The synthesis and characterization of conjugated polyradicals: an approach to organic magnets

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THE SYNTHESIS AND CHARACTERIZATION OF CONJUGATED POLYRADICALS

AN APPROACH TO ORGANIC MAGNETS

by

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ABSTRACT

The thesis describes investigations into the preparation and magnetic properties of new conjugated polymers, with pendant free radical sites, produced from substituted acetylenes.

The first two chapters involve reviews of the literature concerning organic ferromagnetism and the preparation and structure of the materials produced by polymerizing phenylacetylene. The syntheses of esters of propiolic acid and propargyl alcohol, and their polymerization using metathesis catalysts are described in chapter three. The preparation of new substituted triphenylmethanes and triphenylmethanols, and the syntheses of new ethynyl-substituted arylacetylenes, are described in chapters four and five, together with their full characterization. The polymerizations of phenylacetylene and the new substituted arylacetylenes using well-defined tungsten, molybdenum and rhodium catalysts are reported in chapter six, together with electron spin resonance and magnetic susceptibility studies.

All the polymers produced in this study were found to be paramagnetic, and the main target polymer, poly((4-ethynylphenyl)diphenylmethyl) was found to display a reversible increase in spin concentration with increasing temperature. The conclusions drawn from these studies were that conjugated polyradicals were prepared, but that subsequent spin-pairing took place.

ACKNOWLEDGEMENTS

This thesis would not have been possible without the help and expertise of many people, from within Durham University, and from outside. I would particularly like to thank my supervisor, Professor W.J. Feast, for his guidance, encouragement, trust and understanding throughout the project. I would also like to express my thanks to the following: Dr R.H. Friend and his students at Cambridge University for help in carrying out magnetic susceptibility studies; Professor L.H. Sutcliffe at Royal Holloway and Bedford New College, and Dr. A. Bunn at ICI Wilton, for recording the ESR spectra, and Dr A. Kenwright and Mrs J. Say in this department for recording high-resolution NMR spectra.

I would also like to thank the members of the technical staff at Durham, particularly R. Hart and G. Haswell for their skill in turning shards of broken glass into invaluable pieces of laboratory equipment. I extend my thanks to all the members of the Polymer Group, especially Dr E. Khosravi for preparing the molybdenum catalyst used in the polymerizations, and to Dr. M. Mitra and D.H. Cadd for advice concerning column chromatography.

The author gratefully acknowledges the funding of this work by the Science and Engineering Research Council.

Finally, I would like to thank my friends for their support, and most especially I thank my family, for their immense tolerance and understanding, and for staving off the bailiffs.

MEMORANDUM

The work reported in this thesis was carried out in the Chemistry Department of the University of Durham between October 1987 and September 1990. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Aspects of this work have been presented by the author at the following symposia:

International Symposium on Olefin Metathesis (ISOM 8), Bayreuth, Federal Republic of Germany, 4-9 September 1989;

North East Graduate Symposium, Newcastle, 23 April 1990;.

Royal Society of Chemistry Symposium on New Organic Materials, Durham, 10-12 September 1990.

STATEMENT OF COPYRIGHT

NOTE TO THE READER

In this thesis, a number of text formats have been used to aid the reader. The detailed descriptions of experimental procedures have been italicized, and where appropriate, diagrams showing the synthetic transformations have been included with the experimental sections. The characterization of new compounds, including the detailed results of elemental analyses, NMR etc. has been indented slightly from the main text to allow easy identification. In view of the large amount of analytical data, it was not feasible to include spectra with the characterization sections. Thus, all the spectra and chromatograms have been placed at the end of the thesis, with an appendix number corresponding to the chapter in which the characterization results were recorded. For example, Appendix 4-3 contains a spectrum of which the summarized results are reported in chapter 4.

In addition, there are a few terms with specific meaning in this thesis. In the experimental sections, "fresh" molecular sieves refer to material activated prior to use by prolonged heating under reduced pressure (10^{-3} torr). Where solvents are denoted as "double-distilled", the standard procedure was to distil the solvents twice and store on a litre scale. The solvent was then vacuum-transferred before use. The term "canulla wire" refers to a long, syringe-type needle, sharp at both ends.

The naming system for compounds unreported before this thesis has followed IUPAC guidelines wherever possible. There are some differences, as a result, to names derived using the Chemical Abstracts system. For example (4-ethynylphenyl)diphenylmethanol would be named in Chemical Abstracts as α-(4-ethynylphenyl)-α-phenylbenzenemethanol. However, the author believes that system used in this thesis is less cumbersome, and more easy to visualize, than the Chemical Abstracts method. This particularly applies to the compounds described in chapter 5.

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CHAPTER ONE

INTRODUCTION

ORGANIC FERROMAGNETISM

THEORETICAL STUDIES AND REPORTED SYNTHESES

1.1. THEORETICAL STUDIES

This thesis is concerned with an attempt to make organic polyradicals as candidates for new, metal-free, ferromagnetic materials, and thus an introduction to some aspects of the basic theory of magnetism is required.

1.1.i. CLASSIFICATION OF MAGNETS

When a substance is placed in a magnetic field **H**, the field induced inside the substance, **B**, is given by;

$$\mathbf{B/H = 1 + 4\pi I/H = 1 + 4\pi\kappa}$$

where **I** is the magnetization of the substance,

and κ is the volume magnetic susceptibility.

The magnetization is due to the external field **H**, and in most cases **M** is a linear function of **H**, such that;

$$\mathbf{M = \kappa H} \qquad \chi_m = \kappa M/\rho \ (\mathrm{cm^3.mol^{-1}})$$

where χ_m is the molar magnetic susceptibility, **M** is the relative molecular mass and ρ is the density.

Dependent on the sign and magnitude of the magnetic susceptibility, there are three main categories of magnetism:

$\chi < 0$ **diamagnetism**

$\chi > 0$ **paramagnetism**

$\chi \rightarrow \infty$ **ferromagnetism**

The paramagnets can be split further (antiferromagnetic, and ferrimagnetic materials), but this thesis deals only with potentially ferromagnetic substances in the broad sense defined above.

1.1.ii. Organic Ferromagnetic Materials

The possible manufacture of metal-free materials exhibiting bulk ferromagnetic properties has attracted considerable attention over recent years. If such materials could be made, they would offer many potential advantages over metal-based systems, such as reduced weight, and ease of processing. These materials would also be of theoretical interest in terms of the relation between electronic structure at the molecular level and the overall magnetic susceptibility of such systems. The syntheses and characterization studies of these so-called "super-paramagnetic" species are thus of both practical and academic importance.

It was first suggested by Mataga that certain hydrocarbons might exhibit ferromagnetic behaviour[1]. This proposal was in response to earlier theoretical work by McConnell[2] concerning the interactions between organic free radicals, and the possibility of producing ferromagnetic materials. However, it was not until 1977 that a detailed study of the principles underlying the construction of, organic ferromagnets was carried out[3,4].

These theoretical studies in turn have stimulated synthetic work which led to reports of organic ferromagnets[5-9]; nevertheless, at the time of writing, a fully characterized organic material with bulk ferromagnetic properties has yet to be made by a reliable and fully reproducible method.

1.2. ORGANIC FERROMAGNETISM : THEORETICAL STUDIES

1.2.i. Energy Levels and Spin States

The property of magnetism arises from the spinning of charge. The study of theoretical physics has shown that energy is quantised, and hence the energy associated with a spinning charge can only have certain, discrete, values. For an electron, there are two allowed spin states, which have the values +1/2 or -1/2. The overall spin state of a molecule depends on the interactions of all the spinning charged particles, and thus is extremely complex, but can in most cases be approximated to the spin state arising from the interactions of the electron spins. Thus, an expression for the overall spin state is given by:

$$\mathbf{S = 2s + 1}: s = (n/2)$$

where S is the overall spin state, and n is the number of unpaired electrons.

The electrons in organic molecules are generally spin-paired. The overall spin ground states of such molecules are denoted as singlets, since $n = 0$, and $S = 1$. In an applied field, the paired electrons will not align to reinforce the field, and so such molecules are diamagnetic. The presence of one unpaired electron gives a doublet ground state ($S = 2$) resulting in paramagnetism. The generation of organic molecules with triplet or higher multiplicity ground states should, if the spin states can be correctly correlated throughout the bulk, produce observable ferromagnetism in the material as all the unpaired electrons align.

There are, however, few known organic systems with triplet or higher ground states, and thus the syntheses of such species are of prime concern. There are three theoretical classes of high-spin ground state organics, shown overleaf.

Figure 1.2.i. Anti-aromatic annulenes[10-16]

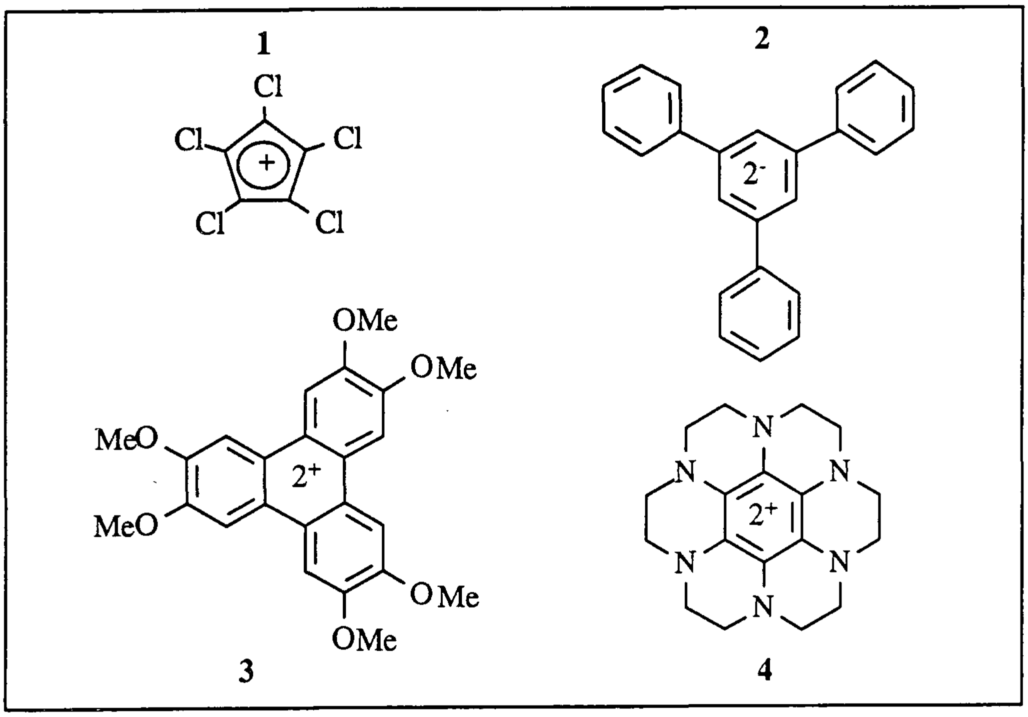


Figure 1.2.ii. Non-Kekulé structures[17-27]

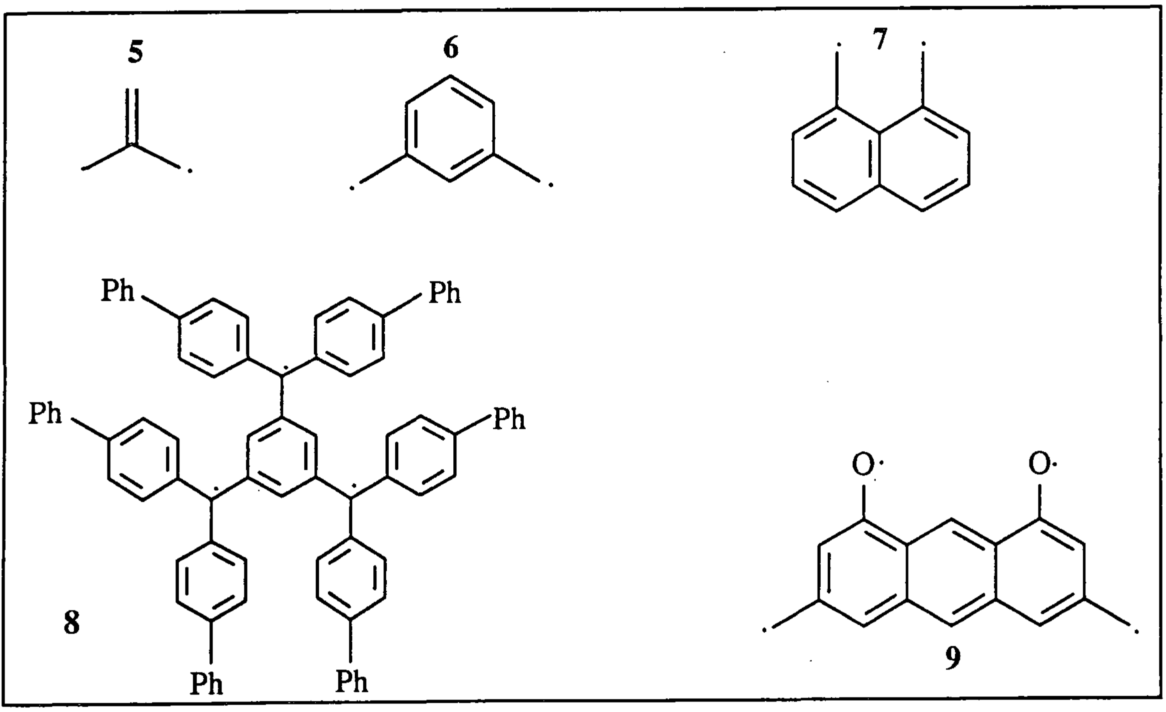
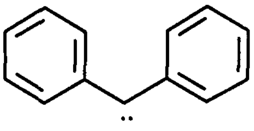


Figure 1.2.iii. Monocentric diradicals[28-33] (i.e. carbenes and nitrenes);

$:CH_2$

10



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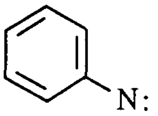

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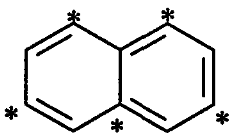
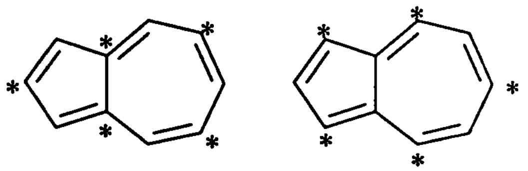
1.2.ii. Polymeric Carbenes and Odd-Alternant Hydrocarbons

The synthesis of polymeric carbenes has been considered as a useful test for organic ferromagnetism theory. A number of model molecules have been characterized[34], based on meta-linked diphenylcarbene units (**11** above). These were designed to fulfil certain conditions set out by Longuet-Higgins[35], concerning "alternant hydrocarbons", of which diphenylcarbene is an example. Alternant hydrocarbons have been defined by molecular orbital (MO) theory such that the carbon atoms can be divided into two sets with no two atoms of the same set being directly linked. Each carbon atom provides a 2p atomic orbital and one electron to the π system. An example of an alternant, and a non-alternant hydrocarbon is shown in Figure 1.2.iv. overleaf:

Figure 1.2.iv.



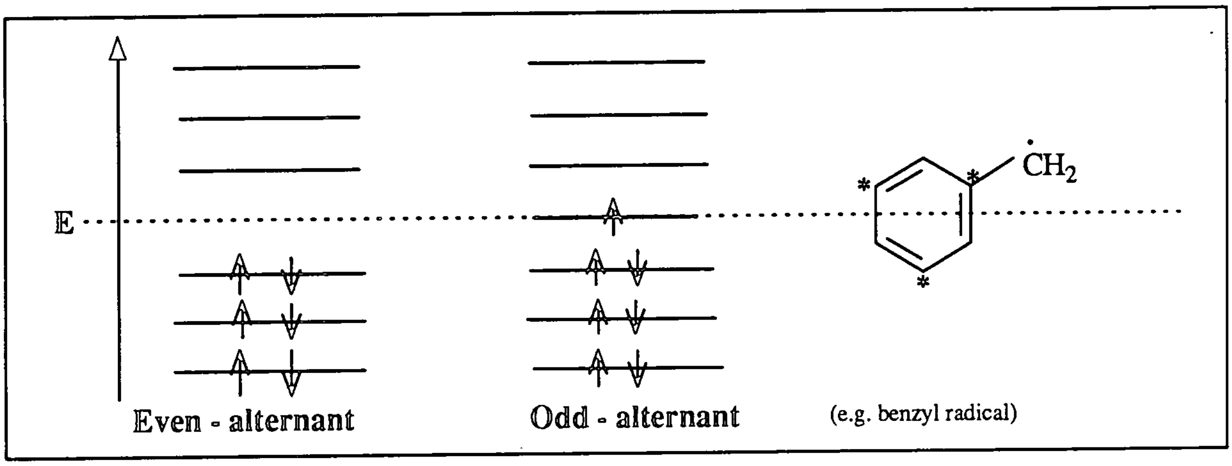
Naphthalene - alternant



Azulene - non-alternant

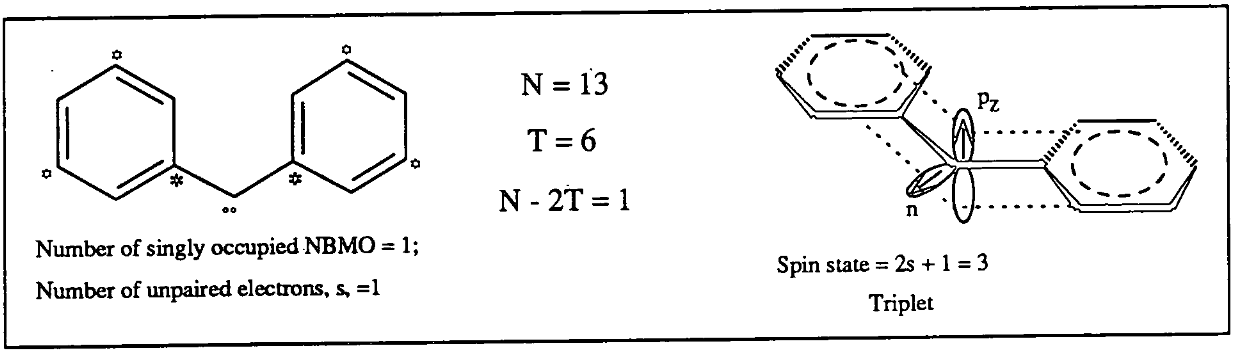
Alternant hydrocarbons have bonding and antibonding orbitals in pairs, with energies symmetrically disposed about the non-bonding position; i.e. for each bonding orbital of energy -E there is an antibonding orbital of energy +E. Those systems with an even number of starred and unstarred atoms are known as *even*-alternant hydrocarbons, and have all the bonding orbitals filled, with the π electrons being uniformly spread over the unsaturated atoms. Odd alternant hydrocarbons, which must be carbocations, free-radicals or carbanions, have a non-bonding orbital, as shown overleaf.

Figure 1.2.v.



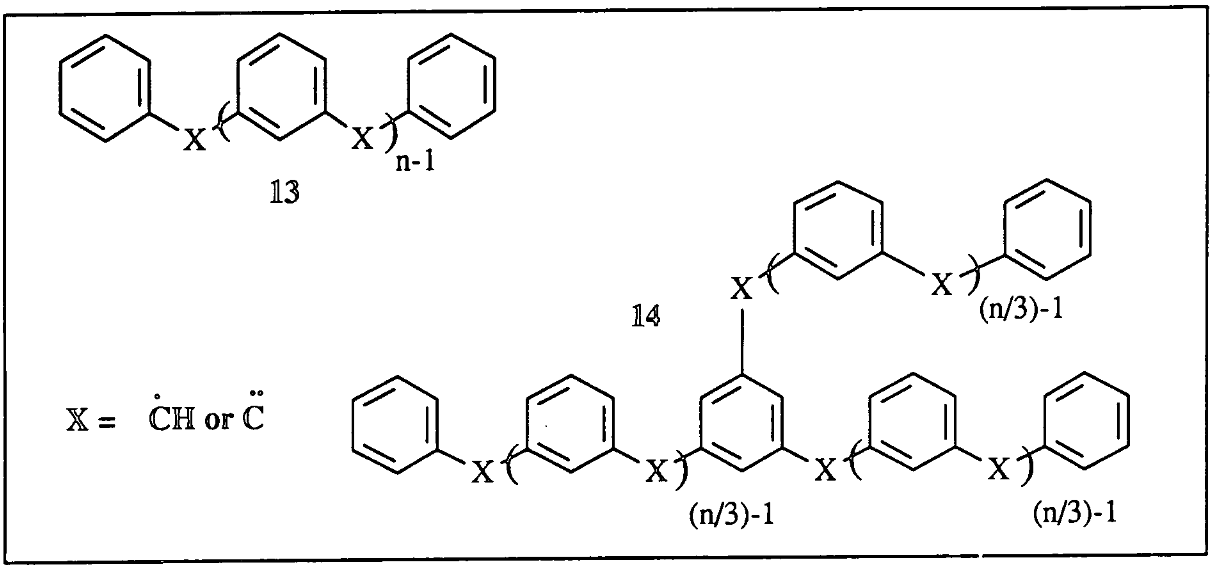
Diphenylcarbene is an odd-alternant hydrocarbon and is known to have a triplet spin ground state. Iwamura[34a] introduced a theoretical treatment applying to alternant hydrocarbons, stating that such species are predicted to have at least N-2T singly occupied non-bonding molecular orbitals (NBMO). Extension and partial confirmation of these theories, has recently been reported by Iwamura and co-workers[34b]. In this model N is the number of carbon atoms in the alternant hydrocarbon and T is the maximum number of double bonds occurring in any resonance structure, as shown in Figure 1.2.vi. below:

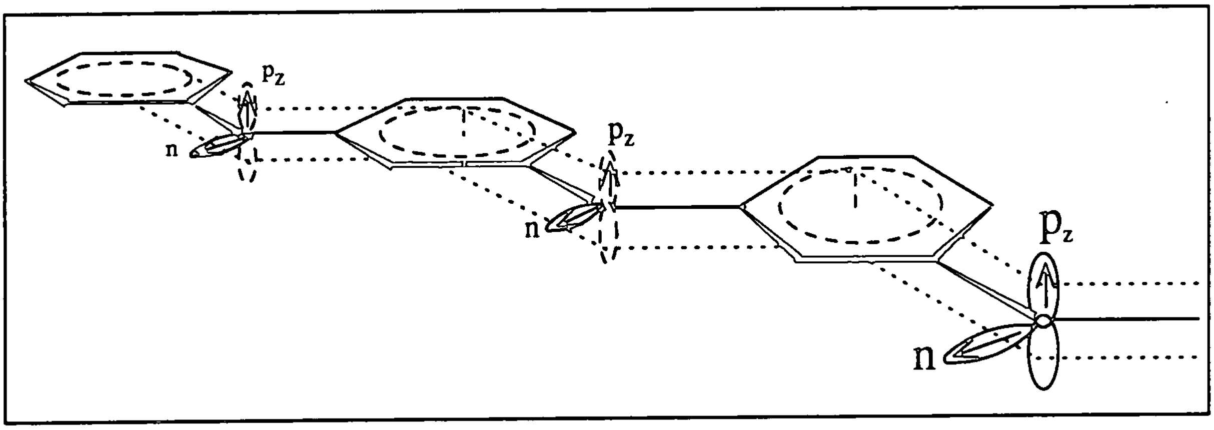
Figure 1.2.vi.



Structures such as **13** and **14**, shown in Figure 1.2.vii. overleaf, are expected to have n degenerate NBMO and, therefore, by application of Hund's Rule, the π-electrons will align parallel as the non bonding shell is half-filled. The overall spin state S will correspond to a ground state of high spin multiplicity as the number of units **n** increases.

Figure 1.2.vii.





More recently, Davidson and Borden have classified the above species as non disjoint (i.e. the Huckel NBMO, and linear combinations thereof, cannot be confined to separate fragments of the molecule, meeting at a node), and have predicted a high spin ground state[36]; this coincides with the conclusions of a Valence-Bond treatment by Ovchinnikov. Replacement of the doublet (>C-H) radical centres by carbenes (>C:) in the above molecules should allow an increase in the total electron spin quantum number as a second singly occupied NBMO is available from each monomer unit of the polymer. Compounds of structures **13** and **14** are therefore predicted to have one- and two-dimensional macroscopic spins as the number of chain links (n in **13** and **14** above),and the number of unpaired electrons tends to infinity.

The n→π interaction between the localized n spins and the delocalized π spins has a close resemblance to the s-d interaction in ferromagnetic metals and alloys.

1.2.iii. Ovchinnikov Models

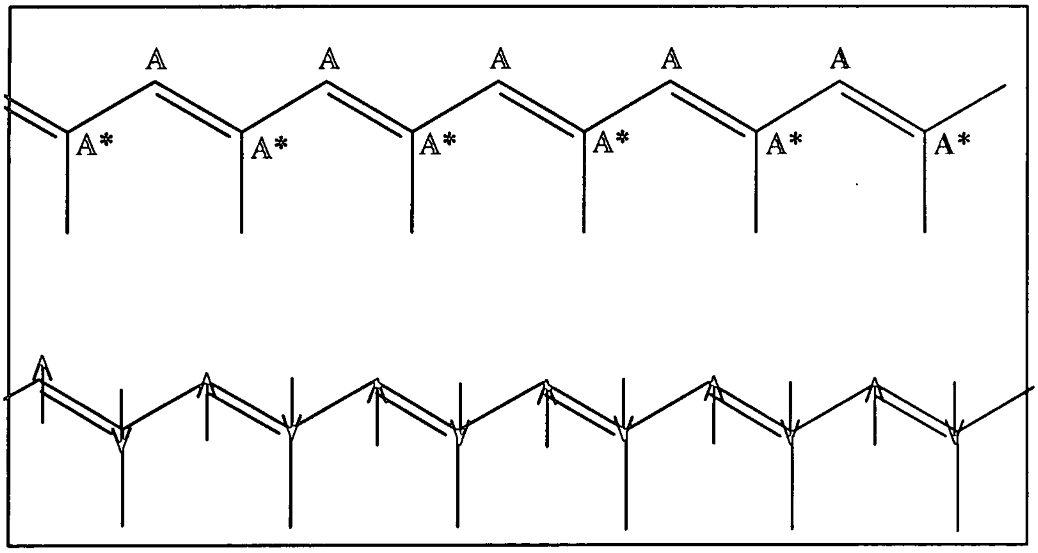
In an extension of the ideas put forward by Mataga[1], the general case for non alternant hydrocarbons, and the inclusion of heteroatoms attached to the hydrocarbon chain, was considered by Ovchinnikov[3,4]. As described earlier, an alternant hydrocarbon contains two groups of atoms (A and A*) where each group is only surrounded by the other group (i.e. AA*AA*AA*AA* etc.).In the case of systems where the number of A and A* atoms is unequal, the total spin was predicted to be positive, and of high multiplicity, given by the expression:

$$S = |n_A - n_{A*}|/2;$$

where n_A is the number of atoms of type A.

Thus a linear conjugated polymer was suggested to have a spin state proportional to the number of chain links, with a true 1-D ferromagnetic polymer resulting at infinite chain length, as shown below:

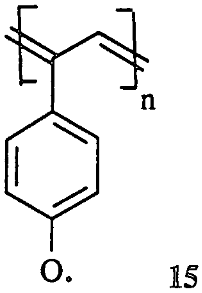
Figure 1.2.viii.



If each type of atom A and A* contributed a p_z electron to the chain, then a perfect alternant hydrocarbon as shown would be fully spin paired. If $n_A \neq n_{A*}$, as in a non alternant, or odd alternant hydrocarbon, then the resultant polymer was predicted to have residual unpaired spins. Clearly, for a given imbalance of A and A* atoms in a monomer unit, the overall spin state of the polymer would increase with chain length.

Ovchinnikov further predicted that the inclusion of heteroatoms, attached to the chain, would enhance ferromagnetic interactions by acting as stabilizing spin traps, and proposed the polyradical (**15** below) as a possible 1-D ferromagnet;

Figure 1.2.ix.



Poly(4-oxylphenylacetylene)

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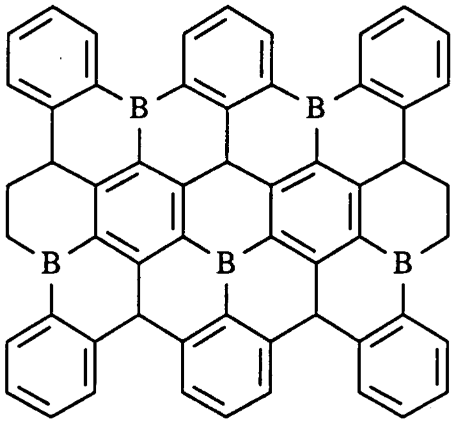
The above polymer has yet to be made, although the 2,6-di-^{t}butyl derivative has recently been reported in the literature[37].

The theoretical consideration above was extended to the field of 2-D and 3-D organic ferromagnets, with the prediction that replacement of carbon atoms in a graphite lattice by boron or nitrogen atoms in the manner below should give rise to a high spin system (**16**);

Figure 1.2.x.



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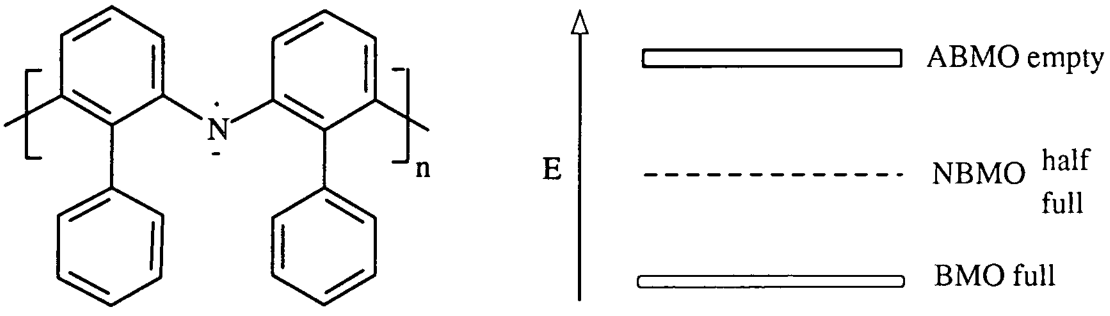
These ideas were extended by Tyutyulkov *et al.*[38] to include the magnetic and electric properties of "non-classical" (i.e. alternant, conjugated) polymers.

The polyconjugation of such systems was expected to stabilise considerably the radical centres present; as with the species **13**-**15** above, the electronic band structure of one dimensional non-classical polymers was anticipated to be as shown below in Figure 1.2.xi. The half-filled NBMO would thus correspond to a ground state of minimum energy for a spin state of maximum multiplicity. However,the replacement of carbon atoms along the chain of a non-classical polymer, and substitution on chain substituents (e.g. by Cl, NO_2, CO_2R etc.), were predicted to perturb the system to enhance stability, despite the non-occurrence in such cases of the NBMO band. In these cases, the BMO band would be half-full, leading to parallel spin alignment, (by Hund's Rule), and thus ferromagnetism. Such a polymer is shown (**17**) in Figure 1.2.xi. below;

Figure 1.2.xi.



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Band structure in **17**

1.2.iv. Torrance Model

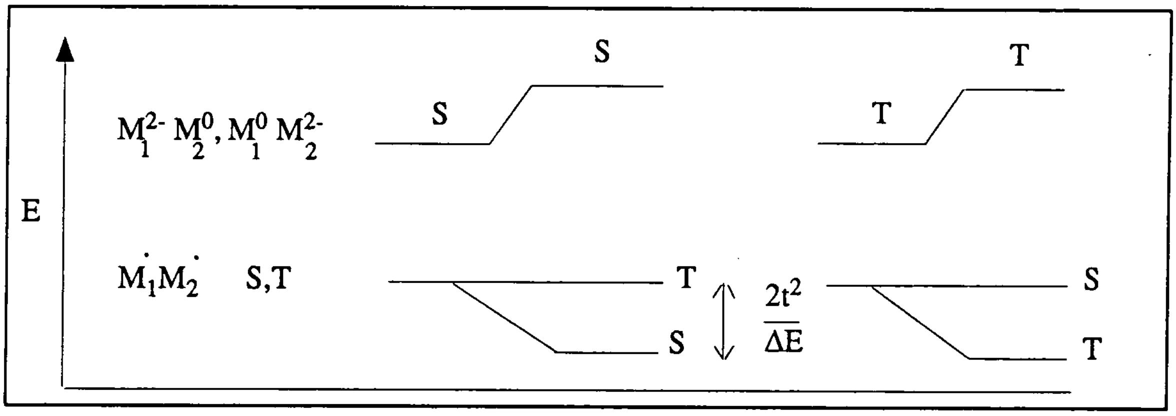
A new, and less complex, model for organic ferromagnetism was put forward by Torrance, Oostra and Nazzal, in their paper claiming the first metal-free organic ferromagnet[9]. In this model segregated stacks of radical ions were considered in order to show which molecular parameters could cause parallel or ferromagnetic alignment of the unpaired electronic spins in the stacks.

In detail, the model consists of a pair of radical anions, $M_1^{\cdot-}$and $M_2^{\cdot-}$, each having an unpaired electron delocalized in a π orbital over an aromatic molecule. The ground state (GS) $M_1^{\cdot}$-$M_2^{\cdot-}$ can have either a singlet S, or a triplet T spin state. The effects of intermolecular overlap can then be described in terms of an induced configuration interaction among the excited charge transfer states of the molecules[39]. The excited state arises by charge transfer of an electron from one molecule to another to form either $M_1^{2-}M_2^{0}$ or $M_1^{0}M_2^{2-}$.

In general, the neutral and dianion compounds are both in S states and hence the excited state is a singlet. The effect of the overlap is for the transfer integral τ, (or the resonance integral β) to mix the ground and excited states, and since this mixture is spin conserving, the excited S state mixes only with the S ground state. Thus the S ground state is stabilized with respect to the T state by $2\tau^2/\Delta E$ where ΔE is the energy difference between the two states.

In physical terms, this is due to the delocalization of the unpaired electron onto the neighbouring molecule; this is only allowed if the spin is antiparallel to its neighbour. Thus charge transfer stabilization energy is spin dependent, and gives rise to the large S-T state splitting observed in most organic compounds. If the lowest excited state is a triplet, then the transfer integral admixes the excited T state, stabilizing the triplet with respect to the S state. In this case therefore, the unpaired spin on M_1 can only gain kinetic energy by delocalization onto M_2, but only if its spin is parallel to that of M_2 as both are in T states. The two cases are shown schematically in Figure 1.2.xii. below:

Figure 1.2.xii.



The above model applies to stacks with identical neighbouring molecules, and thus is highly susceptible to the degree of oxidation or reduction of the homomolecular dimer. The nominal ground state of each of the molecules assuming no overlap is that of one electron, i.e. S=±1/2 and each is a doublet; combined, the total spin is a triplet. The case of a mixed stack of donors and acceptors in a DADADADA arrangement has been extensively studied by Breslow and co-workers[13-15], but has not so far yielded ferromagnetic materials.

However, the creation of a ground state, or lowest excited state of high spin multiplicity, as a precondition of ferromagnetism arises from both models. Thus, if the interaction between neighbouring molecules is of triplet type, then if the molecules form stacks in the solid, the interaction between any two molecules will be ferromagnetic, and thus the entire stack becomes ferromagnetic. Research into the theoretical and experimental aspects of such stacks has recently been carried out by Iwamura[34,40], related to the characterization of poly carbenes.

It has been shown that low dimensional, especially 1-D organic compounds can exhibit the properties of semiconductors, molecular metals, and superconductors[41], and thus the specific goal of producing an organic ferromagnet has been approached by routes to obtain 1-D and 2-D order. It must be remembered, however, that to exhibit bulk (i.e. macroscopic) magnetic properties, there is a need to produce a very highly ordered structure throughout the material.

1.3. EXPERIMENTAL OBSERVATIONS

1.3.i. Ferrocenium Charge-Transfer Compounds

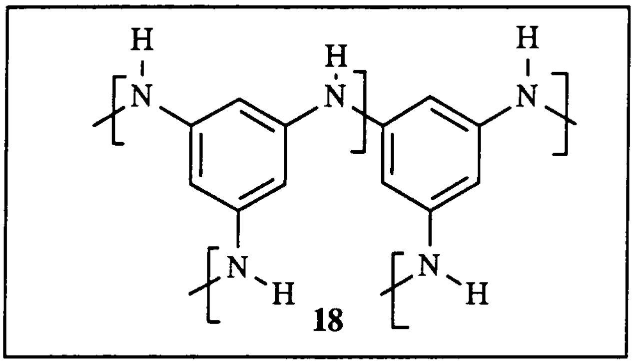
The first claimed molecular-based ferromagnet was decamethylferrocenium tetracyanoethenide $[Fe^{III}C_5Me_5]^{\cdot +}[TCNE]^{\cdot -}$ (Miller *et al*[5-7]). This contains linear chains of alternating donor and acceptor species; ferromagnetic coupling of the free radical spins has been suggested for charge transfer compounds of this type where the donor species has a ground state such that electron transfer forms an S=0 acceptor and an S=1 donor. Thus, the theories of McConnell,[2] (as enlarged by Breslow[13,14]), were partially verified. However, the above system still contained a transition metal, albeit in an organic environment, and so the search for a fully metal-free system has continued.

1.3.ii. Poly(1,3,5-triaminobenzene)

The first such system was claimed by Torrance and Oostra[9] for the reaction product from 1,3,5-triaminobenzene and iodine, in various solvents and in the vapour phase. To date, this reaction has still to be fully understood and only a small fraction (a maximum of 2% of a "Great Batch") gave ferromagnetic material.

The lack of reproducibility has led to an inadequate amount of data on the product, but a tentative assignment of its structure has been made, (**18**, overleaf) from IR and elemental analyses only, and the magnetic behaviour with temperature determined.

Figure 1.3.i.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The material behaved as a ferromagnet up to 700K, when irreversible decomposition occurred. Efforts by Torrance and co-workers[9a] have so far failed to yield a fully-characterized organic ferromagnet.

1.3.iii. Poly(BIPO)

Another recently claimed organic ferromagnet was that synthesized by Korshak *et al*[8]. The stable paramagnetic biradical 1,4-bis(2,2,6,6-tetramethyl-4-hydroxy-4-piperidyl-1- oxyl)-butadiyne, (BIPO), shown below (**19**), was polymerized to give a black powder (polyBIPO) (**20**,**21**), which displayed spontaneous magnetisation. Possible structures for the products are shown in the diagrams below.

Figure 1.3.ii.

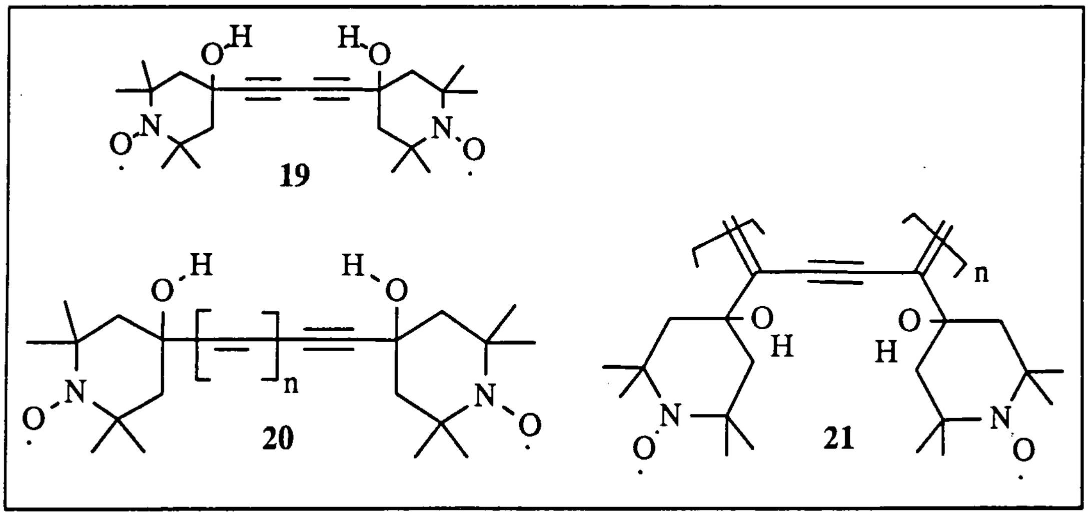
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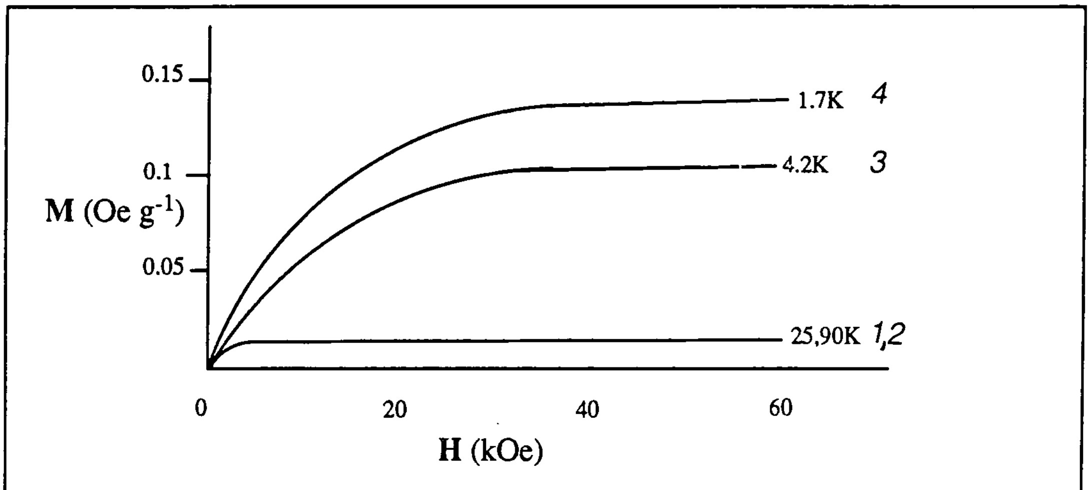
Figure 1.3.iii.



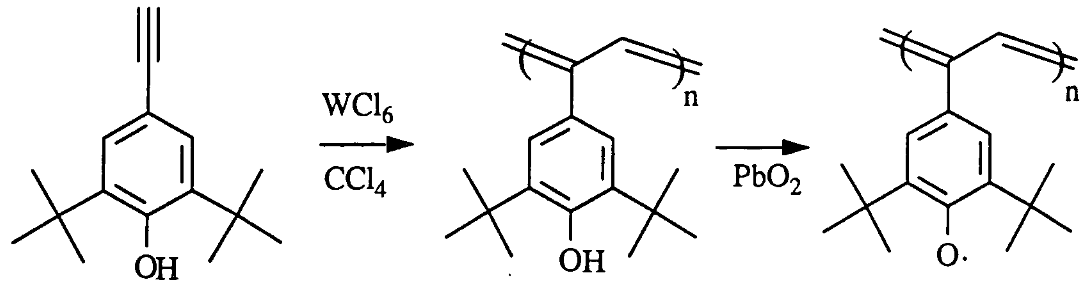
Field dependence of polyBIPO magnetization

At low temperatures (1.7 and 4.2K) the paramagnetic component is dominant (curves 3 and 4 above), typical of ferromagnets, but the spontaneous magnetization measured is only 0.1% of the theoretical value for a 1-D system. This implies that only a very small fraction of the particles are ferromagnetic, and work carried out recently by Miller *et al.*[42] has shown that the BIPO monomer can exist in at least two forms, only one of which can be polymerized in a controlled manner. Magnetic susceptibility measurements are due to be reported later.

1.3.iv. Poly(4-oxylphenylacetylene)

The prediction of Ovchinnikov[4] that poly(4-oxylphenyl)acetylene should exhibit 1-D ferromagnetism has led to work resulting in the reported synthesis of poly(3,5-di-^{t}butyl-4-oxylphenylacetylene)[37], shown below.

Figure 1.3.iv.



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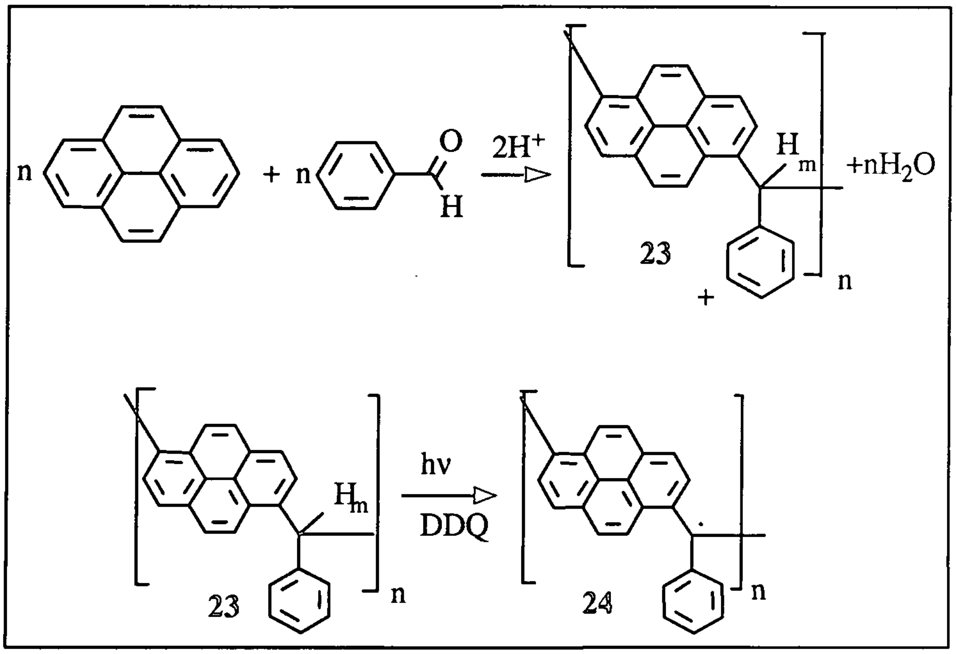
Although magnetic susceptibility and ESR data have not as yet been published, the radical containing polymer is claimed to have a narrow molecular weight distribution, conjugation of the radical sites with the polyene backbone, and high stability in the absence of oxygen. However, the microstructure of the polymer has not been elucidated, and thus direct comparison of this material with the theoretical predictions may not be possible.

1.3.v. COPNA Resins

The most recent claims for the syntheses of organic ferromagnets have been those due to Ota *et al*[43]. The preparation of various condensed polynuclear aromatic ("COPNA") resins in the presence of a magnetic field was studied, and some bulk samples of the resins were found to display a magnetic hysteresis loop. In addition, some powdered resin samples appeared to respond to a permanent magnet. Similar resins prepared in the absence of the magnetic field were found to be diamagnetic. However, these latter polymers were found to exhibit ferromagnetic properties if irradiated in the presence of dehydrogenating agents such as benzoquinone (BQ) or dicyanodichlorobenzoquinone (DDQ). The structures given for the resins are shown in Figure 1.3.v. below.

Figure 1.3.v.



Although little experimental, and no spectral, data has yet been given, the authors proposed that the origin of the ferromagnetic behaviour was the presence of triarylmethyl radicals in the condensed resin. These polymers were described as "B-stage resins", possessing molecular weights of 1500-1900, and were fusible and soluble. Exposure of the dehydrogenated resin to hydrogen chloride gas resulted in a complete loss of response to an applied magnetic field. However, the ferromagnetic properties of the resins were unaffected by atmospheric oxygen or contact with water.The synthesis of a similar polymer and its study by ESR was recently carried out by Nogami and co-workers[44], who claimed the detection of triplet and higher spin states. The polymer was prepared by heating isophthalaldehyde with a catalytic quantity of p-toluenesulphonic acid under nitrogen, to give a black powdery solid, containing acetone soluble, and completely insoluble, fractions. The insoluble polymer fractions were diamagnetic with an estimated monoradical concentration of 3.8 x 10^{18}spins.g^{-1}, as measured by comparison of the ESR signal intensity with a TEMPO (4-hydroxy-2,2,6,6-tetramethylpiperidinoxyl) standard. The ESR spectra showed a single strong absorption assigned to monoradical centres and two further absorptions at low temperatures (4.4K) assigned to triplet and quintet spin state absorptions. However, no information was given about the structure of the polymer, or its chemistry other than elemental analysis.

1.3.vi. High Spin Meta-Linked Triphenylmethyls

Another very recent study of high-spin molecules has been carried out by Rajca[45], who synthesized meta-linked triphenylmethyl radicals to give a molecule with a quintet ground state. Although only a preliminary communication, the work contained in this report has shown that the conjugated polyradical approach to organic ferromagnets appears to be plausible, and may yet give rise to the desired magnetic properties.

1.4. Aims and Objectives of this Project

The apparent lack of correlation between much of the theoretical work concerning ferromagnetism in organic compounds, and the claims in the literature of ferromagnetic behaviour, provided the main objective for this project. Our initial aim was to produce an organic material of well -defined structure to test some of the theories and thus provide an unambiguous reference point. The work of Ovchinnikov[4], suggesting that certain conjugated polyenes, (with radical-containing substituents), should exhibit 1-D ferromagnetism, led us to decide to prepare stable free-radicals connected to a conjugated polyene chain; i.e. conjugated polyradicals.

1.5. Conjugated Polyradicals

At the start of this project, there were only a few reports in the literature describing the preparation of well-defined polymers with attached stable radical substituents[46-49]. All the materials in the above studies were based on substituted polystyrenes or polyphenoxyls, and thus were unconjugated. The preparation of a series of triphenylmethyl-type radicals linked by p-phenylene units was reported by Braun and Lehmann[50], and the characterization of these conjugated systems included an ESR spectral study. However, as this study was not directed towards organic ferromagnetism, there was no discussion of any bulk magnetic properties of the polymers.

Thus, the preparation of a conjugated polyene with stable radical substituents with a view to generating an organic ferromagnet was new at the start of this project.

The route which we chose to employ to synthesise such a conjugated polyene was via the metathesis polymerization of suitably substituted acetylenes. This method appeared to offer the most direct way of controlling the ultimate polymer structure, and thus the most effective means of producing a well-defined conjugated polyradical. The reasons for our choice of metathesis polymerization, and a review of the literature concerning the polymerization of phenylacetylene are discussed in more detail in the following chapter.

CHAPTER TWO

METATHESIS POLYMERIZATION AND POLY(PHENYLACETYLENE)

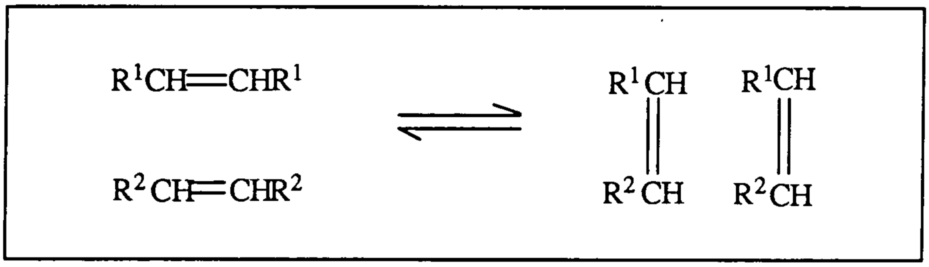
CHAPTER 2 PART 1:
OLEFIN METATHESIS AND POLYMERIZATION OF ACETYLENES

2.1.i. Definition of the Olefin Metathesis Reaction

There are now a number of reviews and general texts on the subject of olefin metathesis and polymerization[51], and therefore this introduction covers only the basic principles and recent results in this field.

Olefin metathesis involves a reorganization of two alkenes, in which the total number and types of chemical bonds remains unchanged during the generation of equimolar amounts of two new alkenes, as shown below:

Figure 2.1.i

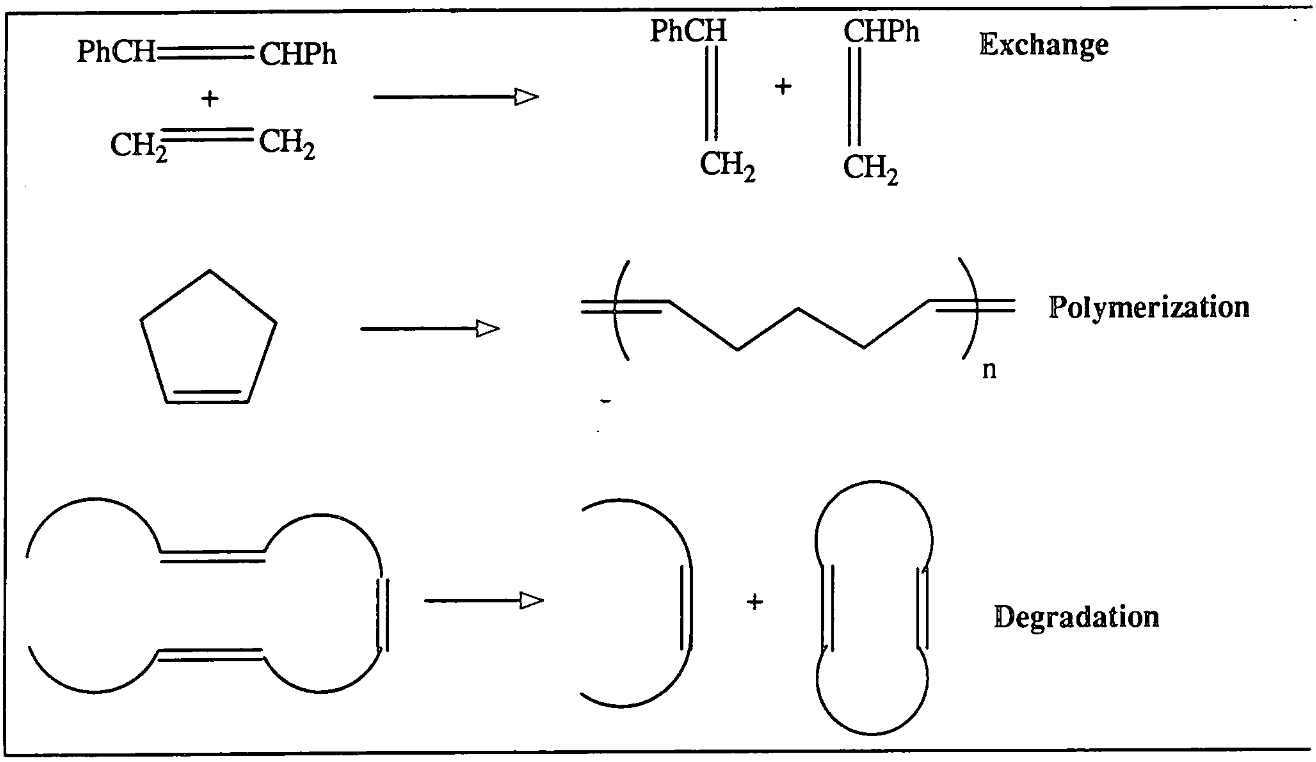


$$\begin{matrix} R^1CH{=}CHR^1 \\ R^2CH{=}CHR^2 \end{matrix} \rightleftharpoons \begin{matrix} R^1CH & R^1CH \\ \| & \| \\ R^2CH & R^2CH \end{matrix}$$

The term "olefin metathesis" was first used by Calderon[52] in 1967, although reactions of olefins in the manner described were first reported some years previously by Eleuterio[53], Truett[54], and Peters[55].

Within the category of the olefin metathesis reaction, three broad sub-groups can be defined: exchange, polymerization, and degradation. These transformations are catalysed by a range of transition metals, either homogeneously or heterogeneously, and can be carried out in the presence of a variety of other functional groups. The reactions generally proceed to equilibrium at a very high rate, and given the correct conditions of catalysts, solvents, and temperature, high yields of the desired products can be attained with a minimum of by-products. These metathesis reactions are not limited to alkenes, and for the work covered in this thesis, the related alkyne metathesis reaction is of more direct relevance. However, some knowledge of the catalyst systems used, and of the mechanism of olefin metathesis, is necessary in order to understand the reactions of acetylenes under similar conditions, and thus a brief outline of each is given below. Figure 2.1.ii. overleaf shows the main sub-groups of the olefin metathesis reaction.

Figure 2.1.ii



2.1.ii. Survey of Catalyst Systems

The number and variety of catalyst systems which can bring about the olefin metathesis reaction is very large. In addition to the transition metal centre, the catalyst can contain a co-catalyst, and, if necessary various "promoters", which adds to the complexity.

Figure 2.1.iii. Metals Active for Olefin Metathesis

IVa	Va	VIa	VIIa	VIIIa
Ti	V	Cr		
Zr	Nb	Mo		Ru Rh Pd
Hf	Ta	W	Re	Os Ir Pt

These systems can be formally heterogeneous or homogeneous, although the precise nature of the catalyst has rarely been ascertained, and therefore whether the activity lies in a heterogeneous or homogeneous part has not always been defined.

The thermodynamics of a given olefin metathesis reaction will also determine to some extent the range and nature of the catalytic systems used. Highly exothermic processes such as the ring-opening polymerization of cyclobutene can be brought about by a large number of catalytic systems, whereas metathesis of certain acyclic alkenes, which are almost thermoneutral processes, require the use of the most active catalysts if equilibrium is to be quickly reached.

The most commonly used catalysts have been the oxides, chlorides, or oxychlorides of tungsten, molybdenum, or rhenium, and such catalysts have been found to be active for all the types of metathesis shown above. Ruthenium, osmium, iridium, and titanium-based catalysts have also been employed, primarily for the ring-opening polymerization of norbornene and its derivatives. Although many other metals have been shown to be active (e.g. zirconium, hafnium, tantalum, and niobium), most have been successful only in promoting highly specific metathesis reactions under very stringent conditions. Despite this wide range, all these catalysts can be divided into three classes:

a- those containing a well-defined metal carbene, such as $(^tBuO)_2W(=CH^tBu)(NAr)$;

b- those containing an alkyl or allyl group in one of the components, e.g. Me_4Sn, from which a carbene ligand can be generated;

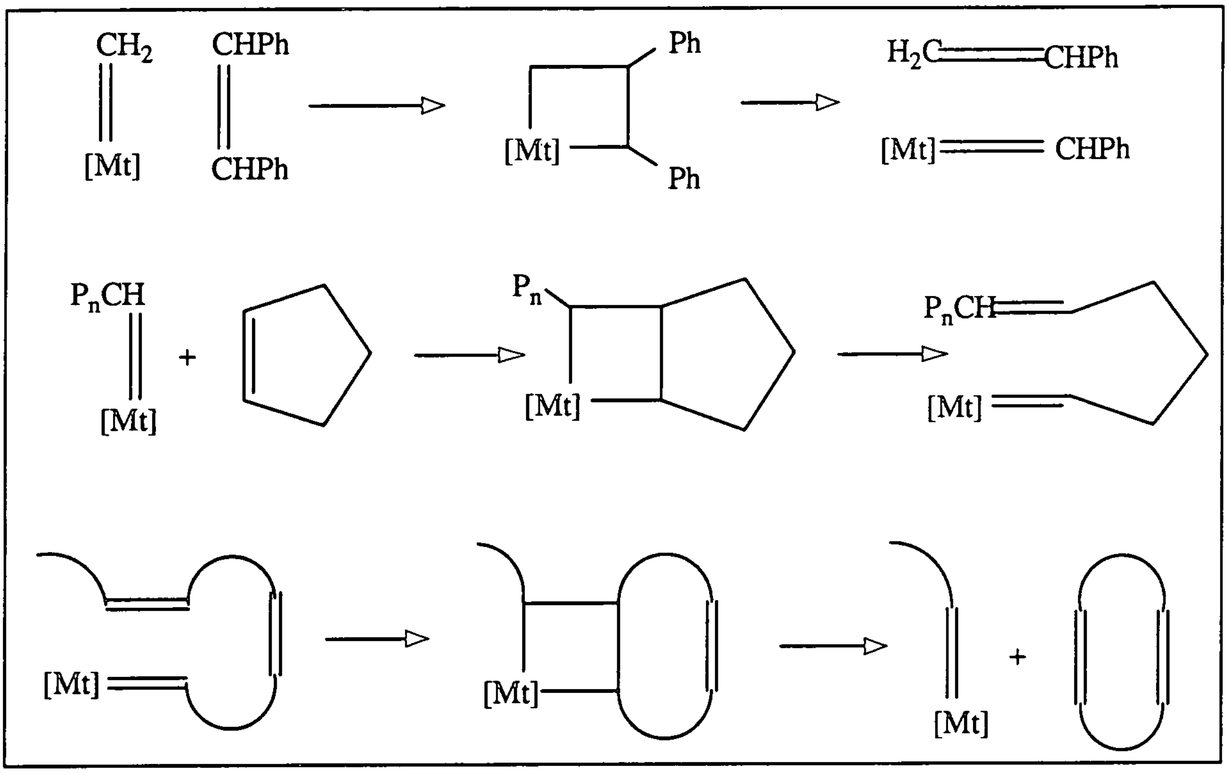
c- those containing neither a pre-formed carbene or an alkyl component, which requires interaction between the metal and the substrate olefin to generate the active catalyst. This class consists mainly of metal oxides on silica/alumina supports and such heterogeneous catalysts have been mainly used for the cross-metathesis of acyclic alkenes. The high temperatures usually employed with these systems renders them unsuitable for the polymerization of olefins, owing to difficulties of product separation from the catalyst, and polymer decomposition.

Class (a) and (b) catalysts have found extensive use in polymerization studies, as reaction conditions are often mild, with conversion of monomer to polymer being rapid, and in high yield. However, the use of co-catalysts and promoters, often derived by empirical observations, has led to an element of irreproducibility, and thus the best catalyst for a given polymerization reaction has often been derived by a process of trial and error.

2.1.iii. The Mechanism of Olefin Metathesis

The active species in the reaction is thought to be a metal carbene, formed either by the components of the catalyst system, by interaction of the catalyst and substrate, or by specific synthesis. This carbene reacts with the alkene to form a metallocyclobutane, which can ring-open to generate a new metal carbene and the new alkene. These steps are shown for exchange, polymerization, and degradation below.

Figure 2.1.iv.



Stable metal carbenes and metallocyclobutanes have been used as initiator systems, and recently "living polymerization" using such catalysts has been reported[56,57,58]. These catalysts have also allowed the detection of intermediates and propagating species, with interconversion of metal carbenes and metallocyclobutanes, in the polymerization process, confirming the metal carbene mechanism in these cases[59].

2.1.iv. Advanced Theory of Olefin Metathesis

In a recent review paper, Schrock[60] has described the metathesis reaction in terms of an electrophilic attack by the olefin on the nucleophilic metal carbene. Formation of the metallocyclobutane is thus dependent on the electron density at the metal centre, as well as the alkene. For example, reaction of cis-2-pentene with tungsten complexes of the type $(RO)_2W(=CH^tBu)(NAr)$ proceded significantly faster in the case where $R=CMe(CF_3)_2$ as opposed to $R=CMe_3$. For a given metal, the activity of these catalysts also increases if electron-withdrawing fluorinated alkoxide ligands replace t-butoxide.

In Ring-Opening Metathesis Polymerization (ROMP), formation of polymer occurs after attack of the cyclic olefin by cleavage of the metallocycle to form a new carbene, followed by reaction of more monomer. The nature of the polymerization depends on whether the rate of initiation is faster than the rate of propagation. Important factors controlling the respective rates and also the stereochemistry and molecular weight distribution of the final polymer include:

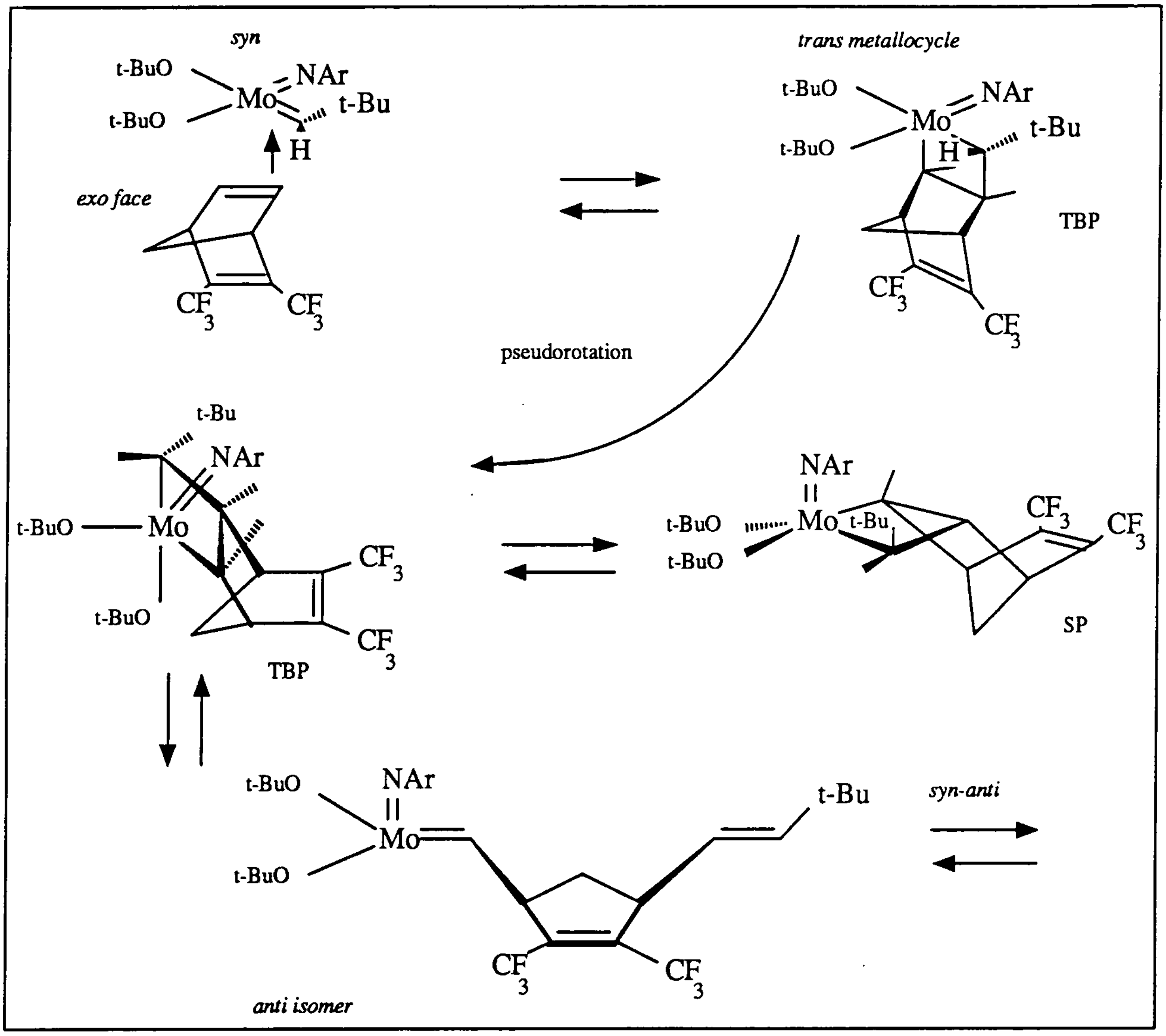
a- Stability of the metallocycle: steric as well as electronic factors are important, with bulky substituents destabilising the metallocycle. It has been shown by Schrock that the well-defined tungsten and molybdenum initiators can exist as two rotamers. Attack of an olefin can lead to cis and trans metallocycles, with the more stable form determined by electronic and steric constraints.

b- Monomer and solvent chemistry: for example norbornene type monomers substituted at the 5 and/or 6 positions have been shown to form stable metallocycles[61]. The secondary co-ordination sphere of the metal and solvent interaction are critical in determining the relative rates of metallocycle formation and decomposition.

c- Core geometry rearrangement: the overall rate of reaction for the Schrock complexes is related to the energy barriers between trigonal and square pyramidal forms of the metallocycle.

These factors are illustrated in figure 2.1.v. overleaf for the reaction between the Schrock molybdenum complex and 5,6-bis(trifluoromethyl)norbornadiene[61].
Attack of the olefin yields a trigonal bipyramidal complex, for which loss of the olefin to create the new carbene is not a favoured path. A pseudorotation about equatorial nitrogen via a square pyramidal intermediate results in a new trigonal bipyramid which can lose the olefin from an axial position to form the new carbene. The subsequent reactions to form the polymer in this case have been shown to proceed in a controlled manner resulting in a highly stereoregular material.

Figure 2.1.v.

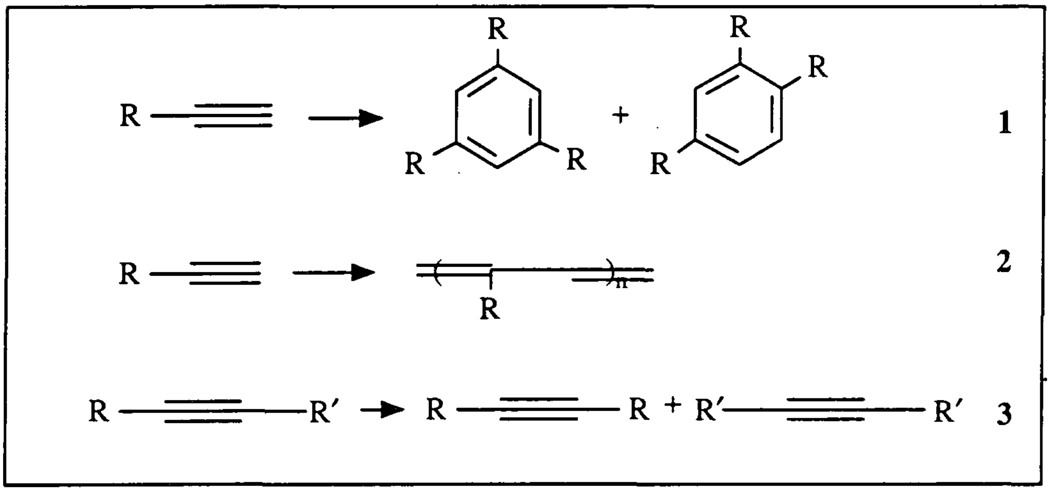


The olefin metathesis reaction is now reasonably well understood allowing the possibility of precise functionalized polyalkenamer synthesis.

2.1.v. The Alkyne Metathesis Reaction

Acetylenes can react with olefin metathesis catalysts to produce three main categories of compounds, resulting from cyclotrimerization, polymerization, and metathesis, as shown in figure 2.1.vi. below.

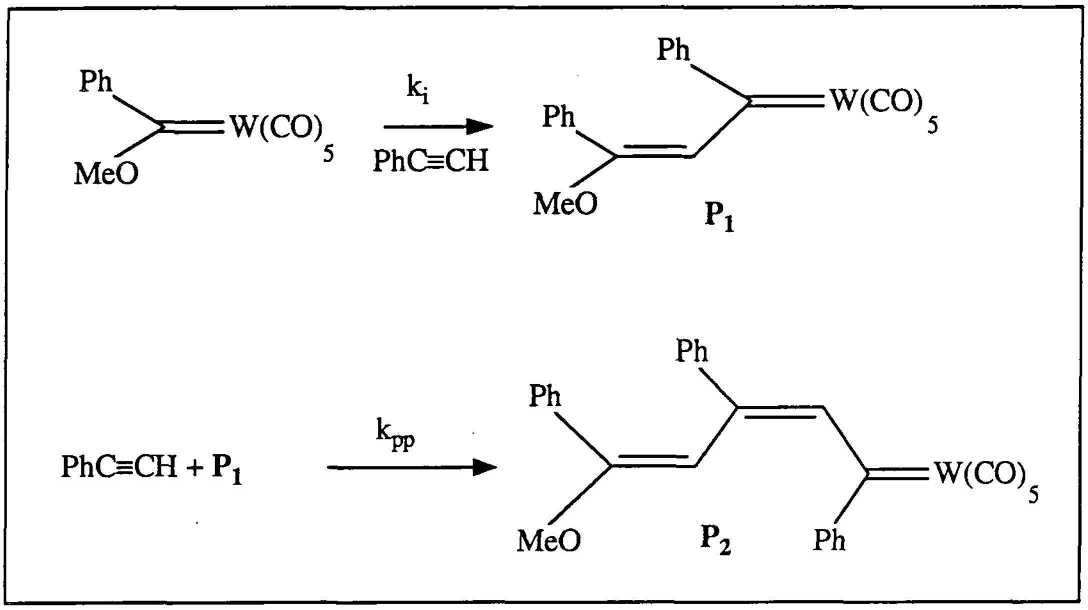
Figure 2.1.vi.



Of these reactions, productive metathesis, as shown in **3** above, has been seen for disubstituted acetylenes only. Monosubstituted acetylenes undergo cyclization or polymerization; the catalysts active for these polymerizations are generally initiators of ROMP also. Thus, a whole range of empirically devised catalytic systems have been used, but the exact details of the mechanism of polymerization have yet to be fully elucidated.

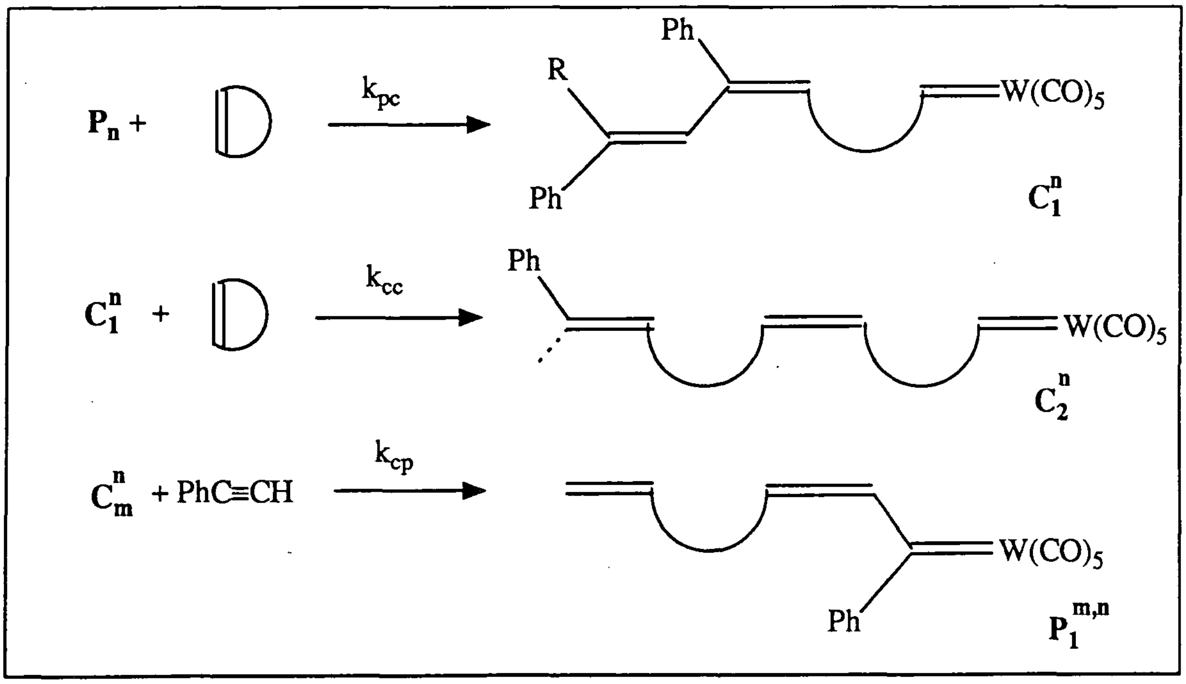
The obvious analogy to the olefin metathesis reaction suggested that an insight into the mechanism might be gained if better-defined catalysts were used. Katz[62,63] employed isolable metal carbenes, known to be active as olefin metathesis catalysts, as initiators. The carbenes were of the form $Ph(X)C=W(CO)_5$, where X=Ph (I) or OMe,(II) and were found to be active for the polymerization of aryl- and alkyl-acetylenes. In addition, (phenylmethoxycarbene)pentacarbonyltungsten (II) polymerized cyclopentene, cycloheptene, and cyclooctene to the corresponding polyalkenamers in the presence of phenylacetylene, but was inactive for these polymerizations without the acetylene. The polymers formed in these cases were very similar to those prepared using (diphenylcarbene)pentacarbonyltungsten (I) as the initiator. The proposed reaction scheme is shown in figure 2.1.vii overleaf.

Figure 2.1.vii.



The new carbene P_2, or a higher homologue P_m, can react with a cyclic olefin to induce metathesis polymerization in the normal way:

Figure 2.1.viii.



Katz found that increased concentration of phenylacetylene relative to cycloalkene reduced the overall molecular weight, implying that termination and/or transfer processes were more facile for polyacetylenes. The observed ratios of k_{cp}/k_{cc} were less than unity for cyclopentene and phenylacetylene in these experiments, indicating that the carbenes directly attached to the growing polyalkenamer (**C species above**) reacted more readily with alkene than acetylene. Ratios for $k_{pp}/_{pc}$ were found to be over 100, showing that the stabilized metal carbenes (**P species**) reacted preferentially with acetylenes.

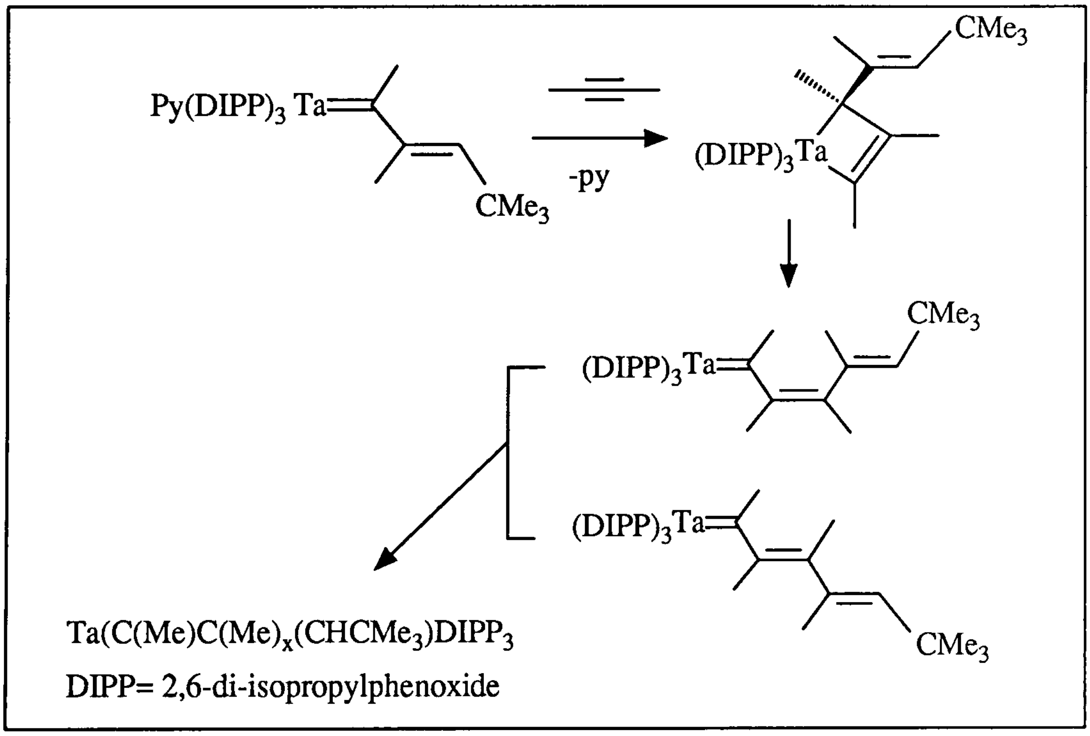
In later experiments Katz[64] was able to demonstrate insertion of an arylacetylene into a metal carbene followed by metathesis with stereochemical control, although no intermediates could be isolated.

The above studies indicated that metal carbenes were involved in the polymerization of acetylenes, but no stable metallocyclobutenes were detected, and thus no final proof could be provided.

2.1.vi. Living Polymerization of Acetylenes

The first living polymerization of an acetylene was achieved by Schrock et al[65]. using tantalum catalysts. The di-substituted acetylene but-2-yne was polymerized in a controlled manner as shown below.

Figure 2.1.ix.



Intermediate compounds were isolated or observed by NMR: up to 200 equivalents of monomer could be added without increasing the polydispersity above 1.1. Terminal acetylenes such as pent-1-yne were found to be too reactive after the initiation stage for controlled polymerization.

Acetylene itself has been polymerized by the tungsten carbene complex $(t\text{-}BuO)_2W(=CH^tBu)(NC_6H_3{}^iPr_2)$ to "living polyenes"[66]. This reaction required the use of quinuclidine to control the catalyst activity, and was only effective for 3-13 equivalents of acetylene before side-reactions took place. Capping with pivaldehyde produced a series of polyenes of structure $(^tBu\text{-}(CH=CH)_x(^tBu)$, with between three and nine double bonds. The predominant polyenes were all-trans and no other organic products, including benzene, were isolated. The quinuclidine was believed to bind more strongly to the living polyene oligomer $W=(CH\text{-}CH)_x$ than to the catalyst $(W=CH^tBu)$ for steric reasons slowing the propagation reaction relative to initiation. Preliminary results for analogous reactions with the related molybdenum complex have, according to Schrock[65], shown that more controlled acetylene polymerizations may be possible. In addition, the isolation of vinylalkylidene complexes of the type $(L)(RO)_2(ArN)W=CHCH=CHMe$ lend support to the idea that living polyenes may be prepared, and that living polymerization of other acetylenes may soon be demonstrated.

CHAPTER 2 PART 2.
POLY(PHENYLACETYLENE) AND RELATED POLYMERS

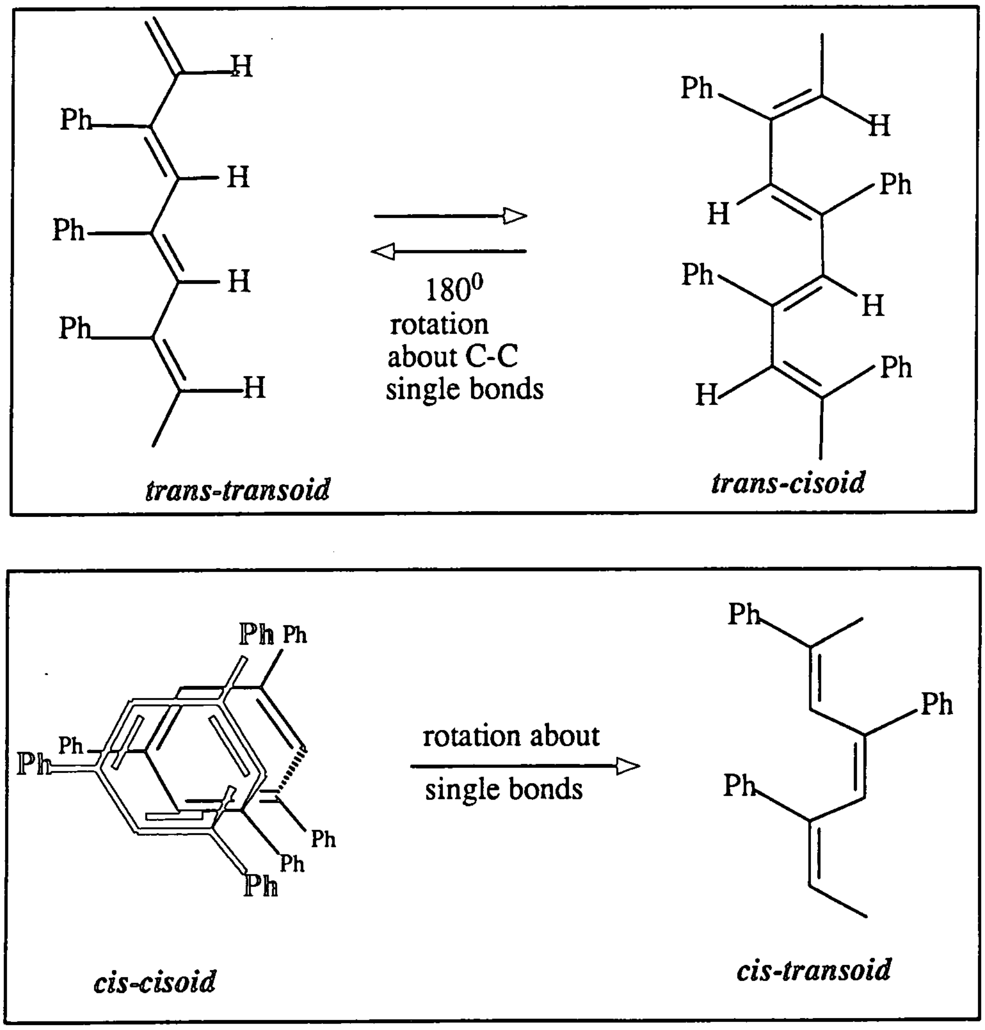
Introduction

The polymerization of phenylacetylene was first reported by Natta[67] in 1955 using Ziegler-Natta coordination catalysts. Since then, it has been shown that phenylacetylene polymerization may be initiated by cationic[68,69], thermal[70,71], radical[70-72], and metathesis[73-76] routes. The highest molecular weight polymers, and the highest yielding polymerizations, have been those employing coordination and metathesis catalysts. The polymers produced have been extensively studied[77], particularly with respect to their electrical and optical properties. However, despite the numerous publications and the efforts of the many workers active in this field, there is still considerable uncertainty as to the structures of many poly(phenylacetylene)s.

The main problems regarding the characterization of polymers produced from phenylacetylene arise from uncertainties concerning the mechanisms of the polymerizations, the difficulty of making an unambiguous structural assignment, and the sensitivity of the polymers to solvent and thermal treatments.

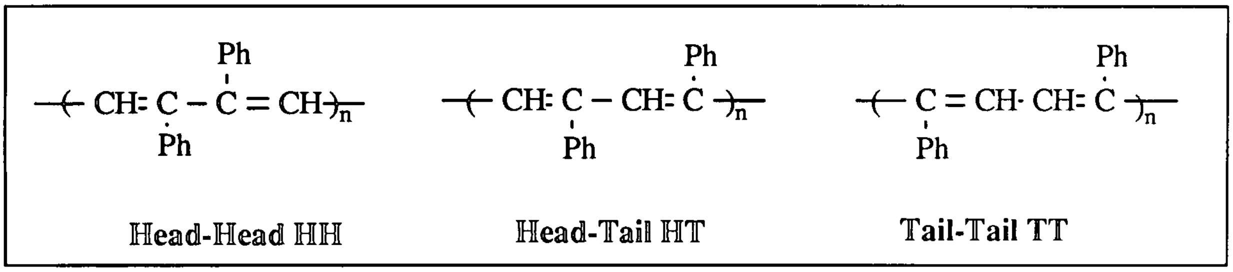
The polymerization of phenylacetylene by almost all the above methods reportedly yields a polymer with the repeat unit $(\text{-CH=C(Ph)-})_n$, and, dependent on the exact conditions of polymerization and work-up, varying proportions of cis and trans double bonds along the polyene backbone. This polyene chain can, in theory at least, adopt a number of conformations, some of which are shown in Figure 2.2.i. in extended chain form, for all head-tail poly(phenylacetylene).

Figure 2.2.i



Since phenylacetylene is an unsymmetrically substituted monomer, the addition of the monomer to the growing polymer can occur in two ways, giving rise to "head-tail effects", as shown below:

Figure 2.2.ii



$-(CH{=}C(Ph)-C(Ph){=}CH)_n-$ $\quad -(CH{=}C(Ph)-CH{=}C(Ph))_n-$ $\quad -(C(Ph){=}CH-CH{=}C(Ph))_n-$

Head-Head HH Head-Tail HT Tail-Tail TT

The various combinations of HH, TT, HT placement, vinylene unit stereochemistry, sequence, and conformations which are possible, mean that there are very many microstructural possiblities for this polymer. Characterization of the different isomeric forms which have been observed has been an important goal for workers in this field. Many workers have described the polymers they have investigated in terms of their method of synthesis. This has led to widely accepted synthesis-structure correlations, and therefore a brief introduction to the polymerization routes is necessary before discussing the reported structures.

2.2.i. Survey of Polymerization Methods

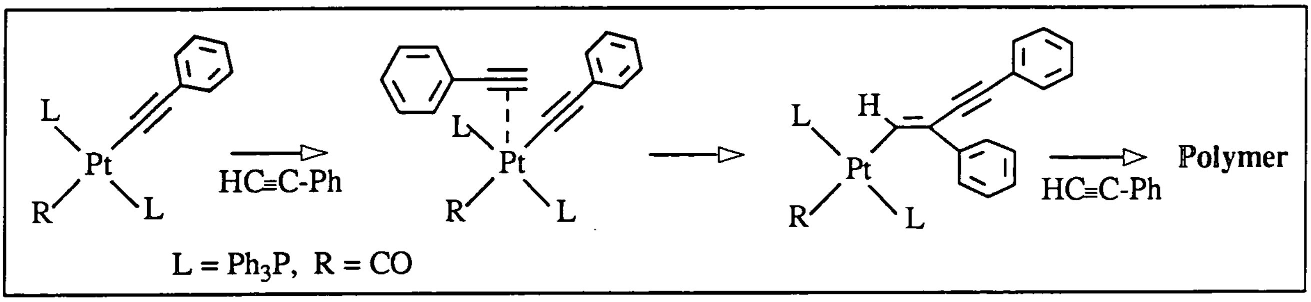
2.2.i(a). Catalytic Methods

The most widely studied routes to poly(phenylacetylene) (PPA) have been those employing Ziegler-Natta, metathesis, and related transition metal complex catalysts. The often elusive natures of the active species in these catalysts have resulted in empirically devised methods, with exact polymerization conditions being critical to the outcome of the process. However, certain catalysts have been extensively used, in particular $TiCl_4/AlR_3$ of the Ziegler-Natta type, and WCl_6- or $MoCl_5$-based metathesis catalysts. These catalysts and the structures of the resulting polymers are considered in detail in later sections of this chapter.

An early study of transition metal systems for phenylacetylene polymerization was carried out by Meriwether[78], and explored further by Furlani *et al*[79]. The catalysts used were phosphine complexes of nickel and platinum, which were found to be active for both cyclization and polymerization reactions.

Furlani isolated a series of platinum-phenylacetylene complexes and showed that both polymerization and cyclization occurred by reaction of these intermediates with more phenylacetylene. The mechanism of polymerization was postulated to be as shown in Figure 2.2.iii.

Figure 2.2.iii



Molecular weights (VPO) for these polymers were 500 or less;, the cyclization products (1,3,5-, and 1,2,4-triphenylbenzene (TPB)) were also produced. Nickel complexes were found to be more active than those of platinum and for these catalysts similar mechanistic rationalizations were proposed[80].

In a later paper[81], Furlani *et al.* compared the properties of PPA synthesised using rhodium catalysts with those of samples prepared using the platinum systems: complexes of the type $[Rh(L)(Chelate)]^+X^-$ were found to polymerize phenylacetylene to number average molecular weights of ~ 10,000 (VPO). The ligands for these complexes were either 1,5-cyclooctadiene (COD), or norbornadiene (NBD), with chelates derived from bidentate heterocycles such as 2,2′-bipyridine (bipy) or 2,2′-dipyridylamine (dipyam); the anions X were non-nucleophilic species (PF_6^-, ClO_4^-, BPh_4^-). Rhodium (0) species were also found to be active for phenylacetylene cyclization and polymerization.

2.2.i(b). Thermal Polymerization

Phenylacetylene readily polymerizes above ~100^{0}C, even in an inert atmosphere, to give a material with a molecular weight of less than 5000. This method of producing PPA gives rise to less well-defined materials than the catalytic methods and has been used mainly to provide reference points for comparison. It should be noted, however, that the polymer is extremely thermally-sensitive regardless of the method of synthesis. Any heating during or after polymerization can have an effect on the structure of the polymer, as revealed by IR spectroscopy, and consequently any sensible comparison of different types of PPA, requires a knowledge of the thermal history of the samples.

2.2.i(c). Electrochemical Polymerization

The polymerization of phenylacetylene using electrochemical methods was first reported by Farafonov[82], using perchlorates as charge carriers in DMF or DMSO. Low molecular weight oligomers (M_n~500-1000) were formed, with the structure assigned as linear and conjugated on the basis of IR spectroscopy. Molecular weights of up to 3000 were claimed by Jakubowski[83], using $NaNO_3$/DMF as the electrolyte, and the polymer was shown to be similar in structure to those prepared by catalytic methods. A 1:1 co-polymer with benzonitrile was also prepared by this technique, but little other information was given concerning its structure.

2.2.i(d). Plasma Polymerization[84]

When phenylacetylene was introduced into a capacitatively coupled argon plasma (discharge power 2-7W, pressure 13Pa, RF source 13.56 MHz), a thin polymeric film was rapidly formed on a gold substrate in the reactor. This polymer was reported to be similar to those prepared by thermal methods, but contained some trapped monomer. The ESCA spectrum of the thin film showed evidence of oxidation, which was said to have occurred during transfer of the sample into the spectrometer. This degradation showed the sensitivity of PPA to oxygen, although whether this oxidation occurred in the reactor, or subsequent to the polymerization process, was not made clear in this report. However, as the authors state, as-made plasma polymers generally have many radical sites, and are therefore prone to atmospheric oxidation.

2.2.ii. Structures and Properties of Poly(phenylacetylene) (PPA):

A brief survey of the literature is necessary in order to understand early attempts to characterize PPA, and to see how this work has influenced current assumptions and thinking concerning the structure of these polymers.

2.2.ii(a). "Kern" PPA

One of the first reports to discuss in detail the variety of polymers produced from phenylacetylene was that due to Kern[85]. In this paper, the preparations and properties of three isomeric polyphenylacetylenes were considered, and the underlying structural differences and spectroscopic features were set out: assignments made therein have been extensively cited by subsequent authors. Kern's classifications are summarised overleaf.

Type IA

This was formed using certain transition metal catalysts in combination with reducing agents. The polymer was bright yellow, was readily soluble in benzene or chloroform at room temperature, and displayed an intense infra-red absorption at 740cm^{-1}, and a broad band between 880-910cm^{-1}. Typical molecular weights were around 5000 (VPO). The catalyst systems studied by Kern to produce PPA-IA were $Fe(acac)_3$/Di-isobutylaluminiumhydride (DIBAL), $RhCl_3$, and $RhCl_3/LiBH_4$, with a combination of diluents and/or solvents. The use of $RhCl_3$ in ethanol with or without $LiBH_4$ resulted in type IA alone: however, addition of tetralin as a diluent or heating of IA (>100^{0}C) gave an orange polymer described as Type IB.

Type IB

This polymer was formed with IA in varying quantities using the combination of catalysts described above, and could also be obtained by dissolving IA in solvent and then treating the solution with 12M HCl. Type IB possessed a softening temperature of 203-204^{0}C, and appeared on the basis of X-Ray Diffraction (XRD) to be partly crystalline. The molecular weights quoted were 4200 (Fe catalyst), and 5400 (Rh catalyst), indicating that no major change of overall macromolecular size range occurred during the transition from Type IA. However, unlike IA, IB displayed no strong IR absorption at 740cm^{-1}, but did show a weak but sharp doublet at 878 and 885cm^{-1}.

Type IC

The crystallinity of IB was increased by immersion in alkylated aromatic solvents such as tetralin or toluene. This process changed the colour to a deep red, and the solid, PPA-IC, displayed a softening point of 198-203^{0}C. However, no distinction could be drawn between types IB and IC in solution.

Type II

Type II PPA was a tan coloured polymer resulting from the use of $RhCl(PPh_3)_3$ at 40-80^{0}C in neat monomer. Unlike type I species, this polymer fluoresced yellow under ultra-violet radiation, and displayed no strong IR absorptions at 740cm^{-1}, or between 880 and 910cm^{-1}. No order was observed by XRD, and the "melt-softening" temperature was 152-153^{0}C. The molecular weight of this polymer was quoted as 1100 (VPO).

If this reaction was carried out at 0-20^{0}C under otherwise identical conditions, up to 50% of the product consisted of 1,4-diphenylbutenyne ($PhCH{=}CH{-}C{\equiv}CPh$). This product was not present in reactions leading to types I and II PPA.

Type III

Thermal polymerization of phenylacetylene gave pale yellow Type III PPA, which was readily soluble at room temperature and non-crystalline. Weak bands were observed in the IR spectrum between 880 and 910 cm^{-1}, and the material fluoresced yellow under ultra-violet radiation. The "melt-softening" temperature was 158-163^{0}C and the molecular weight was between 700-900 (VPO).

Solvent Treatment of Types I,II, and III

Treatment of types I and III PPA with polar solvents such as pyridine or DMF gave a yellow non-crystalline solid which fluoresced yellow under UV radiation. and which exhibited weak IR absorptions between 880 and 910cm^{-1}. Treatment of type II PPA with the same solvents raised the "melt-softening" temperature to 213-217^{0}C, identical to those of pyridine treated I or III, and thus it was concluded that all three types of PPA with such solvents led to the same polymer.

The above classifications by Kern were followed by a number of structure-property correlations, based largely on the observed IR spectra, and the solubility and crystallinity behaviour of the various types.

i- Comparison of the IR spectra of the polyphenylacetylenes with polystyrenes indicated that there were bands in the 880-910cm^{-1} region of the spectrum of PPA which were associated with chain unsaturation. Hydrogenation of types I and III PPA removed these bands, supporting this hypothesis. Polymerization of PhC≡C-D shifted these bands to longer wavelengths, and analogous polymerization of (1-cyclohexyl)acetylene, t-butylacetylene, 3-cyclohexylprop-1-yne, and hex-1-yne all gave materials with IR absorptions in the same 880-910cm^{-1} region. The conclusion drawn was that these bands were due to absorptions associated with vinylic hydrogens on the backbone.

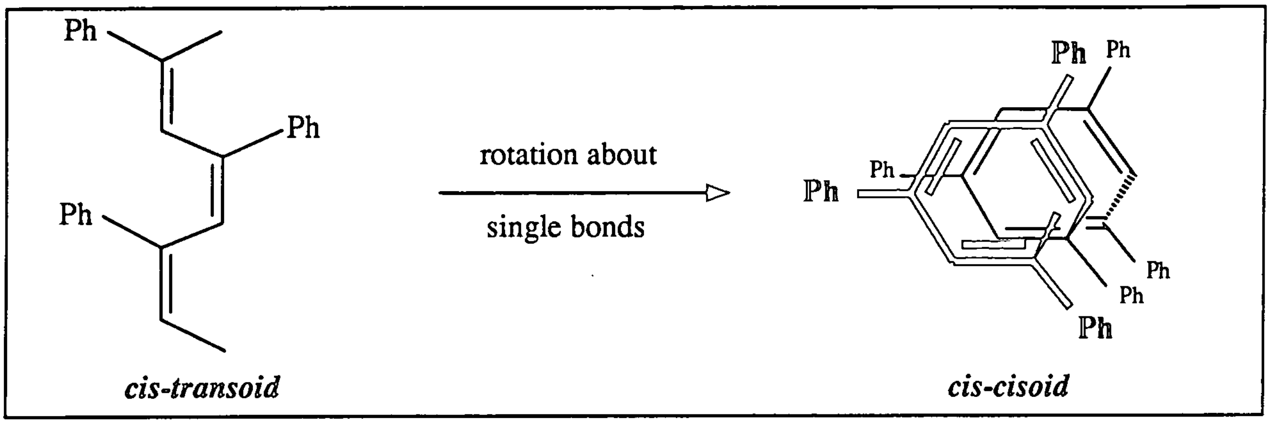
ii- Kern commented that the cis and trans nature of the backbone was analogous to that of tri-substituted ethylenes. However, since the literature at the time of Kern's publication did not readily allow distinction of cis and trans forms of trisubstituted ethylenes, the chief distinguishing criteria available were those of solubility and crystallinity of the polymers.

Kern proposed that Type IA was cis-transoidal following the reasoning set out below.

a- Rotation about the mainchain single bonds in cis-transoidal polyphenylacetylene leads to the cis-cisoidal isomer, which must have a helical conformation.

Such isomerization would be accompanied by a contraction, and since both left- and right-handed helices could be formed, the generation of significant lengths of a helix would require a collaborative process over many repeat units.

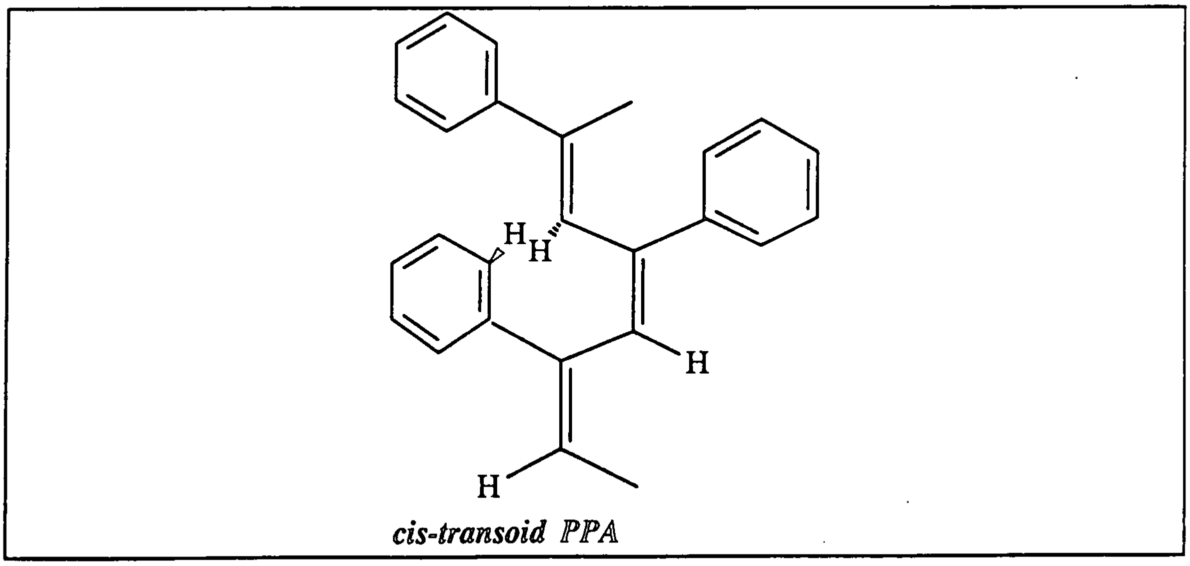
Figure 2.2.iv.



b- Helices often give rise to ordered structure, thence crystallinity, and altered solubility characteristics as observed in IB. Optimisation of the solvent environment leads to higher degrees of crystallinity as shown by IC. An analogy exists for isotactic polystyrene[86].

c- The strong band at 740cm^{-1}disappeared on conversion of IA to IB. Molecular models of HT cis-transoidal PPA suggest strong interaction between phenyl groups and protons two monomer units away.

Figure 2.2.v.



Partial rotation about backbone C-C bonds alleviates this interaction, which may be connected with the disappearance of the 740cm^{-1} band on conversion of IA to IB. Aromatic ring deformations have been reported to occur in this region[87]. Thus type IA was considered to be largely the extended cis-transoid form, and IB and IC were said to contain increasing proportions of cis-cisoid structures.

Type II was assigned as a trans polymer for the reasons given below, assuming types IA-IC were cis polyenes.

a- No bands were observed in the IR spectrum for type II in the 880-910cm^{-1} region assignable to chain unsaturation as in the case of type I. However, hydrogenation of type II PPA yielded a product with a very similar IR spectrum to polystyrene indicating that chain unsaturation must have been present, and of a different kind to that found in type I.

b Weak IR bands were observed for type II at 960-980cm^{-1}, which were removed by hydrogenation. This region was reported to be characteristic of trans unsaturation[86].

c- The IR spectra of trans 1,4-diphenylbutenyne, two oligomers of phenylacetylene (M_n 430 and 925 respectively), and type II PPA (M_n 1150) were compared in the region 960-980cm^{-1}. The intensities of these absorptions were found to decrease with increase in molecular weight, which was taken as an indication that the trans backbone CH modes were obscured in higher molecular weight samples.

d- Rotation about C-C single bonds in trans-transoidal PPA to give the trans-cisoidal polymer does not lead to an ordered helical structure. Type II PPA exhibited no crystallinity and no changes in solubility after heating or solvent treatment analogous to type IA.

Type III was assigned as a cis/trans copolymer as it exhibited weak IR bands between 880-910cm^{-1}(as in type I) but also showed no solubility changes or crystallinity. Like type II PPA, type III fluoresced yellow under UV radiation, and in view of the nature of the polymerization (thermal), a combination of cis and trans units was considered probable.

The effect of polar solvents on the three types of PPA was ascribed to the conversion of some cis double bonds to trans, although the increase in softening temperatures was not understood.

Summary of Kern's Proposals

1- The presence of bands in the IR spectrum of PPA at 880-910cm^{-1} were due to chain unsaturation, and, on the basis of crystallinity and solubility characteristics, were assigned to CH modes of cis double bonds.

2- The presence of bands between 960-980cm^{-1} was indicative of trans double bonds in the backbone.

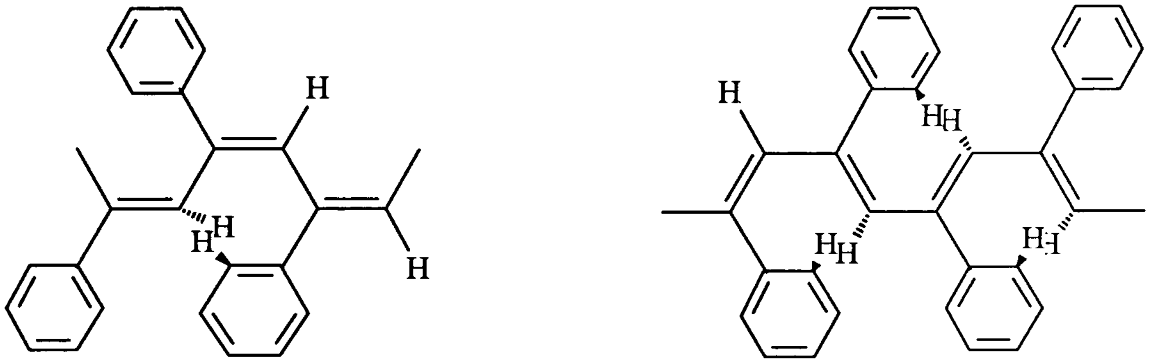
3- Iron acetylacetonate and rhodium trichloride based catalysts in combination with reducing agents generated cis PPA, whereas $RhCl(PPh_3)_3$ gave a trans polymer. Thermal polymerization of phenylacetylene resulted in a cis/trans copolymer.

Discussion

The results reported by Kern assumed an all Head-Tail structure for poly(phenylacetylene), and although this seems the most probable structure, for steric reasons, no evidence for this structural assignment was presented. No NMR data was given, and the correlations between chain microstructure and bulk properties must be considered as unproven, although inherently reasonable. In addition, the IR data cannot be regarded as conclusive proof for the structures claimed. For example, the band at 740cm^{-1} was assigned to a ring deformation due to an out-of-plane aromatic CH bending mode determined by aryl CH-vinyl CH interactions in cis-transoid PPA. As can be seen in Figure 2.2.vi. such interactions seem equally possible for the trans-cisoid isomer.

Figure 2.2.vi.

Proton-Proton Interactions in HT Polyphenylacetylene



cis-transoid PPA ***trans-cisoid PPA***

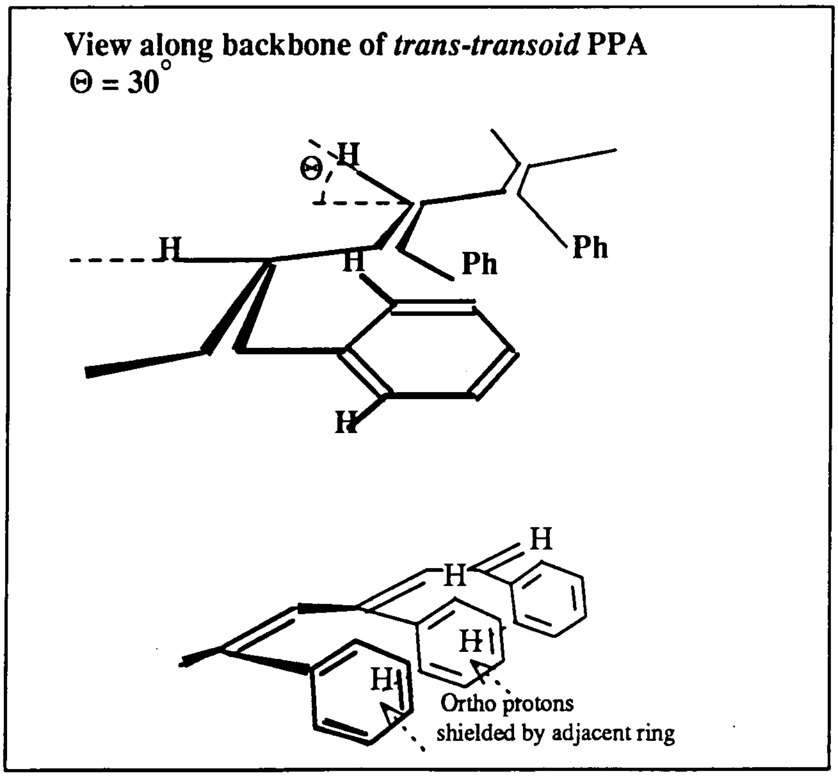
Nevertheless, the work by Kern clearly established a link between the IR spectral characteristics of different types of poly(phenylacetylene), as a function of their method of synthesis.

2.2.ii(b). Berlin PPA

One of the first papers to include NMR spectroscopic studies of PPA was that due to Berlin[88], who attempted to characterize samples of polymer prepared by catalytic (PPA-C), and thermal (PPA-T) methods. These samples were probably equivalent to Kern's Type IA and Type III samples. As a premise to the NMR study, Berlin stated that the sequence of the PPA studied was up to 90% Head-Tail (established by pyrolysis chromatography and ozonolysis), and thus the spectra might have been expected to be relatively simple. However, both PPA-C and PPA-T samples displayed only broad, poorly resolved signals.

PPA-C showed resonances between 5.3-7.8ppm, with peaks at 5.6 and 7.2ppm, whereas PPA-T showed one broad peak. Comparison of these spectra with model polyenes (up to diphenyloctatetraene) led Berlin to suggest that the backbone (conjugated chain) protons should resonate between 6.4-7.0ppm. From this, Berlin stated that the peak at 5.6ppm in the spectrum of PPA-C was due to protons which were shielded by interaction with aryl ring currents. Examination of molecular models led to the view that the trans-transoid configuration should exist as a 12/1 helix, with the ortho protons of each ring shielded by adjacent phenyl substituents.

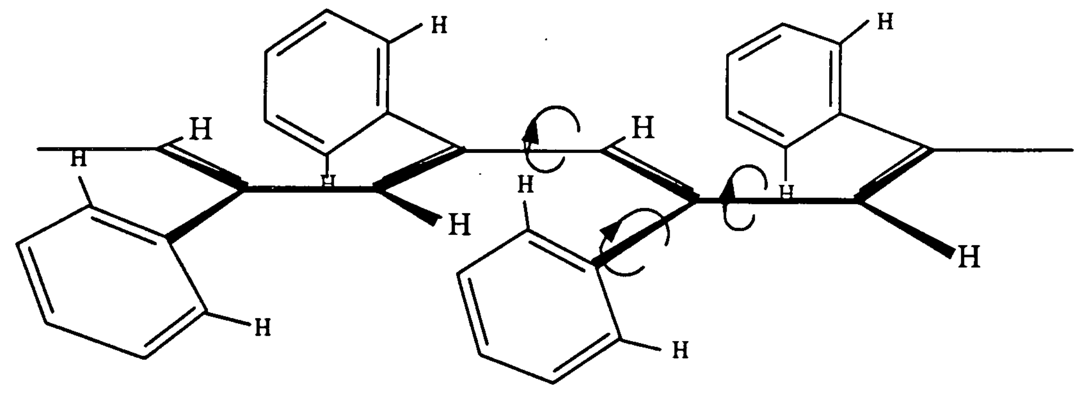
Figure 2.2.vii.



The molecular models showed that no such displacement should occur with the trans-cisoid isomer, for which a 3/1 helix was postulated, and thus no signal at 5.6ppm would occur; for this reason PPA-T was assigned to the trans-cisoid isomer.

Figure 2.2.viii.

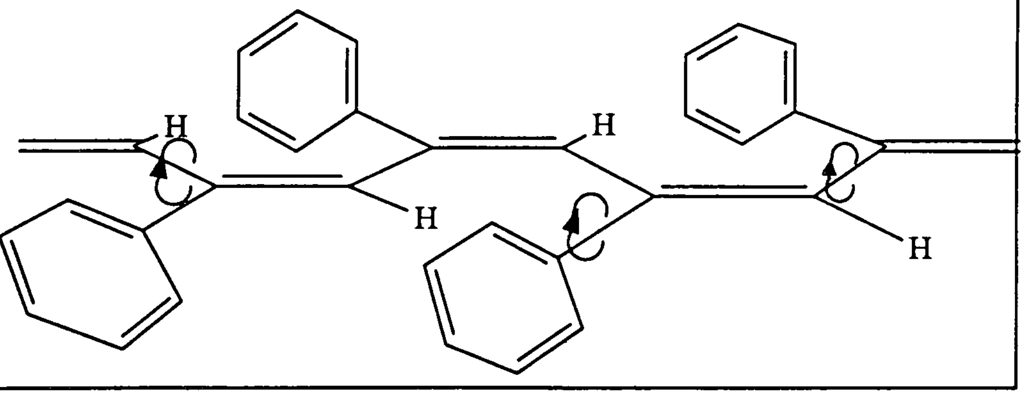
Stereoview of *trans-cisoid* PPA



Berlin asserted that for cis-transoid PPA, molecular models indicated extensive overlap of ring and backbone protons, with considerable distortions of the rings and the main chain. Consequently, some protons might be shielded, giving rise to the signal at 5.6ppm in the ^{1}H NMR spectrum.

Figure 2.2.ix.

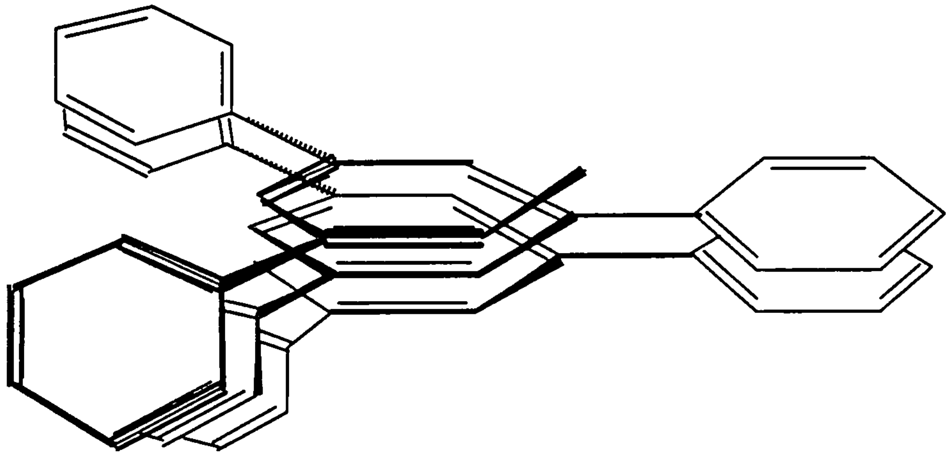
Stereoview of *cis-transoid* PPA



For the cis-cisoid isomer, the models showed less interaction.

No peak at 5.6ppm would therefore be expected for the cis-cisoid isomer, which is shown in figure 2.2.x.. On the basis of this and IR data, Berlin assigned PPA-C to the cis-transoid structure, in agreement with Kern's earlier work.

Figure 2.2.x.



Stereoview of *cis-cisoidal* PPA: hydrogen atoms omitted for clarity

Further evidence to support this hypothesis was the elimination of the 5.6ppm signal for PPA-C on heating, and the emergence of signals due to 1,3,5-, and 1,2,4-triphenylbenzene (70% and 30% respectively). The NMR spectrum of a PPA-T melt did not exhibit these signals: cyclization of the trans-cisoid isomer to benzene derivatives would be less favourable. The IR spectra of PPA-C samples showed absorptions at 873cm^{-1}, which were attributed to cis double bond CH deformations, again in agreement with the assignments of Kern.

Discussion

The work of Berlin assumed an all H-T structure, and from this the conclusions drawn seemed logical, but no firm proof was offered as to the assignment of structure. The use of molecular models in this study relied on the structure being all H-T, and the production of both 1,3,5- and 1,2,4-triphenylbenzenes on heating the polymers suggests that this initial premise was dubious. The assertion that PPA-C was largely of a cis-transoid structure was based on the presence of a poorly resolved shoulder at 5.6ppm in the ^{1}H NMR spectrum, and the other isomers were assigned from this starting point.

Infra-red spectral data and the results of thermal degradation were used to lend credence to the initial hypothesis, and to show that PPA-T must be largely of trans-cisoid structure. It must be stressed that none of these assertions were proved unambiguously, and that if the peak at 5.6ppm were not associated with shielded ring or backbone protons, the argument would lose much of its validity.

2.2.ii(c). Simionescu and Percec PPA

The work of Simionescu, Percec and co-authors has produced a large number of papers concerning the various routes to PPA and the characterization of these polymers[89]. Initial work by Simionescu set out numerous hypotheses, in particular concerning the IR and NMR spectra of PPA, and the conclusions from these studies are still extensively cited.

Simionescu[90] found that the use of Ziegler-Natta catalysts such as $Et_3Al/TiCl_3$ gave two polymer fractions, both of which were insoluble in methanol. Fraction A was insoluble in benzene and was assigned a cis-cisoidal structure by similar reasoning to that of Kern. Fraction B, which was soluble in benzene, was assigned a cis-transoidal structure by comparison with Fraction A. Fraction C PPA, obtained by polymerization of phenylacetylene using $TiCl_4$, $(Ph_3P)_2PdCl_2$, or thermal methods, was denoted as a trans isomer, again by comparison.

Simionescu noted the hazards of assigning structures solely from IR data, and stated that Fractions A and B gave identical IR spectra, with strong absorptions at $740cm^{-1}$ and $895cm^{-1}$. Fraction C did not display these bands, but did absorb strongly at $922cm^{-1}$. By comparison with cis- and trans-stilbene, structure specific bands were assigned as follows:

1265, 970, $922cm^{-1}$: trans-PPA.

1380, 895,740^{-1}: cis-PPA.

The ^1H NMR spectra of all the polymers exhibited broad resonances. Simionescu used the same molecular modelling system as Berlin, and equated structure with theoretically derived NMR spectra. The predicted spectra were:

Trans-transoidal (12/1 helix)- two aromatic protons shifted to high field.
Trans-cisoidal (3/1 helix)- no protons shifted.
Cis-transoidal (3/1 helix)- one aromatic and one backbone proton shifted to high field.
Cis-cisoidal (3/1 helix)- one aromatic proton shifted to high field.

Fraction B, assigned by IR to the cis-transoid form, showed NMR peaks at δ=5.82ppm, with integration corresponding to one proton, δ=6.70ppm (one proton), and δ=6.85ppm (four protons). PPA samples with weaker IR absorptions at 740cm^{-1} were found to show less intense peaks in the NMR at 5.82ppm; thus the IR assignments of Kern and Simionescu's NMR spectra were correlated for materials denoted as predominantly cis-transoid. Fraction C PPA showed broad absorptions between 6 and 8ppm, centred at 7.1-7.25ppm. A weak signal at 7.75ppm was attributed to the 2,4,6 protons of 1,3,5-triphenylbenzene.

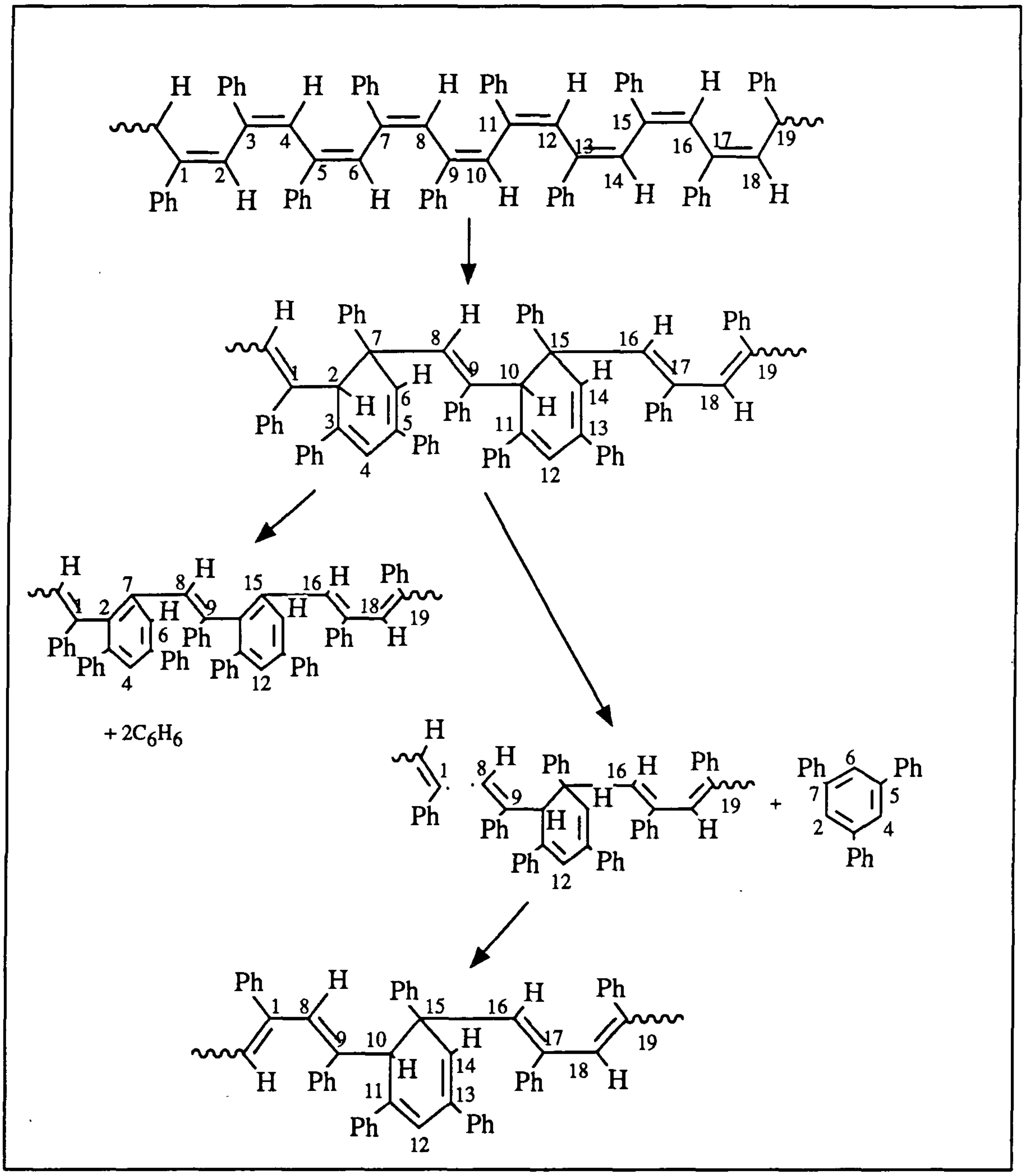
Effect of Temperature

Fractions A and B did not show IR bands at 740, 895, and 1380cm^{-1} after heating under argon, in the solid or solution state. This heating also gave rise to a new band at 1265cm^{-1}. The NMR spectrum of Fraction B changed with increasing temperature to be almost identical with that of Fraction C. From this, it was concluded that thermal treatment of Fractions A and B gave Fraction C, and that these changes were due to cis-trans isomerization of main chain double bonds. The production of triphenylbenzene and the appearance of broad peaks at 3-4ppm after heating were cited as evidence for polymer degradation on heating.

Mechanism of Polymer Thermal Isomerization

The cis-trans isomerization was further studied and a mechanism was proposed by Simionescu and Percec in 1980[91]. This represented a significant advance in as much as the authors acknowledged that PPA is a reactive organic system, inevitably complicating any physical or spectroscopic analysis. The initial premise was that high cis PPA was formed at the active sites of the Ziegler-Natta catalysts and that subsequent thermal isomerization generated trans double bonds. To test this, samples of PPA, assumed to be cis-cisoidal, were assessed for cis content as a function of temperature by monitoring IR bands at 740 and 895cm^{-1}, and the area under the proton signal at 5.82ppm. The loss of cis content was equated with apparent cis-trans isomerization, with the appearance of peaks at 3-4ppm during these reactions being ascribed to the production of cyclohexadiene moieties. Percec offered the mechanistic rationalization shown in figure 2.2.xi. (overleaf) to support these hypotheses.

Figure 2.2.xi.



Aromatization of the cyclohexadiene structures could occur, followed by chain scission. This might account for the production of trisubstituted benzenes, and an increase in the polydispersity of the PPA. Clearly, an all Head-Tail polymer would eliminate 1,3,5-triphenylbenzene, whereas less stereoregular PPA would produce some of the 1,2,4-isomer.

The rates of the "isomerization" reactions were followed by NMR and were found to depend on the initial cis content of the polymer. From this, the authors proposed that opening of the triple bond of phenylacetylene occurred at the catalyst only in a cis sense, with initial rapid thermal isomerizations of some cis- double bonds to trans-, accounting for the various proportions of cis-, trans-. and cyclohexadiene structures in the final polymer. Factors affecting such isomerizations would include the exothermicity of polymerization and of any catalyst deactivation reactions, and the thermal conductivity of the solvent. According to this hypothesis, all-trans PPA could not be produced using Ziegler-Natta catalysts.

Chemical Isomerization of PPA

The production of material assigned as high-trans PPA was effected by reaction of high-cis samples with chlorine to give a partially chlorinated material, which on treatment with acetone, gave a polymer assigned on the basis of NMR and IR as high in trans content[92]. Study by DSC and DTA techniques showed clear differences between these polymers and those prepared originally. The chlorine treated polymers showed no exotherms on heating, whereas non-treated high-cis PPA exhibited strong exothermic maxima, which were assigned to the cis-trans isomerization. This is in agreement with the cis-trans isomerization of poly(acetylene) in the presence of oxidising agents[77].

Poly(pentadeuterophenylacetylene) (PPDPA)

Percec tested the conclusions drawn from previous NMR studies by polymerizing $C_6D_5C\equiv CH$ with Ziegler-Natta catalysts[93]. A strong proton signal was observed at 5.82ppm, with a weaker absorption at 6.85ppm. Chlorine treatment followed by solvent extraction caused the 5.82ppm signal to disappear, and a broad hump was seen around 6.9ppm. Thermal isomerization of the original deuterated polymers gave NMR peaks at 3.5 and 7.3-7.8ppm, as with similarly treated PPA.

Discussion

The NMR assignments of Simionescu and Percec were clear regarding the protons on the backbone chain of PPA. Two peaks were seen, at 5.82ppm and 6.85ppm, for the deuterated polymer, dependent on the method of synthesis or sample history. The assignment of these to cis-, and trans-, double bonds respectively fits with the original assignments of Kern, and is plausible since it is reasonable to expect the thermal, and chloronium ion promoted, isomerizations to proceed from the cis to the trans isomer.

However, the above argument does not constitute unambiguous proof, as it is not impossible that in a highly hindered system, the relative stabilities of the cis and trans isomers may be altered. It is also clear from the authors' previous work that thermal treatments may result in chemical reactions, such as cyclizations and eliminations, other than simple cis/trans isomerization.

2.2.ii(d). "Masuda" Poly(phenylacetylene)

A significant development in the polymerization of phenylacetylene was the use of WCl_6 and $MoCl_5$ based catalysts[74-76]. These metal systems allowed the synthesis of PPA with an average molecular weight of > 10,000, almost twice that of previous samples. Another important difference with the WCl_6 and $MoCl_5$ generated polymers was the solubility of almost all of the reaction product in benzene. In addition to the high polymer, a very small fraction (< 5%) was obtained which was soluble in methanol.

Properties of Masuda PPA

Polymers produced using the WCl_6 and $MoCl_5$ catalysts ("WCl_6 and $MoCl_5$ polymers") were powdery, soluble in benzene, dichloromethane, chloroform, and carbon tetrachloride, and were coloured dark-red and orange-yellow respectively. The effects of various reaction conditions were studied, and, as previously, it was found that changes in solvent, monomer concentration, catalyst system, and post treatment of polymer, all contributed to changes in the final polymer structure. For example PPA produced using $WCl_6.1/2(H_2O)$ in benzene was of significantly higher molecular weight than polymer produced using identical conditions but with dichloromethane as the solvent. The tungsten-based catalyst produced PPA in 90% conversion within 30 minutes, whereas the molybdenum system required 100 minutes for 60% conversion. It was found that WCl_6 polymer degraded substantially at room temperature in the light, with the molecular weight decreasing to roughly half its original value within 4 months: the same sample had not degraded when stored at -20^0C in the dark for 6 months. Photochemical reactions are not unexpected for such conjugated polyenes, but the study did not mention whether atmospheric oxygen played any part in the degradation.

Structure of Masuda PPA

The softening points ($215-226^0C$), solubility characteristics, and the high molecular weights of Masuda PPA samples, suggested that the polymerizations were significantly different to those reported earlier.

The detailed analysis of these samples were based largely on IR spectroscopy, and conclusions drawn by comparison with the work of Kern[85], and Simionescu *et al*[89,90]. For all the polymers, absorptions assigned to stretching vibrations of polyconjugated double bonds were seen at 1550-1600 cm^{-1}. Bands at 777 and 693cm^{-1} were stated to be those of out of plane CH deformations of monosubstituted benzenes. The main conclusions of Masuda were:

i- the polymers were linear polyenes;

ii- catalysis by WCl_6 in polar solvents produced high trans polymers.

iii- catalysis by $MoCl_5$ in non-polar solvents produced high cis polymers.

The main reason behind these assertions was that $MoCl_5$ polymers gave spectra with strong absorptions at 738cm^{-1} and 870cm^{-1}, which were assigned to cis double bonds on the polyene backbone. It was stated that such absorptions were in accordance with those at 740cm^{-1} for cis-polyacetylene (out-of-plane bend)[94,95], and that for PPA such bands were due to out-of-plane CH deformations. Polymers produced using WCl_6 in polar solvents showed a strong absorption at 910cm^{-1}, which was assigned to the trans isomer. Masuda reported that polyalkenamers produced in his laboratories under the same conditions contained a higher trans content for WCl_6 than $MoCl_5$, but recognised that there was no clear reason for this.

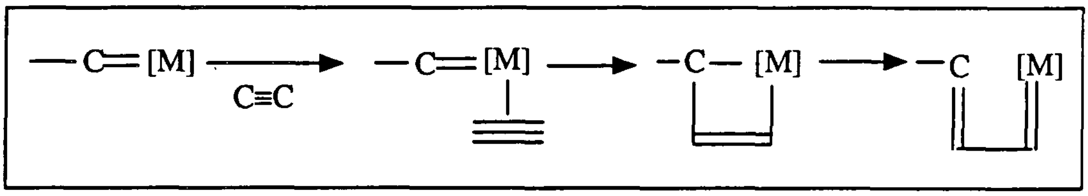
UV Absorption and Emission Spectra for Masuda PPA

In view of the colour of the polymers, it was not surprising that the UV absorption and emission spectra for the PPA samples differed. However, each polymer possessed a maximum absorption at 225nm (ϵ=5-6 x 10^{-3}), with absorption tails up to 500nm. The 500nm absorption was more intense for WCl_6 polymers accounting for their dark-red colour. Emission spectra for these samples (after excitation at 250nm) displayed peaks at 360nm and 430nm, whereas $MoCl_5$ polymers did not emit at 430nm: maximum emission for both types of polymer was at 250nm. No further discussion of these spectra was presented.

Discussion

These preparations of PPA were amongst the first to use catalysts active for olefin metathesis, and this led Masuda to propose that the polymerization took place in a similar way to ring-opening metathesis polymerization (ROMP) of olefins. In this case, the acetylene was behaving as the "ultimate" small ring, with coordination to the catalyst leading to a metallocyclobutene intermediate.

Figure 2.2.xii.



The relatively low polydispersities (M_w/M_n~2) were claimed to indicate that the polymerization proceeded via one propagating species. Masuda recognised that the polymers were not necessarily of an all head-tail microstructure: however, the low activity of PhC≡CMe in similar reaction media was taken as evidence that steric crowding inhibited polymerization. This hindrance would be greater with head-head structures than head-tail in PPA.

As with the work of Kern, the structures of various polyphenylacetylenes were not unambiguously defined, but were nevertheless cited extensively by other workers.

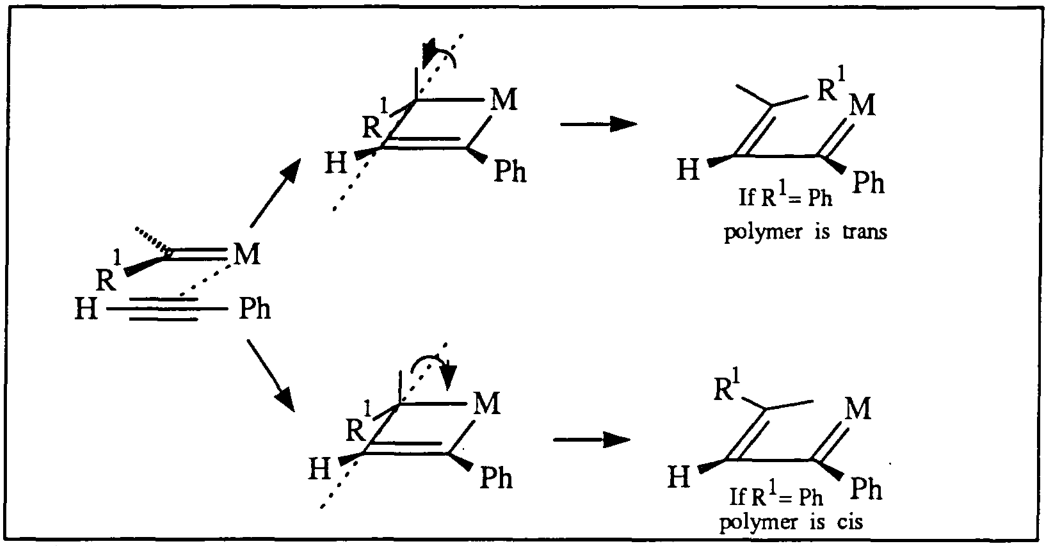
2.2.iii. Further Metathesis Polymerizations of Phenylacetylene

Percec and Rinaldi[96] studied the cis-trans isomerization of PPA synthesized with $MoCl_5$ and WCl_6 catalysts. The conclusions drawn assumed a metathesis mechanism, and the production of cis-, trans-, and cyclohexadiene sequences in the polymer were considered to arise as a result of two main factors.

i- Thermal isomerization in the polymer, as described earlier for the case of Ziegler-Natta catalysed high cis PPA.

ii- Isomerization prior to double bond formation, at the catalyst. Such isomerization would depend on the properties of the metal, the substituents at the metal and the acetylene, and the precise reaction conditions such as solvent and temperature. A mechanistic rationalization for this isomerization at the catalyst was proposed by Percec and is shown overleaf in figure 2.2.xiii.

Figure 2.2.xiii.



Percec used the same analysis as in his previous work for structural elucidation, and included an assessment of cyclohexadiene content by monitoring signals at 3.6ppm in the ^{1}H NMR spectrum. The following conclusions were reported:

a- Catalysis by $MoCl_5$ gave high-cis PPA which partially isomerized after polymerization to give trans-cisoid sequences. Short reaction times gave these trans sequences without producing cyclohexadiene moieties, indicating that cyclization occurred via intrachain mechanisms after polymerization.

b- The use of WCl_6 gave high-trans PPA, as a result of steric interaction between the metal centre and the growing polymer chain. The atomic radius of tungsten is larger than that of molybdenum, and the interactions between the tungsten metal centre and growing polymer were expected to be larger as a result. Isomerization during the initial double bond formation was thus predicted for tungsten catalysts, giving the high-trans polymer.

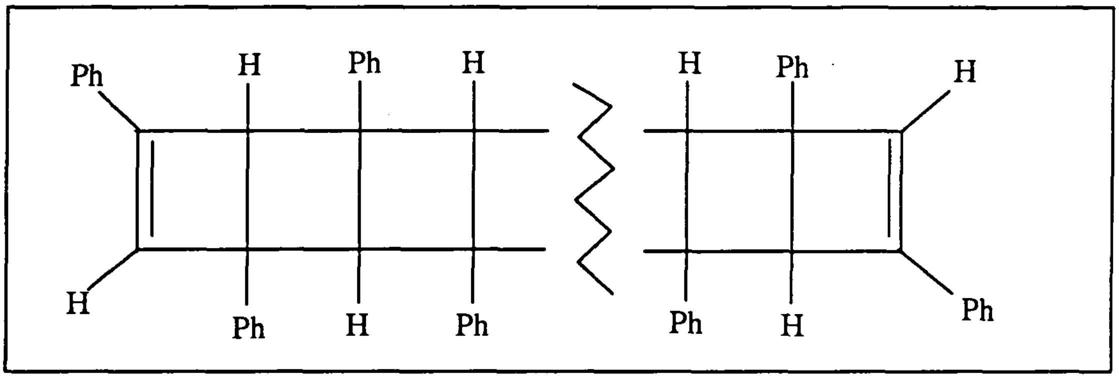
c- The effect of solvent was two-fold. Non-coordinating solvents of differing thermal conductivities changed the proportion of thermal isomerization dependent on ability to dissipate heat from the reactive sites. Coordinating solvents interacted with the metal centre, resulting in changes of steric requirements at the polymerization sites. The observations reported by Masuda and Higashimura's groups[97], in which WCl_6 in 1,4-dioxane produced very high molecular weight PPA, were considered to support this hypothesis.

Coordination of the solvent in this case was believed to cause isomerization at the metal centre, giving almost 100% trans PPA, with no intra-chain isomerization and degradation to cyclohexadienes. The use of metathesis catalysts appeared from these studies to offer the capability of producing high-trans-, as well as high-cis-PPA, and thus more recent work concerning PPA has tended to concentrate on such catalysts.

2.2.iv. Ladder Polymers from Phenylacetylene

The group of Farona and co-workers also used catalysts active for metathesis to produce PPA with molecular weights of ~10,000. However, in these reports[73,98,99], the isolation of an intermediate low-molecular weight oligomer was described, with a ladder structure assigned on the basis of ^1H NMR and IR spectroscopy.

Figure 2.2.xiv.



Further evidence for the proposed structure was the detection of hexamethylbenzene in the reaction of but-2-yne with one of the catalysts used previously ((toluene)Mo(CO)$_3$). Reaction of phenylacetylene with polymer supported molybdenum catalysts, in the presence of carbon monoxide, gave triphenylbenzenes and triphenylDewarbenzenes. These results led Farona to propose that thermally induced 2+2 cycloadditions were taking place at the metal centre.

2.2.v. Recent Advances in Preparation of PPA and Substituted Derivatives

2.2.v(a). Furlani stereoregular PPA[100]

Certain rhodium (I) catalysts have been used to produce highly structurally regular PPA. In particular, $[Rh(COD)bipyam]^+PF_6^-$ and $(Rh(COD)Cl)_2$ catalysts have given PPA of sufficiently stereoregular structure to exhibit a sharp singlet resonance for the protons on the backbone chain.

The polymer spectra also showed AA′MM′N system resonances for the ring protons, with integration in the expected 2:2:1 ratio compared to the vinylic backbone proton. Highly resolved ^{13}C spectra were also obtained, with clearly distinguishable resonances for the quaternary and non-quaternary carbons. IR bands at 740, 895, and 920cm^{-1} were in accord with previous literature assignments of cis-PPA, leading the authors to propose that the polymers, of molecular weights of between 10-100,000, were cis-transoidal and all Head-Tail. However, this study was concluded with some discussion concerning the difficulty of assigning the structure unambiguously, and it was noted that solvent or thermal treatment of these polymers caused considerable changes in the NMR spectra.

2.2.v(b). Iwamura Substituted Poly(phenylacetylene)s

The polymerization of some para substituted poly(phenylacetylene)s was studied by Iwamura and McKelvey[101] in 1988. These workers were attempting to polymerize *p*-ethynylbenzaldehyde using the WCl_6/Ph_4Sn system, but found that this monomer, and *p*-ethynylbenzyl alcohol deactivated the catalyst. However, by polymerizing *p*-ethynylmethylbenzoate, the corresponding hydroxyl and aldehyde containing polymers were accessible by reduction of the ester fuunction followed by oxidation. The structures of all the polymers were reported to be high trans, using ^{13}C NMR spectroscopy in comparison with assignments given by Percec and Rinaldi, but the authors noted that their assignments could not be exact. In addition, bands in the IR spectra at 870 and 910cm^{-1}, used by other authors for evaluation of cis and trans content, were obscured in the spectra of the *p*-substituted polymers. Nevertheless, this work showed that functionalized conjugated polymers could be prepared by metathesis routes, and that synthetic transformations were possible after polymerization.

2.2.v(c). Masuda *o*-MePPA

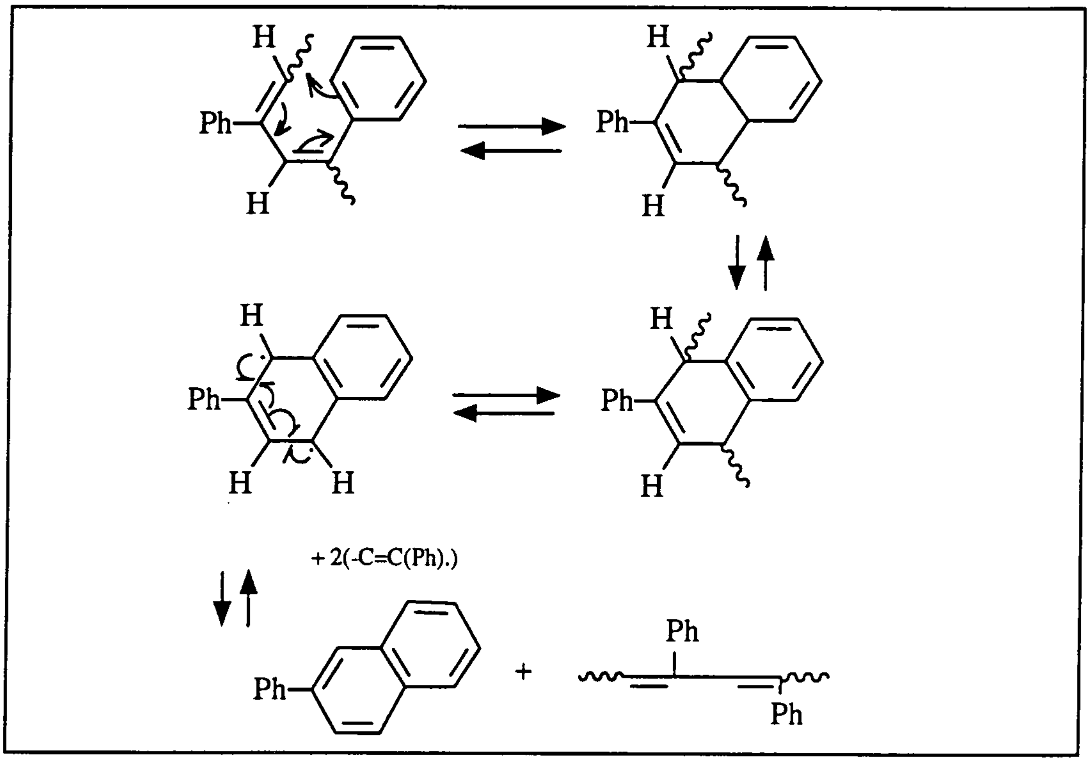
In an investigation into the properties of substituted poly(phenylacetylenes), Masuda[102,103] found that polymerization to unusually high molecular weight was possible, using "classical" metathesis catalysts, if the arylacetylene was substituted in the ortho position. Thus, polymerization of 2-methyl-1-ethynylbenzene (*o*-methylphenylacetylene) with molybdenum- and tungsten-based catalysts in a range of solvents gave materials with molecular weights of up to 800,000 (GPC, compared to polystyrene standards). The highest molecular weights and the narrowest M_w/M_n ratios were achieved with WCl_6/Ph_4Sn in 1,4-dioxane.

The ^{13}C NMR spectra showed broad resonances in the 120-140ppm region, but some resolution was achieved for the signals arising from the *o*-methyl carbons at 18-21ppm. All the catalytic systems gave polymers with at least two signals in this region assigned to the effect of the cis and trans sequences in the conjugated backbone. The higher field signal (19-20.2ppm) was more intense for samples prepared using tunsten catalysts, and was assigned as associated with the trans isomer. Co-polymerization studies with phenylacetylene indicated that *o*-methylphenylacetylene was very slightly less reactive with respect to metathesis, but that the mechanism of polymerization was identical. For *o*-trifluoromethylphenylacetylene, a living mechanism of polymerization was claimed, with a narrow polydispersity resulting from the use of $MoCl_5/Ph_4Sn/EtOH$ as the catalytic system. The UV spectra of poly(*o*-methylphenylacetylene) and poly(*o*-trifluoromethylphenylacetylene) showed significantly red-shifted (λ_{max}= 466nm) absorption as compared to PPA (λ_{max}= 225nm), suggesting increased conjugation despite the bulky ortho substituents. No explanation for these phenomena were offered.

2.2.v(d). Percec "living PPA" and Ortho substituent effect

The results of Masuda's work led Kunzler and Percec[104] to compare the polymerization of phenylacetylene with ortho-substituted phenylacetylenes. The polymerization of phenylacetylene using $MoCl_5$ in C_6D_6 was monitored by ^1H NMR, with spectra recorded at intervals after addition of monomer of one, five and nineteen hours. The initial appearance of singlets at δ=6.2ppm and 7.6ppm were assigned to the backbone protons of the cis-polymer and the 2,4,6 protons of 1,3,5-triphenylbenzene respectively. After five hours (70% monomer conversion), the signal at 6.2ppm had decreased in intensity, whereas the 7.6ppm signal had increased and a broad band had appeared at 3.5-4.5ppm. These changes were assigned to a decrease in the concentration of cis-transoidal PPA, and the production of cyclohexadiene sequences and further amounts of 1,3,5-triphenylbenzene. At 95% conversion, the amounts of cyclohexadiene and 1,3,5-triphenylbenzene were unchanged but no signal at 6.2ppm was observed. The decrease in cis concentration during polymerization was ascribed to thermally-induced double bond isomerizations and intramolecular reactions leading to cyclohexadienes, with 1,3,5-triphenylbenzene arising either from direct cyclotrimerization, or from backbiting of a cis-cisoidal growing chain. A further mechanism for intramolecular cyclization was put forward, suggesting that cyclohexadiene and tetralin type structures could arise from electrocyclic reactions of the kind shown in figure 2.2.xv. overleaf.

Figure 2.2.xv.



Percec proposed that the ^1H NMR signals at 3.5-4.5 ppm could arise from fragments formed during these cyclizations, and that ortho-substituted poly(phenylacetylene)s would be less likely to react in this manner because of steric constraints.

The polymerization of *o*-methylphenylacetylene was also followed by NMR and GPC. A linear molecular weight-conversion plot was obtained to 60% conversion, with a subsequent rapid decrease in molecular weight. Compared to phenylacetylene polymerization, there was a four-fold increase in molecular weight and a three-fold increase in monomer conversion, and no signals were observed in the ^1H NMR between 3.5-4.5 ppm. For *o*-trimethylsilylphenylacetylene, the molecular weight-conversion plot was followed to complete monomer conversion, with no changes of molecular weight with time if the polymer was left in the reaction system after completion of reaction. This was claimed to show that "living" polymerization had occurred, in agreement with Masuda's claims described above. In addition, the polymer was claimed to contain a high proportion of cis double bonds, owing to a strong ^1H NMR signal at δ=6.0ppm, but no intramolecular cyclization products.

Percec quoted reports[105] that the trimerization of arylacetylene derivatives by specific trimerization catalysts was unaffected by bulky substituents, and that the lack of cyclization products after polymerization of *o*-trimethylsilylphenylacetylene was evidence that such products arose only through intramolecular back-biting of cis-cisoidal segments. Percec suggested that the presence of the bulky ortho substituent suppressed cis-transoid to cis-cisoid isomerizations, and thus eliminated intramolecular backbiting.

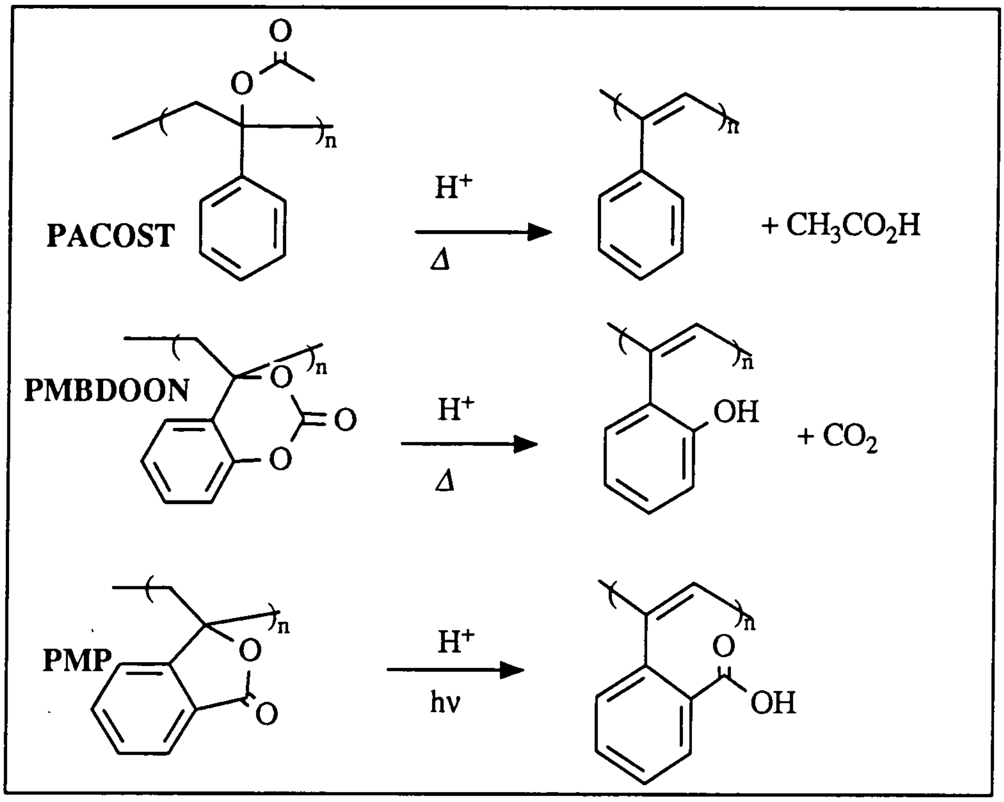
The extended UV absorptions of the ortho-substituted polymers was ascribed to the presence of long conjugated sequences which could not be obtained for unsubstituted PPA because of intramolecular backbiting during the polymerization process.

Percec concluded this study by stating that the important factors in these polymerizations were isomerization prior to double bond formation at the catalyst, which determined the length of cis-transoidal sequences available for intrachain cyclizations, and the extent of the subsequent cyclizations. Bulky ortho substituents suppressed cis-transoid to cis-cisoid isomerizations, and prevented interchain reactions leading to narrow dispersity polymers with no cyclohexadiene or triphenylbenzene fragments.

2.2.v(e). Ito, Ueda PPA Precursor route[106]

A precursor route to PPA and substituted derivatives has recently been described by Ito and Ueda, in which three saturated chain polymers were converted to chain-unsaturated polymers by heat or photochemical acidolysis. The saturated precursors were not stereoregular, and thus the PPA derivatives were not expected to be of well-defined structure. All the conjugated polymers prepared by thermal methods (220-240^{0}C) were suggested to be high in trans content, with cis double bonds reported only for conversion of one of the polymers ("PMP") via the photochemical route. Triphenylsulphonium hexafluoroantimonate was used to generate acidic species on irradiation, but heating was required in some cases to complete the acidolysis. These polymers and the conversion reactions are shown in figure 2.2.xvi. overleaf.

Figure 2.2.xvi.



^1H and ^{13}C NMR spectroscopy showed broad resonances and peak positions in general agreement with reports by other workers. These precursor routes clearly require some optimization, but might allow preparation of stereoregular PPA if the pre-polymers could be prepared in a controlled manner, and if the conversion reactions were to proceed under mild conditions.

2.2.vi. ESR Studies of PPA

The presence of paramagnetic centres in PPA was noted in early studies concerning the preparation of the material. However, the origin of free radicals in PPA has still to be fully established. Benderskii[107] claimed that ESR signals arose from the isolated, uncontaminated macromolecule, whereas Penkovskii and Kuts[108] attributed most of the signals reported by previous workers to charge transfer interactions with oxygen.

An investigation into the structure-paramagnetism relation in PPA was carried out by Ehrlich et al[109]. who prepared PPA by catalytic and thermal methods. Samples polymerised thermally at 120^0C in the absence of oxygen showed single line ESR spectra with no hyperfine structure, with a spin concentration of $\sim 10^{17}$ spins.g^{-1}. PPA prepared using $RhCl_3/LiBH_4$ gave ESR signals corresponding to $\sim 10^{16}$ spins.g^{-1}at 60^0C, which increased to $\sim 10^{18}$spins.g^{-1} at 130^0C, at which temperature the crystallinity af the polymer decreased sharply. From this, Ehrlich concluded that the presence of paramagnetic centres in PPA was due to conformational disorder, and that a perfect crystal lattice of PPA would be diamagnetic.

Further investigation by Holob et al[110] confirmed that samples prepared using $RhCl_3/LiBH_4$ or Ziegler-Natta catalysts, and assigned as partially crystalline high cis PPA attained a maximum ESR peak at 120^0C, with a decrease in intensity up to the melting point of the polymers at 220^0C. However, the samples still displayed paramagnetism well above 220^0C in the absence of oxygen. Holob attributed the origin of paramagnetism to the breaking of skeletal double bonds in a severely distorted cis polymer, causing lattice defects, i.e. free radical centres. The lack of hyperfine structure in the spectra of the PPA samples was not considered as evidence that the free radicals were delocalized; it was suggested that model studies of free radicals in conjugated polymers were required for the proper definition of electronic defects in such materials. The lattice defects in this study of PPA were claimed to lead to kinks in the polymer skeleton after bond rupture, but no NMR or molecular weight distribution data were given to support these assertions.

Well resolved hyperfine structure (hfs) was first observed in ESR spectra by Ehrlich[111] in 1974 in PPA solutions at temperatures just below the order-disorder transition. Fresh samples prepared catalytically were found to display a structureless single line with a peak-peak width of ~10G in the solid and solution states. On heating to 120^0C, hfs was observed, with over 40 resolvable lines spaced equally about 1G apart, and this improved resolution remained partially on cooling. In addition, the ESR spectra did not change with time at 110-120^0C, which was taken as evidence that the polymers were not degrading, and that the origin of the signal was the order-disorder transition from crystalline to amorphous PPA.

The suggestion that the increase in radical concentration was due to a cis to trans isomerization was made by Chang[112]. In this work, it was asserted that the production of such radicals might have accounted for chain termination processes in the polymerization of acetylenes, leading to the relatively low molecular weights reported relative to the polymerisation of alkenes.

The presence of unpaired electrons and electrical conductivity was briefly discussed by Masuda *et al* in their paper describing metathesis polymerization of phenylacetylene[75]. Samples of PPA in this study showed electrical conductivities of 10^{-18}-10^{-15}ohm^{-1}. However, Masuda observed strong ESR signals for all the PPA samples with the same g-values in each case. At room temperature, these signals were broad (peak-peak widths of 10-13G), but with increasing temperature hyperfine structure was apparent with a concomitant increase in spin concentration from ˆ10^{17}spins.g^{-1} to ˆ10^{18}spins.g^{-1} at 150^{0}C. This was ascribed to the formation of biradicals by twisting of double bonds and subsequent polymer degradation, as reported by Holob et *al*[110]. No significant change in these spectra was observed by exposure of the polymers to air.

The application of MO theory and computer modelling by Whitte *et al*[113] to ESR spectra of PPA gave rise to the suggestion that two main types of free radical were present in these samples. Polymers prepared using Fe(acac)$_3$/Et$_3$Al, assigned a cis-cisoid microstructure and melting at 120^{0}C, gave hfs at 100^{0}C superimposed upon a broad single peak (line width 15G). This structure was apparent in samples stored in the dark for several years indicating that essentially irreversible structural changes had taken place during heating. Further heating of the samples under vacuum also failed to effect any changes in the spectra, suggesting that the observed radicals centres did not arise from volatile fragments. First and second derivative spectra agreed well with computer simulations with the results suggesting that the radicals were delocalized over between 1 and 3 monomer units. However, the narrow line width of the hfs suggested that one of the radical species was trapped. The authors suggested that this might occur by formation of cyclohexadienyl radicals during isomerization. These cyclohexadienyl radicals could aromatize, causing chain scission, leading to the production 1,3,5 - TPB, as suggested by other workers, but Whitte pointed out that the computer simulations also indicated that other types of radicals could give rise to the observed ESR spectra. Thus, the origin of this radical accounting for ~10% of the total signal could not be unambiguously assigned by these experiments.

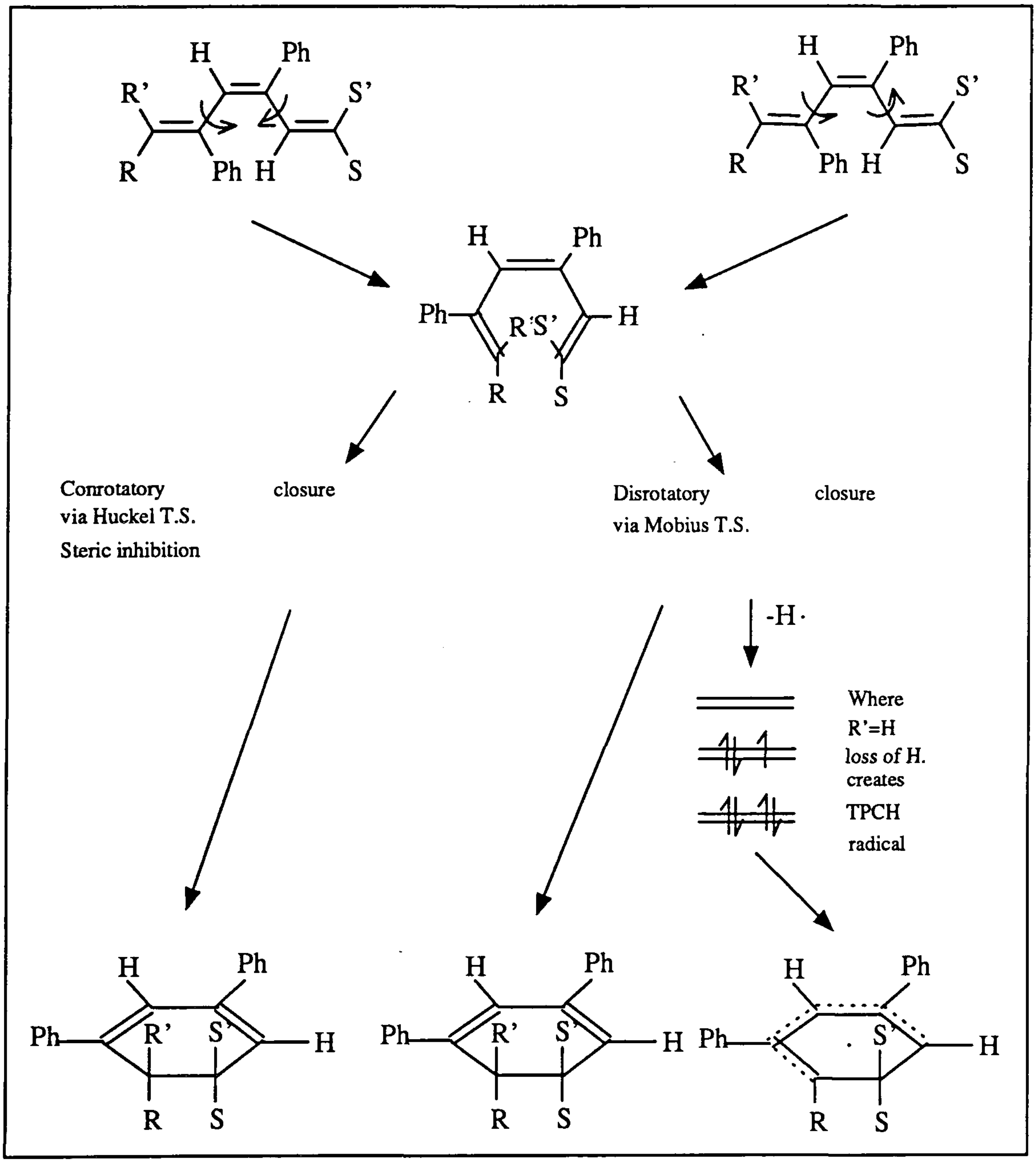
Study of thermally polymerized phenylacetylene by Hwang and Tsonis[114] showed that similar radical species were present in these samples as in those prepared by catalytic methods. These studies showed that polymerization of PA by thermal methods proceeded by a radical mechanism, but did not discuss further the origin of paramagnetism and hfs in heated PPA samples.

The most recent ESR study of PPA has been that due to Langner and Ehrlich[115]. Phenylacetylene was polymerized using $Fe(acac)_3/Et_3Al$ to give two fractions of varying crystallinity. The more crystalline fraction was purified by extraction with chloroform, leaving an insoluble form which was assigned by these authors as cis-cisoidal PPA. ESR spectra were recorded for each fraction, and were found to contain broad absorptions (peak-peak width 18G) with little hfs at room temperature. Typical spin concentrations were $\sim 10^{16}$ spins.g^{-1}, which were found to increase with time in the solid state at room temperature.

The authors conducted a detailed ESR study of the catalytic system, and found that signals arising from the catalyst varied with the polymer fraction. The strengths and characteristics of these signals were different for the insoluble and soluble fractions of a given polymerization batch, with the insoluble fraction apparently corresponding to signals from catalysts with a low Al:Fe ratio. From this, it was concluded that formation of cis-cisoidal PPA was favoured by a low Al:Fe catalyst. However, the authors claimed that even the insoluble crystalline fraction contained cis-transoidal segments disordering the cis-cisoidal helices, and that the cis-cisoidal segments were capable of cyclization. A mechanism was proposed involving rotation of main chain single bonds to produce a segment of three double bonds in a cis-cisoid conformation; i.e. set up for cyclization. A 6π ground state electrocyclic ring closure in a cis-cisoid triad would be required by orbital symmetry arguments to be conrotatory. This is sterically impossible, and thus the authors suggested that loss of a hydrogen atom from the terminus, and closure via a Möbius rather than the Hückel transition state might be preferred. Such a process would give a 1,3,5-triphenylcyclohexadienyl (TPCH) radical, which the authors suggested was the major radical species in the solid. At ambient temperatures it was proposed that cyclization of cis-cisoidal segments produced these radicals, which were delocalized along the chain. However, the insoluble fraction was believed to trap large numbers of isolated radicals, due to the lack of planarity of the cis-cisoidal helix. The hyperfine splittings for these radicals were reported to be similar to those of unsubstituted cyclohexadienyl radicals.

The proposed mechanism of cyclization and the production of TPCH radicals is shown in figure 2.2.xvii overleaf.

Figure 2.2.xvii.



A further contribution to the ESR spectra was stated to be from chemisorbed oxygen, which arose from treatment of the polymers during work-up with HCl/MeOH. These radicals were believed to play an important role in the degradation of the polymers above 100^0C.

2.2.vii. Summary of Structural Data

In spite of the number of papers published in this field, there have been few attempts to summarise the various spectroscopic features of PPA. The tables below give an indication of the IR and NMR characteristics which have been used to differentiate between the different types of polymer reported.

2.2.vii(a). IR Bands

ν/cm^{-1}	Assigned Structure	Reference
740, 880-910	cis	85
960-980	trans	
873	cis-transoid	88
1265, 970, 922	trans	90
1380, 895, 740	cis	
738, 870	cis	75
910	trans	
740, 895, 920	cis	100

2.2.vii(b). ^{1}H NMR Peaks

δ/ppm	Assigned Structure	Reference
5.6, 7.2	cis-transoidal	88
5.82(1), 6.7(1), 6.85(4)	cis-transoidal	90
5.83(β), 6.67(*o*), 6.99(*m*), 7.2(*p*)	cis-cisoidal	116
5.85, 6.70, 7.1	cis (E)	117
5.82, 6.82	cis-transoidal & trans	96
5.84(1), 6.63-6.64(2), 6.93-6.95(2)		100
6.2	cis-transoidal	104

2.2.vii(c). ^{13}C NMR Peaks

δ/ppm	Assigned Structure	Reference
142.6,139.2,131.5,127-128,126.6	cis-cisoidal	118
142.8,139.2,131.7,129.9-127.8,126.6	cis and trans	96
142.8,139.3,131.7,127.6-127.4,126.6		100

In the table, integral intensities for ^{1}H NMR are given in parentheses: assignments of *o,m,p*, refer to benzene ring protons and β to polyene backbone protons.

CONCLUSIONS

The syntheses, properties and microstructures of poly(phenylacetylene) and related materials have attracted considerable attention for around thirty years, but to date these polymers are still incompletely characterized. The work of Kern established the first reference points, particularly relating to the infra-red spectra of PPA. Simionescu and Percec were amongst the first to use NMR spectroscopy for the analysis of the polymers, and the most recent publication by Percec has shown that the polymerization of PPA can be followed by NMR. The use of metathesis catalysts by Masuda and co-workers has enabled the synthesis of high molecular weight PPA to be carried out in high yield, and has allowed the preparation of ortho-substituted PPAs with extended UV absorption similar to poly(acetylene).

However, despite these advances, the exact structures of these polymers are still not known. The preparation of PPA giving very well-resolved NMR spectra was described by Furlani, and has been repeated by this author, but the assignment of each of the resonances has yet to be established unambiguously.

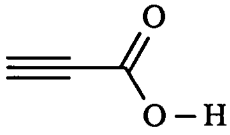
CHAPTER THREE

PREPARATION
CHARACTERIZATION
AND
POLYMERIZATION
OF
PROPIOLIC ACID
AND
PROPARGYL ALCOHOL
ESTERS

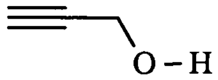
Introduction

The first approach to the preparation of the desired polyradicals involved the polymerization of functionalized acetylenes. The monomers chosen initially were esters of 2-propynoic acid (**3a**) and 2-propyn-1-ol (**3b**), as both acid ("propiolic acid"), and alcohol ("propargyl alcohol") were readily available and inexpensive materials.

Figure 3.1.i.



3a 2-propynoic acid

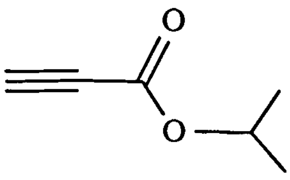


3b 2-propyn-1-ol

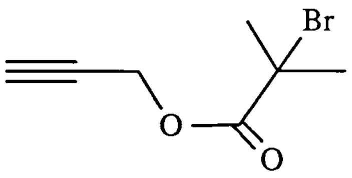
As discussed earlier, the method of polymerization chosen was the acetylene metathesis reaction, and thus the monomers chosen should not contain functional groups likely to deactivate the catalysts. Therefore, it was decided to generate the desired radical centres after polymerization.

The two monomers initially prepared were the isopropyl ester of 2-propynoic acid (**3c**), and the 2-bromo-2-methylpropanoate ester of 2-propyn-1-ol (**3d**).

Figure 3.1.ii.



3c



3d

These monomers were considered to be useful in terms of acquiring the techniques necessary for metathesis polymerization of functionalised acetylenes. In the case of 3d, the presence of the bromine atom at a tertiary carbon was thought to confer a ready means of generating a radical site. Reaction with a suitable metal, such as zinc, might, in the case of the polymer, create free radicals stabilised by the conjugated backbone, and thus provide a test for some of the hypotheses described in Chapter 1.

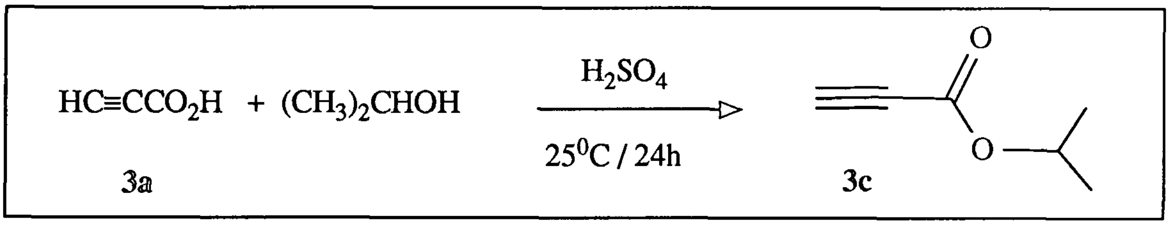
3.2. Experimental

These experiments were carried out during the early stages of this project, and some of the instruments available for characterization were different to those described in the rest of this thesis. In this chapter, NMR spectra were recorded on a Bruker AC 250 spectrometer at 90.13MHz (^1H), or 62.90 MHz (^{13}C). Gel Permeation chromatograms were run using a Waters 590 pump equipped with a refractive index detector, but without the Chromatocorder integration computer described later in this thesis. Thus, the molecular weights quoted in this chapter were determined by direct comparison with traces for polystyrene standards.

3.2.i. Preparation of (1-Methylethyl)prop-2-ynoate

The synthesis of this monomer (3c) was first carried out by Vermeulen and Fierens[119], but the reported yield (62%) proved difficult to repeat and many attempts were made to improve the reaction method; the procedure below gave the best results.

Figure 3.2.i.



Experimental

N.B. 2-Propynoic acid and its volatile ester derivatives, including (1-methylethyl)prop-2-ynoate, are powerful lachrymators, and skin irritants, and thus should be handled with care.

2-Propynoic acid (propiolic acid) was used as supplied by Aldrich. Propan-2-ol (Isopropanol) was dried over calcium oxide and redistilled. Sulphuric acid, and diethyl ether used in the work-up were standard reagent grade, and used without further purification.

Procedure

2-Propynoic acid (10.5g, 150mmol) was added to propan-2-ol (50ml, excess) wth stirring, under a nitrogen atmosphere. Sulphuric acid (10ml) was added dropwise with the temperature maintained at 0°C during addition, after which the contents of the reaction vessel were allowed to reach room temperature. The reaction was continued for 24 hours at room temperature, before pouring into ice-water (200ml).

The aqueous layer was extracted with diethyl ether (3x75ml), the organic layers combined and shaken with saturated sodium bicarbonate solution (3x75ml), washed with water (3x50ml) and dried over magnesium sulphate, to yield, after solvent evaporation, a yellow, lachrymatory oil (11.5g, 69%). The aqueous layers were combined, acidified, extracted with ether and the organic layer dried over magnesium sulphate, to recover unreacted 2-propynoic acid and propan-2-ol.

3.2.ii. Results: (1-Methylethyl)prop-2-ynoate 3c

Distillation under reduced pressure (39°C / 30mm Hg, lit.[119]) yielded 11.25g (67%) of a colourless liquid. The product was stored over 4A molecular sieves, and redistilled prior to polymerization experiments.

Characterization of 3c

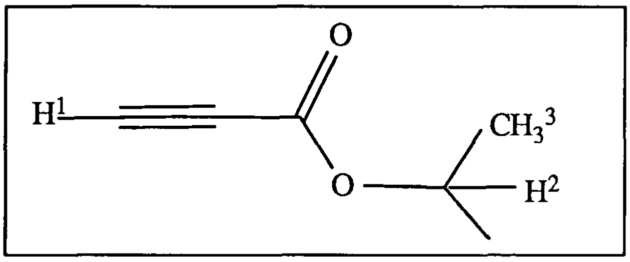
a- Combustion analysis: calculated for $C_6H_8O_2$; C,64.30%; H, 7.30%: found C, 64.80%; H, 7.57%.

b- Gas Chromatography (GC) indicated >99% purity.

c- The infra red spectrum (Appendix 3-1) was consistent with the designated structure. Characteristic bands were: ν (Thin film)/cm^{-1}: 3260 (acetylenic CH), 2980, 2960 (aliphatic CH), 2120 (RC≡CH), 1715 (ester C=O).

d- The ^1H NMR spectrum (Appendix 3-2) provided good evidence of the desired structure.

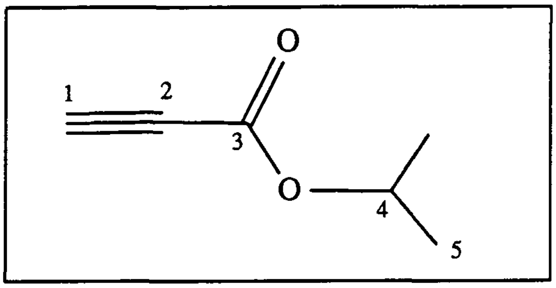
Figure 3.2.ii.



δ/ppm ($CDCl_3$): 1.22 (d,6H,H^3), 2.98 (s,1H,H^1), 5.00 (h,1H,H^2).

e- The ^{13}C NMR spectrum (Appendix 3-3) provided further evidence for the desired compound. The numbering scheme for the spectral assignment is shown overleaf.

Figure 3.2.iii.



δ/ppm ($CDCl_3$): 21.41 (C^5), 70.24 (C^4), 74.24 (C^1), 75.00 (C^2), 152.05 (C^3).

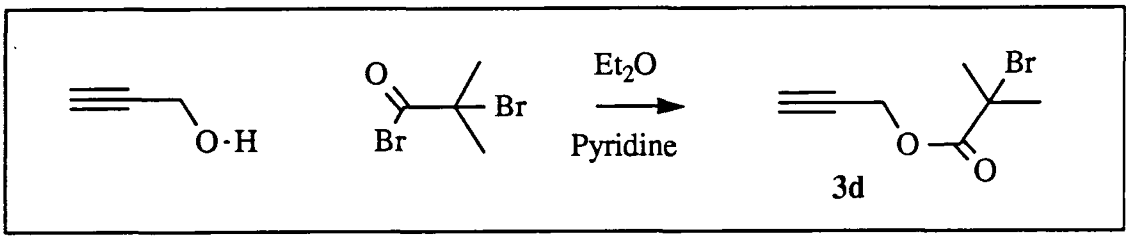
f- The mass spectrum (Appendix 3-4) showed a high intensity peak at m/e 130, corresponding to an MNH_4^+ ion resulting from attachment of the ionising ammonia gas. Electron impact (EI^+) gave a low intensity MH^+ peak at m/e 113, and a fragment ion corresponding to loss of a methyl group.

m/e: 130 (MNH_4^+,7.25,CI^+), 113 (MH^+,1.87,EI^+), 97 (M-Me,17.27), 53 ($HC\equiv CCO$,100).

3.2.iii. Preparation of Prop-2-yne-1-yl(2-bromo-2-methyl)propanoate

This monomer (**3d**, named in Chemical Abstracts as 2-propyn-1-ol,2-bromo-2-methylpropyl ester) was prepared as described by Leudke and Timberlake[120].

Figure 3.2.iv.



Experimental

N.B. The product of the reaction (3d) is a severe irritant causing painful skin burns on contact, and in common with both reagents, is a powerful lachrymator. In addition, 2-propyn-1-ol is extremely toxic, and thus the experiment should be carried out with due caution.

2-Propyn-1-ol, and 2-bromo-isobutyrylbromide were used as supplied by Aldrich. Diethyl ether was distilled, dried over sodium wire and then refluxed over lithium tetrahydroaluminate. Pyridine was distilled from sodium hydroxide pellets onto fresh molecular sieves.

Procedure

2-Bromo-isobutyrylbromide (51.5g, 0.225mol), in dry diethyl ether (100ml), at 0°C under nitrogen, was added slowly to 2-propyn-1-ol (15.0g, 0.225mol), and pyridine (21.5g, 0.225mol), in dry diethyl ether (100ml). The mixture was allowed to reach room temperature and react overnight. The contents were then washed with water (3x100ml), saturated aqueous sodium bicarbonate solution (3x100ml), hydrochloric acid (5%, 3x100ml) and saturated sodium chloride solution (3x100ml), followed by drying over magnesium sulphate. Evaporation of solvent gave a yellow liquid, mass 42g (≈ 92%).

3.2.iv. Results: 2-propyn-1-yl-(2-methyl-2-bromo-propanoate)

The product was distilled under reduced pressure (88°C, 20mm Hg; 86-90°C lit.[120]) to give a clear, colourless liquid (40.74g, 90%).

Characterization of **3d**

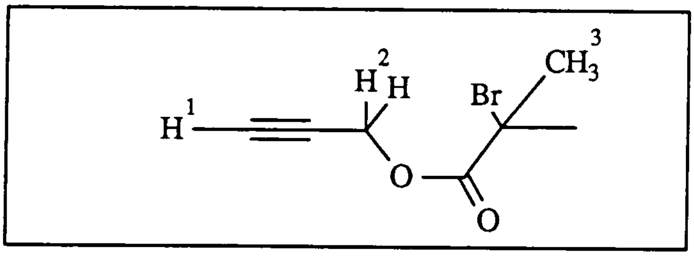
a- Combustion analysis gave the following: calculated for $C_7H_9BrO_2$; C, 40.52%; H, 4.39%; Br 39.02%: found C, 40.90%; H, 4.41%; Br, 40.81%.

b- Gas Chromatography (GC) indicated >99% purity.

c- The infra red spectrum (Appendix 3-5) was consistent with the designated structure. Characteristic bands were: ν (Thin film)/cm^{-1}: 3290 (acetylenic CH), 3000, 2980, 2960 (aliphatic CH), 2130 (RC≡CH), 1740 (ester C=O).

d- The ^{1}H NMR spectrum (Appendix 3-6) provided good evidence of the desired structure.

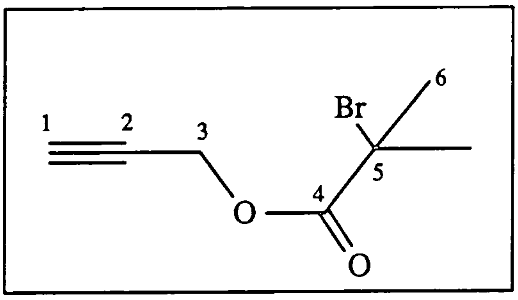
Figure 3.2.v.



δ/ppm (CDCl$_3$): 1.98 (s,6H,H^3), 2.52 (m,1H,H^1), 4.72 (d,2H,H^2).

e- The ^{13}C NMR spectrum (Appendix 3-7) provided further evidence for the desired compound.

Figure 3.2.vi.



δ/ppm ($CDCl_3$): 30.45 (C^6), 53.42 (C^3), 54.95 (C^5), 75.53 (C^1), 76.95 (C^2), 170.80 (C^4).

f- The mass spectrum (Appendix 3-8) showed two medium intensity peaks at m/e 224 and 222, corresponding to the MNH_4^+ ions resulting from attachment of the ionising ammonia gas. These peaks were in the required ratio for the ^{81}Br and ^{79}Br isotopic abundances. The peak at m/e 144 was possibly due to loss of HBr from the MNH_4^+ fragment. Further loss of NH_4^+ gave the ion at m/e 125.

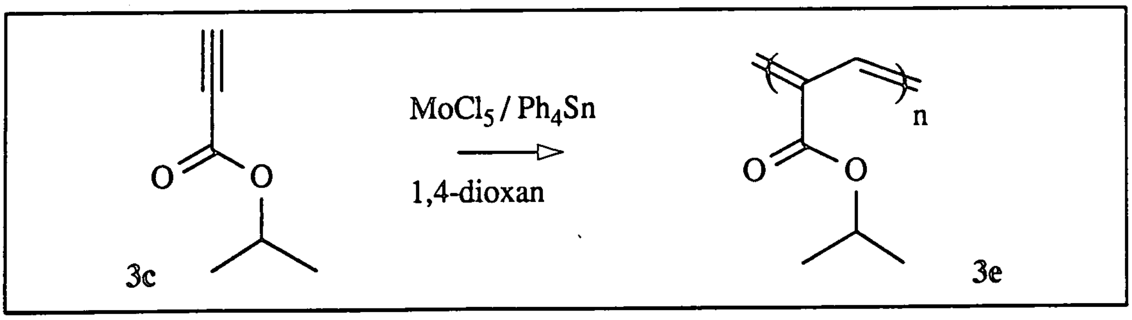
m/e: 224 (MNH_4^+,1.94,^{81}Br,CI^+), 222 (MNH_4^+,1.84,^{79}Br), 125 (M-Br,8.79).

3.3. POLYMERIZATION STUDIES

3.3.i. Polymerization of (1-Methylethyl)prop-2-ynoate (3c)

The method followed was an adaptation of that used by Masuda to polymerize the methyl ester of propiolic acid[121], as this polymer 3e had not hitherto been prepared.

Figure 3.3.i.



Experimental

The monomer was redistilled onto fresh molecular sieves, vacuum transferred, and degassed by several freeze-thaw cycles prior to use. Molybdenum (V) chloride and tetraphenyltin were used as received from Aldrich (99.99% pure). 1,4-Dioxane was distilled over sodium in the presence of benzophenone under nitrogen, and collected when the deep blue colour of sodium benzophenone ketyl persisted. All other solvents were redistilled and degassed by at least two freeze-thaw cycles before use. In general, the catalyst and co-catalyst were mixed until a deep red colour was produced, and then transferred by canulla wire into the monomer solution. The work-up procedure involved addition of acetone (1ml), precipitation in hexane, filtration of solid, resolvation in tetrahydrofuran, and reprecipitation in hexane/diethyl ether. All these procedures were carried out under a nitrogen atmosphere, in glassware assembled hot, evacuated, and purged with a dry nitrogen flow.

Table 3.3.i. Polymerization Conditions

The catalyst/co-catalyst ratio was kept constant at 1:1, and the solvent used throughout was 1,4-dioxan.

Mon.(mmol)	Cat.(mmol)	Temp.(°C)	Time	Yield(%)
10	0.10	25	4h	0.4
10	0.10	60	24h	<1
50	0.50	60	120	3.6
40	0.10	25	120	4.4

The yield quoted is that for material precipitated from hexane; in each case a brown oil was obtained in almost quantitative yield by evaporation of hexane, which was shown by GPC to be of low molecular weight.

3.3.ii. Results: Poly((1-methylethyl)prop-2-ynoate) 3e

The polymer was a brown powdery solid, soluble in tetrahydrofuran, chloroform and dichloromethane.

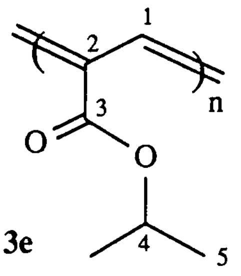
a- Combustion analysis: calculated for $C_6H_8O_2$; C, 64.30%; H, 7.30%: found C, 64.45%; H, 7.61%.

b- Gel Permeation Chromatography (GPC) indicated a highly disperse material with molecular weight of ~10,000.

c- The infra-red spectrum (Appendix 3-9) showed the following diagnostic bands:_v (KBr disc)/cm^{-1}: 3080 (alkenic CH), 2990 (aliphatic CH), 1710 (ester C=O), 1610 (C=C).

d- The ^{13}C NMR spectrum (Appendix 3-10) was very poorly resolved. Assignment was by comparison with the monomer spectrum.

Figure 3.3.ii.



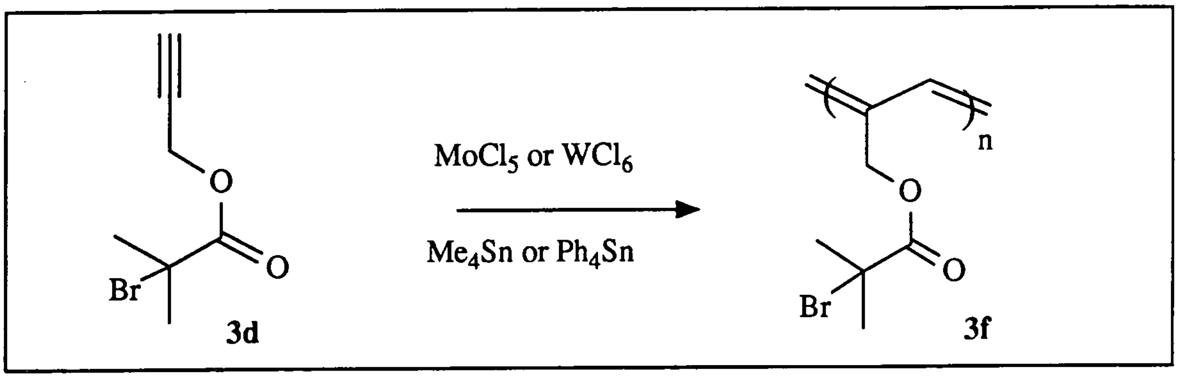
3e

δ/ppm ($CDCl_3$): 21.7 (C^5), 69.3 (C^4), 128-137 ($C^{1,2}$), 164-166 (C^3). The above data showed no bands associated with acetylene moieties, and contained alkenic C=C bonds in a number of environments.

3.3.iii. Polymerization of (Prop-2-yne-1-yl)2-bromo-2-methylpropanoate 3d

The general methodology for the production of this new polymer (3f) was in accordance with that described by Masuda[121], for the polymerization of substituted acetylenes.

Figure 3.3.iii.



Experimental

The monomer was redistilled under nitrogen onto fresh 4A molecular sieves and vacuum transferred prior to use. The catalyst system and solvents were prepared as described in section 3.3.i.

All reactions were carried out under nitrogen using dried glassware, to prevent oxygen or moisture contamination.

Procedure

A range of experimental conditions were employed: the procedure below gave the best results.

Tungsten (VI) chloride (39.6mg, 0.1mmol) in dry chlorobenzene (1ml) was added dropwise to tetramethyltin (35.6mg, 0.2mmol) in chlorobenzene, and the solution was stirred for 20 minutes to generate active catalyst. A solution of (prop-2-yne-1-yl)2-bromo-2-methylpropanoate (3d) (3.29g, 10mmol) in chlorobenzene (5ml) was stirred rapidly at 60^{0}C as addition of the catalyst took place via canulla wire. After 48 hours at 60^{0}C, the reaction was terminated by addition of acetone (1ml). Precipitation in hexane recovered the polymer (3f) as a brown solid.

3.3.iv. Results: Poly((prop-2-yne-1-yl)2-bromo-2-methylpropanoate 3f

The best yield obtained was less than 5%. Combinations of WCl_6 or $MoCl_5$ with either Ph_4Sn, or Me_4Sn, in 1,4-dioxane or chlorobenzene, failed to effect any improvements.

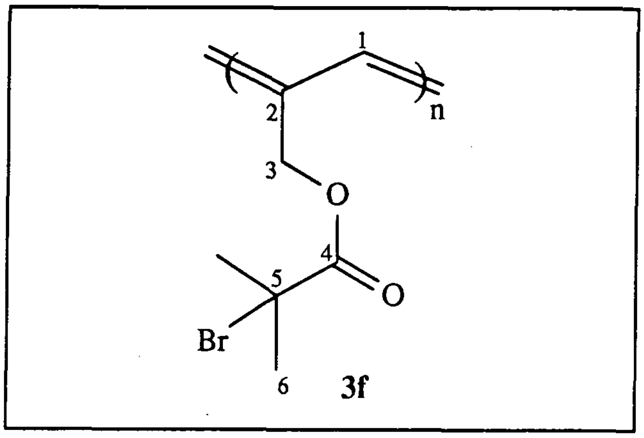
a- Combustion analysis indicated that catalyst residues remained in the polymer: Calculated for $C_7H_9BrO_2$; C, 40.52%; H, 4.39%; Br 39.02%: Found C, 35.50%; H, 4.80%; Br, 38.62%; W, 4.54%.

b- Gel Permeation Chromatography (GPC) indicated a molecular weight of ~10,000.

c- Infra-red spectroscopy (Appendix 3-11) showed the following bands: ν (KBr disc)/ cm^{-1}: 3020 (alkenic CH), 1740 (ester C=O), 1620 (C=C).

d- The ^{13}C NMR spectrum (Appendix 3-12) was assigned by comparison with the monomer. The numbering scheme for spectral assignment is shown overleaf in figure 3.3.iv.

Figure 3.3.iv.



3f

δ ($CDCl_3$)/ppm: 30.7 (C^6), 53.5 (C^3), 55.7 (C^5), 128-129 ($C^{1,2}$), 171.7 (C^4).

The monomer appeared to deactivate the catalyst, since addition of catalyst and monomer to norbornene failed to polymerize norbornene, whereas the same batch of catalyst on its own effected norbornene polymerization instantly. Preliminary experiments with the well-defined metathesis catalysts $(t\text{-}BuO)_2Mo(NAr)(CH\text{-}t\text{-}Bu)$ and $(t\text{-}BuO)_2W(NAr)(CH\text{-}t\text{-}Bu)$ also resulted in deactivation of the metal carbene centres.

CONCLUSIONS

These preliminary experiments allowed experience to be gained of metathesis polymerization techniques, but the yields obtained were too low to carry out any subsequent reactions to generate radical centres. The reasons for the low yields probably lay in the nature of the functional groups on the monomers. In the case of **3c**, the carbonyl function directly attached to the acetylenic bond may have coordinated to the catalyst, whereas in **3d**, the C-Br bond was probably attacked by the catalyst, resulting in each case in catalyst deactivation.

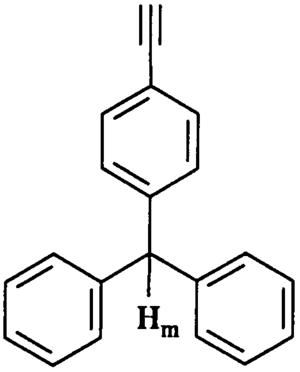
CHAPTER FOUR

PREPARATION
AND
CHARACTERIZATION
OF
(4-ETHYNYLPHENYL)DIPHENYLMETHANE
AND
PRECURSORS

Introduction

This chapter describes the synthesis of a new acetylenic monomer. The target monomer was (4-ethynylphenyl)diphenylmethane (**4a**) which offered several potential advantages over the compounds described previously (Chapter 3). In particular, this compound contained no functional groups likely to deactivate metathesis catalysts. In addition, conjugated polymers made from this substituted acetylene might give access to stable polyradicals through removal of the methine proton (H_m below) in the repeat unit.

Figure 4.1.i.



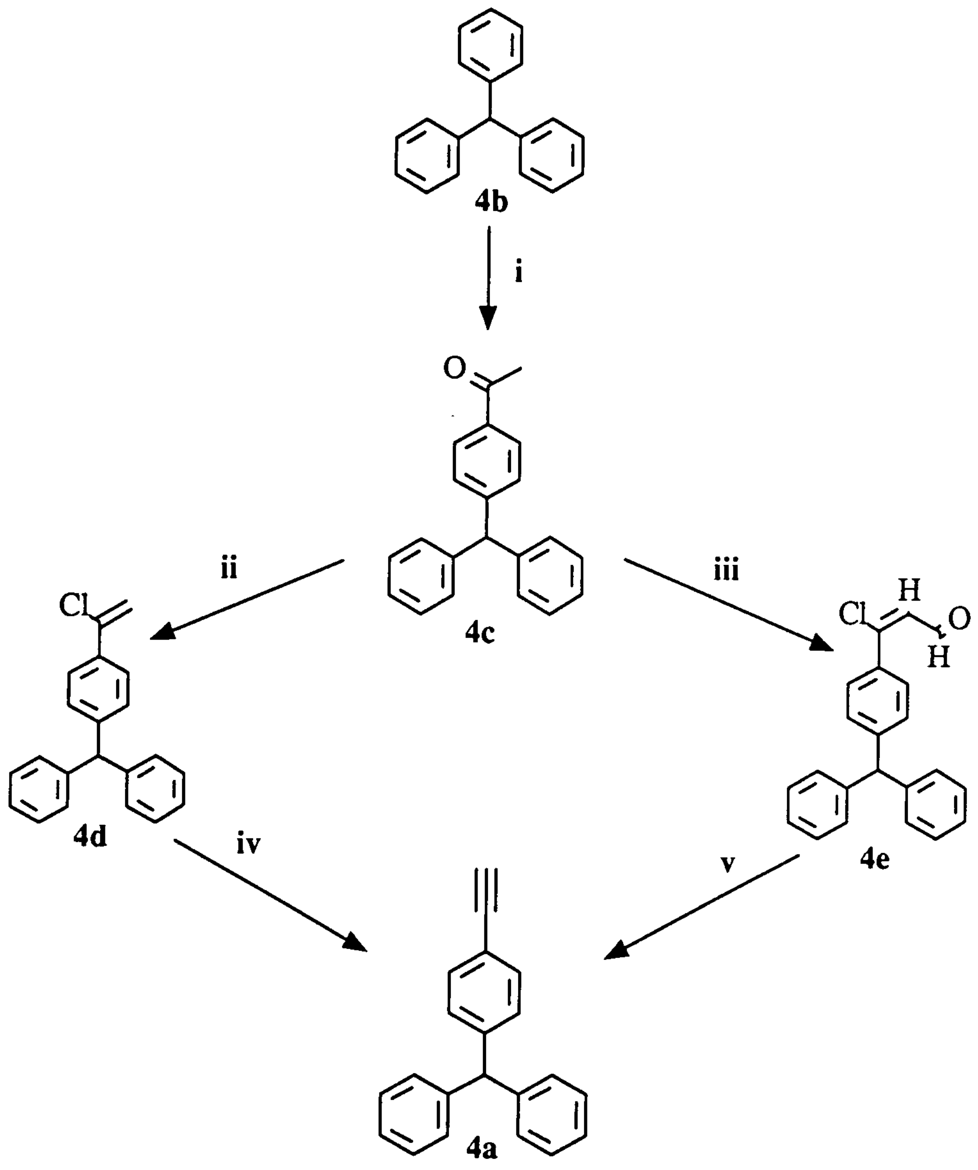
4a

(4-ethynylphenyl)diphenylmethane

The resultant triphenylmethyl radicals, attached to the conjugated backbone, might be more stable than their monomeric counterparts because the steric hindrance associated with a stiff polymer chain, might inhibit their dimerization. The generation of the radical centre could be via photochemically promoted hydrogen abstraction, or radical bromination followed by a one electron reduction by zinc metal. The method chosen would be dependent on whether the conjugated polymer had a suitable "absorption window" for UV radiation, and on the stability of the polymer to radical reagents. Clearly, these factors could not be evaluated until the polymer had been prepared: however, the synthesis and polymerization of the monomer would provide a useful set of standards, in terms of reference spectra, for comparison with known materials such as poly(phenylacetylene), and related conjugated polymers.

There are several routes by which **4a** might be synthesised; the two which we chose to investigate are summarized overleaf in Figure 4.1.ii.

Figure 4.1.ii.



Reagents and Conditions

i- $AcCl/AlCl_3$ **ii-** PCl_3/PCl_5 **iii-** $POCl_3$/DMF **iv-** $K^+t\text{-}BuO^-$ **v-** KOH

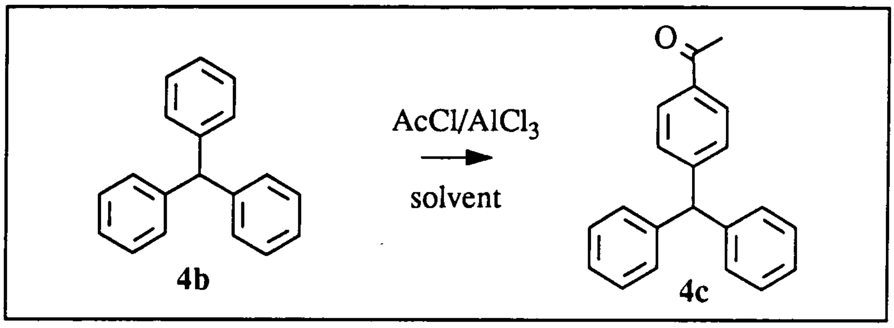
For each of the above routes, the key intermediate is the previously unreported compound (**4c**), (1-(4-diphenylmethyl)phenyl)ethanone.

4.2. Experimental

4.2.i. Preparation of (1-(4-Diphenylmethyl)phenyl)ethanone 4c

The synthesis involved the Friedel-Crafts mono-acylation of triphenylmethane.

Figure 4.2.i.



Experimental

Triphenylmethane was recrystallised from methanol to constant melting point (92°C), and all other reagents were used as supplied (98% purity) from BDH.

Procedure 1

Triphenylmethane (97.6g, 0.4mol) was dissolved in nitrobenzene (700ml), and acetyl chloride (31.2g, 0.4mol) was added dropwise with stirring. The temperature was maintained below 0°C and a nitrogen flow maintained, as powdered aluminium chloride (60g, 0.46mol) was added, in small portions, with vigorous stirring. After complete addition of aluminium chloride the reaction was continued for 6 hours at the same temperature, before pouring onto crushed ice acidified with hydrochloric acid. The layers were separated, and the organic layer washed with water, (3x200ml), saturated sodium bicarbonate (3x200ml), and water again (3x200ml), before drying over magnesium sulphate.

Nitrobenzene was removed by distillation under reduced pressure (b.p.95-100^{0}C/10mmHg), and the residual orange oil obtained decolourised six times with charcoal in boiling methanol. Unreacted triphenylmethane was removed by fractional crystallization from methanol, and the desired product recovered by evaporation of methanol followed by recrystallisation from amixture of petrol (b.p. 60-80°C) and acetone (10:1).

Procedure 2

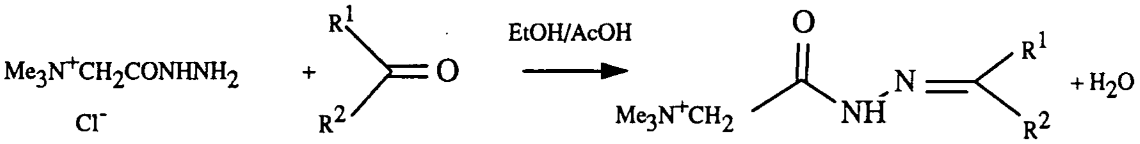
The high toxicity of nitrobenzene, and the difficulty of solvent removal upon completion of the reaction, combined with the low yields (~40%), led to attempts to find a better solvent system.

Cyclohexane as solvent gave only tarry, insoluble products.

Dichloromethane, used at reaction temperatures below -5°C, gave yields of ~65%, but the desired product was contaminated with diarylmethanes and other solvent alkylation products. Thin layer chromatography (TLC), using alumina plates (Merck; elution with hexane/acetone (5:1 v/v)) showed the presence of at least eight resolvable components. Separation by column chromatography using neutral alumina (Merck, Brockmann Grades II-III), with elution by hexane, followed by hexane/acetone (10:1 v/v) yielded the desired component as a colourless oil, which solidified on standing.

Considerable effort was expended to find the best purification method, as the use of column chromatography was time-consuming and impractical for the recovery of the desired compound on the scale required (i.e. more than 100g).

An alternative method of purification employed the Girard "T" reagent, trimethylaminoacetohydrazide chloride. This forms water-soluble hydrazone salts with ketones allowing their ready separation from other organic residues.



Impure (4-diphenylmethyl)phenylethanone (75g, 260mmol) was dissolved in absolute ethanol (750ml) and acetic acid (75ml). Girard "T" reagent (50g, ~10% excess) was added and the mixture refluxed slowly for one hour. After cooling, aqueous sodium bicarbonate (30% w/v, 3l) was added to neutralise 90% of the acid present, and reduce the ethanol concentration to below 20% of the total solution volume.

Exhaustive extraction with diethyl ether removed the non-ketonic compounds, and the ketone was liberated from solution by decomposing the hydrazone salt with aqueous acid to bring the total acid concentration to 0.5M. Extraction of the acidified solution with diethyl ether followed by washing the ether layers with sodium bicarbonate (3x300ml), water (3x300ml) and drying over $MgSO_4$, gave, after solvent evaporation, the product as a white powder, m.p. 90°C.

4.2.ii. Results: *(1-(4-Diphenylmethyl)phenyl)ethanone* (4c)

The best yields obtained for the pure product were 40% for procedure 1, and 60% for procedure 2.

Characterisation of **4c**

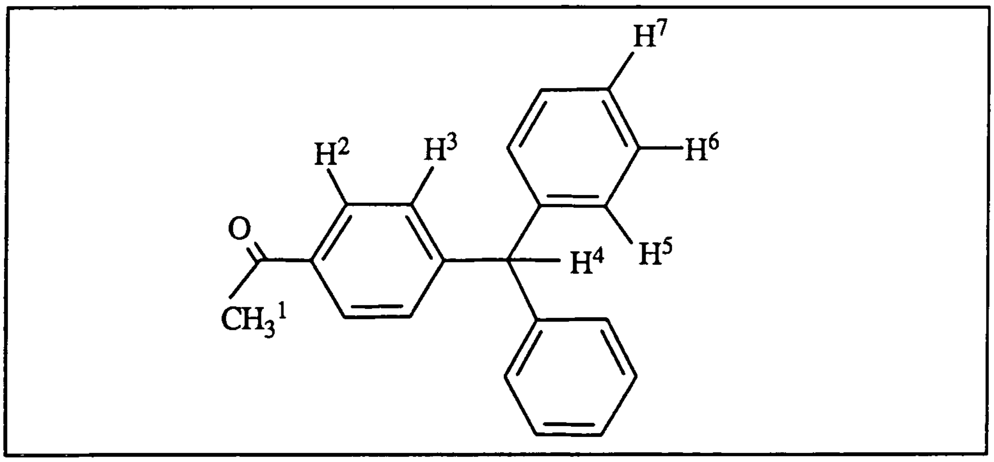
a- Combustion analysis was satisfactory: calculated for $C_{21}H_{18}O$; C, 88.08%; H, 6.33%; found C, 88.41%; H, 6.34%.

b- Chromatography indicated one component: R_f Neutral alumina; elution with hexane/acetone (10:1) 0.60.

c- The infra-red Spectrum (Appendix 4-1) was consistent with the assigned structure. Diagnostic bands were: v (KBr disc)/cm^{-1}; 3060,3020,3000 (aromatic CH), 2920,2860 (aliphatic CH), 1690 (C=O), 1600, (C=C).

d- The ^1H NMR spectrum (Appendix 4-2) provided good evidence of the designated structure. The observed resonances are assigned as shown in figure 4.2.ii.

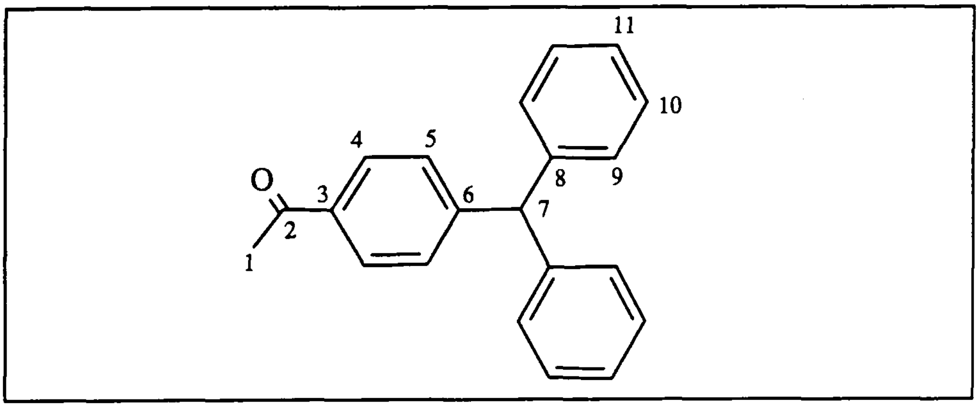
Figure 4.2.ii.



δ/ppm (C_6D_6): 2.46 (s,3H, H^1), 5.50 (s,1H,H^4), 6.99-7.79 (m, 14H, $H^{2,3}$,H^{5-7}).

e- The ^{13}C NMR spectrum (Appendix 4-3) gave further evidence for the structure as shown; the tabulated assignments being supported, in part, by APT spectra and by analogy with known compounds. Problems with a new probe on the spectrometer at the time the spectra were recorded led to an inversion of phase for the methyl carbon C^1. The assignment scheme for these resonances is shown in figure 4.2.iii.

Figure 4.2.iii.



δ/ppm (C_6D_6): 26.48 (C^1), 56.72 (C^7), 126.55 (C^9), 128.36, 128.40, 129.29, 129.58 (C^4,C^5,C^{10},C^{11}), 135.30 (C^3), 142.90 (C^8), 149.44 (C^6), 197.62 (C^2).

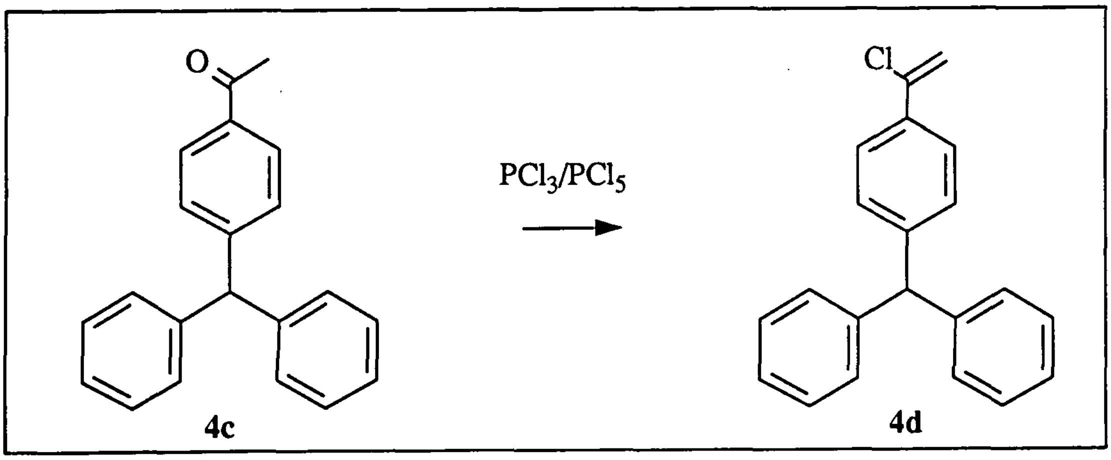
f- The mass spectrum (Appendix 4-4) displayed a molecular ion which was also the base peak, and two major fragmentation routes commensurate with the loss of CH_3CO and C_6H_5 moieties.

m/e: 286 (M^+, 100.0), 243 (M-MeCO, 80.6), 209 (M-Ph,17.8).

4.2.iii. Attempted Synthesis of ((4-Diphenylmethyl)phenyl)-1-chloro-ethene

The synthesis of this material ((**4d**), also previously unreported), was attempted several times using a range of different temperatures and reaction times, all without success. The method employed was a variation on a standard literature procedure[122]:

Figure 4.2.iv.

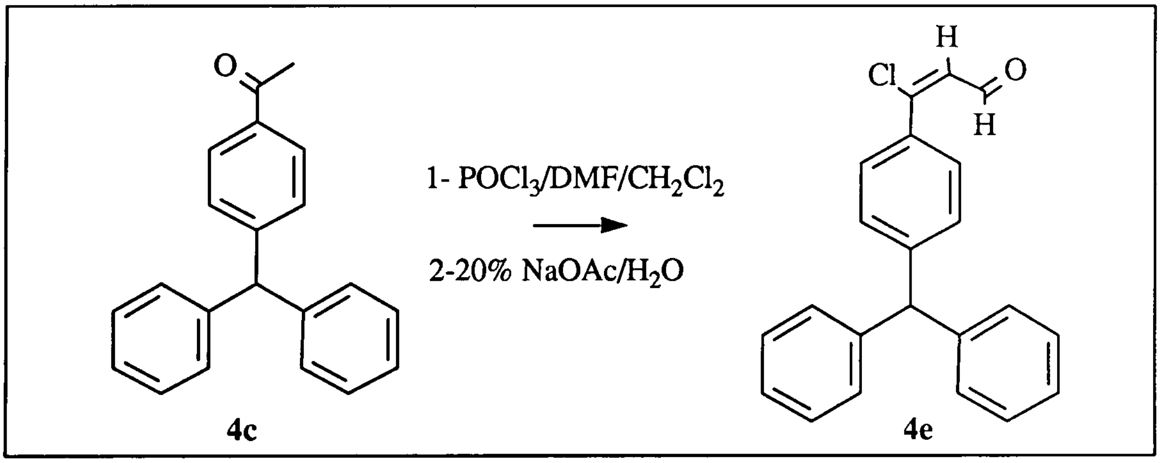


The reaction failed to yield the desired product due possibly to a fault in the nitrogen supply to the laboratory at the time, or degradation during column chromatographic workup, resulting in the hydrolysis of the moisture-sensitive phosphorus reagents, and/or the product. This route was abandoned in favour of the second scheme, which employed less severe reaction conditions in the second stage of the synthetic sequence. An additional factor in the decision to change the route was the potential disadvantage of using potassium t-butoxide to generate the acetylene from **4d**. The dehydrochlorination of the intermediate using such a strong base might have led to side reactions, such as the removal of the methine proton and the subsequent production of tarry residues. Thus, the second scheme appeared to offer the advantages of milder conditions and hence the prevention of impurity materials contaminating the products.

4.2.iv. Preparation of 3-Chloro-(3-(4-diphenylmethyl)phenyl)prop-2-enal (4e)

The method employed, as this compound was previously unreported, was an adaptation of that used by Huang and Marvel[123], for the preparation of precursors to ethynyl-tipped polymers. The Vilsmeier reagent used was prepared *in situ* by reaction of phosphorus oxychloride and dimethylformamide.

Figure 4.2.v.



Experimental

Phosphorus oxychloride as supplied by Aldrich, was degassed and stored under nitrogen.

N,N-dimethylformamide was dried by azeotropic distillation with benzene, followed by passage through neutral alumina (Grade 1 Aldrich), and distillation under nitrogen at reduced pressure (b.p. 76°C/39mm Hg), onto fresh 4A molecular sieves. Dichloromethane was passed through neutral alumina (Grade 1 Aldrich) and distilled onto fresh 4A sieves. Both solvents were stored under a dry nitrogen atmosphere. (4-Diphenylmethyl)phenylethanone was used as prepared above.

Procedure

Phosphorous oxychloride (19.57ml, 210mmol) was added dropwise to N,N-dimethylformamide (35ml, 600mmol) over two hours, under nitrogen at 0°C, with vigorous stirring.

A solution of (4-diphenylmethyl)phenylethanone (20.0g, 70mmol) in dichloromethane (200ml) was added dropwise over one hour and the reaction allowed to proceed for twelve hours at room temperature, before pouring into aqueous sodium acetate (20%, 200ml). The aqueous layer was extracted with dichloromethane (100ml), and the combined organic layers washed with water (4x200ml), before drying over magnesium sulphate. Solvent evaporation yielded yellow waxy crystals, which were recrystallised from petrol(b.p. 60-80°C)/acetone (10:1).

4.2.v. Results: *3-Chloro-(3-(4-diphenylmethyl)phenyl)prop-2-enal* 4e

The yield after several recrystallisations was 16.6g (71%), of light yellow needles m.p. 115-117°C. The product, which decomposes rapidly at room temperature due to loss of HCl, was stored under nitrogen at -20°C.

Characterization of 4e

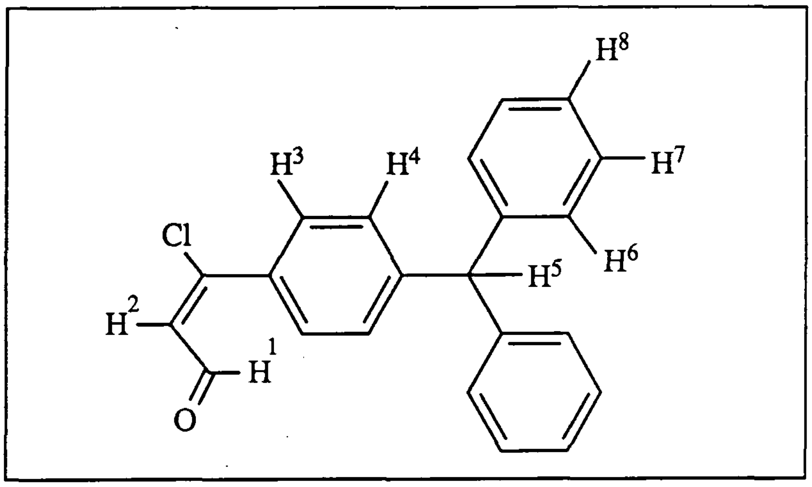
a- Combustion analysis indicated some decomposition, with the best results being: calculated for $C_{22}H_{17}ClO$; C, 79.39%; H, 5.15%; Cl, 10.65%: found; C, 79.61%; H, 4.88%; Cl, 9.77%.

b- Chromatography showed one component; R_f neutral alumina; elution with hexane/acetone (10:1) 0.64.

c- The infra-red spectrum (Appendix 4-5) was consistent with the assigned structure. ν (KBr disc)/cm^{-1}; 3060,3020 (aromatic CH), 2920 (aliphatic CH), 2720, (aldehydic CH),1670 (α-β unsaturated C=O), 1600, (C=C ring).

d- The ^{1}H NMR spectrum (Appendix 4-6) also indicated the correct structure:

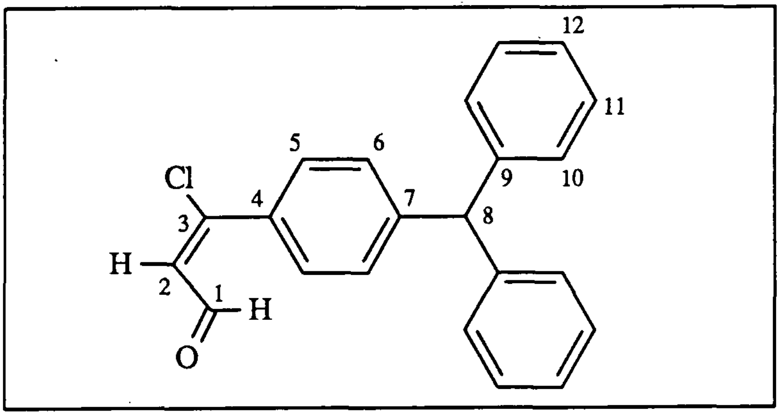
Figure 4.2.vi.



δ/ppm (C_6D_6): 5.72 (s,1H, H^5), 6.66-6.68 (d,1H,H^2), 7.23-7.81 (m, 14H, $H^{3,4}$,H^{6-8}), 10.21-10.22 (d,1H,H^1).

d- The ^{13}C NMR spectrum (Appendix 4-7) was consistent with the desired product, and a provisional assignment made with the aid of APT spectra and comparison with known compounds is given below:

Figure 4.2.vii.



δ/ppm (C_6D_6): 56.57 (C^8), 123.21 (C^2), 126.66, 127.17 (C^{10},C^{12}), 128.40, 129.30, 129.90, (C^5,C^6,C^{11}), 133.48 (C^4), 142.32, 148.43 (C^7,C^9), 151.96 (C^3), 191.32 (C^1).

This compound was probably produced as a mixture of *cis* and *trans* isomers, which,although not resolved into two components by TLC, might account for the presence of the extra peaks visible in the ^{13}C NMR spectrum. Clearly, the presence of an extra isomer would affect the resonances of the ring carbons to which the β-chloroaldehyde was attached, as well as changing the resonance positions of the substituent itself.

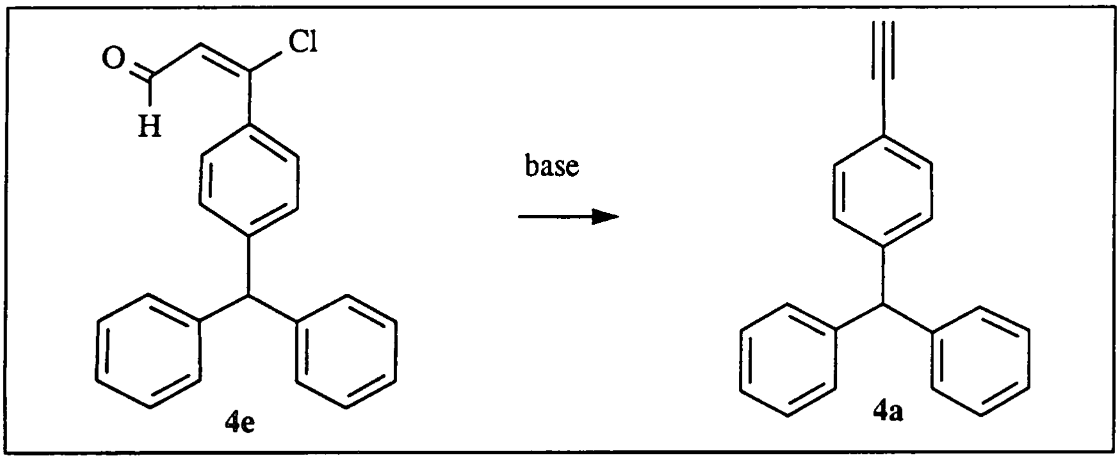
e- The mass spectrum (Appendix 4-8) confirmed the nature of the product, with an intense molecular ion and the expected M-H, and M-Cl fragment ions.

m/e: 335 (M$^+$, ^{37}Cl, 10.84, CI$^+$), 334 (MH$^+$ ^{35}Cl, or M-H ^{37}Cl,7.85), 333 (M$^+$ ^{35}Cl,31.54), 332 (M-H, ^{35}Cl, 3.20, CI$^-$), 299 (M-Cl, 2.5)

4.2.vi. Preparation of (4-Ethynylphenyl)diphenylmethane

The routes used were adaptations of those used by Huang and Marvel[123] and Bodendorf and Meyer[124].

Figure 4.2.viii.



Experimental

Initial attempts to produce the acetylene employed aqueous potassium hydroxide in mixed solvent systems and all such reagents were used as supplied (BDH and Aldrich). The use of potassium t-butoxide as the base required sodium-dried tetrahydrofuran as the solvent, and these reactions were carried out under a dry nitrogen atmosphere.

Procedure

The elimination reaction was performed typically as follows:

3-Chloro-(3-(4-diphenylmethyl)phenyl)prop-2-enal (2.0g, 6mmol) in THF (20ml) was stirred rapidly as potassium hydroxide (1.0g, three-fold excess) in aqueous methanol (75:25 v/v, (20ml) was added dropwise over one hour, at room temperature. The solution was then brought to reflux and reaction continued for three hours, with regular monitoring by TLC (alumina plates; elution with hexane/acetone (10:1)). The organic product was extracted into diethyl ether and the combined ether layers washed with aqueous HCl (1%, 20ml), sodium bicarbonate (10ml), and water (3x20ml), before drying over magnesium sulphate. The product was recovered by evaporation of the solvent.

Results

The product was recovered as a viscous brown oil, shown by TLC to contain starting material and two new products, one subsequently identified as the desired acetylene. The other component showed two strong infra-red absorptions at 2200 and 1670 cm^{-1}*, which were postulated to be due to an α-β acetylenic aldehyde, but the compound was not obtained in a sufficiently pure state to characterize fully. Efforts to prevent contamination of the product with starting material by increasing the reaction time invariably led to the production of tarry insoluble residues. The method shown above gave the best yields, although it should be mentioned that factors such as stirring speed and efficiency seemed to be critical.*

The table below gives the results of various attempts to produce the terminal acetylene using a combination of solvents, bases, and reaction conditions:. this table is presented solely to illustrate the difficulty in finding effective reaction conditions for this process.

Table 4.2.i.

Base	*Solvents*	*Time*	*Temp.(^0C)*	*Yield(%)*
KOH	$EtOH/H_2O/DMF$ 95:5:300	24h	25	3
KOH	$EtOH/H_2O/DMF$ 95:5:300	2h	25	3
KOH	$EtOH/H_2O/DMF$ 95:5:300	2h	0	3
K_2CO_3	$EtOH/H_2O/Et_2O$ 95:5:100	24h	0	1
KO^tBu	THF	20m	25	5
KO^tBu	THF	2h	25	5
KO^tBu	THF	1h	50	4
KOH	$THF/MeOH/H_2O$ 100:25:75	3h	80	60

The yields were not improved by changing the order of addition; i.e. adding the β-chloro-aldehyde to the base.

The initial products from all the above reactions were dark-brown oils, and considerable effort was expended in separating the materials, as TLC analysis indicated at least three different compounds on each occasion. Recrystallisation proved impossible from any solvent system tried (hexane, diethyl ether, dichloromethane, ethyl acetate, ethanol, methanol and combinations thereof), and repeated boiling with activated charcoal in methanol failed to effect decolourisation. Product purification thus required column chromatography.

The most effective stationary phase was found to be neutral alumina (Merck, Brockmann Grades II-III), and the eluants used were hexane/acetone (200:1). The products were loaded as solutions in dichloromethane onto the support (product:gel=1:5 w/w), and the solvent removed on a rotary evaporator, to leave a dry, loaded, gel which could be poured onto the top of the column to give an even layer. Elution and product isolation were carried out according to standard procedures.

The first product eluted from the column was the desired material, which, after evaporation of solvent, was obtained as a white oily solid. Recrystallization from methanol, gave small colourless prisms (m.p. 45^{0}C).

4.2.vii. Results: *(4-Ethynylphenyl)diphenylmethane* (4a)

Characterization of 4a

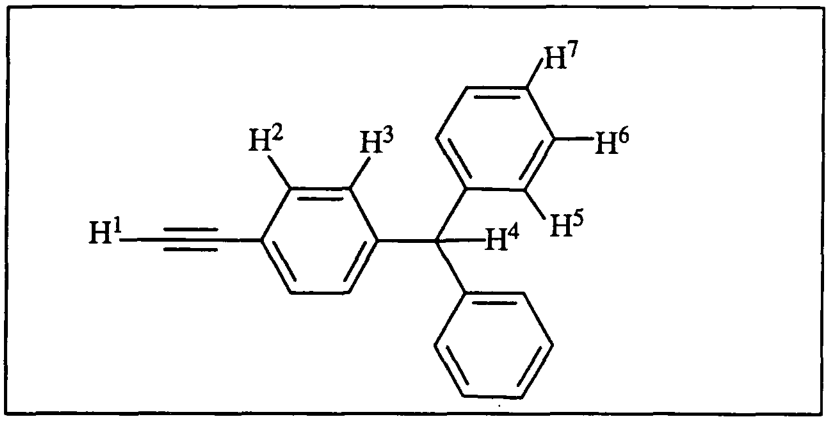
a- Combustion analysis was satisfactory: calculated for $C_{21}H_{16}$; C, 93.99%; H, 6.01%; found; C, 93.76%; H, 6.23%.

b- Chromatography indicated one component: R_f Neutral alumina: elution with hexane/acetone (10:1) 0.96.

c- The infra-red spectrum (Appendix 4-9) gave the following diagnostic bands: ν (KBr disc)/cm^{-1}; 3290 (acetylenic CH), 3060,3020 (aromatic CH), 2980 (aliphatic CH), 2110 (RC≡CH), 1600, (C=C).

d- The ^{1}H NMR spectrum (Appendix 4-10) was in agreement with the assigned structure: the numbering scheme for peak assignment is given overleaf in figure 4.2.ix.

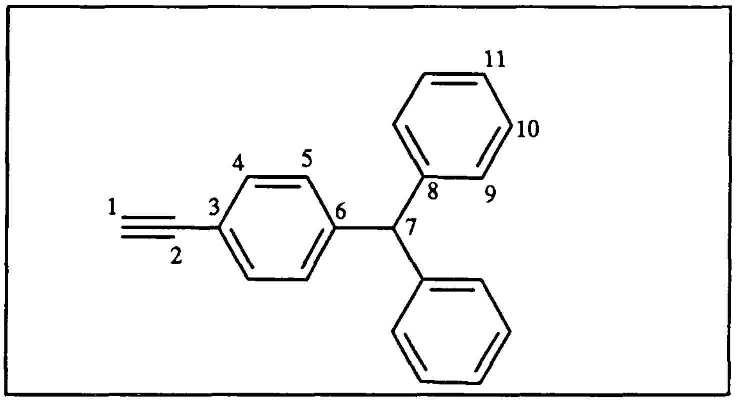
Figure 4.2.ix.



δ/ppm (C_6D_6): 2.70 (s,1H, H^1), 5.27 (s,1H,H^4), 6.84-7.35 (m, 14H, $H^{2,3}$,H^{5-7}).

e- The ^{13}C NMR spectrum (Appendix 4-11) provided further evidence for the structure below, with the assignments based on APT spectra and comparison with known compounds. The resonances for C^1 and C^2 were indistinguishable in the ^{13}C APT spectrum owing to problems with the spectrometer probe, but assignment was possible from peak heights in the proton-decoupled ^{13}C NMR spectrum.

Figure 4.2.x.



δ/ppm (C_6D_6): 56.90 (C^7), 77.63 (C^1), 83.82 (C^2), 120.69 (C^3), 126.63, 128.53, 128.60, (C^9,C^{10},C^{11}), 129.70 (C^5), 132.35 (C^4), 143.69 (C^6), 145.10 (C^8).

f- The mass spectrum (Appendix 4-12) showed a strong parent ion at m/e 268.

m/e: 268 (M^+, 94.23, EI^+), 267 (M^-,23.43, CI^-), 286 (MNH_4^+, (CI^+)

CONCLUSIONS

The desired monomer was produced by a three stage synthesis in a maximum yield of 25%, and three new triphenylmethane derivatives were prepared.

However, the monomer produced appeared to decompose rapidly in air, and even storage in a glove box at -20^{0}C in the dark resulted in slight decomposition over a period of three months. Thus it was decided to store the monomer as its precursor, carrying out the elimination reaction when required, ready for polymerization studies.

CHAPTER FIVE

PREPARATION AND CHARACTERIZATION OF (4-ETHYNYLPHENYL)DIPHENYLCHLOROMETHANE AND PRECURSORS

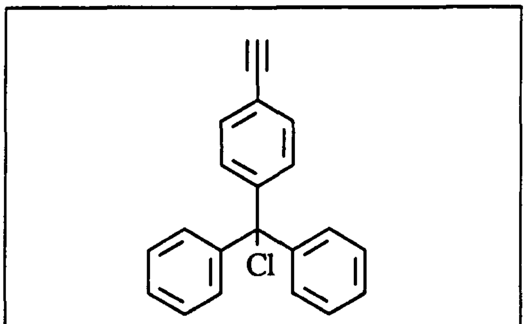
Introduction

The synthesis of a conjugated polymer with a triphenylmethyl radical substituent at each repeat unit in the chain required suitably derivatised monomers. The generation of the radicals could, in principle, be carried out either before, or after polymerization, if the radical centres were readily formed and sufficiently stable. However, the option of polymerization of ethynyl substituted triphenylmethyl radicals to give the conjugated "polyradical" was rejected owing to the possibilities of side reactions: for example it has been suggested[112] that phenylacetylene can polymerize via a radical mechanism. Therefore, the controlled polymerization of a free-radical substituted phenylacetylene was considered to be unlikely. Thus, it was decided that the preparation of the radicals should be carried out subsequent to polymerization.

The most suitable monomers were thought to be ethynyl substituted derivatives of triphenylchloromethane and triphenylmethanol. The acetylene bond provided the route to the conjugated polymer, and the chlorine and hydroxyl functionalities offered suitable means of generating free radical centres.

5.1. Synthetic Routes and Methodology

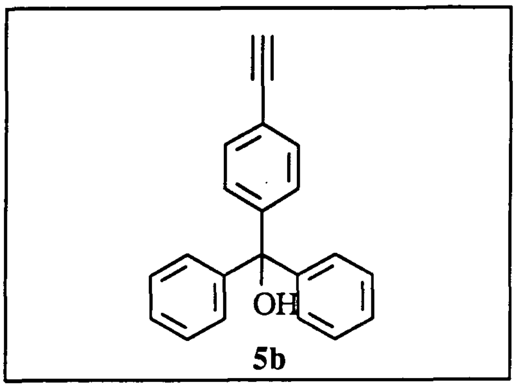
Figure 5.1.i. (4-Ethynylphenyl)diphenylchloromethane



5a

The polymerisation of this monomer was considered to be a route to the desired polyradicals, as the monomer contains a labile chlorine atom. The parent triphenylchloromethane is readily converted to the stable triphenylmethyl radical by reaction with metals, such as zinc, silver, or mercury, under dry, anaerobic conditions[125].

Figure 5.1.ii. (4-Ethynylphenyl)diphenylmethanol

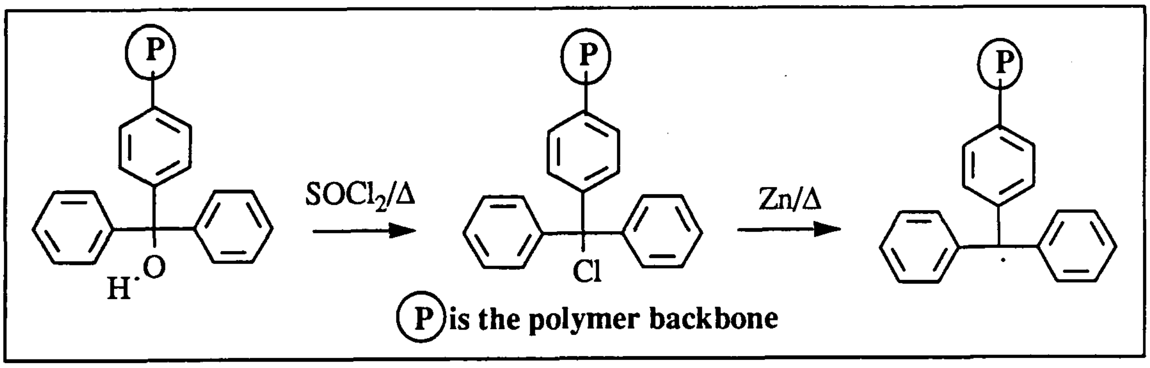


5b

Polymerization of this monomer (**5b**) was also regarded as a potential route to the desired polyradicals. It was hoped that the resulting conjugated polymer could be chlorinated to give the same material as that obtained by the polymerization of (**5a**) above.

The dechlorination reaction to produce the radicals could be the same for both polymers, and similar to standard methods for the generation of triphenylmethyl radical from triphenylchloromethane.

Figure 5.1.iii. Polymer Functional Group Interconversions



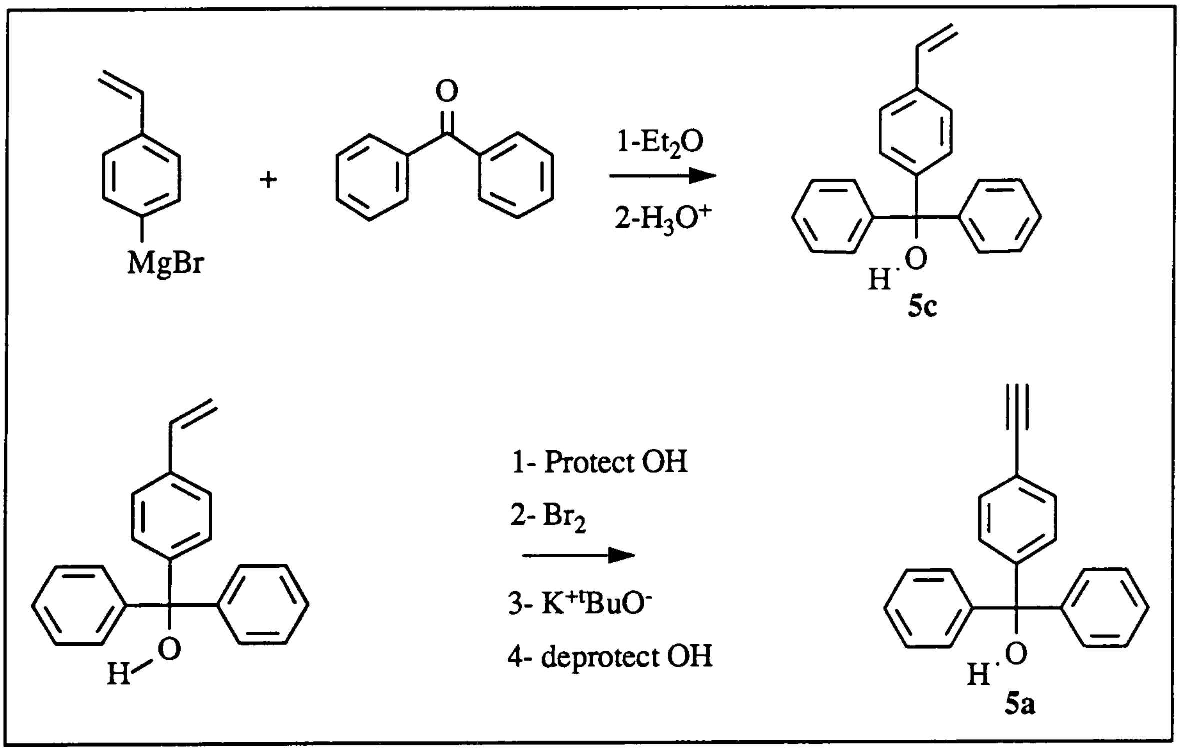
The desired monomers were not previously cited in the literature, and thus a synthetic strategy had to be devised. The facile nature of the chlorination reaction suggested that, if the triphenylmethanol derivative could be synthesized, then the triphenylchloromethane would readily follow. Thus, the first target was (4-ethynylphenyl)diphenylmethanol.

The most obvious route to triphenylmethanol derivatives appeared to be via Grignard type reactions on substituted benzophenones, of which many are available commercially as starting materials. The acetylenic function could be introduced subsequently, or could be protected during the Grignard reaction, to be de-protected at a later stage. In all, three routes were investigated.

Route 1

A disconnection approach indicated that the desired material could be obtained by the procedure outlined below, requiring five stages including the addition and removal of a protecting group.

Figure 5.1.iv.



5.2. Experimental

5.2.i. Preparation of (4-Ethenylphenyl)diphenylmethanol

This monomer was first prepared by Braun[46] but no experimental details were given concerning reaction conditions. Therefore, a typical Grignard procedure, as described by Vogel[126], was used with necessary modifications.

Experimental

4-Bromostyrene was distilled under nitrogen at reduced pressure (b.p. 89°C/2.5mmHg) and stored over fresh 4A molecular sieves. Diethyl ether (May and Baker "Pronalys" grade) was dried over sodium wire, and benzophenone and magnesium turnings were used as supplied by BDH.

Method

4-Bromostyrene (18.2g, 0.10mol) was added dropwise to magnesium turnings (2.5g, 0.11mol) in diethyl ether (50ml) to generate the Grignard reagent. Benzophenone (18.22g, 0.10mol) in diethyl ether (200ml) was added dropwise with rapid stirring to maintain a slow reflux, and the reaction was continued for 4 hours, before pouring into ice water/conc.HCl (100:2 v/v). The organic layer was washed with water (3x50ml), saturated sodium bicarbonate solution (3x50ml), and again with water (3x50ml), before drying over magnesium sulphate. Solvent evaporation yielded an orange oil (28g).

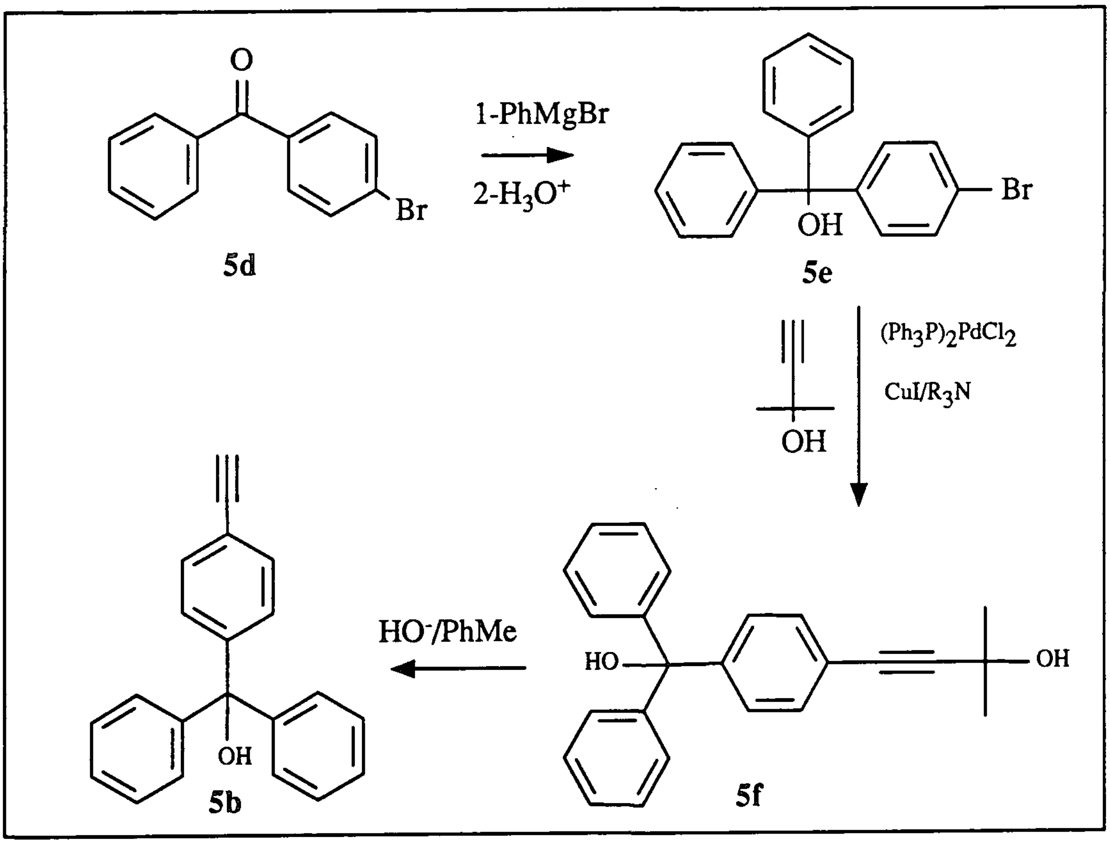
Results

IR spectroscopy showed a strong peak at 1670cm^{-1}, indicating contamination of the product with benzophenone. Removal of unreacted benzophenone was attempted using the Girard "T" reagent, by saturated sodium metabisulphite, and by reaction with 2,4-dinitrophenylhydrazine; none of these methods proved effective. The use of column chromatography was considered to be impractical for the separation of the desired material, since, as the compound was the first stage in a multi-step synthesis, large quantities were likely to be required. The difficulty of purification of the (4-ethenylphenyl)diphenylmethanol, combined with the low yields typically associated with the bromination/dehydrobromination step (~ 40%), and the number of steps in the synthesis, led to the abandonment of this route.

5.3. Synthetic Route 2

The second attempt to synthesize the above monomer was by a three-stage route, starting with a Grignard reaction of 4-bromobenzophenone with phenylmagnesium bromide, and introducing the triple bond as a protected acetylene via a palladium catalysed coupling reaction.

Figure 5.3.i.



5.3.i. Preparation of (4-Bromophenyl)diphenylmethanol

The method of Manning[127] was used without modification.

Experimental

Bromobenzene and 4-bromobenzophenone (Aldrich) were used without further purification. Magnesium turnings (BDH Grignard standard) were also used as supplied. Diethyl ether and benzene were both dried over sodium wire before use.

Procedure

A solution of bromobenzene (47.16g,31.63ml, 0.30mol) in diethylether (30ml) was added dropwise onto magnesium turnings (7.3g, 0.32mol) in diethyl ether (90ml) under a nitrogen atmosphere. 4-Bromobenzophenone (50.0g, 0.19mol) was dissolved in benzene (300ml), under nitrogen, and was stirred rapidly as the phenyl magnesium bromide solution was added dropwise. A red solution formed which deposited a white flocculent precipitate on stirring overnight. The reaction mixture was added to 3N H_2SO_4 *(200ml) and the aqueous phase extracted with benzene (3x50ml). The combined organic layer was washed with 5% sodium bicarbonate solution (200ml), and water (200ml), and dried over magnesium sulphate. Solvent evaporation gave an orange oil (56g ~87%), which was recovered from hexane/diethyl ether at* 0^0C *as a brown oily solid.*

5.3.ii. Results: (4-Bromophenyl)diphenylmethanol 5e

The compound proved impossible to recrystallise in any combination of solvents tried (hexane, carbon tetrachloride, diethyl ether, dichloromethane, acetone, methanol and water). Column chromatography on alumina (neutral, Grade 1) with diethyl ether/hexane (1:10) gave the product as a colourless oil (32g), which solidified after four weeks. Recrystallisation from petrol (b.p. 60-80^0C) gave large colourless prisms (14g) m.p. 95^0C (99-100^0C lit[127]).

Characterization of 5c

a- Combustion analysis: calculated for $C_{19}H_{15}BrO$: C, 67.27%; H, 4.46%; Br, 23.55%. found: C, 67.01%; H, 4.86%; Br, 23.17%.

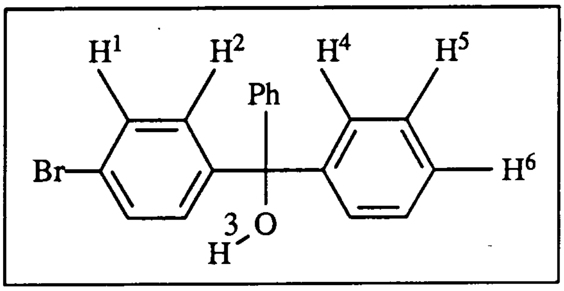
The elemental analyses and the melting point indicated trapping of solvent in the crystals, however the other data left no doubt as to the structure of the product.

b- Chromatography showed one component: R_f Neutral alumina; elution with hexane/acetone (10:1) 0.37.

c- The infra-red spectrum (Appendix 5-1) was consistent with the assigned structure. Diagnostic bands were: ν (KBr disc)/cm^{-1}; 3580,3480 (free, and H-bonded alcohol OH) 3060,3020,3000 (aromatic CH), 1600, (C=C).

d- The ^1H NMR spectrum (Appendix 5-2) gave good evidence for the designated structure. The numbering scheme for peak assignment is shown overleaf.

Figure 5.3.ii.

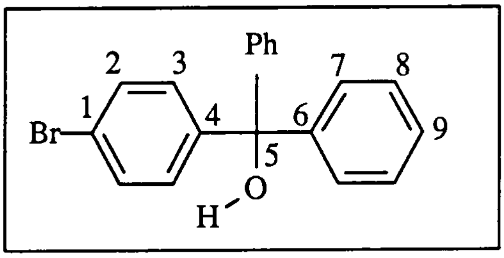


δ/ppm (C_6D_6): 2.80 (s, 1H, H^3), 7.10-7.96 (m, 14H, H^1,H^2, H^{4-6}).

The corresponding literature values were: δ/ppm, 2.80 (s,1H), 7.08-7.38 (m, 14H).

e- The ^{13}C NMR spectrum (Appendix 5-3) provided further evidence for the structure as shown. The tabulated assignments were supported, in part, by APT spectra and by analogy with known compounds. Observed resonances are assigned below: no literature values were given.

Figure 5.3.iii.



δ/ppm ($CDCl_3$): 81.67 (C^5), 121.33 (C^1), 127.45, 127.78, 128.02 (C^{7-9}), 129.69,(C^3), 130.93 (C^2), 145.83 (C^4), 146.32 (C^6).

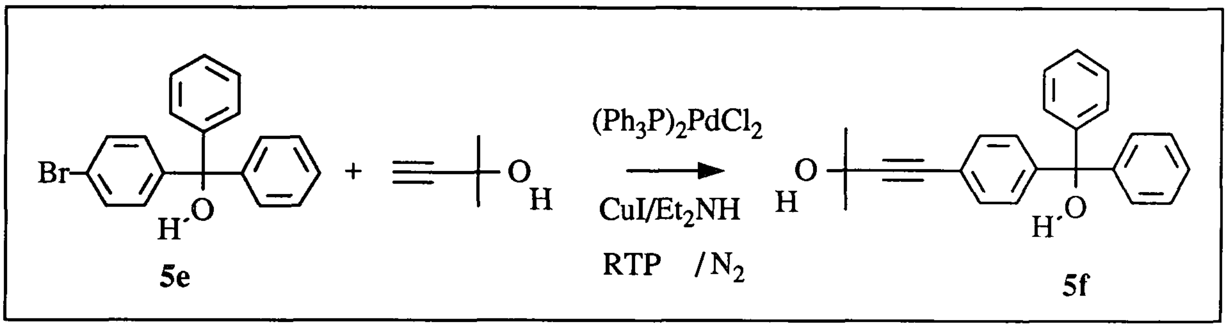
f- The mass spectrum (Appendix 5-4) displayed two molecular ion peaks of low intensity, containing the ^{81}Br and ^{79}Br isotopes in the correct ratio. Loss of the tertiary hydroxyl group gave base peaks at m/e 322 and 320. Loss of a phenyl group accounted for the peaks at m/e 263 and 261.

m/e: 340,338 (MH^+, 6.07,6.08, CI^+), 322,320 (M-OH, 99.0,100),
263,261 (M-Ph, 36.0,37.4).

5.3.iii. Attempted Preparation of (4-(2-Methyl-2-hydroxyl)but-3-ynylphenyl)diphenylmethanol (5f)

The method used to attempt to prepare this new compound was a variation of those used by Ames *et al.*[128] and Trumbo and Marvel[130] to prepare aryl acetylenes.

Figure 5.3.iv.



Experimental

All liquids were distilled and stored under a dry nitrogen atmosphere. 2-methyl-3-butyn-2-ol (Aldrich) was distilled onto fresh 4A molecular sieves; diethylamine (Aldrich) was distilled from solid KOH pellets and stored over fresh KOH. Bis(triphenylphosphine)palladium (II) chloride (Lancaster Synthesis) was stored and manipulated in a Dry Box; copper (I) iodide (Aldrich) was kept at all times in the dark both were used without further purification.

Procedure

2-Methyl-3-butyn-2-ol (1.47g, 17.5mmol) was mixed with diethylamine (50ml) and (4-bromophenyl)diphenylmethanol (5.00g, 14.8mmol) at room temperature, and dry nitrogen bubbled through the solution for 20 minutes.

Bis(triphenylphosphine)palladium (II) chloride (0.103g, 0.15mmol) and copper (I) iodide (0.014g, 0.075mmol) were added successively and the mixture stirred rapidly under nitrogen for 5 days. The diethylamine was then removed under reduced pressure, and water (30ml) added. Extraction of the water layer with diethyl ether (3x50ml), followed by washing of the organic layer with water (3x20ml), and passage of the ether solution through alumina (neutral, grade 1), gave, on solvent evaporation, a brown oily solid.

Results

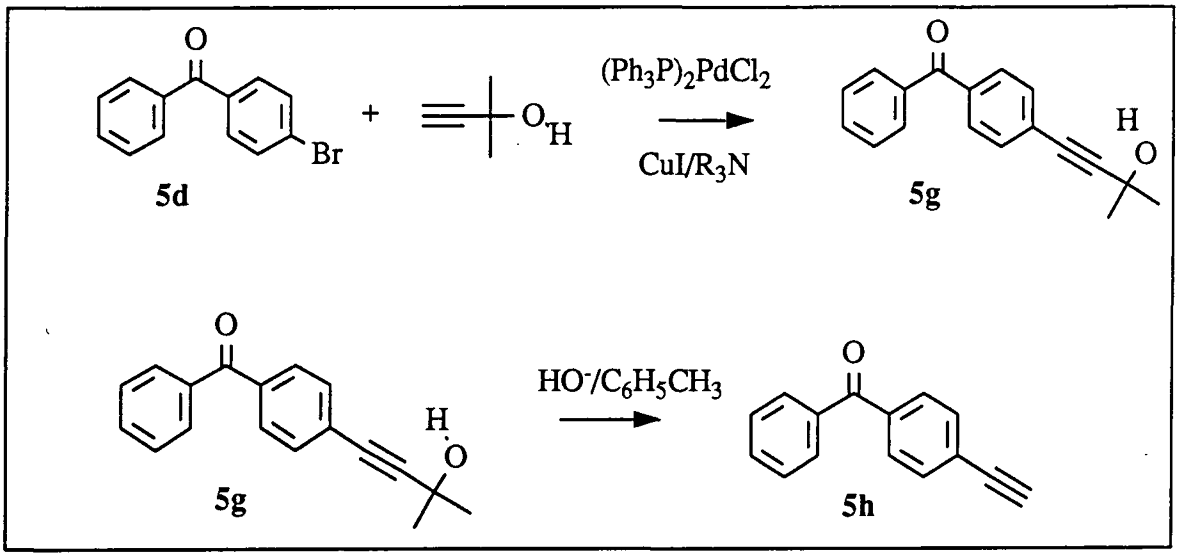
Successive recrystallisations from hexane/diethyl ether removed a white solid shown by IR to be the self-coupled product $HO\text{-}C(CH_3)_2C{\equiv}C\text{-}C{\equiv}C\text{-}C(CH_3)_2OH$. *Other material was recovered by column chromatography on alumina (neutral, grade1), and shown to be largely unchanged starting material, (4-bromophenyldiphenylmethanol).*

The reaction was repeated several times, with rigorous exclusion of oxygen, but without success. The ethynylation reaction[128,129] used was a variation of the Heck reaction[131] (of phenylacetylene and aromatic halides in the presence of organopalladium catalysts), and thus any factors affecting the Heck reaction should also apply to the coupling scheme described above. Austin[132] has reported that electron-withdrawing groups on the aromatic halide facilitate the palladium catalysed coupling reaction, while electron-donating groups impart adverse effects. Therefore, a model compound was chosen to test whether the coupling reaction as described was likely to proceed. Bromobenzene was chosen as the model compound owing to its ready availability, ease of purification and similar ring electron density to (4-bromophenyl)diphenylmethanol. If the bromobenzene did not react with 2-methyl-3-butyn-2-ol, then the electron density on the aromatic ring was presumably too high for the palladium catalysed coupling to proceed. Bromobenzene proved to be unreactive with respect to the alkynylation under the same conditions, and thus it was concluded that the (4-bromophenyl)diphenylmethanol was too electron-rich to react in the desired manner. Thus the above route was abandoned.

5.4. Synthetic Route 3

The previous route was unsuccessful at the alkynylation stage and therefore it was decided to introduce the acetylenic moiety at an earlier stage, on a relatively electron-poor aromatic. 4-bromobenzophenone was available and thus the alkynylation reaction could be attempted on this compound both as a model reaction and as part of the synthetic route.

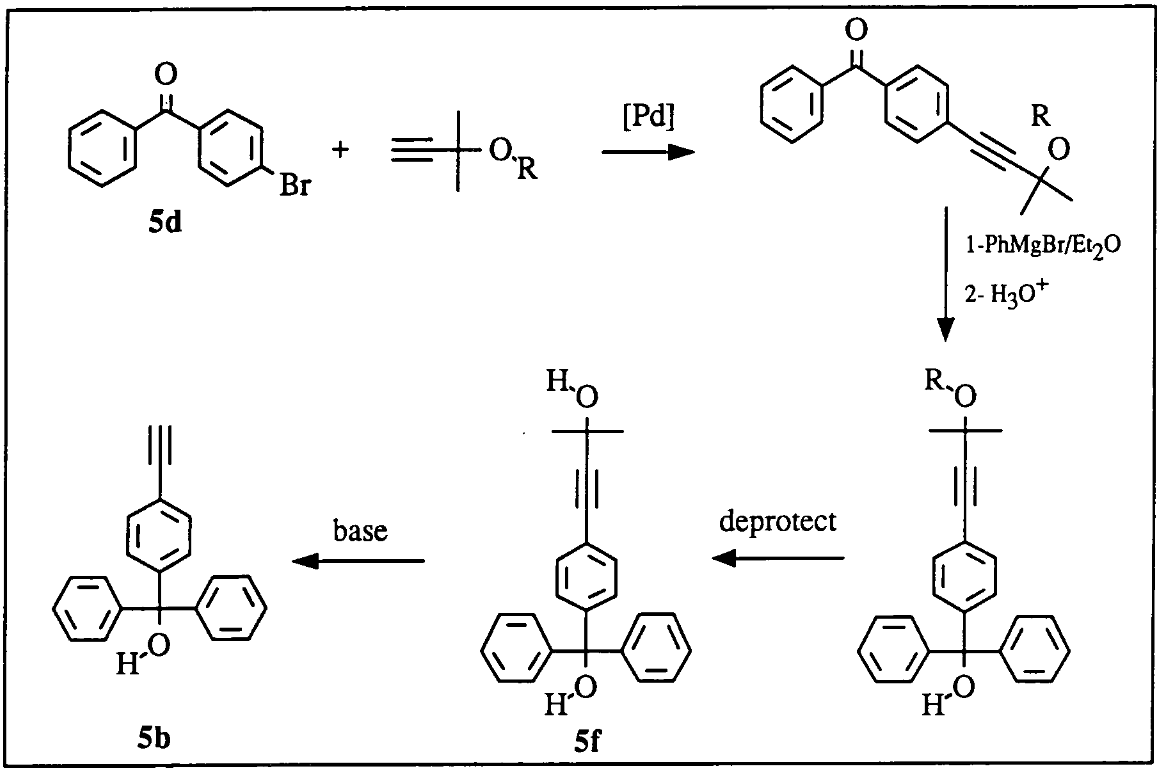
Figure 5.4.i.



The alkynylated benzophenone **5g** would hydrolyse Grignard reagents and thus for the formation of the triphenylmethanol derivative the alcohol group would require protection. The alternative to this method would be to employ trimethylsilylacetylene ($Me_3SiC{\equiv}CH$) as the protected alkyne; cleavage of the trimethylsilyl group readily occurs under mild basic hydrolysis, to give the terminal acetylene. However, the high cost of trimethylsilylacetylene rendered this route unsuitable for the preparation of large quantities of monomer.

It was decided therefore to pursue the sequence below, assuming that the alkynylated benzophenone **5g** above could be synthesized as shown overleaf in figure 5.4.ii.

Figure 5.4.ii.

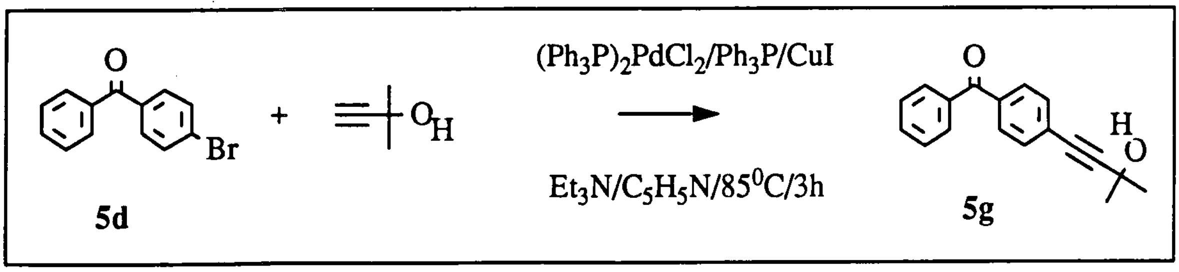


In the above scheme, R is a protecting group for alcohols.

5.4.i. Preparation of (4-(2-Methyl-2-hydroxylbut-3-ynyl)benzophenone) 5g

The compound **5b** and its precursors were all previously unreported, and hence variations of known literature procedures were used. For the alkynylation of benzophenone, the method of Trumbo and Marvel[130] was used with appropriate modifications.

Figure 5.4.iii.



Experimental

All liquids were distilled and stored under dry nitrogen. Copper (I) iodide, triphenylphosphine (Aldrich), bis(triphenylphosphine)palladium (II) chloride, and 4-bromobenzophenone (Lancaster Synthesis) were used as supplied. Triethylamine and pyridine were twice distilled over KOH pellets onto fresh KOH, and 2-methyl-3-butyn-2-ol was purified as described above.

Procedure

In a three-neck flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen bleed was placed 4-bromobenzophenone (6.53g, 25mmol) dissolved in triethylamine (30ml) and pyridine (10ml). 2-Methyl-3-butyn-2-ol (2.6ml, 30mmol), triphenylphosphine (40mg, 0.15mmol) and copper (I) iodide (25mg, 0.125mmol) were added and the mixture was stirred as nitrogen was rapidly bubbled through the solution for 30 minutes. Bis(triphenylphosphine)palladium (II) chloride (175mg, 0.25mmol) was added and the temperature raised slowly to 85^{0}C, whereupon the solution darkened and a grey precipitate appeared. The temperature was retained at 85^{0}C for 3 hours before cooling and allowing the reaction to continue overnight at room temperature. Triethylamine was then removed by rotary evaporation, and diethyl ether added (100ml). The mixture was filtered to remove quaternary amine salts, washed with dilute hydrochloric acid (2%, 3x25ml),and water (3x25ml), and then passed through alumina (neutral, Grade 1), before rotary evaporation of ether, giving an off-white solid.

5.4.ii. Results: 4-(2-methyl-2-hydroxybut-3-ynyl)benzophenone 5g

The yield of crude material was 6.16g (93%). Recrystallisation from hexane/diethyl ether gave lustrous white flakes (m.p. 116-119^{0}C).

Characterization of 5g

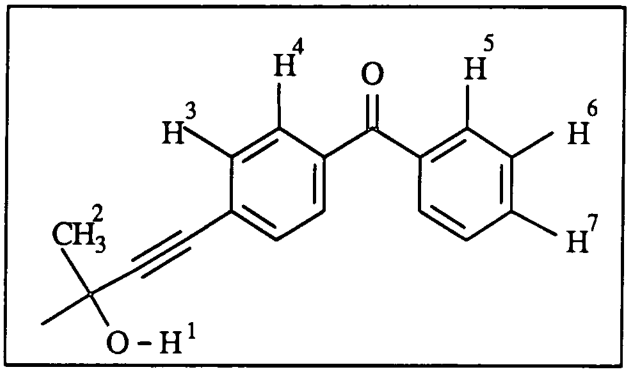
a- Combustion analysis was satisfactory: calculated for $C_{18}H_{16}O_2$: C, 81.80%; H, 6.10%: found: C, 81.70%; H, 6.20%.

b- Chromatography indicated one component. R_f Neutral alumina; elution with hexane/acetone (10:1) 0.28.

c- The infra-red spectrum (Appendix 5-5) showed the following bands: ν (KBr disc)/cm^{-1}; 3480 (broad, OH), 3080,3060 (aromatic CH), 2980 (aliphatic CH),1655 (aromatic C=O), 1600 (C=C).

d- The ^{1}H NMR spectrum (Appendix 5-6) gave good evidence for the structure overleaf.

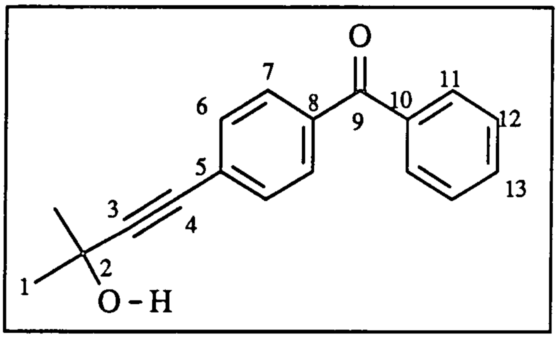
Figure 5.4.iv.



δ/ppm (C_6D_6): 1.49 (s,6H,H^2), 1.91 (s,1H, H^1), 7.00-7.14,7.56-7.66 (m,m,4H,4H,H^{3-6}), 7.30 (m,1H,H^7).

e- The ^{13}C NMR spectrum (Appendix 5-7) provided further evidence for the designated structure, based partially on APT spectra and comparison with known compounds.

Figure 5.4.v.



δ/ppm (C_6D_6): 31.43 (C^1), 65.25 (C^2), 81.60,97.80 (C^3,C^4), 127.32 (C^5), 128.38 (C^{12}), 130.09,130.20 (C^7,C^{11}), 131.61 (C^6), 132.20 (C^{13}), 137.35,137.93 (C^8,C^{10}), 194.97 (C^9).

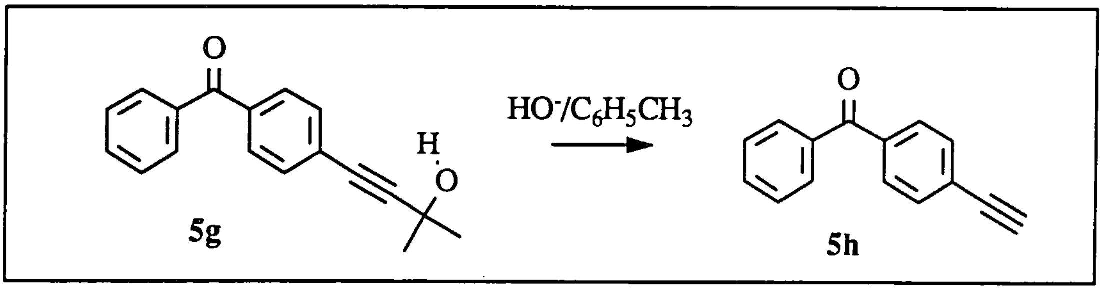
f- The mass spectrum (Appendix 5-8) showed a strong molecular ion, and a base peak corresponding to the loss of the tertiary hydroxyl group.

m/e: 265 (MH^+, 39.3, EI^+,CI^+), 264 (M^+, 11.6), 247 (M-OH, 100).

5.4.iii. Preparation of 4-Ethynylbenzophenone

The method of Trumbo and Marvel[130] was adapted to prepare this new compound.

Figure 5.4.vi.



5g

5h

Experimental

Toluene was dried over sodium wire: all other reagents were used as supplied.

Procedure

(4-(2-methyl-2-hydroxy-but-3-ynyl)benzophenone (2.64g, 10mmol) was dissolved in toluene (50ml) and sodium hydroxide (0.8g, two-fold excess) added. The mixture was refluxed for 2 hours with a flow of nitrogen through the system, and, when cooled, poured into water (50ml). Hydrochloric acid (2%, 3x25ml) and water (3x25ml) were used to wash the organic layer, which was then dried over magnesium sulphate. Evaporation of solvent under reduced pressure gave a brown solid.

5.4.iv. Results: 4-ethynylbenzophenone *5h*

The yield of crude material was 2.0g (97%). Purification of the product was possible via recrystallisation from aqueous ethanol, or sublimation in vacuo. Recrystallisation gave the product as lustrous white flakes, melting at 52-53^{0}C. Sublimation yielded a fine white powder with the same melting point.

Characterization of 5h

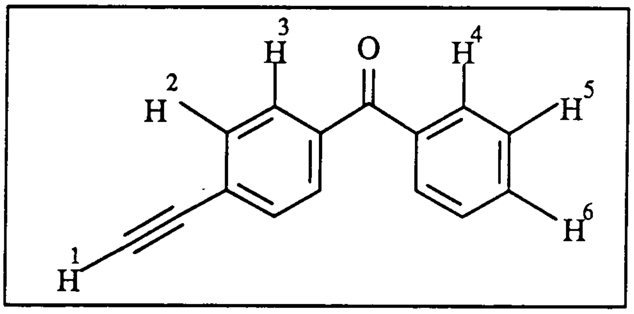
a- Combustion analysis was not satisfactory for carbon, but the other characterization methods confirmed the nature of the product: calculated for $C_{15}H_{10}O$: C, 87.36%; H, 4.89%: found: C, 88.10; H, 4.84%.

b- Chromatography indicated one component. R_f Neutral alumina; elution with hexane/acetone (10:1) 0.71.

c- The infra-red spectrum (Appendix 5-9) showed the following diagnostic bands: ν (KBr disc)/cm^{-1}: 3290 (acetylenic CH), 3080,3060 (aromatic CH) 2100 (RC≡CH), 1655 (aromatic C=O), 1600 (C=C).

d- The ^{1}H NMR spectrum (Appendix 5-10) gave good evidence for the structure below:

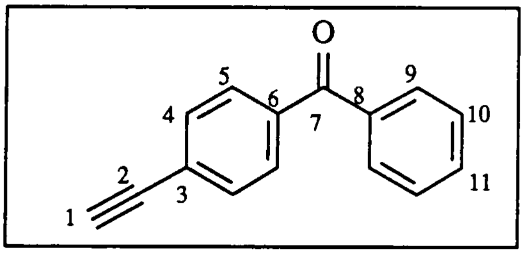
Figure 5.4.vii.



δ/ppm (C_6D_6): 2.76 (s,1H,H^1), 6.98-7.62 (m,9H,H$^{2-6}$).

e- The ^{13}C NMR spectrum (Appendix 5-11) provided further evidence for the designated structure, with the assignments based partially in comparison with known compounds and APT spectra.

Figure 5.4.viii.



δ/ppm (C_6D_6): 80.30 (C^1), 83.08 (C^2), 126.22 (C^3), 128.37, 128.24 (C^9,C^{10}), 130.08 (C^5), 132.10 (C^{11}), 132.23 (C^4), 137.80, 137.91 (C^6,C^8), 194.80 (C^7).

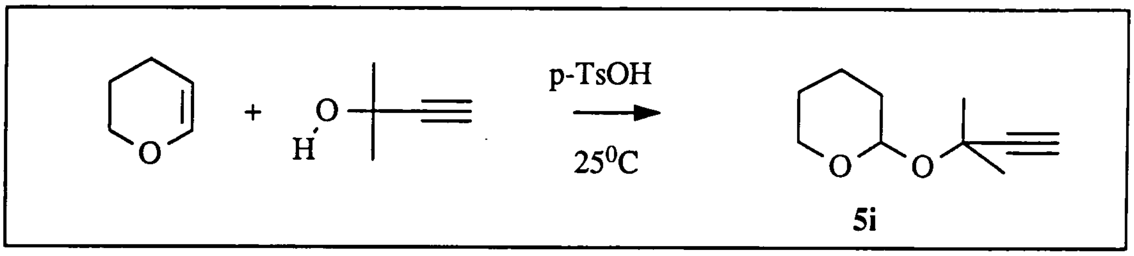
f- The mass spectrum (Appendix 5-12) showed a strong molecular ion peak, and peaks associated with ionization by the CI bombarding gas.

m/e: 224 (MNH_4^+,11.9,CI$^+$), 207 (MH$^+$,74.9), 206 (M$^+$,90.1,EI$^+$).

5.4.v. Preparation of Protected 2-Methyl-3-butyn-2-ol

It was decided to use 2,3-dihydropyran as the protecting reagent, as it readily forms, under acid catalysis, tetrahydropyranyl ethers with alcohols, which are stable to bases (including Grignard reagents) and yet are easily removed under mild acid conditions[133]. The THP ether of 2-methyl-3-butyn-2-ol had been prepared previously[134], and this method was used without modification.

Figure 5.4.ix.



5i

Experimental

All reagents were used as supplied (Lancaster Synthesis).

Procedure

2,3-Dihydropyran (16.8g, 0.2mol) was mixed with 2-methyl-3-butyn-2-ol (8.41g, 0.1mol) at 0^{0}*C. Toluene-4-sulphonic acid (5mg) was added and stirring continued for one hour at* 0^{0}*C. The reaction was allowed to continue overnight at room temperature, after which excess dihydropyran (b.p.* 86^{0}*C) was removed by rotary evaporation. The residue was poured into 5% sodium bicarbonate solution (25ml), extracted with ether (2x20ml), washed with water (20ml), dried and distilled (b.p* 57^{0}*C/3.5mm Hg).*

5.4.vi. Results: (2-Tetrahydropyranyloxy)-2-methylbut-3-yne *5i*

The yield of pure product was 15g (90%). The data agreed well with literature values[134]*, sufficient to confirm the nature of the compound. The compound was produced as a mixture of two enantiomers, b.p.* 57^{0}*C (3.5 torr): (lit.* 57^{0}*C 3.5 torr).*

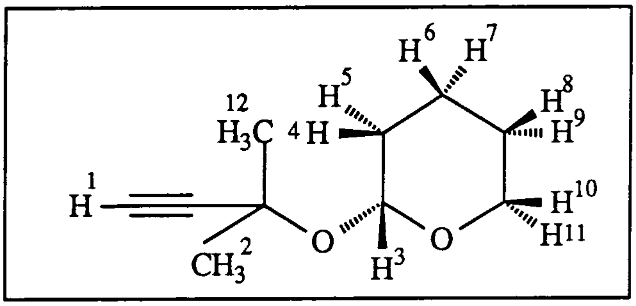
Characterization of 5i

a- Combustion analysis: calculated for $C_{10}H_{16}O_2$: C, 71.4%; H, 9.52%; found: C, 71.31%; H, 9.80.

b- The infra-red spectrum (Appendix 5-13) showed the following diagnostic bands: v (Thin film): 3300 (acetylenic CH), 2980-2860 (aliphatic CH), 2110 ($RC\equiv CH$), 1125 (ether C-O). Lit[134]. ($CHCl_3$): 3310, 1125, 1070, 1030.

c- The ^{1}H NMR spectrum (Appendix 5-14) gave good evidence for the structure below:

Figure 5.4.x.

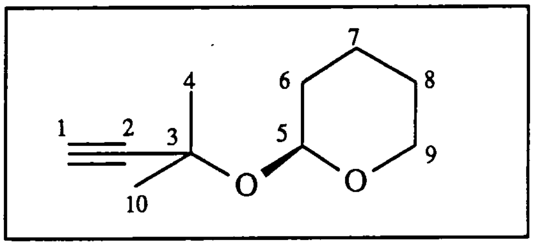


δ/ppm ($CDCl_3$): 1.34-1.70 (s + complex m:broad 12H, H^2,H^4-H^9,H^{12}), 2.32 (s,1H,H^1), 3.32-3.81 (d of complex m,1H,1H,$H^{10,11}$), 4.92 (s,1H,H^3). Lit[134]. δ/ppm ($CDCl_3$): 5.06 m(O-C$\underline{H}$-O), 2.44 s(C≡C$\underline{H}$), 1.51 s(C$\underline{H_3}$), 1.48 s(C$\underline{H_3}$).

The shift values recorded in this work were slightly different to those recorded in the literature; in the previous work the multiplets for the THP protons were ignored, although in our work (even at 400MHz) these the signals overlapped the methyl resonances. However, the spectra obtained were consistent with the desired structure.

d- The ^{13}C NMR spectra (Appendices 5-15, 5-16) provided further evidence for the designated structure. Off Resonance Decoupled (ORD) and DEPT spectra supported the assignments. No literature values were available.

Figure 5.4.xi.



δ/ppm ($CDCl_3$): 19.90 (C^7,t), 25.05 (C^8,t), 29.39 (C^4,q), 30.21 (C^{10},q), 31.47 (C^6,t), 62.58 (C^9,t), 70.40 (C^3,s), 71.72 (C^1,d), 85.85 (C^2,s), 95.54 (C^5,d).

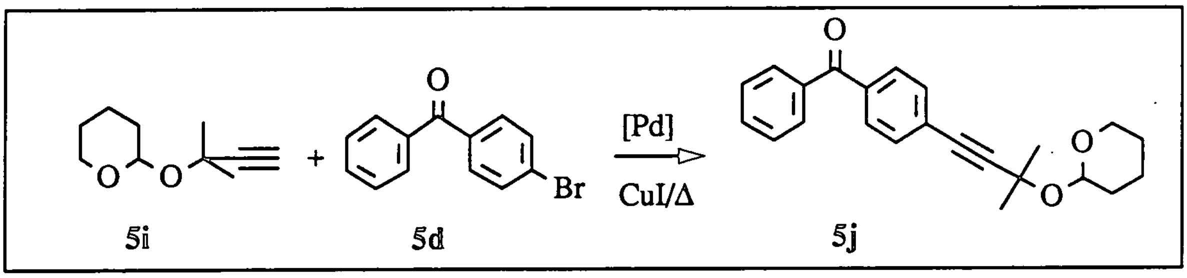
In the DEPT spectrum, problems with the probe at the time the spectrum was recorded led to an inability to distinguish between quaternary and CH carbons. However, the data left no doubt as to the assignments.

f- Mass spectral analysis: spectra obtained under chemical ionization (CI) conditions showed only polymeric products. The gas used for chemical ionization experiments was ammonia, which might have caused polymerization by nucleophilic attack at the triple bond. Experience gained during this project has shown that some aliphatic acetylenes polymerize readily in the presence of reactive amines.

5.4.vii. Preparation of Protected Alkynylbenzophenone

The method of Trumbo and Marvel[130] was used again, with the necessary modifications.

Figure 5.4.xii.



Experimental

The THP ether (2-tetrahydropyranyloxy-2-methyl-but-3-yne) was distilled under nitrogen at reduced pressure (b.p. 57^0C/13.5mmHg) onto fresh 4A molecular sieves and stored under nitrogen. All other reagents were purified as described above for the synthesis of (4-(2-methyl-2-hydroxybut-3-ynyl)benzophenone.

Procedure

4-Bromobenzophenone (6.53g, 25mmol) was mixed with 2-tetrahydropyranyloxy-2-methylbut-3-yne (5.04g, 30mmol), triphenylphosphine (40mg, 0.15mmol), and copper (I) iodide (25mg, 0.125mmol), and the resultant suspension was dissolved in triethylamine (30ml) and pyridine (30ml). Dry nitrogen was bubbled rapidly through the solution for 30 minutes before the addition of bis(triphenylphosphine)palladium (II) chloride (175mg, 0.25mmol).

The temperature was raised to 80^0C to initiate the reaction, which was continued for 6 hours at 80^0C and then overnight at room temperature. The dark brown suspension was poured into water (100ml), extracted with diethyl ether (100ml), and the organic layer filtered and washed again with water (6x100ml) to remove any residual amine. The ether solution was passed through alumina (neutral, Grade 1) to remove water and palladium salts, and the solvent evaporated to leave a light yellow oil.

5.4.viii. Results

4-(2-Tetrahydropyranyloxy-2-methylbut-3-ynyl)benzophenone 5j

The yield of crude material was 8.2g (94%), which was shown by TLC (alumina plates; hexane eluant) to consist of one component. Attempts to crystallise this oil failed despite using a wide range and combination of solvent systems (hexane, carbon tetrachloride, diethyl ether, dichloromethane, acetone, methanol, and water). However, after vacuum drying for one week followed by six weeks standing in air, the oil solidified, and the solid was recrystallised from methanol. The resultant white solid (m.p. 58-59^0C) was found to decompose over a period of several months to the singly protected alkyne and dihydropyran: hence this compound was stored at -20^0C. The compound was prepared as a mixture of two enantiomers.

Characterization of 5j

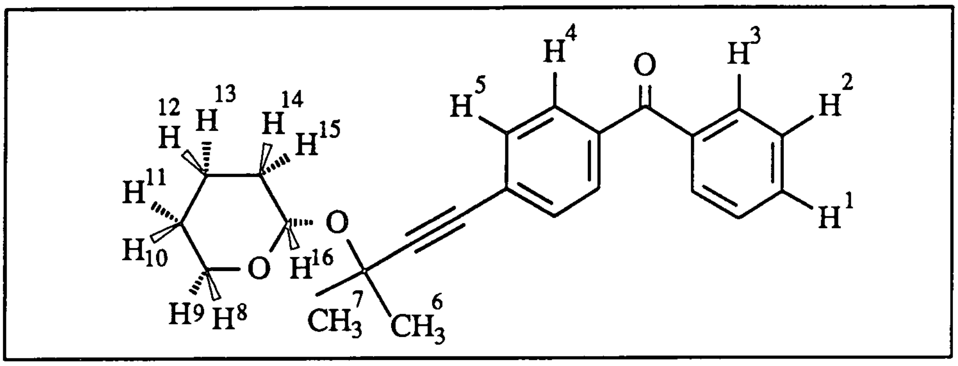
a- Combustion analysis was satisfactory: calculated for $C_{23}H_{24}O_3$: C, 79.28%; H, 6.94%: found: C, 79.34%, H, 6.74%.

b- Chromatography indicated one component. R_f Neutral alumina; elution with hexane/acetone (10:1) 0.69.

c- The infra-red spectrum (Appendix 5-17) showed the following diagnostic bands: v (KBr disc)/cm^{-1}: 3060,3040 (aromatic CH) 2940,2860 (aliphatic CH), 1665 (aromatic C=O), 1605 (C=C).

d- The ^1H NMR spectrum (Appendix 5-18) gave good evidence for the assigned structure. The numbering scheme for peak assignment is shown overleaf in figure 5.4.xiii.

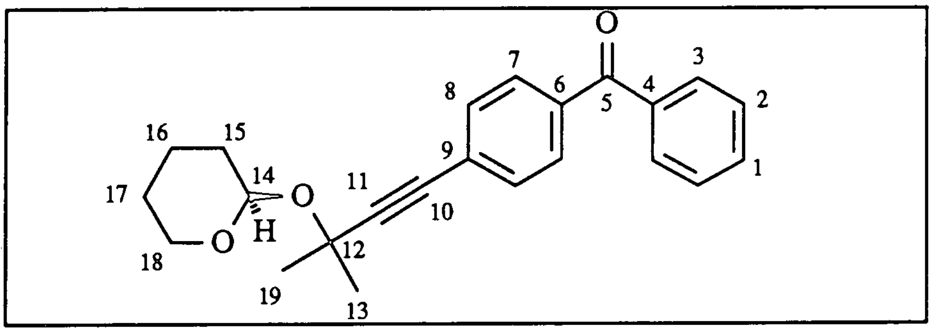
Figure 5.4.xiii.



δ/ppm ($CDCl_3$): 1.20-1.82 (2s + complex m:broad 12H, $H^{6,7}$,H^{10-15}), 3.49-4.01 (d of complex m,1H,1H,$H^{8,9}$), 5.42 (s,1H,H^{16}), 7.01-7.64 (m,9H,H^{1-5}).

e- The ^{13}C NMR spectrum (Appendix 5-19) provided further evidence for the structures as shown: resonances are assigned below, and are assigned with the aid of APT spectra and by comparison with the THP ether **5i**:

Figure 5.4.xiv.



δ/ppm (C_6D_6): 19.38 (C^{16}), 25.34 (C^{17}), 29.71 (C^{13}), 30.27 (C^{19}), 31.60 (C^{15}), 61.68 (C^{18}), 70.96 (C^{12}), 83.44 (C^{10}), 94.83 (C^{11}), 95.29 (C^{14}), 126.58 (C^{9}), 127.84 (C^{2}), 129.54 (C^{7}), 129.57 (C^{3}), 131.20 (C^{1}), 131.68 (C^{8}), 136.87 (C^{6}), 137.38 (C^{4}), 194.26 (C^{5}).

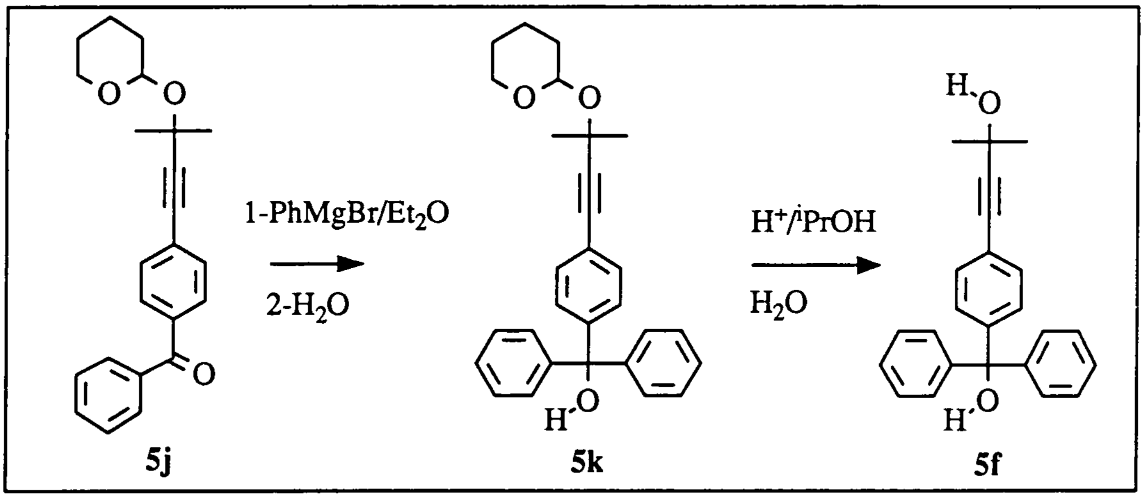
f- The mass spectrum (Appendix 5-20) showed a low intensity molecular ion, and fragment ions corresponding to loss of the THP protecting group. The base peak resulted from the loss of the protecting group and the tertiary alcohol oxygen.

m/e: 348 (M^+,1.4), 264 (MH^+-THP,12.8), 263 (M-THP,31.6), 247 (M-(THP-O),100).

5.4.ix. Preparation of (4-(2-(Tetrahydropyranyloxy)-2-methylbut-3-ynyl)phenyl) -diphenylmethanol 5k and (4-(2-Methyl-2-hydroxyl)but-3-ynylphenyl)diphenylmethanol 5f

The method used was an adaptation of that used by Manning[127] to prepare (4-bromophenyl)diphenylmethanol, described earlier, employing excess Grignard reagent, followed by a new method for removing the tetrahydropyranyl (THP) protecting group. The reaction was in general carried out without isolation of **5k** below: i.e. as a "one pot" procedure. However, for completeness, the following account of the reaction scheme includes the description of the purification and characterization of (4-(2-(tetrahydropyranyloxy)-2-methylbut-3-ynyl)phenyl)-diphenylmethanol (**5k**).

Figure 5.4.xv.



Experimental

Bromobenzene and magnesium turnings were used as supplied. Benzene and diethyl ether were dried over sodium wire, methanol (GPR grade) was used without further purification, and the tetrahydropyranyl ether (5j) used as prepared above.

Procedure

Bromobenzene (2.0ml, 19mmol) was added dropwise to magnesium turnings (0.48g, 20mmol) in diethyl ether (20ml) under nitrogen; complete conversion was ensured by continuing the reaction for 30 minutes under gentle reflux.

A solution of benzene (30ml) and diethyl ether (10ml) containing (4-(2-tetrahydropyranyloxy-2-methyl)but-3-ynyl)benzophenone (5.20g, 15mmol) was stirred rapidly under nitrogen as the Grignard reagent was added dropwise over 2 hours. The reaction was continued overnight at room temperature, before pouring into ice water (100ml). The aqueous layer was extracted with diethyl ether (3x20ml), and the combined organic layers washed with water (3x20ml), and dried over magnesium sulphate. Evaporation of solvent gave a light yellow oil (5k). Isolation and purification of this intermediate was carried out on a small scale: slow crystallisation from hexane/diethyl ether over a period of six months at -20⁰C yielded a white solid (m.p. 96-98⁰C.)

5.4.x. Results

4-(2-(Tetrahydropyranyloxy)-2-methylbut-3-ynyl)phenyl)diphenylmethanol 5k

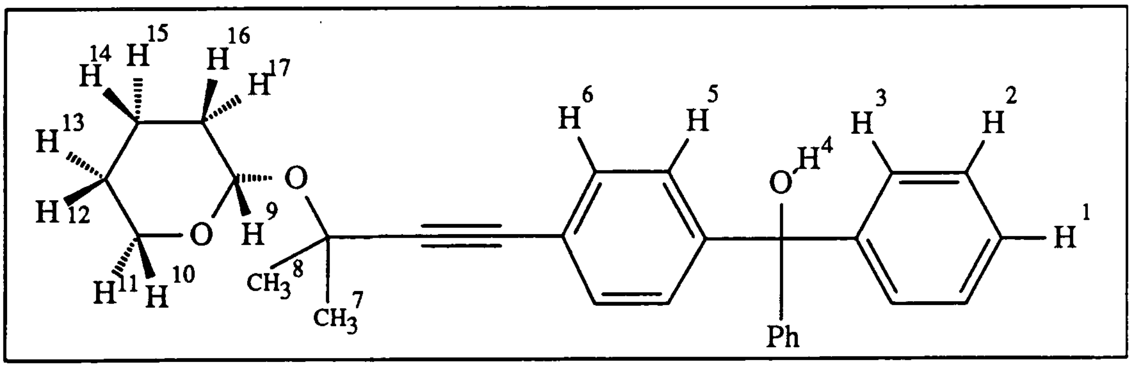
a- Combustion analysis: calculated for $C_{29}H_{30}O_3$: C, 81.66%; H, 7.09%; found: C, 83.05%; H, 7.24%.

b- Chromatography showed one component. R_f Neutral alumina; elution with hexane/acetone (10:1) 0.38.

c- The infra-red spectrum (Appendix 5-21) showed the following diagnostic bands: ν (KBr disc)/cm^{-1}: 3380 (OH), 3060,3040 (aromatic CH) 2940,2860 (aliphatic CH), 1600 (C=C).

d- The ^{1}H NMR spectrum (Appendix 5-22) gave good evidence for the structure.

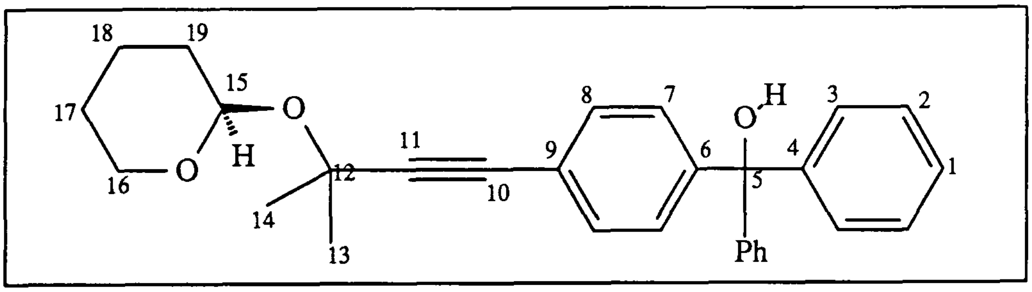
Figure 5.4.xvi.



δ/ppm ($CDCl_3$): 1.20-1.80 (complex m:broad 6H,H^{12,17}), 1.62, 1.74 (s,s,6H,H^{7,8}), 2.6-2.8 (s,broad,1H,H^4), 3.40-3.93 (d of complex m,1H,1H,H^{10,11}), 5.48 (s,1H,H^9), 7.01-7.35 (m,14H,H$^{1-3,5,6}$).

e- The ^{13}C NMR (Appendix 5-23) also provided evidence for the structures above and below: as for **5j** the compound was produced as a mixture of two enantiomers. Conformational effects on the chiral carbon can be seen for **5k** at 95ppm. At high resolution, the peak is seen to split, due to different environments for the chiral carbon caused probably by boat/chair configurations of the THP ring.

Figure 5.4.xvii.



δ/ppm (C_6D_6). 19.99 (C^{18}), 25.87 (C^{17}), 30.38 (C^{13}), 31.01 (C^{14}), 32.18 (C^{19}), 62.22 (C^{16}), 71.69 (C^{12}), 81.88 (C^5), 84.62 (C^{10}), 92.58 (C^{11}), 95.89 (C^{15}), 122.19 (C^9), 127.43 (C^7), 128.13, 128.26, 128.37 ($C^{1,2,3}$), 131.56 (C^8), 147.30 (C^4), 147.73 (C^6).

f- The mass spectrum (Appendix 5-24) showed a low intensity molecular ion, with fragmentation ions corresponding to loss of the protecting group and tertiary hydroxyl moieties.

m/e: 426 (M^+,1.26,CI^+), 341 (MH^+-THP,13.2), 325 (M-THPOH,53.7).

Removal of Tetrahydropyranyl Protecting Group

Isopropanol (200ml) was added to the initial product from the above reaction (5k), and the stirred solution heated to $50^{0}C$. Distilled water (50ml) and toluene-4-sulphonic acid (5mg) were added and the mixture refluxed for 2 hours. The solution was concentrated by rotary evaporation of methanol, and sodium bicarbonate solution (5%, 50ml) added. The organic product was isolated by extraction with diethyl ether (3x50ml): the organic layer being further washed with water (3x10ml), followed by drying over magnesium sulphate, and evaporation of solvent, to give a yellow viscous oil.

5.4.xi. Results: (4-(2-Methyl-2-hydroxybut-3-ynyl)phenyl)diphenylmethanol 5f

Yield of crude material was 4.57g (90%), which was shown by TLC (alumina plates with elution by acetone/hexane 1:20) to consist primarily of one component. The desired product was recrystallised twice from hexane/diethyl ether, and finally from carbon tetrachloride, giving a white solid m.p. 139-140^{0}C.

Characterization of 5f

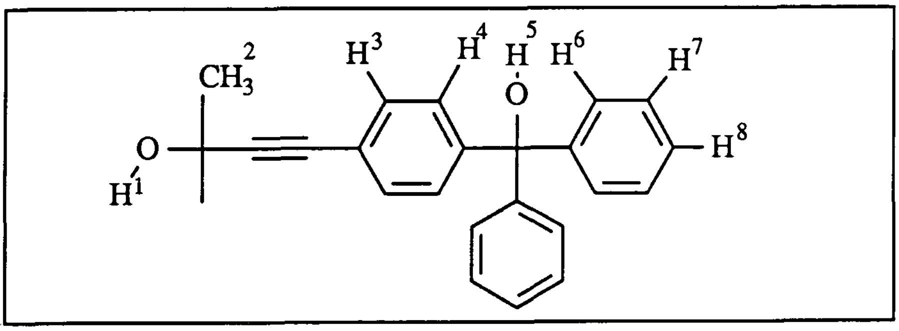
a- Combustion analysis was satisfactory: calculated for $C_{24}H_{22}O_2$: C, 84.18%; H, 6.48%; found: C, 83.84%; H, 6.57%.

b- Chromatography indicated one component. R_f Neutral alumina: elution with hexane/acetone (10:1) 0.06.

c- The infra-red spectrum (Appendix 5-25) showed the following diagnostic bands: ν (KBr disc)/cm^{-1}: 3560,3420,3400 (free, and H-bonded OH), 3080,3060,3040 (aromatic CH), 2980,2920 (aliphatic CH), 2210 (RC≡CR), 1600 (C=C).

d- The ^{1}H NMR spectrum (Appendix 5-26) gave good evidence for the assigned structure.

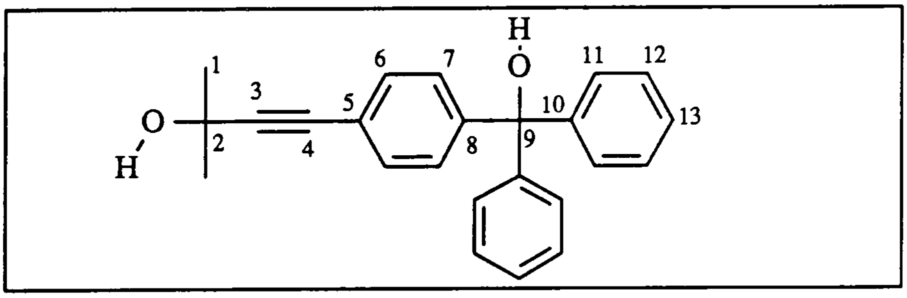
Figure 5.4.xviii.



δ/ppm (C_6D_6): 1.46 (s,6H,H^2), 2.37 (s,1H,H^1), 2.96 (s,1H,H^5). 7.02-7.35 (m,14H,H^{3,4},H$^{6-8}$),

e- The ^{13}C NMR spectrum (Appendix 5-27) provided further evidence for the designated structure. The numbering scheme for peak assignment is shown overleaf in figure 5.4.xix.

Figure 5.4.xix.

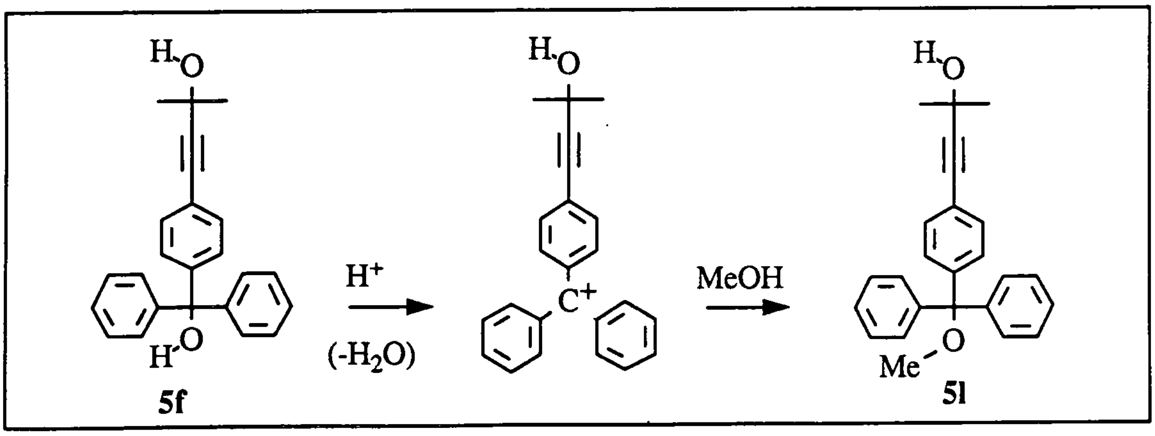


δ/ppm (C_6D_6): 31.62 (C^1), 65.45 (C^2), 82.01 (C^3), 82.28 (C^9), 95.10 (C^4), 122.35 (C^5), 127.44, 127.77 ($C^{12,13}$), 128.25 (C^{11}), 128.43 (C^7), 131.44 (C^6), 147.25, (C^8), 147.67 (C^{10}).

f- The mass spectrum (Appendix 5-28) showed a low intensity molecular ion peak, and fragment ions corresponding to loss of hydroxyl, and phenyl, groups.
m/e: 342(M^+,12.3,EI^+), 325 (M-OH,26.5), 265 (M-Ph,59.0).

Initial attempts to produce the above compound using the standard literature method of removal of the THP protecting group (methanol/pTsOH at 0°C)[133] resulted in substantial quantities (30%) of a low polarity impurity. Subsequent experiments showed the impurity material to be the methoxy ether of (4-(2-methyl-2-hydroxybut-3-ynylphenyl)diphenylmethanol, with the methylation occurring at the triphenylmethyl hydroxy group:

Figure 5.4.xx.



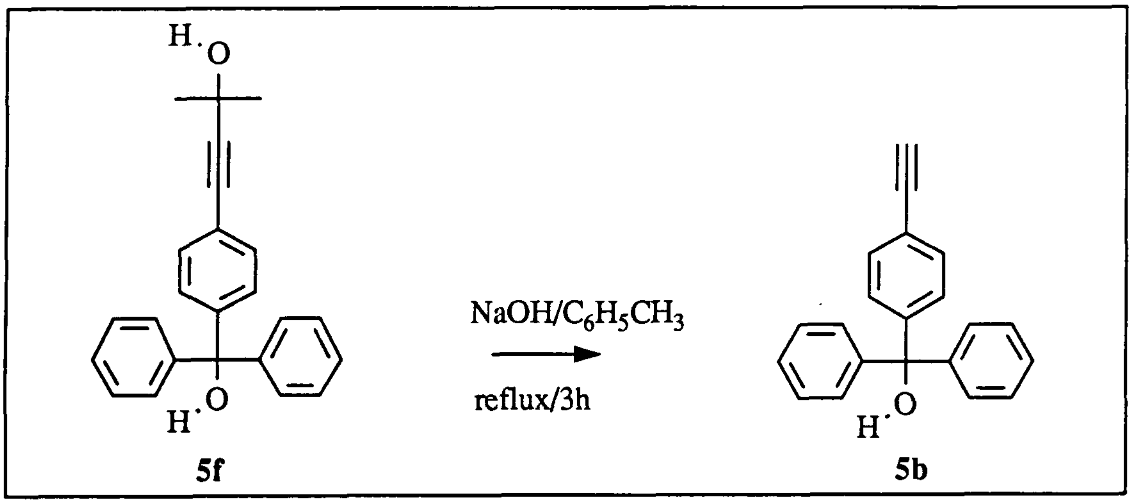
Methylation occured very readily during removal of the tetrahydropyranyl protecting group if the temperature was not controlled carefully; initial problems arose because the rotary evaporation of methanol was carried out at 45^{0}C before the acid catalyst had been removed. The high relative stability of the triphenylmethyl cation would clearly be a contributary factor in this methylation; no evidence was found of methylation at the other hydroxyl site.

However, the mixture of the two alcohols (**5f** and **5l** above) was useful in itself, as the elimination stage could be carried out on both to yield the corresponding terminal acetylenes. The separation and purification of these compounds is described below.

5.4.xii. Preparation of (4-Ethynylphenyl)diphenylmethanol

The elimination of acetone (deprotection of the acetylene) was carried out as shown below:

Figure 5.4.xxi.



Experimental

Toluene was dried over sodium wire prior to use. Sodium hydroxide was used as supplied (GPR grade), and the alcohol (5f) was used as prepared above.

Procedure

Sodium hydroxide (1g, 25mmol) was added to toluene (50ml) containing (4-(2-methyl-2-hydroxybut-3-ynyl)phenyl)diphenylmethanol (4.0g, 12mmol) and the mixture brought to reflux. A flow of nitrogen was maintained through the solution throughout the reflux (3 hours).

After cooling, the solution was poured into ice water containing hydrochloric acid (1%), and diethyl ether (50ml) was used to extract the aqueous layer. The combined organic layers were washed with saturated sodium bicarbonate solution (3x20ml), and water (3x20ml), and dried over magnesium sulphate. Evaporation of solvent left a viscous dark brown oil. Repeated charcoal treatment in methanol produced a dark yellow oil of increased viscosity, but full decolourisation was not achieved. Recrystallisation proved impossible from a range and combination of solvents, despite evidence from TLC (alumina plates, with elution in acetone/hexane 1:20) that the oil was predominantly one product.

Column chromatography on alumina (neutral, Brockmann grades II-III) with elution by hexane/diethyl ether (20:1) yielded a light yellow oily solid, which gave crude yellow crystals from hexane/carbon tetrachloride at -10⁰C. These were successfully recrystallised from carbon tetrachloride (3ml solvent to 1g solid) as large colourless prisms, which yellowed in air and sunlight.

5.4.xiii. Results: (4-Ethynylphenyl)diphenylmethanol 5b

The yield at the final stage, after column chromatography, was 2g (60%).

Characterization of 5b

a- Combustion analysis indicated the presence of solvent trapped in the crystals. Attempts to remove the solvent by prolonged vacuum pumping (10^{-3}torr) resulted in the collapse of the crystals to an oil. However, the other methods of characterization left no doubt as to the nature of the product.

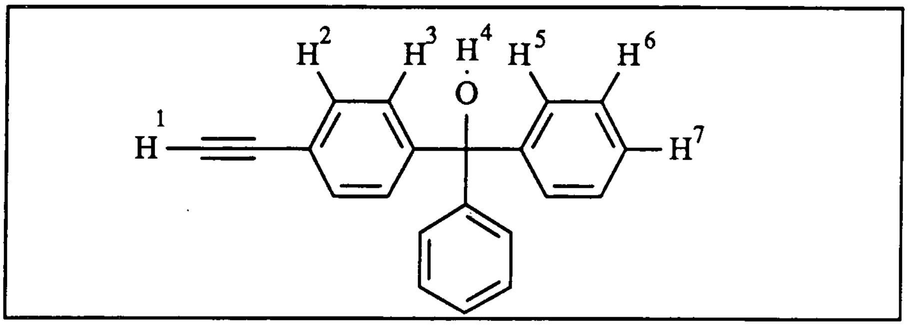
Calculated for $C_{21}H_{16}O$: C, 88.70%; H, 5.67%: found: C, 64.40%; H, 4.71%

b- Chromatography indicated one component. R_f Neutral alumina; elution with hexane/acetone (10:1) 0.39.

c- The infra-red spectrum (Appendix 5-29) showed the following diagnostic bands: v (KBr disc)/cm^{-1}: 3550,3450 (free and H-bonded OH), 3280 (acetylenic CH), 3060,3040,3020 (aromatic CH) 2100 (RC≡CH), 1595 (C=C).

d- The ^1H NMR spectrum (Appendix 5-30) gave good evidence for the assigned structure. The numbering scheme for peak assignment is shown overleaf in figure 5.4.xxii.

Figure 5.4.xxii.

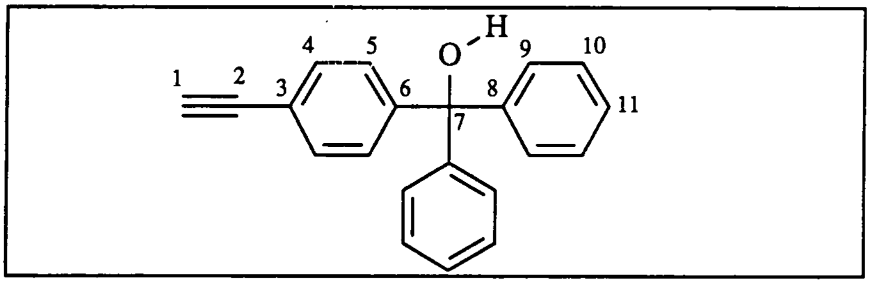


δ/ppm (C_6D_6): 2.86 (s,1H,H^4), 3.07 (s,1H,H^1), 7.25-7.46 (m,14H,$H^{2,3,5-7}$).

The signal for H^4 disappears in D_20.

e- The ^{13}C NMR spectrum (Appendix 5-31) provided further evidence for the designated structure.

Figure 5.4.xxiii.



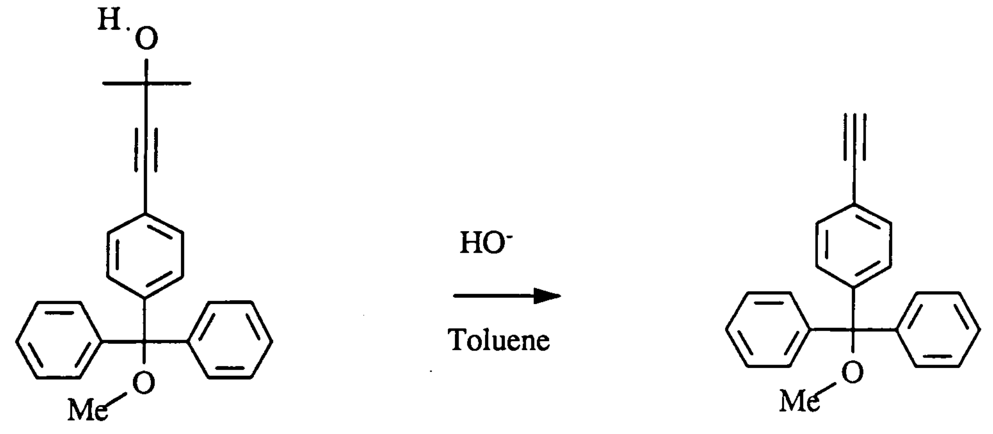
δ/ppm (C_6D_6): 77.95 (C^1), 81.83 (C^7), 83.73 (C^2), 121.45 (C^3), 128.07, 128.14, 128.30 (C^{9-11}), 128.43 (C^5), 131.88 (C^4), 147.05 (C^6), 148.07 (C^8).

f- The mass spectrum (Appendix 5-32) contained a medium intensity molecular ion and ions due to the loss of hydroxyl and phenyl fragments.

m/e: 284 (M^+,24.1,EI^+), 267 (M-OH,3.1), 207 (M-Ph,73).

5.4.xiv. Preparation of (4-Ethynylphenyl)diphenylmethoxymethane

Figure 5.4.xxiv.



5l **5m**

The method used was identical to that described earlier for (4-ethynylphenyl)diphenylmethanol, except that the elimination reaction was carried out on the mixture of the two alcohols (**5f** and **5l**). Separation was by column chromatography on alumina (neutral, grades II-III) with hexane as the eluant. The first compound off the column was (4-ethynylphenyl)diphenylmethoxymethane, (**5m**) which was recovered as white waxy crystals. These were recrystallised from methanol to constant melting point (69^{0}C).

5.4.xv. Results: (4-Ethynylphenyl)diphenylmethoxymethane 5m

Characterization of 5m

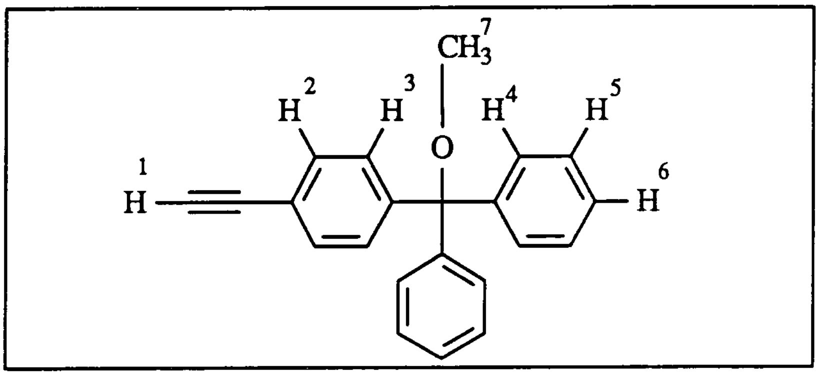
a- Combustion analysis: calculated for $C_{22}H_{18}O$: C, 88.56%; H, 6.08%: found: C, 89.21%; H, 6.29%.

b- Chromatography indicated one component. R_f Neutral alumina; elution with hexane/acetone (10:1) 0.95.

c- The infra-red spectrum (Appendix 5-33) showed the following diagnostic bands: ν (KBr disc)/cm^{-1}: 3280 (acetylenic CH), 3060,3040,3020 (aromatic CH), 2100 (RC≡CH), 1595 (C=C).

d- The ^{1}H NMR spectrum (Appendix 5-34) gave good evidence for the structure shown overleaf in figure 5.4.xxv.

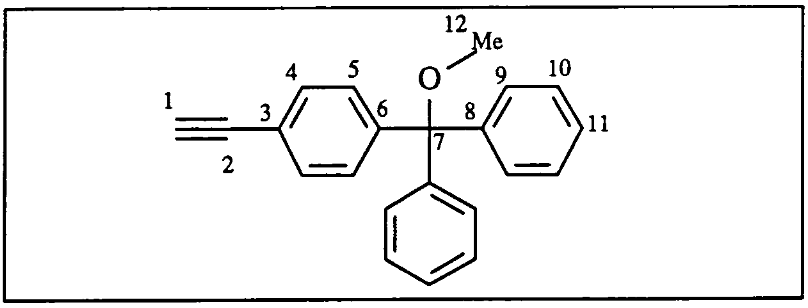
Figure 5.4.xxv.



δ/ppm (C_6D_6): 2.72 (s,1H,H^1), 2.88 (s,3H,H^7), 7.00-7.43 (m,14H,$H^{2,3,4-6}$).

e- The ^{13}C NMR spectrum (Appendix 5-35) provided further evidence for the designated structure. The peak positions for C^1 and C^2 were indistinguishable in the APT spectrum, and thus were assigned by comparison with **5b**.

Figure 5.4.xvi.



δ/ppm (C_6D_6): 51.89 (C^{12}), 77.92 (C^1), 83.78 (C^2), 87.10 (C^7), 121.22 (C^3), 127.30, 128.09, 128.87 (C^{9-11}), 129.15 (C^5), 131.91 (C^4), 143.86 (C^6), 145.61 (C^8).

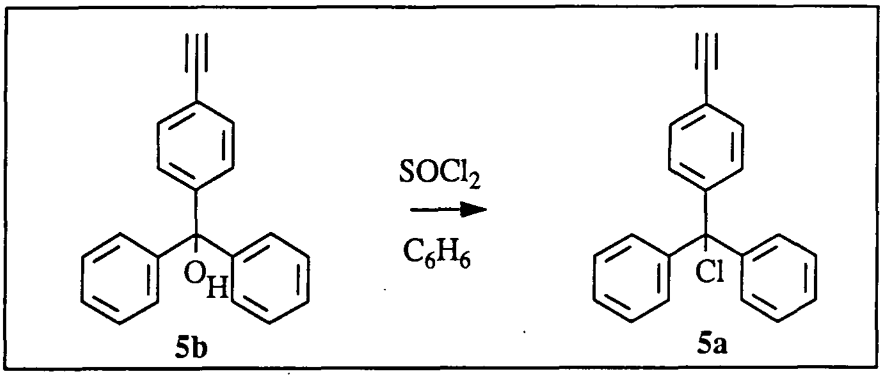
f- The mass spectrum (Appendix 5-36) showed a molecular ion, and fragments corresponding to the loss of methyl and methoxy groups.

m/e: 298 (M^+,30.2,CI^+), 283 (M-Me,24.8), 267 (M-MeO,69.1).

5.4.xvi. Preparation of (4-Ethynylphenyl)diphenylchloromethane

The method used was adapted from that used by Braun[47], for the chlorination of hydroxy functionalized polymers, to prepare this hitherto unreported compound.

Figure 5.4.xvii.



Experimental

Thionyl chloride (99+%, Aldrich) was transferred in vacuo and degassed twice before use. Benzene was distilled over sodium and benzophenone, and collected when the deep blue colour of the ketyl persisted.

Procedure

(4-Ethynylphenyl)diphenylmethanol (2.84g, 10mmol) was dissolved in benzene (20ml) under a dry nitrogen atmosphere. The temperature was reduced to 0^0C before thionyl chloride (3ml, excess) was added via canulla wire, and the solution was stirred rapidly at this temperature for 30 minutes. The reaction was completed by stirring for 4 hours at room temperature. Removal of solvent and excess thionyl chloride in vacuo yielded a green/brown viscous oil, which was recrystallised from hexane/carbon tetrachloride (5:1) to give a light yellow powdery solid.

5.4.xvii. Results: (4-Ethynylphenyl)diphenylchloromethane 5a

The yield after recrystallisation was 2.75g (91%). This new compound was found to hydrolyse rapidly in air to give (4-ethynylphenyl)diphenylmethanol, and hence all the characterization methods were carried out under nitrogen. Melting point 116-118^{0}C.

Characterization of 5a

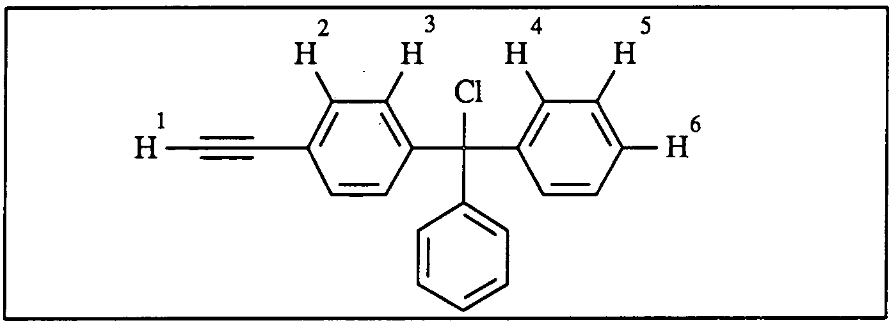
a- Combustion analysis: calculated for $C_{21}H_{15}Cl$: C, 83.30%; H, 4.99%; Cl 11.71%: found: C, 81.96%; H, 5.00%; Cl 11.69%.

b- Chromatography was not possible using neutral silica or alumina owing to hydrolysis on the TLC plates to (4-ethynylphenyl)diphenylmethanol.

c- The infra-red spectrum (Appendix 5-37) showed the following diagnostic bands: ν (KBr disc)/cm^{-1}: 3280 (acetylenic CH), 3060,3040,3020 (aromatic CH), 2100 (RC≡CH), 1595 (C=C), 780 (C-Cl).

d- The ^{1}H NMR spectrum (Appendix 5-38) gave good evidence for the structure below:

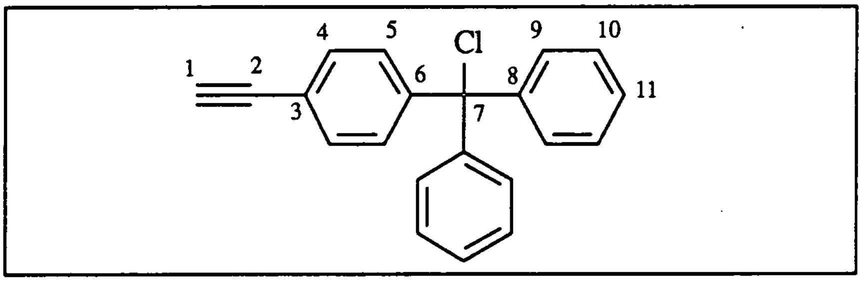
Figure 5.4.xviii.



δ/ppm (C_6D_6): 2.69 (s,1H,H^1), 6.97-7.27 (m,14H,H$^{2-6}$).

e- The ^{13}C NMR spectrum (Appendix 5-39) provided further evidence for the designated structure. The assignments were based, in part, on APT spectra, and by comparison with known compounds, or those synthesized above.

Figure 5.4.xxix.



δ/ppm (C_6D_6): 78.52 (C^1), 81.30 (C^7), 83.30 (C^2), 122.21 (C^3), 128.04, 129.96 (C^9,C^{10,11}), 130.10 (C^5), 131.76 (C^4), 145.26 (C^6), 146.27 (C^8).

oblems with the probe at the time these spectra were recorded meant that C^1 d C^2 were not distinguishable in the APT spectrum, and thus assignment was sed on peak heights on the proton-decoupled spectrum.

e mass spectrum (Appendix 5-40) showed a low intensity molecular ion for th of the ^{37}Cl and ^{35}Cl isotopes in the required 1:3 ratio, and a base peak rresponding to the loss of chlorine.

e: 305 (M$^+$(^{37}Cl),1.05,CI$^+$), 303 (M$^+$(^{35}Cl),3.02), 268 (MH$^+$-Cl,32.3),
7(M-Cl,100).

CONCLUSIONS

e final product (4-ethynylphenyl)diphenylmethanol was produced in an overall b from 4-bromobenzophenone via a four-step route. However, this monomer gradually even when stored at -20^{0}C in the dark inside the glovebox, and thus best stored as its precursor l-2-hydroxybut-3-ynyl)phenyl)diphenylmethanol, which appears not to over a period of several months. It should also be noted that crystals of enyl)diphenylmethanol obtained from carbon tetra chloride contain solvent ng crystallisation, a property shared with triphenylmethanol, which is known rates with many solvents[135]. The approximate composition of the inclusion of (4-ethynylphenyl)diphenylmethanol with carbon tetrachloride is CCl$_4$, as opposed to the 1:1 clathrate reported for triphenylmethanol with

e other desired monomer, (4-ethynylphenyl)diphenylchloromethane, was an overall yield of 42%. Analysis of purity was not possible by conventional monomer hydrolysed on alumina and silica plates, and as this hydrolysis dly on standing in air this monomer too was stored in the glovebox at -20^{0}C.

CHAPTER SIX

POLYMER SYNTHESES AND MANIPULATIONS

POLY(PHENYLACETYLENE)

POLY((4-ETHYNYLPHENYL)DIPHENYLMETHANE)

POLY((4-ETHYNYLPHENYL)DIPHENYLMETHANOL)

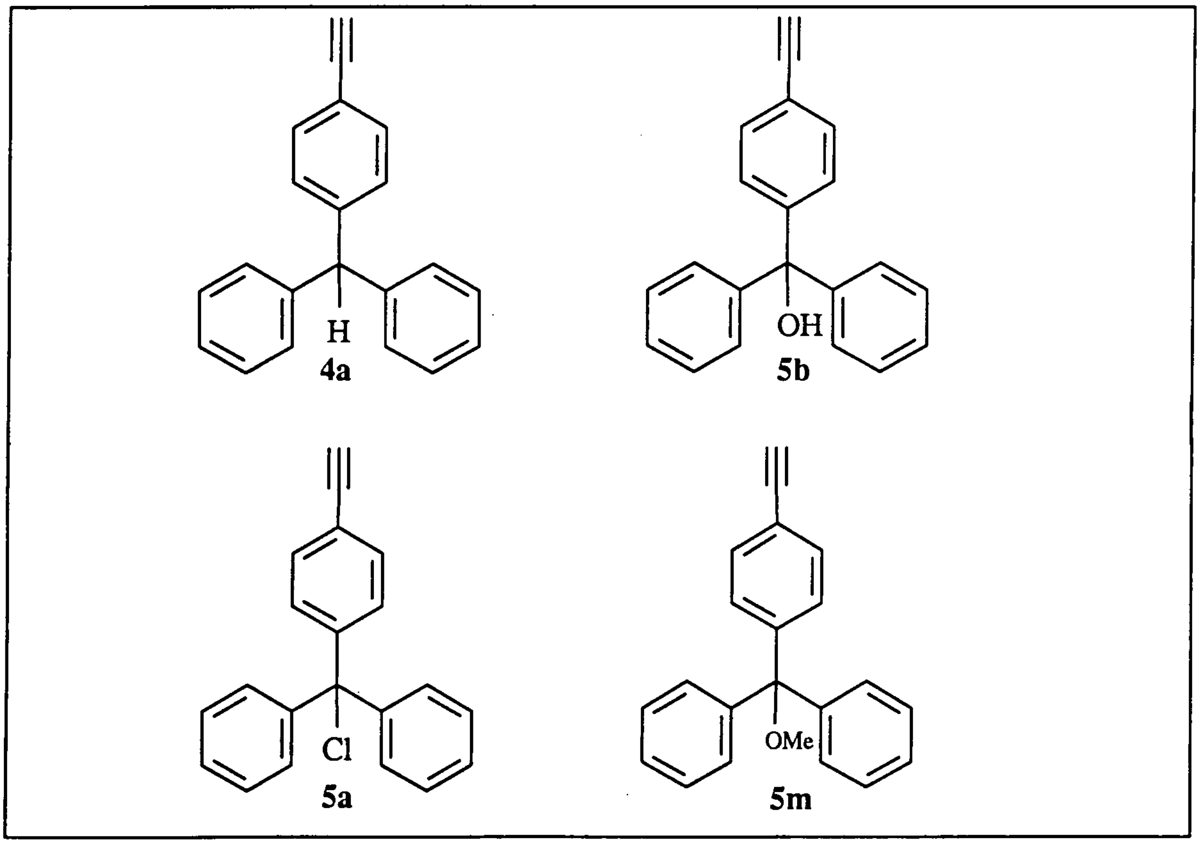
POLY((4-ETHYNYLPHENYL)DIPHENYLCHLOROMETHANE)

POLY((4-ETHYNYLPHENYL)DIPHENYLMETHOXYMETHANE)

Introduction

The main object of this research project was to prepare substituted conjugated polymers in a controlled manner, in an attempt to equate the bulk magnetic properties with chemical structure. The structure of the materials produced by the polymerization of the relatively simple monomer, phenylacetylene, has still to be fully understood. Therefore, initial work was directed towards this goal, in order to establish reference points for the structure of materials produced by polymerization of substituted arylacetylenes. To facilitate these studies, phenylacetylene was polymerized using the well-defined metathesis catalyst ($(({}^tBuO)_2Mo(=NAr)(=CH{}^tBu)$: Ar= 2,6-di-*iso*-propylphenyl), and the rhodium catalyst described by Furlani[100], since both these systems have been shown to be capable of giving polymers with regular microstructures in some cases. Polymerization studies were also carried out on the monomers prepared in chapters 4 and 5 and shown in figure 6.i.

Figure 6.i.



The same catalyst systems were employed for these monomers in an attempt to control the final polymer microstructure as closely as possible.

Polymerizations with "Classical" Metathesis Catalysts

The so-called "classical" metathesis catalysts such as $MoCl_5$ or WCl_6, either alone or in combination with co-catalysts such as Ph_4Sn or Me_4Sn, were also used. Initial experiments with phenylacetylene confirmed the activity of these catalysts, with results in accordance with those of previous reports in the literature[75,76]. However, under conditions where phenylacetylene was readily polymerized, these catalytic systems were deactivated by **5a** and **5b**. The monomers **4a** and **5m** proved difficult to obtain in a pure state and sufficient quantities were not available for tests using the classical catalysts. Since the polymerization of phenylacetylene with these catalysts has been well documented, it was decided to concentrate on the Schrock and Furlani catalysts for the preparation of polyphenylacetylene and the substituted poly(arylacetylenes).

6.1. General Experimental Procedures

6.1.i. Purification of Reagents

The use of metathesis catalysts such as tungsten (VI) chloride, molybdenum (V) chloride and the "Schrock catalysts" required that all reagents be rigorously purified. Phenylacetylene was double-distilled onto fresh 4A molecular sieves and transferred in vacuo *immediately prior to use. All other monomers were recrystallised at least twice before use, and the solvents and reagents were purified under an inert atmosphere as described below, and stored under dry nitrogen.*

Benzene, hexane, tetrahydrofuran and toluene were dried over sodium wire before being distilled over sodium or potassium in the presence of benzophenone. The solvent was collected when the deep-blue colour of the radical anion persisted. Methanol was distilled onto fresh 4A molecular sieves. Dichloromethane, tetrachloromethane and chlorobenzene were twice distilled over phosphorus pentoxide and stored over fresh 4A molecular sieves. All solvents were degassed by several freeze-thaw cycles before use. Tungsten (VI) chloride, molybdenum (V) chloride, tetraphenyltin and tetramethyltin were used as received from Aldrich (Gold label >99.9% pure). The Schrock catalysts were prepared by co-workers in this department using a recently published route[137]. *The rhodium catalyst* $[Rh(COD)Cl]_2$ *was prepared by a literature method*[138].

All glassware was flame dried whilst being evacuated (10^{-3} *torr), and then flushed repeatedly with dry nitrogen. All polymerization reactions and subsequent manipulations of the polymers were carried out under nitrogen, either in Schlenk tubes using conventional vacuum-line techniques, or in a glovebox.*

All glassware was flame dried whilst being evacuated (10^{-3} torr), and then flushed repeatedly with dry nitrogen. All polymerization reactions and subsequent manipulations of the polymers were carried out under nitrogen, either in Schlenk tubes using conventional vacuum-line techniques, or in a GloveBox.

6.1.ii. Characterization Techniques

Elemental Analysis

Samples were sealed in metal or gelatine capsules inside a GloveBox, and removed immediately prior to use.

Gel Permeation Chromatography

Filtered solutions (1% w/v) in THF were prepared in the GloveBox and tranferred into Schlenk tubes. The required amount was withdrawn by airtight syringe and injected immediately to minimise oxidation.

Infra-Red Spectroscopy

Thin films of the polymers were cast from tetrachloromethane or, in the case of the chlorinated materials, benzene, onto NaCl or KBr plates. These plates were assembled between rubber "O" rings inside a metal holder to prevent atmospheric oxidation. Both operations were carried out in a GloveBox.

NMR Spectroscopy

Choroform-d *and benzene*-d_6 *were stirred over* P_2O_5 *and transferred* in vacuo *before being degassed several times by freeze-thaw cycles. Solutions were made up inside a GloveBox. Samples for solid-state CP/MAS were powdered under a nitrogen atmosphere before insertion into the spectrometer.*

6.2. Polymerizations of Phenylacetylene

6.2.i. Schrock Catalyst Route

6.2.i.a. NMR Scale Polymerizations

The controlled polymerization of phenylacetylene was attempted using the well-defined tungsten and molybdenum catalysts. A typical procedure is described overleaf.

Phenylacetylene (19μl, 17.7mg, 0.173mmol) was dissolved in C_6D_6 (200μl) and the solution filtered through dry alumina into a sample vial in a GloveBox. Tungsten catalyst (10mg, 0.017mmol) was dissolved in pre-filtered C_6D_6 (200μl) in a second sample vial. After complete solvation of the catalyst, the monomer solution was added to the catalyst solution with rapid stirring. The reaction was monitored by ^1H NMR after ten minutes, and at hourly intervals. Variations on this typical procedure are shown in table 6.2.i. Norbornene (NBE) was added to test for catalyst activity after full conversion of monomer; quinuclidine was used to modify catalyst activity. All runs were carried out at room temperature.

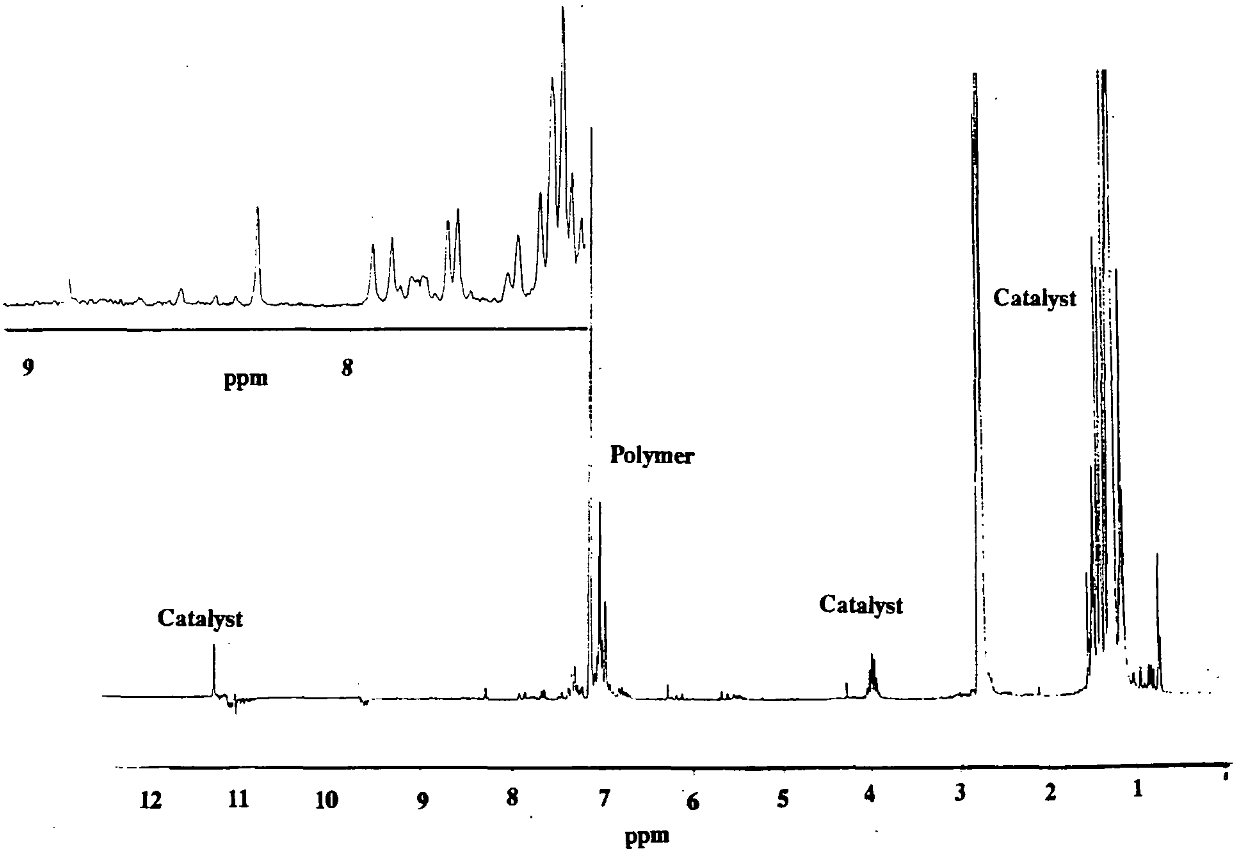
Table 6.2.i. Catalyst was $(t\text{-BuO})_2W(NAr)(CHt\text{-Bu})$ unless otherwise stated; equivalents are relative to catalyst.

Monomer	Catalyst	NBE	Quinuclidine	Result
0.550mmol 35 eq.	0.017mmol	10mmol	none	Gel
0.235mmol 15 eq.	0.017mmol	10 mmol	none	Gel
0.173mmol 5 eq.	0.034mmol	10 mmol	none	Gel
0.205mmol 10 eq.	[Mo] 0.0205mmol	none	none	PPA
0.034mmol 1 eq.	0.035mmol	none	none	PPA
0.045mmol	[Mo] 0.045mmol	none	none	PPA
0.0205mmol	[Mo] 0.0205mmol	none	0.1025mmol,5eq.	PPA
0.01025mmol 0.5 eq.	[Mo] 0.0205mmol	none	0.1025mmol,5eq.	PPA

Results

In all cases, addition of phenylacetylene to the catalyst resulted in polymer formation within ten minutes. The initial yellow colour of the catalyst changed rapidly to the deep red colour of poly(phenylacetylene), with a concurrent increase in the viscosity of the solution. A slight induction period (~1-2 minutes) was apparent in the case of the molybdenum catalyst in the presence of quinuclidine, but the ^1H NMR spectrum showed evidence of polymer formation by the time the NMR tube was placed in the spectrometer. A typical spectrum is shown in Figure 6.2.i. overleaf.

Figure 6.2.i.



Conclusions

The attempted controlled polymerization of phenylacetylene was not successful. The ^{1}H NMR spectra showed the presence of residual catalyst and polymer, with no monomer remaining after one hour in the reaction system. Addition of norbornene caused rapid gelation, indicating that the catalyst was still active after complete conversion of monomer. These results were in general agreement with those of Schrock[65], and indicated that initial reaction of phenylacetylene with the catalyst produced a new catalytic species of higher activity than the original alkylidene. Thus, the rate of propagation was higher than the rate of initiation, and an uncontrolled polymerization resulted. Vinylalkylidenes have been reported to be active initiators of alkyne polymerization and the ^{1}H NMR spectra in these studies displayed resonances between 8-10 ppm in accord with values quoted for molybdenum vinylalkylidenes[139].

6.2.i.b. Preparative Scale Polymerization

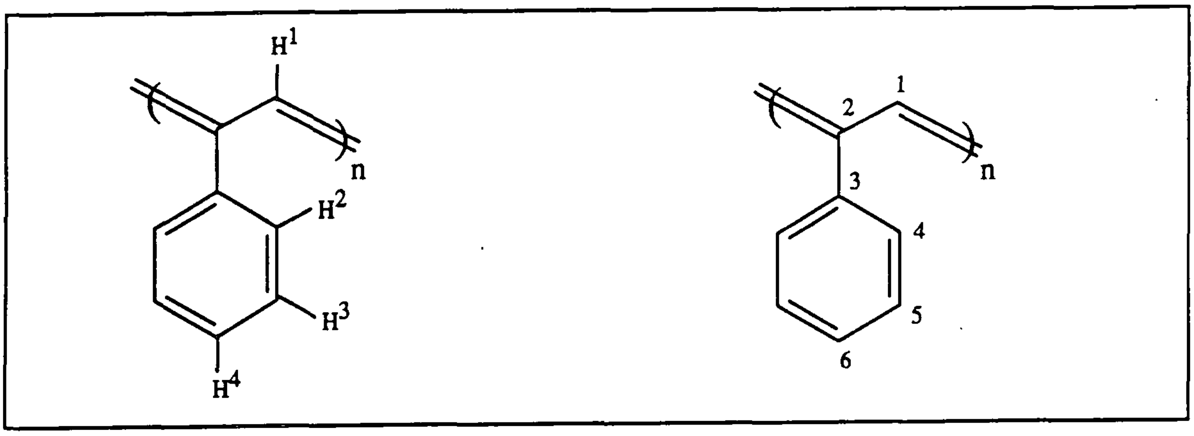
Phenylacetylene (1.02g, 10mmol) was dissolved in toluene (5ml) and added via canulla wire to a Schlenk tube containing a solution of molybdenum catalyst (24.3mg, 0.05mmol) in toluene (5ml). Rapid stirring was maintained throughout. After eighteen hours at room temperature, the reaction was terminated by addition of the solution to methanol (150ml). The polymer was recovered by centrifugation, and purified by redissolving in toluene (15ml) followed by reprecipitation in methanol. This process was carried out three times to remove unreacted monomer and low molecular weight oligomers.

6.2.ii. Results 6a

The polymer (695mg, 70%) was orange in colour, with a similar appearance to PPA prepared with $MoCl_5/Me_4Sn$, following the method of Masuda[75].

Characterization of 6a

Figure 6.2.ii. Numbering System for 6a



a- Combustion analysis: calculated for C_8H_6;C, 94.07%; H, 5.93%: found C, 91.51%; H, 5.93%.

b- Gel Permeation Chromatography (GPC) (Appendix 6-1) indicated a highly disperse polymer. M_w= 92,000; M_n= 18,000; M_w/M_n= 5.2.

c- The infra-red spectrum (Appendix 6-2) showed the following diagnostic bands: ν (thin film)/cm^{-1}: 3080,3060,3020 (aromatic CH), 1605 (C=C), 1380, 970, 920 , 880, 740. Of these bands, previous authors have repeatedly assigned those at 740, 880 and 920 and 1380 to cis-PPA, and the absorption at 970 to trans-PPA (see Chapter 2).

d- The ^{1}H NMR spectrum (Appendix 6-3) exhibited broad, partially resolved resonances. δ/ppm (C_6D_6): 6.18, 6.84, 6.97-7.03, 7.10-7.14. These absorptions are consistent with literature reports of cis and trans-PPA. Integrals were rendered meaningless by overlap with residual solvent protons.

e- The ^{13}C NMR spectrum (Appendix 6-4) displayed the following resonances. δ/ppm ($CDCl_3$): 125.27, 126.68, 127.54, 127.76, 128.19, 129.01, 131.79, 139.32, 142.86. The resonances at 126.68, 127.54, 127.76, 128.19, 129.01, 131.79, 139.32 and 142.86 were strong and relatively sharp and agreed with previous literature values for both cis- and trans-PPA (see Chapter 2).

6.2.iii. Furlani Catalyst Route

The method described by Furlani[100] was modified to ensure that atmospheric oxidation was prevented.

Phenylacetylene (1.02g, 10mmol) was dissolved in dry, degassed methanol (20ml) at 50^{0}C. In a separate Schlenk tube, [Rh(COD)Cl]$_2$ (24.6mg, 0.05mmol) was dissolved in boiling methanol (30ml), with rapid stirring. The monomer solution was added via canulla wire and the temperature was raised to 60^{0}C. The reaction was carried out at for three hours at this temperature. Addition of cold methanol (50ml), followed by filtration and repeated washing of the filtrant left a bright yellow-orange polymer.

6.2.iv. Results 6b

Total yield was 780mg (78%). The polymer was soluble in benzene, dichloromethane, tetrachloromethane and tetrahydrofuran.

Characterization of **6b**

The numbering system for **6b** was as shown above in Figure 6.2.i.

a- Combustion analysis: calculated for C_8H_6; C, 94.07%; H, 5.93%: found C, 92.28%; H, 5.63%.

b- Gel Permeation Chromatography GPC (Appendix 6-5) indicated a relatively low polydispersity material. M_w= 80,000; M_n= 40,000; M_w/M_n= 2.0.

c- The infra-red spectrum (Appendix 6-6) showed the following diagnostic bands: ν (thin film)/cm^{-1}: 3080,3060,3020 (aromatic CH), 1605 (C=C), 1380, 970 (w), 920, 880, 740. These absorptions are consistent with previous reports of PPA assigned to the cis isomer, with the weak band at 970 corresponding to a trace of trans-PPA.

d- The ^{1}H NMR spectrum (Appendix 6-7) was well-resolved, and in close agreement with the original work by Furlani[100]. δ/ppm ($CDCl_3$): 5.87 (s,1H), 6.65-6.66 (d,2H)), 6.96-6.97 (m,3H). Literature values: 5.84, 6.63-6.64, 6.93-6.95.

e- The ^{13}C NMR and ^{13}C NMR APT spectra (Appendix 6-8) were also well-resolved. δ/ppm ($CDCl_3$): 126.68 (C^{1or6}), 127.52,127.61 ($C^{4,5}$), 131.81,(C^{1or6}), 139.28,142.85 ($C^{2,3}$). The APT spectrum confirmed that the resonances at 139.3 and 142.9ppm were due to quaternary carbons. (Lit. 126.6, 127.4-127.6, 131.7, 139.3, 142.8.).

6.3. Polymerization of (4-ethynylphenyl)diphenylmethane (4a),

6.3.i. Schrock Catalyst Route

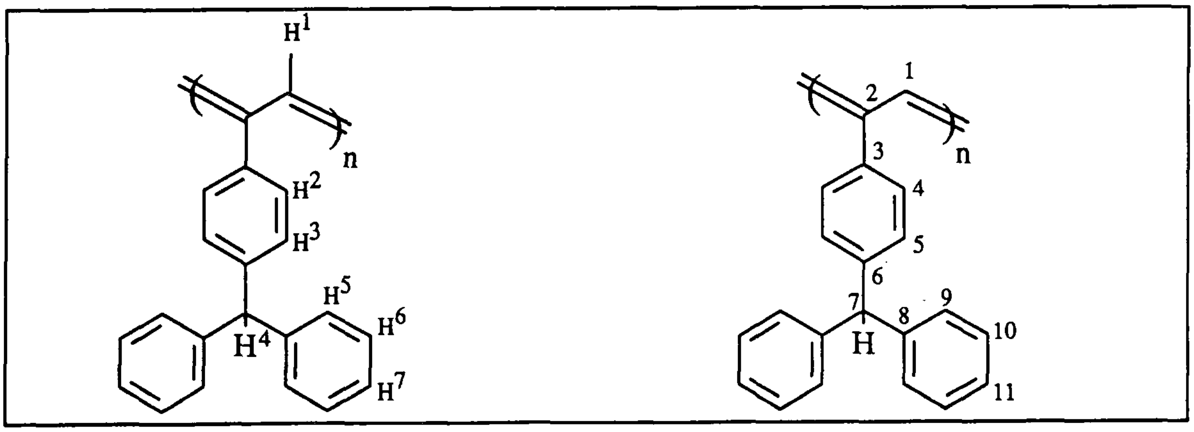
In a Schlenk tube, molybdenum catalyst (50mg, 0.10mmol) was dissolved in benzene (5 ml). A solution of (4-ethynylphenyl)diphenylmethane (2.68g, 10mmol) in benzene was added via canulla wire, and the solution stirred rapidly for 12 hours at room temperature. The reaction was terminated by addition of acetone (2 ml), and the solution added to methanol (200 ml). The polymer was recovered by repeated precipitation in methanol from benzene solution, followed by centrifugation (20000 rpm, 15 minutes).

6.3.ii. Results- Poly(4-Ethynylphenyl)diphenylmethane (6c)

The yield of pure polymer was 1.37g (52%). The polymer was an orange powdery solid soluble in benzene, toluene, chloroform, dichloromethane and tetrahydrofuran.

Characterization of 6c

Figure 6.3.i. Numbering System for 6c



a- Combustion analysis: calculated for $C_{21}H_{16}$; C, 93.99%; H, 6.01%: found C, 92.17%; H, 5.64%.

b- Gel Permeation Chromatography (GPC) (Appendix 6-9) showed the polymer to be of intermediate polydispersity. M_w= 36,300; M_n= 14,200; M_w/M_n= 2.6.

c- The infra-red spectrum (Appendix 6-10) showed the following diagnostic bands: ν (thin film)/cm^{-1}: 3080,3060,3020 (aromatic CH), 2880 (aliphatic CH), 1605 (C=C), 1260, 920, 870, 740.

d- The ^1H NMR spectrum (Appendix 6-11) contained two broad, unresolved peaks, and traces of monomer; assignment was by comparison with the monomer. δ/ppm (C_6D_6): 5.2-5.4 (H^4), 6.6-7.4 ($H^{2,3,5-7}$). A small very broad resonance was evident at 6.0-6.1ppm.

e- The ^{13}C NMR and APT spectra (Appendix 6-12) displayed the following resonances, assigned partially below, by comparison with the monomer. δ/ppm (C_6D_6): 56.92 (C^7), 126.55,127.75,127.99,128.23,128.62,129.26,129.86, 132.38, ($C^{1,4,5,9-11}$), 144.34 ($C^{2,3,6,8}$). The band at 144ppm was very broad, and thus may have contained several peaks. As the cis/trans nature and enchainment sequence were unknown, it is reasonable to assume that there were more carbon environments than are depicted in the numbering system above. The computer running the spectrometer identified several multiple peaks in 140-144ppm region for solutions of the polymer in $CDCl_3$.

6.3.iii. Furlani Catalyst Route

(4-Ethynylphenyl)diphenylmethane (2.68g, 10mmol) was dissolved in dry, degassed methanol (20ml) at 50°C, and added via canulla wire to [Rh(COD)Cl]$_2$ (24.6mg, 0.05mmol) in boiling methanol (30ml). The solution was maintained at 60°C for five hours, giving a yellow-brown flocculent precipitate. The polymer was recovered by centrifugation (20,000 rpm, 10 minutes), and repeated washing with methanol.

6.3.iv. Results- Poly(4-Ethynylphenyl)diphenylmethane (6d)

The polymer produced (1.84g, 70%) was yellow in colour, and was soluble in benzene, toluene, dichloromethane and tetrahydrofuran. However, the solubility was lower than that of the molybdenum-prepared analogue, due possibly to a different chain microstructure.

Characterization of **6d**

The numbering system for **6d** was as shown in Figure 6.3.i.

a- Combustion analysis: calculated for $C_{21}H_{16}$; C, 93.99%; H, 6.01%: found C, 91.52%, H, 5.98%.

b- Gel Permeation Chromatography (GPC Appendix 6-13) showed similar molecular weight distributions to **6b**, and a peak at long retention times, due probably to monomer residues. M_w= 91,600,; M_n= 38,000; M_w/M_n= 2.4.

c- The infra-red spectrum (Appendix 6-14) showed the presence of trapped monomer as well as polymer. ν (thin film)/cm^{-1}: 3280 (acetylenic CH), 3080,3060,3020 (aromatic CH), 2920,2980 (aliphatic CH), 1605 (C=C), 1380, 1270, 970, 880, 740.

d- The ^1H NMR spectrum (Appendix 6-15) contained sharper resonances than the corresponding metathesis polymer **6c**, but with the same general features.

δ/ppm (C_6D_6): 5.2, (H^4),5.3-5.5 (2), 6.0-6.2 (1), 6.7,6.9,7.1,7.3 (13). Integrals are shown in parentheses, but have limited significance because of monomer and solvent impurities.

e- The ^{13}C NMR spectrum (Appendix 6-16) contained eleven peaks: δ/ppm (C_6D_6): 56.93 (C^7), 126.47,126.62,127.84,128.08,128.59,129.70,129.82,132.35 ($C^{1,4,5,9-11}$), 143.71 ($C^{2,3}$), 144.33 ($C^{6,8}$).

6.4. Polymerization of (4-Ethynylphenyl)diphenylmethanol

6.4.i. Schrock Catalyst Route

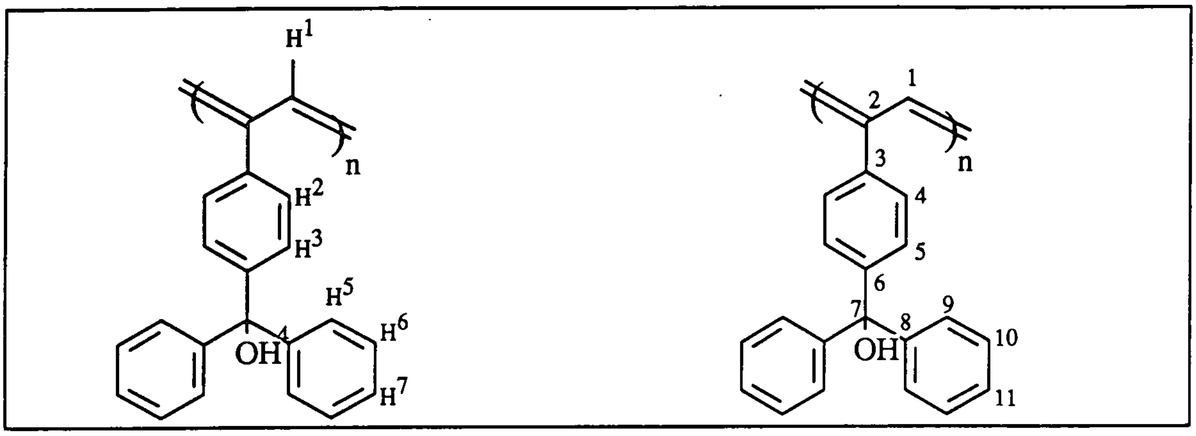
A solution of (4-ethynylphenyl)diphenylmethanol (2.84g, 10mmol) in benzene (5ml) was added via canulla wire to molybdenum catalyst (48.7mg, 0.1mmol) in benzene, with rapid stirring. The reaction was carried out for 24 hours at room temperature before addition to methanol (200ml). Repeated cycles of centrifugation (20,000rpm, 10 minutes), solvation in benzene (15ml), and precipitation in methanol (200ml) gave an orange polymer.

6.4.ii. Results 6e

The best yield obtained for this reaction was 1.70g (60%). However, average yields were 40-50%, with factors such as stirring speed and exact monomer concentration being critical. The presence of the free hydroxyl group was probably the cause of catalyst deactivation. The use of very concentrated solutions favoured polymer formation, but caused problems with precipitation as the polymer chain increased in molecular weight.

Characterization of **6e**

Figure 6.4.i. Numbering System for **6e**



a- Combustion analysis: calculated for $C_{21}H_{16}O$; C, 88.70%; H, 5.67%; O, 5.63%: found C, 88.00%: H, 5.74%.

b- Gel Permeation Chromatography GPC (Appendix 6-17) gave the following molecular weight distributions: M_w= 47,400, M_n=21,000: M_w/M_n= 2.3.

On some occasions bimodal distributions were observed, indicating that the polymerizations may have involved more than one propagating species.

c- The infra-red spectrum (Appendix 6-18) showed the following diagnostic bands: ν (thin film)/cm^{-1}: 3550,3480 (OH), 3080,3060,3020 (aromatic CH), 1605 (C=C), 1380,920 (weak), 730.

d- The ^1H NMR spectrum (Appendix 6-19) contained one broad, poorly resolved absorption. No hydroxyl protons were identified in the spectrum.

δ/ppm (C_6D_6): 6.7-7.4.

e- The solution and solid state ^{13}C NMR spectra (Appendix 6-20) are assigned partially below, by comparison with the monomer. Up to five peaks were indicated by the NMR computer for C^7 in C_6D_6 solution, between 81.7 and 82.3ppm, possibly indicating the variety of environments present in the polymer. Peaks in the aromatic region were best observed in deuteriochloroform.

δ/ppm ($CDCl_3$): 127.07,127.16,127.48,127.87,128.06,128.22,128.48, 128.66,129.03,131.71 ($C^{1,4,5,8-11}$), 146.44 ($C^{2,3,6,8}$).

The ^{13}C NMR CP/MAS spectra confirmed that the peaks at 81 and 146ppm were due to quaternary carbons. δ/ppm: 81.65 (C^7), 127.72 ($C^{1,4,5,8-11}$, 146.30 ($C^{2,3,6,8}$). QS: 127.78. NQS: 82.04, 127.85, 146.30.

6.4.iii. Furlani Catalyst Route

(4-Ethynylphenyl)diphenylmethanol (2.84g, 10mmol) was dissolved in dry, degassed methanol (20ml) at 50^{0}C, and added to [Rh(COD)Cl]$_2$ (24.9mg, 0.05mmol) in boiling methanol (30ml). The solution was stirred at 25^{0}C for four hours and then centrifuged (20,000rpm, 10 minutes). The resultant brown solid was washed repeatedly with dry methanol.

6.4.iv. Results 6f

The yield was 2.20g (78%), of a yellow-brown powdery solid. The reaction was initially carried out in boiling methanol, and the polymer produced exhibited ^{13}C NMR resonances at 52ppm and 87ppm. These were very similar to those obtained for the C-O$\underline{\text{Me}}$ and $\underline{\text{C}}$-OMe peaks of poly((4-ethynylphenyl)diphenylmethoxymethane) and thus may have indicated methylation by the solvent. For polymerizations carried out at room temperature, these resonances disappeared, but IR spectra indicated that the product may have contained small amounts of the methylated polymer. The polymer was considerably less soluble than the corresponding molybdenum prepared precursor.

Characterization of **6f**

The numbering system for **6f** was as shown in Figure 6.4.i.

a- Combustion analysis: calculated for $C_{21}H_{16}O$; C, 88.70%; H, 5.67%; O, 5.63: found C, 86.47%; H, 5.69%.

b- Gel Permeation Chromatography GPC (Appendix 6-21) showed a very broad molecular weight distribution. M_w= 55,400, M_n= 6,500: M_w/M_n= 8.6.

c- The infra-red spectrum (Appendix 6-22) showed the following diagnostic bands: ν (thin film)/cm^{-1}: 3580,3480 (OH), 3080,3060,3020 (aromatic CH), 2980 (w, aliphatic CH),1605 (C=C), 970, 920,740 (shoulder peaks). The hydroxyl mode was weaker than in the metathesis polymer, and the presnece of aliphatic CH modes indicated possible methylation.

d- The ^{1}H NMR spectrum (Appendix 6-23) showed three main resonances. Integrals in parentheses. δ/ppm (C_6D_6): 2.7-3.1 (1,H^4), 6.2-7.1,7.3-7.8 (10,H$^{1-3,5-7}$).

e- The ^{13}C NMR spectrum (Appendix 6-24) was poorly resolved, owing partially to the low solubility of the polymer. δ/ppm (C_6D_6): 82.10 (C^7), 125.61,127.47,127.73,127.98,128.21,128.49,129.24,131.85 C$^{1,4,5,9-11}$), 147.37 (C^{2,3,6,8}).

6.5. Preparation of Poly(4-Ethynylphenyl)diphenylchloromethane 6g

6.5.i. Attempted Polymerizations of (4-Ethynylphenyl)diphenylchloromethane (5a)

Polymerizations were attempted using the Schrock and Furlani catalysts, with procedures similar to those described above for other substituted arylacetylenes. However, in all cases, the yield of polymer was less than 5%.

The polymerizations probably failed owing to impurities in the monomer. As discussed in the previous chapter, purification of (4-ethynylphenyl)diphenylchloromethane was not possible using column chromatography, and analysis by TLC resulted in monomer decomposition. Thus, residual impurities not apparent from NMR or IR spectroscopy may have caused catalyst deactivation.

6.5.ii. Chlorination of 6e and 6f

The method for chlorination was the same for both precursor polymers ***6e*** *and* ***6f****.*

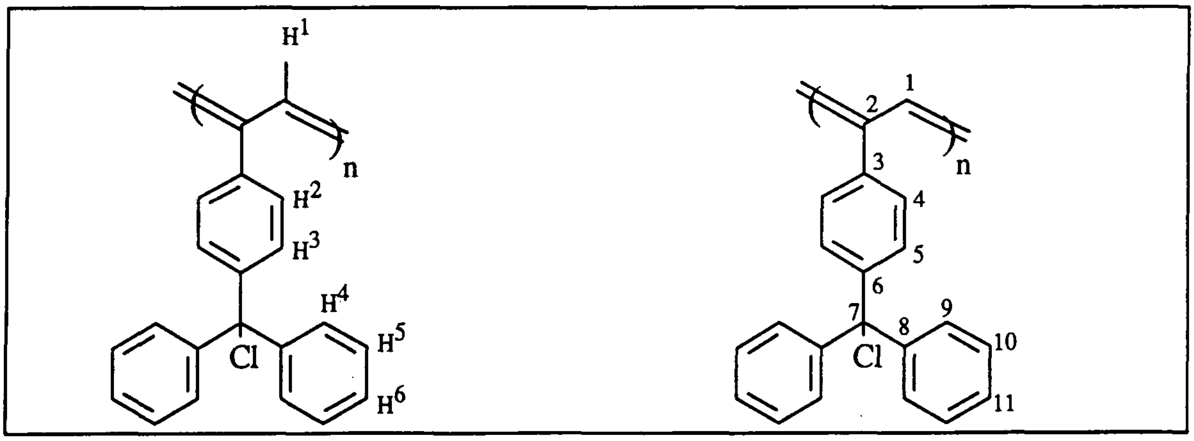
Poly(4-ethynylphenyl)diphenylmethanol (1.34g, 5mmol) was dissolved in benzene (20ml). The solution was stirred as double-distilled thionyl chloride (2ml, ~20mmol) was added via canulla wire. The solution darkened almost immediately, and heat was evolved. Infra-red spectroscopy of films cast from solution indicated complete disappearance of hydroxyl groups after two hours. The solvent and unreacted thionyl chloride were then removed in vacuo *(12hrs, 10^{-3}torr), leaving shiny red-brown flakes of polymer.*

6.5.iii. Results 6g

The yield of the chlorinated polymer from the molybdenum prepared precursor was 1.48g (98%).

Characterization of **6g**

Figure 6.5.i. Numbering System for **6g**



a- Combustion analysis: calculated for $C_{21}H_{15}Cl$; C, 83.29%; H, 5.00%; Cl, 11.71%: found C, 82.62%; H, 5.41%; Cl, 11.75%.

b- Gel Permeation Chromatography GPC (Appendix 6-25) indicated that, although the molecular weight distribution remained virtually unchanged from the hydroxyl precursor, the M_w and M_n values were reduced on chlorination. M_w= 22,900, M_n= 8700: M_w/M_n= 2.6. GPC measures the volumes of polymer coils in solution: thus a change of OH to Cl substitution may have had a significant effect. A sample stored in the light under nitrogen showed significant degradation over three months; this chromatogram is also shown in Appendix 6-25. M_w= 4400; M_n= 3300; M_w/M_n= 1.4.

c- The infra-red spectrum (Appendix 6-26) showed the following diagnostic bands, with complete disappearance of hydroxyl groups: ν (thin film)/cm^{-1}: 3080,3060,3020 (aromatic CH), 1605 (C=C), 1265, 970, 780 (C-Cl).

d- The ^1H NMR spectrum (Appendix 6-27) showed a broad resonance in the aromatic region as expected, and a significant broad band (0.8-2.4ppm) of unknown origin. This may have been due to an impurity such as vacuum grease, but is not assigned with certainty. A further peak at 4.2ppm was present which, from its lineshape, was probably a solvent, rather than a polymer, impurity. δ/ppm (C_6D_6): 6.4-7.6.

e- The ^{13}C NMR CP/MAS spectrum (Appendix 6-28) distinguished the quaternary carbons. The polymer was not sufficiently soluble for solution state ^{13}C NMR spectra to be recorded. The spectrum was virtually superimposable on that of the hydroxy precursor. δ/ppm: 81.29 (C^7), 128.50 ($C^{1,4,5,9-11}$), 144.82 ($C^{2,3,6,8}$). QS: 128.50. NQS: 144.69, 128.42, 81.88.

6.5.iv. Results 6h

The yield from the rhodium prepared precursor was 1.24g (82%): losses were incurred due to precipitation of some polymer on addition of thionyl chloride. The recovered polymer was considerably less soluble in benzene and chloroform than the corresponding molybdenum prepared precursor.

Characterization of **6h**

The numbering system for **6h** was as shown in Figure 6.5.i.

a- Combustion analysis indicated a slightly lower chlorine content than expected. The presence of methyl ether sites as impurities in the precursor **6f** may have accounted for the incomplete chlorination.

Calculated for $C_{21}H_{15}Cl$; C, 83.29%; H, 5.00%; Cl, 11.71%: found C,83.75%; H, 5.20%; Cl, 11.05%.

b- Gel Permeation Chromatography GPC could not be carried out immediately after preparation, and the chromatogram (Appendix 6-29) appeared to indicate that the polymer had degraded during chlorination and/or storage. The low molecular weights recorded may have also been due to the fact that the polymer was not completely soluble in THF. M_w= 3040; M_n= 1760; M_w/M_n= 1.7.

c- The infra-red spectrum (Appendix 6-30) showed the following diagnostic bands: ν (thin film)/cm^{-1}: 3080,3060,3020 (aromatic CH), 1600 (C=C), 1270, 970, 790 (C-Cl).

d- The ^{1}H NMR spectrum (Appendix 6-31) contained a single broad resonance, with two shoulders. δ/ppm ($CDCl_3$): 5.6-5.7, 6.4-6.5, 6.6-7.4. The band at 0.8-2.4ppm, observed for **6g**, was not seen for this polymer, encouraging the belief that in the earlier sample, it was due to an impurity.

e- The ^{13}C NMR CP/MAS spectrum (Appendix 6-32) distinguished the quaternary carbons. The polymer was not sufficiently soluble for solution state ^{13}C NMR spectra to be recorded. δ/ppm: 80.73 (C^{7}), 127.60 ($C^{1,4,5,8-11}$), 144.70 ($C^{2,3,6,8}$). QS: 127.54. NQS: 144.60, 127.70, 80.79.

6.6. Polymerization of (4-Ethynylphenyl)diphenylmethoxymethane (5m).

6.6.i. Schrock Catalyst Route

Attempts to prepare poly((4-ethynylphenyl)diphenylmethoxymethane) using the Schrock molybdenum catalyst proceeded in very low yield. The difficulty in obtaining suitable quantities of the monomer in a state of high purity resulted in the abandonment of this reaction.

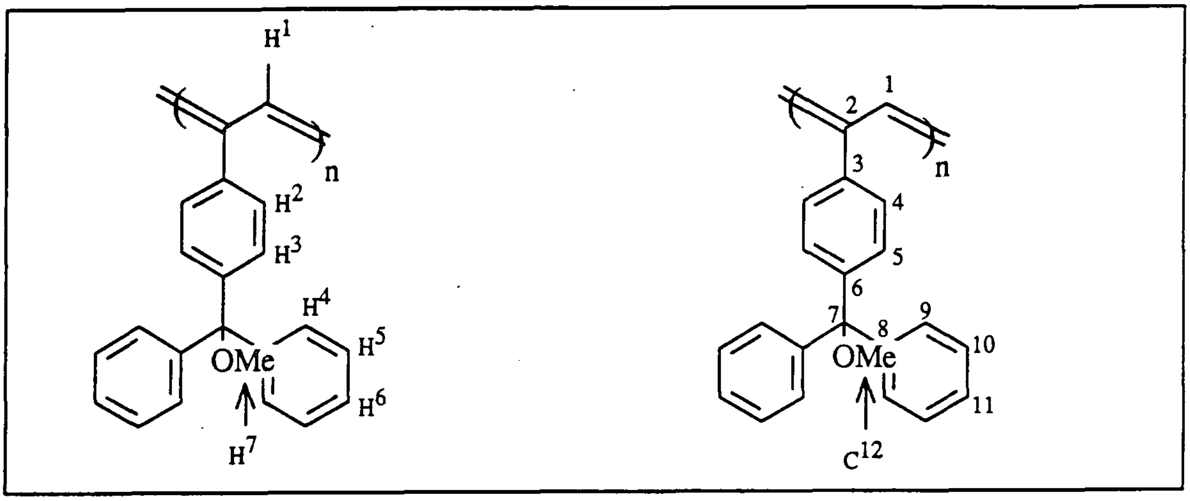
6.6.ii. Furlani Catalyst Route

A solution of (4-ethynylphenyl)diphenylmethoxymethane (1.49g, 5mmol) in dry, degassed methanol (20ml) was heated to 50⁰C and added via canulla wire to [Rh(COD)Cl]$_2$ (24.9mg, 0.05mmol), in boiling methanol (30ml). The solution was refluxed for three hours, allowed to cool and centrifuged (20,000rpm, 10 minutes). Repeated washing with methanol followed by drying in vacuo *left a brown powdery solid.*

6.6.iii. Results 6i

The final yield was 0.94g (60%). The polymer was only slightly soluble in benzene, chloroform and THF.

Figure 6.6.i. Numbering System for 6i



Characterization of 6i

a- Combustion analysis: calculated for $C_{22}H_{18}O$; C, 88.55%; H, 5.36%; O, 6.09%: found C, 85.79%; H, 5.69%.

b- Gel Permeation Chromatography GPC was not carried out immediately after polymer preparation. Thus the low molecular weights recorded (Appendix 6-33) may have indicated some degradation over time. The incomplete solubility may also have accounted for the low values recorded. M_w= 930; M_n= 620; M_w/M_n= 1.5.

c- The infra-red spectrum (Appendix 6-34) showed the following diagnostic bands: ν (thin film)/cm^{-1}: 3080,3060,3020 (aromatic CH), 2980,2940,2840 (aliphatic CH), 1605 (C=C)970, 920, 880 (w), 740.

d- The ^{1}H NMR spectrum (Appendix 6-35) showed two broad bands. δ/ppm ($CDCl_3$): 2.81-3.00 (m,H^7), 6.2-7.5 (H^{1-6}). The integral ratios were 1:7 compared to the 1:5 expected. There was also evidence of residual catalyst.

e- The ^{13}C NMR spectrum (Appendix 6-36) showed two environments for C^{12}. δ/ppm ($CDCl_3$): 52.02,52.12 (C^{12}), 126.82,127.74,128.02,128.48,128.76 ($C^{1,4,5,9-11}$), 143.51 ($C^{2,3,6,8}$). A weak resonance at ~88ppm was present in the spectrum, but was not recorded as a peak by the NMR computer. This was likely to have been the quaternary carbon C^7, which, in the monomer, resonates at 87ppm.

6.7. Dechlorination of Poly(4-Ethynylphenyl)diphenylchloromethane

6.7.i. Model Compound Studies

To test the efficacy of different routes to the desired polyradicals, a study was carried out on a model compound, triphenylchloromethane. The triphenylmethyl radical has been studied extensively[140], and thus literature methods were adapted accordingly to find the best method for generating the radical by dechlorination.

Results

It was found that copper turnings, silver and zinc powders, and a 1% sodium/mercury amalgam all generated the triphenylmethyl radical almost immediately if shaken with a solution of triphenylchloromethane in benzene. The reaction was marked by a change of the solution from colourless to deep yellow. The solution became colourless again if exposed to air, due to peroxide formation. ESR spectra (Appendix 6-50) were recorded to provide confirmation of the presence of the triphenylmethyl radicals.

6.7.ii. Dechlorination Routes

The removal of the tertiary chlorine atoms from the polymer was attempted with a range of metals and other reducing agents. All manipulations were carried out in a GloveBox, or on a vacuum-line with glassware repeatedly dried, evacuated and purged with dry nitrogen.

A typical procedure is outlined below, with exact reagents and conditions recorded in table 6.7.i. overleaf.

A solution of the chlorinated precursor (151mg, 0.5mmol) in dry, degassed solvent was stirred rapidly as the dechlorinating agent (5mmol) was added. After the reaction was adjudged to have reached completion, the mixture was filtered through a canulla wire fitted with glass and paper filters, and then passed twice through a sinter funnel (Porosity 3). Removal of solvent in vacuo *left black shiny flakes of polymer.*

Table 6.7.i.

Reducing Agent	Solvent	Time	Temperature / Conditions
Cu turnings	Benzene	2 hr	25^0C
Cu turnings	Benzene	3 hr	70^0C
Cu turnings	Benzene	6 hr	70^0C
Na/Hg(1%) amalgam	Benzene	14hr	reflux.30 fold xs Na/Hg.
Na/Hg(1%) amalgam	Benzene	14hr	reflux1hr: overnight 25^0C
Zn	Benzene	14hr	25^0C.20 fold xs Zn powder
Zn	Benzene	48hr	25^0C. High dilution: 6mM
Zn	Benzene	1hr	60^0C 100fold xs Zn
Zn	THF	2hr	60^0C Stirred 3 days 25^0C
Zn	Benzene	2hr	25^0C. Ultrasound at 40kHz
Ag	THF	2hr	Reflux
Ag	THF	30min	25^0C. Ultrasound at 40kHz
Ag	THF	2hr	25^0C. Ultrasound at 40kHz

6.8. Results and Characterization of "Polyradicals"

The dechlorination reactions above were repeated many times, but consistent results proved extremely difficult to obtain. Initial characterization of the materials involved elemental analysis and IR spectroscopy: ^{1}H and ^{13}C NMR spectra displayed very broad and poorly resolved signals and thus were of little use in obtaining information about the polymers, which is consistent with reasonable expectation.

Polyradicals made from metathesis precursors are referred to as **6j**, and those from rhodium precursors as **6k**.

a- Elemental Analysis

The desired polyradicals should have contained he repeat unit $(C_{21}H_{15})_n$, giving rise to the folowing elemental analysis figures. Calculated C, 94.34%; H, 5.66%. However, the results indicated that complete removal of chlorine from the polymers was never achieved. The best analysis obtained was for a dechlorination reaction using copper turnings in refluxing benzene.

Found (**6j**) C, 91.41%; H, 5.17%, Cl, 1.21%. These figures were found to be irreproducible.

The most consistent analyses resulted from the use of silver powder in THF at high dilution (2-5mM) with respect to the chlorinated precursor. Sonication of the reaction mixture for periods of 1-2 hours gave the following, repeatable, results for **6j** and **6k**:

Found C, 78.68%; H, 5.96%, Cl, 4.96%.

The silver content of these samples was never higher than 0.29%. The possibility of sulphur residues from previous reactions was tested and found to be less than 1%. These results are discussed later

b- Gel Permeation Chromatography

The molecular weight distributions for **6j** samples were very similar to the chlorinated precursors, indicating that neither chain scission or cross-linking had occurred during dechlorination. A trace for **6j** is shown in Appendix 6-37. M_w= 19,600; M_n= 8000. M_w/M_n= 2.4.

c- Infra-Red Spectroscopy

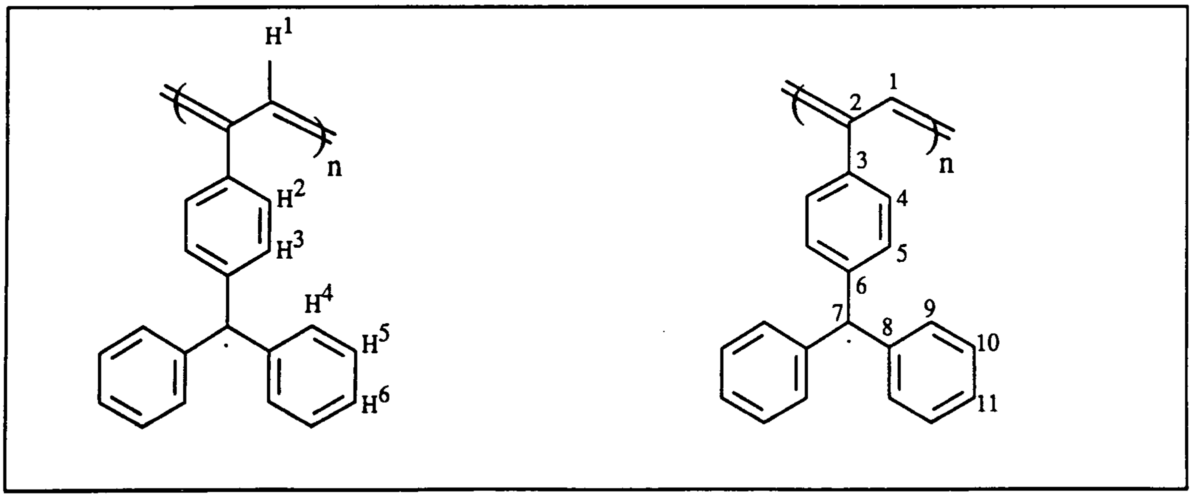
Films were cast from benzene onto KBr plates. Typical spectra are shown in Appendix 6-38.

"Metathesis Precursor" **6j**

ν (thin film)/cm^{-1}: 3580 (weak OH), 3080,3060,3020 (aromatic CH), 1605 (C=C), 1270, 880 (w), 740. In several samples, a broad absorption of uncertain origin occurred between 1000-1200cm^{-1}, due possibly to aliphatic ether (see Discussion below).

d- ^{1}H NMR Spectroscopy

Figure 6.8.i. Numbering System for **6j** and **6k**



The best ^{1}H NMR spectrum obtained is shown in Appendix 6-39.

δ/ppm ($CDCl_3$); 5.2-7.8 (broad, unresolved resonance). Assignment of specific protons was not possible.

e- **^{13}C NMR Spectroscopy**

The CP/MAS solid state ^{13}C NMR spectrum is given in Appendix 6-40. No major differences were observed between **6j** and **6k**. Solution state spectra were poorly resolved and thus yielded little useful information.

CP/MAS: δ/ppm; 67.37, 128.50 ($C^{1,4,5,9-11}$), 141.91.($C^{2,3,6,8}$) Quaternary Suppressed (QS); 128.556. Non-Quaternary Suppressed (NQS); 142.28, 128.37.

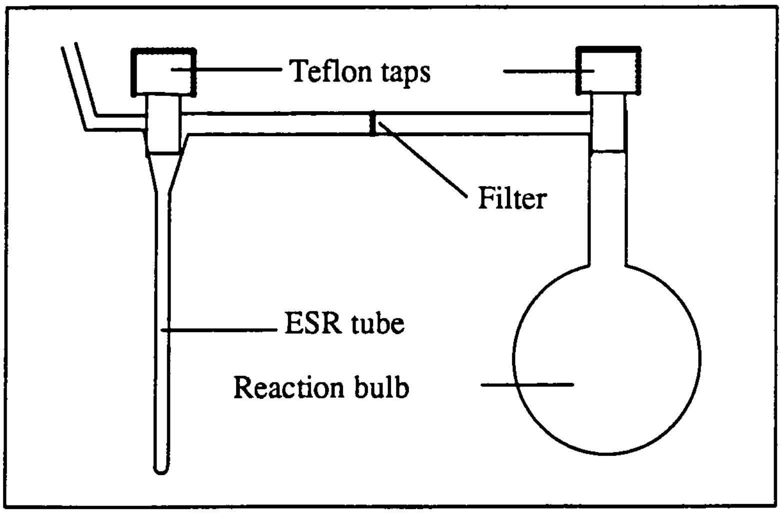
The peak at 67ppm was probably due to C^7, but this could not be confirmed from the solution state spectra. Samples exposed to air for a few minutes lost the band at 67ppm, which was replaced by a new band at 81.1ppm, due possibly to quaternary C-OH or C-OOH sites.

6.9. Electron Spin Resonance (ESR) Spectroscopy

Experimental

Solid state ESR studies were carried out on polymers 6a-c, 6e-h, 6j and 6k. Samples of the polymers (10mg) were placed in 4mm ESR tubes and sealed inside a GloveBox to prevent oxygen contamination. Solution state ESR spectra were recorded for triphenylmethyl radical, 6j and 6k in benzene. For these studies, a special reaction vessel was used, as shown in figure 6.9.i., to ensure complete exclusion of oxygen and moisture.

Figure 6.9.i.



The chlorinated precursor (100mg) was dissolved in dry, degassed benzene (20ml) in the reaction bulb. A rapid nitrogen flow was maintained as silver powder (100mg) was added, and the mixture was stirred for 10 minutes. The tube was then tilted to allow the solution to enter the ESR tube: excess silver and any insolubles were trapped by the filter. The ESR tube arm was then inserted directly into the spectrometer.

All experiments were conducted at room temperature unless stated otherwise.

Results- Solid State ESR

In all cases, single broad peaks were observed. All the resonances, recorded as first derivatives, displayed Dysonian rather than Gaussian lineshapes . No hyperfine structure was observed, suggesting that a number of localized free radical species were present. Peak-peak linewidths varied from 1-1.5mT (10-15G), with g-values deviating from the value for the free electron (2.0023) by less than 0.001. Spin concentrations were calculated by integration: maximum errors were 25% relative to other samples, and absolute values may have been in error by no more than a factor of 2.

6.9.i. Poly(phenylacetylene)- Metathesis Route 6a

The results were in general agreement with previous reports for PPA samples[109-113,115].Peak-peak width = 10G; g= 2.0023. No hyperfine structure was observed. The spectrum is shown in Appendix 6-41. Spin concentration 7.6 x 10^{15}spins.g^{-1}.

6.9.ii. Poly(phenylacetylene)- Rhodium Route 6b

A weak single band was observed. Peak-peak width = 10G; g = 2.0023. The spin concentration (9.1 x 10^{14}spins.g^{-1}) was lower than the metathesis PPA sample, which may have partially accounted for the well-resolved NMR spectra recorded for this sample. The spectrum is shown in Appendix 6-42.

6.9.iii. Poly((4-ethynylphenyl)diphenylmethane) 6c

A strong absorption was observed. Peak-peak width = 12G; g= 2.0023. Spin concentration 3.8 x 10^{16}spins.g^{-1}. Variable Temperature (VT) experiments showed a slight irreversible increase (<10^1) in spin concentration from -50 to +50^{0}C. The spectra are shown in Appendix 6-43.

6.9.iv. Poly((4-ethynylphenyl)diphenylmethanol) (Mo) 6e

A broad band was exhibited. Peak-peak width = 15G; g= 2.0023. Spin concentration 1.3 x 10^{16}spins.g^{-1}. The spectrum is shown in Appendix 6-44.

6.9.v. Poly((4-ethynylphenyl)diphenylmethanol) (Rh) 6f

This polymer absorbed less strongly than the corresponding metathesis sample. Peak-peak width = 12G; g= 2.0023. Spin concentration 3.6 x 10^{15}spins.g^{-1}. However, an aged sample (stored for three months in the GloveBox) showed an increase in spin concentration to 1.5 x 10^{16}spins.g^{-1}. These spectra are shown in Appendix 6-45.

6.9.vi. Poly((4-ethynylphenyl)diphenylchloromethane) (Mo) 6g

The spectrum (Appendix 6-46) showed a single band, almost identical to that of the hydroxyl precursor **6e**. Peak-peak width = 10G; g= 2.0023. Spin concentration 1.2 x 10^{16}spins.g^{-1}.

6.9.vii. Poly((4-ethynylphenyl)diphenylchloromethane) (Rh) 6h

Two signals were visible in the ESR spectrum (Appendix 6-47), corresponding to g-values of 2.002 and 1.947. The peak with g= 2.002 had a peak-peak width of 10G and was due probably to unpaired electrons associated with carbon p-orbitals. The peak with g= 1.947 was of uncertain origin, but was most likely to have arisen from rhodium catalyst residues in the polymer. Spin concentration$_{g=2.002}$= 5.2 x 10^{15}spins.g^{-1}.

6.9.viii. Poly((4-ethynylphenyl)diphenylmethyl) (Mo) 6j

ESR spectra were recorded for a number of samples, differing in their method of preparation. All displayed a strong absorption with g= 2.0027-2.0030, with peak-peak widths of 10-12G. Spin concentrations varied from 8.9 x 10^{15} to 8.1 x 10^{16}spins.g^{-1}. VT experiments showed a significant (>10^1) increase in spins with increasing temperature from -50^{0}C to +90^{0}C. These changes were reversible up to ~100^{0}C. Some of the samples displayed a distinct shoulder absorption to lower field (g > 2.0), which may have been due to peroxy radicals. No hyperfine splitting was observed in any of the spectra, which are shown in Appendix 6-48.

6.9.ix. Poly((4-ethynylphenyl)diphenylmethyl) (Rh) 6k

Two bands were observed in the ESR spectrum, with g= 2.0027 and g= 1.934. The absorption with g= 2.0027 had a peak-peak width of 12G and spin concentration 2.5 x 10^{15}spins.g^{-1}. The second band was considerably more intense and very broad, with an overall width of ~100G. As with the chlorinated precursor **6h**, this band may have been due to catalyst residues. This spectrum is shown in Appendix 6-49.

Results- Solution State ESR

6.9.x. Triphenylmethyl Radical

Freshly prepared solutions of this radical in benzene showed strong absorption with extensive hyperfine structure. The g-value was found to be 2.0023 by comparison with Mn(II) markers, and 2.0025 from the gaussmeter. First and second derivative spectra are shown in Appendix 6-50.

6.9.xi. Poly((4-ethynylphenyl)diphenylmethyl) (Mo) 6j

A single absorption was observed, with a peak-peak width of 7G, and a g-value of 2.0025. No hyperfine structure was apparent (Appendix 6-51).

6.9.xii. Poly((4-ethynylphenyl)diphenylmethyl) (Rh) 6k

A weak, broad absorption occurred, with a peak-peak width of ~15G and a g-value of 2.0019. The low solubility of the precursor **6h** in benzene may have accounted for the low intensity observed. No hyperfine structure was recorded (Appendix 6-52).

6.10. UV/VIS Spectroscopy

Spectra were recorded of 0.1% (w/v) solutions of 6e, 6g, and 6j in chloroform. Samples were prepared in a GloveBox to minimise oxidation.

Results

The spectra are shown in Appendix 6-53. In all cases, maximum absorption occurred below 300nm, with local maxima at 350 and 420nm. The chlorinated polymers and the"polyradical" samples (**6g**, and **6j**) showed stronger absorption at longer wavelength than their precursors, as expected from the deep brown colour. Polymer **6j** absorbed more strongly than the chlorinated samples in the visible region, and displayed a noticeable absorption tail up to ~680nm, corresponding to a band gap of ~2.0eV.

These results were similar to those obtained for other conjugated polymers[77],with the polyradicals showing absorptions intermediate between poly(phenylacetylene) and polyacetylene.

6.11. Magnetic Susceptibility Studies

*"Polyradical" samples **6j** and **6k** were tested for magnetic susceptibility using a Faraday Balance. The polymers were unavoidably exposed to air for approximately 20-30 seconds during placement in the balance, and thus may have been partially oxidised at this stage.*

Results

The results are shown in Appendices 6-54, 6-55 and 6-56.

Both samples displayed a Curie-Weiss dependence of magnetic susceptibility with temperature, with good fitting to the equation below:

$$\chi = \chi^0 + C/(T-\Theta).$$

An analysis of the field dependence of the susceptibility at room temperature indicated that a small amount of ferromagnetic material of unknown origin (<5ppm) was present in the samples. The most likely source of this ferromagnetic material was iron present as an impurity in the silver used to dechlorinate the polymers. Aldrich quote an iron content of 40ppm in the grade of silver used in these reactions.

The results are summarized in table 6.11.i. overleaf. The value of χ^0 agreed well with the calculated diamagnetic contribution of -1.68 x 10^{-4}emu.mol^{-1}, from Pascal's constants[141]. These constants are a measure of the shielding effect of *s*- and *p*- core electrons in carbon based systems, and thus can readily be applied to the polymers in this study. The Curie constant C for this polymer determined from the Curie-Weiss Law above, was found to be 2.03 x 10^{-3}emuK.mol^{-1}. This was compared to the molar Curie constant for S=1/2 spins, such as free electrons, of 0.375 emuK.mol^{-1}, to give the fraction of the number of free spins present over the number expected. These molar fractions appeared, as with the other values, not to depend on exposure to air, but did show a temperature dependence. This correlated well with the ESR data. However, of the expected number of spins, even at the higher temperatures, only 1 in 100 was unpaired.

Table 6.11.i.

	6j(i)	6j(ii)	6j(iii)	
Exposure to air	< 5min	12 days	≤ 3days	
Ferromagnetic Content	3.8ppm	0.3ppm	4.7ppm	
χ^0 (emu.mol^{-1})	-167×10^{-6}	-161×10^{-6}	-161×10^{-6}	
Θ (K)	-0.53	-1	-0.75	
C (emuK.mol^{-1})	2.03×10^{-3}	2.47×10^{-3}	2.81×10^{-3} (0-200K)	4.92×10^{-3} (240-340K)
Molar % of S=1/2 spins	0.54	0.66	0.75	1.3

Similar results were obtained for **6k**.

6.12. Discussion

The two main aims of the work described in this chapter were the controlled polymerization of phenylacetylene, and the synthesis of a well-defined conjugated polymer with pendant free radical sites on each repeat unit.

6.12.i. Polymerization of Phenylacetylene

The controlled polymerization of phenylacetylene was partially achieved, using the rhodium catalyst $[Rh(CODCl]_2$, supporting the results of earlier work by Furlani[100]. High resolution NMR spectroscopy confirmed that the poly(phenylacetylene) produced in this way was stereoregular. The ^1H NMR spectrum displayed three sharp resonances, at 5.75, 6.52-6.54, and 6.83-6.85ppm, with integral ratios 1:2:3. The ^{13}C NMR spectrum showed the presence of six different carbon environments, which could only occur if the polymer was stereoregular. Poly(phenylacetylene) produced by the Furlani catalyst had not previously been studied by ESR spectroscopy, and the results obtained in this work showed a considerably lower free radical concentration than in other PPA samples. This may have accounted, in part, for the high resolution obtainable in the NMR spectra. A corollary to this is that in a controlled, stereoselective polymerization, there is a reduced likelihood of isomerization and chain scission, leading to radical formation.

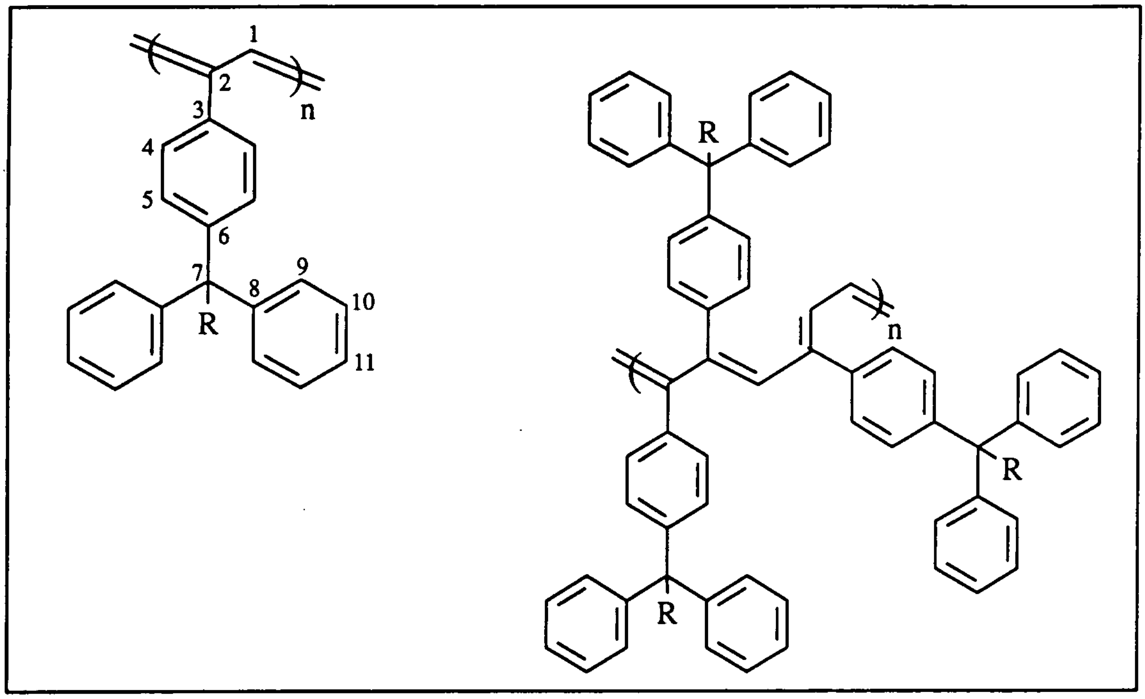
However, the full, unambiguous, characterization of the PPA samples in this study was still not possible. Although the polymer was stereoregular, NMR studies could give no indication of the cis/trans nature of the backbone. It was hoped that the well-defined metathesis catalyst $(^tBuO)_2Mo(NAr)(CH^tBu)$ might polymerize phenylacetylene by a living mechanism, in a similar manner to analogous reactions with norbornene derivatives[60,61]. This might allow monitoring of the polymerization process by NMR, and the isolation of discrete oligomers by controlled termination reactions, as has been demonstrated for short-chain poly(acetylene)s[60]. Unfortunately, despite the addition of quinuclidine to reduce the activity of the catalyst, the polymerization reaction was extremely rapid, once a brief induction period had elapsed. From the presence of residual initiator after monomer conversion was complete, it was deduced that the rate of propagation was faster than the rate of initiation, and that living polymerization did not take place. It was therefore not possible to follow the polymerization by NMR, or to isolate very low molecular weight oligomers. The PPA samples produced using the Schrock catalyst were similar to those prepared using "classical" metathesis catalysts, with corresponding uncertainties as to the microstructure.

6.12.ii. New Conjugated Polymers

The ultimate goal, of preparing well-defined conjugated polyradicals, was also achieved only in part. Four new conjugated polymers
poly((4-ethynylphenyl)diphenylmethane) (**6c**,**6d**),
poly((4-ethynylphenyl)diphenylmethanol) (**6e**,**6f**),
poly((4-ethynylphenyl)diphenylchloromethane) (**6g**,**6h**), and
poly((4-ethynylphenyl)diphenylmethoxymethane) (**6i**), were prepared using the well-defined molybdenum and rhodium catalysts.

The characterization of these polymers was incomplete, owing to uncertainties in the microstructures of the backbone chains. However, the combination of IR, ^{1}H and ^{13}C NMR spectroscopies, GPC, and elemental analysis left no doubt that these materials were the appropriately functionalized polymers. Although all the ^{1}H NMR spectra contained broadened peaks, IR spectra established the nature of the functional groups present, and elemental analysis confirmed that these groups were in the correct abundances. Comparison of ^{13}C NMR spectra of the polymers with the respective monomers enabled unambiguous assignment of the quaternary carbons. Solid-state CP/MAS ^{13}C NMR confirmed these assignments with QS and NQS spectra. In most cases, the solution state ^{13}C NMR indicated more than the "theoretical" number of peaks described in the numbering schemes (as shown below), due probably to a variety of cis/trans chain double bonds and sequence effects. Figure 6.12.i. overleaf illustrates these points.

Figure 6.12.i.



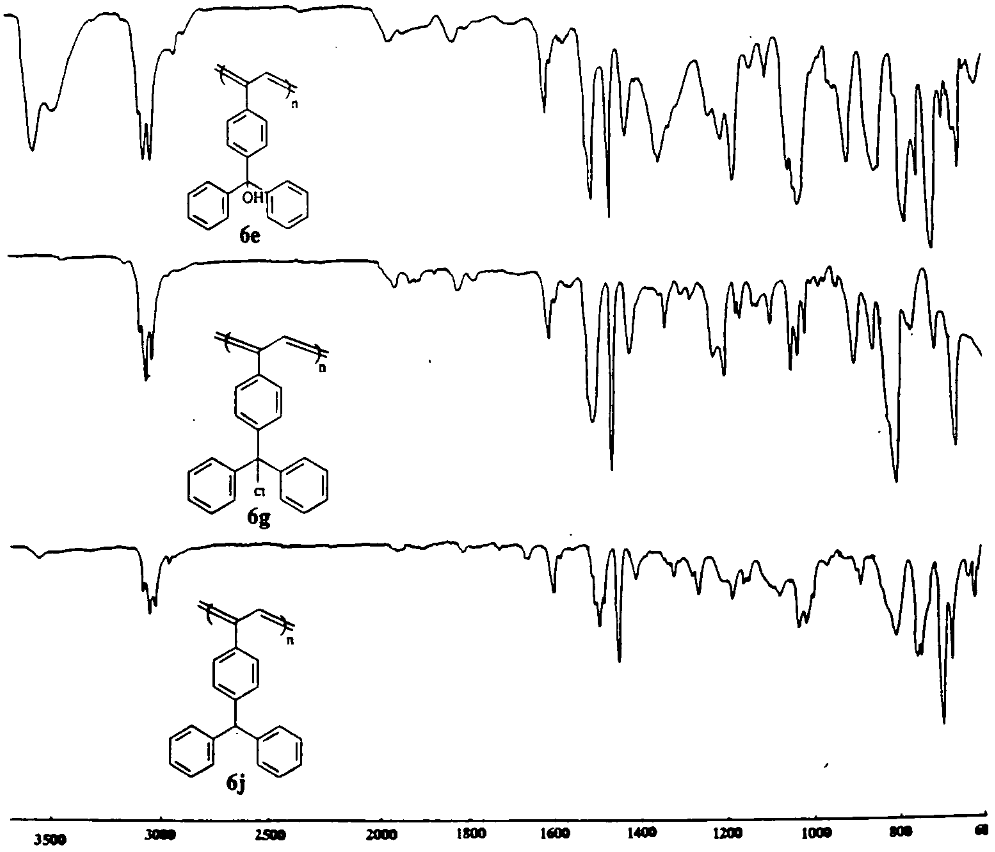
In solution, these polymers are likely to be highly coiled, and any irregularity in sequence or double bond nature could result in close contact between chain and substituent carbon atoms, leading to changes in chemical shift. As with poly(phenylacetylene), the true microstructures of these polymers are only likely to be elucidated if controlled polymerization methods can be found, allowing isolation of discrete oligomers.

6.12.iii. Polyradicals

The target polymer, poly((4-ethynylphenyl)diphenylmethyl) (**6j**,**6k**), was incompletely characterized. Model reactions on triphenylchloromethane established reliable methods of generating the triphenylmethyl radical, and these were extended to reactions on the precursor polymer poly((4-ethynylphenyl)diphenylchloromethane) (**6g**,**6h**). Elemental analysis suggested that removal of the tertiary chlorine atom from the precursor was never completely accomplished. Residual chlorine levels for the final polymers were 1-5%, and for materials produced by some protocols, the analyses were reproducibly lower than expected for carbon by 10%.

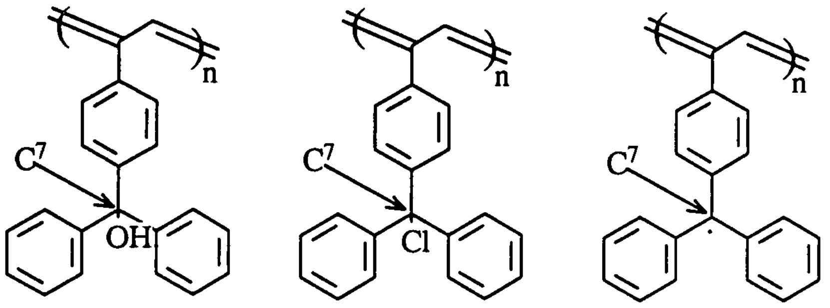
This difference between observed and expected analytical results is difficult to explain, and may have been a result of problems inherent to the analytical process, such as partial hydrolysis prior to combustion. Another factor may have been retention of, or reaction with, THF, used as the solvent for generation of these polyradicals. It has been shown[142], that in the reduction of Ph_3CCl in THF, an important step is the production of $(Ph_3C\text{-}THF)^+Cl^-$ species, which encourages the belief that some THF might be trapped in the polymer. Some IR spectra showed a broad band between 1000-1100cm^{-1}, in a region associated with -C-O- stretches of ethers. These spectra showed the removal of the C-Cl stretch at 790cm^{-1}, but also the presence of a weak band at 3550cm^{-1}, indicating that some hydrolysis had occurred. Figure 6.12.ii. shows the IR spectra of the hydroxy, chlorine and radical polymers, and the changes in the 3500and 800cm^{-1} regions can clearly be seen.

Figure 6.12.ii. IR Spectra



In addition ^{13}C NMR spectra could be used to follow the course of these reactions owing to the difference in shift of the quaternary aliphatic carbons from hydroxyl, chlorine and "radical" substituents.

Figure 6.12.iii.- ^{13}C NMR Shift Positions for Quaternary Carbon C^7



6e δ=81.7ppm (Mo)
6f δ=82.1ppm (Rh)

6g δ=81.3ppm (Mo)
6h δ=80.7ppm (Rh)

6j,k δ=67ppm (Mo and Rh)

(Monomer **5b** δ=81.8ppm **5a** δ=81.3ppm

The small change in shift from hydroxyl to chlorine substituents was also observed in the monomer spectra. Spectra of newly prepared "polyradicals" exhibited a resonance at 67ppm, which did not appear in the QS or NQS spectra. If these samples were exposed to the atmosphere for only 1 minute, resonances at 81ppm were seen, in combination with emerging IR bands at 3550cm^{-1}. Exposure of the chlorinated polymers **6g** and **6h** to the atmosphere also resulted in the emergence of IR bands at 3550cm^{-1}, but this process was slower than for **6j** and **6k** samples. Exposure of **6j** and **6k** to the air for several hours solubilized the polymers to the extent that solution state NMR was possible, and the spectra obtained were very similar to those of **6e**.

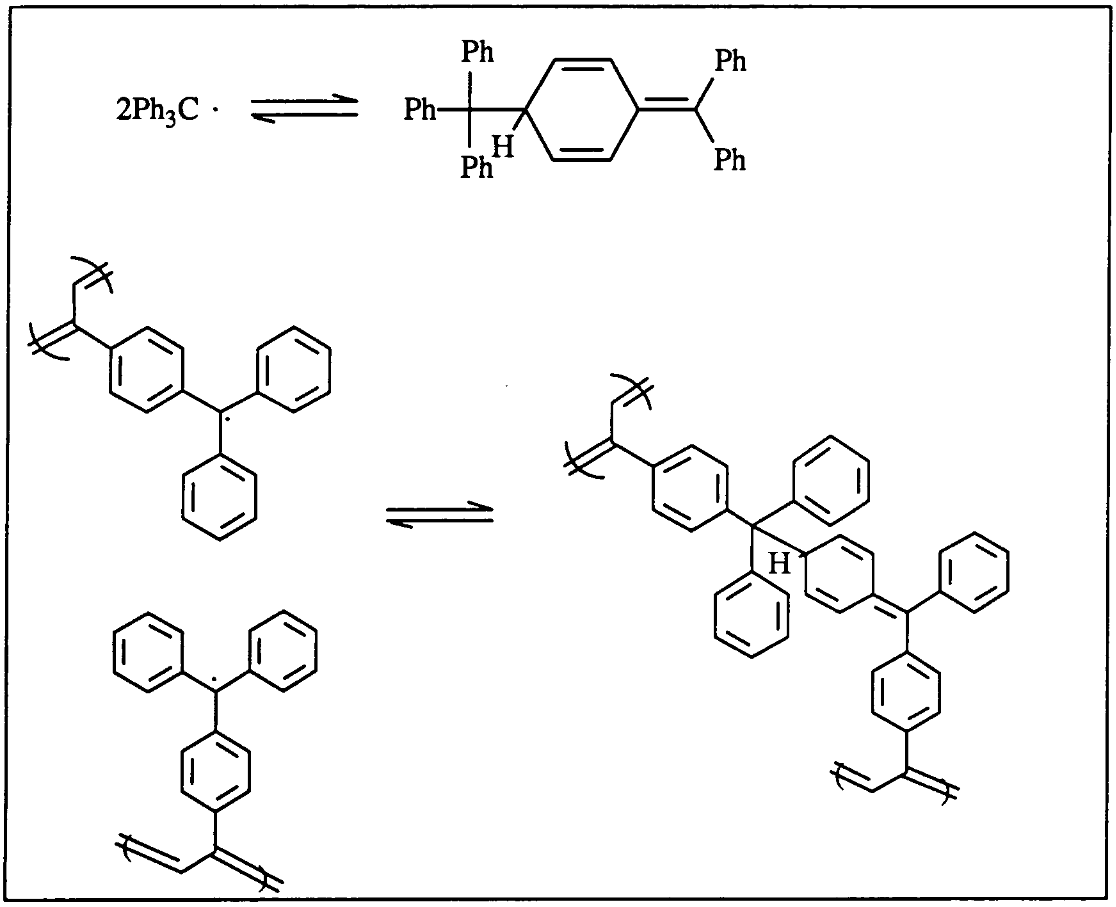
The evidence presented above strongly suggests that (poly(4-ethynylphenyl)diphenylmethyl) radicals were synthesized but that the polymer was extremely sensitive to air and moisture. It is perhaps surprising that the magnetic susceptibility data did not appear to be change with exposure of the polymers to the atmosphere. However, in these studies, all the polymers were exposed to air for at least a short time, and thus oxidation could have taken place in this period.

Elemental analyses also indicated the difficulty of complete removal of all the tertiary chlorine atoms. Since the dechlorination of triphenylchloromethane was carried out successfully under the same reaction conditions, it is clear that access to the C-Cl sites in the polymer must have been impeded to account for the difference between monomer and polymer reactivity.

The reaction of a heterogeneous metal surface with a hindered polymer site is unlikely to be a highly favourable process, as even in dilute solution, these polymers are probably highly coiled. The C-Cl bond might be hindered not only by the triphenylmethyl substituents, but also by the polymer chain itself. The probable occurrence of a variety of HT, HH, and TT sequences, combined with a range of cis/trans environments would decrease access to the chlorine atom. and thus even with sonication, reaction with the metal surface might not occur at all the sites. However, although ESR studies showed the presence of unpaired spins in all the polymers **6c-k**, spin concentrations were highest in **6j** and **6k** samples, supporting the idea that at least some new free radical sites were generated in the dechlorination reaction.

The ESR spectra of the polyradicals indicated a maximum spin concentration of 10^{16}-10^{17}spins.g^{-1} at room temperature, increasing to 10^{18}-10^{19}spins.g^{-1} at 100^{0}C. This is at between 1/1000 and 1/100 of the theoretical spin concentration of 10^{21}spins.g^{-1}, assuming each repeat unit contains one unpaired electron. Magnetic susceptibility measurements suggested that the unpaired spin concentration was 0.5-1% of the expected value for a polymer containing one free electron in each repeat unit. These methods clearly show that the free radical centres were either never produced, or were subsequently spin-paired. The best analysis indicated a residual chlorine concentration of 1.2%, which corresponds to roughly nine out of every ten repeat units bearing a triphenyl methyl radical. For residual chlorine contents of 5%, every second unit should have contained a free radical site. It appears, therefore, that spin pairing must have taken place subsequent to dechlorination. The results of variable temperature ESR studies showed a reversible increase in spins by a factor of 10^{1}-10^{2} for the polyradical sample **6j** between -50-100^{0}C. An irreversible increase by a factor of ~2 in spins was found for poly((4-ethynylphenyl)diphenylmethane) (**6c**) between -50-50^{0}C. These results suggest that a different mechanism of thermal radical formation was operating for the polyradical samples compared to their "non-radical" analogues. The ESR results were borne out by the magnetic susceptibility measurements, which showed an increase in the molar ratio of unpaired spins between 200-340K. In view of the known equilibrium between the triphenylmethyl radical and its dimer[143,144], the implication is that dimerization of triphenylmethyl radical moieties was taking place within the polymer. On heating, the radicals might be regenerated, giving rise to the observed changes in the ESR and magnetic susceptibilty data. Figure 6.12.iii. overleaf shows possible dimerizations.

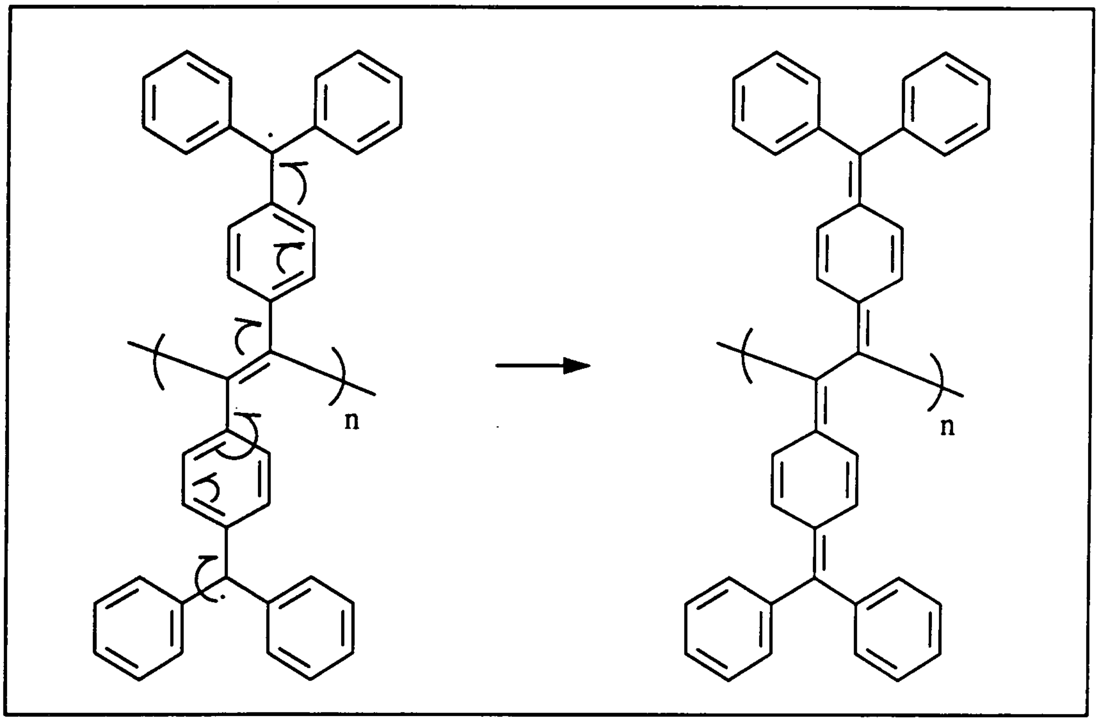
Figure 6.12.iii.



If this were the case, any interchain dimerization would increase the molecular weights of the polymers. This did not appear to be the case as GPC studies indicated that the polyradicals were of very similar molecular weight distributions to the precursors. However, as GPC studies must be carried out in very dilute solutions, this technique would be unsuitable for testing for any dimerization between different polymer chains.

Another possibility for spin pairing to occur might be via isomerization of HH sequences to give quinonoid structures, as shown in figure 6.12.iv. overleaf.

Figure 6.12.iv.



The production of these quinonoid-type structures would cause defects in the conjugated chain, and might also lead to changes in the UV absorption of the polymer. However, despite the "polyradicals" displaying absorption tails to higher wavelength than the chlorinated precursors, the contribution of quinonoid sequences to this extended absorption could not be proved.

These conjugated polymers were all chemically reactive materials, and thus, over a period of time, certain properties were seen to change. For example, ESR studies of poly((4-ethynylphenyl)diphenylmethanol) samples (**6f**, prepared using the rhodium catalyst), showed a marked increase in spin concentration for a sample aged for three months compared to a week-old sample. Both samples had been made in as similar manner as possible, and stored under nitrogen at room temperature throughout. It is likely that the polyradical samples would also be reactive species, undergoing facile hydrogen atom transfer to generate new radical sites, which may have accounted for the variations in spin concentrations observed.

CONCLUSIONS

The polymerizations described in this chapter produced nine new conjugated polymers (**6c,6d,6e,6f,6g,6h,6i,6j** and **6k**) and confirmed the previous results of Furlani[100] regarding the preparation of poly(phenylacetylene) with $[Rh(COD)Cl]_2$. All the polymers were air, moisture, light and temperature sensitive, and thus were stored in the dark, in a GloveBox at -40^0C. Conjugated polymers with pendant radical sites were produced but the radical concentrations were much lower than initially expected, due probably to both inter and intra molecular spin pairing reactions.

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

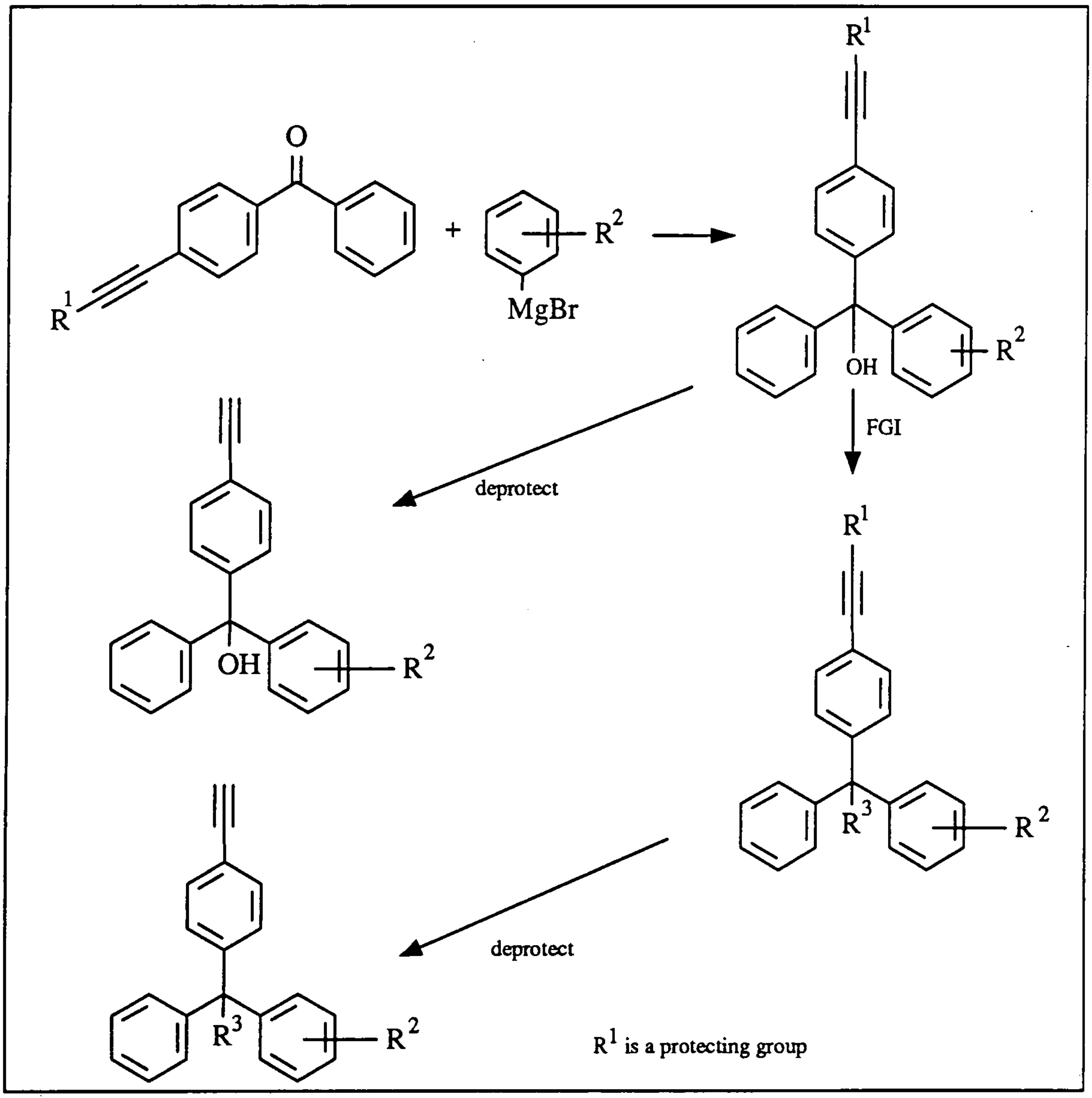
CONCLUSIONS

The original aim of the work in this thesis was to produce conjugated polyradical species, of precisely defined chemical structure, to serve as model compounds to test recent theories concerning the possibility of organic ferromagnetism. In particular, it was hoped that a correlation between the overall spin state and number of repeat units in these conjugated polymers could be drawn. This would have provided the first accurate experimental study of the ideas put forward by Ovchinnikov[3,4]. Therefore, to produce such species required the controlled polymerization of suitably functionalized monomers. These monomers were the first synthetic targets.

7.1 Monomer Syntheses

In total, eleven new compounds, (**4a,4c,4e, 5a,5b,5f,5g,5h,5j,5k,** and **5m**) including four acetylenic triphenylmethyl derivatives were synthesized. The preparations of the compounds were simple, but all the purifications required extensive use of column chromatography, and thus were very time-consuming for multi-gram scale monomer production. The synthetic methodology used to prepare compounds **5a-m** was flexible enough to allow functional group interconversion after the acetylene function had been introduced, and thus could be adapted to produce other substituted (4-ethynlphenyl)diphenylmethyl derivatives. A proposed synthetic route is depicted in figure 7.1.i overleaf.

Figure 7.1.i.



R^1 is a protecting group

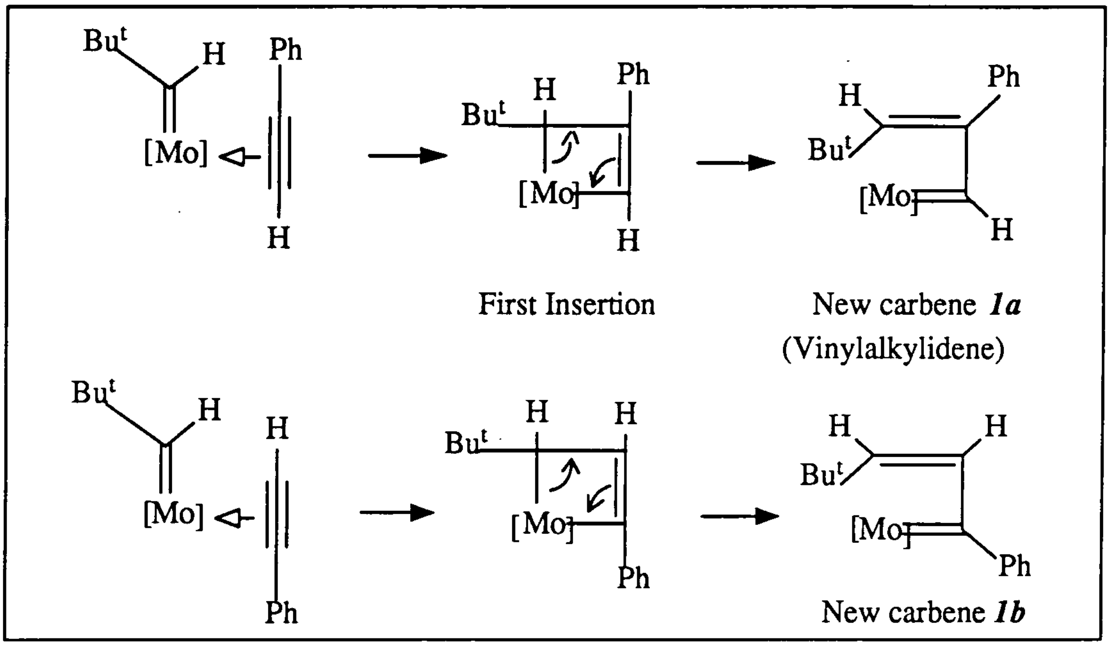
Introduction of further substitution in the benzophenone-based compound would allow the facile synthesis of a whole range of acetylenic triphenylmethyl monomers. The use of flash chromatography and/or preparative scale HPLC would enable sufficient quantities of these monomers to be prepared for polymerization studies.

High-resolution ^{1}H and ^{13}C NMR spectroscopies were used to characterize the materials prepared in this work. Full assignments were possible for these new compounds by comparison with known compounds such as triphenylmethanol and triphenylchloromethane. This enabled the elucidation of peak positions of the carbons attached to the hydroxyl and chlorine substituents, which were useful in the characterization of the polymers. Although the respective resonances differed by less than 1ppm (81.8ppm$_{C\text{-}OH}$, 81.3ppm$_{C\text{-}Cl}$), the assignments, made in conjunction with IR spectra, were unambiguous. Thus the goal of preparing fully characterized monomers was achieved.

7.2. Controlled Polymer Synthesis.

The task of converting the monomers to precisely defined polymers was important if any property-structure correlations were to be made. The use of the acetylene metathesis reaction appeared to offer the best chance of preparing the desired conjugated polymers, by analogy with the Ring Opening Metathesis Polymerization of olefins, which is now well understood. The monomers prepared as described in Chapters 4 and 5 could be considered as substituted phenylacetylenes, and thus if the polymerization of phenylacetylene were to proceed in a controlled manner, the functionalized monomers might polymerize in the same way. However, despite using the well-defined molybdenum catalyst ($(^tBuO)_2Mo(=NAr)(=CH^tBu)$: Ar= 2,6-di-*iso*-propylphenyl), the polymerization of phenylacetylene did not proceed by a living mechanism. The ^{1}H NMR spectra recorded after a reaction time of only 10 minutes were complex, and suggested a mixture of products. The polymerization of phenylacetylene can, in principle, lead to a large number of isomeric products, even using well defined carbene initiators, and some reasons for this are outlined in figure 7.2.i overleaf.

Figure 7.2.i.


Bu^t
H
Ph
[Mo]
H
Bu^t
H
Ph
[Mo]
H
H
Ph
Bu^t
[Mo]
H
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New carbene 1a
(Vinylalkylidene)
Bu^t
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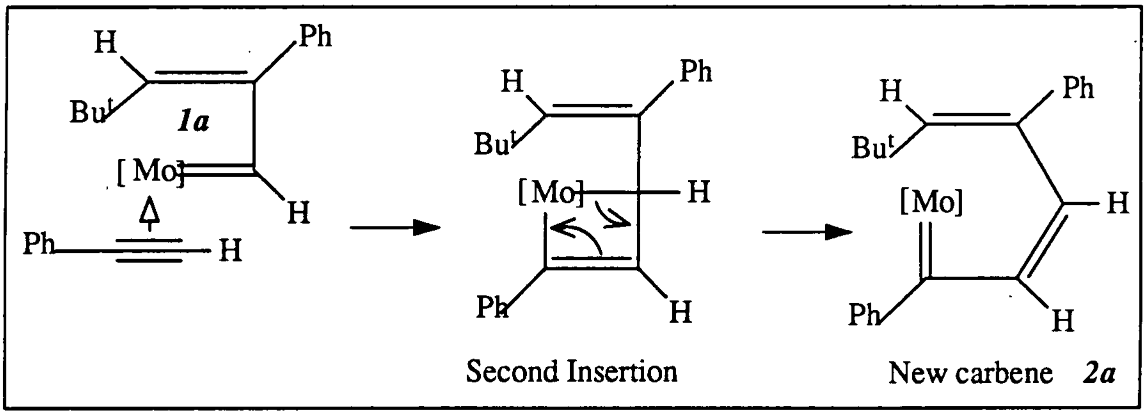
Bu^t
[Mo]
Ph
New carbene 1b


H
Ph
Bu^t
1a
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H
Ph
H
H
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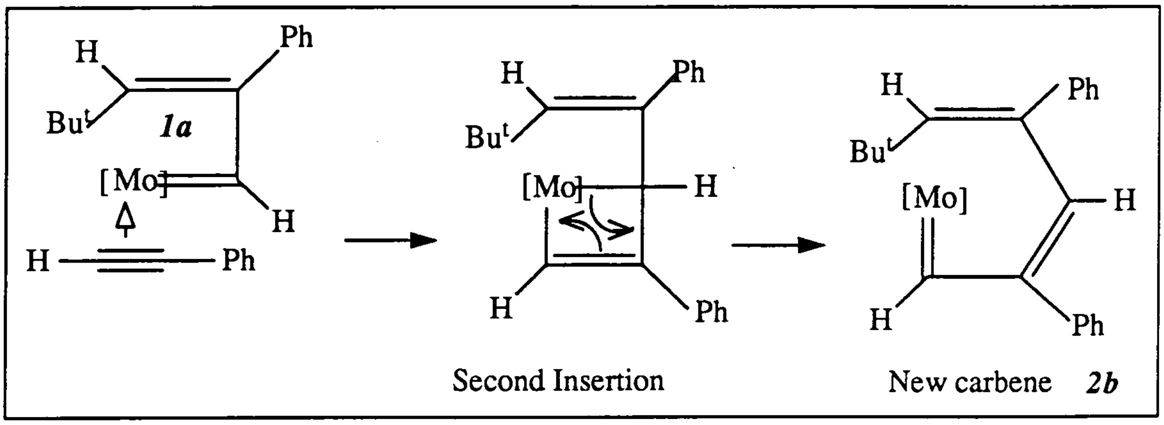
Ph
H
Second Insertion
New carbene 2a



In the diagrams above, ***1b*** can undergo a second insertion to yield two more isomeric products, differing, as with ***2a*** and ***2b*** above, according to whether the second phenylacetylene molecule inserts head-head or head-tail. The third insertion can again take place in two ways, giving rise to eight isomers after three insertions. In addition to these head/tail effects there is also the possibility of cis/trans isomerism, and as a result, it is clear that complex product mixtures are likely even if the polymerization is "living" (i.e. if the rate of initiation is greater than the rate of propagation). If, as appeared to be the case in this work, the propagation was faster than initiation, it is hardly surprising that the NMR spectra of the polymers produced were not fully assignable. The polymerizations with the Schrock catalysts could not be controlled even by addition of quinuclidine, which is thought to bind reversibly to the catalyst, regulating the electron density and steric environment at the metal centre[65]. As a result of these studies, a different catalyst was required.

The rhodium complex [Rh(COD)Cl$_2$ was able to polymerize phenylacetylene to high molecular weights, and appeared to give a stereoregular polymer. The ^{13}C NMR showed six different carbon environments, as in the monomer, and the ^{1}H NMR spectrum was exceptionally well-resolved. We were able to reproduce the results of Furlani's group[100], but were still unable to characterize the polymer completely. The cis/trans nature of the polymer chain backbone could not be determined from the NMR spectra, and the use of IR spectra to solve this problem must still be regarded as incomplete. It seems likely that the full characterization of PPA samples will only be achieved if catalytic species can be found which will allow isolation of discrete oligomers.

7.3. New Conjugated Polymers

A total of eleven new conjugated polymers (**3e,3f,6c-6k**) were produced, if each polymerization method was considered to yield a different material. These polymers were well characterized apart from the cis/trans nature of the backbone, and the sequence of repeat units, which remained uncertain for the reasons discussed above for PPA. However, the target polymers (**6j,6k**) were found to be difficult to synthesize in an easily reproducible manner.

7.4 "Polyradicals"

The syntheses of poly((4-ethynylphenyl)diphenylmethyl) radicals were partially accomplished, and the materials were characterized by conventional techniques. ESR and magnetic susceptibility studies showed the polymers to be highly paramagnetic, but not, as hoped, ferromagnetic. The expected number of unpaired spins was not produced, and so the theories of Ovchinnikov could not be tested directly. The dimerization of the triphenylmethyl radical substituents may have accounted for this low spin concentration. At temperatures where these dimers could dissociate into free radicals, thermal agitation of the material would probably prevent any spin alignment. In addition, the polymers were highly sensitive to atmospheric oxygen and moisture, which rendered characterization and testing of magnetic properties extremely difficult. However, the original goal of producing a conjugated polymer with pendant sites capable of generating free radical centres was achieved.

SUGGESTIONS FOR FURTHER WORK

Poly(phenylacetylene): Synthesis and Characterization

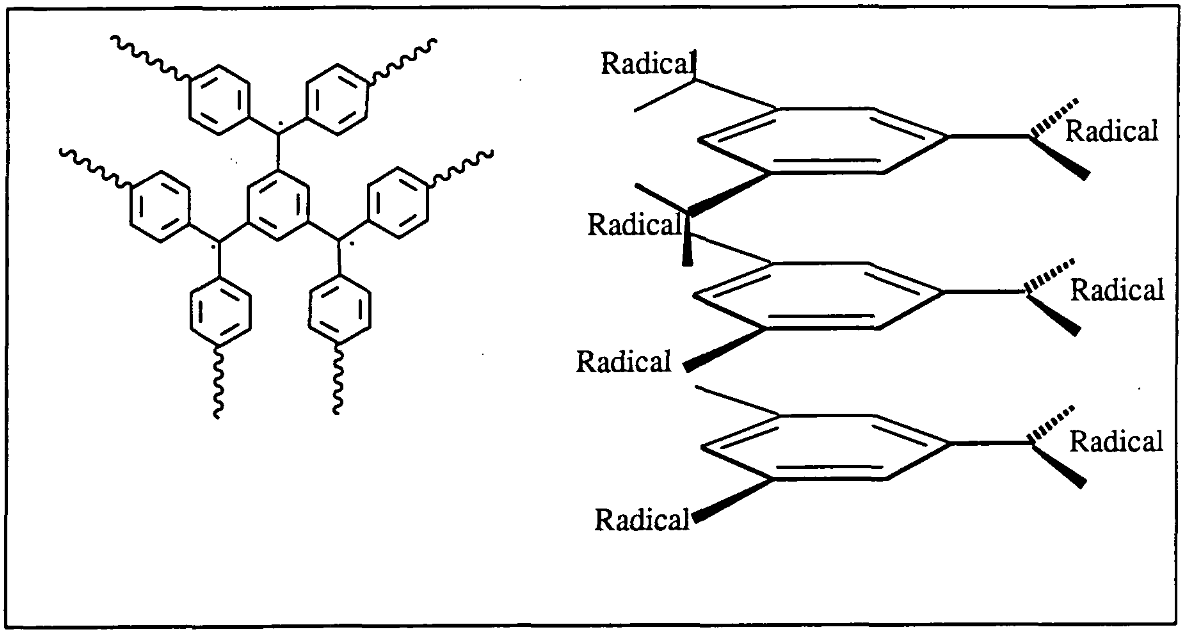
Two methods might be followed for the complete characterization of poly(phenylacetylene). As described earlier, if a catalyst could be found to polymerize phenylacetylene in a controlled, ideally "living", manner, then isolation of dimers, trimers, and low molecular weight oligomers could be carried out. Thus, unambiguous IR and NMR assignments of cis and trans double bonds on the backbone could be made, removing the uncertainty current in the literature regarding polymer microstructure. If such a catalyst is not available, then studies of the polymerization of isotopically substituted phenylacetylene, using the Furlani rhodium catalyst, would yield valuable information. For example, deuterium substitution of the acetylenic hydrogen would identify chain protons, while ^{13}C substitution of the acetylene carbons would allow positive assignment of chain carbon environments. However, correlation of the spectra obtained with the cis/trans nature of the polymer would still be a difficult task, requiring model studies of low molecular weight oligomers prepared by conventional organic syntheses.

Polyradical Syntheses

The main problems to be addressed are those concerning the initial generation of radical centres, and the subsequent fate of these sites. The difficulty of gaining access to all the C-Cl bonds in this study suggests that radical generation would best be achieved prior to polymerization. Thus, the radicals would have to be stable under conditions of polymerization. Suitable radical species are the nitroxyls[144] or the Perchlorinated TriphenylMethyl (PTM) radicals developed by Ballester, Armet and co-workers[145]. The latter species appear particularly promising as some have shown to be air stable over many months. If acetylenic derivatives could be prepared, steric hindrance at the ortho positions of bulky chlorine atoms would also test the results of Masuda and Percec concerning the living polymerization of ortho-substituted phenylacetylenes[103,104], discussed in Chapter 2.

Organic Ferromagnet Syntheses

The preparation of organic ferromagnets requires a high degree of order throughout the material, and thus any syntheses must allow for the generation of a complete 3-D structure. This is obviously a considerable challenge, which has so far been met only by charge transfer salts[5-7]. However, if well-defined, and suitably functionalized, polymer networks can be synthesized, the possibility of spin-spin interactions throughout the material might result in bulk ferromagnetism. Such a material might be synthesized from 1,3,5-trisubstituted benzenes, stacked together as discotic liquid crystals:



Ideally, each sub-unit would be chemically bonded to another sub-unit, ensuring interaction throughout the whole network.

If the synthetic problems could be overcome, then the advantages traditionally associated with organic polymer materials, such as low density and ease of processing, might be combined with ferromagnetism to produce valuable new materials.

APPENDIX 1

INSTRUMENTS

Infra-red

Spectra were recorded on Perkin-Elmer 457 or 577 grating Infra-red spectrometers.

^{1}H and ^{13}C NMR

Spectra were recorded on a Varian VXR400 NMR spectrometer, at 399.952MHz (^{1}H) and 100.577MHz (^{13}C).

Gel Permeation Chromatography

Chromatograms were obtained using a Waters Model 590 pump, Waters Model R401 Differential Refractometer detector, Polymer Laboratories PLgel 5m 300x7.5mm crosslinked polystyrene columns, equipped with an SIC Chromacorder 12 computing integrator.

Elemental Analyses

Results were obtained from a Carlo-Erba Model 1105 elemental analyser.

Mass Spectrometry

Spectra were obtained from a VG Analytical Model 7070E Mass spectrometer.

ESR

Spectra were obtained using a JEOL RE1X ESR spectrometer equipped with an ESPRIT-330 data station.

UV/VIS

Spectra were recorded using a Perkin-Elmer Model Lambda 9 UV/VIS spectrometer controlled by an Apple Macintosh microcomputer

Magnetic Susceptibility Studies

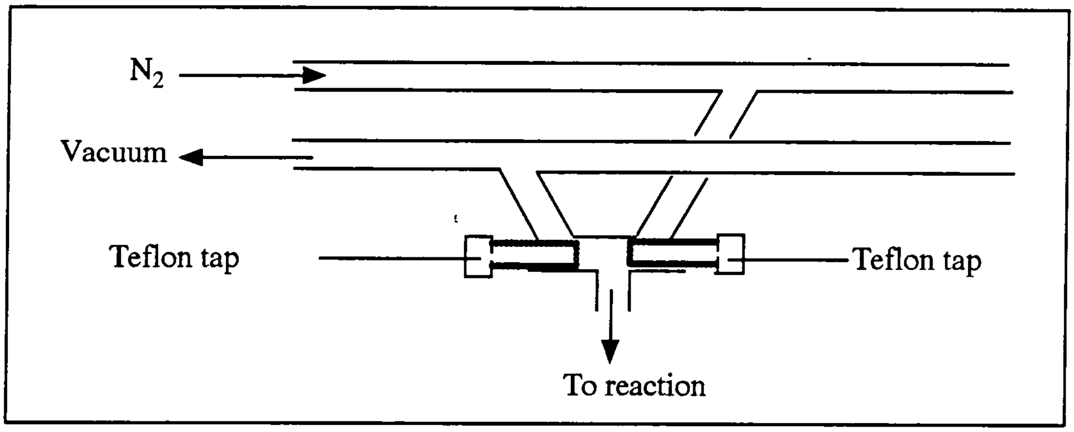
Results were obtained using a Faraday Balance developed and built at the Cavendish Laboratories, University of Cambridge. Data manipulation was by Apple Macintosh microcomputer using LabView software specially adapted for magnetic susceptibility studies.

APPENDIX 2

APPARATUS FOR HANDLING AIR-SENSITIVE MATERIALS

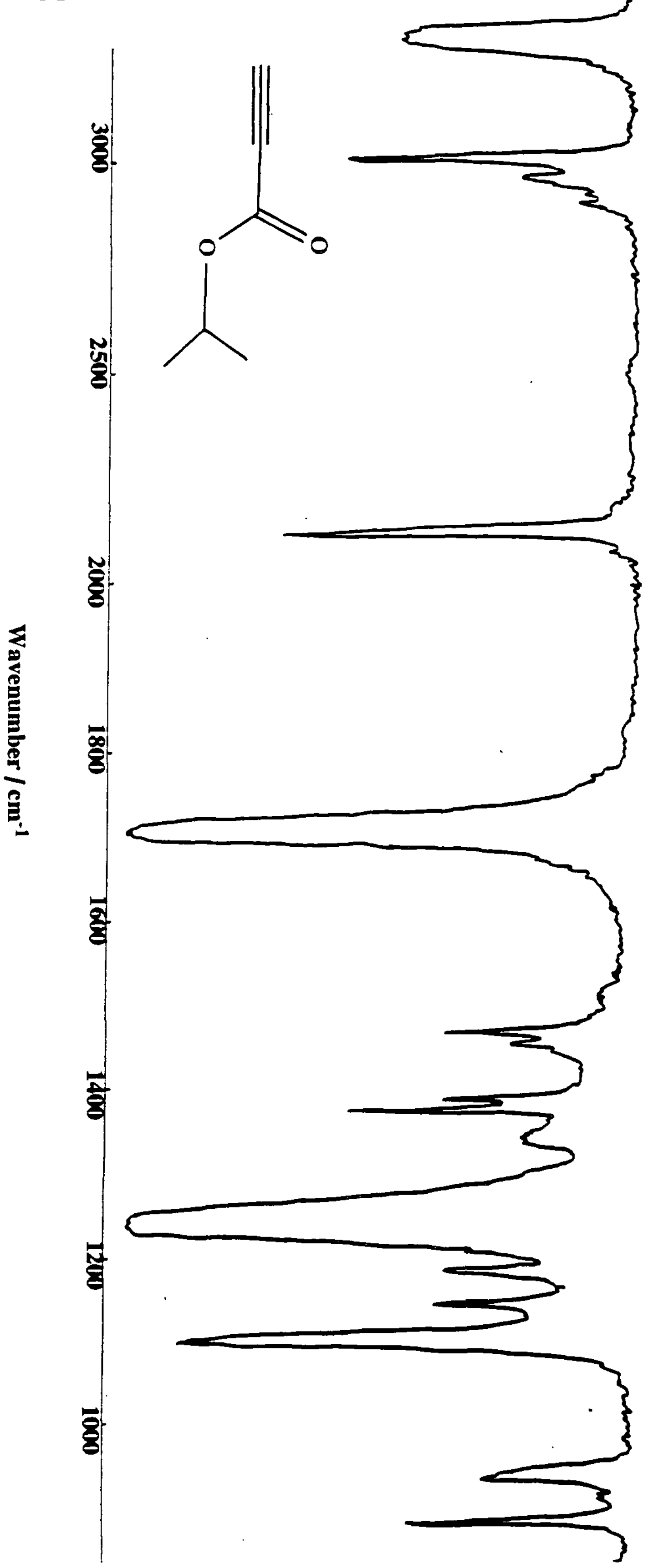
Manipulations of air-sensitive reagents or reaction products were carried out under nitrogen in Faircrest MB41 or Miller-Howe P3131 GloveBoxes equipped with BASF copper alloy and molecular sieve deoxygenating and drying columns, and activated charcoal solvent-removal columns. Typical moisture and oxygen levels were below 10ppm for the Faircrest box, and below 5ppm for the Miller-Howe box.

Where the use of a GloveBox was not practicable, a vacuum line, a part of which is shown below, was used.

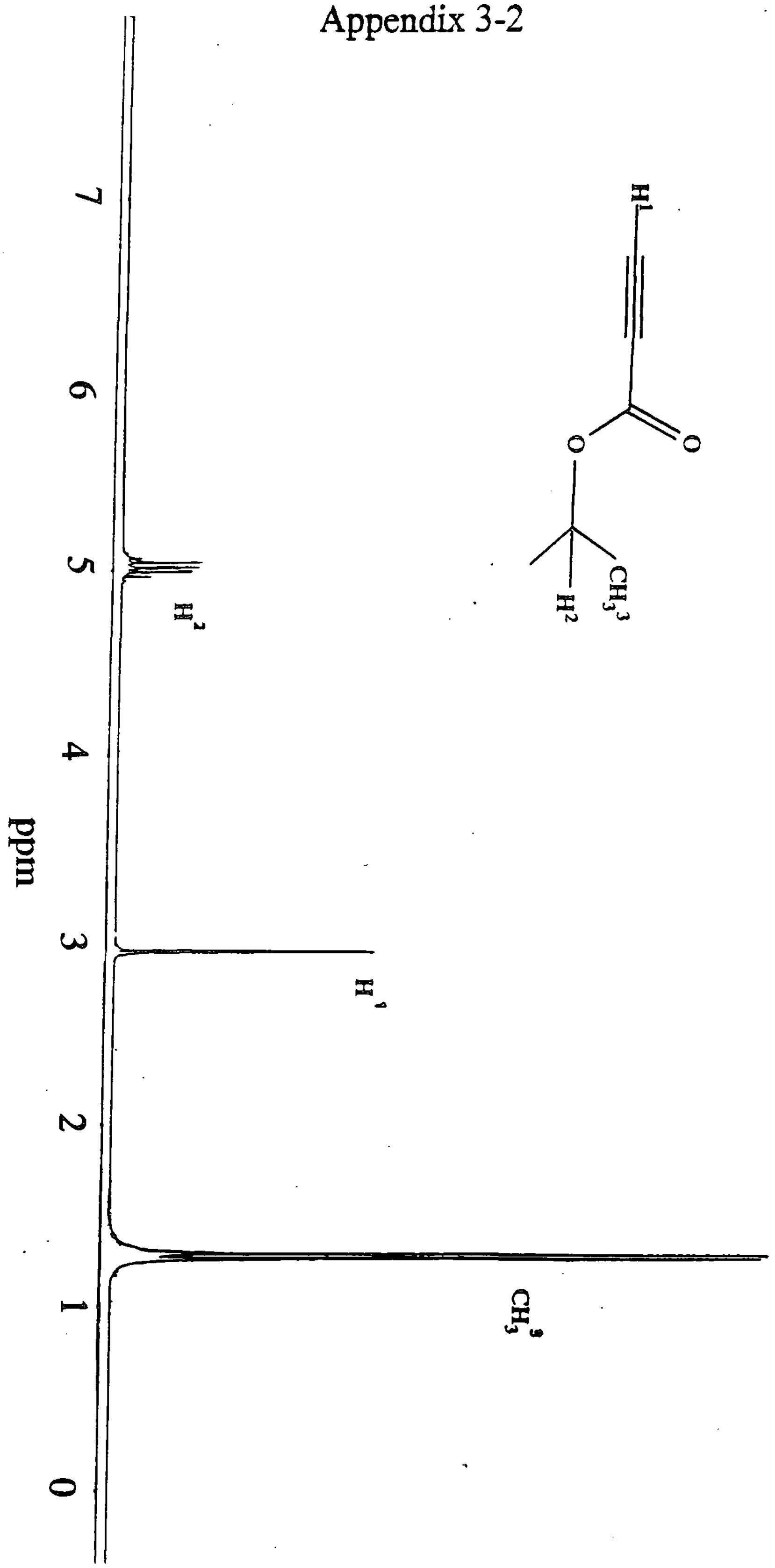


The nitrogen supply was dried by passage through concentrated sulphuric acid, phosphorous pentoxide, and activated 13X and 4A molecular sieves. An Edwards P2 pump was used to provide the vacuum (10^{-3} torr).

Appendix 3-1



Appendix 3-2



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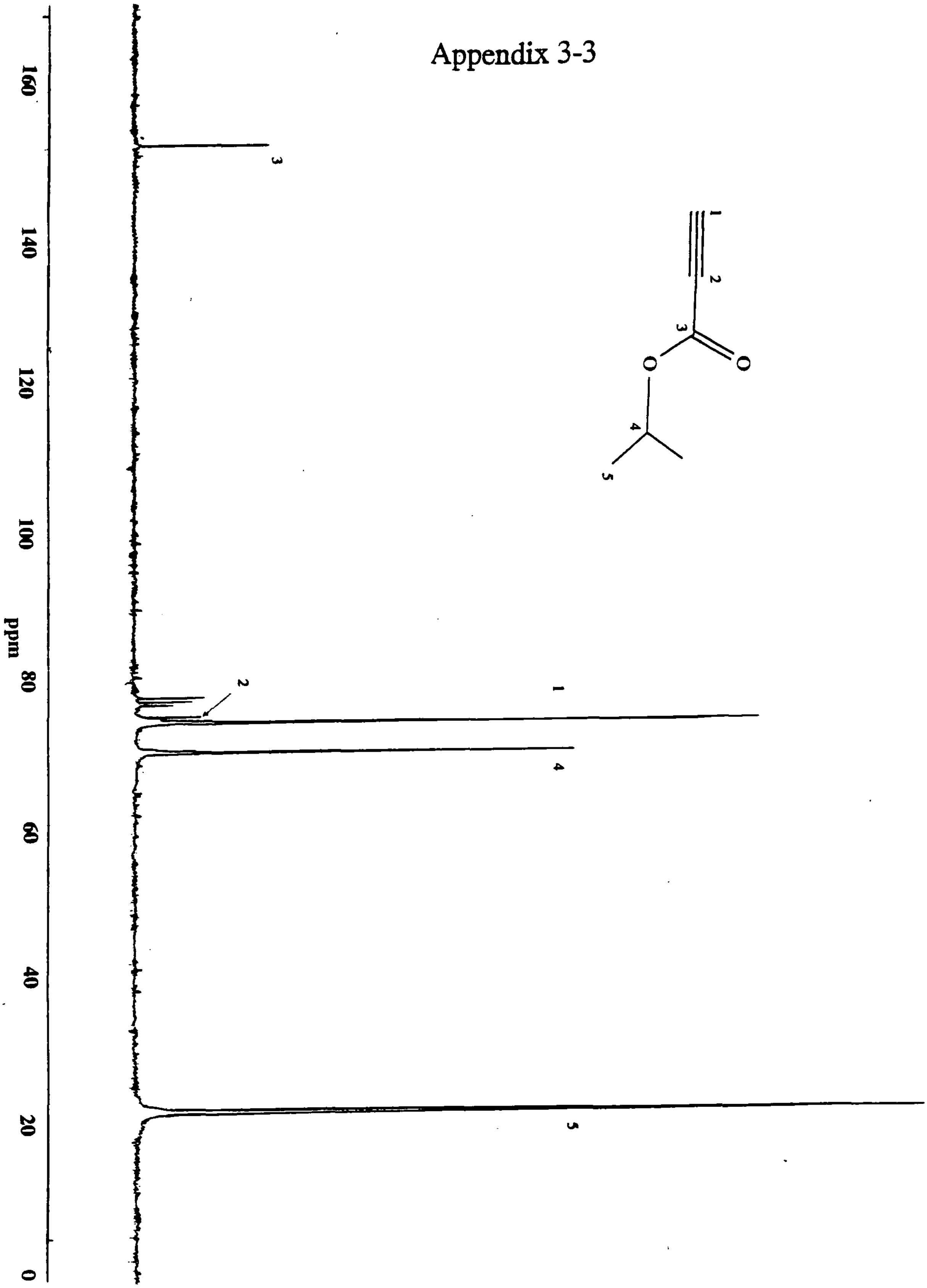

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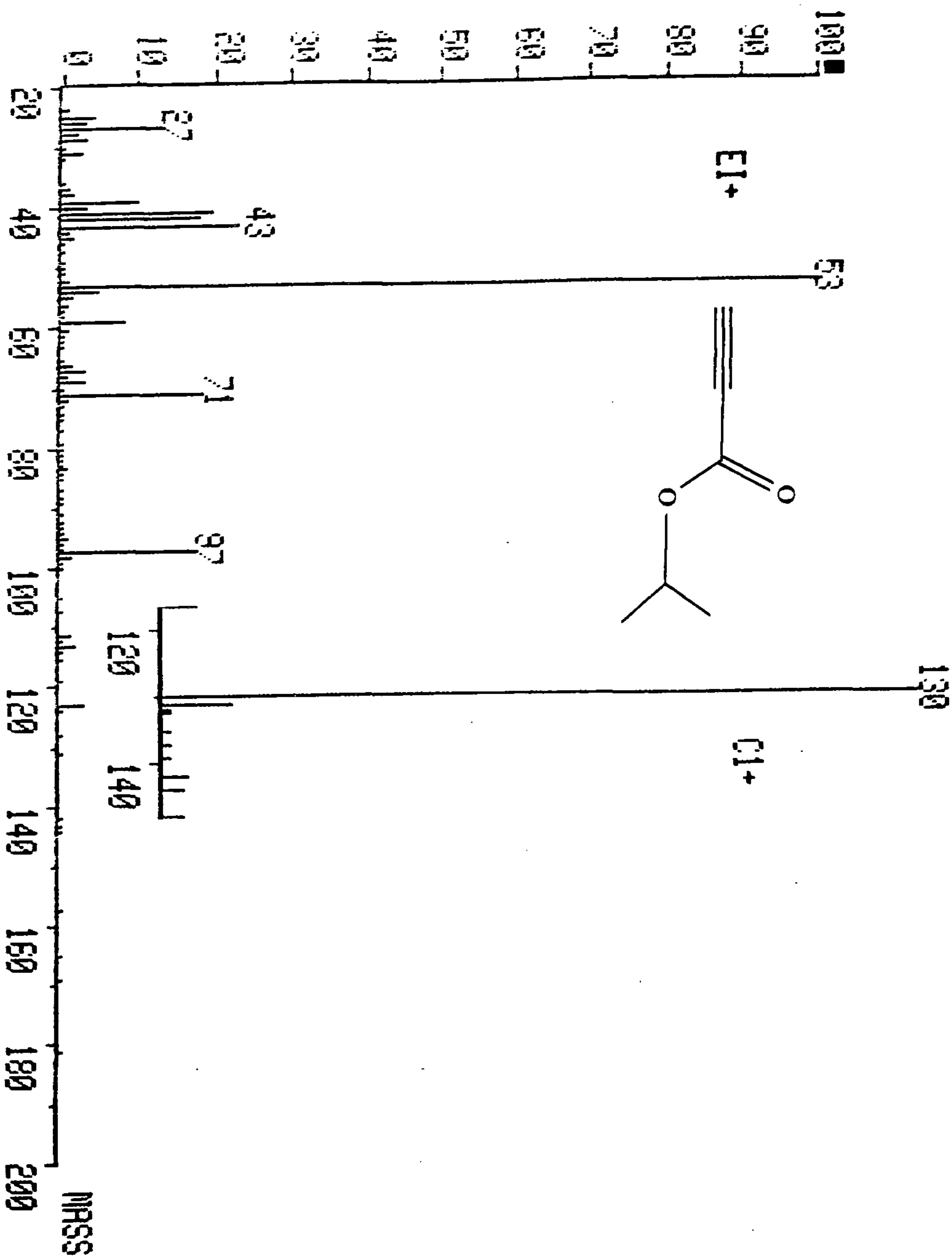
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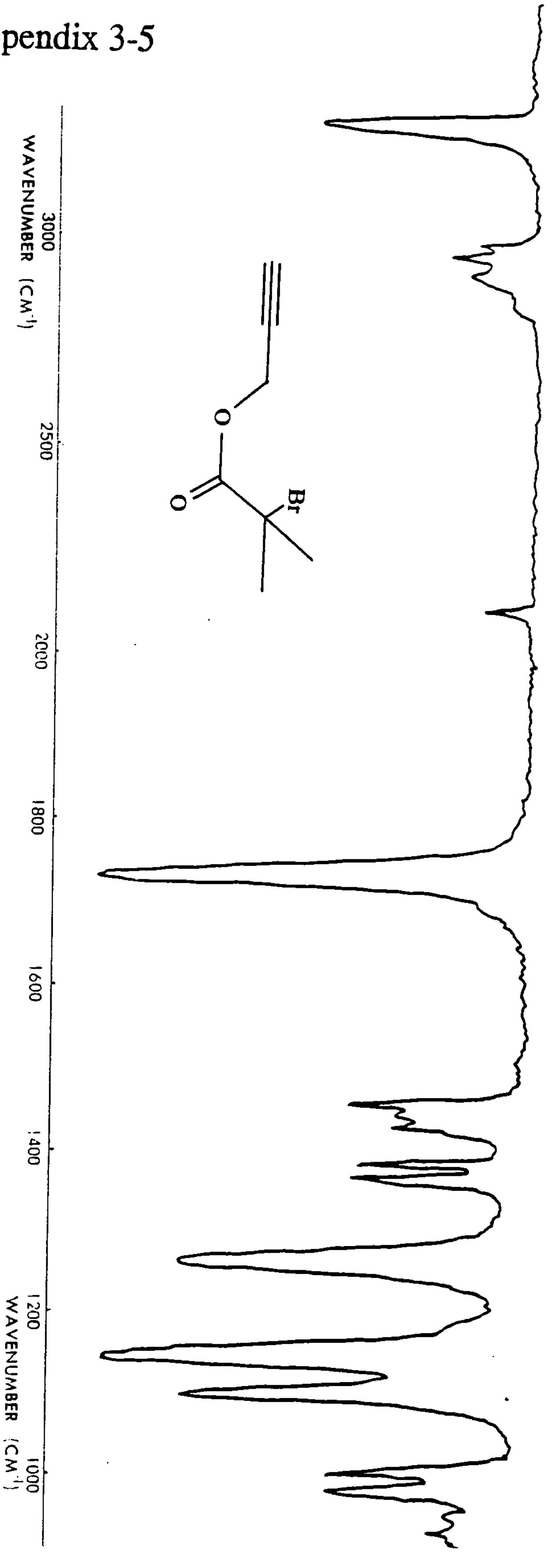
80
70
60
50
40
30
20
10
0
20
40
60
80
100
120
140
160
180
200
MASS
27
43
53
71
97
EI+
O
O
120
130
140
CI+

Appendix 3-5


Br
O
O
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2500
2000
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1600
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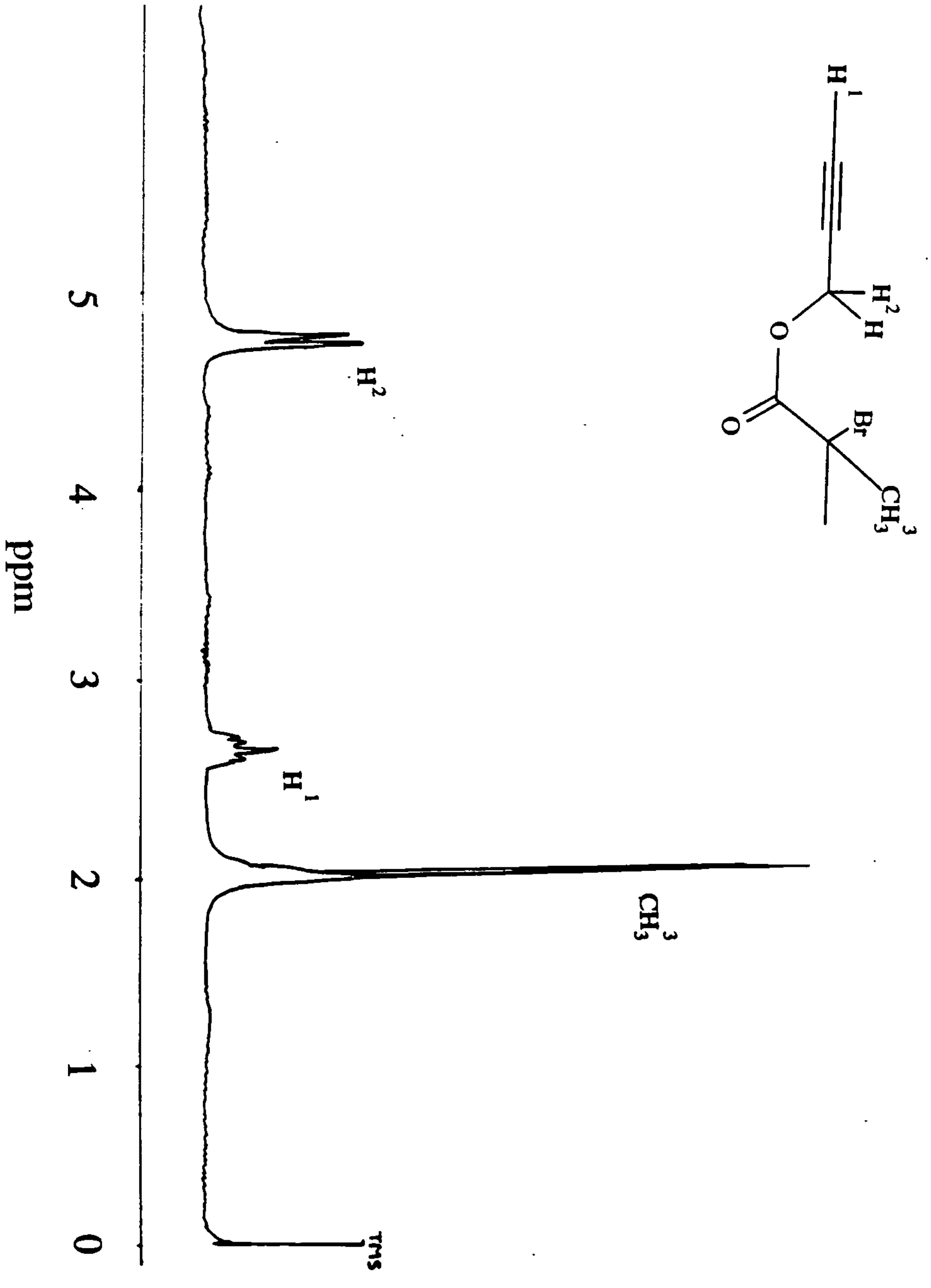
1200
1000
WAVENUMBER (CM-1)
WAVENUMBER (CM-1)

Appendix 3-6



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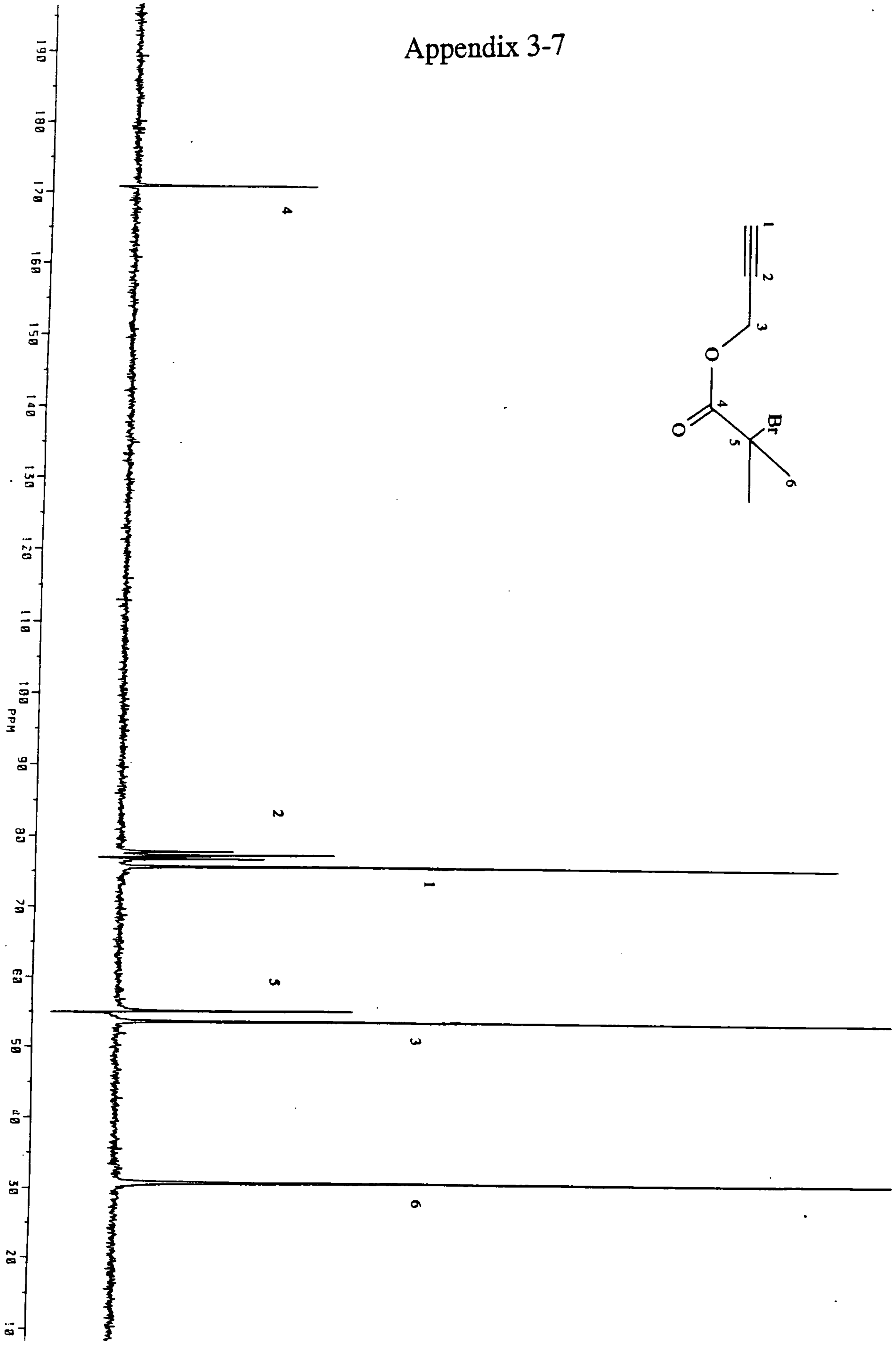
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6
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O
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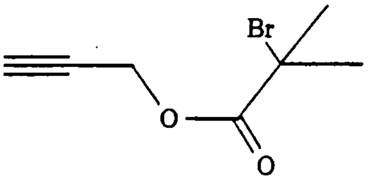
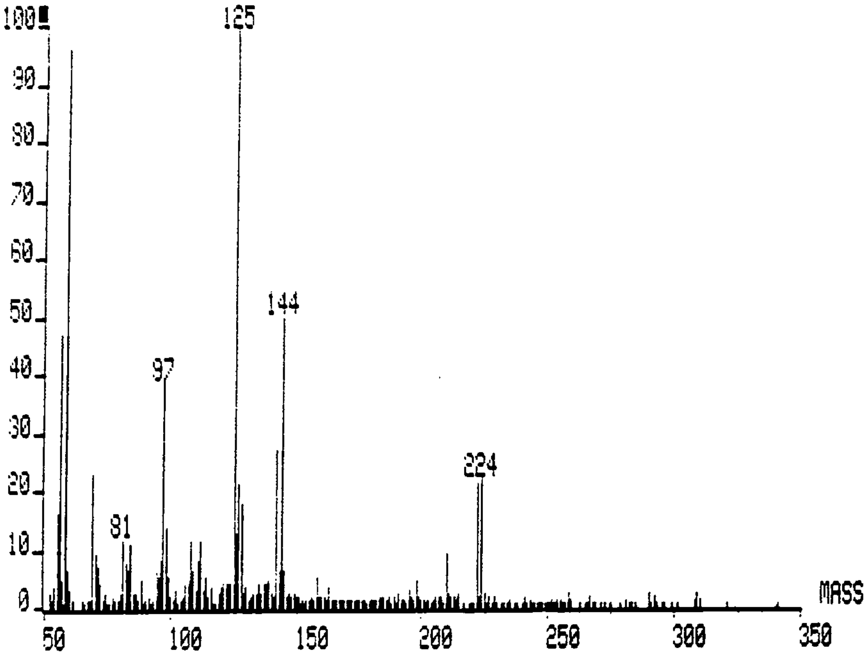
O
Br
5
6

Appendix 3-8


Br
O
O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90
80
70
60
50
40
30
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10
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144
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224
81
MASS
50
100
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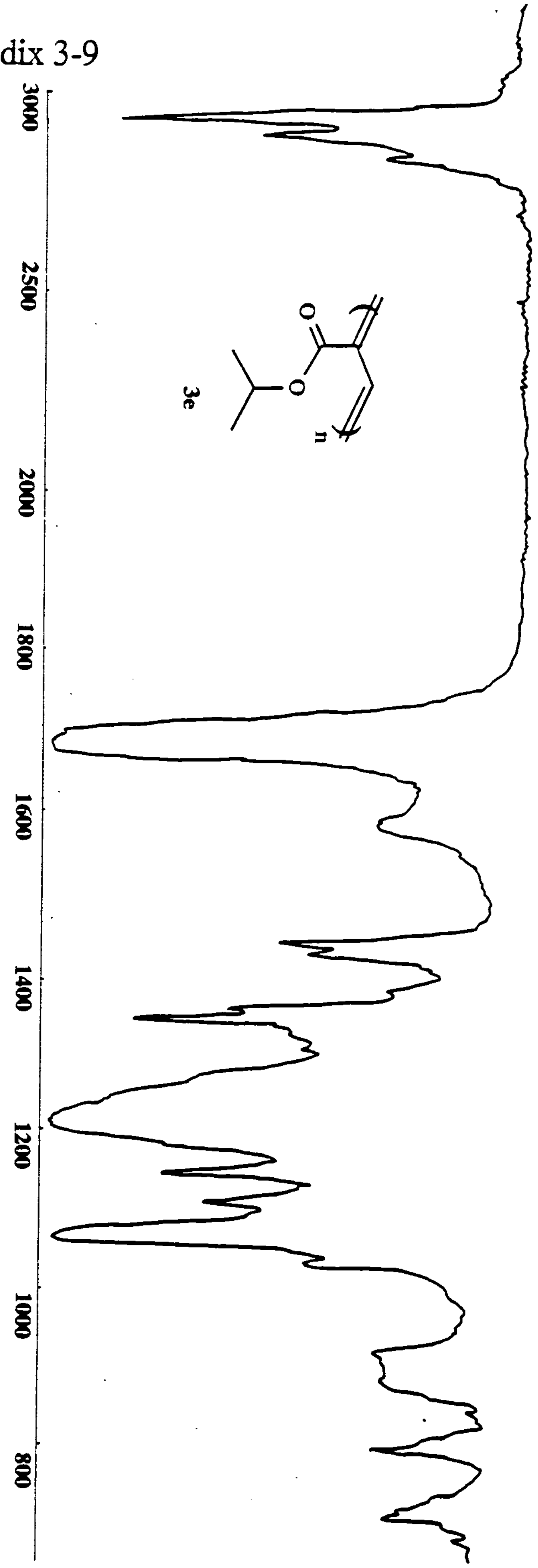
200
250
300
350

Appendix 3-9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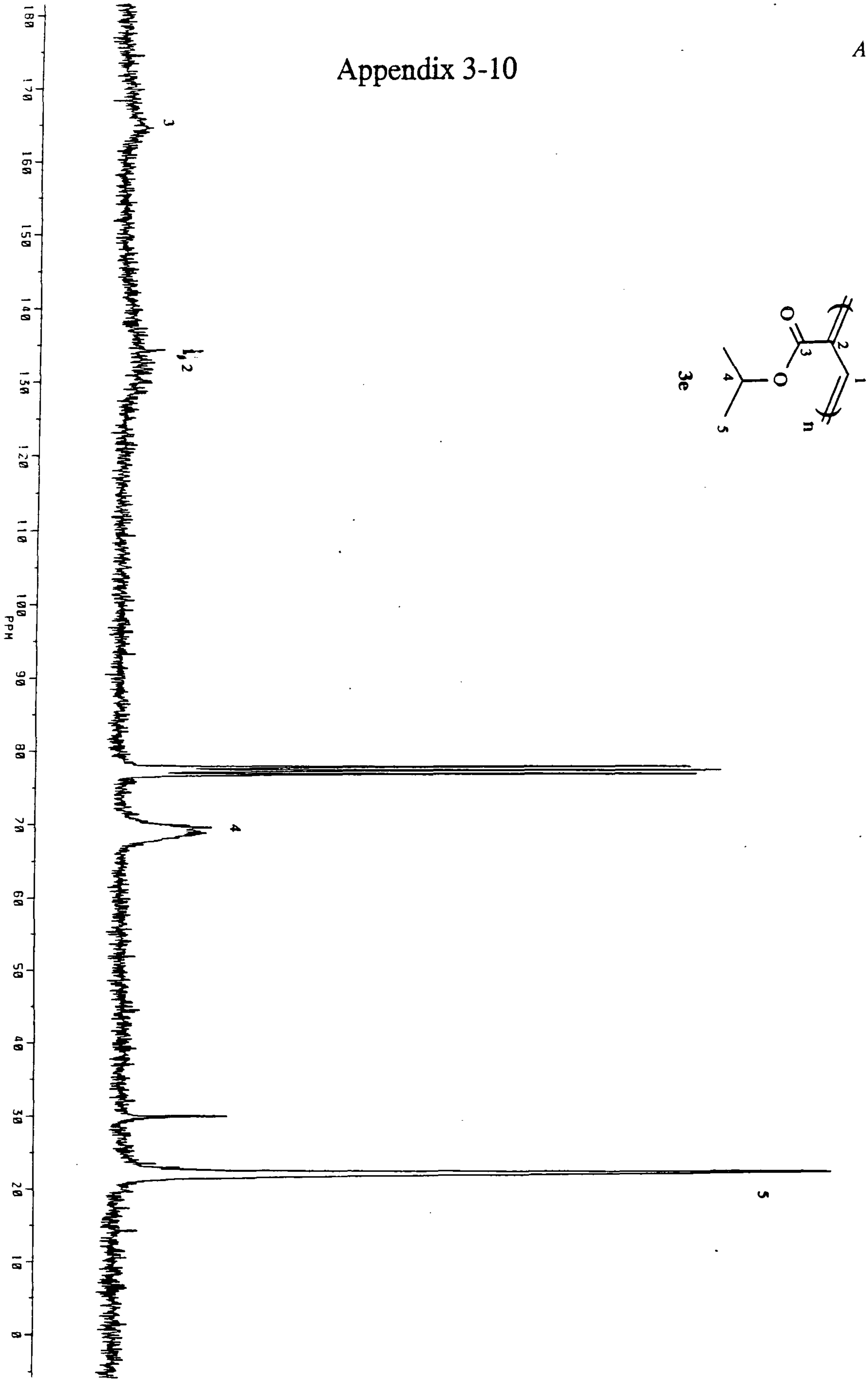
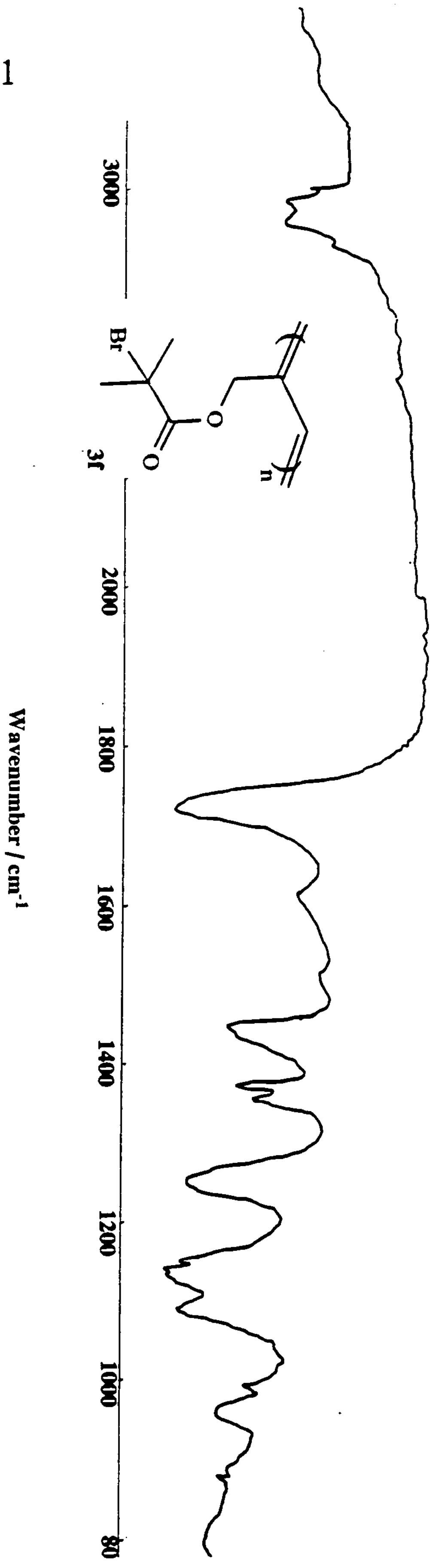
2000
1800
1600
1400
1200
1000
800
Wavenumber / cm-1
O
O
n
3e

Appendix 3-10



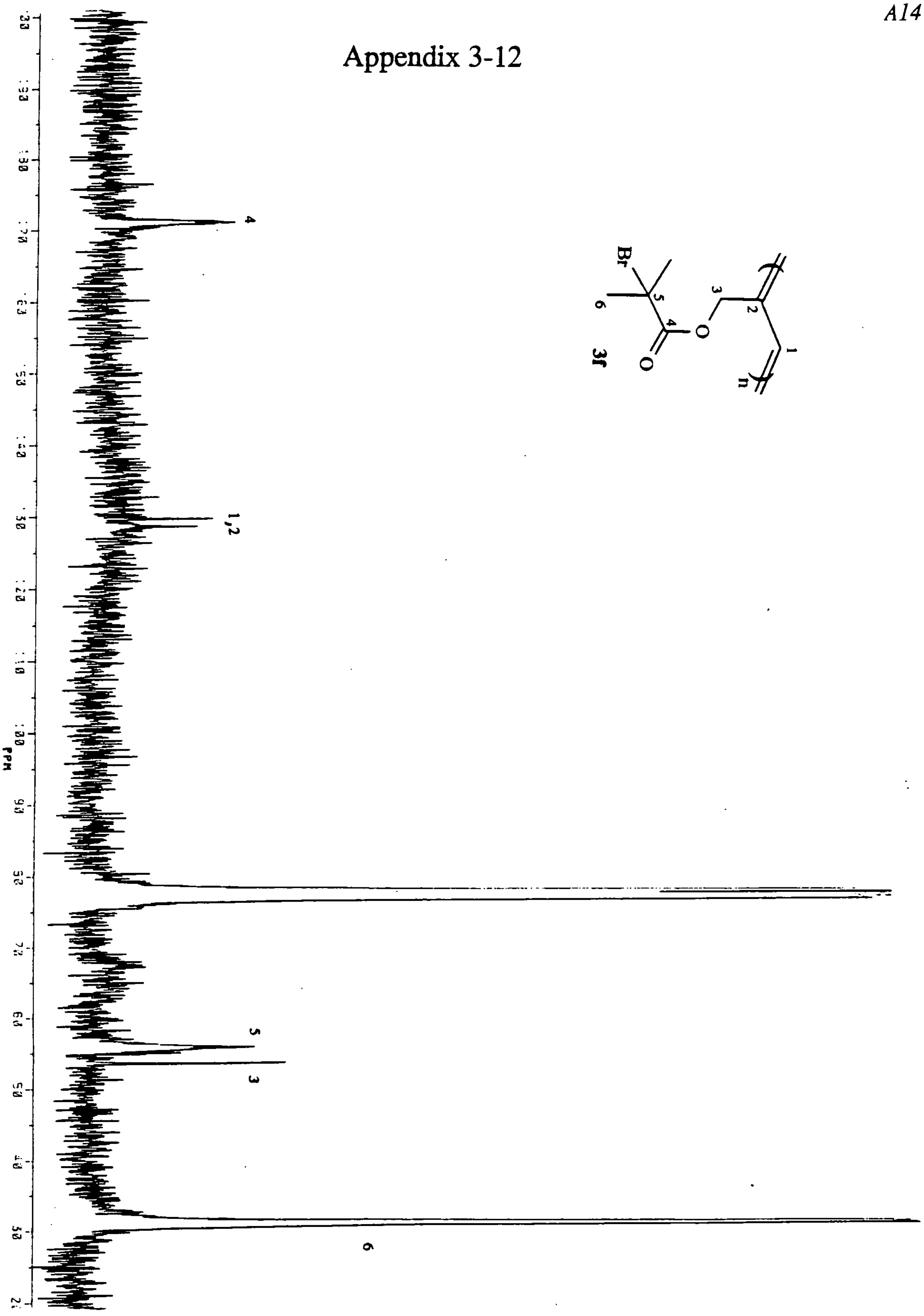
3e

Appendix 3-11



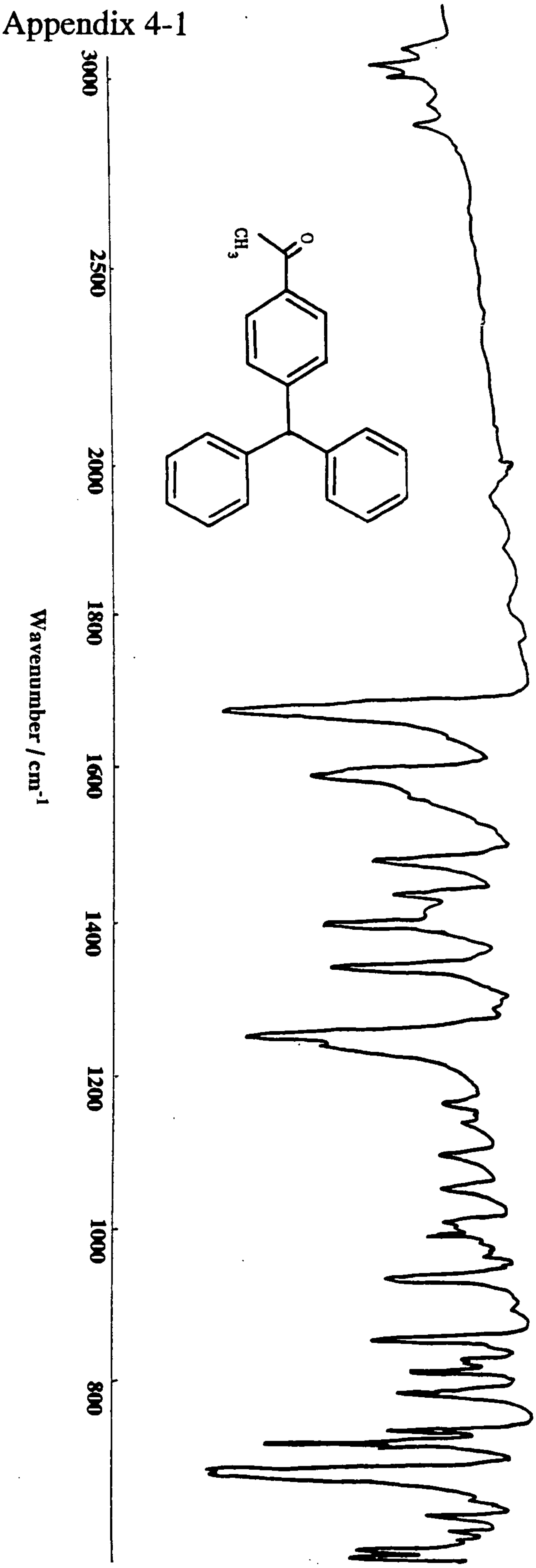
3f

Appendix 3-12

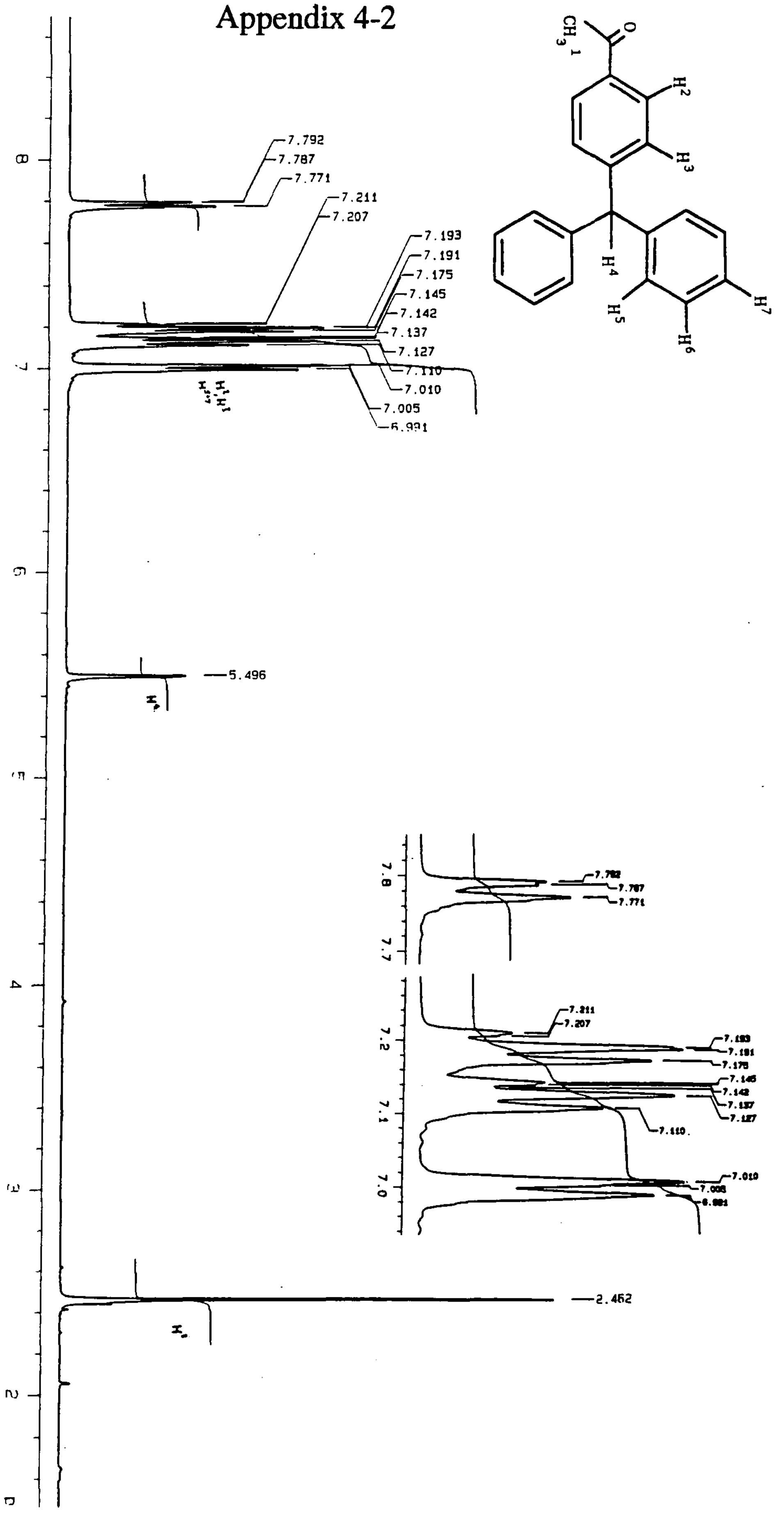


3f

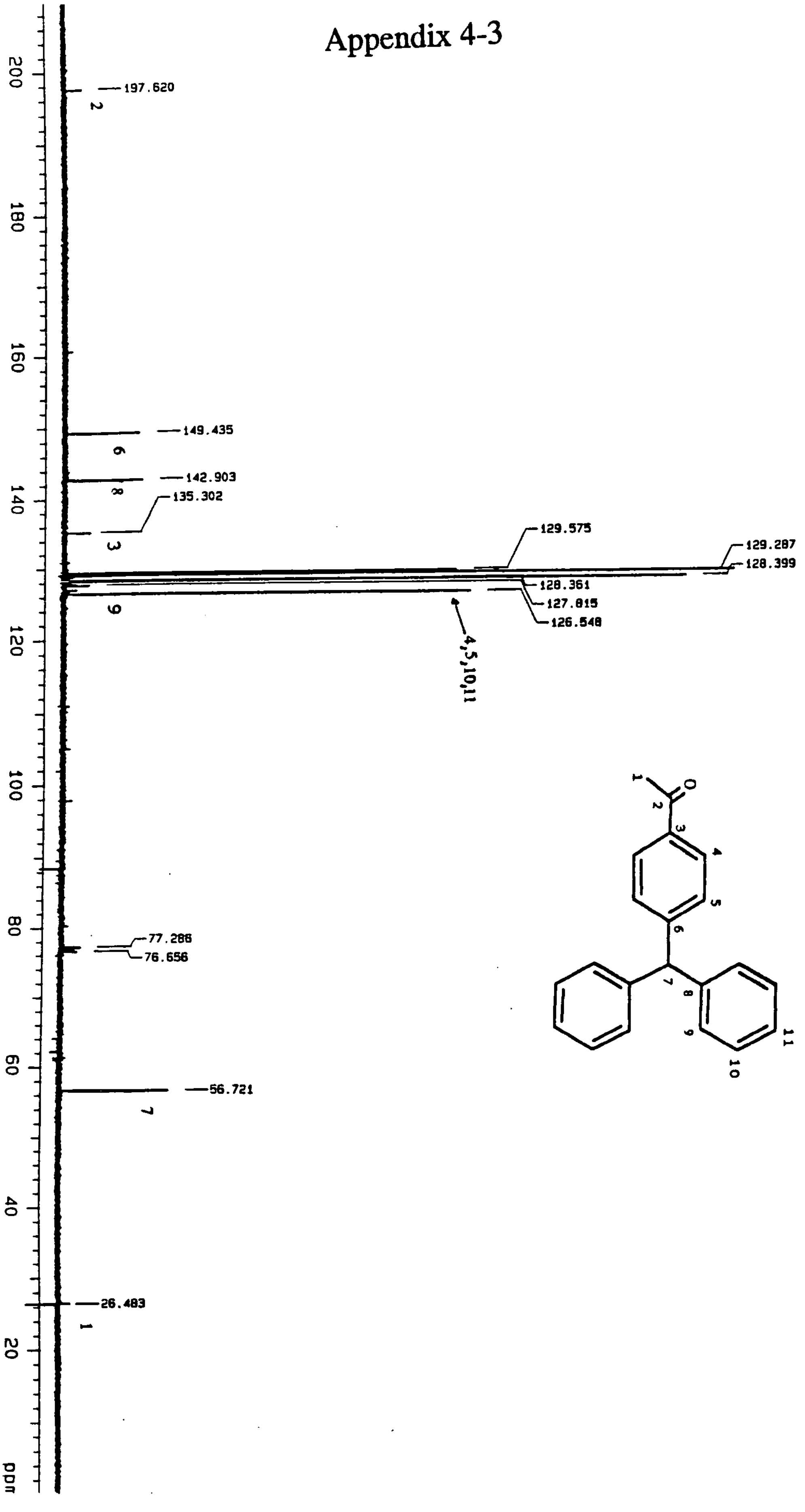
Appendix 4-1


3000
2500
2000
1800
1600
1400
1200
1000
800
Wavenumber / cm-1
O
CH3

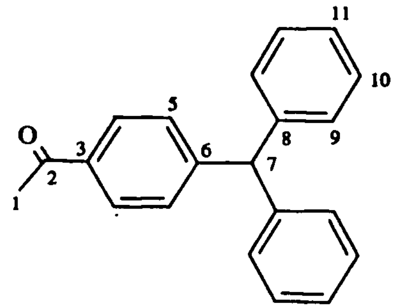
Appendix 4-2


O
CH3 1
H2
H3
H4
H5
H6
H7
8
7
6
5
4
3
2
0
7.792
7.787
7.771
7.211
7.207
7.193
7.191
7.175
7.145
7.142
7.137
7.127
7.110
7.010
7.005
6.991
H2,H3
H5-7
5.496
H4
2.462
H1
7.8
7.7
7.2
7.1
7.0

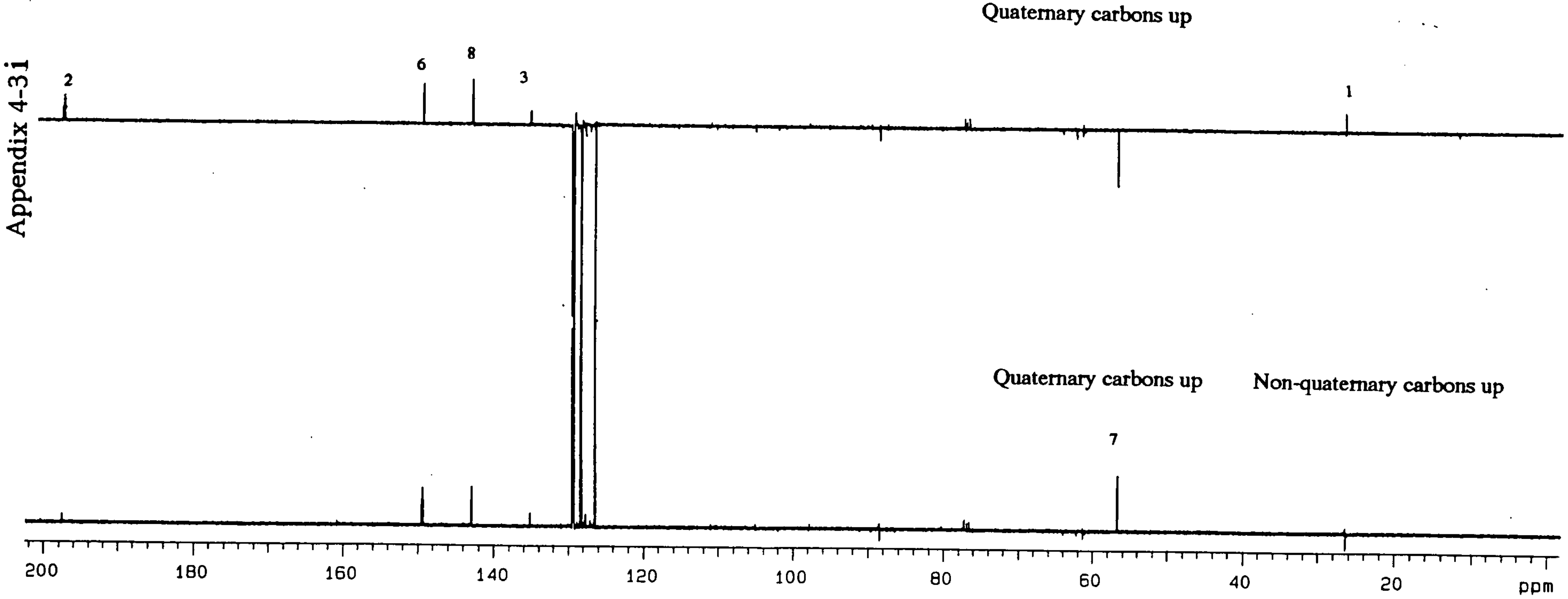
Appendix 4-3


197.620
2
149.435
6
142.903
8
135.302
3
129.575
129.287
128.399
128.361
127.815
126.548
9
4,5,10,11
77.286
76.656
56.721
7
26.483
1
O
1
2
3
4
5
6
7
8
9
10
11
200
180
160
140
120
100
80
60
40
20
ppm

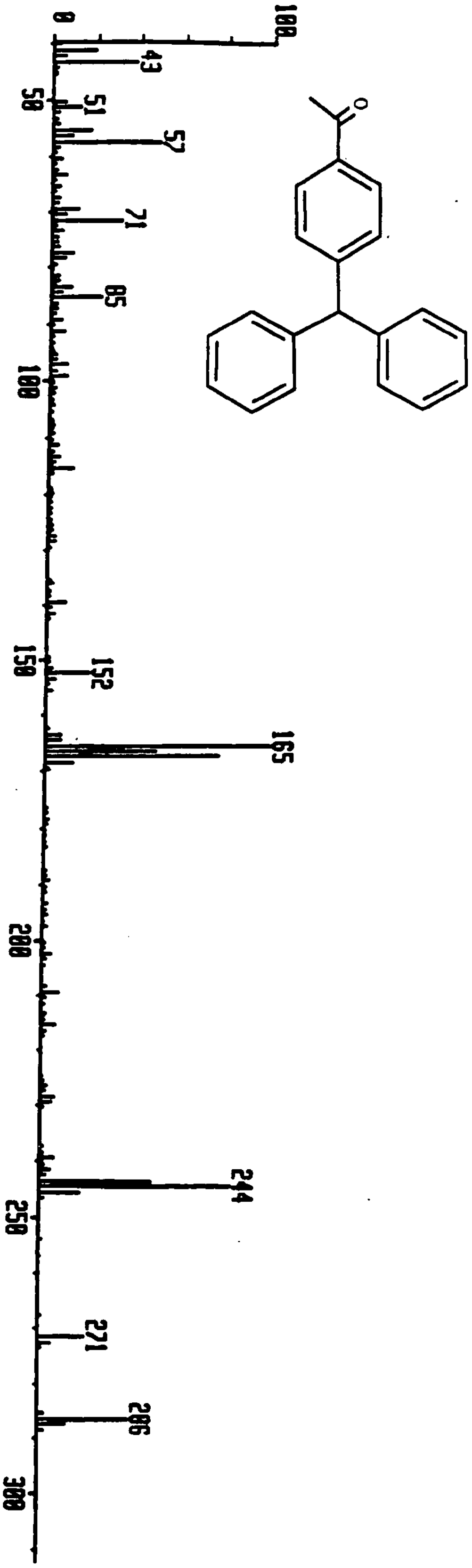
Appendix 4-3i



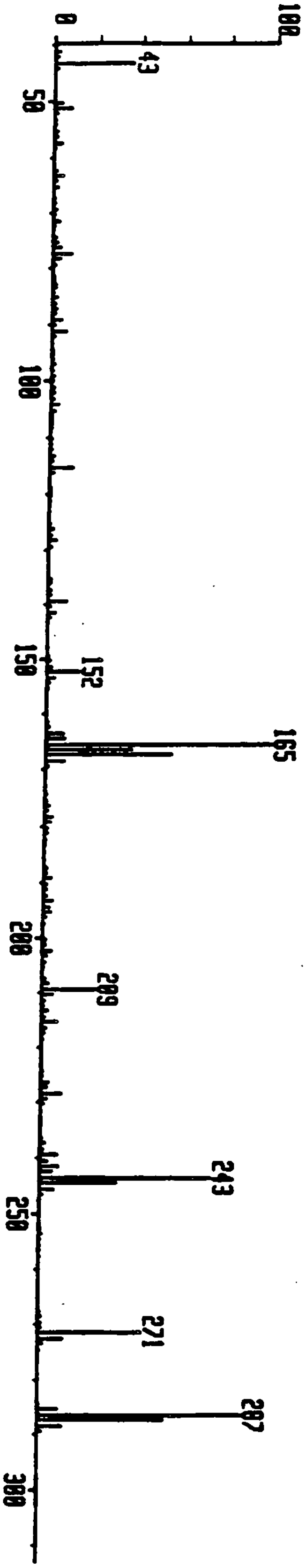
^{13}C NMR APT



Appendix 4-4

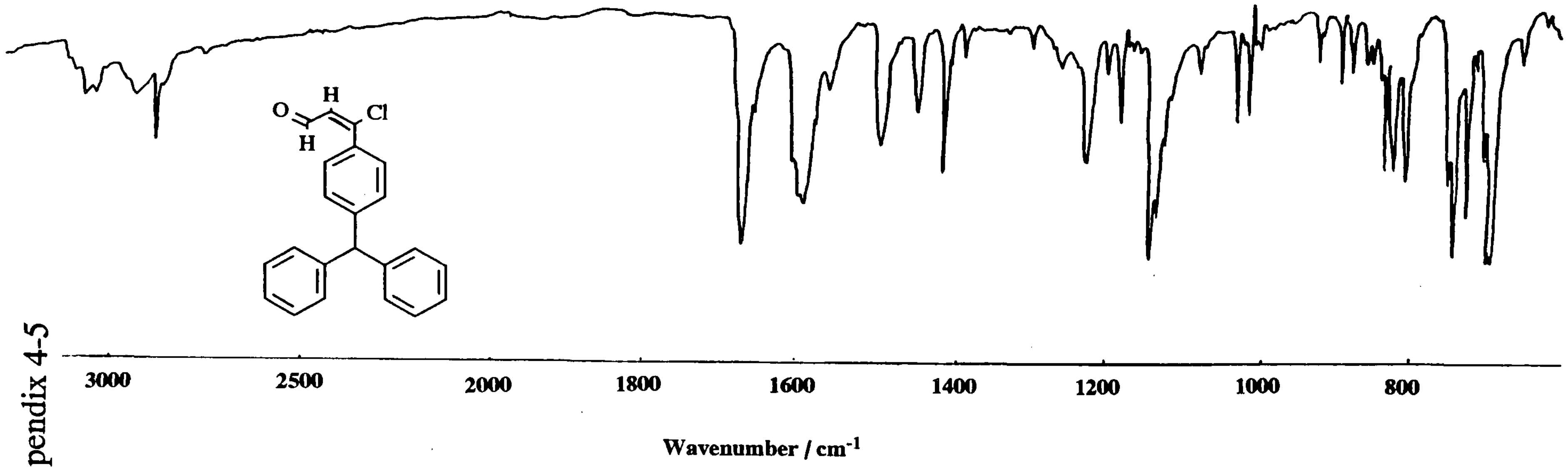


100
0
43
50
51
57
71
85
100
150
152
165
200
244
250
271
286
300
O

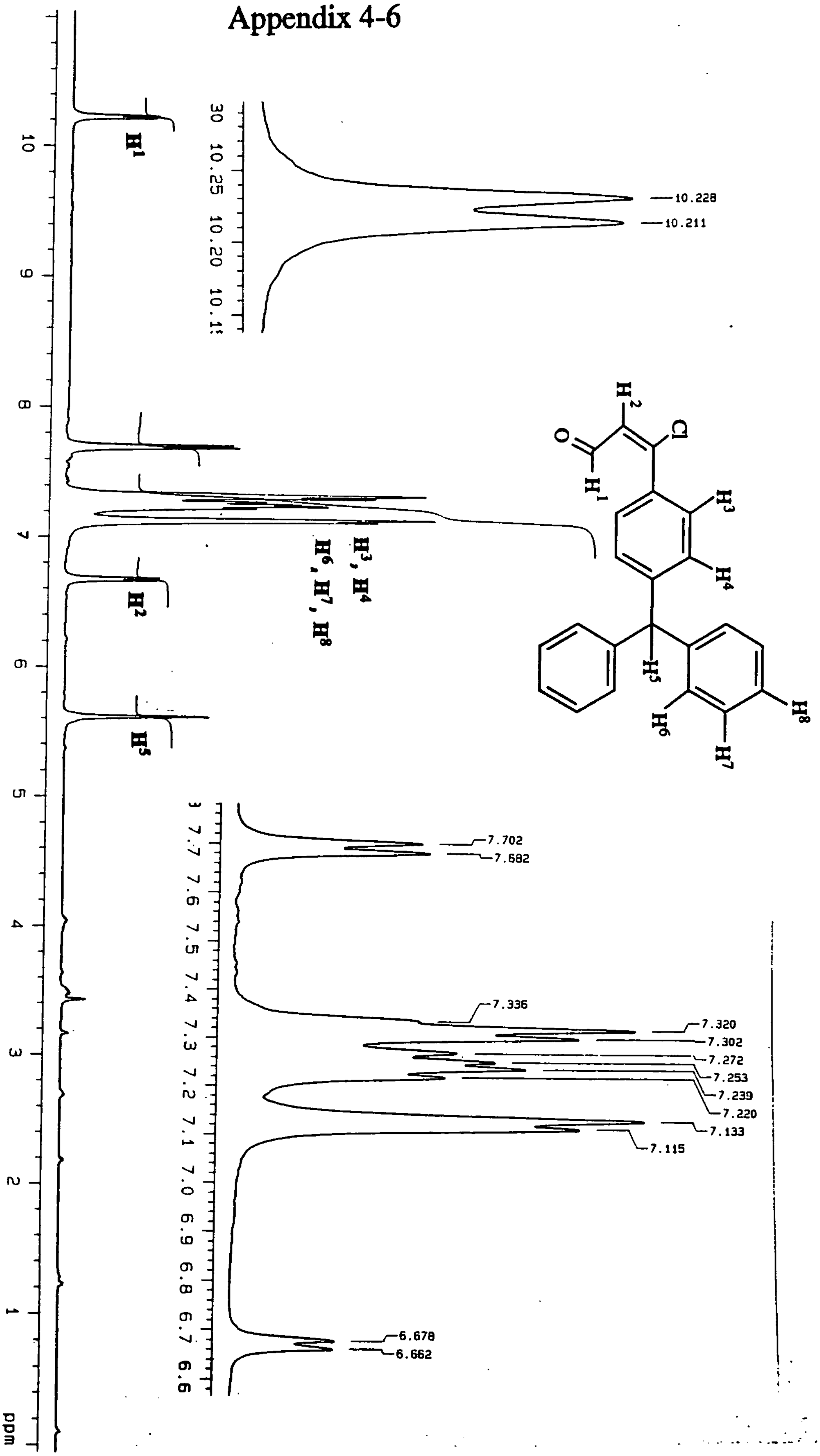


100
0
43
50
100
150
152
165
200
209
243
250
271
287
300

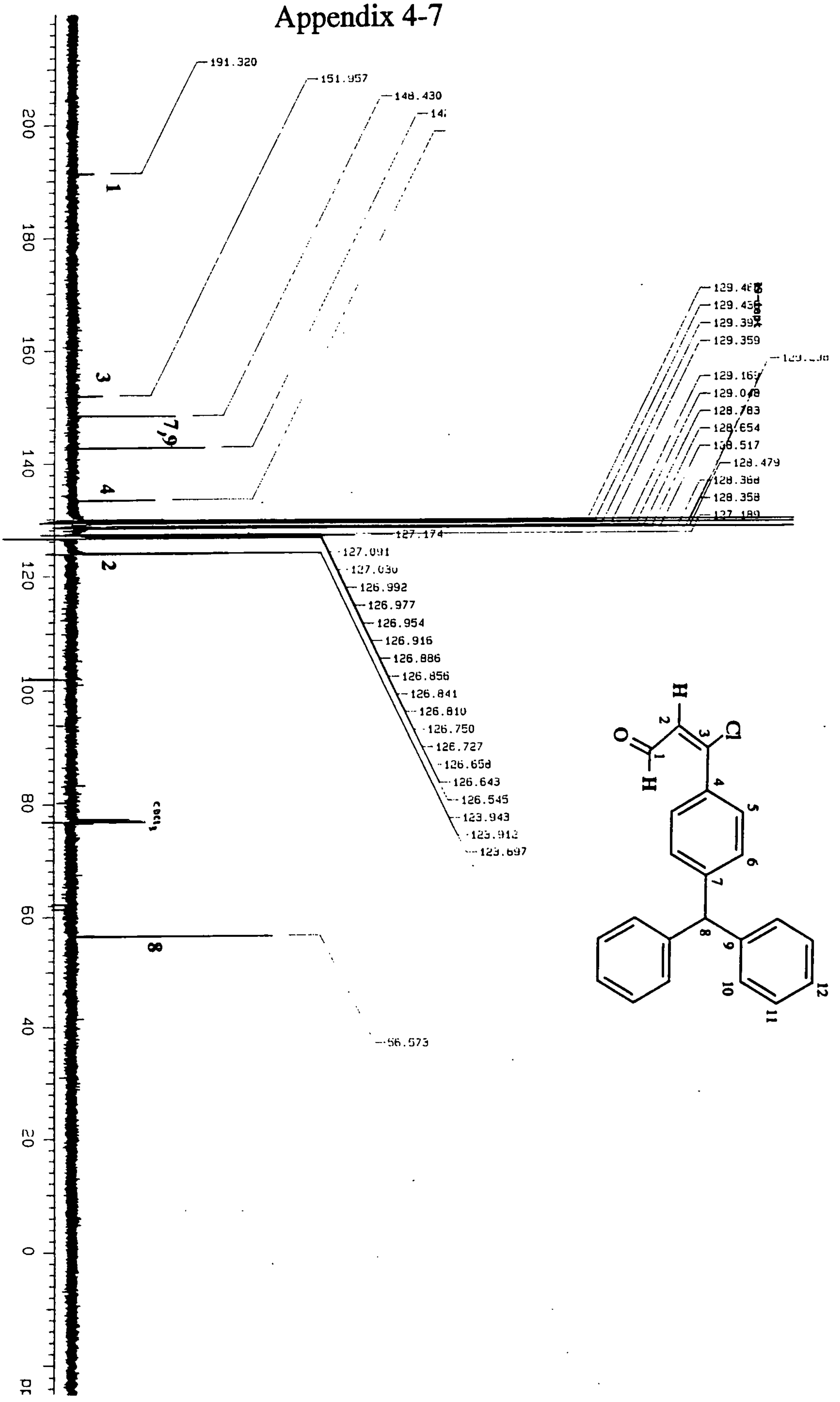
Appendix 4-5


O
H
H
Cl
3000
2500
2000
1800
1600
1400
1200
1000
800
Wavenumber / cm-1

Appendix 4-6


H1
H3, H4
H6, H7, H8
H2
H5
10
9
8
7
6
5
4
3
2
1
ppm
10.228
10.211
7.702
7.682
7.336
7.320
7.302
7.272
7.253
7.239
7.220
7.133
7.115
6.678
6.662
O
Cl
H8
H7
H6

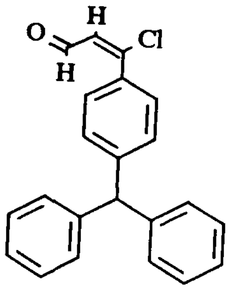
Appendix 4-7

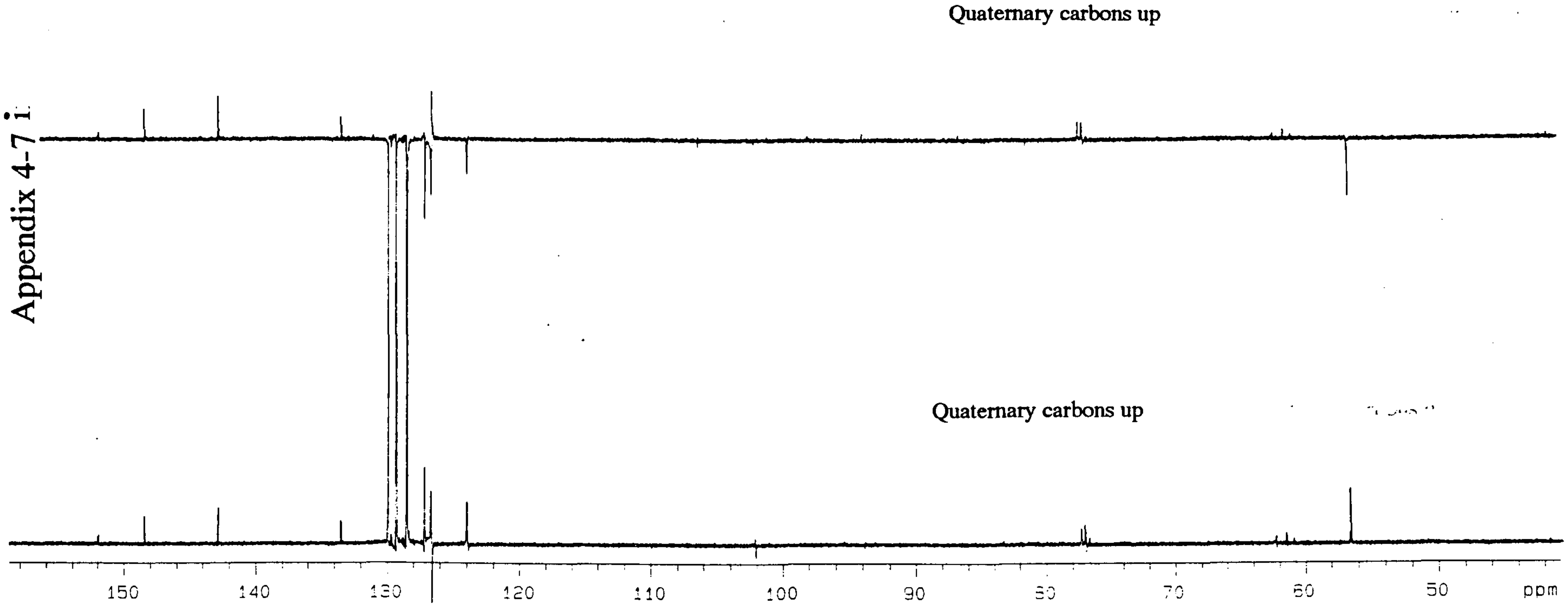


191.320
151.957
148.430
129.436
129.397
129.359
129.169
129.048
128.783
128.654
128.517
128.479
128.368
128.358
127.189
127.174
127.091
127.030
126.992
126.977
126.954
126.916
126.886
126.856
126.841
126.810
126.750
126.727
126.658
126.643
126.545
123.943
123.912
123.697
56.573
1
3
7,9
4
2
CDCl3
8
200
180
160
140
120
100
80
60
40
20
0
ppm
H
O
H
Cl
1
2
3
4
5
6
7
8
9
10
11
12

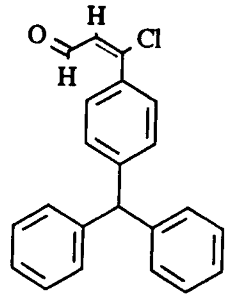
Appendix 4-7 i

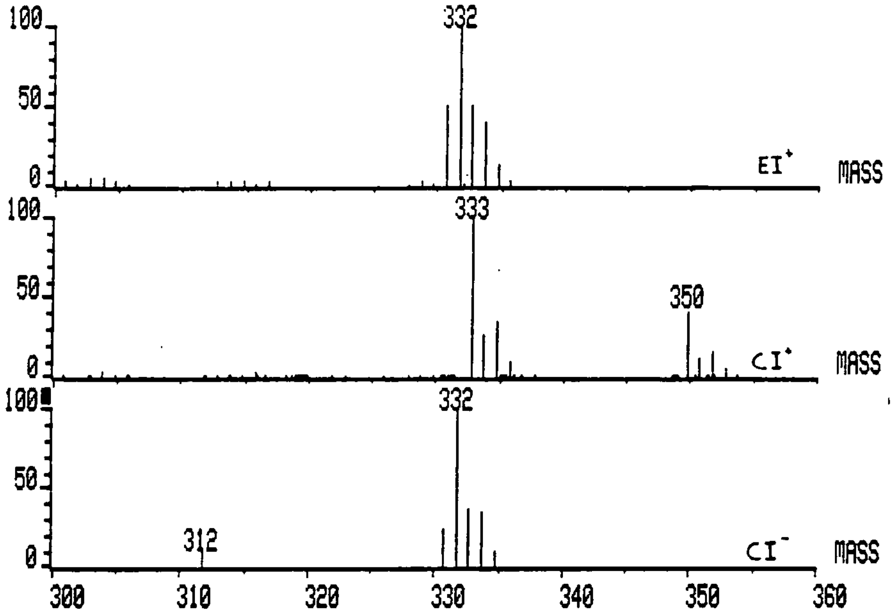
^{13}C NMR APT



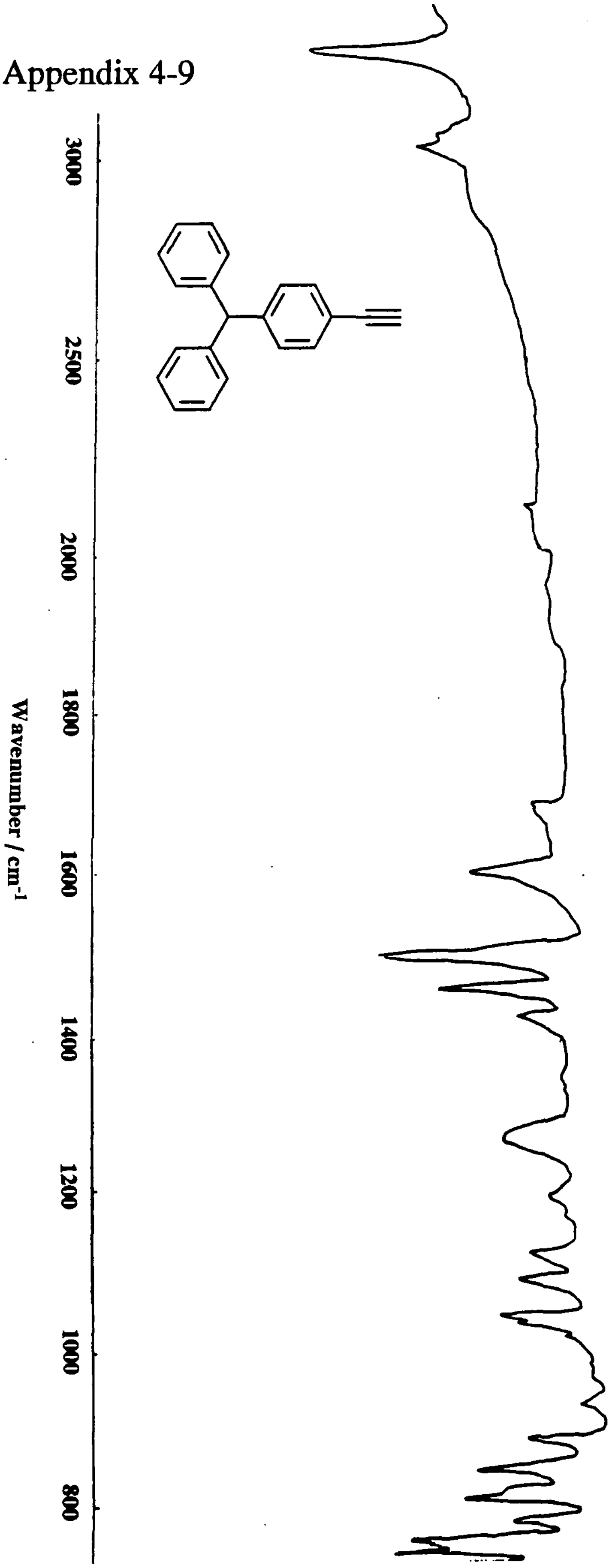


Appendix 4-8

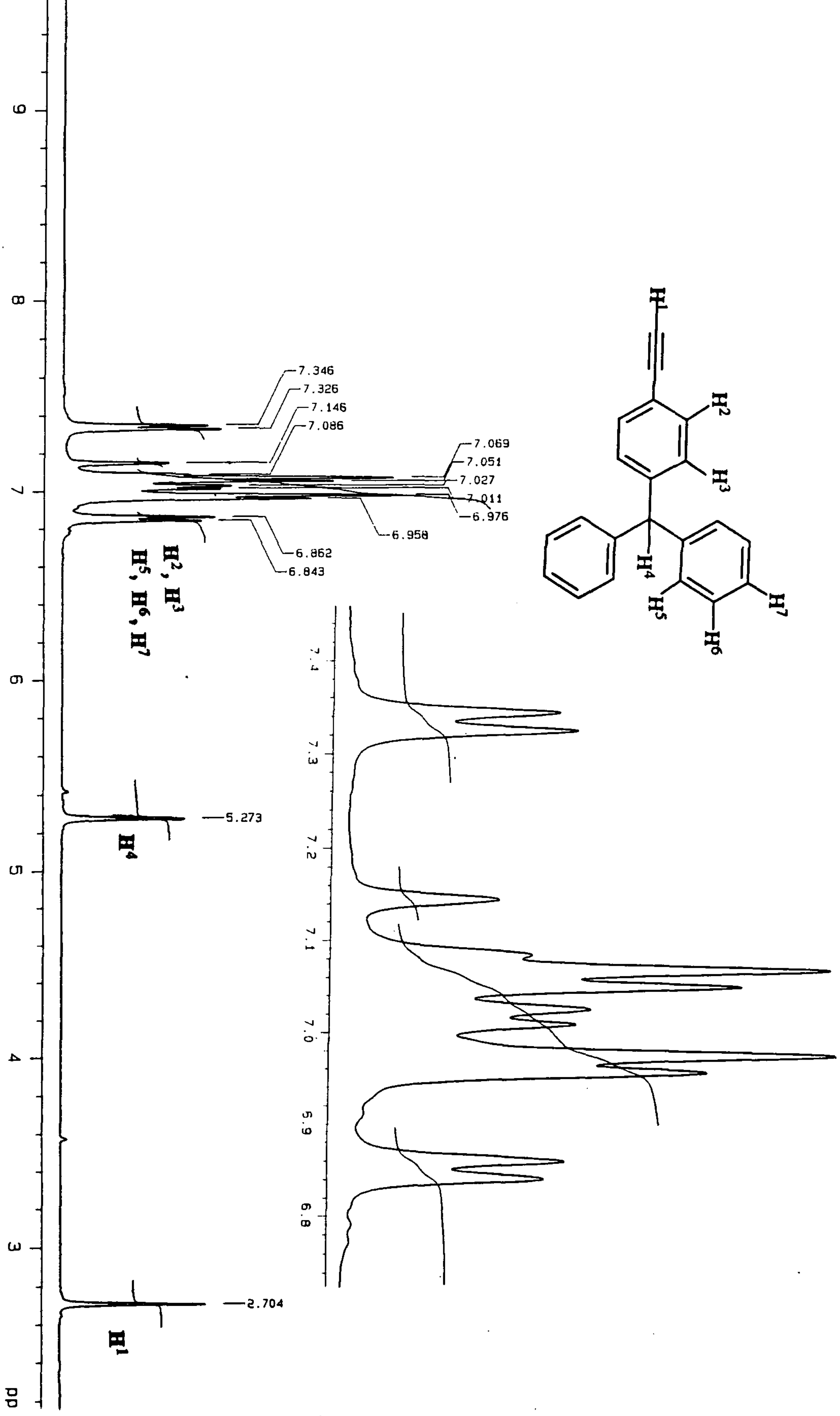

H
O
Cl
H


100
50
0
332
EI$^+$
MASS
100
50
0
333
350
CI$^+$
MASS
100
50
0
332
312
CI$^-$
MASS
300
310
320
330
340
350
360

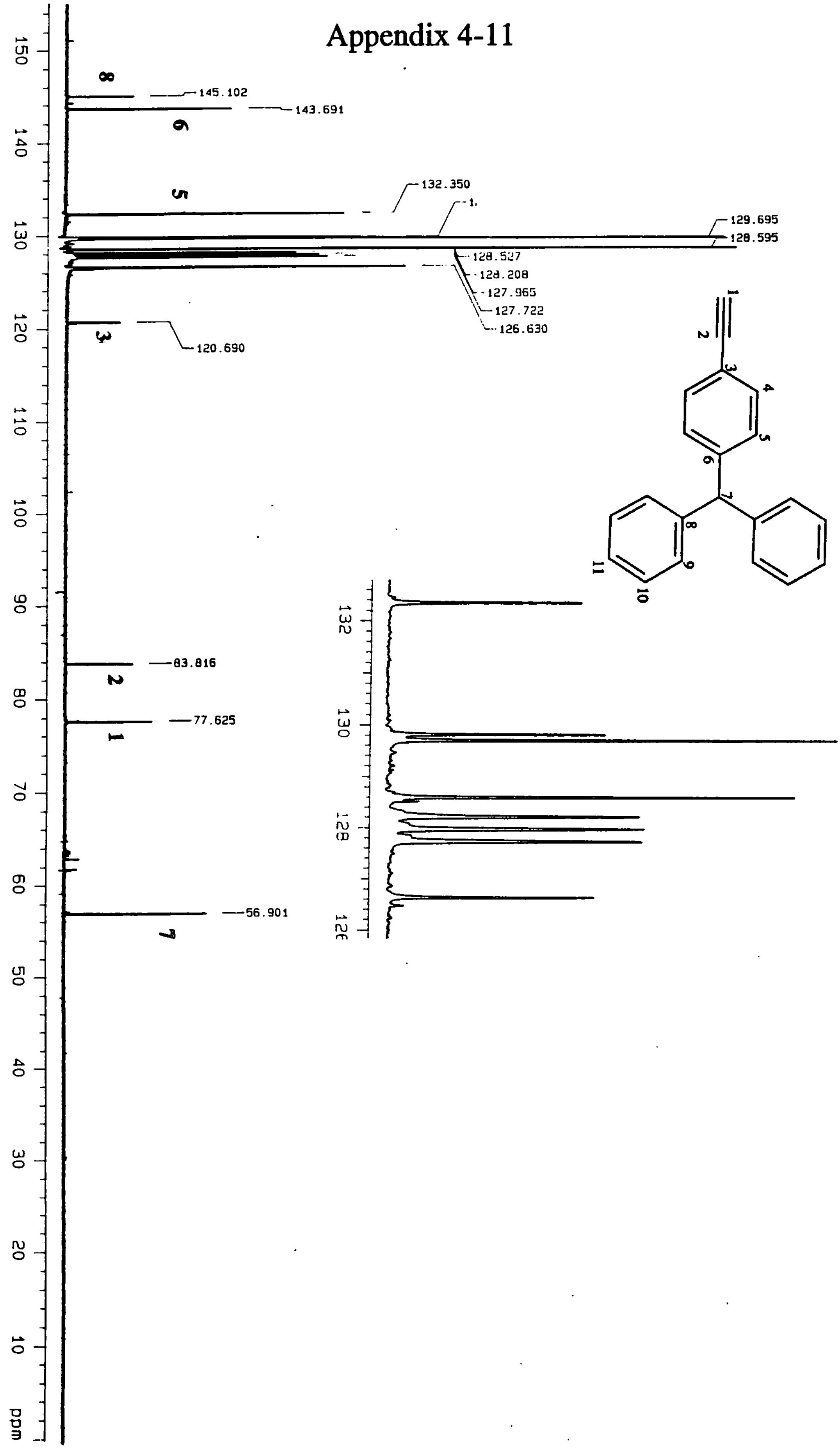
Appendix 4-9



Appendix 4-10

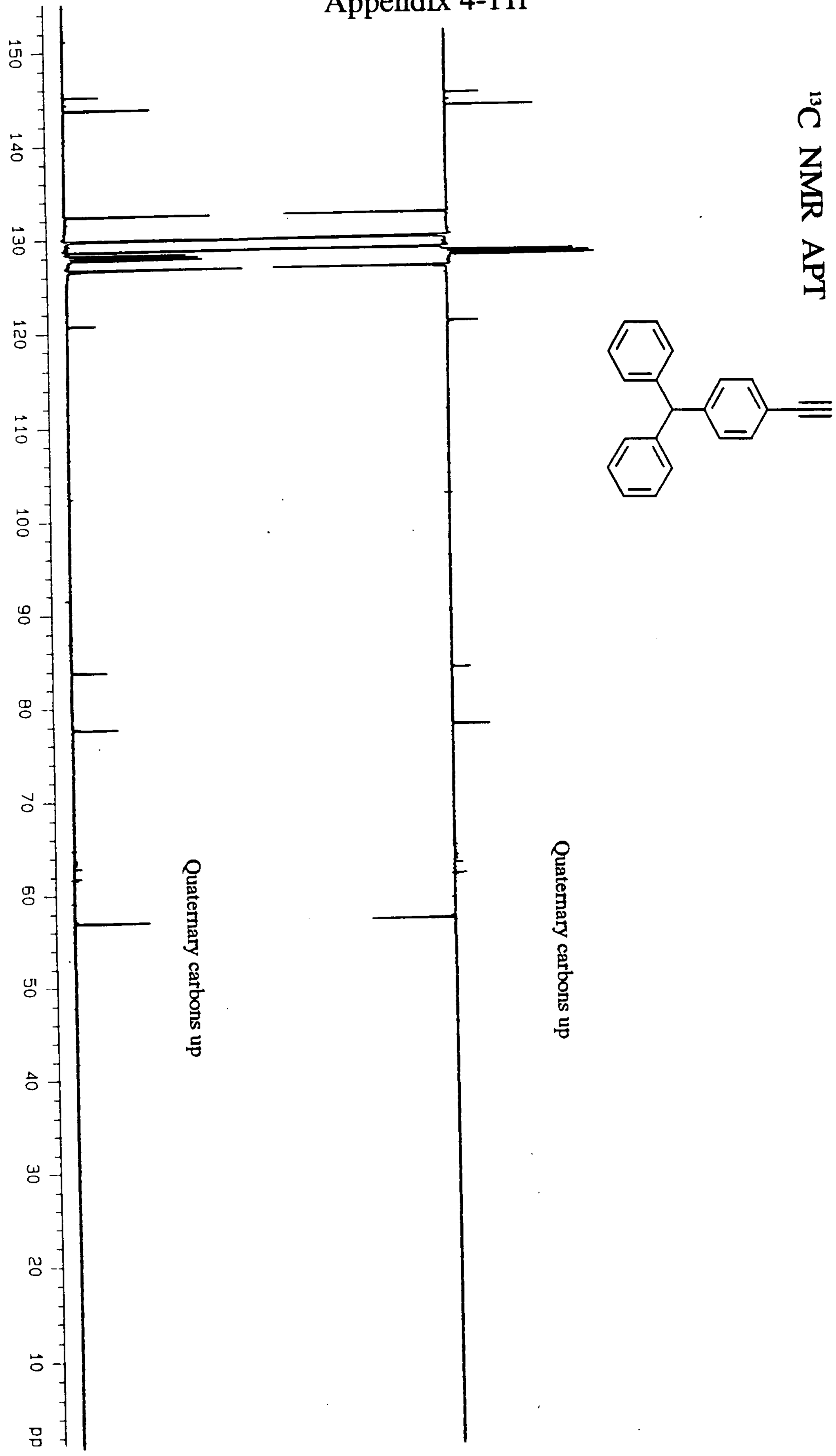


Appendix 4-11

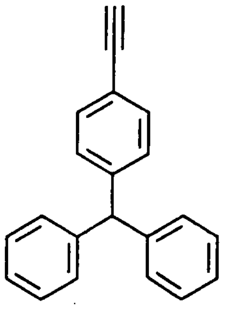


Appendix 4-11i

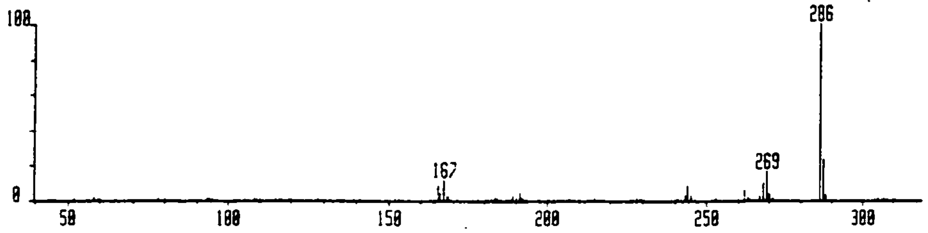
^{13}C NMR APT



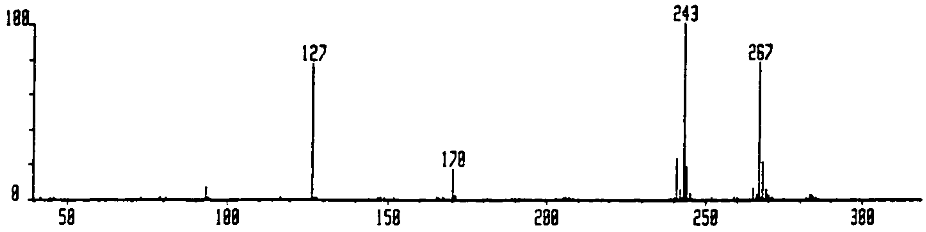
Appendix 4-12



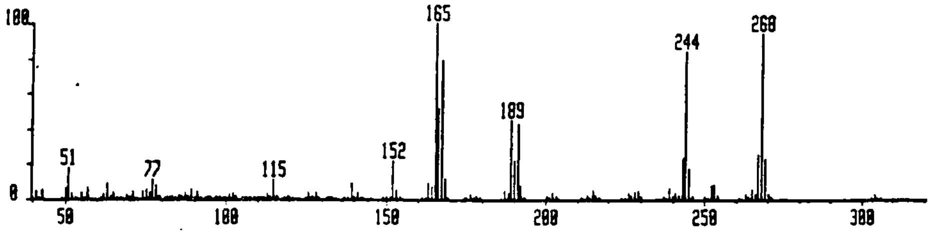
CI+



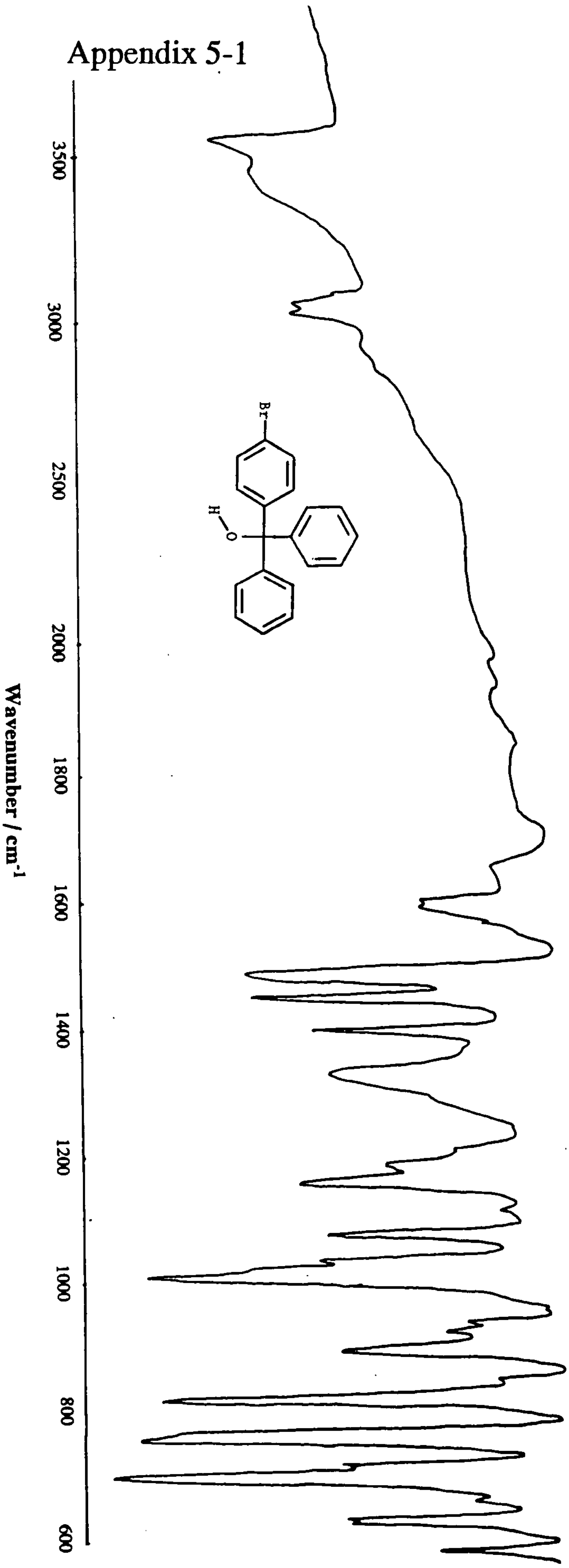
CI-



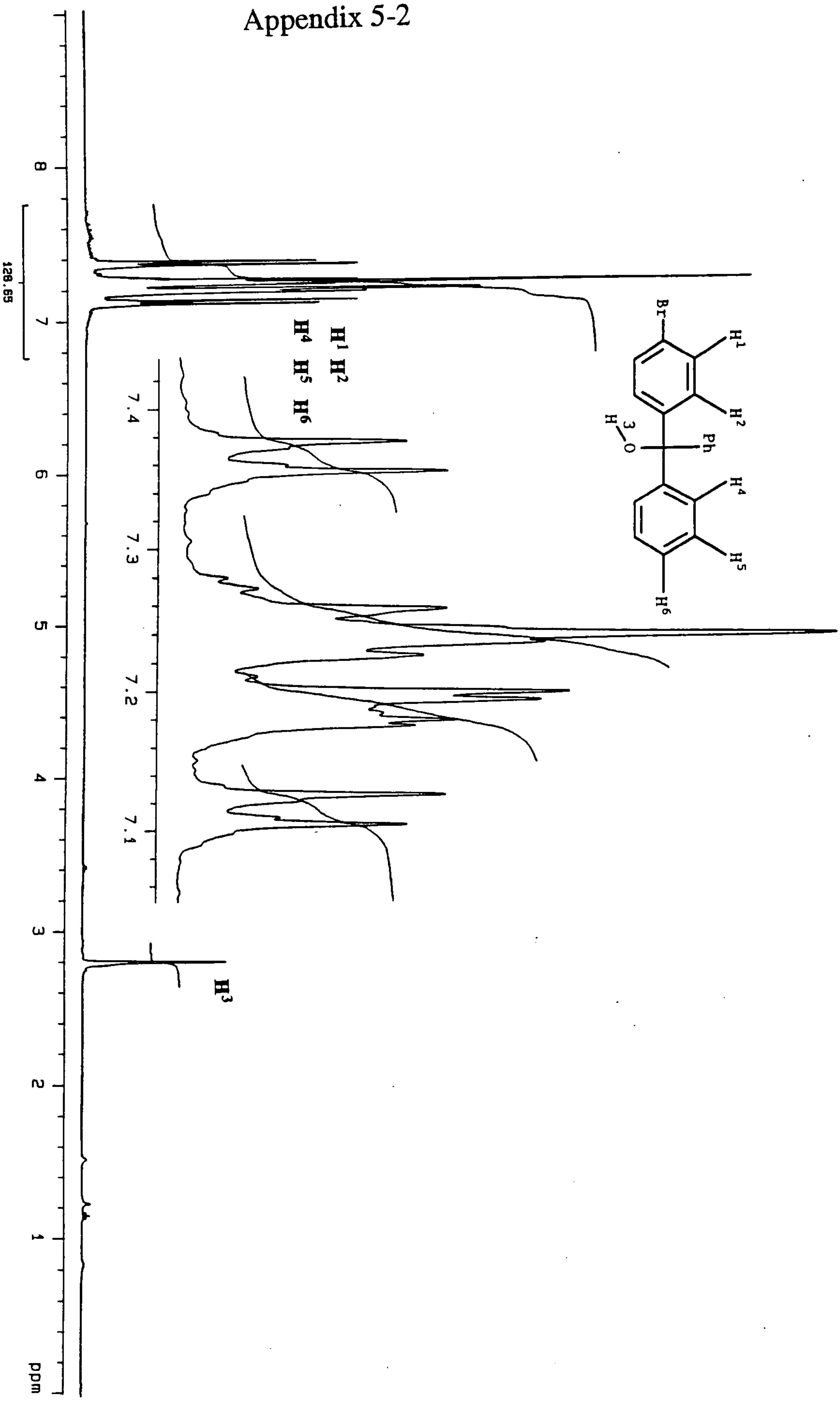
EI+



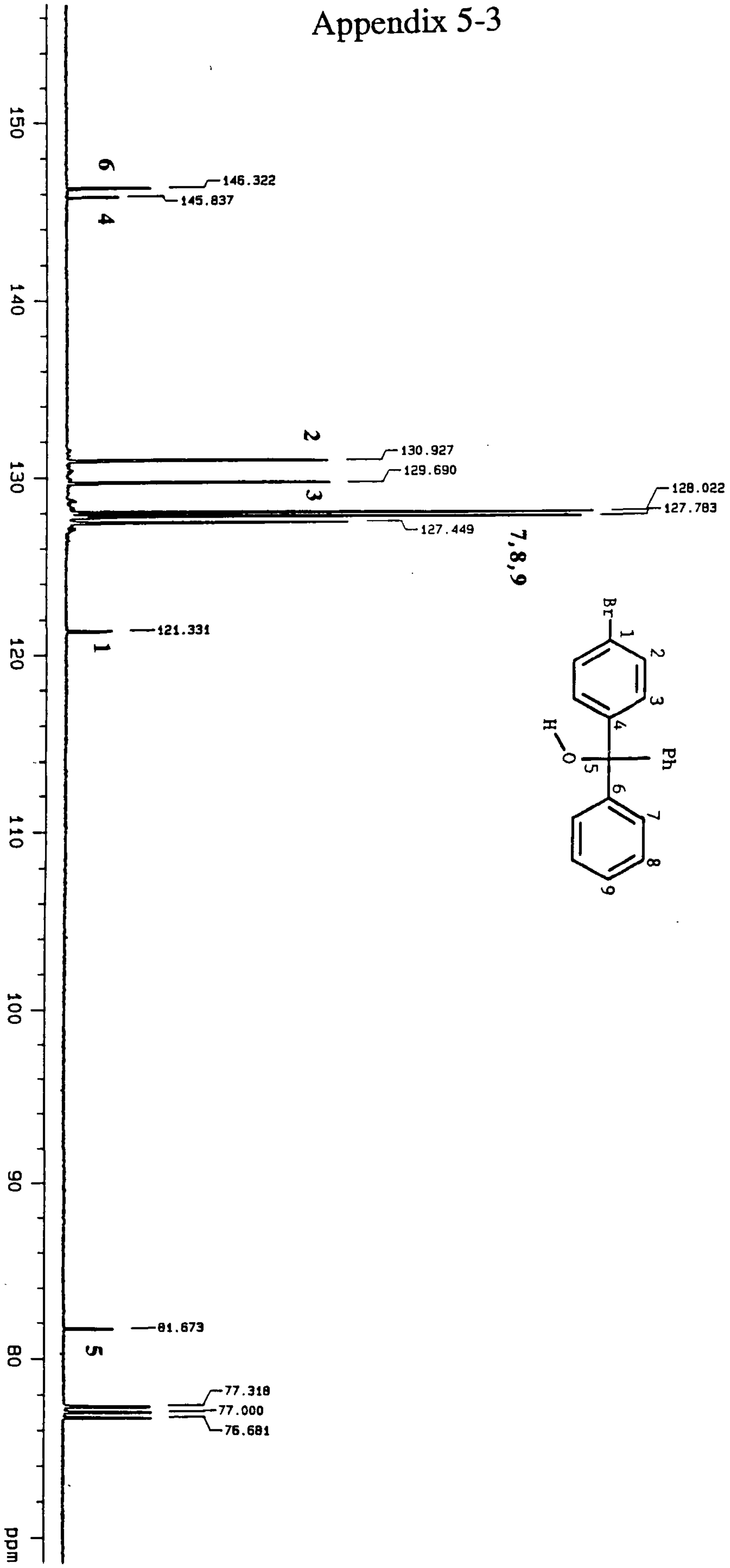
Appendix 5-1


3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
Wavenumber / cm-1
Br
H
O

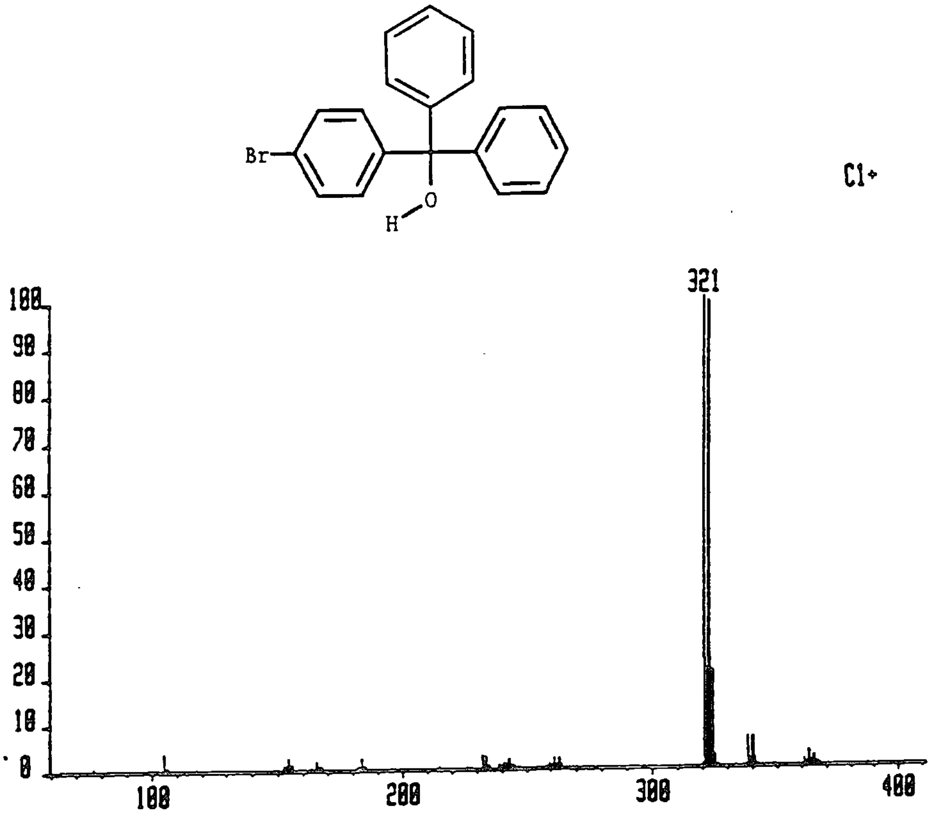
Appendix 5-2


8
7
6
5
4
3
2
1
ppm
128.65
7.4
7.3
7.2
7.1
H^1 **H**^{2}
H^4 **H**^{5} **H**^{6}
H^3
Br
H^1
H^2
H^3
O
Ph
H^4
H^5
H^6

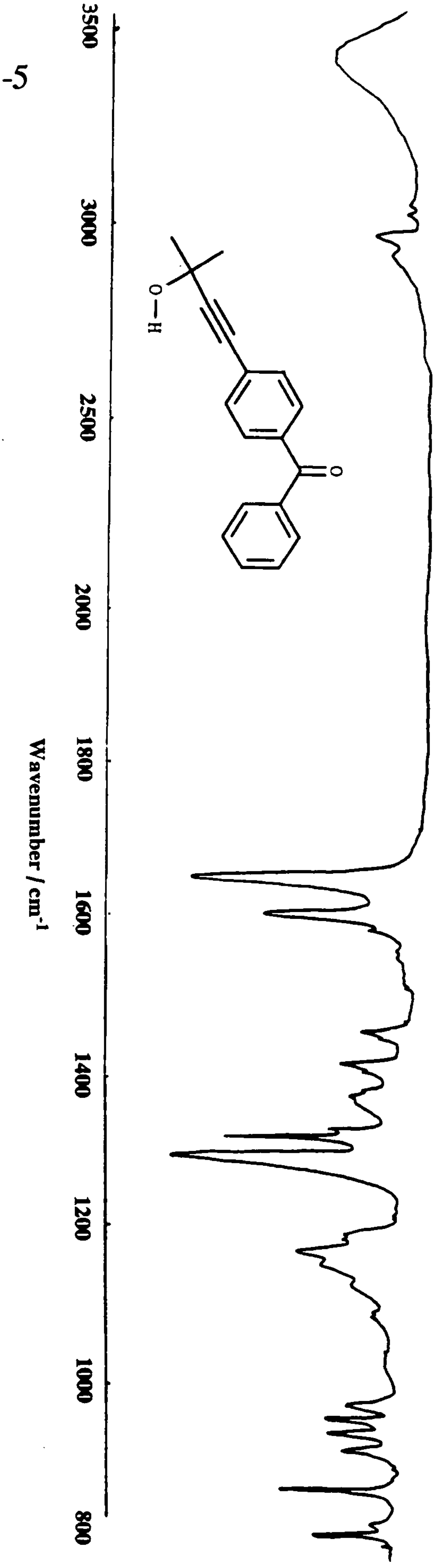
Appendix 5-3


150
140
130
120
110
100
90
80
ppm
6
4
146.322
145.837
2
3
130.927
129.690
128.022
127.783
127.449
7,8,9
1
121.331
81.673
5
77.318
77.000
76.681
Br
1
2
3
4
H
O
5
Ph
6
7
8
9

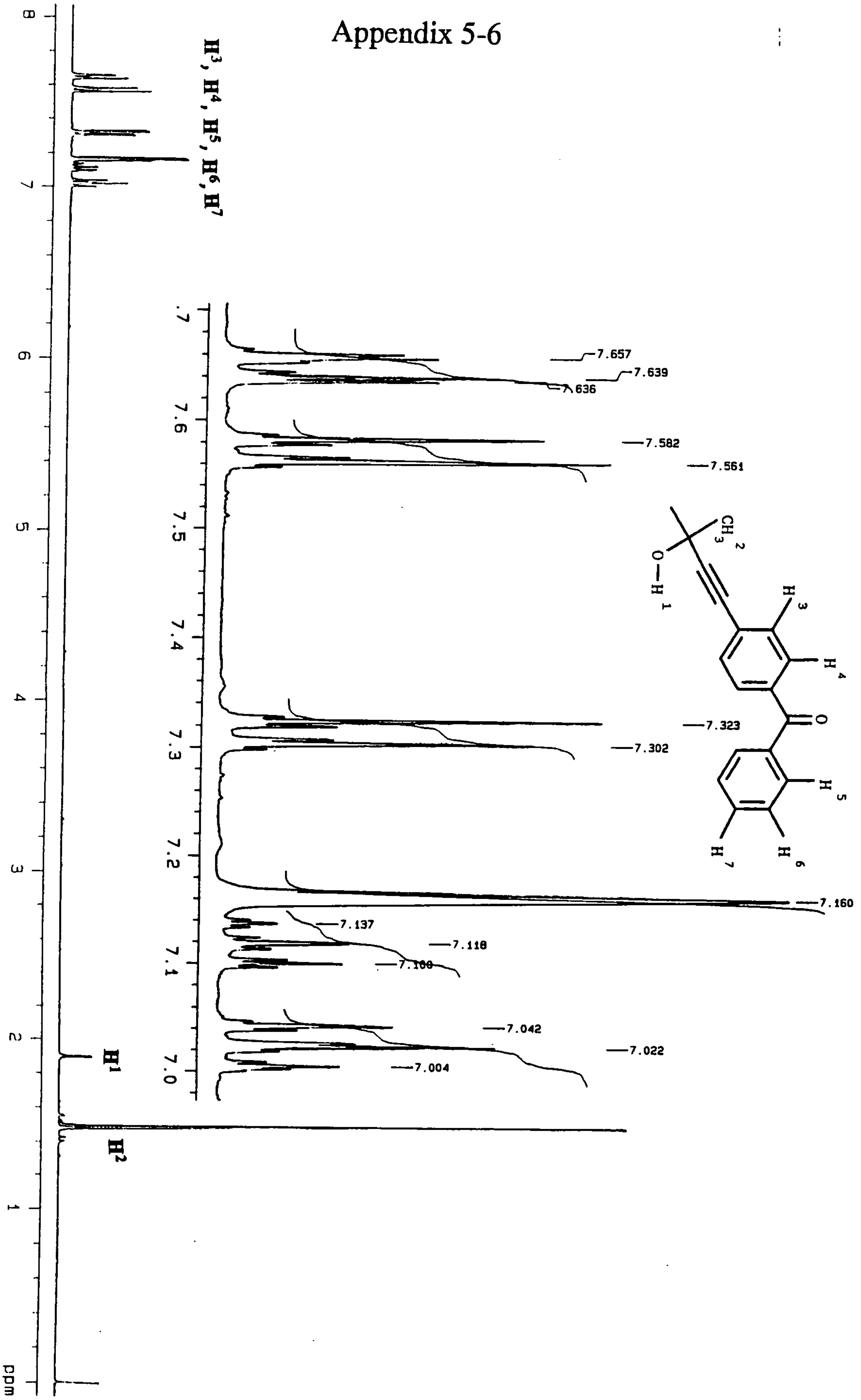
Appendix 5-4



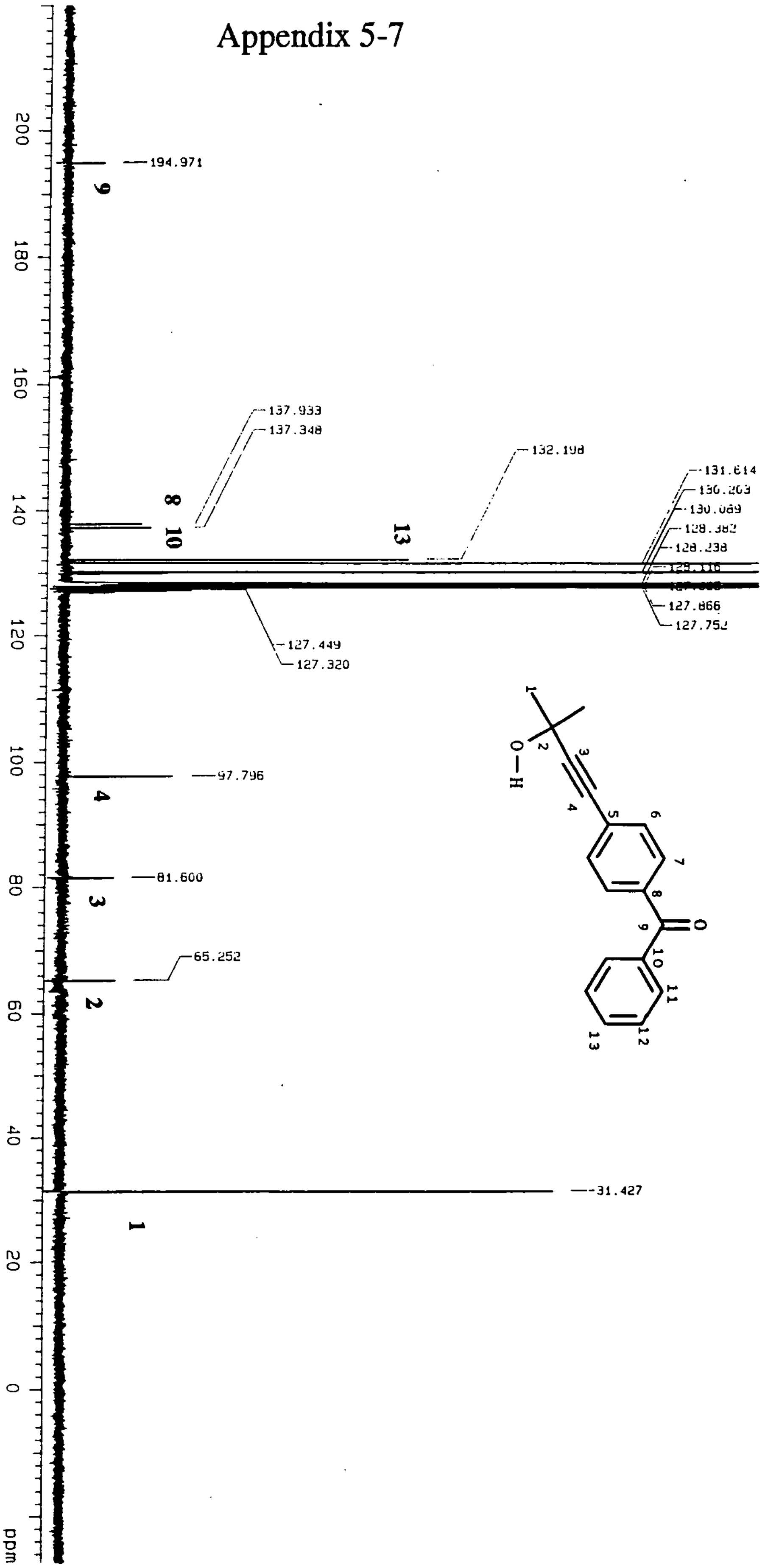
Appendix 5-5


3500
3000
2500
2000
1800
1600
1400
1200
1000
800
Wavenumber / cm-1
O—H
O

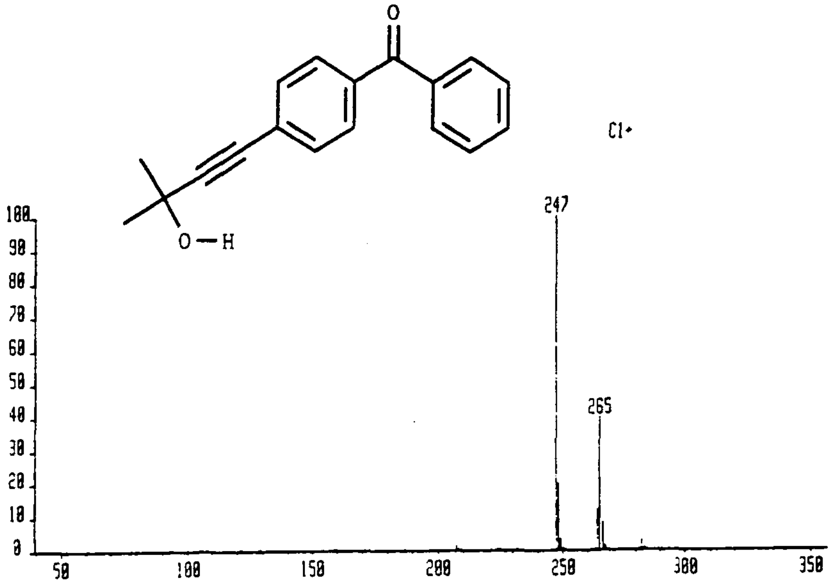
Appendix 5-6

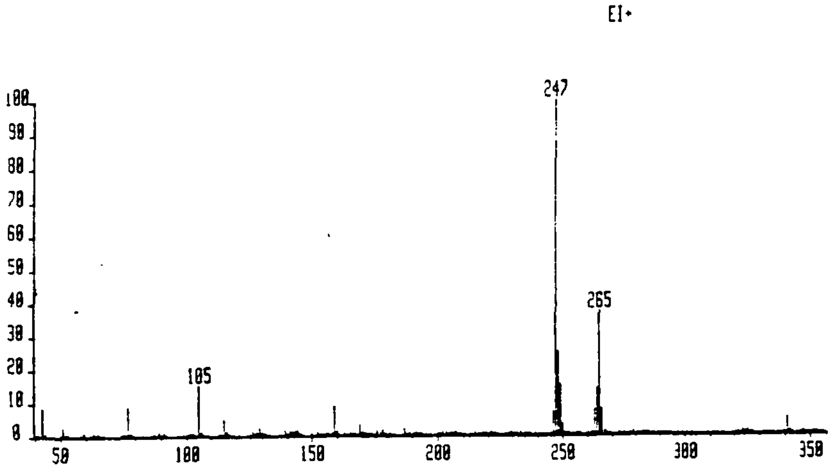

H3, H4, H5, H6, H7
H1
H2
ppm
8
7
6
5
4
3
2
1
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
7.657
7.639
7.636
7.582
7.561
7.323
7.302
7.160
7.137
7.118
7.100
7.042
7.022
7.004
CH3 2
O—H 1
H 3
H 4
O
H 5
H 6
H 7

Appendix 5-7

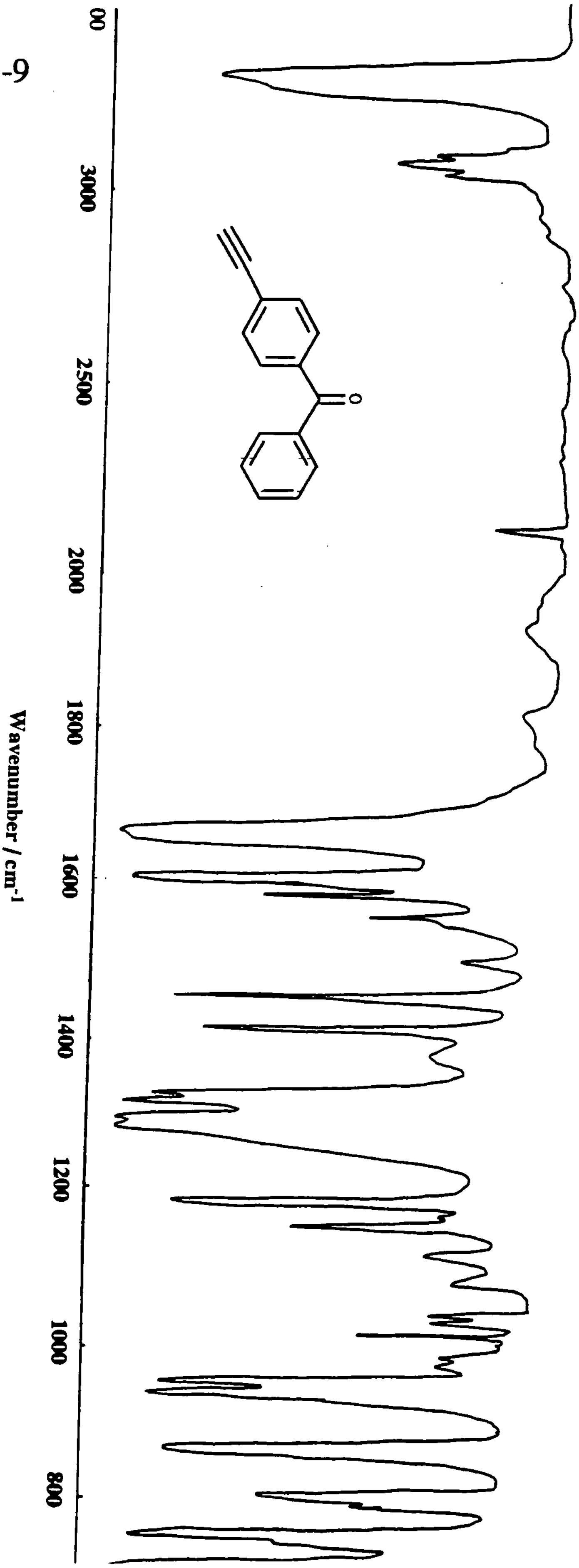

194.971
9
137.933
137.348
8
10
132.198
13
131.614
130.203
130.089
128.382
128.238
128.116
127.866
127.752
127.449
127.320
97.796
4
81.600
3
65.252
2
31.427
1
200
180
160
140
120
100
80
60
40
20
0
ppm
1
2
3
4
5
6
7
8
9
10
11
12
13
O—H
O

Appendix 5-8

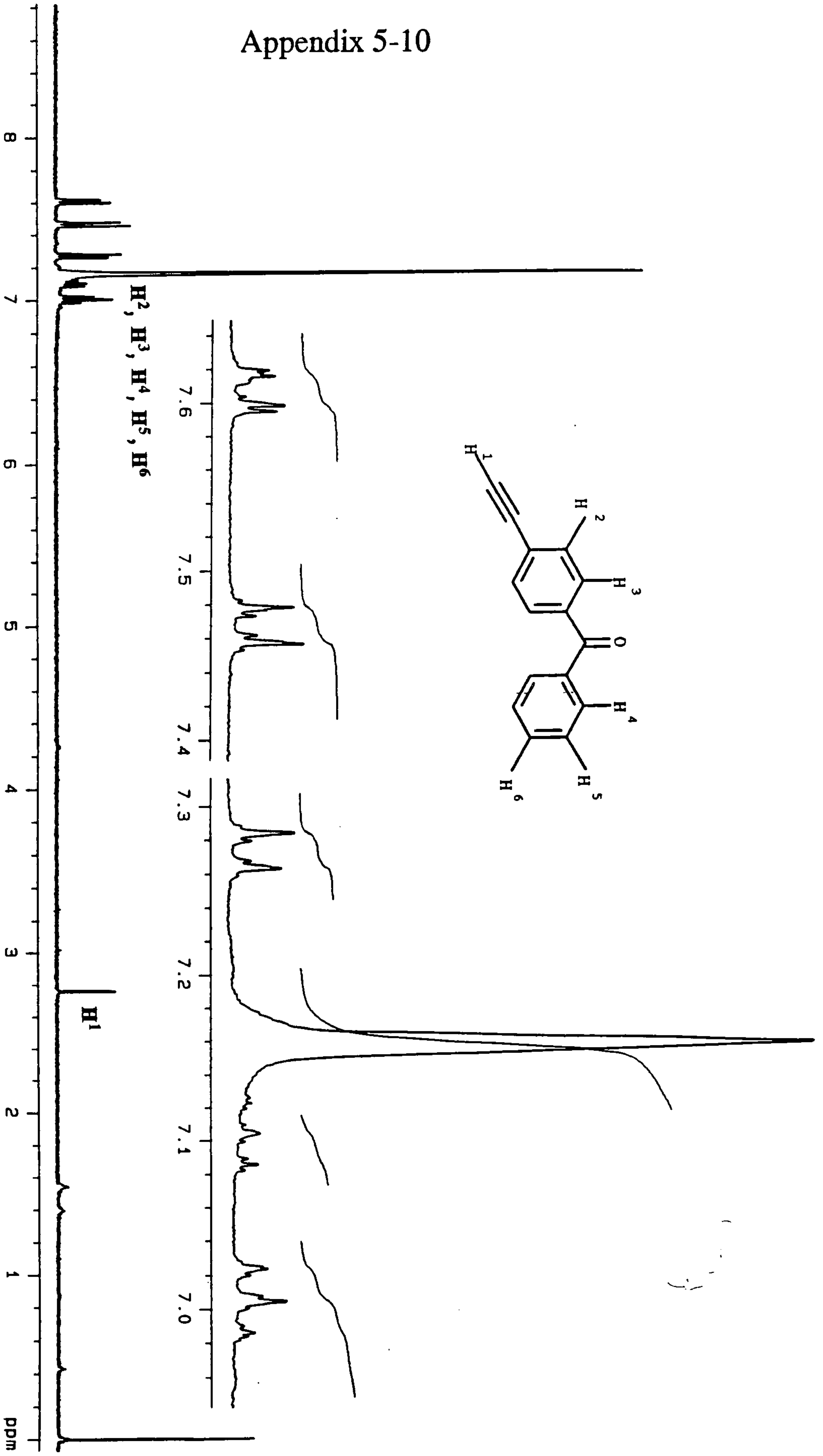

O
O—H
CI+
247
265
100
90
80
70
60
50
40
30
20
10
0
50
100
150
200
250
300
350


EI+
247
265
105
100
90
80
70
60
50
40
30
20
10
0
50
100
150
200
250
300
350

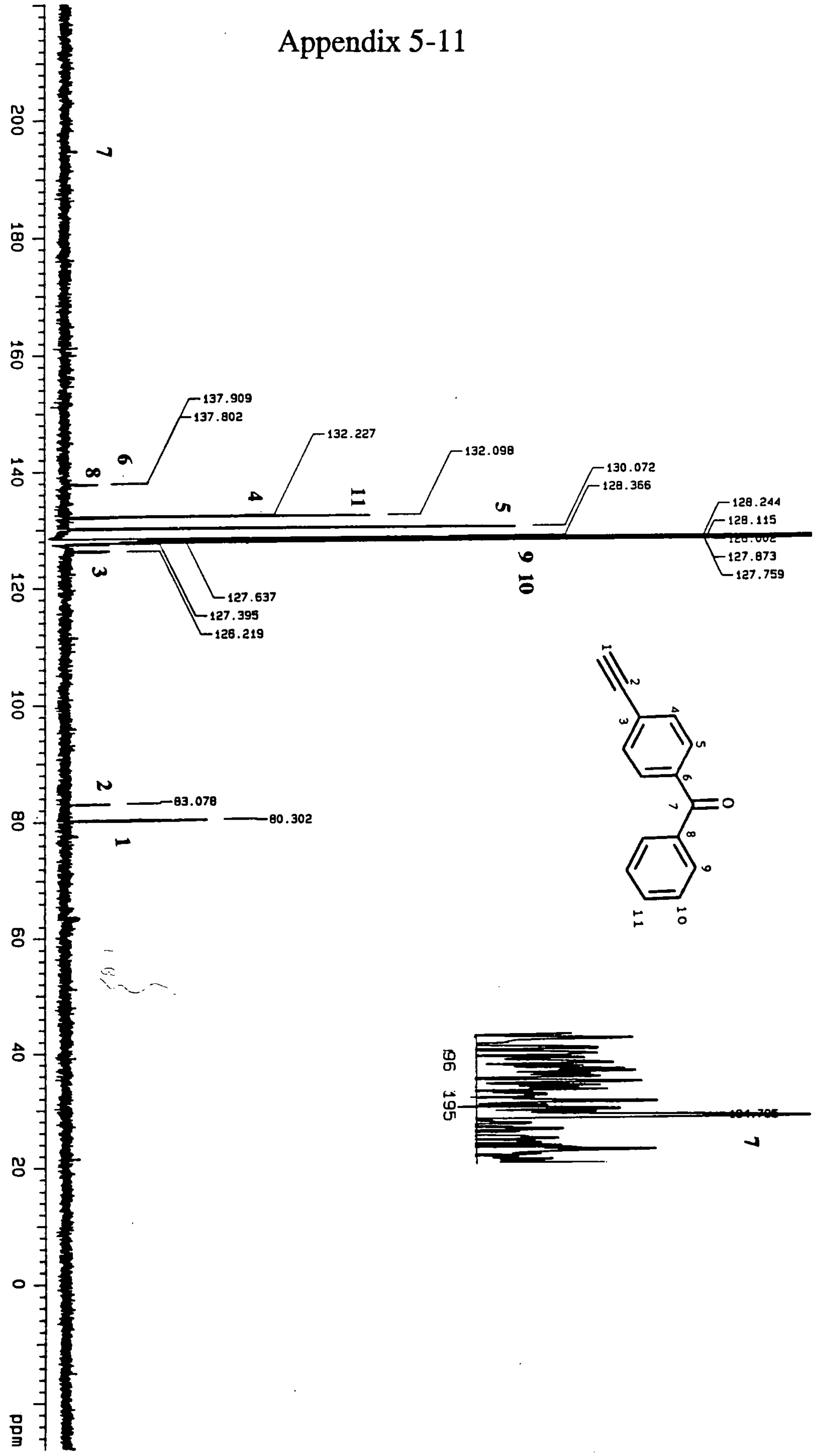
Appendix 5-9


00
3000
2500
2000
1800
1600
1400
1200
1000
800
Wavenumber / cm-1
O

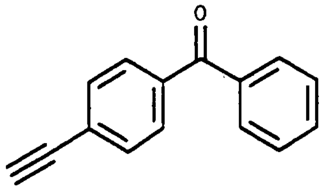
Appendix 5-10

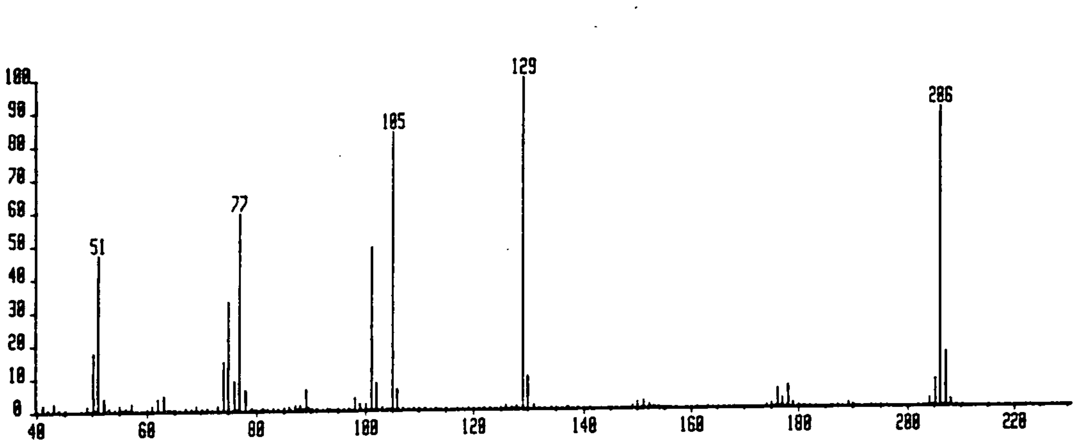


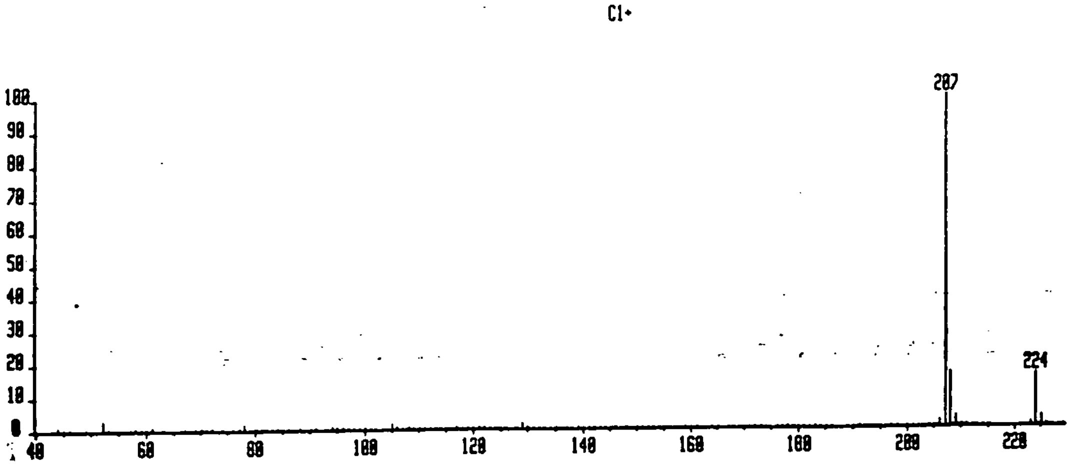
Appendix 5-11



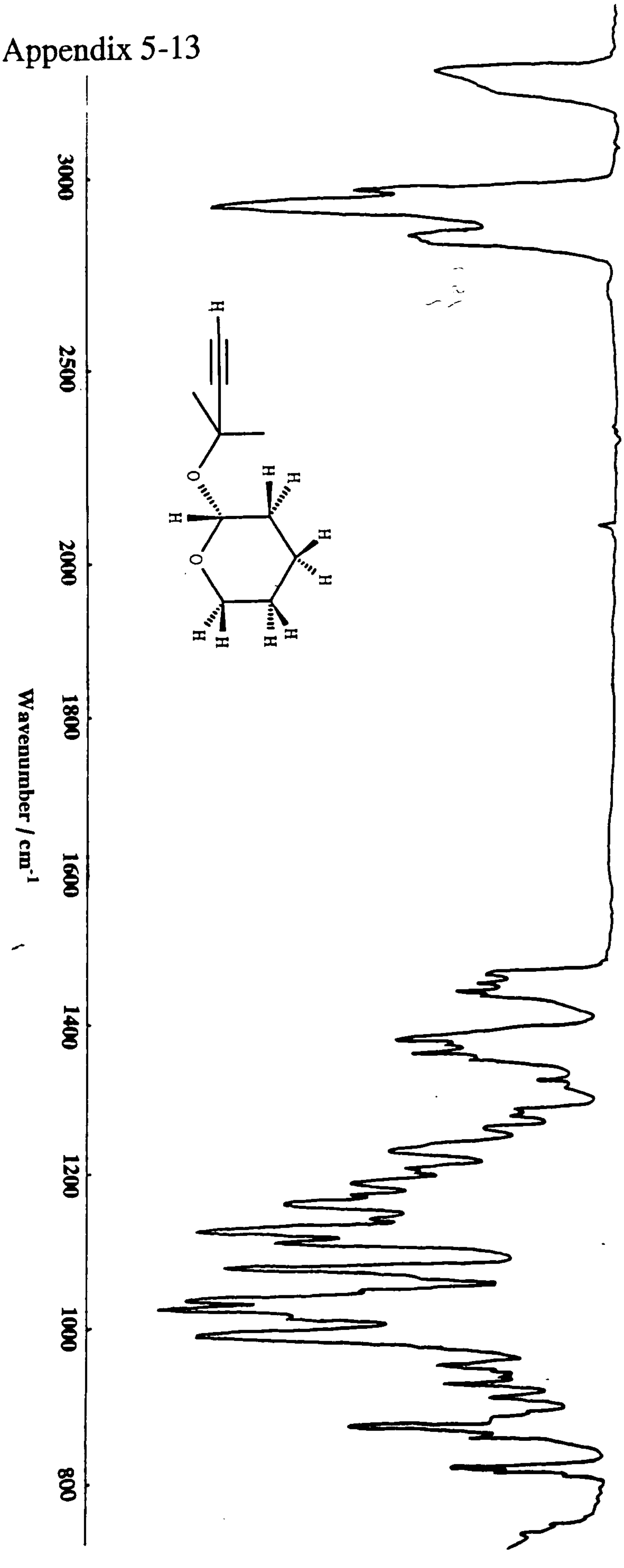
Appendix 5-12



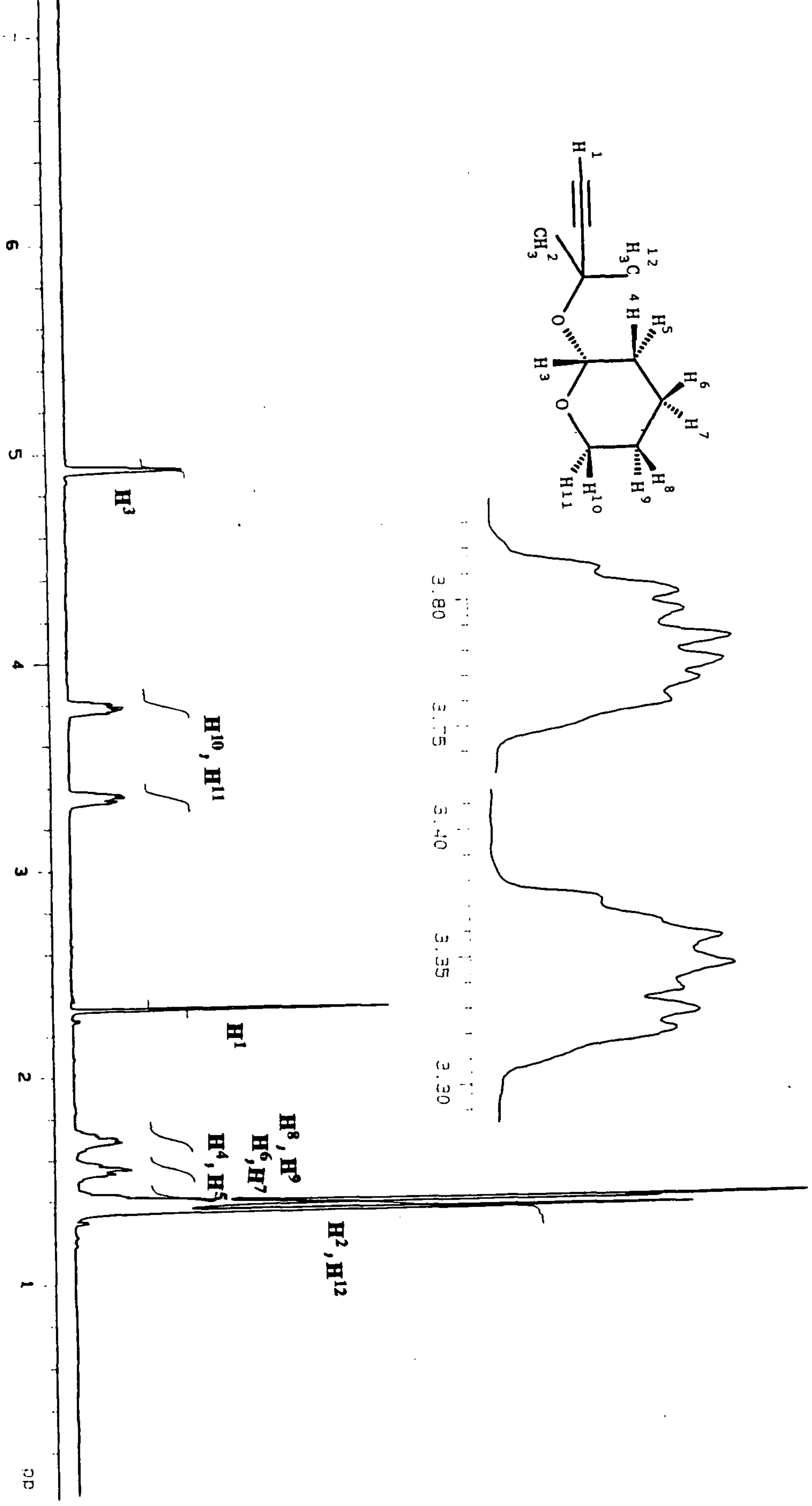




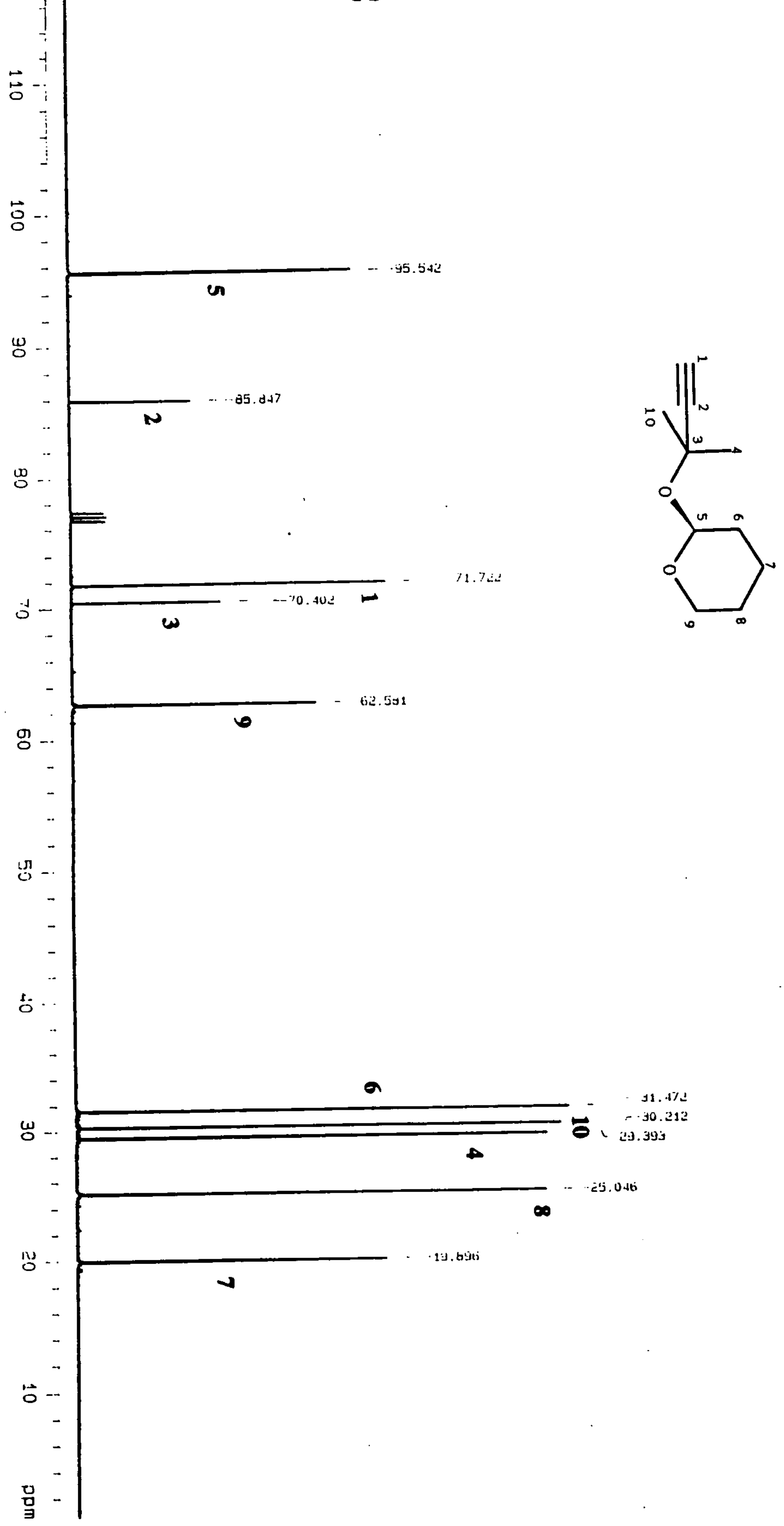
Appendix 5-13



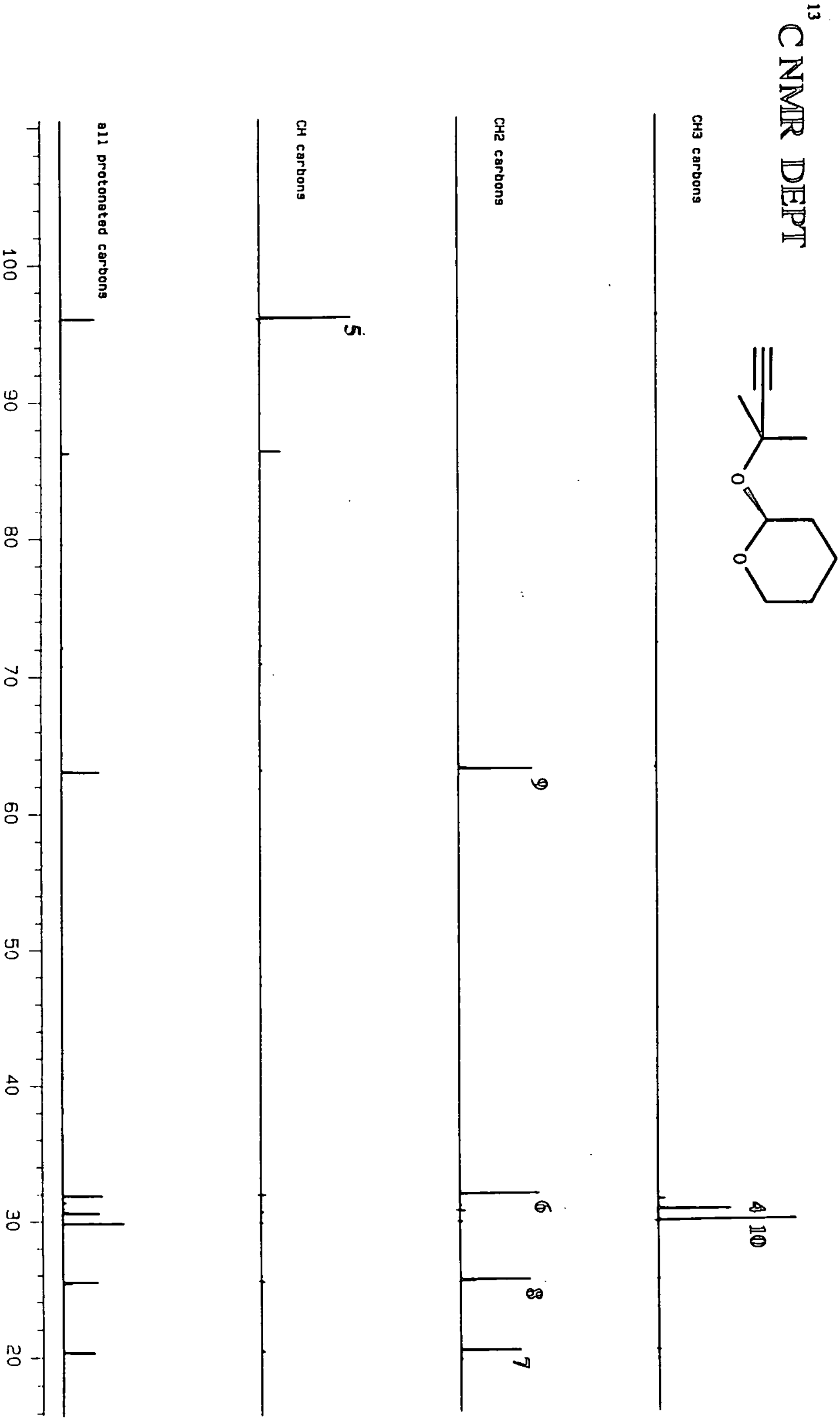
Appendix 5-14



Appendix 5-15

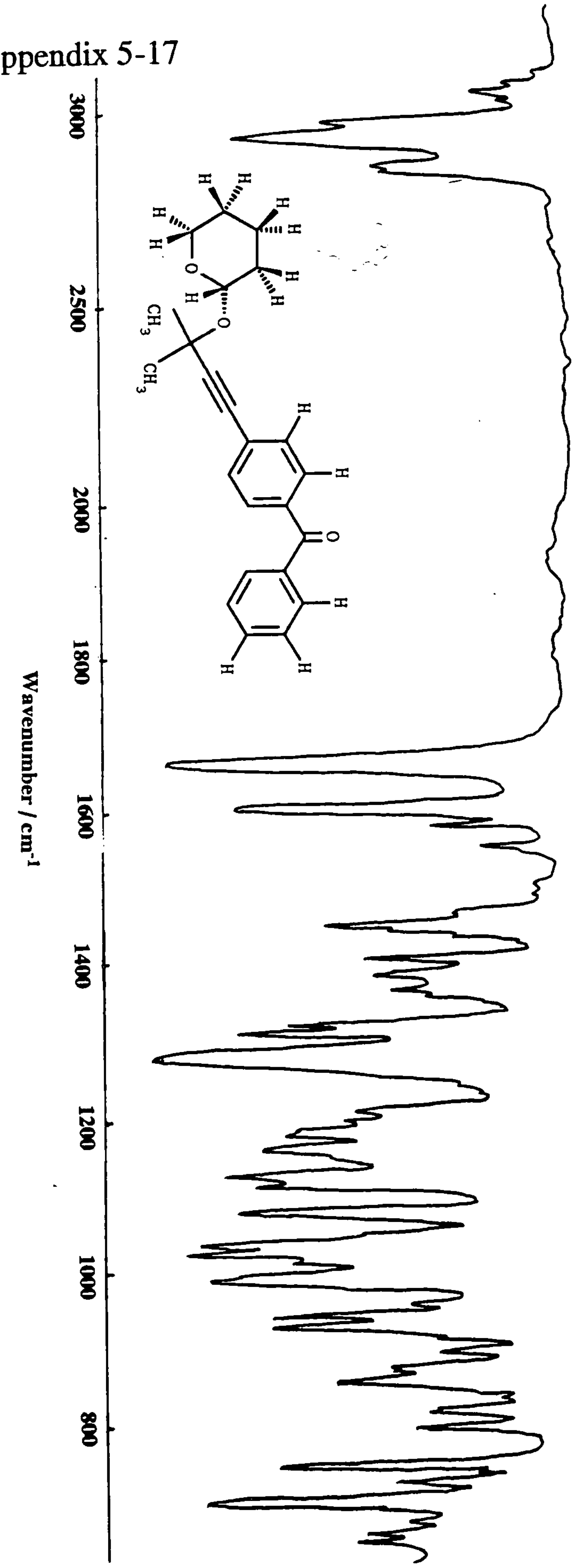


Appendix 5-16

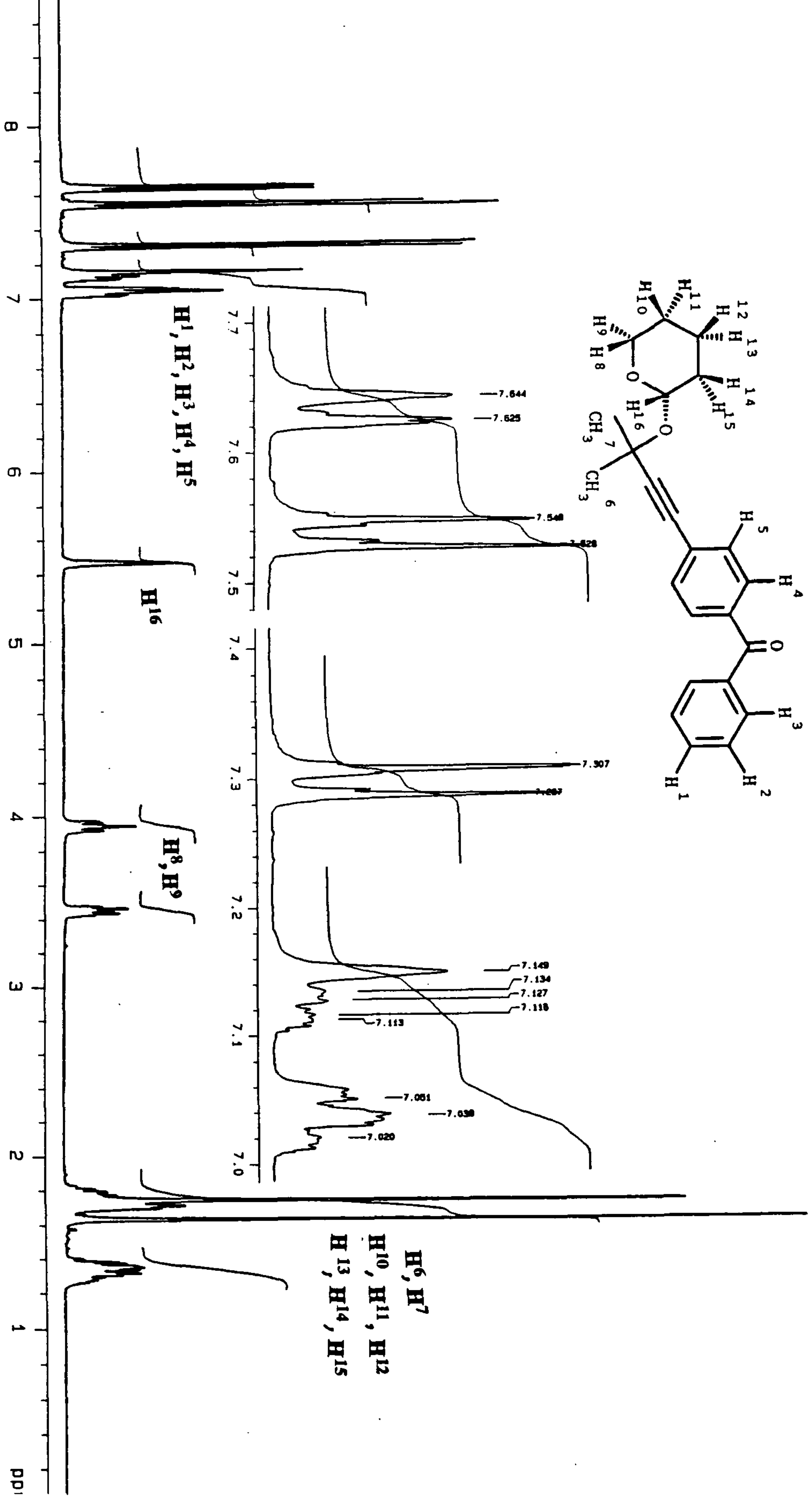


^{13}C NMR DEPT

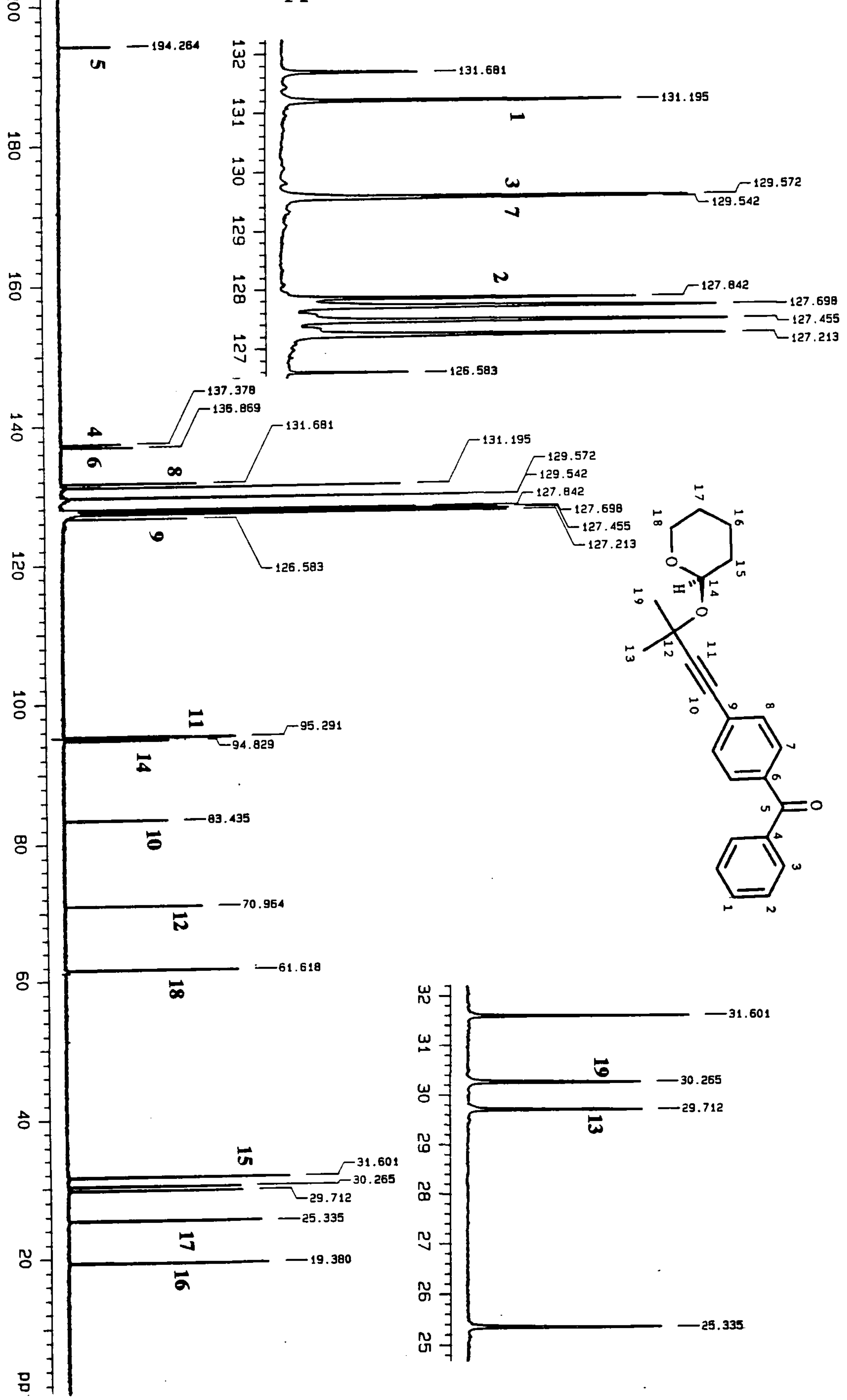
Appendix 5-17



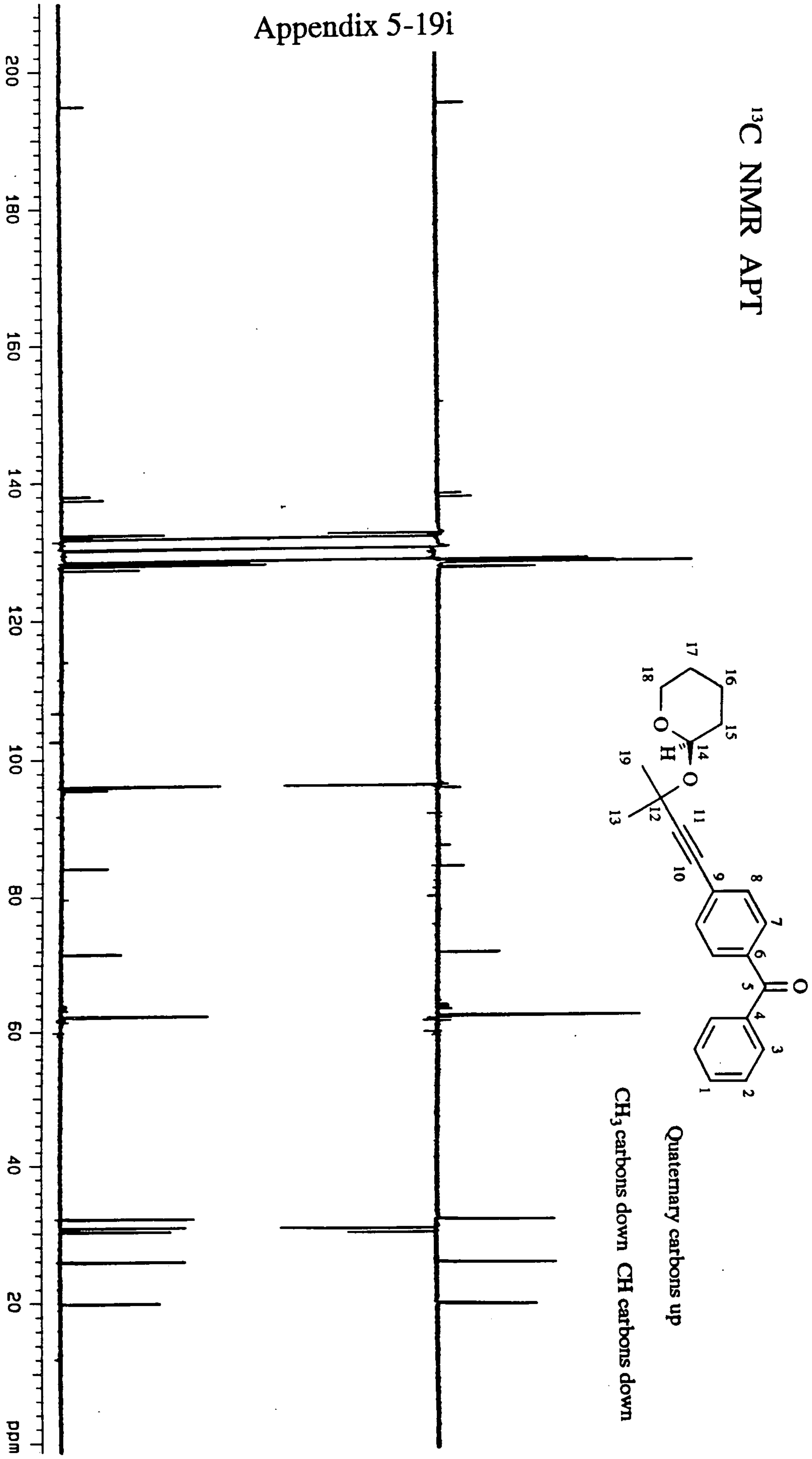
Appendix 5-18



Appendix 5-19



Appendix 5-19i

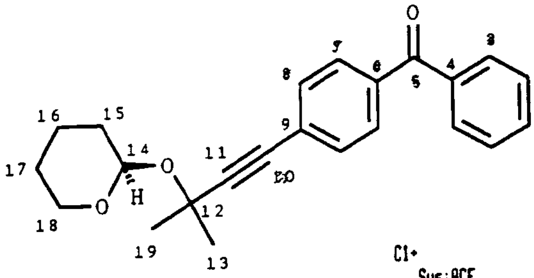


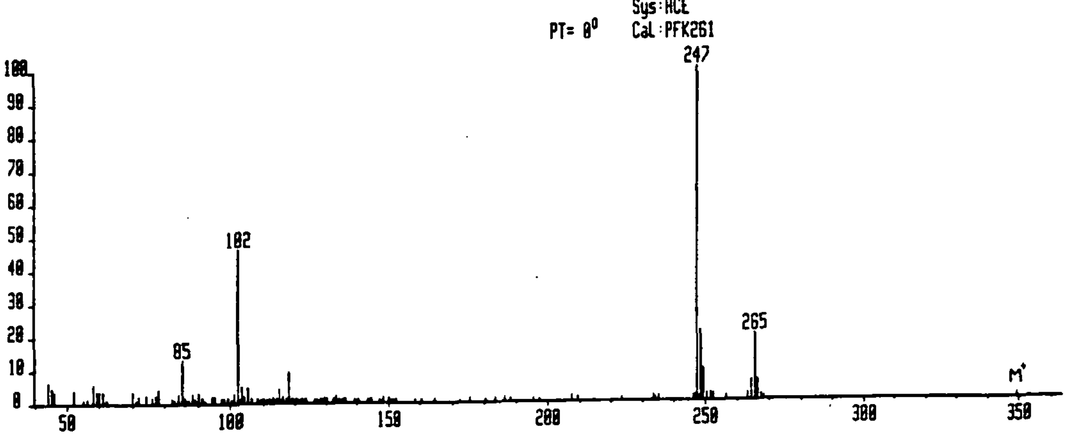
^{13}C NMR APT

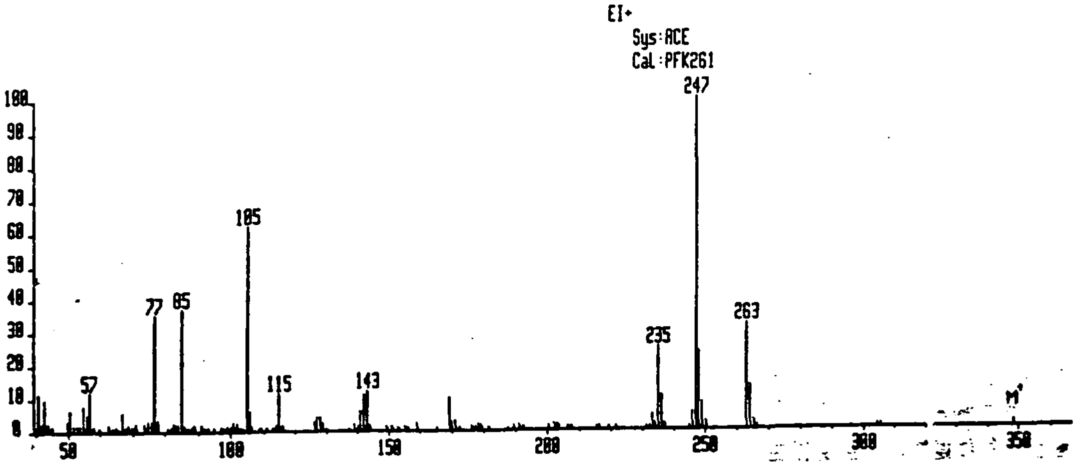
Quaternary carbons up

CH_3 carbons down CH carbons down

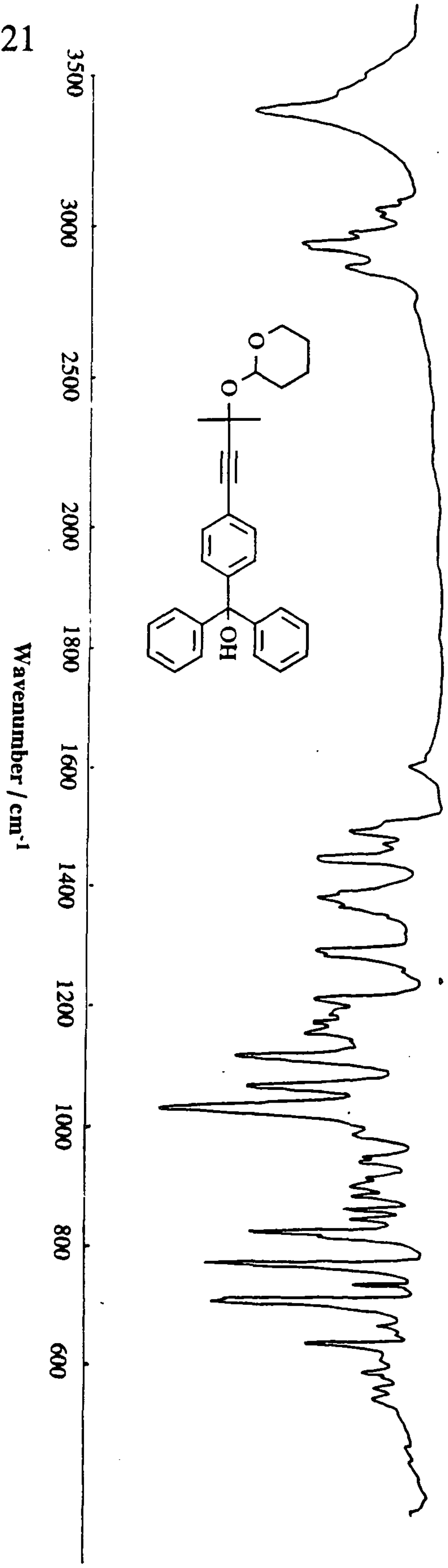
Appendix 5-20



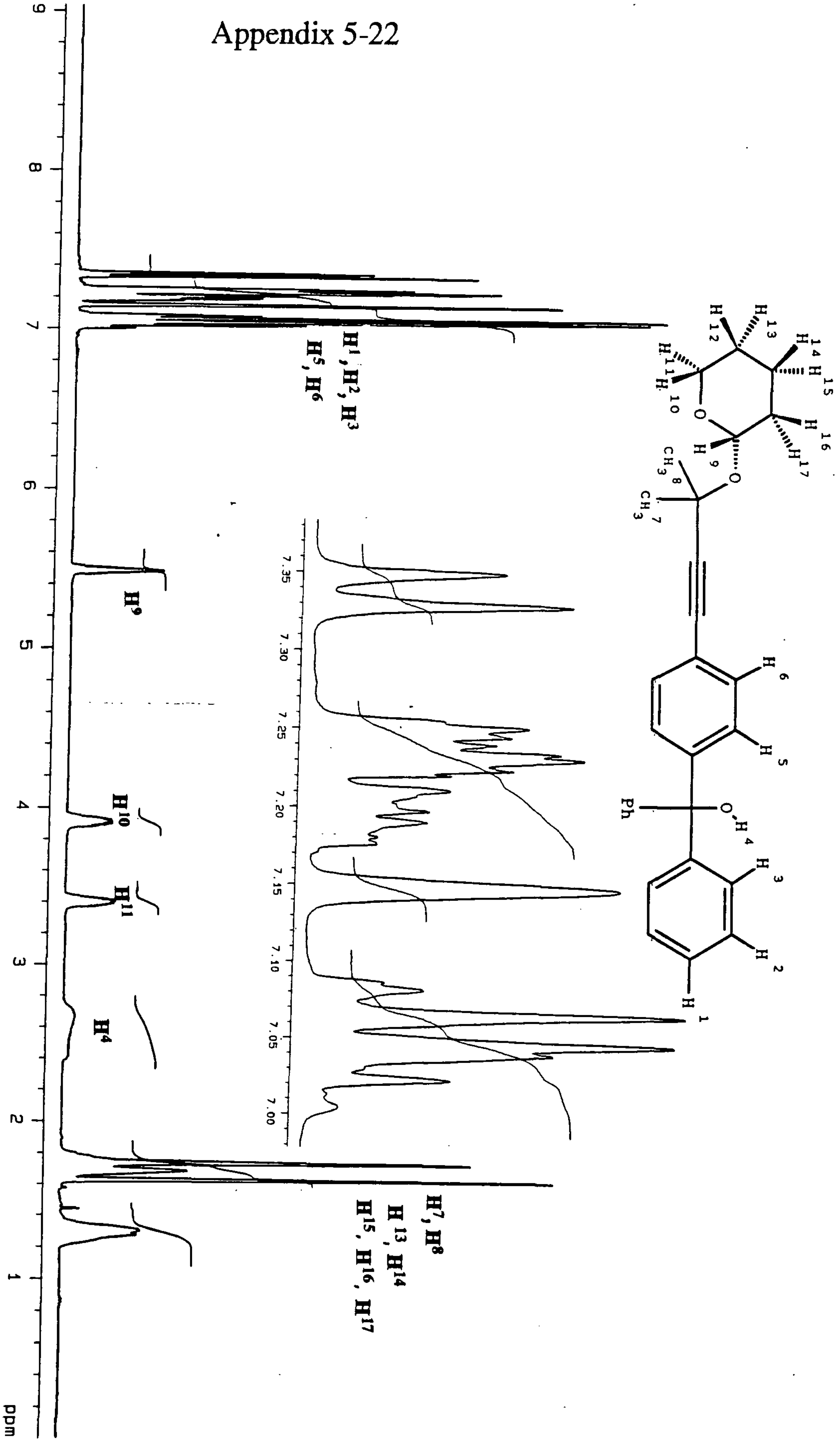




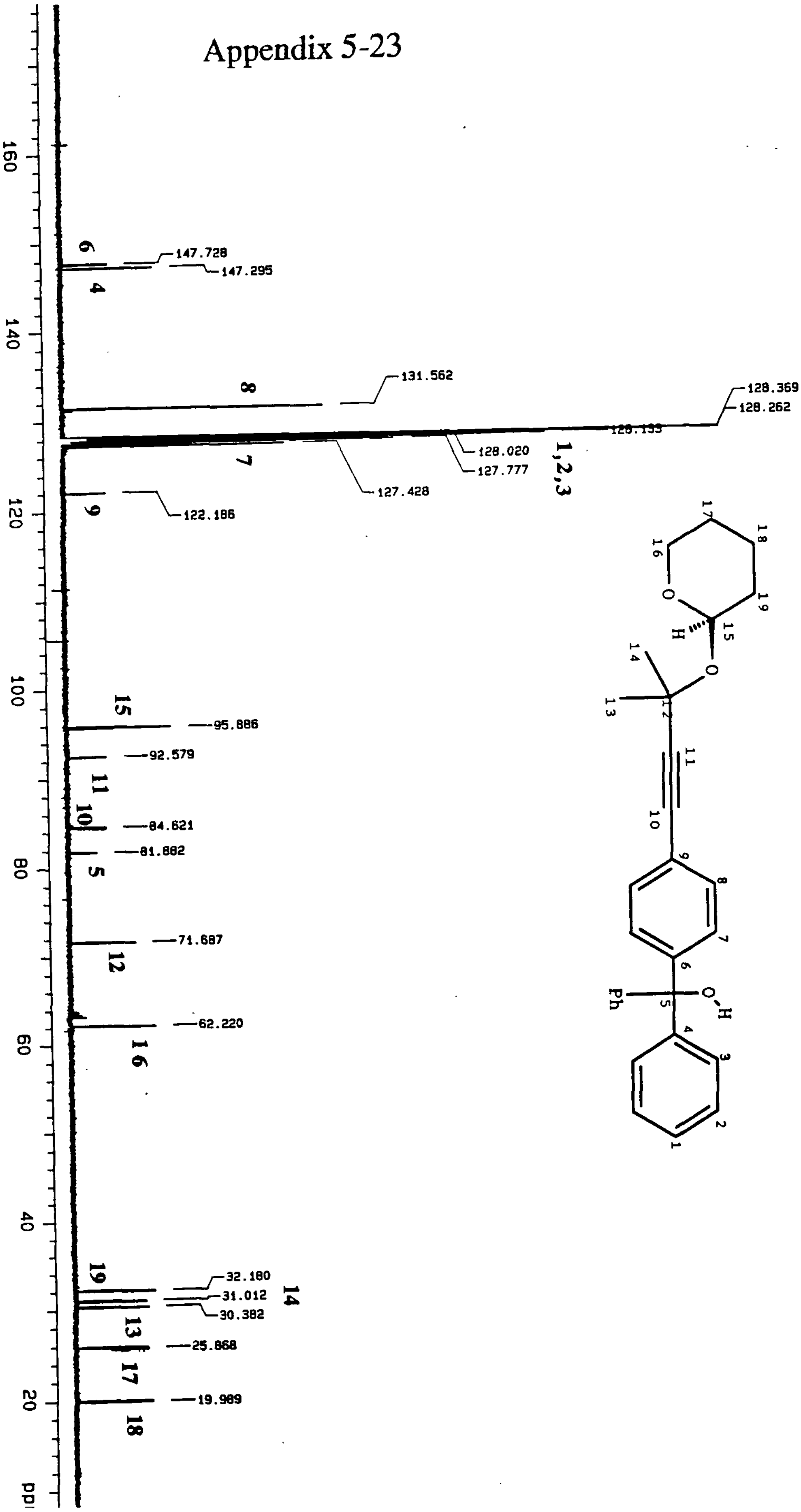
Appendix 5-21



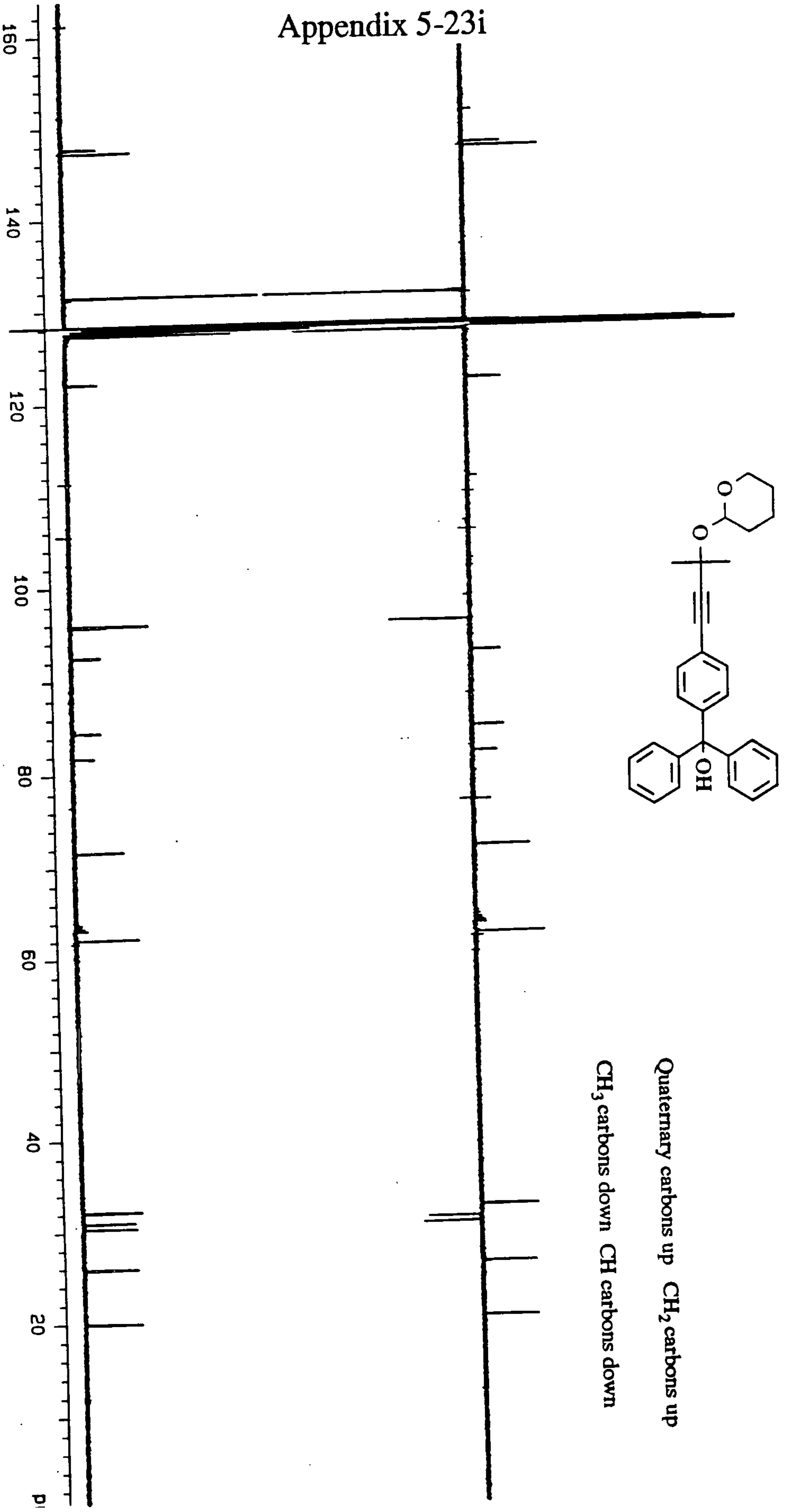
Appendix 5-22



Appendix 5-23



Appendix 5-23i

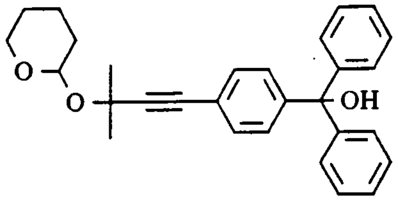


^{13}C NMR APT

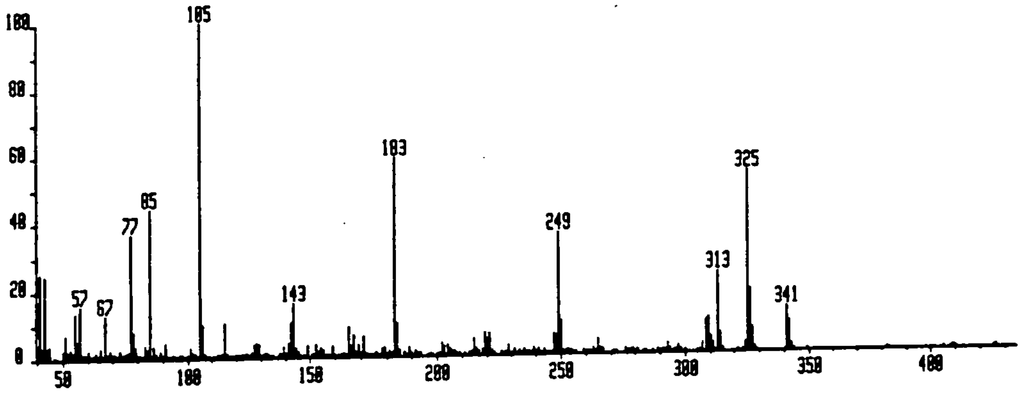
Quaternary carbons up CH_2 carbons up

CH_3 carbons down CH carbons down

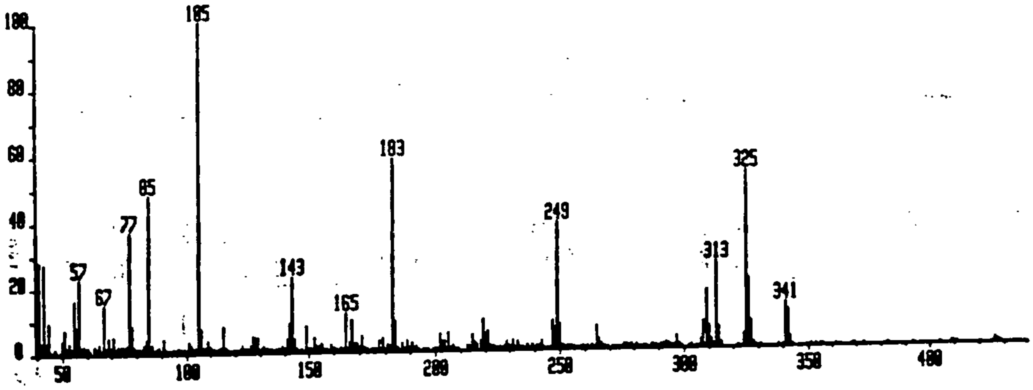
Appendix 5-24



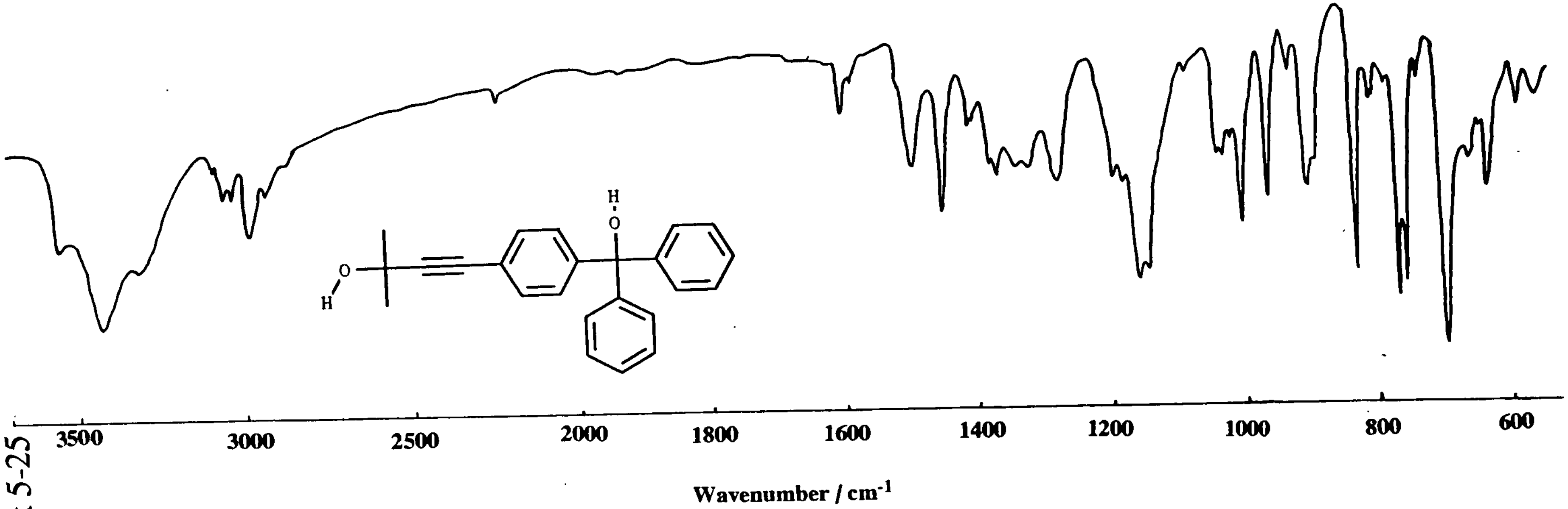
EI+



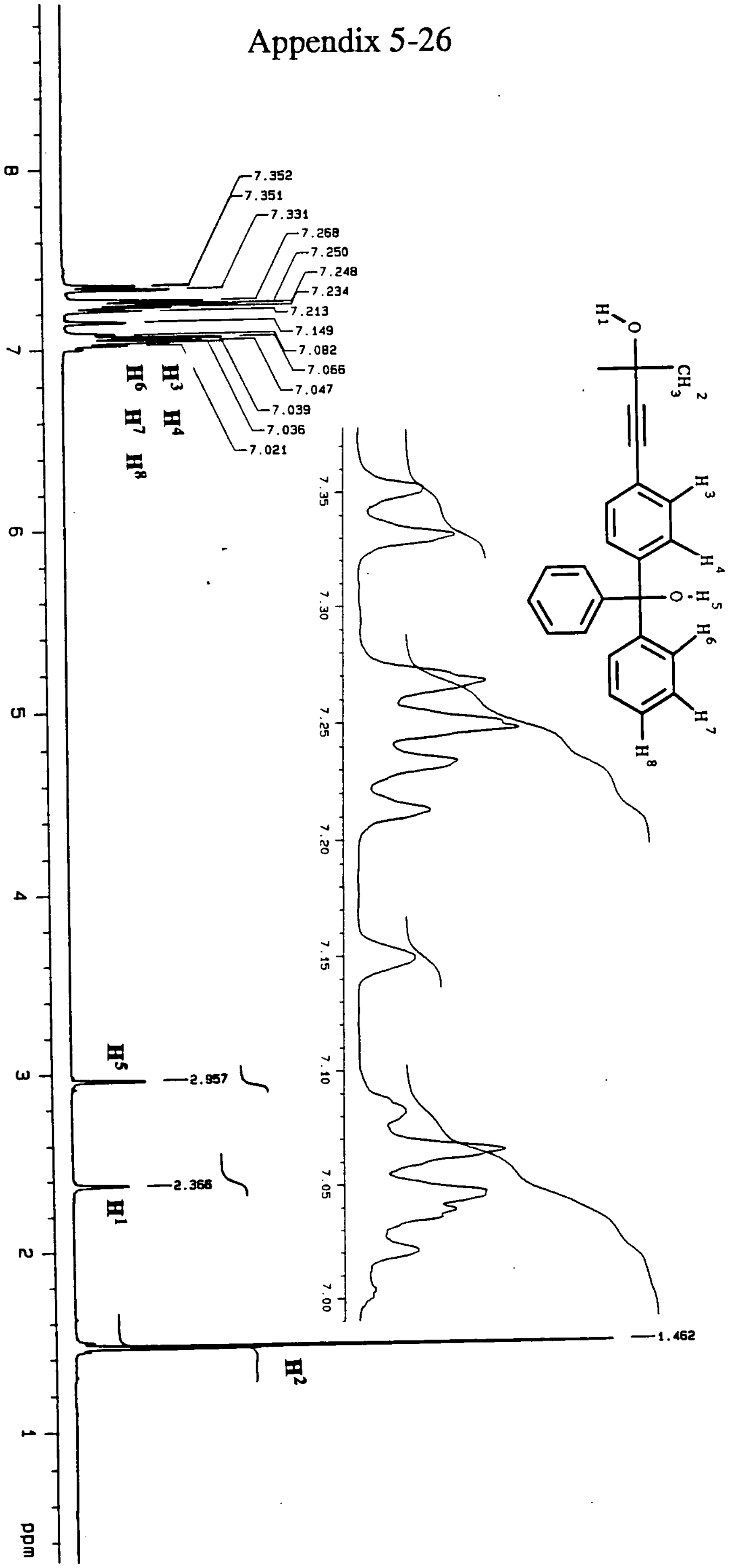
CI+



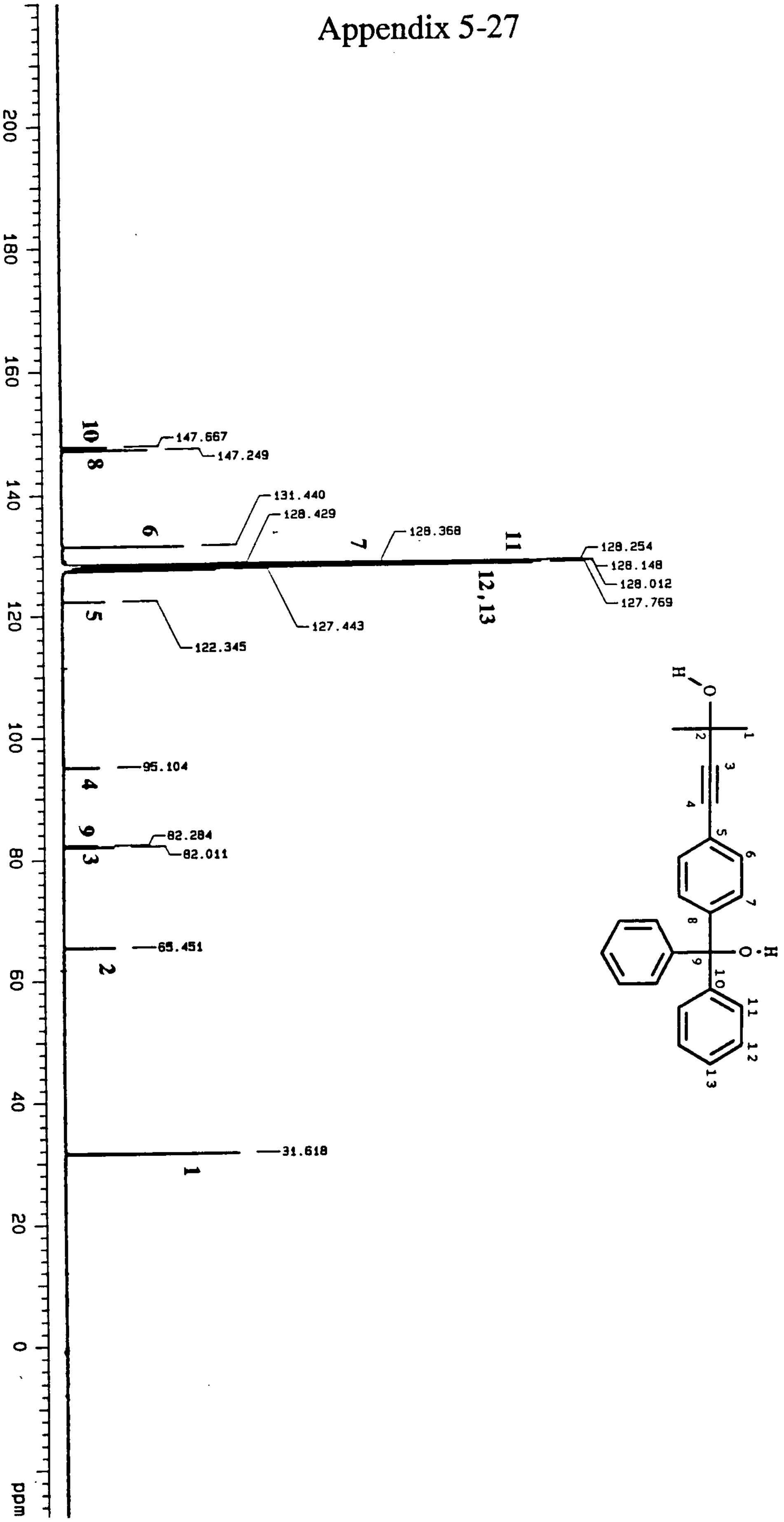
Appendix 5-25



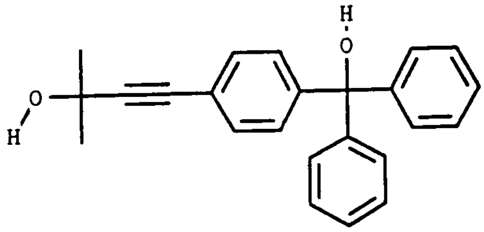
Appendix 5-26

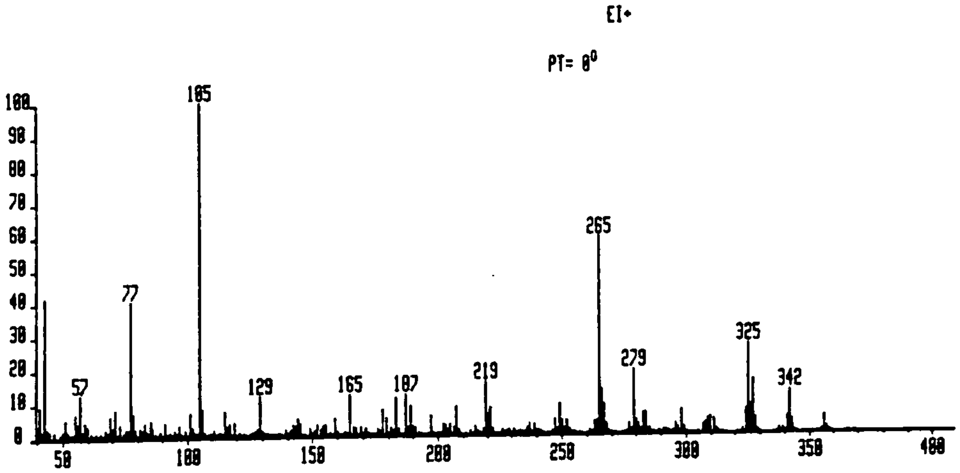


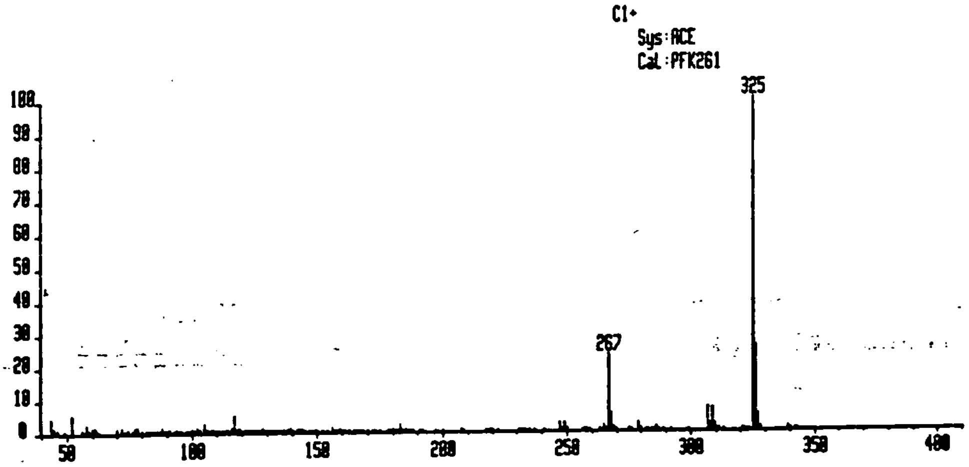
Appendix 5-27



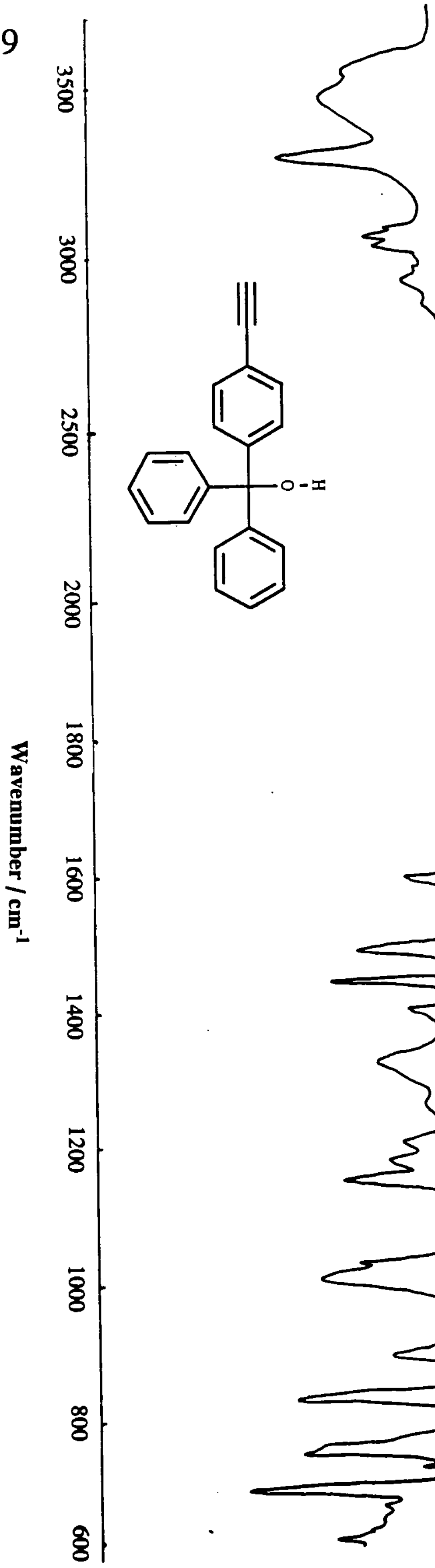
Appendix 5-28



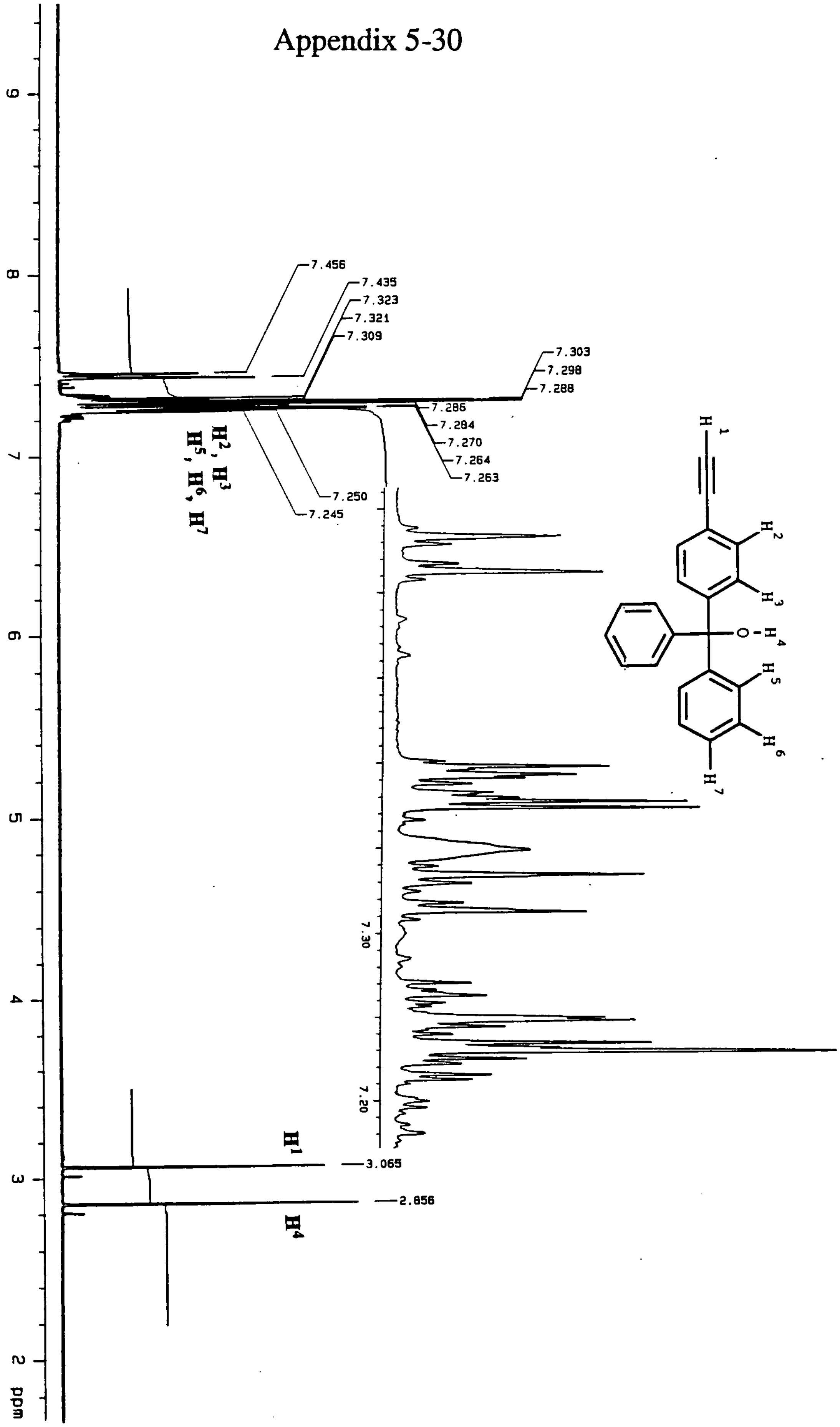




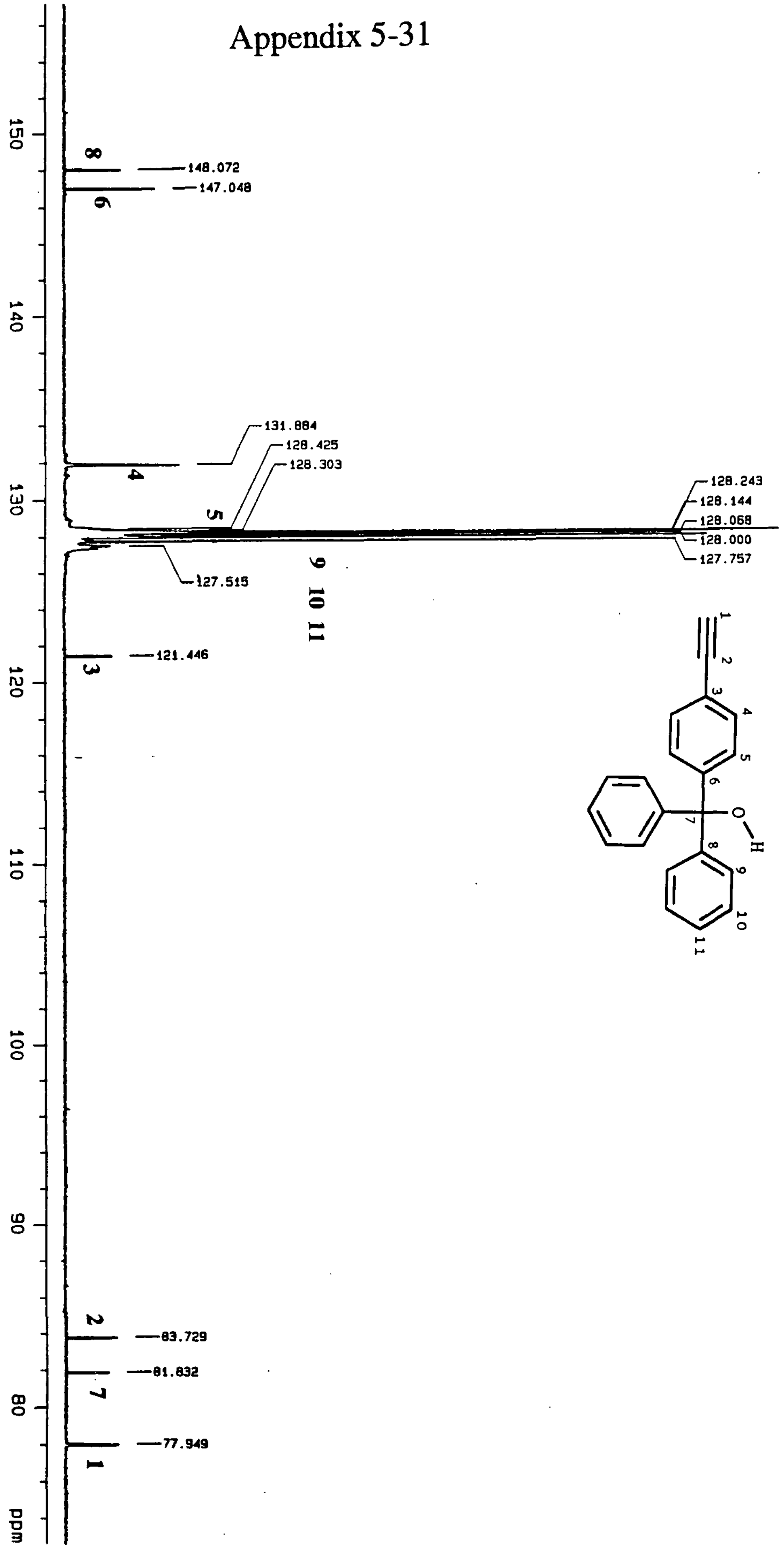
Appendix 5-29



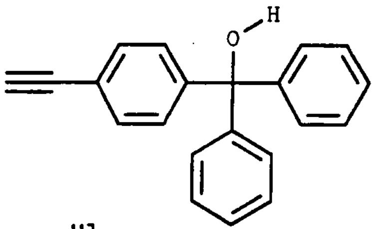
Appendix 5-30

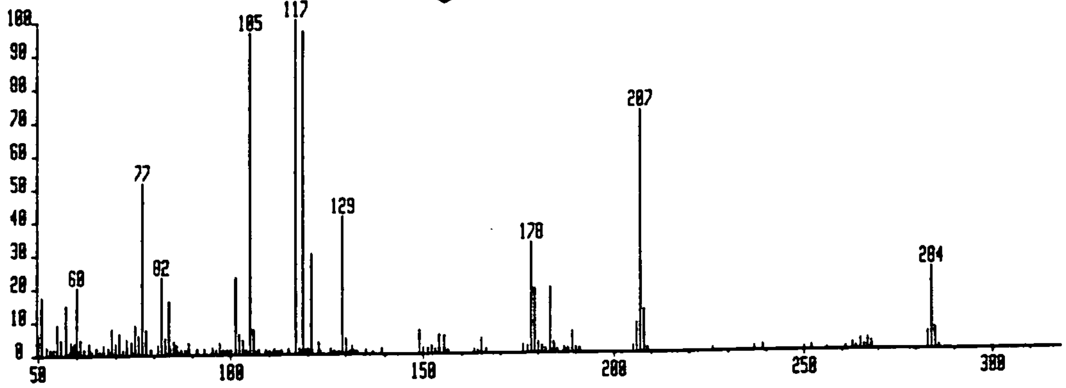


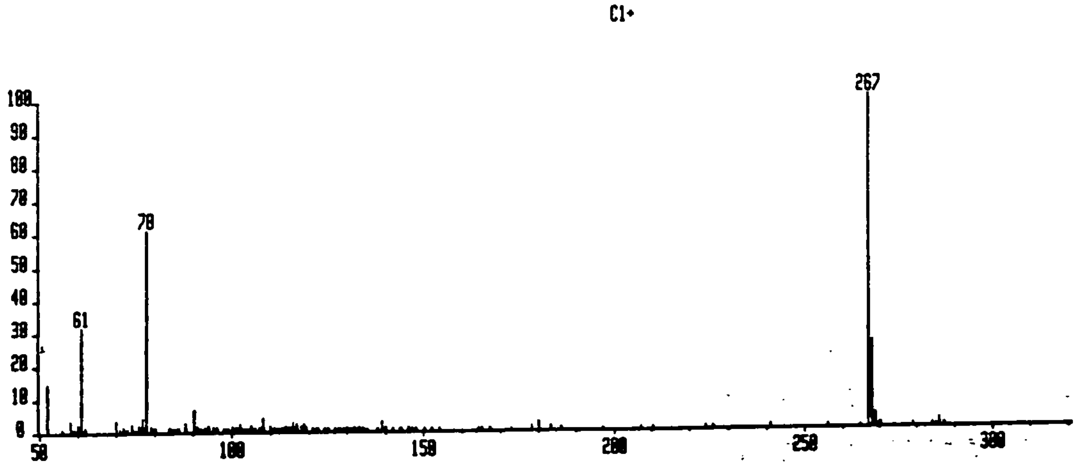
Appendix 5-31



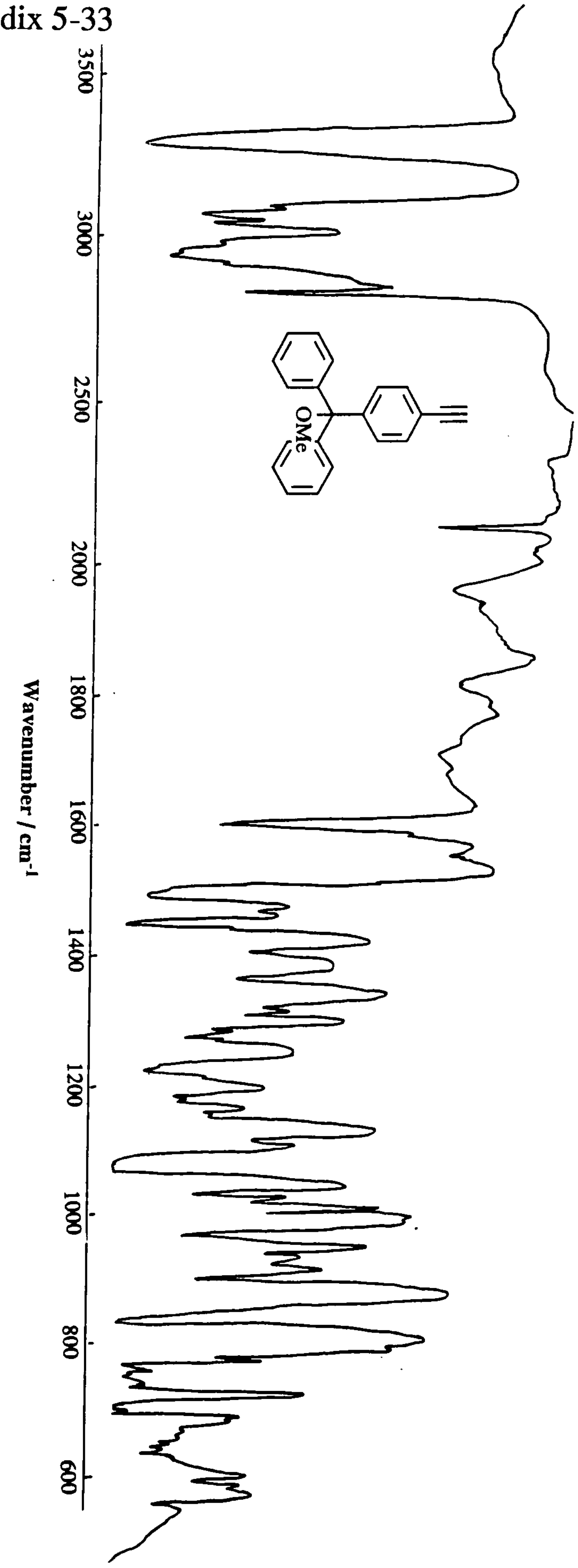
Appendix 5-32



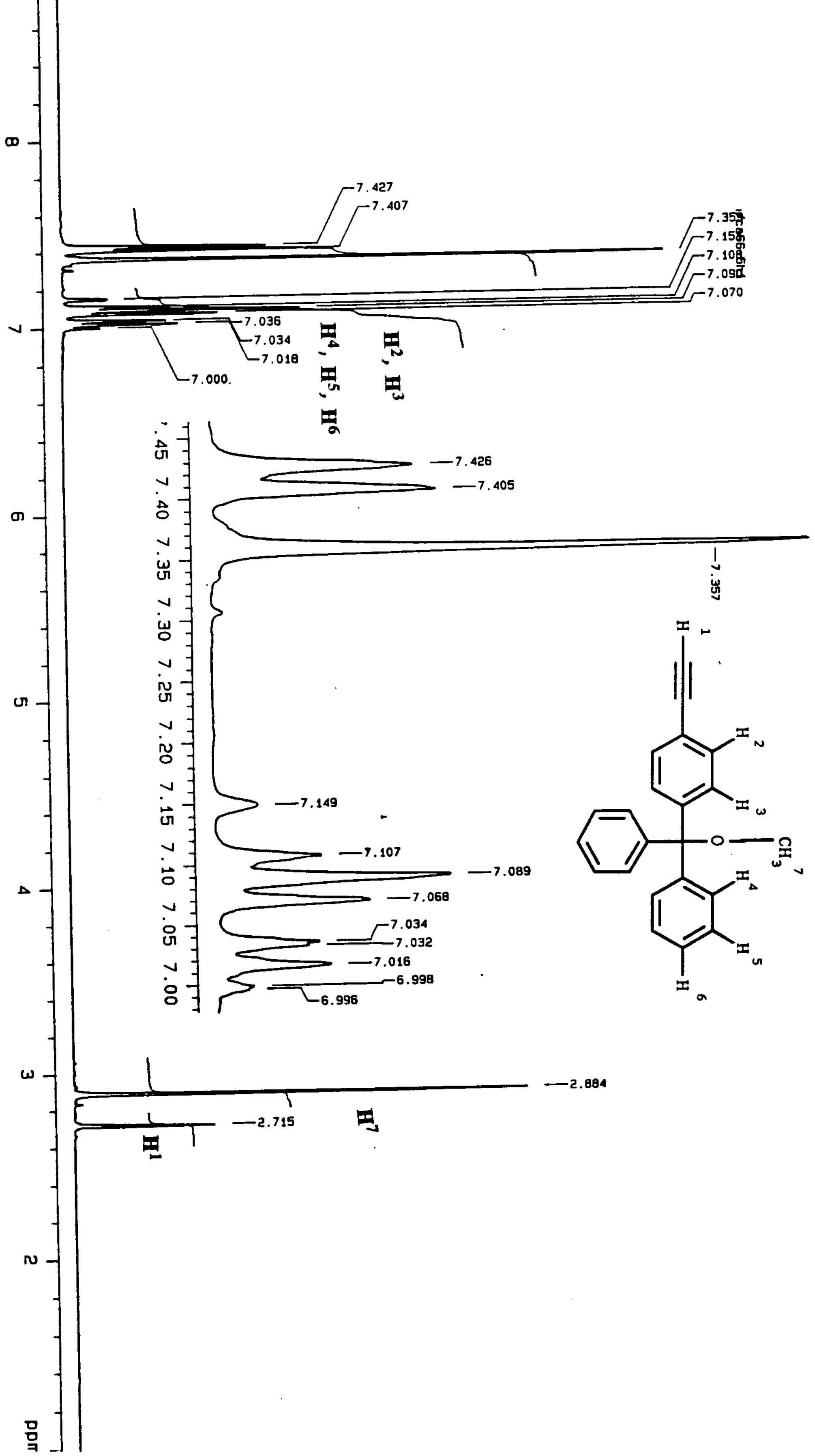




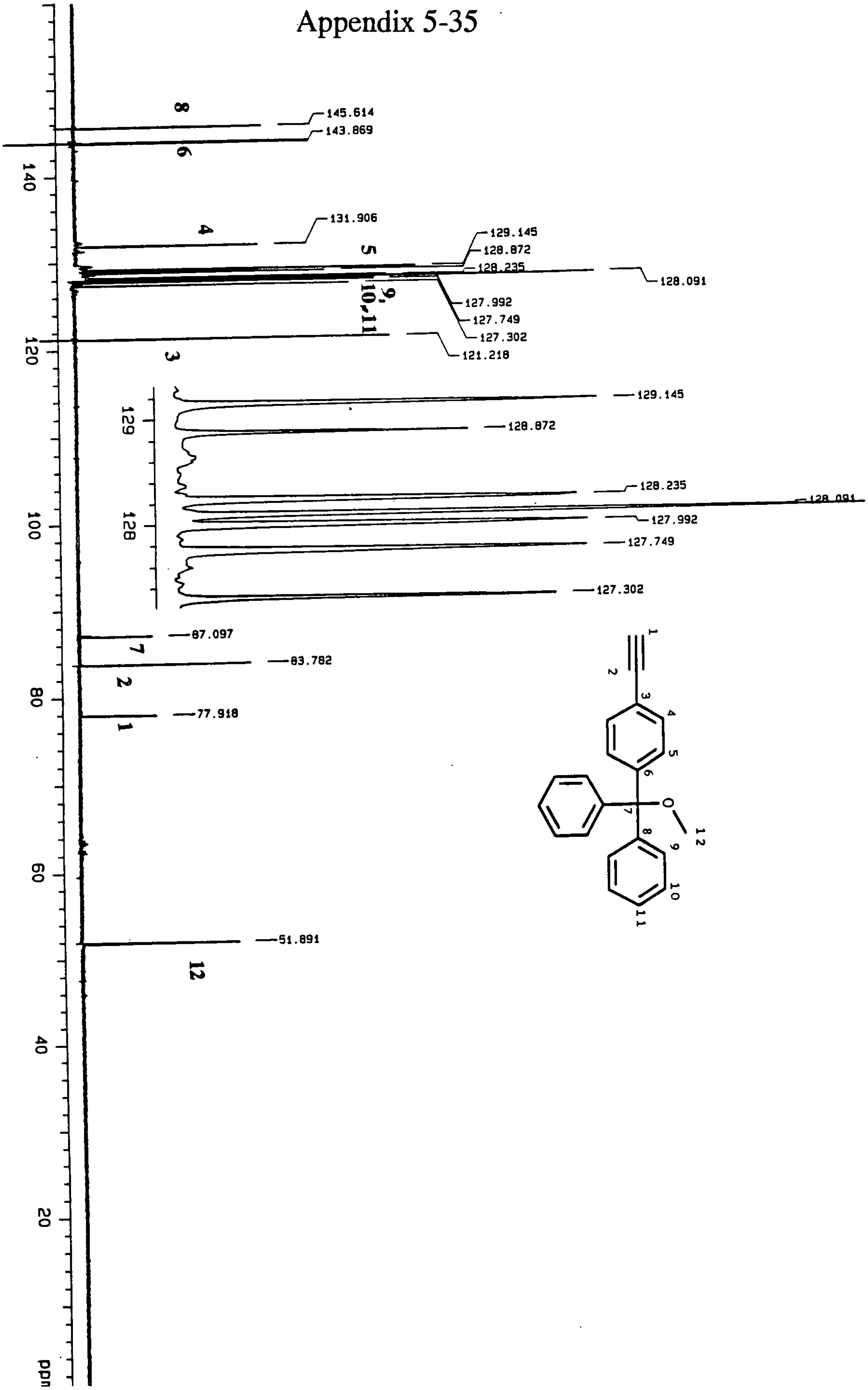
Appendix 5-33



Appendix 5-34

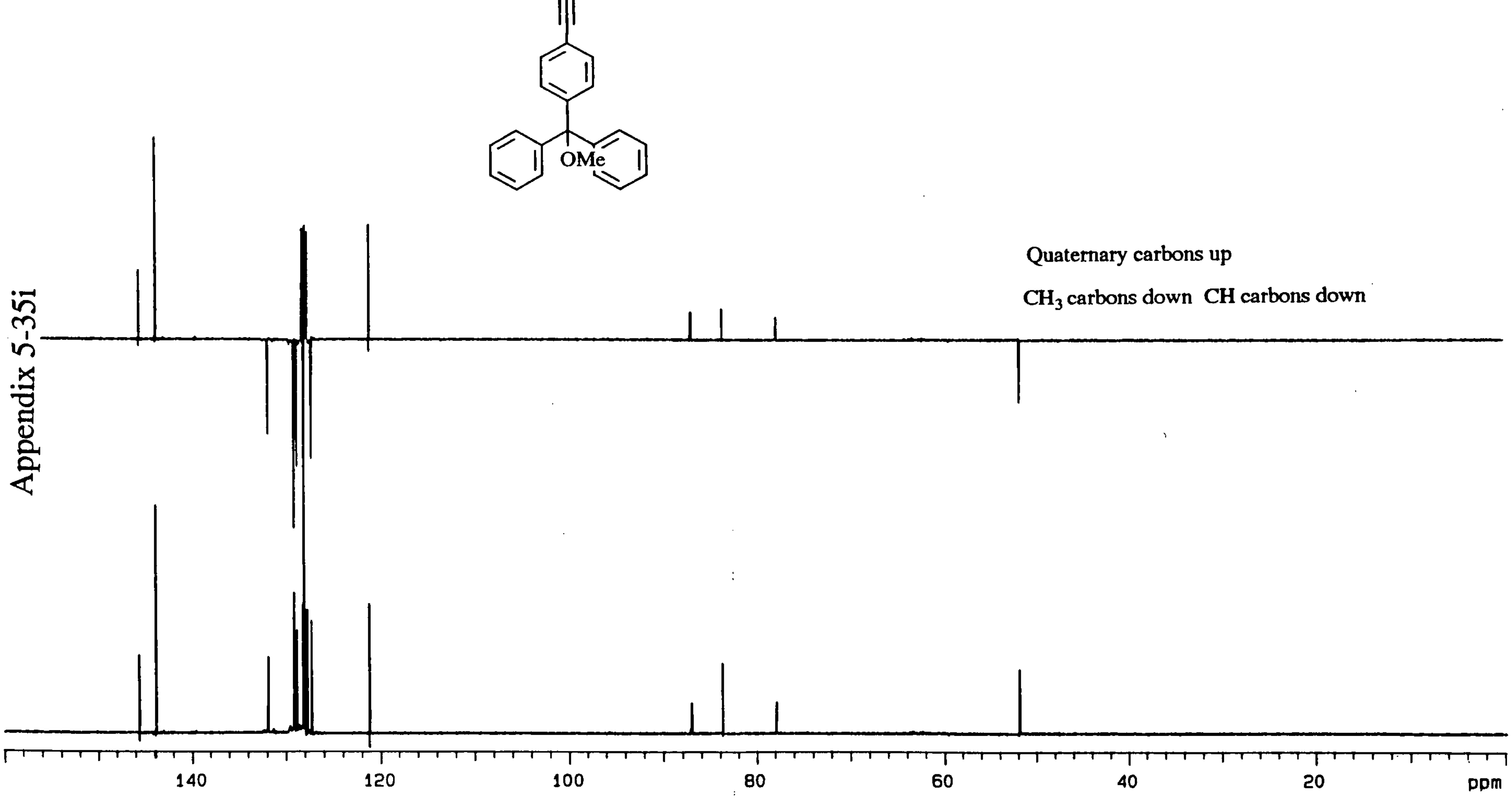


Appendix 5-35



Appendix 5-35i

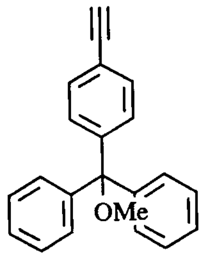
^{13}C NMR APT



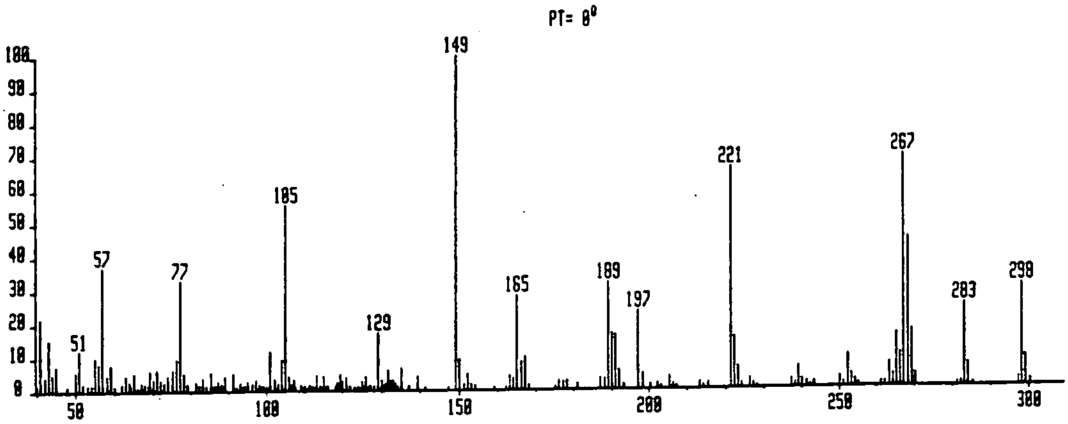
Quaternary carbons up

CH_3 carbons down CH carbons down

Appendix 5-36

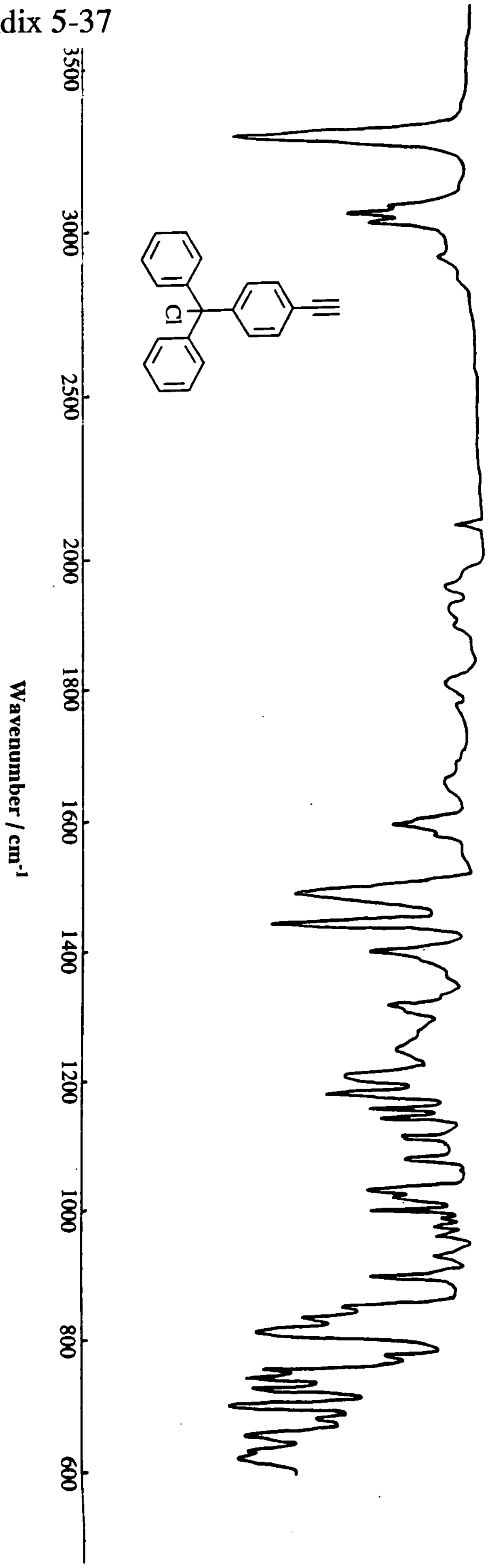


EI+

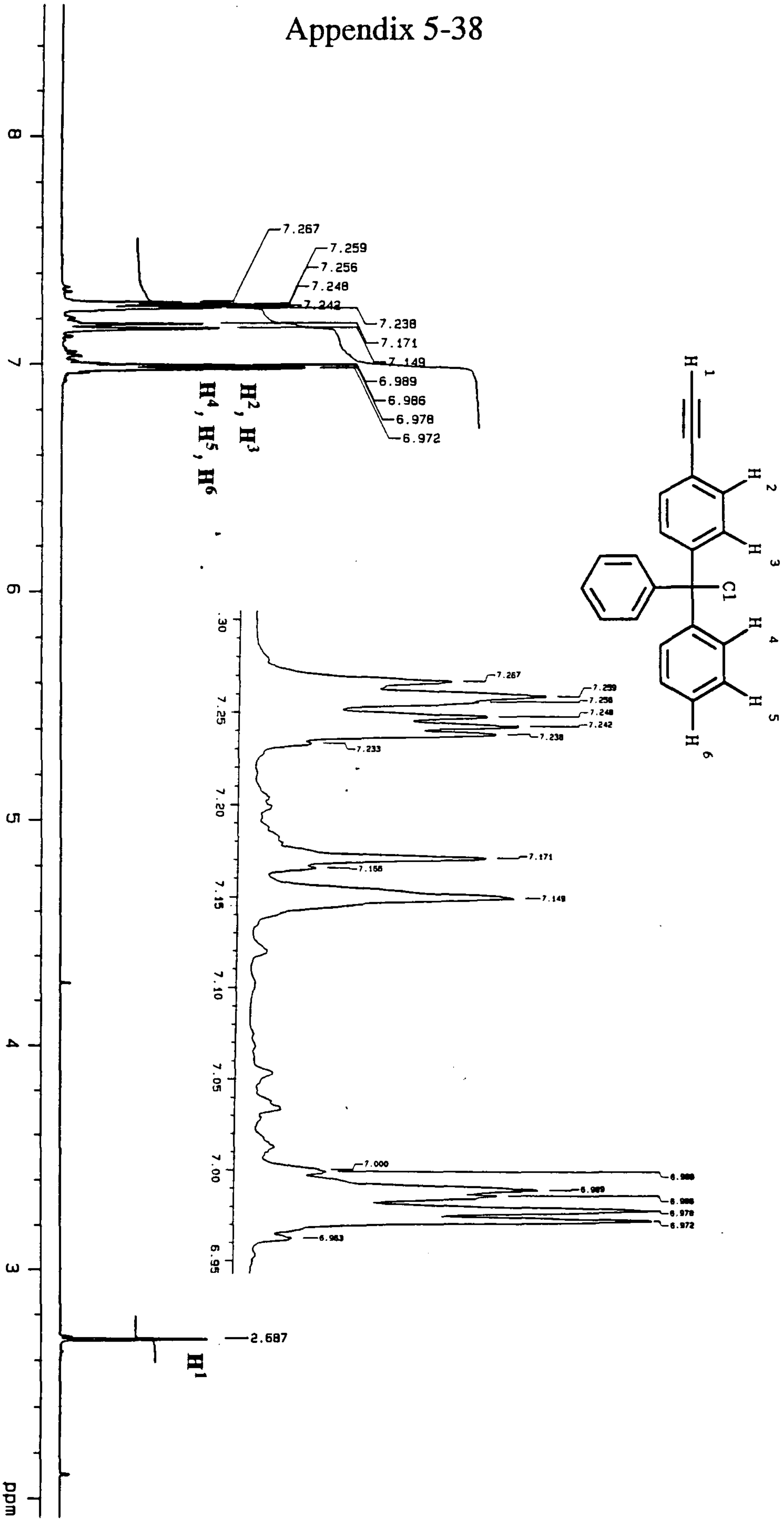


CI+

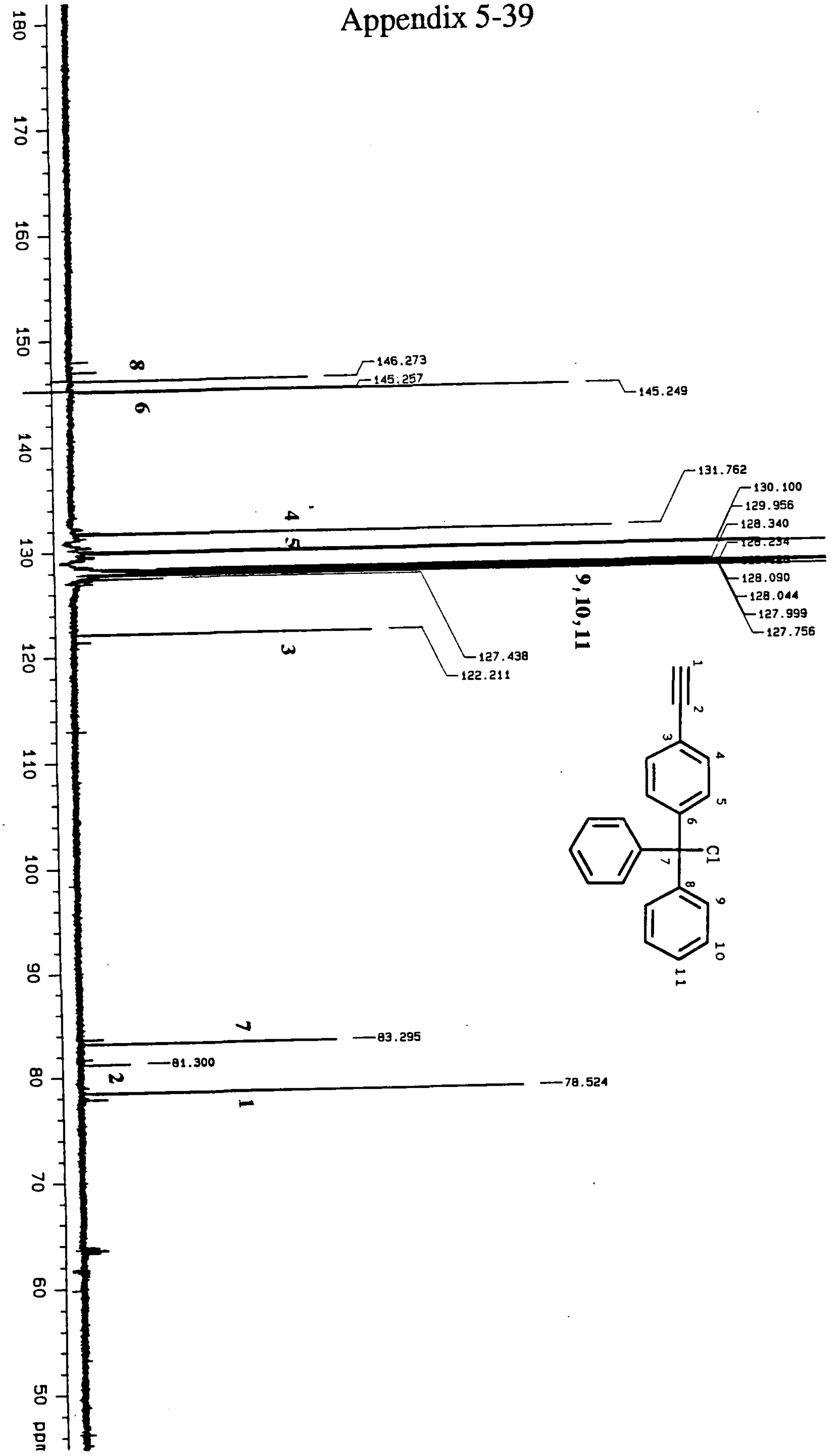
Appendix 5-37



Appendix 5-38

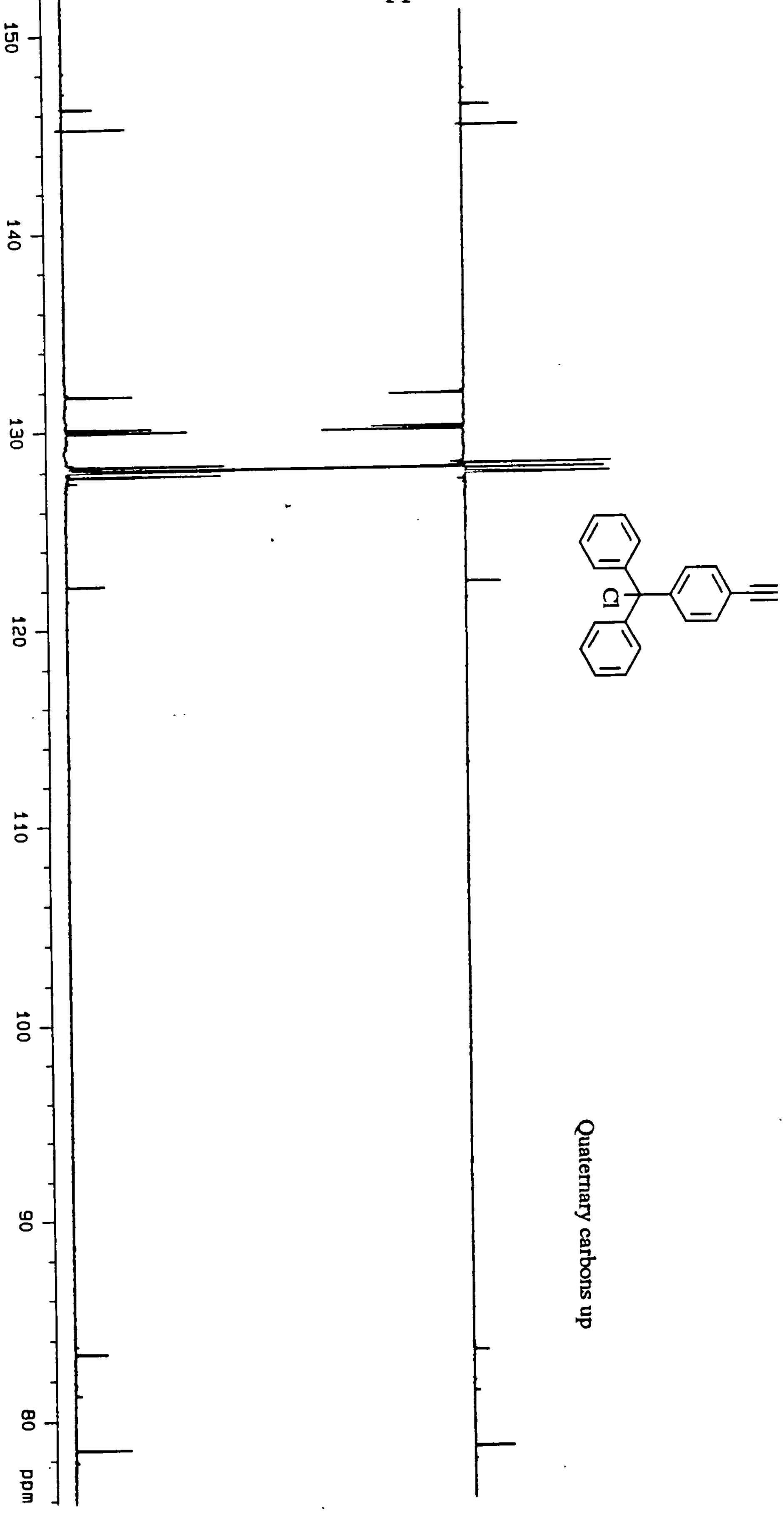


Appendix 5-39

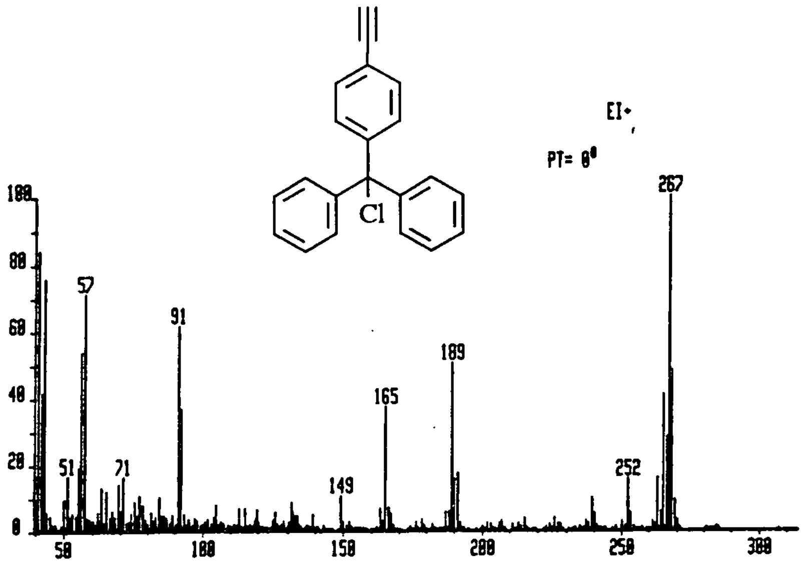


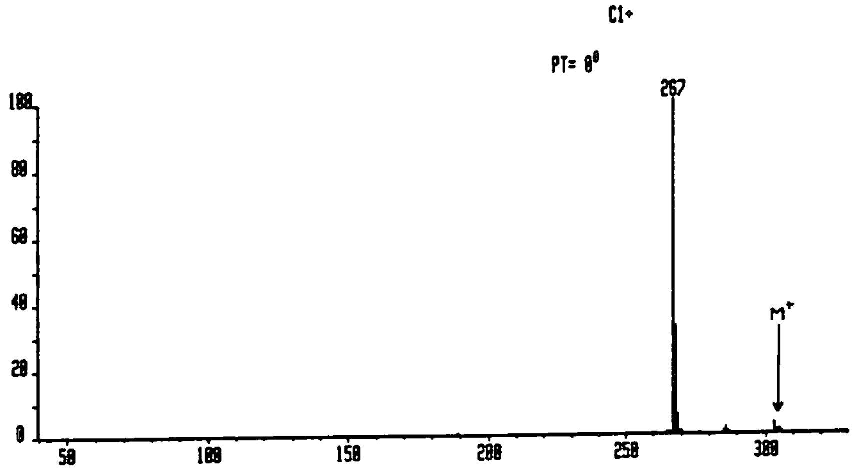
Appendix 5-39i

^{13}C NMR APT

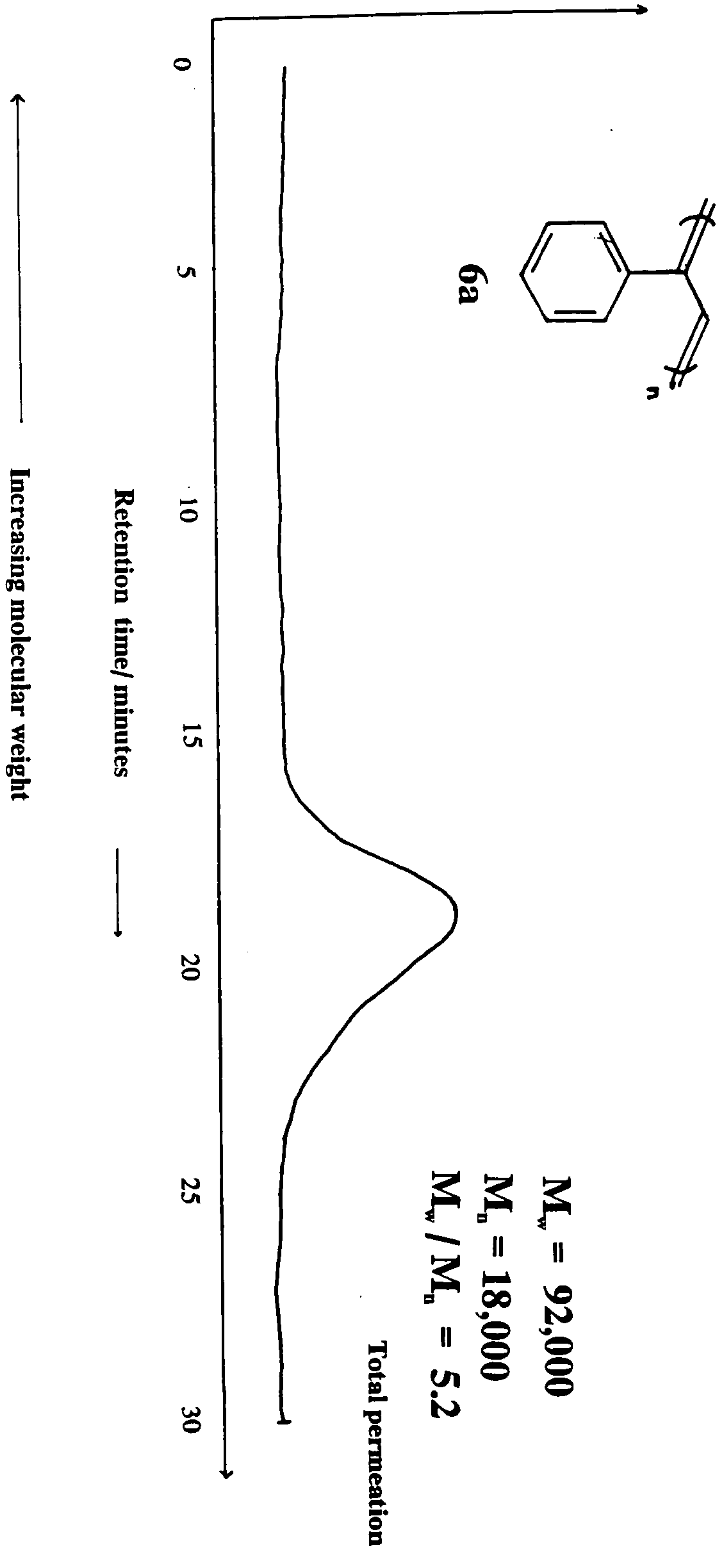


Appendix 5-40

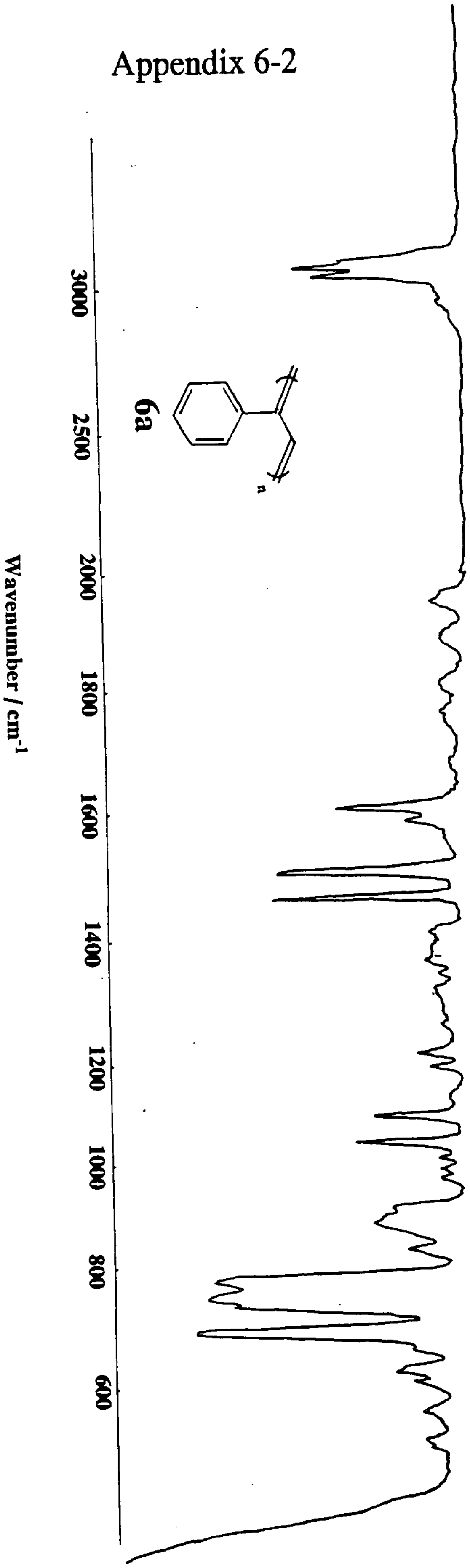




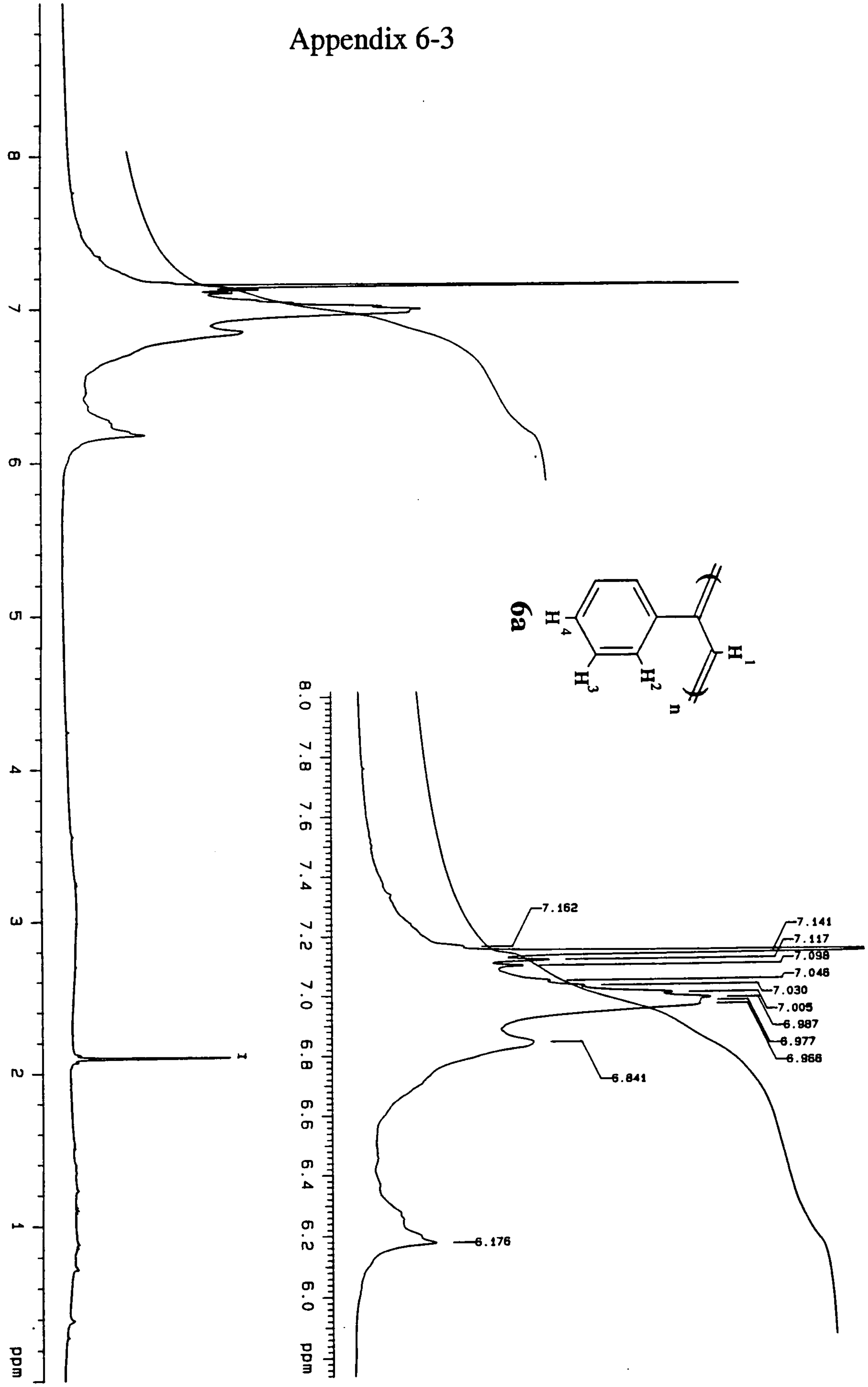
Appendix 6-1


n
6a
M_w = 92,000
M_n = 18,000
M_w / M_n = 5.2
Total permeation
0
5
10
15
20
25
30
Retention time/ minutes
Increasing molecular weight

Appendix 6-2

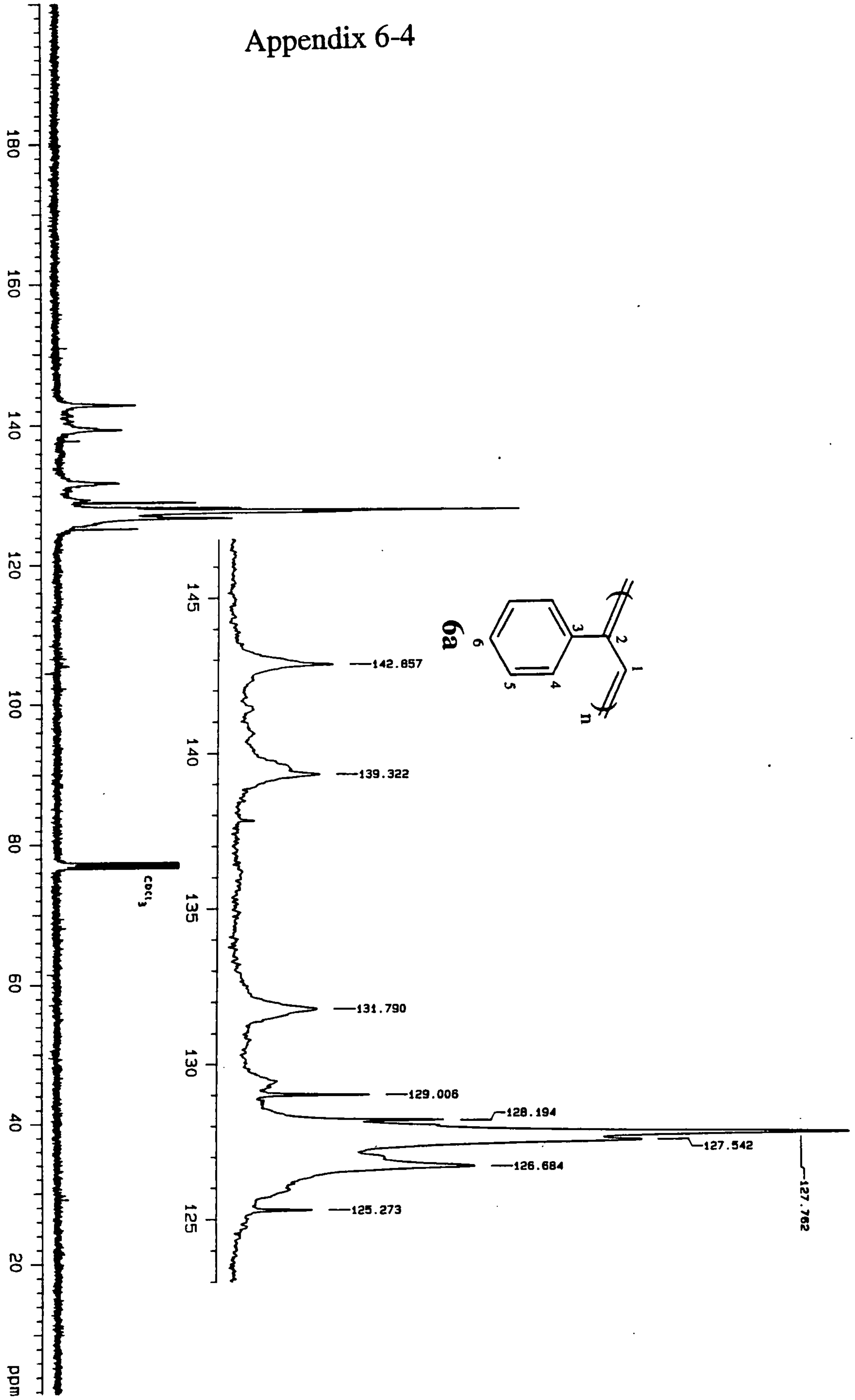

6a
n
3000
2500
2000
1800
1600
1400
1200
1000
800
600
Wavenumber / cm-1

Appendix 6-3



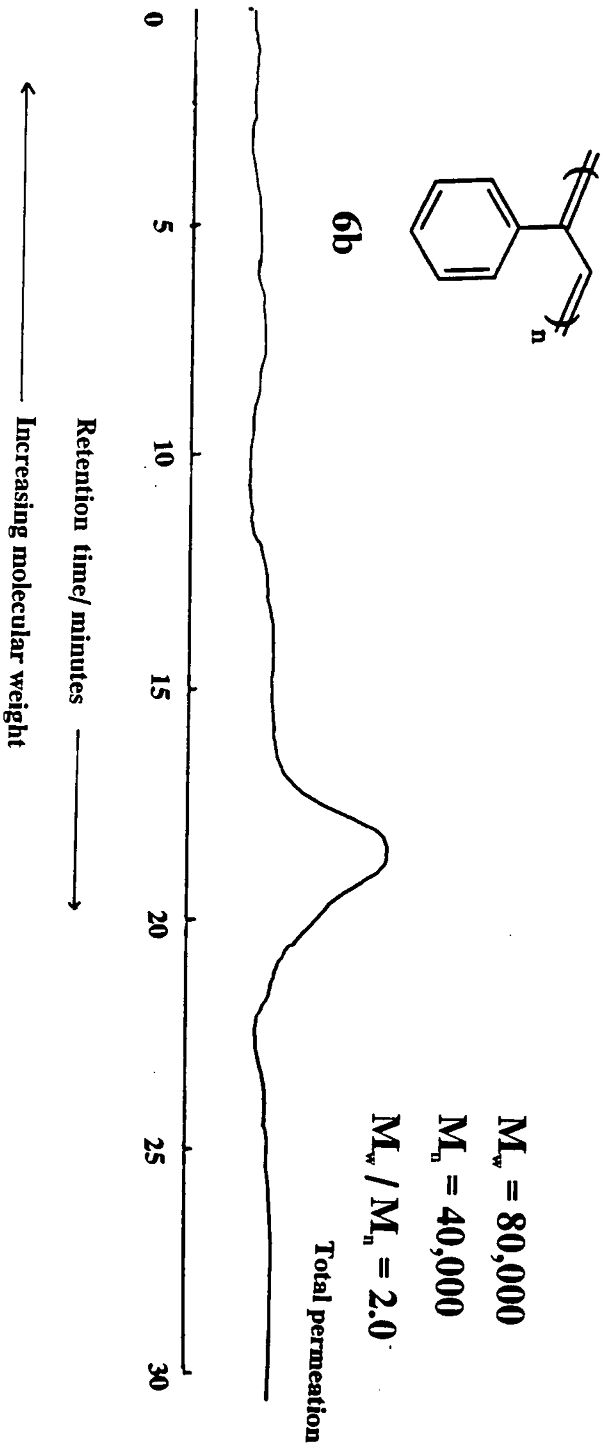
6a

Appendix 6-4



6a

Appendix 6-5

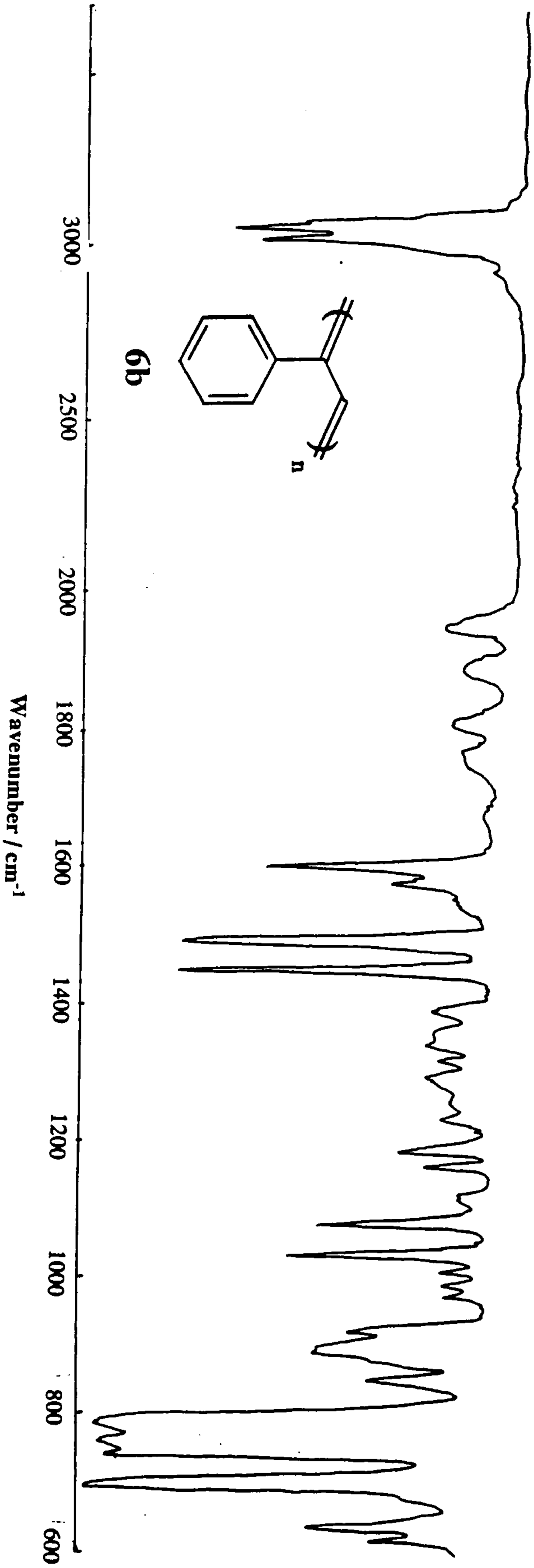


$M_w = 80{,}000$

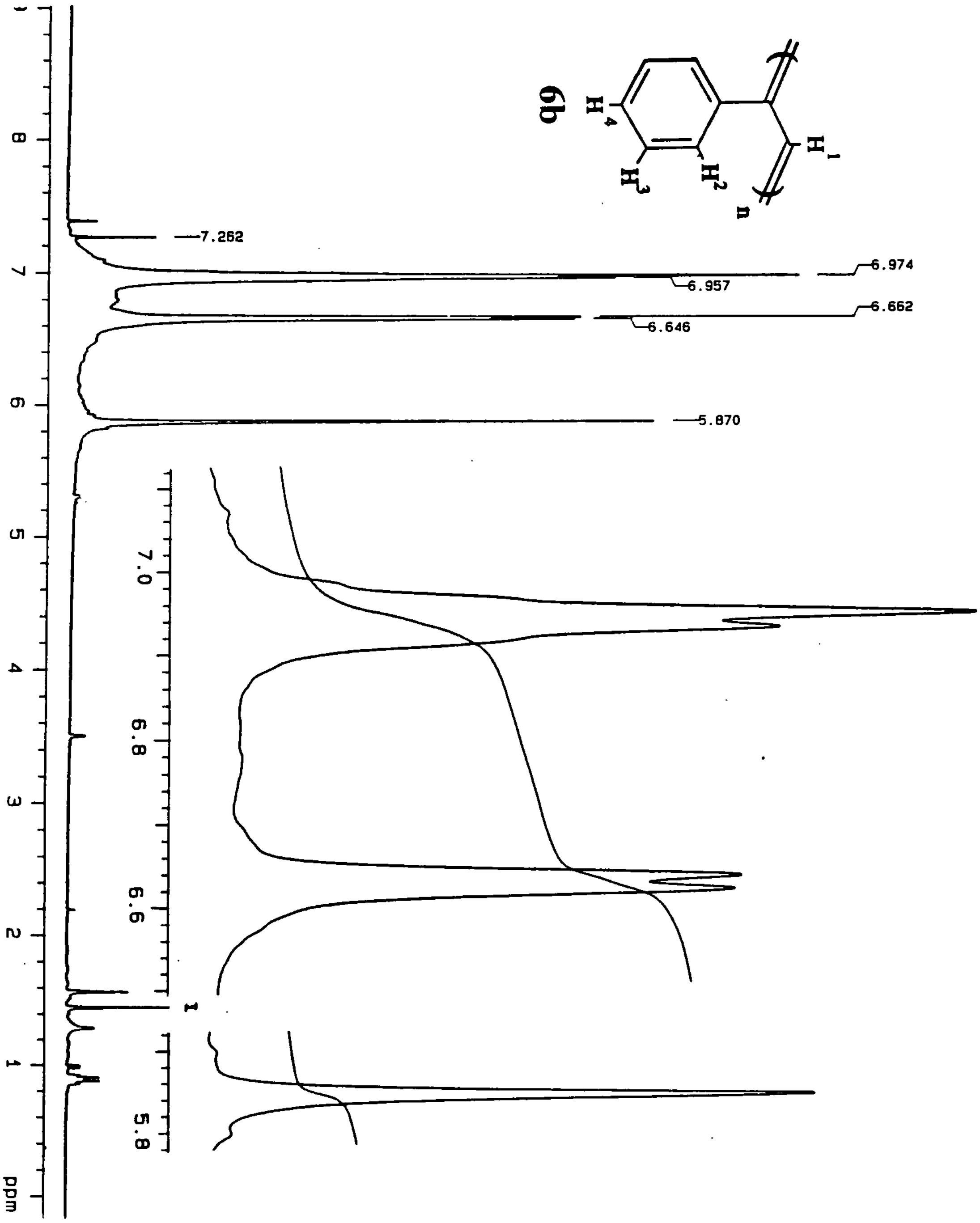
$M_n = 40{,}000$

$M_w / M_n = 2.0$

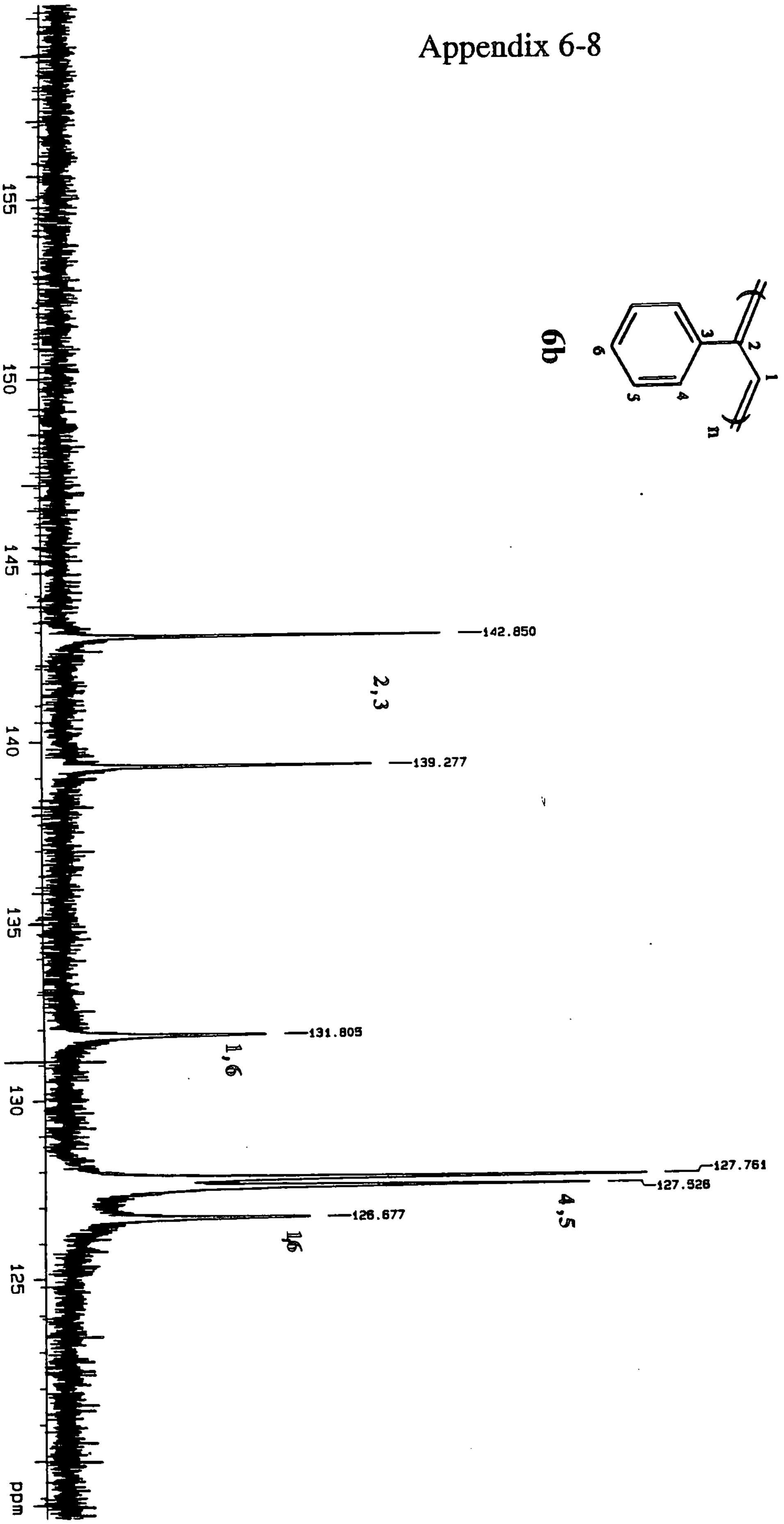
Appendix 6-6


3000
2500
2000
1800
1600
1400
1200
1000
800
600
Wavenumber / cm^{-1}
6b
n

Appendix 6-7

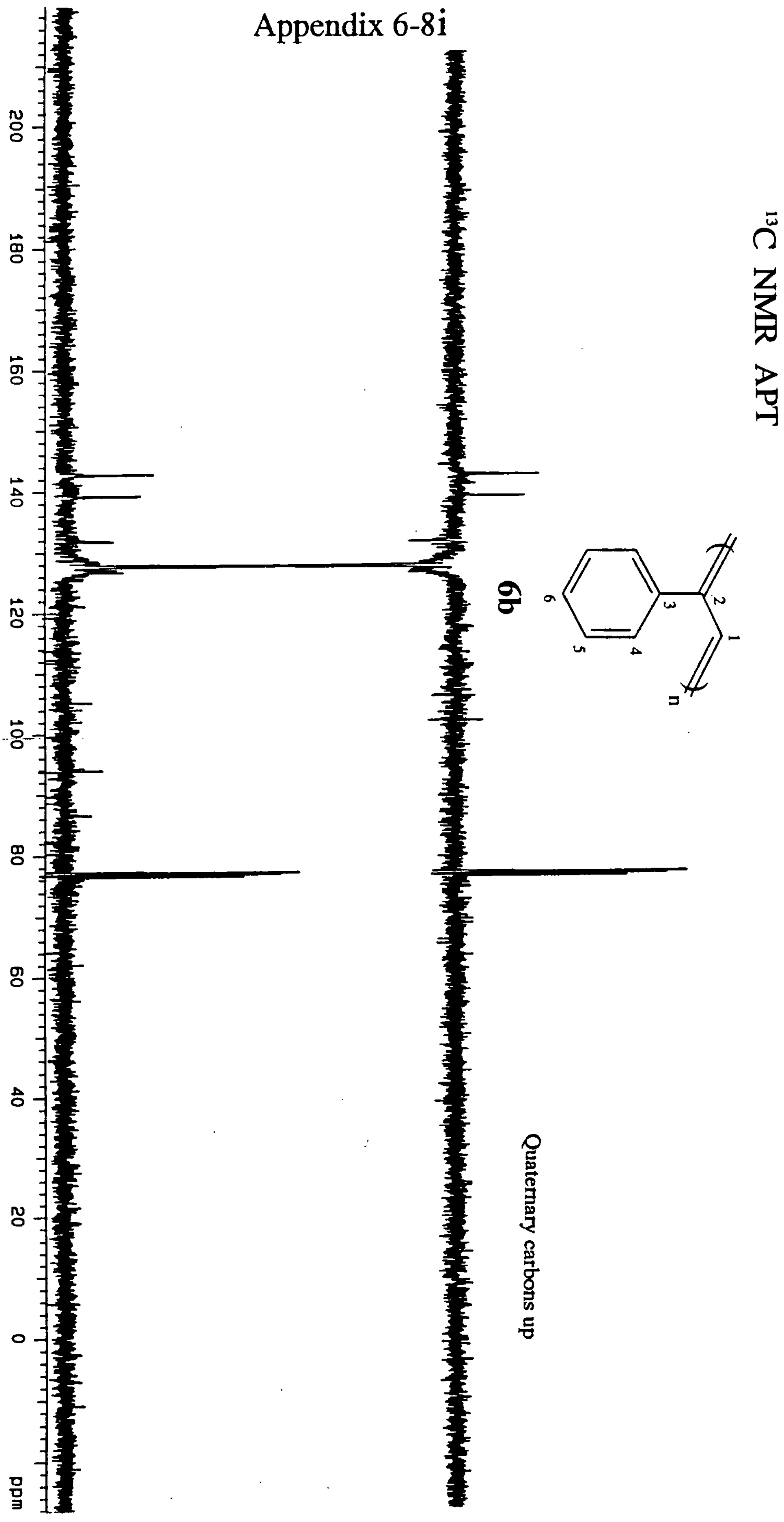

6b
H1
H2
H3
H4
n
7.262
6.974
6.957
6.662
6.646
5.870
8
7
6
5
4
3
2
1
ppm
7.0
6.8
6.6
5.8
1

Appendix 6-8


6b
1
2
3
4
5
6
n
155
150
145
140
135
130
125
ppm
142.850
2,3
139.277
131.805
1,6
127.761
127.526
4,5
126.677
1,6

Appendix 6-8i

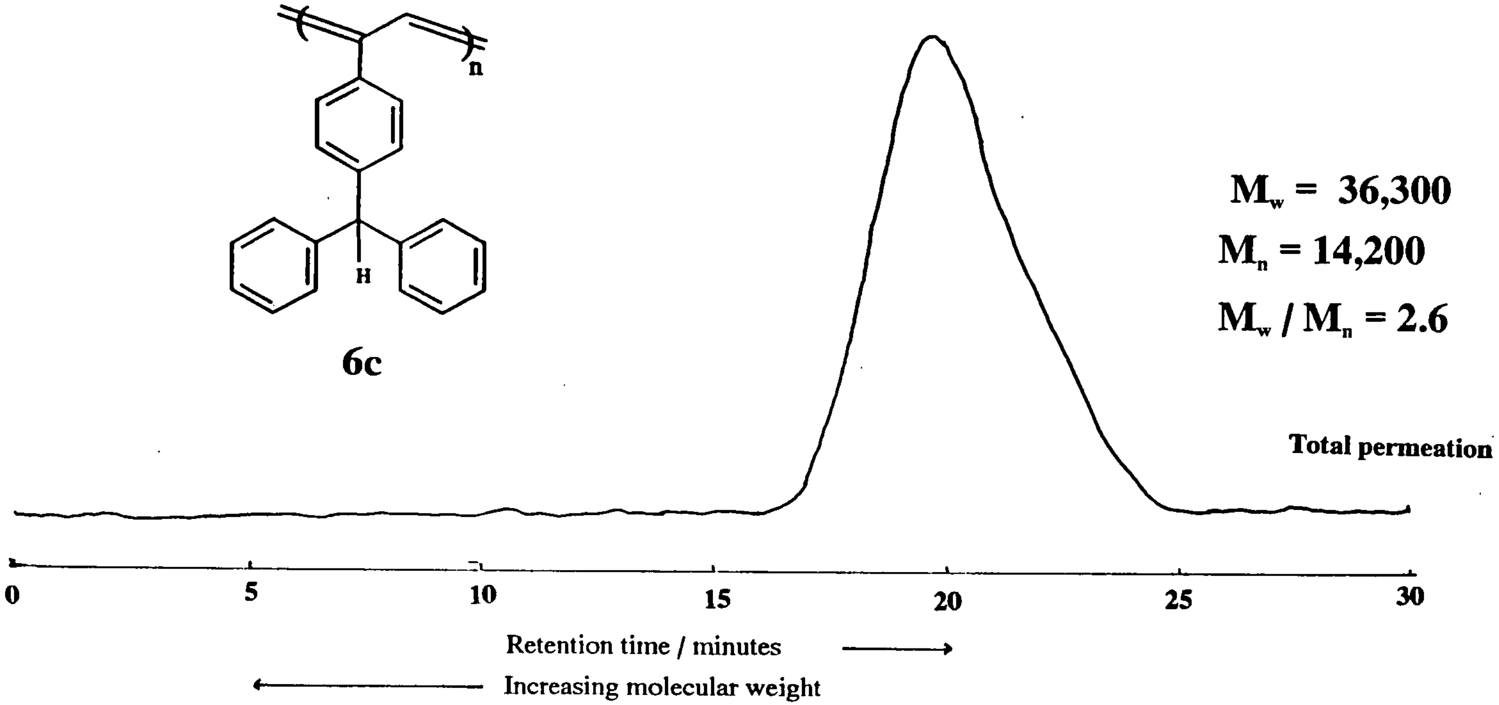
^{13}C NMR APT



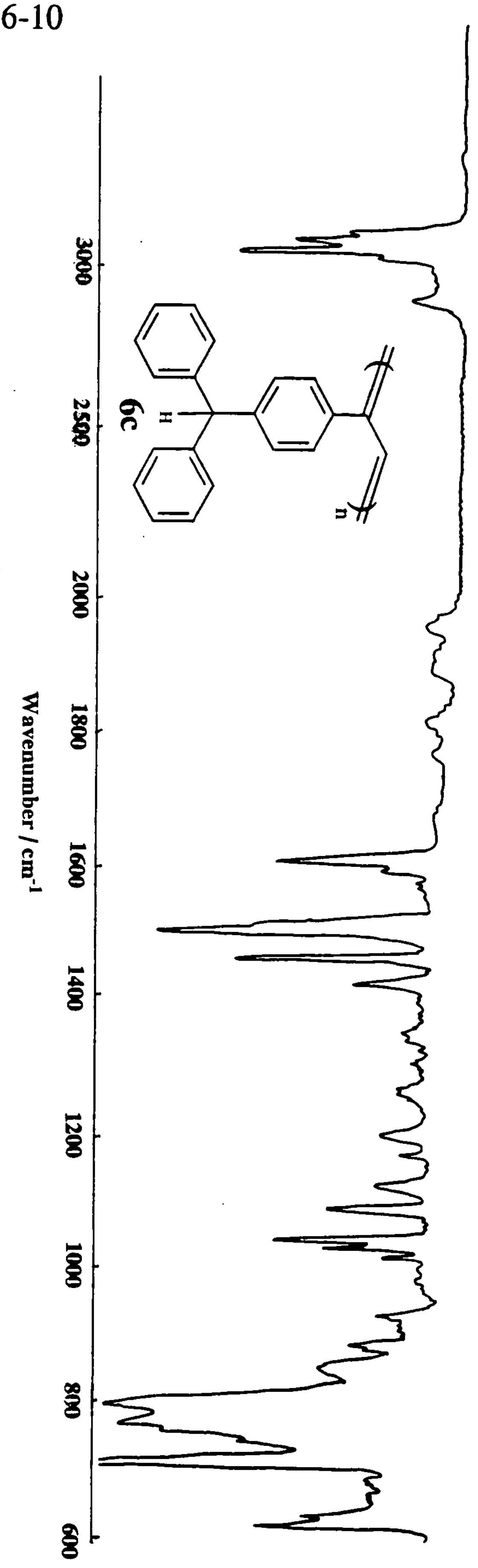
6b

Quaternary carbons up

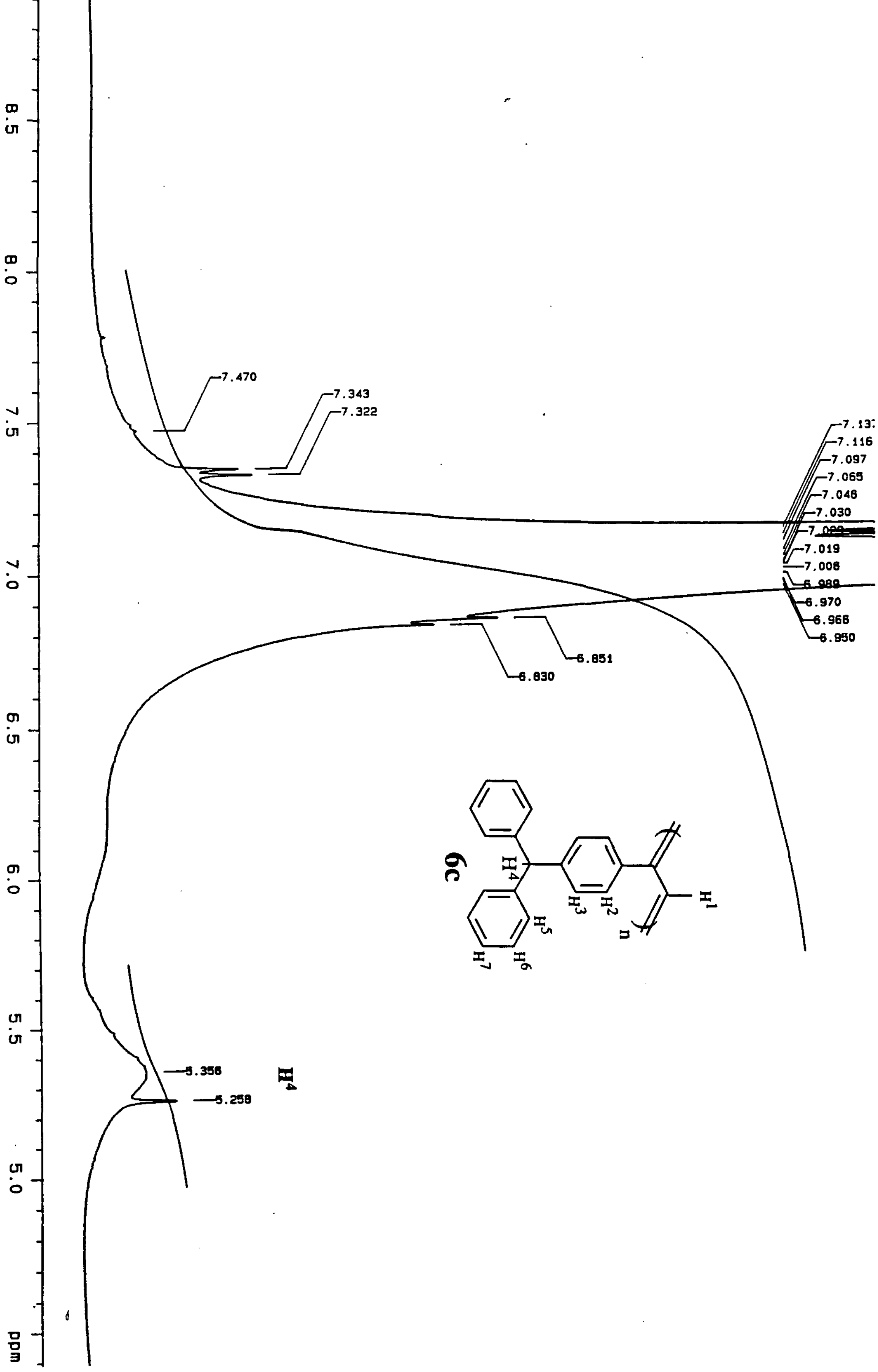
Appendix 6-9


6c
n
H
M$_w$ = 36,300
M$_n$ = 14,200
M$_w$ / M$_n$ = 2.6
Total permeation
0
5
10
15
20
25
30
Retention time / minutes
Increasing molecular weight

Appendix 6-10

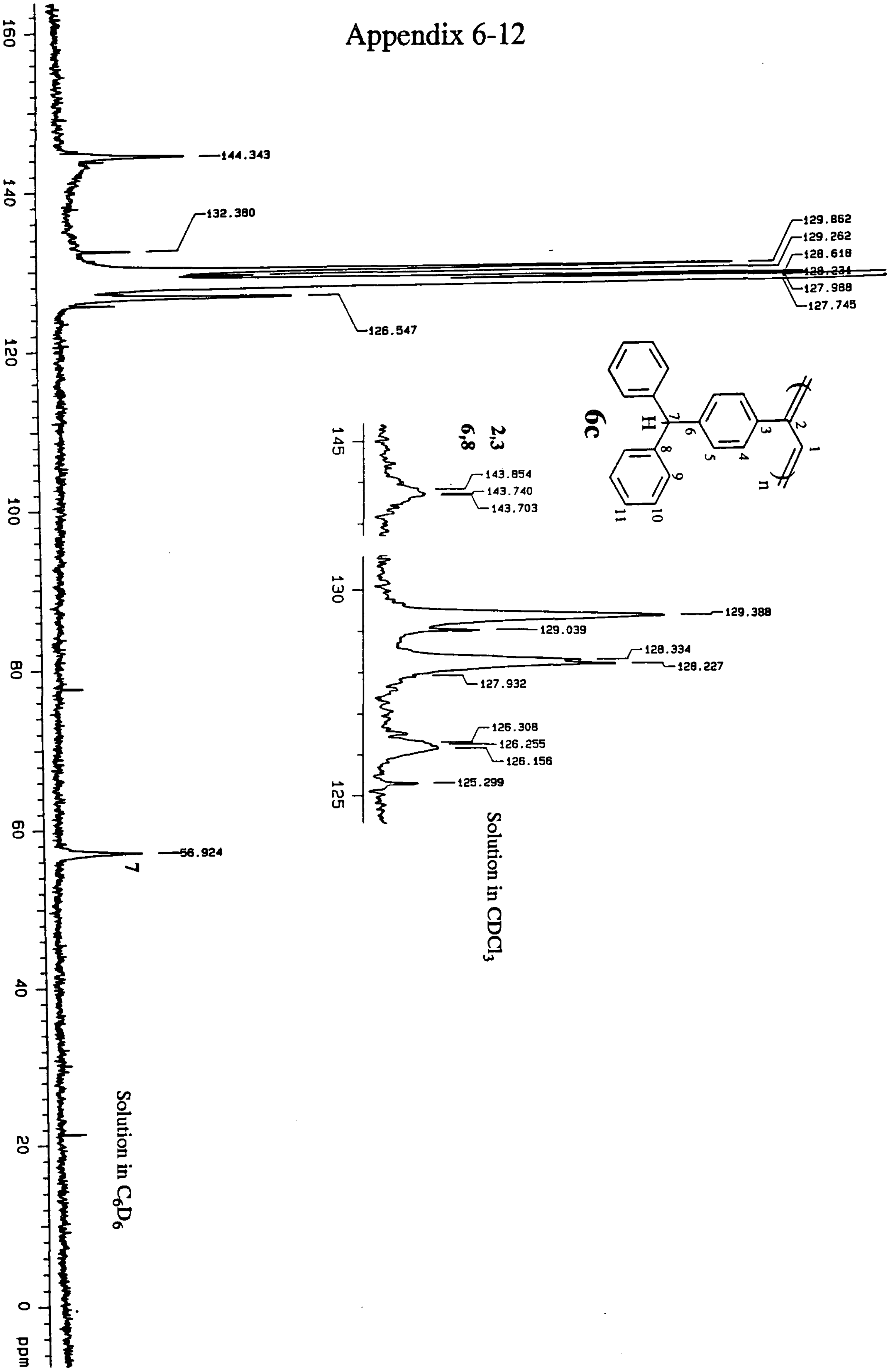


Appendix 6-11



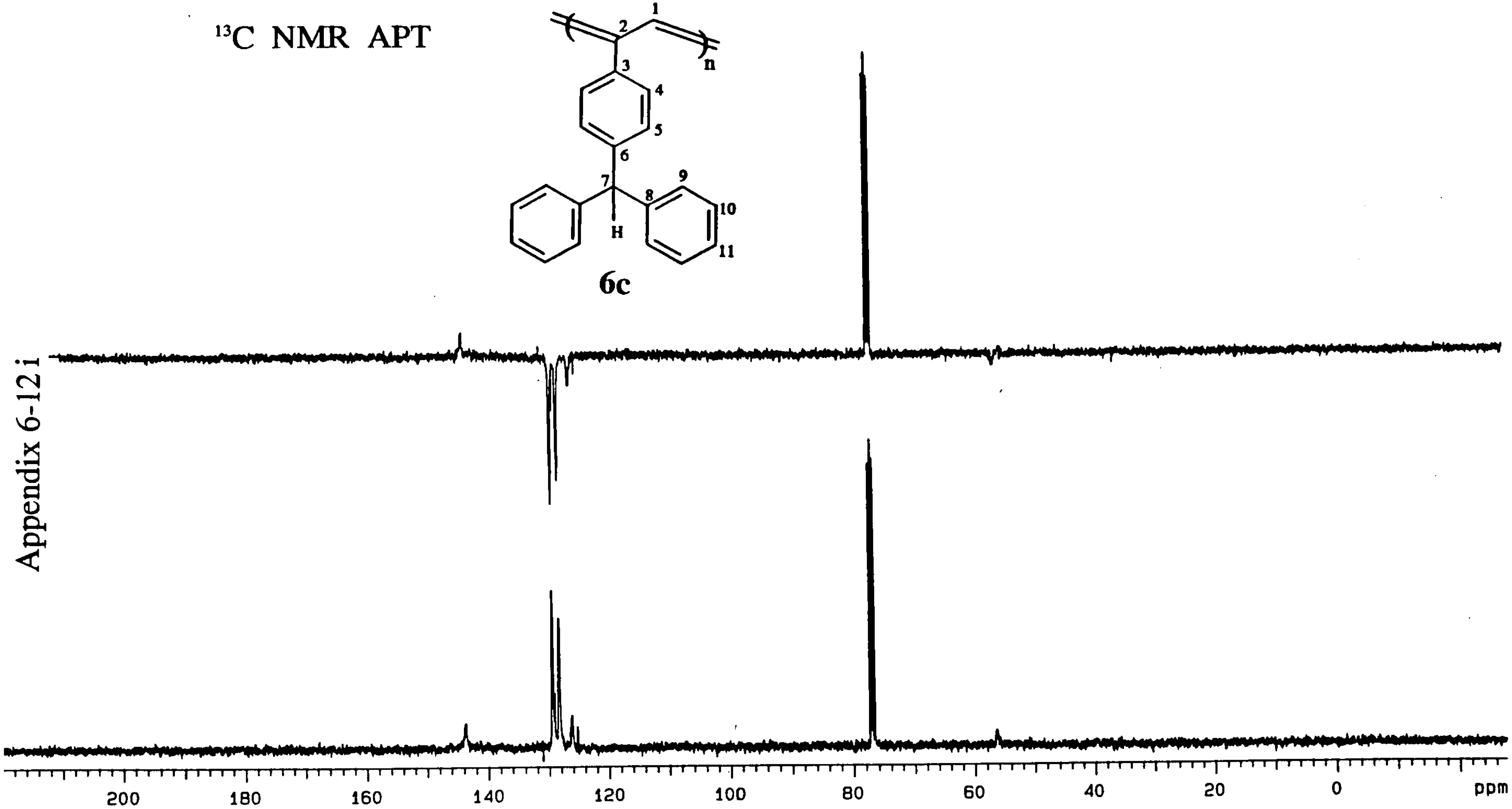
6c

Appendix 6-12



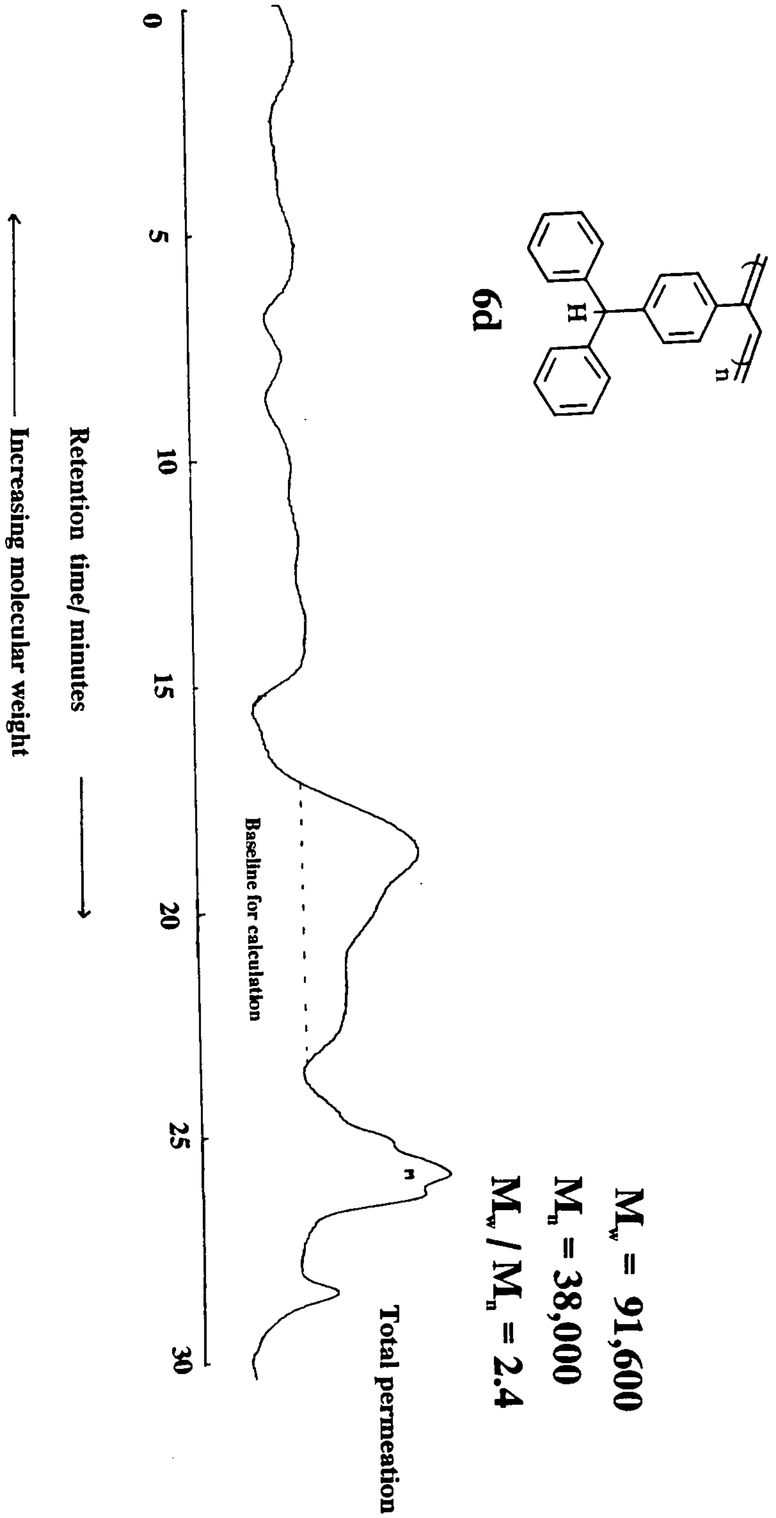
Appendix 6-12 i

13C NMR APT



6c

Appendix 6-13



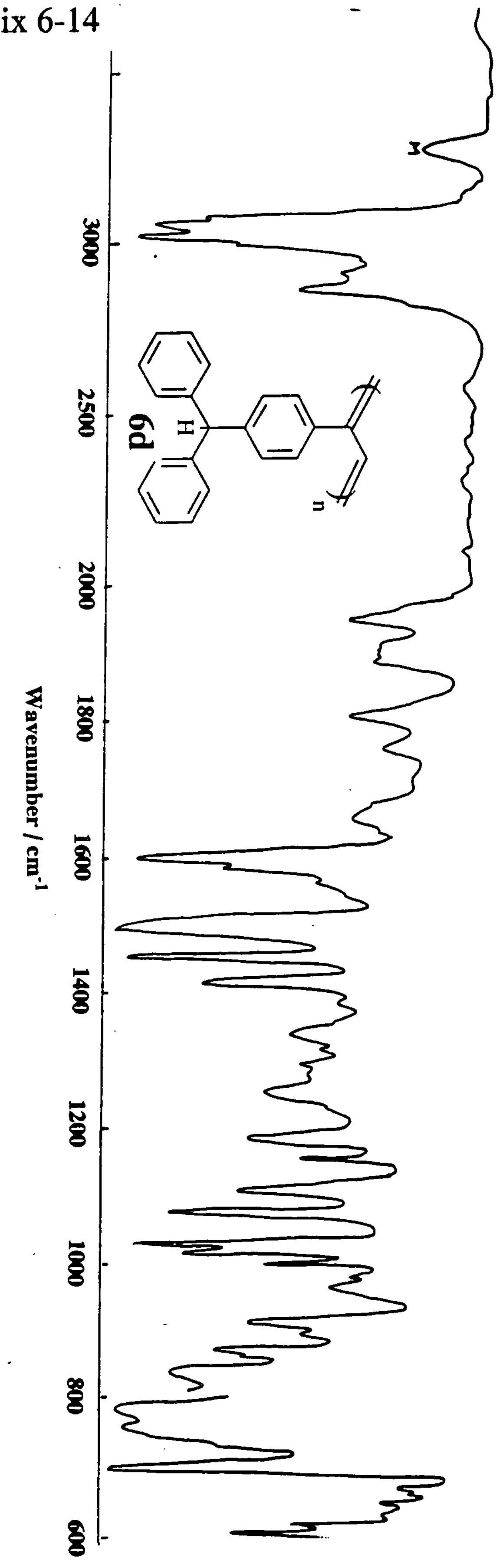
6d

M_w = 91,600

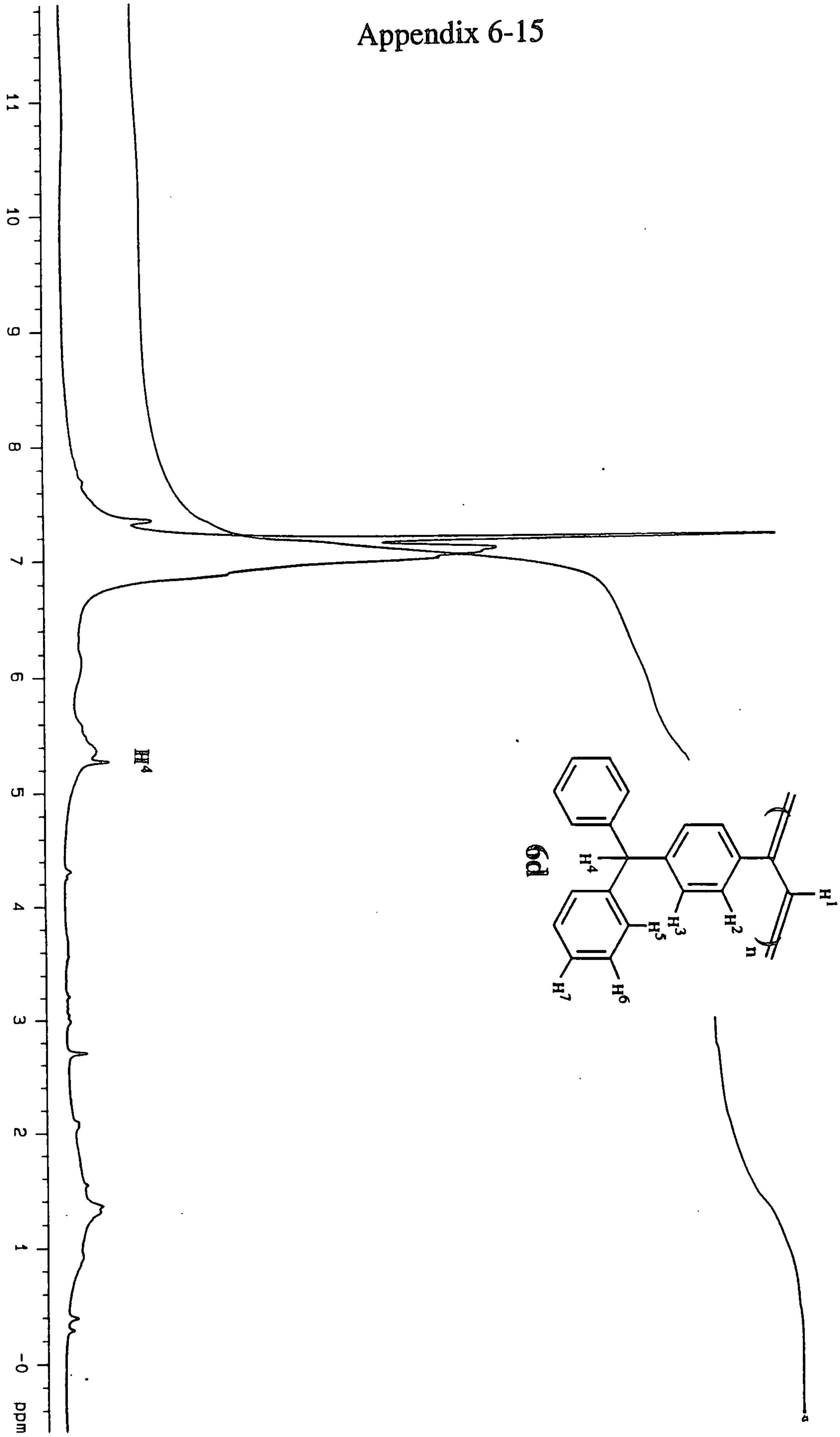
M_n = 38,000

M_w / M_n = 2.4

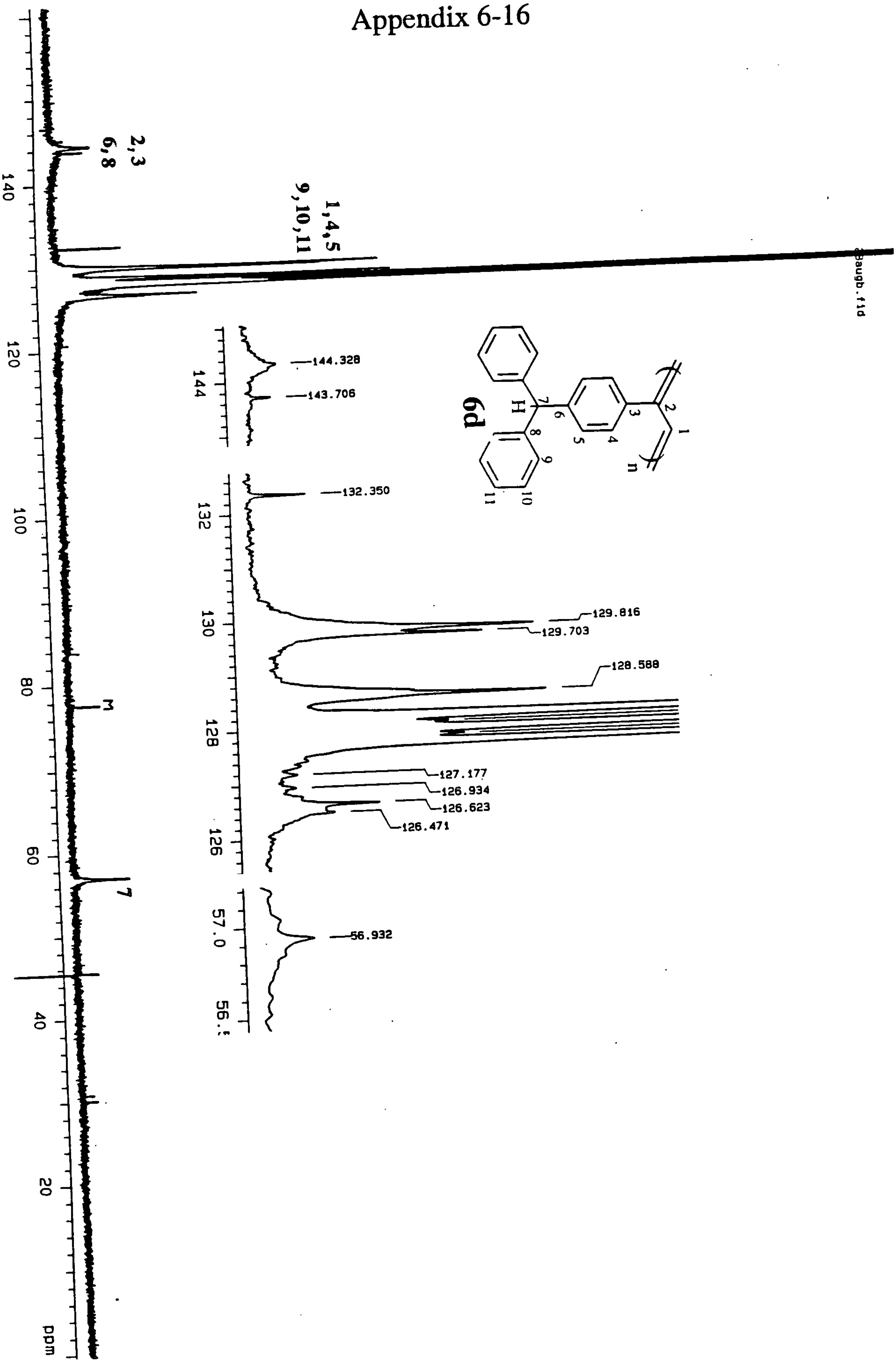
Appendix 6-14



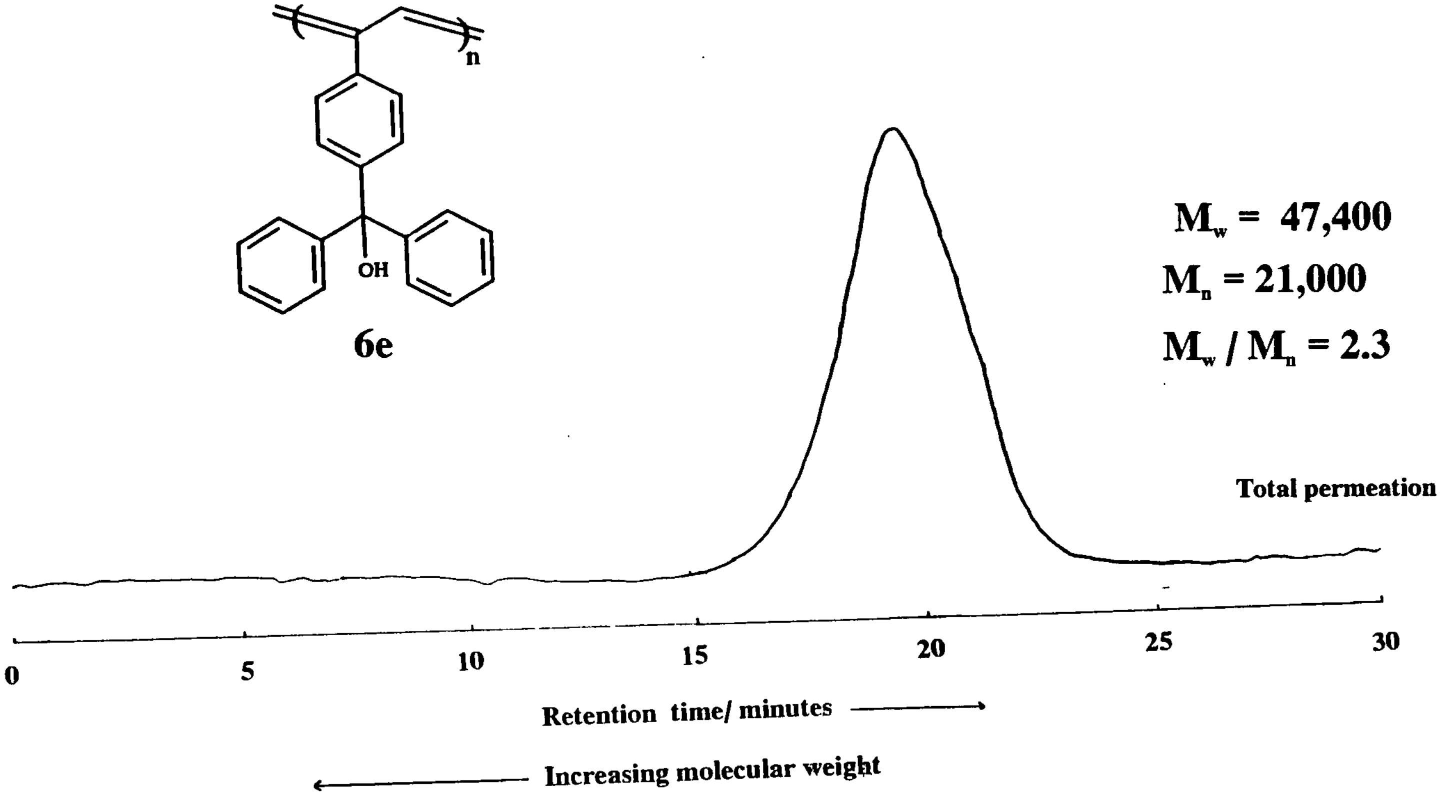
Appendix 6-15



Appendix 6-16



Appendix 6-17



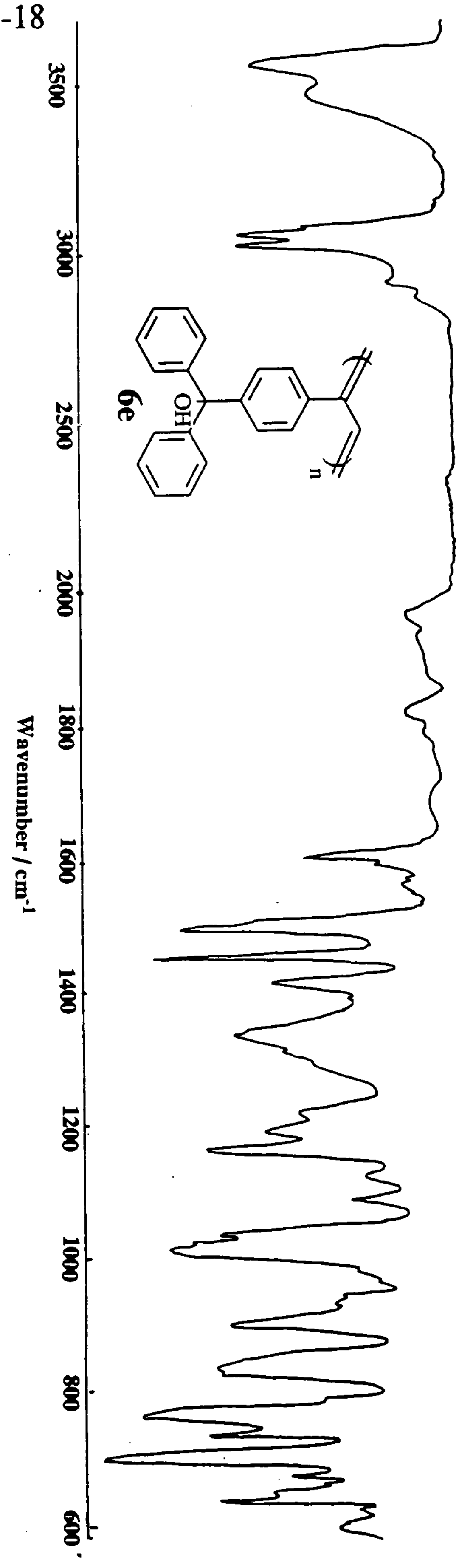
6e

M_w = 47,400

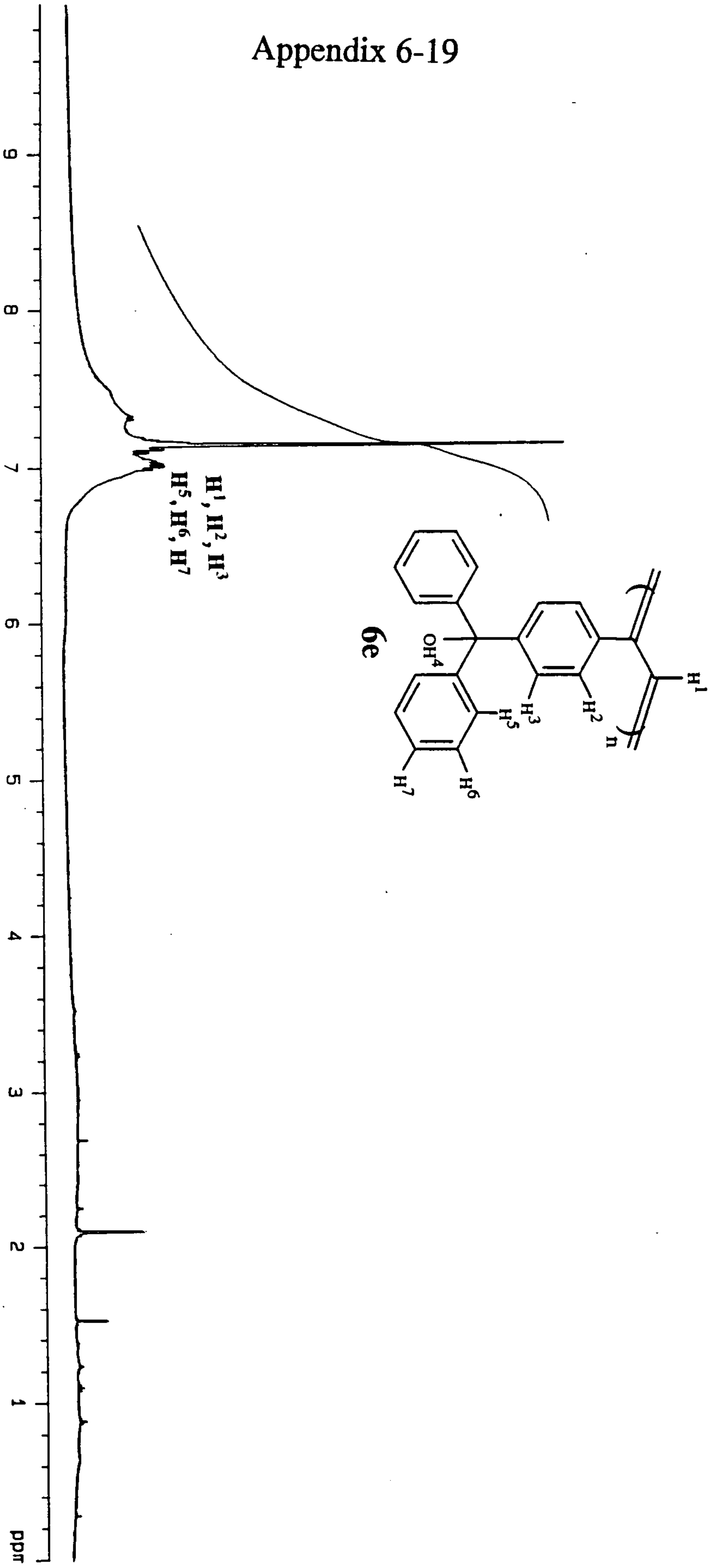
M_n = 21,000

M_w / M_n = 2.3

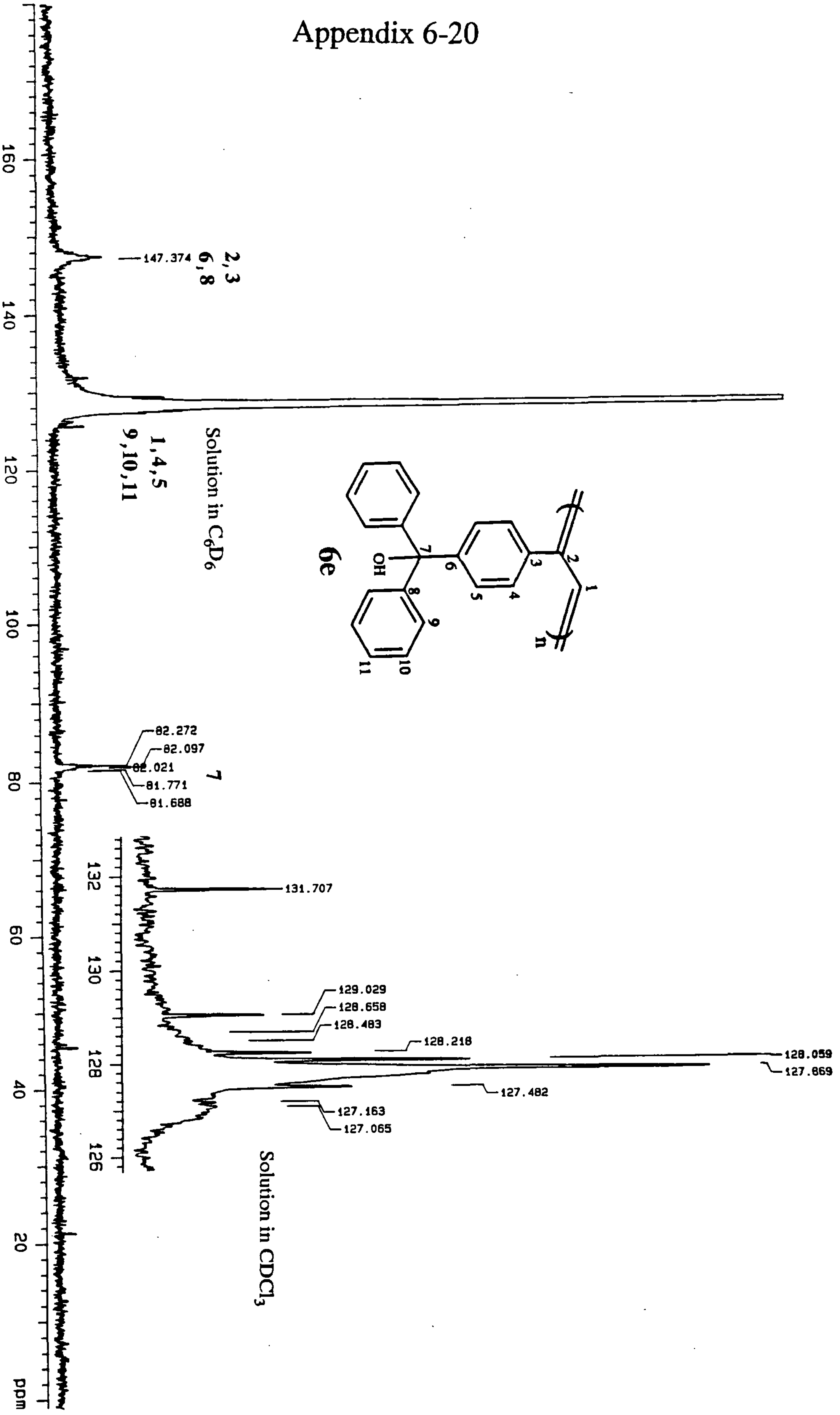
Appendix 6-18



Appendix 6-19

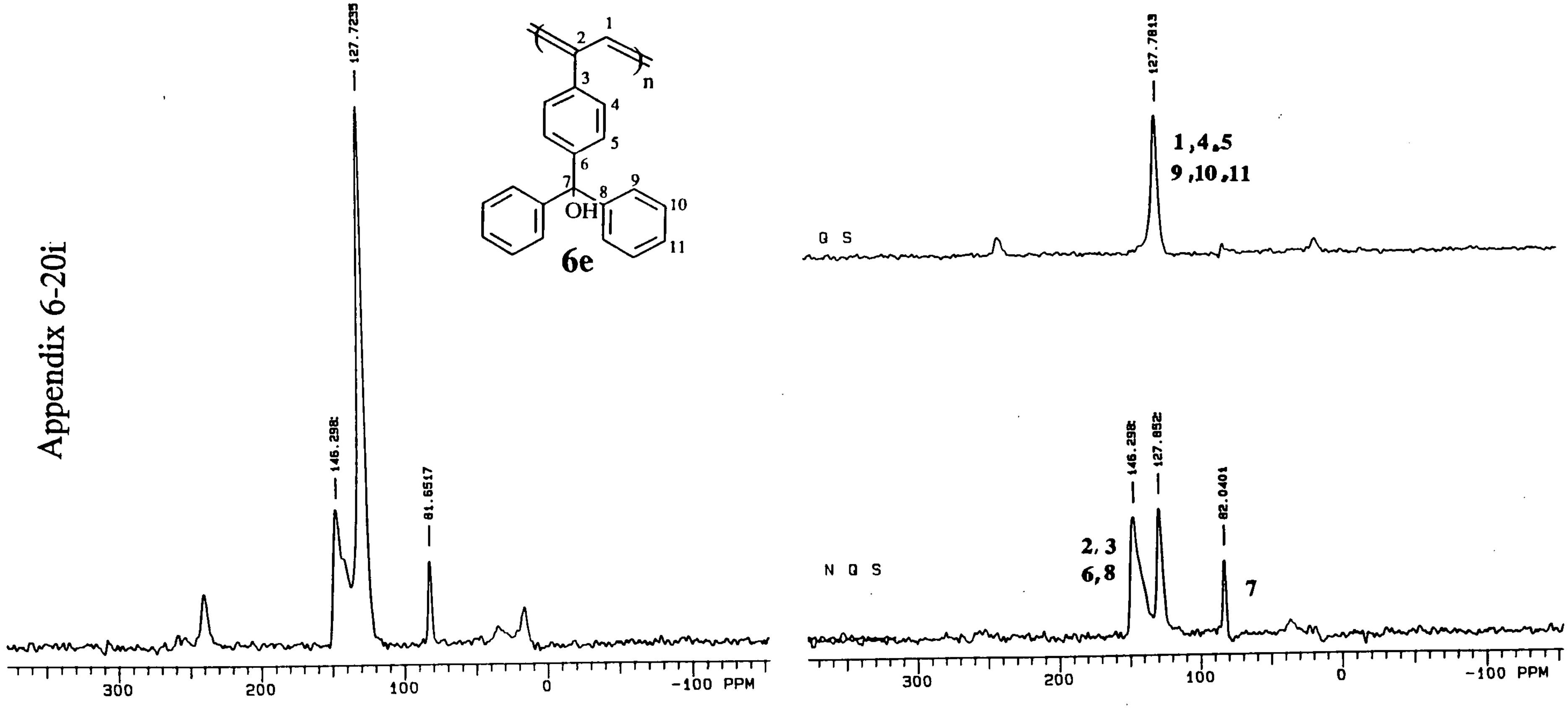


Appendix 6-20

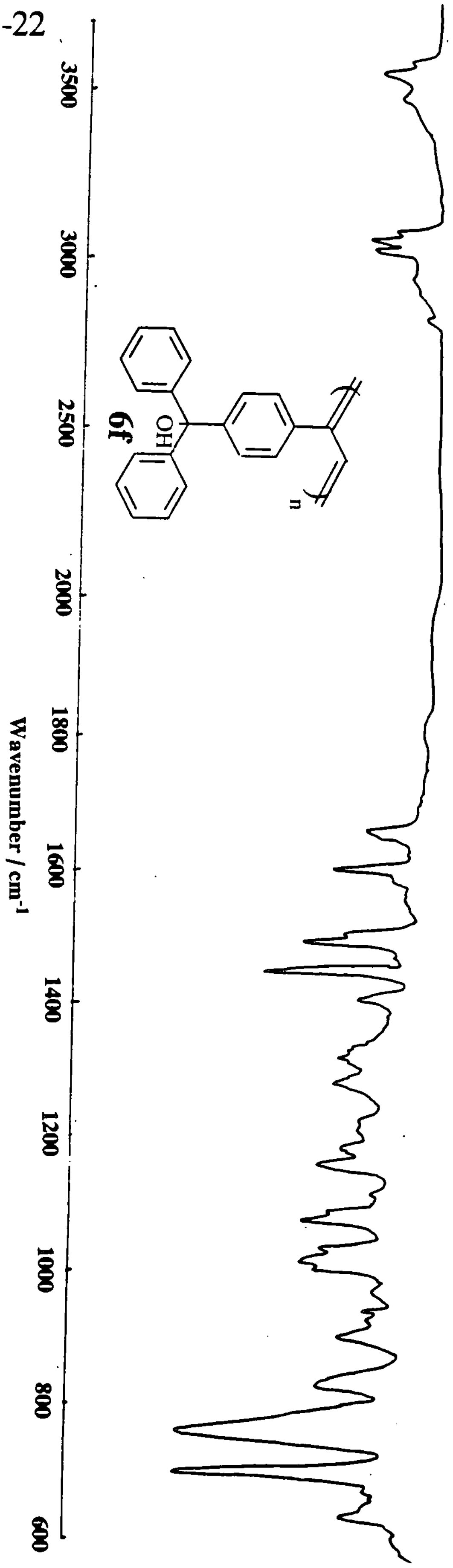


Appendix 6-20i

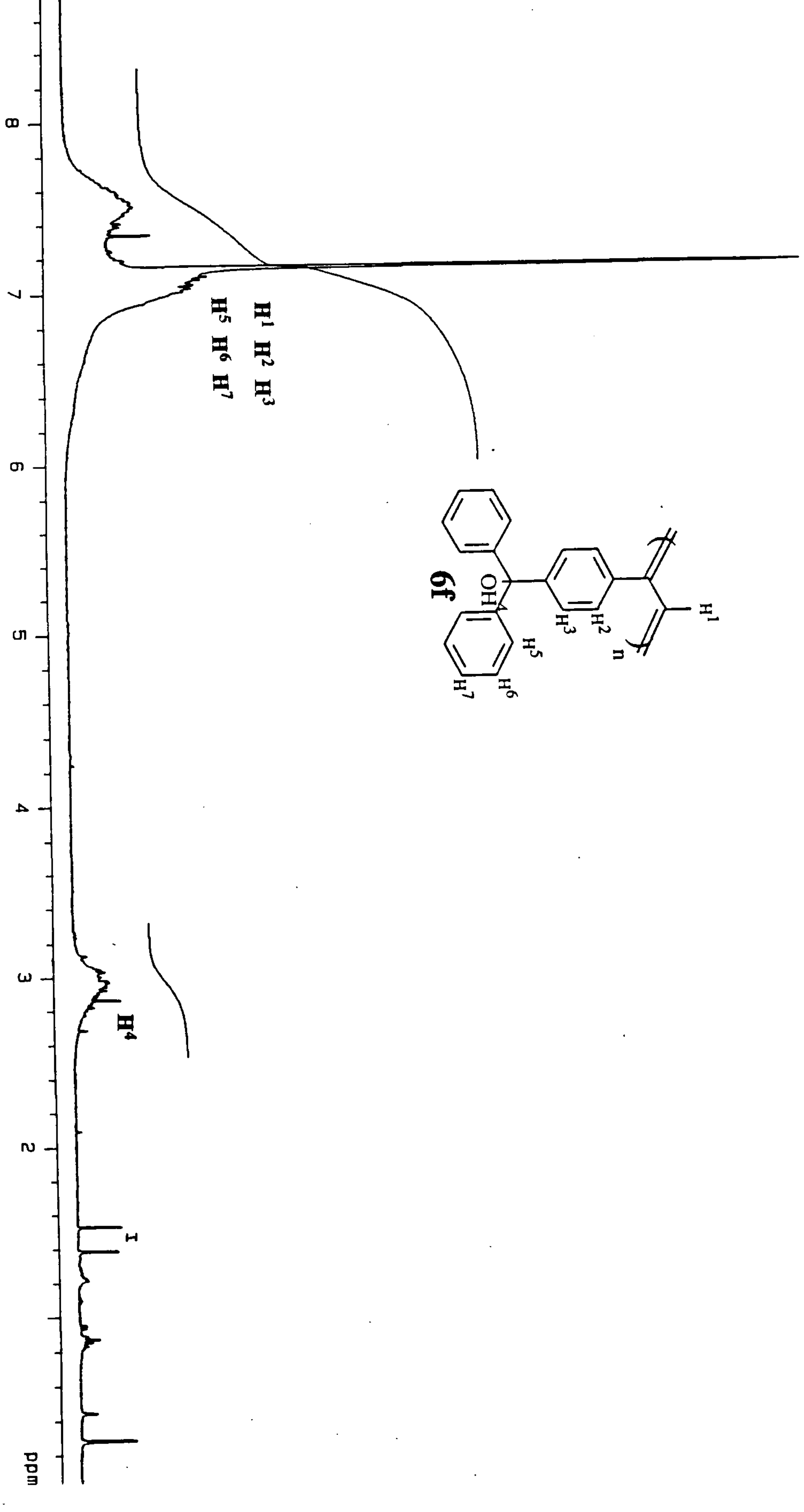
CP/MAS ^{13}C NMR



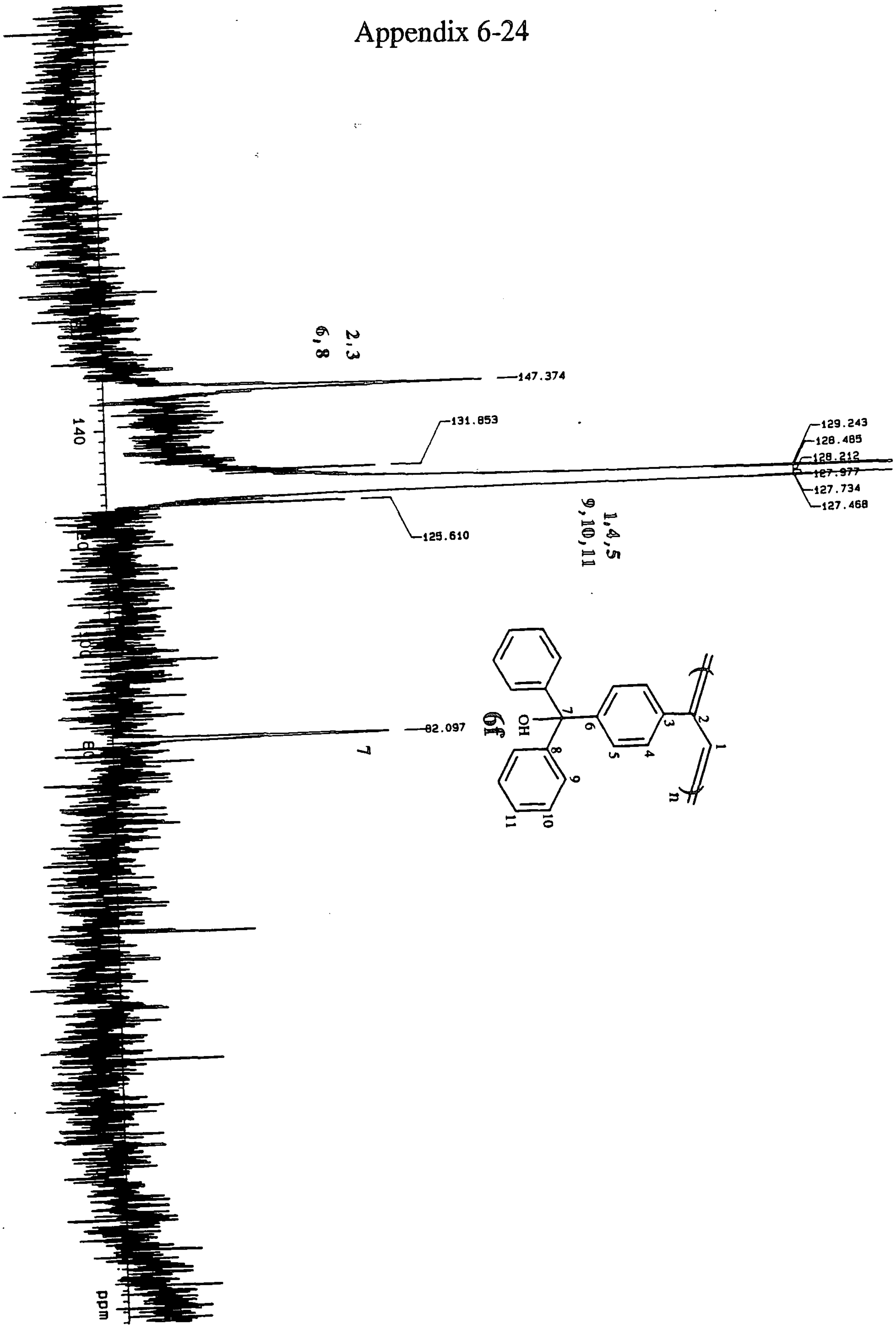
Appendix 6-22



Appendix 6-23

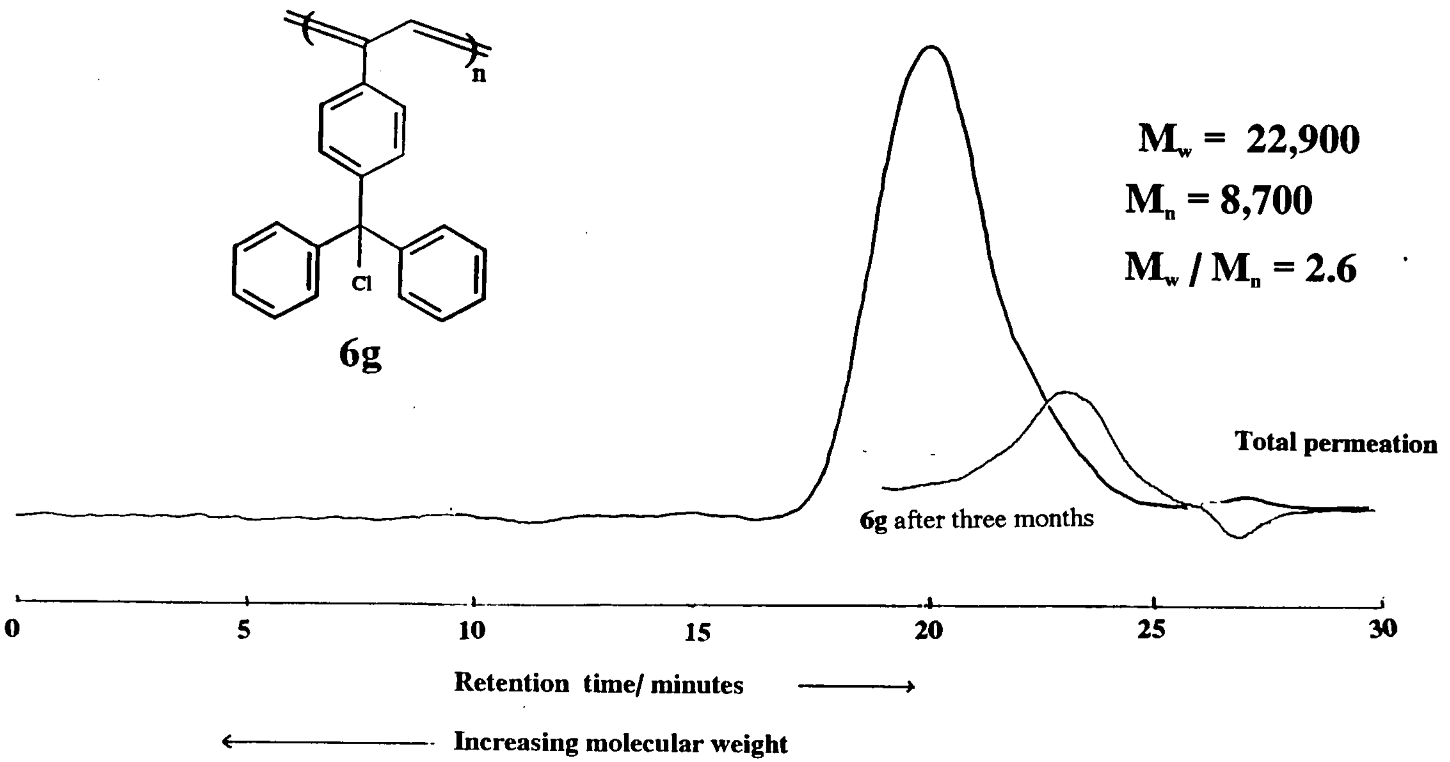


Appendix 6-24

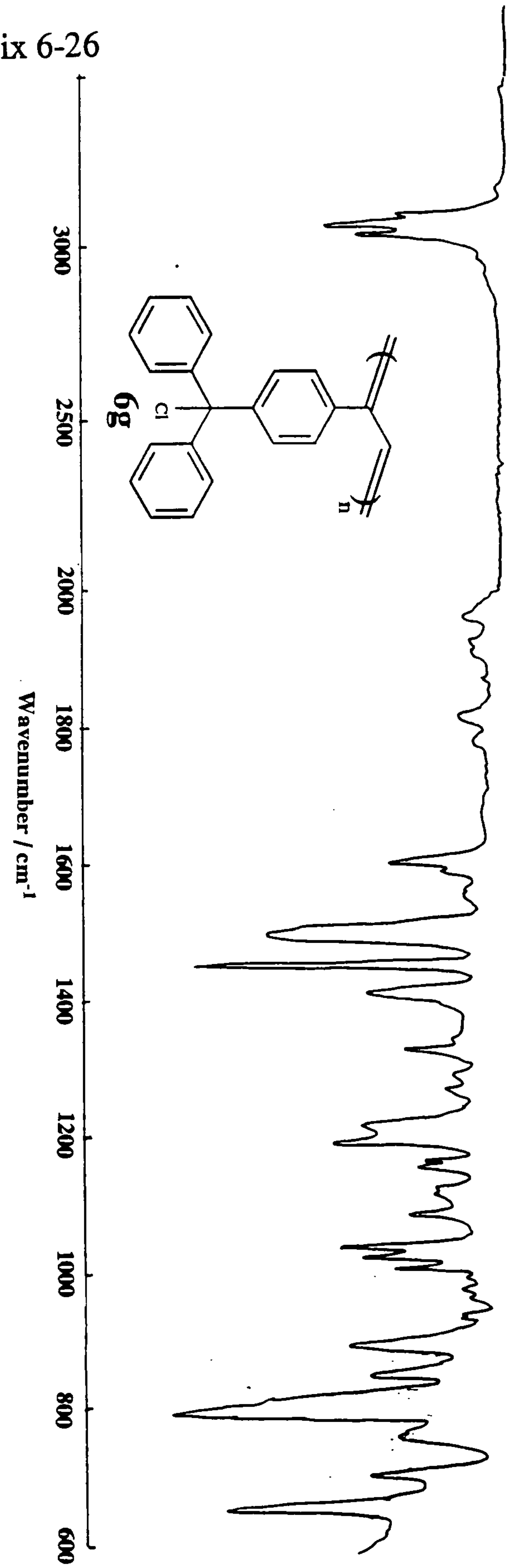


6f

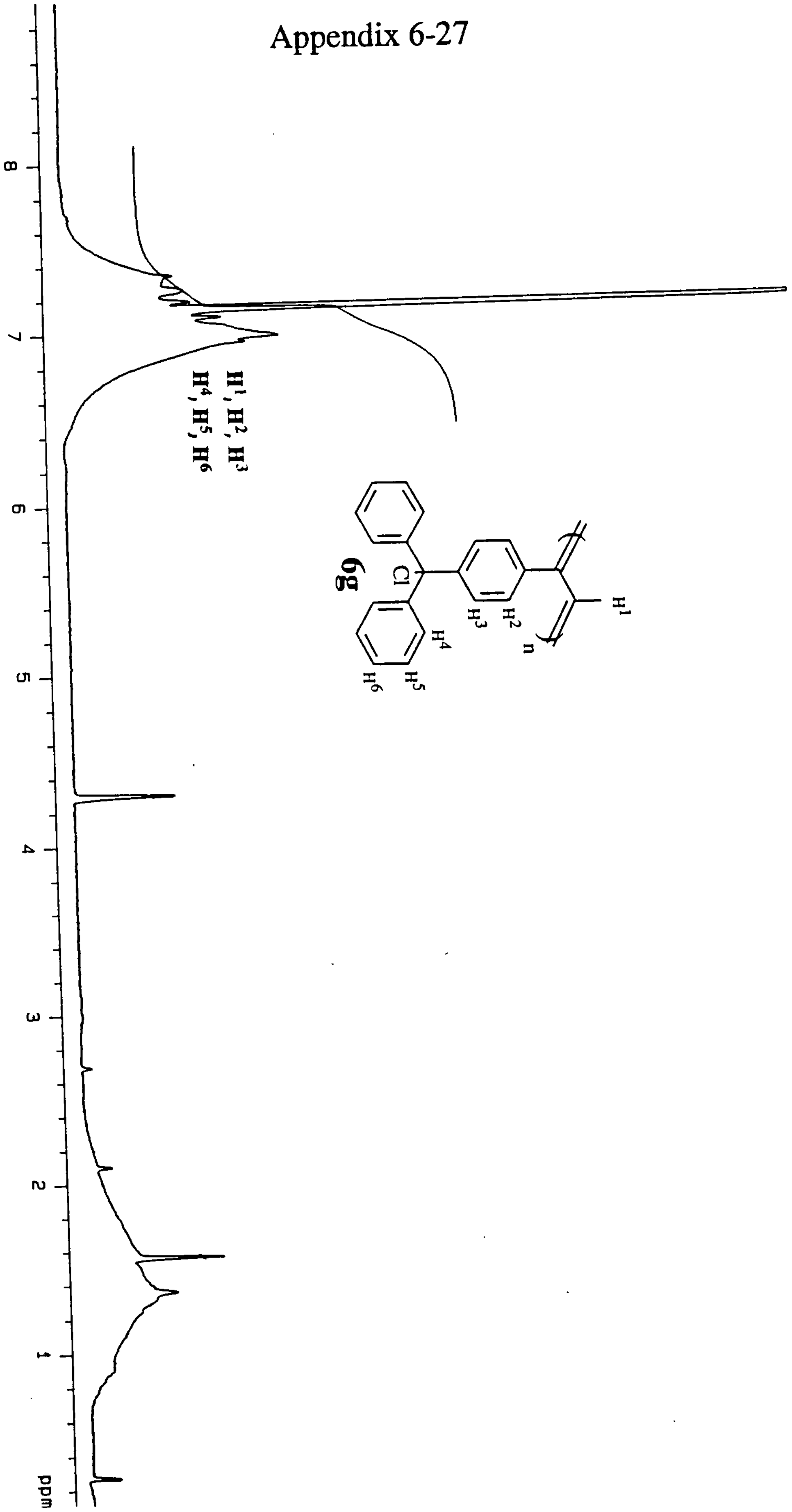
Appendix 6-25



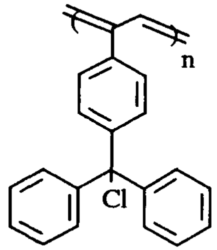
Appendix 6-26



Appendix 6-27



Appendix 6-29

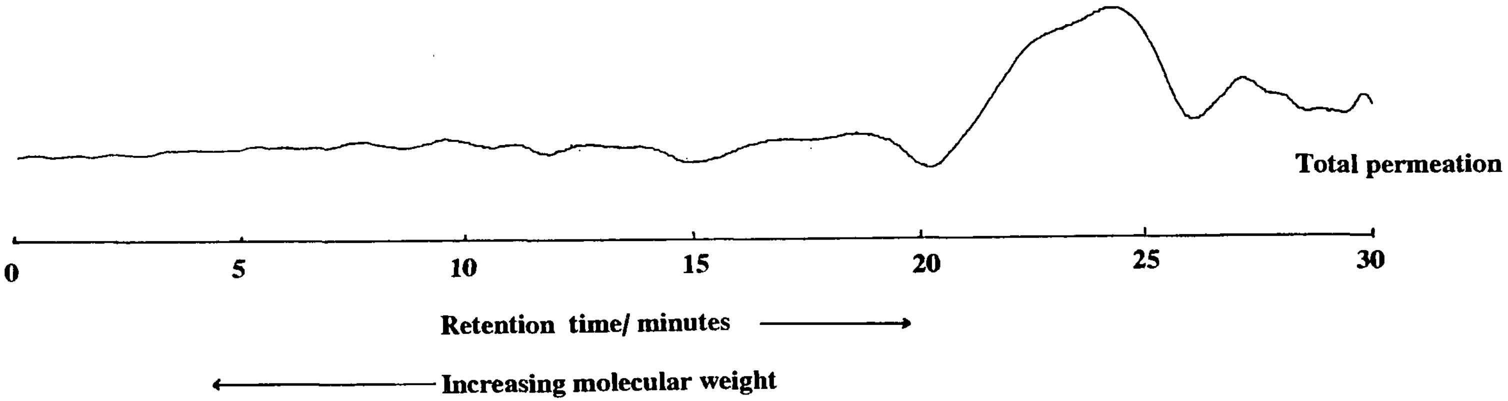


6h

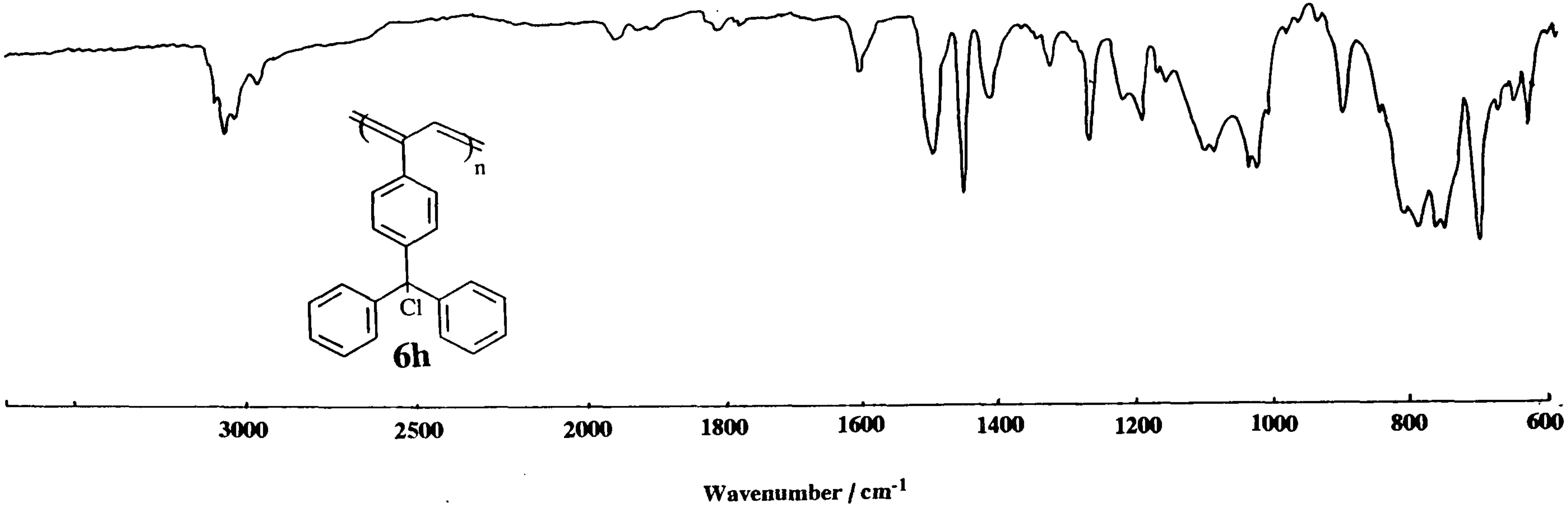
M_w = 3,040

M_n = 1760

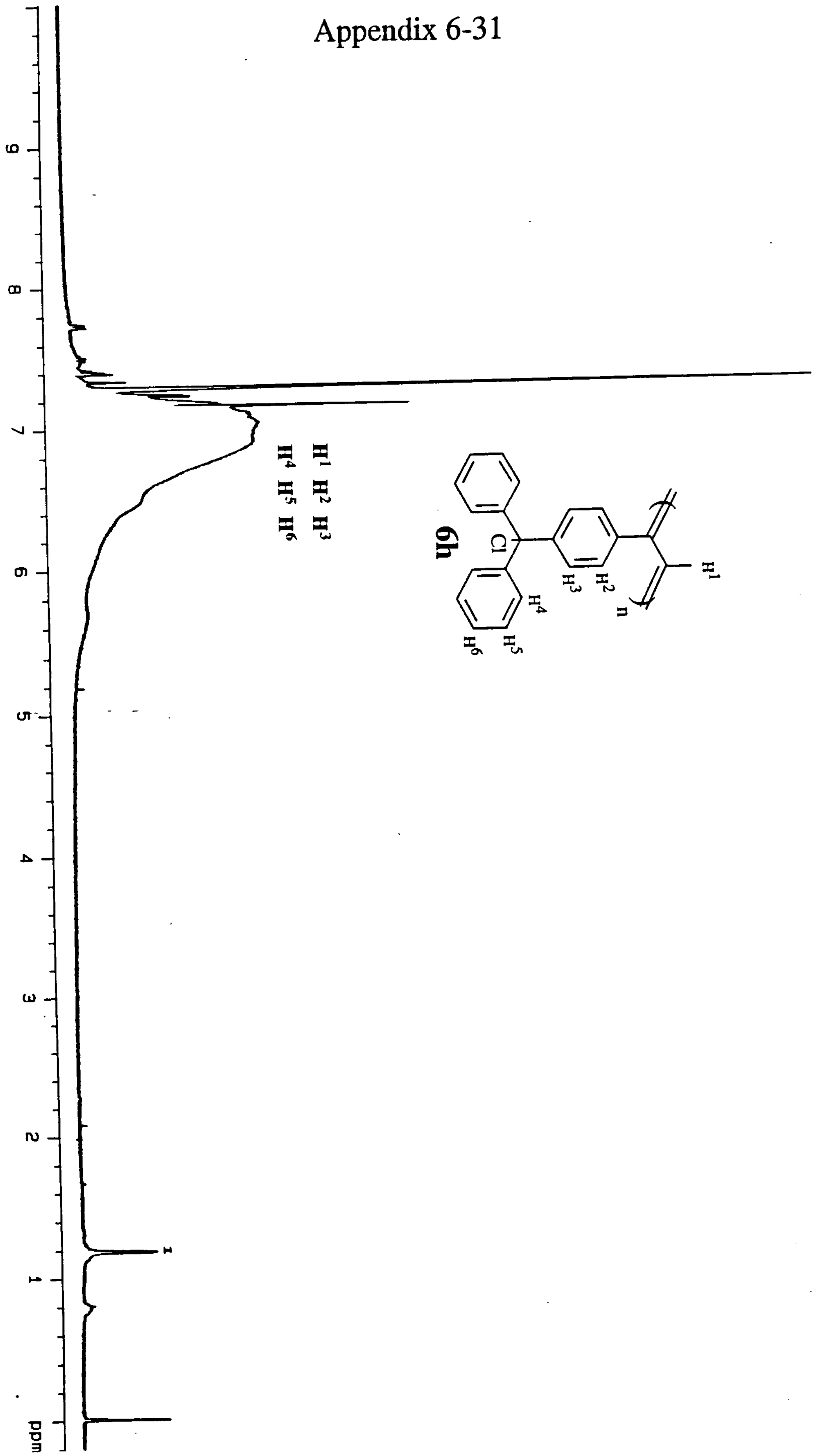
M_w / M_n = 1.7



Appendix 6-30



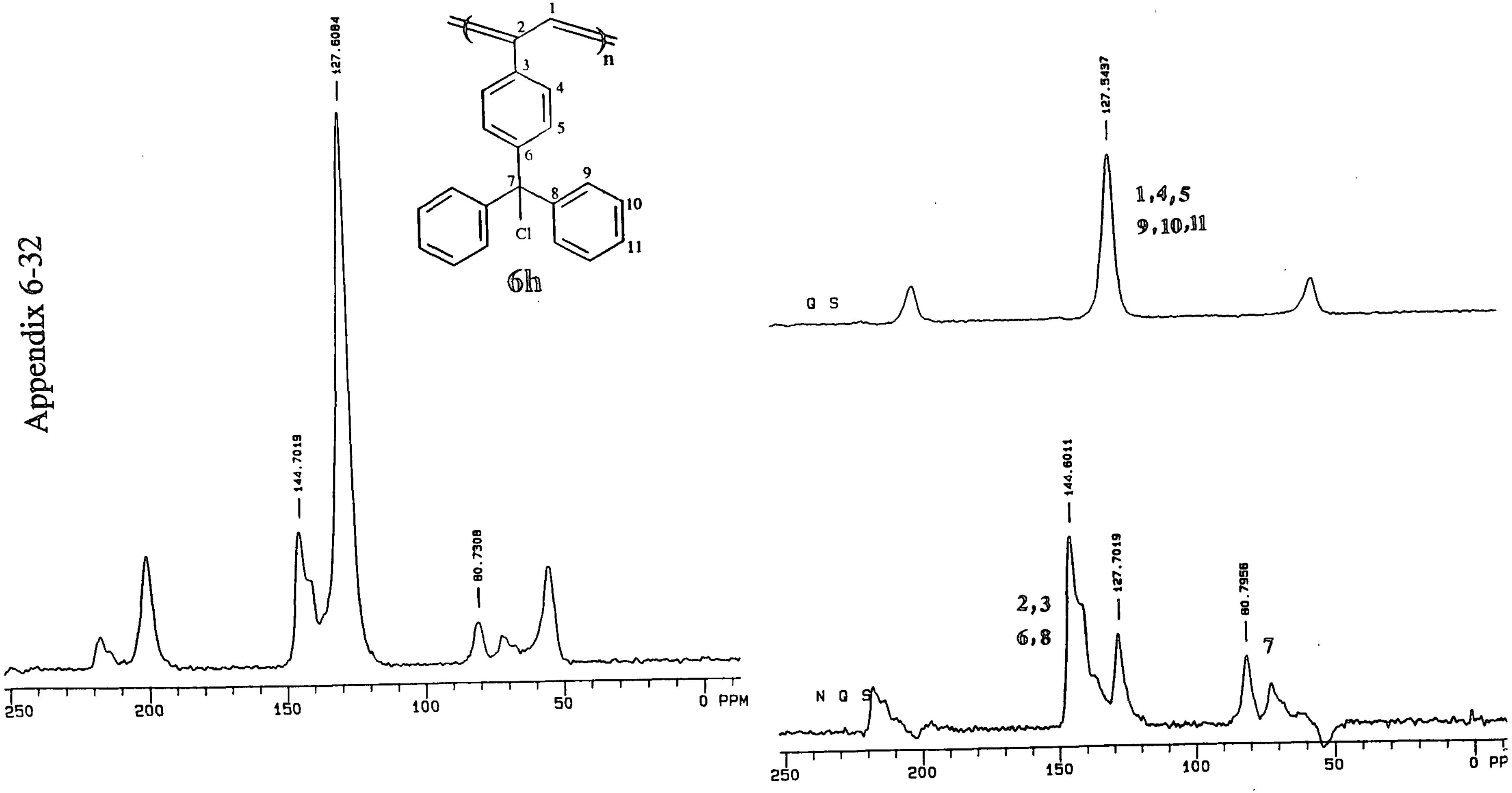
Appendix 6-31



6h

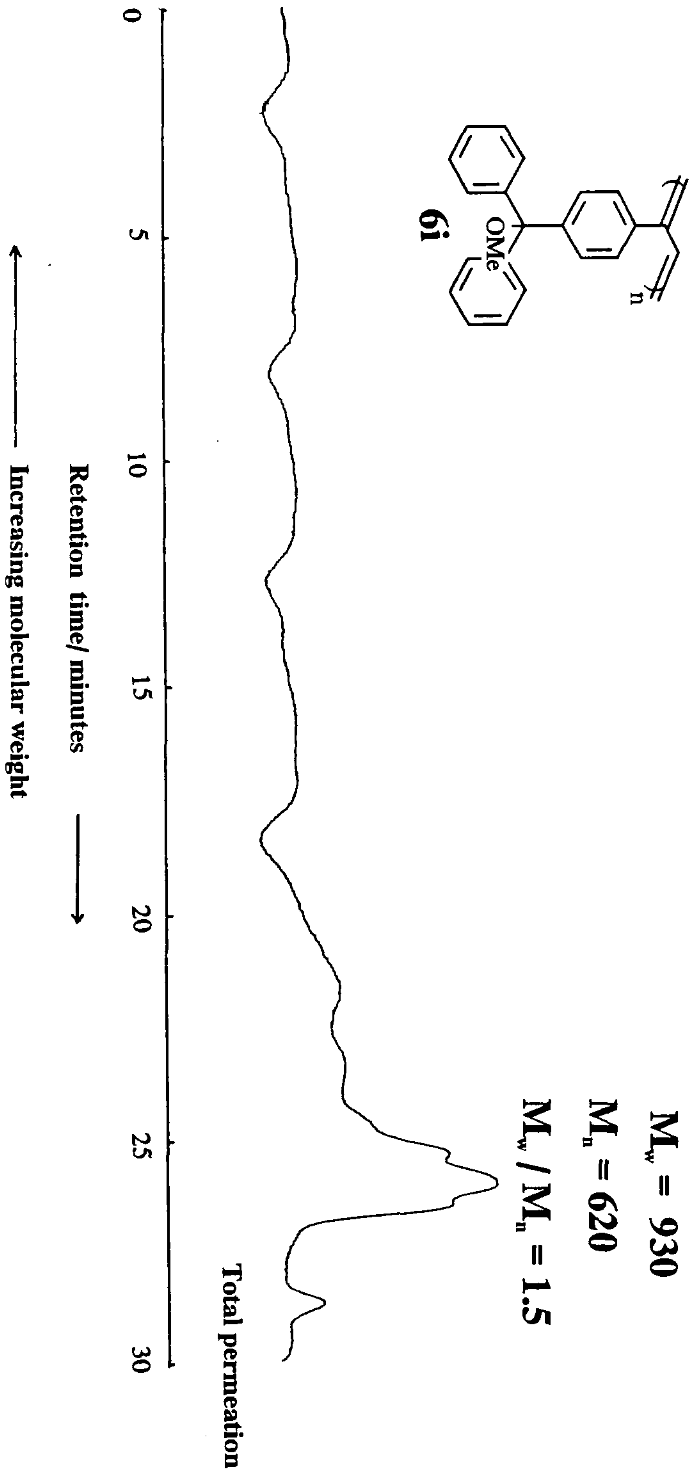
Appendix 6-32

CP/MAS ^{13}C NMR



6h

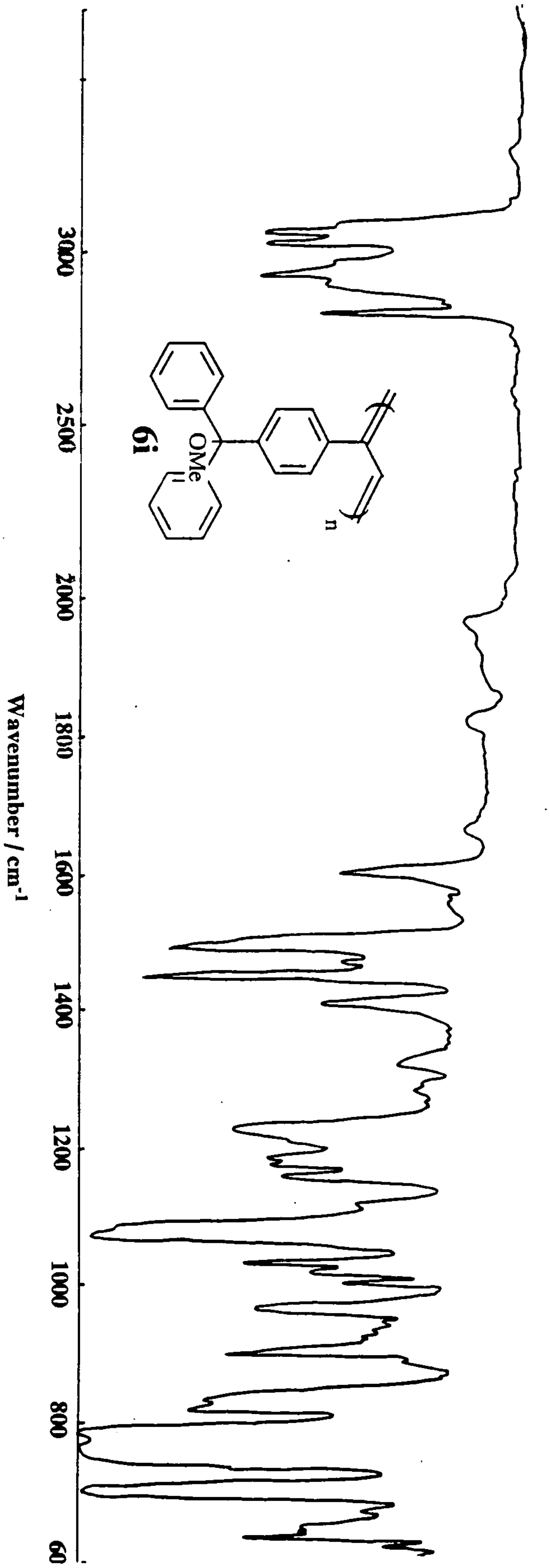
Appendix 6-33



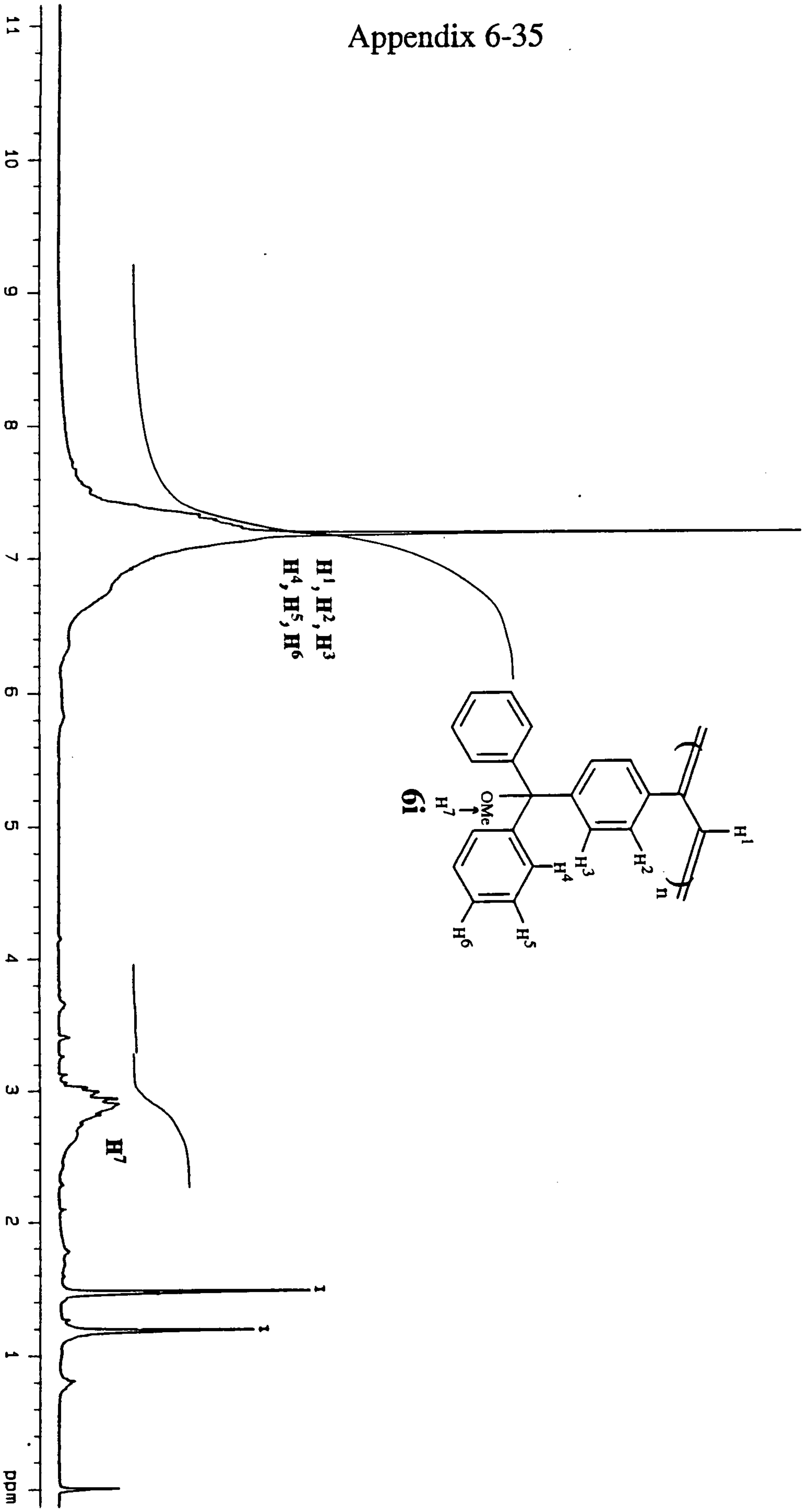
6i

M_w = 930
M_n = 620
M_w / M_n = 1.5

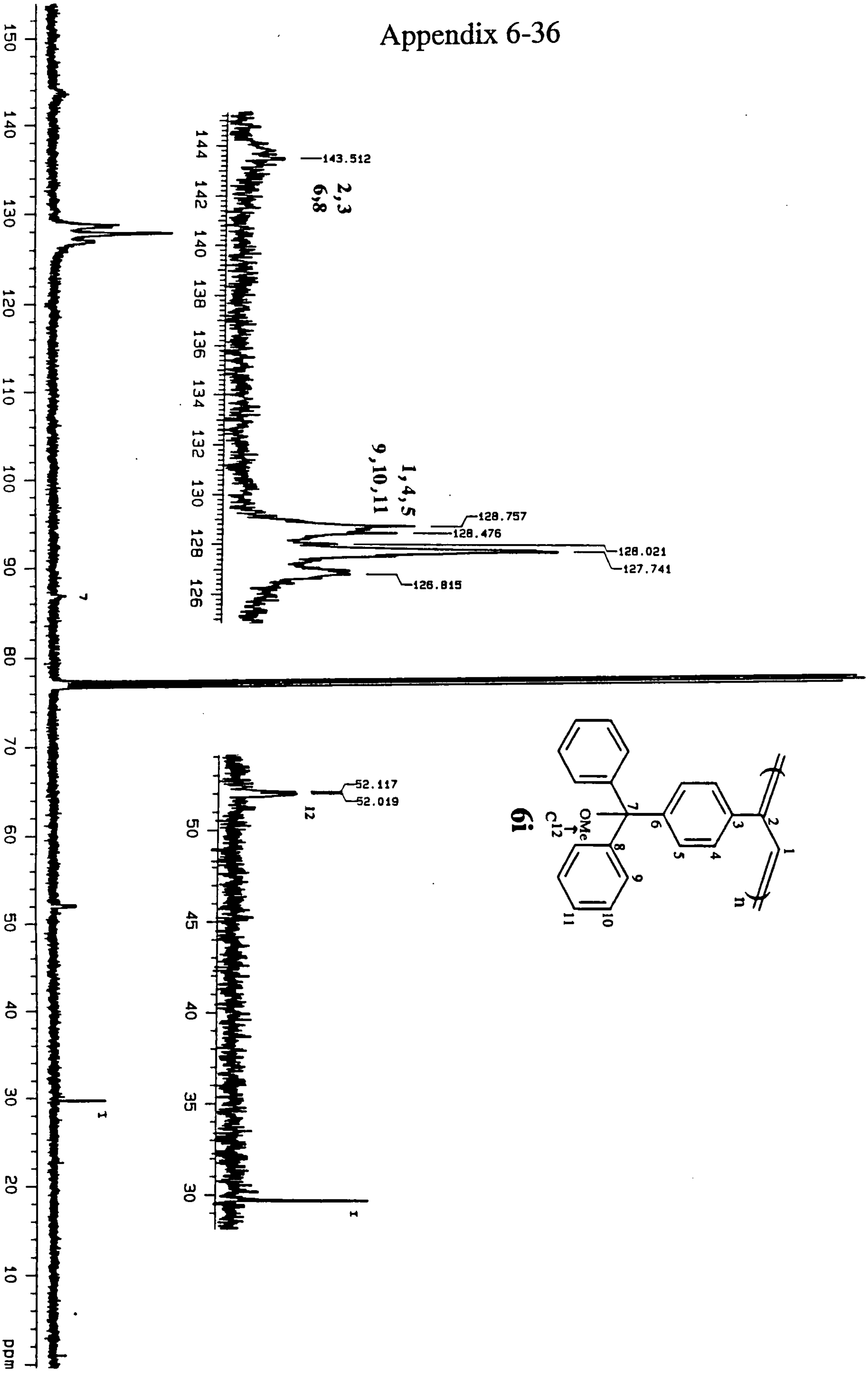
Appendix 6-34



Appendix 6-35

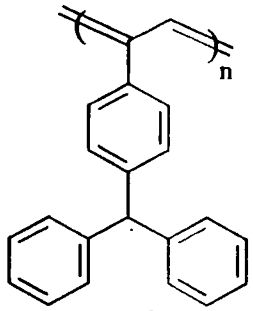


Appendix 6-36



6i

Appendix 6-37

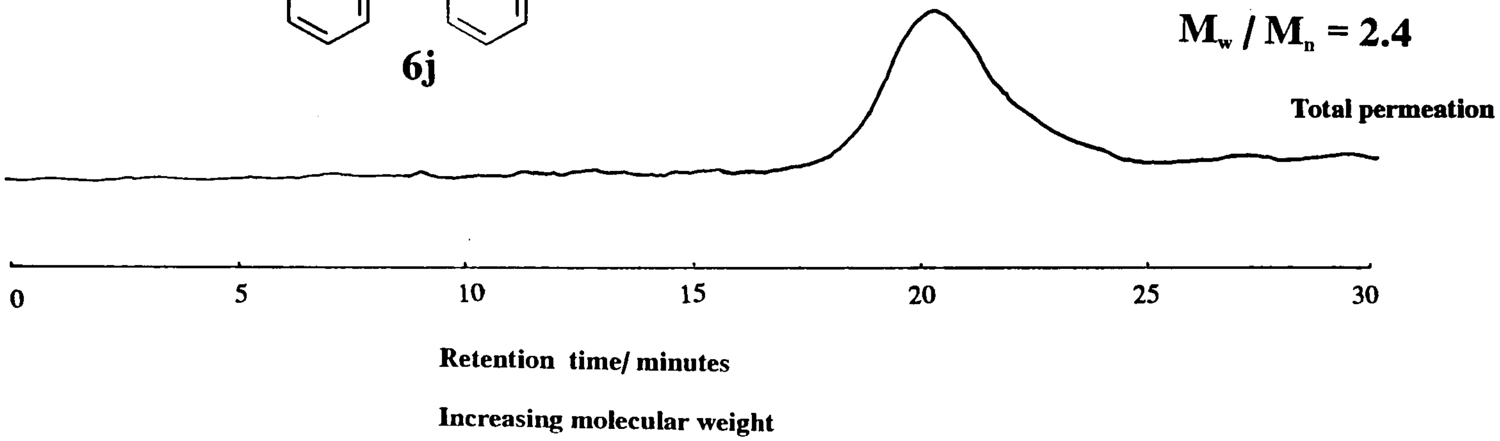


6j

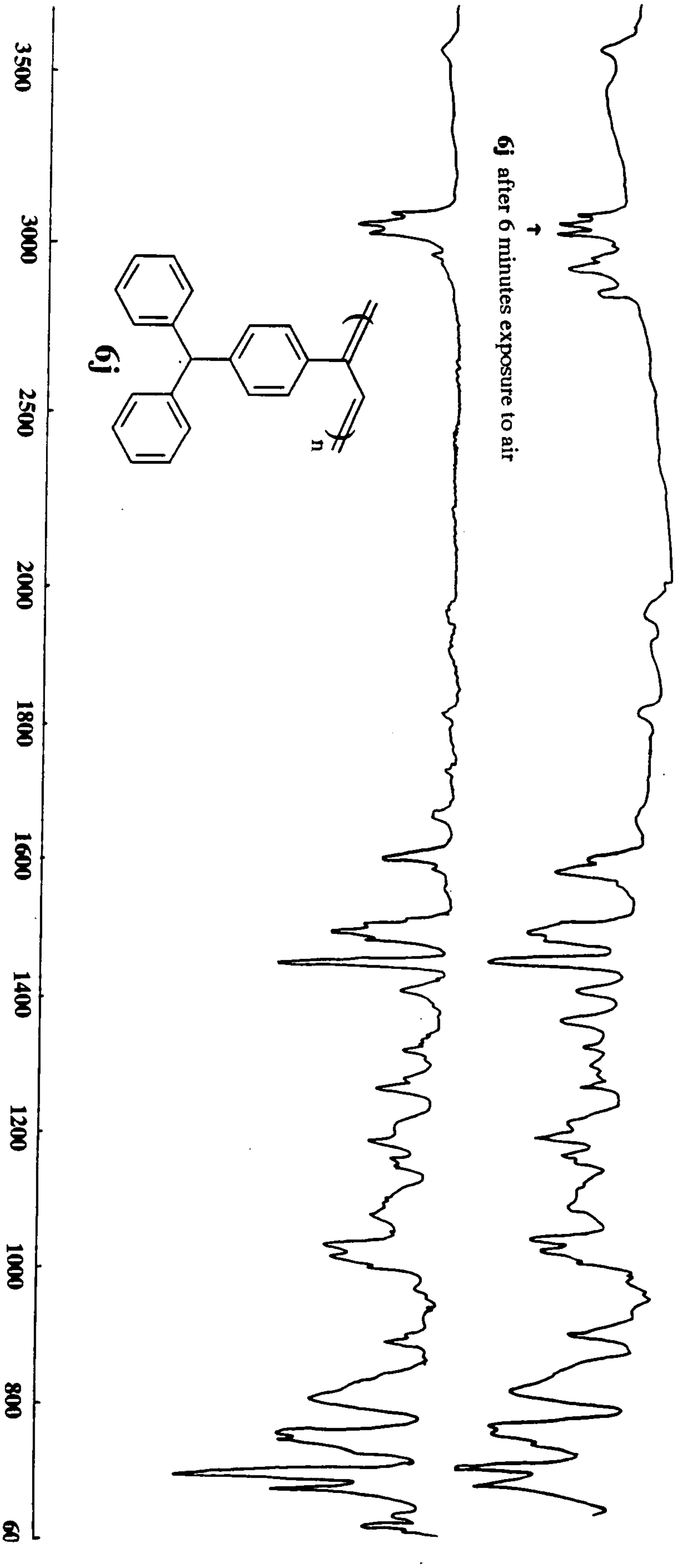
M_w = 19,600

M_n = 8000

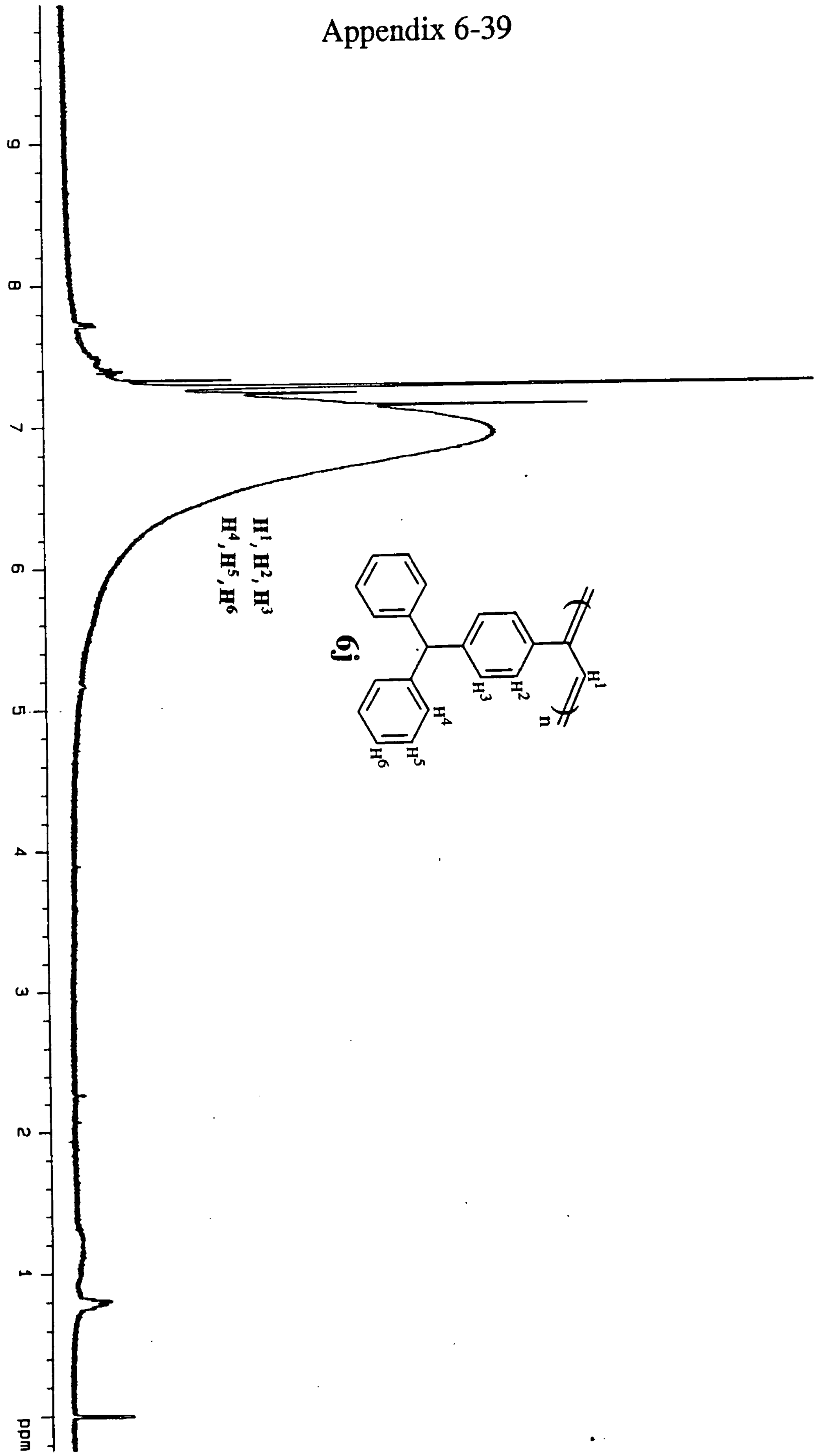
M_w / M_n = 2.4



Appendix 6-38



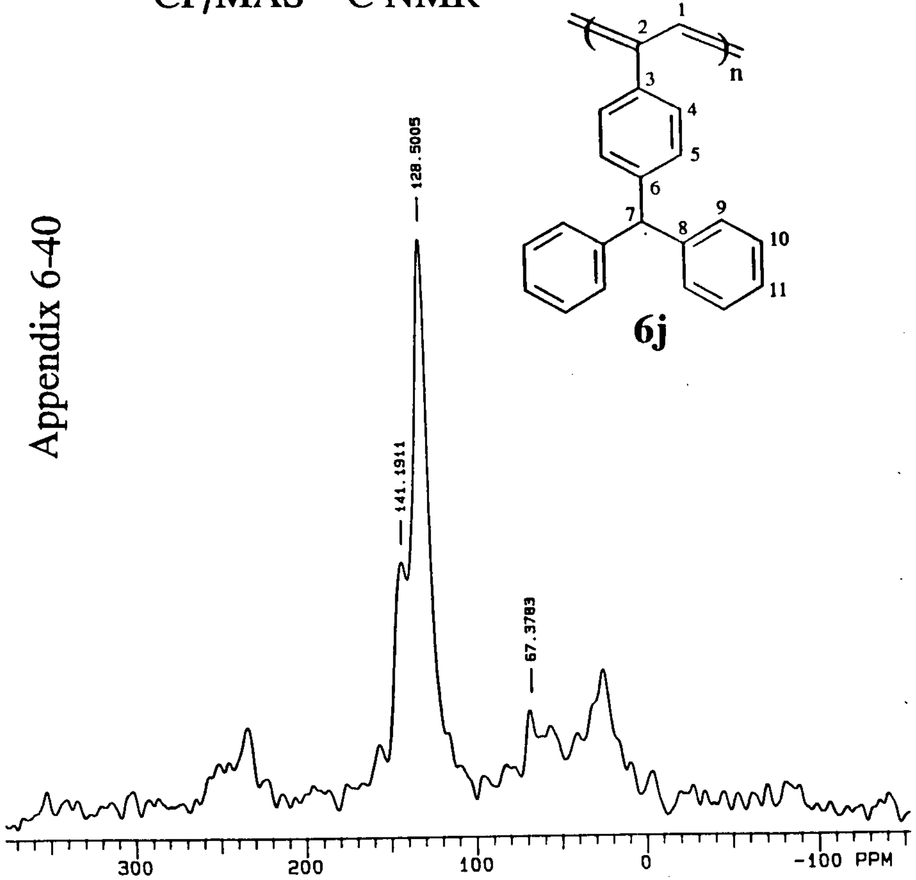
Appendix 6-39



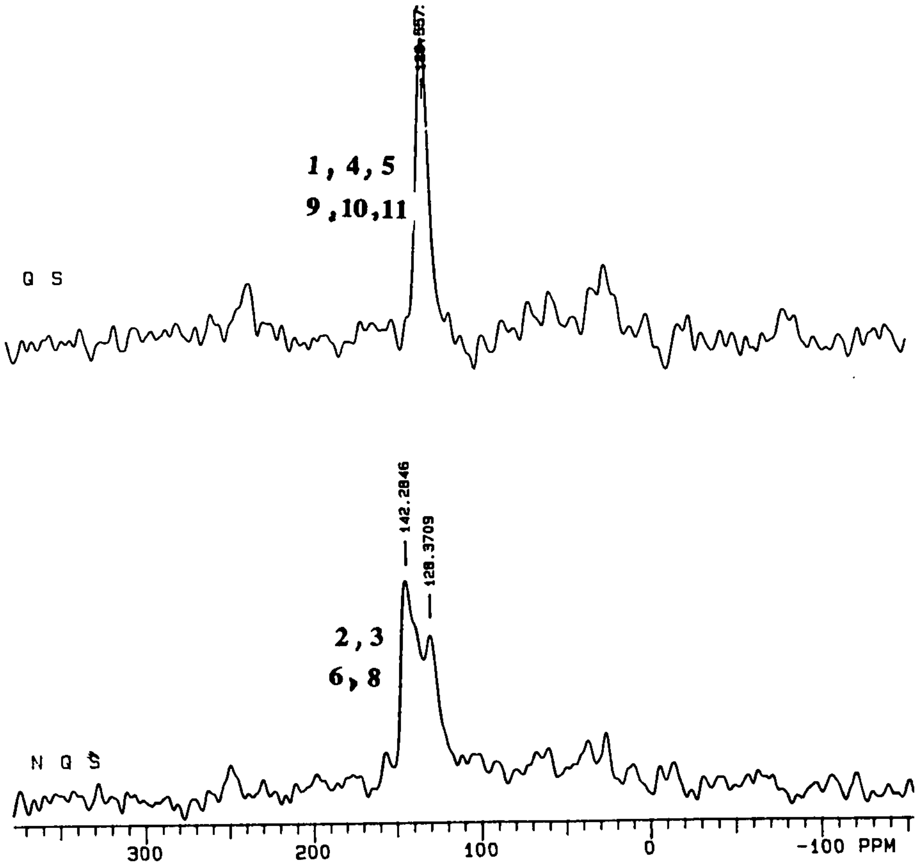
6j

Appendix 6-40

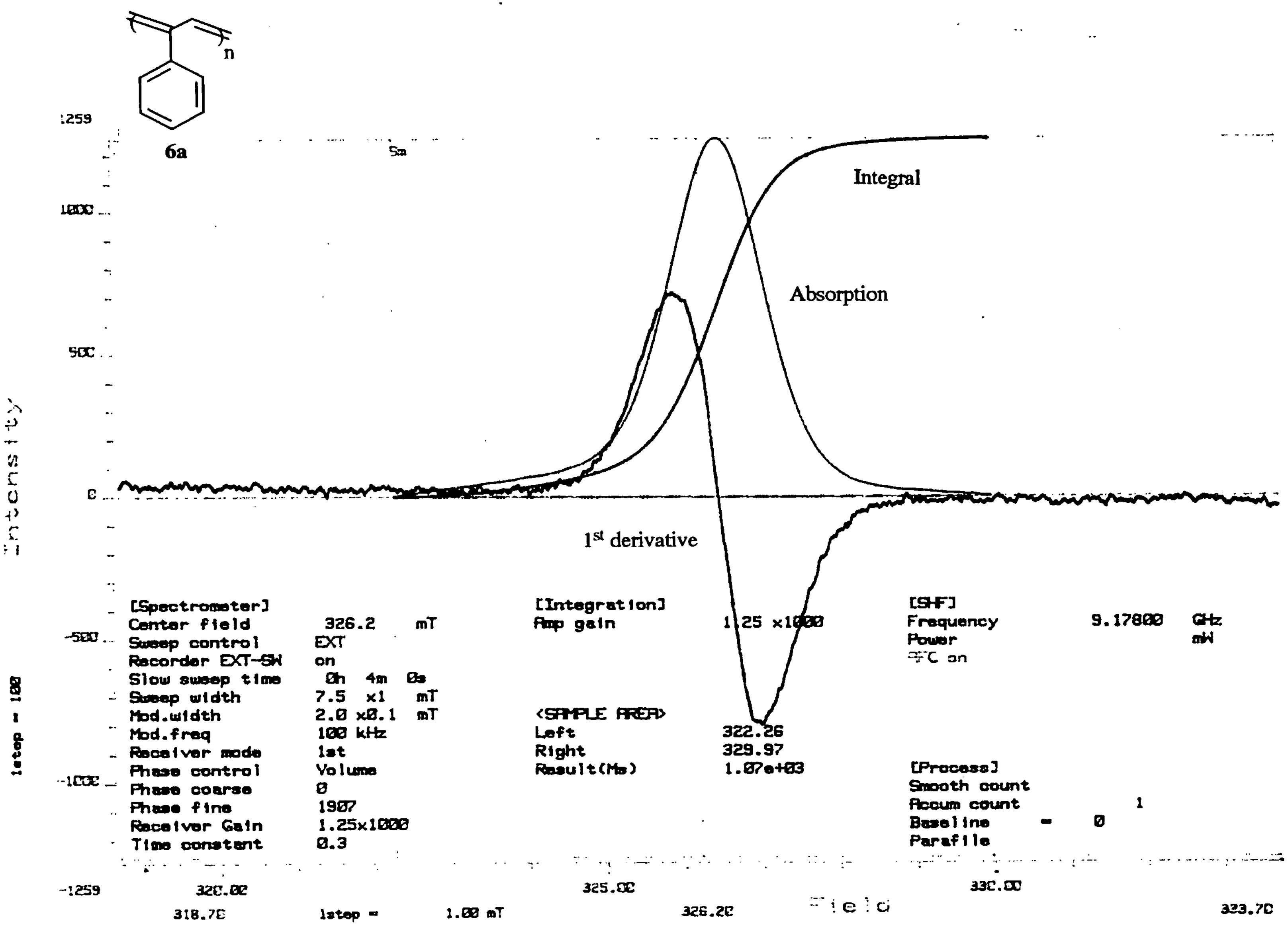
CP/MAS ^{13}C NMR



6j

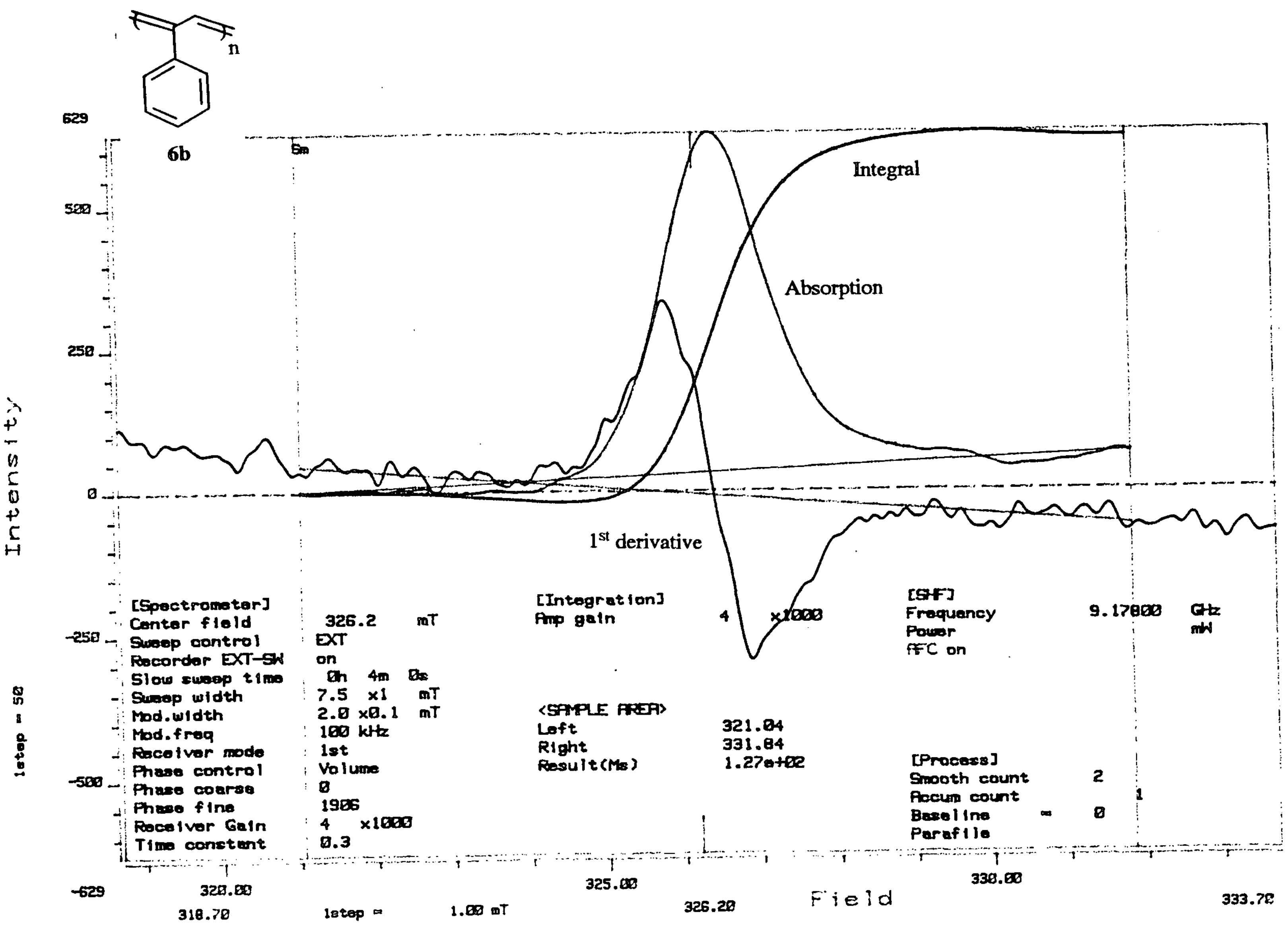


Appendix 6-41



```
[Spectrometer]
Center field        326.2    mT
Sweep control       EXT
Recorder EXT-SW     on
Slow sweep time      0h  4m  0s
Sweep width         7.5  x1    mT
Mod.width           2.0 x0.1  mT
Mod.freq            100 kHz
Receiver mode       1st
Phase control       Volume
Phase coarse        0
Phase fine          1907
Receiver Gain       1.25x1000
Time constant       0.3

[Integration]
Amp gain            1.25 x1000

<SAMPLE AREA>
Left                322.26
Right               329.97
Result(Ms)          1.07e+03

[SHF]
Frequency           9.17800   GHz
Power                         mW
AFC on

[Process]
Smooth count
Accum count                1
Baseline      =     0
Parafile

lstep =        1.00 mT
```

Appendix 6-42



[Spectrometer]
Center field 326.2 mT
Sweep control EXT
Recorder EXT-SW on
Slow sweep time 0h 4m 0s
Sweep width 7.5 x1 mT
Mod.width 2.0 x0.1 mT
Mod.freq 100 kHz
Receiver mode 1st
Phase control Volume
Phase coarse 0
Phase fine 1906
Receiver Gain 4 x1000
Time constant 0.3

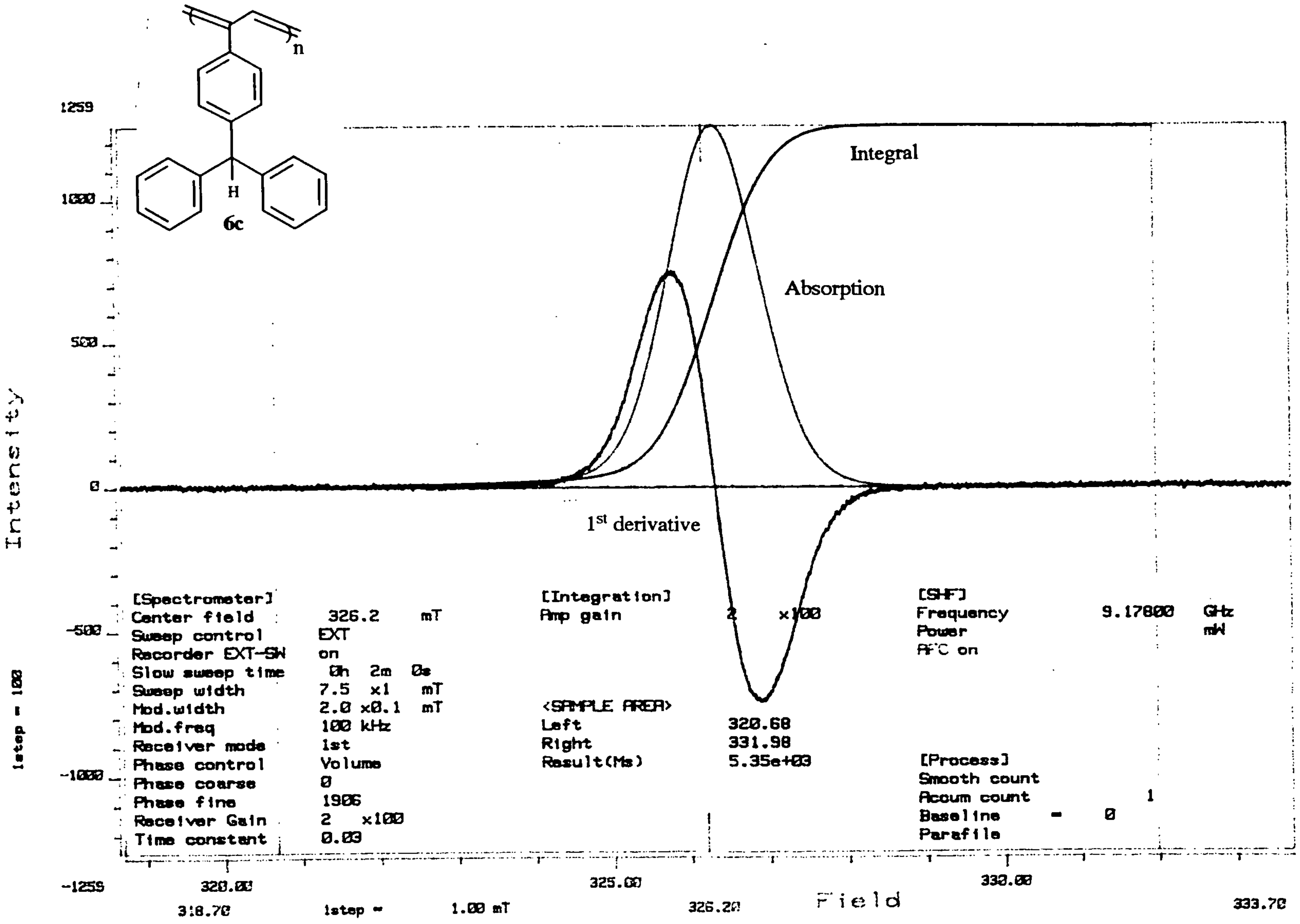
[Integration]
Amp gain 4 x1000

<SAMPLE AREA>
Left 321.04
Right 331.84
Result(Ms) 1.27e+02

[SHF]
Frequency 9.17800 GHz
Power mW
AFC on

[Process]
Smooth count 2
Accum count 1
Baseline = 0
Parafile

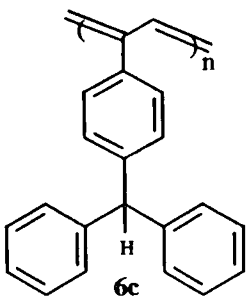
Appendix 6-43



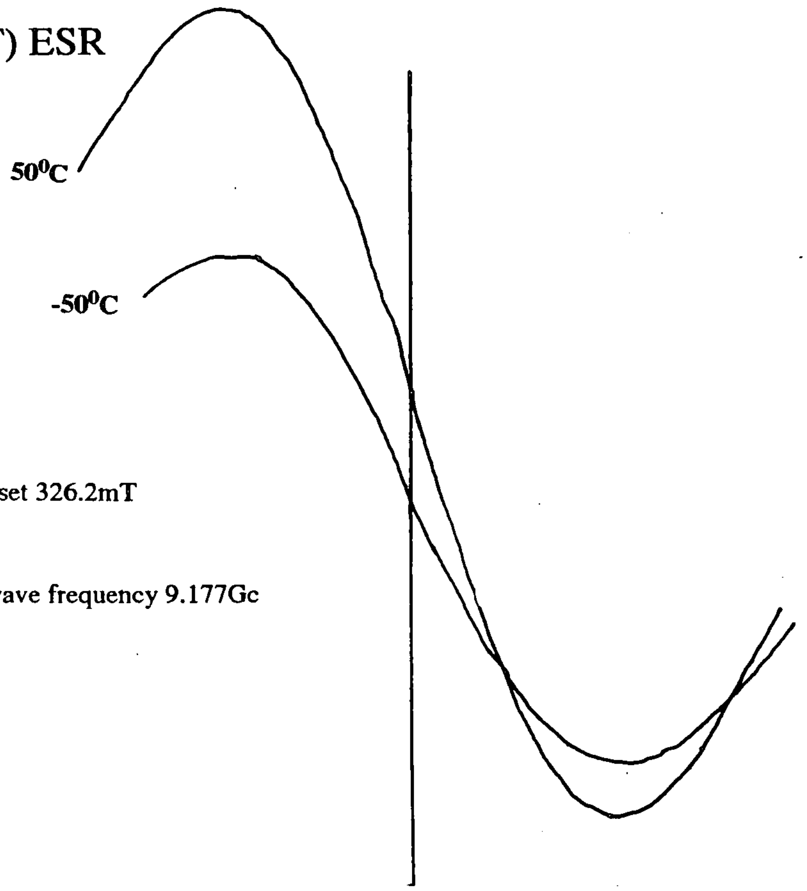
```
[Spectrometer]
Center field        326.2    mT
Sweep control       EXT
Recorder EXT-SW     on
Slow sweep time      0h  2m  0s
Sweep width         7.5  x1   mT
Mod.width           2.0 x0.1  mT
Mod.freq            100 kHz
Receiver mode       1st
Phase control       Volume
Phase coarse        0
Phase fine          1906
Receiver Gain       2   x100
Time constant       0.03

[Integration]
Amp gain                 2     x100

<SAMPLE AREA>
Left                     320.68
Right                    331.98
Result(Ms)               5.35e+03

[SHF]
Frequency           9.17800   GHz
Power                         mW
AFC on

[Process]
Smooth count
Accum count                1
Baseline        -     0
Parafile
```

Appendix 6-43i

Variable Temperature (VT) ESR



6c



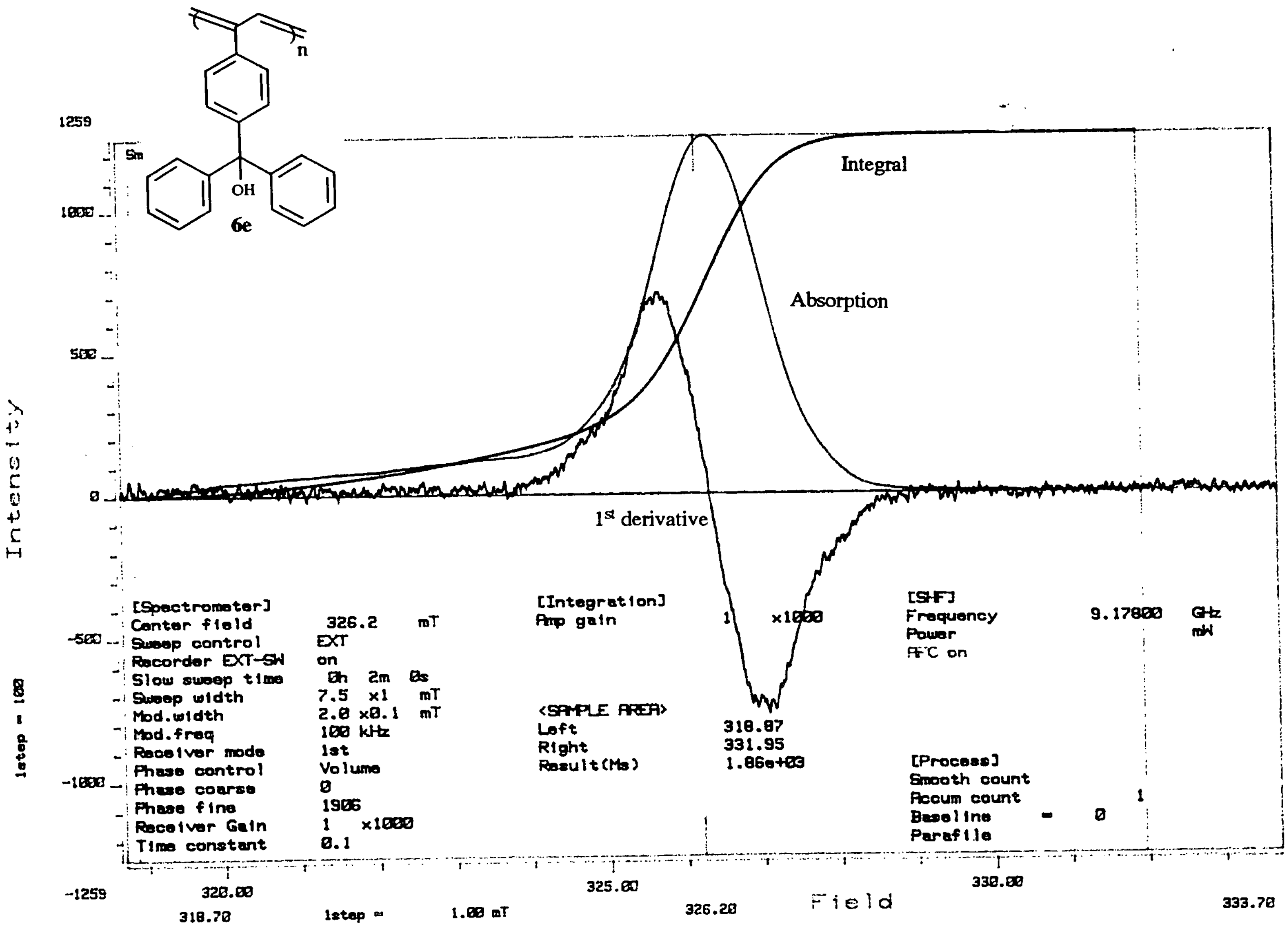
Time constant 0.1s Centre field set 326.2mT

Modulation frequency 100k cps

Microwave power 1mW Microwave frequency 9.177Gc

Receiver gain 1•100

Appendix 6-44



[Spectrometer]
Center field 326.2 mT
Sweep control EXT
Recorder EXT-SW on
Slow sweep time 0h 2m 0s
Sweep width 7.5 x1 mT
Mod.width 2.0 x0.1 mT
Mod.freq 100 kHz
Receiver mode 1st
Phase control Volume
Phase coarse 0
Phase fine 1906
Receiver Gain 1 x1000
Time constant 0.1

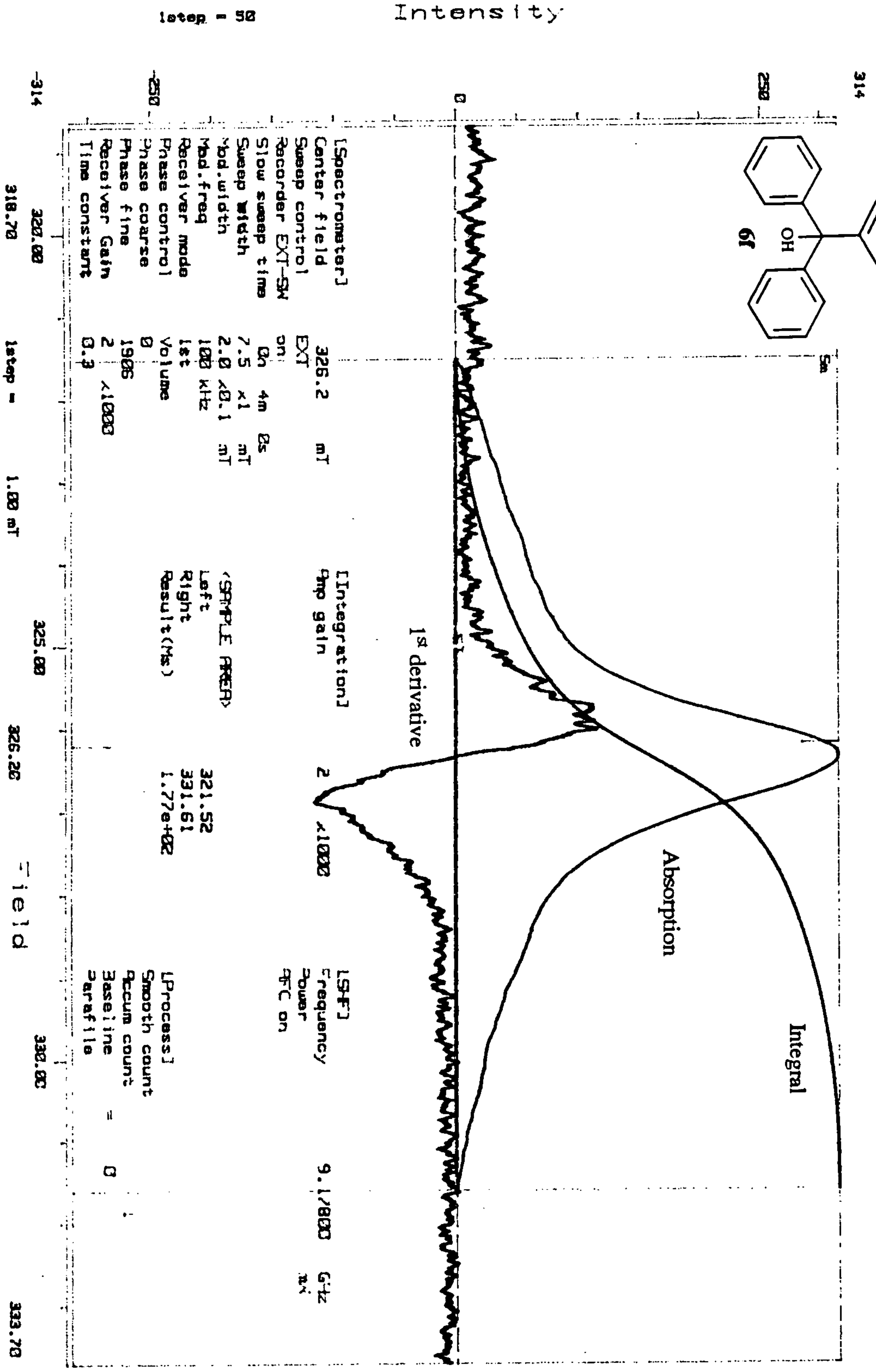
[Integration]
Amp gain 1 x1000

<SAMPLE AREA>
Left 318.87
Right 331.95
Result(Ms) 1.86e+03

[SHF]
Frequency 9.17800 GHz
Power mW
AFC on

[Process]
Smooth count
Accum count 1
Baseline = 0
Parafile

Appendix 6-45



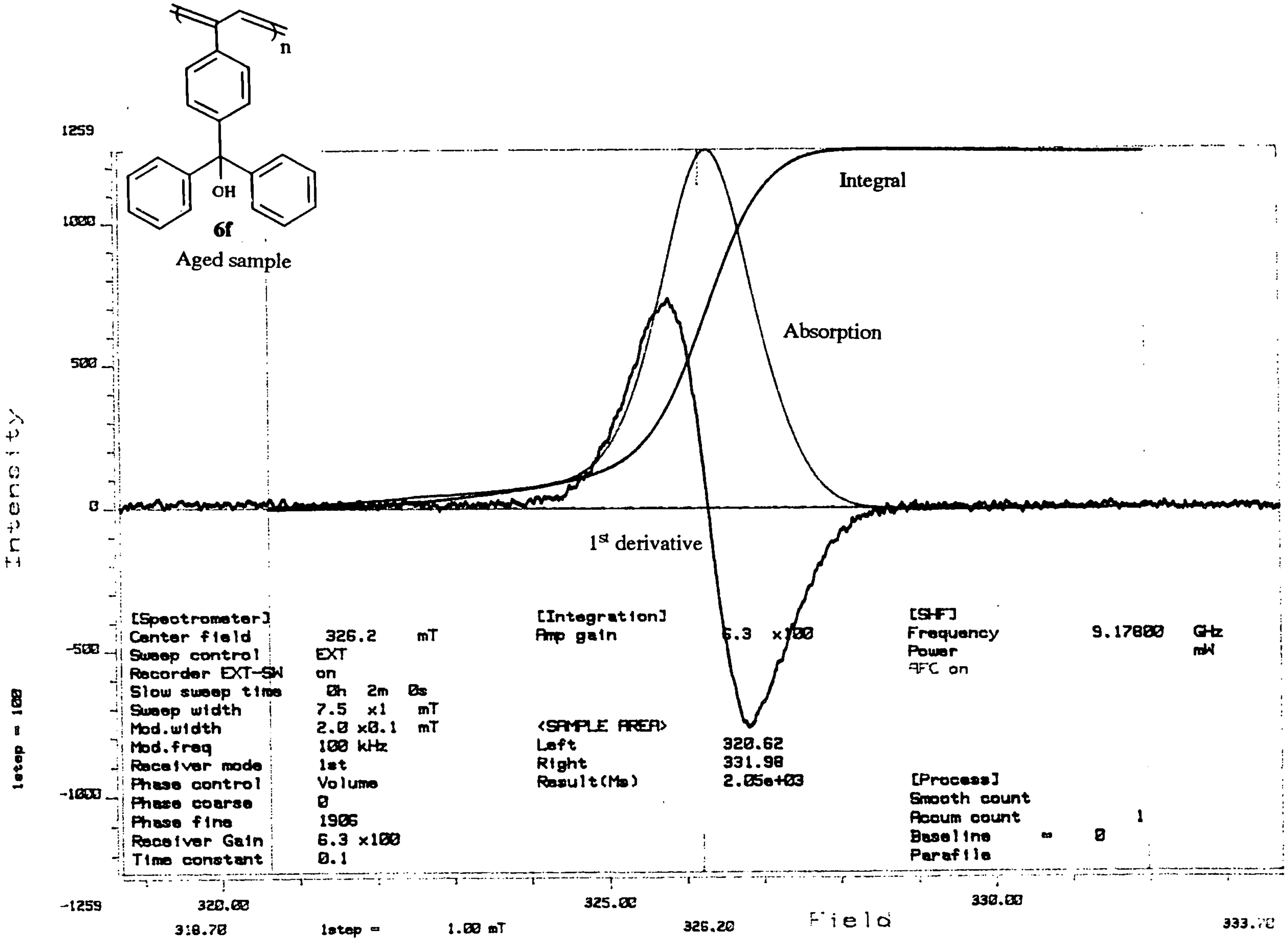
[Spectrometer]
Center field 326.2 mT
Sweep control EXT
Recorder EXT-SW on
Slow sweep time On 4m 0s
Sweep width 7.5 x1 mT
Mod.width 2.0 x0.1 mT
Mod.freq 100 kHz
Receiver mode 1st
Phase control Volume
Phase coarse 0
Phase fine 1906
Receiver Gain 2 x1000
Time constant 0.3

[Integration]
Amp gain 2 x1000
<SAMPLE AREA>
Left 321.52
Right 331.61
Result(Ms) 1.77e+02

[SHF]
Frequency 9.17800 GHz
Power mW
AFC on

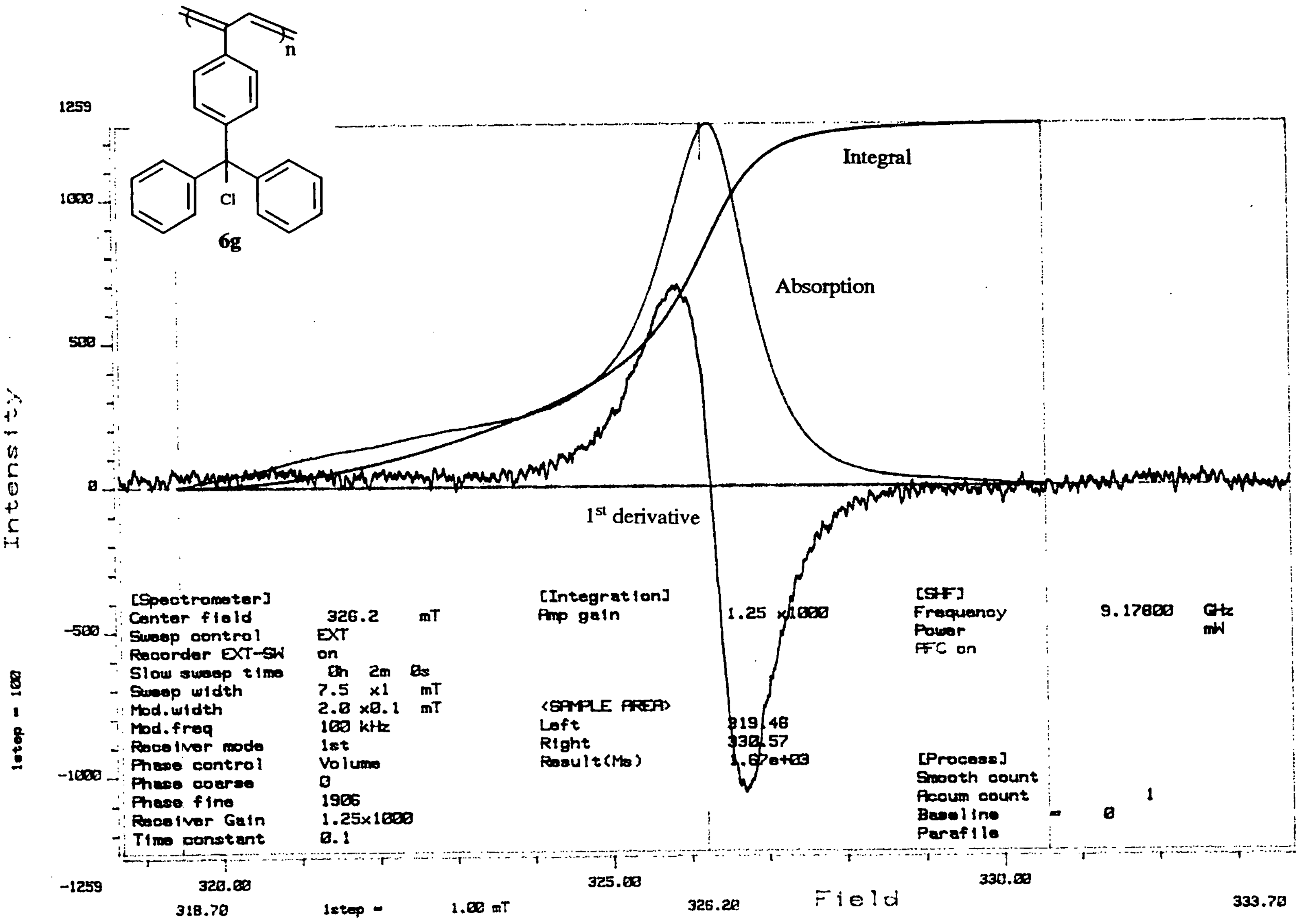
[Process]
Smooth count
Accum count
Baseline = 0
Parafile

Appendix 6-45i



```
[Spectrometer]                              [Integration]                    [SHF]
Center field       326.2    mT              Amp gain         6.3  x100       Frequency       9.17800   GHz
Sweep control      EXT                                                       Power                     mW
Recorder EXT-SW    on                                                        AFC on
Slow sweep time     0h  2m  0s
Sweep width        7.5  x1   mT
Mod.width          2.0 x0.1  mT             <SAMPLE AREA>
Mod.freq           100 kHz                  Left             320.62
Receiver mode      1st                      Right            331.98
Phase control      Volume                   Result(Ms)       2.05e+03        [Process]
Phase coarse       0                                                         Smooth count
Phase fine         1906                                                      Accum count          1
Receiver Gain      6.3 x100                                                  Baseline     =  0
Time constant      0.1                                                       Parafile
```

Appendix 6-46



6g

[Spectrometer]
Center field 326.2 mT
Sweep control EXT
Recorder EXT-SW on
Slow sweep time 0h 2m 0s
Sweep width 7.5 x1 mT
Mod.width 2.0 x0.1 mT
Mod.freq 100 kHz
Receiver mode 1st
Phase control Volume
Phase coarse 0
Phase fine 1906
Receiver Gain 1.25x1000
Time constant 0.1

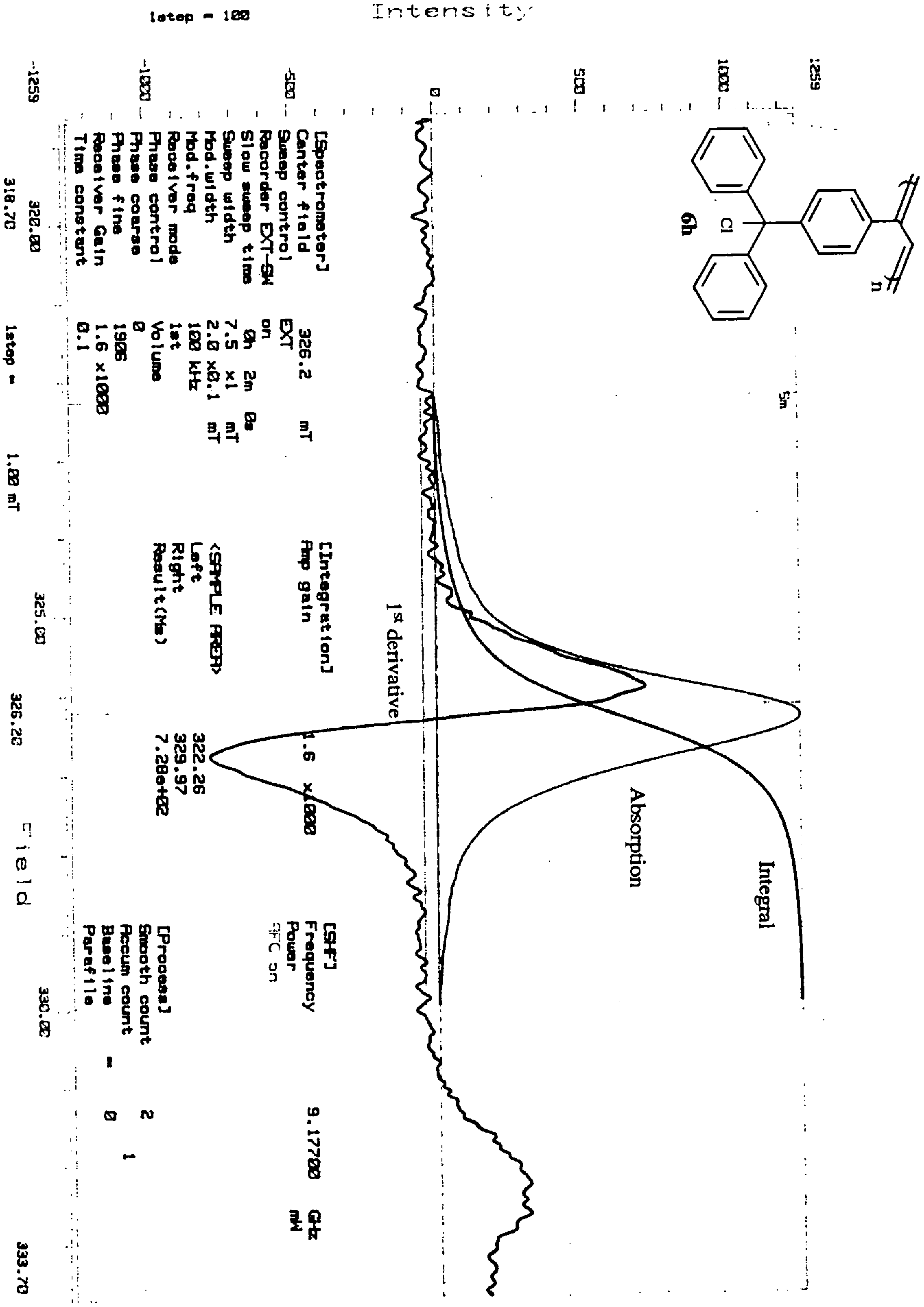
[Integration]
Amp gain 1.25 x1000

<SAMPLE AREA>
Left 319.48
Right 330.57
Result(Ms) 1.67e+03

[SHF]
Frequency 9.17800 GHz
Power mW
AFC on

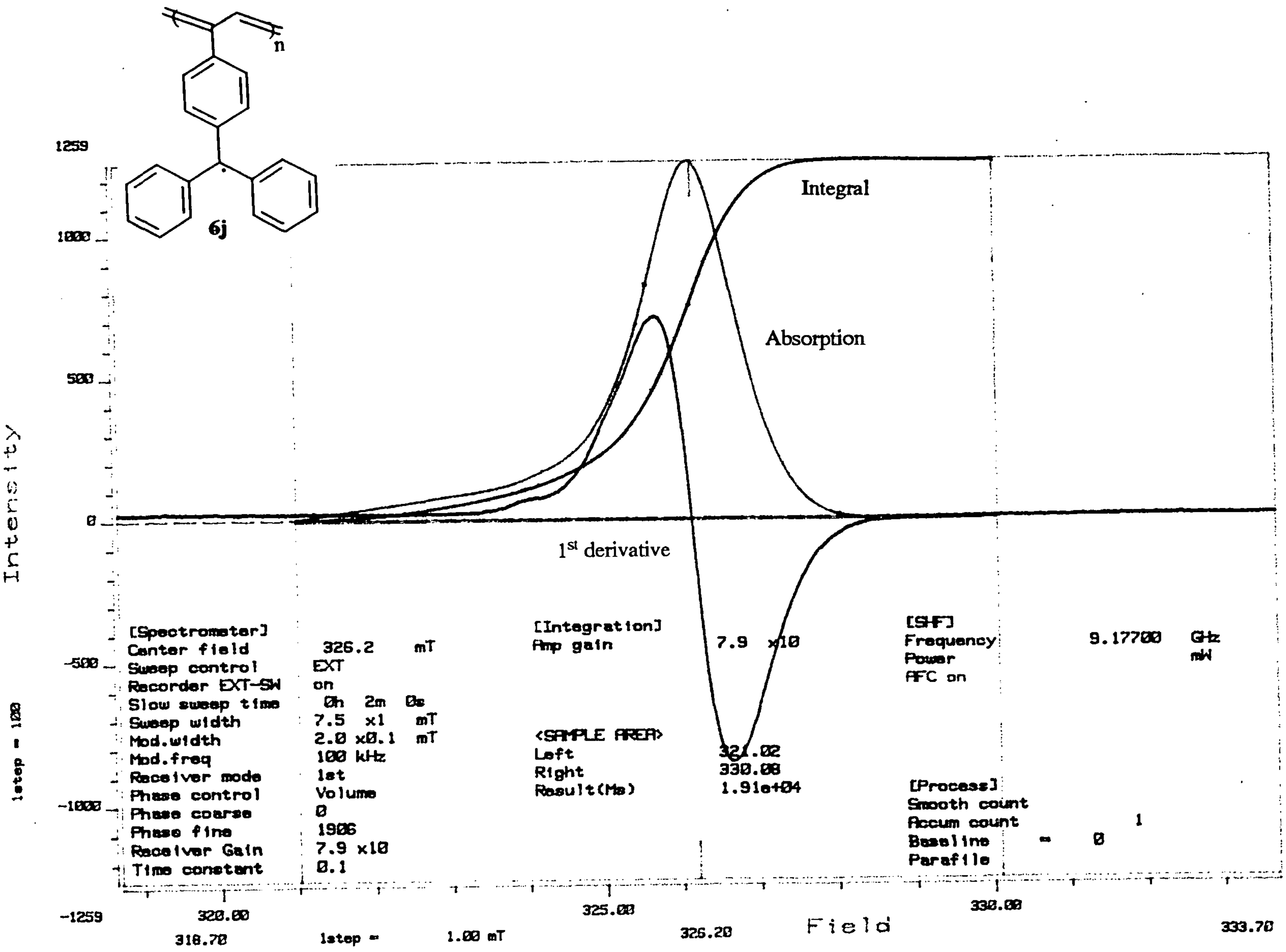
[Process]
Smooth count
Accum count 1
Baseline = 0
Parafile

Appendix 6-47



```
[Spectrometer]
Center field        326.2    mT
Sweep control       EXT
Recorder EXT-SW     on
Slow sweep time      0h  2m  0s
Sweep width         7.5  x1   mT
Mod.width           2.0 x0.1  mT
Mod.freq            100 kHz
Receiver mode       1st
Phase control       Volume
Phase coarse        0
Phase fine          1906
Receiver Gain       1.6 x1000
Time constant       0.1

[Integration]
Amp gain            1.6  x1000

<SAMPLE AREA>
Left                322.26
Right               329.97
Result(Ms)          7.28e+02

[SHF]
Frequency           9.17700   GHz
Power                         mW
AFC on

[Process]
Smooth count        2
Accum count           1
Baseline      =     0
Parafile
```

Appendix 6-48



[Spectrometer]
Center field 326.2 mT
Sweep control EXT
Recorder EXT-SW on
Slow sweep time 0h 2m 0s
Sweep width 7.5 x1 mT
Mod.width 2.0 x0.1 mT
Mod.freq 100 kHz
Receiver mode 1st
Phase control Volume
Phase coarse 0
Phase fine 1906
Receiver Gain 7.9 x10
Time constant 0.1

[Integration]
Amp gain 7.9 x10

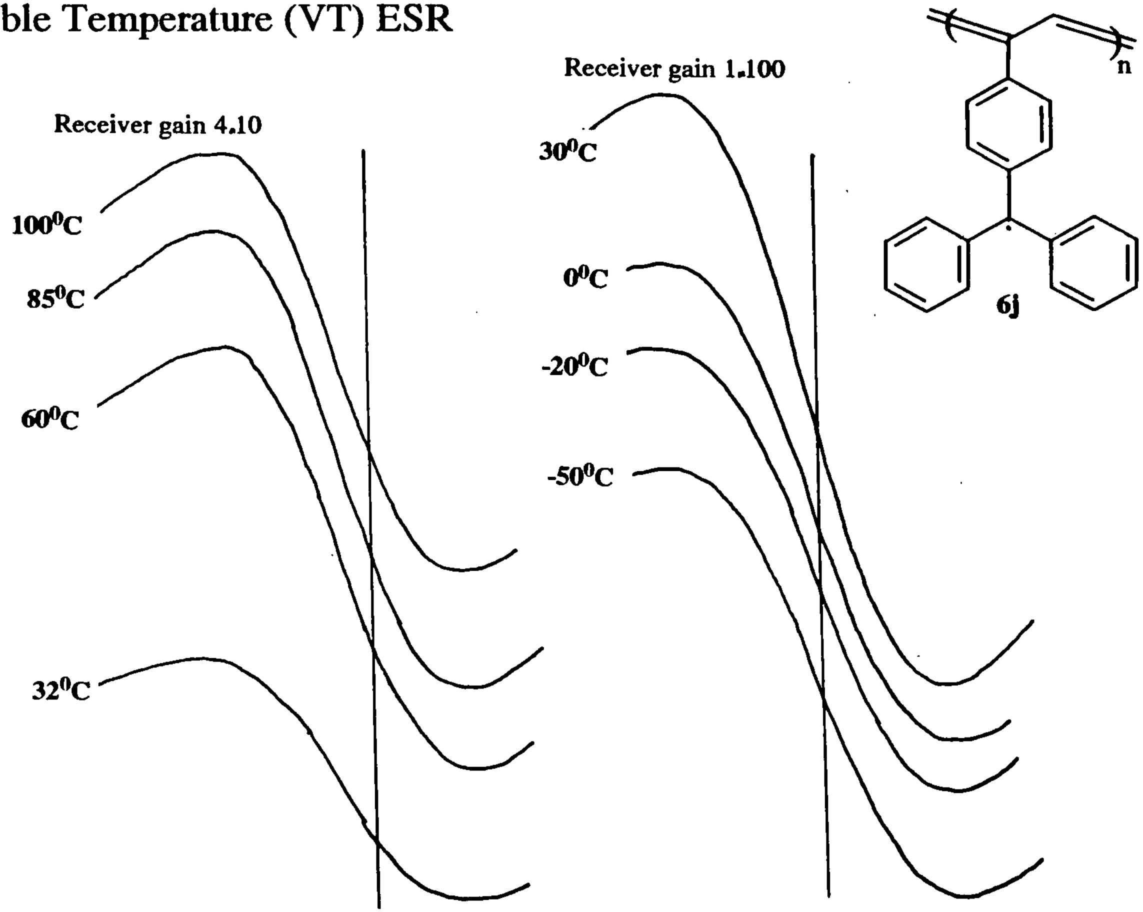
<SAMPLE AREA>
Left 321.02
Right 330.08
Result(Ms) 1.91e+04

[SHF]
Frequency 9.17700 GHz
Power mW
AFC on

[Process]
Smooth count 1
Accum count
Baseline = 0
Parafile

Appendix 6-48i

Variable Temperature (VT) ESR

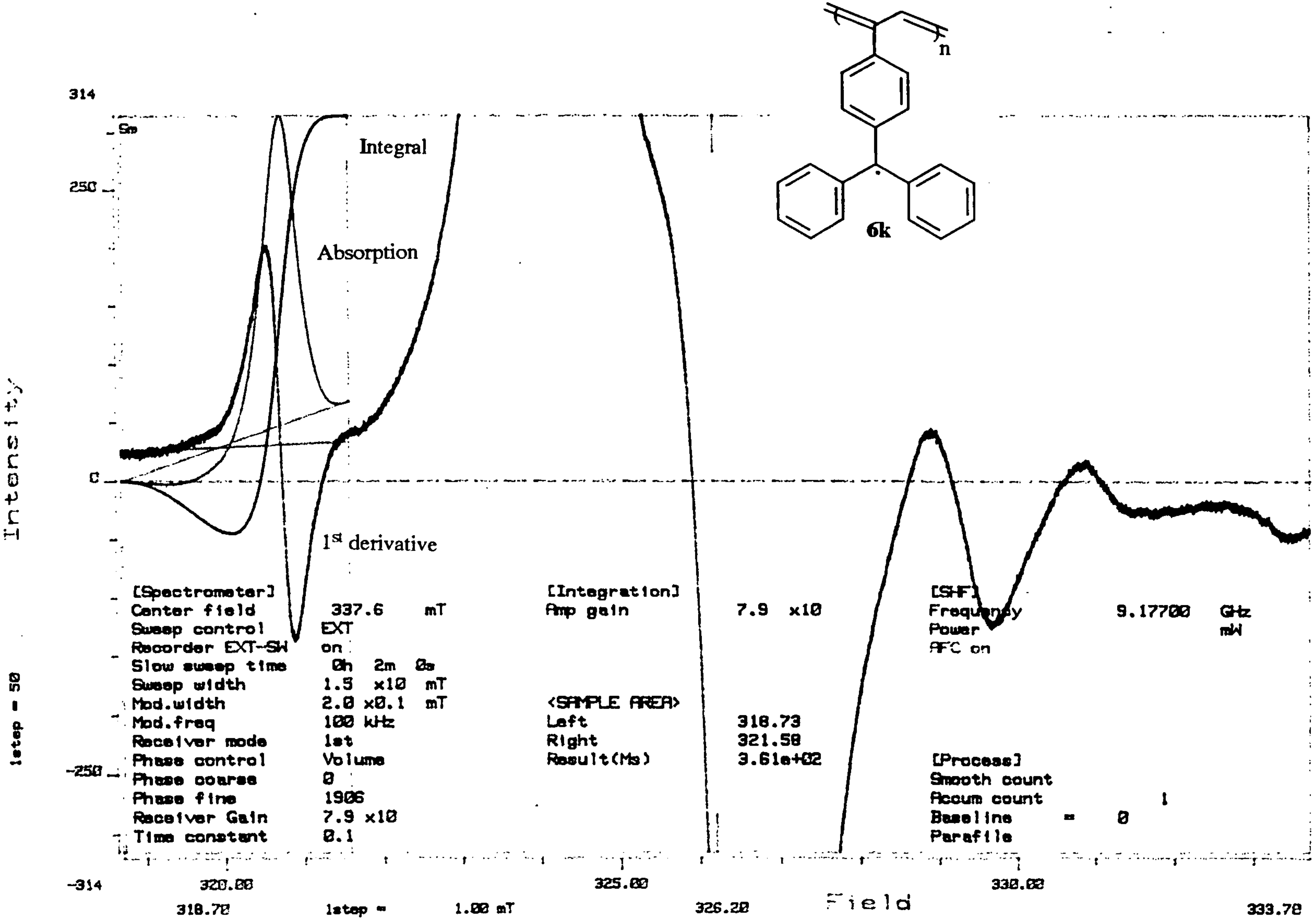


6j

Time constant 0.1s Centre field set 326.2mT

Modulation frequency 100k cps Microwave power 1mW Microwave frequency 9.177Gc

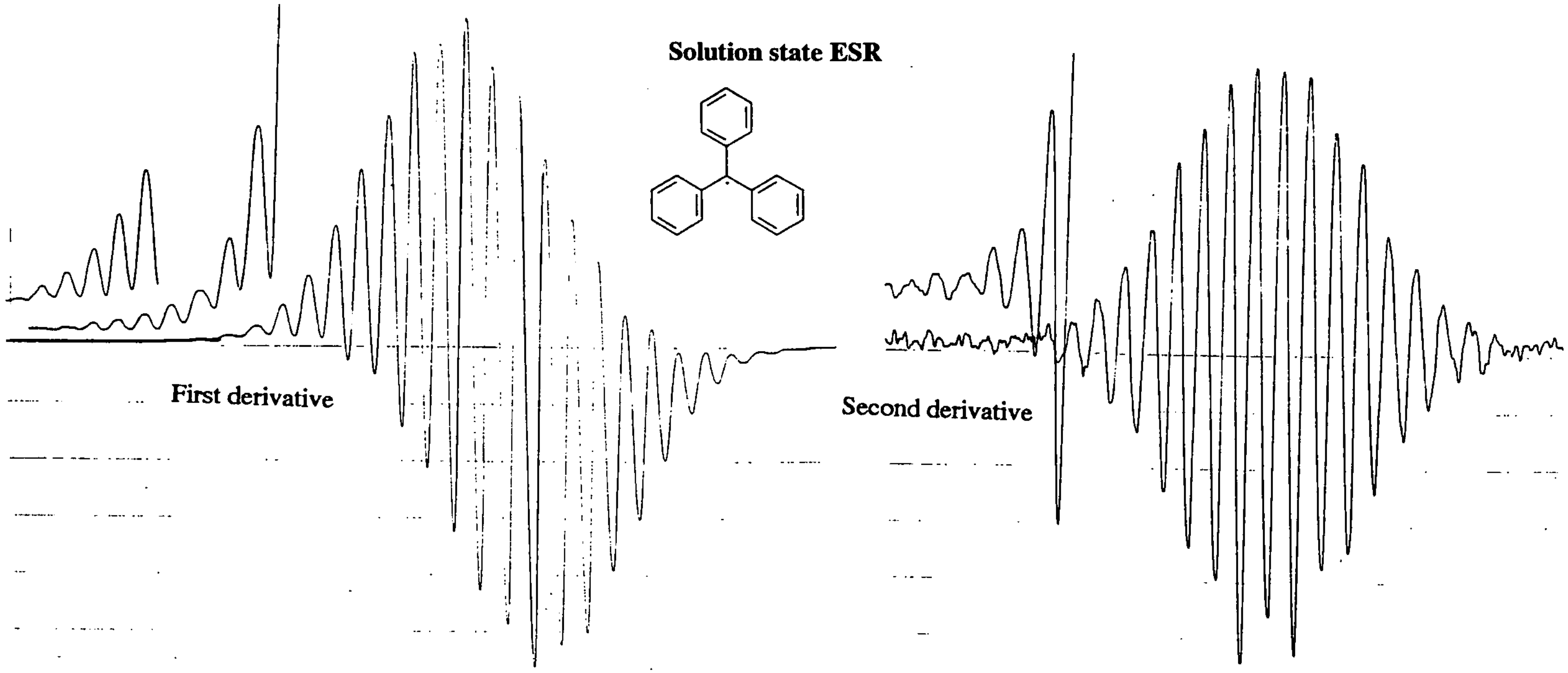
Appendix 6-49



6k

```
[Spectrometer]                                   [Integration]                    [SHF]
Center field      337.6   mT                     Amp gain         7.9  x10        Frequency        9.17700   GHz
Sweep control     EXT                                                             Power                      mW
Recorder EXT-SW   on                                                              AFC on
Slow sweep time    0h  2m  0s
Sweep width       1.5  x10  mT
Mod.width         2.0 x0.1  mT                   <SAMPLE AREA>
Mod.freq          100 kHz                        Left             318.73
Receiver mode     1st                            Right            321.58
Phase control     Volume                         Result(Ms)       3.61e+02        [Process]
Phase coarse      0                                                               Smooth count
Phase fine        1906                                                            Accum count          1
Receiver Gain     7.9 x10                                                         Baseline     =   0
Time constant     0.1                                                             Parafile
```

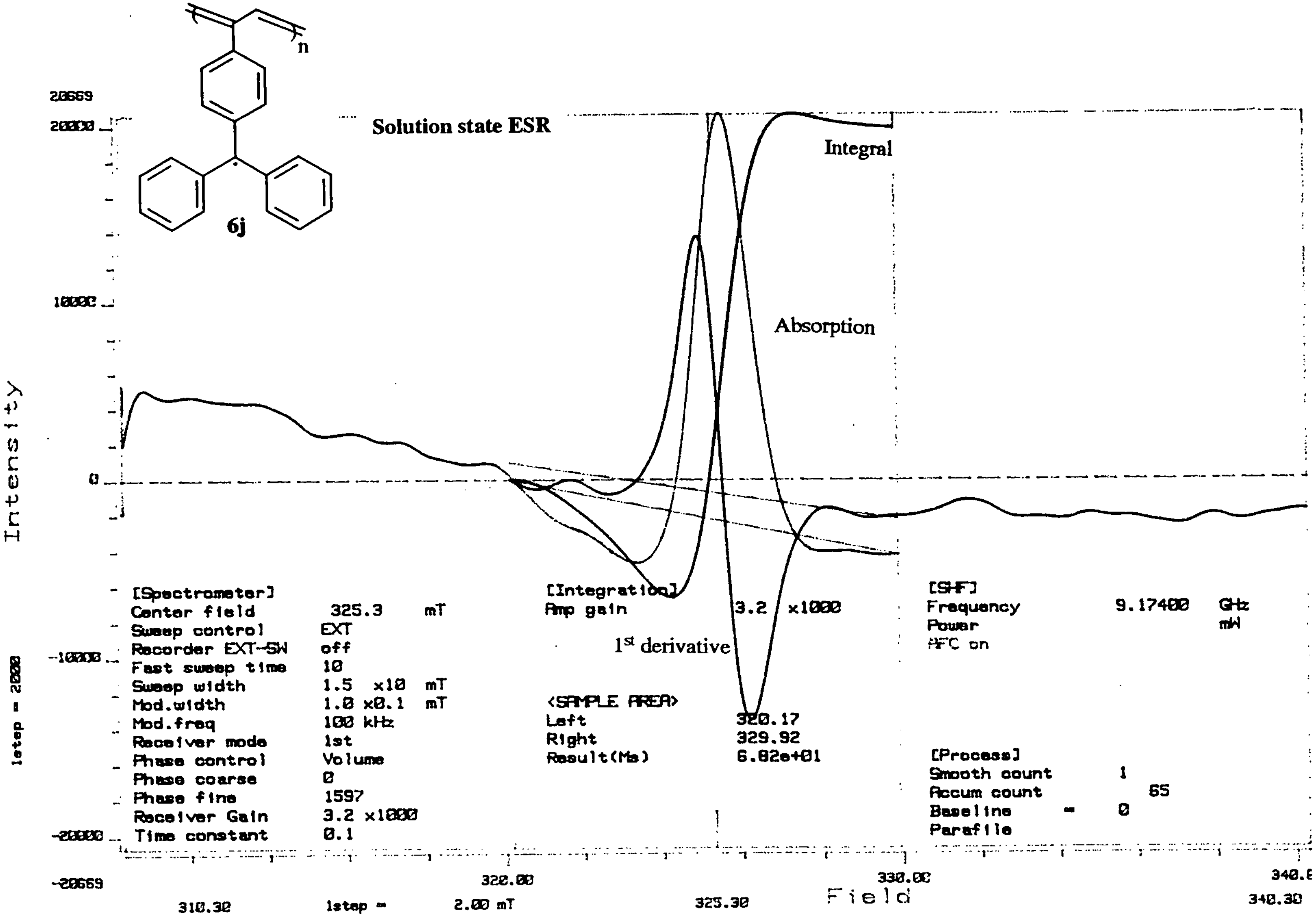
Appendix 6-50



Solution state ESR

Time constant 0.03s Centre field set 326.2mT
Modulation frequency 100k cps Microwave power 1mW Microwave frequency 9.177Gc
Receiver gain 1.100

Appendix 6-51



[Spectrometer]
Center field 325.3 mT
Sweep control EXT
Recorder EXT-SW off
Fast sweep time 10
Sweep width 1.5 x10 mT
Mod.width 1.0 x0.1 mT
Mod.freq 100 kHz
Receiver mode 1st
Phase control Volume
Phase coarse 0
Phase fine 1597
Receiver Gain 3.2 x1000
Time constant 0.1

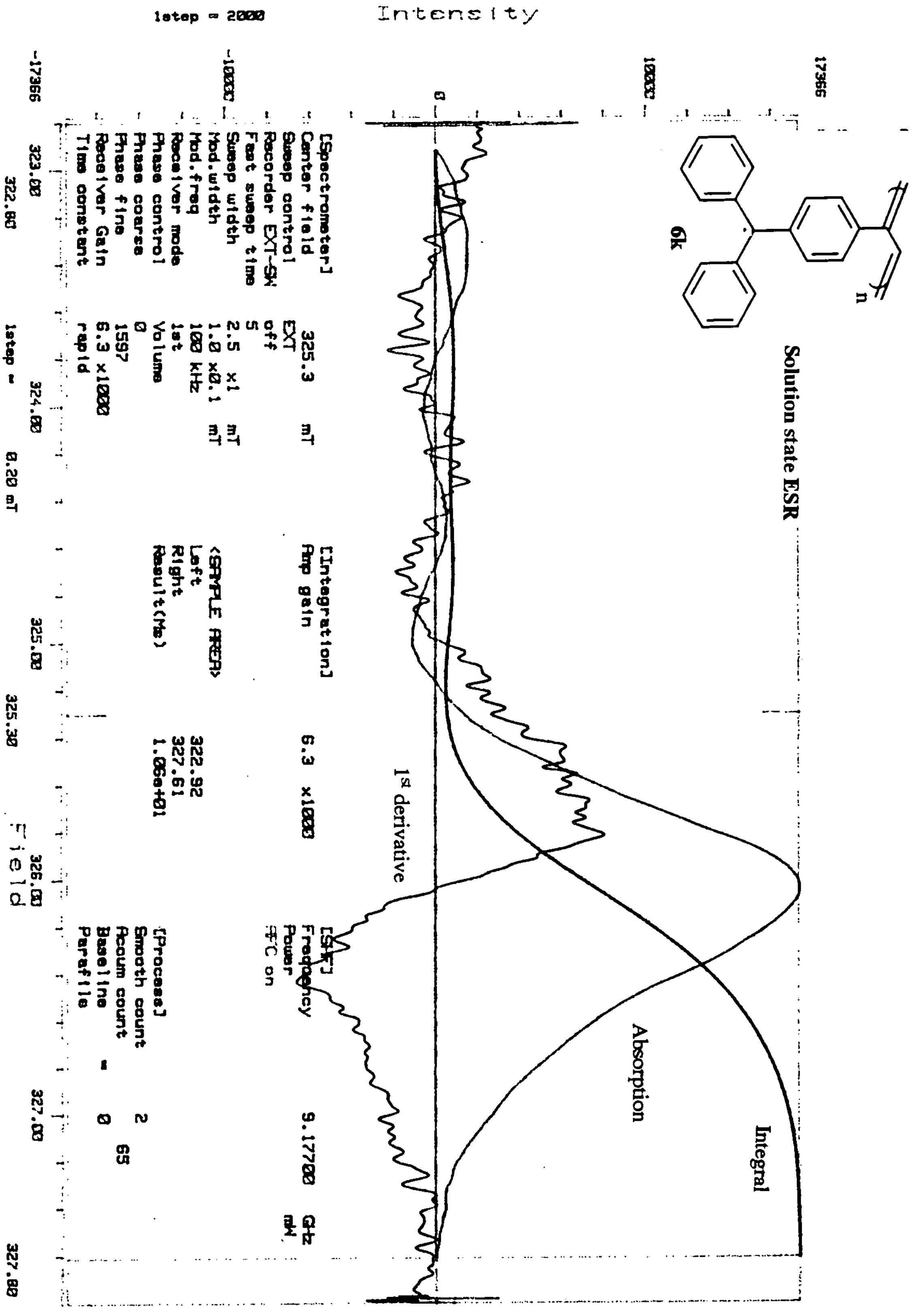
[Integration]
Amp gain 3.2 x1000

<SAMPLE AREA>
Left 320.17
Right 329.92
Result(Ms) 6.82e+01

[SHF]
Frequency 9.17400 GHz
Power mW
AFC on

[Process]
Smooth count 1
Accum count 65
Baseline = 0
Parafile

Appendix 6-52



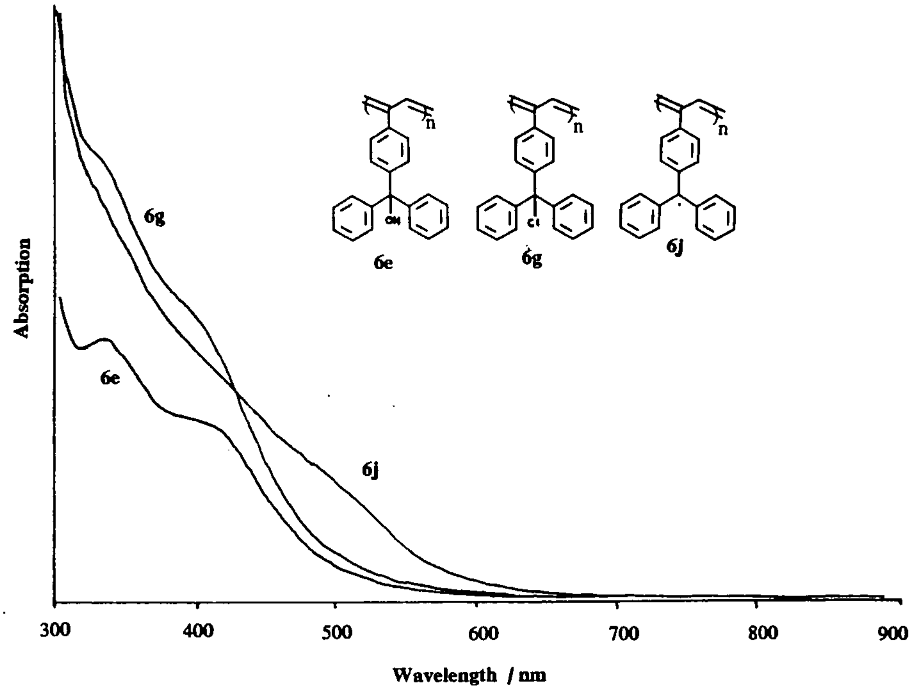
[Spectrometer]
Center field 325.3 mT
Sweep control EXT
Recorder EXT-SW off
Fast sweep time 5
Sweep width 2.5 x1 mT
Mod.width 1.0 x0.1 mT
Mod.freq 100 kHz
Receiver mode 1st
Phase control Volume
Phase coarse 0
Phase fine 1597
Receiver Gain 6.3 x1000
Time constant rapid

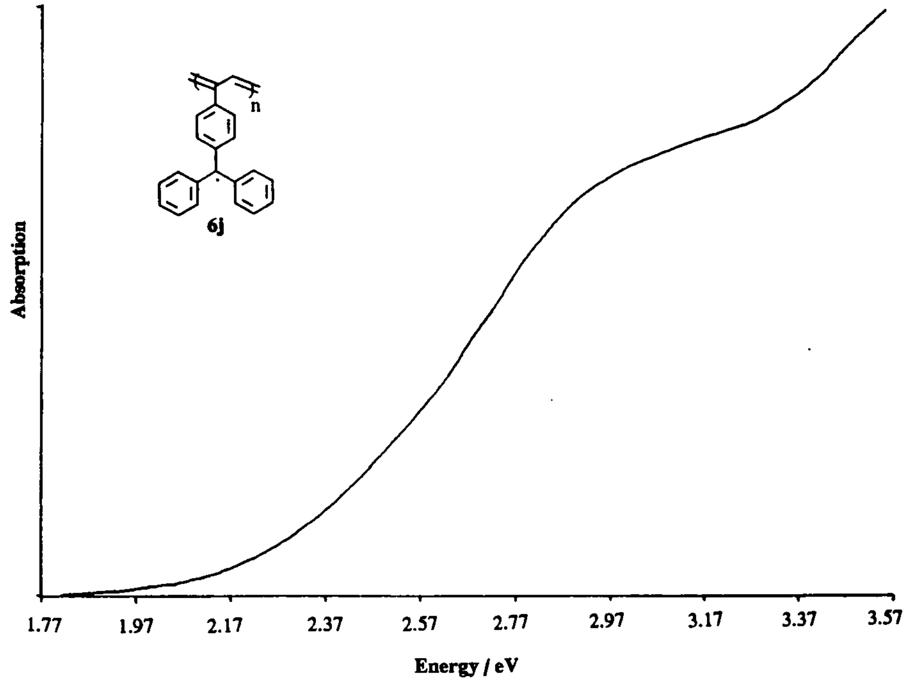
[Integration]
Amp gain 6.3 x1000
<SAMPLE AREA>
Left 322.92
Right 327.61
Result(Ms) 1.06e+01

[SSF]
Frequency 9.17700 GHz
Power mW
AFC on

[Process]
Smooth count 2
Accum count 65
Baseline = 0
Parafile

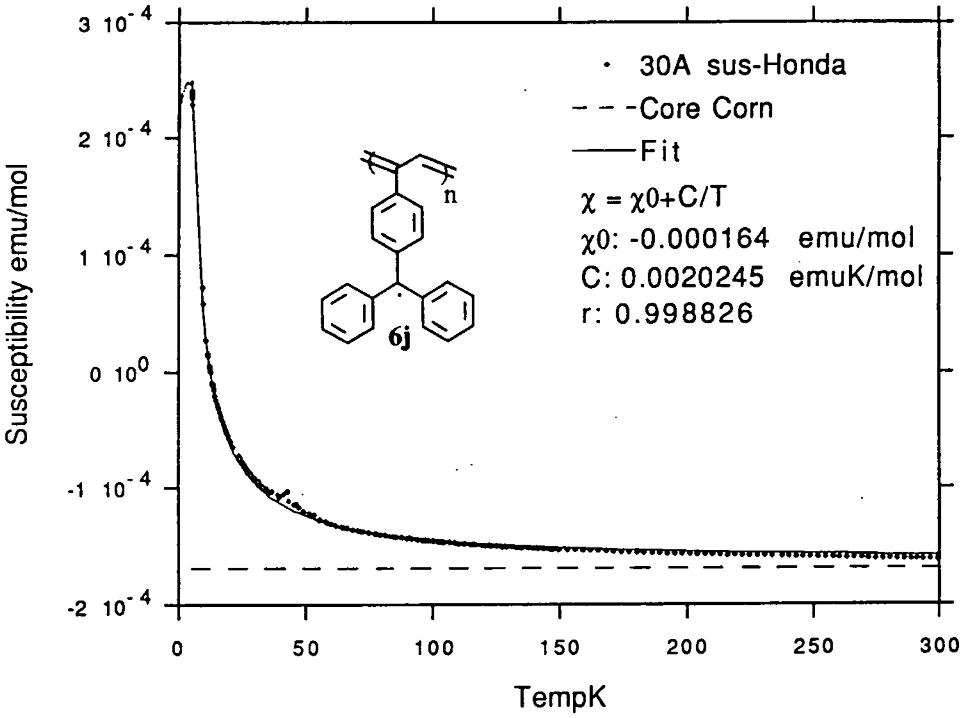
Appendix 6-53



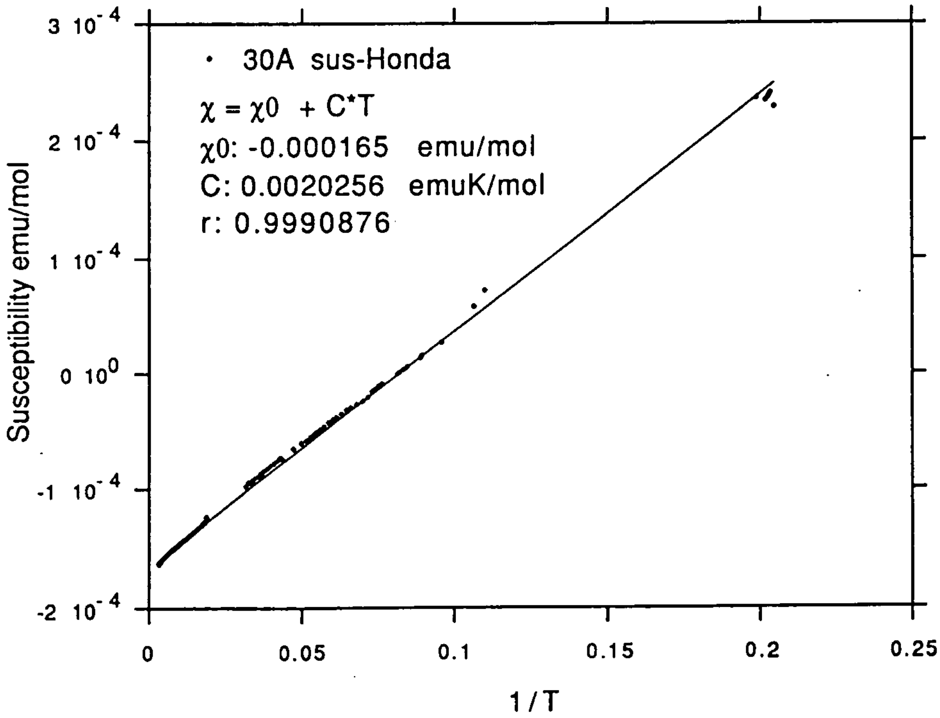


Appendix 6-54

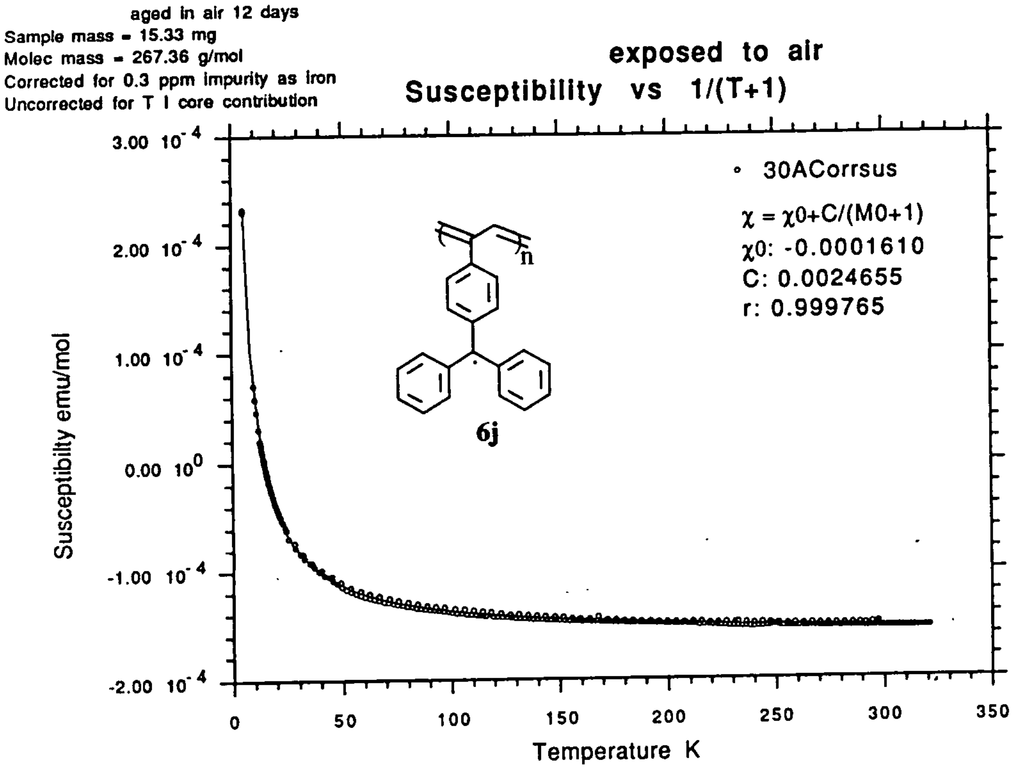
Sample mass = 17.41 mg
Molec. weight = 267.4 g/mol
Corrected for 4ppm Ferr imp as iron
No TIP core contribution added

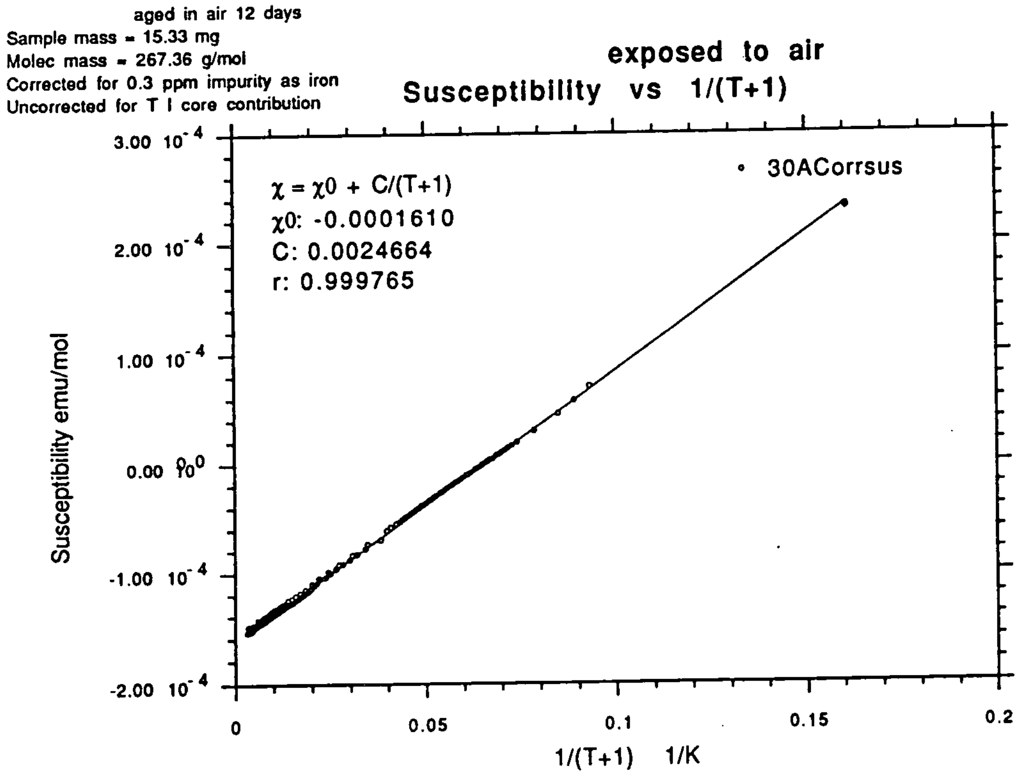


Sample mass = 17.41 mg
Molec. weight = 267.4 g/mol
Corrected for 4ppm Ferr imp as iron
No TIP core contribution added



Appendix 6-55

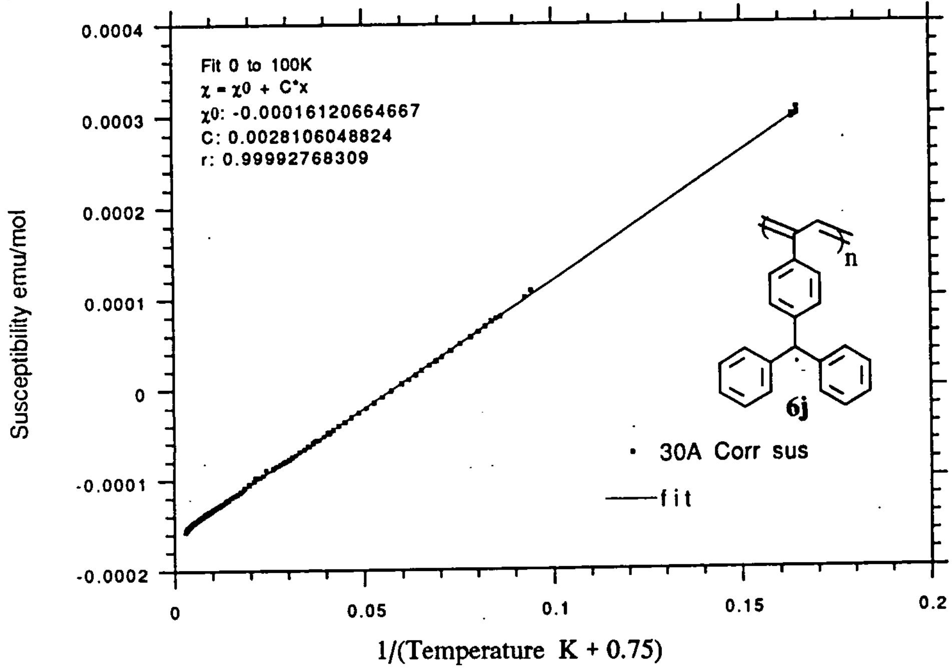




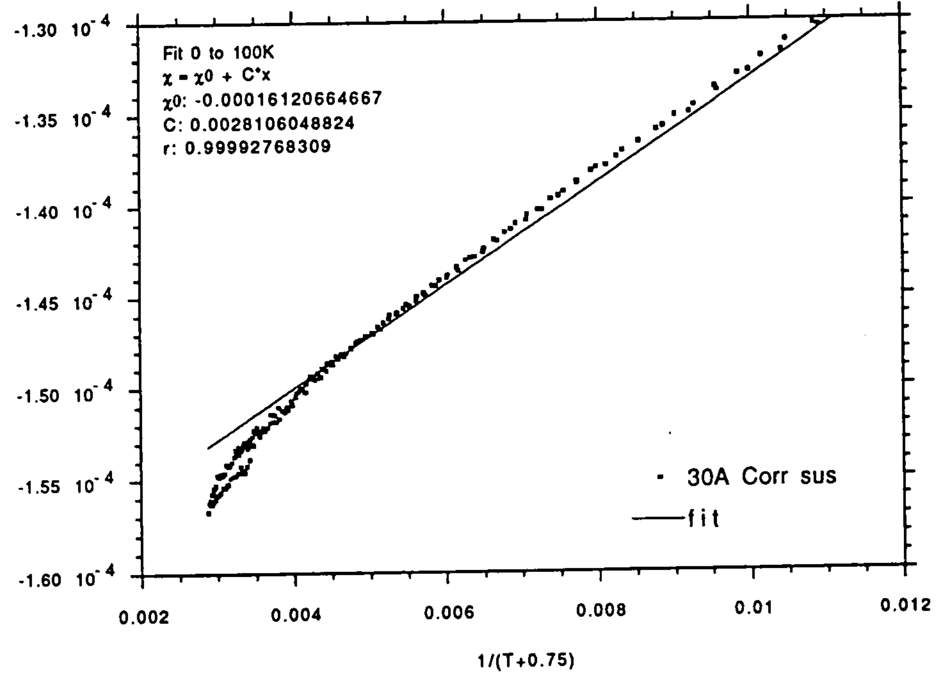
Appendix 6-56

Sample mass = 24.60 mg
Molec mass = 267.4 g/mol
Corrected for 4.7 ppm ferr imp
Uncorrected for Tl core contrib.

Sus vs 1/T



Sample mass = 24.60 mg
Molec mass = 267.4 g/mol
Corrected for 4.7 ppm ferr imp
Uncorrected for Tl core contrib.



UNIVERSITY OF DURHAM

Board of Studies in Chemistry

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS
1ST AUGUST 1987 to 31st JULY 1988

x	BIRCHALL, Prof. D. (I.C.I. Advanced Materials) Environmental Chemistry of Aluminium	25th April 1988
x	BORER, Dr. K. (University of Durham Industrial Research Labs.) The Brighton Bomb - A Forensic Science View	18th February 1988
	BOSSONS, L. (Durham Chemistry Teachers' Centre) GCSE Practical Assessment	16th March 1988
x	BUTLER, Dr. A.R. (University of St. Andrews) Chinese Alchemy	5th November 1987
x	CAIRNS-SMITH, Dr. A. (Glasgow University) Clay Minerals and the Origin of Life	28th January 1988
x	DAVIDSON, Dr. J. (Herriot-Watt University) Metal Promoted Oligomerisation Reactions of Alkynes	November 1987
x	GRADUATE CHEMISTS (Northeast Polytechnics and Universities) R.S.C. Graduate Symposium	19th April 1988
x	GRAHAM, Prof. W.A.G. (University of Alberta, Canada) Rhodium and Iridium Complexes in the Activation of Carbon-Hydrogen Bonds	3rd March 1988
x	GRAY, Prof. G.W. (University of Hull) Liquid Crystals and their Applications	22nd October 1987
	HARTSHORN, Prof. M.P. (University of Canterbury, New Zealand) Aspects of Ipso-Nitration	7th April 1988
x	HOWARD, Dr. J. (I.C.I. Wilton) Chemistry of Non-Equilibrium Processes	3rd December 1987
x	LUDMAN, Dr. C.J. (Durham University) Explosives	10th December 1987
x	McDONALD, Dr. W.A. (I.C.I. Wilton) Liquid Crystal Polymers	11th May 1988
x	MAJORAL, Prof. J.-P. (Université Paul Sabatier) Stabilisation by Complexation of Short-Lived Phosphorus Species	8th June 1988
	MAPLETOFT, Mrs. M. (Durham Chemistry Teachers' Centre) Salters' Chemistry	4th November 1987
	NIETO DE CASTRO, Prof. C.A. (University of Lisbon and Imperial College) Transport Properties of Non-Polar Fluids	18th April 1988

x OLAH, Prof. G.A. (University of Southern California) New Aspects of Hydrocarbon Chemistry)	29th June, 1988
x PALMER, Dr. F. (University of Nottingham) Luminescence (Demonstration Lecture)	21st January 1988
x PINES, Prof. A. (University of California, Berkeley, U.S.A.) Some Magnetic Moments	28th April 1988
x RICHARDSON, Dr. R. (University of Bristol) X-Ray Diffraction from Spread Monolayers	27th April 1988
ROBERTS, Mrs. E. (SATRO Officer for Sunderland) Talk - Durham Chemistry Teachers' Centre - "Links Between Industry and Schools"	13th April 1988
x ROBINSON, Dr. J.A. (University of Southampton) Aspects of Antibiotic Biosynthesis	27th April 1988
x ROSE van Mrs. S. (Geological Museum) Chemistry of Volcanoes	29th October 1987
x SAMMES, Prof. P.G. (Smith, Kline and French) Chemical Aspects of Drug Development	19th December 1987
x SEEBACH, Prof. D. (E.T.H. Zurich) From Synthetic Methods to Mechanistic Insight	12th November 1987
SODEAU, Dr. J. (University of East Anglia) Durham Chemistry Teachers' Centre Lecture: "Spray Cans, Smog and Society"	11th May 1988
SWART, Mr. R.M. (I.C.I.) The Interaction of Chemicals with Lipid Bilayers	16th December 1987
x TURNER, Prof. J.J. (University of Nottingham) Catching Organometallic Intermediates	11th February 1988
x UNDERHILL, Prof. A. (University of Bangor) Molecular Electronics	25th February 1988
x WILLIAMS, Dr. D.H. (University of Cambridge) Molecular Recognition	26th November 1987
x WINTER, Dr. M.J. (University of Sheffield) Pyrotechnics (Demonstration Lecture)	15th October 1987

UNIVERSITY OF DURHAM

Board of Studies in Chemistry

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS
1ST AUGUST 1988 to 31st JULY 1989

ASHMAN, Mr. A. (Durham Chemistry Teachers' Centre) The Chemical Aspects of the National Curriculum	3rd May, 1989
AVEYARD, Dr. R. (University of Hull) Surfactants at your Surface	15th March, 1989
AYLETT, Prof. B.J. (Queen Mary College. London) Silicon-Based Chips:- The Chemist's Contribution	16th February, 1989
BALDWIN, Prof. J.E. (Oxford University) Recent Advances in the Bioorganic Chemistry of Penicillin Biosynthesis	9th February, 1989
BALDWIN & WALKER, Drs. R.R. & R.W. (Hull University) Combustion: Some Burning Problems	24th November, 1988
BOLLEN, Mr. F. (Durham Chemistry Teachers' Centre) Lecture about the use of SATIS in the classroom	18th October, 1988
BUTLER, Dr. A.R. (St. Andrews University) Cancer in Linxiam: The Chemical Dimension	15th February, 1989
CADOGAN, Prof. J.I.G. (British Petroleum) From Pure Science to Profit	10th November, 1988
CASEY, Dr. M. (University of Salford) Sulphoxides in Stereoselective Synthesis	20th April, 1989
CRESSEY & WATERS, Mr. D. & T. (Durham Chemistry Teachers' Centre) GCSE Chemistry 1988: "A Coroner's Report"	1st February, 1989
CRICH, Dr. D. (University College London) Some Novel Uses of Free Radicals in Organic Synthesis	27th April, 1989
DINGWALL, Dr. J. (Ciba Geigy) Phosphorus-containing Amino Acids: Biologically Active Natural and Unnatural Products	18th October, 1988
ERRINGTON, Dr. R.J. (University of Newcastle-upon-Tyne) Polymetalate Assembly in Organic Solvents	1st March, 1989
FREY, Dr. J. (Southampton University) Spectroscopy of the Reaction Path: Photodissociation Raman Spectra of NOCl	11th May, 1989
GRADUATE CHEMISTS, (Polytechs and Universities in North East England) R.S.C. Symposium for presentation of papers by postgraduate students	12th April, 1989

HALL, Prof. L.D. (Addenbrooke's Hospital, Cambridge) NMR - A Window to the Human Body	2nd February, 1989
HARDGROVE, Dr. G. (St. Olaf College, U.S.A.) Polymers in the Physical Chemistry Laboratory	December, 1988
HARWOOD, Dr. L. (Oxford University) Synthetic Approaches to Phorbols Via Intramolecular Furan Diels-Alder Reactions: Chemistry under Pressure	25th January, 1988
JÄGER, Dr. C. (Friedrich-Schiller University GDR) NMR Investigations of Fast Ion Conductors of the NASICON Type	9th December, 1988
JENNINGS, Prof. R.R. (Warwick University) Chemistry of the Masses	26th January, 1989
JOHNSON, Dr. B.F.G. (Cambridge University) The Binary Carbonyls	23rd February, 1989
JONES, Dr. M.E. (Durham Chemistry Teachers' Centre) Discussion Session on the National Curriculum	14th June, 1989
JONES, Dr. M.E. (Durham Chemistry Teachers' Centre) GCSE and A Level Chemistry 1989	28th June, 1989
LUDMAN, Dr. C.J. (Durham University) The Energetics of Explosives	18th October, 1988
MACDOUGALL, Dr. G. (Edinburgh University) Vibrational Spectroscopy of Model Catalytic Systems	22nd February, 1989
MARKO, Dr. I. (Sheffield University) Catalytic Asymmetric Osmylation of Olefins	9th March, 1989
McLAUCHLAN, Dr. K.A. (University of Oxford) The Effect of Magnetic Fields on Chemical Reactions	16th November, 1988
MOODY, Dr. C.J. (Imperial College) Reactive Intermediates in Heterocyclic Synthesis	17th May, 1989
MORTIMER, Dr. C. (Durham Chemistry Teachers' Centre) The Hindenberg Disaster - an Excuse for Some Experiments	14th December, 1988
NICHOLLS, Dr. D. (Durham Chemistry Teachers' Centre) Demo. "Liquid Air"	11th July, 1989
PAETZOLD, Prof. P. (Aachen) Iminoboranes $XB\equiv NR$: Inorganic Acetylenes?	23rd May, 1989
PAGE, Dr. P.C.B. (University of Liverpool) Stereocontrol of Organic Reactions Using 1,3-dithiane-1-oxides	3rd May, 1989

	POLA, Prof. J. (Czechoslovak Academy of Sciences) Carbon Dioxide Laser Induced Chemical Reactions - New Pathways in Gas-Phase Chemistry	15th June, 1989
x	REES, Prof. C.W. (Imperial College London) Some Very Heterocyclic Compounds	27th October, 1988
	REVELL, Mr. P. (Durham Chemistry Teachers' Centre) Implementing Broad and Balanced Science 11-16	14th March, 1989
	SCHMUTZLER, Prof. R. (Technische Universitat Braunschweig) Fluorophosphines Revisited - New Contributions to an Old Theme	6th October, 1988
x	SCHROCK, Prof. R.R. (M.I.T.) Recent Advances in Living Metathesis	13th February, 1989
x	SINGH, Dr. G. (Teesside Polytechnic) Towards Third Generation Anti-Leukaemics	9th November, 1988
x	SNAITH, Dr. R. (Cambridge University) Egyptian Mummies: What, Where, Why and How?	1st December, 1988
	STIBR, Dr. R. (Czechoslovak Academy of Sciences) Recent Developments in the Chemistry of Intermediate-Sited Carboranes	16th May, 1989
x	VON RAGUE SCHLEYER, Prof. P. (Universitat Erlangen Nurnberg) The Fruitful Interplay Between Calculational and Experimental Chemistry	21st October, 1988
x	WELLS, Prof. P.B. (Hull University) Catalyst Characterisation and Activity	10th May, 1989

UNIVERSITY OF DURHAM

Board of Studies in Chemistry

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS
1ST AUGUST 1989 TO 31ST JULY 1990

ASHMAN, Mr. A. (Durham Chemistry Teachers' Centre) The National Curriculum - an update	11th October, 1989
BADYAL, Dr. J.P.S. (Durham University) Breakthoughs in Heterogeneous Catalysis	1st November, 1989
BECHER, Dr. J. (Odense University) Synthesis of New Macrocylic Systems using Heterocyclic Building Blocks	13th November, 1989
BERCAW, Prof. J.E. (California Institute of Technology) Synthetic and Mechanistic Approaches to Ziegler-natta Polymerization of Olefins	10th November, 1989
BLEASDALE, Dr. C. (Newcastle University) The Mode of Action of some Anti-tumour Agents	21st February, 1990
BOLLEN, Mr. F.(Formerly Science Advisor, Newcastle LEA) Whats's New in Satis, 16-19	27th March, 1990
BOWMAN, Prof. J.M. (Emory University) Fitting Experiment with Theory in Ar-OH	23rd March, 1990
BUTLER, Dr. A. (St. Andrews University) The Discovery of Penicillin: Facts and Fancies	7th December, 1989
CAMPBELL, Mr. W.A. (Durham Chemistry Teachers' Centre) Industrial catalysis - some ideas for the National Curriculum	12th September, 1989
CHADWICK, Dr. P. (Dept. of Physics, Durham University) Recent Theories of the Universe (with Reference to National Curriculum Attainment Target 16)	24th January, 1990
CHEETHAM, Dr. A.K. (Oxford University) Chemistry of Zeolite Cages	8th March, 1990
CLARK, Prof. D.T. (ICI Wilton) Spatially Resolved Chemistry (using Natures's Paradigm in the Advanced Materials Arena)	22nd February, 1990
COLE-HAMILTON, Prof. D.J. (St. Andrews University) New Polymers from Homogeneous Catalysis	29th November, 1989

* PARKER, Dr. D. (Durham University) Macrocycles, Drugs and Rock 'n' roll	16th November, 1989
* PERUTZ, Dr. R.N. (York University) Plotting the Course of C-H Activations with Organometallics	24th January, 1990
PLATONOV, Prof. V.E. (USSR Academy of Sciences - Novosibirsk) Polyfluoroindanes: Synthesis and Transformation	9th July, 1990
* POWELL, Dr. R.L. (ICI) The Development of CFC Replacements	6th December, 1989
POWIS, Dr. I. (Nottingham University) Spinning off in a huff: Photodissociation of Methyl Iodide	21st March, 1990
RICHARDS, Mr. C. (Health and Safety Executive, Newcastle) Safety in School Science Laboratories and COSHH	28th February, 1990
ROZHKOV, Prof. I.N. (USSR Academy of Sciences - Moscow) Reactivity of Perfluoroalkyl Bromides	9th July, 1990
* STODDART, Dr. J.F. (Sheffield University) Molecular Lego	1st March, 1990
SUTTON, Prof. D. (Simon Fraser University, Vancouver B.C.) Synthesis and Applications of Dinitrogen and Diazo Compounds of Rhenium and Iridium	14th February, 1990
THOMAS, Dr. R.K. (Oxford University) Neutron Reflectometry from Surfaces	28th February, 1990
* THOMPSON, Dr. D.P. (Newcastle University) The role of Nitrogen in Extending Silicate Crystal Chemistry	7th February, 1990

× CROMBIE, Prof. L. (Nottingham University) The Chemistry of Cannabis and Khat	15th February, 1990
× DYER, Dr. U. (Glaxo) Synthesis and Conformation of C-Glycosides	31st January, 1990
× FLORIANI, Prof. C. (University of Lausanne, Switzerland) Molecular Aggregates - A Bridge between homogeneous and Heterogeneous Systems	25th October, 1989
GERMAN, Prof. L.S. (USSR Academy of Sciences - Moscow) New Syntheses in Fluoroaliphatic Chemistry: Recent Advances in the Chemistry of Fluorinated Oxiranes	9th July, 1990
× GRAHAM, Dr. D. (B.P. Reserch Centre) How Proteins Absorb to Interfaces	4th December, 1989
× GREENWOOD, Prof. N.N. (University of Leeds) Novel Cluster Geometries in Metalloborane Chemistry	9th November, 1989
× HOLLOWAY, Prof. J.H. (University of Leicester) Noble Gas Chemistry	1st February, 1990
× HUGHES, Dr. M.N. (King's College, London) A Bug's Eye View of the Periodic Table	30th November, 1989
× HUISGEN, Prof. R. (Universität München) Recent Mechanistic Studies of [2+2] Additions	15th December, 1989
IDDON, Dr. B. (Univeristy of Salford) Schools' Christmas Lecture - The Magic of Chemistry	15th December, 1989
JONES, Dr. M.E. (Durham Chemistry Teachers' Centre) The Chemistry A Level 1990	3rd July, 1990
JONES, Dr. M.E. (Durham Chemistry Teachers' Centre) GCSE and Dual Award Science as a starting point for A level Chemistry - how suitable are they?	21st November 1989
JOHNSON, Dr. G.A.L. (Durham Chemistry Teachers' Centre) Some aspects of local Geology in the National Science Curriculum (attainment target 9)	8th February, 1990
KLINOWSKI, Dr. J. (Cambridge University) Solid State NMR Studies of Zeolite Catalysts	13th December 1989
× LANCASTER, Rev. R. (Kimbolton Fireworks) Fireworks - Principles and Practice	8th February, 1990
× LUNAZZI, Prof. L. (University of Bologna) Application of Dynamic NMR to the Study of Conformational Enantiomerism	12th February, 1990
× PALMER, Dr. F. (Nottingham University) Thunder and Lightning	17th October, 1989

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