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The Synthesis and Properties of some Well-Defined Fluorinated Polymers

by

Richard Mark Towns

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A thesis submitted for the degree of
Doctor of Philosophy at the University of Durham

March 1996

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4 JUL 1996

Abstract

The Synthesis and Properties of some Well-Defined Fluorinated Polymers

This thesis describes studies directed to the ring opening metathesis polymerisation (ROMP) of some fluorinated compounds using a range of well-defined initiators.

Chapter 1 reviews some general aspects of olefin metathesis and ring opening metathesis polymerisation of relevance to the work described in this thesis. Topics such as piezo- and pyro-electricity and optical and electrical properties of conjugated polymers are introduced and these receive more detailed attention later in the thesis.

Chapter 2 describes the synthesis, characterisation and properties of poly(bis(trifluoromethyl)norbornadiene) in detail. The use of various initiating systems that have been used previously and the effect they have on the tacticity of the resulting polymer microstructure are discussed. The latter part of this chapter reviews some of the current thinking concerning the detailed mechanistic aspects of this polymerisation.

Chapter 3 reviews attempts directed to an improvement in tacticity control in the synthesis of poly(bis(trifluoromethyl)norbornadiene). The synthesis and activity of the new well-defined initiators used in these studies are reported. It is shown that varying the nature of the ancillary ligands surrounding the metal centre can have a dramatic influence on the tacticity of the resulting polymer.

Chapter 4 reports studies directed to an examination of the limits of the well controlled synthesis of poly(bis(trifluoromethyl)norbornadiene). The syntheses of high

trans and high cis, highly tactic poly(bis(trifluoromethyl)norbornadiene samples using well-defined initiating systems are described. It is shown that by varying the monomer:initiator ratio, samples with a wide range of molecular weights can be achieved and these are reported.

Chapter 5 describes experiments concerning the ROMP of fluorinated monomers containing six membered rings. In particular ROMP studies of the monomers, 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene and 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene are described.

Finally, Chapter 6 provides a summary of the work reported and outlines some ideas for future studies.

Memorandum

The work reported in this thesis was carried out at the Interdisciplinary Research Centre in Polymer Science and Technology at Durham University between October 1992 and December 1995. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by an appropiate reference.

Statement of Copyright

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Financial Support

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Acknowledgements

Well, I've finally done it lads! The end of the era is now complete. This is probably the hardest part of the thesis to write as there are so many people I wish to thank. First and foremost the people who actually got me through my "academic" times in Durham. I am indebted to Professor Jim Feast, for his continual guidance and encouragement, and he really has been good to me and showed tremendous patience and kindness through my rough times in my first year, cheers Jim! Also to **all** the people in the IRC, including Ezat Khosravi who certainly does know the "crack" about initiators and chemistry in general, Julia in the NMR room, Gordon in the GPC room, the glassblowers, whom I tried to keep as busy as possible, thanks everyone.

Now to the "social" side of things. This could be a whole thesis in itself, but I will keep it brief. As the self appointed leader of the "lads", I wish to thank you all. Oh and also the honorary lads i.e. the chicks, this is an even longer list, I wish!!

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Chapter 1

General Introduction and Background

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1.1 General introduction

This thesis describes studies directed towards the synthesis of novel fluoropolymers of interest as potential piezoelectric, pyroelectric or electroluminescent materials. Ring Opening Metathesis Polymerisation (ROMP) has been the reaction used in pursuit of these aims.

Fluoropolymers are well established. Although they are expensive, the benefits resulting from their high thermal stability and chemical resistance are well documented and result in their widespread application as speciality materials. Stereoregulation in the polymer backbone is well established as an important determinant of polymer properties. It seems reasonable to expect that the combination of stereoregulation and the benefits conferred by fluorine-substitution may give rise to novel materials with interesting properties. These factors generate the interest in this area of research.

In chapter 1 of this thesis, the main features of olefin metathesis and ROMP are reviewed, the use of well-defined initiators in 'living' ROMP reactions is introduced and receives further attention in chapter 3. Also in chapter 1, established fluoropolymers are reviewed, and the basis of the piezo- and pyro-electric response is discussed with particular reference to poly(vinylidene fluoride) (PVDF), the polymer which is often regarded as the archetypal piezoelectric polymer. The final section of this chapter is devoted to the relatively new and exciting area of the application of electroluminescent conjugated polymers in Light Emitting Diodes (LEDs).

Chapter 2 discusses in detail the ROMP of 2,3-bis(trifluoromethyl)-norbornadiene. The structure and properties of this polymer are discussed, in particular tacticity and its relation to the possibility of producing a poled and highly polar material of potential interest as a component of piezo- or pyro-electric devices. The details of the mechanism of this polymerisation are discussed in the latter part of this chapter.

In chapter 3 the key developments in attempts to improve the tacticity of poly(2,3-bis(trifluoromethyl)norbornadiene) by varying the ligands at the metal centre in "Schrock-type" well-defined initiators are described and discussed.

Chapter 4 describes the syntheses of a wide range of high cis (>98%) and high trans (>98%) poly(2,3-bis(trifluoromethyl)norbornadiene)s. These polymers were made and characterised as standards for detailed studies, using physical measurements such as light scattering, of the solution behaviour of the materials and the correlation of observed properties with predictions based on molecular modelling.

Chapter 5 discusses the ROMP of fluorinated monomers containing 6-membered rings. Attempts to prepare a conjugated polymer of potential interest as the electroluminescent component of an LED is described. Finally, chapter 6 suggests further studies, which could reasonably be undertaken to extend the work described in this thesis.

1.2 Olefin Metathesis and Ring Opening Metathesis Polymerisation (ROMP).

1.2.1 Introduction.

Metathesis chemistry, now more than thirty years old,[1] was, at the time of its discovery, a surprising reaction of olefins which has been used for the synthesis both of small molecules and a wide range of polymers. A lot of information has been established about all aspects of the process and there is a vast literature concerning metathesis,[1-6] covering the initiators, mechanistic features and applications of this reaction in organic and polymer synthesis.

The word "metathesis" is derived from the Greek "*meta*" (change) and "*tithemi*" (place), and grammatically it refers to a transposition of sounds or letters in a word. In chemistry it refers to the interchange of atoms or groups of atoms between two molecules.

Olefin metathesis is the reaction in which molecules of these hydrocarbons are fragmented at their double bonds and new olefin molecules result by the recombination of fragments originating from the different molecules (Figure 1.1.).[7]

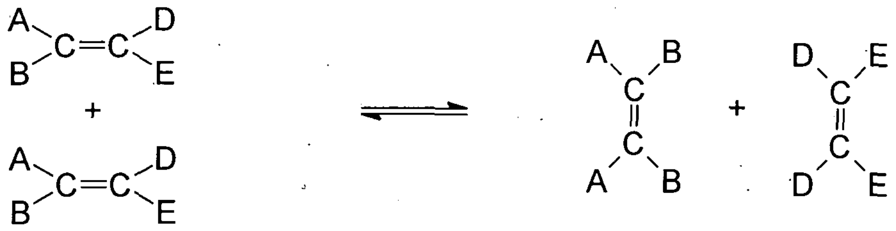


Figure 1.1. Schematic diagram for the metathesis of an acyclic alkene.

This is a bond reorganisation reaction in which the total number and type of chemical bonds remain unchanged during the transformation of the initial alkenes into equimolar amounts of the two new alkenes.

The ring opening metathesis polymerisation (ROMP) of cyclo-olefins is a reaction which is closely related to the metathesis of acyclic alkenes. It is the process by which such molecules are cleaved at the double bond producing unsaturated linear polymers of the polyalkenylene type (Figure 1.2.).

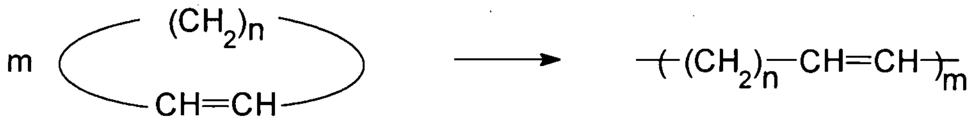
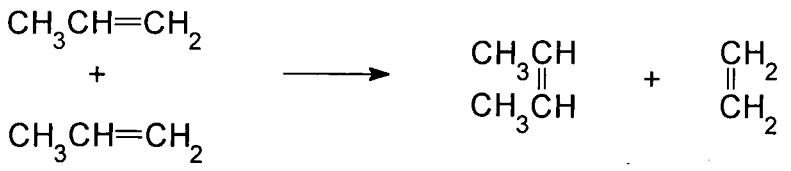


Figure 1.2. Schematic diagram for the ROMP of a cycloalkene.

1.2.2 Brief history.

The expression "Olefin metathesis" was first used by Calderon in 1967.[7] Until then the consideration of the chemistry of exchange reactions, such as the process indicated in equation 1.1a, and of polymerisation reactions as described by equations 1.1b and 1.1c had developed independently.

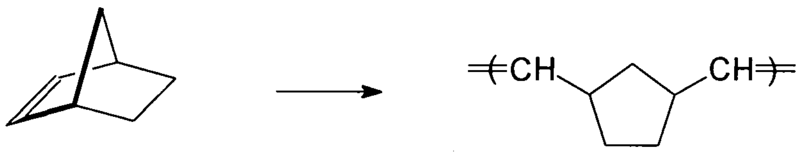
Both types of reaction were surprisingly late to appear on the modern chemistry scene. The first open publications were those of Truett (1960) [8] reporting reaction 1.1c and Banks (1964) [9] reporting the reaction 1.1a.



$$\begin{matrix} CH_3CH{=}CH_2 \\ + \\ CH_3CH{=}CH_2 \end{matrix} \longrightarrow \begin{matrix} CH_3CH \\ \| \\ CH_3CH \end{matrix} + \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}$$

1.1a

1.1b

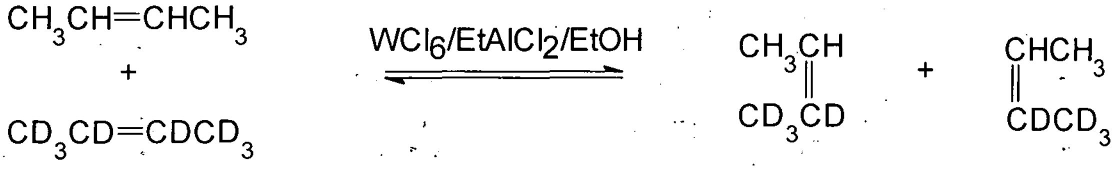


1.1c

However, both these publications were foreshadowed by a patent filed by Eleuterio (1957) [10] concerning the reactions of norbornene, cyclopentene and other cycloalkenes (equations 1.1b and 1.1c). The connection between the two types of reaction was not immediately obvious, mainly due to the fact that different catalysts and conditions were generally employed. The disproportionation of acyclic olefins was usually carried out on supported oxide catalysts such as MoO_3/Al_2O_3 at elevated temperatures (160^0C), whereas the ring opening polymerisation of cycloalkenes was usually initiated by mixtures of reagents which resembled Ziegler-Natta initiators, such as $MoCl_5/Et_3Al$, and the process occurred at room temperature. It should be noted, however, that supported oxide catalysts were in fact used by Eleuterio (1957), but the yield of polymer obtained was relatively low.

The mechanism of these ring opening polymerisations remained unexplained for several years, but a significant advance was made in 1967 when Calderon showed that the disproportionation of acyclic olefins such as pent-2-ene and the ring opening polymerisation of cycloalkenes such as cyclooctene and cycloocta-1,5-diene could be brought about very rapidly at room temperature by the same catalyst, namely, $WCl_6/EtAlCl_2/EtOH$, which is now referred to as the Calderon catalyst. This discovery helped to encourage the view that the reactions of acyclic and cyclic olefins probably proceeded via a common mechanism.[11-14]

Further evidence came from deuterium-labelling experiments (equation 1.2) which showed that the double bond itself was cleaved during the reaction of acyclic olefins, leading to the exchange of alkylidene moieties.[13,14]



$$\begin{matrix} CH_3CH{=}CHCH_3 \\ + \\ CD_3CD{=}CDCD_3 \end{matrix} \quad \xrightleftharpoons{WCl_6/EtAlCl_2/EtOH} \quad \begin{matrix} CH_3CH \\ \| \\ CD_3CD \end{matrix} \quad + \quad \begin{matrix} CHCH_3 \\ \| \\ CDCD_3 \end{matrix}$$

Equation 1.2. Cross metathesis of perhydro and perdeuterobut-2-enes.

Since this discovery, the reaction has become known as Olefin Metathesis or "*transalkylidenation*". Evidence, in the case of cycloalkenes, that the double bond was completely broken during ring opening necessitated a different approach to a mechanistic rationalization of metathesis and the work of Dall'Asta[15] added to the evidence which forced the revisions described in the next section.

1.2.3. The mechanism of olefin metathesis and ROMP.

Early mechanistic rationalizations of olefin metathesis favoured a four-centred process.[16] In these schemes a cycloaddition reaction of two alkenes was promoted by coordination to a transition metal, (Figure 1.3).

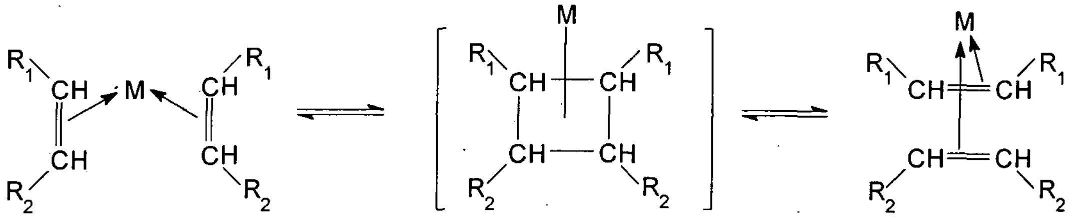


Figure 1.3. The pairwise mechanism of acyclic olefin metathesis.[14]

This mechanism involves the coming together of a pair of double bonds from two alkenes in the proximity of a transition metal centre. It was proposed that the d orbitals of the transition metal overlapped with the π orbitals, associated with the double bonds, in such a way as to allow exchange to occur via a weakly bonded cyclobutane complex. This was termed the pairwise mechanism.

Subsequently, theoretical arguments were developed to support the idea that a normally forbidden [2+2] cycloaddition could be transformed into an allowed process in the prescence of a transition metal in an appropiate oxidation state. However, the acceptance of this scheme was short-lived, and pairwise mechanisms gave way to a mechanism involving the alternation of a metal carbene and a metallocyclobutane as the chain carrying species, the so-called non-pairwise mechanism.[17]

Hérisson and Chauvin, in 1970, observed that some products from metathesis reactions could not be adequately accounted for by the pairwise mechanism, for example high molecular weight polymer is obtained in the presence of monomer which is a characteristic of chain growth rather than step growth polymerisation. They offered an alternative mechanistic rationalization involving the transformation of a metal carbene to a metallacyclobutane which cleaved to regenerate the metal carbene, (Figure 1.4), and this is now the generally accepted mechanism.[18]

The carbon-carbon double bond of the alkene initially coordinates to the transition metal to form a metal π complex. An electronic reorganisation takes place to give a metallacyclobutane, which cleaves to give the new metallo-olefin.

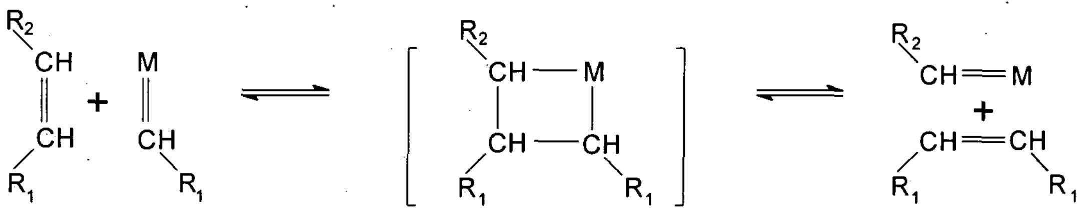


Figure 1.4. The non-pairwise (carbene) mechanism.

Each step in the process is reversible. The metallacyclobutane can revert to the starting metallo-carbene or transform into a new metallo-carbene with equal ease.

The ring opening of cyclic olefins follows a similar non-pairwise mechanism, as summarised in figure 1.5,

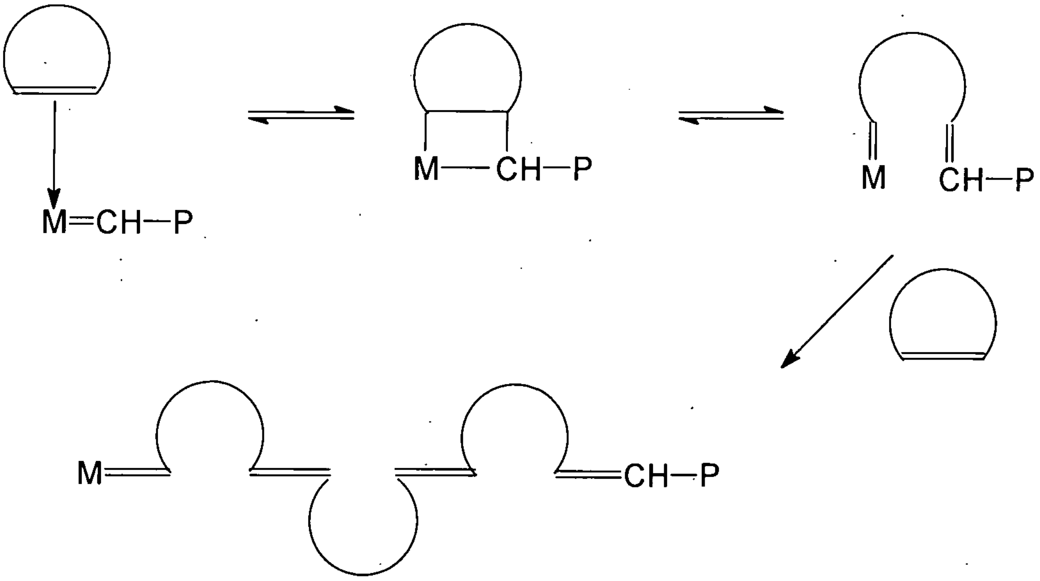


Figure 1.5. Schematic diagram for the ring opening of cyclic olefins.

where the repetition of this cycle results in the formation of unsaturated linear polymer.

1.2.4 Initiating systems.

1.2.4.1 Classifications.

The most widely used initiating systems in olefin metathesis and ROMP are based on compounds of the transition elements, Ti, V, Cr, Nb, Ta, Ru, Os, Rh, Ir. Generally the most effective initiators are those involving Mo, W, Re compounds.[1,4]

The range of initiators suitable for a particular metathesis reaction depends to some extent, on the reaction conditions and the monomer involved. Thus, the polymerisations of monomers with relatively high ring strain, for example norbornenes, are readily initiated by a wide range of transition metal systems, whereas monomers such as cyclopentene, with less ring strain, require more specific and highly active initiators in order for ring opening to occur.

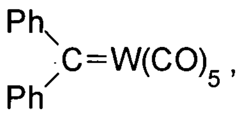
There are various classifications which have been used for initiating systems. The initiator can be of a heterogeneous or homogeneous nature.[3] Heterogeneous initiators normally consist of a transition metal oxide or carbonyl adsorbed onto a support such as alumina or silica. These systems are very rarely used for the ring opening of cycloalkenes and bicycloalkenes. Initiators of a homogeneous nature can consist of one or several components and are the most important class of initiators for ring opening polymerisation of cyclic and bicyclic alkenes. Another classification that has been made is that between the so-called "classical" initiators and the recently developed range of well-defined initiators. Both types have found widespread use in metathesis reactions.

1.2.4.2 Survey of initiator systems.

1.2.4.2a. Transition metal carbene complexes.

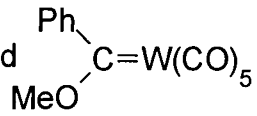
The first examples of compounds of this type which were used to initiate ring opening polymerisation were named after their discoverers, namely:

The Casey compound



$(Ph)_2C{=}W(CO)_5$, and

The Fischer compound



$Ph(MeO)C{=}W(CO)_5$

Ring opening polymerisation by the Casey compound [19,20] is often slow at room temperature and generally works better at elevated temperatures. The elevated temperatures cause carbon monoxide to be evolved, thus creating a vacancy to which the π electrons of the incoming monomer can coordinate in the first step of the reaction. Similarly, in the case of the Fischer compound,[21,22] a temperature of around 80^{0}C is required before the initiator becomes active, presumably because it is again necessary for a carbon monoxide ligand to be ejected before the initiator can become active. The activity of the Fischer compound is also enhanced by the prescence of an excess of $TiCl_4$. It then becomes active enough to initiate the opening of less strained rings such as cyclopentene and cyclooctadiene.

However, in recent years a second class of well-defined transition metal carbene compounds has been discovered. These are the so-called "Schrock" alkylidene complexes and they will be discussed later in this section.

1.2.4.2b. Transition metal halides.

These are often referred to as the "classical initiators" and the following transition metal halides and halide complexes have been used to initiate ring opening metathesis polymerisations:[23-26]

$TiCl_4$, $ZrCl_4$, VCl_4,
$NbCl_5$, $TaCl_5$, $MoCl_5$,
WF_6, WCl_6, $WOCl_4$,
$ReCl_5$, $OsCl_3$, $RuCl_3.3H_2O$.

Some of these compounds, including $MoCl_5$, $ReCl_5$ and WCl_6, (single component), require no deliberately added cocatalyst to bring about the polymerisation of highly strained rings such as norbornene. However, in the case of WCl_6 and $MoCl_5$ the activity of these catalysts seems to improve with the ageing of the sample, an effect which could be due to the cocatalytic action of traces of water or oxygen. Indeed the activity of most of these catalysts can be improved by the use of a cocatalyst (dual-component).

Co-catalysts normally consist of an organometallic compound of a non-transition metal. Common co-catalysts include: BuLi, Et_3Al, Et_2AlCl, Me_4Sn, Bu_4Sn, Ph_4Sn. They are thought to have several functions, such as providing a source of an alkyl ligand at the transition metal site which is subsequently converted into an alkylidene ligand by reductive elimination. It has also been suggested that perhaps the co-catalyst may also act as a ligand, attaching itself to the catalyst complex in some way and modifying the activity of the transition metal centre.

Furthermore, the activity of the transition metal halide when accompanied by an aluminium compound as co-catalyst is often enhanced by the addition of an oxygen containing compound as a third component. One example of such a system is the Calderon catalyst, $WCl_6/EtAlCl_2/EtOH$. This has proved to be very active in metathesis reactions, however it tends to be rather short lived and not very tolerant of functional groups on the monomer.

Co-catalysts carrying an alkyl group can exchange ligands with the transition metal halide compound resulting, eventually, in the formation of the initiating metallocarbene. For example, in the case of the WCl_6/Me_4Sn system, the proposed sequence of events is summarized overleaf.

$$\mathrm{WCl_6 + (CH_3)_4Sn \longrightarrow CH_3WCl_5 + (CH_3)_3SnCl}$$

$$\mathrm{CH_3WCl_5 \longrightarrow HCl + CH_2{=}WCl_4}$$

Proposed initiating carbene

1.2.4.2c. Oxides.

The oxides which are commonly used are those derived from Mo, W, Re.[27-29] They are usually adsorbed onto a support such as alumina or silica. Their catalytic activity is mainly confined to the metathesis of acyclic olefins, and they are very rarely used for the ring opening polymerisation of cycloalkenes, because the yields of polymer tend to be low. The catalyst is usually activated by heating in a specific atmosphere such as oxygen,nitrogen or hydrogen.

1.2.4.2d. Well-defined initiators for living ROMP.

A well-defined living polymerisation reaction, proceeds in the absence of the kinetic steps of termination or chain transfer. [30-32] These polymerisations provide the maximum degree of control of molecular weight and molecular weight distribution for the synthesis of polymers and, in favourable cases well-defined microstructures may also be obtained.

Among the features of a living polymerisation,[33,34] perhaps the most important is that concerning the number average molecular weight, M_n. In a well characterized living polymerization a plot of M_n versus %-conversion is linear with the intercept passing through the origin. This implies that M_n can be controlled by the stoichiometry of the reaction. Furthermore in an ideal living polymerisation, the rate of initiation (k_i) is greater than or of a similar magnitude to the rate of propagation (k_p) meaning that relatively narrow molecular weight distributions are achievable.

Another benefit of living polymerisation is the ability to synthesise block co-polymers. This can be achieved by sequential addition of a second monomer, following the total consumption of the initial monomer fraction.

Until relatively recently, the only metathesis initiators available were the 'classical' type of initiators. But in recent years a new class of well-defined initiators has been developed. These have a major advantage over their classical analogues in that they are able to promote living polymerisations. There are several further differences between classical and well-defined initiator systems. Classical ROMP initiators are ill-defined, and it is uncertain how many and what kind of active sites are present in any particular system. There is a lack of molecular weight control using classical initiators and polymers with broad molecular weight distributions are usually produced. This is due in part to the high activity of the chain end metal-carbon double bond and the fact that the carbon-carbon double bonds in the growing polymer chain can react both intra- or inter- molecularly giving cyclic or linear oligomers. There is an element of irreproducibility shown by classical initiators, and they show a limited tolerance of functional groups and only rarely produce stereoregular polymers. On the other hand, well-defined initiators in favourable cases allow the synthesis of highly stereoregular, virtually monodisperse polymers via a well controlled polymerisation. Indeed the reactivity of certain well-defined initiators can be 'tuned' using a suitable choice of ligands. Different ligands may alter the electronic nature of the metal centre, imparting different reactivities and stereoregulating capabilities on the chain end complex.

There are a variety of well-defined initiators which have found use in ROMP, including the titanacyclobutanes introduced by Grubbs [35] and the four coordinate 'Schrock' alkylidene complexes.[37,38]

I) Titanacyclobutanes

In 1984, Grubbs and Gilliom [35] reported the first examples of a living polymerisation of a cyclic olefin based on titanacyclobutane complexes (figure 1.6).

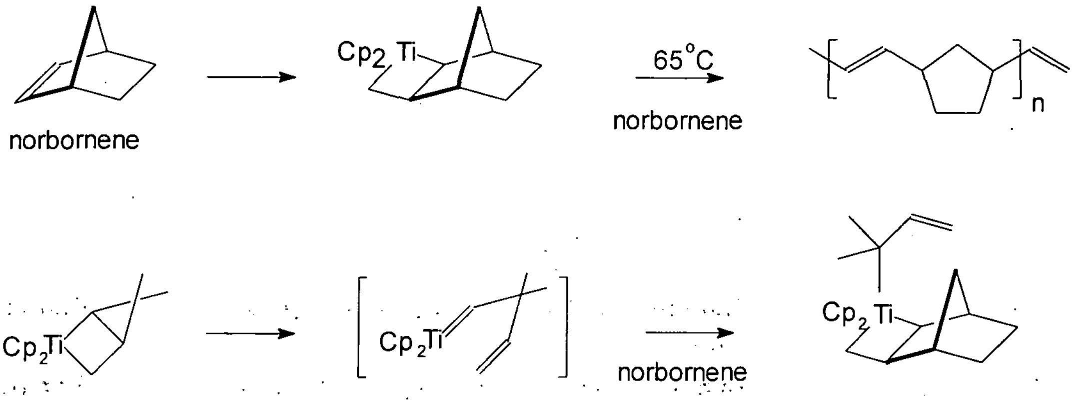


Figure 1.6. The living polymerisation of norbornene by titanacyclobutane complexes.

The titanacyclobutanes shown in figure 1.6 catalysed the polymerisation of norbornene in a living manner to give a polymer of narrow molecular weight distribution. The most stable state for the propagating chain end derived from these initiators appears to be the metallacyclobutane rather than the metal-carbene. This early work by Grubbs and co-workers paved the way for studies of the controlled syntheses of new polymers based on titanacyclobutane initiation, including various diblock and triblock copolymers of norbornenes and substituted norbornenes.[36]

Several key features for the design of living ROMP initiators have emerged from research on titanium metallacycles. The first feature is the low activity of the initiator, which contrasts with the high activity associated with classical catalysts. A highly active catalyst reacts with and degrades the growing polymer chain through chain transfer and termination reactions giving rise to a broadened molecular weight distribution. Secondly, chain growth is extremely sensitive to temperature, which allows the reaction to be stopped and re-initiated over a narrow temperature range.

II) Four coordinate alkylidene complexes.

In addition to the stable metallacyclobutane catalysts described previously, a series of stable alkylidene complexes based on tungsten and molybdenum have been synthesised and have shown to be active initiators of living polymerisations. The basic structure of these complexes is shown in figure 1.7.

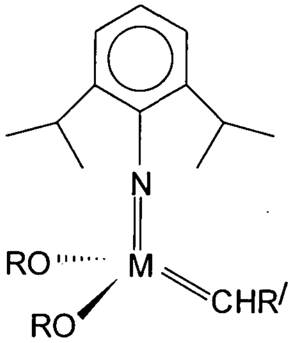


Figure 1.7. Basic structure of the "Schrock" initiator.

At the present time, the most effective catalysts are the four-coordinate neopentylidene (R/=t-Bu) and neophylidene ($R^{/}=CMe_2Ph$) complexes of tungsten and molybdenum. They contain two bulky alkoxide groups (OR) and a bulky diisopropylimido ligand.[37,38] Four coordination allows a relatively small monomer to attack the metal centre to give a five-coordinate intermediate metallacyclobutane complex, whilst the bulky alkoxide and imido ligands provide steric bulk and prevent decomposition reactions that could destroy the alkylidene ligand.

Tungsten complexes of the type $W(CH\text{-}t\text{-}Bu)(NAr)(Ot\text{-}Bu)_2$ where NAr represents the diisopropylimido ligand will bring about the ring opening of strained olefins such as norbornene, yielding polymers with polydispersities as low as 1.05. These living polymerisations can then be terminated or "end-capped" via a Wittig-type reaction using an aldehyde such as benzaldehyde. The well-defined living nature of the polymerization can be attributed to the relative inactivity of the living chain end towards unactivated double bonds, i.e. the internal olefins present in the polymer backbone.[39]

The activity of the catalyst can be altered by modifying the alkoxide ligands. The substitution of the t-butoxide ligands by $-OC(CH_3)_2CF_3$ or $-OCCH_3(CF_3)_2$ leads to increasingly more active catalysts, which are reactive enough to bring about the metathesis of less strained acyclic olefins. For example, $W(NAr)(CHt\text{-}Bu)(OCCH_3\text{-}(CF_3)_2)_2$ will metathesize cis-pent-2-ene at a rate of 10^3 turnovers per minute, however under the same conditions the t-butoxide analogue only achieves a rate of two turnovers per hour.[39,40]

This difference in reactivity is due in part, to the dramatically lower electrophilicity of the metal centre in the t-butoxide complex compared to the fluorinated analogues, making it less susceptible to nucleophilic attack from the carbon -carbon double bond of the reacting olefin. Hence by varying the electronic and steric properties of the alkoxide ligands, the electronic nature and hence the reactivity and stereoregulating ability of the active chain end can be controlled.

Further synthetic utility can be introduced by changing the metal centre in the alkylidene complexes from tungsten to molybdenum. The same trends exist in molybdenum complexes as for tungsten complexes, namely that the hexafluoro t-butoxide complex is more reactive than the t-butoxide complex for metathesis reactions. However, one major difference between the molybdenum and tungsten initiators is the fact that the molybdenum complexes are much less reactive than their tungsten counterparts. This means that molybdenum based initiators are able to tolerate monomers with mildly reactive functionalities such as esters and nitriles, without any significant catalyst deactivation during the polymerisation reaction. For example, the ROMP of 2,3-dicarbomethoxynorbornadiene[41] can be brought about by the molybdenum alkylidene complex, as shown in figure 1.8.

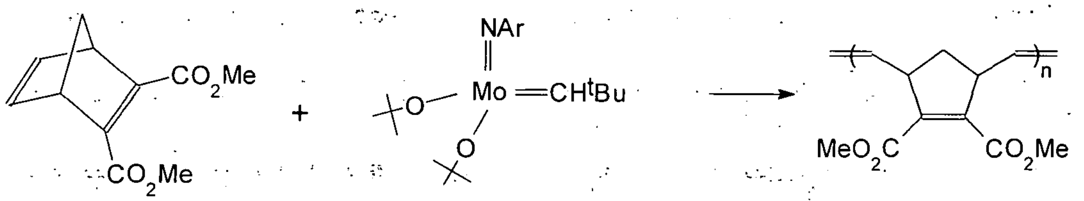


Figure 1.8

Some examples of other functionalised norbornenes and norbornadienes which can be polymerised by the molybdenum initiator are shown overleaf in figure 1.9.[41,42,43]

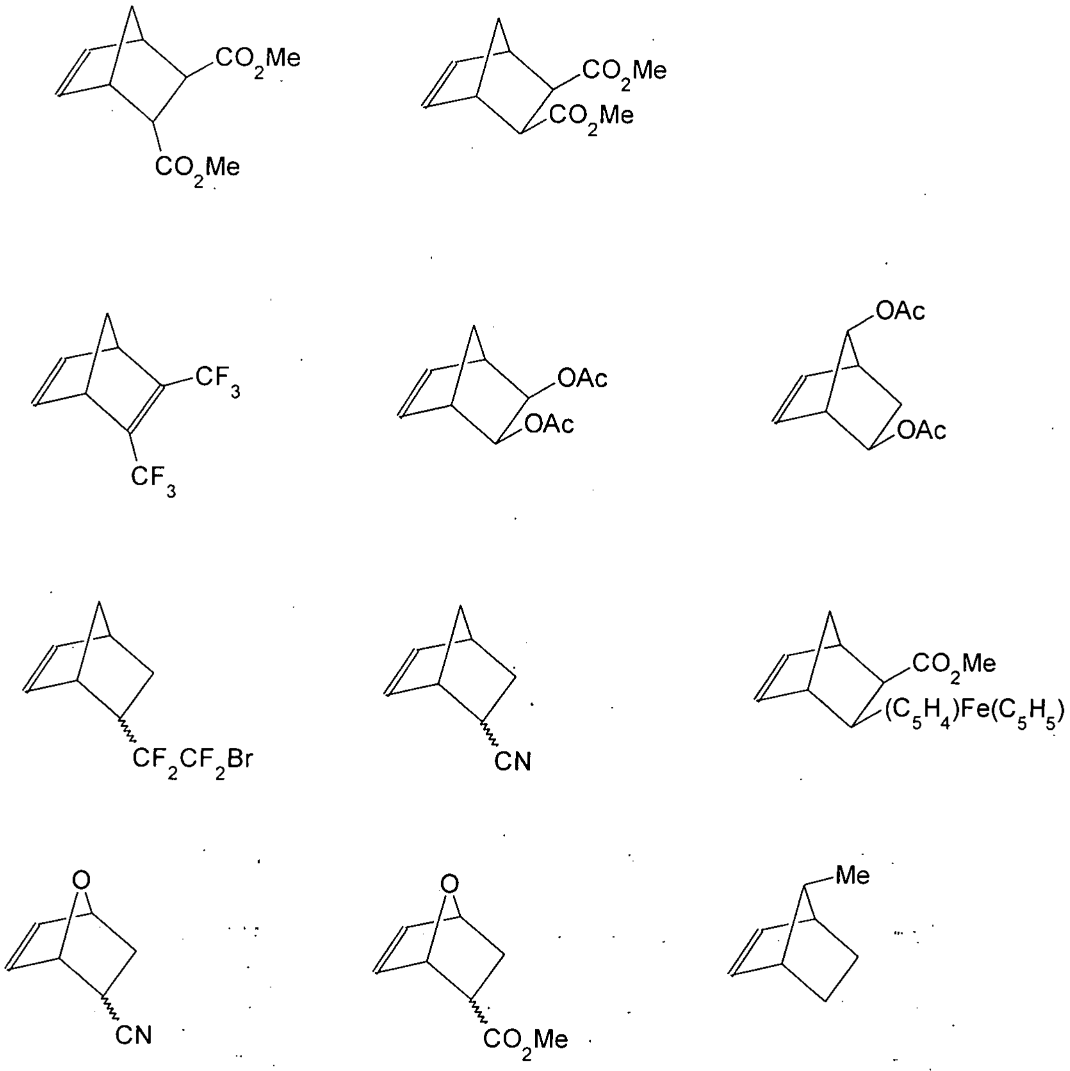


Figure 1.9. Diagram showing some examples of functionalised norbornenes and norbornadienes which can be polymerised by the molybdenum "Schrock" initiator.

It is not yet totally clear why tungsten does not appear to polymerise monomers containing a range of functionalities. Possible reasons include the tungsten alkylidene reacts more readily with the functionality in the polymer chain than molybdenum does, as stated previously. Also tungsten based initiators may be more sensitive to traces of impurities present in the monomer than the molybdenum analogues.[39]

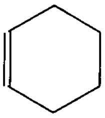
Much research is being performed in this field at present. Well-defined initiators are rapidly becoming the initiators of choice for ROMP reactions, since they give more controlled polymerisations, with the aim of having more control over the resulting polymer microstructure. Detailed discussion concerning the effect the initiator has on the polymer microstructure will be addressed later in this thesis.

1.2.5. Thermodynamics of ring opening metathesis polymerisation.

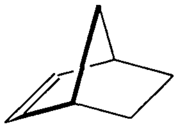
The thermodynamics of ring opening polymerisation is a widely studied subject and the ROMP of cyclic olefins is a special case of this more general topic. The metathesis reaction of linear alkenes is characterised by the cleavage and formation of an equal number of virtually identical chemical bonds and the enthalpy changes associated with such reactions are zero or very small. [1,3] The product distribution is statistically controlled. Whilst the metathesis of linear alkenes gives structures similar to the reactants, the metathesis of cyclic alkenes involves different processes, including ring cleavage and the formation of a distribution of linear and possibly macrocyclic molecules. The ring cleavage is accompanied by the release of ring-strain energy. In this case, the enthalpy of polymerisation is not expected to be zero except when a strain-free monomer is involved, and indeed the ring-strain energy is an important factor when considering the polymerisability of cyclic olefins. The change in entropy on polymerization is, of course, always negative.

Ring opening polymerisations of all types are thermodynamically favourable for 3,4,8 and larger membered rings, and will proceed if a suitable mechanism is available, as in the case of cycloalkenes. [44] For 5,6, and 7 membered rings, the situation is more delicately balanced. The sign of the Gibbs free energy of polymerisation, ΔG, may be influenced by a number of physical factors including monomer concentration, temperature and pressure and also by a number of chemical factors such as the nature and type of substituents present and their positions on the ring. When bridging groups are present i.e. when the compound is bi- or polycyclic, ΔG for the opening of a particular ring maybe more negative, as a result of the increased strain energy.

A good example which illustrates the effect of a bridging group on the ring opening of cycloalkenes is the difference in polymerisability between cyclohexene and norbornene whose structures are shown below.



Cyclohexene



Norbornene

Cyclohexene will not undergo ring opening polymerisation. Its failure to polymerise is due to its low strain energy, its ΔG of polymerisation is positive. However, norbornene will readily undergo ring opening and indeed it is one of the more reactive monomers to be used in ring opening metathesis polymerisations. It may be regarded as being derived from cyclohexene with the introduction of a bridging methylene group which forces the six membered ring into the more strained boat conformation. This results in increased ring strain and ΔG for the polymerisation becomes negative.

For addition polymerisations of any kind, of which ring opening is a particular type, the barrier between polymerisability and non-polymerisability is very distinct,[4] corresponding to negative and positive values of ΔG respectively. A well defined temperature, known as the *Ceiling Temperature,* may be observed, above which polymerisation will not occur, at a given monomer concentration and pressure.

1.2.6 Applications of ROMP polymers.

A variety of polymeric materials have been made via ROMP and some of these have been commercially exploited.[17] These include Norsorex (from norbornene, CdF), Vestenamer (from cyclooctene, HÜls), and Metton (Hercules) and Telene (BF Goodrich) (from dicyclopentadiene RIM) and their structures are shown in figure 1.10.

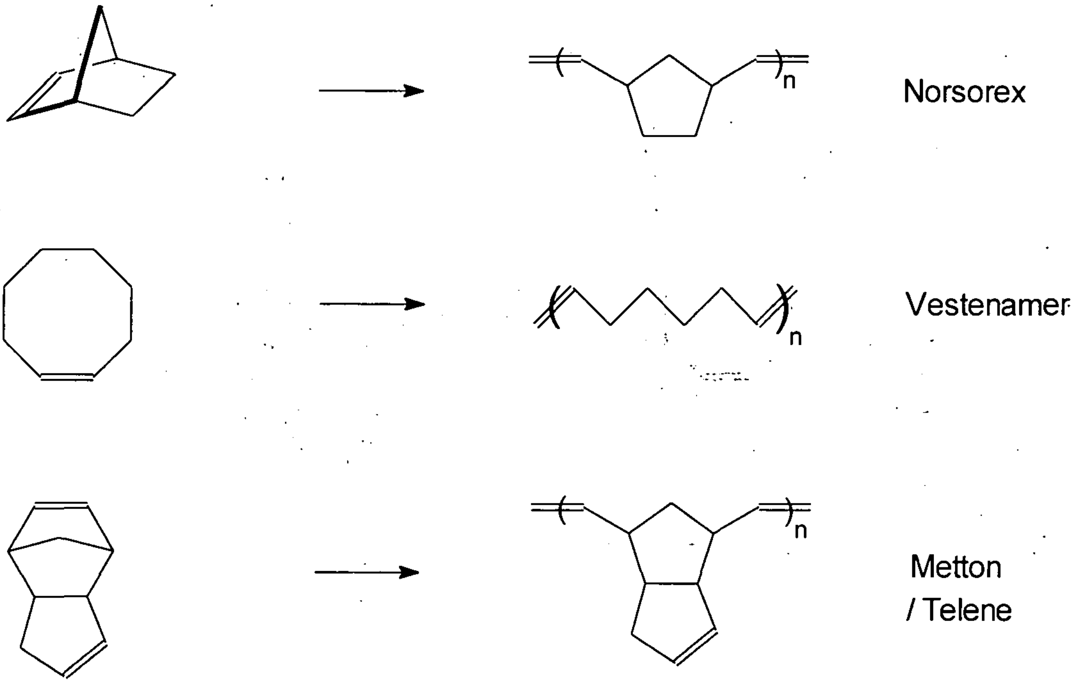


Figure 1.10 Industrial olefin metathesis processes.

In the late seventies, there was a flood of patent activity concerning ROMP polymers but many of these materials have not yet been commercially exploited.

Some of the major patent holders in this area include BF Goodrich, the Japanese Synthetic Rubber Company, Nippon Xeon and Showa Denko.

Norsorex was the first product to be introduced commercially. It was initially manufactured by CdF Chimie in France in 1975 and in 1985 a production output of around 5 Mlb per annum was reported.[45] The polymer has certain unique properties such as a glass transition temperature of around 35^0C and a very high molecular weight of two million.[46] It is the 90% trans polymer of norbornene and is usually sold as a moulding powder, being mainly used in formulations which contain high levels of plasticizing oils. This effectively lowers the T_g of the blend, giving the product elastomeric properties. The vulcanised product has proved important in certain specialist areas. These include vibration-damping applications such as anti-vibration mounts and shock-proof bumpers.

Trans-polyoctenamer was first marketed as Vestenamer 8012, by Chemische Werke Huls in 1980,[47] the polymer containing 80% trans double bonds. At room temperature it is hard with a melting point above 60^0C, the melt viscosity is, however, fairly low. The hardness of the polymer at lower temperatures can be attributed to its crystallinity (33%) whilst its fluid like nature at higher temperatures is due to its relatively low molecular weight (60,000). This combination of properties has made Vestenamer appear suitable for use as a blending agent in conjunction with other elastomers and the material has found speciality applications.

Polymers from dicyclopentadiene (DCPD) have been studied in depth by several research groups, mainly on account of the low cost of the monomer. In the early eighties, BF Goodrich marketed the linear polymer of DCPD under the name

Telene.[48] Subsequently this name was also used for their DCPD RIM (reaction injection moulding) product.

In 1985, Hercules Inc. investigated the development of a RIM technology based on DCPD,[49,50] and named the product Metton. Metton and Telene possess certain advantages including high strength, rigidity, and impact resistance making them desirable materials for a variety of engineering applications. Some of the more attractive uses include components for jet skis, snow mobiles and golf carts. The obnoxious smell of the monomer means that most applications of DCPD RIM products are likely to be for open air use unless a complete consumption of the monomer can be guaranteed.

The first metathesis polymer to be seriously considered for commercial production was the polymer of cyclopentene, Polypentenamer.[51] It possesses attractive elastomeric properties, and the monomer could be obtained relatively cheaply from cyclopentadiene, a by-product from the steam cracking of naphtha. The technology was developed to the pilot plant stage by several companies during the 1970s. However, changes in the availability of the raw materials and a shifting emphasis towards different types of elastomers, coupled with an uncertain economic environment, resulted in the shelving of exploitation plans.

Other ROMP polymers have been test marketed and some new materials have recently appeared. The Nippon Xeon company have an optical polymer which is believed to be the hydrogenation product of a polymer made by the ROMP of a polycyclic alkene. This material already finds application in camera components and optical discs under the name Xeonex.

There also exists a range of new materials which are being investigated, and which have been made possible by the advent of a range of well-defined initiators (discussed in section 1.2.4.). The materials attracting interest include conducting polymers, piezo- and pyroelectric materials, side chain liquid crystal polymers and precursors to ceramics.[52] Due to the well-defined nature of the initiator, more control and information can be gained about the polymer microstructure and molecular weight distribution, making the discovery of new speciality materials more probable. However, to be of significance commercially, these new ROMP materials face stiff competition from the already well-established polymers in use.

1.3 Fluoropolymers and polar polymers.

Highly fluorinated polymers have been investigated and developed on account of their unusually high thermal and chemical stabilities, which are attributed to the strength of the *C-F* bond compared to that of the *C-H* bond and the shielding of the carbon backbone by the fluorine atoms. [53] Dramatic changes in physical properties and chemical reactivities of organic materials can be brought about by fluorination as todays diverse range of fluoro-organic products show. Not only does fluorine form the strongest single bond to carbon in organic chemistry (Table 1.1), [54] but also its steric demands are very modest, especially when compared with other halogens(Table 1.2). [55]

Table 1.1 Bond dissociation energies/KJmol^{-1}

C-F	**485**
C-Cl	339
C-Br	285
C-I	213
C-O	358
C-N	301
C-C	346

Table 1.2 Intermolecular van der Waals radii (r_w / Å)

H	C	N	O	**F**	Cl	Br	I
1.20	1.70	1.55	1.52	**1.47**	1.75	1.85	1.98

Only in the case of fluorine, therefore, can the total replacement of hydrogen by a halogen in any hydrocarbon or functionalised derivative be envisaged, to produce a halogenocarbon analogue. The vast range of fluoro-organic materials available today on the market include; drugs, dyes, surfactants, polymers, anaesthetics and agrochemicals. These all demonstrate the beneficial effects that fluorination produces as well as showing that the behaviour of fluorinated compounds has become fairly well understood.[56]

Important characteristic effects arising from the prescence of carbon-fluorine bonds can be deduced by comparing some fundamental properties of atomic fluorine with those of other elements. For example high ionisation potentials and relatively low polarisabilities imply very weak intermolecular forces and low surface energies for perfluorocarbons (compounds containing only carbon and fluorine). The extreme electronegativity (Pauling values: *F, 4.0; O, 3.4; Cl, 3.2; C, 2.6; H, 2.2*) of bound fluorine will ensure that all *C-F* bonds are polarised; $C^{\delta+}$-$F^{\delta-}$, consequently *C-F* bonds will possess relatively high ionic character and will be stronger than other carbon-element bonds. Owing to the *C-F* bond dipole, partially fluorinated materials (hydrofluorocarbons) should be significantly polar, and therefore expected to possess physical properties quite different from those of their hydrocarbon or perfluorocarbon analogues. It is the combination of the physical and chemical properties associated with fluorinated organic materials that has inspired the extensive commercial development of fluoropolymers (figure 1.11.). The useful properties of fluoropolymers include those described overleaf.

i) **Thermal stability.**

At the heart of commercial interest in fluoropolymers lies the great strength of the *C-F* bond, which increases with accumulation of fluorine. Thus the *C-F* bond dissociation energy rises progressively from 456 to 546 kJmol^{-1} on moving from CH_3F to CF_4, and, as expected, the *C-F* bond lengths decrease progressively.[57] No such trend is observed for other halogenomethanes.

ii) **Chemical inertness and solvent resistance.**

The extraordinary resistance shown by perfluorocarbons towards attack by hostile chemicals (hot, concentrated acids and alkalis) and solvents is well known and this resistance extends to polymeric systems.[58] The inertness could be attributed to (for example in the case of *PTFE*) the shielding of the carbon backbone by fluorine, allied to the great strength of the carbon-fluorine bonds and their lack of polarisability. The fluorine atoms in a saturated perfluorocarbon are of such a size that they form an almost impenetrable sheath, with tightly held electrons, which clearly must provide the carbon backbone with excellent protection from chemical attack.

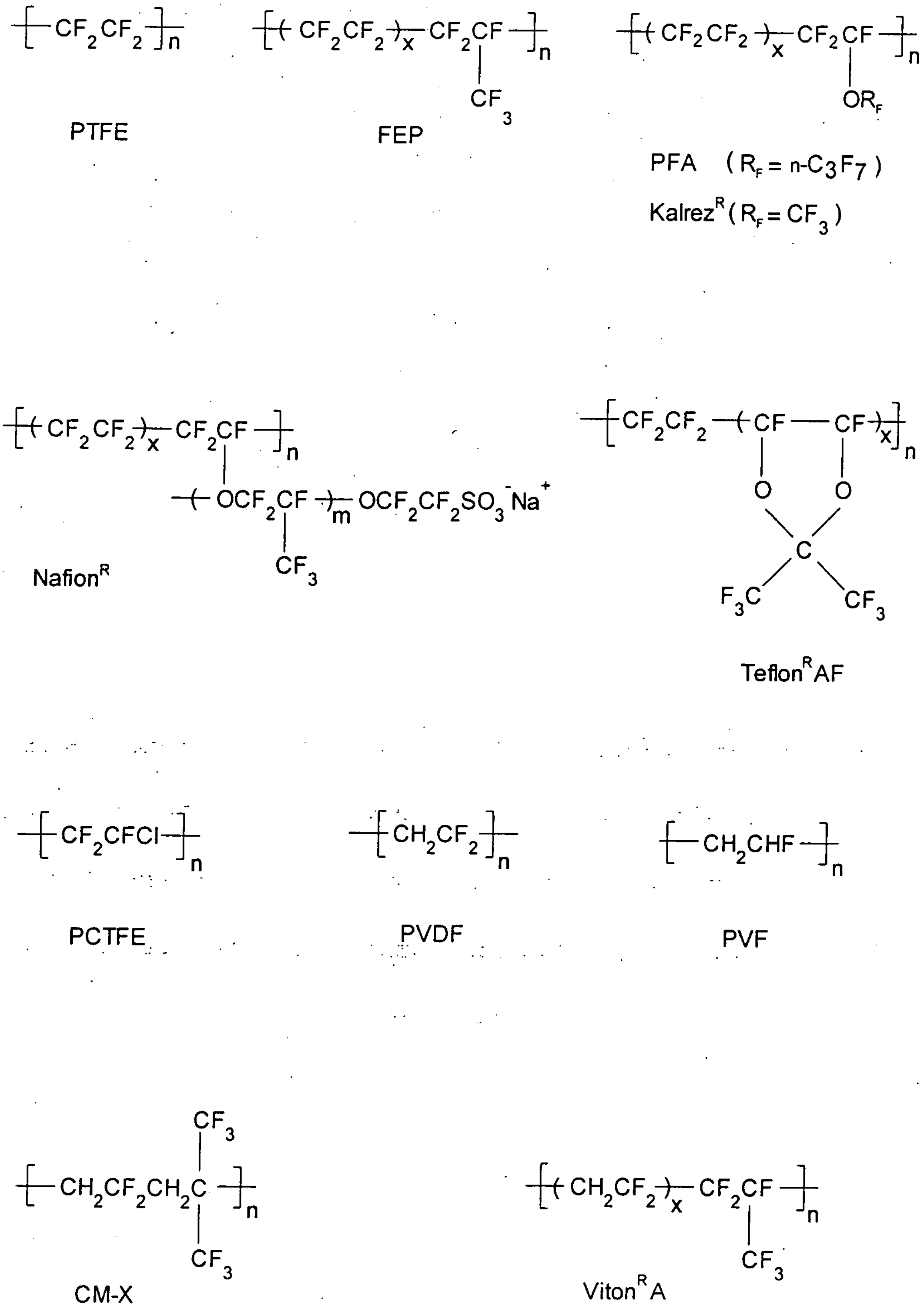


Figure 1.11. Some common fluoropolymers.[53]

(See Table A2.1, Appendix 2, for the full names of the fluoropolymers used in the figure above).

The compact fluorine envelope forms such a protective coating that rates of reaction are greatly reduced even under conditions where reactions are thermodynamically favourable. [59] Naturally, partially fluorinated polymers are less resistant to chemical attack than their perfluorocarbon analogues and are thus more susceptible to attack by nucleophilic reagents. The question then arises of balancing the fluorine content in the polymers with the end product requirements.

It is well accepted that stereoregulation often gives access to improved polymer properties. So the combination of stereoregulation and the advantages conveyed by fluorine substitution, as discussed in this section, might give rise to novel materials, which will display interesting and possibly valuable properties.

1.4 Electroactive polymers.

1.4a. Piezoelectricity and Pyroelectricity.

Historical introduction and definitions

*"**Pyroelectricity**": An electric polarisation produced in certain crystals by a change in temperature.*

*"**Piezoelectricity**": An electric polarisation produced by a mechanical strain in certain crystals.* [60]

The existence of piezoelectricity in certain synthetic and biological polymers has been known for some time. [61-65] In particular, the piezoelectric effect in polymers of biological origin such as bone and tendon has been studied in detail. [66,67] However, the piezoelectric effects generated by these polymers are small, and despite the considerable academic interest in these materials no significant technological activity resulted.

The situation changed greatly in 1969, when Kawai [68] and others showed that substantial piezoelectric and pyroelectric activity could be generated in synthetic polymer films. Because of their flexibility and availability in the form of thin films of large area, these materials provided opportunities for new application and device ideas which could not be realised with the traditional piezo- and pyro-electric materials, which are generally ceramics.

Poly(vinylidene fluoride) (PVDF)

The best known, and commercially most attractive example is poly(vinylidene fluoride) (PVDF), and in recent years it has come to be regarded as the archetypal piezoelectric polymer. Indeed there has been a rapid growth in interest in piezo- and pyro-electricity in synthetic polymers following the discovery of such effects in PVDF. Most activity and interest has centred on PVDF itself, which yields the highest response of all synthetic polymers investigated to date.

PVDF is a semicrystalline thermoplastic polymer with the repeat unit $\mathbf{(CH_2CF_2)_n}$. It is resistant to a wide range of solvents and is chemically inert. It can be easily produced in a wide variety of shapes, and in particular it can be made in film form down to thicknesses of 6μm. As normally produced, it is about 50% crystalline, with the crystalline region having a melting point between 430K and 470K depending on the crystal form present, and the amorphous regions have a T_g around 230K. For many purposes, it has been useful to consider PVDF as a composite material, composed of stiff, crystalline lamellae surrounded by a soft amorphous matrix. [69]

In order to exhibit piezo- or pyro-electric behaviour, it is necessary to obtain a poled sample. This is achieved by subjecting the sample to a large electric field (100MVm^{-1}), usually at a raised temperature. Poling the material produces many effects including orienting the dipoles in the sample. Indeed it is thought that the outstanding piezoelectric properties displayed by PVDF, are due to its high dipolar (*C-F* dipole) alignment in the prescence of an electric field. This explains why PVDF exhibits considerably greater piezoelectric activity than other synthetic polymers which do not show such high dipolar alignment. A thin poled film of PVDF with electrodes on either side is the essential component of a piezoelectric device. When the electrodes are connected as part of a circuit and the film is exposed to a mechanically induced distortion the charge separation across the poled film results in a detectable current in the external circuit.

This is a much simplified version of how piezoelectricity occurs in PVDF. Pyroelectricity requires the same poled structure and the charge separation and current flow is induced by distortions following absorption of heat, usually infra-red radiation. The actual mechanism of these physical processes is much more complicated and has been the subject of intense research by physicists. PVDF consists of at least four different crystalline domains, commonly named the **I, II, III** and **II$_p$** forms. With the forms being interchangeable with each other on the application of heat, electric fields and pressure. This interconversion, combined with the fact that the crystalline and amorphous phases possess different dielectric and elastic properties has been used as the basis for the models used to try and explain the origin of piezoelectricity in PVDF in detail. The detailed physics is beyond the scope of this study and for further detail the reader is referred to more advanced texts.[60,61 69-72]

Commercially, PVDF has been used in a variety of applications. Its main competitors have been ceramic materials, especially the salt; lead zirconate titanate (PZT). It differs in many respects from these more conventional piezoelectric materials, in particular, it is characterised by such properties as flexibility, ruggedness, softness and light weight. It is easily available in thin films and relatively inexpensive to produce. However, one of the drawbacks of PVDF is its poor electrical stability at elevated temperatures, which means its "service" temperature is limited to 80^{0}C. In this respect, the ceramic materials are vastly superior.[73]

Some of the applications proposed and established for PVDF, include; as a pyroelectric polymer film where it has been utilised in infra-red cameras as an optical detector. In this application its small heat capacity permits a rapid response within the camera. Its piezoelectric properties have enabled it to find use in transducers for audio-frequency applications such as in microphones and loudspeakers. It has also found use in the fields of ultrasonic and underwater transducers, and as electromechanical transducers in telephone dials and computer keyboards. For more information on the applications mentioned and other potential uses, the reader is advised to consult the various reviews published on the subject.[74 - 78]

1.4b. Optical and electrical properties of conjugated polymers.

1.4.1b. Introduction.

Conjugated polymers are capable of being modified via oxidation or reduction to states of high electrical conductivity. Previous generations of polymeric materials have been developed to provide various properties; for example, desired mechanical strength, processing possibilities and electrical insulation. This new generation of conjugated polymeric materials possess σ-bonded chains, which provide the conventional polymer strength and processing attributes, coupled to a relatively high density of conjugated π-electrons which give rise to novel electrical and optical properties. The π-electrons are less tightly bound to the atomic framework and electrons may be added, removed or photochemically reorganized [79] to create the charge carriers and excited states on which the novel electrical and optical properties depend.

One of the major challenges in this field is the finding of new synthetic routes with the aim of producing polymers in a form suitable for application. Indeed much research at this present time, is directed towards addressing this problem of polymer processability. This class of materials display many desirable properties which have produced interest for a variety of applications, and some of these will be discussed later in this section.

1.4.2b. Basic properties of conjugated polymers.

In the past, organic materials have not usually been acknowledged for their ability to conduct electronic charge. Indeed the traditional role of organic polymers in electronics has been as insulators. [80] Generally, organic materials which contain mostly saturated bonds have proved to be excellent insulators, on account of their bonding orbitals being tightly bound to form localised covalent bonds.

However, in conjugated polymers, where the polymer backbone consists of alternating single and double bonds, very different electronic properties result. In terms of chemical bonding, the σ bonds connecting adjacent carbon atoms in the polymer chain are formed from sp^2 hybrid atomic orbitals (AOs). A σ bond also binds the hydrogen atoms in the polymer chain. In addition, every sp^2 carbon atom provides an electron in a p_z AO which is used to form a π bond. It is the π electrons which become the most important ones with respect to the electronic properties.[80,81]

These π electrons overlap with adjacent p_z atomic orbitals to form a delocalised π electron cloud which spreads along the polymer backbone. This can be illustrated diagrammatically using poly(p-phenylenevinylene) (PPV) as an example, figure 1.12.[82]

Part a) of figure 1.12 shows the monomeric unit of PPV. It shows the conjugation present in the polymer with alternating single and double bonds along the chain. Part b) shows part of the PPV chain schematically, it displays the p_z orbitals which are combined to form delocalised π-MOs and consequent electron cloud above and below to the planar σ-bonded framework.

When this happens, delocalised π bonding and π^* anti-bonding bands are formed, also termed valence and conduction bands respectively. This is a prerequisite for semi-conducting behaviour. Normally, electrons sit in the lower energy valence band, but if supplied with enough energy they can move into the normally empty upper conduction band. The reader is referred to the excellent reviews that are available in the literature detailing the mechanism of semi-conducting behaviour in polymers.[79,80,83-85]

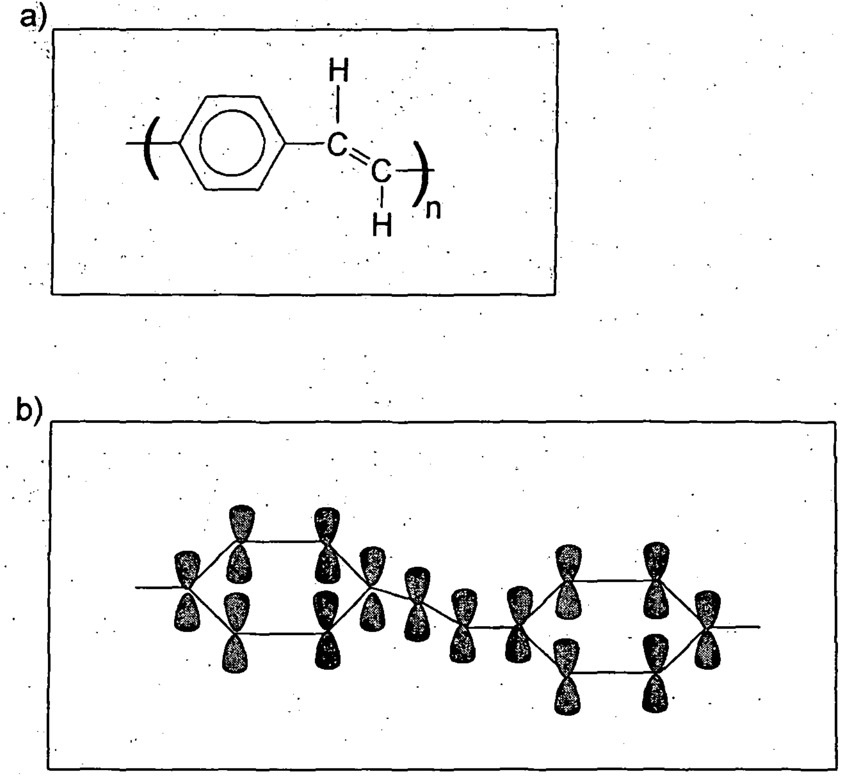


Figure 1.12. Poly(p-phenylene vinylene) and the form of the p_z AOs used to construct the π-molecular orbitals (MOs).

1.4.3b. Examples of conjugated polymers.

Conjugated bond structures are found in several aromatic and heterocyclic polymers. Figure 1.13 lists some of the most thoroughly investigated polymers of this class [79,84]. All of the polymers listed have chemical structures which result in materials capable of semi-conducting behaviour. Charge injection or 'doping' of these materials results in a variety of interesting properties with potentially useful applications. One such application uses conjugated polymers as the active components of light emitting diodes and this area of research will be discussed later.

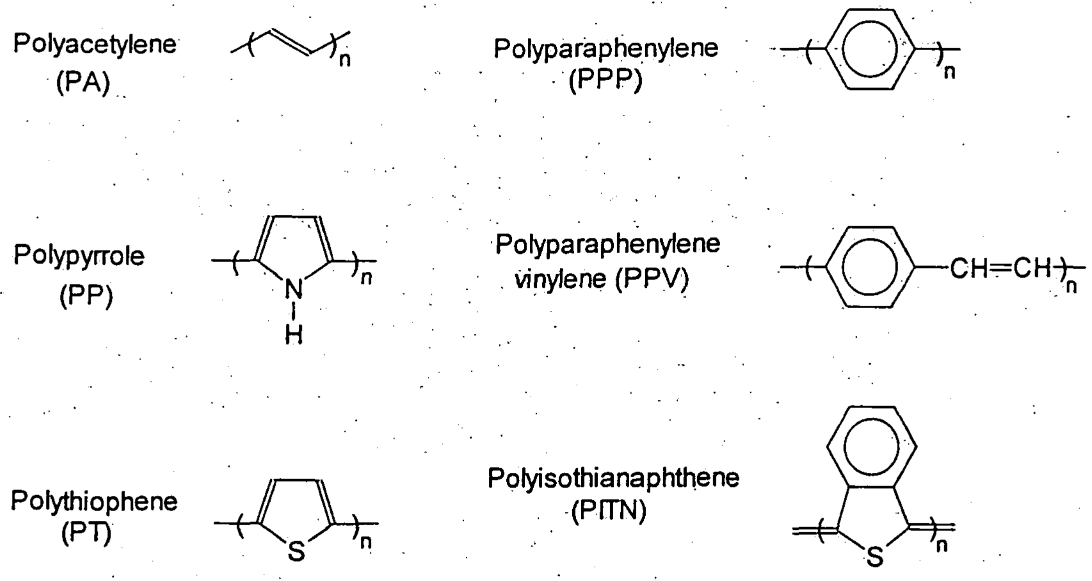


Figure 1.13. Some common conjugated polymers.

1.4.4b. Poly(p-phenylene vinylene)-based light-emitting diodes.

Electroluminescence through charge injection under an applied field, has been known in organic semiconductors for some time, with a considerable amount of interest centred around anthracene.[86,87,88] In 1990, Burroughes *et al.*[89] reported electroluminescence in poly(p-phenylene vinylene) based polymers, and since this discovery, there has been a great flurry of activity in this area.

Basically, the structure of a polymer LED consists of a conjugated polymer, PPV in this case, as the single semi-conductor layer sandwiched between two electrodes.[90,91] The device is fabricated on a glass substrate, with a transparent indium/tin oxide layer as the positive, hole-injecting contact. The polymer is deposited onto this layer and a metal such as aluminium, magnesium or calcium forms the top contact to provide the source of electron injection.

Light generation in a polymer LED involves a series of steps including hole injection (from the indium/tin oxide layer) , electron injection (from the metal), electron transport, electron-hole capture and radiative decay of the singlet exciton produced, and indeed much research has been directed towards understanding the underlying mechanism of electroluminescence in these devices.[92]

Poly(p-phenylenevinylene) is an intractable material with a rigid-rod crystalline structure, it is infusible and insoluble in common solvents, giving it excellent mechanical and thermal properties with good stability to 400^{0}C. These are ideal properties for a film of polymer once formed, but not ideal for the processing of the polymer, and indeed processing cannot be carried out directly with this material which is usually produced via a processible precursor.[93,94]

Variations of the PPV structure have been devised, such as block co-polymers, and substitution with solubilising side chains on the PPV backbone, or groups capable of modifying spectroscopic or electronic properties such as cyano groups.[92,95] By altering the composition of the polymer in the device a variation in the wavelength of light emitted can occur,[96-98] and one of the aims in this field is to produce a wide range of emitted colours from these devices. In chapter 5 of this thesis, attempts to synthesise a highly fluorinated derivative of PPV, of potential interest in this field, are described.

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Chapter 2

Poly(bis(trifluoromethylnorbornadiene)

Synthesis, Characterisation and Properties

2.1 Introduction.

2.1.1. Ring opening metathesis polymerisation of fluoro-cycloolefins.

It has been known for some time that stereoregulation can often give rise to improved polymer properties and the benefits bestowed by fluorine substitution were outlined in Chapter 1 of this thesis. Thus the synthesis of stereoregular fluoropolymers seemed to present a worthwhile challenge in the area of ring opening polymerisation.

It was in 1979 that Wilson showed, for the first time, that fluorinated norbornene type monomers were susceptible to ROM polymerisation using 'classical' initiating systems such as WCl_6/Me_4Sn, however, the polymers produced had mainly atactic microstrucures.[1,2] This finding quashed the scepticism prevalent at that time concerning the polymerisability of fluorinated monomers using Ziegler-Natta-like transition metal initiators. It was perceived that halogenated substrates would act as inhibitors or poisons for polymerisations propagated at the metal centre. The prevalent view being based on the premise that the "active site" or "vacancy", which was proposed as existing at the propagating transition metal at the chain end would react to form metal-halogen bonds in preference to coordinating to the π bond of the incoming olefin.

Since this initial discovery, a wide range of monomer structures with varying degrees of substitution have been investigated and polymerised with a range of transition metal compounds as the initiator (figure 2.1).[1-10] Substituted bicyclo[2.2.1]hept-2-enes and bicyclo[2.2.1]hepta-2,5-dienes proving to be suitable monomers for these studies, attempts to polymerise fluorinated cyclopentenes have so far proved unsuccessful. The section of the periodic table shown, illustrates the transition metals which have been incorporated in initiator systems for use in olefin metathesis reactions and the elements displayed in bold type have generally proved to produce the most effective initiators.

4	5	6	7	8	9
Ti	V	Cr			
Zr	Nb	**Mo**		Ru	Rh
Hf	Ta	**W**	**Re**	Os	Ir

The monomers shown in figure 2.1. are easily prepared by Diels-Alder reactions between cyclopentadiene or dimethylfulvene and the appropiate fluorinated dienophile.[7] The monomers shown vary in their complexity, a few examples from figure 2.1. will illustrate this point. For example, crossing the first row from left to right results in an increase in monomer complexity. Thus, the first monomer, 2,3-bis(trifluoromethyl)norbornadiene, is a single unique compound; the second monomer, 2-trifluoromethylnorbornadiene is chiral and is produced as a racemic mixture; finally, in this row, the 5-substituted norbornenes can display the additional complication of *exo-/endo-* isomerism and, almost invariably, the product of synthesis is a mixture of both isomers and, as both are racemic, the monomer is usually obtained as a combination of four compounds. These examples highlight some of the potential complications of monomer structure that need to be considered when selecting compounds suitable for polymerisation studies.

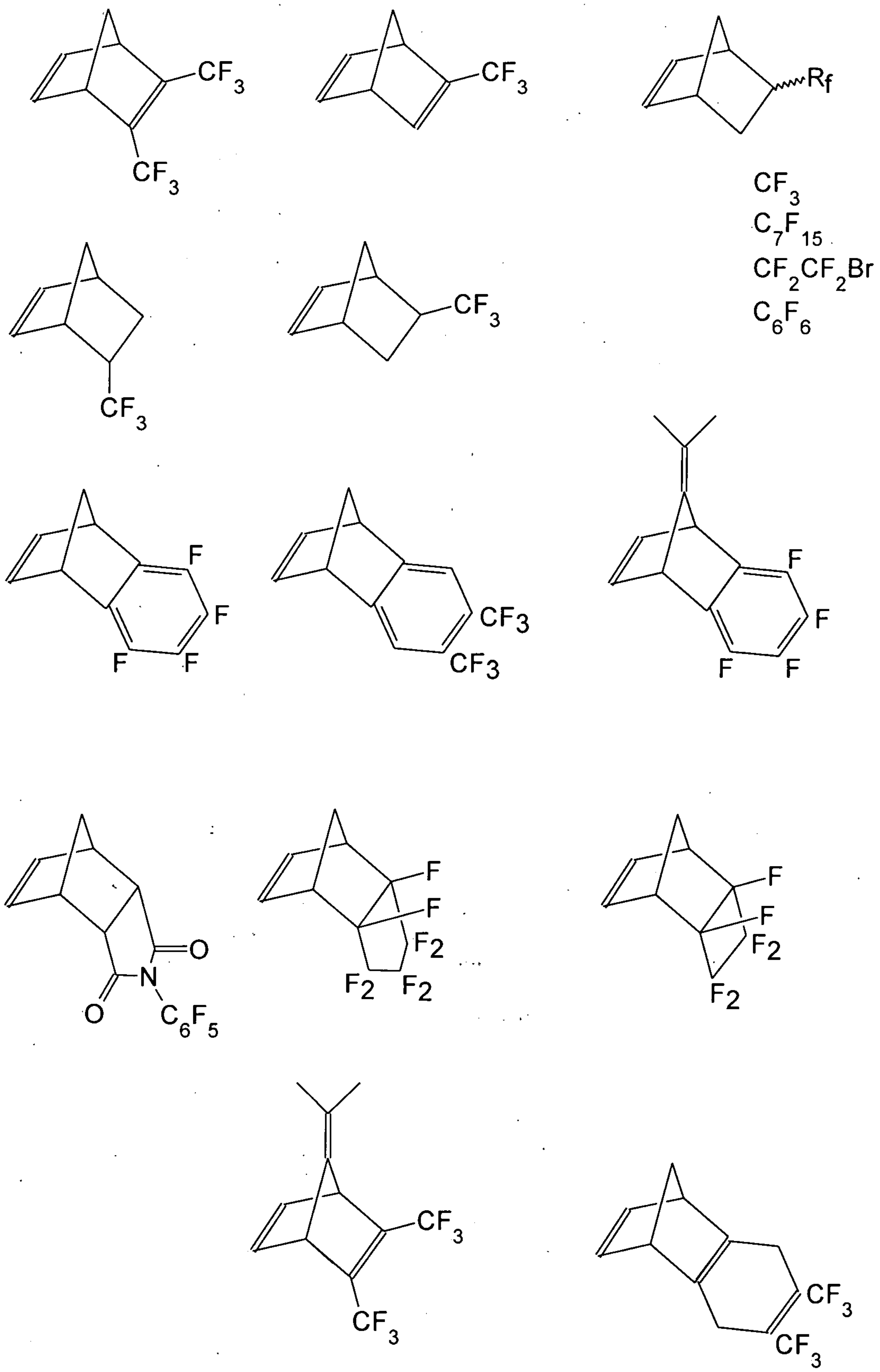


Figure 2.1. A selection of the fluorinated monomers which will undergo ROMP.

2.1.2. Ring Opening Metathesis Polymerisation of 2,3-bis(trifluoromethyl)-norbornadiene.

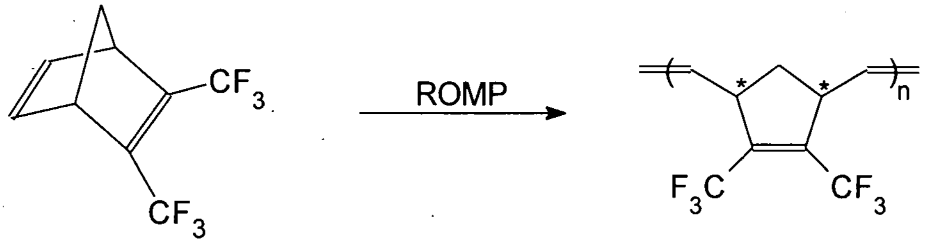
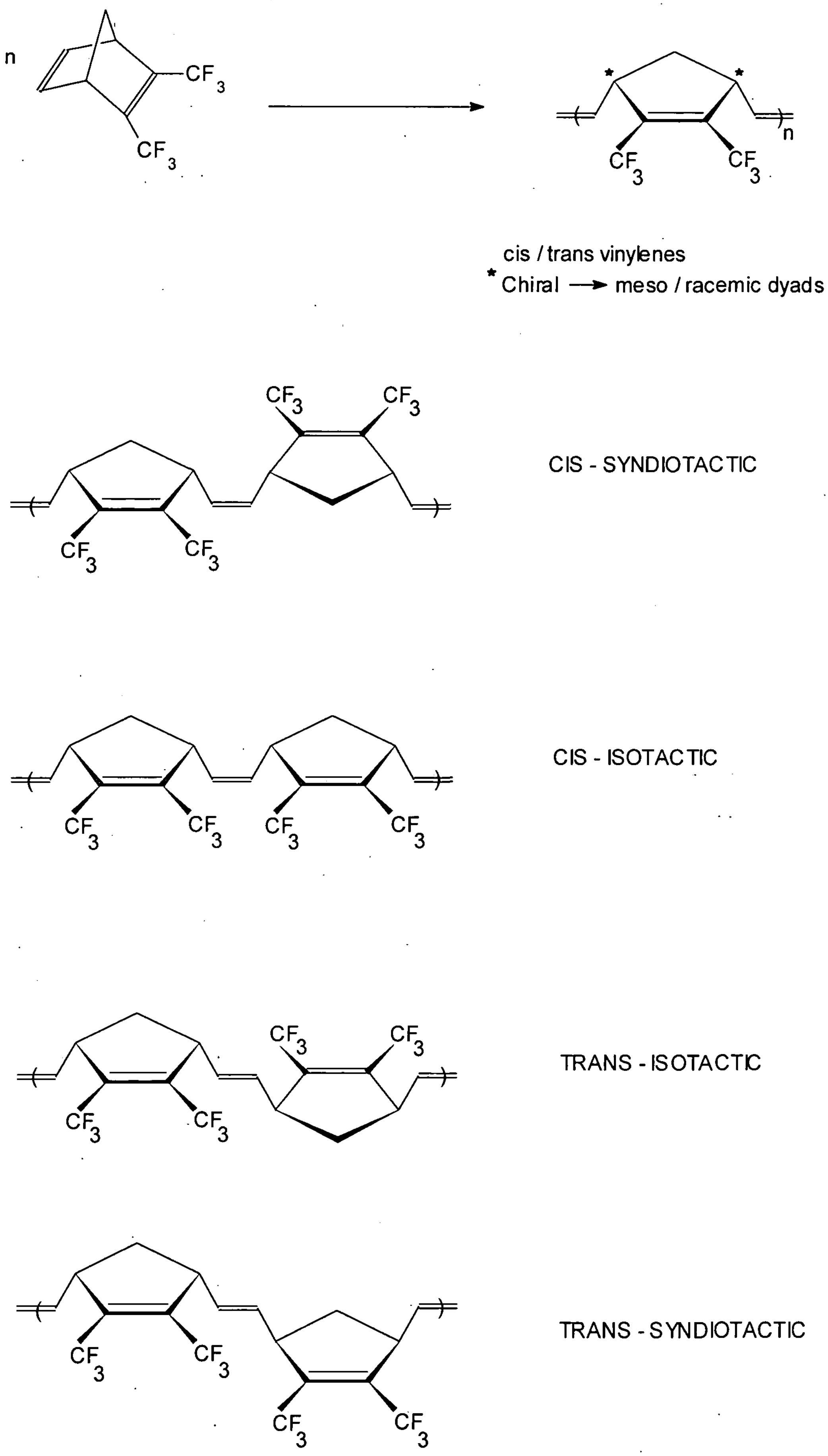


Figure 2.2. Schematic diagram of the ring opening of 2,3-bis(trifluoromethyl)norbornadiene.

Figure 2.2. shows schematically the ring opening of 2,3-bis(trifluoromethyl)norbornadiene to give the unsaturated linear polymer poly(1,4-(2,3-bis(trifluoromethyl)cyclopentenylene)vinylene). Ring opening occurs at the unsubstituted double bond in the monomer giving the repeat unit shown. This monomer has proved to be particularly useful in detailed studies of ring opening metathesis polymerisation and of the microstructures of the product polymers. This monomer contains a plane of symmetry and does not suffer from the complications of endo/exo isomerism. Consequently, the possible microstructures of its polymers are relatively simple. The only variables being the frequency and distribution of cis and trans vinylenes and meso and racemic dyads (see figure 2.3), since head-tail / head-head, tail-tail and exo/endo effects are eliminated as a consequence of repeat unit structure. The four possible homopolymer microstructures are cis and trans syndiotactic and cis and trans isotactic, (figure 2.3 overleaf).

Figure 2.3. The four primary structures of poly(bis(trifluoromethyl)norbornadiene)



2.1.2.1. Classically initiated ROMP of 2,3-bis(trifluoromethyl)norbornadiene.

The metathesis polymerisation of 2,3-bis(trifluoromethyl)norbornadiene has been performed with a wide range of classical initiators. In 1979, Wilson first polymerised this monomer using the initiating system obtained by reacting WCl_6 with Me_4Sn. This procedure gave a polymer with an atactic structure and approximately a 50/50 distribution of cis and trans vinylenes in the backbone.[1,2] Since these initial studies, various other classical systems have been used, and it was established that the proportion of cis vinylenes in the polymer was dependent on the initiator used. For example, catalyst systems based on WCl_6 generally gave σ_c (i.e. the fraction of cis vinylenes) of approximately 0.5. Ruthenium based systems, such as $RuCl_3/Me_4Sn$, afforded $\sigma_c \sim 0.3$, and molybdenum systems, like $MoCl_5/Me_4Sn$, gave $\sigma_c \sim 0.1$. The polymers produced by these classical initiator systems generally possessed broad molecular weight distributions and largely atactic microstructures.[4] The reasons for the limited microstructure control and broad polydispersity were not well understood, but it was generally believed that the initiator systems probably contained several different active species with different reactivities and lifetimes.

2.1.2.2. The living ROMP of 2,3-bis(trifluoromethyl)norbornadiene.

Recently, it has been established that the use of well-defined "Schrock" type initiators based on molybdenum allows a major improvement in the precision and control of the polymerisation of this monomer.

It has been shown that with 2,3-bis(trifluoromethyl)norbornadiene the initiator, $Mo(N\text{-}2,6\text{-}^{i}Pr_2\text{-}C_6H_3)(CHCMe_2Ph)(OCMe_3)$,[11] gives a well-defined living and highly stereoregular polymerisation,[10,12,13] the process is shown in figure 2.4.[14] The initiation of the polymerisation occurs by addition of the molybdenum carbene to the unsubstituted exo-face of the monomer and the resulting metallocyclobutane opens spontaneously to regenerate a metal carbene. Repetition of the process leads to a living poly(bis(trifluoromethyl)norbornadiene) with a molybdenum carbene chain end. In normal practice this polymer is terminated by the addition of an aldehyde, benzaldehyde in figure 2.4. This description outlines the sequence of events in this kind of living polymerisation, the stereochemical details will be discussed later.

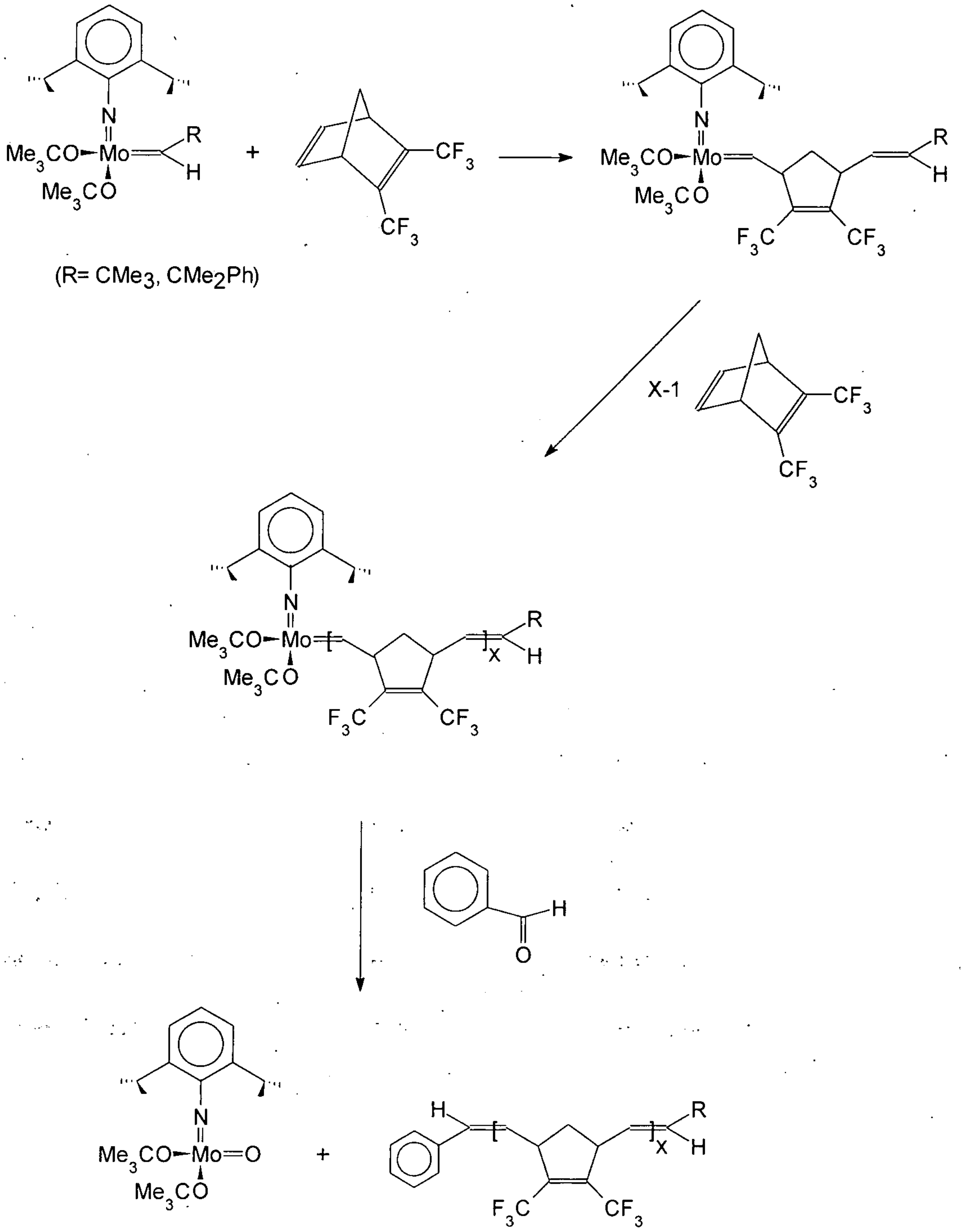


Figure 2.4. The living ROMP of 2,3-bis(trifluoromethyl)norbornadiene.

Analysis by ^{13}C NMR spectroscopy, showed that the polymer contains in excess of 98% trans double bonds, furthermore comparison with the ^{13}C NMR

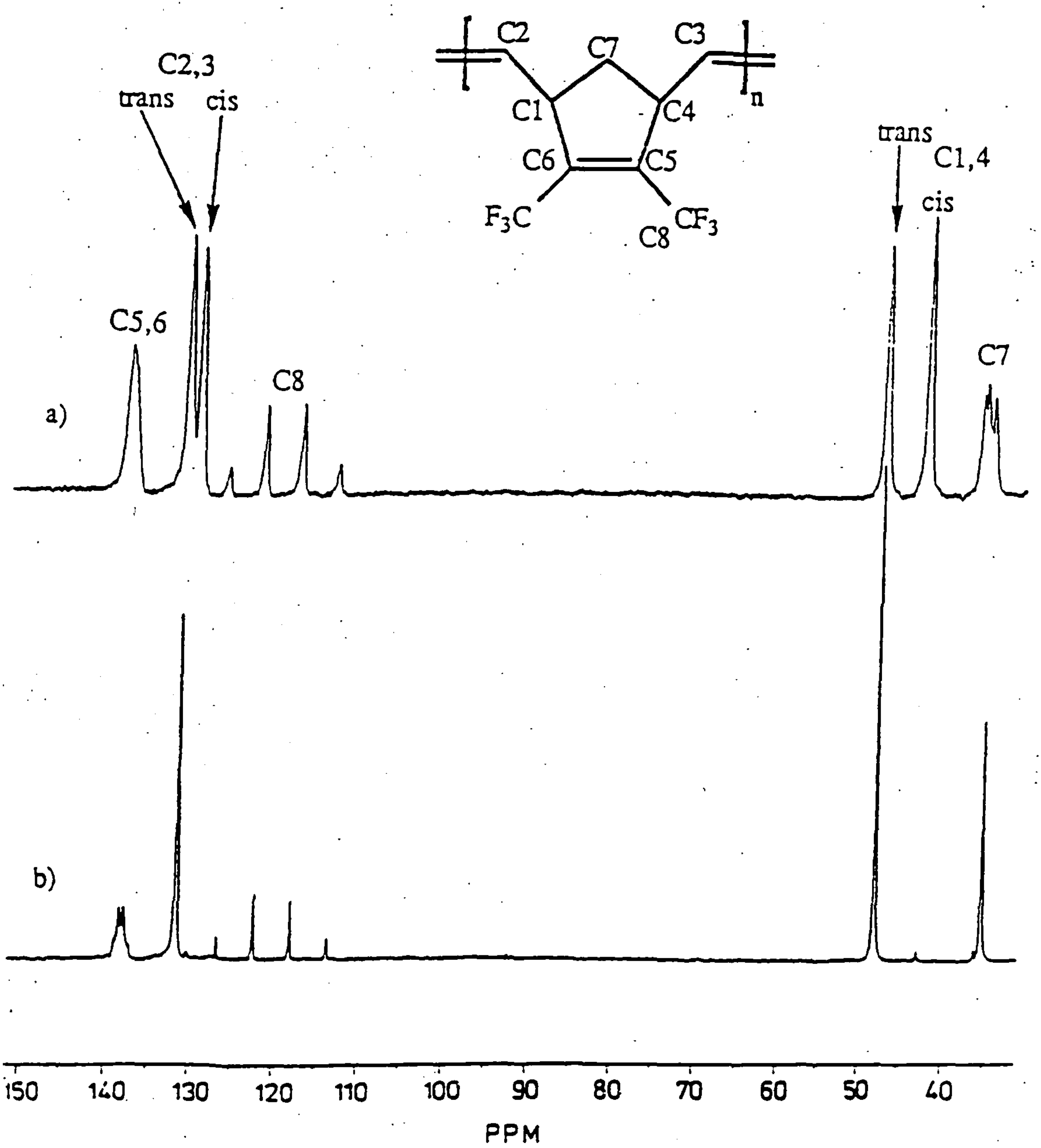


Figure 2.5. The ^{13}C NMR spectra of poly(bis(trifluoromethyl)norbornadiene) initiated by a) WCl_6/Me_4Sn b) $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(OCMe_3)_2$.

spectrum of the polymer formed by the WCl_6/Me_4Sn system revealed that this polymer was highly tactic, (figure 2.5.).[12]

Examination of the spectra in figure 2.5 shows quite clearly that spectrum b), obtained from the $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr_2{}^i\text{-}C_6H_3)(OCMe_3)_2$ initiated polymerization contains distinctly narrower peaks than those of spectrum a), obtained from the WCl_6/Me_4Sn initiated process, which is indicative of a more tactic polymer in the former case. In the allylic carbon region, the carbons adjacent to a cis vinylene always occur about 4 to 5ppm up field from those adjacent to trans vinylenes and along with the integrated intensities this gives the starting point for assigning such spectra. In this case, the spectra unambiguously show the high proportion of trans vinylenes present in the polymer produced with the well-defined initiator compared to the ~ 50/50 cis/trans arrangement in spectrum a). The differences in the C7 methylene regions of the two spectra are of particular significance with respect to the assignment of tacticity effects. In the 98% trans vinylene polymer, the C7 methylene occurs as what appears to be a single resonance, whereas in the case of the product from the classical initiator system, it is a partially resolved multiplet. The multiplet had previously been assigned to the consequences of different dyad sequences in the polymer, thus the apparent appearance of a single resonance suggests a single dyad structure giving rise to a tactic polymer; under higher resolution the C7 methylene peak can be seen to have a shoulder at high field and deconvolution of the peak allowed the assignment of this polymer as 92% tactic.

Further to these initial studies using $Mo(N\text{-}2,6\text{-}{}^iPr_2\text{-}C_6H_3)(CHCMe_2Ph)\mathbf{(OCMe_3)_2}$, it has been shown that replacing two methyl groups in each alkoxy ligand of the initiator by trifluoromethyl groups has a dramatic effect on the resulting polymer microstructure, in as much as the resulting polymer has > 98% **cis** double bond content. [10,14,15] The ^{13}C NMR spectra of samples of poly(bis(trifluoromethyl)norbornadiene) prepared by a) Mo(NAr)(CHCMe$_2$Ph)-**(OCMe$_3$)$_2$** and b) Mo(NAr)(CHCMe$_2$Ph)**(OCMe(CF$_3$)$_2$)$_2$** are compared in figure 2.6. As can be seen from the allylic carbon region, there is a striking change in the microstructure of the polymer on changing the alkoxy ligands. Furthermore, on examining the C7 methylene region, differences in the tacticity of the respective polymers become apparent. In spectrum b) the C7 resonance is clearly resolved into two peaks, indicating the presence of two or more dyad sequences and hence a lowering in tacticity of the polymer as compared to case a). More detailed discussions of tacticity will be presented later in this chapter.

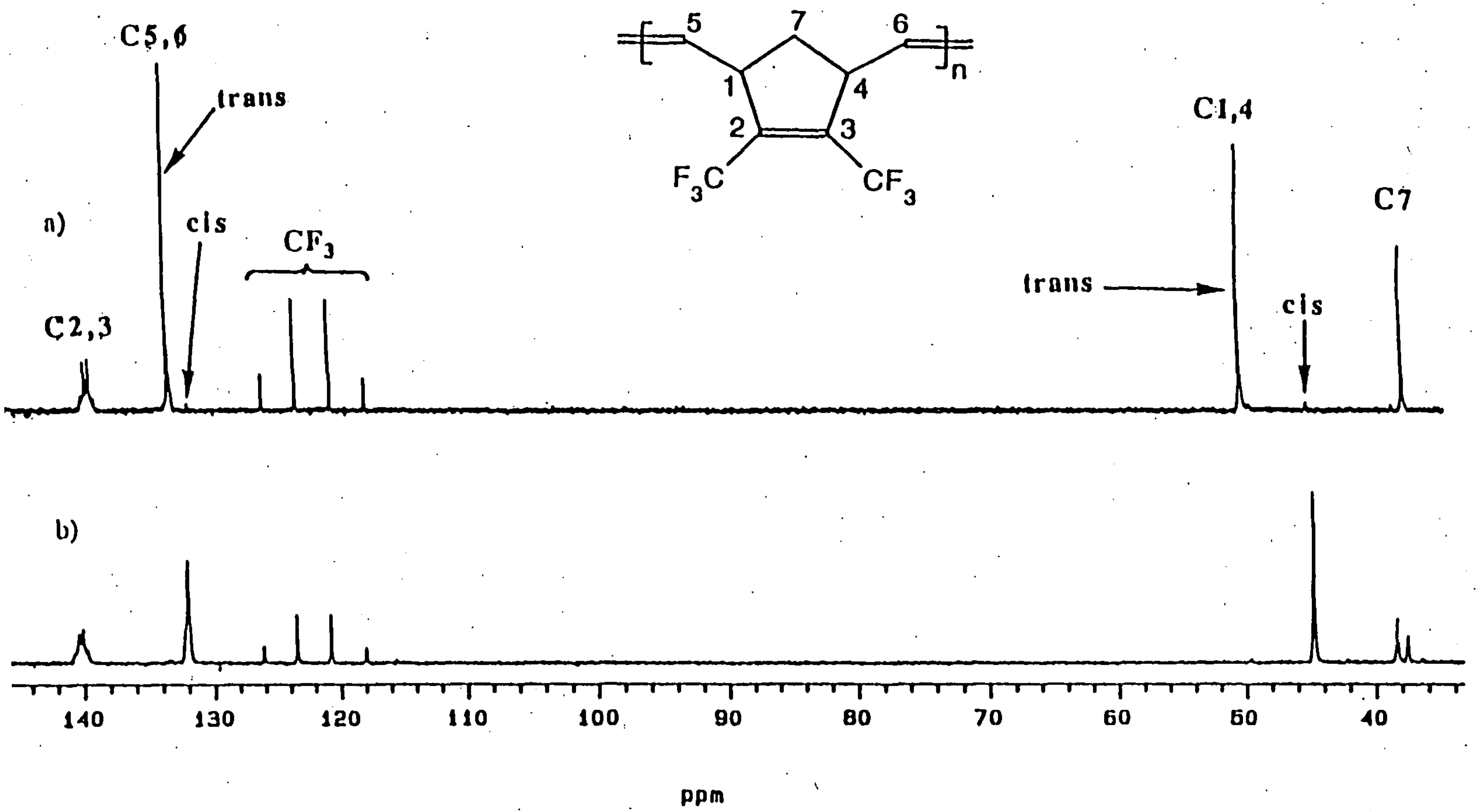


Figure 2.6. The ^{13}C NMR spectra [15] of poly(bis(trifluoromethyl)norbornadiene) samples prepared by initiation with a) Mo(NAr)(CHCMe$_2$Ph)**(OCMe$_3$)$_2$** ,b) Mo(NAr)(CHCMe$_2$Ph)**(OCMe(CF$_3$)$_2$)$_2$**

2.2. Microstructure in polymers produced by ring opening metathesis polymerisation.

2.2.1 General considerations.

The polymerisation of bicyclic olefins by ring opening gives rise to a number of possible types of stereoisomerism during the propagation step.[16] Cis/trans isomerism in the carbon-carbon double bond in the polymer backbone gives rise to the first type of isomerism and complete specification of microstructure requires the determination of the frequency and distribution of cis and trans vinylenes. Next, as mentioned previously, the presence of chiral centres in the polymer repeat unit can give rise to tacticity effects. When successive equivalent chiral centres in the chain have the same configuration they give rise to meso dyads and an isotactic microstructure, if they are present in an alternating configuration, this defines racemic dyads and a syndiotactic microstructure. A random arrangement of chiral centres gives rise to an atactic structure. Figure 2.7 illustrates these configurations for the all cis-vinylene ring-opened polymer of norbornene.

There are many variables which affect the tacticity produced in a particular polymerisation. One of the more important ones is the structure of the initiator and growing chain end involved in the polymerisation process. The effect of initiator structure on the tacticity of the polymer produced from the ring opening of the monomer 2,3-bis(trifluoromethyl)norbornadiene will be discussed in detail later in this chapter. The most powerful tool in the analysis of the microstructure of polymers produced by the ring opening polymerisation of norbornene and its derivatives has proved to be ^{13}C NMR spectroscopy. The technique can yield information on the frequency and distribution of cis/trans double bonds in the polymer chain.[16]

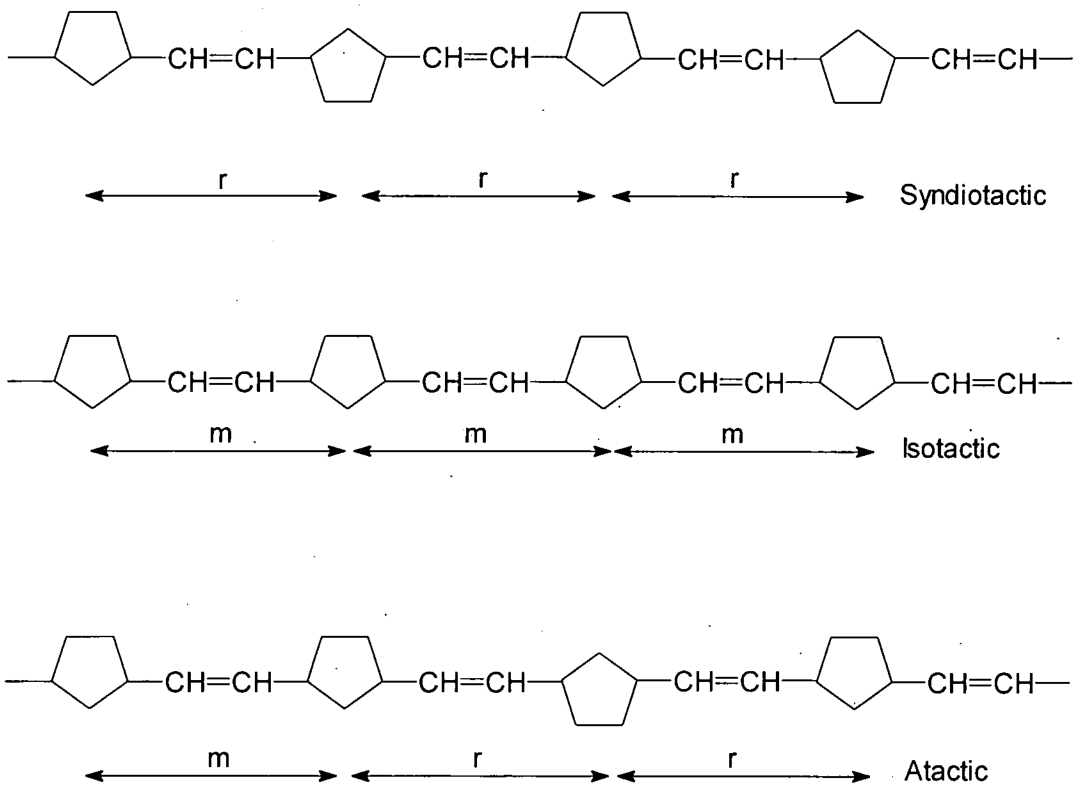


Figure 2.7. The possible configurations for the all cis-vinylene ring-opened polymer of norbornene.[17]

In favourable cases, the analysis can yield a distinction between a random distribution of double bonds and any tendency for alternation or blockiness in a polymer containing both cis and trans double bonds. Ivin and co-workers have studied the polymerisation of norbornene using a variety of initiator systems and prepared polymers with varying proportions of cis double bonds and varying distributions.

2.2.2. Overview of tacticity in polymers produced by ROMP.

The system adopted by Ivin to account for tacticity in these systems is outlined in figure 2.8. The source of tacticity is based on the idea of 'steric fit' of the incoming monomer with the initiating and/or propagating transition metal centre.

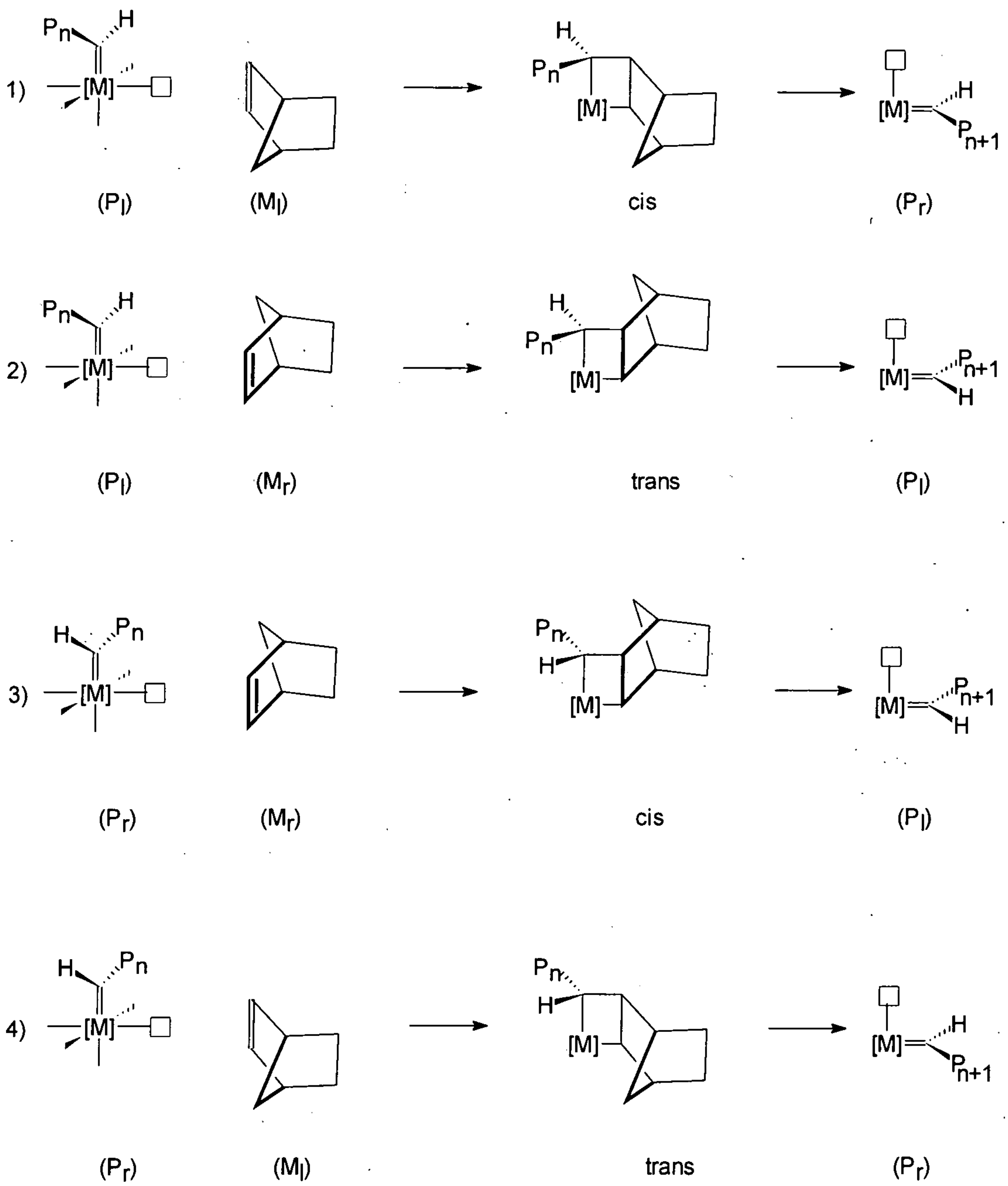


Figure 2.8. The Ivin hypothesis for assembly in ROMP.

In this scheme it is assumed that a metallocarbene is involved in the propagation step of the polymerisation. Ivin et al assumed that the geometry about the metal centre was pseudo-octahedral, with one position occupied by the carbene ligand and at least one position kept vacant to allow coordination to the substrate olefin. The concept of a "vacant site" is widespread but probably hard to justify; however, the picture that was generated is acceptable if one assumes that the incoming π-bond donor creates a pseudo-octahedral intermediate in the first step. The rest of the argument is then exactly as Ivin et al proposed.

The propagating species is represented as **[M]=CHP**, where P is the growing polymer chain. The explanation for the production of tactic polymers proposes that the propagating species may have left (P_l) or right (P_r) handed forms as shown by 1 and 2 and 3 and 4 respectively, the nomenclature being defined by the perception of the incoming olefin with respect to the disposition of the growing polymer chain. Furthermore, the approach of the monomer (in this case, norbornene) is crucial to the resulting tacticity in the ring-opened polymer. It is assumed that the monomer always presents its less hindered *exo* face to the propagating metallocarbene, it can do this in one of two ways depending on which of the two olefinic carbons becomes attached to the carbene carbon, M_l or M_r, see figure 2.8.

Hence, there are four possible modes of addition of the monomer to the propagating species. From a careful consideration of the scheme shown, it is clear that an all *cis* polymer can only be formed by alternation of steps 1 and 3, giving rise to a syndiotactic polymer, where the incorporated rings are in an alternating configuration i.e. successive rings are in a P_l-P_r or P_r-P_l sequence. Conversely, an all *trans* polymer can be formed by the sequence of reactions 2 and 4 producing an isotactic configuration in the polymer i.e. the rings add P_l-P_l or P_r-P_r. As an example of what occurs when both cis and trans double bonds are formed in the polymer, consider the series of reactions (referring to figure 2.8): 1, 3, 2, 2, 1, 4, 3. This will yield a sequence along the polymer chain where every cis double bond is encompassed by a racemic dyad, and every trans double bond by a meso dyad. This is what is observed in tactic polymers prepared using initiating systems such as $ReCl_5/Et_3Al$ [18,19] and WCl_6/Bu_4Sn. The reader is referred to Ivin's publications for a more detailed discussion of this subject. [16,17,20,21]

2.3. Tacticity in poly(bis(trifluoromethyl)norbornadiene)

Various types of initiating systems have been employed to bring about the ROM polymerisation of 2,3-bis(trifluoromethyl)norbornadiene. Table 2.1 below, summarises the key results, which are discussed in detail in this section.

Table 2.1

Initiator	**Vinylene stereochemistry**	**Tacticity by ^{13}C NMR**	**Relaxed dielectric constant**	**Conclusion concerning tacticity**
WCl_6/Me_4Sn	50:50 trans:cis	Atactic	~ 15	Atactic
[Mo]**$(OCMe_3)_2$** *	> 98% trans	~ 92%	> 45	Syndiotactic
[Mo]**$(OCMe(CF_3)_2$** *	> 98% cis	~ 75%	~ 7	Syndiotactic

*{Where [Mo] = $Mo(NAr)(CHCMe_2Ph)$}

As stated previously, the ring opened polymer of 2,3-bis(trifluoromethyl)norbornadiene can give rise to four possible structures; cis/trans isomerism can occur about the double bond in the polymer chain and tacticity effects will be present, due to the presence of the chiral centres in the repeat unit, (see figure 2.3 previously).

Determination of polymer microstructure using ^{13}C NMR spectroscopy.

The definitive assignment of microstructure to polymers produced by the ROMP of symmetrical norbornadienes presents considerable difficulties. For example, the polymers formed are not obtained in a highly crystalline ordered form which would allow X-ray diffraction methods to be applied and so far attempts to obtain crystalline samples by annealing or drawing have been unsuccessful. However, ^{13}C NMR spectroscopy has proved to be a valuable tool in gathering information about the polymers. In the case of 2,3-bis(trifluoromethyl)norbornadiene, substantial fine structure, indicative of splitting due to the prescence of racemic and meso dyads in cis and trans vinylene sequences is revealed in the C7 methylene region of the polymer backbone.[10,12]

Interpretation of the ^{13}C NMR spectra of the all *cis* and all *trans* polymers formed from 2,3-bis(trifluoromethyl)norbornadiene has centred around analysing the polymer structure in terms of the triad frequency. Possible triad structures for the all *cis* polymer are shown in figure 2.9. The all *trans* polymer can also adopt similar configurations to those shown for the *cis* polymer, i.e.(tt mm, tt rr, tt rm/mr).

In the ^{13}C NMR spectrum, it is expected that the central methylene carbon (marked ★ in figure 2.9) will encounter shift effects from the adjacent vinylene units in the chain giving rise to possible cis/cis (cc), cis/trans=trans/cis (ct=tc), and trans/trans (tt) environments. In an all cis or all trans polymer only one environment and hence one signal will be observed (cc or tt). However, the methylene carbon may also experience a meso/racemic(m/r) shift as a result of the varying stereochemistries of the neighbouring rings, this means there can be up to three possible environments (mm, mr=rm and rr).

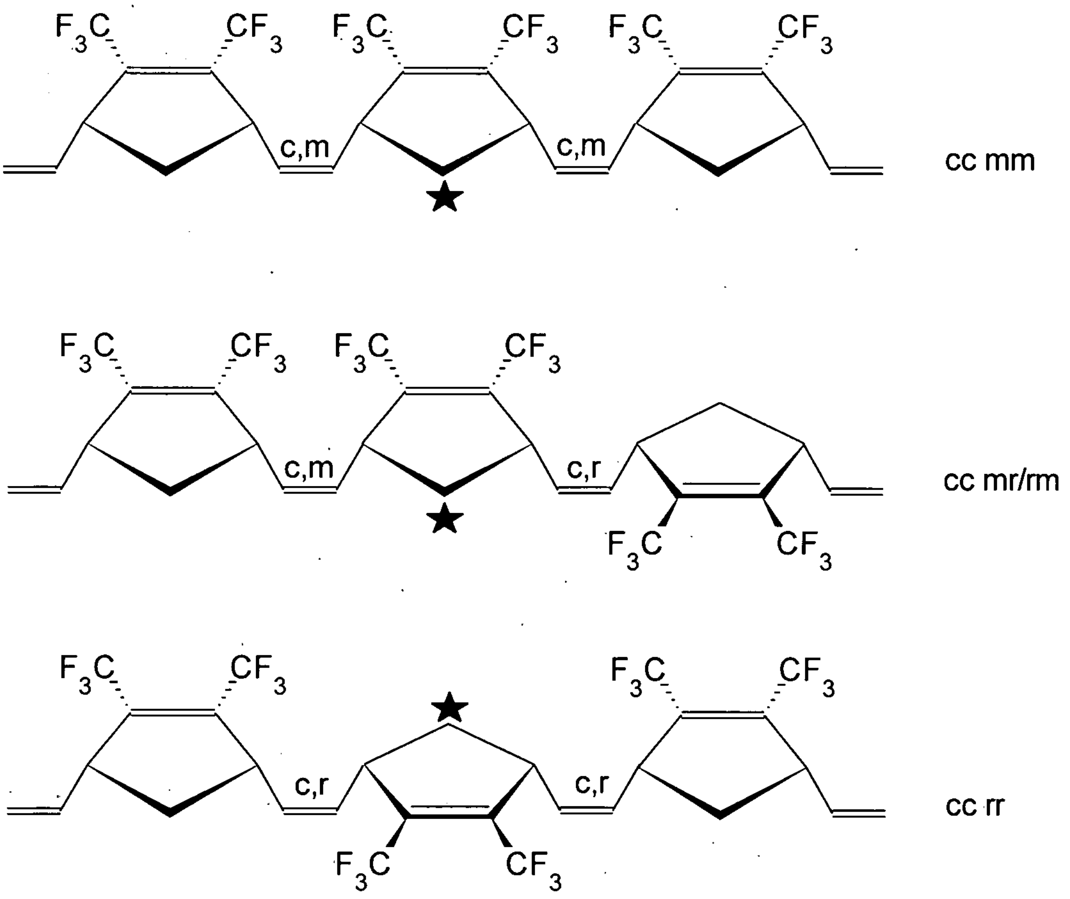
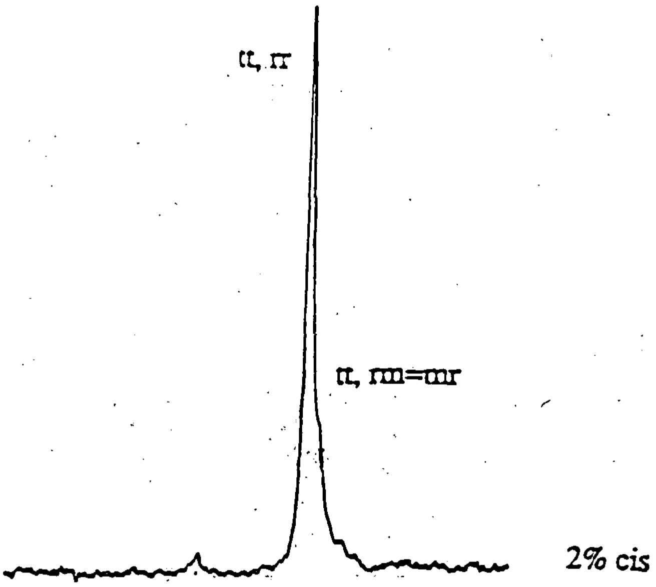


Figure 2.9. Possible triad structures for the all cis polymer.

The ^{13}C NMR spectra for the methylene regions of the high *cis* polymer, prepared using $\mathrm{Mo(N\text{-}2,6\text{-}Pr^i{}_2\text{-}C_6H_3)(CHCMe_2Ph)}\mathbf{(OCMe(CF_3)_2}$, and the high *trans* polymer, prepared using $\mathrm{Mo(N\text{-}2,6\text{-}Pr^i{}_2\text{-}C_6H_3)(CHCMe_2Ph)}\mathbf{(OCMe_3)_2}$, are shown in figure 2.10.[10] In the spectrum of the high cis polymer there are two main resonances. Both are thought to be *cc*, i.e. arising from methylene units between two adjacent cis vinylenes, this assignment was based on the unlikelihood of observing any ct/tt resonances at such a low proportion of trans double bonds. Therefore, the splitting of the cc resonance must have been due to tacticity effects. It was impossible to assign tacticity on the basis of this data but on the basis of relaxed dielectric constant measurements (to be discussed later), the syndiotactic structure was thought to predominate (the structures are shown in figure 2.3), thus mainly racemic dyads were

I) Initiated by $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(OCMe_3)_2$



II) Initiated by $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(OCMe(CF_3)_2)_2$

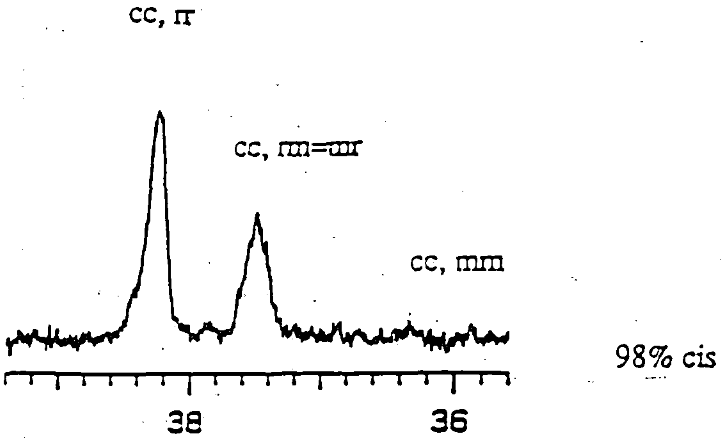


Figure 2.10. A comparison of the C7 methylene regions in high cis and high trans poly(bis(trifluoromethyl)norbornadiene.

thought to be present in the polymer chain. Hence, the peak of greatest intensity was assigned *cc rr*, with the central methylene carbon adjacent to two cis vinylene bonds and placed between two syndiotactic dyads. The signal of lower intensity was designated *cc rm/mr.* This meant that the structure was not 100% syndiotactic i.e. consisting of all racemic dyads. Some meso dyads must be present in the chain which give rise to the splitting shown. Furthermore, on the basis of this analysis, a third signal was predicted to be present and can be just about seen emerging from the noise; (*cc mm*), representing approximately 6% of the total *cc* resonance. Integration of these peaks using quantitative ^{13}C NMR suggested the polymer was 75% tactic.

Conversely, the C7 region of the high trans polymer just showed one major resonance assigned as *tt rr*, (dielectric measurements, see later, suggested a syndiotactic material) the presence of a small shoulder to high field of the signal is probably due to the occurrence of meso/racemic dyads. Deconvolution of these overlapping ^{13}C NMR peaks indicated that this polymer was 92% tactic.

In summary, using ^{13}C NMR to analyse the fine structure established that the high *trans* polymer was 92% tactic and the high *cis* polymer was 75% tactic,[10,12] but the tacticity could not be assigned on the basis of the ^{13}C NMR evidence.

Determination of tacticity using Dielectric spectroscopy.

Although ^{13}C NMR gave an indication of the tacticities in the polymers, a complete assignment was not possible and dielectric spectroscopy provided the vital observations which allow a more comprehensive assignment to be made. As recorded in table 2.1, it was found that the high *trans* polymer has a relaxed dielectric constant >45 whereas the high *cis* polymer has a value less than a quarter of that, with the polymer produced using the WCl_6/Me_4Sn system, which was unambiguously assigned as atactic, giving a value of 15. This leads to the conclusion that in the *trans* polymer, the polar CF_3 groups can act in a collaborative reinforcing sense in response to an electric field giving rise to a high dielectric constant. However, in the high *cis* polymer the CF_3 groups are acting in an opposite sense and their individual effects tend to cancel each other out producing a lower value.[22,23]

With these observations in mind, figure 2.3 shows quite clearly that both polymers possess predominantly syndiotactic structures. It is generally agreed that the high *trans* polymer has a syndiotactic structure, based on these dielectric measurements.[14,22] However, a low dielectric constant for the high *cis* polymer could also be explained if an isotactic structure adopted a conformation which allowed cancellation of dipole moments. This explanation is favoured by Schrock.[28] There is no dispute over the assignment of the high trans polymer since the very high value of the relaxed dielectric constant observed can only be obtained by collaborative alignment of dipoles; however, the low value obtained for the high cis polymer can be explained by cancellation of dipoles in a variety of ways, investigations into the various possibilities are currently being undertaken in the Leeds Physics group of the IRC using various computer modeling techniques.

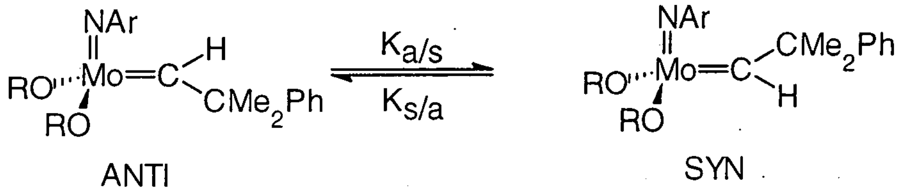
2.4. Mechanistic speculation in ROMP.

Introduction.

In the last few years, well-defined initiators of the general type: $M(NAr)(CHR^{/})(OR^{//})_2$, (where M=Mo,W), have proved to be useful in a variety of olefin metathesis studies. This is due in part to the fact that the activity of these initiators can be varied systematically by altering the electron withdrawing ability of the alkoxide ligands.[24] Molybdenum complexes containing t-butoxide ligands ($-OCMe_3$ and $-OCMe(CF_3)_2$ in particular) and an arylimido ligand, (where NAr = N-2,6-$^iPr_2$-C_6H_3) illustrate how the microstructure of the polymer can vary dramatically depending on the structure of the initiator. Thus, as discussed previously, the polymer may be virtually all trans and highly tactic or all cis depending on the nature of the alkoxide group.

The results from these studies using well-defined initiators are important because the bulk physical properties of the polymer can be expected to vary dramatically with the degree of microstructural regularity attained. This was illustrated previously with respect to polarity as evidenced by the measured relaxed dipole moments. Furthermore, a long term aim in this area of work is to achieve a greater understanding of how to control the structure of ROMP polymers in a systematic fashion and hence how to control such polymer properties.[24]

Recent work performed by Schrock and co-workers has suggested that the question of stereoregularity in the polymer may depend upon *syn/anti* interconversion rates in the initiator. These workers have shown that syn/anti isomerism occurs and that its rate can be measured, see figure 2.11.[25]



{Where R = CMe_3, CMe_2CF_3, $CMe(CF_3)_2$, $C(CF_3)_2CF_2CF_2CF_3$}

Figure 2.11. Syn/anti isomerism in Schrock-type initiators.

Rotamer interconversion rates have been measured for several members of this class of $M(NAr)(CHCMe_2Ph)(OR)_2$ complexes. The most extensive study has involved molybdenum complexes in which *OR* is a phenoxide ligand.[26] This was a suitable choice of ligand system as it allowed both the rotamers to be observed on the time scale of the reaction and as a result of this, standard ^{1}H NMR techniques could be used to obtain rate constants and activation energies.

Rotamer interconversion rates have also been studied in other initiating systems such as rhenium complexes of the general type: $Re(CR')(CHR')(OR'')_2$, (where $R' = CMe_3$ or CMe_2Ph and OR'' is chosen from a range of t-butoxide ligands). This has proved to be a well-behaved system, although the barrier to rotamer interconversion is considerably greater in the rhenium system[27] than in the molybdenum system making the molybdenum system easier to study in relation to syn/anti rotamer isomerization rates.

Syn/Anti rotamer interconversion in $Mo(CHCMe_2Ph)(NAr)(OR)_2$ and the subsequent effect on the reactivities towards 2,3-bis(trifluoromethyl)norbornadiene.

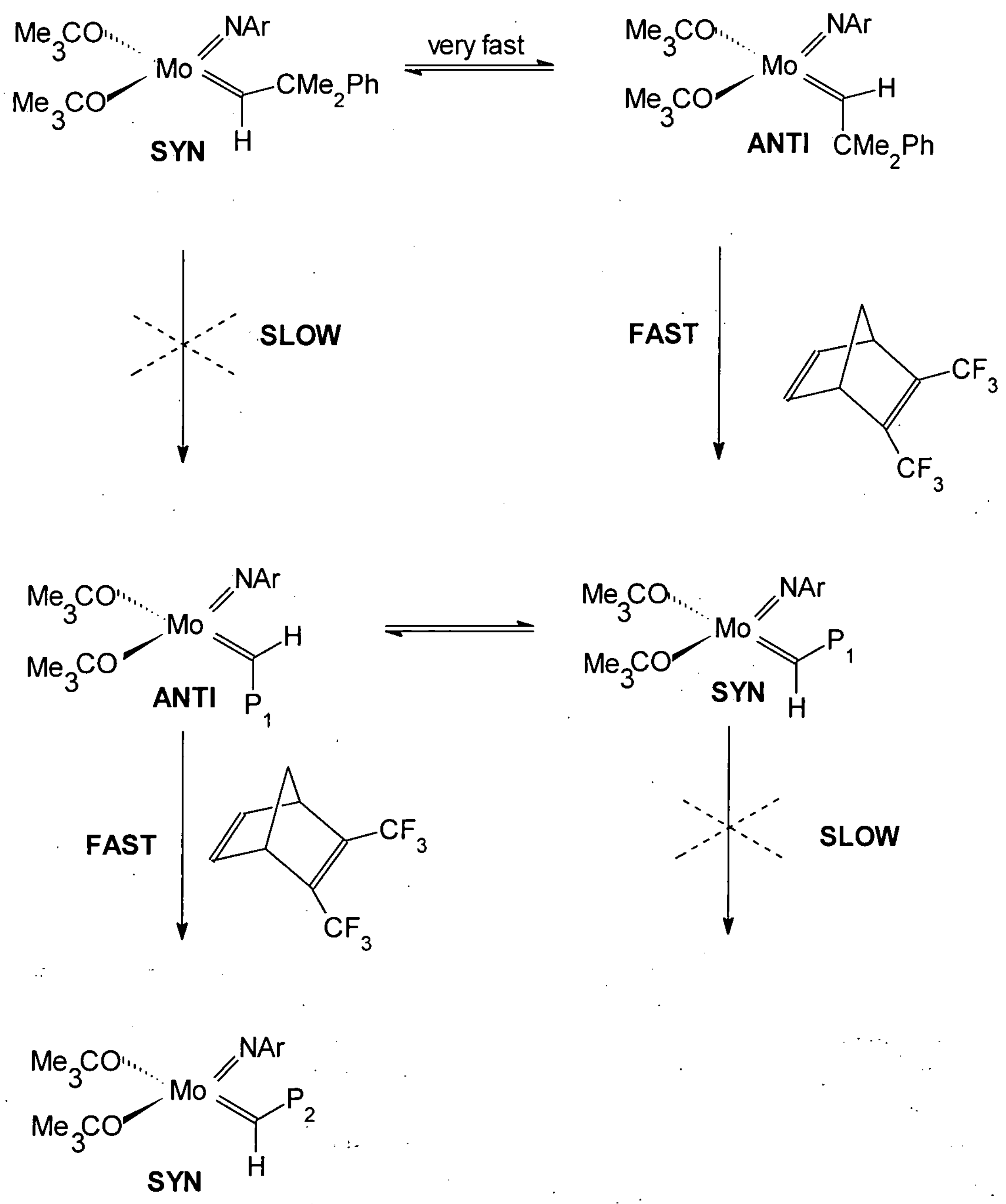
The intriguing question which these studies attempted to address was why should the $Mo(CHCMe_2Ph)(NAr)(OCMe_3)_2$ initiator produce a polymer, poly(bis(trifluoromethyl)norbornadiene), which was virtually all trans, whereas $Mo(CHCMe_2Ph)(NAr)(OCMe(CF_3)_2)_2$ afforded a high cis polymer. The general consensus held by workers in the field is that the concentration and rates of interconversion of *syn/anti* rotamers, figure 2.11, are key factors in determining the detailed mechanism of these polymerisations.

At room temperature, the ^1H NMR spectrum of either of the two initiators shows only one alkylidene resonance, assigned to the *syn* rotamer. However, low temperature photolysis at -80^{0}C of the hexafluoro-t-butoxide initiator yields approximately 35% of the *anti* rotamer, for which the alkylidene ^1H signal can be observed 1ppm downfield of the analogous *syn* alkylidene signal in the ^1H NMR spectrum.

NMR methods have been employed to determine the rates of *syn/anti* interconversion. Such studies have shown that the rate of rotamer isomerisation slows drastically as the alkoxide ligands become more electron withdrawing. Indeed the rate of conversion of the *anti* to the *syn* rotamer is found to vary by at least five orders of magnitude on going from the t-butoxide initiator to the hexafluoro-t-butoxide analogue. It has also been established that the *anti* rotamer is inherently more reactive than its *syn* counterpart. Furthermore, the *anti* form reacts with 2,3-

bis(trifluoromethyl)norbornadiene to give, after forming and cleaving a metallocyclobutane (see later), a trans vinylene and a *syn* alkylidene.[23]

Indeed the results of bulk polymerisation studies have suggested that a relationship exists between the alkylidene rotamer interconversion rates and the cis/trans content in the polymer. In the case of the t-butoxide initiator, the rotamer interconversion rates are fast on the time scale of the polymerisation, and the polymerisation occurs almost exclusively via the highly reactive *anti* isomer, even though this form is present in very small amounts at room temperature, to give a high trans polymer. Since the rate of *syn/anti* interconversion is much slower for initiators containing electron withdrawing alkoxide ligands, for example, $Mo(CHCMe_2Ph)(NAr)(OCMe(CF_3)_2)_2$, the *anti* rotamer cannot be accessed on the time scale of the polymerisation at room temperature. Hence this initiator polymerises 2,3-bis(trifluoromethyl)norbornadiene via the *syn* alkylidene to give a high cis polymer. Figure 2.12 summarises the polymerisation pathway using the t-butoxide initiator.



[P_1 = first insertion product
P_2 = second insertion product]

Figure 2.12 A fast rate of *syn/anti* rotamer interconversion for the t-butoxide initiator allows the polymerisation to occur via the highly reactive *anti* form producing high trans polymers.[14]

In accordance with Ivin's reasoning on polymer microstructure and tacticity effects, discussed earlier in this chapter, the stereoregularity in the polymer is determined by the approach of the monomer to the alkylidene rotamer. The orientation of the monomer is based upon minimization of steric hindrance at the C7 methylene fragment with respect to the ligands around the metal site. Figure 2.13 attempts to illustrate this point.

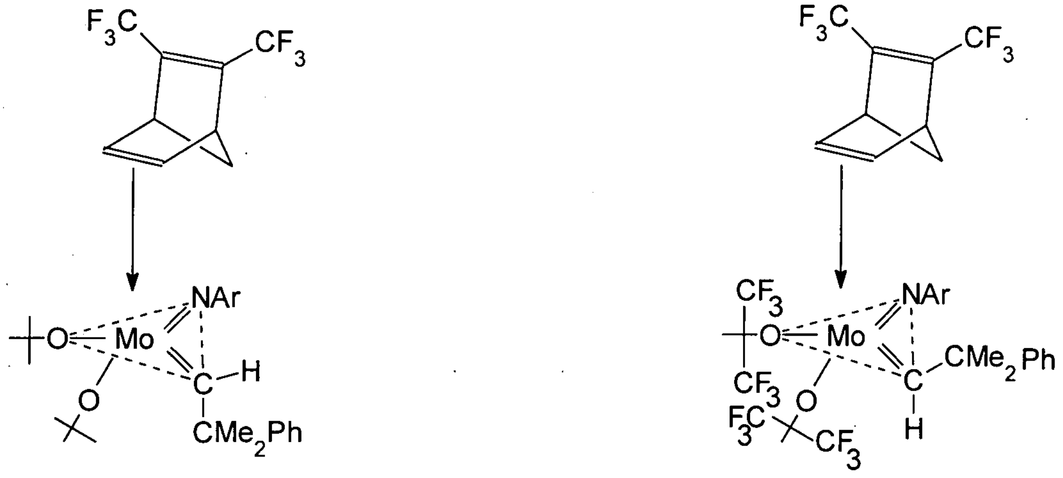


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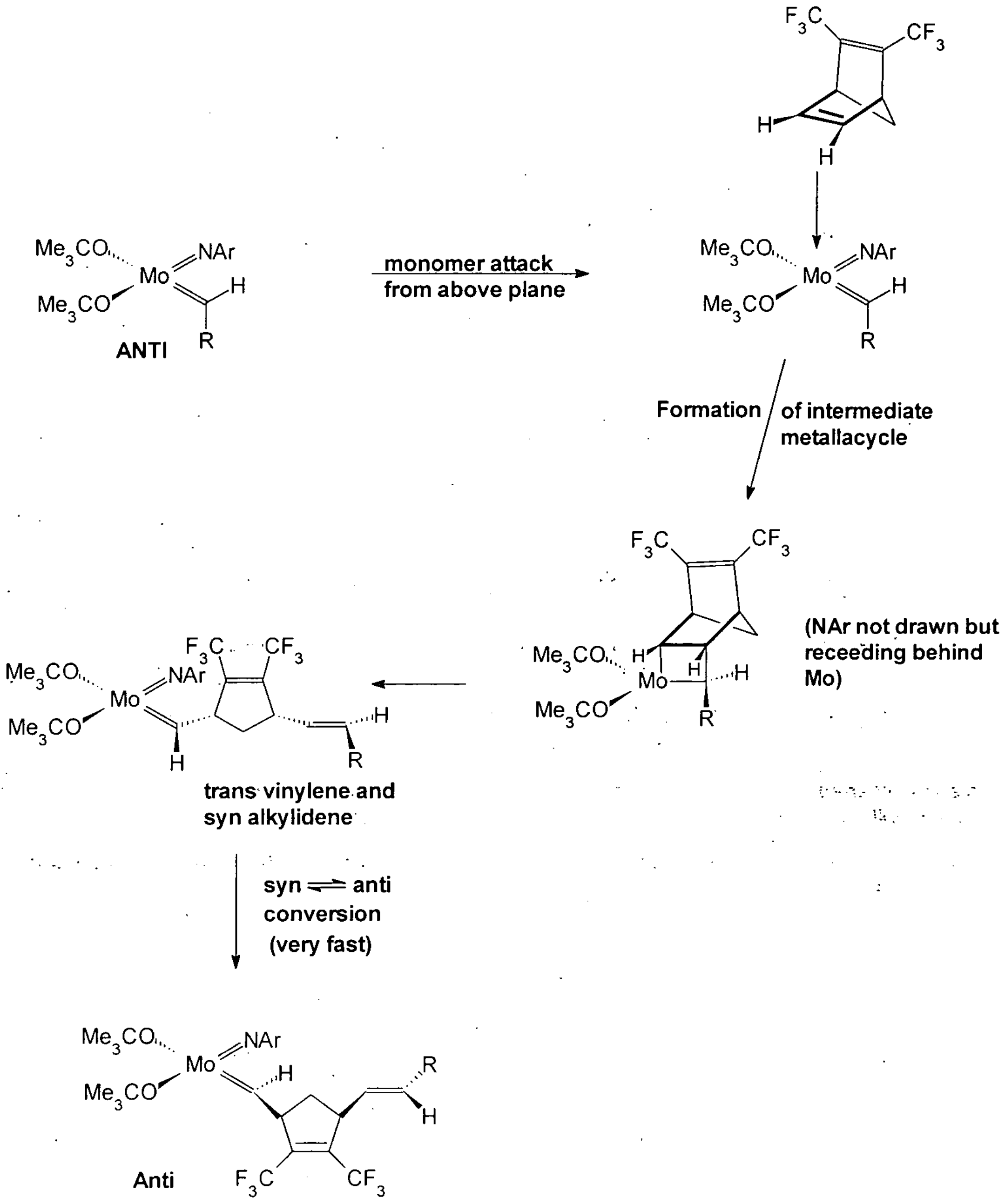
Figure 2.13. The approach pathways of 2,3-bis(trifluoromethyl)norbornadiene to initiators bearing t-butoxide and hexafluoro-t-butoxide ligands (shown as the anti and syn rotamers respectively).

The monomer is thought to approach perpendicular to the NCO face of the initiator (highlighted by the dotted line in figure 2.13) giving a 5-coordinate geometry, where the NCO face forms the equatorial plane of a trigonal bipyramid structure. The exceptional bulkiness of the alkoxide ligands are expected to force the C7 methylene unit in the direction of the arylimido ligand, which is more conformationally flexible than the alkoxide ligand and is able to re-orientate itself in order to accomodate the monomer. However, the monomer can also attack the NCO face from the opposite direction. In other words, rather than approaching from above the plane it can attack the initiator from below it. Thus, there are four possible modes of attack that the monomer can adopt when approaching the active centre. It can attack either the *syn* or *anti* rotamer of the initiator and can approach from the same face or alternating faces giving rise to the four possible microstructures: Cis/trans isotactic, cis/trans syndiotactic.

The diagrams [14] on the following pages attempt to show how the approach of the monomer to the initiator (*syn* or *anti* rotamer) is crucial to the resulting microstructure in the product polymer.

Figure 2.14.a). The production of trans polymers via attack upon the *anti* rotamer of $Mo(CHCMe_2Ph)(NAr)(\mathbf{OCMe_3})_2$.



The next monomer insertion can now occur from above or below the NCO plane as detailed overleaf.

Figure 2.14b) Attack from above the plane

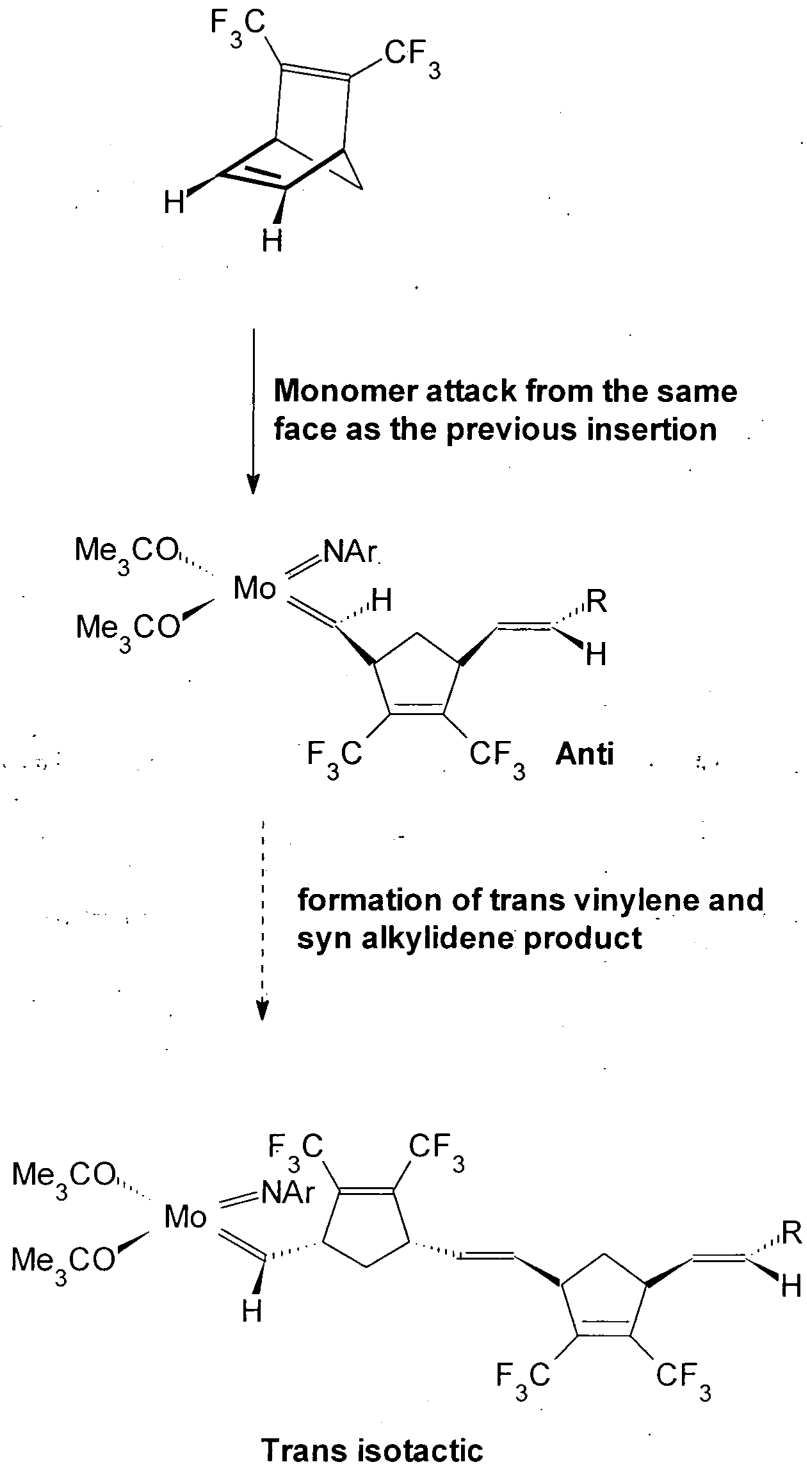
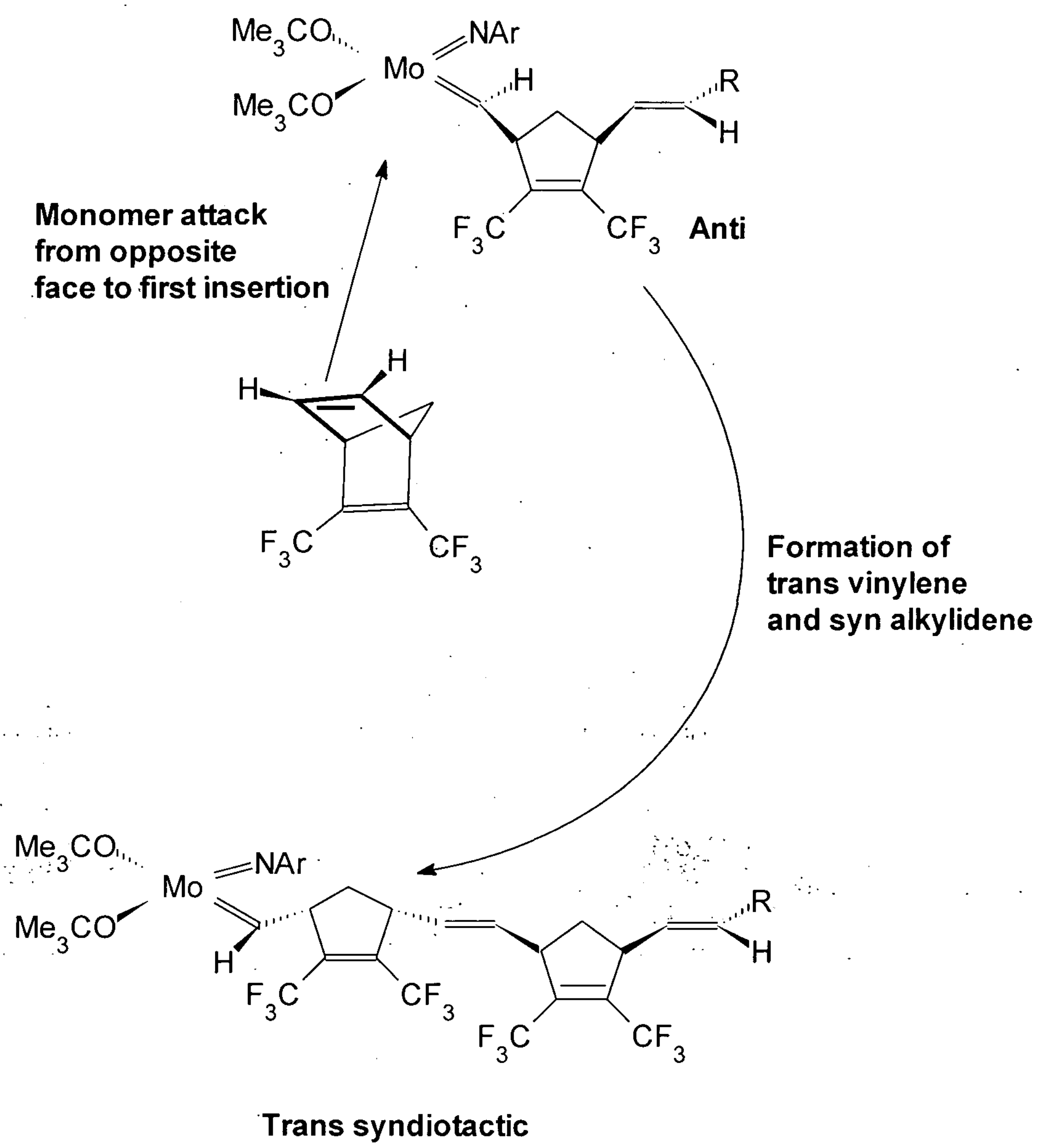


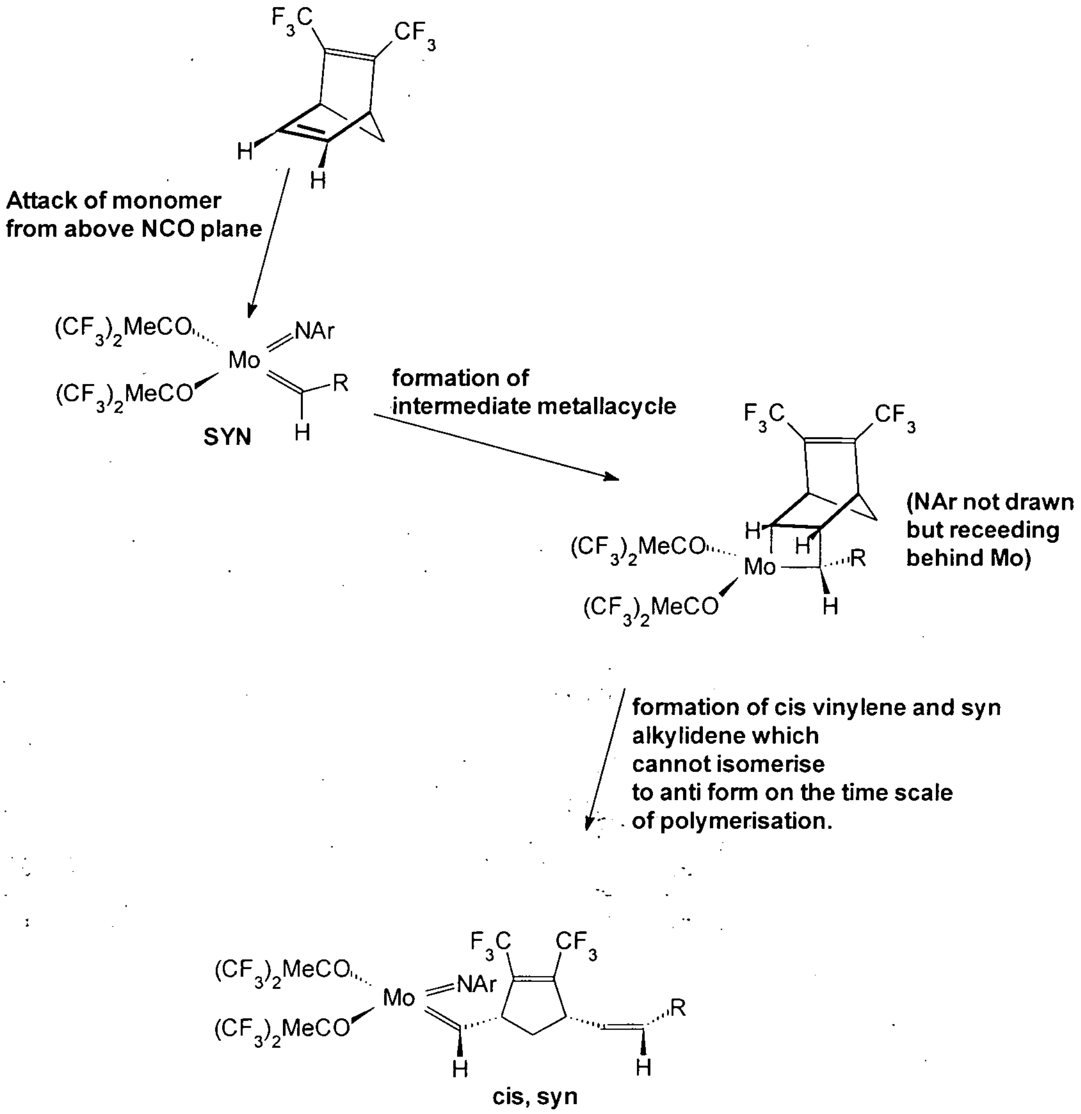
Figure 2.14 c) Attack from below the plane.



The formation of cis polymers can be rationalised in a similar way, where the attack of the monomer occurs on the syn rotamer of the hexafluoro-t-butoxide initiator, as detailed in the following diagrams.

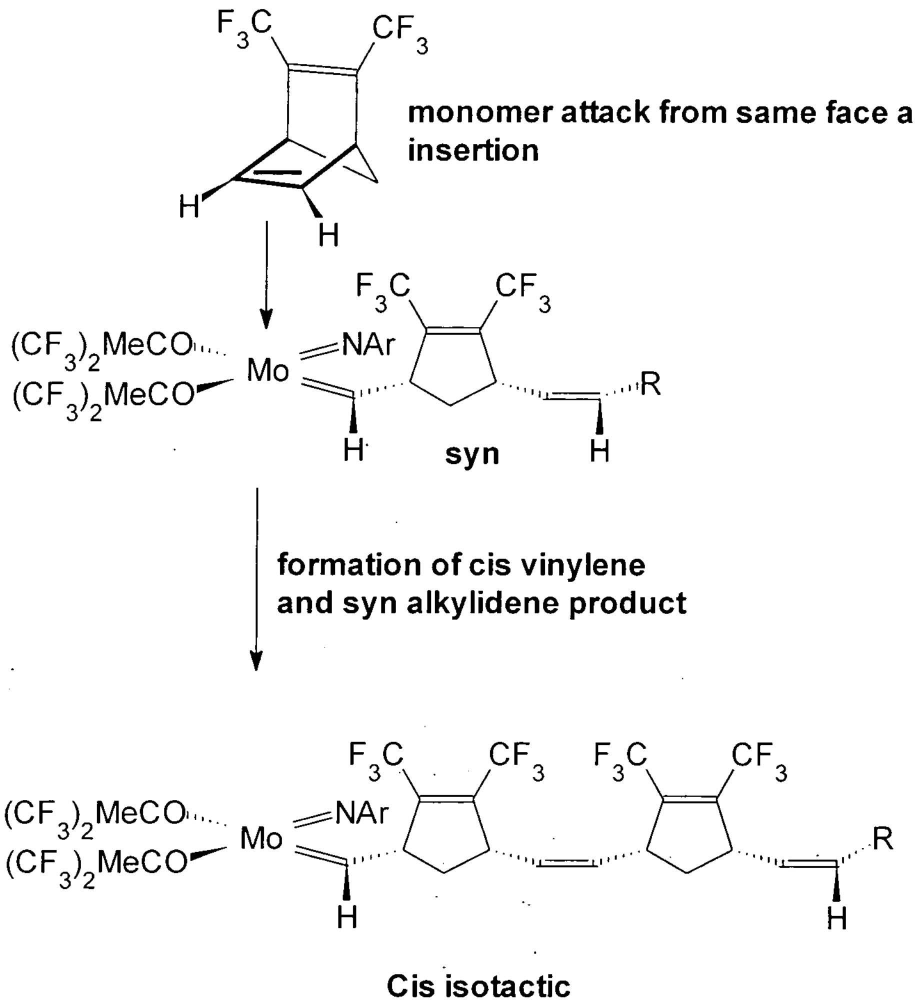
Figure 2.15a). The formation of cis polymers via attack upon the *syn* rotamer of

Mo(CHCMe$_2$Ph)(NAr)**(OCMe(CF$_3$)$_2$)$_2$**.



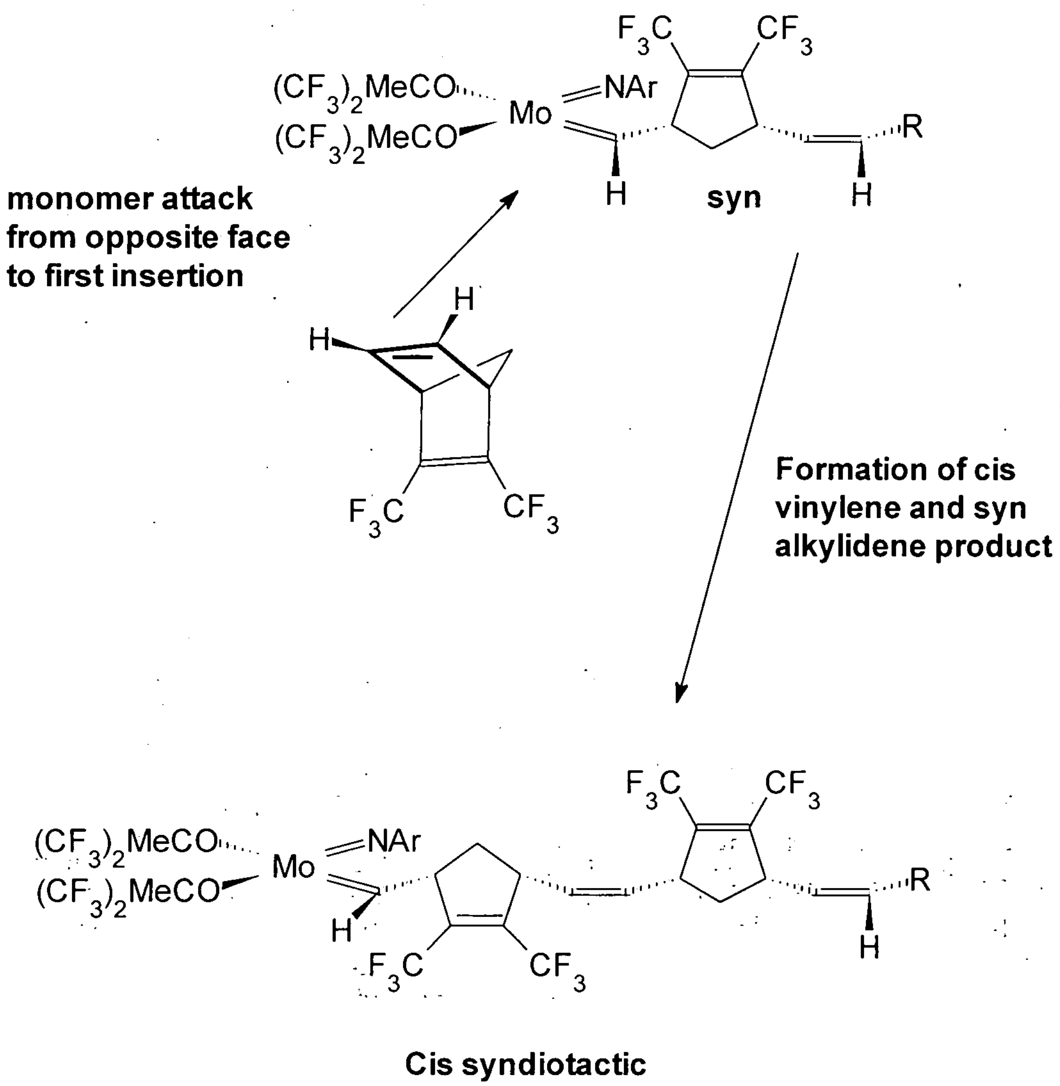
As in the case of the formation of the trans polymers, the tacticity of the resulting polymer is governed by the direction of attack of subsequent monomer units at the metal centre, as shown in the following schemes.

Figure 2.15b) Attack from above the NCO plane.



The formation of this polymer is most probably disfavoured due to the large steric stress present in the polymerisation. The close proximity of the CF_3 groups on the incoming monomer unit and on the backbone of the propagating polymer chain will produce very large F-F repulsions making the formation of a cis, isotactic polymer unlikely based on this speculative mechanistic rationalization.

Figure 2.15c) Attack from below the NCO plane.



In the case of this polymer, the polar CF_3 groups are on opposite sides of the polymer backbone. Thus, the F-F interactions are greatly reduced possibly leading to the formation of this polymer being more favourable than the cis, isotactic polymer.

Summary

The detailed mechanistic studies which have been conducted on the 2,3-bis(trifluoromethyl)norbornadiene system have shown that the resulting polymer microstructure is greatly influenced by a number of factors including: The *syn/anti* interconversion rates in the initiator, which vary dramatically with the electron-withdrawing nature of the alkoxide ligands. Hence, the t-butoxide initiator polymerises almost exclusively via the *anti* rotamer producing high trans polymers. Whereas the slower interconversion rates present in the hexafluoro-t-butoxide initiator result in the *syn* rotamer being the reactive form to give high cis polymers.

Furthermore, the stereoregularity in the polymer is determined by the approach of the monomer to the alkylidene rotamer. The direction of attack of the monomer is based upon the minimization of steric hindrance at the C7 methylene unit with respect to the ligands around the transition metal site. Some of this description is still very speculative and has yet to be proved experimentally, but detailed investigations are being undertaken to address this matter.

In the next chapter of this thesis the author describes attempts to produce a better regulated microstructure in poly(bis(trifluoromethyl)norbornadiene via variation of ligands at the initiating and propagating molybdenum centre. The motivation for this study being both to understand the mechanism better and to produce more highly tactic trans, syndiotactic poly(bis(trifluoromethyl)norbornadiene which might be a technologically useful pyroelectric material.

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Chapter 3

Studies directed to an improvement in tacticity control in the synthesis of poly(bis(trifluoromethyl)norbornadiene) and related materials

3.1 The problem addressed and approaches to its solution.

In the previous chapter of this thesis, the use of well-defined "Schrock-type" initiators in the ROMP studies of 2,3-bis(trifluoromethyl)norbornadiene was described and some of the details concerning the proposed mechanism for this polymerization were outlined.[1,2] From these studies it is evident that a great deal of progress has been made in this field since the first ring opening polymerization of this monomer by Wilson in 1979 using the classical initiating system, WCl_6/Me_4Sn.[3,4] In this early work little control of the resulting polymer microstructure was achieved, however in recent years the use of well-defined initiators has provided a much greater control over the polymerization and hence a more comprehensive knowledge of the polymer has been attained.[5,6,7]

The control over the cis/trans vinylene content in poly(bis(trifluoromethyl)norbornadiene) is excellent. Polymers with virtually all cis and all trans vinylenes are now readily accessible using the initiators described in the previous chapter. The control over tacticity is promising but there is scope for improvement and the purpose of this chapter is to describe efforts directed towards improving the tacticity of this polymer. The high trans polymer which is available at present is 92% tactic and has been unambiguously assigned as syndiotactic using dielectric spectroscopy.[8] If it could be obtained as a 100% tactic material, the pyroelectric response could be expected to be significantly improved with possible technological and commercial significance. The anticipated improvement in the pyroelectric response may not necessarily follow a simple linear increase and if the tacticity can be raised above 92% a disproportionate improvement in properties may result. This possibility is what encouraged an extensive search for an apparently marginal improvement in catalyst performance.

An area of continuing research is the control of tacticity in polymer systems, and much work has centred around the development of "face-selective" initiators. It can be argued that high degrees of tacticity are likely only if in each propagation step, one face of the N-Mo-C plane is attacked (figure 3.1) and hence attempts to increase the tacticity have concentrated on methods of enhancing the face-selectivity of the initiators. For the first reaction between monomer and initiator depicted in figure 3.1 there is, of course, no difference between the two faces as drawn; however when the initiating alkylidene is replaced by a propagating alkylidene the two faces are sterically distinct, (see Chapter 2, figures 2.14a-c and 2.15a-c).

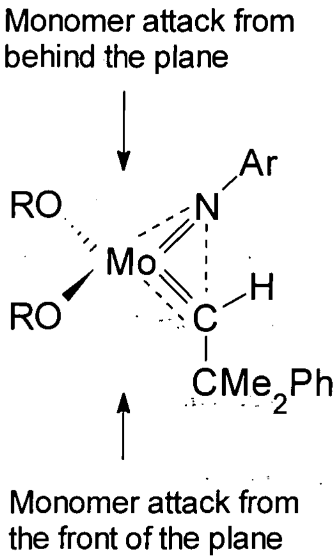
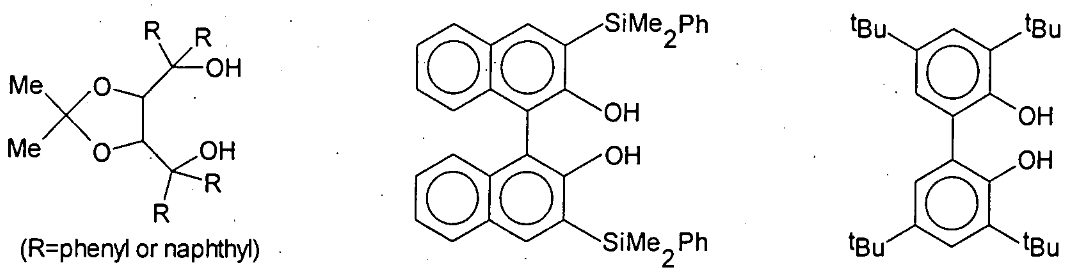


Figure 3.1. Possible approaches of the monomer to N-Mo-C plane.

Various ligand modifications have been employed in the search for control and understanding of tacticity. Schrock and co-workers have shown that chiral catalysts of the general type, $Mo(NAr)(CHCMe_2Ph)(OR)_2$ can be prepared that contain C_2-symmetric chiral diolate ligands such as those shown in figure 3.2,[9,10]



(R=phenyl or naphthyl)

R_4tartH_2 $BINO(SiMe_2Ph)_2H_2$ $Bipheno(t\text{-}Bu)_4H_2$

Figure 3.2. Examples of chiral diolate ligands.

and that poly(bis(trifluoromethyl)norbornadiene and related polymers can be prepared using them that are >99% cis and >99% tactic. It has been suggested that the high levels of tacticity observed are due to the linked and chelating nature of the diols which results in a rigidly fixed stereochemistry at the initiator and propagating chain end active sites.

In the remainder of this chapter attempts to improve the tacticity in poly(bis(trifluoromethyl)norbornadiene will be described. The work which follows is based on the knowledge that the choice of ancillary alkoxide and imido ligands around the transition metal centre in the initiator and propagating chain end active site has a profound effect on the microstructure of this polymer.[11] The work was motivated by the hope that by employing subtle variations in the steric and electronic demands of the ligands, a favourable improvement in the tacticity might result. The steric and electronic properties of the ligands employed are clearly very important. It has been established that the cis/trans vinylene content of the resulting polymer is a function of the electron withdrawing nature of the ligand, and also that the "bulkiness" of the ligands provide a high degree of steric protection for the initiator and living chain ends, thereby preventing bimolecular coupling and other side reactions. With these factors in mind, the initiators described in the following sections were synthesised and used in subsequent polymerisation studies.

3.2. New well-defined ROMP initiators: Synthesis and activity.

The following initiator systems which have been used in polymerization studies by the author were synthesised by Dr.C.Redshaw of the IRC and Chemistry Department, University of Durham, with some minor experimental assistance from the author.

a) Use of bulky chelating ligands.

Developing the theme of bulky chelating ligands described previously, the following achiral diphenol was used and a new initiator system synthesised (figure 3.3). The diphenol can be purchased from the Aldrich chemical company and has the trade name Vulkanox, it finds commercial application as an antioxidant for hydrocarbon polyolefins.

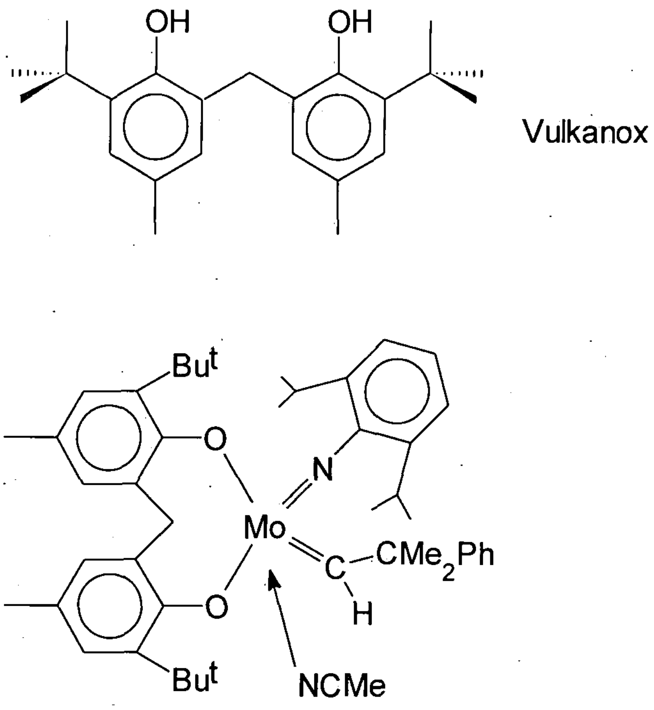


Figure 3.3. Diagram showing the "Vulkanox" ligand and its incorporation into the initiator.

Addition of the above diphenol [$2,2'$-$CH_2(4\text{-}Me,6\text{-}t\text{-}BuC_6H_2OH)_2$] to the Schrock initiator, $Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$[12] in pentane gave, after removal of the t-butanol by-product, crystalline {$Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(CHCMe_2Ph)[2,2'\text{-}CH_2(4\text{-}Me,6\text{-}t\text{-}BuC_6H_2O)_2](CH_3CN)$} in 73% yield. The molecular structure of the initiator is shown in figure 3.4. The molecular geometry is best described as a distorted trigonal bipyramidal structure with one of the oxygen atoms of the chelating diolate ligand and an acetonitrile ligand occupying axial sites and the alkylidene and imido ligands occupying equatorial positions. The distortion arises from the constrained geometry of the diolate ligand, which has the flattened boat conformation seen in other complexes containing this and closely related ligands.[13]

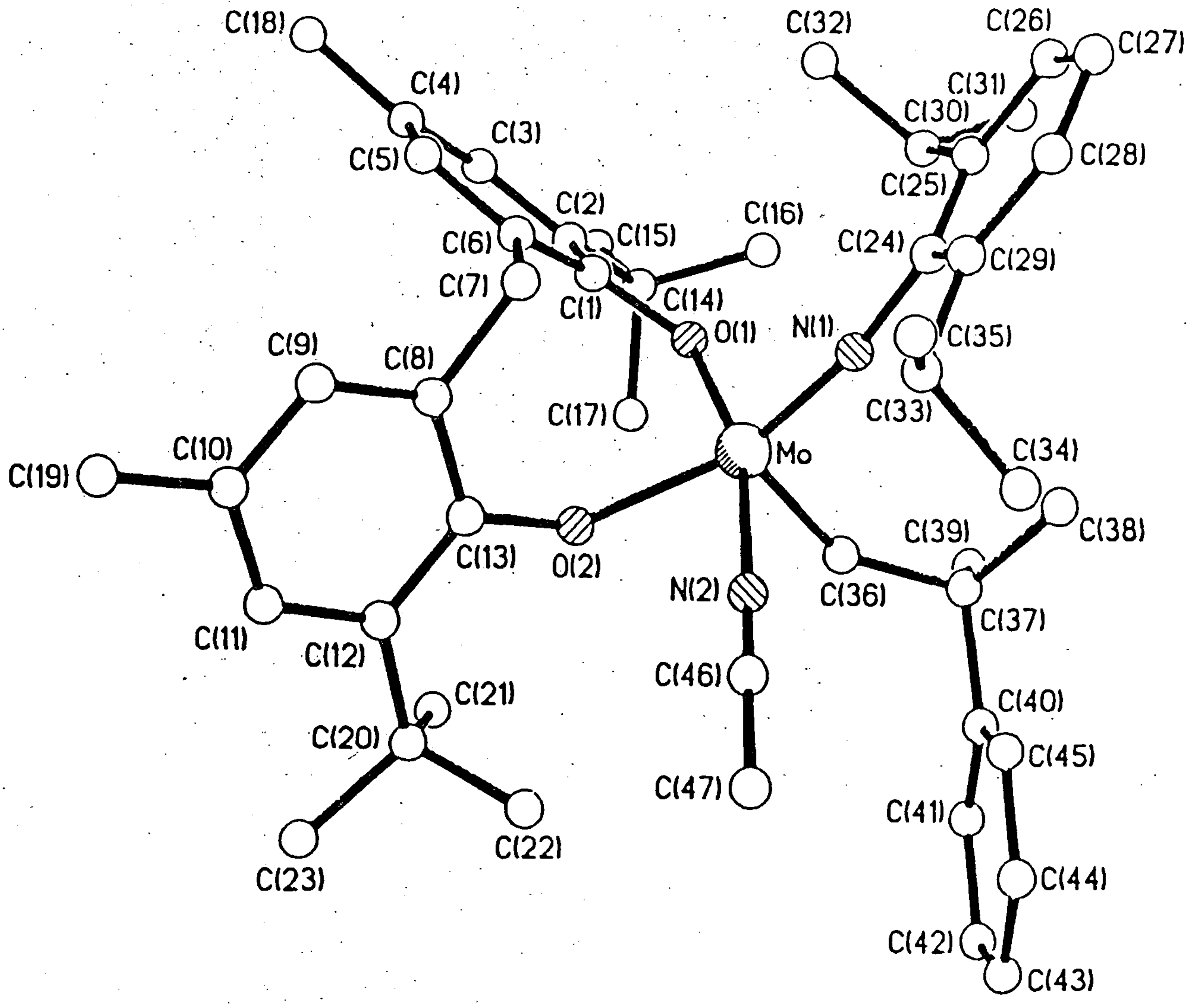
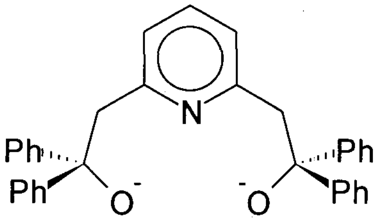


Figure 3.4. X-ray determined structure of Mo(N-2,6-$Pr^i_2C_6H_3$)($CHCMe_2Ph$)[2,2′-CH_2(4-Me,6-t-$BuC_6H_2O)_2$](CH_3CN).

To the author's knowledge, this is the first solid-state structure determination of a well-defined ROMP initiator containing a diolate ligand.[14] Other features of the structure of relevance to its ability to initiate ROMP include the fact that the CMe_2Ph substituent on the alkylidene carbon is orientated towards the imido ligand i.e. the *syn* rotamer is present; the possible implications of *syn* and *anti* rotamers in the initiator and propagating chain end on the resulting polymer structure was discussed in chapter 2 of this thesis. The position of the acetonitrile molecule is interesting, it may be viewed as binding to the C,N,O face of the four-coordinate initiator, one of the postulated sites of attack for the olefinic substrate.[5,7] This initiator thus serves as a possible model for the supposed five-coordinate intermediate in metathesis reactions involving this family of well-defined four-coordinate molybenum initiators.[7] Polymerisation studies (see later) were performed using 2,3-bis(trifluoromethyl)-norbornadiene, which is a useful benchmark monomer for the evaluation of new initiators because of its favourable kinetic profile in polymerisations with these well-defined initiators, i.e. a relatively fast rate of initiation versus propagation and a reasonably slow overall propagation rate which allows optimal control over the resultant polymer molecular weight distribution and microstructure.[5]

The previous synthesis suggested a possible route into a new class of five-coordinate molybdenum(VI) imido-alkylidene complexes utilising tridentate pyridine-2,6-diolate ligands of the form shown overleaf:



Where the addition of this ligand to the Schrock initiator, Mo(N-2,6-$Pr^i_2C_6H_3$)($CHCMe_2Ph$)(O-t-Bu)$_2$[12] gives, after removal of the t-butanol by-product, the crystalline product shown below in figure 3.5.

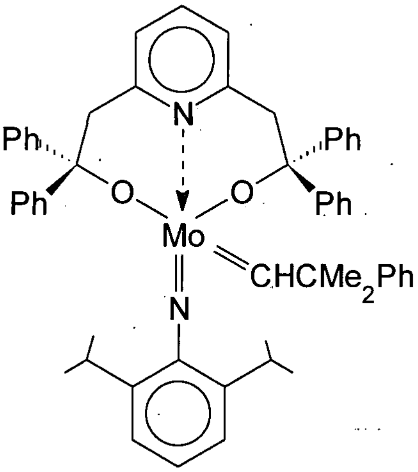


Figure 3.5. Schematic diagram of {Mo(N-2,6-Pr^i_2-C_6H_3)($CHCMe_2Ph$)[2,6-($OCPh_2CH_2$)$_2C_5H_3N$]}

This provides an excellent opportunity to study structural changes resulting from a change in coordination number.[15] Indeed it has been possible to obtain a molecular structure of this complex as displayed in figure 3.6. It is best described as a distorted trigonal bipyrimidal arrangement, with the pyridine fragment of the diolate ligand and the imido group occupying axial sites and the alkylidene group and alkoxide ligands positioned equatorially.

Of particular interest here is the fact that this potential initiator is air stable. The molybdenum initiators described previously are all very air and moisture sensitive and hence all manipulations using them must be performed in a nitrogen atmosphere in a glove box. An air stable initiator would be a major step forward in the design and development of novel initiators for use in ROMP reactions. It was envisaged that at ambient temperatures, this initiator would be inactive towards ROMP due to the coordination of the nitrogen atom of the diolate ligand to the metal centre, but it was hoped that at elevated temperatures the nitrogen-molybdenum bond would be cleaved and the initiator would become active for ROMP. Studies were undertaken to investigate the reactivity of the initiator, using the highly strained and very reactive monomer, norbornene.

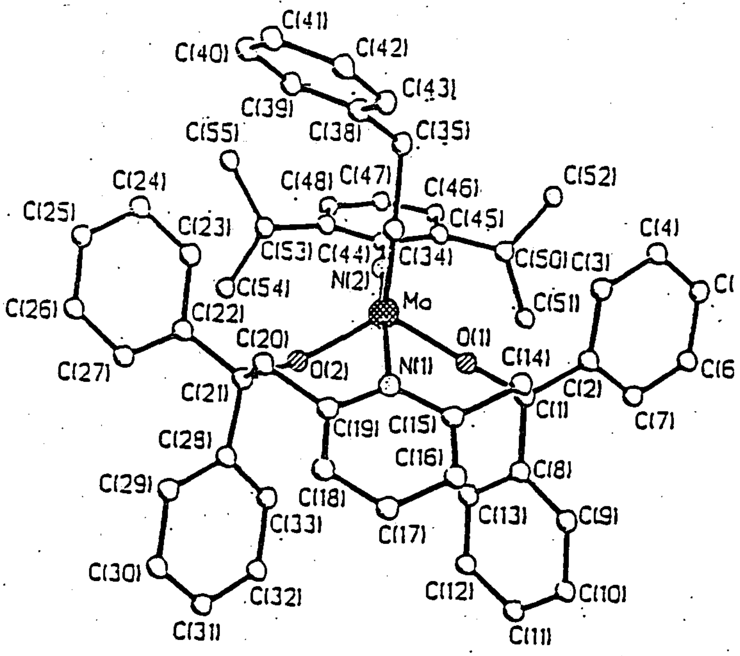


Figure 3.6. The molecular structure of Mo(N-2,6-Pr$^i_2$-C$_6$H$_3$)(CHCMe$_2$Ph)[2,6-(OCPh$_2$CH$_2$)$_2$C$_5$H$_3$N].

b) Use of "quasi-alkoxides".

Previous work by the Durham group and others has shown that by using fluoroalkoxides of the type: $-OCMe_2(CF_3)$ and $-OCMe(CF_3)_2$, the electronic properties of the alkoxide ligand can be changed by the strong electron-withdrawing effect of the CF_3 moiety, and this has a dramatic effect on the microstructure of the resulting polymer.[5,6,16,17] These earlier observations led to investigations being extended to an unusual class of alkoxide ligand, the so-called "quasi-alkoxides", in which the metal bound oxygen has a Lewis-acidic diarylboron group attached. It was envisaged that potential interactions between the Lewis acid boron centres and the Lewis basic fluorine atoms of the norbornadiene CF_3 substituents may lead to an orientating influence on the incoming monomer and thereby affect the resultant polymer microstructure. Transition metal boroalkoxide complexes have been reported in the literature, but to the author's knowledge there are no examples of the use of these ligands in ROMP chemistry.

The treatment of $\{Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(CHCMe_2Ph)(OSO_2CF_3)_2(dme)\}$[12] (where dme = 1,2-dimethoxyethane) with two equivalents of $LiOB(2,4,6\text{-}Me_3C_6H_2)_2$[18] afforded the yellow crystalline product illustrated in figure 3.7.

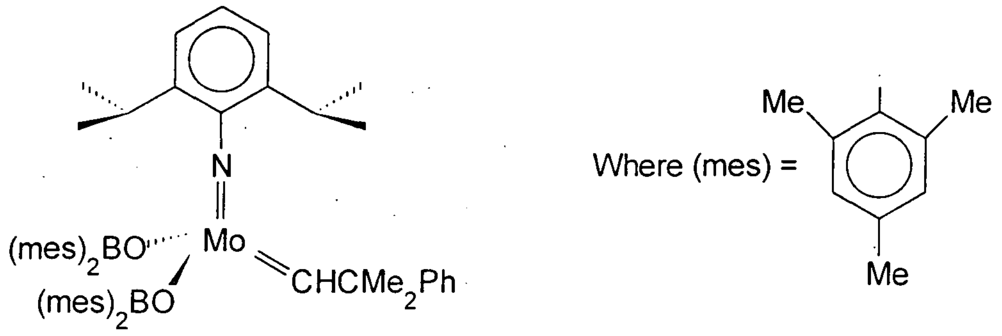
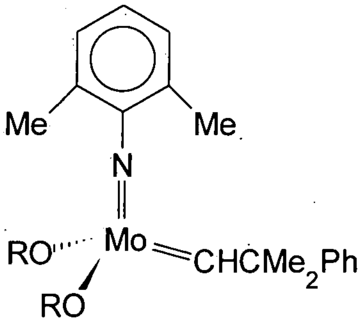


Figure 3.7. Schematic diagram of the four-coordinate boroalkoxide initiator.

The ^1H NMR spectrum of this initiator shows a resonance for the alkylidene proton at δ 11.66ppm, a chemical shift comparable with that observed for the trifluoro-t-butoxide initiator $\{Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(CHCMe_2Ph)[OMe_2(CF_3)]_2\}$ (δ 11.68ppm). Indeed the position of the alkylidene hydrogen is a useful indicator of the electron-withdrawing capacity of the ancillary alkoxide ligands and suggests that the boroxide ligand has a comparable electron-withdrawing capacity to the trifluoro-t-butoxide group. Subsequent polymerisation studies were undertaken using the monomer 2,3-bis(trifluoromethyl)norbornadiene.

c) Variation of the arylimido ligand in the initiator.

Among the questions that have not yet been addressed in relation to the reactivity and stereoregulating capacity of these initiators are to what extent can the electronic and steric properties of the arylimido ligand be varied and what effect will these variations have on subsequent polymerisation products. The function of the imido ligand is almost certainly not just confined to providing steric bulk to the initiator, and both electronically and sterically speaking, it stands a good chance of being able to alter, perhaps drastically, the reactivity of the transition metal centre.[13] Hence using the initiator $Mo(N\text{-}2,6\text{-}Me_2C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$,[13] previously described by Schrock and co-workers, in polymerisation studies on 2,3-bis(trifluoromethyl)norbornadiene also seemed a worthwhile challenge.



{ Where R = $CMe(CF_3)_2$ }

Figure 3.8. Schematic diagram of $Mo(N\text{-}2,6\text{-}Me_2C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$.

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3.3. Experimental.

1) General procedures and techniques.

All manipulations were performed under an atmosphere of nitrogen using standard Schlenk and cannular techniques or in a conventional nitrogen-filled glove-box. The following deuterated NMR solvents were dried by storing over a suitable drying agent (in parentheses) and vacuum transferred immediately prior to use: d_6-benzene (phosphorus (V) oxide), d_2-dichloromethane (calcium hydride), d-chloroform (phosphorus (V) oxide), d_3-acetonitrile (calcium hydride), d_8-toluene (phosphorus (V) oxide), d_5-chlorobenzene (phosphorus (V) oxide). d_6-Acetone was used as received.

Solvents used for the larger scale polymerisations were toluene and THF. Toluene was distilled from sodium metal and passed through a column of activated alumina prior to use. THF was stored over sodium benzophenone ketyl and vacuum transferred prior to use. Both solvents were deoxygenated immediately before use in the glovebox. The monomers used in these experiments were norbornene and 2,3-bis(trifluoromethyl)norbornadiene, and these were prepared as described in the literature.[19,20]

2) Initiator syntheses.

a) Synthesis of $Mo(N\text{-}2,6\text{-}Pr^i{}_2C_6H_3)(CHCMe_2Ph)[2,2'\text{-}CH_2\text{-}(4\text{-}Me,6\text{-}t\text{-}Bu\text{-}C_6H_2O)_2](CH_3CN)$.

$Mo(N\text{-}2,6\text{-}Pr^i{}_2C_6H_3)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$[12] (0.273g, 0.5mmol) and $[2,2'\text{-}CH_2(4\text{-}Me,6\text{-}t\text{-}BuC_6H_2OH)_2]$ (0.17g, 0.5mmol) were stirred in pentane (30cm^3). After 5 minutes, the volatile components were removed and then another 30cm^3 pentane added. This cycle was repeated twice after which the yellow residue was extracted with hot CH_3CN (25cm^3). Yellow prisms formed on standing (1-2 days) 0.28g, 72.7% yield. Found: C, 71.5; H, 8.0; N, 2.8. Calculated for $C_{46}H_{62}N_2O_2Mo$: C, 71.7; H, 8.1; N, 3.6.

^{1}H NMR data (CDCl$_3$, 400MHz, 298K, reference to TMS)

Alkylidene region: 13.02ppm (s), Mo=C*H*CMe$_2$Ph (see Appendix 3.1a)

^{13}C NMR data (CDCl$_3$, 100.59MHz, 298K, reference to TMS)

Alkylidene region: 263.9ppm, Mo=*C*HCMe$_2$Ph (see Appendix 3.1b)

b) Synthesis of $Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(CHCMe_2Ph)(OB(2,4,6\text{-}Me_3C_6H_2)_2)_2$

$Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(CHCMe_2Ph)(OSO_2CF_3)_2(dme)$[12] (1.0g, 1.26mmol) and $LiOB(2,4,6\text{-}Me_3C_6H_2)_2$[18] (0.688g, 2.53mmol) were combined in diethyl ether (40cm^3) at -40^{0}C. After stirring for 4 hours at room temperature, the volatile components were removed under reduced pressure. Extraction of the residue with hot CH_3CN (30cm^3) gave yellow prisms on standing (0.41g, 34.8%). Found: C, 73.9; H, 8.1; N, 2.4. Calculated for $C_{58}H_{73}B_2O_2NMo$: C, 74.6; H, 7.9; N, 1.5.

^{1}H NMR data (C_6D_6, 400MHz, 298K, reference to TMS)

Alkylidene region: 11.66ppm (s), Mo=C*H*CMe$_2$Ph (see Appendix 3.2a)

^{13}C NMR data (C_6D_6, 100MHz, 298K, reference to TMS)

Alkylidene region: 278.8ppm, Mo=*C*HCMe$_2$Ph (see Appendix 3.2b)

c) Synthesis of Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)($OCMe(CF_3)_2$)$_2$.

This was synthesised according to the methods published by Schrock and co-workers, and details are available in the literature.[13] The ^1H NMR spectrum is recorded in Appendix 3.3.

d) Synthesis of Mo(N-2,6-$Pr^i_2C_6H_3$)($CHCMe_2Ph$)[2,6-($OCPh_2CH_2$)$_2C_5H_3N$]

Mo(N-2,6-$Pr^i_2C_6H_3$)($CHCMe_2Ph$)(O-t-Bu)$_2$[12] (0.5g, 0.91mmol) and 2,6-($HOCPh_2CH_2$)$_2C_5H_3N$ (0.43g, 0.91mmol) were stirred in pentane (30cm^3). After 5 minutes, the volatile components were removed and then another 30cm^3 pentane was added. This cycle was repeated twice after which the red residue was extracted with hot CH_3CN (25cm^3). Red needles formed on standing (1-2 days). Found: C, 75.2; H, 6.6; N, 3.3. Calculated for $C_{54}H_{56}N_2O_2Mo$: C, 75.7; H, 6.5; N, 3.2.

^1H NMR data (400MHz, CD_2Cl_2, 298K, reference to TMS)

Alkylidene region: 11.32ppm (s), Mo=C*H*CMe$_2$Ph (see Appendix 3.4a)

^{13}C NMR data (100.57MHz, C_6D_6, 298K, reference to TMS)

Alkylidene region: 268.75ppm, Mo=*C*HCMe$_2$Ph (see Appendix 3.4b)

3) Polymerisation studies.

a) ^{1}H NMR scale polymerisation of 2,3-bis(trifluoromethyl)norbornadiene using $Mo(N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$.

To a rapidly stirring solution of $Mo(N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)(CHCMe_2Ph)\text{-}(OCMe(CF_3)_2)_2$ (0.0127g, 0.0179mmole) in C_6D_6 (350µl) was added a C_6D_6 solution (350µl) of 2,3-bis(trifluoromethyl)norbornadiene (0.0666g,0.292mmole). After twenty minutes the reaction mixture was injected into an NMR tube specially fitted with a Teflon stopcock and a ^{1}H NMR run to observe the propagating alkylidene protons.

<u>^{1}H NMR data.</u> (400MHz, C_6D_6, 298K, reference to TMS)

Alkylidene region: 12.405-12.137ppm (d), Mo=CHP. 12.154ppm (s), Mo=CHC-Me_2Ph (see Appendix 3.6)

b) Scaled-up polymerisation of 2,3-bis(trifluoromethyl)norbornadiene using $Mo(N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$.

A solution of 2,3-bis(trifluoromethyl)norbornadiene (2.17g, 9.5 mmole) in toluene/THF (6ml, 90:10 ratio of toluene:THF) was added dropwise to a rapidly stirred solution of $Mo(N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$ (0.056g, 0.079mmole) in toluene/THF (6ml, 90:10 ratio) over a period of 30 minutes. On addition of the monomer solution, the reaction mixture deepened to a cherry-red colour indicative of the formation of the propagating alkylidene species and within 15 minutes the reaction mixture became extremely viscous and turned noticeably cloudy. In order to maintain the homogenous nature of the polymerisation, a further 5ml toluene/THF was added and stirring continued for 16 hours.

The polymerisation was terminated by the addition of benzaldehyde, (0.08ml, 0.79mmole, 10-fold excess with respect to the initiator), and stirred for a further 60 minutes, and the product polymer was isolated by precipitation from a large volume of hexane. The product was recovered by filtration and dried *in vacuo* to give poly(bis(trifluoromethyl)norbornadiene as a pale-green powder, (1.5g, 69%).

^{1}H NMR data (400MHz, $(CD_3)_2CO$, 298K, reference to TMS)

5.6, 5.55ppm (br), (vinylic protons), 4.22ppm (s,br), (allylic protons), 2.8ppm (s,br), 1.52ppm (s,br) (methylene protons) (see Appendix 3.7a)

^{13}C NMR data (100.58MHz, $(CD_3)_2CO$, 298K, reference to TMS)

140.38ppm (m), (olefinic carbons), 131.84ppm (br), (vinylic carbons), 126.03 (s), 123.30 (s), 120.57 (s), 117.85ppm (s), (CF_3), 50.87 (s), 44.82,44.67ppm (br), (allylic carbons), 38.34 (s), 37.57 (s), (methylene carbons), (see Appendix 3.7b)

^{19}F NMR data (376.32MHz, $(CD_3)_2CO$, 298K, reference to $CFCl_3$)

59.49-60.28ppm (m), (CF_3), (see Appendix 3.7c)

In Appendix 3.7d, a DSC trace of the polymer is recorded.

c) ^{1}H NMR scale polymerisation of 2,3-bis(trifluoromethyl)norbornadiene using $Mo(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(CHCMe_2Ph)(OB(mes)_2)$.

2,3-Bis(trifluoromethyl)norbornadiene (74.8mg, 0.328mmole, 23 equivalents) were dissolved in C_6D_6 (350μl) and the resultant mixture added to a rapidly stirring solution of $Mo(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(CHCMe_2Ph)(OB(mes)_2)$ (0.0135g, 0.0145mmole) in C_6D_6 (350μl). After 30 minutes the reaction was analysed by ^{1}H NMR spectroscopy.

^{1}H NMRdata. (400MHz, C_6D_6, 298K, reference to TMS).

Alkylidene region: 11.693-11.685ppm (d), Mo=CHP (see Appendix 3.8)

d) Scaled-up polymerisation of 2,3-bis(trifluoromethyl)norbornadiene using $Mo(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(CHCMe_2Ph)(OB(mes)_2)$.

2,3-Bis(trifluoromethyl)norbornadiene (4.16g 18.2mmole, 1300 equivalents) were dissolved in a toluene/THF mixture (10ml, 90:10 ratio) and the resultant solution added dropwise, over a period of 40 minutes, to a vigorously stirred solution of $Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(CHCMe_2Ph)(OB(mes)_2)$ (0.013g, 0.0140mmole) in toluene/THF (10ml, 90:10 ratio). No discernible colour change was observed, but within 5 minutes the reaction mixture turned noticeably cloudy and became slightly viscous. In order to maintain the homogenous nature of the reaction, a further 5ml of toluene/THF was added and the reaction stirred continuously for 20 hours.

The polymerisation was terminated by the addition of benzaldehyde (0.014ml, 0.138mmole, 10-fold excess with respect to initiator) and stirring continued for a further 60 minutes. The product polymer was isolated by precipitation from hexane and purified by re-dissolving the polymer in acetone and re-precipitating again in hexane. The product was recovered by filtration and dried *in vacuo* to yield poly(bis(trifluoromethyl)norbornadiene as a white fibrous material (2.84g, 68%)

^{1}H NMR data (400MHz, $(CD_3)_2CO$, 298K, reference to TMS)

5.76, 5.61ppm (br), (vinylic protons), 4.21 (s,br), 3.84ppm (s,br), (allylic protons), 2.85, 2.82 (br), 1.55ppm (s,br), (methylene protons) (see Appendix 3.9a)

^{13}C NMR data (100.58MHz, $(CD_3)_2CO$, 298K, reference to TMS).

140.39ppm (m), (olefinic), 133.04 (s,br), 131.91ppm (s), (vinylic), 125.98 (s), 123.26 (s), 120.53 (s), 117.81ppm (s), (CF_3), 49.11 (m), 44.71ppm (s), (allylic), 38.28 (s), 37.69ppm (m), (methylene) (see Appendix 3.9b)

^{19}F NMR data (376.32MHz, $(CD_3)_2CO$, 298K, reference to $CFCl_3$)

59.11, 59.94, 60.47ppm, (all broad singlets), (CF_3) (see Appendix 3.9c)

In Appendix 3.9d, a DSC trace of the polymer is recorded.

e) Polymerisation of 2,3-bis(trifluoromethyl)norbornadiene using Mo(N-2,6-Pr^i_2-C_6H_3)($CHCMe_2Ph$)[2,2'CH_2(4-Me,6-t-BuC_6H_2O)$_2$](CH_3CN) where 2,2'CH_2(4-Me,6-t-BuC_6H_2O)$_2$ represents the "Vulkanox" ligand.

To a vigorously stirred solution of Mo(N-2,6-Pr^i_2-C_6H_3)($CHCMe_2Ph$)[vulkanox](CH_3CN) (0.013g, 0.017mmole) in toluene/THF (5ml, 90:10 ratio) was added dropwise a toluene/THF (5ml, 90:10 ratio) solution of 2,3-bis(trifluoromethyl)norbornadiene (3.76g, 16.5mmole) over a period of 30 minutes. On addition of the monomer solution, the reaction mixture deepened to a darkish brown colour. The solution remained homogenous and stirring was continued for 24 hours, where upon the reaction mixture had become viscous.

Benzaldehyde (0.017ml, 0.17mmole, 10-fold excess with respect to initiator)was added to terminate the polymerisation and the reaction mixture allowed to stir for a further 60 minutes. The product polymer was recovered by precipitation from hexane and purified by re-dissolving the polymer in acetone and re-precipitating again in hexane. The product was recovered by filtration and dried *in vacuo* to yield poly(bis(trifluoromethyl)norbornadiene as a pale yellow fibrous material, (1.2g, 32%).

^{1}H NMR data (400MHz, $(CD_3)_2CO$, 298K, reference to TMS)

5.71 (s), 5.61ppm (s), (vinylic), 4.23 (s), 3.83ppm (s), (allylic), 2.84 (m), 1.60ppm (m), (methylene) (see Appendix 3.10a)

^{13}C NMR data (100.58MHz, $(CD_3)_2CO$, 298K, reference to TMS)

140.03ppm (m), (olefinic), 133.41, 133.14 (d), 131.80ppm (s,br), (vinylic), 126.02 (s), 123.29 (s), 120.57 (s), 117.87ppm (s), (CF_3), 49.59 (s,br), 44.61ppm (s), (allylic), 38.37 (s,br), 37.82 (s,br), 37.04ppm (m), (methylene) (see Appendix 3.10b)

^{19}F NMR data (376.32MHz, $(CD_3)_2CO$, 298K, reference to $CFCl_3$)

59.47, 59.72, 60.09, 60.40ppm, (all broad singlets), (CF_3) (see Appendix 3.10c)

In Appendix 3.10d, the DSC trace of this polymer is recorded.

f) Reaction of $Mo(N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$ with 2 equivalents of ^{t}BuOH.

To a stirring solution of $Mo(N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$ (0.0236g, 0.033mmole) in C_6D_6 (350μl) was added 2 equivalents of ^{t}BuOH (0.00943g, 0.0665mmole), dissolved in C_6D_6 (350μl). The reaction mixture was stirred for 15 minutes before transferring the reaction vial contents into an NMR tube. The reaction was monitored by ^{1}NMR spectroscopy. The spectroscopic data is shown overleaf.

^{1}H NMR data. (400MHz, C_6D_6, 298K, reference to TMS).

Alkylidene region:

With no ^{t}BuOH added: 12.154ppm (s) (see Appendix 3.11a)

With ^{t}BuOH added (after 1.5 hours): 11.769 (s), 83%. 11.373 (s), 17%.

With ^{t}BuOH added (after 46 hours): 12.177 (s), 3.5%. 11.769 (s), 81%. 11.373 (s), 15.5% (see Appendix 3.11b)

With ^{t}BuOH added (after 5 days): 12.177 (s), 4%. 11.769 (s), 81%. 11.374 (s), 15%.

g) Attempted polymerisation of norbornene using Mo(N-2,6-Pr^i_2-C_6H_3)($CHCMe_2Ph$)(2,6-($OCPh_2CH_2$)$_2C_5H_3N$).

In the glove box, norbornene (0.244g,2.59mmole) was dissolved in d_5-chlorobenzene (400μl). This solution was then added dropwise to a stirring solution of Mo(N-2,6-Pr^i_2-C_6H_3)($CHCMe_2Ph$)(2,6-($OCPh_2$)$_2C_5H_3N$) (0.026g, 0.030mmole) in d_5-chlorobenzene (400μl). No colour change was observed on the addition of the monomer solution i.e. the solution remained a clear orange/brown colour and no signs of the solution becoming viscous could be detected. The reaction mixture was stirred for 10 minutes, prior to injection into an NMR tube, specially fitted with a teflon stopcock. A ^{1}H NMR was recorded and showed that no polymerisation had occurred, (see Appendix 3.12).

The reaction mixture was heated to see if the initiator could be thermally activated, this was performed as follows: The NMR tube was connected to a vacuum line and immersed in an oil bath at 80^{0}C. At regular intervals, the teflon stopcock on the NMR tube was opened to the vacuum line in order to release any pressure building up in the NMR tube due to the heating. The reaction mixture was heated at 80^0C for 24 hours, after which the solution remained a clear orange/brown colour. A ^{1}H NMR was taken and revealed the absence of any signs of polymerisation occurring.

The reaction mixture was heated for a further 48 hours at 90^0C, and once again no signs of polymerisation were evident. Furthermore, increasing the reaction temperature to 100^0C had no effect on the outcome of the reaction.

Different solvent systems were tried to see if this had any effect on the polymerisation. The solvents tried were d_3-acetonitrile and d_8-toluene. Both the neopentylidene and neophylidene initiator complexes were used, however, no signs of polymerisation occurring were observed with either of them.

3.4. Results and discussion.

Polymerisation studies.

The results of the polymerisation studies are summarized in table 3.1. Information relating to the cis/trans vinylene content and tacticity can be deduced from an analysis of the ^{13}C NMR spectra. The characteristic 5ppm upfield shift of an allylic carbon adjacent to a cis vinylene as compared to an analogous carbon adjacent to trans is the usual starting point in such analyses. Spectra recorded under quantitative conditions then allow integration of the relative intensity of cis and trans associated vinylene and allylic carbons. These procedures are well established.[5,6,20] Previous studies on the polymer of 2,3-bis(trifluoromethyl)norbornadiene have shown the C7 methylene region to be especially revealing with respect to tacticity and sequence effects. The C7 methylene signal recorded for polymers produced using Mo(N-2,6-Pr^i_2-C_6H_3)($CHCMe_2Ph$)($OCMe(CF_3)_2$ (I) and the dimethylimido analogue (II) as initiators are reproduced in figure 3.9.

Table 3.1. A table summarising the results of polymerisation studies performed using the new well-defined ROMP initiators.

Initiator	**Monomer**	**Tacticity (%)**	**Cis/Trans (%)**	**T_g (^{0}C)**
Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ * **(I)**	2,3-bis(trifluoromethyl) norbornadiene	~ 75% tactic	>98% cis	144
Mo(N-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ **(II)**	2,3-bis(trifluoromethyl) norbornadiene	~ 75% tactic	>98% cis	144
Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OB(mes)$_2$) **(III)**	2,3-bis(trifluoromethyl) norbornadiene	Some tacticity present in polymer. % not known.	85% cis	130
{Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)[vulkanox](CH$_3$CN)} **(IV)**	2,3-bis(trifluoromethyl) norbornadiene	Some tacticity present in polymer. % not known.	60% cis	115
Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(2,6-(OCPh$_2$)$_2$C$_5$H$_3$N) **(V)**	norbornene	–	–	–

* This initiator has been studied previously, and these results are included in the table for comparison with the new initiators.[16,17]

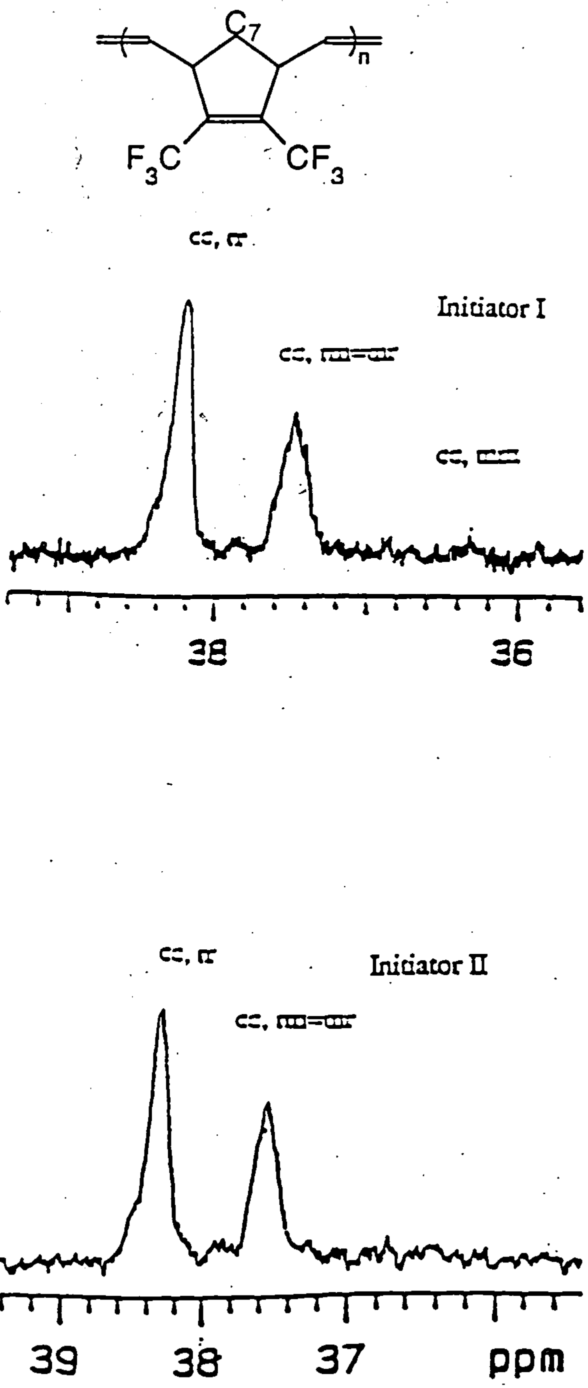

Figure 3.9. A comparison of the C7 methylene regions of poly((bistrifluoromethyl)norbornadiene) produced by initiators I and II.

The two major resonances seen in both spectra must arise from methylene units between two adjacent cis vinylenes since both polymers have >98% cis vinylene content and trans vinylene effects will be so small as to be negligible. Consequently the observed splitting of the C7 resonance must be due to tacticity. As discussed previously, dielectric spectroscopy leads to the hypothesis that racemic dyads are most prevalent in this low relaxed dielectric constant polymer, hence the peak of greater intensity is assigned as cc rr, where cc indicates a cis cis sequence of vinylenes and rr indicates two consecutive racemic ring incorporations. The polymer is not 100% syndiotactic and a further peak of lower intensity is observed and is assigned as cc rm=mr indicating adjacent meso and racemic ring incorporations in the polymer backbone.[5,8] With initiator I there is a very weak signal assigned as cc mm on the same basis. Thus it can be concluded, on the basis of the ^{13}C NMR data, that the substitution of iso-propyl groups on the arylimido ligand by methyl groups has no influence on the resulting polymer microstructure in the case of the related initiators I and II. Further evidence for this conclusion comes from Differential Scanning Calorimetry (DSC) measurements which shows identical glass transition temperatures (T_g) for the products of polymerisations initiated by I and II. This was a disappointing result in view of Schrock's report of the effect of swapping isopropyl for methyl groups in the initiator, $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}R\text{-}C_6H_3)[BINO(SiMe_2Ph)_2]$, where R represents either methyl or isopropyl groups, (figure 3.2 shown previously, illustrates the $[BINO(SiMe_2Ph)_2]$ ligand schematically). In this system, it was reported that the initiator containing isopropyl groups produced a polymer containing 75% cis vinylenes and was 86% tactic. However, on exchanging the isopropyl groups for methyl groups, a remarkable change in the resulting polymer microstructure occurred and a polymer was produced containing >99% cis vinylenes and furthermore it was >99% tactic. This dramatic change in microstructure highlights the exceedingly fine steric balance that exists in these sterically crowded species.[9,10,11]

Experiments were conducted in an attempt to generate the t-butoxide analogue of the dimethylimido initiator (II), using t-butanol exchange. The motivation for these experiments was based on previous work performed by workers in the Durham group. It has been shown that using a 1:1 initiating mixture of the initiator Mo(N-2,6-Pr^i_2-C_6H_3)($CHCMe_2Ph$)($OCMe_3$)$_2$ and its hexafluoro-t-butoxide analogue generates an equilibrium between three alkylidene species,[16,17] more recently, living ligand exchange experiments have been performed by the same group.[21] Results from these experiments have shown that the addition of hexafluoro-t-butanol to the living all trans-vinylene polymer produced when the polymerisation of 2,3-bis(trifluoromethyl)norbornadiene is initiated by Mo(N-2,6-Pr^i_2-C_6H_3)($CHCMe_2Ph$)($OCMe_3$)$_2$, allows ligand exchange to occur between the hexafluoro-t-butanol and the living chain end to give a modified chain end which can initiate the polymerisation of another batch of monomer to produce a stereoblock copolymer with cis and trans vinylene blocks. These results extend the earlier observations of Marshall which showed that the distribution of cis and trans vinylenes in the polymer backbone is controlled by the relative proportion of the different alkoxy ligands in the polymerisation mixture. The expected equilibrium between three alkylidene species, figure 3.10, is observed experimentally when two equivalents of t-butanol are added to the dimethylimido initiator (II), ^1H NMR spectroscopy shows quite clearly the existence of three distinct alkylidene species, figure 3.11. This finding suggests it may also be possible to synthesise a stereoblock copolymer of cis and trans vinylene blocks, as was the case with the isopropylimido initiating system discussed previously; but, as yet, no polymerisation studies have been performed using this equilibrium system.

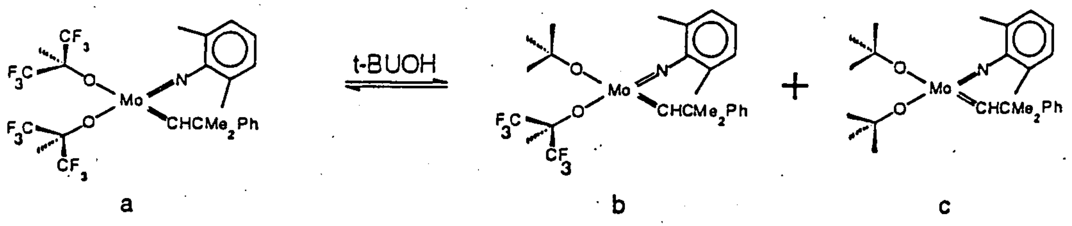

Figure 3.10. The equilibrium between three alkylidene species on the addition of t-butanol to initiator II.

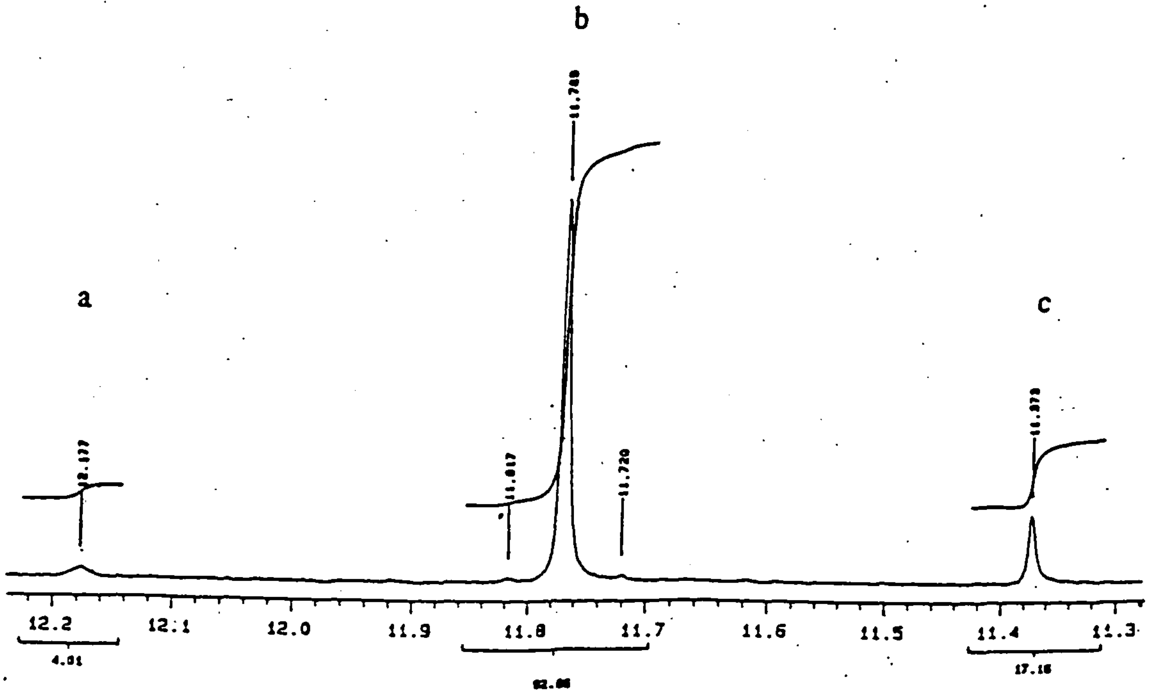

Figure 3.11. ^{1}H NMR spectrum showing the existence of three alkylidene species when two equivalents of t-butanol are added to the dimethylimido initiator (II). (The letters a,b,c refer to the structures shown above in figure 3.10).

As indicated in table 3.1, initiator V displayed no ROMP activity. As discussed previously, it was envisaged that at elevated temperatures the nitrogen-molybdenum bond would be cleaved thereby activating the initiator for ROMP, however this does not seem to be the case and no signs of a polymerisation occurring are evident. Norbornene was used, as this is well established as one of the more reactive monomers in ROMP on account of its high ring strain and relatively good π-donor capacity,[20] furthermore it contains no functional groups which could disrupt the activity of the initiator. Figure 3.12 below, summarises the proposed mode of action of this initiator

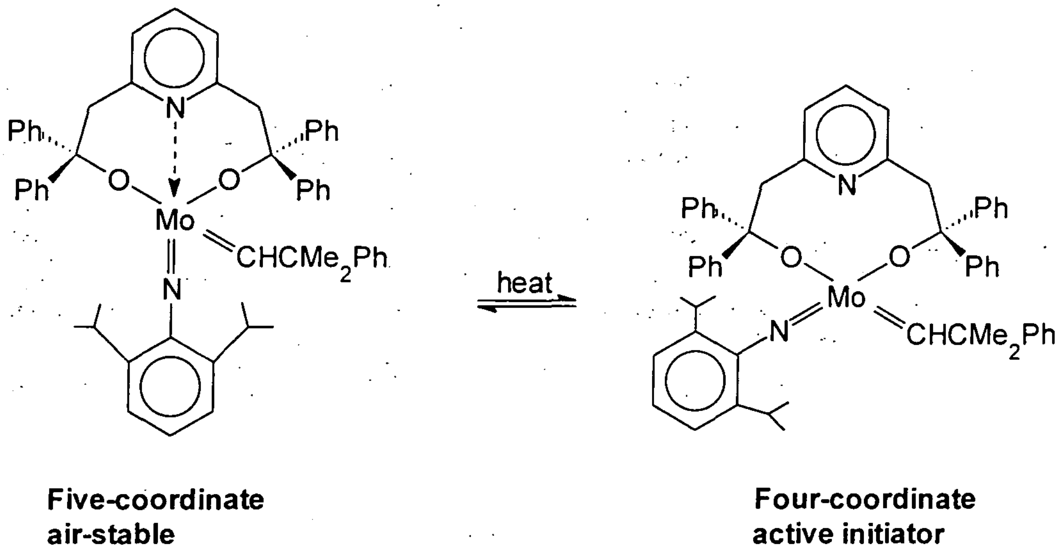

Figure 3.12. The concept for an air-stable, thermally activated ROMP initiator.

The lack of ROMP activity shown by this initiator was a disappointing result in view of the fact that an air-stable initiator for use in ROMP reactions would be a major breakthrough. As discussed previously in this chapter, one of the problems associated with well-defined ROMP initiators is that they are highly sensitive to traces of moisture and oxygen, hence all manipulations using them have to be performed in a nitrogen filled dry-box. The quest for solving this problem provided the motivation for developing an air-stable initiating system. Such a potential initiator system was developed, which was air stable and its structure has been characterised as detailed previously in this chapter. In the initiator, the molybdenum centre was five coordinate and it was hoped that it would become thermally activated to produce an active complex in which the molybdenum was four coordinate (figure 3.12). In the event, this was not the case and no activity was observed, with presumably, the pyridinediolate ligand being too strongly bound to the metal centre. Possible future studies which could reasonably be undertaken on the further development of this initiating system will be described in Chapter 6 of this thesis.

Initiator IV was also an interesting system to study. The motivation for developing this initiating system was provided by previous work performed by Schrock and co-workers involving the use of C_2-symmetric chiral diolate ligands, described previously in this chapter (figure 3.2).[9,10] In this work, samples of poly(bis(trifluoromethyl)norbornadiene were obtained which contained >99% cis vinylenes and were >99% tactic. So this theme of bulky chelating ligands was extended and the achiral phenol, Vulkanox, was incorporated into an initiating system as shown in figure 3.13.

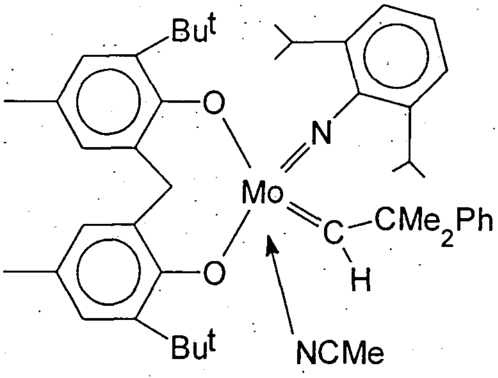

Figure 3.13. The "Vulkanox" initiator.

As discussed previously, the position of the acetonitrile is interesting, as it may be viewed as binding to one of the C,N,O faces of the four-coordinate initiator, the postulated sites of attack for the olefinic substrate. Hence, this is an interesting initiating system to study as it serves as a possible model for the supposed five-coordinate intermediate in metathesis reactions involving this family of well-defined four-coordinate molybdenum initiators.

^{13}C NMR spectroscopy has been used to analyse the microstructure of poly(bis(trifluoromethyl)norbornadiene) obtained using initiator IV and information concerning the tacticity and cis and trans vinylene content has been obtained. Using a similar analysis to that described earlier in this section, it was calculated from the allylic carbon region that this polymer contained 60% cis vinylenes in the backbone. Information relating to tacticity effects can be sought by analysing the C7 methylene region of this polymer. Figure 3.14 displays the methylene region of this polymer and the peak assignments are shown in table 3.2. As can be seen, the region shows substantial splitting indicating that the polymer does not possess a totally stereoregular microstructure. Comparison with the spectra shown in figure 3.15 allows a clearer picture of the tacticity in this polymer to be attained. Figure 3.15[22] displays a series of spectra of the methylene regions of poly(bis(trifluoromethyl)-norbornadiene) samples of varying cis vinylene content. In an all cis or all trans polymer only one environment and one signal will be observed unless the methylene carbon experiences a meso/racemic (m/r) shift effect, caused by the stereochemistries of the nearest ring placements, which means there can be up to three possible environments (mm, mr=rm and rr).

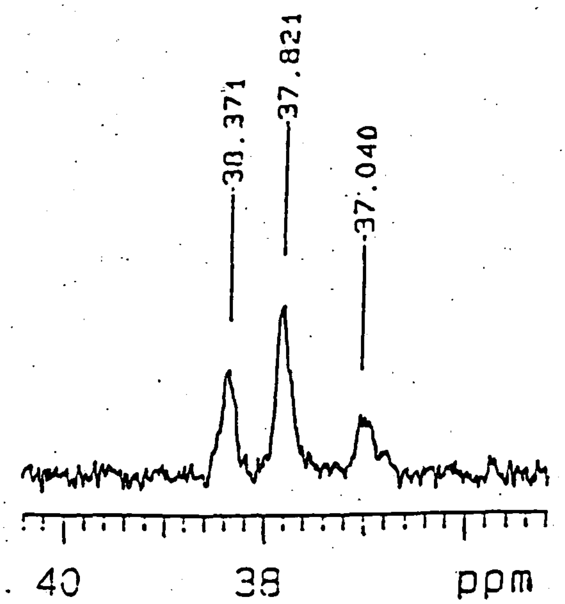

Figure 3.14. The ^{13}C NMR spectrum of the methylene region of poly(bis(trifluoromethyl)norbornadiene) made using initiator IV.

Chemical shift/ppm	Peak assignment
38.37	cc, rr
37.82	ct/tc
37.04	tt

Table 3.2. Peak assignments for the methylene carbon region displayed in figure 3.14.

The peak assignments in table 3.2 were made on the basis of a comparison between the ^{13}C NMR spectrum of the methylene region shown in figure 3.14 and the series of ^{13}C NMR spectra displayed in figure 3.15.

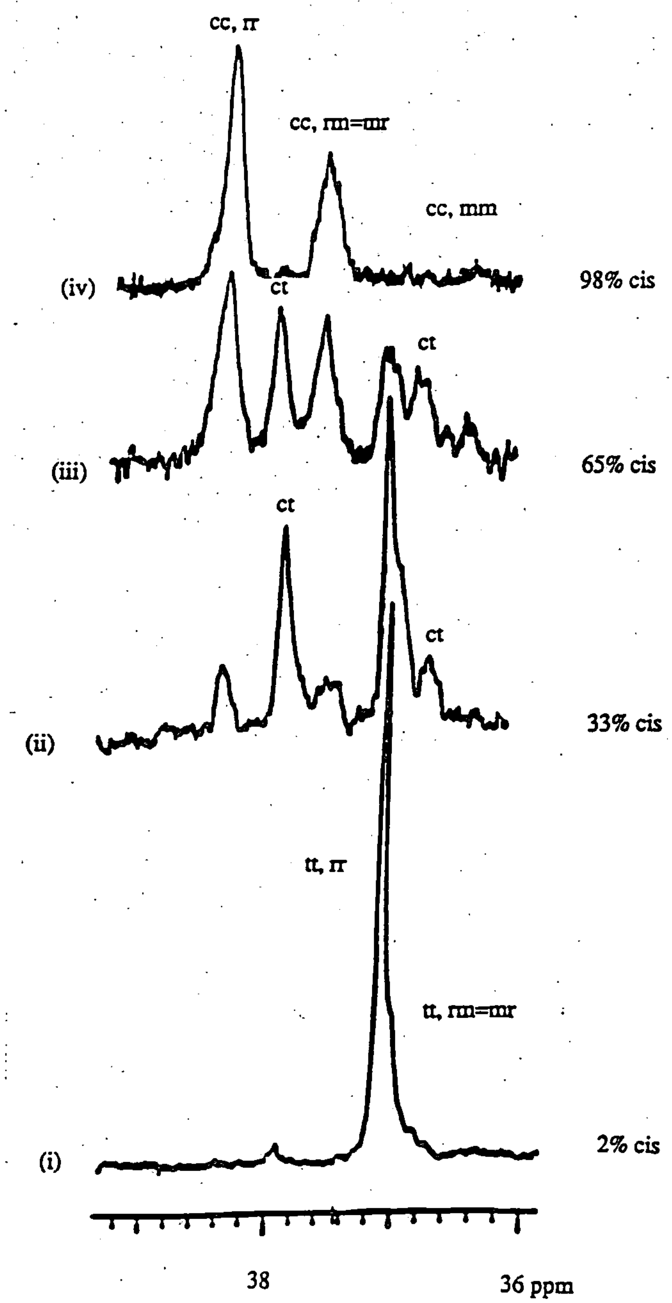

Figure 3.15. ^{13}C NMR spectra of the methylene region of a series of poly(bis(trifluoromethyl)norbornadiene) samples of varying cis vinylene content and their assignments.

With reference to figure 3.15, spectrum i) is for the sample with >98% trans vinylene content, prepared using the $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(OCMe_3)_2$ initiator. It consists of a single peak with a shoulder to lower frequency, deconvolution of the two overlapping peaks indicates that this polymer is 92% tactic, but it is not possible to assign the specific tacticity from this data, as was explained in Chapter 2 of this thesis. The assignment, based on dielectric measurements, is never-the-less secure as shown. As the cis content is increased, spectra (ii and iii), an increase in multiplicity of the methylene carbon peaks occurs which must be due to the presence of cis/trans junctions and all cis sequences. In the spectrum of the polymer with >98% cis vinylene content (iv), prepared using the $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(OCMe(CF_3)_2)_2$ initiator, two well-resolved environments are observed corresponding to two of the three possible triads. Integration of these peaks indicates that this high cis polymer is 75% tactic. Although no assignment of the tacticity can be made on the basis of the NMR data, the dielectric measurements are consistent with a predominantly syndiotactic microstructure. In these assignments workers in this field are in unanimous agreement concerning the assignment of tacticity of the high trans vinylene polymers. There is disagreement over the assignment of tacticity in the high cis polymers, while accepting that there is a measure of uncertainty, the remainder of this work will use the assignments favoured by the Durham/Leeds workers the basis of which was discussed earlier (Chapter 2). The remainder of the ^{13}C NMR spectra shown, are fully consistent with this analysis. Comparing these spectra to the spectrum of the methylene region shown in figure 3.14 allows some detail concerning the tacticity of the polymer produced using initiator IV to be deduced. In figure 3.14, the presence of single peaks for the cc and ct/tc resonances at

38.37 and 37.82 ppm respectively, indicates that in this polymer the cc sequences and ct/tc sequences are predominantly of one tacticity each, however the third peak at 37.04 ppm associated with tt placements, is not sufficiently well resolved to provide any evidence concerning the extent of tacticity in tt sequences. Comparing the methylene region in figure 3.14 with spectrum iii) in figure 3.15, i.e. comparing the two polymers of a similar cis vinylene content, shows that there are more peaks in spectrum iii) than in figure 3.14 which indicates that the polymer produced using initiator IV is significantly more regular in structure than the sample produced with the mixed ligands whose spectrum is reproduced in figure 3.15(iii). In particular in the spectrum of the sample produced by initiation with IV, the cc mr signal is absent showing that all the cc placements are rr. Thus we can conclude that with initiator IV and the living chain end derived from it, when cis vinylene follows cis vinylene the monomers are incorporated in a syndiotactic sense, when cis follows trans or trans follows cis only one signal is seen and this placement is probably tactic but when trans follows trans we are unable to resolve tacticity effects. The fact that in all cis sequences we have only one tacticity is not surprising in view of Schrock's earlier observation of an all cis tactic polymer with the BINO bidentate ligand, see figure 3.2.

Finally, initiator III (Table 3.1) provided an opportunity to study the ROMP activity of an initiator which incorporated the novel boroalkoxide ligands. As a reminder, the structure of the initiator is shown in figure 3.16 overleaf.

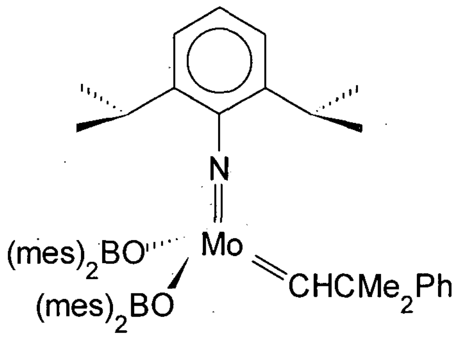

Figure 3.16. Schematic diagram of the four-coordinate boroalkoxide initiator.

As described previously, changing the electronic properties of the ancillary alkoxide ligands in these molybdenum four-coordinate initiators can have a dramatic effect on the microstructure of the resulting polymer. The use of a strong electron-withdrawing ligand such as the CF_3 moiety demonstrates this point and the effect this ligand has on the polymer microstructure has been discussed previously in this thesis. These earlier observations led to investigations being extended to the unusual class of alkoxide ligand, the so-called “quasi-alkoxides”, in which the metal bound oxygen has a Lewis-acidic diarylboron group attached. An initiating system was developed and synthesised incorporating the novel boroalkoxide ligand. The initiator was found to be active for the ROMP of 2,3-bis(trifluoromethyl)norbornadiene and the resulting polymer microstructure was analysed using ^{13}C NMR spectroscopy.

Analysis of the allylic carbon region for this polymer, using similar methods to those previously described revealed that this polymer contained 85% cis vinylenes. Information regarding the tacticity present in this polymer was obtained by analysing the C7 methylene region, illustrated in figure 3.17.

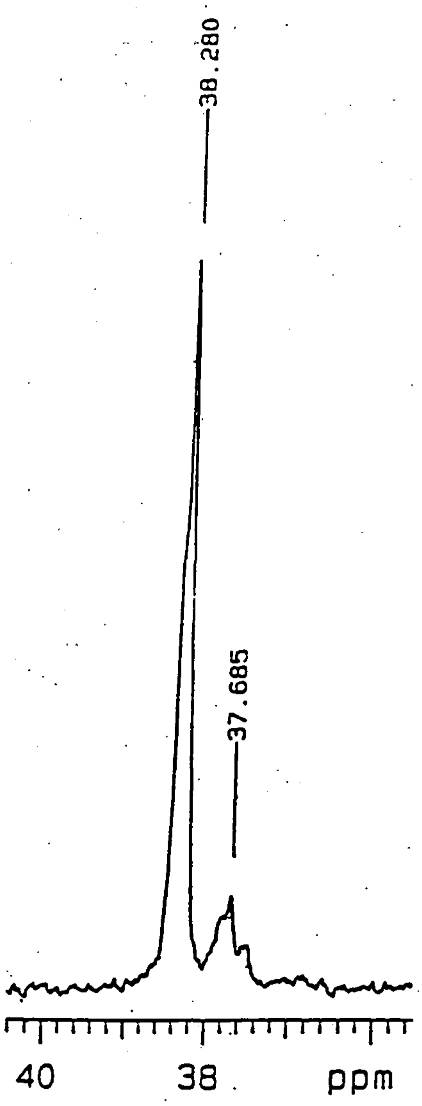

Figure 3.17. ^{13}C NMR spectrum of the C7 methylene region of the polymer made using initiator III.

Figure 3.17 shows the presence of two peaks in the methylene region of this polymer. By the same argument as before the peak of highest intensity at 38.28 ppm can be assigned to cc rr sequences in the polymer and the peaks of lower intensity centred at 37.69 ppm are probably due to tc/ct sequences. Significantly there is no peak at 37ppm which is where tt rr and tt mr signals are expected, which indicates that the trans vinylenes are predominantly found in ctc sequences and the multiplicity of the ct peak at 37.69 suggests the trans vinylenes are not stereoselectively placed. Thus, we can conclude that initiation with III gives a polymer which is 85% cis syndiotactic with the 15% of trans vinylenes being atactically incorporated predominantly in ctc sequences.

3.5. Conclusions.

The purpose of this chapter was to describe efforts directed towards improving the tacticity in poly(bis(trifluoromethyl)norbornadiene, specifically to obtain an all trans all syndiotactic polymer. At present, the best achievable is a high trans 92% syndiotactic material synthesised using the molybdenum hexa-t-butoxide initiator and an increase in the tacticity to approaching 100% could be of great interest both academically and perhaps more importantly be of commercial significance.[8] The studies were undertaken based on the knowledge that variations in the ancillary ligands around the metal centre can have a profound influence on the resulting polymer microstructure.[7] This chapter has described novel initiators which contain variations in both the alkoxide and arylimido ligands. The polymerisation studies have confirmed that changes in the surrounding ligand types do indeed affect the resulting polymer microstructure.

This work shows that the well-defined initiators III and IV give polymers in which cis-cis vinylene sequences are accompanied almost exclusively by stereoregular monomer incorporation, this is interesting, but since our main aim was to produce high tt rr microstructures, not useful. The ideas behind the development of these initiators could still be utilised in future studies and there still exists a vast range of opportunities for workers in this field. Possible future studies which could be conducted in this area will be outlined in Chapter 6 of this thesis.

3.6. References.

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Chapter 4

Studies directed to an examination of the limits of the well controlled synthesis of poly(bis(trifluoromethyl)norbornadiene).

4.1. Introduction.

The ring opening polymerisation of 2,3-bis(trifluoromethyl)norbornadiene initiated by well defined Schrock-type initiators is an example of a living polymerisation, see figure 4.1.

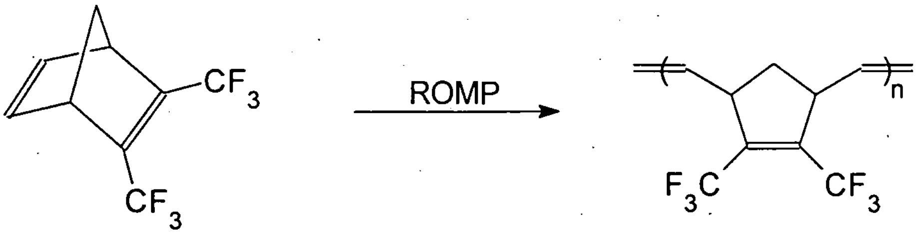


Figure 4.1. The ROMP of 2,3-bis(trifluoromethyl)norbornadiene.

In Chapter 1 of this thesis, some of the features of a living polymerisation were described.[1,2,3] Perhaps the most important is that concerning the number average molecular weight, M_n. In a well characterized living polymerisation a plot of M_n versus %-conversion is linear with the intercept passing through the origin. This implies that M_n can be controlled by the stoichiometry of the reaction. Furthermore in an ideal living polymerisation, the rate of initiation is greater than or of a similar magnitude to the rate of propagation meaning that relatively narrow molecular weight distributions are achievable.

The studies described in this Chapter were directed to the synthesis of a series of high trans, highly tactic poly(bis(trifluoromethyl)norbornadiene) samples and also a series of high cis, highly tactic samples. Using the criteria described previously, it was envisaged that a range of molecular weights of narrow molecular weight distribution should be achievable. One of the aims of this work was to see if molecular weights approaching one million were possible with this polymerisation method. Another aim was to provide samples for the further study of the properties of the high trans and high cis polymers and to see what effect, if any, the molecular weight had on the properties. Light scattering is being used to study the configurations of the trans and cis polymers in solution and work is still in progress using this technique. This work is conducted by Mr P.Almond, a graduate student at Leeds University, who is also working on molecular modelling of this polymer as a function of microstructure. The hope is that the modelling and light scattering measurements on the established high trans syndiotactic material will provide confidence in the predictive value of the modelling and that the experimental data for the high cis polymer will be fitted by the modelling in a way which resolves the debate about its microstructure.

The remainder of this Chapter describes the syntheses of the high trans and high cis poly(bis(trifluoromethyl)norbornadiene) samples and the range of molecular weights attained.

4.2. The synthesis of high trans poly(bis(trifluoromethyl)norbornadiene) samples.

This section describes attempts to synthesise samples of high trans poly(bis(trifluoromethyl)norbornadiene) of varying molecular weight. In Chapter 2 of this thesis the use of well-defined four coordinate molybdenum initiators in the ROM polymerisation of 2,3-bis(trifluoromethyl)norbornadiene[4,5,6] was discussed. It has been shown using the initiator, $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(OCMe_3)_2$, that poly(bis(trifluoromethyl)norbornadiene) can be obtained containing >99% trans vinylenes, a value confirmed by ^{13}C NMR spectroscopy, and furthermore dielectric and ^{13}C NMR spectroscopy measurements have confirmed that this polymer is 92% syndiotactic.[7,8] The polymerisation studies described in the next section are based on the use of this well-defined molybdenum initiator.

4.2.1. Experimental

a) General procedure and techniques.

All polymerisation experiments were performed in a conventional nitrogen-filled glove-box. The solvents used for the polymerisations were toluene and THF. Toluene was distilled from sodium wire and passed through a column of activated alumina prior to use. THF was stored over sodium benzophenone ketyl and vacuum transferred prior to use. Both solvents were deoxygenated immediately before use in the glovebox. The terminating agent used in these polymerisations was benzaldehyde, and this was purchased from the Aldrich chemical company. It was vacuum distilled and stored over molecular sieves, before being deoxygenated and used in the glove-box. The initiator, $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(OCMe_3)_2$ [5]and the monomer, 2,3-bis(trifluoromethyl)norbornadiene,[9] used in these experiments were prepared using the methods described in the literature.

b) Polymerisation procedure.

As discussed previously in this chapter, changing the stoichiometry of this polymerisation results in polymers of varying molecular weight being produced, i.e. by changing the monomer:initiator ratio it is possible to obtain different molecular weight polymers. Thus by using a higher number of monomer equivalents higher molecular weight polymers can be produced. The description which follows is the general procedure which was adopted in the synthesis of the range of molecular weight samples of high trans, highly tactic poly(bis(trifluoromethyl)norbronadiene). For the synthesis of a sample of a particular molecular weight, a specific monomer:initiator ratio was calculated and used.

Firstly, a solution of $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(OCMe_3)_2$ in toluene/THF (90:10 v/v ratio) was prepared. The volume of the solvent mixture used in the polymerisation depended on the stoichiometry of the reaction. The volume used was approximately 3-4 times more than the volume of monomer used. To this rapidly stirring initiator solution was added dropwise the monomer in toluene/THF solution. Usually one third of the monomer solution was added initially to consume all the initiator, after 30 minutes the remaining monomer solution was added dropwise. On addition of the monomer solution, the initiator solution changed from a pale yellow/brown to a deep cherry red, indicative of the formation of the propagating alkylidene species. The polymerisation mixture was stirred continuously for 19-20 hours, after which the reaction mixture had become extremely viscous and in some cases the formation of a gel occurred. The polymerisation was terminated by the addition of benzaldehyde (ten-fold excess with respect to the initiator) and stirred for a further 60 minutes. The product polymer was recovered by dissolving the viscous reaction product in the minimum amount of acetone (AR grade) and precipitating it by dropwise addition to a ten-fold excess of methanol. The polymer was purified by re-dissolving the crude product in acetone and re-precipitating it in methanol. The solid polymer was recovered by filtration and dried *in vacuo* to give a white fibrous material.

The product was analysed by gel permeation chromatography (GPC), using a Viscotek Differential Refractometer/Viscometer Model 200 (column packing PL_{gel} 10_{μ} mixed styrene-divinyl benzene beads, solvent: tetrahydrofuran), and ^{13}C, ^{19}F,^{1}H NMR spectroscopy to check that the polymer samples remained highly trans and highly tactic with variation in molecular weight, and also that they maintained a narrow molecular weight distribution. Table 4.1 overleaf, displays a list of the polymer samples prepared, and in each case high trans (>98%) polymers were obtained.

Table 4.1. Poly(bis(trifluoromethyl)norbornadiene samples prepared using $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(OCMe_3)_2$.

Sample number	**Amount (g)**	**Molecular weight (M_n) relative to polystyrene standards**	**Polydispersity index (PDI)**	**Theoretical molecular weight computed from monomer to initiator ratio**	$\frac{\mathbf{M_n(meas)}}{\mathbf{M_n(calc)}}$
1	2.21	100,900	1.31	52,300	1.9
2	1.79	337,100	1.35	144,000	2.3
3	1.92	245,300	1.08	257,000	0.95
4	2.65	92,200	1.01	47,600	1.9
5	2.54	271,100	1.01	151,200	1.8
6	2.62	75,100	1.08	53,100	1.4
7	3.47	147,700	1.16	136,700	1.1
8	1.23	283,500	1.59	141,000	2.0
9	3.25	203,200	1.27	133,900	1.5
10	1.67	87,400	1.06	61,700	1.4
11	3.58	202,900	1.06	123,900	1.6
12	2.13	321,600	1.08	116,100	2.7
13	3.02	218,300	1.05	164,100	1.3

Sample number	**Amount (g)**	**Molecular weight relative to polystyrene standards**	**Polydispersity index (PDI)**	**Theoretical molecular weight**	$\frac{M_n(\text{meas})}{M_n(\text{calc})}$
14	3.16	84,400	1.01	53,200	1.6
15	4.94	229,600	1.02	161,800	1.4
16	4.50	185,000	1.41	184,700	1.0
17	1.90	85,000	1.36	103,300	0.8
18	4.86	267,800	1.03	181,000	1.5
19	5.70	240,300	1.33	214,500	1.1
20	5.56	303,900	1.18	281,900	1.1
21	3.78	216,300	1.08	104,800	2.1
22	5.02	468,800	1.19	1,028,000	0.46
23	9.62	693,400	1.55	763,100	0.9
24	10.1	893,000	1.49	975,100	0.9

Table 4.1 (continued).

4.2.2. Results and discussion.

The data recorded in Table 4.1 illustrate that a wide range of molecular weights of high trans poly(bis(trifluoromethyl)norbornadiene) have been made. The range encompasses polystyrene equivalent number average molecular weights from under 100,000 to values approaching 900,000. All the samples were characterized using ^{1}H, ^{13}C, ^{19}F NMR spectroscopy which showed that the molecular weight of the polymer does not affect the trans vinylene content or tacticity of the polymer. A detailed discussion of the NMR spectrum of high trans poly(bis(trifluoromethyl)norbornadiene) has been given previously in this thesis (pp58,59 and 68-72), and examples of the spectra obtained for the range of high trans samples of different M_n are shown in Appendix 4.1.

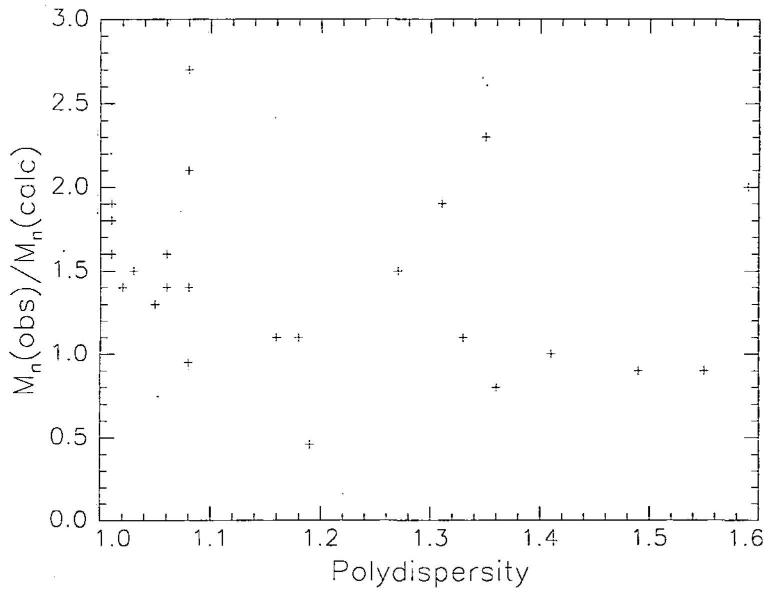
On examination of table 4.1, it can be observed that the majority of samples synthesised possess a relatively narrow molecular weight distribution, however, in some cases a higher polydispersity (>1.3/1.4) is produced. This broadening of molecular weight distribution has been reported previously for systems using fluorinated monomers[10] and can be due to the presence of trace amounts of dioxygen introduced at the termination stage of the polymerisation. A bimolecular termination reaction occurs involving dioxygen and the propagating alkylidene species and results in a dimerization of the living chain ends producing a higher molecular weight impurity, which usually occurs at twice the molecular weight of the major product. If there was a slight leakage of oxygen into the polymerisation vessel this process may occur throughout the polymerisation giving a broadened molecular weight distribution.

This phenomenon highlights the care which must be taken in ensuring that the monomer is fully deoxygenated prior to its use in ROMP reactions and that reaction conditions are carefully regulated. Indeed during the syntheses of the range of molecular weight samples, it became apparent that certain experimental criteria had to be addressed, in order to ensure a well-behaved, living polymerisation took place.

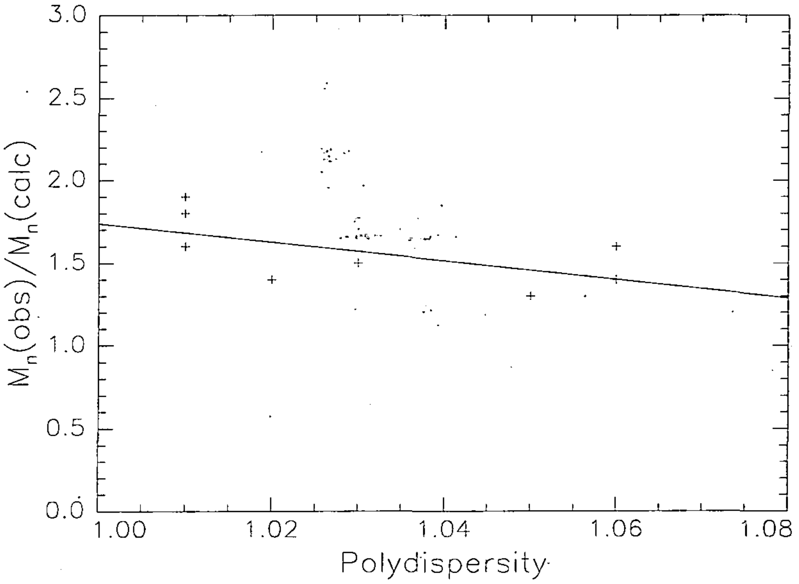
The high purity of the monomer was crucial. Sometimes, during the monomer preparation, small traces of cyclopentadiene were present and this acts as a poison towards the initiator, effectively "killing" the polymerisation, so the monomer had to be carefully re-distilled to ensure its removal. Monomer concentration also proved to be important, it was found that if too much solvent was used in the polymerisation in an attempt to keep the solution viscosity low, then no propagation occurred. In some cases, the monomer was used with no solvent added to produce a high enough concentration for initiation by the active alkylidene species to take place. These considerations became very important when high monomer:initiator ratios were employed and when very small quantities of initiator were used.

As discussed in the introduction of this Chapter, one of the aims of this study was to produce a high trans poly(bis(trifluoromethyl)norbornadiene) sample of a molecular weight approaching one million, and attempts to achieve this have been fairly successful with a polystyrene equivalent molecular weight around 900,000 produced.

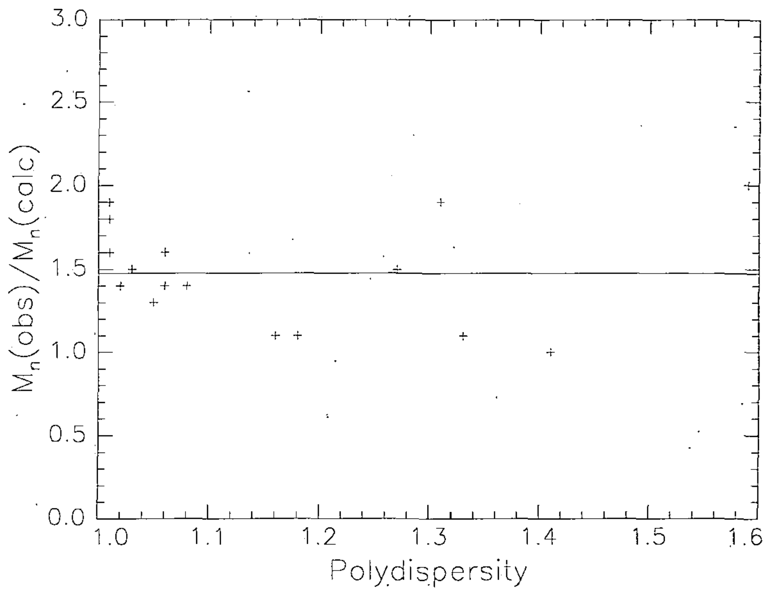
However, the reliability of the data shown in table 4.1 has to be critically examined. In polymerisations of this type where $I + nM \rightarrow IM_n$, I and M representing the initiator and monomer respectively, a "perfect" result requires that a constant value is obtained for the ratio M_n (observed) / M_n (calculated) and that the polydispersity approaches 1. On examination of table 4.1 it can be seen that these two requirements are not met in every case. In some cases a low polydispersity for a polymer sample is obtained but the ratio of the observed molecular weights to the calculated molecular weights is not a constant value. In an ideal polymerisation, a plot of the polydispersity versus M_n (observed) / M_n (calculated) should be linear and parallel to the polydispersity axis, that is the polydispersity should not vary with M_n. The graphs which follow are plots of these two variables using the data in table 4.1.



Graph 4.1. A plot of M_n (observed)/M_n (calculated) versus PDI for all the polymer samples listed in table 4.1.



Graph 4.2. A plot of M_n (observed)/M_n (calculated) versus PDI for the polymer samples having a PDI less than 1.08.



Graph 4.3. A plot of M_n (observed)/M_n (calculated) versus PDI for the polymer samples having a M_n (obs)/M_n (calc) ratio between 1.0 and 2.0.

In graph 4.1, where the data for all the polymer samples are plotted, a high degree of scatter occurs and there is no apparent correlation between the PDI of the polymer and the M_n (obs)/M_n (calc) ratio. In graph 4.2, only those samples possessing a PDI less than 1.08 have been plotted. The reason for this was to see if those samples possessing a low PDI necessarily had a constant M_n (obs)/M_n (calc) ratio as expected for a well behaved system. Graph 4.3 only considers those samples having a M_n(obs)/M_n (calc) ratio between 1.0 and 2.0, which is fairly close to the average value for the low PDI samples plotted in graph 4.2, (1.74). Graphs 4.2 and 4.3 show that more correlation exists between the two variables when only the values approaching the "optimum" are considered as compared to graph 4.1 where higher polydispersities and higher M_n (obs)/M_n (calc) ratios result in very little correlation.

The respective correlation coefficients of the data plotted in graphs 4.2 and 4.3 are also interesting to note; the correlation coefficient of the data in graph 4.2 is 0.61 compared to a value of 0.002 for the data in graph 4.3. The correlation coefficient shows the extent to which a set of data support a linear relationship, it is a number somewhere between -1 and +1. If the value for the correlation coefficient is close to +1 or -1, then the data lie close to some straight line; if the value is close to zero, then the data are uncorrelated with little or no tendency to lie on a straight line. This suggests that in deciding which data for samples from table 4.1 are reliable, M_n(obs)/M_n (calc) ratios approaching a constant value of 1.48 (Graph 4.3), provide a less accurate prediction than using low polydispersities (Graph 4.2) as the sole criterion. Furthermore the observed molecular weights of those samples possessing both low polydispersities (<1.08) and M_n (obs)/M_n (calc) ratios close to the average value of 1.48 may be trusted, with some degree of confidence, to be the most reliable.

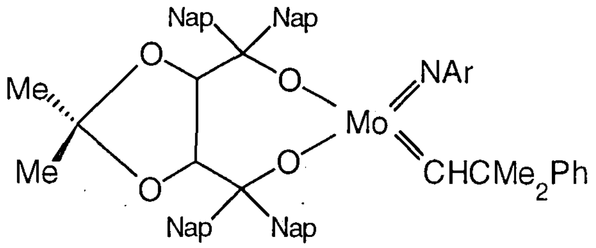
The discrepancies between the observed and calculated molecular weights of the high trans samples reported in table 4.1 highlight the highly delicate nature of this polymerisation particularly on the scale of reaction used in this work. Certain experimental criteria which need to be observed to ensure a well-behaved living polymerisation have been discussed previously. Because of the small amounts of initiator used in these experiments (<8mg) there is much scope for experimental error. On such a small scale, the weighing of the material is subject to an error due to the limits of accuracy inherent in using a balance in the glove box, and the discrepancies observed may be partly due to this. Other reasons for the discrepancies may include the method of stirring and efficiency of mixing; sometimes the size of the stirrer bar used in the reaction vessel had an effect on the time taken for the reaction mixture to become viscous and this may influence the subsequent molecular weights and polydispersities observed.

4.3. The synthesis of high cis poly(bis(trifluoromethyl)norbornadiene) samples.

4.3.1. Introduction.

The synthesis of the high trans samples of this polymer has previously been discussed in section 4.2, using the molybdenum t-butoxide initiator. The fluorinated analogue of this initiator, i.e. $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(OCMe(CF_3)_2)_2$, has also been described in earlier Chapters of this thesis, and polymerises 2,3-bis(trifluoromethyl)norbornadiene to produce a polymer containing >98% cis vinylenes and a tacticity of 75%.[11,12]

In these studies of the properties of high trans and high cis poly(bis(trifluoromethyl)norbornenes), it was necessary to have highly tactic samples of each. The high trans samples prepared using the molybdenum t-butoxide initiator are highly tactic (92% syndiotactic) but the polymer produced using the hexafluoro-t-butoxide initiator does not possess a high enough tacticity. Therefore, for the purpose of these studies, an alternative initiator was used. The one chosen is shown in figure 4.2.



{Where Ar = 2,6-Pr^i_2-C_6H_3 and Nap = Naphthyl }

Figure 4.2. The initiator prepared by Schrock, producing high cis, highly tactic poly(bis(trifluoromethyl)norbornene)

The initiator shown in figure 4.2 was synthesised by Schrock and co-workers,[13] and was reported to polymerise 2,3-bis(trifluoromethyl)norbornadiene to give a polymer containing 97% cis vinylenes and 97% tacticity (it is not known with certainty whether the polymer is syndiotactic or isotactic). The improvement of tacticity in the polymer obtained using this initiator as compared to the molybdenum hexafluoro-t-butoxide initiator can be illustrated by comparing the respective C7 methylene regions of the polymers produced, as shown in figure 4.3.[13] The C7 methylene region of the polymer produced by the hexafluoro-t-butoxide initiator has been discussed previously in this thesis, (see pp69-71), and in figure 4.3 it can be clearly seen that it possesses a more complicated C7 region than the Mo($CHCMe_2Ph$)(NAr)((+)-Nap_4tart) initiator. This is because in the 97% tactic polymer, there are more ring dyad environments of the same configuration giving rise to a simple ^{13}C NMR spectrum with predominantly a single narrow line, whereas in the 75% tactic polymer there are more ring dyad environments having different configurations and the distribution of environments gives rise to two broadened lines in the ^{13}C NMR spectrum.

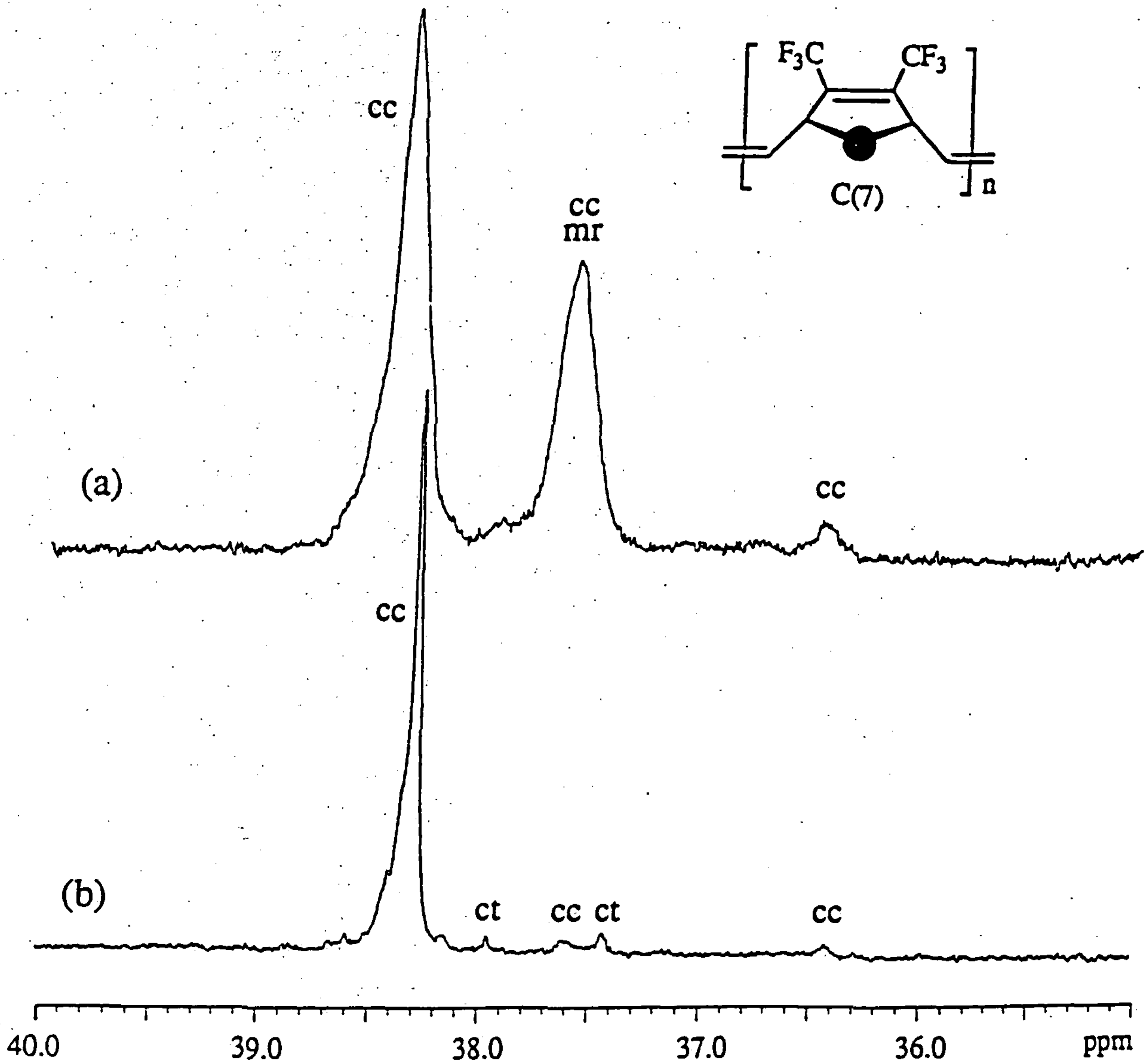


Figure 4.3. The C7 methylene region of poly(bis(trifluoromethyl)norbornadiene) prepared by a) $Mo(CHCMe_2Ph)(NAr)(OCMe(CF_3)_2)_2$ b) $Mo(CHCMe_2Ph)(NAr)((+)$-$Nap_4tart)$.

4.3.2. Experimental

The general polymerisation procedure for the preparation of high cis, high tactic poly(bis(trifluoromethyl)norbornadiene) samples was similar to that adopted for the synthesis of the high trans samples described previously, with all manipulations being performed in a glove-box. To a rapidly stirring solution of $Mo(CHCMe_2Ph)(NAr)((+)-Nap_4tart)$ in toluene/THF (90:10 v/v ratio) (3-4 times more volume than that of the monomer), was added one third of the 2,3-bis(trifluoromethyl)norbornadiene, toluene/ THF (90:10 ratio) solution (concentration ranging from $329gl^{-1}$ - $601gl^{-1}$). After 30 minutes, the remaining monomer solution was added dropwise. After 20 minutes, the contents of the flask had become very viscous and more toluene/THF solution was added in an attempt to keep the solution homogeneous. The reaction mixture was left stirring for 12 hours, and the polymerisation was terminated by the addition of benzaldehyde (ten-fold excess with respect to the initiator) and stirred for a further 60 minutes. The product polymer was recovered by dissolving the viscous reaction product in a minimum amount of acetone (AR grade) and precipitating the polymer by dropwise addition to a ten-fold excess of hexane. It was purified by re-dissolving the crude product in acetone and re-precipitating in hexane. The product was recovered by filtration and the isolated product dried *in vacuo* to give a white fibrous material. Characterisation of the polymer was performed using ^1H, ^{13}C, ^{19}F NMR spectroscopy. Examples of the spectra produced from samples of the high cis, highly tactic polymers are shown in Appendix 4.2.

4.3.3. Results and discussion.

As was the case with the syntheses of the high trans samples of poly(bis(trifluoromethyl)norbornadiene), various initiator:monomer ratios were used in order to produce polymer samples of varying molecular weight, the results are listed in Table 4.2. However, one of the major drawbacks of using this particular initiating system is that the resulting polymer is rather insoluble and tends to precipitate as it forms,[13] the reaction mixture becomes very viscous and this makes the maintenance of an homogeneous solution extremely difficult. Various solvent systems were tried including dichloromethane, dimethoxyethane and toluene/THF (described in section 4.3.2) and in each case the polymer precipitated as it formed. The lack of solubility displayed by this polymer prevented the determination of molecular weight and polydispersity by GPC. However, the polymer is soluble in acetone and this allowed alternative methods of obtaining some measure of the molecular weight to be employed. The techniques of capillary viscometry and light scattering were chosen to investigate the molecular weight and dimensions in solution and work is in progress using these methods.[14]

Table 4.2. Poly(bis(trifluoromethyl)norbornadiene) samples prepared using the initiator; Mo(CHCMe$_2$Ph)(NAr)((+)-Nap$_4$tart).

Sample number	**Amount (g)**	**^{13}C NMR data**	**Theoretical molecular weight.**
1	0.91	>98% cis	160,000
2	3.62	>98% cis	390,000

Sample number	Amount (g)	^{13}C NMR data	Theoretical molecular weight
3	1.87	>98% cis	300,000
4	1.10	>98% cis	210,000
5	0.49	>98% cis	280,000
6	2.30	>98 % cis	520,000
7	3.20	> 98% cis	630,000

Table 4.2 (continued).

Table 4.2 shows the range of high cis, highly tactic poly((bistrifluoromethyl)norbornadiene) samples produced. The theoretical molecular weights are calculated on the basis of the initiator:monomer ratios used in each sample preparation. These samples proved significantly more difficult to prepare than the high trans polymers. Their continued investigation is in progress by other workers in the IRC. The reasons for making these samples were outlined in the introduction but the outcome of this study is not available at the time of writing.

4.4. Summary.

In this Chapter the syntheses of a range of high trans and high cis, highly tactic samples of poly(bis(trifluoromethyl)norbornadienes) has been described. It has been shown that by varying the initiator:monomer ratio, a range of different molecular weights can be attained, and furthermore in the majority of cases, narrow molecular weight distributions are obtained. The work reported in this chapter was undertaken to provide samples for study by other workers in the IRC as described earlier. It was also an experimental test of the applicability of living ROMP to the synthesis of well defined high molecular weight samples of polymers. Most earlier work on living ROMP has addressed the mechanism of polymerisation and has concentrated on spectroscopic studies at low monomer:initiator ratios. In the earlier literature of this field it is common to read of 10:1 and 20:1 monomer:initiator ratios and examples of 200 to 400:1 represent typical "high molecular weight" syntheses. In this work the author has established that ratios of ca. 4000:1 can be effectively used to make truely high molecular weight polymers but that the technique is experimentally very demanding. The experimental problems in this case were accentuated by the scale of the work, for example in the syntheses of highest molecular weight samples the amount of initiator used was as low as 5mg, and handling air and moisture sensitive transition metal complexes safely and precisely on this scale represents a challenge to the worker's skill. As an example, of the discrepancies that can occur in the resulting molecular weights of the high trans polymer samples as a consequence of an error (±0.5mg) in the weighing of small quantities of initiator in the glove box, consider two "perfect" polymerisations where 10g of monomer is added to 5mg and 4.5mg of initiator. The resulting calculated molecular weights of the polymer samples are 980,000 and 1,086,000 respectively, thus a difference of 0.5mg of initiator being used produces a variance of 106,000 in the molecular weights of the polymers; this clearly illustrates the extremely delicate nature of this polymerisation. The results presented here demonstrate that it can be done but the author acknowledges that the reliability of some of the molecular weights reported for the high trans samples may be open to question and that discrepancies do occur between the observed and calculated molecular weights.

4.5. References.

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Chapter 5

Experiments concerning the ROMP of fluorinated monomers containing six membered rings.

5.1. Introduction.

This chapter describes attempts to effect the ROMP of certain fluorinated monomers in which the double bond is located in a six membered ring. In Chapter 1 of this thesis, the thermodynamics of ROMP reactions[1] were discussed. The most important factor governing the probability that a particular compound will polymerise is the change in Gibb's free energy on polymerisation, ΔG. This parameter is linked to the enthalpy and entropy changes by the well-known equation,

$$\Delta G = \Delta H - T\Delta S.$$

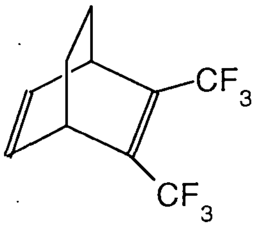
A negative value of ΔG indicates that the polymerisation is thermodynamically favourable and likely to occur providing a suitable mechanism exists. The entropy change, ΔS, on polymerisation is always negative and this fact gives rise to the phenomenon known as the Ceiling Temperature,[2] which can be regarded as the point where the entropic and enthalpic contributions to ΔG are in balance and above which no polymer forms. Most cycloalkenes may undergo ROMP since, in most cases, ΔG for ring opening is negative at normally used reaction temperatures. Ring strain is present in small rings, of three, four and five members, and also in larger rings of seven members and more. Only cyclohexene, which has a low strain energy, has a positive value for its ΔG of polymerisation, meaning it will not undergo ring opening. However, the balance is fine and if some strain is introduced into the six membered ring, the situation might be modified sufficiently to allow such monomers to undergo ROMP. Figure 5.1, shows two such examples.

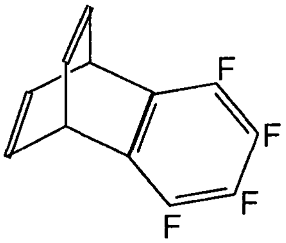
Bicyclo[2.2.2]oct-2-ene Norbornene

Figure 5.1. Examples of increased ring strain in six membered rings.

There are reports in the literature of the ROMP of bicyclo[2.2.2]oct-2-ene,[3,4] and here the cyclohexene ring is forced to adopt a slightly strained conformation due to the restriction placed upon it by the 1,4-ethylene bridge. Further strain can be introduced by placing a 1,4-methylene bridge on the cyclohexene as is the case with norbornene, one of the most reactive ROMP monomers.

In this Chapter, attempts to ring open the monomers shown below will be described.





It was hoped that sufficient ring strain would be present in these monomers to allow ring opening to occur, and the fluorinated polymers produced may well be of interest, in particular their dehydrogenation products would be novel poly(arylene vinylene)s of potential value as emitting layers for polymer based LEDs.

5.2. The ring opening metathesis polymerisation of 2,3-bis(trifluoromethyl)-bicyclo[2.2.2]octa-2,5-diene.

5.2.1. Introduction.

In contrast to bicyclo[2.2.1]heptenes and -heptadienes, few examples of the ROMP of bicyclo[2.2.2]octenes or -octadienes have been reported [3,4] although the strain energies of the two ring systems (16.0 and 20.4 Kcal/mol respectively)[5] are significantly greater than cyclopentene (6.9 Kcal/mol), which is known to successfully undergo ROMP. The lack of easy synthetic routes to simple bicyclo[2.2.2]octenes and-octadienes, as compared to the range of norbornenes and norbornadienes readily available via Diels-Alder reactions of cyclopentadiene, which is cheap and readily accessible has hindered their study as potential monomers for ROMP reactions.

ROMP studies have previously been conducted on a wide range of fluorinated norbornenes and norbornadienes[6,7] and in particular, 2,3-bis(trifluoromethyl)norbornadiene has received a lot of attention due to the potential of its all trans syndiotactic polymer for use in pyroelectric and piezoelectric devices.[8] The aim of this section of work was to extend these studies by investigating the polymerisability of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene, the reaction scheme is shown in figure 5.2 in conjunction with the scheme for the ring opening of 2,3-bis(trifluoromethyl)norbornadiene. Investigations directed to the ring opening of the bicyclooctadiene monomer are discussed in the subsequent sections.

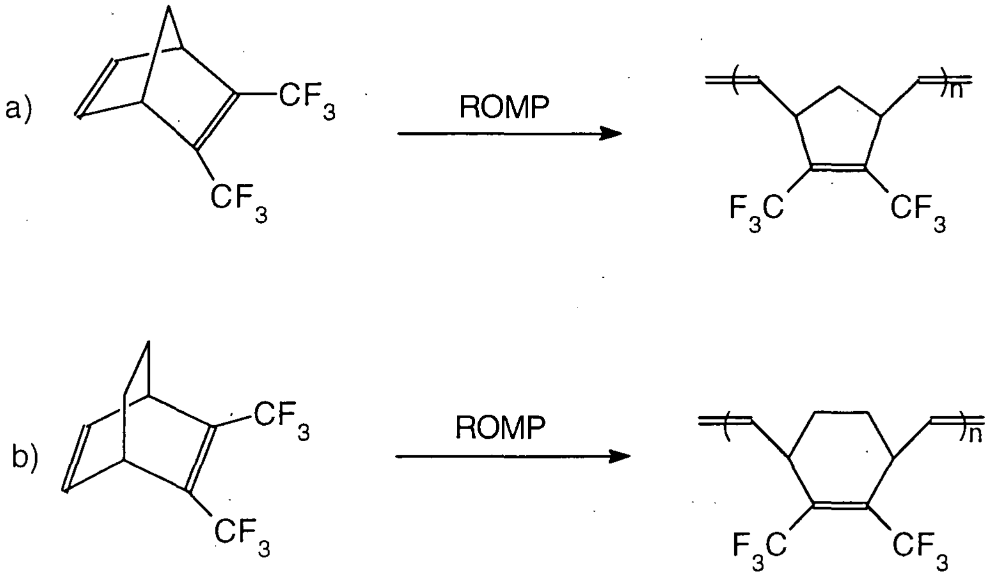


Figure 5.2. Reaction schemes for the ROMP of a) 2,3-bis(trifluoromethyl)norbornadiene, b) 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene.

5.2.2 Experimental.

5.2.2.1 Synthesis of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene.

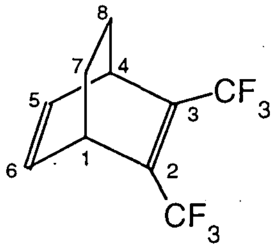
The preparation of this monomer was similar to that described in the literature.[9]

Firstly a hard glass Carius tube (16mm outside diameter, wall thickness 2.5mm) fitted with a Youngs tap and S19 joint was connected to a vacuum line. 1,3-Cyclohexadiene (3.49g, 0.044mole) was pipetted into the tube via the tap and hydroquinone (0.15g, 0.0014mole) was added.

The contents of the Carius tube were then purged with nitrogen and degassed using the 'freeze-thaw' method. After the degassing process, the Carius tube was charged with hexafluorobut-2-yne (7.05g, 0.044mole) by vacuum transfer. Once the Carius tube had been charged with the reagents it was sealed under vacuum (ca. 10^{-3}mmHg). The tube was placed in a thick metal sleeve and heated in a furnace at 80^{0}C for 6 hours.

On removal from the furnace, the reaction solution was pale-yellow with a white precipitate also present, the tube was opened using the 'hot-spotting' technique and the volatile products were recovered by vacuum transfer. The yellowish product which remained in the Carius tube was distilled to give 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene, boiling range 52-54^{0}C @ 20mm Hg, (5.93g, 56% yield).

Prior to the polymerisation studies, the monomer was dried over phosphorus (V) oxide for 12 hours, then vacuum transferred and degassed immediately before use in the glove box. The spectroscopic characterisation data are listed and are consistent with the assigned structure and in agreement with the literature.[9] The spectra are reproduced in Appendix 5.1.



^{1}H NMR data (400MHz, $CDCl_3$, 298K)

1.46 (t), 4H, (methylene), 4.06 (s, broad), 2H, (bridgehead), 6.40 (sextet), 2H, (olefinic), chemical shifts in ppm, reference to TMS, (see Appendix 5.1a).

^{19}F NMR data (376.29MHz, $CDCl_3$, 298K)

61.14(s), **CF_3**, chemical shift in ppm, reference to $CFCl_3$, (see Appendix 5.1b).

^{13}C NMR data (100.57MHz, $CDCl_3$, 298K)

(see the above monomer structure for numbering system of carbon atoms)

24.17, C7 and C8, 37.63, C1 and C4, 121.67 (q, J = 272 Hz, CF_3), 133.51, C5 and C6, 138.98, C2 and C3, chemical shifts in ppm, reference to TMS, (see Appendix 5.1c).

Infra-red data (cm^{-1})

3071.2 (m), 2956.6 (s), 2920.9 (s) (C-H stretch), 1676.8 (s), (substituted double bond stretch), 1400-1000 (s), (C-F stretch), 756.0 (m), (=CH-, out of plane bend). (see Appendix 5.1d).

5.2.2.2 Attempted polymerisation of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene using Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$

To a rapidly stirring solution of Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (0.01g, 0.0131mmole) in CDCl$_3$ (350μl) was added dropwise a solution of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene (0.063g, 0.261 mmole, 20 equivalents) in CDCl$_3$ (350μl). (Before the addition to the initiating solution, the monomer was passed through a column of activated alumina).

The reaction solution was allowed to stir for 15 minutes, after which no discernible colour change could be observed. The reaction was monitored by ^{1}H NMR spectroscopy, (see table 5.1 later and Appendix 5.2).

5.2.2.3 Attempted polymerisation of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene using W(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$

A solution of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene (0.130g, 0.537 mmole, 22 equivalents) in CDCl$_3$ (350μl) was added dropwise to a rapidly stirring solution of W(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$ (0.014g, 0.0244 mmole) in CDCl$_3$ (350μl). The reaction mixture was stirred continuously for a further 15 minutes, after which no noticeable colour change was observed. The reaction was analysed by ^{1}H NMR spectroscopy, (see table 5.2 later and Appendix 5.3).

5.2.2.4 Attempted polymerisation of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene using Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$

To a rapidly stirring solution of Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$ (0.0127g, 0.026 mmole) in CDCl$_3$ (350μl) was added dropwise a solution of 2,3-

bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene (0.130g, 0.537 mmole) in $CDCl_3$ (350μl). The reaction mixture was stirred for 15 minutes, and no noticeable colour change could be detected. After this time, the reaction solution was injected into an NMR tube and the reaction monitored by ^1H NMR spectroscopy, (see Appendix 5.4).

5.2.2.5 Attempted polymerisation of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene using the classical initiating system: WCl_6/Me_4Sn.

In this reaction, a catalyst:co-catalyst:monomer ratio of 1:2:100 was used. Firstly the stock solution of WCl_6 in chlorobenzene was prepared in the glove box. WCl_6 (0.2466g, 0.622 mmole) was dissolved in chlorobenzene (16ml) and stirred in an ampoule for 24 hours in order to ensure all the WCl_6 was in solution.

The polymerisation was performed as follows: In the glove-box, a solution of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene (2g, 8.3mmole) in chlorobenzene (10ml) was injected into an ampoule fitted with a Youngs tap and suba seal. The ampoule was removed from the glove-box and connected to a standard vacuum line, where it was maintained under an atmosphere of nitrogen. A small ampoule containing a magnetic stirrer and fitted with a suba seal was purged with nitrogen for several minutes. Into this ampoule, was placed WCl_6/chlorobenzene stock solution (2.1ml, 0.083mmole) and $(CH_3)_4Sn$ (13μl, 0.166mmole) and the mixture was stirred for 15 minutes, during this time the solution changed from a blue/black colour to a deep red/brown colour as the active species was formed.

After 15 minutes, using an air tight syringe, the catalyst solution was injected into the stirred monomer solution, and the reaction mixture was stirred. After 1 hour, the reaction was terminated by the addition of acetone (5ml) and the reaction solution was added to a ten-fold excess of stirring hexane under nitrogen. No polymer precipitated in the hexane, so a different non-solvent, methanol, was tried but no polymer precipitated from this either. The polymerisation was repeated employing different reaction times and conditions, (see table 5.3 later).

5.2.2.6 The reaction between 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene and Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$, followed by the addition of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene.

To a rapidly stirring solution of Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (0.01g, 0.014mmole) in CDCl$_3$ (350μl) was added dropwise a solution of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene (0.0688g, 0.284mmole) in CDCl$_3$ (350μl). The reaction mixture was stirred for 15 minutes, and then injected into an NMR tube. A ^{1}H NMR spectrum was recorded after 24 hours (at room temperature) and also after 1 week (reaction mixture heated at 65^{0}C).

After 1 week, the reaction mixture was returned to the glove-box and the solution was poured into a sample vial and allowed to stir. To this solution, 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (0.160g, 0.7mmole) was added dropwise. Within a few minutes the reaction contents became very viscous and turned into a solid gel after 5 minutes suggesting polymer formation. Toluene (5ml) was added to try and keep the reaction mixture homogeneous, and the reaction was stirred for a further 60 minutes. After this time, the reaction was capped with benzaldehyde (0.14mmole, 0.148g, ten-fold excess with respect to initiator) and stirred for 30 minutes. The product polymer was recovered by dissolving the viscous reaction product in a minimum amount of acetone and precipitating it by dropwise addition to ten-fold excess of methanol. The solid polymer was recovered by filtration and dried *in vacuo* to give a white fibrous material, (0.033g, 50% yield). The product polymer was analysed by ^{13}C NMR spectroscopy and the analysis was consistent with the formation of high cis poly(bis(trifluoromethyl)norbornadiene). The spectroscopic data are shown below; the spectrum observed was similar to that shown in figure 2.6b, in Chapter 2 of this thesis.

^{13}C NMR data (100.58MHz, $(CD_3)_2CO$, 298K).

140.36 (multiplet), (olefinic), 131.82 (s,broad), (vinylic), 121.93, (q, J = 272 Hz, CF_3), 50.86 (s) and 44.81 (s,broad), (allylic), 38.33 (s) and 37.55 (s), (methylene), chemical shifts in ppm, reference to TMS.

5.2.3. Results and discussion.

The ring opening metathesis polymerisation of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene has been attempted using several different initiating systems, described previously in section 5.2.2. On each occasion, the polymerisation proved unsuccessful. These were disappointing results, as it was envisaged at the beginning of the studies on this monomer system, that the ROMP studies previously conducted on the range of fluorinated norbornenes and norbornadienes[6,7] described earlier in this thesis, could be reasonably extended to include the equivalent fluorinated bicyclo-octadiene compounds. However, this notion has not been realised.

The first initiating systems to be tried in the attempted polymerisation of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene were the well-defined molybdenum initiators; $Mo(CHCMe_2Ph)(NAr)(OCMe_3)_2$ and $Mo(CHCMe_2Ph)(NAr)(OCMe(CF_3)_2)_2$.[10] Both polymerisations were attempted on an NMR-tube scale, at room temperature and also at elevated temperatures for periods up to one week, however no signs of a polymerisation occurring could be observed in any case. Table 5.1 shows the ^{1}H NMR data for the polymerisation attempts using the hexafluoro-t-butoxide molybdenum initiator and in each attempt the only peaks observed were those of the initiating alkylidene and the monomer providing evidence that essentially no polymerisation had occurred.

Table 5.1. ^{1}<u>H NMR data</u> (400MHz, $CDCl_3$, 298K) for the attempted polymerisation of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene using the initiator $Mo(N\text{-}2,6\text{-}Pr^i{}_2\text{-}C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$.

Reaction time	Temperature (^{0}C)	Peak assignment (ppm)
1 hour	25	12.183 (s); Mo=C**H**CMe$_2$Ph 1.52 (t), 4H, (methylene) 4.14 (s,broad), 2H, (bridgehead) 6.42 (sextet), 2H, (olefinic)
24 hours	25	same as after 1 hour
7 days	25	same as after 1 hour
7 days	heated at 50 for 3 hours	same as after 1 hour

The next initiator to be tried was the tungsten analogue of the molybdenum t-butoxide complex, W(CHCMe$_3$)(NAr)(OCMe$_3$).[11] In Chapter 1 of this thesis, it was remarked that four-coordinate tungsten alkylidene complexes are generally more reactive than the equivalent molybdenum complexes,[12] on account of differences in the electronegative character of the two metal centres. Thus, it was envisaged that this more reactive initiator might be able to ring open 2,3-bis(trifluoromethyl)bicyclo-[2.2.2]octa-2,5-diene. Polymerisation attempts were conducted on an NMR-tube scale, at room temperature and at elevated temperatures. However, analysis of the resulting ^{1}H NMR spectra showed that ring opening of the monomer had not occurred, and table 5.2 shows the ^{1}H NMR data for each attempt, the peaks present being due to the initiating alkylidene and the monomer.

Table 5.2. ^{1}H NMR data (400MHz, CDCl$_3$, 298K) for the attempted polymerisation of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene using the initiator W(N-2,6-Pr$^i_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$.

Reaction time	Temperature (^{0}C)	Peak assignment (ppm)
2 hours	25	7.97 (s), WC**H**CMe$_3$ 1.46 (t), 4H, (methylene) 4.08 (s,broad), 2H, (bridgehead) 6.42 (sextet), 2H, (olefinic)
2.5 days	25	same as after 2 hours
6 hours	45	same as after 2 hours

Due to the failure of the well-defined initiators described previously, to bring about the ring opening of this monomer, attention was turned to the use of classical initiating systems based on WCl_6 and Me_4Sn. These classical systems are well known for being more reactive than the well-defined systems. It was thought that this highly reactive system, whilst not producing a high degree of stereoregulation in the polymer, might at least be able to effect ring opening of the monomer. Unfortunately, this initiating system also proved to be unsuccessful in the pursuit of the ring opened polymer of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene, despite varying the temperature and duration of the reaction. Table 5.3 summarises the polymerisation studies performed on this monomer using the classical initiating system based on WCl_6/Me_4Sn.

Table 5.3. Summary of the attempted polymerisation studies performed on 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene using the initiating system, WCl_6/Me_4Sn.

Reaction scale	Reaction time	Temperature (^0C)	Polymerisaton results
1:2:100 ratio 1g monomer	24 hours	25	no reaction
1:2:100 ratio 2g monomer	5 days	25	no reaction
1:2:100 ratio 3g monomer	3 hours	65	no reaction

As a check to make sure the initiator being used in these reactions was still living i.e. it does not decompose on the time scale of the reaction and thus cause the lack of polymerisability shown by this monomer, an NMR-tube scale reaction was performed using the molybdenum hexafluoro-t-butoxide initiator. To this initiator solution, was added a solution of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene and the reaction left for one week at 65^{0}C. To check that the initiator was still living, a solution of 2,3-bis(trifluoromethyl)norbornadiene was added to the reaction mixture. If the initiator was still living, then poly(bis(trifluoromethyl)norbornadiene) would be expected to be produced, and this did in fact occur, proving that the lack of polymerisability shown by 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene was not due to initiator decomposition on the time scale of the attempted reaction.

In summary, a range of initiating systems have been employed in an attempt to effect the ring opening of this fluorinated octadiene monomer. However, on each occasion these attempts have proven unsuccessful, no evidence of a polymerisation occurring was evident.

5.3. The ring opening metathesis polymerisation of 2,3-(tetrafluorobenzo)-bicyclo[2.2.2]octatriene.

5.3.1. Introduction.

The retention of unsaturation in the polymer backbone is one of the useful features of metathesis polymerisation that favours its use as a route to new conjugated polymers. Poly(p-phenylenevinylene), PPV, is one of these relatively new conjugated polymeric materials attracting a great deal of interest on account of its suitability as the emitting layer in light emitting diodes (LEDs). In Chapter 1 of this thesis the basic principles underpinning the operation of these devices was described.[13,14,15] One of the problems associated with PPV is that its extended planar topology renders it infusible and insoluble in a wide range of common solvents, whilst this gives the polymer excellent mechanical and thermal properties with good stability up to 400^0C, it limits the possibilities for post-synthesis fabrication of the material.

Various routes have been devised which make use of a suitable precursor polymer which is subsequently converted into the desired PPV material. One of the most commonly used is the sulphonium precursor which is conveniently processed from solution in methanol, and is converted to PPV by thermal treatment at temperatures ranging from 200^0C-300^0C,[16,17] figure 5.3. In this polymerisation, the sulphonium precursor is a very reactive intermediate and as a consequence of this, certain aspects of the resulting polymer structure are difficult to control such as the degree of polymerisation and polydispersity.

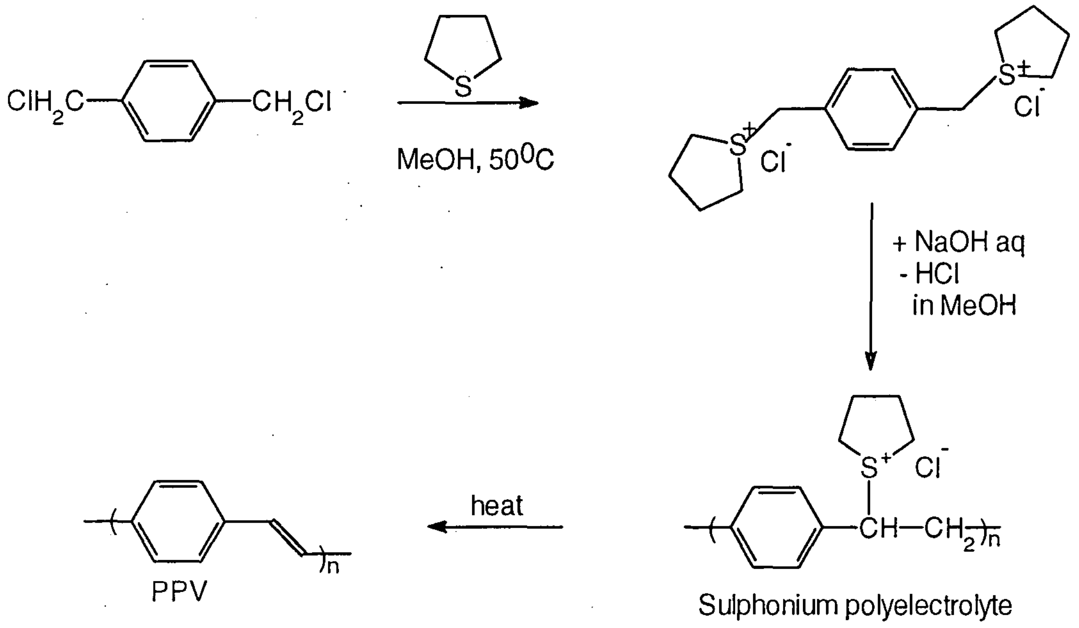


Figure 5.3. Sulphonium precursor route to PPV.

Recently, Grubbs and co-workers have described an alternative precursor synthesis of PPV based on the *living* ROMP of carboxylic ester derivatives of bicyclo[2.2.2]octadienes, see figure 5.4 overleaf.[18] The ROMP of the bis(carboxylic ester) derivative of bicyclo[2.2.2]octadiene was achieved by using Mo(CHCMe$_2$Ph)-(N-2,6-Pr$^i_2$-C$_6$H$_3$)(OCMe$_2$CF$_3$)$_2$ as initiator, to yield the precursor polymer which contained approximately equal proportions of cis and trans vinylenes. Thermal treatment (200^{0}C) of this precursor polymer yielded a free-standing film of PPV containing all trans vinylenes. This method highlights the advantages of using living ROMP reactions, as they allow a high degree of control over the structure of the product polymer, in this case, PPV. In particular, the degree of polymerisation, molecular weight distribution and potentially the sequence structure of block copolymers can be carefully controlled.

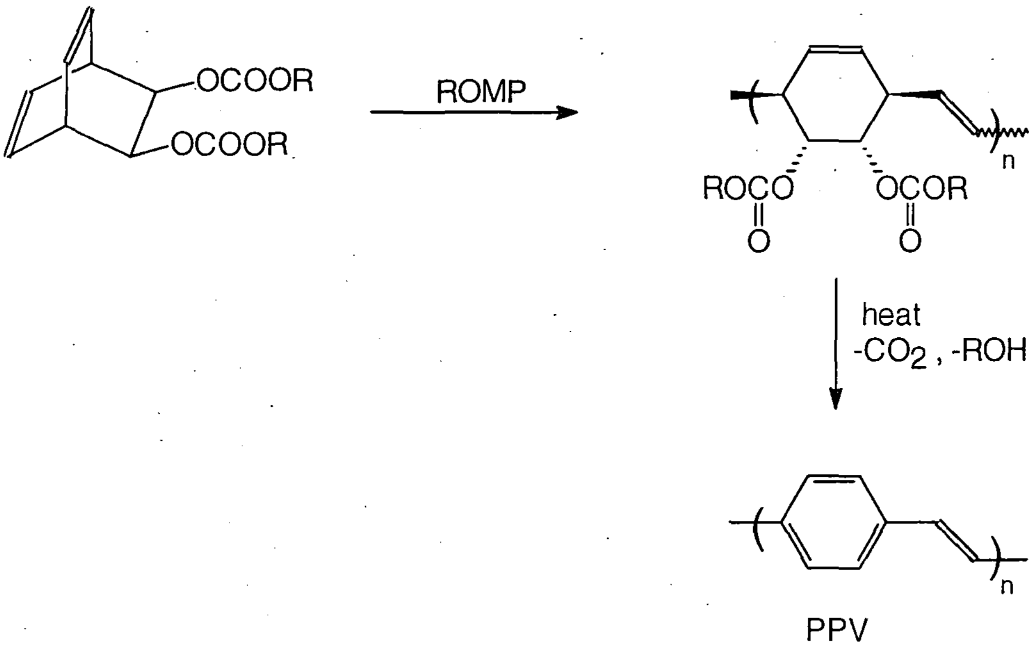


Figure 5.4. The living ROMP synthesis of PPV

Developing the theme of using living ROMP methodology as a route to the precursor polymer synthesis of PPV and related materials was considered to be a worthwhile area of work. The monomer, 2,3-(tetrafluorobenzo)bicyclo[2.2.2]-octatriene was considered to be an interesting monomer to study on account of the presence of the electron withdrawing fluorine atoms in the structure. It has been reported previously that the incorporation of electron withdrawing groups in the backbone of PPV can improve the efficiency of the resulting LEDs, the cyano derivative of PPV shown overleaf, being a good example of this. The polymer shown in figure 5.5 displays a deep red electroluminesence and a very high brightness of colour has been achieved.[15,19]

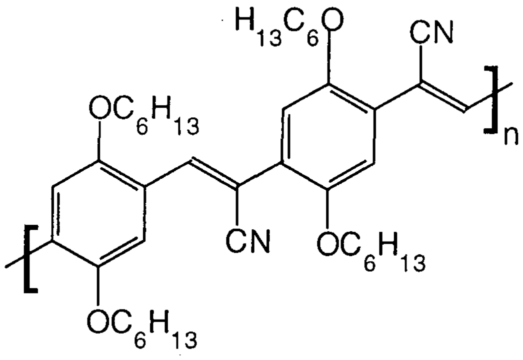


Figure 5.5. The structure of a cyano derivative of PPV.

The idea behind using 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene as a starting material was that if a suitable precursor synthesis to a fluorinated arylene vinylene polymer could be established the resulting material might be of interest as a component in LEDs either as a light emitting layer or an electron-transporting and hole blocking layer. Figure 5.6 outlines the potential scheme for the synthesis of a fluorinated poly(napthylene vinylene). It was proposed that the living ROMP of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene would produce the naphthalene-vinylene derivative as shown in figure 5.6. This ring opened polymer contains two hydrogens which are both tertiary and allylic (indicated as H^* in figure 5.6) and, as a result, they should be relatively weakly bonded to their respective carbon atoms. By using a suitable oxidising agent such as p-chloranil, it may be possible to remove these tertiary protons and produce the novel poly(arylene vinylene), as illustrated in figure 5.6.

Efforts directed to the synthesis of this fluorinated poly(napthylene vinylene) by the route described in figure 5.6 are reported in the following sections of this Chapter.

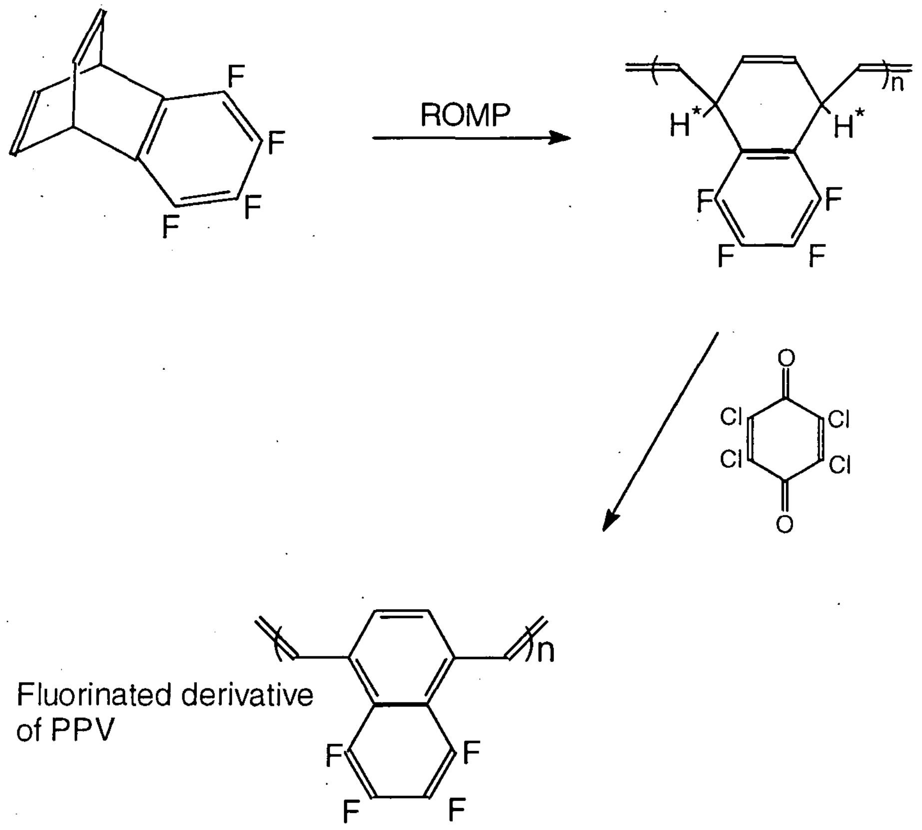


Figure 5.6. A possible synthesis of a fluorinated poly(arylene vinylene) by living ROMP.

5.3.2. Results and discussion.

Using ^1H NMR spectroscopy it has been shown that 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene undergoes living ring opening polymerisation on reaction with the well-defined initiators, $Mo(CHCMe_2Ph)(NAr)(OCMe_3)_2$ and $Mo(CHCMe_2Ph)(NAr)(OCMe(CF_3)_2)_2$, as shown below in figure 5.7.

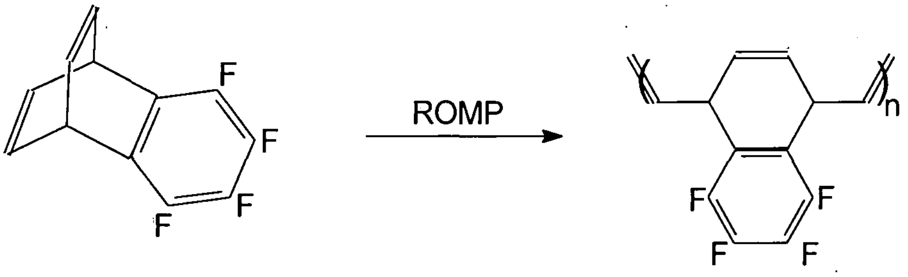
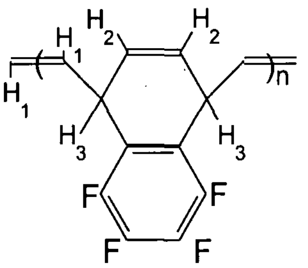


Figure 5.7. The living ROMP of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene.

The ^1H NMR spectrum shows the presence of a peak attributable to the propagating alkylidene species, and also there are signs of polymer growth with three broader peaks present due to the three different proton environments (H_1, H_2, H_3) in the polymer as illustrated below. The chemical shifts are H_1, 5.4ppm, H_2, 5.9ppm, H_3, 4.05ppm, with the relative intensities in the required 1:1:1 ratio.



However, there was one major drawback with this polymerisation, the fact that the polymer precipitated during the course of the reaction. This presented two major problems; firstly, due to the lack of the solubility of the polymer, it was difficult to fully characterise the material by conventional analytical techniques. Furthermore, as regards the long term aim to synthesise a fluorinated poly(arylene vinylene), a soluble precursor polymer was necessary, and this polymer was not soluble, meaning this goal would be difficult to achieve.

A solubility study was undertaken to try and find a suitable solvent system for this polymerisation. As described in the Experimental Section, the solubility of the monomer, 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene, was assessed for a wide range of solvents. It was found to be most soluble in chloroform, tetrahydrofuran, benzene, dichloromethane and toluene, and subsequent polymerisation studies were conducted in these solvent systems. However, none of the solvents tried were able to solve the problem of the polymer precipitating, although a living polymerisation was observed in each case. This solubility problem also accounted for the lack of success achieved in the dehydrogenation reaction of this polymer using the oxidising agent, p-chloranil, as described in the Experimental Section.

Attention was turned to attempts to synthesise a modified monomer, which would hopefully overcome the problem of the polymer precipitating out of solution. It was decided to attempt to synthesise 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene carrying a long alkyl chain, ($-C_{10}H_{21}$), which would hopefully act as a solubilising substituent in the resulting polymer. The attempted synthesis of this monomer was similar to that of the monomer containing no alkyl chain; namely, addition of tetrafluorobenzyne to phenyldecane, only one isomer of the possible products would be useful. It was hoped that this monomer would undergo ring opening to produce a soluble polymer, as shown in figure 5.8.

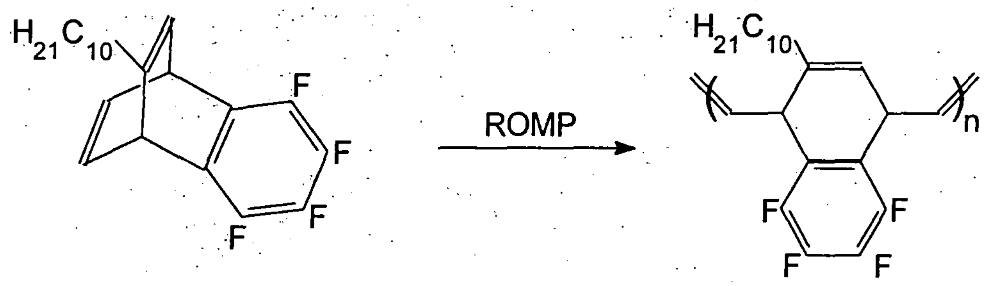
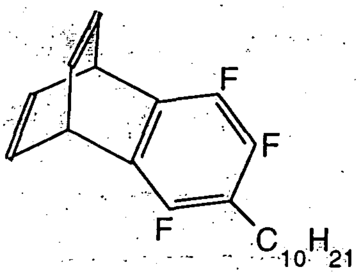


Figure 5.8. Proposed scheme for the ROMP of 7-decyl-2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene.

Unfortunately, attempts to synthesise this monomer were unsuccessful. Possible reasons include the fact that the butyllithium used in the reaction would probably extract a proton from the benzylic methylene of the phenyldecane rather than the pentafluorobenzene as this is probably more easily removable. In this case the reaction would be unsuccessful as the removal of a proton from pentafluorobenzene to form the reactive intermediate, tetrafluorobenzyne, is the necessary first step for this reaction to proceed.

The next attempt to produce a soluble polymerisation system involved the attempted synthesis of 2,3-(trifluoro-decyl-benzo)bicyclo[2.2.2]octatriene, as shown next.



This involved the use of the Grignard reagent, decylmagnesium bromide ($C_{10}H_{21}MgBr$). It has been reported that fluorinated aromatic compounds undergo nucleophilic attack with Grignard reagents,[20] so it was thought that the substitution of a fluorine by a $C_{10}H_{21}$ group in 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene by using $C_{10}H_{21}MgBr$ would be possible. However in the event, this was not achieved and this synthesis was unsuccessful.

The final effort to produce a soluble polymer system, involved the attempted synthesis of an AB block co-polymer incorporating a solubilising block. Poly(bis(trifluoromethyl)norbornadiene) is known to be a polymer soluble in range of solvents, and the idea was that a block- co-polymer combining a block of this polymer and a block of poly(tetrafluorobenzo)bicyclo[2.2.2]octatriene) might provide a soluble system. However, this idea did not come to fruition and on addition of 2,3(tetrafluorobenzo)bicyclo[2.2.2]octatriene to living poly(bis(trifluoromethyl)-norbornadiene), a precipitate formed almost immediately making the synthesis of a soluble block co-polymer unattainable.

5.3.3 Experimental details

5.3.3.1 Synthesis of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene.

The preparation of this monomer was similar to that described in the literature.[21]

To a stirring solution of pentafluorobenzene (20.7g, 0.123mole) and benzene (200ml, 2.23mole) a solution of n-butyllithium in hexane (81.25ml, 1.6M) was added dropwise at 0^0C. The reaction mixture was stirred for 5 hours at 15^0C and washed with 2M H_2SO_4 (50ml) and water (3×50ml), the organic layer was separated, dried ($MgSO_4$) and the solvents evaporated to yield an oily product.

Various methods were employed in an attempt to extract 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene from the oil, the most effective approach involved the use of a temperature gradient vacuum sublimation apparatus (Shinho instruments, model Pt100). At a temperature setting of 62.5^0C and pressure of ca.10^{-3} mmHg, white crystals sublimed from the oil. The product was recovered by recrystallization from hexane and dried *in vacuo* to yield a white crystalline material, melting point $70\text{-}72^0$C. The synthesis of this monomer was performed several times, and on each occasion low yields were obtained (<30%). The product was characterised spectroscopically and key data are recorded below, and the spectra are shown in Appendix 5.5. The evidence is consistent with the assigned structure and in agreement with the literature.[21]

<u>^{1}H NMR data</u> (200MHz, $CDCl_3$, 298K)

6.91ppm (sextet, 4H, vinylic), 5.31ppm (sextet, 2H, bridgehead), reference to TMS.

^{19}F NMR data (376.28MHz, $CDCl_3$, 298K)

149.93ppm, (q, J = 8Hz, 2F), 162.61ppm, (q, J = 4Hz, 2F), reference to $CFCl_3$.

Infra-red data (KBr disc, cm^{-1})

3076.9 (w), 3021.5 (w), (olefinic C-H stretch), 2961.9 (w), (aliphatic C-H stretch), 1630.3 (m), (olefinic C=C stretch), 1497.6 (s), (fluorinated aromatic ring), 1400-1000 (s), (C-F stretch), 744.4 (s), (cis-olefin out - of - plane CH bending).

5.3.3.2 A study to find a suitable solvent system for the polymerisation of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene

A study was performed using a range of common solvent systems in an attempt to find a suitable solvent for the ROM polymerisation of this monomer. The basic procedure was as follows: At room temperature in a sample vial, a saturated solution was prepared with the solvent under investigation and the monomer. Measured volumes of these saturated solutions (ca.0.5ml) of a series of monomer/solvent combinations were prepared and left for approximately 12 hours, to allow the solvent to evaporate. The mass of solid present in the sample vial after solvent evaporation was recorded and this enabled the solubility, in grams per litre, to be calculated for the monomer in the range of solvents listed in table 5.4.

Table 5.4. Solubilities of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene in various solvents.

Solvent	**Solubility grams/litre**
acetone	842.6
chloroform	1275.7
hexane	328.0

Solvent	Solubility grams/litre
toluene	819.1
methanol	106.4
dichloromethane	1195.1
pentane	246.4
tetrahydrofuran	883.5
petroleum ether	224.6
diethyl ether	586.5
ethyl acetate	758.1
ethane diol	127.5
dimethyl sulphoxide	2.43
ethanol	164.1
m-cresol	29.7
pyridine	754.7
N,N-dimethylacetamide	643.6
2-butanone	823.9
benzene	970.2
chlorobenzene	772.03

Table 5.4 (continued)

Subsequent polymerisation studies were performed in the solvents in which the monomer had the highest solubility. The five solvent systems chosen from this study were chloroform, tetrahydrofuran, benzene, dichloromethane and toluene.

5.3.3.3. ^{1}H NMR scale polymerisation of 2,3-(tetrafluorobenzo)bicyclo-[2.2.2]-octatriene using $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i{}_2\text{-}C_6H_3)(OCMe_3)_2$.

^{1}H NMR scale polymerisations of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]-octatriene initiated by $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i{}_2\text{-}C_6H_3)(OCMe_3)_2$ were performed in the solvents chosen from the solubility study described previously. The general procedure was as follows: To a rapidly stirring solution of $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i{}_2\text{-}C_6H_3)(OCMe_3)_2$ (0.01g, 0.0182mmole) in the solvent under investigation (350μl) was added a solution of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene (0.082g, 0.364mmole, 20 equivalents) in the solvent under investigation (350μl). After twenty minutes the reaction mixture was injected into an NMR tube fitted with a Teflon stopcock and after 24 hours a ^{1}H NMR spectrum was recorded in order to observe if the propagating alkylidene species were present. In every solvent system used, the pale orange/brown colour of the initiating solution changed to a deep cherry red colour, indicative of the formation of the propagating species, and a precipitate formed in the bottom of the NMR tube. The ^{1}H NMR data is reported with the spectrum being recorded at 400MHz and 298K. A propagating doublet was observed at 10.82ppm due to the presence of the active alkylidene species. Three distinct environments for the protons due to the growing polymer chain were observed, and these were assigned as follows: 5.9ppm (s,br, 2H), (cyclohexenyl), 5.4ppm (s,br, 2H), (vinylic), 4.05ppm (s,br, 2H), (bridgehead). The spectrum is shown in Appendix 5.6.

5.3.3.4. ^{1}H NMR scale polymerisation of 2,3-(tetrafluorobenzo)-bicyclo[2.2.2]octatriene using $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(OCMe(CF_3)_2)_2$.

^{1}H NMR scale polymerisations of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]-octatriene initiated by $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(OCMe(CF_3)_2)_2$ were performed in the solvents chosen from the solubility study previously described. The general procedure was as follows: To a rapidly stirring solution of $Mo(CHCMe_2Ph)$-$(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(OCMe(CF_3)_2)_2$ (0.01g, 0.0131mmole) in the solvent under investigation (350μl) was added a solution of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]-octatriene (0.059g, 0.2613mmole, 20 equivalents) in the solvent under investigation (350μl). After twenty minutes the reaction mixture was injected into an NMR tube fitted with a Teflon stopcock. After 24 hours, a ^{1}H NMR spectrum was recorded in order to observe if the propagating alkylidene protons were present. As was observed in the series of experiments performed with the molybdenum-t-butoxide initiator, the formation of the propagating species could be detected by the reaction solution changing from a pale orange/brown colour to a deep cherry red, the presence of a precipitate in the NMR tube was also be observed. The ^{1}H NMR data is reported with the spectrum being recorded at 400MHz and 298K. A propagating doublet was observed at 11.66ppm due to the presence of the active alkylidene species. Three distinct environments for the protons due to the growing polymer chain were observed, and these were assigned as follows: 5.9ppm (s,br, 2H), (cyclohexenyl), 5.4ppm (s,br, 2H), (vinylic), 4.05ppm (s,br, 2H), (bridgehead) and the spectrum is shown in Appendix 5.7. The recovered polymer was analysed by DSC indicating a T_g of 164.7^{0}C for this polymer. The DSC trace is reproduced in Appendix 5.8.

5.3.3.5. The attempted dehydrogenation of poly((tetrafluorobenzo)bicyclo[2.2.2]octatriene).

To a rapidly stirring suspension of poly((tetrafluorobenzo)bicyclo[2.2.2]-octatriene) (0.306g) in toluene (25ml), was added p-chloranil, (0.025g, 0.101mmole), previously purified by vacuum sublimation at a temperature of 80^{0}C. The reaction mixture was refluxed under nitrogen for 12 hours. The initial pale yellow colour of the reaction mixture remained after 12 hours, but after this time a yellow/brown precipitate, (0.234g), was present in the reaction vessel. The purification of this precipitate was attempted by the technique of dissolving and reprecipitating of it in a suitable solvent/non-solvent combination but, due to its insolubility in the wide range of common solvents, this purification technique proved unsuitable. This lack of solubility inhibited most analytical procedures and the only characterisation data obtained was from FTIR studies. The FTIR spectrum of the precipitate was compared to the FTIR spectrum of a sample of poly((tetrafluorobenzo)bicyclo[2.2.2]octatriene) and as the spectra were virtually identical suggested that no dehydrogenation had taken place. The attempted dehydrogenation reaction was performed on both the poly((tetrafluorobenzo)bicyclo[2.2.2]octatriene) samples produced by initiation with $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(OCMe_3)_2$ and $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(OCMe(CF_3)_2)_2$ described previously in this section. The evidence from the FTIR data suggested that no dehydrogenation of poly((tetrafluorobenzo)bicyclo[2.2.2]octatriene) had occured in either case. Appendix 5.9 compares samples of poly((tetrafluorobenzo)bicyclo[2.2.2]octatriene) before and after the attempted dehydrogenation.

5.3.3.6. The attempted synthesis of 7-decyl-2,3-(tetrafluorobenzo)bicyclo-[2.2.2]octatriene.

To a stirring solution of pentafluorobenzene (2g, 0.012mole) and phenyldecane (16g, 0.073mole), (dried over benzophenone and sodium wire, and vacuum distilled immediately prior to use) was added dropwise a solution of n-butyl lithium in hexane (15ml, 1.23M) at 0^0C. The reaction mixture was stirred at 15^0C for 6 hours and washed with H_2SO_4 (2M, 30ml) and water (3x30ml). The organic layer was separated, dried ($MgSO_4$) and the solvents evaporated to yield a yellow oil, (4.5g, 44% yield). This yellow oil was analysed by ^{1}H, ^{13}C NMR spectroscopy and the spectra for the starting materials and the reaction product, were almost identical, suggesting the attempted synthesis of 7-decyl-2,3-(tetrafluorobenzo)bicyclo[2.2.2]-octatriene had been unsuccessful, these spectra are recorded in Appendix 5.10.

5.3.3.7. Reaction of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene with decylmagnesium bromide.

Firstly the Grignard reagent, decylmagnesium bromide was prepared: A two-necked 500cm^3 round bottomed flask was connected to a reflux condenser and an addition funnel, both capped with $CaCl_2$ guard tubes. Into the 500cm^3 RB flask were placed dry magnesium turnings (0.42g, 0.0173mole) in dry ether (50ml), and the addition funnel was charged with 1-bromodecane (3.89g, 0.0173mole) in dry ether (20ml). To initiate the reaction, a crystal of iodine was introduced onto the surface of the magnesium without stirring and approximately 5ml of the 1-bromodecane solution was added dropwise. Gentle heating was applied to the flask and the formation of the Grignard reagent could be observed by the disappearance of the iodine colour and the appearance of a cloudy grey colour with small bubbles arising from the area around the original site of the iodine crystal. Stirring of the solution was then started and the reaction was allowed to proceed at such a rate that gentle refluxing of the ether took place. The rate was controlled by the addition of small volumes of the 1-bromodecane solution to maintain the reaction. When all the 1-bromodecane solution had been added the reaction mixture was refluxed gently for a further 2 hours.

After this period, the addition funnel was charged with 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene (4g, 0.0175mole) in dry ether (30ml). This solution was then added slowly to the Grignard reagent solution and a steady reflux was maintained for 12 hours. After 12 hours, the reaction mixture was cooled in ice and hydrochloric acid (50ml, 10%) was added to the solution. The organic layer was separated, dried (Na_2SO_4) and the solvents evaporated to give a colourless liquid (3.93g, 64 % yield). This colourless liquid was analysed by ^1H, ^{19}F NMR spectroscopy and the spectra recorded were compared with the spectra for poly(tetrafluorobenzo)bicyclo[2.2.2]octatriene, the two sets of spectra were virtually identical, suggesting this reaction had been unsuccessful. The spectra are recorded in Appendix 5.11.

5.3.3.8. Attempted synthesis of poly(bis(trifluoromethyl)norbornadiene)-*block*-poly((tetrafluorobenzo)bicyclo[2.2.2]octatriene).

The attempted synthesis of the above AB block co-polymer was performed on an NMR-tube scale. To a rapidly stirring solution of $Mo(CHCMe_3)(N\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)(OCMe_3)_2$ (0.01g, 0.020mmole) in C_6D_6 (350µl) was added a solution of 2,3-bis(trifluoromethyl)norbornadiene (0.468g, 2.05mmole, ca. 100 equivalents) in C_6D_6

(350μl). The reaction mixture was stirred for twenty minutes, after which the solution had changed from a pale orange/brown colour to a deep cherry red indicative of the formation of the propagating alkylidene species. The reaction mixture was injected into a NMR tube and a ^{1}H NMR spectrum (400MHz, C_6D_6, 298K) was obtained, the presence of a doublet at 11.289-11.269ppm confirmed the presence of the propagating alkylidene species, (the spectrum is reproduced in Appendix 5.12).

To the stirring solution of this reaction mixture was added 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene (0.093g, 0.41mmole, ca.20 equivalents) in C_6D_6 (350μl). The resultant reaction mixture was then stirred for twenty minutes. After this time the reaction contents had become a solid gel. This indicated that the proposed synthesis of a soluble block co-polymer had not been achieved and thus further analysis was not carried out.

5.4. Conclusions.

The purpose of this Chapter was to describe efforts directed to the ring opening polymerisation of the fluorinated monomers, 2,3-bis(trifluoromethyl)-bicyclo[2.2.2]octa-2,5-diene and 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene. Unfortunately, these efforts have only been moderately successful. Attempts to ring open the first monomer used a range of well-defined initiators and also the classical initiating system based on WCl_6 and Me_4Sn, however all these attempts were unsuccessful and no ring-opened polymer was obtained.

The ring-opened polymer of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene was obtained using the well-defined initiators, $Mo(CHCMe_2Ph)(NAr)(OCMe_3)_2$ and $Mo(CHCMe_2Ph)(NAr)(OCMe(CF_3)_2)_2$. However, the polymer precipitated from the reaction mixture upon formation. This has presented problems as regards fully characterizing this material and furthermore prevented its use as a precursor polymer for the synthesis of the fluorinated poly(napthylene vinylene), which was the motivation for the attempted synthesis. Various methods have been employed to try and circumvent this problem. These include; varying the solvent system for the polymerisation and the attempted modification of the monomer to incorporate a solubilising alkyl chain in its structure. However, these attempts were unsuccessful and a fluorinated poly(arylene vinylene) via ROMP of 2,3-(tetrafluorobenzo)bicyclo-[2.2.2]octatriene and dehydrogenation has not been realised.

There is a great deal of interest in poly(arylene vinylene)s and related polymers at present which has centred on their application as components in light emitting diodes. A great deal of research at the present time is directed to establishing suitable precursor routes to such polymers and living ROMP provides a possible entry in to this line of research. Future studies which the author believes could reasonably be undertaken in applying living ROMP systems to this area of work will be discussed in Chapter 6 of this thesis.

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Chapter 6

Conclusions and suggestions for future work

6.1. Conclusions.

In Chapter 3, the synthesis and activity of some novel well-defined ROMP initiators was reported. These initiators incorporated variations in both the ancillary alkoxide and imido ligands and their synthesis and use as initiators was directed towards improving the tacticity of poly(bis(trifluoromethyl)norbornadiene). The choice of ancillary alkoxide and imido ligands around the transition metal centre in the initiator and propagating chain end active site is known to have a dramatic effect on the microstructure of this polymer and this provided the motivation for this work.

At present, the best result achievable is a high trans 92% syndiotactic material synthesised using the initiator, $Mo(NAr)(CHCMe_2Ph)(OCMe_3)_2$. An increase in tacticity approaching 100% could be of great interest commercially as the pyroelectric response of poled films of this polymer would be expected to improve significantly. The work reported shows that the well-defined initiators, $Mo(NAr)(CHCMe_2Ph)(OB(mes)_2)_2$ and $Mo(NAr)(CHCMe_2Ph)(vulkanox)(CH_3CN)$ give polymers in which the cis-cis vinylene sequences are accompanied almost exclusively by stereoregular monomer incorporation, in a syndiotactic sense. This was an interesting result but not really useful, since the main aim of this study was to produce a microstructure in which the whole of the polymer backbone was of a highly stereoregular nature.

The practical limits of the well controlled synthesis of poly-(bis-(trifluoromethyl)norbornadiene were studied in Chapter 4. The details of the syntheses of a range of high trans and high cis, highly tactic samples of poly(bis-(trifluoromethyl)norbornadiene) were described. It was shown that by varying the initiator:monomer ratio, a range of different molecular weights could be attained, and furthermore in the majority of cases, narrow molecular weight distributions were obtained. As described in this chapter, one of the reasons for undertaking this program of work was to provide a series of well-defined samples for further study by other workers in the IRC using techniques such as molecular modelling and light scattering, and this is work in progress at the time of writing.

A second aim was the investigation into the applicability of living ROMP to the synthesis of well defined high molecular weight samples of polymers. In this work it was established that high monomer:initiator ratios (ca. 4000:1) could be effectively used to make high molecular weight polymers. A sample with a polystyrene equivalent molecular weight of around 900,000 was produced.

Chapter 5 described efforts directed to the ring opening polymerisation of the fluorinated monomers; 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene and 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene. However, these efforts proved only moderately successful. Attempts to ring open the first monomer using a range of well defined initiators and also the classical initiating system based on WCl_6 and Me_4Sn proved unsuccessful and no ring opened polymer was obtained.

The ring opened polymer of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene was obtained using well defined Schrock-type initiators. However problems were encountered with this polymerisation; namely, the polymer precipitated from the reaction mixture upon formation. This hindered the complete characterisation of the material and furthermore prevented its use as a precursor polymer for the synthesis of the fluorinated poly(arylene vinylene), which was the motivation for this work. Various methods directed towards producing a soluble polymerisation system were tried. These included varying the solvent system for the polymerisation and the attempted modification of the monomer to incorporate a solubilising alkyl chain in its structure. Unfortunately, these attempts proved unsuccessful and the synthesis of a fluorinated poly(arylene vinylene) for potential use as a component in light emitting diodes was not achieved.

6.2. Suggestions for future work.

The scope for modifying well-defined initiators of the general structure shown in figure 6.1, for use in ROMP, remains vast.

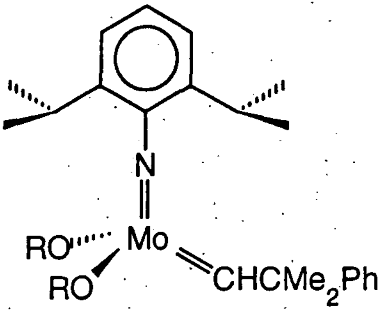

Figure 6.1. General structure of four-coordinate "Schrock" initiator.

The choice of ligand to be used exercises the imagination of the worker in the field. Two important criteria in considering a suitable ligand system are the electronic and steric properties as these have been shown to greatly influence the resulting polymer microstructure.

With particular reference to the improvement of tacticity in poly(bis(trifluoromethyl)norbornadiene). Possible routes to a material of higher tacticity could include the use of modified t-butoxy ligands. Two examples of such ligands are shown in figure 6.2;

Figure 6.2. Examples of modified t-butoxy ligands.

The possible advantages which these ligands may confer, are similar electronic properties to the t-butoxy ligand (i.e. high trans) and also, as they are relatively bulky, they may provide a high degree of steric protection for the initiator and living chain ends. The combination of these two factors may lead to an improvement in the tacticity of the polymer.

There are also further studies possible using some of the novel initiators described in Chapter 3. Firstly, in the case of the molybdenum alkylidene complex utilising the pyridine diolate ligand, whose structure is shown in figure 6.3.

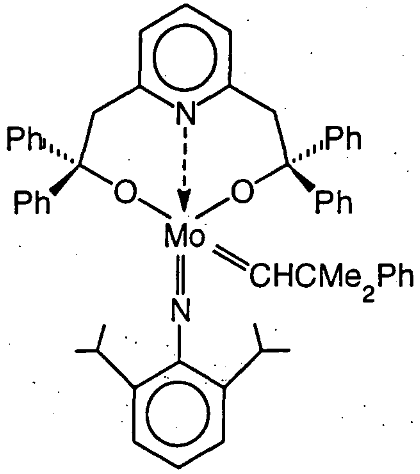

Figure 6.3. Schematic diagram of the molybdenum-pyridine diolate initiator

Studies were directed to the thermal activation of this initiator for use in ROMP reactions. Of particular interest with this initiator system was the fact that it was air stable and the development of an air stable ROMP initiator would be a major breakthrough. Unfortunately, attempts to thermally activate this inititiator were unsuccessful. Further studies which may be worth considering in an attempt to activate this initiator towards ROMP include: Instead of using a pyridine diolate ligand which is coordinated at the 2 and 6 positions, the 3,5 analogue could be used which may produce a more favourable orientation and allow the nitrogen-molybdenum bond to be cleaved more easily, thus activating the initiator. Another method of activation which could be attempted is the use of ultra-violet light. It is evident that the use of heat only serves to decompose the initiator and perhaps the initiator may be activated by light.

Secondly, the use of "quasi-alkoxides" in ROMP initiators was described in Chapter 3. A novel initiator was developed incorporating the boroalkoxide ligands, the initiator is shown in figure 6.4

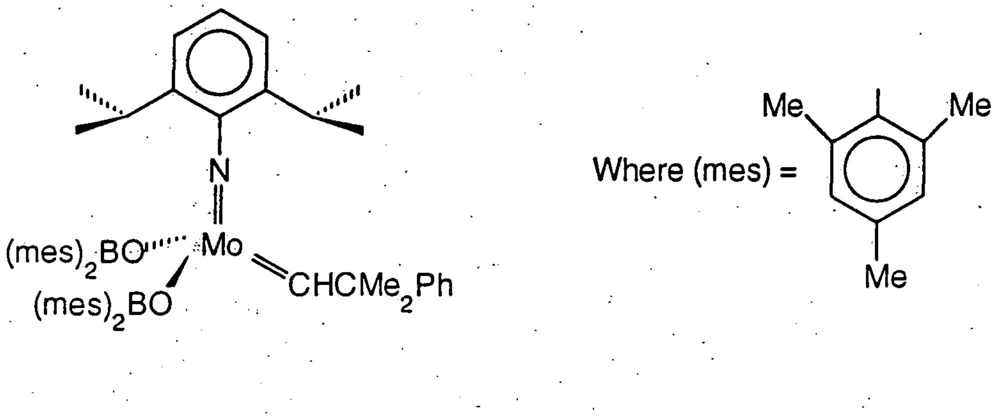

Figure 6.4. Schematic diagram of the four coordinate boroalkoxide initiator.

^{13}C NMR spectroscopy revealed that this initiator produced a poly(bis(trifluoromethyl)norbornadiene) sample containing 85% cis vinylenes, and these cis vinylenes are in a syndiotactic arrangement in the polymer chain. Possible improvements which could be made to this initiator could involve the exchange of the methyl groups on the benzyl ring of the boroalkoxide ligand for trifluoromethyl groups (CF_3), this may increase the electron withdrawing effect of the boroalkoxide ligand even further. This may produce a polymer containing a higher proportion of cis vinylenes which could improve the tacticity of the polymer.

The development of a fluorinated poly(arylene vinylene) in Chapter 5 has proved to be a difficult task. Future studies will need to develop a soluble polymerisation system. Perhaps an alternative solubilising fragment to the alkyl chain needs to be considered; for example, it is known that vinylic phenyl substitution solubilises some poly(arylene vinylene)s.[1] Furthermore, a variation in the type of fluorine group incorporated in the monomer may influence solubility. Perhaps the use of trifluoromethyl groups or even longer chain fluoroalkyls, such as -($CF_2CF_2CF_3$), could aid the solubility problem although, from the point of view of the opto-electronic properties of the material, it is presumed that at least some of the fluorines should be directly attached to the sp^2 carbon framework.

6.3. References.

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Appendix 1

General procedures, equipment and instrumentation

Appendix 1: General experimental procedures

The glove box used in the studies described in this thesis was a modified Miller Howe dry box with a fitted freezer (-40^0C), the inert gas was oxygen-free nitrogen and the normal working conditions were 3-10 ppm oxygen and 10-15 ppm water. The apparatus was transferred in and out of the box via two vacuum/nitrogen ports. All materials were thoroughly dried before use in the glove box and all solvents deoxygenated immediately prior to use in the glove box.

The vacuum / nitrogen line was fitted with Youngs valves and greaseless joints to permit the handling of materials either under nitrogen or under vacuum. The vacuum was provided by an Edwards 5 Two Stage pump and dry oxygen-free nitrogen was supplied via a H_2SO_4 bubbler and a double P_2O_5 column.

Instrumentation

^{1}H, ^{13}C and ^{19}F nuclear magnetic resonance spectra

These were recorded on a Varian VXR 400 NMR spectrometer at 399.95MHz (^{1}H), 100.58MHz (^{13}C) and 376.29MHz (^{19}F) and a Varian Gemini 200 NMR spectrometer at 199.53MHz (^{1}H) and 50.29MHz (^{13}C).

Gel Permeation Chromatography

Measurements using this technique were carried out using a Waters Model 590 refractometer, (column packing Pl_{gel} 5_{μ} mixed styrene-divinyl benzene beads, solvent: Chloroform) and a Viscotek Differential Refractometer/Viscometer Model 200, (column packing Pl_{gel} 10_{μ} mixed styrene-divinyl benzene beads, solvent: Tetrahydrofuran).

Infra-red spectra

Measurements using this technique were recorded on a Perkin Elmer 1600 series FTIR.

Differential Scanning Calorimetry

This was performed using a Perkin Elmer DSC 7 differential scanning calorimeter.

Thermogravimetric Analysis

This was carried out using a Stanton Redcroft TG760 thermobalance.

Elemental Analysis

CHN analysis was performed using a Carlo Erba 1106 elemental analyser.

Appendix 2

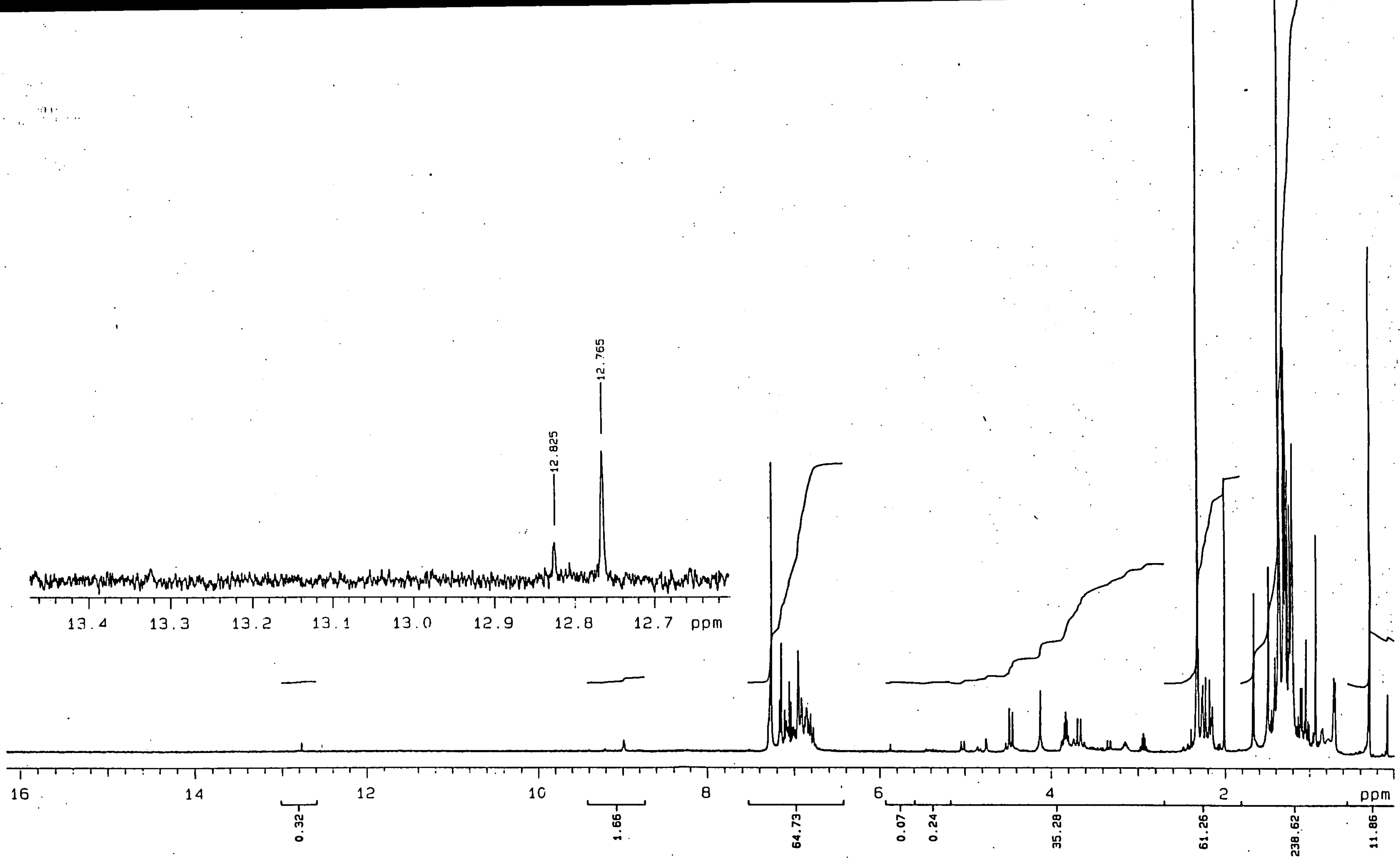
Miscellaneous data for Chapter 1

Table A2.1 The names of the common fluoropolymers, named in abbreviated form in figure 1.11, Chapter 1.

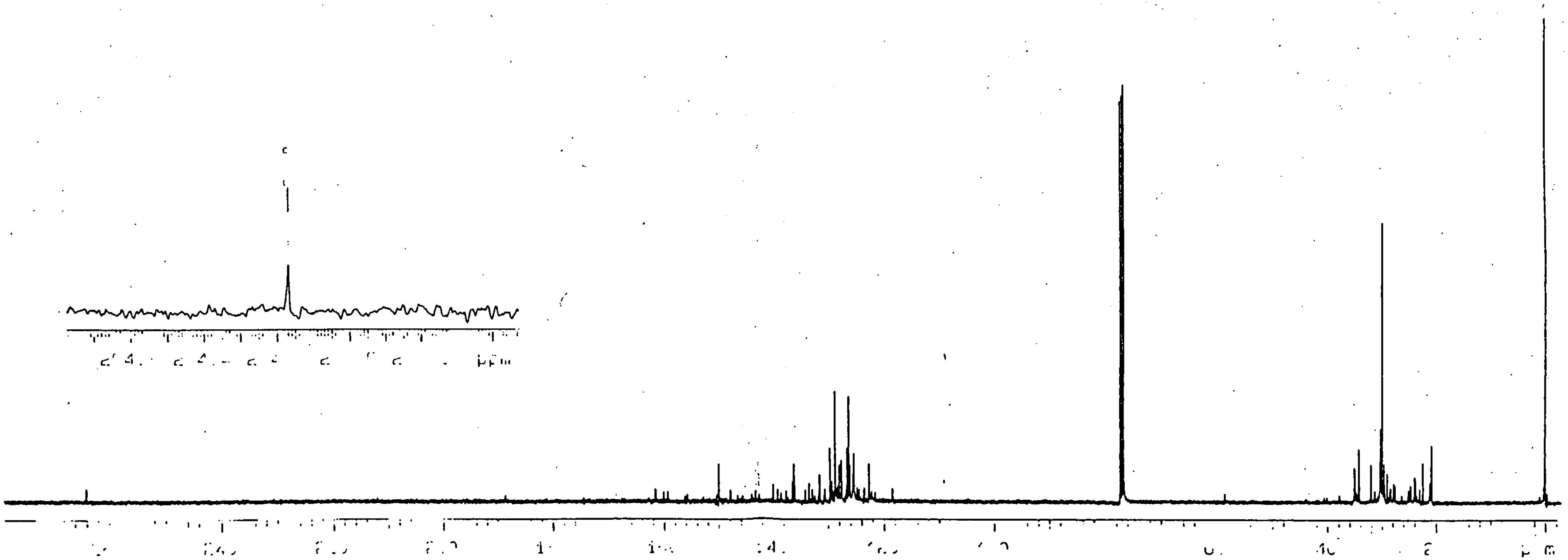
Abbreviation	**Full name**
PTFE	polytetrafluoroethylene
FEP	tetrafluoroethylene/hexafluoropropylene copolymer
PFA/Kalrez	tetrafluoroethylene/perfluoroalkylvinyl-ether copolymer
Nafion	tetrafluoroethylene/perfluorovinylether copolymer containing sulphonyl fluoride groups
Teflon AF	polytetrafluoroethylene /2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole
PCTFE	polychlorotrifluoroethylene
PVDF	polyvinylidenefluoride
PVF	polyvinylchloride
CM-X	hexafluoro-iso-butene/vinylidene fluoride copolymer
Viton-A	vinylidene fluoride/hexafluoropropylene copolymer

Appendix 3

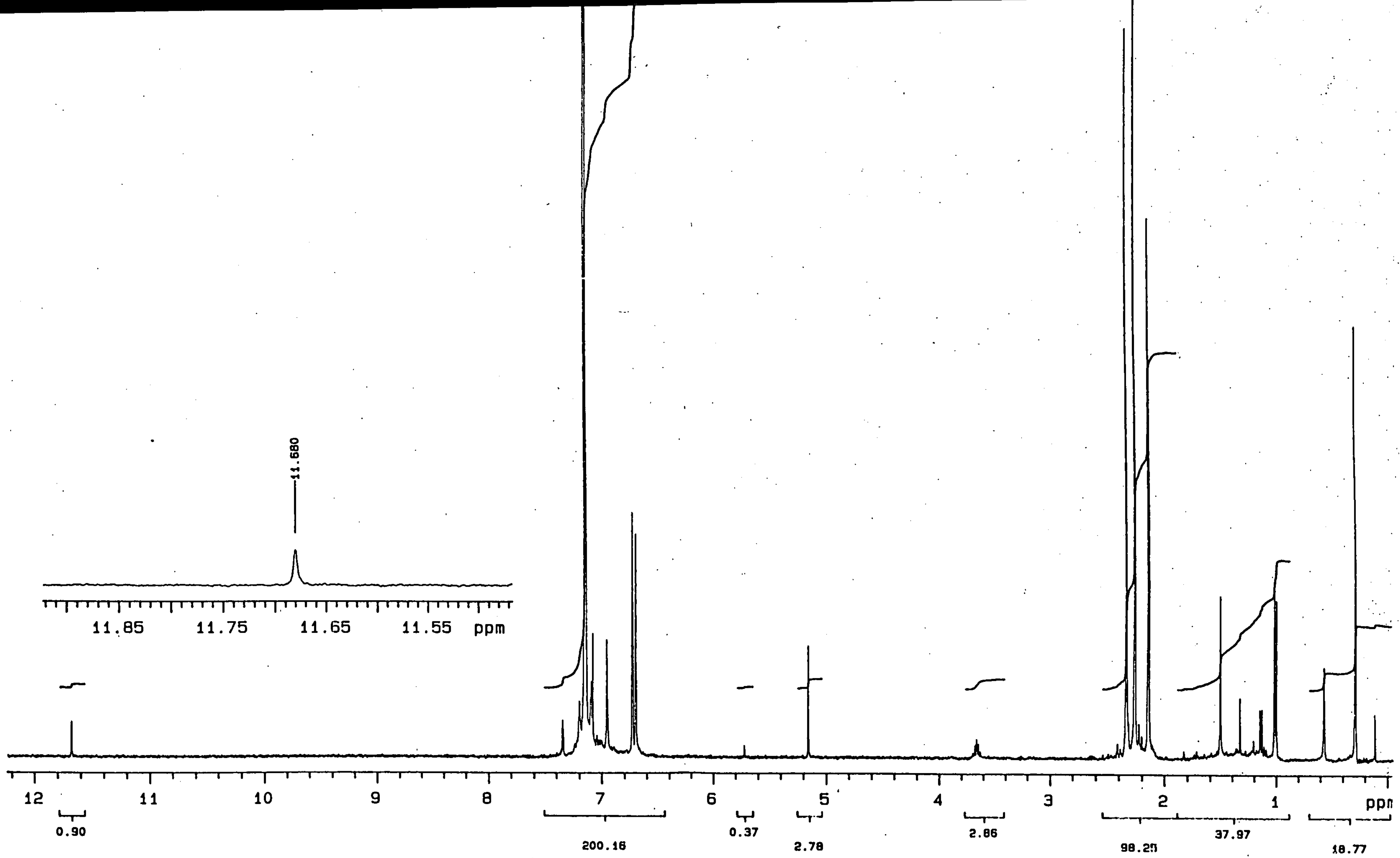
Analytical data for Chapter 3



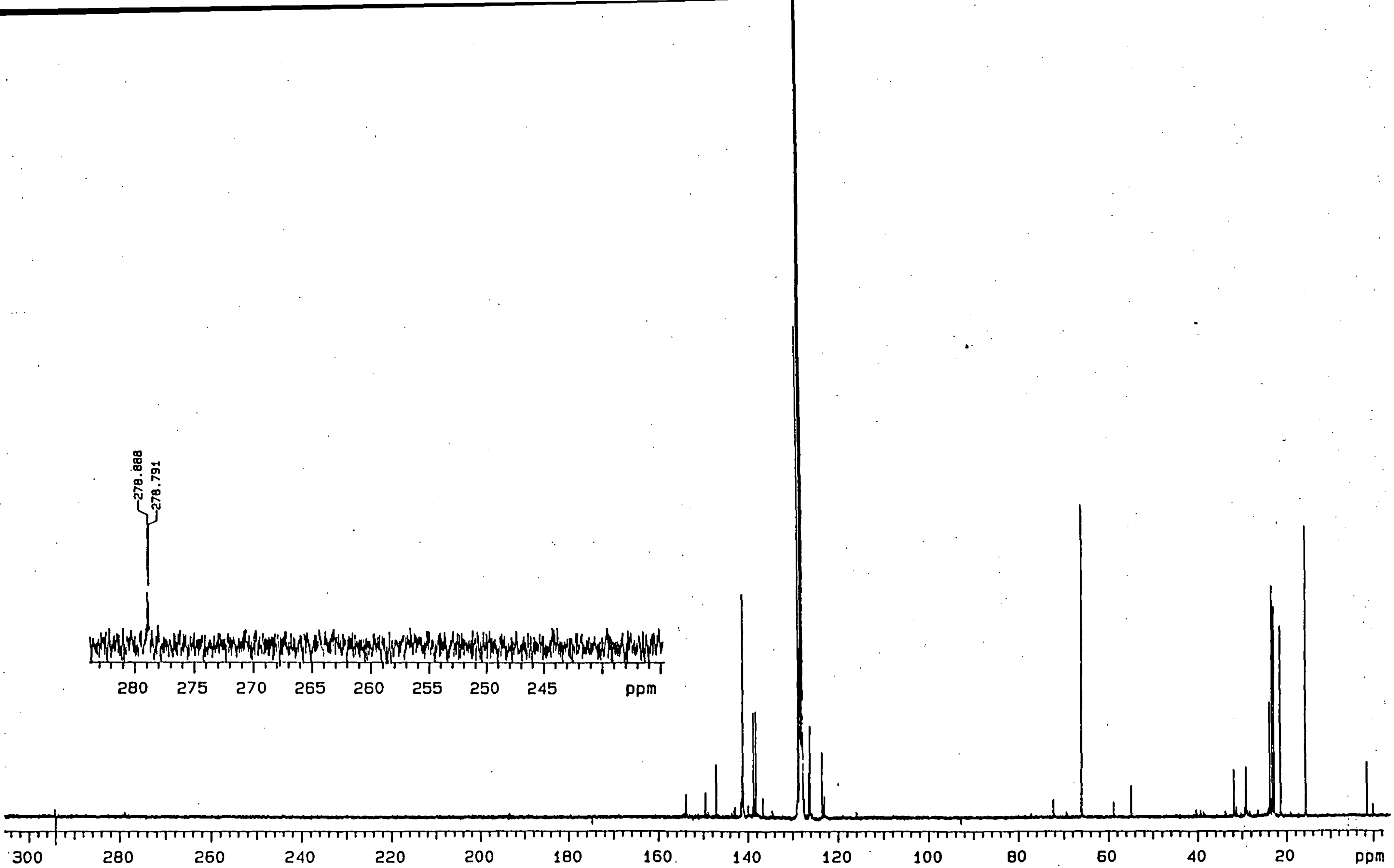
Appendix 3.1a. ^{1}H NMR spectrum of Mo(NAr)(CHCMe$_2$Ph)(2,2′-CH$_2$-(4-Me,-6-t-BuC$_6$H$_2$O)$_2$)(CH$_3$CN) initiator.



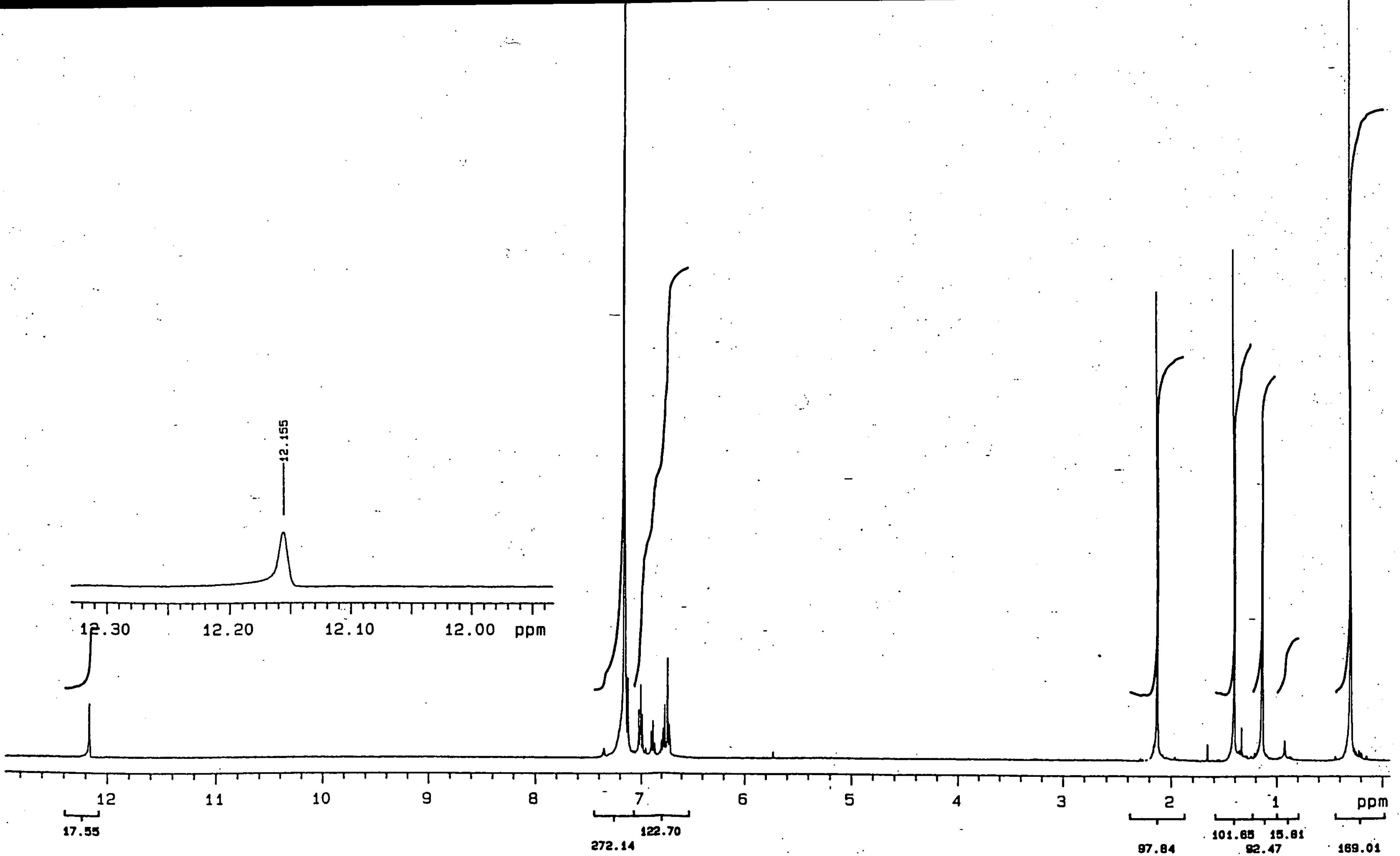
Appendix 3.1b. ^{13}C NMR spectrum of Mo(NAr)(CHCMe$_2$Ph)(2,2′-CH$_2$-(4-Me,-6-t-BuC$_6$H$_2$O)$_2$)(CH$_3$CN) initiator.



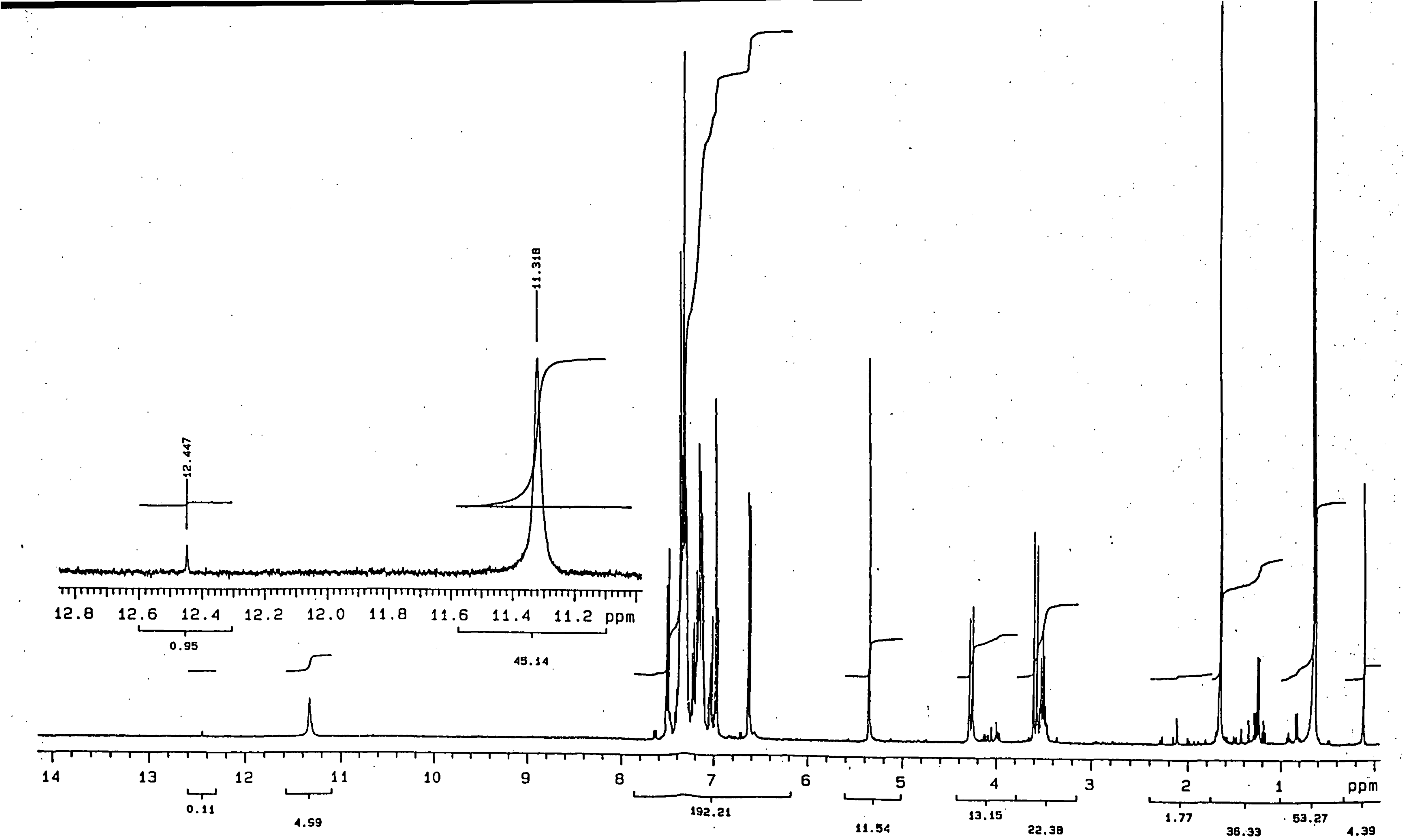
Appendix 3.2a. ^{1}H NMR spectrum of Mo(NAr)(CHCMe$_2$Ph)(OB(2,4,6-Me$_3$C$_6$H$_2$)$_2$) initiator.



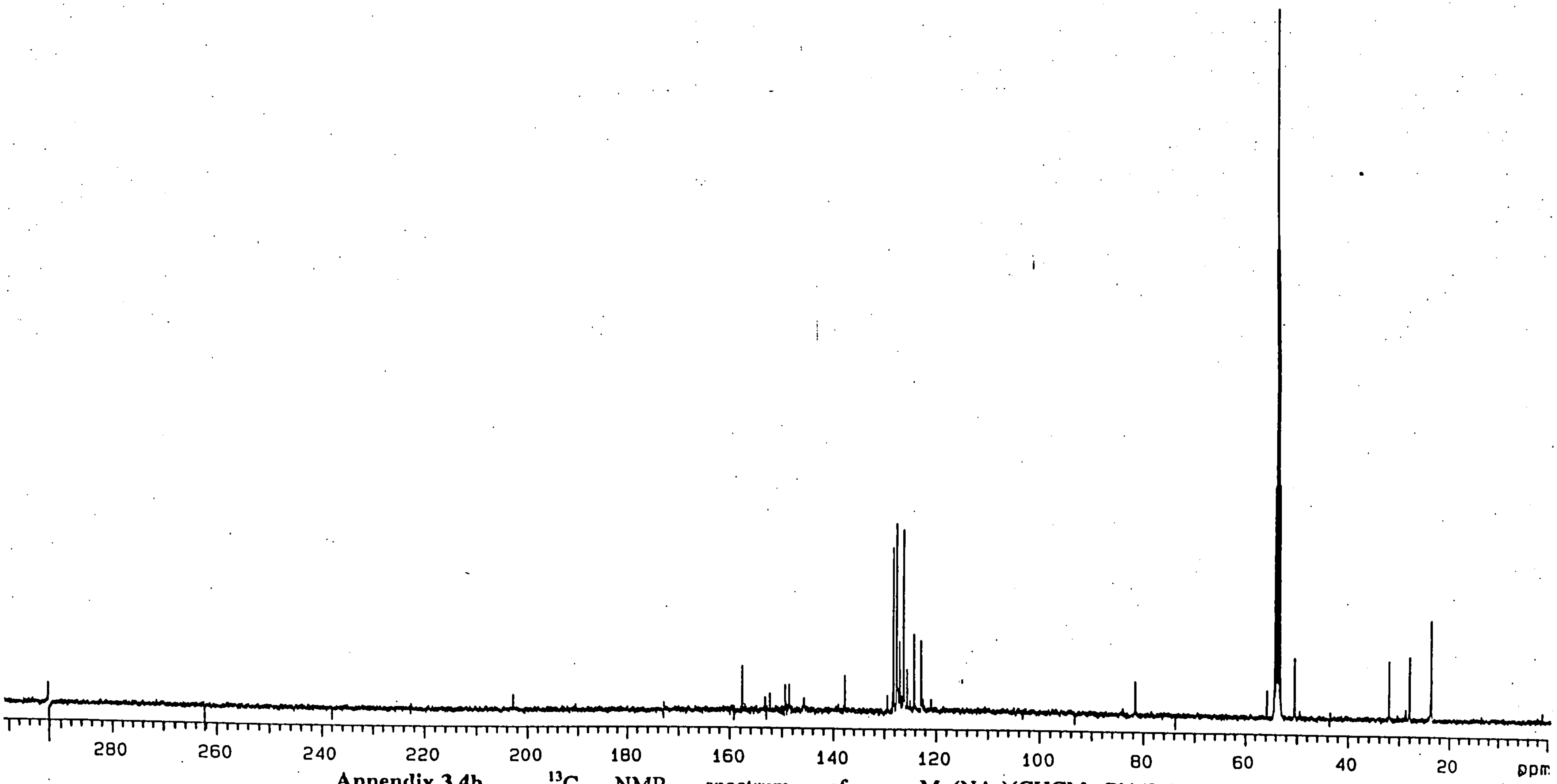
Appendix 3.2b. ^{13}C NMR spectrum of Mo(NAr)(CHCMe$_2$Ph)(OB(2,4,6-Me$_3$C$_6$H$_2$)$_2$ initiator



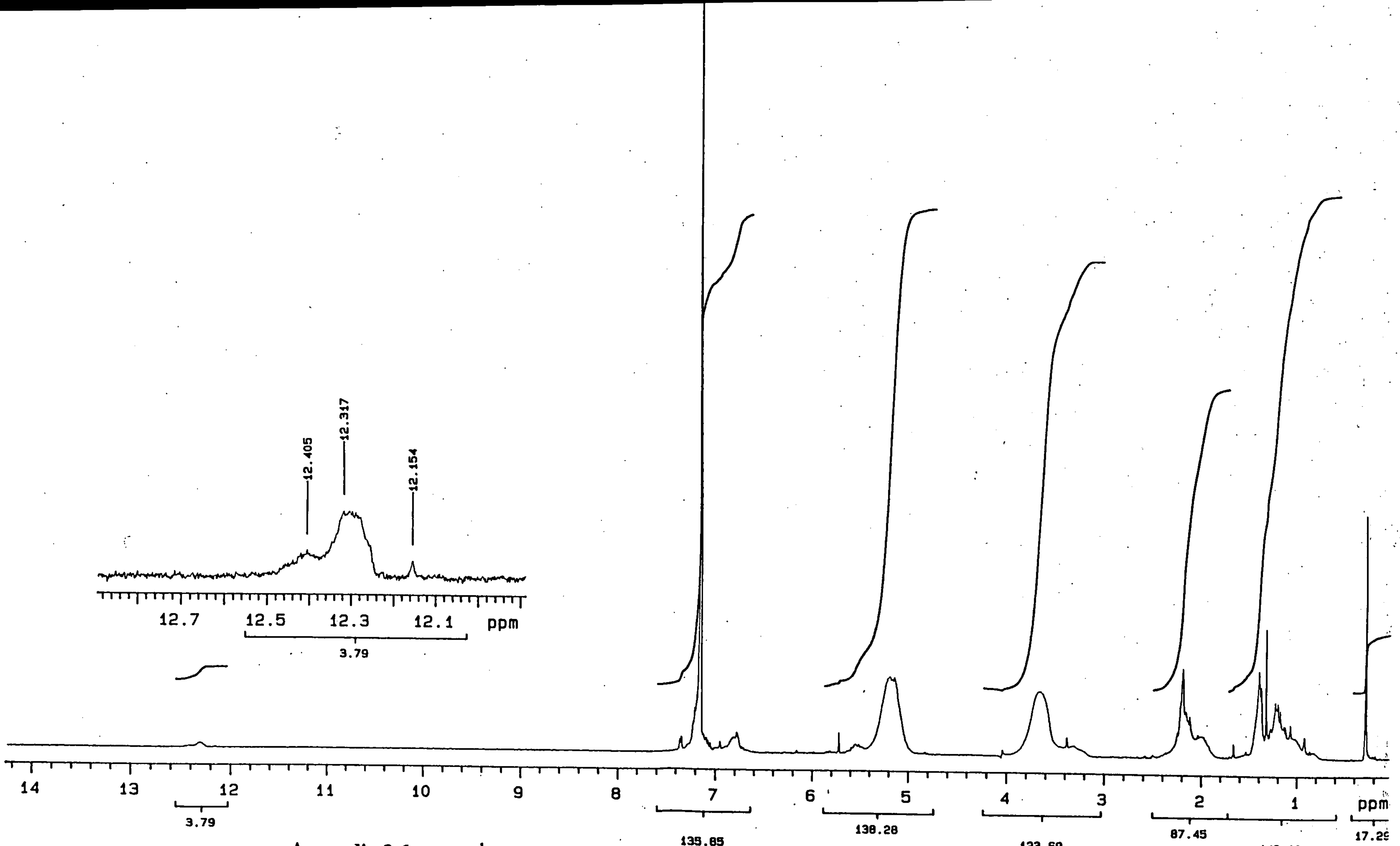
Appendix 3.3. ^1H NMR spectrum of $Mo(N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$ initiator.



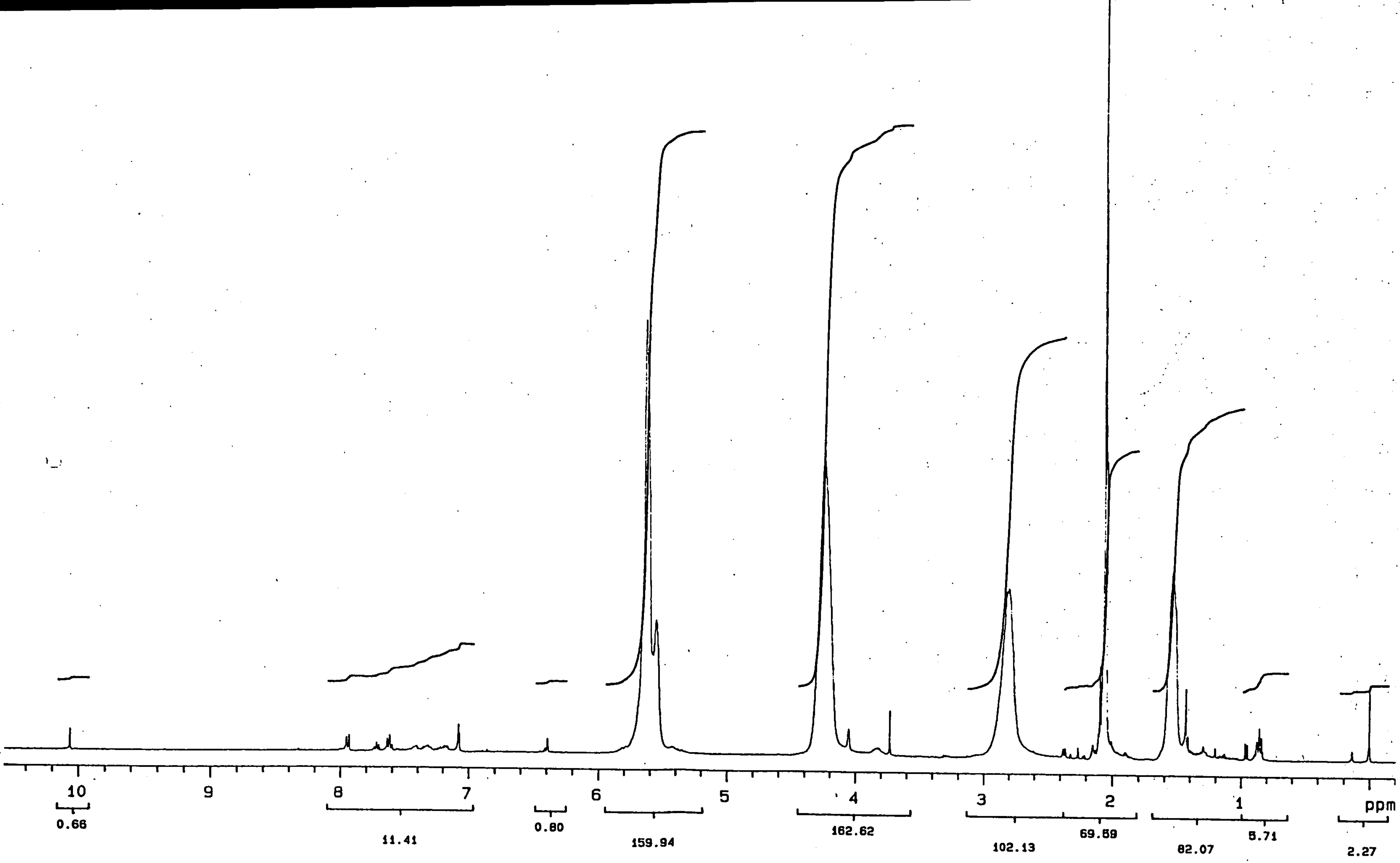
Appendix 3.4. ^{1}H NMR spectrum of Mo(NAr)(CHCMe$_2$Ph)(2,6-(OCPh$_2$CH$_2$)$_2$C$_5$H$_3$N) initiator.



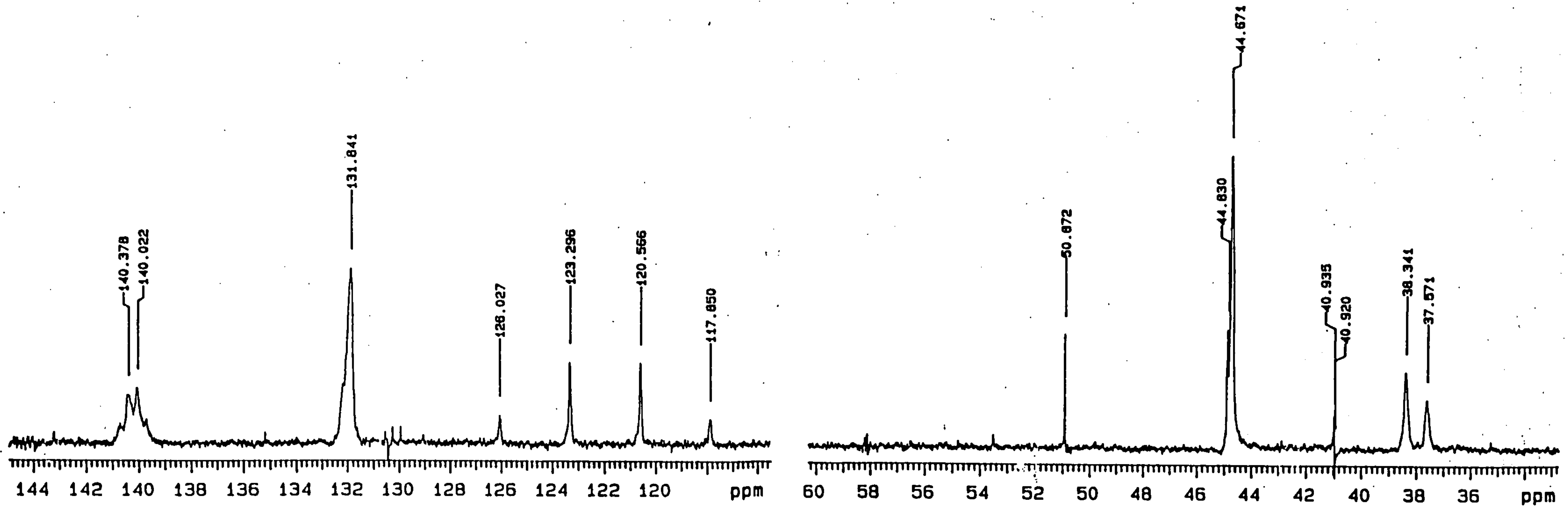
Appendix 3.4b. ^{13}C NMR spectrum of Mo(NAr)(CHCMe$_2$Ph)(2,6-(OCPh$_2$CH$_2$)$_2$C$_5$H$_3$N) initiator



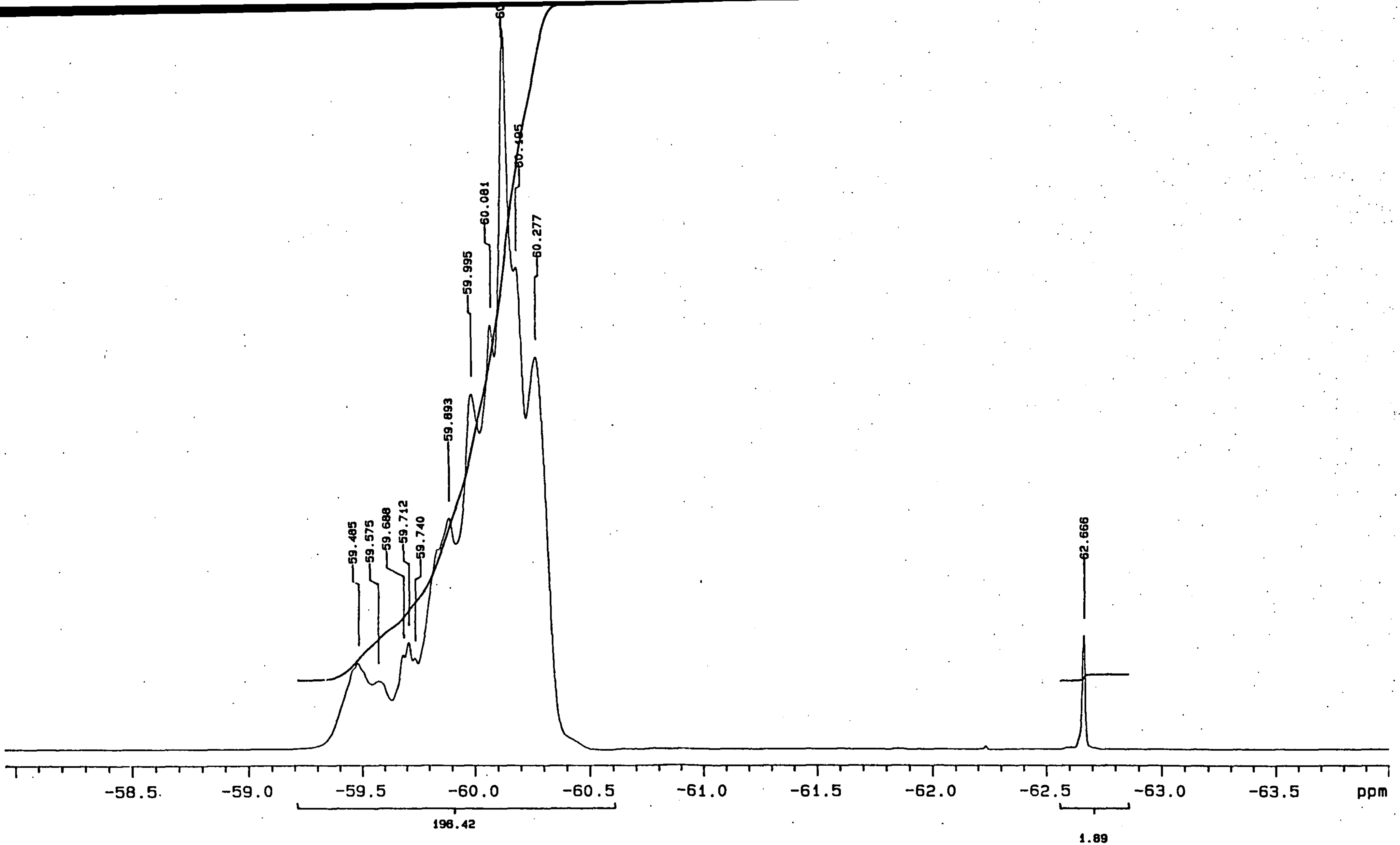
Appendix 3.6. ^1H NMR spectrum of living poly((bistrifluoromethyl)norbornadiene) initiated by Mo(N-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$.



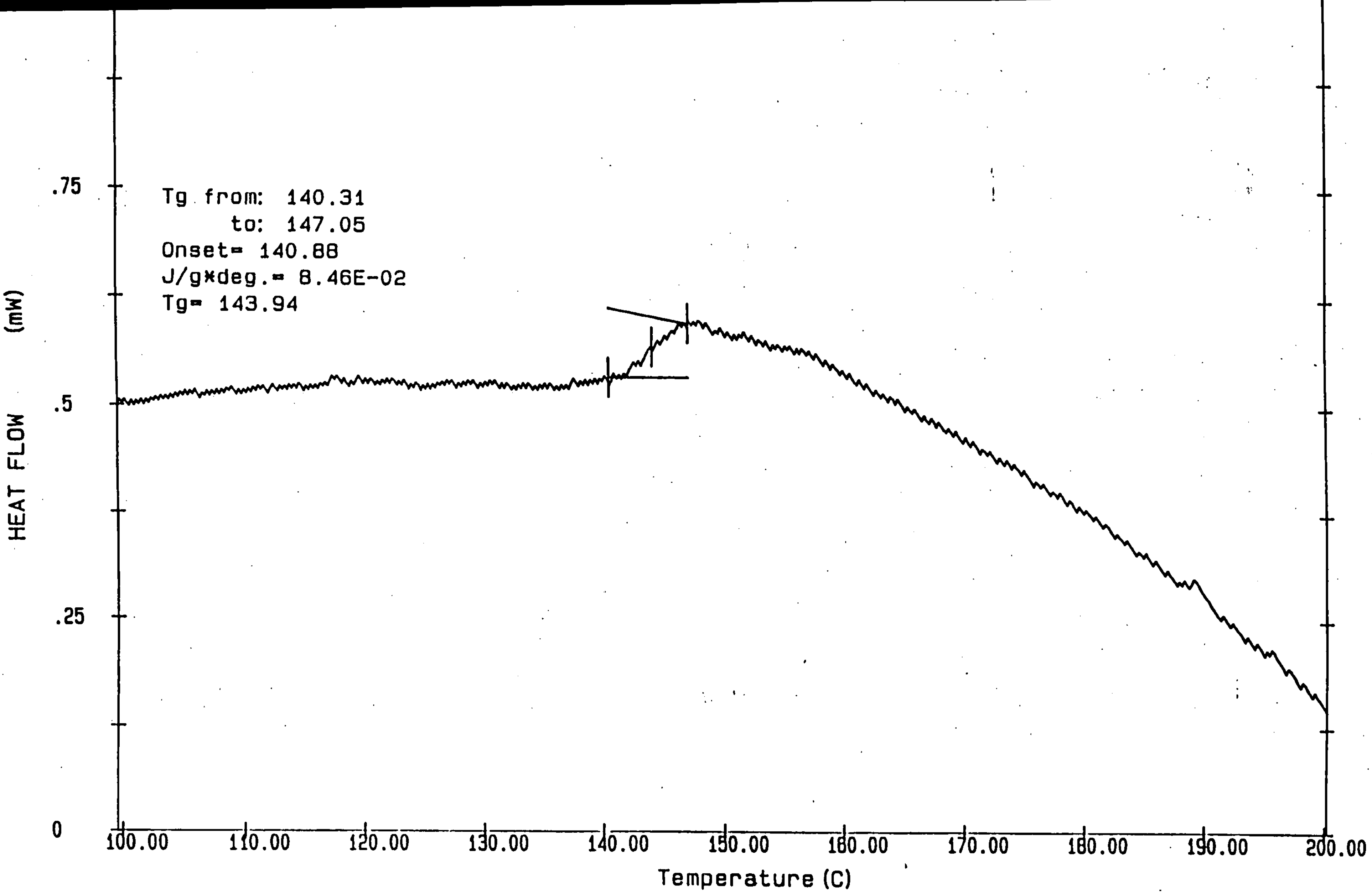
Appendix 3.7a. ^{1}H NMR spectrum of poly((bistrifluoromethyl)norbornadiene) initiated by Mo(N-2,6-Me_2-C_6H_3)($CHCMe_2Ph$)($OCMe(CF_3)_2$)$_2$.



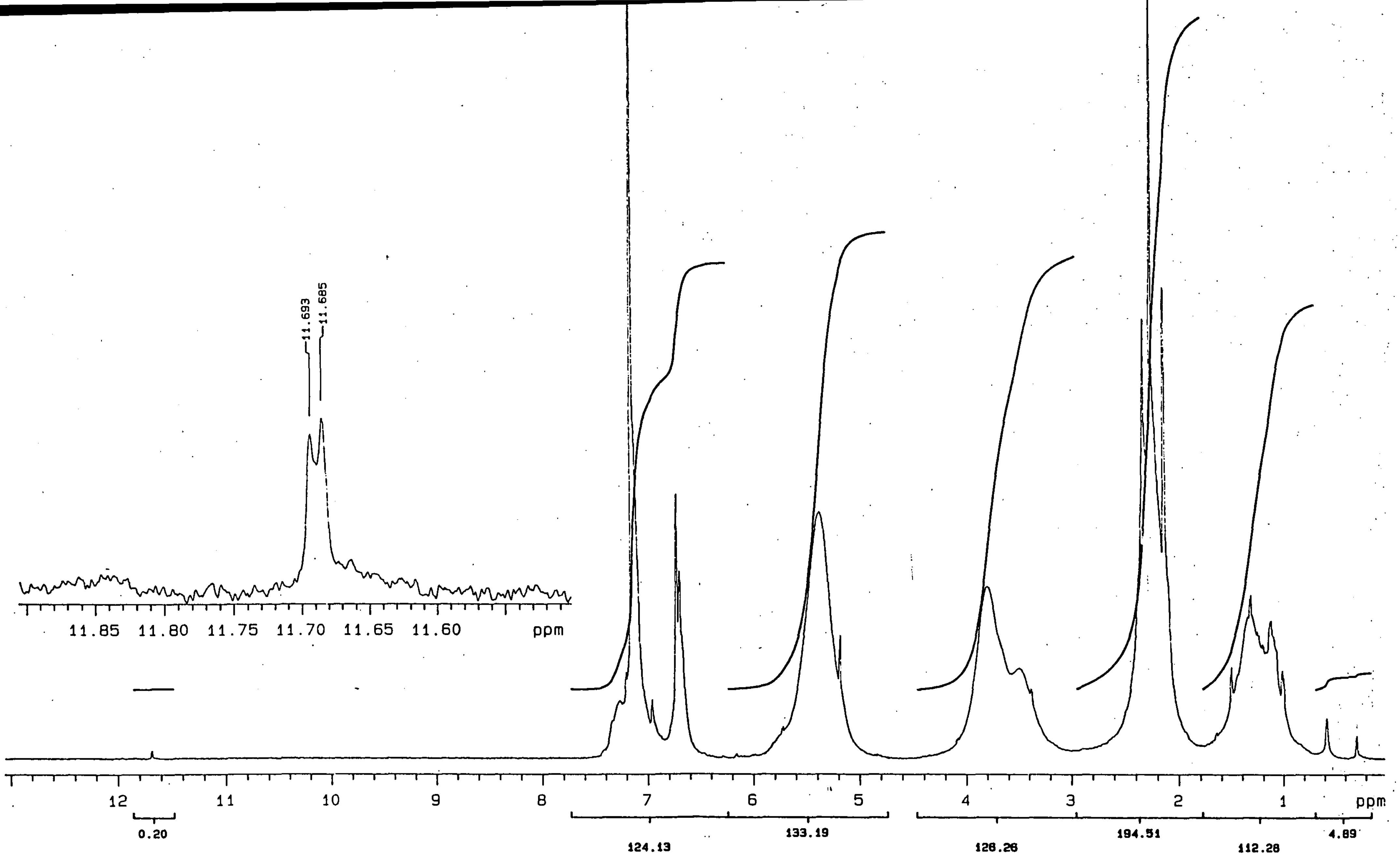
Appendix 3.7b. ^{13}C NMR spectrum of poly((bistrifluoromethyl)norbornadiene) initiated by Mo(N-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$.



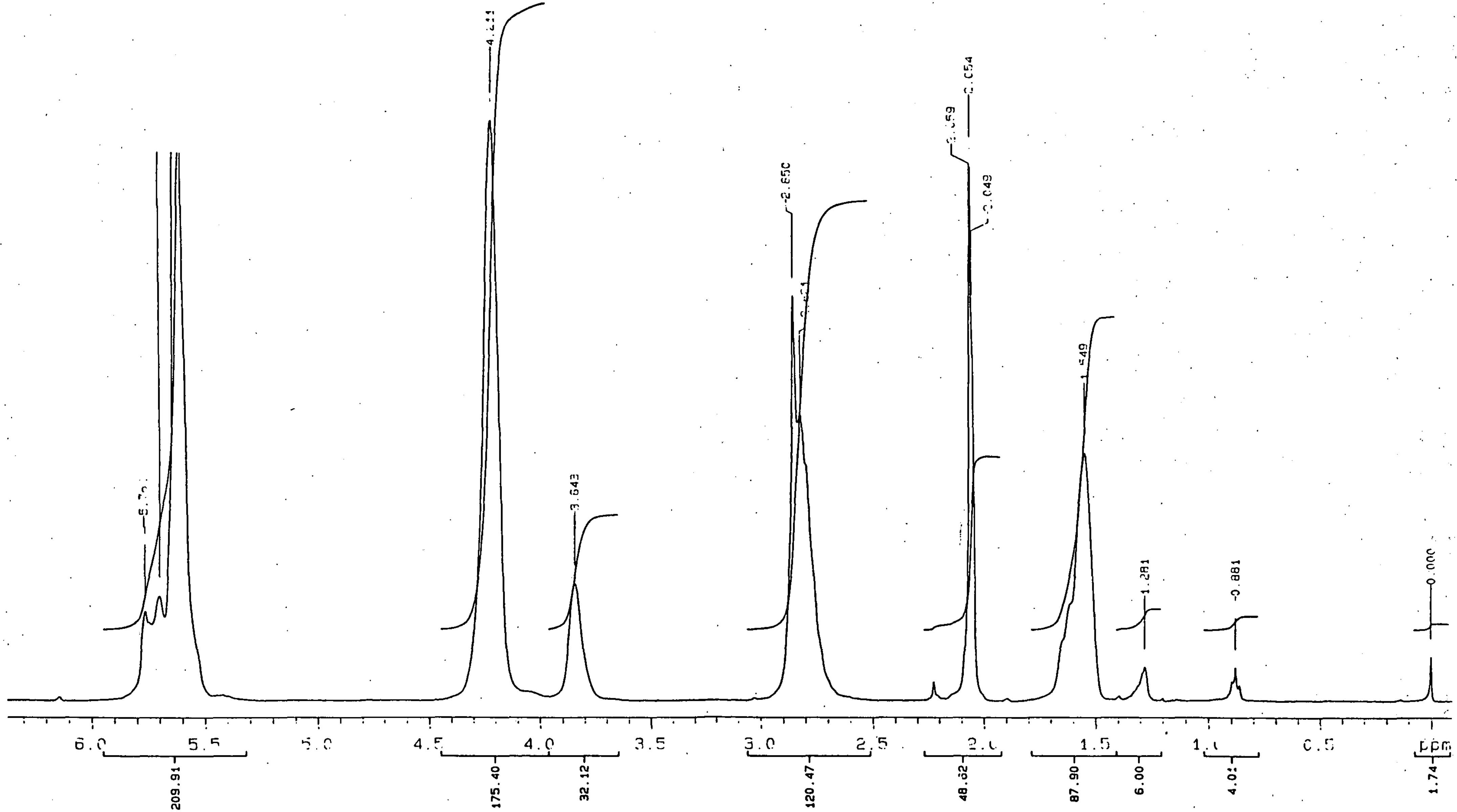
Appendix 3.7c. ^{19}F NMR spectrum of poly((bistrifluoromethyl)norbornadiene) initiated by Mo(N-2,6-Me_2-C_6H_3)($CHCMe_2Ph$)($OCMe(CF_3)_2$)$_2$



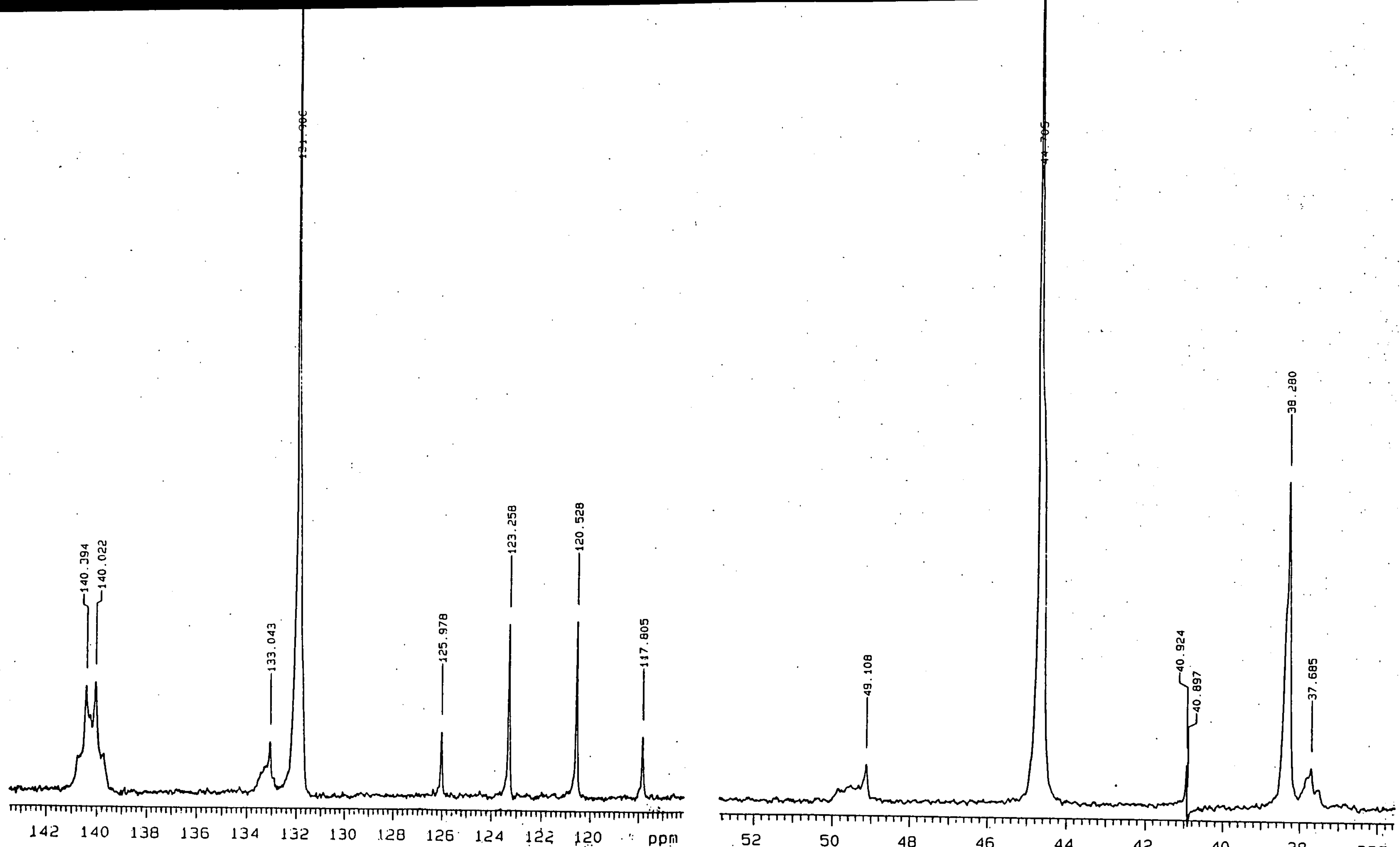
Appendix 3.7d. DSC trace of poly((bistrifluoromethyl)norbornadiene) initiated by $Mo(N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)(OCMe(CF_3)_2)_2$



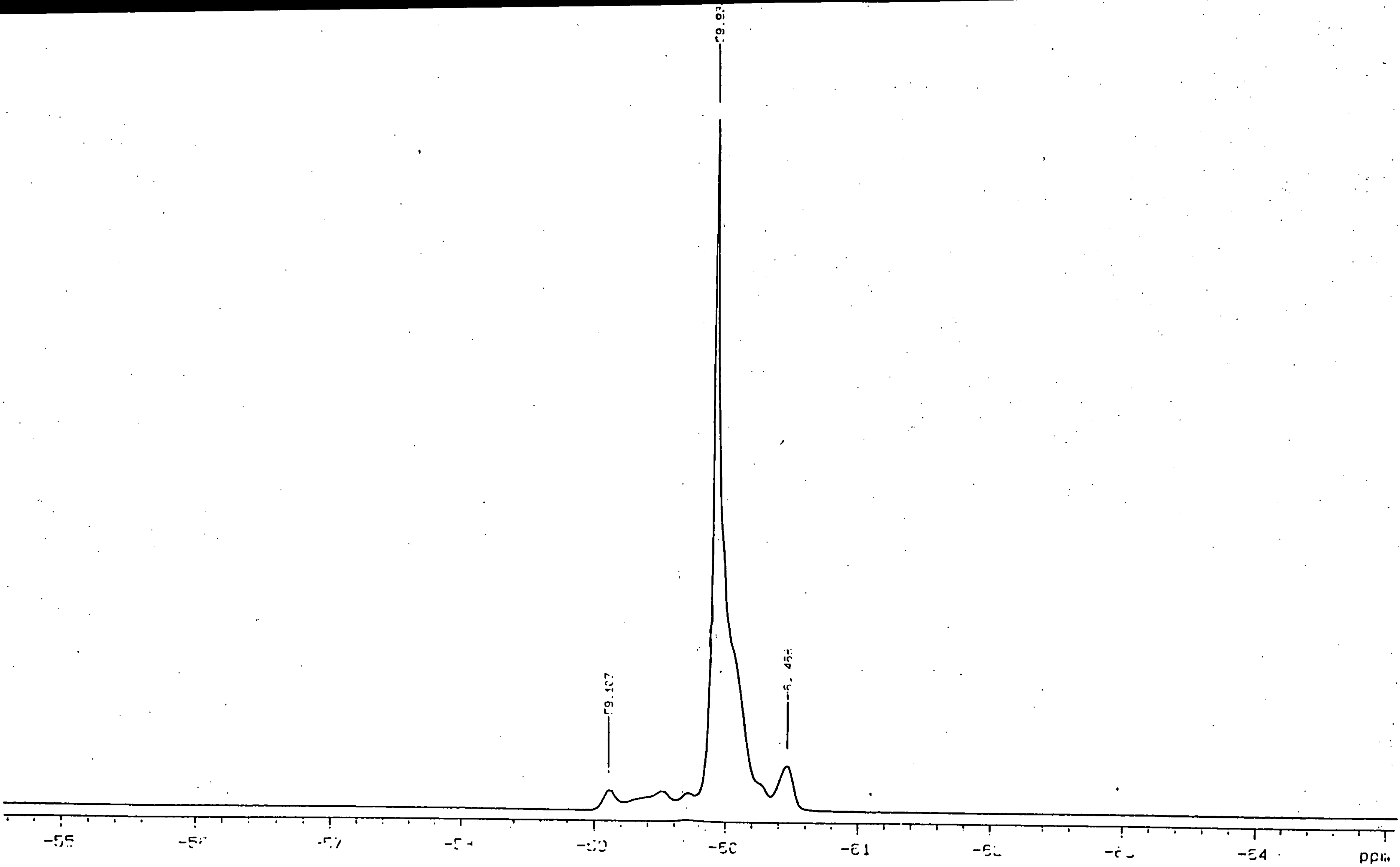
Appendix 3.8. ^1H NMR spectrum of living poly((bistrifluoromethyl)norbornadiene) initiated by $Mo(NAr)(CHCMe_2Ph)(OB(mes)_2)$



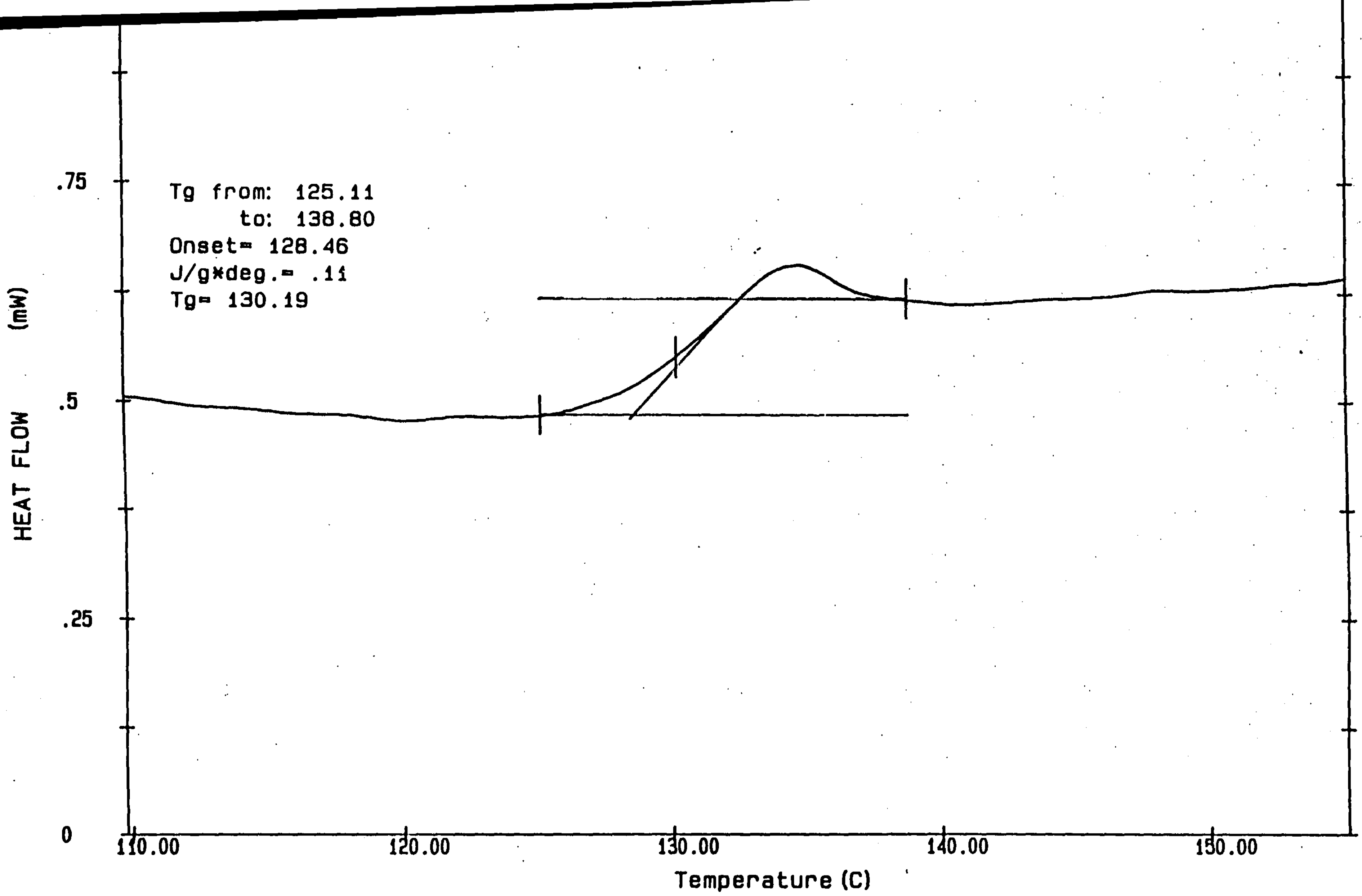
Appendix 3.9a. ^{1}H NMR spectrum of poly((bistrifluoromethyl)norbornadiene) initiated by Mo(NAr)(CHCMe$_2$Ph)(OB(mes)$_2$)



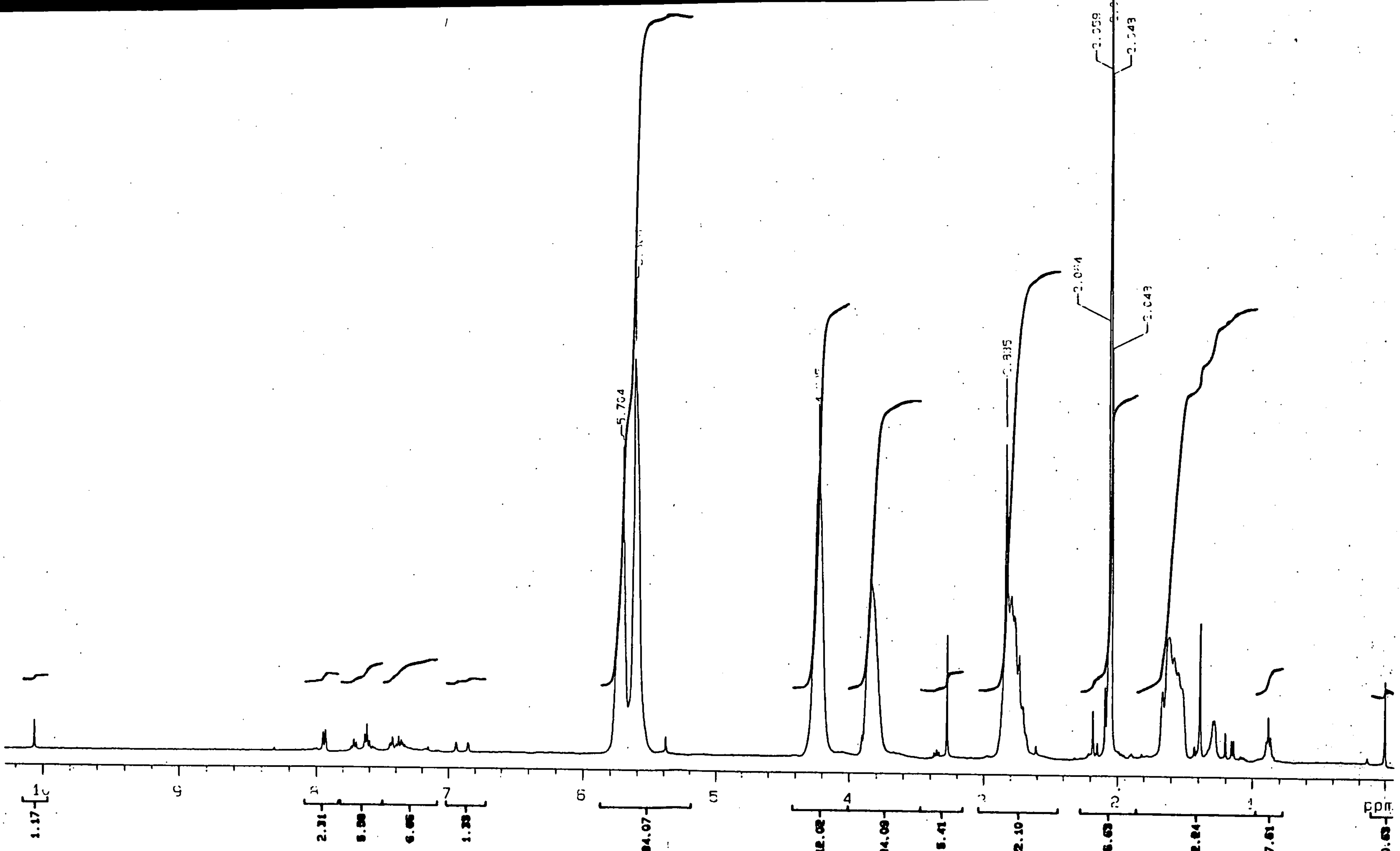
Appendix 3.9b. ^{13}C NMR spectrum of poly((bistrifluoromethyl)norbornadiene) initiated by Mo(NAr)(CHCMe$_2$Ph)(OB(mes)$_2$)



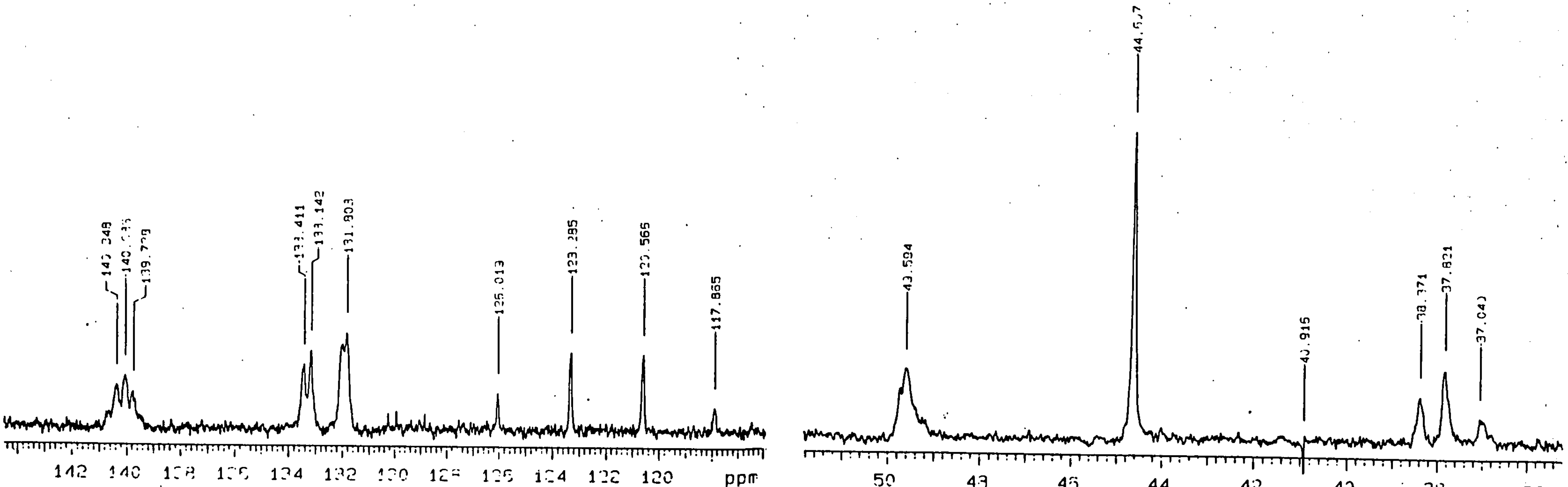
Appendix 3.9c. ^{19}F NMR spectrum of poly((bistrifluoromethyl)norbornadiene) initiated by Mo(NAr)(CHCMe$_2$Ph)(OB(mes)$_2$)



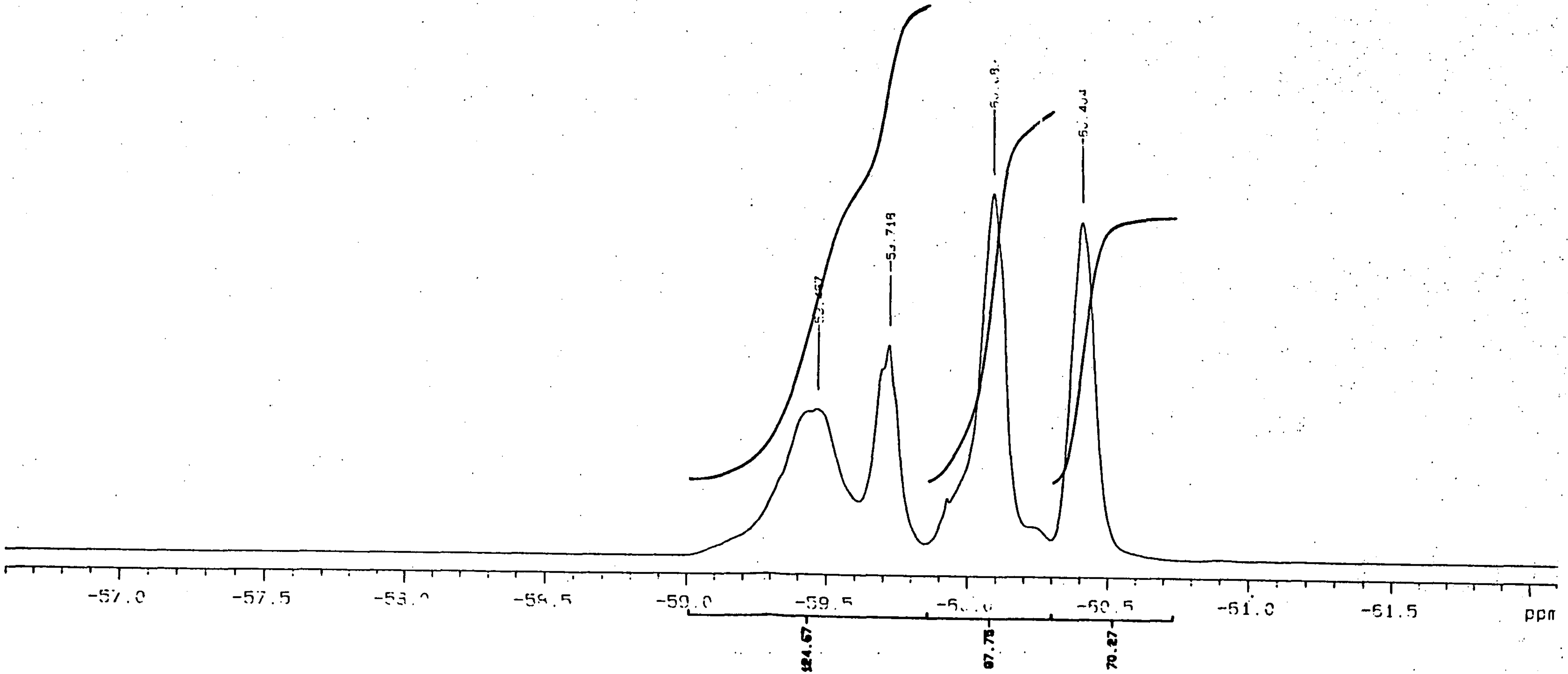
Appendix 3.9d. DSC trace of poly((bistrifluoromethyl)norbornadiene) initiated by $Mo(NAr)(CHCMe_2Ph)(OB(mes)_2)$



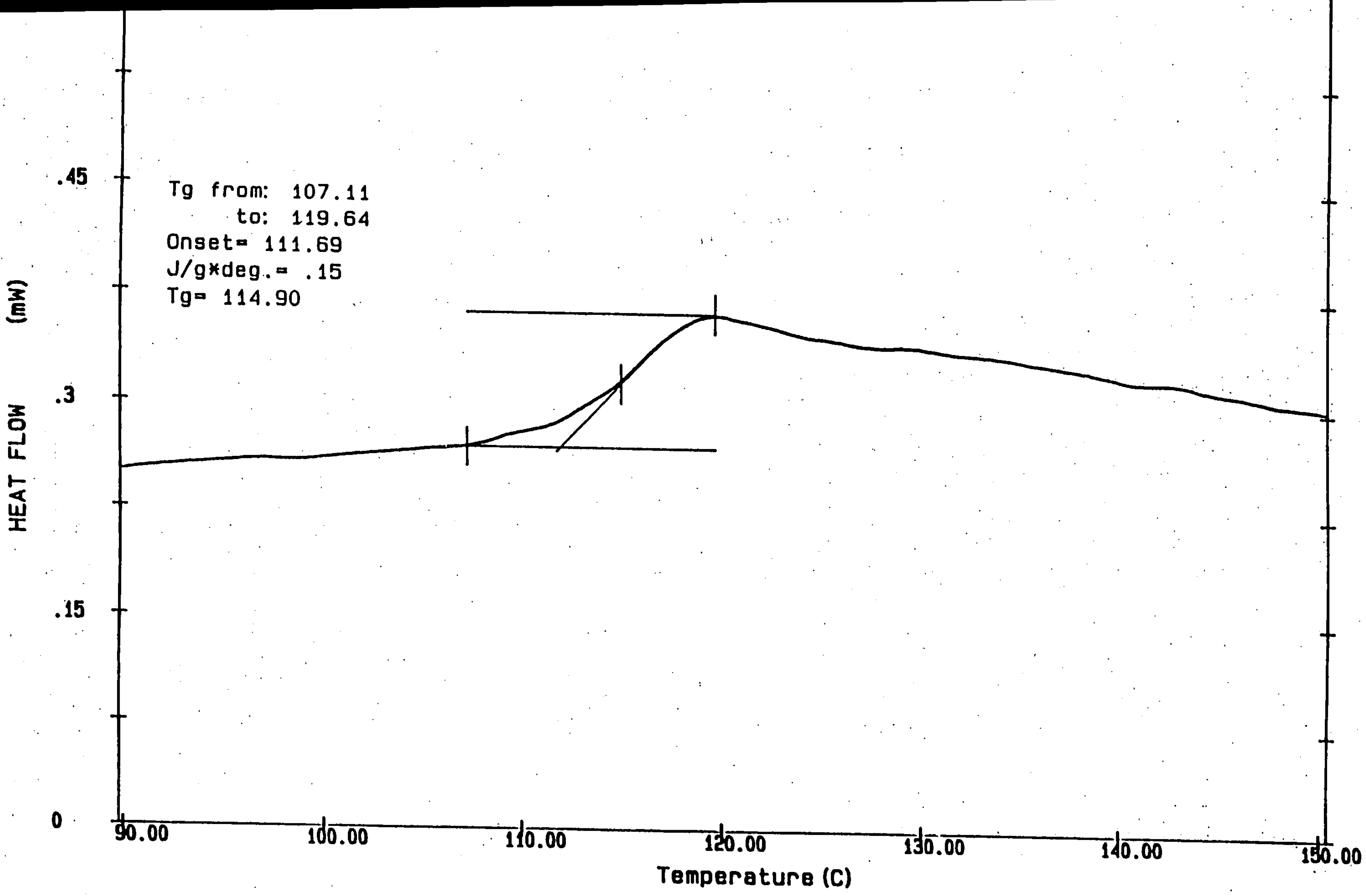
Appendix 3.10a. ^{1}H NMR spectrum of poly((bistrifluoromethyl)norbornadiene) initiated by Mo(NAr)(CHCMe$_2$Ph)(vulkanox)(CH$_3$CN)



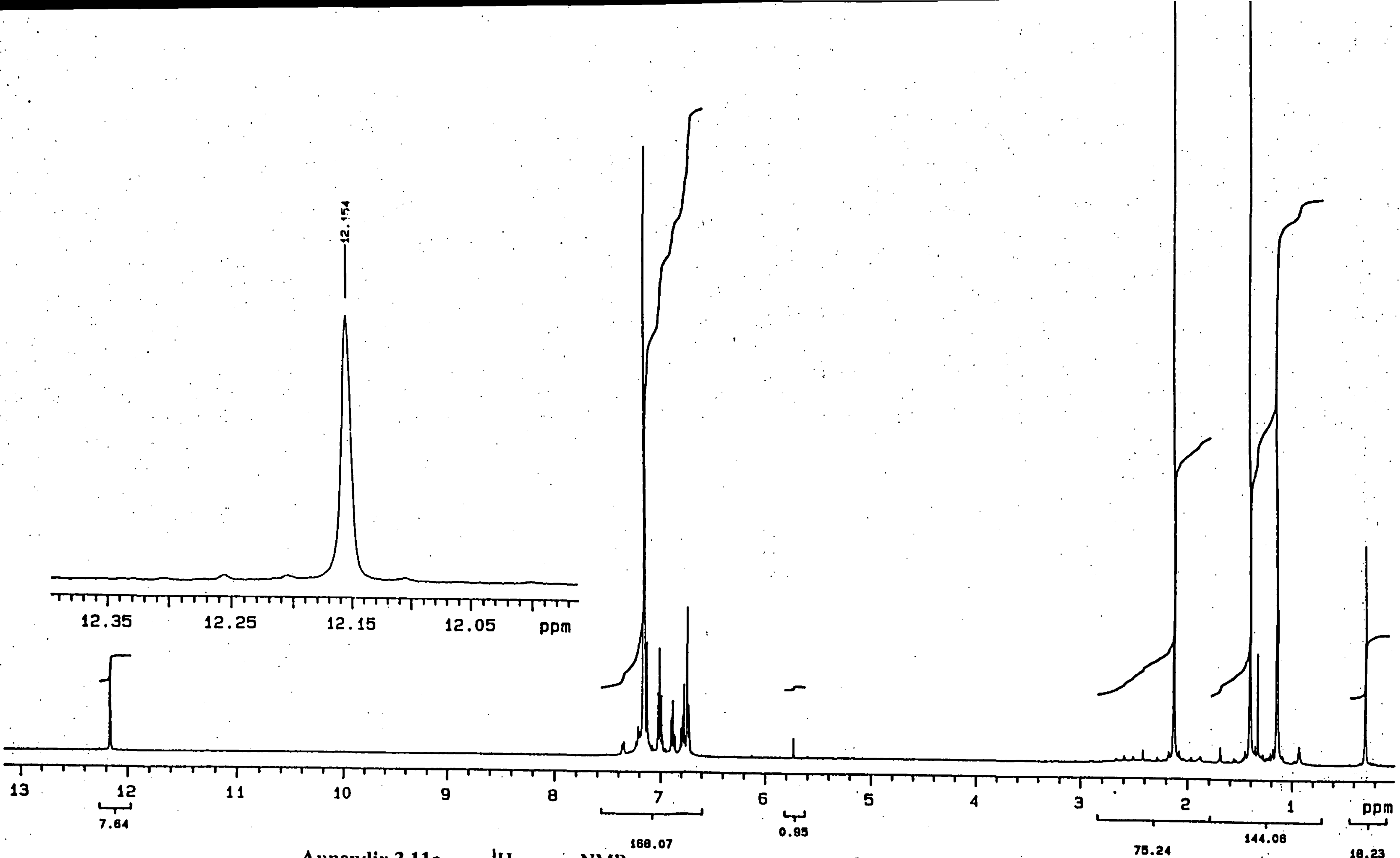
Appendix 3.10b. ^{13}C NMR spectrum of poly((bistrifluoromethyl)norbornadiene) initiated by Mo(NAr)(CHCMe$_2$Ph)(vulkanox)(CH$_3$CN)



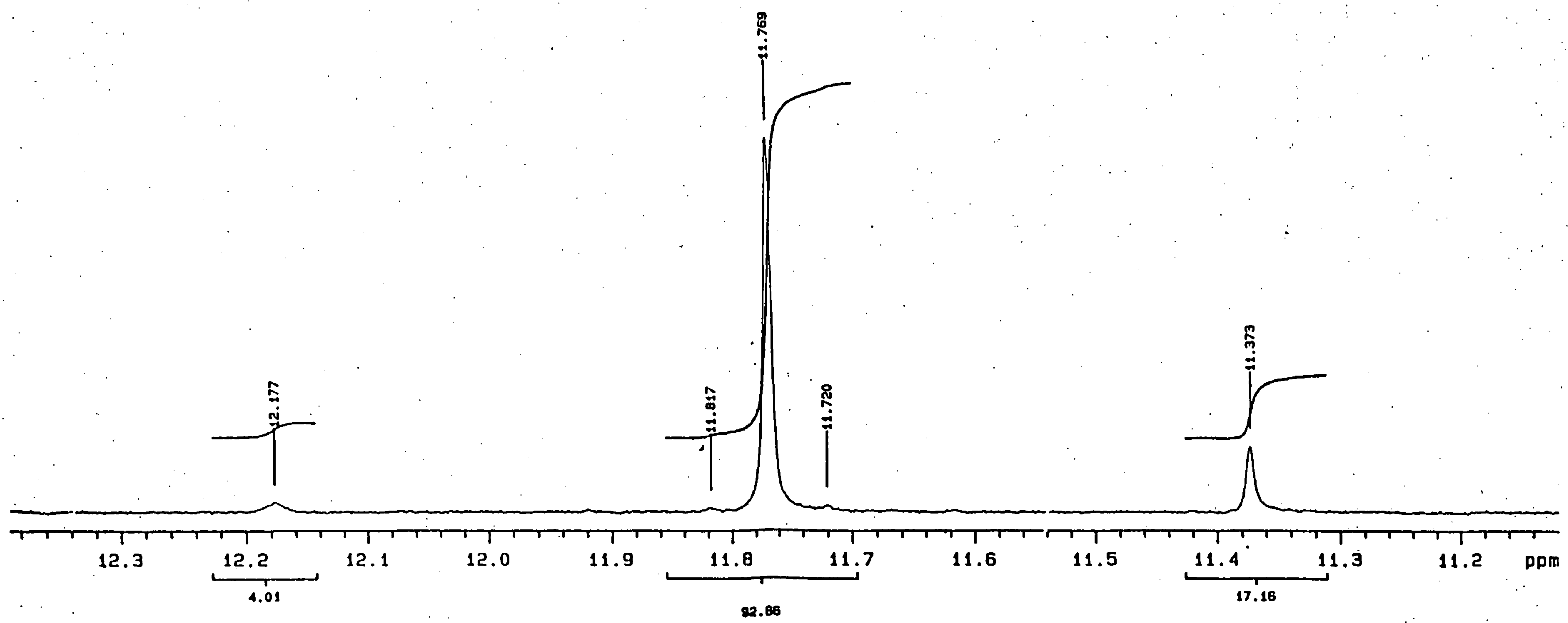
Appendix 3.10c. ^{19}F NMR spectrum of poly((bistrifluoromethyl)norbornadiene) initiated by Mo(NAr)(CHCMe$_2$Ph)(vulkanox)(CH$_3$CN)



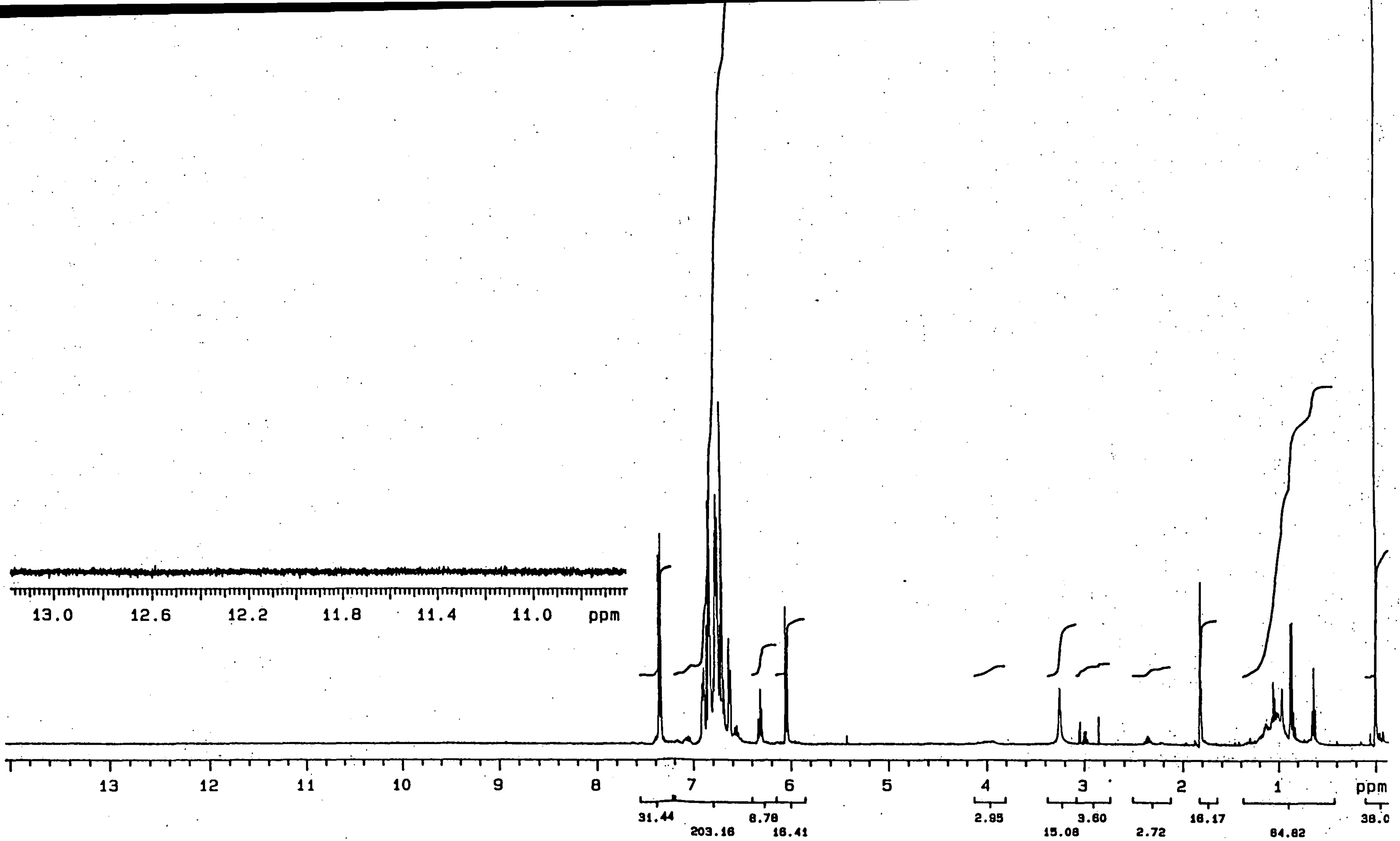
Appendix 3.10d. DSC trace of poly((bistrifluoromethyl)norbornadiene) initiated by Mo(NAr)(CHCMe$_2$Ph)(vulkanox)(CH$_3$CN)



Appendix 3.11a. ^{1}H NMR spectrum of Mo(N-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ with no t-butanol added



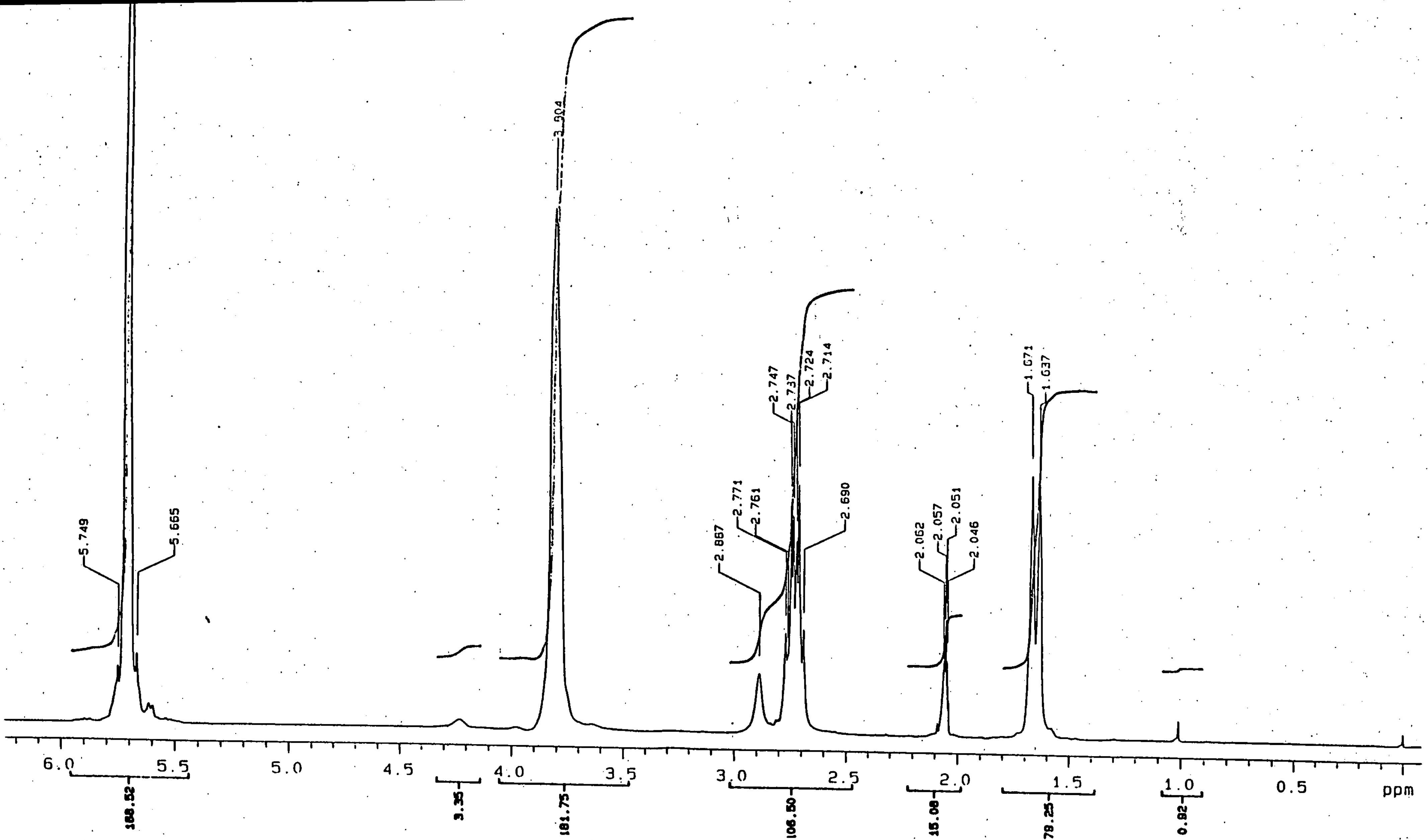
Appendix 3.11b. ^{1}H NMR spectrum (after 46 hours) of Mo(N-2,6-Me_2-C_6H_3)($CHCMe_2Ph$)($OCMe(CF_3)_2$)$_2$ with 2 equivalents of t-butanol added



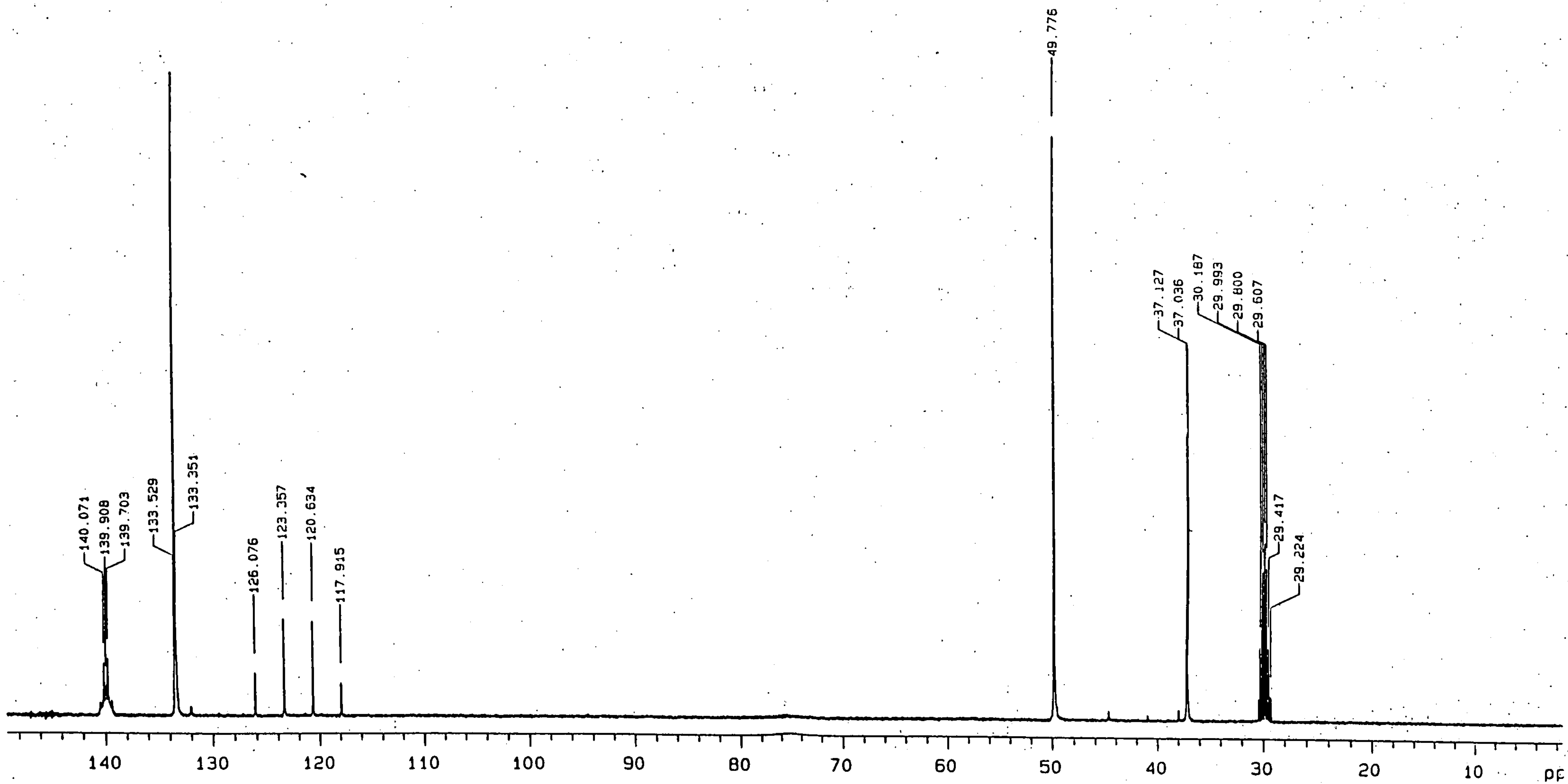
Appendix 3.12. ^{1}H NMR spectrum of the living polymerisation of norbornene initiated by $Mo(NAr)(CHCMe_2Ph)(2,6\text{-}(OCPh_2CH_2)_2C_5H_3N)$

Appendix 4

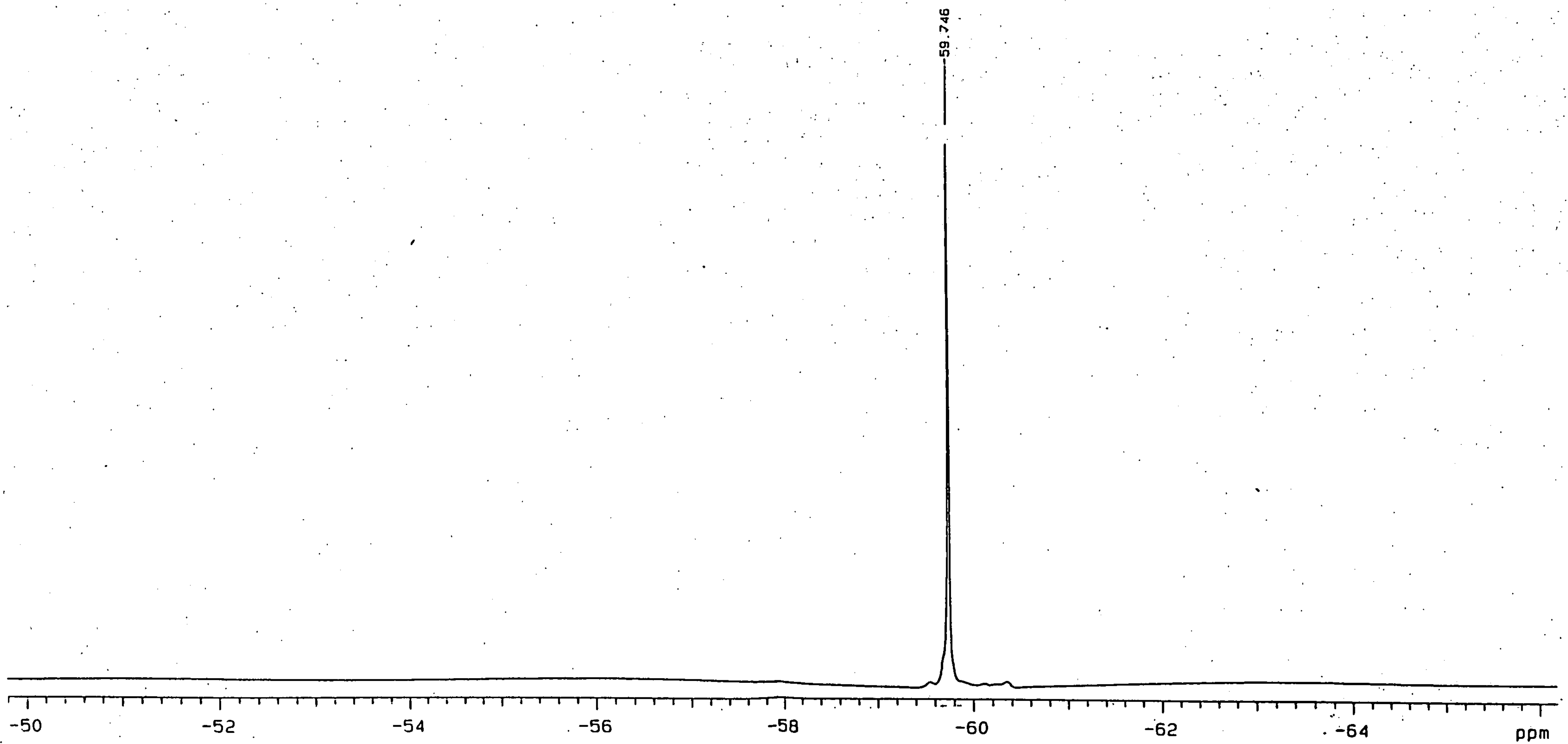
Analytical data for Chapter 4



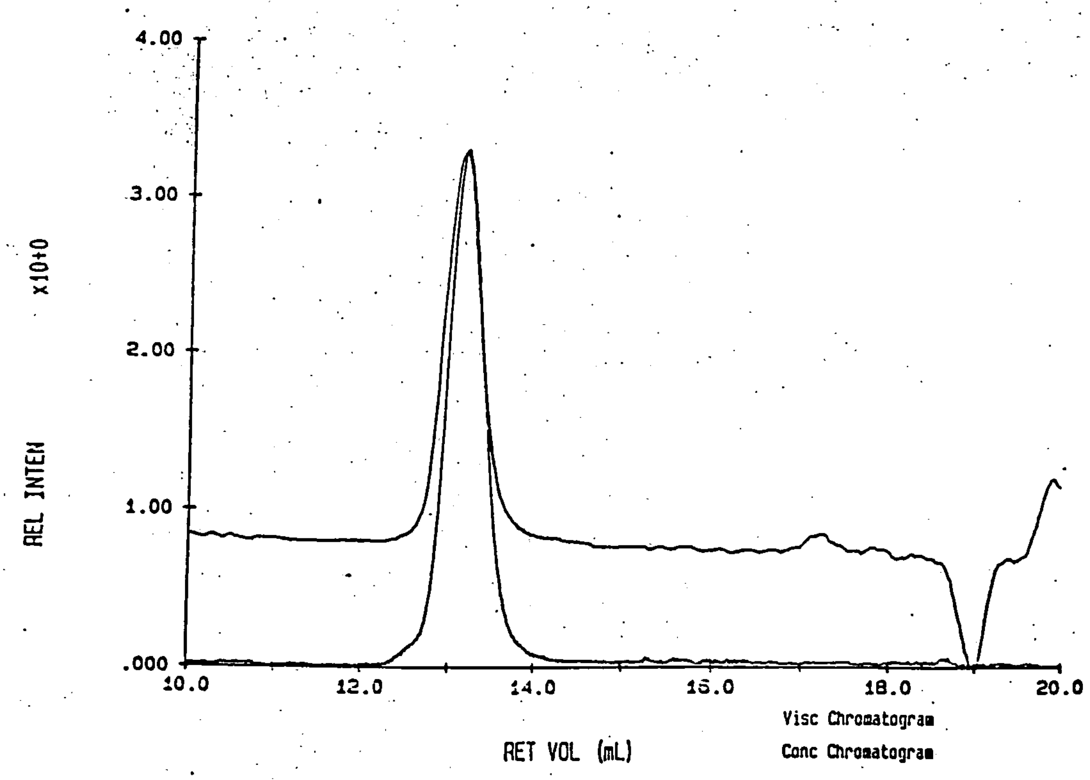
Appendix 4.1a. ^{1}H NMR spectrum of a high trans, highly tactic poly((bistrifluoromethyl)norbornadiene) sample.



Appendix 4.1b. ^{13}C NMR spectrum of a high trans, highly tactic poly((bistrifluoromethyl)norbornadiene) sample.



Appendix 4.1c. ^{19}F NMR spectrum of a high trans, highly tactic poly((bistrifluoromethyl)norbornadiene) sample.



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/ISCOMETER OFFSET (mL)          -.014         Mn(no RI)=         2.065E   5
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\CQ. STOP TIME (min)           20.000         POLYDISPERSITY RATIOS
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;IGMA (mL)                       .177         Mz/Mn =               1.038
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'HRESHOLD                        .020         SKEW(w) =             11.913

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1ARK-HOUWINK CONSTANTS
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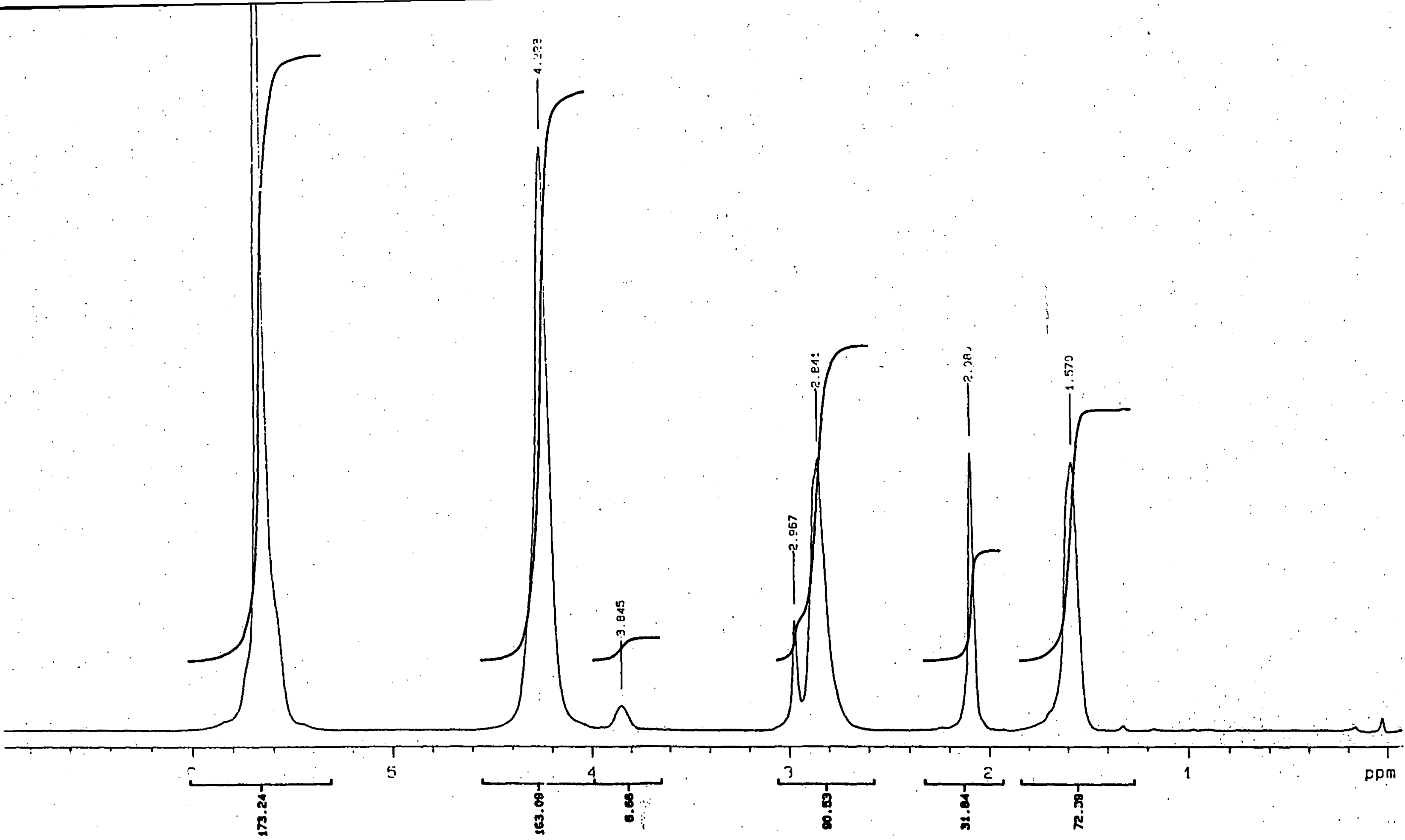
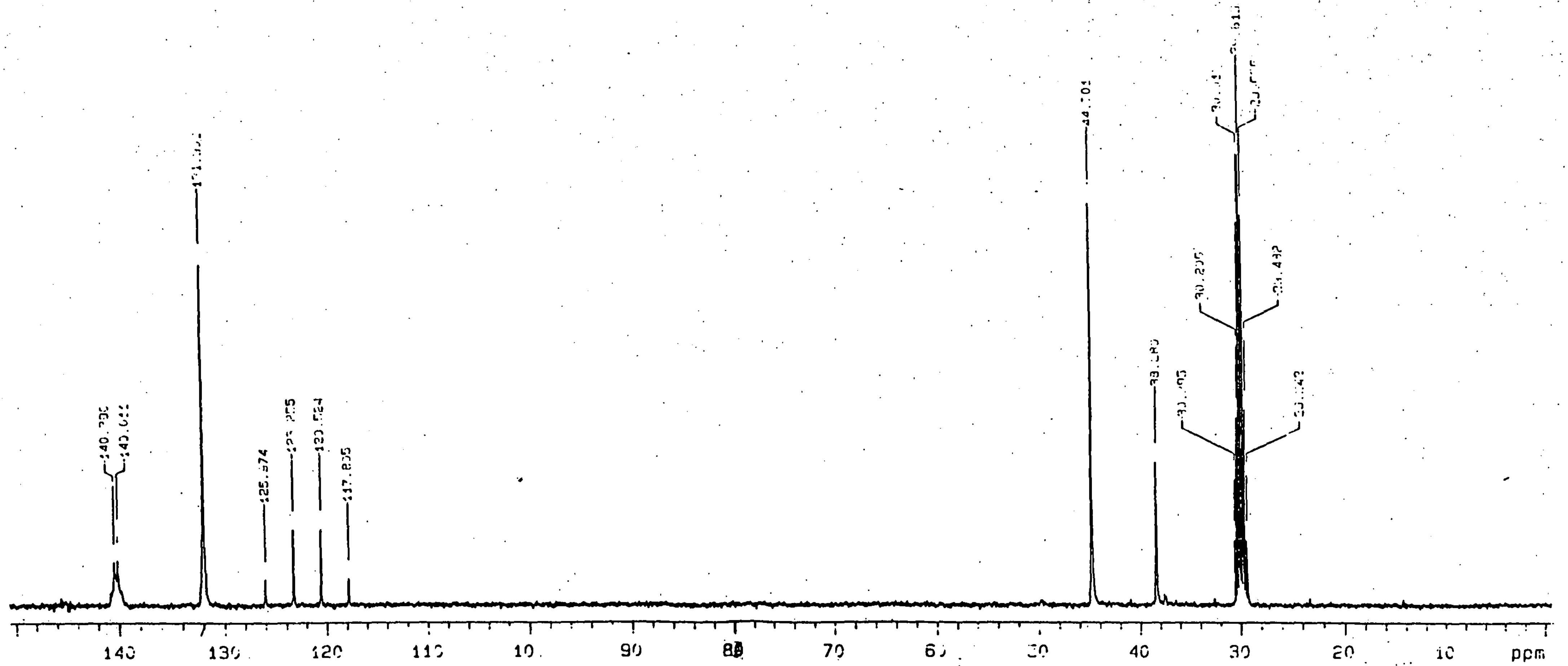
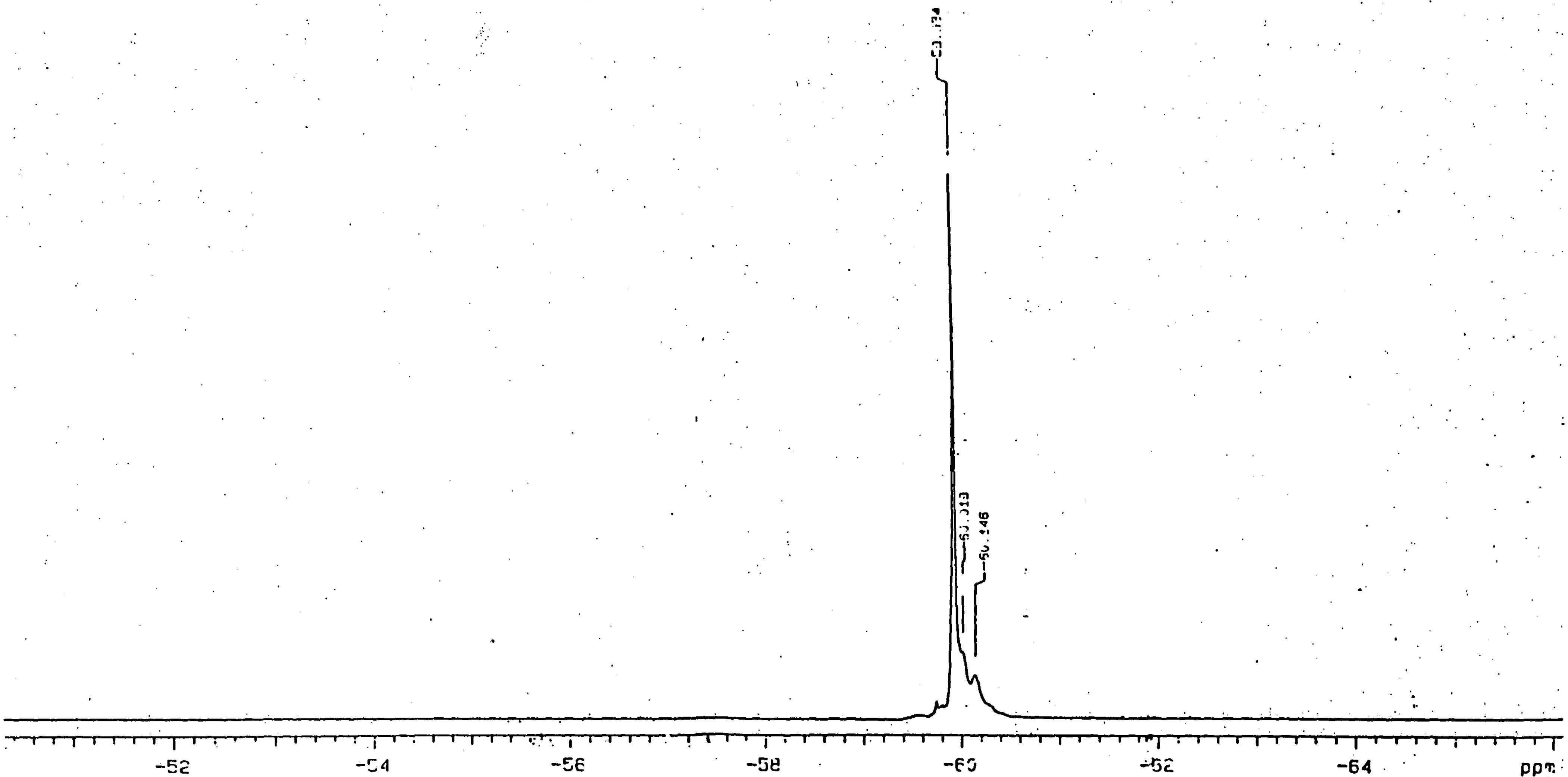
Appendix 4.1d. GPC trace of a high trans, highly tactic poly((bistrifluoromethyl)norbornadiene) sample.



Appendix 4.2a. ^{1}H NMR spectrum of a high cis, highly tactic poly((bistrifluoromethyl)norbornadiene) sample.



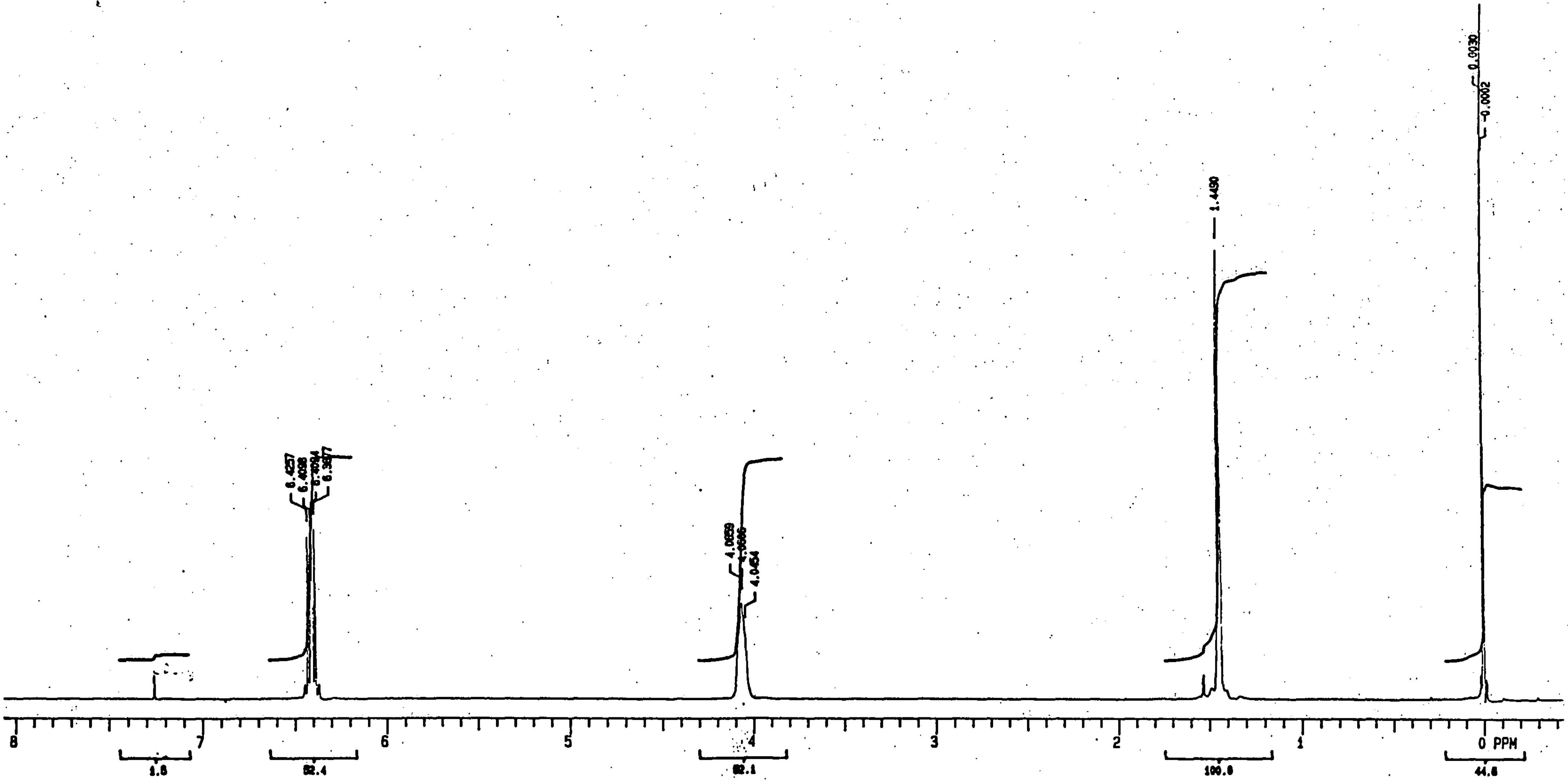
Appendix 4.2b. ^{13}C NMR spectrum of a high cis, highly tactic poly((bistrifluoromethyl)norbornadiene) sample.



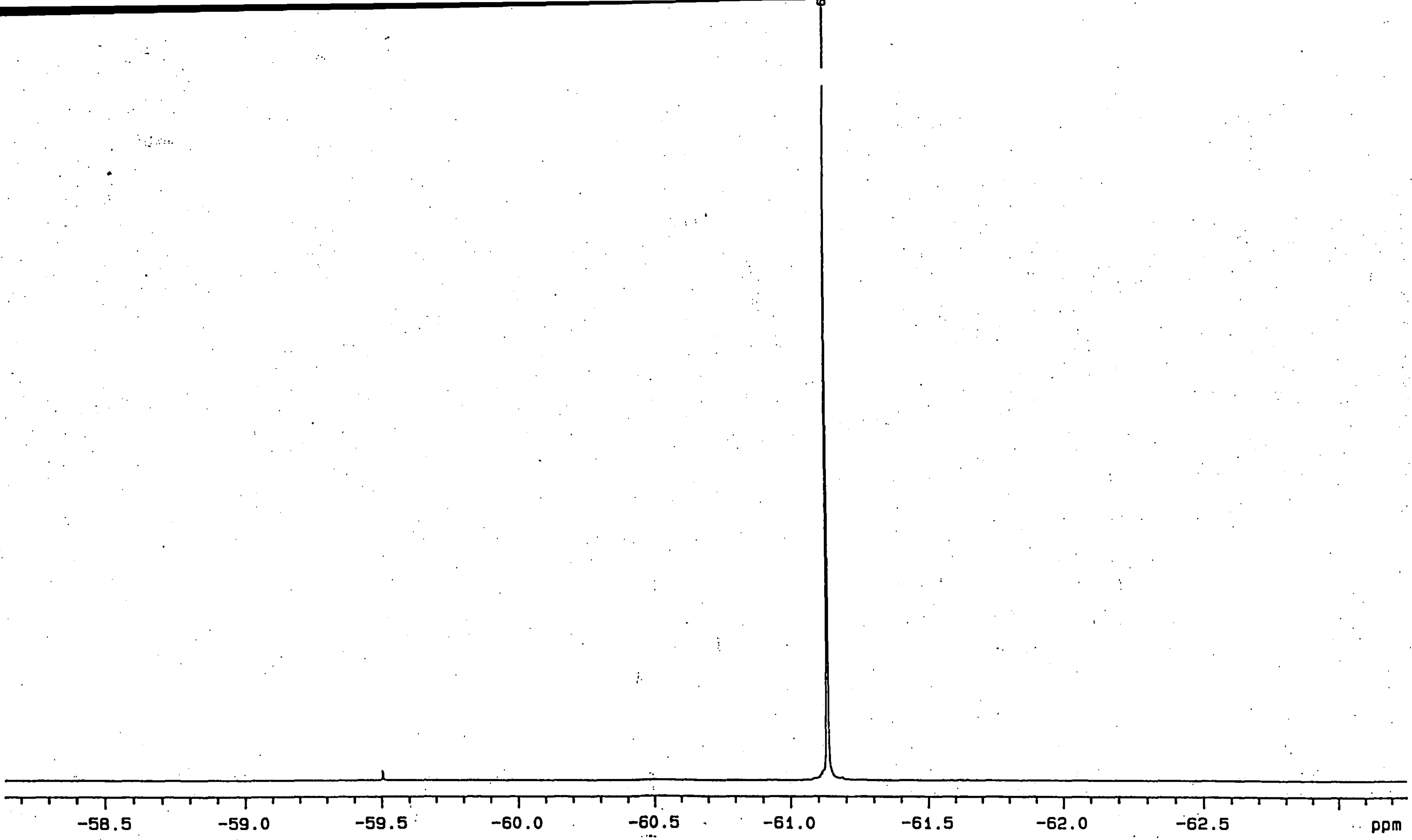
Appendix 4.2c. ^{19}F NMR spectrum of a high cis, highly tactic poly((bistrifluoromethyl)norbornadiene) sample.

Appendix 5

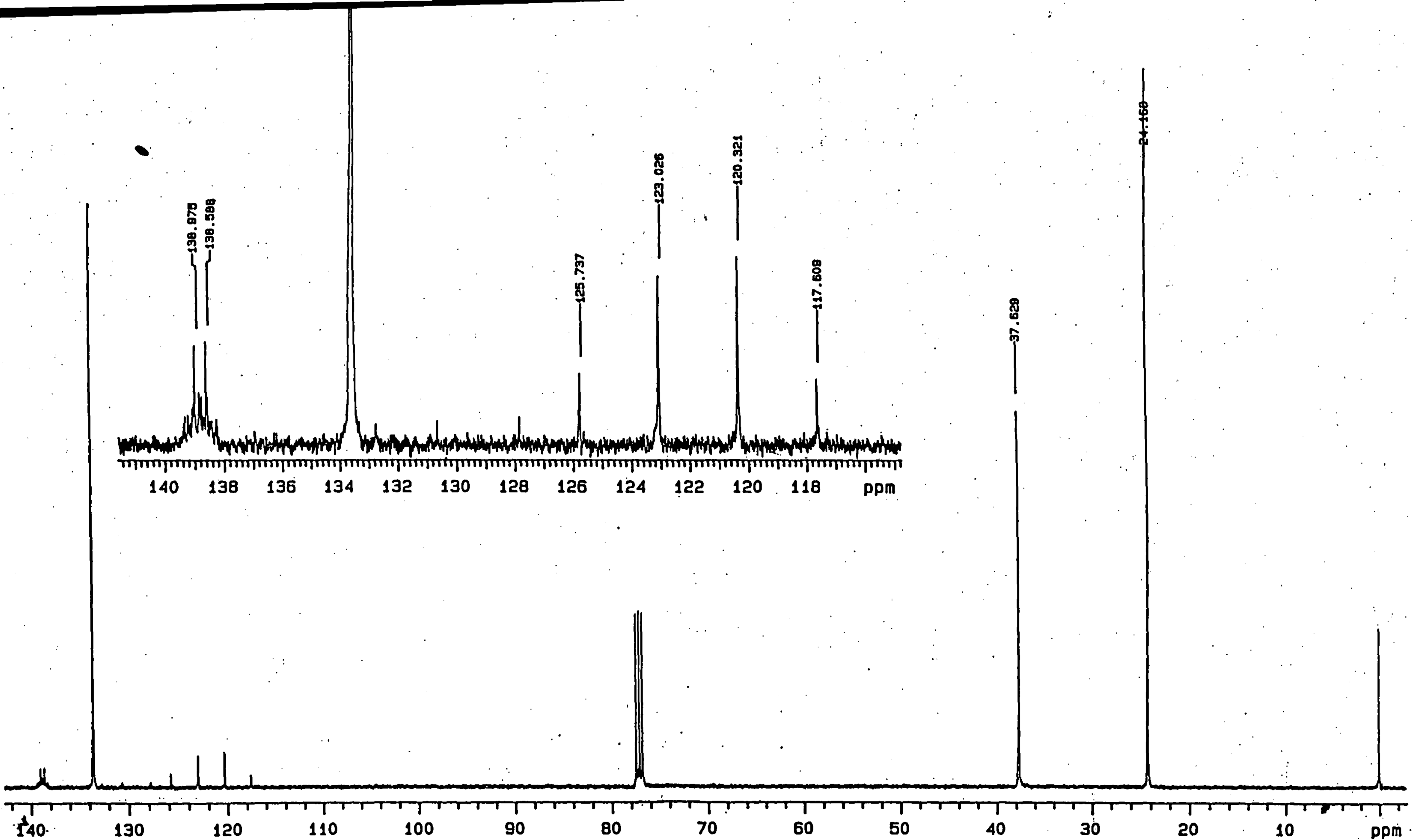
Analytical data for Chapter 5



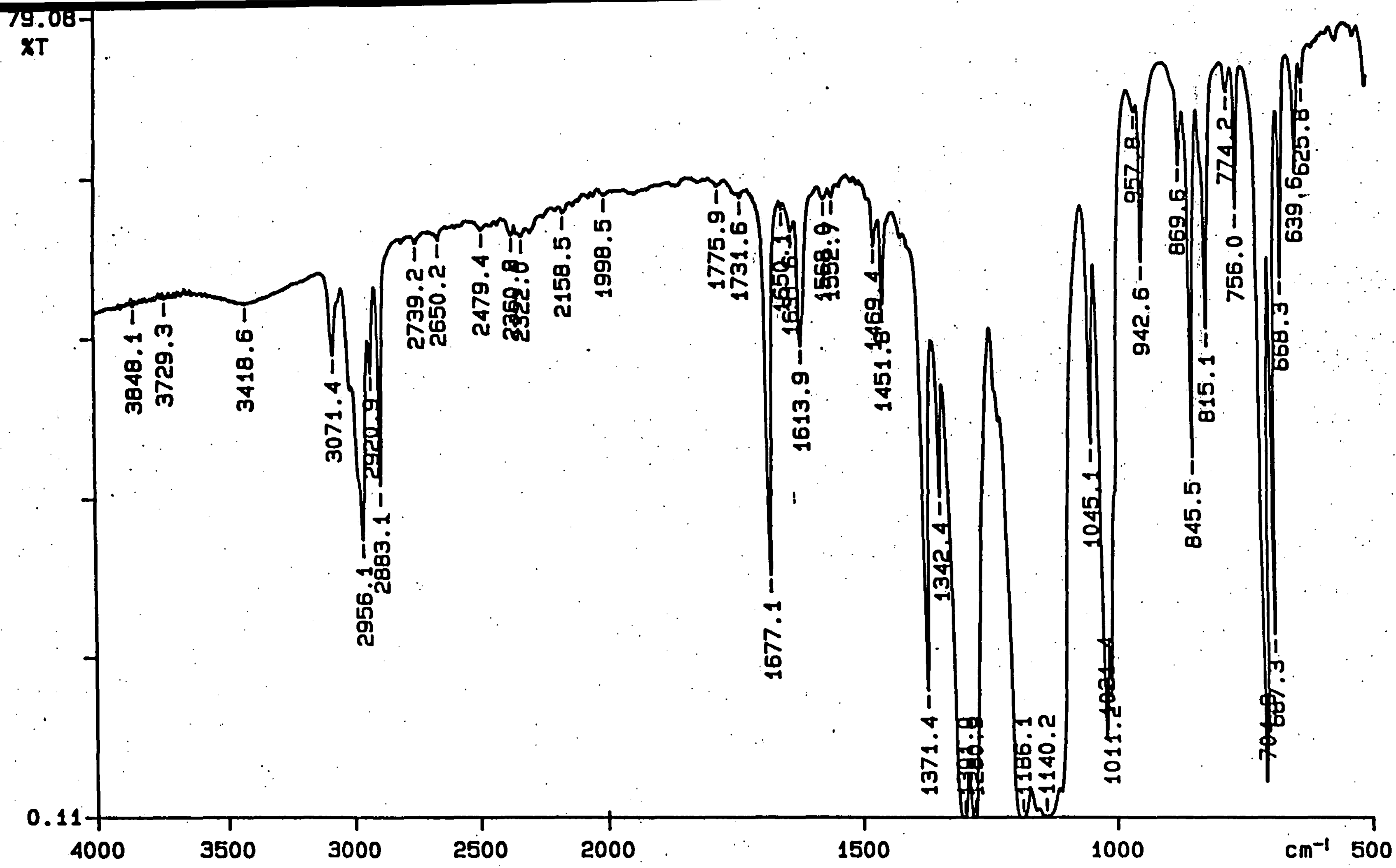
Appendix 5.1a ^{1}H NMR spectrum of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene.



Appendix 5.1b. ^{19}F NMR spectrum of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene.

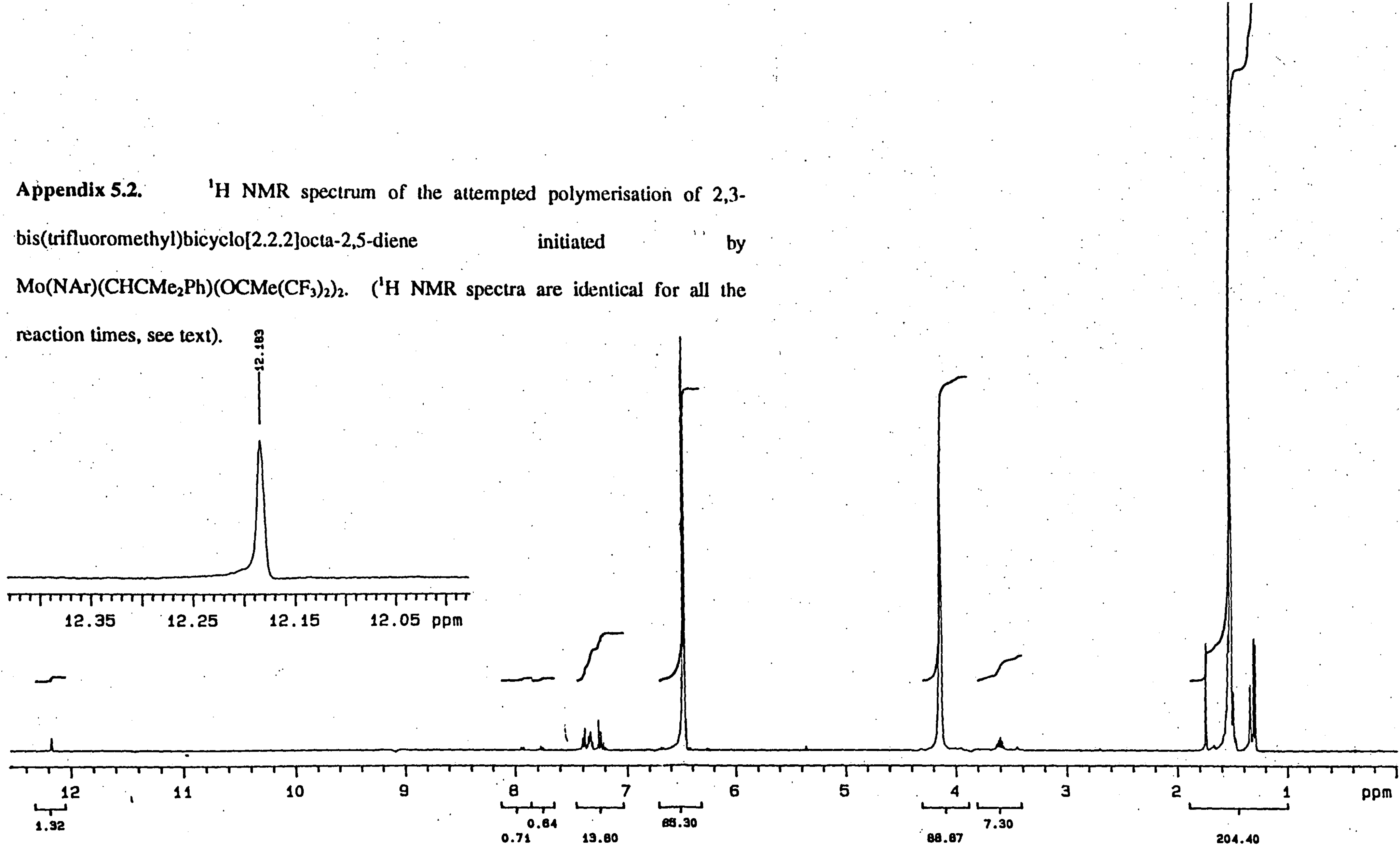


Appendix 5.1c. ^{13}C NMR spectrum of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene.

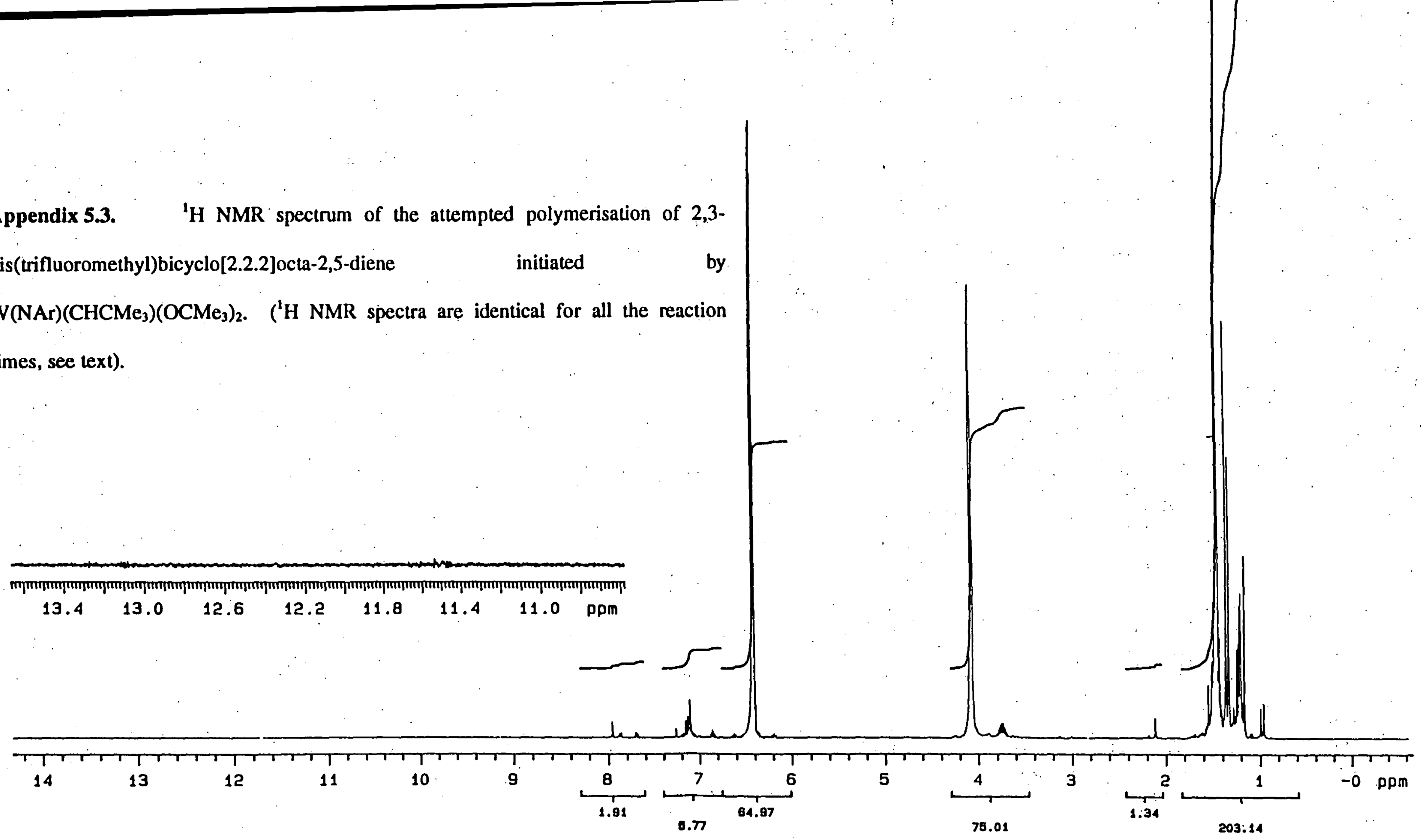


Appendix 5.1d. FTIR spectrum of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene.

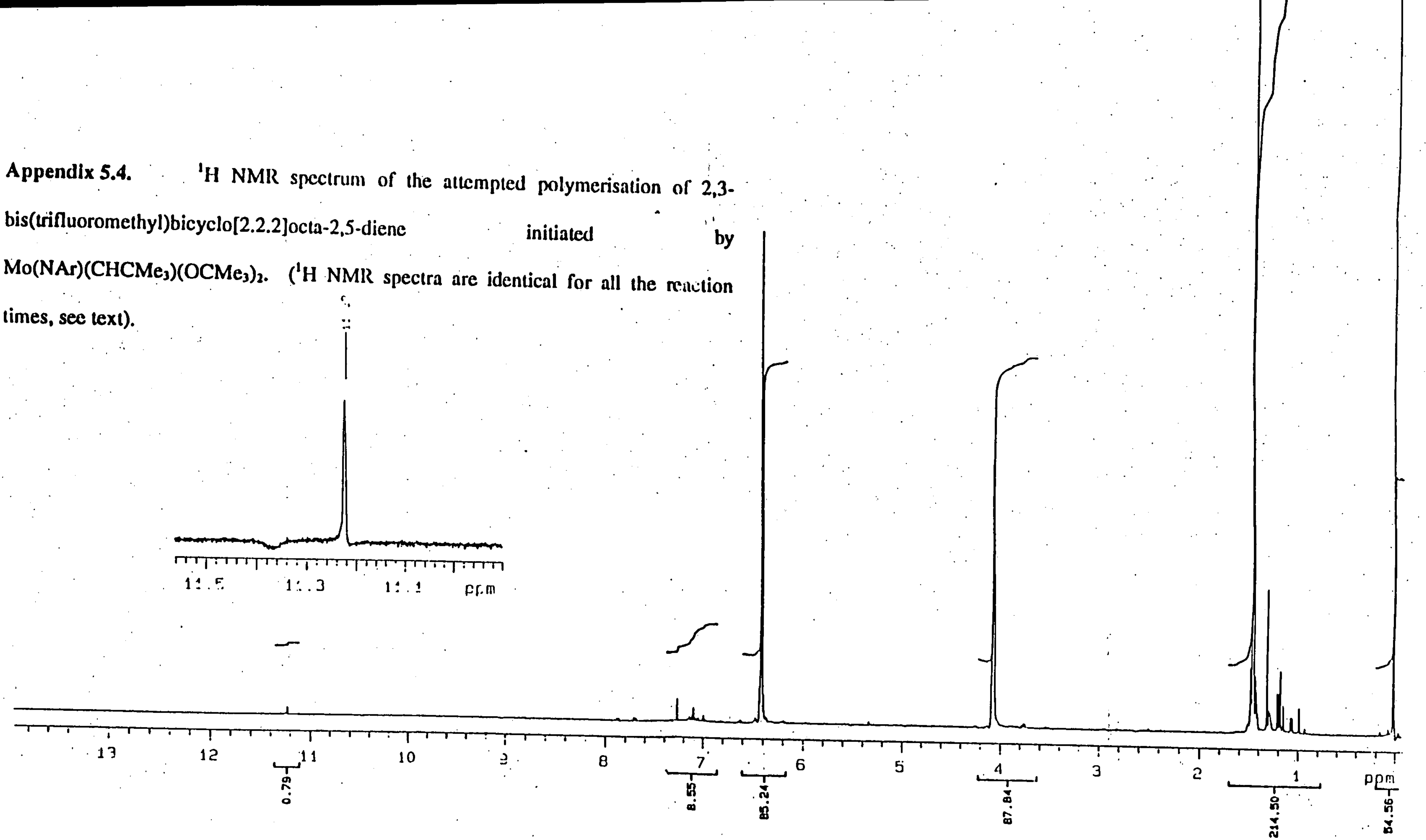
Appendix 5.2. ^1H NMR spectrum of the attempted polymerisation of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene initiated by $Mo(NAr)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$. ($^1H$ NMR spectra are identical for all the reaction times, see text).

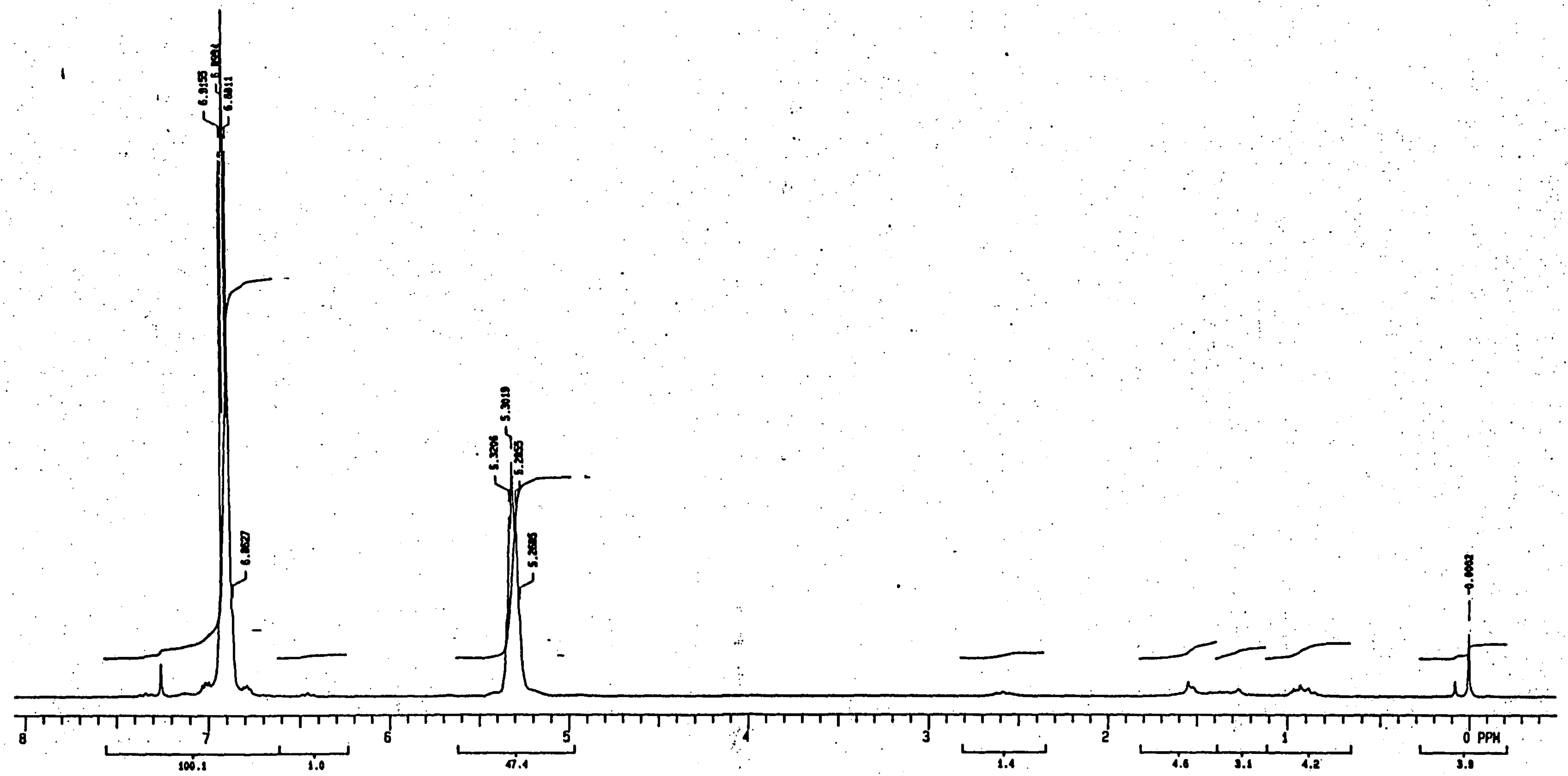


Appendix 5.3. ^1H NMR spectrum of the attempted polymerisation of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene initiated by $W(NAr)(CHCMe_3)(OCMe_3)_2$. ($^1H$ NMR spectra are identical for all the reaction times, see text).

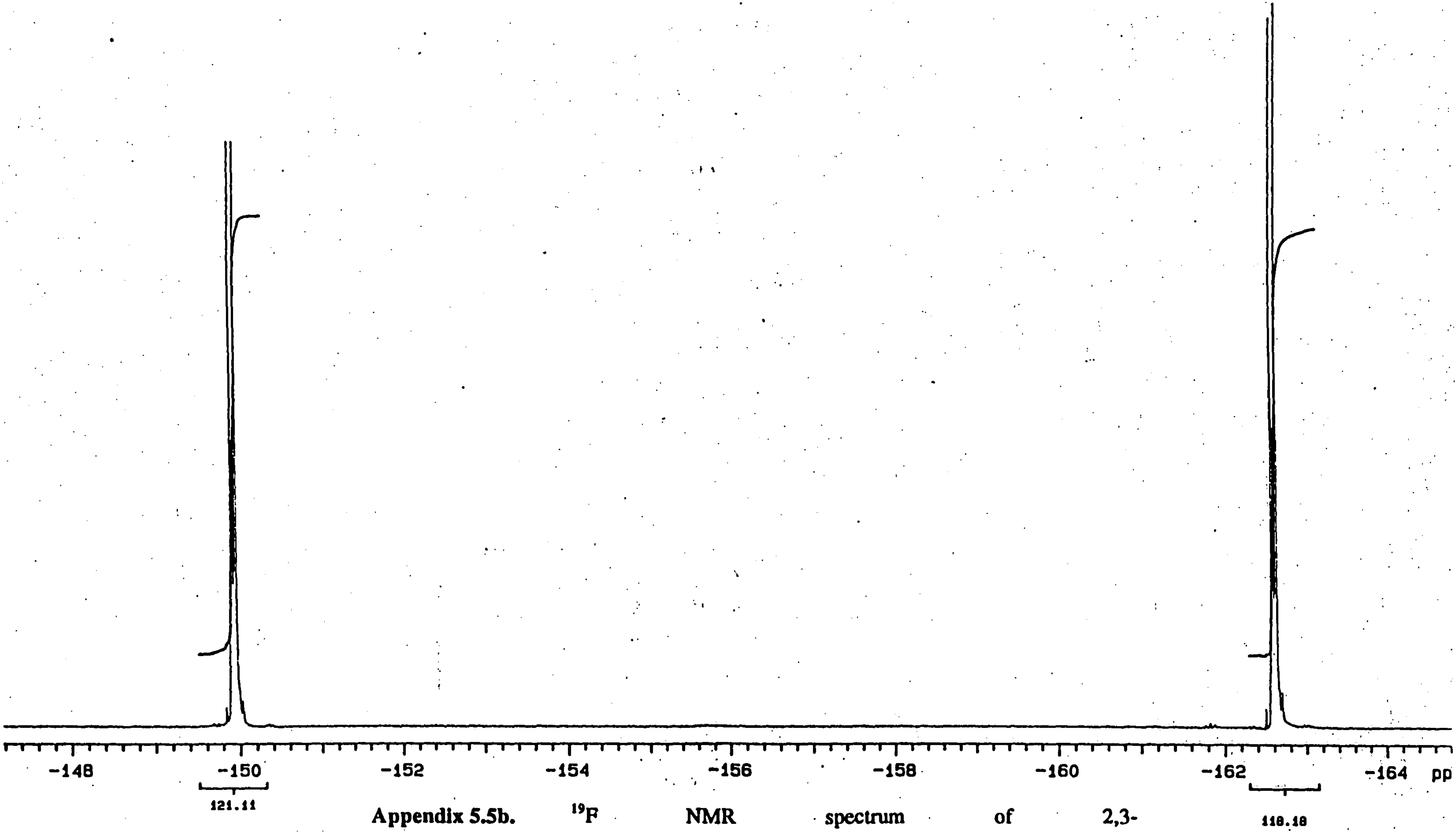


Appendix 5.4. ^{1}H NMR spectrum of the attempted polymerisation of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene initiated by Mo(NAr)(CHCMe$_3$)(OCMe$_3$)$_2$. (^{1}H NMR spectra are identical for all the reaction times, see text).

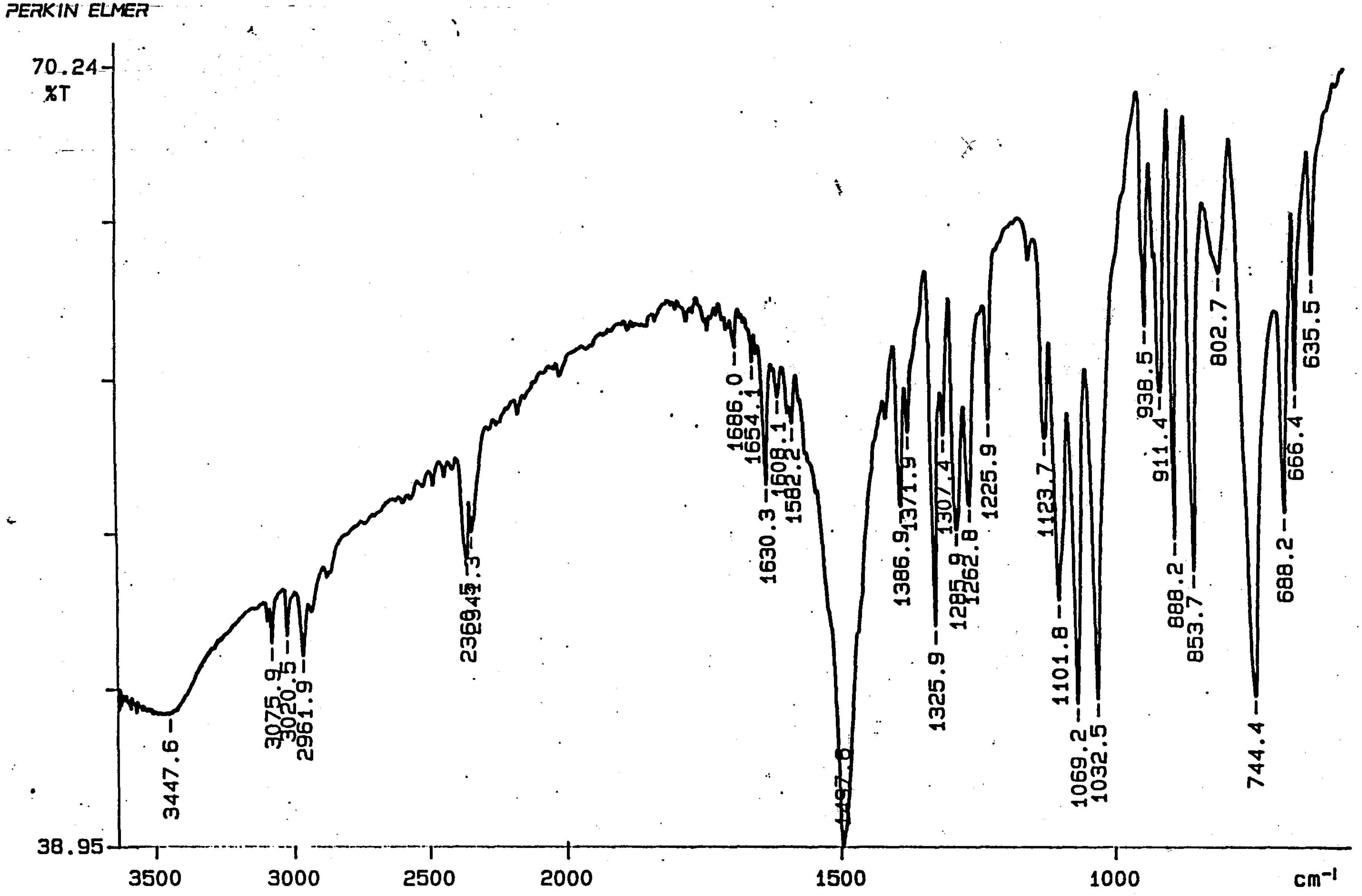




Appendix 5.5a. ^{1}H NMR spectrum of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene.

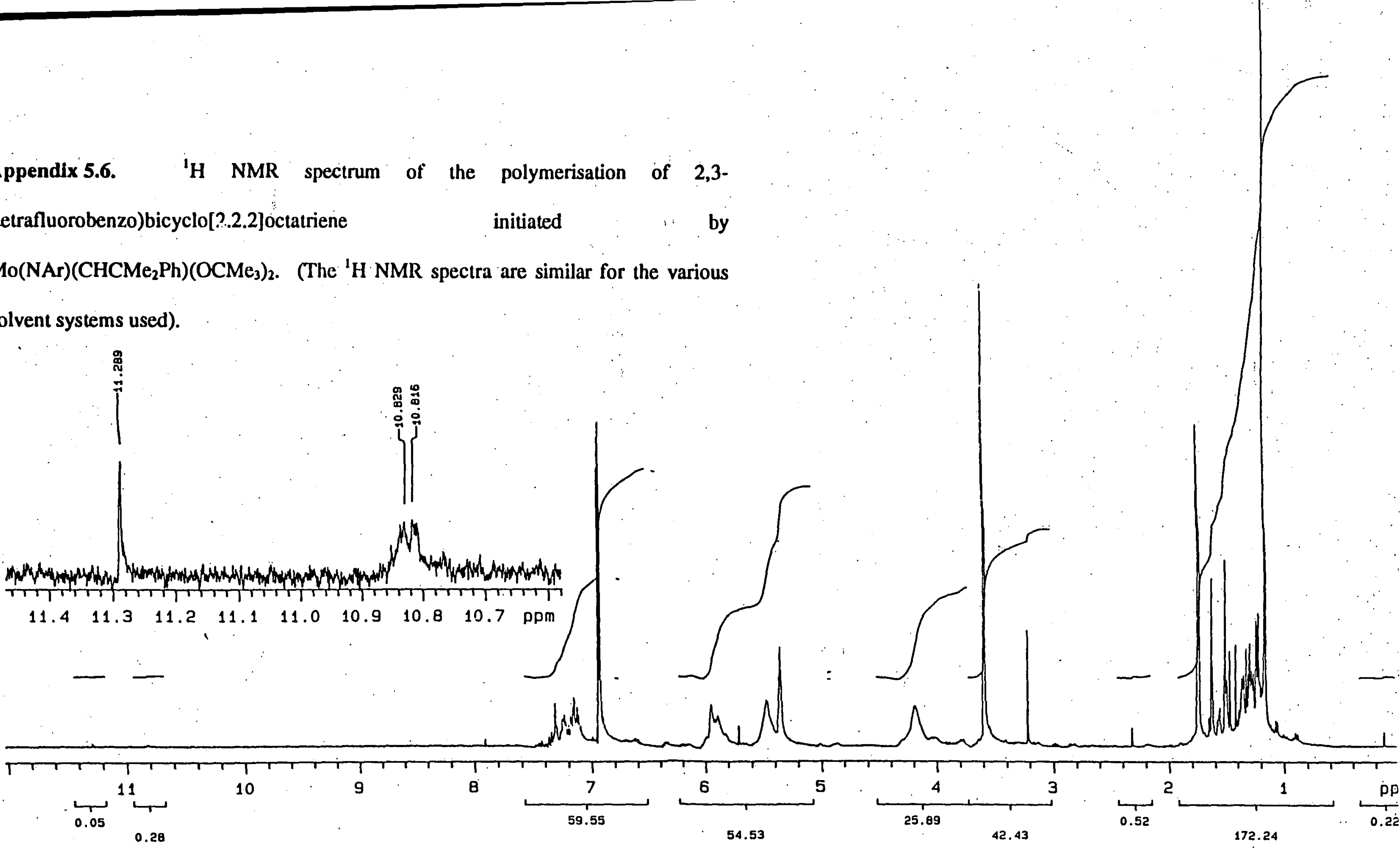


Appendix 5.5b. ^{19}F NMR spectrum of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene.

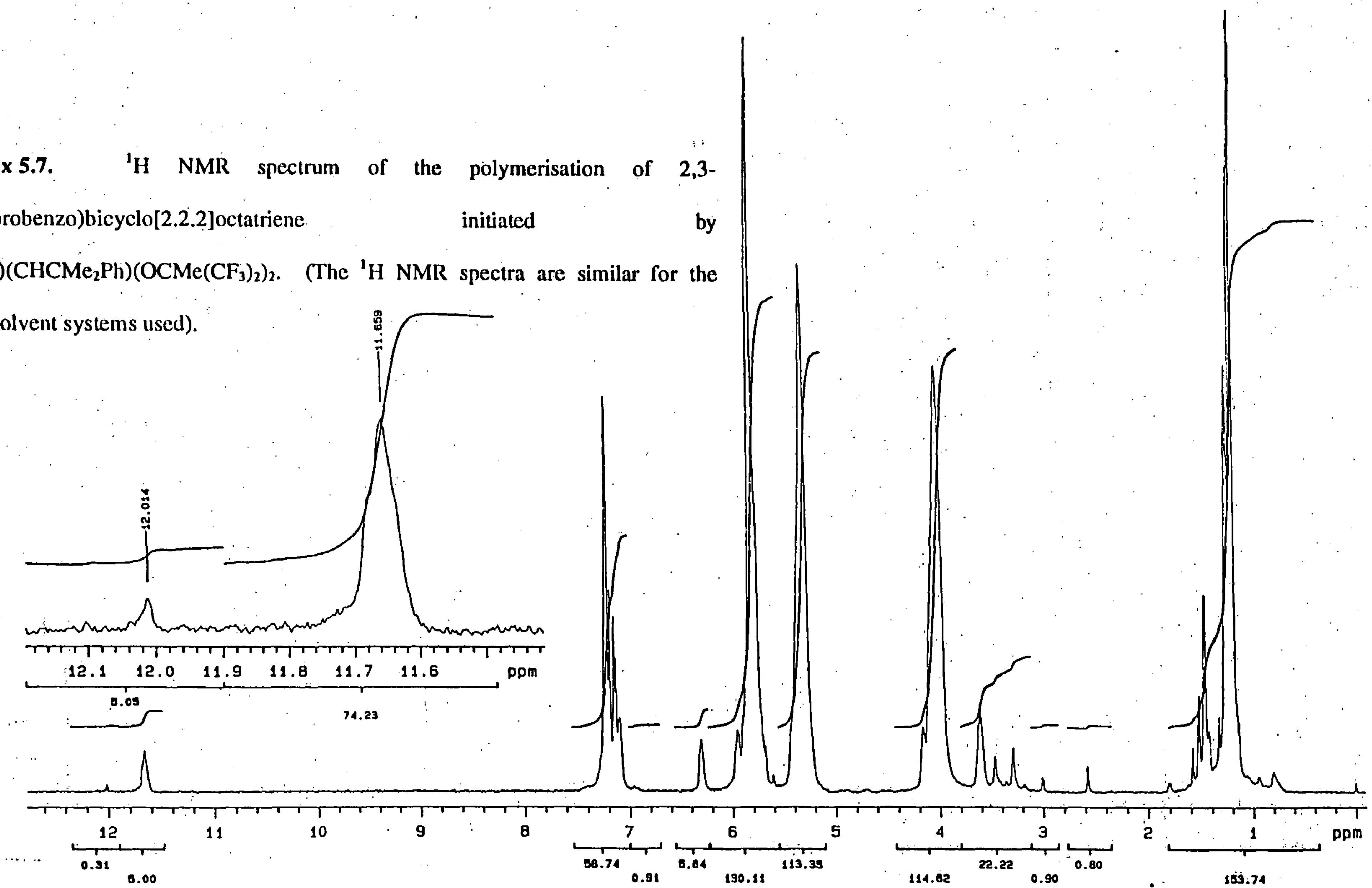


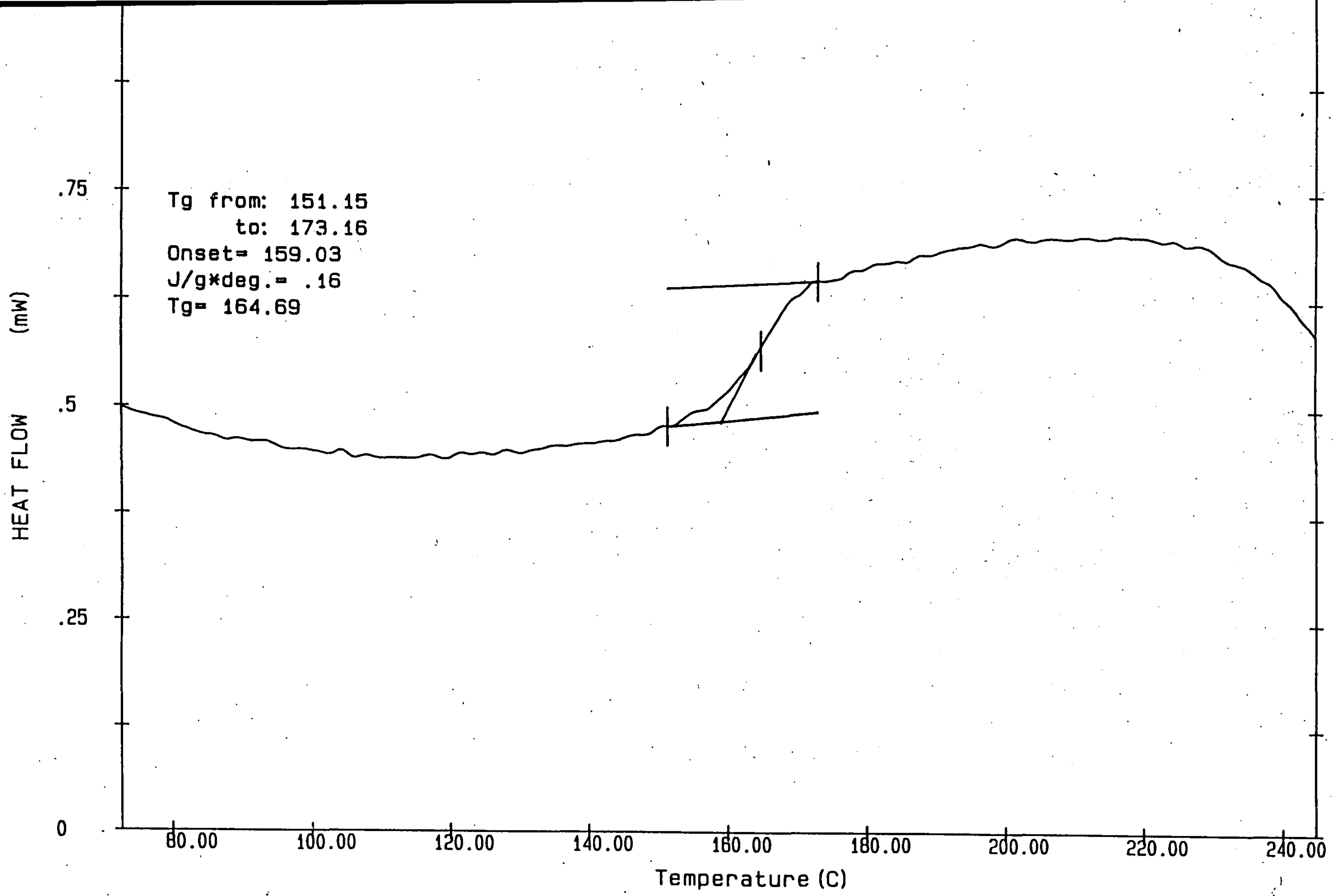
Appendix 5.5c. FTIR spectrum of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene.

Appendix 5.6. ^{1}H NMR spectrum of the polymerisation of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene initiated by Mo(NAr)(CHCMe$_2$Ph)(OCMe$_3$)$_2$. (The ^{1}H NMR spectra are similar for the various solvent systems used).

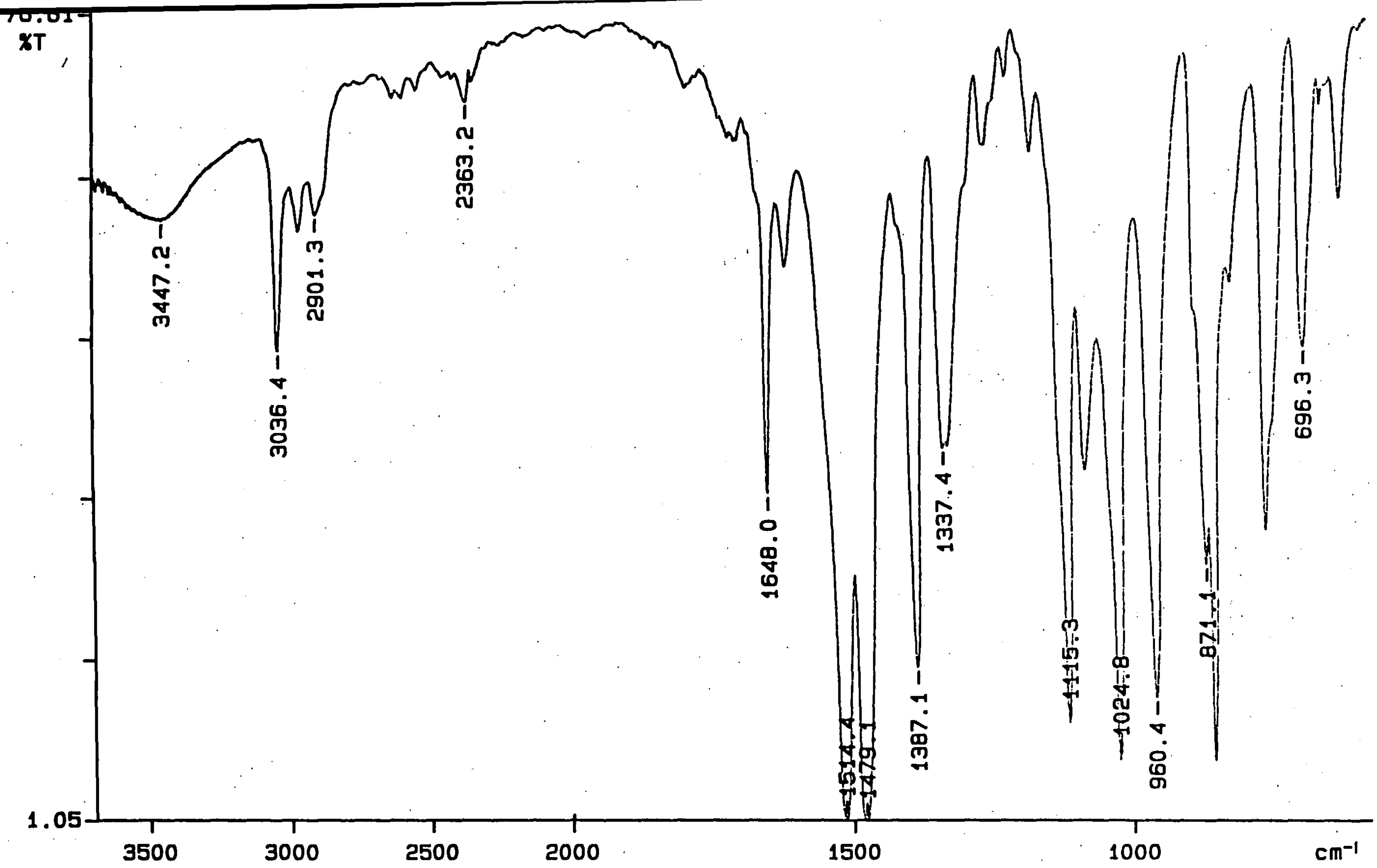


Appendix 5.7. ^{1}H NMR spectrum of the polymerisation of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene initiated by Mo(NAr)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$. (The ^{1}H NMR spectra are similar for the various solvent systems used).

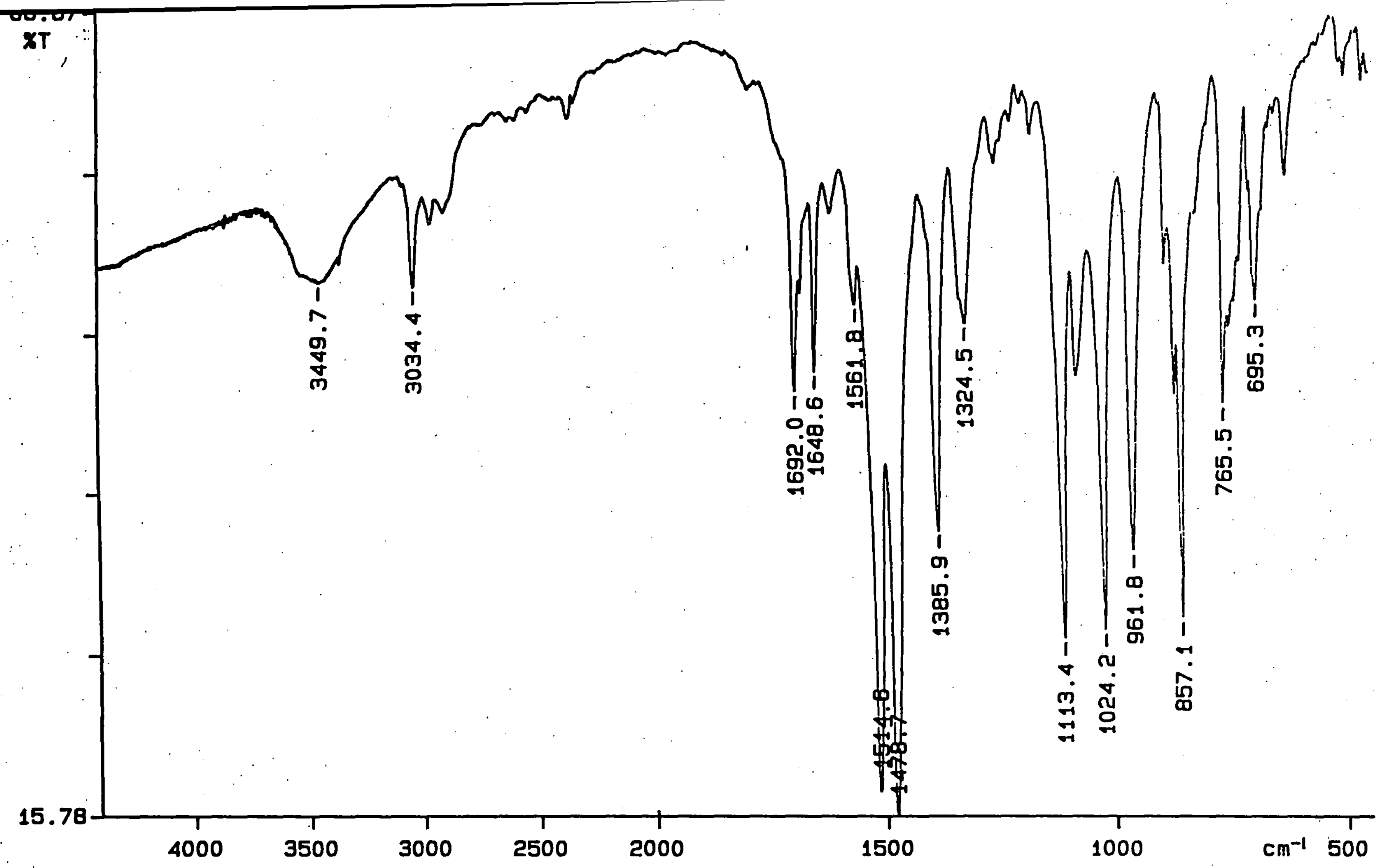




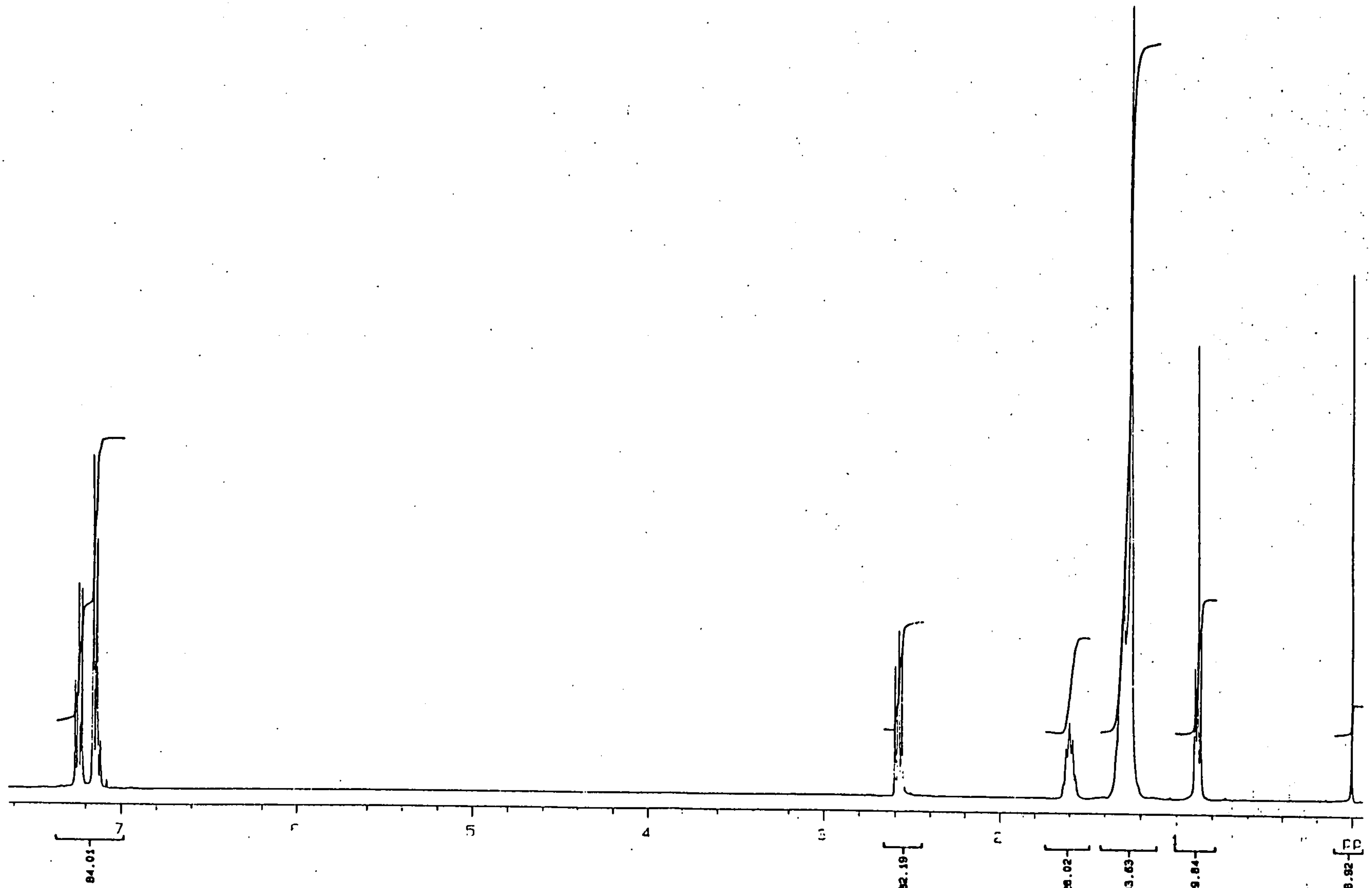
Appendix 5.8. DSC trace of poly((tetrafluorobenzo)bicyclo[2.2.2]octatriene).



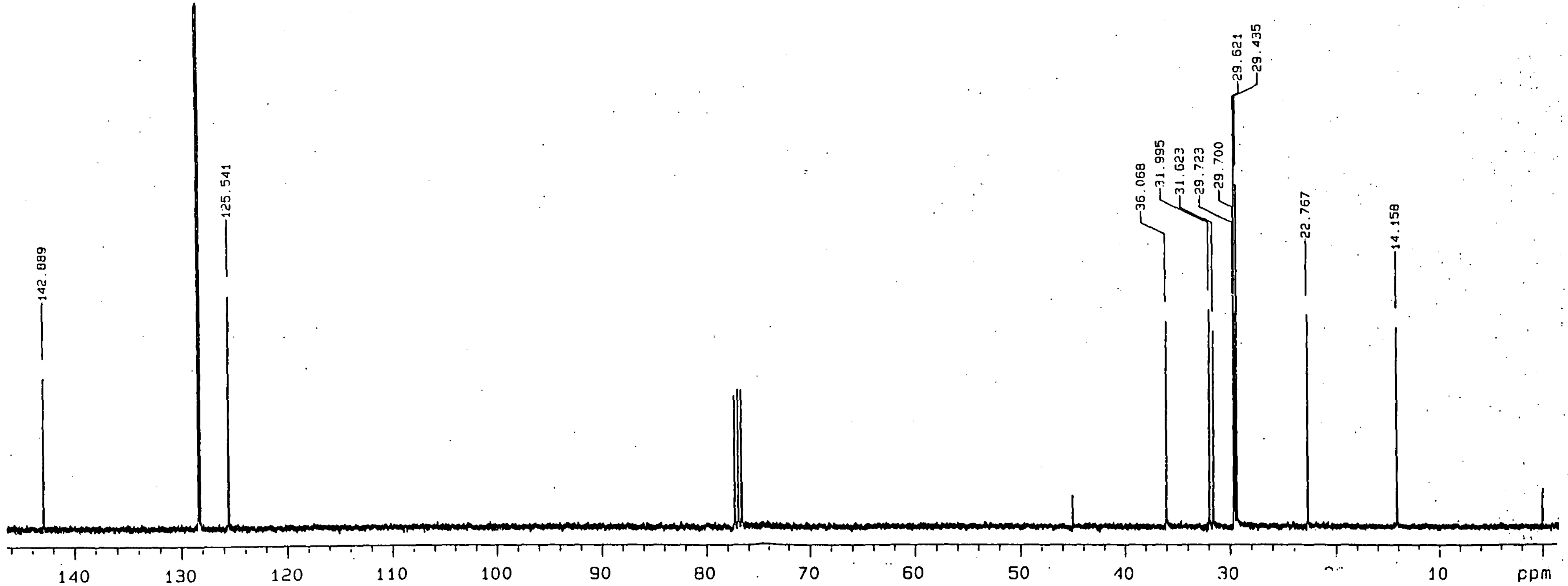
Appendix 5.9a. FTIR spectrum of poly((tetrafluorobenzo)bicyclo[2.2.2]octatriene) initiated by $Mo(NAr)(CHCMe_2Ph)(OCMe_3)_2$



Appendix 5.9b. FTIR spectrum of the attempted dehydrogenation reaction between poly((tetrafluorobenzo)bicyclo[2.2.2]octatriene) and p-chloranil

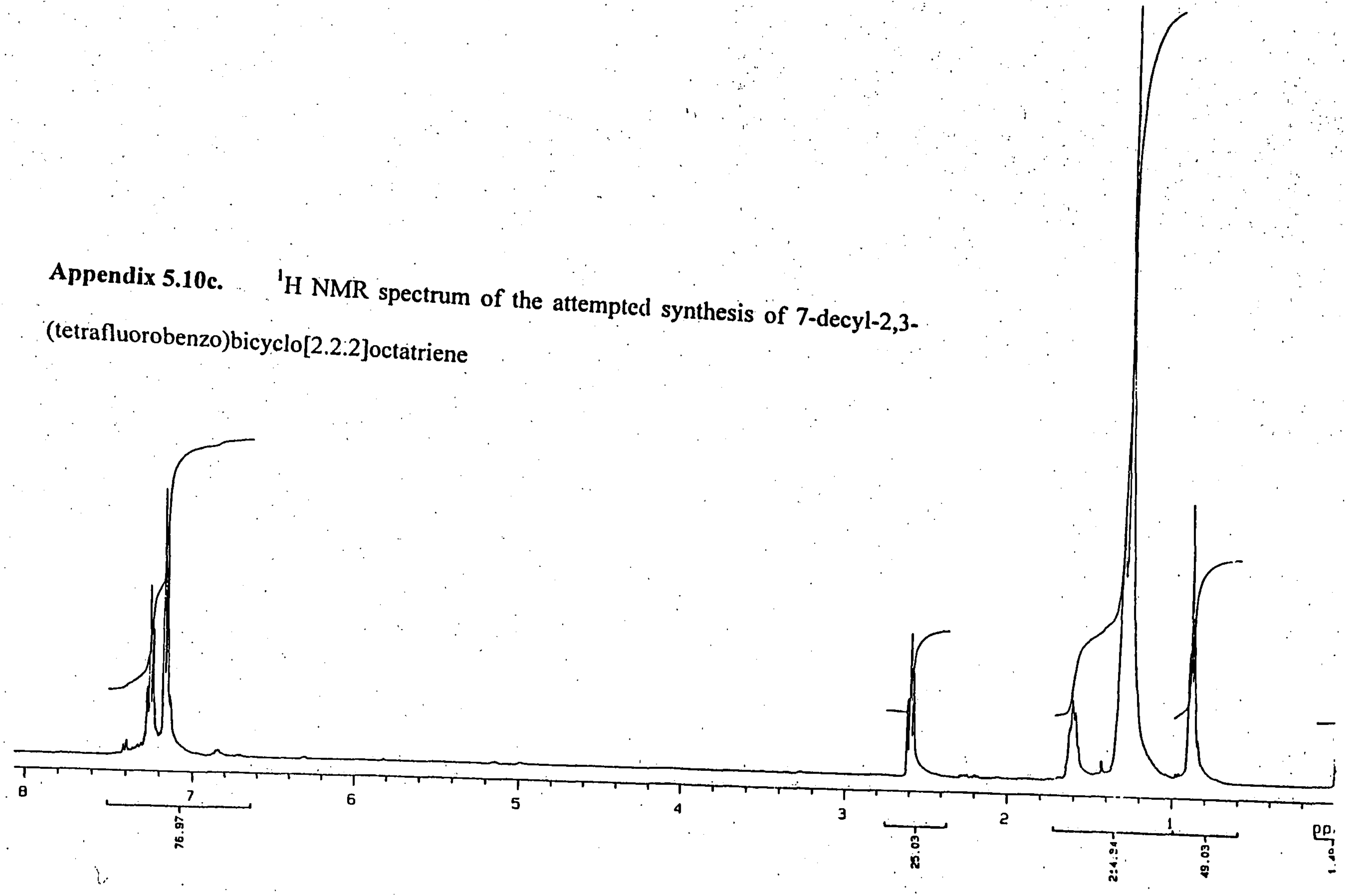


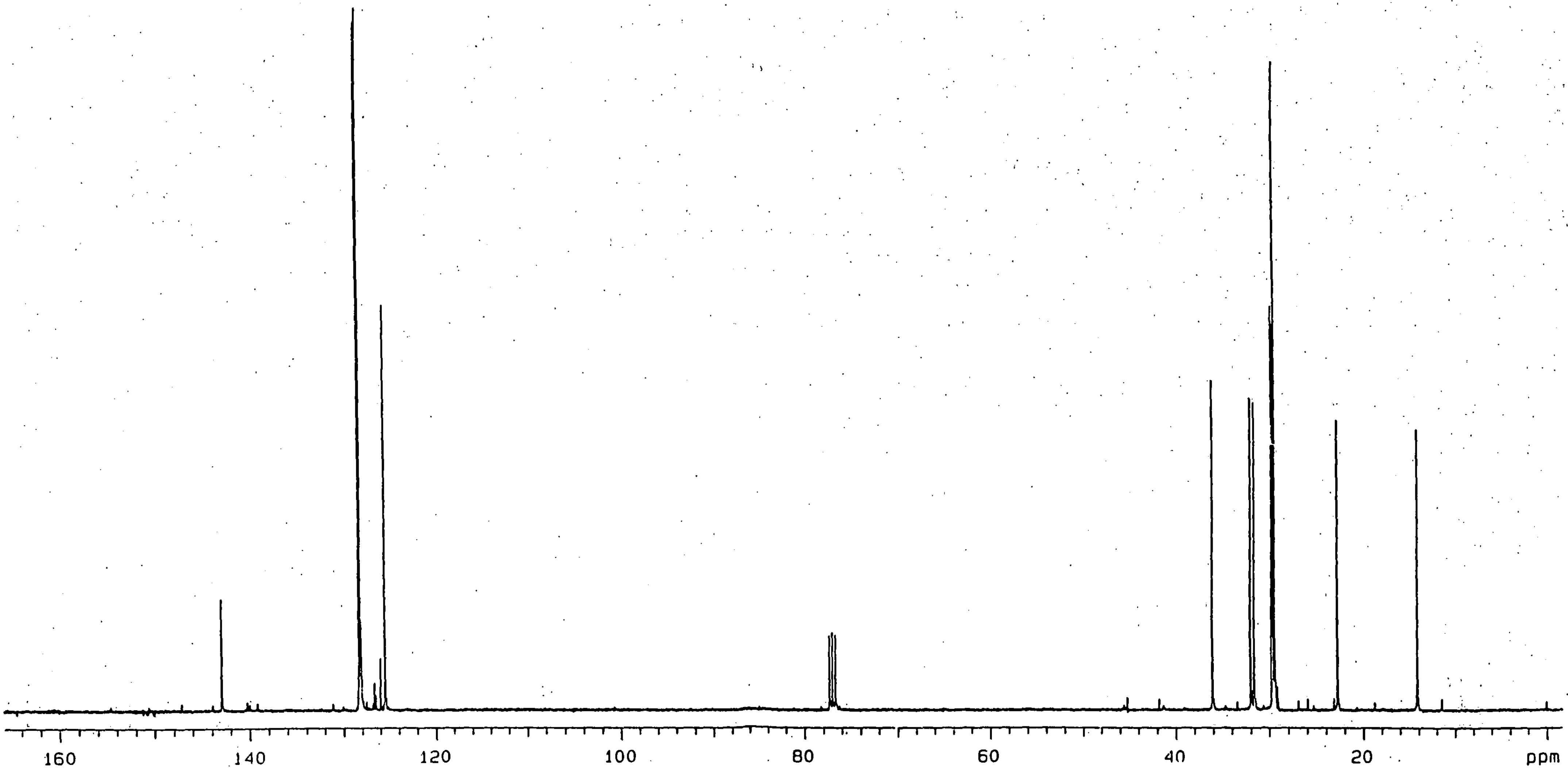
Appendix 5.10a. ^{1}H NMR spectrum of phenyldecane



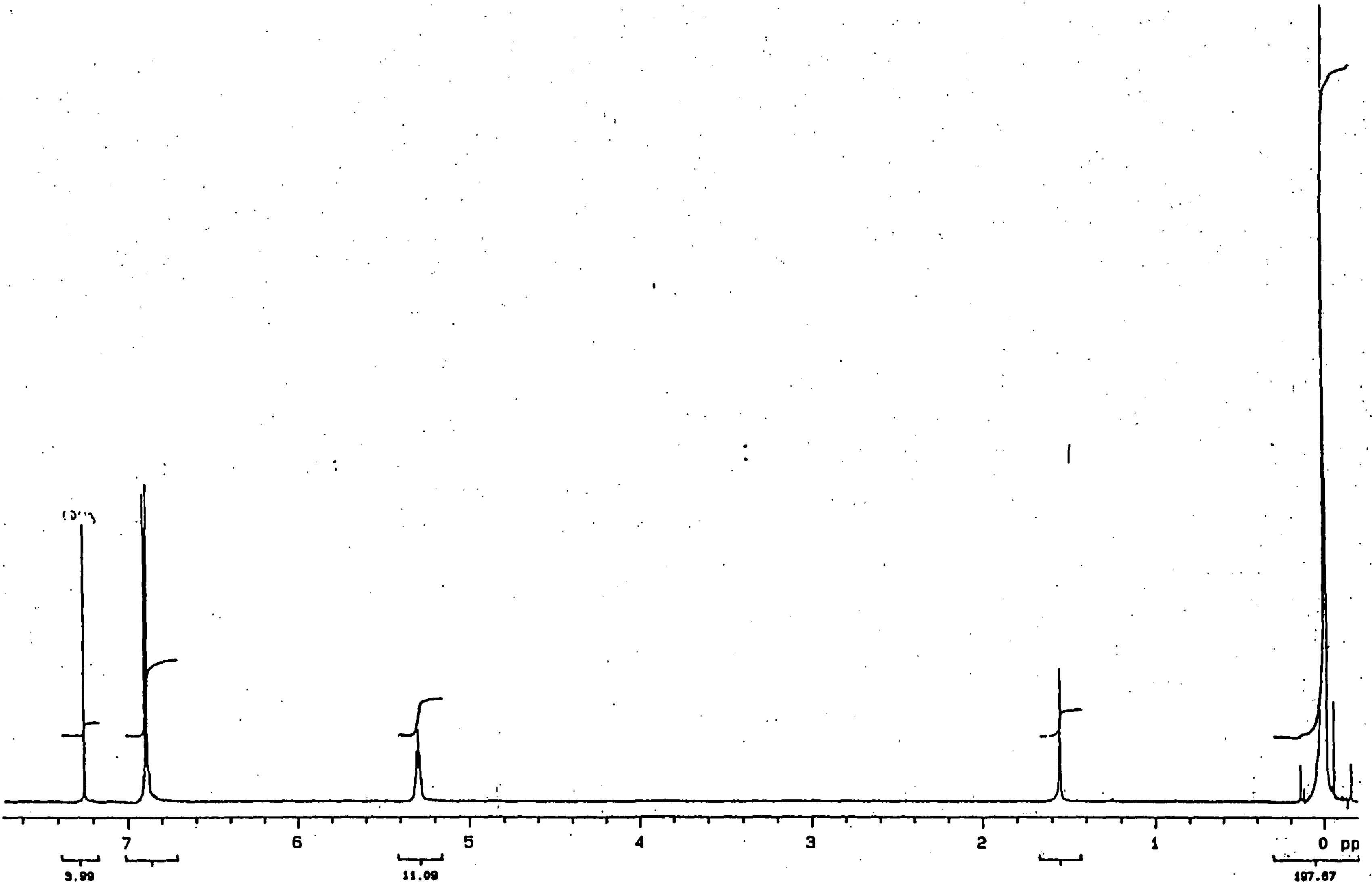
Appendix 5.10b. ^{13}C NMR spectrum of phenyldecane

Appendix 5.10c. ^{1}H NMR spectrum of the attempted synthesis of 7-decyl-2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene

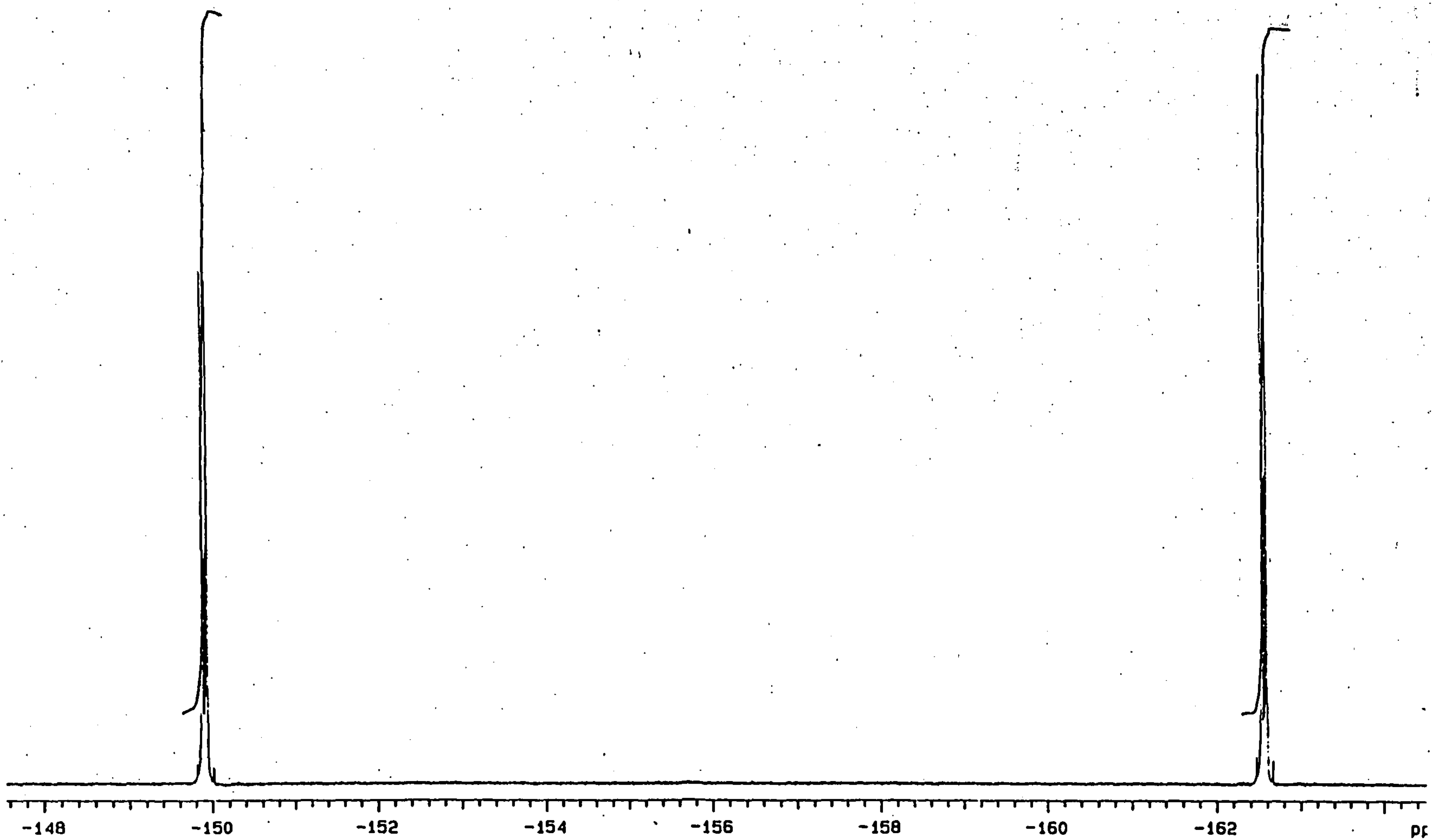




Appendix 5.10d. ^{13}C NMR spectrum of the attempted synthesis of 7-decyl-2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene

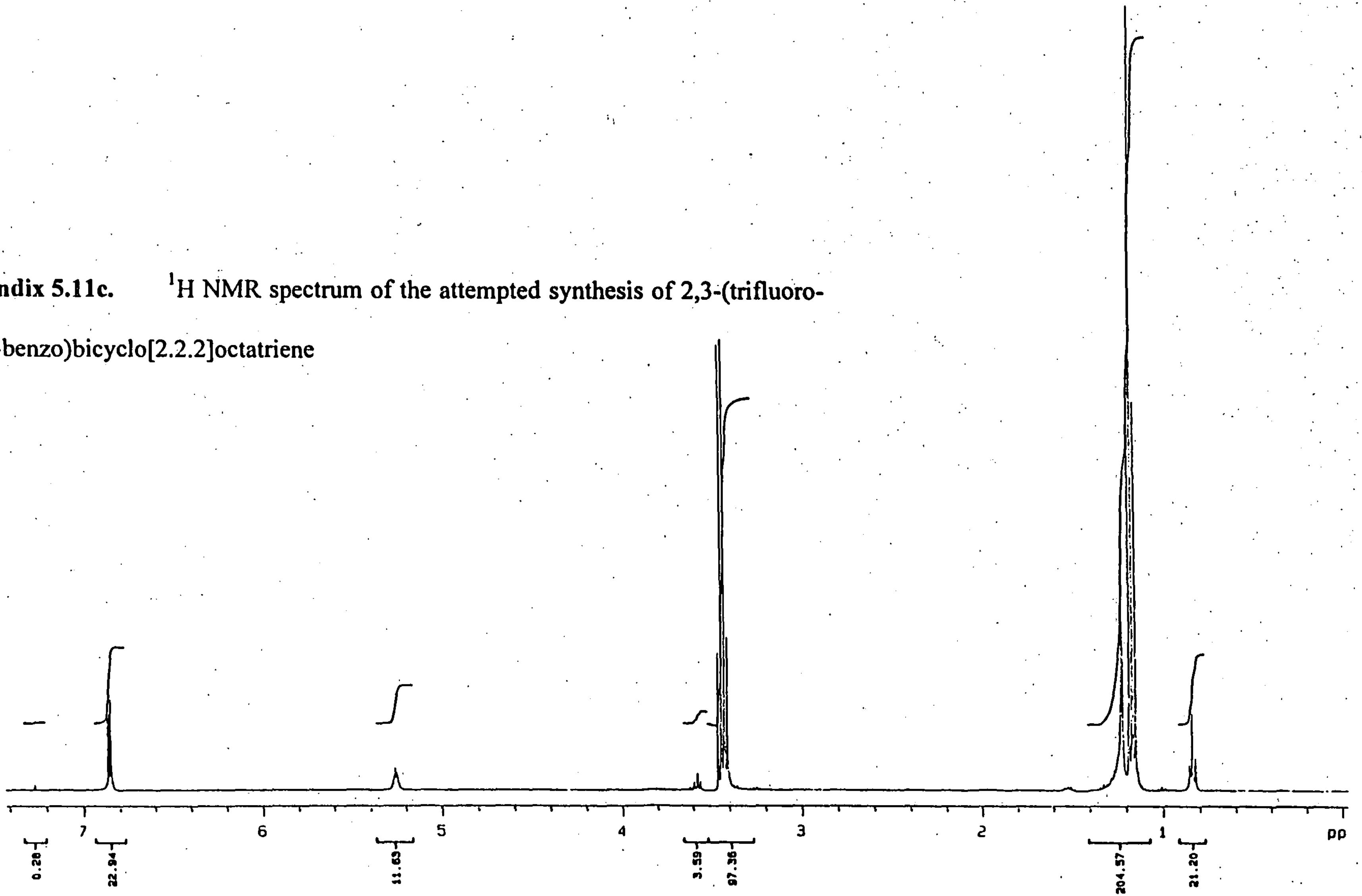


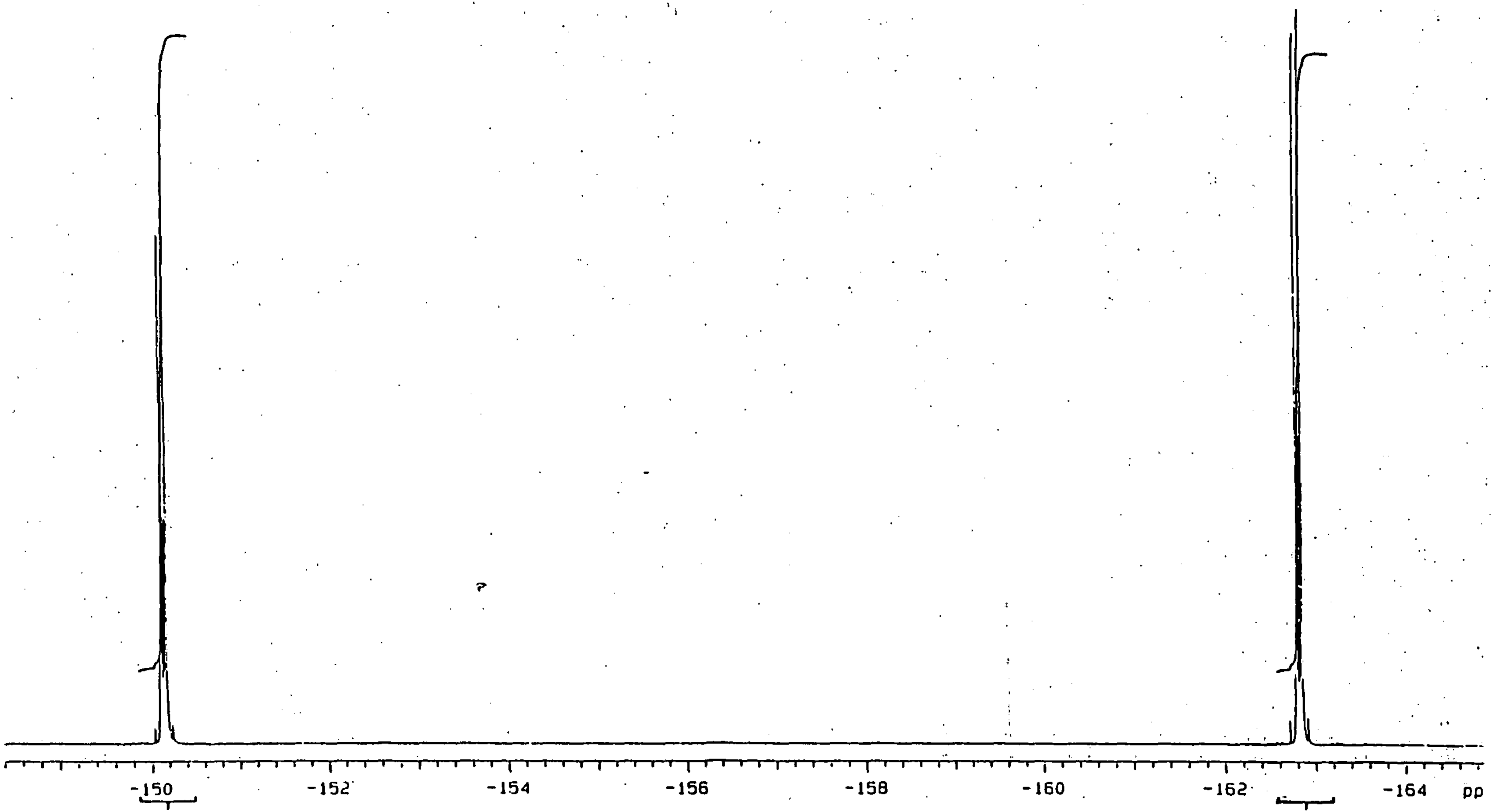
Appendix 5.11a. ^1H NMR spectrum of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene



Appendix 5.11b. ^{19}F NMR spectrum of 2,3-(tetrafluorobenzo)bicyclo[2.2.2]octatriene

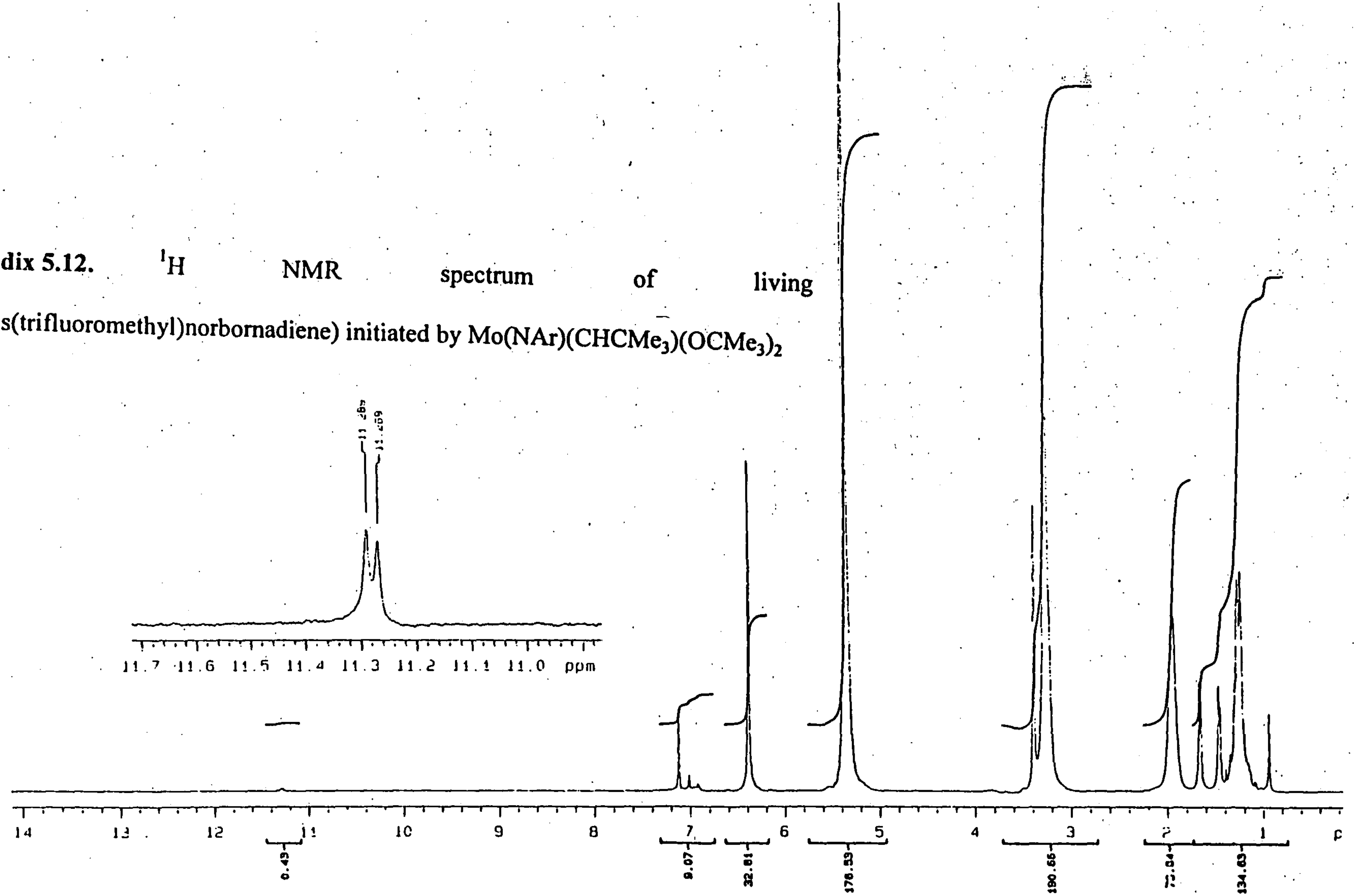
Appendix 5.11c. ^{1}H NMR spectrum of the attempted synthesis of 2,3-(trifluorodecyl-benzo)bicyclo[2.2.2]octatriene





Appendix 5.11d. ^{19}F NMR spectrum of the attempted synthesis of 2,3-(trifluorodecyl-benzo)bicyclo[2.2.2]octatriene

Appendix 5.12. ^1H NMR spectrum of living poly(bis(trifluoromethyl)norbornadiene) initiated by Mo(NAr)(CHCMe$_3$)(OCMe$_3$)$_2$



Appendix 6

Lectures and conferences attended by the author

University of Durham - Board of Studies in Chemistry

Colloquia, Seminars and Lectures given by invited speakers

1992

October 15	Dr. M. Glazer, Oxford University, & Dr. S. Tarling, Birkbeck College, London. It Pays to be British! The Chemist's Role as an Expert Witness in Patent Litigation
October 20	Dr. H.E. Bryndza, Du Pont Central Research. Synthesis, Reactions and Thermochemistry of Metal (Alkyl) Cyanide Complexes and their impact on Olefin Hydrocarbon Metathesis
October 22	Prof. A. Davies. University College, London. The Ingold-Albert Lecture. The behaviour of Hydrogen as a Pseudometal
October 28	Dr. J. K. Cockcroft. University of Durham. Recent Developments in Powder Diffraction
October 29	Dr. J. Emsley. Imperial College, London. The Shocking History of Phosporus
November 4	Dr. T.P. Kee. University of Leeds. Synthesis and Co-ordination Chemistry of Silylated Phosphites
November 5	Dr. C.J. Ludman. University of Durham. Explosions; A Demonstration Lecture
November 11	Prof. D. Robins. Glasgow University, Pyrrolizidine Alkaloids: Biological Activity, Biosynthesis and Benefits
November 12	Prof. M. R. Truter. University College, London. Luck and Logic in Host-Guest Chemistry
November 18	Dr. R. Nix. Queen Mary College, London. Characterisation of Heterogeneous Catalysts
November 25	Prof. Y. Vallee. University of Caen Reactive Tricarbonyl Compounds.
November 25	Prof. L.D. Quin. University of Massachusetts, Amherst. Fragmentation of Phosphorus Heterocycles as a Route to Phosphoryl Species with Uncommon Bonding.
November 26	Dr. D. Humber. Glaxo Greenford. AIDS- The development of a Novel Series of Inhibitors of HIV.

December 2	Prof. A. F. Hegarty, University College Dublin Highly Reactive Enols Stabilised by Steric Protection
December 2	Dr. R. A. Aitken, University of St. Andrews The Versatile Cycloaddition of $Bu_3P.CS_2$
December 3	Prof. P Edwards, Birmingham University The SCI Lecture: What is Metal?
December 9	Dr. A. N. Burgess, ICI Runcorn The structure of Perfluorinated Inonomer Membranes
<u>1993</u>	
January 20	Dr. D. C. Clary, University of Cambridge Energy Flow in Chemical Reactions
January 21	Prof. L. Hall, Cambridge NMR- Window to the Human Body
January 27	Dr. W. Kerr, University of Strathclyde Development of the Pauson-Khand Annulation Reaction: Organocobalt Mediated Synthesis of Natural and Unnatural Products
January 28	Prof. J. Mann, University of Reading Murder, Magic and Medicine
February 3	Prof. M. S. Roberts, University of Exeter Enzymes in Organic Synthesis
February 10	Dr. D. Gillies, University of Surrey NMR and Molecular Motion in Solution
February 11	Prof. S. Knox, Bristol University The Tiden Lecture: Organic Chemistry at Polynuclear Metal Centres
February 17	Dr. W. R. Kemmitt, University of Leicester Oxatrimethylenemethane Metal Complexes
February 18	Dr. I. Fraser, ICI Wilton Reactive Processing of Composite Materials
February 22	Prof. D. M. Grant, Universityof Utah Single Crystals, Molecular Structure and Chemical-Shift Anisotropy
February 24	Prof. C. J. M. Stirling, University of Sheffield Chemistry on the Flat Reactivity of Ordered Systems

March 10	Dr. P. K. Baker, University College of North Wales, Bangor 'Chemistry of Highly Versatile 7-Coordinate Complexes
March 11	Dr. R. A. Y. Jones, University of East Anglia The Chemistry of Wine Making
March 17	Dr. R. J. K. Taylor, University of East Anglia Adventures in Natural Product Synthesis
March 24	Prof. I. O. Sutherland, University of Liverpool Chromogenic Reagents for Cations
May 13	Prof. J. A. Pople, Carnegie-Mellon University, Pittsburgh, USA The Boys-Rahman Lcture: Applications of Molecular Orbital Theory
May 21	Prof. L. Weber, University of Bielefeld Metallo-phospha Alkenes as Synthons in Organometallic Chemistry
June 1	Prof. J. P. Konopelski, University of California Santa Cruz Synthetic Adventures with Enantiomerically Pure Acetals
June 2	Prof. F. Ciardelli, University of Pisa Chiral Discrimination in the Stereospecific Polymerisation of Alpha Olefins
June 7	Prof. R. S. Stein, University of Massachusetts Scattering Studies of Crystaline and Liquid Crystalline Polymers
June 16	Prof A. K. Covington, University of Newcastle Use of Ion Selective Electrodes as Detectors in Ion Chromatography
June 17	Prof. O. F. Nielsen, H. C. Ørsted Institute, University of Copenhagen Low-Frequency IR- and Raman Studies of Hydrogen Bonded Liquids
September 13	Dr A. D. Schluter, Freie Universitat, Berlin, Germany Synthesis and Characterisation of Molecular Rods and Ribbons
September 13	Dr. K. J. Wynne, Office of Naval Research, Washington, USA Polymer Surface Design for Minimal Adhesion
September 14	Prof. J. M. DeSimone, University of North Carolina, Chapel Hill, USA Homogeneous and Heterogeneous Polymerisations in Environmentally Responsible Carbon Dioxide
September 28	Prof. H. Ila, North Eastern Hill University, India Synthetic Strategies for Cyclopentanoids via Oxoketene Duithioacetals
October 4	Prof. F. J. Feher, University of California, Irvine, USA Bridging the Gap Between Surfaces and Solution with Sessilquioxanes

October 14	Dr. P. Hubberstey, University of Nottingham Alkali Metals: Alchemist's Nightmare, Biochemist's Puzzle and Technologist's Dream
October 20	Dr. P. Quayle, University of Manchester Aspects of aqueous ROMP Chemistry
October 21	Prof. R. Adams, University of South Carolina, USA Chemistry of Metal Carbonyl Cluster Complexes: Development of Cluster Based Alkyne Hydrogenation Catalysts
October 27	Dr. R. A. L. Jones, Cavendish Laboratory, Cambridge Perambulating Polymers
November 10	Prof. M. N. R. Ashfold, University of Bristol High Rsolution Photofragment Translational Spectroscopy: A New Way to Watch Photodissociation
November 17	Dr. A. Parker, Rutherford Appleton Laboratory, Didcot Applications of Time Ressolved Resonance Raman Spectroscopy to Chemical and Biochemical Problems
November 24	Dr P. G. Bruce, University of St. Andrews Structure and Properties of Inorganic Solids and Polymers
November 25	Dr. R. P. Wayne, University of Oxford The Origin and Evolution of the Atmosphere
December 1	Prof. M. A. McKervey, Queen's University, Belfast Synthesis and Applications of Chemically Modified Calixarenes
December 8	Prof. O. Meth-Cohn, University of Sunderland Friedel's Folly Revisited- A Super Way to Fused Pyridines
December 16	Prof. R. F. Hudson, University of Kent Close Encounters of the Second Kind

1994

January 26	Prof. J. Evans, University of Southampton Shining Light on Catalysts
February 2	Dr. A. Masters, University of Manchester Modelling Water Without Using Pair Potentials
February 9	Prof. D. Young, University of Sussex Chemical and Biological Studies on the Coenzyme Tetrahydrofolic Acid

February 16	Prof. K. P. Theopold, University of Delaware, USA Paramagnetic Chromium Alkyls: Synthesis and Reactivity
February 23	Prof. P. M. Maitlis, University of Sheffield Across the Border: From Homogeneous to Heterogeneous Catalysis
March 2	Dr. C. Hunter, University of Sheffield Noncovalent Interaction between Aromatic Molecules
March 9	Prof. R. Wilkinson, Loughborough University of Technology Nanosecond and Pecosecond Laser Flash Photolysis
March 10	Prof. S. V. Ley, University of Cambridge New Methods for Organic Synthesis
March 25	Dr. J. Dilworth, University of Essex Technetium and Rhenium Compounds with Applications as Imaging Agents
April 28	Prof. R. J. Gillespie, McMaster University, Canada The Molecular Structure of some Metal Fluorides and Oxofluorides: Apparent Exceptions to the VSEPR Model
May 12	Prof. D. A. Humphreys, McMaster University, Canada Bringing Knowledge to Life
October 5	Prof N. L. Owen, Brigham Young University, Utah, USA Determining Molecular Stuctrure-The INADEQUATE NMR Way
October 19	Professor N. Bartlett, University of California Some Aspects of (AgII) and (AgIII) Chemistry.
October 26	Dr. G. Rumbles, Imperial College Real or Imaginary 3rd Order Non-Linear Optical Materials.
November 2	Dr. P. G. Edwards, University of Wales, Cardiff The Manipulation of Electronic and Structural Diversity in Metal Complexes - New Ligands for New Properties.
November 9	Dr. G. Hogarth, University College, London New Vistas in Metal Imido Chemistry.
November 16	Professor M. Page, University of Huddersfield Four Membered Rings and B-Lactamase.
November 23	Dr. J. Williams, University of Loughborough New Approaches to Asymmetric Catalysis.

November 30	Professor P. Parsons, University of Reading Applications of Tandem Reactions in Organic Synthesis.

1995

January 25	Dr. D. A. Roberts, Zeneca Pharmaceuticals The Design and Synthesis of Inhibitors of the Renin-Angiotensin System.
February 1	Dr. T. Cosgrove, Bristol University Polymers do it at Interfaces.
February 8	Dr. D. O'Hare, Oxford University Synthesis and Solid State Properties of Poly- Oligo- and Multidecker Metallocenes.
February 15	Professor W. Motherwell, University College, London New Reactions for Organic Synthesis.
March 1	Dr. M. Rosseinsky, Oxford University Fullerene Intercalation Chemistry.
April 26	Dr. M. Schroder, University of Edinburgh Redox Active Macrocyclic Complexes: Rings, Stacks and Liquid Crystals.
May 3	Professor E. W. Randall, Queen Mary and Westfield College New Perspectives in NMR imaging.
May 24	Dr. P. Beer, Oxford University Anion Complexation Chemistry.

The author has also attended the following lectures in the IRC in Polymer Science and Technology International Seminar Series.

1993

March 16 Prof. J.M.G. Cowie (Heriot-Watt University), at Bradford University
High Technology in chains : The Role of Polymers in Electronic Applications and Data Processing.

April 1 Prof. H.W. Speiss (Max Planck Institut for Polymerforschung, Mainz), at Durham University.
Multidimensional NMR Studies of Structure and Dynamics of Polymers.

June 2 Prof. F. Ciardelli (University of Pisa), at Durham University
Chiral Discrimination in the Stereospecific Polymerisation of α-olefins.

June 8 Prof. B.E. Eichinger (BIOSYM Technologies Inc. San Diego), at Leeds University.
Recent Polymer Modelling Results and a look into the Future.

Conferences, meetings and courses attended by the author

January 1993	IRC Polymer Engineering Course, University of Bradford
March 1993	IRC Polymer Physics Course, University of Leeds
June 1993	ISOM 10, Tihany-University of Vesprem, Hungary
April 1993	Macro Group (U.K) Family Meeting, University of Lancaster
September 1993	IRC Club Meeting, University of Durham
April 1994	Macro Group (U.K) Family Meeting, University of Birmingham
April 1994	New Electronic Materials, Royal Society of Chemistry, London
September 1994	# IRC Club Meeting, University of Leeds
April 1995	Macro Group (U.K) Family Meeting, Loughborough University of Technology
September 1995	IRC Club Meeting, University of Durham

Poster presentation by the author

Publications

1. "New Well-Defined Molybdenum Initiators for Ring-Opening Metathesis Polymerisation; Their use in the Polymerisation of 2,3-Bis(trifluoromethyl)-norbornadiene", W.J.Feast, V.C.Gibson, C.Redshaw, R.M.Towns, W.Clegg and M.Elsegood, J.Mol.Cat, *in press*.

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