The chemistry of perfluoro-4-isopropylpyridine

Philip R. Hoskin

UNIVERSITY OF DURHAM

A THESIS
entitled

THE CHEMISTRY OF PERFLUORO-4-ISOPROPYLPYRIDINE

submitted by

PHILIP R. HOSKIN B.S.c. (Hons) University of Bath
(St. Mary's College)

A candidate for the degree of Doctor of Philosophy

Department of Chemistry

2000

For my parents, Grandmother and Peter.

Acknowledgements

I would like to thank my supervisors, Professor R. D. Chambers and Dr. G. Sandford for their continued support and encouragement throughout this period of research.

This thesis could not have been completed without the advice and assistance of the technical staff in the department. Many thanks in particular to Mr L. W. Lauchlan (gas chromatography), Dr. M. Jones and Miss. L. M. Turner (mass spectrometry), Dr. A. Kenwright and Mrs. C. F. Heffernen (NMR spectroscopy), Mrs. J. Dostal (elemental analysis), Mr. R. Hart, Mr. G. Haswell and Mr. M. Richardson (glass blowing), Mr. D. Hunter (high pressure synthesis), Mr. J. Peel, Mr. J. Lincoln and Mrs. E. Wood (stores), Dr. A. Royston (computing) and Dr. D. Yufit (X-ray crystallography).

Thanks to all my colleagues in CG.115 and to the many friends that I have made during a memorable three years in Durham. In particular, thanks to Lyndsay (Zip.com), Jarvis, Christianna (Genuine Greek Article), Clare (Black Aubergine), Stephen '10-Bellies' Tindale, Shirley, Fr. Mac, Fr. Curtis, Mr Dicken, Karen and Irene (I managed to survive your 'cooking'), St Mary's girls, Duncan, Robbie and the Guys at St. Mary's (the 'Original Institution'), Angelo, Maria, Lavinia, Nicholas, Mark, Belle, Krissie, Georg (Ja, Ja, Ja!) and of course the inimitable Julian.

Memorandum

The work described in this thesis was carried out at the University of Durham between September 1997 and September 2000. This thesis is the work of the author, except where acknowledged by reference, and has not been submitted for any other degree.

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

P. R. Hoskin, M. Jones, G. Sandford and L. Turner, '*Negative ion mass spectrometry of highly fluorinated compounds*', in *Rapid Commun. Mass Spectrom.* 14, 91-94 (2000).

R. D. Chambers, P. R. Hoskin, P. Richmond and G. Sandford, in *Arkat* 2000, in press.

R. D. Chambers, P. R. Hoskin, P. Richmond and G. Sandford, in *Journal of Fluorine Chemistry*, in press.

and has been presented at:

I.C.I Poster Session
University of Durham.
December, 1999.

ACS 14th Winter Fluorine Conference
St. Petersburg, Florida.
January, 1999.

16th International Symposium on Fluorine Chemistry
University of Durham.
July, 2000.

Nomenclature

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

Abbreviations

The following are used throughout this thesis:

IR	infrared
MS	mass spectrometry
NMR	nuclear magnetic resonance
UV	ultraviolet

Abstract

The Chemistry of Perfluoro-4-isopropylpyridine
by P. R. Hoskin

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

1) Perfluoro-4-isopropylpyridine (1) has been synthesised efficiently by reaction between pentafluoropyridine and hexafluoropropene in the presence of an amine initiator tetrakis-(dimethylamino)ethene (TDAE). A variety of oxygen and nitrogen centred nucleophiles were successfully reacted with (1) to afford a range of model compounds for highly fluorinated macrocycles.

2) Perfluorocarbon soluble macrocycles have been prepared from (1) and the coordination properties of these systems have been determined by metal ion extraction techniques.

3) Bromination of (1) gave the synthetically versatile derivative, 2,6-dibromo-perfluoro-4-isopropylpyridine (37), from which a range of highly substituted pyridine compounds were derived.

Contents

CHAPTER I
The Chemistry of Pentafluoropyridine and Perfluoro-4-isopropylpyridine **1**

1. General Introduction **2**
1.1. Industrial Applications 2

1.2. Pentafluoropyridine and Perfluoro-4-isopropylpyridine **3**

1.3. Preparation of Pentafluoropyridine **3**
1.3. A. Electrochemical Fluorination 3
1.3. B. Direct Fluorination 4
1.3. C. Halogen Exchange 4

1.4. Chemical properties of Pentafluoropyridine **4**
1.4. A. Nucleophilic Aromatic Substitution 5
1.4. B. Activation by *Ipso-*, *Ortho-* and *Meta-* Fluorines and Ring Nitrogen 6
1.4. Bi. Fluorine Initial State Effects 6
1.4. Bii. Fluorine Transition State Effects 6
1.4. Biii. Ring Nitrogen Transition State Effects 8

1.5. Perfluoroalkylation of Pentafluoropyridine by Fluorinated Alkenes **9**
1.5. A. Reactivity of Perfluorinated Alkenes 9
1.5.B. 'Negative Friedel-Crafts' Chemistry 10

1.6. Preparation of Perfluoro-4-isopropylpyridine **10**
1.6. A. Alkali Metal Fluoride Initiated Perfluoroalkylation 10
1.6. B. TDAE Initiated Perfluoroalkylation 11

1.7. Established Chemistry of Perfluoro-4-isopropylpyridine **12**
1.7.A. Further Reaction of Perfluoro-4-isopropylpyridine with Hexafluoropropene 12
1.7.B. Reaction of Perfluoro-4-isopropylpyridine with Decafluorohexene 13
1.7.C. Reaction of Perfluoro-4-isopropylpyridine with Sodium Methoxide 14
1.7. D. Reaction of Perfluoro-4-isopropylpyridine with Sodium Azide 14

CHAPTER II
Synthesis of Perfluoro-4-isopropylpyridine and Derivatives **15**

2. Introduction **16**

2.1. Preparation of Perfluoro-4-isopropylpyridine **16**

2.2. Reactions of Perfluoro-4-isopropylpyridine with Oxygen Nucleophiles **17**
2.2.A. Preparation of 6-methoxy-perfluoro-4-isopropylpyridine 17
2.2.B. Preparation of 2,6-dimethoxy-perfluoro-4-isopropyl-pyridine 19

2.3. Further Reactions of Perfluoro-4-isopropylpyridine with Oxygen-Centred Nucleophiles **20**

2.4. Reaction of Perfluoro-(2,4-diisopropyl)-pyridine with Sodium Methoxide **22**

2.5. Reactions of Perfluoro-4-isopropylpyridine with Nitrogen Nucleophiles **24**
2.5.A. Reaction of Perfluoro-4-isopropylpyridine and Methylamine 24
2.5.B. Preparation of a Highly Fluorinated Bispyridyl-Building Block and Derivatives 25
2.5.B.i. Derivatives (18), (19) and (20) 26

2.6. Conclusions **27**

CHAPTER III
2,6-Pyridine-Bridged-Macrocycles **29**

3. General Introduction **30**

3.1. Introduction into 2,6-Substituted-Pyridine Macrocycles **32**

3.2. 2,6-Carbon-Carbon Bridged Macrocycles **32**
3.2.A. Pyridinophanes from Organometallic Reagents 32
3.2.B. Pyridinophanes from Dithiane Reagents 34
3.2.C. Calixpyridones and Calixpyridines 36

3.3. Carbon-Nitrogen Bridged Macrocycles **37**

3.4. Carbon-Oxygen Bridged Macrocycles **40**

3.4. Carbon-Sulfur Bridged Macrocycles **42**

CHAPTER IV
Synthesis of Highly Fluorinated Macrocycles 44

4. Introduction 45

4.1. Polyether-Macrocycles 45

4.2. Reaction of Perfluoro-4-isopropylpyridine with Resorcinol and 1,3-Dihydroxytoluene 45

4.3. Preparation of Macrocycles (25), (26) and (27) 47

4.4. Preparation of Macrocycles (29) and (31) 50

4.5. Alkali Metal Picrate Studies Involving Macrocycles (27), (29) and (31) 56

4.6. Electrospray Mass Spectrometry Studies Involving Macrocycles (27), (29) and (31) 57

4.7. Preparation of Polyamino-Macrocycles 59

4.8. Preparation of Macrocycle (34) 59

4.9. Attempted Preparation of a Macrocycle Containing 4-Pyridine Subcyclic Units 60

4.10. Conclusions 63

CHAPTER V
Bromination of Perfluorinated Aromatic Heterocycles 64

5. General Introduction 65

5.1. Bromination of Perfluorinated Aromatic Heterocycles 65

5.2. Bromination of Perfluorinated Heterocycles by BBr_3 and $AlBr_3$ 65

5.3. Bromination of Perfluorinated Heterocycles by HBr 67

5.4. Bromination of Perfluorinated Heterocycles by HBr and $AlBr_3$ **68**

5.5. Synthesis of 4-bromotetrafluoropyridine from 4-aminotetrafluoropyridine **69**

5.6. Reactions involving Bromofluoroheterocycles **69**

5.7. Reactions involving 4-Bromo-tetrafluoropyridine **69**

5.8. Reactions involving 2,4,6-Tribromo-difluoropyridine **71**

5.9. Reduction of Bromofluoroheterocycles **72**

5.10. Palladium Catalysed Coupling of Alkynes with Bromofluoroheterocycles **72**

CHAPTER VI
Synthesis of 2,6-Dibromo-perfluoro-4-isopropylpyridine and Derivatives **74**

6. Introduction **75**

6.1. Preparation of 2,6-Dibromo-perfluoro-4-isopropylpyridine **75**

6.2. Preparation of 6-Bromo-perfluoro-4-isopropylpyridine **76**

6.3. Reactions involving 2,6-Dibromo-perfluoro-4-isopropylpyridine **76**
6.3.i. Hydrogenolysis 76
6.3.ii. Methoxylation 77
6.3.iii. Amination 79
6.3.iv. Mono-Lithiation 79
6.3.v. Methoxylation of Bipyridine (46) 81
6.3.vi. Dilithiation 81
6.3.vii. Alkyne Couplings 82

6.4. Pentasubstituted Pyridines Derived from 2,6-Dibromo-perfluoro-4-isopropylpyridine **84**

6.5. Conclusions **86**

Instrumentation and Reagents **88**

Chapter VII
Experimental to Chapter II **91**
Synthesis of *2,3,5,6-Tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* (**1**) and *2,3,5-trifluoro-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* (**2**). **92**

Reactions of (**1**) with Alkoxide Ions. **92**

Reactions of (**2**) with Alkoxide Ions **95**

Reactions of (**1**) with Nitrogen Nucleophiles **96**

Chapter VIII.
Experimental to Chapter IV **98**

Reactions of (**1**) with Dioxygen nucleophiles **99**

Cyclisation Reactions with (**21**) and (**24**) **99**

A Cyclisation Reaction with (**28**) **101**

Reactions of (**1**) with Dinitrogen Nucleophiles **102**

A Cyclisation Reaction with (**32**) **102**

Reaction of (**17**) with N,N' dimethylethylenediamine **103**

Complexation Studies **104**

Chapter IX
Experimental to Chapter VI **105**

Exchange of Fluorine by Bromine Reactions **106**

Catalytic Hydrogenolysis Reaction of the Dibromocompound (**37**) **106**

Reactions of the Bromo-fluoro-compound (**37**) with Sodium Methoxide **107**

Lithiation reactions of the 2,6-dibromocompound (**37**) and Reactions with Electrophiles **108**

Reaction of Compound (**46**) with Sodium Methoxide **109**

Coupling Reactions of the 2,6-Dibromocompound (**37**) with Terminal Alkynes **110**

Preparation of Pentasubstituted Pyridines **111**

Appendices

Appendix A
NMR. Data A.1-A.54

Appendix B
IR. Data B.1-B.18

Appendix C
Mass Spectrometry Data C.1-C.57

Appendix D
Crystallographic Data D.1-D.40

Appendix E
Board of Studies Requirements E.1-E.10

Appendix F
Bibliography F.1-F.10

CHAPTER I

The Chemistry of Pentafluoropyridine and Perfluoro-4-isopropylpyridine

1. General Introduction.

Fluorine is the thirteenth most abundant element in the earth's crust (0.065%)[1] being concentrated in commercially important mineral deposits[2] such as cryolite, Na_3AlF_6 and fluorspar, CaF_2. The principle feedstock of the fluorochemical industry, hydrogen fluoride[3], is obtained by distillation from a mixture of fluorspar and concentrated sulfuric acid.

Despite the widespread distribution of fluorine in the lithosphere, organofluorine natural products are rare[4, 5] and consequently fluorinated organic compounds are almost entirely synthetic.

The first 'man-made' organic fluoride, fluoromethane, was reported in 1835 by Dumas and Péligot[6]. However, it was not until 1890, when Swarts[7, 8] pioneered halogen-exchange techniques to produce aliphatic fluorides that the foundations of organofluorine chemistry were firmly established. In 1883 the preparation of the first fluorinated aromatic compound, fluorobenzene, was published by Paternó and Oliveri[9] and then in 1915 Chichibabin and Rajazancev[10] published the synthesis of the first fluorinated heterocycle, 2-fluoropyridine.

The motivational basis in these and more recent developments, can be attributed to the unique characteristics that fluorine atoms impart to organic systems:

1. The electronegativity[11, 12] of the fluorine atom results in strongly polarised carbon-fluorine bonds.

2. Fluorine forms extraordinarily strong bonds to carbon (C-F, 485 $kJmol^{-1}$)[13] and this feature is exemplified by the enhanced chemical and thermal stability[14-16] associated with some highly fluorinated compounds.

3. Fluorine is the halogen with the smallest van der Waal's radius (F=1.47Å)[17] and this allows multiple substitution of hydrogen by fluorine in C-H containing molecules, with minimal steric disruption.

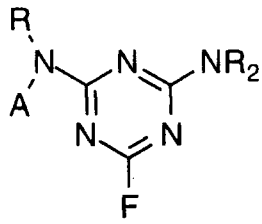
4. Fluorine has three tightly bound non-bonding pairs of electrons.

5. Fluorine is displaced from organofluorine compounds as fluoride ion[18].

1.1. Industrial Applications.

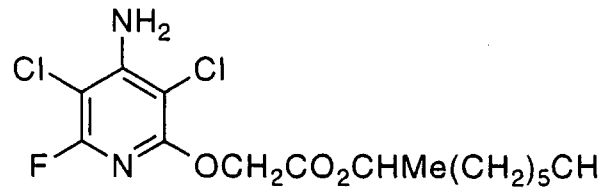
The range of commercially important fluoroorganic products bear testament to the profound effects that fluorine has on the physicochemical properties[15, 16] of

compounds. Fluoropolymers, such as PTFE[19], are characterised by their chemical and thermal stabilities and can be utilised, for example, in laboratory equipment where chemical resistance is important. In the dyestuff[20], agrochemical[21] and pharmaceutical[22] industries there is a wide range of applications for fluoroorganic compounds and some of these are illustrated below:

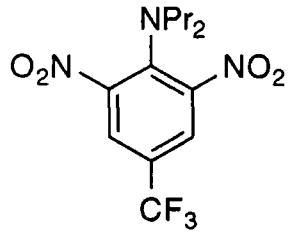


Levafix®
Dye

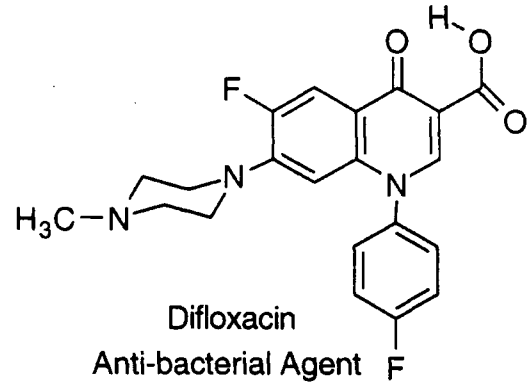
(R = H or C substituent,
A = Chromophore)



Fluroxypyr
Herbicide



Trifluralin
Herbicide



Difloxacin
Anti-bacterial Agent

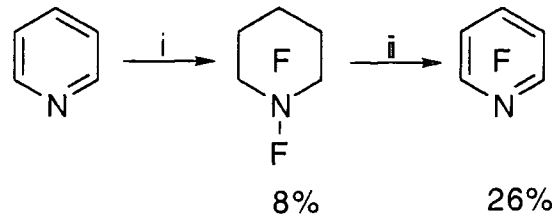
1.2. Pentafluoropyridine and Perfluoro-4-isopropylpyridine.

The aim of the research work described in this thesis has been to explore the chemistry of the pentafluoropyridine derivative, perfluoro-4-isopropylpyridine. Before new work is described, a brief review of fluorinated pyridines and their chemistry is appropriate.

1.3. Preparation of Pentafluoropyridine.

1.3. A. Electrochemical Fluorination.

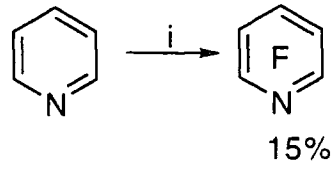
Pentafluoropyridine was first obtained *via* a two-step conversion of pyridine or piperidine[23-25]. Electrochemical fluorination[26] of either compound gives perfluoropiperidine, which upon defluorination using hot iron or nickel, affords pentafluoropyridine in a low overall yield.



Reagents and conditions: i, HF, Electrochemical Fluorination (25A/ 5.5 V).
ii, Fe, 600°C.

1.3. B. Direct Fluorination.

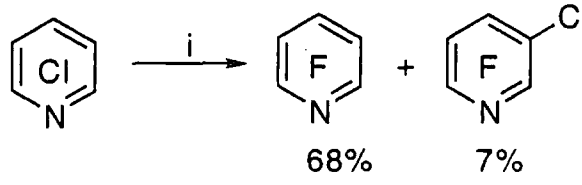
Substitution of hydrogen in pyridine by fluorine potentially offers an efficient route to pentafluoropyridine. The direct fluorination of pyridine by caesium tetrafluorocobaltate[27] has been attempted but gave pentafluoropyridine in a low overall yield.



Reagents and Conditions: i, $CsCoF_4$, 250°C

1.3. C. Halogen Exchange.

A more practical route to pentafluoropyridine, involving the nucleophilic displacement of chlorine by fluorine, has been developed by Musgrave and Chambers[28, 29]. This halogen exchange (Halex) reaction, using an alkali metal fluorides as the source of fluoride ion, occurs in the absence of solvent at high temperatures to give pentafluoropyridine in good yield.

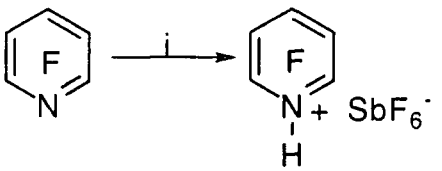


Reagents and Conditions: i. KF, 480°C, Autoclave

1.4. Chemical properties of Pentafluoropyridine.

Pentafluoropyridine (bpt. 84°C) became available in synthetically useful quantities in the 1960's, being prepared *via* the efficient Halex route[28]. Pentafluoropyridine is an extremely weak base (estimated pK_A value -11), owing to

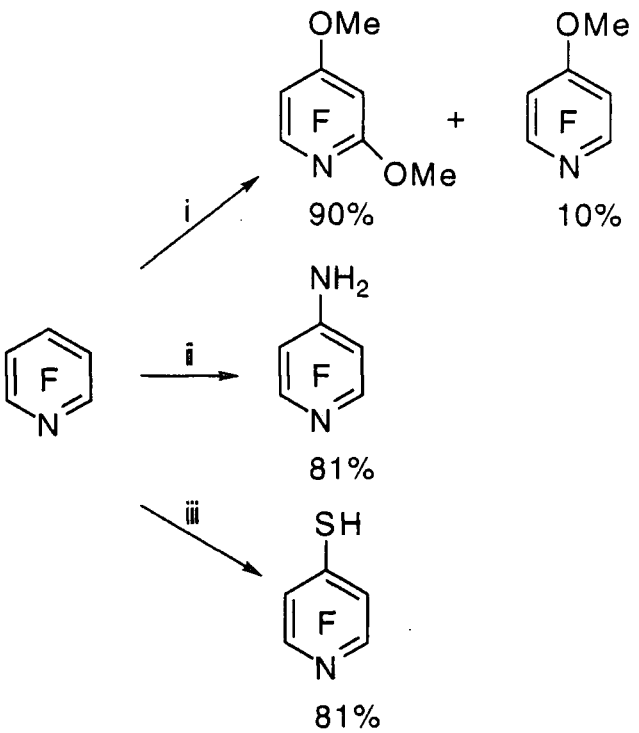
the fluorine atoms *ortho* to the nitrogen and will only form N-protonated salts with super acids such as antimony pentafluoride and boron trifluoride[30].



Reagents: SbF_5/ HF, SO_2

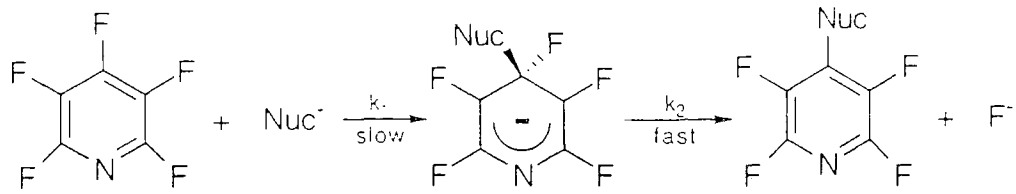
1.4. A. Nucleophilic Aromatic Substitution[31, 32].

Pentafluoropyridine has been shown to react with a range of reagents, including carbon-[33-43], nitrogen-[36, 37, 43-47], oxygen-[36, 37, 48-51] and sulfur-[52, 53]centred nucleophiles to yield products which arise from nucleophilic substitution processes, for example:



Reagents and Conditions: i.MeONa (2 equivs.), 0°C, MeOH.
ii. NH_3 (3 equivs.), 110°C, EtOH, 8 h, Carius Tube.
iii. KSH, -40- -20°C, DMF-glycol, 1.5 h.

The available experimental evidence indicates that nucleophilic attack on pentafluoropyridine proceeds *via* a two-step reaction pathway[54-56], with the first stage (k_1) being rate determining.



In general, monosubstitution in pentafluoropyridine occurs exclusively in the 4-position, while a second nucleophilic group usually enters at the 2-position.

1.4. B. Activation by *Ipso-*, *Ortho-* and *Meta-* Fluorines and Ring Nitrogen.

To account for the regiospecificity observed in reactions between nucleophiles and pentafluoropyridine, it is necessary to consider the activating influences of the fluorine atoms at the positions *ipso-*, *ortho-*, *meta-* and *para-* to the point of nucleophilic attack and also the effect of the ring nitrogen atom on the nucleophilic substitution process.

1.4. Bi. Fluorine Initial State Effects.

In order to explain the greater reactivity of heterocycles bearing fluorine *versus* chlorine, at identical sites, the polar contribution[57-60] to the activating influence of fluorine needs to be appreciated.

i.e.

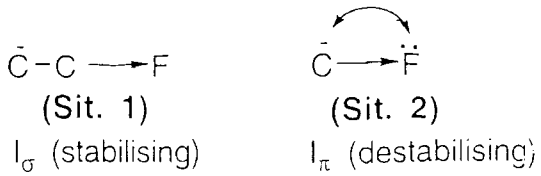
$$\overset{\delta^+}{C}\longrightarrow\overset{\delta^-}{F} \;>>\; \overset{\delta^+}{C}\longrightarrow\overset{\delta^-}{Cl}$$

1.4. Bii. Fluorine Transition State Effects.

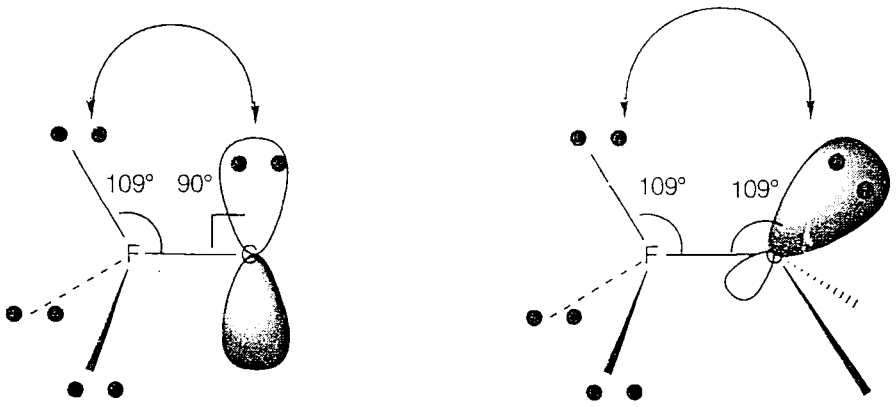
Based upon a range of kinetic data for substitution in fluorinated pyridines[57-60], the quite different effects of fluorine atoms *ortho-*, *meta-* and *para-* to the position of nucleophilic attack have been assessed. From these results, it has been deduced that fluorine atoms *ortho-* and *meta-* to the site of nucleophilic substitution are activating, with respect to hydrogen at the same position, whilst a *para-*fluorine atom is deactivating. To understand these findings it is necessary to understand the distribution of electron density in the transition state.

The factors which determine carbanion stability in fluorinated systems will also influence the transition state formed between a nucleophile and pentafluoropyridine

It is well established that a fluorine atom in situation 1 (Sit.1) is strongly carbanion stabilising by inductive withdrawal (I_σ)[61], whereas, in situation 2 (Sit.2) electron withdrawal is offset by electron pair repulsion (I_π).



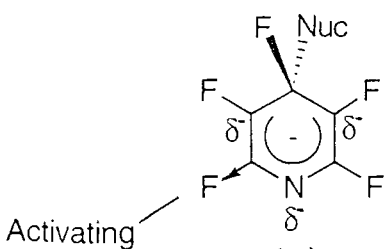
Whether the resultant of the effects shown in situation (Sit. 2) is stabilising or not will be determined by the geometry of the carbanion centre. I_π repulsion is greatest for a planar carbanion (destabilising), in which the carbon centre is sp^2-hybridised, than for a tetrahedral, sp^3-hybridised, carbanion centre (stabilising).



sp^2
Destabilising Overall

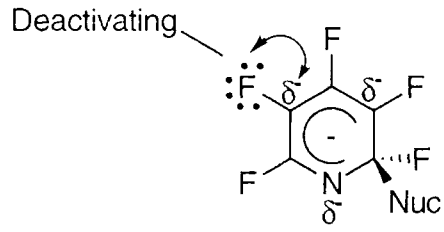
sp^3
Stabilising Overall

For a transition state resulting from nucleophilic attack on the 4-position, it has been deduced that the fluorine atoms at the 2 and 6-positions i.e. *meta* to the point of attack in (α), are activating[57-60]



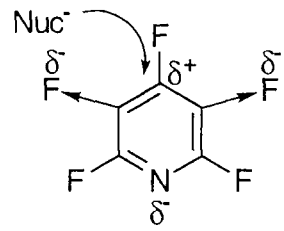
(α)

whereas a transition state obtained from nucleophilic attack at the 2-position in (B) is deactivated by a *para*-fluorine atom.



(B)

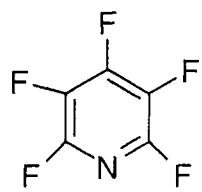
A similar deactivating effect in (α) by fluorine at the *ortho*-position might be anticipated. It has been shown, however, that the *ortho*-fluorines are more activating than the *meta*-fluorines and this behaviour can be attributed to an initial state effect (Section 1.4. Bi.), in which the *ortho*-fluorines make the carbon centre under attack electron deficient (β).



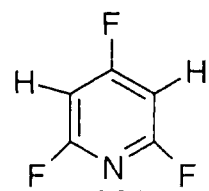
(β)

1.4. Biii. Ring Nitrogen Transition State Effects.

It has been shown that the ring nitrogen atom has an important influence on the orientation of nucleophilic attack in pentafluoropyridine[54]. For example, the preference for nucleophilic attack at the 4-position in the symmetrical compound, (C), has been attributed to the orientating effect of the ring-nitrogen. The exclusive nucleophilic attack observed at the 4-position in (A), is therefore a consequence of both the orientating influence of the ring nitrogen atom and the ring fluorine atoms. In this situation nucleophilic attack occurs so as to maximise the number of activating fluorine atoms (two-*ortho* and two-*meta*-fluorines): note attack at the 2-position in (A) would be activated by only three fluorine atoms (one-*ortho* and two-*meta*).



(A)
(4- : 100%)



(C)
(4- : 78%; 2,6- :22%)

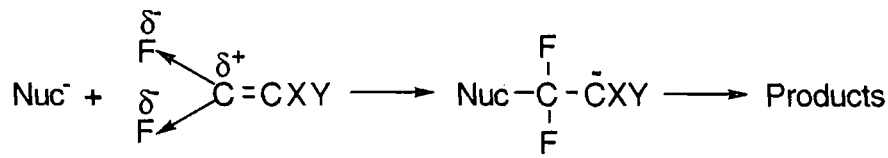
Positions of substitution by aqueous ammonia

1.5. Perfluoroalkylation of Pentafluoropyridine by Fluorinated Alkenes.

This section concerns the perfluoroalkylation of pentafluoropyridine by fluorinated carbanions derived from perfluoroalkenes. The factors which govern the reactivity of fluoroalkenes and the stability of fluorocarbanions will be described, before the trapping of these species by pentafluoropyridine is reviewed.

1.5. A. Reactivity of Perfluorinated Alkenes.

The double bonds of perfluorinated alkenes are inherently electron deficient, due to the inductive influences of substituent fluorine atoms and perfluoroalkyl-groups. Fluorinated alkenes are consequently more susceptible to nucleophilic[62-64, 65], rather than electrophilic attack[66, 67], producing carbanion intermediates.



X,Y = F or R_f

The reactivity order for fluoroalkenes[64, 68-71] reflects the importance of I_π repulsion (Section 1.4.B.ii) in the associated intermediates:

$F_2C{=}CF_2$

$F_2C{=}CFCF_3$ ⇓ Increasing Reactivity

$F_2C{=}C(CF_3)_2$

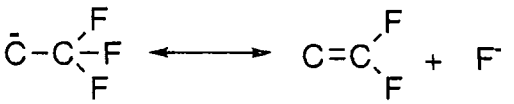
In this series, nucleophilic attack will occur on the less substituted vinylic carbon. The regiospecificity reflects both the initial polar contribution from the α-fluorine atoms and, importantly, the relative reactivity also reflects the formation of the stable carbanion having the highest number of perfluoroalkyl groups attached to the anionic centre.

$NucF_2C{-}\bar{C}F_2$

$NucF_2C{-}\bar{C}FCF_3$ ⇓ Increasing Stability

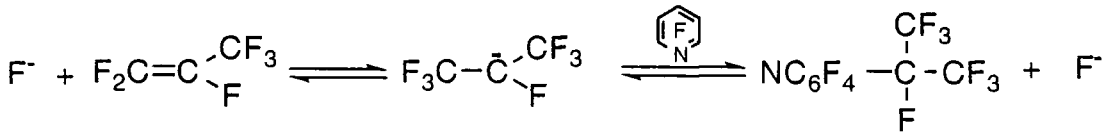
$NucF_2C{-}\bar{C}(CF_3)_2$

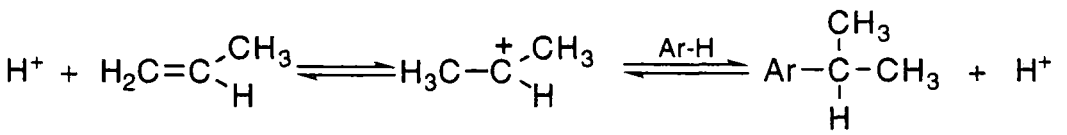
In addition to stabilisation by inductive effects, it has also been proposed that perfluoroalkyl-groups can stabilise carbanion centres by negative hyperconjugation. This concept was originally proposed by Roberts[72] in 1950 and arguments for and against its validity are still a matter of debate[73-78].



1.5.B. 'Negative Friedel-Crafts' Chemistry.

Fluorocarbanions generated by the reaction of fluoroalkenes and fluoride ion can be trapped by aromatics that are activated towards nucleophilic attack such as pentafluoropyridine[35, 79-82] to give mono- and polyfluoroalkylated pyridines. Reactions of this type are redolent of cationic processes, hence they are often referred to as 'nucleophilic Friedel Crafts reactions'[18, 65, 83, 84].



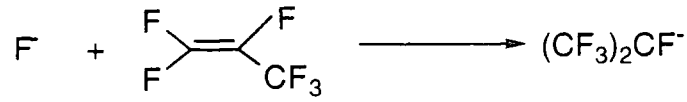


1.6. Preparation of Perfluoro-4-isopropylpyridine.

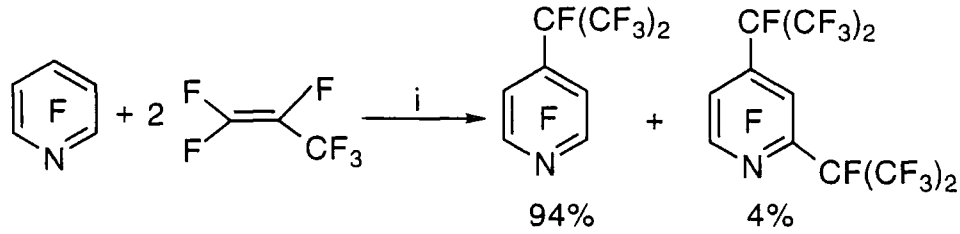
Since this thesis is primarily concerned with the chemistry of perfluoro-4-isopropylpyridine, established methods for the synthesis of this system will be discussed.

1.6. A. Alkali Metal Fluoride Initiated Perfluoroalkylation.

In the presence of a fluoride ion initiator, reaction occurs between hexafluoropropene and pentafluoropyridine to give mono- and polyfluoroalkylated pyridines[85]. Alkali metal fluorides[86, 87] in aprotic solvents were originally used as fluoride ion sources and these react with hexafluoropropene to give perfluoroisopropyl- anions (Section 1.5.A.).

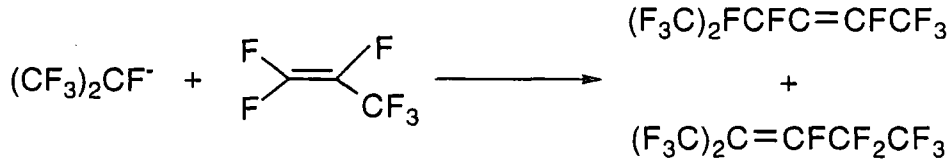


These carbanions can be trapped by pentafluoropyridine in a nucleophilic substitution process (Section 1.4.A.) to afford mono- and polyperfluoroalkylated pyridines. Consistent with the established reactivity pattern of pentafluoropyridine (Section 1.4.Bi.), initial attack occurs exclusively at the 4-position.



Reagents and Conditions: i.KF, Sulfolane, 130°C, 12 hr

In a typical reaction, it is usual to employ twice the theoretical amount of hexafluoropropene in order to compensate for the competing dimerisation reaction that occurs between hexafluoropropene and perfluoroisopropyl-anions[85, 88, 89].

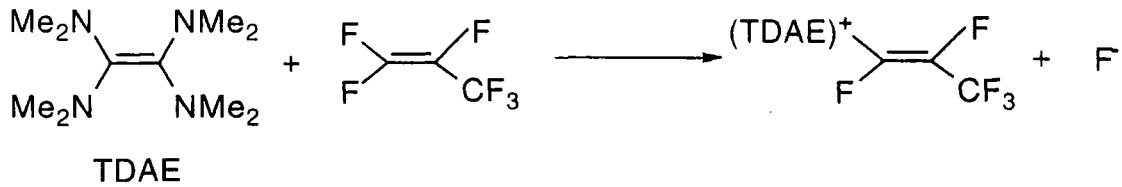


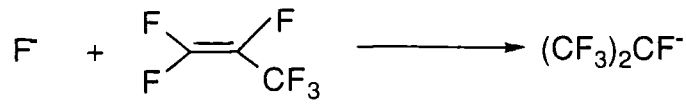
The isolation of perfluoroalkylated pyridines from an aprotic solvent is often problematic and so improved methodology has recently been developed.

1.6. B. TDAE Initiated Perfluoroalkylation.

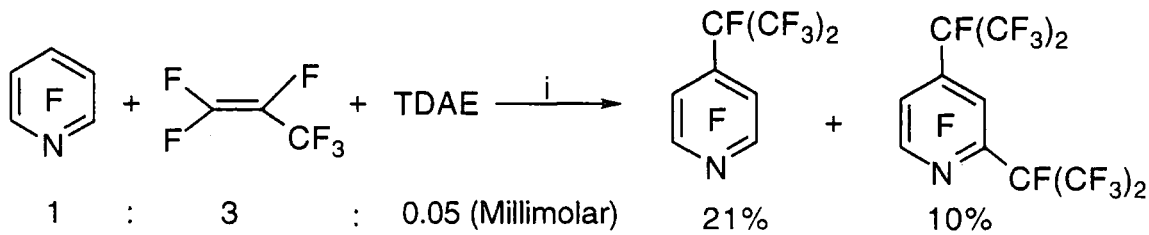
Using tetrakis(dimethylamino)ethene (TDAE) as a catalyst it is possible to effect the perfluoroalkylation of pentafluoropyridine[90] in the *absence of solvent.*

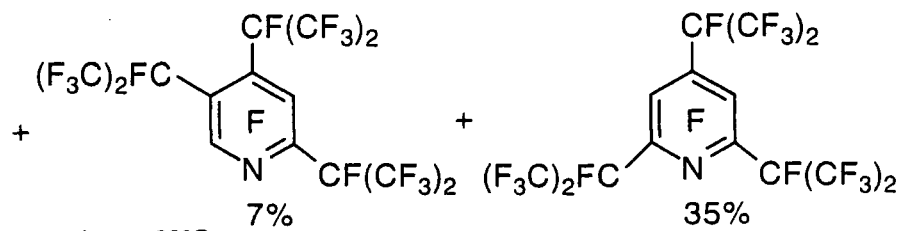
TDAE[91, 92] has been shown to react with perfluorinated alkenes[93] to produce fluoride salts. Under anhydrous conditions, TDAE reacts with hexafluoropropene to produce an '*in situ*' source of fluoride ion which can then react with hexafluoropropene to produce perfluoroisopropyl-anions.





The trapping of fluorinated carbanions by pentafluoropyridine affords mono- and polyperfluoroalkylated pyridines in good yield and it should be noted that the absence of a reaction solvent facilitates considerably product recovery by distillation directly from the reaction mixture.





Conditions: i. 48 h, no solvent, 60°C

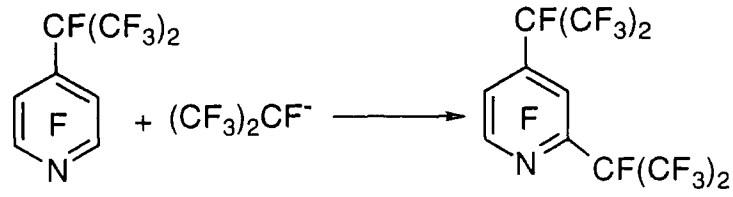
1.7. Established Chemistry of Perfluoro-4-isopropylpyridine.

Until recently, development of the chemistry of perfluoro-4-isopropylpyridine, and indeed related perfluorinated heterocycles, has been severely impeded by the inability to synthesise such compounds efficiently on a preparatively useful scale. As a consequence, there are only a few reported examples of reactions involving perfluoro-4-isopropylpyridine.

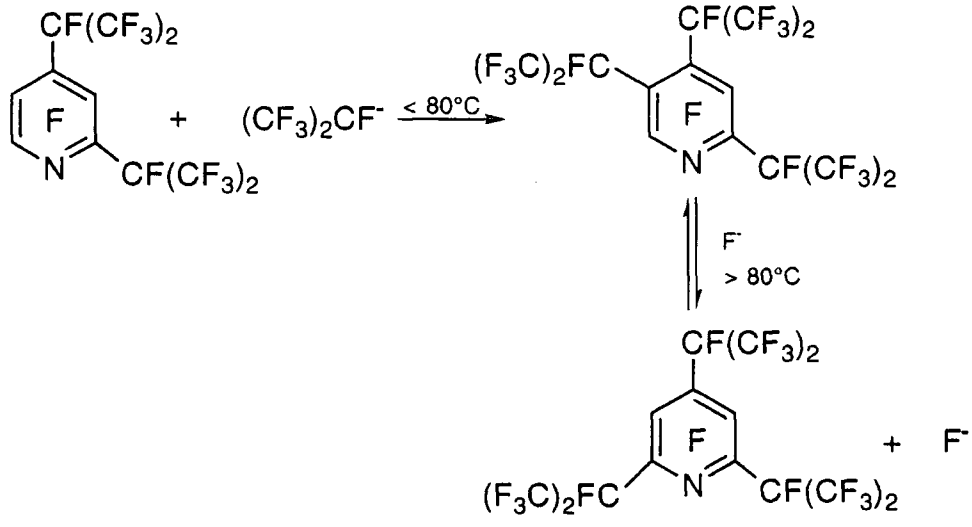
1.7.A. Further Reaction of Perfluoro-4-isopropylpyridine with Hexafluoropropene.

Implicit in the earlier discussion is the ability of perfluoro-4-isopropylpyridine to undergo polyperfluoroalkylation[82, 85, 94], when hexafluoropropene is employed as the perfluoroalkylating agent. It is well established that the second perfluorinated isopropyl-group enters at the 2-position[85, 94, 95] and steric reasons apart, this pattern of

substitution is consistent with the activating effects of the *ortho*-nitrogen and *ortho*-fluorine atoms.

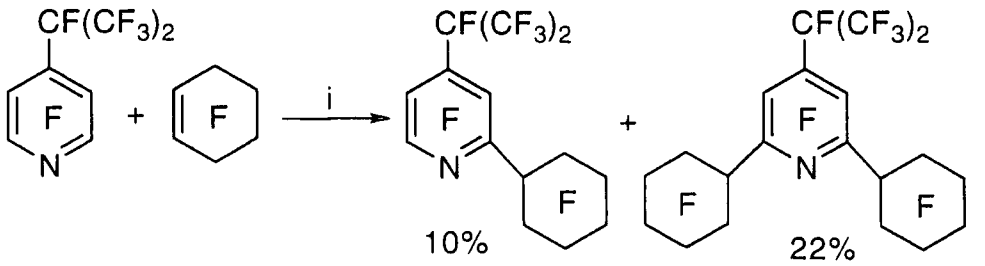


Despite the large steric interactions that exist between adjacent isopropyl-groups, a third perfluoroisopropyl carbanion has been shown to attack the 5-position, in preference to the anticipated 6-position, to yield the kinetically preferred 2,4,5-isomer. At a higher reaction temperature, in the presence of a stoichiometric equivalent of fluoride ion, the intermolecular rearrangement of the 2,4,5-isomer to the more thermodynamically stable 2,4,6-isomer occurs[85, 94, 95].



1.7.B. Reaction of Perfluoro-4-isopropylpyridine with Decafluorohexene.

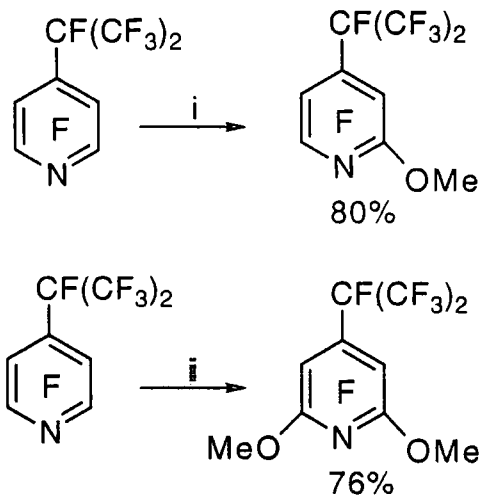
By a similar process, the fluoride induced reaction of perfluoro-4-isopropylpyridine with decafluorocyclohexene was shown by Chambers and co-workers[80] to give the 2- and 2,6-substituted derivatives, the 2,6-substituted product being the result of thermodynamic control.



Reagents and Conditions: CsF, Sulfolane, 165°C, 3 days.

1.7.C. Reaction of Perfluoro-4-isopropylpyridine with Sodium Methoxide.

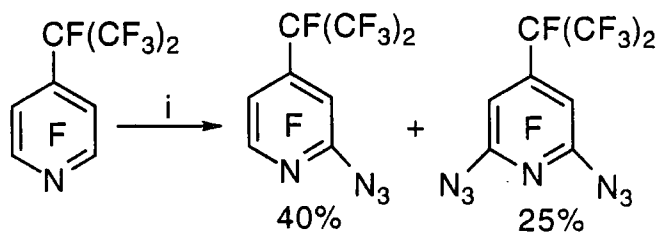
Chambers[85] and Haszeldine[96] have independently shown that perfluoro-4-isopropylpyridine reacts with methoxide ion to give the 2- and 2,6-substituted compounds.



Reagents and Conditions: i, NaOMe (1 equiv.), MeOH, r.t, 15 mins.
ii, NaOMe (2 equivs.), MeOH, reflux, 2h.

1.7. D. Reaction of Perfluoro-4-isopropylpyridine with Sodium Azide.

Banks has shown that perfluoro-(2-azido-isopropylpyridine) and perfluoro-(2,6-diazido-4-isopropylpyridine) can be readily prepared by the treatment of perfluoro-4-isopropylpyridine with sodium azide[97].



Reagents and Conditions: i, NaN_3 (2 equivs.), CH_3CN, r.t, 2 days.

CHAPTER II

Synthesis of Perfluoro-4-isopropylpyridine and Derivatives

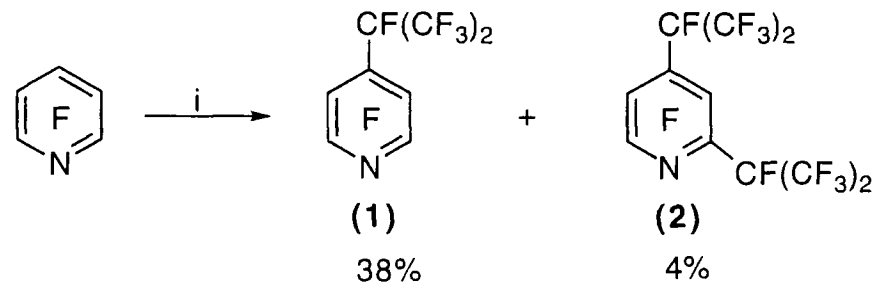
2. Introduction.

The introduction of perfluoroalkyl-groups[83, 84, 98-103] into aromatic or heteroaromatic systems can have a profound effect on the physical[15, 16, 104] and, in certain cases, biological properties[105] of the original compound. For example, the addition of a trifluoromethyl-group into a biologically[21, 22, 106] active molecule will often enhance its surface and lipophilic properties. The introduction of large perfluoroalkyl-groups has been shown to render some compounds completely soluble in perfluorocarbon solvents (a property that is utilised in fluorous-biphase chemistry[107-109]).

This chapter is concerned with the chemistry of the perfluoroalkylated compound, perfluoro-4-isopropylpyridine. The development of the chemistry of this system has been severly impeded by the inability to prepare this compound on a preparatively useful scale. We therefore aimed to provide a convenient route to this compound using established methodology. It was our intention to eventually incorporate this heterocycle into a range of highly coordinating, fluorous soluble macrocycles. However, before this was attempted, it was necessary to synthesise a range of model compounds for fluorous soluble macrocycles from perfluoro-4-isopropylpyridine. The following work therefore describes reactions between perfluoro-4-isopropylpyridine and oxygen- and nitrogen-centred nucleophiles to give model compounds for highly fluorinated macrocycles.

2.1. Preparation of Perfluoro-4-isopropylpyridine.

By optimising the procedure described in Chapter I (Section 1.6B), perfluoro-4-isopropylpyridine[90] (**1**) has been synthesised in good yield, on a large scale, by reaction between pentafluoropyridine and hexafluoropropene in the presence of an amine initiator, tetrakis-(dimethylamino)ethene (TDAE). The experiment was conducted without solvent making isolation of the products (**1**) and (**2**) straightforward by distillation.

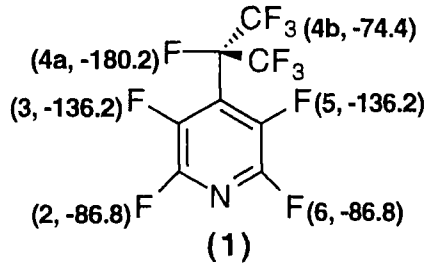


Reagents and conditions: i, HFP (1 equiv.), TDAE (2 mol%), 60°C , autoclave, 21 h.

Although the physical data and spectral data (^{19}F NMR) for compound (**1**) is

available in the literature[85, 90] the NMR data for (**1**), which is pivotal to our work, merits a brief description here.

At room temperature, the ^{19}F NMR spectrum for compound (**1**) consists of four groups of peaks which can be assigned to the fluorine atoms shown:



Figures in parentheses denote: i, chemical shift (ppm)

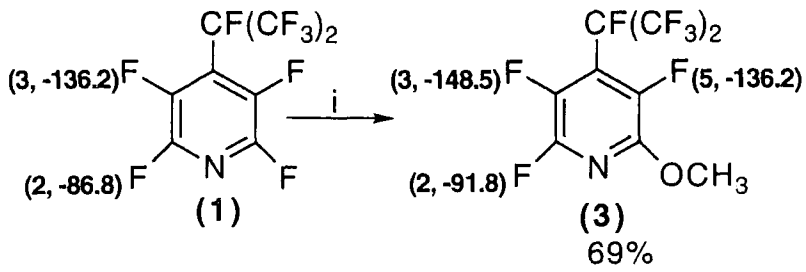
Inspection of the chemical shifts of the ring fluorine atoms reveals a large difference in values between the 2, 6-fluorines (-86.8 ppm) and the 3, 5-fluorines (-136.2 ppm). It will soon become apparent, when we synthesise model compounds for fluorous soluble macrocycles, that substituents have a small effect on these chemical shift values.

2.2. Reactions of Perfluoro-4-isopropylpyridine with Oxygen Nucleophiles.

Reaction of perfluoro-4-isopropylpyridine (**1**) with a series of alkoxide ions has provided a range of model compounds for highly fluorinated macrocycles. A series of detailed studies between compound (**1**) and methoxide ion have identified the 2- and 6-positions as the preferred sites of nucleophilic substitution in (**1**).

2.2.A. Preparation of 6-methoxy-perfluoro-4-isopropylpyridine.

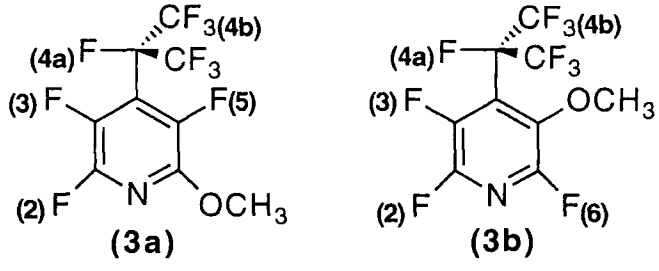
The most reactive site in compound (**1**) was identified using sodium methoxide as a nucleophile. Sodium methoxide (1.2 equivalents) reacted with compound (**1**) to afford the product, 6-methoxy-perfluoro-4-isopropylpyridine (**3**), which was purified by column chromatography.



Reagents and conditions: i,1.2 equivs. NaOMe, THF, reflux , 24 h.
Figures in parentheses denote: i, chemical shift (ppm)

A comparison of the ^{19}F NMR chemical shift values for the ring fluorine atoms, in (**1**) and (**3**), reveals a small substituent effect on the chemical shifts *ortho-*, *meta-* and *para-* to the site of substitution. This feature, together with the loss of a high frequency fluorine atom chemical shift, enabled us to identify the 6-position as the preferred site for methoxylation. Moreover, the calculated fluorine chemical shifts for compounds (**3a**) and (**3b**) (Table 1), derived from substituent chemical shift data, support formation of the 6-substituted product (**3**) rather than a 5-substituted compound.

Table 1.



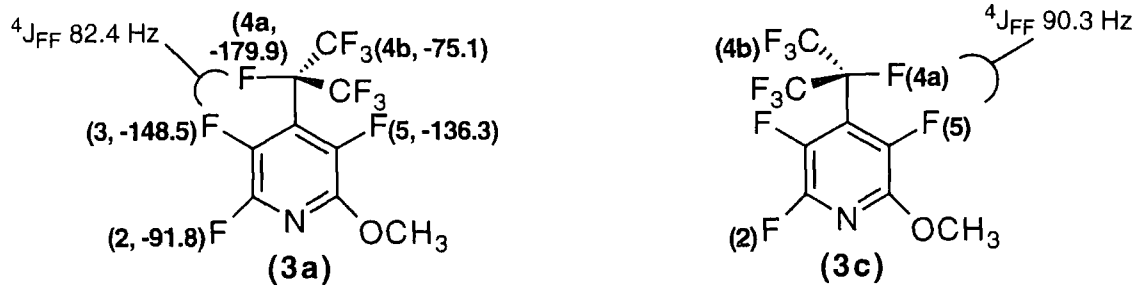
Chemical shifts (ppm) for ring fluorine atoms in (3a) and (3b)

	2	3	5	6
***Calculated (3a)**	-91.3	-149.7	-135.7	-
***Calculated (3b)**	-86.0	-141.0	-	-85.7
Observed	-91.8	-148.5	-136.2	-

*Calculated using pentafluoropyridine[28], 4-methoxytetrafluoropyridine[95] and perfluoro-4-isopropylpyridine[90]. as reference compounds.

At low temperature (-39°C) it was possible to resolve the ^{19}F NMR spectrum

of (3) into five groups of signals, corresponding to the rotamers (**3a**) and (**3c**)[95]. From these data the preferred site of substitution, 6-F, could be identified conclusively.

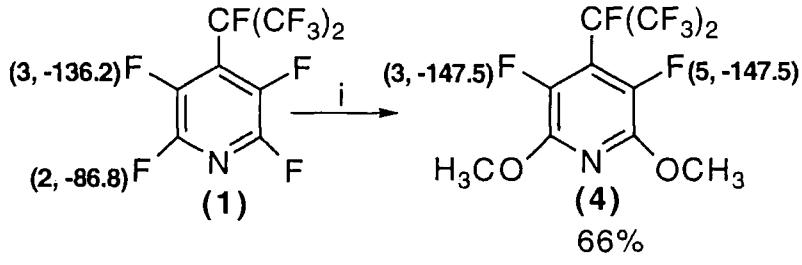


Figures in parentheses denote: i, chemical shift (ppm)

The non-equivalent fluorines $F_{(3)}$ and $F_{(5)}$ gave large through space couplings to $F_{(4a)}$ in the eclipsed conformations (**3a**) and (**3c**) respectively: this observation, together with the relative signal intensities for these fluorine atoms is consistent with a product arising from substitution at the 6-position.

2.2.B. Preparation of 2,6-dimethoxy-perfluoro-4-isopropyl-pyridine.

Having established the 6-position as the most reactive site in compound (**1**), we proceeded to identify the second most reactive centre. Compound (**1**) reacted with sodium methoxide (2.4 equivalents) to afford 2,6-dimethoxy-perfluoro-4-isopropyl-pyridine (**4**) in good yield.



Reagents and conditions: i, 2.4 equivs. NaOMe, THF, reflux , 24 h.
Figures in parentheses denote: i, chemical shift (ppm)

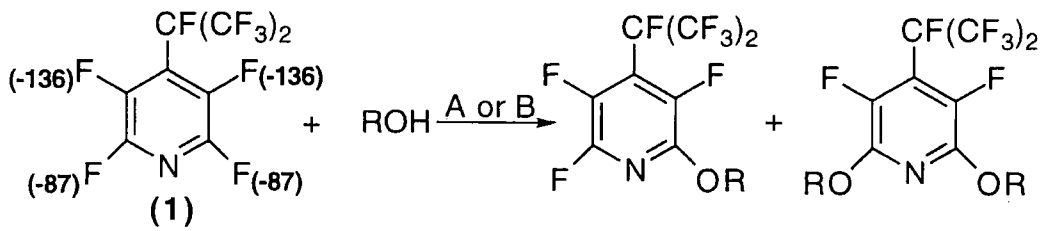
The absence of a resonance at -86.8 ppm corresponding to the 2-F ring atom, in the ^{19}F NMR spectrum for (**4**), indicated that methoxylation had proceeded to afford the 2,6-disubstituted compound (**4**) shown. Significantly, one ring fluorine signal was observed at -147.5 ppm which, together with its relative peak intensity value of two, confirmed the symmetrical nature of the 2,6-disubstituted product. If the second site of nucleophilic substitution had occured at the 5-position then two signals for the 3- and 6-ring fluorine atoms, in the ratio 1:1, would have been recorded.

2.3. Further Reactions of Perfluoro-4-isopropylpyridine with Oxygen-Centred Nucleophiles.

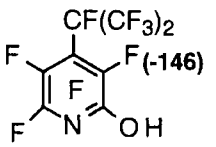
Having identified the substitution pattern between methoxide ion and perfluoro-4-isopropylpyridine (**1**) (Sections 2.2A-B), the reactivity of (**1**) with KOH and a series of related alkoxide ions was explored to give a range of model compounds for fluorous soluble macrocycles (Table 2). Significantly, the ^{19}F NMR chemical shift values for the ring fluorine atoms in the monoalkoxylated products reveal a small substituent effect on the chemical shifts *ortho-*, *meta-* and *para-* to the site of substitution and small substituent effects on the chemical shifts *ortho-* and *para-* to the site of substitution were also recorded for the dialkoxylated products. These features, together with the loss of a high frequency fluorine atom chemical shift, enabled us to identify the 2- and 6-positions as the preferred sites for mono-alkoxylation and dialkoxylation.

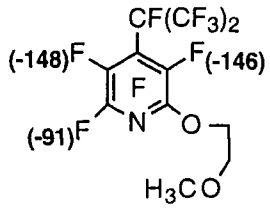
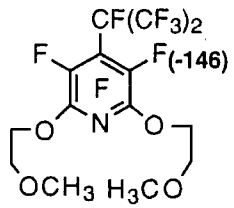
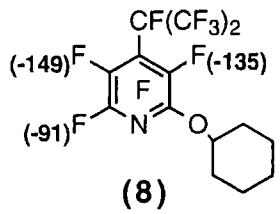
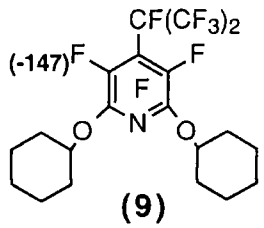
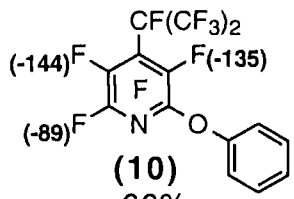
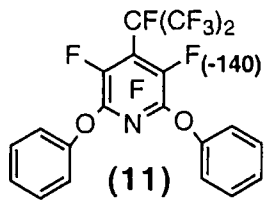
Table 2.

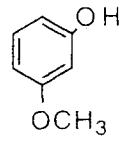
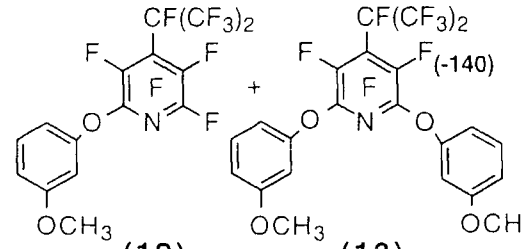
Reactions of Perfluoro-4-isopropylpyridine (**1**) with oxygen nucleophiles.



Figures in parentheses denote fluorine atom chemical shift (ppm)

Nucleophile (ROH)	Conditions	Products (% Yield)
KOH	A	 (5) 61%

Nucleophile (ROH)	Conditions	Products
$CH_3OCH_2CH_2OH$	A	 **(6)** 38%
$CH_3OCH_2CH_2OH$	B	 **(7)** 76%
$C_6H_{11}OH$	A	 **(8)** 64%
$C_6H_{11}OH$	B	 **(9)** 65%
C_6H_5OH	A	 **(10)** 66%
C_6H_5OH	B	 **(11)** 72%

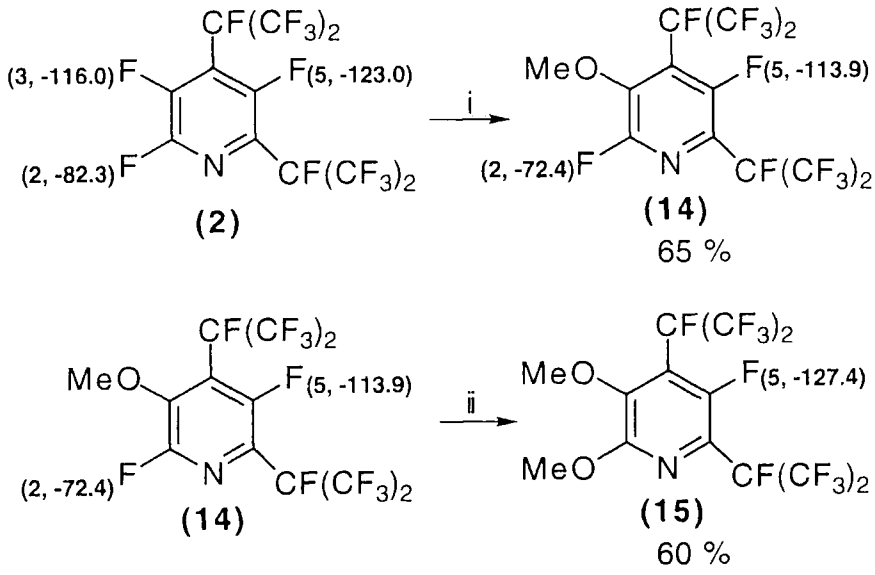
	B	 (12) 3% (13) 69%

Conditions:A, ROH (1 equiv.), Na or K, THF, Reflux, 24 h; Conditions: B. ROH (2 equiv.), Na or K, THF, Reflux, 24 h.

2.4. Reaction of Perfluoro-(2,4-diisopropyl)-pyridine with Sodium Methoxide.

The compound, perfluoro-(2,4-diisopropyl)-pyridine (**2**) was described previously (Section 2.1) as a product formed in the reaction between hexafluoropropene and pentafluoropyridine. Compound (**2**) was identified by comparison of its ^{19}F NMR and MS spectra with an authentic sample[90].

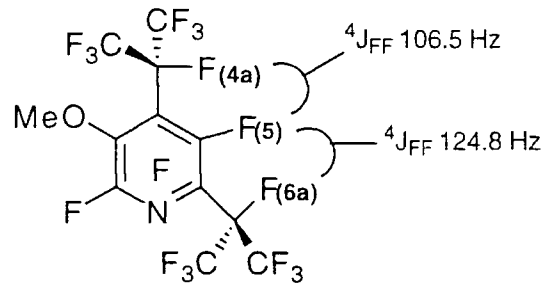
Reaction of (**2**) with 1.25 equivalents of sodium methoxide yielded the monomethoxylated derivative (**14**). Upon isolation, reaction between compound (**14**) and 1.25 equivalents of methoxide ion afforded the dimethoxylated product (**15**).



Reagents and conditions: i and ii, NaOMe (1.25 equivs.), MeOH, Reflux, 20 h.
Figures in parentheses denote: position and chemical shift (ppm)

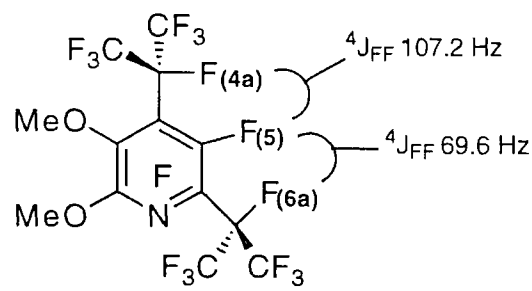
A comparison of the ^{19}F NMR chemical shift values for the ring fluorine atoms in (**2**) and (**14**) reveals a small substituent effect on the chemical shift values *ortho*- and *meta*- to the site of substitution. The absence of a resonance at -116 ppm,

corresponding to the 3-F ring atom, suggested that the reaction had proceeded to afford the 3-methoxylated product shown. In particular, large through space coupling between $F_{(4a)}$-$F_{(5)}$ and $F_{(6a)}$-$F_{(5)}$ respectively provided conclusive evidence for the 3-methoxylated product (**14**):



We conclude from these observations that the activating influence of the perfluoroisopropyl-groups, towards nucleophilic attack on the 3-fluorine atom, is greater than the activating effect of the ring nitrogen on the 2-fluorine atom.

The ^{19}F-NMR spectral data for compound (**15**) confirmed the presence of one ring fluorine atom only. The notable absence of a resonance at -72.4 ppm found in (**14**), corresponding to $F_{(2)}$, together with large through space coupling between $F_{(4a)}$-$F_{(5)}$ and $F_{(6a)}$-$F_{(5)}$ respectively, provided strong evidence for the 2,3-dimethoxylated product (**15**) shown:



(**15**)

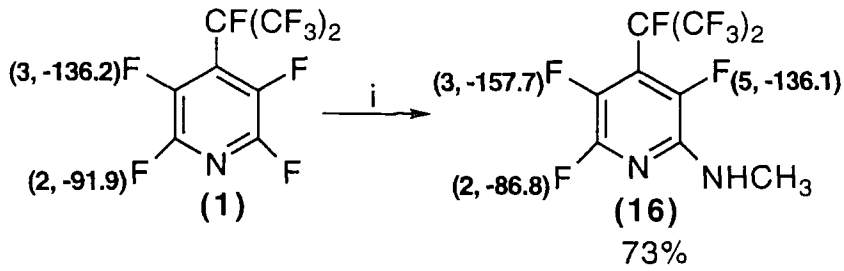
2.5. Reactions of Perfluoro-4-isopropylpyridine with Nitrogen Nucleophiles.

Reactions between perfluoro-4-isopropylpyridine (**1**) and a series of amines yield some potentially useful synthetic building blocks for the preparation of fluorous soluble macrocycles.

2.5.A. Reaction of Perfluoro-4-isopropylpyridine and Methylamine.

The reactivity and regioselectivity of compound (**1**) towards nitrogen-centred reagents has been assessed using methylamine as a model nucleophile. The addition of methylamine to a solution of compound (**1**), in THF, afforded the monoaminated

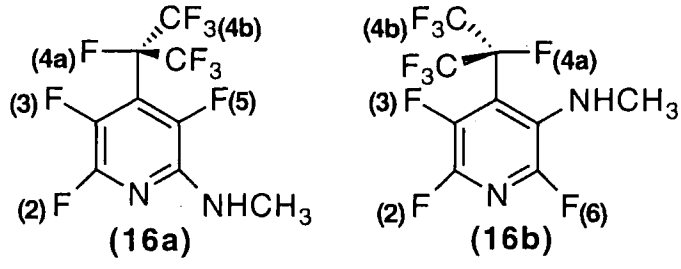
product (**16**) exclusively.



Reagents and conditions: i, $MeNH_2$ (2 equivs.), THF, r.t., 24 h.
Figures in parentheses denote: i, chemical shift (ppm)

Compound (**16**) was identified by considering its NMR and MS-data. A comparison of the ^{19}F NMR chemical shift values for the ring fluorine atoms in (**1**) and (**16**) reveals a small substituent effect on the chemical shift values *ortho-*, *meta-* and *para-* to the site of substitution. This feature together with the loss of a high frequency fluorine atom chemical shift enabled us to identify the 6-position as the preferred site for amination. Moreover, the calculated fluorine chemical shift data for compounds (**16a**) and (**16b**) (Table 3) support amination at the 6-position, to give the product (**16**), rather than at the 5-position.

Table 3.



Chemical shifts (ppm) for ring fluorine atoms in (3a) and (3b)

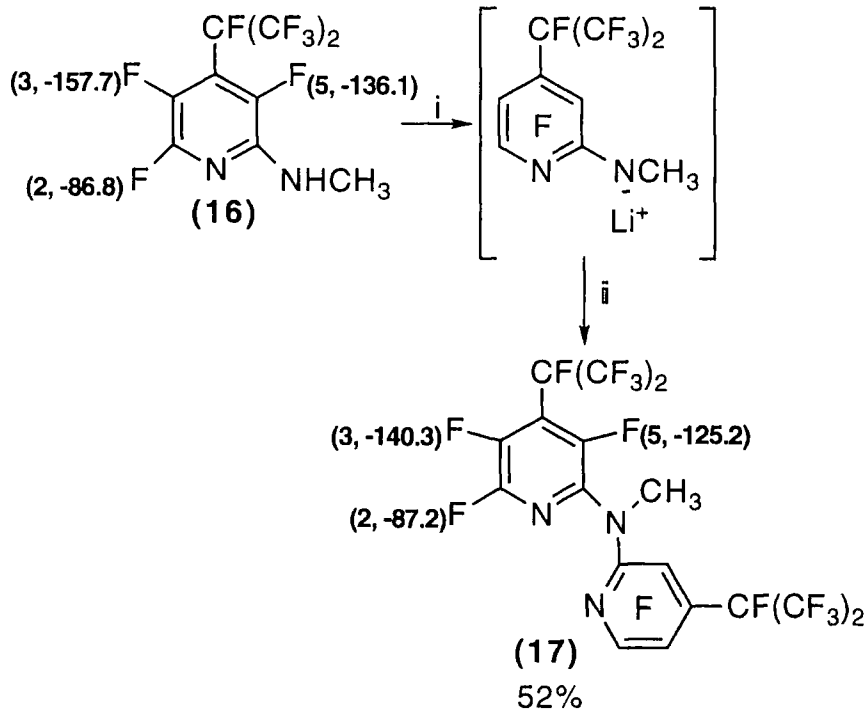
	2	3	5	6
***Calculated (16a)**	-93.4	-157.7	-138.7	-
***Calculated (16b)**	-86.0	-143.1	-	-89.0
Observed	-86.8	-157.7	-136.1	-

*Calculated using pentafluoropyridine[28], 4-aminotetrafluoropyridine[37] and perfluoro-4-isopropylpyridine[90] as reference compounds.

2.5.B. Preparation of a Highly Fluorinated Bispyridyl-Building Block and Derivatives.

In this section, we describe the synthesis of a highly fluorinated bispyridyl-compound and some aza-substituted derivatives. In principle, this class of compound can be used to prepare highly fluorinated macrocycles, incorporating 2,6-disubstituted pyridine subunits and nitrogen-bridging atoms.

The reaction of compound (**16**) with butyl lithium[110, 111] resulted in hydrogen lithium exchange to give a reactive lithium salt. The identity of the lithiated species was confirmed by reaction with perfluoro-4-isopropylpyridine (**1**) to afford the product (**17**). Compound (**17**) was characterised by ^{19}F NMR spectroscopy which, consistent with its symmetry, gives rise to 3 signals, in the ratio 1:1:1, for the ring fluorine atoms shown:

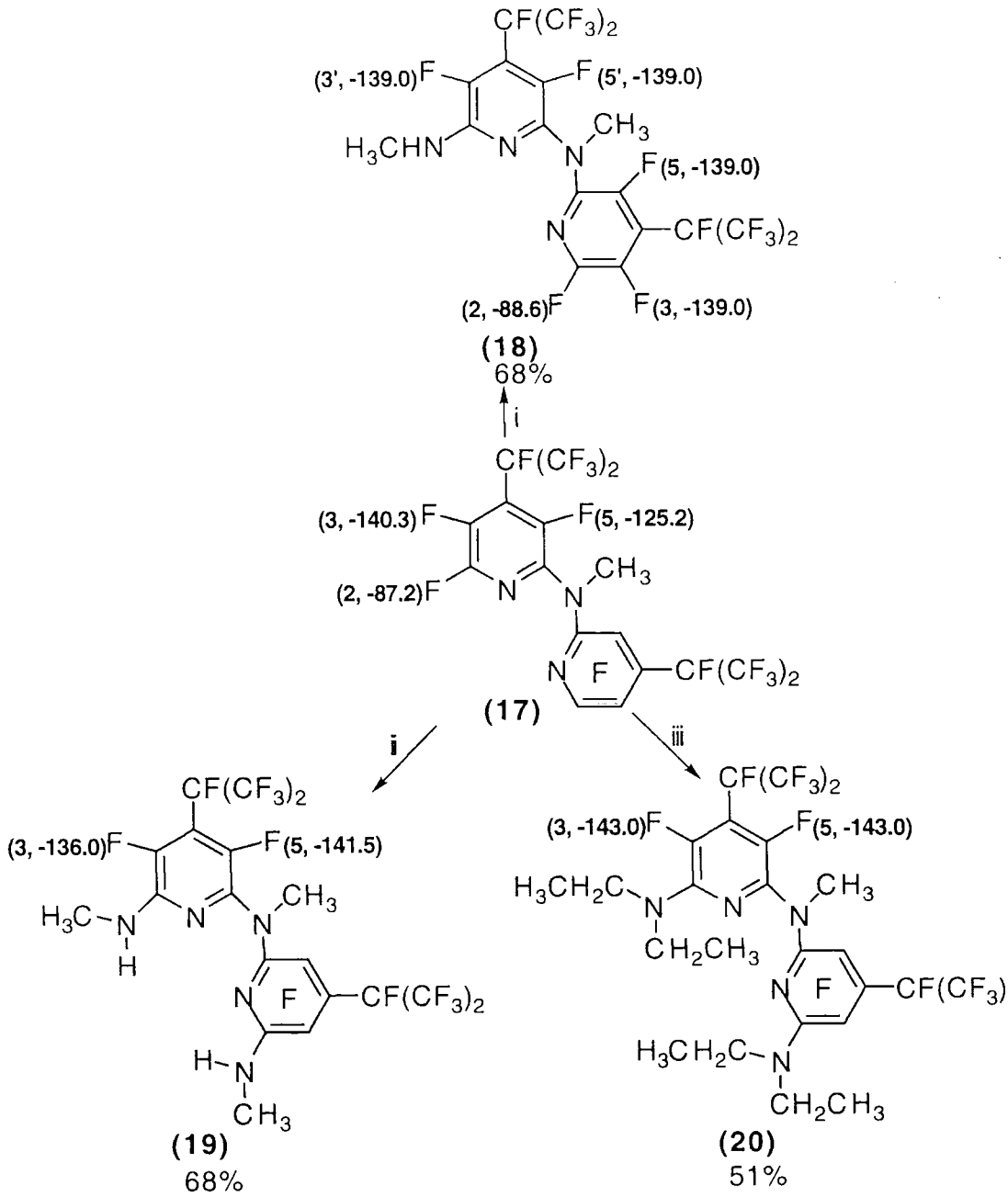


Reagents and conditions: i, nBuLi (1 equiv.), THF, -78°C, 1 h.
ii, Perfluoro-4-isopropylpyridine (1 equiv.), -78°C, 3 h.
Figures in parentheses denote: i, chemical shift (ppm)

2.5.B.i. Derivatives (18), (19) and (20).

The reaction of (**17**) with 2.5 equivalents of methylamine resulted in the displacement of one 2-F atom to give compound (**18**), whilst the reaction of (**17**) with

4 equivalents of either methylamine or diethylamine yielded the products, (**19**) and (**20**) which result from nucleophilic substitution of both 2-F and 2'-F. The identities of compounds (**18**)-(**20**) were established by MS and ^{19}F NMR analysis. In particular, a comparison of the ^{19}F NMR chemical shift values for the ring fluorine atoms in (**17**) and the products (**18**)-(**20**) reveals a small substituent effect on the chemical shift values *ortho-* and *para-* to the site of substitution. In each example the absence of a resonance at -87.2 ppm indicated that amination had occured to yield the 2- and 2'-substituted products shown:



Reagents and conditions: i, $MeNH_2$ (2.5 equivs),THF, r.t., 20 h.
ii, $MeNH_2$ (4 equivs),THF, r.t., 20 h.
iii, Et_2NH (4 equivs),THF, r.t., 20 h.
Figures in parentheses denote: position and chemical shift (ppm)

2.6. Conclusions.

In this chapter, we have demonstrated that perfluoro-4-isopropylpyridine can be prepared conveniently, on a large scale, by reaction of pentafluoropyridine with one stoichiometric equivalent of hexafluoropropene. A series of nucleophilic substitution reactions between perfluoro-4-isopropylpyridine and oxygen- and nitrogen-centered nucleophiles afforded a range of model compounds and building

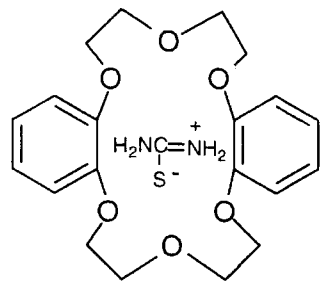
blocks for highly fluorinated macrocycles. The results obtained for reactions involving perfluoro-4-isopropylpyridine were consistent with the preferred 2,6-pattern of substitution described in Section 1.7.

CHAPTER III

2,6-Pyridine-Bridged-Macrocycles.

3. General Introduction.

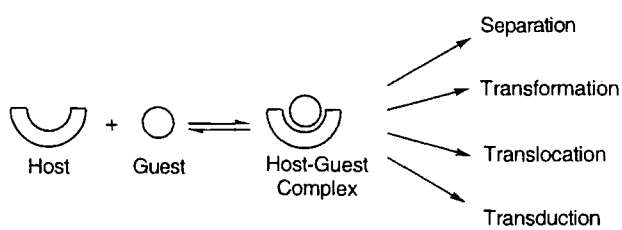
In 1971, Pedersen reported a molecular host-guest complex between dibenzo-18-crown-6 and thiourea[112] (**D**) and since then specific molecular recognition has evolved into a new and increasingly important area of chemistry[113, 114].



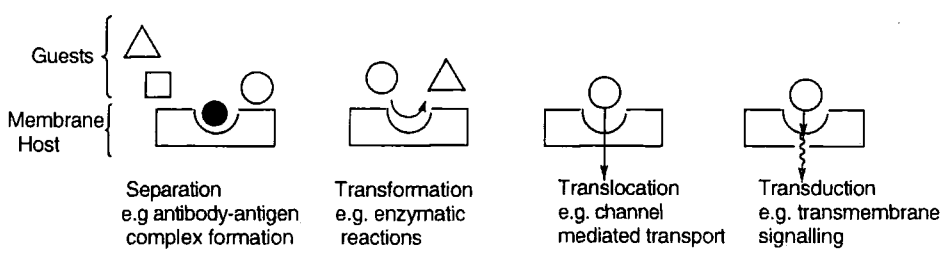
(D)

Molecular recognition[115] can be defined as, "the study of polymolecular entities and assemblies e.g. supramolecular complexes, formed between two or more designed chemical species which are held together by non covalent forces"[116]. In nature, molecular recognition is a fundamental chemical process that controls numerous significant biological reactions including: enzymatic reactions, substrate binding to receptor proteins and cellular recognition[117, 118]. In living organisms, host-guest complexation occurs both in homogeneous solution (A) and on the surfaces of cellular membranes (B).

A. Host-Guest Complexation in a Homogeneous Solution



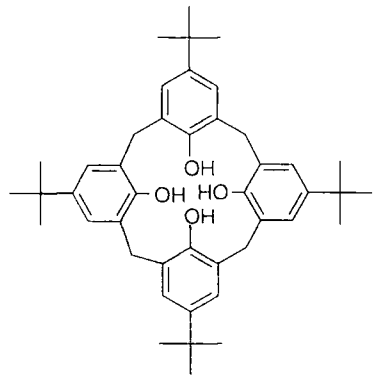
B. Host-Guest Complexation at Membrane Surfaces



Cyclophanes[119, 120], or bridged aromatic macrocycles, represent the central class of *synthetic* receptors in molecular recognition. A feature of cyclophanes is their

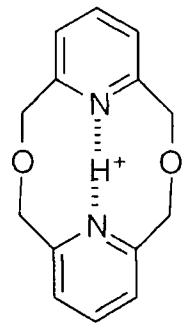
ability to transport ions or neutral molecules *via* their π-electron rich cavities: this property enables them to mimic important biological recognition processes.

Calixarenes[121] are amongst the most studied synthetic meta-cyclophane hosts, having been used to host both neutral guest molecules[122] and metal ions[123]. For example, *para*-t-butylcalix[4]arene (**E**) forms a 1:1 inclusion complex with para-xylene[124] and will also complex alkali-metal ions[125].



(E)

The incorporation of heterocyclic groups into cyclophanes is becoming increasingly important because heterocycles not only provide rigidity to macrocyclic systems, but importantly, they can participate in complexation through their donor atoms. For example, the macrocycle, (**F**), can stabilise a proton through its nitrogen lone-pair orbitals[126]:



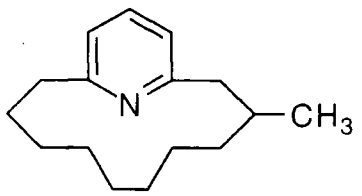
(F)

It was the aim of this work to develop routes to highly fluorinated macrocycles, containing 2,6-disubstituted pyridine subunits and nitrogen and oxygen-bridging atoms. Before new work is described, it is appropriate to outline some of the more important synthetic pathways to 2,6-substituted-pyridine macrocycles. This chapter is not intended to be a comprehensive text of the syntheses of *all* 2,6-bridged pyridine macrocycles, as compounds of this type are too numerous to write an exhaustive review. There are, however, a number of excellent texts[127] and a

particularly comprehensive review article[128], that between them, describe the majority of these compounds.

3.1. Introduction of 2,6-Substituted-Pyridine Macrocycles.

The first recognised 2,6-substituted-pyridine macrocycle, 'muscopyridine'[129, 130], was isolated by Prelog[131] from the odoriferous component of natural musk.

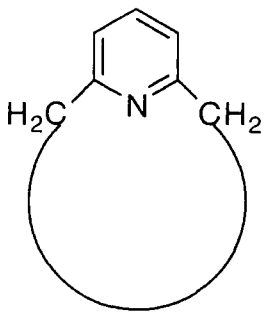


(+)-2-Me

The unique biochemical properties possessed by this compound provided a stimulus to organic chemists to prepare synthetic analogues. In particular, numerous carbon-, nitrogen-, oxygen- and sulfur-2,6-disubstituted pyridine containing macrocycles have been made.

3.2. 2,6-Carbon-Carbon Bridged Macrocycles.

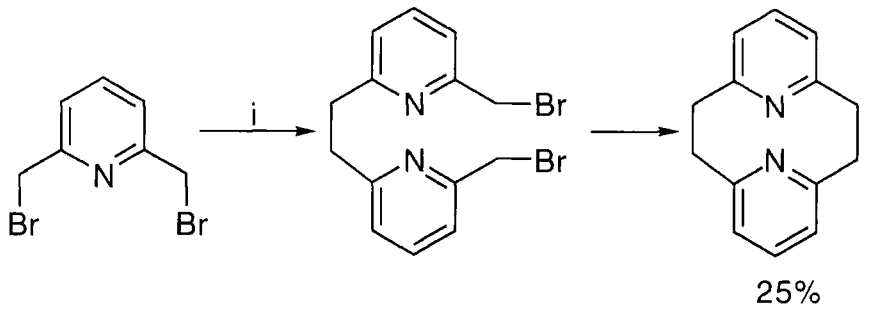
2,6-carbon-carbon bridged macrocycles can be defined as systems in which the bridging carbon atoms are directly attached to the pyridine ring:



3.2.A. Pyridinophanes from Organometallic Reagents.

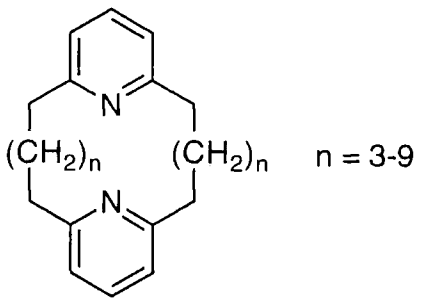
An effective way of generating C-C σ-bonds involves the reaction of an organometallic reagent with an activated site typically possessing a good leaving group[132].

Baker[133, 134] published the first synthesis of a [2.2](2,6)pyridinophane, by the treatment of 1,2-bis(6'-bromomethyl-2'-pyridyl)ethane with either n-butyl- or phenyllithium.

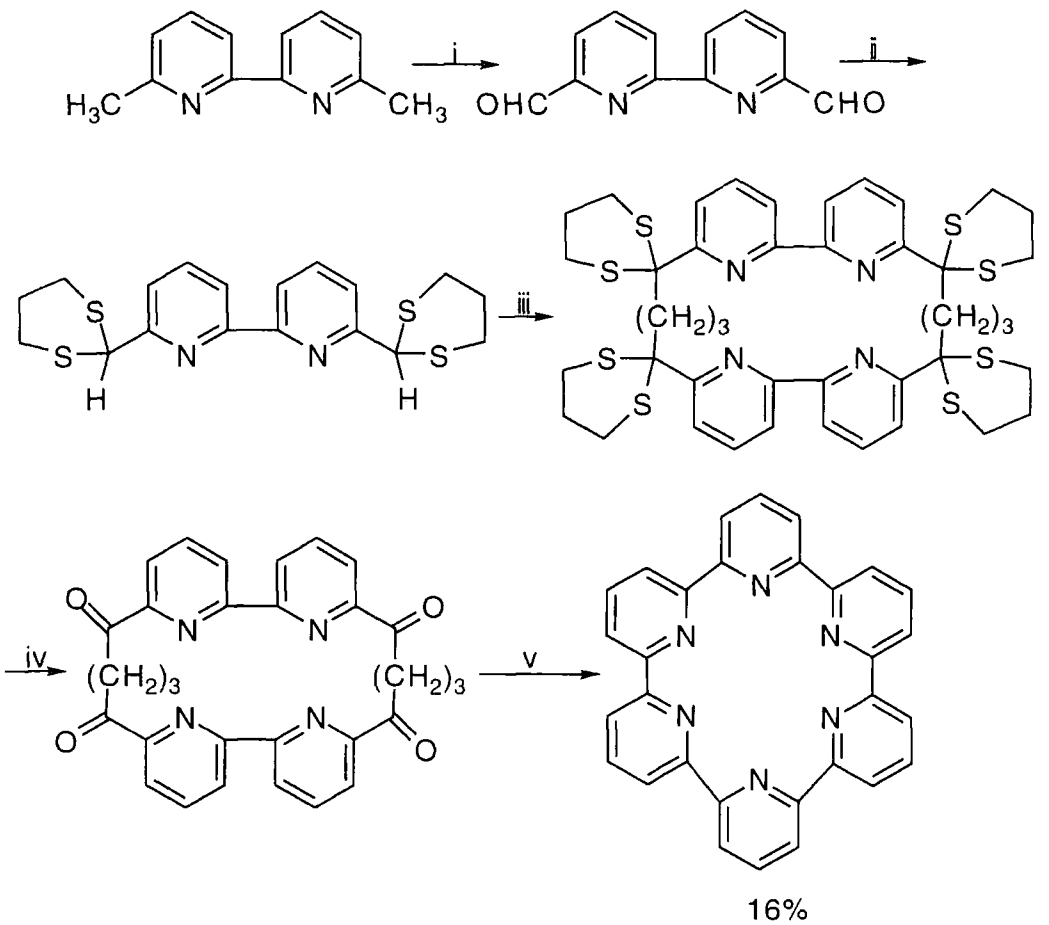


Reagents: i, BuLi or PhLi (2.5 equivs), Benzene-Ether.

This approach has been successfully employed to produce higher pyridinophane homologues (n =3-9[135, 136, 137]):



Similarly, Newkome[138] described the synthesis of a particularly elaborate macrocycle, comprising of six unsubstituted pyridine units. The key step to this synthesis, (iii), involves the cyclisation of an organolithium species to give a polyfunctional macrocycle, from which molecular rigidity is irreversibly introduced.

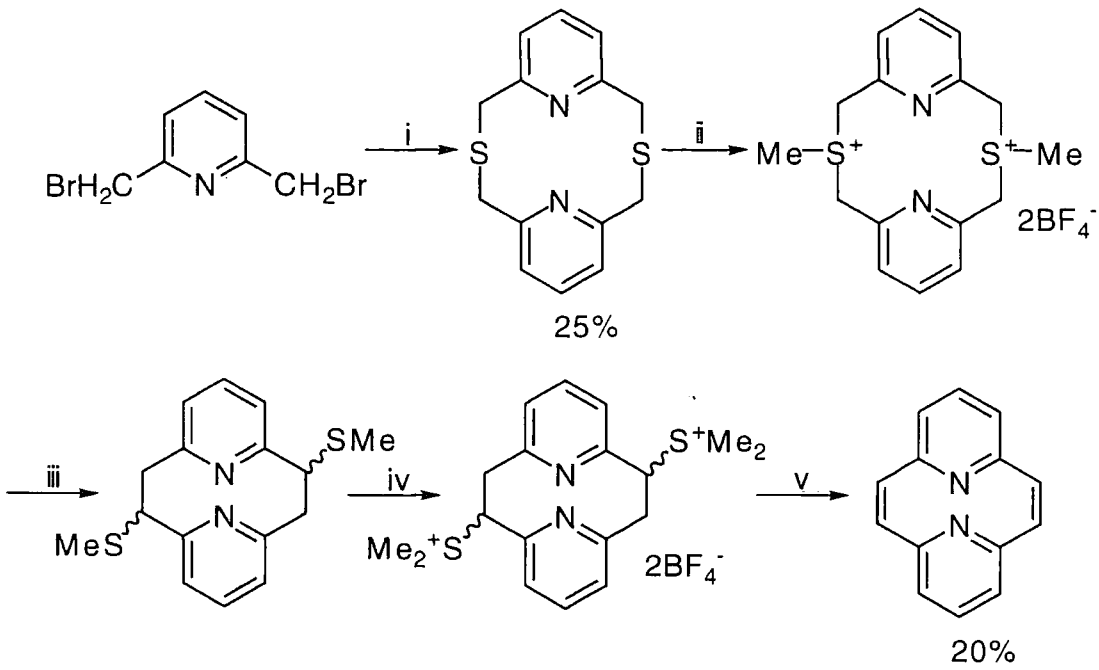


Reagents and conditions: i, SeO_2, AcOH, Reflux, 24 h; ii, $HS(CH_2)_3SH$, Toluene, Reflux, 5 h; iii, nBuLi, THF, $CH_2(CH_2Br)_2$, 3 days, -45°C; iv, NBS, THF, CH_3OH; v, H_2NOH, HCl, AcOH.

3.2.B. Pyridinophanes from Dithiane Reagents.

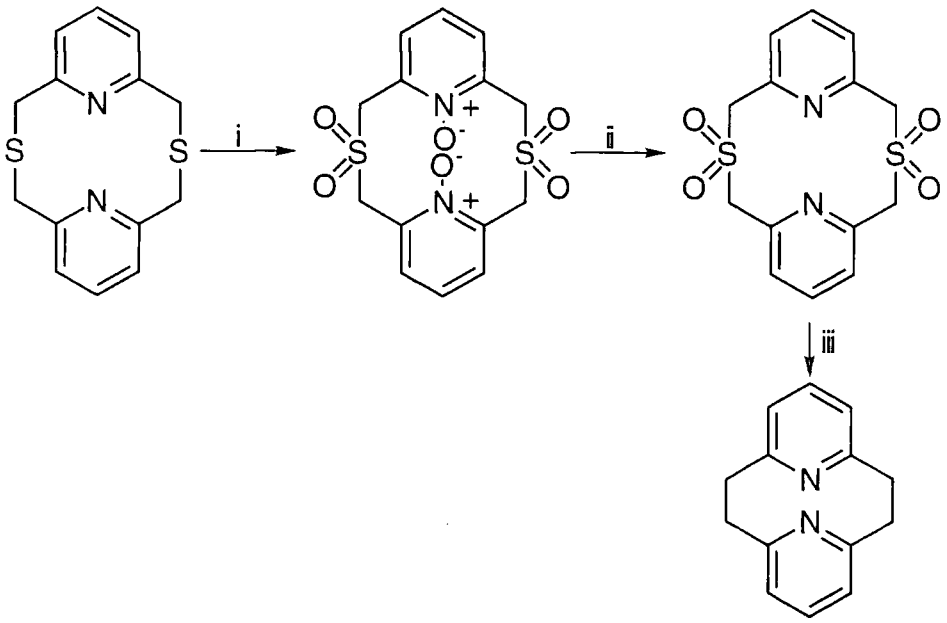
A different approach to 2,6-carbon-carbon bridged macrocycles uses dithiane compounds as starting materials.

Boekelheide and Lawson[139] published an interesting route to pyridinophanes *via* dithiacyclophane precursors: the reaction shown involves a two-step extrusion of sulfur by a Stevens rearrangement.



Reagents: i, Na_2S; ii, Me_3OBF_4; iii, KO^tBu, THF; iv, Me_3OBF_4; v, KO^tBu.

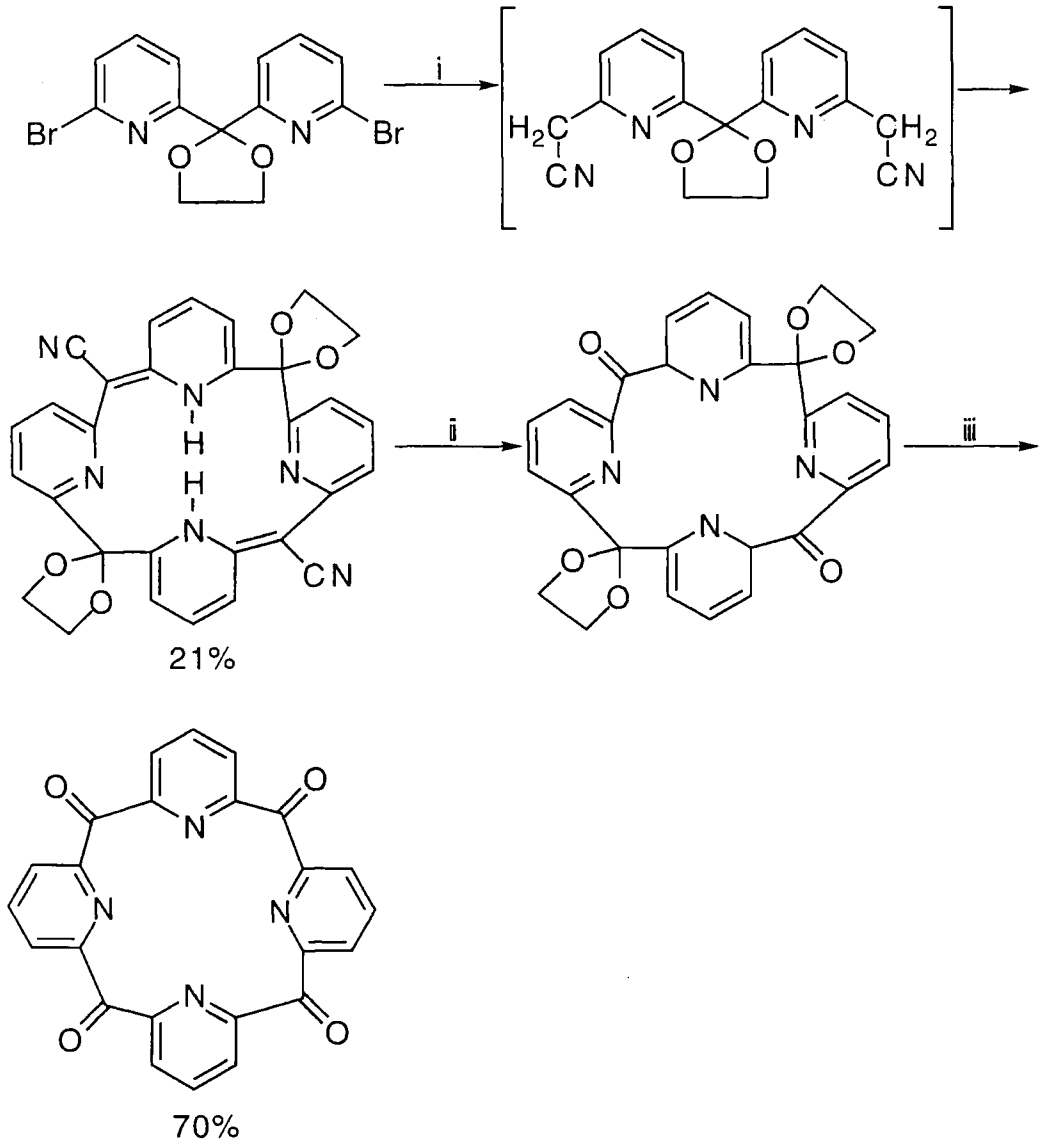
A more efficient route to pyridinophanes has been reported by Martel and Rasmussen[140] involving the thermal expulsion of sulfur dioxide, from the corresponding sulfone:



Reagents: i, (O); ii, Fe, CF_3CO_2H; iii, 680°C/0.01mm.

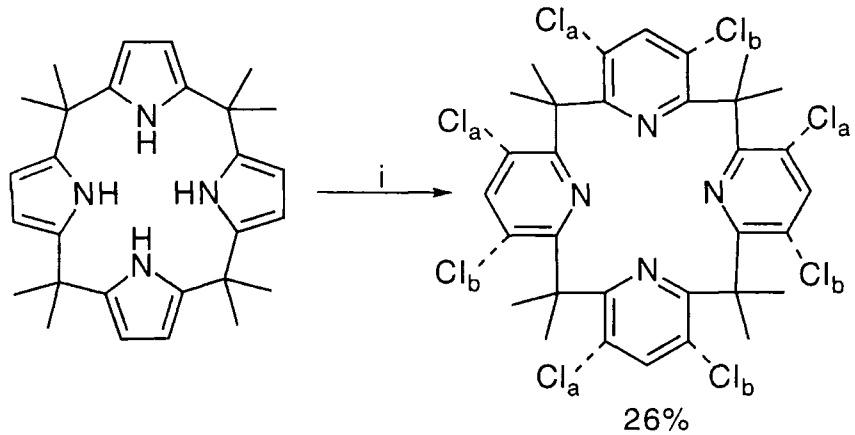
3.2.C. Calixpyridones and Calixpyridines.

In the area of heterocalixarenes, there are few reported examples of calixpyridines. Newkome first published the preparation of a calix[4]pyridine analogue, tetrapyridine tetraone[141], from 2,2-bis(6'-bromopyrid-2'-yl)-1,3-dioxolane:



Reagents: i, LiH, MeCN, 5% TMEDA-Benzene; ii, m-CPBA, $CHCl_3$; iii, c.HCl

The first 'true' calixpyridine, with the pyridine rings linked in the 2- and 6-positions *via* a single sp^3-hybridised carbon has only recently been reported[142]. In this elegant synthesis, dichlorocarbene[143] is used to insert carbon atoms into the 5-membered rings of the parent calix[4]pyrrole. The subsequent elimination of HCl and rearrangement produces a 3-chloropyridyl-ring:

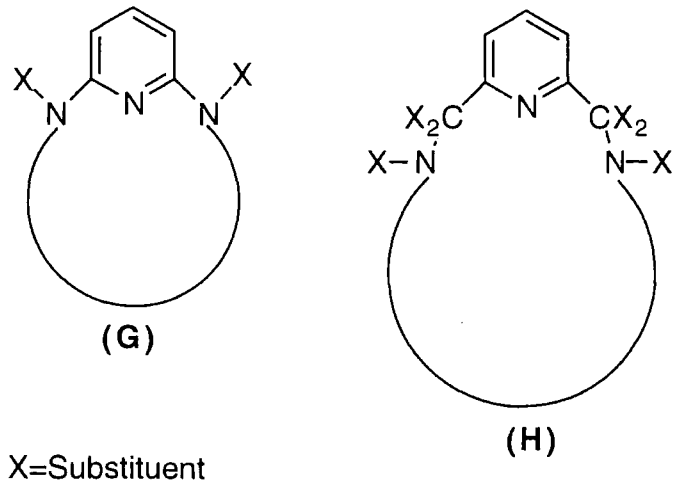


Reagents: i, Cl_3CCO_2Na (15 equivs.), dioxane.
(N.B. The chlorine atoms indicated may be present in positions 'a' **or** 'b')

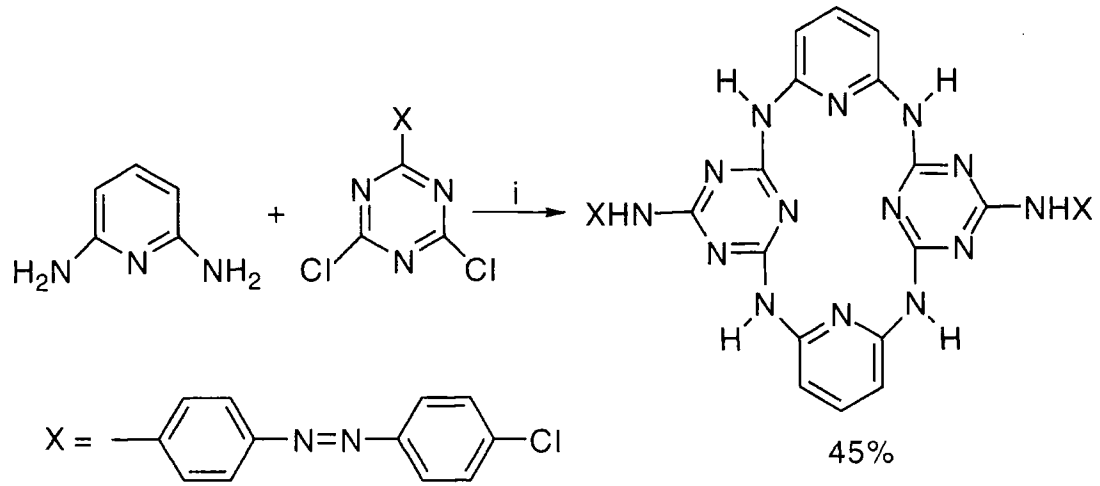
It has been proposed that calixpyridines will eventually be utilised in waste remediation processes, involving the selective complexation of transition- and other heavy-metals.

3.3. Carbon-Nitrogen Bridged Macrocycles.

Carbon-nitrogen bridged pyridino-macrocycles can be categorised as systems in which the bridging nitrogen atoms are directly bonded to the pyridine ring (**G**) or compounds in which the nitrogen atoms are remote from the pyridine nucleus (**H**).

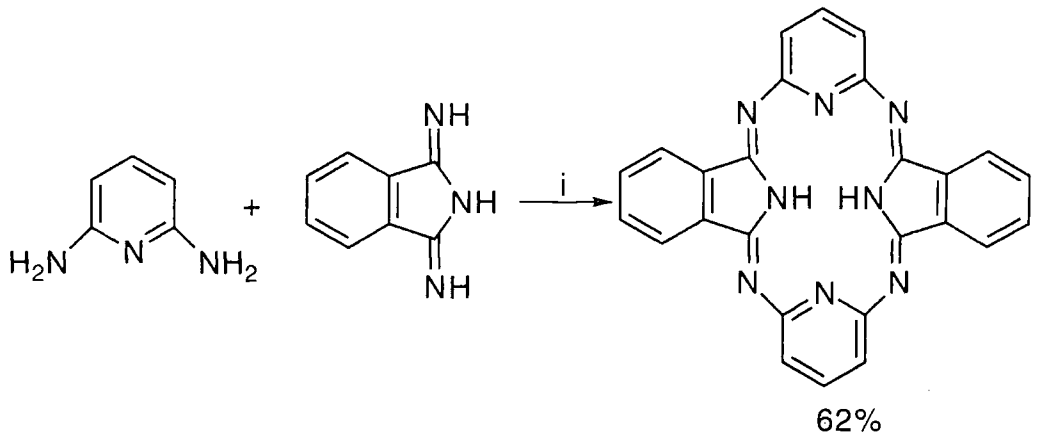


Borodkin[144] has synthesised macroheterocycles (**G**) by heating 2,6-diaminopyridine with appropriate dichlorides:



Conditions: i, Hexanol, Reflux, 10 h.

Similarly, Barnfield and Mack have demonstrated that carbon-nitrogen bridged macrocycles (**G**) can be prepared by a condensation reaction between 1,3-di-iminoisoindole and 2,6-diaminopyridine:

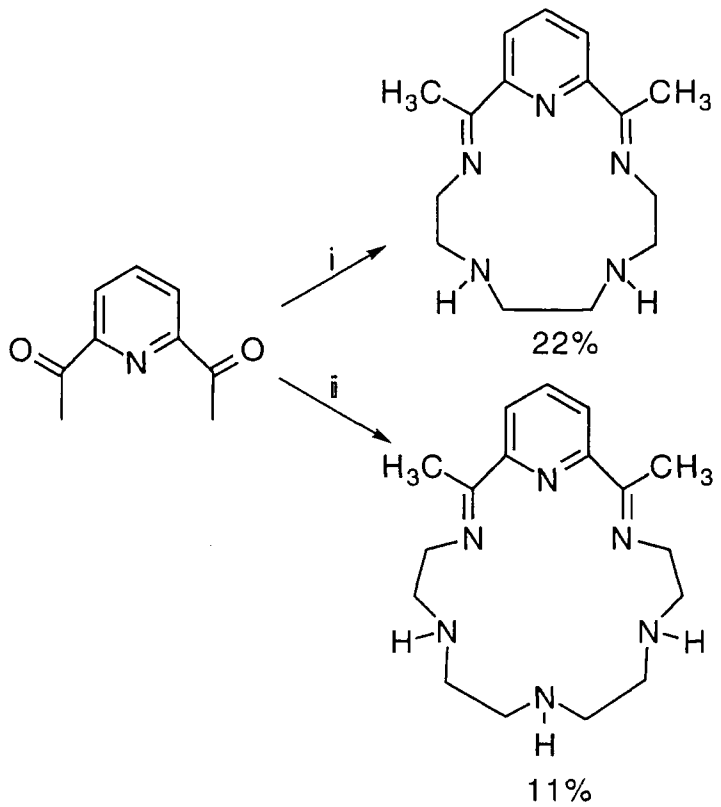


Reagents and conditions: i, Methanol, Reflux, 20 h.

Highly conjugated carbon-nitrogen-bridged macrocycles such as these can be utilised, for example, as paint pigments.

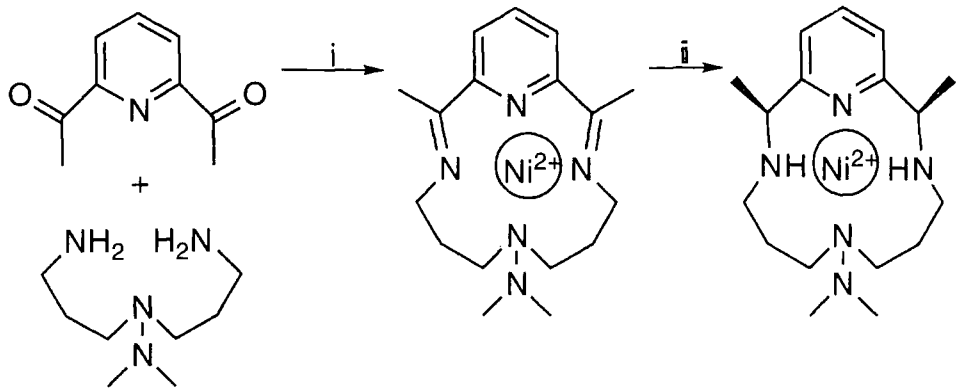
The synthesis of carbon-nitrogen-bridged pyridine macrocycles (**H**) is normally achieved *via* condensation reactions using either 2,6-diacetylpyridine or a 2,6-pyridinedicarboxaldehyde. In these reactions, the final cyclisation step is often facilitated by a carefully selected metal-ion template: it has been shown that the presence of a suitable metal templating agent will always raise the yield of macrocyclic product[145].

Curry and Busch[146] published the metal-ion mediated, Schiff-base condensation reaction between 2,6-diacetylpyridine and triethylenetetraamine and also tetraethylenepentamine to give the pentadentate and hexadentate macrocycles:



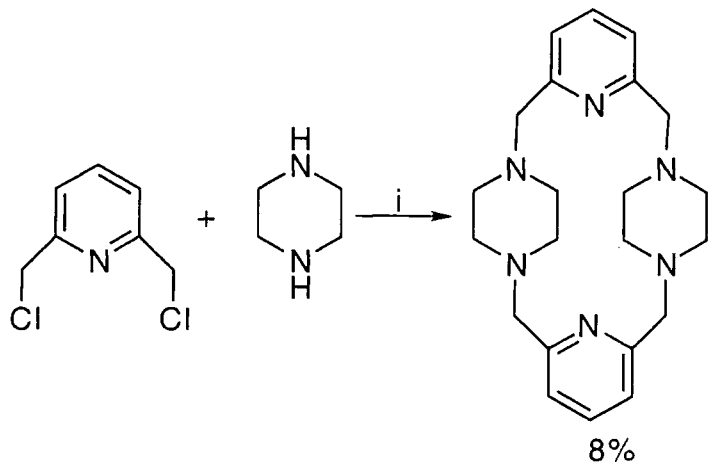
Reagents and conditions: i, $FeCl_2$ (1 equiv.), H_2O, Triethyltetraamine, 36 h.
ii, $FeCl_2$ (1 equiv.), H_2O, Tetraethylpentamine, 24 h.

It is usual to reduce the resulting diimine compounds to the corresponding saturated penta/hexadentate macrocycles. For example, the diimine macrocycle obtained *via* the template directed (Ni^{2+}) condensation of 2,6-diacetylpyridine and 4-(dimethylamino)-1,7-diamino-4-azaheptane was hydrogenated to the saturated Ni^{2+} complex[147]:



Reagents and conditions: i, $NiCl_2 .6H_2O$ (1 equiv.), $EtOH/H_2O$ 1:1, CH_3CO_2H.
ii, PtO_2 /H_2,140 atm, 80°C, 48 h.

Rissanen has published an alternative route to polyazacycles, albeit a low yielding preparation, involving a reaction between 2,6-bis(chloromethyl)pyridine and piperazine, under high dilution conditions[148]:



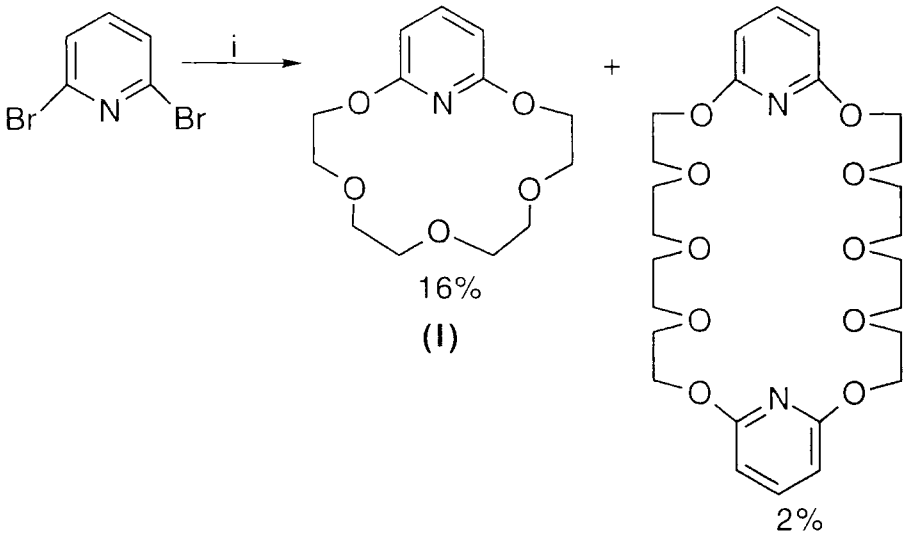
Reagents and conditions: i, Na_2CO_3,THF/CH_3CN (1:1.5), Reflux, 10 h.

The solubility of this particular macrocycle can easily be modified by treatment with acid, thereby protonating the nitrogen atoms of piperazine.

3.4. Carbon-Oxygen Bridged Macrocycles.

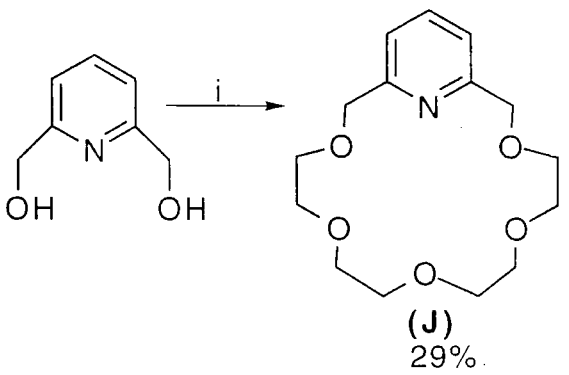
Carbon-oxygen bridged pyridino-macrocycles can also be categorised as: systems in which the bridging oxygen atoms are directly bonded to the pyridine ring (**I**) or systems in which the oxygen atoms are remote from the pyridine nucleus (**J**).

Newkome[149, 150] has reported a low yielding preparative route to pyridine containing macrocyclic ethers (**I**) *via* nucleophilic displacement by alkoxide.

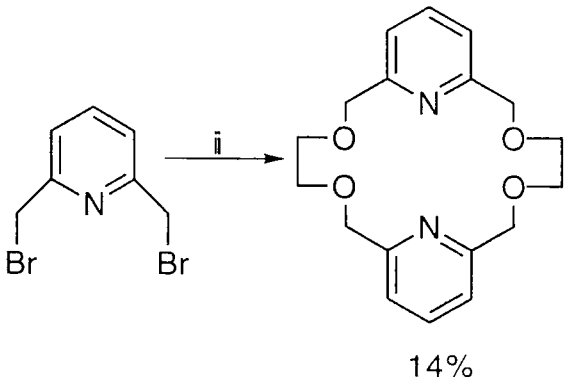


Reagents and conditions: i, Tetraethylene Glycol, NaH, Xylene, 140°C.

Cram has published pyridine containing macrocyclic ethers[126], in which the bridging oxygen atoms are not directly bonded to the pyridine ring (J):

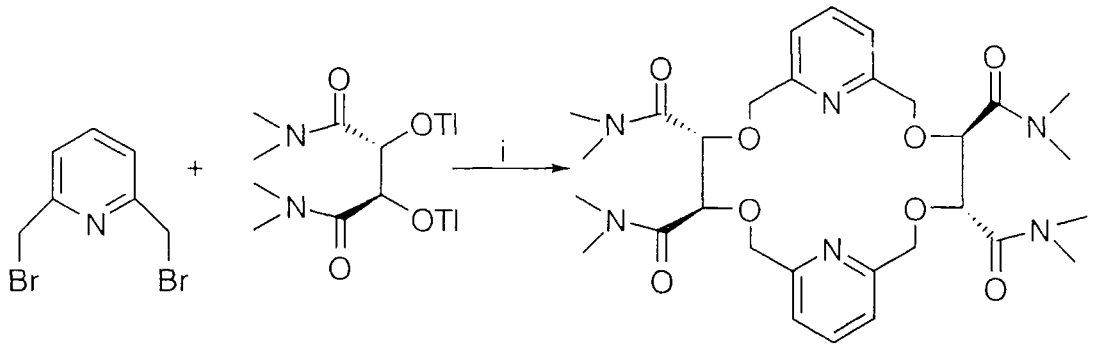


Reagents and conditions: i, ^{t}BuOK, Tetraethyleneglycolditosylate, THF.



Reagents and conditions: ii, NaH, Ethylene glycol, THF.

This general procedure has been applied to prepare not only achiral[151-153] but also chiral macrocycles[154], which display efficient chiral recognition towards various ammonium salts.

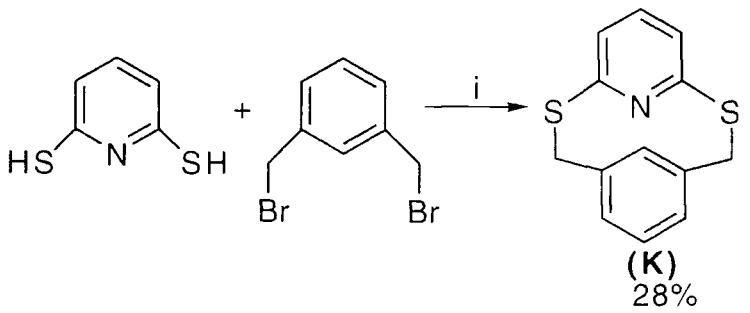


Reagents and conditions: i, DMF, 95°C, N_2.

3.4. Carbon-Sulfur Bridged Macrocycles.

Carbon sulfur bridged pyridino-macrocycles can be also be classified as compounds in which the bridging sulfur atoms are directly bonded to the pyridine ring (**K**) or systems in which the sulfur atoms are remote from the pyridine nucleus (**L**).

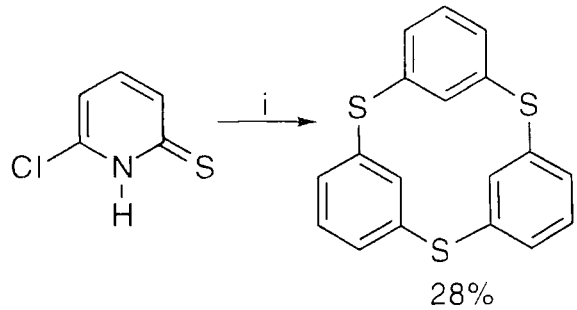
Vogtle[155] published an effective synthesis of carbon-sulfur bridged macrocycles (**K**) in which 2,6-pyridinedithiol was treated with an appropriate dihalide:



Reagents and conditions: i, KOH, MEK, Reflux, 36 h.

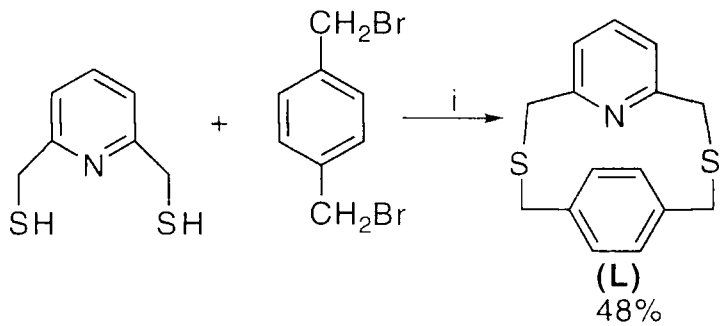
This approach has been successfully employed to produce higher homologues, containing polythioether linkages. These macrocycles readily form complexes with heavy metal ions including, silver-, gold- and mercuric-ions

Reistad[156] has reported an interesting route to a macrocycle (**K**), incorporating three pyridine units, *via* the intermolecular condensation of 6-chloropyridine-2-thione:



Reagents and conditions: i, P_2S_5, 130°C.

Finally, Boekelheide has shown that sulfur-bridged macrocycles (**L**) can be prepared, in reasonable yields, by the nucleophilic substitution of a dihalide with an appropriate bismercaptide[156a].



Reagents and conditions: i, NaOH, Benzene, r.t, 12 h.

CHAPTER IV

Synthesis of Highly Fluorinated Macrocycles.

4. Introduction.

The selective binding of ionic substrates to organic host molecules (e.g. enzymes, antibodies or membrane transporters) is a fundamentally important process in biological systems. Molecular recognition of charged species is now practicable using synthetic hosts, for example, macrocyclic polyamines and polyethers[157-161]. In the previous chapter, low yielding routes towards pyridine containing polyamino- (Section 3.3) and polyether-macrocycles (Section 3.4) were described, and we saw that pyridine inclusion imparts enhanced complexation properties through the basic nitrogen atom (Section 3).

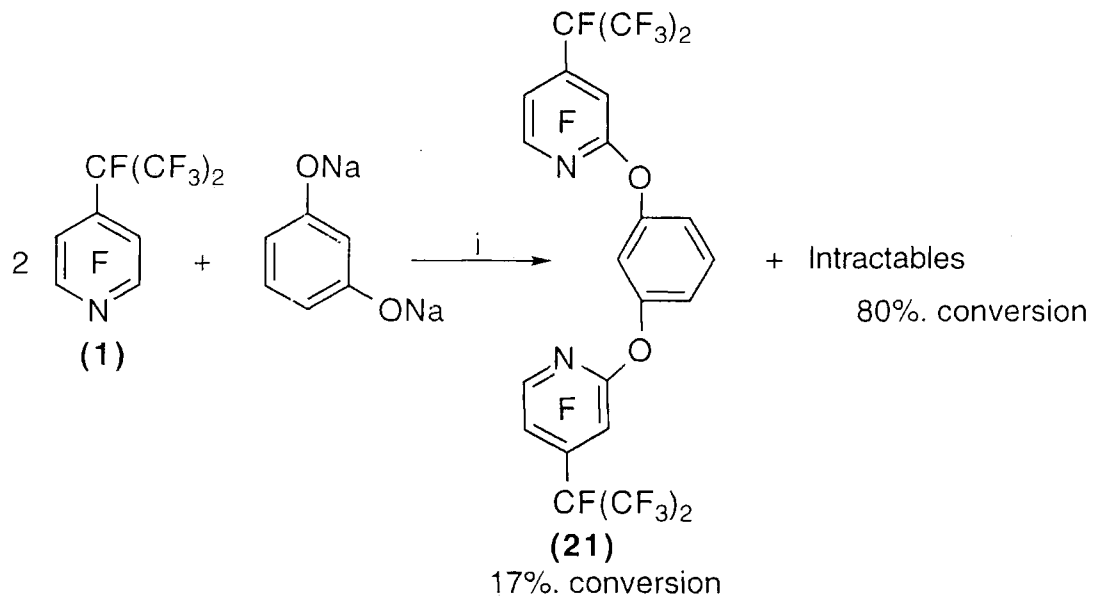
In this chapter, we aim to synthesise a range of highly coordinating, fluorous soluble macrocycles from the compound, perfluoro-4-isopropylpyridine. The coordination properties of these macrocycles will then be determined by metal ion extraction techniques.

4.1. Polyether-Macrocycles.

In this section the syntheses of a range of possible perfluorocarbon soluble macrocycles, containing polyether backbones, from perfluoro-4-isopropylpyridine (**1**) is addressed.

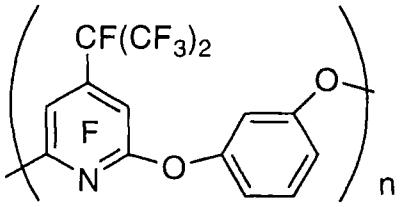
4.2. Reaction of Perfluoro-4-isopropylpyridine with Resorcinol and 1,3-Dihydroxytoluene.

Perfluoro-4-isopropylpyridine (**1**) reacts with the disodium salt of resorcinol to afford a product (**21**) having a mass consistent with the bipyridyl system shown:



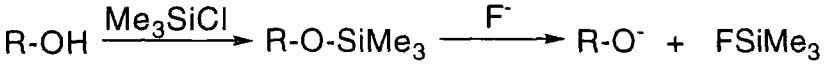
Reagents and Conditions: i, CsF, monoglyme, reflux, 40 h

In this particular experiment, the isolation of (**21**) was not attempted owing to the complexity of the product mixture. The MS data obtained for the intractable components gave fragment ions with masses consistent to those units of general structure:

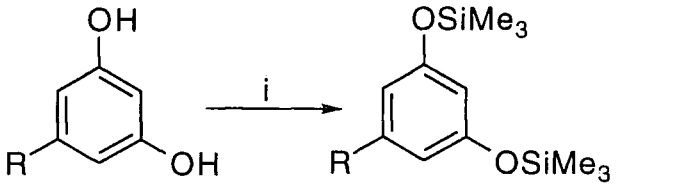


n=2-3

An alternative strategy towards the synthesis of compound (**21**) utilised fluoride ion promoted desilylation methodology[162-164] to give reactive sources of alkoxide ion:



The difunctional silyl ethers, (**22**)[165] and (**23**)[165], were prepared by reaction of the appropriate diols with trimethylsilylchloride.

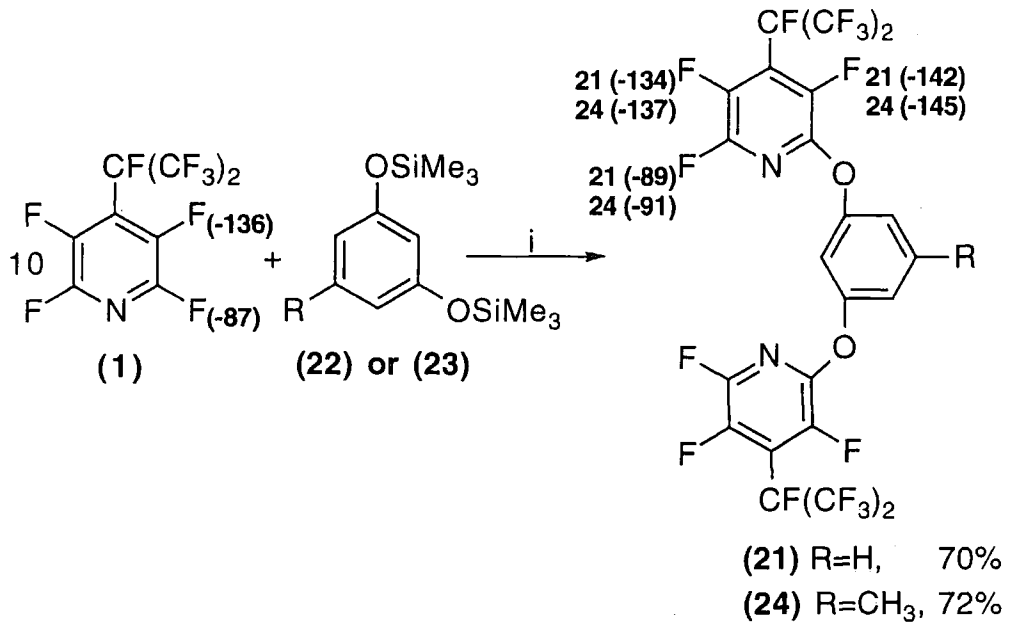


R=H or CH_3

(22) (R=H) 85%
(23) (R=CH_3) 90%

Reagents and conditions: i, Trimethylsilylchloride (2.5 equivs.), Pyridine (2 equivs.), Pet-Ether (60-80°C), Reflux, 4 days.

In the presence of caesium fluoride catalyst, (**22**) or (**23**) reacted with compound (**1**) to afford the compounds (**21**) and (**24**) respectively. In these experiments, it was necessary to employ an excess of reactant (**1**) to inhibit the formation of intractable components. Anhydrous reaction conditions were paramount to the success of these reactions and so both experiments were conducted under an atmosphere of dry nitrogen, in sodium dried solvent and using anhydrous caesium fluoride catalyst.

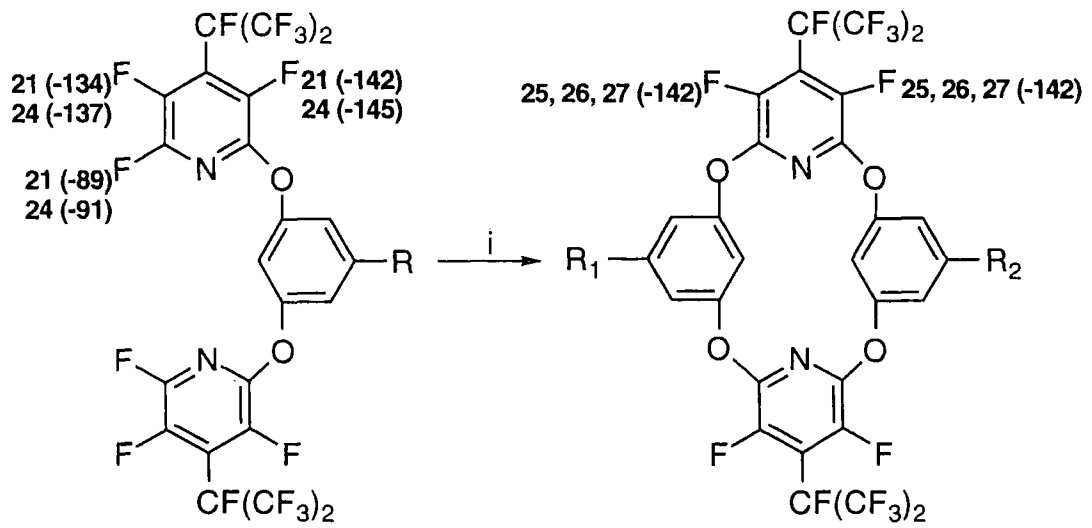


Reagents and conditions: i, CsF, monoglyme, reflux, 40 h.
Figures in parentheses denote fluorine atom chemical shift (ppm).

A comparison of the ^{19}F NMR chemical shift values between the ring fluorine atoms, in (**1**) and (**21**) and (**24**), reveals a small substituent effect on the chemical shifts *ortho-*, *meta-* and *para-* to the site of substitution also the disappearance of high frequency chemical shifts corresponding to ring fluorine atoms was recorded. These observations, together with the data accrued for model compounds in Section 2.3, enabled us to identify the 6-position as the preferred site for alkoxylation in compound (**1**). Mass spectrometry gave molecular ions of mass 708 and 722 corresponding to the structures (**21**) and (**24**) respectively.

4.3. Preparation of Macrocycles (25), (26) and (27).

The fluoride ion induced cyclisation of compounds (**21**) and (**24**) was achieved by reaction with a further equivalent of either (**22**) or (**23**), under high dilution conditions[166-168]. In the absence of excess solvent high molecular weight oligomers (Section 4.2) were formed predominantly.



(21) R=H
(24) R=CH_3

(25) R_1=H, R_2=H, 64%
(26) R_1=H, R_2=CH_3, 64%
(27) R_1=R_2=CH_3, 63%

Reagents and conditions: i, Compound **(22)** or **(23)** (1 equiv.), CsF, monoglyme, reflux, 40 h. Figures in parentheses denote fluorine atom chemical shift (ppm).

In the ^{19}F NMR spectra for compounds **(25)**-**(27)**, the notable absence of resonances between -89 ppm and -91 ppm confirmed that cyclisation had proceeded at the 2-F positions. Only one type of ring fluorine atom was detected for each of the symmetrical products, corresponding to 3-F (-142 ppm). These observations were consistent with data obtained for 2,6-dialkoxylated model compounds (Section 2.3).

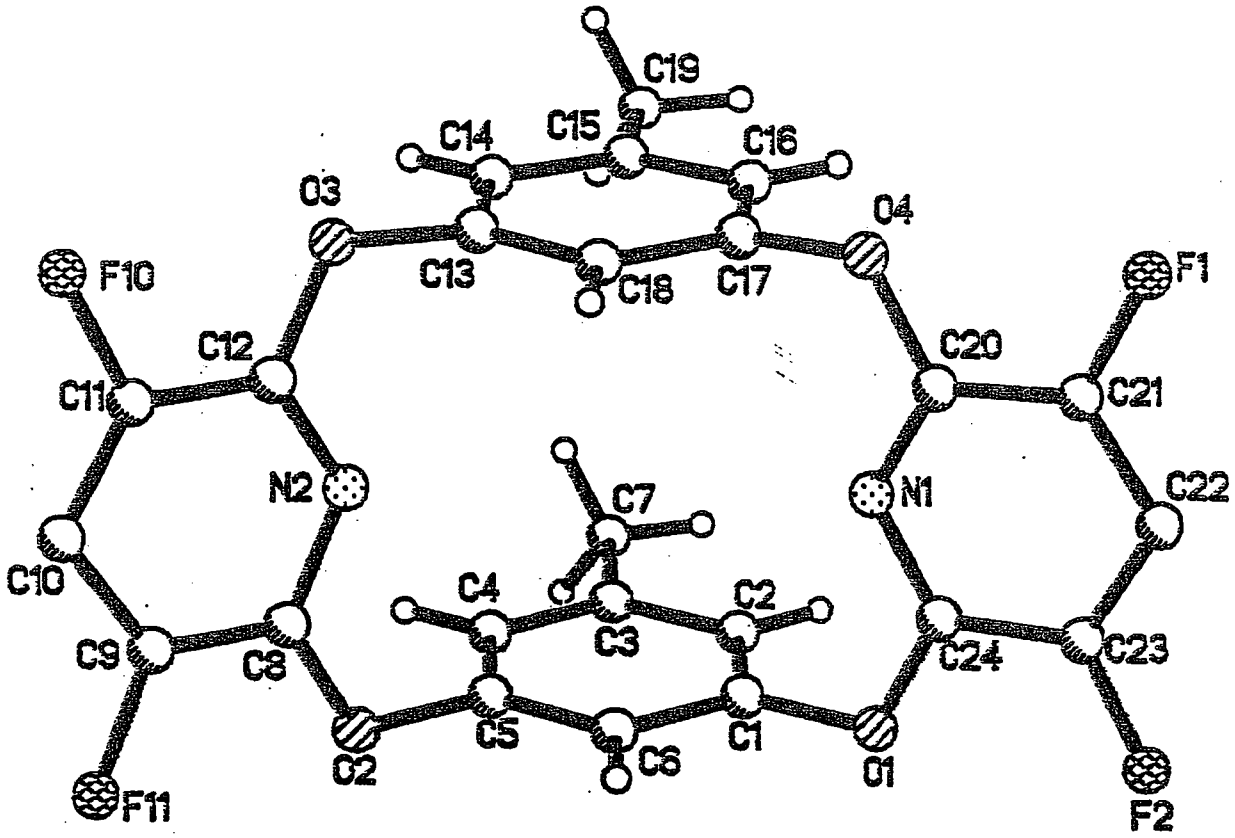
Mass spectrometry gave molecular ions of mass 778, 792 and 806 corresponding to the structures **(25)**, **(26)** and **(27)** respectively.

A crystal of compound **(27)** was grown from toluene and the x-ray crystallographic data obtained confirmed our structural assignment. In the diagram shown the perfluoroisopropyl-groups have been omitted for reasons of clarity; at room temperature, these groups give rise to dynamic disorder resulting from a stepwise movement between energy minima[169]. It was possible to determine the cavity size for the 16-membered ring in **(27)**, by measuring the appropriate interatomic distances (Table 1). Based on these data, a high affinity for Na^+[170] would be anticipated and presumably this would be the case for the analogues **(25)** and **(26)**.

The compounds **(25)**-**(27)** are all soluble (0.5 g in 5 ml) in perfluorodecalin at 110°C.

Table 1. Compound (27), Macroring Interatomic Distances.

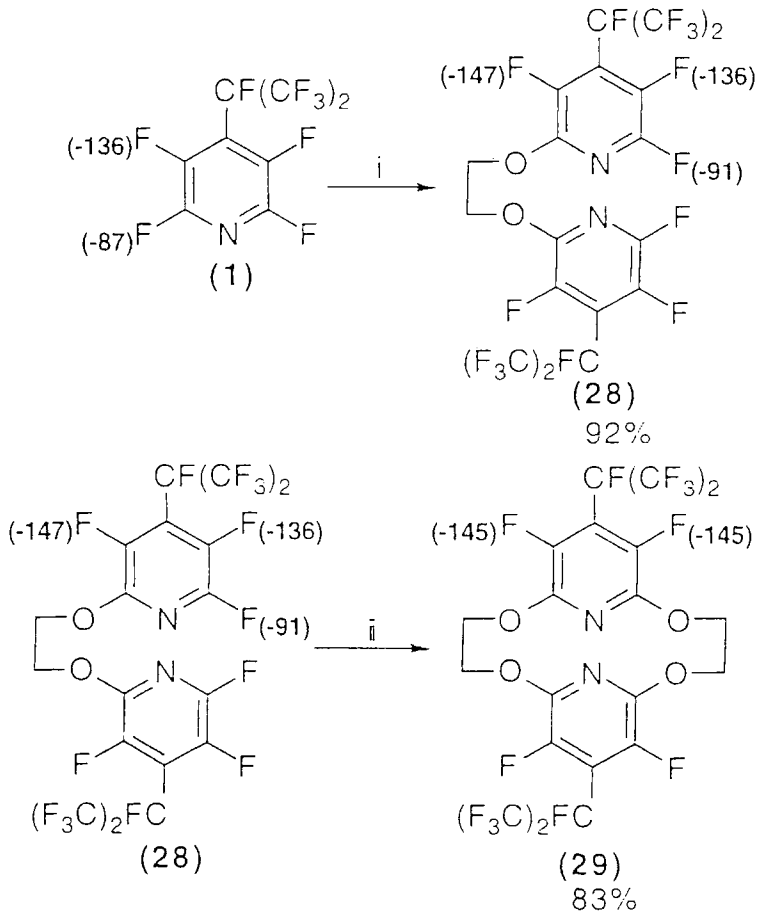
Atoms	Distance (Å)
O2 - O4	6.79
O1 - O3	6.55
N1 - N2	4.79
C6 - C18	4.53



4.4. Preparation of Macrocycles (29) and (31).

By extending the desilylation methodology (section 4.2) we have synthesised two further macrocycles.

Macrocycle (29) was prepared by reacting 1,2-bis(trimethylsilyloxy)ethane with compound (1), in the presence of caesium fluoride catalyst.



Reagents and conditions: i, 1,2-Bis(trimethylsilyloxy)ethane (0.5 equivs.), CsF, Monoglyme, Reflux, 4 days.
ii, 1,2-Bis(trimethylsilyloxy)ethane (1 equiv.), CsF, Monoglyme, Reflux, 4 days.
Figures in parentheses denote fluorine atom chemical shift values.

A comparison of the ^{19}F NMR chemical shift data, for the ring fluorines in compounds (1) and (28), reveals a small substituent effect on the chemical shifts *ortho-*, *meta-* and *para-* to the site of substitution also the disappearance of high frequency chemical shifts corresponding to ring fluorine atoms was recorded. These observations, together with data obtained for model compounds (Section 2.3), enabled us to conclude that alkoxylation had occurred at the 6-position, in (1), to yield (28).

Reaction of (28) with 1,2-bis(trimethylsilyloxy)ethane and CsF in monoglyme gave macrocycle (29) in good yield.

To account for the excellent product yield, we propose that the caesium

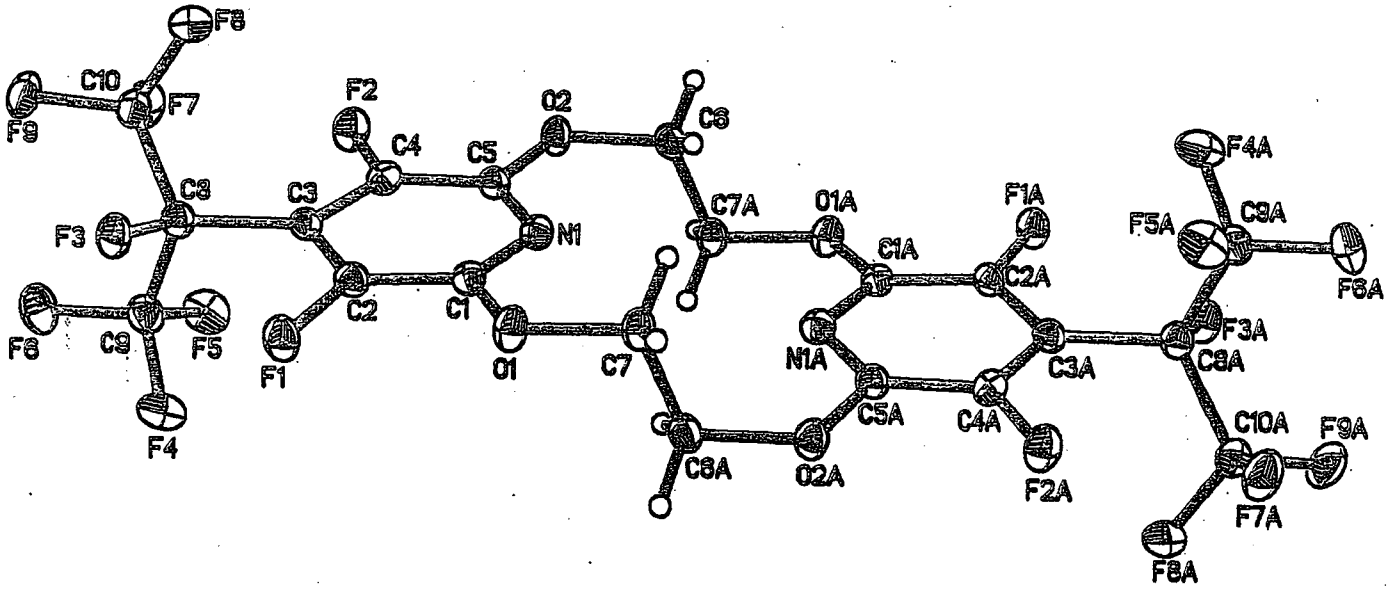
fluoride catalyst facilitated the cyclisation step *via* a templating effect[145]. The elemental analysis data and mass spectrometry data (molecular ion 682) for (**29**) were all in agreement with the structure shown. In the ^{19}F NMR spectrum for (**29**), the notable absence of a resonance at -91 ppm, corresponding to the 2-F ring atom in (**28**), indicated that cyclisation had proceeded to afford the macrocycle shown. Consistent with the symmetrical nature of (**29**), only one type of ring fluorine atom was observed corresponding to 3-F (-145 ppm) and these results were consistent with data obtained for 2,6-dialkoxylated model compounds (Section 2.3).

Using toluene as a recrystallisation solvent, it was possible to grow adequate crystals of (**29**) for structural analysis. The X-ray structure determination for (**29**) showed a product in which the macroring adopts a chair-like conformation with the two nitrogen atoms pointing inwards. It can be seen that the perfluoroisopropyl-groups exist in their minimum energy conformations[95], where the trifluoromethyl-groups are in front of and behind the pyridine ring. The cavity size for the 14-membered ring, in (**29**), was determined by measuring appropriate interatomic distances (Table 2). Based on this ring size and the number of potentially coordinating atoms (2N and 4O), a high affinity for Na^+ would be anticipated[170].

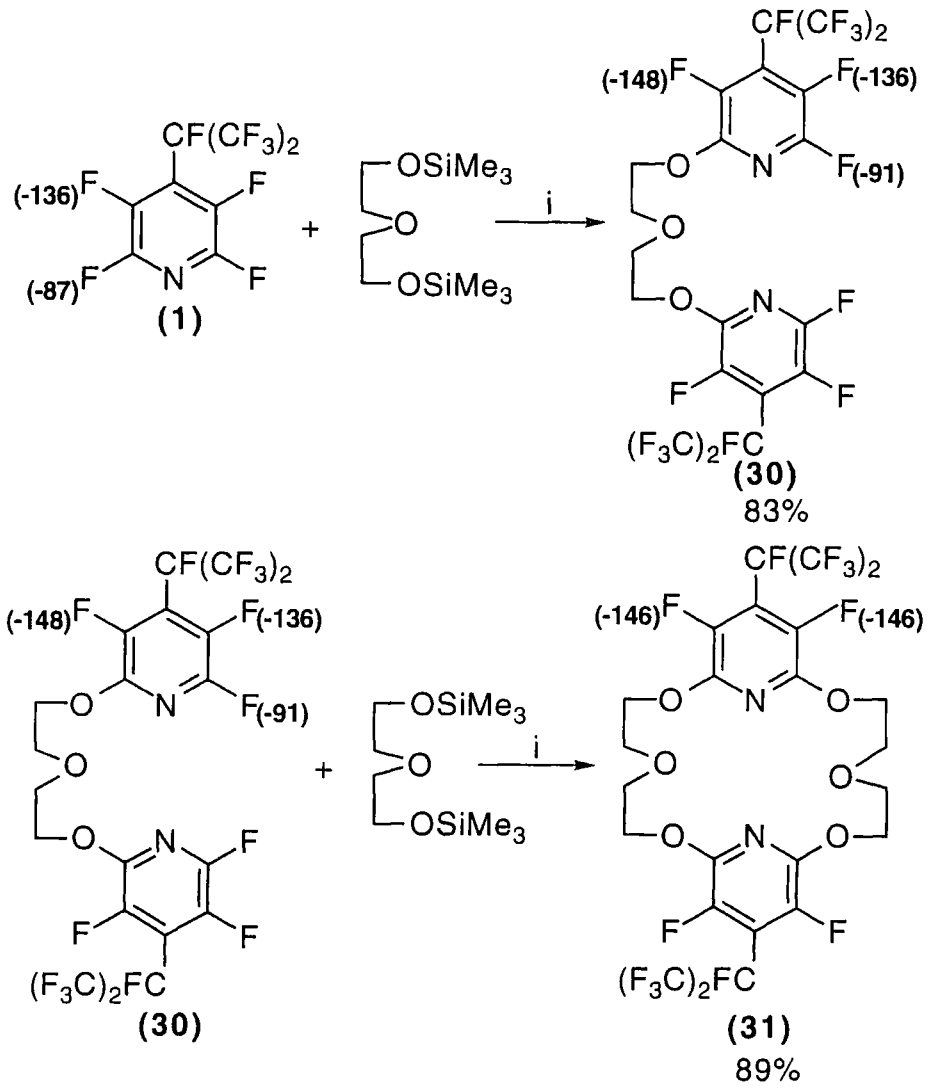
The highly fluorinated macrocycle (**29**) is completely soluble (0.5 g in 5 ml) in perfluorodecalin at 110°C.

Table 2. Compound (29), Macroring Interatomic Distances.

Atoms	Distance (Å)
N_1-N_{1A}	3.61
O_1-O_2	4.67
O_2-O_{2A}	6.04



Similarly, compound (**1**) reacted with the disilylether of diethylene glycol to afford (**30**) in good yield. The identity of (**30**) was confirmed by elemental analysis, mass spectrometry (molecular ion 704) and n.m.r studies. Again a comparison of the ^{19}F NMR chemical shifts for the ring fluorines in (**1**) and (**30**), reveals a small substituent effect on the chemical shifts *ortho-*, *meta-* and *para-* to the site of substitution also the disappearance of high frequency chemical shifts corresponding to ring fluorine atoms was recorded. These observations enabled us to conclude that alkoxylation had occurred at the 6-position.



Reagents and conditions: i, CsF, Monoglyme, Reflux, 4 days.
Figures in parentheses denote fluorine atom chemical shift value (ppm).

Compound (**30**) reacted with a further equivalent of the disilylether of diethylene glycol to afford macrocycle (**31**). The excellent product yield recorded for this reaction can be attributed to a template effect[171, 172] involving Cs^+: because in

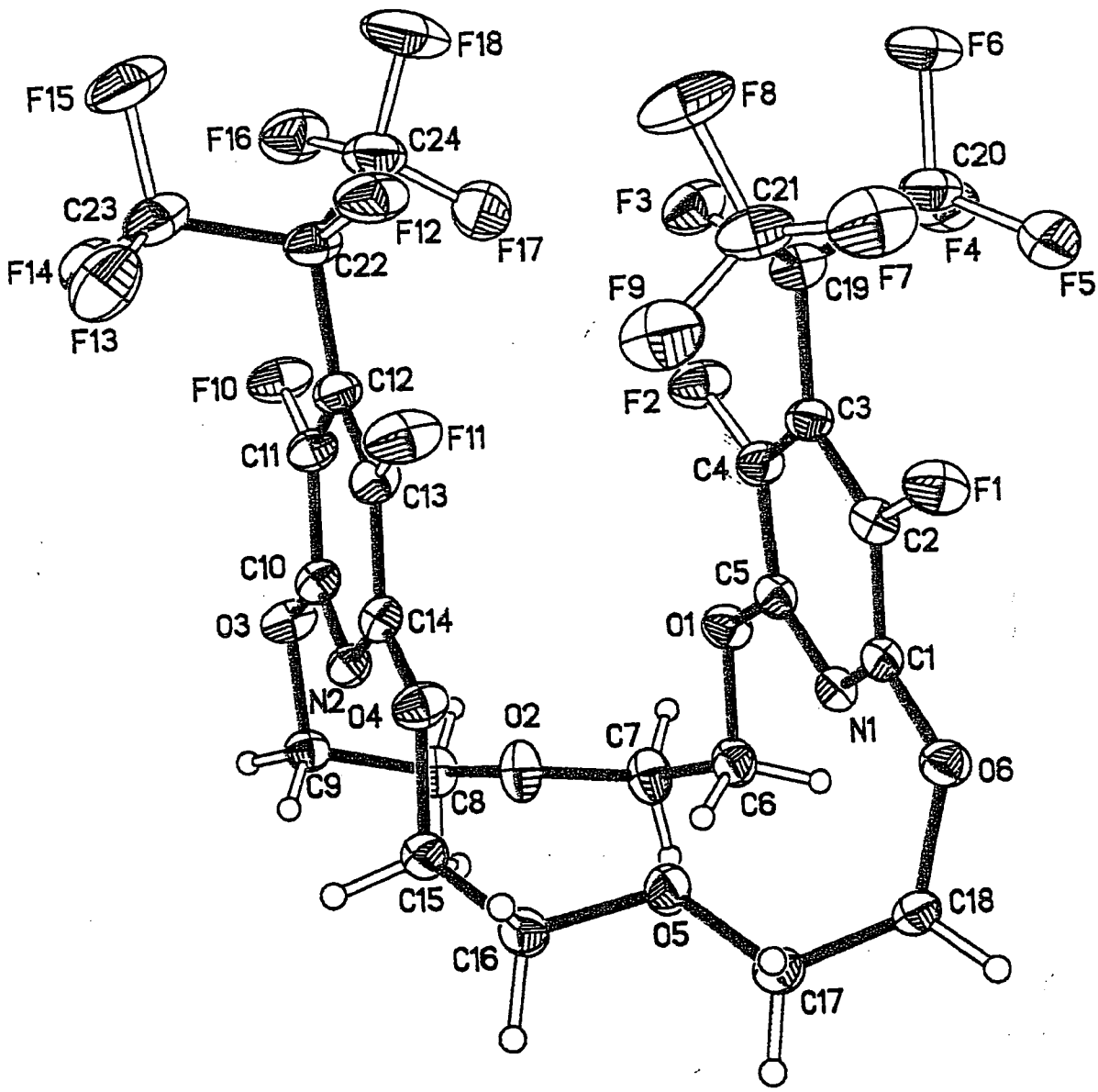
principle this ion can organise the reactive sites to preferentially yield the macrocyclic product (**31**).

In the ^{19}F NMR spectrum for (**31**), the absence of a resonance at -91 ppm indicated that cyclisation had occurred at the 2-F positions, to yield the macrocycle shown. Accordant with the symmetrical nature of (**31**) only one type of ring fluorine atom was observed corresponding to 3-F (-146 ppm). Again these observations were consistent with the data accrued for 2,6-dialkoxylated model compounds (Section 2.3). The elemental analysis data and mass spectrometry data (molecular ion 770) for (**31**) were all in agreement with the structure shown. This highly fluorinated macrocycle (**31**) is completely soluble (0.5 g in 5 ml) in perfluorodecalin at 110°C.

A crystal of (**31**) was grown from toluene and the X-ray crystallographic data obtained agreed with our structural assignment. The macrocycle adopts a boat-like conformation which is perhaps surprising given the proximity of the sterically demanding perfluoroisopropyl-groups and so we attribute this conformation to π–π electrostatic interactions[173] between the adjacent pyridine rings. By measuring the interatomic distances between appropriate atoms it was possible to determine the cavity size for this 20-membered macroring (Table 3) and based on the metal ion-macroring size compatibility theory[170], a high affinity for K^+ is anticipated for (**31**).

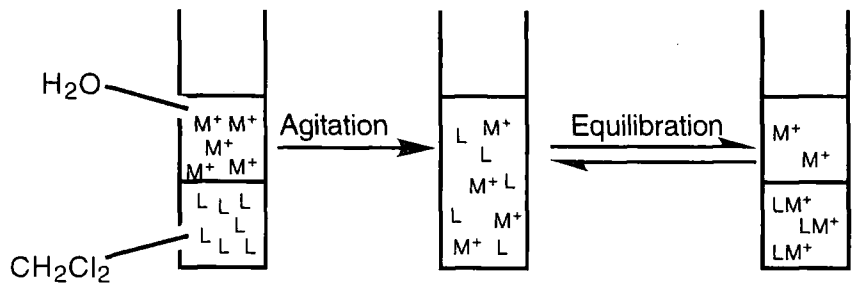
Table 3. Compound (31), Macroring Interatomic Distances.

Atoms	Distance (Å)
N_1-N_2	4.95
O_2-O_5	4.84
N_2-O_2	2.91
N_1-O_5	2.86



4.5. Alkali Metal Picrate Studies Involving Macrocycles (27), (29) and (31).

Having synthesised the macrocycles (**27**), (**29**) and (**31**), we then proceeded to investigate the abilities of these systems to complex metal cations. Ultimately, it is our intention to synthesise macrocycles that can extract metal ions into fluorocarbon solvents, from organic or aqueous *media*, at room temperature. It has been shown, however, that the compounds (**27**), (**29**) and (**31**) are only soluble in perfluorocarbons, such as perfluorodecalin, at elevated temperatures. Therefore, in order to assess the metal-ion transport properties of these compounds at room temperature, aqueous solutions of Li^+, Na^+, K^+ and Cs^+ picrates were extracted with CH_2Cl_2 in the presence of either (**27**), (**29**) or (**31**). It should be noted that the hosts and their complexes were soluble only in the CH_2Cl_2 layer upon equilibration.



L = Macrocycle (**27**), (**29**) or (**31**)
M^+= Group I metal ion
LM^+= Macrocycle-Metal Ion Complex

After agitation and equilibration, the distribution of metal ions in the aqueous phase were determined by UV-spectrometry[174-176]. In this approach the % of metal picrate extracted by the macrocycle was calculated from:

$$\% \text{ Extraction} = 100\ (\mathbf{Abs_{before}} - \mathbf{Abs_{after}})/\mathbf{Abs_{before}}$$

where, $\mathbf{Abs_{before}}$ is the absorbance of a similarly diluted sample of the unextracted alkali metal and $\mathbf{Abs_{after}}$ is the absorbance of the alkali metal picrate after extraction. The results obtained for the extraction experiments are outlined in Table 4:

Table 4. Alkali metal picrate extractions from aqueous solutions into dichloromethane by macrocycles (**27**), (**29**) and (**31**).

Macrocycle	Picrate Extracted (%)			
	Li^+	Na^+	K^+	Cs^+
27	15	40	10	10
29	10	45	10	-
31	10	70	15	15

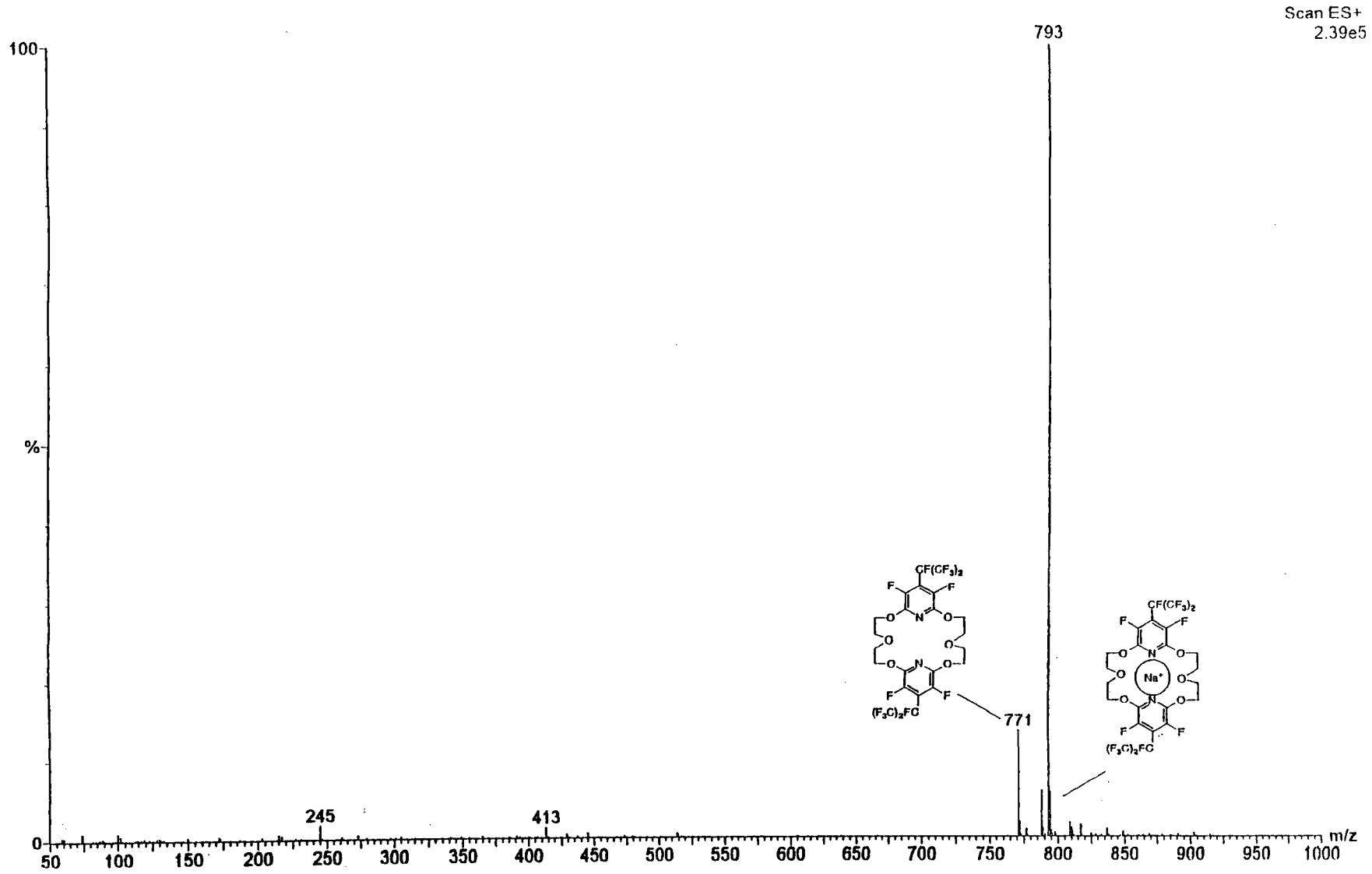
Analysis of these results shows the selectivity order for each macrocycle to be: (**27**), $Na^+ > Li^+ > K^+=Cs^+$; (**29**) $Na^+ > Li^+=K^+$ and (**37**), $Na^+ >> K^+=Cs^+ > Li^+$. Evidently, each macrocycle has a higher selectivity for sodium ions: in particular, the 20-membered macrocycle (**31**) exhibited strong binding towards Na^+ ions. The highest extraction of Na^+ is observed for both (**27**) and (**29**)[170]: overall, the extraction efficiencies and selectivities of these macrocycles were comparable.

4.6. Electrospray Mass Spectrometry Studies Involving Macrocycles (27), (29) and (31).

Electrospray mass spectrometry (ESMS) was also used to demonstrate the complexation of metal-ions (M^+) by suitable ligating agents (L)[177]. Using the ESMS technique we have attempted to determine the complexation abilities of the macrocycles (**27**), (**29**) and (**31**) towards group I metal ions. All spectra were recorded using 1:1 M^+:L ratios over a range of concentrations, from 10^{-4} to 10^{-5}M in methanolic solution, employing alkali metal triflates as cation sources.

Macrocycles (**27**) and (**29**) underwent fragmentation in the mass spectrometer and so meaningful ESMS data could not be obtained for their corresponding metal-ion complexes. However, in a competition experiment between the ions, Li^+, Na^+, K^+ and Cs^+, macrocycle (**31**) showed exclusive discrimination for Na^+. This result was consistent with our earlier liquid-liquid extraction results (Section 4.5).

Mass Spectrum showing the Sodium ion Complex of (31)

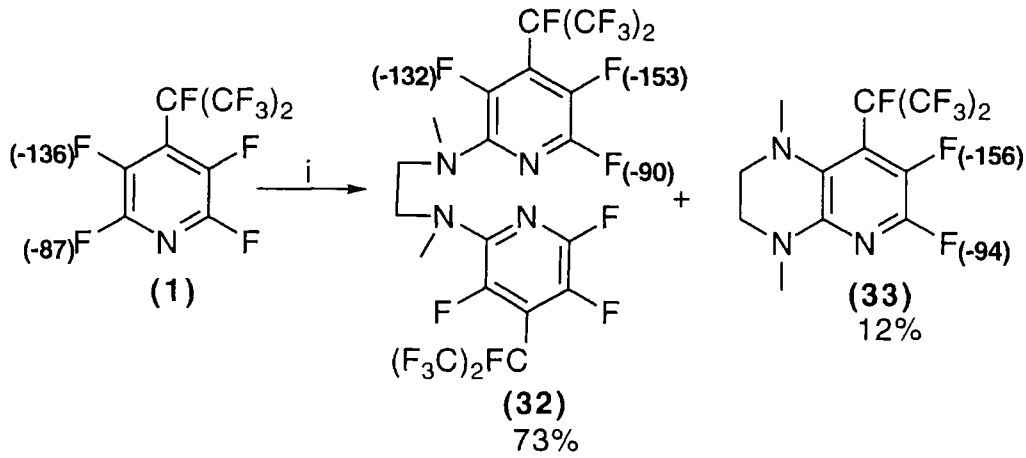


4.7. Preparation of Polyamino-Macrocycles.

In this section we aimed to synthesise a range of fluorous soluble macrocycles, containing polyamine backbones, from perfluoro-4-isopropylpyridine (**1**). In principle, such compounds ought to complex metal ions through their nitrogen lone-pair orbitals[126].

4.8. Preparation of Macrocycle (34).

Reaction of N,N'-dimethylethylenediamine with compound (**1**) gave the products (**32**) and (**33**):

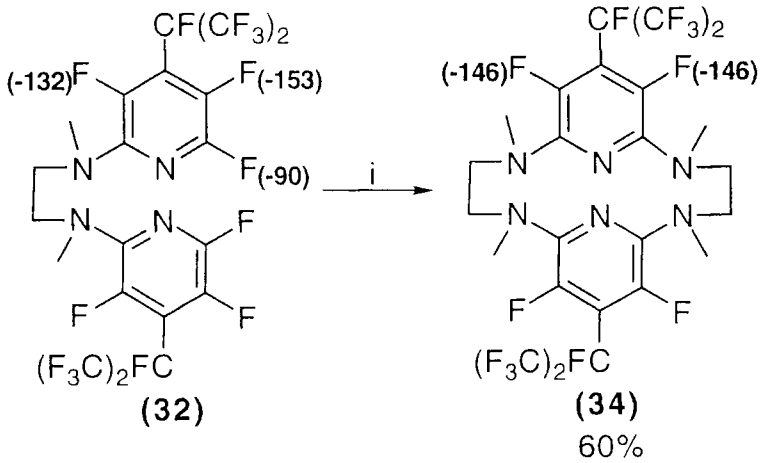


Reagents and conditions: i, N,N'-dimethylethylene-diamine (0.5 equivs.), THF, rt, 1hr.
Figures in parentheses denote fluorine atom chemical shifts (ppm)

The compounds (**32**) and (**33**) were separated and characterised by elemental analysis, mass spectrometry (molecular ions 686 and 367 respectively) and n.m.r studies. A comparison of the ^{19}F NMR chemical shift values in (**1**) and (**32**) reveals a small substituent effect on the chemical shifts *ortho-*, *meta-* and *para-* to the site of substitution also the disappearance of a high frequency chemical shift corresponding to a ring fluorine atom was recorded. These observations, together with the data accrued for model compounds (Section 2.5.A), enabled us to identify the 6-position as the preferred site for amination in (**1**). Similarly, there is a small substituent effect on the chemical shift values *meta-* and *para-* to the sites of substitution in (**33**) which allowed us to elucidate the substitution pattern illustrated.

Reaction of (**32**) with N,N'-dimethylethylene-diamine afforded the macrocycle (**34**) in reasonable yield. In the ^{19}F NMR spectrum for (**34**), the absence of a resonance at -90 ppm confirmed that cyclisation had proceeded at the 2-F position. Accordant with the symmetrical nature of (**34**) one type of ring fluorine atom was observed corresponding to 3-F (-146 ppm). The elemental analysis and mass

spectrometry (molecular ion 734) results obtained for (**34**) were in agreement with the structure illustrated:

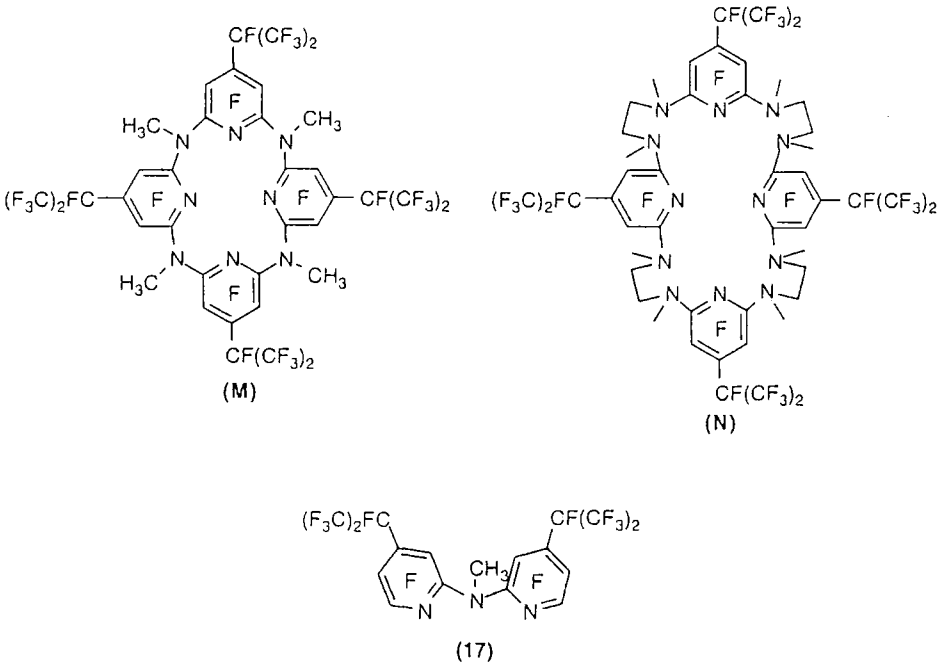


Reagents and conditions: i, N,N'-dimethylethylene-diamine (2.0 equivs.), THF, rt, 20 hr.
Figures in parentheses denote fluorine atom chemical shifts (ppm)

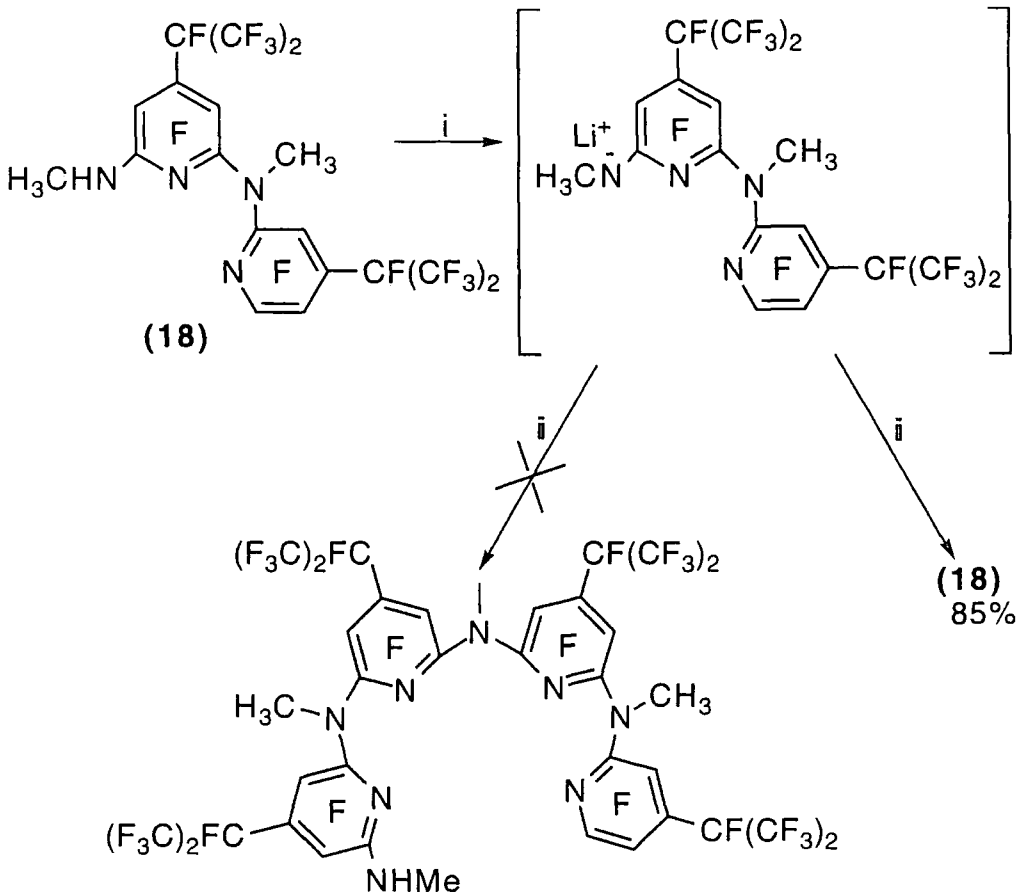
This highly fluorinated macrocycle (34) was shown to be completely soluble in perfluorodecalin at 110°C.

4.9. Attempted Preparation of a Macrocycle Containing Four Pyridine Subcyclic Units.

The primary objective of the work described in this section was to synthesise perfluorocarbon soluble macrocycles, (**M**) or (**N**); which contain alternating pyridyl units derived from the building block (**17**).

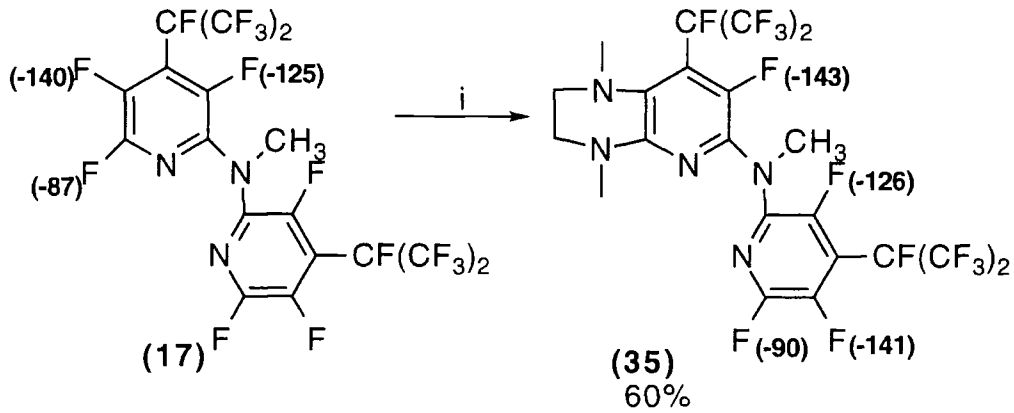


Under anhydrous reaction conditions, compound (**18**) was reacted with *n*BuLi (1.25 equivs.) to give the lithio-salt shown. Trapping of the lithiated species by (**18**) (1 equiv.) proved unsuccessful and after work-up only starting material was recovered.



Reagents and conditions: i, *n*BuLi (1.25 equivs.), THF, -78°C, 0.5 h.
ii, Compound (**18**) (1 equiv.), THF, -78°C-25°C, 3 h.

We then examined the prospect of cyclisation of compound (**17**) with N,N'-dimethylethylene-diamine to potentially yield macrocycle (**N**). The reaction of (**17**) with 1 equivalent of N,N'-dimethylethylene-diamine resulted in the formation of product (**35**):

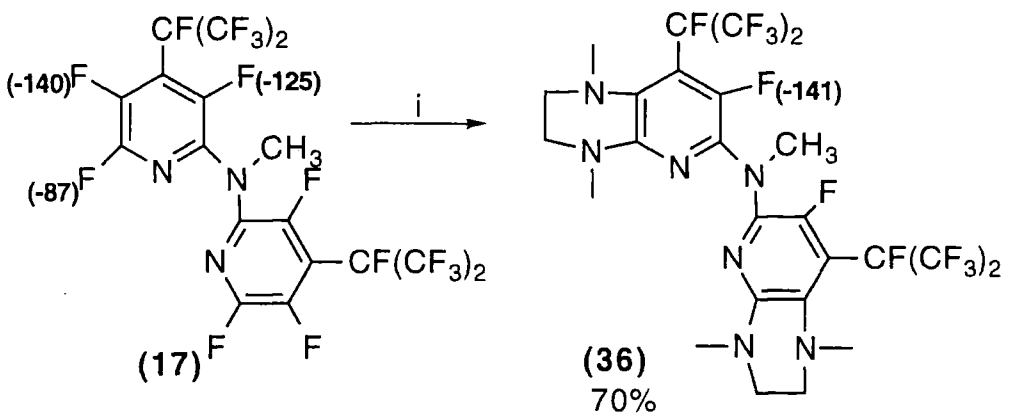


Reagents and conditions: i, N,N'-dimethylethylene-diamine (1 equiv.), THF, reflux, 40 h.
Figures in parentheses denote fluorine chemical shift (ppm).

The identity of (**35**) was confirmed by its mass spectra (molecular ion 677), elemental analysis data and n.m.r spectra. The ^{19}F NMR spectrum showed four resonances, in the ratio 1:1:1:1, corresponding to the ring fluorines illustrated.

We attempted to suppress the intramolecular cyclisation process, leading to compound (**35**), by employing a deficiency of N,N'-dimethylethylene-diamine. However, under identical reaction conditions compound (**17**) (5 equivs) was shown to react with N,N'-dimethylethylene-diamine (1 equiv.) to give (**35**) exclusively.

Similarly, the reaction of (**17**) with two equivalents of N,N'-dimethylethylene-diamine proceeded efficiently and substitution of the ring fluorines shown occurred to afford (**36**). As a consequence we were unable to synthesise the range of polyaminated macrocycles outlined earlier.



Figures in parentheses denote fluorine chemical shift (ppm).
Reagents and conditions: i, N,N'-dimethylethylene-diamine (2 equivs.), THF, reflux, 40 h.

The elemental analysis data and mass spectrometry data (molecular ion 725) for (**36**) were all in agreement with the structure shown and the ^{19}F NMR spectrum showed one ring fluorine signal, at -141 ppm.

4.10. Conclusions.

A series of highly fluorinated have been conveniently prepared from the compound perfluoro-4-isopropylpyridine. The metal ion complexation properties of the polyether macrocycles were determined by the solvent extraction of alkali metal picrates, from aqueous solutions into dichloromethane. These macrocycles were soluble in perfluorodecalin, at 110°C, and are therefore expected to have applications in fluorous-phase metal ion separation[107, 108, 178].

CHAPTER V

Bromination of Perfluorinated Aromatic Heterocycles.

5. General Introduction.

Owing to the importance of pyridine derivatives, in for example, medicinal and agricultural applications[179], numerous synthetic pathways have been developed towards functionalised pyridines. There are essentially two main approaches for the synthesis of highly substituted pyridines: i) the modification of a preformed pyridine nucleus[180] and ii) formation from heterocycloaddition methodologies[181].

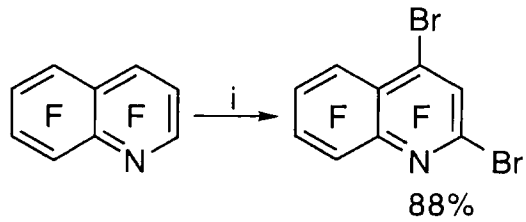
It was our aim to synthesise a range of highly substituted pyridine derivatives from 2,6-dibromo-perfluoro-4-isopropylpyridine. Before the new work is described, it is appropriate to review procedures for the replacement of fluorine by bromine in perfluorinated heterocycles. The chemistry of these polyhalogenated compounds will then be outlined.

5.1. Bromination of Perfluorinated Aromatic Heterocycles.

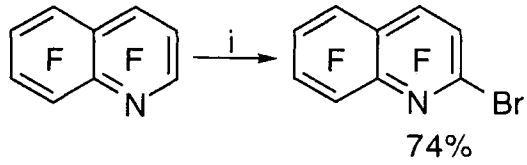
The introduction of bromine atoms into perfluorinated aromatic systems is useful in synthesis because brominated centres exhibit different reactivities to those in the parent compound. There are principally two approaches for exchanging fluorine by bromine in perfluorinated heterocycles: i) using Lewis acids (BBr_3 and $AlBr_3$) and ii) using Brönsted acids (HBr).

5.2. Bromination of Perfluorinated Heterocycles by BBr_3 and $AlBr_3$.

Musgrave[182] has published an account of bromine-fluorine exchange reactions between perfluoroquinoline and the Lewis acids, BBr_3 and $AlBr_3$.

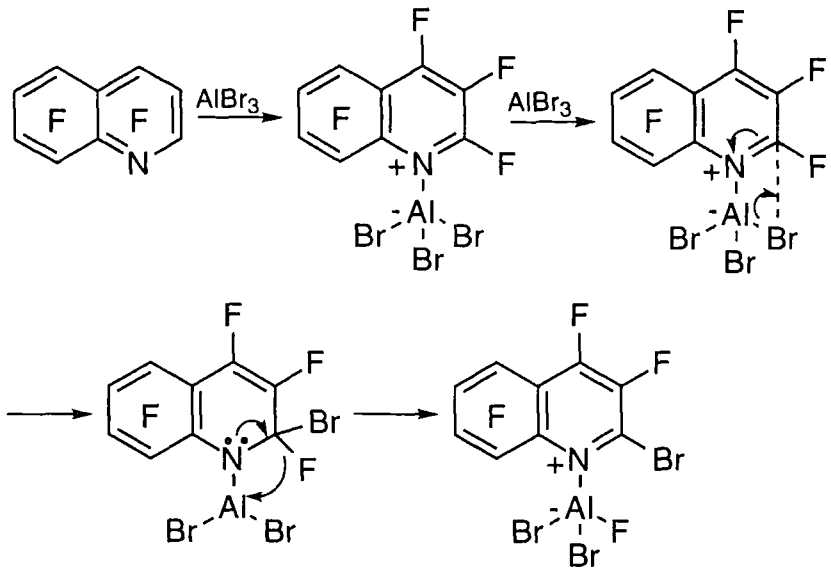


Reagents and conditions: i, Excess BBr_3, Carius Tube,150°C, 55 h.

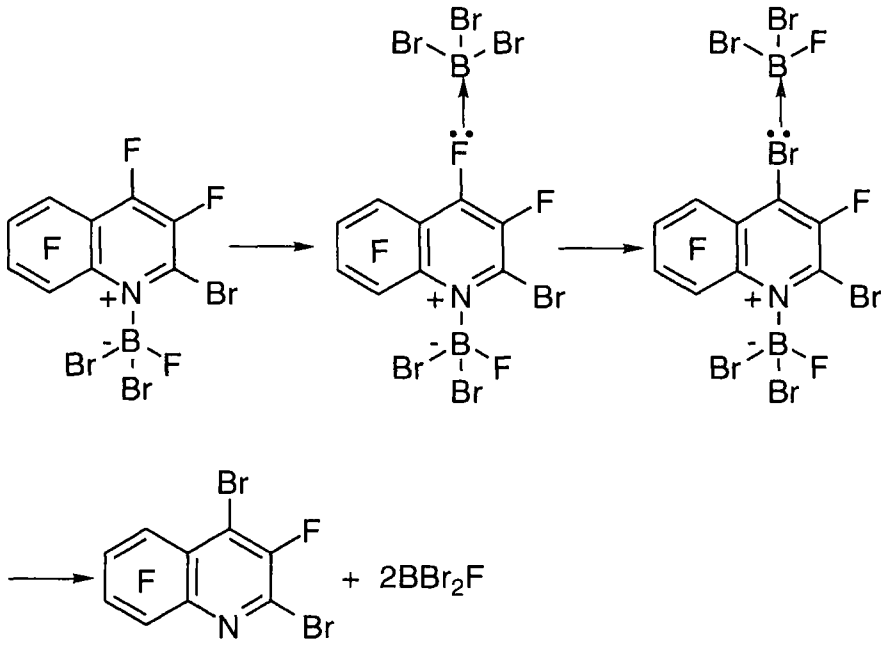


Reagents and conditions: i, Excess $AlBr_3$, Carius Tube,120°C,120 h.

In the case of the reaction involving $AlBr_3$, an intramolecular reaction mechanism was proposed for bromination at the site *ortho*- to the ring nitrogen:

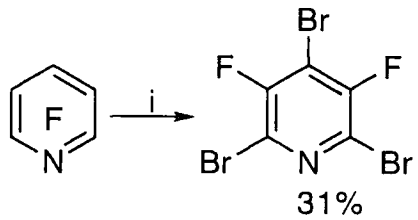


For the reaction involving BBr_3, it seems likely that reaction at the site *ortho-* to the ring nitrogen also operates *via* an intramolecular reaction. However, an intermolecular reaction must occur at the position *para-* to the ring nitrogen. This would involve the donation of a pair of electrons by the 4-F atom to BBr_3, followed by the exchange of bromine for fluorine.

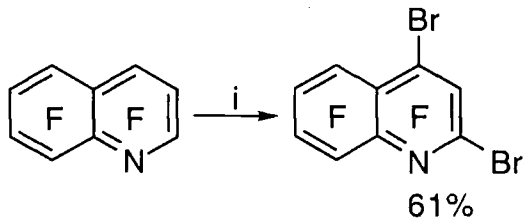


5.3. Bromination of Perfluorinated Heterocycles by HBr.

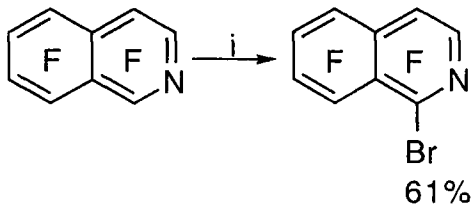
Chambers[183] reported the acid-induced replacement of fluorines *ortho-* and *para-* to the ring nitrogen in pentafluoropyridine, heptafluoroquinoline and heptafluoroisoquinoline, to give the brominated derivatives shown:



Reagents and conditions: i, HBr (2.5 mol), Sulfolane, Carius Tube, 100°C for 20 h then 130-160°C for 48 h.

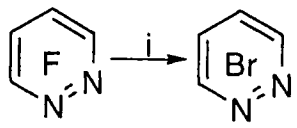


Reagents and conditions: i, HBr (4 mol), Sulfolane, Carius Tube, r.t, 48 h.



Reagents and conditions: i, HBr (3 mol), Sulfolane, Carius Tube,135-145°C,142 h.

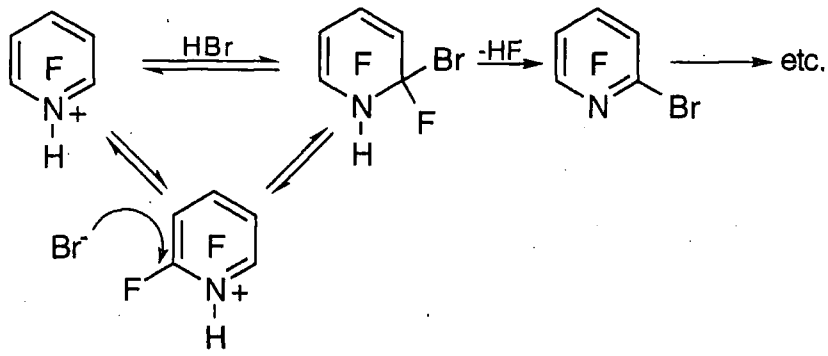
Similarly, Musgrave[182] has reported that when HBr is bubbled through an ethereal solution of tetrafluoropyridazine all of the fluorine atoms are substituted:



Reagents and conditions: i, HBr, Ether, 20°C.

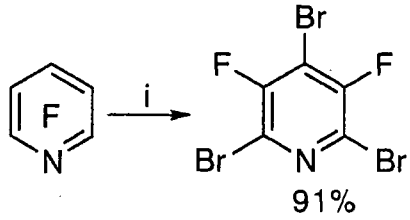
The tetrabromopyridazine formed is unstable and so an accurate yield for this product has not been reported.

The reactivity displayed in these experiments can be attributed to initial protonation of the ring nitrogen which activates fluorines at the positions *ortho*- and *para*- to the ring nitrogen to reaction, for example:

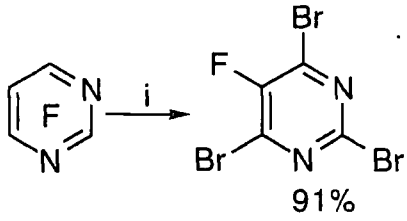


5.4. Bromination of Perfluorinated Heterocycles by HBr and $AlBr_3$.

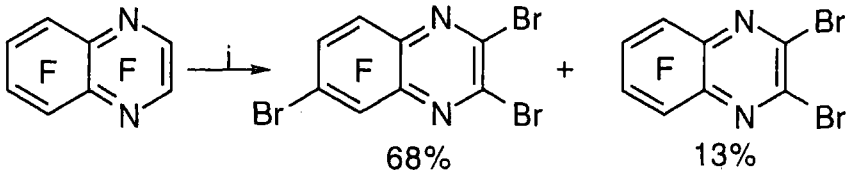
Chambers[184] has recently reported an efficient acid-induced exchange of fluorine by bromine, in pentafluoropyridine, tetrafluoropyrimidine and hexafluoroquinoxaline, by heating the appropriate heterocycle with the superacid formed between HBr and $AlBr_3$. Musgrave has proposed that reactions of this type proceed by attack of $AlBr_4^-$ on the protonated heterocycle.



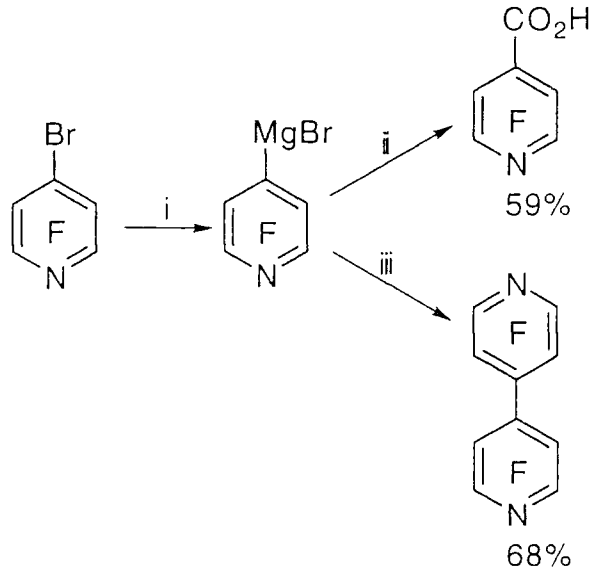
Reagents and conditions: i, HBr, $AlBr_3$, Autoclave,150°C, 84 h.



Reagents and conditions: i, HBr, $AlBr_3$, Autoclave,150°C, 43 h.

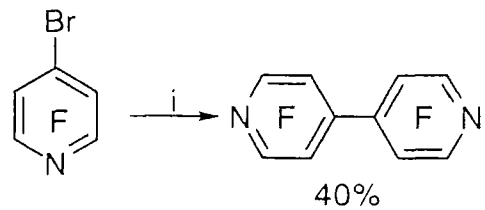


Reagents and conditions: i, HBr, $AlBr_3$, Autoclave,150°C, 68 h.



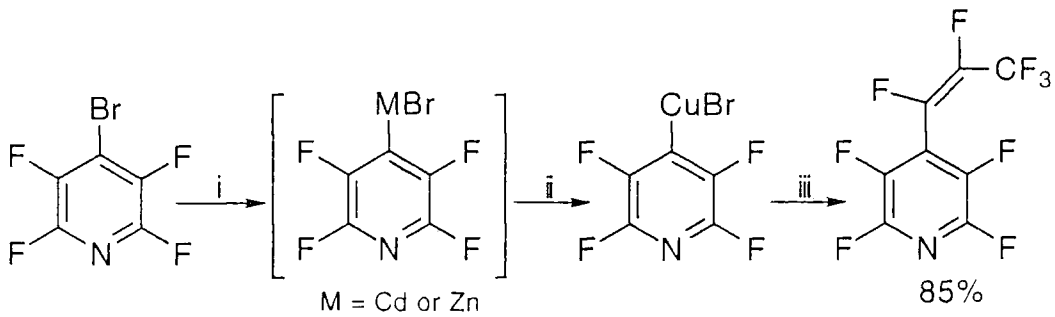
Reagents and conditions: i, Mg, THF, -20 to -10°C, 1h.
ii, CO_2, -10°C, 2h, H_2SO_4.
iii, Pentafluoropyridine, -35 to -40°C, 1h.

The 4,4'-octafluorobipyridine compound was also obtained by the Ullman coupling[186] technique.



Reagents and conditions: i, Cu,DMF, Reflux, 5h.

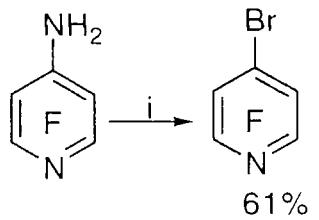
Similarly, 4-bromo-tetrafluoropyridine can be converted into the corresponding zinc[187], cadmium[187] and copper[187, 188] derivatives, from which a range of 4-substituted pyridine compounds can be synthesised.



Reagents and conditions: i, Zn or Cd, DMF, r.t., 5 min; ii, CuBr, DMF, r.t., 10 min;
iii, 1-Iodo-perfluoropropene.

5.5. Synthesis of 4-bromotetrafluoropyridine from 4-aminotetrafluoropyridine.

Chambers[41] published the synthesis of 4-bromotetrafluoropyridine from 4-aminotetrafluoropyridine.



Reagents and conditions: i, HF (aq), $NaNO_2$, CuBr, KBr, -20°C, 1 h.

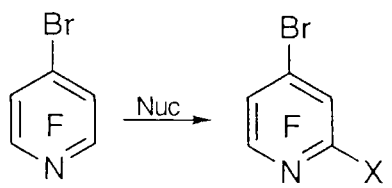
In this reaction, the reduction of 4-nitrotetrafluoropyridine to the 4-amino-compound occurs prior to diazotization by hydrofluoric acid. The diazonium salt formed then reacts with cuprous bromide and is converted into 4-bromotetrafluoropyridine.

5.6. Reactions involving Bromofluoroheterocycles.

Bromofluoroheterocycles are known to react with a wide range of nucleophiles giving the exclusive displacement of either fluorine or bromine.

5.7. Reactions involving 4-Bromo-tetrafluoropyridine.

Chambers[41] published a series of reactions involving 4-bromo-tetrafluoropyridine. The reaction of 4-bromo-tetrafluoropyridine with nucleophilic reagents e.g. aqueous ammonia, potassium hydroxide and sodium methoxide resulted in exclusive displacement of fluorine, rather than bromine, to give 4-bromo-2-amino-, -2-hydroxy- and -2-methoxytrifluoropyridine shown:

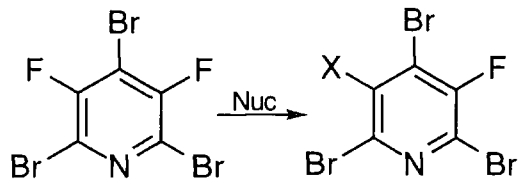


Nuc	X	Reagents and conditions:
NH_3	$-NH_2$	NH_3 (aq), Carius tube, 85°C, 2h.
KOH	-OH	KOH, tBuOH, Reflux, 2h.
$NaOCH_3$	$-OCH_3$	NaOMe, MeOH, 0°C, 30min.

At low temperature, 4-Bromo-tetrafluoropyridine can be readily converted into a Grignard reagent[185]. The reactant, tetrafluoro-4-pyridylmagnesium bromide was readily carboxylated and also reacted with pentafluoropyridine to give a 4,4'-octafluorobipyridine.

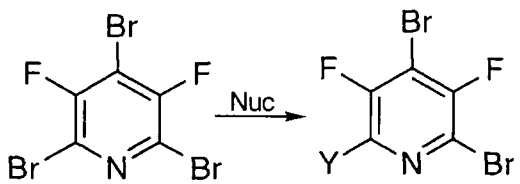
5.8. Reactions involving 2,4,6-Tribromo-difluoropyridine.

Chambers[184] has published a series of reactions involving 2,4,6-tribromodifluoropyridine and a range of nucleophiles. Hard nucleophiles, including methoxide ion, displaced fluorine exclusively.



Nuc	X	Reagents and conditions:
NH_3	$-NH_2$	NH_3 (aq), CH_3CN, Carius tube, 85°C, 2h.
KOH	-OH	KOH, tBuOH, Reflux, 3h.
$NaOCH_3$	$-OCH_3$	NaOMe, MeOH, r.t., 60h.
NaOPh	-OPh	NaOPh, Et_2O, Reflux, 23h.

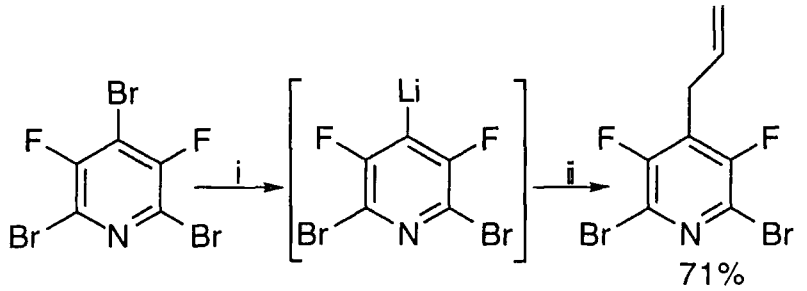
In contrast soft nucleophiles, such as diethylamine, displaced bromine exclusively.



Nuc	Y	Reagents and conditions:
Et_2NH	Et_2N-	Et_2NH, CH_3CN, Carius tube, 50°C, 95h.
PhSH	PhS-	PhSH, CH_3CN, Reflux, 19h.
Piperidine	Piperidinyl-	Piperidine,CH_3CN, Reflux, 23h.

This apparent selectivity has been attributed to the established preference for hard nucleophiles to react at hard sites (C-F) and soft nucleophiles to react at soft sites (C-Br)[189].

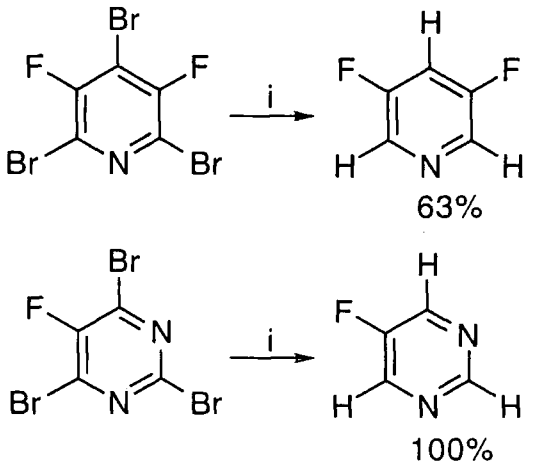
2,4,6-Tribromodifluoropyridine[184] has been shown to undergo lithium-bromine exchange readily, exclusively at the 4-position, with n-butyllithium. The lithiated species is readily converted into the 4-allyl-derivative upon reaction with allyl-bromide:



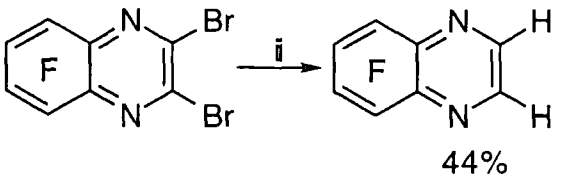
Reagents and conditions: i, BuLi, Et_2O, -78°C; ii, CH_2CHCH_2Br, -78°C.

5.9. Reduction of Bromofluoroheterocycles.

Chambers[184] recently reported the catalytic reduction[190] of bromofluoroheterocycles as a viable route to a range of hydrofluoroheterocycles.



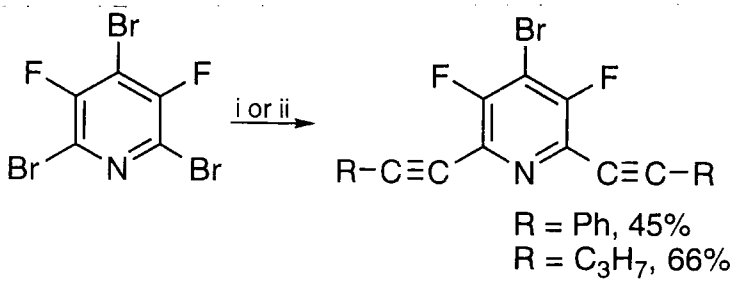
Reagents and conditions: i, Pd/C, H_2 (4 bar), Et_3N, CH_2Cl_2, r.t.

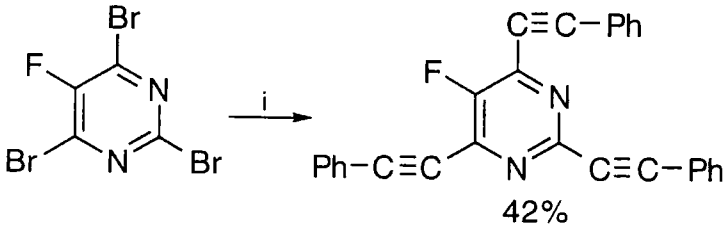


Reagents and conditions: i, H_2 (4 bar), Lindlar cat., 120h.

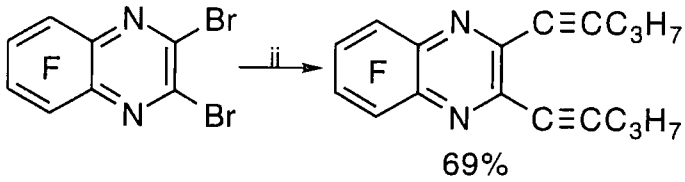
5.10. Palladium Catalysed Coupling of Alkynes with Bromofluoroheterocycles.

Chambers[184] has published palladium catalysed coupling reactions between bromofluoroheterocycles and alkynes.





Reagents and conditions: i, CuI, $(Ph_3P)_3PdCl_2$, Et_3N, Phenylacetylene;
ii, CuI, $(Ph_3P)_3PdCl_2$, Et_3N,Pent-1-yne.



Reagents and conditions: ii, CuI, $(Ph_3P)_3PdCl_2$, Et_3N, Pent-1-yne.

CHAPTER VI

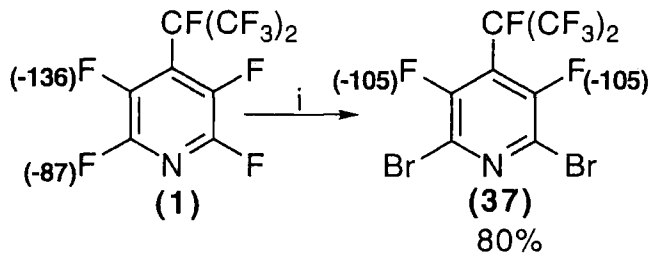
Synthesis of 2,6-Dibromo-perfluoro-4-isopropylpyridine and Derivatives

6. Introduction.

The preparation of brominated fluoroheterocycles were described in chapter V. In this chapter we describe attempts to develop a convenient route towards the compound, 2,6-dibromo-perfluoro-4-isopropylpyridine and then synthesise a range of highly substituted pyridine derivatives from this unit. In particular, reactions between 2,6-dibromo-perfluoro-4-isopropylpyridine and hard and soft nucleophiles will be investigated as well as palladium-mediated coupling reactions involving a range of alkynes.

6.1. Preparation of 2,6-Dibromo-perfluoro-4-isopropylpyridine.

Perfluoro-4-isopropylpyridine (**1**) reacted with a combination of $AlBr_3$ and HBr ($H^+AlBr_4^-$)[184] to afford 2,6-dibromo-perfluoro-4-isopropylpyridine (**37**) as a single product in high yield.



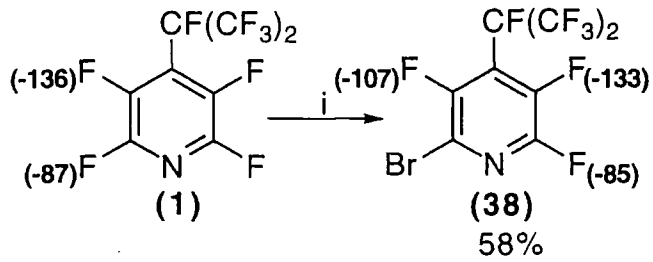
Reagents and conditions: i, $AlBr_3$ (2.2 equivs.), HBr (2.2 equivs.), 160°C, Hastalloy Autoclave, 48 h
Figures in parentheses denote fluorine atom chemical shift (ppm).

The identity of (**37**) was confirmed by its NMR, MS and elemental analysis data. In the ^{19}F NMR spectrum, one ring fluorine signal was observed at -105 ppm which, together with its relative peak intensity value of two, confirmed the symmetrical nature of the 2,6-disubstituted product. If the second site of nucleophilic substitution had occured at the 5-position then two signals for the 3- and 6-ring fluorine atoms, in the ratio 1:1, would have been recorded. The ^{13}C NMR spectrum for (**37**) showed a doublet of triplets splitting pattern for the 4-C centre which is consistent with bromination at the 2- and 6-positions. This pattern can be attributed to coupling between 4-C and the tertiary fluorine atom ($^2J_{CF}$ 22.5 Hz) and then to the magnetically equivalent 3,5-F atoms ($^2J_{CF}$ 13.3 Hz).

Mass spectra for molecular ions or fragment ions containing two bromine atoms exhibit characteristic isotope patterns[191]: notably, the parent ions for compound (**37**) (M^+ 439, 441 and 443) displayed such an isotope pattern.

6.2. Preparation of 6-Bromo-perfluoro-4-isopropylpyridine.

A combination of $AlBr_3$ (2 equivs.) and HBr (1 equiv.) [184] reacted with compound (**1**) to afford the product, 6-bromo-perfluoro-4-isopropylpyridine (**38**), exclusively.



Reagents and conditions: i, $AlBr_3$ (2 equivs.), HBr (1 equiv.), 160°C, Hastalloy Autoclave, 48 h.
Figures in parentheses denote fluorine atom chemical shift (ppm).

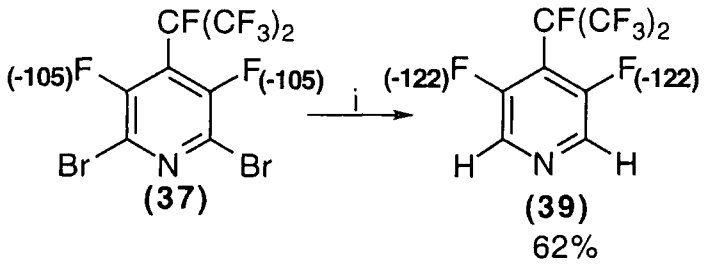
Compound (**38**) was identified by considering its elemental analysis, NMR and MS-data. A comparison of the ^{19}F NMR chemical shift values and relative intensities for the ring fluorines in (**1**) and (**38**), together with the data accrued for model compounds (Section 2.3), enabled us to assign the ring fluorines and therefore identify the 6-position as the site of bromination.

The mass spectrum of (**38**) exhibited the characteristic isotope pattern for a molecule containing one bromine atom[191] giving two parent ions (M^+ 379 and 381).

6.3. Reactions involving 2,6-Dibromo-perfluoro-4-isopropylpyridine.

6.3.i. Hydrogenolysis.

The reduction of (**37**) occurred efficiently in the presence of a palladium catalyst[190] to afford 2,6-dihydro-perfluoro-4-isopropylpyridine (**39**).

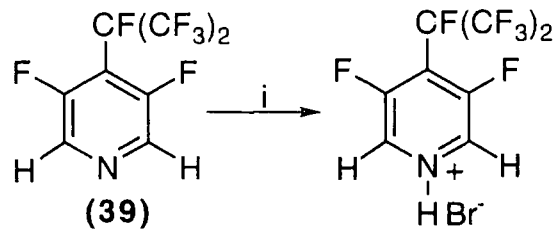


Reagents and conditions: i, H_2 (4 atm), DCM, Pd(5%)/C, Et_3N, 20 h.
Figures in parentheses denote fluorine atom chemical shift (ppm).

The elemental analysis, MS (molecular ion 283) and NMR results obtained for (**39**) were all in agreement with the structure illustrated. Significantly, one ring fluorine signal was observed at -122 ppm, in the ^{19}F NMR spectrum, which, together

with its relative peak intensity value of two, confirmed the symmetrical nature of the 2,6-disubstituted product. Similarly, the ^{1}H NMR spectrum for (**39**) gave one signal at 8.5 ppm corresponding to 2- and 6-H.

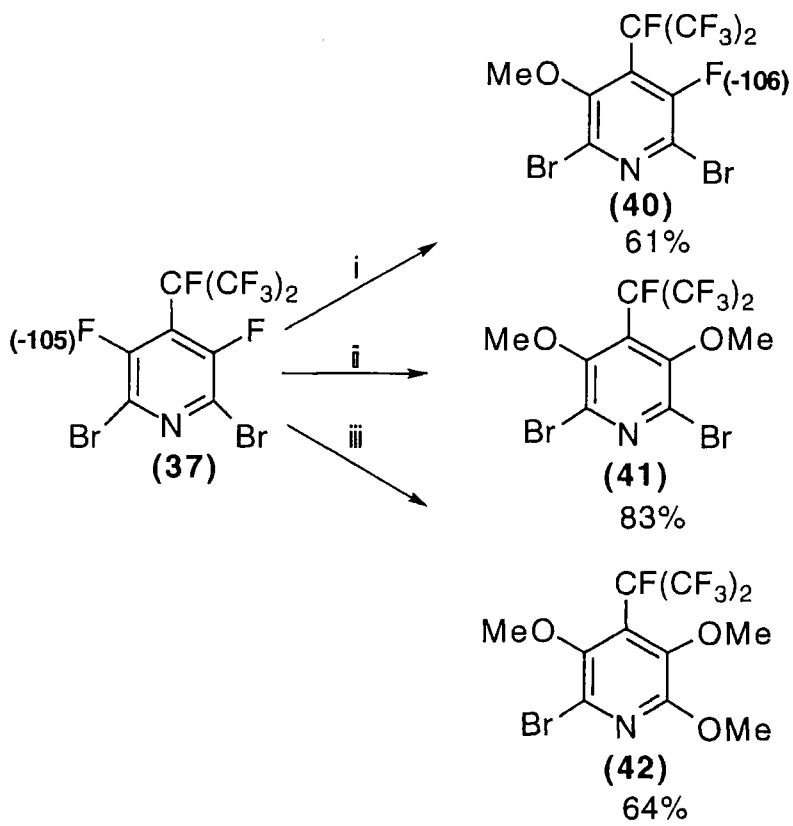
Compound (**39**) exhibited basic properties forming a salt when anhydrous HBr was bubbled through an ethereal solution.



Reagents and conditions: i, HBr, Et_2O, r.t.

6.3.ii. Methoxylation.

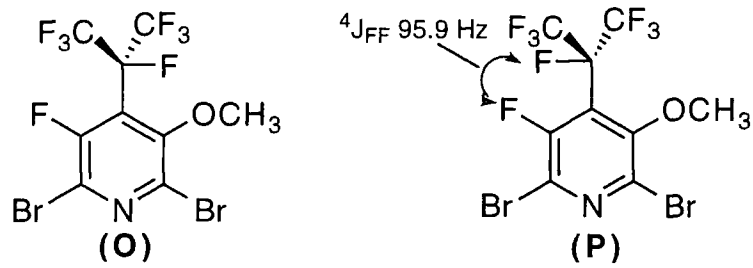
Reaction of (**37**) with sodium methoxide (1.5 and 3.0 equivalents) led to the displacement of ring fluorines to afford the methoxylated derivatives (**40**) and (**41**); whilst excess methoxide ion gave the trimethoxylated compound (**42**).



Reagents and conditions: i, NaOMe (1.5 equivs.), MeOH, Reflux, 24 h;
ii, NaOMe (3 equivs.); iii, NaOMe (6 equivs.).
Figures in parentheses denote fluorine atom chemical shift (ppm).

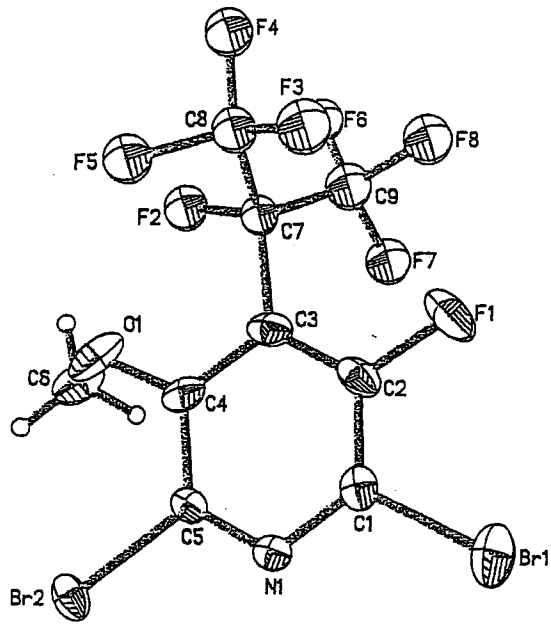
The substitution of fluorine (instead of bromine) by methoxide ion in (**37**), to give (**40**) and (**41**), was confirmed by NMR, MS and X-ray crystallographic analysis. The selectivity observed can be attributed to the well known preference of hard nucleophiles to attack hard centres (C-F)[189].

The ^{19}F NMR spectrum for (**40**) confirmed the presence of only one ring fluorine. Significantly, the presence of the 3-methoxy-group, in (**40**), acts to hinder rotation of the perfluoroisopropyl-group thereby increasing the barrier to rotation[95]. As a consequence it is possible to observe the rotamers (**O**) and (**P**), at room temperature, in the corresponding ^{19}F NMR spectrum.

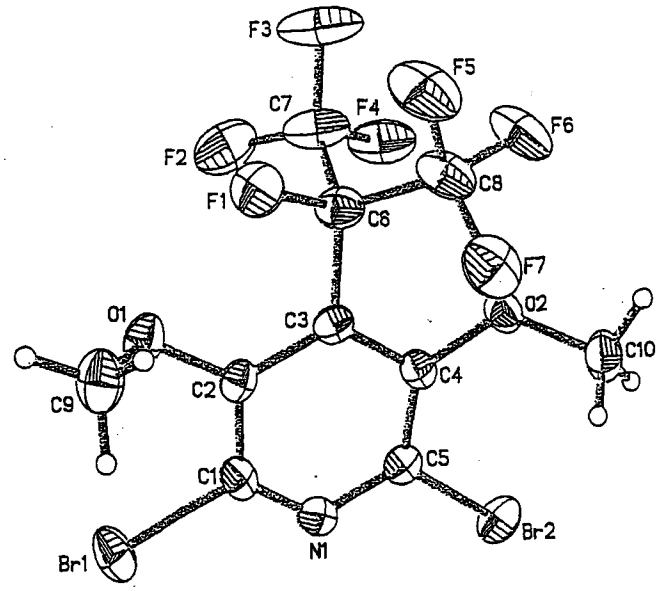


Crystals of compounds (**40**) and (**41**) were grown from hexane and the X-ray data obtained unequivocally confirmed our structural assignments. The crystallographic results revealed products in which the perfluoroisopropyl-groups are in front of and behind the aromatic plane[95] at room temperature.

Compound (40)

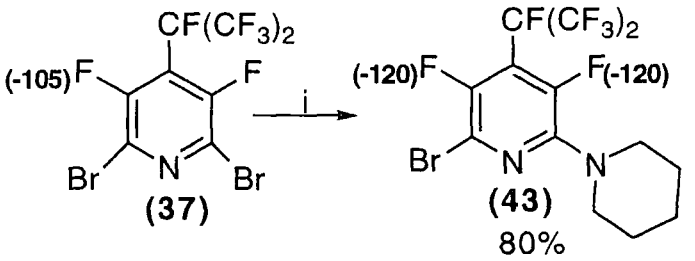


Compound (41)



6.3.iii. Amination.

Reaction of the dibromo derivative (**37**) with piperidine resulted in the exclusive displacement of bromine to give compound (**43**).

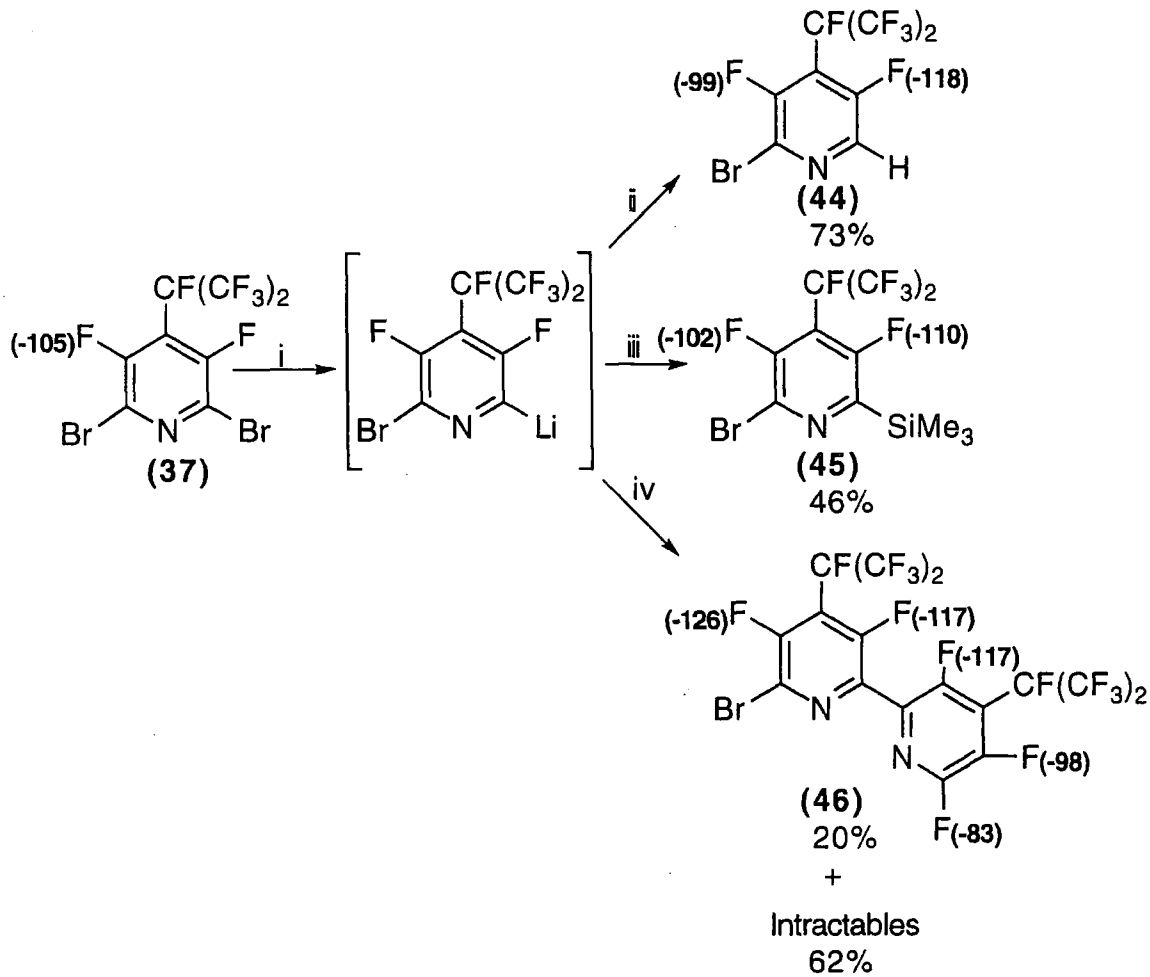


Reagents and conditions: i. Piperidine (2 equivs.), Acetonitrile, Reflux, 24h.
Figures in parentheses denote fluorine atom chemical shift value (ppm).

The preference for the substitution of bromine by piperidine was deduced by considering the NMR, MS and elemental analysis data for compound (**43**). The ^{19}F NMR data confirmed the presence of two ring fluorines, whilst the MS data gave two parent ions (M^+ 458, M^+ 456), in the ratio 1:1, which is consistent with a one bromine pattern (Section 6.2). The regioselectivity observed can be attributed to the well known preference of soft nucleophiles to attack soft centres (C-Br)[189].

6.3.iv. Mono-Lithiation.

The reaction of compound (**37**) with *n*-butyl-lithium resulted in metal-halogen exchange[192-194] to give the 2-lithio-derivative shown. Quenching of the metalation reaction with ethanol, at -78°C, afforded the monohydrido compound (**44**), whilst independent trapping of the lithio-salt with trimethylsilylchloride and perfluoro-4-isopropylpyridine (**1**) afforded the silylated (**45**) and bipyridyl (**46**) compounds respectively.



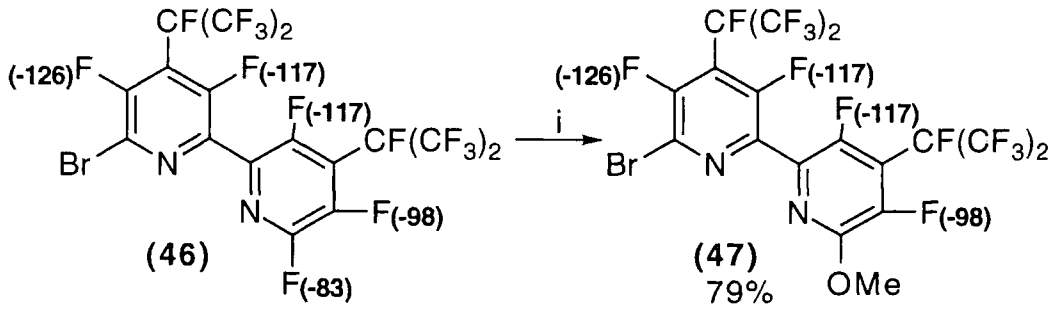
Reagents and conditions: i. nBuLi (1.2 equivs), THF, -78°C.
ii. Excess EtOH, -78°C-r.t.
iii. Me_3SiCl (4 equivs), -78°C-r.t.
iv. Compound (1) (4 equivs), -78°C-r.t.
Figures in parentheses denote fluorine chemical shift (ppm).

Products **(44)**-**(46)** were characterised by NMR, MS and elemental analysis. A comparison of the ^{19}F NMR chemical shift values for the ring fluorine atoms in **(37)** and **(44)**, **(37)** and **(45)**, reveals a small substituent effect on the chemical shifts *ortho* and *para* to the site of substitution. This observation, together with the data accrued for model compounds (Section 2.3), enabled the assignment of the ring fluorine atoms. Significantly, the ^{19}F NMR spectrum for compound **(46)** showed one fluorine atom (-83 ppm) *ortho* to the ring nitrogen, thus providing strong evidence for the bipyridine shown. The monohydrido-derivative **(44)** gave a singlet at 8.3 ppm, in the ^{1}H NMR spectrum, corresponding to 2-CH; whilst the monosilylated compound **(45)** gave a singlet at 0.4 ppm which can be assigned to $-CH_3$. MS data for each product, **(44)**-**(46)**, revealed two parent ions (M^+ 361, M^+ 363; M^+ 433, M^+ 435 and M^+ 660,

M^+ 662 respectively), in a ratio of 1:1, which is characteristic of compounds containing one bromine atom (Section 6.2).

6.3.v. Methoxylation of Bipyridine (46).

Reaction between compound (**46**) and methoxide ion afforded the methoxy-derivative (**47**), which was purified by column chromatography.

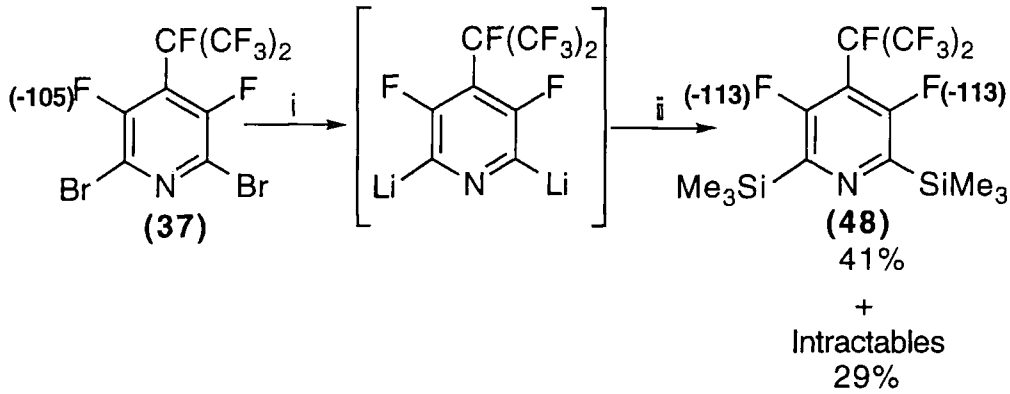


Reagents and conditions: i, NaOMe (1 equivs), MeOH, Reflux, 24h.
Figures in parentheses denote fluorine chemical shift (ppm).

A comparison of the ^{19}F NMR chemical shift values for the ring fluorine atoms, in (**46**) and (**47**), reveals the absence of a resonance at -83 ppm, corresponding to the 6-F ring atom. This observation, together with relative signal intensity values for the remaining ring fluorines, allowed us to conclude that the reaction had proceeded to afford the 6-methoxylated product shown. The elemental analysis and MS (M^+ 672 and M^+ 674) results obtained for (**47**) were in agreement with the structure illustrated.

6.3.vi. Dilithiation.

Compound (**37**) was treated with 2.4 molar equivalents of n-butyllithium[192-194] in THF at -79°C and then silylated to give the product (**48**) shown:

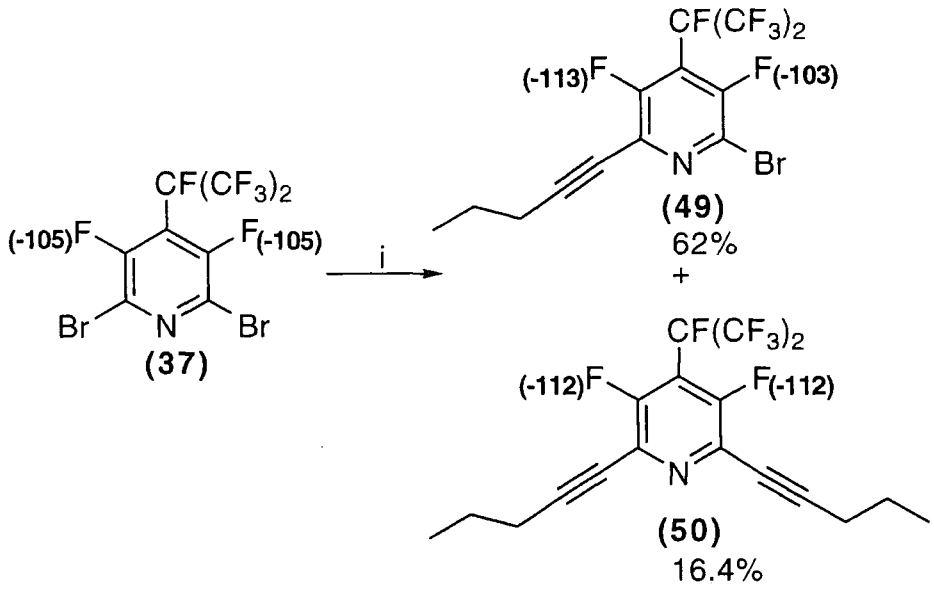


Reagents and conditions: i, nBuLi (2.4 equivs), THF, -78°C.
ii, Me_3SiCl (4.9 equivs), -78°C-r.t.
Figures in parentheses denote fluorine chemical shift (ppm).

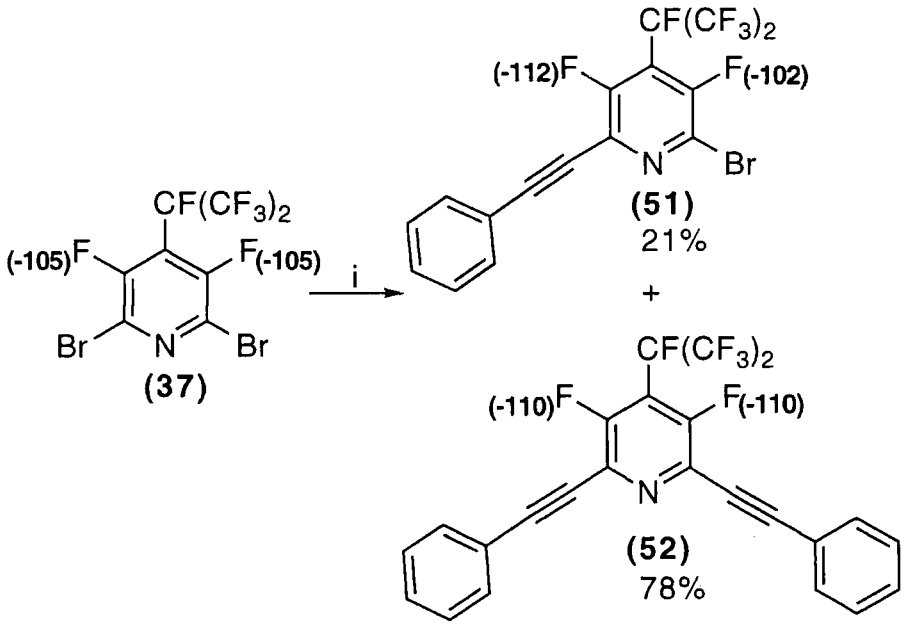
The elemental analysis, MS (M^+ 427) and NMR results obtained for **(48)** were accordant with the compound shown. Significantly, one ring fluorine signal was observed at -113 ppm in the ^{19}F NMR spectrum which, together with its relative peak intensity value of two, confirmed the symmetrical nature of the 2,6-disubstituted product. Similarly, the ^1H NMR spectrum for **(48)** gave one signal at 0.38 ppm corresponding to $-CH_3$.

6.3.vii. Alkyne Couplings.

At room temperature, 2,6-dibromo-perfluoro-4-isopropylpyridine **(37)** underwent palladium mediated coupling reactions with pent-1-yne and phenylacetylene, to give a mixture of 2- and 2,6-substituted products **(49)-(52)**. When the reactants were heated to 45°C it was possible to obtain the 2,6-disubstituted products, **(50)** and **(52)**, exclusively.



Reagents and conditions: i,Pent-1-yne (2 equivs.),CuI, $Pd(OAc)_2$, PPh_3, Et_3N, r.t., 3 days.



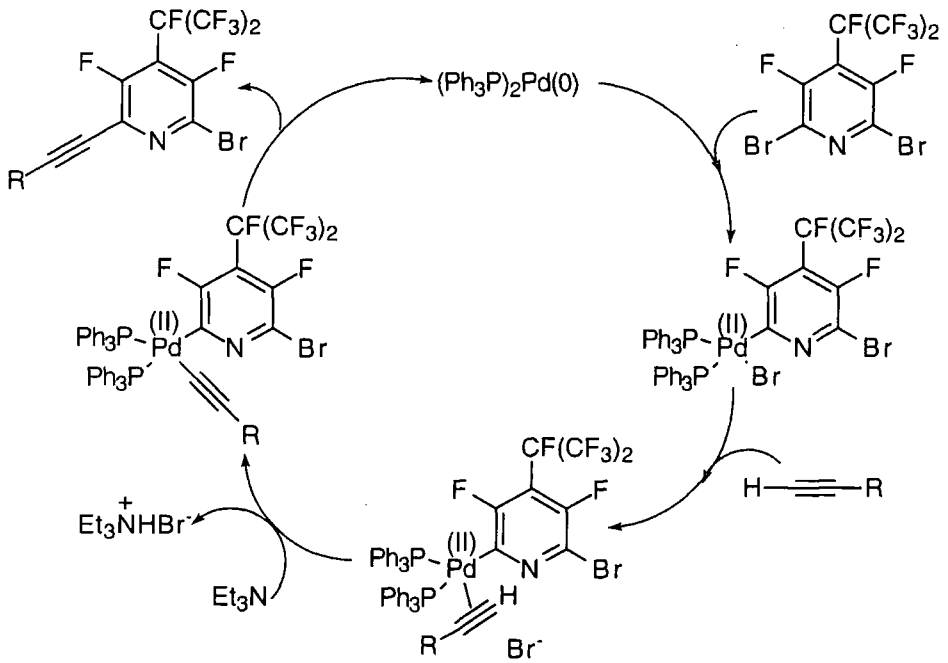
Reagents and conditions: i,Phenylacetylene (2 equivs.),CuI, $(Ph_3P)_2PdCl_2$, Et_3N, r.t., 16h.
Figures in parentheses denote fluorine atom chemical shift (ppm).

The ^{19}F NMR spectra for compounds (**50**) and (**52**) showed only one ring fluorine signal, at -112 ppm and -110 ppm respectively, which is consistent with the symmetry of these 2,6-disubstituted products. A comparison of the chemical shift values for the ring fluorine atoms in (**37**) and (**49**); (**37**) and (**51**), reveals a small substituent effect on the chemical shifts *ortho* and *para* to the site of substitution.

This feature, together with the data accrued for model compounds (Section 2.3), enabled us to identify the chemical shifts of the individual ring fluorines.

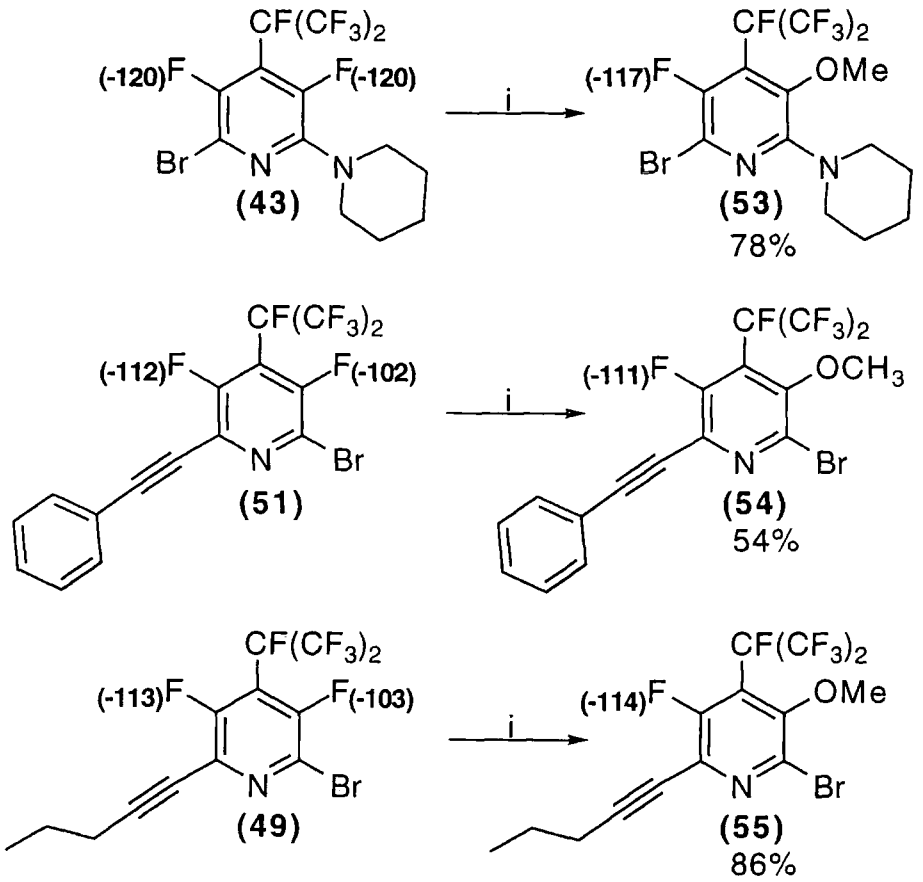
The preference for substitution of the bromines at the 2- and 6-positions by the alkynes was also deduced by mass spectroscopy. Thus compounds **(49)** and **(51)** showed characteristic one bromine patterns (Section 6.2) (M^+ 427 and M^+ 429; M^+ 462 and M^+ 464 respectively): whilst the mass spectra for compounds **(50)** and **(52)** showed no bromine patterns (M^+ 415 and M^+ 483 respectively).

The mechanistic pathway for these coupling reactions most likely proceeds *via* the oxidative addition of **(37)** to a Pd(0) species[195-197]. This is then followed by the formation of an intermediate "Py-Pd^{II}-Alkyne" species, which undergoes reductive elimination to afford the coupled product and the regenerated Pd(0) catalyst.



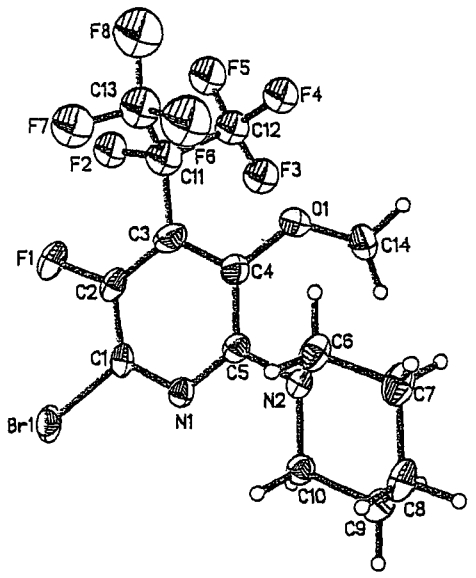
6.4. Pentasubstituted Pyridines Derived from 2,6-Dibromo-perfluoro-4-isopropylpyridine.

Three pentasubstituted pyridine compounds **(53)**-**(55)** have been prepared by methoxylation of the substrates **(43)**, **(49)** and **(51)**. The identities of these compounds were confirmed by NMR, MS, elemental and in the case of **(53)** x-ray analysis.



Reagents and conditions: i, NaOMe (1.7 equivs), MeOH, Reflux, 24h.
Figures in parentheses denote fluorine atom chemical shift (ppm).

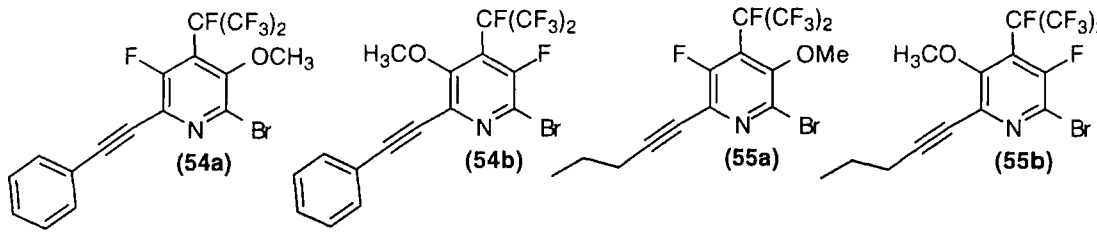
The order of the substituents in compound (**53**) was confirmed by X-ray structural data.



A comparison of the ^{19}F NMR chemical shift values for the ring fluorines in (**51**) and (**54**), and also in (**49**) and (**55**), reveals a small substituent effect on the

chemical shift values *meta* to the site of substitution. This feature allowed us to identify the 3-position in compounds (**54**) and (**55**) as the preferred site for methoxylation. Moreover, the calculated fluorine chemical shifts for compounds (**54a**) and (**54b**) and also (**55a**) and (**55b**), derived from substituent chemical shift data, support formation of the 3-substituted products (**54**) and (**55**) rather than the 5-substituted compounds.

Table 1.



Chemical shifts (ppm) for ring fluorine atoms in (54a), (54b), (55a) and (55b)

	3	5
***Calculated (54a)**	-113.7	-
***Calculated (54b)**	-	-103.4
Observed	-114.0	-
***Calculated (55a)**	-110.8	-
***Calculated (55b)**	-	-102.3
Observed	-111.0	-

*Calculated using pentafluoropyridine[28], 4-methoxytetrafluoropyridine[95], perfluoro-4-isopropylpyridine[90] and compounds (**49**) and (**51**) as reference compounds.

6.5. Conclusions.

In this chapter a convenient synthesis of the compound, 2,6-dibromo-perfluoro-4-isopropylpyridine (**37**) has been achieved. Reactions of the dibromo derivative (**37**) with hard nucleophiles resulted in the exclusive displacement of fluorine, whereas softer nucleophiles gave exclusive displacement of bromine. We

attribute this selectivity to the well known tendency of hard nucleophiles to react at hard centres (C-F) and soft nucleophiles to react at soft centres (C-Br).

The reaction of (**37**) with butyllithium resulted in lithium bromine exchange to give the mono or dilithium derivatives, depending upon the reaction stoichiometry. Evidence for the lithiated species was provided by a series of trapping experiments involving appropriate electrophiles.

The palladium mediated coupling reactions between (**37**) and alkynes proceeded efficiently to give a mixture of 2- and 2,6-alkynylated products.

Efficient routes to a series of pentasubstituted pyridines were developed.

Instrumentation and Reagents.

Reagents and Solvents.

All starting materials were obtained commercially (Aldrich, Lancaster or Fluorochem) unless stated otherwise. Solvents were dried using literature procedures and then stored over molecular sieves (4Å) or sodium wire.

Column chromatography.

Column chromatography was carried out on silica gel (Merck no. 109385, particle size 0.040-0.063nm) and TLC analysis was performed on silica gel TLC plates using the stated eluent .

Gas Liquid Chromatography.

Chromatographic analyses were performed on a Shimadzu GC8A system using an SE30 column. Preparative scale GC was performed on a Varian Aerograph Model 920 gas chromatograph, fitted with a 3m 10% SE30 packed column.

Distillation/ Boiling Points/ Melting Points.

Fractional distillations were performed using a Fischer Spaltruhr MS220 microdistillation apparatus. Boiling points were either recorded during distillation or at atmospheric pressure (Siwoboloff's method) using a Gallankamp apparatus and are uncorrected. Melting points were all carried out at tmospheric pressure using the Gallankamp apparatus and are also uncorrected.

NMR Spectra.

^{1}H (399.96 MHz), ^{13}C (100.58 MHz) and ^{19}F (376.29 MHz) spectra were all obtained from a Varian VXR 400S spectrometer. All spectra were recorded with TMS and/or $CFCl_3$ as internal references, and J values are given in Hz.

Mass Spectra.

Mass spectra were recorded on a Fisons VG-Trio 1000 Spectrometer coupled with a Hewlett Packard 5890 series II gas chromatograph using a 25m HP1 (methyl - silicone) column.

Elemental Analyses.

Elemental analyses were obtained on an Exeter Analytical CE-440 elemental analyser.

FT-IR Spectra.

Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer, using thin films between sodium chloride plates, as either neat liquids or Nujol mulls.

Chapter VII.

Experimental to Chapter II

Synthesis of *2,3,5,6-Tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* **(1)** and *2,3,5-trifluoro-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* **(2)**.

A stainless steel autoclave was charged with pentafluoropyridine (20.0 g, 0.12 mol) and tetrakis(dimethylamino)-ethylene (0.4 g, 2.0 mmol). The mixture was degassed, by freeze-thawing under vacuum, before hexafluoropropene (16.5 g, 0.11 mol) was transferred into the autoclave. The autoclave was sealed and heated to 60°C for 21 h in a thermostatically controlled rocking furnace. The product mixture (36.0 g) was shown, by GC-MS, to consist of *2,3,5,6-tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* **(1)** (57%), *pentafluoropyridine* (25%), *hexafluoropropene-dimers* (12%), *2,3,5-trifluoro-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* **(2)** (4%) and a mixture of *3,6-difluoro-2,4,5-tri-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* and *3,5-difluoro-2,4,6-tri-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* (2%). Fractional distillation gave *2,3,5,6-tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine)* **(1)** (13.3 g, 38 %) as a colourless liquid bp 128-9°C (Found: C, 29.8; N, 4.3. $C_8F_{11}N$ requires C, 30.1; N, 4.4%) **NMR spectrum no. 1; Mass spectrum no. 1; IR spectrum no. 1**; and *2,3,5-trifluoro-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* **(2)** (1.0 g, 4 %) as a colourless liquid bp 158-9°C (Found: C, 27.7; N, 2.9. $C_{11}F_{17}N$ requires C, 28.1; N, 3.0%) **NMR spectrum no. 2; Mass spectrum no. 2; IR spectrum no. 2.**

Reactions of (1) with Alkoxide Ions.

General Procedure:

(i) Under an atmosphere of dry nitrogen, sodium metal was added to a solution of the alcohol in THF (20 cm^3) and stirred until hydrogen evolution was complete. 2,3,5,6-Tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (1) (1.75 g, 5.5 mmol) was added to the solution which was stirred at reflux temperature for 24 h before water (25 cm^3) was added. The mixture was continuously extracted with DCM, dried ($MgSO_4$) and evaporated to yield crude material. The isolation of pure products was achieved by column chromatography, using hexane and dichloromethane (6:1) as the eluent.

(ii) *2,3,5-Trifluoro-6-methoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine.***(3)**.

Compound (1) in (i) and sodium methoxide (0.36 g, 6.5 mmol) gave crude product (1.9 g) which after column chromatography, afforded *2,3,5-trifluoro-6-methoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* **(3)** (1.4 g, 77%) as a

colourless liquid bp 173-173.5°C (Found: C, 32.3; H, 0.9; N, 4.2. $C_9H_3F_{10}NO$ requires C, 32.6; H, 0.9; N, 4.2%) **NMR spectrum no. 3; Mass spectrum no. 3; IR spectrum no. 3.**

(iii) *3,5-Difluoro-2,6-dimethoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* (**4**)

Compound (1) in (i) and sodium methoxide (0.72 g, 13.1 mmol) gave crude material (2.2 g) which after column chromatography, afforded *3,5-difluoro-2,6-dimethoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* (**4**) (1.44 g, 77%) as a yellow liquid bp 217-8°C (Found: C, 34.7; H, 1.6; N, 4.3. $C_{10}H_6F_9NO_2$ requires C, 34.9; H, 1.8; N, 4.1%) **NMR spectrum no. 4; Mass spectrum no. 4; IR spectrum no. 4.**

Preparation of *3,5,6-Trifluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridin-2-ol* (**5**).

Potassium hydroxide (0.7 g, 12.5 mmol) was added to a solution of 2,3,5,6-tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (**1**) (1.75 g, 5.5 mmol) in 2-methylpropanol (25 cm^3).and the mixture was stirred at reflux temperature for 24 h. Dilute HCl was added until the solution was pH 1 and the mixture was continuously extracted with DCM, dried ($MgSO_4$), and evaporated to yield crude material (4.2 g). Column chromatography, using dichloromethane as the eluent, yielded pure *3,5,6-trifluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridin-2-ol* (**5**) (2.4 g, 60%) as a white solid mp 88.9-89.3°C (Found: C, 29.9; H, 0.4; N, 4.4. $C_8HF_{10}NO$ requires C, 30.3; H, 0.3; N, 4.4%) **NMR spectrum no. 5; Mass spectrum no. 5; IR spectrum no. 5.**

iv. *3,5,6-Trifluoro-2-(methoxyethanoxy)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl]-pyridine* (**6**).

Compound (1) in (i) and sodium metal (0.13 g, 5.5 mmol) which had been reacted with 2-methoxyethanol (0.42 g, 5.5 mmol) gave crude material (2.2 g) which after column chromatography afforded *3,5,6-trifluoro-2-(methoxyethanoxy)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl]-pyridine* (**6**) (0.79 g, 38%) as a yellow oil bp 256.8-257°C (Found C, 35.1; H, 1.9; N, 3.9. $C_{11}H_7F_{10}NO_2$ requires C, 35.2; H, 1.9; N, 3.7%) **NMR spectrum no. 6; Mass spectrum no. 6; IR spectrum no. 6.**

(v)*2,6-Bis(2-methoxyethanoxy)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-pyridine* (**7**).

Compound (1) in (i) and sodium metal (0.52 g, 22.1 mmol) which had been reacted with 2-methoxyethanol (1.68 g, 22.0 mmol) gave crude material (2.5 g) which after column chromatography afforded *2,6-bis(2-methoxyethanoxy)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-pyridine* (**7**) (1.8g, 76%) as a clear liquid bp >300°C (Found: C, 39.0; H, 3.2; N, 3.2. $C_{14}H_{14}F_9NO_4$ requires C, 38.9; H, 3.2; N, 3.2%) **NMR spectrum no. 7; Mass spectrum no. 7; IR spectrum no. 7.**

(vi) *6-Cyclohexyloxy-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-pyridine* (**8**).

Compound (1) in (i) and sodium hydride (0.13 g, 5.3 mmol) which had been reacted with cyclohexanol (0.55 g, 5.5 mmol) gave crude material (2.3 g), which after column chromatography afforded *6-cyclohexyloxy-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-pyridine* (**8**) (1.4 g, 64 %) as a colourless oil bp >300°C (Found C, 41.8; H, 2.6; N, 3.5. $C_{14}H_{11}F_{10}NO$ requires C, 42.1; H, 2.8; N, 3.5%) **NMR spectrum no. 8; Mass spectrum no. 8; IR spectrum no. 8.**

(vii) *2,6-dicyclohexyloxy-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-pyridine* (**9**).

Compound (1) in (i) and sodium hydride (0.26 g, 11.0 mmol) which had been reacted with cyclohexanol (1.1 g, 11.0 mmol) gave crude material (2.9 g)which after column chromatography afforded *2,6-dicyclohexyloxy-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-pyridine* (**9**) (1.7g, 65%) as a white solid mp 68.5-69.0°C (Found: C, 49.8; H, 4.5; N, 2.8. $C_{20}H_{22}F_9NO_2$ requires C, 50.1; H, 4.6; N, 2.9%) **NMR spectrum no. 9; Mass spectrum no. 9; IR spectrum no. 9.**

(viii) *2,3,5-Trifluoro-6-phenoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine.* (**10**).

Compound (1) in (i) and sodium metal (0.13 g, 5.5 mmol) which had been reacted with phenol (0.52 g, 5.5 mmol) gave crude material (2.6 g), which after column chromatography afforded *2,3,5-trifluoro-6-phenoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* (**10**) (1.42 g, 66 %) as a colourless oil bp 252.6-253.0°C (Found C, 42.5; H, 1.2; N, 3.5. $C_{14}H_5F_{10}NO$ requires C, 42.7; H, 1.3; N, 3.6%) **NMR spectrum no. 10; Mass spectrum no. 10; IR spectrum no. 10.**

(ix) *3,5-Difluoro-2,6-diphenoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine.* (**11**).

Compound (1) in (i) and sodium metal (0.26 g, 11.7 mmol) which had been reacted with phenol (1.1 g, 11.7 mmol) gave crude material (3.1g) which after column chromatography afforded *3,5-difluoro-2,6-diphenoxy-4-[1,2,2,2-tetrafluoro-1-*

(trifluoromethyl)ethyl]pyridine (**11**) (1.86 g, 72%) as a white solid mp 45.1-45.8°C (Found C, 51.5; H, 2.1; N, 3.0. $C_{20}H_{10}F_9NO_2$ requires C, 51.4; H 2.1; N, 3.0%) **NMR spectrum no. 11; Mass spectrum no. 11; IR spectrum no. 11.**

(x) *2,6-Bis-(3-methoxyphenoxy)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl]pyridine* (**13**) and (**12**).

Compound (1) in (i) and sodium metal (0.26 g, 11.0 mmol) which had been reacted with 3-methoxyphenol (1.36 g, 11.0 mmol) gave crude material (3.2 g) which after column chromatography afforded *2,6-bis-(3-methoxyphenoxy)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl]pyridine* (**13**) (2.0 g, 69 %) as a white solid mp 54.1-54.8°C (Found: C, 50.2; H, 2.7; N, 2.7 $C_{22}H_{14}F_9NO_4$ requires C, 50.1; H 2.7; N, 2.7%) **NMR spectrum no. 13; Mass Spectrum no. 13; IR spectrum no. 13** and compound (**12**) (3%) which could not be obtained pure.

Reactions of (2) with Alkoxide Ions.

General Procedure:

(i) Under an atmosphere of dry nitrogen, sodium metal was added to a solution of the alcohol (20 cm^3) and stirred until hydrogen evolution was complete. 2,3,5-trifluoro-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (**2**) (1.2 g, 2.7 mmol) or 2,5-difluoro-3-methoxy-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (**14**) (2.2 g, 4.5 mmol) was added to the solution which was stirred at reflux temperature for 48 h before water (25 cm^3) was added. The mixture was continuously extracted with DCM, dried ($MgSO_4$) and evaporated to yield crude material. The isolation of pure products was achieved by column chromatography, using hexane and dichloromethane (8:1) as the eluent.

(ii) *2,5-Difluoro-3-methoxy-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* (**14**).

Compound (2) in (i) and sodium metal (0.06 g, 2.7 mmol) added to methanol gave crude material (1.32 g) which after column chromatography afforded *2,5-difluoro-3-methoxy-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* (**14**) (0.8 g, 63 %) as a colourless liquid bp 187.1-188.5°C (Found: C, 29.9; H, 0.6; N, 2.9. $C_{12}H_3F_{16}NO$ requires C, 29.9; H, 0.6; N, 2.9%) **NMR spectrum no. 14; Mass spectrum no. 14; IR spectrum no. 14.**

(iii) ***5-Fluoro*** *-2,3-dimethoxy-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* (**15**).

Sodium metal (0.1 g, 4.5 mmol) in methanol and *2,5-difluoro-3-methoxy-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* (**14**) (2.2 g, 4.5 mmol) gave

crude material (2.4 g) which after column chromatography afforded *5-fluoro-2,3-dimethoxy-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* **(15)** (1.35 g, 60 %) as a colourless liquid bp 229.1-231.0°C (Found: C, 31.5; H, 1.1; N, 2.8. $C_{13}H_6F_{15}NO_2$ requires C, 31.6; H, 1.2; N, 2.8%) **NMR spectrum no. 15; Mass spectrum no. 15; IR spectrum no. 15.**

Reactions with Nitrogen Nucleophiles.

Methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl}amine **(16)**.

Under an atmosphere of dry nitrogen, methylamine (11.2 g, 0.36 mol) was added dropwise to a solution of 2,3,5,6-tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine **(1)** (60.0 g, 0.18 mol) in tetrahydrofuran (200 cm^3) and the mixture was then stirred at room temperature for 24 h before water (250 cm^3) was added. The mixture was continuously extracted with DCM, dried ($MgSO_4$) and evaporated to yield crude material (62 g). Vacuum distillation gave *methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}amine* **(16)** (45.0 g, 73%) as a white solid bp 45°C at 8 mbar mp 36°C (Found: C, 32.6; H, 1.2; N, 8.5. $C_9H_4F_{10}N_2$ requires C, 32.7; H, 1.2; N, 8.5%) **NMR spectrum no. 16; Mass Spectrum no. 16; IR spectrum no.16.**

Bis{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}methylamine **(17)**.

Under an atmosphere of dry nitrogen, at -78°C, *n*-butyllithium (5.8 g, 91 mmol) was added to a solution of methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amine **(16)** (30 g, 91 mmol) in THF (300 cm^3) and then stirred for 1 h before adding 2,3,5,6-tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine **(1)** (29.0 g, 91 mmol). The mixture was then stirred for a further 3 h before water (200 cm^3) was added. The organics were continuously extracted with DCM, dried ($MgSO_4$) and then evaporated to yield crude material (58 g). Distillation, under vacuum, afforded *bis{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}methylamine* **(17)** (29.8 g, 52 %) as a yellow solid bp 95°C at 8 mbar mp 81.2-83°C (Found: C, 32.7; H, 0.6; N, 6.9. $C_{17}H_3F_{20}N_3$ requires C, 32.4; H, 0.5; N, 6.7%); **NMR spectrum no. 17; Mass spectrum no. 17; IR spectrum no. 17.**

{3,5-Difluoro-6-N-methylamino-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}methyl{3,5,6-trifluoro-4[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}amine **(18)**.

Under an atmosphere of dry nitrogen, methylamine (1.24 g, 40.0 mmol) was added to a solution of bis{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}methylamine **(17)** (10.1 g, 16 mmol) in THF (75 cm^3) and the mixture was stirred at r.t for 20 h before water (100 cm^3) was added. The mixture was continuously extracted with DCM, dried ($MgSO_4$) and evaporated to yield crude material (10.1 g) which after column chromatography, using hexane and ether (3:1) as the eluent, afforded *{3,5-difluoro-6-methylamino-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}methyl{3,5,6-trifluoro-4[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl-2-pyridyl}amine* **(18)** (7.0 g, 68 %) as a yellow solid mp 60.2°C (Found: C, 33.5; H, 1.1; N, 8.7. $C_{18}H_7F_{19}N_4$ requires C, 33.8; H, 1.1 N, 8.8%); **NMR spectrum no. 18; Mass spectrum no. 18; IR spectrum no. 18.**

Bis{3,5-difluoro-6-(N-methylamino)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl}methylamine **(19)**.

Under an atmosphere of dry nitrogen, methylamine (0.6 g, 19.4 mmol) was added to a solution of bis{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}methylamine **(17)** (3.1 g, 4.9 mmol) in THF (100 cm^3) and the mixture was stirred at room temperature for 20 h before water (100 cm^3).was added. The mixture was continuously extracted with DCM, dried ($MgSO_4$) and evaporated to yield crude material (3.3 g) which after column chromatography, using hexane and DCM (2:1) as the eluent, afforded *bis{3,5-difluoro-6-(methylamino)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}methylamine* **(19)** (2.2 g, 68 %) as a blue liquid bp 105°C at 8 mbar (Found: C, 34.5; H, 1.7; N, 10.5. $C_{19}H_{11}F_{18}N_5$ requires C, 35.0; H, 1.7; N, 10.8 %); **NMR spectrum no. 19; Mass spectrum no. 19; IR spectrum no. 19.**

Bis{6-(N,N-diethylamino)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}methylamine **(20)**.

Under an atmosphere of dry nitrogen, diethylamine (0.94 g, 13.1 mmol) was added to a solution of bis{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}methylamine **(17)** (2.0 g, 3.18 mmol) in THF (50 cm^3) and the mixture was stirred at reflux temperature for 20 h before water (100 cm^3) was added. The organics were continuously extracted with DCM, dried ($MgSO_4$) and then evaporated to yield crude material (2.3 g) which after column chromatography using hexane and ethylacetate (8:1) as the eluent afforded *bis{6-(N,N-diethylamino)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]2-pyridyl}methylamine* **(20)** as a yellow solid (1.2 g, 51 %) mp 74.6-76°C (Found: C, 40.8; H, 3.1; N, 9.4. $C_{25}H_{23}F_{18}N_5$ requires C, 40.8; H, 3.1; N, 9.4%); **NMR spectrum no. 20; Mass spectrum no. 20; IR spectrum no. 20.**

Chapter VIII.

Experimental to Chapter IV

Reactions with Dioxygen nucleophiles.

Synthesis of *2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl]-6-(3-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl](2-pyridyloxy)}phenoxyloxy)pyridine* (**2 1**) and *2,3,5-trifluoro-6-(5-methyl-3-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}phenoxy)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* (**24**)

Under an atmosphere of dry nitrogen, either 1,3-bis-(trimethylsiloxy)benzene (**22**) (1.8 g, 7.1mmol) or 1,3-bis-(trimethylsiloxy)-toluene (**23**) (1.9 g, 7.1 mmol) was added to a solution consisting of caesium fluoride (2.5 g, 16.5 mmol), 2,3,5,6-tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (**1**) (22.5 g, 70.5 mmol) and monoglyme (175 cm^3) and heated to reflux for 40 h, before water (250 cm^3) was added. The mixture was continuously extracted into ether and dried ($MgSO_4$) and the excess 2,3,5,6-tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (**1**) present in the ether fraction was recovered by further extraction into perfluorocyclohexane. The ether layer was evaporated to yield crude products and the isolation of *2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl]-6-(3-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl](2-pyridyloxy)}phenoxyloxy)pyridine* (**2 1**) or *2,3,5-trifluoro-6-(5-methyl-3-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}phenoxy)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* (**24**)
as white solids was achieved by recrystallisation in cyclohexane to give *2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl]-6-(3-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl](2-pyridyloxy)}phenoxyloxy)pyridine* (**21**) from (**22**) (3.5 g, 70%) mp 138.0-138.4°C (Found: C, 37.3; H, 0.5; N, 3.9. $C_{22}H_4F_{20}N_2O_2$ requires C, 37.3; H, 0.6; N, 3.9%); **NMR spectrum no. 21; Mass spectrum no. 21; IR spectrum no. 21.**, and *2,3,5-trifluoro-6-(5-methyl-3-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}phenoxy)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* (**24**).from (**23**) (3.7 g, 72%) mp 161-161.5°C (Found: C, 38.0; H, 0.8; N, 3.9. $C_{23}H_6F_{20}N_2O_2$ requires C, 38.2; H, 0.8; N, 3.9%); **NMR spectrum no. 24; Mass spectrum no. 24; IR spectrum no. 24.**

Cyclisation Reactions with (21) and (24).

Under an atmosphere of dry nitrogen, either 1,3-bis-(trimethylsiloxy)-benzene (**22**) (0.36 g, 1.4 mmol) or 1,3-bis-(trimethylsiloxy)-toluene (**23**) (0.38 g, 1.4 mmol) was added to a solution of caesium fluoride (0.35 g, 2.3 mmol *2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl]-6-(3-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl](2-pyridyloxy)}phenoxyloxy)pyridine* (**21**) (1.0 g, 1.4 mmol) or 2,3,5-trifluoro-6-(5-methyl-3-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}phenoxy)-4-[1,2,2,2-tetrafluoro-1-

(trifluoromethyl)ethyl]pyridine (**24**) (1.0 g, 1.4 mmol) in monoglyme (300 cm^3) and heated to reflux temperature for 40 h, before water (300 cm^3) was added. The mixture was continuously extracted into DCM, dried ($MgSO_4$) and evaporated to yield crude material. The isolation of pure products, as white solids, was achieved by column chromatography, using dichloromethane as the eluent.

From compound (**21**) and (**22**), was obtained *26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(25),3,5,7(26),9,11,13 (27),15,17,19(28),21,23-dodecaene* (**25**) (0.71 g, 64%) mp 118.7-118.9°C (Found: C, 43.0; H, 1.0; N, 3.6. $C_{28}H_8F_{18}N_2O_4$ requires C, 43.0; H, 1.0; N, 3.6%); **NMR spectrum no. 25; Mass spectrum no. 25; IR spectrum no. 25.**

From compound (**22**) and (**24**), was obtained *26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-11-methyl-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(25),3,5,7(26),9,11,13 (27),15,17,19(28),21,23-dodecaene* (**26**) (0.72 g, 64%) mp 143.9-144.3°C (Found: C, 43.7; H, 1.2; N, 3.4. $C_{29}H_{10}F_{18}N_2O_4$ requires C, 43.9 ; H, 1.3; N, 3.5%); **NMR spectrum no. 26; Mass spectrum no. 26; IR spectrum no. 26.**

From compound (**23**) and (**24**) was obtained *6,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-11,23-dimethyl-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(25),3,5,7(26),9,11,13 (27),15,17,19(28),21,23-dodecaene* (**27**) (0.72 g, 63%) mp 230°C (Found: C, 44.9; H, 1.6; N, 3.4. $C_{30}H_{12}F_{18}N_2O_4$ requires C, 44.7; H, 1.5; N, 3.5%); **NMR spectrum no. 27; Mass spectrum no. 27; IR spectrum no. 27.**

Synthesis of *2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-(trifluoromethyl)ethyl]-6-(-2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}ethoxy)pyridine* (**28**).

Under an atmosphere of dry nitrogen, 1,2-bis(trimethylsilyloxy)ethane (0.16 g, 0.79 mmol) was added to a solution of 2,3,5,6-tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (**1**) (5.0 g, 15.7 mmol) and caesium fluoride (0.12 g, 0.79 mmol) in monoglyme (50 cm^3) and the mixture was stirred at reflux temperature for 4 days before water (100 cm^3) was added. The organics were continuously extracted with DCM, dried ($MgSO_4$) and then evaporated to yield crude material (0.54 g) which after column chromatography, using hexane and ethyl acetate (8:1) as the eluent on a silica-gel support, afforded *2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-(trifluoromethyl)ethyl]-6-(-2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}ethoxy)pyridine* (**28**), as clear liquid (0.47

g, 92%) bp >300°C (Found: C, 32.6; H, 0.6; N, 4.2. $C_{18}H_4F_{20}N_2O_2$ requires C, 32.7; H, 0.6; N, 4.2%); **NMR spectrum no. 28; Mass spectrum no. 28; IR spectrum no. 28.**

A Cyclisation Reaction with (28).

Under an atmosphere of dry nitrogen, 1,2-bis(trimethylsilyloxy)ethane (0.31 g, 1.5 mmol) was added to a solution 2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-(trifluoromethyl)ethyl]-6-(-2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}ethoxy)pyridine **(28)** (1.0 g, 1.52 mmol) and caesium fluoride (0.23 g, 1.5 mmol) in monoglyme (50 cm^3) and the mixture was stirred at reflux temperature for 4 days before water (75 cm^3) was added. The organics were continuously extracted with DCM, dried ($MgSO_4$) and then evaporated to yield crude material (1.2 g) which after column chromatography, using hexane and dichloromethane (4:1) as the eluent on a silica-gel support, afforded 19,20-diaza-8,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl][-7,9,16,18-tetrafluoro-2,5,11,14-tetraoxatricyclo[13.3.1.1<6,10>]icosa-1(18),6(20),7,9,15(19),16-hexaene **(29)** as a white solid (0.85 g, 83%)
mp 207.6-209.0°C (Found: C, 35.1; H, 1.2; N, 4.3. $C_{20}H_8F_{18}N_2O_4$ requires C, 35.2; H, 1.2; N, 4.1%); **NMR spectrum no. 29; Mass Spectrum no. 29; IR spectrum no. 29.**

Synthesis of *2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)oxy}-1-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1(trifluoromethyl)ethyl](2-pyridyloxy)}ethoxy)ethane* **(30)**.

Under an atmosphere of dry nitrogen, 1-{2-[2-1,1-dimethyl-1-(silaethoxy)ethoxy]ethoxy}-1,1-dimethyl-1-silaethane (3.92 g, 15.7 mmol) was added to a solution of 2,3,5,6-tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine **(1)** (10.0 g, 31.3 mmol) and caesium fluoride (4.75 g, 31.3 mmol) in monoglyme (100 cm^3) and the mixture was stirred at reflux temperature for 4 days before water (100 cm^3) was added. The organics were continuously extracted with DCM, dried ($MgSO_4$) and then evaporated to yield crude material (11.5 g) which after flash column chromatography, using dichloromethane as the eluent on a silica-gel support, afforded *2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)oxy}-1-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1(trifluoromethyl)ethyl](2-pyridyloxy)}ethoxy)ethane* **(30)** as a colourless liquid (9.17 g, 83%) bp 280-282°C (Found: C, 34.1; H, 1.1; N, 3.9. $C_{20}H_8F_{20}N_2O_3$ requires C, 34.1; H, 1.1; N, 3.9%); **NMR spectrum no. 30; Mass spectrum no. 30; IR spectrum no. 30.**

A Cyclisation Reaction with (30).

Under an atmosphere of dry nitrogen, 1-{2-[2-1,1-dimethyl-1-(silaethoxy)ethoxy]ethoxy}-1,1-dimethyl-1-silaethane (2.1 g, 8.4 mmol) was added to a solution of 2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)oxy}-1-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1(trifluoromethyl)ethyl](2-pyridyloxy)}ethoxy)ethane **(30)** (6.0 g, 8.5 mmol) and caesium fluoride (3.2 g, 21.1 mmol) in monoglyme (150 cm^3) and the mixture was stirred at room temperature for 5 days before water (150 cm^3) was added. The organics were continuously extracted with DCM, dried ($MgSO_4$) and then evaporated to yield crude material (6.6 g) which after flash column chromatography, using dichloromethane as the eluent on a silica-gel support, afforded *25,26-diaza-11,23-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-10,12,22,24-tetrafluoro-2,5,8,14,17,20-hexaoxatricyclo[19.3.1.1<9,13>]hexacosa-1(24),9(26),10,12,21(25),22-hexaene* **(31)** as a white solid (5.8 g, 90%) mp 147.2-149.0°C (Found: C, 37.3; H, 2.0; N, 3.5. $C_{24}H_{16}F_{18}N_2O_6$ requires C, 37.4, H, 2.1; N, 3.6%) **NMR spectrum no. 31; Mass spectrum no. 31; IR spectrum no. 31.**

Reactions with Dinitrogen Nucleophiles.

Synthesis of *Methyl[2-(methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amino)ethyl]{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amine* **(32)** *and 2,3-difluoro-5,8-dimethyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethylethyl)]-5,6,7,8-tetrahydroquinoline* **(33)**.

Under an atmosphere of dry nitrogen, N,N'-dimethylethylene-diamine (2.76 g, 31.3 mmol) was added to a solution of 2,3,5,6-tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine **(1)** (20.0 g, 62.6 mmol) in THF (50 cm^3) and the mixture was stirred at r.t for 1 h before water (100 cm^3) was added. The organic material was continuously extracted with DCM, dried ($MgSO_4$) and then evaporated to yield crude material (19.6 g) which after column chromatography, using hexane and ethyl acetate (8:1) as the eluent, afforded *methyl[2-(methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amino)ethyl]{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amine* **(32)** (15.7 g, 73%) as a brown oil bp >300°C (Found: C, 35.0; H, 1.4; N, 8.2. $C_{20}H_{10}F_{20}N_4$ requires C, 34.9; H, 1.4, N, 8.2%); **NMR spectrum no. 32; Mass spectrum no. 32; IR spectrum no. 32** and *2,3-difluoro-5,8-dimethyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethylethyl)]-5,6,7,8-tetrahydroquinoline* **(33)** (2.8 g, 12%) as a purple solid mp 66.2-68°C (Found: C, 39.1; H, 2.7; N, 11.3. $C_{12}H_{10}F_9N_3$ requires C, 39.2; H, 2.7; N, 11.4%); **NMR spectrum no. 33; Mass spectrum no. 33; IR spectrum no. 33.**

A Cyclisation Reaction with (32).

Under an atmosphere of dry nitrogen, N,N'-dimethylethylene-diamine (0.46 g, 5.2 mmol) was added to a solution of methyl[2-(methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amino)ethyl]{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amine **(32)** (1.0 g, 1.5 mmol) in THF (50 cm^3) and the mixture was stirred at r.t for 20 h before water (100 cm^3) was added. The organic material was continuously extracted with DCM, dried ($MgSO_4$) and then evaporated to yield crude material (1.98 g) which after recrystallisation, using toluene, afforded *2,5,11,14,19,20-hexaaza-8,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11,14-tetramethyltricyclo[13.3.1.1<6,10>]icosa-1(18),6(20),7,9,15,(19),16-hexaene.* **(34)** (0.6 g, 60%) as a white solid mp -299.3-300.0°C (Found: C, 39.0; H, 2.7; N, 11.3. $C_{24}H_{20}F_{18}N_6$ requires C, 39.2; H, 2.7; N, 11.4%); **NMR spectrum no. 34; Mass spectrum no. 34; IR spectrum no. 34.**

Reaction of (17) with N,N' dimethylethylenediamine.

(i) Under an atmosphere of dry nitrogen, N,N'-dimethylethylene-diamine (0.28 g, 3.2 mmol) was added to a solution of bis{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}methylamine **(17)** (2.0 g, 3.18 mmol) in THF (50 cm^3) and the mixture was stirred at reflux temperature for 40 h before water (100 cm^3) was added. The organic layer was continuously extracted with DCM, dried ($MgSO_4$) and then evaporated to yield crude material (2.1 g) which after column chromatography, using hexane and ethyl acetate (8:1) as the eluent, afforded *{7-fluoro-1,4-dimethyl-8-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](1,2,3,4-tetrahydropyridino[2,3-b]pyrazin-6-yl)}methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl}amine* **(35)** (1.3 g, 60 %) as a yellow solid mp 112.4-113.0°C (Found: C, 37.2; H, 1.9; N, 10.4. $C_{21}H_{13}F_{18}N_5$ requires C, 37.2; H, 1.9; N, 10.3%); **NMR spectrum no. 35; Mass spectrum no. 35; IR spectrum no. 35.**

(ii) Under an atmosphere of dry nitrogen, N,N'-dimethylethylene-diamine (0.13 g, 1.48 mmol) was added to a solution of *bis{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}methylamine* **(17)** (0.5 g, 0.79 mmol) in THF (50 cm^3) and the mixture was stirred at reflux temperature for 40 h before water (100 cm^3) was added. The organic layer was continuously extracted with DCM, dried ($MgSO_4$) and then evaporated to yield crude material (0.6 g) which after column chromatography, using hexane and ethylacetate (6:1) as the eluent, afforded *bis{7-fluoro-1,4-dimethyl-8-[1,2,2,2-trifluoromethyl)ethyl](1,2,3,4-tetrahydropyridino[2,3-b]pyrazin-6-yl)}methylamine* **(36)** as a green solid (0.38 g, 71 %) mp 169.3-170.2°C

(Found: C, 41.4; H, 3.2; N, 13.5. $C_{25}H_{23}F_{16}N_7$ requires C, 41.4; H, 3.2, N, 13.5%); **NMR spectrum no. 36; Mass spectrum no. 36; IR spectrum no. 36.**

Complexation Studies.

In order to determine the metal-ion transport ability of (**27**), (**29**) and (**31**) across an aqueous-dichloromethane membrane, alkali metal picrates were used and the distribution of these ions, in the aqueous phase, were measured at equilibrium.

Aqueous solutions containing picric acid (10.0 mM) and the alkali metal fluoride (60.0 mM) were prepared. Into a plastic capped vial was placed 1.0 ml of the metal picrate solution and 1.0 ml of a 10.0 mM dichloromethane solution of the ionophore. The resulting two-phase system was then mixed together for 5 minutes using a Fisons Whirlimixer. Phase separation was induced using a MSE Centaur 2 centrifuge for 10 minutes. A sample (10 μl) of the aqueous phase was then removed and added to HPLC-grade acetonitrile (5.0 ml). The absorption spectrum of the solution was then measured, in a 1 cm silica-cell, using a UV2 UV/VIS spectrometer. When lithium picrate was used the absorbance of the solution was measured at 263 nm; for sodium picrate, 260 nm; for potassium picrate, 260 nm and for caesium picrate 262 nm respectively. The % of metal picrate extracted by the macrocycle was calculated by:

$$\% \text{ Extraction} = 100\,(\mathbf{Abs_{before}} - \mathbf{Abs_{after}})/\mathbf{Abs_{before}}$$

where, $\mathbf{Abs_{before}}$ is the absorbance of a similarly diluted sample of the unextracted alkali metal and $\mathbf{Abs_{after}}$ is the absorbance of the alkali metal picrate after extraction.

Chapter IX.

Experimental to Chapter VI

Exchange of Fluorine by Bromine Reactions

2,6-Dibromo-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine **(37)**.

A Hastalloy autoclave (equipped with a copper gasket and an Inconel bursting disc) was charged with aluminium bromide (34.1 g, 0.13 mol), 2,3,5,6-tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine **(1)** (19.2 g, 0.06 mol) and hydrogen bromide (10.2 g, 0.13 mol). The autoclave was heated at 160°C for 48 h, cooled, then excess gaseous hydrogen bromide was neutralised by release into a sodium hydrogen carbonate solution. The autoclave was opened and ice water was cautiously added to the solid contents. This mixture was then extracted with DCM, and the dried extracts were distilled to give *2,6-dibromo-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* **(37)** (21.6 g, 81%) as a colourless liquid bp 56°C (4mmHg) (Found: C, 21.8; N, 3.1. $C_8Br_2F_9N$ requires C, 21.8; N, 3.2%); **NMR spectrum no. 37; Mass spectrum no. 37; IR spectrum no. 37.**

6-Bromo-2,3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine **(38)**.

A Hastalloy autoclave (equipped with a copper gasket and an Inconel bursting disc) was charged with aluminium bromide (67 g, 0.25 mol), 2,3,5,6-tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine **(1)** (40.0 g, 0.13 mol) and hydrogen bromide (10.2 g, 0.13 mol). The autoclave was heated at 160°C for 18 h, cooled, then excess gaseous hydrogen bromide was neutralised by release into a sodium hydrogen carbonate solution. The autoclave was opened and ice water was cautiously added to the solid contents. This mixture was then extracted with DCM, and the dried extracts were distilled to give *6-bromo-2,3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* **(38)** (27.7 g, 58%) as a colourless liquid bp 25-30°C (4mmHg) (Found: C, 25.4; N, 3.7. $C_8BrF_{10}N$ requires C, 25.3; N, 3.7%); **NMR spectrum no. 38; Mass spectrum no. 38; IR spectrum no. 38.**

Catalytic Hydrogenolysis Reaction of the Dibromocompound (37).

2,6-Dihydrido-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine **(39)**.

A solution of 2,6-dibromo-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine **(37)** (12.0 g, 27.2 mmol) was stirred in DCM (80 cm^3) with activated carbon and then filtered. A palladium catalyst (5% Pd/C) and triethylamine were added to the filtrate and the mixture was hydrogenated on a Parr apparatus, at 4 Bar, for 20 h. The mixture was filtered before water was added (40 cm^3). The organic material was continually extracted with DCM, dried ($MgSO_4$) and then evaporated to yield crude material (8.8 g) which after flash column chromatography, using DCM as the eluent on a silica-gel support, afforded *2,6-*

dihydrido-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (**39**) (4.8 g, 62 %) as a colourless liquid bp 132.3-133.1°C (Found: C, 34.1; H, 0.7; N, 4.9. $C_8H_2F_9N$ requires C, 33.9; H, 0.7; N, 4.9%); **NMR spectrum no. 39; Mass spectrum no. 39; IR spectrum no. 39.**

Reactions of the Bromo-fluoro-compound (37) with Sodium Methoxide. General Procedure:

(i) Under an atmosphere of dry nitrogen, sodium metal was added to methanol (20 cm^3) and stirred until hydrogen evolution was complete. 2,6-Dibromo-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (**37**) (2.0 g, 4.5 mmol) was used in each experiment was added to the solution which was stirred at reflux temperature for 24 h before water (25 cm^3) was added. The mixture was continuously extracted with DCM, dried ($MgSO_4$) and evaporated to yield crude material. The isolation of pure products was achieved by column chromatography, using dichloromethane and hexane (2:1) as the eluent.

2,6-Dibromo-3-fluoro-5-methoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (**40**).

(ii) Compound (**37**) in (i) and sodium methoxide (0.38g, 6.9 mmol) gave crude product (2.21 g) which after column chromatography, afforded *2,6-dibromo-3-fluoro-5-methoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* (**40**) (1.26g, 61%) as a colourless liquid bp 254-255.6°C (Found: C, 23.8; H, 0.6; N, 3.1. $C_9H_3Br_2F_8NO$ requires C, 23.8; H, 0.7; N, 3.1%); **NMR spectrum no. 40; Mass spectrum no. 40; IR spectrum no. 40.**

2,6-Dibromo-3,5-dimethoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (**41**).

(iii) Compound (**37**) in (i) and sodium methoxide (0.76g, 13.9 mmol) gave crude product (2.2 g) which after column chromatography afforded *2,6-dibromo-3,5-dimethoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* (**41**) (1.75g, 83%) as a white solid mp 72.7-74.0°C (Found: C, 26.1; H, 1.3; N, 2.9. $C_{10}H_6Br_2F_7NO_2$ requires C, 25.8; H, 1.3; N, 3.0%); **NMR spectrum no. 41; Mass spectrum no. 41; IR spectrum no. 41.**

2-bromo-3,5,6-trimethoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine.

(iv) Compound (**37**) in (i) and sodium methoxide (1.5g, 27.5 mmol) gave crude product (1.6 g) which after column chromatography afforded *2-bromo-3,5,6-trimethoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* (**42**) (1.2g, 64.0%)

as a colourless liquid bp 260.5-262°C (Found: C, 31.6; H, 2.0; N, 3.3. $C_{11}H_9BrF_7NO_3$ requires C, 31.7; H, 2.2; N, 3.4%); **NMR spectrum no. 42; Mass spectrum no. 42; IR spectrum no. 42.**

Reaction of the Bromofluorocompound (37) with piperidine.

6-bromo-3,5-difluoro-2-piperidyl-4-[1,2,2,2-tetrafluoro-1 -(trifluoromethyl)ethyl]pyridine (**43**).

A solution of 2,6-dibromo-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (**37**) (1.0 g, 2.3 mmol) and piperidine (0.4 g, 4.5 mmol) in acetonitrile (15 cm^3) was stirred under reflux for 24 hours. Water (30 cm^3) was added and the mixture was filtered and extracted into DCM. The DCM solution was dried ($MgSO_4$) and evaporated affording a liquid (1.9 g). Flash-column chromatography, using DCM as the eluent, yielded *6-bromo-3,5-difluoro-2-piperidyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* (**43**) (0.8 g, 80.2%) as a yellow liquid bp 284.5-286.6°C (Found: C, 35.2; H, 2.0; N, 6.3. $C_{13}H_{10}BrF_9N_2$ requires C, 35.1; H, 2.2; N, 6.3%); **NMR spectrum no. 43; Mass spectrum no. 43; IR spectrum no. 43.**

Lithiation reactions of the 2,6-dibromocompound (37) and Reactions with Electrophiles:

A *2-Bromo-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-6-lithiopyridine.*

(i) A solution of butyllithium (3.5 cm^3, 5.5 mmol of 1.6 M solution in hexanes) was added to a solution to 2,6-dibromo-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (2.0 g, 4.5 mmol) in tetrahydrofuran (25 cm^3) at -78°C, with stirring, under an atmosphere of dry nitrogen.

(ii) *2-Bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl]pyridine* (**44**). Ethanol (30 cm^3) was added to a solution of 2-bromo-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-6-lithiopyridine as prepared in (i) and the mixture was stirred for 0.5 h at -78°C, then warmed to room temperature. Water (30 cm^3) was added and the organic components were extracted into DCM. The DCM solution was dried ($MgSO_4$) and evaporated to give a residue which after column chromatography, using hexane and dichloromethane (4:1) as the eluent yielded *2-bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl]pyridine* (**44**) (1.2 g, 73%) as a colourless liquid bp 180.6-182.2°C (1 atm) (Found: C, 26.4; H, 0.2; N, 3.8.

C_8HBrF_9N requires C, 26.5; H, 0.3; N, 3.9%); **NMR spectrum no. 44; Mass spectrum no. 44; IR spectrum no. 44**

2-{6-Bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl](2-pyridyl)}-2-methyl-2-silapropane (**45**).

(iii) Trimethylsilylchloride (2.4 g, 22.2 mmol) was added to a solution of 2-bromo-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-6-lithiopyridine as prepared in (i) and the mixture was stirred for 0.5 h at -78°C, then warmed to room temperature. Water (30 cm^3) was added and the organic components were extracted into DCM. The DCM solution was dried ($MgSO_4$) and evaporated to give a residue which after column chromatography, using hexane and dichloromethane (6:1) as the eluent yielded *2-{6-bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl]}pyridyl-2-methyl-2-silapropane* (**45**) (0.9 g, 46%) as a colourless liquid bp 211.0-212.1°C (1 atm) (Found: C, 30.3; H, 2.0; N, 3.2. $C_{11}H_9BrF_9NSi$ requires C, 30.4; H, 2.1; N, 3.2%); **NMR spectrum no. 45; Mass spectrum no. 45; IR spectrum no. 45.**

2-Bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl]-6-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}pyridine (**46**).

(iv) 2,3,5,6-tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (**1**) (7.1 g, 22.2 mmol) was added to a solution of 2-bromo-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-6-lithiopyridine as prepared in (i) and the mixture was stirred for 0.5 h at -78°C, then warmed to room temperature. Water (30 cm^3) was added and the organic components were extracted into DCM. The DCM solution was dried ($MgSO_4$) and evaporated to give a residue which after column chromatography, using hexane and dichloromethane (4:1) as the eluent yielded *2-bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl]-6-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}pyridine* (**46**) (0.6 g, 20%) as a white solid; mp 68-69.5°C; (Found C, 29.1; N, 4.2. $C_{16}BrF_{19}N_2$ requires C, 29.1; N, 4.2%); **NMR spectrum no. 46; Mass spectrum no. 46; IR spectrum no. 46.**

Reaction of Compound (46) with Sodium Methoxide.

2-{6-Bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl](2-pyridyl)}{3,5,-difluoro-6-methoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (**47**).

Under an atmosphere of dry nitrogen, sodium metal (0.02 g, 0.8 mmol) was added to methanol (20 cm^3) and stirred until hydrogen evolution was complete. 2-Bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl]-6-{3,5,6-trifluoro-

4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}pyridine (**46**) (0.5 g, 0.8 mmol) was added to the solution which was stirred at reflux temperature for 24 h. Water (30 cm^3) was added and the organic components were extracted into DCM. The DCM solution was dried ($MgSO_4$) and evaporated to give a residue which after column chromatography, using hexane and dichloromethane (4:1) as the eluent yielded *2-{6-bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl](2-pyridyl)}{3,5,-difluoro-6-methoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* (**47**) (0.4 g, 79%) as a white solid mp 79.8-81.6°C (Found: C, 30.3; H, 0.4, N, 4.2. $C_{17}H_3BrF_{18}N_2$ requires C, 30.3; H, 0.5; N, 4.2%); **NMR spectrum no. 47; Mass spectrum no. 47; IR spectrum no. 47.**

B Preparation of *3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-2,6-dilithiopyridine.*

(i) A solution of butyllithium (7.0 cm^3, 11.0 mmol of 1.6 M solution in hexanes) was added to a solution to 2,6-dibromo-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (**37**) (2.0 g, 4.5 mmol) in tetrahydrofuran (25 cm^3) at -78°C, with stirring, under an atmosphere of dry nitrogen.

(ii) *2-{6-(1,1-Dimethyl-1-silaethyl)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl](2-pyridyl)}-2-methyl-2-silapropane* (**48**).

Trimethylsilylchloride (2.4 g, 22.2 mmol) was added to a solution of 2-bromo-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-6-lithiopyridine as prepared in (i) and the mixture was stirred for 0.5 h at -78°C, then warmed to room temperature. Water (30 cm^3) was added and the organic components were extracted into DCM. The DCM solution was dried ($MgSO_4$) and evaporated to give a residue which after column chromatography, using hexane and dichloromethane (6:1) as the eluent yielded *2-{6-(1,1-dimethyl-1-silaethyl)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl](2-pyridyl)}-2-methyl-2-silapropane* (**48**) (0.8 g, 41%) as a colourless liquid bp 138.0-140.0°C (1 atm) (Found: C, 39.9; H, 4.2; N, 3.3. $C_{14}H_{18}F_9NSi_2$ requires C, 39.3; H, 4.2; N, 3.3%); **NMR spectrum no. 48; Mass spectrum no. 48; IR spectrum no. 48.**

Coupling Reactions of the 2,6-Dibromocompound (37) with Terminal Alkynes.

6-Bromo-3,5-difluoro-2-pent-1-ynyl-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (**49**) and *3,5-difluoro-2,6-dipent-1-ynyl-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* (**50**).

A mixture of 2,6-dibromo-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (**37**) (1.0 g, 2.3 mmol), pent-1-yne (0.31 g, 4.5 mmol), copper(I) iodide (0.01 g, 0.05 mmol), palladium(II) acetate (0.04 g),

triphenylphosphine (0.08 g) and triethylamine (15 cm^3) was stirred at room temperature, under an atmosphere of dry nitrogen, for 3 days. Water (30 cm^3) was added and the mixture was filtered and extracted into DCM. The DCM solution was dried ($MgSO_4$) and evaporated affording a solid (1.29g). Column chromatography, using hexane/DCM (1:2) as the eluent, yielded *6-bromo-3,5-difluoro-2-pent-1-ynyl-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* **(49)** (0.6 g, 62%) as white crystals mp 55.2-56.5°C (Found: C, 36.5; H, 1.6; N, 3.2. $C_{13}H_7BrF_9N$ requires C, 36.5; H, 1.6; N, 3.3%); **NMR spectrum no. 49; Mass spectrum no. 49; IR spectrum no. 49** and *3,5-difluoro-2,6-dipent-1-ynyl-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* **(50)** (0.15 g, 16%) as a yellow oil (bp >300°C) (Found; C, 52.2; H, 3.4; N, 3.3. $C_{18}H_{14}F_9N$ requires C, 52.0; H, 3.4; N, 3.4%); **NMR spectrum no. 50; Mass spectrum no. 50; IR spectrum no. 50.**

6-Bromo-3,5-difluoro-2-phenylethynyl-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine **(51)** *and 2,6-bis(2-phenylethynyl)-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* **(52)**.

A mixture of 2,6-dibromo-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine **(37)** (1.0 g, 2.3 mmol), phenylacetylene (0.5 g, 4.5 mmol), copper(I) iodide (0.01 g, 0.05 mmol), bis(triphenylphosphine)palladium dichloride (0.04 g, 0.06 mmol) and triethylamine (10 cm^3) was stirred at room temperature, under an atmosphere of dry nitrogen, for 16 hours. Water (30 cm^3) was added and the mixture was filtered and extracted into DCM. The DCM solution was dried ($MgSO_4$) and evaporated affording a solid (1.24 g). Column chromatography, using hexane/DCM (1:2) as the eluent, yielded *6-bromo-3,5-difluoro-2-phenylethynyl-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* **(51)** (0.23 g, 22%) as white crystals mp 84.7-86.2°C (Found: C, 41.9; H, 1.1; N, 3.1. $C_{16}H_5BrF_9N$ requires C, 41.6; H, 1.1; N, 3.0%); **NMR spectrum no. 51; Mass spectrum no. 51; IR spectrum no. 51** and *2,6-bis(2-phenylethynyl)-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine* **(52)** (0.86g, 78%) as white crystals mp 172.8-173.2°C (Found: C, 59.5; H, 2.0; N, 2.8. $C_{24}H_{10}F_9N$ requires C, 59.6; H, 2.1; N, 2.9%); **NMR spectrum no. 52; Mass spectrum no. 52; IR spectrum no. 52.**

Preparation of Pentasubstituted Pyridines.
General Procedure.

Under an atmosphere of dry nitrogen, sodium methoxide (0.3 g, 5.9 mmol) was added to methanol (35 cm^3) and stirred. To the resulting solution either 6-bromo-3,5-difluoro-2-piperidyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine **(43)** (1.5 g, 3.4 mmol), 6-bromo-3,5-difluoro-2-phenylethynyl-4-(1,2,2,2-tetrafluoro-1-

trifluoromethyl-ethyl)-pyridine (**51**) (1.8 g, 4.0 mmol) or 6-bromo-3,5-difluoro-2-pent-1-ynyl-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (**49**) (1.7 g, 4.0 mmol) was added and then stirred at reflux temperature for 24 h before water (25 cm^3) was added. The mixture was continuously extracted with DCM, dried ($MgSO_4$) and evaporated to yield crude material. The isolation of pure products was achieved by column chromatography, using dichloromethane and hexane (1:1) as the eluent.

From compound (**43**) was obtained *4-[1-(trifluoromethyl)-1,2,2,2-tetrafluoroethyl]-2-bromo-3-fluoro-5-methoxy-6-piperidylpyridine* (**53**) (1.2 g, 78%) a white solid mp 81.1-83.0°C (Found; C, 36.6; H, 2.8; N, 6.0. $C_{14}H_{13}BrF_8N_2O$ requires C, 36.8; H, 2.8; N, 6.1%); **NMR spectrum no. 53; Mass spectrum no. 53; IR spectrum no. 53.**

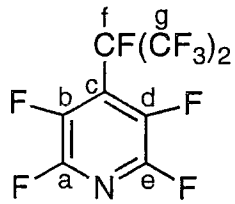
Compound (**51**) gave *4-[1-(trifluoromethyl)-1,2,2,2-tetrafluoroethyl]-2-bromo-3-methoxy-5-fluoro-6-(2-phenylethynyl)pyridine* (**54**) (1.0 g, 54%) a yellow oil bp >300°C (Found: C, 42.6; H, 1.6; N, 2.8. $C_{17}H_8BrF_8NO$ requires C, 43.0; H, 1.7; N, 2.9%); **NMR spectrum no. 54; Mass spectrum no. 54; IR spectrum no. 54.**

Compound (**49**) gave *4-[1-(trifluoromethyl)-1,2,2,2-tetrafluoroethyl]-2-bromo-3-methoxy-5-fluoro-6-pent-1-ynylpyridine* (**55**) (1.5 g, 86%) a yellow oil; bp >300°C; (Found; C, 38.5; H, 2.2; N, 3.2. $C_{14}H_{10}BrF_8NO$ requires C, 38.2; H, 2.3; N, 3.2%); **NMR spectrum no. 55; Mass spectrum no. 55; IR spectrum no. 55.**

Appendix A.

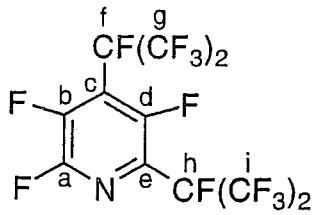
NMR. Data

2,3,5,6-tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (1)



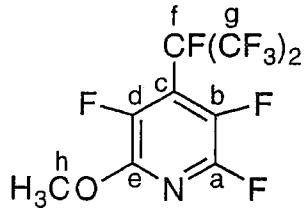
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-74.4	m		6	g
-86.8	br s		2	a and e
-134.9	s		1	b or d
-137.4	s		1	b or d
-180.2	m		1	f
^{13}C				
91.7	d sept	$^1J_{CF}$ 215.5 $^2J_{CF}$ 36.3		f
119.2	d t	$^2J_{CF}$ 22.9 $^2J_{CF}$ 11.9		c
119.6	q d	$^1J_{CF}$ 288.4 $^2J_{CF}$ 27.1		g
143.3	m			b and d
145.8	m			a and e

2,3,5-trifluoro-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (2)



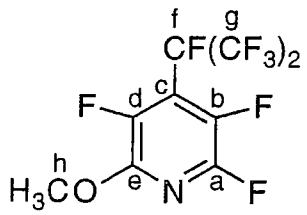
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.7	m		6	g
-75.8	m		6	i
-82.3	m		1	a
-116.0	s		1	b
-123.0	s		1	d
-181.0	m		1	f
-181.4	m		1	h
^{13}C				
91.7	d sept	$^1J_{CF}$ 209.8 $^2J_{CF}$ 36.3		f and h
118.8	brs			c and e
119.6	q d	$^1J_{CF}$ 295.6 $^2J_{CF}$ 14.9		g
119.9	q d	$^1J_{CF}$ 288.4 $^2J_{CF}$ 14.6		i
126.9	brs			b
147.7	d	$^1J_{CF}$ 244.9		d
152.8	d	$^1J_{CF}$ 277.4		a

2,3,5-trifluoro-6-methoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (3)



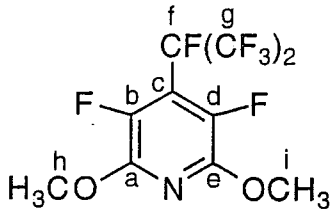
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.1	m		6	g
-91.2 and -92.4	br s		1	a
-134.9 and -137.6	br s		1	d
-146.9 and -150.1	br s		1	b
-179.9	m		1	f
^{1}H				
4.0	s		3	h
^{13}C				
55.2	s			h
91.8	d sept	$^{1}J_{CF}$ 214.4 $^{2}J_{CF}$ 36.2		f
116.5	d t	$^{2}J_{CF}$ 24.4 $^{2}J_{CF}$ 10.7		c
119.8	q d	$^{1}J_{CF}$ 288.6 $^{2}J_{CF}$ 27.6		g
144.0-147.0	br m			a, b, d and e

2,3,5-trifluoro-6-methoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (a low temperature ^{19}F-NMR experiment) (3)



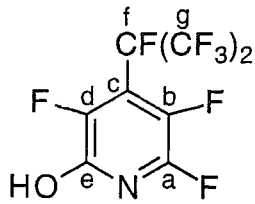
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F (room temp.)				
-75.1	m		6	g
-91.2 and -92.4	br s		1	a
-134.9 and -137.6	br s		1	d
-146.9 and -150.1	br s		1	b
-179.9	m		1	f
^{19}F (-39°C)				
-75.1	m		6	g
-91.7	dd	$^{3}J_{FF}$ 21.8 $^{5}J_{FF}$ 30.4	1	a
-92.69	dd	$^{3}J_{FF}$ 23.3 $^{5}J_{FF}$ 29.4	1	a
-138.4	dd	$^{4}J_{FF}$ 90.3 $^{5}J_{FF}$ 30.5	1	d
-135.7	m		1	d
-147.5	m		1	b
-150.6	dd	$^{4}J_{FF}$ 84.2 $^{3}J_{FF}$ 14.3	1	b
-181.2	dd	$^{4}J_{FF}$ 84.5 $^{4}J_{FF}$ 74.1	1	c

3,5-difluoro-2,6-dimethoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (4)



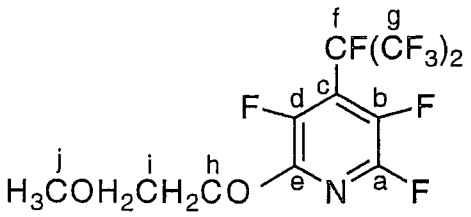
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.3	m		6	g
-145.9	br s		1	b or d
-149.0	br s		1	b or d
-179.9	m		1	f
^{1}H				
4.0	s		6	h and i
^{13}C				
54.2	s			h and i
92.0	d sept	$^{1}J_{CF}$ 213.3 $^{2}J_{CF}$ 35.5		f
114.6	d t	$^{2}J_{CF}$ 21.7 $^{2}J_{CF}$ 10.4		c
120.9	q d	$^{1}J_{CF}$ 288.2 $^{2}J_{CF}$ 27.1		g
134-141.0	br m			b and d
147.6	m			a and e

3,5,6-trifluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridin-2-ol (5)



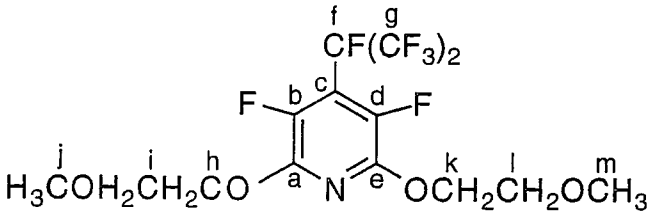
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-71.3	m		6	g
-86.8 and -87.8	br s		1	a
-131.1 and -133.8	s		1	d
-141.6 and -144.8	s		1	b
-176.4	m		1	f
^{1}H				
2.2	s		1	e
^{13}C				
95.5	d sept	$^{1}J_{CF}$ 213.5 $^{2}J_{CF}$ 36.0		f
120.7	m			c
123.3	q d	$^{1}J_{CF}$ 287.0 $^{2}J_{CF}$ 27.5		g
140.0-150.0	br m			a, b, d and e

3,5,6-trifluoro-2-(methoxyethanoxy)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl]-pyridine (6)



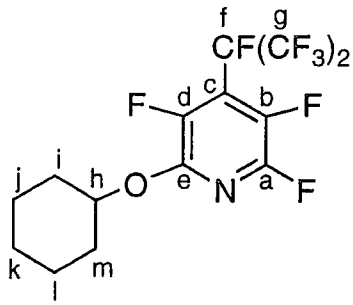
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.0	m		6	g
-90.4 and -91.6	br s		1	a
-133.4 and -136.1	br s		1	d
-146.1 and -149.1	br s		1	b
-180.0	m		1	f
^{1}H				
3.4	s		3	j
3.8	d t	$^{2}J_{HH}$ 5.2 $^{3}J_{HH}$ 1.2	2	i
4.5	d t	$^{2}J_{HH}$ 5.2 $^{3}J_{HH}$ 1.2	2	h
^{13}C				
58.9	s			j
63.7	s			i
69.9	s			h
91.6	d sept	$^{1}J_{CF}$ 214.2 $^{2}J_{CF}$ 33.9		f
116.4	d t	$^{2}J_{CF}$ 24.4 $^{2}J_{CF}$ 12.9		c
119.9	q d	$^{1}J_{CF}$ 281.6 $^{2}J_{CF}$ 27.6		g
143.6-146.1	br m			a, b, d and e

2,6-bis(2-methoxyethanoxy)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-pyridine (7)



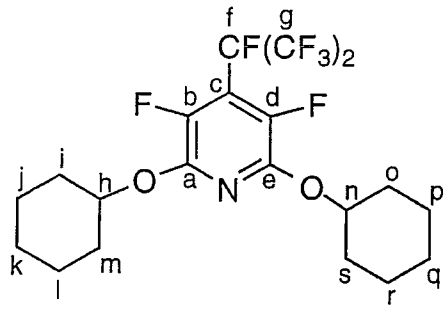
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.6	m		6	g
-144.5	br s		1	b or d
-147.6	br s		1	b or d
-180.3	m		1	f
^{1}H				
3.4	s		6	j and m
3.7	d t	$^{2}J_{HH}$ 5.2 $^{3}J_{HH}$ 1.2	4	i and l
4.5	d t	$^{2}J_{HH}$ 5.2 $^{3}J_{HH}$ 1.2	4	h and k
^{13}C				
58.9	s			j and m
66.5	s			i and l
70.3	s			h and k
91.9	d sept	$^{1}J_{CF}$ 212.8 $^{2}J_{CF}$ 35.8		f
114.8	d t	$^{2}J_{CF}$ 22.1 $^{2}J_{CF}$ 11.1		c
119.9	q d	$^{1}J_{CF}$ 288.6 $^{2}J_{CF}$ 28.7		g
134.0-140.0	br m			b and d
146.2	br s			a and e

6-cyclohexyloxy-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-pyridine (8)



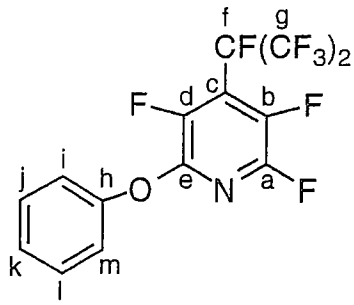
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.3	m		6	g
-90.8 and -91.9	br s		1	a
-134.1 and -136.7	br s		1	d
-147.5 and -150.6	br s		1	b
-180.0	m		1	f
^{1}H				
5.0	t t	$^{3}J_{HH}$ 17.9 $^{3}J_{HH}$ 3.9	1	h
1.7	m		10	i-m
^{13}C				
23.6	s			j and l
25.4	s			k
31.4	s			i and m
77.2	s			h
91.9	d sept	$^{1}J_{CF}$ 214.0 $^{2}J_{CF}$ 38.1		f
116.4	d t	$^{2}J_{CF}$ 22.5 $^{2}J_{CF}$ 9.2		c
119.9	q d	$^{1}J_{CF}$ 288.7 $^{2}J_{CF}$ 27.6		g
143.9-146.5	br m			a, b, d and e

2,6-dicyclohexyloxy-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-pyridine (9)



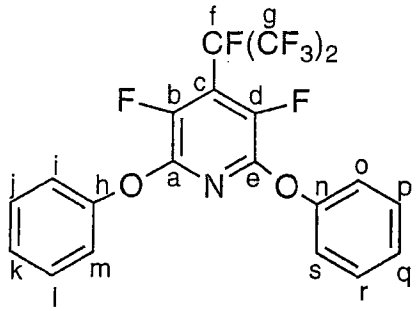
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.0	m		6	g
-145.4	br s		1	b or d
-148.5	br s		1	b or d
-180.0	m		1	f
^{1}H				
4.8	t t	$^{3}J_{HH}$ 17.9 $^{3}J_{HH}$ 3.9	2	h and n
1.6	m		20	i-m and o-s
^{13}C				
23.9	s			j,l,p and r
25.5	s			k and q
31.7	s			i,m,o and s
75.8	s			h and n
91.9	d sept	$^{1}J_{CF}$ 212.8 $^{2}J_{CF}$ 35.7		f
114.3	d t	$^{2}J_{CF}$ 21.6 $^{2}J_{CF}$ 14.3		c
120.1	q d	$^{1}J_{CF}$ 288.3 $^{2}J_{CF}$ 27.7		g
134.0-140.0	br m			b and d
145.9	m			a and e

2,3,5-trifluoro-6-phenoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (10)



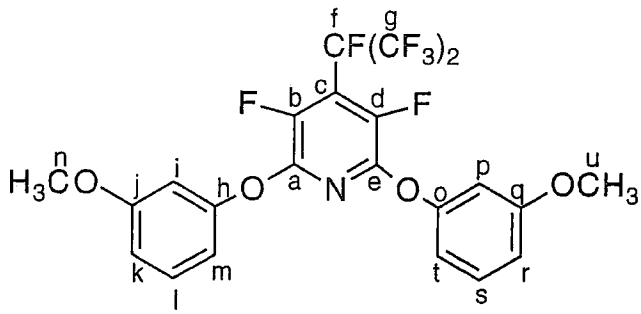
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-74.9	m		6	g
-88.6 and -89.6	br s		1	a
-133.1 and -135.8	br s		1	d
-142.0 and -145.0	br s		1	b
-180.1	m		1	f
^{1}H				
7.1-7.6	m		5	i-m
^{13}C				
91.9	d sept	$^{1}J_{CF}$ 214.3 $^{2}J_{CF}$ 36.2		f
117.5	m	$^{2}J_{CF}$ 10.7		c
119.9	q d	$^{1}J_{CF}$ 292.7 $^{2}J_{CF}$ 27.1		g
120.9	s			i and m
125.9	s			k
129.8	s			j and l
135.0-140.0	br m			b and d
143.8	br s			e
146.2	br s			a
152.3	s			h

3,5-difluoro-2,6-diphenoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (11)



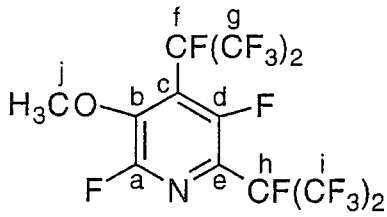
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.0	m		6	g
-138.7	br s		1	b
-141.6	br s		1	d
-179.0	m		1	f
^{1}H				
7.0-7.4	m		10	i-m and o-s
^{13}C				
92.1	d sept	$^{1}J_{CF}$ 213.6 $^{2}J_{CF}$ 35.8		f
115.9	d t	$^{2}J_{CF}$ 20.7 $^{2}J_{CF}$ 11.0		c
120.1	q d	$^{1}J_{CF}$ 291.7 $^{2}J_{CF}$ 27.2		g
120.8	s			i,m,o and s
125.1	s			k and q
129.2	s			j,l,p and r
137.0-142.0	br m			b and d
145.3	br s			a and e
152.3	s			h and n

2,6-bis-(3-methoxyphenoxy)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl]pyridine (13)



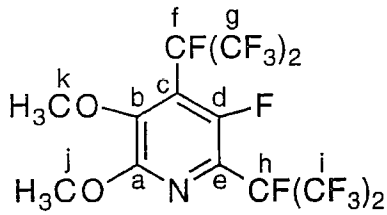
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.6	m		6	g
-138.5 and -141.5	br s		2	b and d
-180.0	m		1	f
^{1}H				
3.7	s		6	n and u
6.6	m		4	i,m,p and t
6.7	m	$^{3}J_{HH}$8.4	2	k and r
7.2	m	$^{3}J_{HH}$ 8.4	2	l and s
^{13}C				
55.4	s			n and u
92.2	d sept	$^{1}J_{CF}$ 212.8 $^{2}J_{CF}$ 57.6		f
106.9	s			l and s
111.4	s			j and q
112.9	s			h and o
119.5	d t	$^{2}J_{CF}$ 22.1 $^{2}J_{CF}$ 11.0		c
120.2	q d	$^{1}J_{CF}$ 288.0 $^{2}J_{CF}$ 26.5		g
129.9	s			k and r
137.0-140.0	br m			b and d
145.2	br s			a and e
154.0	s			m and t
160.7	s			i and p

2,5-difluoro-3-methoxy-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (14)



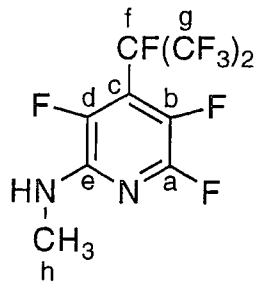
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-71.3	s		12	g and i
-72.4	m		1	a
-112.5 and -115.2	m		1	d
-175.4	m		1	f
-180.6	m		1	h
^{1}H				
4.15 and 4.17	s		3	j
^{13}C				
61.7 and 62.8				j
91.9	m			f and h
120.1	q d	$^{1}J_{CF}$ 287.0 $^{2}J_{CF}$ 9.5		g
120.3	q d	$^{1}J_{CF}$ 286.0 $^{2}J_{CF}$ 9.6		i
120.6	brm			c and e
144.0	dm	$^{2}J_{CF}$ 22.8		b
149.2	d	$^{1}J_{CF}$ 245.5		d
155.7	d	$^{1}J_{CF}$ 279.4		a

5-fluoro-2,3-dimethoxy-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (15)



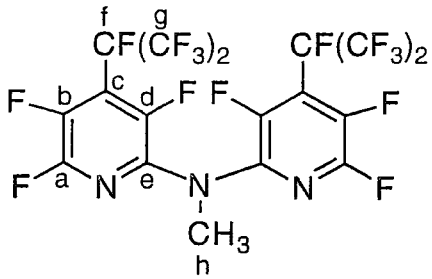
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.1	s		12	g and i
-125.7	m		1	d
-129.1	dd	$^4J_{FF}$ 107.6 $^4J_{FF}$ 56.4	1	d
-177.9	d	$^4J_{FF}$ 107.2	1	f
-180.4	m		1	f
-184.6 and -184.9	d d	$^4J_{FF}$ 69.6 $^4J_{FF}$ 56.4	1	h
^1H				
3.95	s		6	j and k
^{13}C				
54.6 and 54.7	s			j
61.0 and 61.8	s			k
91.5	d sept	$^1J_{CF}$ 231.6 $^2J_{CF}$ 32.1		f
92.9	d sept	$^1J_{CF}$ 211.7 $^2J_{CF}$ 35.1		h
118.3	dd	$^2J_{CF}$ 20.0 $^2J_{CF}$ 9.6		c
120.4	q d	$^1J_{CF}$ 296.7 $^2J_{CF}$ 27.1		g and i
123.8	dd	$^2J_{CF}$ 24.3 $^2J_{CF}$ 14.5		e
144.8	d	$^3J_{CF}$ 6.0		b
147.3	s			b
149.0 and 151.3	s			a
152.8	dd	$^1J_{CF}$ 271.5 $^3J_{CF}$ 33.1		d

Methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amine (16)



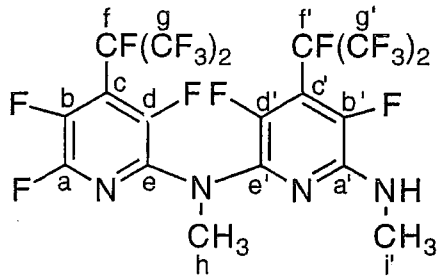
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.5	m		6	g
-91.3 and -92.5	br s		1	a
-139.3 and -141.9	br s		1	d
-156.1 and -159.3	br s		1	b
-180.3	m		1	f
^{1}H				
2.96	d	$^{3}J_{HH}$ 4.8	3	h
4.76	br s		1	h
^{13}C				
28.2	s			h
91.9	d sept	$^{1}J_{CF}$ 215.2 $^{2}J_{CF}$ 35.5		f
114.2	m			c
120.1	q d	$^{1}J_{CF}$ 285.7 $^{2}J_{CF}$ 27.1		g
132.0-149.0	br m			a, b, d and e

Bis{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}methylamine (17)



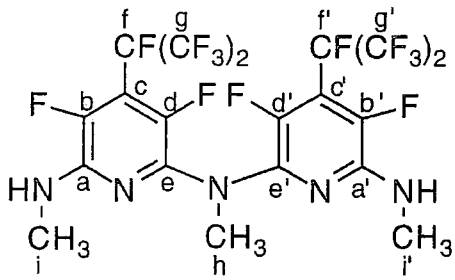
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.5	m		12	g
-86.6 and -87.8	br s		2	a
-124.0 and -126.3	br s		2	d
-138.8 and -141.8	br s		2	b
-179.9	m		2	f
^{1}H				
3.5	m		3	h
^{13}C				
37.8	s			h
91.9	d sept	$^{1}J_{CF}$ 213.7 $^{2}J_{CF}$ 40.8		f
117.0	m			c
119.9	q d	$^{1}J_{CF}$ 293.8 $^{2}J_{CF}$ 27.1		g
137.0-149.0	br m			a, b, d and e

{3,5-difluoro-6-(methylamino)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}methyl{3,5,6-trifluoro-4[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amine (18)



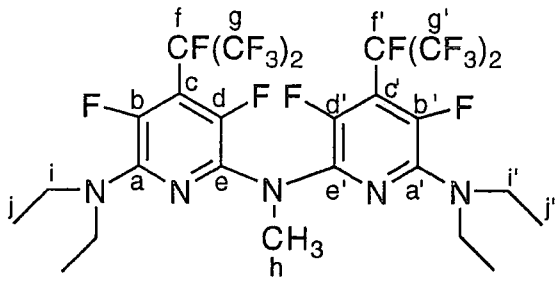
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.5 and -75.6	m		12	g and g'
-88.6 and -89.7	br s		1	a
-125.1	br s		1	d or d'
-130.0- -148.0	m		3	b, b', d or d'
-180.0	br s		2	f and f'
^{1}H				
2.9	m		3	i'
3.5	s		3	h
4.7	br s		1	i'
^{13}C				
27.7	s			h
37.4	s			i'
91.8	d sept	$^{1}J_{CF}$ 215.1 $^{2}J_{CF}$ 37.8		f and f'
111.9	br s			c and c'
119.7	q d	$^{1}J_{CF}$ 289.9 $^{2}J_{CF}$ 21.4		g and g'
138.0-148.0	br m			a, a', b, b', d, d', e and e'

Bis{3,5-difluoro-6-(methylamino)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}methylamine (19)



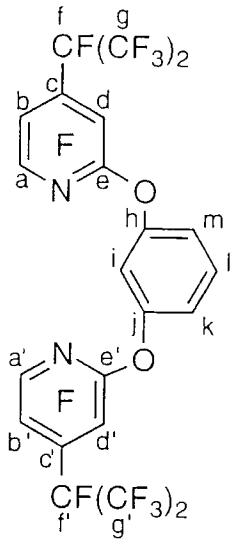
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.6	m		12	g and g'
-140.0- -146.0	m		4	b, b', d and d'
-179.8	br s		2	f and f'
^{1}H				
2.9	d	$^{3}J_{HH}$ 3.2	6	i and i'
3.5	s		3	h
4.6	br s		2	i and i'
^{13}C				
27.8	s			h
36.9	s			i and i'
92.2	d sept	$^{1}J_{CF}$ 211.8 $^{2}J_{CF}$ 35.1		f and f'
111.9	br s			c and c'
120.3	q d	$^{1}J_{CF}$ 288.4 $^{2}J_{CF}$ 27.1		g and g'
139.5-144.5	br m			a, a', b, b', d, d', e and e'

Bis{6-(diethylamino)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}methylamine (20)



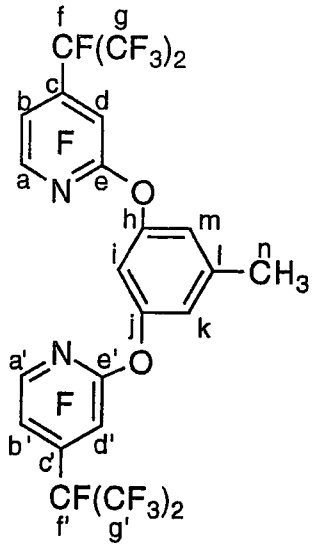
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.5	m		12	g and g'
-135.0 and -137.0	br s		2	d and d'
-139.0 and -142.0	br s		2	b and b'
-179.4	br s		2	f and f'
^{1}H				
1.16	m		12	j and j'
3.41	m		8	i and i'
3.48	s		3	h
^{13}C				
13.5	s			j and j'
36.9	s			h
44.3	m			i and i'
92.2	m			f and f'
113.1	m			c and c'
120.2	q d	$^{1}J_{CF}$ 288.6 $^{2}J_{CF}$ 27.2		g and g'
136.0-148.0	br m			a, a', b, b', d, d', e and e'

2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl]-6-(3-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl](2-pyridyloxy)} phenoxy)pyridine (21)



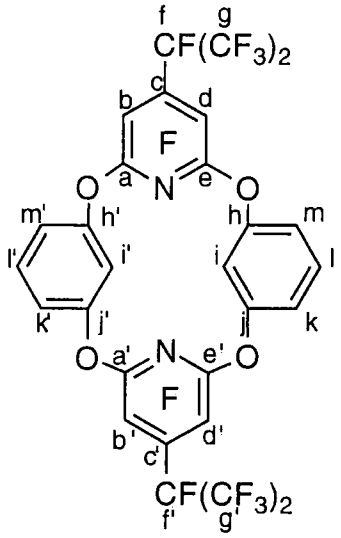
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.2	m		12	g and g'
-87.9 and -89.0	br s		2	a and a'
-132.8 and -135.3	brs		2	b and b'
-140.9 and -143.6	brs		2	d and d'
-180.3	m		2	f and f'
^{1}H				
7.07	s		1	i
7.14	dd	$^{3}J_{HH}$ 8.4 $^{4}J_{HH}$ 2.0	2	k and m
7.5	t	$^{3}J_{HH}$ 8.4	1	l
^{13}C				
91.9	d sept	$^{1}J_{CF}$ 212.9 $^{2}J_{CF}$ 38.5		f and f'
114.6	s			i
118.0	m	$^{2}J_{CF}$ 9.6		c and c'
118.4	s			k and m
119.9	q d	$^{1}J_{CF}$ 289.6 $^{2}J_{CF}$ 26.7		g and g'
130.9	s			l
139.0-145.8	br m			a, a', b, b', d, d', e and e'
153.1	s			h and j

2,3,5-trifluoro-6-(5-methyl-3-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}phenoxy)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (24)



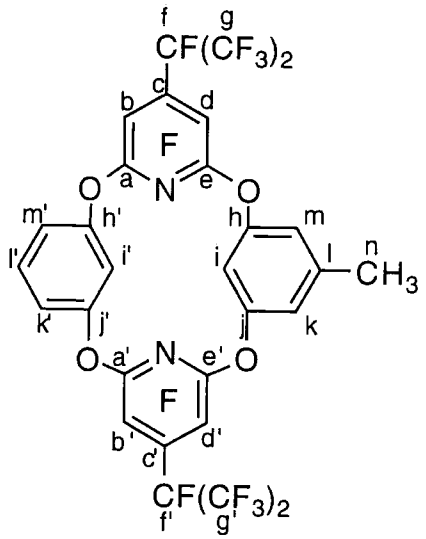
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-76.2	m		12	g and g'
-90.8 and -91.9	br s		2	a and a'
-135.2 and -137.7	brs		2	b and b'
-143.8 and -146.4	brs		2	d and d'
-180.8	m		2	f and f'
^{1}H				
2.4	s		3	n
7.1	m		3	i, k and m
^{13}C				
20.7	s			n
92.1	d sept	$^{1}J_{CF}$ 213.2 $^{2}J_{CF}$ 35.8		f and f'
111.2	s			i
116.7	m			c and c'
119.0	s			k and m
120.0	q d	$^{1}J_{CF}$ 288.2 $^{2}J_{CF}$ 27.1		g and g'
141.9	s			l
142.0-144.0	br m			a, a',b, b', d, d', e and "
153.6	s			h and j

26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(25),3,5,7(26),9,11,13 (27),15,17,19(28),21,23-dodecaene (25)



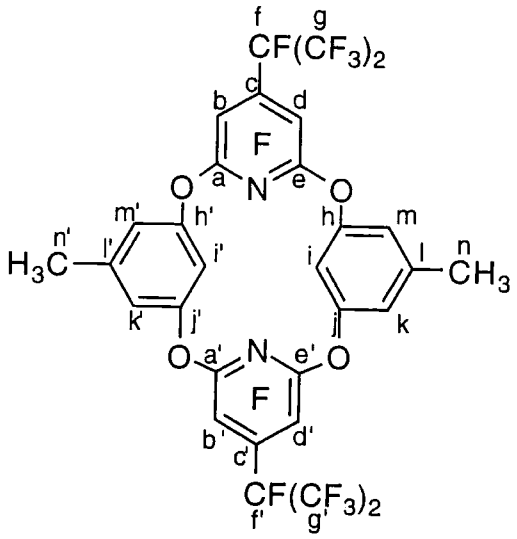
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.3	m		12	g and g'
-140.8 and -143.7	brs		4	b, b', d and d'
-180.1	m		2	f and f'
^{1}H				
6.69	s		2	i and i'
6.86	m		4	k, k', m and m'
7.27	t	$^{3}J_{HH}$ 9.6	2	l and l'
^{13}C				
91.9	d sept	$^{1}J_{CF}$ 214.4 $^{2}J_{CF}$ 24.8		f and f'
116.2	s			i and i'
119.3	m			c and c'
119.5	s			k, k', m and m'
119.9	q d	$^{1}J_{CF}$ 288.6 $^{2}J_{CF}$ 27.5		g and g'
130.4	s			l and l'
139.0-146.0	br m			a, a', b, b', d, d', e and e'
152.8	s			h, h' j and j'

26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-11-methyl-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(25),3,5,7(26),9,11,13 (27),15,17,19(28),21,23-dodecaene (26)



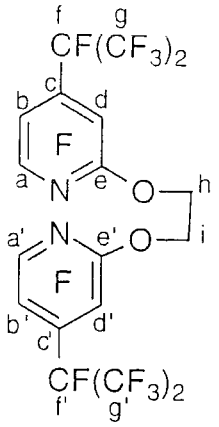
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.3	m		12	g and g'
-140.7 and -143.6	brs		4	b, b', d and d'
-180.1	m		2	f and f'
^{1}H				
2.25	s		3	n
6.67	s		2	i and i'
6.87	m		4	k, k', m and m'
7.29	t	$^{3}J_{HH}$ 8.0	2	l'
^{13}C				
21.1	s			n
91.9	d sept	$^{1}J_{CF}$ 214.0 $^{2}J_{CF}$ 35.9		f and f'
112.7	s			i
116.1	s			i'
119.4	m			c and c'
119.95	s			k, k', m and m'
119.99	q d	$^{1}J_{CF}$ 288.3 $^{2}J_{CF}$ 27.2		g and g'
130.2	s			l
138.0-146.0	br m			b, b', d and d'
141.0	s			l'
146.0	br s			a, a', e and e'
152.7	s			h and j
152.9	s			h' and j'

26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-11,23-dimethyl-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(25),3,5,7(26),9,11,13 (27),15,17,19(28),21,23-dodecaene (27)



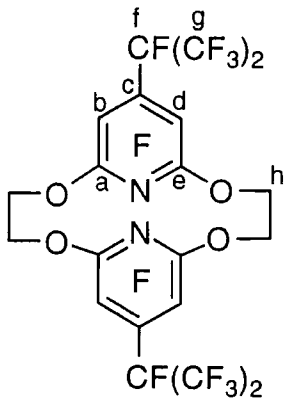
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.3	m		12	g and g'
-140.7 and -144.0	brs		4	b, b', d and d'
-180.2	m		2	f and f'
^{1}H				
2.3	s		6	n and n'
6.5	s		2	i and i'
6.7	m		4	k, k', m and m'
^{13}C				
21.1	s			n and n'
91.9	d sept	$^{1}J_{CF}$ 213.6 $^{2}J_{CF}$ 35.5		f and f'
112.7	s			i and i'
116.1	m			c and c'
119.8	s			k, k', m and m'
119.9	q d	$^{1}J_{CF}$ 281.7 $^{2}J_{CF}$ 28.1		g and g'
136.0-140.0	br m			b, b', d and d'
141.0	s			l and l'
146.0	br s			a, a', e and e'
152.6	s			h, h' j and j'

2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-6-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)ethoxy}pyridine) (28)



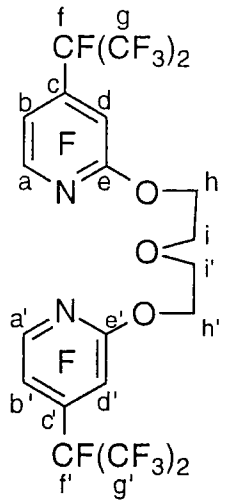
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.6	m		12	g and g'
-90.6 and -91.8	s		2	a and a'
-134.2 and -137.7	s		2	b and b'
-145.4 and -148.3	brs		2	d and d'
-180.5	m		2	f and f'
^{1}H				
4.8	s		4	h and i
^{13}C				
65.6	s			h and i
91.8	d sept	$^{1}J_{CF}$ 214.9 $^{2}J_{CF}$ 38.2		f and f'
117.0	m			c and c'
120.3	q d	$^{1}J_{CF}$ 288.5 $^{2}J_{CF}$ 27.1		g and g'
132.0-146.2	br m			a, a',b, b', d, d', e and e'

19,20-diaza-8,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11,14-tetraoxatricyclo[13.3.1.1<6,10>]icosa-1(18),6(20),7,9,15(19),16-hexaene (29)



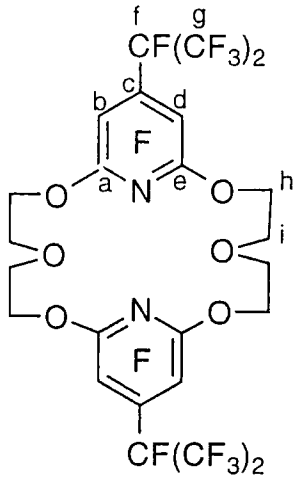
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.3	m		12	g
-143.4 and -146.4	br s		4	b and d
-180.2	m		2	f
^{1}H				
4.7	br s		8	h
^{13}C				
62.0	s			h
90.0-92.0	m			f
116.2	m			c
120.1	q d	$^{1}J_{CF}$ 288.7 $^{2}J_{CF}$ 27.2		g
130.0-144.0	br m			a,b,d and e

2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)oxy}-1-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1(trifluoromethyl)ethyl](2-pyridyloxy)}ethoxy)ethane (30)



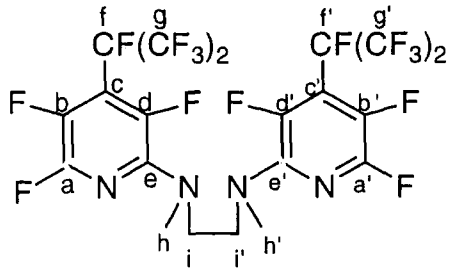
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.8	m		12	g and g'
-91.2 and -91.8	br s		2	a and a'
-134.5 and -137.2	br s		2	b and b'
-146.6 and -149.9	br s		2	d and d'
-180.6	m		2	f and f'
^{1}H				
3.9	t	$^{3}J_{HH}$ 6.8	4	i and i'
4.5	t	$^{3}J_{HH}$ 6.8	4	h and h'
^{13}C				
67.5	s			i and i'
69.2	s			h and h'
91.9	d sept	$^{1}J_{CF}$ 213.5 $^{2}J_{CF}$ 36.0		f and f'
116.9	m			c and c'
119.9	q d	$^{1}J_{CF}$ 287.0 $^{2}J_{CF}$ 26.9		g and g'
132.0-146.8	br m			a, a',b, b', d, d', e and e'

25,26-diaza-11,23-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-10,12,22,24-tetrafluoro-2,5,8,14,17,20-hexaoxatricyclo[19.3.1.1<9,13>]hexacosa-1(24),9(26),10,12,21(25),22-hexaene (31)



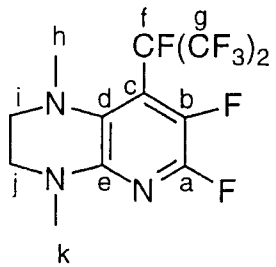
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.5	m		12	g
-144.4 and -147.6	br s		4	b and d
-180.2	m		2	f
^{1}H				
3.9	t	$^{3}J_{HH}$ 5.6	4	i
4.6	t	$^{3}J_{HH}$ 5.2	4	h
^{13}C				
65.8	s			i
69.4	s			h
92.1	d sept	$^{1}J_{CF}$ 213.6 $^{2}J_{CF}$ 35.5		f
115.2	dt	$^{2}J_{CF}$ 22.1 $^{2}J_{CF}$ 10.3		c
120.2	q d	$^{1}J_{CF}$ 288.8 $^{2}J_{CF}$ 27.5		g
144.0-147.0	br m			a,b,d and e

Methyl[2-(methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amino)ethyl]{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amine (32)



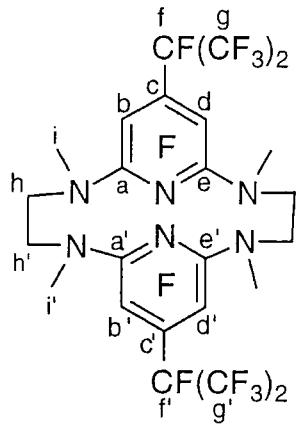
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.6	m		12	g and g'
-89.2 and -90.4	s		2	a and a'
-130.9 and -133.1	s		2	d and d'
-151.2 and -154.6	m		2	b and b'
-179.9	m		2	f and f'
^{1}H				
3.1	s		6	h and h'
3.6	s		4	i and i'
^{13}C				
38.5	s			i and i'
49.8	s			h and h'
92.2	d sept	$^{1}J_{CF}$ 212.8 $^{2}J_{CF}$ 34.9		f and f'
116.5	m			c and c'
120.1	q d	$^{1}J_{CF}$ 289.1 $^{2}J_{CF}$ 27.1		g and g'
130.0-147.0	br m			a, a', b, b', d, d', e and e'

2,3-difluoro-5,8-dimethyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5,6,7,8-tetrahydroquinoline (33)



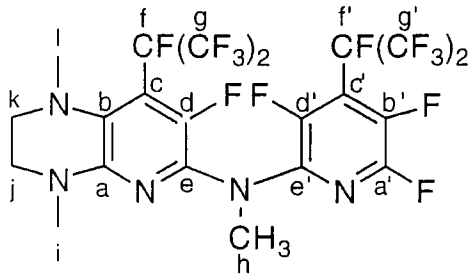
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-70.0 and -80.0	broad overlapping m		6	g
-94.4	m		1	a
-155.7	br s		1	b
-179.7	m		1	f
^{1}H				
2.63	s		3	k
2.98	s		2	j
3.12	s		3	h
3.48	s		2	i
^{13}C				
37.0	s			k
42.9	s			j
45.4	s			h
46.8	s			i
90.0-94.0	br m			f
119.0-120.5	br m			c
120.7	q d	$^{1}J_{CF}$ 288.2 $^{2}J_{CF}$ 29.4		g
128.0-149.0	br overlapping m			a, b, d and e

2,5,11,14,19,20-hexaaza-8,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11,14-tetramethyltricyclo[13.3.1.1<6,10>]icosa-1(18),6(20),7,9,15,(19),16-hexaene (34)



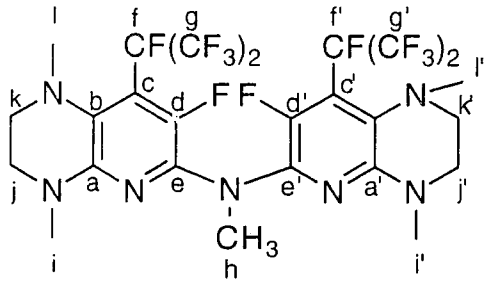
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-76.1	m		12	g and g'
-144.8 and -147.8	s		4	b, b', d and d'
-179.9	m		2	f and f'
^{1}H				
2.8	m		12	i and i'
3.2	m		8	h and h'
^{13}C				
37.9	m			h and h'
48.3	s			i and i'
88.0-92.0	broad m			f and f'
113.9	m			c and c'
120.6	q d	$^{1}J_{CF}$ 286.7 $^{2}J_{CF}$ 27.9		g and g'
130.0-145.0	br m			a, a', b, b', d, d', e and e'

{7-fluoro-1,4-dimethyl-8-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](1,2,3,4-tetrahydropyridino[2,3-b]pyrazin-6-yl)}methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl}amine (35)



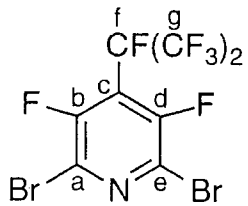
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.5	m		12	g and g'
-89.1 and -90.4	br s		1	a'
-125.6 and -126.5	s		1	d'
-140.5	s		1	b'
-145.7 and -148.7	s		1	d
-179.0	br s		2	f and f'
^{1}H				
2.6	s		3	i
2.92	s		2	j
2.98	s		3	l
3.38	m		2	k
3.44	m		3	h
^{13}C				
36.8	s			i
37.5	s			j
42.9	m			k
45.7	m			l
47.0	m			h
90.0-94.0	m			f and f'
119.0-119.5	m			c and c'
120.4	q d	$^{1}J_{CF}$ 220.1 $^{2}J_{CF}$ 29.8		g and g'
128.4				a
138.0-148.0	br m			a', b, b', d, d', e and e'

Bis{7-fluoro-1,4-dimethyl-8-[1,2,2,2-trifluoromethyl)ethyl](1,2,3,4-tetrahydropyridino[2,3-b]pyrazin-6-yl)}methylamine (36)



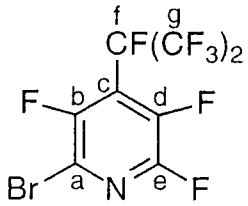
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-70.8 and -80.0	br m		12	g and g'
-141.3	m		2	d and d'
-178.9	s		2	f and f'
^{1}H				
2.6	s		6	i
2.99	s		4	j
3.1	s		6	l
3.44	s		4	k
3.51	s		3	h
^{13}C				
36.9	s			i and i'
37.3	s			j and j'
43.1	s			h and h'
45.6	m			k and k'
47.5	m			l and l'
94.3	d sept	$^{1}J_{CF}$ 181.9 $^{2}J_{CF}$ 33.9		f and f'
117.4	d d	$^{2}J_{CF}$ 19.1 $^{2}J_{CF}$ 11.8		c and c'
120.8	q d	$^{1}J_{CF}$ 282.7 $^{2}J_{CF}$ 28.6		g and g'
124.9	s			a and a'
137.6 and 140.1	s			b and b'
140.8	d	$^{2}J_{CF}$ 13.7		e and e'
147.6	s			d and d'

2,6-dibromo-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (37)



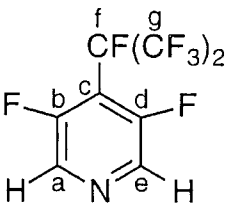
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.8	m		6	g
-103.7 and -105.8	s		2	b and d
-180.0	m		1	f
^{13}C				
91.5	d sept	$^{1}J_{CF}$ 216.3 $^{2}J_{CF}$ 36.0		f
114.1	d t	$^{2}J_{CF}$ 22.5 $^{2}J_{CF}$ 13.3		c
119.7	q d	$^{1}J_{CF}$ 288.7 $^{2}J_{CF}$ 27.1		g
124.0-126.2	broad overlapping m			a and e
148.0-155.0	broad overlapping m			b and d

6-bromo-2,3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (38)



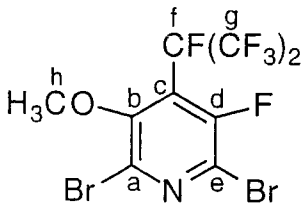
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.7	m		6	g
-84.3 and -85.4	br m		1	e
-106.8 and -109.2	br m		1	b
-131.3 and -134.2	br m		1	d
-180.4	s		1	f
^{13}C				
91.7	d sept	$^{1}J_{CF}$ 215.1 $^{2}J_{CF}$ 37.3		f
117.2	m			c
119.8	q d	$^{1}J_{CF}$ 291.7 $^{2}J_{CF}$ 27.2		g
121.0-123.0	br s			a
138.0-156.0	broad overlapping m			b, d and e

2,6-dihydrido-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (39)



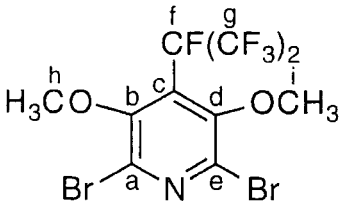
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.9	m		6	g
-120.4 and -123.3	s		2	b and d
-180.4	m		1	f
^{1}H				
8.5	s		2	a and e
^{13}C				
91.6	d sept	$^{1}J_{CF}$ 212.8 $^{2}J_{CF}$ 36.3		f
112.1	dt	$^{2}J_{CF}$ 21.4 $^{2}J_{CF}$ 11.8		c
119.9	q d	$^{1}J_{CF}$ 284.9 $^{2}J_{CF}$ 27.4		g
136.4	broad s			a and e
154.0-158.4	broad overlapping m			b and d

2,6-dibromo-3-fluoro-5-methoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (40)



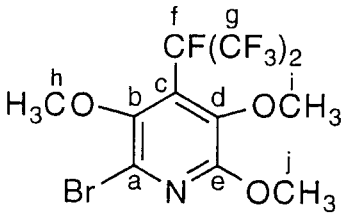
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-74.6	m		6	g
-104.3	s		1	d
-106.5	d	$^4J_{FF}$ 95.9	1	d
-176.3	d	$^4J_{FF}$ 94.5	1	f
-181.5	s		1	f
^1H				
3.88	s		3	h
3.99	s		3	h
^{13}C				
62.3	s			h
63.2	s			h
92.2	d sept	$^1J_{CF}$ 215.8 $^2J_{CF}$ 34.7		f
119.9	q d	$^1J_{CF}$ 289.1 $^2J_{CF}$ 27.4		g
120.1	m			a
124.4	m			c
129.6	s			e
134.1	s			b
151.7	d d	$^1J_{CF}$ 277.6 $^3J_{CF}$ 210.9		d
152.7	d	$^1J_{CF}$ 153.8		d

2,6-dibromo-3,5-dimethoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (41)



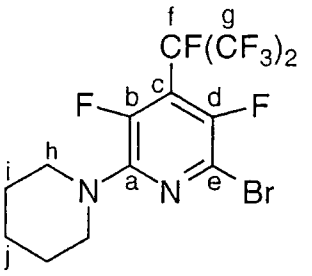
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-73.9	m		6	g
-177.2	m		1	f
^{1}H				
3.9	s		6	h and i
4.0	s		6	h and i
^{13}C				
62.3	s			h and i
63.2	s			h and i
93.3	d sept	$^{1}J_{CF}$ 212.6 $^{2}J_{CF}$ 35.1		f
119.9	q d	$^{1}J_{CF}$ 291.7 $^{2}J_{CF}$ 27.9		g
120.5	m			a
126.4	d	$^{2}J_{CF}$ 19.8		c
129.4	s			a and e
133.1	s			a and e
152.0	m			b and d
153.8	s			b and d

2-bromo-3,5,6-trimethoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (42)



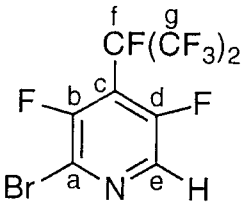
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-74.6	m		6	g
-176.7	m		1	f
-179.3			1	f
^{1}H				
3.8	s		3	h
3.9	s		3	i
4.0	s		3	j
^{13}C				
54.4	s			h
54.6	s			h
60.4	s			i
61.5	s			i
62.4	s			j
62.5	s			j
93.5	d sept	$^{1}J_{CF}$ 210.5 $^{2}J_{CF}$ 35.1		f
120.5	q d	$^{1}J_{CF}$ 286.6 $^{2}J_{CF}$ 28.3		g
123.6	d	$^{2}J_{CF}$ 20.2		c
124.9	d	$^{2}J_{CF}$ 18.7		c
125.4	s			a
127.8	s			a
141.2	m			b
146.9	s			d
152.6	s			e

6-bromo-3,5-difluoro-2-piperidyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (43)



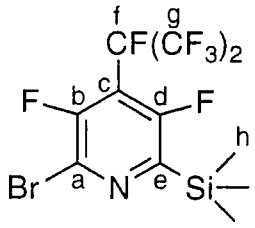
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-73.3	m		6	g
-117.6 and -122.8	broad m		2	b and d
-177.3	m		1	f
^{1}H				
1.6	s		3	i and j
3.99	s		2	h
^{13}C				
24.4	s			j
25.6	s			h
49.2	s			i
91.8	d sept	$^{1}J_{CF}$ 214.3 $^{2}J_{CF}$ 38.2		f
113.9	br s			c
120.2	q d	$^{1}J_{CF}$ 286.7 $^{2}J_{CF}$ 27.5		g
142.0-149.0	broad overlapping m			a,b,d and e

2-bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl]pyridine (44)



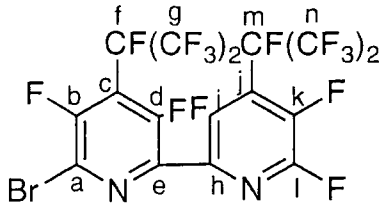
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-71.2	m		6	g
-97.0 and -100.0	s		1	b
-116.0 and -119.0	s		1	d
-175.6	m		1	f
^{1}H				
8.27	s		1	e
^{13}C				
91.5	d sept	$^{1}J_{CF}$ 214.4 $^{2}J_{CF}$ 36.2		f
113.8	dt	$^{2}J_{CF}$ 22.4 $^{2}J_{CF}$ 12.3		c
119.8	q d	$^{1}J_{CF}$ 290.6 $^{2}J_{CF}$ 27.5		g
127.0	broad s			e
135.4	broad s			a
150.0-158.0	broad overlapping m			b and d

2-{bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl](2-pyridyl)}-2-methyl-2-silapropane (45)



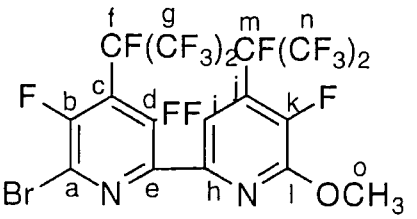
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-73.4	m		6	g
-100.4 and -103.0	s		1	b
-108.6 and -110.6	s		1	d
-177.3	m		1	f
^{1}H				
0.38	s		1	h
^{13}C				
-1.8	s			h
91.8	d sept	$^{1}J_{CF}$ 214.1 $^{2}J_{CF}$ 36.3		f
111.9	m			c
120.1	q d	$^{1}J_{CF}$ 288.9 $^{2}J_{CF}$ 27.1		g
128.2	broad s			e
151.8	broad s			a
154.0-160.0	broad overlapping m			b and d

2-bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl]-6-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}pyridine (46)



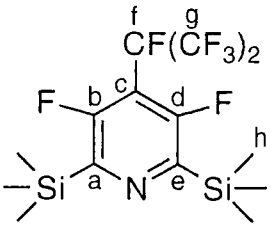
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.2	m		12	g and n
-82.9 and -83.8	br m		1	l
-97.3 and -99.5	m		1	k
-115.0 and -119.8	m		2	d and i
-124.7 and -127.5	m		1	b
-179.6	m		2	f and m
^{13}C				
91.8	d sept	$^{1}J_{CF}$ 215.2 $^{2}J_{CF}$ 35.5		f and m
114.8	dt	$^{2}J_{CF}$ 35.2 $^{2}J_{CF}$ 14.1		c
117.2	m			j
119.8	q d	$^{1}J_{CF}$ 289.7 $^{2}J_{CF}$ 30.5		g and n
127.0-159.0	broad overlapping m			a,b,d,e,h,i,k and l

2-{6-bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl](2-pyridyl)}{3,5,-difluoro-6-methoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (47)



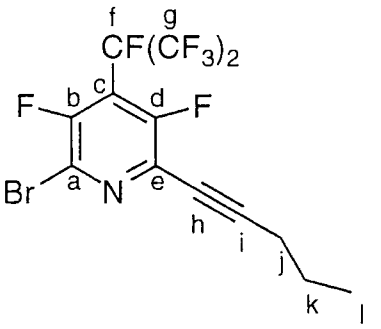
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.4	m		12	g and n
-97.3 and -99.5	m		1	k
-115.2 and -119.6	m		2	d and i
-124.7 and -127.1	m		1	b
-179.9	m		2	f and m
^{1}H				
4.0	s		3	o
^{13}C				
62.3	s			o
91.8	d sept	$^{1}J_{CF}$ 214.9 $^{2}J_{CF}$ 35.1		f and m
114.4	dt	$^{2}J_{CF}$ 34.9 $^{2}J_{CF}$ 14.3		c
117.2	m			j
119.9	q d	$^{1}J_{CF}$ 289.2 $^{2}J_{CF}$ 30.1		g and n
127.0-159.0	broad overlapping m			a,b,d,e,h,i,k and l

2-{6-(1,1-dimethyl-1-silaethyl)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl](2-pyridyl)}-2-methyl-2-silapropane (48)



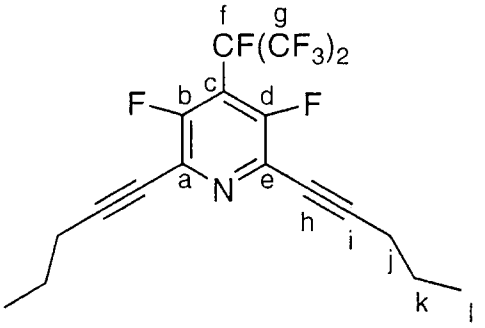
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-73.4	m		6	g
-111.4 and -114.3	s		2	b and d
-179.6	m		1	f
^{1}H				
0.38	s		1	h
^{13}C				
-1.8	s			h
92.1	d sept	$^{1}J_{CF}$ 212.6 $^{2}J_{CF}$ 35.5		f
107.7	dt	$^{2}J_{CF}$ 21.8 $^{2}J_{CF}$ 13.3		c
120.4	q d	$^{1}J_{CF}$ 288.9 $^{2}J_{CF}$ 27.2		g
158.6	broad s			b and d
178.1	s			a and b

6-bromo-3,5-difluoro-2-pent-1-ynyl-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (49)



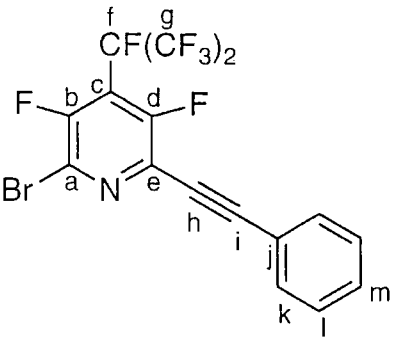
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.4	m		6	g
-101.2 and -104.2	m		1	b
-111.9 and -114.2	m		1	d
-179.8	m		1	f
^{1}H				
1.05	t	$^{3}J_{HH}$ 6.2	3	l
1.67	q	$^{3}J_{HH}$ 7.2	2	k
2.48	t	$^{3}J_{HH}$ 7.2	2	j
^{13}C				
13.4	s			l
21.4	s			j or k
21.5	s			j or k
72.3	s			i
91.5	d sept	$^{1}J_{CF}$ 215.0 $^{2}J_{CF}$ 36.2		f
101.4	s			h
113.5	m			c
119.8	q d	$^{1}J_{CF}$ 275.6 $^{2}J_{CF}$ 25.6		g
124.0-135.0	broad overlapping m			a,b,d and e

3,5-difluoro-2,6-dipent-1-ynyl-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (50)



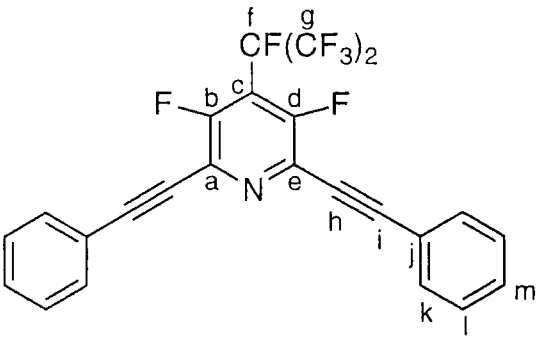
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-76.1	m		6	g
-111.2 and -113.7	m		1	b and d
-180.5	m		1	f
^{1}H				
0.95	t	$^{3}J_{HH}$ 7.2	3	l
1.57	q	$^{3}J_{HH}$ 7.2	2	k
2.38	t	$^{3}J_{HH}$ 6.8	2	j
^{13}C				
12.9	s			l
21.2	s			j or k
21.3	s			j or k
72.7	s			i
91.6	d sept	$^{1}J_{CF}$ 214.1 $^{2}J_{CF}$ 35.8		f
99.1	s			h
112.1	m			c
119.8	q d	$^{1}J_{CF}$ 288.7 $^{2}J_{CF}$ 27.5		g
128.0-132.0	broad singlet			a and e
150.0-159.0	broad overlapping m			b and d

6-bromo-3,5-difluoro-2-phenylethynyl-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (51)



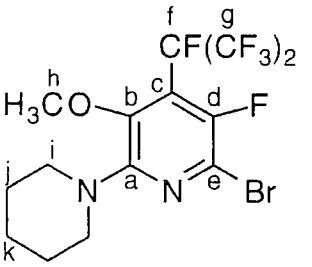
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.2	m		6	g
-100.2 and -103.0	m		1	b
-110.7 and -113.0	m		1	d
-179.7	m		1	f
^{1}H				
7.34	m		3	l and m
7.56	m		2	k
^{13}C				
80.1	m			i
91.7	d sept	$^{1}J_{CF}$ 215.5 $^{2}J_{CF}$ 35.8		f
98.6	m			h
114.2	dt	$^{2}J_{CF}$ 22.1 $^{2}J_{CF}$ 13.3		c
119.9	q d	$^{1}J_{CF}$ 290.0 $^{2}J_{CF}$ 27.1		g
121.0	s			j
128.8	s			l
130.4	s			m
132.5	s			k
126.0-131.0	broad overlapping m			a,b,d and e

2,6-bis(2-phenylethynyl)-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine (52)



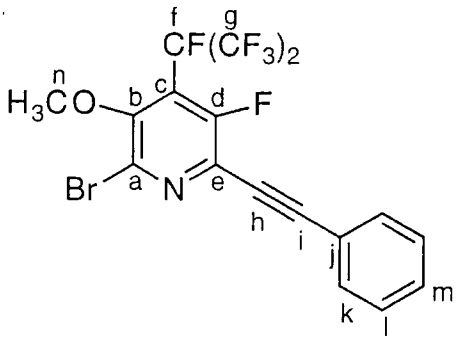
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-75.3	m		6	g
-108.5 and -110.9	m		1	d
-179.9	m		1	f
^{1}H				
7.33	m		3	l and m
7.55	m		2	k
^{13}C				
80.3	m			i
91.8	d sept	$^{1}J_{CF}$ 214.8 $^{2}J_{CF}$ 35.9		f
97.4	m			h
112.9	dt	$^{2}J_{CF}$ 22.1 $^{2}J_{CF}$ 13.1		c
120.2	q d	$^{1}J_{CF}$ 305.8 $^{2}J_{CF}$ 27.5		g
121.3	s			j
128.8	s			l
130.2	s			m
132.5	s			k
128.0-133.0	broad overlapping m			a,b,d and e

4-[1-(trifluoromethyl)-1,2,2,2-tetrafluoroethyl]-2-bromo-3-fluoro-5-methoxy-6-piperidylpyridine (53)



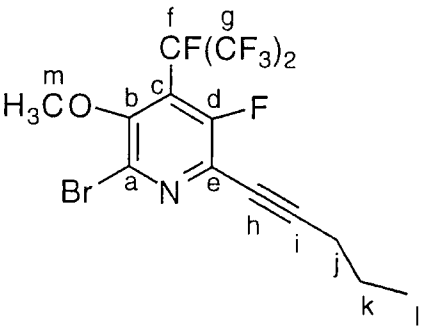
Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-73.4	m		6	g
-116.0	s		1	$d_{conformer1}$
-118.4	d	$^4J_{FF}$ 89.9	1	$d_{conformer2}$
-174.9	d	$^4J_{FF}$ 95.9	1	$f_{conformer2}$
-179.3	s		1	$f_{conformer1}$
^1H				
1.6	s		6	j and k
3.3	s		4	i
3.7	s		3	h
^{13}C				
24.3	s			k
25.8	s			i
49.2	m			j
57.7	s			$h_{conformer1}$
59.0	s			$h_{conformer2}$
92.8	d sept	$^1J_{CF}$ 210.9 $^2J_{CF}$ 35.1		f
120.2	q d	$^1J_{CF}$ 286.7 $^2J_{CF}$ 28.2		g
121.2	m			c
142.0-149.0	broad overlapping m			a,b,d and e

4-[1-(trifluoromethyl)-1,2,2,2-tetrafluoroethyl]-2-bromo-3-methoxy-5-fluoro-6-(2-phenylethynyl)pyridine (54)



Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-72.9	m		6	g
-109.6	m		1	$d_{conformer\ 1}$
-112.0	d	$^4J_{FF}$ 89.9	1	$d_{conformer\ 2}$
-174.6	d	$^4J_{FF}$ 89.9	1	$f_{conformer\ 2}$
-179.6	s		1	$f_{conformer\ 1}$
^1H				
3.91	br s		3	$n_{conformer\ 1}$
3.99	br s		3	$n_{conformer\ 2}$
7.34	m		3	l and m
7.53	m		2	k
^{13}C				
62.8	br s			n
63.7	br s			n
80.8	m			i
92.6	d sept	$^1J_{CF}$ 214.1 $^2J_{CF}$ 35.5		f
98.1	m			h
119.5	m			c
120.3	q d	$^1J_{CF}$ 288.9 $^2J_{CF}$ 27.5		g
121.3	s			j
128.5	s			l
129.9	s			m
132.2	s			k
126.0-131.0	broad overlapping m			a,b,d and e

4-[1-(trifluoromethyl)-1,2,2,2-tetrafluoroethyl]-2-bromo-3-methoxy-5-fluoro-6-pent-1-ynylpyridine (55)



Chemical Shift (ppm)	Multiplicity	Coupling constants (J /Hz)	Relative Intensity	Assignment
^{19}F				
-74.9	m		6	g
-112.6	m		1	$d_{conformer\ 1}$
-115.1	d	$^4J_{FF}$ 96.0	1	$d_{conformer\ 2}$
-176.6	d	$^4J_{FF}$ 96.0	1	$f_{conformer\ 2}$
-181.5	m		1	$f_{conformer\ 1}$
^{1}H				
0.99	t	$^3J_{HH}$ 7.2	3	l
1.61	q	$^3J_{HH}$ 7.2	2	k
2.41	t	$^3J_{HH}$ 7.2	2	j
3.86	br s		3	m
3.96	br s		3	m
^{13}C				
13.5	s			l
21.48	s			j or k
21.51	s			j or k
62.36	br s			$m_{conformer1}$
63.17	br s			$m_{conformer2}$
72.7	s			i
92.5	d sept	$^1J_{CF}$ 214.4 $^2J_{CF}$ 38.1		f
100.5	br s			h
118.9	d d	$^2J_{CF}$ 20.8 $^2J_{CF}$ 10.2		c
120.2	q d	$^1J_{CF}$ 289.6 $^2J_{CF}$ 27.1		g
124.0-135.0	broad overlapping m			a,b,d and e

Appendix B.

IR. Data

Compound Number:	IUPAC Name:
(1)	*2,3,5,6-tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(2)	*2,3,5-trifluoro-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(3)	*2,3,5-trifluoro-6-methoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine.*
(4)	*3,5-difluoro-2,6-dimethoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(5)	*3,5,6-trifluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridin-2-ol*
(6)	*3,5,6-trifluoro-2-(methoxyethanoxy)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl]-pyridine*
(7)	*2,6-bis(2-methoxyethanoxy)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-pyridine*
(8)	*6-cyclohexyloxy-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-pyridine*
(9)	*2,6-dicyclohexyloxy-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-pyridine*
(10)	*2,3,5-trifluoro-6-phenoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine*
(11)	*3,5-difluoro-2,6-diphenoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine*
(13)	*2,6-bis-(3-methoxyphenoxy)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl]pyridine*
(14)	*2,5-difluoro-3-methoxy-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(15)	*5-fluoro-2,3-dimethoxy-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(16)	*Methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amine*
(17)	*Bis{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}methylamine*

(18) *{3,5-difluoro-6-(methylamino)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}methyl{3,5,6-trifluoro-4[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amine*

(19) *Bis{3,5-difluoro-6-(methylamino)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}methylamine*

(20) *Bis{6-(diethylamino)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}methylamine*

(21) *3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl]-2-3-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl](2-pyridyloxy)}phenoxy)pyridine*

(24) *2,3,5-trifluoro-6-(5-methyl-3-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}phenoxy)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine*

(25) *26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.<15,19>]octacosa-1(25),3,5,7(26),9(27),10,12,15,17,19(28),21,23-dodecaene*

(26) *26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-11-methyl-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(25),3,5,7(26),9(27),10,12,15,17,19(28),21,23-dodecaene*

(27) *26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-11,23-dimethyl-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(25),3,5,7(26),9(27),10,12,15,17,19(28),21,23-dodecaene*

(28) *2-1',2'-dioxyethyl-bis-3,5,6-trifluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*

(29) *6-(2-{3,5-difluoro-6-propoxy-4[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}ethoxy)-3,5-difluoro-4-1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridin-2-ol*

(30) *2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)oxy}-1-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1(trifluoromethyl)ethyl](2-pyridyloxy)}ethoxy)ethane*

(31) *25,26-diaza-11,23-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-10,12,22,24-tetrafluoro-2,5,8,14,17,20-hexaoxatricyclo[19.3.1.1<9,13>]hexacosa-1(24),9(26),10,12,21(25),22-hexaene*

(32) *Methyl[2-(methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amino)ethyl]{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amine*

(33) *2,3-difluoro-5,8-dimethyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethylethyl)]-5,6,7,8-tetrahydroquinoline*

(34) *2,5,11,14,19,20-hexaaza-8,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11,14-tetramethyltricyclo[13.3.1.1<6,10>]icosa-1(18),6(20),7,9,15,(19),16-hexaene*

(35) *{7-fluoro-1,4-dimethyl-8-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](1,2,3,4-tetrahydropyridino[2,3-b]pyrazin-6-yl)}methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl}amine*

(36) *Bis{7-fluoro-1,4-dimethyl-8-[1,2,2,2-trifluoromethyl)ethyl](1,2,3,4-tetrahydropyridino[2,3-b]pyrazin-6-yl)}methylamine*

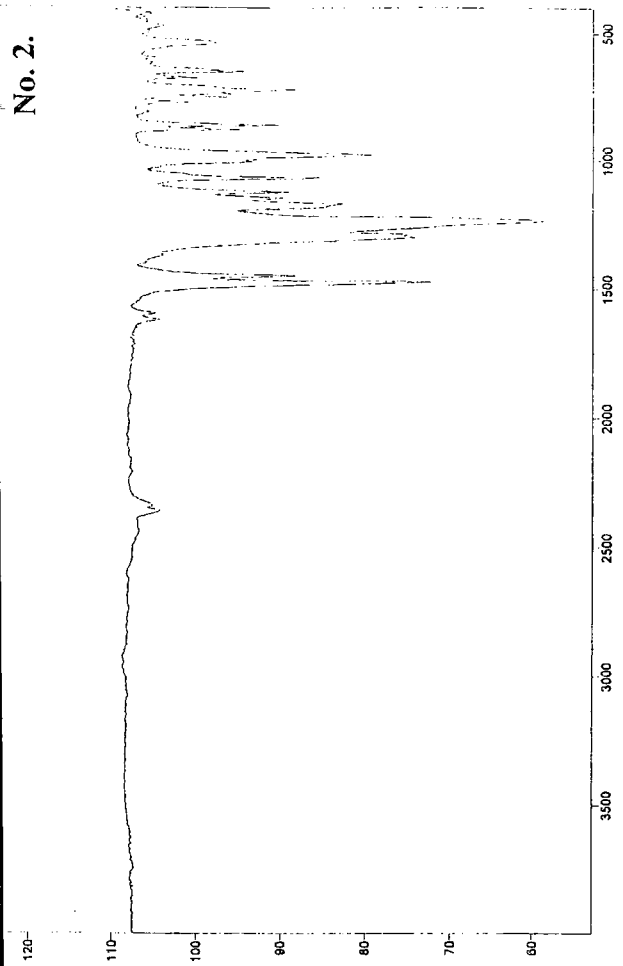
(37) *2,6-dibromo-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*

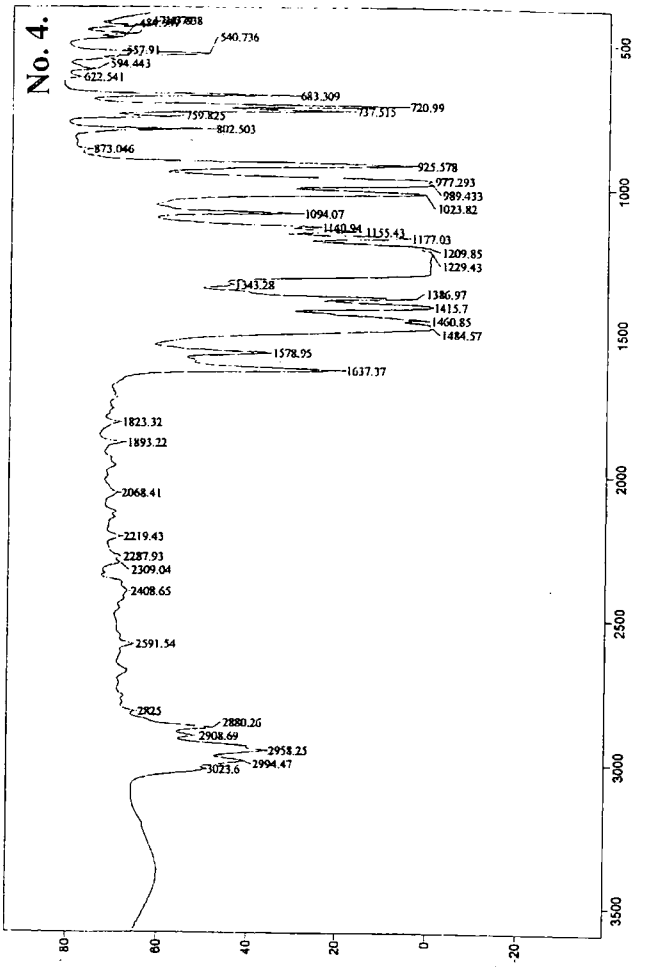
(38) *6-bromo-2,3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*

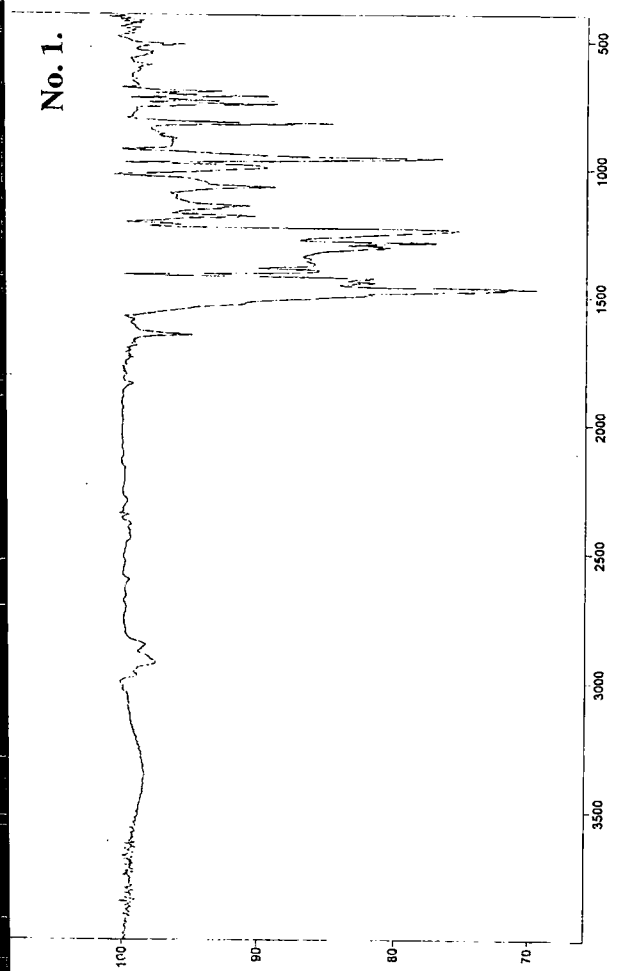
(39) *2,6-dihydrido-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*

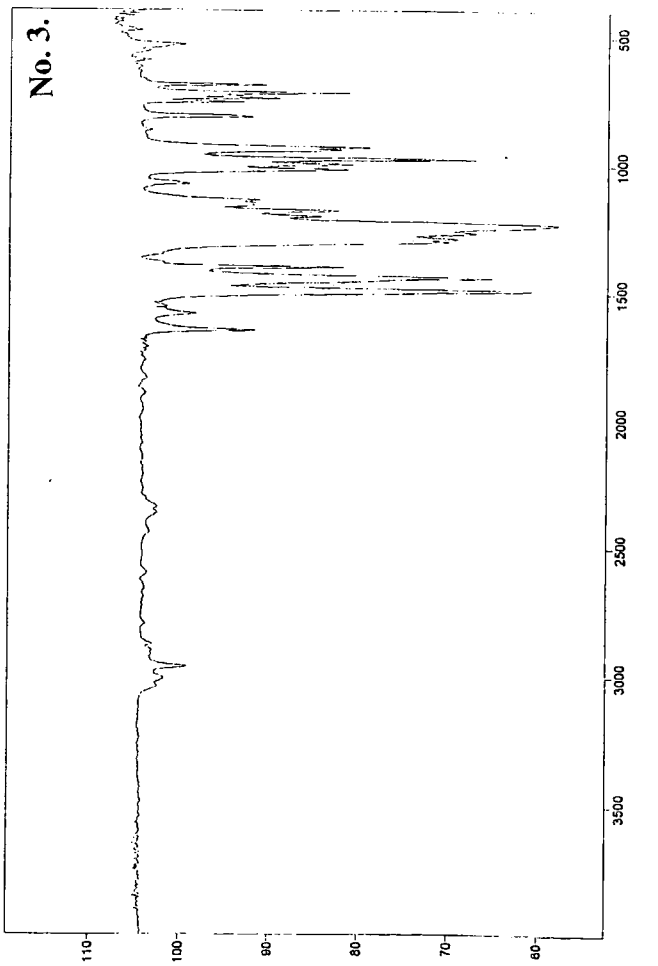
(40) *2,6-dibromo-3-fluoro-5-methoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*

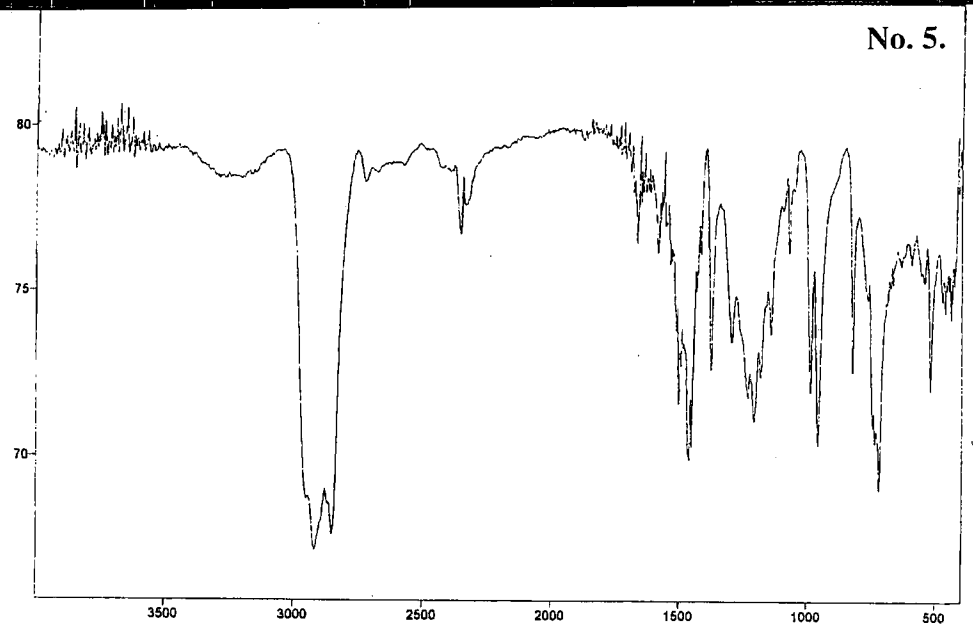
(41)	*2,6-dibromo-3,5-dimethoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(42)	*2-bromo-3,5,6-trimethoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(43)	*6-bromo-3,5-difluoro-2-piperidyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine*
(44)	*2-bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl]pyridine*
(45)	*2-{bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl](2-pyridyl)}-2-methyl-2-silapropane*
(46)	*2-bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl]-6-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}pyridine*
(47)	*2-{6-bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl](2-pyridyl)}{3,5,-difluoro-6-methoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine*
(48)	*2-{6-(1,1-dimethyl-1-silaethyl)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl](2-pyridyl)}-2-methyl-2-silapropane*
(49)	*6-bromo-3,5-difluoro-2-pent-1-ynyl-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(50)	*3,5-difluoro-2,6-dipent-1-ynyl-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(51)	*6-bromo-3,5-difluoro-2-phenylethynyl-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(52)	*2,6-bis(2-phenylethynyl)-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(53)	*4-[1-(trifluoromethyl)-1,2,2,2-tetrafluoroethyl]-2-bromo-3-fluoro-5-methoxy-6-piperidylpyridine*
(54)	*4-[1-(trifluoromethyl)-1,2,2,2-tetrafluoroethyl]-2-bromo-3-methoxy-5-fluoro-6-(2-phenylethynyl)pyridine*
(55)	*4-[1-(trifluoromethyl)-1,2,2,2-tetrafluoroethyl]-2-bromo-3-methoxy-5-fluoro-6-pent-1-ynylpyridine*

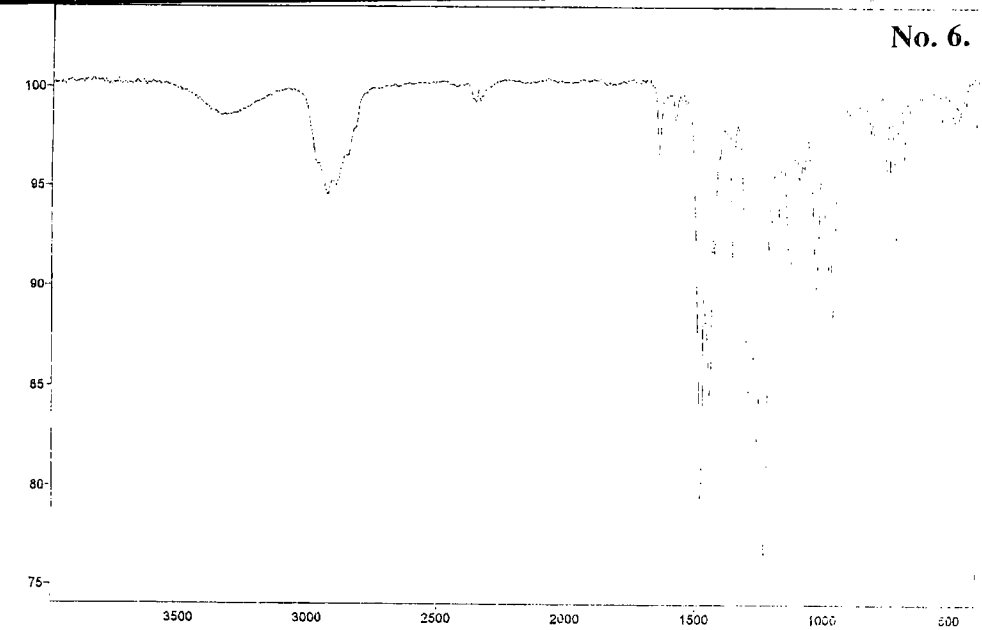

No. 2.

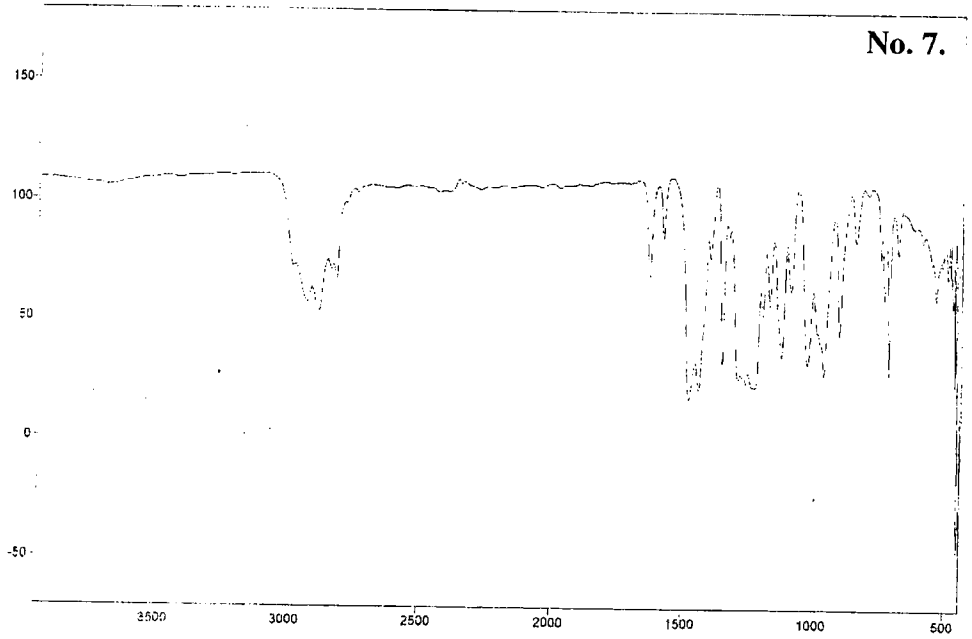

No. 4.
540.736
557.91
594.443
622.541
683.309
720.99
737.515
759.825
802.503
873.046
925.578
977.293
989.433
1023.82
1094.07
1140.94
1155.43
1177.03
1209.85
1229.43
1343.28
1386.97
1415.7
1460.85
1484.57
1578.95
1637.37
1823.32
1893.22
2068.41
2219.43
2287.93
2309.04
2408.65
2591.54
2925
2880.26
2908.69
2958.25
2994.47
3023.6

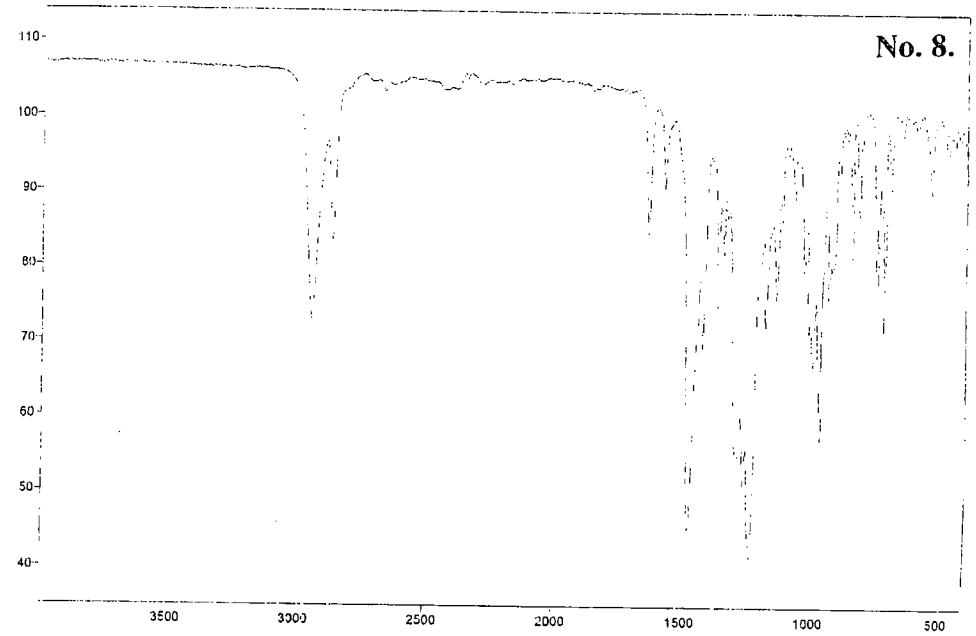

No. 1.


No. 3.

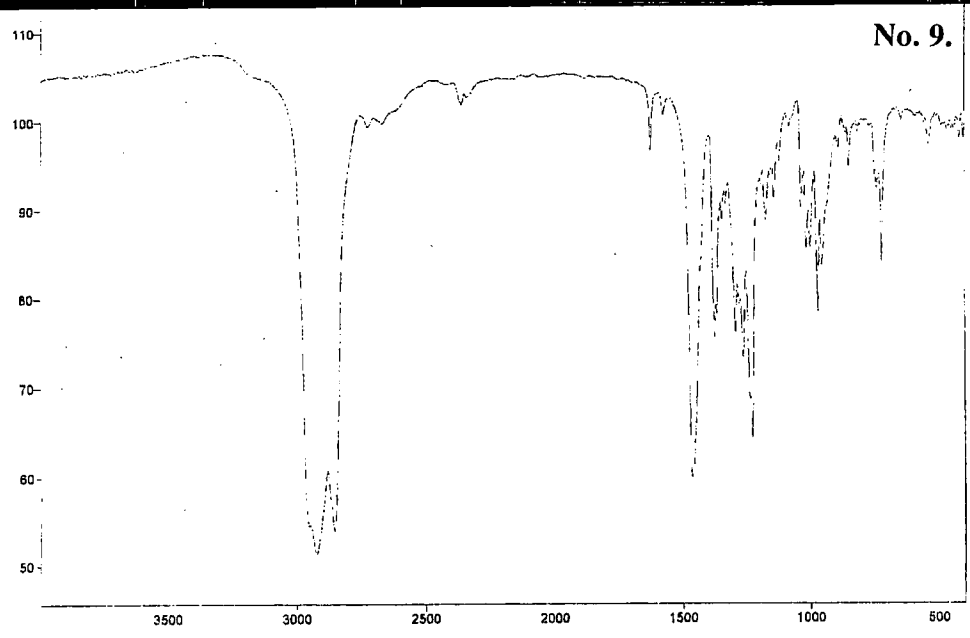

No. 5.
80
75
70
3500
3000
2500
2000
1500
1000
500

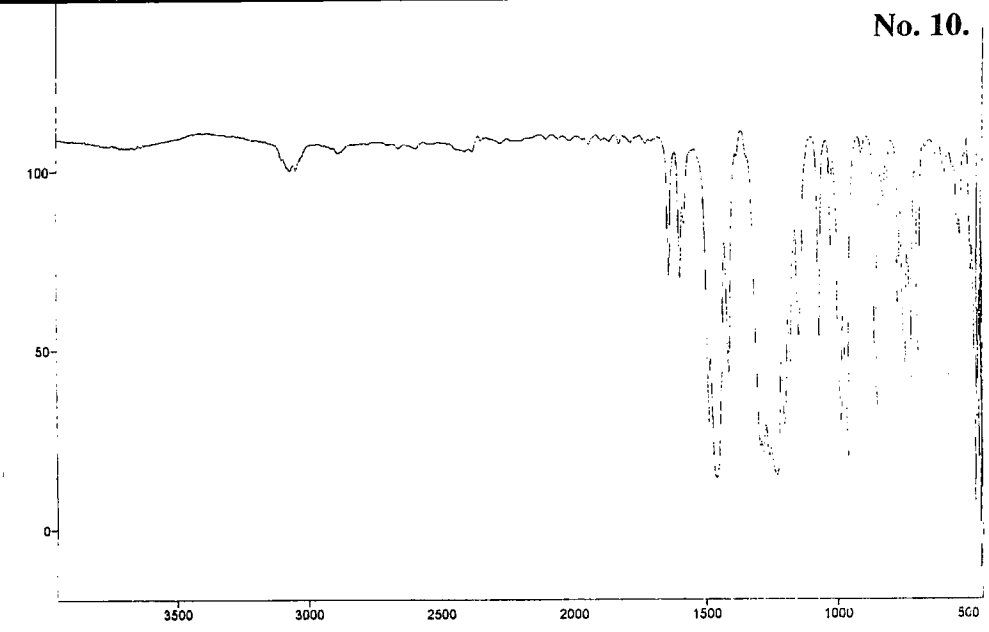

No. 6.
100
95
90
85
80
75
3500
3000
2500
2000
1500
1000
500

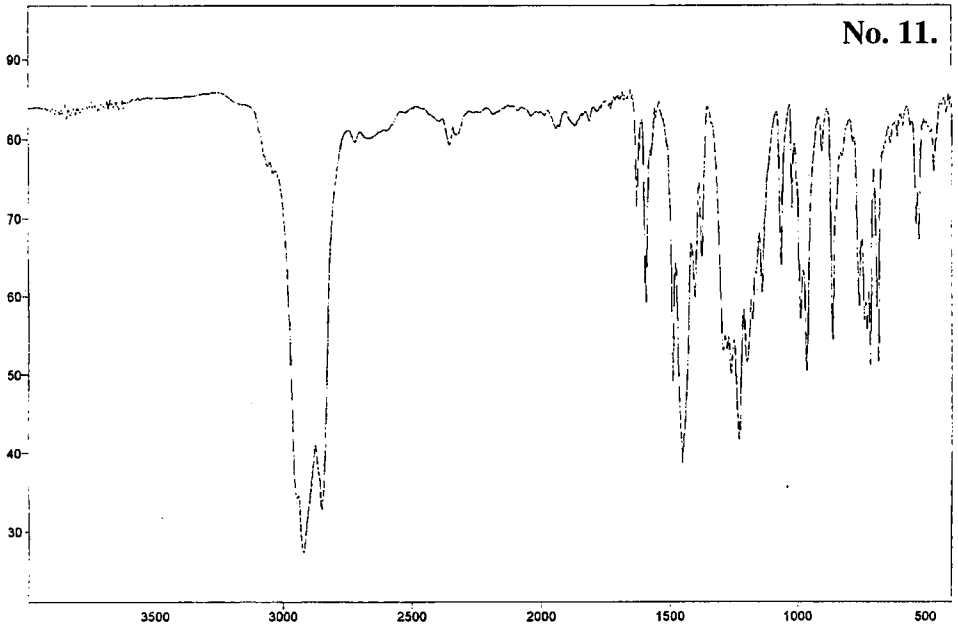

No. 7.
150
100
50
0
-50
3500
3000
2500
2000
1500
1000
500

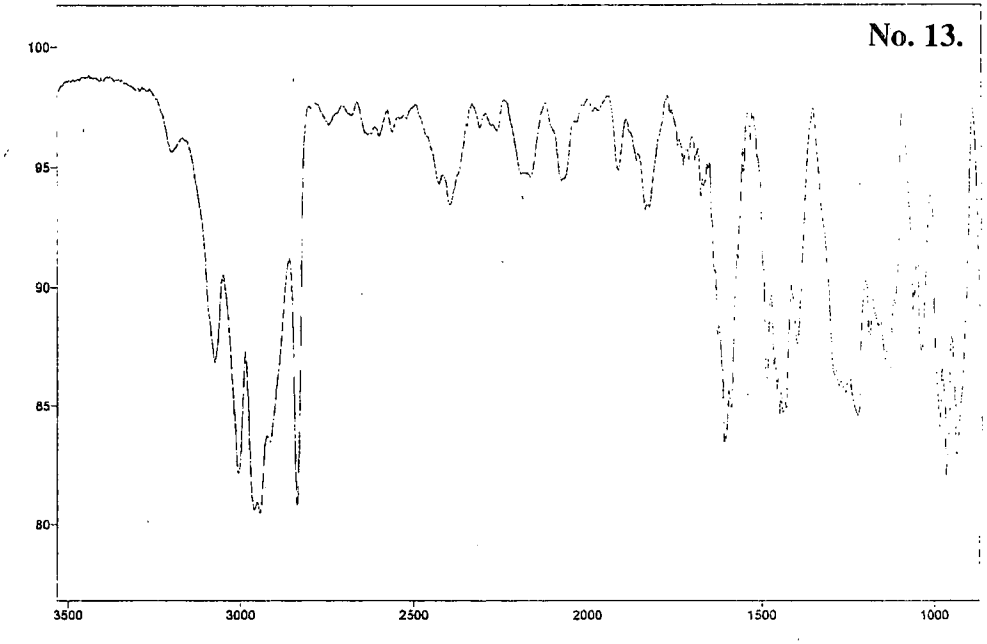

No. 8.
110
100
90
80
70
60
50
40
3500
3000
2500
2000
1500
1000
500

B. 7.

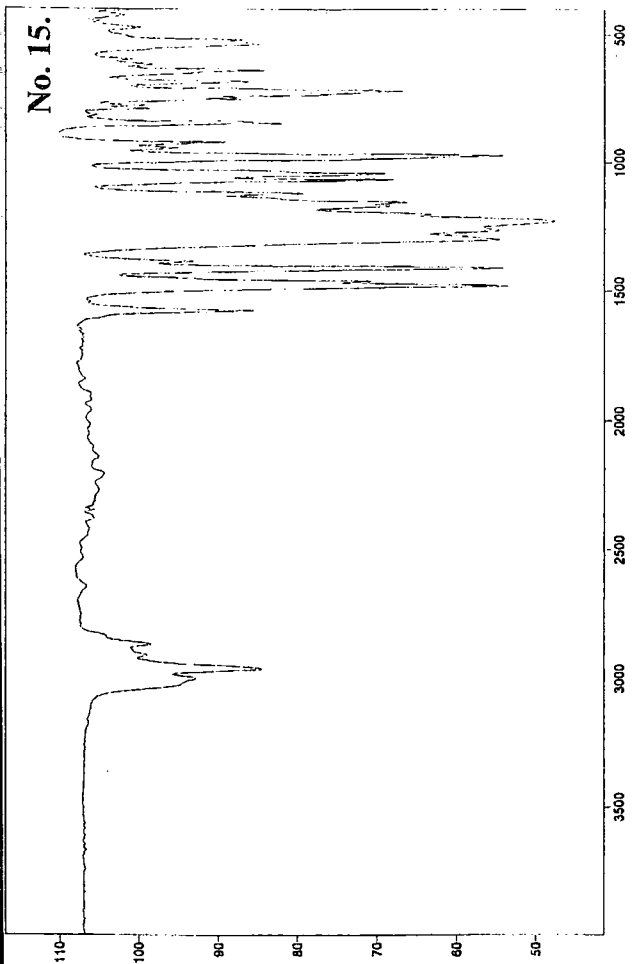

No. 9.
110
100
90
80
70
60
50
3500
3000
2500
2000
1500
1000
500

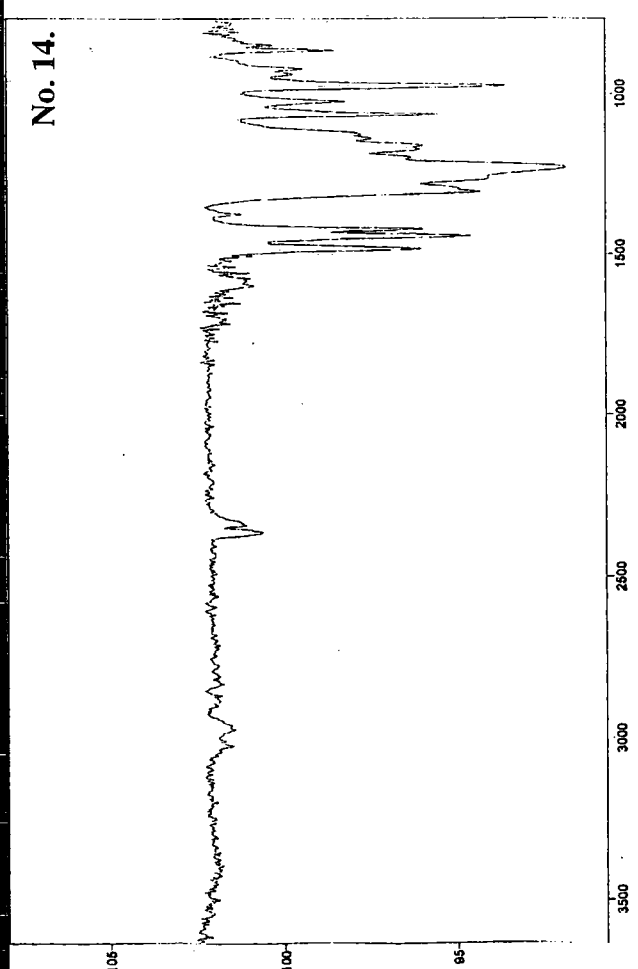

No. 10.
100
50
0
3500
3000
2500
2000
1500
1000
500

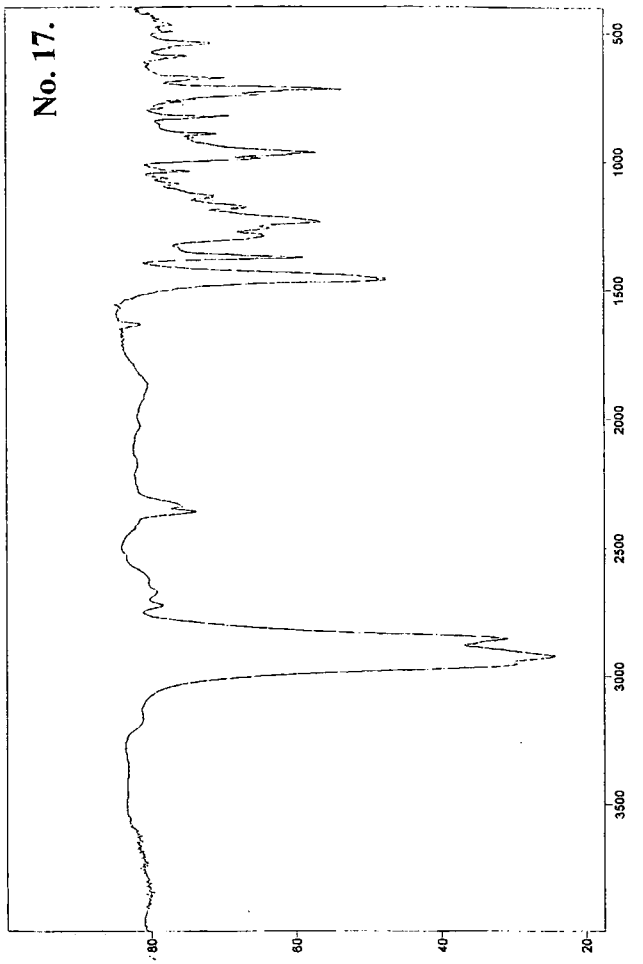

No. 11.
90
80
70
60
50
40
30
3500
3000
2500
2000
1500
1000
500

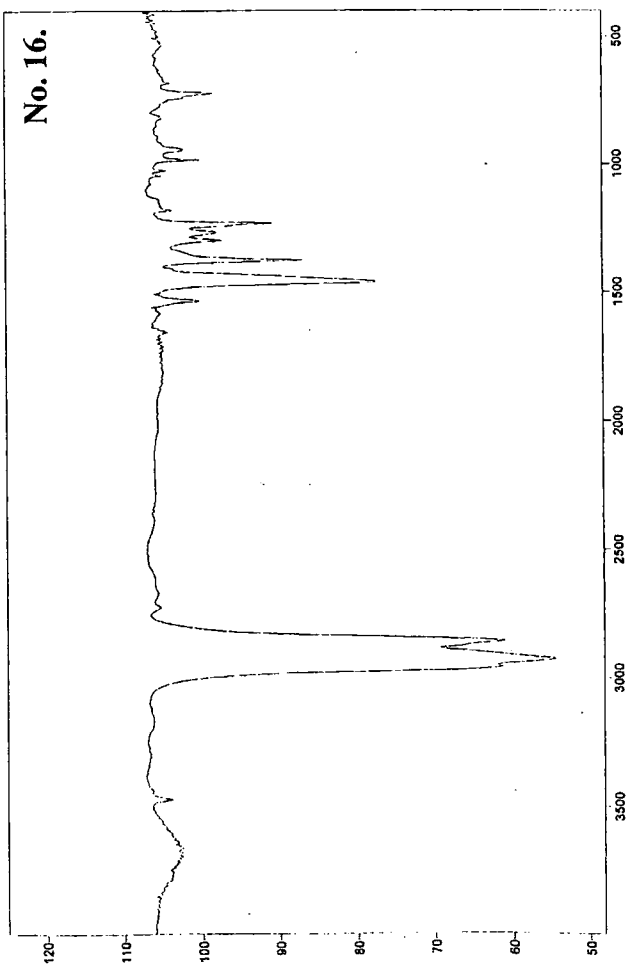

No. 13.
100
95
90
85
80
3500
3000
2500
2000
1500
1000

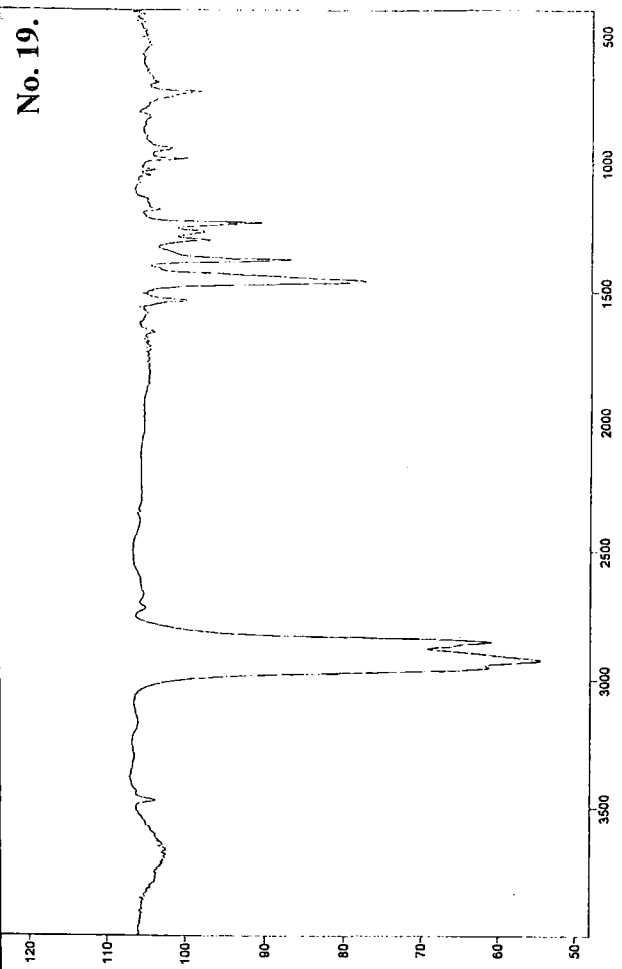
B. 8.

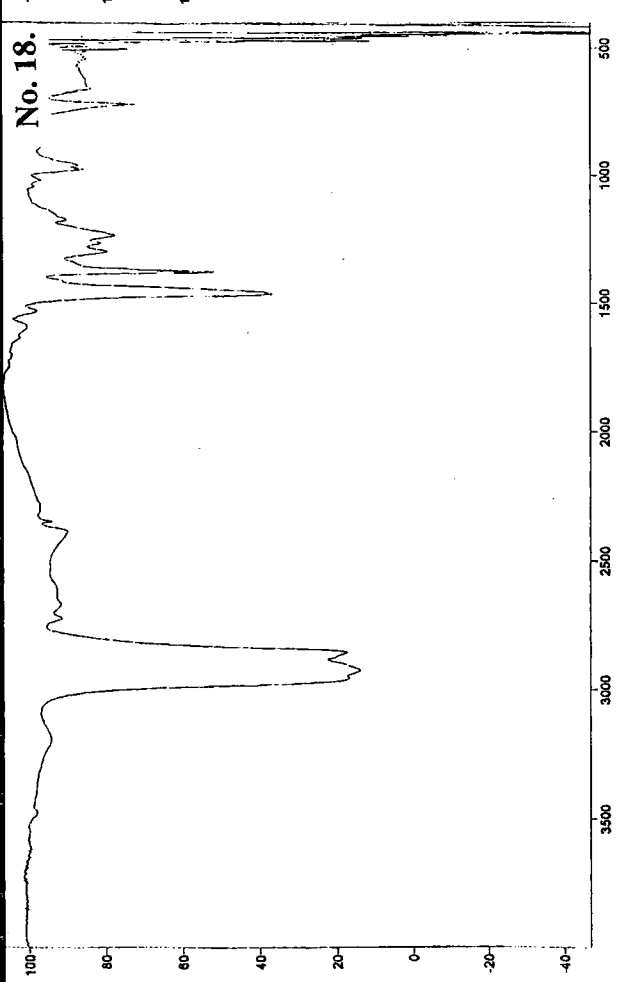

No. 15.
110
100
90
80
70
60
50
500
1000
1500
2000
2500
3000
3500

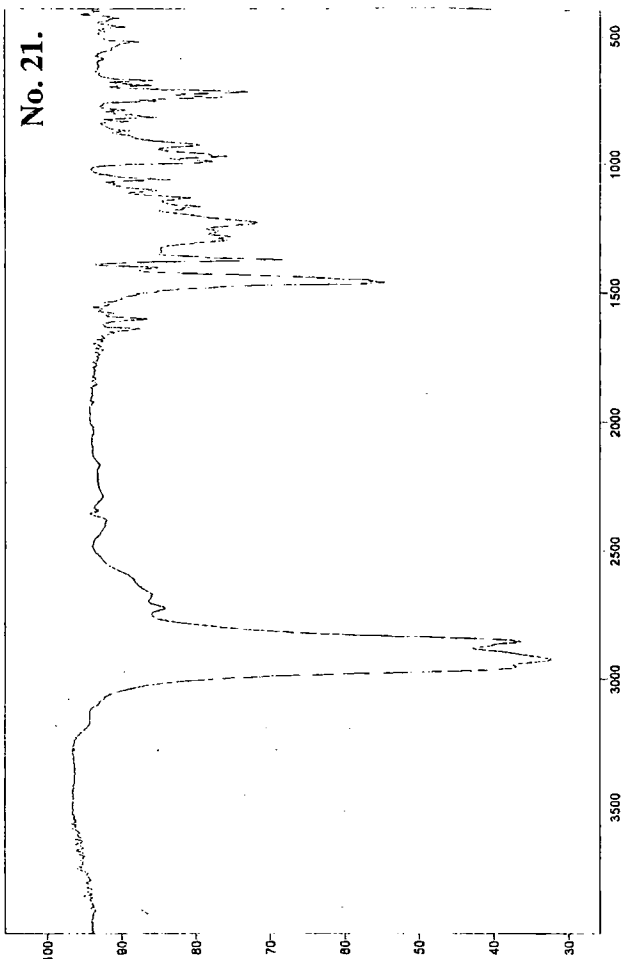

No. 14.
105
100
95
1000
1500
2000
2500
3000
3500

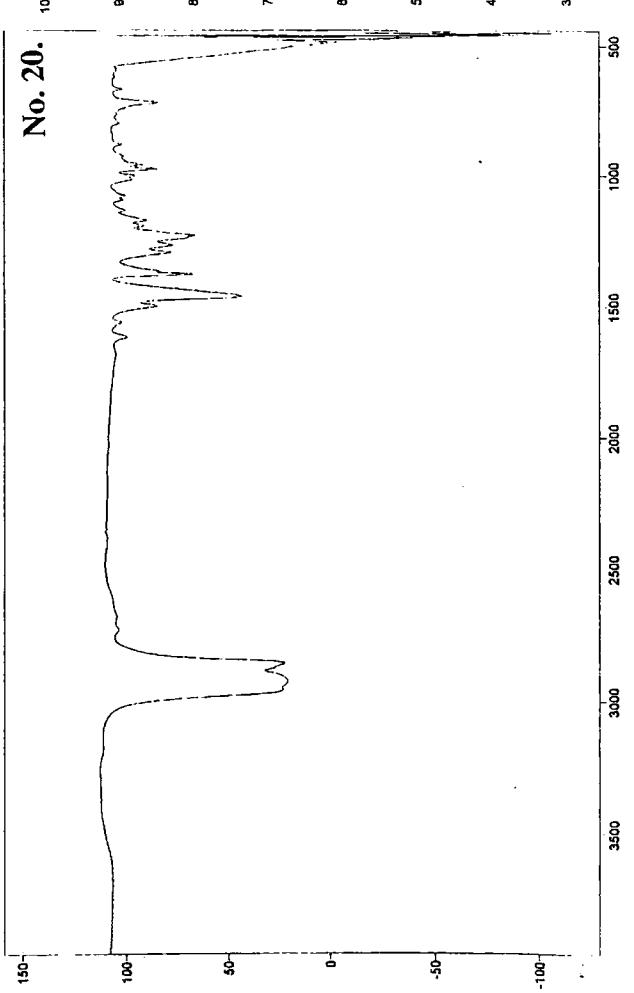

No. 17.
80
60
40
20
500
1000
1500
2000
2500
3000
3500

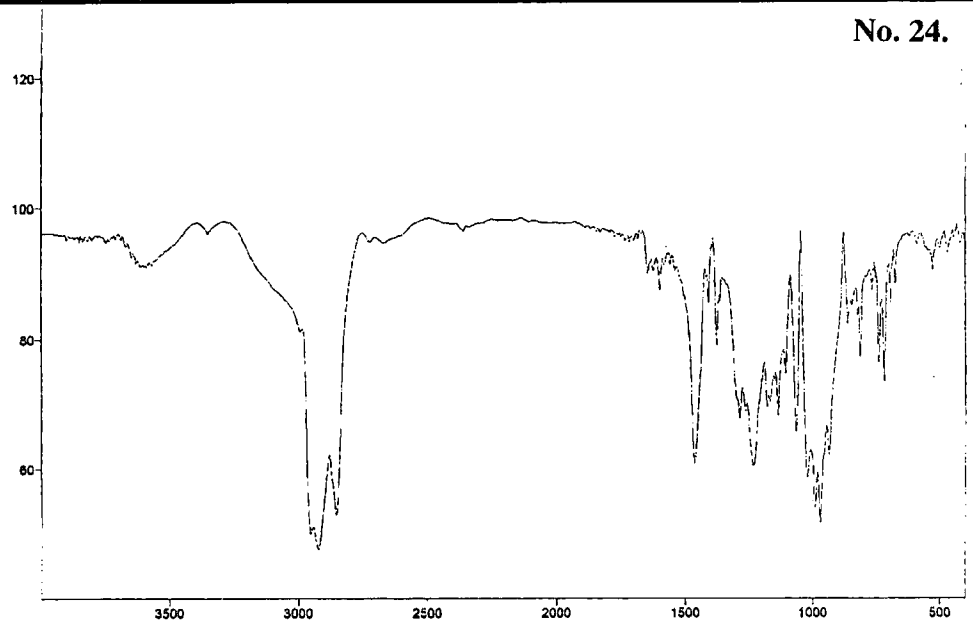

No. 16.
120
110
100
90
80
70
60
50
500
1000
1500
2000
2500
3000
3500

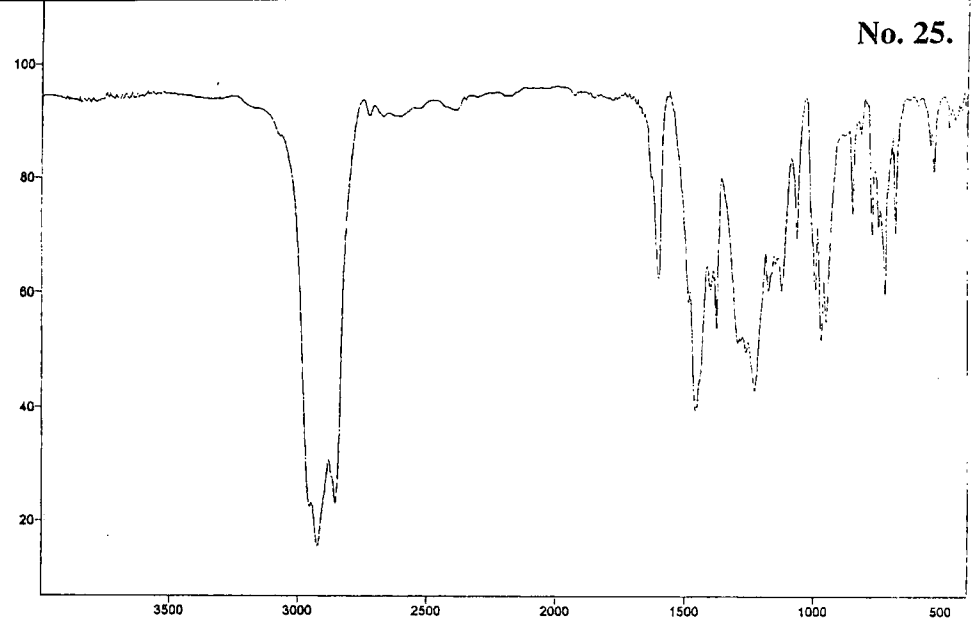

No. 19.
120
110
100
90
80
70
60
50
500
1000
1500
2000
2500
3000
3500

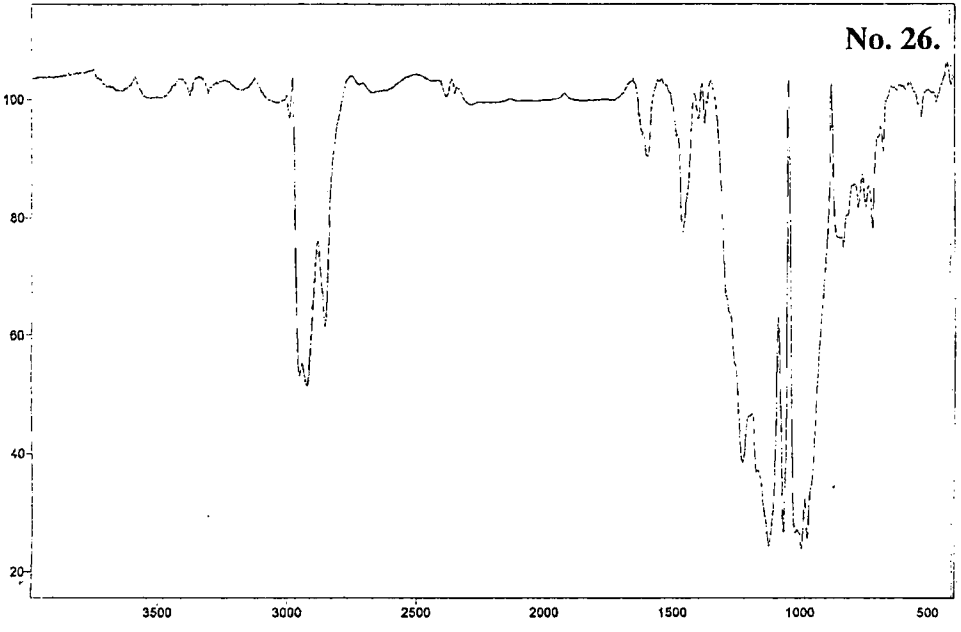

No. 18.
100
80
60
40
20
0
-20
-40
500
1000
1500
2000
2500
3000
3500

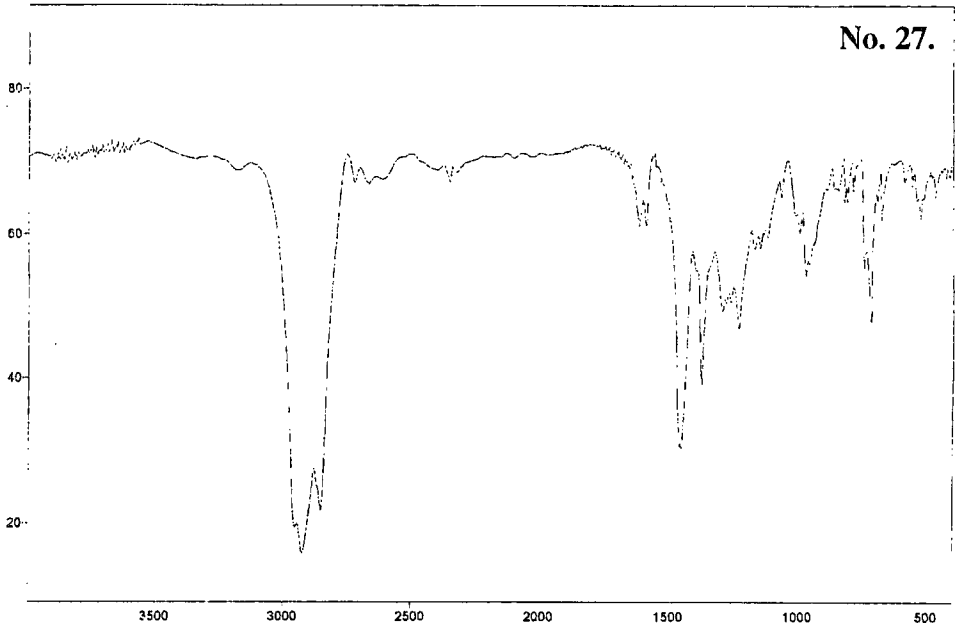

No. 21.
100
90
80
70
60
50
40
30
500
1000
1500
2000
2500
3000
3500


No. 20.
150
100
50
0
-50
-100
500
1000
1500
2000
2500
3000
3500

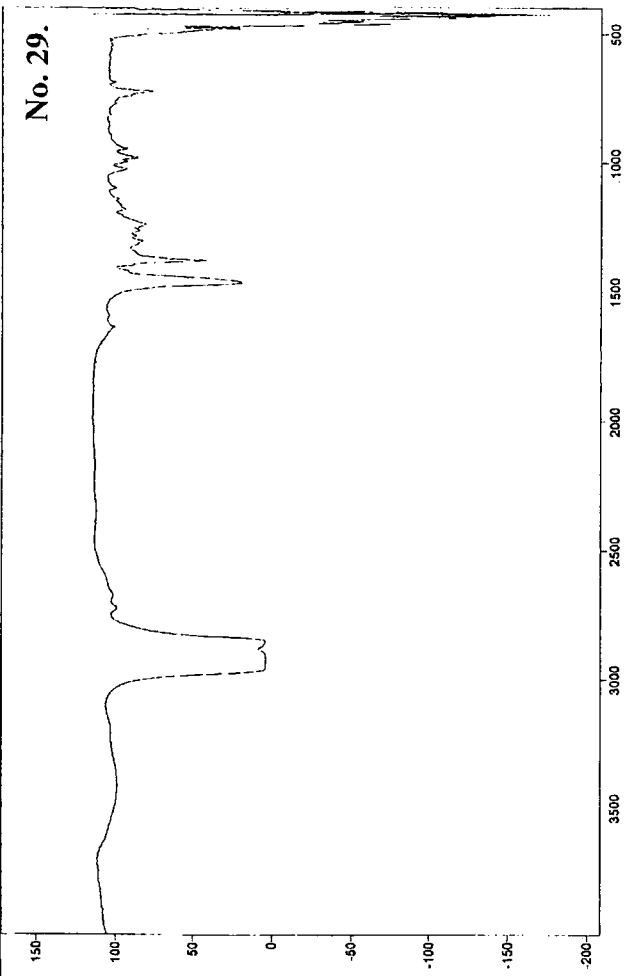

No. 24.
120
100
80
60
3500
3000
2500
2000
1500
1000
500

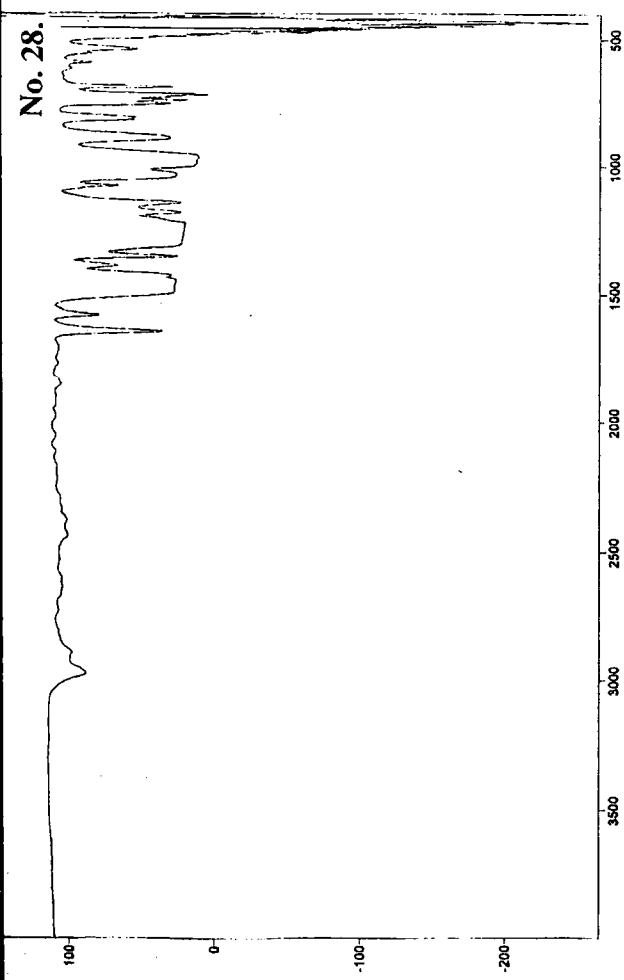

No. 25.
100
80
60
40
20
3500
3000
2500
2000
1500
1000
500

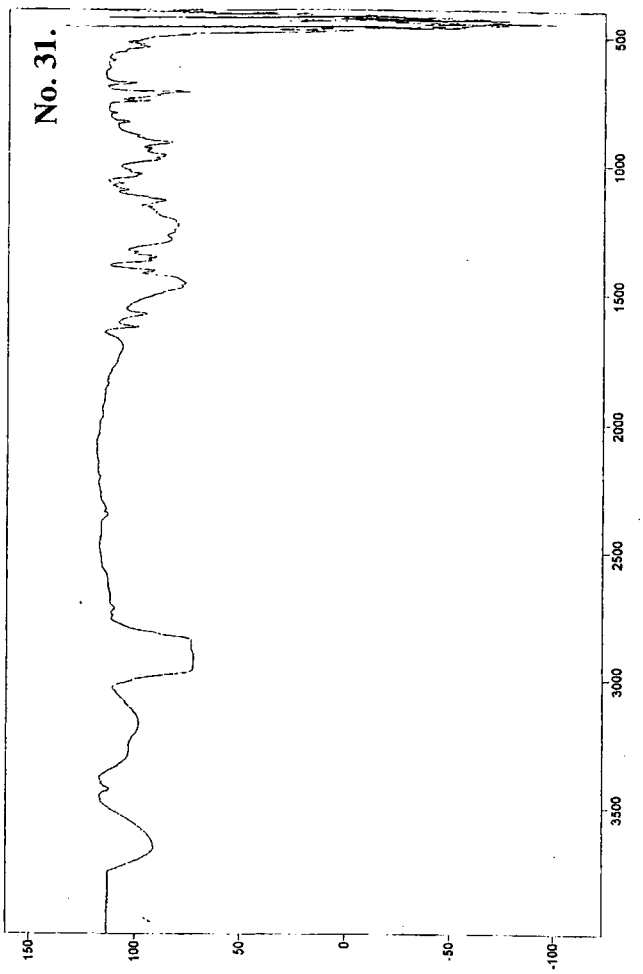

No. 26.
100
80
60
40
20
3500
3000
2500
2000
1500
1000
500

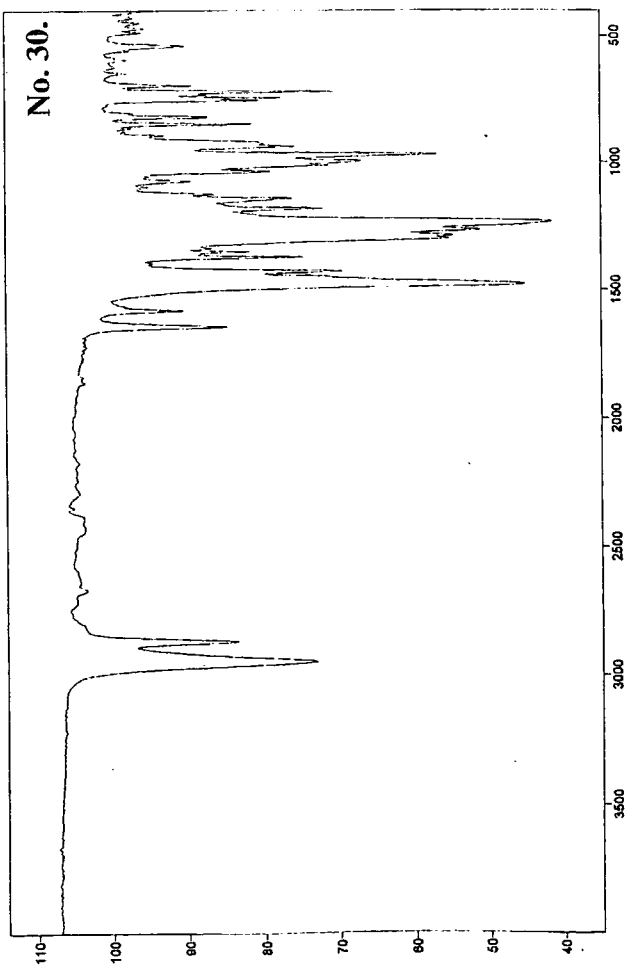

No. 27.
80
60
40
20
3500
3000
2500
2000
1500
1000
500

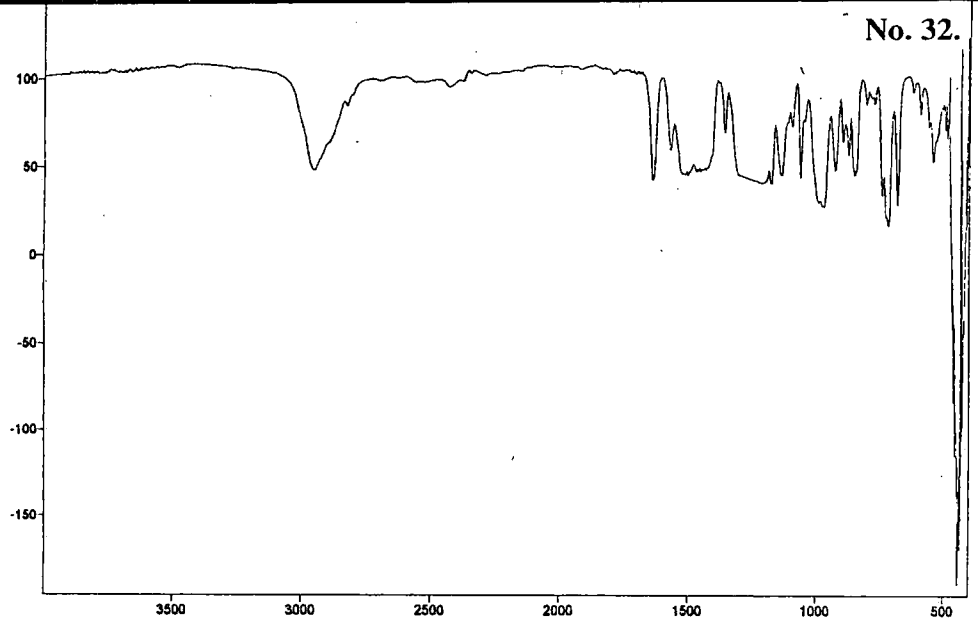
B. 11.

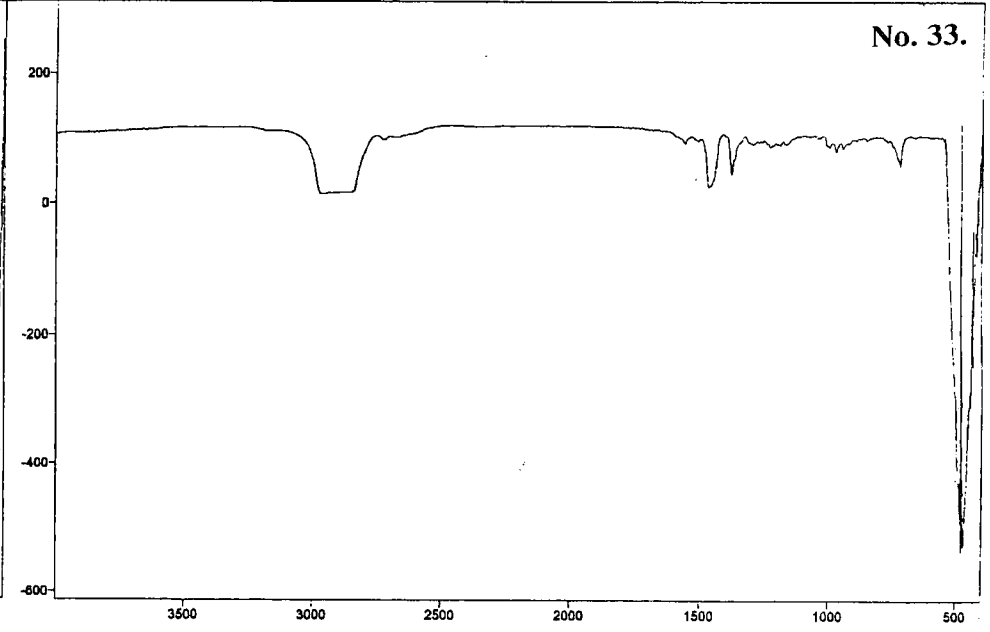

No. 29.
150
100
50
0
-50
-100
-150
-200
500
1000
1500
2000
2500
3000
3500

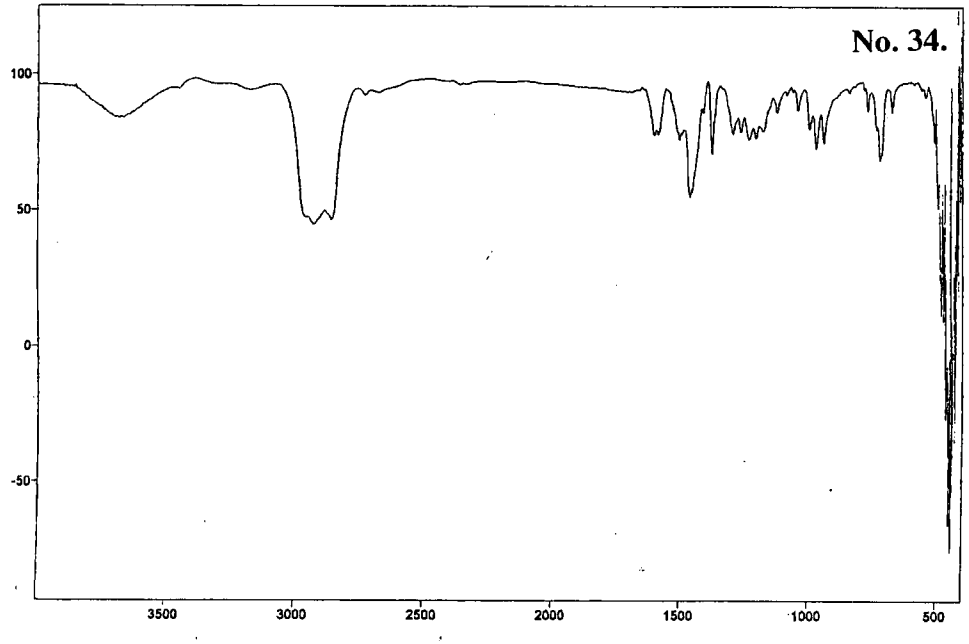

No. 28.
100
0
-100
-200
500
1000
1500
2000
2500
3000
3500

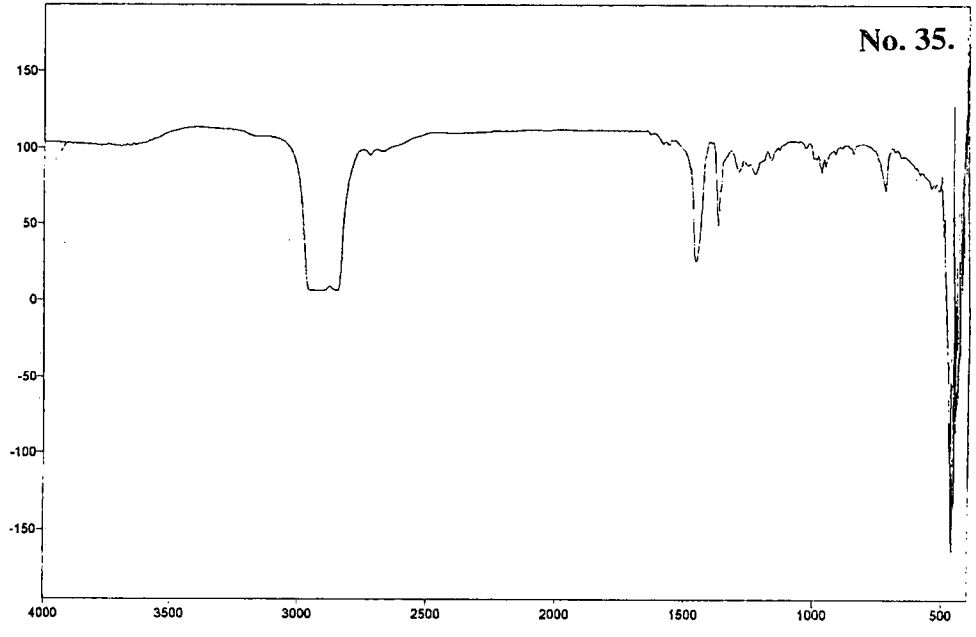

No. 31.
150
100
50
0
-50
-100
500
1000
1500
2000
2500
3000
3500


No. 30.
110
100
90
80
70
60
50
40
500
1000
1500
2000
2500
3000
3500

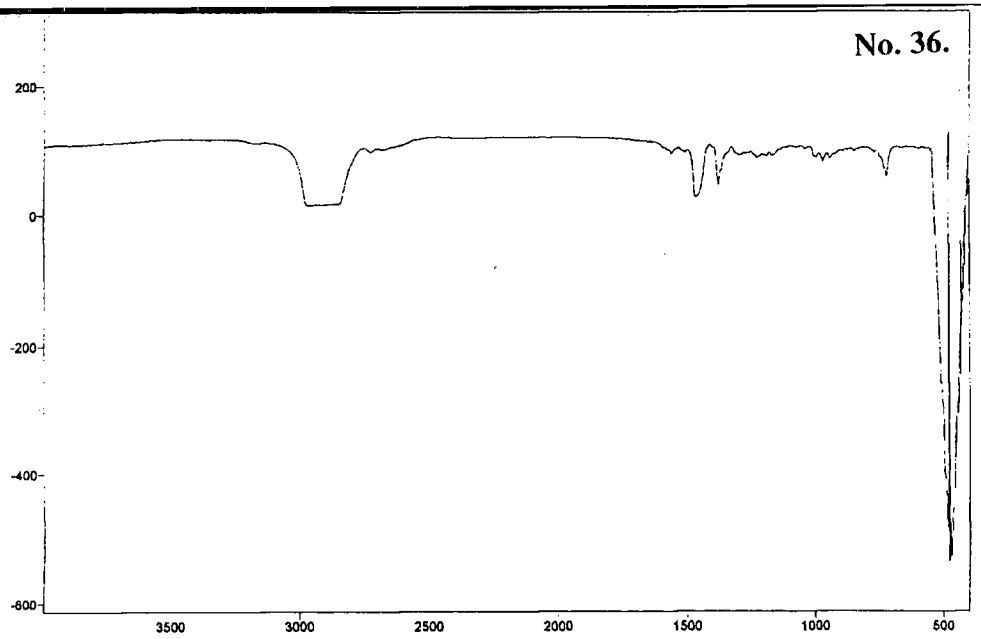

No. 32.
100
50
0
-50
-100
-150
3500
3000
2500
2000
1500
1000
500

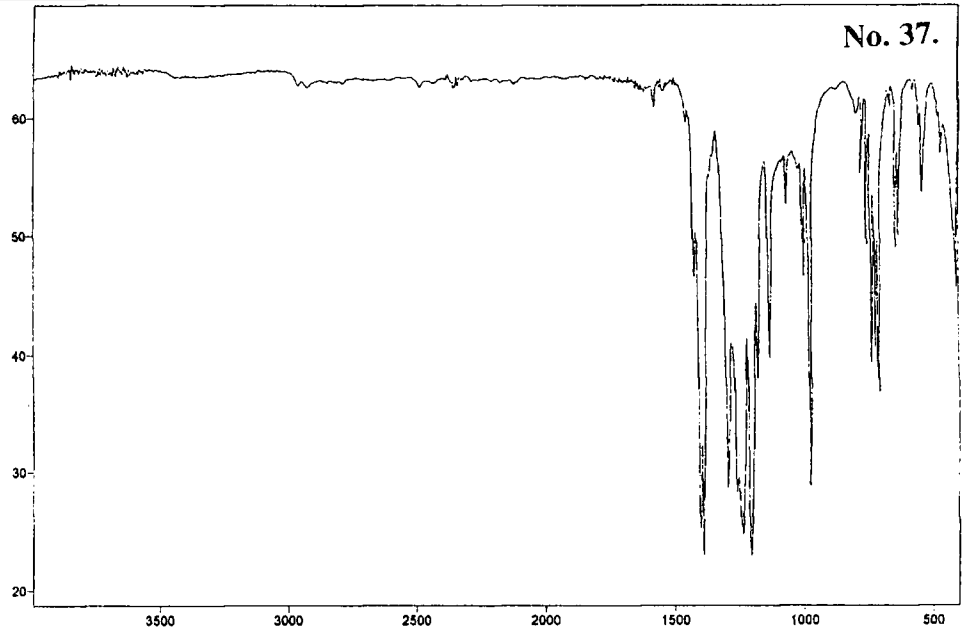

No. 33.
200
0
-200
-400
-600
3500
3000
2500
2000
1500
1000
500

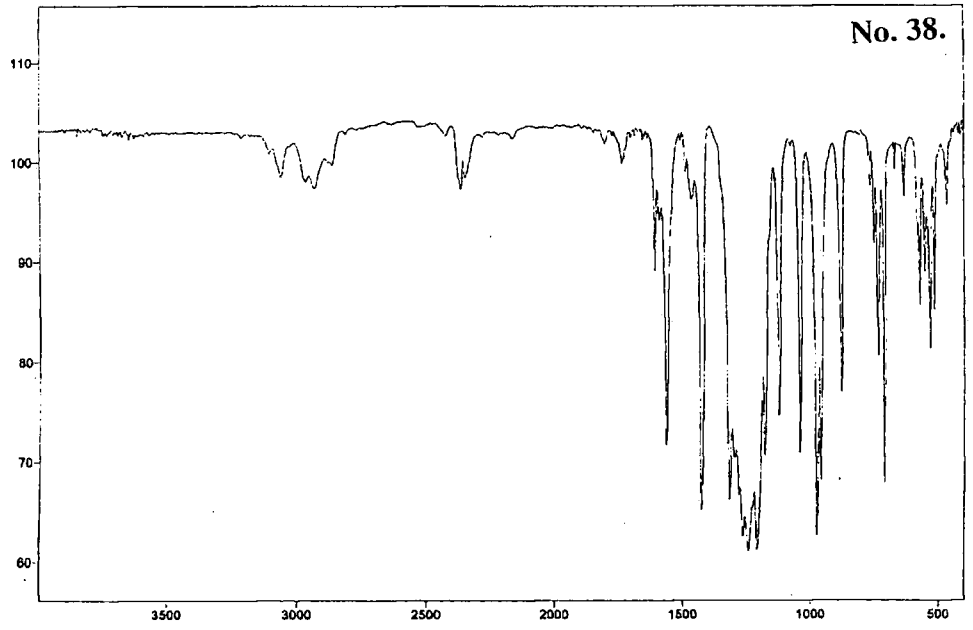

No. 34.
100
50
0
-50
3500
3000
2500
2000
1500
1000
500

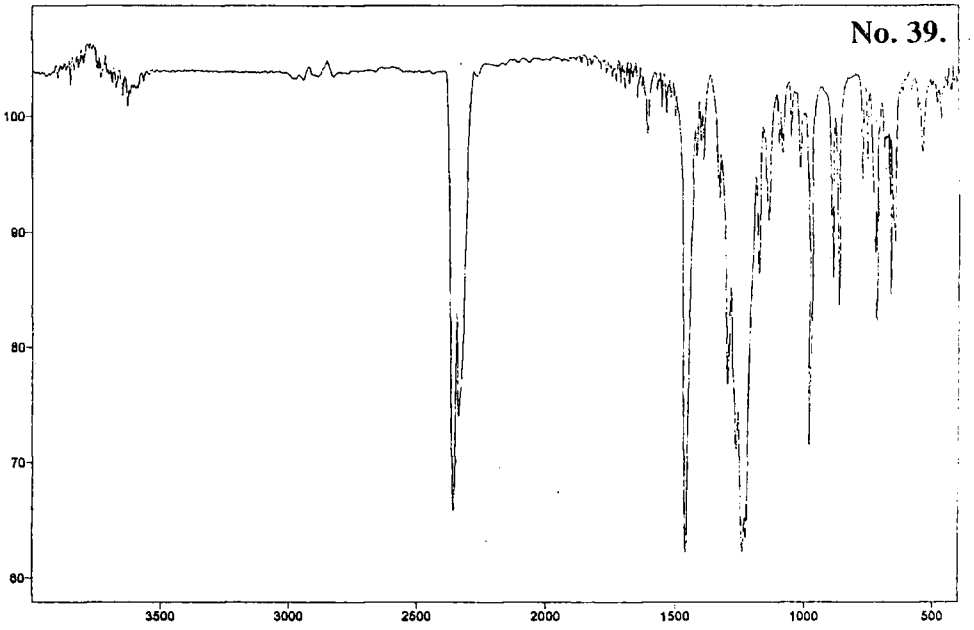

No. 35.
150
100
50
0
-50
-100
-150
4000
3500
3000
2500
2000
1500
1000
500

B. 13.

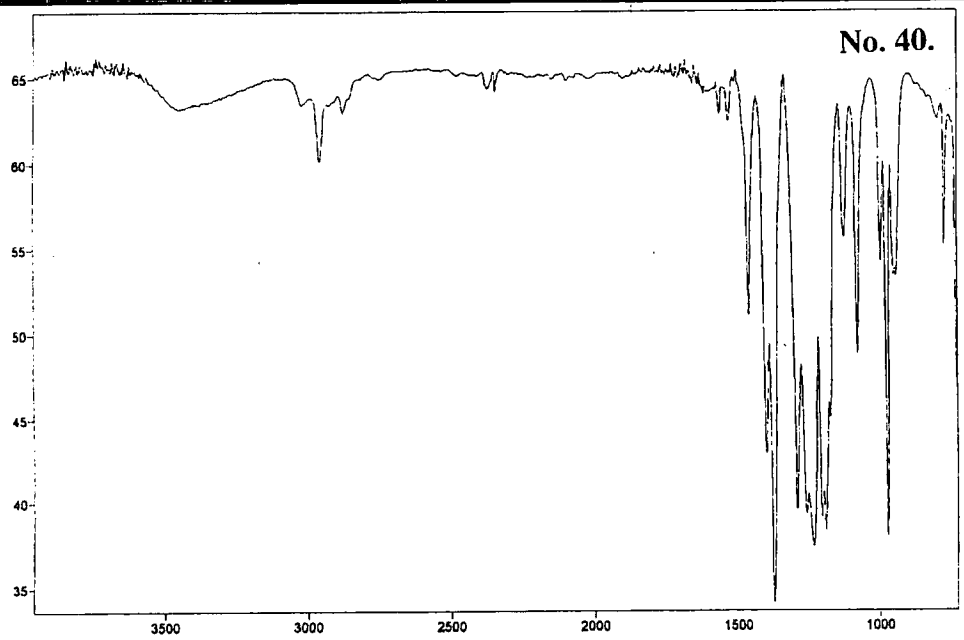

No. 36.
200
0
-200
-400
-600
3500
3000
2500
2000
1500
1000
500

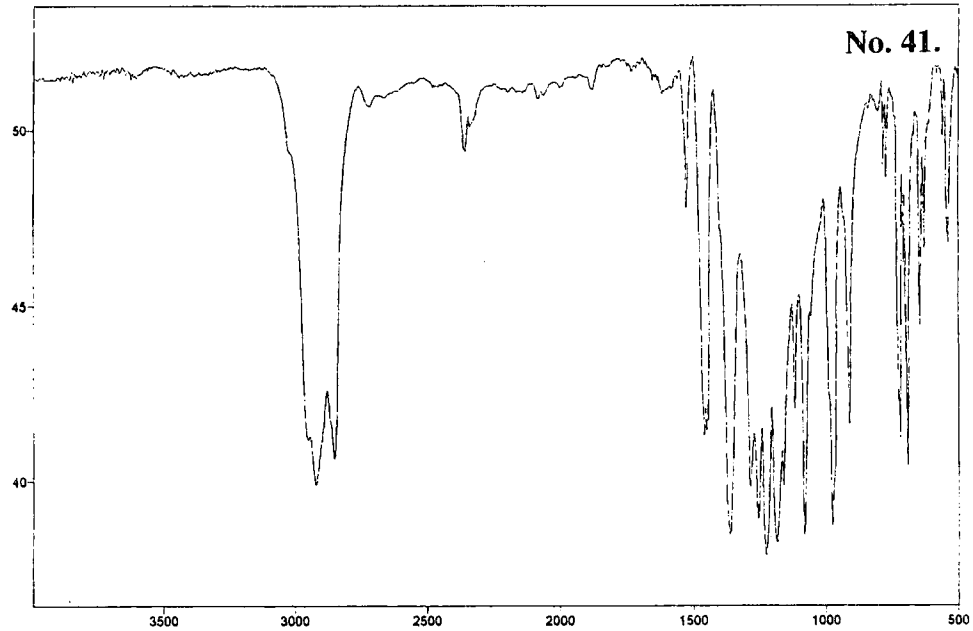

No. 37.
60
50
40
30
20
3500
3000
2500
2000
1500
1000
500

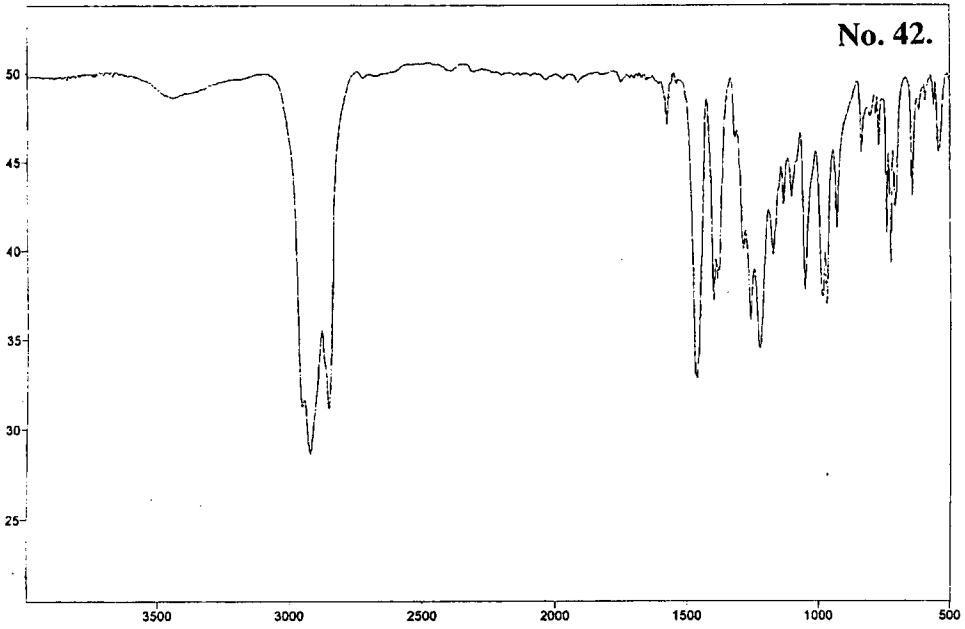

No. 38.
110
100
90
80
70
60
3500
3000
2500
2000
1500
1000
500

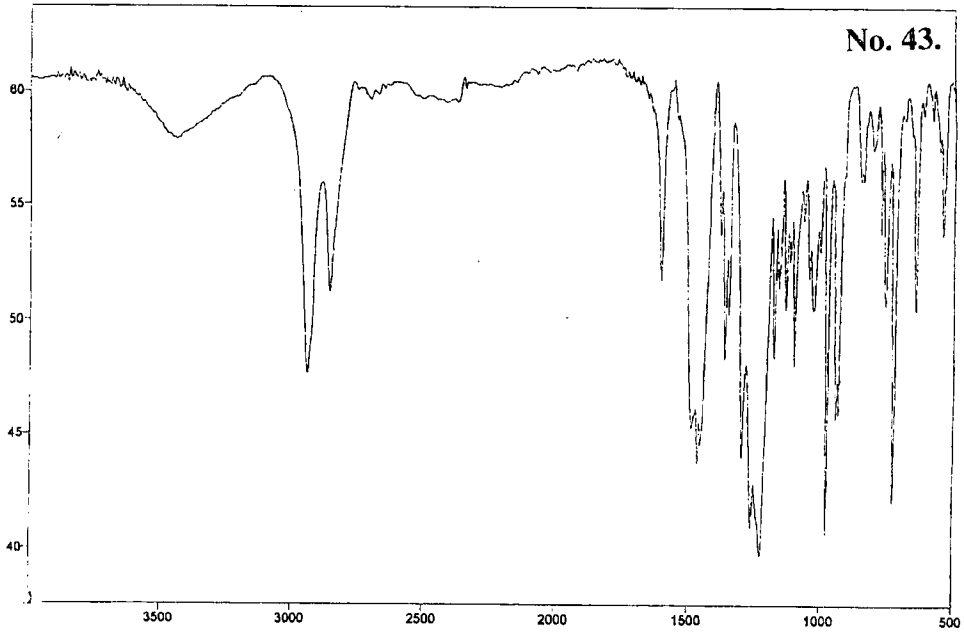

No. 39.
100
90
80
70
60
3500
3000
2500
2000
1500
1000
500

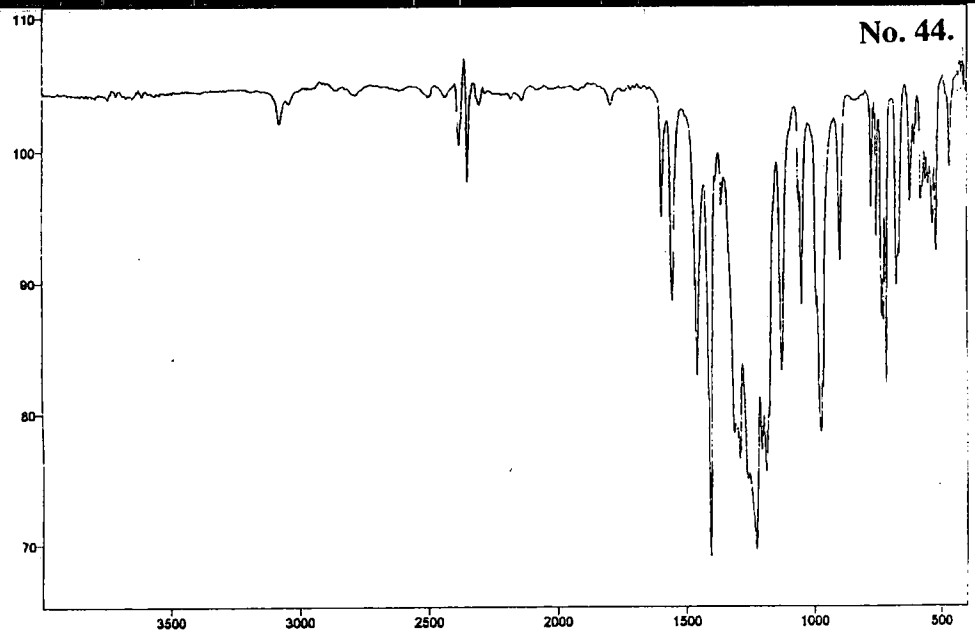
R 14.

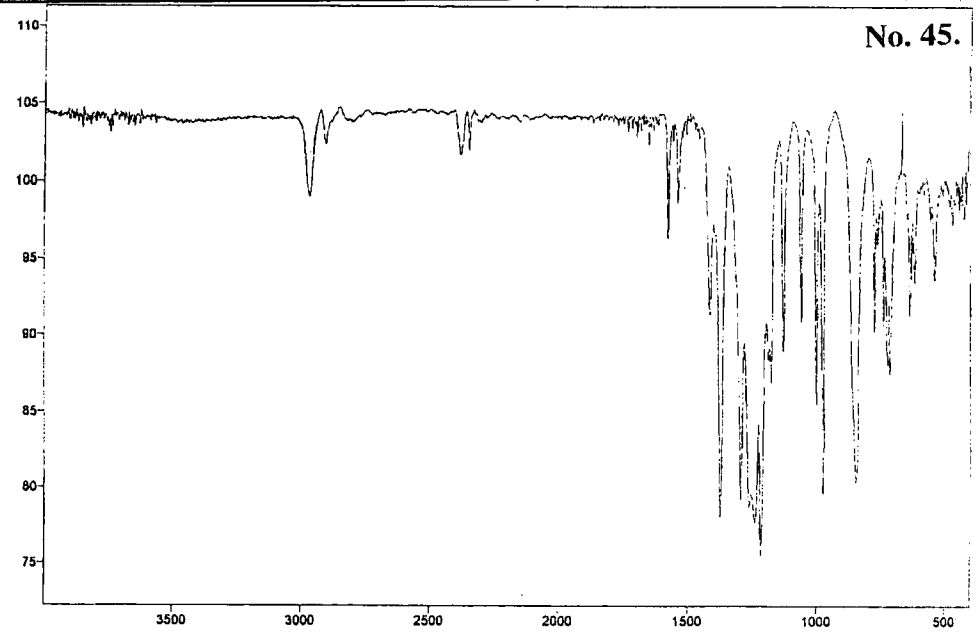

No. 40.
65
60
55
50
45
40
35
3500
3000
2500
2000
1500
1000

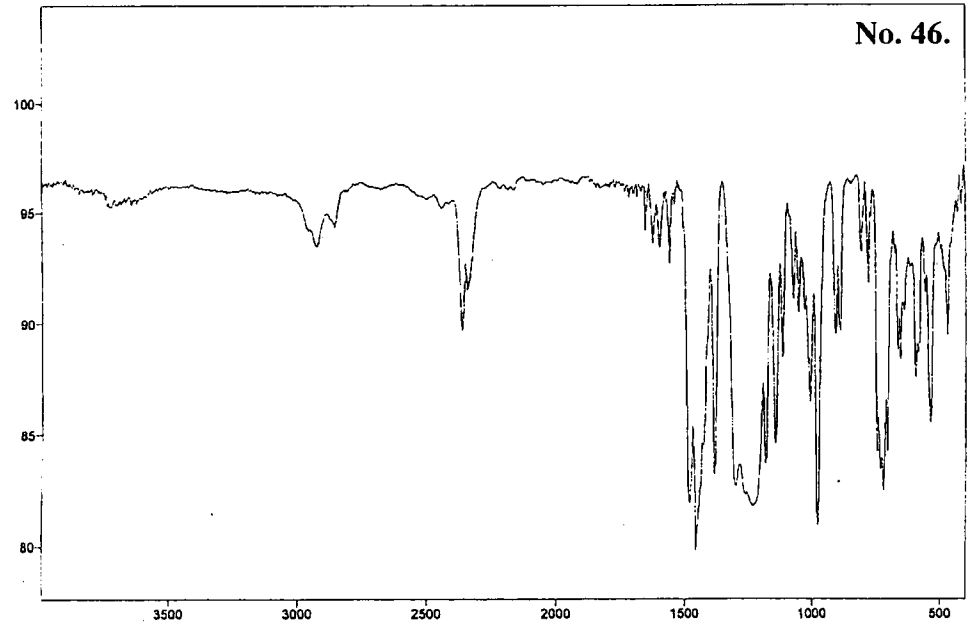

No. 41.
50
45
40
3500
3000
2500
2000
1500
1000
500

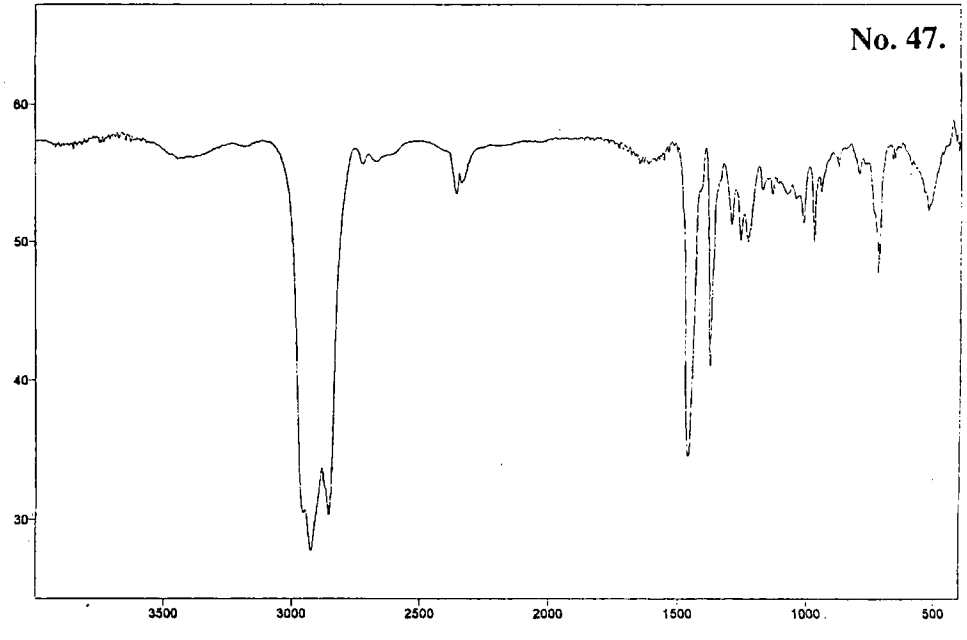

No. 42.
50
45
40
35
30
25
3500
3000
2500
2000
1500
1000
500

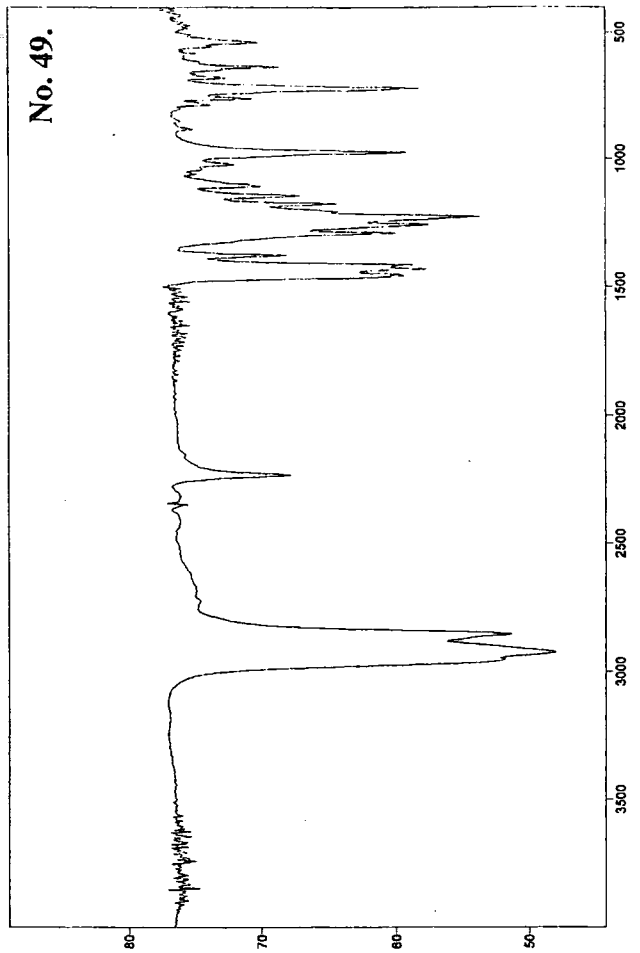

No. 43.
60
55
50
45
40
3500
3000
2500
2000
1500
1000
500

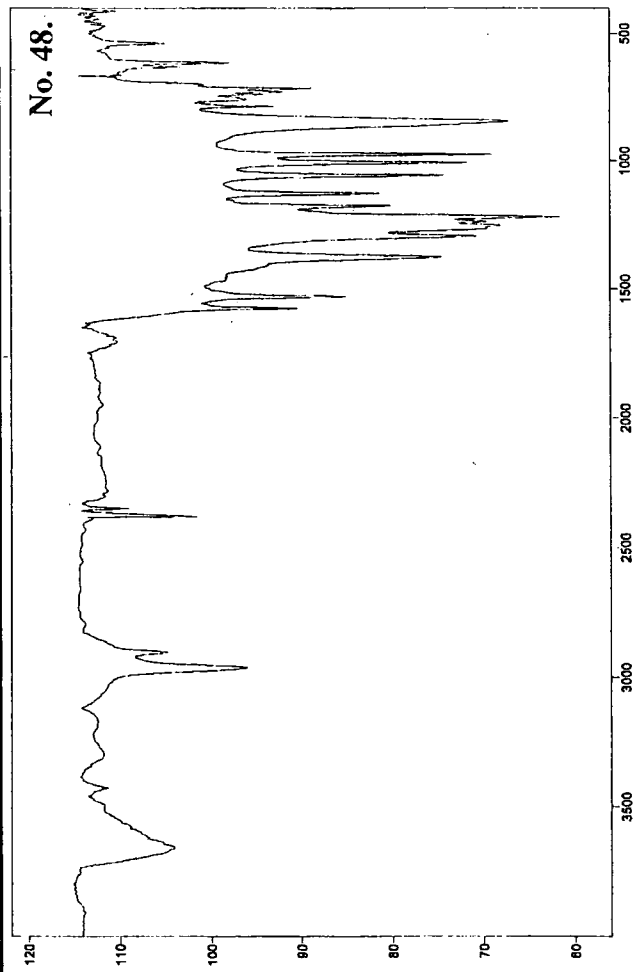

No. 44.
110
100
90
80
70
3500
3000
2500
2000
1500
1000
500

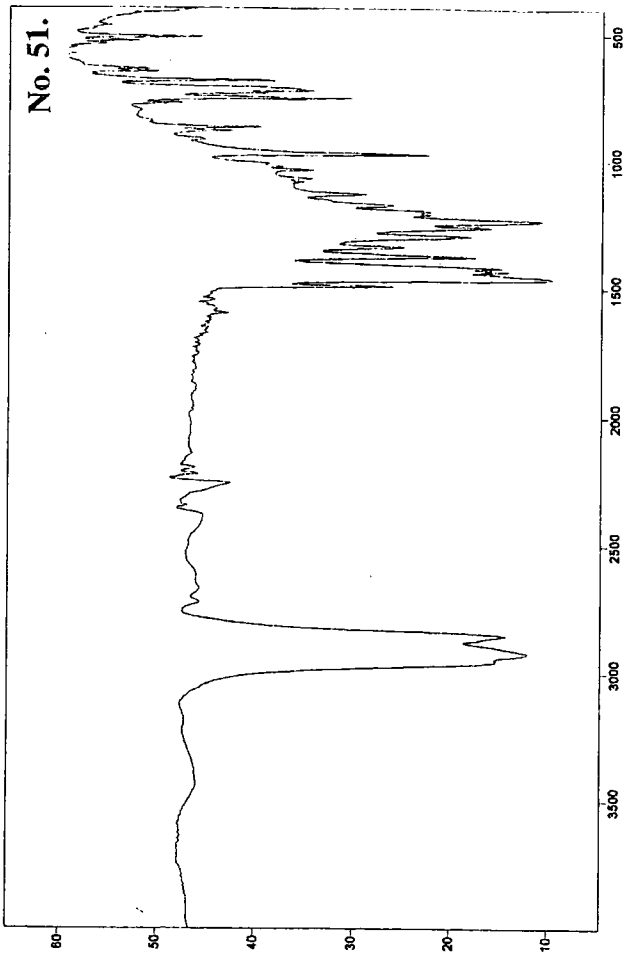

No. 45.
110
105
100
95
90
85
80
75
3500
3000
2500
2000
1500
1000
500

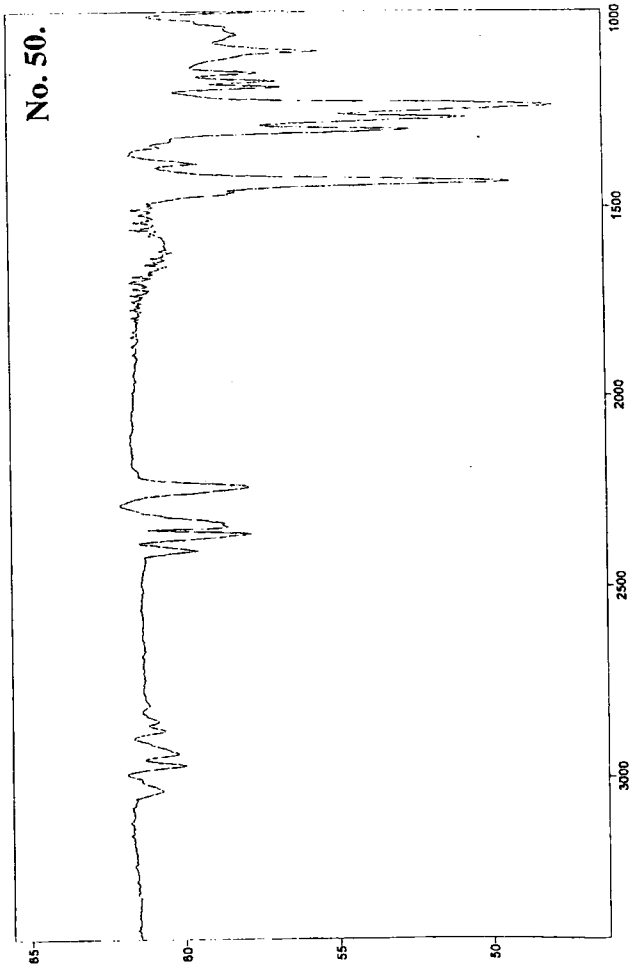

No. 46.
100
95
90
85
80
3500
3000
2500
2000
1500
1000
500

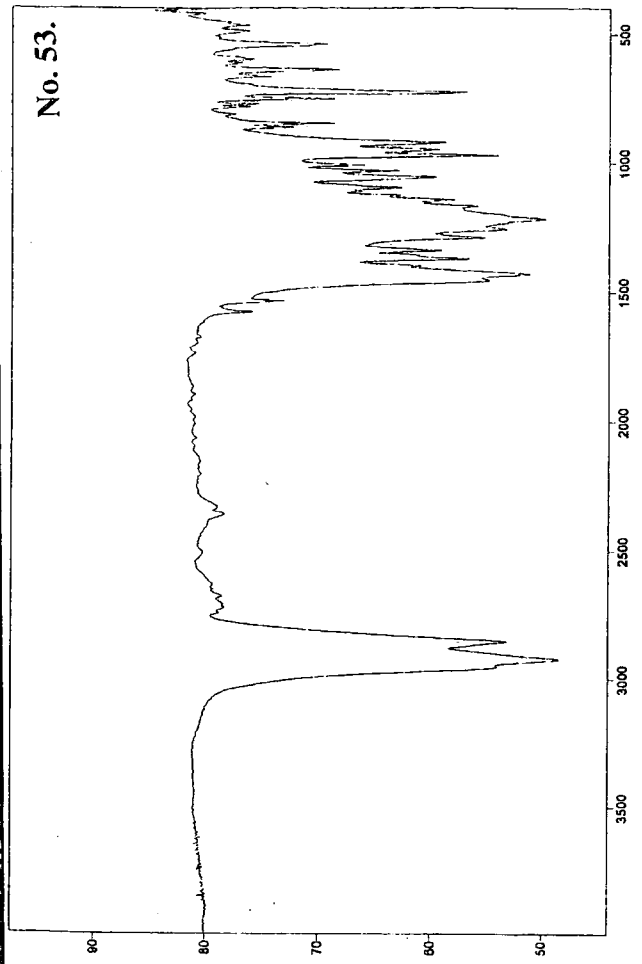

No. 47.
60
50
40
30
3500
3000
2500
2000
1500
1000
500

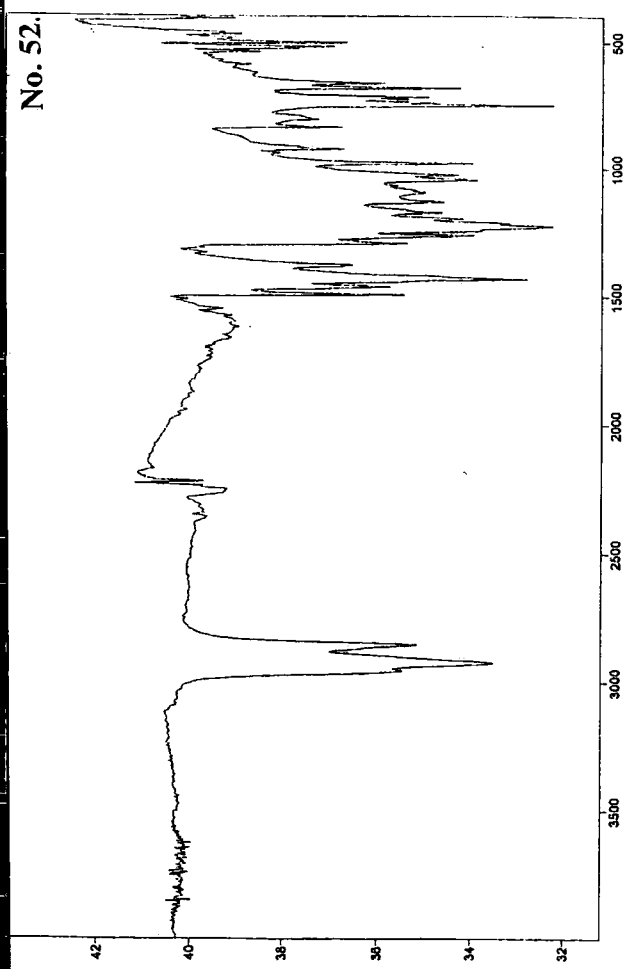

No. 49.
500
1000
1500
2000
2500
3000
3500
80
70
60
50

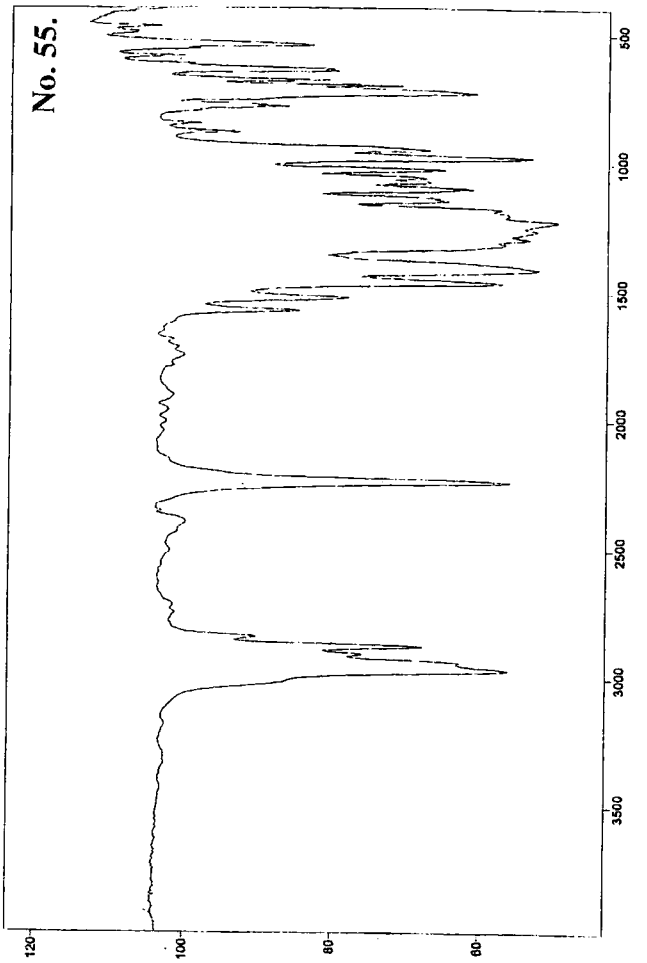

No. 48.
500
1000
1500
2000
2500
3000
3500
120
110
100
90
80
70
60

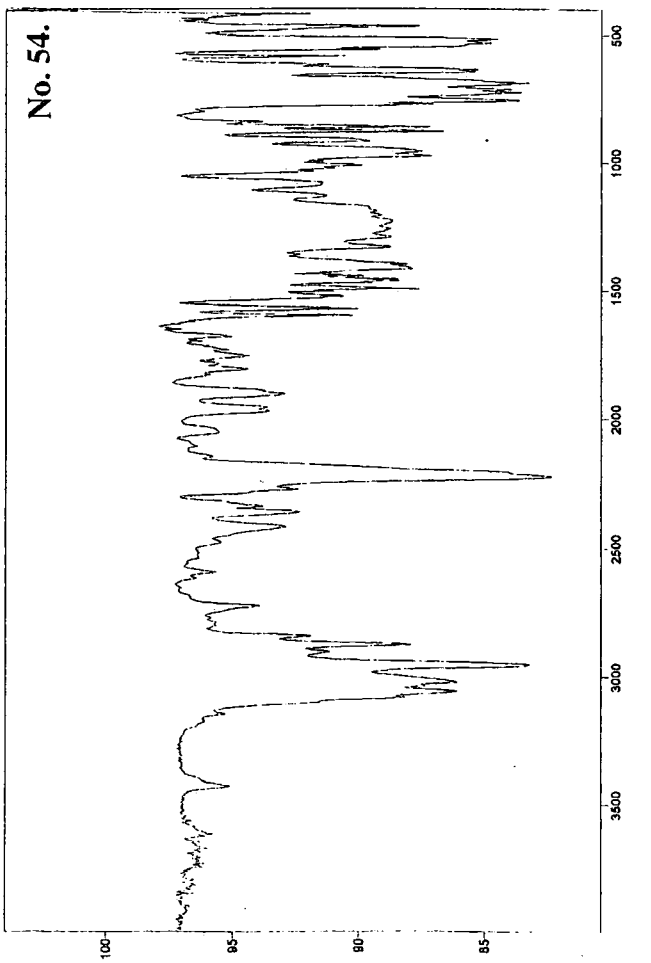

No. 51.
500
1000
1500
2000
2500
3000
3500
80
50
40
30
20
10


No. 50.
1000
1500
2000
2500
3000
65
60
55
50


No. 53.
90
80
70
60
50
3500
3000
2500
2000
1500
1000
500


No. 52.
42
40
38
36
34
32
3500
3000
2500
2000
1500
1000
500


No. 55.
120
100
80
60
3500
3000
2500
2000
1500
1000
500


No. 54.
100
95
90
85
3500
3000
2500
2000
1500
1000
500

Appendix C.

Mass Spectrometry Data.

Compound Number:	IUPAC Name:
(1)	*2,3,5,6-tetrafluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(2)	*2,3,5-trifluoro-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(3)	*2,3,5-trifluoro-6-methoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine.*
(4)	*3,5-difluoro-2,6-dimethoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(5)	*3,5,6-trifluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridin-2-ol*
(6)	*3,5,6-trifluoro-2-(methoxyethanoxy)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl]-pyridine*
(7)	*2,6-bis(2-methoxyethanoxy)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-pyridine*
(8)	*6-cyclohexyloxy-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-pyridine*
(9)	*2,6-dicyclohexyloxy-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-pyridine*
(10)	*2,3,5-trifluoro-6-phenoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine*
(11)	*3,5-difluoro-2,6-diphenoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine*
(13)	*2,6-bis-(3-methoxyphenoxy)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl]pyridine*
(14)	*2,5-difluoro-3-methoxy-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(15)	*5-fluoro-2,3-dimethoxy-4,6-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(16)	*Methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amine*
(17)	*Bis{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}methylamine*

(18) *{3,5-difluoro-6-(methylamino)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}methyl{3,5,6-trifluoro-4[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amine*

(19) *Bis{3,5-difluoro-6-(methylamino)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}methylamine*

(20) *Bis{6-(diethylamino)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}methylamine*

(21) *3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl]-2-3-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethyl](2-pyridyloxy)}phenoxy)pyridine*

(24) *2,3,5-trifluoro-6-(5-methyl-3-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}phenoxy)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine*

(25) *26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.<15,19>]octacosa-1(25),3,5,7(26),9(27),10,12,15,17,19(28),21,23-dodecaene*

(26) *26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-11-methyl-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(25),3,5,7(26),9(27),10,12,15,17,19(28),21,23-dodecaene*

(27) *26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-11,23-dimethyl-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(25),3,5,7(26),9(27),10,12,15,17,19(28),21,23-dodecaene*

(28) *2-1',2'-dioxyethyl-bis-3,5,6-trifluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*

(29) *6-(2-{3,5-difluoro-6-propoxy-4[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}ethoxy)-3,5-difluoro-4-1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridin-2-ol*

(30) *2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)oxy}-1-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1(trifluoromethyl)ethyl](2-pyridyloxy)}ethoxy)ethane*

(31) *25,26-diaza-11,23-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-10,12,22,24-tetrafluoro-2,5,8,14,17,20-hexaoxatricyclo[19.3.1.1<9,13>]hexacosa-1(24),9(26),10,12,21(25),22-hexaene*

(32) *Methyl[2-(methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amino)ethyl]{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amine*

(33) *2,3-difluoro-5,8-dimethyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethylethyl)]-5,6,7,8-tetrahydroquinoline*

(34) *2,5,11,14,19,20-hexaaza-8,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11,14-tetramethyltricyclo[13.3.1.1<6,10>]icosa-1(18),6(20),7,9,15,(19),16-hexaene*

(35) *{7-fluoro-1,4-dimethyl-8-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](1,2,3,4-tetrahydropyridino[2,3-b]pyrazin-6-yl)}methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl}amine*

(36) *Bis{7-fluoro-1,4-dimethyl-8-[1,2,2,2-trifluoromethyl)ethyl](1,2,3,4-tetrahydropyridino[2,3-b]pyrazin-6-yl)}methylamine*

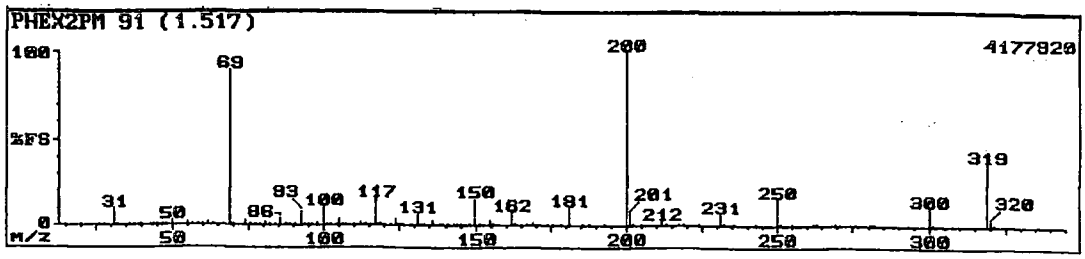
(37) *2,6-dibromo-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*

(38) *6-bromo-2,3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*

(39) *2,6-dihydrido-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*

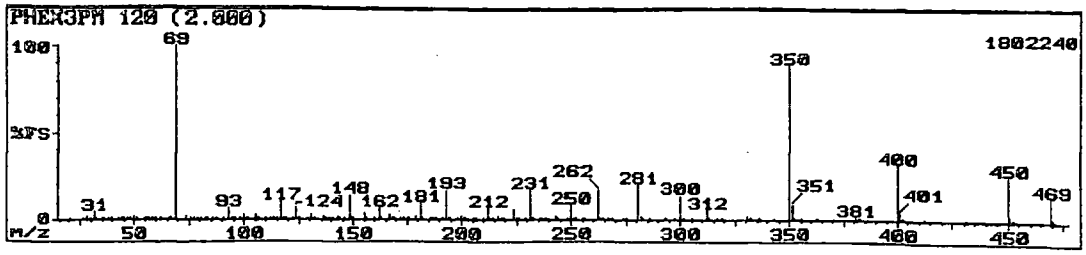
(40) *2,6-dibromo-3-fluoro-5-methoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*

(41)	*2,6-dibromo-3,5-dimethoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(42)	*2-bromo-3,5,6-trimethoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(43)	*6-bromo-3,5-difluoro-2-piperidyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine*
(44)	*2-bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl]pyridine*
(45)	*2-{bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl](2-pyridyl)}-2-methyl-2-silapropane*
(46)	*2-bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl]-6-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}pyridine*
(47)	*2-{6-bromo-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl](2-pyridyl)}{3,5,-difluoro-6-methoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine*
(48)	*2-{6-(1,1-dimethyl-1-silaethyl)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl](2-pyridyl)}-2-methyl-2-silapropane*
(49)	*6-bromo-3,5-difluoro-2-pent-1-ynyl-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(50)	*3,5-difluoro-2,6-dipent-1-ynyl-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(51)	*6-bromo-3,5-difluoro-2-phenylethynyl-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(52)	*2,6-bis(2-phenylethynyl)-3,5-difluoro-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*
(53)	*4-[1-(trifluoromethyl)-1,2,2,2-tetrafluoroethyl]-2-bromo-3-fluoro-5-methoxy-6-piperidylpyridine*
(54)	*4-[1-(trifluoromethyl)-1,2,2,2-tetrafluoroethyl]-2-bromo-3-methoxy-5-fluoro-6-(2-phenylethynyl)pyridine*
(55)	*4-[1-(trifluoromethyl)-1,2,2,2-tetrafluoroethyl]-2-bromo-3-methoxy-5-fluoro-6-pent-1-ynylpyridine*

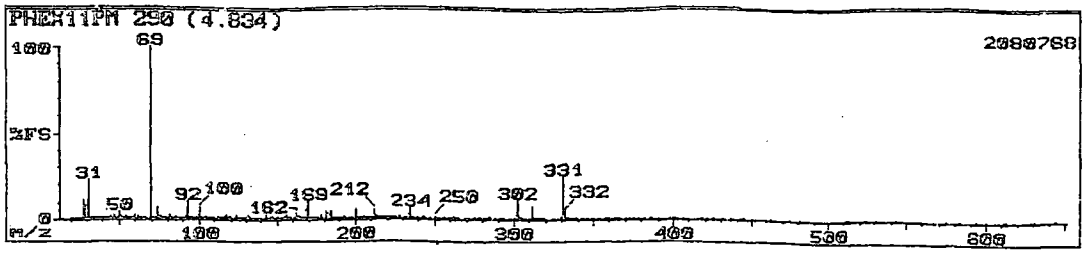


PHEX2PM 91 (1.517) 4177920

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.00	82	0.08	124	3.95	193	0.61
26	0.01	84	0.08	125	0.18	200	100.00
28	0.47	86	3.82	126	0.04	201	7.06
31	10.10	87	0.17	129	0.19	202	0.23
32	0.17	88	0.22	131	7.25	205	0.59
36	0.04	89	0.01	132	0.29	212	3.38
38	0.10	90	0.02	133	0.01	213	0.17
39	0.01	93	7.84	136	2.82	217	0.08
40	0.01	94	0.24	138	0.36	219	0.52
43	0.07	95	0.08	139	0.02	224	0.01
44	0.02	96	0.04	141	0.01	231	6.47
45	0.03	98	2.38	143	0.58	232	0.35
47	0.04	100	10.49	144	0.03	236	0.03
48	0.05	101	0.37	145	0.01	243	0.01
50	2.45	102	0.01	148	0.72	250	15.69
55	1.96	104	0.63	150	4.24	251	0.86
57	0.05	105	3.90	151	0.17	255	0.01
58	0.02	106	0.19	155	2.65	262	0.40
60	0.02	107	0.09	156	0.04	263	0.02
62	1.67	110	0.10	162	8.04	269	0.06
63	0.03	112	1.96	163	0.38	281	0.31
67	0.28	113	0.07	167	0.63	282	0.01
69	89.80	114	0.17	169	2.13	300	10.88
70	0.63	115	0.15	174	0.12	301	0.64
74	2.99	117	15.88	176	0.02	319	36.86
76	0.75	118	0.80	179	0.02	320	2.97
77	0.10	119	0.30	181	10.49	321	0.08
79	1.21	120	0.02	186	1.04		
81	2.13	122	0.01	188	0.07		



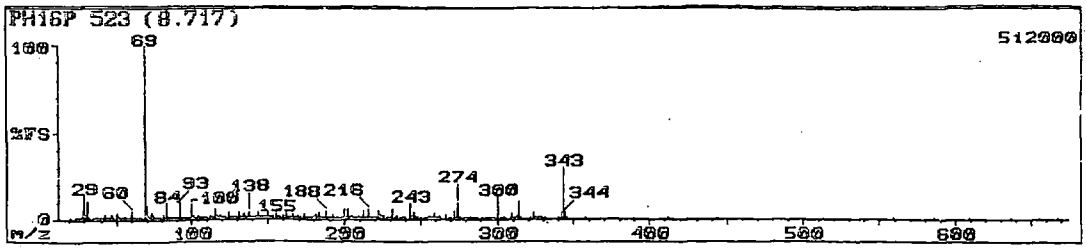
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.05	101	0.08	182	0.58	268	0.03
26	0.01	105	2.60	186	1.31	274	0.60
28	2.12	106	0.12	187	0.08	275	0.05
29	0.03	107	0.08	188	0.19	281	20.23
31	4.89	110	0.31	191	0.04	282	1.69
32	0.52	112	1.14	193	5.91	283	0.07
35	0.02	114	0.38	194	0.38	286	0.08
36	0.01	115	0.14	198	0.95	293	0.37
38	0.01	117	10.68	200	2.32	294	0.04
40	0.05	118	0.48	201	0.13	298	0.02
43	0.03	119	0.63	205	1.35	300	3.34
44	0.10	122	0.05	206	0.09	301	0.27
45	0.02	124	6.65	207	0.01	305	0.02
47	0.09	125	0.32	210	0.05	312	5.63
48	0.02	129	1.11	212	6.82	313	0.50
50	1.97	131	3.10	213	0.49	317	0.02
51	0.05	132	0.13	214	0.01	319	0.08
55	0.67	136	1.75	217	1.53	331	1.93
56	0.03	137	0.07	218	0.10	332	0.22
57	0.05	138	0.51	219	0.15	336	0.01
58	0.02	139	0.02	224	5.80	343	0.04
60	0.01	141	0.57	225	0.46	350	89.09
62	0.50	143	1.92	226	0.03	351	8.69
66	0.02	144	0.08	229	0.16	352	0.44
67	0.07	146	0.01	231	17.95	355	0.12
69	100.00	148	2.43	232	1.24	362	1.26
74	1.70	149	0.12	233	0.04	363	0.13
76	0.58	150	0.38	236	0.37	381	2.20
78	0.02	155	3.98	237	0.03	382	0.25
79	0.64	156	0.20	238	0.01	383	0.01
81	0.77	160	0.21	243	1.61	400	32.50
82	0.05	162	6.42	244	0.14	401	3.64
84	0.02	163	0.36	248	0.13	402	0.18
86	1.34	167	3.01	250	8.64	412	0.03
88	0.13	168	0.16	251	0.62	431	0.07
91	0.01	169	0.63	252	0.03	450	25.91
93	6.99	172	0.02	255	0.38	451	3.13
94	0.15	174	1.36	256	0.03	452	0.17
95	0.02	175	0.09	262	16.59	469	14.77
96	0.02	176	0.03	263	1.25	470	1.73
98	1.01	179	1.48	264	0.05	471	0.10
100	3.10	181	9.32	267	0.36		



PHEX11PM 290 (4.834) 2080766

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.84	79	0.51	134	0.98	188	1.41
21	0.02	81	3.20	135	0.56	189	0.12
24	0.12	82	1.70	136	0.97	190	0.05
25	0.11	83	0.34	137	1.05	191	0.07
26	1.41	85	0.55	138	1.06	193	1.06
27	0.71	86	1.92	139	0.13	193	2.01
28	11.47	87	0.26	140	0.18	194	0.49
29	9.15	87	0.58	141	0.05	195	0.26
30	1.18	88	0.56	142	1.69	196	0.98
31	23.23	89	0.29	143	3.20	197	1.34
32	0.87	90	0.10	144	0.98	198	0.22
33	1.35	91	3.20	145	0.41	200	3.54
34	0.05	92	10.58	146	1.64	200	5.51
35	0.79	93	7.23	147	2.10	201	0.55
36	0.73	94	0.33	148	0.31	202	0.29
37	0.61	95	0.49	149	1.01	203	0.06
38	1.12	96	0.21	150	2.09	205	0.92
39	0.84	97	0.06	151	0.41	205	1.61
40	0.40	98	0.48	152	0.12	206	0.21
41	0.56	99	2.76	154	0.05	207	0.05
42	0.58	100	6.94	155	1.92	209	0.04
43	1.38	101	0.51	155	3.30	209	0.07
44	1.41	102	0.23	157	0.41	211	0.03
45	1.57	103	0.04	157	0.57	212	2.79
46	0.82	104	1.09	158	0.09	212	5.56
47	2.46	105	2.31	159	0.03	213	1.70
48	0.17	106	0.62	161	0.04	214	1.38
49	0.29	107	0.41	162	2.02	215	0.51
50	5.12	108	0.13	162	3.54	216	0.12
51	1.57	109	0.16	163	1.75	217	0.10
52	0.19	110	0.20	164	1.76	219	0.92
53	0.05	112	1.53	165	0.84	219	1.14
54	0.17	113	1.32	166	0.34	221	0.53
55	2.23	113	0.70	167	0.38	221	0.40
56	0.45	114	1.33	169	5.46	222	0.05
57	0.85	115	0.62	169	10.63	224	0.26
58	0.13	116	1.75	170	1.09	224	0.35
59	0.11	117	3.05	171	0.21	225	0.07
60	3.15	118	1.38	172	0.05	228	1.92
62	1.61	119	2.28	174	0.65	231	0.31
63	0.37	120	0.43	174	1.18	232	1.43
64	0.79	121	0.13	175	0.33	233	3.40
65	1.17	122	0.16	176	0.16	234	6.74
66	0.26	123	2.01	178	1.39	234	6.99
67	0.22	124	3.35	178	2.49	236	0.08
69	100.00	125	0.40	179	0.23	238	0.89
71	0.34	126	0.22	181	1.51	240	0.09
72	0.27	127	0.07	181	5.12	242	0.23
73	0.19	128	0.05	182	4.23	243	2.09
74	6.84	129	0.07	183	3.35	244	0.48
75	1.50	130	1.54	184	4.82	247	0.65
76	1.60	131	3.15	185	0.63	250	2.20
77	0.09	132	1.66	186	0.63	251	0.51
78	0.32	133	1.08	188	1.06	252	0.16

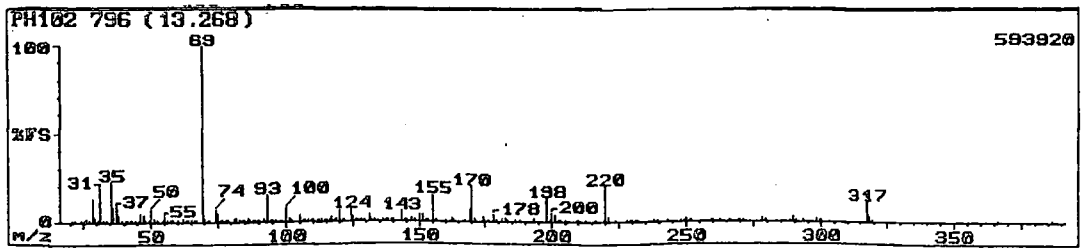
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
253	0.08	298	0.09	346	0.07	417	0.01
255	0.09	300	0.64	347	0.02	418	0.01
257	0.03	301	3.15	349	0.01	421	0.01
259	0.04	302	11.71	350	0.04	424	0.09
260	0.04	303	1.69	353	0.01	425	0.02
261	0.16	304	0.11	354	0.01	431	0.02
262	1.87	305	0.06	357	0.02	436	0.02
263	0.82	308	0.03	358	0.02	443	0.01
264	0.75	310	0.10	360	0.03	445	0.01
265	0.51	312	8.02	362	0.20	450	0.02
269	0.30	313	0.79	363	0.03	463	0.02
270	0.02	314	0.06	364	0.04	474	0.04
271	0.15	315	0.02	365	0.01	481	0.02
272	0.04	316	0.06	366	0.02	512	0.03
274	0.18	317	0.04	367	0.02	513	0.02
275	0.07	318	0.03	370	0.03	524	0.01
276	0.02	319	0.06	372	0.01	531	0.01
278	0.17	324	0.02	374	0.03	543	0.01
279	0.03	326	0.01	375	0.01	574	0.01
281	0.45	328	0.28	376	0.01	583	0.01
282	0.41	330	1.73	378	0.05	593	0.01
283	0.09	331	24.80	379	0.01	600	0.01
284	1.85	332	5.07	381	0.01	611	0.01
285	0.06	333	0.39	382	0.02	612	0.02
288	0.70	334	0.07	385	0.01	613	0.02
289	0.04	335	0.02	386	0.02	628	0.01
290	0.42	336	0.02	390	0.03	631	0.02
291	0.07	337	0.01	398	0.01	643	0.09
292	0.24	338	0.03	400	1.40	644	0.02
293	0.38	340	0.01	401	0.15		
294	0.05	343	0.02	402	0.01		
297	0.79	344	0.01	406	0.01		



PH16P 523 (8.717) 51200(

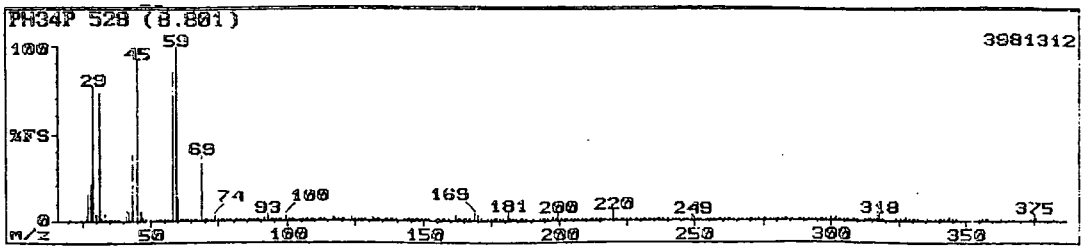
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.24	81	3.25	139	0.38	199	0.12
24	0.14	82	0.84	140	0.12	200	5.75
25	0.18	84	9.75	141	0.06	201	0.37
26	0.89	85	0.73	142	0.11	202	0.72
27	0.40	86	0.90	143	3.85	203	5.35
28	6.15	87	0.35	144	1.43	204	0.21
29	14.80	88	0.67	145	0.41	205	1.91
30	2.99	89	0.67	146	0.58	206	0.26
31	10.45	90	0.31	147	0.52	207	0.29
32	0.22	91	0.10	148	0.28	208	0.19
33	0.73	92	0.86	150	3.40	209	1.80
35	0.65	93	9.50	151	1.20	210	0.59
36	0.36	94	0.65	152	1.15	211	0.30
37	0.25	95	0.41	153	1.98	212	4.50
38	0.68	96	0.32	155	4.15	214	0.53
39	0.80	97	0.21	156	0.44	215	0.45
40	0.34	98	0.36	157	0.35	216	6.15
41	0.38	99	0.39	159	1.56	217	0.81
42	1.35	100	8.55	160	0.64	218	0.08
43	2.53	101	1.84	162	4.10	219	1.09
44	0.94	102	1.13	163	0.63	220	0.08
45	0.74	103	1.05	164	1.30	221	0.23
46	0.32	104	1.75	165	0.33	222	5.15
47	3.25	105	1.66	166	2.48	224	2.75
48	0.10	106	0.50	167	0.38	225	1.73
50	3.85	107	0.40	168	0.16	226	2.26
51	1.49	108	0.12	169	1.61	228	0.60
52	0.31	109	0.37	170	0.38	229	0.24
53	0.13	110	0.18	171	0.26	230	0.30
54	0.50	112	1.61	172	0.68	231	6.10
55	1.35	113	0.68	174	2.78	233	0.13
56	1.65	114	0.84	175	0.95	234	1.90
57	0.78	115	0.39	176	0.50	236	0.16
58	0.66	116	5.75	177	0.21	238	0.45
59	0.33	117	1.76	178	0.76	239	0.07
60	4.55	118	0.31	179	0.22	240	0.45
61	0.14	119	1.91	180	0.41	243	9.40
62	0.91	120	0.44	181	2.20	244	1.80
63	0.40	121	0.24	182	2.58	245	3.40
64	0.44	122	0.14	183	0.72	246	0.91
65	0.73	124	3.45	184	3.40	248	0.04
66	0.29	125	0.54	185	0.17	250	1.29
67	0.14	126	0.41	186	0.15	252	0.26
69	100.00	127	0.26	187	0.39	253	0.15
70	7.30	128	0.30	188	4.75	254	0.85
71	0.98	129	0.35	189	0.17	255	1.49
72	1.75	131	3.50	190	0.26	257	0.10
73	0.38	132	0.75	191	0.06	258	0.28
74	3.65	133	0.53	193	3.08	259	4.05
75	1.66	134	2.53	194	0.98	260	0.21
76	0.78	135	0.30	195	0.34	261	0.09
77	0.28	136	0.44	196	0.67	262	1.81
78	0.25	137	0.57	197	0.72	263	0.40
79	0.27	138	3.75	198	0.13	266	3.00

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
269	0.06	286	0.22	305	0.32	340	0.29
270	0.29	287	0.18	309	4.10	342	3.65
272	4.60	290	0.04	310	0.24	343	30.00
273	0.64	293	0.09	312	1.31	344	4.35
274	9.40	294	0.78	313	1.73	345	0.43
275	0.60	295	0.19	314	10.30	358	0.06
276	0.58	296	0.85	315	0.80	412	0.06
278	0.12	297	0.17	322	0.11	559	0.07
279	0.04	298	0.29	324	3.75	586	0.07
280	0.12	299	0.33	325	0.34	609	0.06
281	0.15	300	14.00	326	0.21	636	0.06
282	0.04	301	0.58	327	0.05	637	0.05
283	0.25	302	0.10	328	0.70	655	0.05
284	0.20	303	0.07	329	0.08	667	0.03
285	0.05	304	0.39	331	0.05		



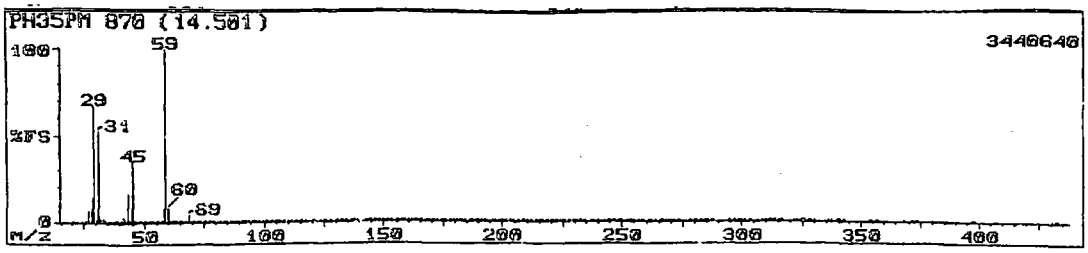
PH102'713 (11.884) REFINE 61696

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.85	60	1.12	143	2.41	229	0.58
24	0.88	62	0.41	147	1.08	230	0.92
25	1.41	63	0.38	150	2.00	231	0.62
26	8.92	69	46.06	151	1.16	232	0.52
27	40.66	73	4.25	152	0.26	238	0.88
28	37.76	74	2.88	155	2.59	243	2.96
29	2.41	75	0.81	162	2.44	249	11.20
30	0.82	81	1.30	169	5.32	250	3.53
31	6.56	82	0.68	170	15.35	251	2.13
35	21.06	86	1.30	171	0.56	265	1.50
36	5.45	92	1.79	174	0.70	269	0.75
37	12.55	93	5.29	178	2.54	270	1.01
38	16.29	98	0.35	181	3.86	275	0.54
39	62.24	100	3.86	182	1.92	279	0.28
40	12.45	101	0.39	188	1.45	281	6.38
41	90.46	105	1.13	191	1.71	282	3.03
42	29.46	112	0.91	193	4.15	283	2.18
43	100.00	114	0.45	198	13.38	288	2.88
44	7.78	117	1.30	199	4.41	289	10.27
45	1.52	119	1.28	200	5.08	290	0.77
47	4.05	120	2.13	201	1.84	298	3.97
49	0.81	124	2.77	202	0.65	300	0.40
50	2.28	125	0.83	205	1.59	301	1.00
51	1.26	131	2.67	207	1.30	317	49.38
55	1.15	132	0.76	212	1.12	318	10.68
56	0.70	133	1.07	219	2.20	344	1.47
58	0.95	136	0.32	220	37.76	359	2.36
59	27.39	138	0.51	228	0.93		



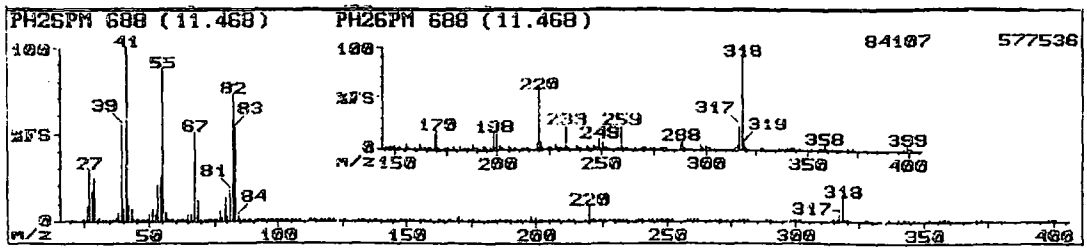
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.12	86	0.56	156	0.10	226	0.05
24	0.01	87	0.08	157	0.05	228	0.27
26	3.22	88	0.17	158	0.04	229	0.07
27	15.33	89	0.04	159	0.04	230	0.27
28	20.88	90	0.06	162	2.65	231	0.71
29	76.95	92	1.88	163	0.24	232	0.32
30	4.27	93	3.55	164	0.40	233	1.36
31	72.84	94	0.22	165	0.06	234	0.95
32	1.95	95	0.11	166	0.04	235	0.06
33	3.83	96	0.07	167	0.27	236	0.02
34	0.08	97	0.06	169	3.68	237	0.01
35	0.06	98	0.24	170	2.70	238	0.54
36	0.05	100	3.29	171	0.16	240	0.03
37	0.07	101	0.25	174	0.41	242	0.11
38	0.03	102	0.08	175	0.08	243	0.79
39	0.58	105	1.01	176	0.12	244	0.10
41	5.61	106	0.23	177	0.02	246	0.62
42	4.53	107	0.08	178	0.66	247	0.27
43	38.27	108	0.02	179	0.06	249	3.24
45	92.59	109	0.02	181	4.42	250	1.72
46	4.73	110	0.02	182	1.33	251	0.17
47	1.53	112	0.63	183	0.43	252	0.06
48	0.04	113	0.20	184	0.50	255	0.07
50	0.69	114	0.27	186	0.13	256	0.09
51	0.51	117	1.50	187	0.12	257	0.10
52	0.03	118	0.07	188	1.14	259	0.03
53	0.05	119	0.86	190	0.03	260	0.07
54	0.15	120	0.37	193	0.82	261	0.05
55	0.69	121	0.07	194	0.15	262	0.22
56	0.22	124	2.01	195	0.06	263	0.09
58	85.19	125	0.32	196	0.15	264	0.11
59	100.00	126	0.07	198	1.65	266	0.04
60	13.58	127	0.06	199	0.78	267	0.01
61	1.13	128	0.05	200	4.32	269	0.07
62	0.61	131	2.24	201	0.35	270	0.12
63	0.69	132	0.37	202	0.07	271	0.02
64	0.14	133	0.32	203	0.02	272	0.03
65	0.13	134	0.05	205	0.95	273	0.08
66	0.07	136	0.46	206	0.10	275	0.68
67	0.11	137	0.21	207	0.05	276	0.08
69	37.86	138	0.46	209	0.02	278	0.03
70	0.42	139	0.03	210	0.03	279	0.02
71	0.08	140	0.02	212	1.27	280	0.11
72	0.03	143	1.00	213	0.15	281	0.09
74	3.01	144	0.11	214	0.46	282	0.05
75	0.57	145	0.03	215	0.05	283	0.18
76	0.62	146	0.06	216	0.02	284	0.03
77	0.12	147	0.60	217	0.04	286	0.03
78	0.17	148	0.13	219	0.56	288	0.77
79	0.12	149	0.14	220	6.28	289	1.15
81	1.14	150	1.02	221	0.60	290	0.30
82	0.36	151	0.31	223	0.06	292	0.04
83	0.11	152	0.12	224	0.09	293	0.03
84	0.04	155	1.42	225	0.17	294	0.02

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
296	0.05	312	0.06	329	0.16	346	0.01
297	0.03	313	0.03	330	0.71	355	0.32
298	0.10	314	0.09	331	0.14	356	0.14
300	1.72	315	1.21	332	0.05	357	0.02
301	0.35	316	0.32	336	0.01	358	0.02
302	1.83	317	3.52	339	0.01	363	0.02
303	0.14	318	4.19	340	0.03	374	0.29
305	0.02	319	0.26	341	0.39	375	4.12
306	0.01	324	0.07	342	0.38	376	0.37
308	0.02	326	0.77	343	0.19	383	0.02
309	0.00	327	0.04	344	1.85		
310	0.03	328	1.95	345	0.16		



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.15	78	0.01	144	0.05	209	0.01
24	0.01	79	0.02	145	0.03	210	0.02
25	0.05	81	0.09	146	0.02	212	0.09
26	1.12	82	0.08	147	0.03	214	0.18
27	7.02	83	0.02	148	0.01	215	0.06
28	14.29	84	0.03	150	0.44	216	0.59
29	66.67	85	0.02	151	0.05	217	0.06
30	2.23	86	0.02	152	0.07	218	0.62
31	52.86	87	0.02	153	0.02	219	0.29
32	2.35	88	0.02	155	0.19	220	0.04
33	2.14	89	0.03	156	0.03	221	0.02
34	0.05	90	0.03	157	0.02	222	0.03
35	0.03	91	0.01	158	0.02	224	0.05
36	0.04	92	0.03	159	0.03	225	0.11
37	0.01	93	0.52	160	0.02	226	0.03
38	0.03	94	0.04	162	0.25	227	0.01
39	0.31	95	0.01	163	0.05	228	0.16
40	0.15	96	0.02	164	0.12	229	0.02
41	2.77	97	0.01	165	0.03	230	0.06
42	1.76	98	0.01	166	0.09	231	0.14
43	16.79	100	0.74	167	0.02	232	0.10
44	1.10	101	0.10	168	0.17	233	0.02
45	34.76	102	0.04	169	0.18	234	0.01
46	0.89	103	0.01	170	0.06	237	0.02
47	0.38	104	0.01	171	0.03	238	0.03
48	0.03	105	0.03	172	0.02	239	0.04
49	0.02	106	0.02	174	0.18	240	0.03
50	0.11	107	0.02	175	0.13	243	1.11
51	0.18	108	0.01	176	0.03	244	0.12
52	0.03	109	0.02	178	0.05	245	0.04
53	0.03	110	0.01	179	0.01	246	0.01
54	0.10	112	0.09	181	0.14	247	0.12
55	0.12	113	0.04	182	0.08	248	0.03
56	0.10	114	0.02	183	0.02	249	0.01
57	0.77	115	0.01	184	0.02	250	0.05
58	7.32	116	0.11	186	0.02	252	0.03
59	100.00	117	0.05	187	0.07	253	0.03
60	8.10	119	0.19	188	0.10	254	0.02
61	0.66	120	0.05	189	0.05	255	0.02
62	0.08	121	0.01	190	0.02	257	0.10
63	0.11	124	0.22	191	0.01	258	0.02
64	0.07	125	0.04	193	0.15	259	0.04
65	0.03	126	0.02	194	0.06	261	0.02
66	0.03	128	0.02	195	0.01	262	0.01
67	0.03	130	0.02	196	0.06	264	0.01
69	3.63	131	0.25	197	0.06	266	0.16
70	0.52	132	0.04	198	0.03	267	0.02
71	0.11	133	0.02	200	0.87	268	0.09
72	0.04	134	0.01	201	0.09	269	0.02
73	0.07	136	0.02	202	0.16	270	0.03
74	0.28	137	0.05	203	0.04	271	0.04
75	0.16	138	0.11	205	0.07	272	0.07
76	0.06	139	0.02	207	0.05	273	0.05
77	0.02	143	0.19	208	0.04	274	0.01

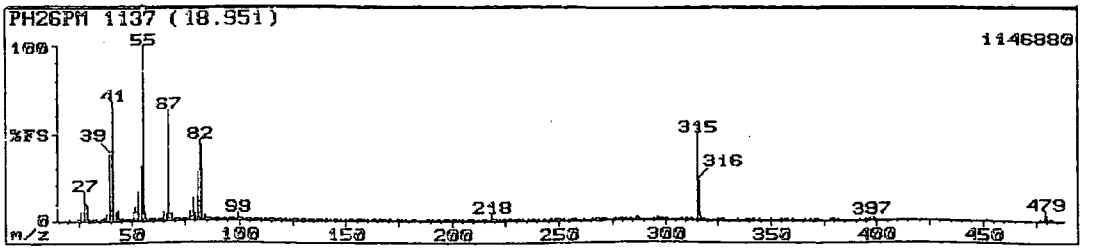
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
278	0.01	299	0.04	324	0.02	356	0.27
279	0.01	300	0.21	325	0.01	357	0.03
280	0.02	301	0.02	326	0.05	368	0.04
281	0.01	303	0.01	327	0.01	371	0.09
282	0.01	306	0.03	328	0.08	372	0.03
283	0.03	308	0.01	329	0.07	373	0.15
284	0.06	310	0.02	330	0.07	374	0.02
285	0.03	311	0.02	336	0.01	380	0.02
286	0.22	312	0.23	337	0.01	386	0.01
287	0.17	313	0.14	339	0.28	397	0.07
288	0.03	314	0.05	340	0.14	398	0.01
294	0.03	315	0.49	341	0.47	431	1.26
295	0.01	316	0.15	342	0.35	432	0.18
296	0.02	317	0.02	343	0.04	433	0.02
297	0.05	322	0.13	353	0.01		
298	0.01	323	0.02	354	0.06		



PH26PM 688 (11.468) 577536

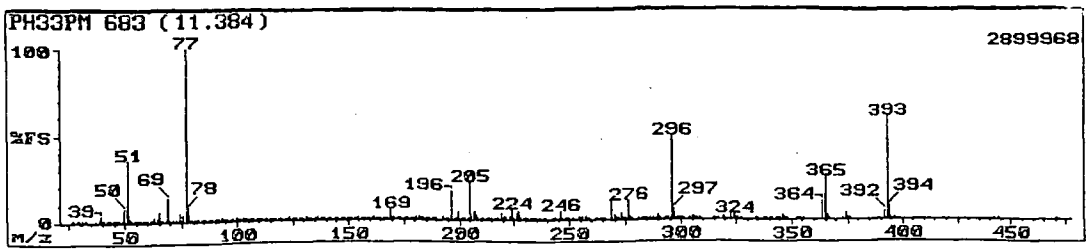
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.67	79	13.65	150	0.38	234	0.07
24	0.58	80	3.37	151	0.26	238	0.47
25	1.35	81	17.20	152	0.08	239	0.11
26	8.51	82	72.34	155	0.68	240	0.13
27	28.90	83	53.19	156	0.06	243	0.49
28	16.13	84	3.28	159	0.12	244	0.06
29	24.11	85	0.25	162	0.70	246	0.45
30	0.72	86	0.20	163	0.15	247	0.08
31	2.06	87	0.14	164	0.12	248	0.22
32	0.37	88	0.10	166	0.06	249	1.40
33	0.11	89	0.07	167	0.10	250	0.84
35	0.11	91	0.24	169	2.19	251	0.17
36	0.27	92	0.76	170	2.54	252	0.06
37	2.24	93	0.93	171	0.22	258	0.12
38	4.43	94	0.21	174	0.23	259	0.49
39	54.61	95	0.19	175	0.07	260	0.04
40	7.23	96	0.10	176	0.08	262	0.07
41	100.00	97	0.07	178	0.45	266	0.05
42	9.22	98	0.12	181	0.36	269	0.27
43	6.38	99	1.00	182	0.40	270	0.21
44	0.83	100	0.90	183	0.17	271	0.08
45	0.17	101	0.16	184	0.08	273	0.08
46	0.27	102	0.03	186	0.14	275	0.09
47	0.33	103	0.05	188	0.66	278	0.07
48	0.10	104	0.23	189	0.11	279	0.11
49	0.44	105	0.48	190	0.22	280	0.22
50	4.08	106	0.16	193	0.47	281	0.13
51	7.05	107	0.06	194	0.07	288	1.19
52	3.90	108	0.05	196	0.11	289	1.15
53	20.21	112	0.21	198	2.44	290	0.32
54	25.00	113	0.12	199	0.29	298	0.74
55	87.23	114	0.11	200	2.23	299	0.20
56	4.74	115	0.10	201	0.46	300	0.58
57	0.70	117	0.64	202	0.10	301	0.22
58	0.09	118	0.08	205	0.45	302	0.24
59	0.09	119	0.41	206	0.07	314	0.09
61	0.15	120	0.25	208	0.10	315	0.26
62	0.47	121	0.06	209	0.12	316	0.67
63	1.12	124	0.84	212	0.34	317	3.41
64	0.28	125	0.15	213	0.15	318	13.48
65	4.30	126	0.07	214	0.09	319	1.00
66	3.41	131	0.73	219	0.96	320	0.08
67	50.35	132	0.20	220	8.29	327	0.05
68	2.06	133	0.09	221	0.89	328	0.24
69	11.88	136	0.21	222	0.05	336	0.07
70	0.41	137	0.16	224	0.09	340	0.07
71	0.12	138	0.13	225	0.07	342	0.21
72	0.05	140	0.04	226	0.07	343	0.13
73	0.13	143	0.33	228	0.62	344	0.24
74	0.40	144	0.08	229	0.12	346	0.10
75	0.53	145	0.05	230	0.14	352	0.06
76	0.39	147	0.23	231	0.20	356	0.30
77	5.81	148	0.07	232	0.24	357	0.08
78	2.26	149	0.07	233	0.44	358	0.71

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
359	0.05	372	0.23	399	0.64	401	0.03
370	0.20	398	0.20	400	0.32		



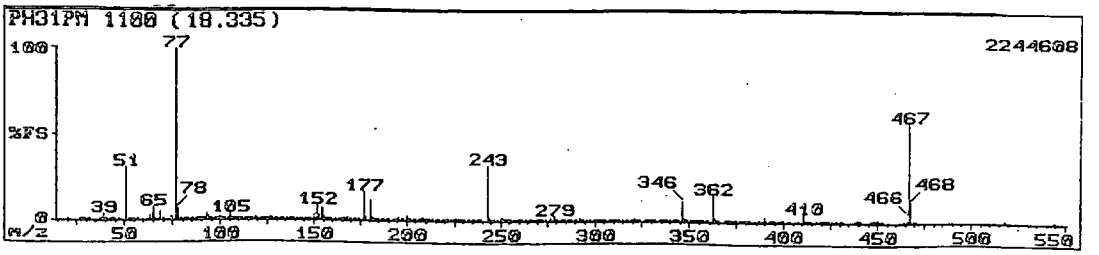
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.56	78	1.81	134	0.03	209	0.02
24	0.27	79	13.04	135	0.03	210	0.03
25	0.70	80	4.22	136	0.03	212	0.04
26	5.04	81	27.50	137	0.09	214	0.04
27	16.79	82	45.71	138	0.08	216	0.19
28	9.38	83	42.50	139	0.03	218	3.68
29	8.84	84	2.75	140	0.03	219	0.41
30	0.32	85	0.11	141	0.02	220	0.13
31	0.88	86	0.09	143	0.11	221	0.06
32	0.28	87	0.09	144	0.04	222	0.03
33	0.04	88	0.04	145	0.04	224	0.10
35	0.21	89	0.09	146	0.04	225	0.06
36	0.36	90	0.07	147	0.05	226	0.11
37	1.72	91	0.29	150	0.30	227	0.32
38	3.91	93	0.73	151	0.09	228	0.52
39	37.50	94	0.19	152	0.07	229	0.07
40	5.40	95	0.21	153	0.02	230	0.04
41	67.50	96	0.07	155	0.12	231	0.11
42	5.00	97	0.15	156	0.04	232	0.03
43	5.49	98	0.66	157	0.03	233	0.03
44	0.71	99	3.86	158	0.02	236	0.04
45	0.13	100	0.90	160	0.03	237	0.04
46	0.12	101	0.10	162	0.08	238	0.04
47	0.18	102	0.06	163	0.04	239	0.06
48	0.13	103	0.03	164	0.03	240	0.06
49	0.61	104	0.02	165	0.04	243	0.54
50	4.62	105	0.10	166	0.03	244	0.06
51	7.86	106	0.10	168	0.34	246	0.56
52	4.71	107	0.07	169	0.12	247	0.65
53	16.07	108	0.05	170	0.12	248	0.31
54	31.07	109	0.09	171	0.03	249	0.16
55	100.00	110	0.02	174	0.11	250	0.05
56	5.31	112	0.10	175	0.07	251	0.05
57	0.84	113	0.07	176	0.03	252	0.05
58	0.13	114	0.05	178	0.03	255	0.02
59	0.17	115	0.07	181	0.08	256	0.02
60	0.08	116	0.07	182	0.06	257	0.07
61	0.22	117	0.09	183	0.04	258	0.04
62	0.52	118	0.05	188	0.06	262	0.03
63	1.42	119	0.13	189	0.05	266	0.30
64	0.32	120	0.23	191	0.04	267	0.06
65	4.53	121	0.06	193	0.12	268	0.16
66	3.57	122	0.04	194	0.05	269	0.08
67	62.86	123	0.11	196	0.50	270	0.08
68	3.64	124	0.15	197	0.11	271	0.04
69	4.20	125	0.06	198	0.06	272	0.07
70	0.71	126	0.03	199	0.09	276	0.04
71	0.13	127	0.05	200	0.78	277	0.47
72	0.05	128	0.04	201	0.11	278	0.16
73	0.08	129	0.03	202	0.15	279	0.05
74	0.47	130	0.03	203	0.04	280	0.06
75	0.50	131	0.18	205	0.12	281	0.03
76	0.21	132	0.05	207	0.04	284	0.07
77	5.18	133	0.04	208	0.06	286	1.41

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
287	2.03	315	49.64	350	0.03	380	0.20
288	0.28	316	22.32	354	0.29	381	0.04
295	0.06	317	1.79	355	0.05	392	0.05
296	1.63	318	0.15	356	0.80	395	0.04
297	0.41	325	0.04	357	0.10	396	0.52
298	0.31	326	0.28	358	0.04	397	3.17
299	0.24	327	0.06	360	0.06	398	1.58
300	0.97	328	0.04	366	0.05	399	0.21
301	0.05	334	0.03	368	0.13	452	0.04
307	0.02	338	0.07	369	0.92	477	0.03
308	0.02	339	0.04	370	1.26	479	5.56
310	0.05	340	0.23	371	0.16	480	2.59
311	0.05	341	0.15	372	0.03	481	0.41
312	0.03	342	0.10	378	0.22	482	0.04
313	0.16	344	0.07	379	0.07		



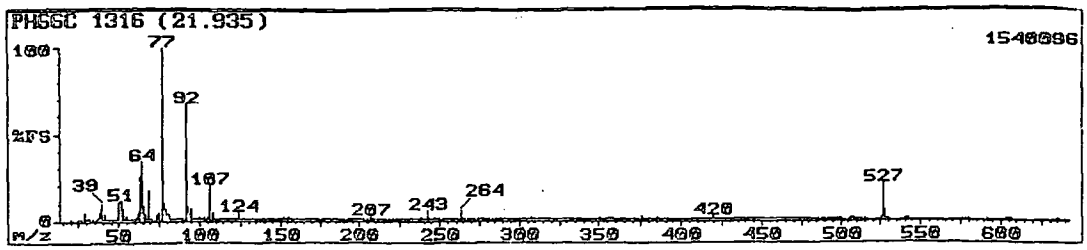
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.04	86	0.26	141	0.58	199	0.24
27	0.28	87	0.07	142	0.07	200	4.45
28	0.25	88	0.11	143	1.36	201	1.26
29	0.01	89	0.04	144	0.14	202	0.55
31	0.25	90	0.04	145	0.20	203	0.05
32	0.08	91	0.10	146	0.17	204	0.22
37	0.20	92	1.32	147	0.33	205	21.61
38	0.92	93	2.22	148	0.14	206	3.04
39	3.78	94	0.25	149	0.17	207	4.77
40	0.18	95	0.17	150	1.11	208	2.44
41	0.05	96	0.46	151	1.00	209	0.30
42	0.02	97	0.04	152	0.62	210	0.03
43	0.01	98	0.16	153	0.48	211	0.10
44	0.02	99	0.12	154	0.31	212	0.25
45	0.02	100	1.84	155	1.59	213	0.23
46	0.13	101	0.11	156	0.16	214	0.32
47	0.14	102	0.05	157	0.13	215	0.05
48	0.01	103	1.46	158	0.50	216	0.04
49	0.27	104	0.15	159	0.06	217	0.06
50	8.02	105	0.61	161	0.13	218	0.14
51	34.60	106	0.12	162	2.26	219	3.53
52	1.63	107	0.14	163	0.24	220	1.45
53	0.36	108	0.12	164	0.09	221	2.17
54	0.03	109	0.03	165	0.11	222	0.14
55	0.17	110	0.03	166	0.04	223	2.07
56	0.03	111	0.03	167	0.21	224	6.25
57	0.05	112	0.47	168	0.19	225	1.02
58	0.02	113	0.37	169	5.76	226	3.71
59	0.01	114	0.25	170	1.45	227	4.56
60	0.03	115	0.02	171	0.22	228	1.07
61	0.31	116	0.07	172	0.07	229	0.13
62	1.19	117	1.05	173	0.02	230	0.04
63	3.28	118	0.08	174	0.56	231	0.85
64	1.82	119	0.57	175	0.19	232	0.26
65	5.86	120	0.12	176	2.22	233	0.08
66	0.49	122	0.28	177	0.87	234	0.04
67	0.05	123	0.21	178	0.37	235	0.10
68	0.23	124	1.69	179	0.09	236	0.40
69	13.84	125	0.26	180	0.13	237	0.06
70	0.22	126	0.19	181	2.33	238	1.17
71	0.03	127	0.68	182	1.57	239	0.15
73	0.49	128	0.18	183	0.26	242	0.04
74	4.41	129	0.05	184	0.22	243	1.23
75	3.32	130	0.06	185	0.05	244	0.40
76	3.53	131	1.84	186	0.28	245	0.34
77	100.00	132	0.33	187	0.18	246	4.94
78	8.02	133	0.10	188	1.40	247	0.62
79	0.34	134	0.18	189	0.23	248	0.03
80	0.07	135	0.03	190	0.03	249	0.13
81	0.57	136	0.49	193	1.79	250	0.93
82	0.10	137	1.54	194	0.55	251	1.03
83	0.06	138	0.32	195	0.23	252	0.16
84	0.02	139	0.05	196	16.10	254	2.26
85	0.04	140	0.05	198	0.31	255	0.86

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
256	2.26	284	0.09	315	0.21	353	0.03
257	1.47	285	0.17	317	0.07	354	0.27
258	0.64	286	0.10	319	1.54	355	0.08
259	0.10	288	0.30	320	0.21	364	10.73
262	0.28	289	0.05	323	3.00	365	24.58
263	0.03	290	3.21	324	3.28	366	3.07
264	0.05	291	0.16	325	0.49	367	0.21
265	0.16	293	0.01	326	1.24	373	0.23
266	0.09	294	0.08	327	0.18	374	3.71
269	10.45	295	0.66	334	0.05	375	0.52
270	2.68	296	47.46	335	0.02	376	0.07
271	0.23	297	5.79	338	0.06	392	4.56
272	0.05	298	0.36	339	0.94	393	58.76
273	3.50	299	0.02	340	0.09	394	7.63
274	0.67	300	0.36	341	0.02	395	0.61
275	0.14	301	0.10	343	0.02	396	0.05
276	10.88	304	1.09	344	0.05	442	0.03
277	1.87	305	1.69	345	0.23	444	0.02
278	0.20	306	0.58	346	2.54	470	0.12
281	0.13	307	0.13	347	0.30	471	0.02
282	0.02	308	0.04	348	0.02		
283	0.15	314	0.11	352	0.33		



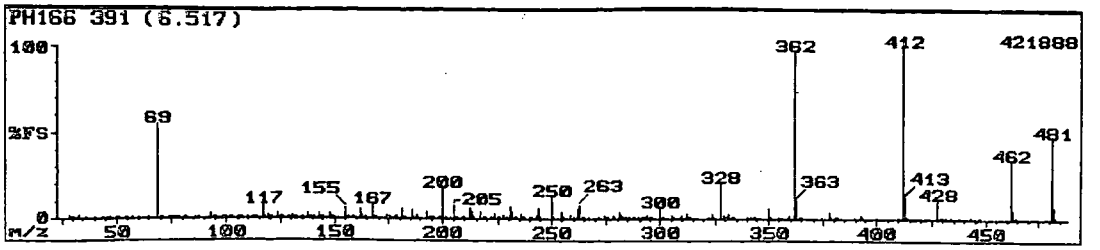
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
21	0.01	104	0.46	165	0.61	229	0.48
26	0.02	105	4.11	166	0.52	230	0.28
27	0.36	106	0.38	167	1.04	231	0.37
28	0.36	107	0.18	168	1.53	232	0.33
29	0.01	108	0.20	169	0.46	234	1.06
31	0.09	109	0.06	170	0.45	235	0.13
32	0.09	110	0.02	171	0.10	236	0.25
37	0.10	111	0.05	172	0.12	238	0.88
38	0.60	112	0.29	174	1.17	239	0.40
39	3.47	113	0.11	177	16.97	240	0.17
40	0.17	114	0.15	178	1.86	243	31.57
41	0.04	115	0.88	180	11.27	244	1.68
42	0.02	116	0.17	181	1.90	245	0.07
43	0.02	117	0.18	182	0.73	246	0.73
44	0.05	119	1.96	183	0.29	247	0.34
47	0.03	120	0.34	184	0.09	248	0.11
51	31.02	121	0.09	185	0.12	250	2.29
52	1.22	122	0.27	187	0.19	251	2.30
53	0.25	123	0.12	187	0.06	252	0.45
54	0.01	124	0.53	188	0.38	253	0.76
55	0.05	125	0.15	189	0.37	254	0.32
57	0.06	126	0.33	190	0.06	255	0.31
63	2.67	127	1.63	193	1.20	256	0.36
65	7.80	128	0.35	194	0.53	257	1.05
66	0.57	129	0.07	195	0.99	258	0.95
69	4.38	131	1.17	196	2.33	259	0.28
70	0.23	132	0.17	197	0.38	260	0.08
74	1.93	133	0.06	198	0.54	261	0.15
75	2.36	134	0.16	200	2.91	262	0.08
77	100.00	135	0.08	201	0.83	264	0.69
78	7.21	136	0.07	202	0.13	265	0.52
79	0.38	137	0.06	204	0.42	266	0.37
81	0.20	138	0.22	205	1.37	267	0.27
82	0.06	139	0.41	206	0.25	268	0.20
83	0.05	141	0.99	207	0.83	269	0.20
85	0.03	143	0.80	208	1.98	270	0.65
86	0.07	144	0.16	209	0.35	271	0.98
87	0.03	146	0.45	210	0.19	272	0.44
88	0.03	146	0.27	211	0.09	273	0.64
89	0.05	147	0.05	212	0.09	274	0.54
90	0.12	148	0.03	214	1.31	276	0.95
91	0.67	150	2.66	215	0.78	277	1.60
92	0.94	151	3.74	216	0.23	279	3.28
93	3.70	152	9.12	217	0.17	280	0.63
94	1.87	153	3.01	219	1.44	281	0.41
95	0.32	154	6.48	220	0.39	282	0.22
96	0.27	155	1.89	221	0.27	283	0.10
97	0.03	156	0.07	222	1.12	284	0.09
98	0.04	157	0.06	223	0.55	286	0.16
99	0.22	158	0.42	224	0.66	287	0.03
100	1.47	159	0.07	225	0.15	288	0.04
101	0.17	162	0.65	226	0.75	289	0.04
102	0.36	163	0.11	227	0.56	290	0.07
103	0.45	164	0.39	228	0.27	292	1.96

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
293	0.41	330	0.18	371	0.25	414	0.03
294	0.14	331	0.08	372	0.25	418	0.58
296	0.88	332	0.06	373	0.41	419	0.32
297	0.08	334	1.16	374	0.90	420	0.99
298	0.82	335	0.23	375	0.14	421	0.31
299	0.20	336	0.36	376	0.02	422	0.14
300	0.07	337	0.06	377	0.03	423	0.04
301	0.25	338	0.02	378	0.15	424	0.04
302	0.47	340	0.08	379	0.21	426	0.08
303	0.18	341	0.27	380	0.09	427	0.03
304	0.35	342	0.92	381	0.13	428	0.08
305	0.46	343	0.25	382	0.04	430	0.27
306	0.45	344	0.28	384	0.04	431	0.06
307	0.11	346	12.04	386	0.05	438	0.44
308	0.16	347	1.73	387	0.06	439	1.92
309	0.09	348	0.87	389	0.78	440	0.32
310	0.10	349	0.28	390	2.61	441	0.04
311	0.05	350	0.58	391	0.45	446	0.20
312	0.18	351	0.16	392	0.41	447	0.33
313	0.04	352	0.16	393	0.09	448	2.09
314	0.04	353	0.11	394	0.05	449	0.42
315	0.16	354	0.10	395	0.06	450	1.63
316	0.13	355	0.91	397	0.64	451	0.32
317	0.11	356	0.13	398	0.20	452	0.04
319	1.33	357	0.05	399	0.11	464	0.06
320	0.30	358	0.03	400	0.08	466	3.51
321	1.70	359	0.04	402	0.04	467	57.66
322	0.69	362	15.88	403	0.02	468	11.27
323	0.18	363	1.98	406	0.03	469	1.30
324	0.11	364	0.36	408	0.02	470	0.13
326	1.27	365	0.04	410	4.88	518	0.02
327	0.23	368	0.02	411	0.86	544	0.10
328	0.05	369	0.14	412	0.07	545	0.03
329	0.04	370	0.66	413	0.13		

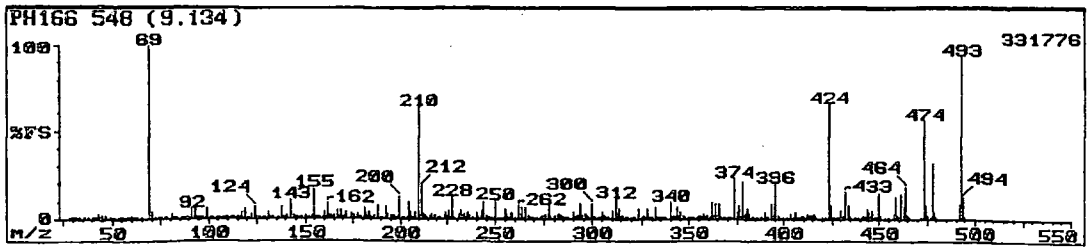


Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel I
20	0.03	83	0.86	139	1.23	194	0.88	252	0.53	308	0.91	362	0.44	417	0.
24	0.03	84	0.14	140	0.91	195	0.73	253	0.41	309	0.40	363	0.25	418	0.
25	0.07	85	0.30	141	0.90	196	0.52	254	0.47	310	0.63	364	0.57	419	0.
26	0.33	86	0.37	142	0.36	197	0.50	255	0.52	311	0.24	365	0.24	420	3.
28	4.45	87	0.33	143	0.59	198	1.45	256	0.61	312	0.18	366	0.37	421	0.
29	1.41	88	0.29	144	0.62	199	0.23	257	0.43	313	0.15	367	0.23	422	0.
30	0.62	89	0.56	145	0.39	200	0.90	258	0.57	314	0.42	368	0.17	423	0.
31	1.86	90	0.74	146	0.15	201	0.61	259	0.18	315	0.23	369	0.16	424	0.
32	0.88	92	67.02	147	0.11	202	0.52	260	0.17	316	0.32	370	0.44	425	0.
33	0.04	93	7.91	148	0.33	203	0.10	261	0.21	317	0.11	371	0.20	426	0.
34	0.02	94	3.77	149	1.11	205	0.44	262	0.12	318	0.22	372	0.37	427	0.
36	0.17	95	6.72	150	0.86	207	3.27	264	5.59	319	0.33	373	0.25	428	0.
37	1.89	96	0.88	151	0.83	208	0.69	265	0.39	320	0.42	374	0.28	429	0.
38	4.52	97	0.23	152	1.51	209	0.23	266	0.39	321	0.52	376	2.71	430	0.
39	9.71	98	0.46	153	0.80	210	0.34	267	0.20	322	1.20	377	0.62	431	0.
40	1.21	99	0.58	154	0.70	211	0.35	268	0.30	323	0.43	378	0.41	432	0.
41	3.86	100	1.46	155	1.93	212	0.64	269	0.37	324	0.33	379	0.15	433	0.
42	0.77	101	0.28	156	0.54	213	0.59	270	0.24	325	0.15	380	0.16	434	0.
43	1.11	102	0.34	157	0.47	214	1.11	271	0.27	326	0.89	381	0.10	435	0.
44	1.35	103	2.04	158	0.38	215	0.35	272	0.37	327	0.31	382	0.21	436	0.
45	0.50	104	0.34	159	0.44	216	0.22	274	0.22	328	0.28	383	0.08	437	0.
46	0.34	105	2.18	160	0.11	217	0.09	275	0.16	329	0.16	384	0.36	438	0.
47	0.63	107	20.21	161	0.21	218	0.26	276	0.45	330	0.31	385	1.65	439	0.
48	0.42	108	4.85	162	0.54	219	0.33	277	0.56	331	0.27	386	0.49	440	0.
49	0.53	109	0.95	163	0.40	220	0.32	278	0.33	332	0.34	387	0.17	441	0.
50	10.51	110	0.41	164	0.52	221	0.34	279	0.34	333	0.39	388	0.17	442	0.
51	11.17	111	0.55	165	0.34	223	0.41	280	0.69	334	0.64	389	0.25	443	0.
52	11.24	112	0.46	166	0.26	224	0.44	281	0.86	335	0.52	390	0.50	444	0.
53	6.85	113	0.31	167	0.69	225	0.86	282	0.20	336	0.84	391	0.28	445	0.
54	0.73	114	0.25	168	1.15	226	0.87	283	0.27	337	0.34	392	1.31	446	0.
55	2.66	115	0.69	169	1.25	227	0.25	284	0.12	338	0.52	393	0.28	447	0.
56	0.38	116	0.27	170	0.86	228	0.30	285	0.21	339	0.60	394	0.17	448	0.
57	0.85	117	0.53	171	0.62	229	0.34	286	0.33	340	0.33	395	0.13	449	0.
58	0.05	118	0.36	172	0.25	230	0.19	287	0.30	341	0.09	396	0.14	450	0.
59	1.06	119	0.83	173	0.17	231	0.31	288	1.13	342	0.55	397	0.18	451	0.
60	0.13	120	0.62	174	0.44	232	0.56	289	0.24	343	0.21	398	0.21	452	0.
61	1.88	121	0.95	175	0.27	233	0.12	290	0.17	344	0.25	399	0.12	453	0.
62	4.45	122	0.62	176	0.63	234	0.26	291	0.25	345	0.18	400	0.29	454	0.
63	25.00	123	1.20	177	0.37	235	0.39	292	1.33	346	0.53	401	0.19	455	0.
64	34.04	124	4.99	178	0.12	236	0.16	293	0.16	347	0.38	402	0.34	456	0.
65	9.11	125	0.79	179	0.25	237	0.37	294	0.61	348	0.34	403	0.32	457	0.
66	3.59	126	0.56	180	0.57	238	1.66	295	0.43	349	0.53	404	1.40	458	0.
67	1.20	127	0.89	181	1.25	239	0.68	296	0.38	350	0.25	405	1.03	459	0.
69	17.29	128	0.76	182	1.11	240	0.54	297	0.23	351	1.61	406	0.32	460	0.
70	0.73	129	0.34	183	1.40	241	0.43	298	0.31	352	0.44	407	0.11	461	0.
71	0.38	130	0.13	184	0.94	243	5.98	299	0.29	353	0.16	408	0.17	462	0.
74	3.62	131	0.85	185	0.31	244	1.04	300	0.16	354	0.25	409	0.10	463	0.
75	5.32	132	0.37	186	0.18	245	0.39	301	0.62	355	0.13	410	0.26	464	0.
77	100.00	133	0.83	187	0.51	246	0.17	302	0.23	356	1.70	411	0.09	465	0.
78	9.51	134	0.48	188	0.50	247	0.20	303	0.47	357	0.43	412	0.10	466	0.
79	6.91	135	1.16	189	0.27	248	0.08	304	0.54	358	1.83	413	0.11	467	0.
80	4.06	136	0.28	190	0.22	249	0.10	305	0.26	359	0.43	414	0.13	468	0.
81	3.41	137	0.68	192	0.68	250	0.48	306	0.61	360	0.32	415	0.12	469	0.
82	0.72	138	0.84	193	0.61	252	0.59	307	1.51	361	0.35	416	0.17	470	0.

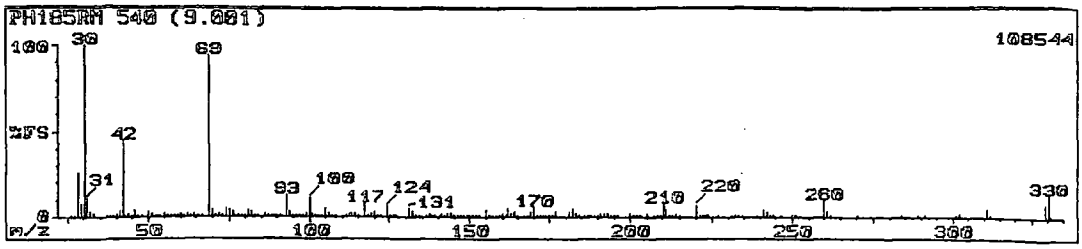
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
471	0.04	486	0.04	507	1.50	541	0.03
472	0.03	488	0.16	508	1.80	542	0.03
473	0.04	489	0.13	509	0.42	576	0.01
474	0.02	490	0.12	510	0.48	578	0.02
475	0.10	492	0.34	511	0.10	580	0.03
476	0.15	493	0.08	512	0.59	592	0.03
477	0.11	494	0.08	513	0.12	603	0.04
478	0.22	495	0.12	515	0.04	604	0.42
479	0.20	496	0.52	526	1.50	605	0.13
480	0.34	497	0.18	527	21.28	606	0.04
481	0.16	498	0.47	528	5.92	634	0.16
482	0.12	499	0.84	529	0.95	635	0.04
484	0.57	500	0.16	530	0.09		
485	0.12	506	0.18	540	0.02		



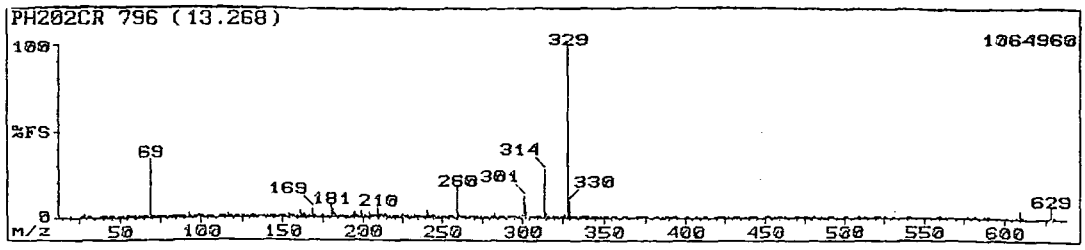
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	1.52	129	0.24	224	3.37	312	2.64
29	0.49	131	2.06	225	0.45	313	0.62
30	0.06	132	0.17	226	0.69	314	0.42
31	0.64	136	0.97	228	1.93	322	0.20
32	1.06	138	2.90	229	0.35	324	3.19
33	1.97	139	0.21	231	6.43	325	0.31
36	0.07	141	0.13	232	3.88	328	20.39
40	0.10	143	2.96	233	1.30	329	1.84
43	0.08	144	0.83	234	0.18	330	0.10
44	0.45	145	0.08	236	2.81	331	0.70
45	0.07	148	2.70	237	0.31	332	2.85
47	0.93	149	0.38	238	0.19	333	0.46
50	0.61	150	0.51	240	0.66	334	0.10
51	0.33	155	6.01	241	0.24	340	0.57
54	0.17	156	0.46	243	2.20	342	0.31
55	0.11	159	0.20	244	5.40	343	0.09
57	0.07	162	4.43	245	0.69	344	0.38
60	0.06	163	1.88	250	12.74	350	5.52
65	0.17	164	0.44	251	0.88	351	0.52
69	54.37	167	7.83	255	3.79	355	0.13
70	0.69	168	0.74	256	0.44	359	0.14
71	0.52	169	1.03	259	1.53	360	2.32
74	0.63	174	1.56	260	1.15	362	97.09
75	0.13	175	1.02	262	6.25	363	10.56
76	0.20	176	0.23	263	7.40	364	0.88
77	0.06	178	1.33	264	1.32	365	0.19
79	0.16	179	1.71	265	0.17	374	0.24
81	0.59	181	5.70	267	0.97	378	4.19
82	0.07	182	1.11	272	0.40	379	0.39
86	0.39	183	0.27	274	2.21	381	0.09
87	0.06	186	4.43	275	0.28	382	0.36
93	3.13	187	0.38	276	0.18	390	0.28
94	0.13	188	2.37	278	2.41	393	1.87
95	0.24	193	3.55	279	0.14	394	0.26
98	0.58	194	0.79	281	3.56	400	0.97
99	0.49	195	0.31	282	2.32	410	0.80
100	1.40	196	0.19	283	0.55	412	100.00
101	0.13	198	1.11	284	0.11	413	12.20
102	0.05	199	0.49	286	0.41	414	0.91
105	0.89	200	17.48	287	0.17	428	10.80
106	0.22	201	1.02	288	0.34	429	1.26
107	0.12	204	0.67	290	1.38	430	0.11
110	0.11	205	7.71	291	0.26	432	0.33
112	0.63	206	1.40	292	0.19	434	0.16
113	0.39	207	0.36	293	0.97	438	0.21
114	0.89	209	0.27	294	1.53	443	0.16
117	7.34	210	0.21	295	0.28	447	0.19
118	0.49	212	6.25	296	0.08	462	33.74
119	2.32	213	3.88	300	6.25	463	4.55
120	0.13	214	0.84	301	0.51	464	0.36
121	0.14	217	4.19	305	1.50	481	47.33
124	2.96	218	0.33	306	0.13	482	6.49
125	0.26	219	0.19	309	0.34	483	0.47
126	0.10	222	0.20	310	1.53		



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	0.53	101	0.21	167	5.32	228	12.19
29	0.66	102	0.20	168	1.00	229	1.33
30	0.14	105	0.97	169	4.80	231	2.66
31	0.74	106	0.56	170	0.52	232	4.84
32	0.76	107	0.21	171	0.60	233	1.83
33	0.33	108	0.12	172	4.22	234	3.11
36	0.10	109	0.56	174	3.20	235	0.24
38	0.05	110	0.57	175	2.33	236	3.86
40	0.11	112	1.20	176	2.28	237	1.81
41	0.09	113	0.68	178	2.62	238	1.37
42	0.53	114	0.68	179	1.43	240	4.26
43	2.55	115	0.22	180	0.32	241	1.41
44	0.46	116	0.77	181	5.86	243	4.48
45	1.68	117	3.61	182	2.76	244	9.41
47	1.99	119	5.40	183	0.58	245	1.83
50	0.56	120	0.35	184	3.74	246	1.29
51	0.28	122	3.28	185	0.27	247	1.27
54	1.14	124	6.33	186	2.04	248	0.67
55	0.37	125	0.93	187	2.12	250	11.03
56	0.33	126	1.13	188	7.72	251	0.53
57	0.40	127	0.29	190	0.64	252	0.25
58	0.16	128	0.21	191	0.53	253	1.23
59	0.41	129	0.34	193	6.64	254	0.57
60	1.47	131	4.36	194	2.72	255	6.25
61	0.22	132	0.43	195	1.89	256	2.58
62	0.24	133	0.33	196	2.01	257	0.59
63	0.20	134	0.56	197	2.31	258	0.85
65	0.26	136	1.08	198	1.22	259	3.88
69	100.00	138	7.18	199	0.44	260	1.41
70	1.79	139	0.31	200	12.58	262	7.48
71	3.94	140	0.36	201	0.60	263	2.58
72	0.25	141	2.41	202	0.28	264	6.56
74	0.96	143	11.03	204	1.09	265	1.43
75	0.37	144	2.06	205	9.80	266	6.79
76	0.99	145	0.75	206	3.55	267	2.10
77	0.18	146	0.28	207	1.33	268	0.52
78	0.25	148	1.43	208	0.75	269	0.51
81	2.51	149	0.36	209	3.99	270	0.25
82	0.32	150	1.95	210	64.51	271	0.62
83	0.33	151	0.34	211	2.30	272	1.08
84	0.77	152	0.31	212	18.13	273	0.20
86	0.26	154	1.87	213	2.51	274	2.37
87	0.26	155	5.40	214	2.04	275	1.68
88	0.38	156	1.33	215	1.08	276	2.70
89	0.13	157	1.10	216	1.79	278	7.33
90	0.57	158	0.49	217	3.07	279	1.01
92	6.17	159	0.88	218	0.81	281	2.10
93	5.56	160	3.49	219	1.70	282	2.84
94	0.39	161	0.27	221	0.80	283	2.60
95	0.49	162	8.95	222	1.21	284	1.64
96	0.23	163	1.54	224	4.28	285	0.51
97	0.20	164	1.72	225	1.87	286	1.39
98	0.32	165	0.69	226	5.32	287	0.97
100	5.79	166	2.12	227	0.71	288	0.63
290	3.97	335	0.12	380	3.05	432	2.12
291	0.52	336	1.16	381	6.02	433	15.35
292	1.52	337	0.52	382	2.91	434	7.56
293	2.33	338	0.59	383	1.45	435	0.77
294	8.64	340	9.95	384	0.56	438	0.32
295	2.03	341	1.31	386	0.51	440	1.37
296	2.43	342	1.89	388	0.18	441	0.19
297	2.16	343	0.18	389	0.53	442	1.49
298	0.79	344	6.87	390	3.76	443	1.37
300	8.95	345	1.68	391	0.59	444	5.63
301	0.81	346	3.59	392	0.55	445	3.88
302	0.91	347	2.16	394	9.03	446	0.93
303	0.17	348	0.77	395	1.47	447	5.02
304	0.62	350	0.75	396	20.06	448	1.31
305	3.99	351	0.34	397	2.08	449	0.09
306	1.62	352	0.91	398	0.35	450	14.35
307	0.63	353	0.24	400	0.26	451	1.50
308	0.48	354	0.48	402	0.44	454	0.13
309	0.62	355	1.60	404	2.82	455	0.11
310	5.17	356	2.22	405	1.35	458	3.36
312	11.65	357	0.32	406	4.01	459	12.27
313	2.66	358	2.66	407	0.40	460	1.47
314	5.40	359	0.55	408	1.16	461	0.16
315	0.95	360	1.68	409	0.90	462	14.20
316	1.83	361	1.25	410	1.60	463	6.64
317	0.34	362	9.88	411	0.24	464	18.06
318	0.27	363	2.14	412	2.58	465	2.03
320	0.20	364	8.56	413	1.50	466	0.09
321	0.20	365	1.93	414	2.33	472	0.31
322	0.50	366	8.95	415	2.01	474	56.48
324	5.71	367	0.93	416	2.47	475	7.56
325	1.10	368	0.25	417	0.23	476	1.70
326	2.31	370	0.47	420	0.13	477	0.21
327	0.79	371	0.30	422	0.53	478	31.79
328	5.56	372	0.58	424	66.36	479	3.78
329	0.60	374	22.84	425	7.56	480	0.36
330	0.41	375	3.53	426	0.80	492	8.72
331	0.80	376	8.02	428	0.66	493	93.83
332	7.02	377	0.71	429	0.61	494	12.81
333	1.35	378	21.30	430	4.63	495	1.15
334	1.23	379	2.35	431	0.48		

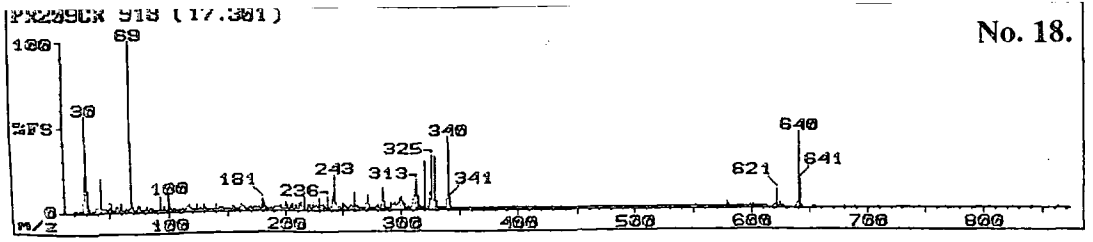


Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.22	81	3.71	140	0.12	195	0.24
27	0.60	82	3.29	141	1.46	196	0.25
28	26.42	83	0.51	142	0.48	200	2.23
29	7.96	84	0.82	143	2.03	201	0.89
30	100.00	86	2.42	144	2.31	202	0.20
31	11.03	87	1.14	145	0.83	203	0.19
32	3.07	88	1.30	146	1.27	205	1.53
33	1.67	89	0.61	147	0.18	207	0.76
37	0.33	90	0.50	148	0.53	208	0.27
38	0.36	91	1.37	149	0.39	209	0.33
39	0.53	93	12.38	150	1.43	210	8.20
40	1.89	94	2.43	151	1.27	211	4.36
41	4.25	95	1.02	152	0.50	212	1.39
42	45.05	96	1.05	153	0.28	213	0.80
43	1.44	97	0.31	155	4.30	214	1.83
44	2.39	98	1.27	156	0.60	215	0.27
45	0.97	99	1.78	157	0.40	220	6.49
46	3.69	100	10.26	158	0.17	221	0.80
47	0.15	101	2.09	159	0.36	222	0.28
48	0.53	102	0.49	160	2.09	223	0.16
50	2.45	103	0.20	161	0.87	224	0.20
51	2.15	104	0.26	162	4.60	227	0.64
52	0.74	105	5.19	163	1.49	231	0.48
53	1.15	106	2.11	164	3.30	232	1.30
55	1.71	107	1.25	165	1.09	233	1.37
56	0.78	108	0.72	167	0.79	234	0.79
57	1.06	111	0.35	168	0.45	239	0.28
58	0.76	112	2.20	169	2.87	241	3.77
59	0.45	113	2.02	170	5.72	242	2.76
60	1.58	114	2.27	171	0.97	243	1.22
61	0.23	115	1.02	172	0.84	244	0.20
62	1.49	117	7.72	173	0.45	246	0.21
63	0.65	118	0.91	174	0.71	250	0.55
64	1.78	119	1.90	175	0.44	251	0.33
65	0.41	120	2.62	176	1.05	260	9.61
66	0.50	121	0.72	177	2.45	261	3.29
67	0.85	122	0.42	181	2.84	262	0.40
69	94.34	124	5.90	182	4.66	270	0.22
70	3.55	125	1.19	183	1.53	284	0.17
71	0.97	126	0.88	184	0.78	289	0.26
72	2.03	127	0.83	186	0.83	291	0.57
73	0.46	131	5.13	187	0.44	301	1.15
74	4.60	132	3.05	188	0.53	302	2.37
75	3.43	133	1.34	189	0.19	311	4.95
76	2.59	134	1.31	190	0.35	312	0.55
77	0.80	136	1.30	191	2.03	329	7.31
78	0.56	137	1.65	192	2.00	330	13.56
79	0.84	138	0.69	193	1.50	331	1.27
80	0.54	139	0.30	194	0.72		



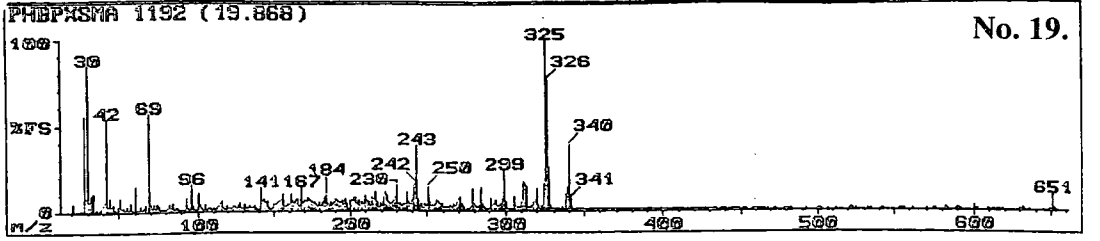
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.08	94	0.28	163	0.80	229	0.04
26	0.02	95	0.16	164	1.47	231	1.43
27	0.08	96	0.12	165	0.31	232	2.12
28	1.75	98	0.11	167	0.58	233	1.88
29	0.09	99	0.17	169	5.10	234	0.87
31	0.75	100	2.19	170	0.71	235	0.08
32	0.29	101	0.10	171	0.18	236	0.14
33	0.20	102	0.04	172	0.07	237	0.19
38	0.02	105	0.76	174	0.52	238	0.68
39	0.04	106	0.23	175	0.30	239	0.38
40	0.14	107	0.18	176	1.88	240	0.19
41	0.26	108	0.05	177	0.23	241	3.85
42	0.03	112	0.28	179	0.06	242	0.35
44	0.13	113	0.22	181	6.44	243	0.85
45	0.13	114	0.45	182	5.26	244	0.55
46	0.24	115	0.10	183	1.63	245	1.97
50	0.21	117	1.52	184	0.66	246	0.32
51	0.56	118	0.09	186	0.94	248	0.06
52	0.07	119	0.41	187	0.49	250	1.27
53	0.03	119	0.23	188	1.07	251	0.61
55	0.17	121	0.04	189	0.28	252	0.14
56	0.07	122	0.07	190	0.30	253	0.10
57	0.13	124	1.02	191	0.72	255	1.12
58	0.02	125	0.20	193	1.29	256	0.10
59	0.07	126	0.22	194	0.82	257	0.14
60	0.63	129	0.06	195	2.81	258	0.30
62	0.21	131	1.15	196	0.44	260	17.79
63	0.06	132	1.85	197	0.06	261	1.63
64	0.21	132	0.84	198	0.04	262	0.39
65	0.08	133	0.40	200	3.63	263	0.23
66	0.03	134	0.08	201	0.41	264	1.29
67	0.13	136	0.34	202	0.14	265	0.09
69	35.38	137	0.50	203	0.09	267	0.05
70	0.55	138	0.49	205	3.15	268	0.04
71	0.09	138	0.17	206	1.22	269	0.15
72	0.14	139	0.05	207	1.06	270	0.13
74	0.64	141	0.38	208	0.20	271	0.09
75	0.41	141	0.17	209	0.61	272	0.23
76	0.60	143	0.55	210	5.48	274	0.21
77	0.05	144	0.77	211	0.34	275	0.15
78	0.14	144	0.59	212	2.24	276	0.51
79	0.06	146	0.24	213	1.32	277	0.08
81	0.70	146	0.06	214	1.63	279	0.08
82	0.56	148	0.16	215	0.32	280	0.05
83	0.07	150	0.56	217	0.23	281	0.33
84	0.07	151	0.41	219	0.83	282	0.40
85	0.03	152	0.17	220	0.54	283	2.91
86	0.37	152	0.08	221	0.35	284	0.21
87	0.09	155	2.31	222	0.28	286	0.12
88	0.20	156	0.26	224	0.41	287	0.08
89	0.05	157	0.22	225	0.14	288	0.69
90	0.06	158	0.09	226	1.59	289	0.14
91	0.06	160	0.88	227	0.17	291	0.90
93	2.57	162	3.51	228	0.02	292	0.10

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
293	0.27	345	0.06	413	0.07	490	0.11
294	0.36	346	0.03	414	0.02	491	0.36
295	0.12	348	0.02	419	0.04	492	0.06
296	0.07	350	0.16	420	0.04	493	0.02
298	0.05	351	0.10	421	0.20	500	0.02
300	2.43	352	0.24	422	0.17	501	0.02
301	12.50	353	0.16	423	0.03	502	0.02
302	6.63	355	0.06	424	0.03	503	0.02
303	0.63	356	0.03	425	0.04	509	0.37
305	0.13	357	0.25	426	0.18	510	0.11
306	0.10	358	0.06	427	0.04	513	0.06
307	0.36	362	0.11	431	0.10	514	0.03
308	0.10	363	0.05	432	0.04	519	0.41
309	0.79	364	0.04	433	0.02	520	0.13
310	0.65	369	0.07	434	0.03	521	0.09
311	0.05	370	0.04	438	0.05	522	0.21
312	0.19	371	0.28	440	0.07	523	0.04
314	27.69	372	0.25	441	0.43	526	0.04
315	3.32	373	0.04	442	0.08	527	0.02
316	0.20	374	0.07	443	0.05	532	0.03
317	0.07	375	0.13	444	0.09	540	0.36
319	0.10	376	0.44	445	0.09	541	0.69
320	0.05	377	0.08	450	0.10	542	0.12
321	0.12	381	0.18	451	0.08	559	0.37
322	0.18	382	0.11	452	0.09	560	0.29
324	0.11	383	0.07	453	0.13	561	0.05
325	0.16	384	0.06	454	0.02	577	0.04
326	0.45	386	0.03	457	0.05	582	0.03
327	1.61	388	0.19	459	0.05	583	0.02
329	100.00	389	0.04	460	0.19	588	0.06
330	9.52	390	0.06	461	0.04	590	0.08
331	0.69	391	0.25	463	0.08	591	0.04
332	0.24	392	0.02	469	0.22	601	0.02
333	0.12	393	0.11	470	0.07	608	0.02
334	0.17	394	0.07	471	0.21	610	4.57
336	0.07	395	0.04	472	0.24	611	0.87
337	0.03	400	0.10	473	0.05	612	0.07
338	0.25	401	0.10	474	0.02	628	0.85
339	0.08	402	0.15	476	0.17	629	6.83
340	0.06	403	0.15	477	0.03	630	1.39
341	0.17	407	0.16	481	0.07	631	0.13
343	0.15	408	0.03	482	0.04		
344	0.11	412	0.05	486	0.02		



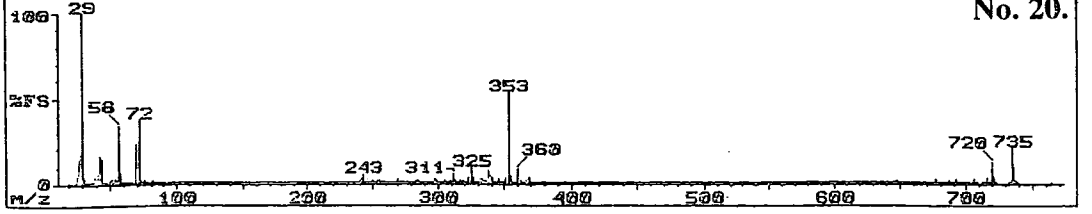
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.37	79	0.77	134	1.04	187	1.83	242	6.20	296	3.01	351	0.34	405	0.23
21	0.02	80	0.70	135	0.20	188	1.48	243	20.06	297	3.65	352	0.56	406	0.10
24	0.10	81	3.06	136	0.74	189	1.17	244	4.06	298	5.71	353	0.64	407	0.27
25	0.13	82	1.72	137	1.34	190	1.64	245	1.77	299	6.79	354	0.44	408	0.28
26	2.24	83	0.57	138	1.22	191	1.65	246	1.56	300	7.41	355	0.42	409	0.19
27	5.38	84	0.89	139	0.72	192	0.59	247	0.68	301	5.32	356	0.80	410	0.50
28	21.50	85	1.88	140	0.48	193	1.67	248	0.59	302	2.67	357	0.51	411	0.41
29	3.65	86	1.58	141	3.52	193	1.14	249	0.46	303	0.79	358	0.36	412	0.39
30	56.79	87	1.11	142	0.40	194	1.90	250	3.91	304	0.51	359	0.34	413	0.52
31	12.86	88	1.13	143	1.72	195	1.80	251	2.49	305	2.13	360	0.26	414	0.38
32	2.19	89	0.77	144	2.34	196	2.73	252	2.06	306	1.32	361	0.51	415	0.46
33	1.83	90	0.44	145	1.70	197	1.43	253	1.22	307	0.66	362	0.46	416	0.26
35	0.18	91	0.68	146	1.58	198	0.35	254	0.60	308	0.67	363	0.45	417	0.27
36	0.36	93	9.05	147	1.08	199	0.26	255	1.77	309	1.59	364	0.38	418	0.18
37	0.48	94	1.45	148	0.66	200	4.84	256	2.26	310	5.71	365	0.29	419	0.23
38	2.75	95	1.07	149	0.45	201	1.70	257	2.73	311	12.04	366	0.23	420	0.21
39	2.91	96	2.78	150	1.39	202	3.22	258	1.59	312	11.73	367	0.15	421	0.34
40	3.24	97	0.64	151	1.39	203	1.21	259	1.26	313	17.18	368	0.21	422	0.94
41	5.04	98	0.92	152	1.75	205	2.93	260	10.19	314	7.30	369	0.35	423	0.36
42	19.75	99	1.34	153	0.89	206	0.62	261	1.88	315	1.14	370	0.30	424	0.42
43	1.59	100	9.57	154	0.66	207	3.42	262	1.70	316	2.42	371	0.50	425	0.20
44	2.29	101	1.65	155	2.73	208	0.96	263	0.98	317	0.62	372	0.74	426	0.48
45	1.38	102	0.89	155	2.19	209	1.65	264	1.34	318	0.42	373	0.46	427	0.33
46	1.72	103	0.56	157	0.95	210	2.78	265	1.28	319	0.96	374	0.54	428	0.34
47	1.90	104	0.24	158	0.79	211	0.67	266	1.12	320	27.98	375	0.31	429	0.22
48	0.44	105	2.39	159	0.95	212	3.65	267	1.04	322	0.60	376	0.48	430	0.34
50	5.81	106	1.14	160	0.94	213	1.29	268	0.22	323	1.83	377	0.27	431	0.38
51	4.55	107	0.95	161	1.57	214	4.78	269	4.19	324	10.19	378	0.19	432	0.49
52	1.24	108	0.59	162	3.58	215	2.21	270	3.11	325	32.10	379	0.18	433	0.45
53	1.03	109	0.32	162	2.96	216	7.51	271	8.44	326	6.69	380	0.18	434	0.42
54	0.39	110	0.37	164	2.49	217	1.35	272	3.24	327	5.09	381	0.53	435	0.23
55	3.11	111	0.22	165	2.31	219	2.49	273	0.91	328	1.67	382	0.37	436	0.22
56	1.54	112	1.47	165	1.22	220	0.96	274	0.56	329	30.86	383	0.62	437	0.27
57	2.75	113	1.25	167	0.99	221	2.88	275	0.85	330	4.58	384	0.44	438	0.20
58	0.74	114	1.70	167	0.86	222	1.09	276	0.82	331	0.82	385	0.25	439	0.19
59	0.36	115	1.43	169	2.24	223	3.32	277	0.51	332	0.58	386	0.31	440	0.71
60	5.04	116	2.96	169	1.54	224	2.42	278	1.55	333	0.44	387	0.26	441	0.73
61	0.51	117	3.50	170	1.75	225	2.26	279	2.47	334	0.46	388	0.36	442	0.66
62	1.28	118	0.39	171	1.05	226	2.67	280	0.67	335	0.26	389	0.44	443	0.30
63	0.96	119	1.95	172	1.42	227	1.28	281	0.95	336	1.00	390	0.28	444	0.22
64	2.06	120	0.93	173	1.46	228	1.93	282	1.11	337	0.52	391	0.35	445	0.35
65	0.53	121	0.51	174	1.98	229	3.47	283	2.62	338	6.02	392	0.40	446	0.33
66	0.97	122	0.77	175	1.72	230	6.40	284	12.24	339	2.19	393	0.19	447	0.19
67	1.63	123	0.39	176	2.11	231	2.57	285	4.81	340	42.39	394	0.31	448	0.18
69	100.00	124	3.81	177	1.53	232	2.52	286	1.59	341	6.40	395	0.35	449	0.24
70	2.70	125	0.81	178	0.71	233	2.31	287	1.03	342	0.82	396	0.34	450	0.26
71	0.95	126	1.11	179	0.79	234	1.67	288	0.92	343	0.40	397	0.27	451	0.70
72	1.28	127	1.64	180	0.21	235	0.87	289	0.89	344	0.37	398	0.86	452	0.65
73	0.46	128	0.63	181	6.56	236	8.02	290	0.53	345	0.40	399	0.23	453	0.44
74	3.34	129	0.66	182	4.96	237	2.26	291	3.65	346	0.55	400	0.32	454	0.35
75	4.22	130	0.18	183	1.50	238	1.31	292	1.55	347	0.17	401	0.35	455	0.23
76	2.78	131	3.86	184	2.03	239	1.00	293	2.55	348	0.31	402	0.54	456	0.15
77	0.70	132	1.64	185	0.25	240	1.72	294	4.01	349	0.17	403	0.41	457	0.14
78	0.38	133	0.66	186	1.41	241	9.16	295	0.85	350	0.34	404	0.28	458	0.28

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
459	0.19	504	0.33	549	0.09	594	0.05
460	0.48	505	0.14	550	0.20	595	0.03
461	0.48	506	0.21	551	1.85	596	0.03
462	0.31	507	0.14	552	1.33	597	0.17
463	0.46	508	0.41	553	0.36	598	2.39
464	0.32	509	0.31	554	0.16	599	0.75
465	0.19	510	1.34	555	0.32	600	0.32
466	0.16	511	0.83	556	0.50	601	1.45
467	1.25	512	0.27	557	0.18	602	2.08
468	0.32	513	0.33	558	0.07	603	0.69
469	0.25	514	0.35	559	0.19	604	0.16
470	0.28	515	0.21	560	0.51	605	0.24
471	0.68	516	0.10	561	0.25	606	0.16
472	0.49	517	0.48	562	0.22	607	0.09
473	0.26	518	0.14	563	0.19	608	0.05
474	0.27	519	0.13	564	1.04	609	0.34
475	0.11	520	0.30	565	0.99	610	0.30
476	0.25	521	0.23	566	0.18	611	0.17
477	0.20	522	0.60	567	0.07	612	0.98
478	0.11	523	0.29	568	0.05	613	0.19
479	0.13	524	0.26	569	0.09	619	0.51
480	0.11	525	0.07	570	0.42	620	1.48
481	0.66	526	0.13	571	1.34	621	11.01
482	0.82	527	0.13	572	0.47	622	2.52
483	0.66	528	0.19	573	0.16	623	0.92
484	0.26	529	0.69	574	0.20	624	0.21
485	0.17	530	0.47	575	0.05	625	3.34
486	0.20	531	0.38	576	0.03	626	0.76
487	0.23	532	0.35	577	0.15	627	0.08
488	0.16	533	0.44	578	0.72	637	0.12
489	0.22	534	0.18	579	3.70	638	0.78
490	0.34	535	0.15	580	1.60	639	2.73
491	0.62	536	0.16	581	0.41	640	44.86
492	0.30	537	0.42	582	0.21	641	16.67
493	0.15	538	0.12	583	0.48	642	2.11
494	0.11	539	0.10	584	0.30	643	0.20
495	0.54	540	0.35	585	0.13	653	0.08
496	0.35	541	0.53	586	0.06	654	0.04
497	0.09	542	0.21	587	0.23	680	0.02
498	0.08	543	0.19	588	0.09	689	0.02
499	0.15	544	0.06	589	0.05	709	0.05
500	0.15	545	0.08	590	0.12	863	0.03
501	0.36	546	0.10	591	0.95		
502	0.55	547	0.07	592	0.99		
503	0.32	548	0.06	593	0.22		



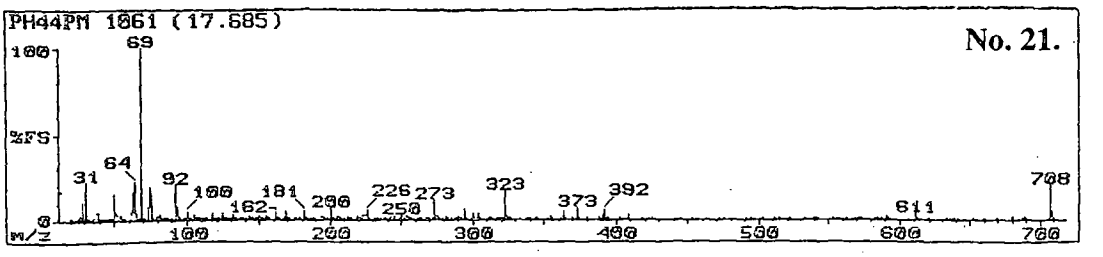
s	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
0	4.41	86	1.63	140	1.41	194	5.42	248	3.96	303	0.68	357	0.41	412	0.28
6	0.37	87	2.36	141	13.47	195	4.24	249	2.66	304	0.85	358	0.43	413	0.33
8	55.56	88	1.35	142	4.65	196	6.88	250	13.54	305	7.85	359	0.33	414	0.21
9	7.50	89	1.11	143	6.18	197	4.93	251	5.07	306	6.25	360	0.41	415	0.21
0	84.44	90	1.00	144	6.32	198	4.01	252	3.89	307	2.60	361	0.56	416	0.27
1	5.97	91	1.28	145	4.72	199	1.18	253	3.25	308	2.01	362	0.56	417	0.39
2	10.00	92	1.01	146	5.90	200	5.90	254	2.97	309	2.20	363	0.50	418	0.23
3	11.04	93	7.64	147	1.67	201	5.56	255	3.63	310	5.14	364	0.44	419	0.23
6	0.57	94	1.60	148	1.42	202	7.57	256	6.11	311	16.88	365	0.45	421	0.39
8	0.80	95	1.42	149	1.51	203	8.13	257	4.44	312	15.97	366	0.43	421	0.47
9	1.91	96	15.49	150	3.82	204	4.25	258	4.17	313	13.26	367	0.59	422	0.34
0	3.70	97	2.67	151	3.45	205	5.90	259	3.91	314	2.08	368	0.42	423	0.20
1	5.42	98	1.20	152	4.65	206	2.59	260	2.10	315	1.79	369	0.30	424	0.23
2	53.06	99	1.37	153	5.49	207	4.44	261	2.10	316	2.92	370	0.27	425	0.21
3	3.32	100	10.76	154	6.88	208	3.85	262	2.05	318	5.07	371	0.29	426	0.14
4	7.43	101	3.61	155	9.38	209	4.72	263	2.03	318	5.63	372	0.55	427	0.49
5	2.73	102	2.03	156	3.33	210	9.17	264	2.17	319	1.75	373	0.35	428	0.25
6	4.25	103	1.49	157	2.48	211	5.42	265	2.60	320	12.29	374	0.43	429	0.31
7	0.62	104	1.44	158	2.50	212	4.79	266	2.10	321	2.59	375	0.30	430	0.31
8	0.78	105	3.40	159	3.63	213	2.76	267	3.51	322	1.25	376	0.36	431	0.31
0	2.81	106	1.37	160	3.45	214	7.92	268	2.52	323	2.60	377	0.33	432	0.79
1	7.50	107	1.55	161	9.86	215	6.81	269	4.65	325	15.69	378	0.53	433	0.33
2	1.48	108	1.61	162	5.56	216	10.21	270	6.74	325	100.00	379	0.43	434	0.20
3	1.49	109	1.22	163	4.44	217	4.72	271	8.13	326	75.56	380	0.42	436	0.22
4	1.35	110	1.75	164	6.74	218	2.17	272	3.98	327	25.56	381	0.50	437	0.25
5	2.80	111	1.34	165	6.46	219	3.59	273	2.38	328	3.13	382	0.38	438	0.38
6	1.41	112	1.81	166	3.39	220	2.78	275	0.88	329	0.73	383	0.39	440	0.30
7	5.00	113	2.85	167	13.47	221	7.85	276	1.28	330	0.55	384	0.52	442	1.01
8	0.86	114	4.58	168	4.65	222	10.63	277	1.32	331	0.60	385	0.50	442	1.37
0	14.72	115	4.11	169	5.42	223	8.26	278	1.88	332	0.63	386	0.26	443	0.40
1	0.95	116	5.42	170	5.07	224	6.60	279	12.50	333	0.51	388	0.19	444	0.19
2	0.66	117	2.26	171	5.90	225	5.14	280	4.34	334	0.62	389	0.16	445	0.44
3	0.59	118	1.01	172	7.64	226	3.89	281	2.97	335	0.62	390	0.21	446	0.21
4	2.69	119	3.30	173	6.60	227	4.72	282	2.24	336	2.05	391	0.22	447	0.46
5	0.91	120	2.31	174	5.69	228	6.11	283	2.60	337	0.98	392	0.45	448	0.34
6	1.58	121	1.94	175	4.79	229	7.57	284	13.19	338	10.07	393	0.57	449	0.25
7	4.24	122	2.17	176	4.51	230	14.44	285	3.99	339	14.03	394	0.46	451	0.37
9	56.11	123	2.45	177	3.70	231	3.91	286	2.22	340	38.33	395	0.36	452	0.27
0	3.72	124	3.28	178	2.62	232	3.92	287	1.01	341	6.53	396	0.33	453	0.21
1	1.89	125	1.75	179	4.44	233	3.14	288	0.76	342	1.05	397	0.36	458	0.28
2	3.94	126	3.56	180	3.06	234	4.25	289	0.85	343	0.62	398	0.28	459	0.25
3	1.81	127	5.14	181	4.86	235	4.27	290	1.11	344	0.41	399	0.19	460	0.36
4	1.53	128	1.96	182	8.19	236	10.42	291	6.32	345	0.41	400	0.21	461	0.22
5	3.44	129	1.55	183	5.90	237	4.43	292	3.07	346	0.46	401	0.40	462	0.62
6	2.76	130	0.93	184	8.40	238	4.08	293	3.99	347	0.52	402	0.35	463	0.84
7	1.16	131	3.70	185	4.01	239	4.06	294	5.69	348	0.51	403	0.28	464	0.23
8	1.20	132	2.27	186	2.97	240	5.90	295	3.09	349	0.30	404	0.34	465	0.36
9	0.60	133	1.67	187	4.51	241	14.31	296	2.92	350	0.57	405	0.42	467	0.20
0	1.41	134	3.19	188	3.77	242	15.28	297	4.22	351	0.88	406	0.26	472	0.28
1	1.46	135	1.48	189	4.65	243	37.78	298	6.53	352	1.11	407	0.30	473	0.17
2	3.73	136	1.46	190	6.67	244	6.88	299	23.33	353	0.38	408	0.23	478	0.37
3	1.48	137	3.19	191	6.25	245	2.92	300	5.14	354	0.47	409	0.19	480	0.27
4	4.86	138	2.33	192	4.72	246	3.44	301	0.95	355	0.36	410	0.26	481	0.33
5	1.25	139	0.99	193	4.43	247	2.15	302	1.02	356	0.43	411	0.30	482	1.27

s	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
3	0.37	541	0.68	590	1.74	630	0.22
3	0.28	542	0.62	591	0.51	631	0.31
0	0.29	553	0.29	592	0.22	632	1.96
1	0.36	554	0.19	601	2.62	633	0.41
2	0.33	555	0.69	602	0.64	636	0.31
6	0.27	556	0.38	603	0.22	649	0.35
2	0.31	562	0.30	609	1.01	650	0.82
1	0.27	570	0.38	610	0.47	651	9.24
2	2.26	575	0.60	612	0.56	652	1.94
3	0.68	576	0.43	613	0.18	653	0.21
5	0.21	582	1.51	616	0.36		
2	0.28	583	0.67	617	0.41		
5	0.25	589	0.23	619	0.24		



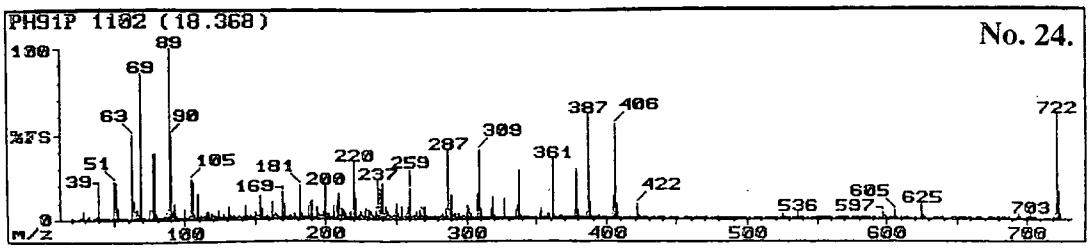
ss	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.71	80	0.44	135	0.24	189	0.54	243	5.35	297	2.50	354	4.44	410	0.28
24	0.13	81	0.91	136	0.33	190	0.72	244	0.73	298	1.93	355	1.08	411	0.14
25	0.67	82	1.64	137	0.59	191	0.38	245	0.64	299	1.35	356	0.14	412	0.12
26	4.90	83	0.46	138	0.33	192	0.36	246	0.37	301	0.17	357	0.51	413	0.24
27	14.44	84	0.50	139	0.30	193	0.30	247	0.44	302	0.33	358	0.49	414	0.21
28	17.92	85	0.67	140	0.43	194	0.55	248	0.66	303	0.49	360	8.33	415	0.09
29	100.00	86	0.36	141	0.95	195	0.44	249	0.55	304	0.86	362	1.60	416	0.22
30	5.80	87	0.43	142	0.28	196	0.51	250	1.53	305	1.67	363	0.77	417	0.18
31	2.60	88	0.30	143	0.25	197	0.23	251	0.66	306	0.94	364	0.54	418	0.24
32	0.76	89	0.19	144	0.95	198	0.32	252	0.51	307	1.06	365	0.46	419	0.23
33	0.54	90	0.30	145	0.59	199	0.16	253	0.64	308	1.30	366	2.01	420	0.20
35	0.57	91	0.26	146	0.42	200	0.39	254	1.81	309	1.54	367	2.92	421	0.18
36	0.61	93	1.35	147	0.30	201	0.52	255	1.48	310	1.07	368	4.27	422	0.28
37	0.61	94	0.63	148	0.16	202	0.60	256	1.09	311	5.42	369	0.56	423	0.17
38	2.00	95	0.56	149	0.38	203	0.56	257	1.07	312	2.26	370	0.24	424	0.20
39	3.51	96	0.74	150	0.50	204	0.25	258	0.44	313	1.86	371	0.33	425	0.22
40	3.13	97	0.30	151	0.65	205	0.63	259	1.00	314	0.89	372	0.25	426	0.21
41	5.97	98	0.11	152	0.56	206	0.37	260	0.62	315	0.69	373	0.13	427	0.25
42	16.81	99	0.95	153	0.36	207	0.45	261	0.27	316	0.40	374	0.25	428	0.11
43	3.09	100	0.82	154	0.52	208	0.25	262	0.62	317	2.08	375	0.21	429	0.19
44	14.58	101	0.73	155	0.71	209	0.47	263	0.89	318	1.34	376	0.25	430	0.21
45	0.82	102	0.46	156	0.34	210	0.46	264	0.88	319	1.77	377	0.23	431	0.29
46	0.82	103	0.18	157	0.40	211	0.35	265	0.83	320	0.69	378	0.22	432	0.27
47	0.87	104	0.08	158	0.59	212	0.25	266	0.89	321	0.76	379	0.43	433	0.25
48	0.12	105	0.29	159	0.43	213	0.27	267	1.01	322	0.47	380	0.61	434	0.31
50	1.74	106	0.49	160	0.25	214	1.26	268	0.63	323	4.20	381	0.25	435	0.28
51	2.71	107	0.36	161	0.15	215	0.86	269	2.92	325	10.14	382	0.74	436	0.25
52	1.20	108	0.51	162	0.54	216	0.77	270	1.75	326	3.54	383	1.02	437	0.16
53	1.09	109	0.34	163	0.70	217	0.49	271	0.74	327	1.55	384	0.32	438	0.23
54	2.88	110	0.70	164	0.81	218	0.38	272	0.28	328	0.40	385	0.26	439	0.22
55	2.04	111	0.28	165	0.49	219	0.71	273	0.89	329	0.69	386	0.12	440	0.14
56	33.75	112	0.32	166	0.25	220	0.31	274	0.43	330	0.74	387	0.12	441	0.18
57	3.13	113	0.71	167	0.43	221	0.45	275	0.38	331	1.68	388	0.20	442	0.16
58	6.98	114	0.67	168	0.47	222	0.74	276	0.27	332	3.13	389	0.14	443	0.20
59	0.37	115	0.40	169	0.41	223	0.49	277	0.15	333	2.60	390	0.24	444	0.23
60	1.28	116	0.19	170	0.56	224	0.60	278	0.53	334	1.57	391	0.22	445	0.18
61	0.16	117	0.47	171	0.36	225	0.54	279	1.08	335	0.95	392	0.23	446	0.15
62	0.47	118	0.14	172	0.50	226	0.63	280	1.20	336	1.60	393	0.33	447	0.26
63	0.76	119	0.52	173	0.21	227	0.66	281	0.87	337	2.21	394	0.22	448	0.25
64	0.67	120	0.45	174	0.38	228	1.11	282	0.74	338	7.29	395	0.22	449	0.22
65	0.52	121	0.19	175	0.35	229	0.96	283	2.17	339	5.17	396	0.26	450	0.21
66	0.62	122	0.36	176	0.46	230	0.56	284	1.72	340	4.03	397	0.21	451	0.23
67	1.12	123	0.34	177	0.39	231	0.31	285	2.13	341	1.68	398	0.12	452	0.27
69	23.61	124	0.61	178	0.15	232	0.56	286	0.72	342	0.56	399	0.18	453	0.22
70	9.31	125	0.37	179	0.30	233	0.75	287	0.41	343	1.12	400	0.18	454	0.28
71	1.15	126	0.53	180	0.16	234	0.44	288	0.50	344	0.63	401	0.16	455	0.15
72	37.78	127	0.86	181	0.34	235	0.85	289	0.15	345	2.71	402	0.22	456	0.15
73	1.87	128	0.40	182	0.59	236	0.99	290	0.33	346	2.14	403	0.12	457	0.12
74	0.98	129	0.31	183	0.29	237	0.70	291	1.19	347	0.66	404	0.31	458	0.29
75	1.81	130	0.36	184	0.48	238	0.57	292	1.18	348	0.77	405	0.22	459	0.23
76	1.02	131	0.79	185	0.52	239	0.43	293	1.05	349	0.73	406	0.12	460	0.36
77	0.51	132	0.41	186	0.27	240	2.07	294	1.10	350	1.86	407	0.25	461	0.26
78	0.37	133	0.21	187	0.28	241	2.57	295	0.42	351	3.92	408	0.21	462	0.36
79	0.49	134	0.35	188	0.44	242	1.25	296	0.62	353	53.33	409	0.16	463	0.22

ss	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
54	0.22	518	0.36	572	0.22	626	0.14	680	0.47	692	3.09	705	0.31	720	12.92
55	0.22	519	0.31	573	0.25	627	0.16	681	0.14	693	0.89	706	3.13	721	3.54
56	0.24	520	0.20	574	0.42	628	0.23	682	0.30	694	0.20	707	0.95	722	0.51
57	0.14	521	0.14	575	0.26	629	0.63	683	0.10	695	0.36	708	0.12	732	0.04
58	0.24	522	0.22	576	0.17	630	0.19	684	0.13	696	0.27	712	0.04	733	0.15
59	0.13	523	0.22	577	0.19	631	0.34	685	0.11	697	0.43	713	0.25	734	1.15
70	0.13	524	0.16	578	0.11	632	0.48	686	1.62	698	0.45	714	0.25	735	21.25
71	0.16	525	0.18	579	0.16	633	0.24	687	0.51	699	0.12	715	0.36	736	10.00
72	0.26	526	0.18	580	0.21	634	0.31	688	0.23	700	0.69	716	3.51	737	1.69
73	0.35	527	0.22	581	0.20	635	0.31	689	0.08	701	0.23	717	1.18	738	0.20
74	0.41	528	0.13	582	0.16	636	0.43	690	1.27	702	0.13	718	0.34	764	0.04
75	0.27	529	0.17	583	0.16	637	0.23	691	0.68	704	0.48	719	0.12		
76	0.32	530	0.17	584	0.16	638	0.34								
77	0.25	531	0.31	585	0.11	639	0.18								
78	0.20	532	0.29	586	0.30	640	0.14								
79	0.21	533	0.29	587	0.21	641	0.14								
80	0.14	534	0.25	588	0.61	642	0.61								
81	0.14	535	0.16	589	0.31	643	0.51								
82	0.18	536	0.14	590	0.29	644	0.27								
83	0.11	537	0.12	591	0.19	645	0.69								
84	0.26	538	0.20	592	0.33	646	0.49								
85	0.16	539	0.15	593	0.11	647	0.31								
86	0.21	540	0.21	594	0.24	648	1.78								
87	0.16	541	0.21	595	0.30	649	1.36								
88	0.34	542	0.16	596	0.14	650	0.47								
89	0.21	543	0.08	597	0.20	651	0.15								
90	0.46	544	0.08	598	0.18	652	0.88								
91	0.26	545	0.21	599	0.08	653	0.16								
92	0.19	546	0.33	600	0.13	654	0.26								
93	0.24	547	0.26	601	0.47	655	0.14								
94	0.14	548	0.22	602	1.22	656	0.52								
95	0.16	549	0.19	603	0.46	657	0.21								
96	0.13	550	0.21	604	0.50	658	0.36								
97	0.22	551	0.15	605	0.13	659	0.22								
98	0.18	552	0.26	606	0.24	660	0.31								
99	0.20	553	0.17	607	0.24	661	0.16								
00	0.23	554	0.16	608	0.26	662	0.67								
01	0.18	555	0.09	609	0.15	663	0.56								
02	0.29	556	0.12	610	0.12	664	0.56								
03	0.25	557	0.06	611	0.18	665	0.14								
04	0.34	558	0.17	612	0.17	666	0.82								
05	0.28	559	0.19	613	0.15	667	0.25								
06	0.20	560	0.26	614	0.22	668	0.26								
07	0.18	561	0.21	615	0.34	669	0.11								
08	0.13	562	0.19	616	0.35	670	0.53								
09	0.11	563	0.17	617	0.47	671	0.35								
10	0.15	564	0.12	618	0.43	672	1.01								
11	0.21	565	0.18	619	0.32	673	0.30								
12	0.10	566	0.21	620	0.18	674	0.24								
13	0.22	567	0.26	621	0.62	675	0.23								
14	0.20	568	0.23	622	0.51	676	2.64								
15	0.14	569	0.16	623	0.27	677	1.29								
16	0.13	570	0.09	624	0.33	678	0.69								
17	0.19	571	0.09	625	0.28	679	0.19								



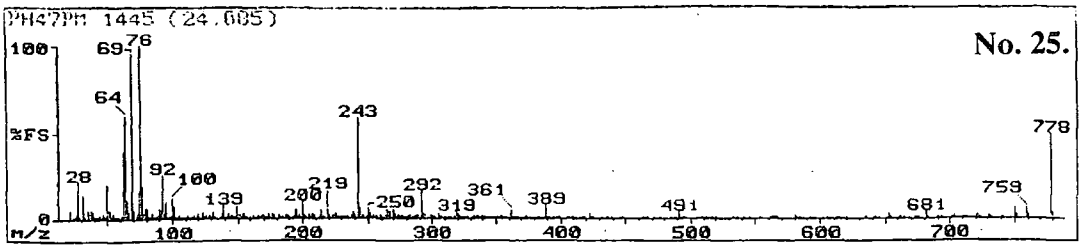
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	2.24	87	0.50	163	0.54	254	1.56
21	0.10	88	0.35	164	0.13	254	1.83
24	0.35	90	0.47	167	0.81	256	0.97
25	0.53	92	20.77	169	5.08	257	0.25
26	2.57	93	8.01	170	1.45	262	0.81
27	1.43	94	0.72	171	0.26	262	0.71
28	10.83	95	2.02	174	0.61	264	0.33
29	1.04	96	0.20	175	0.18	268	0.23
31	22.18	98	0.81	176	1.29	269	0.90
32	0.62	99	1.22	178	0.46	270	0.52
33	0.17	100	4.82	181	5.19	272	0.98
35	0.63	101	0.47	182	0.83	273	11.71
36	0.41	102	0.62	183	1.31	273	12.06
37	2.02	103	0.08	184	0.15	274	2.31
38	4.67	105	2.51	186	0.25	276	2.42
39	4.93	106	0.57	188	0.91	276	1.30
40	0.24	107	0.50	189	0.08	277	0.21
41	0.19	108	0.23	193	2.16	279	0.40
42	0.22	109	0.13	194	1.56	281	1.85
43	0.35	110	0.29	195	1.07	282	0.39
44	0.57	111	0.17	198	0.81	283	1.43
45	0.37	112	1.26	200	6.87	285	0.12
46	0.75	113	0.43	201	0.48	288	0.51
47	0.67	114	0.16	202	0.26	289	1.34
48	0.28	117	3.85	205	1.56	290	1.63
50	15.76	118	0.26	206	1.54	291	0.15
51	5.17	119	0.80	207	0.53	292	0.34
52	3.04	120	0.40	210	0.05	295	5.90
53	1.85	121	0.24	212	2.11	296	0.61
55	2.51	124	3.48	213	0.26	299	0.24
56	0.65	125	0.51	214	0.41	300	3.68
57	1.05	126	0.13	219	1.02	301	0.51
61	1.06	128	0.32	220	1.61	302	0.07
62	4.71	129	0.14	220	1.41	303	0.76
63	16.37	131	2.90	221	0.95	304	3.74
64	22.27	132	0.48	223	2.93	305	0.40
65	4.12	133	0.14	223	2.64	311	0.81
66	1.23	136	0.85	225	2.44	312	0.33
67	0.64	137	0.45	226	6.07	314	0.67
69	100.00	138	0.49	227	0.50	317	0.90
70	1.20	140	0.13	231	0.98	318	0.13
71	0.25	143	1.58	232	0.31	320	0.88
74	7.66	144	0.44	233	0.72	321	0.72
75	19.37	145	0.28	236	0.24	322	1.01
76	15.40	147	0.50	238	0.88	323	16.73
77	1.45	148	0.41	239	0.17	324	2.13
79	1.61	149	0.18	242	0.24	325	0.50
80	1.50	150	1.50	243	1.87	326	0.28
81	2.55	151	0.52	244	1.00	333	0.23
82	0.93	152	0.35	245	1.50	338	0.72
83	0.50	155	2.05	249	0.24	339	1.17
84	0.09	156	0.24	250	3.01	340	0.09
85	0.77	157	0.16	252	0.09	344	0.44
86	1.45	162	3.92	253	0.13	345	0.30

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
354	2.02	423	0.09	553	0.15	639	0.21
356	0.08	425	0.28	563	0.28	641	0.26
361	0.56	445	0.04	569	0.36	652	0.75
363	0.92	453	0.16	571	0.14	659	0.09
364	4.67	463	0.08	572	0.20	660	0.21
365	0.67	472	0.17	573	0.16	661	0.18
370	0.11	475	0.13	583	1.40	669	0.18
373	6.51	491	0.18	584	1.07	670	0.26
374	0.89	494	0.13	585	0.13	679	0.11
380	0.43	503	0.10	588	0.24	680	2.29
389	0.17	511	0.62	591	2.09	681	0.32
391	3.35	515	0.16	592	0.44	688	0.22
392	5.35	522	1.19	611	3.96	689	2.33
393	0.86	523	0.17	612	0.67	690	0.63
394	0.12	534	0.21	619	0.36	707	0.91
403	0.14	539	0.31	620	0.48	708	20.07
408	2.79	541	0.24	621	0.16	709	5.24
409	0.69	542	0.15	634	0.13	710	0.72
418	0.22	543	0.14	638	0.52		



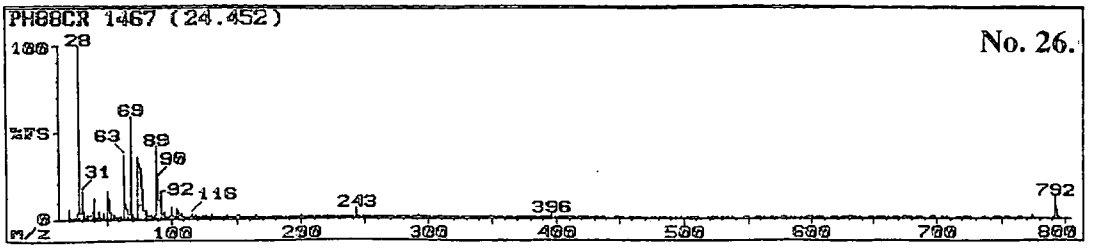
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.08	87	4.17	141	0.34	197	2.13	251	2.59	306	0.80	364	0.64	421	0.67
26	0.12	88	6.19	142	1.53	198	3.72	252	1.04	307	1.85	365	0.37	422	9.03
27	0.86	89	100.00	143	7.45	199	1.53	253	6.82	308	14.77	366	1.61	423	1.50
28	4.42	90	49.24	144	1.80	200	19.70	255	0.98	309	39.39	367	1.07	424	0.32
29	0.17	91	4.29	145	0.81	201	2.95	256	2.38	310	5.37	368	1.63	425	0.19
31	1.39	92	3.50	146	0.94	202	2.57	257	2.79	311	0.56	369	0.42	427	0.16
32	1.55	93	8.52	147	2.30	203	0.48	258	6.94	312	0.44	370	0.28	428	0.21
36	0.20	94	1.61	148	0.57	204	0.27	259	17.93	313	0.60	371	0.15	429	0.10
37	0.34	95	0.78	149	0.64	205	7.77	260	2.43	314	1.28	372	0.12	431	0.34
38	2.27	96	0.56	150	3.84	206	3.13	261	0.52	315	0.60	374	0.68	432	1.15
39	19.19	97	0.43	151	2.15	207	4.23	262	1.83	316	1.33	375	1.33	433	0.23
40	3.49	98	0.39	152	1.75	208	10.73	263	1.80	317	5.74	376	1.04	434	0.08
41	0.67	99	0.57	153	0.46	209	14.90	264	3.95	318	12.18	377	5.18	436	0.43
42	0.21	100	5.93	154	13.13	210	1.77	265	1.09	319	2.00	378	29.04	437	0.49
43	1.17	101	1.33	155	6.19	211	1.09	266	1.12	320	1.14	379	4.42	438	0.21
44	0.65	102	0.86	156	0.90	212	5.43	267	4.73	321	0.34	380	0.60	439	0.64
45	0.18	103	1.40	157	0.69	213	4.80	268	6.50	322	0.39	381	0.12	440	0.18
46	0.47	104	1.55	158	1.53	214	2.87	269	5.37	323	0.37	382	0.17	441	0.10
47	0.66	105	23.23	159	0.94	215	0.57	270	7.13	324	0.52	383	0.41	444	0.11
49	0.18	106	21.46	160	0.22	216	0.51	271	1.94	325	1.22	384	0.43	445	0.09
50	8.40	107	2.73	162	9.72	217	1.06	272	0.77	327	11.30	385	0.28	446	0.10
51	22.22	108	0.79	163	2.23	218	3.58	273	0.67	328	1.37	386	3.74	447	0.31
52	21.46	109	14.39	164	2.89	219	6.25	274	1.03	329	0.26	387	61.36	448	0.33
53	6.69	110	1.14	165	1.56	220	32.83	275	1.06	330	0.10	388	10.04	449	0.15
54	0.54	111	0.28	166	1.99	221	11.49	276	1.33	331	0.09	389	1.44	450	0.07
55	1.28	112	1.75	167	1.39	222	1.18	277	1.03	332	0.61	390	0.31	451	0.10
56	0.21	113	0.82	168	1.10	223	0.88	278	1.77	333	1.36	391	0.30	455	0.08
57	0.54	114	1.47	169	15.47	224	2.02	279	0.54	334	1.06	392	0.31	456	0.25
58	0.15	115	1.10	170	8.71	225	3.66	280	0.69	335	4.92	393	0.25	457	0.15
59	0.22	116	4.29	171	2.30	226	2.34	281	1.44	336	7.89	394	1.82	458	0.24
61	0.67	117	3.77	172	0.39	227	0.60	282	1.96	337	28.54	395	0.39	459	0.17
62	8.40	118	0.84	173	0.25	228	6.12	283	3.19	338	6.06	396	0.15	460	0.13
63	49.24	119	3.19	174	2.38	229	0.95	284	2.35	339	1.47	397	0.23	463	0.12
64	10.29	120	1.59	175	1.61	230	1.45	285	1.14	340	0.82	398	0.22	464	0.17
65	4.86	121	1.94	176	1.88	231	4.48	286	5.74	341	0.31	399	0.17	465	0.15
66	6.19	122	0.51	177	0.87	232	3.41	287	39.39	342	0.42	400	0.14	466	0.15
67	2.83	123	0.41	178	2.59	233	1.96	288	10.35	343	0.23	401	0.14	467	0.72
69	85.86	124	4.48	179	0.43	234	1.04	289	12.56	344	0.19	402	0.32	468	0.28
70	1.18	125	1.25	181	18.94	235	1.20	290	13.57	345	0.15	403	0.68	469	0.22
71	0.26	126	0.82	182	6.44	236	6.44	291	1.63	346	0.27	404	2.45	470	0.12
73	0.26	127	2.51	183	3.31	237	22.73	292	3.28	347	0.79	405	13.45	471	0.07
74	3.87	128	0.65	184	0.68	238	17.42	293	1.06	348	0.53	406	55.56	475	0.10
75	6.00	129	0.28	185	0.23	239	16.92	294	2.67	349	0.35	407	8.78	477	0.59
76	5.62	130	0.47	186	1.22	240	20.20	295	0.75	350	0.40	408	1.20	478	0.18
77	38.64	131	7.13	187	1.63	241	2.70	296	1.42	352	3.14	409	0.24	480	0.13
78	38.89	132	1.64	188	7.45	242	2.38	297	2.35	353	5.62	410	0.08	481	0.16
79	3.16	133	0.98	189	10.10	243	6.69	298	1.69	354	1.26	412	0.17	482	0.20
80	0.31	134	1.20	190	10.42	244	3.44	299	0.65	355	0.36	413	0.22	483	0.20
81	1.45	135	1.66	191	1.39	245	1.47	300	7.58	356	0.36	414	0.12	484	0.15
82	0.42	136	1.45	192	0.62	246	1.39	301	5.81	357	0.36	416	0.17	485	0.15
83	1.34	137	1.00	193	7.07	247	1.89	302	5.74	358	3.39	417	0.39	486	0.34
84	0.15	138	2.08	194	3.25	248	1.42	303	2.57	359	2.75	418	0.21	487	0.17
85	0.40	139	0.56	195	3.33	249	3.96	304	0.58	361	35.10	419	0.28	488	0.22
86	1.80	140	1.22	196	2.16	250	9.03	305	1.03	363	0.45	420	0.37	489	0.53

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
490	0.14	537	1.07	585	0.36	654	0.30
491	0.06	538	0.26	586	0.56	655	0.84
493	0.11	539	0.17	587	0.21	656	0.22
494	0.12	543	0.09	588	0.13	659	0.39
495	0.12	545	0.19	590	0.09	660	0.11
496	0.13	546	0.10	591	0.08	665	0.15
497	0.63	547	0.10	595	0.06	666	0.75
498	0.25	548	0.66	597	3.55	667	0.20
499	0.08	549	0.14	598	1.94	673	0.18
501	0.07	550	0.08	599	0.34	674	0.46
505	1.40	552	0.12	602	0.28	675	0.31
506	0.39	553	0.97	603	0.09	676	0.08
507	0.24	554	0.27	604	0.07	679	0.37
508	0.81	555	0.40	605	5.11	680	0.10
509	0.25	556	0.26	606	1.31	683	0.29
510	0.13	557	0.41	607	0.20	684	0.22
513	0.13	558	0.21	610	0.05	685	0.08
514	0.19	559	0.06	613	0.08	688	0.06
515	0.15	560	0.12	614	0.23	693	0.32
516	0.27	563	0.14	615	0.12	694	2.97
517	0.59	564	0.34	620	0.10	695	0.71
518	0.18	565	0.23	625	8.40	696	0.11
519	0.11	566	0.15	626	2.05	701	0.07
520	0.11	567	0.21	627	0.36	702	0.26
521	0.09	568	0.07	633	0.62	703	3.31
524	0.06	569	0.09	634	0.86	704	0.88
525	3.38	570	0.23	635	0.29	705	0.17
526	0.80	571	0.10	636	0.07	707	0.08
527	0.30	572	0.07	638	0.13	720	0.11
528	0.15	575	0.18	639	0.05	721	3.17
529	0.34	577	1.06	646	0.10	722	61.62
530	0.11	578	0.31	647	0.11	723	16.10
532	0.10	579	0.11	648	0.39	724	2.48
533	0.35	580	0.06	649	0.10	725	0.26
534	0.22	582	0.07	651	0.40		
535	0.26	583	0.53	652	0.87		
536	3.52	584	0.20	653	0.78		



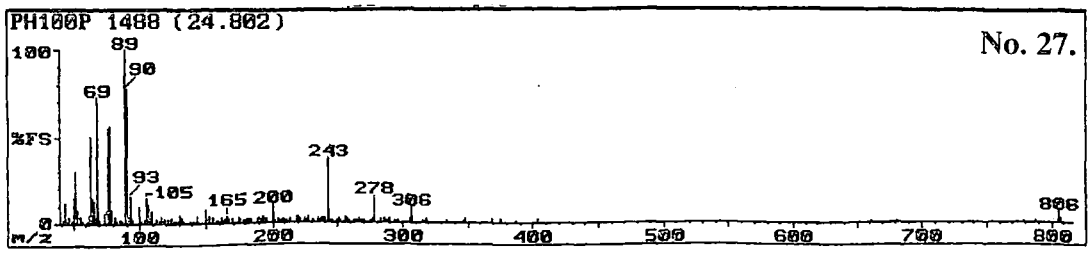
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	4.69	86	1.07	144	1.23	214	5.11	275	1.05	333	1.76	390	1.38	519	0.37
24	0.93	87	1.15	145	2.15	215	1.37	276	2.34	334	1.31	391	0.27	533	0.44
25	0.95	88	0.91	146	0.63	216	0.90	277	1.15	335	1.30	392	0.31	534	0.36
26	3.18	89	1.67	148	0.27	219	4.62	278	0.95	336	1.69	394	0.91	536	0.28
27	1.81	90	5.68	150	6.68	220	2.11	279	1.07	337	0.39	395	0.67	541	0.37
28	21.02	91	4.76	151	1.58	221	1.74	280	1.01	338	0.72	396	0.34	545	0.24
29	1.37	92	25.28	152	1.65	222	0.48	281	1.90	339	1.76	397	0.18	553	0.85
31	13.64	93	22.16	153	0.60	223	2.29	282	1.60	340	1.15	398	0.36	561	0.27
32	0.33	94	2.93	154	0.75	224	1.30	283	1.09	341	0.67	399	0.19	562	0.20
35	5.04	95	9.66	155	2.97	225	1.74	284	0.56	342	1.01	405	0.18	564	1.01
36	1.94	96	0.83	156	0.97	226	3.25	285	1.44	343	0.40	405	0.87	565	0.45
37	2.65	98	0.59	157	0.53	227	1.46	286	1.33	344	0.60	406	0.55	566	0.14
38	4.76	98	0.29	159	0.52	228	1.38	287	0.89	345	0.55	407	0.26	581	1.69
39	3.59	99	1.92	162	2.01	229	0.66	288	1.97	346	1.33	408	0.56	582	0.30
40	0.24	100	11.36	163	1.12	230	0.44	289	2.01	347	0.82	409	0.58	584	0.41
41	0.54	101	1.92	164	1.01	231	1.31	290	0.51	348	0.79	410	0.28	585	0.29
42	0.26	102	6.75	165	0.50	232	1.21	292	15.34	349	0.58	415	0.81	592	0.34
43	1.19	103	1.14	166	1.69	233	0.69	293	2.89	350	0.44	416	0.43	605	0.50
44	2.04	104	0.90	167	1.33	235	0.82	294	1.63	351	0.29	417	0.41	612	0.25
45	0.39	105	1.67	168	1.86	237	1.86	295	1.00	352	0.26	418	0.62	613	0.53
47	2.52	106	0.99	169	1.88	238	2.52	296	1.15	353	0.25	419	0.57	614	0.41
48	0.49	107	1.37	170	1.62	239	3.55	297	0.89	354	1.62	422	2.77	620	0.61
50	19.32	108	0.22	171	0.87	240	2.15	298	1.60	355	0.84	423	0.73	633	1.30
51	4.76	109	0.30	172	0.25	243	58.24	299	2.13	356	0.46	424	0.51	634	0.55
52	4.69	110	0.29	174	2.88	244	6.04	300	1.44	357	0.33	425	0.39	635	0.23
53	1.06	111	0.70	175	0.60	245	1.09	301	1.24	358	0.41	432	0.32	641	0.4
54	0.61	112	2.04	176	3.05	246	1.62	302	0.80	359	0.39	435	0.58	642	0.2
55	2.50	113	1.13	177	2.20	247	0.78	304	2.81	360	2.50	436	0.79	645	0.3
56	0.42	114	0.55	178	0.71	249	0.94	305	1.42	361	4.51	437	0.46	652	0.4
57	1.23	115	0.90	181	2.18	250	5.54	306	0.91	362	1.85	439	0.38	653	2.8
59	0.23	116	1.58	182	1.11	251	2.68	307	1.03	363	0.68	446	0.72	654	0.7
61	1.51	117	0.80	183	1.03	252	2.31	308	0.99	364	0.65	447	0.54	661	0.8
62	4.15	118	0.93	184	0.59	253	0.96	309	0.60	365	0.33	448	0.17	662	0.6
63	39.20	119	3.09	185	0.19	254	2.10	310	0.92	366	0.66	463	0.71	665	0.6
64	59.09	120	0.82	187	1.99	255	0.92	311	0.31	367	1.23	464	0.56	673	0.3
65	10.72	121	0.32	188	1.63	256	2.22	312	0.25	368	0.69	465	0.31	674	0.3
66	3.59	122	0.20	189	0.44	257	1.94	313	0.58	369	0.32	467	0.47	675	0.3
67	1.23	124	4.31	192	1.14	258	1.30	314	0.58	370	0.54	472	0.25	681	4.2
69	95.45	125	1.21	193	4.62	259	2.22	315	0.54	371	0.59	475	0.32	682	1.3
70	4.46	127	1.88	194	4.69	260	0.88	316	0.92	372	0.67	477	0.32	683	0.6
71	2.54	127	0.96	195	1.21	261	0.45	317	0.91	373	1.56	484	0.28	689	0.4
73	2.75	128	1.63	196	1.23	262	0.95	318	1.76	374	0.59	487	0.22	690	0.5
74	17.68	129	0.19	197	1.99	263	2.18	319	3.46	375	0.69	489	0.38	693	0.5
75	71.88	130	0.88	198	0.51	264	4.90	320	3.04	376	0.54	491	4.30	701	0.4
76	100.00	131	3.55	200	9.94	265	0.86	321	1.90	377	0.54	492	0.73	702	0.4
77	18.75	132	0.21	201	1.76	266	3.80	322	0.65	378	0.40	493	0.30	703	1.9
78	3.02	133	0.24	202	1.17	267	3.66	323	0.93	380	0.47	495	0.44	704	0.4
79	5.68	136	0.19	204	0.60	268	1.11	324	0.51	381	0.24	505	0.51	709	1.1
80	4.40	137	0.78	205	3.04	269	4.24	325	0.92	382	0.30	507	0.90	710	0.4
81	5.40	138	2.86	206	0.50	270	4.55	326	1.40	383	0.32	508	0.36	711	0.4
82	0.93	139	7.32	207	2.86	271	2.89	327	0.75	384	0.15	509	0.28	712	0.2
83	0.88	140	1.46	208	1.03	272	1.19	328	0.49	386	0.24	512	0.31	721	1.5
84	0.43	141	0.47	209	1.92	273	1.88	330	0.47	387	1.44	516	0.41	722	2.2
85	2.45	143	3.39	212	1.28	274	0.77	332	1.28	389	3.10	517	0.33	723	0.6

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
729	0.28	740	1.44	759	6.18	779	15.91
730	0.34	741	0.30	760	2.02	780	2.81
731	2.41	749	1.23	761	0.25		
732	0.81	750	5.40	777	0.47		
739	0.20	751	1.76	778	48.86		



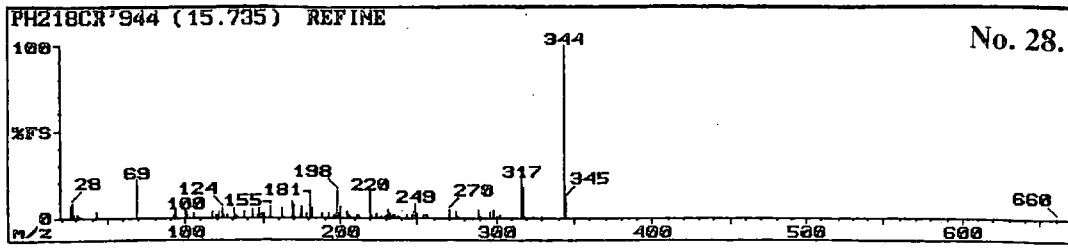
Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
5.78	84	0.61	139	0.86	197	0.29	262	0.18	319	0.22	380	0.27	451	0.12
0.09	85	2.04	140	0.56	198	0.10	263	0.39	320	0.31	381	0.23	452	0.07
0.85	86	1.36	141	0.82	200	2.26	264	0.76	321	0.19	382	0.22	453	0.06
1.23	87	1.80	142	0.57	201	0.41	265	0.41	322	0.21	383	0.07	458	0.06
3.97	89	41.76	143	1.55	202	0.14	266	0.24	323	0.10	384	0.10	460	0.12
2.68	90	23.14	144	0.34	203	0.09	267	0.20	324	0.13	386	0.18	460	0.07
100.00	91	10.90	145	0.46	205	0.60	268	0.30	326	0.20	387	0.32	461	0.14
3.76	92	13.30	146	0.21	206	0.25	269	0.33	327	0.18	388	0.12	463	0.03
0.52	93	12.97	147	0.14	207	0.37	270	0.42	328	0.07	389	0.34	465	0.06
16.02	94	2.56	148	0.17	208	0.42	271	0.35	329	0.16	390	0.32	466	0.05
5.32	95	3.47	149	0.55	209	0.45	271	0.13	330	0.14	391	0.06	476	0.09
0.55	96	0.85	150	2.24	211	0.15	273	0.22	331	0.18	392	0.07	478	0.26
2.54	97	0.45	151	1.45	212	0.13	274	0.20	332	0.19	393	0.04	478	0.20
2.34	98	0.55	152	2.43	214	0.81	276	0.51	333	0.88	394	0.08	481	0.09
3.19	99	2.11	153	1.30	216	0.15	277	0.49	334	0.41	395	0.16	485	0.07
4.39	100	6.52	154	0.38	218	0.20	278	0.64	335	0.42	396	3.19	486	0.08
12.23	101	1.13	155	1.21	219	0.55	279	0.17	337	0.33	398	0.05	489	0.08
2.34	102	1.86	156	0.19	220	0.55	280	0.30	338	0.16	401	0.21	493	0.05
0.84	103	1.15	157	0.14	221	0.45	281	0.40	339	0.28	402	0.28	498	0.08
0.88	104	2.46	158	0.35	222	0.13	282	0.40	340	0.12	403	0.39	503	0.15
0.96	105	5.72	159	0.32	223	0.18	283	0.44	341	0.08	404	0.15	505	0.42
4.65	106	4.52	160	0.14	224	0.11	284	0.54	342	0.25	405	0.13	506	0.17
5.05	107	1.75	161	0.19	225	0.49	284	0.22	343	0.22	406	0.05	507	0.13
0.36	108	1.28	162	0.84	226	0.56	286	0.30	344	0.14	407	0.09	508	0.07
4.16	109	3.19	163	0.70	228	0.22	287	0.32	345	0.15	408	0.20	509	0.07
0.50	110	0.70	164	1.16	231	0.27	288	0.26	346	0.53	409	0.14	510	0.12
16.16	111	0.48	165	1.98	232	0.15	289	0.39	347	0.39	410	0.14	511	0.05
11.70	112	1.45	166	0.74	233	0.32	290	0.44	348	0.25	412	0.07	519	0.07
10.84	113	0.47	167	0.26	234	0.37	292	1.93	349	0.23	413	0.04	521	0.09
3.61	114	0.88	168	0.49	235	0.11	293	0.37	350	0.15	414	0.07	522	0.11
2.61	115	1.85	169	0.90	237	0.15	294	0.32	351	0.16	417	0.06	524	0.03
0.98	116	3.22	170	0.37	238	0.39	295	0.20	352	0.24	418	0.09	526	0.11
1.23	117	1.40	171	0.15	239	0.39	296	0.09	353	0.24	419	0.15	529	0.07
0.16	118	0.52	172	0.10	239	0.22	296	0.10	354	0.35	420	0.07	530	0.15
0.15	119	1.56	174	0.69	240	0.27	297	0.07	355	0.16	421	0.11	531	0.10
0.25	120	0.69	175	0.36	241	0.09	298	0.05	356	0.05	422	0.27	533	0.10
1.63	121	0.62	176	0.57	243	6.12	299	0.27	358	0.17	423	0.07	534	0.04
36.97	122	0.18	177	0.57	243	3.41	300	0.16	360	0.47	424	0.06	535	0.09
23.67	123	0.66	178	0.42	245	0.57	302	0.26	361	0.86	425	0.06	538	0.06
8.84	124	1.78	179	0.15	246	0.27	303	0.28	362	0.57	428	0.04	546	0.07
5.65	125	0.52	180	0.49	246	0.15	304	0.31	363	0.24	429	0.10	547	0.17
2.93	126	0.46	181	0.92	249	0.13	305	0.32	364	0.19	430	0.13	548	0.10
59.04	127	1.51	182	0.36	250	0.50	306	0.96	365	0.15	431	0.12	549	0.10
2.49	128	0.53	183	0.46	251	0.50	307	0.76	366	0.10	432	0.07	550	0.12
1.08	129	0.21	184	0.22	252	0.53	308	0.21	368	0.34	433	0.08	551	0.06
35.90	130	0.76	185	0.13	252	0.18	309	0.13	369	0.17	435	0.06	555	0.13
32.18	131	2.48	187	0.34	253	0.52	310	0.13	370	0.16	437	0.29	556	0.10
28.99	132	1.06	188	0.46	254	0.40	312	0.27	371	0.10	437	0.09	557	0.10
17.29	133	0.62	190	0.58	256	0.40	313	0.18	372	0.12	438	0.16	558	0.16
4.52	134	0.22	191	0.58	257	0.33	314	0.14	374	0.76	446	0.11	559	0.10
2.43	135	0.21	193	0.91	258	0.51	315	0.16	375	0.64	447	0.06	563	0.10
4.92	136	0.23	194	0.37	259	0.45	316	0.08	376	0.31	448	0.08	567	0.27
1.75	137	0.57	195	0.44	260	0.15	317	0.14	377	0.12	449	0.15	568	0.11
1.50	138	0.88	196	0.27	261	0.09	318	0.63	378	0.09	450	0.32	569	0.05

Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
0.08	621	0.08	668	0.38	722	0.12
0.13	623	0.06	669	0.11	723	0.36
0.08	625	0.15	670	0.07	724	0.14
0.09	626	0.19	673	0.08	725	0.15
0.32	627	0.24	674	0.08	726	0.09
0.14	628	0.12	675	0.44	735	0.48
0.08	629	0.06	676	0.26	736	0.62
0.09	630	0.04	677	0.09	737	0.18
0.06	631	0.05	679	0.12	743	0.15
0.04	632	0.06	680	0.07	744	0.15
0.06	634	0.06	684	0.09	745	0.71
0.07	635	0.08	685	0.05	746	0.25
0.37	637	0.06	687	0.05	747	0.06
0.13	639	0.08	688	0.04	749	0.14
0.12	645	0.10	694	0.07	753	0.08
0.20	646	0.08	695	0.93	754	0.33
0.18	647	0.61	696	0.32	755	0.10
0.07	648	0.37	697	0.09	763	0.31
0.06	649	0.13	698	0.06	764	1.43
0.09	652	0.08	699	0.05	765	0.46
0.10	654	0.06	703	0.18	766	0.10
0.14	655	0.18	704	0.22	773	1.60
0.12	656	0.14	705	0.11	774	0.58
0.07	657	0.09	707	0.12	775	0.15
0.06	658	0.07	708	0.08	791	0.33
0.08	659	0.09	715	0.09	792	12.37
0.08	661	0.05	716	0.17	793	4.45
0.08	665	0.06	717	0.52	794	0.79
0.17	666	0.11	718	0.16	795	0.08
0.17	667	1.16	721	0.12		

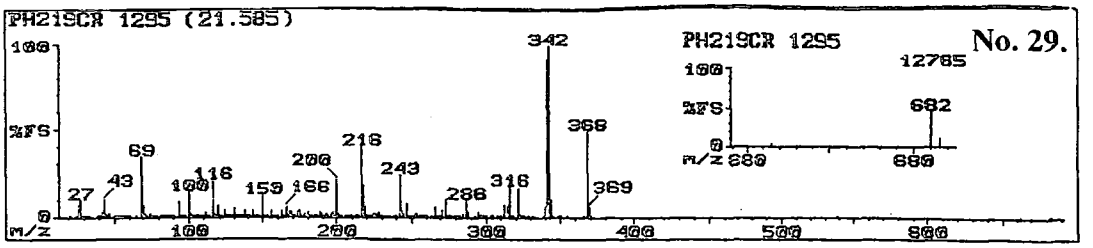


No. 27.

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
41	2.25	103	2.07	183	1.55	263	0.73
42	0.90	104	2.25	188	2.07	264	1.45
43	2.13	105	14.58	189	1.50	265	0.92
44	12.04	106	11.07	190	2.62	266	2.29
45	1.16	107	2.70	191	1.90	267	0.92
47	3.45	109	6.51	192	0.68	268	1.37
49	1.06	112	1.82	193	4.30	269	0.85
50	15.04	115	1.37	194	1.82	270	0.87
51	27.60	116	4.23	195	2.23	276	1.14
52	30.21	117	1.17	200	10.29	277	1.55
53	7.36	119	2.34	201	0.84	278	4.02
55	4.12	121	1.51	202	1.30	283	1.50
56	0.79	124	2.54	205	1.97	286	2.29
57	0.92	127	1.07	206	0.86	287	0.92
61	0.55	128	0.90	207	1.14	289	0.64
62	5.01	131	4.49	208	2.20	290	1.73
63	50.78	132	2.75	209	1.17	294	0.81
64	14.13	133	1.19	211	0.54	296	1.06
65	7.42	138	0.92	213	1.69	305	1.71
66	12.63	141	0.89	218	1.46	306	8.40
67	3.34	143	3.66	219	3.39	307	1.40
69	72.92	150	8.07	220	3.11	316	0.70
70	2.02	151	2.29	221	1.55	318	1.81
74	5.40	152	4.30	225	1.51	333	0.69
75	8.07	153	1.99	226	1.29	334	1.12
77	55.21	155	3.34	228	2.78	346	0.85
78	56.25	158	1.14	232	0.65	347	1.64
79	8.07	159	1.33	236	1.58	348	1.11
81	4.00	162	2.65	237	1.35	168	1.48
82	1.79	163	0.93	238	1.51	375	2.21
83	0.87	164	1.89	239	1.50	387	1.06
86	1.66	165	4.15	240	1.68	403	1.87
87	1.33	166	1.66	243	37.24	661	0.68
89	100.00	167	1.09	246	1.09	681	1.02
90	78.13	169	2.05	249	0.69	778	0.75
91	40.89	174	2.78	251	1.48	787	0.68
92	3.69	176	1.69	252	0.90	806	6.77
93	15.30	178	1.37	256	3.11	807	2.44
94	2.13	179	1.00	257	0.67		
100	9.31	181	1.76	258	1.99		
101	0.88	182	1.76	259	1.12		



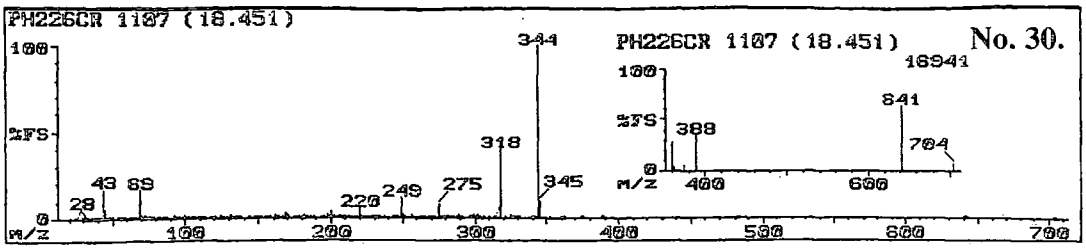
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
27	7.75	138	3.53	200	6.49	250	3.20
28	8.53	143	4.57	204	3.70	254	1.82
29	1.88	146	1.92	205	1.92	255	1.70
31	2.15	147	5.59	207	0.74	256	1.82
32	0.35	148	1.79	211	1.89	270	5.29
43	4.15	149	2.84	212	2.01	274	1.37
44	1.04	150	3.09	219	1.43	275	3.44
69	22.36	151	1.71	220	15.87	276	0.94
92	1.47	155	7.15	221	2.21	288	1.22
93	4.87	162	5.47	224	2.55	289	4.99
100	5.05	169	10.10	227	1.31	290	1.13
101	4.27	170	8.11	229	1.23	296	3.80
105	2.99	174	2.19	230	1.53	298	4.51
117	4.03	175	7.27	231	4.81	300	1.11
119	2.34	178	2.82	232	2.85	302	1.62
120	2.16	181	12.62	233	1.02	317	22.84
121	3.55	182	5.41	235	2.21	318	17.79
124	5.53	188	3.31	236	1.47	319	1.29
125	1.86	193	2.55	238	1.40	324	0.55
127	2.24	196	1.67	243	1.55	330	1.35
131	5.47	197	2.82	246	1.68	344	100.00
132	1.95	198	15.38	248	3.85	345	11.96
133	1.01	199	3.23	249	8.53	660	1.20



No. 29.

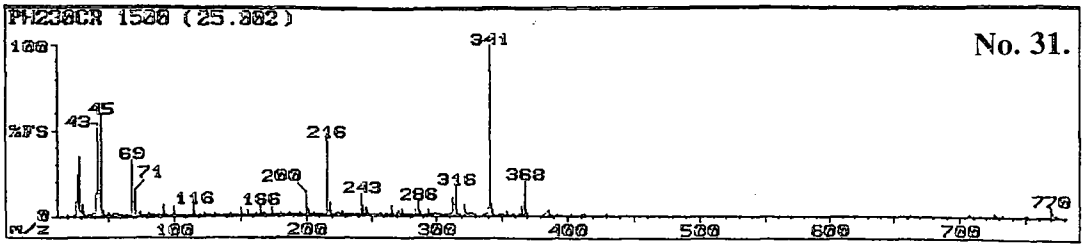
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.05	97	0.16	159	0.08	224	1.49
26	0.41	98	0.20	160	0.15	225	2.09
27	6.37	100	14.60	162	3.91	226	0.82
27	9.99	101	2.00	163	0.65	228	2.80
28	6.83	102	0.99	164	0.99	229	0.46
29	1.05	103	0.14	165	0.24	230	0.80
30	0.37	105	0.47	166	5.61	231	1.15
31	0.79	105	0.30	167	0.31	232	0.43
32	0.36	107	0.69	168	2.95	233	0.10
33	0.12	108	0.30	168	1.75	234	0.07
39	0.18	109	0.23	169	3.11	236	0.44
40	0.23	110	0.19	170	1.10	238	0.44
41	1.20	112	3.34	171	0.50	239	0.75
42	2.94	113	0.71	174	2.61	240	0.83
43	9.35	114	0.34	174	1.47	243	24.30
44	1.46	116	10.05	175	4.15	244	4.26
45	2.16	117	1.85	176	0.46	245	1.47
46	0.73	118	0.19	178	1.58	247	8.24
47	2.13	119	6.37	179	0.32	248	1.33
50	0.42	120	0.98	181	2.47	249	1.05
51	0.77	121	0.55	182	0.77	250	0.87
52	0.07	122	0.06	183	0.26	251	0.62
53	0.52	124	3.86	184	0.14	253	2.10
54	1.04	125	0.78	186	0.19	254	1.65
55	0.98	126	0.35	188	3.34	256	1.20
56	0.32	127	0.47	189	1.49	257	1.07
57	0.20	128	1.24	190	0.38	258	0.47
58	0.10	129	0.21	191	0.31	259	0.26
59	0.14	130	0.66	193	1.78	260	0.14
60	0.09	131	5.26	193	1.61	264	0.18
65	0.38	132	0.88	194	1.12	266	6.07
69	35.05	133	0.52	196	2.19	267	1.15
70	7.18	134	0.09	197	2.44	268	1.45
71	2.09	135	0.30	198	1.11	269	1.26
72	0.45	136	0.32	200	21.03	270	3.40
74	1.87	137	0.96	201	2.28	271	2.48
75	1.14	138	3.91	202	1.30	273	9.23
76	0.40	139	0.48	203	0.44	274	0.82
77	0.30	140	0.19	205	1.45	275	0.08
78	0.12	141	0.17	206	0.22	276	0.14
81	0.82	143	4.26	207	0.91	278	0.27
82	0.61	144	0.90	208	1.01	280	0.54
83	0.19	145	1.18	209	0.26	281	0.56
84	0.09	146	1.24	210	0.35	282	1.39
85	0.12	147	1.05	212	0.80	284	1.94
86	0.15	148	0.52	213	0.21	286	9.99
87	0.20	150	12.38	214	1.05	287	2.61
88	0.79	151	1.27	216	40.42	288	0.42
89	0.92	152	1.08	218	18.22	292	0.12
90	0.68	153	0.30	219	5.61	294	2.44
93	8.64	155	3.91	220	0.98	295	0.33
94	0.78	156	0.67	221	0.82	296	0.70
95	0.47	157	0.38	222	0.31	297	0.47
96	1.18	158	0.32	223	1.39	299	0.56

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
299	1.23	316	17.06	331	0.28	354	0.14
300	0.45	317	0.92	338	0.20	366	0.25
303	0.33	318	0.28	339	0.45	368	50.00
304	0.28	322	16.12	340	5.49	369	5.96
308	0.15	323	2.19	341	91.59	370	0.54
310	0.44	324	0.30	342	100.00	538	0.08
312	0.86	325	0.42	343	9.93	663	0.10
313	7.18	326	0.19	344	0.93	682	1.27
314	3.02	328	0.23	349	0.37	683	0.30
315	5.90	330	0.14	350	0.11		



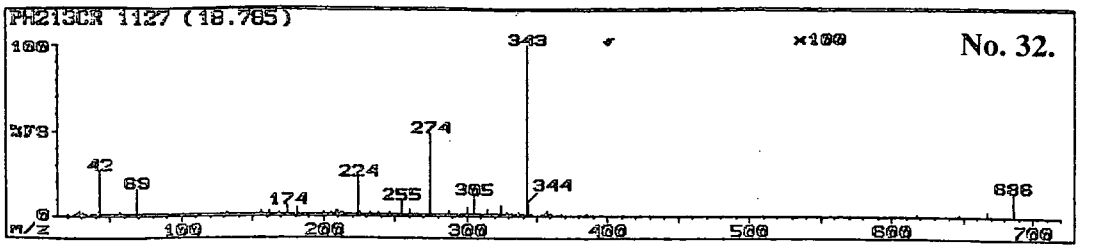
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.30	86	0.39	169	3.37	251	0.37
24	0.10	87	0.11	170	1.70	256	1.80
25	0.28	88	0.11	171	0.09	257	0.17
26	1.75	92	1.03	174	0.39	260	0.06
27	5.11	93	1.97	175	0.58	262	0.29
28	5.72	94	0.17	176	0.11	263	0.07
29	3.84	95	0.10	178	0.99	264	0.05
30	0.66	96	0.06	180	0.48	266	0.10
31	2.79	98	0.18	181	1.88	268	0.02
32	0.21	100	2.00	182	1.36	269	0.15
33	0.07	101	0.20	183	0.24	270	0.25
35	0.06	102	0.05	184	0.06	271	0.05
36	0.10	105	0.78	186	0.08	272	0.07
37	0.05	106	0.13	186	0.08	273	0.08
38	0.09	107	0.36	188	0.81	275	7.63
39	0.12	109	0.23	189	0.04	276	0.48
40	0.07	110	0.05	193	0.55	278	0.18
41	0.96	112	0.56	194	0.18	279	0.16
42	1.39	113	0.32	196	0.25	280	0.68
43	5.49	114	0.22	198	1.75	281	0.09
44	2.49	117	1.09	199	0.59	282	0.10
45	5.13	118	0.04	200	3.46	283	0.06
46	0.29	119	0.60	201	0.46	284	0.03
47	0.48	120	0.36	202	0.26	286	0.07
48	0.04	121	0.05	205	0.73	288	0.99
50	0.57	124	1.59	206	0.14	289	1.56
51	0.23	125	0.32	207	0.09	290	0.30
54	0.07	126	0.08	208	0.09	291	0.04
55	0.20	127	0.07	210	0.12	296	0.19
56	0.10	129	0.06	212	0.81	297	0.27
57	0.58	131	1.56	213	0.12	298	0.11
58	0.31	132	0.40	214	0.14	299	0.38
59	0.04	133	0.13	216	0.14	300	1.94
62	0.25	134	0.12	217	0.03	301	0.81
63	0.06	136	0.34	220	6.02	302	1.94
64	0.04	137	0.32	221	0.50	303	0.12
65	0.08	138	0.30	223	0.05	304	0.06
66	0.05	143	0.68	224	0.15	306	1.05
67	0.04	144	0.12	225	0.79	310	0.06
69	16.90	147	0.89	226	0.10	314	0.09
70	1.54	148	0.07	227	0.07	315	0.65
71	0.91	148	0.12	228	0.73	316	2.96
72	0.30	149	0.27	230	1.19	317	5.34
73	1.49	150	0.67	231	0.67	318	39.44
74	1.09	151	0.21	232	0.48	322	0.03
75	0.30	152	0.10	233	0.89	325	1.83
76	0.23	155	1.24	234	0.12	326	0.40
77	0.06	156	0.19	238	0.69	327	0.03
78	0.06	157	0.04	243	1.00	328	0.08
79	0.14	158	0.07	244	0.07	330	0.96
81	0.65	162	1.57	246	0.34	331	0.12
82	0.22	163	0.29	247	1.05	339	0.12
83	0.06	164	0.09	249	11.50	341	0.09
85	0.35	167	0.17	250	2.20	342	0.57

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
344	100.00	361	0.55	375	0.04	642	0.21
345	10.09	362	0.04	388	0.65	704	0.12
352	0.05	363	0.05	389	0.09	705	0.05
360	0.07	374	0.10	641	1.25		



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.44	79	0.28	144	0.89	204	0.12
24	0.36	80	0.16	145	0.76	205	1.06
25	1.44	81	1.47	146	1.34	206	1.47
26	8.28	82	0.92	147	1.16	207	1.40
27	24.13	83	0.41	148	0.36	208	0.41
28	35.17	84	0.10	150	4.61	209	0.12
29	20.06	85	0.45	151	1.27	210	0.37
30	2.53	86	0.81	152	1.15	211	0.08
31	6.98	87	0.65	153	0.29	212	0.67
32	0.80	88	0.43	155	2.83	213	0.19
33	0.47	89	0.83	156	0.58	214	1.06
35	0.52	90	0.58	157	0.27	215	0.69
36	1.08	91	0.18	158	0.29	216	45.06
37	0.62	92	0.53	159	0.15	217	3.29
38	1.00	93	6.32	160	0.11	218	7.85
39	1.67	94	0.86	162	1.96	219	3.25
40	1.54	95	0.55	163	0.90	220	0.92
41	13.30	96	0.96	164	0.93	221	0.35
42	9.81	97	0.42	166	5.81	223	0.42
43	51.16	99	0.47	168	1.11	224	1.47
44	15.19	100	6.10	168	1.62	225	1.78
45	59.30	101	0.83	169	1.29	226	0.42
46	3.11	102	0.54	170	0.67	227	0.21
47	3.85	103	0.12	171	0.50	228	2.47
48	0.27	105	0.62	172	0.18	229	0.22
49	0.32	106	0.83	173	0.15	230	0.93
50	1.69	107	0.24	174	1.10	231	1.31
51	2.27	108	0.17	175	5.01	232	0.53
52	0.52	109	0.14	176	0.34	233	0.07
53	0.51	110	0.13	178	1.20	234	0.04
54	1.62	112	1.18	179	0.14	235	0.05
55	1.54	113	0.50	180	0.11	236	0.29
56	0.97	114	0.49	181	2.05	237	0.16
57	1.62	116	6.47	182	1.24	238	0.54
58	0.40	117	1.44	183	0.58	239	0.87
59	0.51	119	1.01	184	0.28	240	0.91
60	0.17	120	0.51	186	0.16	242	0.45
61	0.16	121	0.26	187	0.40	243	12.72
62	0.40	124	2.20	188	1.64	244	5.74
63	0.38	125	0.69	189	1.22	245	0.94
64	0.56	126	0.30	190	0.30	247	4.38
65	0.54	127	0.16	191	0.13	248	1.47
66	0.19	128	0.55	192	0.12	249	0.30
67	0.21	129	0.08	193	1.42	250	0.65
69	33.14	131	2.18	194	1.33	251	0.35
70	8.79	132	0.50	195	0.30	252	0.54
71	14.68	133	0.25	196	2.02	253	0.78
72	1.40	135	0.16	197	1.36	254	0.77
73	1.69	137	1.16	198	0.97	255	0.33
74	2.23	138	1.29	199	0.36	256	0.42
75	2.54	139	0.46	200	11.56	257	1.51
76	0.64	140	0.18	201	1.67	258	0.33
77	0.29	141	0.10	202	4.02	260	0.16
78	0.28	143	2.18	203	0.32	262	0.04

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
264	0.17	296	0.64	329	0.28	383	0.07
266	5.52	297	0.91	330	0.28	384	1.87
267	0.44	298	0.38	336	0.68	385	2.63
268	1.15	299	1.64	338	0.36	386	4.00
270	1.91	300	2.25	339	1.73	387	0.41
270	3.13	301	0.17	340	4.65	392	0.06
271	2.43	302	0.22	341	100.00	403	0.14
272	0.96	303	1.22	342	82.56	410	1.20
273	4.22	304	0.66	343	7.19	412	1.31
274	0.66	307	0.09	344	0.69	413	0.15
275	0.15	308	0.28	348	0.45	430	0.20
276	0.07	310	0.68	349	0.26	663	0.13
277	0.13	311	0.14	350	0.16	707	0.49
278	0.21	312	2.03	352	0.15	708	0.11
280	0.36	313	10.61	354	2.91	726	1.84
281	0.21	314	1.27	355	0.62	727	0.49
282	0.12	315	7.19	356	0.43	732	0.07
284	4.36	316	17.30	358	0.07	750	0.14
285	2.58	317	1.07	359	0.21	751	0.47
286	8.72	318	0.35	363	0.26	752	0.17
287	3.34	322	6.90	365	0.52	770	5.96
288	0.37	323	2.31	366	5.92	771	2.47
289	0.05	324	0.88	367	0.67	772	0.56
292	0.15	325	1.12	368	20.64	773	0.08
293	0.39	326	2.34	369	2.33		
294	3.76	327	0.36	370	0.26		
295	0.61	328	1.47	382	0.07		

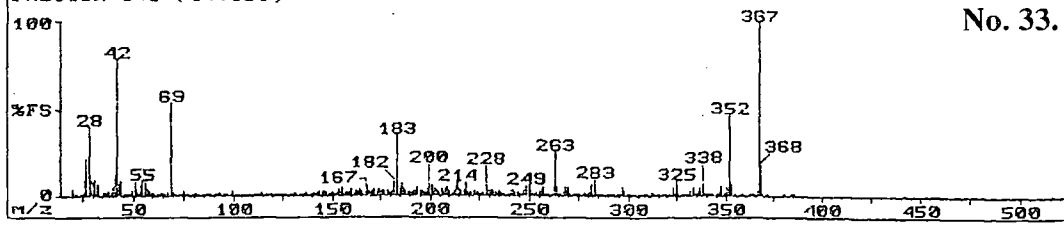


Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.20	83	0.21	140	0.21	195	1.25
25	0.01	84	0.12	141	0.55	196	0.67
26	0.13	85	0.23	142	0.09	197	0.50
27	1.76	86	0.54	143	0.57	198	0.33
28	2.60	87	0.17	144	0.84	199	0.42
29	0.91	88	0.28	145	0.42	200	2.07
30	1.53	89	0.09	146	0.81	201	0.39
31	0.76	90	0.10	147	0.25	202	0.17
32	0.10	91	0.13	148	0.22	203	0.76
33	0.29	93	1.41	149	0.19	204	0.58
37	0.02	94	0.26	150	0.60	205	2.14
38	0.04	95	0.23	151	0.52	206	0.77
39	0.20	96	0.16	152	0.42	207	0.46
40	0.30	97	0.04	153	0.15	208	0.38
41	1.71	98	0.14	154	0.40	209	2.65
42	26.05	99	0.35	155	2.47	210	3.31
43	6.12	100	1.27	156	0.35	211	0.42
44	0.82	101	0.28	157	0.23	212	2.15
45	0.14	102	0.13	158	0.43	213	1.56
46	0.20	103	0.04	159	0.46	214	0.73
47	0.11	104	0.06	160	0.62	215	0.28
48	0.03	105	0.54	161	0.13	216	0.15
50	0.31	106	0.39	162	2.66	217	1.03
51	0.36	107	0.17	163	0.88	218	0.43
52	0.11	108	0.13	164	1.43	219	0.56
53	0.08	109	0.04	165	0.30	220	1.09
54	0.86	110	0.07	166	0.09	221	0.91
55	1.10	111	0.04	167	0.74	222	0.87
56	1.66	112	0.31	168	0.81	223	0.69
57	0.89	113	0.50	169	1.68	224	22.63
58	0.13	114	0.48	170	1.25	225	2.34
59	0.13	115	0.24	171	0.44	226	0.58
60	0.46	117	0.94	172	0.38	227	0.46
61	0.04	118	0.19	173	0.79	228	0.53
62	0.12	119	0.55	174	5.92	229	0.65
63	0.05	120	0.36	175	0.92	230	0.08
64	0.26	121	0.16	176	0.85	231	1.32
65	0.09	122	0.07	177	0.60	232	2.07
66	0.07	124	0.83	178	0.44	233	1.07
67	0.18	125	0.23	179	0.11	234	0.89
69	15.79	126	0.30	181	3.80	235	0.31
70	0.42	127	0.25	182	5.33	236	0.86
71	0.14	128	0.20	183	1.41	237	0.40
72	0.14	129	0.11	184	0.60	238	2.29
73	0.06	130	0.07	185	0.46	239	0.68
74	0.36	131	1.35	186	0.86	240	0.37
75	0.45	132	1.74	187	0.49	241	0.84
76	0.41	133	0.70	188	1.18	242	0.24
77	0.13	134	0.24	189	0.45	243	0.45
78	0.22	135	0.06	190	0.50	244	0.36
79	0.09	136	0.32	191	0.42	245	0.57
80	0.04	137	0.61	192	0.17	246	1.74
81	0.44	138	0.40	193	0.82	247	0.48
82	0.67	139	0.21	194	0.58	248	0.53

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
249	0.19	276	0.45	304	0.05	335	0.07
250	1.18	277	0.16	305	11.91	336	0.14
251	0.49	278	0.13	306	1.40	337	2.01
252	0.10	279	0.35	307	0.10	338	0.57
253	0.88	280	0.06	308	0.04	339	1.07
254	0.60	281	0.25	309	0.20	340	0.17
255	8.42	282	0.27	310	0.12	341	1.22
256	1.13	283	0.19	311	0.19	343	100.00
257	0.13	284	0.11	312	0.04	344	6.97
258	0.32	285	0.09	314	1.38	345	0.41
259	0.51	286	1.10	315	3.52	346	0.04
260	4.28	287	0.38	316	0.56	353	0.03
261	0.49	288	3.04	317	0.74	355	0.61
262	0.79	289	0.46	318	0.10	356	1.64
263	0.89	290	0.09	319	0.26	357	2.86
264	0.34	291	0.12	320	0.03	358	0.37
265	0.15	292	0.05	322	0.04	359	0.03
266	0.10	293	0.06	323	0.30	361	0.02
267	0.50	294	0.05	324	5.39	367	0.03
268	0.42	296	0.15	325	1.09	368	0.03
269	0.67	297	0.40	326	0.12	384	0.16
270	0.17	298	0.08	327	1.04	385	0.04
271	0.22	299	0.07	328	0.64	617	0.01
272	1.17	300	2.34	329	1.61	647	0.01
273	0.60	301	5.07	330	1.22	667	0.03
274	47.89	302	0.83	331	0.21	686	0.14
275	5.46	303	0.35	332	0.03	687	0.04

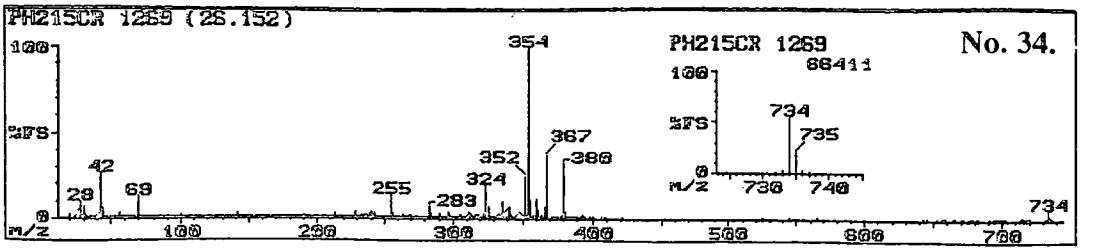
PH231CR 843 (14.051)

No. 33.



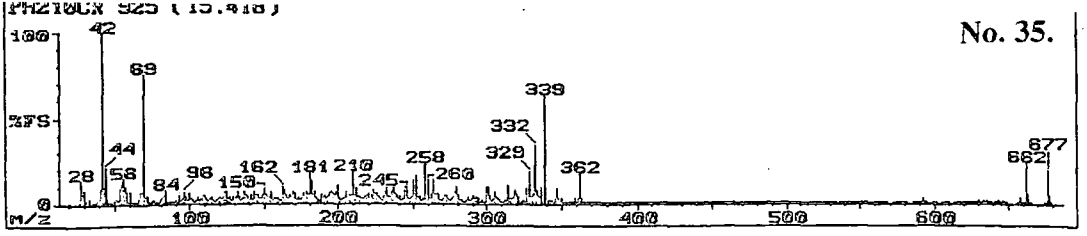
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	3.50	78	0.73	132	1.01	186	6.72
21	0.06	79	0.49	133	0.70	187	3.55
24	0.45	80	0.37	134	0.77	188	3.17
25	1.05	81	1.54	135	0.65	189	2.11
26	9.00	82	1.13	136	0.73	190	1.51
27	20.93	83	0.85	137	1.49	191	1.87
28	39.77	84	1.32	138	1.20	192	3.31
29	9.19	85	0.35	139	1.04	193	2.53
30	7.86	86	0.54	140	1.38	194	4.43
31	8.33	87	0.38	141	2.04	195	2.46
32	0.99	88	0.82	142	0.77	196	3.05
33	6.44	89	0.25	143	1.61	197	1.92
35	1.99	90	0.36	144	2.68	198	1.70
36	2.34	91	0.57	145	1.70	199	3.74
37	1.40	92	0.12	146	2.75	200	7.10
38	3.39	93	2.23	147	1.54	201	6.06
39	4.81	94	0.73	148	1.30	202	1.39
40	5.49	95	0.61	149	1.68	203	3.46
41	12.97	96	0.49	150	1.80	204	3.01
42	78.41	97	0.33	151	1.27	205	1.70
43	6.63	99	1.08	152	0.84	206	4.02
44	3.33	100	2.72	153	2.15	207	2.25
45	1.23	101	0.97	154	4.36	208	3.43
46	1.42	102	0.79	155	2.01	209	4.52
47	1.08	103	0.32	156	4.45	210	3.27
48	0.34	105	1.02	156	1.33	211	0.99
49	0.59	105	0.67	157	1.94	212	2.82
50	3.08	106	0.67	158	2.13	213	5.42
51	7.57	107	0.54	159	1.82	214	7.48
52	2.06	108	0.51	160	4.02	215	3.43
53	1.40	109	0.31	161	1.04	216	2.91
54	5.56	110	0.22	162	2.84	217	2.53
55	8.52	111	0.11	163	1.51	218	7.48
56	7.95	112	0.43	164	3.67	219	1.73
57	3.43	113	0.72	165	2.68	220	0.98
58	2.49	114	2.15	166	1.33	221	2.27
59	0.48	115	1.33	167	6.82	222	2.77
60	2.13	116	1.08	168	5.75	223	1.40
61	0.36	117	0.72	169	3.08	224	2.39
62	0.98	118	0.57	170	1.87	225	0.44
63	1.01	119	0.69	171	3.22	226	1.31
64	1.96	120	0.34	172	4.00	227	1.87
65	0.56	121	0.39	173	2.39	228	5.85
66	1.44	122	0.31	174	4.31	229	3.27
67	2.13	123	1.06	175	1.87	230	2.77
69	53.79	124	1.38	176	2.75	231	2.79
70	1.59	125	0.63	177	2.79	232	3.34
71	1.00	126	1.31	178	2.49	233	1.70
72	0.19	127	0.91	179	1.66	234	1.01
73	0.06	128	1.45	180	1.78	235	3.39
74	0.91	129	0.47	181	2.72	236	1.85
75	2.46	129	0.80	182	7.58	237	0.79
76	1.38	130	0.24	183	34.47	238	1.00
77	0.58	131	1.87	185	4.19	239	0.70

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
240	0.91	274	0.41	308	0.33	342	0.04
241	2.34	275	0.30	309	0.28	343	0.05
242	2.89	276	0.89	310	0.35	344	0.05
243	2.25	277	0.46	311	2.32	345	0.21
244	2.11	278	2.06	312	2.08	346	0.46
245	0.78	279	0.67	313	0.36	347	3.48
246	1.04	280	1.73	314	0.22	348	5.56
247	2.68	281	5.52	315	0.29	349	0.72
248	4.40	282	6.72	316	0.43	350	5.16
249	5.16	283	9.56	317	0.59	351	4.12
250	5.80	284	1.34	318	0.96	352	46.59
251	1.05	285	0.31	319	0.60	353	6.91
252	0.25	286	0.09	320	1.07	354	0.62
253	0.67	287	0.29	321	0.24	355	0.04
254	2.30	288	0.05	322	0.16	358	0.02
255	3.14	289	0.06	323	5.04	359	0.04
256	4.00	290	0.03	324	1.44	362	0.03
257	5.00	291	0.38	325	9.09	363	0.03
258	1.08	292	0.58	326	1.00	364	0.44
259	0.59	293	0.36	327	0.38	365	0.42
260	0.86	294	0.71	328	0.65	366	3.39
261	0.38	295	0.25	329	0.32	367	100.00
262	4.66	296	1.34	330	0.26	368	17.42
263	25.00	297	4.88	331	1.12	369	1.33
264	5.28	298	2.60	332	2.46	371	0.02
265	0.77	299	0.72	333	4.64	380	0.03
266	1.40	300	0.36	334	0.82	381	0.03
267	2.08	301	0.06	335	1.02	384	0.03
268	5.16	302	0.25	336	2.30	385	0.03
269	2.56	303	0.06	337	4.56	386	0.04
270	4.50	304	0.18	338	6.82	442	0.02
271	0.38	305	0.82	339	0.94	516	0.01
272	0.23	306	0.22	340	0.12		
273	0.13	307	1.31	341	0.07		



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.96	80	0.29	135	0.16	192	0.57
24	0.11	81	0.91	136	0.24	193	0.74
25	0.24	82	0.76	137	0.63	194	0.76
26	1.91	83	0.40	138	0.41	195	0.40
27	4.57	84	0.30	139	0.42	196	0.80
28	9.73	85	0.39	140	1.18	197	0.55
29	1.82	86	0.61	141	2.81	198	0.55
30	6.36	87	0.26	142	0.57	199	0.72
31	2.32	88	0.40	143	0.68	200	0.78
32	0.36	89	0.21	144	0.86	201	0.86
33	0.52	90	0.19	145	0.51	202	0.31
35	0.08	91	0.15	146	0.81	203	0.62
36	0.17	93	1.33	147	0.36	204	0.26
37	0.23	94	0.56	148	0.38	205	0.78
38	1.00	95	0.48	149	0.68	206	0.64
39	1.34	96	0.64	150	0.83	207	0.40
40	2.26	97	0.29	151	0.65	208	0.93
41	2.96	98	0.19	152	0.60	209	0.64
42	25.75	99	0.72	153	0.30	210	0.64
43	3.18	100	2.25	155	1.35	211	0.43
44	5.61	101	0.60	156	0.65	212	0.61
45	0.42	102	0.35	157	0.22	213	0.34
46	0.29	103	0.17	158	0.54	214	2.73
47	0.29	104	0.09	159	0.49	215	1.19
48	0.07	105	0.30	160	0.39	216	0.78
50	0.82	106	0.48	161	0.54	217	0.65
51	1.09	107	0.28	162	0.65	218	0.41
52	0.44	108	0.33	163	0.93	219	0.65
53	0.26	109	0.22	164	1.26	220	0.45
54	0.79	110	0.33	165	0.76	221	0.74
55	1.43	111	0.24	167	0.71	222	0.86
56	2.47	112	0.41	168	0.81	223	1.08
57	1.41	113	0.50	169	0.30	224	0.63
58	0.65	114	0.77	170	0.70	225	0.60
59	0.10	115	0.47	171	0.85	226	0.68
60	0.60	116	0.45	172	0.80	227	0.66
61	0.14	117	0.47	173	0.43	228	4.08
62	0.35	118	0.15	174	0.57	229	1.26
63	0.13	119	0.55	175	0.62	230	0.57
64	0.70	120	0.25	176	0.67	231	0.71
65	0.09	121	0.32	177	0.52	232	0.33
66	0.33	122	0.25	178	0.60	233	2.28
67	0.60	123	0.60	179	0.52	234	0.51
69	12.28	124	0.85	181	1.06	235	0.90
70	0.67	125	0.43	182	0.66	236	1.62
71	0.31	126	0.63	183	0.72	237	1.50
72	0.29	127	0.68	184	0.91	238	0.63
73	0.26	128	0.56	185	0.49	239	0.22
74	0.44	129	0.31	186	1.12	240	2.84
75	0.97	130	0.29	187	0.57	241	4.15
76	0.65	131	0.82	188	0.65	242	1.78
77	0.16	132	0.40	189	0.35	243	2.81
78	0.23	133	0.23	190	1.82	244	0.80
79	0.31	134	0.14	191	0.84	245	0.60

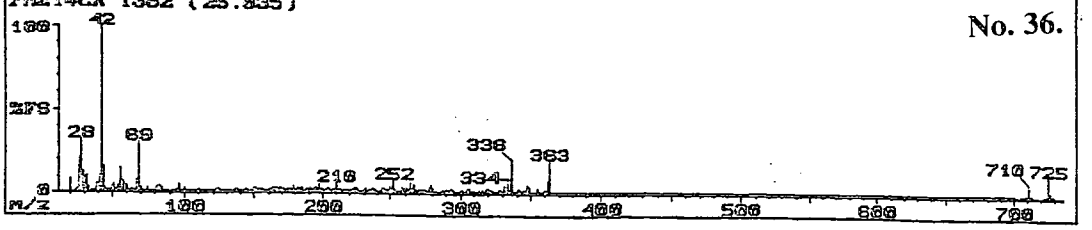
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
246	0.39	293	1.28	340	1.86	421	0.08
247	0.74	294	0.62	341	7.26	525	0.06
248	0.42	295	1.17	342	1.95	545	0.11
249	1.03	296	1.16	343	0.28	565	0.07
250	1.30	297	3.78	344	1.38	642	0.02
251	0.73	298	1.68	345	0.71	645	0.04
252	0.48	299	1.38	346	2.02	652	0.05
253	0.84	300	0.82	347	2.96	656	0.06
254	0.83	301	0.50	348	4.04	657	0.05
255	14.07	302	0.28	349	2.62	658	0.05
256	2.58	303	0.40	350	2.01	659	0.03
257	1.13	304	0.43	352	24.40	665	0.10
258	0.49	305	1.88	353	2.12	666	0.03
259	1.00	306	0.86	354	100.00	671	0.03
260	0.17	307	0.92	355	10.48	672	0.04
261	0.26	308	0.83	356	0.84	676	0.04
262	0.61	309	0.90	358	1.53	677	0.04
263	0.83	310	1.96	360	12.13	678	0.02
264	1.73	311	4.08	361	1.84	679	0.04
265	0.94	312	2.03	362	4.68	682	0.02
266	1.07	313	2.73	363	0.66	683	0.03
267	0.92	314	1.53	364	2.20	690	0.13
268	1.01	315	0.33	366	6.55	691	0.11
269	1.95	316	1.66	367	37.28	694	0.10
270	1.82	317	0.73	372	0.37	695	0.08
271	0.90	318	1.74	373	0.60	696	0.14
272	1.21	319	1.96	374	1.38	697	0.14
273	0.62	320	1.24	375	0.59	698	0.05
274	0.31	321	0.69	376	0.27	699	0.12
275	0.32	322	1.37	378	1.94	700	0.05
276	0.56	323	2.58	380	31.74	701	0.05
277	0.86	324	19.01	381	4.12	702	0.08
278	1.08	325	4.04	382	1.07	713	0.04
279	0.91	326	7.00	383	0.17	714	0.73
280	0.53	327	1.08	384	0.05	715	2.00
281	0.95	328	0.78	386	0.08	716	0.82
282	0.67	329	0.48	387	0.11	717	0.20
283	7.19	330	0.38	388	0.05	718	0.04
284	1.87	331	0.75	389	0.21	719	0.04
285	2.92	332	1.76	392	0.44	720	0.10
286	1.11	333	1.38	393	1.77	721	0.03
287	0.59	334	2.81	394	0.51	732	0.06
288	0.40	335	1.75	395	0.10	733	0.29
289	0.20	336	9.28	398	0.19	734	5.43
290	0.38	337	3.44	400	0.08	735	1.94
291	2.88	338	5.05	407	0.08	736	0.31
292	1.45	339	5.35	409	0.22	737	0.04



No. 35.

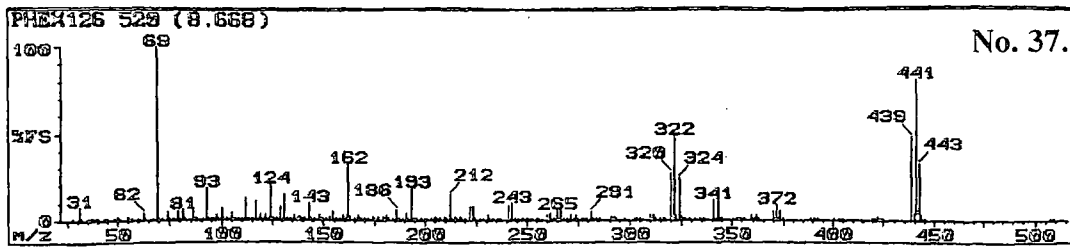
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.31	82	4.36	136	6.82	190	2.92	244	9.66	298	1.32	355	0.73	409	0.69
26	0.77	83	4.59	137	4.30	191	3.98	245	9.82	299	1.15	356	0.69	410	0.60
27	5.84	84	7.95	138	5.03	192	2.94	246	5.60	300	9.58	357	1.08	411	0.41
28	13.96	85	1.34	139	4.14	193	4.06	247	2.68	301	9.25	358	0.81	412	0.44
29	5.44	86	0.94	140	2.25	194	5.44	248	3.15	302	4.44	359	3.25	413	0.46
30	7.39	87	0.68	141	4.91	195	6.98	249	3.59	303	1.83	360	0.98	414	0.38
31	2.23	88	1.15	142	2.03	196	6.09	250	13.31	304	3.04	361	3.39	415	0.56
32	1.04	89	1.09	143	6.90	197	4.63	251	6.17	305	6.90	362	17.21	416	0.44
33	2.92	90	1.14	144	4.61	198	6.49	252	16.88	306	3.88	363	2.92	417	0.37
36	0.16	91	1.93	145	5.19	199	2.19	253	4.18	307	3.39	364	0.70	418	0.42
37	0.10	92	0.70	146	5.05	200	10.96	254	4.24	308	1.89	365	0.60	419	0.45
38	0.28	93	4.63	147	3.10	201	2.48	255	2.29	309	1.02	366	0.61	420	0.59
39	1.54	94	1.50	148	2.74	202	1.97	256	1.83	310	0.98	367	0.56	421	0.43
40	2.60	95	2.76	149	4.50	203	3.10	257	2.78	311	0.80	368	0.48	422	0.66
41	8.77	96	6.49	150	8.36	204	3.08	258	23.05	312	1.70	369	0.56	423	0.55
42	100.00	97	3.59	151	4.81	205	7.22	259	5.52	313	1.62	370	0.70	424	0.57
43	9.66	98	2.01	152	3.49	206	2.84	260	14.04	314	11.12	371	0.65	425	0.33
44	21.75	99	1.44	153	3.61	207	5.11	261	3.13	315	2.58	372	0.59	426	0.40
45	2.17	100	5.60	154	5.44	208	1.83	262	5.76	316	3.23	373	0.72	427	0.52
46	1.16	101	3.00	155	6.57	209	4.42	263	5.52	317	2.62	374	0.72	428	0.34
47	0.68	102	1.93	156	1.60	210	18.34	264	13.31	318	3.49	375	0.74	429	0.31
48	0.15	103	1.24	157	2.82	211	4.40	265	6.09	319	7.39	376	0.84	430	0.31
50	1.58	104	1.68	158	2.48	212	8.44	266	5.84	320	6.17	377	0.96	431	0.38
51	3.27	105	4.20	159	2.68	213	3.59	267	5.68	321	3.55	378	0.47	432	0.30
52	1.64	106	1.93	160	2.41	214	3.43	268	1.60	323	1.21	379	0.53	433	0.36
53	1.68	107	1.54	161	2.01	215	2.44	269	1.97	324	1.68	380	0.47	434	0.56
54	9.01	108	3.21	162	9.33	216	2.60	270	2.70	325	0.98	381	0.61	435	0.70
55	12.01	109	4.89	163	6.09	217	3.67	271	2.48	326	1.16	382	0.46	436	0.46
56	15.02	110	5.03	164	7.39	218	2.96	272	4.69	327	9.09	383	0.45	437	0.31
57	9.25	111	2.80	165	4.87	219	4.67	273	5.28	328	3.43	384	0.66	438	0.39
58	6.33	112	1.50	166	3.33	220	5.68	274	2.44	329	18.67	385	0.64	439	0.32
59	1.18	113	2.80	167	5.15	221	3.04	275	1.72	330	3.81	386	0.56	440	0.38
60	6.90	114	3.41	168	3.59	222	5.19	276	2.56	331	6.09	387	0.34	441	0.41
61	0.41	115	1.66	169	7.06	223	8.20	277	3.47	332	34.09	388	0.48	442	0.40
62	0.45	116	0.71	170	5.60	224	6.01	278	6.66	333	8.20	389	0.53	443	0.36
63	0.46	117	1.72	171	2.07	225	5.93	279	9.58	334	5.19	390	0.53	444	0.31
64	1.26	118	1.11	172	2.66	226	4.00	280	4.48	335	3.61	391	0.70	445	0.43
65	0.81	119	2.84	173	1.23	227	2.84	281	1.93	336	9.98	392	0.47	446	0.38
66	2.62	120	3.41	174	2.41	228	2.07	282	1.56	337	1.79	393	0.37	447	0.36
67	7.22	121	3.25	175	3.00	229	2.29	283	1.77	339	62.66	394	0.54	448	0.38
68	7.22	122	4.30	176	5.36	230	3.96	284	1.20	341	2.19	395	0.68	449	0.45
69	75.32	123	6.82	177	4.20	231	7.22	285	1.12	342	1.91	396	0.61	450	0.48
70	3.94	124	6.98	178	6.33	232	8.60	286	1.99	343	1.81	397	0.55	451	0.52
71	4.55	125	2.70	179	4.50	233	4.26	287	3.69	344	0.72	398	0.50	452	0.34
72	1.12	126	4.08	180	1.81	234	3.79	288	2.29	345	1.75	399	0.34	453	0.32
73	0.77	127	1.56	181	17.13	235	3.73	289	2.64	346	2.76	400	0.53	454	0.63
74	0.79	128	1.44	182	12.74	236	6.49	290	2.29	347	9.17	401	0.36	455	0.43
75	1.99	129	3.49	183	4.73	237	8.52	291	4.46	348	2.58	402	0.38	456	0.36
76	2.23	130	2.35	184	6.57	238	5.84	292	3.06	349	1.60	403	0.48	457	0.32
77	1.04	131	4.14	185	3.33	239	4.59	293	3.90	350	2.48	404	0.66	458	0.51
78	1.14	132	6.82	186	1.68	240	2.44	294	3.13	351	0.74	405	0.55	459	0.38
79	1.03	133	3.51	187	1.38	241	4.30	295	0.92	352	0.66	406	0.41	460	0.63
80	0.95	134	2.01	188	4.46	242	1.97	296	2.01	353	0.67	407	0.51	461	0.41
81	2.64	135	3.35	189	2.90	243	3.27	297	1.18	354	0.70	408	0.64	462	0.47

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
463	0.54	510	0.38	558	0.38	619	0.42
464	0.52	511	0.45	559	0.31	620	0.15
465	0.47	512	0.22	560	0.50	621	1.25
466	0.31	513	0.18	561	0.32	622	0.59
467	0.73	514	0.14	562	0.11	623	0.15
468	0.41	515	0.15	563	0.11	624	0.30
469	0.46	516	0.14	564	0.41	625	0.13
470	0.33	517	0.21	565	0.54	626	0.18
471	0.33	518	0.31	566	0.30	627	0.20
472	0.45	519	0.22	567	0.34	628	0.22
473	0.40	520	0.11	568	0.16	629	0.24
474	0.57	521	0.19	572	0.43	630	1.81
475	0.31	522	0.32	573	0.56	631	0.50
476	0.45	523	0.52	574	1.05	632	0.20
477	0.55	524	0.61	575	0.29	633	1.79
478	0.83	525	0.32	576	0.15	634	0.62
479	0.38	526	0.23	577	0.25	635	2.29
480	0.31	527	0.18	578	0.48	636	0.57
481	0.50	528	0.21	579	0.54	637	0.09
482	0.28	529	0.25	580	1.10	638	0.23
483	0.60	530	0.19	581	0.34	639	0.22
484	0.62	531	0.34	586	0.08	641	0.48
485	0.29	532	0.22	587	0.17	642	0.65
486	0.20	533	0.23	588	0.20	643	2.03
487	0.14	534	0.15	589	0.63	644	0.59
488	0.36	536	0.08	590	0.27	645	0.40
489	0.72	537	0.18	591	0.20	646	0.87
490	0.44	538	0.30	592	0.91	647	1.89
491	0.47	539	0.20	593	2.48	648	1.19
492	0.70	540	0.23	594	0.78	649	0.24
493	0.86	541	0.19	595	0.21	656	0.08
494	0.33	542	0.20	599	0.06	657	0.13
495	0.30	543	1.25	600	0.09	658	3.71
496	0.48	544	0.38	601	0.25	659	0.93
497	0.30	545	0.33	602	0.13	660	0.81
498	0.22	546	0.24	605	0.11	661	0.57
499	0.19	547	0.31	606	0.19	662	24.68
500	0.20	548	0.13	607	0.49	663	5.93
501	0.09	549	0.15	608	0.40	664	0.65
502	0.23	550	0.19	609	0.22	665	0.06
503	0.30	551	0.18	610	0.15	675	0.11
504	0.89	552	0.25	613	0.15	676	0.43
505	0.40	553	0.46	614	0.11	677	20.78
506	0.22	554	0.35	615	0.30	678	5.01
507	0.20	555	0.13	616	0.12	679	0.61
508	0.43	556	0.10	617	0.30		
509	0.29	557	0.14	618	0.38		



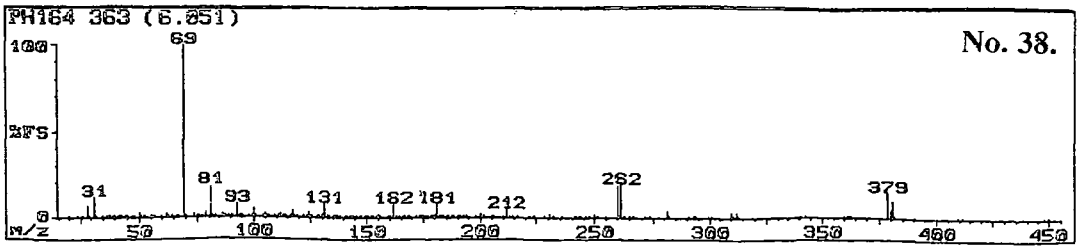
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	7.69	79	0.88	134	0.66	188	1.67	242	1.43	296	1.10	350	1.23	404	0.24
21	0.55	80	1.04	135	1.43	189	1.97	243	1.18	297	0.70	351	0.39	405	0.22
24	0.56	81	2.98	136	1.80	190	2.08	244	2.78	298	1.18	352	0.81	406	0.19
25	1.53	82	3.52	137	2.08	191	2.12	245	3.04	299	1.31	353	0.82	407	0.20
26	10.66	83	3.92	138	1.45	192	2.05	246	2.19	300	1.95	354	1.13	408	0.21
27	20.24	84	3.37	139	1.26	193	2.16	247	1.50	301	1.45	355	2.65	409	0.24
28	31.75	85	0.95	140	1.17	194	2.73	248	1.71	302	1.92	356	0.86	410	0.23
29	12.55	86	0.71	141	1.26	195	1.96	249	1.92	303	1.09	357	0.94	411	0.24
30	8.78	87	0.37	142	1.04	196	2.69	250	4.07	304	1.33	358	0.87	412	0.22
31	10.07	88	1.10	143	1.51	197	1.95	251	2.91	305	2.55	359	1.57	413	0.20
32	1.04	89	0.36	144	1.19	198	4.51	252	7.89	306	2.13	360	0.79	414	0.18
33	2.81	90	0.40	145	1.66	199	1.66	253	2.22	307	2.55	361	2.31	415	0.18
35	0.12	91	0.47	146	1.26	200	2.34	254	0.77	308	1.28	362	7.84	416	0.19
36	0.44	92	1.33	147	1.19	201	1.28	255	1.09	309	0.88	363	19.84	417	0.18
37	0.68	94	1.12	148	1.02	202	1.12	256	0.76	310	0.77	364	1.10	418	0.18
38	3.03	95	1.77	149	2.37	203	1.60	257	0.83	311	0.78	365	0.33	419	0.16
39	4.46	96	4.71	150	3.10	204	2.77	258	3.92	312	0.91	366	0.27	420	0.18
40	4.71	97	2.08	151	2.44	205	2.02	259	2.55	313	1.36	367	0.46	421	0.19
41	9.62	98	0.42	152	1.65	206	1.43	260	2.34	314	1.88	368	0.34	422	0.24
42	100.00	99	0.89	153	1.74	207	2.02	261	1.08	315	1.10	369	0.29	423	0.25
43	8.13	100	2.67	154	1.61	208	2.41	262	2.52	316	1.80	370	0.25	424	0.24
44	15.48	101	1.40	155	1.65	209	2.01	263	2.22	317	1.08	371	0.34	425	0.20
45	2.08	102	0.73	156	1.07	210	6.05	264	5.41	318	2.44	372	0.45	426	0.20
46	0.79	103	0.35	157	1.28	211	2.24	265	3.22	319	3.05	373	0.64	427	0.19
47	1.09	104	0.22	158	1.36	212	2.18	266	3.01	320	3.22	374	0.75	428	0.21
48	0.28	105	0.76	159	1.24	213	1.40	267	4.96	321	1.76	375	0.56	429	0.22
50	4.37	106	0.86	160	1.46	214	1.51	268	1.80	322	1.55	376	0.98	430	0.19
51	4.66	107	1.00	161	1.43	215	1.41	269	0.99	323	0.88	377	1.29	431	0.19
52	2.36	108	1.19	162	2.42	216	1.51	270	1.48	324	0.84	378	0.78	432	0.21
53	2.06	109	1.29	163	2.64	217	1.88	271	1.23	325	0.87	379	0.35	433	0.18
54	3.72	110	1.54	164	3.37	218	1.67	272	1.57	326	0.91	380	0.28	434	0.19
55	8.33	111	0.92	165	2.55	219	1.64	273	1.88	327	1.30	381	0.25	435	0.18
56	14.29	112	0.54	166	2.13	220	1.20	274	1.56	328	2.05	382	0.28	436	0.25
57	6.40	113	1.09	167	2.57	221	1.76	275	1.53	329	2.29	383	0.28	437	0.21
58	5.80	114	0.87	168	1.96	222	1.91	276	1.40	330	1.43	384	0.27	438	0.32
60	3.47	115	0.67	169	2.69	223	2.52	277	1.80	331	1.35	385	0.25	439	0.20
61	0.51	116	0.88	170	2.00	224	2.50	278	3.57	332	4.71	386	0.28	440	0.20
62	0.98	117	1.45	171	1.71	225	2.22	279	4.61	333	3.47	387	0.34	441	0.19
63	1.45	118	0.40	172	1.40	226	1.53	280	2.64	334	5.41	388	0.44	442	0.23
64	1.75	119	1.05	173	1.26	227	1.19	281	1.22	335	2.17	389	0.43	443	0.19
65	1.10	120	0.95	174	1.59	228	1.28	282	0.89	336	17.06	390	0.24	444	0.17
66	1.13	121	1.08	175	1.76	229	0.70	283	0.84	337	2.85	391	0.25	445	0.16
67	4.12	122	1.55	176	2.24	230	1.92	284	0.73	338	0.87	392	0.22	446	0.16
68	8.04	123	1.77	177	1.80	231	1.49	285	1.00	339	0.91	393	0.23	447	0.19
69	30.56	124	1.64	178	4.12	232	2.46	286	1.09	340	1.23	394	0.25	448	0.20
70	3.32	125	1.00	179	2.70	233	1.40	287	1.82	341	1.35	395	0.24	449	0.19
71	1.29	126	1.20	180	2.26	234	1.64	288	1.33	342	3.17	396	0.23	450	0.20
72	0.42	127	0.91	181	2.23	235	1.61	289	1.54	343	1.98	397	0.24	451	0.19
73	0.36	128	0.92	182	3.05	236	2.53	290	1.38	344	1.19	398	0.30	452	0.25
74	0.57	129	1.22	183	1.98	237	3.27	291	1.76	345	1.67	399	0.24	453	0.19
75	2.96	130	0.51	184	2.77	238	2.22	292	1.97	346	2.06	400	0.23	454	0.20
76	1.14	131	1.31	185	1.74	239	1.76	293	2.68	347	4.37	401	0.22	455	0.17
77	0.81	132	0.69	186	1.31	240	1.38	294	1.59	348	4.61	402	0.33	456	0.27
78	0.51	133	0.65	187	1.19	241	1.34	295	1.04	349	3.82	403	0.24	457	0.20

ass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
58	0.19	512	0.15	566	0.09	620	0.12	674	0.12	685	1.09	696	0.45	711	2.15
59	0.14	513	0.09	567	0.06	621	0.12	675	0.19	686	0.40	697	0.21	712	0.40
60	0.15	514	0.07	568	0.09	622	0.12	676	0.30	687	0.19	698	0.07	713	0.07
61	0.17	515	0.10	569	0.07	623	0.08	677	0.24	688	0.08	699	0.08	723	0.20
62	0.18	516	0.12	570	0.08	624	0.11	678	0.42	689	0.05	704	0.08	724	0.38
63	0.20	517	0.10	571	0.12	625	0.12	679	0.24	690	0.35	705	0.41	725	12.60
64	0.15	518	0.10	572	0.12	626	0.18	680	1.18	691	0.73	706	0.57	726	3.32
65	0.15	519	0.10	573	0.09	627	0.13	681	0.46	692	0.29	707	0.24	727	0.57
66	0.17	520	0.23	574	0.09	628	0.21	682	0.16	693	0.19	708	0.33	728	0.06
67	0.16	521	0.28	575	0.06	629	0.10	683	0.13	694	0.37	709	0.27		
68	0.15	522	0.22	576	0.09	630	0.06	684	0.13	695	0.52	710	5.41		
69	0.15	523	0.14	577	0.10	631	0.09								
70	0.15	524	0.14	578	0.12	632	0.06								
71	0.16	525	0.10	579	0.11	633	0.11								
72	0.15	526	0.17	580	0.11	634	0.09								
73	0.11	527	0.11	581	0.08	635	0.13								
74	0.15	528	0.09	582	0.09	636	0.12								
75	0.14	529	0.10	583	0.09	637	0.12								
76	0.16	530	0.10	584	0.09	638	0.09								
77	0.16	531	0.11	585	0.13	639	0.13								
78	0.18	532	0.10	586	0.16	640	0.20								
79	0.16	533	0.06	587	0.08	641	0.13								
80	0.15	534	0.09	588	0.07	642	0.12								
81	0.16	535	0.08	589	0.06	643	0.08								
82	0.17	536	0.23	590	0.09	644	0.06								
83	0.17	537	0.16	591	0.13	645	0.11								
84	0.14	538	0.12	592	0.17	646	0.10								
85	0.16	539	0.09	593	0.11	647	0.13								
86	0.23	540	0.13	594	0.10	648	0.21								
87	0.14	541	0.16	595	0.08	649	0.14								
88	0.15	542	0.15	596	0.09	650	0.14								
89	0.12	543	0.11	597	0.14	651	0.18								
90	0.15	544	0.08	598	0.23	652	0.13								
91	0.17	545	0.09	599	0.15	653	0.24								
92	0.17	546	0.07	600	0.12	654	0.16								
93	0.17	547	0.07	601	0.08	655	0.17								
94	0.13	548	0.07	602	0.08	656	0.18								
95	0.16	549	0.07	603	0.05	657	0.12								
96	0.17	550	0.09	604	0.08	658	0.06								
97	0.16	551	0.10	605	0.09	659	0.08								
98	0.17	552	0.12	606	0.16	660	0.13								
99	0.15	553	0.09	607	0.10	661	0.12								
00	0.14	554	0.10	608	0.08	662	0.20								
01	0.13	555	0.08	609	0.05	663	0.14								
02	0.16	556	0.17	610	0.12	664	0.13								
03	0.12	557	0.11	611	0.15	665	0.29								
04	0.16	558	0.08	612	0.22	666	0.30								
05	0.13	559	0.10	613	0.11	667	0.21								
06	0.23	560	0.09	614	0.06	668	0.12								
07	0.18	561	0.06	615	0.08	669	0.09								
08	0.16	562	0.05	616	0.09	670	0.32								
09	0.14	563	0.05	617	0.08	671	0.17								
10	0.15	564	0.05	618	0.08	672	0.11								
11	0.15	565	0.08	619	0.08	673	0.10								

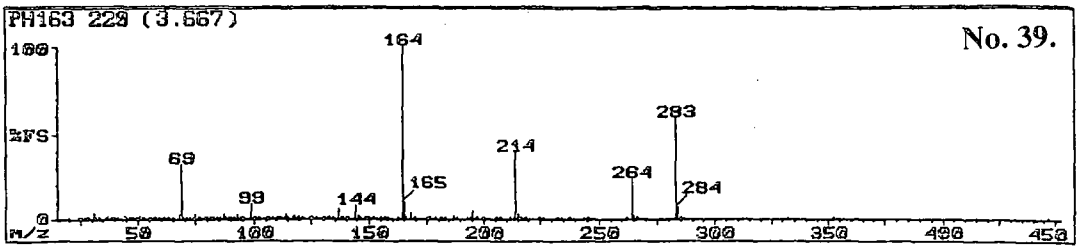


Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	0.14	117	10.50	193	18.54	274	3.23
31	7.53	118	0.55	194	1.26	275	0.25
32	0.19	119	2.55	195	0.02	277	0.07
35	0.02	120	0.48	196	0.22	279	0.04
36	0.37	122	2.89	198	1.32	281	5.06
37	0.04	123	0.19	200	1.43	282	0.41
38	0.31	124	20.07	201	0.18	284	0.26
39	0.03	125	1.23	203	0.56	286	0.20
40	0.02	126	0.06	205	1.89	291	1.81
43	0.20	127	0.08	206	0.06	292	0.13
44	0.05	129	7.78	208	0.06	293	1.72
45	0.02	131	14.46	210	2.17	294	0.14
48	0.14	132	0.51	211	0.06	298	0.02
50	1.72	134	0.43	212	14.46	303	0.03
51	0.06	136	3.36	213	1.12	304	0.03
55	1.61	137	0.20	215	2.05	305	0.03
56	0.03	138	1.73	216	0.08	310	2.76
57	0.22	139	0.11	217	2.42	311	0.20
60	0.19	141	0.74	218	0.13	312	2.72
62	3.40	143	9.35	220	0.07	313	0.21
63	0.17	144	0.59	222	7.40	315	0.07
67	0.66	146	1.16	223	0.39	317	0.08
69	100.00	148	2.93	224	7.70	320	27.04
70	1.18	149	0.13	225	0.56	321	1.69
72	0.02	150	1.13	227	0.64	322	48.30
74	4.55	151	0.18	229	0.69	323	3.27
75	0.17	153	2.37	231	3.32	324	24.15
76	1.12	155	4.38	232	0.13	325	1.57
77	0.04	156	0.22	234	0.27	326	0.06
79	5.23	158	0.15	236	1.13	327	0.15
80	0.32	160	3.02	237	0.06	329	0.08
81	5.40	161	0.44	241	8.80	332	0.04
82	0.35	162	32.14	242	0.54	334	0.09
86	4.89	163	2.05	243	9.31	336	0.03
87	0.23	165	1.25	244	0.64	341	11.22
88	0.08	167	3.02	246	0.30	342	0.94
91	0.92	168	0.17	248	0.33	343	10.63
93	18.03	169	0.34	249	0.02	344	0.95
94	0.77	170	0.09	250	0.23	345	0.05
95	0.05	172	0.80	251	0.10	351	0.66
96	0.17	174	2.07	253	0.95	352	0.05
98	2.93	175	0.18	255	1.11	353	1.23
99	0.13	177	2.02	256	0.05	354	0.10
100	6.76	179	2.42	260	2.44	355	0.61
101	0.30	180	0.09	261	0.13	356	0.05
103	0.09	181	2.60	262	3.87	360	2.93
105	4.08	182	0.15	263	0.28	361	0.28
106	0.24	184	0.80	265	5.57	362	2.85
107	0.24	186	5.82	266	0.29	363	0.29
108	0.09	187	0.33	267	5.57	370	4.72
110	0.54	188	0.09	268	0.32	371	0.33
112	12.24	189	0.07	270	0.09	372	9.06
113	0.70	191	4.04	272	3.36	373	0.73
115	0.23	192	0.09	273	0.22	374	4.51

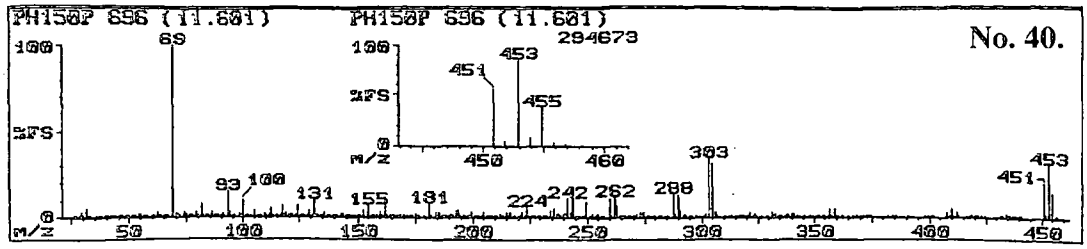
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
375	0.37	405	0.03	425	0.09	444	2.63
389	0.03	420	0.84	439	48.30	445	0.15
391	0.05	421	0.09	440	4.04	508	0.02
393	0.03	422	1.59	441	81.63	510	0.03
401	0.03	423	0.18	442	6.21		
403	0.05	424	0.79	443	32.65		



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.46	93	7.29	153	0.13	224	0.37
24	0.05	94	0.34	154	0.38	229	0.09
26	0.54	95	0.05	155	1.54	231	1.53
28	6.55	98	0.87	156	0.10	232	0.25
29	0.26	99	1.13	159	0.09	236	0.08
31	11.46	100	4.76	160	0.43	241	0.15
32	1.23	101	0.22	161	1.75	242	0.06
35	0.29	104	0.31	162	7.59	243	0.20
36	0.37	105	1.47	163	0.66	244	0.10
37	0.26	106	0.19	164	0.04	246	0.03
38	0.36	107	0.20	165	0.13	248	0.02
39	0.06	110	0.11	166	0.15	250	1.58
40	0.07	111	0.36	167	0.70	251	0.11
41	0.04	112	1.62	168	0.07	255	0.04
42	0.06	113	0.34	169	0.23	260	18.01
43	0.24	114	0.09	172	0.04	261	0.66
44	0.49	116	0.89	173	0.05	262	19.05
45	0.15	117	3.98	174	0.24	263	1.19
47	0.22	118	0.33	175	0.03	265	0.07
48	0.09	119	0.36	176	0.02	267	0.07
50	2.46	122	0.10	177	0.08	272	0.15
51	0.48	123	0.58	178	0.02	274	0.16
52	0.03	124	2.49	179	0.09	281	4.26
55	1.07	125	0.17	180	1.45	282	0.48
56	0.16	126	0.02	181	8.04	291	0.76
57	0.17	128	0.11	182	1.09	293	0.77
60	0.07	129	0.48	183	0.07	294	0.04
62	2.06	130	1.79	184	0.04	300	1.21
63	0.30	131	7.89	185	0.11	301	0.54
64	0.04	132	0.53	186	0.53	310	2.62
66	0.12	133	0.03	187	0.03	311	0.14
67	0.33	135	0.26	188	0.07	312	2.59
69	100.00	136	1.13	190	0.03	313	0.23
70	1.12	137	0.23	191	0.13	341	0.15
74	2.31	138	0.36	193	1.17	343	0.14
75	0.51	140	0.01	194	0.13	360	1.15
76	0.91	141	0.07	198	0.04	361	0.09
77	0.05	142	0.15	200	2.42	362	0.84
79	2.88	143	0.70	201	0.14	363	0.10
81	6.99	144	0.25	205	0.95	379	14.14
82	0.53	146	0.07	206	0.06	380	4.84
83	0.04	147	0.07	210	0.29	381	9.38
86	2.33	148	0.30	212	5.13	382	0.91
87	0.20	149	0.13	213	0.53	410	0.06
88	0.30	150	0.47	215	0.21	412	0.06
89	0.03	151	0.06	217	0.30	448	0.27
91	0.17	152	0.03	222	0.28	450	0.18

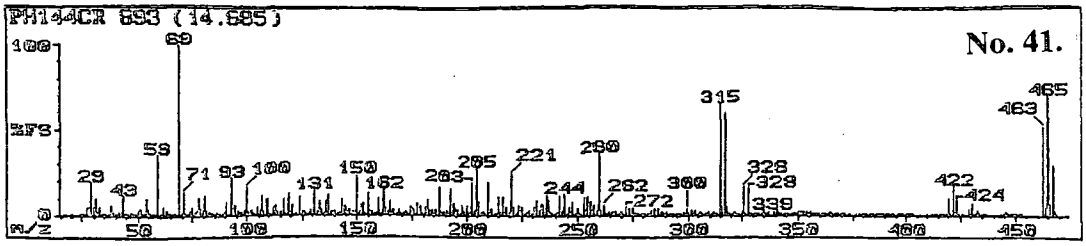


Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	73	0.06	124	0.94	187	1.62
24	0.01	74	1.17	125	0.26	188	0.10
25	0.02	75	2.63	126	1.22	193	0.09
26	0.05	76	0.83	127	0.09	194	0.56
27	0.04	77	0.04	130	0.38	195	4.40
28	1.09	79	0.66	131	0.34	196	0.34
29	0.02	80	0.98	132	0.10	197	0.02
31	4.36	81	0.33	133	0.20	199	0.44
32	0.34	82	0.36	134	0.01	200	0.05
33	0.03	83	0.03	137	5.39	205	0.02
36	0.08	84	0.06	138	0.36	206	0.16
37	1.79	86	0.53	139	0.01	207	0.05
38	0.20	87	3.21	140	0.04	212	0.13
39	0.09	88	0.24	141	0.01	214	38.49
40	0.18	89	0.03	144	7.48	215	3.25
41	0.01	90	0.25	145	1.50	216	0.13
44	1.93	91	0.02	146	0.22	217	0.12
45	0.16	93	2.75	148	0.16	218	0.26
46	0.21	94	0.86	149	1.08	219	0.04
47	0.02	95	0.40	150	0.30	224	0.17
48	0.07	96	0.06	151	0.06	225	0.03
49	0.32	99	8.84	152	0.05	226	0.13
50	1.14	100	1.25	155	0.15	232	0.23
51	1.80	101	0.08	156	0.43	233	0.36
52	0.77	102	0.02	157	0.09	234	0.03
53	0.04	105	0.36	158	0.01	237	0.58
55	0.51	106	1.15	162	0.29	238	0.04
56	1.08	107	0.12	164	100.00	244	1.37
57	0.33	108	0.02	165	9.50	245	0.34
58	0.12	110	0.04	166	0.36	246	0.02
59	0.04	111	0.08	168	3.45	262	0.03
61	0.52	112	0.15	169	0.30	264	22.86
62	0.22	113	0.85	170	0.04	265	1.95
63	0.56	114	2.84	175	1.20	266	0.08
64	1.41	115	0.16	176	1.30	283	58.55
65	0.05	117	1.43	177	0.11	284	6.33
68	2.71	118	1.59	179	0.03	285	0.24
69	31.91	119	0.43	181	0.02	332	0.02
70	0.87	120	0.12	182	0.51	352	0.06
71	0.36	121	0.01	183	0.08	447	0.03



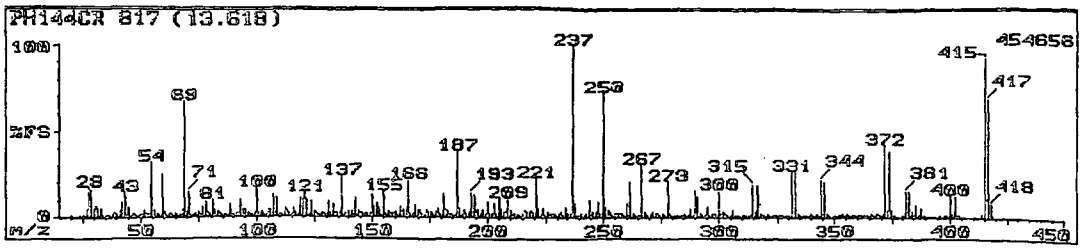
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.10	86	3.40	144	2.34	205	2.66
27	0.24	87	0.19	145	0.41	206	0.73
28	0.36	88	0.25	146	0.62	207	0.12
29	3.01	89	0.08	147	0.21	208	0.17
30	0.71	90	0.25	148	0.88	209	0.16
31	4.39	91	2.04	149	0.28	210	1.12
32	0.12	93	14.74	150	0.70	211	0.14
33	1.21	94	2.44	151	0.18	212	2.40
36	0.13	95	1.35	153	3.91	213	0.61
37	0.08	96	0.60	155	7.02	214	0.13
38	0.57	98	1.78	156	0.47	215	3.04
39	0.13	99	1.35	157	0.13	216	0.39
40	0.10	100	9.62	159	0.13	217	3.37
41	0.10	101	0.76	160	2.69	218	0.39
42	0.17	102	0.31	161	0.12	219	0.08
43	0.63	103	0.08	162	5.61	220	0.16
44	0.16	105	3.97	163	0.71	221	0.10
45	0.12	106	1.10	164	0.16	222	2.79
46	0.04	107	1.35	165	0.42	223	0.50
47	0.51	108	0.37	166	0.11	224	5.42
48	0.09	109	1.68	167	0.95	225	0.99
49	0.09	110	0.36	168	0.54	226	0.44
50	1.05	111	0.24	169	0.35	227	0.45
51	0.87	112	4.78	170	0.20	228	0.13
52	0.33	113	1.05	172	0.41	229	0.65
53	0.14	114	0.23	173	0.25	230	0.11
54	1.63	115	0.26	174	1.27	231	1.15
55	2.34	116	0.36	175	1.60	232	0.17
56	0.31	117	6.70	176	0.44	233	0.05
57	0.37	118	0.56	177	0.79	234	4.17
58	0.06	119	2.05	179	0.91	235	0.52
60	0.37	120	0.31	181	7.92	236	4.78
61	0.14	121	0.74	182	0.67	237	1.63
62	2.66	122	0.68	184	2.88	238	2.05
63	0.18	123	0.35	185	0.23	239	0.41
64	0.18	124	7.18	186	3.11	240	1.87
65	0.11	125	0.76	187	0.68	241	1.68
66	0.15	126	0.51	188	0.23	242	10.77
67	0.48	127	0.27	189	0.18	243	2.63
69	100.00	128	0.33	190	0.38	244	10.51
70	1.57	129	3.62	191	1.48	245	0.91
71	2.18	130	0.54	192	0.12	246	0.30
72	0.23	131	9.74	193	4.13	247	0.23
74	2.56	132	0.54	194	3.94	248	0.37
75	1.55	133	0.21	195	0.31	249	0.21
76	0.93	134	0.78	196	1.20	250	8.46
77	0.13	135	0.15	197	0.25	251	0.79
78	0.37	136	3.14	198	0.48	252	0.28
79	3.33	137	0.23	199	0.25	253	1.81
80	1.08	138	0.31	200	2.95	254	0.83
81	7.63	139	0.10	201	0.28	255	1.87
82	1.33	140	0.43	202	0.07	256	0.82
83	0.18	141	0.14	203	0.30	257	0.25
84	0.63	143	1.97	204	0.44	258	0.23

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
260	10.26	300	0.40	340	1.59	400	0.19
261	0.72	301	0.07	341	2.00	401	0.03
262	11.41	302	1.82	342	0.64	402	0.10
263	7.28	303	34.36	343	1.28	408	2.72
264	1.01	304	4.87	344	0.57	409	0.21
265	1.39	305	31.28	345	0.10	410	4.84
266	0.20	306	3.40	346	0.04	411	0.44
267	1.29	307	0.18	348	0.15	412	2.44
268	0.11	310	0.53	349	0.06	413	0.21
269	0.40	311	0.06	350	0.28	417	0.71
270	0.54	312	0.53	351	0.22	418	0.07
271	0.27	313	0.15	352	0.28	419	1.38
272	2.15	314	0.09	353	0.81	420	0.14
273	2.92	315	0.26	354	0.23	421	0.72
274	2.02	316	0.18	355	0.62	422	0.07
275	2.95	317	0.19	356	0.14	423	0.03
276	0.41	318	0.10	357	4.74	425	0.02
277	0.29	319	0.22	358	0.94	432	1.05
278	0.40	320	1.45	359	4.52	433	0.10
279	0.67	321	0.26	360	1.35	434	2.05
280	0.07	322	2.82	361	0.09	435	0.20
281	0.54	323	0.25	362	0.51	436	1.35
282	0.13	324	1.52	363	0.14	437	0.14
283	0.08	325	0.17	365	0.23	438	0.74
284	0.60	326	0.05	367	0.14	439	0.09
285	0.13	327	0.05	369	0.04	440	0.35
286	0.57	329	1.15	370	0.14	441	0.05
288	13.46	330	0.19	371	0.09	451	20.51
289	2.31	331	3.14	372	0.32	452	2.04
290	12.82	332	0.44	373	0.10	453	31.41
291	3.46	333	2.05	374	0.19	454	2.92
292	0.93	334	0.30	375	0.04	455	14.10
293	1.76	335	0.14	382	0.11	456	1.23
294	0.73	336	0.08	384	0.22	457	0.09
295	0.14	337	0.05	386	0.11		
296	0.05	338	1.66	391	0.03		
298	0.20	339	0.83	398	0.10		



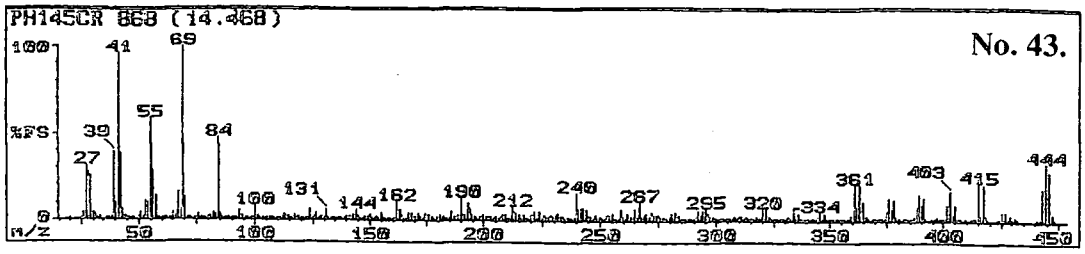
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.18	79	3.93	138	2.22	193	15.98
24	0.08	80	2.53	139	1.83	194	6.86
25	0.12	81	11.75	140	1.71	195	3.35
26	1.41	82	2.53	141	1.31	196	3.35
27	4.61	83	1.55	142	0.86	197	1.28
28	5.33	84	0.63	143	8.88	198	6.18
29	19.26	85	0.22	144	4.54	199	1.79
30	5.19	86	2.03	145	4.34	200	6.18
31	9.84	87	0.89	146	2.22	201	0.94
32	1.51	88	1.03	147	3.38	202	1.73
33	5.12	89	0.80	148	1.65	203	18.99
34	0.13	90	1.62	149	1.13	204	2.49
35	0.06	91	7.75	150	11.48	205	28.14
36	0.85	93	22.13	151	1.79	206	7.96
37	1.24	94	3.62	152	5.57	207	2.08
38	5.60	95	5.81	153	7.27	208	1.52
39	1.91	96	2.53	155	12.57	209	1.12
40	0.84	97	0.44	156	2.25	210	18.99
41	0.80	98	1.48	157	2.29	211	1.62
42	1.84	99	3.07	158	1.31	212	4.13
43	11.20	100	16.80	159	0.97	213	1.35
44	0.64	101	2.25	160	9.29	214	0.63
45	1.16	102	2.49	161	0.55	215	10.52
46	0.14	103	0.31	162	14.34	216	1.62
47	1.65	105	5.16	163	4.17	217	10.79
48	0.20	106	3.24	164	2.07	218	2.02
49	0.45	107	11.20	165	7.51	219	4.58
50	2.66	108	1.77	166	1.06	220	1.50
51	3.65	109	10.11	167	3.38	221	24.04
52	2.73	110	0.38	168	1.25	222	4.61
53	1.42	111	0.30	169	2.46	223	1.06
54	9.97	112	4.85	170	0.67	224	6.18
55	2.66	113	5.60	171	0.83	225	2.97
56	1.14	114	1.51	172	2.15	226	4.88
57	1.12	115	1.54	173	0.64	227	1.40
59	35.52	117	9.56	174	5.16	228	1.47
60	1.17	118	1.34	175	3.83	229	2.90
61	0.48	119	12.84	176	3.11	230	0.37
62	4.54	120	2.22	177	6.93	231	5.33
63	2.66	121	6.18	178	3.48	232	8.64
64	1.28	122	1.36	179	4.37	233	2.66
65	0.99	124	10.93	180	0.45	234	6.97
66	0.69	125	1.57	181	5.02	235	5.64
67	0.98	126	1.55	182	9.15	236	11.61
69	100.00	127	0.66	183	2.66	237	8.74
70	1.55	128	0.78	184	2.53	238	2.22
71	13.93	129	2.94	185	0.53	239	0.41
72	1.07	131	14.21	186	3.07	240	1.23
73	0.05	132	2.19	187	16.12	241	1.52
74	3.18	133	8.20	188	1.96	242	11.48
75	4.37	134	2.49	189	0.62	243	2.56
76	1.59	135	0.43	190	1.76	244	12.16
77	2.60	136	7.45	191	2.56	245	0.86
78	10.38	137	11.75	192	0.67	246	5.33

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
247	1.82	296	0.38	345	0.34	399	0.05
248	7.68	297	0.38	346	0.20	400	0.09
249	0.88	298	2.06	347	0.08	401	0.10
250	3.42	299	0.35	348	0.26	402	0.08
251	0.78	300	4.00	349	0.81	403	0.09
252	1.18	301	1.02	350	1.83	410	0.08
253	10.52	302	3.11	351	2.19	412	0.07
254	2.83	303	1.20	352	1.81	414	0.29
255	10.25	304	2.73	353	2.18	415	0.06
256	7.82	305	0.93	354	2.19	416	0.47
257	3.24	306	1.78	355	1.03	417	0.63
258	5.84	307	0.53	356	2.02	418	0.29
259	2.60	308	0.80	357	0.35	419	1.08
260	36.07	309	0.42	358	0.87	420	9.56
261	3.21	310	2.29	359	0.07	421	1.30
262	5.91	311	0.58	360	1.43	422	17.62
263	0.66	312	1.99	361	0.29	423	1.55
264	0.65	313	0.61	362	0.83	424	8.67
265	1.47	314	0.74	363	1.14	425	0.73
266	2.36	315	66.12	364	0.37	426	0.05
267	1.72	316	5.05	365	1.96	429	3.59
268	2.02	317	60.66	366	0.49	430	0.33
269	0.67	318	4.71	367	1.05	431	6.86
270	2.39	319	0.51	368	0.27	432	0.72
271	0.59	320	1.38	369	0.88	433	3.38
272	4.88	321	0.38	370	0.19	434	0.50
273	2.46	322	2.36	371	0.85	435	0.13
274	3.96	323	0.45	372	0.21	436	0.09
275	4.10	324	1.20	374	0.08	437	0.04
276	1.36	325	0.29	377	0.04	444	0.88
277	0.93	326	16.80	379	0.36	445	0.10
278	0.49	327	1.26	380	0.06	446	1.75
279	0.99	328	15.57	381	0.61	447	0.21
280	0.34	329	1.25	382	0.24	448	0.96
281	0.54	330	0.26	383	0.46	449	0.17
282	0.76	331	0.48	384	0.48	450	0.18
283	0.38	332	0.40	385	0.24	451	0.12
284	2.60	333	0.65	386	0.57	452	0.09
285	3.96	334	0.47	387	0.13	453	0.06
286	3.11	335	2.56	388	0.57	463	51.91
287	3.96	336	1.44	389	0.11	464	4.92
288	1.72	337	2.32	389	0.17	465	69.95
289	1.10	338	2.87	391	0.16	466	6.93
290	1.31	339	3.07	392	0.12	467	28.96
291	1.49	340	1.92	393	0.10	468	3.04
292	1.23	341	3.04	394	0.17	469	0.33
293	0.68	342	0.40	396	0.18		
294	1.24	343	0.47	397	0.02		
295	0.36	344	0.19	398	0.12		



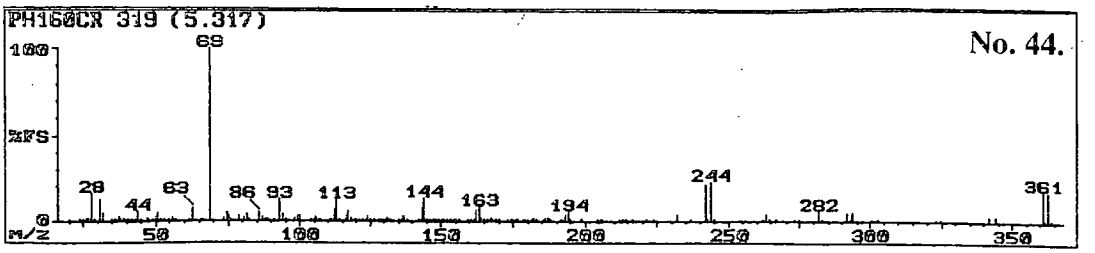
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.27	77	5.52	131	8.50	185	0.54
24	0.06	78	9.18	132	2.34	186	1.39
25	0.06	79	2.94	133	7.15	187	37.61
26	0.87	80	2.21	134	2.32	188	4.50
27	4.79	81	9.91	135	2.25	189	1.07
28	17.57	82	3.60	136	1.98	190	3.60
29	15.77	83	2.77	137	11.20	191	2.10
30	4.45	84	1.87	138	2.03	192	2.58
31	7.21	85	0.40	139	1.41	193	13.40
32	5.24	86	0.93	140	2.66	194	12.73
33	5.29	87	0.61	141	2.51	195	2.53
34	0.17	88	7.15	142	1.31	196	3.51
35	0.10	89	1.17	143	10.70	197	1.56
36	0.35	90	1.00	144	3.08	198	4.05
37	0.65	91	2.06	145	2.08	199	2.08
38	1.69	92	1.52	146	2.01	200	8.73
39	2.48	93	9.52	147	2.06	201	1.91
40	2.22	94	3.66	148	1.72	202	2.21
41	3.45	95	3.94	149	1.49	203	8.22
42	8.78	96	2.07	150	13.01	204	1.80
43	14.36	97	0.94	151	5.41	205	10.42
44	1.38	98	0.91	152	7.77	206	4.50
45	5.41	99	1.46	153	4.67	207	2.55
46	0.33	100	16.67	154	1.00	208	2.46
47	2.27	101	2.28	155	14.64	209	4.73
48	0.08	102	3.10	156	2.25	210	4.28
49	0.22	103	0.39	157	2.44	211	0.79
50	1.46	104	0.21	158	2.00	212	2.17
51	4.28	105	3.55	159	1.93	213	1.28
52	2.06	106	3.66	160	3.21	214	1.42
53	2.39	107	12.50	161	1.28	215	2.36
54	31.76	108	1.90	162	5.80	216	4.11
55	2.79	109	10.75	163	2.91	217	2.55
56	3.83	110	0.63	164	3.58	218	2.56
57	1.84	111	0.47	165	5.80	219	4.05
58	1.27	112	4.67	166	9.74	220	2.60
59	24.77	113	4.05	167	2.01	221	21.85
60	3.08	114	1.79	168	2.15	222	5.12
61	0.48	115	1.30	169	7.26	223	1.41
62	1.62	116	5.18	170	4.17	224	4.50
63	1.58	117	2.41	171	4.17	225	1.28
64	1.06	118	0.65	172	1.66	226	2.94
65	1.65	119	10.47	173	0.72	227	0.87
66	1.31	120	9.46	174	4.05	228	1.96
67	0.90	121	13.85	175	2.79	229	2.36
68	3.83	122	9.52	176	3.07	230	1.04
69	66.67	123	0.51	177	2.18	231	2.22
70	2.44	124	8.45	178	3.21	232	2.44
71	14.36	125	2.60	179	4.39	233	1.22
72	1.20	126	1.65	180	1.98	234	5.80
73	0.23	127	0.99	181	13.18	235	1.75
74	2.20	128	1.46	182	4.73	236	2.39
75	2.97	129	1.70	183	3.41	237	100.00
76	1.32	130	0.53	184	1.52	238	7.49

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
239	1.07	280	0.67	321	1.84	363	0.14
240	1.15	281	0.46	322	0.62	364	0.12
241	2.20	282	0.80	323	0.25	365	0.15
242	1.44	283	0.69	324	0.44	366	1.49
243	2.17	284	1.31	325	0.24	367	0.43
244	9.68	285	1.03	326	1.38	368	2.08
245	1.35	286	1.48	327	0.30	369	2.31
246	3.17	287	1.01	328	1.45	370	1.22
247	2.74	288	4.67	329	0.26	371	1.89
248	8.78	289	0.77	330	0.49	372	41.44
249	2.42	290	15.99	331	25.90	373	3.53
250	72.07	291	11.88	332	2.10	374	37.84
251	5.35	292	1.83	333	25.00	375	3.55
252	4.00	293	0.58	334	2.32	376	0.36
253	2.55	294	0.56	335	1.07	380	0.49
254	1.14	295	5.74	336	0.58	381	14.41
255	1.79	296	0.60	337	0.33	382	2.51
256	1.68	297	1.96	338	0.79	383	14.30
257	1.49	298	1.86	339	0.73	384	2.90
258	2.08	299	1.98	340	1.75	385	0.53
259	1.45	300	3.77	341	0.76	386	6.36
260	7.43	301	1.56	342	1.91	387	0.83
261	6.42	302	2.90	343	0.29	388	5.24
262	20.27	303	2.25	344	21.62	389	0.58
263	2.11	304	1.03	345	1.79	396	0.13
264	1.34	305	0.97	346	20.05	398	0.37
265	0.88	306	3.83	347	1.69	399	0.23
266	0.86	307	0.86	348	0.23	400	12.95
267	30.18	308	1.35	350	0.36	401	1.51
268	2.89	309	0.23	351	0.88	402	12.11
269	1.32	310	0.90	352	1.53	403	1.37
270	0.72	311	0.27	353	1.00	404	0.11
271	1.49	312	0.90	354	2.04	414	1.55
272	2.60	313	0.84	355	1.32	415	92.79
273	1.53	314	0.67	356	1.63	416	10.42
274	1.83	315	18.69	357	1.24	417	69.37
275	1.20	316	2.55	358	0.79	418	7.77
276	2.04	317	18.02	359	1.25	419	0.84
277	0.74	318	2.14	360	0.15		
278	20.05	319	0.45	361	1.15		
279	2.03	320	0.62	362	0.17		



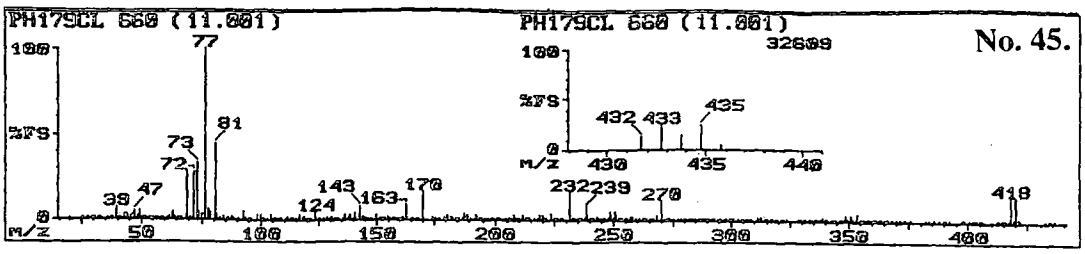
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.16	82	4.21	137	1.38	191	2.67
25	0.11	83	3.20	138	1.27	192	2.81
26	3.80	84	46.52	139	1.23	193	9.97
27	30.70	85	3.11	140	1.70	194	6.96
28	27.22	86	0.92	141	1.66	195	2.77
29	25.00	87	0.45	142	0.56	196	1.76
30	3.44	88	0.64	143	3.36	197	1.12
31	2.51	89	0.40	144	6.17	198	1.56
32	1.31	90	0.42	145	2.02	199	1.70
33	1.46	91	0.14	146	0.65	200	3.22
36	0.13	92	0.20	147	0.60	201	1.70
37	0.37	93	4.55	148	1.86	202	1.56
38	1.68	94	1.74	149	1.78	203	1.56
39	39.24	95	1.58	150	2.57	204	1.09
40	9.97	96	0.87	151	1.42	205	2.12
41	96.20	97	0.48	152	1.12	206	1.40
42	37.66	98	0.66	153	1.94	207	1.92
43	6.25	99	1.21	154	0.86	208	2.67
44	1.94	100	8.15	155	3.66	209	3.05
45	0.36	101	1.62	156	1.02	210	1.31
46	0.57	102	0.63	157	1.14	211	0.63
47	0.30	103	0.12	158	1.00	212	8.23
48	0.19	105	0.89	159	0.88	213	4.49
50	1.66	106	1.13	160	0.90	214	4.13
51	3.44	107	1.14	161	0.65	215	2.83
52	2.27	108	1.05	162	10.92	216	0.77
53	10.52	109	0.48	163	5.38	217	2.47
54	10.05	110	0.20	164	2.83	218	0.70
55	57.91	111	0.31	165	1.17	219	1.14
56	27.85	112	2.71	166	0.76	220	2.63
57	13.53	113	3.11	167	3.96	221	3.03
58	0.90	114	1.90	168	3.98	222	4.73
59	0.61	115	0.32	169	2.14	223	0.95
60	0.19	116	0.16	170	2.23	224	4.47
61	0.14	117	3.24	171	3.62	225	1.03
62	0.55	118	0.57	172	1.66	226	3.09
63	0.84	119	2.00	173	0.86	227	2.16
64	1.40	120	0.89	174	3.62	228	2.06
65	3.44	121	1.36	175	2.81	229	2.63
66	1.86	122	0.59	176	3.01	230	1.74
67	15.27	123	0.30	177	2.02	231	3.03
68	5.85	124	5.38	178	1.19	232	3.94
69	100.00	125	1.10	179	1.92	233	1.50
70	12.82	126	1.46	180	0.91	234	1.70
71	1.38	127	3.78	181	3.01	235	1.08
72	0.35	128	0.64	182	1.96	236	1.80
74	0.85	129	2.02	183	0.87	237	0.81
75	1.19	130	0.42	184	1.26	238	0.71
76	2.69	131	5.46	185	0.96	239	1.92
77	0.49	132	1.31	186	4.53	240	15.27
78	0.74	133	0.57	187	2.39	241	6.41
79	1.23	134	0.64	188	2.06	242	6.65
80	1.84	135	0.65	189	2.95	243	6.88
81	2.02	136	1.36	190	12.18	244	5.93

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
245	1.48	292	6.09	339	0.21	388	7.67
246	1.78	293	2.87	340	0.13	389	14.48
247	1.34	294	5.93	341	0.66	390	8.31
248	3.32	295	6.41	342	0.75	391	12.18
249	1.38	296	4.02	343	0.76	392	1.29
250	1.56	297	1.84	344	1.02	395	0.76
251	0.85	298	1.62	345	1.58	396	0.73
252	0.98	299	0.54	346	4.47	397	1.96
253	3.16	300	0.65	347	1.09	398	0.95
254	3.07	301	1.38	348	3.44	399	1.21
255	3.82	302	0.79	349	1.33	400	0.76
256	1.05	303	1.44	350	0.27	401	8.78
257	1.22	304	0.44	351	0.90	402	2.14
258	0.91	305	0.72	352	0.19	403	16.61
259	7.12	306	1.42	353	0.42	404	2.59
260	1.70	307	0.77	354	0.12	405	8.62
261	0.62	308	1.88	355	0.61	406	1.04
262	3.40	309	1.36	356	0.36	407	0.18
263	2.02	310	2.16	357	0.73	409	0.10
264	0.62	311	2.27	358	0.70	412	0.20
265	6.88	312	1.21	359	0.39	413	0.38
266	1.48	313	1.94	360	3.24	414	0.41
267	10.28	314	0.38	361	20.25	415	21.52
268	2.23	315	1.26	362	7.44	416	2.93
269	2.55	316	0.47	363	19.94	417	20.17
270	4.11	317	1.80	364	5.46	418	2.67
271	1.98	318	1.07	365	10.60	419	0.23
272	5.22	319	0.70	366	1.62	423	0.24
273	2.43	320	6.88	367	0.22	424	0.28
274	2.69	321	1.34	369	0.27	425	4.75
275	3.20	322	6.88	370	0.33	426	0.95
276	1.46	323	1.54	371	0.79	427	4.61
277	1.82	324	1.04	372	0.44	428	0.71
278	1.02	325	0.60	373	0.58	429	2.67
279	0.99	326	0.65	374	1.34	430	0.35
280	2.25	327	1.44	375	4.53	431	2.25
281	3.46	328	0.65	376	12.74	432	0.33
282	5.30	329	1.33	377	6.65	441	0.28
283	1.72	330	0.47	378	11.47	442	0.34
284	2.61	331	0.43	379	2.00	443	18.51
285	0.53	332	2.22	380	0.18	444	32.91
286	1.04	333	0.67	382	0.20	445	19.46
287	0.62	334	4.96	383	0.33	446	27.85
288	0.54	335	1.36	384	0.31	447	3.86
289	0.88	336	3.68	385	0.34	448	0.29
290	0.84	337	1.31	386	0.25		
291	1.84	338	0.40	387	2.22		



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.48	82	1.45	143	7.49	192	0.67
24	0.15	86	5.34	144	13.77	193	4.18
25	0.32	87	1.97	145	1.10	194	5.47
26	1.97	88	0.22	146	0.14	195	0.61
27	1.59	89	0.35	147	0.31	198	0.12
28	16.90	91	0.16	148	0.95	199	0.19
29	1.35	93	12.25	149	1.18	204	0.16
31	12.96	94	3.64	150	0.40	205	0.22
32	4.68	95	0.30	151	0.30	206	0.07
35	0.21	98	2.35	152	0.23	212	1.16
36	0.35	99	3.16	153	0.52	213	1.31
37	2.43	100	2.73	154	0.58	214	0.52
38	1.72	104	0.40	155	1.20	217	1.04
39	1.57	105	1.58	156	0.43	222	0.67
40	0.73	106	1.95	159	0.09	224	1.00
41	0.74	107	0.17	160	0.18	232	3.59
42	0.49	110	0.09	161	1.30	237	0.14
43	0.79	111	0.58	162	6.88	242	21.46
44	5.64	112	6.88	163	8.60	243	0.64
45	0.63	113	12.25	164	2.13	244	23.48
47	2.05	114	0.84	165	0.62	245	1.21
48	0.25	116	3.04	166	0.78	262	0.54
49	0.63	117	5.36	167	1.95	263	3.42
50	3.37	118	1.61	168	0.96	264	0.50
51	4.50	119	1.16	169	0.19	267	0.11
52	0.18	120	0.66	170	0.12	273	0.69
53	0.24	121	0.14	173	0.28	275	0.66
55	1.21	122	0.16	174	0.95	282	5.39
56	1.67	123	1.25	175	1.13	283	1.08
57	0.17	124	2.86	176	0.24	292	4.66
62	0.93	125	0.32	177	0.22	293	0.21
63	7.49	126	0.08	178	0.15	294	4.68
66	0.46	128	0.53	179	0.21	301	0.17
66	0.20	129	1.20	180	0.08	303	0.12
69	100.00	130	1.33	181	1.06	323	0.14
74	1.51	131	2.10	182	1.92	325	0.16
74	4.91	132	0.58	183	0.12	342	2.68
75	2.43	135	0.80	185	0.49	344	2.66
76	0.89	136	2.94	186	1.77	361	18.02
79	3.09	137	2.48	187	1.72	362	0.72
80	2.28	138	0.36	188	0.09	363	17.91
81	3.95	142	0.60	191	0.17	364	1.03

No. 45.

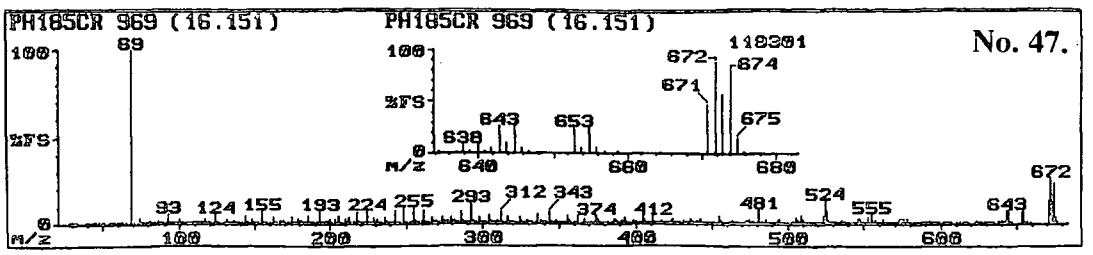


Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.05	86	0.98	152	0.33	215	0.82
25	0.01	87	0.85	153	0.81	217	1.37
26	0.21	88	1.65	154	0.14	218	0.56
27	1.05	89	0.85	155	2.35	219	2.90
28	1.43	91	0.76	156	0.44	220	3.26
29	1.36	93	4.63	157	0.64	221	0.34
30	0.07	94	0.81	158	0.66	222	0.81
31	1.26	95	0.88	159	0.61	224	3.99
32	0.19	96	0.25	160	0.15	225	0.59
33	0.14	99	2.50	161	0.84	226	0.14
36	0.01	100	2.74	162	2.07	227	0.75
37	0.09	101	1.10	163	8.66	228	0.14
38	0.10	102	0.36	165	0.27	229	0.66
39	7.07	103	0.14	166	0.35	232	16.22
40	0.29	105	2.47	167	0.75	233	1.01
42	0.65	106	1.35	168	0.50	234	0.22
43	2.65	107	1.15	170	16.34	235	0.12
43	3.32	108	0.97	174	2.01	236	0.33
44	2.26	109	0.93	175	0.72	237	0.31
45	2.32	111	0.37	176	0.28	238	1.20
47	2.90	112	1.59	177	0.75	239	7.47
47	5.06	113	1.36	179	1.95	240	0.47
48	1.90	114	0.24	180	0.19	241	0.62
49	4.45	115	0.19	181	2.44	242	1.07
50	0.61	117	2.56	182	1.85	243	1.98
51	1.33	118	0.19	183	0.40	244	1.34
52	0.26	119	1.84	184	0.75	245	0.21
53	1.32	120	1.36	185	0.38	246	0.13
54	0.45	121	0.11	186	1.21	247	0.21
55	0.75	122	0.24	187	0.45	248	0.78
56	0.45	124	5.27	188	4.18	249	4.60
57	1.12	125	0.90	189	2.77	250	1.04
58	1.12	126	0.59	190	1.43	251	5.09
59	0.25	127	0.44	192	0.83	252	0.51
61	0.80	129	1.95	193	2.44	253	0.19
62	1.75	130	0.25	194	1.07	254	0.55
63	3.48	131	2.32	195	0.20	255	0.58
64	0.54	132	0.91	196	0.09	256	0.50
65	0.42	133	0.37	198	1.27	257	1.86
66	0.24	134	0.38	199	0.59	258	2.16
67	0.67	136	1.39	200	0.47	259	0.45
69	27.07	137	2.62	201	0.86	261	0.37
70	0.77	138	0.52	202	0.14	262	0.33
72	27.44	139	3.17	203	0.41	263	0.37
73	31.71	140	0.31	205	1.22	264	0.32
74	3.69	141	4.18	206	0.42	265	1.01
75	3.20	143	7.44	207	0.22	266	0.40
77	100.00	144	1.65	208	2.68	267	1.08
78	6.16	145	0.82	209	0.26	268	3.11
79	3.78	146	0.21	210	0.26	270	11.34
81	43.41	147	0.55	211	0.26	271	1.18
82	2.84	148	1.14	212	3.29	272	0.69
83	1.25	150	2.84	213	1.00	273	0.11
85	1.69	151	0.76	214	0.39	274	0.85

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
275	0.07	309	0.04	347	0.10	390	0.28
277	1.33	311	1.95	348	0.21	391	0.03
279	0.24	312	0.18	349	2.44	392	0.06
280	0.92	313	1.89	350	0.41	398	0.04
281	0.24	315	0.07	351	2.53	399	0.06
282	0.96	316	0.03	352	0.29	401	0.05
283	0.12	317	0.16	354	3.90	402	0.02
284	0.37	318	0.38	355	0.49	403	0.05
285	1.11	319	0.33	356	0.14	404	0.07
286	0.25	320	0.41	357	0.48	405	0.06
287	0.43	322	0.24	358	0.04	406	0.07
288	0.27	323	0.04	359	0.45	412	0.24
289	0.43	324	0.52	360	0.17	413	0.07
290	0.29	329	0.31	361	0.05	414	0.30
291	0.88	330	0.14	362	0.17	415	0.05
292	0.12	331	0.34	363	0.08	416	0.28
293	0.84	332	0.16	364	0.10	417	0.40
295	0.05	333	0.04	365	0.03	418	14.88
296	0.19	334	0.20	366	0.08	419	2.35
297	0.05	335	0.22	367	0.02	420	14.27
298	0.73	336	0.18	368	0.06	421	2.04
299	1.00	337	1.18	370	0.07	422	0.55
300	0.85	338	0.26	372	0.02	432	0.12
301	0.96	339	1.68	374	0.01	433	0.25
303	0.08	340	0.35	376	0.01	434	0.15
304	0.28	341	0.13	382	0.02	435	0.24
305	0.09	343	0.12	384	0.04	436	0.04
306	0.08	344	0.03	386	0.05		
307	0.03	345	0.12	388	0.23		

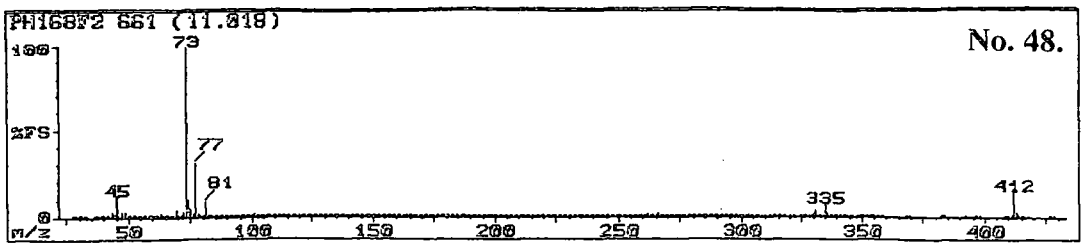
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	0.82	147	0.33	248	4.81	360	0.32
31	0.37	148	1.87	249	0.36	362	1.63
32	0.42	149	0.23	250	0.40	363	0.16
40	0.12	150	0.26	253	0.42	367	1.12
41	0.06	153	0.47	255	8.33	372	0.84
43	0.06	155	3.63	256	0.89	374	4.81
44	0.36	156	0.26	257	0.08	375	0.63
50	0.82	160	0.66	260	2.50	379	0.17
55	0.47	162	2.59	262	3.50	381	0.85
57	0.11	163	0.16	263	0.29	384	0.33
62	0.13	165	0.66	265	0.70	386	0.95
67	0.11	167	2.32	267	1.76	391	0.19
69	100.00	168	0.18	268	0.10	393	7.83
74	0.78	169	0.55	269	0.35	394	0.61
76	0.57	172	0.88	270	0.36	398	0.54
79	0.48	174	1.01	272	0.84	403	1.42
81	0.77	177	0.57	274	3.41	404	0.16
82	0.09	179	2.03	275	0.41	405	2.03
86	1.81	181	2.08	278	0.09	406	0.28
87	0.05	182	0.12	279	2.80	412	1.35
93	3.65	184	0.29	280	0.32	415	0.09
94	0.13	186	3.68	281	0.93	417	1.51
98	0.17	187	0.57	284	0.18	422	1.65
98	0.37	188	0.31	286	3.70	423	0.17
100	0.46	191	0.53	287	0.37	424	1.34
100	1.15	193	2.64	291	0.23	425	0.45
103	0.07	194	0.21	293	7.04	431	0.67
104	0.29	198	1.08	294	0.81	434	0.22
105	1.03	200	1.54	298	1.85	436	1.58
106	0.08	203	0.83	299	0.16	437	0.22
107	0.07	205	3.23	300	0.11	441	4.08
110	0.25	207	0.34	303	0.17	442	0.42
111	0.11	210	2.16	305	3.04	443	9.20
112	0.33	211	2.12	306	0.40	444	1.20
113	0.04	212	3.66	310	1.56	446	0.64
114	0.21	215	0.84	312	1.47	448	0.68
116	0.76	217	2.68	315	0.31	449	0.08
117	4.17	219	0.18	317	1.78	453	1.87
118	0.25	222	0.70	322	0.28	454	0.23
119	0.54	224	6.47	324	6.61	455	2.05
122	0.14	225	0.54	325	0.65	456	0.25
124	2.17	227	0.23	329	0.78	462	2.68
125	0.16	229	2.42	330	0.62	463	0.51
129	1.04	230	0.13	331	0.77	467	0.26
131	1.65	231	2.14	336	1.10	472	1.54
132	0.06	234	0.34	337	0.17	473	0.15
134	0.07	236	3.04	341	0.15	474	1.81
136	1.51	237	0.26	343	8.26	475	0.26
137	0.09	238	0.24	344	0.75	477	0.05
138	0.31	241	1.07	348	0.92	479	0.07
140	0.13	242	0.13	350	1.10	481	0.55
141	0.88	243	1.90	353	0.67	486	2.80
143	1.87	244	0.18	355	3.48	487	0.42
144	0.10	246	0.23	356	0.40	491	1.81

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
492	0.25	522	0.70	546	0.15	593	1.63
493	3.48	523	0.11	548	0.15	594	0.29
494	0.52	524	0.67	562	0.49	641	4.81
496	0.29	525	0.09	563	0.11	642	0.79
498	0.29	531	0.57	572	0.58	643	4.81
503	0.50	532	0.10	573	0.10	644	0.82
504	0.08	536	0.16	574	0.59	660	18.97
505	1.03	541	7.40	581	3.23	661	3.20
506	0.13	542	1.06	582	0.66	662	18.97
512	4.47	543	7.33	591	1.56	663	3.20
513	0.74	544	1.07	592	0.27	664	0.23



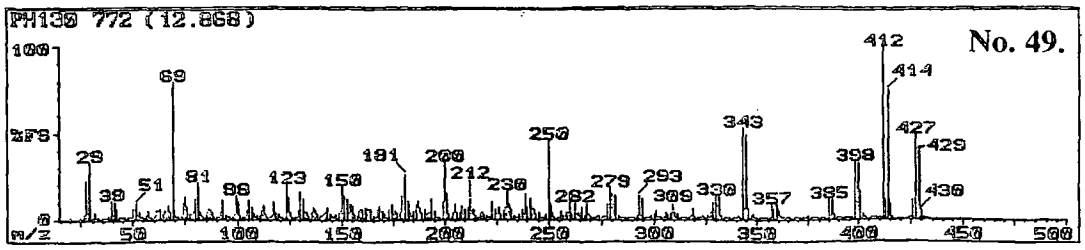
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel In
28	0.41	105	1.34	172	1.02	236	4.31	299	0.86	366	0.19	423	1.39	478	0.1
29	0.45	106	0.32	174	4.06	237	2.20	300	0.48	367	2.67	424	2.33	479	1.0
30	0.17	107	0.24	175	0.60	238	1.13	301	0.22	368	0.76	425	2.94	480	0.1
31	0.43	108	0.14	176	0.40	239	0.31	302	0.19	369	0.58	426	0.80	481	8.6
32	0.19	109	0.19	177	0.80	240	0.15	303	0.63	370	0.20	427	1.22	482	1.1
33	0.13	110	0.24	178	0.27	241	1.33	305	5.00	371	0.75	428	0.37	483	0.1
39	0.06	111	0.28	179	3.23	242	0.25	306	1.81	372	1.23	429	0.70	484	1.9
40	0.05	112	0.73	180	0.32	243	8.06	307	0.57	373	0.12	431	2.42	485	0.6
41	0.07	113	0.32	181	1.59	244	1.05	308	0.78	374	5.19	432	0.37	486	2.8
43	0.48	114	0.33	182	0.65	245	0.13	309	0.21	375	3.11	433	0.26	487	0.9
44	0.24	115	0.15	183	0.54	246	0.36	310	2.08	376	0.77	434	1.23	488	0.6
45	0.13	116	1.14	184	0.74	248	9.25	311	0.36	377	0.83	435	1.38	489	0.2
47	0.39	117	3.19	186	5.13	249	1.05	312	6.94	378	0.20	436	3.36	490	0.3
50	0.86	118	0.39	187	1.39	250	1.03	313	1.00	379	0.82	437	1.67	491	1.0
51	0.48	119	1.09	188	1.22	251	0.27	315	0.47	380	0.22	438	0.70	492	0.1
54	0.30	120	0.16	189	0.60	253	0.71	317	3.78	381	1.27	439	0.31	493	1.5
55	0.33	122	0.19	191	1.03	254	0.22	318	1.00	382	0.18	440	0.65	494	2.4
56	0.17	124	1.61	192	0.38	255	9.44	319	0.65	384	0.68	441	1.80	495	0.7
57	0.23	124	5.69	193	7.44	256	1.83	320	0.27	385	0.56	442	0.29	496	0.6
60	0.58	125	0.45	194	0.96	257	1.16	321	0.40	386	3.00	443	2.63	497	0.2
61	0.03	126	0.17	196	0.48	258	0.54	322	0.88	387	1.48	444	1.19	498	0.5
62	0.15	129	1.06	196	0.22	260	1.92	324	3.41	388	0.68	445	0.52	499	0.0
63	0.07	130	0.75	198	1.91	261	0.75	325	2.50	389	0.42	446	0.46	500	0.2
65	0.25	131	2.44	199	0.59	262	7.31	326	0.91	390	0.62	447	0.19	502	0.3
67	0.14	132	0.20	200	2.72	263	0.86	327	0.78	391	1.92	448	0.77	503	1.5
69	100.00	133	0.23	201	0.44	264	0.41	329	1.78	392	0.26	449	0.15	504	0.6
71	0.17	134	0.24	203	2.59	265	1.06	330	0.55	393	3.81	450	0.51	505	3.5
73	0.11	136	1.75	204	0.50	267	4.06	331	0.85	394	1.17	451	0.09	506	1.2
74	4.06	137	0.58	205	4.50	268	1.27	332	0.66	395	0.52	452	0.25	507	1.8
75	0.58	138	0.65	206	1.41	269	1.73	334	0.93	396	0.61	453	1.02	508	0.8
76	1.17	139	0.26	207	1.28	270	0.34	336	6.25	398	1.67	454	0.64	509	4.3
79	0.72	141	1.23	208	0.79	271	0.50	337	2.28	399	0.57	455	4.75	510	2.1
80	0.13	143	5.00	210	2.97	272	0.90	339	0.49	400	0.45	456	1.92	511	0.3
81	1.64	144	0.46	211	0.73	274	3.78	340	0.43	401	0.34	457	1.20	512	1.3
82	0.21	145	0.13	212	3.78	275	1.80	341	1.00	403	1.25	458	1.13	513	0.9
83	0.23	146	0.36	213	0.79	276	1.17	343	6.69	404	1.22	459	1.28	514	0.3
84	0.22	148	2.94	215	1.66	277	0.73	344	1.11	405	4.50	460	0.71	515	0.3
86	1.47	149	0.43	217	7.00	277	1.69	345	0.25	406	2.83	461	0.17	516	0.3
87	0.20	150	1.22	218	2.58	279	4.13	346	0.25	407	1.11	462	0.68	517	0.3
88	0.14	151	0.17	219	1.61	280	0.95	348	2.28	408	0.91	463	1.77	518	0.1
89	0.08	153	1.03	220	0.32	281	1.55	349	0.34	409	0.45	464	0.38	519	0.7
92	0.34	155	7.56	221	0.18	282	1.13	350	0.50	410	0.61	465	0.94	520	0.1
92	3.67	156	0.75	222	1.45	284	1.38	351	0.30	411	0.10	466	0.50	521	0.6
93	5.50	157	0.23	223	0.29	286	6.75	352	0.20	412	5.00	467	1.31	522	0.2
94	0.41	158	0.25	224	7.31	287	2.33	353	0.97	413	0.49	468	0.80	523	4.8
95	0.24	160	0.92	225	1.06	288	0.87	354	0.55	414	0.19	469	0.79	524	13.8
96	0.11	162	3.64	226	0.42	289	0.57	355	4.63	415	1.16	470	0.13	525	7.5
97	0.19	163	0.81	227	1.14	290	0.35	356	2.00	416	0.41	471	0.54	526	1.8
98	0.40	164	0.30	229	3.95	291	0.94	357	1.16	417	2.25	472	0.63	527	0.9
99	1.38	165	0.73	230	1.20	293	11.38	358	0.75	418	0.71	473	1.48	528	0.6
100	2.44	167	2.31	231	2.86	294	1.50	360	0.86	419	0.87	474	1.66	529	0.2
102	0.84	168	1.03	232	0.77	295	0.25	361	0.17	420	0.18	475	2.69	530	0.3
103	0.12	169	1.53	233	0.21	296	0.13	362	4.56	421	0.75	476	1.14	531	0.3
104	0.48	170	0.54	234	1.00	298	3.80	365	0.73	422	1.20	477	1.56	532	0.0

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
533	0.77	561	0.19	591	0.21	630	0.06
534	0.79	562	0.82	592	0.08	631	0.38
535	1.47	563	3.09	593	1.69	632	0.06
536	1.11	564	0.71	594	0.41	633	0.12
537	0.80	565	0.38	595	0.04	635	0.08
538	0.61	566	0.11	596	0.09	638	2.30
539	0.14	567	0.13	597	0.12	639	0.43
540	0.34	569	0.51	598	0.12	640	2.23
541	0.65	570	0.11	599	0.12	641	0.59
542	0.12	571	0.55	602	0.95	642	1.50
543	0.78	572	0.32	603	0.77	643	7.88
544	0.25	573	1.81	604	1.27	644	2.77
545	1.03	574	3.33	605	0.80	645	7.81
546	2.78	575	2.58	606	0.35	646	1.31
547	0.48	576	2.86	607	0.17	647	0.07
548	2.53	577	1.06	610	0.11	653	7.00
549	0.42	578	2.58	612	0.10	654	1.44
550	0.69	579	0.57	615	0.39	655	7.00
551	0.15	580	0.08	616	0.07	656	1.42
552	0.34	581	0.14	617	0.39	657	0.32
553	4.13	583	0.96	618	0.07	659	0.17
554	1.19	584	0.71	622	0.96	671	13.75
555	5.75	585	1.03	623	0.55	672	25.75
556	1.33	586	0.76	624	1.80	673	16.50
557	1.58	587	0.16	625	0.84	674	23.50
558	0.39	588	0.57	626	0.89	675	4.13
559	0.62	589	0.08	627	0.34	676	0.41
560	0.95	590	0.52	629	0.41		



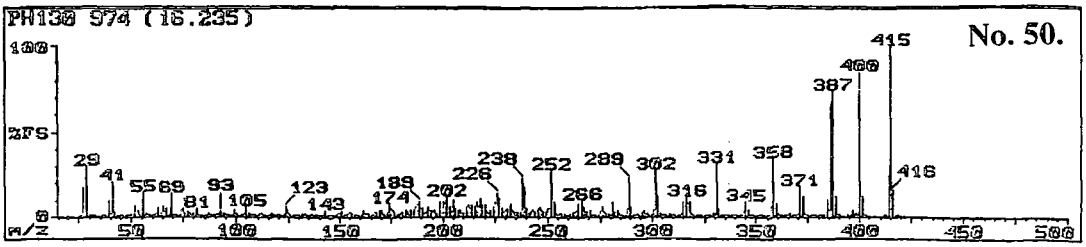
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
27	0.04	83	0.54	137	0.21	191	0.08
28	0.34	84	0.29	138	0.17	192	0.08
29	0.12	85	0.43	139	0.28	193	0.29
30	0.01	86	0.20	140	0.22	194	0.25
31	0.08	87	0.77	141	0.11	195	0.22
32	0.22	88	0.68	142	0.08	196	0.37
33	0.02	89	0.61	143	0.49	197	0.32
36	0.02	90	0.17	144	0.26	198	0.15
37	0.02	91	0.34	145	0.58	199	0.11
38	0.03	92	0.13	146	0.25	200	0.18
39	0.37	93	0.53	147	0.30	201	0.10
40	0.07	94	0.21	148	0.13	202	0.11
41	0.09	95	0.31	149	0.23	203	0.06
42	0.25	96	0.14	150	0.27	204	0.07
43	3.08	97	0.13	151	0.19	205	0.07
44	1.70	98	0.19	152	0.12	206	0.07
45	11.75	99	0.80	153	0.25	207	0.09
46	0.82	100	0.61	154	0.10	208	0.09
47	3.10	101	1.46	155	0.22	209	0.08
48	0.18	102	0.38	156	0.13	210	0.52
49	3.31	103	0.18	157	0.34	211	0.15
50	0.32	104	0.41	158	0.17	212	0.16
51	0.57	105	0.47	159	0.20	213	0.21
52	0.13	106	0.34	160	0.10	214	0.18
53	0.48	107	0.22	161	0.21	215	0.16
54	0.31	108	0.26	162	0.28	216	0.41
55	0.57	109	0.21	163	0.72	217	0.13
56	0.26	110	0.09	164	0.20	218	0.08
57	1.01	111	0.12	165	0.20	219	0.14
58	1.25	112	0.29	166	0.74	220	0.23
59	0.89	113	0.48	167	0.18	221	0.10
60	0.11	114	0.17	168	0.14	222	0.07
61	0.18	115	0.23	169	0.81	223	0.09
62	0.51	116	0.13	170	1.08	224	0.62
63	2.08	117	0.31	171	0.20	225	0.13
64	0.25	118	0.48	172	0.06	226	0.20
65	0.18	119	0.29	173	0.06	227	0.18
66	0.10	120	0.25	174	0.23	228	0.20
67	0.25	121	0.12	175	0.21	229	0.12
68	0.11	122	0.18	176	0.44	230	0.12
69	4.01	123	0.22	177	0.13	231	0.26
70	0.47	124	0.48	178	0.08	232	0.63
71	0.54	125	0.36	179	0.24	233	0.15
72	2.66	126	0.15	180	0.24	234	0.19
73	100.00	127	0.17	181	0.27	235	0.10
74	10.07	128	0.08	182	0.15	236	0.09
75	5.15	129	0.08	183	0.13	237	0.04
76	1.80	130	0.14	184	0.29	238	0.10
77	31.34	131	0.23	185	0.33	239	0.05
78	2.43	132	0.26	186	0.21	240	0.09
79	1.27	133	0.27	187	0.15	241	0.07
80	0.47	134	0.25	188	0.20	242	0.27
81	8.96	135	0.17	189	0.28	243	0.13
82	0.75	136	0.36	190	0.24	244	0.08

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
245	0.12	278	0.06	314	0.57	350	0.38
246	0.72	279	0.13	315	0.21	351	1.03
247	0.63	280	0.31	316	0.83	352	0.25
248	0.18	281	0.23	317	0.17	353	0.19
249	0.06	282	0.12	318	0.11	354	1.39
250	0.12	283	0.06	320	0.44	355	0.24
251	0.19	284	0.11	321	0.11	356	0.07
252	0.07	285	0.21	322	0.05	357	0.02
253	0.05	286	0.07	324	0.15	358	0.02
254	0.28	287	0.02	325	0.04	368	0.04
255	0.12	288	0.11	326	0.06	369	0.01
256	0.06	289	0.02	327	0.24	382	0.09
257	0.06	290	0.05	328	0.24	383	0.03
258	0.33	291	0.02	329	0.14	384	0.04
259	0.13	292	0.06	330	1.63	392	0.03
260	0.24	293	0.28	331	4.34	396	0.62
261	0.32	294	0.10	332	0.88	397	0.13
262	1.49	295	0.04	333	0.27	398	0.06
263	0.35	296	0.11	334	1.25	408	0.24
264	0.26	297	0.05	335	6.34	409	0.05
265	0.46	298	0.02	336	2.24	410	0.20
266	1.66	299	0.01	337	0.49	411	0.14
267	0.48	300	0.10	338	0.11	412	14.37
268	0.14	301	0.06	339	0.17	413	3.15
269	0.09	302	0.06	340	0.11	414	1.09
270	0.24	303	0.03	341	0.10	415	0.17
271	0.09	304	0.03	342	0.18	416	0.03
272	0.08	306	0.09	343	1.20	426	0.21
273	0.04	307	0.03	344	0.30	427	0.07
274	0.17	308	0.03	345	0.12	428	0.03
275	0.12	310	0.03	346	0.03		
276	0.09	312	0.10	348	0.38		
277	0.16	313	0.10	349	0.13		



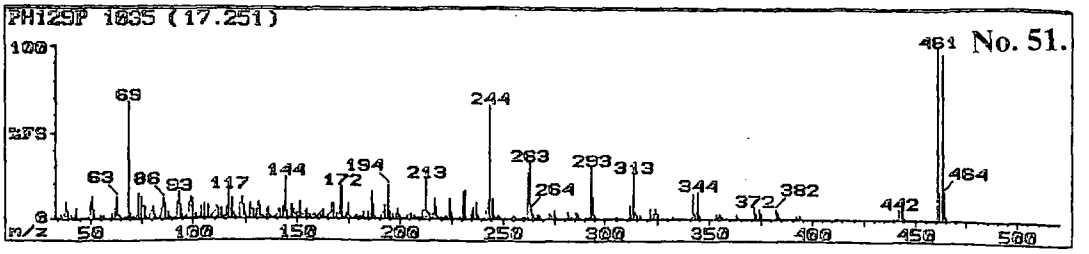
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.11	79	3.58	134	1.94	188	6.38
25	0.11	80	11.23	135	4.34	189	3.94
26	2.74	81	21.12	136	6.58	190	6.12
27	21.93	82	3.68	137	5.25	191	2.44
28	4.28	83	1.76	138	2.84	192	3.84
29	33.42	84	0.56	139	1.99	193	4.21
30	0.89	85	3.44	140	2.03	194	11.23
31	3.78	86	5.75	141	2.61	195	4.98
32	0.70	87	4.95	142	3.78	196	0.79
33	0.24	88	4.01	143	7.12	197	0.39
35	0.04	89	1.04	144	3.38	198	1.38
36	0.18	90	0.48	145	2.00	199	9.63
37	0.64	91	0.78	146	1.28	200	33.16
38	1.74	92	4.28	147	2.44	201	14.30
39	10.83	93	10.56	148	3.78	202	3.07
40	1.99	94	2.27	149	5.08	203	1.45
41	9.49	95	1.15	150	18.98	204	3.48
42	6.08	96	0.67	151	13.90	205	8.96
43	0.32	97	0.37	152	11.76	206	4.28
44	0.18	98	3.07	153	4.01	207	4.24
45	0.19	99	13.90	154	8.46	208	7.65
46	0.28	100	9.63	155	8.09	209	3.28
47	0.31	101	2.03	156	2.97	210	6.28
48	0.08	102	0.57	157	1.86	211	6.38
49	0.53	103	1.24	158	5.15	212	12.03
50	5.98	104	5.05	159	5.75	213	5.31
51	8.56	105	10.29	160	5.75	214	5.78
52	2.11	106	6.92	161	7.19	215	2.11
53	3.91	107	2.91	162	6.25	216	0.48
54	0.58	108	1.33	163	5.75	217	2.61
55	0.59	109	2.34	164	5.68	218	4.21
56	1.59	110	1.69	165	1.56	219	3.28
57	4.85	111	4.85	166	0.53	220	2.17
58	0.36	112	7.42	167	6.05	221	0.56
59	1.09	113	2.94	168	7.89	222	0.31
60	0.15	114	1.07	169	4.61	223	10.03
61	4.51	115	0.47	170	3.34	224	5.61
62	4.78	116	2.17	171	0.96	225	2.84
63	6.12	117	10.16	172	0.36	226	6.65
64	3.21	118	3.54	173	6.12	227	2.57
65	5.15	119	2.91	174	9.09	228	4.91
66	3.78	120	0.83	175	3.24	229	6.62
67	7.39	121	0.46	176	4.78	230	16.71
68	3.78	123	20.19	177	3.58	231	8.56
69	79.14	124	13.10	178	3.98	232	6.22
70	2.06	125	3.48	179	13.64	233	1.84
71	0.48	126	1.40	180	8.56	234	0.72
72	0.29	127	1.38	181	26.47	235	0.58
73	0.68	128	0.78	182	10.43	236	2.97
74	8.32	129	4.41	183	4.34	237	5.65
75	12.17	130	15.11	184	1.60	238	2.87
76	6.89	131	11.36	185	4.41	239	14.71
77	2.91	132	3.88	186	8.39	240	7.22
78	2.67	133	3.94	187	10.83	241	11.90

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
242	5.45	287	0.99	332	12.83	378	0.17
243	5.68	288	1.44	333	2.37	379	0.43
244	3.01	289	1.09	334	0.44	380	0.40
245	3.51	290	1.23	335	0.16	381	0.53
246	0.83	291	0.78	336	0.23	382	0.43
247	0.34	292	2.21	337	0.14	383	0.16
248	1.45	293	13.37	338	1.45	385	11.36
249	2.91	294	2.12	339	1.33	386	2.14
250	45.99	295	12.03	340	1.26	387	11.10
251	8.82	296	1.41	341	1.52	388	2.44
252	4.11	297	0.40	342	0.88	389	0.37
253	1.09	298	1.34	343	52.41	390	0.29
254	1.11	299	1.62	344	6.15	391	0.07
255	1.39	300	3.11	345	48.66	392	0.05
256	4.45	301	4.48	346	6.12	393	0.17
257	2.27	302	1.14	347	1.51	394	0.10
258	4.31	303	0.56	348	2.61	395	0.15
259	3.71	304	0.91	349	0.91	396	0.08
260	10.16	305	0.69	350	0.51	397	0.20
261	3.21	306	3.64	351	0.53	398	33.02
262	3.88	307	3.34	352	0.08	399	16.71
263	2.87	308	3.14	353	0.04	400	32.49
264	3.58	309	3.58	354	0.18	401	16.44
265	1.93	310	3.41	355	0.22	402	2.51
266	6.52	311	0.86	356	1.32	403	0.25
267	2.24	312	2.71	357	9.09	406	0.07
268	9.09	313	0.74	358	6.08	407	0.14
269	3.21	314	1.17	359	8.82	408	0.80
270	1.78	315	0.56	360	5.11	409	0.22
271	0.71	316	1.45	361	1.81	410	0.79
272	0.94	317	1.28	362	0.54	412	100.00
273	1.56	318	2.17	363	1.34	413	10.70
274	1.59	319	5.41	364	0.36	414	74.33
275	0.74	320	1.15	365	0.06	415	9.09
276	1.88	321	1.30	366	0.04	416	0.63
277	1.61	322	0.33	368	0.26	424	0.04
278	8.49	323	0.23	369	0.03	425	0.11
279	18.05	324	2.05	370	0.24	426	10.56
280	14.84	325	0.29	371	0.14	427	48.66
281	12.17	326	1.97	372	0.08	428	12.57
282	13.64	327	0.33	373	0.09	429	38.50
283	1.91	328	3.51	374	0.76	430	4.95
284	0.35	329	9.76	375	1.47	431	0.37
285	0.34	330	13.90	376	0.76		
286	0.87	331	10.29	377	1.41		



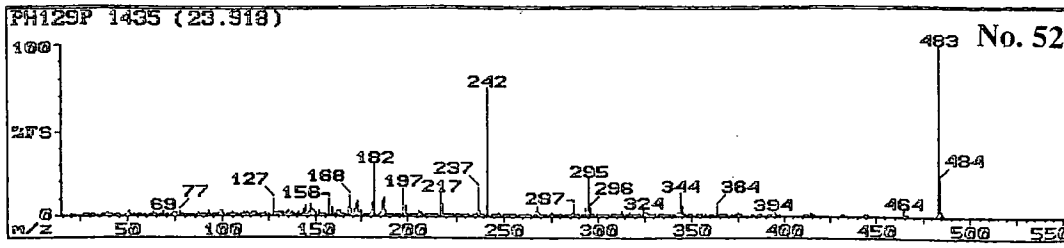
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.18	80	2.02	134	0.63	188	7.80
25	0.07	81	5.13	135	1.33	189	8.99
26	1.41	82	0.81	136	1.79	190	4.46
27	17.59	83	0.92	137	1.25	191	2.18
28	4.43	84	0.26	138	1.31	192	3.08
29	30.16	85	0.88	139	0.60	193	5.56
30	0.77	86	1.27	140	0.44	194	4.00
31	0.81	87	2.35	141	0.90	195	2.81
32	1.37	88	1.19	142	1.17	196	3.84
33	0.11	89	0.65	143	4.03	197	2.35
36	0.11	90	0.38	144	1.22	198	8.47
37	0.29	91	0.95	145	0.97	199	4.93
38	0.92	92	1.60	146	0.68	200	8.37
39	9.39	93	3.27	147	0.98	201	7.87
40	1.50	94	1.78	148	1.21	202	11.51
41	9.79	95	0.78	149	2.08	203	6.02
42	2.55	96	0.56	150	2.04	204	3.24
43	1.07	97	0.37	151	2.78	205	9.66
44	0.27	98	1.19	152	1.18	206	5.26
45	0.12	99	4.10	153	0.75	207	3.84
46	0.18	100	1.50	154	1.78	208	3.67
47	0.28	101	1.22	155	2.98	209	2.00
48	0.09	102	0.52	156	1.98	210	1.97
49	0.12	103	0.57	157	1.07	211	5.62
50	2.12	104	1.79	158	0.98	212	7.04
51	6.65	105	5.69	159	0.80	213	5.22
52	2.81	106	1.54	160	0.86	214	6.78
53	3.51	107	1.14	161	3.47	215	6.08
54	0.49	108	0.43	162	2.03	216	9.13
55	14.15	109	0.92	163	1.88	217	5.46
56	0.94	110	0.79	164	1.79	218	10.85
57	2.25	111	1.74	165	0.90	219	6.78
58	0.16	112	1.51	166	0.77	220	6.65
59	0.58	113	1.20	167	2.55	221	2.81
60	0.05	114	0.69	168	3.01	222	2.38
61	0.93	115	0.83	169	4.37	223	4.10
62	1.60	116	1.05	170	3.54	224	5.99
63	4.53	117	1.89	171	1.50	225	9.13
64	2.35	118	0.89	172	1.34	226	13.62
65	6.12	119	0.93	173	2.68	227	10.32
66	2.65	120	0.77	174	7.54	228	5.06
67	4.89	121	0.22	175	4.46	229	3.31
68	0.96	122	0.52	176	3.41	230	3.60
69	13.89	123	5.65	177	3.04	231	4.99
70	0.62	124	4.27	178	1.16	232	7.34
71	0.25	125	2.25	179	1.27	233	3.77
72	0.12	126	1.35	180	2.22	234	2.58
73	0.20	127	1.08	181	2.78	235	1.44
74	3.47	128	0.63	182	3.70	236	2.88
75	4.56	129	1.04	183	2.51	237	2.78
76	2.05	130	1.41	184	1.38	238	22.09
77	3.34	131	1.60	185	3.64	239	17.33
78	1.88	132	1.18	186	3.70	240	4.53
79	1.01	133	1.87	187	5.59	241	1.52

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
242	2.55	284	2.05	326	1.07	368	0.94
243	3.87	285	0.55	327	1.03	369	0.37
244	3.27	286	0.57	328	0.76	370	1.62
245	5.13	287	1.45	329	1.71	371	17.86
246	5.46	288	4.46	330	1.35	372	11.38
247	3.57	289	22.62	331	31.22	373	1.97
248	3.21	290	5.42	332	5.06	374	0.66
249	3.34	291	1.43	333	1.17	375	0.15
250	4.76	292	0.71	334	1.18	376	0.24
251	4.66	293	1.53	335	0.28	377	0.12
252	27.51	294	1.17	336	0.42	378	0.14
253	8.86	295	2.74	337	0.09	379	0.07
254	1.74	296	4.07	338	0.43	380	0.85
255	1.32	297	2.38	339	0.23	381	0.25
256	2.38	298	2.38	340	0.47	382	0.42
257	1.47	299	1.07	341	0.19	383	0.19
258	2.18	300	1.40	342	0.26	384	9.66
259	0.83	301	4.30	343	0.55	385	4.10
260	1.03	302	26.98	344	3.31	386	65.08
261	1.55	303	12.70	345	8.37	387	72.49
262	2.65	304	2.38	346	3.51	388	11.38
263	3.11	305	0.51	347	0.88	389	1.05
264	3.94	306	0.55	348	0.53	390	0.11
265	8.20	307	0.79	349	0.32	394	0.27
266	9.52	308	2.15	350	0.20	395	0.68
267	5.49	309	0.48	351	0.17	396	4.10
268	2.81	310	1.00	352	0.37	397	0.98
269	2.45	311	0.94	353	0.26	398	1.66
270	3.47	312	1.38	354	0.31	399	0.43
271	1.20	313	1.12	355	0.09	400	72.49
272	0.74	314	1.69	356	0.45	401	11.77
273	0.84	315	8.47	357	5.62	402	1.01
274	1.33	316	11.24	358	34.39	403	0.08
275	3.41	317	8.20	359	7.64	412	0.22
276	5.49	318	9.13	360	1.58	413	0.37
277	2.61	319	1.75	361	0.27	414	24.21
278	1.87	320	1.05	362	0.32	415	100.00
279	2.04	321	0.65	363	1.07	416	15.34
280	0.88	322	0.42	364	0.30	417	1.36
281	8.47	323	0.11	365	0.14	418	0.12
282	3.14	324	0.25	366	1.73		
283	3.77	325	0.22	367	1.03		



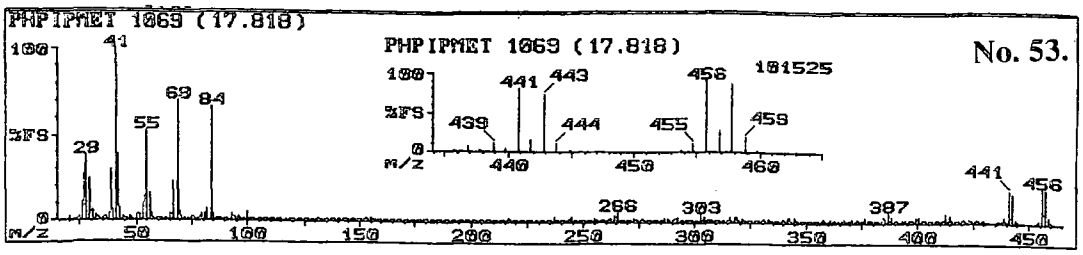
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
36	2.43	107	7.38	167	9.04	242	5.19
37	1.03	108	2.11	168	9.11	243	9.77
38	2.99	109	3.09	169	2.94	244	66.22
39	9.31	110	4.26	170	1.70	245	11.50
40	3.77	111	6.85	171	17.29	246	1.58
41	1.56	112	5.39	172	18.09	247	1.04
43	1.04	113	6.18	174	3.39	248	1.56
44	6.18	114	0.95	175	8.58	249	0.80
49	0.73	115	1.11	176	1.43	254	1.21
50	9.91	116	7.18	178	0.55	255	2.18
51	12.77	117	16.69	179	1.70	256	0.89
52	4.72	118	11.30	181	0.90	260	0.82
55	1.56	119	3.27	182	3.71	261	1.10
56	0.78	120	1.16	185	3.47	262	26.86
57	1.99	122	8.44	186	15.89	263	32.98
61	3.24	123	13.03	187	8.11	264	5.39
62	5.52	124	7.91	188	0.98	265	2.81
63	12.83	125	1.86	191	1.94	266	1.16
64	1.93	127	8.51	192	4.19	267	2.86
65	0.84	128	4.85	193	8.05	268	2.31
67	0.83	129	4.72	194	19.68	273	3.31
69	68.09	130	4.92	195	3.44	274	1.89
70	3.08	131	9.77	197	2.58	275	4.79
71	0.97	132	6.45	198	2.83	276	0.65
73	1.86	133	0.84	199	5.39	282	4.12
74	14.63	134	0.98	200	1.48	283	0.83
75	12.90	135	4.79	204	1.63	286	3.89
76	6.98	136	6.05	205	2.38	287	3.19
77	6.45	137	1.43	206	3.31	291	0.77
78	1.00	139	0.66	207	1.91	292	1.18
79	3.39	140	1.75	209	1.00	293	30.32
80	4.92	141	4.65	210	0.94	294	12.83
81	6.32	142	4.79	211	4.65	295	1.91
82	1.60	143	6.45	212	4.45	305	0.58
84	2.14	144	23.94	213	23.40	311	0.78
85	5.59	145	3.54	214	3.92	312	7.58
86	11.30	147	7.98	215	2.84	313	26.33
87	8.91	148	4.59	216	3.04	314	4.26
88	3.64	149	1.46	217	12.03	315	1.85
89	1.40	150	2.83	218	6.91	317	1.76
91	0.49	151	10.17	219	1.11	322	5.39
92	9.31	152	1.83	220	0.48	323	3.26
93	15.89	153	1.56	222	0.89	324	5.85
94	8.24	154	4.14	223	2.31	325	3.14
95	2.21	155	4.45	224	11.44	332	1.36
96	0.89	156	2.23	225	3.72	341	0.57
97	1.99	158	2.39	229	0.80	342	14.89
98	10.17	159	1.98	231	15.36	343	3.26
99	12.63	160	1.89	232	16.42	344	15.16
100	11.24	161	3.24	235	3.03	345	2.39
101	2.53	162	3.76	236	6.98	353	3.11
103	1.25	163	5.05	237	9.57	354	0.78
104	6.38	165	1.89	238	1.48	355	2.86
105	8.58	166	2.63	241	0.45	356	0.85

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
363	2.59	375	2.61	394	2.11	461	100.00
364	0.85	382	5.52	442	5.92	462	16.76
372	6.32	383	3.44	443	1.13	463	95.74
373	2.81	384	0.64	444	5.72	464	16.76
374	6.18	392	2.11	445	1.26	465	1.70



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.05	91	0.15	147	7.06	203	0.29
26	0.09	92	1.09	148	3.81	204	0.45
27	0.34	93	2.55	149	3.06	205	0.68
28	1.09	94	0.90	150	1.54	206	2.76
29	0.04	95	0.31	151	2.46	207	1.60
31	0.14	96	0.21	152	1.04	208	0.27
32	1.28	97	0.11	153	0.74	209	0.61
36	0.15	98	1.82	154	0.32	210	0.52
37	0.07	99	2.48	155	1.35	211	1.14
38	0.27	100	2.67	156	9.71	212	0.51
39	1.97	101	1.04	158	3.56	213	0.77
40	0.29	102	0.37	159	5.08	214	0.23
41	0.15	103	0.19	160	1.19	215	0.42
42	0.08	104	0.98	162	2.87	216	0.97
43	0.06	105	1.49	162	2.50	217	13.41
44	0.73	106	0.51	163	2.44	218	7.22
45	0.06	107	0.25	164	0.58	219	1.23
49	0.08	108	0.24	165	0.68	220	0.38
50	1.69	109	0.41	166	0.85	221	0.27
51	2.72	110	0.84	167	4.52	222	0.72
52	1.38	111	1.47	168	11.69	223	0.81
53	0.13	112	0.93	169	3.46	224	1.19
55	0.11	113	1.64	170	0.32	225	0.49
56	0.09	114	0.49	171	4.12	226	0.98
57	0.28	115	0.23	172	6.66	227	0.37
59	0.03	116	1.54	173	8.28	228	0.62
61	0.22	117	1.79	174	1.65	229	0.60
62	0.60	118	1.59	175	2.81	230	0.50
63	2.25	119	0.62	176	0.56	231	0.37
64	0.27	120	0.67	177	0.50	232	0.88
65	0.07	121	1.21	178	0.93	234	0.23
67	0.05	122	0.49	179	1.16	235	1.28
68	0.10	123	2.31	180	1.52	236	2.30
69	3.14	124	0.71	181	7.37	237	16.87
70	0.29	125	0.84	182	30.08	238	2.62
71	0.06	127	9.45	184	0.58	239	0.31
73	0.23	128	1.99	185	1.79	240	0.48
74	2.02	129	1.51	186	8.94	242	74.80
75	2.34	130	1.50	187	10.21	244	0.83
76	1.47	131	1.69	188	2.90	245	0.33
77	3.06	132	1.08	189	0.33	246	0.26
78	0.30	133	1.82	190	0.19	247	0.70
79	0.30	134	2.27	191	0.95	248	1.47
80	0.35	135	2.49	192	0.86	249	0.74
81	0.76	136	1.28	193	0.85	250	0.45
82	0.17	137	2.05	194	0.40	251	0.48
83	0.17	138	1.00	195	0.14	252	0.20
84	0.12	140	1.30	197	4.42	253	0.23
85	0.74	141	1.58	197	2.06	254	0.38
86	1.03	142	1.37	198	2.95	255	0.66
87	1.88	143	4.07	199	6.30	256	0.51
88	0.84	144	5.84	200	1.31	257	0.23
89	0.33	145	1.40	201	0.30	258	0.21
90	0.10	146	2.34	202	0.34	259	0.30

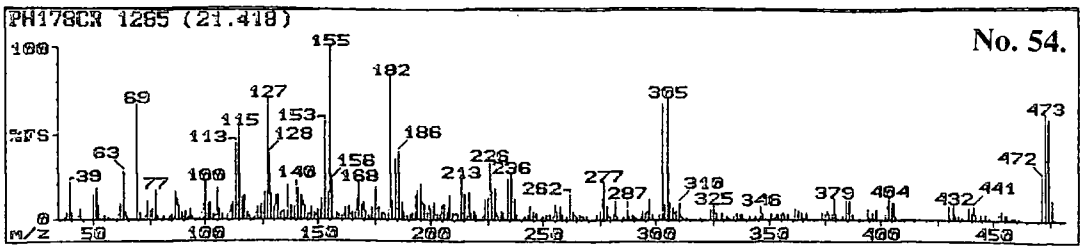
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
260	0.50	296	5.08	332	0.09	374	0.60
261	0.73	297	1.30	333	0.08	375	1.65
262	0.83	298	0.74	334	0.10	376	0.49
263	0.33	299	0.99	335	0.26	377	0.08
264	0.29	300	0.46	336	0.47	382	0.03
265	0.32	301	0.13	337	0.99	383	0.04
266	1.27	302	0.10	338	0.34	386	0.05
267	2.55	303	0.17	339	0.09	387	0.11
268	5.59	304	0.61	340	0.12	388	0.05
269	1.94	305	0.58	341	0.19	391	0.07
270	0.45	306	0.85	342	1.91	392	0.24
271	0.46	307	0.24	343	1.49	393	0.95
272	0.44	308	0.08	344	13.21	394	3.14
273	0.66	309	0.14	345	5.64	395	1.65
274	0.94	310	0.29	346	1.03	396	0.31
275	1.63	311	0.80	347	0.19	397	0.05
276	0.50	312	1.11	348	0.24	411	0.06
277	0.22	313	2.58	349	0.23	412	0.36
278	0.30	314	1.27	350	0.08	413	0.93
279	0.51	315	0.50	353	0.12	414	1.68
280	0.40	316	0.54	354	0.22	415	0.54
281	0.40	317	1.51	355	0.60	416	0.10
282	0.26	318	1.24	356	0.52	431	0.04
283	0.16	319	0.84	357	0.15	432	0.07
284	0.29	320	0.24	360	0.11	444	0.07
285	0.58	321	0.09	361	0.18	445	0.55
286	2.36	322	0.53	362	1.45	446	0.12
287	7.16	323	0.63	363	2.35	464	3.71
288	1.28	324	4.17	364	5.79	465	1.14
289	0.30	325	1.56	365	1.30	466	0.22
290	0.20	326	2.27	366	0.27	482	0.39
291	0.49	327	0.53	367	0.14	483	100.00
292	0.99	328	0.17	368	0.12	484	21.34
293	4.78	329	0.17	369	0.05	485	2.63
294	3.15	330	0.20	372	0.08	486	0.22
295	22.36	331	0.18	373	0.67		



No. 53.

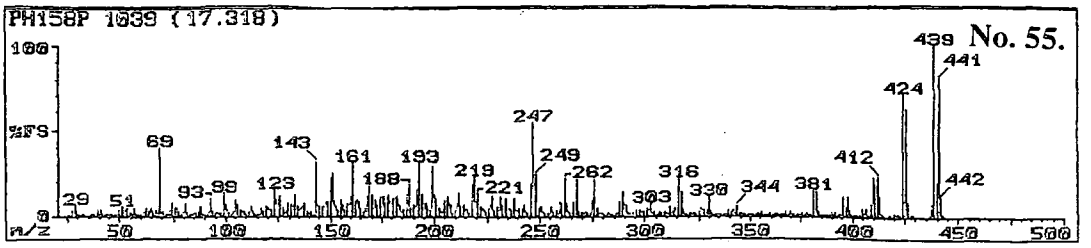
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	2.14	80	3.59	139	0.26	193	1.00
24	0.61	81	4.22	140	0.64	194	1.32
25	1.63	82	6.81	141	0.33	195	1.03
26	11.04	84	65.77	142	0.26	196	0.81
27	27.03	85	3.83	143	1.28	197	0.99
28	37.39	86	0.72	144	1.18	198	0.61
29	24.32	87	0.26	145	0.71	199	0.35
30	4.73	88	0.52	146	0.39	200	0.89
31	6.14	89	0.36	147	0.24	201	0.38
32	2.79	90	0.44	148	0.68	202	0.36
33	2.11	91	0.42	149	0.76	203	0.66
34	0.06	93	3.66	150	1.34	204	0.61
35	1.20	94	2.34	151	0.62	205	0.87
36	1.75	95	1.49	152	0.68	206	0.46
37	1.84	96	1.48	153	1.48	207	0.49
38	3.49	97	0.73	154	0.63	208	0.52
39	29.05	98	0.64	155	1.94	209	1.03
40	5.91	100	4.62	156	0.50	210	1.11
41	100.00	101	0.71	157	0.43	211	0.41
42	37.84	102	0.36	158	0.28	212	1.22
43	6.76	103	0.20	159	0.87	213	0.39
44	2.42	105	0.84	160	0.48	214	1.17
45	0.70	106	1.07	161	0.44	215	1.13
46	0.41	107	1.08	162	1.38	216	1.34
47	2.00	108	0.94	163	0.76	217	1.59
48	0.27	109	1.14	164	0.80	218	0.67
50	3.20	110	0.50	165	1.27	219	0.89
51	4.00	111	0.15	166	0.91	220	0.40
52	2.87	112	0.90	167	0.62	221	1.01
53	9.91	113	0.84	168	0.84	222	1.22
54	13.68	114	0.48	169	1.37	223	0.96
55	52.25	115	0.21	170	0.85	224	1.28
56	15.09	117	0.84	171	0.51	225	1.06
57	4.28	118	0.20	172	0.53	226	0.63
58	0.60	119	0.94	173	0.49	227	0.51
59	0.49	120	0.26	174	0.86	228	0.44
60	0.39	121	0.78	175	1.13	229	0.76
61	0.23	122	0.57	176	1.41	230	0.30
62	1.01	123	0.72	177	0.90	231	0.89
63	1.25	124	1.24	178	0.53	232	0.73
64	0.63	125	0.24	179	0.38	233	0.54
65	4.28	126	0.70	180	0.25	234	0.93
66	3.38	127	0.34	181	1.25	235	0.27
67	22.75	128	0.34	182	0.80	236	1.42
69	70.27	129	0.63	183	0.57	237	2.67
70	4.67	130	0.59	184	0.79	238	0.57
71	1.68	131	1.82	185	0.38	239	0.30
72	0.33	132	0.50	186	0.62	240	1.28
74	1.24	133	0.43	187	0.49	241	0.38
75	2.07	134	0.40	188	0.69	242	1.30
76	1.86	135	0.25	189	0.55	243	0.86
77	0.38	136	0.88	190	0.73	244	1.86
78	1.10	137	0.99	191	0.74	245	3.03
79	2.31	138	0.71	192	0.39	246	0.40

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
247	0.65	297	0.65	347	1.10	399	3.13
248	0.35	298	0.70	348	0.80	400	1.65
249	0.96	299	0.38	349	0.39	401	3.35
250	1.08	300	0.32	350	0.14	402	1.34
251	1.30	301	0.94	351	0.43	403	0.80
252	1.31	302	0.43	352	0.60	404	0.17
253	0.91	303	5.01	353	0.72	405	0.06
254	0.63	304	0.70	354	0.75	406	0.13
255	1.55	304	2.65	355	0.70	407	0.26
256	0.52	306	1.07	356	0.55	408	0.17
257	0.59	307	0.59	357	1.04	409	0.45
258	0.60	308	0.29	358	1.68	410	0.16
259	0.73	309	0.27	359	1.44	411	0.96
260	1.31	310	0.60	360	1.37	412	0.45
261	0.67	311	0.35	361	1.63	413	4.45
262	1.93	312	0.56	362	0.96	414	0.89
263	1.91	313	1.17	363	0.36	415	4.05
264	3.42	314	1.04	365	0.64	416	0.67
265	2.46	315	1.17	366	0.32	417	0.55
266	5.41	316	2.66	367	1.80	418	0.23
267	0.87	317	1.21	368	0.47	419	0.25
268	0.46	318	2.66	369	1.37	420	0.12
269	0.57	319	2.89	370	0.50	421	1.75
270	0.39	320	0.59	371	1.55	422	1.44
271	0.91	321	2.35	372	1.00	423	1.69
272	0.58	322	0.56	373	2.04	424	1.34
273	1.52	323	0.57	374	0.90	425	0.88
274	1.28	324	0.88	375	1.03	426	0.17
275	0.93	325	0.99	376	0.38	427	1.51
276	0.57	326	0.93	377	3.35	428	0.29
277	1.94	327	1.07	378	0.67	429	0.91
278	1.21	328	0.49	379	0.80	430	0.12
279	1.24	329	1.07	380	0.22	436	0.13
280	0.65	330	0.86	381	1.27	437	1.45
281	0.59	331	2.21	382	0.31	438	0.46
282	0.44	332	0.81	383	1.10	439	2.53
283	0.30	333	2.29	384	1.14	440	0.90
284	0.58	334	0.53	385	3.39	441	18.02
285	0.65	335	0.26	386	1.76	442	3.15
286	0.81	336	0.18	387	5.91	443	16.22
287	1.72	337	0.24	388	1.11	444	2.31
288	1.55	338	0.41	389	3.27	445	0.22
289	0.94	339	0.99	390	0.45	454	0.48
290	1.35	340	2.01	391	0.20	455	2.18
291	1.66	341	1.13	393	1.17	456	20.27
292	2.04	342	2.46	394	0.22	457	6.08
293	2.74	343	2.51	395	1.28	458	19.37
294	1.01	344	0.97	396	0.52	459	4.05
295	0.64	345	2.58	397	0.73	460	0.44
296	0.34	346	1.30	398	0.57		



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
37	0.68	116	6.96	174	3.86	231	2.62
38	1.99	117	7.29	175	9.95	232	1.99
39	11.69	118	2.32	176	3.29	234	12.50
40	2.22	119	0.88	177	3.60	235	1.96
43	1.00	121	0.46	178	1.83	236	13.84
44	3.26	122	1.92	179	2.13	237	6.52
50	7.06	123	3.70	180	1.58	238	1.32
51	9.41	124	4.70	181	3.36	241	0.73
52	3.97	125	1.39	182	44.62	242	1.23
55	0.81	126	8.13	183	5.98	243	1.77
57	0.51	127	37.63	184	18.95	244	4.07
61	1.76	128	20.16	185	3.13	245	2.39
62	4.64	129	8.06	186	20.70	246	0.96
63	14.38	130	3.80	187	5.04	247	1.87
64	1.86	131	7.33	188	1.87	249	0.75
65	1.28	132	7.53	189	0.92	250	1.01
69	36.02	133	1.92	191	1.42	251	1.73
71	2.10	134	2.45	192	1.94	253	1.42
73	1.17	135	2.72	193	7.16	254	0.82
74	5.78	136	10.48	194	9.01	255	4.47
75	2.79	137	3.23	195	11.16	256	2.55
76	3.02	138	4.23	196	5.04	257	4.17
77	8.87	139	3.70	197	4.54	258	1.76
78	1.10	140	9.41	198	1.92	260	1.11
81	1.23	141	9.14	199	4.07	262	7.93
84	0.93	142	7.33	200	3.09	263	2.79
85	1.34	143	5.81	201	5.48	264	1.42
86	8.53	144	4.37	202	1.60	265	0.88
87	6.25	145	1.53	203	1.65	266	1.50
88	4.33	146	1.41	204	1.50	267	0.92
89	2.10	147	3.80	205	4.33	268	1.24
90	0.57	148	1.83	206	4.74	269	0.93
91	2.49	149	1.81	207	2.07	274	1.36
92	0.70	150	2.89	208	7.43	275	2.69
93	3.16	151	6.28	209	1.94	276	6.32
94	1.17	153	30.11	210	1.44	277	11.42
97	0.50	154	8.23	211	1.89	278	4.33
98	2.15	155	53.76	212	1.64	279	1.26
99	4.60	156	11.83	213	12.50	280	0.81
100	11.29	158	1.85	214	2.10	281	1.72
101	4.87	159	1.36	215	7.80	282	5.98
102	5.38	160	0.95	216	0.87	283	1.28
103	1.65	161	1.45	217	8.33	285	0.66
104	1.20	162	3.60	218	2.22	286	1.19
105	9.27	163	4.30	219	2.55	287	3.09
106	3.02	164	1.63	220	1.52	288	1.09
107	1.55	165	2.01	223	0.86	289	1.50
109	1.82	166	2.25	224	6.45	290	1.21
110	1.97	167	6.45	225	6.65	291	0.70
111	4.07	168	11.56	226	11.56	293	0.97
112	5.44	169	4.54	227	8.74	294	2.55
113	23.52	170	5.21	228	9.14	295	2.22
114	4.44	171	2.76	229	2.09	296	2.72
115	28.90	172	0.92	230	0.92	297	6.45

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
298	1.42	337	1.79	377	1.69	436	0.57
301	1.68	338	1.36	378	1.69	439	3.80
303	36.02	339	0.76	379	6.22	440	2.01
304	4.54	342	0.94	380	1.35	441	3.93
305	37.63	344	1.06	383	0.94	442	1.81
306	5.28	346	4.44	384	5.51	444	1.33
307	3.39	347	1.97	385	2.13	446	1.58
308	2.15	351	2.07	386	5.58	448	0.43
309	2.42	352	0.70	387	1.47	452	1.69
310	5.48	353	1.43	394	2.96	453	1.42
311	1.22	354	1.34	395	0.66	454	2.86
312	0.34	355	1.65	396	1.95	455	1.66
313	0.44	356	2.15	398	3.33	456	1.39
319	0.73	357	0.84	402	1.54	458	0.39
324	3.19	358	1.82	403	4.33	459	0.40
325	4.50	361	3.09	404	6.82	460	0.41
326	1.92	362	0.70	405	5.04	461	0.40
327	1.98	363	2.86	406	5.31	472	13.44
329	1.83	364	2.15	407	0.92	473	32.66
331	0.79	365	0.68	430	4.44	474	18.55
332	0.61	366	1.89	431	0.76	475	31.18
334	1.14	374	2.05	432	4.74	476	6.22
335	1.65	375	1.80	433	1.23	477	0.57
336	2.15	376	2.49	434	1.22		



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.34	82	1.73	136	5.14	190	6.50
27	3.58	83	1.40	137	6.00	191	5.39
28	1.36	84	0.32	138	8.06	192	15.30
29	6.74	85	1.90	139	2.58	193	31.09
30	0.31	86	1.93	140	2.18	194	12.50
31	0.69	87	2.92	141	2.58	195	3.91
32	0.21	88	5.88	142	1.25	196	7.61
33	0.24	89	1.17	143	30.59	197	5.43
36	0.05	90	0.69	144	6.74	198	3.82
37	0.19	91	1.03	145	6.21	199	28.95
38	0.52	92	3.08	146	5.55	200	12.99
39	3.66	93	10.69	147	5.51	201	10.28
40	0.64	94	2.44	148	8.88	202	5.30
41	4.32	95	2.21	149	8.39	203	2.51
42	1.26	96	2.00	150	22.37	204	2.60
43	0.93	97	0.62	151	24.84	205	9.91
44	0.40	98	1.59	152	8.31	206	11.35
45	0.24	99	13.65	153	6.04	207	7.94
46	0.26	100	6.74	154	3.54	208	7.28
47	1.31	101	4.24	155	10.03	209	2.31
48	0.15	102	1.89	156	6.33	210	4.19
49	0.36	103	1.10	157	3.50	211	7.57
50	3.70	104	3.08	158	7.57	212	13.98
51	6.21	105	10.07	159	7.20	213	6.29
52	2.01	106	7.24	160	11.51	214	6.87
53	3.99	107	3.95	161	31.09	215	4.32
54	5.10	108	3.25	162	8.39	216	3.50
55	2.17	109	3.25	163	9.42	217	2.30
56	0.85	110	0.96	164	8.63	218	18.09
57	4.48	111	3.04	165	4.61	219	22.86
58	0.19	112	6.21	166	2.61	220	8.88
59	0.89	113	2.84	167	4.44	221	13.98
60	1.10	114	1.31	168	11.18	222	6.21
61	2.05	115	0.87	169	17.60	223	5.26
62	2.51	116	1.21	170	12.83	224	4.07
63	4.40	117	5.06	171	4.52	225	3.33
64	2.53	118	2.96	172	9.42	226	4.93
65	4.85	119	5.96	173	6.87	227	6.91
66	3.21	120	4.98	174	11.84	228	11.68
67	3.41	121	4.19	175	5.84	229	4.28
68	2.12	122	4.11	176	11.51	230	5.51
69	40.13	123	15.95	177	7.44	231	4.07
70	1.59	124	9.95	178	12.83	232	12.01
71	2.71	125	6.37	179	8.92	233	7.03
72	0.27	126	11.51	180	7.52	234	10.53
73	0.63	127	5.26	181	10.69	235	3.62
74	3.91	128	1.93	182	11.84	236	4.56
75	7.98	129	2.80	183	7.03	237	3.70
76	5.18	130	7.65	184	5.63	238	10.86
77	4.69	131	7.20	185	3.29	239	3.50
78	2.63	132	5.88	186	3.91	240	4.28
79	0.88	133	12.83	187	12.83	241	4.77
80	3.37	134	5.76	188	18.75	242	5.02
81	7.52	135	3.99	189	5.14	243	7.28

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
244	3.21	292	2.43	340	3.91	388	0.17
245	2.33	293	2.07	341	2.75	389	0.20
246	19.24	294	1.59	342	4.07	390	2.47
247	54.61	295	1.01	343	2.26	391	0.43
248	23.85	296	4.07	344	5.35	392	2.50
249	24.67	297	4.36	345	2.41	393	0.46
250	4.85	298	2.58	346	1.60	394	0.68
251	6.00	299	2.67	347	0.21	395	1.20
252	2.96	300	2.47	348	0.78	396	12.01
253	2.42	301	5.06	349	0.36	397	5.43
254	1.46	302	3.41	350	0.28	398	12.01
255	2.15	303	7.61	351	0.35	399	4.36
256	5.67	304	2.15	352	0.43	400	0.87
257	2.75	305	2.75	353	0.25	401	0.14
258	3.45	306	1.27	354	2.42	402	0.09
259	2.06	307	3.17	355	1.04	404	1.11
260	8.63	308	1.61	356	2.60	405	5.10
261	7.89	309	3.25	357	1.01	406	1.70
262	22.53	310	2.24	358	0.85	407	5.10
263	7.65	311	1.28	359	0.54	408	0.81
264	3.25	312	5.76	360	1.75	409	7.89
265	2.01	313	2.92	361	0.79	410	23.52
266	8.31	314	5.02	362	0.21	411	19.24
267	1.28	315	2.55	363	0.68	412	23.68
268	21.71	316	22.37	364	0.26	413	11.18
269	3.33	317	14.31	365	0.30	414	1.59
270	2.75	318	3.62	366	0.22	415	0.18
271	2.29	319	0.97	367	0.11	418	0.08
272	2.80	320	0.61	368	2.53	420	1.49
273	1.92	321	2.13	369	0.44	421	0.27
274	2.37	322	0.91	370	2.59	422	1.79
275	9.25	323	1.69	371	0.45	423	1.10
276	21.71	324	1.17	372	1.43	424	70.39
277	5.10	325	3.13	373	0.30	425	9.79
278	1.88	326	5.26	374	1.33	426	62.50
279	1.93	327	4.07	375	0.25	427	8.59
280	1.57	328	4.28	376	2.37	428	0.69
281	1.18	329	3.66	377	0.69	429	0.08
282	2.04	330	11.18	378	2.38	437	0.12
283	2.06	331	2.54	379	0.82	438	7.85
284	0.82	332	0.59	380	0.50	439	100.00
285	1.00	333	0.29	381	15.13	440	20.39
286	1.49	334	0.24	382	2.23	441	80.92
287	1.52	335	0.49	383	14.80	442	11.51
288	8.47	336	0.61	384	2.52	443	1.08
289	14.47	337	0.52	385	0.42		
290	6.70	338	0.76	386	0.64		
291	7.11	339	0.53	387	0.33		

Appendix D.

Crystallographic Data

Compound Number:	Name:
(27)	*26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-11,23-dimethyl-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(25),3,5,7(26),9(27),10,12,15,17,19(28),21,23-dodecaene*

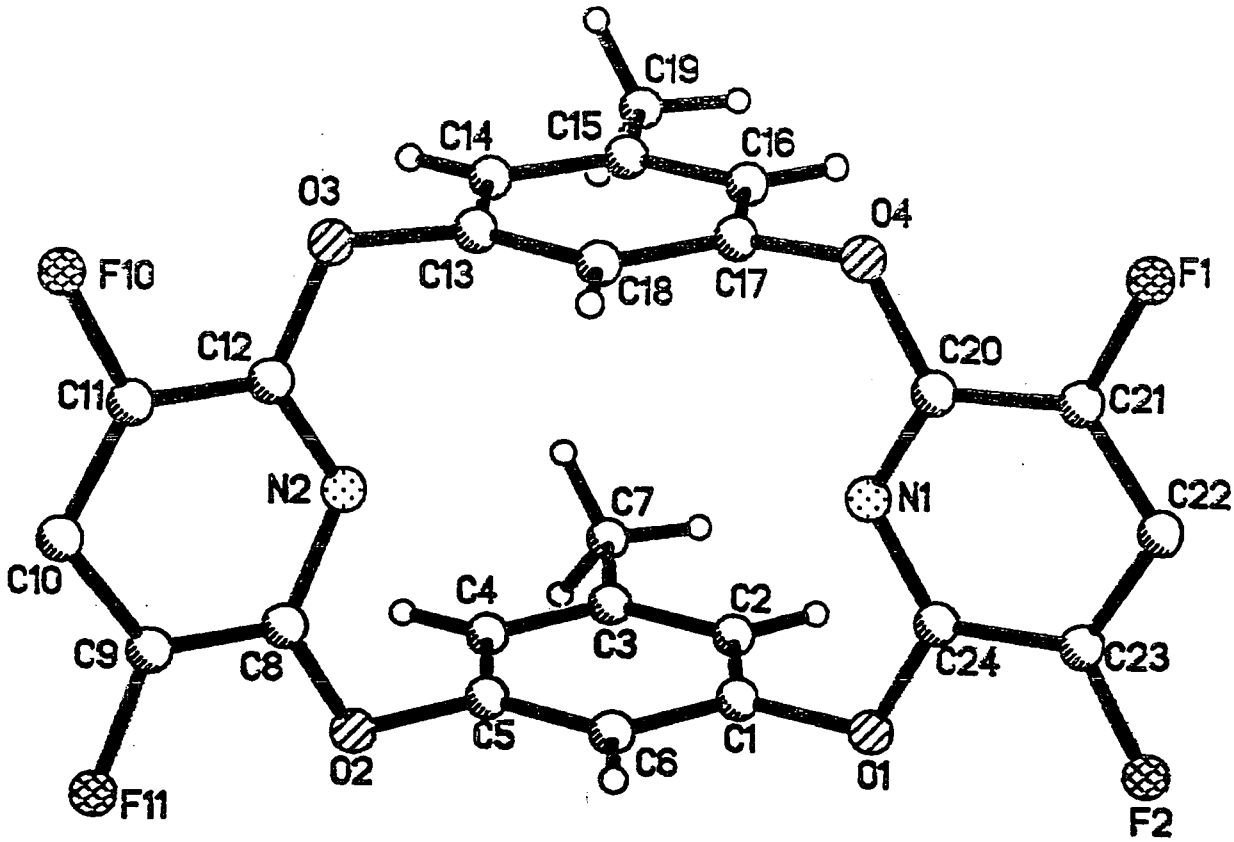


Table 1. Crystal data and structure refinement for (27)

Identification code	103s	
Empirical formula	$C_{30}H_{12}F_{18}N_2O_4$	
Formula weight	806.42	
Temperature	120.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C c	
Unit cell dimensions	a = 13.473(3) Å	α = 90°.
	b = 23.261(5) Å	β = 113.78(3)°.
	c = 11.079(2) Å	γ = 90°.
Volume	3177.2(11) $Å^3$	
Z	4	
Density (calculated)	1.686 Mg/m^3	
Absorption coefficient	0.182 mm^{-1}	
F(000)	1600	
Crystal size	0.46 x 0.40 x 0.20 mm^3	
Theta range for data collection	1.75 to 25.50°.	
Index ranges	-16<=h<=16, -28<=k<=28, -13<=l<=13	
Reflections collected	15431	
Independent reflections	5778 [R(int) = 0.0281]	
Completeness to theta = 25.50°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9644 and 0.9208	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5778 / 2 / 408	
Goodness-of-fit on F^2	1.095	
Final R indices [I>2sigma(I)]	R1 = 0.1168, wR2 = 0.2795	
R indices (all data)	R1 = 0.1322, wR2 = 0.3100	
Absolute structure parameter	0.1(18)	
Largest diff. peak and hole	0.745 and -0.645 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (27) U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
O(1)	8676(4)	8924(2)	4069(5)	42(1)
O(2)	10025(6)	7507(2)	1959(7)	57(2)
O(3)	11385(5)	8909(3)	61(6)	53(2)
O(4)	9668(5)	10316(3)	1763(6)	50(1)
N(1)	9165(5)	9628(3)	2904(6)	35(1)
N(2)	10697(6)	8216(3)	1005(6)	46(2)
C(1)	9541(6)	8590(3)	4038(7)	40(2)
C(2)	10543(7)	8662(3)	4992(8)	47(2)
C(3)	11430(7)	8341(4)	5011(9)	50(2)
C(4)	11217(8)	7964(4)	3959(9)	54(2)
C(5)	10187(8)	7902(3)	2986(8)	49(2)
C(6)	9339(8)	8207(3)	2997(8)	46(2)
C(7)	12584(9)	8416(5)	6116(14)	77(3)
C(8)	10254(7)	7683(4)	959(10)	50(2)
C(9)	10063(8)	7340(4)	-107(9)	60(2)
C(10)	10310(9)	7489(5)	-1185(10)	67(3)
C(11)	10736(9)	8023(5)	-1077(8)	59(2)
C(12)	10927(7)	8378(4)	-6(8)	48(2)
C(13)	11393(7)	9291(4)	1042(8)	43(2)
C(14)	12396(7)	9392(5)	2091(9)	58(2)
C(15)	12474(7)	9796(5)	3070(10)	59(2)
C(16)	11542(7)	10100(4)	2943(9)	50(2)
C(17)	10568(6)	9984(3)	1909(8)	41(2)
C(18)	10468(6)	9580(3)	943(7)	39(2)
C(19)	13524(16)	9908(10)	4211(19)	145(8)
C(20)	9034(6)	10135(3)	2397(7)	38(2)
C(21)	8283(7)	10529(4)	2476(8)	45(2)
C(22)	7638(6)	10380(4)	3116(8)	45(2)
C(23)	7778(6)	9823(3)	3650(8)	40(2)
C(24)	8560(6)	9457(3)	3530(7)	37(2)
C(25)	6777(9)	10785(5)	3232(11)	65(2)

C(26)	5790(18)	10502(9)	3180(20)	65(5)
F(6)	5840(11)	10428(6)	4342(14)	78(3)
C(26')	5730(20)	10673(11)	2300(30)	77(6)
F(6')	5836(10)	10773(6)	1096(13)	73(3)
C(27)	7286(15)	11189(8)	4410(20)	50(4)
F(9)	7717(9)	10898(5)	5411(11)	61(3)
C(27')	7133(17)	11347(9)	3740(20)	59(4)
F(9')	6916(12)	11662(6)	2615(15)	88(4)
C(28)	10132(11)	7108(6)	-2368(14)	83(3)
C(29)	9042(10)	7197(5)	-3448(12)	76(3)
C(30)	10935(16)	6932(9)	-2770(20)	56(4)
F(16)	10773(12)	6412(6)	-3303(14)	67(3)
F(17)	11877(11)	7024(6)	-1781(14)	78(3)
F(18)	10795(14)	7328(7)	-3730(20)	95(4)
C(30')	10689(11)	6543(6)	-2045(13)	31(3)
F(16')	11146(10)	6335(5)	-2824(12)	53(3)
F(17')	11551(8)	6535(4)	-824(10)	51(2)
F(18')	9977(10)	6207(6)	-1936(12)	61(3)
F(12)	9740(11)	6477(6)	-2041(13)	72(3)
F(12')	10993(11)	7381(6)	-2984(15)	73(3)
F(1)	8231(4)	11061(2)	1969(5)	54(1)
F(2)	7197(4)	9621(2)	4312(5)	55(1)
F(3)	6373(11)	11170(6)	1958(14)	77(3)
F(3')	6761(11)	10555(6)	4645(14)	77(3)
F(4)	4975(9)	10995(5)	2507(11)	128(3)
F(5)	5402(7)	10128(4)	2319(9)	97(2)
F(7)	6609(6)	11580(3)	4488(7)	82(2)
F(8)	8135(6)	11477(3)	4349(8)	91(2)
F(10)	11029(6)	8252(3)	-2037(7)	78(2)
F(11)	9619(6)	6802(3)	-77(7)	81(2)
F(13)	8294(7)	7093(4)	-2963(9)	108(3)
F(14)	8832(7)	6853(4)	-4469(9)	104(2)
F(15)	8919(6)	7744(3)	-3864(8)	87(2)

Table 3. Bond lengths [Å] and angles [°] for (27)

O(1)-C(24)	1.358(9)	C(2)-C(3)	1.402(12)	C(13)-C(14)	1.403(13)
O(1)-C(1)	1.414(10)	C(3)-C(4)	1.393(13)	C(14)-C(15)	1.406(14)
O(2)-C(8)	1.329(11)	C(3)-C(7)	1.552(15)	C(15)-C(16)	1.397(12)
O(2)-C(5)	1.409(10)	C(4)-C(5)	1.379(14)	C(15)-C(19)	1.491(19)
O(3)-C(12)	1.368(11)	C(5)-C(6)	1.349(13)	C(16)-C(17)	1.377(12)
O(3)-C(13)	1.400(9)	C(8)-C(9)	1.361(12)	C(17)-C(18)	1.389(11)
O(4)-C(20)	1.374(9)	C(9)-F(11)	1.392(13)	C(20)-C(21)	1.394(10)
O(4)-C(17)	1.392(9)	C(9)-C(10)	1.406(16)	C(21)-F(1)	1.348(10)
N(1)-C(20)	1.287(10)	C(10)-C(11)	1.355(16)	C(21)-C(22)	1.370(12)
N(1)-C(24)	1.326(9)	C(10)-C(28)	1.518(17)	C(22)-C(23)	1.405(12)
N(2)-C(12)	1.331(11)	C(11)-F(10)	1.382(12)	C(22)-C(25)	1.540(14)
N(2)-C(8)	1.369(11)	C(11)-C(12)	1.383(12)	C(23)-F(2)	1.355(9)
C(1)-C(2)	1.348(12)	C(13)-C(18)	1.380(11)	C(23)-C(24)	1.401(10)
C(1)-C(6)	1.394(11)				

C(24)-O(1)-C(1)	116.2(6)	N(2)-C(12)-O(3)	117.5(7)
C(8)-O(2)-C(5)	117.4(6)	N(2)-C(12)-C(11)	121.8(9)
C(12)-O(3)-C(13)	118.5(6)	O(3)-C(12)-C(11)	120.6(8)
C(20)-O(4)-C(17)	117.5(6)	C(18)-C(13)-O(3)	121.6(7)
C(20)-N(1)-C(24)	119.7(6)	C(18)-C(13)-C(14)	121.4(8)
C(12)-N(2)-C(8)	118.1(7)	O(3)-C(13)-C(14)	117.0(7)
C(2)-C(1)-C(6)	121.9(8)	C(13)-C(14)-C(15)	119.9(8)
C(2)-C(1)-O(1)	119.1(7)	C(16)-C(15)-C(14)	118.4(9)
C(6)-C(1)-O(1)	118.9(7)	C(16)-C(15)-C(19)	120.2(12)
C(1)-C(2)-C(3)	121.5(8)	C(14)-C(15)-C(19)	121.3(12)
C(4)-C(3)-C(2)	115.9(8)	C(17)-C(16)-C(15)	120.0(8)
C(4)-C(3)-C(7)	122.2(9)	C(16)-C(17)-C(18)	122.5(7)
C(2)-C(3)-C(7)	121.9(9)	C(16)-C(17)-O(4)	118.8(8)
C(5)-C(4)-C(3)	121.5(8)	C(18)-C(17)-O(4)	118.5(7)
C(6)-C(5)-C(4)	121.8(8)	C(13)-C(18)-C(17)	117.7(7)
C(6)-C(5)-O(2)	119.6(8)	N(1)-C(20)-O(4)	120.0(6)
C(4)-C(5)-O(2)	118.7(8)	N(1)-C(20)-C(21)	123.5(7)
C(5)-C(6)-C(1)	117.4(8)	O(4)-C(20)-C(21)	116.5(7)
O(2)-C(8)-C(9)	121.1(8)	F(1)-C(21)-C(22)	120.7(7)

O(2)-C(8)-N(2)	119.5(8)	F(1)-C(21)-C(20)	119.7(7)
C(9)-C(8)-N(2)	119.5(9)	C(22)-C(21)-C(20)	119.5(8)
C(8)-C(9)-F(11)	116.1(9)	C(21)-C(22)-C(23)	116.5(7)
C(8)-C(9)-C(10)	124.4(10)	C(21)-C(22)-C(25)	123.0(8)
F(11)-C(9)-C(10)	119.5(8)	C(23)-C(22)-C(25)	120.5(8)
C(11)-C(10)-C(9)	112.9(8)	F(2)-C(23)-C(24)	117.5(7)
C(11)-C(10)-C(28)	121.6(11)	F(2)-C(23)-C(22)	122.6(6)
C(9)-C(10)-C(28)	125.5(11)	C(24)-C(23)-C(22)	119.9(6)
C(10)-C(11)-F(10)	121.9(8)	N(1)-C(24)-O(1)	121.1(6)
C(10)-C(11)-C(12)	123.3(9)	N(1)-C(24)-C(23)	120.8(7)
F(10)-C(11)-C(12)	114.7(9)	O(1)-C(24)-C(23)	118.0(6)

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for (27) The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + \ldots + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	45(3)	39(3)	47(3)	8(2)	24(2)	4(2)
O(2)	90(5)	37(3)	61(4)	-4(3)	47(4)	-2(3)
O(3)	74(4)	57(4)	41(3)	5(3)	38(3)	11(3)
O(4)	55(3)	53(3)	53(3)	18(3)	35(3)	15(3)
N(1)	46(3)	36(3)	32(3)	-3(2)	23(3)	2(2)
N(2)	70(4)	47(4)	31(3)	-5(3)	31(3)	5(3)
C(1)	40(4)	47(4)	35(4)	7(3)	19(3)	-3(3)
C(2)	71(6)	41(4)	37(4)	0(3)	31(4)	2(4)
C(3)	44(4)	57(5)	47(5)	10(4)	15(4)	4(4)
C(4)	82(7)	43(4)	55(5)	10(4)	46(5)	0(4)
C(5)	76(6)	34(4)	42(4)	2(3)	29(4)	-2(4)
C(6)	67(5)	40(4)	33(4)	1(3)	21(4)	-16(4)
C(7)	55(6)	81(7)	91(8)	1(6)	24(6)	6(5)
C(8)	58(5)	39(4)	60(5)	-5(4)	29(4)	10(4)
C(9)	63(6)	58(6)	48(5)	-14(4)	12(4)	12(4)
C(10)	65(6)	66(6)	51(5)	-11(5)	3(5)	35(5)
C(11)	82(6)	76(6)	24(4)	2(4)	28(4)	24(5)
C(12)	59(5)	52(5)	32(4)	2(3)	16(4)	17(4)
C(13)	48(5)	53(5)	38(4)	2(3)	27(4)	-3(4)
C(14)	46(5)	87(7)	52(5)	4(5)	31(4)	12(4)
C(15)	38(5)	77(6)	63(6)	8(5)	20(4)	6(4)
C(16)	47(5)	57(5)	45(5)	-8(4)	18(4)	-4(4)
C(17)	43(4)	46(4)	47(4)	10(3)	32(4)	5(3)
C(18)	41(4)	45(4)	31(3)	9(3)	17(3)	1(3)
C(19)	113(14)	174(18)	102(13)	-38(13)	-3(11)	-33(13)
C(20)	32(4)	46(4)	38(4)	1(3)	16(3)	10(3)
C(21)	54(5)	43(4)	37(4)	2(3)	18(4)	11(4)
C(22)	33(4)	60(5)	37(4)	-17(4)	9(3)	1(3)
C(23)	27(4)	53(4)	46(4)	-7(3)	21(3)	-6(3)
C(24)	31(4)	43(4)	37(4)	0(3)	14(3)	-2(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for (27)

Atom	x	y	z	U(eq)
H(2A)	10651	8937	5667	56
H(4A)	11795	7745	3910	64
H(6A)	8632	8163	2322	56
H(7A)	12560	8698	6761	116
H(7B)	13079	8551	5728	116
H(7C)	12840	8047	6555	116
H(14A)	13022	9188	2142	70
H(16A)	11581	10387	3571	60
H(18A)	9788	9506	238	46
H(19A)	13419	10203	4779	217
H(19B)	14062	10041	3887	217
H(19C)	13780	9552	4717	217

Compound Number:	Name:
(29)	*6-(2-{3,5-difluoro-6-propoxy-4[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}ethoxy)-3,5-difluoro-4-1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridin-2-ol*

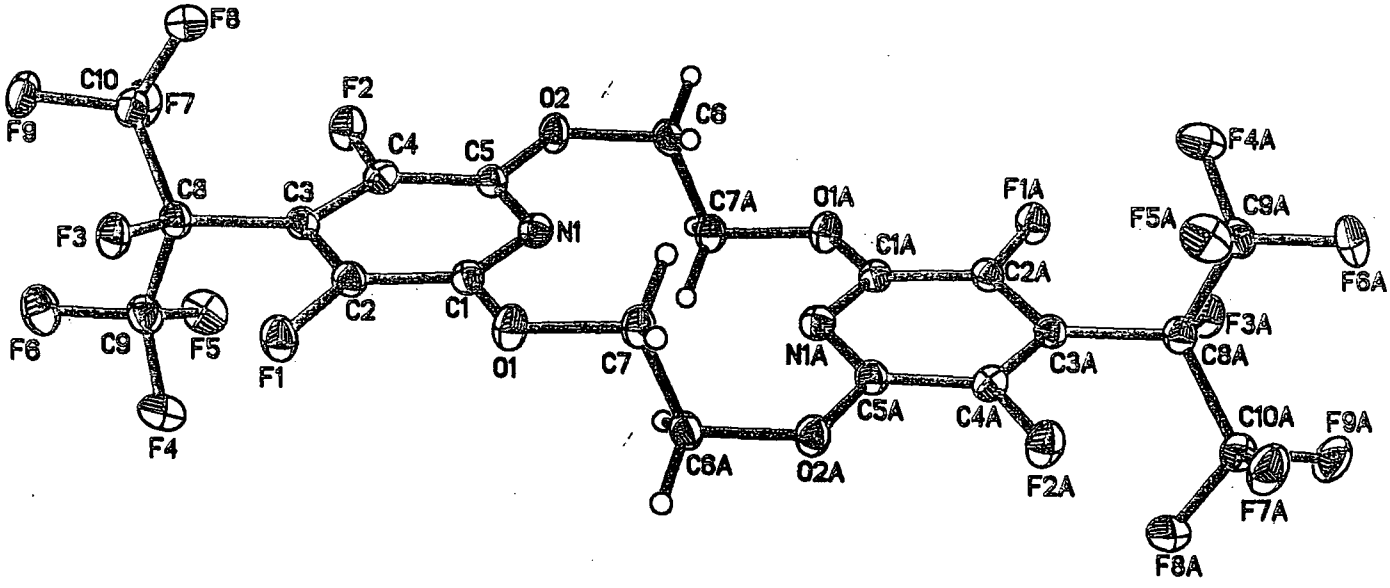


Table 1. Crystal data and structure refinement for (29)

Identification code	s139	
Empirical formula	$C_{20}H_8F_{18}N_2O_4$	
Formula weight	682.28	
Temperature	120.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 14.2011(5) Å	α = 90°.
	b = 8.4725(3) Å	β = 102.114(1)°.
	c = 9.4479(3) Å	γ = 90°.
Volume	1111.45(7) $Å^3$	
Z	2	
Density (calculated)	2.039 Mg/m^3	
Absorption coefficient	0.240 mm^{-1}	
F(000)	672	
Crystal size	0.32 x 0.26 x 0.06 mm^3	
Theta range for data collection	1.47 to 30.31°.	
Index ranges	-19<=h<=19, -11<=k<=11, -13<=l<=12	
Reflections collected	12347	
Independent reflections	3089 [R(int) = 0.0516]	
Completeness to theta = 30.31°	92.9 %	
Absorption correction	None	
Max. and min. transmission	0.9858 and 0.9273	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3089 / 0 / 215	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0429, wR2 = 0.0997	
R indices (all data)	R1 = 0.0643, wR2 = 0.1101	
Largest diff. peak and hole	0.538 and -0.284 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(29)** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
O(1)	5187(1)	1388(2)	2974(1)	20(1)
O(2)	2922(1)	79(2)	-1180(1)	20(1)
N(1)	4077(1)	651(2)	900(2)	17(1)
C(1)	4288(1)	942(2)	2305(2)	16(1)
C(2)	3599(1)	861(2)	3161(2)	16(1)
C(3)	2634(1)	558(2)	2521(2)	16(1)
C(4)	2441(1)	264(2)	1036(2)	18(1)
C(5)	3174(1)	324(2)	264(2)	17(1)
C(6)	3676(1)	154(2)	-1991(2)	19(1)
C(7)	5900(1)	1479(2)	2079(2)	18(1)
C(8)	1861(1)	516(2)	3421(2)	18(1)
C(9)	1717(1)	-1189(2)	3917(2)	22(1)
C(10)	877(1)	1305(2)	2694(2)	23(1)
F(1)	3899(1)	1097(1)	4594(1)	22(1)
F(2)	1545(1)	-65(1)	314(1)	24(1)
F(3)	2167(1)	1377(1)	4671(1)	22(1)
F(4)	2533(1)	-1675(1)	4793(1)	28(1)
F(5)	1518(1)	-2171(1)	2797(1)	29(1)
F(6)	1018(1)	-1274(2)	4652(1)	35(1)
F(7)	282(1)	311(2)	1870(1)	31(1)
F(8)	1034(1)	2539(1)	1901(1)	31(1)
F(9)	445(1)	1825(2)	3727(1)	33(1)

Table 3. Bond lengths [Å] and angles [°] for (29)

O(1)-C(1)	1.354(2)	C(2)-C(3)	1.401(2)	C(8)-C(9)	1.546(3)
O(1)-C(7)	1.450(2)	C(3)-C(4)	1.394(2)	C(8)-C(10)	1.570(3)
O(2)-C(5)	1.352(2)	C(3)-C(8)	1.524(2)	C(9)-F(6)	1.327(2)
O(2)-C(6)	1.442(2)	C(4)-F(2)	1.342(2)	C(9)-F(5)	1.329(2)
N(1)-C(1)	1.321(2)	C(4)-C(5)	1.392(3)	C(9)-F(4)	1.340(2)
N(1)-C(5)	1.326(2)	C(6)-C(7)#1	1.518(3)	C(10)-F(7)	1.324(2)
C(1)-C(2)	1.396(2)	C(7)-C(6)#1	1.518(3)	C(10)-F(9)	1.331(2)
C(2)-F(1)	1.346(2)	C(8)-F(3)	1.379(2)	C(10)-F(8)	1.332(2)

C(1)-O(1)-C(7)	116.60(13)	O(1)-C(7)-C(6)#1	108.49(14)
C(5)-O(2)-C(6)	117.43(13)	F(3)-C(8)-C(3)	109.30(14)
C(1)-N(1)-C(5)	119.24(15)	F(3)-C(8)-C(9)	105.81(14)
N(1)-C(1)-O(1)	120.93(15)	C(3)-C(8)-C(9)	110.35(15)
N(1)-C(1)-C(2)	122.31(15)	F(3)-C(8)-C(10)	103.96(14)
O(1)-C(1)-C(2)	116.73(15)	C(3)-C(8)-C(10)	115.19(14)
F(1)-C(2)-C(1)	117.64(15)	C(9)-C(8)-C(10)	111.61(15)
F(1)-C(2)-C(3)	122.36(15)	F(6)-C(9)-F(5)	108.99(15)
C(1)-C(2)-C(3)	120.00(15)	F(6)-C(9)-F(4)	107.78(15)
C(4)-C(3)-C(2)	115.75(15)	F(5)-C(9)-F(4)	108.13(15)
C(4)-C(3)-C(8)	123.02(15)	F(6)-C(9)-C(8)	111.74(16)
C(2)-C(3)-C(8)	121.21(15)	F(5)-C(9)-C(8)	111.26(15)
F(2)-C(4)-C(5)	118.36(15)	F(4)-C(9)-C(8)	108.81(15)
F(2)-C(4)-C(3)	120.92(16)	F(7)-C(10)-F(9)	107.85(15)
C(5)-C(4)-C(3)	120.71(16)	F(7)-C(10)-F(8)	109.24(15)
N(1)-C(5)-O(2)	121.05(15)	F(9)-C(10)-F(8)	108.04(16)
N(1)-C(5)-C(4)	121.88(16)	F(7)-C(10)-C(8)	112.66(15)
O(2)-C(5)-C(4)	117.05(15)	F(9)-C(10)-C(8)	108.97(15)
O(2)-C(6)-C(7)#1	109.66(15)	F(8)-C(10)-C(8)	109.96(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for (29) The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	16(1)	25(1)	18(1)	-6(1)	5(1)	-3(1)
O(2)	17(1)	30(1)	14(1)	-3(1)	4(1)	1(1)
N(1)	18(1)	15(1)	18(1)	-1(1)	4(1)	0(1)
C(1)	17(1)	13(1)	17(1)	-1(1)	5(1)	0(1)
C(2)	19(1)	17(1)	14(1)	-1(1)	4(1)	0(1)
C(3)	19(1)	13(1)	17(1)	1(1)	7(1)	1(1)
C(4)	16(1)	18(1)	19(1)	-1(1)	3(1)	0(1)
C(5)	19(1)	17(1)	15(1)	0(1)	5(1)	1(1)
C(6)	19(1)	23(1)	15(1)	1(1)	5(1)	0(1)
C(7)	15(1)	21(1)	18(1)	-2(1)	5(1)	-3(1)
C(8)	18(1)	20(1)	16(1)	-2(1)	4(1)	0(1)
C(9)	22(1)	23(1)	21(1)	3(1)	6(1)	-2(1)
C(10)	21(1)	29(1)	21(1)	2(1)	7(1)	6(1)
F(1)	21(1)	31(1)	15(1)	-4(1)	4(1)	-2(1)
F(2)	16(1)	34(1)	20(1)	-5(1)	3(1)	-3(1)
F(3)	23(1)	26(1)	19(1)	-6(1)	7(1)	0(1)
F(4)	30(1)	25(1)	26(1)	7(1)	1(1)	1(1)
F(5)	33(1)	23(1)	29(1)	-2(1)	3(1)	-7(1)
F(6)	32(1)	39(1)	40(1)	10(1)	21(1)	-4(1)
F(7)	17(1)	47(1)	28(1)	-3(1)	2(1)	0(1)
F(8)	33(1)	31(1)	31(1)	11(1)	11(1)	12(1)
F(9)	26(1)	48(1)	27(1)	-1(1)	12(1)	14(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for (**29**)

Atom	x	y	z	U(eq)
H(71)	6386(15)	2160(20)	2580(20)	12(5)
H(72)	5601(14)	1870(20)	1150(20)	13(5)
H(61)	3348(17)	480(30)	-2930(30)	28(6)
H(62)	4180(16)	870(30)	-1550(20)	24(6)

Table 6. Torsion angles [°] for (**29**)

C(5)-N(1)-C(1)-O(1)	-175.33(15)	C(1)-O(1)-C(7)-C(6)#1	-84.91(18)
C(5)-N(1)-C(1)-C(2)	2.5(2)	C(4)-C(3)-C(8)-F(3)	-158.50(15)
C(7)-O(1)-C(1)-N(1)	-1.8(2)	C(2)-C(3)-C(8)-F(3)	23.1(2)
C(7)-O(1)-C(1)-C(2)	-179.69(15)	C(4)-C(3)-C(8)-C(9)	85.5(2)
N(1)-C(1)-C(2)-F(1)	176.55(15)	C(2)-C(3)-C(8)-C(9)	-92.86(19)
O(1)-C(1)-C(2)-F(1)	-5.6(2)	C(4)-C(3)-C(8)-C(10)	-41.9(2)
N(1)-C(1)-C(2)-C(3)	-4.0(3)	C(2)-C(3)-C(8)-C(10)	139.66(17)
O(1)-C(1)-C(2)-C(3)	173.85(15)	F(3)-C(8)-C(9)-F(6)	64.55(19)
F(1)-C(2)-C(3)-C(4)	-177.09(15)	C(3)-C(8)-C(9)-F(6)	-177.33(14)
C(1)-C(2)-C(3)-C(4)	3.5(2)	C(10)-C(8)-C(9)-F(6)	-47.9(2)
F(1)-C(2)-C(3)-C(8)	1.4(3)	F(3)-C(8)-C(9)-F(5)	-173.38(13)
C(1)-C(2)-C(3)-C(8)	-177.95(16)	C(3)-C(8)-C(9)-F(5)	-55.3(2)
C(2)-C(3)-C(4)-F(2)	178.94(15)	C(10)-C(8)-C(9)-F(5)	74.18(19)
C(8)-C(3)-C(4)-F(2)	0.5(3)	F(3)-C(8)-C(9)-F(4)	-54.35(18)
C(2)-C(3)-C(4)-C(5)	-1.8(2)	C(3)-C(8)-C(9)-F(4)	63.77(18)
C(8)-C(3)-C(4)-C(5)	179.70(16)	C(10)-C(8)-C(9)-F(4)	-166.79(14)
C(1)-N(1)-C(5)-O(2)	177.46(15)	F(3)-C(8)-C(10)-F(7)	-152.64(15)
C(1)-N(1)-C(5)-C(4)	-0.6(2)	C(3)-C(8)-C(10)-F(7)	87.81(19)
C(6)-O(2)-C(5)-N(1)	1.2(2)	C(9)-C(8)-C(10)-F(7)	-39.0(2)
C(6)-O(2)-C(5)-C(4)	179.43(15)	F(3)-C(8)-C(10)-F(9)	-32.99(19)
F(2)-C(4)-C(5)-N(1)	179.64(15)	C(3)-C(8)-C(10)-F(9)	-152.55(16)
C(3)-C(4)-C(5)-N(1)	0.4(3)	C(9)-C(8)-C(10)-F(9)	80.61(19)
F(2)-C(4)-C(5)-O(2)	1.5(2)	F(3)-C(8)-C(10)-F(8)	85.25(17)
C(3)-C(4)-C(5)-O(2)	-177.80(15)	C(3)-C(8)-C(10)-F(8)	-34.3(2)
C(5)-O(2)-C(6)-C(7)#1	91.13(18)	C(9)-C(8)-C(10)-F(8)	-161.15(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z

Compound Number:	Name:
(31)	*25,26-diaza-11,23-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-10,12,22,24-tetrafluoro-2,5,8,14,17,20-hexaoxatricyclo[19.3.1.1<9,13>]hexacosa-1(24),9(26),10,12,21(25),22-hexaene*

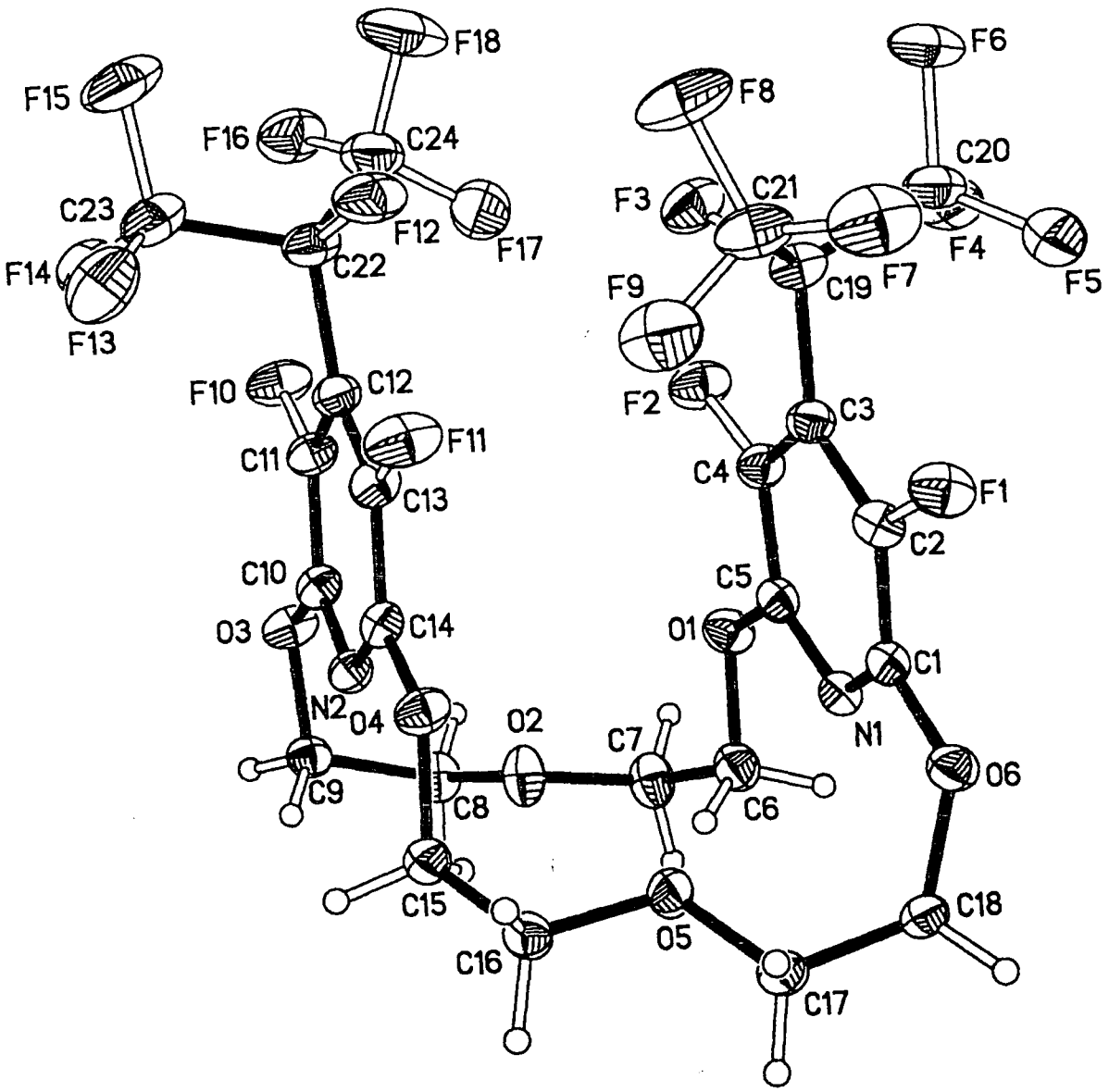


Table 1. Crystal data and structure refinement for (31)

Identification code	s138	
Empirical formula	$C_{24} H_{16} F_{18} N_2 O_6$	
Formula weight	770.39	
Temperature	120.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.0542(4) Å	α= 90°.
	b = 14.1784(5) Å	β= 102.96(1)°.
	c = 18.7552(6) Å	γ = 90°.
Volume	2864.64(17) $Å^3$	
Z	4	
Density (calculated)	1.786 Mg/m^3	
Absorption coefficient	0.202 mm^{-1}	
F(000)	1536	
Crystal size	0.36 x 0.32 x 0.32 mm^3	
Theta range for data collection	1.89 to 30.20°.	
Index ranges	-14<=h<=14, -19<=k<=19, -26<=l<=26	
Reflections collected	33009	
Independent reflections	7801 [R(int) = 0.0287]	
Completeness to theta = 30.20°	91.6 %	
Absorption correction	None	
Max. and min. transmission	0.9382 and 0.9308	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7801 / 0 / 515	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0439, wR2 = 0.1101	
R indices (all data)	R1 = 0.0532, wR2 = 0.1175	
Largest diff. peak and hole	0.674 and -0.314 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(31)** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
O(1)	4876(1)	7654(1)	7477(1)	25(1)
O(2)	3569(1)	8946(1)	6412(1)	27(1)
O(3)	5317(1)	10202(1)	5903(1)	26(1)
O(4)	5381(1)	10492(1)	8395(1)	24(1)
O(5)	3611(1)	9417(1)	8971(1)	25(1)
O(6)	4436(1)	7757(1)	9876(1)	24(1)
N(1)	4659(1)	7656(1)	8676(1)	20(1)
N(2)	5308(1)	10370(1)	7146(1)	20(1)
C(1)	5162(1)	7696(1)	9383(1)	20(1)
C(2)	6447(1)	7669(1)	9647(1)	22(1)
C(3)	7243(1)	7654(1)	9160(1)	22(1)
C(4)	6678(1)	7644(1)	8420(1)	23(1)
C(5)	5379(1)	7649(1)	8200(1)	21(1)
C(6)	3538(2)	7753(1)	7273(1)	25(1)
C(7)	3209(2)	7995(1)	6472(1)	27(1)
C(8)	3416(2)	9271(1)	5683(1)	25(1)
C(9)	3974(1)	10243(1)	5711(1)	22(1)
C(10)	5907(1)	10207(1)	6616(1)	21(1)
C(11)	7184(1)	10060(1)	6767(1)	23(1)
C(12)	7892(1)	10086(1)	7481(1)	23(1)
C(13)	7234(1)	10234(1)	8025(1)	23(1)
C(14)	5947(1)	10361(1)	7835(1)	20(1)
C(15)	4050(1)	10649(1)	8214(1)	23(1)
C(16)	3579(2)	10414(1)	8887(1)	23(1)
C(17)	3044(2)	9108(1)	9540(1)	25(1)
C(18)	3153(1)	8048(1)	9592(1)	25(1)
C(19)	8658(1)	7613(1)	9419(1)	25(1)
C(20)	9087(2)	6579(1)	9584(1)	32(1)
C(21)	9224(2)	8277(2)	10073(1)	35(1)
C(22)	9307(2)	10057(1)	7648(1)	29(1)
C(23)	9794(2)	11049(2)	7493(1)	35(1)
C(24)	9881(2)	9255(2)	7259(1)	39(1)
F(1)	6909(1)	7653(1)	10374(1)	29(1)
F(2)	7323(1)	7617(1)	7891(1)	32(1)
F(3)	9207(1)	7907(1)	8867(1)	34(1)
F(4)	8741(1)	6071(1)	8980(1)	39(1)
F(5)	8595(1)	6193(1)	10100(1)	41(1)
F(6)	10326(1)	6529(1)	9802(1)	48(1)
F(7)	9275(1)	7867(1)	10717(1)	49(1)
F(8)	10387(1)	8501(1)	10051(1)	50(1)
F(9)	8572(1)	9069(1)	10043(1)	46(1)
F(10)	7726(1)	9914(1)	6199(1)	32(1)
F(11)	7798(1)	10295(1)	8740(1)	37(1)
F(12)	9775(1)	9909(1)	8384(1)	40(1)
F(13)	9440(1)	11676(1)	7937(1)	47(1)
F(14)	9341(1)	11326(1)	6810(1)	37(1)
F(15)	11031(1)	11060(1)	7620(1)	53(1)
F(16)	10078(1)	9513(1)	6612(1)	43(1)
F(17)	9149(1)	8501(1)	7164(1)	51(1)
F(18)	10981(1)	9005(1)	7676(1)	61(1)

Table 3. Bond lengths [Å] and angles [°] for **(31)**

O(1)-C(5)	1.3456(18)	C(2)-C(3)	1.403(2)	C(19)-C(20)	1.551(2)
O(1)-C(6)	1.4497(19)	C(3)-C(4)	1.388(2)	C(19)-C(21)	1.563(2)
O(2)-C(7)	1.4165(19)	C(3)-C(19)	1.531(2)	C(20)-F(4)	1.325(2)
O(2)-C(8)	1.4173(19)	C(4)-F(2)	1.3473(17)	C(20)-F(5)	1.329(2)
O(3)-C(10)	1.3503(18)	C(4)-C(5)	1.402(2)	C(20)-F(6)	1.3409(19)
O(3)-C(9)	1.4476(18)	C(6)-C(7)	1.505(2)	C(21)-F(9)	1.329(2)
O(4)-C(14)	1.3504(17)	C(8)-C(9)	1.507(2)	C(21)-F(7)	1.330(2)
O(4)-C(15)	1.4511(18)	C(10)-C(11)	1.391(2)	C(21)-F(8)	1.333(2)
O(5)-C(16)	1.4215(18)	C(11)-F(10)	1.3504(16)	C(22)-F(12)	1.3776(19)
O(5)-C(17)	1.4225(17)	C(11)-C(12)	1.392(2)	C(22)-C(23)	1.555(3)
O(6)-C(1)	1.3555(17)	C(12)-C(13)	1.394(2)	C(22)-C(24)	1.561(3)
O(6)-C(18)	1.4581(18)	C(12)-C(22)	1.526(2)	C(23)-F(14)	1.325(2)
N(1)-C(1)	1.3202(19)	C(13)-F(11)	1.3489(17)	C(23)-F(15)	1.334(2)
N(1)-C(5)	1.3219(19)	C(13)-C(14)	1.398(2)	C(23)-F(13)	1.336(2)
N(2)-C(14)	1.3259(19)	C(15)-C(16)	1.506(2)	C(24)-F(17)	1.329(2)
N(2)-C(10)	1.3326(18)	C(17)-C(18)	1.510(2)	C(24)-F(16)	1.332(2)
C(1)-C(2)	1.396(2)	C(19)-F(3)	1.3768(18)	C(24)-F(18)	1.337(2)
C(2)-F(1)	1.3444(17)				

C(5)-O(1)-C(6)	115.63(12)	O(4)-C(14)-C(13)	116.23(13)
C(7)-O(2)-C(8)	114.23(12)	O(4)-C(15)-C(16)	107.05(12)
C(10)-O(3)-C(9)	119.12(11)	O(5)-C(16)-C(15)	107.99(12)
C(14)-O(4)-C(15)	117.50(11)	O(5)-C(17)-C(18)	108.24(12)
C(16)-O(5)-C(17)	112.65(11)	O(6)-C(18)-C(17)	111.21(13)
C(1)-O(6)-C(18)	116.45(11)	F(3)-C(19)-C(3)	109.94(13)
C(1)-N(1)-C(5)	119.80(13)	F(3)-C(19)-C(20)	105.73(13)
C(14)-N(2)-C(10)	118.68(13)	C(3)-C(19)-C(20)	110.13(13)
N(1)-C(1)-O(6)	120.51(13)	F(3)-C(19)-C(21)	103.98(13)
N(1)-C(1)-C(2)	121.36(13)	C(3)-C(19)-C(21)	115.26(13)
O(6)-C(1)-C(2)	118.13(13)	C(20)-C(19)-C(21)	111.21(14)
F(1)-C(2)-C(1)	118.94(13)	F(4)-C(20)-F(5)	108.18(15)
F(1)-C(2)-C(3)	120.58(13)	F(4)-C(20)-F(6)	108.16(14)
C(1)-C(2)-C(3)	120.47(14)	F(5)-C(20)-F(6)	108.27(15)
C(4)-C(3)-C(2)	116.27(14)	F(4)-C(20)-C(19)	109.01(14)
C(4)-C(3)-C(19)	121.06(13)	F(5)-C(20)-C(19)	112.27(14)
C(2)-C(3)-C(19)	122.63(14)	F(6)-C(20)-C(19)	110.84(14)
F(2)-C(4)-C(3)	122.84(14)	F(9)-C(21)-F(7)	108.66(15)
F(2)-C(4)-C(5)	117.39(14)	F(9)-C(21)-F(8)	108.37(16)
C(3)-C(4)-C(5)	119.77(14)	F(7)-C(21)-F(8)	106.74(15)
N(1)-C(5)-O(1)	120.33(13)	F(9)-C(21)-C(19)	110.97(15)
N(1)-C(5)-C(4)	122.21(14)	F(7)-C(21)-C(19)	112.24(16)
O(1)-C(5)-C(4)	117.45(13)	F(8)-C(21)-C(19)	109.71(14)
O(1)-C(6)-C(7)	106.80(13)	F(12)-C(22)-C(12)	110.29(13)
O(2)-C(7)-C(6)	106.61(13)	F(12)-C(22)-C(23)	104.97(14)
O(2)-C(8)-C(9)	107.74(12)	C(12)-C(22)-C(23)	108.61(14)
O(3)-C(9)-C(8)	111.14(13)	F(12)-C(22)-C(24)	104.81(14)
N(2)-C(10)-O(3)	121.99(13)	C(12)-C(22)-C(24)	115.43(15)
N(2)-C(10)-C(11)	121.67(13)	C(23)-C(22)-C(24)	112.17(14)
O(3)-C(10)-C(11)	116.32(13)	F(14)-C(23)-F(15)	108.60(15)
F(10)-C(11)-C(12)	120.62(13)	F(14)-C(23)-F(13)	107.78(16)
F(10)-C(11)-C(10)	118.18(13)	F(15)-C(23)-F(13)	108.20(15)
C(12)-C(11)-C(10)	121.18(13)	F(14)-C(23)-C(22)	112.17(15)
C(11)-C(12)-C(13)	115.78(14)	F(15)-C(23)-C(22)	111.16(16)
C(11)-C(12)-C(22)	121.74(13)	F(13)-C(23)-C(22)	108.82(14)
C(13)-C(12)-C(22)	122.19(14)	F(17)-C(24)-F(16)	108.49(18)
F(11)-C(13)-C(12)	122.42(14)	F(17)-C(24)-F(18)	108.16(17)
F(11)-C(13)-C(14)	117.52(13)	F(16)-C(24)-F(18)	107.01(15)
C(12)-C(13)-C(14)	120.02(13)	F(17)-C(24)-C(22)	110.51(14)
N(2)-C(14)-O(4)	121.17(13)	F(16)-C(24)-C(22)	113.09(16)
N(2)-C(14)-C(13)	122.59(13)	F(18)-C(24)-C(22)	109.41(17)

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for **(31)** The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	25(1)	28(1)	22(1)	0(1)	6(1)	5(1)
O(2)	39(1)	21(1)	20(1)	0(1)	2(1)	-6(1)
O(3)	20(1)	40(1)	18(1)	-3(1)	4(1)	-2(1)
O(4)	20(1)	34(1)	18(1)	0(1)	6(1)	-1(1)
O(5)	30(1)	22(1)	27(1)	5(1)	16(1)	4(1)
O(6)	22(1)	30(1)	21(1)	6(1)	7(1)	6(1)
N(1)	20(1)	18(1)	23(1)	2(1)	5(1)	2(1)
N(2)	19(1)	21(1)	19(1)	-1(1)	5(1)	-2(1)
C(1)	20(1)	18(1)	24(1)	1(1)	7(1)	2(1)
C(2)	21(1)	23(1)	21(1)	-1(1)	3(1)	3(1)
C(3)	18(1)	20(1)	28(1)	-2(1)	5(1)	1(1)
C(4)	22(1)	23(1)	26(1)	-1(1)	10(1)	1(1)
C(5)	23(1)	17(1)	24(1)	0(1)	6(1)	2(1)
C(6)	24(1)	23(1)	26(1)	1(1)	3(1)	0(1)
C(7)	33(1)	21(1)	25(1)	-2(1)	0(1)	-4(1)
C(8)	27(1)	27(1)	18(1)	-2(1)	0(1)	-2(1)
C(9)	20(1)	25(1)	19(1)	1(1)	2(1)	1(1)
C(10)	20(1)	23(1)	19(1)	-3(1)	4(1)	-3(1)
C(11)	21(1)	29(1)	21(1)	-2(1)	9(1)	-1(1)
C(12)	18(1)	27(1)	24(1)	2(1)	5(1)	0(1)
C(13)	21(1)	30(1)	18(1)	2(1)	3(1)	-2(1)
C(14)	21(1)	20(1)	19(1)	0(1)	6(1)	-3(1)
C(15)	21(1)	24(1)	24(1)	4(1)	7(1)	2(1)
C(16)	25(1)	22(1)	25(1)	2(1)	11(1)	4(1)
C(17)	24(1)	29(1)	26(1)	7(1)	14(1)	7(1)
C(18)	19(1)	31(1)	28(1)	9(1)	10(1)	3(1)
C(19)	19(1)	31(1)	26(1)	-3(1)	7(1)	-1(1)
C(20)	18(1)	35(1)	43(1)	0(1)	7(1)	5(1)
C(21)	23(1)	49(1)	34(1)	-12(1)	5(1)	-6(1)
C(22)	18(1)	42(1)	25(1)	6(1)	3(1)	1(1)
C(23)	23(1)	49(1)	32(1)	2(1)	4(1)	-9(1)
C(24)	25(1)	49(1)	45(1)	8(1)	12(1)	8(1)
F(1)	26(1)	38(1)	21(1)	-2(1)	2(1)	5(1)
F(2)	27(1)	44(1)	27(1)	-2(1)	13(1)	2(1)
F(3)	28(1)	45(1)	30(1)	1(1)	12(1)	-5(1)
F(4)	33(1)	34(1)	53(1)	-11(1)	17(1)	4(1)
F(5)	32(1)	47(1)	44(1)	15(1)	8(1)	5(1)
F(6)	19(1)	52(1)	69(1)	6(1)	5(1)	10(1)
F(7)	39(1)	80(1)	26(1)	-7(1)	1(1)	-2(1)
F(8)	24(1)	70(1)	55(1)	-25(1)	10(1)	-18(1)
F(9)	41(1)	40(1)	57(1)	-21(1)	12(1)	-7(1)
F(10)	24(1)	51(1)	24(1)	-6(1)	11(1)	0(1)
F(11)	24(1)	66(1)	18(1)	2(1)	1(1)	-1(1)
F(12)	23(1)	67(1)	28(1)	13(1)	2(1)	5(1)
F(13)	48(1)	50(1)	42(1)	-13(1)	8(1)	-20(1)
F(14)	30(1)	47(1)	33(1)	9(1)	6(1)	-7(1)
F(15)	21(1)	82(1)	53(1)	14(1)	1(1)	-16(1)
F(16)	33(1)	57(1)	43(1)	0(1)	20(1)	3(1)
F(17)	46(1)	36(1)	79(1)	5(1)	32(1)	8(1)
F(18)	31(1)	91(1)	62(1)	17(1)	12(1)	30(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for (**31**)

Atom	x	y	z	U(eq)
H(61)	3290(18)	8260(14)	7543(10)	23(5)
H(62)	3190(20)	7170(16)	7368(11)	31(5)
H(71)	3630(20)	7566(15)	6194(12)	32(5)
H(72)	2310(20)	7907(15)	6296(11)	29(5)
H(81)	3824(19)	8862(15)	5394(11)	27(5)
H(82)	2520(20)	9302(16)	5435(13)	40(6)
H(91)	3660(18)	10632(14)	6046(10)	22(4)
H(92)	3780(18)	10532(14)	5224(11)	23(5)
H(151)	3660(20)	10249(15)	7820(12)	30(5)
H(152)	3877(19)	11291(16)	8077(11)	29(5)
H(161)	2732(18)	10648(13)	8835(10)	21(4)
H(162)	4080(20)	10724(16)	9322(12)	34(5)
H(171)	3428(19)	9396(14)	9999(11)	26(5)
H(172)	2190(19)	9270(14)	9434(11)	24(5)
H(181)	2826(18)	7751(14)	9118(11)	25(5)
H(182)	2731(19)	7809(15)	9943(11)	29(5)

Table 6. Torsion angles [°] for **(31)**

C(5)-N(1)-C(1)-O(6)	176.33(13)	C(14)-O(4)-C(15)-C(16)	159.21(13)
C(5)-N(1)-C(1)-C(2)	-4.3(2)	C(17)-O(5)-C(16)-C(15)	-172.80(13)
C(18)-O(6)-C(1)-N(1)	-17.2(2)	O(4)-C(15)-C(16)-O(5)	-72.88(15)
C(18)-O(6)-C(1)-C(2)	163.35(13)	C(16)-O(5)-C(17)-C(18)	-178.83(13)
N(1)-C(1)-C(2)-F(1)	-175.94(13)	C(1)-O(6)-C(18)-C(17)	-83.71(16)
O(6)-C(1)-C(2)-F(1)	3.5(2)	O(5)-C(17)-C(18)-O(6)	69.53(17)
N(1)-C(1)-C(2)-C(3)	3.8(2)	C(4)-C(3)-C(19)-F(3)	21.7(2)
O(6)-C(1)-C(2)-C(3)	-176.78(13)	C(2)-C(3)-C(19)-F(3)	-160.70(14)
F(1)-C(2)-C(3)-C(4)	178.14(13)	C(4)-C(3)-C(19)-C(20)	-94.40(17)
C(1)-C(2)-C(3)-C(4)	-1.6(2)	C(2)-C(3)-C(19)-C(20)	83.18(18)
F(1)-C(2)-C(3)-C(19)	0.4(2)	C(4)-C(3)-C(19)-C(21)	138.80(16)
C(1)-C(2)-C(3)-C(19)	-179.29(14)	C(2)-C(3)-C(19)-C(21)	-43.6(2)
C(2)-C(3)-C(4)-F(2)	-179.14(14)	F(3)-C(19)-C(20)-F(4)	-58.52(16)
C(19)-C(3)-C(4)-F(2)	-1.4(2)	C(3)-C(19)-C(20)-F(4)	60.21(17)
C(2)-C(3)-C(4)-C(5)	0.0(2)	C(21)-C(19)-C(20)-F(4)	-170.76(13)
C(19)-C(3)-C(4)-C(5)	177.78(14)	F(3)-C(19)-C(20)-F(5)	-178.37(13)
C(1)-N(1)-C(5)-O(1)	-176.81(13)	C(3)-C(19)-C(20)-F(5)	-59.64(18)
C(1)-N(1)-C(5)-C(4)	2.7(2)	C(21)-C(19)-C(20)-F(5)	69.39(18)
C(6)-O(1)-C(5)-N(1)	5.36(19)	F(3)-C(19)-C(20)-F(6)	60.41(18)
C(6)-O(1)-C(5)-C(4)	-174.15(13)	C(3)-C(19)-C(20)-F(6)	179.14(14)
F(2)-C(4)-C(5)-N(1)	178.68(13)	C(21)-C(19)-C(20)-F(6)	-51.83(19)
C(3)-C(4)-C(5)-N(1)	-0.5(2)	F(3)-C(19)-C(21)-F(9)	86.94(16)
F(2)-C(4)-C(5)-O(1)	-1.8(2)	C(3)-C(19)-C(21)-F(9)	-33.5(2)
C(3)-C(4)-C(5)-O(1)	178.95(13)	C(20)-C(19)-C(21)-F(9)	-159.72(15)
C(5)-O(1)-C(6)-C(7)	165.54(12)	F(3)-C(19)-C(21)-F(7)	-151.27(14)
C(8)-O(2)-C(7)-C(6)	175.22(13)	C(3)-C(19)-C(21)-F(7)	88.32(18)
O(1)-C(6)-C(7)-O(2)	-73.68(16)	C(20)-C(19)-C(21)-F(7)	-37.92(19)
C(7)-O(2)-C(8)-C(9)	-173.46(13)	F(3)-C(19)-C(21)-F(8)	-32.8(2)
C(10)-O(3)-C(9)-C(8)	-87.71(16)	C(3)-C(19)-C(21)-F(8)	-153.18(15)
O(2)-C(8)-C(9)-O(3)	73.19(16)	C(20)-C(19)-C(21)-F(8)	80.57(19)
C(14)-N(2)-C(10)-O(3)	179.77(13)	C(11)-C(12)-C(22)-F(12)	-168.41(15)
C(14)-N(2)-C(10)-C(11)	-2.1(2)	C(13)-C(12)-C(22)-F(12)	18.0(2)
C(9)-O(3)-C(10)-N(2)	-8.7(2)	C(11)-C(12)-C(22)-C(23)	77.07(19)
C(9)-O(3)-C(10)-C(11)	173.07(13)	C(13)-C(12)-C(22)-C(23)	-96.49(18)
N(2)-C(10)-C(11)-F(10)	-179.02(13)	C(11)-C(12)-C(22)-C(24)	-49.9(2)
O(3)-C(10)-C(11)-F(10)	-0.8(2)	C(13)-C(12)-C(22)-C(24)	136.56(16)
N(2)-C(10)-C(11)-C(12)	-0.6(2)	F(12)-C(22)-C(23)-F(14)	-175.25(14)
O(3)-C(10)-C(11)-C(12)	177.59(14)	C(12)-C(22)-C(23)-F(14)	-57.29(19)
F(10)-C(11)-C(12)-C(13)	-179.45(14)	C(24)-C(22)-C(23)-F(14)	71.50(19)
C(10)-C(11)-C(12)-C(13)	2.2(2)	F(12)-C(22)-C(23)-F(15)	62.95(18)
F(10)-C(11)-C(12)-C(22)	6.6(2)	C(12)-C(22)-C(23)-F(15)	-179.09(14)
C(10)-C(11)-C(12)-C(22)	-171.74(15)	C(24)-C(22)-C(23)-F(15)	-50.3(2)
C(11)-C(12)-C(13)-F(11)	-178.63(15)	F(12)-C(22)-C(23)-F(13)	-56.10(17)
C(22)-C(12)-C(13)-F(11)	-4.7(2)	C(12)-C(22)-C(23)-F(13)	61.86(18)
C(11)-C(12)-C(13)-C(14)	-1.2(2)	C(24)-C(22)-C(23)-F(13)	-169.35(15)
C(22)-C(12)-C(13)-C(14)	172.76(15)	F(12)-C(22)-C(24)-F(17)	90.14(18)
C(10)-N(2)-C(14)-O(4)	-177.95(13)	C(12)-C(22)-C(24)-F(17)	-31.4(2)
C(10)-N(2)-C(14)-C(13)	3.2(2)	C(23)-C(22)-C(24)-F(17)	-156.52(15)
C(15)-O(4)-C(14)-N(2)	-0.4(2)	F(12)-C(22)-C(24)-F(16)	-148.01(15)
C(15)-O(4)-C(14)-C(13)	178.53(13)	C(12)-C(22)-C(24)-F(16)	90.45(19)
F(11)-C(13)-C(14)-N(2)	176.04(14)	C(23)-C(22)-C(24)-F(16)	-34.7(2)
C(12)-C(13)-C(14)-N(2)	-1.6(2)	F(12)-C(22)-C(24)-F(18)	-28.8(2)
F(11)-C(13)-C(14)-O(4)	-2.9(2)	C(12)-C(22)-C(24)-F(18)	-150.37(15)
C(12)-C(13)-C(14)-O(4)	179.55(14)	C(23)-C(22)-C(24)-F(18)	84.50(19)

Compound Number:	Name:
(40)	*2,6-dibromo-3-fluoro-5-methoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*

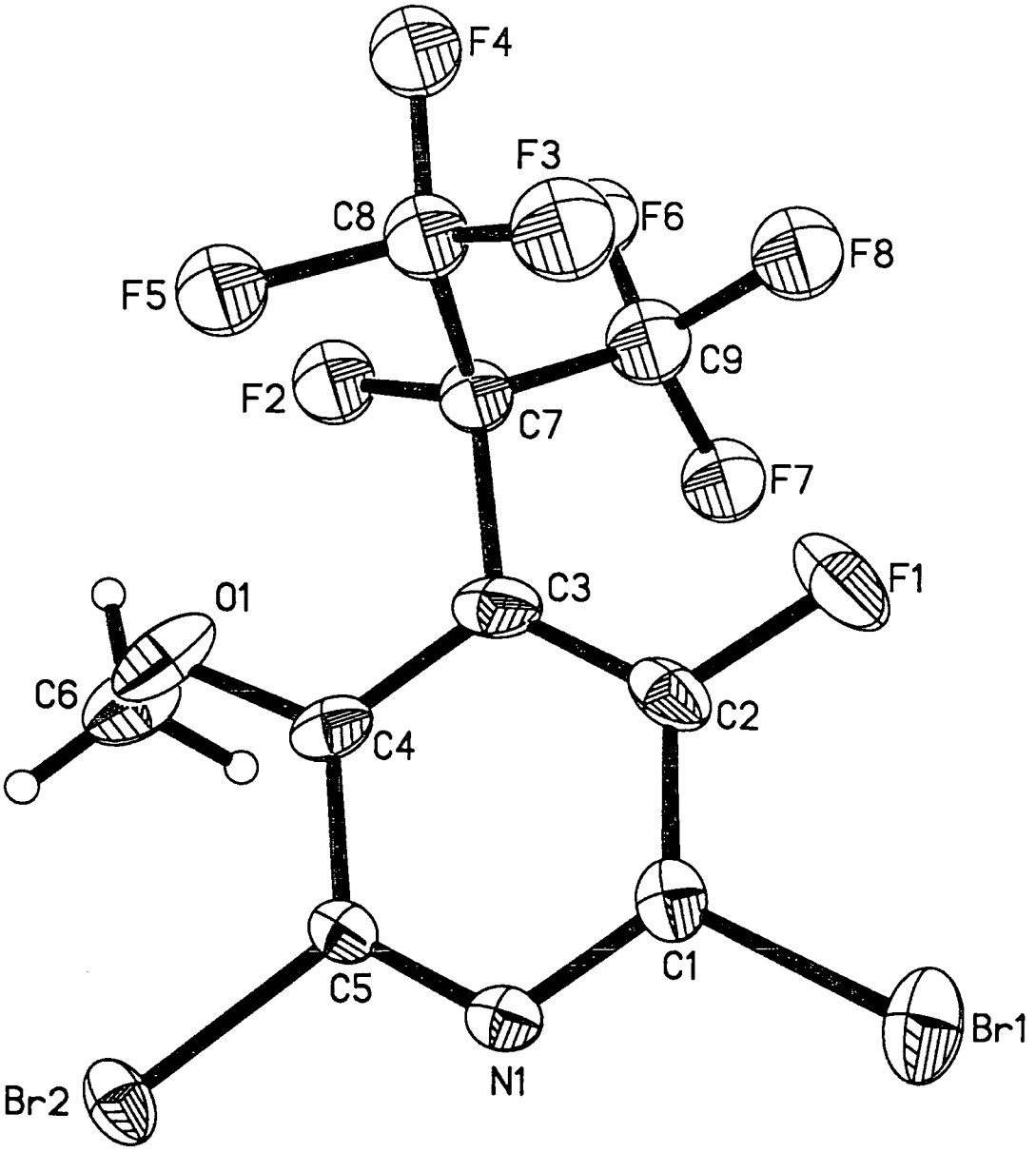


Table 1. Crystal data and structure refinement for **(40)**

Identification code	s194s	
Empirical formula	C9 H3 Br2 F8 N O	
Formula weight	452.94	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2(1)/c	
Unit cell dimensions	a = 10.446(2) Å	α= 90°.
	b = 7.122(1) Å	β= 93.71(3)°.
	c = 17.251(4) Å	γ = 90°.
Volume	1280.8(4) $Å^3$	
Z	4	
Density (calculated)	2.349 Mg/m^3	
Absorption coefficient	6.424 mm^{-1}	
F(000)	856	
Crystal size	0.50 x 0.32 x 0.26 mm^3	
Theta range for data collection	1.95 to 27.50°.	
Index ranges	-13<=h<=13, -9<=k<=9, -22<=l<=22	
Reflections collected	12605	
Independent reflections	2941 [R(int) = 0.0321]	
Completeness to theta = 27.50°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2859 and 0.1415	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2941 / 0 / 176	
Goodness-of-fit on F^2	1.008	
Final R indices [I>2sigma(I)]	R1 = 0.0528, wR2 = 0.1338	
R indices (all data)	R1 = 0.0677, wR2 = 0.1435	
Largest diff. peak and hole	1.341 and -1.793 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(40)** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	11564(1)	8405(1)	8186(1)	48(1)
Br(2)	10184(1)	6911(1)	11125(1)	34(1)
N(1)	10581(4)	7670(6)	9602(2)	25(1)
O(1)	7464(4)	7660(6)	10415(3)	50(1)
C(1)	10257(6)	8095(7)	8871(3)	29(1)
C(2)	8989(6)	8321(7)	8604(3)	35(1)
C(3)	7996(6)	8142(8)	9095(4)	35(1)
C(4)	8335(5)	7704(7)	9872(3)	30(1)
C(5)	9656(5)	7478(7)	10081(3)	24(1)
C(6)	7084(7)	5823(10)	10685(5)	50(2)
F(1)	8727(5)	8748(6)	7854(2)	59(1)
F(2)	5746(5)	7484(8)	9412(3)	47(1)
F(2')	6929(13)	10030(20)	8003(8)	51(3)
F(3)	6832(6)	11405(9)	8397(4)	54(1)
F(3')	5214(15)	8750(20)	9558(9)	61(4)
F(4)	5032(7)	10887(11)	8654(4)	49(2)
F(4')	4792(13)	10430(20)	8731(7)	32(3)
F(5)	6345(6)	10982(9)	9653(4)	45(1)
F(5')	6655(12)	11379(17)	9464(7)	33(3)
F(6)	4836(6)	6867(9)	8137(4)	43(2)
F(6')	4879(12)	7470(20)	7978(7)	34(3)
F(7)	6692(6)	5740(9)	8031(4)	49(1)
F(7')	6812(13)	6360(20)	7730(9)	49(3)
F(8)	6220(6)	8404(8)	7498(3)	53(1)
F(8')	6122(13)	5600(20)	8842(8)	53(3)
C(7)	6518(8)	8315(12)	8885(5)	33(2)
C(7')	6766(18)	8740(30)	8624(11)	27(4)
C(8)	6188(10)	10472(14)	8861(6)	41(2)
C(8')	5930(17)	10020(30)	9113(10)	24(3)
C(9)	6087(7)	7308(11)	8149(4)	48(2)

Table 3. Bond lengths [Å] and angles [°] for (40)

Br(1)-C(1)	1.875(6)
Br(2)-C(5)	1.893(5)
N(1)-C(5)	1.318(7)
N(1)-C(1)	1.319(7)
O(1)-C(4)	1.347(7)
O(1)-C(6)	1.453(8)
C(1)-C(2)	1.383(8)
C(2)-F(1)	1.340(6)
C(2)-C(3)	1.388(9)
C(3)-C(4)	1.399(8)
C(3)-C(7')	1.53(2)
C(3)-C(7)	1.57(1)
C(4)-C(5)	1.412(7)
C(5)-N(1)-C(1)	118.0(5)
C(4)-O(1)-C(6)	117.1(5)
N(1)-C(1)-C(2)	121.7(5)
N(1)-C(1)-Br(1)	118.5(4)
C(2)-C(1)-Br(1)	119.8(4)
F(1)-C(2)-C(1)	118.7(6)
F(1)-C(2)-C(3)	119.8(5)
C(1)-C(2)-C(3)	121.6(5)
C(2)-C(3)-C(4)	116.9(5)
O(1)-C(4)-C(3)	122.0(5)
O(1)-C(4)-C(5)	120.9(5)
C(3)-C(4)-C(5)	116.9(5)
N(1)-C(5)-C(4)	124.9(5)
N(1)-C(5)-Br(2)	116.0(4)
C(4)-C(5)-Br(2)	119.1(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for (**40**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	63(1)	41(1)	42(1)	1(1)	21(1)	-4(1)
Br(2)	54(1)	23(1)	25(1)	-1(1)	-5(1)	1(1)
N(1)	27(2)	18(2)	30(2)	-2(2)	-3(2)	1(2)
O(1)	39(2)	30(2)	83(4)	-1(2)	27(2)	7(2)
C(1)	40(3)	19(2)	28(2)	-2(2)	4(2)	-1(2)
C(2)	53(4)	23(3)	29(3)	-3(2)	-12(2)	12(2)
C(3)	34(3)	27(3)	44(3)	-13(2)	-13(2)	10(2)
C(4)	27(3)	16(2)	46(3)	-6(2)	1(2)	4(2)
C(5)	29(3)	15(2)	26(2)	-2(2)	-5(2)	2(2)
C(6)	40(4)	42(4)	71(5)	11(3)	19(3)	6(3)
F(1)	95(3)	47(2)	31(2)	0(2)	-19(2)	22(2)

Table 5. Hydrogen coordinates ($x 10^4$) and isotropic displacement parameters ($Å^2 x 10^3$) for (**40**).

	x	y	z	U(eq)
H(61)	6146	5724	10641	60
H(62)	7395	5660	11229	60
H(63)	7453	4847	10367	60

Compound Number:	Name:
(41)	*2,6-dibromo-3,5-dimethoxy-4-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-pyridine*

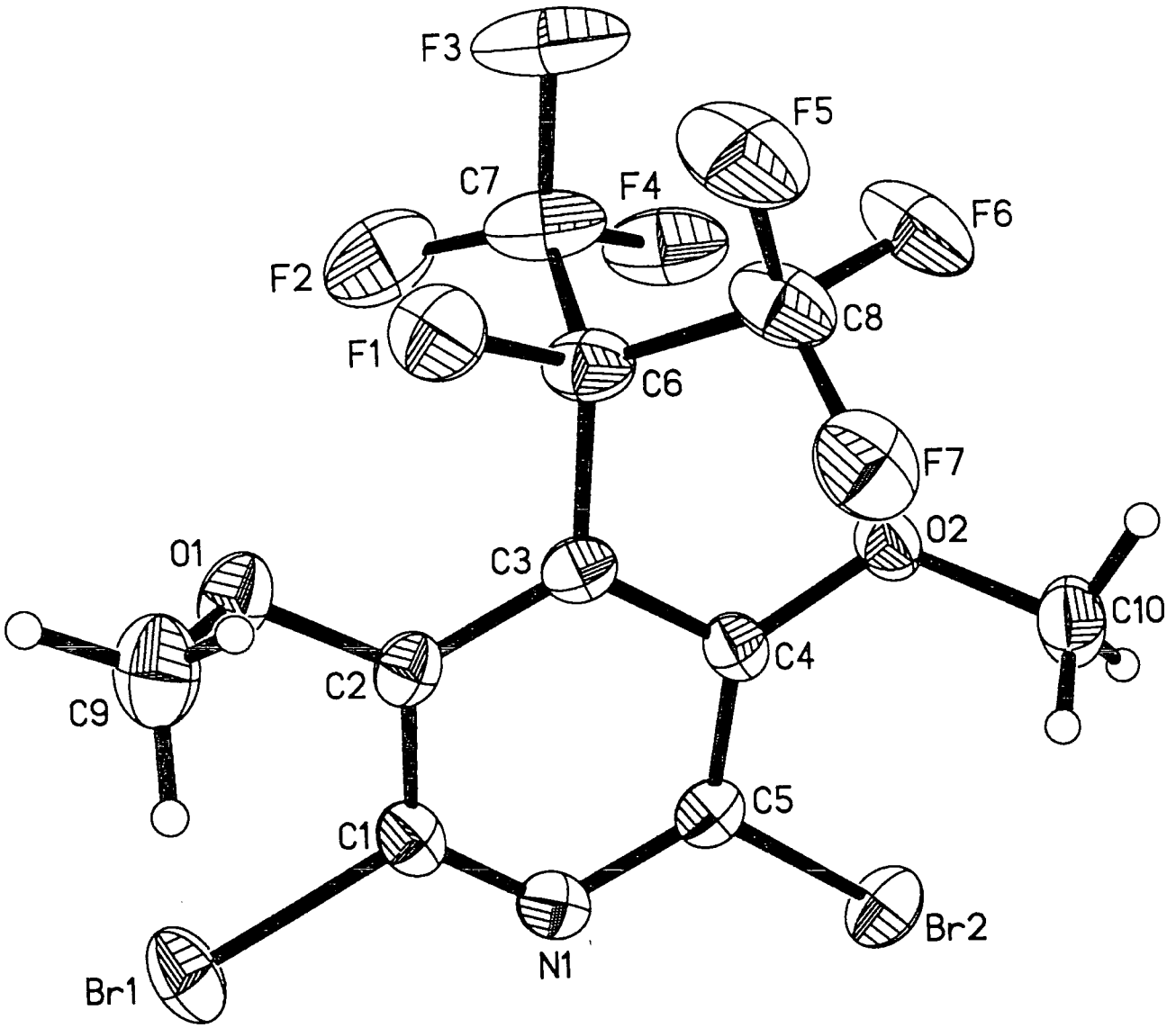


Table 1. Crystal data and structure refinement for **(41)**

Identification code	s197	
Empirical formula	$C_{10} H_6 Br_2 F_7 N O_2$	
Formula weight	464.98	
Temperature	120(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P 2_1/c$	
Unit cell dimensions	a = 8.7159(2) Å	α= 90°.
	b = 12.5425(3) Å	β= 91.50(1)°.
	c = 12.8367(3) Å	γ = 90°.
Volume	1402.82(6) $Å^3$	
Z	4	
Density (calculated)	2.202 Mg/m^3	
Absorption coefficient	5.864 mm^{-1}	
F(000)	888	
Crystal size	0.30 x 0.15 x 0.06 mm^3	
Theta range for data collection	2.27 to 30.55°.	
Index ranges	-10<=h<=12, -17<=k<=16, -17<=l<=17	
Reflections collected	16148	
Independent reflections	3888 [R(int) = 0.0426]	
Completeness to theta = 30.55°	90.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7199 and 0.2722	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3888 / 0 / 223	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0321, wR2 = 0.0634	
R indices (all data)	R1 = 0.0518, wR2 = 0.0689	
Largest diff. peak and hole	0.627 and -0.640 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (**41**) U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Br(1)	6727(1)	8044(1)	11328(1)	34(1)
Br(2)	3147(1)	4514(1)	11223(1)	28(1)
F(1)	2739(2)	8616(1)	8087(1)	35(1)
F(2)	1134(2)	9112(2)	9762(2)	50(1)
F(3)	-318(2)	8861(2)	8398(2)	56(1)
F(4)	-252(2)	7690(2)	9625(1)	42(1)
F(5)	1189(2)	7726(2)	6783(1)	46(1)
F(6)	41(2)	6629(2)	7766(1)	41(1)
F(7)	2428(2)	6375(2)	7403(1)	38(1)
N(1)	4771(2)	6359(2)	11003(2)	21(1)
O(1)	4562(2)	8863(1)	9616(2)	27(1)
O(2)	1367(2)	5754(1)	9399(1)	24(1)
C(1)	5068(3)	7316(2)	10649(2)	22(1)
C(2)	4228(3)	7831(2)	9855(2)	21(1)
C(3)	2995(3)	7271(2)	9393(2)	19(1)
C(4)	2652(3)	6246(2)	9770(2)	19(1)
C(5)	3587(3)	5839(2)	10582(2)	20(1)
C(6)	1952(3)	7812(2)	8572(2)	26(1)
C(7)	599(4)	8377(3)	9100(2)	38(1)
C(8)	1386(3)	7114(3)	7629(2)	32(1)
C(9)	5811(4)	9016(3)	8896(3)	34(1)
C(10)	1505(4)	4696(2)	8940(3)	30(1)

Table 3. Bond lengths [Å] and angles [°] for **(41)**

Br(1)-C(1)	1.903(3)	F(7)-C(8)	1.334(4)	C(1)-C(2)	1.397(4)
Br(2)-C(5)	1.898(2)	N(1)-C(1)	1.311(3)	C(2)-C(3)	1.403(4)
F(1)-C(6)	1.377(3)	N(1)-C(5)	1.324(3)	C(3)-C(4)	1.408(3)
F(2)-C(7)	1.329(4)	O(1)-C(2)	1.363(3)	C(3)-C(6)	1.533(3)
F(3)-C(7)	1.335(3)	O(1)-C(9)	1.458(3)	C(4)-C(5)	1.402(3)
F(4)-C(7)	1.331(4)	O(2)-C(4)	1.355(3)	C(6)-C(7)	1.548(4)
F(5)-C(8)	1.338(3)	O(2)-C(10)	1.459(3)	C(6)-C(8)	1.563(4)
F(6)-C(8)	1.337(3)				

C(1)-N(1)-C(5)	117.9(2)	F(1)-C(6)-C(3)	110.0(2)
C(2)-O(1)-C(9)	115.8(2)	F(1)-C(6)-C(7)	104.9(2)
C(4)-O(2)-C(10)	118.7(2)	C(3)-C(6)-C(7)	110.2(2)
N(1)-C(1)-C(2)	124.9(2)	F(1)-C(6)-C(8)	102.2(2)
N(1)-C(1)-Br(1)	115.8(2)	C(3)-C(6)-C(8)	117.0(2)
C(2)-C(1)-Br(1)	119.3(2)	C(7)-C(6)-C(8)	111.6(2)
O(1)-C(2)-C(1)	119.5(2)	F(2)-C(7)-F(4)	108.4(3)
O(1)-C(2)-C(3)	123.1(2)	F(2)-C(7)-F(3)	108.1(3)
C(1)-C(2)-C(3)	117.2(2)	F(4)-C(7)-F(3)	107.7(3)
C(2)-C(3)-C(4)	118.6(2)	F(2)-C(7)-C(6)	109.8(3)
C(2)-C(3)-C(6)	120.2(2)	F(4)-C(7)-C(6)	111.5(2)
C(4)-C(3)-C(6)	120.9(2)	F(3)-C(7)-C(6)	111.2(2)
O(2)-C(4)-C(5)	123.7(2)	F(7)-C(8)-F(6)	108.5(3)
O(2)-C(4)-C(3)	118.4(2)	F(7)-C(8)-F(5)	107.2(2)
C(5)-C(4)-C(3)	117.6(2)	F(6)-C(8)-F(5)	105.9(2)
N(1)-C(5)-C(4)	123.7(2)	F(7)-C(8)-C(6)	110.8(2)
N(1)-C(5)-Br(2)	114.8(2)	F(6)-C(8)-C(6)	114.4(2)
C(4)-C(5)-Br(2)	121.4(2)	F(5)-C(8)-C(6)	109.8(2)

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for **(41)**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	30(1)	41(1)	29(1)	-11(1)	-4(1)	-10(1)
Br(2)	38(1)	23(1)	24(1)	5(1)	7(1)	2(1)
F(1)	37(1)	36(1)	32(1)	15(1)	1(1)	-6(1)
F(2)	54(1)	39(1)	58(1)	-6(1)	10(1)	21(1)
F(3)	42(1)	73(1)	52(1)	32(1)	5(1)	29(1)
F(4)	30(1)	57(1)	41(1)	18(1)	13(1)	14(1)
F(5)	46(1)	66(1)	24(1)	18(1)	-9(1)	-7(1)
F(6)	27(1)	62(1)	35(1)	13(1)	-9(1)	-13(1)
F(7)	40(1)	49(1)	25(1)	-7(1)	1(1)	-1(1)
N(1)	22(1)	26(1)	16(1)	-4(1)	0(1)	2(1)
O(1)	31(1)	20(1)	31(1)	-1(1)	9(1)	-3(1)
O(2)	18(1)	25(1)	28(1)	-3(1)	0(1)	-3(1)
C(1)	20(1)	27(1)	19(1)	-7(1)	2(1)	-1(1)
C(2)	23(1)	19(1)	20(1)	-2(1)	6(1)	1(1)
C(3)	20(1)	20(1)	19(1)	1(1)	3(1)	2(1)
C(4)	17(1)	22(1)	19(1)	-3(1)	2(1)	-1(1)
C(5)	23(1)	20(1)	17(1)	0(1)	4(1)	2(1)
C(6)	25(1)	29(1)	24(1)	9(1)	1(1)	2(1)
C(7)	35(2)	48(2)	31(2)	13(1)	4(1)	17(2)
C(8)	25(2)	48(2)	22(1)	9(1)	-1(1)	-3(1)
C(9)	36(2)	32(2)	34(2)	1(1)	11(1)	-10(1)
C(10)	32(2)	26(1)	32(2)	-8(1)	-1(1)	-5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for (**41**)

Atom	x	y	z	U(eq)
H(91)	6070(50)	9710(40)	8870(30)	69(13)
H(92)	6680(50)	8580(40)	9070(30)	69(13)
H(93)	5610(50)	8760(30)	8260(30)	66(13)
H(101)	2550(40)	4560(30)	8720(30)	44(10)
H(102)	1250(40)	4210(30)	9410(30)	36(9)
H(103)	840(50)	4710(30)	8340(30)	56(11)

Compound Number:	Name:
(53)	*4-[1-(trifluoromethyl)-1,2,2,2-tetrafluoroethyl]-2-bromo-3-fluoro-5-methoxy-6-piperidylpyridine*

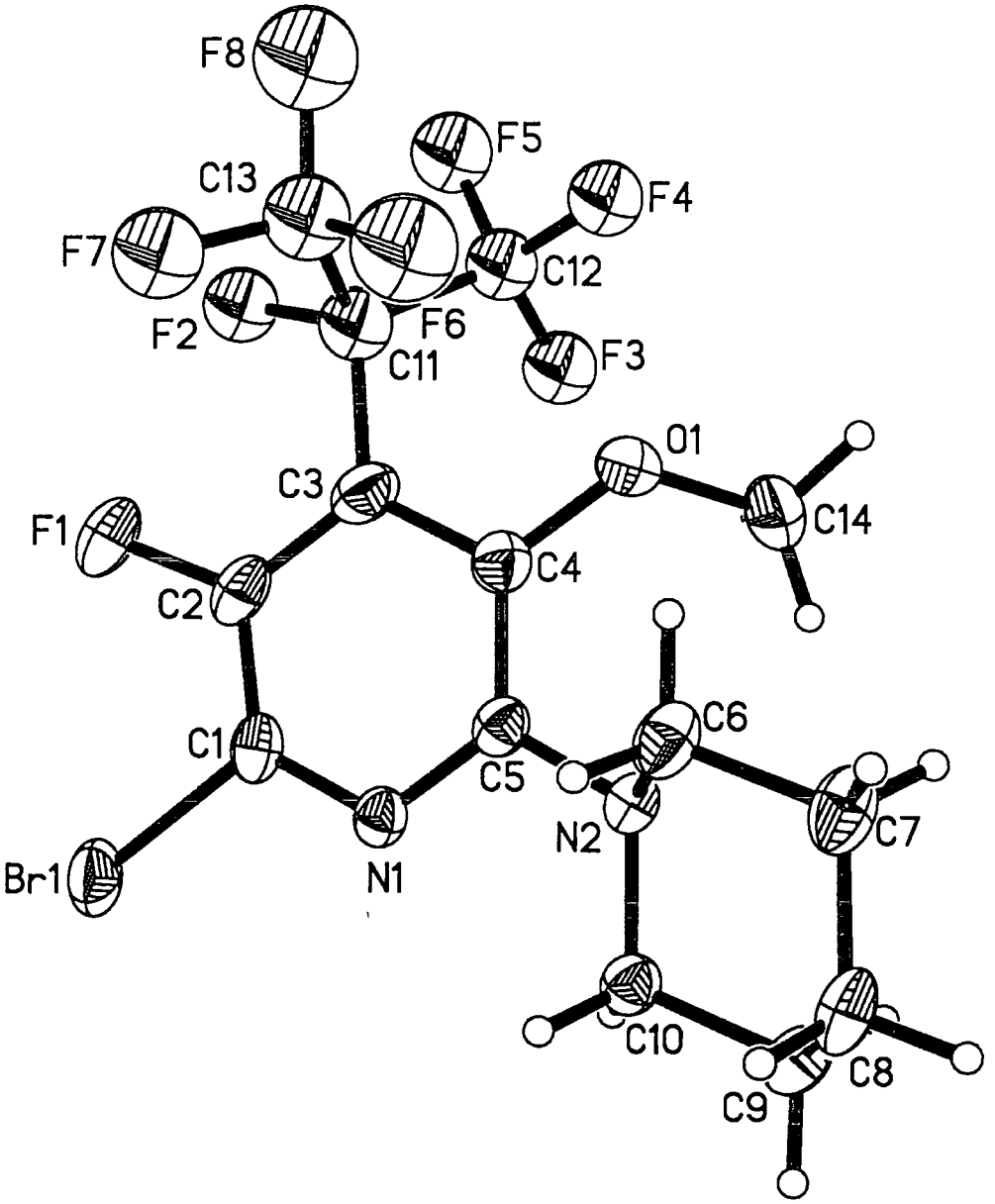


Table 1. Crystal data and structure refinement for (53)

Identification code	187s	
Empirical formula	$C_{14} H_{13} Br F_8 N_2 O$	
Formula weight	457.17	
Temperature	120(1), K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.530(2), Å	α= 90°.
	b = 13.802(3), Å	β= 90.86(3),°.
	c = 11.485(2), Å	γ = 90°.
Volume	1669.1(6), $Å^3$	
Z	4	
Density (calculated),	1.819 Mg/m^3	
Absorption coefficient	2.553 mm^{-1}	
F(000),	904	
Crystal size	0.52 x 0.45 x 0.24 mm^3	
Theta range for data collection	1.93 to 27.50°.	
Index ranges	-13<=h<=13, -16<=k<=17, -14<=l<=14	
Reflections collected	17323	
Independent reflections	3834 [R(int), = 0.0278]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5794 and 0.3503	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3834 / 0 / 238	
Goodness-of-fit on F^2	1.118	
Final R indices [I>2sigma(I),]	R1 = 0.0692, wR2 = 0.1712	
R indices (all data),	R1 = 0.0827, wR2 = 0.1802	
Extinction coefficient	0.005(1),	
Largest diff. peak and hole	2.249 and -1.279 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4), and equivalent isotropic displacement parameters ($Å^2$x 10^3), for (53) U(eq), is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	Y	z	U(eq)
Br(1)	21667(1)	5069(1)	3271(1)	39(1)
F(1)	19361(3)	3966(2)	3933(2)	41(1)
O(1)	16669(3)	4920(3)	762(3)	39(1)
N(1)	19888(4)	5627(3)	1598(3)	24(1)
N(2)	18556(3)	6335(3)	172(3)	24(1)
C(1)	20060(5)	5043(3)	2503(4)	27(1)
C(2)	19121(5)	4460(3)	2942(4)	31(1)
C(3)	17966(5)	4391(4)	2344(4)	34(1)
C(4)	17789(5)	4987(3)	1358(4)	30(1)
C(5)	18751(4)	5648(3)	1057(4)	24(1)
C(6)	17490(5)	7008(4)	391(4)	33(1)
C(7)	17183(5)	7598(4)	-701(4)	36(1)
C(8)	18358(5)	8156(3)	-1107(4)	33(1)
C(9)	19436(5)	7444(3)	-1299(4)	32(1)
C(10)	19710(4)	6846(3)	-201(4)	27(1)
C(14)	16750(5)	4708(4)	-472(5)	40(1)
F(2)	17543(5)	2978(4)	3471(4)	45(1)
F(3)	17194(4)	2816(3)	930(4)	45(1)
F(4)	15346(4)	3399(4)	1292(4)	44(1)
F(5)	16021(5)	2151(4)	2224(5)	55(1)
F(6)	15447(8)	5170(6)	2945(7)	76(2)
F(7)	16514(6)	4510(5)	4422(5)	57(2)
F(8)	14987(8)	3684(7)	3805(7)	78(2)
C(11)	16994(8)	3650(6)	2733(7)	42(2)
C(12)	16411(7)	2973(5)	1716(6)	41(2)
C(13)	16001(9)	4158(8)	3463(8)	53(2)
F(1D)	15778(12)	2350(9)	3059(11)	27(3)
F(2D)	17783(13)	2447(10)	2889(12)	32(3)
F(3D)	14740(16)	4149(13)	3958(14)	40(4)
F(4D)	17040(20)	2960(16)	4344(19)	68(5)
F(5D)	17060(20)	3895(18)	4350(20)	70(6)
F(6D)	15376(8)	4793(7)	2838(8)	35(2)
F(7D)	15206(15)	3328(13)	3771(13)	32(3)
F(8D)	14810(20)	4176(19)	2180(20)	29(5)
F(9D)	15641(19)	4532(16)	3323(18)	45(4)
F(10D)	16381(13)	4861(12)	4374(12)	24(3)
C(11D)	16630(30)	3900(20)	2810(20)	32(6)
C(12D)	16750(30)	2840(20)	2950(30)	46(6)
C(13D)	15690(20)	3690(17)	1750(20)	26(4)

Table 3. Bond lengths [Å] and angles [°] for (53)

Br(1)-C(1)	1.897(5)	C(1)-C(2)	1.376(7)	F(2)-C(11)	1.378(9)
F(1)-C(2)	1.348(5)	C(2)-C(3)	1.391(7)	F(3)-C(12)	1.251(8)
O(1)-C(4)	1.357(6)	C(3)-C(4)	1.411(7)	F(4)-C(12)	1.351(8)
O(1)-C(14)	1.451(6)	C(3)-C(11)	1.518(9)	F(5)-C(12)	1.342(9)
N(1)-C(1)	1.325(6)	C(4)-C(5)	1.410(6)	F(6)-C(13)	1.622(13)
N(1)-C(5)	1.341(6)	C(6)-C(7)	1.526(6)	F(7)-C(13)	1.313(10)
N(2)-C(5)	1.402(5)	C(7)-C(8)	1.535(7)	F(8)-C(13)	1.317(12)
N(2)-C(10)	1.474(6)	C(8)-C(9)	1.520(7)	C(11)-C(13)	1.521(13)
N(2)-C(6)	1.482(6)	C(9)-C(10)	1.530(6)	C(11)-C(12)	1.611(10)

C(4)-O(1)-C(14)	116.3(4)	C(9)-C(8)-C(7)	109.1(4)
C(1)-N(1)-C(5)	119.2(4)	C(8)-C(9)-C(10)	111.1(4)
C(5)-N(2)-C(10)	115.0(3)	N(2)-C(10)-C(9)	110.6(4)
C(5)-N(2)-C(6)	113.8(3)	F(2)-C(11)-C(3)	110.8(6)
C(10)-N(2)-C(6)	112.2(4)	F(2)-C(11)-C(13)	104.9(7)
N(1)-C(1)-C(2)	123.5(4)	C(3)-C(11)-C(13)	108.9(7)
N(1)-C(1)-Br(1)	117.6(4)	F(2)-C(11)-C(12)	102.0(6)
C(2)-C(1)-Br(1)	118.8(3)	C(3)-C(11)-C(12)	115.4(6)
F(1)-C(2)-C(1)	118.6(4)	C(13)-C(11)-C(12)	114.1(7)
F(1)-C(2)-C(3)	122.2(4)	F(3)-C(12)-F(5)	112.1(6)
C(1)-C(2)-C(3)	119.2(4)	F(3)-C(12)-F(4)	111.6(6)
C(2)-C(3)-C(4)	117.4(4)	F(5)-C(12)-F(4)	105.5(6)
C(2)-C(3)-C(11)	119.3(5)	F(3)-C(12)-C(11)	112.1(6)
C(4)-C(3)-C(11)	123.2(5)	F(5)-C(12)-C(11)	106.9(6)
O(1)-C(4)-C(5)	122.8(4)	F(4)-C(12)-C(11)	108.4(6)
O(1)-C(4)-C(3)	118.0(4)	F(7)-C(13)-F(8)	105.0(8)
C(5)-C(4)-C(3)	119.1(4)	F(7)-C(13)-C(11)	110.8(8)
N(1)-C(5)-N(2)	118.1(4)	F(8)-C(13)-C(11)	120.2(9)
N(1)-C(5)-C(4)	120.8(4)	F(7)-C(13)-F(6)	97.6(7)
N(2)-C(5)-C(4)	121.1(4)	F(8)-C(13)-F(6)	104.4(9)
N(2)-C(6)-C(7)	110.3(4)	C(11)-C(13)-F(6)	116.2(7)
C(6)-C(7)-C(8)	110.8(4)		

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$), for (53) The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	41(1)	51(1)	26(1)	6(1)	-8(1)	4(1)
F(1)	57(2)	39(2)	27(1)	13(1)	3(1)	6(1)
O(1)	31(2)	55(2)	32(2)	-1(2)	1(1)	-13(2)
N(1)	30(2)	22(2)	21(2)	-1(1)	0(1)	0(1)
N(2)	27(2)	24(2)	20(2)	2(1)	2(1)	1(1)
C(1)	35(2)	26(2)	20(2)	-2(2)	-1(2)	6(2)
C(2)	48(3)	23(2)	23(2)	4(2)	4(2)	3(2)
C(3)	43(3)	30(2)	30(2)	5(2)	7(2)	-7(2)
C(4)	33(2)	31(2)	26(2)	-1(2)	0(2)	-4(2)
C(5)	31(2)	21(2)	21(2)	-1(2)	2(2)	0(2)
C(6)	35(2)	38(3)	26(2)	4(2)	6(2)	9(2)
C(7)	40(3)	37(3)	30(2)	7(2)	1(2)	15(2)
C(8)	49(3)	27(2)	22(2)	5(2)	1(2)	10(2)
C(9)	40(3)	27(2)	29(2)	5(2)	5(2)	2(2)
C(10)	29(2)	24(2)	26(2)	2(2)	1(2)	-1(2)
C(14)	38(3)	51(3)	31(3)	-3(2)	-8(2)	-3(2)

Table 5. Hydrogen coordinates (x 10^4), and isotropic displacement parameters ($Å^2$x 10^{-3}), for (53)

Atom	x	y	z	U(eq)
H(6A)	17722	7450	1039	39
H(6B)	16732	6635	622	39
H(7A)	16491	8061	-535	43
H(7B)	16886	7159	-1330	43
H(8A)	18158	8504	-1840	39
H(8B)	18613	8639	-511	39
H(9A)	20210	7804	-1516	38
H(9B)	19208	7005	-1950	38
H(10A)	20387	6369	-361	32
H(10B)	20014	7279	431	32
H(14A)	15893	4671	-813	60
H(14B)	17184	4086	-579	60
H(14C)	17228	5222	-858	60

Appendix E.

Board of Studies Requirements

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

A) All research colloquia, seminars and lectures arranged by both the Department and the Durham University Chemical Society during the period of the Author's residence as a postgraduate student.

B) Details of postgraduate induction courses.

C) All research conferences attended and papers presented by the Author during the period of residence as a postgraduate student.

Research Colloquia, Seminars and Lectures

1997

October 15 Dr. R. Mark Ormerod, Department of Chemistry, Keele University.
Studying Catalysts in Action.*

October 21 Prof. A. F. Johnson, IRC, Leeds.
Reactive Processing of Polymers: Science and Technology.

October 22 Prof. R. J. Puddephatt (RSC Endowed Lecture), University of Western Ontario.
Organoplatinum Chemistry and Catalysis.*

October 23 Prof. M. R. Bryce, University of Durham, Inaugural Lecture.
New Tetrathiafulvalene Derivatives in Molecular, Supramolecular and Macromolecular Chemistry: Controlling the Electronic Properties of Organic Solids.*

October 29 Prof. Bob Peacock, University of Glasgow.
Probing Chirality with Circular Dichroism.

October 28 Prof. A P de Silva, The Queen's University, Belfast.
Luminescent Signalling Systems.

November 5 Dr. Mini Hii, Oxford University.
Studies of the Heck Reaction.*

November 11 Prof. V. Gibson, Imperial College, London.
Metallocene Polymerisation.*

November 12 Dr. Jeremy Frey, Department of Chemistry, Southampton University.
Spectroscopy of Liquid Interfaces: from Bio-organic Chemistry to Atmospheric Chemistry.

November 19 Dr. Gareth Morris, Department of Chemistry, Manchester University.
Pulsed Field Gradient NMR Techniques: Good news for the Lazy and DOSY.

November 20 Dr. Leone Spiccia, Manash University, Melbourne, Australia.
Polynuclear Metal Complexes.

November 25 Dr. R. Withnall, University of Greenwich.
Illuminated Molecules and Manuscripts.

November 26 Prof. R. W. Richards, University of Durham, Inaugural Lecture.
A Random Walk in Polymer Science.*

December 2 Dr. C. J. Ludman, University of Durham.
Explosions.*

December 3 Prof. A. P. Davis, Department of Chemistry, Trinity College Dublin.
Steroid-based Frameworks for Supramolecular Chemistry.*

December 10 Sir Gordon Higginson, former Professor of Engineering in Durham and retired Vice-Chancellor of Southampton University.
1981 and all that.

December 10 Prof. Mike Page, Department of Chemistry, University of Huddersfield.
The Mechanism and Inhibition of Beta-lactamases.

1998

January 14 Prof. David Andrews, University of East Anglia.
Energy Transfer and Optical Harmonics in Molecular Systems.

January 20	Prof. J. Brooke, University of Lancaster. What's in a Formula? Some Chemical Controversies of the 19th century.*
January 21	Prof. David Cardin, University of Reading. Aspects of Metal and Carbon Cluster Chemistry.*
January 27	Prof. Richard Jordan, Dept. of Chemistry, University of Iowa, USA. Cationic Transition Metal and Main Group Metal Alkyl Complexes in Olefin Polymerisation.*
January 28	Dr. Steve Rannard, Courtaulds Coatings (Coventry). The Synthesis of Dendrimers using Highly Selective Chemical Reactions.*
February 3	Dr. J. Beacham, ICI Technology. The Chemical Industry in the 21st Century.*
February 4	Prof. P. Fowler, Department of Chemisty, Exeter University. Classical and Non-classical Fullerenes.*
February 11	Prof. J. Murphy, Dept. of Chemistry, Strathclyde University.
February 17	Dr S. Topham, ICI Chemicals and Polymers. Perception of Environmental Risks; The River Tees, Two Different Rivers.
February 18	Prof. Gus Hancock, Oxford University. Surprises in the Photochemistry of the Tropospheric Ozone.
February 24	Prof. R. Ramage, University of Edinburgh. The Synthesis and Folding of Proteins.
February 25	Dr. C. Jones, Swansea University. Low Coordination Arsenic and Antimony Chemistry.
March 4	Prof. T. C. B. McLeish, IRC of Polymer Science Technology, Leeds University.

The Polymer Physics of Pyjama Bottoms (or the Novel Rheological Characterisation of Long Branching in Entangled Macromolecules).

March 11 — Prof. M. J. Cook, Department of Chemistry, UEA.
How to make Phthalocyanine Films and what to do with them.*

March 17 — Prof. V. Rotello, University of Massachusetts, Amherst.
The Interplay of Recognition and Redox Processes- from Flavoenzymes to Devices.

March 18 — Dr. John Evans, Oxford University.
Materials which Contract on Heating (from Shrinking Ceramics to Bullet Proof Vests).

26 March — Prof. G. S. Wilson, University of Kansas, USA
The Applications of Microbiosensors to Continuous *in vivo* Monitoring.

23 April — Prof. T. Cass, Imperial College London, UK
Protein design: Engineering Novel Functions in Bioeletronics

6 July — Dr. S. Althorpe, Steacie Institute for Molecular Sciences, NRCC, Ottawa, Canada
New Theoretical Methods for State-to-State Reactive Scattering

29 July — Dr. A. Cooper, University of Cambridge, UK
Polymer Synthesis in Supercritical Carbon Dioxide*

7 September — Prof. K. Shull, Northwestern University, Evanston, Illinois, USA
Axisymmetric Adhesion Tests of Soft Materials

7 October — Dr. S. Rimmer, Polymer Centre, University of Lancaster, UK
New Polymer Colloids*

9 October — Prof. M. F. Hawthorne, UCLA, Los Angeles, USA
Carboranes: Exploitation of their Unusual Geometries and Reactivities

21 October — Dr. P. Unwin, University of Warwick, UK

Dynamic Electrochemistry: Small is Beautiful

23 October Prof. J. C. Scaiano, University of Ottawa, Canada
In Search of Hypervalent Free Radicals

26 October Dr. W. Piers, University of Calgary, Canada
Reactions of the Highly Electrophilic Boranes $HB(C_6F_5)_2$ and $B(C_6F_5)_3$ Zirconium and Tantalum Based Metallocenes

28 October Prof. J. P. S. Badyal, University of Durham, UK
Tailoring Solid Surfaces*

4 November Dr. N. Kaltscoyannis, University College London, UK
Computational Adventures of d- and f-Element Chemistry

11 November Dr. Martin. Wills, University of Warwick, UK
New Methodology for the Asymmetric transfer Hydrogenation of Ketones*

12 November Prof. Stephen. Loeb, University of Windsor, Ontario, Canada
From Macrocycles to Metallo-Supramolecular Chemistry*

18 November Dr. R. Cameron, University of Cambridge, Dept of Materials Science and Metallurgy, UK
Biodegradable Polymers

2 December Dr. Marcel. Jaspers, University of Aberdeen, UK
Bioactive Compounds Isolated from Marine Invertebrates and Cyanobacteria*

9 December Dr. Mark. Smith, University of Warwick, Dept of Physics, UK

1999

20 January Dr. Anita. Jones, University of Edinburgh, UK
Luminescence of Large Molecules: from Conducting Polymers to Coral Reefs*

27 January Prof. Ken. Wade, University of Durham, UK

Foresight or Hindsight?
Some Borane Lessons and Loose Ends*

3 February — Dr. Christopher. Schofield, University of Oxford, UK
Studies on the Stereoelectronics of Enzyme Catalysts

10 February — Dr. Colin. Bain, University of Oxford, UK
Surfactant Adsorption and Marangori Flow at Expanding Liquid Surfaces

17 February — Dr. Ben. Horrocks, University of Newcastle, UK
Microelectrode techniques for the Study of Enzymes and Nucleic Acids at Interfaces

24 February — Dr. Anne-Kathrin Duhme, University of York, UK
Bioinorganic Aspects of Molybdenum Transport in Nitrogen-Fixing Bacteria

3 March — Prof. B. Gilbert, University of York, UK
Biomolecular Damage by Free Radicals: New Insights through ESR Spectroscopy

10 March — Dr. Andrew. Harrison, University of Edinburgh, UK
Designing Model Magnetic Materials

17 March — Dr. Jeremy. Robertson, University of Oxford, UK
Recent Developments in the Synthesis of Heterocyclic Natural Products*

13 October — Prof. G. Fleet, University of Oxford, UK
Sugar Lactone and Amino Acids*

19 October — Prof. Karsten. Gloe, TU Dresden, Germany
Tailor Made Molecules for the Selective Binding of Metal Ions*

20 October — Prof. S. Lincoln, University of Adelaide, Australia
Aspects of Complexation and Supramolecular Chemistry*

25 October — Prof. Scott. Collins, University of Waterloo, Canada

Methacrylate Polymerisation using Zirconium Enolate Initiators: Polymerisation Mechanisms and Control of Polymer Tacticity*

27 October Dr. C. Braddock, Imperial College, UK
Novel Catalysts for Atom Economic Transformations

3 November Prof. Derek. Smith, University of Waikato, New Zealand
The Strengths of C-C and C-H Bonds in Organic and Organometallic Molecules: Empirical, Semi-empirical and *Ab Initio* Calculations*

10 November Dr. Ifor. Samuel, Department of Physics, University of Durham, UK
Improving Organic Light Emitting Diodes by Molecular, Optical and Device Design

17 November Dr. G. Siligardi, Kings College London, UK
The Use of Circular Dichroism to Detect and Characterise Biomolecular Interactions in Solution

24 November Prof. Tim. Jones, Imperial College, London, UK

8 December Prof. David. Crout, University of Warwick, UK
More than Simply Sweet: Carbohydrates in Medicine and Biology*

2000

12 January Prof. David. Haddleton, University of Warwick, UK
Atom Transfer Polymerisation-what's all the Hype About?

19 January Dr. P. R. Fielden, UMIST, UK
Miniturised Chemical Analysis (Lab-on-a-Chip): Functional or Merely Fashionable?*

26 January Prof. Sabina Flisch, University of Edinburgh

2 February Chick Wilson, *Head of Crystallography*, ISIS, Rutherford Appleton Lab, UK
Protons in Motion? Neutron Diffraction Studies of Hydrogen Atoms in Organic Crystal Structures

9 February	Dr. Steve. Moratti, University of Cambridge, UK Shape and Stereoselectivity in Polymers
16 February	Prof. Kocienski, University of Glasgow, UK Asymmetric Synthesis using Planar Chiral TT-Allyl Cationic Complexes*
23 February	Dr. Nigel. Clarke, UMIST, UK The Flow of Polymer Bends
1 March	Prof. Dominic. Tildsley, Unilever (Head of Research), UK Computer Simulation of Interfaces: Fact and Fiction
8 March	Prof. J. Courtieu, Universite de Paris-Sud, Orsay, France
5 May	Prof. Robin. Hochstrasser, University of Pennsylvania, USA RSC Centenary Lecture

* lectures attended.

Postgraduate Induction Courses

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

Departmental Organisations-	Dr. E. J. F. Ross
Safety Matters-	Mr. D. Hunter
Electrical Appliances-	Mr. B. T. Barker
Library Facilities-	Mrs. M. Hird
Mass Spectroscopy-	Dr. M. Jones
NMR Spectroscopy-	Dr. A. Kenwright
Glass-blowing Techniques-	Mr. R. Hart
	Mr. G. Haswell
Chromatographic Analysis-	Mr. L. W. Lauchlan

Research Conferences Attended

May 1999	Spring 1999 Fluorine Technology Bureau Meeting, UMIST, Manchester, England.

May 1999	The 2nd Sunderland Pre-Grasmere Conference, University of Sunderland, England.
July 2000	16th International Symposium on Fluorine Chemistry , Durham University, Durham, England.

Appendix F.

Bibliography

1. A. F. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry,* Wiley-Interscience, Chichester, 1988.
2. G.C.Finger, *Adv. Fluorine Chem.,* 1961, **2**, 35.
3. A. K. Barbour, in *Organofluorine Chemicals and Their Industrial Applications,* ed. R. E. Banks, Horwood, Chichester, 1979, p. 44.
4. M. Meyer and D. O'Hagan, *Chem. Br.* 1992, **28**, 785.
5. D. O'Hagan and D. B. Harper, *J. Fluorine Chem.,* 1999, 127-133.
6. R. D. Chambers, *Fluorine in Organic Chemistry,* Wiley and Sons, New York, 1973 and references therein.
7. F. Swarts, *Bull. Acad. Roy. Belg,* 1892, **24**, 474.
8. R. E. Banks, D. W. A. Sharp and J. C. Tatlow, *Fluorine: The First Hundred Years (1886-1986),* Elsevier Sequoia, Lausanne and New York, 1986.
9. E. Paterno and V. Oliveri, *Gazzetta,* 1883, **13**, 533.
10. A. E. Chichibabin and M. D. Rajazancev, *J. Russ. Phys. Chem. Soc.,* 1915, **46**, 1571.
11. L. Pauling, *The Nature of the Chemical Bond,* Cornell Univ. Press, Ithaca, N.Y., 1960.
12. K. D. Sen and C. K. Jorgensen, *Electronegativity,* Springer-Verlag, New York, 1987.
13. C. R. Patrick, *Adv. Fluorine Chem.*, 1961, **2**, 1.
14. H. F. Koch, *Acc. Chem. Res.,* 1984, **17**, 137.
15. B. E. Smart, in *The Chemistry of Functional Groups,* ed. S. Patai and Z. Rappoport, Wiley, New York, 1983, vol. Supplement D, Part 2.
16. B. E. Smart, in *Molecular Structure and Energetics,* ed. J. F. Liebman and A. Greenberg, VCH Publishers, Deerfield Beach, Florida, 1986.
17. A. Bondi, *J. Phys. Chem.,* 1964, **68**, 441.
18. R. D. Chambers, *Fluorine in Organic Chemistry,* Wiley and Sons, New York, 1973.
19. R. E. Banks, in *Organofluorine Chemistry: Principles and Commercial Applications,* Plenum Press, New York, 1994.
20. K. J. Herd, in *Organofluorine Chemistry: Principles and Commercial Applications,* Plenum Press, New York, 1994.
21. D. Cartwright, in *Organofluorine Chemistry: Principles and Applications,* ed. R. E. B. *et. al,* Plenum Press, New York, 1994, p. 237.
22. P. N. Edwards, in *Organofluorine Chemistry: Principles and Applications,* ed. B. *et. al,* Plenum Press, New York, 1994, p. 501.
23. R. E. Banks, A. E. Ginsberg and R. N. Haszeldine, *Proc. Chem. Soc.,* 1960, 211.
24. R. E. Banks, A. E. Ginsberg and R. N. Haszeldine, *J. Chem. Soc.,* 1961, 1740.

25. J. Burdon, D. J. Gilman, C. R. Patrick, M. Stacey and J. C. Tatlow, *Nature,* 1960, **186**, 231.
26. J. H. Simmons, *J. Am. Chemical Soc.,* 1957, **79**, 3429.
27. A. J. Edwards, R. G. Plevey and J. C. Tatlow, *Brit. Patent*; 1975, no. 1,392,571.
28. R. D. Chambers, J. Hutchinson and W. K. R. Musgrave, *J. Chem. Soc.,* 1964, 3573-3576.
29. R. E. Banks, R. N. Haszeldine, J. V. Latham and I. M. Young, *Chem. Ind.,* 1964, 835.
30. R. D. Chambers, M. Hole and W. K. R. Musgrave, *J. Chem. Soc. (C),* 1970, 61.
31. J. Miller, *Aromatic Nucleophilic Substitution,* Elsevier, London, 1968.
32. T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry,* Harper and Row, 1987.
33. R. D. Chambers and M. Todd, *J. Fluorine Chem.,* 1985, **27**, 237.
34. V. M. Vlasov, V. V. Aksenov and G. G. Yakobson, *Zh. Org. Khim,* 1979, **15**, 2156.
35. R. D. Chambers, J. A. Jackson, S. Partington, P. D. Philpot and A. C. Young, *J. Fluorine Chem.,* 1975, **6**, 5.
36. R. E. Banks, J. E. Burgess, W. M. Cheng and R. N. Haszeldine, *J. Chem. Soc,* 1965, 575-581.
37. R. D. Chambers, J. Hutchinson and W. K. R. Musgrave, *J. Chem. Soc.,* 1964, 3736.
38. R. E. Banks, R. N. Hazeldine, E. Phillips and I. M. Young, *J. Chem. Soc. (C),* 1967, 2091-2095.
39. R. D. Chambers, B. Iddon and W. K. R. Musgrave, *Tetrahedron,* 1968, **24**, 877.
40. E. R. Biehl, H. M. Refat and A. A. Fadda, *Heterocycles,* 1995, **41**, 1431-1434.
41. R. D. Chambers, J. Hutchinson and W. K. R. Musgrave, *J. Chem. Soc.,* 1965, 5040-5044.
42. M. Green, A. Taunton-Rigby and F. G. A. Stone, *J. Chem. Soc. (A),* 1968, 4762.
43. C. L. Cheong and B. J. Wakefield, *J. Chem. Soc., Perkin Trans. 1,* 1988, 3301-3305.
44. A. O. Miller and G. G. Furin, *J. Fluorine Chem.,* 1987, **36**, 247.
45. R. E. Banks and G. R. Sparkes, *J. Chem. Soc. Perkin Trans. 1,* 1972, 2964.
46. A. O. Miller and G. G. Furin, *J. Fluorine Chem.,* 1995, **75**, 169.
47. R. E. Banks and S. M. Hitchen, *J. Fluorine Chem.,* 1978, **12**, 159.

48. R. D. Chambers, J. Hutchinson and W. K. R. Musgrave., *J. Chem. Soc., suppl. 1,* 1964, 5634.
49. R. E. Banks, W. Jondi and A. E. Tipping, *J. Fluorine Chem.,* 1989, **44**, 441.
50. R. E. Banks, M. S. Falou, R. Fields, N. O. Olaware and A. E. Tipping, *J. Fluorine Chem,* 1988, **38**, 217.
51. R. E. Banks, W. Jondi and A. E. Tipping, *J. Chem. Soc. Chem. Commun.,* 1989, 1268.
52. R. E. Banks, R. N. Haszeldine, D. R. Karsa, F. E. Rickett and M. I. Young, *J. Chem. Soc. (C),* 1969, 1660.
53. W. Dmowski and A. Haas, *J. Chem. Soc., Perkin Trans. 1,* 1987, 2119-2124.
54. R. D. Chambers, J. S. Waterhouse and D. L. H. Williams., *J. Chem. Soc., Perkin Trans. 2,* 1977, 585-588.
55. R. D. Chambers, D. Close, W. K. R. Musgrave, J. S. Waterhouse and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2,* 1977, 1774-1778.
56. R. D. Chambers and S. R. James, in *Comprehensive Organic Chemistry,* ed. D. H. R. Barton and W. D. Ollis, Pergamon, Oxford, 1979, vol. 1, p. 493.
57. D. T. Clark, N. J. Murrell and J. M. Tedder, *J. Chem. Soc.,* 1963, 1250.
58. R. D. Chambers, W. K. R. Musgrave, J. S. Waterhouse, D. L. H. Williams, J. Burdon, W. B. Hollyhead and J. C. Tatlow, *J. Chem. Soc. Chem.Commun.,* 1974, 239.
59. R. D. Chambers, M. J. Seabury, D. L. H. Williams and N. Hughes, *J. Chem. Soc., Perkin Trans. 1,* 1988, 255-257.
60. R. D. Chambers, M. J. Seabury and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 1,* 1988, 251-254.
61. S. Andreades, *J. Am. Chem. Soc.,* 1964, **86**, 2003.
62. W. T. Miller, J. H. Fried and H. Goldwhite, *J. Am. Chem. Soc.,* 1960, **82**, 3901.
63. W. T. Miller, W. Frass and P. R. Resnnick, *J. Am. Chem. Soc.,* 1961, **83**, 1767.
64. R. D. Chambers and R. H. Mobbs, *Adv. Fluorine Chem.,* 1965, **4**, 50.
65. R. D. Chambers and M. R. Bryce, in *Comprehensive Carbanion Chemistry, Part C,* ed. E. Buncel and T. Durst, Elsevier, Amsterdam, 1987, vol. 6, p. 271.
66. B. L. Dyatkin, E. P. Mochalina and I. L. Knunyants, *Fluorine Chem Rev.,* 1969, **3**, 45.
67. L. S. German and I. L. Knunyants, *Angew . Chem. Int. Ed.* 1969, **8**, 349.
68. J. D. Park, W. M. Sweeny, S. L. Hopwood and J. R. Lacher, *J. Am. Chem. Soc.,* 1956, **78**, 1685.
69. R. J. Koshar, J. C. Simmons and F. W. Hoffmann, *J. Am. Chem. Soc.,* 1957, **79**, 1741.

70. D. C. England, L. R. Melby, M. A. Deitrich and R. V. Lindsey, *J. Am. Soc.*, 1960, **82**, 5116.
71. R. D. Chambers, A. A. Lindley and H. C. Fielding, *J. Fluorine Chem.*, 1978, **12**, 85.
72. J. D. Roberts, R. L. Webb and E. A. McElhill, *J. Am. Chem. Soc.*, 1950, **72**, 408.
73. D. A. Dixon, *J. Phys. Chem.*, 1986, **90**, 2038.
74. D. A. Dixon, T. Fukunaga and B. E. Smart, *J. Am. Chem. Soc.*, 1986, **108**, 1585.
75. D. A. Dixon, T. Fukunaga and B. E. Smart, *J. Am. Chem. Soc.*, 1986, **108**, 4027.
76. W. B. Farnham, D. A. Dixon and J. C. Calabrese, *J. Am. Chem. Soc.*, 1988, **110**, 2607.
77. D. Holtz, *Prog. Phys. Org.Chem.*, 1971, **8**, 1.
78. A. Streitweiser, C. M. Berke, G. W. Schriver, D. Grier and J. B. Collins, *Tetrahedron Supplements*, 1981, **37**, 345.
79. R. D. Chambers, R. P. Corbally, M. Y. Gribble and W. K. R. Musgrave, *Chem. Commun.*, 1971, 1345.
80. R. D. Chambers, M. Y. Gribble and E. Marper, *J. Chem. Soc. Perkin Transactions I*, 1973, 1710.
81. C. J. Drayton, W. T. Flowers and R. N. Haszeldine, *Journal of the Chemical Society, Perkin Transactions I*, 1973, 2750.
82. S. L. Bell, R. D. Chambers, M. Y. Gribble and J. R. Maslakiewicz, *J. Chem. Soc., Perkin Transactions I*, 1973, 1716.
83. R. D. Chambers and C. R. Sargent, *Adv. Heterocycl. Chem.*, 1981, **28**, 1-72.
84. M. J. Silvester, *Adv. Heterocycl. Chem.*, 1994, **59**, 1.
85. R. D. Chambers, J. A. Jackson, W. K. R. Musgrave and R. A. Storey, *J. Chem. Soc. (C)*, 1968, 2221.
86. A. G. Sharpe, *Quart. Rev.*, 1937, **11**, 49.
87. M. Hudlicky, *Chemistry of Organic Fluoride Compounds*, Pergamon, Oxford, 1961.
88. W. J. Brehm, K. G. Bremer, H. S. Elevterio and R. W. Meschke, *Chem. Abstr.*, 1960, **54**, 20875.
89. W. Brunskill, W. T. Flowers, R. Gregory and R. N. Haszeldine, *Chem. Commun.*, 1970, 1444.
90. R. D. Chambers, W. K. Gray and S. R. Korn, *Tetrahedron*, 1995, **51**, 13167.
91. W. Carpenter, *J. Org. Chem.*, 1965, **30**, 3082.
92. N. Wiberg, *Angew .Chem. Int. Ed. Engl.*, 1968, **7**, 766.

93. R. D. Chambers, M. W. Briscoe, S. J. Mullins, J. F. S. Vaughan, T. Nakamura and F. D. Drakesmith, *J. Chem. Soc. Perkin Trans. I,* 1994, 3115.
94. R. D. Chambers, R. P. Corbally and W. K. R. Musgrave, *J. Chem. Soc., Perkin Trans. 1,* 1972, 1281.
95. R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, L. H. Sutcliffe and G. J. T. Tiddy, *Tetrahedron,* 1970, **26**, 71.
96. C. J. Drayton, W. T. Flowers and R. N. Haszeldine, *J. Chem. Soc. (C),* 1975, 1029.
97. R. E. Banks and A. Prakash, *J. Chem. Soc. Perkin Trans. I,* 1974, 2479.
98. D. J. Burton and Z. Y. Yang, *Tetrahedron,* 1994, **50**, 2993.
99. W. R. Dolbier, *Chem. Rev.,* 1996, **96**, 1557.
100. W. B. Farnham, *Chem. Rev.,* 1996, **96**, 1633.
101. T. Umemoto, *Chem. Rev.,* 1996, **96**, 1757.
102. G. J. Chen and L. S. Chen, *J. Fluorine Chem.,* 1995, **73**, 113.
103. M. A. McClinton and D. A. McClinton, *Tetrahedron,* 1992, **48**, 6555.
104. B. E. Smart, in *Organofluorine Chemistry: Principles and Commercial Applications,* ed. R. E. B. *et. al*, Plenum Press, New York, 1994, p. 57.
105. J. T. Welch and S. Eswarakrishnan, *Fluorine in Bioorganic Chemistry,* Wiley, New York, 1991.
106. G. G. Furin, *Targets in Heterocyclic Chemistry,* 1998, **2**, 355.
107. D. W. Zhu, *Synthesis,* 1993, 953.
108. I. T. Hovarth and J. Rabai, *Science,* 1994, **266**, 72.
109. R. H. Fish, *Chem. Eur. J.,* 1999, **5**, 1677.
110. B. J. Wakefield, *The Chemistry of Organolithium Compounds,* Pergamon, Oxford, 1974.
111. J. L. Wardell, in *Comprehensive Organometallic Chemistry,* ed. G. Wilkinson, Pergamon, Oxford, 1982, p. Chapter 2.
112. C. J. Pedersen, *J. Org. Chem.,* 1971, **36**, 1690.
113. J. M. Lehn, *Angew. Chem. Int. Ed. Engl.,* 1990, **29**, 1304.
114. B. Dietrich, P. Viout and J. M. Lehn, *Macrocyclic Chemistry (Aspects of Organic and Inorganic Supramolecular Chemistry),* VCH, Weinheim, 1990.
115. E. Fischer, *Ber. Dtsch. Chem. Ges,* 1894, **27**, 2985.
116. D. Hamilton, in *Biooganic Frontiers,* ed. H. Dugas, Springer, Berlin, 1991, vol. 2, p. 115.
117. J. M. Lehn, *Angew. Chem. Int. Ed. Engl.,* 1988, **27**, 89.
118. J. M. Lehn, *Supramolecular Chemistry,* VCH, Weinheim, 1995.
119. F. Vogtle, *Cyclophane Chemistry,* Wiley, Chichester, 1993.
120. F. Diederich, *Cyclophanes,* Royal Society of Chemistry, 1991.
121. V. Bohmer, *Angew. Chem. Int. Ed. Engl.,* 1995, **34**, 713.

122. M. Perrin, F. Gharnati, D. Oehler, R. Perrin and S. Lecocq, *J. Inclusion Phenom., Mol. Recognit. Chem.,* 1992, **14**, 257.
123. D. N. Reinhoudt, P. J. Dijkstra, P. J. A. I. t. Veld, K. E. Brugge, S. Harkema, R. Ungaro and E. Ghidini, *J. Am. Chem. Soc.,* 1987, **109**, 4761.
124. M. Perrin, F. Gharnati, D. Oehler, R. Perrin and S. Lecocq, *J. Inclusion. Phenom., Mol. Recognit Chem.,* 1992, **14**, 257.
125. R. M. Izatt, J. D. Lamb, R. T. Hawkins, P. R. Brow, S. R. Izatt and J. J. Christensen, *J. Am. Chem. Soc.,* 1983, **105**, 257.
126. M. Newcomb, J. M. Timko, D. M. Walba and D. J. Cram, *J. American Chem. Soc.,* 1977, **99**, 6392.
127. J. M. Lehn, in *Comprehensive Supramolecular Chemistry,* eds. J. L. Atwood, J. E. D. Davies, D. D. Macnicol, F. Vogtle, Elsevier, Oxford, 1990.
128. R. M. Izatt, K. Pawlak and J. S. Bradshaw, *Chem. Rev.,* 1991, **91**, 1721.
129. K. Biemann, G. Buchi and B. H. Walker, *J. Am. Chem. Soc.,* 1957, **79**, 5558.
130. K. Tamao, S. I. Kodama, T. Nakatsuka, Y. Kiso and M. Kumada, *J. Am. Chem. Soc.,* 1975, **97**, 4405.
131. H. Schinz, L. Ruzicka, V. Geyer and V. Prelog, *Helv. Chim. Acta.,* 1946, **29**, 1524.
132. D. C. Billington, *Comprehensive Organic Synthesis,* Pergamon Press, Oxford,
133. W. Baker, K. M. Buggle, J. F. W. McOmie and D. A. M. Baker, *J. Chem. Soc.* 1958, 3594.
134. W. Baker, *Chem. Br.,* 1965, **1**, 250.
135. V. Boekelheide and J. A. Lawson, *Chem. Commun.,* 1970, 1558.
136. W. Jenny and H. Holzrichter, *Chimia,* 1968, **22**, 306.
137. T. Kauffmann, G. Beissner, W. Sahm and A. Woltermann, *Angew. Chem. Int. Ed. Engl,* 1970, **9**, 808.
138. G. R. Newkome and H. W. Lee, *J. Am. Chem. Soc.,* 1983, **105**, 5956.
139. V. Boekelheide and J. A. Lawson, *Chem. Commun.,* 1970, 1558.
140. H. J. J. B. Martel and M. Rasmussen, *Tetrahedron Letters,* 1971, 3843.
141. G. R. Newkome, Y. J. Joo and F. R. Fonczek, *J. Chem. Soc. Chem. Commun.* 1987, 854.
142. V. Kral, P. A. Gale, P. A. Jr., K. Jurikova, V. Lynch and J. L. Sessler, *Chem. Commun.,* 1998, 9.
143. C. W. Rees and C. E. Smithen, *J. Chem. Soc,* 1964, 928.
144. I. Borodkin, *Chem. Abst.,* 1974, **80**, 70791j.
145. N. A. Bailey, M. M. Eddy, D. E. Fenton, S. Moss and A. Mukkopadhyay, *J. Chem. Soc. Dalton Trans.,* 1984, 2281.
146. J. D. Curry and D. H. Busch, *J. Am. Chem.. Soc.,* 1964, **86**, 592.
147. T. J. Lotz and T. A. Kaden, *Helv. Chim. Acta.,* 1978, **61**, 1376.

148. J. Huuskonen and K. Rissanen, *J. Chem. Soc. Chem.. Commun.*, 1993, 771.

149. G. R. Newkome, G. L. McClure, J. Broussard-Simpson and F. D. Khoshboo, *J. Am. Chem. Soc.*, 1975, **97**, 3232.

150. G. R. Newkome, A. Nayak, G. L. McClure, J. Broussard-Simpson and F. D. Khoshboo, *J. Org. Chem.*, 1977, **42**, 1500.

151. C. J. V. Staveren, V. M. L. J. Aarts, P. D. J. Groothuis, W. J. H. Droppers, J. V. Eerden, S. Harkema and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1988, **110**, 8134.

152. J. A. Tucker, C. B. Knobler, I. Goldberg and D. J. Cram, *J. Org. Chem.*, 1989, **54**, 5460.

153. E. Weber, H. J. Kohler and H. Reuter, *J. Org. Chem.*, 1991, **54**, 1236.

154. J. M. Girodeau, J. M. Lehn and J. P. Sauvage, *Angew. Chem. Int. Ed. Eng.*, 1975, **14**, 764.

155. F. Vogtle and A. H. Effler, *Chem. Ber.*, 1969, **102**, 3071.

156. K. R. Reistad, P. Groth, R. Lie and K. Undheim, *J. Chem. Soc.Chem. Commun.*, 1972, 1059.

156a. R. Boekelheide, *J. Am. Chem. Soc.*, 1974, **96**, 1578.

157. J. D. Lamb, R. M. Izatt and J. J. Christensen, *Chemistry of Macrocyclic Compounds*, Plenum Press, New York, 1979.

158. M. R. Izatt, J. D. Lamb, N. E. Izatt, B. E. R. Jr., J. Christensen and B. L. Haymore, *J . Am. Chem. Soc.*, 1979, **101**, 6273.

159. D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, 1978, **11**, 8.

160. T. J. V. Bergen and R. M. Kellogg, *J. Am. Chem. Soc.*, 1977, **99**, 3882.

161. M. Kodama, E. Kimura and S. Yamaguchi, *J. Chem. Soc. Dalton Trans.*, 1980, 2536.

162. R. J. P. Corriu and J. C. Young, *The Chemistry of Organosilicon Compounds*, Wiley, New York, 1989.

163. W. B. Farnham, in *Synthetic Fluorine Chemistry*, ed. G. A. Olah, R. D. Chambers and G. K. S. Prakash, John Wiley and Sons, Inc., 1992, p. 247.

164. W. B. Farnham, D. C. Roe, D. A. Dixon, J. C. Calabrese and R. L. Harlow, *J. Am. Chem. Soc.*, 1990, 7707.

165. S. H. Langer, S. Connell and I. Wender, *J. Org. Chem.*, 1958, **23**, 50.

166. P. Ruggli, *Liebigs. Ann. Chem.*, 1917, 4121.

167. A. Luttringhaus and K. Ziegler, *Liebigs Ann. Chem.*, 1937, **528**, 155.

168. K. E. Krakowiak, J. S. Bradshaw and D. Zamecka-Krakowiak, *Chem. Rev.*, 1989, **89**, 929.

169. C. Giacovazzo, H. L. Monaco, D. Viterbo, F. Scordari, G. Gilli, G. Zanotti and M. Catti, *Fundamentals of Crystallography*, Oxford University Press, Oxford, 1992.

170. C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017.

171. M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.,* 1964, **86**, 213.
172. R. N. Greene, *Tetrahedron Letters,* 1972, 1793.
173. C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.,* 1990, **112**, 5525.
174. S. S. Moore, T. L. Tarnowski and M. Newcomb, *J. Am. Chem. Soc.,* 1977, **99**, 6398.
175. R. J. M. Nolte and D. J. Cram, *J. Am. Chem. Soc.,* 1984, **106**, 1416.
176. K. A. Connors, in *Binding Constants, The Measurement of Molecular Complex Stability*, Wiley Interscience, p. 141.
177. M. Goodall, P. M. Kelly, D. Parker, K. Gloe and H. Stephan, *J. Chem. Soc. Perkin Trans. 2,* 1997, 59.
178. J. A. Gladysz, *Science,* 1994, **266**, 55.
179. F. S. Yates, in *Comprehensive Heterocyclic Chemistry,* ed. A. J. Boulton and A. McKillop, Pergamon Press, Oxford, 1984, vol. 2, p. 511.
180. E. F. V. Scriven, in *Comprehensive Heterocyclic Chemistry,* ed. A. J. Boulton and A. McKillop, Pergamon Press, Oxford, 1984, vol. 2, p. 165.
181. D. L. Bodger, *Comprehensive Organic Synthesis,* Pergamon Press, Oxford, 1991.
182. W. K. R. Musgrave, *Chem. Ind.,* 1969, 943.
183. R. D. Chambers, M. Hole, W. K. R. Musgrave and J. G. Thorpe, *J. Chem. Soc., (C),* 1971, 61.
184. R. D. Chambers, C. W. Hall, J. Hutchinson and R. W. Millar, *J. Chem. Soc. Perkin Trans. 1,* 1998, 1705.
185. R. D. Chambers, J. Hutchinson, W. K. R. Musgrave, *J. Chem. Soc. C, (1965),* 5040.
186. R. D. Chambers, D. Lomas, W. K. R. Musgrave, *Tetrahedron,* 24, 1968, 5633.
187. B. V. Nguyen and D. J. Burton, *J. Fluorine Chem.,* 1994, **67**, 205-206.
188. E. J. Soloski, W. E. Ward and C. Tamborski, *J. Fluorine Chem,* 1972, **2**, 361.
189. I. Fleming, *Frontier Orbitals and Organic Chemical Reactions,* Wiley, 1976.
190. R. D. Chambers, F. G. Drakesmith and W. K. R. Musgrave., *J. Chem. Soc.,* 1965, 5045.
191. D. W. Brown, A. J. Floyd and M. Sainsbury, *Organic Spectroscopy,* John Wiley and Sons Ltd., Bath, 1988.
192. G. R. Newkome and J. M. Roper, *J. Organomet. Chem,* 1980, **186**, 147-153.
193. M. Schlosser, in *Organometallics in Synthesis- A Manual,* ed. M. Schlosser, J. Wiley, 1994, p. 1.
194. G. Queguiner, F. Marsais, V. Snieckus and J. Epsztajn, *Adv. Heterocyclic Chem.,* 1991, **52**, 187-304.
195. H. A. Dieck and R. F. Heck, *J. Organomet. Chem.,* 1975, 259.
196. L. Cassar, *J. Organomet. Chem.,* 1975, 253.

197. K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, 1975, 4467-4470.