H), 1721 (C=O), 1591 (C=C), 1338-1200 (br C-O and C-F); n.m.r. spectrum No 26, recorded in deuterated acetonitrile; m/z (EI^+) 537 (M^+, 0.1 %) 438 (69) 82 (100); Mass spectrum No 26; IR spectrum No 20.

VI.3. DYES SOLUBLE IN FLUOROCARBON FLUIDS

VI.3.A. PREPARATION OF 1-AMINO-4-[(PERFLUORO-2-METHYL PENTAN-2-YL)METHYL]BENZENE.

A flask was charged with 1-nitro-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (10) (5.1 g, 11.2 mmol) and 10% of Pt on activated carbon (0.5 g) in ethanol (50 ml). The mixture was stirred under 3 bar of hydrogen gas over night at room temperature[139, 140]. The solution was cautiously filtered to remove the excess of the catalyst and the evaporation of ethanol afforded **1-amino-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene** (32) (3.9 g, 82%);as a yellow liquid; b.p.230°C; (Found: C, 36.1; H, 2.1; N, 3.6%.$C_{13}H_8F_{13}N$ requires C, 36.7; H, 1.9; N, 3.3%); ν_{max}/cm^{-1} 3370 (N-H), 1626 (C=C), 1520 (N-H), 1241 (br C-F); n.m.r. spectrum No 27, recorded in deuterated acetone; m/z (EI^+) 425 (M^+, 7%), 106 (100); Mass spectrum No 27; IR spectrum No 21.

VI.3.B. PREPARATION OF 1-AMINO-3-[(PERFLUORO-2-METHYL PENTAN-2-YL)METHYL]BENZENE.

A flask was charged with 1-nitro-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (11) (5.1 g, 11.2 mmol) and 10% of Pt on activated carbon (0.5 g) in ethanol (50 ml). The mixture was stirred under 3 bar of hydrogen gas over night at room temperature[139, 140]. The solution was cautiously filtered to remove the excess of the catalyst and the evaporation of ethanol afforded **1-amino-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene** (33) (4.0 g, 85%);as a yellow liquid; b.p.238°C; (Found: C, 36.7; H, 2.0; N, 3.3%.$C_{13}H_8F_{13}N$ requires C, 36.7; H, 1.9; N, 3.3%); ν_{max}/cm^{-1} 3373 (N-H), 1624 (C=C), 1497 (N-H), 1243 (br C-F); n.m.r. spectrum No 28, recorded in deuterated acetone; m/z (EI^+) 425 (M^+, 2%), 106 (100); Mass spectrum No 28; IR spectrum No 22.

VI.3.C. REDUCTION OF THE NITRO MIXTURE

A flask was charged with a mixture of three isomers of nitro-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (21), (11) and (10) (5.1 g, 11.2 mmol) in the ratio 1/3.8/3.8 respectively and 10% of Pt on activated carbon (0.5 g) in ethanol (50 ml). The mixture was stirred under 3 bar hydrogen gas over night at room temperature[139, 140]. The solution was cautiously filtered to remove the excess of the catalyst, and the distillation of ethanol afforded the three amines with 100% conversion and in the ratio respectively 1/3.8/3.8.

The product was characterised as a mixture (3.8 g, 81%): 1-amino-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (34), 1-amino-3-[(perfluoro-2-methylpentan-2-

yl)methyl]benzene (33), 1-amino-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (32); pale yellow liquid; M^+ 425.04490 $C_{13}H_8F_{13}N$ requires M^+ 425.04490; ν_{max}/cm^{-1} 3419 (br N-C), 1625 (C=C), 1521 (N-C), 1247 (br C-F); δ_H (400 MHz; CD_3COCD_3, Me_4Si) 7.3-7.2 (m), 7.0 (m), 6.5-6.7 (m), 3.74 (2H, s, CH_2) 3.71 (2H, s, CH_2) 3.56 (2H, s, CH_2); δ_F (235 MHz; CD_3COCD_3, $CFCl_3$) -62.2 (6F, s, $C(\underline{CF}_3)_2$), -62.8 (12F, s, $C(\underline{CF}_3)_2$), -80.8 (9F, s, $CF_2\underline{CF}_3$), -106.3 (6F, s, $\underline{CF}_2CF_2CF_3$), -123.2 (6F, s, $\underline{CF}_2CF_3$); δ_C {H} (100 MHz; CD_3COCD_3, Me_4Si) 157.5 (s), 156.9 (s), 151.1 (s), 149.9 (s), 140.2 (s), 132.6 (s), 130.3 (s), 123.1 (s), 122.7 (s), 115.0 (s), 110.9 (s), 105.9 (s); compound 32 m/z (EI^+) 425 (M^+, 8%) 106 (100) 69 (26); compound 34 m/z (EI^+) 425 (M^+, 19%) 106 (100) 69 (24), Mass spectrum No 29; compound 33 m/z (EI^+) 425(M^+, 5%) 106 (100) 69 (14). Spectroscopy and glc-ms data were identical to the data obtained previously section VI.3.C.A and VI.3.C.B for compounds 32 and 33.

VI.3.C. SYNTHESIS OF AZO-DYES

VI.3.C.1. With 1-amino-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene

1-Amino-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (32) (1.0 g, 2.3 mmol) was dissolved by heating in water (7 ml) and 1.5 ml of 10 % HCl. The mixture was cooled in ice and sodium nitrite (0.16 g) in water (2 ml) was added[142, 141, 136, 143] with stirring ensuring that the temperature of the mixture was kept below 5°C. A solution of β-naphthol (0.31 g, 2.2 mmol) in 2 ml of 10 % NaOH was added to the diazonium salt prepared in the first stage, maintaining a temperature not higher than 5°C. Coupling occured rapidly and the dye separated within few minutes. The mixture was cooled in ice and collected by filtration to give azo-dye (35) as an orange solid, after purification by repeated column chromatography using methanol/water as the eluent; (0.7 g, 53%); mp. 110-115°C; (M^+ 580.08200 $C_{26}H_{13}F_{13}N_2O$ requires M^+ 580.08203); $\lambda_{max}(CH_3CN)/nm$ 199 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 120,359), 250 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 16,249), sh 420 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 7,999), sh 500 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 7,999); ν_{max}/cm^{-1} 3412 (O-H), 3062 (C-H), 2968 (C-H), 1622 (C=C), 1517-1454 (br N=N), 1330-1145 (N-C and C-F); n.m.r. spectrum No 29, recorded in deuterated acetone; m/z (FAB^+) 580 (M^+, 1%), 425 (25), 125 (100), 106 (100), 69 (59); Mass spectrum No 30; IR spectrum No 23.

VI.3.C.2. With 1-amino-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene

VI.3.C.2.i. Reaction with naphthalenesulphonic acid derivative

1-Amino-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (33) (0.5 g, 1.17 mmol) was dissolved by heating in water (7 ml) and 1.5 ml of 10 % HCl. The mixture was cooled in ice and sodium nitrite (0.09 g) in water (2 ml) was added[142, 141, 136, 143] with stirring ensuring that the temperature of the mixture was kept below 5°C. A solution of 4-hydroxy-1-naphthalenesulphonic acid sodium salt hydrate (0.27 g, 1.1 mmol) in 3 ml of 18 % Na_2CO_3 was added to the diazonium salt prepared in the first stage, maintaining a temperature not higher than 5°C. Coupling occured rapidly and the dye was extracted with Fluorinert (FC-84, bp. 80°C). The azo-dye (36) as a reddish solid was obtained after distillation of the solvent and repeated column chromatography using methanol/water as the eluent; (0.7 g, 48%); mp. 195-200°C; (MH^+ 661.14101 $C_{23}H_{13}F_{13}N_2O_4S$ requires MH^+ 661.04671); λ_{max}(CH_3CN)/nm 198 (ε/dm^3 mol^{-1} cm^{-1} 184,812), sh 235 (ε/dm^3 mol^{-1} cm^{-1} 11,331), 350 (ε/dm^3 mol^{-1} cm^{-1} 2,331), 490 (ε/dm^3 mol^{-1} cm^{-1} 3,716); ν_{max}/cm^{-1} 3470 (br O-H), 3084 (br C-H), 1620 (br C=C), 1593-1577 (br N=N), 1270-1158 (N-C and C-F) 1030 (S=O), 680 (S-O); n.m.r. spectrum No 30, recorded in deuterated acetone; m/z (Electrospray, EI^+) 660 (M^+, 20%), 659 (100), 425 (48), 223 (40); Mass spectrum No 31; IR spectrum No 24.

VI.3.C.2.ii. Reaction with pyridone derivative

1-Amino-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (33) (0.5 g, 1.17 mmol) was dissolved by heating in water (7 ml) and 1.5 ml of 10 % HCl. The mixture was cooled in ice. Sodium nitrite (0.09 g) in water (2 ml) was added[142, 141, 136, 143] with stirring ensuring that the temperature of the mixture was kept below 5°C. A solution of 1-*n*-butyl-2-hydroxy-3-cyano-4-methyl-1-pyridone-2 (0.27 g, 1.1 mmol) in 3 ml of 18 % Na_2CO_3.was added to the diazonium salt prepared in the first stage, maintaining a temperature not higher than 5°C. Coupling occured rapidly and the dye was extracted with Fluorinert (FC-84, bp. 80°C). The fluorinated layer was separated from the aqueous layer and concentrated. The azo-dye (37) was obtained as a yellow solid after repeating column chromatography using methanol/water as the eluent; (0.7 g, 51%); mp. 75-80°C; (M^+ 642.130000 $C_{24}H_{19}F_{13}N_4O_2$ requires M^+ 642.130043); λ_{max}(CH_3CN)/nm 199 (ε/dm^3 mol^{-1} cm^{-1} 1,369,732), sh 263 (ε/dm^3 mol^{-1} cm^{-1} 55,401), 420 (ε/dm^3 mol^{-1} cm^{-1} 7,035); ν_{max}/cm^{-1} 3450 (br O-H), 2959 (C-H), 2235 (cyano group), 1698-1640 (C=O and C=C), 1525 (br N=N), 1280-1145 (N-C and C-F); n.m.r. spectrum No 31, recorded in deuterated acetone; m/z (EI^+) 642 (M^+, 4%), 218 (19), 106 (83); Mass spectrum No 32; IR spectrum No 25.

VI.4. SYNTHESIS OF PHOSPHINE DERIVATIVES

VI.4.A. REACTION WITH 1-BROMO-4-[(PERFLUORO-2-METHYL PENTAN-2-YL)METHYL]BENZENE

Under nitrogen atmosphere at -75 °C, tert-butyllithium (2.9 ml, 5 mmol) was added to a solution of 1-bromo-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (7) (1.2 g, 2.4 mmol) in dry diethyl ether (30 ml). After 1h of vigorous stirring at -75°C, phosphorus trichloride (66µl, 0.76 mmol) was added[145, 129, 146, 147, 118]. The mixture containing the phosphine derivative (38) was analysed by ^{31}P and ^{19}F NMR: δ_F (235 MHz, diethyl ether, $CFCl_3$) -62.8 (6F, s, $C(\underline{CF_3})_2$), -81.0 (3F, s, $CF_2\underline{CF_3}$), -106.3 (2F, s, $\underline{CF_2}CF_2CF_3$), -123.4 (2F, s, $\underline{CF_2}CF_3$); δ_P (100 MHz, diethyl ether, H_3PO_4) +23 ($Ph_3P=O$), -7.6 (Ph_3P). The mixture was then allowed to stand at room temperature. A white very fine powder was formed at the bottom of the flasked. The solid was filtered and washed under nitrogen. The filtrate was analysed by ^{31}P and ^{19}F NMR and gave very weak signals. The white powder was found insoluble in organic solvent: THF, acetone, methanol, pentane, benzene (at room temperature or reflux). The solubility of

(38) was studied in fluorocarbon solvent (FC-84 and PP-11), the experiment was done in an NMR tube and the progress was followed by ^{31}P NMR. The NMR was run in both cases at room temperature and 80°C, but with very little success as no peak was observed confirming that compound (38) is insoluble in fluorocarbon solvent. IR was done with nugol, ν_{max}/cm^{-1} 1638 (C=C), 1462 (P-Ph + nugol), 1263-1220 (P-O and C-F); an attempt was made to obtain a mass spectrum but the solid was found highly resistant to temperature (>300°C).

VI.4.B. REACTION WITH 1-BROMO-3-[(PERFLUORO-2-METHYL PENTAN-2-YL)METHYL]BENZENE

Under nitrogen atmosphere at -75 °C, tert-butyllithium (2.9 ml, 5 mmol) was added to a solution of 1-bromo-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (8) (1.2.g, 2.4 mmol) in dry diethyl ether (30 ml). After 1h of vigorous stirring at -75 °C, phosphorus trichloride (66μl, 0.76 mmol) was added[145, 129, 146, 147, 118]. The mixture containing the phosphine derivative (39) was analysed by ^{31}P and ^{19}F NMR: δ_F (235 MHz, diethyl ether, $CFCl_3$) -62.3 (6F, s, $C(\underline{CF_3})_2$), -80.5 (3F, s, $CF_2\underline{CF_3}$), -105.8 (2F, s, $\underline{CF_2}CF_2CF_3$), -122.9 (2F, s, $\underline{CF_2}CF_3$); δ_P (100 MHz, diethyl ether, H_3PO_4) +24.7 (triphenyl phosphine oxide derivative), -5.2 (triphenyl phosphine derivative). The mixture was then allowed to stand at room temperature. A white very fine powder was formed at the bottom of the flasked. The solid was filtered and washed under nitrogen. The filtrate was analysed by ^{31}P and ^{19}F NMR and gave very weak signals. The white powder was found insoluble in organic solvent: THF, acetone, methanol, pentane, benzene (at room temperature or reflux). The solubility of (39) was studied in fluorocarbon solvent (FC-84 and PP-11), the experiment was done in an NMR tube and the progress was followed by ^{31}P NMR. The NMR was run in both cases at room temperature and 80°C, but with very little success no peak was observed confirming that compound (39) is insoluble in fluorocarbon solvent. An attempt was made to obtain a mass spectrum but the solid was found highly resistant to temperature (>300°C).

CHAPTER VII
EXPERIMENTAL TO CHAPTER IV

VII.1. PREPARATION OF 2,4,6-TRIFLUORO-S-TRIAZINE

An autoclave (460 cm^3, No. 14) was charged with 2,4,6-trichloro-s-triazine (35 g, 0.189 mol) and flame dried potassium fluoride (127 g, 2.19 mol), evacuated and then heated at 310 °C for 16h (furnace No.3)[151]. The volatile products were transfered from the hot autoclave to a trap which was cooled in liquid air. The product 2,4,6-trifluoro-s-triazine (40) did not require any further purification and was stored in a rotaflo tube; (24.3 g, 95%) as colourless liquid; b.p. 74°C (lit.[151] 74°C); δ_F (235 MHz, $CDCl_3$, $CFCl_3$) -32.5 ppm.

VII.2. PREPARATION OF PERFLUOROISOPROPYL-S-TRIAZINES

VII.2.A. USE OF POTASSIUM FLUORIDE

A flask was charged with 2,4,6-trifluoro-s-triazine (40) (12.1 g, 89 mmol), potassium fluoride (4 g, 68.9 mmol) and dry sulpholane (80 cm^3). The flask was frozen down in liquid air and evacuated. Hexafluoropropene (14.1 g, 94 mmol) was added via a bladder and the reaction mixture was heated at 70°C for 19 h with vigourous stirring[151, 154]. All volatile products were removed by transfer under vacuum. Glc-ms data showed the presence of a mixture of 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41), 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) and 2,4,6-perfluorotri-isopropyl-s-triazine (43) in the following ratio 1.3/2.2/1. Fluorinated solvent (PP-11, bp 211°C) was used to extract the mixture containing compounds (41), (42) and (43) from sulpholane. Distillation of the product mixture on the Fischer Spahltrohr gave: 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41) as a colourless liquid, b.p. 104-106°C, n.m.r spectrum No 32, m/z (EI$^+$) 285 (M$^+$, 9%) 69 (100), as compared to the literature data[151]; 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) as a colourless liquid, b.p. 134-136°C, n.m.r. spectrum No 33, run in $CDCl_3$, m/z (EI$^+$) 435 (M$^+$, 4%) 69 (100), as compared to the literature data[151]; 2,4,6-perfluorotri-isopropyl-s-triazine (43) as a solid, m.p. 30°C, n.m.r. spectrum No 34, m/z (EI$^+$) 585 (M$^+$, 1%) 69 (100). Single crystals were grown from FC-84, bp 80°C over one week at -15°C and X-ray crystallographic structure was obtained.

VII.2.B. USE OF TRIMETHYLAMINE

General Procedure - A Carius tube was charged with hexafluoropropene, 2,4,6-trifluoro-s-triazine (40) and a catalytic amount of trimethylamine. The tube was sealed and agitated for 10-12 h at 60°C and then was opened. Volatile materials were transfered to a cold trap under reduced pressure. The mixture was kept under nitrogen atmosphere and analysed by glc-ms.

VII.2.B.1. Sealed glass tubes- pressure below 12 atm.

2,4,6-Trifluoro-s-triazine (40) (1.0 g, 7.4 mmol), hexafluoropropene (3.42 g, 22.8 mmol) and trimethylamine (20 mg, 0.34 mmol) gave a mixture (3.3 g) containing 2,4,6-perfluorotri-isopropyl-s-triazine (43) 35%, 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) 55% and 2,4-difluoro-6-perfluoro-isopropyl-s-triazine (41) 10% (by glc-ms).

2,4,6-Trifluoro-s-triazine (40) (1.0 g, 7.4 mmol), hexafluoropropene (4.5 g, 30 mmol) and trimethylamine (20 mg, 0.34 mmol) gave a mixture (2.8 g) containing 2,4,6-perfluorotri-isopropyl-s-triazine (43) 16%, 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) 65% and 2,4-difluoro-6-perfluoro-isopropyl-s-triazine (41) 19% (by glc-ms).

VII.2.B.2. Sealed quartz tubes - pressure below 200 atm.

2,4,6-Trifluoro-s-triazine (40) (2.4 g, 17.7 mmol), hexafluoropropene (10.3 g, 68.6 mmol) and trimethylamine (0.1 g, 1.7 mmol) were heated together at 80°C, the maximum theoritical pressure was 190 atm. The reaction gave 100% 2,4,6-perfluorotri-isopropyl-s-triazine (43), (8.2 g, 80%), as a solid, m.p. 30°C, n.m.r. spectrum No 34, m/z (EI^+) 585 (M^+, 1%) 69 (100). Single crystals were grown from FC-84, bp 80°C over one week at -15°C.

A mixture of 2,4,6-trifluoro-s-triazine (40) (0.7 g, 5.1 mmol), hexafluoropropene (3.6 g, 24.1 mmol) and trimethylamine (0.1 g, 1.7 mmol) were heated together at 80°C, the maximum theoritical pressure was 179 atm. The reaction gave 100% of 2,4,6-perfluorotri-isopropyl-s-triazine (43) (2.1 g, 73 %)..as a solid, m.p. 30°C, n.m.r. spectrum No 34, m/z (EI^+) 585 (M^+, 1%) 69 (100). Single crystals were grown from FC-84, bp 80°C over one week at -15°C.

2,4,6-Trifluoro-s-triazine (40) (1.1 g, 8.1 mmol), hexafluoropropene (5.5 g, 36.6 mmol) and trimethylamine (0.1 g, 1.7 mmol) gave 100% 2,4,6-perfluorotri-isopropyl-s-triazine (43) (3.7 g, 78 %), the maximum theoritical pressure was 150 atm; n.m.r. spectrum No 34, m/z (EI^+) 585 (M^+, 1%) 69 (100). Single crystals were grown from FC-84, bp 80°C over one week at -15°C.

2,4,6-Trifluoro-s-triazine (40) (2.9 g, 21.4 mmol), hexafluoropropene (10.2 g, 68 mmol) and a catalytic amount of trimethylamine (0.1 g, 1.7 mmol) gave a mixture (10.7 g) containing 2,4,6-perfluorotri-isopropyl-s-triazine (43) 85%, 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) 14% and 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41) 1% (by glc-ms). The maximum theoritical pressure was ~100 atm.

VII.2.B.3. Sealed metal tube

2,4,6-Trifluoro-s-triazine (40) (6.9 g, 51.4 mmol), hexafluoropropene (35.8 g, 0.24 mol) and trimethylamine (0.6 g, 10 mmol) gave a mixture (21.3 g) containing 2,4,6-perfluorotri-isopropyl-s-triazine (43) 38%, 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) 37% and 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41) 25% (by glc-ms). The maximum theoritical pressure was 80 atm.

VII.3. NUCLEOPHILIC REACTIONS

VII.3.A. REACTION WITH SODIUM METHOXIDE

Sodium methoxide (0.3 g, 5mmol), dissolved in methanol (4 cm^3), was added dropwise at 0°C to a rapidly stirred solution of methanol (10 cm^3) containing a mixture of 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41) and 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) (1 g) 26% / 74%. The mixture was stirred for a further 2 h at room temperature under a nitrogen atmosphere. The reaction mixture was poured into ether.

The extract was washed with water and dried ($MgSO_4$). The glc-ms data showed trace of 2-methoxy-4,6-perfluorodi-isopropyl-s-triazine (44): m/z (EI^+) 447 (M^+, 7%) 69 (100); 84% of 2,4-dimethoxy-6-perfluoroisopropyl-s-triazine (45): m/z (EI^+) 309 (M^+, 25%) 69 (94) and 16% of 2,4,6-trimethoxy-s-triazine. No further purification was attempted[163].

VII.3.B. WITH METHANOL

A mixture of 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41) and 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) (1 g) 26% / 74% was added to methanol (14 cm^3) at 0°C under a nitrogen atmosphere. The mixture was stirred for a further 2 h at room temperature. The reaction mixture was poured into ether. The extract was washed with water and dried ($MgSO_4$). The glc-ms data showed two compounds 2-methoxy-4,6-perfluorodi-isopropyl-s-triazine (44) and 2,4-dimethoxy-6-perfluoro-isopropyl-s-triazine (45) in the ratio ~74% / 26%. The mixture (0.97 g) was separated by preparative scale GC using a 30% SE30 column at 80 °C to give **2-methoxy-4,6-perfluorodi-isopropyl-s-triazine** (44) as colourless liquid[163] (Found: C, 26.7; H, 0.5; N, 10.0. $C_{10}H_3F_{14}ON_3$ requires C, 26.8; H, 0.6; N, 9.3%); ν_{max}/cm^{-1} 2962 (C-H), 1254 (br C-F), 1076 (br C-O); n.m.r. spectrum No 35, run in $CDCl_3$; m/z (EI^+) 447 (M^+, 7%) 69 (100), Mass spectrum No 33, IR spectrum No 26; **2,4-dimethoxy-6-perfluoroisopropyl-s-triazine** (45) as white crystals[163]; m.p. 32-33°C; (Found: C, 31.2; H, 1.8; N, 13.4. $C_8H_6F_7O_2N_3$ requires C, 31.0; H, 1.9; N, 13.5%); ν_{max}/cm^{-1} 2958 (C-H), 1240 (C-F), 1096-1020 (br C-O); n.m.r. spectrum No 36, run in $CDCl_3$; m/z (EI^+) 309 (M^+, 25%) 69 (94); Mass spectrum No 34, IR spectrum No 27.

VII.3.C. WITH ISOPROPANOL

A mixture of 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41) and 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) (1 g) 26% / 74% was added to isopropanol (14 cm^3) at room temperature under a nitrogen atmosphere. The mixture was stirred for a further 2 h. The reaction mixture was poured into ether. The extract was washed with water and dried ($MgSO_4$). The glc-ms data showed two compounds 2-isopropyloxy-4,6-perfluorodi-isopropyl-s-triazine (46) and 2,4-di-isopropoxy-6-perfluoroisopropyl-s-triazine (47) in the ratio ~74% / 26%. The mixture (0.97 g) was separated by preparative scale GC using a 30% SE30 column at 100°C to give **2-isopropoxy-4,6-perfluorodi-isopropyl-s-triazine** (46) as a colourless liquid; (Found: C, 30.3; H, 1.4; N, 8.8. $C_{12}H_7F_{14}ON_3$ requires C, 30.3; H, 1.4; N, 8.8%); ν_{max}/cm^{-1} 2989 (C-H), 1574 (conj. C=N), 1540 (conj. C=C), 1306-1247 (C-Fbr), 1058-1050 (C-Obr); n.m.r. spectrum No 37, run in $CDCl_3$; m/z (EI^+) 475 (M^+, 5%) 460 (9) 43 (100); Mass spectrum No 35, IR spectrum No 28 and **2,4-di-isopropoxy-6-perfluoroisopropyl-s-triazine** (47) as a colourless liquid; (Found: C, 39.4; H, 3.7; N, 11.6. $C_{12}H_{14}F_7O_2N_3$ requires C, 39.4; H, 3.8; N, 11.5%); ν_{max}/cm^{-1} 1577 (conj. C=N), 1247 (C-F), 1095 (C-Obr); n.m.r spectrum No 38, run in $CDCl_3$; m/z (EI^+) 322 (M^+, 1%) 292 (11) 43 (100); Mass spectrum No 36, IR spectrum No 29.

VII.3.D. WITH PHENOL

A mixture of 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41) and 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) (1 g) 26% / 74% was added to phenol (376 mg, 4 mmol) in acetonitrile (10 cm^3). The reaction was refluxed overnight. The solution was washed with water (2x10cm^3) and dried ($MgSO_4$). The glc-ms showed two compounds 2-phenoxy-4,6-perfluorodi-isopropyl-s-triazine (48A) and the disubstituted product (49A) in the same ratio 24% / 76%. The purificaton of the mixture (1.0 g) was allowed by column chromatography using CH_2Cl_2/hexane as the eluent, **2-phenoxy-4,6-perfluorodi-isopropyl-s-triazine** (48A) (0.3 g, 35%) as a solid; m.p. 130-140°C; n.m.r. spectrum No 39, run in $CDCl_3$; m/z (EI^+) 509 (M^+, 26%) 340 (100) 69 (40); Mass spectrum No 37, IR spectrum No 30.

VII.3.E. WITH p-CRESOL

A mixture of 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41) and 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) (1.14 g) 26% / 74% was added to p-cresol (0.38 g, 3.4 mmol) in acetonitrile (10 cm^3). The reaction was refluxed overnight. The solution was washed with water (2x10cm^3) and dried ($MgSO_4$). The glc-ms showed two compounds 2-(p-cresoxy)-4,6-perfluorodi-isopropyl-s-triazine (48B) [m/z (EI^+) 523 (M^+, 29%) 354 (100) 91 (41) 69 (20)] and 2,4-di(p-cresoxy)-6-perfluoroisopropyl-s-triazine (49B) [m/z (EI^+) 461 (M^+, 27%) 196 (87)]. The purificaton was carried out by column chromatography using CH_2Cl_2/hexane as the eluent to give **2-(p-cresoxy)-4,6-perfluorodi-isopropyl-s-triazine** (48B) (0.94 g, 51%) as a white solid; m.p. 165-167°C; (M^+ 523.03660 requires M^+ 523.03656); ν_{max}/cm^{-1} 2962 (C-H), 1659 (C=N), 1636 (C=C), 1300-1200 (br C-F), 1105-1020 (br C-O); n.m.r. spectrum No 40, run in deuterated acetone; m/z (EI^+) 523 (M^+, 29%) 354 (100) 91 (41) 69 (20); Mass spectrum No 38, IR spectrum No 31.

VII.3.F. REACTION OF CYCLOHEXANOL

VII.3.F.1. With 2,4-difluoro-6-perfluoroisopropyl-s-triazine

2,4-Difluoro-6-perfluoroisopropyl-s-triazine (41) (0.8 g) 89% pure, was added to cyclohexanol (1.2 g, 12 mmol) in acetonitrile (10 cm^3). The mixture was refluxed overnight, the glc-ms data showed the presence of two compounds 2-cyclohexanoxy-4-fluoro-6-perfluoroisopropyl-s-triazine (50) [m/z (EI^+) 434 (M^+, 1%); mass spectrum No 39, and 2,4-dicyclohexanoxy-6-perfluoroisopropyl-s-triazine (51) [m/z (EI^+) 365 (M^+, 1%) 284 (45) 99 (30)] in the ratio 84%/16%. After addition of cyclohexanol (1.2 g, 12 mmol), the reaction was left overnight, the glc-ms data showed the presence of (50) and (51) in the ratio 45%/55%. Finally, the reaction was left another night for completion, the glc-ms data showed the presence of (50) and (51) in the ratio 4%/96%. The solution was washed with water (2x10cm^3) and dried ($MgSO_4$). The purificaton was carried out by column chromatography using CH_2Cl_2/hexane as the eluent to give **2,4-dicyclohexanoxy-6-perfluoroisopropyl-s-triazine** (51) (0.72 g, 66%) was isolated as white crystals; m.p. 56-60°C; (MH^+ 446.16780 requires MH^+ 446.16785);

ν_{max}/cm^{-1} 2942 (C-H), 1688 (C=N), 1620-1540 (br C=C), 1303-1230 (br C-F), 1168 (br C-O); n.m.r. spectrum No 41, run in $CDCl_3$; m/z (CI^+) 445 (M^+, 8%) 309 (70) 69 (32); Mass spectrum No 40, IR spectrum No 32.

VII.3.F.2.With 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine

VII.3.F.2.i. Use of acetonitrile

2-Fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) (0.6 g) 90% pure, was added to cyclohexanol (0.3 g, 3 mmol) in acetonitrile (10 cm^3). The mixture was refluxed overnight. The mixture was washed with wated and dried ($MgSO_4$). The purificaton was performed by column chromatography using CH_2Cl_2/hexane as the eluant to give **2-cyclohexanoxy-4,6-perfluorodi-isopropyl-s-triazine** (52) (0.54 g, 63%) was isolated as a liquid; b.p. 197°C; (Found: C, 34.7; H, 2.0; N, 8.0. $C_{15}H_{11}N_3OF_{14}$ requires C, 34.9; H, 2.1; N, 8.1%); ν_{max}/cm^{-1} 2943 (C-H), 2866 (C-H), 1575-1530 (C=N and C=C), 1350-1175 (br C-F and br C-O); n.m.r. spectrum No 42, run in deuterated acetone; m/z (EI^+) 515 (M^+, 100%) 346 (10); Mass spectrum No 41, IR spectrum No 33.

VII.3.F.2.ii. Use of fluorinated solvent

The reaction was repeated in the same conditions using a different solvent: FC-84.

2-Fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) (0.6 g) 90% pure, was added to cyclohexanol (0.3 g, 3 mmol) in FC-84 (15 cm^3). The mixture was refluxed overnight. The mixture was washed with wated and dried ($MgSO_4$). The purificaton was performed by column chromatography using CH_2Cl_2/hexane as the eluent, the isolation yielded the desired product in 63%.

VII.3.G. REACTION WITH CELLULOSE

A mixture of 2,4-difluoro-6-perfluoroisopropyl-s-triazine (41) and 2-fluoro-4,6-perfluorodi-isopropyl-s-triazine (42) (1 g) 26% / 74% was placed in a flask with standard filter paper in PP-11/CH_3CN (1/4). The mixture was refluxed overnight. The progress of the reaction was followed by glc-ms, completion of the reaction was obtained after no starting materials was detected. After removal of the solvent by pumping it off, the filter paper was found water and oil repellent in comparison to the standard fiter paper.

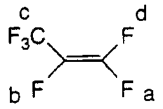
Appendix One

NMR Data

1. Hexafluoropropene
2. Hexafluoropropene dimer
3. [(Perfluoro-2-methylpentan-2-yl)methyl]benzene (**4**)
4. 2-[(Perfluoro-2-methylpentan-2-yl)methyl]naphthalene (**5**)
5. 1-Bromo-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**7**)
6. 1-Bromo-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**8**)
7. 1-Bromo-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**9**)
8. 1-Nitro-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**10**)
9. 1-Nitro-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**11**)
10. 1,3-Xylylene-bis(perfluoro-2-methylpentan-2-yl) (**12**)
11. 1-Fluoromethyl-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**14**)
12. 1,4-Xylylene-bis(perfluoro-2-methylpentan-2-yl) (**15**)
13. 1-Fluoromethyl-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**16**)
14. 1,2-Xylylene-bis(perfluoro-2-methylpentan-2-yl) (**17**)
15. 1-Fluoromethyl-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**18**)
16. 2,6-Bis[(perfluoro-2-methylpentan-2-yl)methyl]pyridine (**19**)
17. 2-Fluoromethyl-6-[(perfluoro-2-methylpentan-2-yl)methyl]pyridine (**20**)
18. 3-[(Perfluoro-2-methylpentan-2-yl)methyl]benzenesulphonyl chloride (**22**)
19. 4-[(Perfluoro-2-methylpentan-2-yl)methyl]benzenesulphonyl chloride (**23**)
20. 3-[(Perfluoro-2-methylpentan-2-yl)methyl]benzenesulphanilide (**24**)
21. 4-[(Perfluoro-2-methylpentan-2-yl)methyl]benzenesulphanilide (**25**)
22. 4-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoic acid (**27**)
23. 3-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoic acid (**28**)
24. 4-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoyl chloride (**29**)
25. 3-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoyl chloride (**30**)
26. Cyclohexyl 3-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoate (**31**)
27. 1-Amino-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**32**)
28. 1-Amino-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**33**)
29. Azo-dye (**35**)
30. Azo-dye (**36**)
31. Azo-dye (**37**)
32. 2,4-Difluoro-6-perfluoroisopropyl-s-triazine (**41**)
33. 2-Fluoro-4,6-perfluorodi-isopropyl-s-triazine (**42**)
34. 2,4,6-Perfluorotri-isopropyl-s-triazine (**43**)
35. 2-Methoxy-4,6-perfluorodi-isopropyl-s-triazine (**44**)
36. 2,4-Dimethoxy-6-perfluoroisopropyl-s-triazine (**45**)
37. 2-Isopropoxy-4,6-perfluorodi-isopropyl-s-triazine (**46**)
38. 2,4-Di-isopropoxy-6-perfluoroisopropyl-s-triazine (**47**)

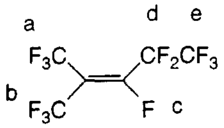
39. 2-Phenoxy-4,6-perfluorodi-isopropyl-s-triazine (**48A**)
40. 2-(p-Cresoxy)-4,6-perfluorodi-isopropyl-s-triazine (**48B**)
41. 2,4-Dicyclohexanoxy-6-perfluoroisopropyl-s-triazine (**51**)
42. 2-Cyclohexanoxy-4,6-perfluorodi-isopropyl-s-triazine (**52**)

Spectrum No 1



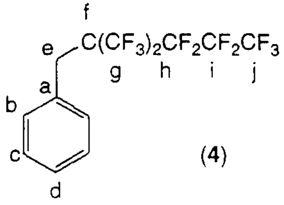
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{19}F	-69.4	ddd	J_{cd} 21 J_{cb} 13 J_{ca} 8.5	3	c
	-94.1	ddq	J_{ad} 58 J_{ab} 40 J_{ac} 8.5	1	a
	-107.6	ddq	J_{db} 117 J_{da} 58 J_{dc} 21	1	d
	-193.1	dqd	J_{bd} 117 J_{bc} 13 J_{ba} 40	1	b

Spectrum No 2



Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{19}F	-60.3	m		3	a
	-63.0	dq	J_{bc} 33 J_{ba} 9	3	b
	-86.4	m		3	e
	-100.4	br s	J_{de} 20	1	c
	-119.5	qd	J_{dc} 5	2	d

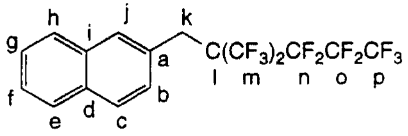
Spectrum No 3



(4)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	7.11	s		5	Ph
	3.36	s		2	e
^{19}F	-62.7	s		6	g
	-80.5	s		3	j
	-106.4	s		2	h
	-123.4	s		2	i
^{13}C	131.4	s			b
	130.8	s			a
	128.0	s			c
	127.9	s			d
	122.3	q	$^{1}J_{CF}$ 290		g
	117.7	qt	$^{1}J_{CF}$ 290 $^{2}J_{CF}$ 34		j
	114.9	tt	$^{1}J_{CF}$ 270 $^{2}J_{CF}$ 33		h
	109.8	tsext	$^{1}J_{CF}$ 271 $^{2}J_{CF}$ 37		i
	61.7	sept	$^{2}J_{CF}$ 25		f
	32.1	s			e

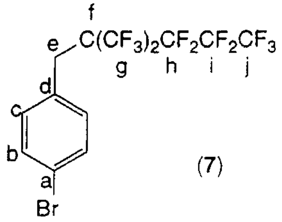
Spectrum No 4



(5)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	7.8-7.3	m		7	
	3.67	s		2	k
^{19}F	-62.2	s		6	m
	-80.1	s		3	p
	-105.9	s		2	n
	-122.8	s			o
^{13}C	133.0	s			i
	132.8	s			d
	131.1	s			a
	128.7	s			b
	128.3	s			j
	127.9	s			
	127.7	s			
	127.5	s			
	126.5	s			
	126.4	s			
	126.3	s			
	122.1	q	$^1J_{CF}$ 290		m
	117.7	qt	$^1J_{CF}$ 290 $^2J_{CF}$ 34		p
	114.9	tt	$^1J_{CF}$ 270 $^2J_{CF}$ 33		n
	109.7	tsext	$^1J_{CF}$ 271 $^2J_{CF}$ 37		o
	61.6	sept	$^2J_{CF}$ 25		l
	32.8	s			k

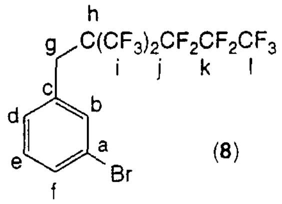
Spectrum No 5



(7)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	7.44	d	$^3J_{HH}$ 8.4	2	b
	7.16	d	$^3J_{HH}$ 8.4	2	c
^{19}F	3.49	s		2	e
	-62.9	s		6	g
	-80.8	s		3	j
	-106.6	s		2	h
	-123.6	s		2	i
^{13}C	133.1	s			b
	131.4	s			c
	129.9	s			d
	122.5	s			a
	121.9	q	$^1J_{CF}$ 290		g
	117.5	qt	$^1J_{CF}$ 289 $^2J_{CF}$ 33		j
	114.7	tt	$^1J_{CF}$ 270 $^2J_{CF}$ 32		h
	109.6	tsext	$^1J_{CF}$ 272 $^2J_{CF}$ 38		i
	62.4	sept	$^2J_{CF}$ 24		f
	32.1	s			e

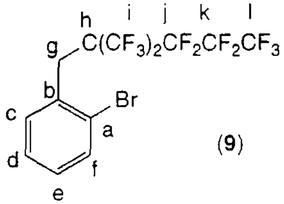
Spectrum No 6



(**8**)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	7.45	s		1	b
	7.44	d	$^{3}J_{HH}$ 8.4	1	f
	7.22	d	$^{3}J_{HH}$ 7.2	1	d
	7.16	t	$^{3}J_{HH}$ 7.6	1	e
	3.49	s		1	g
^{19}F	-62.7	s		6	i
	-80.5	s		3	l
	-106.3	s		2	j
	-123.3	s		2	k
^{13}C	134.7	s			b
	133.3	s			f
	131.5	s			d
	130.2	s			e
	129.7	s			c
	122.3	s			a
	122.0	q	$^{1}J_{CF}$ 290		i
	117.5	qt	$^{1}J_{CF}$ 285 $^{2}J_{CF}$ 34		l
	114.9	tt	$^{1}J_{CF}$ 270 $^{2}J_{CF}$ 33		j
	109.6	tsext	$^{1}J_{CF}$ 272 $^{2}J_{CF}$ 37		k
	61.7	sept	$^{2}J_{CF}$ 24		h
	32.1	s			g

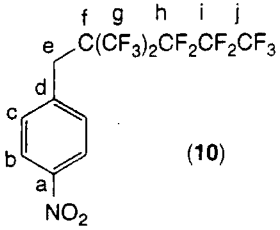
Spectrum No 7



(**9**)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	7.59	d	$^{3}J_{HH}$ 7.9	1	f
	7.43	d	$^{3}J_{HH}$ 7.9	1	c
	7.25	t	$^{3}J_{HH}$ 7.6	1	d
	7.13	t	$^{3}J_{HH}$ 7.9	1	e
	3.84	s		6	g
^{19}F	-61.5	s		3	i
	-80.6	s		2	l
	-107.9	s		2	j
	-122.7	s		1	k
^{13}C	133.7	s			f
	132.6	s			c
	131.5	s			b
	129.7	s			e
	127.2	s			a, d
	122.0	q	$^{1}J_{CF}$ 290		i
	116.4	qt	$^{1}J_{CF}$ 289 $^{2}J_{CF}$ 34		l
	114.9	tt	$^{1}J_{CF}$ 270 $^{2}J_{CF}$ 33		j
	109.6	tsext	$^{1}J_{CF}$ 272 $^{2}J_{CF}$ 37		k
	61.9	sept	$^{2}J_{CF}$ 25		h
	31.6	s			g

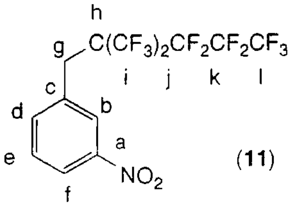
Spectrum No 8



(10)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^1H	8.16	d	$^3J_{HH}$ 9.2	2	b
	7.58	d	$^3J_{HH}$ 9.2	2	c
	3.67	s		2	e
^{19}F	-62.8	s		6	g
	-81.0	s		3	j
	-106.4	s		2	h
	-123.3	s		2	i
^{13}C	148.8	s			a
	139.6	s			d
	133.9	s			c
	124.1	s			b
	121.9	q	$^1J_{CF}$ 290		g
	117.5	qt	$^1J_{CF}$ 289 $^2J_{CF}$ 33		j
	114.7	tt	$^1J_{CF}$ 270 $^2J_{CF}$ 32		h
	109.6	tsext	$^1J_{CF}$ 272 $^2J_{CF}$ 38		i
	62.4	sept	$^2J_{CF}$ 24		f
	32.7	s			e

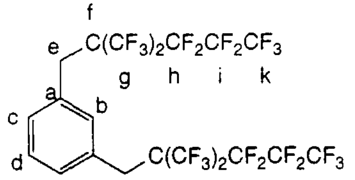
Spectrum No 9



(11)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^1H	8.2	s		1	b
	8.19	d	$^3J_{HH}$ 8.8	1	f
	7.75	d	$^3J_{HH}$ 7.6	1	d
	7.58	t	$^3J_{HH}$ 8	1	e
	3.8	s		2	g
^{19}F	-62.8	s		6	i
	-81.0	s		3	l
	-106.4	s		2	j
	-123.3	s		2	k
^{13}C	149.0	s			a
	139.0	s			d
	134.1	s			c
	130.5	s			e
	127.4	s			b
	124.3	s			f
	122.0	q	$^1J_{CF}$ 290		i
	117.5	qt	$^1J_{CF}$ 285 $^2J_{CF}$ 34		l
	114.9	tt	$^1J_{CF}$ 270 $^2J_{CF}$ 33		j
	109.6	tsext	$^1J_{CF}$ 272 $^2J_{CF}$ 37		k
	61.7	sept	$^2J_{CF}$ 24		h
	32.1	s			g

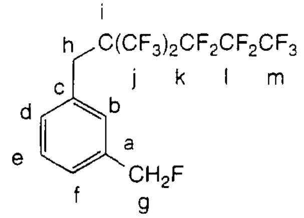
Spectrum No 10


f
e
C(CF3)2CF2CF2CF3
g h i k
a
b
c
d
C(CF3)2CF2CF2CF3

(12)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^1H	7.2	m		4	Ph
	3.5	s		4	e
^{19}F	-62.9	s		12	g
	-80.8	s		6	h
	-106.5	s		4	i
	-123.5	s		4	j
^{13}C	135.1	s			d
	131.7	s			c
	131.5	s			a
	128.3	s			b
	122.3	q	$^1J_{CF}$ 289		g
	117.9	qt	$^1J_{CF}$ 289 $^2J_{CF}$ 34		j
	115.1	tt	$^1J_{CF}$ 270 $^2J_{CF}$ 33		h
	110.0	tsext	$^1J_{CF}$ 271 $^2J_{CF}$ 37		i
	61.8	sept	$^2J_{CF}$ 24		f
	32.8	s			e

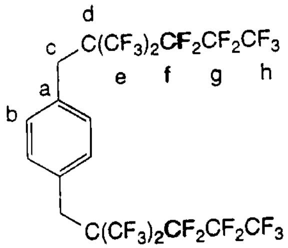
Spectrum No 11


i
h
C(CF3)2CF2CF2CF3
j k l m
c
d
b
a
e
CH2F
f
g

(14)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^1H	7.3	m		4	Ph
	5.35	d	$^1J_{HF}$ 48	2	g
	3.56	s		2	h
^{19}F	-62.7	s		6	j
	-80.5	s		3	m
	-106.3	s		2	k
	-123.3	s		2	l
	-208.8	t	$^1J_{HF}$ 47	2	g
^{13}C	136.5	d	$^2J_{CF}$ 17		a
	131.9	s			d
	131.5	s			c
	130.6	d	$^3J_{CF}$ 6		f
	128.6	d	$^4J_{CF}$ 1		e
	127.3	d	$^3J_{CF}$ 6		b
	122.1	q	$^1J_{CF}$ 290		j
	117.7	qt	$^1J_{CF}$ 285 $^2J_{CF}$ 34		m
	114.9	tt	$^1J_{CF}$ 270 $^2J_{CF}$ 33		k
	109.7	tsext	$^1J_{CF}$ 272 $^2J_{CF}$ 37		l
	84.2	d	$^1J_{CF}$ 167		g
	61.6	sept	$^2J_{CF}$ 24		i
	32.6	s			h

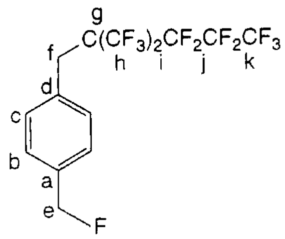
Spectrum No 12


d
c
C(CF3)2CF2CF2CF3
e f g h
a
b
C(CF3)2CF2CF2CF3

(15)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	7.26	s		4	b
	3.54	s		4	c
^{19}F	-62.8	s		12	e
	-80.7	s		6	h
	-106.3	s		4	f
	-123.3	s		4	g
^{13}C	131.4	s			b
	131.1	s			a
	122.1	q	$^{1}J_{CF}$ 290		e
	117.7	qt	$^{1}J_{CF}$ 289 $^{2}J_{CF}$ 33		h
	114.8	tt	$^{1}J_{CF}$ 270 $^{2}J_{CF}$ 33		f
	109.7	tsext	$^{1}J_{CF}$ 270 $^{2}J_{CF}$ 37		g
	61.6	sept	$^{2}J_{CF}$ 24		d
	32.3	s			c

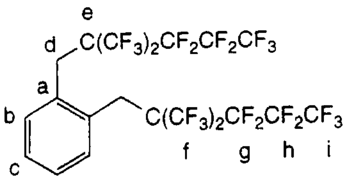
Spectrum No 13


g
f
C(CF3)2CF2CF2CF3
h i j k
d
c
b
a
e
F

(16)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	7.26	m		4	Ph
	5.30	d	$^{1}J_{HF}$ 47	2	e
	3.48	s		2	f
^{19}F	-62.7	s		6	h
	-80.4	s		3	k
	-106.4	s		2	i
	-123.4	s		2	j
	-209.4	t	$^{1}J_{HF}$ 46	2	e
^{13}C	136.2	d	$^{2}J_{CF}$ 17		a
	131.7	s			c
	131.3	s			d
	127.1	d	$^{3}J_{CF}$ 6		b
	121.9	q	$^{1}J_{CF}$ 285		h
	117.5	qt	$^{1}J_{CF}$ 289 $^{2}J_{CF}$ 33		k
	114.7	tt	$^{1}J_{CF}$ 270 $^{2}J_{CF}$ 33		i
	109.7	tsext	$^{1}J_{CF}$ 271 $^{2}J_{CF}$ 37		j
	83.9	d	$^{1}J_{CF}$ 167		e
	61.2	sept	$^{2}J_{CF}$ 21		g
	32.4	s			f

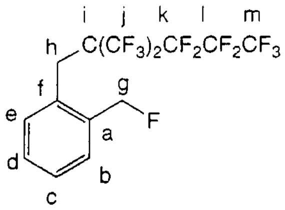
Spectrum No 14


e
d
C(CF3)2CF2CF2CF3
a
b
C(CF3)2CF2CF2CF3
c
f g h i

(17)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	7.37-7.28	m		4	b, c
	3.65	s		4	d
^{19}F	-61.7	s		12	f
	-80.4	s		6	i
	-107.6	s		4	g
	-123.0	s		4	h
^{13}C	131.2	s			b
	130.4	s			a
	127.1	s			c
	120.9	q			f
	116.5	qt	$^{1}J_{CF}$ 290		i
			$^{1}J_{CF}$ 289		
	113.9	tt	$^{2}J_{CF}$ 34		g
			$^{1}J_{CF}$ 270		
	108.4	tsext	$^{2}J_{CF}$ 33		h
			$^{1}J_{CF}$ 272		
	60.5	sept	$^{2}J_{CF}$ 38		e
	32.3	s	$^{2}J_{CF}$ 24		d

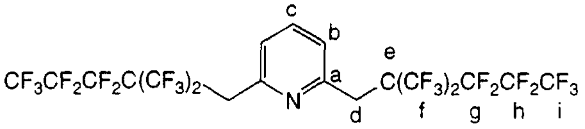
Spectrum No 15


i j k l m
h
C(CF3)2CF2CF2CF3
f
g
e
a
F
d
b
c

(18)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	7.4-7.3	m		4	Ph
	5.48	d	$^{1}J_{HF}$ 47	2	g
	3.75	s		2	h
^{19}F	-61.8	s		6	j
	-80.5	s		3	m
	-107.8	s		2	k
	-123.0	s		2	l
	-205.0	t	$^{1}J_{HF}$ 48	2	g
^{13}C	136.2	d	$^{2}J_{CF}$ 17		a
	132.0	m			e
	130.4	d	$^{3}J_{CF}$ 7		b
	130.1	s			f
	128.7	d	$^{5}J_{CF}$ 3		c
	128.3	d	$^{6}J_{CF}$ 1.5		d
	122.2	q	$^{1}J_{CF}$ 290		j
	117.7	qt	$^{1}J_{CF}$ 289		m
			$^{2}J_{CF}$ 34		
	115.1	tt	$^{1}J_{CF}$ 270		k
			$^{2}J_{CF}$ 33		
	109.7	tsext	$^{1}J_{CF}$ 272		l
			$^{2}J_{CF}$ 38		
	82.7	d	$^{1}J_{CF}$ 164		g
	62.0	sept	$^{2}J_{CF}$ 24		i
	28	s			h

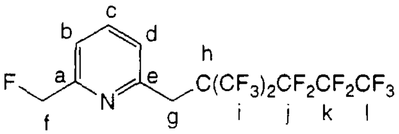
Spectrum No 16


c
b
a
e
N
d
f
g
h
i
$CF_3CF_2CF_2C(CF_3)_2$
$C(CF_3)_2CF_2CF_2CF_3$

(**19**)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	7.61	t	$^{3}J_{HH}$ 8	1	c
	7.22	d	$^{3}J_{HH}$ 8	2	b
	3.67	s		4	d
^{19}F	-62.9	s		12	f
	-80.7	s		6	i
	-106.4	s		4	g
	-123.4	s		4	h
^{13}C	151.6	s			a
	136.5	s			c
	124.6	s			b
	121.9	q	$^{1}J_{CF}$ 290		f
	117.5	qt	$^{1}J_{CF}$ 289 $^{2}J_{CF}$ 33		i
	114.7	tt	$^{1}J_{CF}$ 270 $^{2}J_{CF}$ 32		g
	109.5	tsext	$^{1}J_{CF}$ 272 $^{2}J_{CF}$ 38		h
	61.1	sept	$^{2}J_{CF}$ 24		e
	34.9	s			d

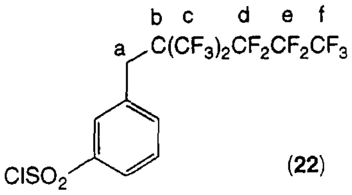
Spectrum No 17


c
b
d
a
e
h
F
N
f
g
i
j
k
l
$C(CF_3)_2CF_2CF_2CF_3$

(**20**)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	7.70	t	$^{3}J_{HH}$ 8	1	c
	7.40	d	$^{3}J_{HH}$ 8	1	d or b
	7.25	d	$^{3}J_{HH}$ 8	1	b or d
	5.43	d	$^{2}J_{HF}$ 46		f
^{19}F	-62.8	s		1	i
	-80.6	s		6	l
	-106.2	s		3	j
	-123.2	s		2	k
	-222.9	t	$^{2}J_{HF}$ 47	2	f
^{13}C	156.2	d	$^{2}J_{CF}$ 22		a
	151.3	s			e
	137.0	s			c
	124.7	s			d
	121.9	q	$^{1}J_{CF}$ 290		i
	119.3	d	$^{3}J_{CF}$ 5		b
	117.5	qt	$^{1}J_{CF}$ 289 $^{2}J_{CF}$ 33		l
	114.7	tt	$^{1}J_{CF}$ 270 $^{2}J_{CF}$ 32		j
	109.6	tsext	$^{1}J_{CF}$ 27 $^{2}J_{CF}$ 38		k
	84.1	d	$^{1}J_{CF}$ 169		h
	62.4	sept	$^{2}J_{CF}$ 24		f
	32.6	s			g

Spectrum No.18

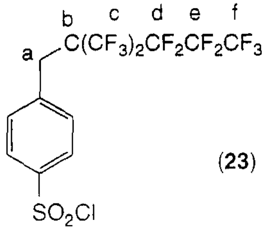


(22)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	7.92	br s		2	Ph
	7.80	d	$^{3}J_{HH}$ 7.6	1	Ph
	7.6	m		1	Ph
	3.8	br s		2	a
^{19}F	-62.5	s		1	c
	-80.5	s		2	f
	-106.5	s		3	d
	-123.1	s		2	e
^{13}C	142.3	s			
	135.2	s			
	132.1	s			
	132.0	s			
	128.7	s			
	126.2	s			
	128.5	s			
	126.5	s			
	121.9	q	$^{1}J_{CF}$ 290		
	61	m			
	31.6	br s			a

In the area between 125-115 ppm, the ^{13}C NMR spectrum showed small peaks overlapping due to the presence of CF_3 and CF_2 groups. The chemical shifts were not fully assigned due to a lack of sample to carry on experiments such as DEPT, COSY and NOE.

Spectrum No 19

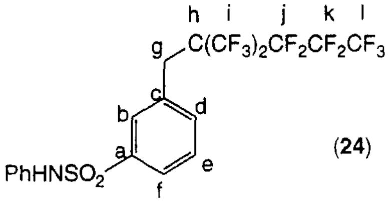


(23)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	8.01	d	$^{3}J_{HH}$ 8.8	2	Ph
	7.67	d	$^{3}J_{HH}$ 8.8	2	Ph
	3.9	s		2	a
^{19}F	-62.4	s		6	c
	-80.8	s		3	f
	-106.2	s		2	d
	-123.2	s		2	e
^{13}C	32.6	s			a

In the area between 145-115 ppm, the ^{13}C NMR spectrum showed small peaks overlapping due to the presence of CF_3 and CF_2 groups. The chemical shifts were not fully assigned due to a lack of sample to carry on experiments such as DEPT, COSY and NOE.

Spectrum No.20

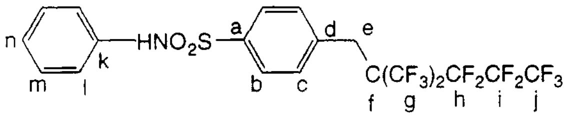


(**24**)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^1H	7.74	d	$^3J_{HH}$ 8.4	1	f
	7.73	s		1	b
	7.5	d		1	d
	7.46	t	$^3J_{HH}$ 7.9	1	e
	7.1	m		2	Ph
	7.0	m		3	Ph
	3.70	s		2	g
^{19}F	-62.2	s		6	i
	-80.5	s		3	l
	-105.6	s		2	j
	-122.8	s		2	k
^{13}C	141.6	s			
	139.8	s			
	137.1	s			
	135.6	s			
	132.1	s			
	129.8	s			
	128.5	s			
	126.5	s			
	124.2	s			
	120.7	s			
	32.7	s			g

In the area between 120-115 ppm, the ^{13}C NMR spectrum showed small peaks overlapping due to the presence of CF_3 and CF_2 groups. The chemical shifts were not fully assigned due to a lack of sample to carry on experiments such as DEPT, COSY.

Spectrum No 21

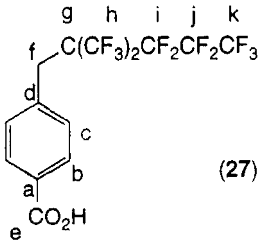


(25)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^1H	7.68	d	$^3J_{HH}$ 6.8	2	c
	7.44	d	$^3J_{HH}$ 8.4	2	b
	7.17	t	$^3J_{HH}$ 8	1	n
	7.0	m		3	m, l
	3.72	s		2	e
^{19}F	-63.3	s		6	g
	-81.5	s		3	j
	-106.6	s		2	h
	-123.7	s		2	i
^{13}C	140.8	s			
	138.7	s			
	137.6	s			
	133.4	s			
	130.0	s			
	128.0	s			
	126.0	s			
	123.1	q	$^1J_{CF}$ 290		g
	118.0	qt	$^1J_{CF}$ 285 $^2J_{CF}$ 34		j
	115.2	tt	$^1J_{CF}$ 270 $^2J_{CF}$ 33		h
	109.1	tsext	$^1J_{CF}$ 272 $^2J_{CF}$ 37		i
	62.5	m			f
	32.5	s			e

The chemical shifts were not fully assigned due to a lack of sample to carry on experiments such as DEPT, COSY.

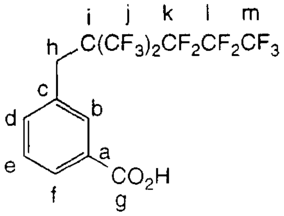
Spectrum No 22



(27)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	8.03	d	$^{3}J_{HH}$ 8.4	2	c
	7.56	d	$^{3}J_{HH}$ 7.9	2	b
	3.86	s		2	f
^{19}F	-62.2	s		6	h
	-80.5	s		3	k
	-105.6	s		2	i
	-122.8	s		2	j
^{13}C	167.0	s			e
	136.9	s			a
	132.7	s			c
	131.3	s			d
	130.1				b
	121.9	q	$^{1}J_{CF}$ 290		h
	117.5	qt	$^{1}J_{CF}$ 289 $^{2}J_{CF}$ 33		k
	114.7	tt	$^{1}J_{CF}$ 270 $^{2}J_{CF}$ 25		i
	109.6	tsext	$^{1}J_{CF}$ 272 $^{2}J_{CF}$ 38		j
	62.4	sept	$^{2}J_{CF}$ 24		g
	32.7	s			f

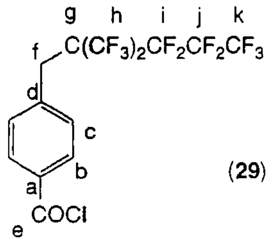
Spectrum No 23



(28)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	8.07	s		1	b
	8.00	dd	$^{3}J_{HH}$ 7.9 $^{4}J_{HH}$ 1.2	1	f
	7.60	d	$^{3}J_{HH}$ 8	1	d
	7.50	t	$^{3}J_{HH}$ 7.6	1	e
	3.84	s		2	h
^{19}F	-62.3	s		6	j
	-80.4	s		3	m
	-105.8	s		2	k
	-122.7	s		2	l
^{13}C	167	s			g
	136.8	s			a
	133.7	s			b
	132.3	s			c
	131.5	s			f
	130.2	s			d
	129.2	s			e
	122.9	q	$^{1}J_{CF}$ 290		j
	118.4	qt	$^{1}J_{CF}$ 289 $^{2}J_{CF}$ 33		m
	115.7	tt	$^{1}J_{CF}$ 270 $^{2}J_{CF}$ 24		k
	110.4	tsext	$^{1}J_{CF}$ 272 $^{2}J_{CF}$ 37		l
	62.6	sept	$^{2}J_{CF}$ 24		i
	32.1	s			h

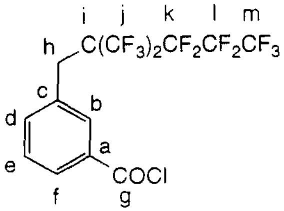
Spectrum No 24



(29)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	8.7	d	$^{3}J_{HH}$ 7.9	2	c
	8.15	d	$^{3}J_{HH}$ 8.3	2	b
	3.93	s		2	f
^{19}F	-62.6	s		6	h
	-80.8	s		3	k
	-106.2	s		2	i
	-123.2	s		2	j
^{13}C	168.2	s			e
	140.5	s			a
	133.6	s			c
	131.8	s			d
	130.2				b
	123.1	q	$^{1}J_{CF}$ 290		h
	118.0	qt	$^{1}J_{CF}$ 285 $^{2}J_{CF}$ 34		k
	115.2	tt	$^{1}J_{CF}$ 270 $^{2}J_{CF}$ 33		i
	109.1	tsext	$^{1}J_{CF}$ 272 $^{2}J_{CF}$ 37		j
	62.5	sept	$^{2}J_{CF}$ 24		g
	32.8	s			f

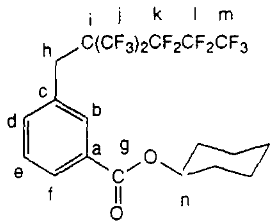
Spectrum No 25



(30)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	8.2	br s		1	b
	8.16	dd	$^{3}J_{HH}$ 7.9 $^{4}J_{HH}$ 1.2	1	f
	7.8	br d	$^{3}J_{HH}$ 7.6	1	d
	7.69	t	$^{3}J_{HH}$ 7.9	1	e
	3.84	s		2	h
^{19}F	-62.6	s		6	j
	-80.4	s		3	m
	-106.3	s		2	k
	-123.3	s		2	l
^{13}C	168.3	s			g
	139.9	s			a
	137.0	s			b
	133.7	s			c
	132.0	s			f
	130.2	s			d
	129.3	s			e
	123.1	q	$^{1}J_{CF}$ 290		j
	118.0	qt	$^{1}J_{CF}$ 285 $^{2}J_{CF}$ 34		m
	115.2	tt	$^{1}J_{CF}$ 270 $^{2}J_{CF}$ 33		k
	109.1	tsext	$^{1}J_{CF}$ 272 $^{2}J_{CF}$ 37		l
	62.5	sept	$^{2}J_{CF}$ 24		i
	32.8	s			h

Spectrum No 26



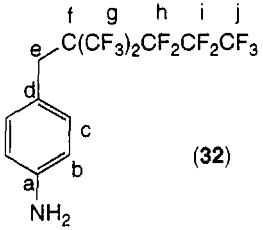
(**31**)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^1H	8.02	s		1	b
	7.97	d	$^3J_{HH}$ 6.4		f
	7.58	d	$^3J_{HH}$ 7	1	d
	7.46	t	$^3J_{HH}$ 7.9	1	e
	3.74	s		2	h
^{19}F	-62.8	s		6	j
	-80.8	s		3	m
	-106.2	s		2	k
	-123.2	s		2	l
^{13}C	166.0	s			g
	137.0	s			a
	133.5	s			b
	132.5	s			c
	132.1	s			f
	130.0	s			d
	129.5	s			e
	123.1	q	$^1J_{CF}$ 290		j
	118.0	qt	$^1J_{CF}$ 285 $^2J_{CF}$ 34		m
	115.2	tt	$^1J_{CF}$ 270 $^2J_{CF}$ 33		k
	109.1	tsext	$^1J_{CF}$ 272 $^2J_{CF}$ 37		l
	61.3	sept	$^2J_{CF}$ 24		i
	31.9	s			h

For the cyclohexanyl of compound (**31**)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^1H	1.2-1.9	m		5	cyclohexan
	4.98	m		1	n
^{13}C	74.0	s			cyclohexan
	34.1	s			cyclohexan
	32.9	s			cyclohexan
	32.1	s			cyclohexan
	26.2	s			cyclohexan
	24.2	s			cyclohexan

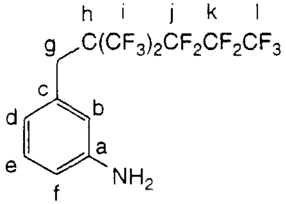
Spectrum No 27



(**32**)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	7.03	d	$^{3}J_{HH}$ 7.9	2	c
	6.63	d	$^{3}J_{HH}$ 8.4	2	b
	3.56	s		2	e
^{19}F	-62.7	s		6	g
	-80.9	s		3	j
	-106.3	s		2	h
	-123.2	s		2	i
^{13}C	152.7	s			a
	149.2	s			c
	133.1	s			d
	114.7	s			b
	123.1	q	$^{1}J_{CF}$ 291		g
	118.6	qt	$^{1}J_{CF}$ 289 $^{2}J_{CF}$ 33		j
	115.9	tt	$^{1}J_{CF}$ 270 $^{2}J_{CF}$ 25		h
	110.4	tsext	$^{1}J_{CF}$ 272 $^{2}J_{CF}$ 38		i
	62	m			f
	32.8	s			e

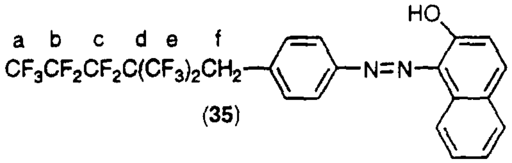
Spectrum No 28



(**33**)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	7.02	t	$^{3}J_{HH}$ 7.9	1	e
	6.69	br s		1	b
	6.66	d	$^{3}J_{HH}$ 7.6	1	f
	6.57	d	$^{3}J_{HH}$ 7.2	1	d
	3.70	t		1	g
^{19}F	-62.3	s		6	i
	-80.7	s		3	l
	-107.7	s		2	j
	-123.2	s		2	k
^{13}C	152.9	s			a
	149.2	s			b
	132.2	s			c
	129.6	s			f
	120.1	s			d
	114.9	s			e
	123.0	q	$^{1}J_{CF}$ 290		i
	118.0	qt	$^{1}J_{CF}$ 285 $^{2}J_{CF}$ 34		l
	115.2	tt	$^{1}J_{CF}$ 270 $^{2}J_{CF}$ 33		j
	109.1	tsext	$^{1}J_{CF}$ 272 $^{2}J_{CF}$ 37		k
	62.5	sept	$^{2}J_{CF}$ 24		h
	33.3	s			g

Spectrum No 29

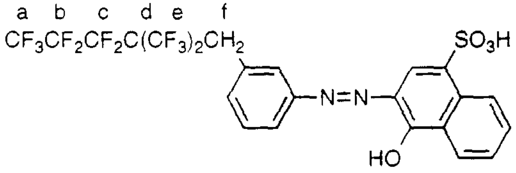


(35)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	8.6-6.6	m		10	aromatic
	3.8	s		2	f
^{19}F	-62.6	s		6	e
	-80.8	s		3	a
	-106.2	s		2	c
	-123.2	s		2	b
^{13}C	31.7	s			f

Problems have been encountered to assign the chemical shifts from the ^{1}H and ^{13}C NMR due to the low solubility of these azo-dyes in organic solvents.

Spectrum No 30

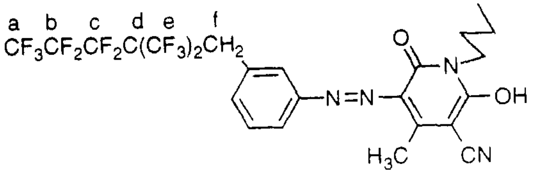


(36)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	8.6-7	m		9	aromatic
	3.8	s		2	f
^{19}F	-62.6	s		6	e
	-80.7	s		3	a
	-106.3	s		2	c
	-123.0	s		2	b
^{13}C	29.7	s			f

Problems have been encountered to assign the chemical shifts from the ^{1}H and ^{13}C NMR due to the low solubility of these azo-dyes in organic solvents.

Spectrum No 31

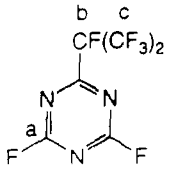

a b c d e f
$CF_3CF_2CF_2C(CF_3)_2CH_2$
O
N
N=N
OH
H_3C
CN

(37)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{19}F	-62.6	s		6	e
	-80.8	s		3	a
	-106.2	s		2	c
	-123.2	s		2	b

Problems have been encountered to assign the chemical shifts from the ^1H and ^{13}C NMR due to the low solubility of these azo-dyes in organic solvents.

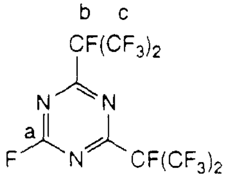
Spectrum No 32


b c
$CF(CF_3)_2$
N
N
a
F
N
F

(41)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{19}F	-30.4	s		2	a
	-74.4	d	$^3J_{FF}$ 7.5	6	c
	-188.8	sept	$^3J_{FF}$ 7.5	1	b

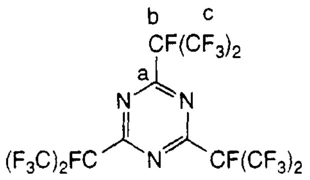
Spectrum No 33


b c
$CF(CF_3)_2$
N
N
a
F
N
$CF(CF_3)_2$

(42)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{19}F	-30.0	s		1	a
	-75.7	d	$^3J_{FF}$ 7.5	12	c
	-186.4	sept	$^3J_{FF}$ 7.5	2	b

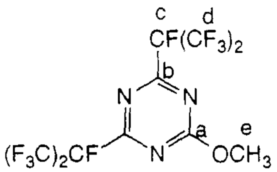
Spectrum No 34


b
c
CF(CF3)2
a
N
N
(F3C)2FC
N
CF(CF3)2

(43)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{19}F	-73.7	d	$^3J_{FF}$ 7.5	18	c
	-186.4	sept	$^3J_{FF}$ 7.5	3	b
^{13}C	88.8	dsept	$^1J_{CF}$ 215 $^2J_{CF}$ 33		b
	118.3	qd	$^1J_{CF}$ 286 $^2J_{CF}$ 26		c
	166.6	d	$^2J_{CF}$ 22		a

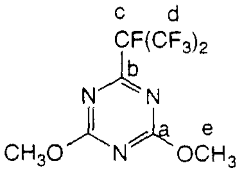
Spectrum No 35


c
d
CF(CF3)2
b
N
N
a
e
(F3C)2CF
N
OCH3

(44)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^1H	4.26	s		3	e
^{19}F	-74.4	d	$^3J_{FF}$ 7.5	12	d
	-184.8	sept	$^3J_{FF}$ 7.5	2	c
^{13}C	171.4	t	$^4J_{CF}$ 3		a
	168.1	dd	$^2J_{CF}$ 22 $^4J_{CF}$ 3		b
	119.5	qd	$^1J_{CF}$ 289 $^2J_{CF}$ 27		d
	89.2	dsept	$^1J_{CF}$ 215		c
			$^2J_{CF}$ 33		c
	57.3	s			e

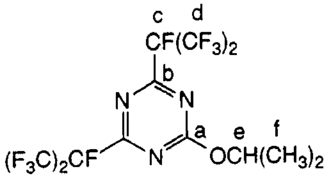
Spectrum No 36


c
d
CF(CF3)2
b
N
N
a
e
CH3O
N
OCH3

(45)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^1H	4.12	s		6	e
^{19}F	-74.4	d	$^3J_{FF}$ 7.5	6	d
	-184.8	sept	$^3J_{FF}$ 7.5	1	c

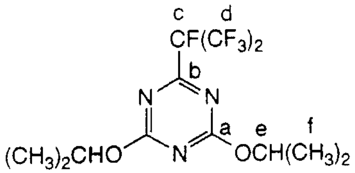
Spectrum No 37


c
d
CF(CF$_3$)$_2$
b
N
N
a
e
f
(F$_3$C)$_2$CF
N
OCH(CH$_3$)$_2$

(46)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	5.47	sep	$^3J_{HH}$ 6	1	e
	1.50	d	$^3J_{HH}$ 6	6	f
^{19}F	-74.4	d	$^3J_{FF}$ 7.5	12	d
	-184.8	sept	$^3J_{FF}$ 7.5	2	c
^{13}C	170.3	s			a
	168	d	$^2J_{CF}$ 22		b
	119.5	qd	$^1J_{CF}$ 287 $^2J_{CF}$ 26		d
	89.2	dsept	$^1J_{CF}$ 215 $^2J_{CF}$ 33		c
	78	s			e
	21.2	s			f

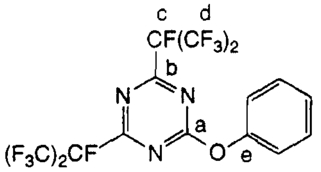
Spectrum No 38


c
d
CF(CF$_3$)$_2$
b
N
N
a
e
f
(CH$_3$)$_2$CHO
N
OCH(CH$_3$)$_2$

(47)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	5.30	sept	$^3J_{HH}$ 6	2	e
	1.35	d	$^3J_{HH}$ 6	12	f
^{19}F	-74.3	d	$^3J_{FF}$ 7.5	6	d
	-184.7	sept	$^3J_{FF}$ 7.5	1	c
^{13}C	171.6	d	$^4J_{CF}$ 3		b
	167.8	d	$^2J_{CF}$ 22		a
	119.5	qd	$^1J_{CF}$ 275 $^2J_{CF}$ 26		d
	89.2	dsept	$^1J_{CF}$ 215 $^2J_{CF}$ 33		c
	73.5	s			e
	21.2	s			f

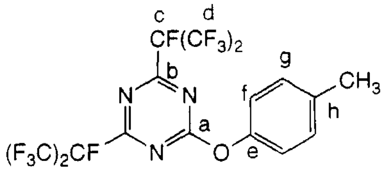
Spectrum No 39



(48A)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	7.4	br		2	Ph
	7.3	br		1	Ph
	7.1	br		2	Ph
^{19}F	-74.4	d	$^{3}J_{FF}$ 7.5	12	d
	-184.8	sept	$^{3}J_{FF}$ 7.5	2	c
^{13}C	170.1	s			a
	167.6	d	$^{2}J_{CF}$ 22		b
	149.8	s			Ph
	128.9	s			Ph
	126.2	s			Ph
	119.6	s			e
	117.2	qd	$^{1}J_{CF}$ 275 $^{2}J_{CF}$ 26		d

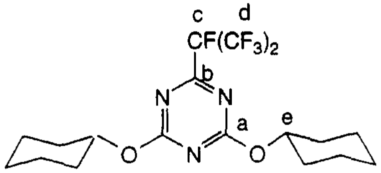
Spectrum No 40



(48B)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	7.4-7.2	m		4	Ph
	2.38	s		3	CH_3
^{19}F	-74.5	d	$^{3}J_{FF}$ 7.5	12	d
	-184.5	sept	$^{3}J_{FF}$ 7.5	2	c
^{13}C	172.7	s			a
	168.1	d	$^{2}J_{CF}$ 25		b
	150.1	s			e
	137.5	s			h
	131.0	s			f or g
	121.0	s			f or g
	119.5	qd	$^{1}J_{CF}$ 287 $^{2}J_{CF}$ 26		d
	89.2	dsept	$^{1}J_{CF}$ 215 $^{2}J_{CF}$ 33		c
	20.8	s			CH_3

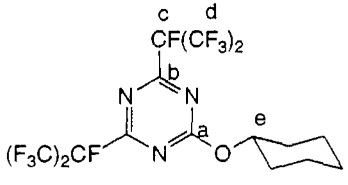
Spectrum No 41



(51)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	5.1	m		1	e
	2.0-1.2	m		10	cyclohexan.
^{19}F	-73.8	d	$^{3}J_{FF}$ 7.5	6	d
	-184.2	sept	$^{3}J_{FF}$ 7.5	1	c
^{13}C	171.5	s			a
	167.7	d	$^{2}J_{CF}$ 23		b
	120.9	m			d
	90.1	m			c
	78.2	s			e
	31.1	s			cyclohexan
	25.1	s			cyclohexan
	23.5	s			cyclohexan

Spectrum No 42

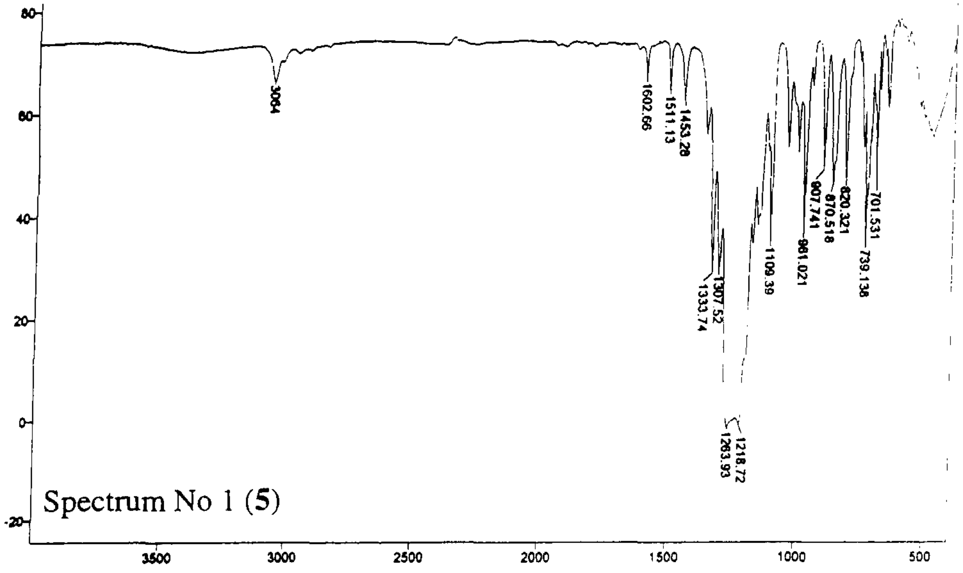


(52)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling constant (Hz)	Integral	Assignment
^{1}H	5.30	m		1	e
	1.2-1.8	m			cyclohexan.
	0.8	m			cyclohexan.
^{19}F	-74.6	d	$^{3}J_{HH}$ 6	12	d
	-184.6	sept	$^{3}J_{HH}$ 6	2	c
^{13}C	171.7	s			a
	167.8	d	$^{2}J_{CF}$ 22		b
	120.6	qd	$^{2}J_{CF}$ 22 $^{1}J_{CF}$ 287		d
	90.1	dsept	$^{2}J_{CF}$ 26 $^{1}J_{CF}$ 215		c
	81.0	s			e
	32.3	s			cyclohexan.
	31.4	s			cyclohexan.
	25.7	s			cyclohexan.
	24.0	s			cyclohexan.
	23.3	s			cyclohexan.

Appendix Two
Infra Red spectra

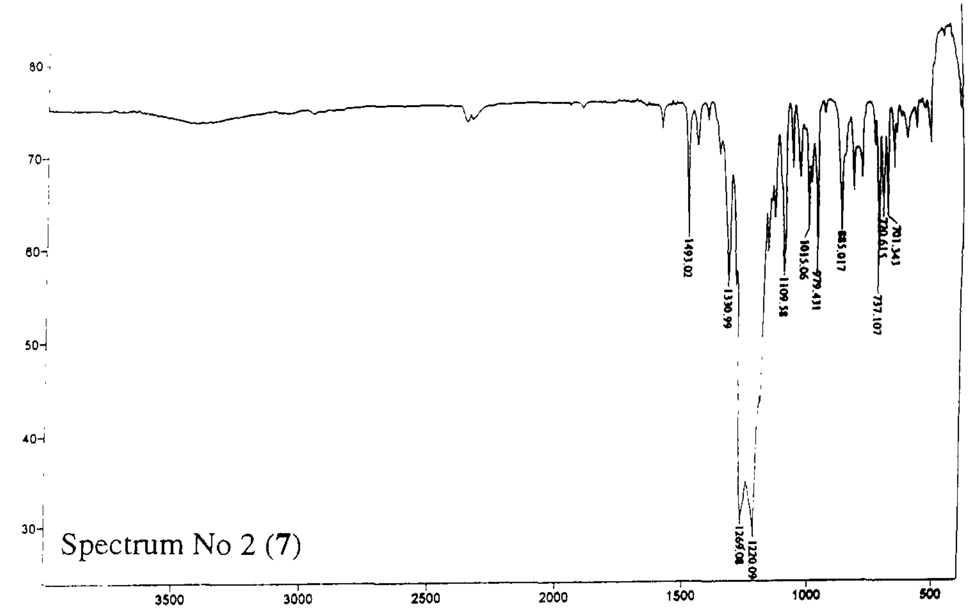
1. 2-[(Perfluoro-2-methylpentan-2-yl)methyl]naphthalene (**5**)
2. 1-Bromo-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**7**)
3. 1-Bromo-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**8**)
4. 1-Bromo-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**9**)
5. 1-Nitro-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**10**)
6. 1-Nitro-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**11**)
7. 1,3-Xylylene-bis(perfluoro-2-methylpentan-2-yl) (**12**)
8. 1-Fluoromethyl-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**14**)
9. 1,4-Xylylene-bis(perfluoro-2-methylpentan-2-yl) (**15**)
10. 1-Fluoromethyl-4-[(perfluoro-2-methylpentan-2-ylmethyl]benzene (**16**)
11. 1,2-Xylylene-bis(perfluoro-2-methylpentan-2-yl) (**17**)
12. 1-Fluoromethyl-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**18**)
13. 2,6-Bis[(perfluoro-2-methylpentan-2-yl)methyl]pyridine (**19**)
14. 2-Fluoromethyl-6-[(perfluoro-2-methylpentan-2-yl)methyl]pyridine (**20**)
15. 4-[(Perfluoro-2-methylpentan-2-yl)methyl]benzenesulphonyl chloride (**23**)
16. 4-([Perfluoro-2-methylpentan-2-yl)methyl]benzoic acid (**27**)
17. 3-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoic acid (**28**)
18. 4-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoyl chloride (**29**)
19. 3-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoyl chloride (**30**)
20. Cyclohexyl 3-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoate (**31**)
21. 1-Amino-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**32**)
22. 1-Amino-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**33**)
23. Azo-dye (**35**)
24. Azo-dye (**36**)
25. Azo-dye (**37**)
26. 2-Methoxy-4,6-perfluorodi-isopropyl-s-triazine (**44**)
27. 2,4-Dimethoxy-6-perfluoroisopropyl-s-triazine (**45**)
28. 2-Isopropoxy-4,6-perfluorodi-isopropyl-s-triazine (**46**)
29. 2,4-Di-isopropoxy-6-perfluoroisopropyl-s-triazine (**47**)
30. 2-Phenoxy-4,6-perfluorodi-isopropyl-s-triazine (**48A**)
31. 2-(p-Cresoxy)-4,6-perfluorodi-isopropyl-s-triazine (**48B**)
32. 2,4-Dicyclohexanoxy-6-perfluoroisopropyl-s-triazine (**51**)
33. 2-Cyclohexanoxy-4,6-perfluorodi-isopropyl-s-triazine (**52**)



Spectrum No 1 (**5**)

Number of Scans= 8 Apodization= Strong

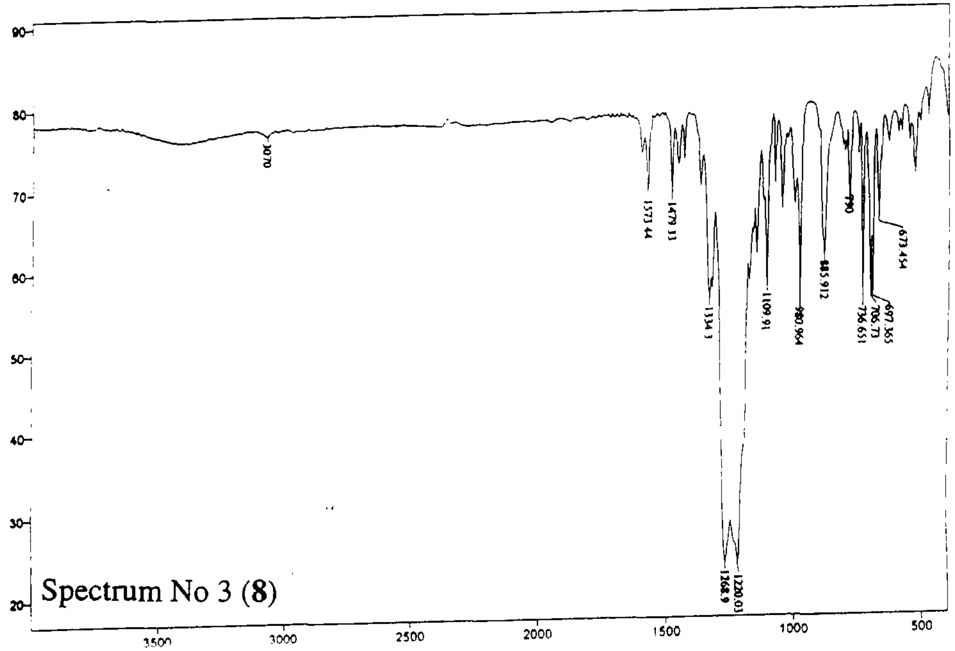
13/03/96 15:06 Res=4 cm-1



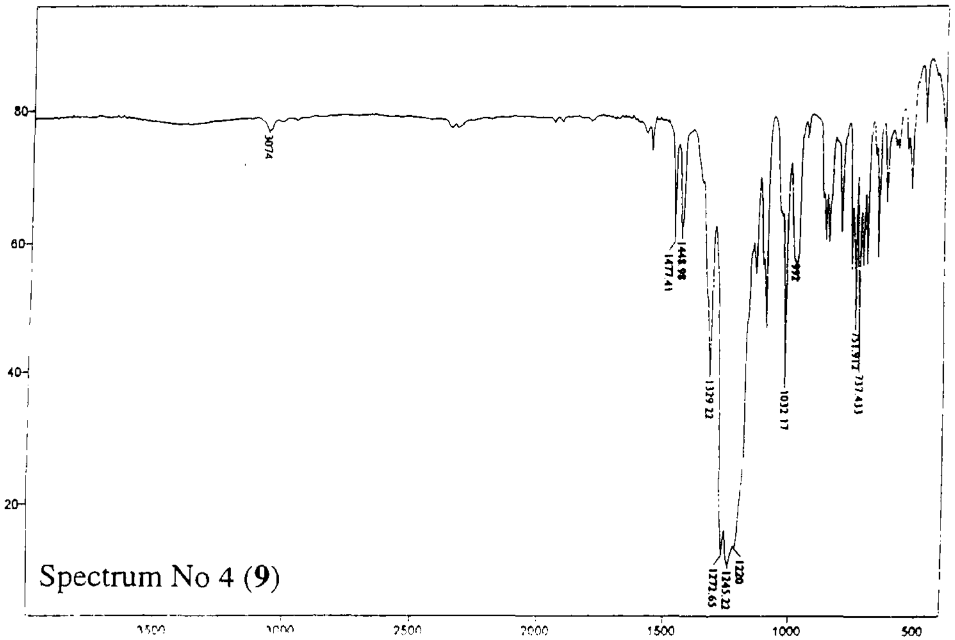
Spectrum No 2 (**7**)

Number of Scans= 4 Apodization= Strong

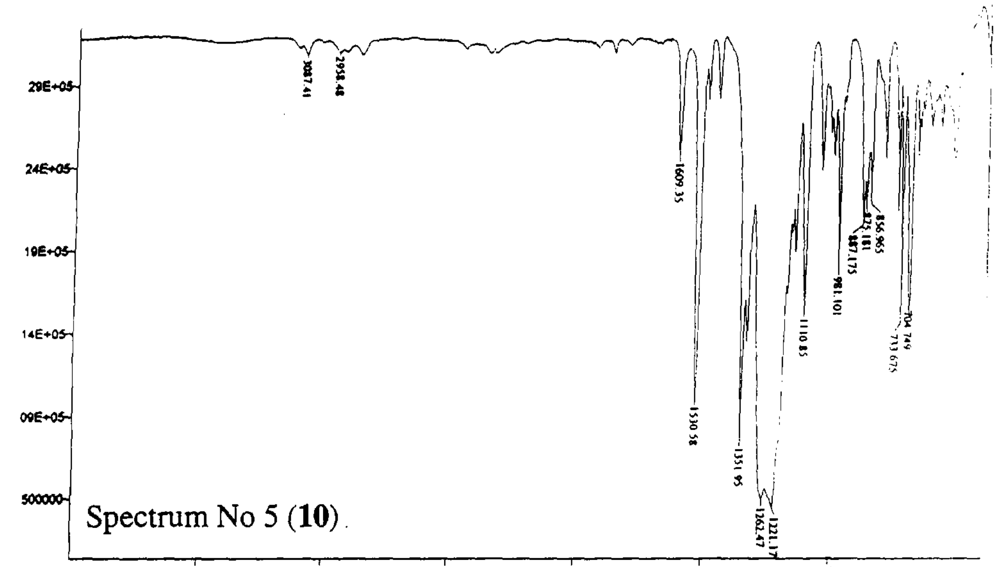
01/05/96 15:11 Res=4 cm-1



Spectrum No 3 (**8**)



Spectrum No 4 (**9**)

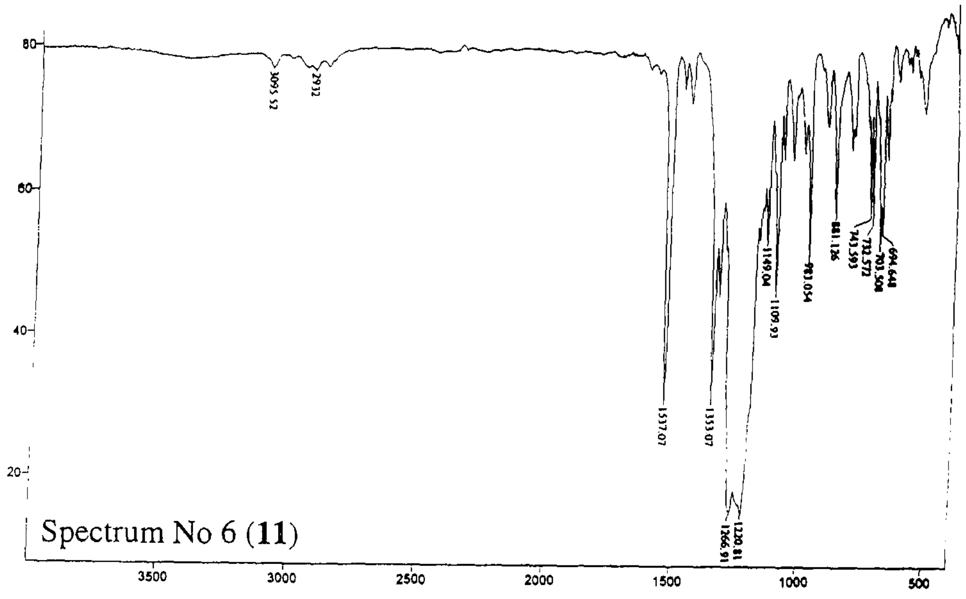


Spectrum No 5 (**10**)

ansmittance / Wavenumber (cm-1)

Number of Scans= 4 Apodization= Strong

22/11/96 13:51 Res=4 cm-1

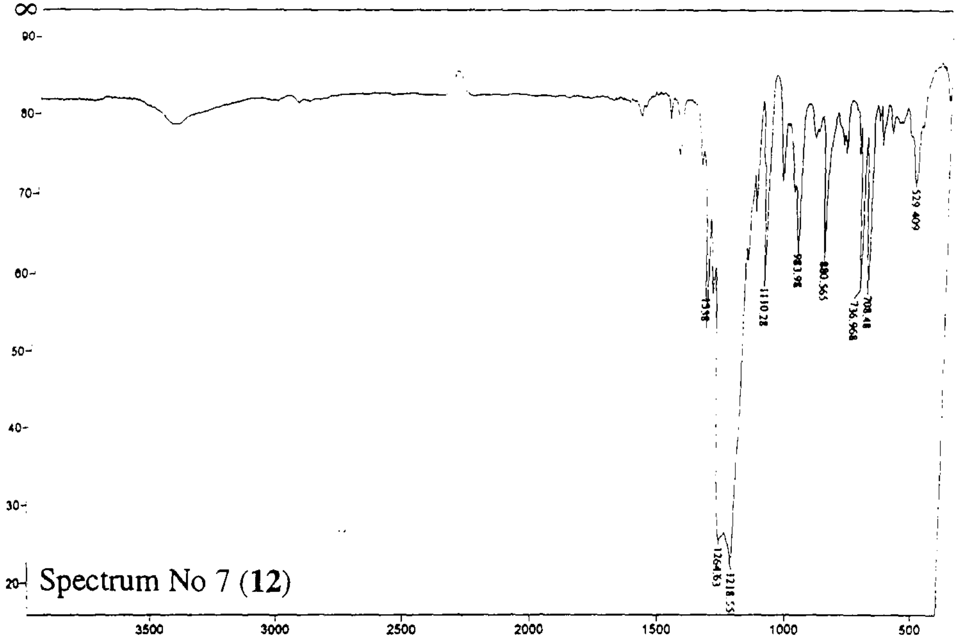


Spectrum No 6 (**11**)

ansmittance / Wavenumber (cm-1)

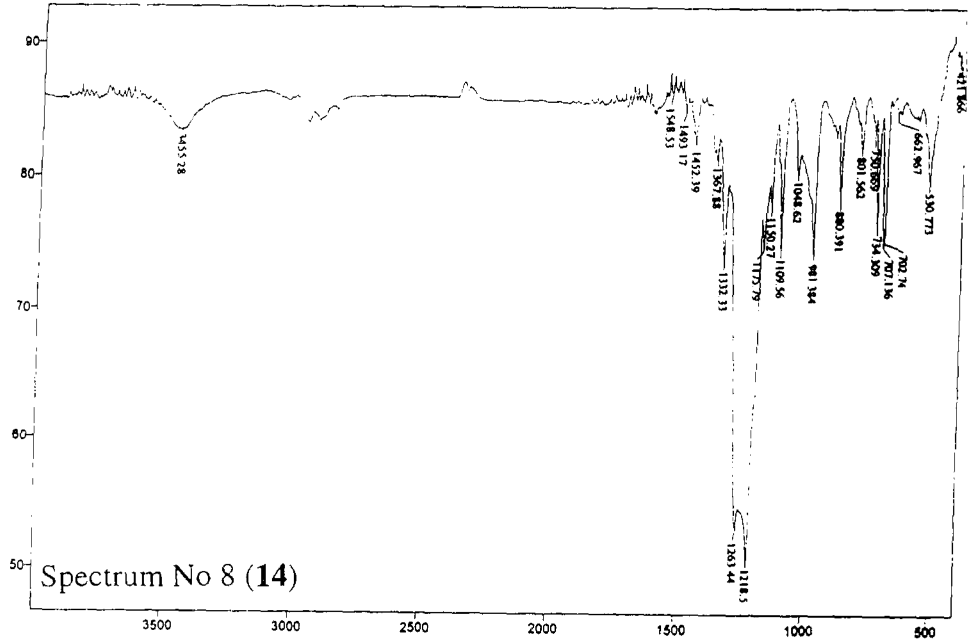
Number of Scans= 4 Apodization= Strong

22/11/96 14:05 Res=4 cm-1

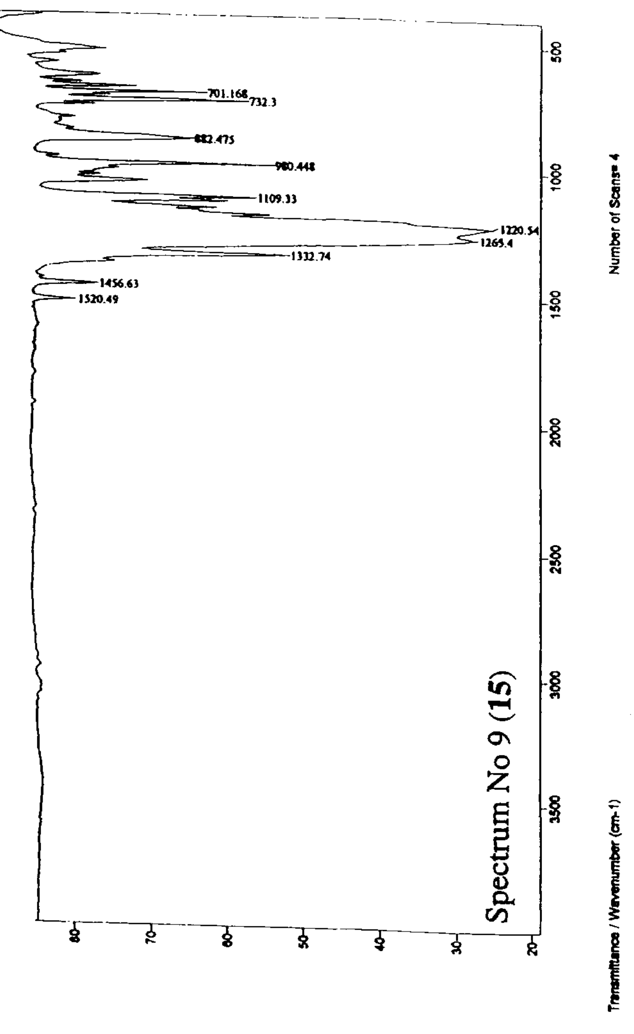


Spectrum No 7 (**12**)

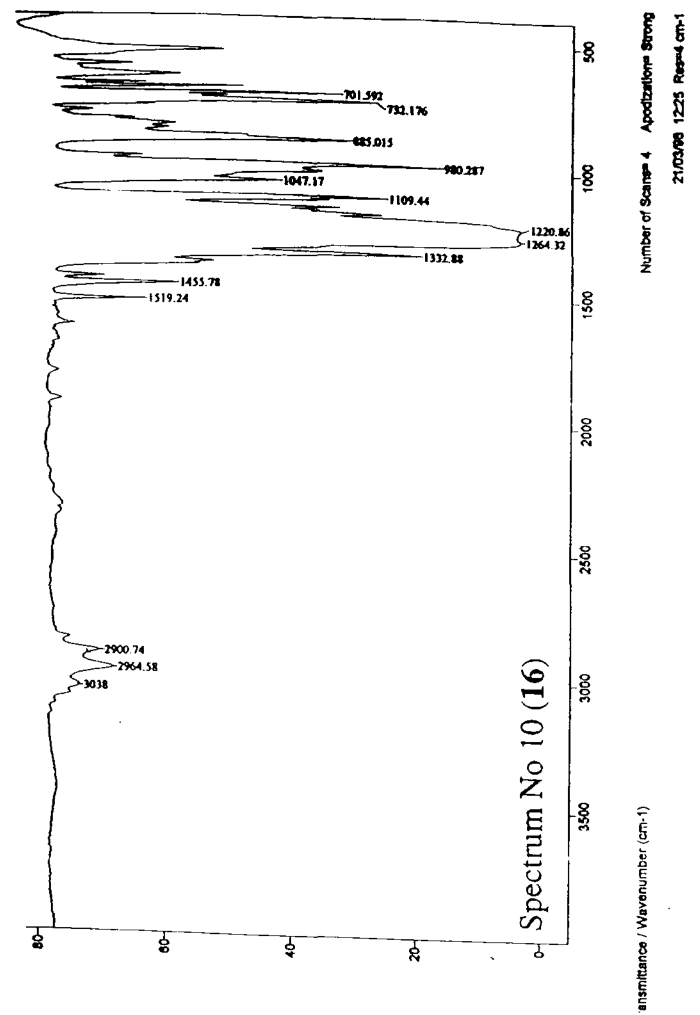
Number of Scans= 4 Apodization= Strong



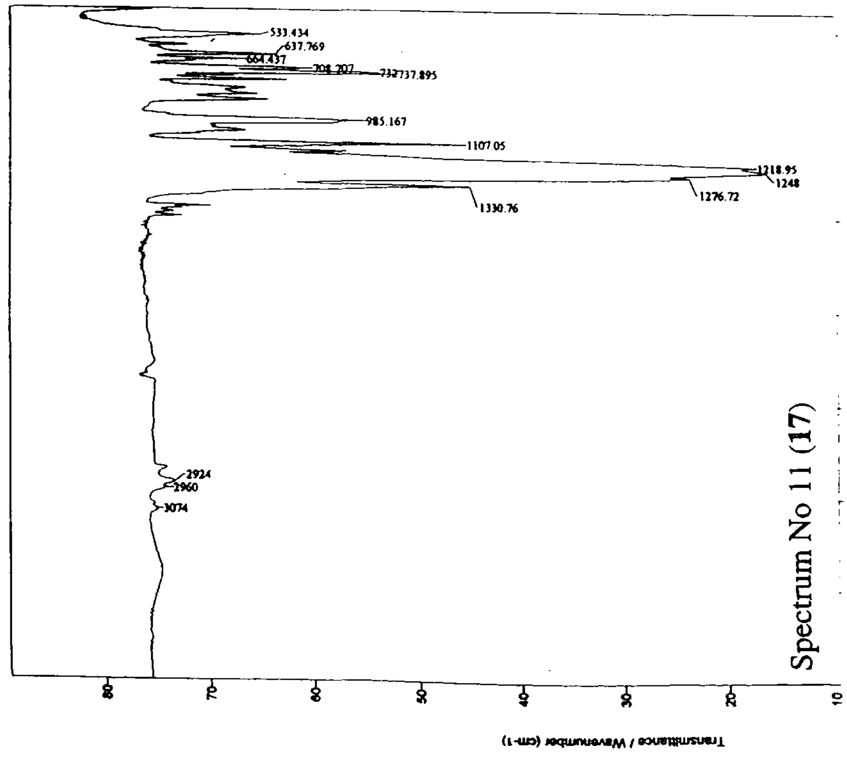
Spectrum No 8 (**14**)



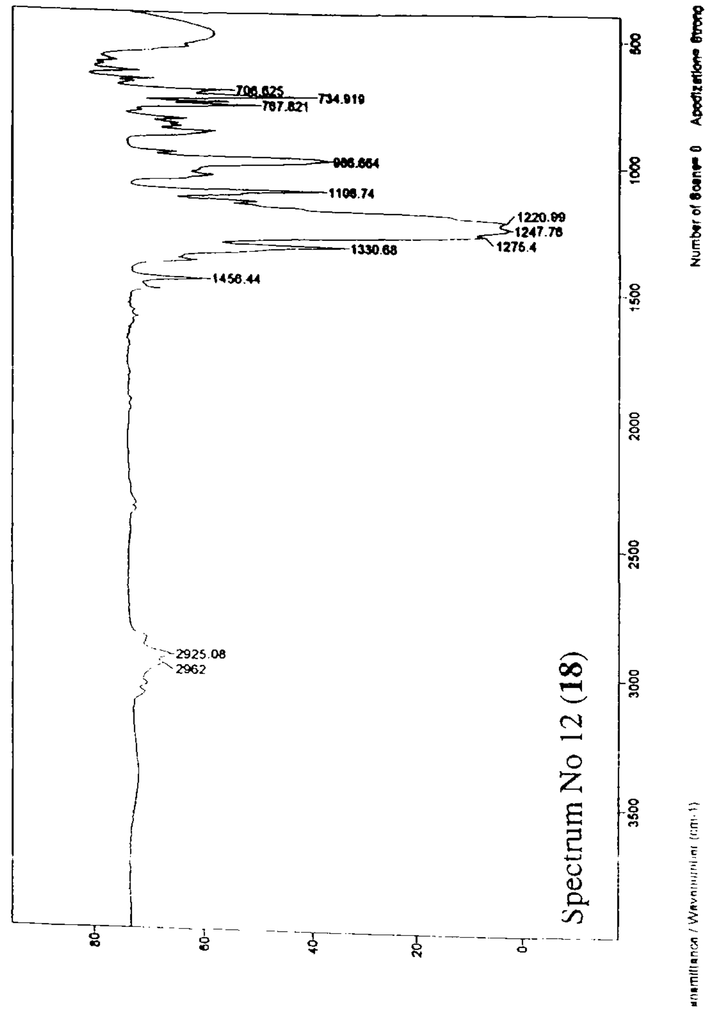
Spectrum No 9 (**15**)



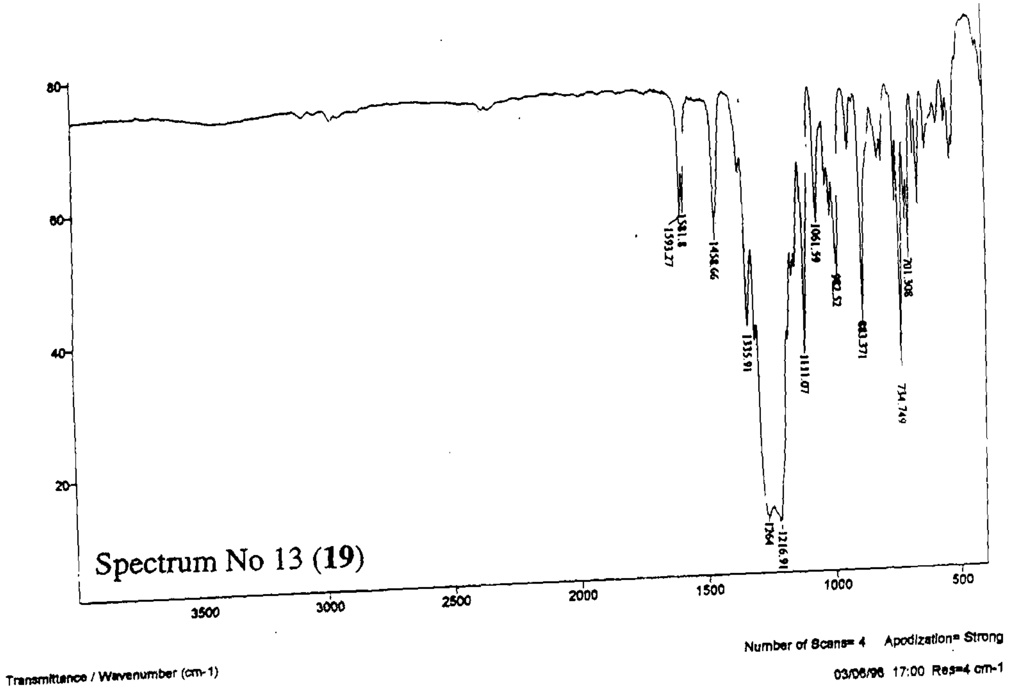
Spectrum No 10 (**16**)



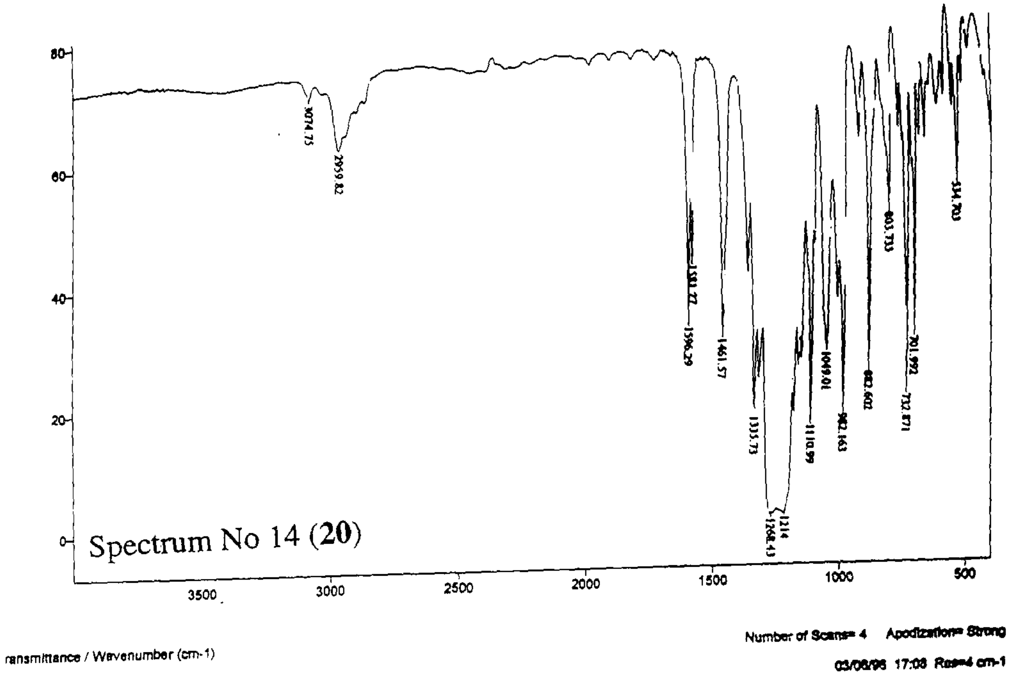
Spectrum No 11 (**17**)



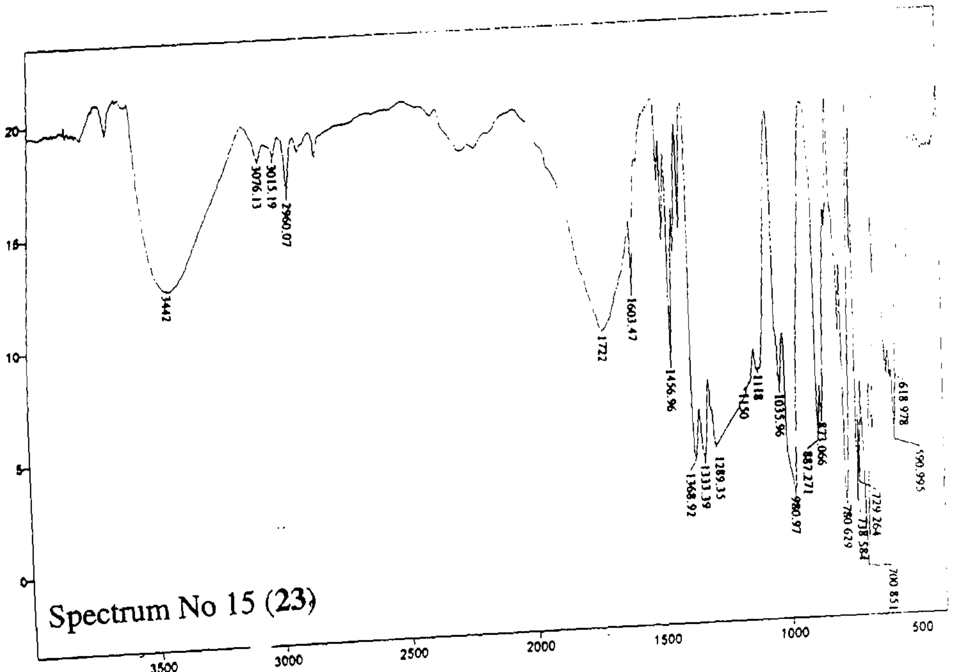
Spectrum No 12 (**18**)



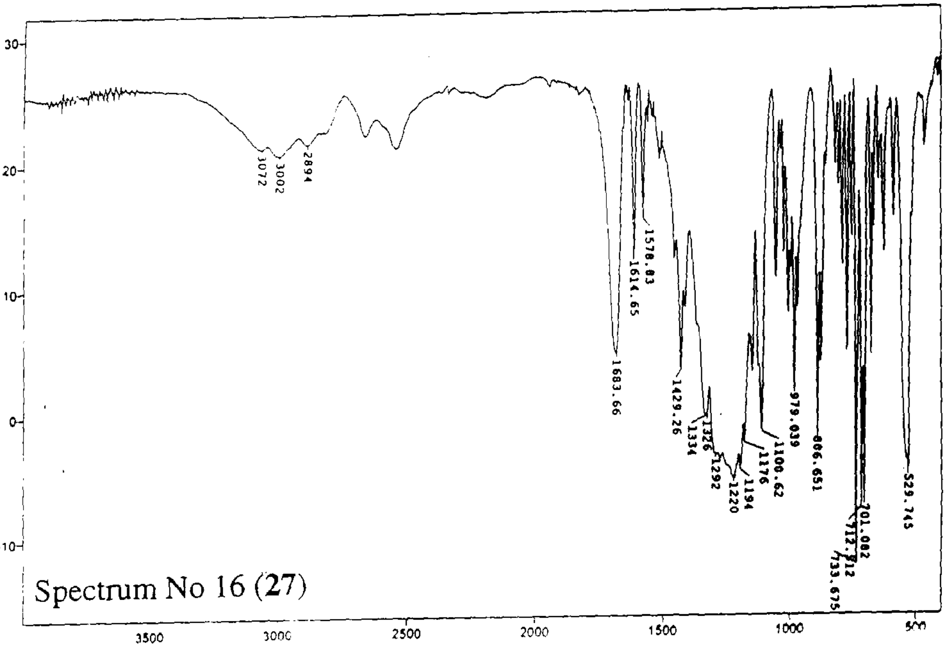
Spectrum No 13 (**19**)



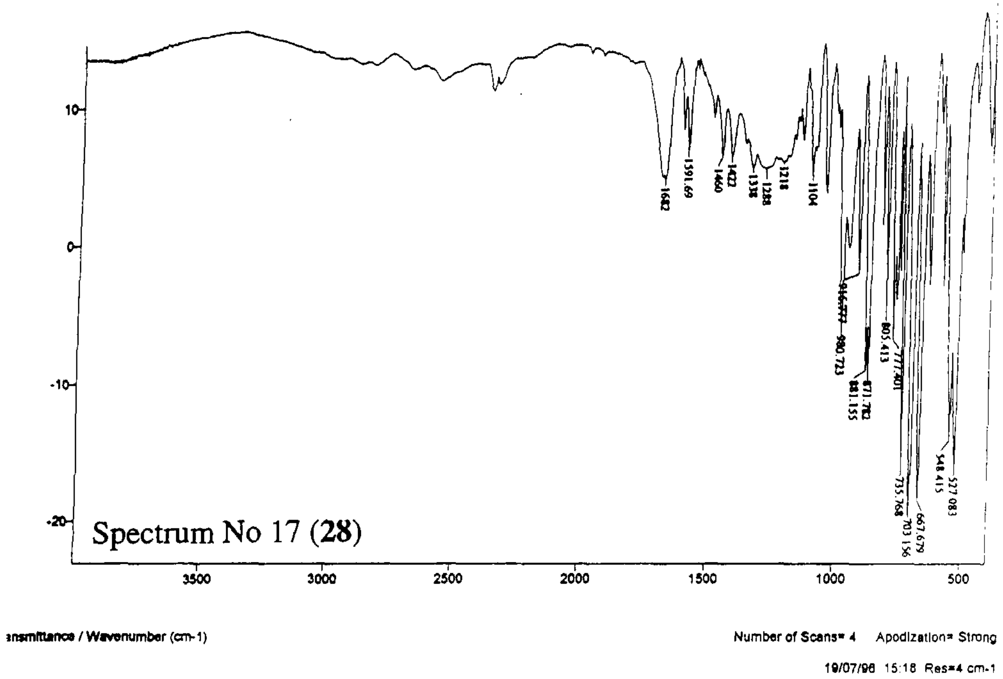
Spectrum No 14 (**20**)

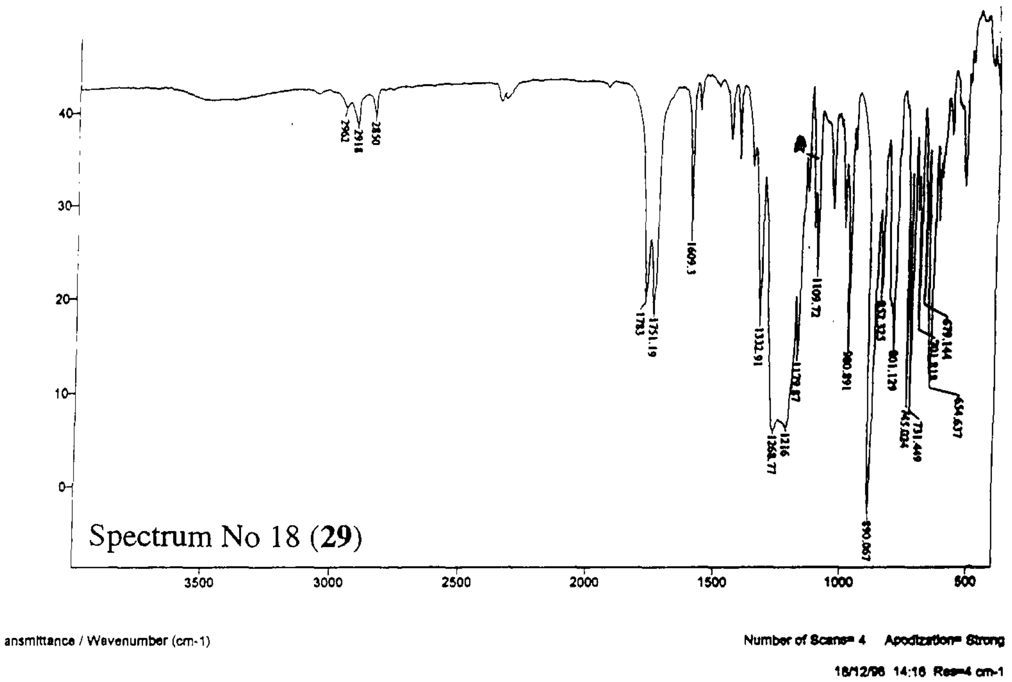


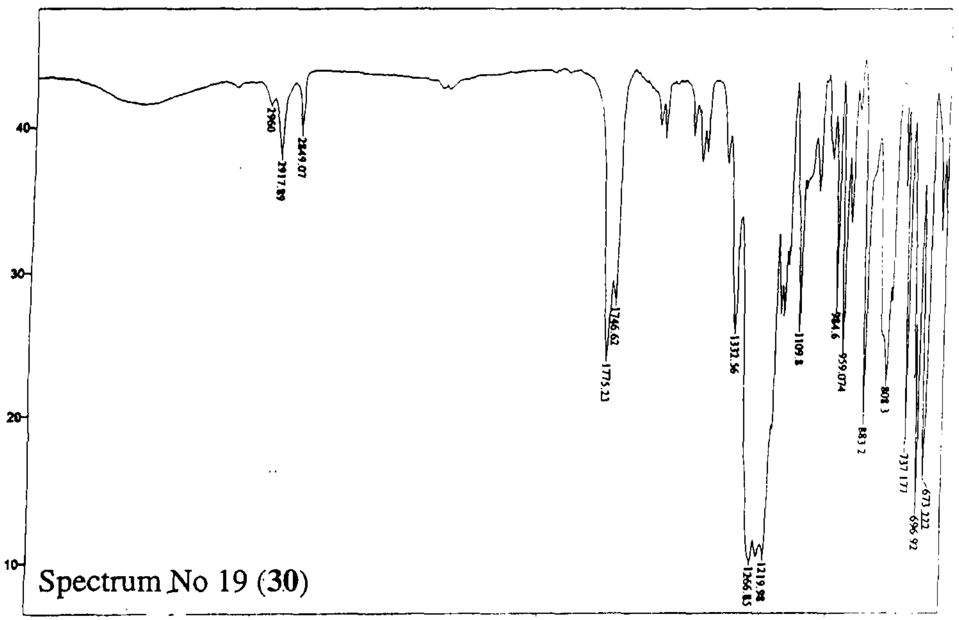
Spectrum No 15 (**23**)

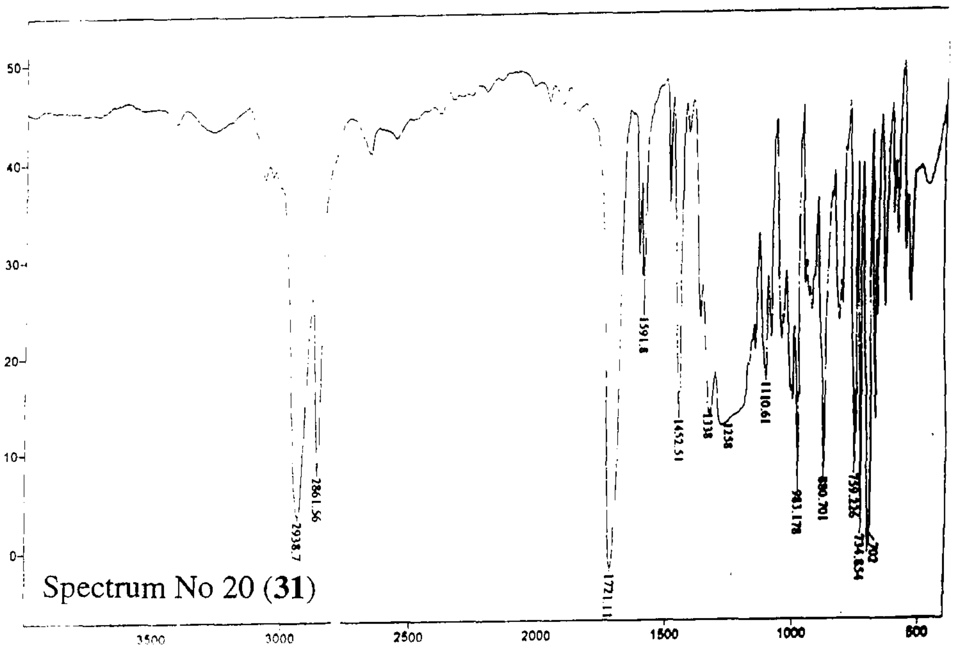


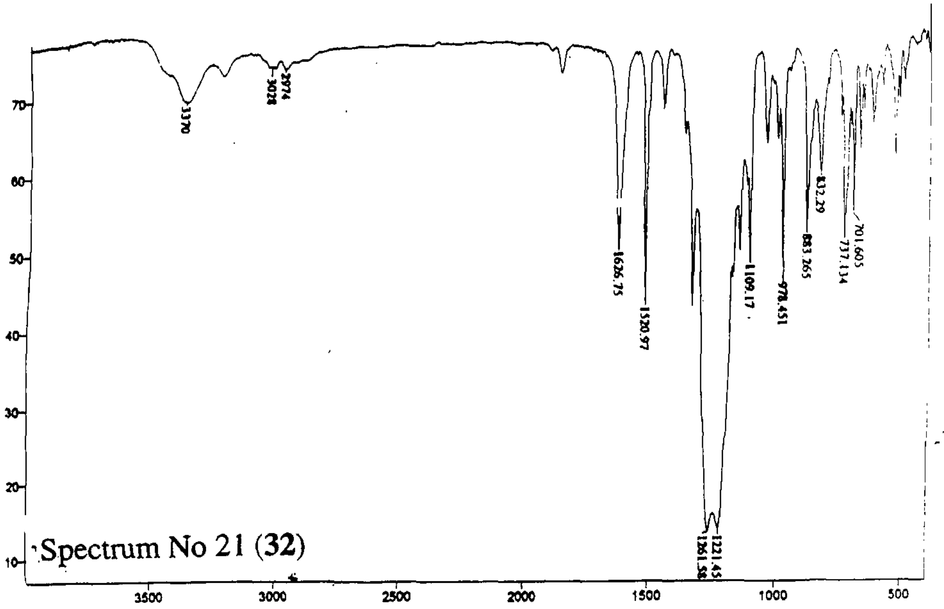
Spectrum No 16 (**27**)


Spectrum No 17 (**28**)


Spectrum No 18 (**29**)


Spectrum No 19 (**30**)

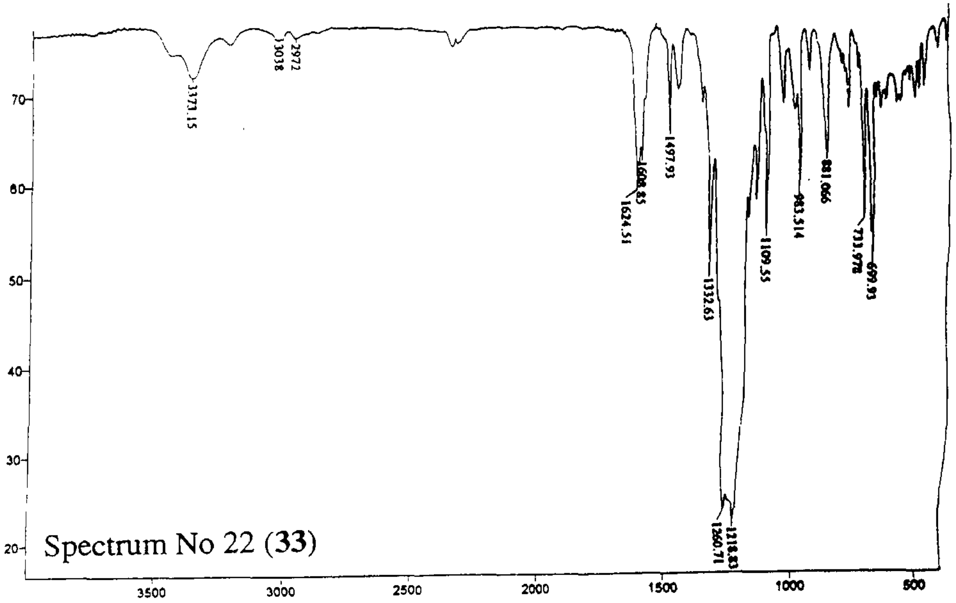

Spectrum No 20 (**31**)


Spectrum No 21 (**32**)

ransmittance / Wavenumber (cm-1)

Number of Scans= 4 Apodization= Strong

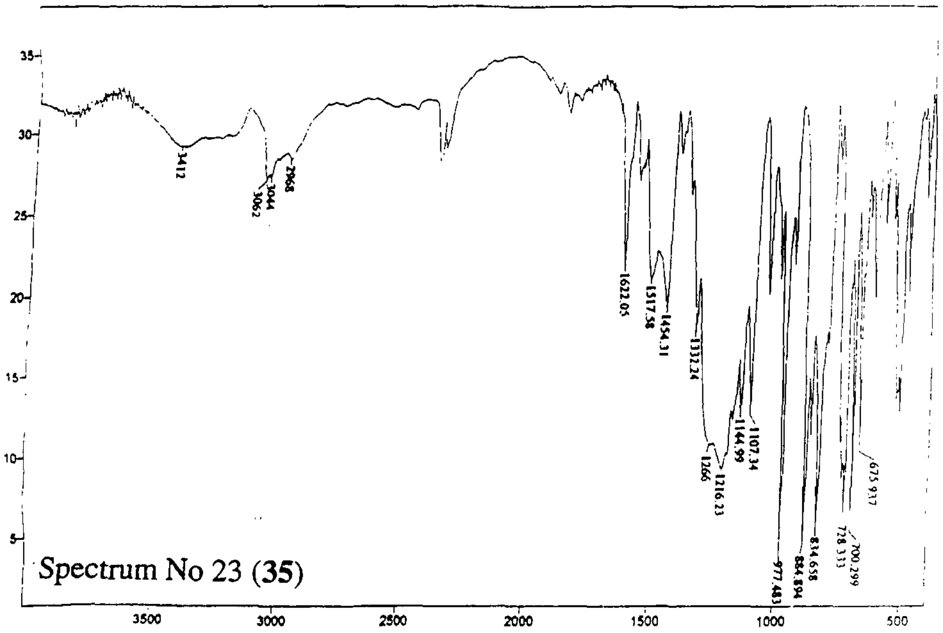
27/11/96 16:24 Res=4 cm-1

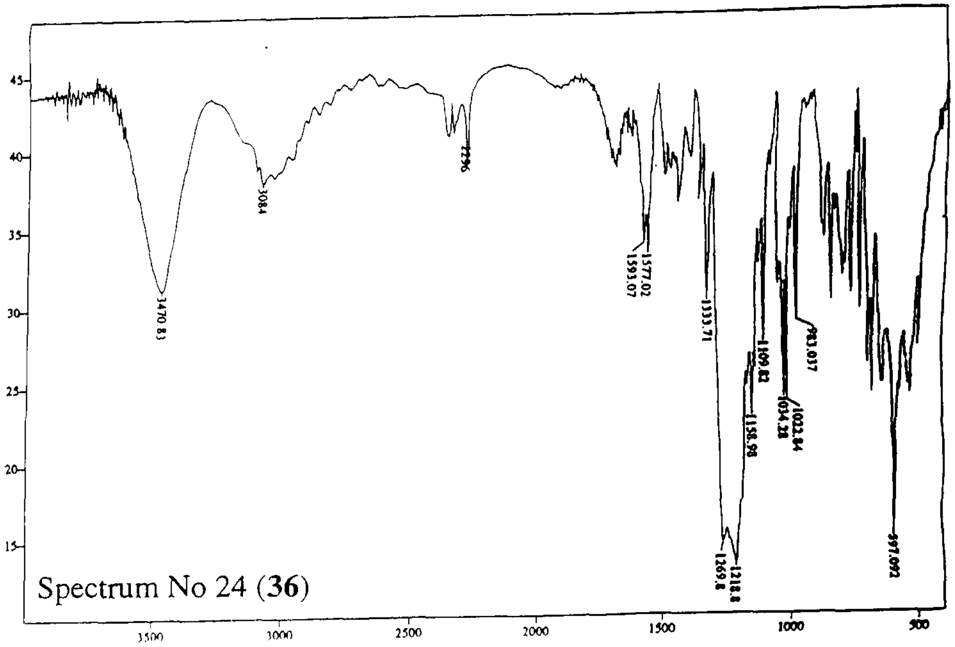

Spectrum No 22 (**33**)

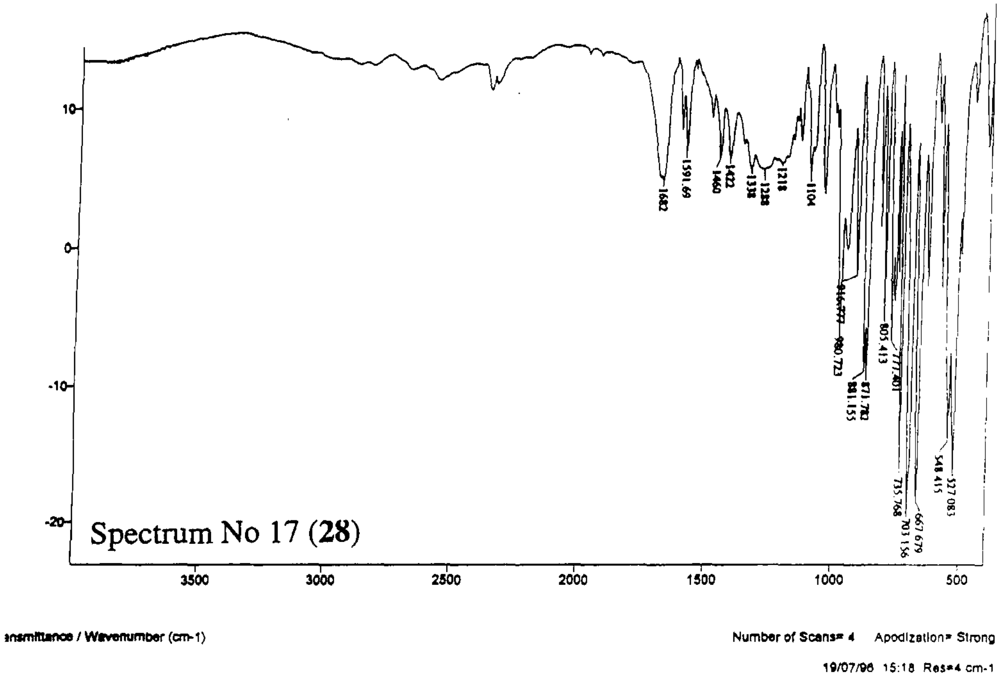
ransmittance / Wavenumber (cm-1)

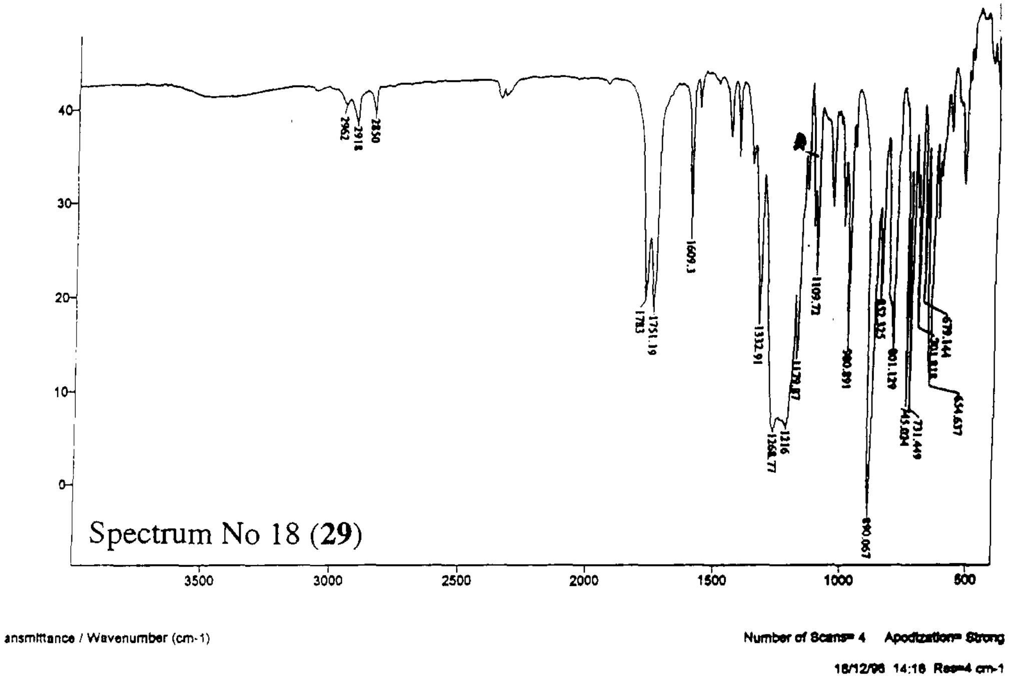
Number of Scans= 4 Apodization= Strong

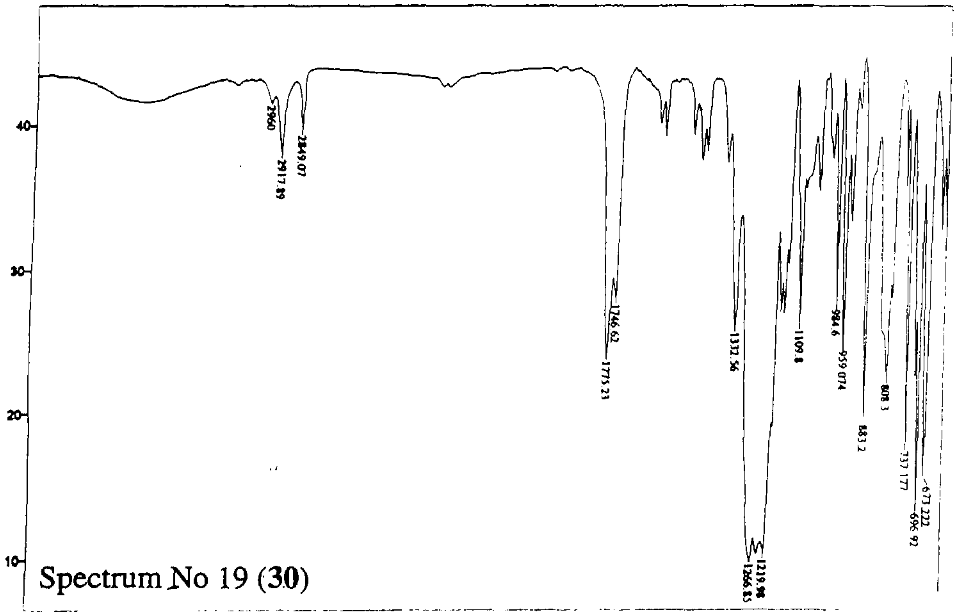
27/11/96 16:12 Res=4 cm-1

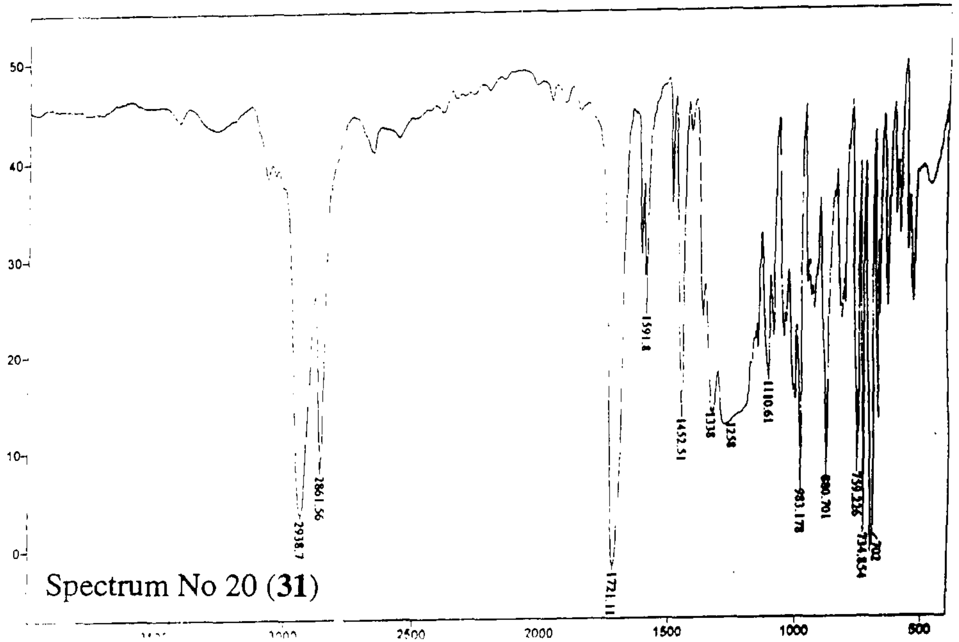

Spectrum No 23 (**35**)

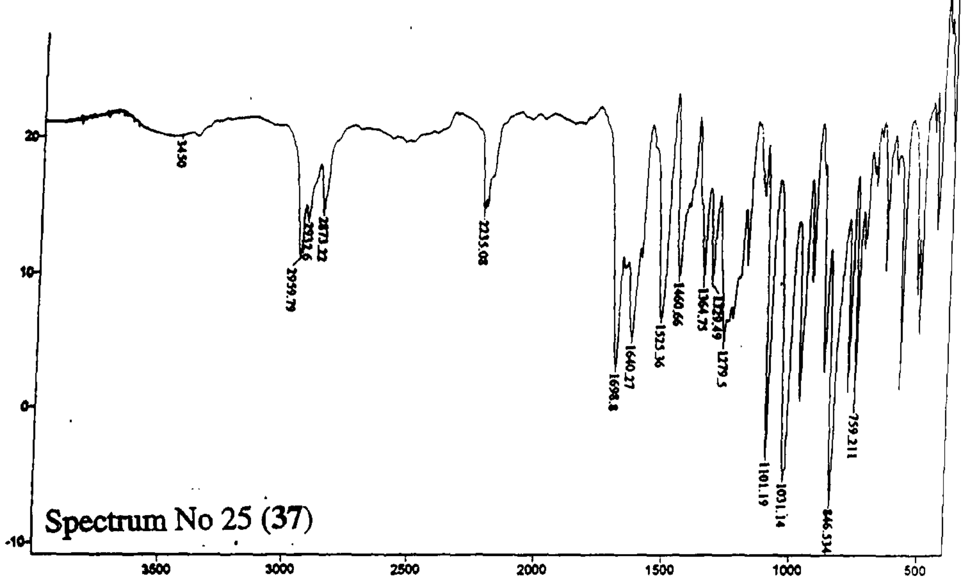

Spectrum No 24 (**36**)


Spectrum No 17 (**28**)


Spectrum No 18 (**29**)


Spectrum No 19 (**30**)


Spectrum No 20 (**31**)

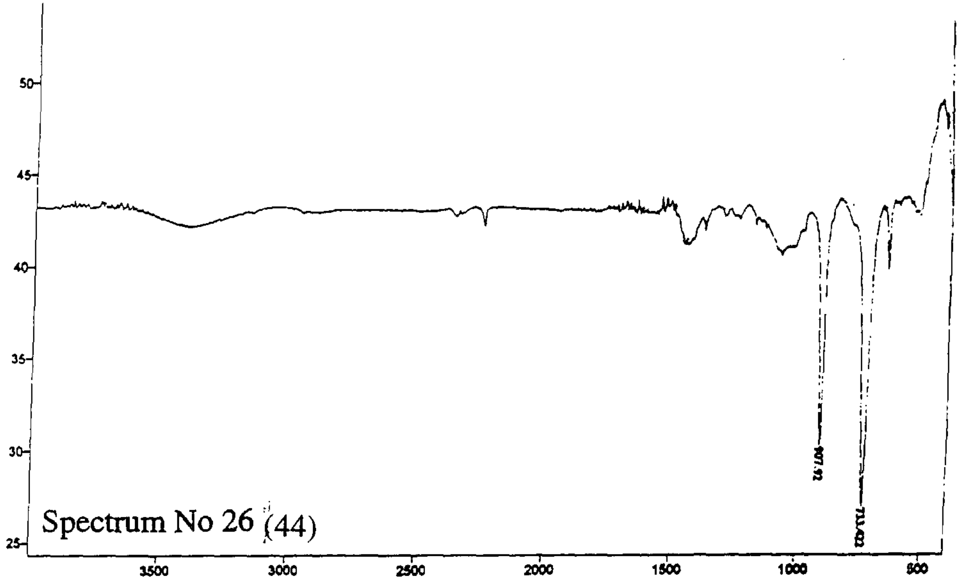


Spectrum No 25 (37)

ansmittance / Wavenumber (cm-1)

Number of Scans= 4 Apodization= Strong

06/03/97 17:15 Res=4 cm-1

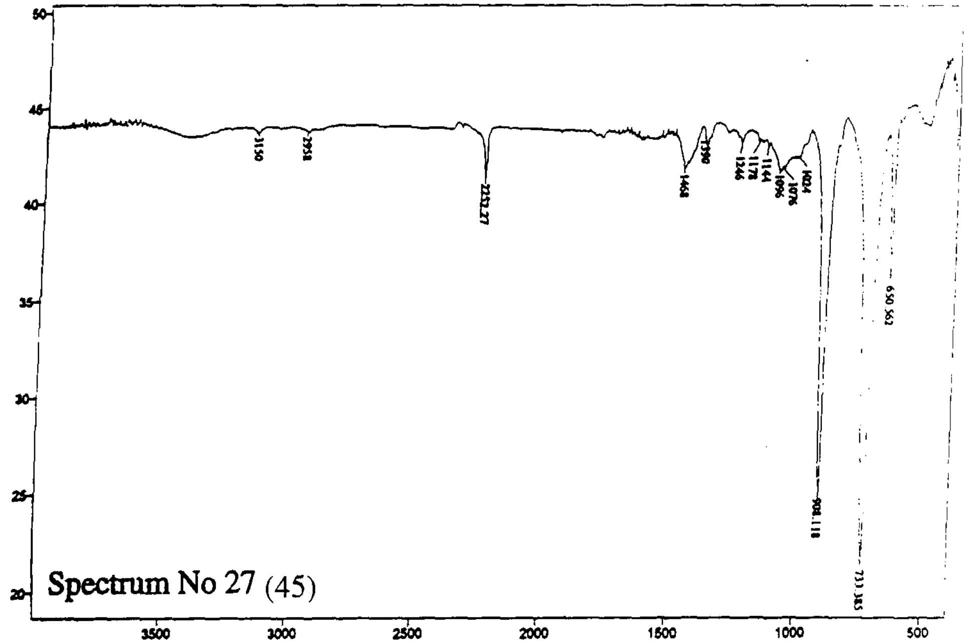


Spectrum No 26 (44)

Transmittance / Wavenumber (cm-1)

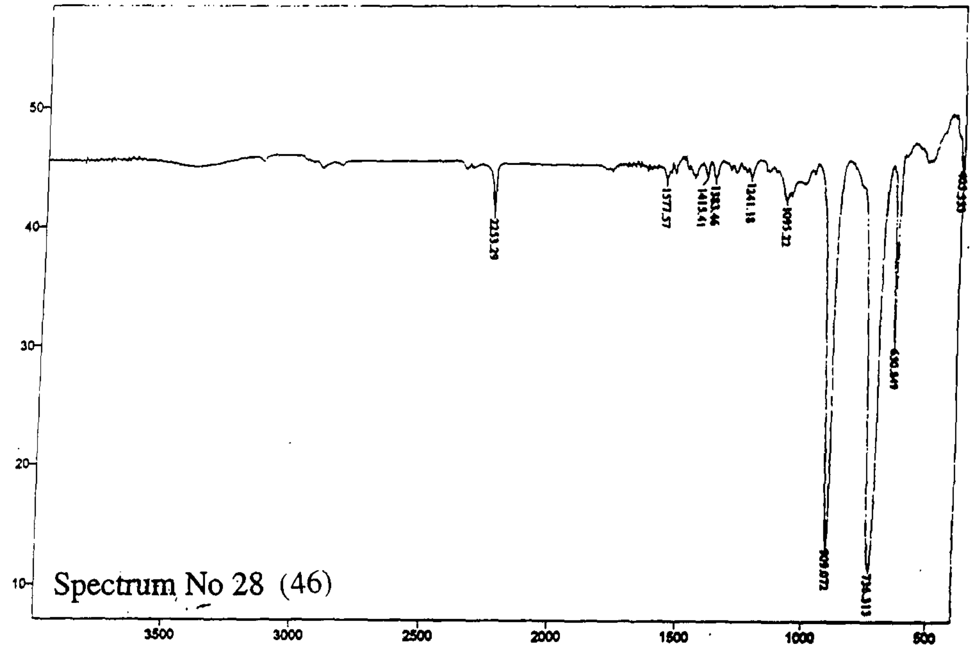
Number of Scans= 4 Apodization= Strong

19/05/95 15:27 Res=4 cm-1



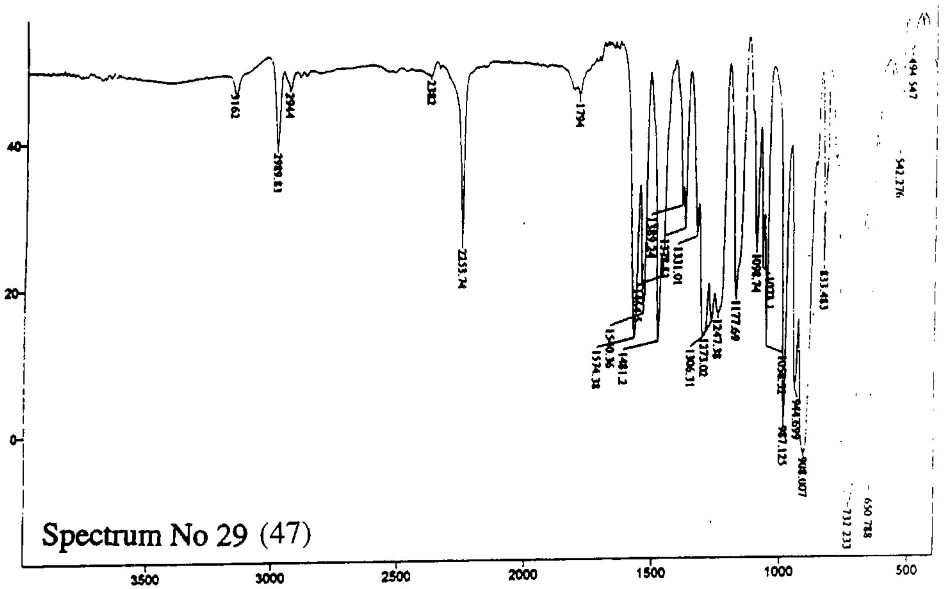
Spectrum No 27 (45)

Number of Scans= 4 Apodization= Strong



Spectrum No 28 (46)

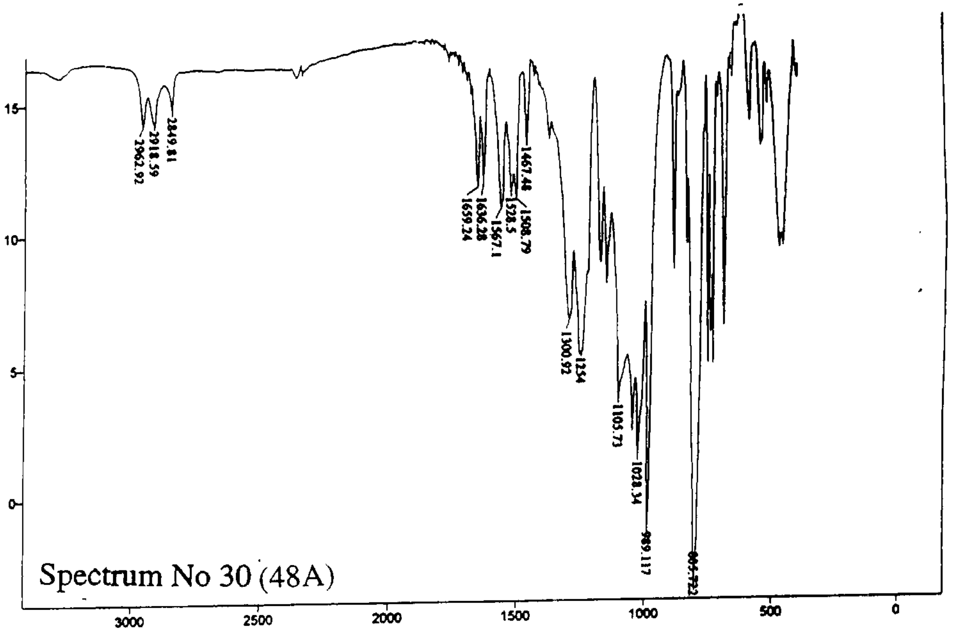
Transmittance / Wavenumber (cm-1)



Spectrum No 29 (47)

Number of Scans= 4 Apodization= Strong

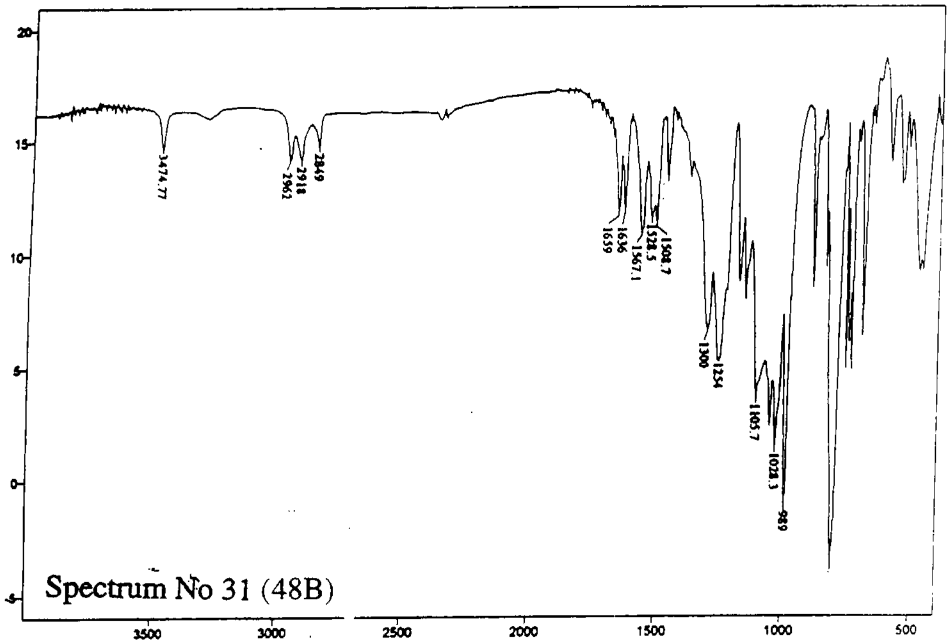
19/05/95 15:04 Res=4 cm-1



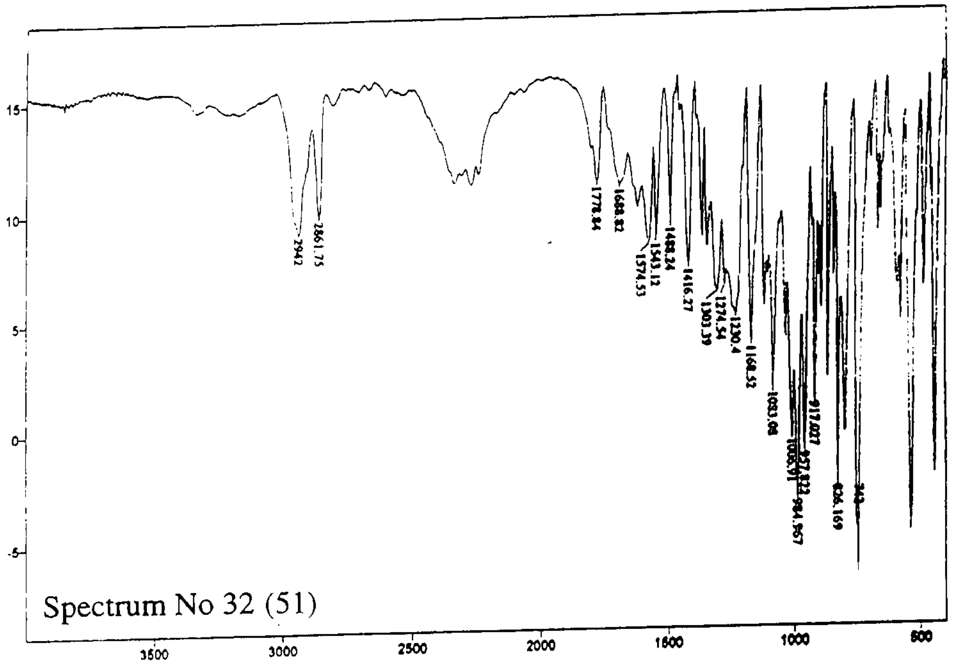
Spectrum No 30 (48A)

Number of Scans= 8 Apodization= Strong

28/04/97 14:43 Res=4 cm-1

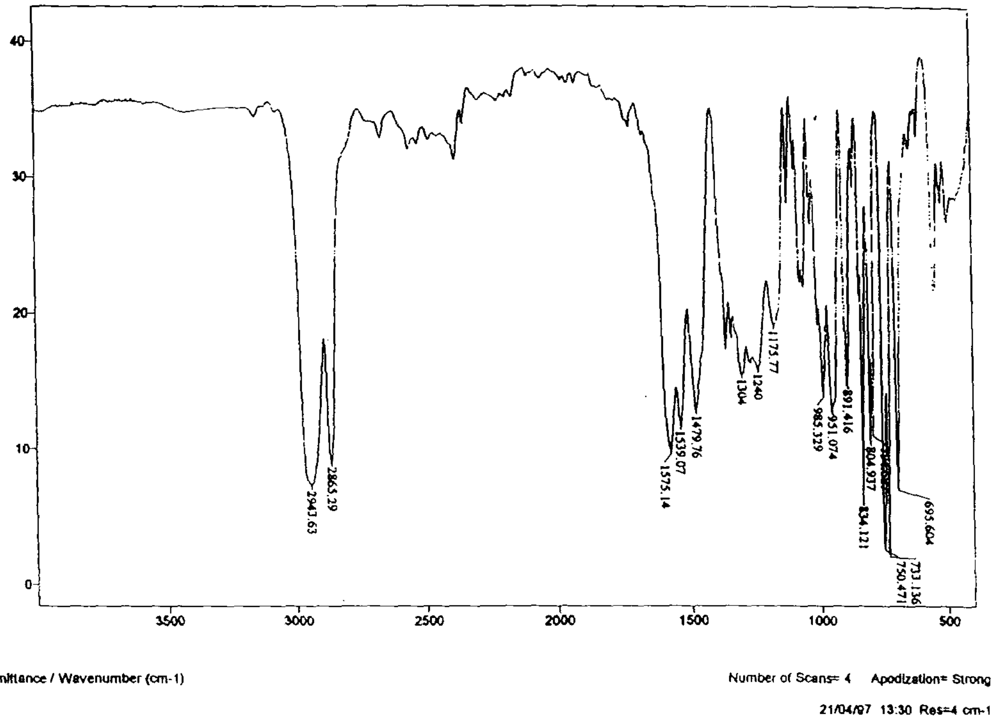


Spectrum No 31 (48B)



Spectrum No 32 (51)

Spectrum No 33 (52)

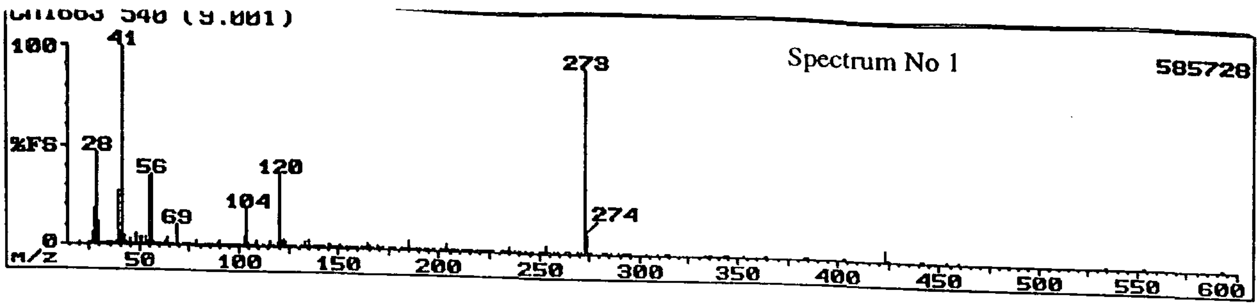


Appendix Three

Mass spectra (EI unless otherwise stated)

1. 1-Fluoromethyl-3-[(perfluoro-2-methyl-3-isopropylpentan-2yl)methyl]benzene
2. 1-Fluoromethyl-3-[(perfluoro-isopropyl)methyl]benzene
3. 2-[(Perfluoro-2-methylpentan-2-yl)methyl]naphthalene (**5**)
4. 1-Bromo-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**7**)
5. 1-Bromo-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**8**)
6. 1-Bromo-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**9**)
7. 1-Nitro-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**10**)
8. 1-Nitro-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**11**)
9. 1,3-Xylylene-bis(perfluoro-2-methylpentan-2-yl) (**12**)
10. 1-Fluoromethyl-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**14**)
11. 1,4-Xylylene-bis(perfluoro-2-methylpentan-2-yl) (**15**)
12. 1-Fluoromethyl-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**16**)
13. 1,2-Xylylene-bis(perfluoro-2-methylpentan-2-yl) (**17**)
14. 1-Fluoromethyl-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**18**)
15. 2,6-bis[(perfluoro-2-methylpentan-2-yl)methyl]pyridine (**19**)
16. 2-Fluoromethyl-6-[(perfluoro-2-methylpentan-2-yl)methyl]pyridine (**20**)
17. 1-Nitro-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**21**)
18. 3-[(Perfluoro-2-methylpentan-2-yl)methyl]benzenesulphonyl chloride (**22**)
19. 4-[(Perfluoro-2-methylpentan-2-yl)methyl]benzenesulphonyl chloride (**23**)
20. 3-[(Perfluoro-2-methylpentan-2-yl)methyl]benzenesulphanilide (**24**)
21. 4-[(Perfluoro-2-methylpentan-2-yl)methyl]benzenesulphanilide (**25**)
22. 4-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoic acid (**27**)
23. 3-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoic acid (**28**)
24. 4-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoyl chloride (**29**)
25. 3-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoyl chloride (**30**)
26. Cyclohexyl 3-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoate (**31**)
27. 1-Amino-4-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**32**)
28. 1-Amino-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**33**)
29. 1-Amino-2-[(perfluoro-2-methylpentan-2-yl)methyl]benzene (**34**)
30. Azo-dye (**35**)
31. Azo-dye (**36**)
32. Azo-dye (**37**)
33. 2-Methoxy-4,6-perfluorodi-isopropyl-s-triazine (**44**)
34. 2,4-Dimethoxy-6-perfluoroisopropyl-s-triazine (**45**)
35. 2-Isopropoxy-4,6-perfluorodi-isopropyl-s-triazine (**46**)
36. 2,4-Di-isopropoxy-6-perfluoroisopropyl-s-triazine (**47**)
37. 2-Phenoxy-4,6-perfluorodi-isopropyl-s-triazine (**48A**)
38. 2-(p-Cresoxy)-4,6-perfluorodi-isopropyl-s-triazine (**48B**)

39. 2-Fluoro-4-cyclohexanoxy-6-perfluoroisopropyl-s-triazine (**50**)
40. 2,4-Dicyclohexanoxy-6-perfluoroisopropyl-s-triazine (**51**)
41. 2-Cyclohexanoxy-4,6-perfluorodi-isopropyl-s-triazine (**52**)



CM1663 540 (9.001)

585728

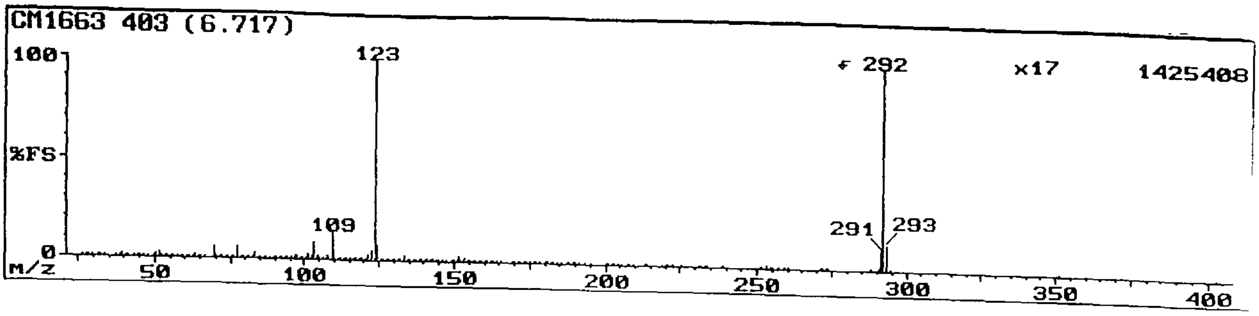
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
30	0.37	85	0.18	142	0.14	205	0.11
31	0.62	86	0.09	143	0.29	206	0.15
32	1.15	87	0.23	144	0.09	207	0.13
33	0.47	88	0.46	145	2.34	208	0.04
34	0.25	89	1.92	146	1.48	209	0.04
35	0.10	90	2.67	147	0.43	211	0.04
36	0.08	91	0.67	148	0.05	212	0.04
37	0.90	92	1.09	149	0.09	213	0.79
38	2.37	93	0.41	150	0.28	214	0.75
39	26.75	94	0.13	151	2.43	215	0.63
40	6.95	95	0.64	152	0.47	216	0.12
41	100.00	96	0.35	153	0.60	218	0.06
42	4.46	97	0.11	154	0.27	219	0.37
43	2.23	98	0.06	155	0.06	220	0.12
44	0.48	99	0.21	156	0.09	221	0.43
45	3.19	100	0.71	157	0.17	222	0.06
46	1.22	101	0.81	158	0.14	223	0.03
47	0.99	102	0.76	159	0.20	224	0.17
48	5.86	103	4.76	161	0.06	225	0.14
49	1.04	104	19.06	162	0.09	226	0.05
50	3.72	105	1.96	163	0.53	227	0.05
51	3.89	106	0.16	164	2.68	231	0.14
52	1.27	107	0.45	165	2.08	232	0.22
53	3.54	108	0.66	166	0.30	233	0.94
54	1.62	109	2.58	167	0.03	234	0.23
55	34.79	110	0.22	169	2.28	235	2.69
56	36.01	111	0.03	170	0.35	236	0.31
57	2.29	112	0.19	171	0.30	237	0.10
58	0.78	113	0.32	172	0.05	238	0.02
59	0.71	114	0.28	175	0.24	239	0.18
60	0.34	115	2.68	176	0.06	240	0.03
61	0.18	116	0.63	177	0.32	242	0.04
62	0.31	117	0.31	178	0.07	243	0.08
63	1.49	119	2.04	181	1.31	245	0.37
64	3.54	120	37.06	182	1.04	246	0.09
65	1.40	121	3.23	183	1.09	250	0.04
66	0.49	122	3.80	184	0.54	251	0.25
67	0.09	123	3.32	185	4.81	252	0.06
69	10.84	124	0.33	186	0.52	253	3.85
70	0.19	125	0.30	187	0.24	254	0.53
71	0.37	126	0.20	188	0.12	255	0.09
72	0.09	127	0.74	189	0.18	257	0.05
73	0.17	128	0.09	190	0.28	259	0.04
74	0.14	131	0.40	191	0.06	263	0.15
75	0.43	132	0.18	193	0.19	264	0.07
76	0.36	133	3.37	194	0.05	265	0.11
77	1.31	134	1.33	195	1.06	269	0.06
78	3.15	135	3.45	196	0.30	271	0.38
79	0.21	136	0.39	197	0.08	273	94.41
80	0.08	137	0.17	200	0.37	274	10.14
81	0.19	138	0.23	201	0.93	275	0.62
82	0.12	139	0.19	202	0.22	276	0.06
83	0.49	140	0.76	203	3.72	281	0.08
84	0.05	141	0.85	204	0.74	282	0.03

CM1663 540 (9.001)

585728

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
283	0.05	314	0.06	365	0.04	453	0.05
285	0.08	315	0.08	383	0.13	459	0.04
289	0.03	333	0.06	384	0.06	533	0.16
291	1.44	335	0.30	385	0.03	534	0.02
292	0.18	336	0.05	403	0.11	553	0.23
293	0.04	343	0.04	404	0.07	554	0.03
294	0.05	344	0.04	423	6.08	592	1.04
295	0.04	345	0.03	424	0.79	593	0.18
303	0.06	353	0.08	425	0.06		
309	0.16	363	0.10	441	0.25		
313	0.07	364	0.06	442	0.05		

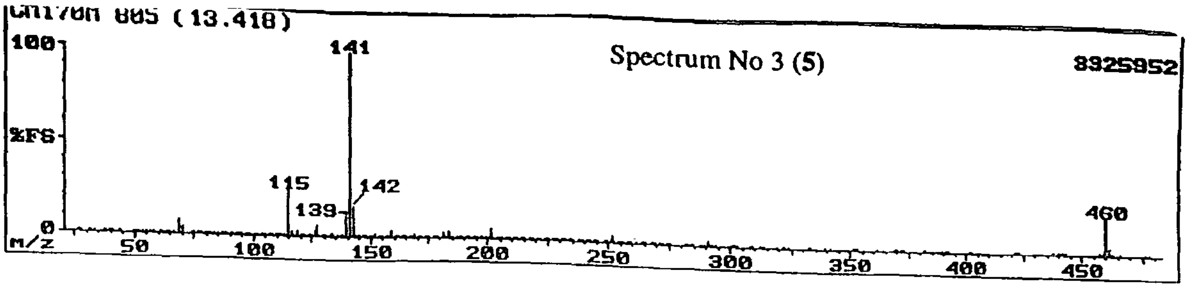
Spectrum No 2



CM1663 403 (6.717)

1425408

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
31	0.32	86	0.27	134	0.86	188	0.04
32	0.23	87	0.34	135	0.33	189	0.11
33	0.62	88	0.27	136	0.04	190	0.17
37	0.12	89	1.35	137	0.09	191	0.03
38	0.49	90	0.35	138	0.16	193	0.02
39	2.26	91	0.40	139	0.15	195	0.04
40	0.18	92	0.11	140	0.40	200	0.15
41	0.08	93	0.23	141	1.38	201	0.44
43	0.01	94	0.31	142	0.43	202	0.10
44	0.08	95	1.20	143	0.19	203	0.89
45	0.13	96	2.37	144	0.07	204	0.15
46	0.06	97	1.67	145	0.29	205	0.02
47	0.03	98	0.21	146	0.04	207	0.02
49	0.05	99	0.40	147	0.01	208	0.01
50	1.51	100	0.80	149	0.15	209	0.02
51	2.87	101	3.02	150	0.21	213	0.18
52	0.51	102	1.81	151	2.62	214	0.03
53	0.26	103	8.76	152	0.54	219	0.17
54	0.02	104	2.01	153	1.53	220	0.02
55	0.01	105	0.42	154	0.27	221	0.51
56	0.09	106	0.16	155	0.04	222	0.12
57	1.45	107	1.80	156	0.06	223	0.03
58	0.09	108	0.80	157	0.05	225	0.02
59	0.39	109	13.15	158	0.10	231	0.04
60	0.11	110	0.97	159	0.34	232	0.02
61	0.39	111	0.10	160	0.03	233	0.19
62	0.72	112	0.14	161	0.06	234	0.02
63	1.90	113	0.25	162	0.08	239	0.07
64	0.43	114	0.26	163	0.28	251	0.04
65	0.31	115	0.51	164	0.43	253	2.01
66	0.06	116	0.08	165	0.09	254	0.22
69	6.18	117	0.06	169	0.81	255	0.02
70	0.55	118	0.05	170	0.20	257	0.02
71	0.15	119	0.66	171	0.40	259	0.12
72	0.02	120	0.71	172	0.08	260	0.01
73	0.05	121	2.75	173	0.03	271	0.05
74	0.54	122	4.74	174	0.01	272	0.01
75	1.31	123	100.00	175	0.02	273	0.45
76	0.52	124	8.19	176	0.02	274	0.05
77	6.03	125	0.65	177	0.10	288	0.01
78	1.15	126	0.16	178	0.01	291	0.02
79	0.09	127	0.69	180	0.01	291	0.56
80	0.09	128	0.08	181	0.08	292	7.83
81	0.77	129	0.02	182	0.61	293	0.76
82	0.26	130	0.03	183	0.64	294	0.04
83	2.78	131	0.23	184	0.13	351	0.02
84	0.21	132	0.16	185	0.02	403	0.03
85	0.12	133	3.00	187	0.09		



Spectrum No 3 (5)

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CM170E 789 (13.151)
                                                                          2834432
Mass   Rel Int | Mass   Rel Int | Mass   Rel Int | Mass   Rel Int
  31     0.40  |  107     0.09  |  170     0.50  |  231     0.11
  32     0.35  |  109     0.06  |  171     0.23  |  232     0.50
  33     0.04  |  110     0.06  |  172     0.13  |  233     0.56
  36     0.01  |  111     0.15  |  173     0.04  |  234     0.08
  37     0.04  |  112     0.21  |  175     0.21  |  237     0.06
  38     0.18  |  113     0.86  |  176     0.05  |  238     0.04
  39     1.63  |  114     0.47  |  177     0.69  |  239     0.06
  40     0.12  |  115    14.60  |  178     0.09  |  240     0.07
  41     0.11  |  116     1.53  |  179     0.05  |  241     0.01
  43     0.02  |  117     0.10  |  180     0.05  |  243     0.02
  44     0.12  |  119     1.17  |  181     1.84  |  245     0.03
  50     1.00  |  120     0.08  |  182     0.32  |  248     0.02
  51     1.35  |  122     0.04  |  183     2.75  |  250     0.21
  52     0.28  |  123     0.07  |  184     0.48  |  251     2.19
  53     0.06  |  124     0.06  |  185     0.05  |  252     0.76
  55     0.03  |  125     0.27  |  186     0.03  |  253     0.16
  58     4.70  |  126     1.65  |  187     0.04  |  257     0.03
  61     0.07  |  127     3.36  |  188     0.26  |  261     0.02
  62     0.67  |  128     0.75  |  189     0.10  |  263     0.05
  63     1.99  |  129     0.11  |  190     0.11  |  264     0.03
  64     0.27  |  131     0.24  |  191     0.03  |  268     0.02
  65     0.56  |  133     0.86  |  192     0.02  |  269     0.37
  67     0.17  |  134     0.09  |  193     0.13  |  270     0.11
  69     8.38  |  136     0.08  |  194     0.06  |  271     0.13
  71    10.55  |  137     0.18  |  195     0.14  |  272     0.38
  74     0.68  |  138     0.21  |  196     0.04  |  273     0.05
  75     0.98  |  139     5.65  |  199     0.40  |  281     0.09
  76     0.64  |  140     2.24  |  200     0.36  |  282     0.09
  77     0.88  |  141   100.00  |  201     4.15  |  283     0.10
  78     0.16  |  142    12.43  |  202     0.80  |  284     0.02
  80     0.89  |  143     0.79  |  203     0.27  |  289     0.07
  81     0.14  |  144     0.11  |  204     0.04  |  290     1.48
  82     0.02  |  145     0.25  |  205     0.02  |  291     0.41
  83     0.03  |  146     0.72  |  206     0.10  |  292     0.05
  85     0.08  |  147     0.10  |  207     0.07  |  301     0.04
  86     0.32  |  149     0.07  |  208     0.03  |  302     0.05
  87     0.68  |  150     0.36  |  209     0.06  |  308     0.03
  88     0.41  |  151     0.58  |  210     0.02  |  319     0.01
  89     1.18  |  152     1.35  |  211     0.08  |  321     0.15
  90     0.13  |  153     0.63  |  212     0.13  |  322     0.06
  91     0.58  |  154     0.08  |  213     0.07  |  332     0.09
  92     0.09  |  155     0.05  |  214     0.26  |  333     0.01
  93     0.16  |  156     0.05  |  215     0.05  |  351     0.06
  94     0.05  |  157     0.32  |  217     0.06  |  352     0.14
  95     0.11  |  158     0.08  |  218     0.05  |  353     0.01
  96     0.02  |  159     2.60  |  219     0.79  |  371     0.06
  98     0.20  |  160     0.36  |  220     0.31  |  372     0.08
  99     0.29  |  161     0.06  |  221     0.42  |  381     0.04
 100     0.64  |  162     0.06  |  222     0.72  |  390     0.03
 101     0.57  |  163     0.14  |  223     0.10  |  391     0.04
 102     0.43  |  164     0.07  |  224     0.03  |  401     0.09
 103     0.06  |  165     0.03  |  225     0.03  |  402     0.02
 105     0.05  |  167     0.02  |  227     0.04  |  421     0.51
 106     0.04  |  169     0.70  |  230     0.24  |  422     0.08
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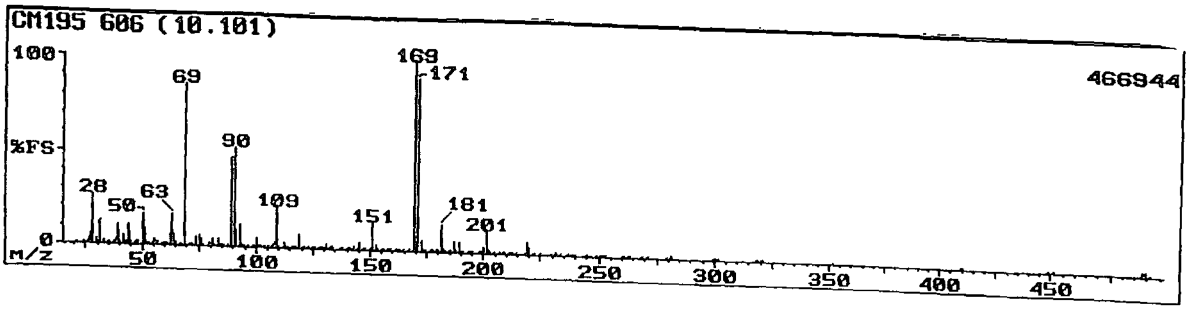
CM170E 789 (13.151)
                                                                          2834432
Mass   Rel Int | Mass   Rel Int | Mass   Rel Int | Mass   Rel Int
 441     0.25  |  459     0.09  |  461     1.89  |  476     0.05
 442     0.04  |  460    11.42  |  462     0.16  |
```

Spectrum No 4 (7)

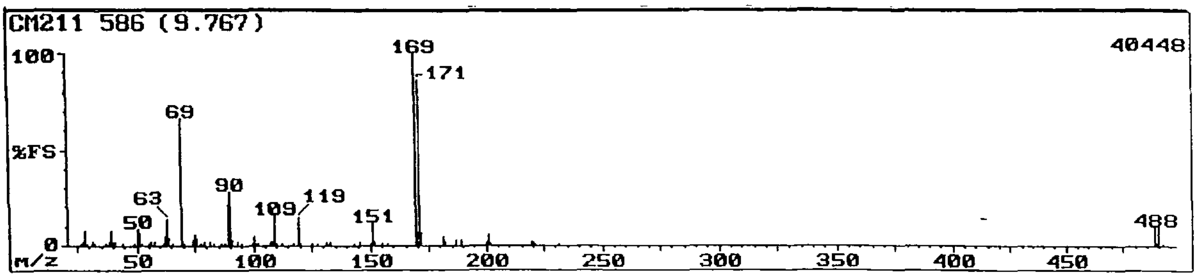


CM195 606 (10.101)

466944

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.07	79	1.55	144	0.16	212	0.33
24	0.53	80	0.23	145	3.56	213	0.48
25	0.75	81	3.89	146	0.11	214	0.11
26	3.11	82	0.92	147	0.07	218	0.24
27	5.54	83	3.43	150	0.89	219	6.69
28	26.54	84	0.37	151	14.69	220	3.89
29	2.97	85	0.54	152	2.75	221	1.37
30	0.26	86	0.53	153	0.28	222	0.18
31	12.28	87	1.14	155	1.00	225	0.04
32	1.73	89	47.59	156	0.17	229	0.28
33	0.30	90	52.41	157	0.64	231	1.51
34	0.26	91	8.72	158	0.12	232	0.92
35	0.73	93	11.24	159	0.09	233	0.30
36	0.37	94	0.90	161	0.29	237	0.19
37	1.78	95	0.83	162	0.73	238	0.30
38	3.17	96	0.14	163	0.70	239	0.86
39	10.31	98	0.15	164	0.22	240	0.14
40	2.11	100	5.26	167	0.10	245	0.12
41	4.55	101	1.44	169	100.00	249	0.16
42	0.92	102	1.15	170	5.32	250	0.90
43	2.11	104	0.25	171	91.23	251	0.90
44	10.47	105	0.53	172	6.03	252	0.38
45	1.62	106	0.45	173	0.14	253	0.07
46	0.39	107	2.01	174	0.21	260	0.07
47	1.88	108	2.52	176	0.24	261	0.11
48	1.99	109	21.27	177	0.09	262	0.13
50	16.23	110	1.30	179	0.04	263	0.09
51	9.21	112	3.07	180	0.17	268	0.13
52	1.34	113	1.12	181	14.69	269	0.26
53	1.03	114	0.09	182	2.10	270	0.27
54	0.42	115	0.07	183	0.71	271	0.12
55	2.70	116	0.08	184	0.07	279	0.26
56	2.22	117	0.55	185	0.07	281	1.78
57	1.82	119	7.73	187	5.81	282	0.13
58	0.20	120	1.07	188	0.37	299	0.39
59	0.29	121	0.26	189	5.92	300	0.25
60	0.36	123	0.49	190	0.54	301	0.44
61	1.22	124	0.74	191	0.07	302	0.24
62	5.48	125	0.64	193	0.64	318	0.43
63	16.45	126	0.53	194	0.09	319	0.36
64	5.48	127	1.15	195	0.14	320	0.73
65	2.19	128	0.21	198	0.11	321	0.33
66	0.51	129	0.25	199	0.18	351	0.04
67	0.18	131	2.54	200	3.10	409	0.05
69	85.09	132	0.88	201	11.40	410	0.15
70	0.66	133	2.01	202	2.10	449	0.10
71	0.17	134	0.24	203	0.11	451	0.13
72	0.07	137	0.12	205	0.29	488	2.67
74	5.32	138	0.21	207	0.57	489	0.29
75	6.30	140	0.49	208	0.03	490	2.54
76	4.22	141	0.14	209	0.06	491	0.34
77	0.77	143	2.36	211	0.16		

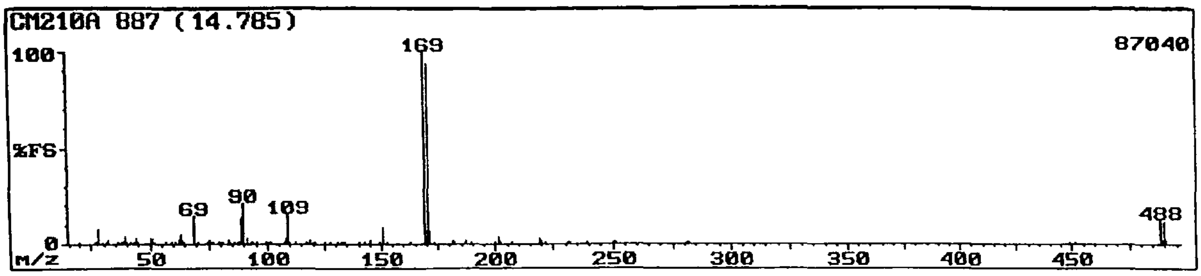
Spectrum No 5 (**8**)



CM211 586 (9.767) 4044

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	1.12	63	13.29	101	1.02	169	100.00
27	2.13	64	4.31	102	0.53	170	6.76
28	8.07	65	0.91	107	1.68	171	86.71
29	0.57	69	65.82	108	2.03	172	6.37
31	1.73	70	1.14	109	15.82	181	4.67
32	0.85	74	2.89	110	1.29	182	1.50
37	0.76	75	5.38	112	0.69	187	3.32
38	2.39	76	3.48	117	0.70	189	3.09
39	7.52	77	0.87	119	14.56	200	1.50
40	1.61	79	1.71	120	0.93	201	6.29
41	2.07	81	2.38	125	0.57	202	0.42
44	0.84	83	1.23	127	0.70	219	2.41
49	0.64	86	0.97	131	2.02	220	1.60
50	9.14	87	0.84	133	2.07	221	1.07
51	6.69	89	21.52	143	1.40	231	0.59
52	1.08	90	28.16	145	2.26	488	10.13
55	0.97	91	2.69	150	1.34	489	1.36
56	1.73	93	1.72	151	11.71	490	10.05
57	1.74	95	1.06	152	2.32	491	1.32
61	1.08	99	0.42	155	0.89		
62	4.63	100	5.14	157	0.86		

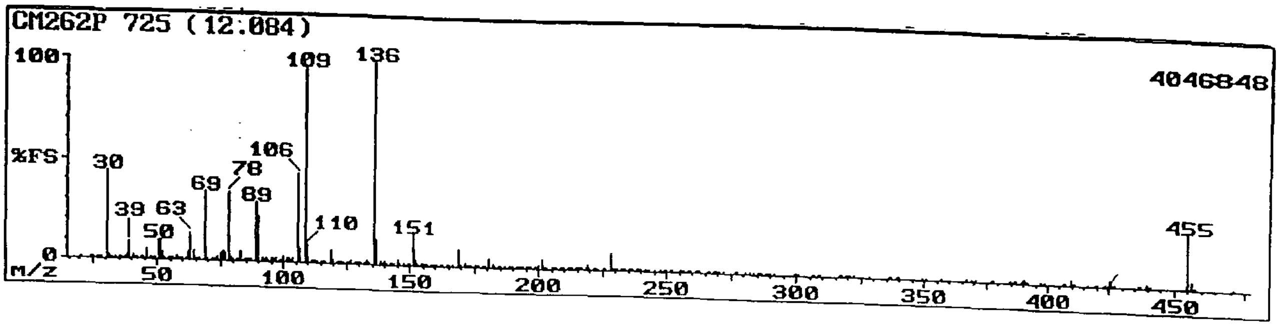
Spectrum No 6 (9)



CM210A 887 (14.785) 87040

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.30	69	14.12	109	15.51	182	0.84
26	0.44	70	0.38	110	1.38	187	2.37
27	0.48	74	0.96	112	0.37	189	1.29
28	8.09	75	1.93	117	0.42	200	1.34
29	0.46	76	1.13	119	2.35	201	3.60
31	0.91	77	0.40	120	0.70	202	0.67
32	1.62	79	0.38	121	0.34	207	0.49
36	0.33	80	0.31	125	0.54	219	2.57
37	0.31	81	0.82	127	0.65	220	1.53
38	1.14	83	2.33	131	0.88	221	0.19
39	3.92	84	0.23	132	0.41	231	0.46
40	0.82	86	0.44	133	1.29	232	0.33
41	0.45	87	0.32	134	0.24	239	0.42
43	0.45	88	0.48	140	0.33	250	0.36
44	2.48	89	13.82	143	0.81	251	0.50
45	0.35	90	21.47	145	1.91	281	0.33
50	2.48	91	2.48	149	0.44	282	0.34
51	2.61	93	0.64	151	8.68	449	0.31
52	0.25	94	0.24	152	1.43	451	0.32
57	0.82	95	0.46	163	0.35	488	12.87
59	0.33	99	0.57	169	100.00	489	1.60
61	0.47	100	1.00	170	7.06	490	12.06
62	1.67	101	0.56	171	94.12	491	1.67
63	5.29	102	0.70	172	6.76		
64	1.69	107	1.40	173	0.25		
65	0.51	108	2.61	181	1.88		

Spectrum No 7 (**10**)



CM262P 725 (12.084)

4046848

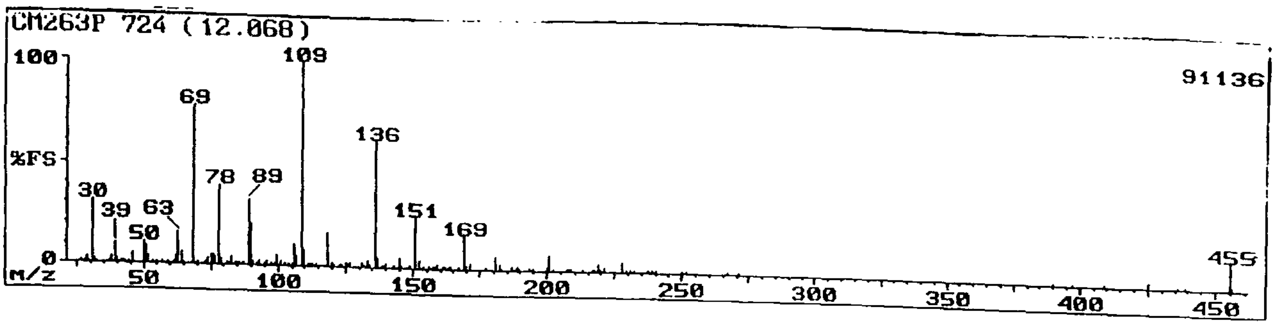
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
21	0.09	81	1.04	140	1.60	199	0.22
24	0.02	82	0.22	141	0.11	200	2.07
25	0.05	83	4.68	142	0.06	201	4.73
26	0.41	84	0.31	143	0.84	202	0.66
27	1.14	85	0.18	144	0.17	203	0.06
28	1.08	86	0.62	145	3.37	205	0.12
30	43.72	87	0.97	146	0.23	206	0.06
31	1.67	89	29.15	147	0.04	207	0.36
32	0.32	90	22.17	149	0.59	208	1.35
33	0.24	91	2.07	150	0.47	209	0.69
35	0.02	92	0.51	151	15.89	210	0.07
36	0.07	93	1.50	152	2.61	211	0.12
37	0.40	94	0.34	153	0.20	212	0.11
38	2.05	95	1.58	154	0.58	213	0.35
39	9.01	96	1.38	155	0.11	214	0.10
40	1.70	97	2.30	156	0.33	215	0.02
41	0.23	98	0.33	157	0.26	216	0.03
42	0.05	99	1.27	158	0.17	217	0.33
43	0.11	100	2.71	159	1.42	218	0.39
44	0.31	101	2.00	160	0.13	219	3.19
46	4.61	102	1.62	161	0.21	220	1.11
47	0.07	103	0.30	162	0.19	221	1.38
48	0.03	104	2.02	163	0.72	222	0.14
49	0.23	106	43.72	164	0.42	223	0.02
50	10.02	107	6.68	165	0.09	225	0.05
51	9.72	109	96.36	167	0.34	226	0.05
52	3.77	110	9.11	169	8.50	228	8.30
53	0.52	111	0.53	170	1.21	229	0.70
54	0.10	112	0.68	171	2.15	230	0.04
55	0.20	113	0.56	172	0.26	231	0.53
56	0.11	114	0.64	173	0.02	232	0.39
57	1.87	115	0.10	174	0.10	233	0.07
58	0.09	116	0.05	175	0.19	234	0.01
59	0.56	117	0.12	176	0.17	235	0.05
60	0.05	119	6.88	177	0.56	236	0.14
61	0.53	120	2.33	178	0.09	237	0.27
62	3.44	121	0.76	179	0.06	238	0.16
63	13.56	122	0.15	181	4.58	239	0.58
64	5.31	123	0.47	182	1.87	240	0.53
65	0.87	124	0.60	183	0.46	241	0.06
66	0.14	125	1.36	184	0.07	242	0.01
67	0.05	126	0.69	185	0.06	243	0.02
69	34.01	127	2.00	187	1.34	245	0.07
70	0.59	128	0.20	188	0.31	248	0.03
71	0.09	129	0.07	189	1.15	249	0.13
72	0.02	130	0.06	190	0.42	250	0.39
73	0.17	131	1.45	191	0.06	251	0.40
74	2.05	132	0.62	192	0.01	252	0.07
75	3.85	133	2.15	193	0.26	255	0.09
76	4.45	134	0.26	194	0.13	256	0.26
77	3.57	136	100.00	195	0.33	257	0.06
78	33.60	137	12.45	196	0.05	258	0.15
79	2.30	138	1.64	197	0.02	259	0.05
80	0.27	139	1.21	198	0.09	261	0.01

CM262P 725 (12.084)

4046848

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
262	0.01	291	0.06	351	0.02	411	0.02
263	0.02	299	0.03	357	0.16	416	0.03
266	0.05	300	0.08	367	0.01	419	0.16
267	0.21	301	0.13	369	0.05	420	0.03
268	0.09	306	0.04	371	0.02	423	0.04
269	0.38	307	0.05	377	0.02	425	3.09
270	0.10	308	0.02	378	0.03	426	0.38
271	1.30	309	0.02	385	0.02	427	0.03
272	0.14	317	0.12	386	0.02	436	0.56
277	0.01	318	0.01	387	0.05	437	0.08
278	0.02	319	0.06	389	0.08	439	1.80
281	0.30	320	0.03	390	1.62	440	0.24
282	0.04	321	0.32	391	0.22	441	0.02
284	0.04	322	0.04	392	0.01	455	26.72
285	0.02	328	0.05	397	0.42	456	4.05
286	0.08	336	0.18	398	0.05	457	0.38
287	0.22	337	0.09	406	0.07	458	0.03
288	0.07	339	0.07	407	0.02	471	0.03
289	0.14	340	0.04	409	2.86		
290	0.55	349	0.02	410	0.38		

Spectrum No 8 (**11**)

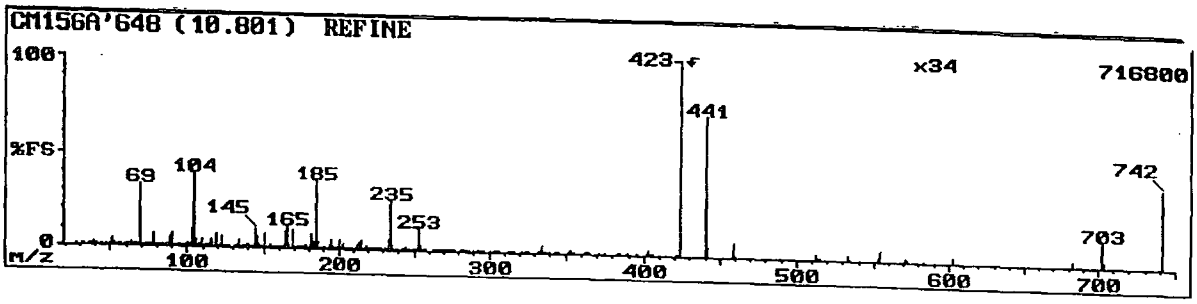


CM263P 724 (12.068)

91136

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.42	79	2.91	127	2.23	190	0.34
27	1.40	81	1.33	131	2.30	193	0.42
28	2.53	83	3.44	132	0.53	195	0.29
29	0.90	84	0.36	133	2.69	200	2.35
30	31.46	85	0.29	134	0.18	201	7.72
31	2.18	86	0.60	136	62.08	202	1.14
32	0.62	87	0.65	137	5.13	207	0.39
37	0.28	89	32.30	138	0.77	208	0.95
38	2.53	90	20.22	139	1.18	209	0.48
39	10.04	91	1.86	140	2.12	213	0.52
40	1.79	92	0.32	143	0.80	217	0.66
41	1.01	93	1.72	145	4.63	218	0.42
42	0.32	95	1.44	146	0.30	219	4.27
43	0.87	96	1.47	149	0.90	220	1.25
44	0.80	97	0.86	151	25.00	221	2.02
46	5.20	99	1.39	152	4.13	228	4.37
50	10.60	100	4.49	154	0.30	229	0.48
51	8.92	101	1.93	156	0.50	231	0.42
52	3.90	102	0.86	157	0.36	232	0.57
53	0.37	104	0.55	158	0.45	237	0.44
55	0.50	105	0.68	159	1.65	239	0.47
57	0.84	106	10.32	161	0.53	240	0.52
59	0.58	107	4.39	162	0.34	250	0.52
61	0.73	109	100.00	163	1.11	251	0.72
62	4.27	110	7.87	164	0.39	267	0.60
63	16.01	111	0.58	167	0.58	271	0.85
64	5.90	112	0.77	169	16.57	390	0.77
65	1.03	113	0.65	170	1.97	397	0.38
69	77.53	114	0.78	171	2.55	409	0.94
70	1.19	119	16.64	177	0.47	425	2.49
73	0.38	120	2.33	181	6.60	436	0.25
74	2.67	121	0.91	182	2.72	439	1.00
75	4.49	123	0.58	183	0.71	455	13.62
76	4.56	124	0.66	187	1.72	456	2.25
77	4.28	125	1.76	188	0.32		
78	38.48	126	0.79	189	1.60		

Spectrum No 9 (12)



CM156A'648 (10.801) REFINE

716800

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
31	0.59	98	0.12	155	0.32	212	0.19
32	0.35	99	0.26	156	0.20	213	3.04
33	0.13	100	1.79	157	0.50	214	3.50
36	0.03	101	1.29	158	0.41	215	5.21
37	0.04	102	1.54	159	0.63	216	0.94
38	0.17	103	9.29	160	0.07	217	0.10
39	1.63	104	38.86	161	0.13	218	0.21
40	0.17	105	3.89	162	0.29	219	2.04
41	0.16	106	0.31	163	1.43	220	0.77
43	0.04	107	0.63	164	9.00	221	1.09
45	0.04	108	1.88	165	11.29	222	0.12
47	0.10	109	3.96	166	1.86	223	0.05
50	1.38	110	0.35	167	0.19	224	0.42
51	3.43	111	0.06	169	9.43	225	0.59
52	2.00	112	0.49	170	0.86	226	0.32
53	0.37	113	0.53	171	0.82	227	0.60
54	0.05	114	0.42	172	0.31	228	0.11
55	0.06	115	4.32	173	0.12	231	0.74
57	0.52	116	1.67	174	0.08	232	1.27
59	0.14	117	0.88	175	0.93	233	6.21
60	0.06	119	7.00	176	0.27	234	1.31
61	0.29	120	0.63	177	1.56	235	26.14
62	0.42	121	1.13	178	0.44	236	3.36
63	1.91	122	5.46	179	0.07	237	0.55
64	0.71	123	3.25	180	0.08	238	0.16
65	0.84	124	0.45	181	7.46	239	1.08
66	0.09	125	0.52	182	3.79	240	0.24
69	33.00	126	0.43	183	3.75	242	0.08
70	0.53	127	1.04	184	1.90	243	0.20
71	0.08	128	0.28	185	36.14	244	0.13
73	0.05	131	1.18	186	4.07	245	1.64
74	0.33	132	0.33	187	0.82	246	0.50
75	0.82	133	3.46	188	0.42	247	0.17
76	0.74	134	1.04	189	0.42	249	0.06
77	3.64	135	0.56	190	0.32	250	0.22
78	6.57	136	0.08	191	0.04	251	1.19
79	0.56	137	0.34	193	0.59	252	0.27
80	0.05	138	0.41	194	0.14	253	11.86
81	0.30	139	0.43	195	5.07	254	2.61
82	0.15	140	2.06	196	1.74	255	0.46
83	0.94	141	0.46	197	0.60	256	0.31
84	0.11	142	0.09	198	0.08	257	0.21
86	0.07	143	0.41	199	0.10	258	0.05
87	0.15	144	0.23	200	1.96	263	0.48
88	0.22	145	9.29	201	4.89	264	0.33
89	4.50	146	6.11	202	1.06	265	0.89
90	7.21	147	2.10	203	3.18	266	0.28
91	1.21	148	0.23	204	0.44	267	0.05
92	0.10	149	0.09	205	0.15	269	0.46
93	1.22	150	0.59	206	0.83	270	0.13
94	0.12	151	7.29	207	0.52	271	0.58
95	1.09	152	1.31	208	0.19	272	0.14
96	0.71	153	0.78	209	0.13	273	0.13
97	0.23	154	2.36	211	0.10	274	0.33

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 CM156A'648 (10.801)  REFINE
---------------+---------------+---------------+------------------------
                                                                  716800
 Mass   Rel Int | Mass   Rel Int | Mass   Rel Int | Mass   Rel Int
---------------+---------------+---------------+------------------------
 275     0.54  | 306     0.08  | 351     0.15  | 441     2.14
 276     0.21  | 307     0.07  | 353     1.65  | 442     0.14
 277     0.11  | 313     0.16  | 354     0.34  | 459     0.23
 281     0.39  | 314     0.09  | 355     0.09  | 460     0.04
 282     0.17  | 315     0.53  | 363     0.08  | 513     0.09
 283     0.41  | 316     0.09  | 364     0.08  | 514     0.03
 284     0.35  | 321     0.09  | 365     0.10  | 515     0.03
 285     1.28  | 323     0.06  | 371     0.07  | 533     0.07
 286     0.19  | 324     0.08  | 375     0.06  | 534     0.03
 287     0.12  | 325     0.26  | 383     0.26  | 553     0.06
 289     0.38  | 326     0.06  | 384     0.11  | 554     0.17
 292     0.05  | 332     0.03  | 385     0.15  | 571     0.05
 293     0.16  | 333     0.68  | 389     0.08  | 572     0.04
 294     0.10  | 334     0.11  | 395     0.05  | 583     0.04
 295     0.47  | 335     4.04  | 401     0.11  | 603     0.08
 296     0.13  | 336     0.51  | 403     2.89  | 683     0.09
 297     0.06  | 337     0.07  | 404     0.26  | 703     0.39
 301     0.14  | 339     0.11  | 405     0.06  | 704     0.08
 303     1.13  | 343     0.15  | 421     0.11  | 742     1.21
 304     0.22  | 344     0.23  | 423   100.00  |
 305     0.13  | 345     0.14  | 424    10.00  |
---------------+---------------+---------------+------------------------
```
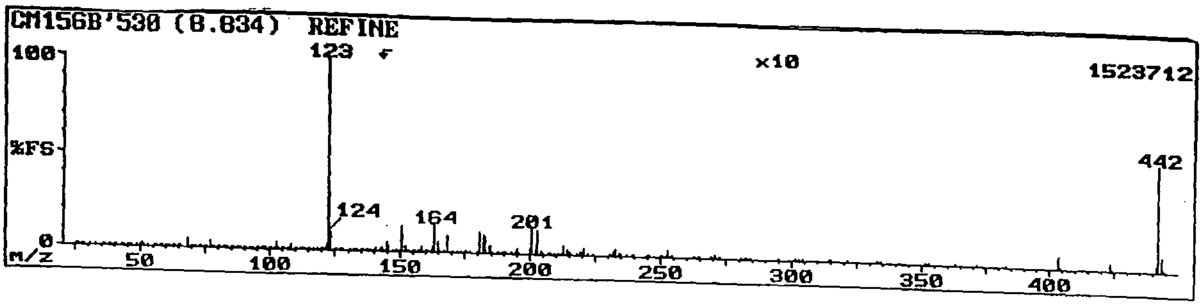

Spectrum No 10 (**14**)

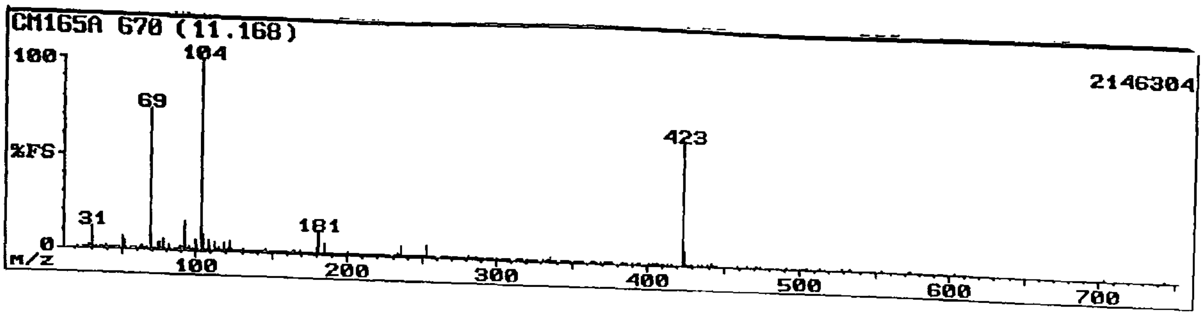


CM156B'530 (8.834) REFINE

1523712

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
31	0.17	94	0.11	152	0.25	216	0.03
33	0.27	95	0.62	153	0.09	218	0.02
36	0.02	96	1.13	154	0.04	219	0.20
37	0.03	97	0.92	155	0.03	220	0.04
38	0.18	98	0.09	156	0.06	221	0.34
39	1.03	99	0.14	157	0.05	222	0.05
40	0.10	100	0.37	158	0.09	224	0.02
41	0.06	101	1.41	159	0.32	231	0.14
43	0.02	102	0.90	160	0.03	232	0.21
44	0.12	103	4.10	161	0.07	233	0.42
45	0.05	104	1.34	162	0.12	234	0.23
46	0.03	105	0.27	163	0.28	235	0.09
47	0.04	106	0.07	164	1.43	237	0.02
49	0.02	107	0.75	165	0.58	239	0.05
50	0.57	108	0.73	166	0.07	240	0.02
51	1.65	109	3.36	167	0.02	245	0.06
52	0.32	110	0.27	169	0.83	246	0.02
53	0.19	111	0.04	170	0.09	250	0.03
56	0.03	112	0.11	171	0.11	251	0.11
57	0.70	113	0.10	172	0.05	252	0.04
58	0.05	114	0.10	174	0.02	253	0.39
59	0.22	115	0.51	175	0.08	254	0.11
60	0.10	116	0.11	176	0.04	263	0.03
61	0.30	117	0.06	177	0.09	264	0.06
62	0.28	119	0.95	180	0.03	265	0.05
63	0.94	120	0.28	181	1.13	269	0.02
64	0.20	121	1.41	182	0.98	271	0.17
65	0.20	122	3.31	183	0.84	272	0.09
66	0.03	123	100.00	184	0.37	273	0.02
69	4.44	124	9.68	185	0.34	281	0.06
70	0.29	125	0.57	186	0.04	282	0.03
71	0.09	126	0.10	187	0.09	283	0.03
72	0.02	127	0.29	188	0.02	284	0.05
73	0.03	128	0.05	189	0.03	295	0.03
74	0.17	131	0.22	190	0.01	301	0.02
75	0.55	132	0.12	191	0.03	303	0.14
76	0.23	133	1.19	193	0.10	304	0.02
77	3.60	134	0.26	194	0.02	314	0.02
78	0.59	135	0.19	195	0.24	315	0.02
79	0.06	136	0.02	196	0.05	321	0.02
80	0.02	137	0.07	200	0.31	333	0.04
81	0.26	138	0.10	201	1.28	334	0.07
82	0.11	139	0.09	202	0.26	351	0.02
83	1.08	140	0.19	203	1.19	353	0.06
84	0.09	141	1.86	204	0.16	363	0.02
85	0.02	142	0.19	205	0.03	371	0.02
86	0.07	143	0.20	207	0.05	383	0.07
87	0.12	144	0.09	208	0.03	403	0.65
88	0.09	145	0.48	209	0.03	404	0.09
89	0.71	146	0.26	211	0.02	423	0.34
90	0.30	147	0.05	212	0.03	424	0.06
91	0.24	149	0.04	213	0.52	441	0.27
92	0.06	150	0.10	214	0.28	442	5.38
93	0.24	151	1.31	215	0.23	443	0.79

Spectrum No 11 (**15**)



CM165A 670 (11.168)

2146304

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
31	11.74	101	1.36	161	0.20	216	0.25
32	0.37	104	100.00	162	0.56	217	0.07
33	0.33	105	8.97	163	0.79	218	0.16
35	0.03	106	0.65	164	1.87	219	0.53
36	0.09	107	0.46	165	1.62	220	0.31
37	0.37	109	5.58	166	0.33	221	0.32
38	0.51	110	0.39	167	0.09	222	0.08
39	2.06	112	5.10	168	0.78	223	0.14
40	0.22	113	0.91	169	1.80	224	0.16
41	0.40	115	2.16	170	0.21	225	0.16
42	0.09	116	0.54	171	0.21	226	0.12
43	0.61	117	0.30	172	0.10	227	0.16
44	0.50	119	4.39	173	0.10	228	0.04
45	0.21	120	0.41	174	0.12	230	0.14
47	0.28	121	1.63	175	0.19	231	1.06
48	0.12	122	5.39	176	0.15	232	0.62
50	6.58	123	1.69	177	0.28	233	1.79
51	4.91	124	0.76	178	0.09	234	1.28
52	1.26	125	0.29	180	4.25	235	5.44
53	0.33	126	0.28	181	11.59	236	0.62
55	0.69	127	0.49	182	1.18	237	0.16
56	0.27	128	0.14	183	0.88	238	0.09
57	0.73	129	0.06	184	2.21	239	0.19
58	0.04	130	0.50	185	5.96	240	0.13
59	0.14	131	1.55	186	0.70	241	0.04
62	1.31	132	0.46	187	0.19	242	0.05
63	1.94	133	0.91	188	0.12	243	0.10
64	0.54	134	0.28	189	0.17	244	0.09
65	0.80	135	0.19	190	0.12	245	0.42
66	0.19	136	0.07	191	0.04	246	0.18
69	74.05	137	0.15	192	0.20	247	0.08
70	0.64	138	0.17	193	0.69	248	0.02
71	0.09	139	0.29	194	0.38	249	0.02
74	3.63	140	0.57	195	1.11	250	0.08
75	3.77	141	0.20	196	0.41	251	0.41
76	1.41	142	0.47	197	0.16	253	7.16
77	3.82	143	1.16	198	0.02	254	1.23
78	5.96	144	0.80	199	0.47	255	0.20
79	0.74	145	2.15	200	1.96	256	0.08
81	2.65	146	1.24	201	1.17	257	0.06
82	0.55	147	0.41	202	0.38	258	0.06
83	0.89	148	0.07	203	0.74	259	0.02
85	0.58	149	0.25	204	0.15	262	0.05
86	0.24	150	1.04	205	0.08	263	0.14
87	0.34	151	1.37	206	0.22	264	0.14
89	1.93	152	0.26	207	0.07	265	0.29
90	1.85	153	0.28	208	0.04	266	0.12
91	1.42	154	0.32	209	0.03	267	0.02
93	15.46	155	0.05	210	0.02	268	0.02
94	0.75	156	0.10	211	0.18	269	0.13
95	1.60	157	0.14	212	0.73	270	0.07
96	0.46	158	0.13	213	0.82	271	0.22
97	0.19	159	0.11	214	1.11	272	0.08
100	6.25	160	0.03	215	1.32	273	0.08

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-------------------------------------------------------------------------
CM165A 670 (11.168)                                               2146304
-----------------+------------------+------------------+-----------------
Mass   Rel Int   | Mass   Rel Int   | Mass   Rel Int   | Mass   Rel Int
-----------------+------------------+------------------+-----------------
 274    0.10     | 316     0.07     | 364     0.04     | 427     0.04
 275    0.15     | 317     0.01     | 365     0.15     | 428     0.12
 276    0.07     | 319     0.03     | 366     0.03     | 430     0.02
 277    0.04     | 320     0.02     | 369     0.03     | 433     0.01
 278    0.01     | 321     0.05     | 371     0.06     | 435     0.01
 281    1.92     | 322     0.01     | 372     0.01     | 439     0.05
 282    0.17     | 323     0.02     | 373     0.02     | 441     1.91
 283    0.17     | 324     0.03     | 375     0.04     | 443     0.25
 284    0.13     | 325     0.10     | 376     0.01     | 444     0.03
 285    0.36     | 326     0.04     | 382     0.01     | 445     0.01
 286    0.07     | 327     0.01     | 383     0.16     | 445     0.02
 287    0.06     | 331     0.02     | 384     0.09     | 460     0.06
 288    0.02     | 333     0.35     | 385     0.20     | 466     0.01
 289    0.11     | 334     0.12     | 386     0.04     | 472     0.01
 290    0.02     | 335     2.66     | 389     0.08     | 474     0.01
 291    0.01     | 336     0.31     | 390     0.02     | 492     0.12
 293    0.06     | 337     0.05     | 393     0.01     | 505     0.01
 294    0.04     | 338     0.01     | 394     0.02     | 514     0.03
 295    0.20     | 339     0.04     | 395     0.03     | 528     0.02
 296    0.06     | 343     0.09     | 401     0.06     | 534     0.02
 297    0.03     | 344     0.12     | 403     1.37     | 535     0.02
 300    0.05     | 345     0.08     | 404     0.22     | 554     0.04
 301    0.11     | 346     0.02     | 405     0.05     | 555     0.02
 303    0.34     | 347     0.01     | 406     0.01     | 573     0.04
 304    0.07     | 349     0.01     | 407     0.01     | 574     0.02
 305    0.06     | 351     0.11     | 409     0.03     | 604     0.02
 306    0.04     | 353     1.37     | 410     0.01     | 704     0.02
 307    0.03     | 354     0.25     | 413     0.01     | 743     0.04
 308    0.01     | 355     0.07     | 415     0.01     | 744     0.01
 313    0.09     | 356     0.04     | 423    64.12     |
 314    0.07     | 357     0.03     | 425     7.87     |
 315    0.38     | 363     0.08     | 426     0.55     |
-----------------+------------------+------------------+-----------------
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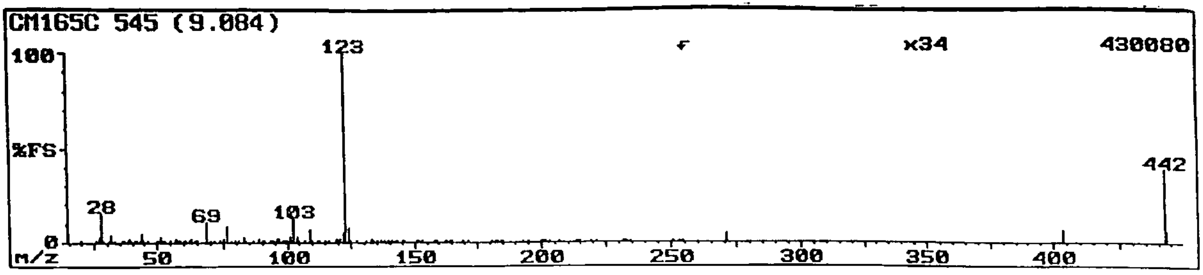
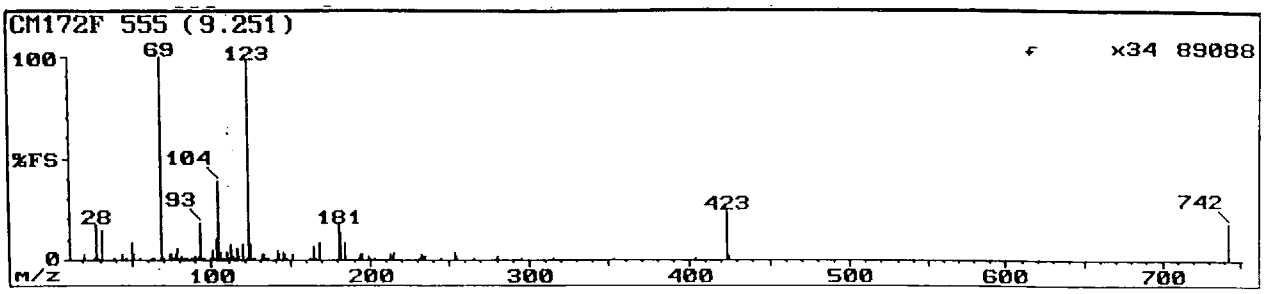
Spectrum No 12 (16)



CM165C 545 (9.084) 430080

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
31	0.62	74	0.47	116	0.14	181	1.09
32	3.87	75	1.47	119	1.62	182	0.90
33	0.68	77	8.63	120	0.26	183	0.66
36	0.21	78	1.28	121	1.55	184	0.24
37	0.09	79	0.15	122	4.52	185	0.18
38	0.26	81	0.68	123	100.00	193	0.12
39	2.43	83	2.50	124	7.68	195	0.22
40	0.53	84	0.18	125	0.45	200	0.22
41	0.84	87	0.29	127	0.39	201	1.24
42	0.47	89	1.46	131	0.25	202	0.20
43	1.06	90	0.44	133	1.49	203	0.67
44	5.06	91	0.57	134	0.27	207	0.21
45	0.22	93	0.63	135	0.21	213	0.42
46	0.10	94	0.13	137	0.07	214	0.23
50	1.41	95	1.21	138	0.09	215	0.15
51	3.07	96	2.10	140	0.11	219	0.17
52	0.60	97	1.83	141	1.32	221	0.37
53	0.42	98	0.18	142	0.12	231	0.12
55	0.21	99	0.21	143	0.23	232	0.17
57	1.50	100	0.69	145	0.51	233	0.29
58	0.13	101	2.50	146	0.17	234	0.09
59	0.28	102	1.09	151	1.44	251	0.08
60	0.12	103	13.10	152	0.23	253	0.26
61	0.18	104	3.02	153	0.12	254	0.11
62	0.61	105	0.49	158	0.11	271	0.13
63	1.98	107	1.04	159	0.18	403	0.19
64	0.45	109	6.67	163	0.28	442	1.13
65	0.28	110	0.48	164	1.35	443	0.18
69	10.30	112	0.15	165	0.47		
70	0.51	113	0.15	169	0.84		
71	0.14	115	0.70	171	0.11		

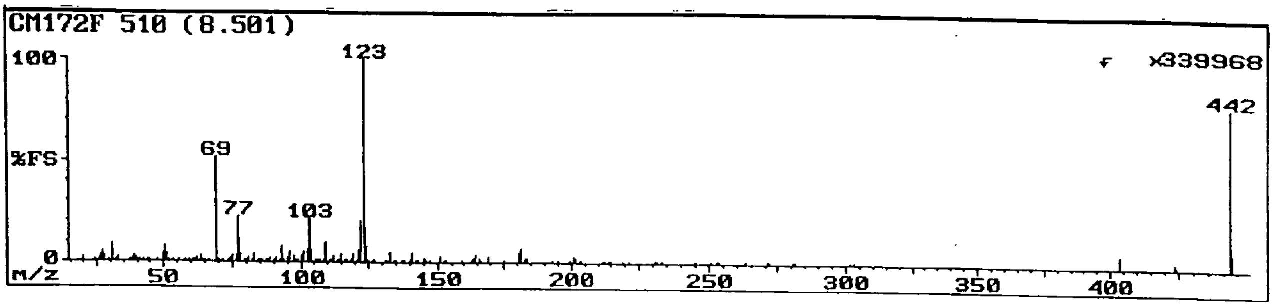
Spectrum No 13 (**17**)



CM172F 555 (9.251) 89088

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
31	14.37	91	0.88	124	7.90	203	0.62
32	2.21	92	1.76	125	0.77	213	2.80
39	1.06	93	18.18	127	0.51	213	2.07
44	3.14	94	0.94	131	2.78	215	3.90
47	1.17	95	1.26	133	2.50	215	2.44
50	8.26	96	0.48	134	0.92	231	1.22
51	3.29	99	0.57	135	0.53	231	1.04
55	1.17	100	5.24	141	5.24	233	2.89
62	0.92	101	1.17	143	3.04	234	1.56
63	1.04	102	1.42	145	4.33	235	1.98
69	100.00	103	10.27	146	3.18	245	0.42
70	0.55	104	38.79	147	0.67	253	2.23
74	3.36	105	4.18	151	3.09	254	4.09
75	2.55	107	0.43	162	0.86	254	2.10
76	0.58	108	0.66	165	3.39	265	0.63
77	3.16	109	3.92	165	6.54	281	1.89
78	5.75	110	0.35	166	0.79	295	0.54
79	0.47	111	0.48	169	8.69	315	0.69
81	2.24	112	7.33	181	17.46	353	0.53
82	0.65	113	1.80	181	13.43	403	1.15
83	0.52	114	0.62	185	8.91	423	23.85
85	0.64	115	5.89	193	0.87	424	2.30
87	0.29	116	1.92	195	2.64	742	0.53
88	0.25	119	7.40	195	2.50		
89	1.53	121	0.48	200	1.69		
90	0.93	123	97.70	200	1.10		

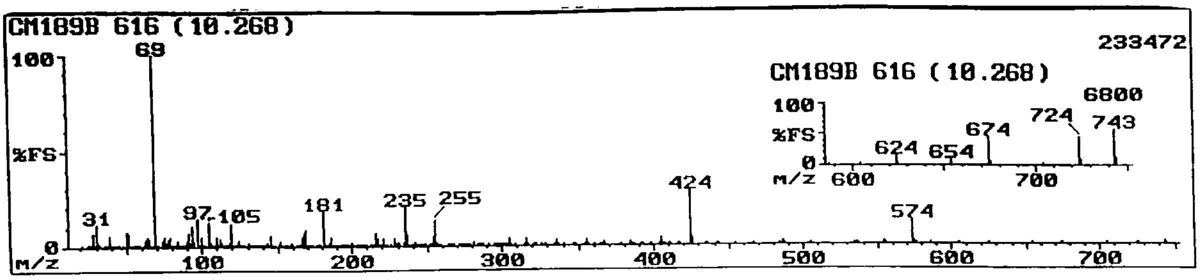
Spectrum No 14 (18)



CM172F 510 (8.501) 339968

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
31	8.43	79	0.46	116	0.76	181	7.08
32	0.81	80	0.22	117	0.16	183	2.01
33	1.56	81	1.69	118	0.30	183	2.18
37	0.64	82	0.76	119	4.14	193	0.65
38	0.40	83	4.35	120	1.05	195	0.65
39	2.56	84	0.38	121	6.17	200	0.95
39	1.90	85	0.32	122	20.18	201	3.24
40	0.16	86	0.26	123	100.00	201	2.20
41	0.22	87	0.41	124	8.13	203	1.26
43	0.30	88	0.40	125	0.68	204	0.72
44	1.10	89	1.90	126	0.14	212	0.30
45	0.69	90	0.89	127	0.63	213	1.32
47	0.21	91	2.28	131	1.22	214	1.28
50	3.73	92	0.78	133	4.82	214	0.49
51	7.30	93	7.68	134	1.28	219	0.35
51	4.14	94	0.72	135	0.46	221	0.42
52	1.28	95	2.26	137	0.20	231	0.49
53	0.45	96	5.20	138	0.22	232	0.79
55	0.20	97	3.20	140	1.37	233	0.88
57	1.12	98	0.34	141	4.56	234	0.58
59	0.48	99	0.49	142	0.70	245	0.14
60	0.13	100	2.99	143	1.13	251	0.20
61	0.48	101	4.97	145	1.52	253	0.32
62	1.75	102	5.42	146	0.71	254	0.17
63	3.18	103	21.08	147	0.09	263	0.14
64	0.74	104	5.65	151	2.45	271	0.15
65	0.90	105	1.37	152	0.49	272	0.07
66	0.16	106	0.36	153	0.20	281	0.57
69	51.20	107	1.19	159	0.33	281	0.42
70	1.03	108	1.45	163	0.38	301	0.16
71	0.41	109	9.56	164	1.83	303	0.16
73	0.35	110	0.65	164	3.75	403	0.42
74	2.30	111	0.30	165	2.07	423	0.21
75	3.11	112	2.90	166	0.23	424	0.05
76	2.75	113	0.79	169	2.52	442	5.42
77	22.59	114	0.53	175	0.15	443	0.50
78	4.18	115	3.93	181	4.73		

Spectrum No 15 (19)



CM189B 616 (10.268) 233472

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.23	86	0.10	146	0.58	207	0.75
24	0.11	87	0.27	147	0.60	208	1.01
25	0.29	88	0.39	148	0.73	209	0.96
26	1.22	89	0.51	150	1.18	210	0.07
27	1.04	90	2.49	151	1.34	212	0.95
28	6.55	91	6.83	152	2.47	213	0.75
29	0.16	92	1.47	153	1.22	214	1.32
31	11.51	93	10.96	154	0.28	215	0.84
32	1.81	94	0.80	156	0.29	216	7.24
33	0.40	95	2.44	156	0.11	217	4.28
35	0.16	97	14.91	157	0.30	218	0.61
36	0.19	98	0.64	159	0.18	219	0.14
37	0.51	100	5.15	159	1.49	220	0.57
38	0.84	101	0.93	160	0.23	221	3.62
39	5.59	102	0.66	162	0.81	222	0.96
40	0.92	104	3.97	163	1.08	223	0.07
41	1.19	105	12.72	164	0.39	225	0.25
42	0.18	106	2.08	165	0.25	226	0.28
43	0.38	107	0.45	166	5.02	228	4.22
44	0.83	109	0.75	167	6.39	229	0.43
45	0.33	109	0.57	169	8.77	231	1.53
47	0.20	110	4.85	170	1.14	232	0.40
48	0.09	111	0.67	171	0.42	234	2.06
50	7.57	112	4.30	172	1.21	235	19.96
51	6.52	113	1.69	173	0.08	236	5.59
52	1.50	114	0.51	174	0.09	237	0.57
53	0.47	115	0.45	176	0.68	238	0.24
54	0.28	116	0.23	177	0.64	239	0.09
55	0.44	117	0.38	178	0.20	240	0.47
56	0.28	118	1.58	179	0.11	241	1.48
57	0.87	119	11.29	181	18.09	242	0.11
59	0.32	120	0.61	182	0.92	244	0.15
61	0.27	121	0.37	183	0.35	245	0.47
62	1.81	122	0.35	184	0.56	246	0.44
63	3.73	123	1.23	185	1.51	247	0.17
64	4.88	124	3.07	186	4.47	248	0.75
65	4.19	125	0.61	187	0.89	249	0.06
66	0.91	126	0.39	188	0.35	251	0.17
67	0.26	127	0.36	189	0.52	252	0.15
69	100.00	128	0.28	190	0.51	253	0.57
70	1.22	131	1.89	191	0.18	254	4.66
71	0.21	132	0.25	193	0.77	255	13.82
74	2.63	133	0.16	194	0.75	256	1.81
75	4.69	134	0.31	195	0.91	257	0.27
76	1.70	135	0.22	196	1.02	258	0.45
77	3.95	136	0.14	197	0.25	259	0.14
78	4.77	137	0.38	198	0.40	264	0.13
79	1.08	138	0.33	200	1.89	265	0.14
80	0.22	139	0.70	201	1.10	266	0.66
81	1.07	140	0.45	202	0.76	267	0.32
82	0.27	141	0.23	203	0.49	268	0.14
83	3.04	143	2.06	204	0.47	271	0.24
84	1.48	144	0.28	205	0.10	272	0.16
85	0.39	145	5.70	206	0.06	273	0.45

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 CM189B 616 (10.268)                                                233472
-----------------+------------------+------------------+-------------------
 Mass   Rel Int  | Mass   Rel Int   | Mass   Rel Int   | Mass   Rel Int
-----------------+------------------+------------------+-------------------
 274     0.06    | 316      3.84    | 385      0.58    | 487      0.22
 275     0.17    | 317      0.60    | 386      0.32    | 504      0.17
 276     0.36    | 321      0.69    | 391      0.62    | 534      0.09
 277     0.16    | 322      0.07    | 392      0.09    | 536      1.21
 278     0.45    | 326      0.09    | 397      0.17    | 537      0.17
 281     2.38    | 328      0.15    | 398      0.21    | 554      1.86
 284     0.21    | 334      0.19    | 404      0.47    | 555      0.30
 285     0.32    | 335      2.52    | 405      3.87    | 574     12.83
 286     1.28    | 336      2.82    | 406      0.26    | 575      2.03
 287     0.09    | 337      0.35    | 407      0.12    | 576      0.15
 291     0.97    | 341      0.68    | 410      1.38    | 586      0.08
 295     0.13    | 346      0.30    | 411      0.23    | 604      0.11
 296     0.49    | 347      0.11    | 416      0.65    | 624      0.44
 297     0.38    | 348      0.14    | 417      0.08    | 625      0.07
 298     0.60    | 354      0.35    | 424     28.07    | 654      0.29
 299     0.08    | 355      2.44    | 425      3.73    | 674      1.32
 300     0.07    | 356      0.25    | 426      0.32    | 675      0.14
 301     0.17    | 360      0.24    | 434      0.06    | 704      0.13
 302     0.11    | 364      0.27    | 436      0.75    | 724      1.36
 303     0.06    | 365      0.30    | 442      1.06    | 725      0.28
 305     4.28    | 366      1.67    | 443      0.12    | 743      1.72
 306     0.55    | 367      0.29    | 454      0.13    | 744      0.33
 308     0.13    | 377      0.10    | 466      0.35    |
 314     0.41    | 378      0.09    | 484      0.23    |
 315     0.10    | 384      1.97    | 486      1.50    |
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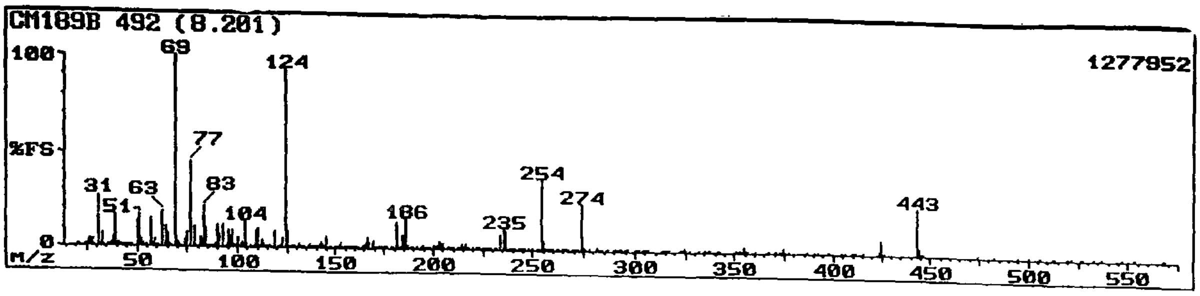
Spectrum No 16 (20)



CM189B 492 (8.201) 1277952

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.36	84	9.86	141	0.18	198	0.22
21	0.02	85	0.92	142	3.23	200	1.56
24	0.55	86	0.25	143	1.98	201	1.00
25	0.75	87	0.57	144	0.52	202	2.20
26	3.61	88	0.91	145	5.69	203	3.45
27	3.81	89	1.96	146	1.34	204	2.92
28	4.13	90	11.62	147	0.23	205	3.00
29	0.17	91	6.81	148	0.27	206	0.36
31	15.38	93	12.10	149	0.13	207	0.86
32	1.27	94	1.40	150	1.13	208	0.48
33	7.05	95	9.21	151	0.82	209	0.21
34	0.08	96	6.17	152	2.48	210	0.04
35	0.07	97	8.65	153	1.38	212	0.94
36	0.34	98	2.08	154	0.34	213	0.45
37	2.28	99	1.36	155	0.17	214	2.50
38	5.21	100	5.29	156	0.45	215	0.90
39	16.19	101	1.14	157	0.73	216	3.19
40	1.88	102	3.00	158	0.59	217	0.92
41	1.94	103	2.40	159	0.56	218	0.15
42	0.58	104	13.38	160	0.56	220	1.11
43	0.63	105	2.32	161	0.29	221	1.34
44	1.04	106	0.75	162	0.66	222	0.99
45	0.90	107	0.59	163	1.38	223	0.10
46	0.35	108	0.78	164	1.72	224	0.02
47	0.41	109	8.41	165	2.74	225	0.23
48	0.50	110	10.18	166	6.25	226	0.23
50	13.94	111	1.38	167	3.04	227	0.24
51	16.27	112	3.97	169	4.17	228	0.32
52	4.15	113	1.88	170	1.01	229	0.03
53	1.84	114	0.79	171	0.37	231	1.09
54	0.87	115	0.92	172	0.81	232	0.51
55	0.81	116	0.84	173	0.16	234	8.17
57	14.42	117	0.60	174	0.24	235	10.74
58	1.94	118	1.30	175	0.32	236	9.46
59	3.71	119	9.13	176	0.82	237	1.00
60	0.86	120	0.70	177	0.79	238	0.07
61	1.19	121	0.86	178	0.22	239	0.06
63	18.51	122	5.13	179	0.04	240	0.32
64	10.66	124	93.59	181	13.86	241	0.12
65	6.97	125	8.57	182	0.94	243	0.06
66	1.52	126	1.38	183	0.85	244	0.13
67	0.33	127	0.95	184	7.13	245	0.25
69	100.00	128	0.37	185	6.65	246	0.38
70	2.68	129	0.08	186	15.87	247	0.08
71	2.14	131	2.02	187	2.30	248	0.07
72	0.64	132	0.71	188	0.54	249	0.03
74	3.63	133	0.47	189	0.43	250	0.05
75	7.45	134	1.00	190	0.30	252	0.97
77	44.23	135	1.36	191	0.12	254	36.86
78	11.14	136	1.98	193	0.91	255	4.43
79	1.24	137	0.81	194	1.62	256	0.24
81	4.43	138	0.65	195	0.91	257	0.07
82	3.91	139	0.96	196	0.82	258	0.02

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 CM189B 492 (8.201)                                                      1277952
-------------------+-------------------+-------------------+--------------------
 Mass    Rel Int   | Mass    Rel Int   | Mass    Rel Int   | Mass    Rel Int
-------------------+-------------------+-------------------+--------------------
  260      0.01    |  294      0.03    |  342      0.04    |  424      1.68
  262      0.05    |  295      0.06    |  350      0.01    |  424      7.93
  263      0.05    |  296      0.05    |  353      0.04    |  425      1.01
  264      0.09    |  300      0.03    |  354      2.46    |  426      0.08
  265      0.14    |  301      0.05    |  355      0.36    |  443     24.04
  266      0.74    |  302      0.06    |  356      0.02    |  444      4.17
  267      0.13    |  304      0.46    |  360      0.09    |  445      0.34
  269      0.03    |  305      0.61    |  366      0.01    |  446      0.01
  270      0.03    |  306      0.06    |  370      0.02    |  474      0.02
  271      0.07    |  307      0.02    |  372      0.06    |  482      0.05
  272      0.63    |  313      0.02    |  373      0.06    |  494      0.02
  274     24.36    |  314      0.08    |  374      2.94    |  500      0.03
  275      2.16    |  315      0.02    |  375      0.33    |  506      0.02
  276      0.16    |  316      0.11    |  376      0.02    |  512      0.07
  278      0.01    |  317      0.03    |  386      0.02    |  513      0.02
  281      1.66    |  322      0.06    |  390      0.02    |  520      0.08
  282      0.15    |  323      0.17    |  392      0.02    |  521      0.02
  283      0.03    |  324      2.06    |  397      0.01    |  526      0.07
  284      0.15    |  325      0.24    |  404      0.22    |  527      0.02
  286      1.32    |  327      0.01    |  405      0.06    |  533      0.05
  287      0.18    |  332      0.02    |  406      0.02    |  536      0.01
  290      0.05    |  334      0.08    |  410      0.02    |  547      0.04
  291      0.05    |  336      0.48    |  410      0.08    |  553      0.02
  292      0.03    |  337      0.06    |  411      0.01    |  567      0.29
  293      0.02    |  341      0.03    |  415      0.01    |  568      0.07
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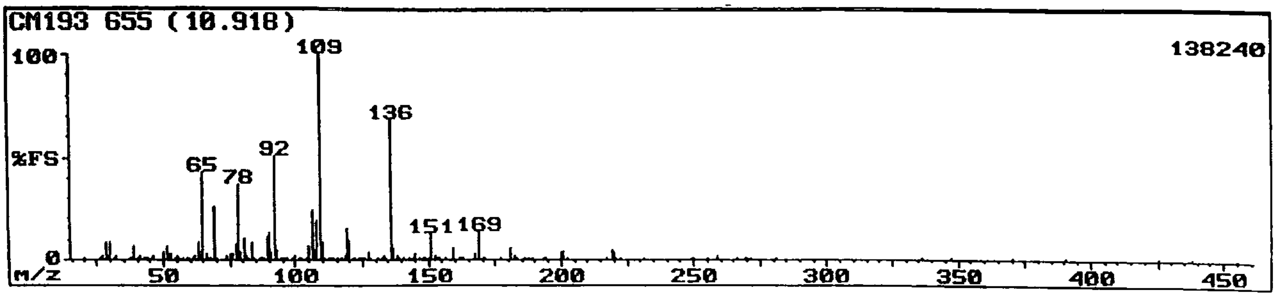
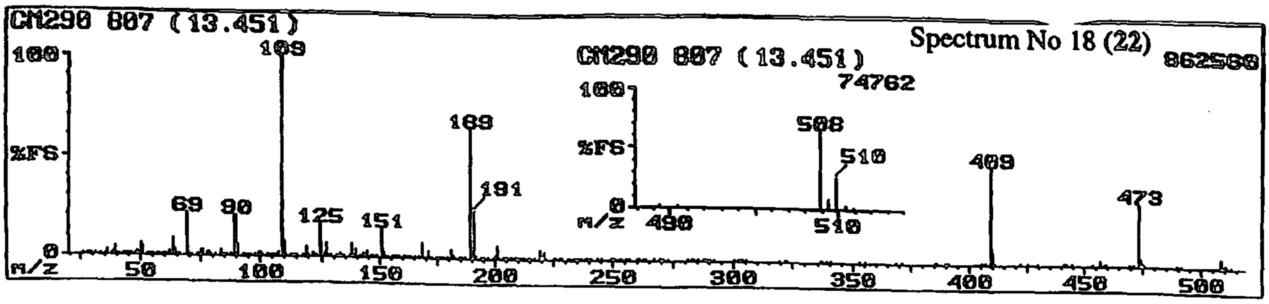
Spectrum No 17 (**21**)



CM193 655 (10.918) 138240

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.22	74	1.49	115	0.34	167	2.96
26	0.64	75	3.19	117	0.27	169	13.89
27	2.15	76	2.86	118	1.69	170	1.16
28	8.38	77	8.01	119	15.19	171	0.47
29	1.61	78	37.22	120	9.63	177	0.52
30	8.47	79	4.17	121	1.15	181	5.79
31	1.16	80	10.97	122	0.34	182	1.47
32	1.96	81	2.21	123	0.82	183	0.36
37	0.32	82	0.25	124	0.56	186	0.54
38	1.34	83	8.33	125	1.37	187	0.35
39	6.67	84	0.54	126	0.80	189	0.24
40	1.12	86	0.43	127	3.70	193	0.24
41	2.35	87	0.72	128	0.32	194	0.17
42	0.18	88	0.42	131	1.11	200	3.89
43	0.16	89	12.04	132	0.64	201	3.52
44	1.26	90	13.70	133	1.48	202	0.58
45	0.32	91	3.89	134	0.58	217	1.26
46	1.56	92	50.37	136	68.15	219	5.00
50	3.98	93	5.05	137	5.37	220	3.56
51	6.76	94	0.67	138	1.63	221	0.60
52	3.15	95	0.87	139	0.74	222	0.43
53	2.96	96	0.65	140	0.57	231	0.60
54	0.36	97	0.86	143	0.78	249	0.71
55	1.52	99	1.01	144	0.26	250	0.96
56	1.37	100	2.09	145	2.71	255	0.29
57	1.37	101	1.45	146	0.26	259	1.64
59	0.84	102	0.96	148	0.35	266	0.43
60	0.16	104	1.24	149	0.66	269	0.39
61	0.32	105	7.18	150	0.68	270	0.20
62	2.21	106	24.26	151	12.59	271	0.30
63	8.75	107	4.68	152	1.93	281	0.21
64	3.94	108	19.26	153	0.54	336	0.22
65	42.59	109	100.00	154	0.20	347	1.19
66	3.24	110	8.89	156	0.23	370	0.29
67	0.28	111	0.68	159	5.37	390	0.36
68	0.32	112	0.61	161	0.23	425	0.78
69	25.93	113	0.55	162	0.29	438	0.53
70	0.55	114	0.47	163	0.47	455	1.20



CM290 807 (13.451)

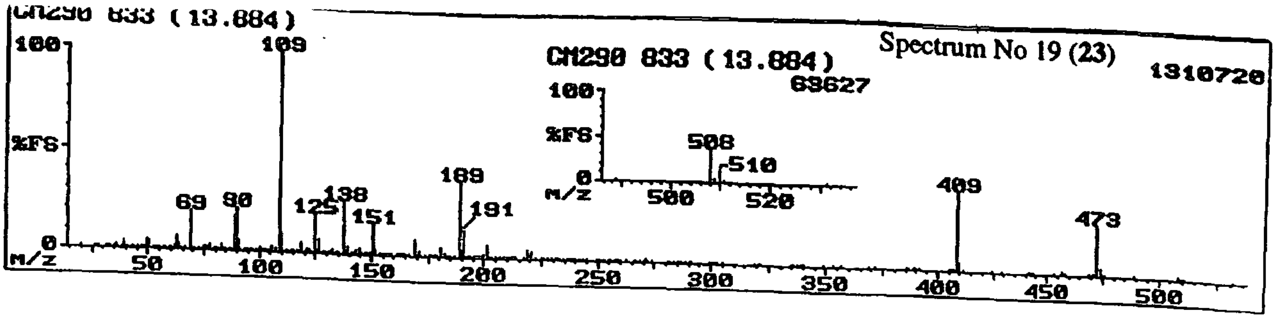
962560

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.05	90	20.21	154	0.11	217	0.16
27	0.08	91	6.20	155	0.31	219	4.55
28	0.91	92	0.62	156	0.71	220	2.26
29	0.05	93	0.78	157	0.49	221	3.51
31	0.38	94	0.23	158	0.23	222	0.38
32	0.40	95	0.89	159	0.68	225	0.07
33	0.07	96	0.59	160	0.14	226	0.11
35	0.68	97	0.37	161	0.42	227	0.03
36	2.95	99	1.70	162	0.33	228	0.30
37	0.42	100	1.48	163	0.64	231	0.69
38	1.94	101	1.26	164	0.40	232	0.70
39	5.00	102	0.80	165	0.09	233	0.28
40	1.01	103	0.10	167	0.24	234	0.08
41	0.19	104	0.03	169	7.87	235	0.21
42	0.02	105	0.32	170	1.44	236	0.12
43	0.06	106	0.37	171	3.88	237	0.23
44	0.52	107	1.65	172	0.44	238	0.22
45	1.38	109	100.00	173	0.43	239	1.06
46	0.04	110	8.09	174	0.15	240	1.06
47	0.03	111	0.81	175	0.49	241	0.15
48	1.78	112	0.52	176	0.30	243	0.04
49	0.09	113	0.40	177	0.78	245	0.05
50	5.61	114	0.35	178	0.05	249	0.15
51	4.89	115	0.08	179	0.09	250	0.57
52	1.00	117	0.10	181	5.00	251	0.74
53	0.12	119	4.79	182	2.18	252	0.20
54	0.09	120	0.82	183	0.92	253	0.05
55	0.12	121	1.89	184	0.11	255	0.11
57	1.14	122	0.88	185	0.14	256	0.09
58	0.08	123	1.30	187	0.76	257	0.07
59	0.24	125	16.60	189	65.53	260	0.52
60	0.05	126	1.73	190	5.98	261	0.06
62	1.99	127	6.65	191	23.94	262	0.02
63	8.62	128	0.54	192	1.89	263	0.03
64	2.87	129	0.09	193	0.82	267	0.05
65	1.36	131	0.98	194	0.18	269	0.34
66	0.37	132	0.41	195	0.39	270	0.08
69	21.70	133	1.99	197	0.07	271	1.24
70	0.59	134	0.32	199	0.45	272	0.17
71	0.23	135	0.05	200	1.86	281	0.47
73	0.26	137	0.55	201	6.38	282	0.07
74	1.14	138	7.23	202	1.22	283	0.03
75	2.58	139	1.42	203	0.17	285	0.49
76	3.27	140	3.40	204	0.06	287	0.15
77	1.69	141	0.45	205	0.16	288	0.03
78	1.97	143	1.73	207	1.23	289	0.30
79	0.22	144	0.25	208	0.15	290	0.37
81	0.59	145	3.11	209	0.47	291	0.04
83	2.69	146	0.25	210	0.11	300	0.07
84	0.30	147	0.07	211	0.07	301	0.25
85	0.31	149	0.44	212	0.07	302	0.07
86	0.29	151	14.15	213	0.40	303	0.07
87	0.48	152	2.63	214	0.09	305	0.04
89	19.36	153	0.30	215	0.04	319	0.15

CM290 807 (13.451)

962560

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
321	0.48	386	0.07	429	0.03	474	4.34
322	0.05	389	1.14	441	0.30	475	1.66
336	0.06	390	0.98	442	0.35	476	0.20
337	0.04	391	0.13	444	0.09	489	0.09
339	0.14	405	0.11	453	0.16	491	0.03
340	0.07	407	0.06	457	2.58	508	5.08
353	0.08	409	48.51	458	0.49	509	0.66
355	0.04	410	6.36	459	0.15	510	2.02
369	0.17	411	0.44	469	0.26	511	0.26
371	0.10	422	0.04	471	0.09	512	0.10
385	0.06	425	0.10	473	31.49		



CM290 833 (13.884)

1310720

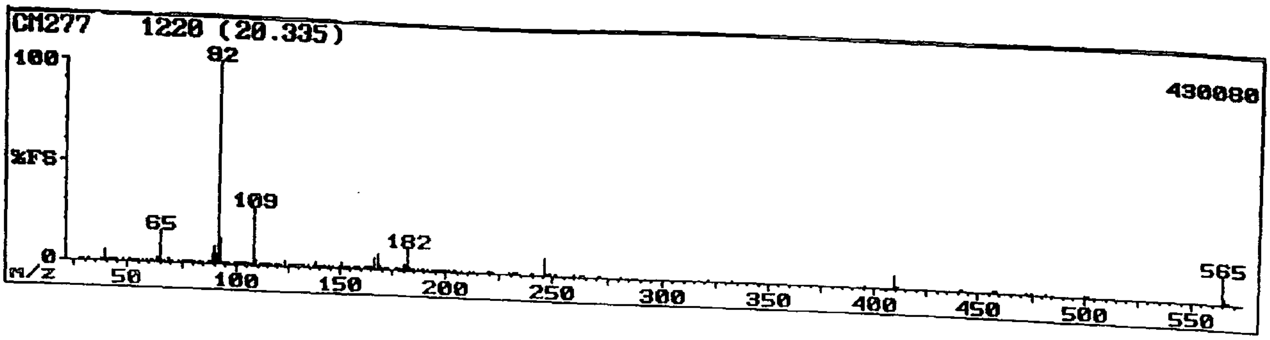
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	91	6.09	157	0.49	221	3.55
26	0.02	92	0.53	158	0.25	222	0.36
27	0.15	93	0.74	159	0.62	225	0.09
28	0.64	94	0.56	161	0.39	226	0.11
31	0.33	95	0.81	162	0.29	228	1.10
32	0.28	96	0.48	163	0.68	229	0.12
33	0.09	97	0.25	164	0.42	231	0.70
35	0.47	99	1.04	165	0.08	232	0.74
36	1.76	100	1.48	167	0.22	233	0.26
37	0.30	101	1.14	169	8.36	235	0.24
38	1.35	102	0.78	170	1.37	236	0.13
39	3.96	103	0.10	171	3.11	237	0.23
40	0.84	104	0.02	172	0.35	238	0.21
41	0.14	105	0.27	173	0.11	239	0.88
43	0.08	106	2.62	174	0.13	240	0.63
44	0.32	107	1.80	175	0.34	241	0.06
45	0.96	109	100.00	176	0.28	243	0.04
47	0.04	110	8.28	177	0.79	245	0.09
48	1.35	111	0.60	178	0.10	249	0.11
49	0.05	112	0.42	179	0.09	250	0.51
50	4.71	113	0.31	181	4.88	251	0.76
51	4.10	114	0.31	182	2.32	252	0.19
52	0.65	115	0.08	183	0.90	253	0.07
53	0.12	117	0.06	184	0.10	255	0.13
54	0.04	119	4.98	185	0.17	256	0.05
55	0.04	120	0.88	187	0.83	257	0.07
57	0.91	121	1.97	189	37.50	258	0.04
58	0.15	122	1.99	190	3.54	259	0.04
59	0.28	123	1.27	191	13.59	260	0.04
60	0.13	125	19.14	192	1.05	263	0.02
62	1.70	126	1.95	193	0.85	266	0.03
63	6.72	127	7.27	194	0.13	267	0.03
64	3.18	128	0.58	195	0.39	269	0.41
65	1.01	129	0.07	196	0.04	270	0.11
66	0.36	131	1.00	197	0.04	271	1.56
69	19.61	132	0.44	198	0.08	272	0.18
70	0.35	133	2.01	199	0.21	274	0.05
71	0.14	134	0.29	200	2.25	281	0.42
72	0.04	135	0.06	201	6.64	282	0.05
74	0.97	138	14.92	202	1.04	283	0.03
75	1.78	139	2.11	203	0.18	285	0.77
76	1.82	140	3.81	205	0.14	286	0.08
77	1.27	141	0.41	206	0.06	287	0.24
78	3.16	143	2.03	207	0.60	288	0.03
79	0.29	145	3.30	208	0.31	289	0.34
80	0.08	146	0.22	209	0.28	290	0.38
81	0.49	147	0.07	210	0.05	291	0.03
83	2.75	149	0.46	211	0.07	299	0.02
84	0.34	151	15.63	212	0.10	300	0.07
85	0.28	152	2.79	213	0.42	301	0.24
86	0.28	153	0.29	214	0.03	302	0.04
87	0.44	154	0.27	217	0.16	303	0.06
89	17.73	155	0.28	219	4.53	305	0.05
90	21.25	156	0.49	220	2.23	319	0.13

CM290 833 (13.884)

1310720

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
321	0.55	385	0.07	429	0.04	474	3.42
322	0.07	386	0.02	441	0.16	475	1.18
335	0.03	389	1.33	442	0.20	476	0.15
336	0.02	390	1.17	443	0.03	489	0.06
337	0.04	391	0.14	444	0.07	508	1.78
339	0.14	405	0.11	453	0.11	509	0.21
340	0.07	406	0.03	457	1.72	510	0.63
349	0.01	407	0.03	458	0.29	511	0.08
353	0.10	409	39.38	459	0.09	531	0.04
357	0.01	410	4.80	469	0.11		

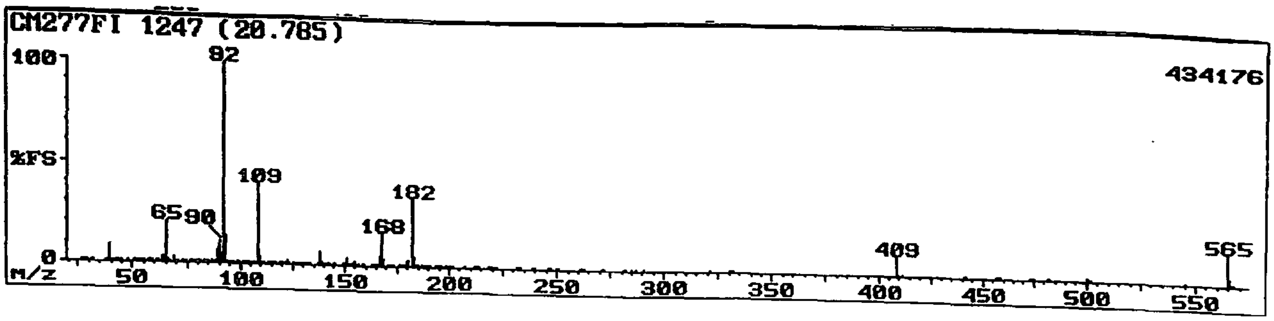
Spectrum No 20 (24)



CM277 1220 (20.335) 430080

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
27	0.16	92	100.00	146	0.07	211	0.06
28	0.77	93	12.20	150	0.13	213	0.11
29	0.06	94	0.75	151	2.95	219	0.74
31	0.11	95	0.23	152	0.93	220	0.34
32	0.28	96	0.23	153	0.51	221	0.40
37	0.15	97	0.19	154	0.58	222	0.16
38	0.73	99	0.05	155	1.19	229	0.06
39	5.77	100	0.23	156	0.39	231	0.12
40	0.70	101	0.20	157	0.16	232	0.15
41	0.41	102	0.25	158	0.18	233	0.06
42	0.08	103	0.09	159	0.10	239	0.21
43	0.11	104	0.46	162	0.04	240	0.27
44	0.23	105	0.10	163	0.14	246	8.45
45	0.11	106	0.32	164	0.17	247	1.29
48	0.18	107	0.63	165	0.52	248	0.54
50	0.54	108	1.29	166	0.58	249	0.11
51	0.90	109	28.10	167	5.95	250	0.13
52	0.78	110	2.53	168	7.50	251	0.11
53	0.18	111	0.25	169	2.19	260	0.16
54	0.12	112	0.12	170	0.41	262	0.19
55	0.06	113	0.09	171	0.94	263	0.34
57	0.15	114	0.09	172	0.10	264	0.13
59	0.06	115	0.33	173	0.09	271	0.08
61	0.08	116	0.12	177	0.17	272	0.08
62	0.39	117	0.20	178	0.09	281	0.13
63	2.25	119	0.38	179	0.15	321	0.06
64	2.23	120	0.19	180	2.87	332	0.09
65	15.06	121	0.44	181	2.84	395	0.07
66	1.44	122	0.32	182	10.42	409	6.55
67	0.12	123	2.54	183	1.73	410	0.91
69	1.96	124	0.28	184	0.21	411	0.07
70	0.10	125	0.19	185	0.12	441	0.11
71	0.05	126	0.20	187	0.11	442	0.19
74	0.14	127	0.50	189	0.11	457	1.15
75	0.33	128	0.33	190	0.09	458	0.18
76	0.68	129	0.20	191	0.09	459	0.07
77	0.90	130	0.09	193	0.11	473	0.28
78	0.49	131	0.10	194	0.07	474	0.34
79	0.32	132	0.08	195	0.14	475	0.08
80	0.09	133	0.41	196	0.08	482	0.25
81	0.12	134	0.03	197	0.13	500	1.25
83	0.78	137	0.20	198	0.21	501	0.81
84	0.19	138	2.54	199	0.15	502	0.13
85	0.09	139	0.97	200	0.48	565	13.69
87	0.07	140	0.70	201	0.94	566	2.96
88	0.05	141	0.50	202	0.23	567	0.95
89	4.82	142	0.17	203	0.08	568	0.16
90	8.87	143	0.27	204	0.06		
91	4.52	145	0.57	207	0.10		

Spectrum No 21 (25)

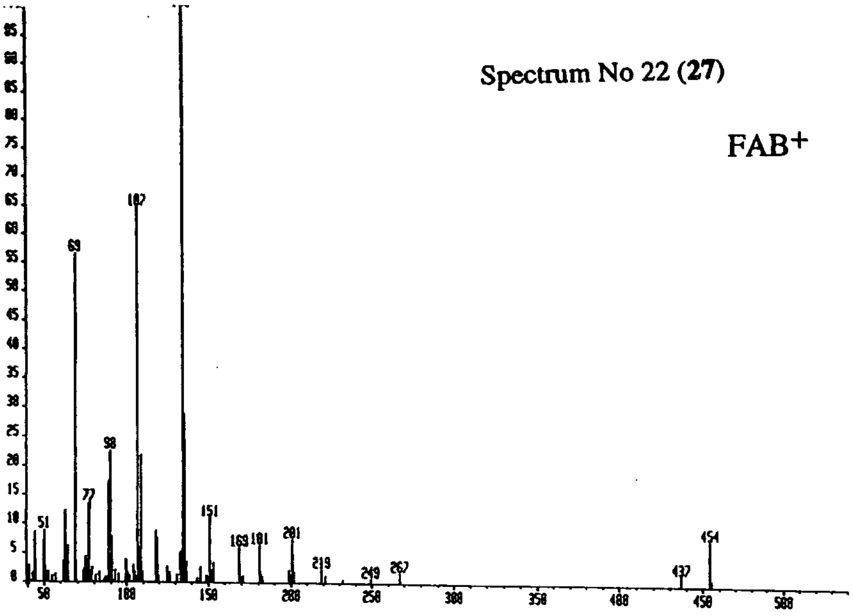


CM277FI 1247 (20.785) 434176

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.05	91	5.01	149	0.11	219	1.02
27	0.18	92	100.00	150	0.20	220	0.48
28	0.67	93	13.33	151	4.30	221	0.58
29	0.06	94	0.93	152	1.15	222	0.18
31	0.12	95	0.29	153	0.56	231	0.24
32	0.31	96	0.15	154	0.84	232	0.14
37	0.19	97	0.15	155	1.96	233	0.07
38	1.08	99	0.13	156	0.42	239	0.17
39	8.31	100	0.28	157	0.12	240	0.20
40	1.02	101	0.24	158	0.12	246	0.61
41	0.59	102	0.31	159	0.11	247	0.11
42	0.07	103	0.08	163	0.17	250	0.17
43	0.12	104	0.21	164	0.22	251	0.13
44	0.25	105	0.12	165	0.33	261	0.07
45	0.15	106	0.35	166	0.69	262	0.18
48	0.24	107	1.16	167	4.66	263	0.20
50	0.84	108	0.97	168	16.51	271	0.09
51	1.33	109	40.09	169	3.83	272	0.05
52	1.18	110	3.52	170	0.58	281	0.20
53	0.25	111	0.35	171	1.06	282	0.10
54	0.18	112	0.16	172	0.16	285	0.06
55	0.09	113	0.14	173	0.06	287	0.07
57	0.26	114	0.10	176	0.09	290	0.08
58	0.05	115	0.37	177	0.27	321	0.08
59	0.07	116	0.17	178	0.18	330	0.10
61	0.09	117	0.12	179	0.22	331	0.49
62	0.52	119	0.53	180	3.39	332	0.11
63	3.18	120	0.20	181	3.18	409	10.08
64	3.18	121	0.49	182	34.43	410	1.33
65	20.75	122	1.00	183	5.19	411	0.08
66	1.99	123	1.89	184	0.48	441	0.08
67	0.18	124	0.21	185	0.09	442	0.05
69	2.76	125	0.26	187	0.18	457	1.11
70	0.12	126	0.24	188	0.08	458	0.15
71	0.08	127	0.60	189	0.12	459	0.05
73	0.05	128	0.34	190	0.16	473	0.68
74	0.18	129	0.20	191	0.07	474	0.22
75	0.33	130	0.09	193	0.08	475	0.05
76	0.69	131	0.16	194	0.04	482	0.65
77	1.18	132	0.11	195	0.09	483	0.15
78	0.64	133	0.54	196	0.04	500	1.92
79	0.33	134	0.08	198	0.11	501	0.67
80	0.12	137	0.12	199	0.11	502	0.08
81	0.14	138	7.02	200	1.28	545	0.06
83	0.96	139	1.74	201	1.33	565	15.80
84	0.26	140	1.14	202	0.27	566	3.45
85	0.07	141	0.57	207	0.13	567	1.11
87	0.10	142	0.21	212	0.08	568	0.20
88	0.10	143	0.15	213	0.15		
89	6.37	145	0.73	214	0.09		
90	11.03	146	0.09	218	0.20		

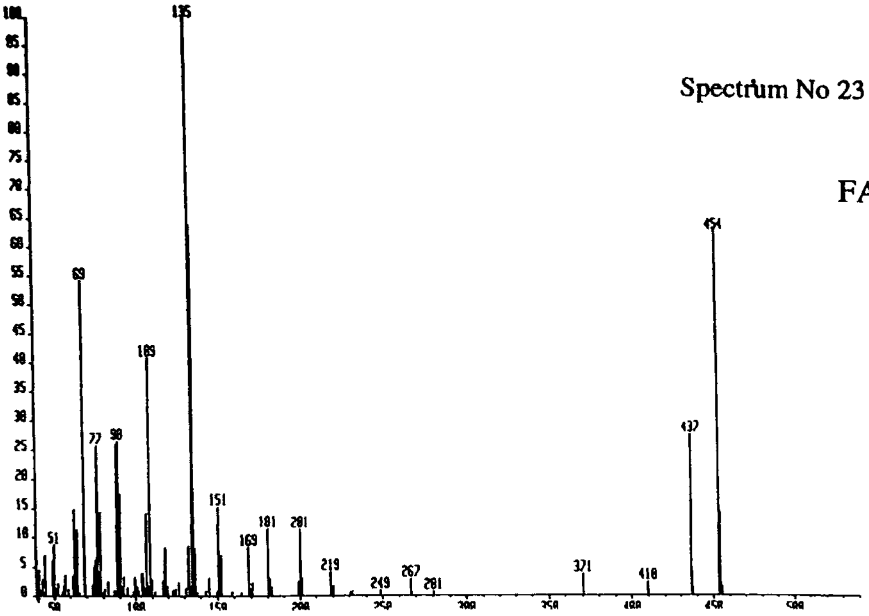
Spectrum No 22 (27)

FAB+



Mass	% Base	
40.06	1.04	
41.07	2.70	
43.05	0.69	
43.09	1.50	
45.03	8.41	
50.05	6.98	
51.05	8.77	
52.06	1.75	
53.06	1.80	
55.07	1.08	
57.05	1.31	
57.11	1.17	
62.05	3.51	
63.06	12.31	
64.07	4.16	
65.08	6.09	
69.03	56.63	
69.11	0.45	
74.05	2.04	
75.06	4.25	
76.07	3.82	
77.08	13.62	
78.09	1.93	
79.09	2.45	
81.05	1.14	F
81.09	1.09	F
83.07	1.60	
87.07	0.74	
88.08	0.66	
89.09	17.34	
90.10	22.44	
91.10	7.70	
92.10	0.33	
93.06	2.07	
95.07	1.38	
99.07	0.74	
100.05	3.79	
101.08	1.48	
102.10	0.95	
104.09	2.95	
105.09	1.63	
106.10	0.98	
107.11	64.78	
108.11	5.71	
109.11	21.96	
110.11	1.72	
118.10	8.76	
119.06	7.46	
120.09	1.04	
125.10	2.65	
127.10	1.55	
131.07	1.14	
133.11	5.10	
134.11	1.68	
135.11	100.00	0
136.12	29.02	
137.12	3.49	

Mass	% Base
150.10	0.67
151.11	10.99
152.12	2.05
153.12	3.33
169.09	5.85
170.11	0.74
171.12	0.96
181.07	6.31
182.12	1.54
183.14	1.01
199.14	2.03
200.12	1.37
201.13	7.28
202.14	1.69
219.14	2.22
221.15	1.24
232.15	0.50
249.14	0.66
267.14	1.64
437.23	1.65
454.23	7.63
455.23	1.05



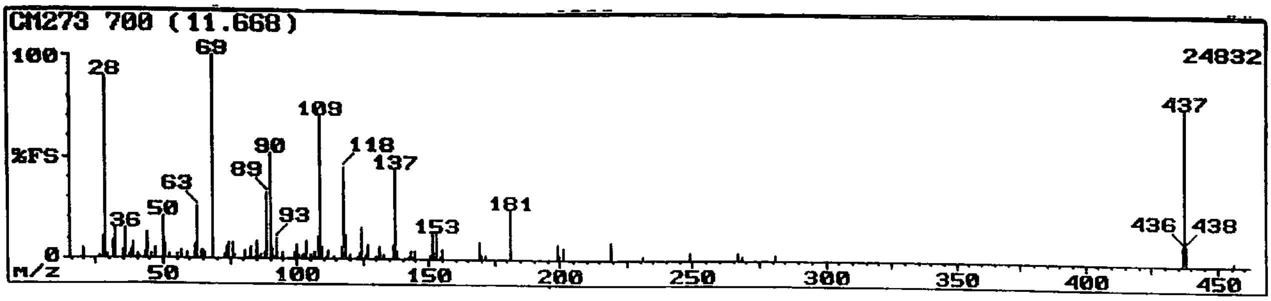
Spectrum No 23 (28)

FAB+

Mass	% Base
40.99	4.43
42.00	1.04
43.00	2.74
43.94	0.57
44.95	6.91
49.96	5.92
50.97	8.67
51.98	1.32
52.98	2.01
54.97	0.59
56.01	1.57
56.96	1.31 F
57.02	3.45 F
58.97	1.01
61.96	3.34
62.97	14.75
63.98	4.50
64.98	11.21
65.98	0.42
68.94	54.08
73.95	1.81
74.96	4.97
75.97	6.14
76.97	25.52
77.98	4.13
78.99	14.32
79.99	0.63
80.95	1.06
82.96	2.30
86.95	0.72
87.96	0.61
88.97	25.81
89.97	26.31
90.98	17.37
91.98	1.60
92.92	3.17
94.94	1.33
98.93	0.64
99.92	3.02
100.95	1.60
101.97	0.86
103.95	3.76
104.95	3.05
105.96	1.28
106.97	14.07
107.96	1.67
108.96	40.56
109.97	2.76
111.92	0.54
116.94	2.45
117.95	6.13
118.91	8.16
119.94	1.66
122.92	0.85
124.93	0.98
126.94	2.17
130.90	1.23

Mass	% Base
135.95	64.10
136.95	8.03
137.94	0.54
142.91	0.68
144.91	2.89
149.91	0.80
150.93	15.18
151.94	3.15
152.93	6.90
158.93	0.63
163.93	0.38
168.90	8.14
169.91	1.18
170.92	2.25
180.86	11.38
181.90	2.93
182.91	1.46
198.90	2.20
199.88	2.45
200.90	11.27
201.91	2.85
218.88	3.90
219.89	0.41
220.90	1.65
230.85	0.47
231.89	0.75
248.88	0.68
266.87	2.74
267.87	0.34
280.82	0.64
370.82	3.50
409.81	2.26
436.78	27.29
437.78	3.74
453.78	62.51
454.78	14.32
455.78	1.46

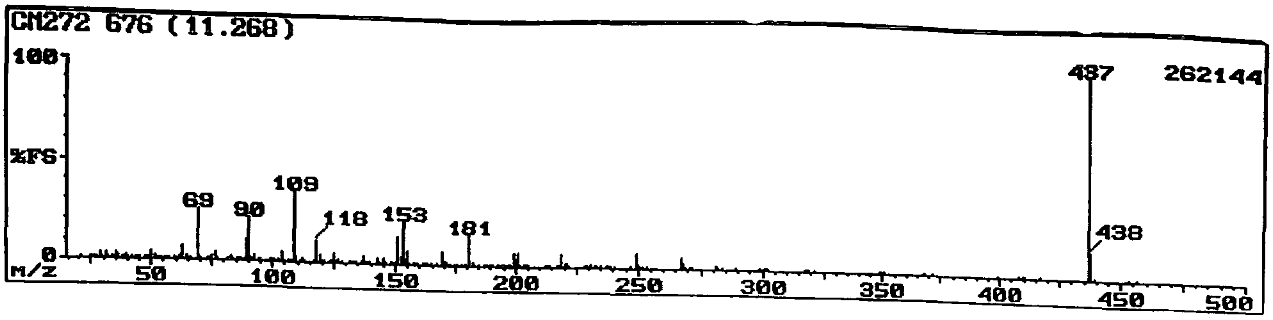
Spectrum No 24 (29)



CM273 700 (11.668) 24832

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
21	5.22	65	3.90	104	9.15	144	0.87
27	1.14	66	2.72	105	1.95	145	4.32
28	10.57	69	100.00	106	0.57	150	2.27
28	89.69	73	1.63	107	3.00	151	13.02
29	2.08	74	5.48	108	11.02	152	2.67
31	8.31	75	8.18	109	70.10	153	13.08
32	14.56	76	7.86	110	5.67	154	1.35
35	4.03	77	2.16	111	0.77	155	4.96
36	14.63	81	3.79	112	3.82	169	9.15
37	2.27	82	0.60	114	1.42	170	1.66
38	3.98	83	6.19	117	6.12	171	1.77
39	7.86	84	1.29	118	44.33	181	24.48
40	2.16	85	8.63	119	11.34	199	7.99
41	1.19	86	1.34	120	1.66	200	2.22
43	2.66	87	1.63	123	0.99	201	5.80
44	12.44	88	3.27	124	2.74	219	8.83
45	2.08	89	32.22	125	15.72	231	2.38
47	4.70	90	51.80	126	1.76	249	3.72
50	20.10	91	4.90	127	6.83	267	4.19
51	6.83	92	1.35	130	0.81	268	1.64
52	1.66	93	9.34	131	5.73	281	2.50
55	1.85	95	3.08	133	1.84	436	10.12
57	4.19	99	2.63	136	6.31	437	76.29
59	3.01	100	6.51	137	43.30	438	9.92
62	6.83	101	2.34	138	4.32	456	2.21
63	25.52	102	1.53	142	0.47		
64	4.01	103	1.47	143	3.77		

Spectrum No 25 (30)

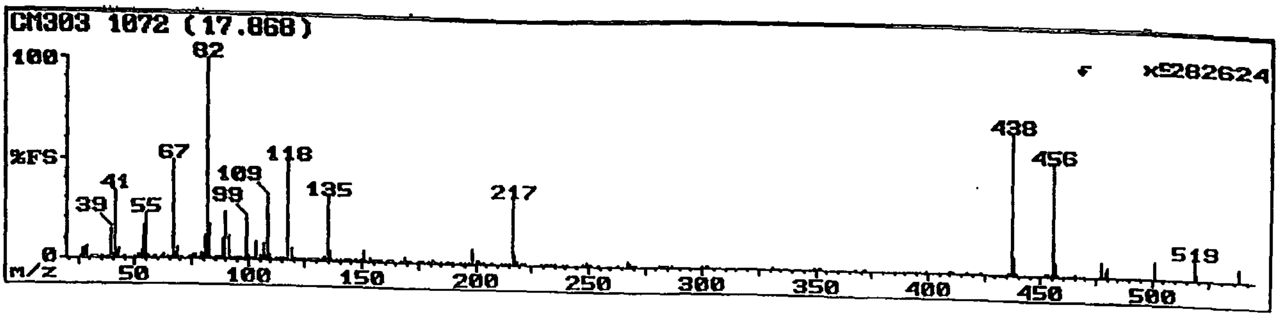


CM272 676 (11.268)

262144

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
21	0.09	87	0.31	153	21.00	228	0.08
24	0.07	88	0.20	154	2.54	229	0.36
25	0.07	89	10.94	155	7.03	231	1.66
26	0.26	90	21.39	156	0.50	232	0.75
27	0.19	91	2.12	157	0.17	233	0.43
28	2.78	92	0.24	158	0.06	235	0.26
29	0.09	93	2.49	159	0.10	237	0.23
31	2.56	94	0.21	161	0.30	238	0.23
32	0.43	95	0.49	162	0.73	239	1.44
33	0.09	99	0.60	163	0.29	240	0.40
35	2.64	100	1.36	164	0.29	247	0.29
36	1.88	101	0.57	167	0.18	249	7.91
37	1.25	102	0.51	169	6.45	250	1.83
38	1.21	104	5.13	170	1.73	251	0.51
39	1.93	105	0.61	171	2.29	252	0.09
40	0.40	106	0.09	172	0.43	253	0.09
41	0.11	107	0.71	173	0.26	267	6.25
43	0.28	108	1.18	174	0.15	268	3.20
44	0.52	109	34.77	175	0.16	269	0.54
45	0.63	110	2.81	176	0.29	270	0.12
47	0.11	111	0.30	177	0.26	271	0.34
48	0.10	112	1.50	179	0.27	281	2.10
49	0.26	113	0.39	181	15.33	282	0.14
50	3.93	117	0.63	182	2.27	283	0.10
51	2.29	118	10.84	183	0.34	289	0.07
52	0.29	119	3.42	185	0.12	299	0.43
53	0.19	120	0.51	187	0.40	300	0.13
54	0.05	121	0.23	188	0.19	301	0.41
55	0.20	123	0.21	189	0.27	302	0.09
56	0.14	124	0.84	190	0.40	317	0.20
57	0.56	125	4.44	193	0.79	318	0.21
59	1.31	126	0.57	194	0.12	319	0.21
61	0.33	127	2.25	195	0.26	321	0.10
62	1.61	128	0.12	197	0.25	349	1.14
63	6.54	131	0.76	198	0.21	350	0.13
64	1.54	132	0.15	199	6.93	367	0.72
65	1.09	133	1.07	200	3.71	368	0.23
66	0.09	134	0.14	201	6.45	371	0.24
69	24.90	136	0.93	202	1.09	399	0.20
70	0.34	137	3.49	203	0.14	408	0.53
73	0.21	138	0.77	204	0.57	409	1.13
74	1.18	139	0.23	205	0.16	410	0.22
75	1.98	140	0.30	212	0.71	417	0.58
76	3.59	143	2.76	213	0.46	437	100.00
77	0.50	144	0.29	214	0.10	438	13.77
81	0.52	145	3.03	217	0.11	439	1.08
82	0.14	146	0.12	218	0.33	453	0.18
83	1.66	149	0.24	219	6.93	456	0.24
84	0.14	150	0.87	220	1.71		
85	0.15	151	13.48	221	1.98		
86	0.24	152	3.98	222	0.26		

Spectrum No 26 (31)



CM303 1072 (17.868)

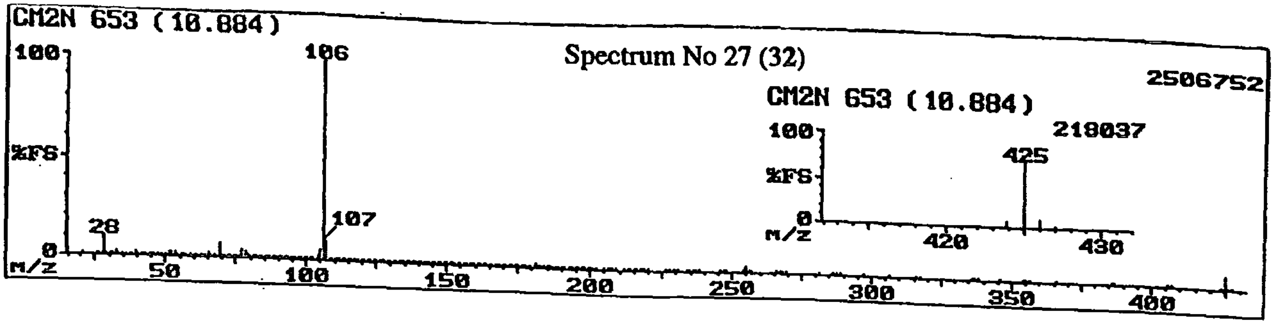
282624

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
30	0.21	93	0.49	149	0.31	232	0.33
31	0.53	94	0.14	150	0.22	233	0.08
32	0.96	95	0.42	151	5.80	235	0.14
33	0.05	96	0.09	152	1.31	239	0.24
35	0.06	97	0.21	153	2.38	240	0.12
36	0.35	98	1.04	154	0.75	247	0.10
37	0.18	99	19.93	155	0.09	249	2.08
38	0.56	100	1.90	156	0.07	250	0.53
39	14.31	101	0.58	157	0.11	251	0.15
40	2.42	102	0.45	158	0.06	254	0.05
41	34.06	103	0.23	159	0.12	263	0.07
42	4.35	104	8.51	161	0.07	267	2.90
43	4.94	105	1.83	162	0.04	268	1.77
44	1.37	106	0.36	163	0.16	269	0.26
45	0.68	107	8.24	164	0.12	270	0.07
50	1.18	108	2.31	167	0.22	271	0.09
51	1.72	109	30.80	169	2.76	281	0.32
52	0.64	110	2.51	170	0.65	282	0.14
53	3.96	111	0.13	171	0.95	283	0.10
54	16.67	112	0.20	172	0.23	284	0.09
55	22.46	113	0.19	175	0.13	285	0.17
56	1.79	114	0.10	176	0.06	286	0.08
57	1.22	115	0.17	177	0.17	299	0.11
58	0.06	116	0.11	179	0.09	301	0.16
59	0.25	117	0.72	181	2.26	302	0.08
62	0.36	118	49.28	182	0.95	331	0.08
63	1.86	119	5.59	183	0.24	349	0.37
64	0.95	120	0.72	185	0.32	351	0.25
65	1.29	121	0.26	187	0.18	352	0.05
66	0.86	122	0.15	188	0.08	367	0.29
67	49.64	123	0.08	189	0.15	371	1.04
68	3.01	124	0.07	190	0.07	372	0.15
69	5.55	125	0.83	193	0.11	400	0.09
70	0.42	126	0.31	195	0.18	409	0.18
71	0.09	127	0.94	197	0.20	410	0.07
74	0.24	128	0.16	199	7.97	412	0.06
75	0.61	129	0.18	200	1.65	418	0.23
76	1.70	130	0.08	201	2.15	424	0.08
77	2.31	131	0.45	202	1.17	436	0.28
78	0.63	132	0.19	203	0.34	437	0.24
79	3.37	133	1.70	204	0.17	438	69.93
80	1.74	134	1.14	207	0.08	439	8.88
81	11.68	135	31.88	212	0.04	440	0.82
82	100.00	136	4.46	213	0.21	453	0.55
83	17.21	137	0.59	215	0.12	454	0.26
84	0.99	138	0.12	217	0.55	455	0.19
85	0.09	139	0.04	217	33.33	456	55.43
86	0.06	140	0.15	218	5.16	457	6.97
87	0.09	142	0.11	219	2.29	458	0.66
88	0.27	143	0.29	220	0.45	466	0.07
89	9.87	144	0.10	221	0.41	478	0.16
90	23.19	145	1.27	222	0.06	480	0.06
91	11.50	146	0.13	229	0.09	481	0.09
92	1.06	147	0.07	231	0.34	501	0.17

CM303 1072 (17.868)

282624

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
519	0.19	520	0.05	537	0.14		



CM2N 653 (10.884)

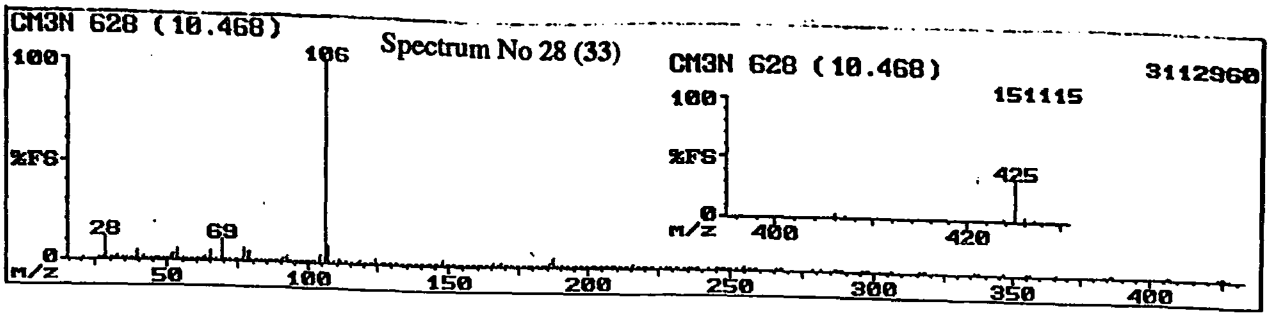
2506752

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.02	82	0.03	137	0.27	193	0.02
25	0.01	83	0.13	138	0.20	194	0.06
26	0.16	84	0.08	139	0.29	195	0.04
27	0.66	85	0.02	140	0.10	196	0.22
28	9.68	86	0.02	141	0.02	197	0.26
29	0.27	87	0.08	142	0.32	198	0.29
30	0.53	88	0.12	143	0.15	199	0.05
31	0.37	89	0.51	144	0.04	200	0.13
32	1.76	90	0.21	145	0.27	201	0.04
33	0.05	91	0.55	146	0.16	202	0.02
34	0.01	92	0.56	147	0.08	205	0.18
36	0.01	93	0.63	148	0.98	206	0.02
37	0.07	94	0.07	149	0.17	207	0.05
38	0.33	95	0.19	150	0.10	208	0.04
39	1.76	96	0.11	151	0.30	209	0.03
40	0.46	97	0.09	152	0.07	212	0.03
41	0.81	98	0.05	153	0.06	213	0.02
42	0.37	99	0.16	154	0.02	214	0.09
43	0.13	100	0.52	155	0.17	215	0.11
44	0.41	101	0.18	156	0.04	216	0.75
45	0.05	102	0.14	157	0.05	217	0.40
46	0.03	104	2.38	158	0.05	218	0.17
47	0.01	105	4.37	159	0.07	219	0.03
48	0.03	106	100.00	160	0.02	220	0.02
50	0.68	107	9.48	161	0.03	226	0.01
51	1.60	108	0.44	162	0.04	228	0.14
52	2.01	109	0.31	163	0.12	229	0.03
53	1.49	110	0.04	164	0.04	231	0.03
54	0.65	111	0.56	165	0.05	234	0.12
55	0.09	112	0.24	166	1.19	235	0.05
56	0.03	113	0.13	167	0.39	236	0.46
57	0.16	114	0.14	168	0.16	237	0.79
59	0.05	115	0.05	169	1.05	238	0.10
60	0.01	116	0.13	170	0.09	246	0.01
61	0.06	117	0.18	171	0.03	247	0.04
62	0.30	118	0.29	172	0.02	248	0.07
63	0.83	119	1.16	173	0.03	254	0.17
64	0.42	120	0.26	174	0.03	255	2.90
65	1.56	121	0.13	175	0.02	256	0.26
66	0.47	122	0.09	176	0.17	257	0.03
67	0.25	123	0.05	177	0.03	266	0.01
69	6.90	124	1.40	178	0.04	267	0.03
70	0.13	125	0.20	179	0.10	268	0.02
71	0.04	126	0.10	181	1.61	269	0.01
72	0.02	127	0.14	182	0.08	281	0.04
73	0.03	128	0.09	183	0.02	286	0.08
74	0.16	129	0.02	184	0.09	287	0.02
75	0.31	130	0.03	185	0.25	289	0.01
76	0.29	131	0.25	186	0.52	297	0.02
77	3.84	132	0.11	187	1.06	306	0.03
78	3.23	133	0.07	188	0.17	316	0.02
79	1.58	134	0.05	189	0.22	317	0.04
80	0.59	135	0.10	190	0.05	336	0.05
81	0.15	136	0.07	191	0.01	337	0.13

CM2N 653 (10.884)

2506752

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
338	0.02	356	0.06	406	0.56	426	0.73
346	0.02	366	0.01	407	0.07	427	0.05
354	0.03	386	0.22	424	0.53		
355	0.02	387	0.02	425	6.41		



CM3N 628 (10.468)

3112960

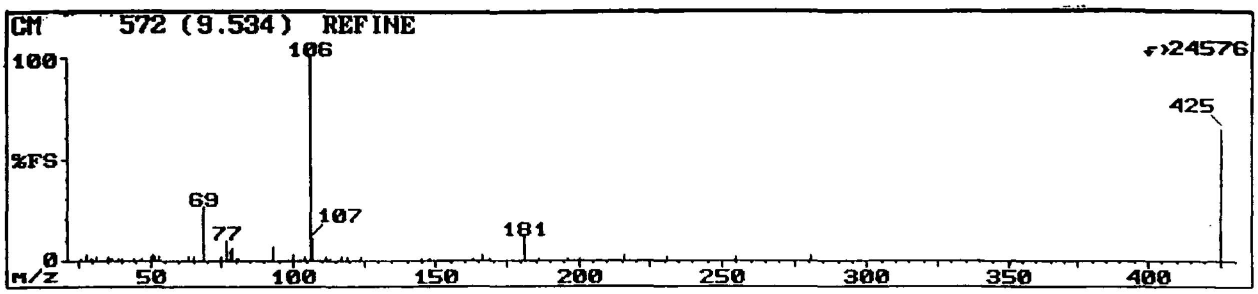
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
21	0.02	83	0.26	141	0.06	195	0.05
26	0.19	84	0.13	142	0.89	196	0.88
27	0.76	86	0.06	143	0.22	197	0.44
28	11.18	87	0.14	144	0.08	198	0.75
29	0.31	88	0.21	145	0.54	199	0.12
30	1.24	89	1.00	146	0.28	200	0.18
31	0.54	90	0.19	147	0.14	201	0.10
32	2.09	91	1.79	148	2.60	202	0.02
33	0.06	92	2.86	149	0.42	203	0.02
34	0.02	93	0.95	150	0.18	204	0.03
36	0.02	94	0.12	151	0.63	205	0.14
37	0.11	95	0.39	152	0.15	206	0.03
38	0.99	96	0.28	153	0.09	207	0.12
39	4.64	97	0.71	154	0.04	208	0.17
40	1.00	98	0.14	155	0.25	209	0.07
41	1.87	99	0.28	156	0.10	210	0.01
42	0.86	100	0.71	157	0.11	211	0.01
43	0.14	101	0.40	158	0.17	212	0.03
44	0.45	102	0.26	159	0.27	213	0.03
45	0.09	104	3.91	160	0.07	214	0.16
46	0.04	106	100.00	161	0.08	215	0.11
47	0.02	107	8.68	162	0.05	216	2.00
48	0.08	108	0.29	163	0.17	217	1.02
50	1.22	109	0.47	164	0.13	218	0.45
51	2.83	111	1.50	165	0.13	219	0.13
52	3.22	112	0.27	166	1.77	220	0.03
53	5.46	113	0.16	167	0.50	221	0.02
54	1.16	114	0.24	168	0.51	222	0.02
55	0.15	115	0.09	169	1.73	223	0.02
56	0.12	116	0.20	170	0.25	226	0.02
57	0.34	117	0.72	171	0.13	228	0.36
58	0.05	118	0.54	172	0.06	229	0.07
59	0.11	119	1.59	173	0.06	231	0.05
60	0.03	120	0.47	174	0.08	232	0.02
61	0.08	121	0.39	175	0.03	234	0.20
62	0.66	122	0.17	176	0.40	235	0.13
63	1.79	123	0.07	177	0.13	236	0.26
64	1.00	124	2.83	178	0.14	237	0.71
65	5.26	125	0.41	179	0.24	238	0.08
66	1.18	126	0.18	180	0.05	239	0.02
67	0.53	127	0.27	181	1.37	242	0.02
69	10.79	128	0.19	182	0.14	245	0.02
70	0.20	129	0.05	183	0.04	246	0.03
71	0.06	130	0.02	184	0.16	247	0.07
72	0.06	131	0.24	185	0.19	248	0.13
74	0.33	132	0.16	186	1.78	249	0.02
75	0.61	133	0.14	187	5.10	250	0.01
76	0.45	134	0.08	188	0.59	252	0.00
77	6.97	135	0.12	189	0.52	254	0.06
78	5.03	136	0.11	190	0.14	255	1.51
79	4.38	137	0.29	191	0.02	256	0.57
80	1.27	138	0.33	192	0.04	257	0.04
81	0.26	139	0.49	193	0.04	258	0.01
82	0.06	140	0.22	194	0.14	259	0.02

CM3N 628 (10.468)

3112960

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
266	0.03	289	0.02	336	0.05	406	0.18
267	0.04	296	0.01	337	0.03	407	0.02
268	0.04	297	0.03	346	0.01	424	0.08
278	0.01	298	0.01	355	0.03	425	1.64
281	0.03	306	0.07	356	0.03	426	0.20
286	0.18	316	0.02	366	0.02	427	0.01
287	0.12	317	0.08	386	0.15		
288	0.02	318	0.02	387	0.02		

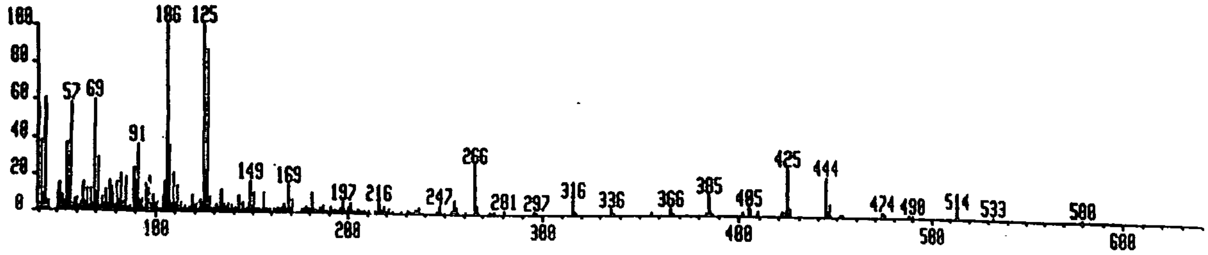
Spectrum No 29 (34)



CM 572 (9.534) REFINE

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel In
30	0.83	53	2.10	104	1.95	169	1.1
31	2.34	63	1.61	106	100.00	181	11.3
35	1.46	65	2.18	107	10.48	186	1.4
36	0.72	69	25.78	112	1.51	196	1.1
37	0.37	75	1.68	113	1.11	200	0.7
39	0.98	77	9.64	117	1.92	216	2.9
40	0.63	78	4.69	119	2.41	231	1.6
44	0.75	79	6.25	124	1.69	255	2.3
47	0.81	80	0.77	145	0.80	281	3.2
50	1.94	81	1.22	148	1.16	425	8.2
51	2.88	93	6.90	163	0.62		
52	1.95	100	2.59	166	2.88		

Spectrum No 30 (35) FAB+



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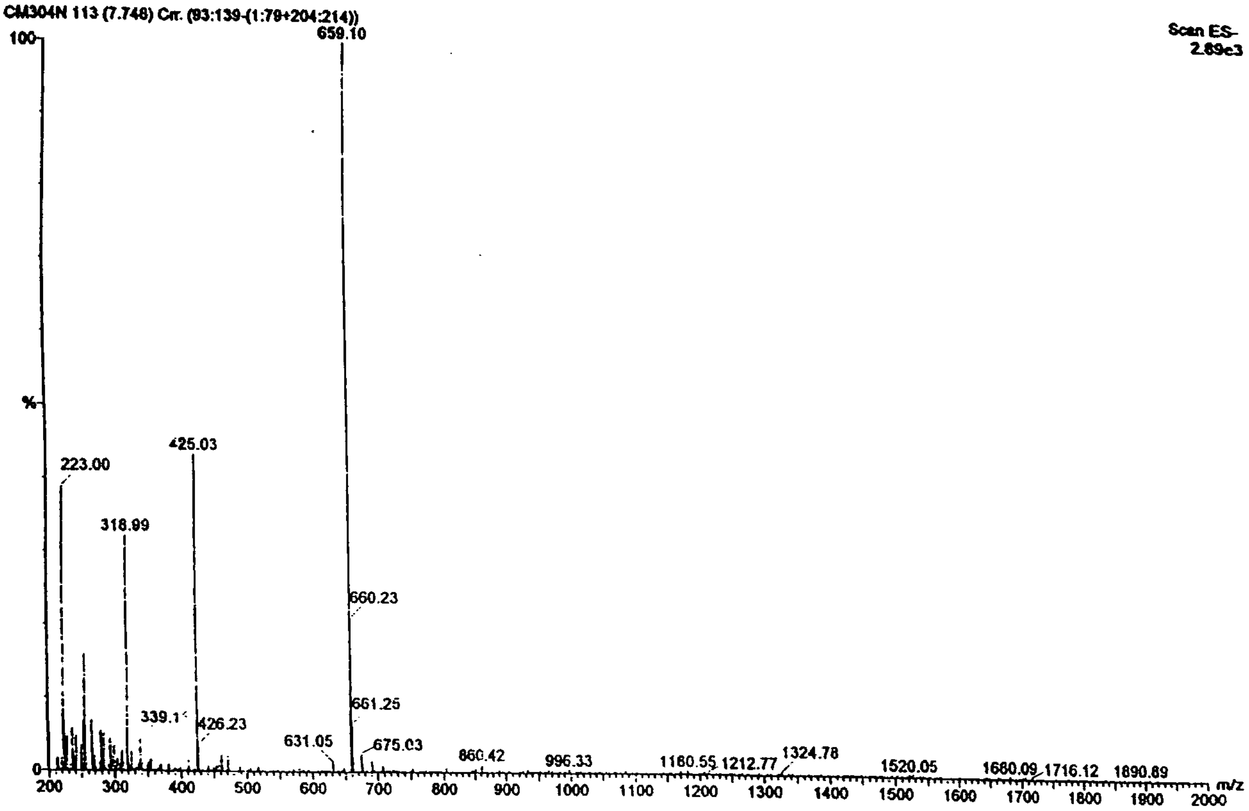
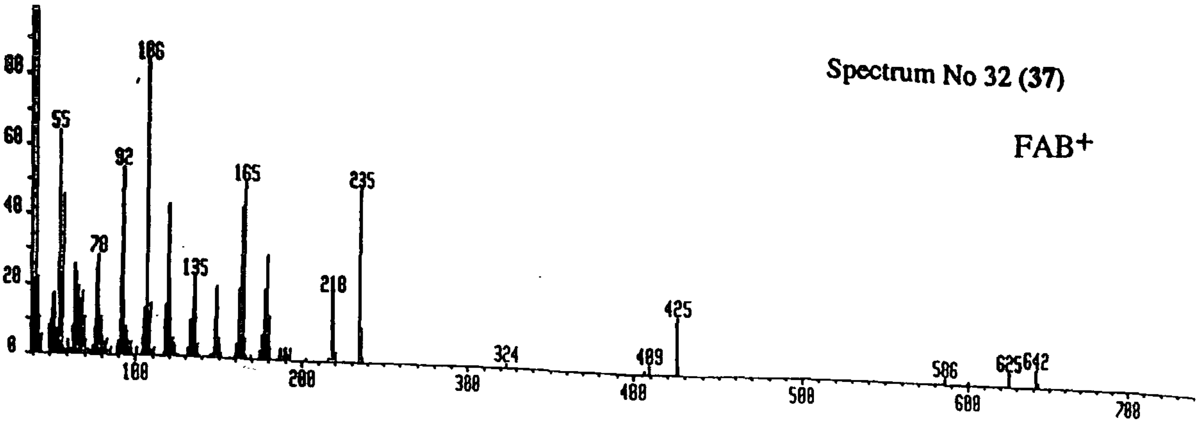
BpM=0         I=10v       Hm=579     TIC=1111021000                      EI+
CORINNE                                                     Acnt:
                                                                              Sys:AC
                                                                   PT= 0      Cal:PFK
```

Mass	% Base
160.95	1.11
161.95	0.42
163.00	1.67
164.01	0.48
165.05	2.06
165.99	3.94
167.00	3.24
168.01	1.00
168.93	14.21
169.95	1.99
170.90	6.21
175.95	1.08
177.02	1.03
177.98	2.35
179.03	1.73
180.01	1.21
180.93	10.51
181.97	1.89
183.07	0.98
183.96	0.33
184.95	1.75
185.95	1.45
186.96	3.47
187.96	0.58
188.96	0.82
191.05	2.29
193.03	1.01
194.02	0.67
195.03	1.52
195.98	1.79
196.97	4.93
197.95	1.84
198.97	0.64
199.92	2.37
200.94	4.58
201.96	2.24
202.98	0.39
204.97	1.17
205.99	0.68
207.01	0.90
207.96	0.34
209.08	0.38
211.11	0.33
213.95	0.59
215.94	4.90
216.94	2.40
217.95	1.03
218.93	3.30
219.94	0.35
220.98	1.91
223.01	0.91
227.93	0.90
230.89	1.04
231.92	0.39
233.94	0.32
234.92	1.63
235.94	1.56
236.94	2.63
238.99	0.31
245.92	0.33
246.91	4.10
247.91	0.73
253.90	1.42
254.90	7.24
255.91	2.95
256.91	0.64
260.96	0.79
265.90	26.12
266.90	4.43
267.89	0.77
273.83	0.85
275.89	0.60
280.84	1.00
295.86	0.43
296.88	0.69
315.85	7.77
316.84	1.32
335.84	2.75
336.84	0.77
355.82	1.02
365.79	3.25
366.80	0.45
383.78	0.74
384.80	10.08
385.79	2.50
386.79	0.41
401.75	1.03
404.76	3.55
405.78	3.04
408.76	0.65
409.74	1.82
421.71	1.87
423.73	2.86
424.75	24.70
425.75	3.94
443.70	20.59
444.70	2.72
445.69	6.47
446.70	0.34
451.75	0.69
452.76	0.92
473.76	2.24
474.75	1.14
487.61	0.32
489.60	0.34
513.70	4.06
514.70	0.58
532.67	0.50
579.67	0.39

Spectrum No 31 (36)

ELECTROSPRAY$^+$





Spectrum No 32 (37)

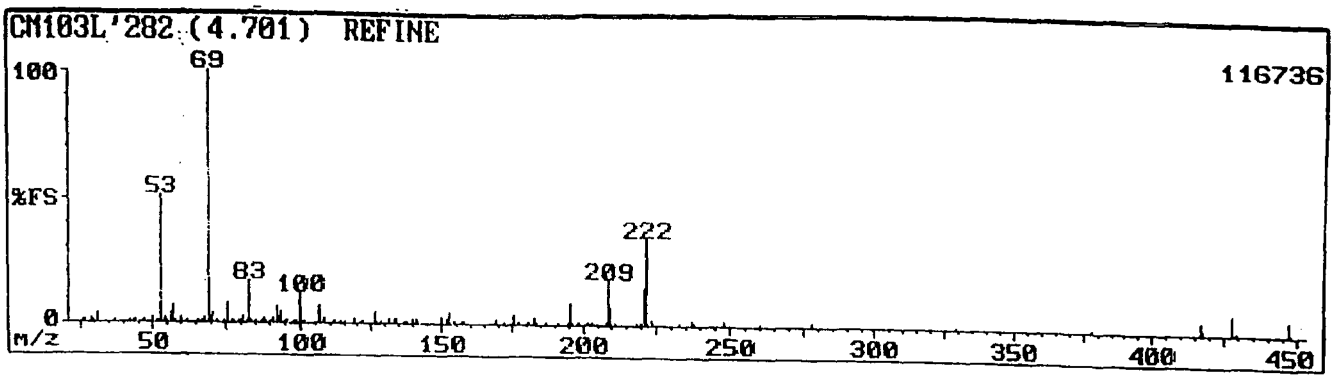
FAB+

Mass	% Base	
40.17	20.98	
41.18	100.00	
42.17	16.51	
43.16	15.84	F
43.19	21.55	F
44.16	10.12	
45.14	5.15	
50.12	7.54	
51.13	12.49	
52.12	16.66	
53.13	11.83	
54.13	7.15	
55.15	63.22	
56.10	18.50	F
56.15	24.47	F
57.16	45.35	
58.16	1.57	
59.12	0.95	
60.10	3.28	
62.08	1.39	
63.08	7.56	
64.08	25.20	
65.09	23.32	
66.09	19.29	
67.08	15.41	
68.08	5.52	
69.06	17.40	
70.06	10.24	
71.11	3.70	
72.11	1.40	
73.07	1.03	
75.05	2.21	
76.05	7.22	
77.05	24.43	
78.06	28.22	
79.07	10.76	
80.06	8.76	
81.07	4.77	
82.08	3.35	
83.10	4.08	
84.10	1.17	
85.12	1.67	
89.06	2.11	
90.06	3.45	
91.06	21.90	
92.07	53.13	
93.07	14.93	
94.07	7.88	
95.08	6.65	
96.09	3.76	
97.11	3.37	
98.12	1.61	
100.09	1.66	
103.07	0.58	
104.08	4.64	
105.07	13.06	
106.09	83.28	
107.08	12.06	
108.07	11.19	
109.08	14.39	

Mass	% Base
110.10	1.28
111.12	1.69
117.10	0.60
118.07	13.95
119.08	42.82
120.09	21.14
121.10	10.22
122.10	4.64
123.11	3.42
124.11	2.69
125.18	0.50
131.09	2.14
132.10	0.94
133.09	9.98
134.08	13.00
135.08	21.75
136.10	10.59
137.11	3.42
138.12	0 34
145.10	0.50
146.11	0.79
147.10	2.26
148.10	11.22
149.09	19.72
150.10	5.01
151.10	3.48
152.10	0.86
160.11	1.13
161.09	3.74
162.09	19.53
163.10	7.17
164.10	42.84
165.11	49.66
166.12	5.51
167.13	0.68
169.09	0.55
174.14	1.95
175.12	1.47
176.12	6.48
177.12	19.60
178.12	2.17
179.11	29.39
180.12	11.99
181.10	2.92
186.12	1.04
187.13	2.61
188.14	0.54
189.16	2.89
190.16	3.21
191.19	1.98
192.13	1.60
193.12	3.18
202.16	0.49
216.12	0.62
218.17	18.88
219.18	10.85
220.19	2.45
235.18	48.99
236.19	9.67
237.17	1.23

Mass	% Base
324.28	0.54
406.17	0.58
409.13	1.91
425.16	16.07
426.16	2.24
586.16	1.11
600.19	0.56
625.08	3.37
642.16	4.31
643.17	1.04

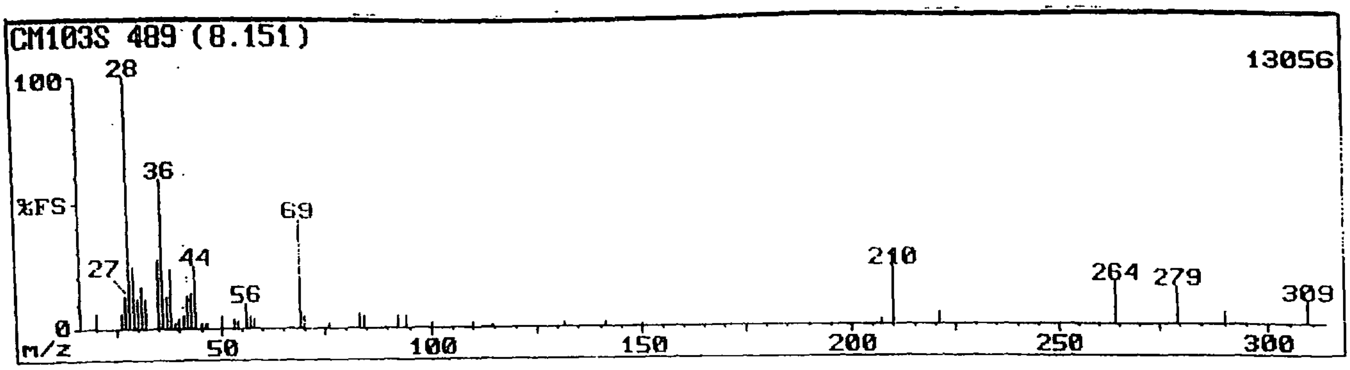
Spectrum No 33 (44)



CM103L'282 (4.701) REFINE 116736

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
30	0.82	55	0.76	74	0.54	89	0.45	107	7.02	134	1.58	172	0.35	203	0.84	248	1.54
31	3.43	56	3.78	76	7.46	90	0.42	108	1.05	137	0.31	176	3.50	208	0.25	260	1.11
37	0.87	57	6.74	77	0.37	91	1.91	112	0.84	138	0.52	177	0.73	209	17.54	270	1.52
42	0.49	58	0.35	78	1.03	92	6.63	114	1.30	140	2.06	181	0.61	210	6.85	329	0.25
43	0.63	60	1.00	79	0.39	93	2.06	115	0.35	141	2.15	183	2.62	211	0.43	370	0.26
44	1.45	62	0.41	80	0.34	94	4.58	119	1.09	142	1.41	184	0.61	218	0.76	417	4.66
46	1.34	66	0.43	81	3.29	95	0.04	121	0.06	150	3.15	187	0.73	220	0.19	418	1.40
47	0.60	67	0.34	82	0.06	96	0.56	122	0.49	152	1.51	192	0.74	221	14.25	428	7.09
50	2.25	68	1.97	83	16.23	98	0.23	126	5.04	153	4.39	195	0.32	222	34.43	429	0.95
51	0.47	69	100.00	84	0.90	99	0.89	127	1.10	154	0.65	196	0.94	223	2.80	447	6.80
52	1.43	70	1.51	85	0.29	100	11.35	128	0.43	157	0.35	197	1.04	233	1.44	448	1.01
53	50.00	71	4.06	87	0.30	101	0.96	131	1.92	158	0.25	199	0.72	237	1.02		
54	2.21	72	0.96	88	1.66	102	0.30	133	1.71	169	1.01	202	1.11	238	0.34		

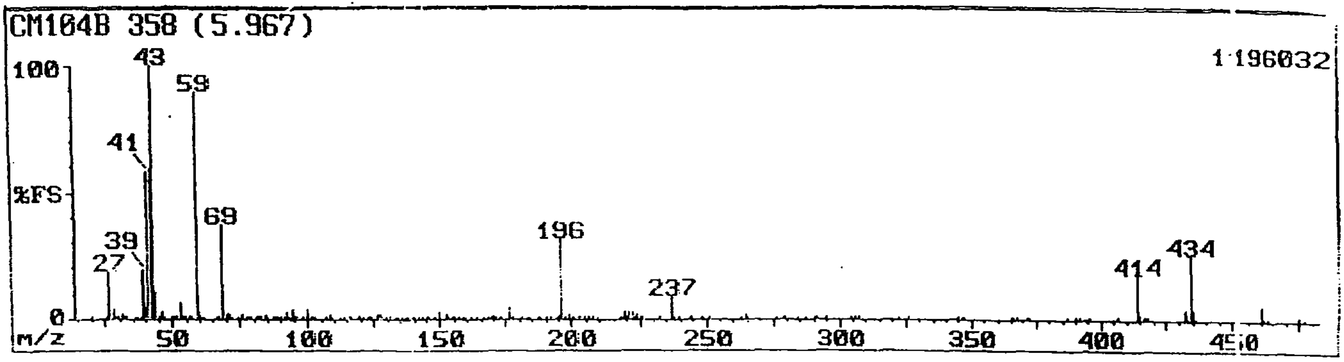
Spectrum No 34 (45)



CM103S'489 (8.151) REFINE 6016

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
30	25.00	38	12.90	43	29.52	50	10.44	58	9.71	84	10.70	114	2.43	210	47.07	309	24.73
31	36.44	39	5.12	44	21.28	53	8.31	69	93.62	92	9.91	131	3.39	221	9.64		
35	17.29	40	7.70	45	5.25	54	6.65	70	11.30	94	10.11	141	4.72	264	38.03		
36	19.60	41	10.11	46	3.97	56	20.21	76	4.39	100	5.25	150	2.69	279	30.05		
37	0.44	42	27.66	47	5.25	57	10.77	83	12.57	110	3.49	207	4.65	290	10.04		

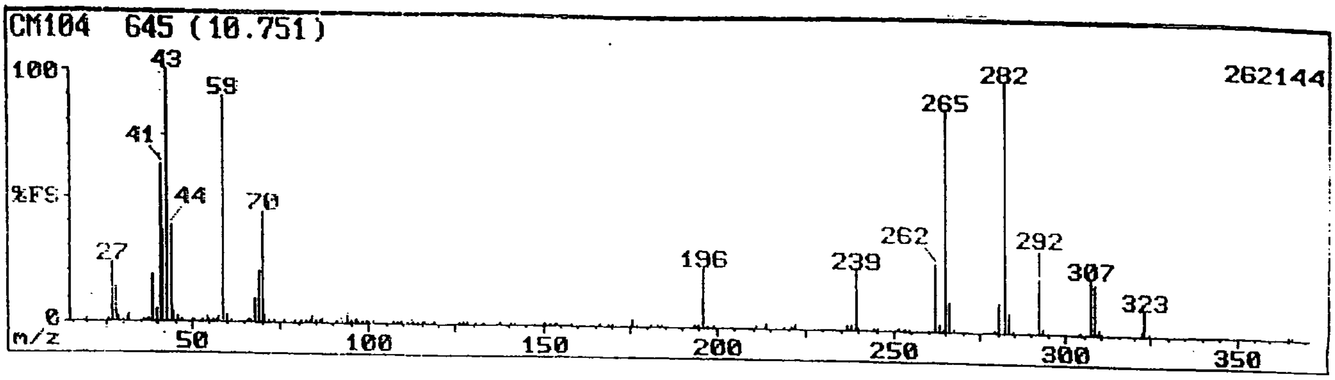
Spectrum No 35 (46)



CM104B'358 (5.967) REFINE 1179646

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
30	0.07	56	0.44	85	0.22	115	0.09	145	0.10	176	5.08	219	3.36	279	0.23	391	0.13
31	1.02	57	0.46	87	0.13	116	0.17	146	0.06	177	0.55	220	0.13	284	0.07	395	0.04
33	0.03	59	90.28	88	0.21	119	1.15	147	0.04	178	0.07	221	2.91	287	0.34	406	0.25
36	0.02	60	3.02	89	0.09	121	0.31	148	0.04	181	0.33	222	3.04	290	0.20	414	17.36
37	0.34	61	0.30	90	0.14	122	0.06	150	2.63	183	0.40	223	0.23	291	0.05	415	1.71
38	1.12	62	0.08	91	0.20	123	0.10	152	1.69	184	0.06	224	1.74	295	0.12	416	0.14
39	19.44	66	0.27	92	2.91	124	0.05	153	0.58	187	0.73	225	0.10	304	0.05	417	0.10
40	4.95	67	0.39	93	0.40	126	1.54	154	0.07	188	0.07	226	0.16	306	1.10	418	0.04
41	58.33	69	36.01	94	4.28	127	1.87	155	0.07	190	0.03	232	0.05	307	0.14	432	4.19
42	60.07	70	2.32	95	0.46	128	0.19	157	0.25	192	0.25	237	9.29	322	0.07	433	0.37
43	100.00	71	1.69	96	0.12	129	0.04	158	0.73	195	0.58	238	0.71	326	0.11	434	25.69
44	10.33	72	0.11	97	0.05	131	0.91	159	0.04	196	31.25	239	0.58	345	0.14	435	3.60
45	0.86	74	1.48	98	0.08	133	1.03	161	0.06	197	1.38	244	0.11	346	0.55	436	0.20
46	2.17	76	1.56	100	4.28	134	0.17	164	0.08	199	1.54	248	0.06	347	0.06	460	5.90
47	0.41	77	0.11	101	0.14	136	0.11	166	0.08	200	0.11	249	0.04	365	0.52	461	0.63
50	0.53	78	0.25	102	0.10	137	0.35	168	0.24	202	0.12	251	0.14	366	0.74	462	0.05
51	0.16	79	0.03	107	0.07	138	0.36	169	1.22	203	0.06	263	0.07	367	0.07	475	2.21
52	0.18	81	0.40	108	1.00	139	0.02	170	0.08	204	0.09	264	2.21	371	0.22	476	0.20
53	5.90	82	0.11	109	0.12	140	0.36	171	0.09	206	0.07	265	0.39	372	0.15		
54	0.69	83	0.95	112	0.26	142	1.15	172	0.06	209	0.12	276	0.08	387	0.08		
55	0.18	84	2.21	114	0.94	143	0.07	173	0.14	210	0.20	278	0.10	390	0.20		

Spectrum No 36 (47)

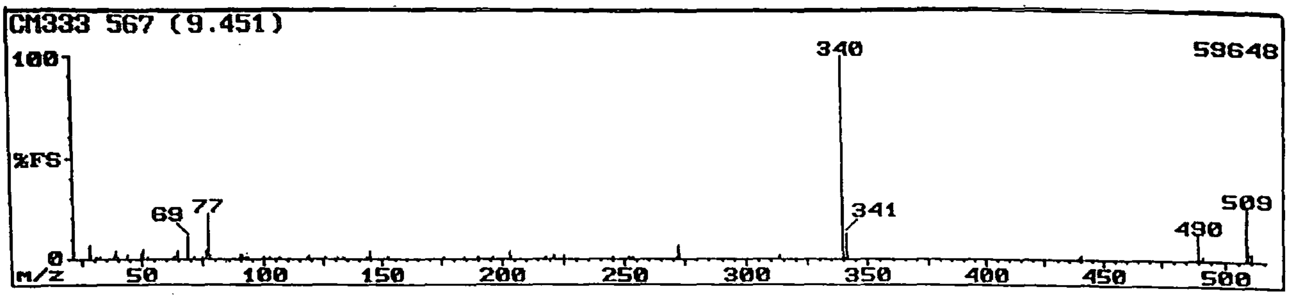


CM104. 645 (10.751)

262144

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
31	1.71	51	0.14	71	2.56	92	1.53	114	0.07	153	0.37	193	0.79	262	25.76	308	19.53
32	3.00	53	1.20	72	0.31	94	3.74	115	0.50	154	0.76	211	0.10	263	2.66	309	1.78
36	0.24	54	1.47	73	0.17	95	0.52	116	0.23	158	0.57	214	2.25	264	1.20	310	0.07
37	0.28	55	0.73	76	0.49	96	1.70	119	0.25	166	0.24	219	0.70	265	85.94	322	1.53
38	0.83	56	1.14	78	0.34	97	0.28	126	0.57	169	0.24	221	1.31	266	11.51	323	9.28
39	10.65	57	1.40	79	0.20	98	0.15	127	0.70	170	0.32	222	1.76	267	0.95	324	1.41
40	4.52	58	1.55	81	0.25	99	0.15	128	0.17	176	3.08	237	1.08	279	0.34	365	0.74
41	62.11	59	89.06	82	0.28	100	0.69	131	0.26	177	0.81	238	1.71	280	11.23	366	0.25
42	35.55	60	3.25	83	0.66	101	0.20	133	0.33	181	0.07	239	23.14	282	96.44		
43	100.00	61	0.25	84	2.64	107	0.27	138	0.26	183	0.13	240	1.35	283	7.42		
44	37.50	66	0.34	85	0.57	108	0.59	141	0.29	184	0.20	244	0.37	284	0.72		
45	4.35	67	0.81	86	0.18	109	0.14	142	0.27	194	0.31	245	0.22	292	20.50		
46	1.76	68	9.67	87	1.59	111	0.08	150	0.40	195	0.74	251	0.36	293	1.95		
47	0.25	69	20.41	88	0.13	112	1.01	151	0.24	196	23.14	253	0.54	304	0.29		
50	0.24	70	43.36	91	0.38	113	0.32	152	0.86	197	1.12	254	0.95	307	21.60		

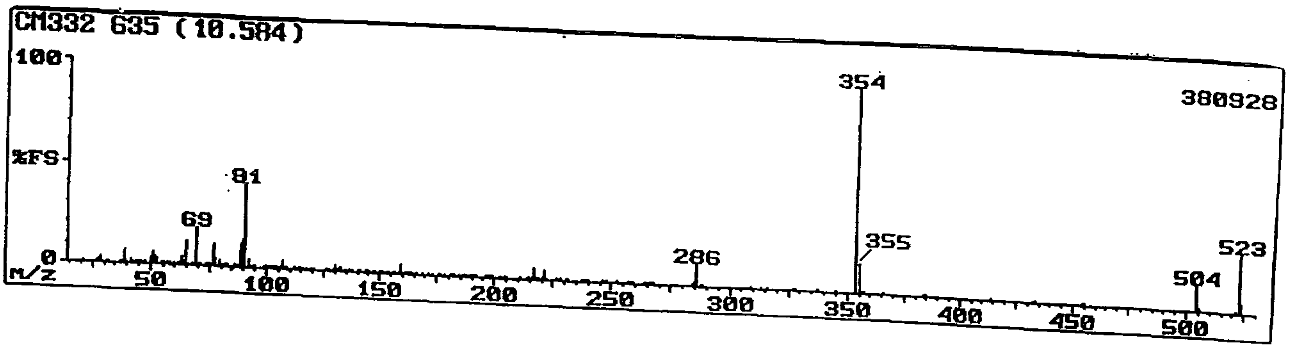
Spectrum No 37 (48A)



CM333 567 (9.451) 59648

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	7.19	75	1.01	131	0.53	252	1.00
31	1.10	76	3.84	133	0.49	253	0.72
32	0.72	77	21.89	143	0.50	271	1.10
38	1.01	78	1.85	144	0.60	272	6.44
39	3.67	90	1.72	145	3.41	313	2.04
40	0.46	91	1.46	152	0.97	340	100.00
44	1.72	92	0.59	176	0.81	341	12.66
50	2.44	93	0.76	184	0.65	439	0.58
51	4.59	94	0.78	190	0.68	440	2.39
52	0.50	100	0.92	196	0.72	490	12.88
63	1.13	103	0.45	203	3.92	491	2.31
64	0.50	107	0.47	218	1.30	509	25.86
65	3.89	118	0.47	221	2.39	510	4.16
69	10.94	119	1.55	225	2.39		
71	0.27	126	0.33	245	1.36		

Spectrum No 38 (48B)

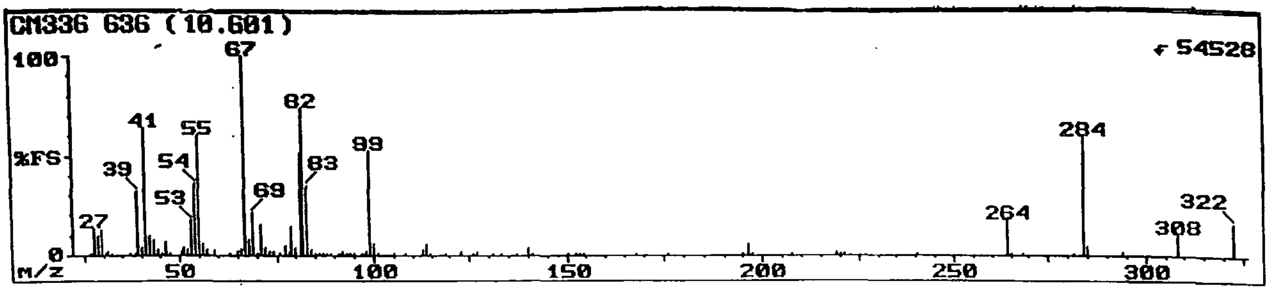


CM332 635 (10.584)

380928

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.07	87	0.26	150	0.58	226	0.05
27	0.28	88	0.46	151	0.13	228	0.09
27	1.46	89	11.29	152	0.54	231	0.15
28	3.11	90	13.37	153	0.05	232	1.19
29	0.13	91	41.13	154	0.65	237	0.14
31	0.48	92	3.70	156	0.33	238	0.05
32	0.89	93	0.30	157	1.05	239	0.84
37	0.18	94	0.40	158	0.22	240	0.09
38	0.86	95	0.12	159	4.77	246	0.12
39	7.06	99	0.05	160	0.53	248	0.19
40	0.93	100	1.44	161	0.10	252	0.31
41	1.83	101	0.09	162	0.17	257	0.12
42	0.27	102	0.22	163	1.09	258	0.14
43	0.26	103	0.52	164	0.91	259	0.77
44	0.53	104	1.21	165	0.09	264	0.37
45	0.13	105	0.39	166	0.55	266	1.44
46	0.65	106	0.16	169	0.95	267	0.22
47	0.13	107	3.41	171	0.08	268	0.07
50	3.06	108	0.60	173	0.27	284	1.09
51	6.25	109	0.29	176	1.08	285	1.97
52	3.48	112	0.13	177	0.23	286	10.95
53	3.34	114	0.35	178	0.07	287	1.23
54	0.45	115	0.11	181	0.40	288	0.12
55	0.19	116	0.91	182	0.40	309	0.18
57	0.09	117	0.59	183	0.24	313	0.05
58	0.04	119	0.78	184	0.11	316	0.11
59	0.04	120	0.10	186	0.13	327	0.90
61	0.19	121	0.19	187	0.13	328	0.11
62	1.23	126	0.62	188	0.14	337	0.09
63	4.05	127	0.17	189	0.20	345	0.08
64	1.61	128	0.04	190	0.20	354	100.00
65	11.96	129	0.15	191	0.09	355	14.38
66	0.81	130	2.82	192	0.04	356	1.21
67	0.08	131	1.01	196	1.38	357	0.10
69	18.82	132	1.85	197	0.25	366	0.04
70	0.24	133	2.42	198	1.43	384	0.07
71	0.90	134	0.16	199	0.30	385	0.14
73	0.10	135	0.07	202	0.12	414	0.16
74	0.38	136	0.09	204	0.86	433	0.34
75	0.59	137	0.13	205	0.08	434	0.15
76	1.44	138	0.09	211	0.11	454	0.43
77	10.42	140	0.11	214	0.11	455	0.11
78	3.86	141	0.21	216	0.71	504	12.30
79	2.86	142	0.28	217	5.65	505	2.05
80	0.29	144	0.07	218	0.67	506	0.20
81	0.23	145	0.03	219	0.20	522	0.51
82	0.04	146	0.16	220	0.09	523	29.03
83	0.07	147	0.24	221	4.91	524	5.04
86	0.20	148	0.08	222	0.10		

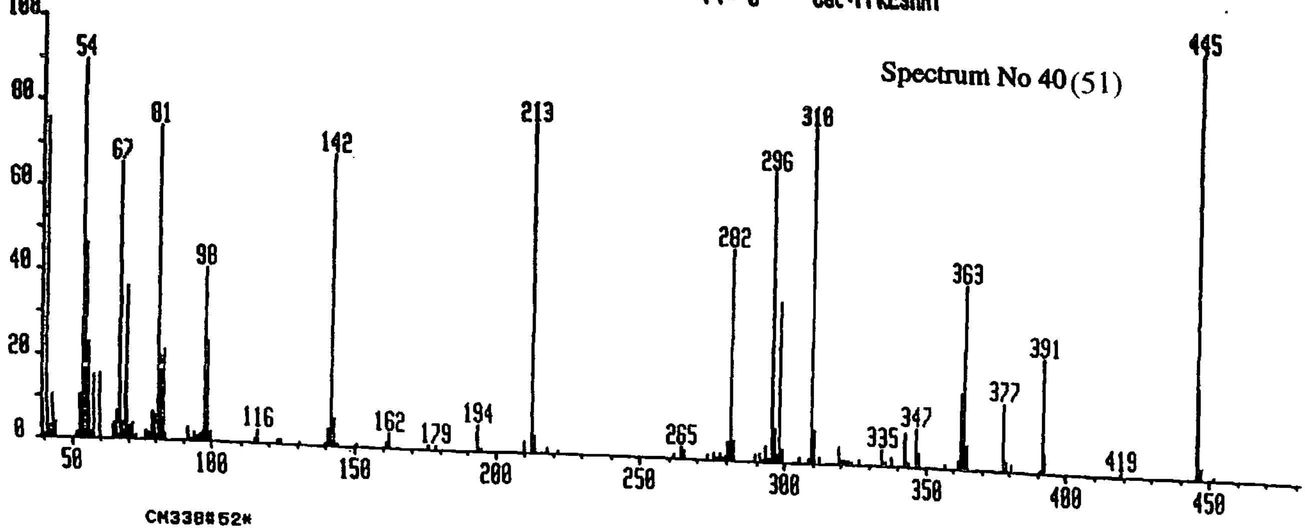
Spectrum No 39 (50)



CM336 636 (10.601) 54528

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
30	0.39	65	1.61	91	0.39	150	1.33
31	1.70	66	2.85	92	1.50	152	0.65
32	1.09	67	100.00	93	0.41	153	0.54
37	0.35	68	7.86	94	1.09	154	0.99
39	0.51	69	21.83	95	0.32	168	0.51
39	32.39	70	1.12	97	0.55	176	0.85
40	3.49	71	15.96	98	1.55	195	0.31
41	64.32	72	4.31	99	52.58	196	5.96
42	9.27	73	2.11	100	5.84	197	0.54
43	7.63	74	1.52	101	1.06	207	0.55
44	2.46	76	0.93	105	0.39	219	1.55
45	0.62	77	4.69	108	0.97	220	0.26
46	6.78	78	1.64	113	2.61	221	0.47
47	1.44	79	14.55	114	6.25	240	0.51
50	1.88	80	3.84	115	0.51	264	17.14
51	3.93	81	51.17	119	0.59	265	0.80
52	2.82	82	74.18	123	2.26	268	0.25
53	17.25	83	35.21	126	1.31	281	0.48
54	36.15	84	2.52	127	1.69	284	59.62
55	60.09	85	0.64	131	0.62	285	4.40
56	6.07	86	0.59	133	0.82	294	1.48
57	2.46	87	1.31	137	1.39	308	0.43
59	2.70	88	0.49	140	4.31	322	0.65
63	0.56	89	0.97	141	0.26		

```
BpM=0      I=9.5V    HA=451    TIC=844484032              Acnt:            Sys:ACE
CORINNE                                                        PT= 0°      Cal:PFK23MAY
```



Spectrum No 40(51)

```
CM338#52*
BpM=0         I=10v
CORINNE
           Mass        % Base
           40.11         5.20
           41.04        22.64 F
           41.12       100.00 FO
           42.11        10.03
           43.10        10.36
           44.01         6.91 F
           44.08        29.74 F
           46.07         1.07
           50.05         2.78
           51.04         8.44
           52.06         2.34
           53.06        23.95
           53.98        13.56 F
           54.07        66.01 F
           54.97        31.09 F
           55.07       100.00 FO
           56.06        19.73
           57.03        10.05
           58.02         1.01
           60.03         1.07
           62.99         1.29
           64.98        13.12
           65.99        10.34
           66.26         0.39
           66.98       100.00 O
           67.96        21.44
           68.92       100.00 O
           69.83        34.81 F
           69.92        64.20 F
           70.95         2.54
           75.93         0.60
           76.94         5.09
           77.96         1.12
           78.95        18.81
           79.96         6.50
           80.95        76.63
           81.96        42.03
           82.97        58.41
           83.98         3.39
           86.92         1.41
           91.90         2.21
           93.91         2.81
           94.93         0.62
           95.94         1.17
           96.97         2.15
           97.81         4.00 F
           97.97        22.98 F
           98.80        28.10 F
           98.97       100.00 FO
           99.95        10.08
          107.90         0.32
          111.89         1.28
          122.95         0.86
          123.95         0.98
          141.96         0.50
          175.80         1.11
          193.83         5.06
          194.83         0.58
```

```
           Mass        % Base
          213.76         0.58
          218.02         0.59 F
          218.67         0.88 F
          220.74         0.50
          236.74         0.83
          238.67        11.15
          261.27         3.24 F
          261.68        19.54 F
          262.69         1.91
          263.68         2.27
          264.62        13.80 F
          265.28         4.48 F
          265.69        25.62 F
          266.70         1.59
          276.70         0.44
          277.75         2.20
          278.70         1.28
          280.59         2.67 F
          281.21        76.28 F
          281.66       100.00 FO
          282.24         5.60 F
          282.67        28.93 F
          283.67         1.99
          291.68         2.60
          293.70         0.43
          295.70         1.62 F
          296.57         0.89 F
          297.24         0.54 F
          305.64         1.36
          307.62         0.42
          309.63         2.77
          318.60         7.80
          320.65         0.82
          321.69         5.95
          334.63         5.09
          335.65         2.81
          346.19         1.35 F
          346.65         8.52 F
          347.65         3.73
          349.57         0.38
          350.65         1.09
          361.53         3.01 F
          362.13         3.11 F
          362.63        18.06 F
          363.16        11.35 F
          363.61        63.14 F
          364.21         1.36 F
          364.62         8.50 F
          365.60         0.37
          444.50         2.45 F
          444.99         8.18 F
          445.55        65.33 F
          446.55        10.49 F
          447.52         0.69
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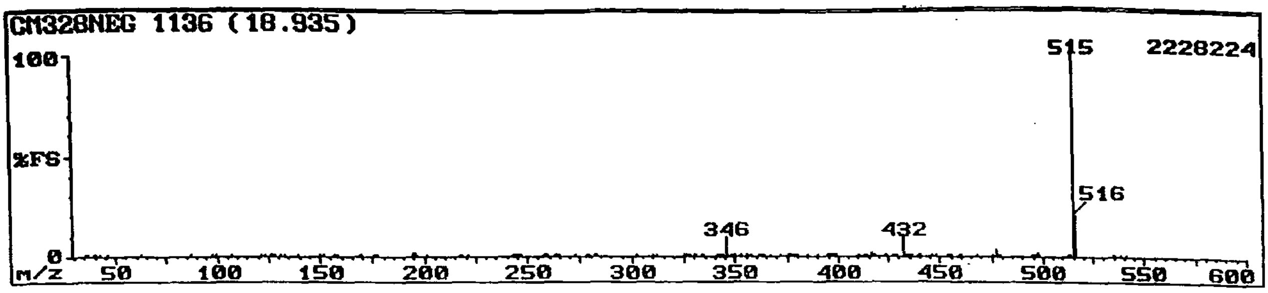
Spectrum No 41 (52)



CM328NEG 1136 (18.935) 2228224

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
35	0.01	221	0.03	349	0.01	428	0.03
36	0.01	243	0.01	352	0.02	432	9.47
39	0.12	243	0.05	355	0.04	433	1.09
40	0.02	244	0.05	357	0.01	434	0.10
42	0.09	245	0.05	361	0.20	435	0.02
46	0.02	246	0.06	362	0.09	436	0.01
62	0.08	247	0.01	363	0.02	439	0.04
87	0.01	257	0.02	364	0.03	440	0.01
97	0.02	258	0.02	366	0.03	446	0.76
99	0.04	259	0.01	371	0.01	447	0.11
107	0.06	264	0.16	375	0.05	453	0.22
121	0.01	264	0.28	376	0.02	454	0.04
123	0.01	265	0.02	377	0.01	455	0.07
126	0.02	272	0.01	378	0.01	459	0.10
127	0.03	278	0.03	379	0.01	460	0.01
128	0.01	279	0.01	380	0.01	467	0.01
131	0.01	282	0.01	385	0.01	475	0.10
133	0.02	283	0.01	389	0.01	477	4.00
139	0.02	302	0.01	394	0.11	478	0.53
150	0.01	309	0.01	395	0.08	479	0.09
152	0.02	311	0.01	396	0.06	494	0.07
157	0.25	325	0.03	397	0.16	495	0.58
157	0.57	326	0.03	398	0.06	496	1.21
158	0.03	327	0.31	399	0.01	497	1.60
169	0.38	328	0.32	409	0.06	498	0.17
169	0.63	329	0.07	410	0.01	513	0.07
170	0.02	330	0.01	412	0.22	513	0.30
176	0.17	333	0.01	413	0.59	515	100.00
176	0.24	334	0.01	414	0.30	516	20.40
177	0.02	341	0.27	416	2.06	534	0.53
195	1.62	342	0.05	417	0.24	535	0.03
195	1.56	343	0.01	418	0.02	538	0.13
196	0.07	344	0.06	423	0.03	541	0.03
202	0.02	346	10.16	424	0.01		
218	0.01	347	1.17	426	0.01		
218	0.01	348	0.11	427	0.04		

Appendix Four
Crystallgraphy Data

1. 4-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoic acid (**27**)
2. 2,4,6-Perfluorotri-isopropyl-s-triazine (**43**)

Data No. 1 (27)

Identification code	77m
Empirical formula	C14 H7 F13 O2
Formula weight	454.20
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	a = 8.3406(3) A alpha = 107.875(2) deg. b = 13.4143(6) A beta = 99.124(2) deg. c = 15.3048(6) A gamma = 90.991(2) deg.
Volume, Z	1605.10(11) A^3, 4
Density (calculated)	1.880 Mg/m^3
Absorption coefficient	0.224 mm^-1
F(000)	896
Crystal size	0.01 x 0.2 x 0.4 mm
Theta range for data collection	1.42 to 30.34 deg.
Limiting indices	-11<=h<=11, -18<=k<=17, -21<=l<=21
Reflections collected	12512
Independent reflections	8341 [R(int) = 0.1204]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8262 / 0 / 525
Goodness-of-fit on F^2	1.121
Final R indices [I>2sigma(I)]	R1 = 0.0942, wR2 = 0.1420
R indices (all data)	R1 = 0.2690, wR2 = 0.2391
Largest diff. peak and hole	0.395 and -0.433 e.A^-3

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

	x	y	z	U(eq)
C(101)	-2985(8)	5698(6)	1345(5)	40(2)
F(1C)	-4429(5)	5802(3)	1590(3)	57(1)
F(1B)	-2170(5)	5114(3)	1795(3)	66(1)
F(1A)	-3173(5)	5219(3)	444(3)	71(1)
C(102)	-2089(7)	6800(5)	1609(4)	29(2)
F(2B)	-1812(4)	7174(3)	2551(2)	40(1)
F(2A)	-3160(4)	7411(3)	1297(3)	44(1)
C(103)	-501(7)	6843(5)	1221(4)	27(2)
F(3B)	320(4)	6033(3)	1383(2)	35(1)
F(3A)	-949(4)	6586(3)	291(2)	37(1)
C(104)	716(7)	7870(5)	1606(4)	25(1)
C(105)	-209(8)	8854(5)	1590(5)	34(2)
F(5C)	801(4)	9681(3)	1719(3)	46(1)
F(5B)	-1233(4)	8712(3)	797(3)	47(1)
F(5A)	-1091(4)	9121(3)	2278(3)	45(1)
C(106)	1987(8)	7736(6)	952(5)	37(2)
F(6C)	3164(4)	8510(3)	1260(2)	48(1)
F(6B)	1321(5)	7750(3)	96(3)	58(1)
F(6A)	2694(5)	6844(3)	853(3)	61(1)
C(107)	1577(7)	7959(5)	2619(4)	31(2)
C(108)	2995(7)	8755(5)	3099(4)	24(1)
C(109)	2769(7)	9791(5)	3572(4)	27(2)
C(110)	4093(7)	10500(5)	4012(4)	28(2)
C(111)	5663(7)	10189(5)	4001(4)	23(1)
C(112)	5901(7)	9150(5)	3556(4)	32(2)
C(113)	4580(7)	8436(5)	3107(4)	29(2)
C(114)	7090(7)	10963(5)	4454(4)	28(2)
O(101)	8504(5)	10602(3)	4466(3)	38(1)
O(102)	6843(5)	11920(3)	4803(3)	36(1)
C(201)	5930(9)	1426(6)	1290(6)	48(2)
F(1F)	7284(5)	2058(4)	1614(3)	64(1)
F(1E)	5418(5)	1397(4)	419(3)	70(1)
F(1D)	6323(5)	470(4)	1304(3)	72(1)
C(202)	4627(7)	1781(5)	1912(4)	30(2)
F(2E)	3462(4)	1011(3)	1641(3)	47(1)
F(2D)	5352(4)	1894(3)	2792(2)	39(1)
C(203)	3891(7)	2835(5)	1870(4)	27(2)
F(3E)	5173(4)	3501(3)	1923(2)	30(1)
F(3D)	3009(4)	2619(3)	1000(2)	36(1)
C(204)	2830(6)	3404(5)	2605(4)	22(1)
C(205)	1948(7)	4266(5)	2260(4)	28(2)
F(5F)	681(4)	3872(3)	1583(2)	34(1)
F(5E)	2950(4)	4809(3)	1946(2)	37(1)
F(5D)	1375(4)	4966(3)	2962(2)	34(1)
C(206)	1457(7)	2638(5)	2679(4)	29(2)
F(6F)	691(4)	2024(3)	1849(2)	34(1)
F(6E)	2089(4)	1995(3)	3147(2)	37(1)
F(6D)	357(4)	3161(3)	3143(2)	38(1)
C(207)	3827(6)	3883(5)	3616(4)	24(1)
C(208)	5224(7)	4719(5)	3797(4)	23(1)
C(209)	4967(7)	5779(5)	3970(4)	26(2)
C(210)	6264(7)	6515(5)	4203(4)	26(1)
C(211)	7855(7)	6209(5)	4283(4)	27(2)
C(212)	8130(7)	5157(5)	4123(4)	27(2)
C(213)	6818(7)	4423(5)	3896(4)	25(1)
C(214)	9231(7)	7037(5)	4571(4)	28(2)
O(201)	10688(5)	6686(3)	4618(3)	39(1)
O(202)	9000(5)	7993(3)	4766(3)	35(1)

Bond lengths [A] and angles [deg]

C(101)-F(1A)	1.313(8)
C(101)-F(1C)	1.314(7)
C(101)-F(1B)	1.323(7)
C(101)-C(102)	1.551(8)
C(102)-F(2B)	1.352(7)
C(102)-F(2A)	1.352(6)
C(102)-C(103)	1.543(8)
C(103)-F(3A)	1.345(6)
C(103)-F(3B)	1.360(6)
C(103)-C(104)	1.593(8)
C(104)-C(105)	1.545(8)
C(104)-C(106)	1.547(9)
C(104)-C(107)	1.569(7)
C(105)-F(5C)	1.326(7)
C(105)-F(5B)	1.329(6)
C(105)-F(5A)	1.342(7)
C(106)-F(6A)	1.321(7)
C(106)-F(6C)	1.334(7)
C(106)-F(6B)	1.345(7)
C(107)-C(108)	1.508(7)
C(107)-H(10A)	0.97
C(107)-H(10B)	0.97
C(108)-C(109)	1.389(8)
C(108)-C(113)	1.396(8)
C(109)-C(110)	1.382(8)
C(109)-H(109)	0.93
C(110)-C(111)	1.382(8)
C(110)-H(110)	0.93
C(111)-C(112)	1.383(8)
C(111)-C(114)	1.493(8)
C(112)-C(113)	1.387(8)
C(112)-H(112)	0.93
C(113)-H(113)	0.93
C(114)-O(102)	1.265(7)
C(114)-O(101)	1.282(7)
O(101)-H(101)	0.82
C(201)-F(1E)	1.323(8)
C(201)-F(1F)	1.331(8)
C(201)-F(1D)	1.334(8)
C(201)-C(202)	1.543(9)
C(202)-F(2E)	1.326(6)
C(202)-F(2D)	1.348(6)
C(202)-C(203)	1.566(8)
C(203)-F(3E)	1.358(6)
C(203)-F(3D)	1.358(6)
C(203)-C(204)	1.563(8)
C(204)-C(205)	1.562(8)
C(204)-C(206)	1.565(8)
C(204)-C(207)	1.569(7)
C(205)-F(5F)	1.329(6)
C(205)-F(5E)	1.334(7)
C(205)-F(5D)	1.350(7)
C(206)-F(6D)	1.327(7)
C(206)-F(6F)	1.336(6)
C(206)-F(6E)	1.345(6)
C(207)-C(208)	1.534(7)
C(207)-H(20A)	0.97
C(207)-H(20B)	0.97
C(208)-C(209)	1.391(8)
C(208)-C(213)	1.393(7)
C(209)-C(210)	1.377(8)
C(209)-H(209)	0.93
C(210)-C(211)	1.393(8)
C(210)-H(210)	0.93
C(211)-C(212)	1.386(8)
C(211)-C(214)	1.497(8)

C(212)-C(213)

C(212)-H(212)	0.93
C(213)-H(213)	0.93
C(214)-O(202)	1.250(7)
C(214)-O(201)	1.311(7)
O(201)-H(201)	0.82
F(1A)-C(101)-F(1C)	108.7(5)
F(1A)-C(101)-F(1B)	109.4(6)
F(1C)-C(101)-F(1B)	108.0(6)
F(1A)-C(101)-C(102)	111.1(6)
F(1C)-C(101)-C(102)	109.1(6)
F(1B)-C(101)-C(102)	110.5(5)
F(2B)-C(102)-F(2A)	107.4(5)
F(2B)-C(102)-C(103)	111.0(5)
F(2A)-C(102)-C(103)	109.4(5)
F(2B)-C(102)-C(101)	106.2(5)
F(2A)-C(102)-C(101)	106.4(5)
C(103)-C(102)-C(101)	116.0(6)
F(3A)-C(103)-F(3B)	106.4(5)
F(3A)-C(103)-C(102)	105.8(5)
F(3B)-C(103)-C(102)	104.6(5)
F(3A)-C(103)-C(104)	110.5(5)
F(3B)-C(103)-C(104)	107.9(4)
C(102)-C(103)-C(104)	120.7(5)
C(105)-C(104)-C(106)	108.9(5)
C(105)-C(104)-C(107)	111.3(5)
C(106)-C(104)-C(107)	110.2(5)
C(105)-C(104)-C(103)	110.5(5)
C(106)-C(104)-C(103)	107.3(5)
C(107)-C(104)-C(103)	108.5(5)
F(5C)-C(105)-F(5B)	107.8(5)
F(5C)-C(105)-F(5A)	106.5(5)
F(5B)-C(105)-F(5A)	106.9(5)
F(5C)-C(105)-C(104)	111.8(5)
F(5B)-C(105)-C(104)	112.7(5)
F(5A)-C(105)-C(104)	110.9(5)
F(6A)-C(106)-F(6C)	107.3(6)
F(6A)-C(106)-F(6B)	107.5(6)
F(6C)-C(106)-F(6B)	105.3(5)
F(6A)-C(106)-C(104)	111.8(5)
F(6C)-C(106)-C(104)	112.4(5)
F(6B)-C(106)-C(104)	112.1(5)
C(108)-C(107)-C(104)	120.2(5)
C(108)-C(107)-H(10A)	107.3(3)
C(104)-C(107)-H(10A)	107.3(3)
C(108)-C(107)-H(10B)	107.3(3)
C(104)-C(107)-H(10B)	107.3(3)
H(10A)-C(107)-H(10B)	106.9
C(109)-C(108)-C(113)	118.6(5)
C(109)-C(108)-C(107)	121.8(5)
C(113)-C(108)-C(107)	119.5(6)
C(110)-C(109)-C(108)	120.4(6)
C(110)-C(109)-H(109)	119.8(4)
C(108)-C(109)-H(109)	119.8(3)
C(111)-C(110)-C(109)	120.8(6)
C(111)-C(110)-H(110)	119.6(4)
C(109)-C(110)-H(110)	119.6(4)
C(110)-C(111)-C(112)	119.2(6)
C(110)-C(111)-C(114)	120.6(6)
C(112)-C(111)-C(114)	120.1(6)
C(111)-C(112)-C(113)	120.3(6)
C(111)-C(112)-H(112)	119.8(4)
C(113)-C(112)-H(112)	119.8(4)
C(112)-C(113)-C(108)	120.5(6)
C(112)-C(113)-H(113)	119.7(4)
C(108)-C(113)-H(113)	119.7(3)
O(102)-C(114)-O(101)	124.1(6)
O(102)-C(114)-C(111)	119.0(6)
O(101)-C(114)-C(111)	116.9(6)

C(114)-O(101)-H(101)

F(1E)-C(201)-F(1F)	108.0(7)
F(1E)-C(201)-F(1D)	109.2(6)
F(1F)-C(201)-F(1D)	107.2(6)
F(1E)-C(201)-C(202)	112.4(6)
F(1F)-C(201)-C(202)	111.4(6)
F(1D)-C(201)-C(202)	108.4(7)
F(2E)-C(202)-F(2D)	109.4(5)
F(2E)-C(202)-C(201)	106.9(5)
F(2D)-C(202)-C(201)	106.6(5)
F(2E)-C(202)-C(203)	110.2(5)
F(2D)-C(202)-C(203)	109.4(5)
C(201)-C(202)-C(203)	114.2(6)
F(3E)-C(203)-F(3D)	106.7(4)
F(3E)-C(203)-C(204)	108.7(5)
F(3D)-C(203)-C(204)	109.5(4)
F(3E)-C(203)-C(202)	106.0(5)
F(3D)-C(203)-C(202)	105.8(5)
C(204)-C(203)-C(202)	119.5(5)
C(205)-C(204)-C(203)	107.8(5)
C(205)-C(204)-C(206)	106.3(4)
C(203)-C(204)-C(206)	111.7(5)
C(205)-C(204)-C(207)	111.3(5)
C(203)-C(204)-C(207)	113.5(4)
C(206)-C(204)-C(207)	106.0(4)
F(5F)-C(205)-F(5E)	107.7(5)
F(5F)-C(205)-F(5D)	106.8(5)
F(5E)-C(205)-F(5D)	106.8(5)
F(5F)-C(205)-C(204)	112.6(5)
F(5E)-C(205)-C(204)	111.9(5)
F(5D)-C(205)-C(204)	110.7(5)
F(6D)-C(206)-F(6F)	108.3(5)
F(6D)-C(206)-F(6E)	107.0(5)
F(6F)-C(206)-F(6E)	106.6(5)
F(6D)-C(206)-C(204)	111.3(5)
F(6F)-C(206)-C(204)	113.0(5)
F(6E)-C(206)-C(204)	110.4(5)
C(208)-C(207)-C(204)	119.3(5)
C(208)-C(207)-H(20A)	107.5(3)
C(204)-C(207)-H(20A)	107.5(3)
C(208)-C(207)-H(20B)	107.5(3)
C(204)-C(207)-H(20B)	107.5(3)
H(20A)-C(207)-H(20B)	107.0
C(209)-C(208)-C(213)	118.6(5)
C(209)-C(208)-C(207)	122.4(5)
C(213)-C(208)-C(207)	118.6(5)
C(210)-C(209)-C(208)	120.6(5)
C(210)-C(209)-H(209)	119.7(4)
C(208)-C(209)-H(209)	119.7(3)
C(209)-C(210)-C(211)	120.4(6)
C(209)-C(210)-H(210)	119.8(4)
C(211)-C(210)-H(210)	119.8(3)
C(212)-C(211)-C(210)	119.7(6)
C(212)-C(211)-C(214)	121.6(6)
C(210)-C(211)-C(214)	118.7(6)
C(213)-C(212)-C(211)	119.6(6)
C(213)-C(212)-H(212)	120.2(3)
C(211)-C(212)-H(212)	120.2(4)
C(212)-C(213)-C(208)	121.1(5)
C(212)-C(213)-H(213)	119.4(3)
C(208)-C(213)-H(213)	119.4(3)
O(202)-C(214)-O(201)	122.7(6)
O(202)-C(214)-C(211)	122.2(6)
O(201)-C(214)-C(211)	115.1(6)
C(214)-O(201)-H(201)	109.5(3)

Symmetry transformations used to generate equivalent atoms:

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

	U11	U22	U33	U23	U13	U12
C(101)	30(4)	35(4)	52(5)	17(4)	-2(4)	-11(3)
F(1C)	37(2)	52(3)	84(3)	22(2)	19(2)	-12(2)
F(1B)	47(3)	50(3)	116(4)	49(3)	8(2)	-5(2)
F(1A)	81(3)	59(3)	53(3)	-9(2)	11(2)	-38(3)
C(102)	22(3)	32(4)	32(4)	11(3)	1(3)	-1(3)
F(2B)	38(2)	47(3)	34(2)	10(2)	11(2)	-10(2)
F(2A)	31(2)	41(2)	63(3)	23(2)	5(2)	7(2)
C(103)	27(4)	29(4)	25(4)	9(3)	5(3)	2(3)
F(3B)	34(2)	24(2)	48(2)	12(2)	5(2)	3(2)
F(3A)	42(2)	41(2)	26(2)	9(2)	5(2)	-5(2)
C(104)	24(3)	27(4)	26(3)	12(3)	5(3)	-3(3)
C(105)	36(4)	23(4)	39(4)	10(3)	-1(4)	-9(3)
F(5C)	56(3)	31(2)	53(3)	24(2)	-5(2)	-8(2)
F(5B)	52(2)	41(2)	48(3)	27(2)	-13(2)	-2(2)
F(5A)	54(3)	31(2)	56(3)	15(2)	20(2)	11(2)
C(106)	39(4)	39(5)	32(4)	7(3)	9(3)	-13(4)
F(6C)	40(2)	67(3)	39(2)	22(2)	8(2)	-19(2)
F(6B)	59(3)	88(3)	29(2)	20(2)	12(2)	-22(2)
F(6A)	54(3)	50(3)	90(3)	22(3)	47(2)	13(2)
C(107)	32(4)	33(4)	32(4)	17(3)	2(3)	1(3)
C(108)	22(3)	24(4)	24(3)	11(3)	-3(3)	-5(3)
C(109)	22(3)	38(4)	26(3)	15(3)	9(3)	12(3)
C(110)	32(4)	29(4)	24(4)	12(3)	1(3)	0(3)
C(111)	26(3)	26(4)	17(3)	8(3)	4(3)	2(3)
C(112)	26(4)	43(5)	29(4)	15(3)	2(3)	5(3)
C(113)	33(4)	23(4)	28(4)	5(3)	2(3)	4(3)
C(114)	29(4)	29(4)	29(4)	15(3)	-1(3)	-1(3)
O(101)	24(2)	37(3)	46(3)	7(2)	-2(2)	-6(2)
O(102)	39(3)	21(3)	45(3)	8(2)	8(2)	-3(2)
C(201)	37(5)	50(6)	53(5)	7(4)	11(4)	9(4)
F(1F)	31(2)	72(3)	90(3)	20(3)	23(2)	6(2)
F(1E)	61(3)	102(4)	46(3)	10(3)	26(2)	25(3)
F(1D)	66(3)	52(3)	98(4)	13(3)	29(3)	29(3)
C(202)	22(3)	29(4)	36(4)	10(3)	0(3)	-4(3)
F(2E)	38(2)	30(2)	69(3)	11(2)	8(2)	-4(2)
F(2D)	42(2)	37(2)	43(2)	19(2)	4(2)	11(2)
C(203)	22(3)	36(4)	25(4)	14(3)	2(3)	-8(3)
F(3E)	25(2)	35(2)	36(2)	14(2)	12(2)	-4(2)
F(3D)	33(2)	46(2)	27(2)	12(2)	1(2)	2(2)
C(204)	16(3)	27(4)	25(3)	11(3)	5(3)	3(3)
C(205)	23(3)	32(4)	29(4)	13(3)	3(3)	1(3)
F(5F)	27(2)	38(2)	36(2)	15(2)	-4(2)	4(2)
F(5E)	33(2)	41(2)	47(2)	29(2)	10(2)	1(2)
F(5D)	34(2)	29(2)	39(2)	7(2)	8(2)	6(2)
C(206)	30(4)	31(4)	30(4)	17(3)	3(3)	-4(3)
F(6F)	27(2)	34(2)	39(2)	9(2)	3(2)	-8(2)
F(6E)	38(2)	34(2)	48(2)	26(2)	6(2)	-6(2)
F(6D)	28(2)	40(2)	51(2)	14(2)	21(2)	1(2)
C(207)	25(3)	27(4)	23(3)	10(3)	7(3)	-1(3)
C(208)	26(3)	25(4)	20(3)	11(3)	4(3)	1(3)
C(209)	18(3)	31(4)	31(4)	11(3)	2(3)	3(3)
C(210)	30(4)	20(4)	29(4)	11(3)	3(3)	2(3)
C(211)	32(4)	32(4)	17(3)	8(3)	5(3)	-5(3)
C(212)	22(3)	23(4)	37(4)	10(3)	5(3)	-2(3)
C(213)	30(4)	17(3)	31(4)	14(3)	4(3)	9(3)
C(214)	26(4)	33(4)	25(4)	12(3)	0(3)	-1(3)
O(201)	31(3)	30(3)	47(3)	1(2)	1(2)	-5(2)
O(202)	35(3)	19(3)	49(3)	12(2)	0(2)	-4(2)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3)

	x	y	z	U(eq)
H(10A)	752(7)	8099(5)	3013(4)	37
H(10B)	1950(7)	7274(5)	2603(4)	37
H(109)	1720(7)	10010(5)	3594(4)	32
H(110)	3926(7)	11194(5)	4319(4)	34
H(112)	6953(7)	8930(5)	3557(4)	39
H(113)	4752(7)	7739(5)	2810(4)	35
H(101)	9174(14)	11041(22)	4845(36)	57
H(20A)	3063(6)	4185(5)	4025(4)	29
H(20B)	4277(6)	3306(5)	3809(4)	29
H(209)	3910(7)	5992(5)	3927(4)	32
H(210)	6078(7)	7220(5)	4309(4)	31
H(212)	9187(7)	4945(5)	4167(4)	32
H(213)	7006(7)	3720(5)	3809(4)	30
H(201)	11342(15)	7145(20)	4986(38)	59

Data No 2 (43)

Empirical formula	$C_{12} F_{21} N_3$
Formula weight	585.15
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C c
Unit cell dimensions	a = 16.510(3) Å, $\alpha = 90°$
	b = 29.181(6) Å, $\beta = 110.38(3)°$
	c = 12.048(2) Å, $\gamma = 90°$
Volume	5441(2) $Å^3$
Z	12
Density (calculated),	2.143 Mg/m^3
Absorption coefficient	0.282 mm^{-1}
F(000)	3384
Crystal size	0.4 x 0.2 x 0.2 mm
Theta range for data collection	1.40 to 30.34°
Index ranges	$-23 \leq h \leq 22$, $-40 \leq k \leq 40$, $-16 \leq l \leq 17$
Reflections collected	32956
Independent reflections	14439 [R(int) = 0.0601]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14402 / 56 / 945
Goodness-of-fit on F^2	1.046
Final R indices [I>2 σ (I)]	$R_1 = 0.0798$, $wR_2 = 0.1819$
R indices (all data)	$R_1 = 0.1467$, $wR_2 = 0.2385$

Largest diff. peak and hole 0.733 and -0.533 e.$Å^{-3}$

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

Atom	x	y	z	U(eq)	Atom	x	y	z	U(eq)
F(101)	858	2946(1)	7022	37(1)	F(311)	-6516(5)	-618(2)	6302(7)	75(2)
F(102)	-450(4)	3496(1)	6150(6)	42(1)	F(312)	-6944(4)	-680(2)	9041(6)	48(1)
F(103)	-810(5)	2828(2)	5421(6)	62(2)	F(313)	-5736(4)	-348(2)	9916(6)	70(2)
F(104)	-1296(4)	3103(2)	6760(7)	54(1)	F(314)	-5820(4)	-866(2)	8601(7)	61(2)
F(105)	521(4)	3528(1)	8568(6)	47(1)	F(315)	-3036(4)	230(1)	7431(6)	44(1)
F(106)	1092(4)	2897(2)	9338(6)	58(2)	F(316)	-2258(4)	-444(2)	8970(6)	48(1)
F(107)	-250(5)	3030(2)	9026(6)	56(2)	F(317)	-2764(4)	93(2)	9725(7)	74(2)
F(108)	1055(4)	873(1)	7338(6)	43(1)	F(318)	-3413(4)	-549(2)	9405(7)	70(2)
F(109)	2181(4)	1815(1)	6803(6)	46(1)	F(319)	-3052(4)	-589(2)	6604(6)	43(1)
F(110)	2184(4)	1084(2)	6408(6)	40(1)	F(320)	-4131(5)	-812(2)	7105(7)	62(2)
F(111)	1034(4)	1473(2)	5548(5)	58(2)	F(321)	-4288(4)	-282(2)	5767(6)	60(1)
F(112)	2359(4)	1738(2)	9146(6)	58(2)	N(11)	725(5)	2084(2)	7423(6)	28(1)
F(113)	2733(4)	1064(2)	8850(6)	45(1)	N(12)	-70(5)	1441(2)	7672(7)	28(1)
F(114)	1717(5)	1186(2)	9563(6)	62(2)	N(13)	-644(4)	2188(2)	7606(7)	26(1)
F(115)	-1914(4)	1876(1)	8204(6)	36(1)	N(21)	799(5)	-1118(2)	7635(7)	37(2)
F(116)	-1949(4)	1084(2)	9146(6)	43(1)	N(22)	-582(5)	-1188(2)	7832(7)	47(2)
F(117)	-1014(4)	782(1)	8520(6)	44(1)	N(23)	169(5)	-1862(2)	7621(7)	26(1)
F(118)	-621(4)	1322(2)	9793(6)	49(1)	N(31)	-5748(5)	575(2)	7968(7)	31(1)
F(119)	-2361(4)	1704(2)	5911(6)	55(1)	N(32)	-5016(5)	-107(2)	7845(7)	30(1)
F(120)	-2815(4)	1172(2)	6770(6)	51(1)	N(33)	-4331(4)	616(2)	7841(6)	26(1)
F(121)	-1736(4)	1047(2)	6198(6)	46(1)	C(101)	74(5)	2340(2)	7461(7)	25(1)
F(201)	2066(4)	-1474(1)	7110(6)	38(1)	C(102)	613(5)	1638(2)	7539(7)	28(1)
F(202)	1083(4)	-2550(1)	6787(6)	45(1)	C(103)	-679(5)	1738(2)	7713(7)	26(1)
F(203)	2042(4)	-2268(2)	6159(6)	44(1)	C(104)	172(4)	2863(2)	7364(7)	22(1)
F(204)	759(4)	-2005(2)	5496(6)	49(1)	C(105)	-632(5)	3078(2)	6418(6)	28(1)
F(205)	2907(4)	-2161(2)	8589(6)	42(1)	C(106)	364(5)	3086(2)	8595(7)	32(2)
F(206)	1800(4)	-2289(2)	9075(6)	53(1)	C(107)	1354(5)	1312(2)	7556(8)	32(2)
F(207)	2411(4)	-1635(2)	9432(6)	44(1)	C(108)	1714(4)	1435(2)	6547(7)	34(2)
F(9)	537(4)	205(2)	9076(6)	53(1)	C(109)	2069(5)	1328(2)	8802(7)	31(2)
F(13)	-475(4)	248(2)	6718(6)	56(1)	C(110)	-1498(5)	1541(2)	7847(8)	29(2)
F(8)	-767(5)	-332(3)	8264(7)	37(2)	C(111)	-1267(5)	1165(2)	8856(7)	34(2)

F(10)	1424(8)	-250(4)	8687(11)	65(3)	C(112)	-2120(5)	1353(2)	6652(8)	35(2)
F(11)	897(7)	-466(3)	9902(10)	53(2)	C(201)	792(5)	-1573(2)	7570(7)	28(2)
F(12)	-1288(9)	-249(5)	7169(13)	87(4)	C(202)	90(7)	-948(2)	7761(9)	51(2)
F(14)	-1047(7)	-413(3)	5960(10)	48(2)	C(203)	-489(6)	-1646(2)	7766(8)	31(2)
F(8')	837(7)	-230(3)	7237(10)	56(2)	C(204)	1590(5)	-1795(2)	7435(7)	26(1)
F(10')	-152(11)	-376(5)	9387(15)	101(4)	C(205)	1362(4)	-2167(2)	6456(7)	31(2)
F(11')	1218(8)	-411(3)	9533(11)	55(2)	C(206)	2191(5)	-1975(2)	8639(7)	29(2)
F(12')	382(9)	-269(4)	6352(12)	70(3)	C(27)	-74(8)	-439(4)	7977(12)	20(2)
F(14')	-687(7)	-383(3)	5725(10)	50(2)	C(27')	172(11)	-401(5)	7656(16)	40(3)
F(215)	-956(4)	-2400(1)	8020(6)	40(1)	C(28)	565(8)	-226(4)	8923(11)	67(3)
F(216)	-2612(4)	-2222(2)	6490(6)	52(1)	C(29)	-437(8)	-205(4)	6755(12)	72(3)
F(217)	-1617(4)	-2133(2)	5768(6)	67(2)	C(210)	-1242(5)	-1955(2)	7766(7)	33(2)
F(218)	-2239(4)	-1540(2)	6193(6)	69(2)	C(211)	-1949(5)	-1963(2)	6533(8)	40(2)
F(219)	-2051(5)	-1437(2)	8500(7)	69(2)	C(212)	-1603(5)	-1827(2)	8763(8)	49(2)
F(220)	-2099(4)	-2160(2)	8922(6)	52(1)	C(301)	-5035(5)	797(2)	7924(7)	26(1)
F(221)	-932(4)	-1769(2)	9780(6)	59(1)	C(302)	-5675(5)	125(2)	7929(7)	28(1)
F(301)	-5801(3)	1453(1)	8212(5)	40(1)	C(303)	-4357(5)	161(2)	7816(7)	25(1)
F(302)	-6000(4)	1308(2)	5929(6)	54(1)	C(304)	-5121(4)	1329(2)	7898(8)	26(1)
F(303)	-5421(4)	1956(1)	6613(6)	45(1)	C(305)	-5286(5)	1505(2)	6657(7)	34(2)
F(304)	-4645(4)	1404(2)	6268(6)	45(1)	C(306)	-4303(5)	1544(2)	8860(7)	36(2)
F(305)	-3609(4)	1520(2)	8572(6)	45(1)	C(307)	-6491(5)	-150(2)	7934(8)	32(2)
F(306)	-4127(4)	1320(2)	9873(6)	56(1)	C(308)	-6974(5)	-330(2)	6682(8)	42(2)
F(307)	-4466(4)	1973(1)	9057(6)	49(1)	C(309)	-6241(5)	-525(2)	8881(8)	41(2)
F(308)	-7030(4)	134(1)	8241(7)	50(1)	C(310)	-3537(5)	-79(2)	7728(8)	32(2)
F(309)	-7689(4)	-540(2)	6634(6)	56(1)	C(311)	-2982(5)	-257(2)	8983(7)	36(2)
F(310)	-7177(5)	26(2)	5962(7)	86(2)	C(312)	-3760(5)	-456(2)	6789(7)	35(2)

Bond lengths [Å] and angles [°]

F(101)-C(104)	1.356(6)	F(315)-C(310)	1.353(6)
F(102)-C(105)	1.321(6)	F(316)-C(311)	1.319(6)
F(103)-C(105)	1.347(6)	F(317)-C(311)	1.323(7)
F(104)-C(105)	1.301(6)	F(318)-C(311)	1.319(7)
F(105)-C(106)	1.318(6)	F(319)-C(312)	1.322(6)
F(106)-C(106)	1.342(7)	F(320)-C(312)	1.329(6)
F(107)-C(106)	1.299(7)	F(321)-C(312)	1.336(6)
F(108)-C(107)	1.366(6)	N(11)-C(101)	1.324(9)
F(109)-C(108)	1.326(6)	N(11)-C(102)	1.326(9)
F(110)-C(108)	1.329(6)	N(12)-C(102)	1.324(9)
F(111)-C(108)	1.334(6)	N(12)-C(103)	1.340(9)
F(112)-C(109)	1.302(7)	N(13)-C(103)	1.323(9)
F(113)-C(109)	1.325(6)	N(13)-C(101)	1.332(9)
F(114)-C(109)	1.313(6)	N(21)-C(202)	1.326(12)
F(115)-C(110)	1.349(6)	N(21)-C(201)	1.331(8)
F(116)-C(111)	1.312(6)	N(22)-C(202)	1.339(12)
F(117)-C(111)	1.307(6)	N(22)-C(203)	1.351(9)
F(118)-C(111)	1.335(7)	N(23)-C(203)	1.319(10)
F(119)-C(112)	1.327(6)	N(23)-C(201)	1.347(9)
F(120)-C(112)	1.314(7)	N(31)-C(302)	1.320(9)
F(121)-C(112)	1.320(7)	N(31)-C(301)	1.361(9)
F(201)-C(204)	1.364(6)	N(32)-C(302)	1.315(9)
F(202)-C(205)	1.321(6)	N(32)-C(303)	1.350(9)
F(203)-C(205)	1.326(6)	N(33)-C(301)	1.312(9)
F(204)-C(205)	1.324(6)	N(33)-C(303)	1.328(8)
F(205)-C(206)	1.321(6)	C(101)-C(104)	1.545(8)
F(206)-C(206)	1.329(6)	C(102)-C(107)	1.545(9)
F(207)-C(206)	1.336(6)	C(103)-C(110)	1.530(10)
F(215)-C(210)	1.380(7)	C(104)-C(106)	1.548(9)
F(216)-C(211)	1.316(7)	C(104)-C(105)	1.549(9)
F(217)-C(211)	1.323(7)	C(107)-C(109)	1.554(10)
F(218)-C(211)	1.334(7)	C(107)-C(108)	1.568(10)
F(219)-C(212)	1.333(7)	C(110)-C(112)	1.549(10)
F(220)-C(212)	1.328(7)	C(110)-C(111)	1.581(10)
F(221)-C(212)	1.345(7)	C(201)-C(204)	1.526(10)
F(301)-C(304)	1.354(6)	C(203)-C(210)	1.535(11)
F(302)-C(305)	1.330(7)	C(204)-C(206)	1.537(10)
F(303)-C(305)	1.332(6)	C(204)-C(205)	1.551(9)
F(304)-C(305)	1.331(7)	C(210)-C(211)	1.537(10)
F(305)-C(306)	1.309(7)	C(210)-C(212)	1.561(10)
F(306)-C(306)	1.325(7)	C(301)-C(304)	1.558(8)
F(307)-C(306)	1.318(6)	C(302)-C(307)	1.571(9)
F(308)-C(307)	1.358(6)	C(303)-C(310)	1.559(9)
F(309)-C(308)	1.314(7)	C(304)-C(305)	1.514(10)
F(310)-C(308)	1.321(7)	C(304)-C(306)	1.572(9)
F(311)-C(308)	1.314(7)	C(307)-C(309)	1.531(10)
F(312)-C(309)	1.321(6)	C(307)-C(308)	1.532(11)
F(313)-C(309)	1.340(7)	C(310)-C(312)	1.528(10)
F(314)-C(309)	1.322(7)	C(310)-C(311)	1.560(10)

C(101)-N(11)-C(102)	113.8(6)	F(204)-C(205)-C(204)	108.9(5)
C(102)-N(12)-C(103)	113.9(5)	F(203)-C(205)-C(204)	110.9(5)
C(103)-N(13)-C(101)	114.4(6)	F(205)-C(206)-F(206)	107.5(5)
C(202)-N(21)-C(201)	112.9(7)	F(205)-C(206)-F(207)	108.2(5)
C(202)-N(22)-C(203)	113.6(7)	F(206)-C(206)-F(207)	106.1(5)
C(203)-N(23)-C(201)	112.7(5)	F(205)-C(206)-C(204)	113.0(5)
C(302)-N(31)-C(301)	112.3(6)	F(206)-C(206)-C(204)	111.5(5)
C(302)-N(32)-C(303)	113.6(5)	F(207)-C(206)-C(204)	110.2(5)
C(301)-N(33)-C(303)	112.4(6)	F(215)-C(210)-C(203)	109.7(5)
N(11)-C(101)-N(13)	126.0(6)	F(215)-C(210)-C(211)	106.7(5)
N(11)-C(101)-C(104)	116.6(6)	C(203)-C(210)-C(211)	110.6(6)
N(13)-C(101)-C(104)	117.4(5)	F(215)-C(210)-C(212)	104.3(5)
N(12)-C(102)-N(11)	126.5(6)	C(203)-C(210)-C(212)	112.7(6)
N(12)-C(102)-C(107)	115.7(5)	C(211)-C(210)-C(212)	112.5(6)
N(11)-C(102)-C(107)	117.7(6)	F(216)-C(211)-F(217)	107.3(6)
N(13)-C(103)-N(12)	125.4(6)	F(216)-C(211)-F(218)	108.3(6)
N(13)-C(103)-C(110)	117.0(6)	F(217)-C(211)-F(218)	108.9(7)
N(12)-C(103)-C(110)	117.6(6)	F(216)-C(211)-C(210)	112.8(6)
F(101)-C(104)-C(101)	108.7(5)	F(217)-C(211)-C(210)	108.6(6)
F(101)-C(104)-C(106)	107.6(5)	F(218)-C(211)-C(210)	110.7(5)
C(101)-C(104)-C(106)	109.6(5)	F(220)-C(212)-F(219)	109.9(6)
F(101)-C(104)-C(105)	107.2(5)	F(220)-C(212)-F(221)	108.3(6)
C(101)-C(104)-C(105)	111.8(5)	F(219)-C(212)-F(221)	108.8(6)
C(106)-C(104)-C(105)	111.8(5)	F(220)-C(212)-C(210)	110.8(6)
F(104)-C(105)-F(102)	108.4(5)	F(219)-C(212)-C(210)	110.5(6)
F(104)-C(105)-F(103)	111.4(6)	F(221)-C(212)-C(210)	108.5(6)
F(102)-C(105)-F(103)	106.3(5)	N(33)-C(301)-N(31)	127.8(6)
F(104)-C(105)-C(104)	112.9(5)	N(33)-C(301)-C(304)	118.4(6)
F(102)-C(105)-C(104)	110.1(5)	N(31)-C(301)-C(304)	113.6(6)
F(103)-C(105)-C(104)	107.6(5)	N(32)-C(302)-N(31)	127.1(6)
F(107)-C(106)-F(105)	108.8(6)	N(32)-C(302)-C(307)	118.1(6)
F(107)-C(106)-F(106)	108.9(6)	N(31)-C(302)-C(307)	114.8(6)
F(105)-C(106)-F(106)	106.3(5)	N(33)-C(303)-N(32)	126.7(6)
F(107)-C(106)-C(104)	113.7(5)	N(33)-C(303)-C(310)	115.4(6)
F(105)-C(106)-C(104)	111.3(5)	N(32)-C(303)-C(310)	117.9(6)
F(106)-C(106)-C(104)	107.6(5)	F(301)-C(304)-C(305)	107.6(5)
F(108)-C(107)-C(102)	110.2(5)	F(301)-C(304)-C(301)	109.9(5)
F(108)-C(107)-C(109)	108.4(5)	C(305)-C(304)-C(301)	110.0(5)
C(102)-C(107)-C(109)	109.0(5)	F(301)-C(304)-C(306)	105.7(5)
F(108)-C(107)-C(108)	105.9(5)	C(305)-C(304)-C(306)	113.9(5)
C(102)-C(107)-C(108)	111.2(5)	C(301)-C(304)-C(306)	109.5(5)
C(109)-C(107)-C(108)	112.1(5)	F(302)-C(305)-F(304)	107.6(6)
F(109)-C(108)-F(110)	110.8(5)	F(302)-C(305)-F(303)	107.7(5)
F(109)-C(108)-F(111)	112.2(6)	F(304)-C(305)-F(303)	110.3(5)
F(110)-C(108)-F(111)	107.2(5)	F(302)-C(305)-C(304)	108.5(5)
F(109)-C(108)-C(107)	111.0(5)	F(304)-C(305)-C(304)	112.4(5)
F(110)-C(108)-C(107)	108.6(5)	F(303)-C(305)-C(304)	110.2(5)
F(111)-C(108)-C(107)	106.9(5)	F(305)-C(306)-F(307)	110.6(5)
F(112)-C(109)-F(114)	105.7(6)	F(305)-C(306)-F(306)	106.7(6)
F(112)-C(109)-F(113)	108.3(6)	F(307)-C(306)-F(306)	107.1(6)
F(114)-C(109)-F(113)	110.2(5)	F(305)-C(306)-C(304)	112.9(5)
F(112)-C(109)-C(107)	114.0(5)	F(307)-C(306)-C(304)	109.5(5)
F(114)-C(109)-C(107)	107.1(6)	F(306)-C(306)-C(304)	109.7(5)
F(113)-C(109)-C(107)	111.3(5)	F(308)-C(307)-C(309)	105.4(6)
F(115)-C(110)-C(103)	109.1(5)	F(308)-C(307)-C(308)	108.2(6)

F(115)-C(110)-C(112)	107.9(5)	C(309)-C(307)-C(308)	113.7(5)
C(103)-C(110)-C(112)	111.0(5)	F(308)-C(307)-C(302)	109.5(5)
F(115)-C(110)-C(111)	105.8(5)	C(309)-C(307)-C(302)	111.0(5)
C(103)-C(110)-C(111)	110.9(5)	C(308)-C(307)-C(302)	108.9(5)
C(112)-C(110)-C(111)	112.0(5)	F(311)-C(308)-F(309)	107.7(6)
F(117)-C(111)-F(116)	109.0(5)	F(311)-C(308)-F(310)	108.6(8)
F(117)-C(111)-F(118)	108.0(6)	F(309)-C(308)-F(310)	108.6(6)
F(116)-C(111)-F(118)	110.1(5)	F(311)-C(308)-C(307)	113.4(6)
F(117)-C(111)-C(110)	111.9(5)	F(309)-C(308)-C(307)	110.8(6)
F(116)-C(111)-C(110)	109.3(5)	F(310)-C(308)-C(307)	107.6(6)
F(118)-C(111)-C(110)	108.6(5)	F(312)-C(309)-F(314)	110.3(6)
F(120)-C(112)-F(121)	109.7(6)	F(312)-C(309)-F(313)	106.9(6)
F(120)-C(112)-F(119)	108.3(6)	F(314)-C(309)-F(313)	108.5(7)
F(121)-C(112)-F(119)	108.6(6)	F(312)-C(309)-C(307)	109.3(6)
F(120)-C(112)-C(110)	111.2(6)	F(314)-C(309)-C(307)	112.1(6)
F(121)-C(112)-C(110)	111.5(5)	F(313)-C(309)-C(307)	109.7(6)
F(119)-C(112)-C(110)	107.4(5)	F(315)-C(310)-C(312)	107.1(5)
N(21)-C(201)-N(23)	127.8(7)	F(315)-C(310)-C(303)	110.1(5)
N(21)-C(201)-C(204)	116.0(6)	C(312)-C(310)-C(303)	112.5(5)
N(23)-C(201)-C(204)	116.2(5)	F(315)-C(310)-C(311)	105.8(5)
N(21)-C(202)-N(22)	126.6(6)	C(312)-C(310)-C(311)	112.7(5)
N(23)-C(203)-N(22)	126.5(7)	C(303)-C(310)-C(311)	108.3(5)
N(23)-C(203)-C(210)	115.2(5)	F(318)-C(311)-F(316)	110.5(6)
N(22)-C(203)-C(210)	118.2(7)	F(318)-C(311)-F(317)	107.2(6)
F(201)-C(204)-C(201)	110.2(5)	F(316)-C(311)-F(317)	107.0(6)
F(201)-C(204)-C(206)	105.0(5)	F(318)-C(311)-C(310)	112.1(5)
C(201)-C(204)-C(206)	110.0(5)	F(316)-C(311)-C(310)	110.8(5)
F(201)-C(204)-C(205)	105.9(5)	F(317)-C(311)-C(310)	109.0(6)
C(201)-C(204)-C(205)	112.8(5)	F(319)-C(312)-F(320)	109.9(5)
C(206)-C(204)-C(205)	112.5(5)	F(319)-C(312)-F(321)	106.7(5)
F(202)-C(205)-F(204)	109.3(5)	F(320)-C(312)-F(321)	110.1(6)
F(202)-C(205)-F(203)	108.1(5)	F(319)-C(312)-C(310)	109.7(5)
F(204)-C(205)-F(203)	107.1(6)	F(320)-C(312)-C(310)	111.5(5)
F(202)-C(205)-C(204)	112.4(5)	F(321)-C(312)-C(310)	108.7(5)

Anisotropic displacement parameters ($Å^2 \times 10^3$) The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2} U_{11} + ... + 2hka^*b^*U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F(101)	29(2)	27(2)	63(3)	9(2)	28(2)	0(2)
F(102)	43(2)	28(2)	48(3)	17(2)	7(2)	-2(2)
F(103)	91(4)	46(3)	24(2)	-4(2)	-13(2)	12(3)
F(104)	21(2)	59(3)	82(4)	33(3)	17(2)	16(2)
F(105)	67(3)	22(2)	44(3)	-6(2)	8(2)	-13(2)
F(106)	53(3)	50(3)	42(3)	0(2)	-22(2)	-2(2)
F(107)	74(4)	66(3)	45(3)	-29(2)	43(3)	-31(3)
F(108)	36(2)	29(2)	67(3)	2(2)	21(2)	2(2)
F(109)	41(3)	33(2)	72(3)	-1(2)	30(3)	-6(2)
F(110)	37(2)	47(2)	40(3)	-1(2)	18(2)	17(2)
F(111)	52(3)	94(4)	25(2)	4(2)	10(2)	30(3)
F(112)	41(3)	43(3)	67(4)	-19(2)	-11(3)	4(2)
F(113)	31(2)	63(3)	36(3)	5(2)	6(2)	25(2)
F(114)	63(3)	87(4)	42(3)	15(3)	26(3)	25(3)
F(115)	32(2)	31(2)	48(3)	-2(2)	19(2)	7(2)
F(116)	45(3)	40(2)	45(3)	13(2)	19(2)	3(2)
F(117)	55(3)	30(2)	50(3)	9(2)	20(2)	15(2)
F(118)	41(3)	64(3)	29(2)	7(2)	-4(2)	-8(2)
F(119)	47(3)	67(3)	38(3)	16(2)	0(2)	0(2)
F(120)	37(3)	66(3)	45(3)	0(2)	7(2)	-16(2)
F(121)	41(3)	50(3)	41(3)	-18(2)	7(2)	-5(2)
F(201)	43(3)	29(2)	43(3)	0(2)	18(2)	-15(2)
F(202)	49(3)	34(2)	58(3)	-12(2)	28(2)	-10(2)
F(203)	30(2)	67(3)	38(2)	-15(2)	14(2)	-2(2)
F(204)	50(3)	51(3)	31(3)	-5(2)	-4(2)	8(2)
F(205)	23(2)	50(3)	48(3)	7(2)	5(2)	12(2)
F(206)	40(3)	69(3)	40(3)	25(2)	3(2)	-8(2)
F(207)	36(3)	52(3)	35(2)	-15(2)	1(2)	-3(2)
F(215)	36(2)	30(2)	62(3)	-1(2)	27(2)	1(2)
F(216)	41(3)	71(3)	44(3)	-9(2)	14(2)	-21(2)
F(217)	55(3)	114(5)	37(3)	-39(3)	22(3)	-28(3)
F(218)	51(3)	80(4)	50(3)	13(3)	-17(3)	4(3)
F(219)	80(4)	66(3)	67(4)	2(3)	34(3)	36(3)
F(220)	48(3)	73(3)	41(3)	0(2)	25(2)	-2(2)
F(221)	59(3)	78(3)	30(2)	-9(2)	3(2)	-5(3)
F(301)	29(2)	38(2)	60(3)	-9(2)	24(2)	-3(2)
F(302)	46(3)	48(3)	42(3)	6(2)	-16(2)	-4(2)
F(303)	55(3)	28(2)	48(3)	5(2)	15(2)	8(2)
F(304)	45(3)	59(3)	33(2)	7(2)	17(2)	10(2)
F(305)	20(2)	61(3)	51(3)	-16(2)	8(2)	-8(2)
F(306)	61(3)	61(3)	32(2)	4(2)	-2(2)	-22(2)
F(307)	45(3)	39(2)	52(3)	-19(2)	5(2)	-7(2)
F(308)	32(2)	30(2)	96(4)	-4(2)	32(3)	3(2)
F(309)	45(3)	55(3)	52(3)	1(2)	-2(2)	-23(2)
F(310)	70(4)	92(4)	59(4)	37(3)	-26(3)	-30(3)
F(311)	55(3)	88(4)	78(4)	-44(3)	18(3)	-11(3)
F(312)	43(3)	54(3)	45(3)	8(2)	13(2)	-14(2)
F(313)	59(4)	103(4)	36(3)	16(3)	0(3)	-38(3)
F(314)	63(4)	37(3)	87(4)	15(3)	33(3)	16(2)
F(315)	32(2)	25(2)	78(3)	2(2)	21(2)	0(2)

F(316)	32(3)	59(3)	46(3)	4(2)	5(2)	15(2)
F(317)	46(3)	83(4)	65(4)	-37(3)	-16(3)	14(3)
F(318)	52(3)	101(4)	54(3)	41(3)	13(3)	15(3)
F(319)	43(3)	45(2)	44(3)	-3(2)	17(2)	10(2)
F(320)	77(4)	47(3)	75(4)	-12(3)	44(3)	-23(3)
F(321)	60(3)	75(3)	31(2)	-2(2)	-1(2)	19(3)
N(11)	28(3)	33(3)	24(3)	0(2)	10(2)	4(2)
N(12)	25(3)	32(3)	24(3)	-1(2)	6(2)	4(2)
N(13)	25(3)	26(3)	30(3)	3(2)	12(2)	8(2)
N(21)	37(4)	17(2)	41(4)	-2(2)	-6(3)	-3(2)
N(22)	41(4)	39(4)	40(4)	-12(3)	-10(3)	16(3)
N(23)	22(3)	25(3)	28(3)	-4(2)	4(2)	-8(2)
N(31)	28(3)	32(3)	31(3)	0(2)	10(2)	-8(2)
N(32)	33(3)	28(3)	26(3)	1(2)	5(2)	-8(3)
N(33)	17(3)	36(3)	20(3)	1(2)	0(2)	-3(2)
C(101)	24(3)	29(3)	23(3)	0(2)	7(3)	5(3)
C(102)	26(3)	29(3)	26(3)	-1(3)	5(3)	7(3)
C(103)	24(3)	33(3)	21(3)	-1(3)	6(3)	2(3)
C(104)	17(3)	23(3)	26(3)	4(2)	9(2)	1(2)
C(105)	25(3)	31(3)	17(3)	2(2)	-6(2)	-4(3)
C(106)	34(4)	28(3)	26(3)	0(3)	1(3)	-5(3)
C(107)	25(3)	36(4)	32(4)	0(3)	7(3)	9(3)
C(108)	29(4)	46(4)	27(3)	6(3)	9(3)	4(3)
C(109)	29(4)	48(4)	20(3)	1(3)	12(3)	17(3)
C(110)	27(4)	25(3)	34(4)	1(3)	9(3)	8(3)
C(111)	44(4)	29(3)	28(4)	0(3)	12(3)	1(3)
C(112)	29(4)	39(4)	33(4)	3(3)	3(3)	7(3)
C(201)	31(4)	18(3)	29(4)	3(2)	2(3)	-3(3)
C(202)	55(5)	20(3)	50(5)	-7(3)	-18(4)	13(3)
C(203)	34(4)	30(3)	23(3)	-4(3)	2(3)	1(3)
C(204)	30(4)	23(3)	26(3)	3(3)	10(3)	-3(3)
C(205)	24(4)	30(3)	29(4)	-2(3)	-3(3)	-6(3)
C(206)	24(4)	35(4)	27(4)	2(3)	8(3)	-1(3)
C(210)	27(4)	45(4)	24(3)	-4(3)	6(3)	4(3)
C(211)	29(4)	54(5)	32(4)	-8(3)	6(3)	-3(3)
C(212)	47(5)	61(5)	34(4)	-6(4)	9(4)	13(4)
C(301)	22(3)	30(3)	19(3)	6(3)	1(2)	-3(3)
C(302)	20(3)	42(4)	20(3)	3(3)	3(3)	-5(3)
C(303)	19(3)	35(3)	18(3)	1(3)	3(2)	-1(3)
C(304)	17(3)	24(3)	32(3)	-6(3)	5(3)	-4(2)
C(305)	31(4)	30(3)	33(4)	2(3)	0(3)	8(3)
C(306)	27(4)	33(4)	35(4)	4(3)	-4(3)	-7(3)
C(307)	26(3)	26(3)	43(4)	0(3)	10(3)	-4(3)
C(308)	26(4)	40(4)	51(5)	-5(4)	5(4)	-4(3)
C(309)	32(4)	42(4)	55(5)	7(4)	20(4)	-7(3)
C(310)	23(3)	34(3)	41(4)	-5(3)	13(3)	-5(3)
C(311)	30(4)	44(4)	27(4)	-4(3)	2(3)	9(3)
C(312)	32(4)	36(4)	35(4)	4(3)	8(3)	1(3)

Appendix Five
Requirements for the Board of Studies

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

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

ii. lectures organised by Durham University Chemical Society;

iii. details of the postgraduate induction course; and

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

First Tear Induction Courses

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. G. M. Brooke
Electrical Appliances -	Mr. B. T. Barker
Library Facilities -	Mrs. M. Hird
Mass Spectroscopy -	Dr. M. Jones
Nuclear Magnetic Resonance Spectroscopy -	Dr. A. Kenwright
Glass-blowing Techniques -	Mr. R. Hart and Mr. G. Haswell

Research Conferences Attended

August 2-7, 1997	15th International Symposium on Fluorine Chemistry Vancouver, Canada

COLLOQUIA, LECTURES AND SEMINARS FROM INVITED SPEAKERS

1994- 1995

October 5	Prof. N. L. Owen, University of Brigham Young, Utah, USA *Determining Molecular Structure - the INADEQUATE NMR way* *
October 19	Prof. N. Bartlett, University of California *Some Aspects of Ag(II) and Ag(III) Chemistry* *
November 2	Dr. P. G. Edwards, University of Wales, Cardiff *The Manipulation of Electronic and Structural Diversity in Metal Complexes - New Ligands*
November 3	Prof. B. F. G. Johnson, University of Edinburgh *Arene-metal Clusters* *
November 9	Dr. G. Hogarth, University College, London *New Vistas in Metal-imido Chemistry*
November 10	Dr. M. Block, Zeneca Pharmaceuticals, Macclesfield *Large-scale Manufacture of ZD 1542, a Thromboxane Antagonist Synthase Inhibitor* *
November 16	Prof. M. Page, University of Huddersfield *Four-membered Rings and b-Lactamase* *
November 23	Dr. J. M. J. Williams, University of Loughborough *New Approaches to Asymmetric Catalysis* *
December 7	Prof. D. Briggs, ICI and University of Durham *Surface Mass Spectrometry*
January 11	Prof. P. Parsons, University of Reading *Applications of Tandem Reactions in Organic Synthesis* *
January 18	Dr. G. Rumbles, Imperial College, London *Real or Imaginary Third Order Non-linear Optical Materials*
January 25	Dr. D. A. Roberts, Zeneca Pharmaceuticals

The Design and Synthesis of Inhibitors of the Renin-angiotensin System

February 1 Dr. T. Cosgrove, University of Bristol
Polymers do it at Interfaces

February 8 Dr. D. O'Hare, University of Oxford
Synthesis and Solid-state Properties of Poly-, Oligo- and Multidecker Metallocenes

February 22 Prof. E. Schaumann, University of Clausthal
Silicon- and Sulphur-mediated Ring-opening Reactions of Epoxide *

March 1 Dr. M. Rosseinsky, University of Oxford
Fullerene Intercalation Chemistry

March 22 Dr. M. Taylor, University of Auckland, New Zealand
Structural Methods in Main-group Chemistry

April 26 Dr. M. Schroder, University of Edinburgh
Redox-active Macrocyclic Complexes : Rings, Stacks and Liquid Crystals

May 4 Prof. A. J. Kresge, University of Toronto
The Ingold Lecture Reactive Intermediates : Carboxylic-acid Enols and Other Unstable Species

1995-1996

October 11 Prof. P. Lugar, Frei University of Berlin, FRG
Low Temperature Crystallography

October 13 Prof. R. Schmutzler, University of Braunschweig, FRG.
Calixarene-Phosphorus Chemistry: A New Dimension in Phosphorus Chemistry

October 18 Prof. A. Alexakis, University of Pierre et Marie Curie, Paris,
Synthetic and Analytical Uses of Chiral Diamines *

October 25 Dr. D. Martin Davies, University of Northumbria
Chemical reactions in organised systems

November 1	Prof. W. Motherwell, UCL London *New Reactions for Organic Synthesis* *
November 3	Dr. B. Langlois, University of Claude Bernard, Lyon *Radical Anionic and Psuedo Cationic Trifluoromethylation* *
November 8	Dr. D. Craig, Imperial College, London *New Stategies for the Assembly of Heterocyclic Systems* *
November 15	Dr. Andrea Sella, UCL, London Chemistry of Lanthanides with Polypyrazoylborate Ligands
November 17	Prof. David Bergbreiter, Texas A&M, USA *Design of Smart Catalysts, Substrates and Surfaces from Simple Polymers*
November 22	Prof. I Soutar, University of Lancaster *A Water of Glass? Luminescence Studies of Water-Soluble Polymers.*
November 29	Prof. Dennis Tuck, University of Windsor, Ontario, Canada *New Indium Coordination Chemistry*
December 8	Prof. M.T. Reetz, Max Planck Institut, Mulheim *Perkin Regional Meeting*
January 10	Dr. Bill Henderson, University of Waikato, NZ *Electrospray Mass Spectrometry - a new sporting technique*
January 17	Prof. J. W. Emsley , University of Southampton *Liquid Crystals: More than Meets the Eye*
January 24	Dr. Alan Armstrong, University of Nottingham *Alkene Oxidation and Natural Product Synthesis* *
January 31	Dr. J. Penfold, Rutherford Appleton Laboratory, *Soft Soap and Surfaces*
February 7	Dr. R.B. Moody, University of Exeter *Nitrosations, Nitrations and Oxidations with Nitrous Acid*

February 12	Dr. P. Pringle, University of Bristol *Catalytic Self-Replication of Phosphines on Platinum(O)*
February 14	Dr. J. Rohr, University of Gottingen, FRG *Goals and Aspects of Biosynthetic Studies on Low Molecular Weight Natural Products*
February 21	Dr. C. R. Pulham , University of Edinburgh *Heavy Metal Hydrides - an exploration of the chemistry of stannanes and plumbanes*
February 28	Prof. E. W. Randall, Queen Mary & Westfield College *New Perspectives in NMR Imaging*
March 6	Dr. R. Whitby, University of Southampton *New approaches to chiral catalysts: Induction of planar and metal centred asymmetry* *
March 7	Dr. D.S. Wright, University of Cambridge *Synthetic Applications of Me_2N-p-Block Metal Reagents*
March 12	RSC Endowed Lecture - Prof. V. Balzani, University of Bologna *Supramolecular Photochemistry*
March 13	Prof. Dave Garner, University of Manchester *Mushrooming in Chemistry*
April 30	Dr. L.D.Pettit, Chairman, IUPAC Commission of Equilibrium Data *pH-metric studies using very small quantities of uncertain purity*
1996-1997	
October 9	Prof. G. Bowmaker, University of Aukland, NZ *Coordination and Materials Chemistry of the Group 11 and Group 12 Metals : Some Recent Vibrational and Solid State NMR Studies*
October 14	Prof. A. R. Katritzky, University of Gainesville, University of Florida, USA *Recent Advances in Benzotriazole Mediated Synthetic Methodology* *

October 16	Prof. Ojima, Guggenheim Fellow, University of New York at Stony Brook *Silylformylation and Silylcarbocyclisations in Organic Synthesis*
October 22	Prof. Lutz Gade, University of Wurzburg, Germany *Organic transformations with Early-Late Heterobimetallics: Synergism and Selectivity*
October 22	Prof. B. J. Tighe, Department of Molecular Sciences and Chemistry, University of Aston *Making Polymers for Biomedical Application - can we meet Nature's Challenge?, Joint lecture with the Institute of Materials*
October 23	Prof. H. Ringsdorf (Perkin Centenary Lecture), Johannes Gutenberg-Universitat, Mainz, Germany *Function Based on Organisation*
October 29	Prof. D. M. Knight, Department of Philosophy, University of Durham. *The Purpose of Experiment - A Look at Davy and Faraday*
October 30	Dr. Phillip Mountford, University of Nottingham *Recent Developments in Group IV Imido Chemistry*
November 6	Dr. Melinda Duer, Chemistry Department, Cambridge *Solid-state NMR Studies of Organic Solid to Liquid-crystalline Phase Transitions*
November 12	Prof. R. J. Young, Manchester Materials Centre, UMIST *New Materials - Fact or Fantasy?,Joint Lecture with Zeneca & RSC* *
November 13	Dr. G. Resnati, Milan *Perfluorinated Oxaziridines: Mild Yet Powerful Oxidising Agents* *
November 18	Prof. G. A. Olah, University of Southern California, USA *Crossing Conventional Lines in my Chemistry of the Elements* *
November 19	Prof. R. E. Grigg, University of Leeds *Assembly of Complex Molecules by Palladium-Catalysed Queueing Processes*

November 20	Prof. J. Earnshaw, Deptartment of Physics, Belfast *Surface Light Scattering: Ripples and Relaxation*
November 27	Dr. Richard Templer, Imperial College, London *Molecular Tubes and Sponges*
December 3	Prof. D. Phillips, Imperial College, London *"A Little Light Relief"*
December 4	Prof. K. Muller-Dethlefs, University of York *Chemical Applications of Very High Resolution ZEKE Photoelectron Spectroscopy*
December 11	Dr. Chris Richards, University of Cardiff *Stereochemical Games with Metallocenes* *
January 15	Dr. V. K. Aggarwal, University of University *Sulfur Mediated Asymmetric Synthesis* *
January 16	Dr. Sally Brooker, University of Otago, NZ *Macrocycles: Exciting yet Controlled Thiolate Coordination Chemistry*
January 21	Mr. D. Rudge, Zeneca Pharmaceuticals *High Speed Automation of Chemical Reactions*
January 22	Dr. Neil Cooley, BP Chemicals, Sunbury *Synthesis and Properties of Alternating Polyketones*
January 29	Dr. Julian Clarke, UMIST *What can we learn about polymers and biopolymers from computer-generated nanosecond movie-clips?*
February 4	Dr. A. J. Banister, University of Durham *From Runways to Non-metallic Metals - A New Chemistry Based on Sulphur*
February 5	Dr. A. Haynes, University of Sheffield *Mechanism in Homogeneous Catalytic Carbonylation*

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

* lectures attended.

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