The development of supported materials as potentially reusable heterogeneous catalysts for fine chemical synthesis.

Buckle, Richard

Buckle, Richard (2004) *The development of supported materials as potentially reusable heterogeneous catalysts for fine chemical synthesis..* thesis, Swansea University.
http://cronfa.swan.ac.uk/Record/cronfa42938

The Development of Supported Materials as Potentially Reusable Heterogeneous Catalysts for Fine Chemical Synthesis

By

Richard Buckle

Acknowledgments

Firstly, I would like to acknowledge Dr. Andrew E. Graham for his guidance, help and patience through the course of this project.

I would also like to thank Wei Li and Louise for their company and assistance in the laboratory.

I would like to express my thanks to Myron for running countless NMRs for me.

I am greatly appreciative of Eileen Jones for organising of the binding of this thesis and the administrative paperwork.

I would also like to thank Dr. Justin Holmes and Puadie Harrington from University College Cork for supplying the catalysts.

Finally, I would like to acknowledge Dr. Dave Hughes and Dr. Mark Bagley from the University of Wales Cardiff for their help and advice with regard to the microwave chapter of this thesis.

DECLARATION

This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree.

Signed . .....(candidate)

Date ....12/10/04........................

STATEMENT 1

This thesis is the result of my own investigations except where otherwise stated.

Other sources are acknowledged by footnotes giving explicit references. A bibliography is appended.

Signed .... .(candidate)

Date ....12/10/04.....................

STATEMENT 2

I hereby give consent for my thesis, if accepted, to be available for photocopying and for inter-library loan and for the title and summary to be made available to outside organisations.

Signed ... ...(candidate)

Date ....12/10/04....................

Abstract

Mesoporous catalysts with a variety of characteristics were utilised in a number of fine chemical synthesis reactions. Variation between the catalysts was determined at the synthetic stage, where differing loadings of aluminium and surfactants were used.

This study focused its attention upon using these catalysts in two specific types of reaction. Firstly, addition of alcohols to a range of epoxides and secondly, rearrangement of epoxides into their respective carbonyl analogue.

The final aspect of this study involved an investigation into microwave enhanced reactions. Here we show how microwaves dramatically reduce reaction times, with specific reference to addition of alcohols to epoxides using copper (II) tetraflouroborate as a catalyst.

Table of Contents

Chapter 1

Introduction

Introduction

In the modern global market place the chemical industry accounts for approximately twenty percent of the world's gross national product (GNP). The utilisation of catalytic materials represents a large and growing component of the chemical industry. A major component of this increased interest in catalytic materials over recent years has come about due to tightening legislation regarding the environment[1]. It is a well known fact that the chemical industry produces large amounts of toxic waste and emissions every year. This has resulted in calls from both inside and outside of the chemical industry to reduce the impact that the chemical industry has upon the environment. The interest in catalytic materials is also encouraged for financial and economic reasons.

The production of fine or speciality chemicals is an important sector of the chemical industry[2]. However, many of the reaction conditions used in the production of these chemicals were developed at the turn of the twentieth century when the chemical industry did not face the same challenges as it does now. Historically, the emphasis of a reaction was to improve the overall yield of the desired product. This often resulted in harsh reaction conditions that produced vast quantities of waste liquid, much of which was of a toxic or acidic nature. There is still a heavy emphasis on the overall yield, however in recent times environmental and economic issues have also been taken into consideration. Increased environmental legislation and a desire to decrease waste for economic reasons have pushed the chemical industry towards finding heterogenous catalysts for use in fine

---

[1] Clark, J. H.; Macquarrie, D. J. *Chem. Soc. Rev.* (1996), 303.
[2] Choudary, B. M.; Lakshmi Kantam, M.; Lakshmi Santhi, P. *Catal. Today* 57, (2000), 17-32.

chemical synthesis. For many years, the petrochemical industry has used zeolites as heterogenous catalysts in the process of petrochemical cracking of hydrocarbons.

Zeolite characteristics

Zeolites can be defined as a microporous crystalline solid containing a well defined structure which is built up of a silicon, aluminium and oxygen framework[3]. Within this framework lies an intricate network of pores that may contain cations, water or other small molecules which may alter the properties of the zeolite. There are approximately one hundred and fifty different types of zeolites, of which fifty occur naturally. Due to the porous nature of zeolites they have a plethora of applications. As mentioned earlier, the petrochemical industry was amongst the first to develop and utilize zeolites in the cracking of hydrocarbons. They have also found other applications in the form of water scavenging, separation and removal of gases and solvents. They also have applications in the agricultural and construction industry as well more domestic uses such as washing powders.

The defining feature of the zeolite framework is that it is made up of tetrahedral array of silicon and oxygen molecules as shown in **Figure 1**. Another attractive feature of these materials is that silicon atoms can be substituted by a small number aluminium atoms in a controlled fashion hence acid sites can be incorporated into the catalyst[4].

---

[3] Weller, M. T. *Inorganic Materials Chemistry*, Oxford University Press (1994), 71.

[4] Shriver, D. F.; Atkins, P. W. *Inorganic chemistry Third edition*, Oxford University Press, (1999), 366.

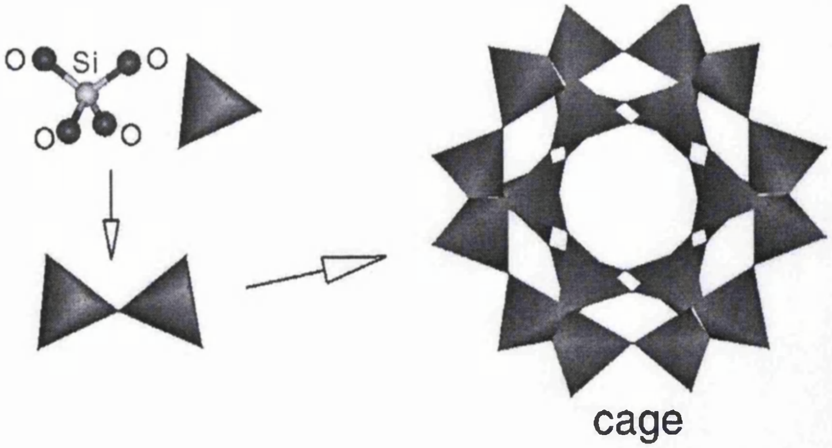


Figure 1: Diagram to show the nature of a zeolite framework[5]

The tetrahedral array of silicon (and aluminium if it is incorporated) atoms are linked together *via* the corners that results in a framework structure that can contain channels, cages or cavites. This framework structure allows molecules to enter, permitting reactions to occur within the framework. However, there is a limiting factor in that only pore sizes of approximately 3-10 Å are found. As a consequence, only reactants with the correct dimensions can be used in conjunction with zeolites for fine chemical synthesis. This limitation on reactant dimension has meant that a new type of porous material needed to be developed that could accommodate larger reactants.

Mesoporous catalysts

In 1992 the Mobil group disclosed a class of mesoporous catalysts named MCM-41s[6] which featured a hexagonal pore ordered system. The pore diameters ranged from 2 to 10

---

[5] Diagram taken from www.bza.org/zeolites.

[6] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359, (1992), 710.

nm and contained a large internal surface area[7] (between the region of 600-1000 m^2 g^{-1}). The primary difference in the synthesis of these mesoporous materials compared with their microporous counterparts (zeolites) lay in the size of the templating surfactant molecule. Typically in zeolite synthesis single molecules were used as templates resulting in small pore diameters. In the synthesis of the MCM-41s, Mobil used large surfactant molecules which after calcination left an ordered structure of pores. The distribution of pore sizes in mesoporous catalysts are somewhat larger than that of microporous materials being between 20-100 Å.

The ability to control pore size to a much greater degree by careful control over the surfactant and reaction conditions has seen significant interest in the development of mesoporous materials[8,9]. The primary reason for this is an enhanced molecular size and shape selectivity being available which is inherent in the mesopore structure. Selectivity results from pore dimensions (i.e. shape selectivity, size selectivity) and the type of active site located within the structure. Typically a mesoporous material will have between 50-80% void space within the volume of the solid depending upon the pore size.

The ability to customise mesoporous catalysts has resulted in a re-think of possible applications for their use. Whereas acid-catalysed reactions were limited (due to reactant size) in microporous catalysts, the increase in the range of pore dimensions available in mesoporous materials has meant that the applications for fine chemical synthesis are

---

[7] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T.Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, *J.Am. Chem. Soc.* 114, (1992), 10834.
[8] Sierra, L.; Guth, J.-L. *Micro and Meso Mater.* 27, (1999), 243-253.

greatly increased. The increase in pore dimensions means that bulky organic molecules can now be used as reagents in fine chemical synthesis. This is of particular importance where diffusional problems exist when microporous catalysts are utilized. A good example of this is the benefit of using Al-MCM-41, in which the weak acid sites catalyse the Beckmann rearrangement of bulky oximes, compared to the use of zeolites[10]

Another advantage associated with mesoporous materials is that many metallic elements can be introduced into the aluminosilicate framework. This gives the catalysts additional catalytic properties and greatly increases the number of applications. For example Ti-MCM-41 has been used in oxidation reactions of a range of organic molecules[11] and displays distinct advantages over catalysts such as Ti-Beta zeolites when large organic molecules are used. Mesoporous materials do, however, have drawbacks in part due to an increase in the number of silanol groups which can strongly adsorb the reaction products. This can lead to a reduction in the rate of reaction and can sometimes result in a loss of selectivity[12].

In our studies a range of aluminium containing mesoporous catalysts[13] were investigated for their ability to perform a limited number of simple transformations. The catalysts used had been designed to have a number of subtle differences, for example in the quantity of aluminium contained in the framework. The aim was to investigate what

---

[9] Øye, G.; Sjöblom, J.; Stöcker, M. *Adv. Collid and Interface Sci.* 89-90, (2001), 439-466.

[10] Brunel, D.; Blanc, A.C.; Galarneau, A.; Fajula, F. *Catal. Today* 73, (2002), 139-152 and ref [11] within.

[11] Blasco, T.; Corma, A.; Navarro, M.T.; Pariente, J.P. *J. Catal.* 156, (1995), 65-74.

[12] Climent, M.J.; Corma, A.; Velty, A.; Susarte, M. *J. Catal*, 196, (2002), 345-351.

[13] All catalyst were synthesised and analysed at University of Cork, Ireland.

effect these changes would have upon their catalytic ability. Another variable investigated was the effect of a change in the amount of surfactant used in the synthesis of the catalyst. It was expected that an increase in the amount of surfactant would result in an increase in the number of pores contained within the catalyst. It has been noted that the variation of the surfactant to silicon alkoxide ratios is important in the formation of the mesoporous material[14]. We were interested in how changing this ratio would affect the catalytic abilities of our mesoporous catalyst. The majority of the catalysts synthesised used hexadecyl trimethylammonium bromide (CTAB) as the surfactant. In later studies the surfactant itself was changed in order to investigate what effect this might have upon catalytic activity for a given reaction.

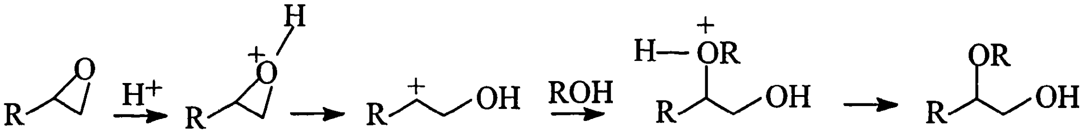
The activity of these catalysts was tested using simple chemical transformations, in particular, the nucleophilic addition of alcohols to epoxides and the rearrangement of epoxides to the corresponding carbonyl compound. The inherent reactive nature of epoxides has led to them becoming key intermediates in many organic reactions. The strain and polarity associated with the three-membered ring system leads to a tendency for epoxides to react with a wide range of reagents. In this particular study, our main focus was the reactions of epoxides with nucleophiles. This is of particular interest due to the fact that ring opening results in the formation of a 1,2-difunctionalised product. In addition to this, one of the oxygen atoms is protected and hence it is possible to selectively manipulate one functional group in the presence of the other. It has also been

---

[14] Yu-de, W.; Chan-lai, M.; Xiao-dans, S.; Heng-de, L. *Applied Catal. A: General* 246, (2003), 161-170.

observed[15] in most cases ring opening occurs with almost exclusively *trans*-stereochemistry where applicable.

It has been well documented that the presence of acid in the reaction of epoxides with nucleophiles catalyses the ring-opening reaction[16]. The mechanism for this reaction proceeds *via* protonation of the oxygen atom of the epoxide three-membered ring. Consequently, ring opening results in the formation of a carbocation intermediate. It is at the carbocation position that the nucleophile attacks, via an S_N1 type mechanism (**Scheme 1**) with attack from either side of the planer intermediate.

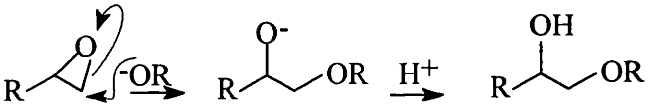


Scheme 1: Ring-opening of epoxide under acidic conditions

The structure of the epoxide, as well as the reaction conditions, determines the position of nucleophillic attack. In the case of unsymmetrical epoxides such as styrene oxide in an acidic reaction mixture, nucleophillic attack will in most cases occur at the more substituted carbon. This is because the carbocation intermediate is stabilised by adjacent groups. In the case of neutral or basic solutions, then nucleophilic attack occurs at the less substituted carbon due to the S_N2 type mechanism that occurs as a result of steric hinderance (**Scheme 2**).

---

[15] Posner, G. H; Rogers, P. Z, *J. Am. Chem. Soc.*, 99:LS, December, 7, (1997), 8108.
[16] Smith, J. G, *Synthesis*, (1984), 629-656.



Scheme 2: Ring-opening of epoxides under basic conditions

The use of reaction conditions utilising catalysts such as hydrochloric acid or sulphuric acid has been problematic in recent years, due to the environmental concerns about the disposal of the waste acidic material. These harsh reaction conditions employed plus mounting environmental pressure has led to a search for new heterogenous acidic catalysts in order to alay these concerns. In particular, heterogenous catalysts are a particularly attractive proposition and there have been numerous attempts to develop such catalysts for ring-opening/addition reactions using alcohols as the nucleophilic species[17]. To date, this reaction was limited to the addition of primary alcohols, however, Barluenga has recently introduced copper (II) tetrafluoroborate as an efficent catalyst for the addition of sterically hindered alcohols[18]. It was found that using this catalyst, good yields of the β-alkoxy alcohol product were produced from the addition reaction of primary, secondary and tertiary alcohols at room temperature. The main disadvantage with this method is that the catalyst is not recoverable and that an aqueous work-up is required that creates waste material and lowers atom efficiency. Furthermore, with sterically hindered alcohols the addition reactions were very slow and only produced synthetically useful yields over extended reaction times.

---

[17] Likhar, P. R.; Kumar, M. P.; Bandyopadhyay, A. K. *Synlett*, 6, (2001), 836-838.
[18] Barluenga, J; Vazquez-villa, Henar; Ballesteros, A; Gonzalez, J.M, *Organic Letters*, (2002), Vol.4, No.17, 2817-2819.

In view of these limitations, we sought to introduce new aluminium based mesoporous catalysts that produce high yields of β-alkoxy alcohols under similar reaction conditions to those used by Barluenga. However, our catalysts are recoverable so giving our approach a decisive practical and economic advantage.

The rearrangement of epoxides under acidic conditions has been noted as a common side reaction, and indeed, mesoporous materials have been used previously to perform such rearrangement reactions[19]. Rearrangement of epoxides to carbonyl compounds has been accomplished using a number of Lewis acid catalysts, such as bismuth (III) oxide perchlorate[20] and bismuth triflate[21] as well as zeolites[22]. In addition to the addition reactions of alcohols we also investigated the rearrangement of epoxides to carbonyl compounds using our mesoporous materials as catalysts.

Microwave reactions

In recent years the use of microwave technology has been utilized to perform a wide range of organic reactions[23]. The principle of microwave heating differs from that of conventional heating. Microwave reactions work on the principle that the frequency of molecular rotation is similar to that of microwave radiation. As a consequence, when a molecule which has a permanent dipole is subjected to a microwave field it will try to

---

[19] Carati, A.; Ferraris, G.; Guidotti, M.; Moretti, G.; Psaro, R.; Rizzo, C. *Catal. Today* 77, (2003), 315-323.

[20] Anderson, A.M.; Blazek, J.M; Garg, P.; Payne, B.J.; Mohan, R.S. *Tetrahedron Lett.* 41, (2000), 1527-1530.

[21] Bhatia, K.A.; Eash, K.J.; Leonard, M.N.; Oswald, M.C.; Mohan, R.S. *Tetrahedron Lett.* 42, (2001), 8129-8132.

[22] R.A Sheldon et al *J. Molecular Catalysis A: Chemical* 134, (1998), 129-135.

[23] Caddick, S. *Tetrahedron* 51, (1995), 10403-10432.

align itself with the applied field. If the applied field oscillates the molecule is constantly trying to realign itself and in the process the electromagmetic energy is transformed to heat energy. The main advantage of this approach is that the reactions are very quick. In addition, due to the nature of the radiation, there is increased uniformity with regard to the heating which leads to a decrease in the number of by-products formed.

We have also investigated the effect of microwave heating upon the rate, overall yields and selectivity of the addition of alcohols to epoxides using copper (II) tetrafluoroborate as a catalyst under Barluenga's reaction conditions. This reaction acts as an ideal benchmark to assess the potential of microwave heating to accelerate addition reactions and to assess the selectivity of this reaction.

It has been claimed that it is possible to utilise microwave technology to improve the overall yields of reactions where solid catalysts are used[24]. As the use of microwave technology is a relatively new field, little is known about the applications of mesoporous materials under these conditions. In previous studies[25], silica gel and alumina have been used under microwave conditions to perform a number of reactions with success. With this in mind, it was expected that the use of microwave conditions may prove to be an ideal approach for the acceleration of the addition of alcohols to epoxides using our mesoporous catalysts.

---

[24] Taken from the CEM Microwave operations manual.

[25] Deshayes, S.; Liagre, M.; Loupy, A.; Luche, J.-L.; Petit, A. *Tetrahedron*, 55, (1999), 10851-10870.

Chapter 2

Addition of alcohols to epoxides using mesoporous catalysts

Introduction

The addition of a range of alcohols to epoxides has been studied and well documented due to the synthetic value of the 1,2-disubstituted products formed[26]. Previously, the conditions employed for this reaction were homogenous and required the use strong acid[27], elevated reaction temperatures[28] and extensive reaction times[29] to promote the reaction. In many cases these harsh reaction conditions resulted in polymerisation and a lack of control over the regiochemistry. Another drawback to these reactions is the low atom efficiency and the associated chemical waste problems. In more recent studies[30] metal salts such as copper (II) tetrafluoroborate and ytterbium trifluoromethanesulfonate[31] have been used at room temperature with successful results. In the case of the copper catalyst, however, the catalytic material is near impossible to recover. Limited studies have been undertaken using titanium based zeolites as catalysts using methanol[32] as the nucleophile, however, these studies met with only limited success. In our study, the addition of alcohols to epoxides was utilised as a test reaction in order to gather information on a number of different mesoporous aluminosilcate based catalysts[33]. We were also interested in how changes in the preparation of the catalysts would affect their efficiency in these reactions.

---

[26] March, J. *Advanced Organic Chemistry*, 3rd ed., John Wiley, New York, (1985), 346.

[27] Olah, G. A.; Fung, A. P.; Meider, D. *Synthesis* (1981), 280.

[28] Posner, G. H.; Rogers, D. Z.; Kinzig, C. H.;Gurria, G. M. *Tetrahedron Lett.* 31, (1975), 3591.

[29] Iranpoor, N.; Mohammadpour Baltork, I, *Tetrahedron Lett.* 31, (1990), 735.

[30] Barluega, J.; Vaszquez-Villa, H.; Ballesteros, A.; Gonzalez, J.M. *Organic Letters* 17, (2002), 2817-2819.

[31] Likhar, P. R.; Kumar, M. P.; Bandyopadhyay, A. K. *Synlett* 6, (2001), 836-838.

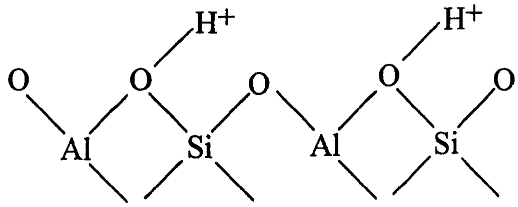
[32] Zhuang, J.; Yan, Z.; Liu, X.; Liu, X.; Han, X.; Bao, X.; Mueller, U. *Catalysis Letters* 83, (2002), 87-91.

[33] Provided by Dr. Justin Holmes, UCC.

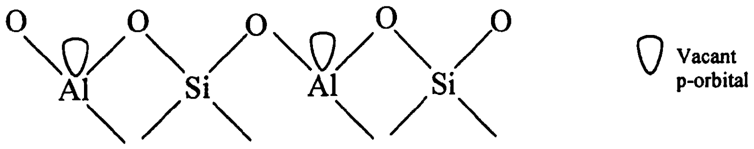
The synthesis of the mesoporous catalysts is typically carried out under standard sol-gel conditions. During their preparation, a number of parameters were varied in order to give a range of individual characteristics to the catalysts. For example, by varying the amount of aluminium the Lewis acidity and Brønsted acidity of the material can be altered. In addition to this, the properties of the catalysts can be changed by varying the type and quantity of surfactant chosen. It is hoped on the basis of the information gathered in this initial study that we will be able to "engineer" the catalysts to further enhance activity and selectivity of the catalyst in subsequent reactions.

The ring opening reaction of epoxides is catalysed by the presence of both Brønsted and Lewis acid sites. The function and structure of both types of acid sites are important factors in determining the activity and selectivity of mesoporous catalysts[34]. Brønsted acidity in the mesoporous material is due to the hydroxy (OH) group which is bridged between the silicon (Si) and aluminium (Al) atoms within the framework structure. Substitution of Si (IV) atoms by Al (III) atoms places a negative charge upon an adjacent oxygen atom. The negative charge on the oxygen atom is balanced out by protonation. Alternatively, the negative charge on the oxygen can be neutralised by the formation of cations (Lewis acidity). Lewis acidity can also be achieved by dehydration of the Brønsted sites *via* calcination (**Figure 2**)

It is possible, using spectroscopic techniques, to distinguish between the two different types of acidic sites. In recent years, many different approaches have been utilised to this end. Characterisation of the acid sites within the catalysts is possible using adsorption of a variety of probe molecules then, analysing the catalysts by Fourier transform infra-red spectroscopy (FTIR) or UV-visible spectroscopy[35,36] It is also possible to distinguish the acid sites using ^{27}Al magic angle spinning nuclear magnetic resonance (MAS-NMR)[37]. Alternatively, it is also possible to use temperature-programmed desorption of probe molecules (such as pyridine[38]) with mass spectroscopic detection. We had hoped to study our mesoporous catalysts using the aforementioned methodologies, however time restrictions meant that this was not possible. Characterisation of our catalyst using these methods is an area for future investigation.



Bronsted acid sites



Lewis acid sites

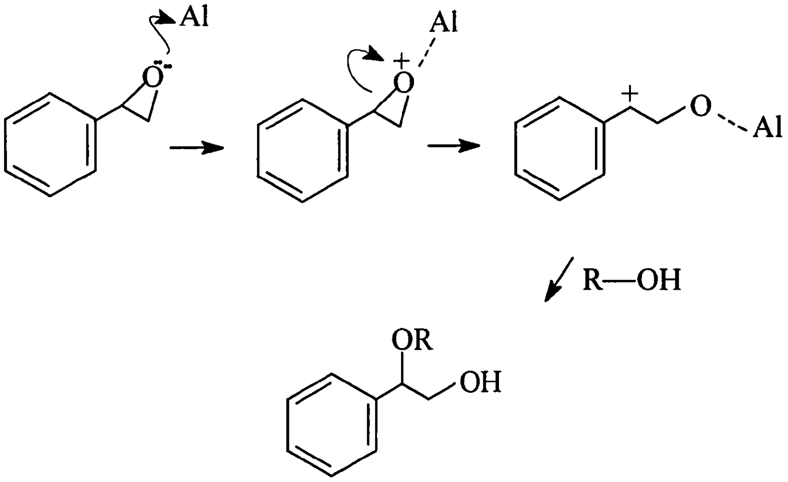
Figure 2: Acidic sites

For the ring opening reaction of epoxides in an acidic environment, the mechanism proceeds through an initial formed cyclic alkyloxonium ion. Cyclic alkyloxonium ion

---

[34] Deng, F.; Du, Y.; Ye, C.; Wang, J.; Ding, T.; Li, H. *J. Phys. Chem.* 99, (1995), 15208-15214.
[35] Coluccia, S.; Marchese, L.; Martra, G. *Micro. And Meso. Mater.* 30, (1999), 43-56.
[36] Bevilacqua, M.; Busca, G. *Catalysis Comm.* 3, (2002), 497-502.
[37] Sakthivel, A.; Daparkar, S. E.; Gupta, N. M.; Kulshreshta, S. K.; Selvan, P. *Micro. And Meso. Mater.* 65, (2003), 177-187.

formation occurs *via* donation of electrons from oxygens lone pair to the vacant p-orbital on the aluminium atom, followed by nucleophilic attack of the alcohol.



Scheme 3: Acid catalysed ring opening of an unsymetrical epoxide

It is apparent from **Scheme 3** that acid catalysed ring opening of unsymmetrical epoxides results in a reaction that is regioselective[39]. As highlighted earlier, the structure of the epoxide and the reaction conditions are critical and determine the position of nucleophilic attack. When the oxygen atom in the epoxide ring donates electrons to the p-orbital of aluminium, the intermediate carbocation formed has a polarised carbon-oxygen bond. Consequently, a partial positive charge (caused by polarisation) is placed on one of the carbon atoms of the epoxide ring, with the carbon atom which has the greatest ability to stabilise the positive charge being favoured. A tertiary carbon atom is better able to stabilise a positive charge than a primary carbon atom due to hyperconjugation. Aryl

---

[38] Selli, E.; Forni, L. *Micro. And Meso. Mater.* 31, (1999), 129-140.

groups which act as electron donors assist in stabilising the positive charge where appropriate.

In the case of cyclic epoxides, such as cyclohexene oxide, a *trans* diaxial product is commonly observed upon ring opening, (due to an inherent lack of free rotation about the carbon-carbon bonds). This occurs as a result of an attempt by the three-membered ring to maximise co-planarity of the participating centres of the transition state[40].

Results

In our study two epoxides were used. The first epoxide was styrene oxide which is an unsymmetrical, aromatic epoxide, the second epoxide was cyclohexene oxide which is a symmetrical, cyclic epoxide. A series of acidic mesoporous catalysts were tested and their abilitity to catalyse the alcoholysis of epoxides was assessed.

Styrene oxide

Cyclohexene oxide

Figure 3: Test epoxides

---

[39] Katritzky, A. R.; Rees, C. W.; Lwowski, W. *Comprehensive Heterocyclic Chemistry*, Oxford: Pergamon, Vol. 7, (1984), 100-113.

[40] Anselmi; Berti; Catelani; Leece; Monti *Tetrahedron* 33, (1977), 2771.

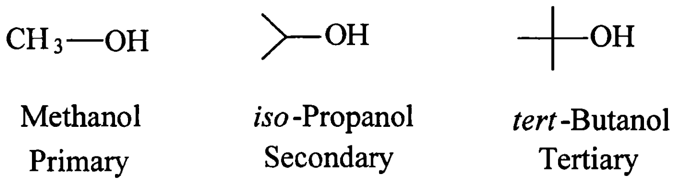


Figure 4: Selected alcohols

Initially it was important to establish that acidic materials from within the mesoporous catalyst did not leech into the reaction mixture and catalyse the reaction in a homogenous manner. In order to establish this, a reaction was carried out in which methanol was added to styrene oxide in the presence of a mesoporous catalyst. After two hours the reaction was divided into two halves; one half remained unaltered whilst the other half had all traces of catalyst removed by filtration through a celite plug. Both reactions were then stirred for a further 22 hours. The results are shown in **Table 1.**

Reaction time (hours)	**% conversion to β-alkoxy alcohol**	
0	0	0
	Catalyst removed	**Catalyst remained**
2	42	42
4	42	76
24	42	100

Note - Percentages are established from ^{1}H NMR spectrum
Reaction conditions: rt, 1:4 epoxide:alcohol, catalyst 1g Al/4g CTAB (100mg)

Table 1: Split reaction results

As **Table 1** clearly demonstrates, when the catalyst is removed from the reaction mixture methanol addition ceases completely. However, in the sample where the catalyst remains, the reaction continues to completion. This indicates that no acidic materials leach from the catalyst and the reaction is truly heterogenous. The reaction was also performed using a selection of catalyst that had not been calcined and as a consequence still contained the surfactant. The results are shown in **Table 2**.

Al sec butoxide (g)	**CTAB surfactant (g)**	**Product (%)**
0	4	0
1	4	0
5	4	0
10	4	0

Reaction conditions: rt, 1:4 epoxide:alcohol, catalyst (100mg)

Table 2: Methanolysis of styrene oxide using uncalcined catalysts

The results in **Table 2** indicate that it is likely that all of the active sites responsible for activity reside inside the catalyst. The results also show that there is little or no surface activity on the outside of the catalyst indicating that the reaction is taking place within the porous framework of the catalyst. This is important as, if reactions occur on the outside surface of the catalyst, any attempts to fine tune the pore structure of the catalysts for selectivity are made redundant. The results from this table also show that the surfactant itself does not catalyse the reaction.

Reactions of styrene oxide with alcohols

Once it was established that catalytic activity resided within the framework of the materials a series of test reactions were commenced. The purpose of these reactions was to investigate how subtle changes in the synthesis of the catalyst would affect the outcome of the reactions. Three main variables of the catalyst were investigated;

I. The loading of aluminium in the catalyst which relates directly to the nature of the active sites,
II. The quantity of the surfactant used (cetyl trimethyl ammonium bromide (CTAB)) which determines the pore shape and quantity,
III. The type of surfactant used which controls the size of the pores.

In the first set of experiments in which a series of alcohols were added to styrene oxide, the amount of surfactant used was kept constant and the aluminium quantity was varied. The results of these experiments are shown in **Table 3 and Table 4**. It was expected that with an increase in the quantity of aluminium present there would be a corresponding increase in the conversion of the starting material to the product. This assumption was made upon the basis that as the quantity of aluminium used increases there will be a greater number of acidic sites present. A possible explanation for why this trend was not observed is that when a greater aluminium quantity is used the strength of the acidic centres decreases[41]. This is due to an increase in the number of anionic centres which disperse the positive charge.

---

[41] Sen, S.E.; Smith, S.M.; Sullivan, K.A. *Tetrahedron* 55, (1999), 12657-12698.

As can be seen in **Table 3,** increasing the aluminium content of the catalyst does not lead to an increase in the amount of product generated. From this information it can be concluded that in order to maximise the yield of product obtained it requires more than just increasing the number of active sites. It appears that the location of the active site within the pore may be of primary importance for the reaction. This issue is raised by Weitkamp[42] who points out that the location of the acid sites is paramount to the ability of the material to function as a catalyst. For example, the acid sites may be located in large pores where they are accessible to bulky substrates, or they could possibly be located in less accessible areas of the catalyst such as in the walls or small cavities. As mentioned earlier, future investigation of the acid sites using spectroscopic methods will help to clarify these issues.

The results in **Table 3** show that two products where observed to have formed. The ^{1}H NMR data showed a competing rearrangement reaction was occuring to form an aldehyde product, which was identified as phenylacetaldehyde. The formation of the competing aldehyde by-product occurs due to the position of the carbocation intermediate that is formed (**Scheme 3**). The carbocation intermediate will form the aldehyde if the alcohol is unable to attack the cation *via* nucleophillic addition. This situation can occur due to the properties of the catalyst and/or the reaction conditions.

---

[42] Weitkamp, J. *Solid State Ionics* 131, (2000), 175-188.

Al sec butoxide	**CTAB**	**Methanol**			***iso*-Propanol**			***t*-Butanol**		
		Conversion	**Product selectivity (%)**		**Conversion**	**Product selectivity (%)**		**Conversion**	**Product selectivity (%)**	
(g)	**(g)**	(%)	*Alcohol*	*Aldehyde*	(%)	*Alcohol*	*Aldehyde*	(%)	*Alcohol*	*Aldehyde*
1	4	100	71.5	28.5	68	40	60	55	25	75
2	4	67.5	67.5	32.5	43	34	66	31	32	68
3	4	100	73.5	26.5	82	35	65	74	24	76
4	4	79.5	71.5	28.5	8	37	63	19.5	37	63
5	4	100	74.5	25.5	61	32	68	70	31	69
6	4	0	0	0	0	0	0	0	0	0
7	4	100	80.5	19.5	86	32	68	70	21	79
8	4	0	0	0	0	0	0	0	0	0
10	4	57.5	69	31	31	33	67	18	23	77

Reaction conditions: RT, 24hr, 1:4 epoxide:alcohol, catalyst (100mg)

Table 3: Addition of a series of alcohols to styrene oxide using a variety of catalysts based on ^1H NMR

Al sec butoxide	**CTAB**	**Methanol**			***iso*-Propanol**			***t*-Butanol**		
		Conversion	**Product selectivity (%)**		**Conversion**	**Product selectivity (%)**		**Conversion**	**Product selectivity (%)**	
(g)	**(g)**	(%)	*Alcohol*	*Aldehyde*	(%)	*Alcohol*	*Aldehyde*	(%)	*Alcohol*	*Aldehyde*
3	**4**	100	*74*	*26*	86	*43*	*57*	65	*25*	*75*
5	**4**	100	*73*	*27*	63	*33*	*67*	71	*32*	*68*
7	**4**	100	*78*	*22*	81	*35*	*65*	70	*24*	*76*

Reaction conditions: RT, 24hr, 1:4 epoxide:alcohol, catalyst (100mg)

Table 4: Addition of a series of alcohols to styrene oxide using selected catalysts based on isolated yields

Catalysts with 1g Al/4g CTAB, 3g Al/4g CTAB, 5g Al/4g CTAB and 7g Al/4g CTAB all showed 100% conversion of styrene oxide to products (from the methanol addition reactions) with a general ratio of products being 70% addition product and 30% rearrangement, with the exception of the catalyst containing 7g Al/4g CTAB which showed 80% and 20% respectively. The results in **Table 3** also show that the 5g Al/4g CTAB catalyst, which performed relatively poor in subsequent rearrangement reactions (only 37 % conversion see **Table 11**) showed a marked improvement in efficiency when used for addition reactions. Catalysts with 2g Al/4g CTAB, 4g Al/4g CTAB, 10g Al/4g CTAB also show improved performance for addition reactions in comparison with their rearrangement reactions, however, their activity is noticeably lower (**Table 3**). Catalysts containing 6g Al/4g CTAB or 8g Al/4g CTAB showed no signs of reactivity and no products were observed. These results show that different quantities of aluminium used in the synthesis affect the catalytic activity of the mesoporous catalyst.

Product selectivity for the β-alkoxy alcohol or the aldehyde can be attained in some cases by changing the reaction conditions. By increasing the amount of alcohol in the reaction mixture, the product distribution is pushed towards the formation of the β-alkoxy alcohol. Likewise, if the amount of alcohol in the reaction is limited then the catalyst is able to effectively promote the competing rearrangement reaction. Therefore product selectivity can be attained by manipulation of the ratio of epoxide:alcohol as is shown in **Table 5**.

Epoxide Equivalents	**Alcohol Equivalents**	**Product Distribution (%)**	
		Aldehyde	β-Alkoxy alcohol
1	1	60	40
1	4	30	70
1	8	20	80
1	12	10	90
1	16	0	100

Reaction conditions: RT, catalyst 1g Al/4g CTAB (100mg)

Table 5: Effect on product distribution by varying epoxide to alcohol ratio

The primary drawback to manipulating the reaction selectivity in this manner is that the atom efficiency of the reaction is reduced, although volatile alcohols can be recovered. We initially thought that formation of the aldehyde product was favoured if entry of the alcohol to the active sites is restricted by the pore size of the catalyst. This would then correlate the increase in aldehyde formation to the increase in size of the alcohol. However, upon reviewing the data concerning the pore size (**Figure 5**) this was deemed not to be the case. The data from **Figure 5** shows that the most abundant pore size for catalysts synthesised using 5g Al/4g CTAB is 17.8 Å, which will easily accommodate all of the alcohols and the products formed. As all the alcohols apparently experience no difficulty entering the pores, a logical conclusion might be that the position of the acidic sites within the pores may hinder the formation of the bulkier β-alkoxy alcohols, thus favouring rearrangement. Another explanation could be that the epoxide to alcohol ratio could affect the product selectivity depending on the alcohol used. Additionally there is a possibility that the catalyst is decomposing the secondary and tertiary alcohols to form the respective alkene and water. This reduces the amount of alcohol present and therefore favours the rearrangement reaction. Decomposition of the primary alcohol would be expected to be an unfavourable process.

Effect on the addition reactions of increasing the quantity of surfactant used in synthesis

Using the information obtained from our initial experiments, a second series of catalysts were synthesised in an attempt to improve selectivity in the addition reactions. In order to overcome the possible problems associated with steric hinderance, the amount of surfactant (CTAB) used in the synthesis of the catalysts was increased. This leads to a larger pore volume and additionally increases the surface area inside the pore. The results of varying the amount of surfactant used in catalyst synthesis were compared by analysis of the pore volume and the surface area with respect to average pore diameter, between catalysts containing 5g Al/4g CTAB and 5g Al/6g CTAB The results are displayed in **Figures 5 and 6** respectively.

From the graphs in **Figure 5** it can be seen that as the surfactant quantity increases there is a considerable increase in the cumulative volume (cubic centimetres/gram) of the catalyst pores. This can be seen by looking at the pore diameter at approximately 18Å for both catalysts. The catalyst containing 5g Al/4g CTAB has a cumulative pore volume of 0.043 cubic centimetres/gram (cc/g) whereas the catalyst containing 5g Al/6g CTAB has a cumulative pore volume of 0.179 cc/g as shown from a BJH adsorption pore distribution report[43]. From this analysis it is clear that as the amount of surfactant used in the synthesis of the catalyst is increased there is a corresponding increase in the pore volume. In conjunction with this, the surface area of the pores inside the catalyst also increases with an increase in the amount of surfactant used at the synthesis stage. It is noteworthy to mention that an increase in the quantity of surfactant used does not result in larger pore diameters. It has been found that the pore diameter of silicon based catalysts is directly related to the alkyl chain length of the surfactant used in the synthesis stage[44]. Therefore in order to increase the pore diameter a different, larger surfactant would have to be employed.

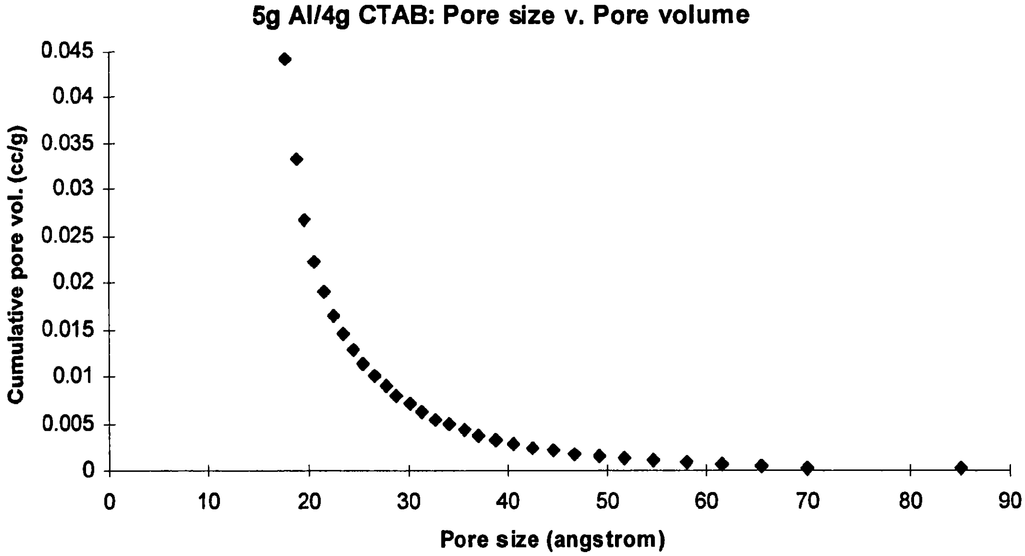
Recently, it has been found that for silica based materials, the variation of the surfactant to silicon alkoxide ratio at the synthesis stage is important in the formation of the mesoporous materials[45]. At different ratios of surfactant-to-silicon, there is a change in the crystalline structure of the mesoporous material. The general trend is that for surfactant-to-silicon ratios of 0.6:1 a hexagonal structure emerges (similar to MCM-41), at a ratio of 1.0-1.2:1 a cubic I_n three-dimensional structure occurs (similar to MCM-48). Finally, at ratios above 1.2:1 a lamellar structure is formed (similar to MCM-50). After calculating the surfactant-to-silicon ratios for the catalysts containing 5g Al/4g CTAB, 5g Al/5g CTAB and 5g Al/6g CTAB, some interesting differences emerged between the catalysts. The catalyst containing 5g Al/4g CTAB have a surfactant-to-silicon ratio of 1.57:1 (lamellar structure), the catalyst containing 5g Al/5g CTAB ratio was 1.2:1 (cubic

---

[43] Characterisation of catalysts carried out at University College Cork, Cork, Ireland.
[44] McIntosh, D. J.; Kydd, R. A. *Micro.and Meso. Mater.* 37, (2000), 281-289.
[45] Wang, Y.-D.; Ma, C.-L.; Sun, X..-D.; Li, H.-D. *Applied Catalysis A: General* 246, (2003), 161-170.

structure) and the catalyst containing 5g Al/6g CTAB had a ratio of 1.05:1 (cubic structure).

The information from **Figures 5 and 6** lends supporting evidence to the theory that differences in the structure of the catalysts emerge when different amounts of surfactant are used at the synthesis stage. The catalysts containing 5g Al/6g CTAB has a far greater surface area and pore volume than the catalyst containing 5g Al/4g CTAB. This is to be expected, as derived from the surfactant-to-silicon ratio the 5g Al/6g CTAB catalyst has a cubic framework which characteristically has a high surface area. The 5g Al/4g CTAB catalysts has a lamellar framework, which due to its more layered structure suffers a decrease in its pore volume and surface area.



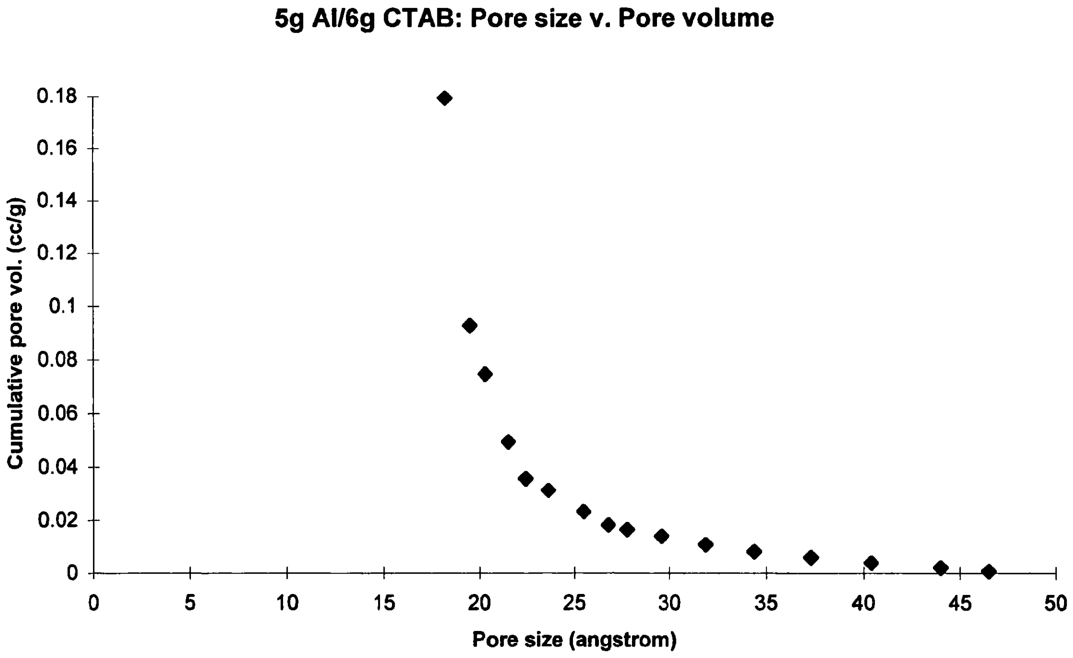


Figure 5: Effect of increase in CTAB on cumulative pore volume

Figure 6 shows the corresponding increase in surface area that occurs when the surfactant quantity is increased.

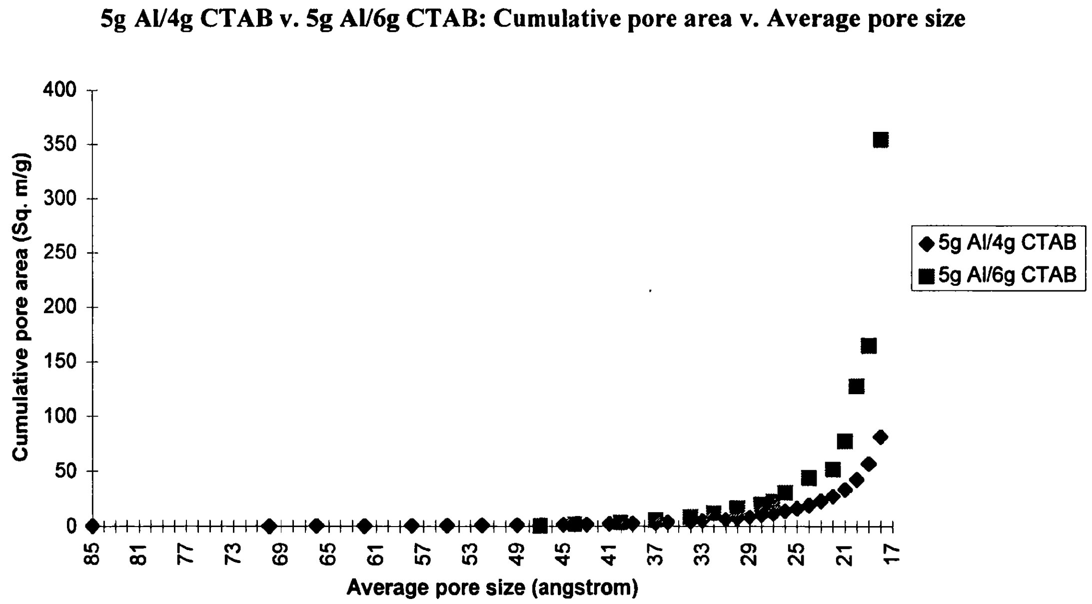


Figure 6: Effect of an increase in CTAB on cumulative surface area

Again it can be seen that an increase in surfactant quantity results in an increase in the area inside of the pores as shown in **Figure 5**.

The effect of variation of surfactant quantity on methanolysis of styrene oxide

It was decided to investigate the methanolysis of styrene oxide using the catalysts synthesized using a variable amount of surfactant with a constant amount of aluminium. The results of these experiments can be seen in **Table 6**.

Al sec butoxide (g)	CTAB surfactant (g)	Product (%)	Product selectivity	
			β-alkoxy-alcohol (%)	aldehyde (%)
5	4	100	74	26
5	5	100	67	33
5	6	100	77	23
5	8	100	80	20

Reaction conditions: RT, 24hr, 1:4 epoxide:alcohol, catalyst (100mg)

Table 6: The effect of variation of surfactant quantity on methanolysis of styrene oxide

As can be seen from **Table 6** an increase in the quantity of the surfactant appears to change the product selectivity to favour the alcohol product although the changes are relatively small. The conversion of starting material to product remains constant across the four catalysts. This leads to the conclusion that here (i.e. in this series) it is the amount of aluminium that is important in promoting the conversion of starting material to product. It may be that variation of the surfactant quantity may indeed allow for the product ratios of alcohol to aldehyde to be changed. In the future it may be possible that catalysts can be designed using this information to help improve the selectivity of the reaction.

In accordance with this, a new series of mesoporous catalysts were produced in which the amount of surfactant was increased to five grams whilst the aluminium quantities were varied. A similar set of experiments were conducted using the addition of alcohols to styrene oxide as a standard reaction to compare the differences between the catalysts.

Results from these experiments are shown in **Table 7**. In comparison with the results shown in **Table 3**, a number of similarities and differences are clear. Firstly, it can be seen that addition of increased amounts of surfactant has the effect of increasing the yield of the reaction with a limited number of exceptions. For example, comparison of the results obtained for the catalysts containing 2g Al/4g CTAB and 2g Al/5g CTAB show that an increase in the quantity of surfactant used (from 4g CTAB to 5g CTAB), increases the product yield by approximately thirty percent. However, it is interesting to note that whilst the overall yield increases the product distribution between the β-alkoxy alcohol and the aldehyde by-product essentially remains the same. These results suggest that an increase in surfactant does not increase the pore diameters, but leads to a change in the structure of the pores as discussed earlier. This hypothesis is supported by the graphs in **Figures 5 and 6**. They show that when amount of surfactant is increased there is a large increase in the cumulative volume and surface area of the pores. This supports the idea that as the surfactant quantity increases there is a change from a lamellar type structure towards a cubic structure.

The catalysts containing *X*g Al/4g CTAB and *X*g Al/5g CTAB (where *X* denotes a varied amount of aluminium used) contain pores with openings of similar dimensions. The catalyst series containing *X*g Al/5g CTAB have a more cubic structure and hence a greater surface area and volume within the pores. The catalyst series containing *X*g Al/4g CTAB have a more lamellar type structure and hence a lower surface area and volume within the pores by comparison. As a consequence reactants entering the pores of a catalyst synthesised using 5g CTAB have an increased probability of interacting with an active site. Therefore as seen in the results in **Table 7** there is an increase in the amount of product observed compared with when 4g CTAB catalyst are used (for results see **Table 3**). Product selectivity appears to stay similar between both types of catalysts. This shows that selectivity is probably a function of the nature of the acid sites or is perhaps dependant upon the epoxide-to-alcohol ratio.

Reactions of cyclohexene oxide with alcohols

After the success of addition of alcohols to styrene oxide, a selection of the more efficent catalysts were used to attempt the addition of a series of alcohols to cyclohexene oxide. Ring opening of cyclohexene oxide with methanol using chromatographic alumina as a catalyst had reported good yields[46]. We hoped that our mesoporous aluminium based catalyst might also help catalyse this reaction. Cyclohexene oxide is a symmetrical, aliphatic epoxide and addition of alcohols is slightly more complex due to the nature of the carbocation intermediate species. The intermediate is not as stable as the corresponding species for styrene oxide since cyclohexene oxide lacks electron donating groups such as phenyl which help to stabilize the carbocation intermediate. As a consequence the intermediate species is short lived therefore if nucleophilic attack is slow dimerisation or hydrolysis reactions may compete.

---

[46] Posner, G. H.; Rogers, D. Z. *J. Am. Chem. Soc.* (1977), 8208-8213.

Al sec butoxide (g)	**CTAB (g)**	**Methanol**			***iso*-Propanol**			***t*-Butanol**		
		Conversion (%)	**Product selectivity (%)**		**Conversion (%)**	**Product selectivity (%)**		**Conversion (%)**	**Product selectivity (%)**	
			Alcohol	*Aldehyde*		*Alcohol*	*Aldehyde*		*Alcohol*	*Aldehyde*
1	5	100	75	25	100	46	52	100	30	70
2	5	100	74	26	100	37	63	96	20	80
3	5	100	77	23	74	34	66	47	20	80
4	5	100	73	27	95	45	55	92	22	78
5	5	100	67	33	78	37	63	59	25	75
7	5	100	70	30	91	38	62	83	19	81
10	5	100	62	38	63	41	59	38	17	83

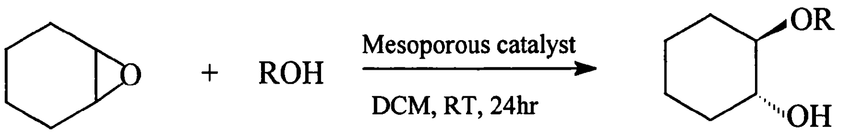
Reaction conditions: RT, 24hr, 1:4 epoxide:alcohol, catalyst (100mg)

Table 7: Results of addition of a series of alcohols to styrene oxide based on ^{1}H NMR

Al sec butoxide (g)	**CTAB (g)**	**Methanol**			***iso*-Propanol**			***t*-Butanol**		
		Conversion (%)	**Product selectivity (%)**		**Conversion (%)**	**Product selectivity (%)**		**Conversion (%)**	**Product selectivity (%)**	
			Alcohol	*Aldehyde*		*Alcohol*	*Aldehyde*		*Alcohol*	*Aldehyde*
1	5	100	*76*	*24*	93	*51*	*49*	98	*28*	*72*
7	5	100	*72*	*28*	87	*39*	*61*	76	*18*	*82*

Reaction conditions: RT, 24hr, 1:4 epoxide:alcohol, catalyst (100mg)

Table 8: Addition of a series of alcohols to styrene oxide using selected catalysts based on isolated yield



R = CH_3, $(CH_3)_2CH$, $(CH_3)_3C$

Scheme 4: Addition of alcohols to cyclohexene oxide

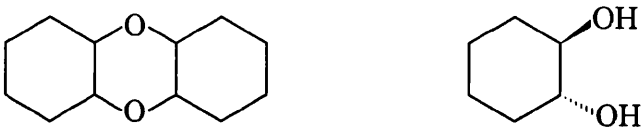
As can be seen from **Scheme 4** the product is stereospecific, in that nucleophilic attack results in formation of the *trans*-isomer. Results from these addition experiments are presented in **Table 9**.

Al sec Butoxide (g)	**CTAB surfactant (g)**	**Alcohol**	**Conversion (%)**
3	4	MeOH	95
4	4	MeOH	89
5	4	MeOH	90
7	4	MeOH	92
3	4	iPrOH	*
3	4	t-BuOH	*

Reaction conditions: RT, 24hr, 1:4 epoxide:alcohol, catalyst (100mg)
* White crystalline solid formed, analysed by EI MS

Table 9: Addition of alcohols to cyclohexene oxide

From the results in **Table 9** it can be seen that the catalysts employed were highly effective in addition of primary alcohols such as methanol to cyclohexene oxide. Where secondary and tertiary alcohols were employed the addition reaction was not successful. These results are most likely due to the increasing size and bulkiness of the respective alcohols. As a consequence the secondary and tertiary alcohols react slower with the epoxide. Due to this and the relative instability of the cyclohexene oxide intermediate, a number of potential side reactions may occur which result in the desired β-alkoxy alcohol not being formed. It appears that in an absence of alcohol the intermediate species may dimerise (**Figure 7(i)**), or if water is present the formation of a diol is possible (**Figure 7(ii)**). This is supported by low resolution EI/CI mass spectrometry data and ^{1}H NMR data (see appendix D). Again, it is also possible that the catalyst may decompose the secondary and tertiary alcohols to form the alkene.



(i) Dimer

(ii) Diol

Figure 7: By-products of cyclohexene oxide in the absence of alcohols

Reaction of methanol and stilbene oxide

After the success of the methanolysis of styrene oxide and cyclohexene oxide, a catalyst containing 3g Al/4g CTAB was investigated for it ability to catalyse the addition of methanol to stilbene oxide. The results of these experiments were largely unsuccessful. This is most likely due to the fact that stilbene oxide is a far larger molecule than other epoxides tested and somewhat less reactive. As a result it may have experienced difficulties entering the pores. Consequently, the reaction conditions may need to be reviewed for this particular reaction.

The use of other mesoporous catalysts

A limited range of other catalysts where tested using the methanolysis of styrene oxide as a standard reaction. Some of the catalysts had been synthesized using different surfactant templates, others had different metals inserted into the framework of the catalyst to assess the ability to catalyse the addition reactions. The results from these experiments can be seen in **Table 10**.

Epoxide	**Alcohol**	**Catalyst**	**Conversion (%)**	**Product selectivity (%)**	
				β-alkoxy alcohol	*Aldehyde*
Styrene oxide	MeOH	P85(1)	0	-	-
Styrene oxide	MeOH	P85(2)	5	100	-
Styrene oxide	MeOH	P123(20)	10	100	-
Styrene oxide	MeOH	P123(40)	10	100	-
Styrene oxide	MeOH	P123(4g)/Al	100	79	21
Styrene oxide	MeOH	Titanium 1	28	100	-

Reaction conditions: RT, 24hr, 1:4 alcohol:epoxide, catalyst (100mg)

Table 10: Methanolysis of styrene oxide using a variety of catalysts

It can be seen in **Table 10** that a small number of catalysts are highly selective towards the addition product (100% selectivity) even though the yields are low. These results are quite significant in that they show that these catalysts only promote one reaction pathway. Spectroscopic study of these catalysts is required to acquire a greater understanding of how the selectivity for this type of reaction is produced. It may be possible to increase the yield by manipulation of the reaction conditions such as an increased reaction time or increasing the amount of catalyst present.

Addition of amines to epoxides

In addition to alcoholysis of epoxides, the ability of the mesoporous catalysts to catalyse the addition of amines to epoxides was investigated. Work previously done using lanthanide triflates[47] to promote aminolysis of 1,2-epoxides had been very successful. It was hoped that using mild reaction conditions (analogous to alcoholysis of epoxides) and a mesoporous catalyst would result in good yields. Initial experiments were mostly unsuccessful with no product being observed. This could have been due to the co-ordination of the amine to the acidic sites within the catalyst. It is also a possiblity that the mild reaction conditions we used are not suited to this type of reaction, however, potential for further study exists. It was also deemed worthy to look into the possibility of thiol addition to epoxides. Due to time restrictions experimental work was not undertaken, yet like the addition of amines there is potential for development in this direction.

Experimental

In order to obtain quantitative conversion results ^{1}H NMR spectroscopy was employed using a Bruker Av 400 NMR. From the resulting spectrum, quantitative conversion yields can be obtained by comparison of the integral values of the peaks present. Mass spectrometry (MS) and Gas Chromatography Mass Spectrometry (GC-MS) where performed at the EPSRC national mass spectrometry service centre, University of Wales Swansea. MS was carried out on a QUATTRO mass spectrometer. For GC-MS samples a GC chromatogram was included along with the sample. The GC used

---

[47] Chini, M.; Crotti, P.; Favero, L.; Macchia, F.; Pineschi, M. *Terahedron Lett.* 35, (1994), 433-436.

was a Zebron ZB-5 using a 30m x 0.32mm x 1.0μm, 5% phenyl polysiloxane column. The injector temperature was set at 300°C, the detector temperature was set at250°C. The oven was heated at 40°C (splitless injection) and then ramped at 3°C min^{-1} to 180°C where it was held for one hour. GC-MS was carried out on a MD800 GC-MS. Infra-red spectra where performed on a Perkin Elmer IR spectrometer. Note that yields for all of the catalysts are displayed in **Tables 4 and 8**. See appendix B for spectra.

Preparation of 2-phenyl-2-methoxy ethanol from styrene oxide

Styrene oxide (0.120g, 1mmol) and four equivalents of methanol (0.128g, 4mmol) was dissolved in CH_2Cl_2 (20ml) and the selected mesoporous catalyst (100mg) was added and the reaction mixture stirred for 24 hours at room temperature. After the reaction time had elapsed, the reaction mixture was filtered through a cellite plug to remove the catalyst and the solvent was removed under reduced pressure. A crude sample was analysed by ^{1}H NMR to determine the conversion. The remainder of the product mixture was then purified by flash column chromatography using hexane/ethyl acetate (1-10% gradient) to give the product as a clear oil. The product was identifed *via* comparison with Barluengas reported results (Barluenga, J; et al, *Organic Letters*, (2002), Vol. 4, No.17, 2817-2819.) and the Aldrich spectral library. Spectrum reference is RB295.1.

^{1}H NMR ($CDCl_3$): δ2.25(s, 1H), δ3.30(s, 3H), δ3.55-3.65(m, 2H), δ4.25-4.30 (q, 1H), δ7.10-7.40(m, 5H), ^{13}C NMR ($CDCl_3$): δ57.30, δ67.78, δ85.03, δ127.27, δ127.81, δ128.54, δ 128.95, δ129.40, δ130.00, I.R cm^{-1} 3450, 3080, 3060, 3040, 2920, 2900, 2850

Preparation of 2-phenyl-2-*iso*propoxy ethanol from styrene oxide

Styrene oxide (0.120g, 1mmol) and four equivalents of *iso*-propanol (0.240g, 4mmol) was dissolved in CH_2Cl_2 (20ml) and the selected mesoporous catalyst (100mg) was added and the reaction mixture stirred for 24 hours at room temperature. After the reaction time had elapsed, the reaction mixture was filtered through a cellite plug to remove the catalyst and the solvent was removed under reduced pressure. A crude sample was analysed by ^1H NMR to determine the conversion. The remainder of the product mixture was then purified by flash column chromatography using hexane/ethyl acetate (1-10% gradient) to give the product as a clearless oil. The product was identifed *via* comparison with Barluengas reported results (Barluenga, J; et al, *Organic Letters*, (2002), Vol. 4, No.17, 2817-2819.) and the Aldrich spectral library. Spectrum reference is RB318.1.

^1H NMR ($CDCl_3$): δ1.10-1.25(dd, 6H), δ2.30(s, 1H), δ3.50-3.60(m, 2H), δ4.50-4.55 (q, 1H), δ7.10-7.40(m, 5H) ^{13}C NMR ($CDCl_3$): δ21.75, δ23.84, δ67.79, δ80.3, δ 127.27, δ127.81, δ128.55, δ 128.95, δ129.40, δ130.00, I.R cm^{-1} 3460, 3100, 3030, 2990, 2950, 2910

Preparation of 2-phenyl-2-*tert*-butoxy ethanol from styrene oxide

Styrene oxide (0.120g, 1mmol) and four equivalents of *tert*-butanol (0.298g, 4mmol) was dissolved in CH_2Cl_2 (20ml) and the selected mesoporous catalyst (100mg) was added and the reaction mixture stirred for 24 hours at room temperature. After the reaction time had elapsed, the reaction mixture was filtered through a cellite plug to remove the catalyst and the solvent was removed under reduced pressure. A crude sample was analysed by ^1H NMR to determine the conversion. The remainder of the product mixture was then purified by flash column chromatography using hexane/ethyl acetate (1-10% gradient) to give the product as a clearless oil. The product was identifed *via* comparison with Barluengas reported results (Barluenga, J; et al, *Organic Letters*, (2002), Vol. 4, No.17, 2817-2819.) and the Aldrich spectral library. Spectrum reference is RB320.1.

^{1}H NMR ($CDCl_3$): δ1.10(s, 9H), δ2.10-2.25(s, 1H), δ3.40-3.50(m, 2H), δ4.50-4.55(q, 1H), δ7.10-7.40(m, 5H) ^{13}C NMR ($CDCl_3$): δ29.10, δ68.28, δ75.30, δ77.42 δ127.74, δ127.81, δ128.63, δ 128.98, δ129.40, δ130.00, I.R cm^{-1} 3450, 3080, 3060, 3040, 2920, 2900, 2850

Preparation of *trans*-2-methoxy cyclohexanol

Cyclohexene oxide (0.098g, 1mmol) and four equivalents of methanol (0.128g, 4mmol) was dissolved in CH_2Cl_2 (20ml) and the selected mesoporous catalyst (100mg) was added and the reaction mixture stirred for 24 hours at room temperature. After the reaction time had elapsed, the reaction mixture was filtered through a cellite plug to remove the catalyst and the solvent was removed under reduced pressure. A crude sample was analysed by ^{1}H NMR to determine the conversion. The remainder of the product mixture was then purified by flash column chromatography using hexane/ethyl acetate (1-10% gradient) to give a colourless oil. The product was identifed *via* comparison with Barluengas reported results (Barluenga, J; et al, *Organic Letters*, (2002), Vol. 4, No.17, 2817-2819.) and the Aldrich spectral library. Spectrum reference is RB302.1.

^{1}H NMR ($CDCl_3$): δ1.00-1.30(bd, 4H), δ1.55-1.75(m, 2H), δ1.90-2.15(m, 2H), δ 2.60-2.70(bs, 1H) δ2.85-2.95(bt, 2H), δ3.40(s, 3H) ^{13}C NMR ($CDCl_3$): δ24.55, δ 24.68, δ28.74, δ32.45, δ56.70, δ74.19, δ85.40, I.R cm^{-1} 3470, 2950, 2880, 2760

Chapter 3

Rearrangment reactions of epoxides using mesoporous catalysts

Introduction

Whilst performing alcohol additions to epoxides using our mesoporous Lewis-acid catalysts it was noted that some rearrangement of the epoxides had occurred to give carbonyl products. We were particularly interested in further investigating this reaction as carbon skeletal rearrangements are extremely valuable synthetic tools for new carbon structures.

Rearrangement of epoxides under acidic conditions leads to the formation of carbonyl compounds. Due to the synthetic usefulness of this reaction, a number of reagents have been studied and their catalytic properties assessed. These studies have investigated $BF_3{\cdot}Et_2O$ and $MgBr_2$[48], lithium salts[49], $InCl_3$[50], $Pd(OAc)_2$ bound to phosphine ligands[51] and $BiOClO_4{\cdot}{}_nH_2O$[52]. However, a number of these reagents have drawbacks with regards to toxicity, handling or cost. Hence, our mesoporous Lewis-acid catalysts have advantages over these materials given their reusability and the potential to fine-tune the catalysts selectivity. It is worth noting that zeolites have already been used in the rearrangement of α-pinene oxide to campholenic aldehyde with good yields and selectivity[53]

In rearrangement reactions, a group moves from one atom to another in the same molecule which can result in a change of functionality and/or rearrangement of the carbon skeleton. In the majority of cases, the group (or atom) migrating moves to an

---

[48] House, H. O. *J. Am. Chem. Soc.* 70, (1955), 3070.
[49] Rickborn, B.; Gerkin, R. M. *J. Am. Chem. Soc.* 93, (1971), 1693.
[50] Ranu, B. C.; Jana, U. *J. Am. Chem. Soc.* 63, (1998), 8212.
[51] Kulasegaram, S.; Kulawiec, R. J. *J. Am. Chem. Soc.* 62, (1997), 6547.
[52] Anderson, A. M.; Blazek, J. M.; Garg, P.; Payne, B. J.; Mohan, R. S. *Tetrahedron Letters 41*, (2000), 1527.

adjacent atom. In cases where more than one group can migrate, the identity of the group that moves is determined by the migratory aptitude of the candidates. In the case of an epoxide, rearrangement leads to the formation of an aldehyde or ketone depending upon the initial structure of the epoxide and the reaction conditions employed.

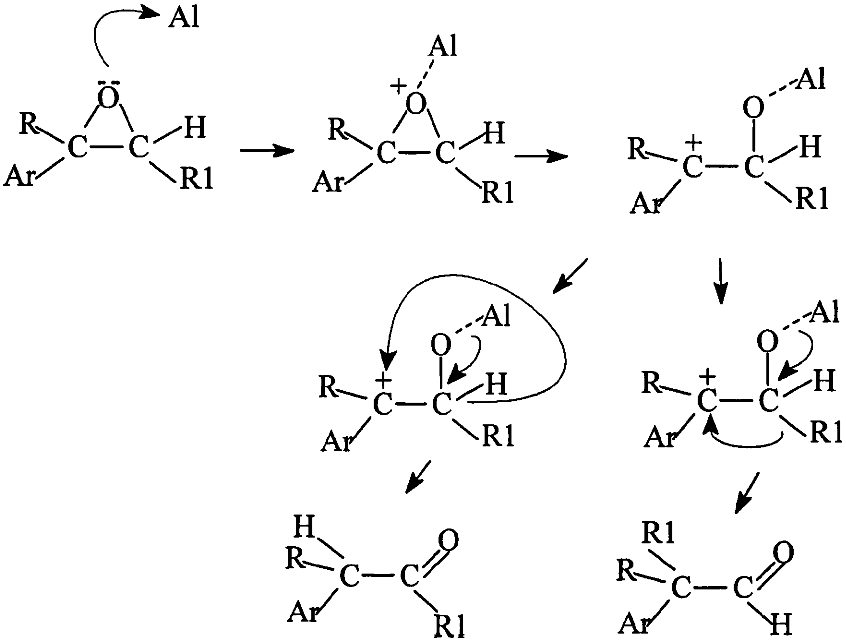
The reaction mechanism proceeds by oxygen donating an electron pair into the empty *p*-orbital on aluminium located in the catalyst. Electron donation occurs from the carbon-oxygen bond to the positively charged oxygen to give a carbocation, the position of which is determined by the ability of the adjacent groups to stabilise the cation intermediate. Where aromatic epoxides are concerned, the carbocation is situated on the benzylic carbon due to the ability of the phenyl group to stabilise the intermediate. The relative migratory aptitudes of the substituents on the carbon bonded to the oxygen atom determine whether the final product is an aldehyde or a ketone (**Scheme 5**).

Zeolite and zeotype materials have been employed in a number of rearrangement reactions. The primary advantages of employing zeolites and zeotypes to perform these reactions is that selectivity can be built into the catalysts. This selectivity can be utilised in allowing only certain starting materials to react (particularly important in one-pot synthesis) and in limiting the formation of unwanted by-products. This can be achieved by tuning the pore size/shape and other catalyst characteristics. It is also

---

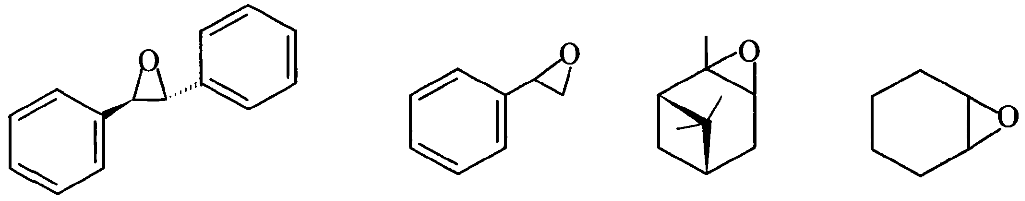
[53] Kunkeler, P. J.; van Der Waal, J. C.; Bremmer, J.; Zuurdeeg, B. J.; Downing. R. S.; van Bekkum, H. *Catal. Lett.* 53, (1998), 135-138.

possible to re-use the catalyst upon reactivation which has economic and environmental benefits.



Scheme 5: General mechanistic pathway for rearrangement of epoxides

In this study it was decided to investigate the ability of the mesoporous catalysts to rearrange a small selection of epoxides under mild reaction conditions. The aim was to investigate a number of different catalyst parameters such as pore distribution and aluminium loadings (Lewis acidity) to discover the effect they had on the efficiency of the rearrangements. It was hoped to use this information and engineer the catalyst to obtain a greater degree of selectivity (if required) and yield for desired reactions. The structures of the epoxides chosen for study are shown in **Figure 8**.



trans - stilbene oxide Styrene oxide pinene oxide Cyclohexene oxide

Figure 8: Epoxides chosen for rearrangement

As can be seen from **Figure 8**, two aromatic epoxides and two aliphatic epoxides were used. Epoxides displaying a range of sizes were employed in order to get an appreciation of the way the catalyst structure allowed the molecules to move within the pores.

Results

In the first set of experiments the epoxides were rearranged to their carbonyl analogue. The catalysts used had a variable amount of aluminium, between 1-10g, used in the synthesis and the amount of surfactant (CTAB) was kept constant (4g used in synthesis). The reactions were all conducted at room temperature in dichloromethane (20ml). Assessment of the conversion to carbonyl analogues was carried out using ^{1}H NMR and are shown in **Table 11.**

Al sec butoxide (g)	**CTAB (g)**	**Conversion to carbonyl analogue (%)**			
		Styrene oxide	*trans-Stilbene oxide*	*α-pinene oxide*	*Cyclohexene oxide*
1	4	100	83	38	0
2	4	25	0	0	0
3	4	100	62	0	0
4	4	13	11	0	0
5	4	37	28	18	0
6	4	0	0	0	0
7	4	100	100	14	0
8	4	0	0	0	0
10	4	7	0	0	0

Reaction conditions: RT, 24hr, 1mmol epoxide, catalyst (100mg)
* Based on ^{1}H NMR spectra

Table 11: Comparison of catalysts ability to rearrange a selection of epoxides

The corresponding graph can be seen in **Figure 9**.

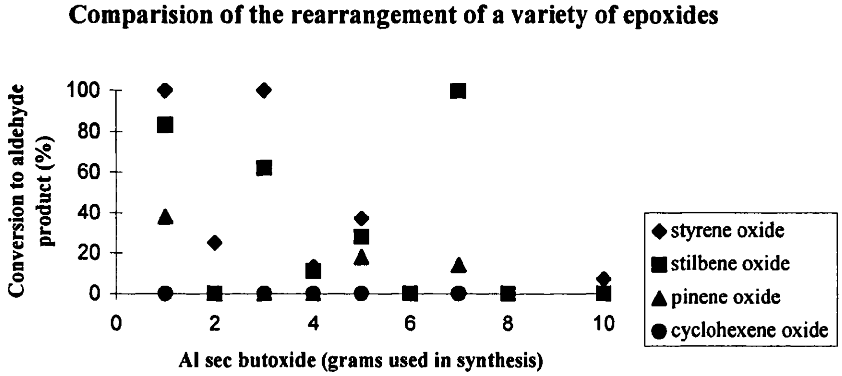


Figure 9: Comparison of catalysts ability to rearrange a selection of epoxides

There are a number of interesting trends that can be observed in **Table 11** and **Figure 9**. The first and most obvious trend is related to the loading of aluminium in the catalysts. It appears that at certain loadings there is a significant reduction in the ability of the catalyst to perform the rearrangement regardless of the epoxide. Catalysts containing 1g Al/4g CTAB, 3g Al/4g CTAB, and 7g Al/4g CTAB appear to have a high ability to catalyse the rearrangement reactions of *trans*-stilbene oxide and styrene oxide. These catalyst were also the only catalysts with the ability to rearrange α-pinene oxide to campholenic aldehyde, although only in limited amounts under the reaction conditions employed. It is also interesting to note that the catalyst containing 5g Al/4g CTAB did not perform rearrangements as well as expected. The predicted behaviour of the 5g Al/4g CTAB catalyst would be similar to that of the catalysts containing 1g Al/4g CTAB, 3g Al/4g CTAB and 7g Al/4g CTAB based on the results observed in **Table 3**. However, the data shows in **Table 11** that the catalyst containing 5g Al/4g CTAB has a distinct decrease in activity in comparison with the three aforementioned catalysts for the rearrangement reactions. This is of interest as this catalyst (5g Al/4g CTAB) performed addition reactions well which indicates that some selectivity in the reaction may be possible. Catalysts containing 2g Al/4g CTAB or 4g Al/4g CTAB were relatively poor catalysts, only performing rearrrangment of styrene oxide to phenyl acetaldehyde in small amounts. For an unknown reason, catalysts containing 6g Al/4g CTAB or 8g Al/4g CTAB were completely unreactive, regardless of the epoxide employed.

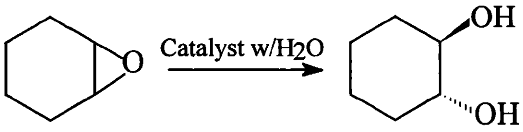
Another factor that affected the outcome of the rearrangements was the ability of the epoxide to stabilise the carbocation intermediate. With our catalysts it has been observed that if a carbocation intermediate is not easily stabilised, then rearrangement is retarded. This effect can be seen quite significantly by comparing the ability of catalysts to rearrange styrene oxide, α-pinene oxide and cyclohexene oxide. The intermediate cation species formed in the rearrrangement of styrene oxide is stabilised by hyperconjugation from the adjacent phenyl group. As a consequence, this stabilisation allows, catalyst permitting, for a high conversion of epoxide to aldehyde.

The intermediate formed by α-pinene oxide is a non-classical carbocation. In a non-classical carbocation the positive charge is delocalisd by a double bond that is not in the allylic position. This species lacks some of the stability associated with styrene oxides intermediate. Therefore only the catalyst with optimum parameters will perform the rearrangement and the conversions are consequently low. Ring opening of cyclohexene oxide results in a secondary carbocation intermediate which is relatively unstable. As a result no rearrangement to the desired product was observed, although a number of dimerised species were identified by mass spectrometry.

Although *trans*-stilbene oxide benefits from electron donation from its phenyl groups to help stabilise the carbocation intermediate the conversion was not as high as styrene oxide. One reason for this may be that steric factors may inhibit the epoxide from reaching active sites.

Investigation into the rearrangement of cyclohexene oxide

It was observed that although the desired carbonyl compound was not produced, a significant amount of the starting material had been consumed. This lead to the conclusion that something other than rearrangement had occurred, due to the instability of the carbocation intermediate. With this in mind samples were sent for gas chromatography-mass spectrometry (GC/MS) and EI mass spectrometery. The EI mass spectrometry showed a peak at m/z 116. This we believe is representative of the *trans*-1,2-cyclohexene diol formed by hydrolysis of the epoxide (**Scheme 6**).



Scheme 6: Suspected product from rearrangement of cyclohexene oxide

It is conceivable that water may been present and therefore hydrolysis of the epoxide led to the formation of the *trans*-diol. In subsequent attempts at the rearrangement of cyclohexene oxide additional by-products were also observed with peaks at m/z 207, 210, 212 being observed from the GC/MS. Two of the by-products contained a similar core structure to each other with m/z peaks at 210 and 212 respectivly (see appendix C). It is possible that some dimerization occurred between the diol and the starting material.

Investigation into change of surfactant quantity

Differences in the quantity of surfactant (CTAB) used in the synthesis of the catalyst were investigated using the rearrangement of styrene oxide to phenyl acetaldehyde as a test reaction. The results can be seen in **Table 12.**

Al sec butoxide (g)	**CTAB (g)**	**Conversion to aldehyde (%)**
5	4	20.5
5	5	85
5	6	100
5	8	100

Reaction conditions: RT, 24hr, 1mmol epoxide, catalyst (100mg)

Table 12: Effect of changing surfactant quantity

From the results in **Table 12** it is clear that a small increase in the amount of surfactant used had a large effect upon the conversion of styrene oxide to phenyl acetaldehyde. As with the addition of methanol to styrene oxide, the reaction seems to have a threshold at 6 grams of surfactant with respect to the conversion to product. This information can be used in the next generation of catalysts engineered to improve the yield.

The next series of experiments focused on varying the aluminium content of catalysts and keeping the amount of CTAB surfactant used in the synthesis constant at 5 grams. The results are shown in **Table 13**.

Al sec butoxide (g)	**CTAB (g)**	**Conversion to aldehyde (%)**
1	5	90
2	5	77
3	5	45
4	5	93
5	5	78
7	5	92
10	5	96

Reaction conditions: RT, 24hr, 1mmol epoxide, catalyst (100mg)

Table 13: Rearrangement of styrene oxide using catalysts containing 5g CTAB

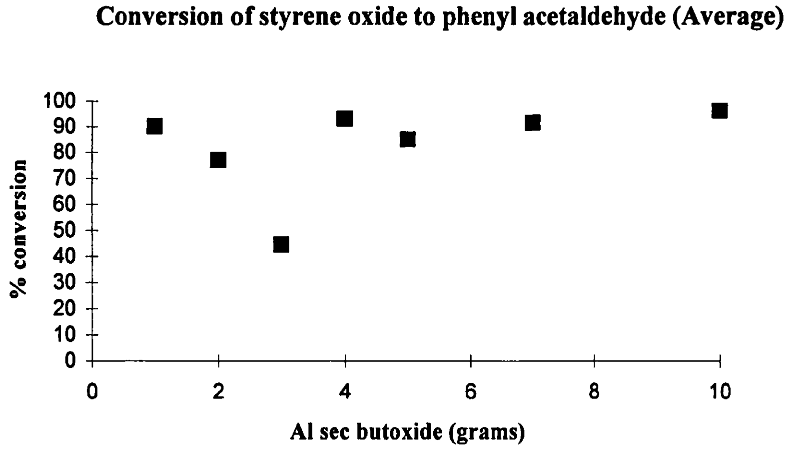


Figure 10: Rearrangement of styrene oxide using catalysts containing 5g CTAB

The results from this experiment show a number of interesting features. Firstly, the catalyst containing 3g Al/5g CTAB showed a decrease in its ability to perform the rearrangement reaction, in comparison to its counterpart containing 3g Al/4g CTAB. This catalyst (3g Al/5g CTAB) performed well in the methanolysis of styrene oxide reactions with a 100% conversion to product (product distribution: 2-phenyl-2-methoxy ethanol 77%, phenyl acetaldehyde 23%). Over the methanolysis series this catalyst (3g Al/5g CTAB) showed the least affinity towards performing the rearrangement reaction. In contrast to this, the catalysts containing 5g Al/4g CTAB and 5g Al/5g CTAB appear to favour the rearrangement reaction. By increasing the surfactant quantity, an increase in conversion to the carbonyl product of approximately 40% is observed. In the methanolysis of styrene oxide this catalyst (5g Al/5g CTAB) showed a higher affinity towards rearrangement than the other catalysts (product distribution; 2-phenyl-2-methoxy ethanol 67% : phenyl acetaldehyde 33%) as shown in **Table 7**. Therefore signs that selectivity can be achieved have begun to become apparent. The catalyst containing 3g Al/5g CTAB appears to favour addition reactions whereas increasing the aluminium content by two grams results in a catalyst (5g Al/*x*g CTAB) which appears to favour the rearrangement reaction under the reaction conditions.

Catalyst synthesised from reactions containing 2, 4 and 10g aluminium and 5g CTAB all show a remarkable increase in the conversion of styrene oxide to phenyl acetaldehyde. This can be mostly attributed to the increase in the pore density that accompanies an increase the amount of in surfactant used in their synthesis (see **Table 12** and **Figures 5 and 6**). The observation that the catalyst containing 3g Al/5g CTAB shows an aversion to rearrangement and an increased selectivity towards addition reactions when the surfactant is increased is of interest. An explanation for this is that particular combinations of aluminium and CTAB may result in a slight change in the crystalline structure and pore shape of the catalyst. As a result this catalysts may favour a particular reaction and so selectivity may be achieved by judicious choice of conditions for catalyst synthesis. It is intended that future work will assess these features (i.e. particular combinations of aluminium and CTAB) and Lewis/Brønsted acidity using physical methods.

Comparison of calcined and uncalcined catalysts.

All of the samples of catalysts used in the aforementioned reactions had been fully calcined. A calcined catalyst has had the templating surfactant "burnt out" leaving the framework structure. A sample of uncalcined catalyst was used in the rearrangement of styrene oxide to phenyl acetaldehyde. The results are outlined in **Table 14.**

	Uncalcined			**Calcined**	
Al sec butoxide (g)	CTAB (g)	Conversion to aldehyde (%)	Al sec butoxide (g)	CTAB (g)	Conversion to aldehyde (%)
*			1	5	90
*			2	5	77
3	5	0	3	5	44
4	5	0	4	5	93
5	5	0	5	5	78
10	5	0	7	5	92
*			10	5	96

Reaction conditions: RT, 24hr, 1mmol epoxide, catalyst (100mg)
* catalyst not provided for comparison

Table 14: Calcined v. uncalcined catalyst - rearrangement of styrene oxide

It is immediately obvious that the uncalcined catalysts are not performing the reaction. This is because the surfactant is still present and therefore blocks access to the active sites. This experiment also proves that it is the catalytic sites within the pore structure that are performing the reactions and not acid sites at the surface of the material.

A comparison of catalysts containing 4 and 5 grams of CTAB

A comparison of catalysts containing 4 and 5 grams of CTAB effect on the rearrangement of styrene oxide is outlined in **Figure 11** and **Table 15**.

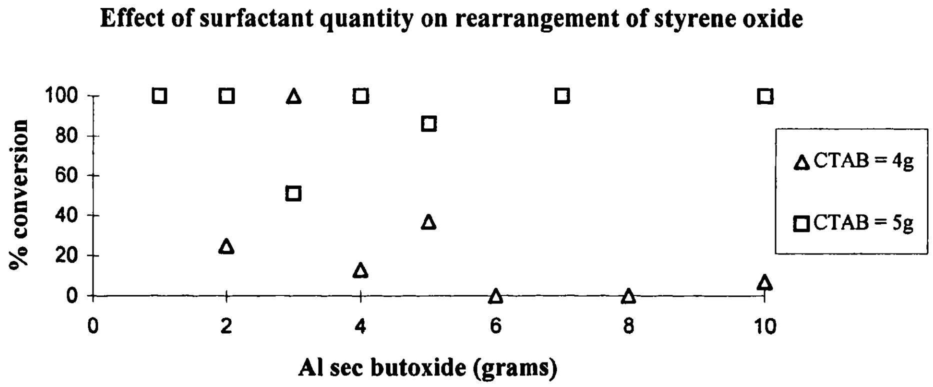


Figure 11: Effect of catalysts with 4 and 5g CTAB on rearrangement of styrene oxide

Al sec butoxide (g)	Conversion to aldehyde (%) CTAB (4g)	CTAB (5g)
1	100	90
2	25	77
3	100	44.5
4	13	93
5	37	81
6	0	*
7	100	91.5
8	0	*
10	7	96

Reaction conditions: RT, 24hr, 1mmol epoxide, catalyst (100mg)
* no catalysts available

Table 15: Effect of catalysts with 4 and 5g CTAB on rearrangement of styrene oxide

From investigation of **Figure 11** and **Table 15** it is clear to see that an increase in CTAB has the general affect of increasing the conversion of epoxide to carbonyl compound, in some cases very dramatically. Again, this type of information may be useful when engineering the next generation of these catalysts.

Comparison of different types of surfactant

The surfactant used in the catalysts initially was cetyltrimethyl ammonium bromide (CTAB). A batch of catalysts were synthesised which used polyoxyethylene lauryl ether (BRIJ 58) as the surfactant. The aluminium content was varied between 1-10 grams and the surfactant was kept constant at 4 grams. The test reaction was the rearrangement of styrene oxide to phenyl acetaldehyde under identical conditions to those previously used. The results are shown in **Table 16**.

Al sec butoxide (g)	CTAB (g)	Conversion (%)
1	4	100
2	4	25
3	4	100
4	4	13
5	4	37
6	4	0
7	4	100
8	4	0
10	4	7

Al sec butoxide (g)	BRIJ (g)	Conversion (%)
1	4	3
2	4	2
3	4	6
4	4	*
5	4	5
6	4	12
7	4	*
8	4	*
10	4	8

Reaction conditions: RT, 24hr, 1mmol epoxide, catalyst (100mg)
*catalysts not available for comparison

Table 16: Comparison of surfactants

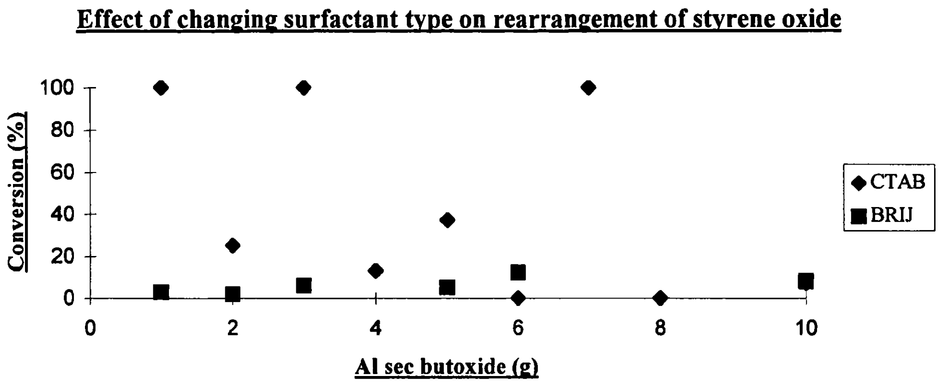


Figure 12: Comparison of surfactants

The results show that changing the surfactant to BRIJ 58 does not improve the reaction and indeed a number of catalysts made with this material are inactive. The reason for the dramatic difference between the two sets of results could be due to the size and shape of the surfactants. CTAB ($CH_3(CH_2)_{15}N^+(CH_3)_3\ Br^-$) appears to be a more bulky surfactant due to the fact that it is a quaternary ammonium salt. BRIJ 58 ($CH_3(CH_2)_{11}(OCH_2CH_2)_nOH$) appears to be a more linear surfactant. It is possible that CTAB forms pore structures with larger dimensions (due to its bulkiness) which can accommodate the reactant molecules easier. A more detailed analysis of this aspect of the study needs to be carried out using physical methods.

Experimental

Please see **Tables 11 and 13** respectively, for data regarding conversions and isolated yields for individual catalysts. For instrument specification please refer to the experimental section in chapter 2. See appendix C for spectra.

Preparation of phenyl acetaldehyde

Styrene oxide (0.120g, 1mmol) was dissolved in CH_2Cl_2 (20ml) and the selected mesoporous catalyst (100mg) was added. The reaction mixture was allowed to stir for 24 hours at room temperature. After the reaction time had elapsed the reaction mixture was filtered through a cellite plug to remove the catalyst. The remaining solvent was removed under reduced pressure. A crude sample was sent for ^{1}H NMR analysis (100% conversion to product). The remainder of the product mixture was purified by flash column chromatography using hexane/ethyl acetate (1-10% gradient) to give the product as a colourless oil. The product was identifed via comparison with the Aldrich spectral library. Spectrum reference is RB281B

^{1}H NMR ($CDCl_3$): δ3.60(s, 2H), δ7.0-7.5(m, 5H), δ9.7(s, 1H) ^{13}C NMR ($CDCl_3$): δ 50.97, δ125.89, δ127.81, δ128.89, δ129.40 δ130.00, δ132.26, δ199.74

Preparation of 2,2-biphenyl ethanal

Stilbene oxide (0.194g, 1mmol) dissolved in CH_2Cl_2 (20ml) and the selected mesoporous catalyst (100mg) was added. The reaction mixture was allowed to stir for 24 hours at room temperature. After the reaction time had elapsed the reaction mixture was filtered through a cellite plug to remove the catalyst. The remaining solvent was removed under reduced pressure. A sample of the colourless oil was sent for ^{1}H NMR and ^{13}C NMR analysis on which the quantitative conversion was based by comparison of the intergrated peaks present. The product was identifed via comparison with the Aldrich spectral library. Spectrum reference is RB325

^{1}H NMR ($CDCl_3$): δ4.85(s, 1H), δ7.0-7.5(m, 10H), δ9.7(s, 1H) ^{13}C NMR ($CDCl_3$): δ64.52, δ125.92, δ127.55, δ128.03, δ128.69, δ128.73, δ129.41, δ129.57, δ130.47, δ 132.82, δ198.95

Preparation of isomeric aldehyde from α-pinene oxide

α-pinene oxide (0.152g, 1mmol) was dissolved in CH_2Cl_2 (20ml) and the selected mesoporous catalyst (100mg) was added. The reaction mixture was allowed to stir for 24 hours at room temperature. After the reaction time had elapsed the reaction mixture was filtered through a cellite plug to remove the catalyst. The remaining solvent was removed under reduced pressure. A crude sample was sent for ^1H NMR and ^{13}C NMR analysis. The product was identifed via comparison with the Aldrich spectral library.

Preparation of cyclohexanone from cyclohexene oxide

Cyclohexene oxide (0.098g, 1mmol) was dissolved in CH_2Cl_2 (20ml) and the selected mesoporous catalyst (100mg) was added. The reaction mixture was allowed to stir for 24 hours at room temperature. After the reaction time had elapsed the reaction mixture was filtered through a cellite plug to remove the catalyst. The remaining solvent was removed under reduced pressure. A white crystalline solid was observed. A crude sample was sent for ^1H NMR and ^{13}C NMR analysis. The resulting spectrum did not show the desired product so MS and GC-MS where performed. Spectrum referance is 204820 Buckle. It was attempted to identify the product *via* comparison with the Aldrich spectral library to no avail.

Chapter 4

Microwave reactions

Introduction

Microwaves occur in the electromagnetic spectrum with wavelengths in the range of $1x10^{-3}$ to $3x10^{-2}$m. Their frequency is in the range of approximately 10^{-2}-10^{-3}m although for ovens it is fixed by law at 2450MHz. In recent years microwave ovens have found a unique niche in the realm of organic synthesis[54]. Initial reactions performed under microwave conditions found that in some cases, classical organic reaction rates could be greatly enhanced. It was also discovered that microwave conditions could enhance selectivity and so the production of complicated reaction mixtures could be avoided[55]. It has now become well established that, in comparison with conventional heating, microwave methods offer substantial advantages in reducing the formation of unwanted by-products. The process of microwave heating of reactants differs in many fundamental ways to that of conventional heating methodologies.

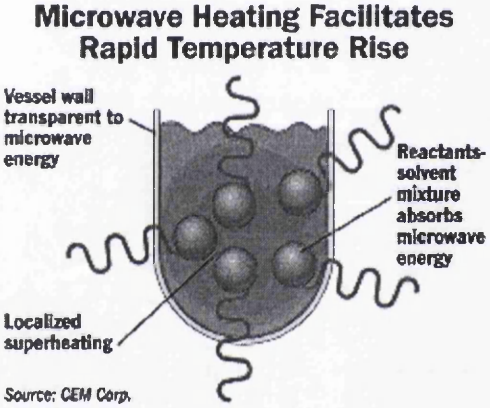
When an electric field is applied to a molecule with a permanent dipole the molecule will align itself with the field. As a consequence of oscillation of the electric field the molecule will itself begin to oscillate. The agitation of the molecule as a result of the oscillating field causes rapid heating of the molecule in a homogeneous and selective fashion. This has obvious advantages over conventional heating. Firstly microwave heating provides an even heating process unlike that of conventional heating methods. A result of this is few by-products in the reaction mixture occur due to local over heating in comparison to when conventional heating systems are employed. Another

---

[54] *S. Deshayes et al. Tetrahedron* 55, (1999), 10851-10870.
[55] *G. Cardillo et al. Tetrahedron* 57, (2001), 2807-2812.

advantage is that energy is transfered extremely quickly into the reaction mixture. The ease of use of microwave equipment also makes this approach highly attractive.

Although domestic microwaves can be used, the electric field is not distributed evenly and consequently there is localised heating of the reaction mixture. Where more accurate experimental data is required it is possible to use a microwave reactor which have dimensioned waveguides which are focused to give an even energy distribution (**Figure 13**). With this type of microwave reactor it is possible to monitor and vary pressure and temperature parametres.



Source: CEM Corp.

Figure 13: Focused microwave reactor effect[56]

There have been a large number of examples[26] of reactions carried out under microwave conditions. As previously mentioned, the effect microwaves have when applied to organic synthesis result in a cleaner, faster reaction. We decided that the application of microwave technology to the study of our mesoporous catalysts might help in accelerating the rate of these reactions. In order to show that potential existed for acceleration of these types of reaction we employed copper (II) tetrafloroborate as the catalyst for the addition reactions of epoxides. Work previously carried out by Barluenga *et al*[18] showed the potential for this catalyst to promote ring-opening reactions of epoxides at room temperatures. Although yields for the reactions where good, reaction times in particular for addition of tertiary alcohols were long. We hoped that by using microwave conditions we could improve upon the initial results presented by Barluenga. In addition to these experiments we wanted to test the ability of our mesoporous catalysts to perform ring opening reactions under microwave conditions, in particular to enhance the rate of reaction for both types of Lewis acid catalysts and to study the effect of microwave acceleration on product selectivity.

Results

This study investigated the ability of copper (II) tetrafluoroborate to induce ring opening of epoxides resulting in the formation of 1,2-disubstituted products. The epoxides chosen where styrene oxide, an aromatic unsymmetrical epoxide, and cyclohexene oxide, a symmetrical aliphatic epoxide. A series of primary, secondary and tertiary alcohols where chosen as nucleophiles to investigate the affect of steric hinderance on the reaction rates and yields and the ability of a microwave reactor to overcome them.

Microwave technology allows a number of variables to be controlled and monitored. The primary variable of interest was the Wattage, however the Wattage has a relationship with the temperature. In order to try to eliminate the effects of conventional heating it was deemed necessary to keep the temperature of the reaction as low as possible. In order to achieve a high Wattage, a high temperature value was

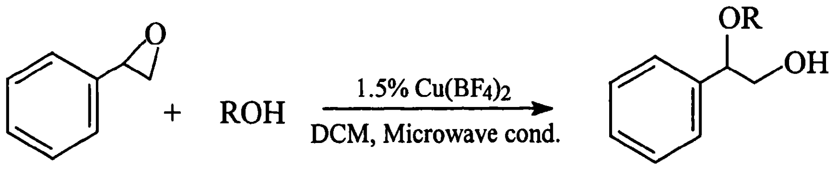
---

[56] diagram from www.rdmag.com/images.

entered into the computer. This allows an in-built cooling function to be activated which has the effect of keeping the temperature low whilst maintaining a high Wattage.

Addition of a series of alcohols to styrene oxide under microwave conditions

A series of primary, secondary and tertiary alcohols were added to styrene oxide under microwave conditions (**Scheme 7**). The results are shown in **Tables 19-21.**



R = CH_3
$(CH_3)_2CH$
$(CH_3)_3C$

Scheme 7: Addition of alcohols to styrene oxide under microwave condition

Microwave conditions (°C/Watts/min)	Catalyst (%)	epoxide:alcohol	Final	reaction	mixture
			Styrene oxide (%)	Alcohol (%)	Aldehyde (%)
40/40/2.5	1	1:4	78	22	
40/40/5	1	1:4	48	52	
40/40/10 (+3min cooling)	1	1:4	22	78	
40/50/10	1	1:4	32	64	5
65/90/10	1	1:4	22	70	9
35/100/15	1	1:4	16	75	9
35/100/15	1.5	1:4	0	91	9
35/100/15	1.5	1:6	0	95	5
35/100/15	1.5	1:8	0	100	0

Reaction conditions: As specified in table

* Results based on ^{1}H NMR

Table 19: Results of addition of methanol to styrene oxide

Microwave conditions (°C/Watts/min)	Catalyst (%)	epoxide:alcohol	Final	reaction	mixture
			Styrene oxide (%)	Alcohol (%)	Aldehyde (%)
40/40/2.5	1	1:4	38	54	8
40/40/5	1	1:4	32	57	12
40/40/10	1	1:4	44	48	8
35/100/15	1	1:4	26	65	9
35/100/15	1	1:4	18	73	9
35/100/15	1.5	1:6	0	92	8
35/100/15	1.5	1:8	0	100	0

Reaction conditions: As specified in table

* Results based on ^{1}H NMR

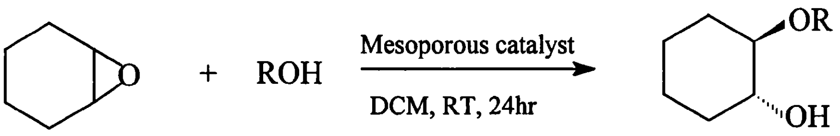
Table 20: Results of addition of *iso*-propanol to styrene oxide

Microwave conditions (°C/Watts/min)	**Catalyst (%)**	**epoxide:alcohol**	**Final**	**reaction**	**mixture**
			Styrene oxide (%)	Alcohol (%)	Aldehyde (%)
40/25/10	1	1:4	33	58	9
40/25/20	1	1:4	44	43	13
40/40/10	1	1:4	45	41	14
40/40/20	1	1:4	44	43	13
50/40/10	1	1:4	22	65	13
50/40/20	1	1:4	43	43	14
60/40/10	1	1:4	50	38	12
60/40/20	1	1:4	48	40	12
50/40/10	1	1:8	35	53	12
65/60/10	1	1:4	48	39	13
40/40/5	1	1:4	73	23	4
35/100/15	1	1:4	56	36	8
35/100/15	1.5	1:6	0	88	12
35/100/15	1.5	1:8	7	83	10

Reaction conditions: As specified in table
* Results based on ^{1}H NMR

Table 21: Results of addition of *t*-Butanol to styrene oxide

As can be seen from the results in **Tables 19-21** a very good conversion of starting materials to products occurs upon the optimization of the reaction conditions. The reaction time is dramatically reduced under the microwave conditions. This is demonstrated for the addition of *t*-butanol to styrene oxide where previously this reaction has taken 12 hours to produce an equivalent yield. The original Barluenga conditions did not report the presence of any aldehyde product however, in this microwave study varying amounts were observed. Selectivity for the alcohol product was obtained by manipulating the reaction conditions, mainly by increasing the amount of alcohol present. After the success of these reactions, we decided to investigate the addition of a series of alcohols to cyclohexene oxide using copper (II) tetrafluoroborate as a catalyst under microwave conditions (**Scheme 8**). The results for these experiments can be seen in **Table 22**.



R = CH_3, $(CH_3)_2CH$, $(CH_3)_3C$

Scheme 8: Addition of alcohols to cyclohexene oxide

Microwave conditions (C/Watts/min)	Alcohol	Catalyst (%)	epoxide:alcohol	Reaction mixture	
				Cyclohexene oxide (%)	Alcohol (%)
40/40/5	MeOH	1	1:4	50	50
40/40/5	*i*PrOH	1	1:4	17	83
40/40/5	*t*-BuOH	1	1:4	68	32
35/70/10	MeOH	1	1:4	0	100
35/70/10	iPrOH	1	1:4	0	100
35/70/10	*t*-BuOH	1	1:4	9	91
35/70/15	*t*-BuOH	1	1:4	5	95
35/70/25	*t*-BuOH	1	1:4	5	95

Reaction conditions: As specified in table
* Results based on ^1H NMR

Table 22: Addition of alcohols to cyclohexene oxide

The results in **Table 22** show that high selectivity and good yields are obtained by application of the correct microwave conditions.

As well as improving upon previous work on the of alcoholysis of epoxides using copper (II) tetrafluoroborate, it was hoped that the microwave conditions would enhance the reactions using mesoporous materials as the catalyst. It was decided to investigate the effect the microwave would have upon the methanolysis of styrene oxide using a selection of aluminium substituted mesoporous catalysts. However, the results obtained were poor with nearly all the starting material remaining. There may have been several reasons for these observations. It is possible that the microwave conditions need to be optimised for reactions of mesoporous materials, as the conditions used in these experiments were based upon the best conditions found for experiments where copper (II) tetrafluoroborate was used as a catalysts. Another reason may have been that the reaction vessel shape was not suitable for the reaction when heterogenous catalysts are used. It was noted that it was hard for the stirrer to reach the catalyst in the reaction vessel and efficient mixing of the catalyst was not acheived.

Experimental

All experiments were conducted in a microwave oven manufactured by CEM microwaves. The microwave had variable wattage, temperature and pressure facilities. The products where deemed to be between 95-100% pure based on ^1H NMR spectra and where therefore not purifed further.

Preparation of 2-phenyl-2-methoxy ethanol from styrene oxide under microwave conditions

Styrene oxide (0.200g, 1.66mmol) was pippetted into the vessel. Eight equivalents of methanol (0.424g, 13.28mmol) was then added to the epoxide inside the reaction vessel. The epoxide and alcohol were then both dissolved in CH_2Cl_2 (5ml) and copper (II) tetrafluoroborate (1.5% mol, 0.006g, 0.024mmol) was added. The reaction mixture was then placed into the microwave oven and the desired reaction conditions were input into the computer. After the reaction time had elapsed the reaction mixture was washed with water and extracted with dichloromethane (3 x 20ml). The combined extracts were then dried over $MgSO_4$, then filtered and the solvent was removed under reduced pressure on a rotary evaporator. A sample was sent for ^1H NMR and ^{13}C NMR analysis to give the product as a colourless oil. The product was identifed *via* comparison with Barluengas reported results (Barluenga, J; et al, *Organic Letters*, (2002), Vol. 4, No.17, 2817-2819.) and the Aldrich spectral library.

^1H NMR ($CDCl_3$):, δ2.25(s, 1H), δ3.30(s, 3H), δ3.60-3.65 (m, 2H), δ4.25-4.30(q, 1H), δ7.10-7.40(m, 5H), ^{13}C NMR ($CDCl_3$): δ57.30, δ67.78, δ85.03, δ127.27, δ127.81, δ 128.54, δ 128.95, δ129.40, δ130.00

Preparation of 2-phenyl-2-*iso*propoxy ethanol from styrene oxide under microwave conditions

Styrene oxide (0.200g, 1.66mmol) was pippetted into the vessel. Eight equivalents of *iso*-propanol (0.797g, 13.32mmol) was then added to the epoxide inside the reaction vessel. The epoxide and alcohol were then both dissolved in CH_2Cl_2 (5ml) and copper (II) tetrafluoroborate (1.5% mol, 0.006g, 0.024mmol) was added. The reaction mixture was then placed into the microwave oven and the desired reaction conditions were input into the computer. After the reaction time had elapsed the reaction mixture was washed with water and extracted with dichloromethane (3 x 20ml). The combined extracts were then dried over $MgSO_4$, then filtered and the solvent was removed under reduced pressure on a rotary evaporator. A sample was sent for ^1H NMR and ^{13}C NMR analysis to give the product as a colourless oil. The product was identifed *via* comparison with Barluengas reported results (Barluenga, J; et al, *Organic Letters*, (2002), Vol. 4, No.17, 2817-2819.) and the Aldrich spectral library.

^1H NMR ($CDCl_3$): δ1.10-1.20(dd, 6H), δ2.35(s, 1H), δ3.50-3.60(m, 2H), δ4.50-4.55 (q, 1H), δ7.10-7.40(m, 5H) ^{13}C NMR ($CDCl_3$): δ21.80, δ23.84, δ67.80, δ80.31 δ 127.27, δ127.8,1 δ128.5,5 δ128.95, δ 129.41, δ130.00

Preparation of 2-phenyl-2-*tert*butoxy ethanol from styrene oxide under microwave conditions

Styrene oxide (0.200g, 1.66mmol) was pippetted into the vessel. Eight equivalents of *t*-butanol (0.982g, 13.32mmol) was then added to the epoxide inside the reaction vessel. The epoxide and alcohol were then both dissolved in CH_2Cl_2 (5ml) and copper (II) tetrafluoroborate (1.5% mol, 0.006g, 0.024mmol) was added. The reaction mixture was then placed into the microwave oven and the desired reaction conditions were input into the computer. After the reaction time had elapsed the reaction mixture was washed with water and extracted with dichloromethane (3 x 20ml). The combined extracts were then dried over $MgSO_4$, then filtered and the solvent was removed under reduced pressure on a rotary evaporator. A sample was sent for ^1H NMR and ^{13}C NMR analysis to give the product as a colourless oil. The product was identifed *via* comparison with Barluengas reported results (Barluenga, J; et al, *Organic Letters*, (2002), Vol. 4, No.17, 2817-2819.) and the Aldrich spectral library.

^{1}H NMR ($CDCl_3$): δ1.10(s, 9H), δ2.10-2.20(s, 1H), δ3.40-3.45(m, 2H), δ4.55-4.60 (q, 1H), δ7.10- 7.40(m, 5H) ^{13}C NMR ($CDCl_3$): δ29.10, δ68.28, δ75.35, δ127.75, δ 127.81, δ128.63, δ128.98, δ129.40, δ130.00

Preparation of *trans*-2-methoxy cyclohexanol from cyclohexene oxide under microwave conditions

Cyclohexene oxide (0.163g, 1.66mmol) was pippetted into the vessel. Four equivalents of methanol (0.213g, 6.64mmol) was then added to the epoxide inside the reaction vessel. The epoxide and alcohol were then both dissolved in CH_2Cl_2 (5ml) and copper (II) tetrafluoroborate (1% mol, 0.004g, 0.016mmol) was added. The reaction mixture was then placed into the microwave oven and the desired reaction conditions were input into the computer. After the reaction time had elapsed the reaction mixture was washed with water and extracted with dichloromethane (3 x 20ml). The combined extracts were then dried over $MgSO_4$, then filtered and the solvent was removed under reduced pressure on a rotary evaporator. A sample was sent for ^{1}H NMR and ^{13}C NMR analysis to give the product as a colourless oil. The product was identifed *via* comparison with Barluengas reported results (Barluenga, J; et al, *Organic Letters*, (2002), Vol. 4, No.17, 2817-2819.) and the Aldrich spectral library.

^{1}H NMR ($CDCl_3$): δ1.00-1.30(bd, 4H), δ1.55-1.75(m, 2H), δ1.95-2.15(m, 2H), δ2.60-2.70(bs, 1H) δ2.90-2.95(bt, 2H), δ3.40(s, 3H) ^{13}C NMR ($CDCl_3$): δ24.55, δ24.70, δ 28.7, δ 32.45, δ56.71, δ74.19, δ85.40,

Preparation of *trans*-2-*iso*propoxy cyclohexanol from cyclohexene oxide under microwave conditions

Cyclohexene oxide (0.163g, 1.66mmol) was pippetted into the vessel. Four equivalents of *iso*-propanol (0.399g, 6.64mmol) was then added to the epoxide inside the reaction vessel. The epoxide and alcohol were then both dissolved in CH_2Cl_2 (5ml) and copper (II) tetrafluoroborate (1% mol, 0.004g, 0.016mmol) was added. The reaction mixture was then placed into the microwave oven and the desired reaction conditions were input into the computer. After the reaction time had elapsed the reaction mixture was washed with water and extracted with dichloromethane (3 x 20ml). The combined extracts were then dried over $MgSO_4$, then filtered and the solvent was removed under reduced pressure on a rotary evaporator. A sample was sent for ^1H NMR and analysis to give the product as a colourless oil. The product was identifed *via* comparison with Barluengas reported results (Barluenga, J; et al, *Organic Letters*, (2002), Vol. 4, No.17, 2817-2819.) and the Aldrich spectral library.

^1H NMR ($CDCl_3$): δ1.05-1.40(m, 10H), δ1.65-1.80(m, 2H), δ1.95-2.15(m, 2H), δ 2.95-3.20(m, 2H), δ3.30-3.50(s, 1H), δ3.70-3.85(m, 1H).

Preparation of *trans*-2-*tert*butoxy cyclohexanol from cyclohexene oxide under microwave conditions

Cyclohexene oxide (0.163g, 1.66mmol) was pippetted into the vessel. Four equivalents of *t*-butanol (0.493g, 6.64mmol) was then added to the epoxide inside the reaction vessel. The epoxide and alcohol were then both dissolved in CH_2Cl_2 (5ml) and copper (II) tetrafluoroborate (1% mol, 0.004g, 0.016mmol) was added. The reaction mixture was then placed into the microwave oven and the desired reaction conditions were input into the computer. After the reaction time had elapsed the reaction mixture was washed with water and extracted with dichloromethane (3 x 20ml). The combined extracts were then dried over $MgSO_4$, then filtered and the solvent was removed under reduced pressure on a rotary evaporator. A sample was sent for ^1H NMR and analysis to give the product as a colourless oil. The product was identifed *via* comparison with Barluengas reported results (Barluenga, J; et al, *Organic Letters*, (2002), Vol. 4, No.17, 2817-2819.) and the Aldrich spectral library.

^1H NMR, δ1.20-1.30(bs, 9H), δ1.67(s, 4H), δ1.90-2.00(bd, 4H), δ2.60(s, 1H), δ3.20-3.30(m, 2H).

Chapter 5

Conclusions

In this study we have demonstrated that our mesoporous materials can be utilised for fine chemical synthesis. The investigation primarily focused on two types of reactions, the addition of alcohols to epoxides to give a 1,2-difunctionalised product and the rearrangement of epoxides to carbonyls. Due to the wide range of catalysts studied and the time constraints upon the study, it was only possible to investigate the aforementioned reactions in depth. Another noteworthy point is the fact that these catalysts had not previously been used in these types of organic reaction. As a consequence, we only had a small idea about what type of reactions they could be successfully utilised in. Therefore this initial study into the our mesoporous catalysts has proved to be quite successful.

With a number of our catalysts, we have achieved very good results with respect to the addition of alcohols to epoxides. We have shown that it is possible to use them to catalyse the nucleophillic addition of primary, secondary, and tertiary alcohols (with varied results) to epoxides at room temperature, under mild conditions. It is hoped that the results from the wide range of catalyst parameters (i.e. the variation of the quantity of Al and CTAB used in the synthesis of the catalysts) investigated in this study can and will be used in order to engineer new catalysts. It is also worth noting that a small selection of our catalysts showed one hundred percent selectivity even though the conversions were low (**Table 10**). This is quite significant as the idea of designing catalysts with inherent product selectivity is paramount in the synthesis of future mesoporous catalysts.

We have also shown that our mesoporous catalysts can be used in the rearrangements of epoxides. The selection of epoxides rearranged in this study was unfortunately limited, again due to time constraints. However, we believe that the results produced in our investigation show that these catalysts have a great deal of potential in this area. We have achieved some very pleasing results for the rearrangement of styrene oxide using our catalysts. These results highlight the inherent selectivity built into our catalysts. Rearrangement of the other test epoxides were not as successful as the styrene oxide rearrangements. However, the results from these experiments show it is consistently the same catalyst which performed the rearrangements best (**Table 11**). We were also interested in looking at rearranging epoxides that contained electron donating and withdrawing groups using our mesoporous catalysts. However, due to time restrictions we were unable to undertake this work. This would be an excellent avenue for future investigation.

After the success of the previously mentioned reactions we embarked upon a limited investigation of our catalysts abilities to perform the pinacol rearrangement on a series of diols. Initial experiments under our mild reaction conditions proved to be unsuccessful. It is possible that our catalysts are unsuited to these types of reactions hence showcasing their selectivity.

Another brief investigation was undertaken toward the end of this study into the ability of some of our mesoporous catalysts containing heteroatoms (i.e. boron) to perform cyclisation reactions. The initial results, although limited suggest that our catalysts have potential in this area. There is excellent opportunity for further investigation as these types of reactions are used commonly in the terpene industry.

In our study into the use of microwave technology we have found that this technology can be extremely useful when applied to fine chemical synthesis. Using the application of microwaves we have significantly reduced the rate of the alcholysis of epoxides using copper (II) tetrafluoroborate as a catalyst. At the same time producing high yields with excellent selectivity towards the desired α-alkoxy alcohol products. A limited number of trial reactions using our mesoporous catalysts to catalyse the addition of alcohols to epoxides were undertaken. Preliminary results were poor, however it does take time in order to find the optimal conditions for a specific reaction when microwave technology is employed. We believe that future studies will show that our catalysts can be used effectively in conjunction with microwave technology.

In this study we would have very much liked to have conducted a more in-depth study of our catalysts from a spectroscopic viewpoint. In recent years a number of exciting new approaches to studying mesoporous materials have emerged. This type of investigation into our catalysts is important in order to broaden our knowledge of there activity beyond this study. Unfortunately, persistant equipment failure and time restrictions meant that such an analysis could not be completed for inclusion in this study.

Appendix A

Data concerning catalyst synthesis and characterisation

Data concerning the synthesis and characterization of the mesoporous catalysts

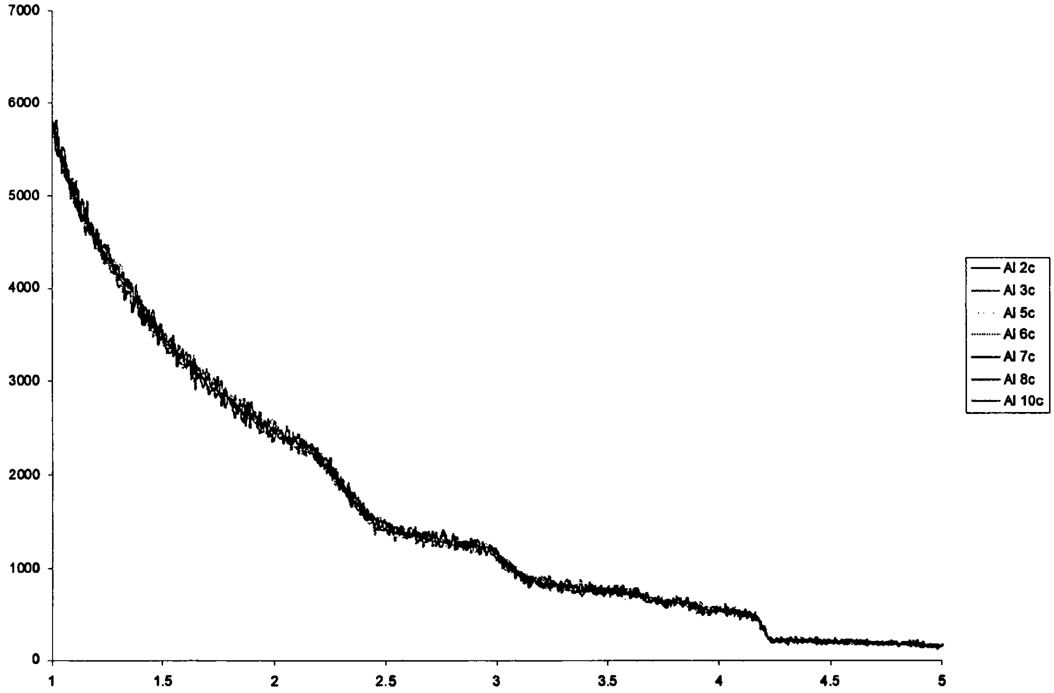
The synthesis of the mesoporous catalysts is as follows:

Hexadecyltrimethylammonium bromide (CTAB) surfactant was dissolved in of ethanol (EtOH) (13.5 g) and HCl 0.12 M (2.5 ml). Tetraethoxyorthosilane (TEOS) (25 ml) was added and the solution was stirred at 40°C for 10 min. The resultant solution was cooled to room temperature in ice. of Aluminium-sec-butoxide (1 g) was added and the mixture was stirred. Water (2ml) was added to complete the hydrolysis reaction. The resultant gel was left age for a week and then calcined in air at 150°C.

Several variations of the above reaction were carried out. The amount of CTAB was kept constant at 4 grams, the quantity of aluminium-sec-butoxide was varied. Quantities of from 1 gram to 10 grams, increasing in 1gram increments were used.

Another variation was to increase the amount of CTAB to 5 grams and use 1 gram increments of aluminium-sec-butoxide.

Figure 14 displays the x-ray diffraction data for the catalysts synthesized using four grams of CTAB and varying amounts of aluminium (between one and ten grams).



Two catalysts (5g Al/4g CTAB and 5g Al/6g CTAB) were synthesised using different quantites of surfactant and a similar amount of aluminium and were characterised and compared. The results seen below show data concerning the surface area and volume of the pores. The results are used courtesy of Paudie Harrington from Cork University, Ireland.

Catalyst containing 5g Al/4g CTAB

Gemini 0
2375 V5
Instrument ID: 1403
Setup Group: 91 Ads Isotherm

Sample D: C4Al5		Started: 04/04/03	11:04:19
Sample weight:	0.3195 g	Completed: 04/04/03	13:36:56
Evacuation Rate:	300.0 mm Hg/min	Evacuation time:	5.0 min
No Free Space Correction applied		Saturation pressure:	796.51 mmHg
Analysis Mode: Equilibration		Equilibration Time:	5 sec

BET Multipoint Surface Area Report

Surface Area :	489.4225 sq m/g
Slope:	0.009084
Y-Intercept:	-0.000189
C:	-47.057407
Vm:	112.428246
Correlation coefficient:	9.58E-02

BET Single Point Surface Area 489.3512 sq. m/g

Langmuir Surface Area Report

Surface Area :	732.0090 sq. m/g
Slope:	0.005947
Y-Intercept:	0.000056
b:	0.009449
Vm:	168.154282
Correlation coefficient:	1.00E-01

Adsorption Total Pore Volume at 0.8707 P/Po: 0.2564 cc/g

Analysis Log

Relative Pressure	Pressure (mmHg)	Vol. Adsorbed (cc/g STP)	Elapsed Time,(h:m)	Surface Area Point
0.0098	7.8	106.344	0:31	
0.0298	23.7	127.801	0:39	
0.0498	39.65	139.419	0:46	*
0.0697	55.53	146.968	0:52	*
0.0897	71.47	152.015	0:57	*
0.1097	87.41	155.301	1:01	*
0.1297	103.33	157.379	1:04	*
0.1497	119.26	158.753	1:07	*
0.1698	135.23	159.731	1:10	*
0.1897	151.13	160.442	1:12	*
0.2098	167.07	161.029	1:14	*
0.2298	183.02	161.523	1:17	*
0.2499	199.05	161.946	1:19	*

Gemini
2375 V5
Instrument ID: 1403
Setup Group: 9 Ads Isotherm

Sample D: C4Al5 Started: 04/04/03 11:04:19
Sample Weight: 0.3195 g Completed: 04/04/03 13:36:56
Evacuation Rate: 300.0 mm Hg/min Evacuation Time: 5.0 min
No Free Space Correction Applied Saturation Pressure: 796.51 mmHg
Analysis Mode: Equilibration Equilibration Time: 5 sec

Analysis Log

Relative pressure	Pressure (mmHg)	Vol. Adsorbed (cc/g STP)	Elapsed Time,(h:m)	Surface Area Point
0.2698	214.91	162.328	1:21	*
0.2898	230.86	162.685	1:23	*
0.3098	246.76	162.988	1:25	*
0.3298	262.72	163.279	1:27	
0.3499	278.69	163.525	1:30	
0.3699	294.61	163.749	1:32	
0.3899	310.6	163.967	1:34	
0.4098	326.45	164.153	1:36	
0.4299	342.4	164.341	1:38	
0.4498	358.26	164.503	1:40	
0.4698	374.21	164.651	1:42	
0.4898	390.13	164.79	1:45	
0.5099	406.14	164.916	1:47	
0.5298	421.95	165.028	1:49	
0.5499	438.04	165.129	1:51	
0.57	453.97	165.224	1:53	
0.59	469.91	165.318	1:55	
0.6101	485.92	165.401	1:58	
0.6301	501.86	165.473	2:00	
0.6501	517.82	165.551	2:02	
0.6702	533.82	165.609	2:04	
0.6903	549.84	165.663	2:06	
0.7102	565.66	165.711	2:08	
0.7302	581.63	165.773	2:11	
0.7505	597.78	165.83	2:13	
0.7703	613.54	165.869	2:15	
0.7905	629.6	165.921	2:17	
0.8103	645.45	165.957	2:19	
0.8304	661.39	166.002	2:21	
0.8504	677.33	166.038	2:23	
0.8705	693.38	166.076	2:26	
0.8707	693.51	165.773	2:31	

Gemini 2375 V5
Instrument ID: 1403
Setup Group: 9 - Full Ads Isotherm

Sample D: C4Al5			Started: 04/04/03	11:04:19
Sample weight:	0.3195 g		Completed: 04/04/03	13:36:56
Evacuation Rate:	300.0 mm	Hg/min	Evacuation time:	5.0 min
No Free Space Correction Applied			Saturation pressure:	796.51 mmHg
Analysis Mode: Equilibration			Equilibration Time:	5 sec

BJH Adsorption pore distribution report

0 3330
t = 3.5 400 [-5.0000/ ln(P/Po)]

Pore diameter Range (A)		Average Diameter (A)	Incremental Pore Volume (cc/g)	Cumulative Pore Volume (cc/g)	Incremental Pore Area (sq. m/g)	Cumulative Pore Area (sq. m/g)
160.5-	72.5	85.1	0.000149	0.000149	0.07	0.07
72.5-	67.8	69.9	0.000125	0.000273	0.071	0.141
67.8-	63.5	65.5	0.00014	0.000413	0.085	0.227
63.5-	59.8	61.5	0.000156	0.000569	0.101	0.328
59.8-	56.4	58	0.000211	0.00078	0.145	0.473
56.4-	53.4	54.8	0.000198	0.000978	0.145	0.618
53.4-	50.6	51.9	0.000231	0.001208	0.178	0.796
50.6-	48	49.2	0.00027	0.001478	0.219	1.015
48.0-	45.7	46.8	0.000272	0.00175	0.233	1.247
45.7-	43.6	44.6	0.000297	0.002047	0.266	1.514
43.6-	41.6	42.5	0.000334	0.002381	0.314	1.828
41.6-	39.7	40.6	0.000383	0.002763	0.377	2.205
39.7-	38	38.8	0.000433	0.003197	0.447	2.651
38.0-	36.4	37.1	0.000467	0.003664	0.503	3.154
36.4-	34.9	35.6	0.000521	0.004185	0.586	3.74
34.9-	33.4	34.1	0.00062	0.004805	0.727	4.467
33.4-	32.1	32.7	0.000618	0.005423	0.756	5.223
32.1-	30.8	31.4	0.000748	0.006171	0.954	6.176
30.8-	29.5	30.1	0.000774	0.006945	1.027	7.204
29.5-	28.4	28.9	0.000869	0.007814	1.202	8.406
28.4-	27.2	27.8	0.001061	0.008875	1.529	9.935
27.2-	26.1	26.7	0.001118	0.009993	1.677	11.613
24.1-	23.1	23.6	0.00167	0.0145	2.836	18.981
23.1-	22.1	22.6	0.002014	0.016514	3.569	22.549
22.1-	21.2	21.6	0.002476	0.018991	4.582	27.132
21.2-	20.2	20.7	0.003111	0.022101	6.02	33.152
20.2-	19.3	19.7	0.004536	0.026637	9.195	42.346
19.3-	18.4	18.8	0.006735	0.033373	14.336	56.682

Catalyst containing 5g Al/6g CTAB

Gemini 2375 V 5
Instrument ID: 1403
Setup Group: 9 - None

Sample D: C6Al5
Sample weight: 0.7963 g
Evacuation Rate: 300.0 mmHg /min
No free space correction applied

Started: 27/03/03 17:48:37
Completed: 27/03/03 19:10:04
Evacuation Time: 5.0 min
Saturation Pressure: 776.36 mmHg

Analysis Mode: Equilibration
Equilibration Time: 5 sec

BET Multipoint Surface Area Report

Surface Area: 683.1268 sq. m/g
Slope: 0.006543
Y-Intercept: -0.000171
C: -37.269981
Vm: 156.92523
Correlation co-efficient: 9.96E-01

t-Method Micropore report

Micropore volume: 0.198504 cc/g
Micropore area 340.9084 sq. m/g
External Surface Area: 342.2184 sq. m/g
Slope: 22.124283
Y-Intercept: 128.33189
Correlation co-efficient: 9.03E-01
Thickness value between 3.500 and 5.000 A
Area correction factor: 1

t= [13.9900/ (0.0340 - log(P/Po))]

Adsorption total pore volume at 0.5548 P/Po: 0.3671 cc/g

Gemini 2375 V
Instrument ID: 1403
Setup Group: 9 - None

Sample ID: C6Al5 Started: 27/03/03 17:48:37
Sample weight: 0.7963 g Completed: 27/03/03 19:10:04
Evacuation Rate: 300.0 mmHg /min Evacuation Time: 5.0 min
No Free Space Correction Applied Saturation Pressure: 776.36 mmHg
Analysis Mode: Equilibration Equilibration Time: 5 sec

BJH Adsorption Pore Distribution Report

0 0.333
t = 3.540 0 [-5.0000 /ln(P/Po)]

Pore diameter Range (A)	Average Diameter (A)	Incremental Pore Volume (cc/g)	Cumulative Pore Volume (cc/g)	Incremental Pore Area (sq. m/g)	Cumulative Pore Area (sq. m/g)
46.8- 46.2	46.5	0.000546	0.000546	0.47	0.47
46.2- 42.3	44	0.001519	0.002065	1.38	1.849
42.3- 38.9	40.4	0.00172	0.003785	1.701	3.55
38.9- 35.9	37.3	0.002001	0.005786	2.148	5.698
35.9- 33.2	34.4	0.002297	0.008083	2.668	8.366
33.2- 30.8	31.9	0.002701	0.010784	3.387	11.753
30.8- 28.6	29.6	0.00322	0.014004	4.354	16.107
28.6- 27.2	27.8	0.002465	0.016469	3.542	19.649
27.2- 26.5	26.8	0.001613	0.018082	2.404	22.053
26.5- 24.6	25.5	0.005166	0.023248	8.118	30.171
24.6- 22.8	23.6	0.007938	0.031186	13.471	43.641
22.8- 22.2	22.4	0.004424	0.03561	7.886	51.527
22.2- 21	21.5	0.013732	0.049343	25.523	77.05
21.0- 19.8	20.3	0.025325	0.074668	49.791	126.841
19.8- 19.2	19.5	0.018031	0.092699	36.981	163.822
19.2- 17.4	18.2	0.086348	0.179047	189.794	353.616

The method for the synthesis of some of the titanium based catalysts is outlined below courtesy of Dr. Justin Holmes, Cork University, Ireland.

Preparation of 20:1 Si:Ti modified P123 (catalyst called Titanium 1)

4g of mesoporous P123 (assumed it was made entirely f SiO2)

Therefore concentration =4/28.09 + 32 =0.0665 moles

Want 20:1 ratio

Therefore 0.0665/20 = 0.0033 moles of Ti (IV) propoxide required

Weight of Ti (IV) propoxide = 284.26

Therefore, 0.9461g required

Density of Ti (IV) propoxide = 1.033

Therefore, 0.915ml required

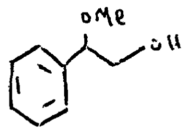
Ti (IV) propoxide was added to mesoporous P123 to which 200m of toluene was added. The solution was slowly stirred for 24hr and was then sucked dry and washed. This was then followed by calcination at 550°C for 15 hours

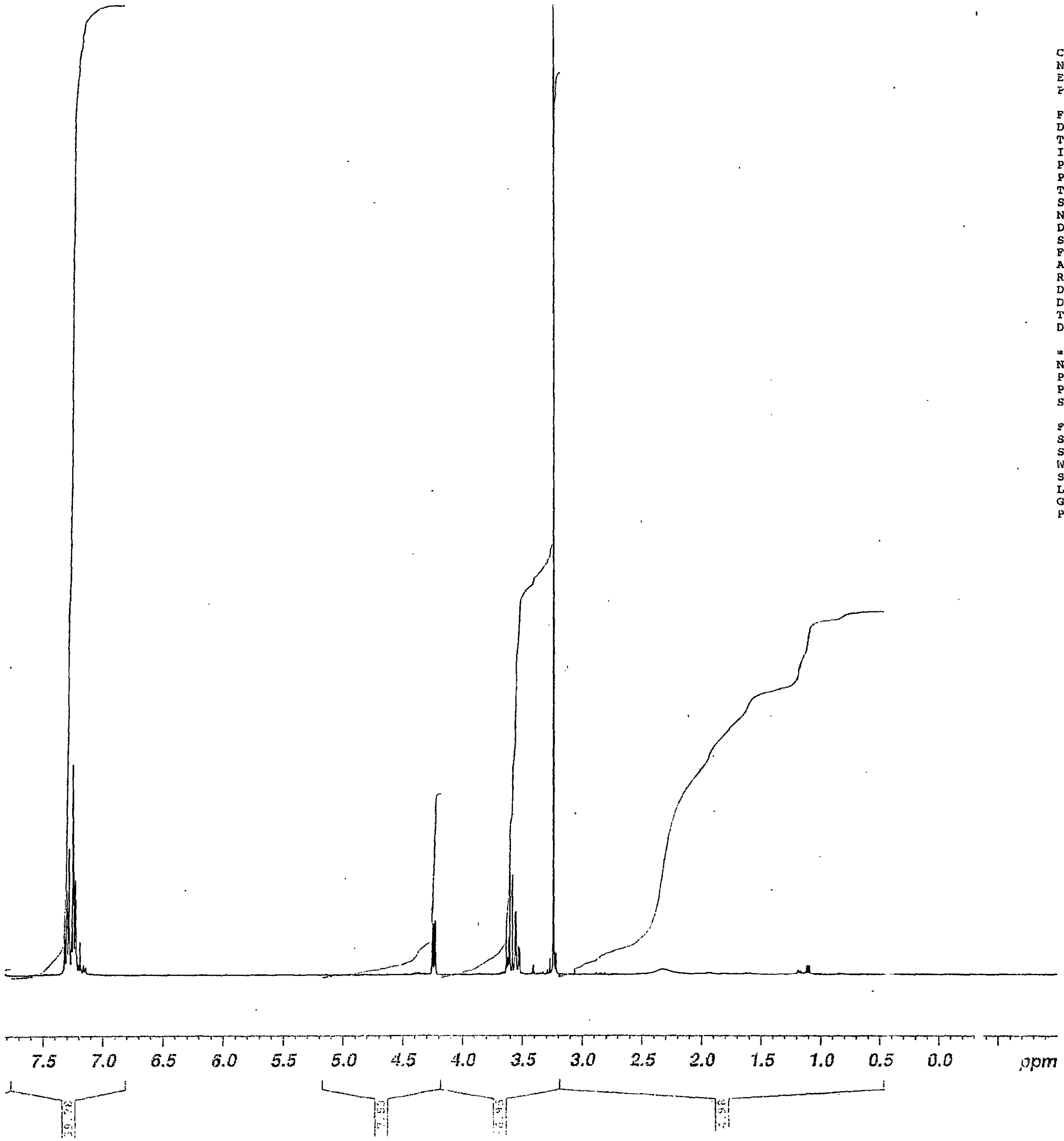
Samples were analysed using X-ray diffraction, BET/BJH, xrt

Appendix B

Spectral data from addition of alcohols to epoxides

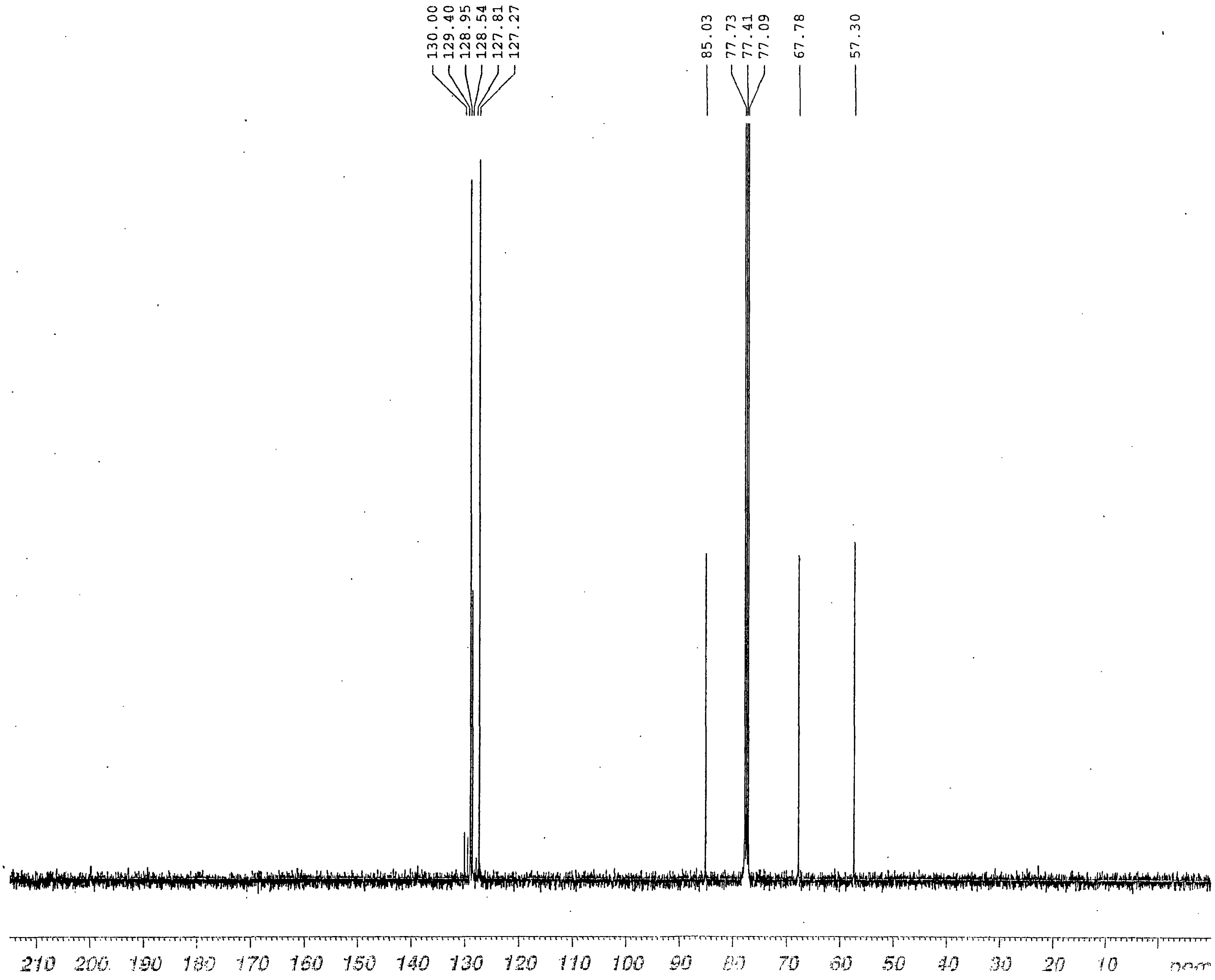
4096 Richard RB295.1



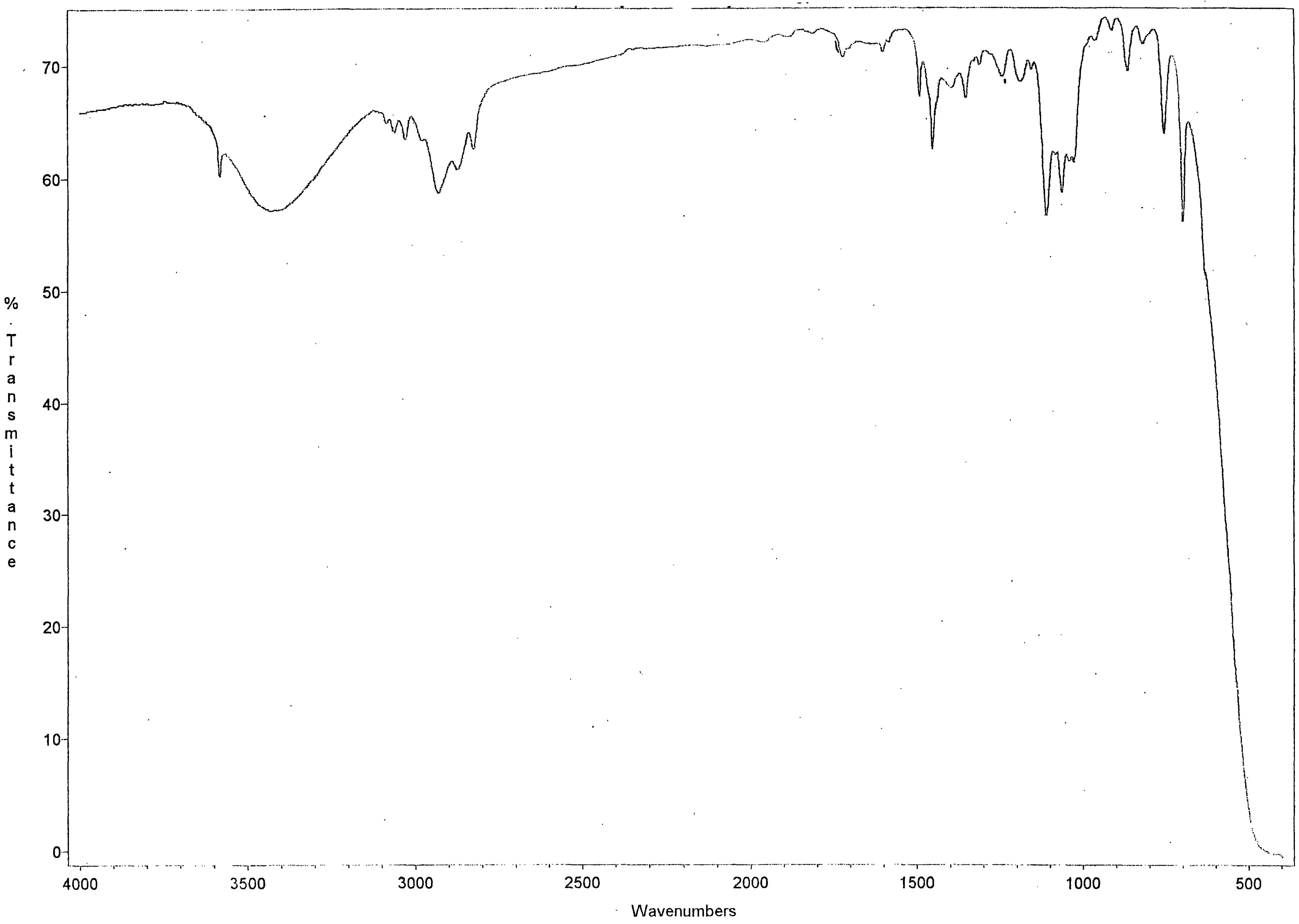


```
Current Data Parameters
NAME          Sep25-2003
EXPNO                 60
PROCNO                 1

F2 - Acquisition Paramete
Date_           20030925
Time               13.09
INSTRUM            av400
PROBHD    5 mm QNP  1H/1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8802.817 Hz
FIDRES          0.134320 Hz
AQ             3.7224948 se
RG                  90.5
DW                56.800 us
DE                  6.00 us
TE                 300.0 K
D1            1.00000000 se

======== CHANNEL f1 ======
NUC1                  1H
P1                  8.00 us
PL1                 4.00 dB
SFO1         400.1328009 MH

F2 - Processing parameters
SI                 32768
SF           400.1300392 MH
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

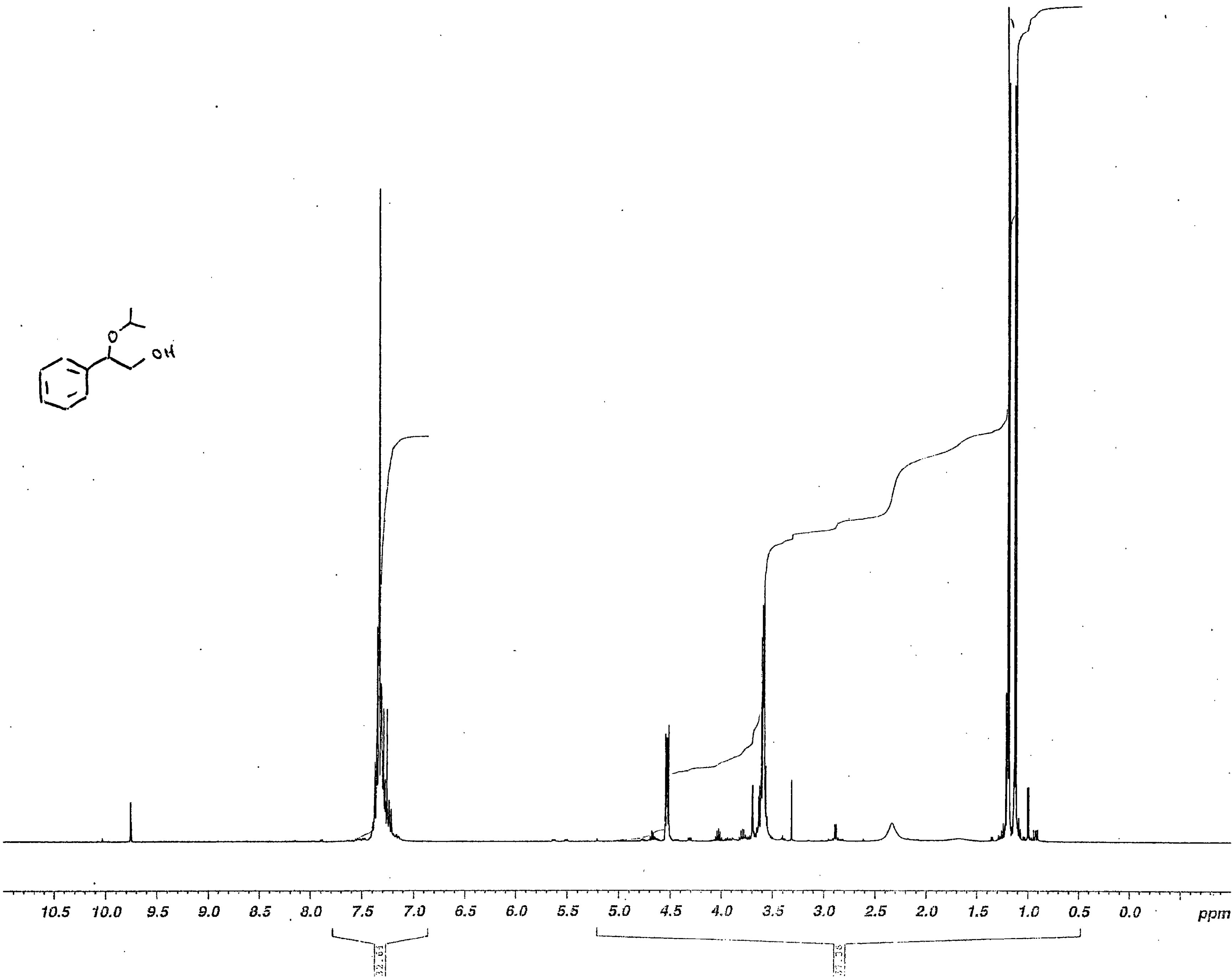
4096 Richard RB295.1



```
Current Data Parameters
NAME          Sep25-2003
EXPNO                 61
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030925
Time               13.39
INSTRUM            av400
PROBHD   5 mm QNP  1H/1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     2
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG               18390.4
DW                20.850 usec
DE                 20.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  6.35 usec
PL1                 2.00 dB
SFO1         100.6227298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              83.00 usec
PL2                 4.00 dB
PL12               24.50 dB
PL13               24.50 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127290 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

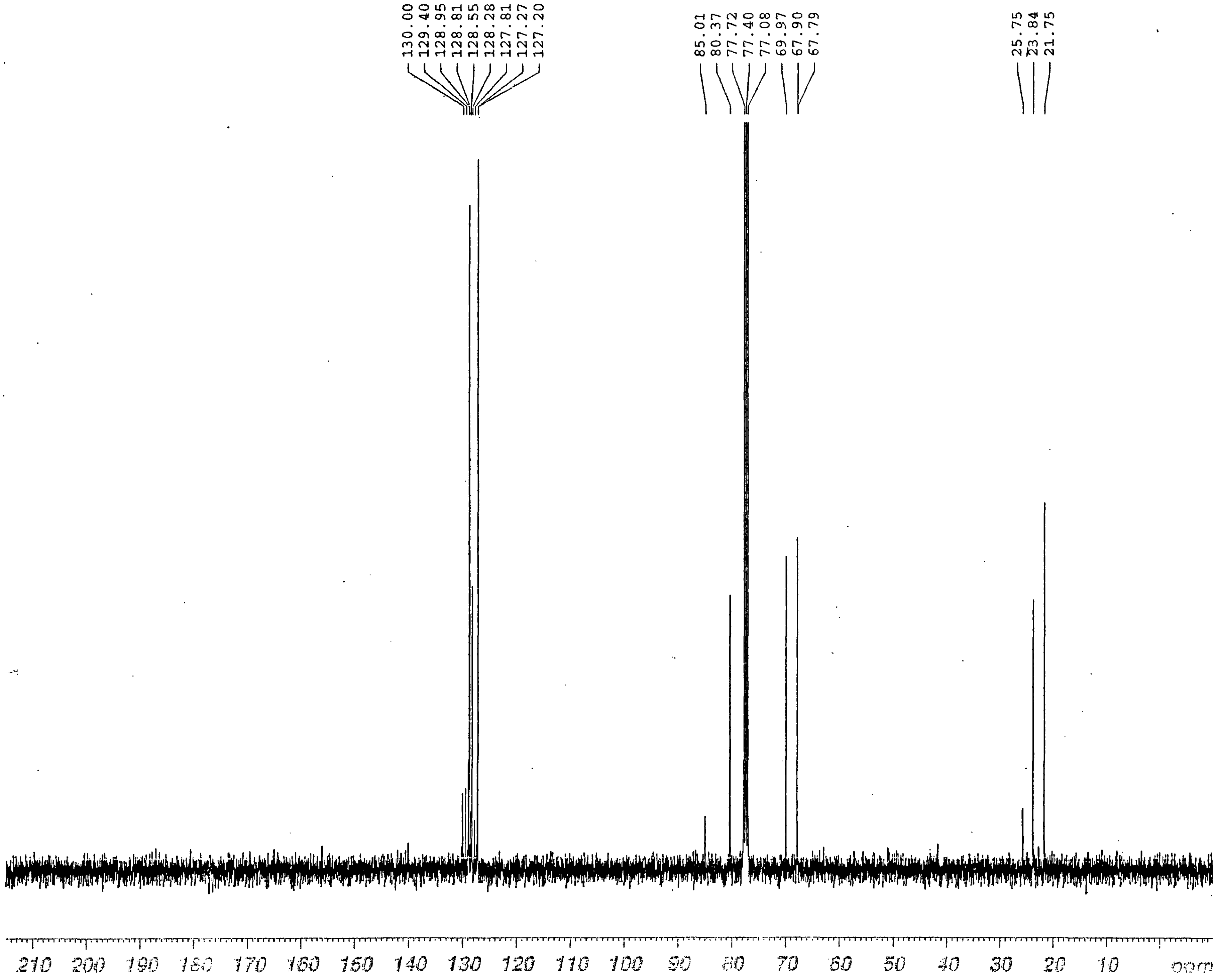

70
60
50
40
30
20
10
0
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers

4047 Richard RB313.1

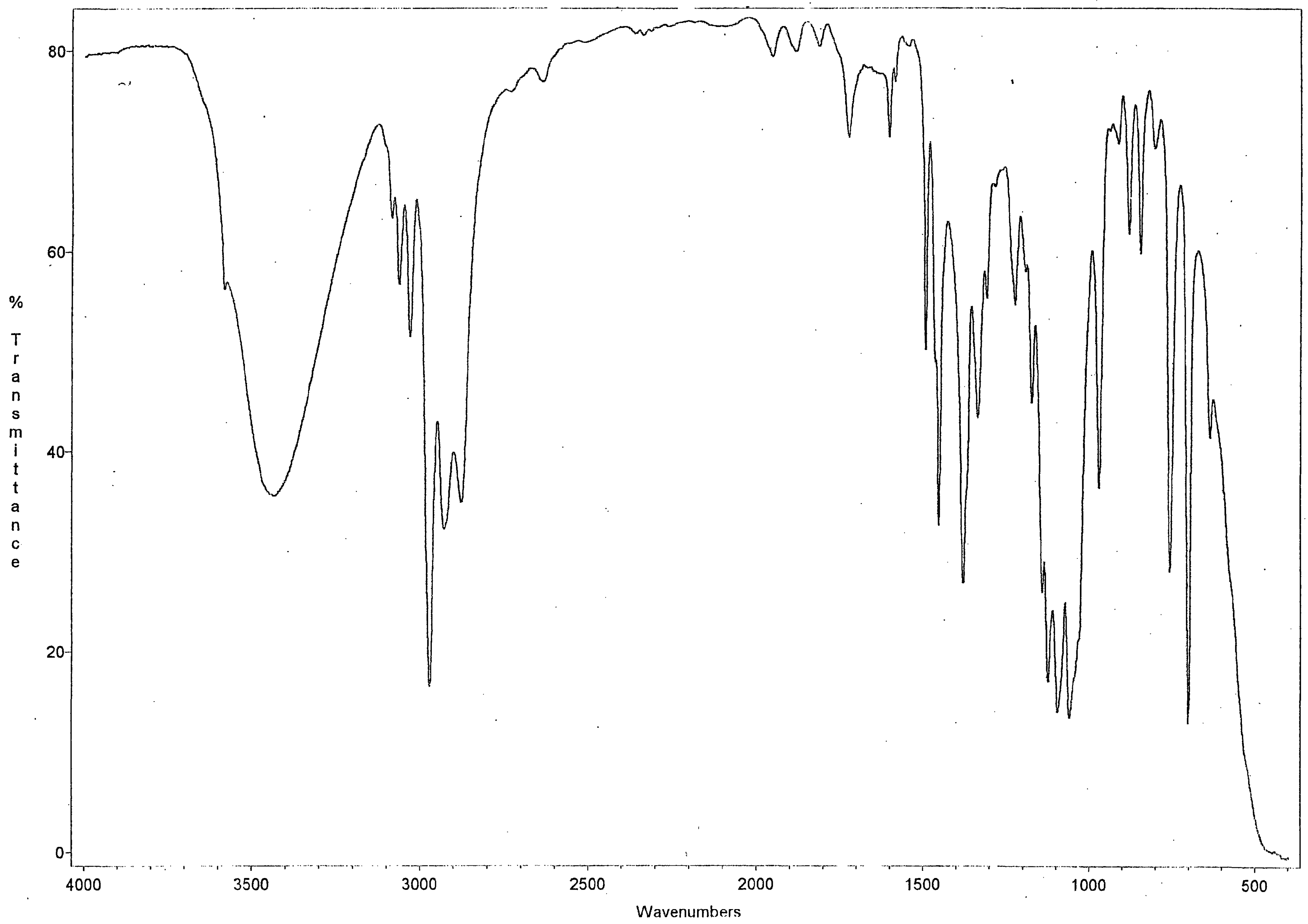


```
Current Data Parameters
NAME           Sep24-2003
EXPNO                  50
PROCNO                  1

F2 - Acquisition Parameters
Date_            20030924
Time                17.25
INSTRUM             av400
PROBHD   5 mm QNP  1H/1
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             8802.817 Hz
FIDRES          0.134320 Hz
AQ             3.7224948 sec
RG                  161.3
DW                 56.800 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.00 usec
PL1                  4.00 dB
SFO1          400.1328009 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300102 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

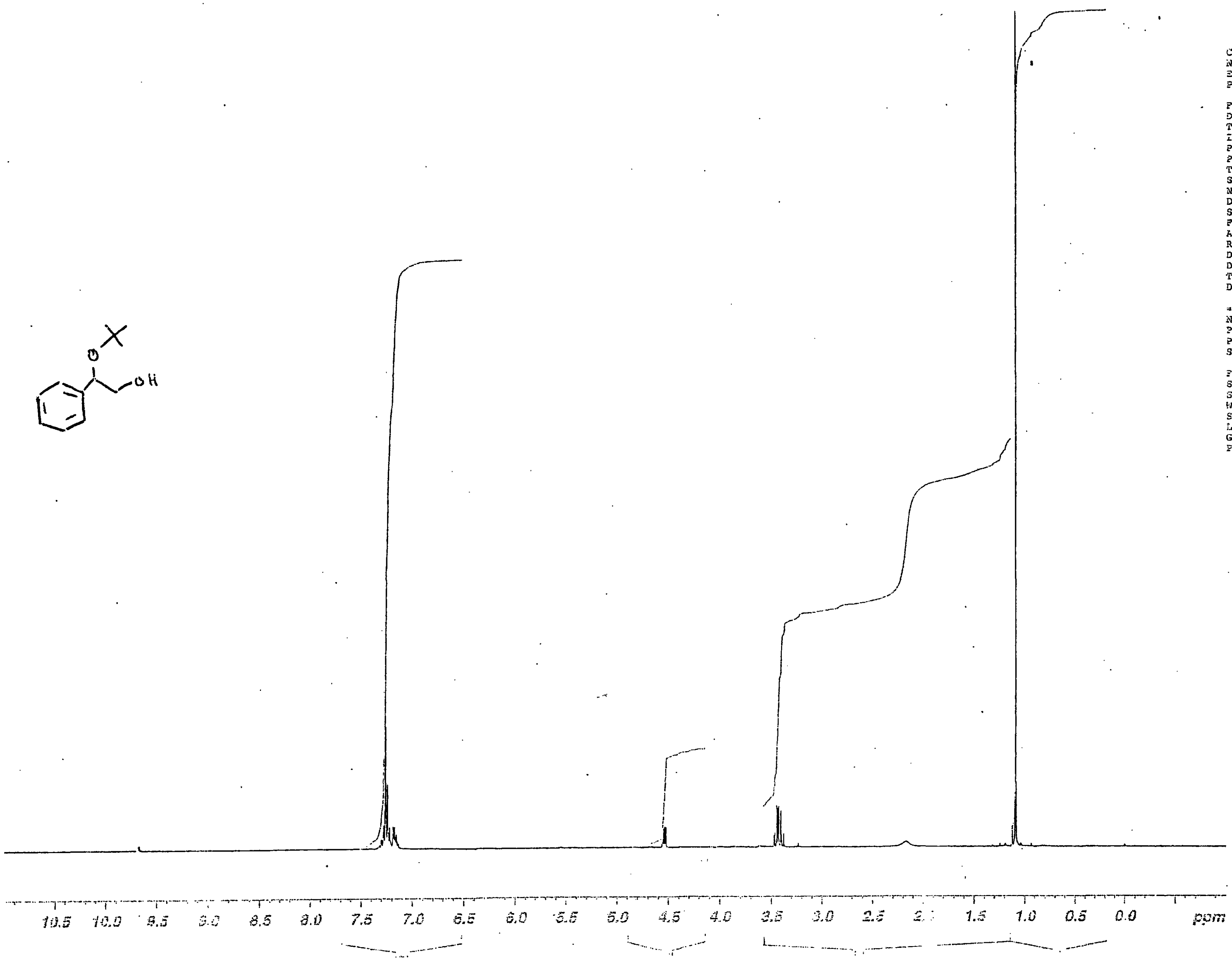
4047 Richard RB318.1



```
Current Data Parameters
NAME          Sep24-2003
EXPNO                 51
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030924
Time               17.55
INSTRUM            av400
PROBHD   5 mm QNP  1H/1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  512
DS                    2
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG              18390.4
DW               20.850 usec
DE                20.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  6.35 usec
PL1                 2.00 dB
SFO1         100.6227898 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                  1H
PCPD2              83.00 usec
PL2                 4.00 dB
PL12               24.50 dB
PL13               24.50 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127290 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

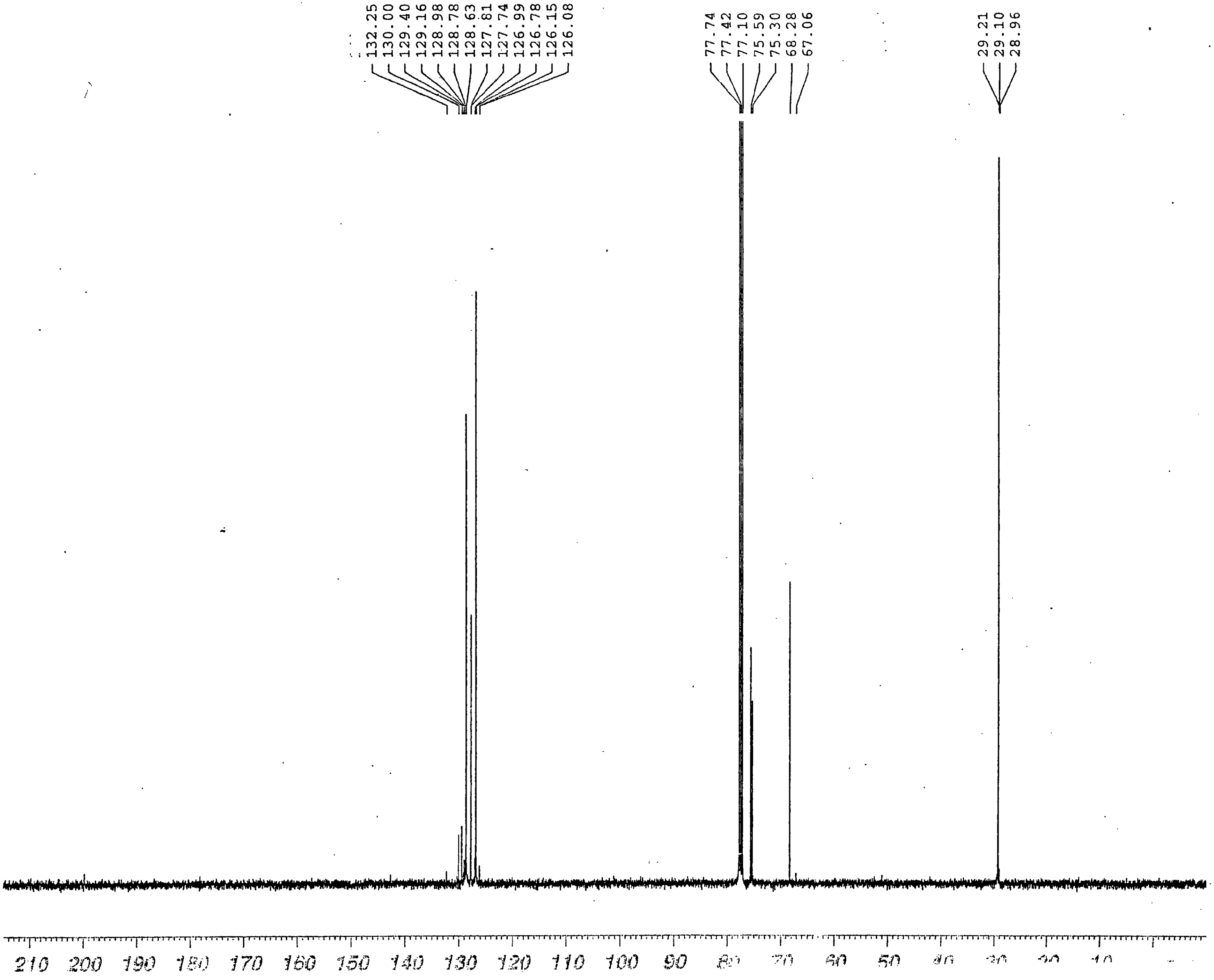

80
60
40
20
0
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers

4055 Richard RB320.1

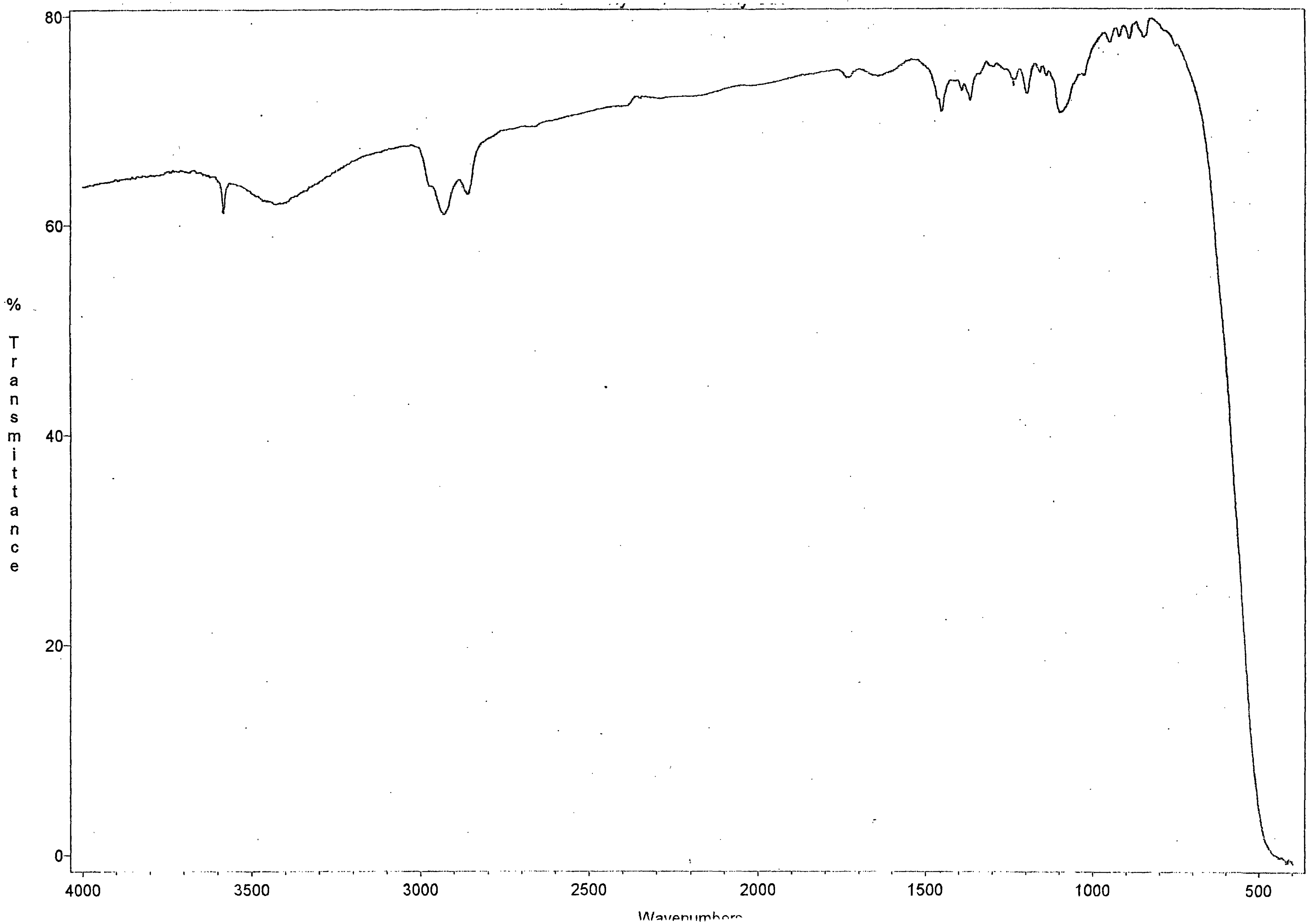


```
Current Data Parameters
NAME              Sep25-2003
EXPNO                     80
PROCNO                     1

F2 - Acquisition Parameters
Date_               20030925
Time                   15.25
INSTRUM                av400
PROBHD    5 mm QNP      1H/1
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8802.817 Hz
FIDRES              0.134320 Hz
AQ                 3.7224948 sec
RG                      90.5
DW                    56.800 usec
DE                      6.00 usec
TE                     300.0 K
D1                1.00000000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                      8.00 usec
PL1                     4.00 dB
SFO1          400.1328009 MHz

F2 - Processing parameters
SI                     32768
SF            400.1300414 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

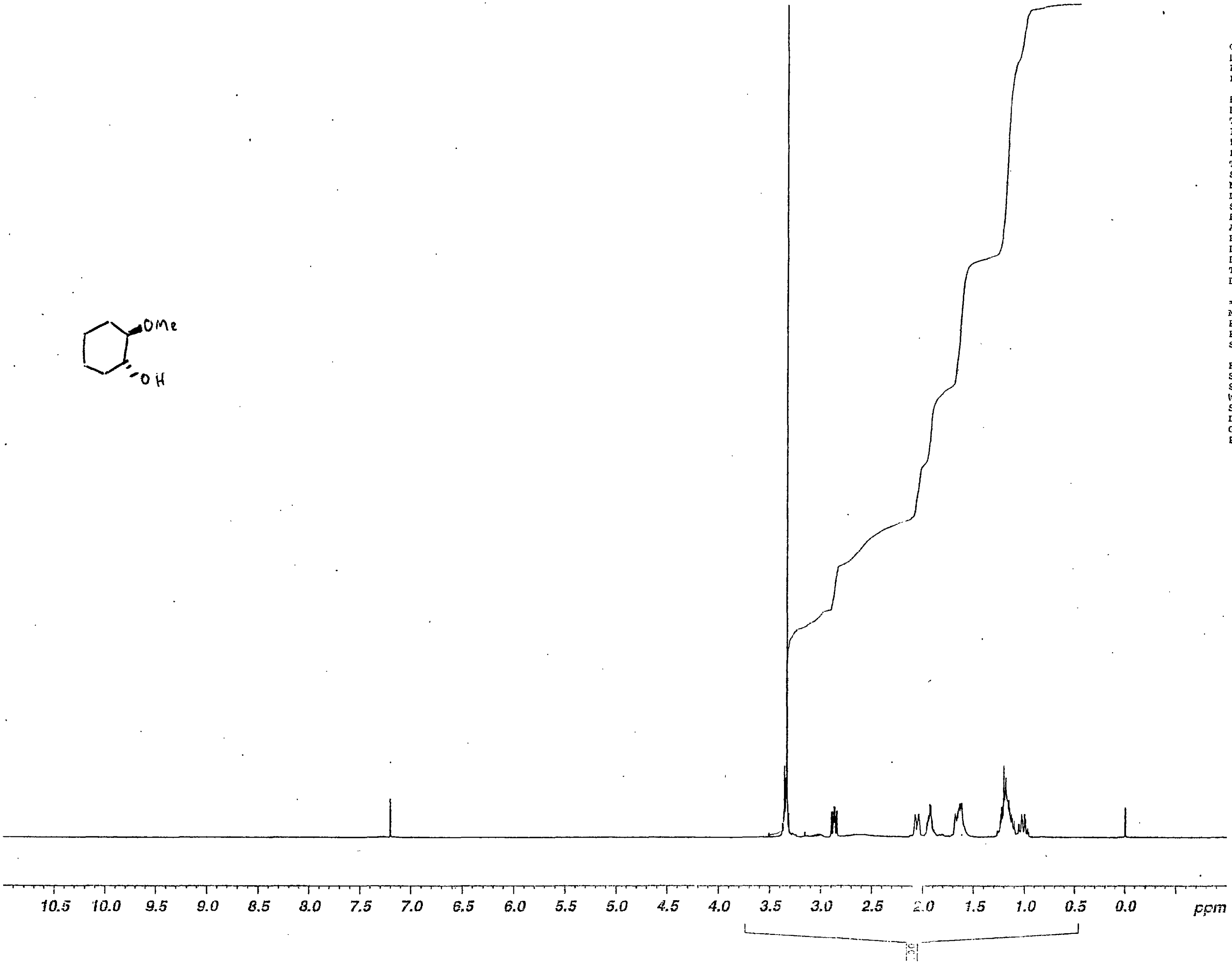
4055 Richard RB320.1



```
Current Data Parameters
NAME             Sep25-2003
EXPNO                    50
PROCNO                    1

F2 - Acquisition Parameters
Date_              20030925
Time                  17.07
INSTRUM               av400
PROBHD   5 mm QNP  1H/1
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      512
DS                        2
SWH               23980.814 Hz
FIDRES             0.365918 Hz
AQ                1.3664756 sec
RG                  18390.4
DW                   20.850 usec
DE                    20.00 usec
TE                    300.0 K
D1               2.00000000 sec
d11              0.03000000 sec
d12              0.00002000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     6.35 usec
PL1                    2.00 dB
SFO1            100.6227898 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 83.00 usec
PL2                    4.00 dB
PL12                  24.50 dB
PL13                  24.50 dB
SFO2            400.1316005 MHz

F2 - Processing parameters
SI                    32768
SF              100.6127290 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

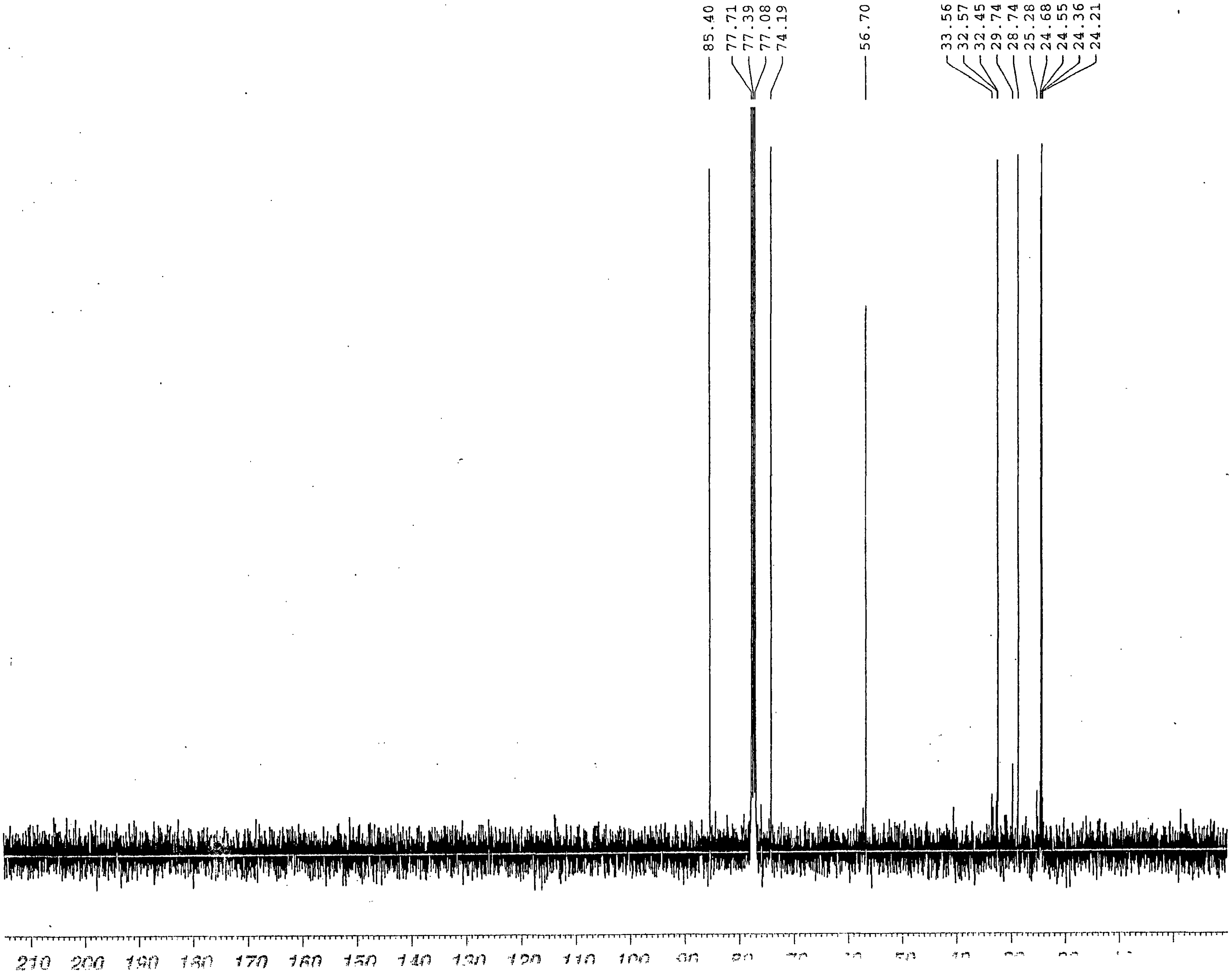

80
60
40
20
0
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers

4054 Richard RB 302.1

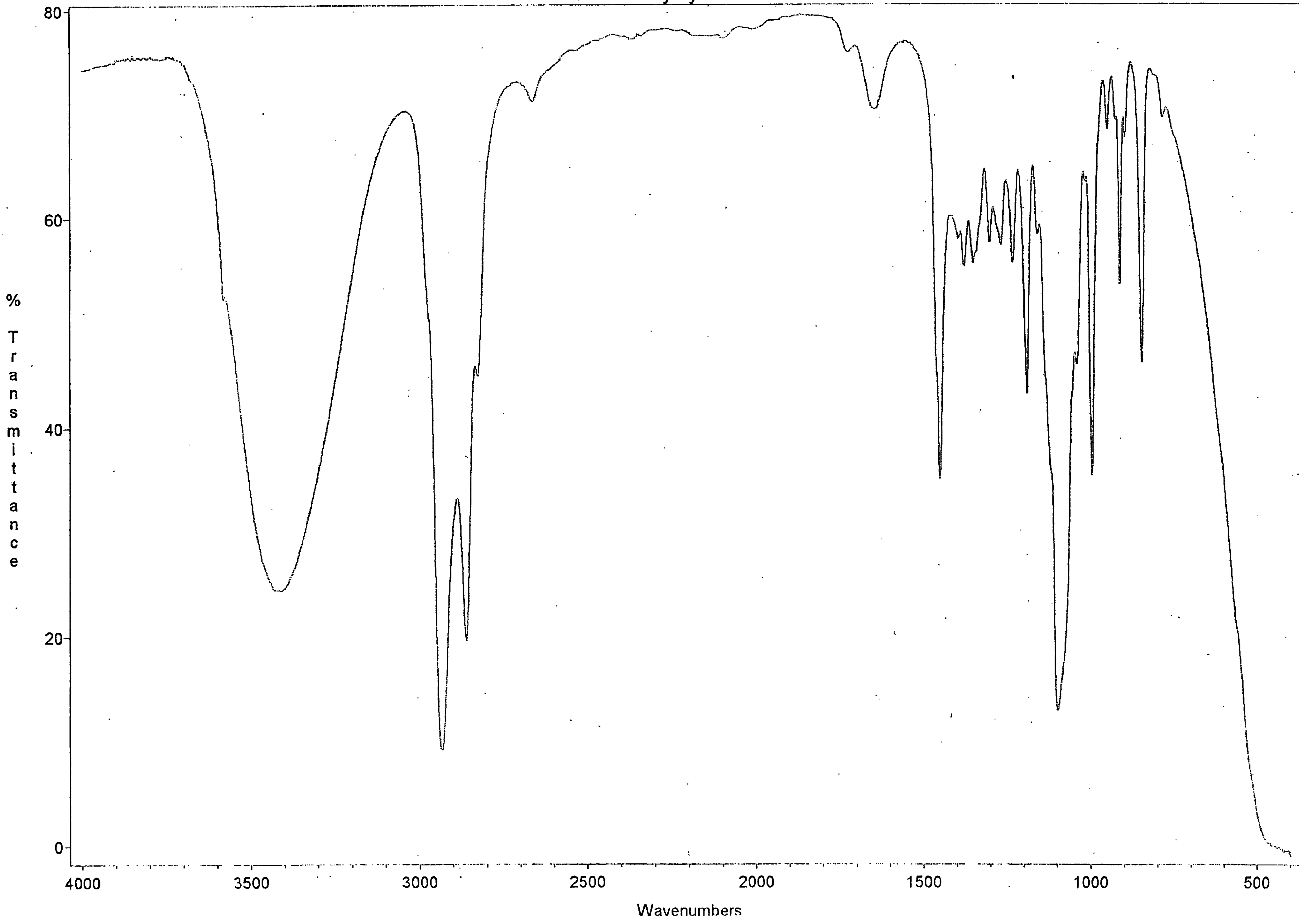


```
Current Data Parameters
NAME          Sep25-2003
EXPNO                 90
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030925
Time               17.15
INSTRUM            av400
PROBHD   5 mm QNP  1H/1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8802.817 Hz
FIDRES          0.134320 Hz
AQ             3.7224948 sec
RG                 161.3
DW                56.800 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  8.00 usec
PL1                 4.00 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300333 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

4054 Richard RB 302.1



```
Current Data Parameters
NAME          Sep25-2003
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030925
Time               17.45
INSTRUM            av400
PROBHD   5 mm QNP  1H/1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     2
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG               20642.5
DW                20.850 usec
DE                 20.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  6.35 usec
PL1                 2.00 dB
SFO1        100.6227398 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              83.00 usec
PL2                 4.00 dB
PL12               24.50 dB
PL13               24.50 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127290 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

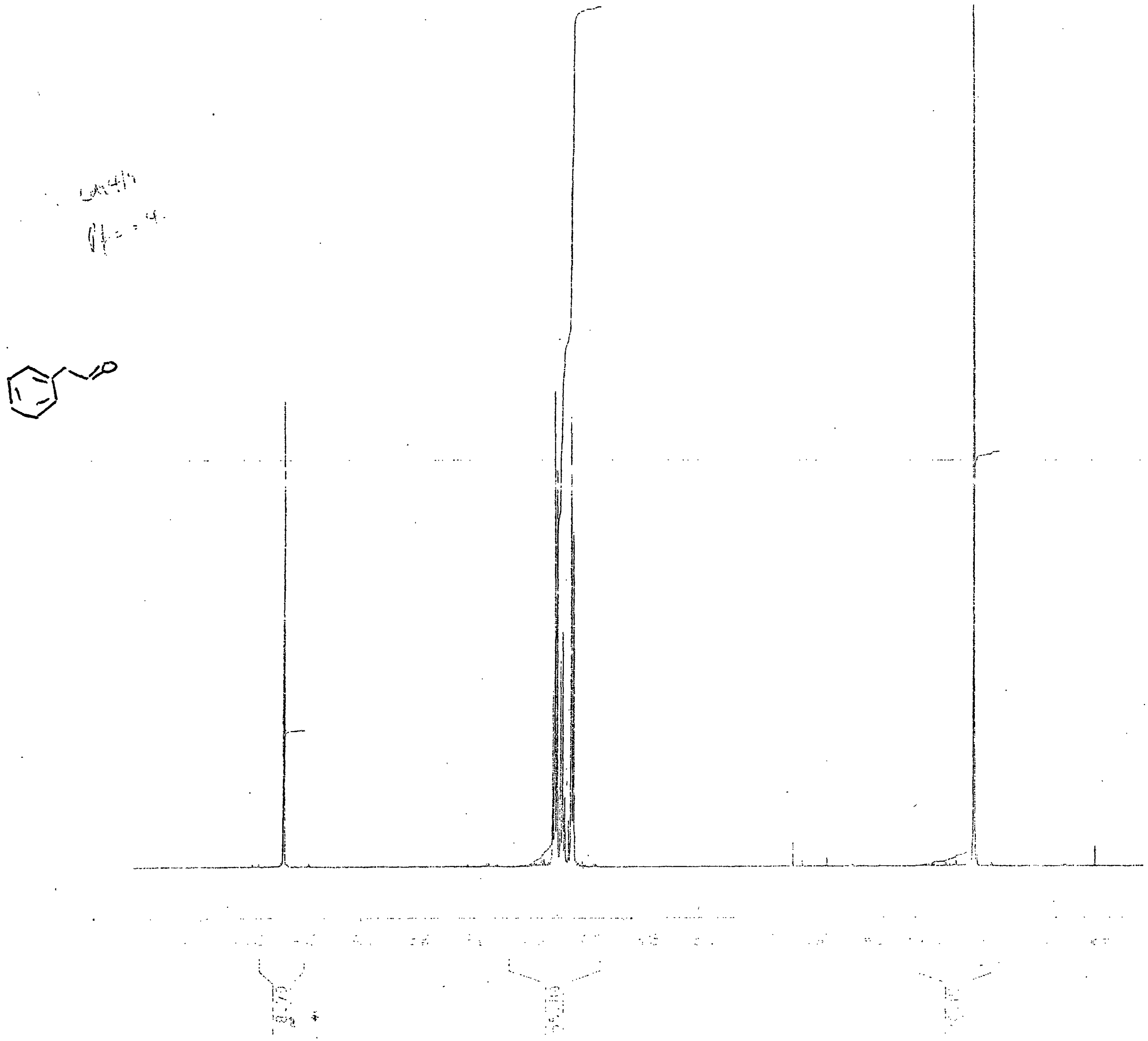


2-methoxy cyclohexanol

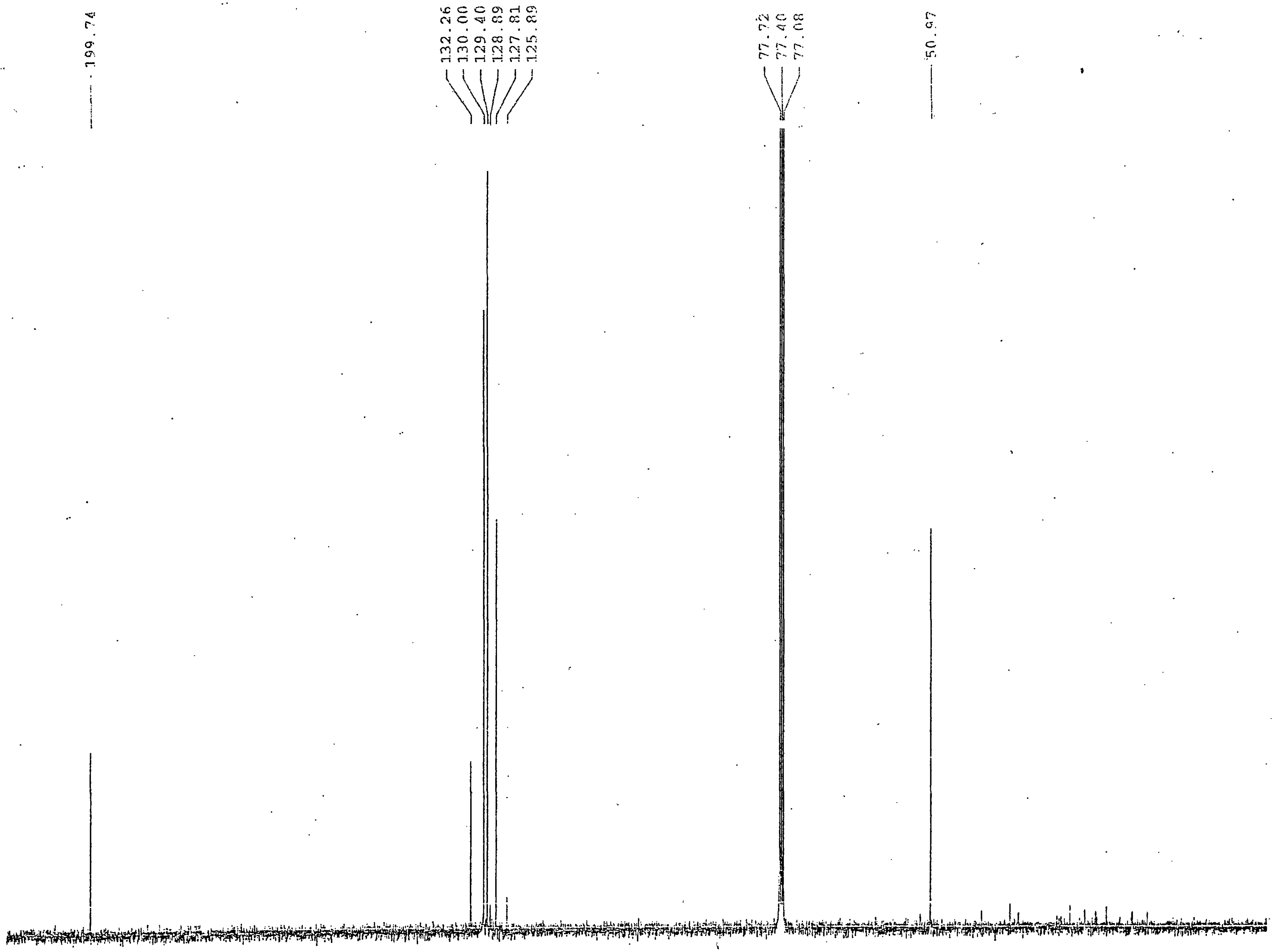
Appendix C

Spectral data from rearrangement reactions of epoxides

3306 Buckle 281B

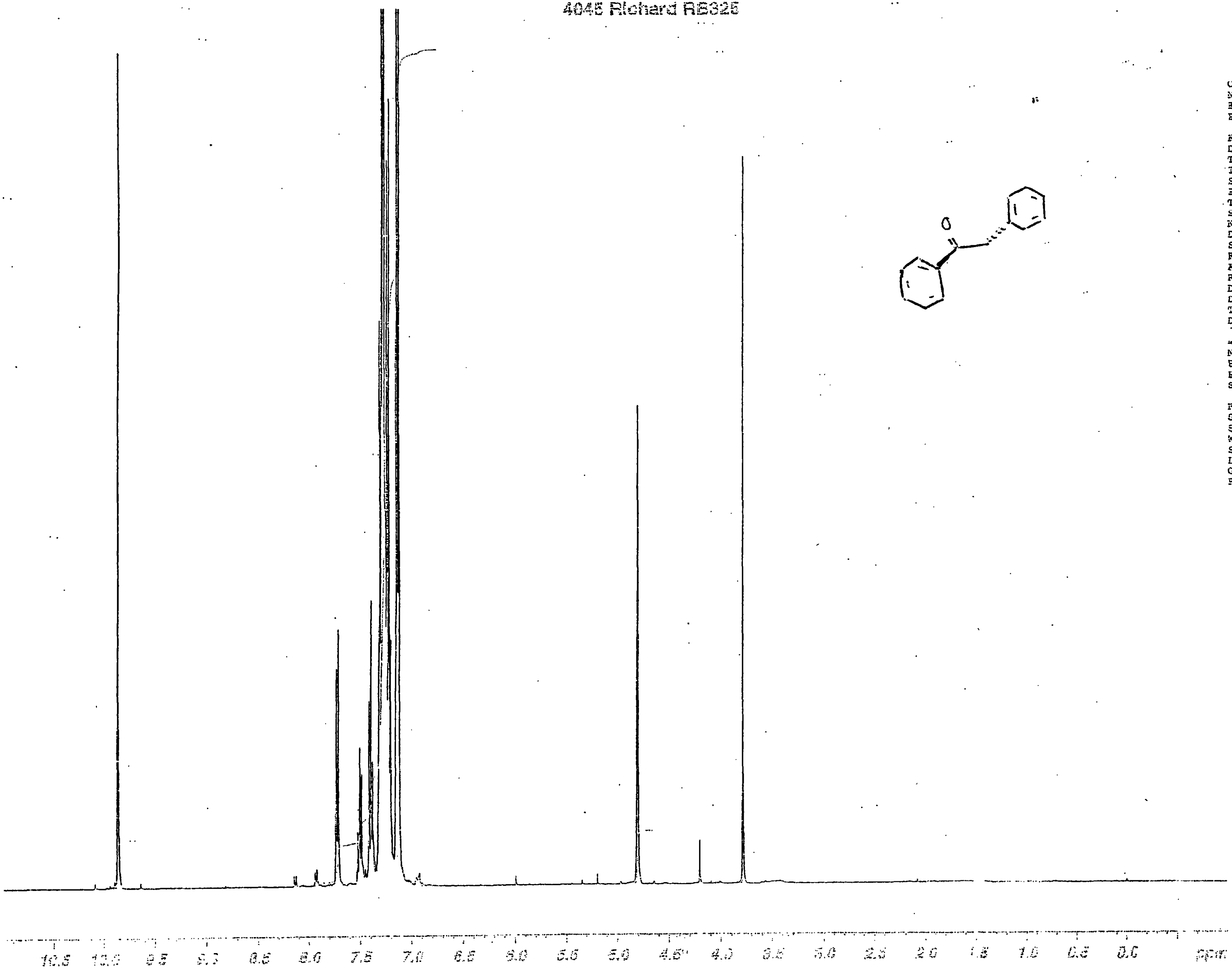


4049 Richard RB324



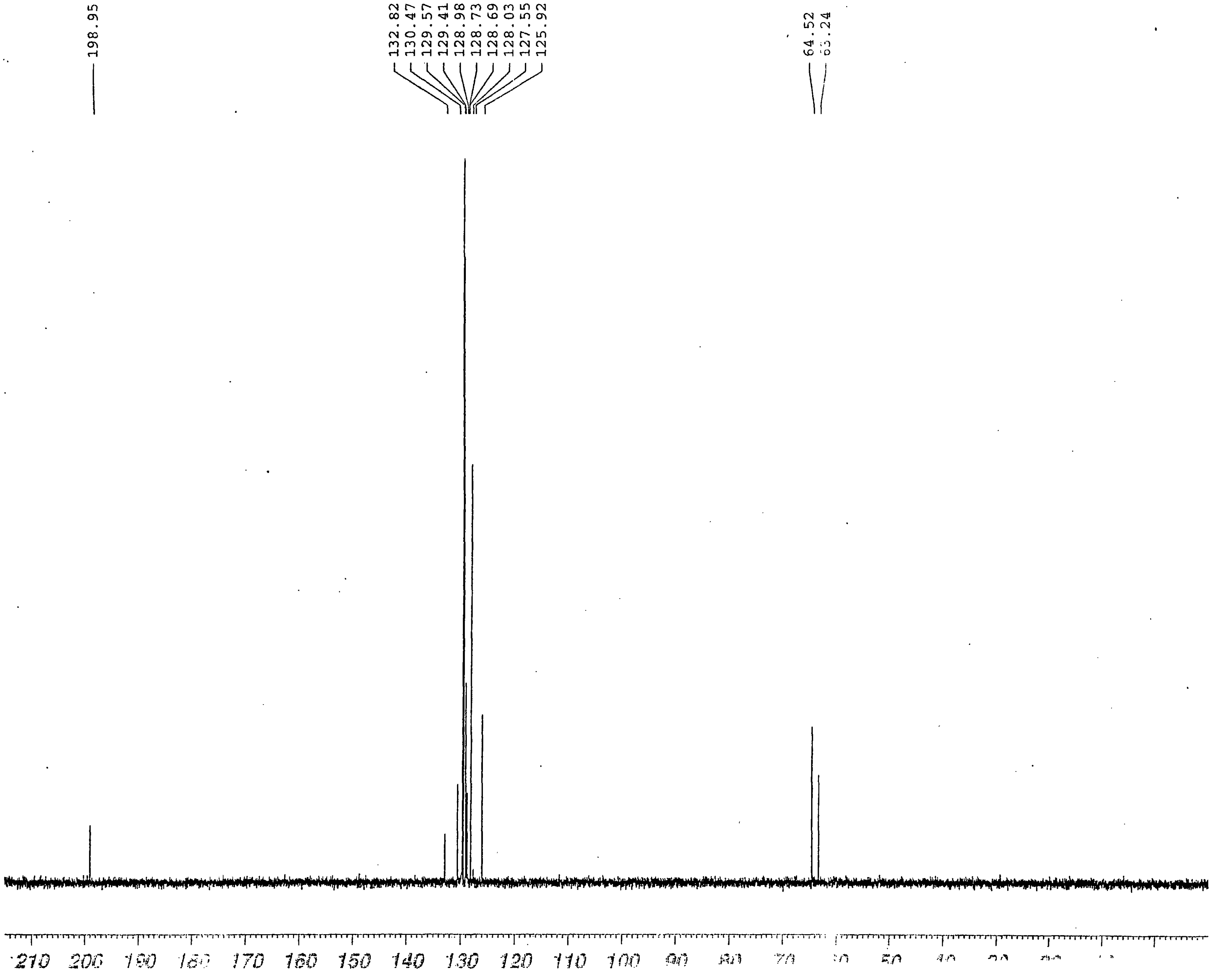
```
Current Data Parameters
NAME            Sep24-2003
EXPNO                   41
PROCNO                   1

F2 - Acquisition Parameters
Date_             20030924
Time                 15.18
INSTRUM              av400
PROBHD   5 mm QNP 1H/1
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       2
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                 18390.4
DW                  20.850 usec
DE                   20.00 usec
TE                   300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
d12             0.00002000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    6.35 usec
PL1                   2.00 dB
SFO1           100.6227898 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 83.00 usec
PL2                    4.00 dB
PL12                  24.50 dB
PL13                  24.50 dB
SFO2            400.1316005 MHz

F2 - Processing parameters
SI                    32768
SF              100.6127290 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

4045 Richard RB325



```
Current Data Parameters
NAME          Sep24-2003
EXPNO                 70
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030924
Time               18.35
INSTRUM            av400
PROBHD   5 mm QNP  1H/1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8802.817 Hz
FIDRES          0.134320 Hz
AQ             3.7224948 sec
RG                  90.5
DW                56.800 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  8.00 usec
PL1                 4.00 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300492 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

4045 Richard RB325



```
Current Data Parameters
NAME          Sep24-2003
EXPNO                 72
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030924
Time               19.35
INSTRUM            av400
PROBHD   5 mm QNP  1H/1
PULPROG          dept135
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                 16384
DW                20.850 usec
DE                  6.00 usec
TE                 300.0 K
CNST2        145.0000000
D1            2.00000000 sec
d2            0.00344828 sec
d12           0.00002000 sec
DELTA         0.00000809 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  6.35 usec
p2                 12.70 usec
PL1                 2.00 dB
SFO1         100.6227898 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
P3                  8.00 usec
p4                 16.00 usec
PCPD2              83.00 usec
PL2                 4.00 dB
PL12               24.50 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127290 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

204820 MW=98?

Buckle

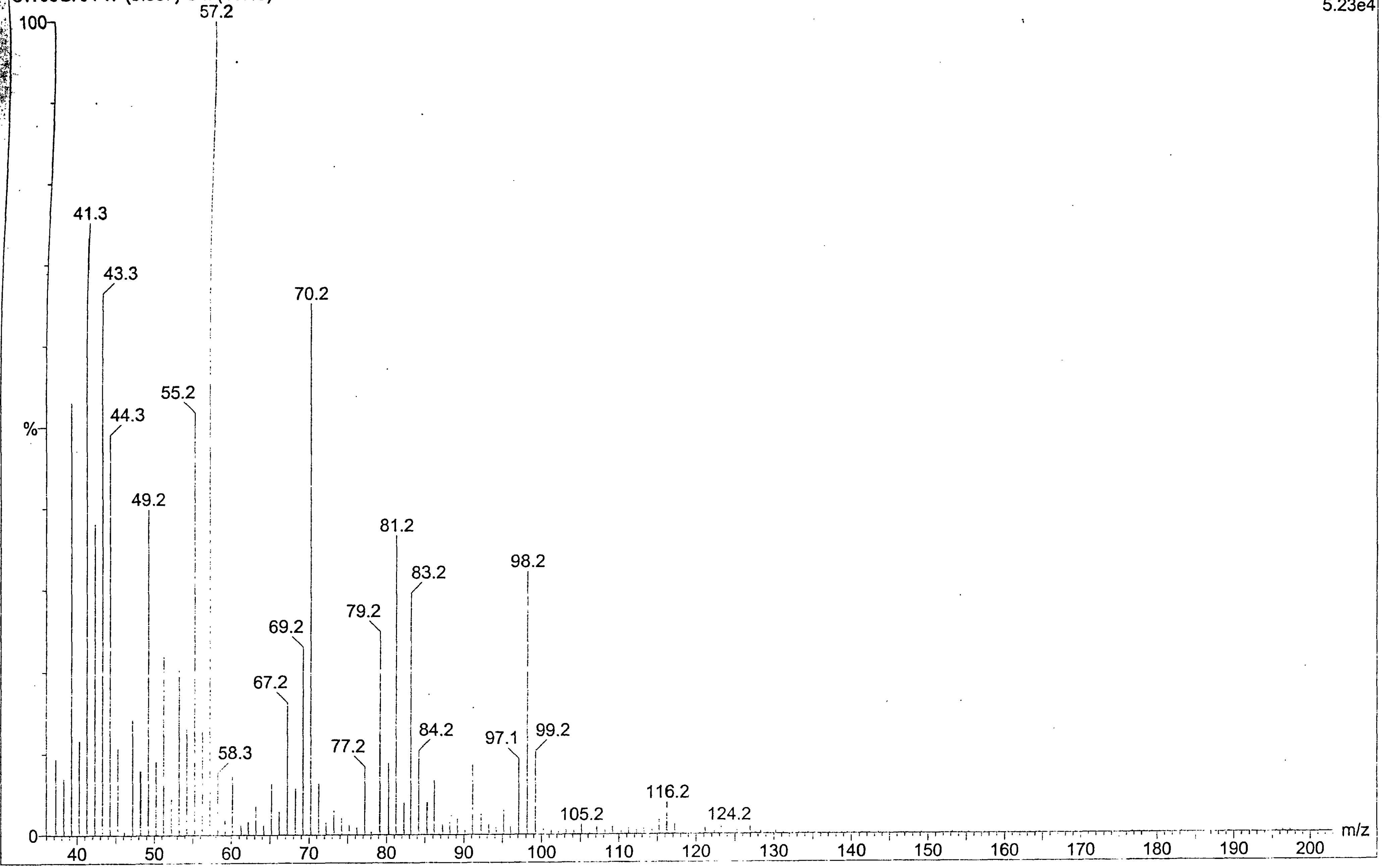
SW03GRA 47 (0.887) Cm (45:49)

EPSRC National Centre, Swansea

QUATTRO

27-Jan-2003

Scan EI+
5.23e4



204820 **MW=98?**
Buckle
SW03GR2 42 (0.887) Cm **(41:46)**

EPSRC National Centre, Swansea
QUATTRO

28-Jan-2003
CI+(NH3)
2: Scan CI+
3.17e4