

THE INFLUENCE OF MICROSTRUCTURE
ON THE THERMAL DEGRADATION
BEHAVIOR OF POLY(VINYL CHLORIDE)

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Master of Arts

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Hoang Vi Tran

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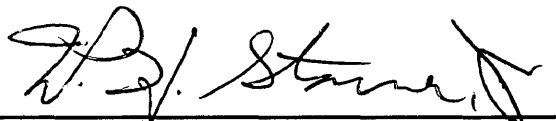
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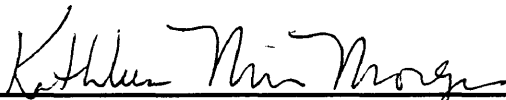


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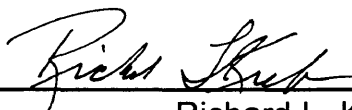
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ABSTRACT

Several model compounds were synthesized in order to study the initiating importance of labile structures in the thermal dehydrochlorination of poly(vinyl chloride): (E)-[(2-decenyl)thio]benzene, (E)-[(1-heptyl-2-decenyl)thio]benzene, [(1,1-dioctylpentyl)thio]benzene, and [(1-pentylhexyl)thio]benzene. Most workers agree that the most important of the labile structures in PVC are the internal allylic chloride and/or tertiary chloride structures. However, a few other researchers have claimed instead that high-energy isotactic conformers in PVC are the principal initiating structures for the thermal dehydrochlorination.

To reconcile these two points of view, the ^{13}C NMR chemical shifts of the model compounds were compared to those of a PVC sample modified by sodium benzenethiolate and then reduced by tri-*n*-butyltin hydride PVC sample. It was believed that PhS- substituted internal allylic and tertiary structures would be formed in the initial fast substitution reaction instead of the PhS- substituted structures relating to the high-energy isotactic conformers.

The resonances of the substituted internal allylic and tertiary structures were found in the polymer spectrum, while those of the terminal allylic structure were not detected. Resonances of the substituted secondary structure also were found. The concentrations of these structures in the polymer were calculated and did not agree with previously reported literature values. Further research needs to be done to determine with absolute certainty what happens to the (internal allylic + tertiary) structures and high-energy isotactic conformers during the initial fast reaction of PVC with the benzenethiolate anion.

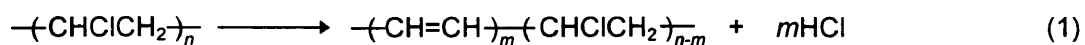
**THE INFLUENCE OF MICROSTRUCTURE
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Chapter 1

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most important and widely used commercial polymers. It is, however, thermally unstable and degrades at temperatures greater than ca. 100-120°C.¹⁻⁵ For this reason, an enormous amount of research has been done to study and improve the low thermal stability of PVC.⁵⁻¹⁸ Most of this research has focused on the nature and concentration of unstable fragments of macromolecules of PVC and their influence on the initial stage of polymer degradation.⁵⁻¹⁴ There have also been attempts to improve the stability of PVC, either by the addition of one or more stabilizers or by chemical modifications of the polymer structure.¹⁹⁻²⁸

It has been well established that the initial instability of PVC occurs primarily from a sequential dehydrochlorination process that forms conjugated polyene sequences (**Equation 1**). Most researchers agree that the thermal dehydrochlorination of PVC originates primarily from low concentrations of structural defects that have unusually low stabilities. Some of the proposed labile groups have included internal allylic chloride and/or tertiary chloride structures, $-\text{CO}(\text{CH}=\text{CH})_n\text{CHCl}-$ (with $n \geq 1$) structures, and high-energy conformers that occur in isotactic PVC segments.²⁹



A majority of researchers agree that the most important labile structures in PVC responsible for the initiation of thermal dehydrochlorination are the internal allylic chloride and/or tertiary chloride structures. However, in recent years, Millán and co-workers have proposed that the tacticity distribution in PVC has a noticeable influence on the thermal degradation mechanism. Specifically, they claim that the GTTG⁻ conformation of isotactic triads is the principle initiating structure for the thermal dehydrochlorination of PVC. Furthermore, Millán *et al.* have argued that rates of chlorine substitution depend on these isotactic triads and that the thermal improvement of

the chemically modified polymer is due to the transformation by thiophenoxy substitution of some of the least stable isotactic triads into more stable structures.^{15,30-45} These improvements were mainly attributed to the removal of the GTTG⁻ arrangement. Also, it was suggested that rather long polyene sequences were generated from the dehydrochlorinations starting from the GTTG⁻ arrangement.

Other workers have challenged some of these proposals. It has been argued, for example, that the changes in the temperature of polymerization cause both isotacticity and the number of allylic and tertiary chloride defects to change in parallel ways. Thus the improved stability caused by thiophenoxy substitution might actually be due to the removal of the aforementioned conventional defect sites (internal allylic and tertiary chloride).⁴⁶⁻⁴⁸ In a recent study, treatment with trimethylaluminum produced a polymer whose greater stability could be explained by the replacement of allylic and tertiary halogens by methyl groups.⁴⁹ It was found that the total amount of methylation was much less than the concentration of the GTTG⁻ conformation. In another study, the correlation of stability with isotacticity was found to be much weaker than the correlation with the (internal allylic + tertiary) chloride content, and it was suggested that the formation of longer polyene sequences in highly isotactic polymers results from enhanced catalysis of the dehydrochlorination process by HCl (whose concentration would be higher in samples that are less stable).⁴⁶

After all this evidence, there is still some debate over the initiating importance of the GTTG⁻ isotactic triad in the thermal dehydrochlorination of PVC. It would therefore be of great interest to know with absolute certainty what happens to the internal allylic and tertiary chloride structures during the initial fast reaction of PVC with the benzenethiolate anion. To reconcile these two points of view, model compounds were prepared and their ¹³C NMR chemical shifts were compared to those of a modified and then reduced PVC sample in an attempt to locate PhS-substituted internal allylic and tertiary structures in this polymer. It was believed that these structures would indeed be found, a result that would prove that the initial fast substitution by sodium benzenethiolate actually occurred at the (internal allylic + tertiary) sites. This result would

suggest that the most important labile structures in PVC are the internal allylic and tertiary chloride structures and not the high-energy isotactic conformers proposed by Millán and co-workers.

Chapter 2

BACKGROUND

The reasons for the low thermal stability of poly(vinyl chloride), one of the most widely used commercial polymers, have been intensively studied in recent years. Much research has been done to suppress the harmful effects of heat and light on the properties of the polymer. As mentioned earlier, PVC undergoes a spontaneous dehydrochlorination reaction via an ionic or quasiionic (polar concerted) mechanism (**Figure 2-1**)²⁹ that generates long conjugated polyene sequences (**Equation 1** in the Introduction). This process occurs when PVC is exposed to temperatures above ca. 100-120°C or to radiation in the ultraviolet region. Even small amounts of dehydrochlorination may lead to these intensely colored sequences, an undesirable effect on the appearance of useful articles constructed from PVC. If dehydrochlorination is not curtailed or halted completely, the physical properties of the polymer may be altered in ways that eventually lead to their complete deterioration. It is therefore necessary to understand how the thermal degradation of PVC is initiated and what may be done to prevent this initiation.

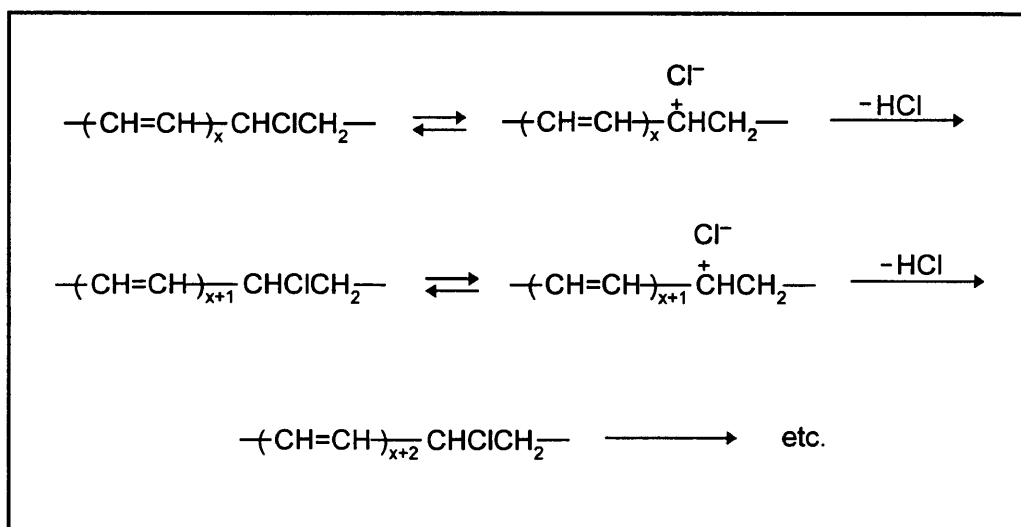


Figure 2-1: Ionic mechanism for the growth of a conjugated polyene sequence in PVC.

2.1 Possible Initiation Sites

It is widely agreed that defect sites in the PVC chain have an essential role in the low stability of the polymer. The determination of the structures and concentrations of irregularities in the polymer has been difficult, because the concentrations are very low and scarcely analyzable. Nevertheless, some powerful methods have been developed and used for the determination of the microstructure of PVC, especially ^{13}C NMR spectroscopy. Starnes and co-workers have developed a novel approach to the structural defect problem which involves the reductive dehalogenation of PVC with a metallic hydride and/or deuteride (LiAlH_4 , LiAlD_4 , Bu_3SnH , and Bu_3SnD), followed by ^{13}C NMR analysis of the reduction product(s).^{6,50-60} This method shows its advantages because the monodeuteration of a ^{13}C atom converts its proton-decoupled NMR signal from a singlet into a triplet and causes both that signal and those of neighboring carbons to undergo upfield shifts. This result allows identification of the original points of chlorine attachment from the spectrum of a deuteride-reduced material. Since the detailed structure of the carbon skeleton can also be derived from the ^{13}C spectra of hydride- or deuteride-reduced PVC, it is possible to deduce the entire microstructure of the original polymer from the spectral data. This method was used successfully to identify and enumerate the structural defects found in PVC.

If it contained no labile structural defects, PVC would be thermally stable up to ca. 200°C .²⁹ However, low concentrations of chain irregularities in PVC have been found (**Table 1**), and the nature, number, relative stability, and formation mechanisms for these defects have been investigated. Of the structures shown in **Table 1**, those containing allylic or tertiary halogen^{20,25,61-63} are considered by most researchers to be the most important ones for initiating the thermal dehydrochlorination. Some workers have proposed, however, that other candidates should be considered as the most important labile structures, including adventitious oxygenated moieties such as $-\text{CO}(\text{CH}=\text{CH})_n\text{CHCl}-$ (with $n \geq 1$)²², high-energy isotactic conformers derived from ordinary monomer units^{15,30}, and α,β -unsaturated ketone structures which supposedly catalyze the dehydrochlorination.⁶⁴ This thesis will only consider the importance of the internal allylic and tertiary chloride structures as compared to the isotactic conformers in the ordinary (head-to-tail) monomer units.

2.2 Formation of Structures Containing Allylic or Tertiary Chloride

During polymerization, head-to-head addition of vinyl chloride (VC) to the ordinary macroradical, P• (**Figure 2-2**), followed by a very rapid, exothermic 1,2 shift of Cl, produces radical **1**. Radical **2** is formed by another 1,2 shift of Cl. Previously, radical **1** (or **2**) was thought to react, in part, by ejecting a chlorine atom in a unimolecular β scission (**Equation 2**):



The resultant allylic end group was considered to be very unstable to heat. Moreover, the Cl• formed was also believed to affect stability adversely by abstracting hydrogen from the polymer in order to give $\text{—CH}_2\dot{\text{C}}\text{ClCH}_2\text{—}$ and $\text{—CHCl}\dot{\text{C}}\text{HCHCl—}$ radicals whose addition to monomer and β scission produced, respectively, unstable tertiary chloride and internal chloroallylic groups. However, the terminal chloroallylic group (**A1** and **A2**) is now known to be relatively stable, and reaction 2 is known not to occur during polymerization to any appreciable extent.^{29,65,66} The β Cl scissions of radicals **1** and **2** actually result, instead, from a *bimolecular* process involving monomer as a reactant (**Figure 2-2**).⁶⁵ The chloromethyl branch (**MB**) and dichloroethyl branch (**EB**) are formed from the addition of monomer to **1** and **2**, respectively. It is important here to note that the structures shown in **Figure 2-2** (**A1**, **A2**, **MB**, and **EB**) are indeed structural defects in PVC, but they are not considered less stable, thermally, than the ordinary monomer units. In other words, they are not regarded as important labile groups. Thus it is agreed that head-to-head emplacement of monomer is not the ultimate source of the thermal instability of PVC.²⁹ There are, instead, other authentic labile sites, namely, the internal allylic and tertiary chloride segments.

Figure 2-3 illustrates the process that gives rise to a thermally labile internal allylic group.^{29,65,67,68} The process begins with the inter- or intramolecular delivery of a methylene hydrogen from the finished PVC segment to the polymeric radical, P•. The resultant radical, **3**, can add to monomer, giving **4**, which starts the growth of a long-branch segment bearing "tertiary hydrogen" on the branch-point carbon. Some NMR evidence for the presence of structure **4** has been obtained.^{14,61} However, **4** is not an important structural defect in PVC. On the other hand,

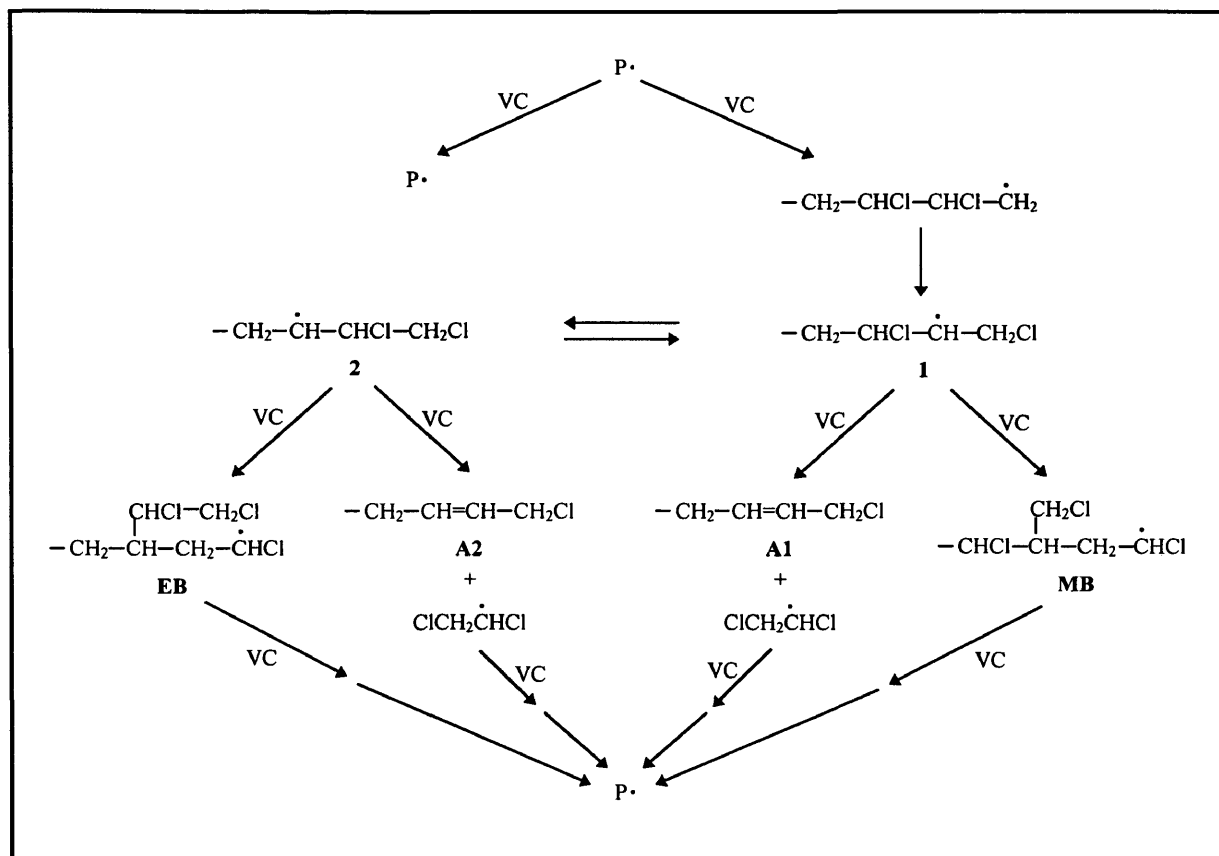


Figure 2-2: Chemical consequences of head-to-head emplacement during the free-radical polymerization of vinyl chloride (VC), where $P\cdot$ is the propagating head-to-tail macroradical.

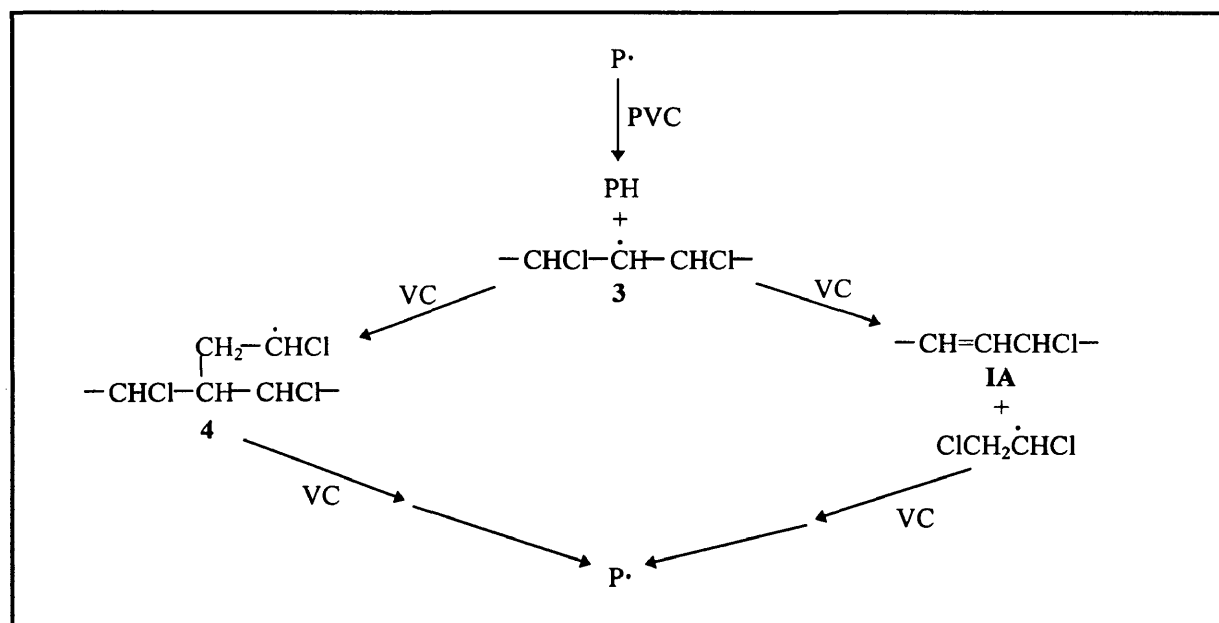


Figure 2-3: Chemical consequences of methylene hydrogen abstraction from PVC by the head-to-tail macroradical, $P\cdot$.

radical **3** can undergo a transfer reaction with VC that gives both an internal allylic chloride (**IA**) moiety and a radical whose addition to monomer starts the growth of another polymer chain. The **IA** structure produced is, indeed, important to the thermal instability of PVC and dehydrochlorinates thermally much more rapidly than do structures **A1** and **A2**.²⁹

Relatively unstable structures containing tertiary chloride result from other H abstraction reactions of $P\cdot$. These abstractions occur from CHCl moieties and yield radicals whose addition to monomer leads to branch formation. The major structures formed are the short-branch segment, **5**, and the long-branch starting point, **6**, whose mechanisms of formation⁶ are shown in **Figure 2-4**. The dichlorobutyl branch, **5**, arises from intramolecular hydrogen transfer, while in the case of the long branch, **6**, intermolecular abstraction is involved.^{6,29} As expected, the decreased thermal stability of PVC samples made at a given temperature can be correlated with the higher observed concentrations of (**IA** + tertiary) chloride that these polymers contain.⁶⁹ Starnes and Girois concluded that this drop in stability cannot be explained satisfactorily in any other reasonable way.²⁹

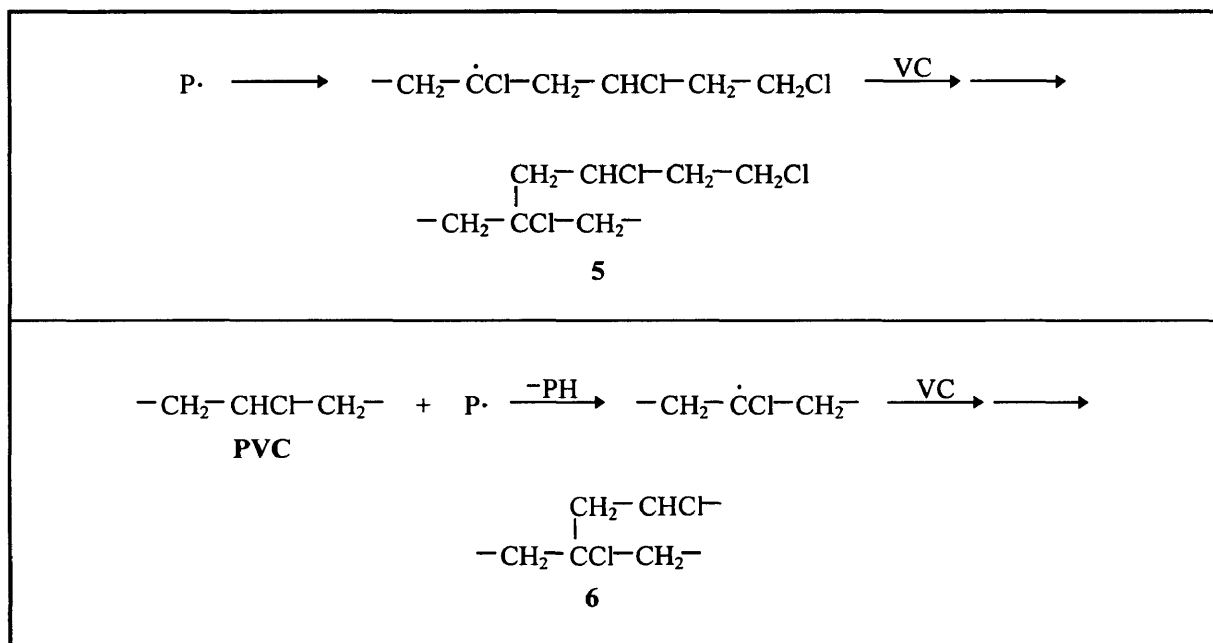


Figure 2-4: Mechanisms of tertiary chloride formation.

2.3 Relative Importance of Internal Allylic and Tertiary Chloride

To determine whether the internal allylic or tertiary chloride is the major destabilizer in PVC, Starnes *et al.* obtained first-order rate constants for the thermal dehydrochlorination of several model compounds (7-12) in dilute solutions in two different solvents (Table 2).^{29,70,71} The heated solutions were bubbled with argon at the indicated flow rates in order to sweep the evolving HCl into water, where it was titrated with standard base. They found that *k* for the tertiary chloride model, 7, varied only slightly from run to run and showed no clear-cut dependence on the rate of argon flow. However, when the argon flow rate was raised, the dehydrochlorination rates of the stereoisomeric allylic chlorides 8 and 9 decreased significantly. These structures were observed to be *less* reactive than 7 at the highest flow rate selected and *more* reactive than 7 at the lowest flow rates. Since increasing the argon flow rate reduces the molar concentration of HCl in the reacting solutions, it was concluded that the internal allylic chloride structure is much more susceptible than the tertiary chloride structure to HCl catalysis.

Also of interest in Table 2 is the low reactivity⁶⁶ found for the stereoisomeric chain-end models, 10 and 11, whose *k* values were comparable to those of the simple *sec*-alkyl chloride, 12, in both of the solvents used. There also seems to be rather small effects of alkene stereoconfiguration on the reactivity differences between compounds 8 and 9 or compounds 10 and 11. This result argues against a proposed mechanism for the thermal dehydrochlorination of PVC that requires *cis*-allylic chloride to be much more reactive than *trans*-allylic chloride.^{70,72}

2.4 Initiation by the Ordinary Monomer Units

Although the effects of structural defects undoubtedly are important, they are not the only factors that influence the thermal stability of PVC. The ordinary monomer units (i.e. those not associated with structural defects) can initiate dehydrochlorination to some extent, and the amounts of HCl that are released after initiation takes place (and thus the lengths of the polyene sequences) are influenced by tacticity.^{29,63,73,74} For example, the decreased stability of a PVC sample made at a very low temperature³³ was best explained by a polyene length enhancement caused by syndiotacticity.⁷³ Since the concentrations of (internal allylic + tertiary) chloride should

model	$k_a \times 10^5, (\text{min})^{-1}$	
	$o\text{-Cl}_2\text{C}_6\text{H}_4$	Ph_2CO
7	780 ^b 1100 950 ^c	5800
8	3120 ^b 600 290 ^c	3300
9	2000 860 ^c	4900
10	6	21
11	7	22
12	2	20

^a At $170 \pm 0.5^\circ\text{C}$ with an argon flow rate of 0.14 mL/s unless noted otherwise; reproducibilities were $\leq (\pm 7\%)$.
^b Argon flow, $\ll 0.14$ mL/s (too slow for accurate measurement).
^c Argon flow, 1.3 mL/s.

(R = n-Pr; R' = n-Bu)

Table 2: Dehydrochlorination rate constants for model compounds.^{29,71}

decrease with decreasing temperature of polymerization, the lowered stability of the polymer could not be related to a faster initiation resulting from the presence of more of these labile structural defects. Another study found that the thermal dehydrochlorination of PVC continued at a constant rate after the kinetic effects of labile defects introduced deliberately were no longer detectable.^{63,64} This steady rate seemed to be initiated by the ordinary monomer units, which was converted to allylic chloride by HCl catalysis.

2.5 Correlation Between Stability and Tacticity

Millán *et al.*¹⁵ demonstrated that the degradation rate of PVC depends on the isotactic content in the manner shown by **Figure 2-5**. The stability is higher as the isotactic content decreases up to a certain point, then the stability decreases again. The minimum in the curve agrees with a Bernoullian distribution of tacticity. They conclude that these data clearly suggest that the instability is associated with the presence of tactic sequences. Furthermore, the tactic sequences, isotactic or syndiotactic, favor the ready propagation of the unzipping reaction involving the sequential loss of hydrogen chloride, since the relative proportion of longer polyene sequences is higher the greater the tactic sequence content of either type (**Figure 2-6**).³¹⁻⁴² They found that polymers which do not have pronounced tactic sequences because the polymerization process obeys Bernoullian propagation statistics have a higher degree of thermal stability and a relatively low content of longer polyene sequences after degradation.

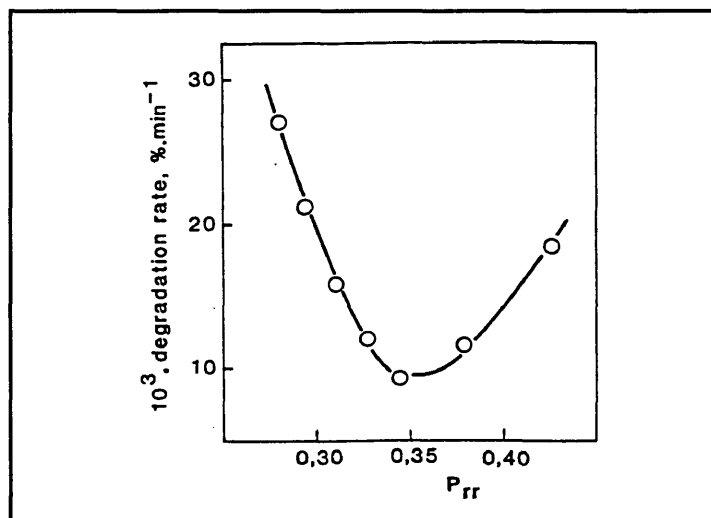


Figure 2-5: Dependence of degradation rate on syndiotactic content of PVC (inert atmosphere; 180°C).

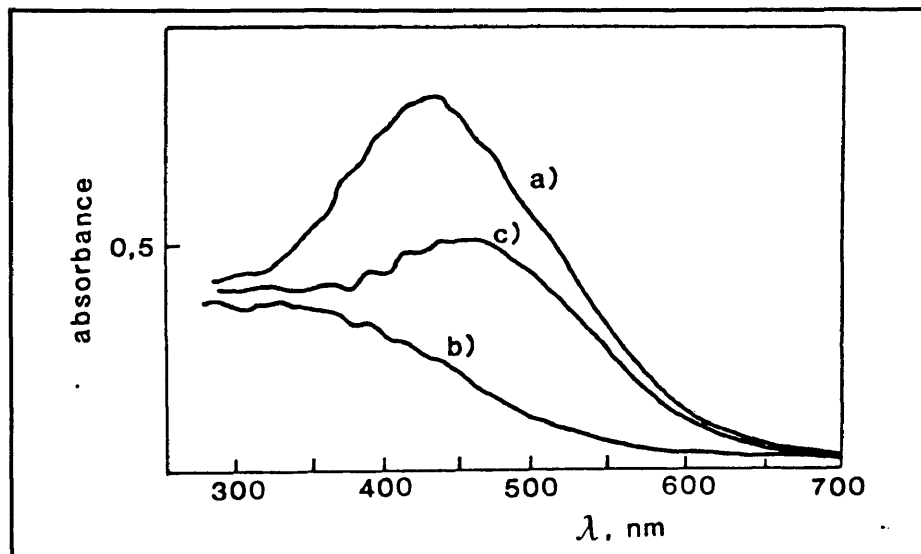


Figure 2-6: UV-Visible spectra of 0.3% degraded (180°C) PVC samples.
 a) Isotactic polymer ($P_{mm} = 21.4\%$);
 b) Bernoullian polymer ($P_{mm} = 16.7\%$);
 c) Syndiotactic polymer ($P_{mm} = 13.2\%$).

2.6 Role of GTTG⁻ Isotactic Triads and Reaction of PVC with Sodium Benzenethiolate

Although the above results concern the propagation of degradation, according to Millán and co-workers, the non-Bernoullian and favored isotactic polymers contain a higher number of initiation sites relative to syndiotactic non-Bernoullian polymers. This hypothesis suggests the occurrence of a higher content of labile structures in the former polymers. Recently, Millán and co-workers have proposed that the initiation of the thermal dehydrochlorination of PVC is due, to the greatest extent, to the occurrence of the GTTG⁻ conformation of isotactic triads (Figure 2-7) formed either during the polymerization or during the degradation process as a result of thermally induced conformational changes.^{15,30,31-45} Their conclusions were based on studies of PVC modified by nucleophilic substitution with sodium benzenethiolate, which was suggested to occur preferentially at isotactic triads in the GTTG⁻ conformation. The substitution also was suggested to involve exclusive attack at the central carbon atom since both the nucleophilic attack and the chlorine atom separation would be sterically more favored in that case. This reaction involved a fast initial period followed by a slower steady period, and it never reached a high degree of

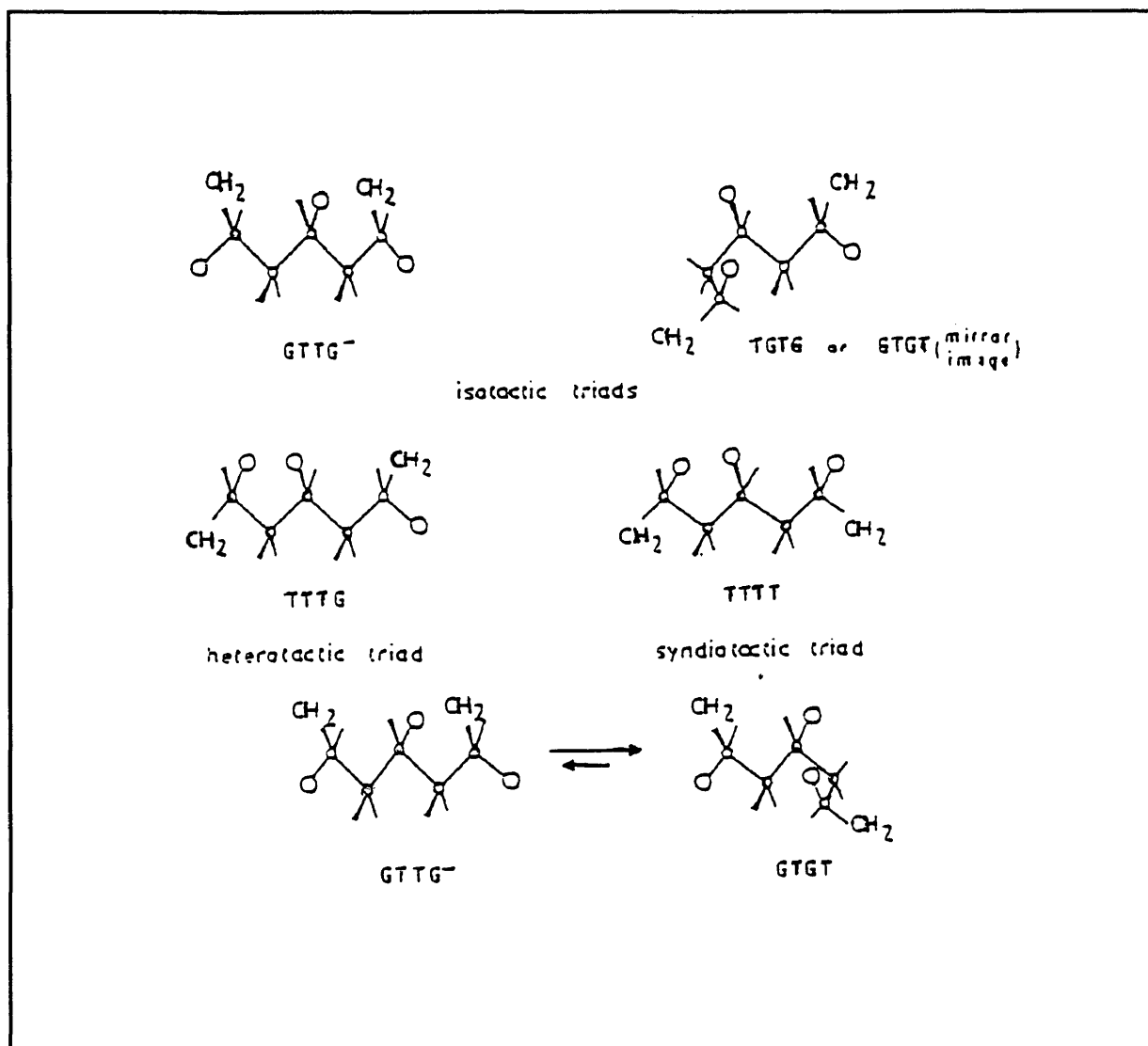


Figure 2-7: Conformations of triads in PVC.

Reaction	Mol/L PVC $\times 10^2$	Mol/L $\text{C}_6\text{H}_5\text{SNa}$ $\times 10^2$	Rate const $\times 10^2$ (L/mol \cdot min)		
			k_1	k_2	k_3
A	6.4	7.6	25	1.5	0.3
B	6.4	5.1	25	1.5	0.4
C	3.2	5.1	25	1.4	0.4

Table 3: Substitution conditions for reactions A, B, and C (Figure 2-8) and rate constant values (Figure 2-9).

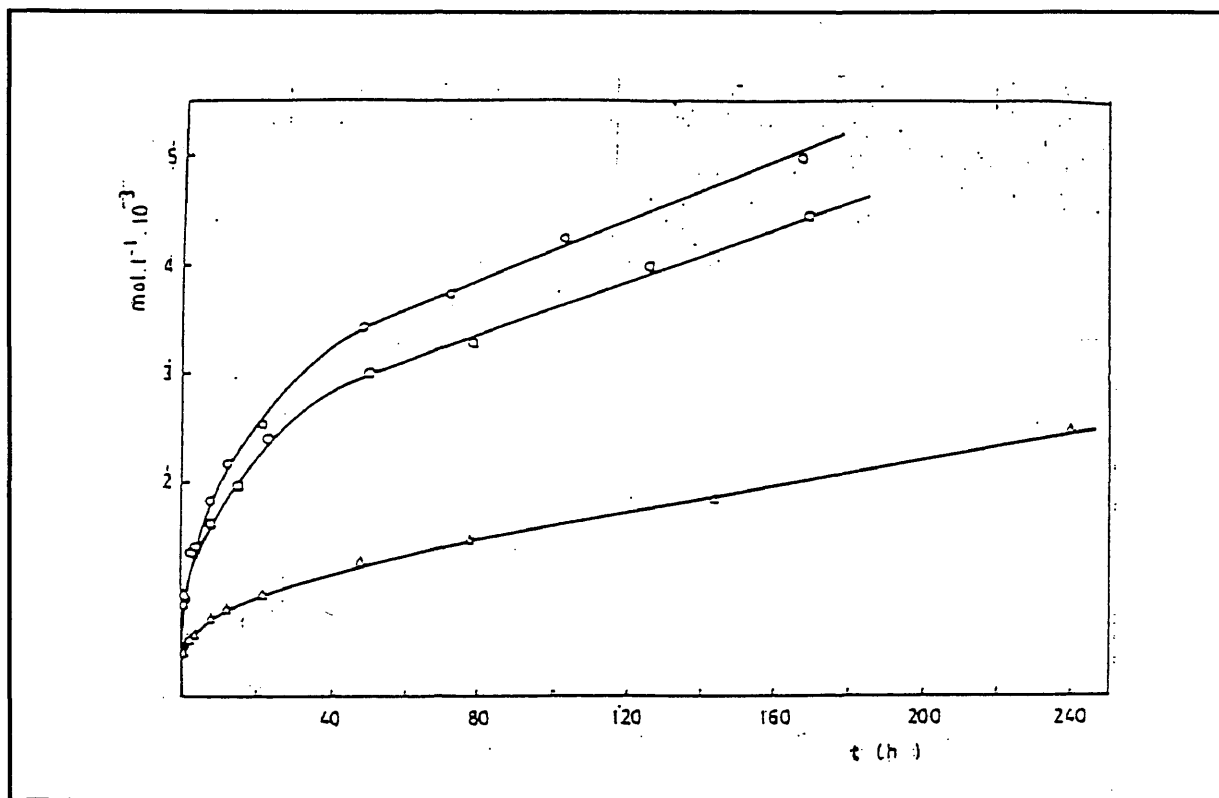


Figure 2-8: Nucleophilic substitution on PVC with sodium benzenethiolate:
 (○) Reaction A, (□) Reaction B, (Δ) Reaction C (See Table 3).

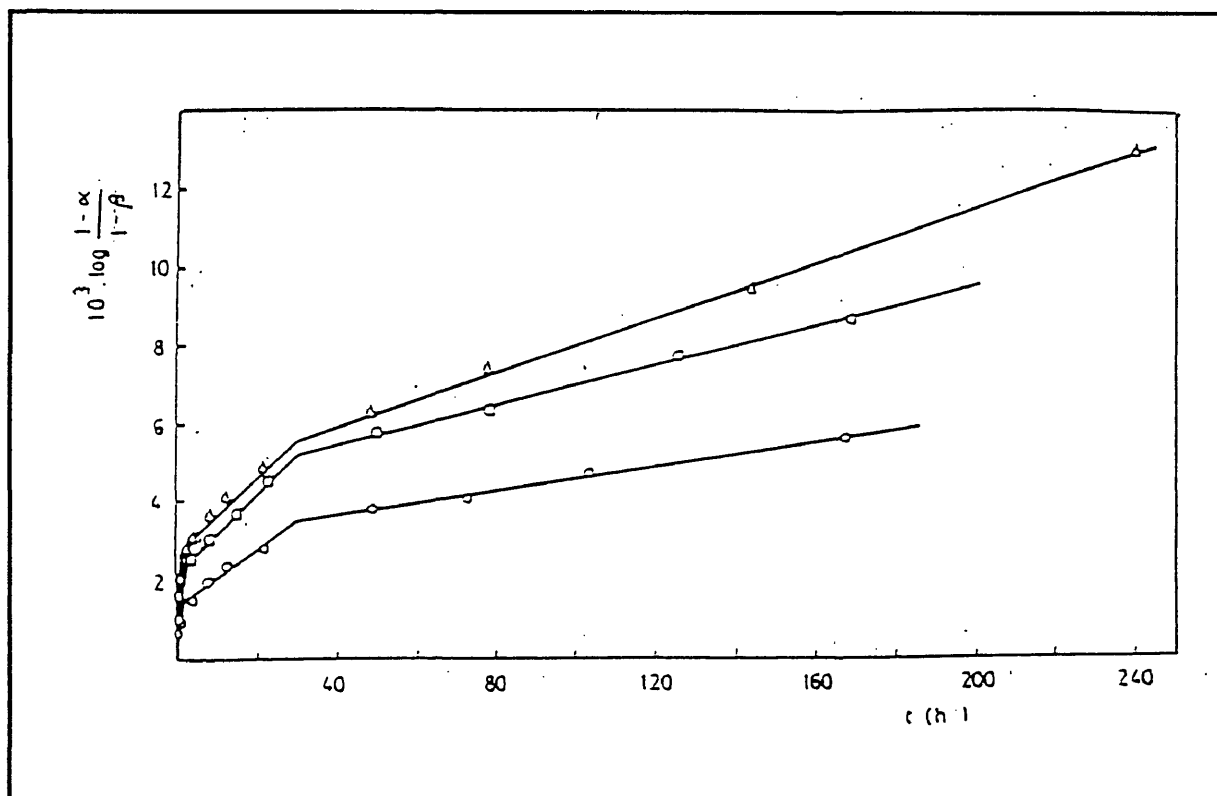


Figure 2-9: Kinetic plots of nucleophilic substitution on PVC with sodium benzenethiolate:
 (○) Reaction A, (□) Reaction B, (Δ) Reaction C (See Table 3).

conversion.³⁵ The reaction conditions are given in **Table 3**, and the conversion curves are plotted in **Figure 2-8**. The reaction was found to fit second-order kinetics (**Figure 2-9**); thus it was believed to be an S_N2 substitution reaction. These results, they believe, indicate the existence of a fraction of chlorine atoms which are much more reactive than the others in PVC.

Since the chlorine atoms in the internal allylic and tertiary structures do not satisfy the best conditions for an S_N2 substitution, Millán *et al.* concluded that the fast initial reaction, shown by the reaction constant k_1 , is related to the displacement of chlorine atoms at some "normal" structures in PVC, particularly the central chlorine atoms in the GTTG⁻ isotactic triad. Three reasons were given for this backside S_N2 attack by the nucleophile: 1. There is no axial interaction of the nucleophile with groups larger than hydrogen atoms; 2. The chlorine atoms on both neighboring units are as far as possible from the attack point; and 3. The transition state and, consequently, the central chlorine separation is favored by the relief of two H, Cl interactions. Also, it was inferred that every act of substitution occurred either at the meso-meso (**mm**) triad of an **mmr** tetrad or at the meso-racemic (**mr**) triad of an **rmrr** pentad (i.e., the **mm** or the **mr** triads located at the end of isotactic or syndiotactic sequences, respectively), and that the only three stereospecific mechanisms operative in this substitution reaction are the ones shown in **Figure 2-10**.

Recently, Millán *et al.* have found that during the first stages of substitution the number of modified triads agrees with the number of isotactic triads that has disappeared. If any labile structure but the isotactic labile conformation had reacted, they argue, appreciable deviations from this behavior should have been detected. In addition, no systematic correlation between "abnormal" labile structures and the type of polyene distribution has been described as it has, supposedly, for the tacticity.¹⁵ The proposed reason for the lability of some chlorines in the GTTG⁻ isotactic triad conformer was that the chlorine atoms, except for the central one, possess a much higher degree of freedom than the remaining chlorines in PVC. This condition, they conclude, would make it easy for these chlorine atoms to vibrate, thus giving rise to an easier initiation.³⁵

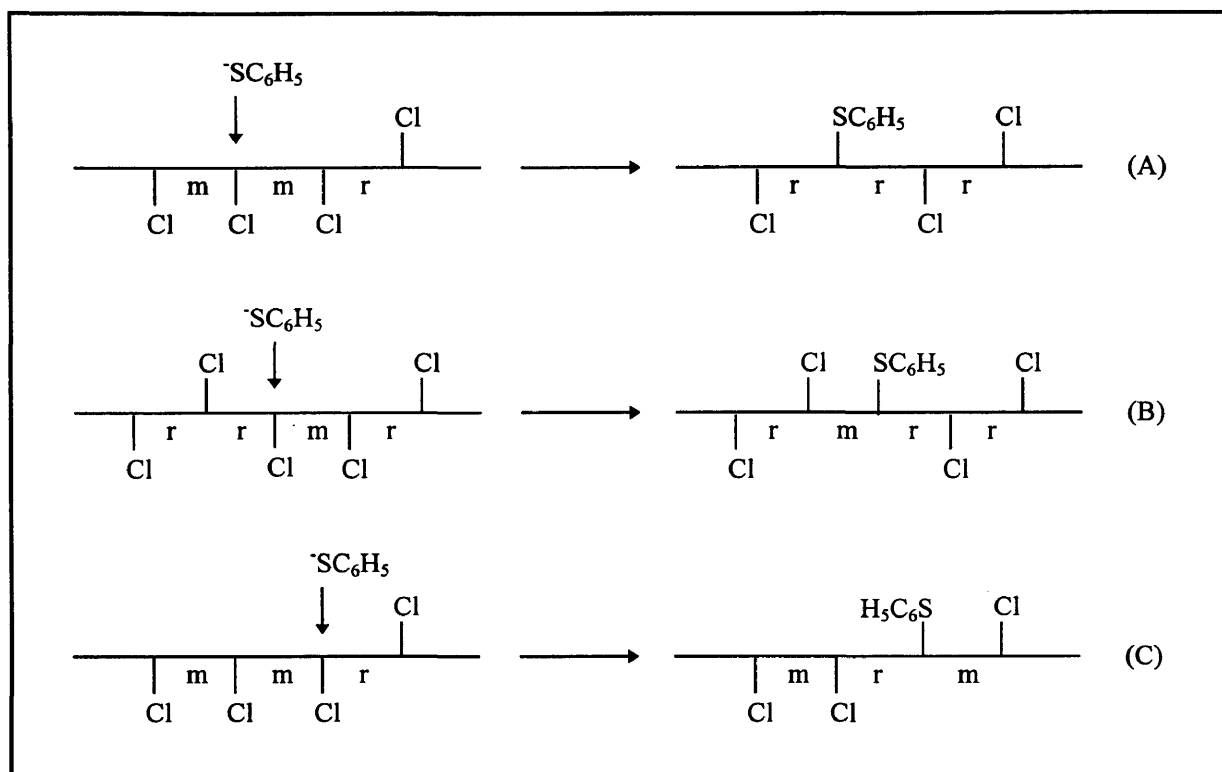


Figure 2-10: Proposed stereospecific mechanisms for the S_N2 substitution of PVC with sodium benzenethiolate.

Hjertberg, on the other hand, questions the findings of Millán and co-workers. From experiments on the degradation behavior of four commercial PVC resins with different polymerization temperatures, Hjertberg and Rogestedt found a definite relationship between the dehydrochlorination rate and the content of internal allylic and tertiary chlorine (**Figure 2-11**).⁴⁶ Their results showed that the dehydrochlorination rate increases with the amount of these structures. Furthermore, their attempt to identify a definite correlation between the degradation rate of PVC and the overall content of isotactic triads was not as successful (**Figure 2-12**). Since the isotacticity was almost the same in the four different samples used, while there was a significant difference in the content of labile chlorine in the samples, Hjertberg and Rogestedt concluded that the labile chlorine structures associated with defects contribute most to the initial degradation rate and that tacticity is of minor importance. In similar experiments, Troitskii *et al.* reached the same conclusions.⁷⁵

Hjertberg also argues that both the content of labile defects and the stereostructure are changed by varying the polymerization temperature, so that the conclusion drawn by Millán *et al.* that the polyene sequence distribution markedly depends on the tacticity of the polymer is questionable. In one study Hjertberg and Rogestedt alkylated a sample of PVC with trimethylaluminum and found that the dehydrochlorination rate of this new polymer was reduced to 20% that of untreated PVC. This result was best explained by the replacement of allylic and tertiary chlorine by methyl groups. They pointed out that the degree of substitution was considerably lower than the content of GTTG⁻ isotactic triads.⁴⁹ Therefore, the concentration of HCl in the sample, which depends on the dehydrochlorination rate, is the major factor determining the polyene sequence distribution, and it seems most likely that tacticity is of minor importance.

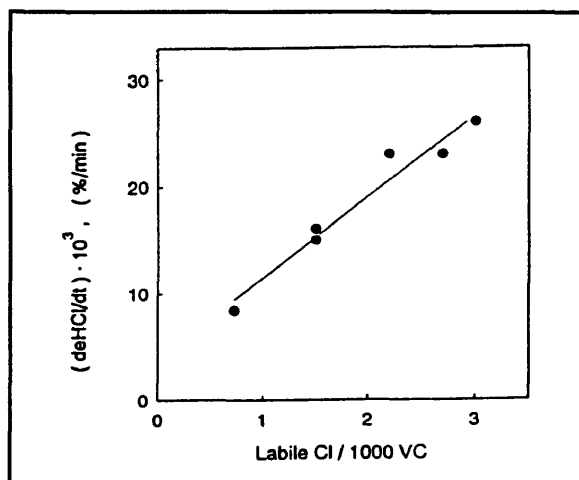


Figure 2-11: Relation between the dehydrochlorination rate and the content of labile chlorine.

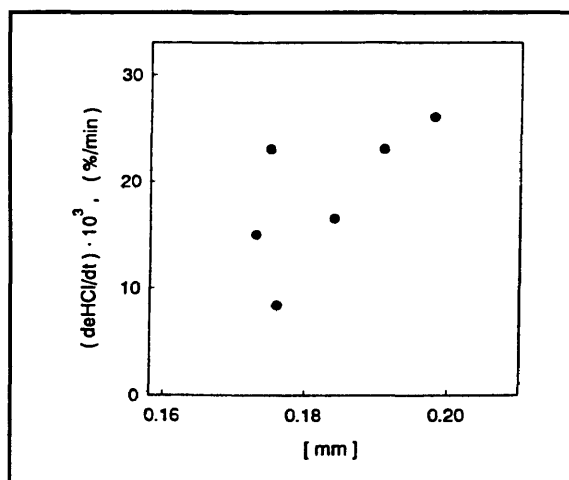


Figure 2-12: Relation between the dehydrochlorination rate and the content of isotactic triads.

Chapter 3

EXPERIMENTAL

3.1 Materials

All starting chemicals were commercial products that were used as received.

1. Thionyl chloride, SOCl_2 , 23,046-4, 99+%, bp 79°C , Aldrich Chemical Company, Inc.
2. N,N-Dimethylformamide (DMF), $\text{HCON}(\text{CH}_3)_2$, 22,705-6, 99.8%, anhydrous, bp 153°C , Aldrich.
3. (E)-2-Decen-1-ol, $\text{CH}_3(\text{CH}_2)_6\text{CH}=\text{CHCH}_2\text{OH}$, 32689, Alfa Aesar Johnson Matthey.
4. Magnesium sulfate, MgSO_4 , M65-500, anhydrous, Fisher Scientific Company.
5. Lithium diisopropylamide (LDA), $[(\text{CH}_3)_2\text{CH}]_2\text{NLi}$, 36,179-8, 2.0 M solution in heptane/tetrahydrofuran/ethylbenzene, Aldrich.
6. Tetrahydrofuran (THF), $\text{C}_4\text{H}_8\text{O}$, 40,175-7, anhydrous, 99.9%, bp $65\text{--}67^\circ\text{C}$, Aldrich.
7. 1-Bromoheptane, $\text{CH}_3(\text{CH}_2)_6\text{Br}$, B6,757-0, 99%, bp 180°C , Aldrich.
8. Pentane, $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$, O4062-4, 98%, bp 36°C , Fisher.
9. Ammonium chloride, NH_4Cl , A661-500, 99.5%, Fisher.
10. Sodium thiophenolate (thiophenol sodium salt), $\text{C}_6\text{H}_5\text{Na}$, 89027, 97%, Fluka Chemical Corporation.
11. Hexadecyltributylphosphonium bromide (HDTP), $\text{CH}_3(\text{CH}_2)_{15}\text{P}[(\text{CH}_2)_3\text{CH}_3]_3\text{Br}$, 27,620-0, 97%, mp $56\text{--}58^\circ\text{C}$, Aldrich.
12. Calcium chloride, CaCl_2 , 22,231-3, -40 mesh, 96+%, Aldrich.
13. Thiophenol, $\text{C}_6\text{H}_5\text{SH}$, 22004-0500, 99+%, bp $169\text{--}170^\circ\text{C}$, Acros Organics.
14. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), $\text{C}_9\text{H}_{16}\text{N}_2$, 13,900-9, 98%, bp $80\text{--}83^\circ\text{C}/0.6\text{mm}$, Aldrich.
15. Benzene, C_6H_6 , B245-4, 99%, bp 80°C , Fisher.
16. 1-Bromobutane, $\text{CH}_3(\text{CH}_2)_3\text{Br}$, 10677-2500, 99%, bp $100\text{--}104^\circ\text{C}$, Acros Organics.
17. Magnesium metal turnings, Mg, for Grignard reaction, M11-500, Fisher.

18. 9-Heptadecanone, $\text{CH}_3(\text{CH}_2)_7\text{CO}(\text{CH}_2)_7\text{CH}_3$, H0536, TCI America.
19. Sodium sulfate, Na_2SO_4 , S415-500, 99%, anhydrous, granular, 10-60 mesh, Fisher.
20. Phosphorus pentachloride, PCl_5 , 15,777-5, 95%, mp 179-181°C, Aldrich.
21. Calcium carbonate, CaCO_3 , 23,921-6, 99+%, powder, Aldrich.
22. Chloroform, CHCl_3 , C298-1, 99.8%, bp 61°C, Fisher.
23. (E)-1-Chloro-2-butene (crotyl chloride), $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Cl}$, 25,458-4, 95%, bp 84-85°C, Aldrich.
24. Iodomethane (methyl iodide), CH_3I , I-850-7, 99%, bp 41-43°C, Aldrich.
25. (E)-3-Penten-2-ol, $\text{CH}_3\text{CH}=\text{CHCH}(\text{OH})\text{CH}_3$, 11,128-7, 96%, bp 119-121°C, Aldrich.
26. Hydrochloric acid, HCl , A144-212, 36.5-38.0%, Fisher.
27. Chloroform-*d*, CDCl_3 , 15,183-1, 99.8 atom % D, contains 1% v/v TMS, bp 60.9°C, Aldrich.
28. Tetramethylsilane (TMS), $\text{Si}(\text{CH}_3)_4$, T2,400-7, 99.9+%, NMR grade, bp 26-28°C, Aldrich.
29. 1,1,2,2-Tetrachloroethane-*d*₂, $\text{Cl}_2\text{CDCDCl}_2$, 99.6 atom % D, bp 145-146°C/737mm, Cambridge Isotope Laboratories.
30. Diethyl ether, $(\text{CH}_3\text{CH}_2)_2\text{O}$, E198-4, 99.9%, anhydrous, bp 34.6°C, Fisher.

3.2 Instrumentation

Nuclear Magnetic Resonance:

All ^1H and ^{13}C NMR spectra were obtained on a 300 MHz General Electric NMR spectrometer (GE QE 300 FT-NMR). For identification of the model compounds, CDCl_3 was used as the solvent in ca. 10-20% (w/v) solutions at room temperature. For spectra used to compare with the PVC spectrum obtained by Dr. G. M. Benedikt of the B. F. Goodrich Company, the solvent for the model compounds was a mixture of 1,4-dioxane- d_8 , 1,1,2,2-tetrachloroethane, and 1,1,2,2-tetrachloroethane- d_2 in a 1:4:1 ratio by volume, respectively. These spectra were obtained at 90 ± 5 °C (363 °K) using a variable temperature controller, and the instrument was uncalibrated at this temperature. Tetramethylsilane (TMS) was used as an internal reference for all the spectra.

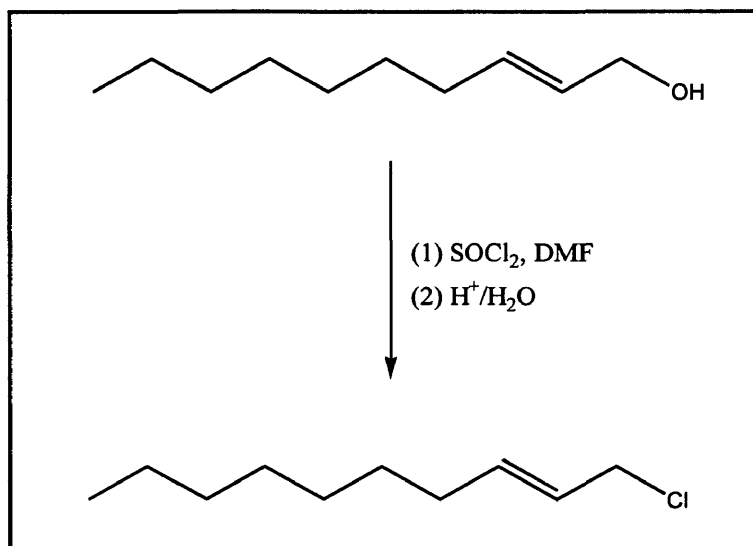
Gas Chromatography-Mass Spectroscopy (GC-MS):

The gas chromatogram/mass spectra were obtained on a Hewlett-Packard (HP) 5890 Series II GC instrument coupled to a Hewlett-Packard 5971A MSD apparatus operating in total ion concentration (TIC) mode. The instrument was equipped with an ULTRA-1 crosslinked methyl silicone gum fused-silica capillary column containing a 95:5 dimethylpolysiloxane:diphenylpolysiloxane mixture (12 m x 0.2 mm ID x 0.33 μm film thickness). Helium was used as the carrier gas, and the heating rate was 5-10 °C/min.

Infrared Spectroscopy:

All IR spectra were recorded on a Perkin-Elmer 1600 Series FTIR instrument using NaCl plates.

3.3 Synthesis of (E)-1-chloro-2-decene



The synthesis of *trans*-1-chloro-2-decene was based on a literature method for converting an allylic alcohol into the corresponding chloride.⁷⁶ Thionyl chloride (10.5 mL, 17.13 g, 144 mmol) was added dropwise to *N,N*-Dimethylformamide (DMF) (81.8 mL, 77.19g, 1.06 mol) at 0-10 °C under N₂ with stirring. To this mixture *trans*-2-decen-1-ol (15 g, 96 mmol) was added dropwise, and the resulting mixture was heated at 85-90 °C for 0.5 h. The reaction was quenched with approximately 35 mL of deionized water, and the organic layer was extracted with ether (4x35 mL). The ether solution was washed with water (3x100 mL), dried with magnesium sulfate, filtered, and concentrated on a rotary evaporator at 50 °C. Upon vacuum distillation (~2 mm Hg, 60-64 °C) of the crude product, 15 g (90%) of 95% pure (by GC/MS) *trans*-1-chloro-2-decene was obtained. The mass spectrum (**Figure 3-1**) showed a molecular ion peak at 174 *m/e*. ¹H NMR (**Figure 3-2**): δ 0.80-1.00 (3H, CH₃, triplet), 1.10-1.50 (10H, CH₂, multiplet), 2.00-2.15 (2H, CH₂, quadruplet), 3.95-4.15 (2H, CH₂, doublet), and 5.53-5.82 (2H, HC=CH, multiplet) ppm vs. Me₄Si. ¹³C NMR (**Figure 3-3**): δ 136.15, 126.08, 45.33, 32.12, 31.89, 29.18, 29.11, 28.98, 22.70, and 14.05 ppm vs. Me₄Si.

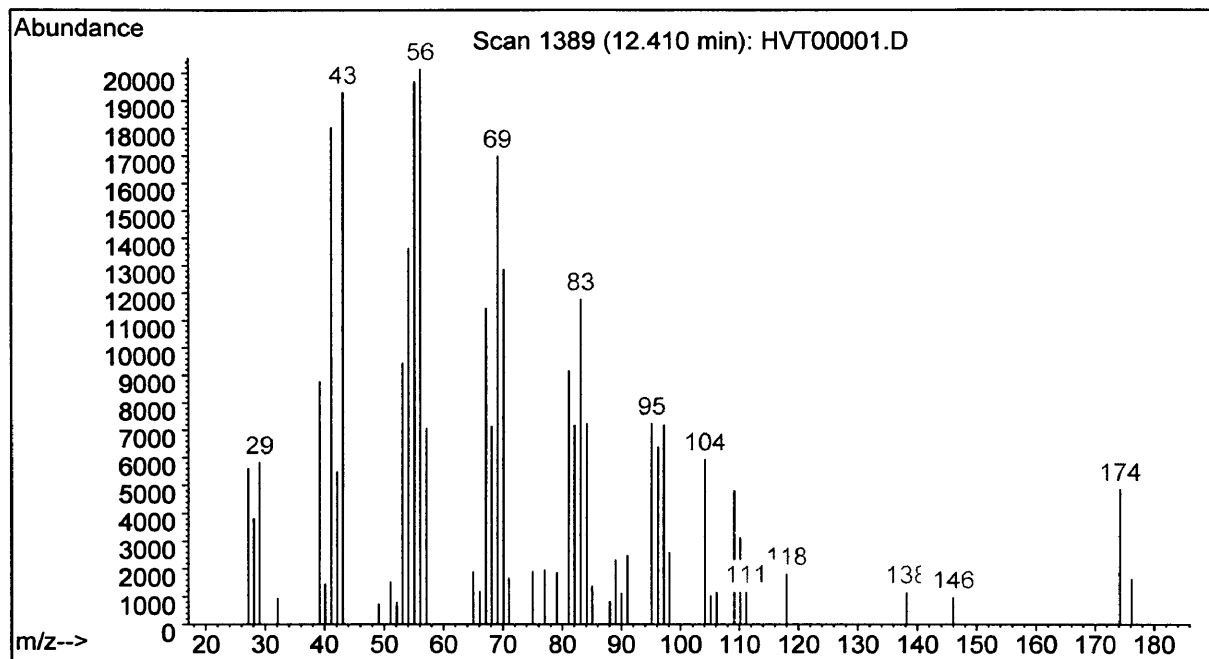


Figure 3-1: Mass spectrum of (E)-1-chloro-2-decene

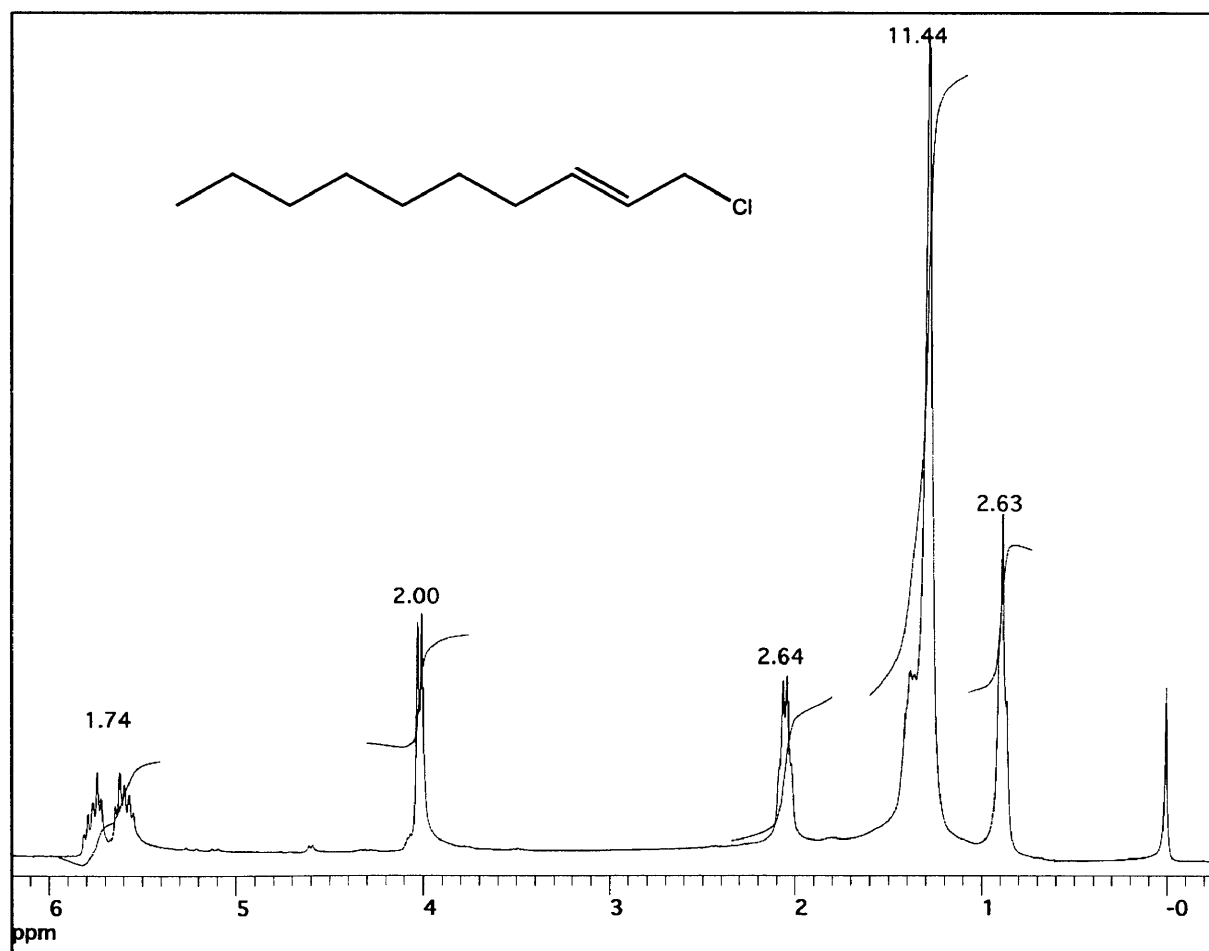


Figure 3-2: ^1H NMR spectrum of (E)-1-chloro-2-decene

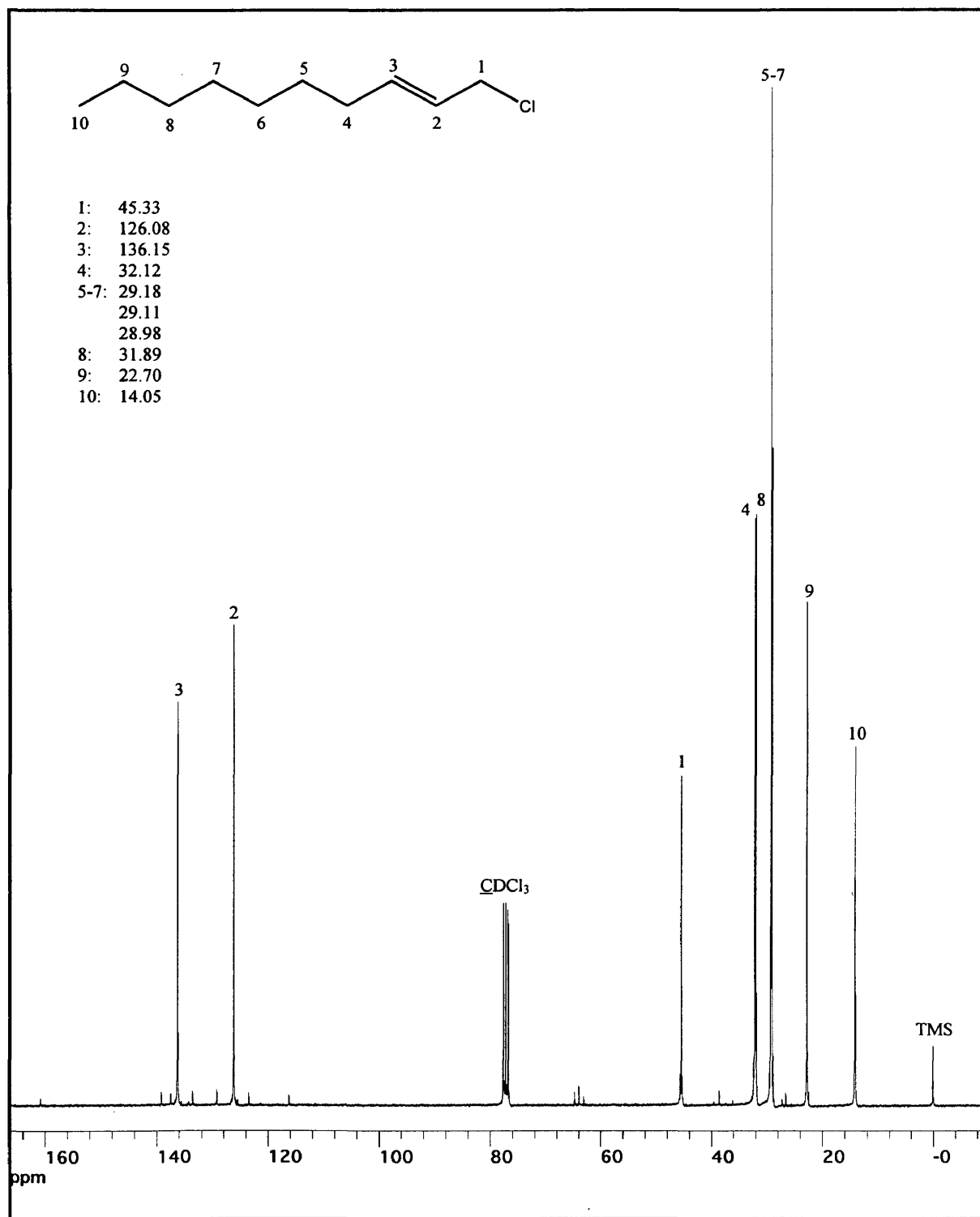
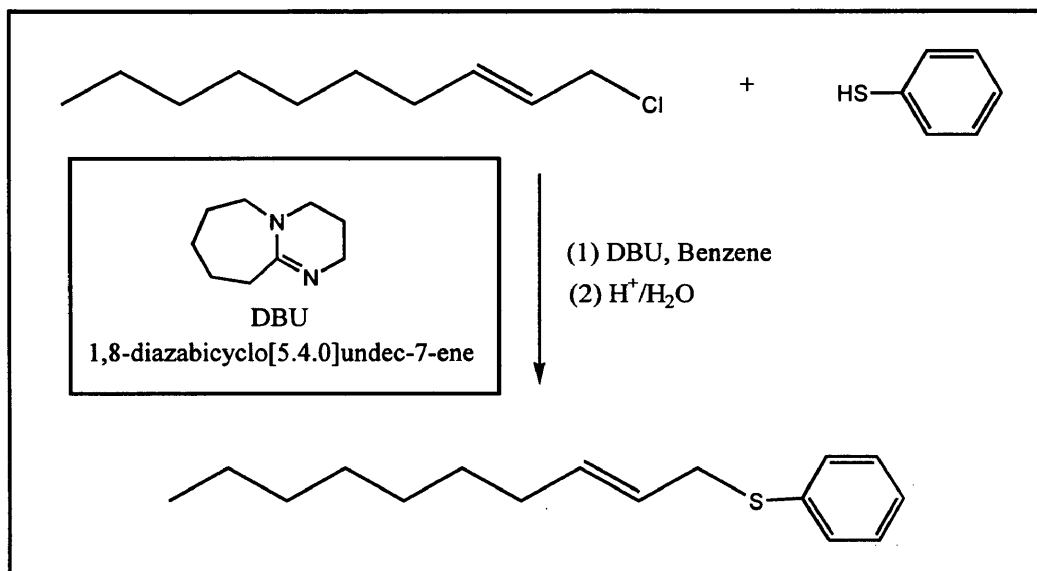


Figure 3-3: ^{13}C NMR spectrum of (E)-1-chloro-2-decene

3.4 Synthesis of (E)-[(2-decenyl)thio]benzene



The synthesis of *trans*-[(2-butenyl)thio]benzene was based on a literature method⁷⁷ for the conversion of a thiol and alkyl halide into a sulfide. The previously made *trans*-1-chloro-2-decene (1.74 g, 0.01 mol) was added to a stirred mixture of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1.52 g, 0.01 mol) and thiophenol (1.10 g, 0.01 mol) in benzene (30 mL), and the resulting reaction mixture was stirred at room temperature for 2 h under N₂. The precipitated DBU-HCl salt was removed by filtration. The filtrate was washed with water and dried with anhydrous magnesium sulfate. Benzene was evaporated in vacuo and the residue was distilled under reduced pressure, yielding 0.85 g (34%) of 97% pure (by GC-MS) product. Mass spectral analysis (**Figure 3-4**) showed a molecular ion peak at 248 *m/e*. ¹H NMR (**Figure 3-5**): δ 0.80-1.00 (3H, CH₃, triplet), 1.10-1.50 (10H, CH₂, multiplet), 1.90-2.10 (2H, CH₂, quadruplet), 3.45-3.56 (2H, CH₂, doublet), 5.38-5.60 (2H, HC=CH, multiplet), and 7.10-7.50 (5H, phenyl H, multiplet) ppm vs. Me₄Si. ¹³C NMR (**Figure 3-6**): δ 136.89, 134.44, 130.33, 128.70, 126.13, 125.37, 36.85, 32.26, 31.89, 29.30, 29.16, 29.08, 22.65, 13.94 ppm vs. Me₄Si.

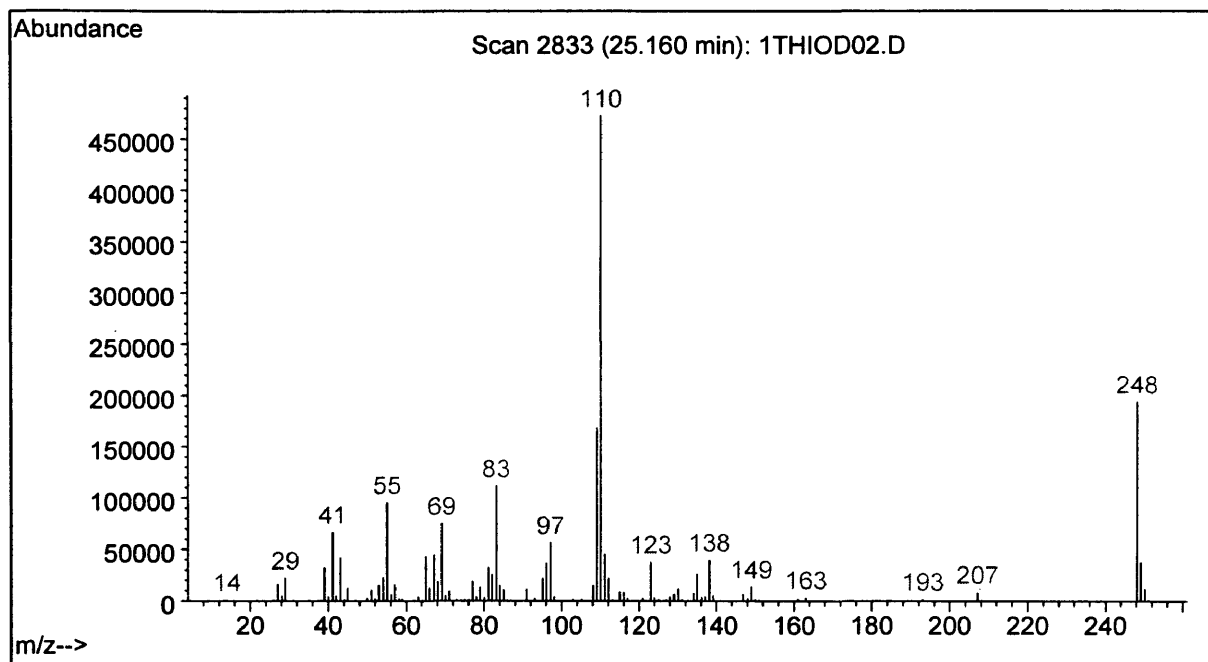


Figure 3-4: Mass spectrum of (E)-[(2-decenyl)thio]benzene

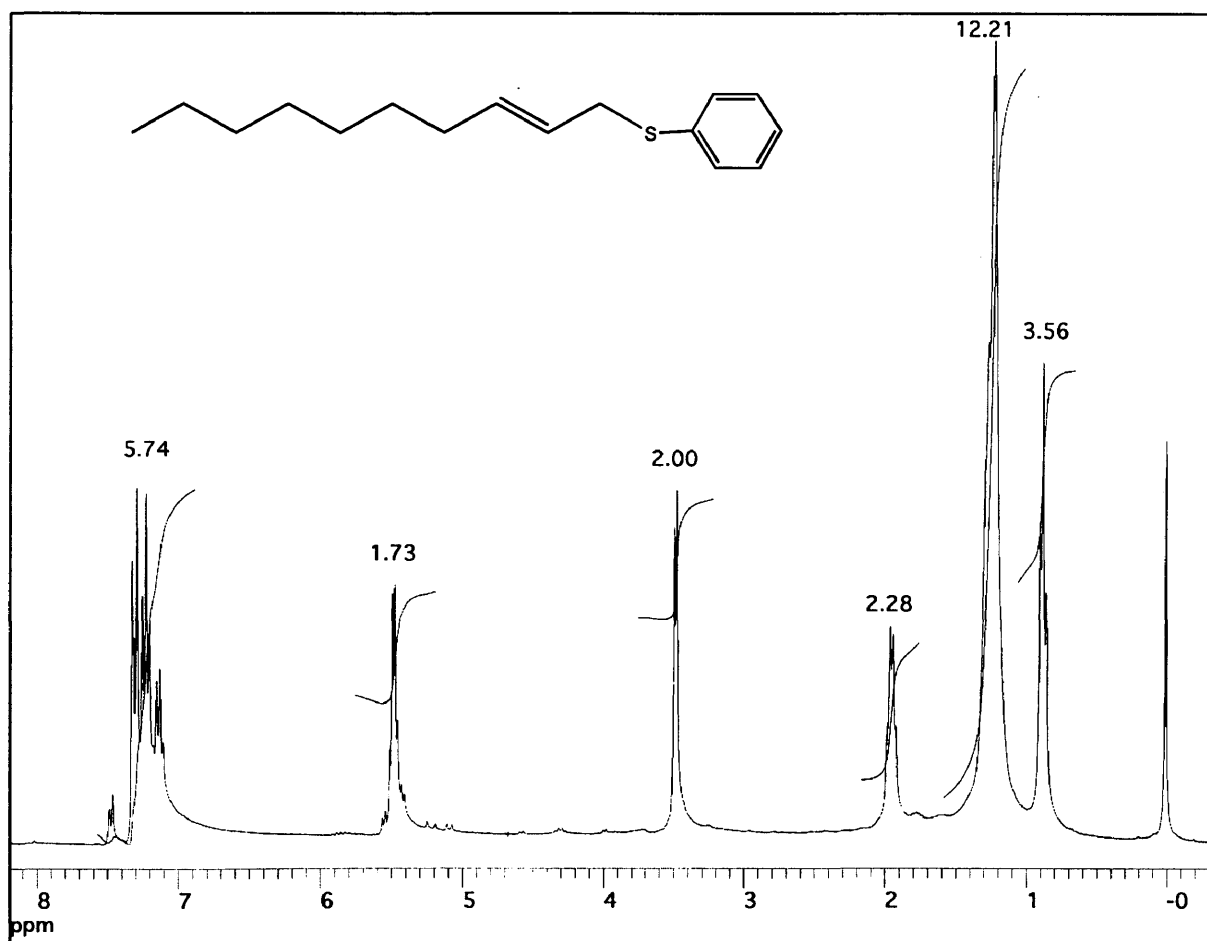


Figure 3-5: ^1H NMR spectrum of (E)-[(2-decenyl)thio]benzene

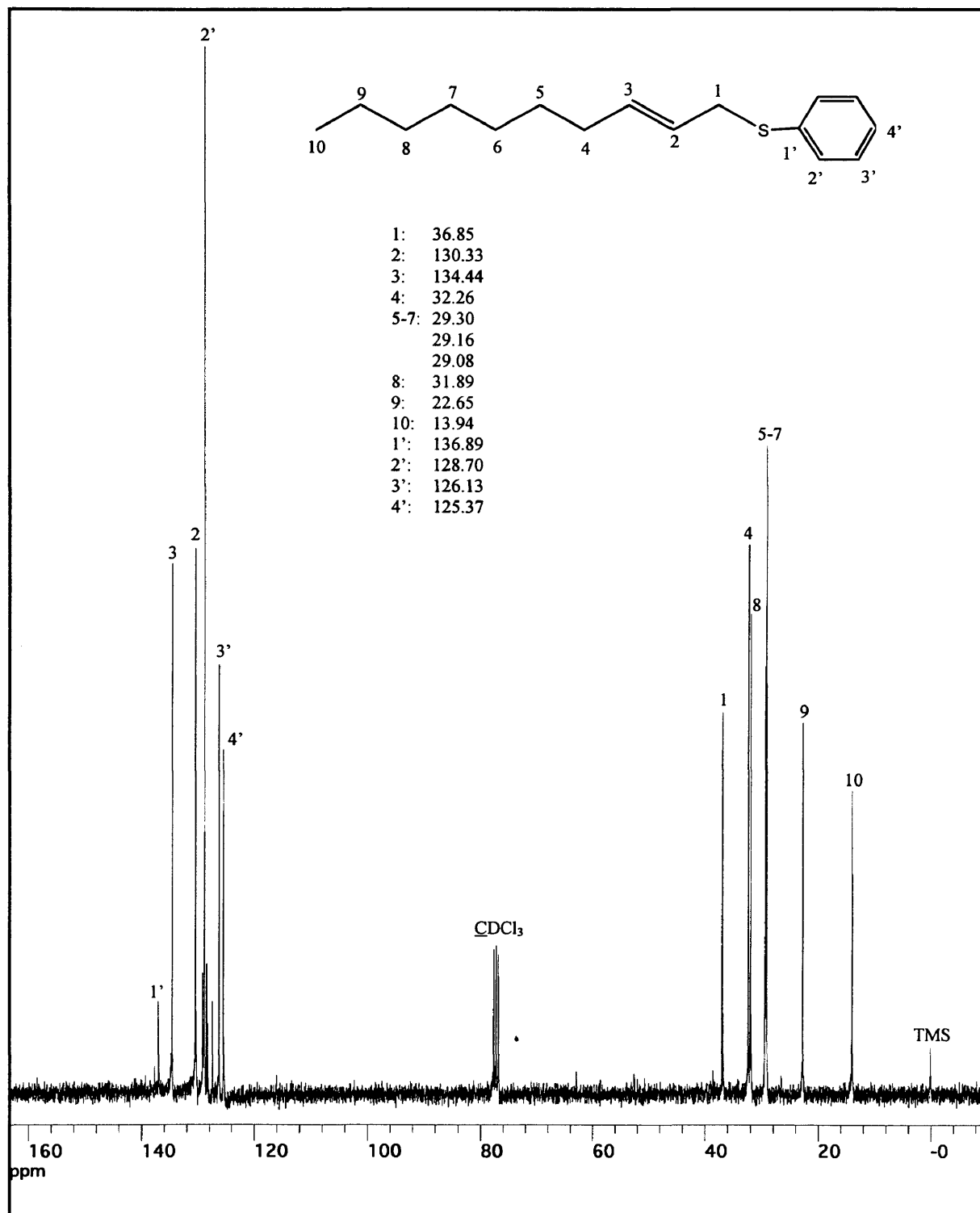
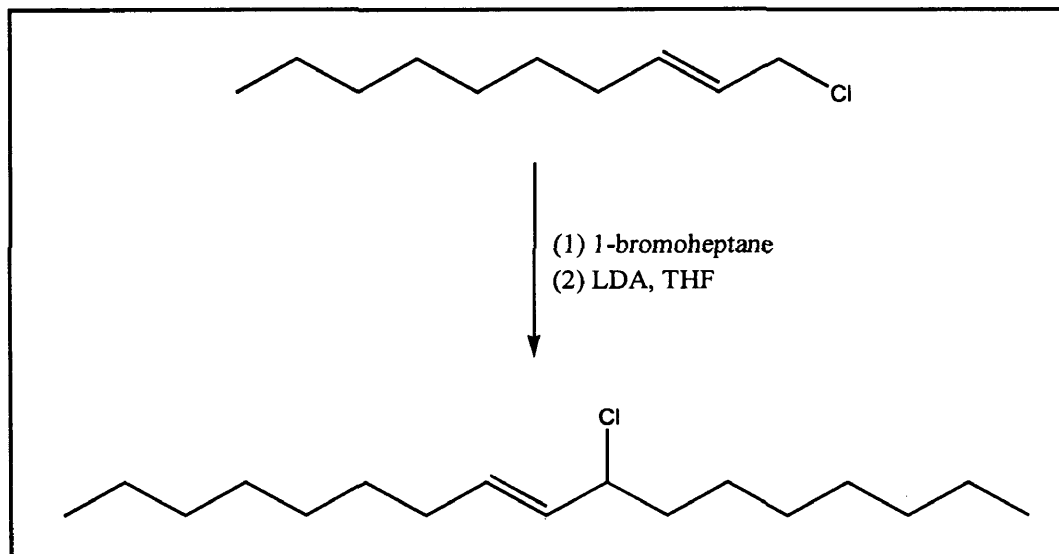


Figure 3-6: ^{13}C NMR spectrum of (E)-[(2-decenyl)thio]benzene

3.5 Synthesis of (E)-10-chloro-8-heptadecene



The method of conversion of *trans*-1-chloro-2-decene into *trans*-10-chloro-8-heptadecene was based on a literature method⁷⁸ for synthesizing internal allylic chlorides from primary allylic chlorides. A solution of lithium diisopropylamide (LDA) (28.7 mL, 2.0 M in THF, 57 mmol) in additional THF (~102 mL) was added dropwise with stirring to a mixture of *trans*-1-chloro-2-decene (5.00 g, 29 mmol), 1-bromoheptane (10.26 g, 57 mmol), and THF (62 mL) at -78 °C under N₂. After 15 min the reaction mixture was diluted with pentane (~200 mL) and then added to a saturated aqueous solution of ammonium chloride (NH₄Cl) (~200 mL). The *trans*-10-chloro-8-heptadecene was extracted with ether (4x100 mL), and the ether solution was dried with anhydrous magnesium sulfate (MgSO₄), filtered, and concentrated by rotary evaporation. After vacuum distillation (~2 mm Hg, 125-132 °C), 4.1 g (52%) of product (95% pure by GC/MS) was obtained. The mass spectrum (**Figure 3-7**) showed a molecular ion peak at 272 *m/e*. ¹H NMR (**Figure 3-8**): δ 0.80-0.95 (6H, CH₃, triplet), 1.10-1.50 (20H, CH₂, multiplet), 1.68-1.90 (2H, CH₂, multiplet), 2.00-2.10 (2H, CH₂, quadruplet), 4.25-4.38 (1H, CHCl, quadruplet), and 5.42-5.78 (2H, CH=CH, multiplet) ppm vs. Me₄Si. ¹³C NMR (**Figure 3-9**): δ 133.35, 131.53, 63.28, 39.17, 32.02, 31.94, 31.91, 29.19, 26.70, 22.68, and 13.96 ppm vs. Me₄Si.

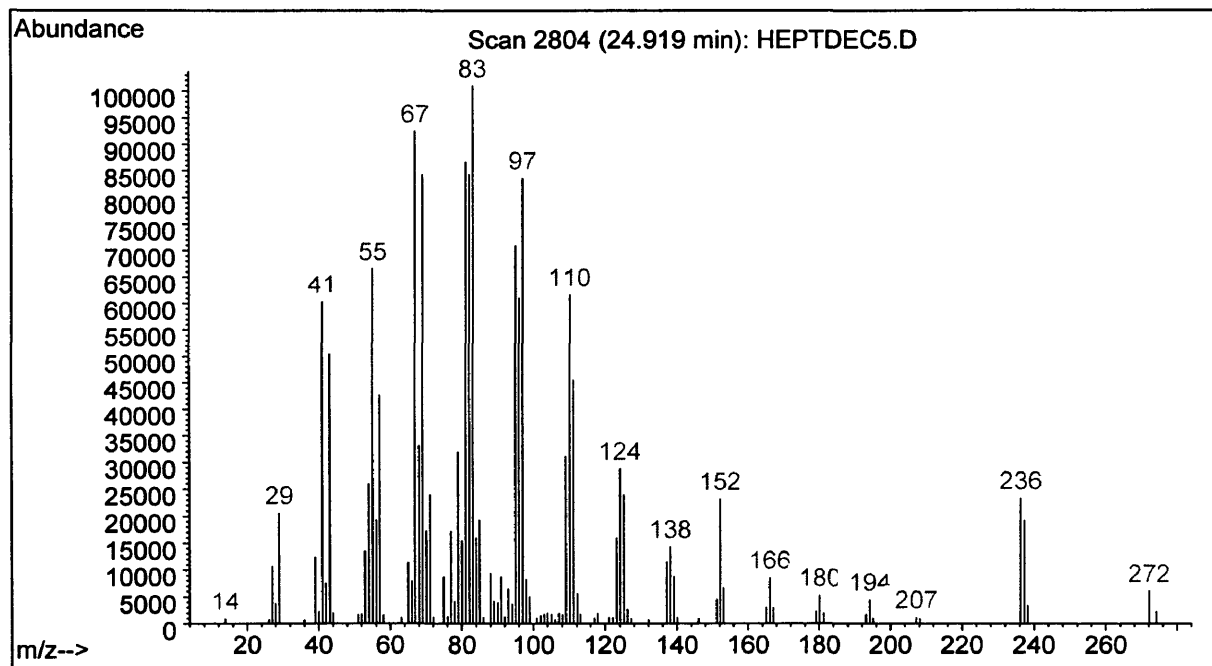


Figure 3-7: Mass spectrum of (E)-10-chloro-8-heptadecene

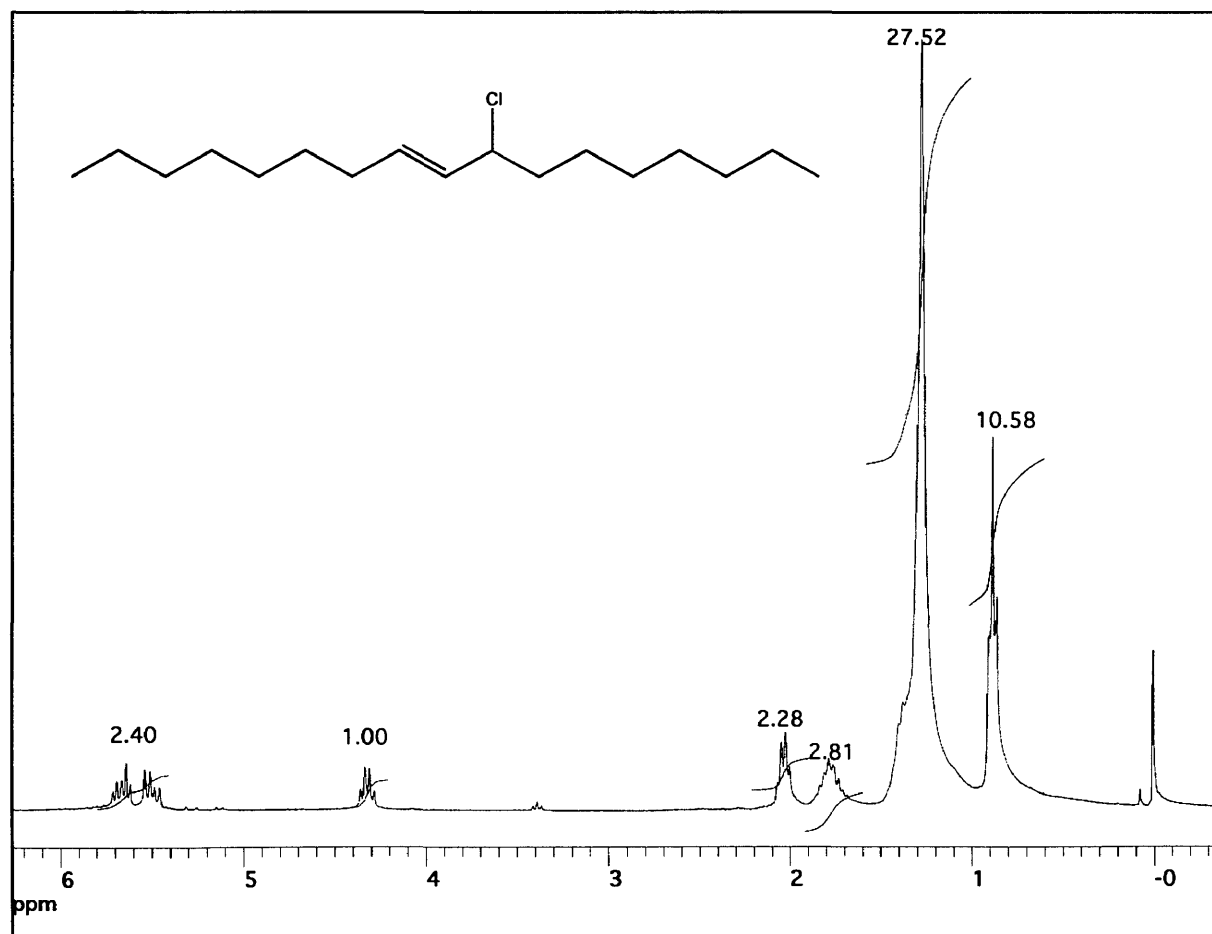


Figure 3-8: ^1H NMR spectrum of (E)-10-chloro-8-heptadecene

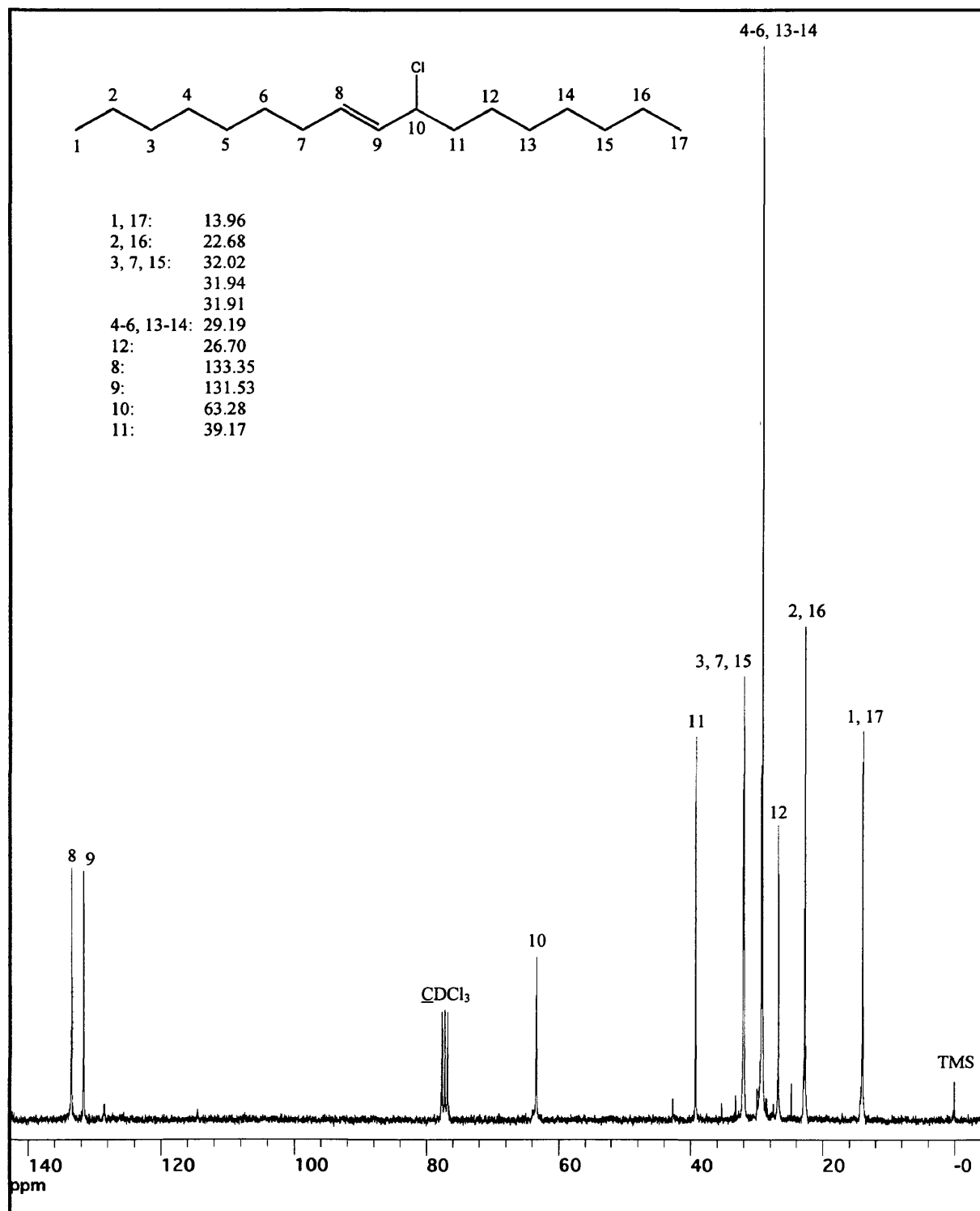
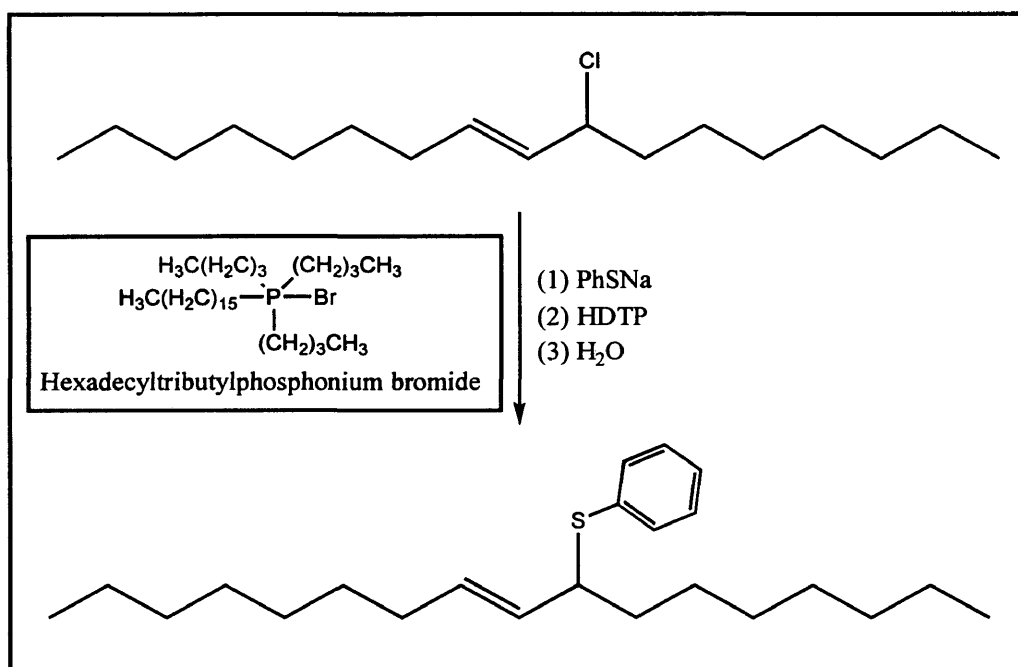


Figure 3-9: ^{13}C NMR spectrum of (E)-10-chloro-8-heptadecene

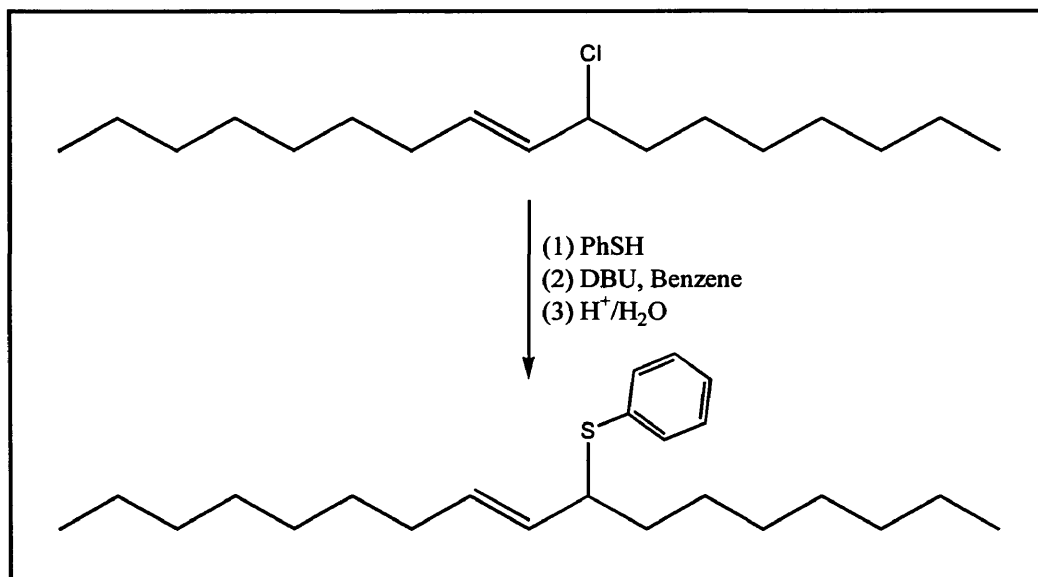
3.6 Synthesis of (E)-[(1-heptyl-2-decenyl)thio]benzene

Two methods were used for the synthesis of *trans*-[(1-heptyl-2-decenyl)thio]benzene. They were based on literature methods for making sulfides from alkyl halides.

Method 1:



The first method⁷⁹ involved the synthesis of thioethers in the presence of a small amount of a phase-transfer catalyst. The reactants, *trans*-10-chloro-8-heptadecene (1.00 g, 3.67 mmol), sodium thiophenolate (0.291 g, 2.20 mmol), and hexadecyltributylphosphonium bromide (HDTP) (0.186 g, 0.367 mmol) were mixed with 1.1 mL of water in a flask equipped with a magnetic stirrer and reflux condenser. After heating at 70 °C (bath temperature) for 3 h under nitrogen, the mixture was cooled to room temperature, and 6 mL of ether was added. The organic layer was separated, washed with water (3x3 mL), dried over calcium chloride, filtered, and subjected to rotary evaporation. After vacuum distillation, no significant amount of product was obtained.

Method 2:

The synthesis of *trans*-[(1-heptyl-2-deceny)thio]benzene was based on a previously reported method⁷⁷ for the conversion of a thiol and primary alkyl halide into a sulfide. The previously made *trans*-10-chloro-8-heptadecene (1.00 g, 3.67 mmol) was added to a stirred mixture of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.56 g, 3.7 mmol) and thiophenol (0.40 g, 3.7 mmol) in benzene (11 mL), and the resulting reaction mixture was stirred at 50 °C for 2 h under N₂. The precipitated DBU-HCl salt was removed by filtration. The filtrate was washed with water and dried with anhydrous magnesium sulfate. Benzene was evaporated in vacuo, and the residue was distilled under reduced pressure, yielding 0.59 g (46%) of 87% pure (by GC-MS) product. Mass spectral analysis (**Figure 3-10**) showed a molecular ion peak at 346 *m/e*. ¹H NMR (**Figure 3-11**): δ 0.82-1.00 (6H, CH₃, triplet), 1.05-1.50 (20H, CH₂, multiplet), 3.50-3.62 (1H, CHSPh, quadruplet), 5.18-5.33 (2H, HC=CH, multiplet), and 7.10-7.50 (5H, phenyl H, multiplet) ppm vs. Me₄Si. ¹³C NMR (**Figure 3-12**): δ 135.84, 133.10, 132.37, 131.19, 128.51, 126.83, 51.97, 35.14, 32.21, 31.91, 29.43, 29.19, 29.08, 27.37, 22.68, and 13.96 ppm vs. Me₄Si.

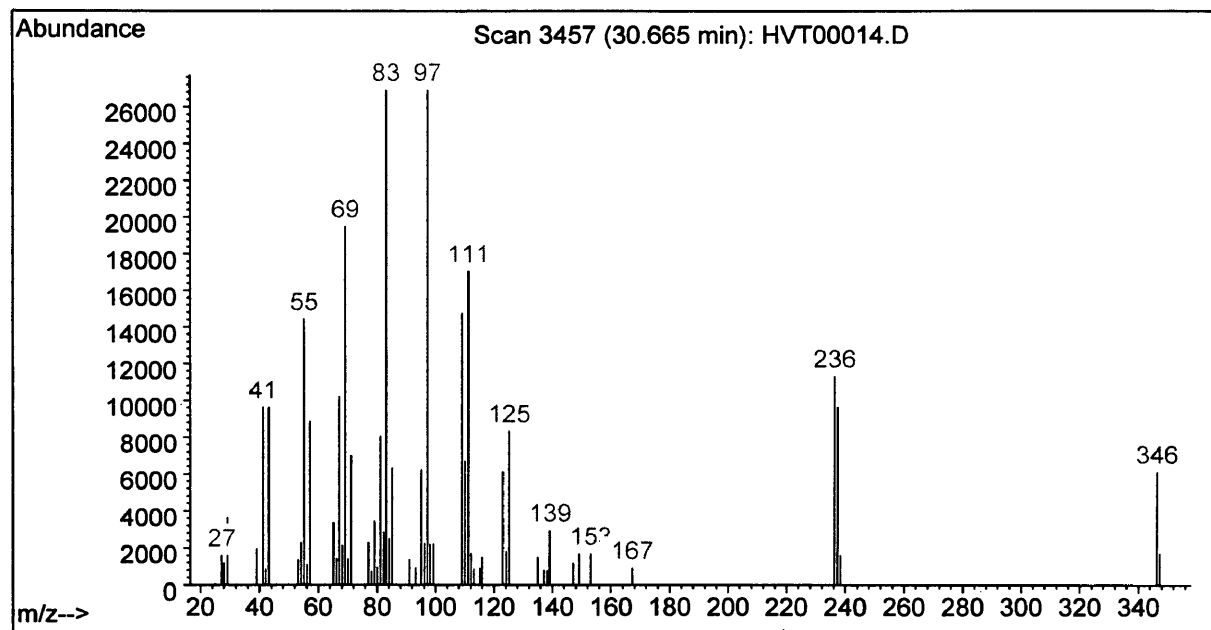


Figure 3-10: Mass spectrum of (E)- [(1-heptyl-2-decenyl)thio]benzene

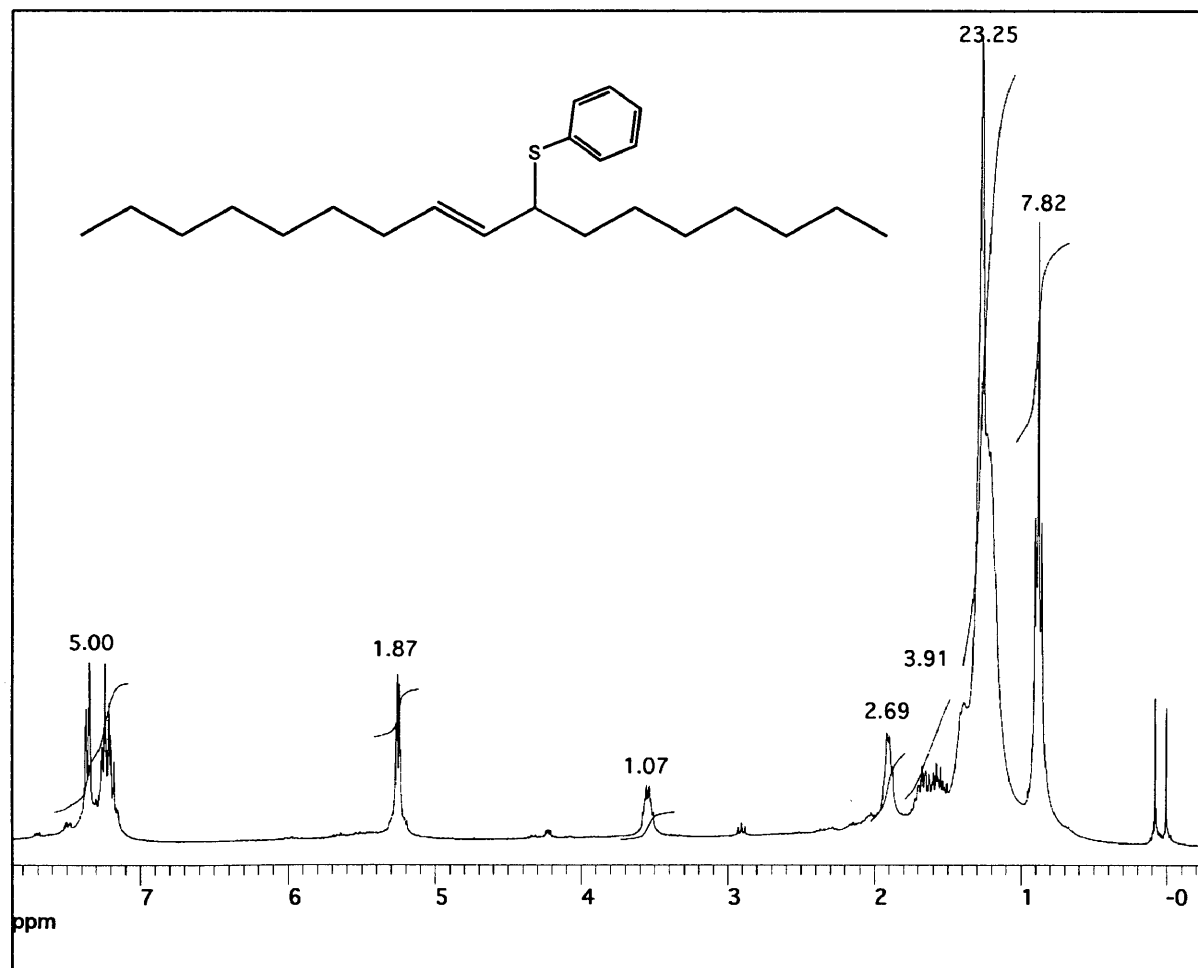


Figure 3-11: ¹H NMR spectrum of (E)- [(1-heptyl-2-decenyl)thio]benzene

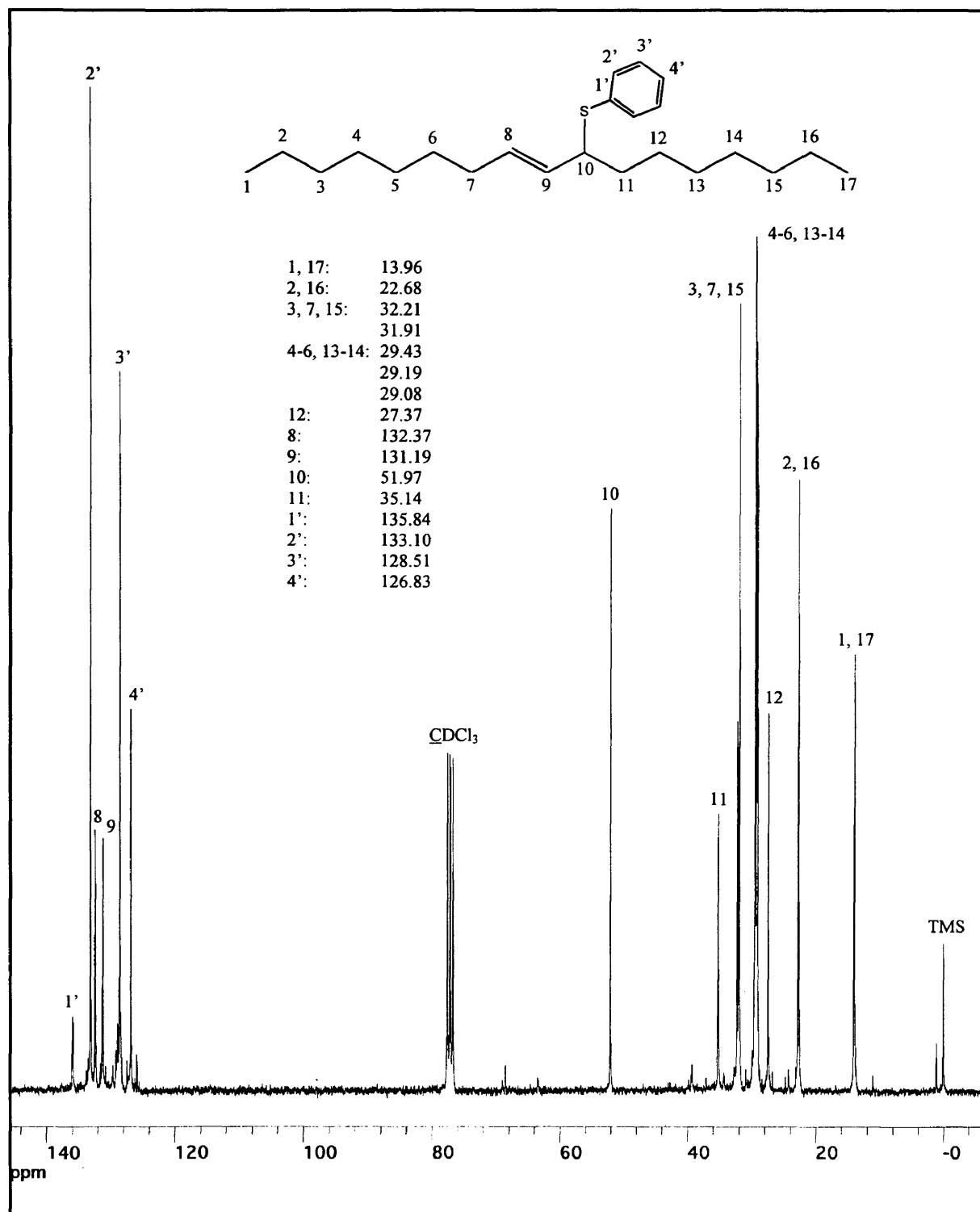
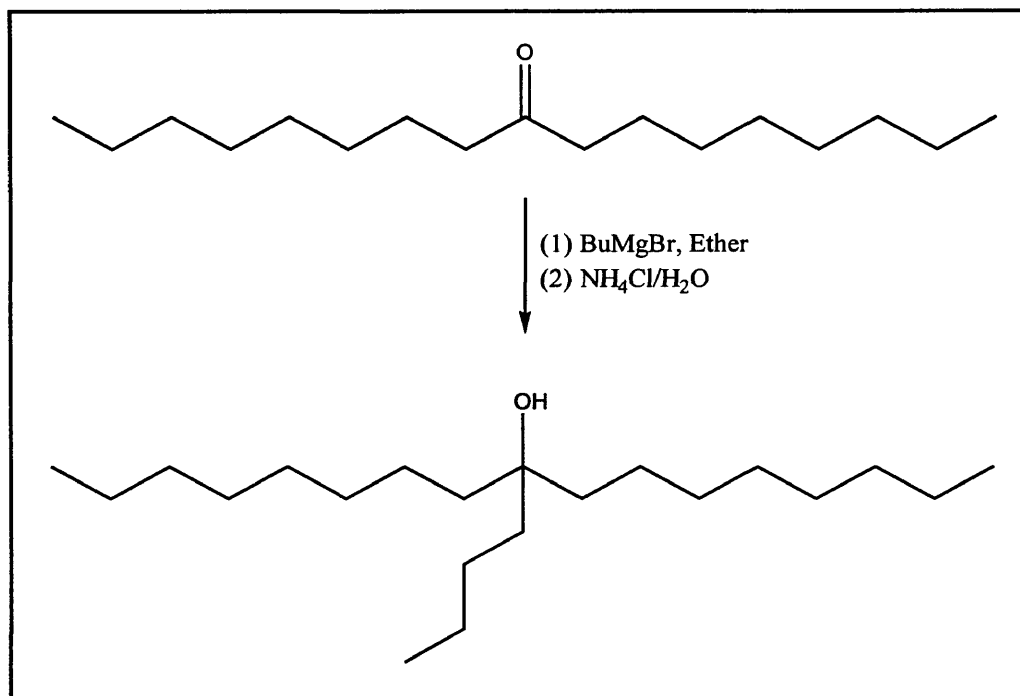


Figure 3-12: ^{13}C NMR spectrum of (E)- [(1-heptyl-2-decyl)thio]benzene

3.7 Synthesis of 9-butylheptadecan-9-ol



A Grignard reaction was used to make the tertiary alcohol from the ketone.⁸⁰ To ~27 mL of ether, *n*-butyl bromide (2.69 g, 19.7 mmol) and magnesium turnings (0.48 g, 20 mmol) were added. The mixture was allowed to react under N₂, with occasional cooling in an ice bath at 0 °C, until almost all of the magnesium was used. After the Grignard reagent was formed, 9-heptadecanone (5.00 g, 19.7 mmol) was added to the mixture with another 27-mL portion of ether. The mixture was allowed to react for 2 hours at 0 °C under nitrogen. The resulting mixture was poured into an icy solution of ammonium chloride (NH₄Cl) and water (~50 mL). The organic phase was separated, dried with sodium sulfate (Na₂SO₄), and subjected to rotary evaporation. Upon vacuum distillation (~2 mm Hg), 3.23 g (53%) of tertiary alcohol (98% purity by GC/MS) was obtained. The IR spectrum showed a broad OH peak at 3300-3500 cm⁻¹ (**Figure 3-13**), and the mass spectrum showed a peak at 294 *m/e* (M⁺ - H₂O) (**Figure 3-14**). ¹H NMR (**Figure 3-15**): δ 0.80-1.00 (9H, CH₃, triplet), 1.10-1.40 (28H, CH₂, multiplet), 1.40-1.50 (6H, CCH₂, multiplet), and 1.40-1.50 (1H, OH, singlet) ppm vs. Me₄Si. ¹³C NMR (**Figure 3-16**): δ 74.49, 39.77, 39.45, 37.87, 32.07, 30.53, 29.93, 29.74, 29.63, 29.42, 25.98, 25.85, 23.71, 23.50, 22.75, and 13.97 ppm vs. Me₄Si.

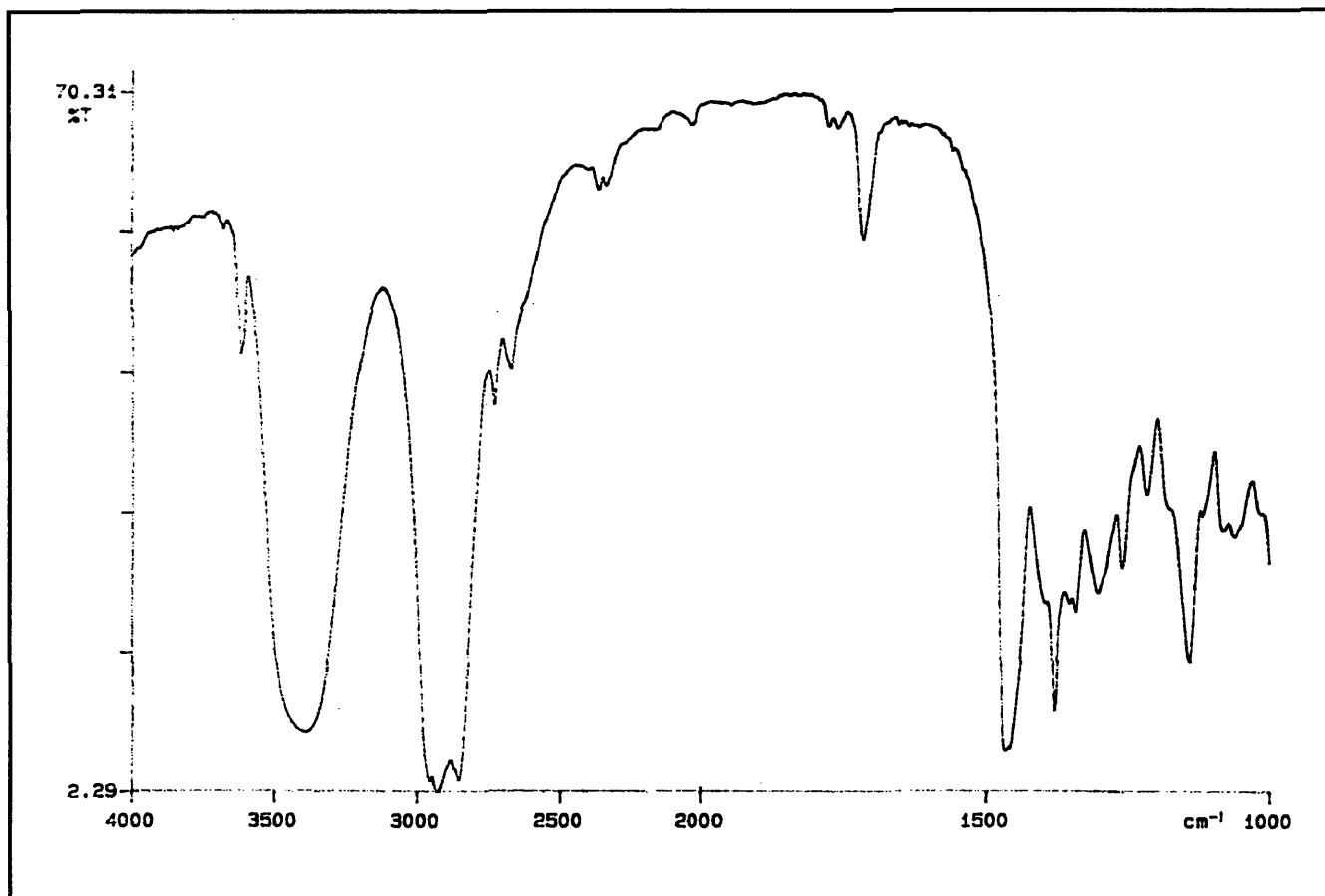


Figure 3-13: IR spectrum of 9-butylheptadecan-9-ol

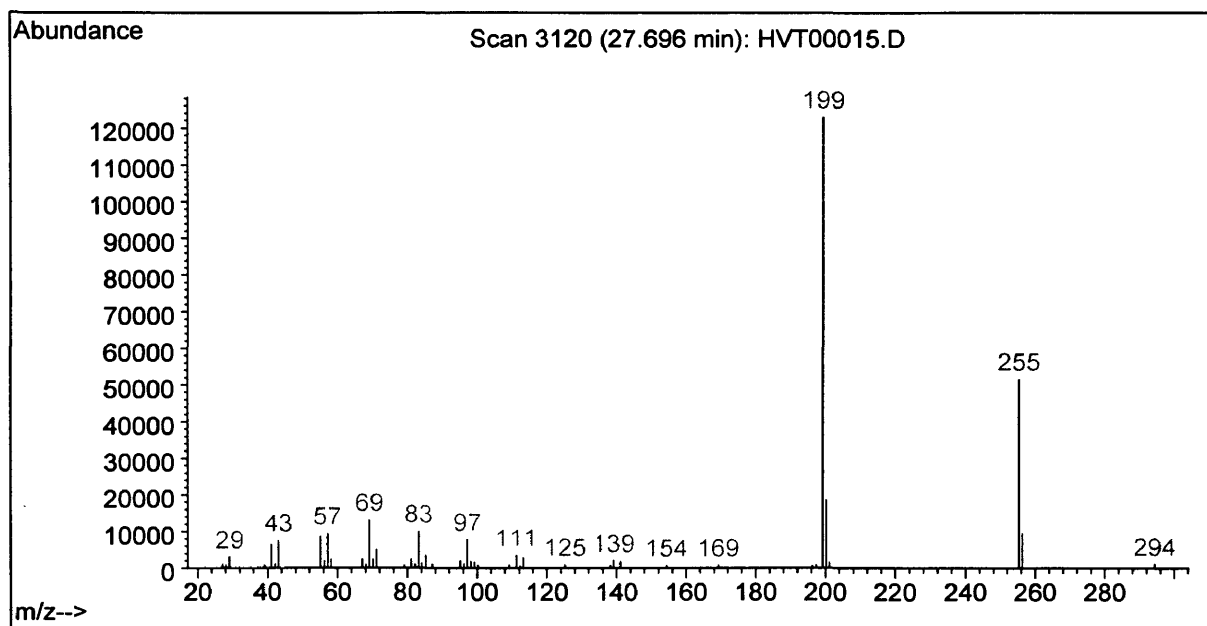


Figure 3-14: Mass spectrum of 9-butylheptadecan-9-ol

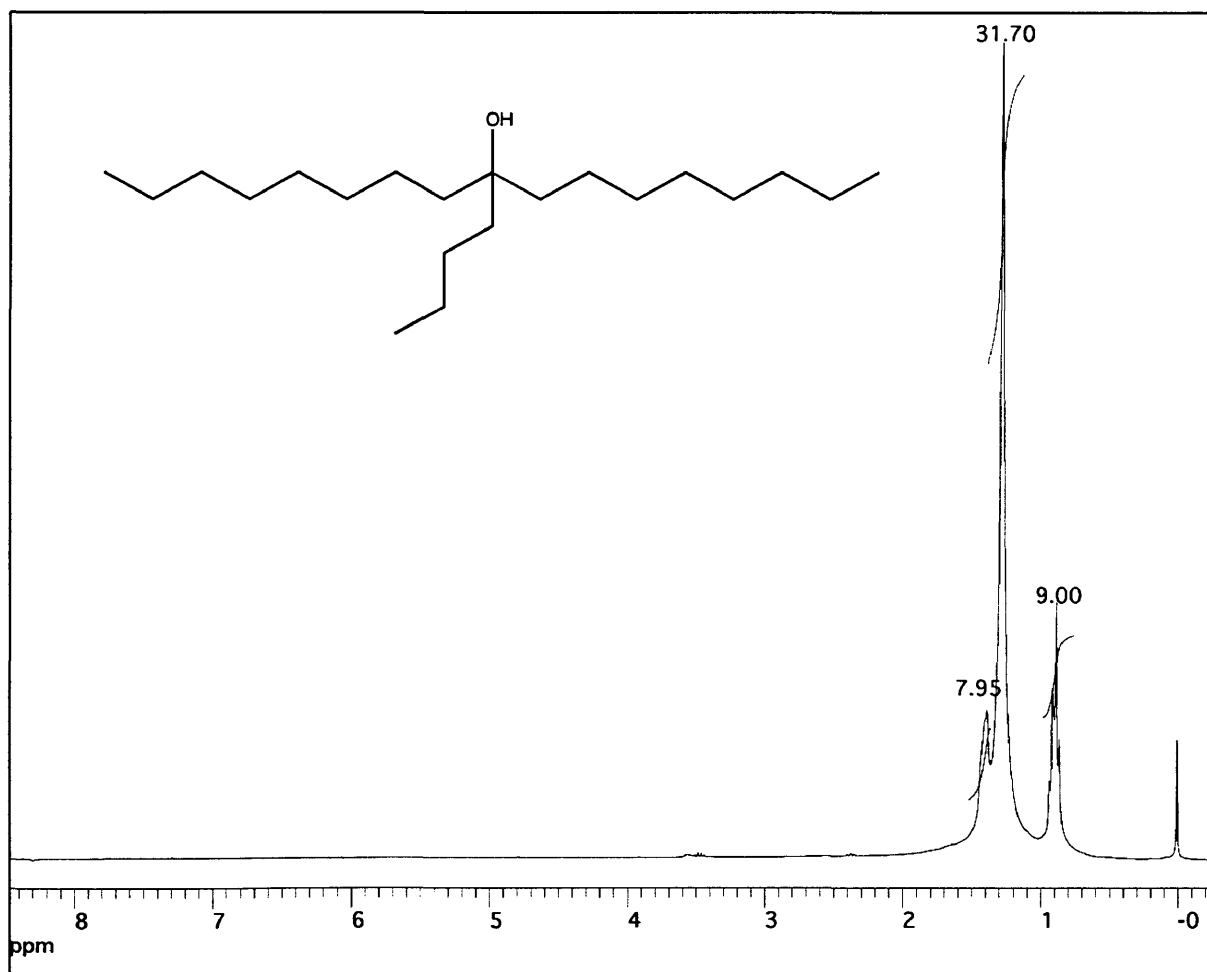


Figure 3-15: ^1H NMR spectrum of 9-butylheptadecan-9-ol

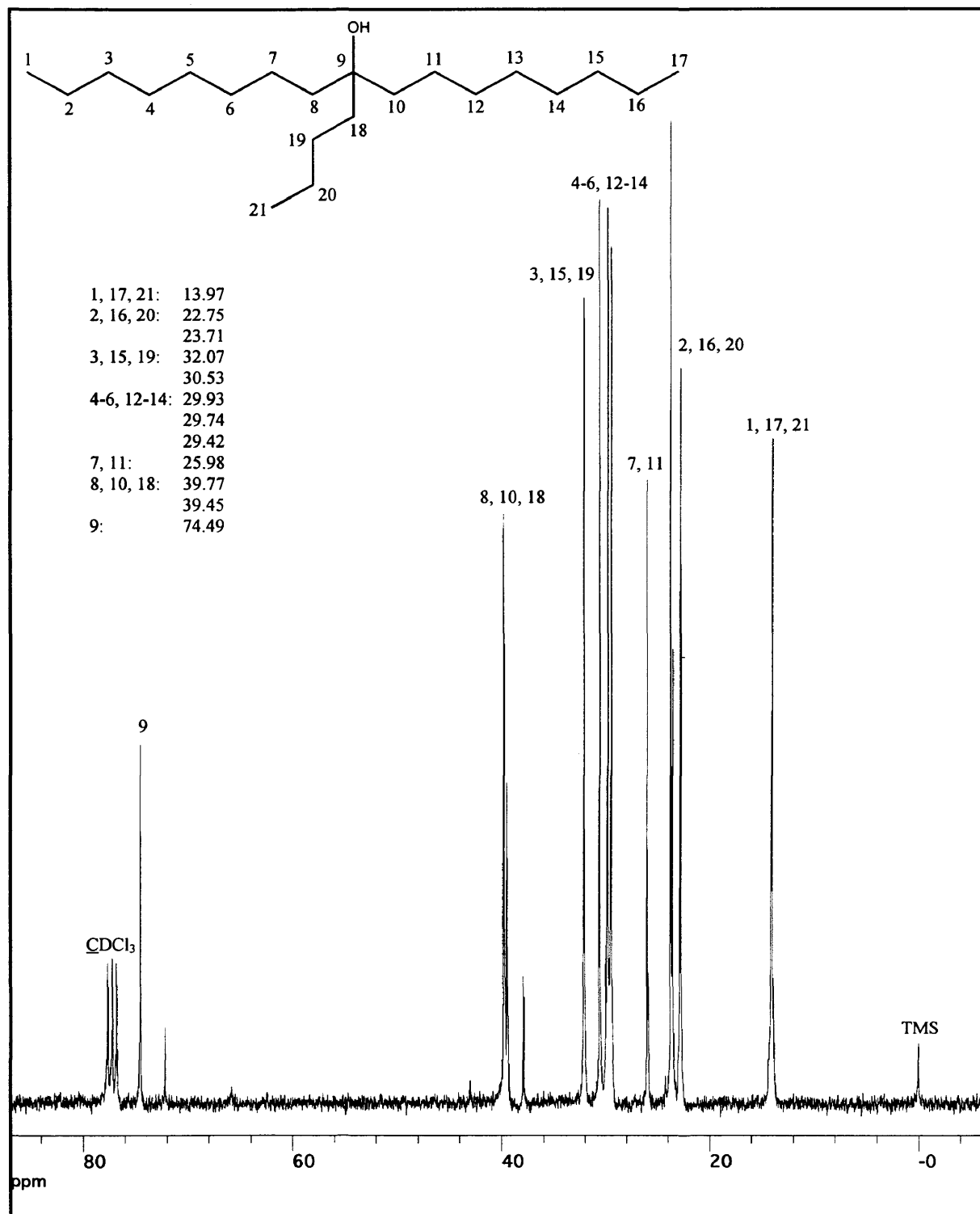
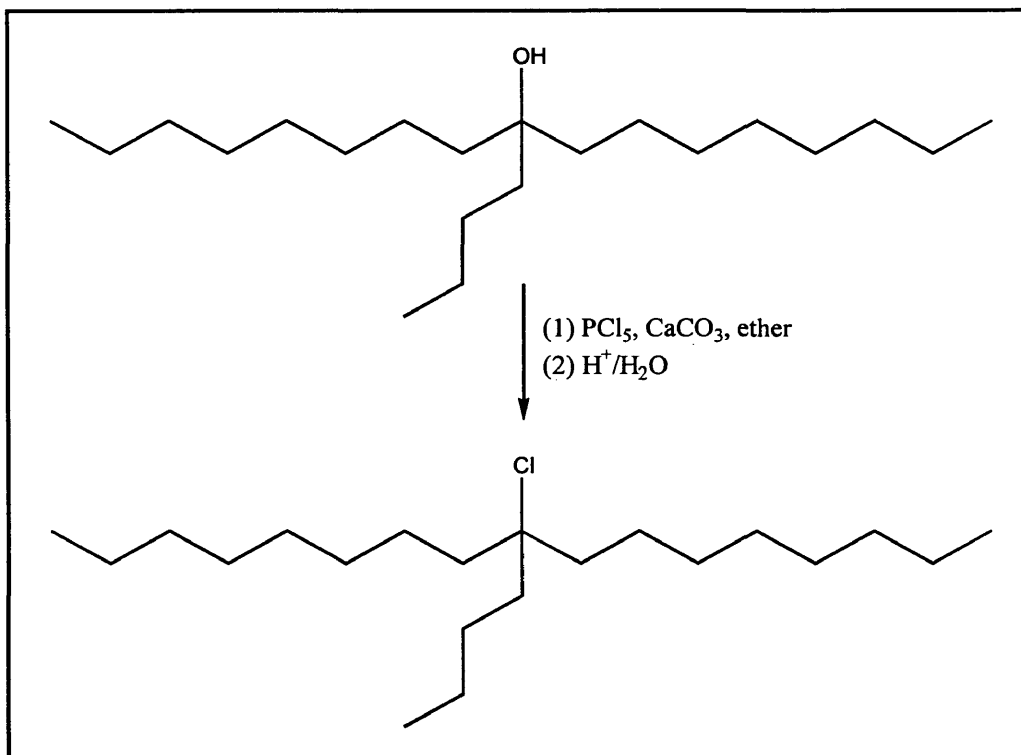


Figure 3-16: ^{13}C NMR spectrum of 9-butylheptadecan-9-ol

3.8 Synthesis of 9-butyl-9-chloroheptadecane



The synthesis of 9-butyl-9-chloroheptadecane was based on a literature method⁸¹ for converting a tertiary alcohol to the corresponding chloride. The previously made 9-butyl-heptadecan-9-ol (1.00 g, 3.20 mmol) was added to a slurry of phosphorus pentachloride (PCl₅) (0.866 g, 4.16 mmol) and calcium carbonate (CaCO₃) (0.320 g, 3.20 mmol) in ether at 0 °C under N₂. After stirring for 3 min, the mixture was filtered and washed with cold water. The ether layer was dried with sodium sulfate, filtered, and concentrated by rotary evaporation. Upon vacuum distillation (~2 mm Hg), 0.38 g (36%) of product (78% purity by GC/MS) was obtained. The IR spectrum showed CH₂ peaks at 2800-3000 cm⁻¹ without the OH peak at 3300-3500 cm⁻¹ (**Figure 3-17**), and the mass spectrum showed a peak at 294 *m/e* (M⁺ - HCl) (**Figure 3-18**). ¹H NMR (**Figure 3-19**): δ 0.80-1.00 (9H, CH₃, triplet), 1.15-1.55 (28H, CH₂, multiplet), and 1.60-1.80 (6H, CCH₂, multiplet) ppm vs. Me₄Si. ¹³C NMR (**Figure 3-20**): δ 78.70, 41.66, 41.36, 38.79, 32.00, 30.08, 29.60, 29.37, 26.75, 24.51, 23.08, 22.73, and 13.97 ppm vs. Me₄Si.

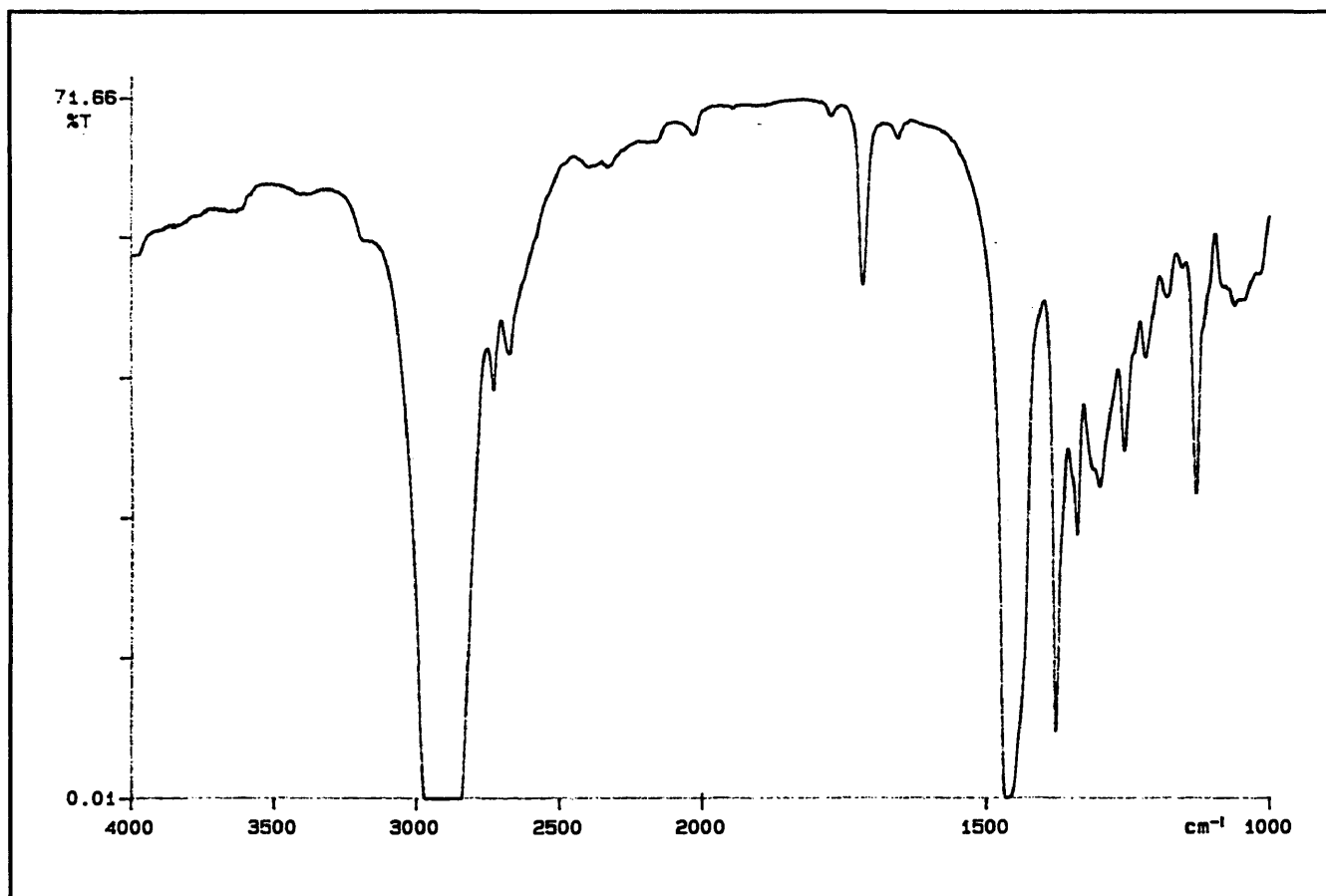


Figure 3-17: IR spectrum of 9-butyl-9-chloroheptadecane

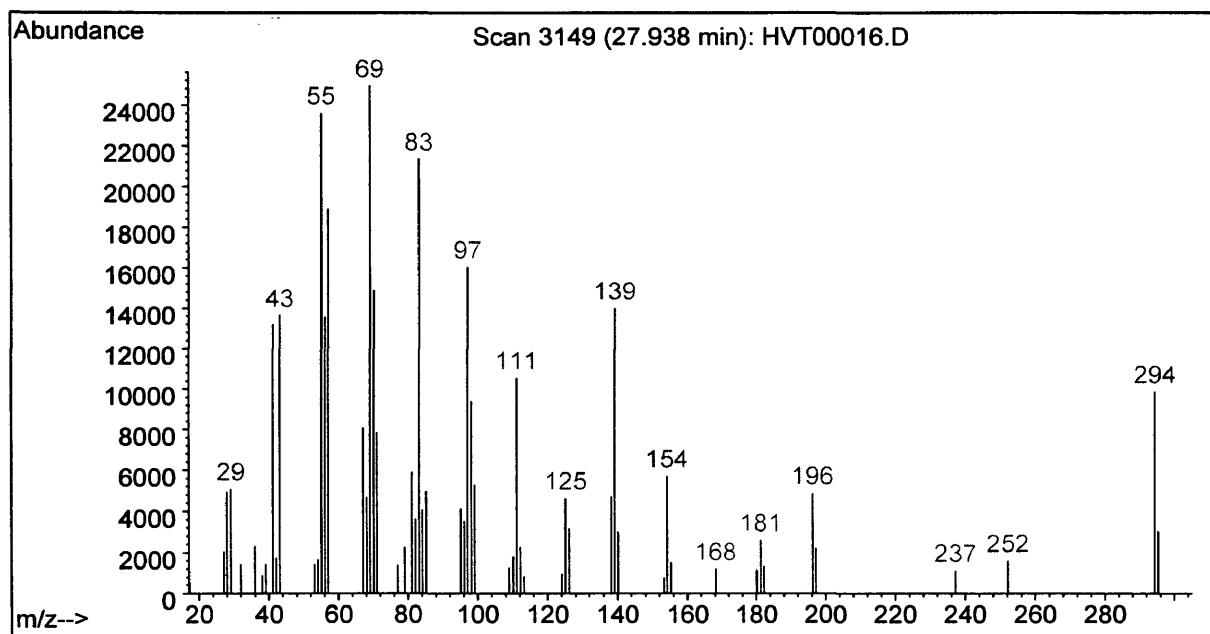


Figure 3-18: Mass spectrum of 9-butyl-9-chloroheptadecane

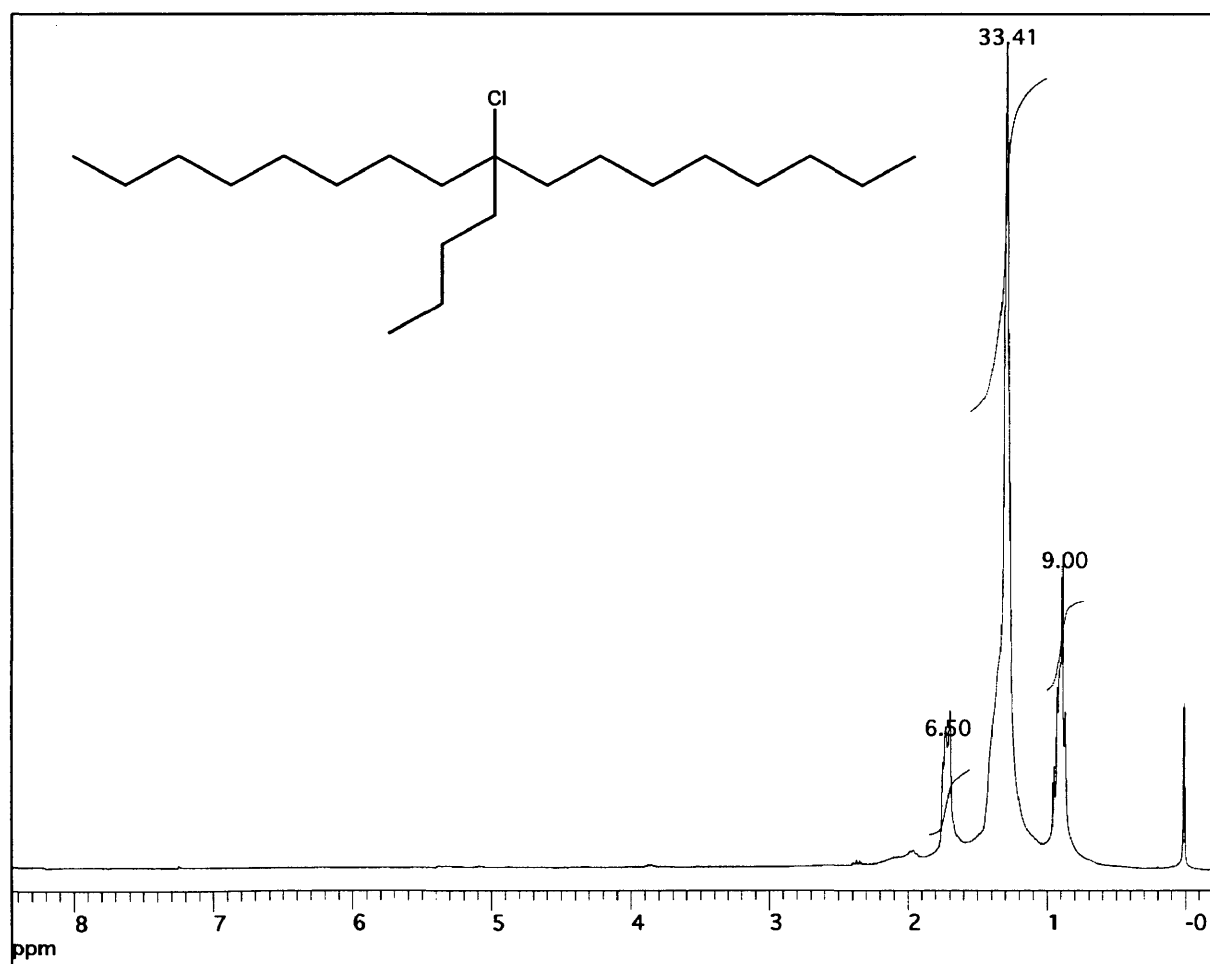


Figure 3-19: ^1H NMR spectrum of 9-butyl-9-chloroheptadecane

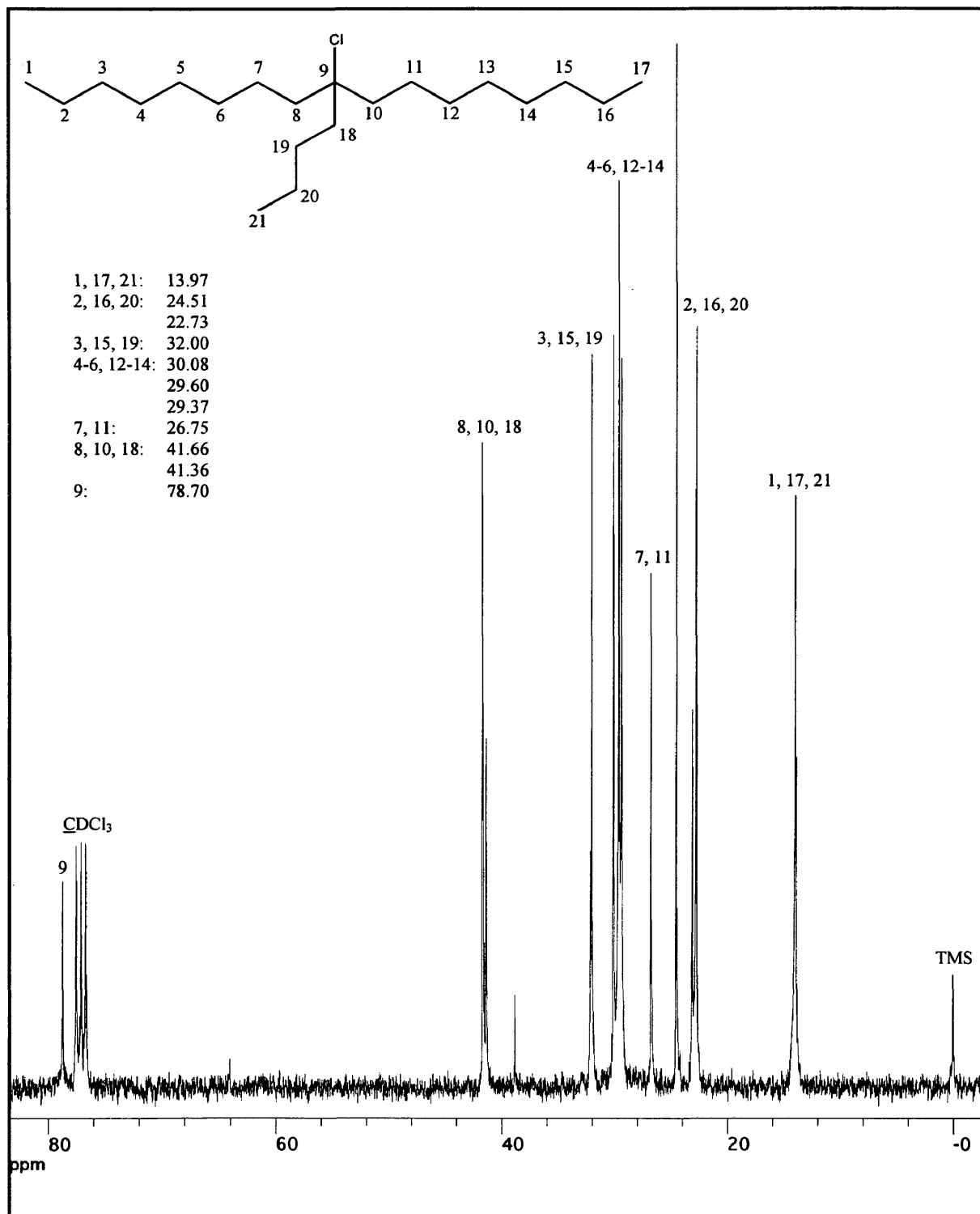
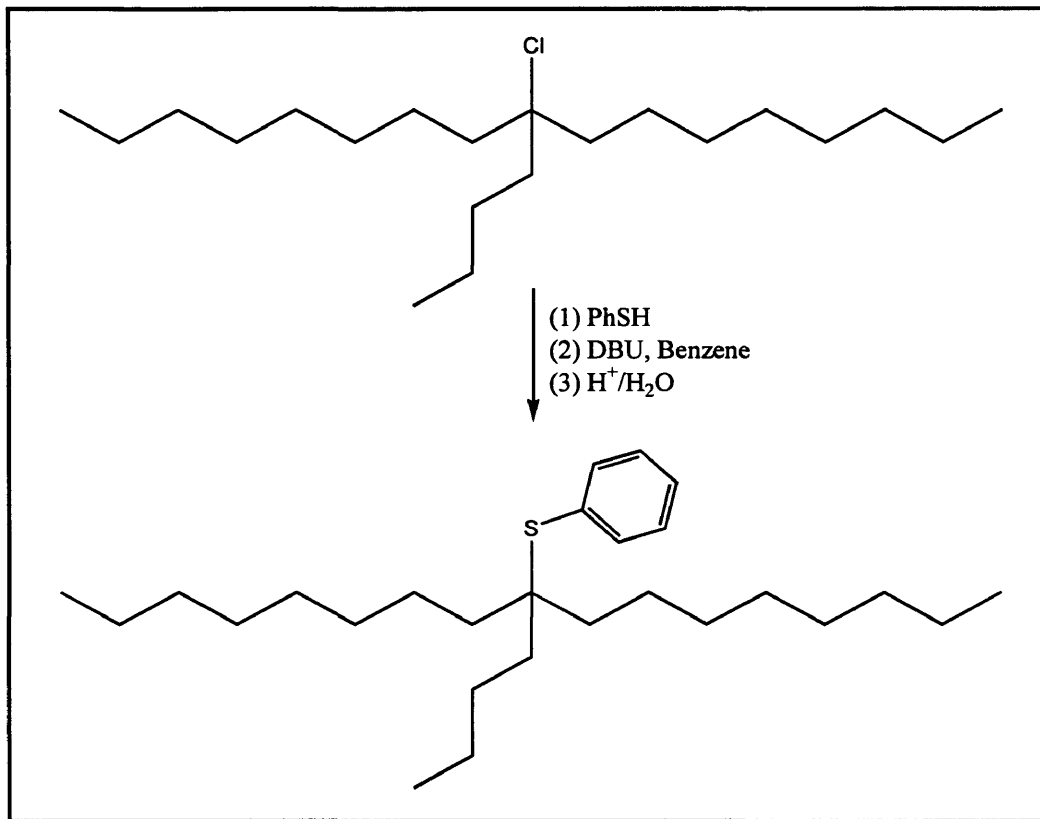


Figure 3-20: ¹³C NMR spectrum of 9-butyl-9-chloroheptadecane

3.9 Attempted synthesis of [(1,1-dioctylpentyl)thio]benzene



The synthesis of [(1,1-dioctylpentyl)thio]benzene was based on the previous method for converting a thiol and alkyl halide into a sulfide.⁷⁷ The previously made 9-butyl-9-chloroheptadecane (2.00 g, 6.0 mmol) was added to a stirred mixture of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.92 g, 6.0 mmol) and thiophenol (0.67 g, 6.0 mmol) in benzene (~18 mL), and the resulting reaction mixture was stirred at 50 °C for 2 h under N₂. The precipitated DBU-HCl salt was removed by filtration. The filtrate was washed with water and dried with anhydrous magnesium sulfate. Benzene was evaporated in vacuo, and the residue was distilled under reduced pressure (~2 mm Hg), yielding 0.63 g (26%) of 45% pure (by GC-MS) product (see Results and Discussion). Mass spectral analysis (**Figure 3-21**) showed a peak at 294 *m/e* (M⁺ - HSPh). ¹H NMR (**Figure 3-22**): δ 0.82-1.00 (9H, CH₃, triplet), 1.05-1.45 (28H, CH₂, multiplet), 1.65-2.04 (6H, CCH₂, multiplet), and 7.15-7.53 (5H, phenyl H, multiplet) ppm vs. Me₄Si. ¹³C NMR (**Figure 3-23**): δ 137.42, 129.06, 127.99, 127.25, 74.41, 39.58, 39.27, 31.99, 30.44, 29.68, 29.55, 29.35, 25.86, 23.60, 23.44, 22.71, and 14.02 ppm vs. Me₄Si.

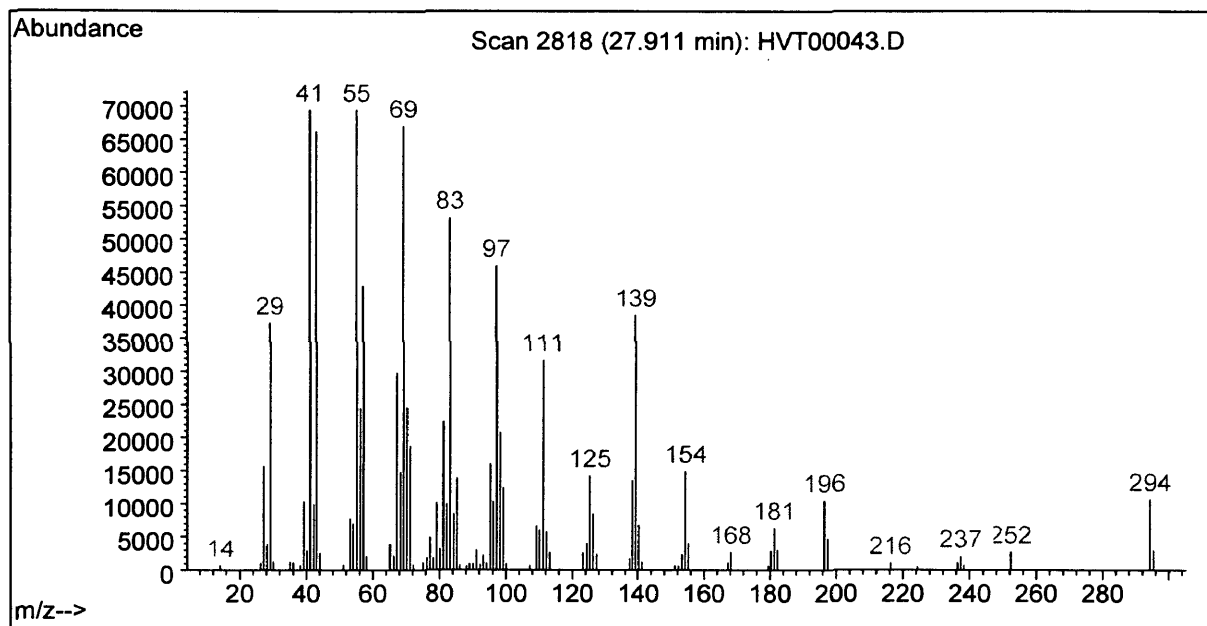


Figure 3-21: Mass spectrum of [(1,1-dioctylpentyl)thio]benzene (See Results and Discussion)

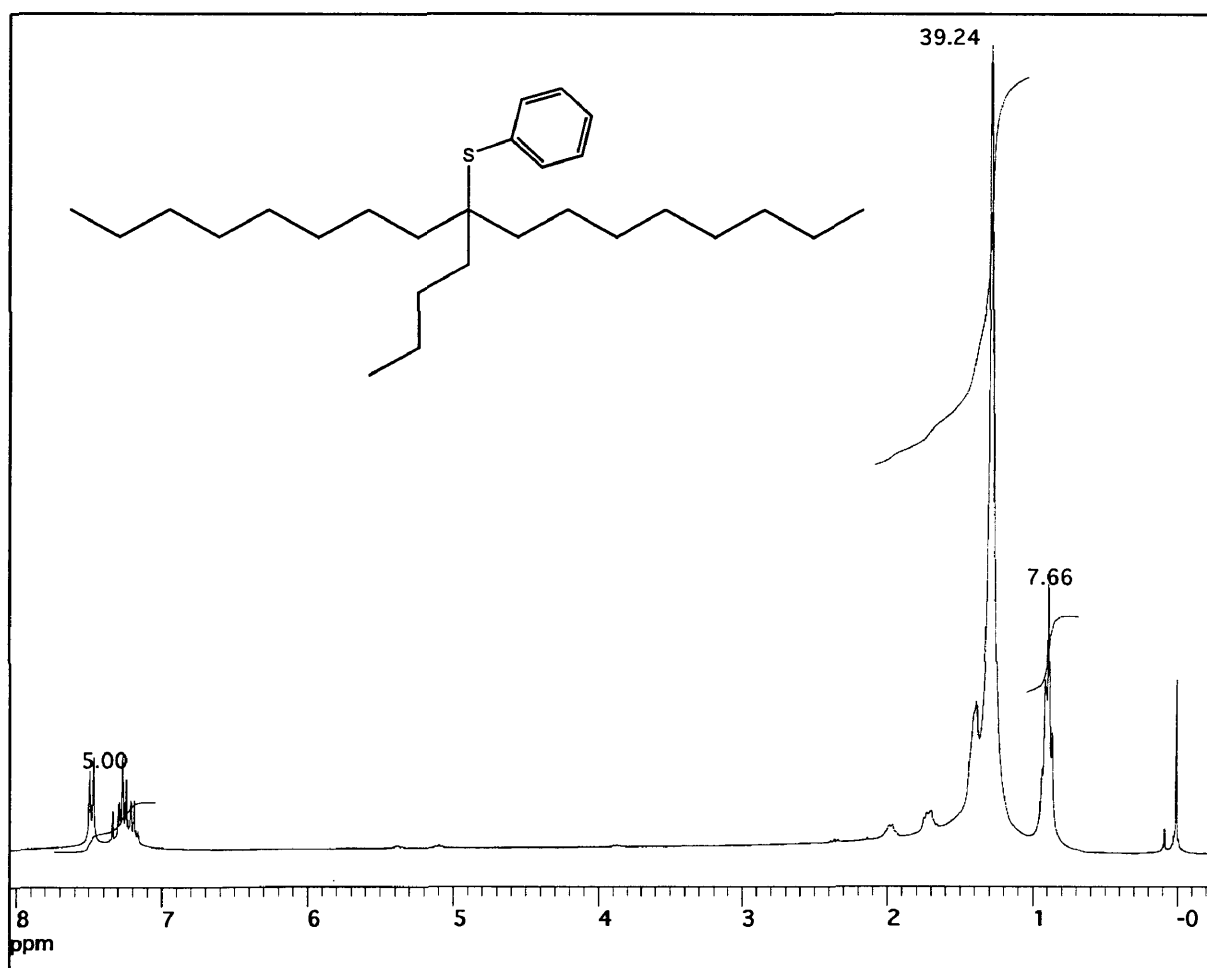


Figure 3-22: ^1H NMR spectrum of [(1,1-dioctylpentyl)thio]benzene (See Results and Discussion)

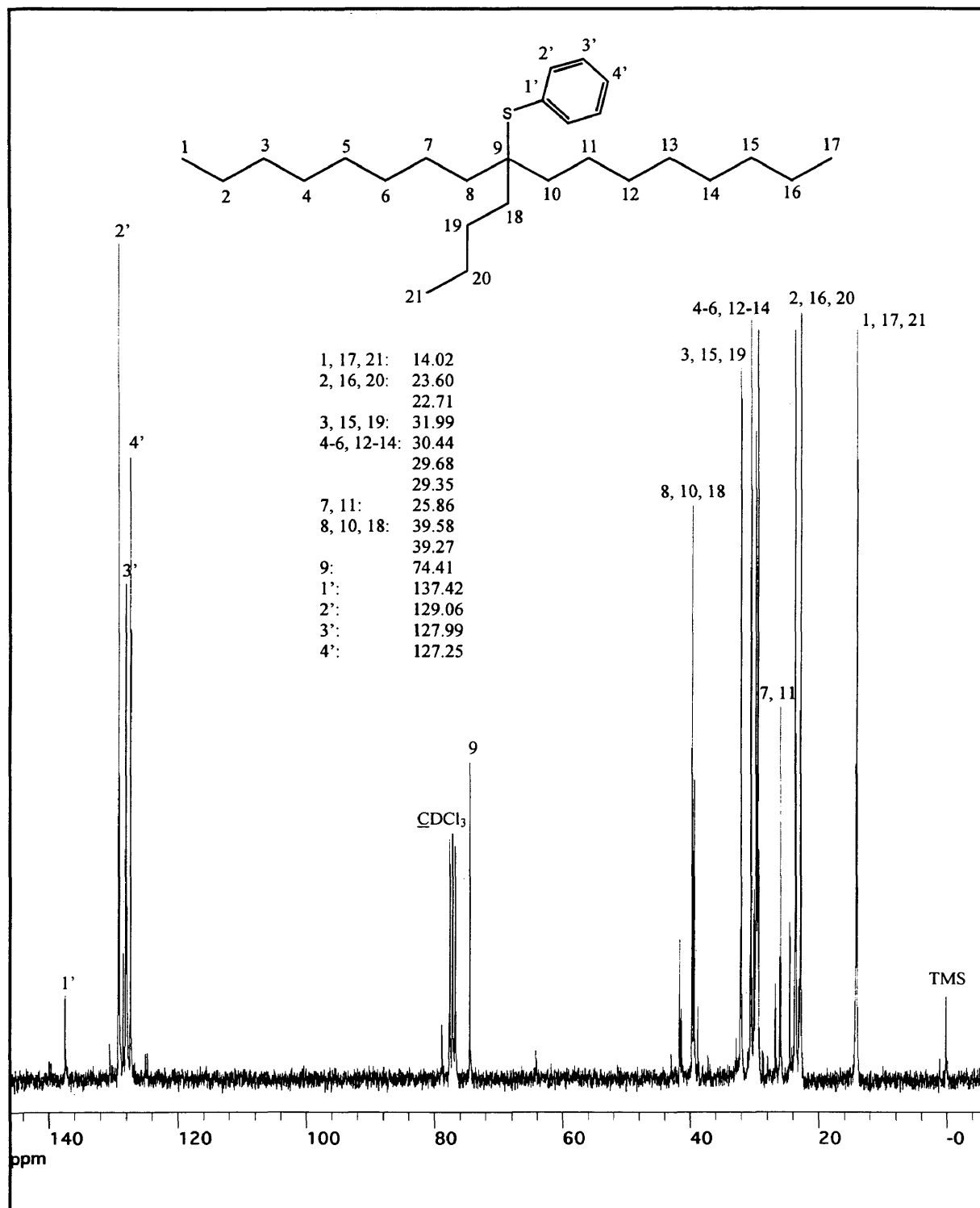
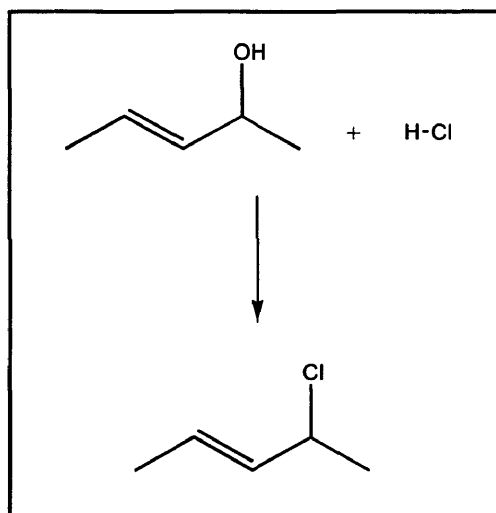


Figure 3-23: ¹³C NMR spectrum of [(1,1-dioctylpentyl)thio]benzene (See Results and Discussion)

3.10 Synthesis of (E)-4-chloro-2-pentene



The synthesis of *trans*-4-chloro-2-pentene was based on the classical method of using concentrated HCl to convert alcohols to the corresponding chlorides.⁸² The starting alcohol, *trans*-3-penten-2-ol (6.00 g, 69.7 mmol), was stirred with concentrated hydrochloric acid (7.62 g, 209 mmol) for 15-20 min at room temperature under N₂. The organic layer was separated, dried with calcium chloride (CaCl₂), and distilled under reduced pressure (~2 mm Hg) to give 5.17 g (71%) of product (90% purity by GC/MS). The mass spectrum showed molecular ion peaks at 104 and 106 *m/e* in the expected 3:1 ratio (**Figure 3-24**). ¹H NMR (**Figure 3-25**): δ 1.40-1.63 (3H, CHClCH₃, doublet), 1.63-1.78 (3H, CH=CHCH₃, doublet), 4.45-4.58 (1H, CHCl, quintet), and 5.45-5.80 (2H, CH=CH, multiplet) ppm vs. Me₄Si. ¹³C NMR (**Figure 3-26**): δ 133.79, 127.12, 58.06, 25.44, and 17.27 ppm vs. Me₄Si.

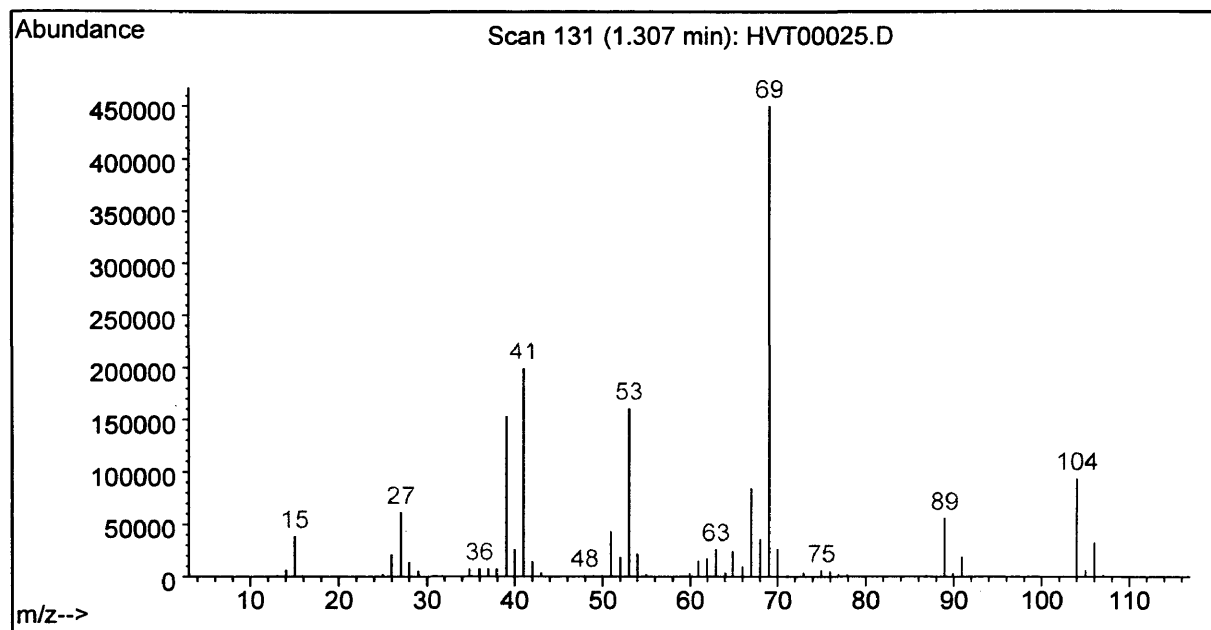


Figure 3-24: Mass spectrum of (E)-4-chloro-2-pentene

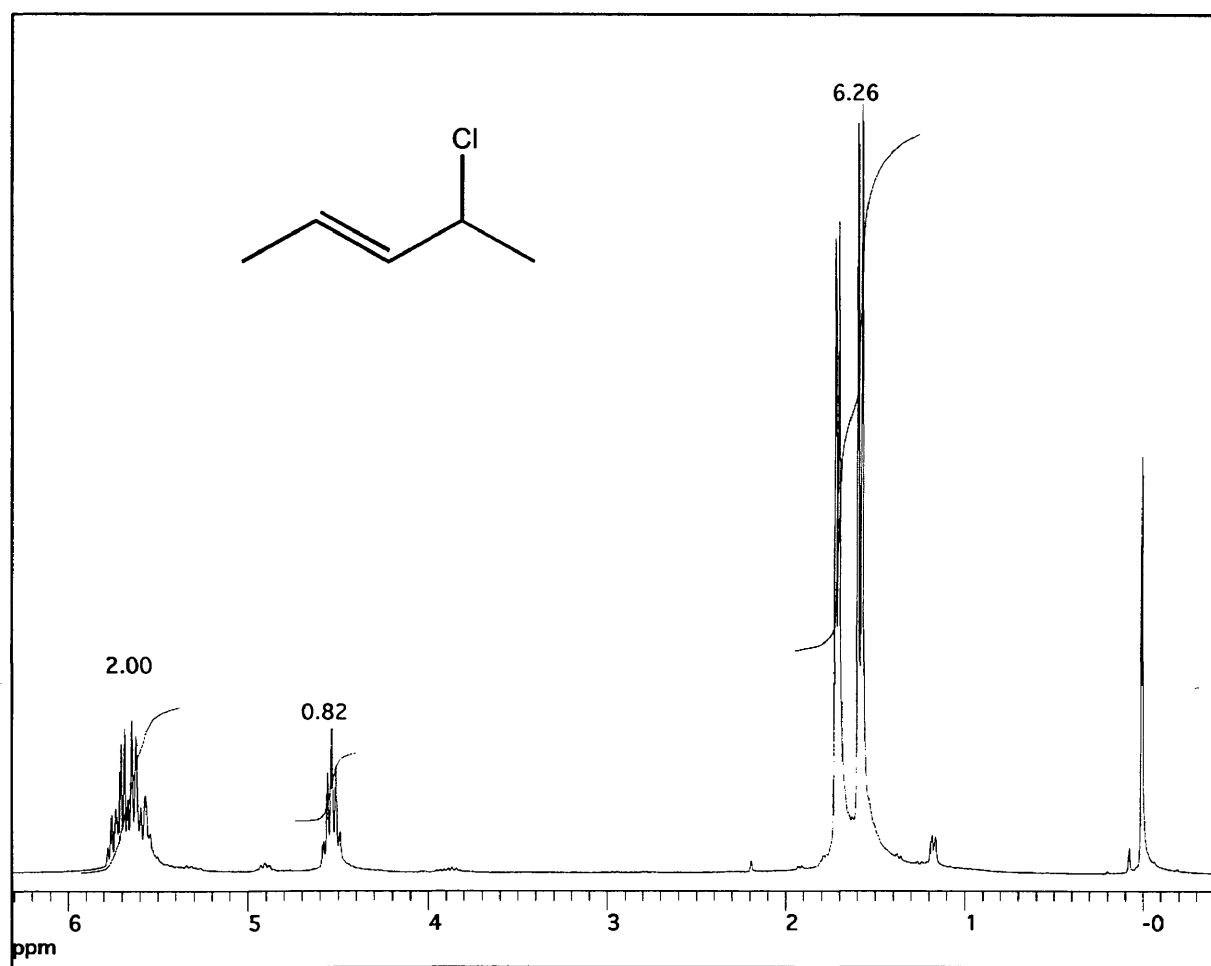


Figure 3-25: ^1H NMR spectrum of (E)-4-chloro-2-pentene

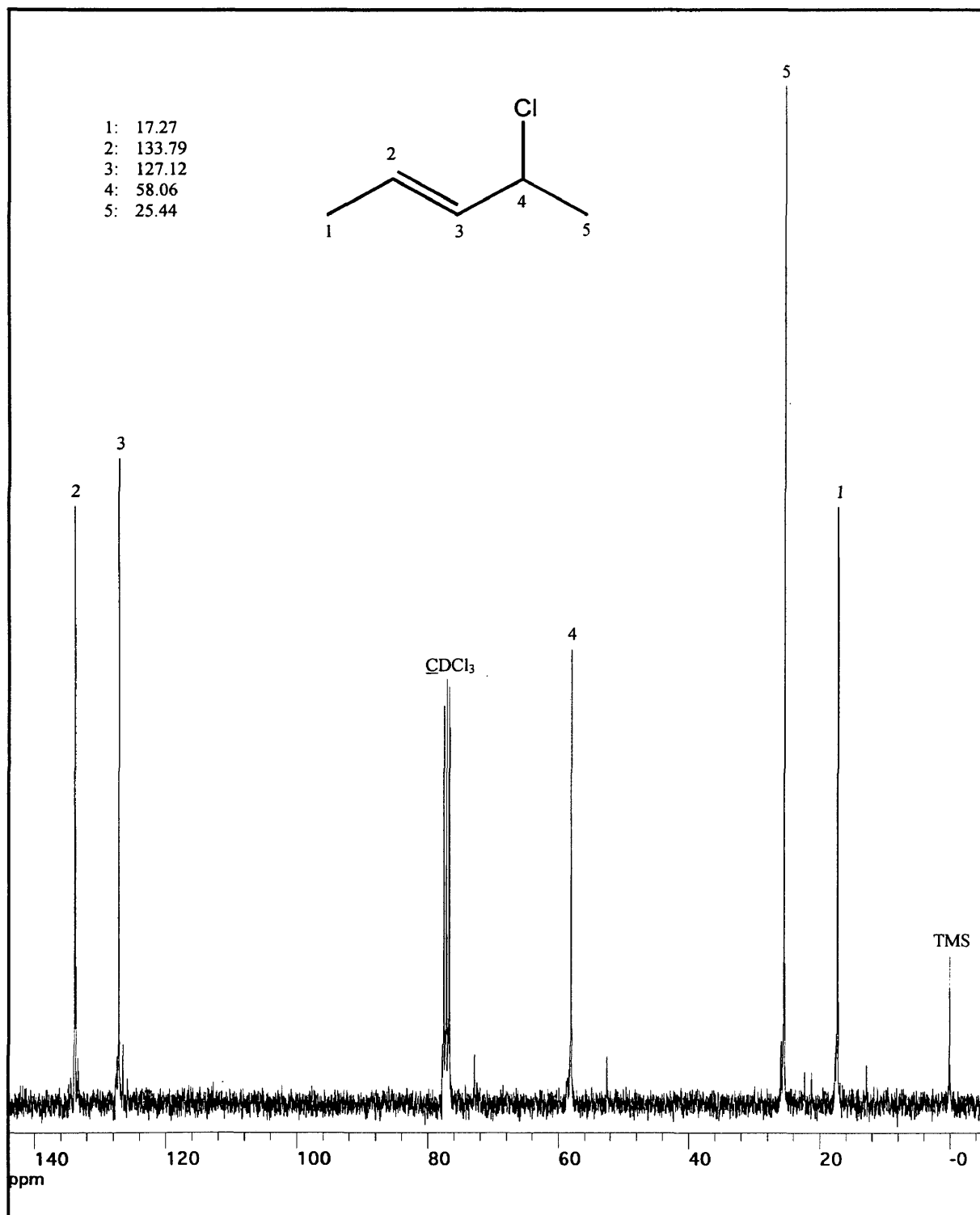
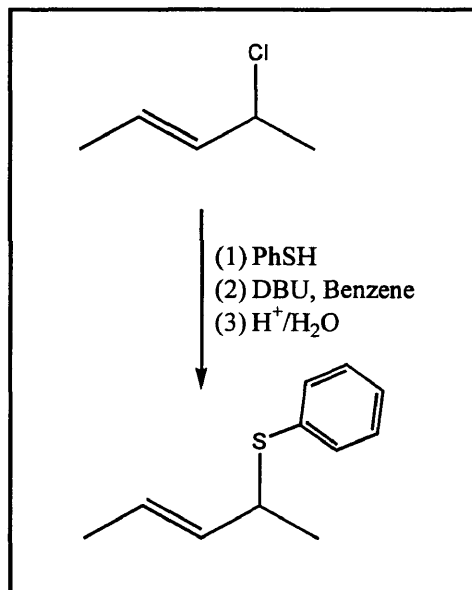


Figure 3-26: ¹³C NMR spectrum of (E)-4-chloro-2-pentene

3.11 Synthesis of (E)-[(1-methyl-2-butenyl)thio]benzene



The synthesis of *trans*-[(1-methyl-2-butenyl)thio]benzene was based on the previously reported method for the conversion of a thiol and alkyl halide into a sulfide.⁷⁷ The previously made *trans*-4-chloro-2-pentene (1.00 g, 9.57 mmol) was added to a stirred mixture of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1.46 g, 9.57 mmol) and thiophenol (1.05 g, 9.57 mmol) in benzene (~29 mL), and the resulting reaction mixture was stirred at room temperature for 2 h under N₂. The precipitated DBU-HCl salt was removed by filtration. The filtrate was washed with water and dried with anhydrous magnesium sulfate. Benzene was evaporated in vacuo, and the residue was distilled under reduced pressure (~2 mm Hg), yielding 0.86 g (50%) of 78% pure (by GC-MS) product. Mass spectral analysis (**Figure 3-27**) showed a molecular ion peak at 178 *m/e* and a diphenyldisulfide impurity peak at 218 *m/e*. ¹H NMR (**Figure 3-28**): δ 1.26-1.49 (3H, CHSCH₃, doublet), 1.49-1.65 (3H, CH=CHCH₃, doublet), 3.67-3.80 (1H, CHSPh, quintet), 5.23-5.65 (2H, HC=CH, multiplet), and 7.10-7.50 (5H, phenyl H, multiplet) ppm vs. Me₄Si. ¹³C NMR (**Figure 3-29**): δ 135.58, 133.19, 132.92, 129.09, 128.57, 126.96, 45.83, 20.89, and 17.43 ppm vs. Me₄Si.

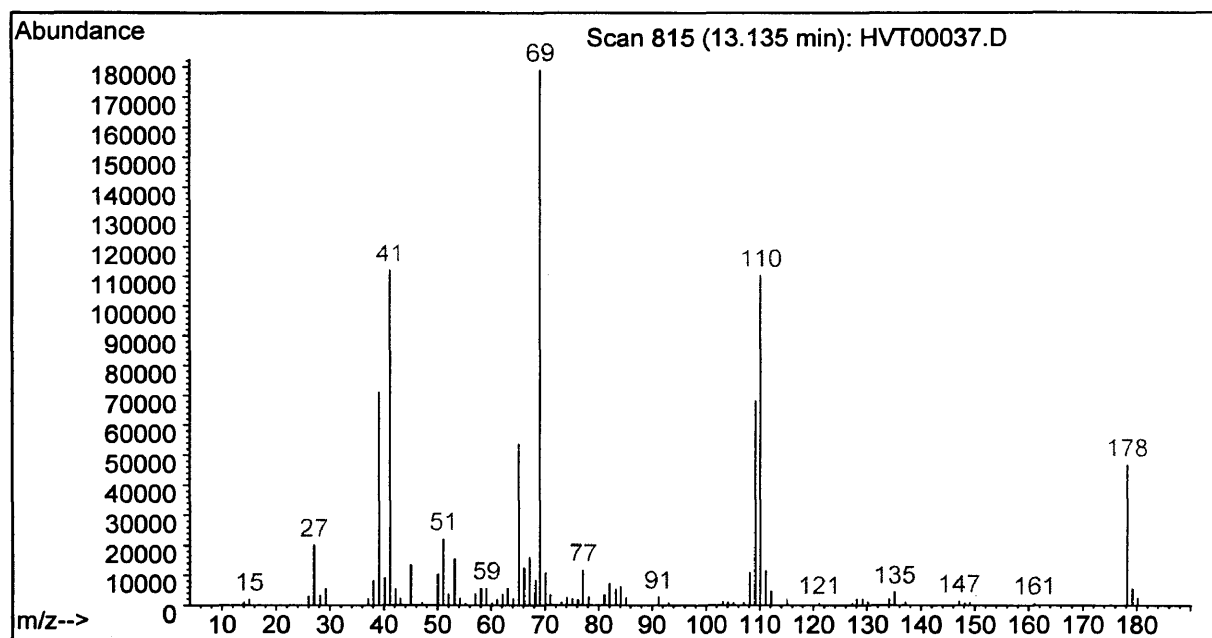


Figure 3-27: Mass spectrum of (E)-[(1-methyl-2-butenyl)thio]benzene

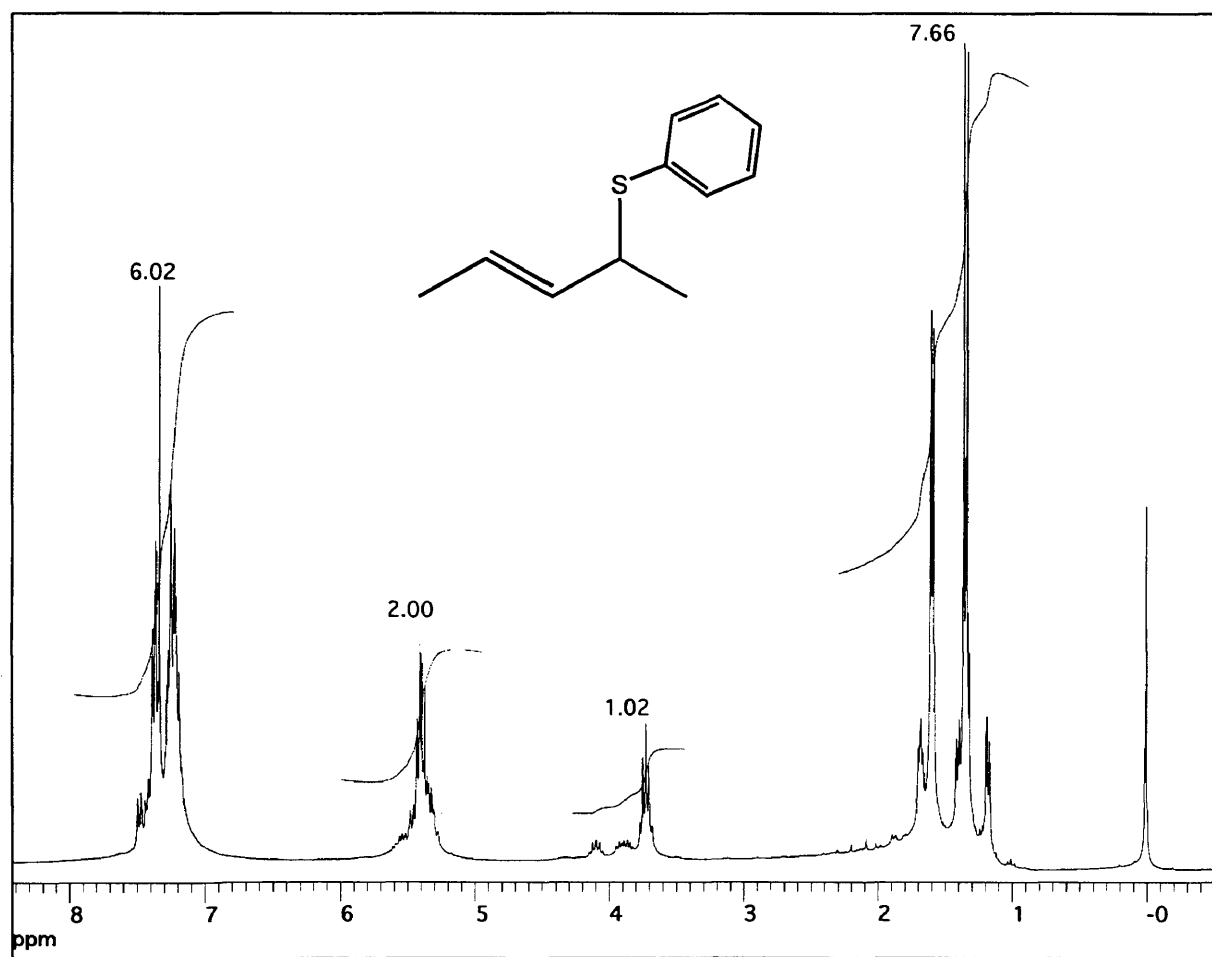


Figure 3-28: ¹H NMR spectrum of (E)-[(1-methyl-2-butenyl)thio]benzene

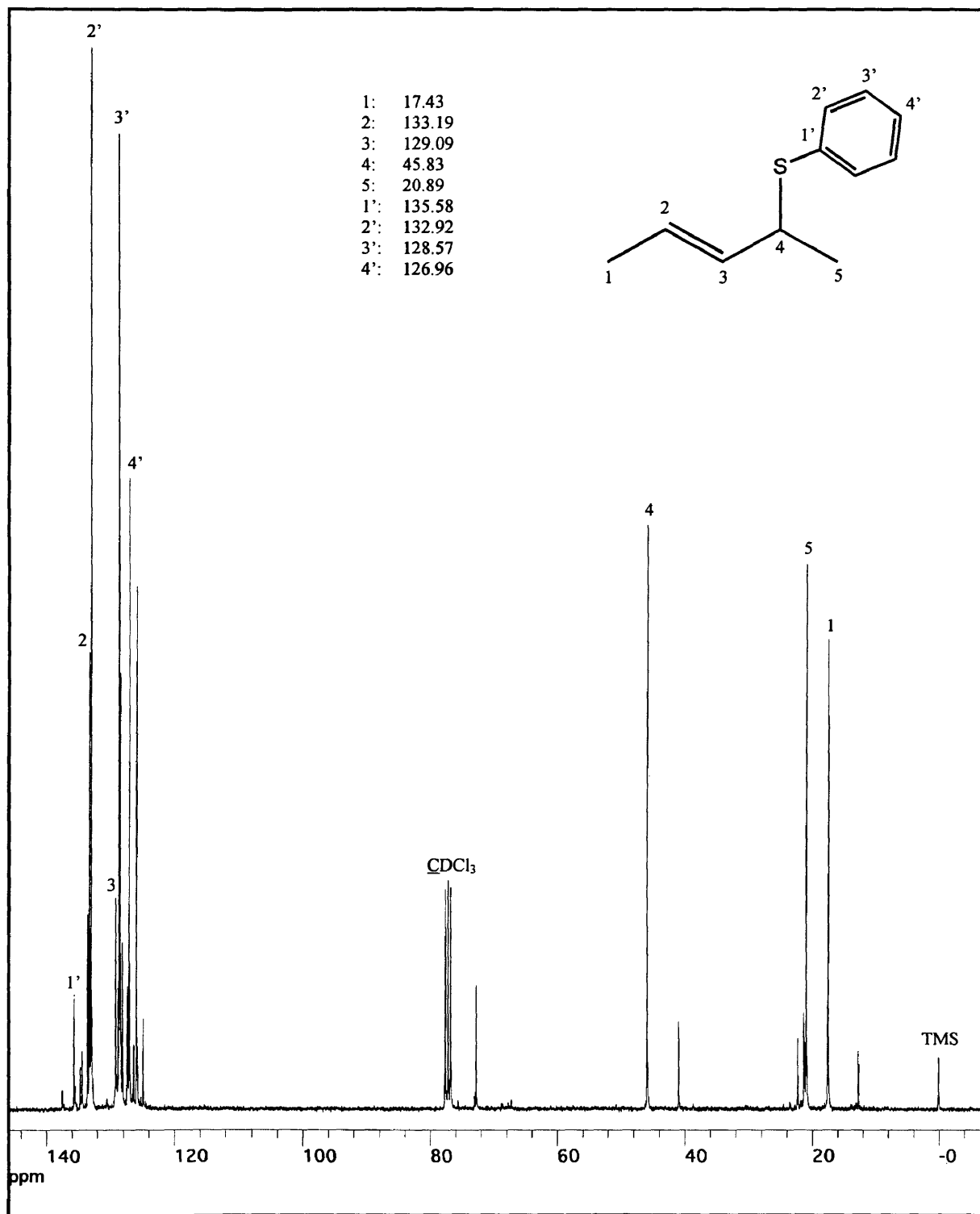


Figure 3-29: ¹³C NMR spectrum of (E)-[(1-methyl-2-butenyl)thio]benzene

Chapter 4

RESULTS AND DISCUSSION

The following three model compounds were made and their ^{13}C NMR chemical shifts were assigned: (E)-[(2-decenyl)thio]benzene, (E)-[(1-heptyl-2-decenyl)thio]benzene, and [(1,1-dioctylpentyl)thio]benzene (see **Figures 3-6, 3-12, and 3-23**). The fourth model compound, (E)-[(1-methyl-2-butenyl)thio]benzene (**Figure 3-29**), was used to verify the shift assignments of the longer-chain internal allylic thiophenyl compound. No problems were encountered in the synthesis of the terminal allylic thiophenyl compound (97% pure by GC/MS). However, the highest purity obtained for the internal allylic thiophenyl compound was 87% (by GC/MS). For our purposes, this value was acceptable, since we only needed ^{13}C chemical shifts of the main component. The smaller peaks belonging to the impurities could be ignored. The synthesis of the tertiary alcohol was straightforward, but its ^{13}C NMR showed a few extra peaks that could not be assigned. Previous work by someone in our group, however, indicated that the starting ketone contained *ca.* 9% of an isomer as an impurity. Also, as seen in the IR spectrum (**Figure 3-13**), some of the ketone was unreacted. This probably explains the extra NMR peaks in the alcohol.

Conversion of the tertiary alcohol into the chloride only gave 78% (purity, by GC/MS) of the product. The facile dehydrochlorination of this tertiary chloride to form an alkene and the impurity from the starting ketone may explain this low value and the presence of several extra peaks in the ^{13}C NMR spectrum. Synthesis of the tertiary thiophenyl compound yielded a product whose purity was only 45% by GC/MS. This low value was attributed to the formation of diphenyl disulfide (confirmed by the presence of a molecular ion peak at 218 *m/e*) and the dehydrochlorination of the tertiary chloride in the reaction mixture. Also, the conversion of the tertiary chloride to the corresponding sulfide was not complete, as shown by similar peaks in the ^{13}C NMR spectra of the chloride (**Figure 3-20**) and sulfide (**Figure 3-23**). The tertiary carbon

resonance of the chloride, at 78.70 ppm, is also seen in the spectrum of the sulfide. Therefore, the peak at 74.41 ppm was, at first, thought to be attributable to the tertiary carbon in the sulfide. However, upon further examination, this peak was actually found to be the tertiary carbon peak in the alcohol (**Figure 3-16**). The product obtained was indeed a mixture of the tertiary chloride and alcohol. Hence, a second reaction was performed on a more nearly pure sample of tertiary chloride (78% by GC/MS), but the conversion to the corresponding tertiary thiophenyl compound still was not successful (the final ^{13}C NMR spectrum looked exactly like the tertiary chloride spectrum, with diphenyl disulfide carbon resonances from 120-140 ppm).

With this realization late in the project, there was no more time to try to synthesize the tertiary thiophenyl compound. Instead, ^{13}C NMR chemical shifts were found for undecane⁸³, **13**, and [(1-pentylhexyl)thio]benzene⁸⁴, **14**, and the shift corrections for substitution of the hydrogen at carbon 6 by PhS^- were calculated (**Figure 4-1**). These shift corrections were used to calculate the shift increments for a butyl branch structure⁶, **15** and **16**, upon substitution by PhS^- . As can be seen, the calculated shift for the quaternary carbon is 16.08 ppm lower than the erroneous one shown in **Figure 3-23**.

Spectra of the model compounds were compared to spectra of similar compounds in the *Aldrich Library of ^{13}C and ^1H FT NMR Spectra*⁸³ and *Carbon-13 NMR Spectroscopy*⁸⁵ and to previously published chemical shift corrections (see **Table 4**). Rows H, J, and L contain shift assignments for the internal allylic, tertiary, and terminal allylic thiophenyl compounds, respectively. The last three rows contain unsorted peaks for a sample of Bu_3SnH -reduced PVC that had been modified with sodium benzenethiolate for 25 h according to the method described by Millán *et al.*³⁵ This was done previously in our research group.⁸⁴ The ^{13}C NMR spectrum (125.76 MHz) for the modified PVC sample (PVC-101X377, polymerized at 82 °C) was obtained by Dr. G. M. Benedikt using a 1:4:1 solvent ratio of 1,4-dioxane- d_6 , 1,1,2,2-tetrachloroethane, and 1,1,2,2-tetrachloroethane- d_2 , respectively, at a temperature of 90 °C (**Figure 4-2**). Therefore, it was necessary to obtain spectra of the three model compounds under the same conditions. **Figures 4-3, 4-4, and 4-5** show the ^{13}C NMR spectra of the three compounds under these conditions, and rows Q, O, and P in **Table 4** show their chemical shift assignments. It should be

noted that all the peak positions in **Figure 4-2** were corrected by subtracting 2.1 ppm to account for the $-\text{CH}_2-$ peak occurring at 32.14 ppm instead of 30.04 ppm, and that the measured chemical shift data for the tertiary model compound are erroneous (as explained previously).

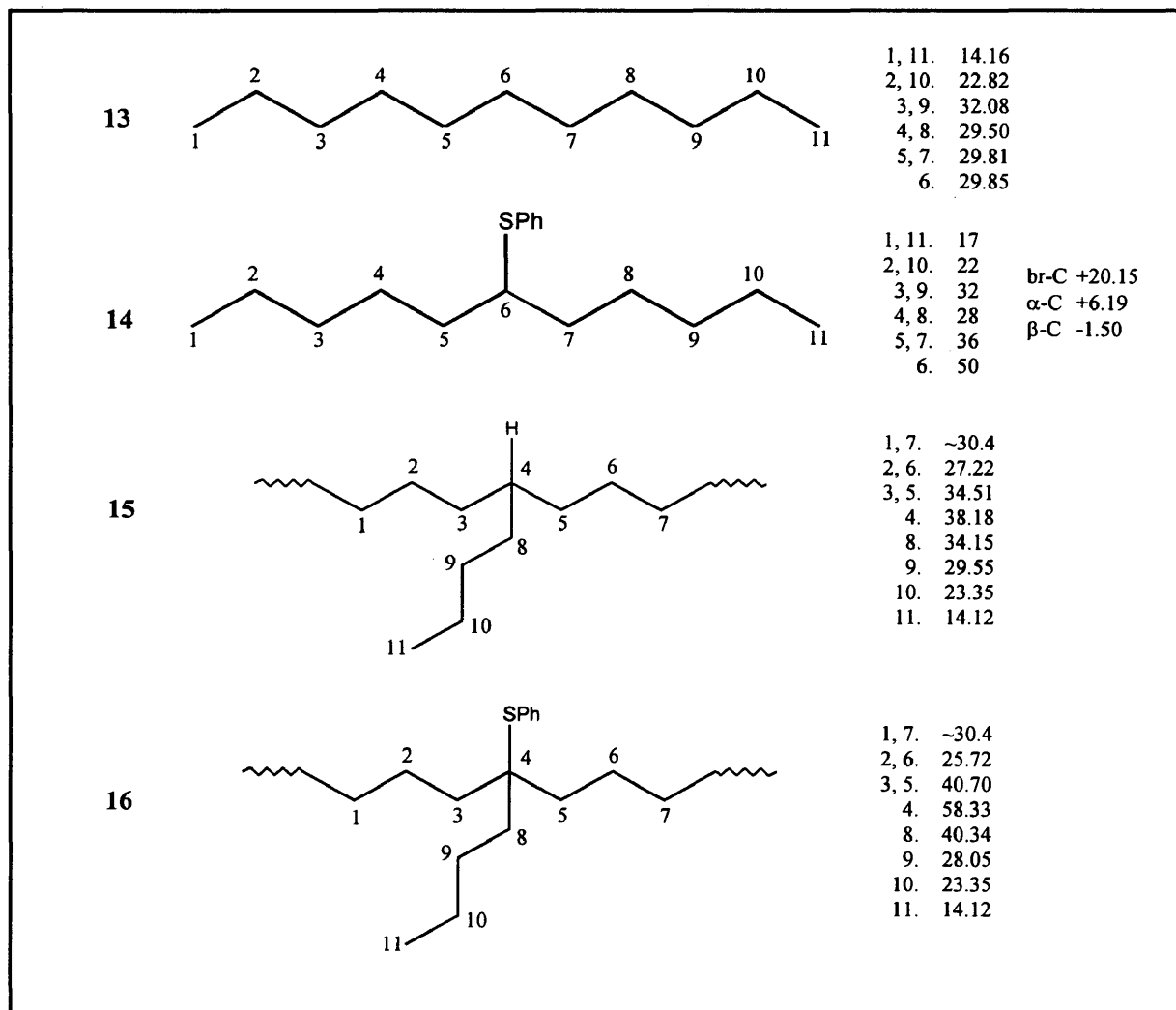


Figure 4-1: ^{13}C NMR chemical shifts (in ppm, vs. Me_4Si) calculated for the substituted butyl branch.

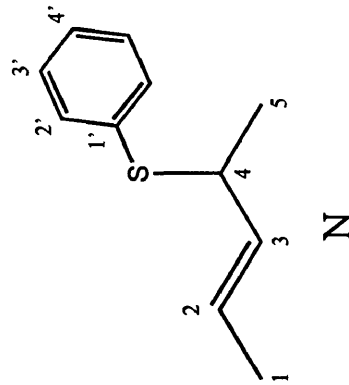
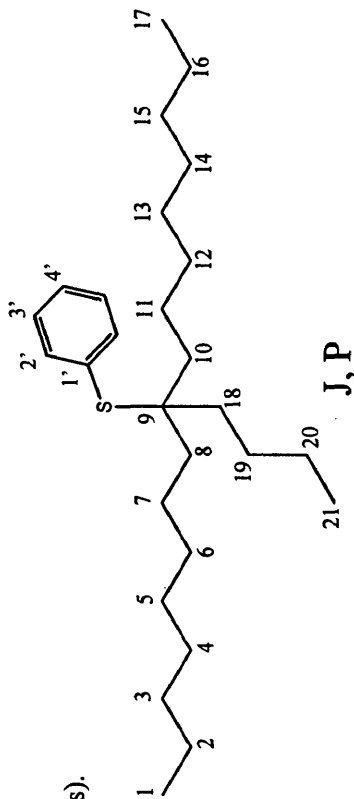
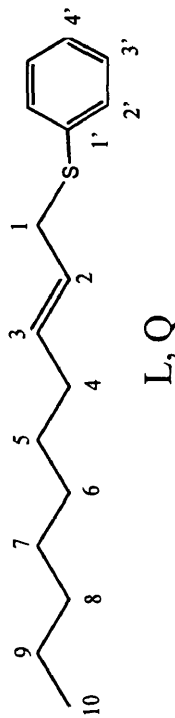
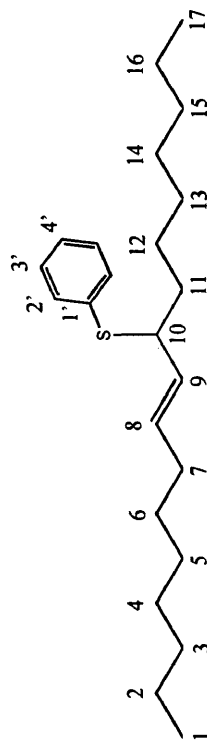
Incorporation of the benzenethiolate into the PVC sample was previously proven by UV spectra (**Figure 4-6**)⁸⁴, and the percentages of conversion for the substitution reaction were calculated and plotted (**Figure 4-7**)⁸⁴. Also, the kinetic data were previously plotted as in **Figure 4-8**⁸⁴, showing that the substitution reaction involved two steps—a fast substitution within the first 25 h and a slow substitution which never reached a high degree of conversion. The decrease in

Table 4: ^{13}C Chemical Shift Data for Model Compounds

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16	C-17
A	13.62	22.23	34.06	133.18	131.44	63.61	38.73	28.87	22.23	13.96							
B	14.11	22.67	31.79	29.65	28.86	32.63	130.31	130.31	32.63	28.86	29.65	31.79	22.67	14.11			
C				-0.1	-0.9	-0.8	3.1	0.6	29.6	9.1	-2.8	-0.5	-0.1				
D	14.11	22.67	31.79	29.55	27.96	31.83	133.41	130.91	62.23	37.96	26.85	31.29	22.57	14.11			
E	14.11	22.67	31.79	29.55	*29.55	*27.96	31.83	133.83	130.91	62.23	37.96	*26.85	*26.85	*26.85	31.29	22.57	14.11
F	13.96	22.68	31.94	*29.19	*29.19	*29.19	32.02	133.35	131.53	63.28	39.17	26.70	*29.19	*29.19	31.91	22.68	13.96
G	14.11	22.67	31.79	29.55	*29.55	*27.96	*34.06	133.18	131.44	>50	38.73	*28.87	*26.85	*26.85	*31.29	22.57	14.11
G(Ph)	136.64	128.81	129.02	125.73													
H	13.96	22.68	*31.91	*29.43	*29.19	*29.08	32.21	132.37	131.19	51.97	35.14	27.37	*29.19	*29.43	*31.91	22.68	13.96
H(Ph)	135.84	133.10	128.51	126.83													
I	13.97	*22.73	*32.00	*30.08	*29.60	*29.37	*26.75	*41.36	78.70	*41.36	*26.75	*29.37	*29.60	*30.08	*32.00	*22.73	13.97
I(Bu)	*41.66	*32.00	*24.51	13.97													
J	14.02	*23.60	*31.99	*30.44	*29.55	*29.35	*25.86	*39.58	74.41	*39.58	*25.86	*29.35	*29.68	*30.44	*31.99	*23.60	14.02
J(Bu)	*39.27	*31.99	*22.71	14.02													
J(Ph)	137.42	129.06	127.99	127.25													
K	45.33	126.08	136.15	32.12	*29.18	*29.11	*28.98	31.89	22.70	14.05							
L	36.85	130.33	134.44	32.26	*29.30	*29.16	*29.08	31.89	22.65	13.94							
L(Ph)	136.89	128.70	126.13	125.37													
M	17.27	133.79	127.12	58.06	25.44												
N	17.43	133.19	129.09	45.83	20.89												
N(Ph)	135.58	132.92	128.57	126.96													
O	13.94	22.58	*31.81	*29.35	*29.11	*29.08	32.10	132.32	131.04	51.76	35.07	27.25	*29.11	*29.35	*31.81	22.58	13.94
P	13.97	*22.63	*31.92	*30.42	*29.61	*29.29	*25.83	*39.64	74.21	*39.64	*25.83	*29.29	*29.61	*30.42	*31.92	*22.63	13.97
P(Bu)	*39.30	*31.92	*23.57	13.97													
Q	36.65	130.09	134.44	32.18	*29.24	*29.08	*29.01	31.81	22.60	13.94							
R	13.73	13.86	18.09	23.15	24.46	27.03	27.13	27.28	27.49	27.59	27.70	27.97	28.23	29.10	29.55	29.63	30.04
	30.41	31.12	32.87	34.02	35.46	37.27	38.60	39.37	39.80	43.23	46.40	50.08	66.21	66.39	66.56	66.73	66.91
	67.10	72.71	74.24	74.47	74.80	76.87	80.48	126.00	126.80	128.10	128.40	129.10	129.90	130.80	132.40	137.00	

*Overlapped.

- A = (E)-6-chloro-4-decene, from Starnes and Katz.⁸⁶
 B = (E)-7-tetradecene, Aldrich.
 C = Corrections in substituting Cl for H from alkene, Starnes and Katz.⁸⁶
 D = (E)-9-chloro-7-tetradecene, predicted from corrections, row C.
 E = (E)-10-chloro-8-heptadecene, predicted from row D.
 F = (E)-10-chloro-8-heptadecene shift assignments, measured.
 G = (E)-[(1-heptyl-2-decyl)thio]benzene, predicted from Aldrich spectra and E.
 H = (E)-[(1-heptyl-2-decyl)thio]benzene shift assignments, measured.
 I = 9-butyl-9-chloroheptadecane shift assignments, measured.
 J = [(1,1-dioctylpentyl)thio]benzene shift assignments, measured (See Results).
 K = (E)-1-chloro-2-decene shift assignments, measured.
 L = (E)-[(2-decyl)thio]benzene shift assignments, measured.
 M = (E)-4-chloro-2-pentene shift assignments, measured.
 N = (E)-[(1-methyl-2-butyl)thio]benzene shift assignments, measured.
 O = (E)-[(1-heptyl-2-decyl)thio]benzene shift assignments, measured in 1:4:1.
 P = [(1,1-dioctylpentyl)thio]benzene shift assignments, measured in 1:4:1 (See Results).
 Q = (E)-[(2-decyl)thio]benzene shift assignments, measured in 1:4:1.
 R = Reduced PVC modified for 25 h, from Benedikt, unsorted.



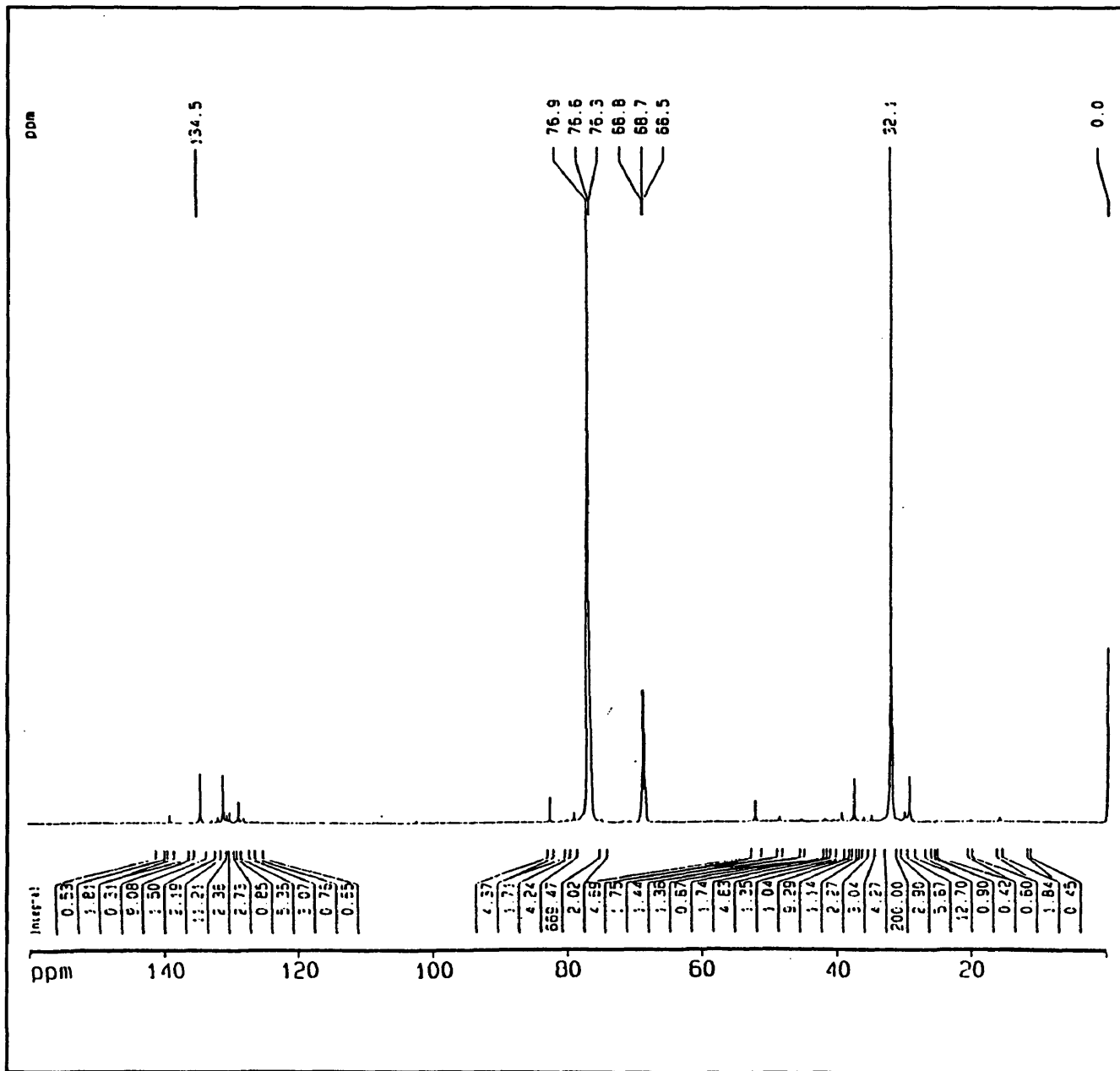


Figure 4-2: ^{13}C NMR spectrum of PVC modified for 25 h and then reduced by Bu_3SnH .

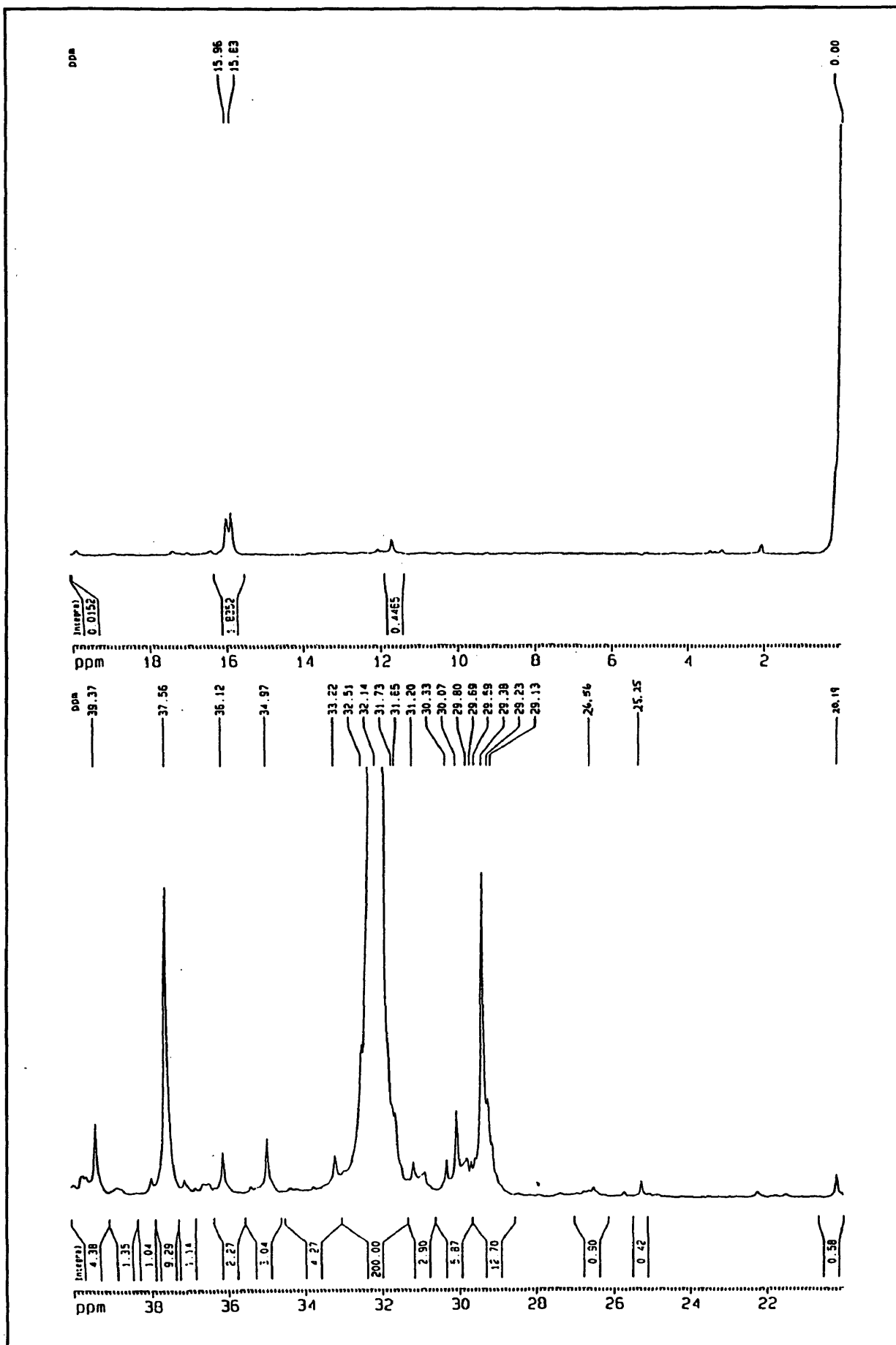


Figure 4-2 (continued): ^{13}C NMR spectrum of PVC modified for 25 h and then reduced by Bu_3SnH .

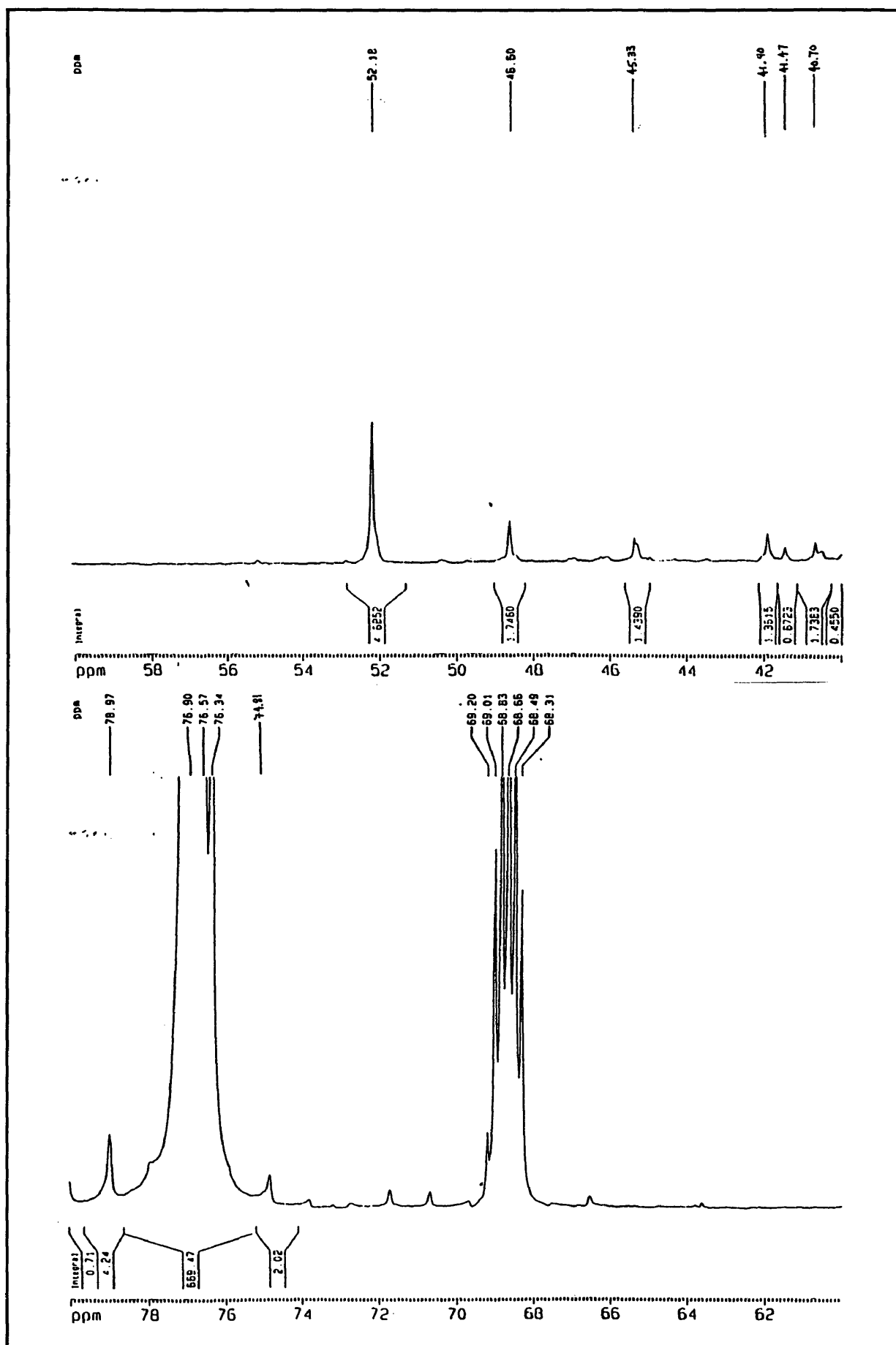


Figure 4-2 (continued): ^{13}C NMR spectrum of PVC modified for 25 h and then reduced by Bu_3SnH .

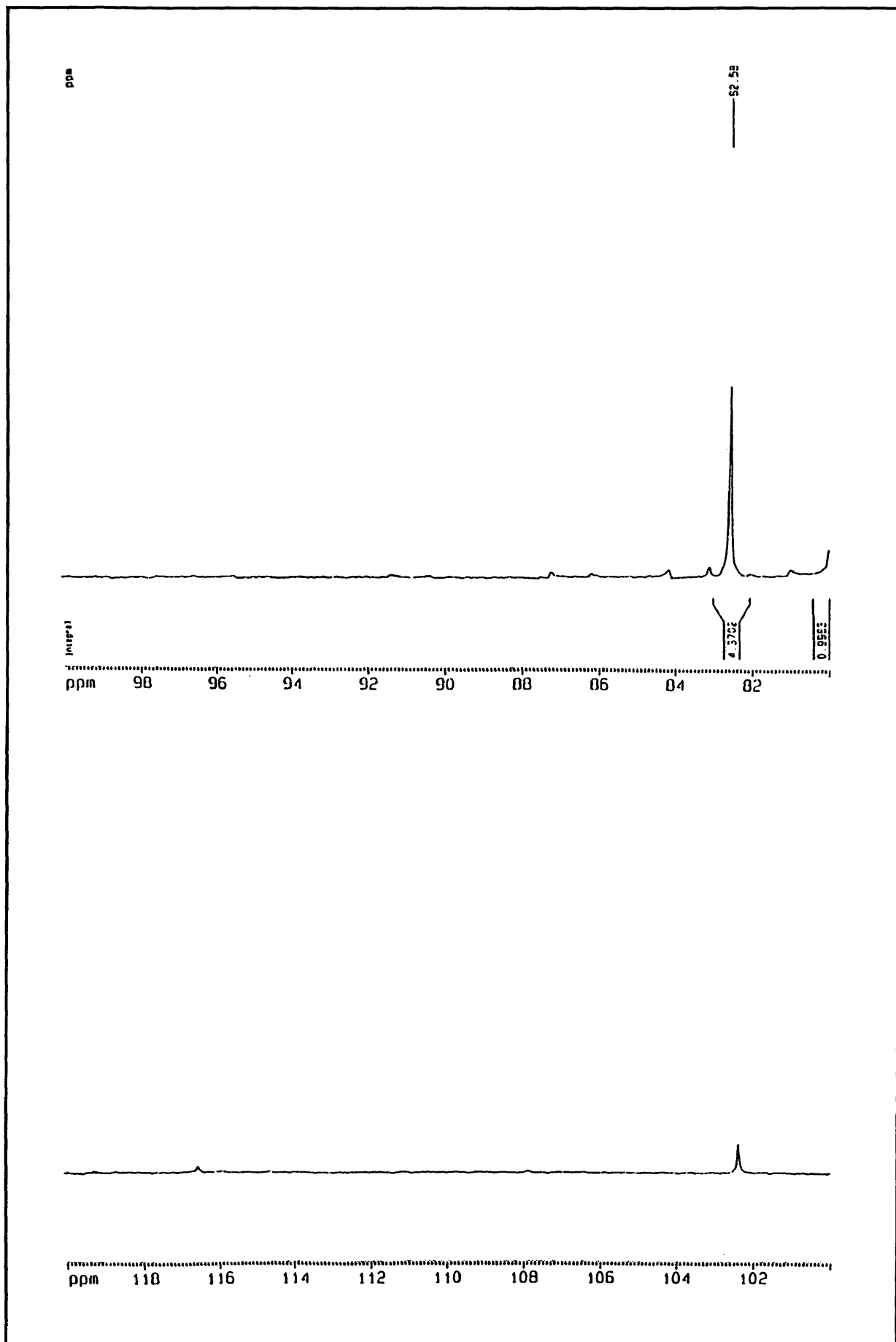


Figure 4-2 (continued): ^{13}C NMR spectrum of PVC modified for 25 h and then reduced by Bu_3SnH .

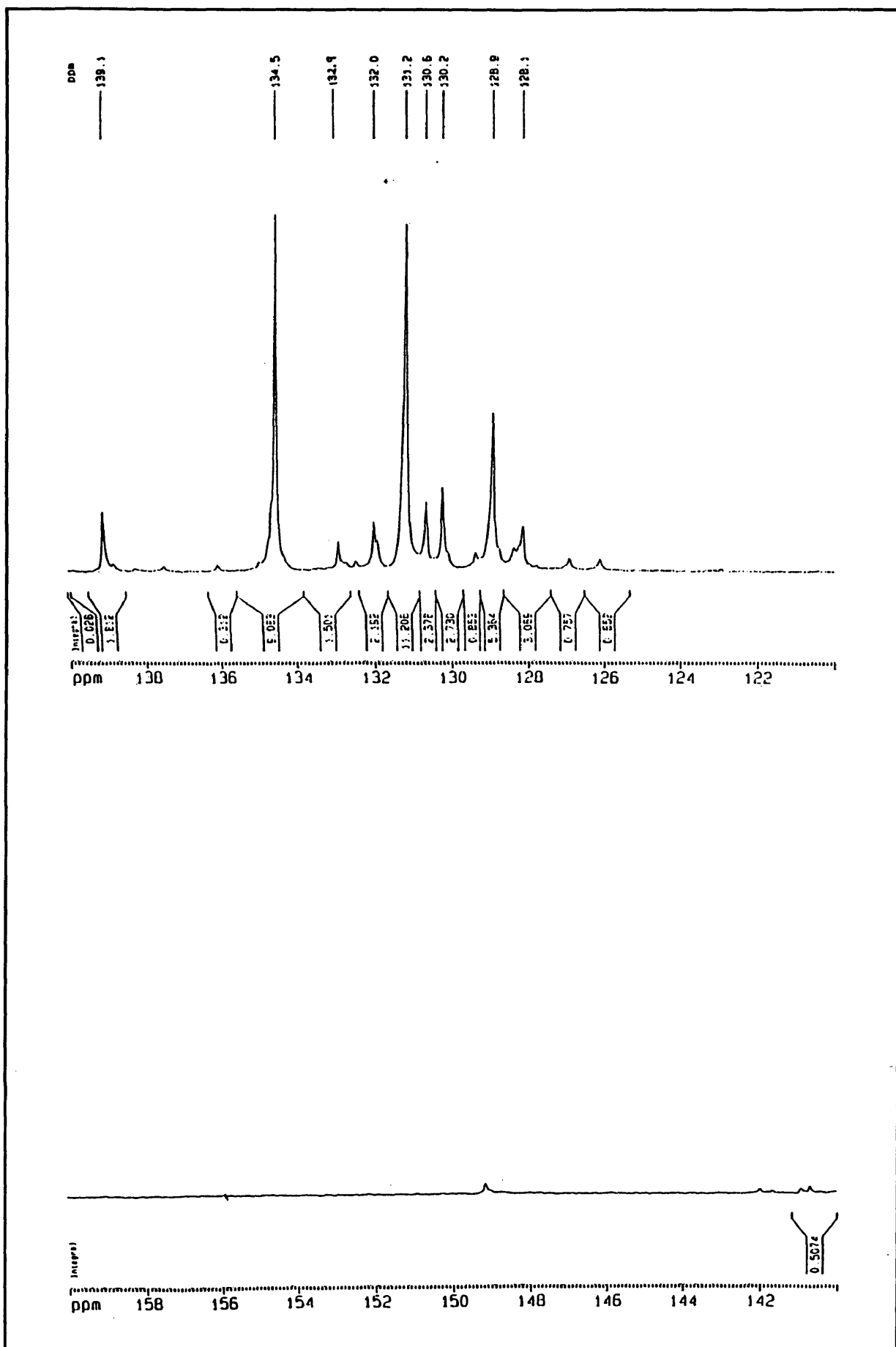


Figure 4-2 (continued): ^{13}C NMR spectrum of PVC modified for 25 h and then reduced by Bu_3SnH .

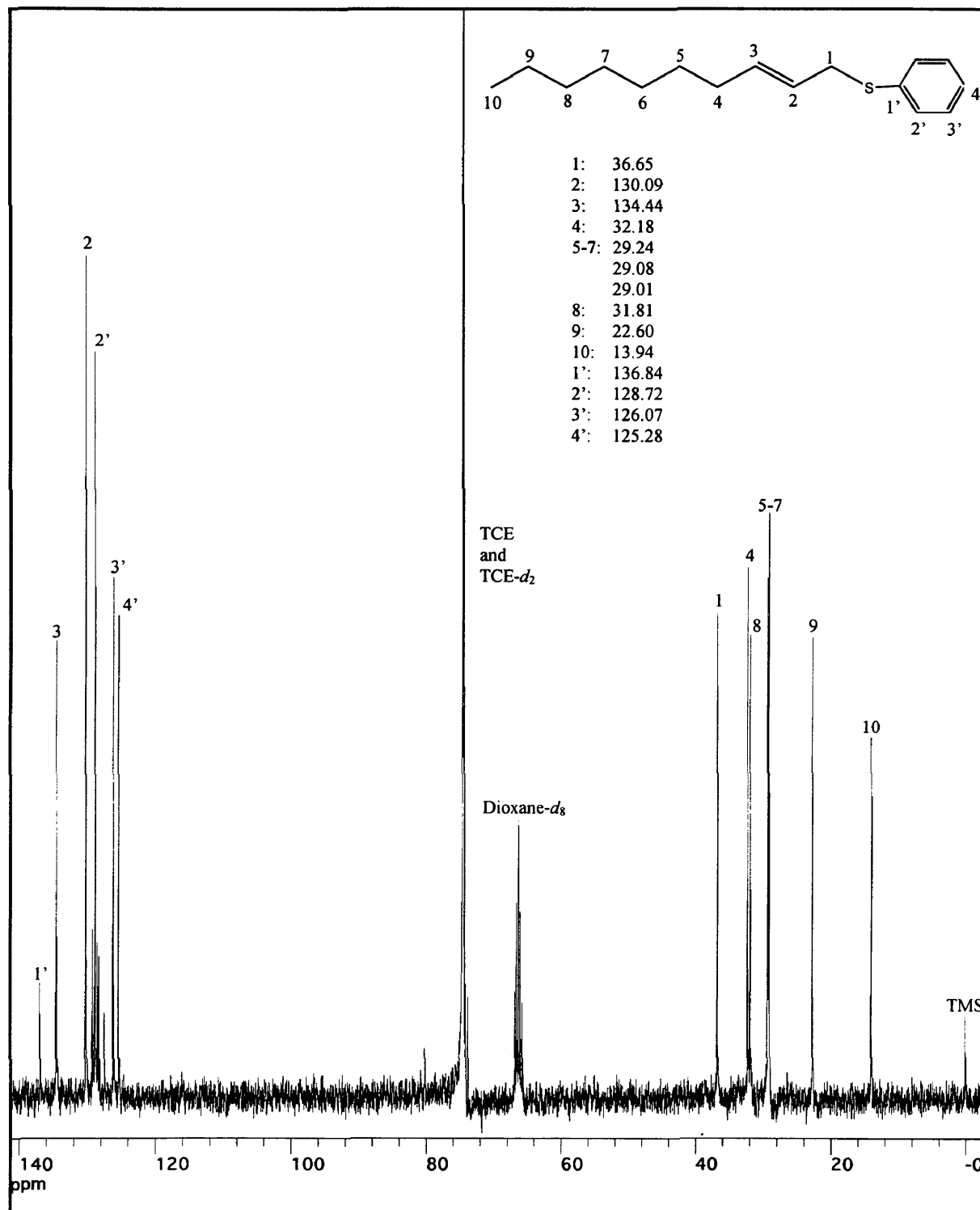


Figure 4-3: ^{13}C NMR spectrum of (E)-[(2-decenyl)thio]benzene in 1:4:1 Tetrachloroethane- d_2 :Tetrachloroethane:1,8-Dioxane- d_8 at 90 °C

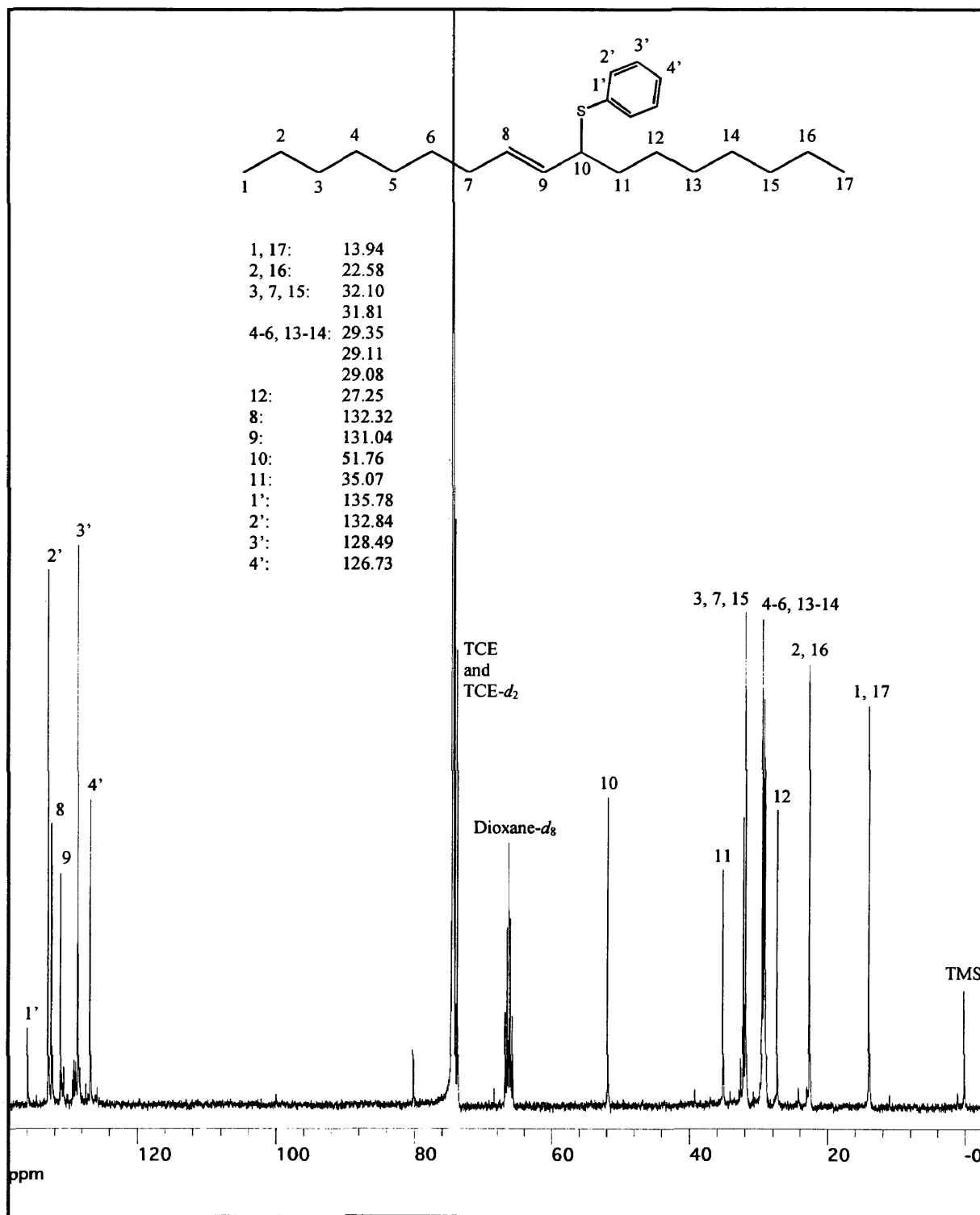


Figure 4-4: ^{13}C NMR spectrum of (E)-[(1-heptyl-2-decyl)thio]benzene in 1:4:1 Tetrachloroethane- d_2 :Tetrachloroethane:1,8-Dioxane- d_8 at 90 °C

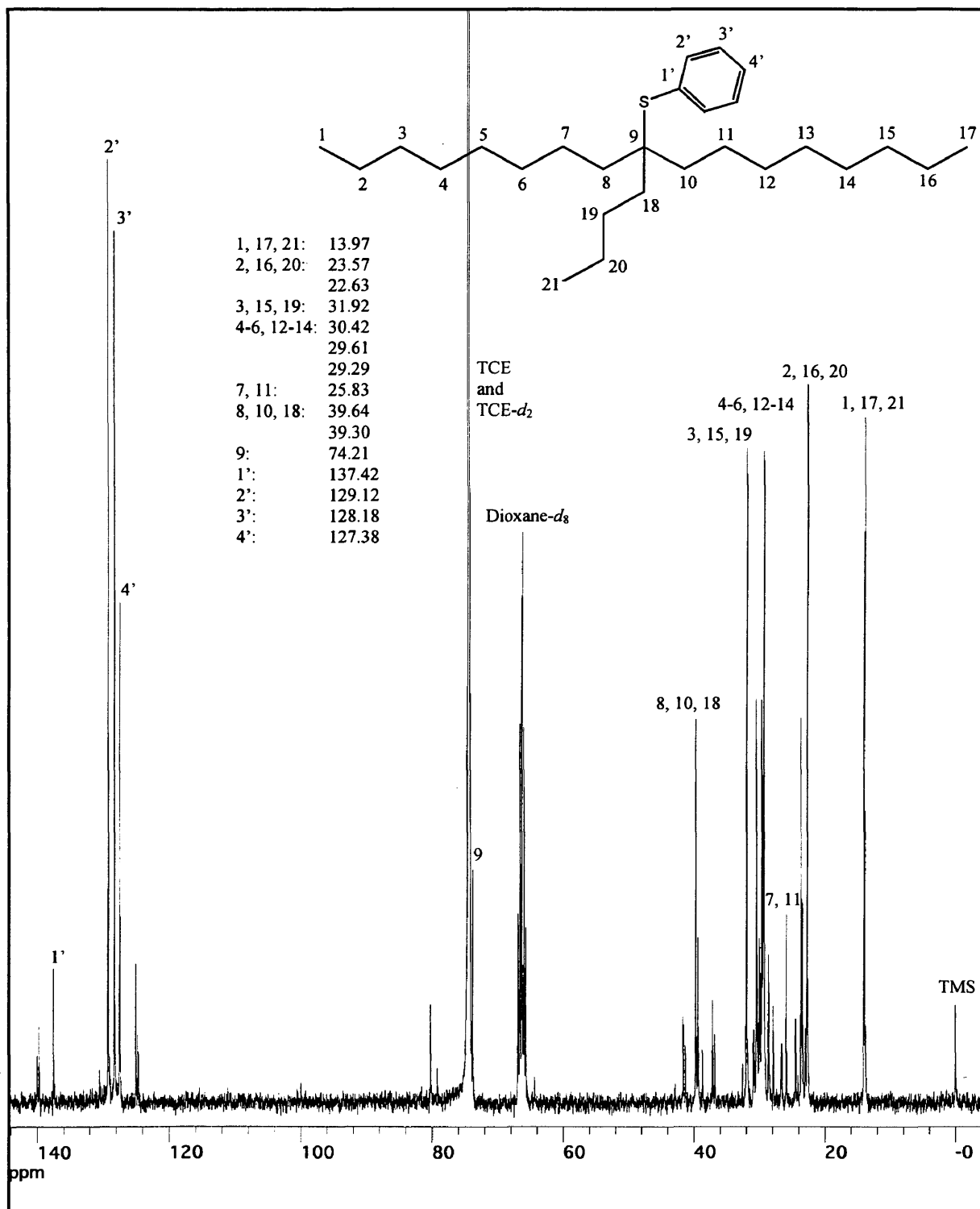


Figure 4-5: ¹³C NMR spectrum of [(1,1-dioctylpentyl)thio]benzene in 1:4:1 Tetrachloroethane-*d*₂:Tetrachloroethane:1,8-Dioxane-*d*₈ at 90 °C (See Results)

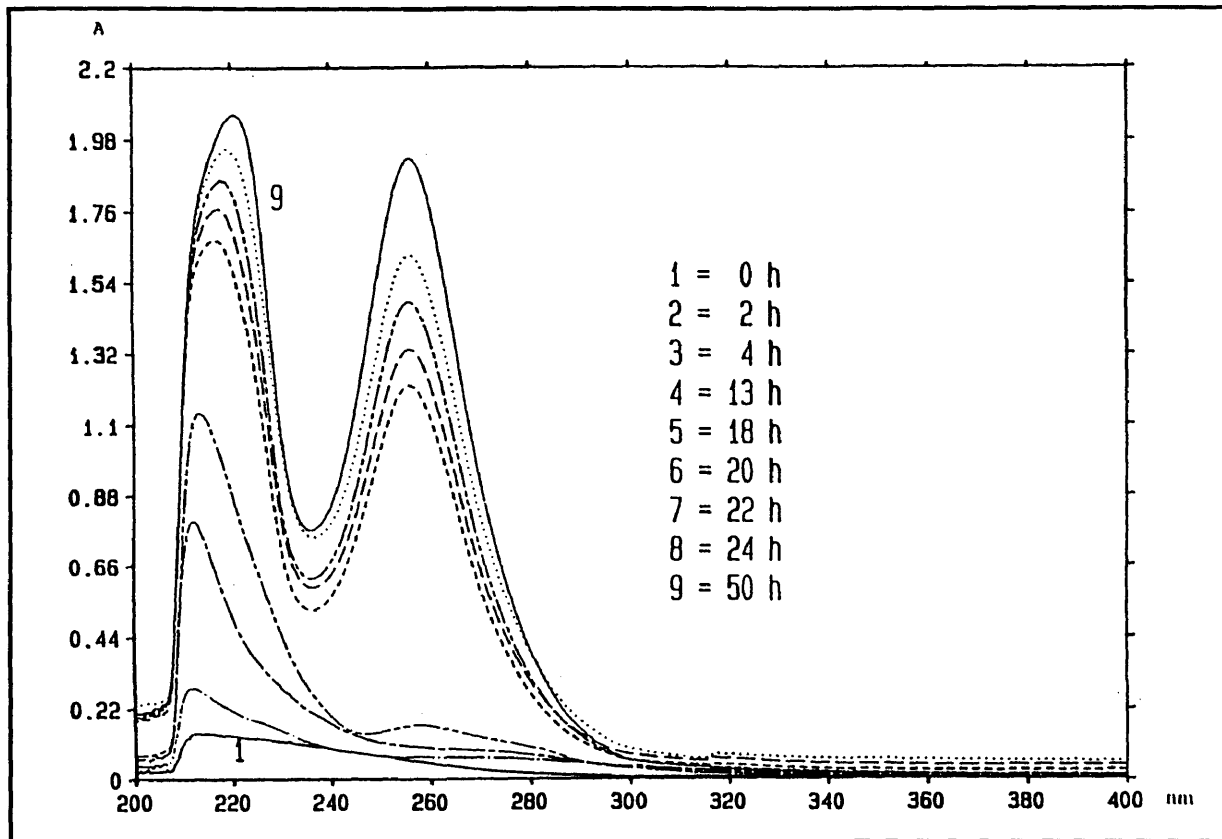


Figure 4-6: UV spectrum of modified PVC samples in THF (concentration, 0.8 g/L).

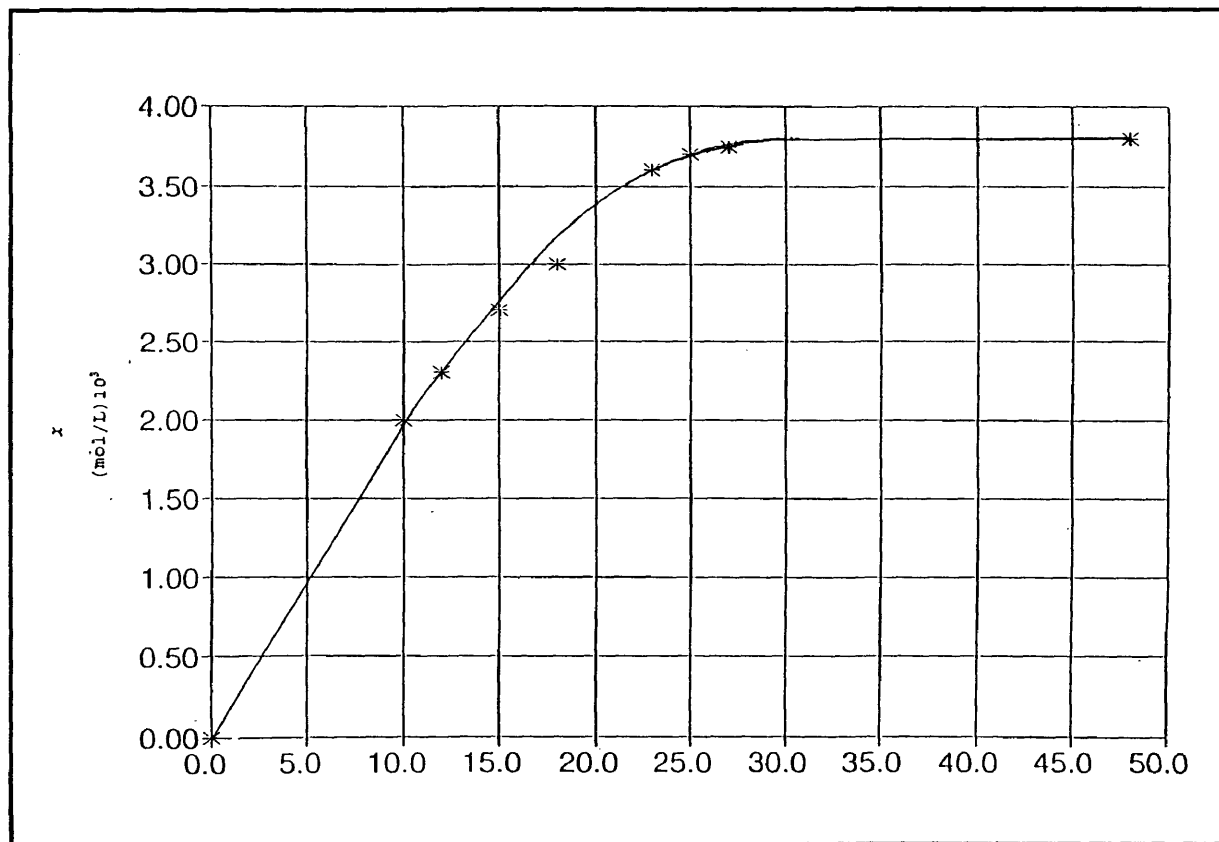


Figure 4-7: Percent conversion for the nucleophilic substitution on PVC with PhSNa at 18 °C.

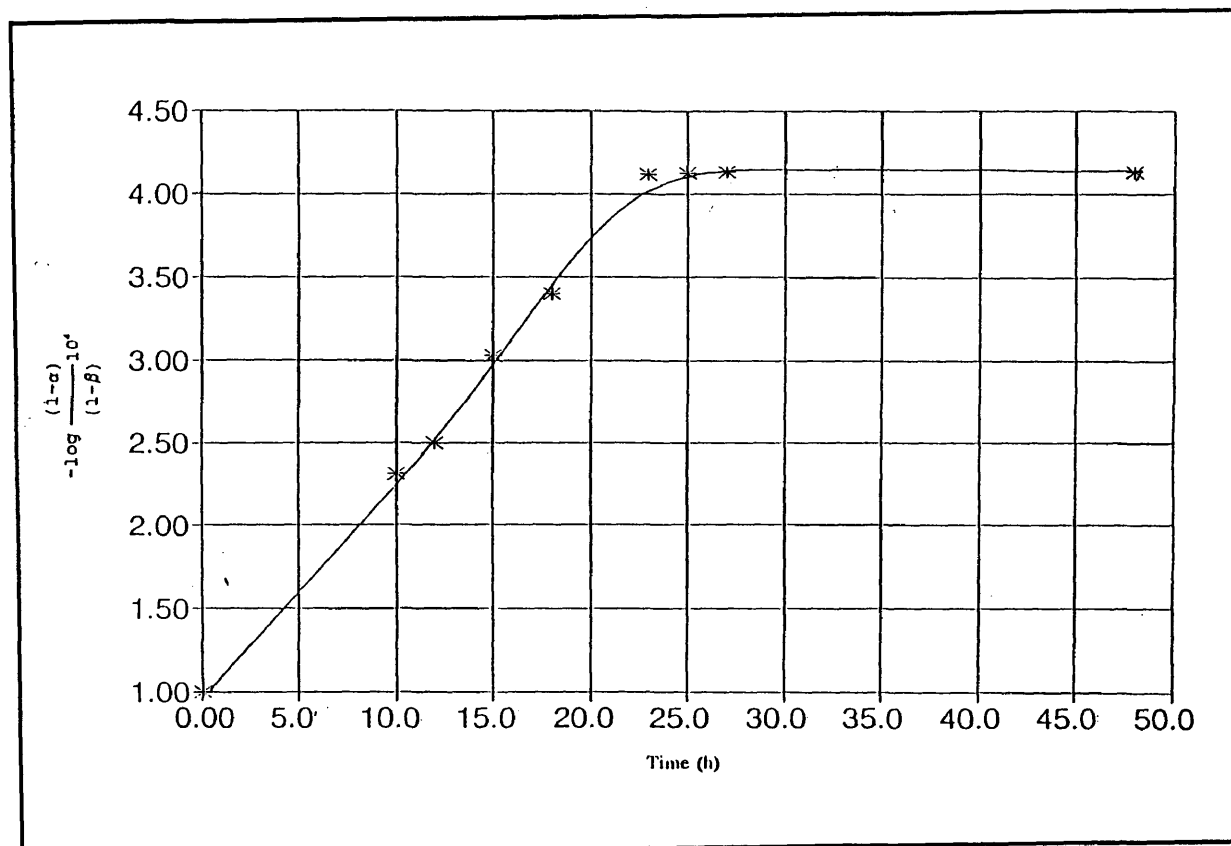


Figure 4-8: Kinetic plot for the nucleophilic substitution on PVC with PhSNa at 18 °C.

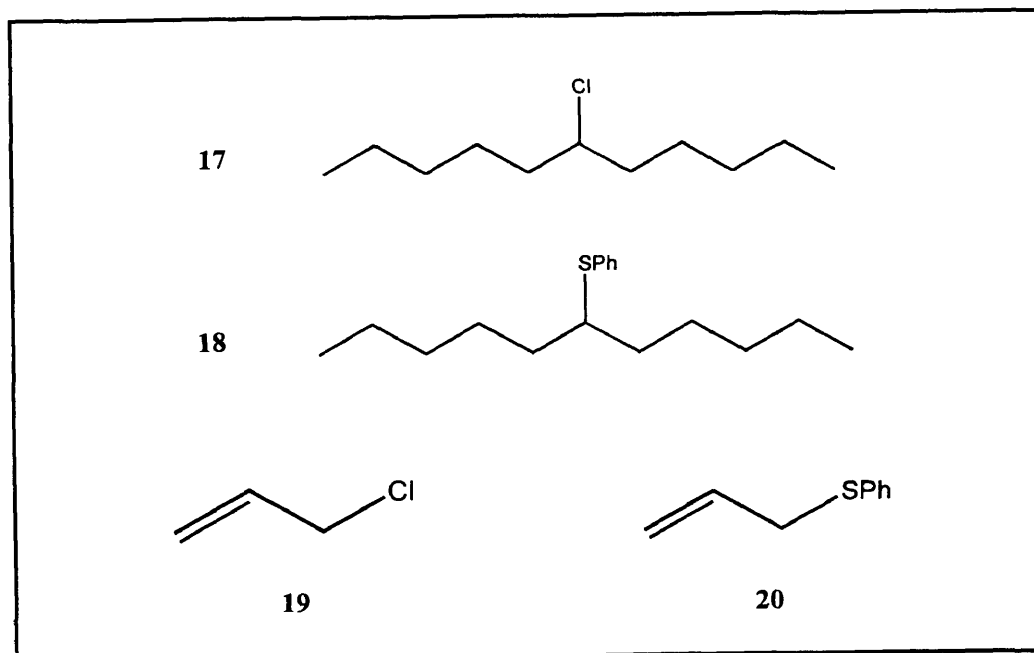


Figure 4-9: Model compounds prepared for competitive reductions by Bu_3SnH .

rate can be attributed to the replacement of almost all of the labile chlorine by the more stable benzenethiolate group (i.e., as more and more labile chlorines were replaced by benzenethiolate, the rate of substitution decreased). After 25 h of reaction, the modified PVC sample was subjected to reductive dechlorination with tri-*n*-butyltin hydride, Bu_3SnH . Before the final sample was analyzed by ^{13}C NMR spectroscopy, it was necessary to learn whether Bu_3SnH also replaced the $\text{C}_6\text{H}_5\text{S}^-$ groups with hydrogen. Accordingly, model compounds **17-20** (**Figure 4-9**) were previously prepared and their competitive reductions by Bu_3SnH were studied.⁸⁴ Earlier studies had established the relative reactivities of various sulfides, selenides, and halides toward $\text{S}_{\text{H}2}$ attack by tributyltin radicals.⁸⁷ The order of reactivity, according to Beckwith and co-workers, was $\text{Br} > \text{PhSe} > \text{Cl} > p\text{-CNC}_6\text{H}_4\text{S} > \text{PhS} > p\text{-MeC}_6\text{H}_4\text{S} > \text{MeS}$. In experiments with the four model compounds, both chlorides were reduced while both sulfides remained unreduced.⁸⁴ Therefore, the lower reactivity of the $\text{C}-\text{SPh}$ bond compared to the $\text{C}-\text{Cl}$ bond was confirmed, and reduction by Bu_3SnH of the modified PVC sample did not affect the benzenethiolate groups, a result required by this investigation.

By comparison of the chemical shifts of the reduced and modified PVC sample with those found for the model compounds, we can determine if there are allylic or tertiary structures involved in the fast substitution by sodium benzenethiolate. The strongest peak at 30.04 ppm (after the 2.1 ppm correction) in **Figure 4-2** was assigned to the $-\text{CH}_2^-$ carbons resulting from the reduction of the ordinary monomer units. The peaks at 66.21, 66.39, 66.56, 66.73, and 66.91 ppm (strike-through values in row R in **Table 4**) all belong to the carbons in *p*-dioxane- d_8 . The other solvent peaks, from tetrachloroethane and tetrachloroethane- d_2 , occur at 74.24, 74.47, and 74.80 ppm. The underlined values between and including 126 and 137 ppm were assigned to the carbons in the phenyl group. All the other peaks arise from structural defects or other branch structures in PVC, or from minor impurities in the sample. These peaks are the ones that occupy our interest.

To determine if any tertiary halogen were substituted by the benzenethiolate group, we planned to compare the spectra of our tertiary model compound with that of the modified and reduced PVC sample. Since the synthesis of the tertiary thiophenyl compound was not successful, we instead compared predicted shifts of this compound to the PVC spectrum. A

significant peak involves the tertiary carbon, carbon 4 of structure **16** in **Figure 4-1**, at 58.33 ppm. A matching peak could not be found in the PVC spectrum. The resonances of carbons 3 and 5 in the tertiary compound were both calculated to be at 40.70 ppm. Carbon 8 in the same compound is predicted to resonate at 40.34 ppm. These peaks were found in the PVC spectrum, at 39.80 and 39.37 ppm (the italicized values in row R). The 0.90-0.97 ppm difference may be attributed to solvent effects. Approximately matching the peak at 24.46 ppm were peaks for carbons 2 and 6 (both at 25.72 ppm), a 1.26 ppm difference. This difference may be small enough to be accounted for by both the solvent effect and experimental error. The predicted peaks for the other three carbons in the butyl branch, at 28.05, 23.35, and 14.12 ppm, were all found in the PVC spectrum at 27.97, 23.15, and 13.86 ppm, respectively. These correlations indicate, firstly, the existence of a butyl branch structural defect in PVC, and secondly, the existence of a substituted (by PhS⁻) tertiary structure. Based on our initial findings, the tertiary structure may have been involved in the initial fast substitution of PVC by sodium benzenethiolate, tentatively indicating the importance of this labile structure in the reaction. These results are only preliminary, since a model compound was not successfully made to determine exact chemical shifts. More research will need to be done in this area.

The concentration per 1000 monomer units of the tertiary branch carbon could not be calculated because the peak was not seen in the polymer spectrum. In any case, the calculated concentration would be lower than that of the other carbons in the branch structure because of a long T_1 and a low NOE for the tertiary carbon. However, the concentration per vinyl chloride unit of the carbons in the PVC sample corresponding to carbons 2, 3, 5, 6, 8, 9, 10 and 11 of the tertiary structure could be calculated. This was done by taking the integrals of the peaks and multiplying by a factor of 10, since the integral of the $-\text{CH}_2-$ peak was set to 200. Multiplying 200 by 5 would give 1000, but there are two $-\text{CH}_2-$ groups per monomer unit after reduction, so the peaks are multiplied by $5 \times 2 = 10$. Consequently, the concentrations of the peaks corresponding to carbons 3 and 5 (39.80 ppm), carbon 8 (39.37 ppm), carbons 2 and 6 (24.46 ppm), and carbon 10 (23.15 ppm) are 13.5 units/1000 VC, 8.7 units/1000 VC, 9.0 units/1000 VC, and 4.2 units/1000 VC, respectively. The concentrations for carbon 9 (27.97 ppm) and carbon 11 (13.86 ppm) could

not be calculated because their integrals were not separately measured (see **Figure 4-2**). Since carbons 3 and 5 are both shown by the same peak in the PVC spectrum, their concentration must be divided by 2 to get the concentration of the tertiary structure per 1000 monomer units. This procedure gives 6.8 units/1000 VC. Doing the same for carbons 2 and 6 gives 4.5 units/1000 VC. Taking the average of the four values obtained (8.7, 6.8, 4.5, and 4.2 ppm) gives 6.1 tertiary structures/1000 VC. Hjertberg and Rogestedt⁴⁶ found the concentration of tertiary chlorine in one of their reduced PVC samples to be 2.0 units/1000 VC, while Starnes *et al.*⁸⁸ found the value to be 2.4 units/1000 VC. The difference in concentration (a factor of about 3) between that found in the current investigation and previously reported literature values cannot yet be accounted for.

Comparison of the peaks of the internal allylic thiophenyl model compound to that of the modified and reduced PVC sample also suggests substitution by the benzenethiolate group at the internal allylic chloride defect site. However, the intensities of the resonances are mutually inconsistent and much higher than expected. Carbon 10 in the model compound (row O in **Table 4**) shows a peak at 51.76 ppm. The corresponding peak in the PVC spectrum might be the one at 50.08 ppm (46.9 units/1000 VC), but this shift is too low. Peaks for the sp^2 carbons (carbons 8 and 9) occur at 132.32 and 131.04 ppm in the model compound. Matching peaks in the PVC sample might be the ones at 132.40 and 130.80 ppm (90.8 units/1000 VC and 15.0 units/1000 VC, respectively). However, peaks from alkene carbons can easily be confused with aromatic peaks, and the difference in intensities for these two peaks is much too large. Carbon 7 at 32.10 ppm can be compared to the peak at 32.87 ppm (30.4 units/1000 VC) in the PVC spectrum, and carbon 11 at 35.07 ppm is closely matched by the peak at 35.46 ppm (92.9 units/1000 VC). Carbon 12, at 27.25 ppm, can be related to any of the peaks from 27.03 to 27.97 ppm (58.7 units/1000 VC to 127 units/1000 VC) in the PVC sample. Starnes and co-workers previously reported the concentration of internal allylic (IA) structures in a PVC sample polymerized at 82 °C to be 0.6 IA/1000 VC.⁶⁸ The much higher concentrations found compared to this value may be due to elimination promoted by the PhS^- anion to form unsaturation points in the polymer chain.

The involvement of the terminal allylic structure in the fast substitution reaction was not confirmed. Carbon 1 in row Q shows a peak at 36.65 ppm, corresponding to the peak at 37.27

ppm (43.8 units/1000 VC) in the PVC spectrum. Carbon 2 at 130.09 ppm can be matched to the peak at 129.90 ppm (21.9 units/1000 VC), but carbon 3 at 134.44 ppm was not found in the polymer spectrum. Carbon 4 at 32.18 ppm may also be matched to the peak at 32.87 ppm (30.4 units/1000 VC). A previously reported concentration⁶⁸ for the terminal allylic structure was 2.2 units/1000 VC, so the above concentrations are much too high. Therefore the assigned peaks are unlikely to be the ones associated with the terminal allylic structure. One very likely reason that the terminal allylic structure could not be detected is the formation of structure **25** in **Figure 4-10**, as suggested by earlier work.⁸⁹ Since the allylic Cl of **21** would be substituted by NaSPh in the first reaction, Bu₃SnH would then cause radical **23** to form in the second step. This radical might be transformed into **25** via a 1,5 free-radical cyclization. This reaction may also occur with the internal allylic structure, forming an internal cyclopentane group in the polymer chain.

Examination of the modified and reduced PVC spectrum for peaks relating to the secondary thiophenyl substituted structure also suggests modification at the ordinary monomer units of PVC by NaSPh. **Figure 4-11** shows the approximate chemical shifts of the model compound, **27**, previously prepared⁸⁴ from the corresponding chloride, 6-chloroundecane (**26**). Carbon 6, at about 50 ppm, can be related to the peak at 50.08 ppm in the polymer spectrum. Carbons 5/7 (both at 36 ppm) and 4/8 (both at 28 ppm) can also be related to the peaks at 35.46 and 27.97 ppm, respectively, in the PVC spectrum. The peaks at 50.08, 35.46, and 27.97 ppm have been accounted for earlier. However, because of their high intensities, these peaks are more likely to arise from carbons in the ordinary monomer units.

The above results indicate that the initial fast substitution by sodium benzenethiolate on PVC occurs at conventional defect sites (internal allylic + tertiary) and/or at the ordinary monomer units. The chemical shifts of structure **27** in **Figure 4-11** are so similar to those of some of the internal allylic and tertiary thiophenyl carbons that their distinction in the PVC spectrum was difficult. As a result, we could not establish with confidence the exclusive involvement of the (internal allylic + tertiary) structures in the initial fast substitution by the benzenethiolate anion. More evidence needs to be obtained to show what happens to these structures and to the structures involving the ordinary monomer units during the initial fast substitution. It is believed that the work described in this thesis will be a useful starting point for further research in this area.

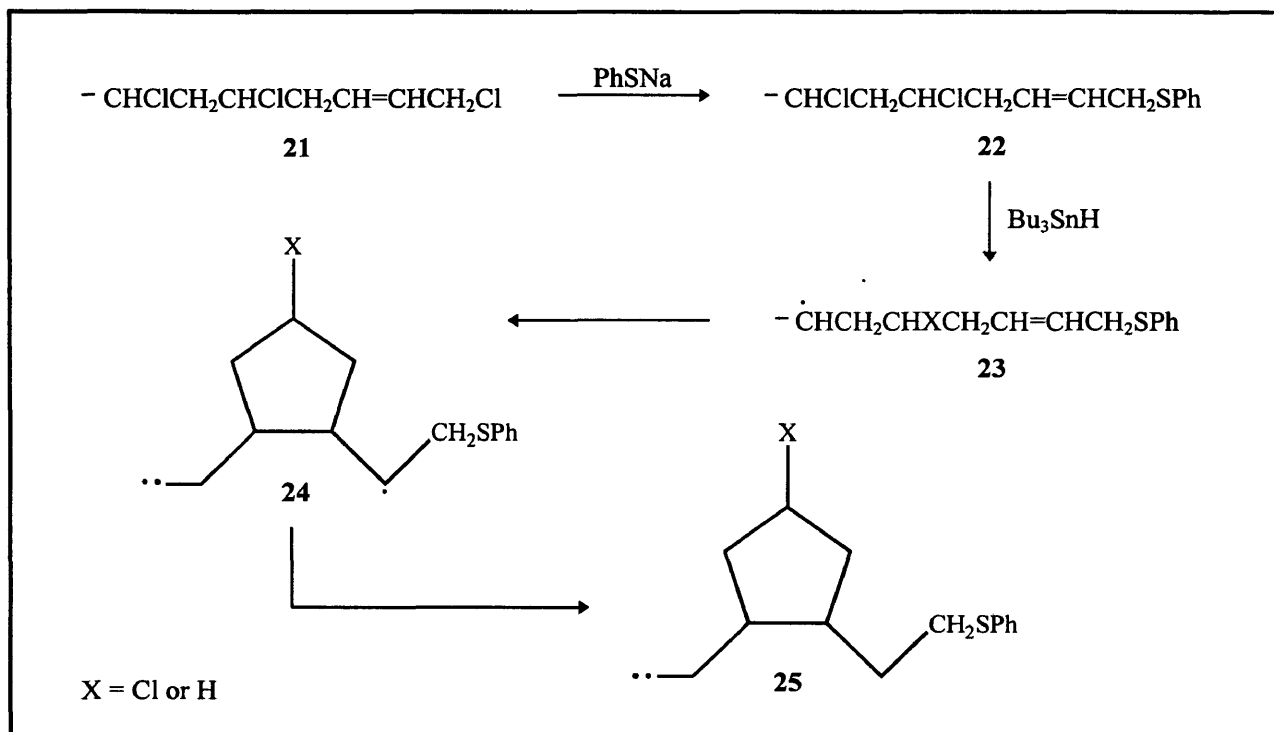


Figure 4-10: Formation of a cyclopentane end group during organotin hydride reduction of modified PVC.

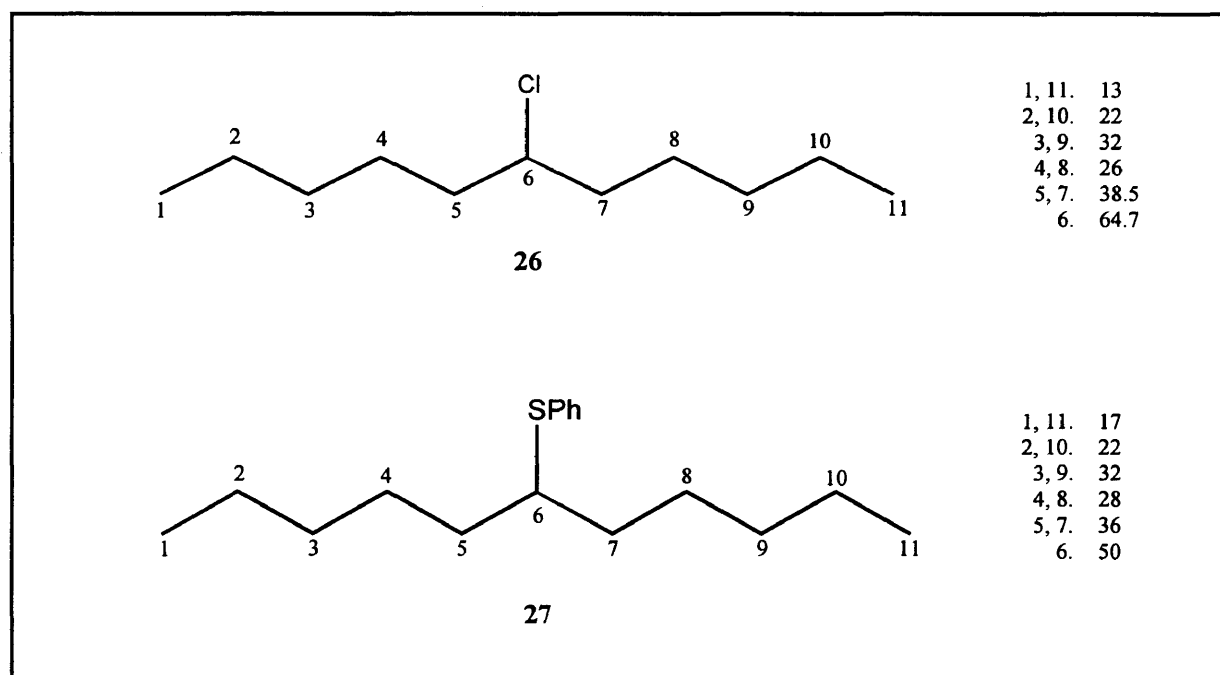


Figure 4-11: ^{13}C chemical shifts (in ppm, vs. Me_4Si) of 6-chloroundecane and the corresponding sulfide.

Chapter 5

CONCLUSIONS

The initial fast substitution by sodium benzenethiolate on poly(vinyl chloride) was suggested by the present investigation to occur at (internal allylic + tertiary) chloride structures and at the ordinary monomer units. Comparison of the ^{13}C NMR spectra of several model compounds to the spectrum of modified and reduced PVC indicated the involvement of both PhS—substituted (internal allylic + tertiary) structures and PhS—substituted structures on the ordinary monomer units. The substituted terminal allylic structure was not found, but this structure may have easily formed the cyclopentane end groups suggested earlier.

The exclusive involvement of the internal allylic and tertiary structures in the thermal dehydrochlorination of poly(vinyl chloride) was not successfully established. Problems with the synthesis of the tertiary model compound were not solved, and there was difficulty in assigning peaks to the polymer spectrum. Also, calculated concentrations of the labile structures did not correlate well with previously reported literature values. The reduced PVC sample used to obtain the ^{13}C NMR spectrum might have been allowed to react with NaSPh for too long. Modification may have initially occurred at the labile chlorine sites and then at the ordinary monomer units after a certain time period. This would explain our findings for the secondary PhS—substituted structure in the polymer spectrum. A sample of PVC should be modified for a shorter time period and then analyzed. Therefore, further work would need to be done in this area.

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